

# Validation of Capillarity Theory at the Nanometer Scale. II: Stability and Rupture of Water Capillary Bridges in Contact with Hydrophobic and Hydrophilic Surfaces

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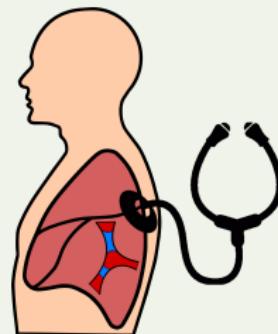
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<sup>3</sup> Department of Physics - Yeshiva University



Capillarity occurs due to the **cohesion and adhesion forces** between the surface of a liquid and another medium, and it is evidenced when this liquid is subjected to the confinement.

### Capillary bridges in lung physiology



[Alencar, Phys. Rev. Lett. (2001)]

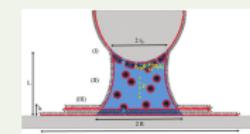
- The capillary bridges can block the small airways in a diseased lung.
- The bridge rupture generates the crackle sounds, which can be used as a qualitative diagnostic tool.

### Capillary bridges at the nanoscale

- Ink transport in the Dip-pen nanolithography
- The capillary adhesion force causes instability and damage on the substrate when making images with AFM.



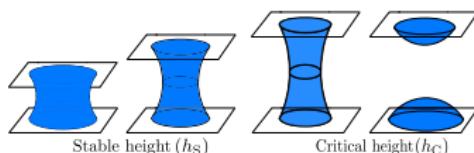
[Weeks, Langmuir (2005)]



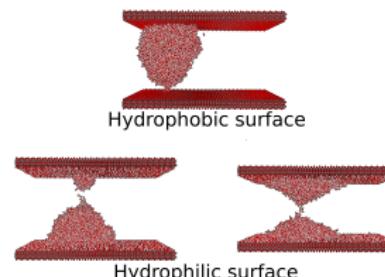
[Urtizberea, Nanoscale (2015)]

# Evaluate the macroscopic capillary theory (CT) at the nanoscale by studying the stability of water axisymmetric capillary bridges (AS bridges).

- Phase diagram: dependence of height and contact angle on the rupture of capillary bridges.



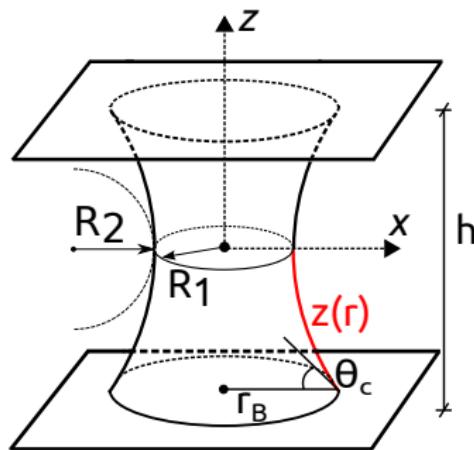
Molecular dynamics simulation of water AS bridges attached to silicon dioxide walls.



## Validation of Capillarity Theory at the Nanometer Scale. II: Stability and Rupture of Water Capillary Bridges in Contact with Hydrophobic and Hydrophilic Surfaces

Alexandre B. Almeida,<sup>†</sup> Nicolas Giovambattista,<sup>‡§</sup> Sergey V. Buldyrev,<sup>||</sup> and Adriano M. Alencar<sup>\*,†</sup>

