COLLEGE OF ENGINEERING
LAMAR UNIVERSITY™

Hydrogel Tribology on Silanized Silicon

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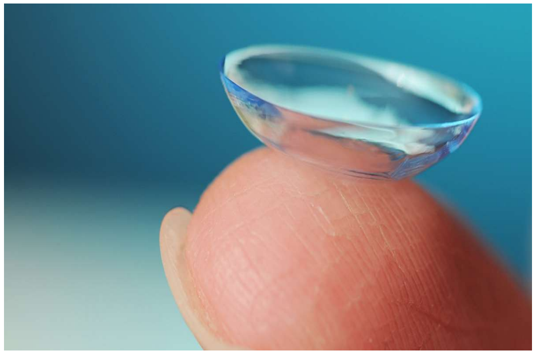
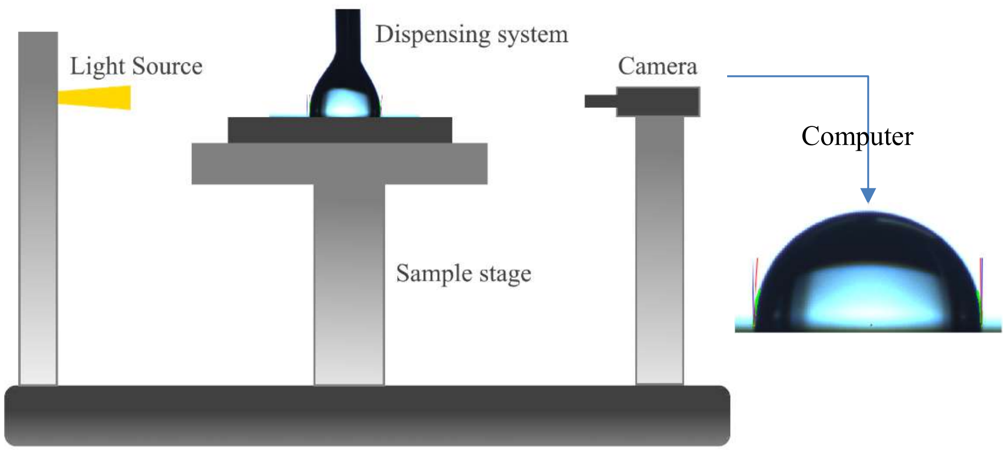
PhD Thesis Defense 09/25/2020

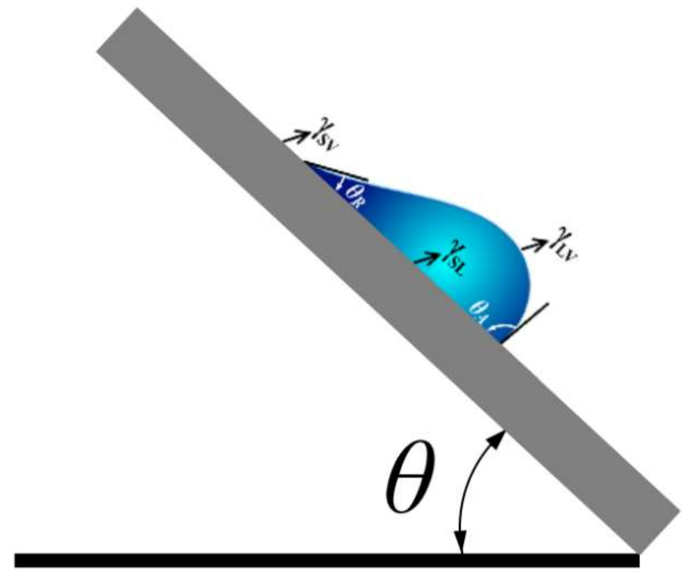
Solid-Liquid Interaction

- Cleaning Industry
- Skin care Industry
- Health care
- Mining, oil and gas
- Electronics



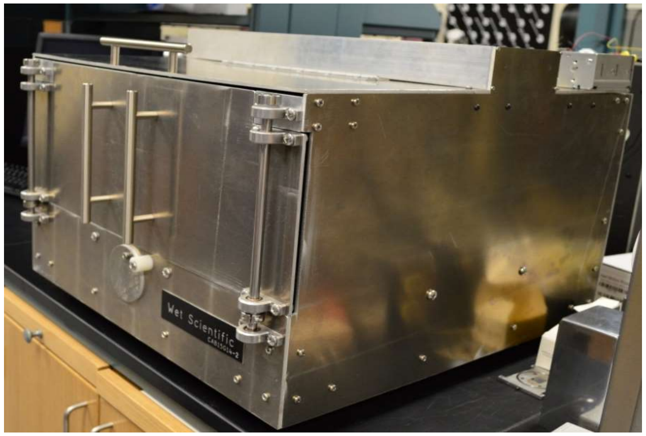
History



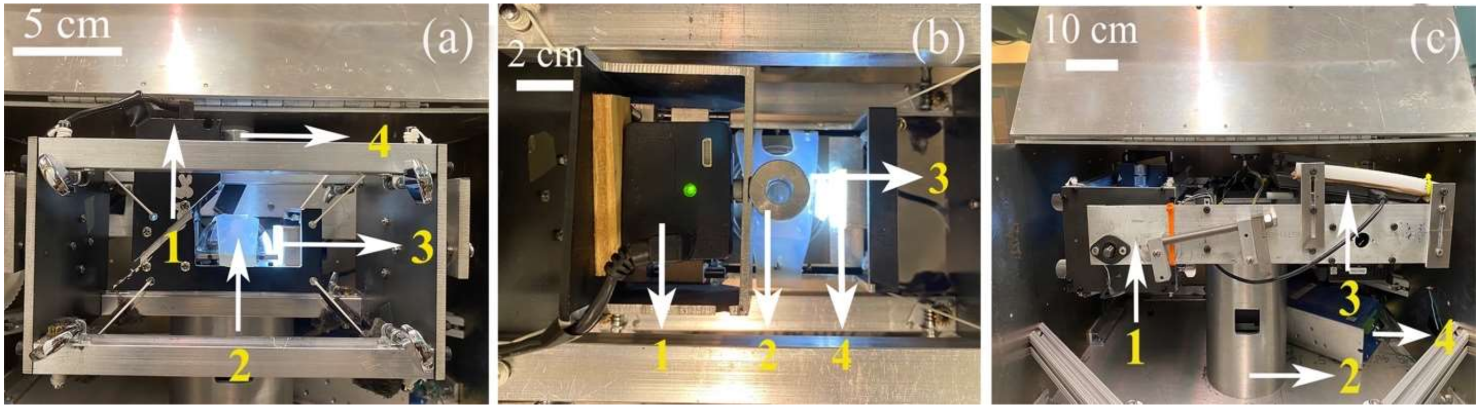


Tadmor et al. 2009

Centrifugal Adhesion Balance (CAB)



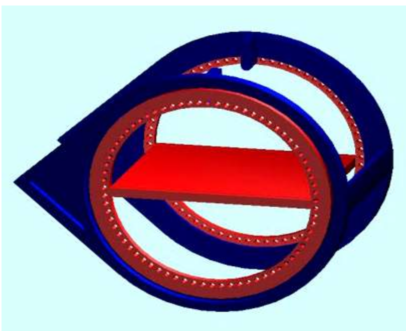
Outside image of CAB

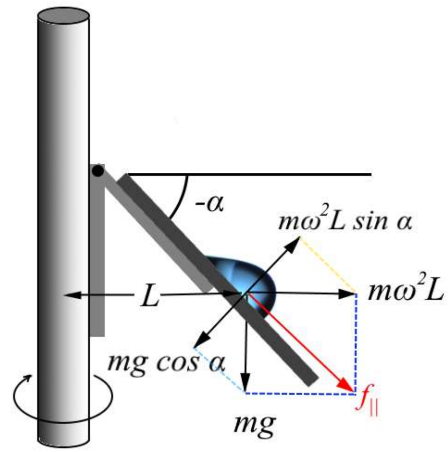


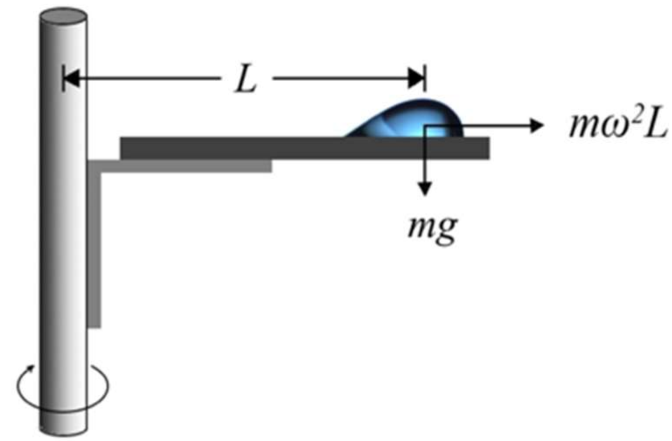
Operation of CAB

Lateral Force & Normal Force

Tilt Plate







m : mass of the droplet
L : distance from drop to axis of rotation
ω: angular velocity
$f_{\parallel}$: lateral force
$f_{\perp}$: normal force

$$f_{\parallel} = m(\omega^2 L cos\alpha - g sin\alpha) \qquad (1)$$

$$f_{\perp} = m(\omega^2 L sin\alpha + g cos\alpha) \qquad (2)$$

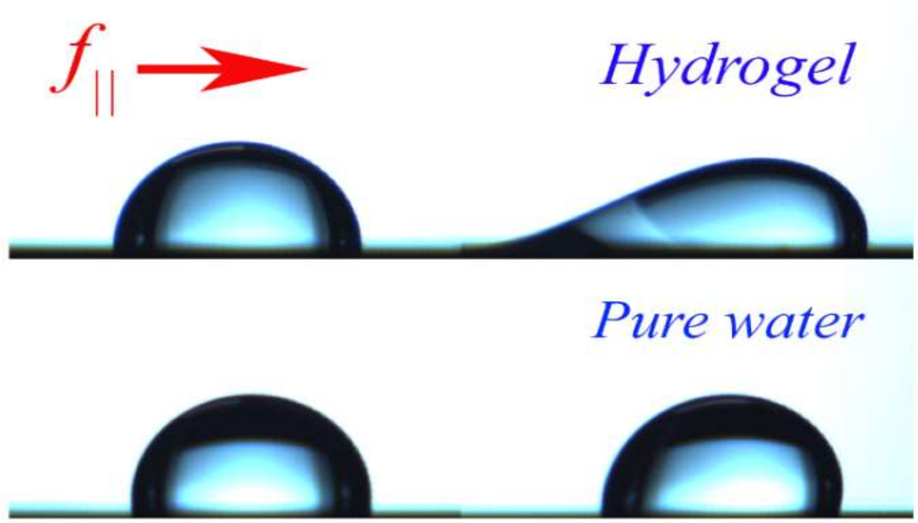
$$f_{\parallel} = m\omega^2 L \qquad (3)$$

