La physique du mouillage

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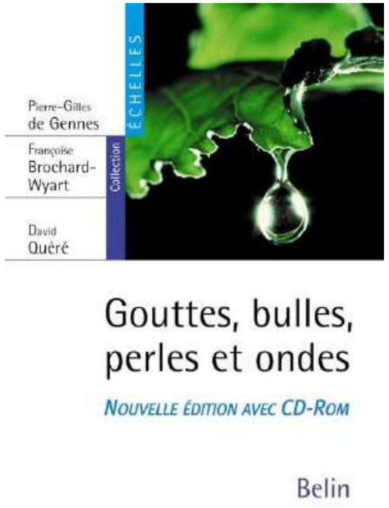
Outline

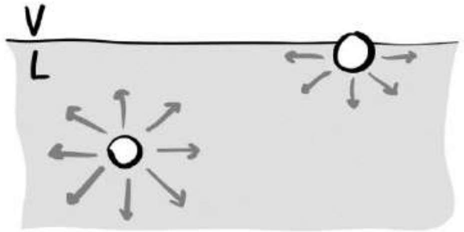
- **Surface tension**
- **Statics of wetting**
  - Contact angle
  - Hysteresis
  - Structured surfaces
  - Nanoscale wetting
  - Wetting of fibers
- **Wetting dynamics: the moving contact line issue**
  - Dynamical contact angle
  - Spreading dynamics
  - Simulations
  - Intertial wetting
  - Impact
- **Wetting in complex situations**
  - Volatile liquids
  - Reactive liquids
  - Surfactants
- **Wetting and adsorption**
  - Contamination by airborne molecules or particles
  - Cleaning



