25.03.2022
Lecture 31
Extra class, Fri 5 PM

Spontaneous Instability in Ultra Thin Polymer Films:-

Liquid Thin Film Hydrodynamics

↳ Film thk will keep on changing.

Dewetted Features → They will slowly evaporate

→ Preferred model system is a Polymer Thi Film

→ Solid Like at Room

→ Liquid State only when heated above T_g.

All the evolution takes place in the Liquid state

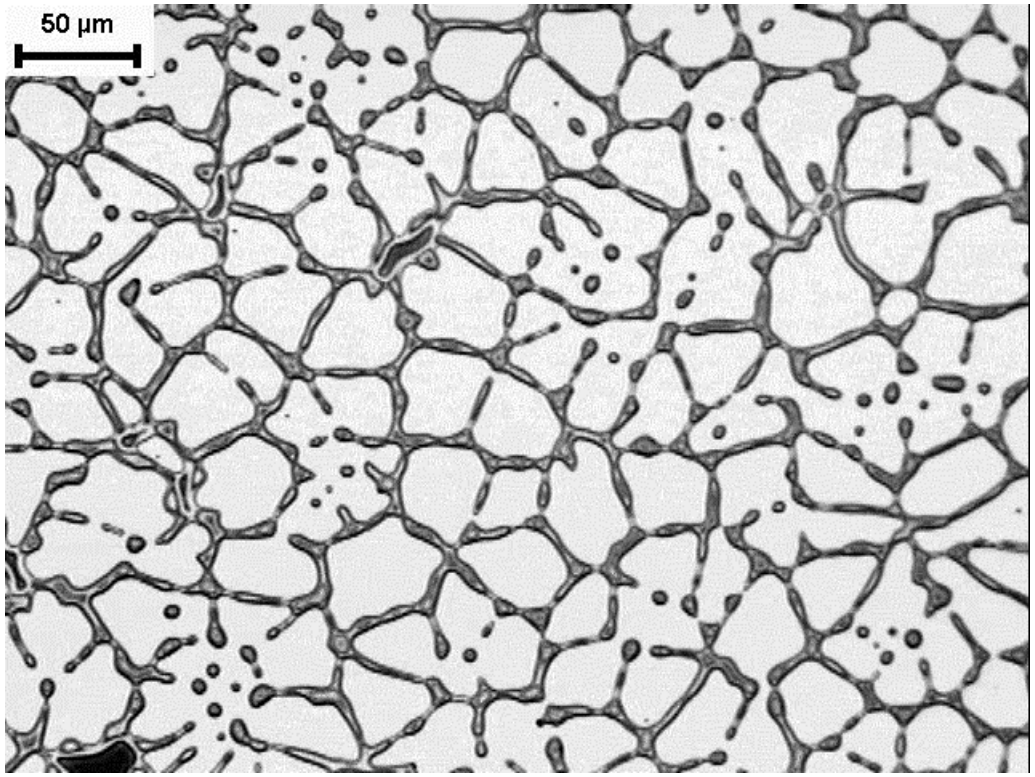
→ Cool down the Sample → So the dewetted features can again be converted to Solid and made permanent.

Spin Coated Film : ~ 40nm

At Room Temp $< T_G$

A_E +ve

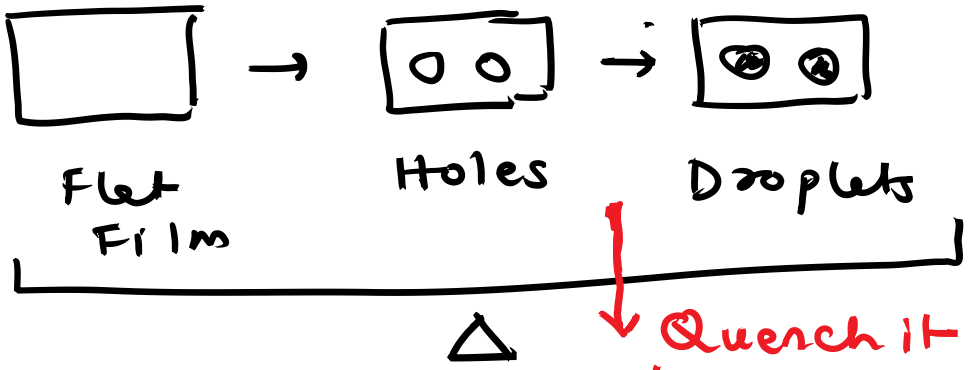
→ Film is solid Like. Viscosity is ∞.