# Theoretical profiles $r(z)$ of stable AS bridges, and its main properties.

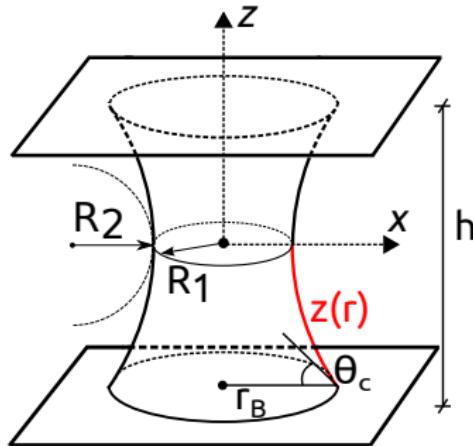


$$\frac{dz}{dr} = \pm \frac{|H(r^2 - r_0^2) + r_0|}{\sqrt{r^2 - [H(r^2 - r_0^2) + r_0]^2}}$$

$$r_0 = R_1$$

$$H = \frac{1}{2} \left( \frac{1}{R_1} + \frac{1}{R_2} \right)$$

# Theoretical profiles $r(z)$ of stable AS bridges, and its main properties.



## Contact angle

$$\theta_c \rightarrow \left. \frac{dz}{dr} \right|_{r_B}$$

## Adhesion forces and surface tension

$$F = F_\gamma + F_P$$

$$F_{z,\text{base}} = 2\pi\gamma r_B \sin \theta_c - 2\pi\gamma H r_B^2$$

$$F_{z,\text{neck}} = 2\pi\gamma C = 2\pi\gamma(r_0 - H r_0^2)$$

$$F_{z,\text{base}} = F_{z,\text{neck}}$$

## Laplace pressure

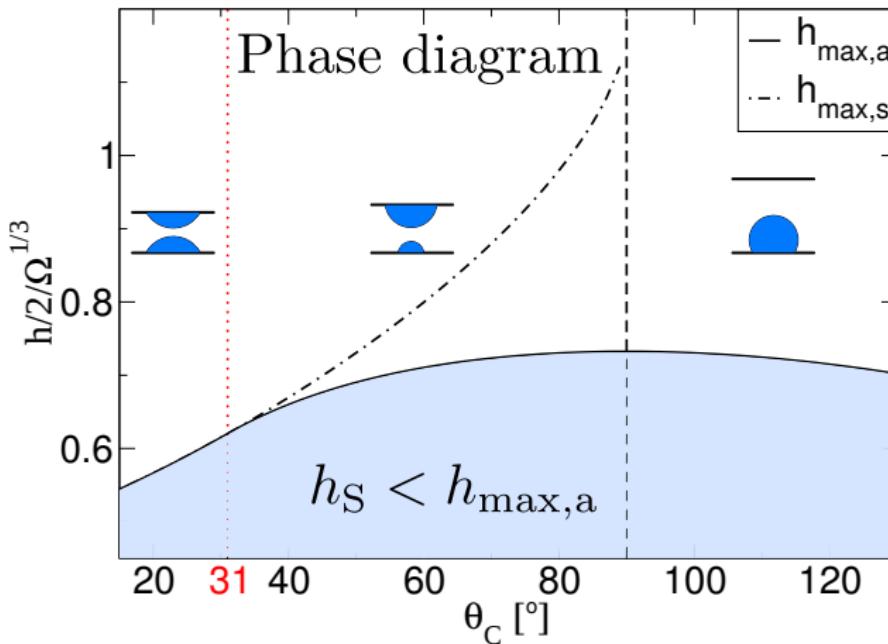
$$P_L = \frac{F_\gamma - \langle F_{z,\text{base}} \rangle}{A_{\text{base}}}$$

$$P_L = 2\gamma H$$

## Surface free energy

$$\mathcal{F}(h) = \gamma(A_{\text{LG}}(h) - \cos \theta_c A_{\text{LS}}(h))$$

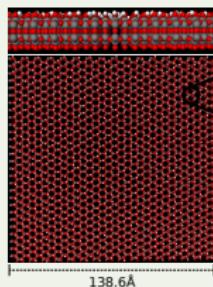
## Analytical solution of AS bridge



- $h_{\max,s}$  ( $h_{\max,a}$ ) is the maximum height for symmetrical (asymmetrical) rupture.
- For  $h_{\max,s} < h_{\max,a}$ , we can analytically calculate the  $F_{z,\text{base}}$ ,  $\mathcal{F}(h)$  and  $P_L$  from the parameters  $h$ ,  $\theta_c$  and volume  $\Omega$ .

