Delayed coating of a liquid film on a deformable substrate, in a partially wetted condition

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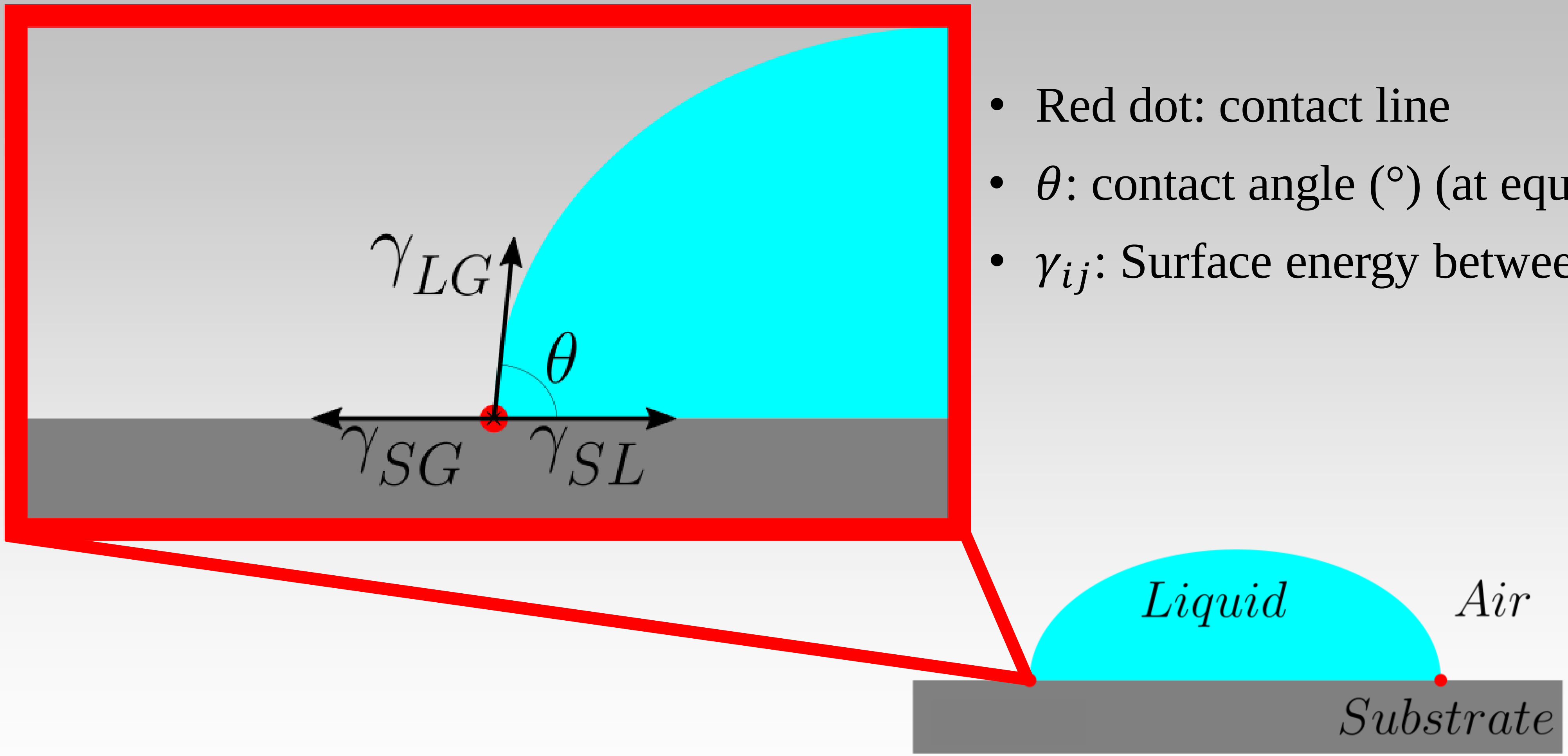
Co-director: Laurent Limat
Supervisor: Julien Dervaux
Co-supervisor: Matthieu Roché

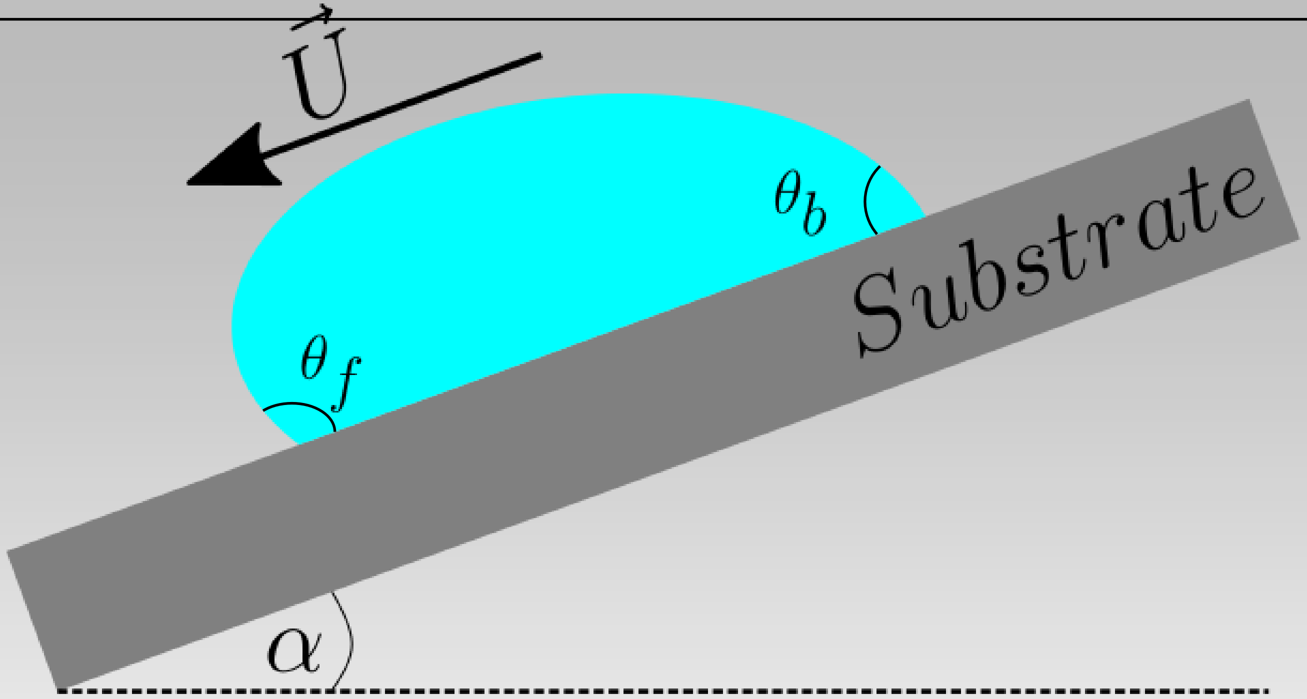
ANTHONY VARLET

Introduction : Wetting statics



- Red dot: contact line
- θ: contact angle (°) (at equilibrium)
- γ_{ij}: Surface energy between phases i and j (J/m²)

Introduction : Wetting dynamics



- Drop in movement → induces viscous stress

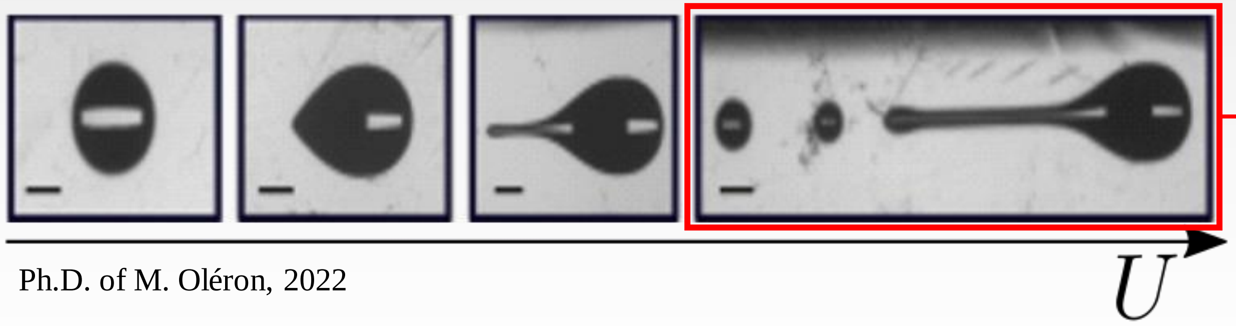
→ $Ca = \frac{\eta U}{\gamma_{LG}}$: Capillary number

- $\theta_f = \theta + f(Ca) > \theta$

→ forward contact angle (°)

- $\theta_b = \theta - f(-Ca) < \theta$

→ backward contact angle (°)