Evolution Starts only $T > T_G$.

↳ growth of fluctuation
formation of holes.
retraction of contact line

* At room temp (any $T < T_g$), the film despite being thermodynamically unstable, the film actually remains stable. → Thermodynamically unstable but kinetically stable



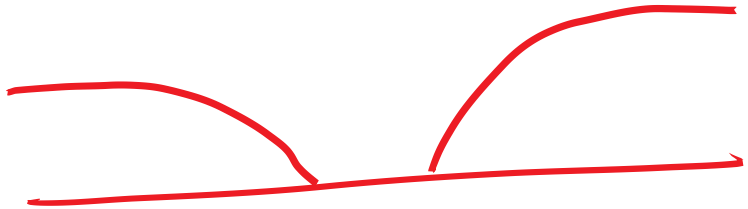
Conclusions from the video:

(1) Film is unstable.

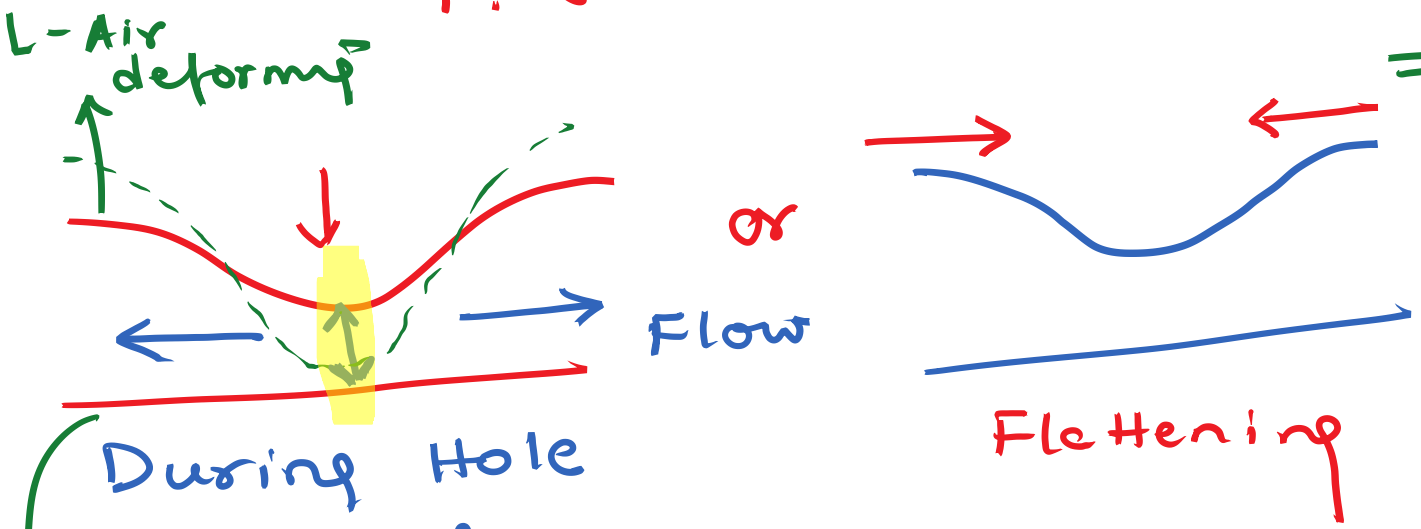
(2) Film must be at $T > T_g$.

If Complete dewetting is allowed → Film evolves to droplets.

Can you control the extent upto which the film has evolved / dewetted ? → By Controlling the Temp / Quenching the Film → Arrest the evolution.



Stop! (As film is Quenched)



(Both require Flow)

Liquid - Solid interface is Rigid

⇒

Laplace Pr. mediated flattening and

Π mediated growth

both require Flow.

Now if you bring

$T < T_G \rightarrow$

$\mu \rightarrow$ Shoots up.

(Flow gets stopped)

Instability in a Thin Polymer Bilayer :-

⇒ The system must be heated above T_G of both polymers.

⇒ How does one create such a sample ?

Sequential Spin Coating.