$$f_{\perp} = mg \qquad (4)$$

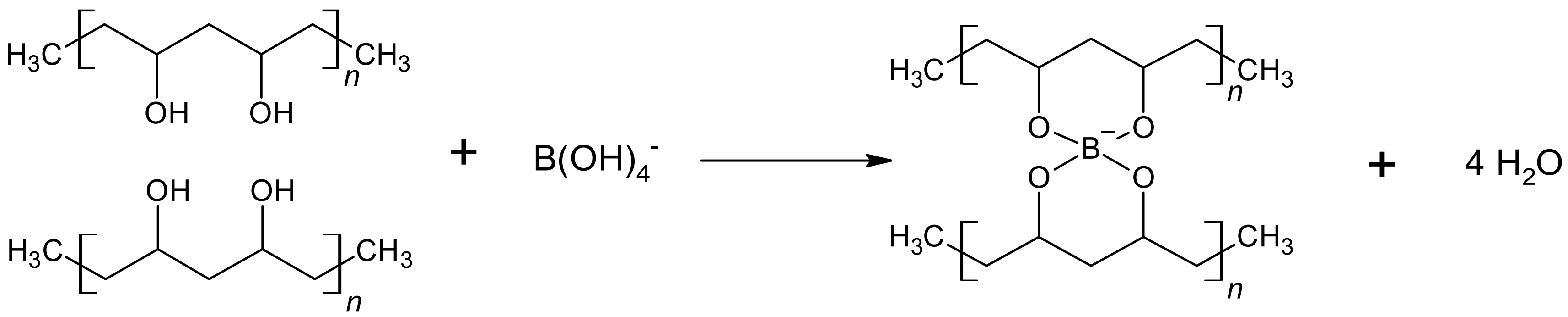
Changing one force at a time, keeping the other force a constant

Tadmor et al. 2009

Tribological study of a hydrogel in comparison to that of pure water



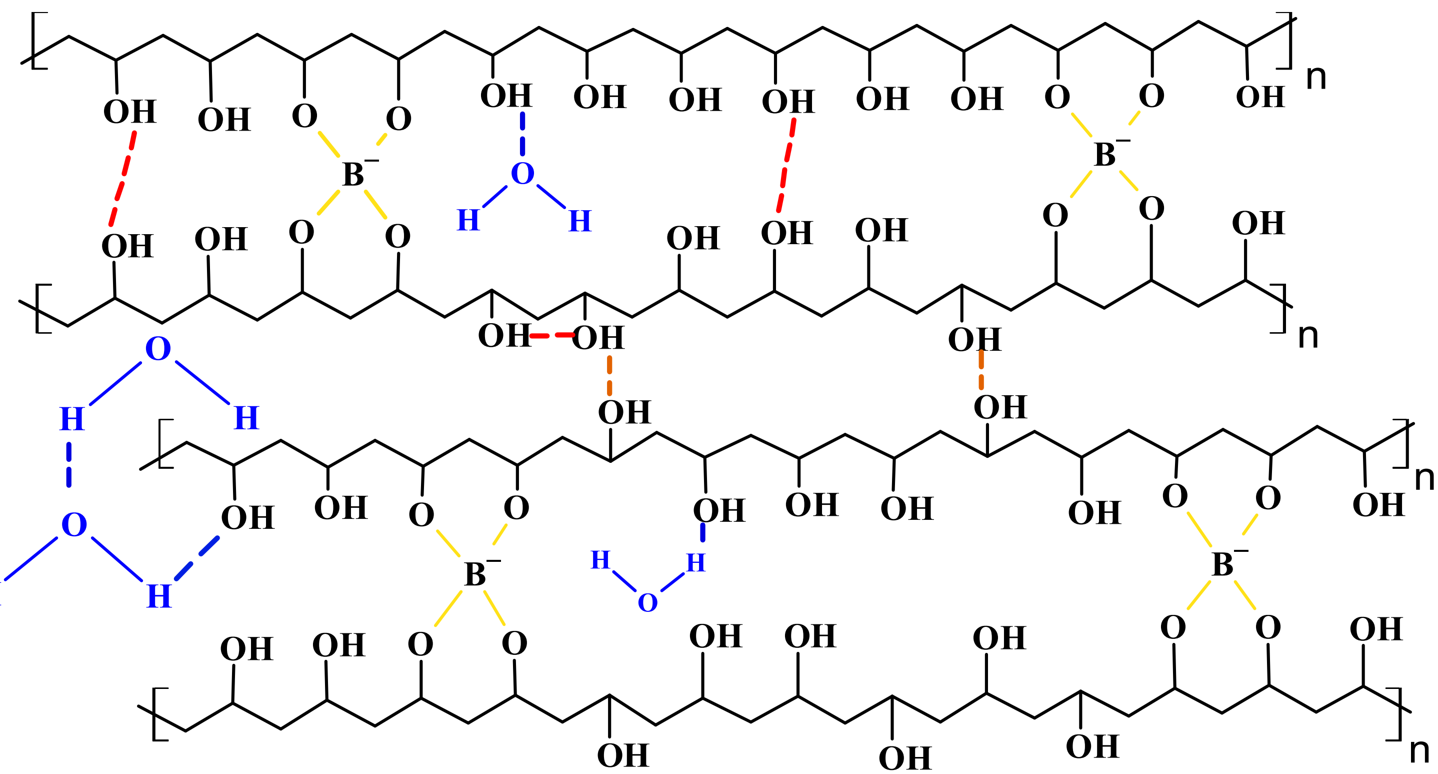
PVA Hydrogel crosslinked using boron ions



The H_2O molecules of borate ion are replaced by the OH molecules of PVA resulting in cross linking