De Gennes, *Rev. Mod. Phys.* 1986
Bonn *et al.*, *Rev. Mod. Phys.* 2009

Surface tension

➤ Surface energy

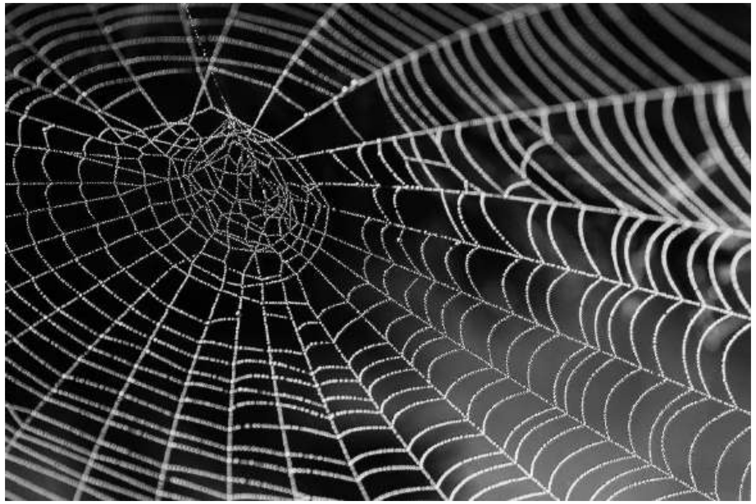


$$\gamma = \frac{energy}{surface} \sim \frac{kT}{a^2}$$

$$\gamma \sim \frac{4.10^{-21}}{(2.10^{-10})^2} \sim 100\ mJ/m^2$$

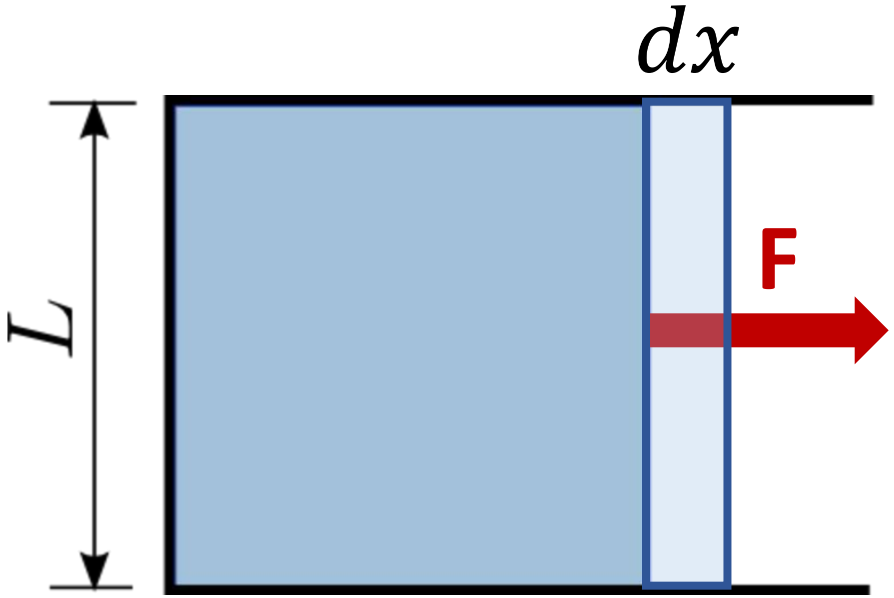
→ **Surface area minimization**

✓ **Ex: Rayleigh-Plateau instability**



Interfacial tension

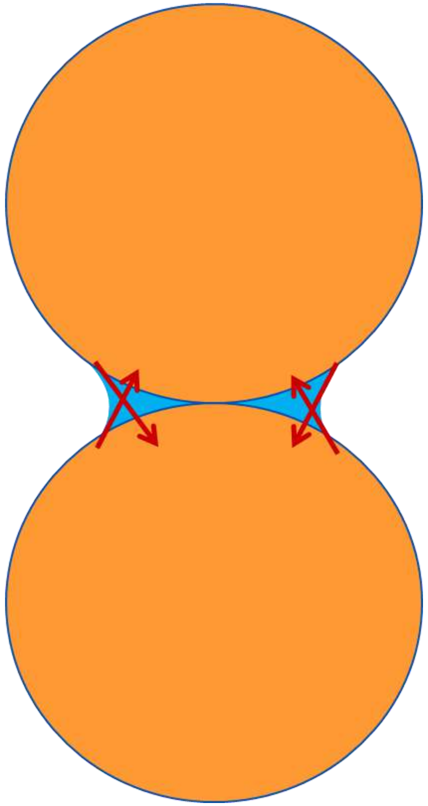
- **Force per unit length**



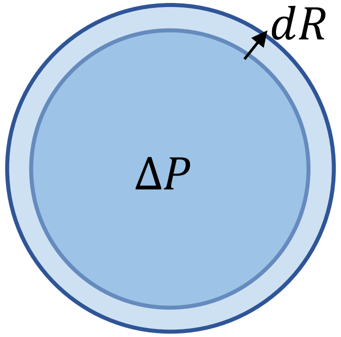
$$\delta W = \gamma L dx = F . dx$$

$$\gamma = \frac{F}{L}$$

- **Ex: sand castle**

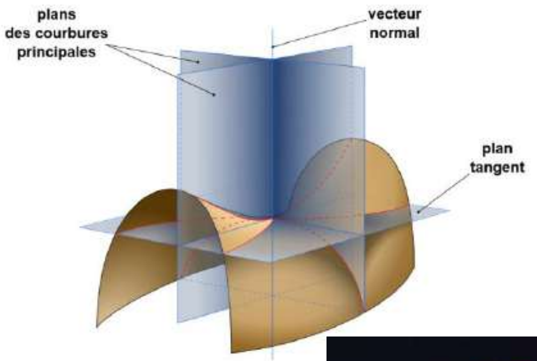


Laplace pressure



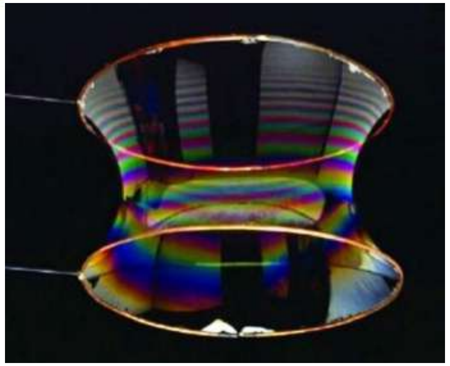
$$\delta W = \Delta P.4\pi R^2 dR = \gamma d(4\pi R^2) = \gamma 8\pi R dR$$