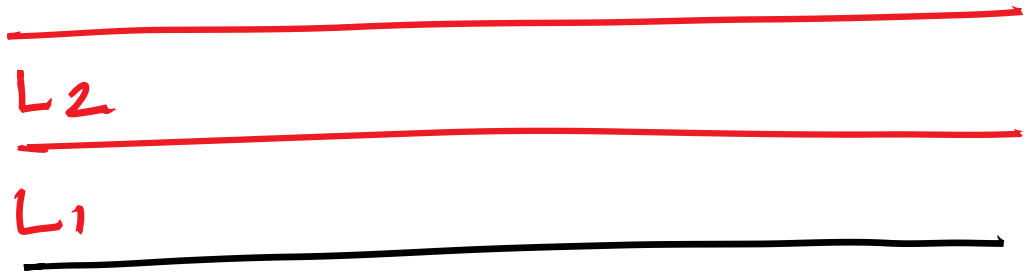
→ Coat L_1 → Allow all solvent to evaporate →
Then Coat L_2 → allow all solvent to evaporate.

Any restriction during Second spin Coating operation?
↳ in terms of choice of solvent used for Spin Coating!!

Mutually exclusive Solvent

Solvent used for Coating L_2 should not be a solvent for Layer L_1.

In case solvent for L_2 layer can dissolve the polymer used for L_1 Layer → then there will be insite disolution of film L_1 during the second Spin Coating operation.



* L_1, L_2 are both thin

$(L_1 + L_2) < 100$ nm

$T > T_{G_1}, T_{G_2} \rightarrow$

Stacked Liquids.

Evolution Sequence:-

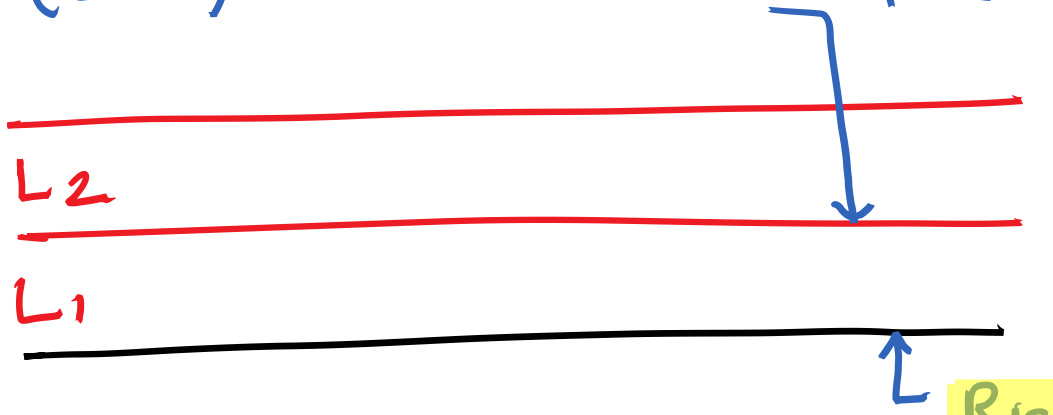
Two possible different Situations depending on which Layer becomes unsteble First.

Parameters that Can decide which Layer will become unsteble first

(1) Relative value of their h (h_1, h_2)

(2) Their thickness → vis-a-vis – Π_1, Π_2

(L-L) Deformable interface



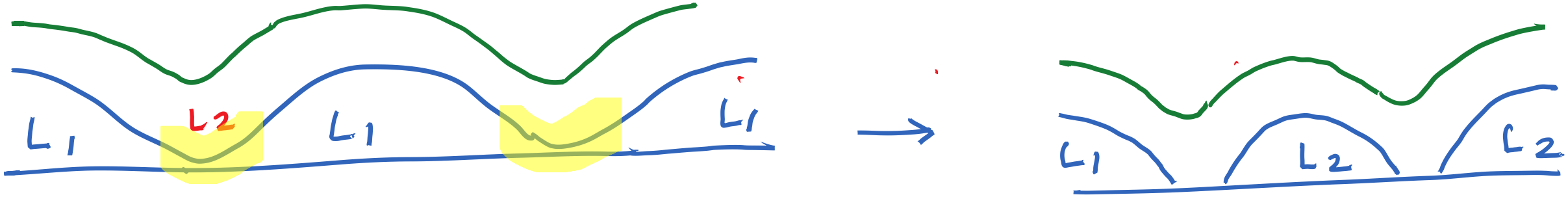
* L_1, L_2 are both thin

$(L_1 + L_2) < 100$ nm

$T > T_{G_1}, T_{G_2}$ → Stacked Liquids.