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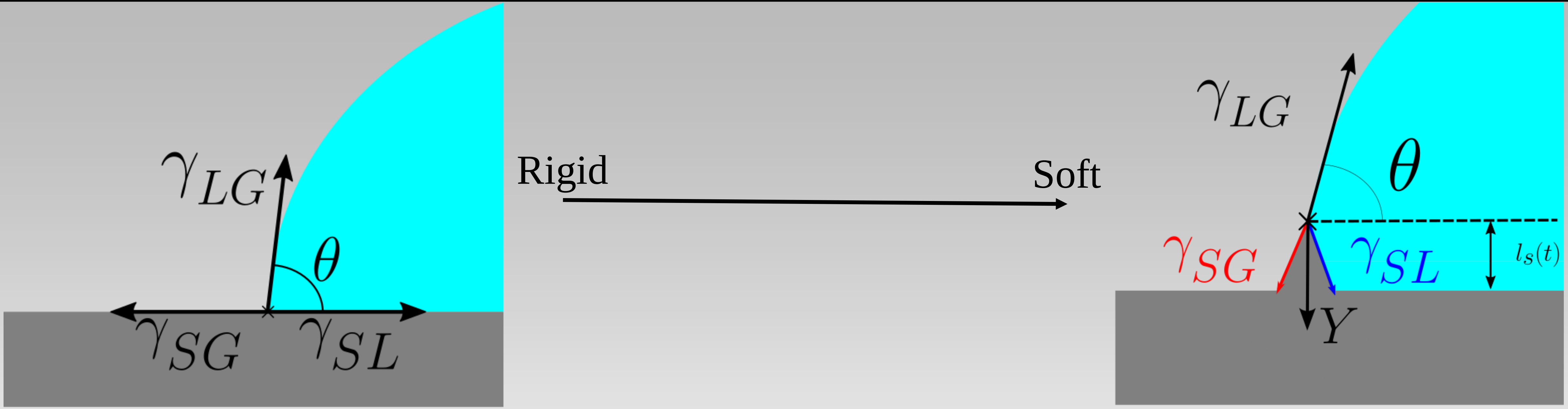
Above a critical droplet speed
→ liquid deposition regime

Context of this study



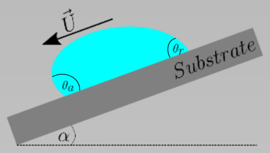
Questions

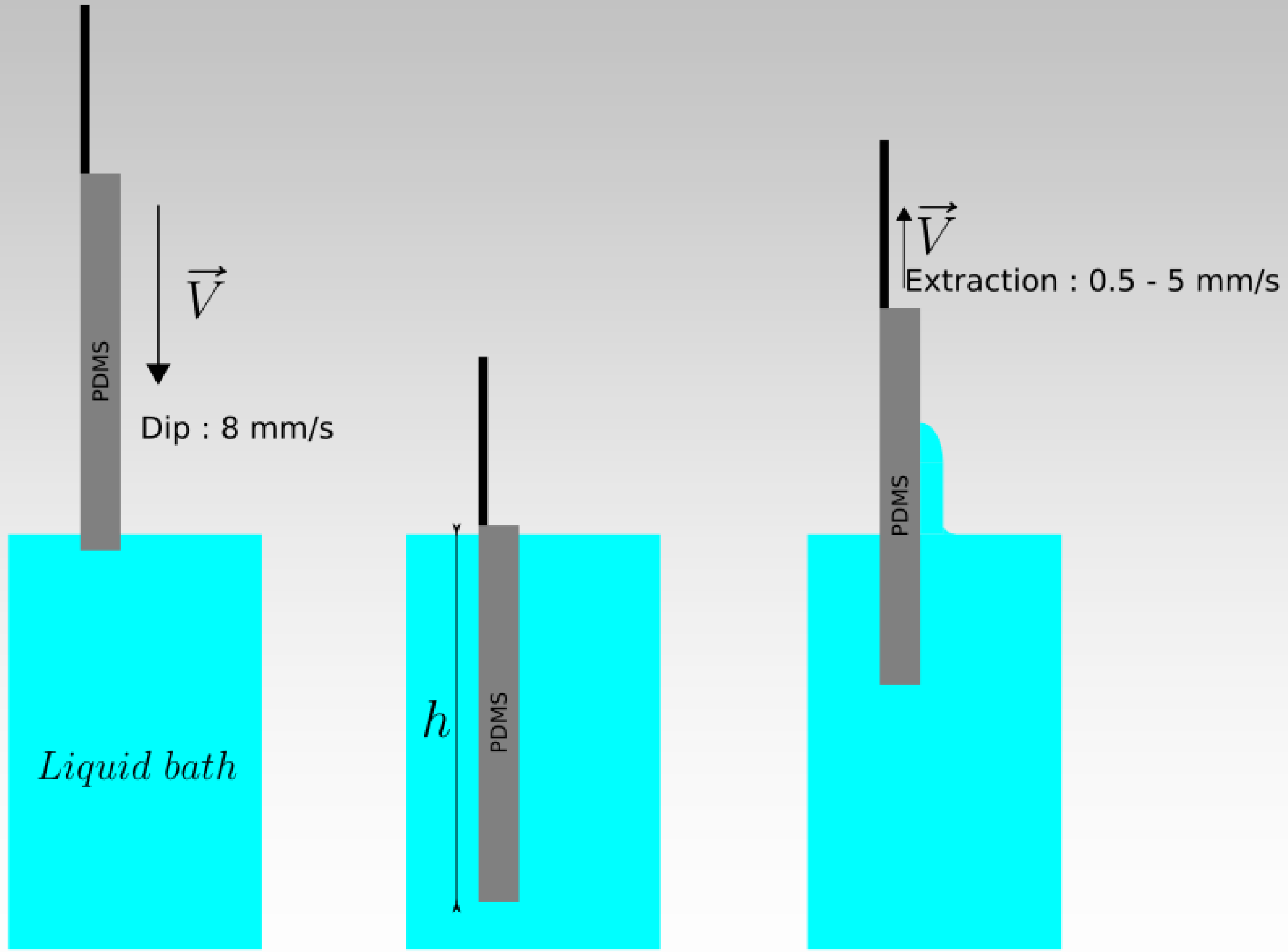
1. Deformation at contact line → Additional dissipation → What changes?
2. Substrate deformation → Favors or damps instabilities at contact line?

Experimental set-up

2 classic set-ups:

- Sliding droplet
- Dip-coating





- Straight contact line
- Pulling speed: controlable parameter

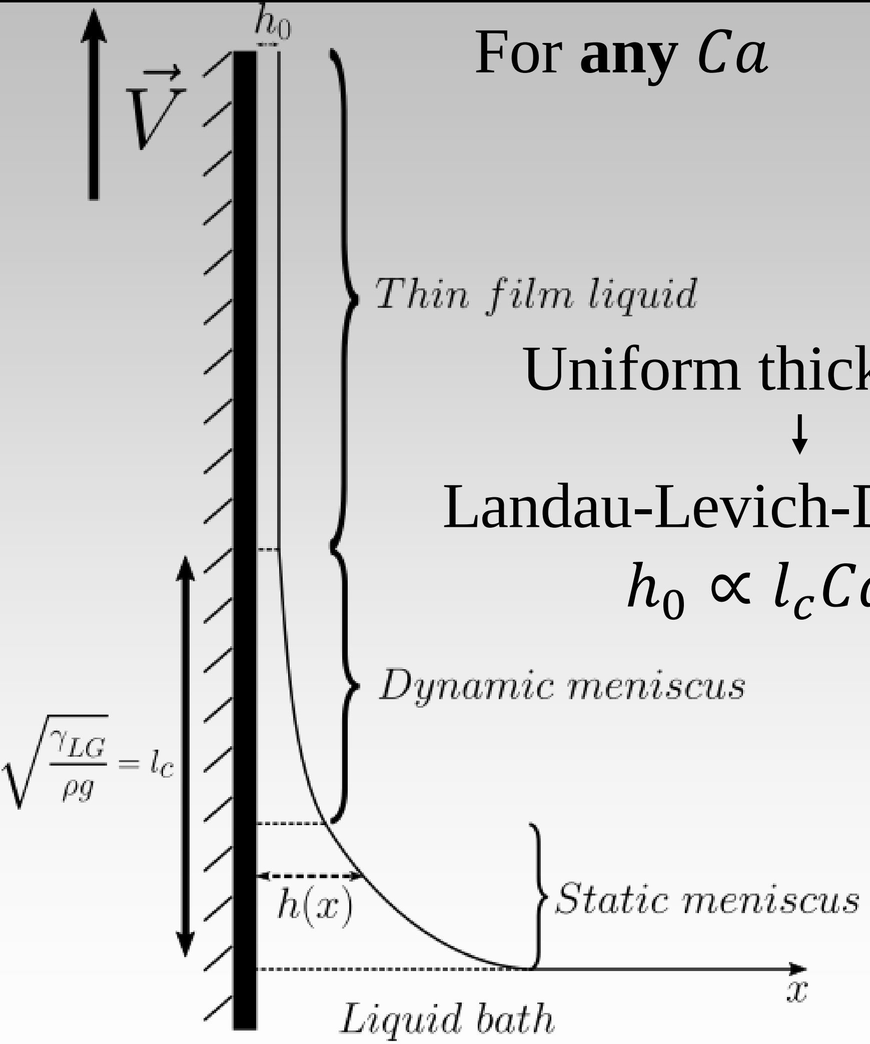
Liquid used : Pure Glyverol ($\eta = 1{,}291 \pm 0{,}301\ Pa.s$)

Sylgard 184™ Elastomeric Gel (Dow Corning)
→ Young modulus : 7 kPa – 1,6 MPa *

* Glover, J. D. *et al*, 2020 JOURNAL OF POLYMER SCIENCE

Dip-coating : Non-deformable case

Total wetting



For **any** Ca

Uniform thickness h_0

↓

Landau-Levich-Derjaguin*:

$$h_0 \propto l_c Ca^{2/3}$$

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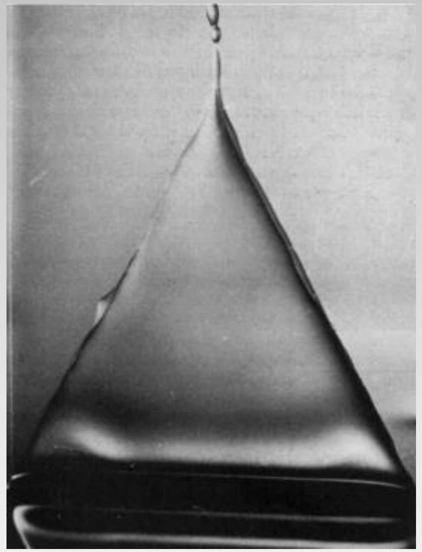
*L. D. Landau and B. V. Levich, 1942 Acta Physicochim.