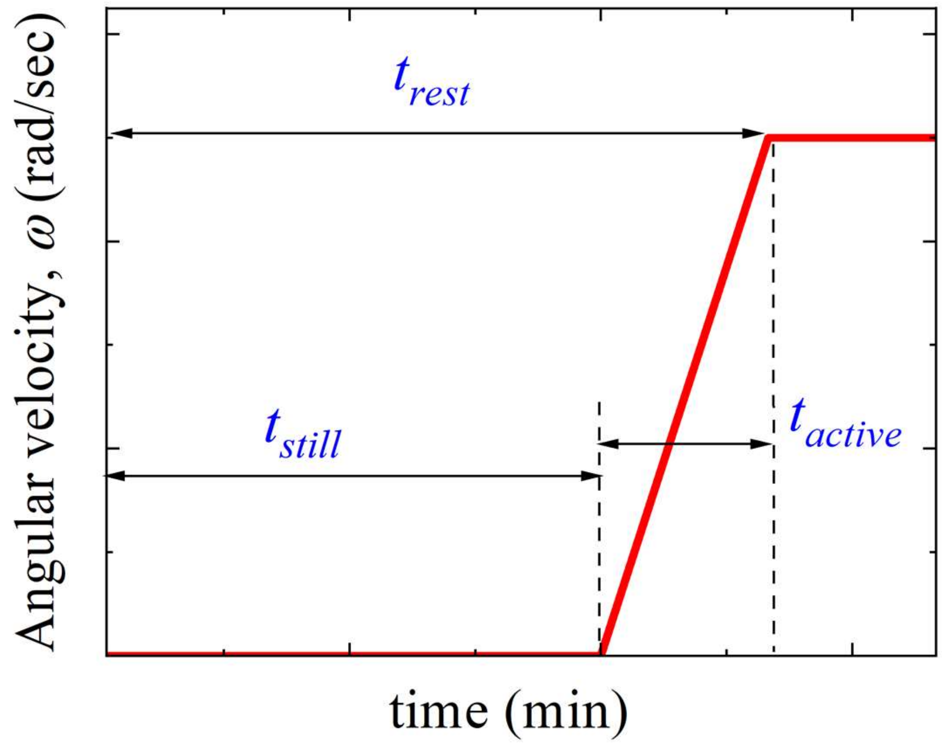
Sinton et al 1987

A possible structure of the PVA hydrogel



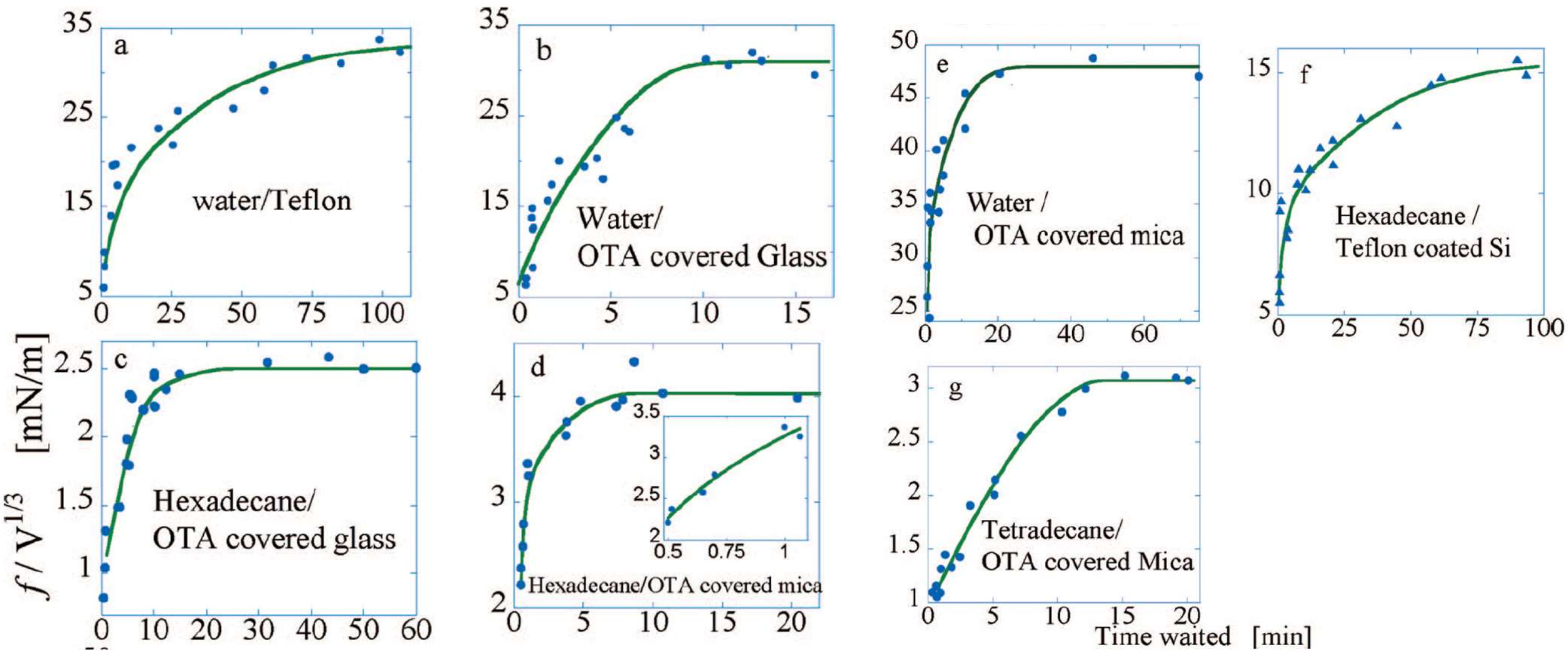
Zhang et al. ACS Macro Lett. 2012

Prescribed Parameter, t_{still}



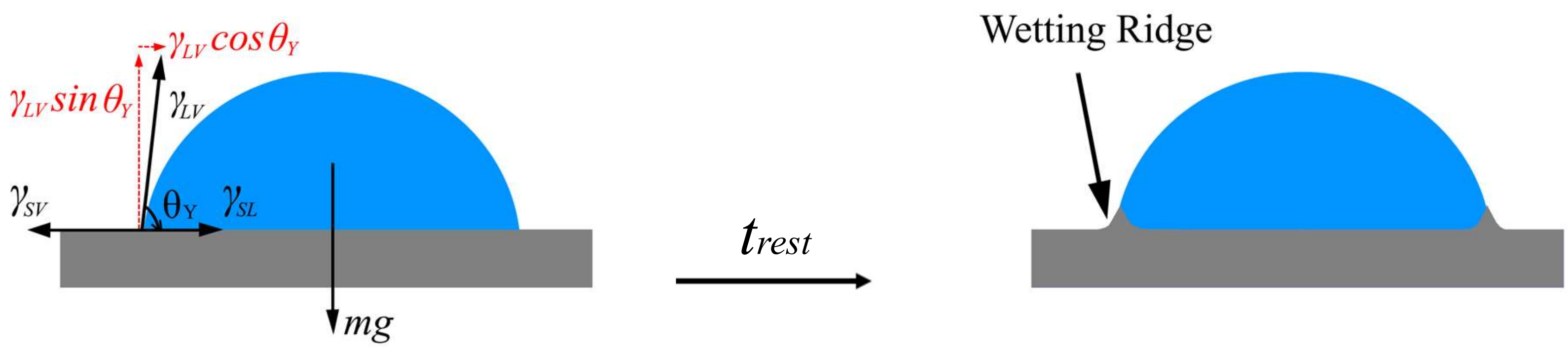
Tadmor et al. 2008

Classic Results: Various systems



Bormashenko et al 2014
Tadmor et al. 2008

Why $f_{||}$ increases with t_{rest} ?

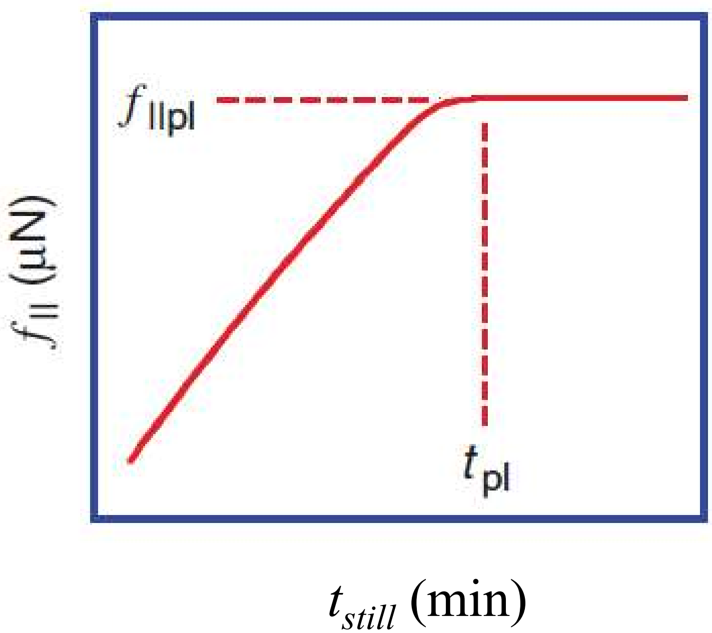


$$\gamma_{SV} = \gamma_{SL} + \gamma_{LV} \cos \theta_Y$$

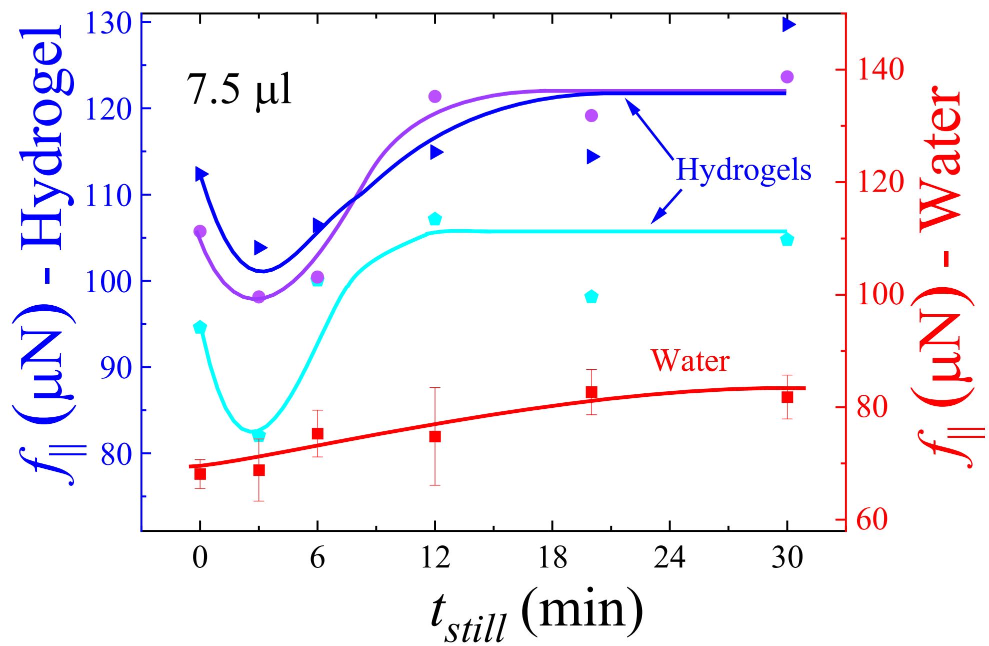
Shanahan and de Gennes 1986

Classic Results vs Current Result

Other systems



PVA Hydrogel on C18 silanized silicon



Tadmor et al. 2008.

3.0 μl of droplets on C18 Silanized Silicon

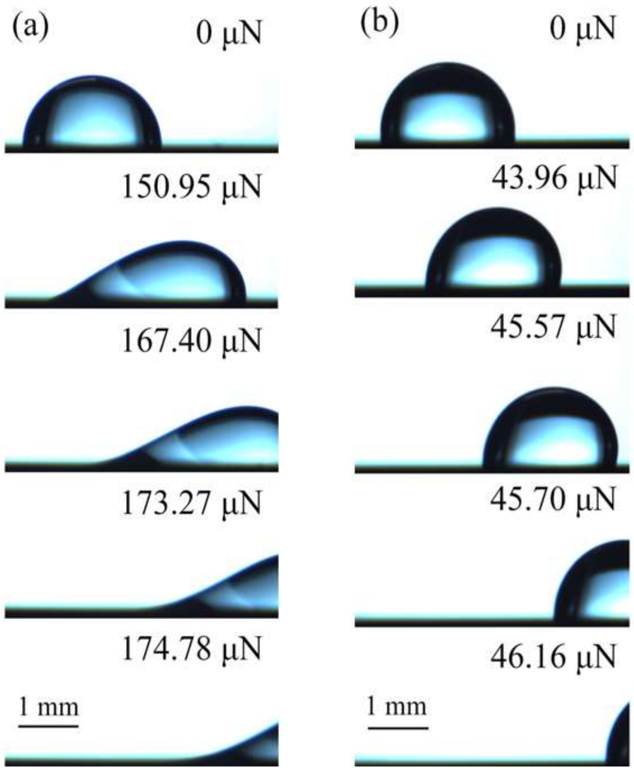
CAB accelerating at 3 rpm/ sec, and t_{still}: 0 minutes (ASAP)