# Molecular dynamics and atomistic model.

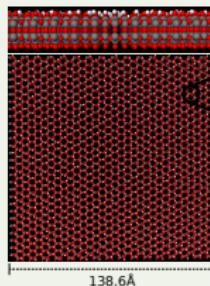
## Silicon dioxide walls, water model and simulation parameters



- Four layers of SiO<sub>2</sub>
  - Partial charges on silanol group
  - Si and O fixed
  - H can move in a circle
  - OH
  - Changing  $\theta_c$ :
- $$\vec{p} = k \times \vec{p}_0$$
- $$\vec{p}_0 = \vec{p}_{SiO} + \vec{p}_{OH}$$

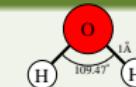
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SPC/E water model

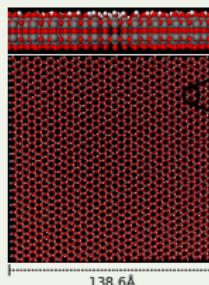
LAMMPS



- $r_c = 10 \text{ \AA}$
- PPPM:  $10^{-5}$
- velocity-Verlet
- Nosé-Hoover
- SHAKE

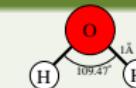
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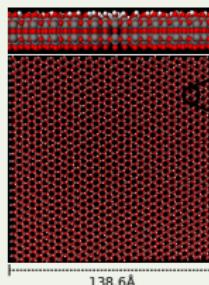
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## Simulations procedure:

- Total water molecules: 3375
- Polarity:  $0 < k < 0.67$

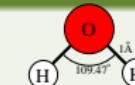
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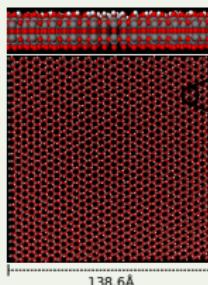
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## Stable heights ( $h_S$ )

- $h_f = h_i + 5 \text{ \AA}$  (0.01  $\text{\AA}$  for 250 fs)
- 1 ns to equilibrate
- 2 ns for the averages

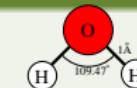
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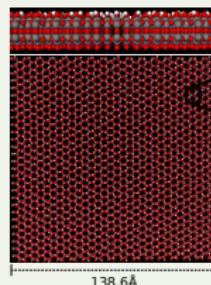
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- First rupture:  $h_{C'} = h_S + 5 \text{ \AA}$
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- $\Delta t_{\text{sim}} = 20 \text{ ns}$ :  $h = (h_S + 2.5) + 1.25 \text{ \AA}$