Partial wetting

Criteria of coating $\Leftarrow Ca_{thresh}$

Snoeijier, J. *et al.*, 2006 PRL



T. D. & Ruschak, K. J., 1979 Nature

Trapezoidal shape

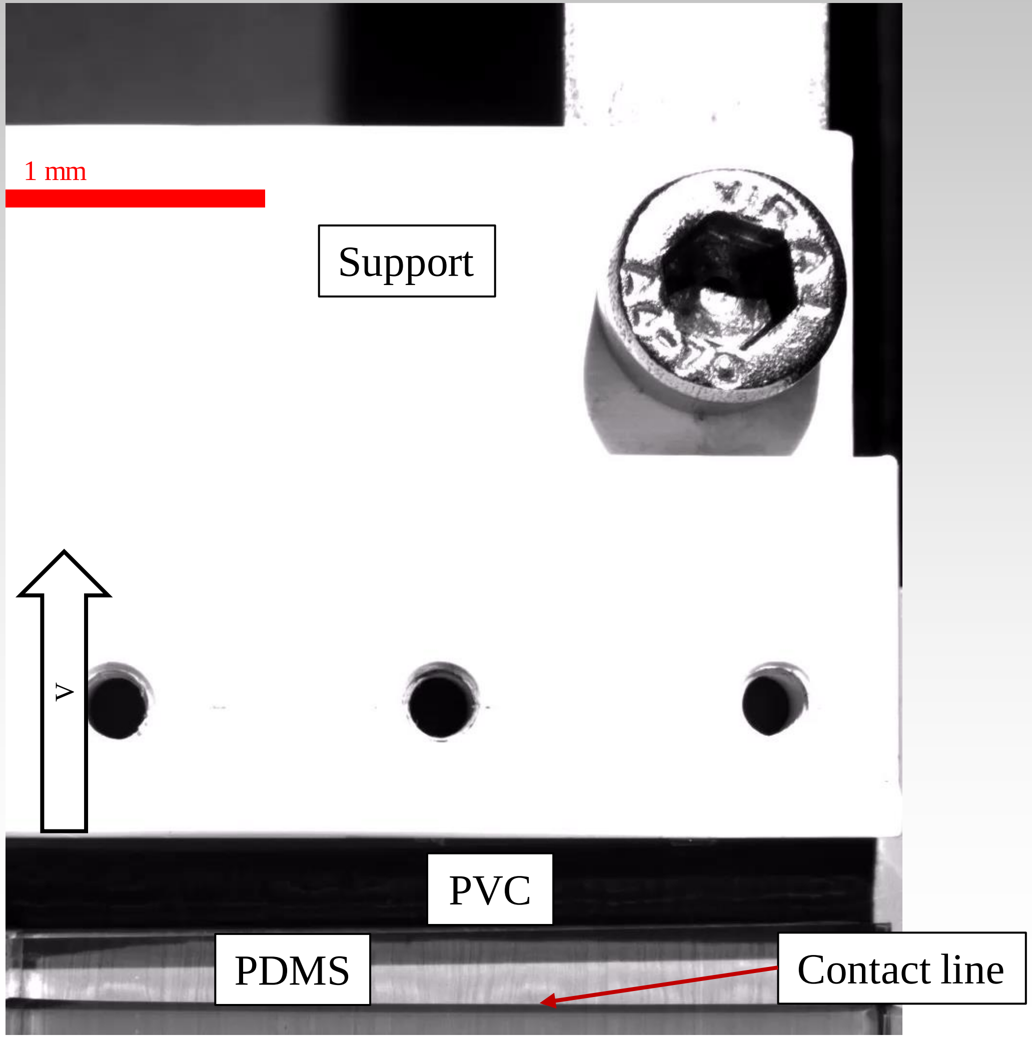
↳ Contact line on the side receding during extraction

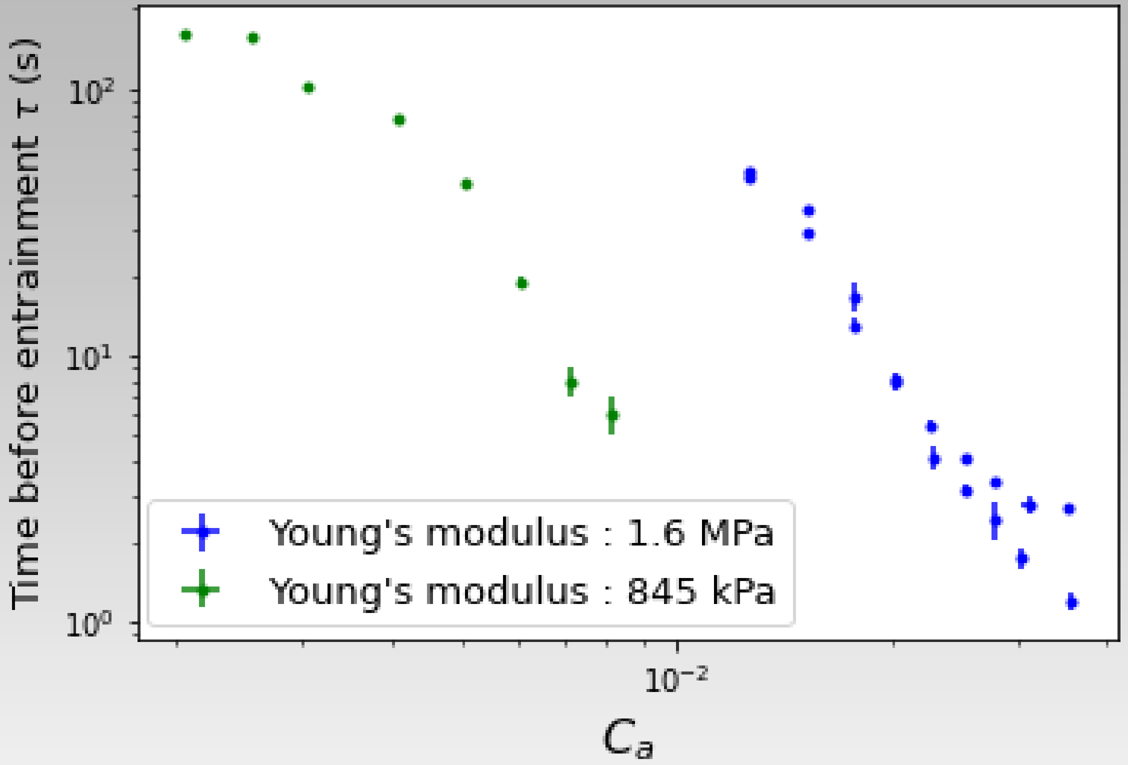
Bulge near the contact line

↳ Separate edge of contact line with rest of the film (LLD-like)

Observation with deformable substrate

Coating with treshold in Ca, like rigid case
Coating not instantaneous, unlike rigid case
→ Delay of liquid entrainment





Lower Young Modulus shifts the range toward lower Ca
Sharp decrease of τ with Ca
↓
Origin?

Phenomenom 1 : Slowly deforming surface of substrate

Force balance at contact line:

- Horizontal: balance of capillary forces and viscous shear stress
- Vertical: elasticity of substrate counterbalances capillary force