$$\Delta P = \frac{2\gamma}{R}$$



$$\Delta P = \gamma\left(\frac{1}{R_1} + \frac{1}{R_2}\right)$$

R > 0 or < 0



- ✓ **Ex : loi de Jurin**

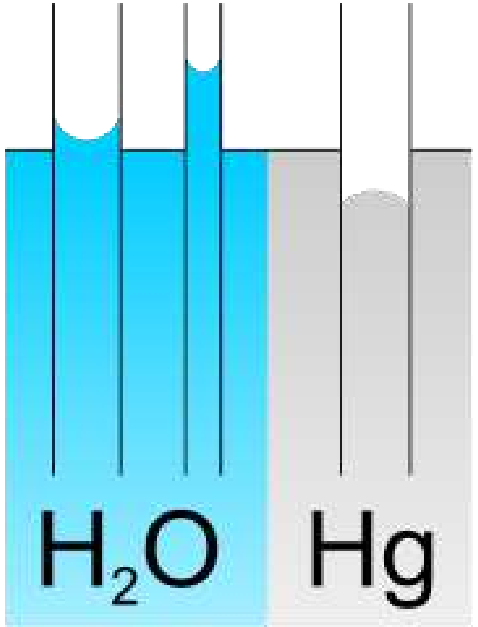
$$\Delta P_{Laplace} + \rho g h = 0$$

$$h = \pm\frac{2\gamma}{\rho g\, R}$$

$\Delta P_{Laplace}$

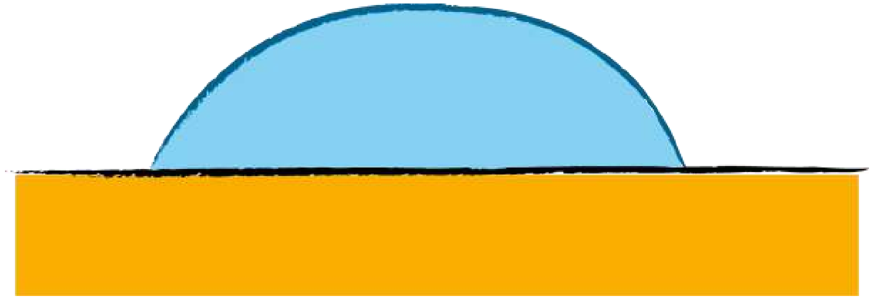
$-\frac{2\gamma}{R}$ $\quad h > 0$

$\frac{2\gamma}{R}$ $\quad h < 0$



Capillary length

- **Laplace pressure *vs.* hydrostatic pressure**



$$\frac{2\gamma}{h} \sim \rho g h$$

$$K^{-1} = \sqrt{\frac{\gamma}{\rho g}} \sim 2 \text{ mm}$$

Surface tension measurement

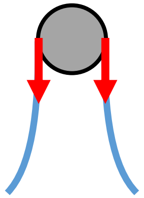
➢ Mesure tension

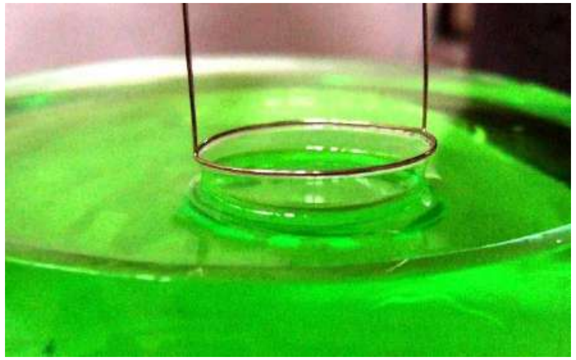
✓ Pendant drop method

Balance surface tension force - weight

✓ Du Noüy tensiometer

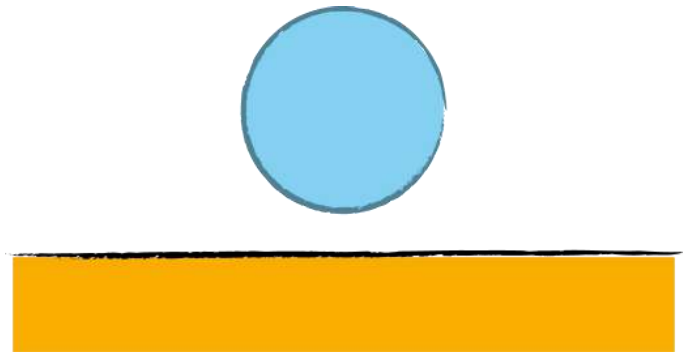
$$F = 2 * 2\pi r\gamma$$





Liquid	γ (mN/m)
Water	72,8
Glycerol	63
Ethylene glycol	48
Ethanol	22,4
Hexane	17,9
PDMS	20,4
Mercure	486

Wetting: thermodynamics

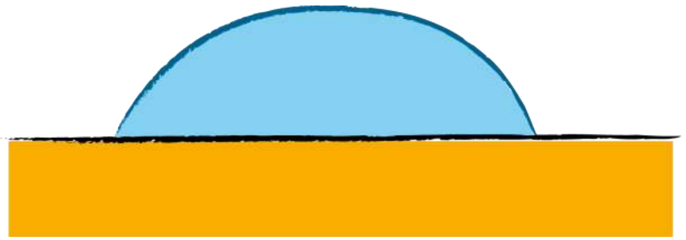


➤ **Spreading parameter**

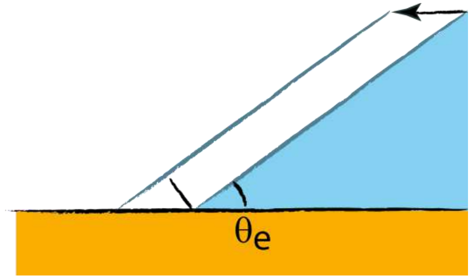
$$S = \gamma_{SG} - (\gamma_{SL} + \gamma)$$