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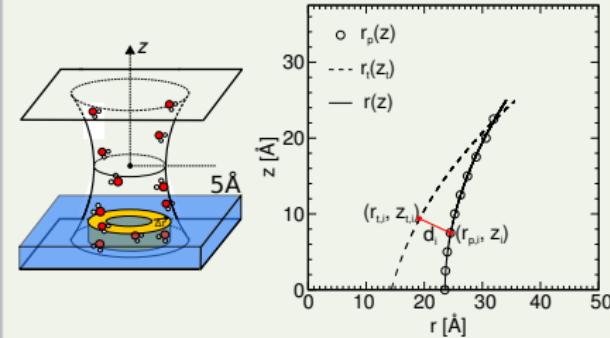
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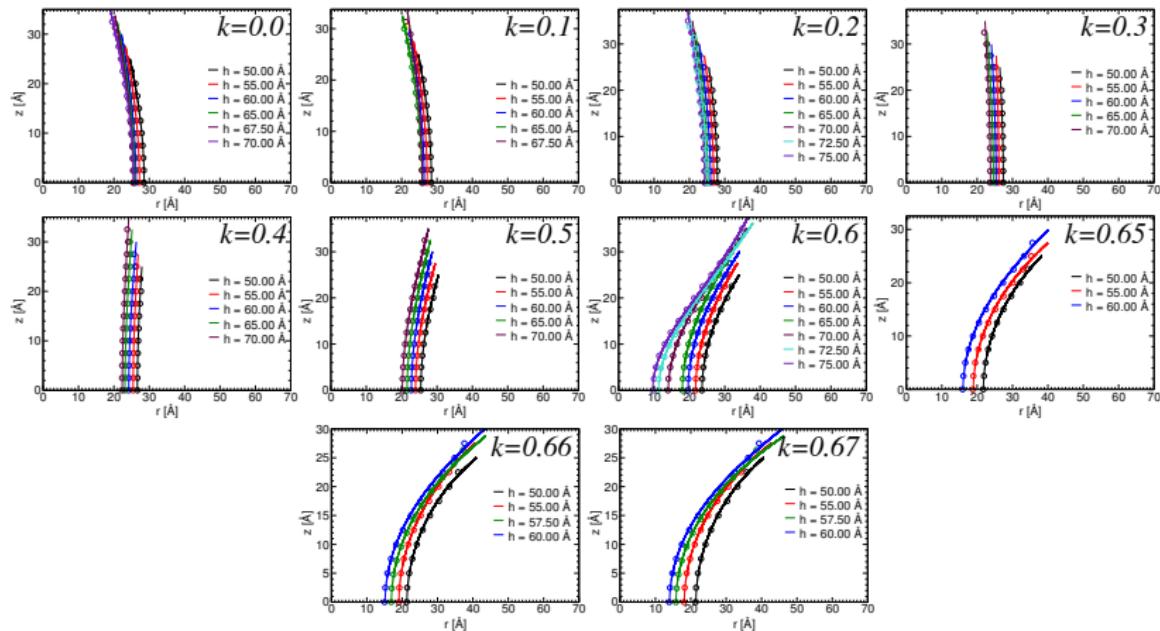
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## Calculation of the average profile $r_p(z)$



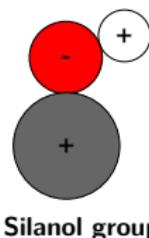
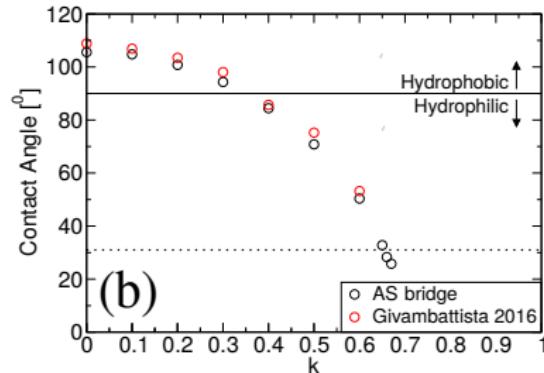
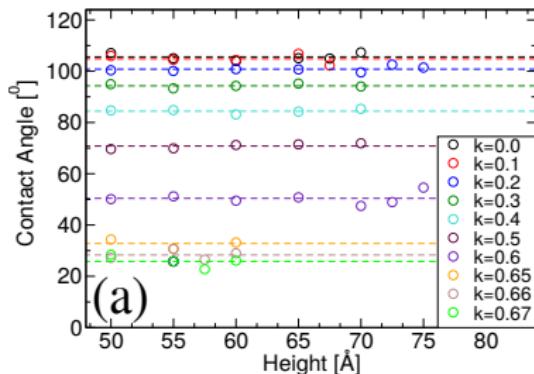
- $r_0$ ,  $r_B$ ,  $\theta_c$ ,  $H$ ,  $\Omega$ ,  $A_R$  and  $A_B$

# Numerical fitting of the profiles $r(z)$ (—) to the average profiles $r_p(z)$ (○) obtained from the 2 ns simulation.



$\theta_c [^\circ]$	0	0.1	0.2	0.3	0.4	0.5	0.6	0.65	0.66	0.67
	105.6	104.8	100.8	94.3	84.4	70.8	50.4	32.8	28.3	25.8