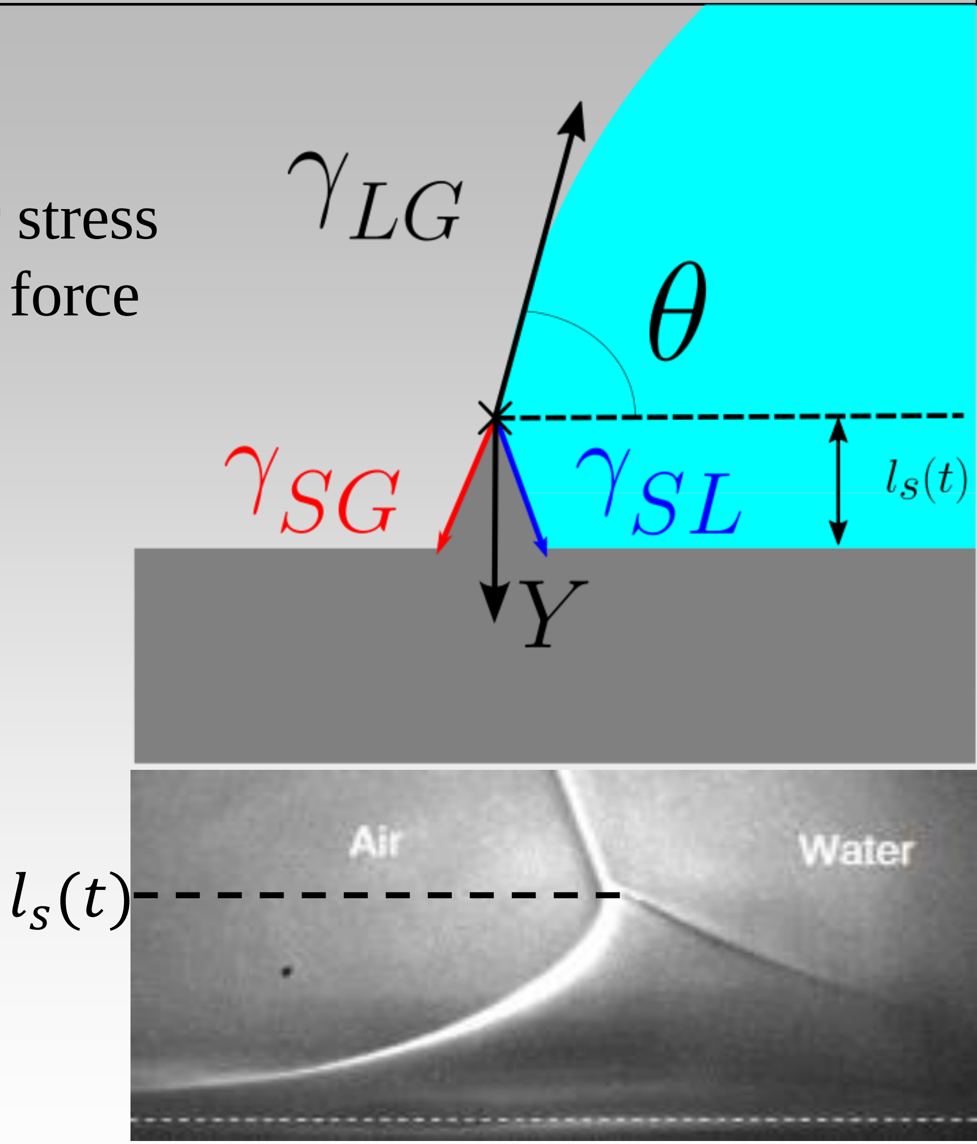
Deformation at contact line

Elastocapillary length: $l_s \propto \frac{\gamma_s}{Y}$

More (slowly increasing) dissipation

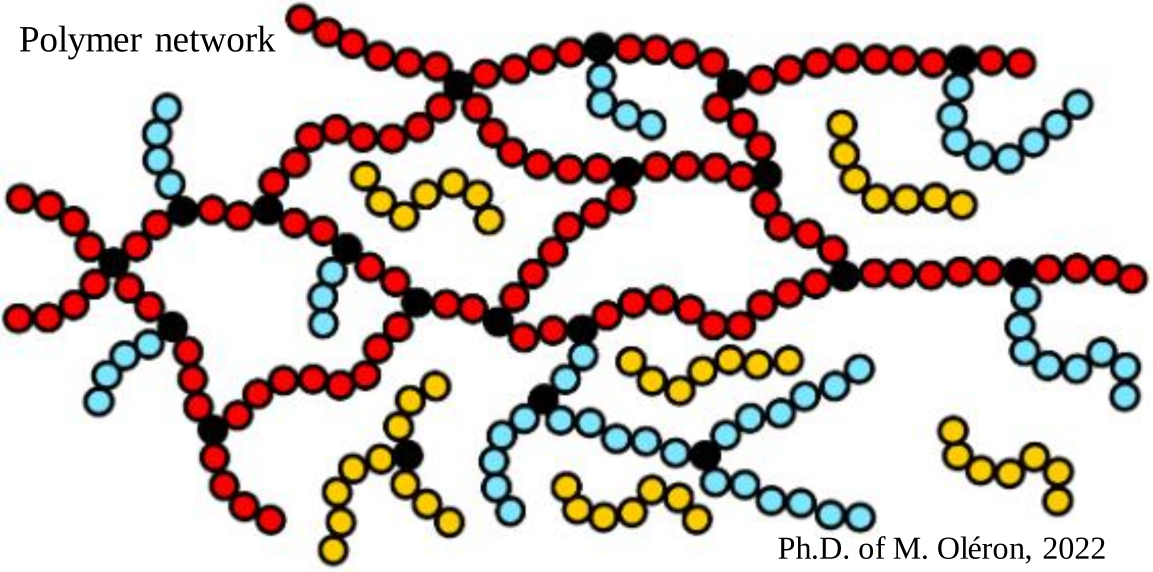
Inside the solid

1. Contact line in movement → Propagating ridge
2. Slow & progressive growth of the ridge



S.J. Park *et al.*, 2014 Nature

Phenomenom 2 : Free-chains slowly moving toward the surface



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Red chain

Blue chain

Yellow chain « Free-chain »
⮡ Poroelasticity

Free-chain washing
↓
Entrainement delay should be suppressed
↓

During extraction
Close to the contact line
Slow reorganization of free-chains

Conclusion

- Unlike rigid case: delay for liquid entrainment

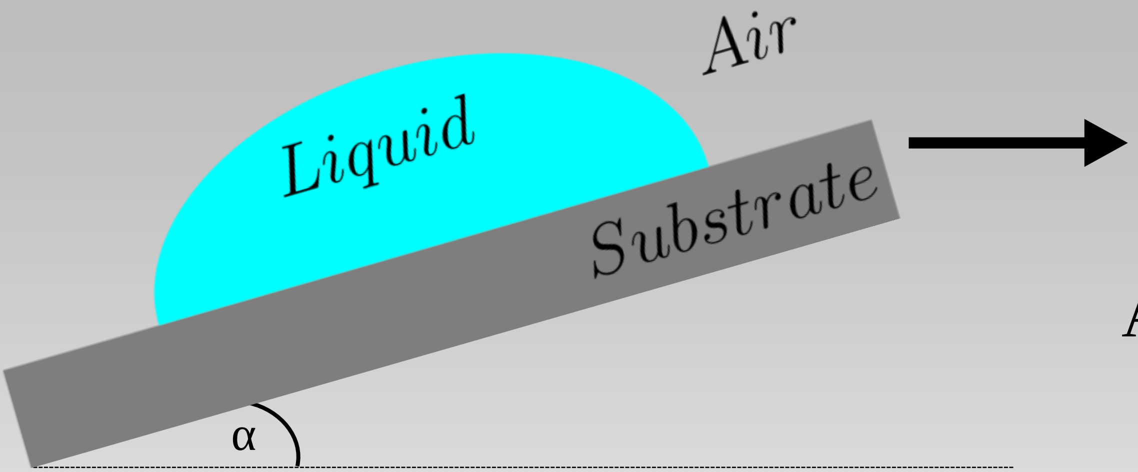
  ⇒ delay time decreases strongly with C_a

- Possible mechanisms underlying delay:
  1. presence of free-chains in substrate ⇒ Work in progress
  2. substrate deformability ⇒ Smaller range of C_a for a smaller Young's modulus

     ⇒ favor liquid entrainment?

Thanks everyone for your attention !!!

Introduction : Context of this work

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Above a critical droplet speed → liquid deposit regime

Characterize this regime with θ

In theory

$C_a \nearrow \Rightarrow \theta \searrow$

$C_{a_c} \Rightarrow \theta = 0$

In practice

$C_a \nearrow \Rightarrow \theta \searrow$

$C_{a_c} \Rightarrow \theta \neq 0$

(near 30°)

Contradiction with the experiment not well understood
→ back of a drop not fully understood

Change experimental system
→ study contact line with simpler geometry

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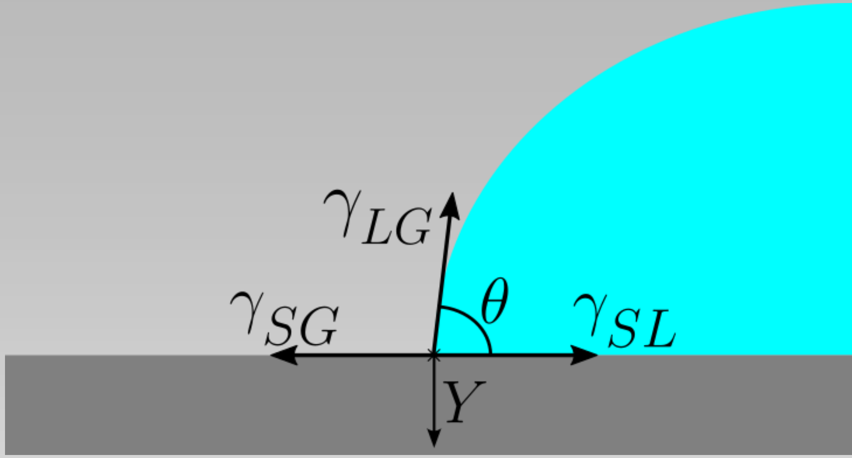
Origin 1 : Deformable surface

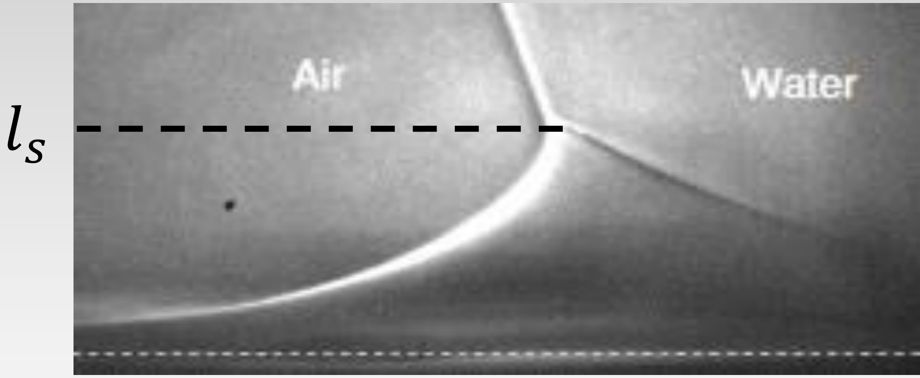
Force balance at contact line:

- Horizontal: balance of capillary forces ($\gamma_{SL} \sim \gamma_{SG}$)
- Vertical: elasticity of substrate meet capillary force



Deformation at contact line

Elastocapillary length: $l_s \propto \frac{F_{cap}}{Y}$



S.J. Park *et al.*, 2014 Nature

$$GP_a > Y > MP_a$$

$$10^{-11} m < l_s < \boxed{10^{-8}\ m}$$

Rigid

~~Deformation~~

[Thickness film ~ 10-100 µm]