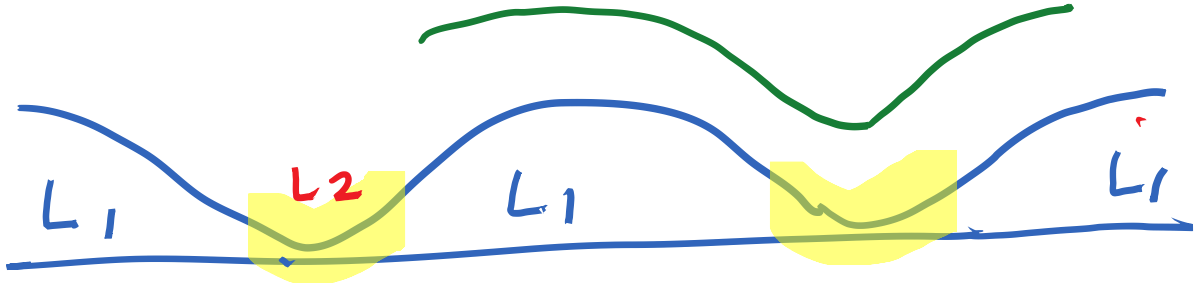
Evolution Sequence:-

Case 1: Bottom layer Becomes unstable first



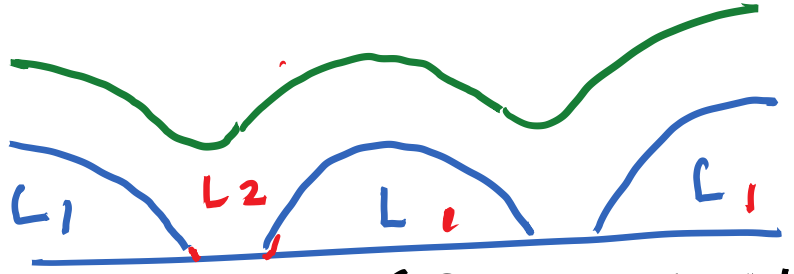
* Bottom layer Ruptures first
* Top layer Deforms in phase with the Bottom layer

Bottom layer becomes unstable first



-ve $\begin{cases} AE_{L_1-L_2} \\ AE_{L_2-S} \end{cases}$

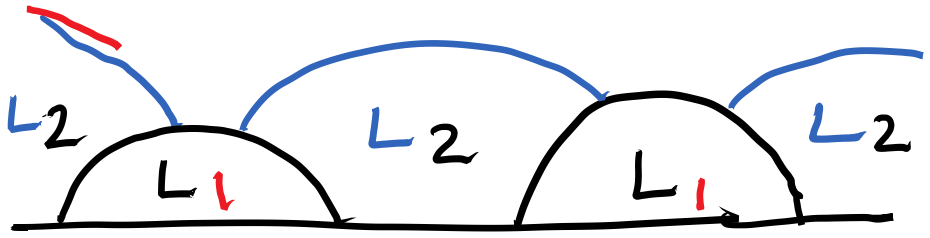
Can be the Final configuration



(Due to instb in one Layer)

* Bottom layer Ruptures first
* Top layer Deforms in Phase with the Bottom layer

Case A: The intact top layer has ruptured over the L_2 droplets

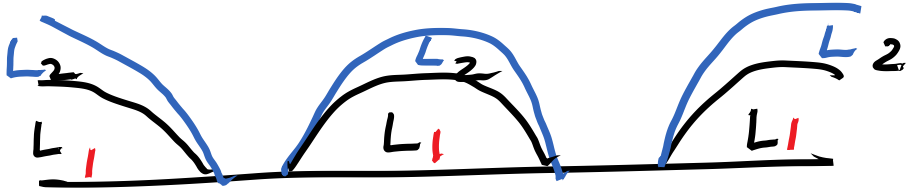


L_2 is unstable over L_1

Case B:

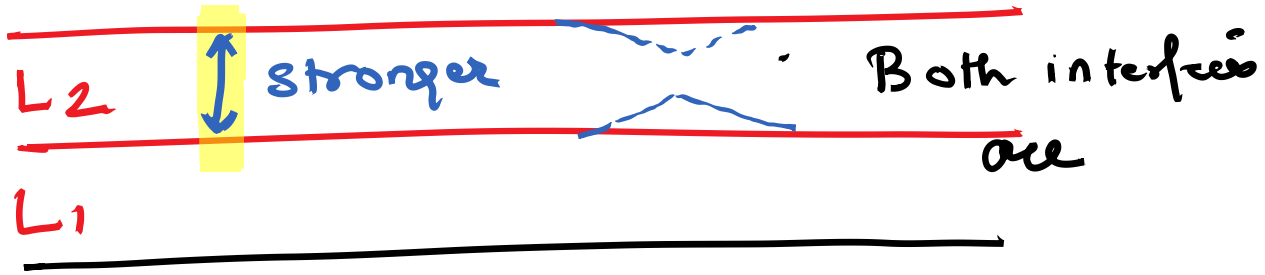
The intact L_2 unstable over the solid Surface.

If any of the Disjoining Pressure → $S-L_2$ interaction, L_1-L_2 interaction } will lead to instability →



Core Shell droplets

Interaction is between two deformable interfaces —



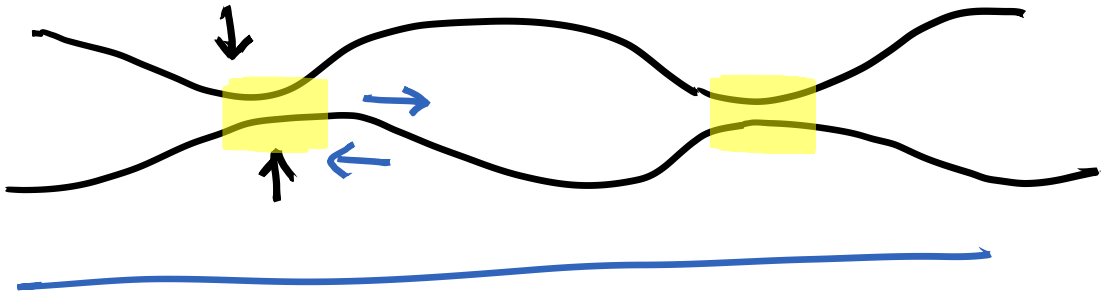
Both interfaces are

* L_1, L_2 are both thin $(L_1 + L_2) < 100$ nm

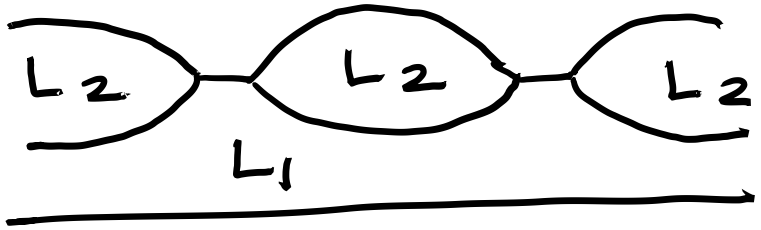
$T > T_{G_1}, T_{G_2}$ → Stacked Liquids.

Evolution Sequence:-

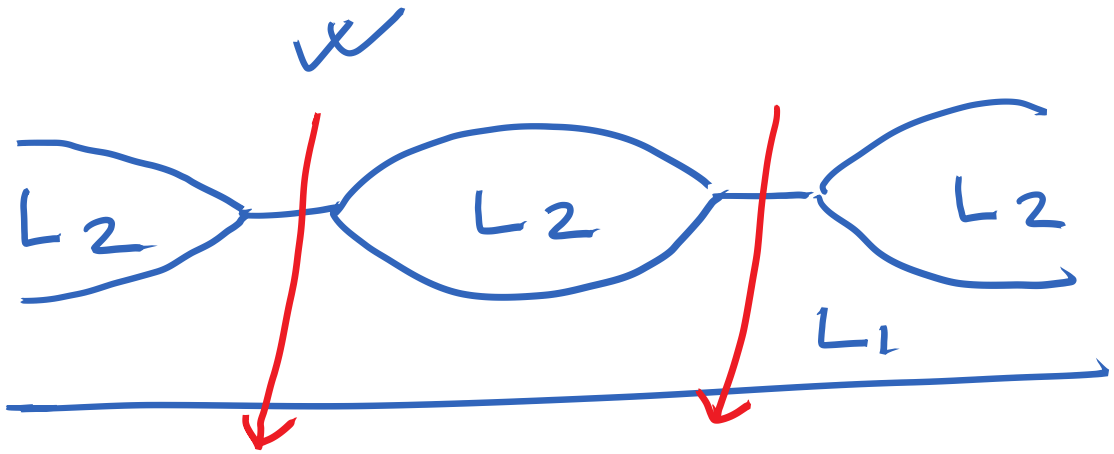
Case 2: Top layer Becomes unstable first:



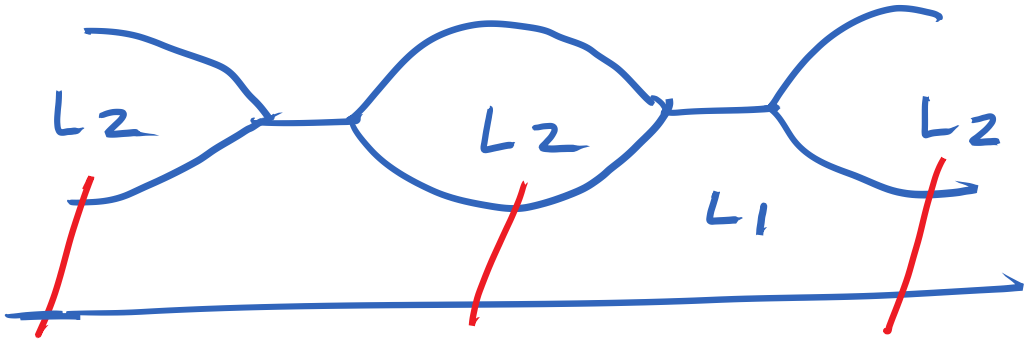
The instability is manifesting between two deformable Interfaces

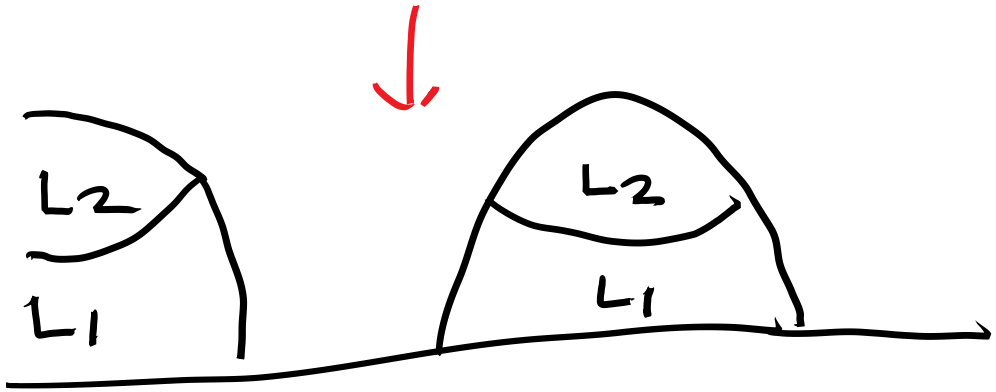


* Top layer Ruptures first
* Bottom layer Deforms out of phase wrt the Top layer

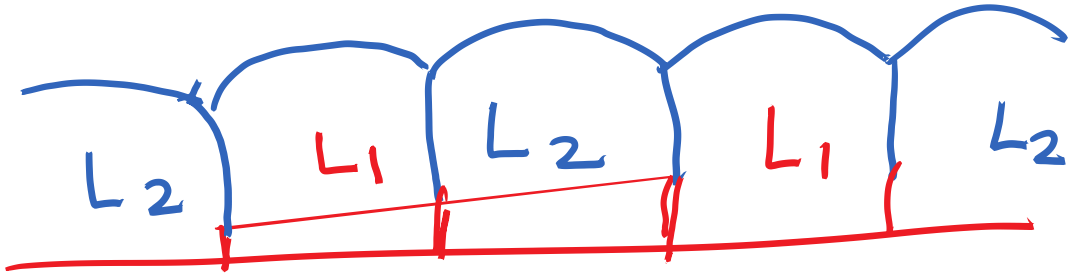


Either the





Crown type droplets



Laterally co-existing structures.