# Contact angle as a function of (a) height and (b) polarity $k$ .



$$\vec{p} = k \times \vec{p}_0$$

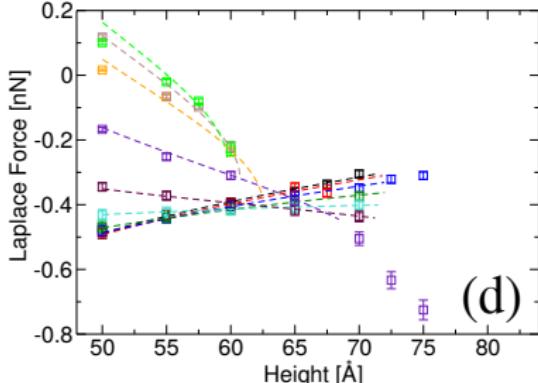
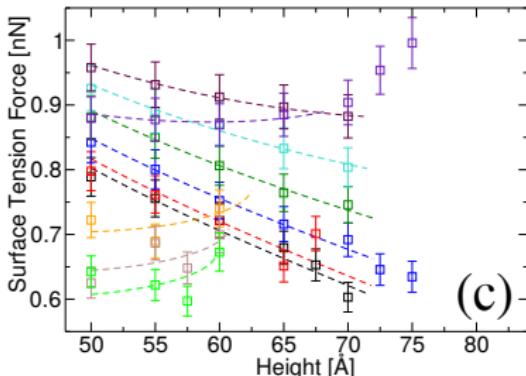
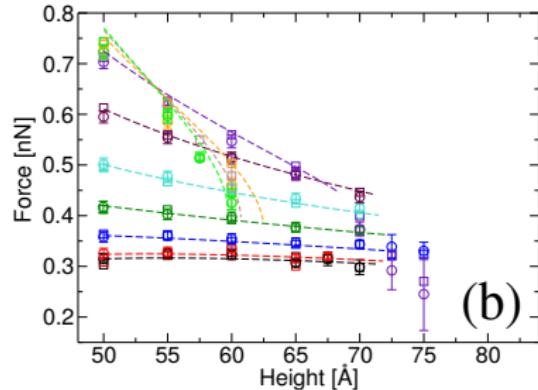
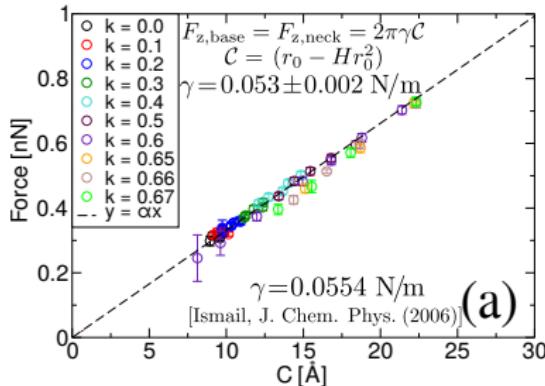
$$\vec{p}_0 = \vec{p}_{SiO} + \vec{p}_{OH}$$