- **S > 0 Total wetting**

- **S < 0 Partial wetting**

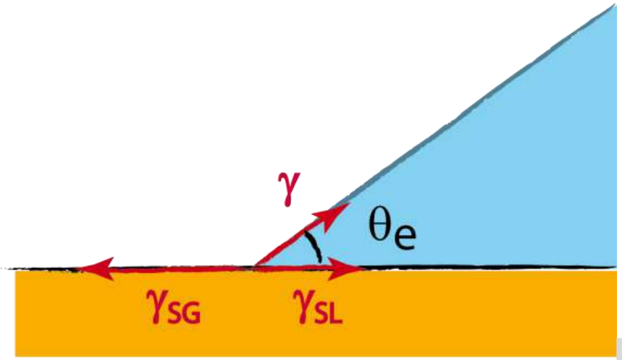


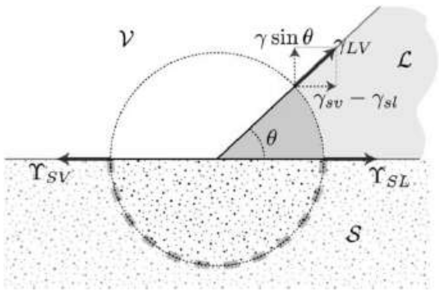
Partial wetting



$$\cos\theta_e = \frac{\gamma_{SG} - \gamma_{SL}}{\gamma}$$

$$dE = (\gamma_{SL} - \gamma_{SG})dx + \gamma.\cos\theta.dx$$

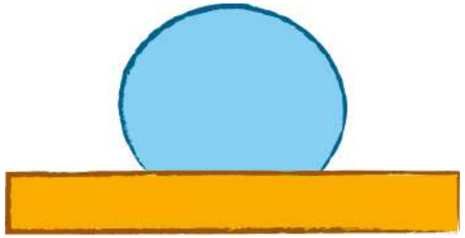




Marchand *et al.*, *Am. J Phys.* 2011

Hydrophilic

$\theta_e < 90\,°$

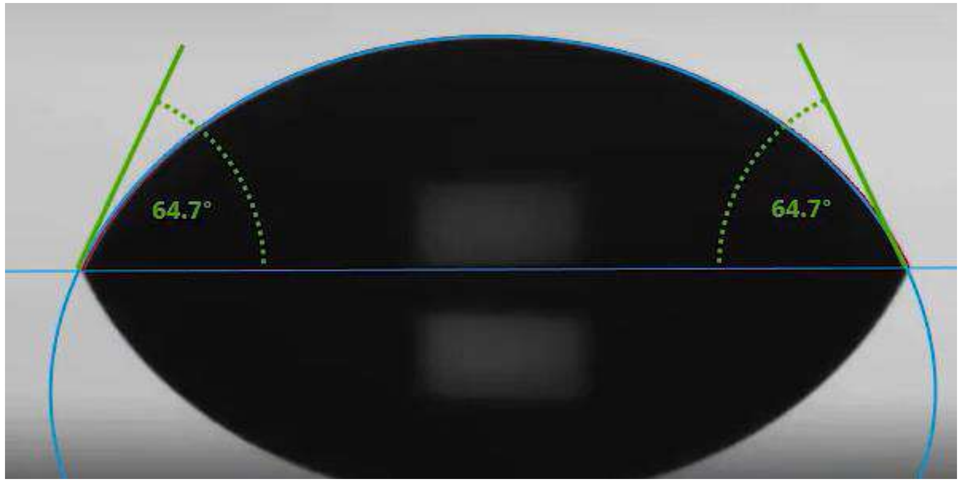


Hydrophobic

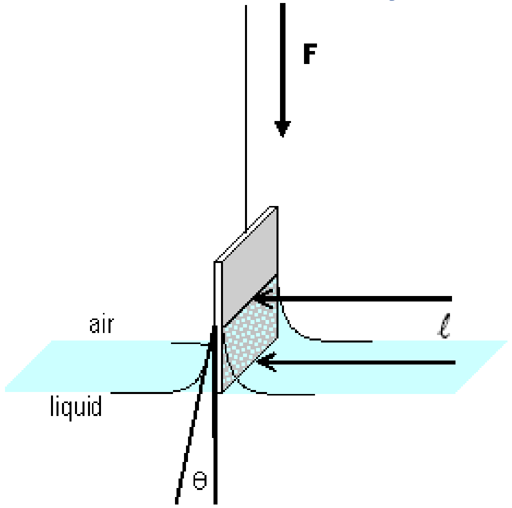
$\theta_e > 90\,°$

Contact angle measurements

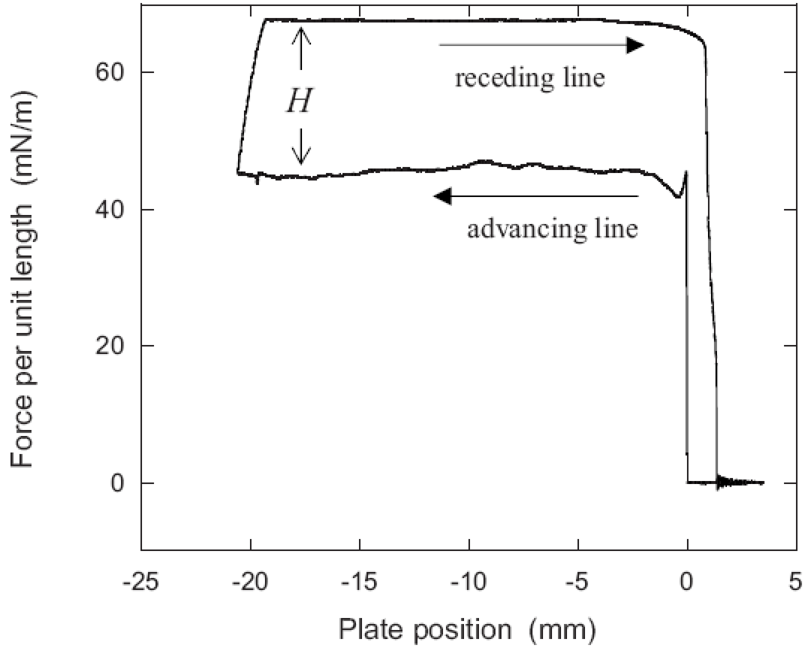
- Goniometer



- Wilhelmy balance

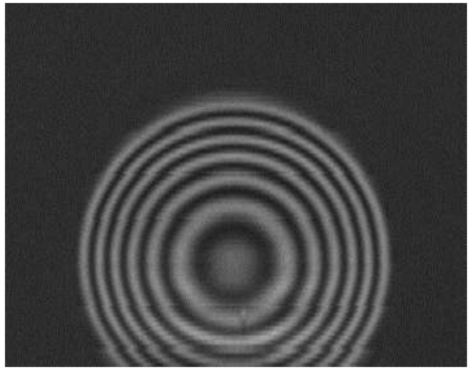


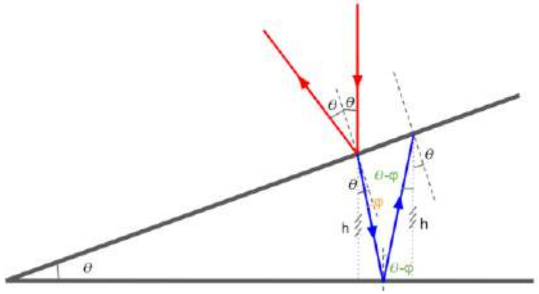
$$F = 2L\gamma \cos\theta$$