Movie speed: Real experiment x 2 faster

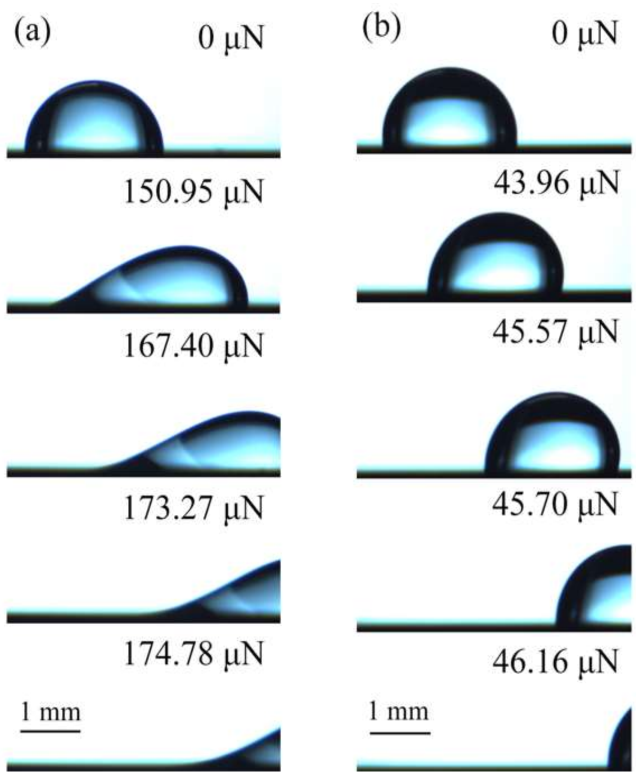
(a) PVA Hydrogel

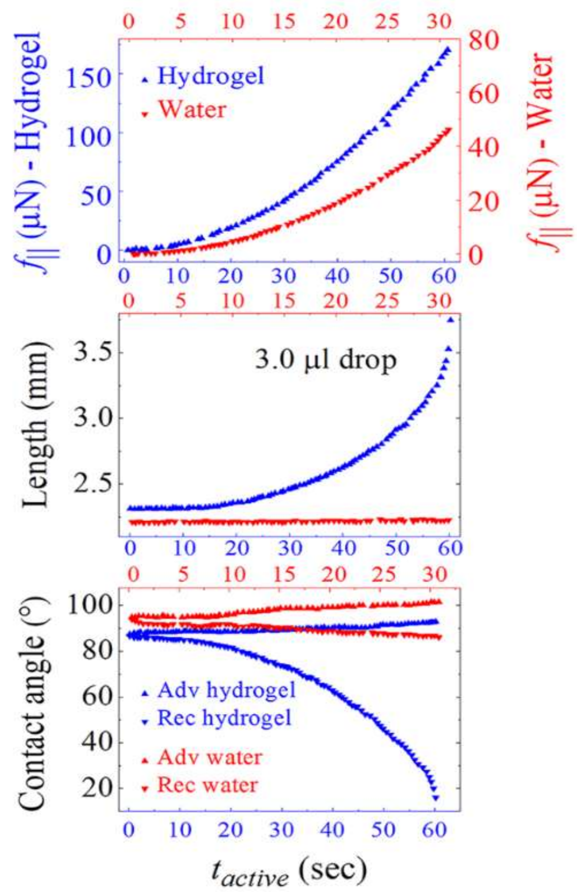
(b) Water

Comparison of contact angles

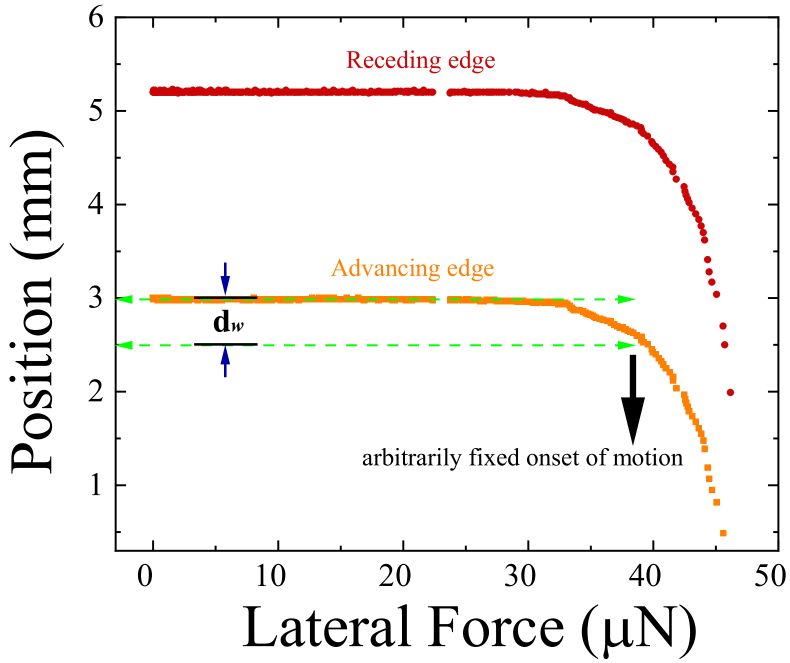


Comparison of contact angles

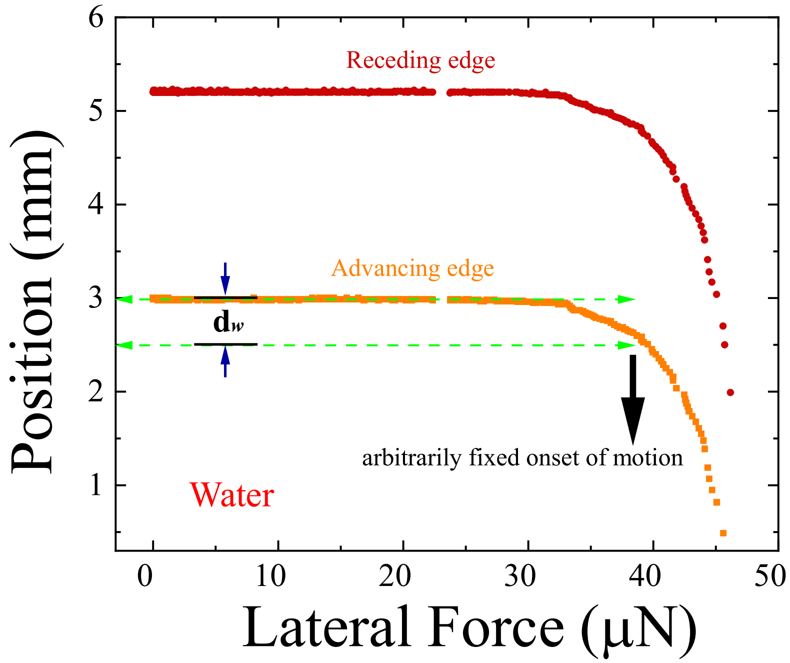


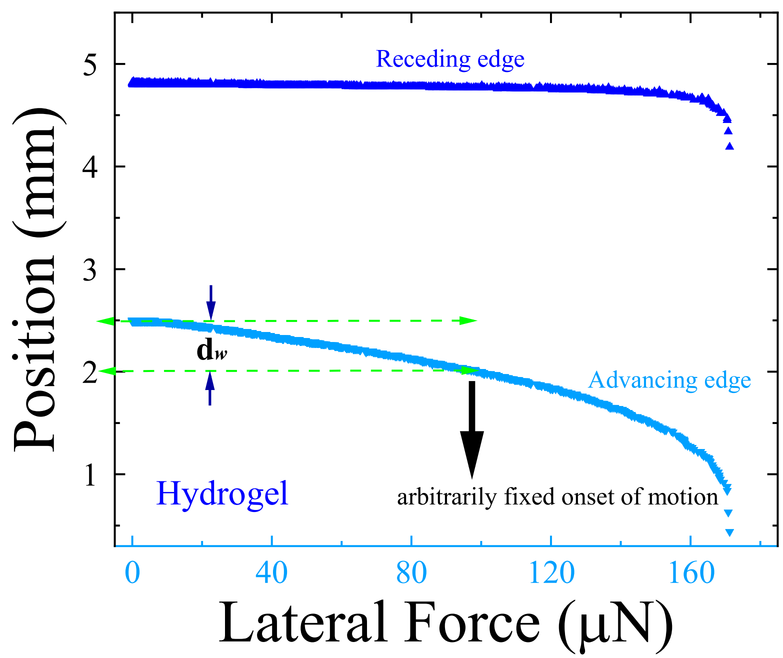


Determination of onset of motion

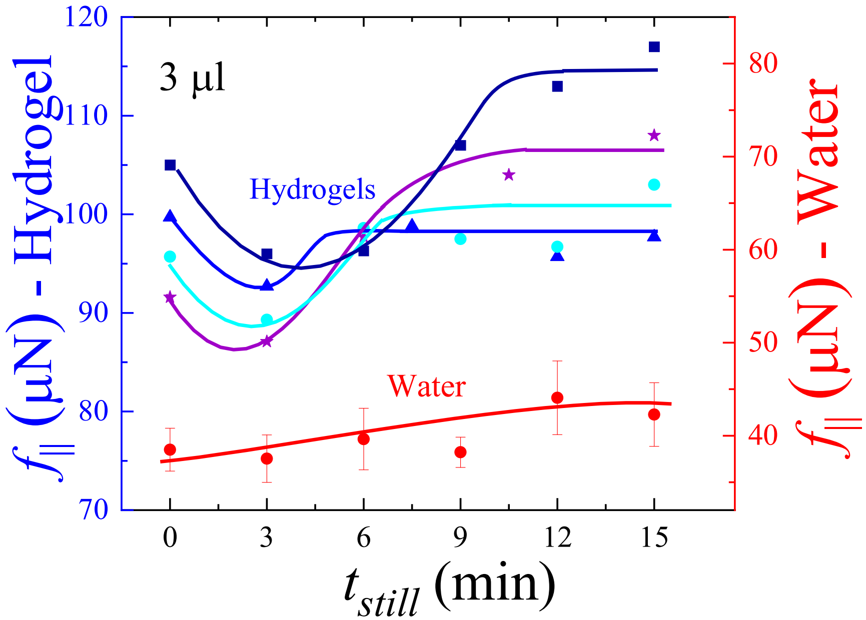


Determination of onset of motion

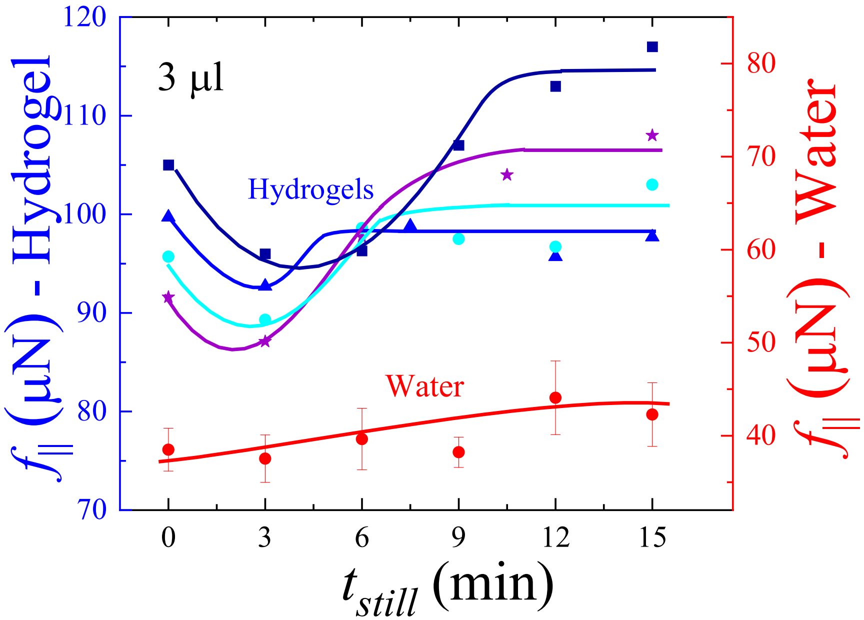


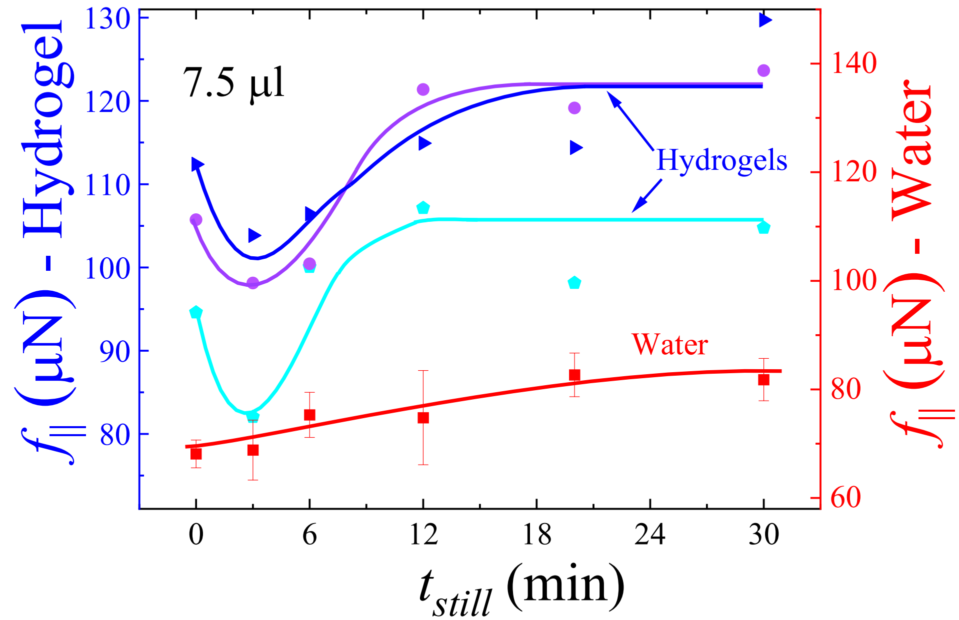


Lateral force vs t_{still}

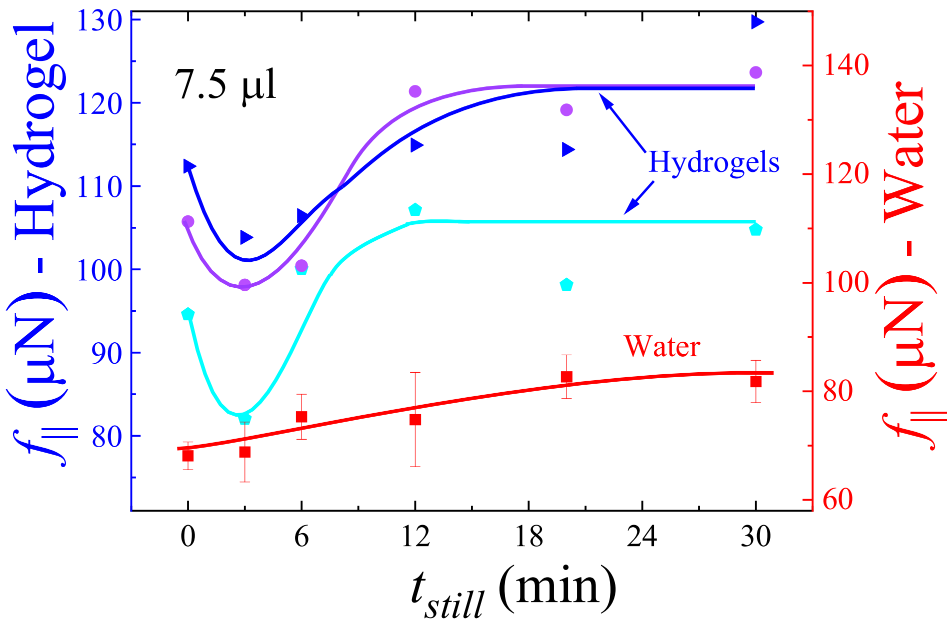


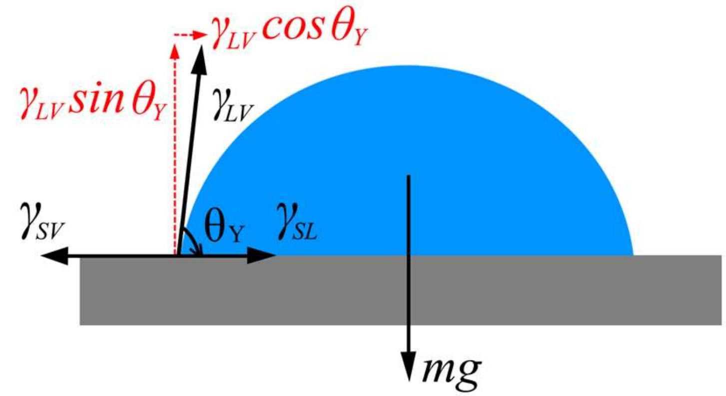
Lateral force vs t_{still}





Higher Retention Force





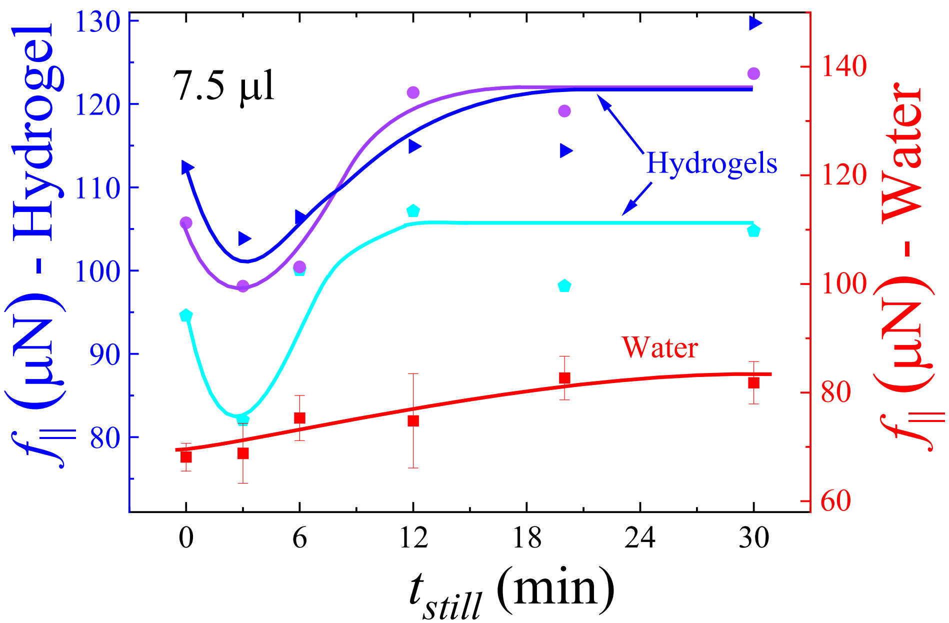
$$\gamma_{SV} = \gamma_{SL} + \gamma_{LV} \cos\theta_Y$$

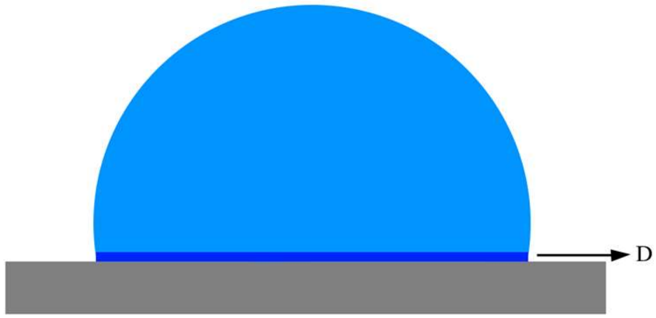
Tadmor et al. Langmuir 2008