## Wetting criteria:

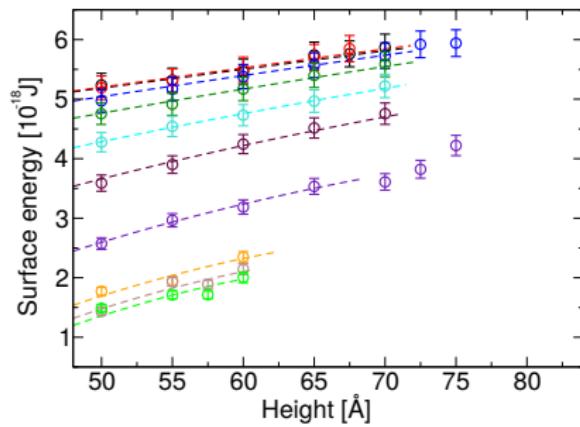
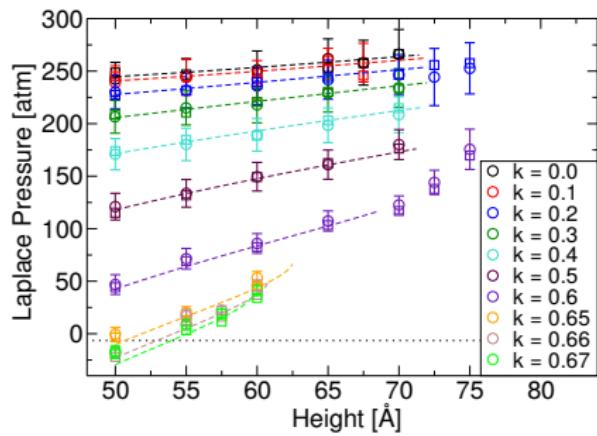
- $k > 0.35$ : Hydrophilic surface;
- $k < 0.35$ : Hydrophobic surface.

Capillary adhesion force = Surface tension force + Laplace force.

The dashed lines are the analytical solution based on  $\theta$ ,  $\Omega$  and  $h$ .



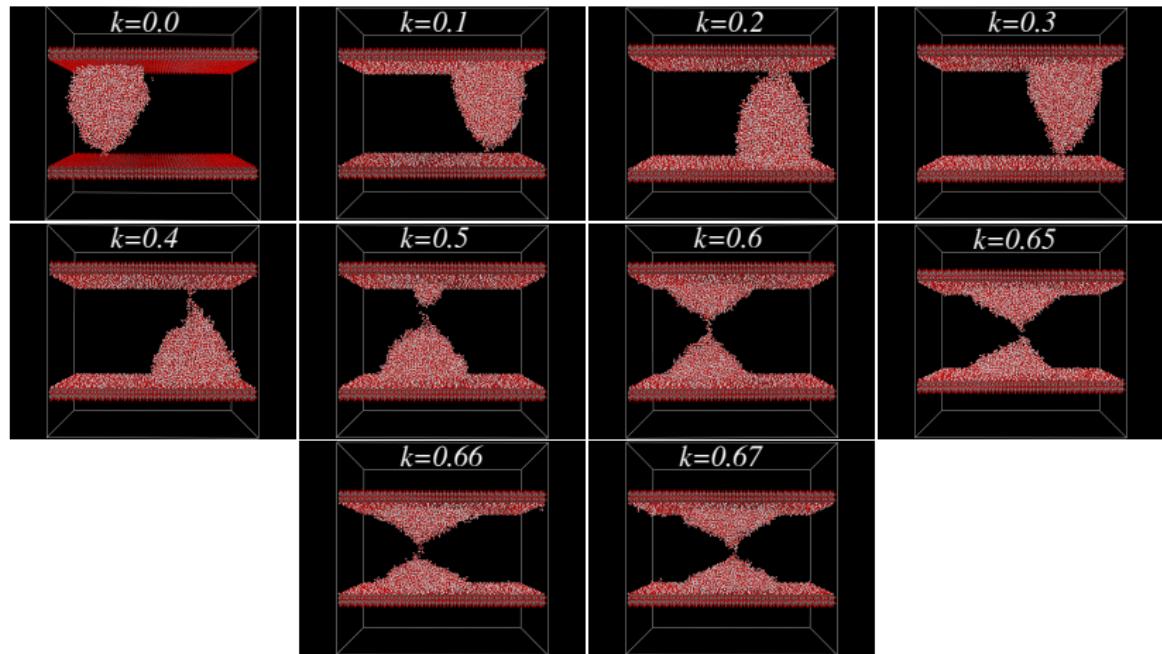
# Laplace pressure and surface free energy.