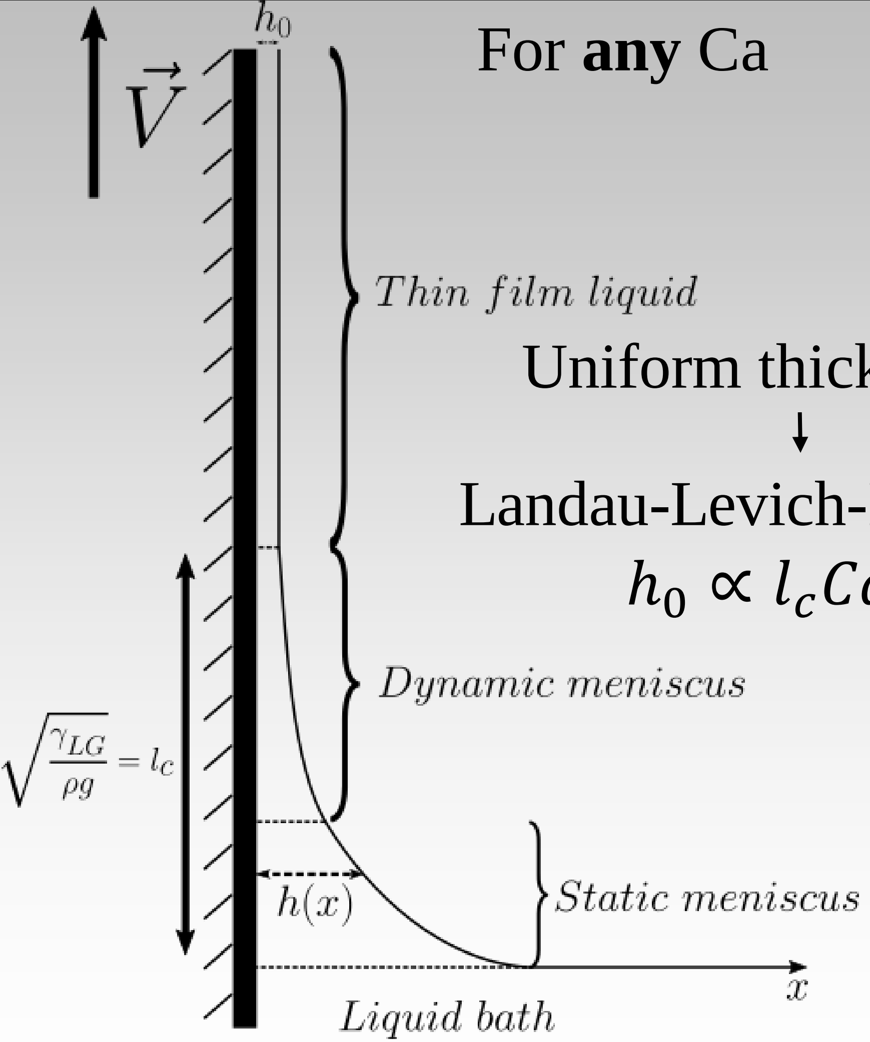
Soft

Can impact the flow

Slow & progressive growth of the ridge at contact line in movement

Dip-coating : Non-deformable case

Total wetting



For **any** Ca

Uniform thickness h_0

↓

Landau-Levich-Derjaguin:

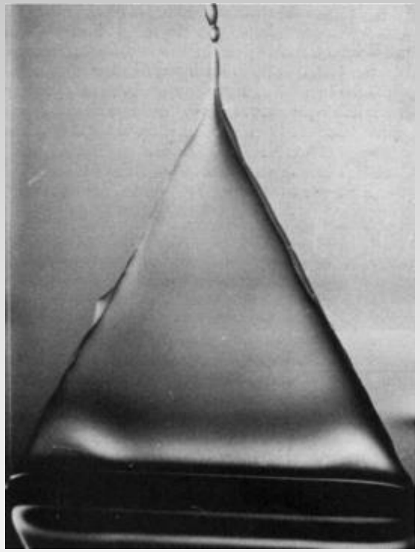
$$h_0 \propto l_c Ca^{2/3}$$

Partial wetting

$\boxed{\text{Criteria of coating}} \Leftarrow Ca_{thresh}$

↳ Viscous dissipation $D = f(Ca) > D_{thresh}$

Snoeijier, J. *et al.*, 2006 PRL



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Trapezoidal shape

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Bump at contact line

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Properties of sample & liquid used

Sample used : PDMS (polydimethyl-siloxane) used:

1. Sylgard 527™ Dielectric Gel (Dow Corning)
   → Young's modulus : 3 kPa
2. Sylgard 184™ Elastomeric Gel (Dow Corning)
   → Young's modulus : 7 kPa – 1,6 MPa

Liquid used :

- Glycerol (more & less) pure, G100 :
  $\gamma \sim (63{,}1 \pm 0{,}5)10^{-3}\ J/m^2,\ \eta \sim 1{,}291 \pm 0{,}301\ Pa.s$
- Ucon (lubricant, Dow Corning) :
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Dissipation ratio

Liquid in movement

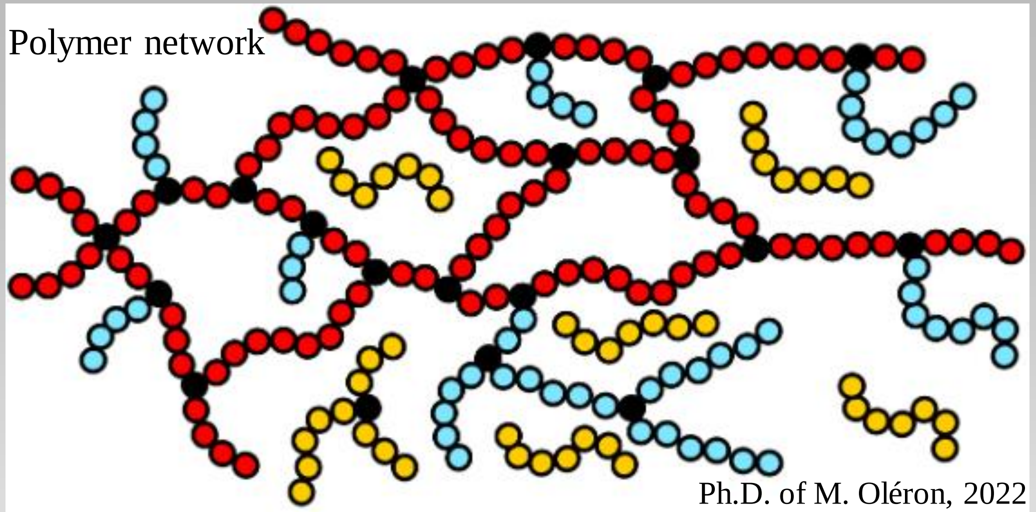
- Viscous energy dissipation in the liquid
- Propagation of the deformation

→ Energy dissipation in solids of viscoelastic origin

Importance of viscoelastic energy dissipation: relaxation ratio $R \propto \frac{E_{solid}}{E_{liquid}}$

$$\begin{cases} R \gg 1\text{, most of the energy dissipated in the solid state} \\ R \sim 1\text{, equivalent energy dissipation in solids and liquids} \\ R = 0\text{, energy dissipation exclusively in the liquid} \end{cases}$$

Phenomenom 2 : Free-chains slowly moving toward the surface



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Free-chain washing

↓

Entrainement delay should be suppressed

↓

During extraction
Close to the contact line
Slow reorganization of free-chains

Red chain

Under stress: stretch and store elastic energy

Blue chain

Yellow chain « Free-chain »

} Under stress: can relax and/or move in the network

↳ mechanical response with viscoelastic contribution

Poroelasticity

Phenomenom 1 : Slowly deforming surface of substrate

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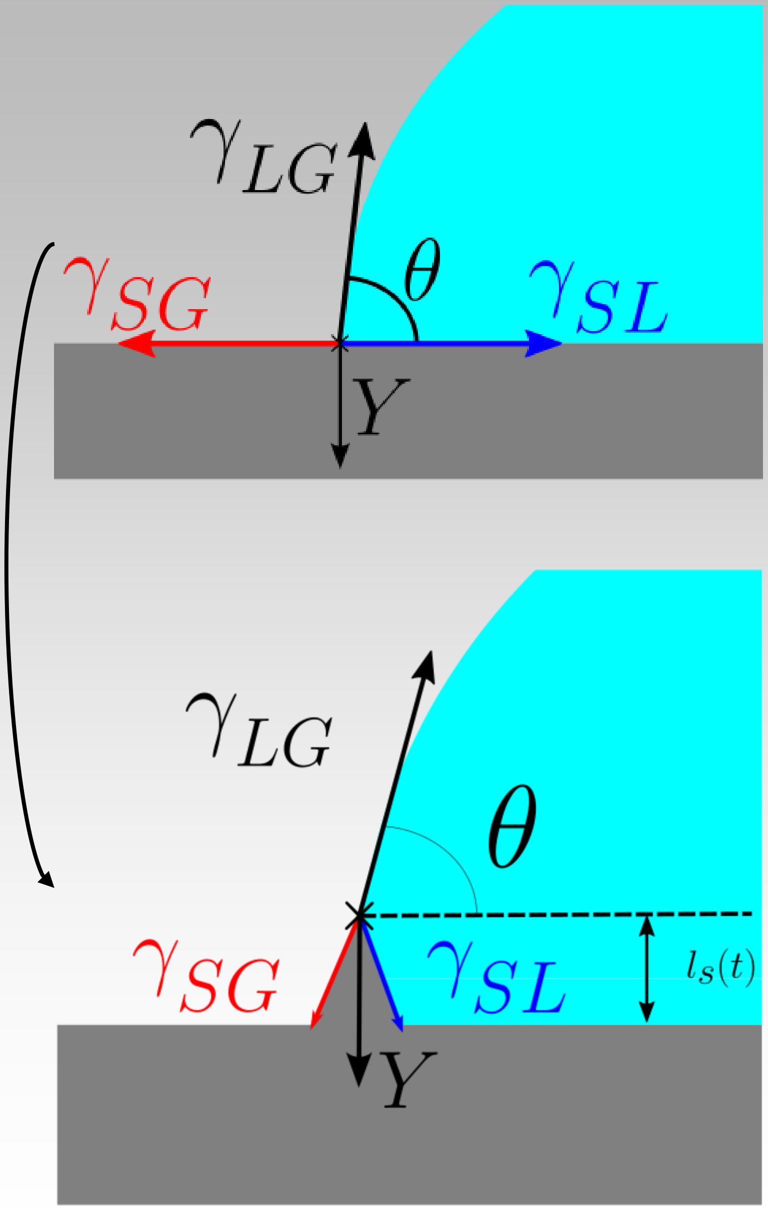


Time condition

Transition time : time between of dip velocity to pulling velocity

In experiment : 200-500 ms

Augment this time ⇒ Influence?