Carre et al. Nature 1996

Zhao et al. 2003

Reduced Retention Force





1. *Yasuda et al. Langmuir 1992.*
2. *Alexander, S. J Phys 1977.*

Reduced Retention Force

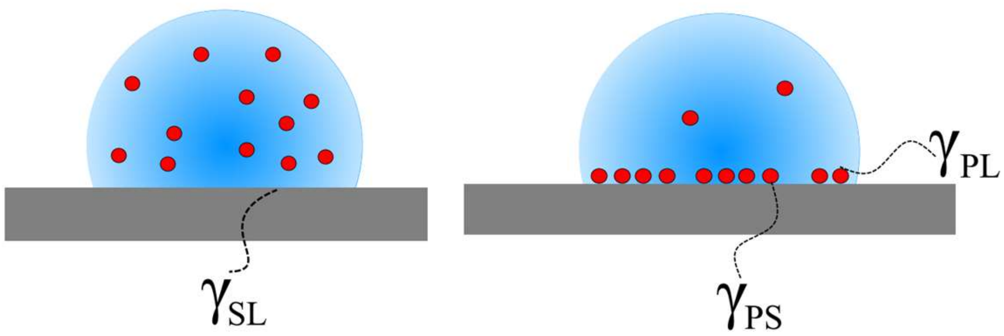
- Reorientation: $\gamma_{SL,(t=0)} > \gamma_{SL,(t>0)}$

Reduced Retention Force

- Reorientation: $\gamma_{SL,(t=0)} > \gamma_{SL,(t>0)}$
- Our case: $\gamma_{SL,(t=0)} < \gamma_{SL,(t>0)}$

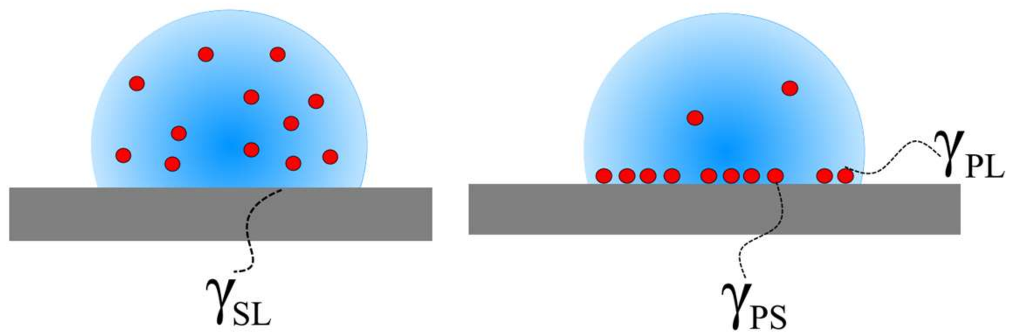
Reduced Retention Force

- Reorientation: $\gamma_{SL,(t=0)} > \gamma_{SL,(t>0)}$
- Our case: $\gamma_{SL,(t=0)} < \gamma_{SL,(t>0)}$
- Adsorption: $\gamma_{SL,(t=0)} < \gamma_{PL,(t>0)}$



Reduced Retention Force

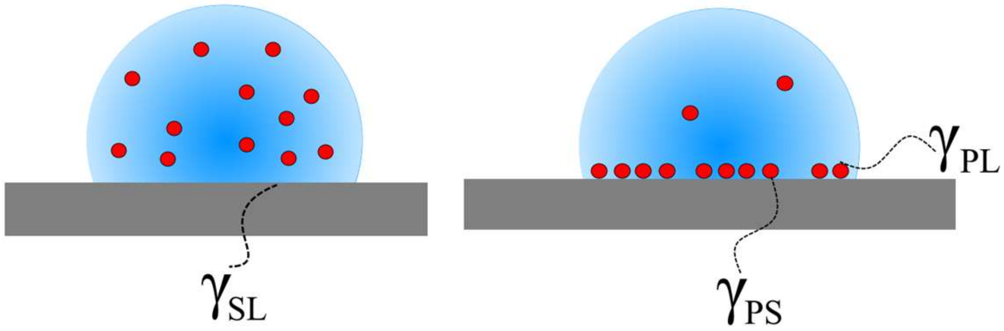
- Reorientation: $\gamma_{SL,(t=0)} > \gamma_{SL,(t>0)}$
- Our case: $\gamma_{SL,(t=0)} < \gamma_{SL,(t>0)}$
- Adsorption: $\gamma_{SL,(t=0)} < \gamma_{PL,(t>0)}$