- $P_L = 2\gamma H$
- $P_L = \frac{F_\gamma - \langle F_{z,\text{base}} \rangle}{A_{\text{base}}}$

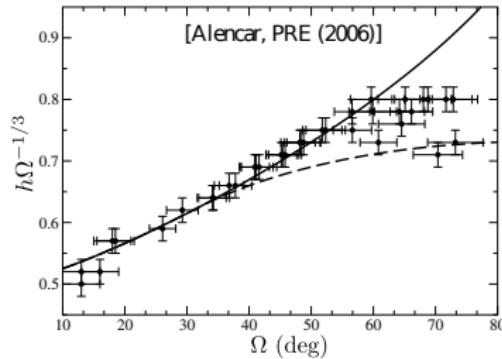
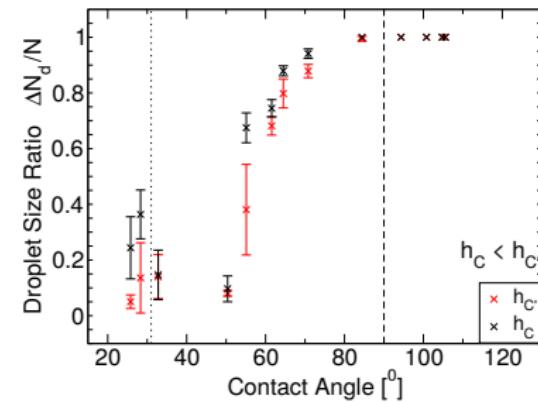
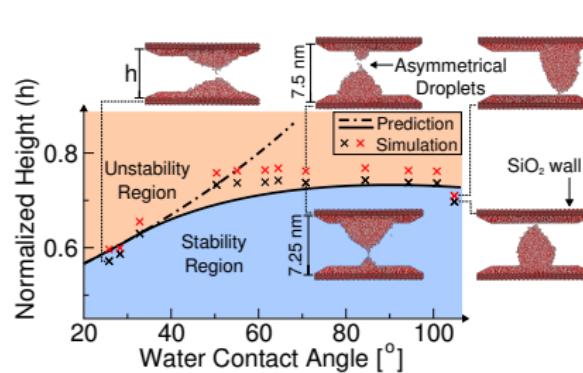
- $\mathcal{F}(h) = \gamma(A_{\text{LG}}(h) - \cos \theta_c A_{\text{LS}}(h))$

Snapshots of water configurations at the rupture time  $\tau_R$  and at the critical height  $h_{C'} = h_S + 5 \text{ \AA}$ .

Polarity ( $k$ )

$\theta_c [^\circ]$	0	0.1	0.2	0.3	0.4	0.5	0.6	0.65	0.66	0.67
$\tau_R$ (ps)	105.6	104.8	100.8	94.3	84.4	70.8	50.4	32.8	28.3	25.8

# Phase diagram ( $\theta_c$ , $h$ ) of AS bridges rupture.



$$\frac{\Delta N_d}{N} = \left| \frac{N_{\text{droplet1}} - N_{\text{droplet2}}}{3375} \right|$$

- $\times \rightarrow$  First rupture:  $h_{C'} = h_S + 5 \text{ \AA}$
- $\times \rightarrow$  Second rupture:  $h_C = h_S + 2.5 \text{ \AA}$   
 $\Delta t_{\text{sim}} = 20 \text{ ns: } h = (h_S + 2.5) + 1.25 \text{ \AA}$

# Conclusions

## Stable AS bridges

- The macroscopic CT predicts the profile of nanometric capillary bridges.
- The contact angle is independent of the height.
- The surface tension calculation based on CT concepts is in agreement with literature.
- The analytical solution ( $\Omega$ ,  $\theta_c$  and  $h$ ) of AS bridges predicts the forces and pressures at the nanoscale.

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## Unstable AS bridges

- The rupture heights  $h_{C'}$  and  $h_C$  are in agreement with analytical solution  $h_{\max,a}$  and  $h_{\max,s}$ .