Contact angle measurements

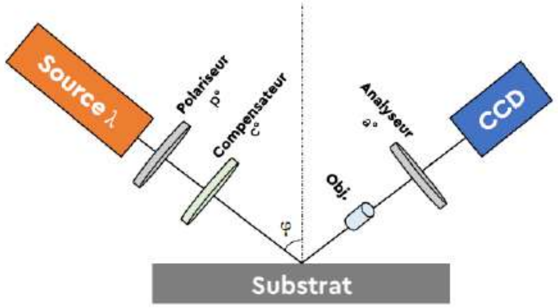
- Interferences



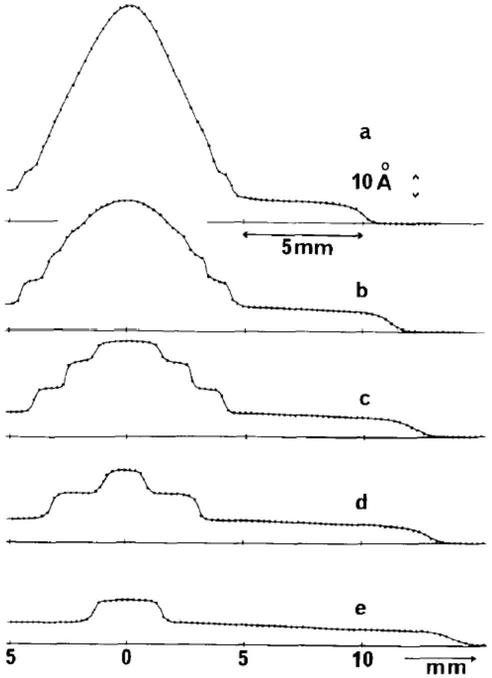


$$\Delta h = \frac{\lambda}{2n}$$

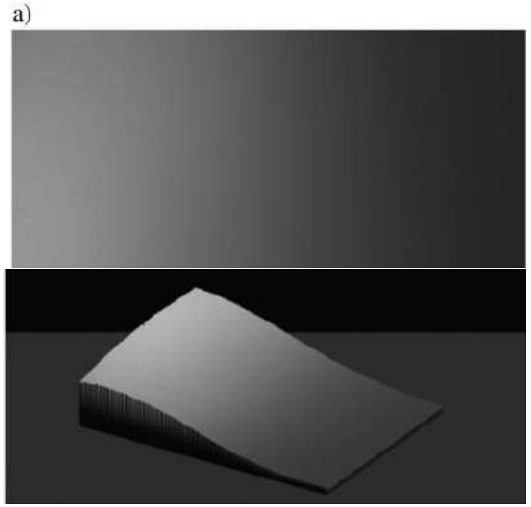
- Ellipsométrie



Heslot *et al.*, Nature 1989

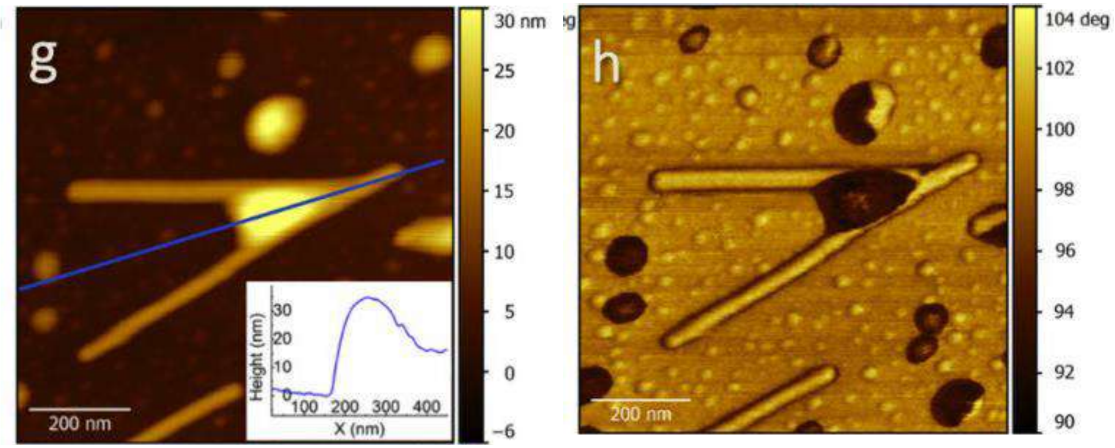


- Fluorescence



Huang *et al.*, Phys. Rev. Lett. 2011

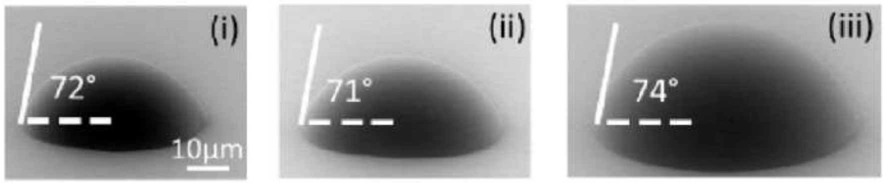
- AFM



Calo *et al.*, *Molecules*. 2021

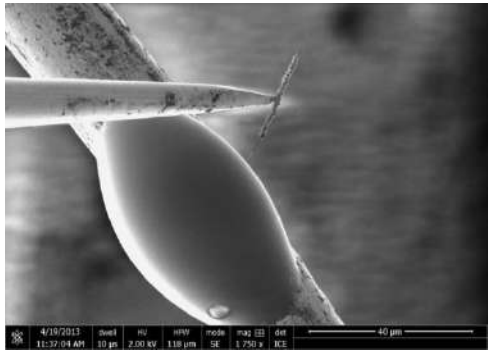
Contact angle measurements

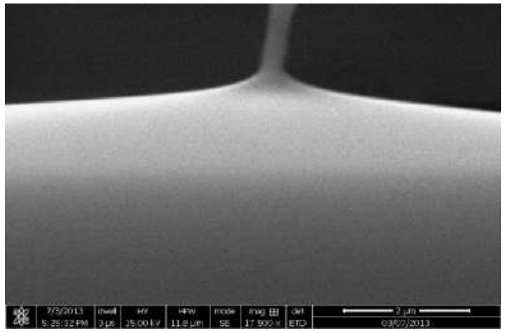
➢ ESEM



Chatre *et al.*, *Langmuir* 2023

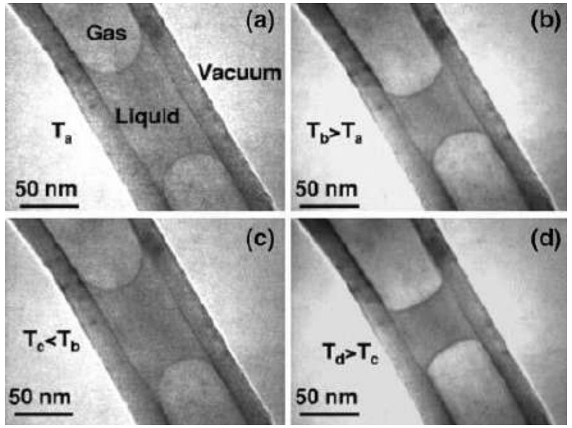
➢ SEM with ionic liquids





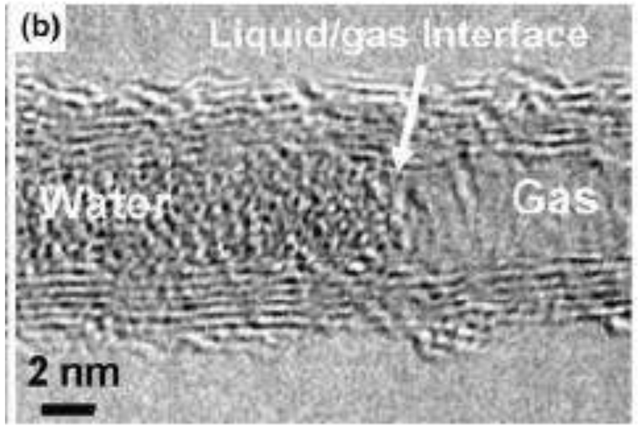
Dupré de Baubigny *et al.*, *Langmuir*. 2015