- ***G* before adsorption**: $\Delta G_{\text{mixing}} + \gamma_{SL\,(t=0)}A$

Reduced Retention Force

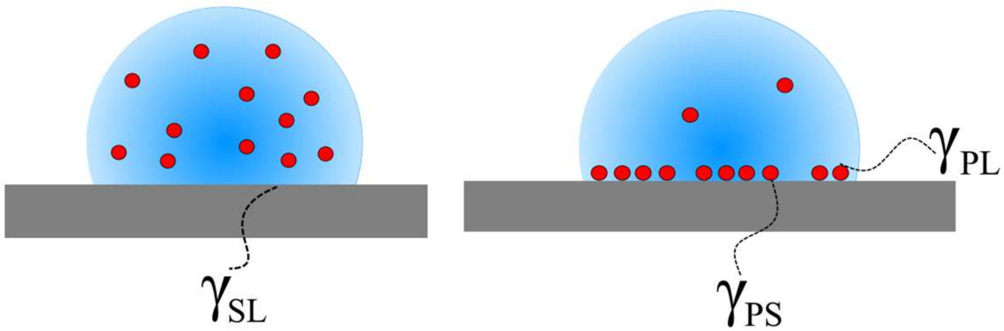
- Reorientation: $\gamma_{SL,(t=0)} > \gamma_{SL,(t>0)}$
- Our case: $\gamma_{SL,(t=0)} < \gamma_{SL,(t>0)}$
- Adsorption: $\gamma_{SL,(t=0)} < \gamma_{PL,(t>0)}$



- ***G* before adsorption**: $\Delta G_{\mathrm{mixing}} + \gamma_{SL\,(t=0)} A$
- ***G* after adsorption**: $\left(\gamma_{PL,(t>0)} + \gamma_{PS,(t>0)}\right) A$

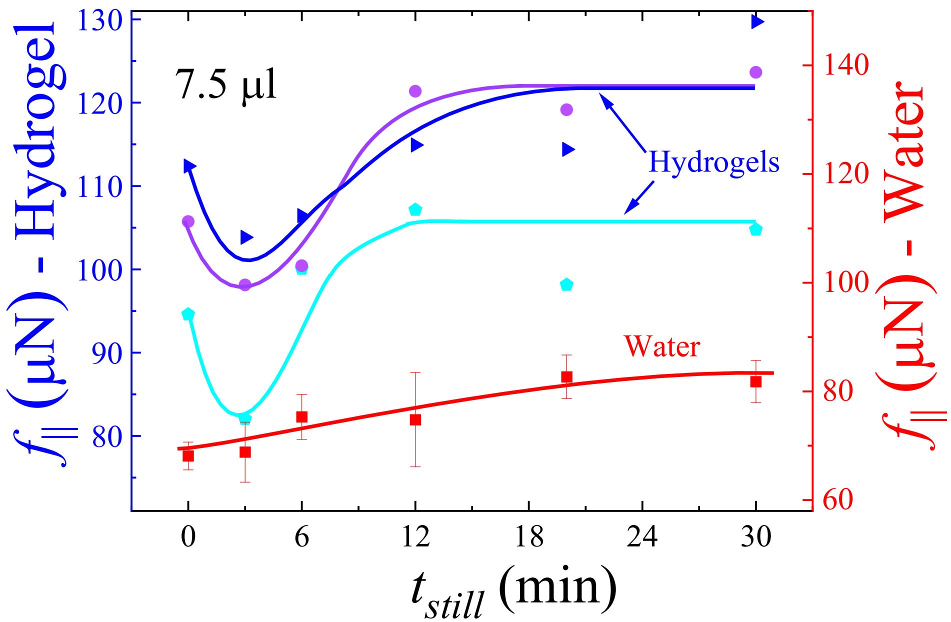
Reduced Retention Force

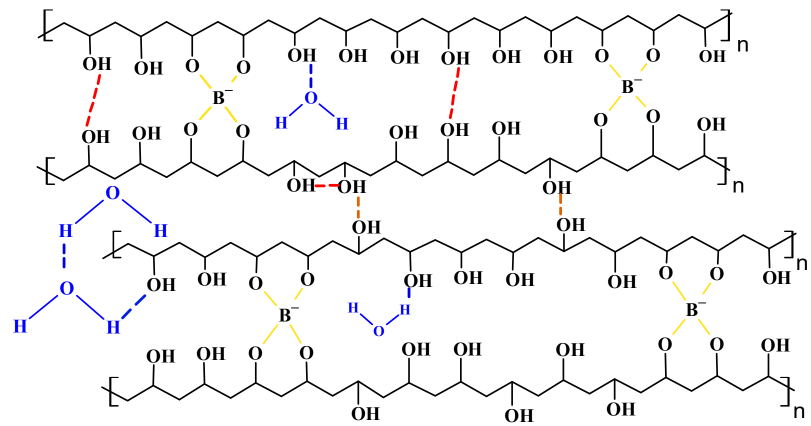
- Reorientation: $\gamma_{SL,(t=0)} > \gamma_{SL,(t>0)}$
- Our case: $\gamma_{SL,(t=0)} < \gamma_{SL,(t>0)}$
- Adsorption: $\gamma_{SL,(t=0)} < \gamma_{PL,(t>0)}$



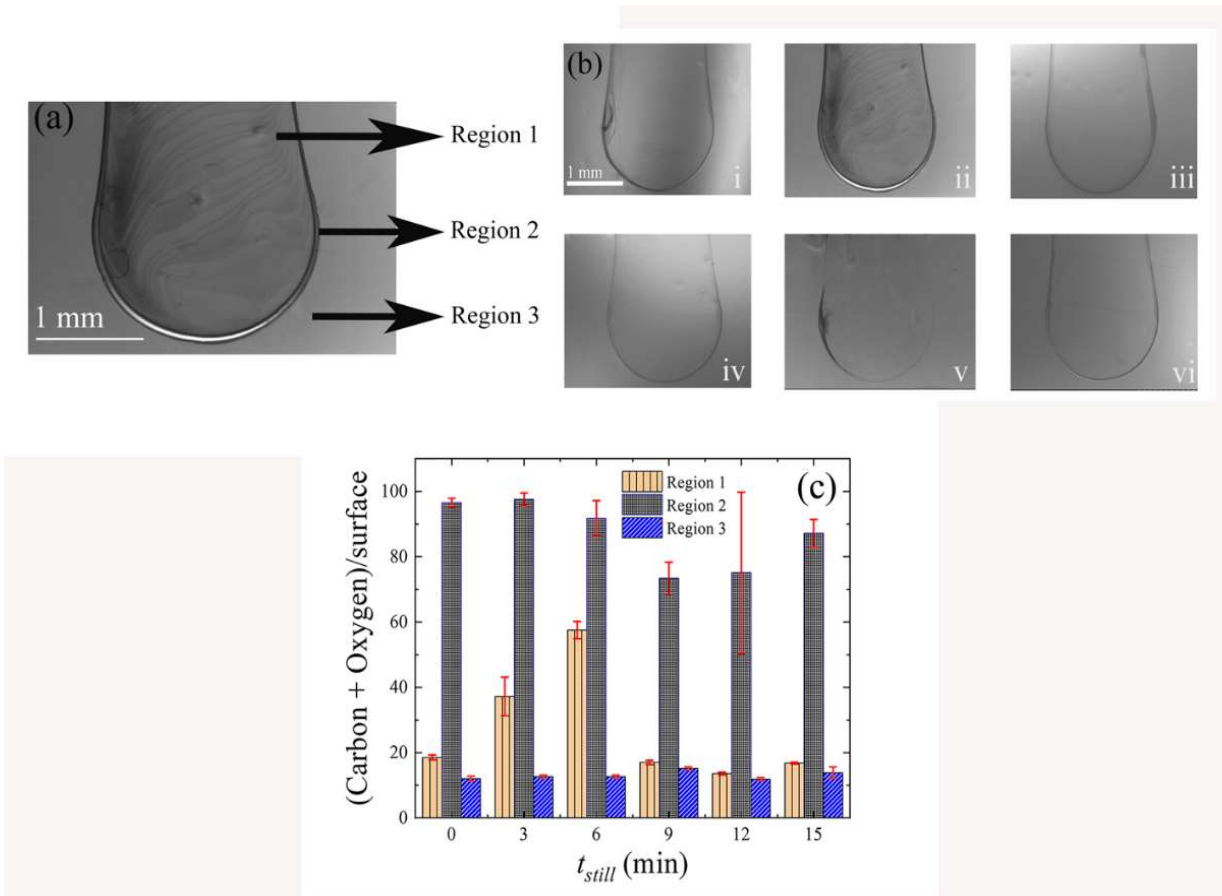
- ***G* before adsorption**: $\Delta G_{mixing} + \gamma_{SL\,(t=0)} A$
- ***G* after adsorption**: $(\gamma_{PL,(t>0)} + \gamma_{PS,(t>0)})\, A$
- $\boldsymbol{\Delta G_{mixing} + \gamma_{SL\,(t=0)} A > (\gamma_{PL,(t>0)} + \gamma_{PS,(t>0)})\, A}$