Waiting time between diping

Substrate as a time to come-back to is initial state

Influence the coating ⇒ Have an « history »

Video 2 – Time between dip : 30 secondes.
Left : n°1, middle : n°3, right : n°5.

How many secondes waiting?

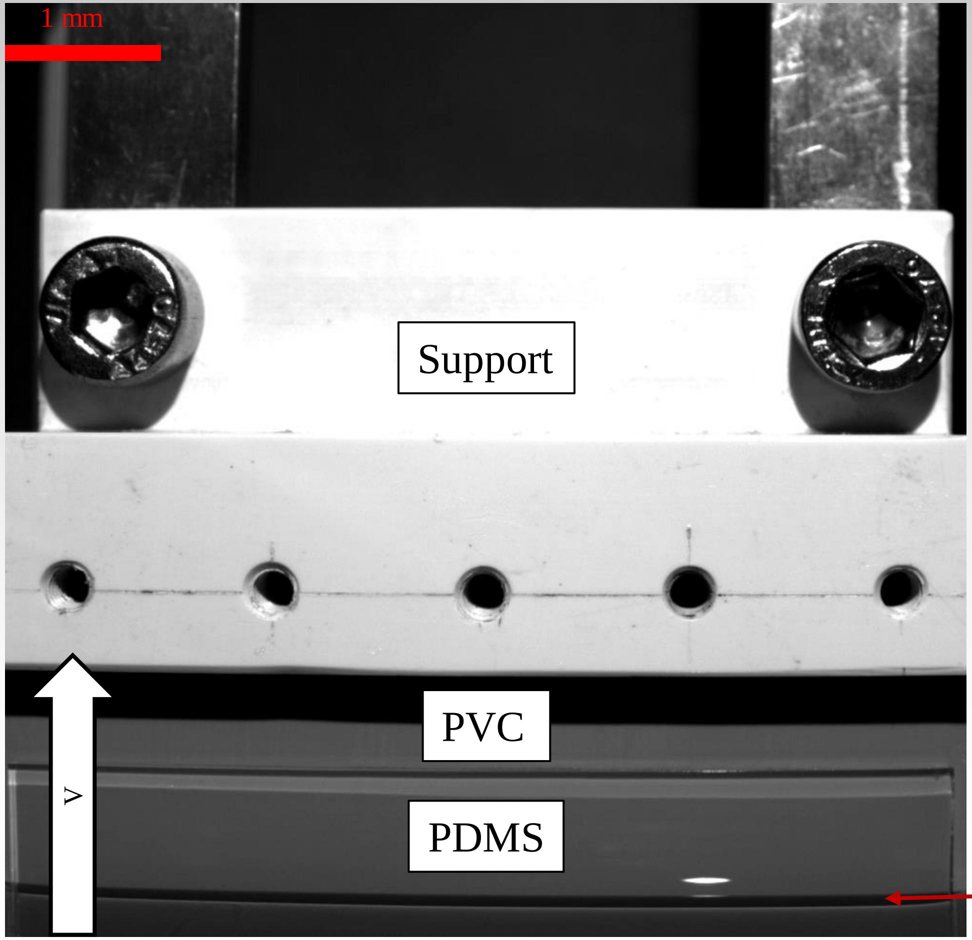
↓

Experiment at fixed Ca and compared coating delayed for 30, 100 and 1000 secondes

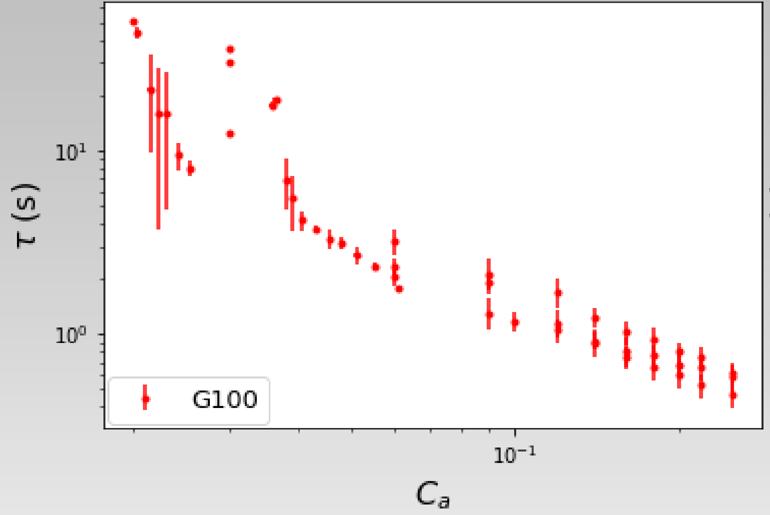
Observation with deformable surfaces

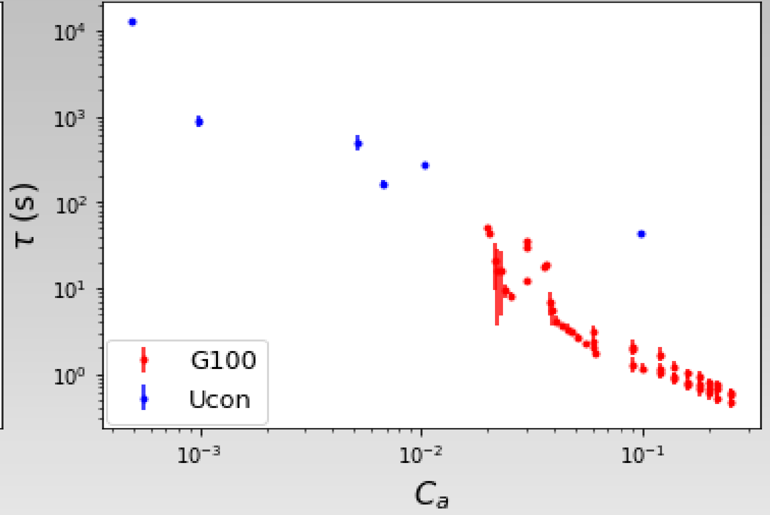
Coating not instantaneous, unlike rigid case

→ Delay at liquid entrainment



Contact line



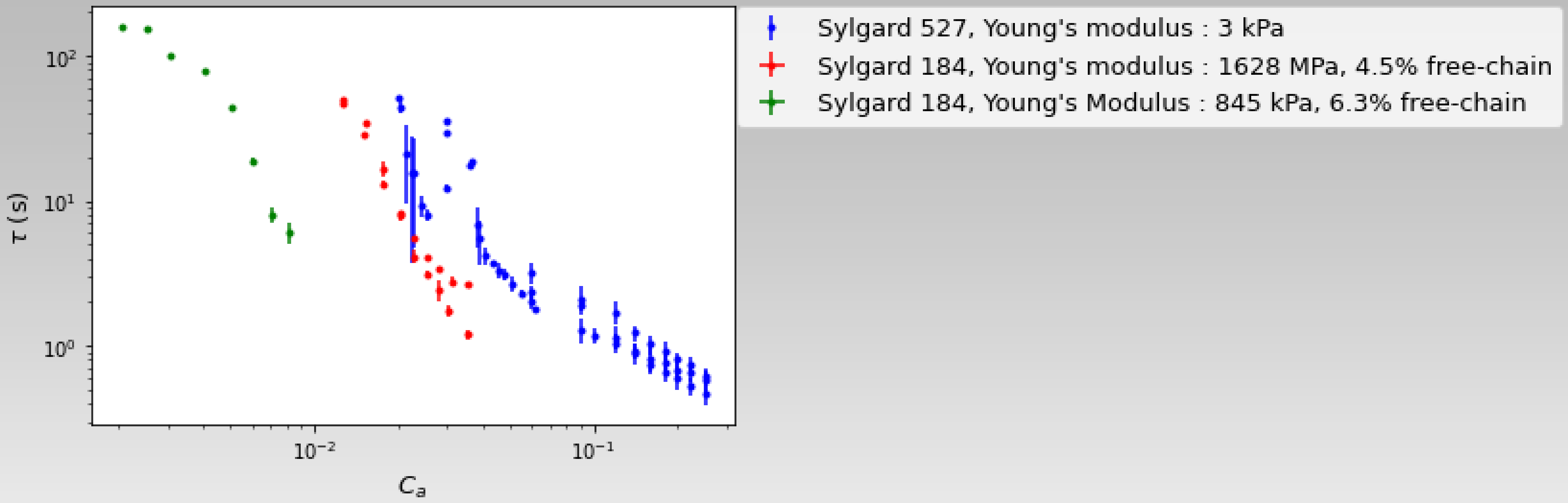


Possible master curve guiding the delay time with C_a

↓

Origin?