➢ TEM



Gogotsi *et al.*, *Appl. Phys.* Lett. 2001

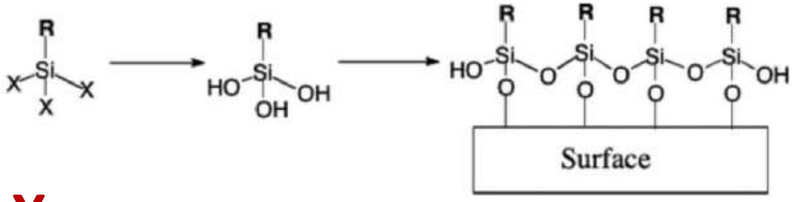
➢ HRTEM



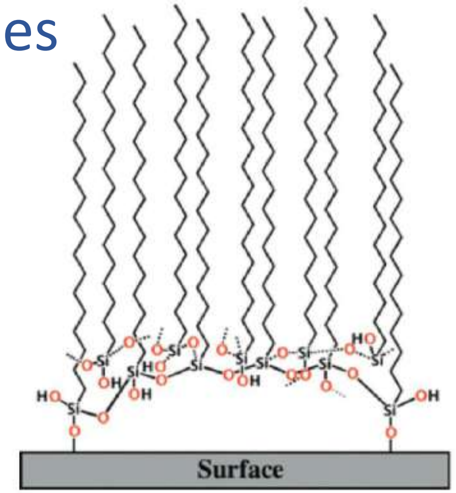
Naguib *et al.*, *Nano*. Lett. 2004

Controlling contact angle

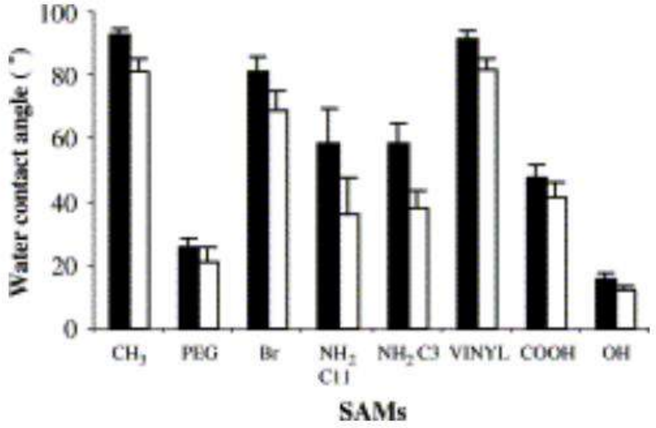
➢ Surface fonctionnalisation by silanes



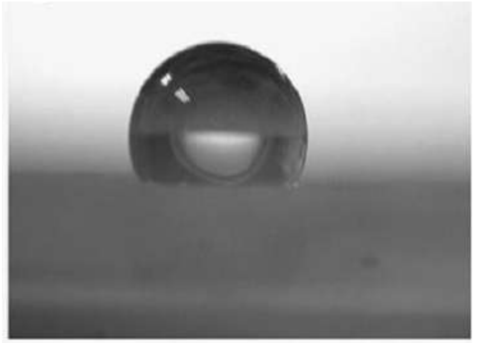
X = Cl, OEth, ..



Liquid or vapor phase



R



Maximum achievable contact angle on flat surface

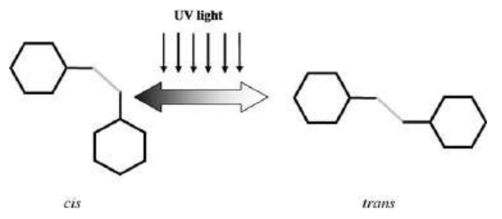
$\boldsymbol{\theta} \approx \mathbf{120°}$