Highest Retention Forces

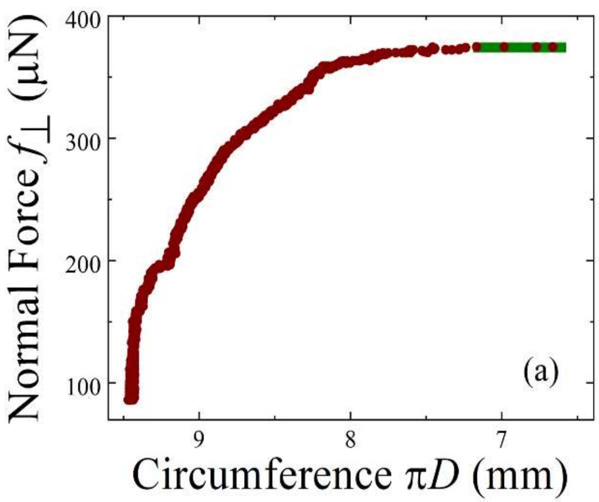


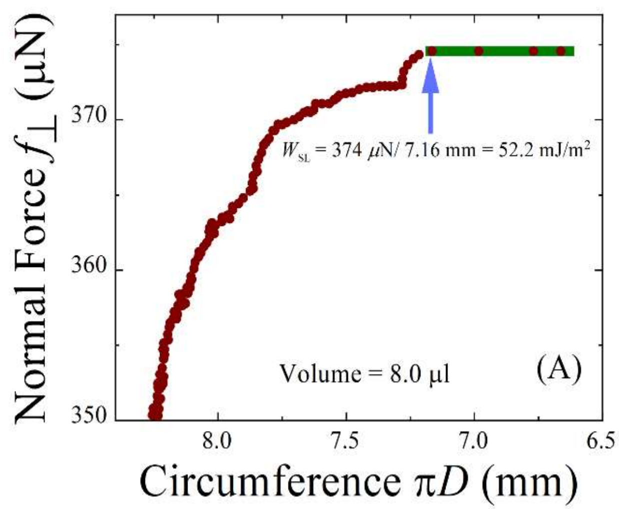


Topographical study and Elemental analysis

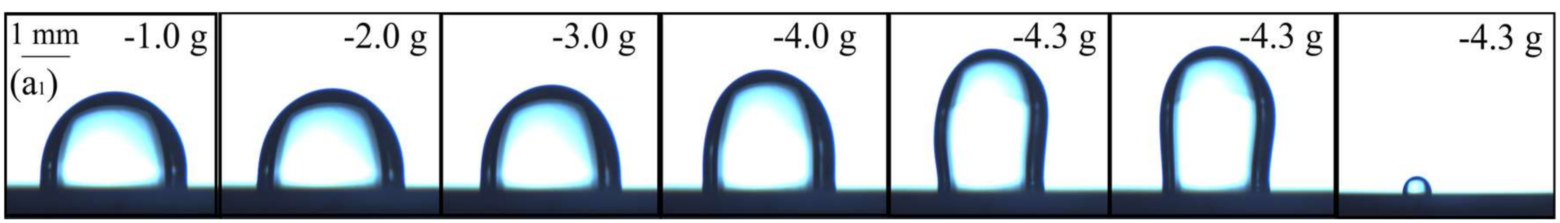


Work of Adhesion water 0 mins t_{still}

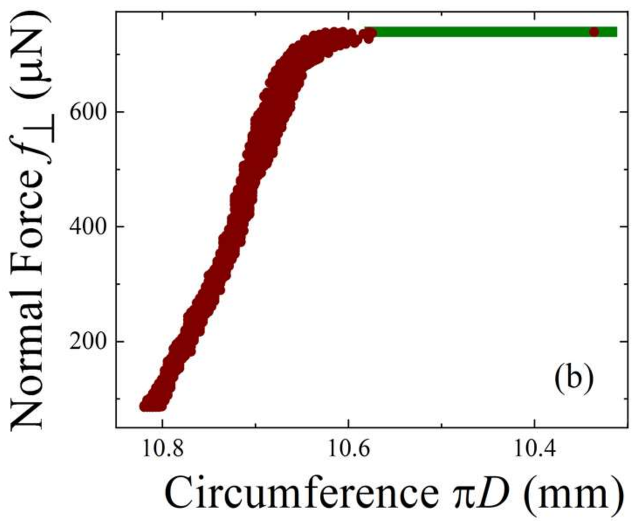


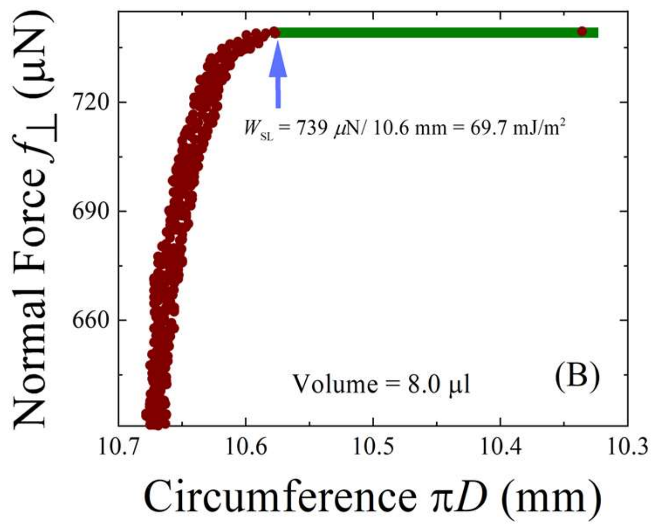


$$W_{SL} = \frac{374\ \mu\text{N}}{7.16\ \text{mm}} = 52.2\ \text{mJ/m}^2$$

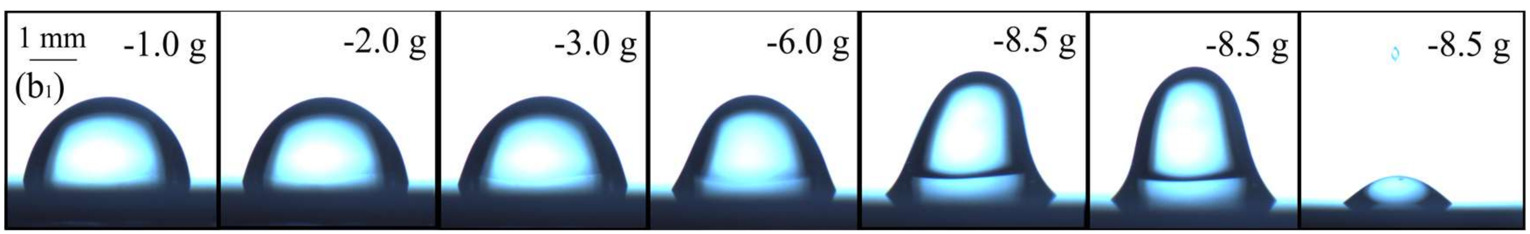


Work of Adhesion Hydrogel 0 mins t_{still}

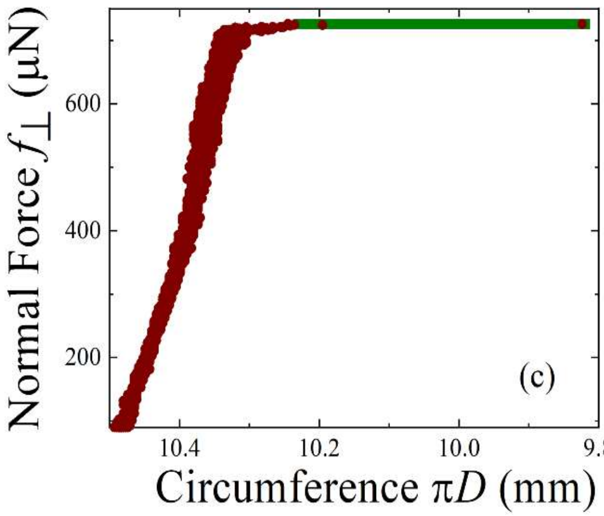


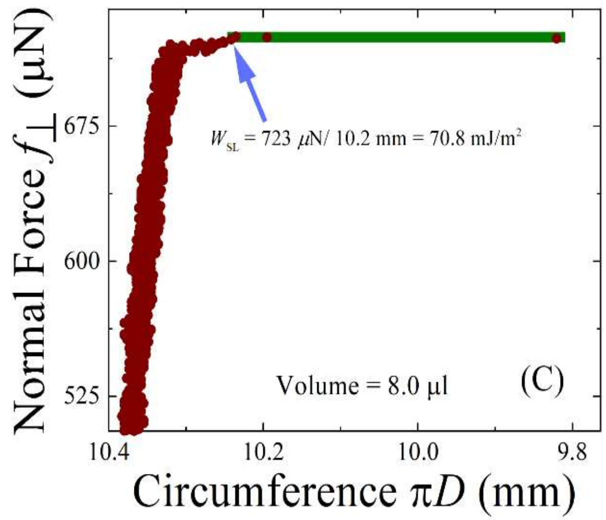


$$W_{SL} = \frac{739\ \mu\text{N}}{10.6\ \text{mm}} = 69.7\ \text{mJ/m}^2$$

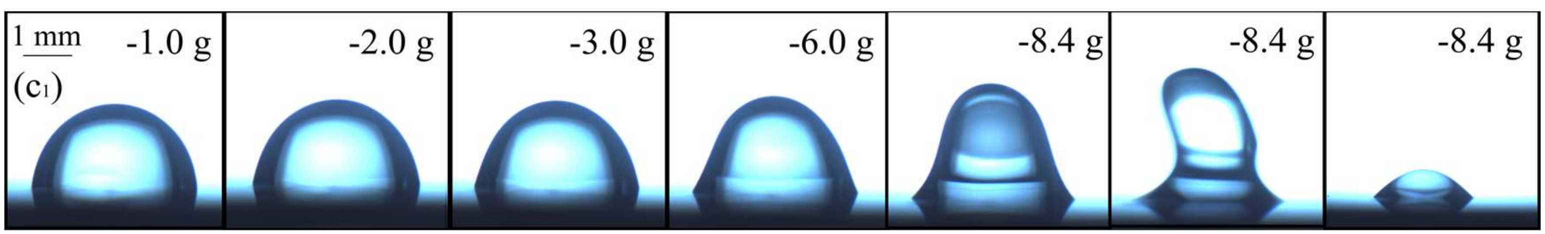


Work of Adhesion Hydrogel 3 mins t_{still}

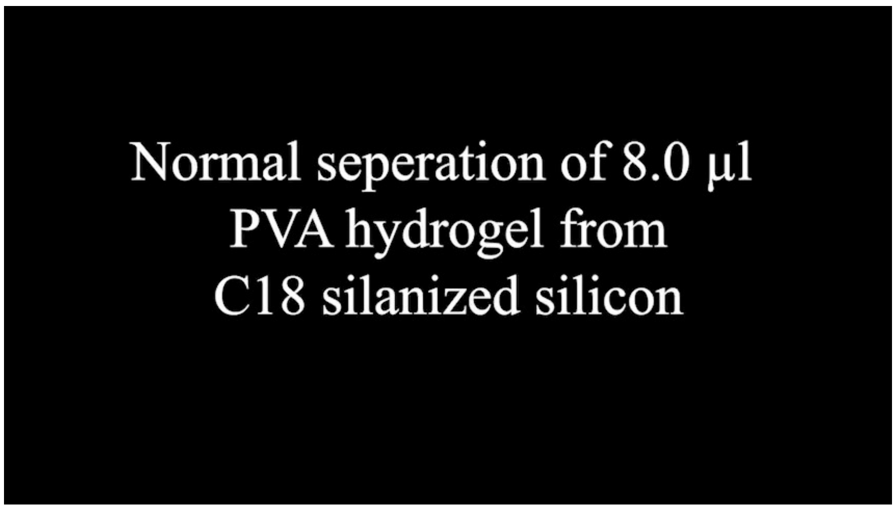


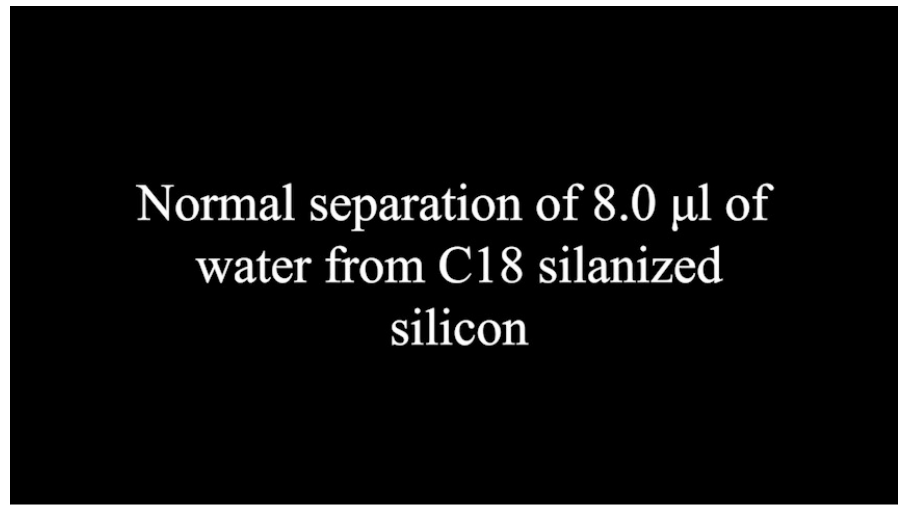


$$W_{SL,} = \frac{723\ \mu\text{N}}{10.2\ \text{mm}} = 70.8\ \text{mJ/m}^2$$



Work of adhesion movie





Summary

- Water's $f_{||}$ grows with t_{still}, and plateaus.
- Gel's high $f_{||}$ at short t_{still} due to strong gel's solid surface adhesion.
- With increase t_{still}, polymer adsorbs on solid reduces the interfacial tension
- Afterwards, the entire droplet gets converted to a hydrogel

Summary

- The already formed thin layer of polymer acts as a bridge that connects the newly formed aqueous hydrogel to the surface
- This strong intermolecular attraction of the newly formed hydrogel to the existing layer of polymer makes it difficult for the drop to slide over the surface.