Origin 1 : Young modulus effect



Sylgard 184 :

- 1,6 Mpa → Shift lower Ca for delay ($\sim 10^{-2}$)
- 845 kPa → Shift less lower Ca for delay ($\sim 10^{-3}$)

↓

Same results with lower Young’s modulus (7, 59, 245 & 845 kPa) ?

Less free chain in Sylgard 184

↓

add free-chain ?

Introduction : Context of this study

In theory

$$Ca \nearrow \Rightarrow \theta_{back} \searrow$$

$$Ca_c \Rightarrow \theta_{back} = 0$$

In practice

$$Ca \nearrow \Rightarrow \theta_{back} \searrow$$

$$Ca_c \Rightarrow \theta_{back} \neq 0$$

(near 30°)

Contradiction with the experiment not well understood
→ back of a drop not fully understood

Change experimental system
→ study contact line with simpler geometry

Time condition : Sylgard 527 (3 kPa)

Figure 11 – Waiting time for Sylgard 527 between dipping of the substrate at Ca = $4\ 10^{-2}$.
Left : Wait time = 30s. Middle : 100s. Rigth : 1000s.

Sylgard 527 → not reliable enough

Time condition : Sylgard 184 (1,6 MPa)

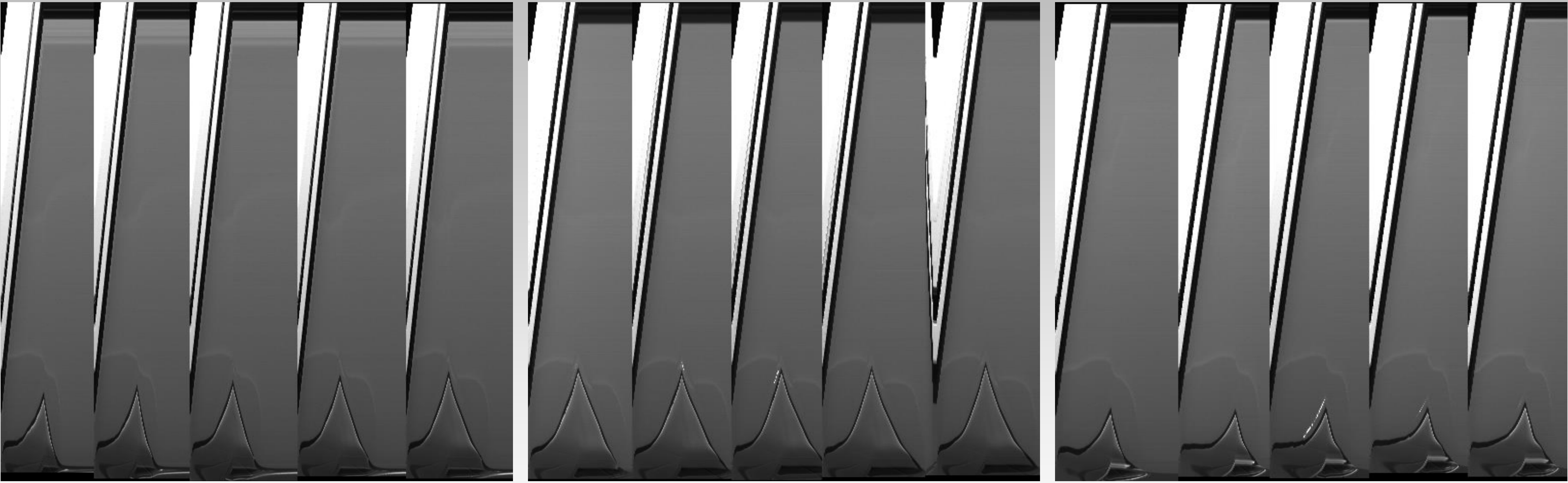


Figure 12 – Waiting time for Sylgard 184 between dipping of the substrate at Ca = 4 10^{-2} .
Left : Wait time = 30s. Middle : 100s. Rigth : 1000s.

Sylgard 184 at 1,6 MPa → wait time of 100s sufficient reliable

Time condition : Sylgard 184 (7 kPa)

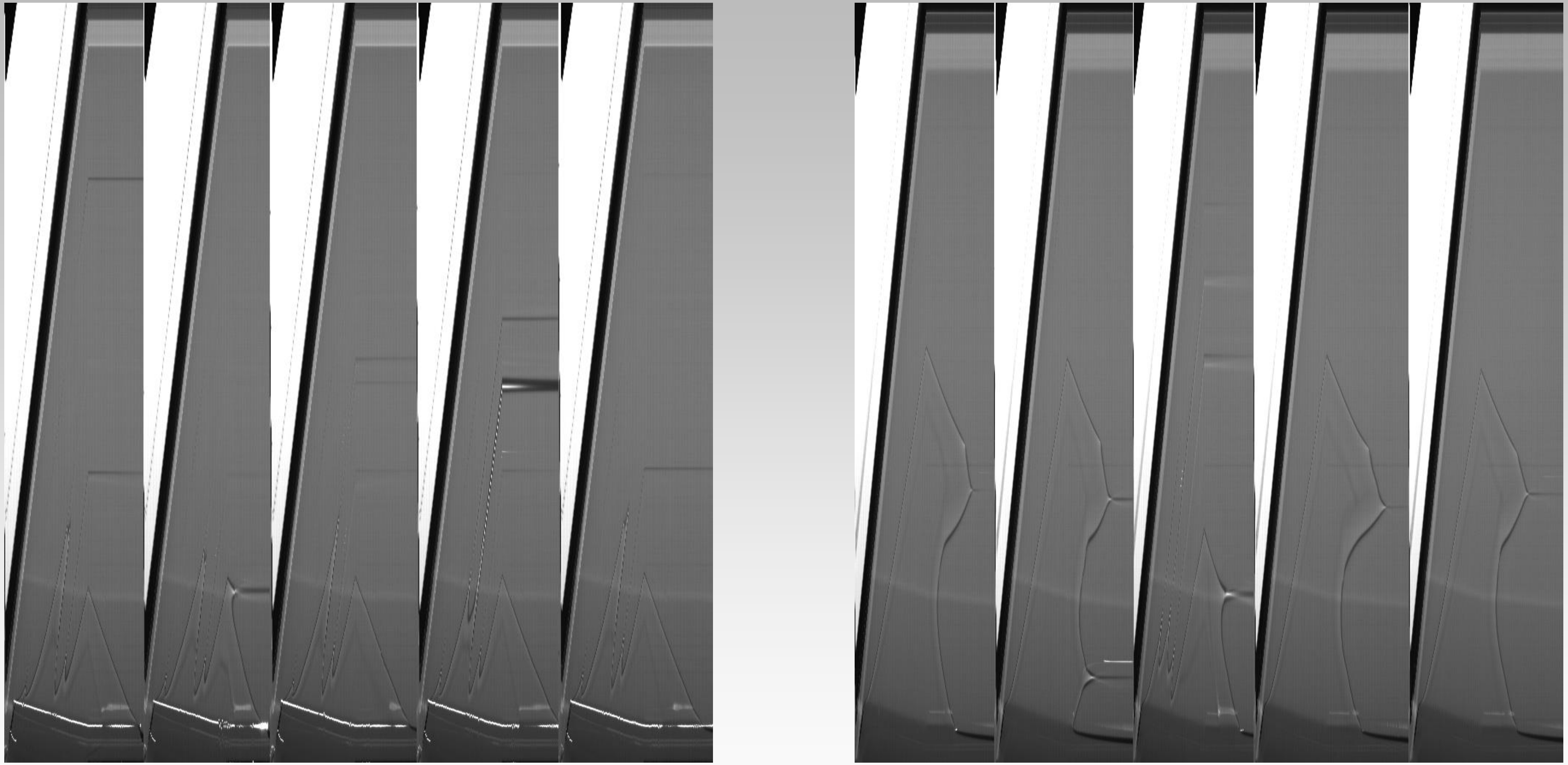


Figure 13 – Waiting time for Sylgard 184 between dipping of the substrate at Ca = 9,4 10^{-5} .
Left : Wait time = 100s. Rigth : 1000s.