1H, 1H, 2H, 2H, perfuorodecyltrichlorosilane

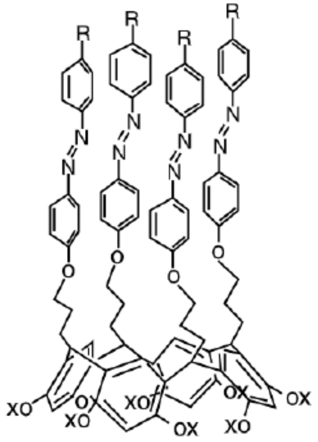
~ Teflon®

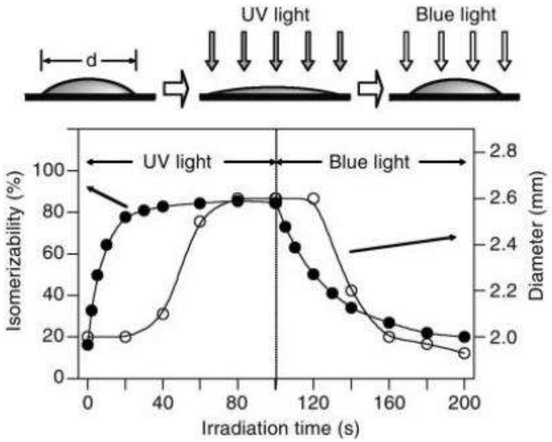
Switchable surfaces

➢ Photoswitching

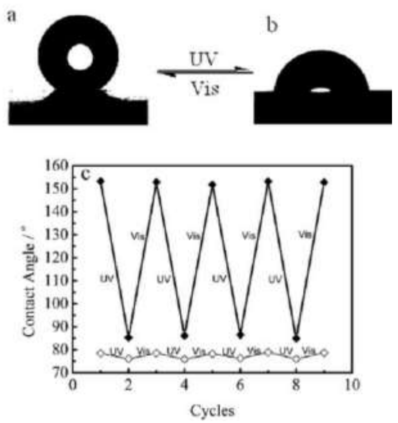


Ishimura, Science 200



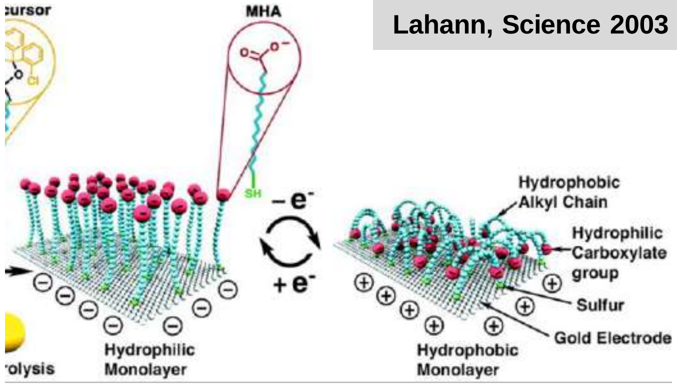


On rough surfaces

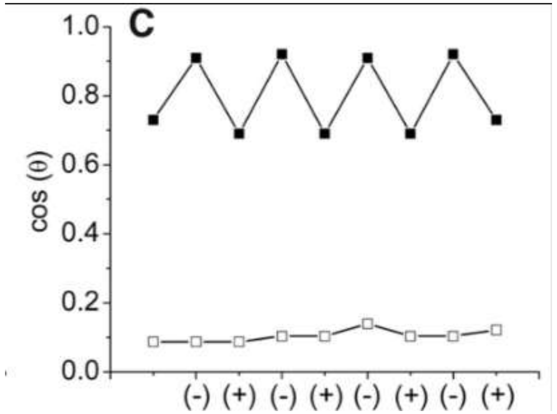


Jiang et al., Chem. Comm. 2005

➢ Photoswitching



Lahann, Science 2003

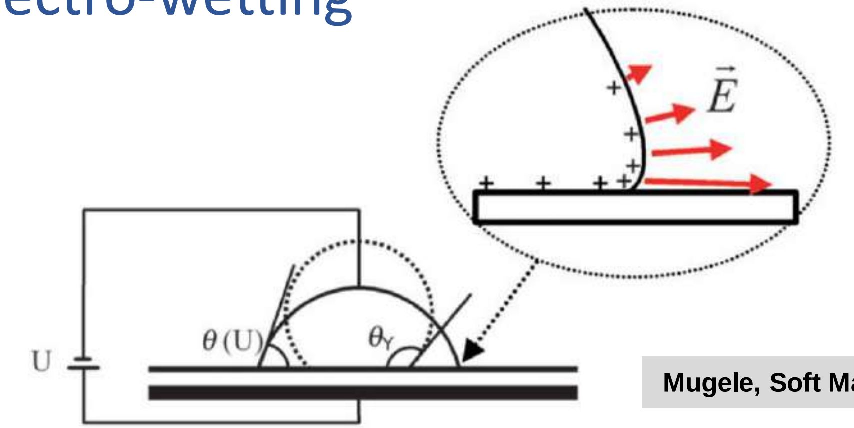


➢ Others

Gras et al., ChemPhysChem 2007

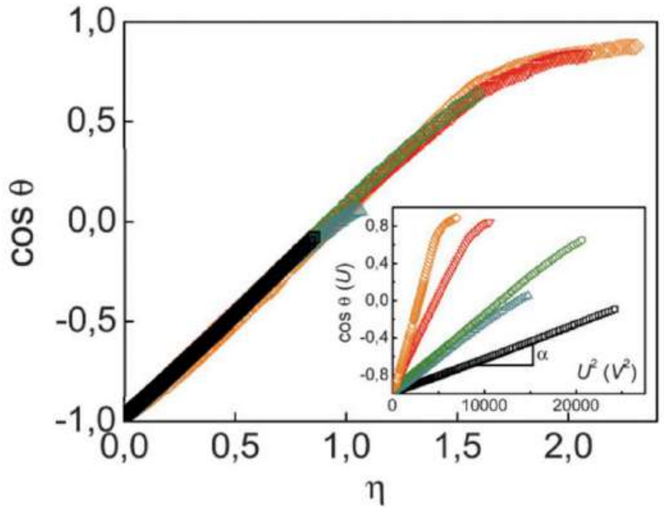
Controlling contact angle

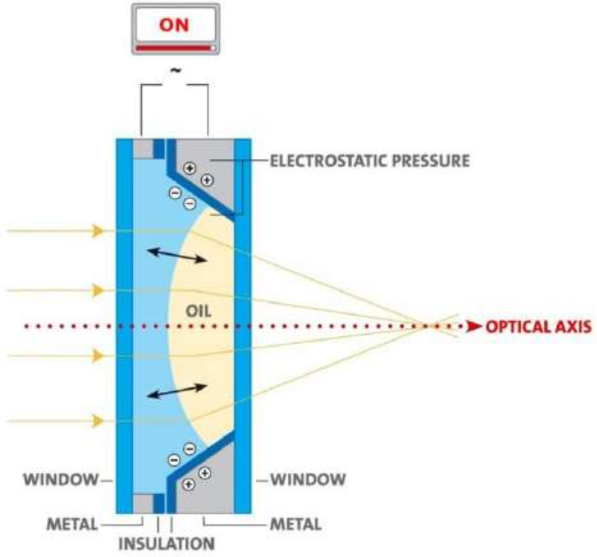
- Electro-wetting



Mugele, Soft Matt 2009

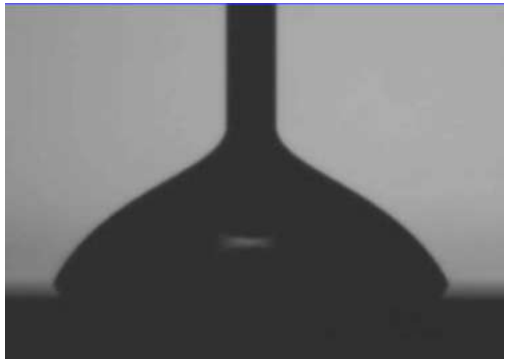
$$\cos\theta = \cos\ \theta_e + \frac{\epsilon\ \epsilon_0 U^2}{2\gamma d}$$