PVA Hydrogel: Mucus secreted by Gastropods

- *PVA hydrogel is reminiscent of the mucus secreted by gastropods*
    - The reduction in the lateral retention force at early waiting times facilitates locomotion of gastropods
    - Increase in the lateral force at longer waiting time can be useful for its adhesion

Reference: Denny, M. Locomotion: The Cost of Gastropod Crawling. Science (80-.). ***1980****. https://doi.org/10.1126/science.208.4449.1288.*

Acknowledgements

- Surface Science Lab
  - Yagna Bhimavarapu
  - Akash K Jena
  - Semih Gulec
  - Ratul Das
  - Hartmann N'guessan
  - Sirui Tang
  - Dr. Rafael Tadmor*

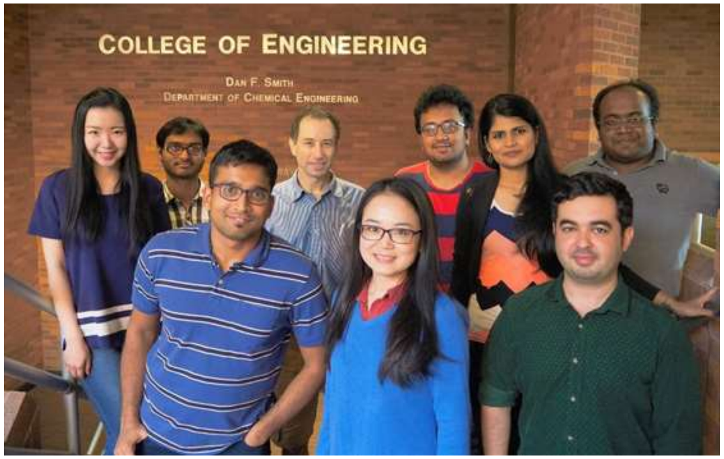
(Professor and Simmons Distinguished Faculty Fellow)

Dr. Prabir Patra

(Chair, Biomedical Engineering, Professor of Biomedical Engineering and Mechanical Engineering, School of Engineering)

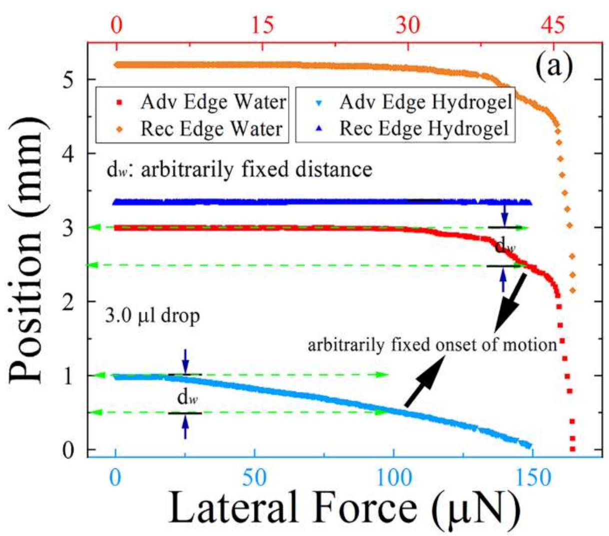
Dr. Robert Vajtai

(Research professor Rice University)



Thank you

Reason for a fixed distance



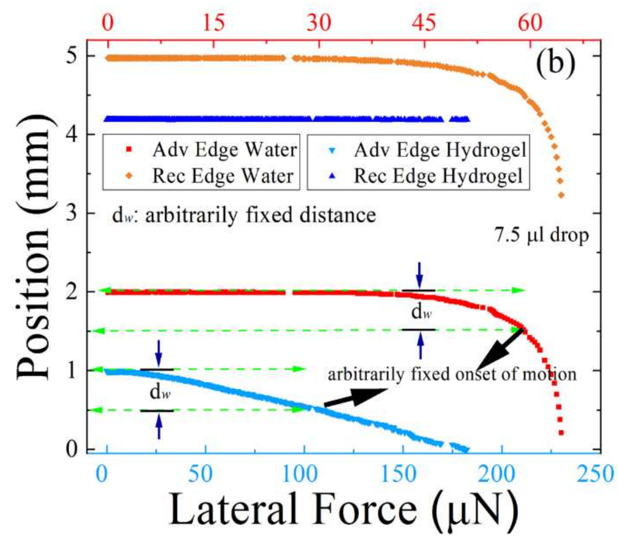


Figure. S4. Determination of onset of motion of drops on silanized silicon surface **(a)** 3.0 µl and **(b)** 7.5 µl of a different t_{still} from Figure. S3.

SEM-EDS Analysis

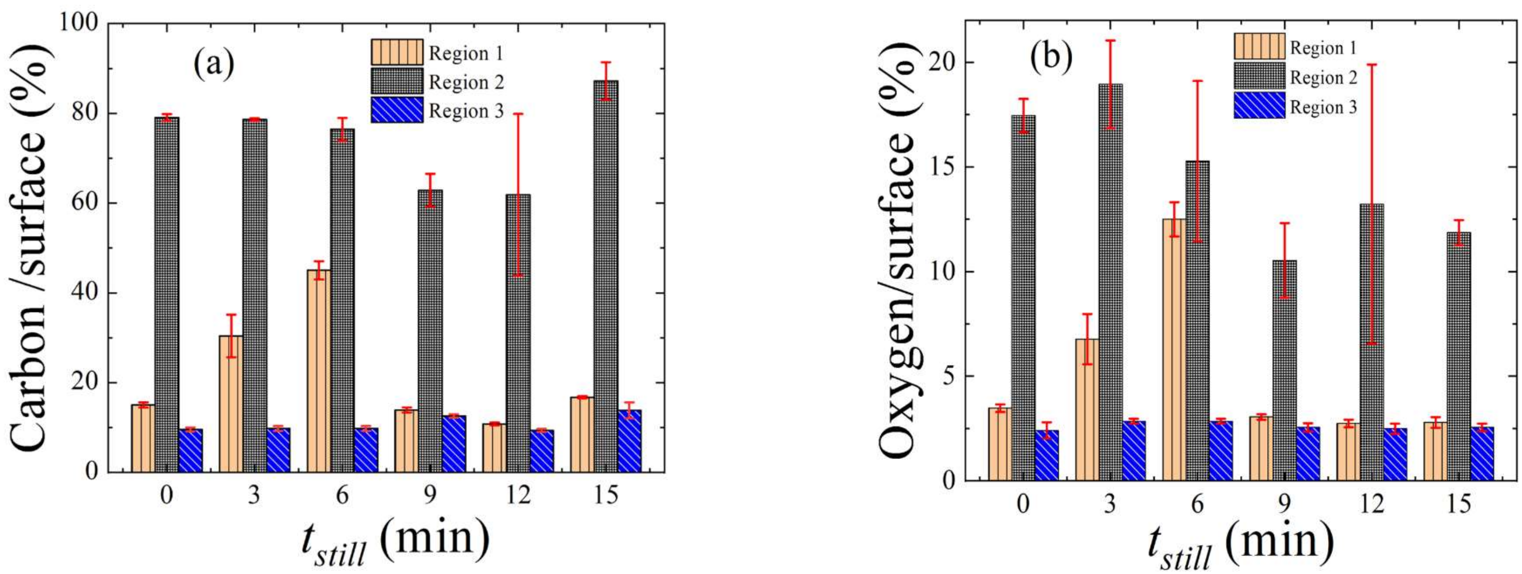


Figure. S5. Quantification of elements at the surface from hydrogel and trimethoxy (octadecyl) silane with variation in t_{still} **(a)** Carbon **(b)** Oxygen.

- Dissociation of sodium tetraborate decahydrate
- Make sure the letters are covered properly

Further details

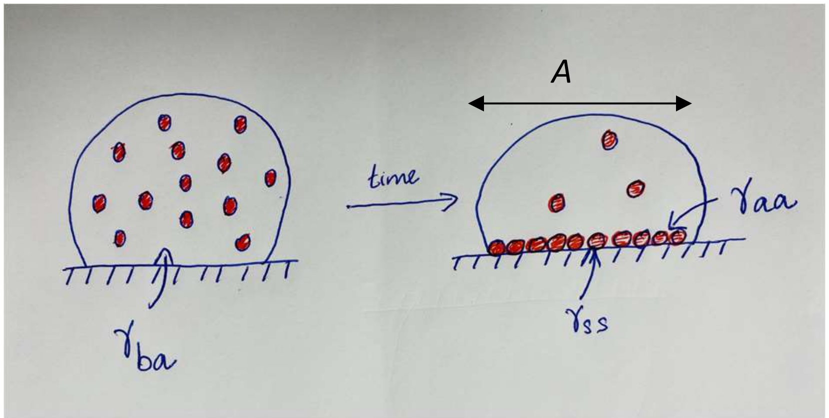
- $CH_3(CH_2)_{17}Si(OCH_3)_3$
- Molecular weight 374.67
- Density 0.883 g/mL at 25 °C (lit.)
- Borax is the sodium tetraborate decahydrate (Na2B4O7 · 10H2O) that, when dissolved in water, is hydrolyzed to boric acid and OH− anions, yielding a pH of about 9.13

Experimental procedure for surface preparation

Fig. 2: Procedure for preparation of Silanized Silicon Surface.

Einai, H et al Electrochim Acta 2009, 54(25), 6063-6069

Reduced Retention Force



Reorientation: $\gamma_{SL}(t=0) > \gamma_{SL}(t>0)$
Adsorption (our case): $\gamma_{SL}(t=0) < \gamma_{SL}(t>0)$

- $E_{sol} + \gamma_{SL\,(t=0)}A > (\gamma_{aa} + \gamma_{ss})A$

  - *E_{sol} = Free energy associated with the existence of the solute (polymer) in the solvent (water).*
  - *γ_{ba} = interfacial tension before polymer adsorption*
  - *γ_{aa} = interfacial tension after polymer adsorption*
  - *γ_{SS} = interfacial tension between the adsorbed polymer layer and the surface*

- *As opposed to molecular reorientation of time effect in which the interfacial energy must go down, because the solid-liquid interaction must go up, in the case of adsorption the interfacial energy can either go up or down because of the above equation.*