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## Main conclusion

**The macroscopic capillary theory is able to predict the properties of capillary bridges with volumes in the order of  $100 \text{ nm}^3$ .**

## Acknowledgements



## Main references

- A. B. Almeida, N. Giovambattista, S. V. Buldyrev and A. M. Alencar, J. Phys. Chem. C **122**, 1556 (2018)
- N. Giovambattista, A. B. Almeida, A. M. Alencar and S. V. Buldyrev, J. Phys. Chem. C **120**, 1597 (2016)
- A. M. Alencar, E. Wolfe and S. V. Buldyrev, Phys. Rev. E **74**, 026311 (2006)
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## Acknowledgements



INCT-Fcx



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Thank you!!

Questions??

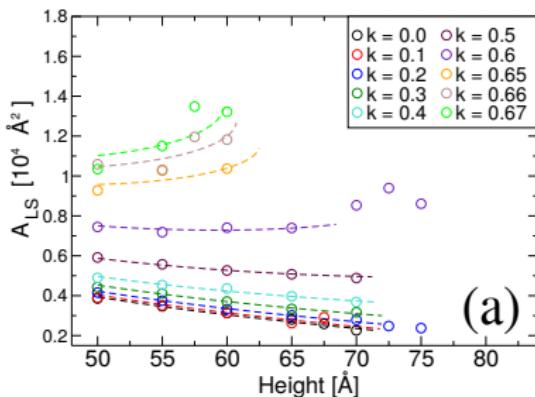


LabM²

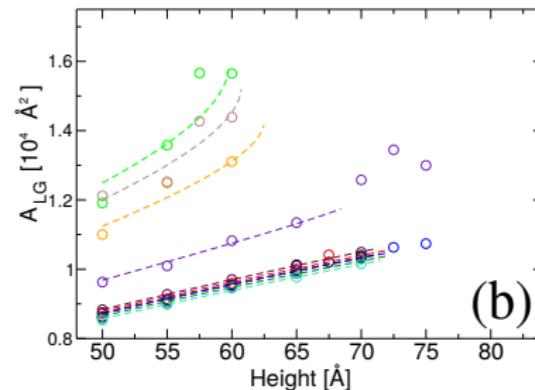
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# Liquid-solid and liquid-gas interface areas, volume and surface free energy.

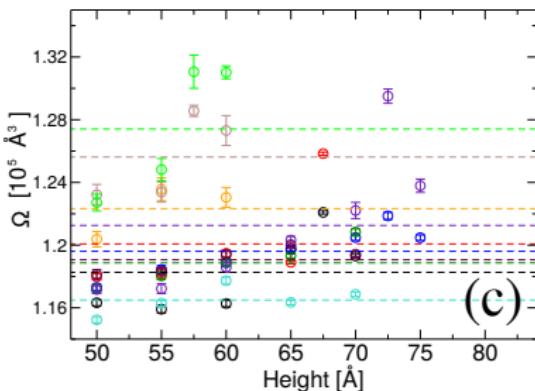
The dashed lines are the analytical solution based on  $\theta$ ,  $\Omega$  and  $h$ .



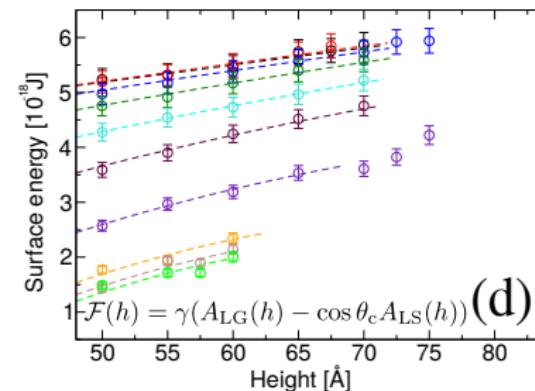
(a)



(b)



(c)



(d)

Validation of capillary theory for  $h \leq 50.0\text{\AA}$ .