Sylgard 184 at 7 kPa → Hard to define wich waiting time

Perspectives : Shape of contact line

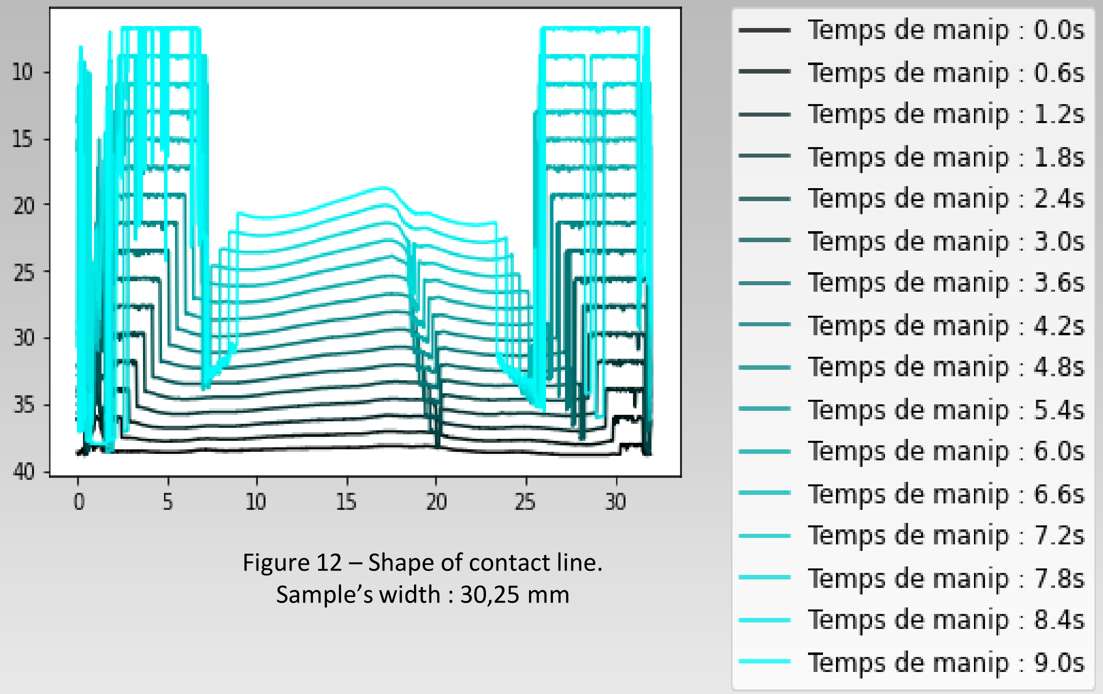


Figure 12 – Shape of contact line.
Sample's width : 30,25 mm

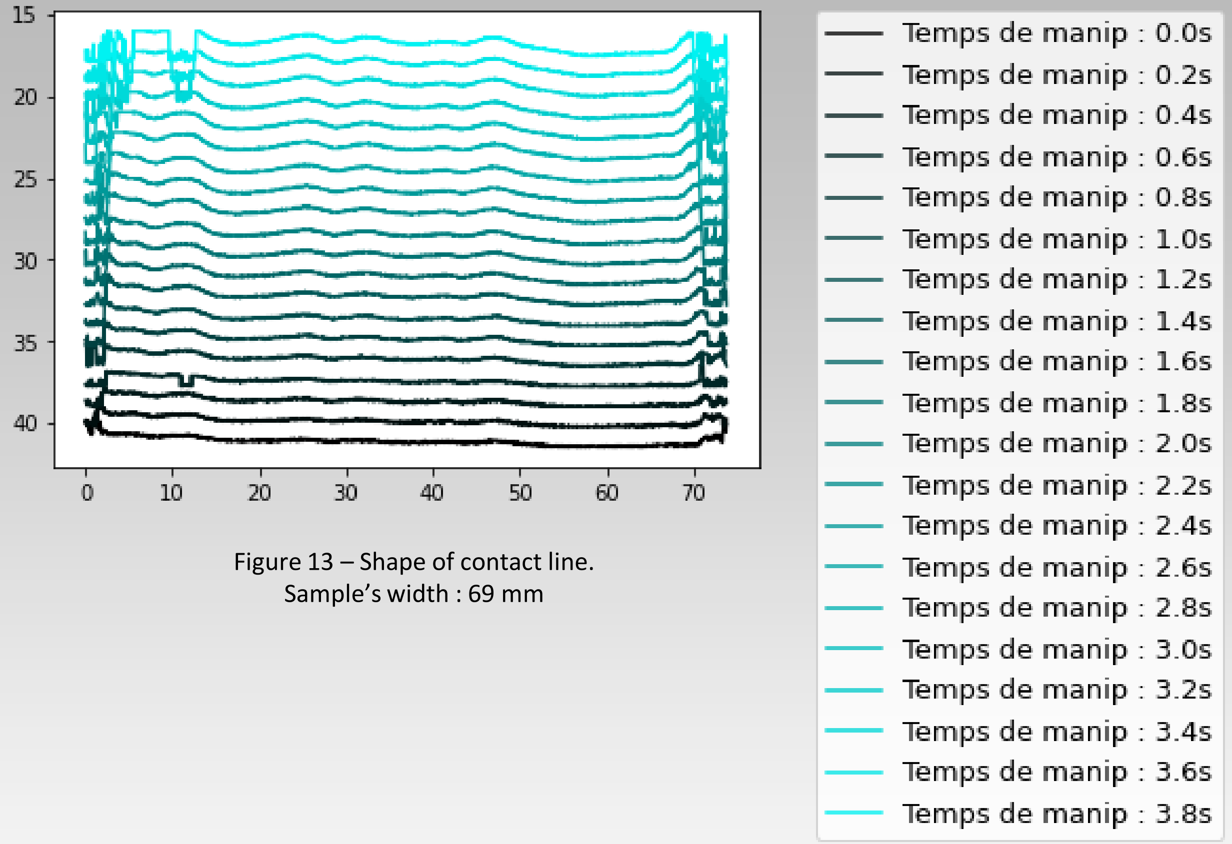


Figure 13 – Shape of contact line.
Sample's width : 69 mm

Instability-like?
- Average « wavelength » of ondulation?
- Size dependent?

→ Upgrade program & ligthing of set-up

Introduction : Context of this work

u_C

(near 30°)

From a critical droplet speed
→ liquid deposit regime

Same in rigid case

Characterize this regime as a function of the contact angle

$$Bo = \frac{\Delta\rho g R^2}{\gamma_{LG}} \Rightarrow Bo_\alpha = Bo \times sin\alpha$$

Figure 2 - Shape of droplet in function of Bond number Bo_α (PHD of M. Oléron, 2022).
The images framed in red are for the case of a rigid (T. Podgorski *et al.*, *PRL* 2001)

Contradiction with the experiment not well understood because the back of a drop not fully understood

Need to change experimental system to study contact line with simpler geometry

Theoretically

(rigid and soft)

$$C_a \nearrow \Rightarrow \theta \searrow$$

$$\left[Capillary\ number\ Ca = \frac{\eta U}{\gamma_{LG}}\right]$$

$$C_{a_c} \Rightarrow \theta = 0$$

In practice

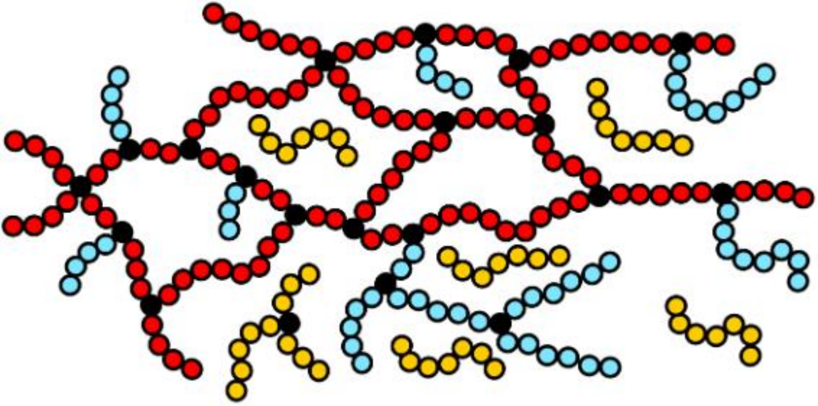
(rigid and soft)

$$C_a \nearrow \Rightarrow \theta \searrow$$

$$C_{a_c} \Rightarrow \theta \neq 0$$

(near 30°)

Origin 2 : Presence of free-chain in the substrate



Red chain

Under stress:
stretch and store elastic energy

Blue chain

Yellow chain
« Free-chain »

Under stress: can relax and/or move in the network
↳ mechanical response with viscoelastic contribution

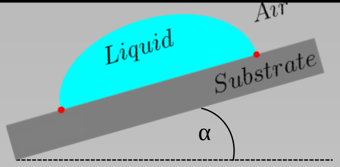
Free-chain extract ⟶ If coating instantaneous

1 lead for delayed coating:
slow reorganization of free chains near the contact line during extraction

Experimental set-up

2 classical set-up :

- Sliding droplet
- Dip-coating



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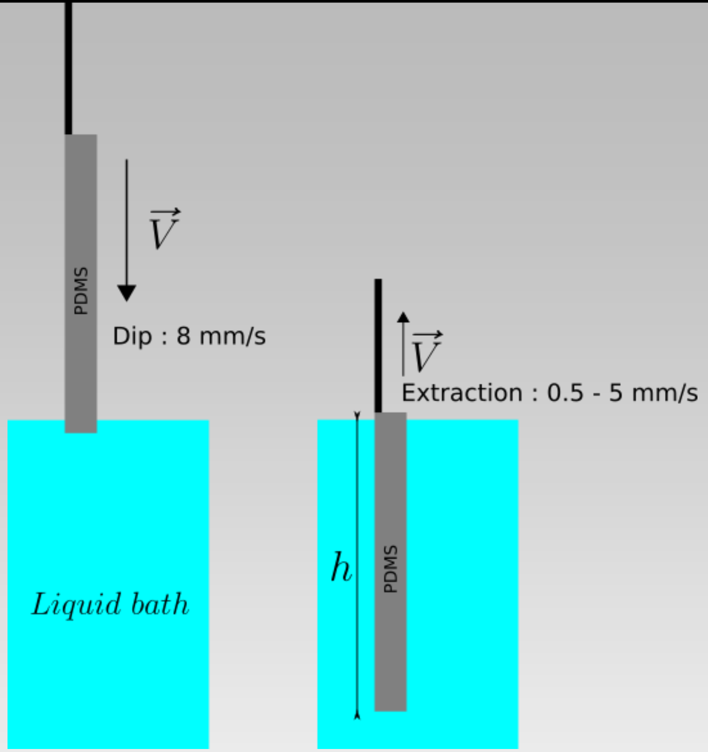

Figure 3 – Experimental set-up : dip-coating

- Straight contact line
- Pulling speed : controlable parameter