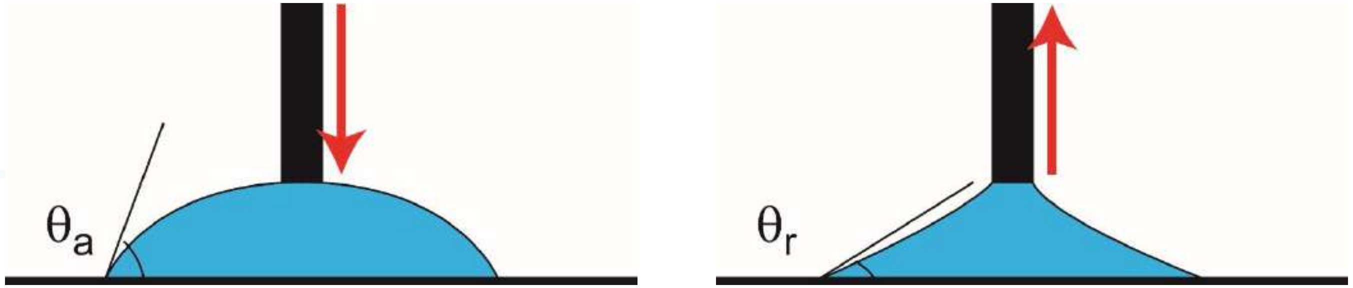




Corning

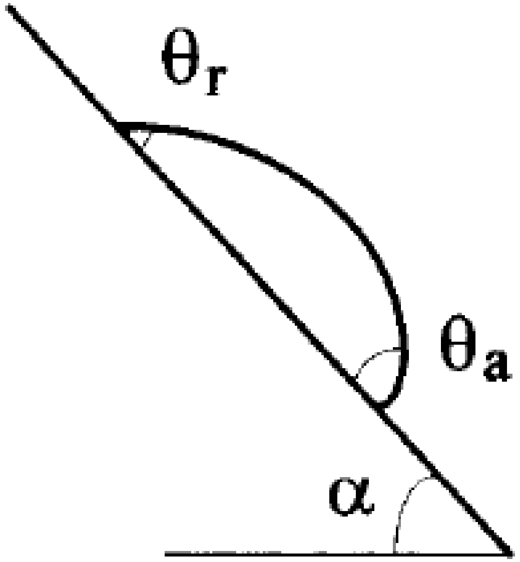
Contact angle hysteresis





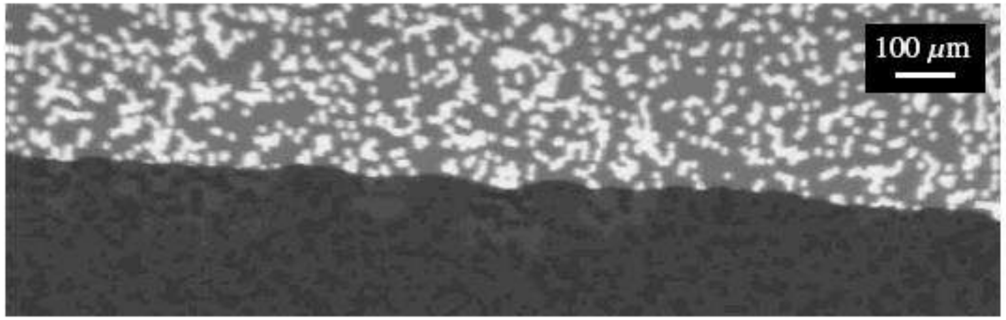
Advancing

Receding



$$\pi r \gamma (\cos\theta_r - \cos\theta_a) \geq \rho \Omega g \sin\alpha$$

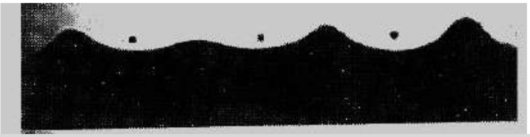
Origin: pinning of the contact line on surface defects



Contact angle hysteresis: individual defect

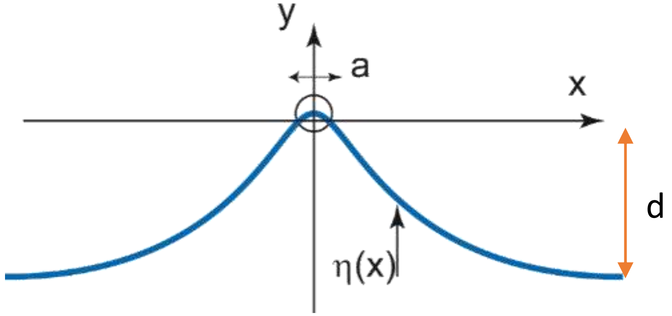
➢Contact line elastic energy

$$E_{él} = \frac{1}{4}\gamma \sin^2\theta \int |q||\tilde{\eta}(q)|^2 \frac{dq}{2\pi}.$$



Ondarçuhu, Veyssié *Nature* 1991

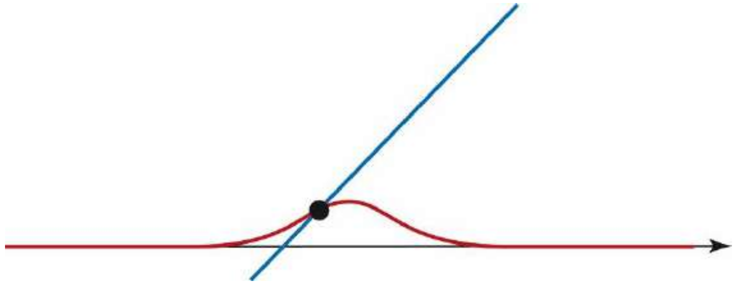
Joanny and de Gennes *J. Chem. Phys.* 1984



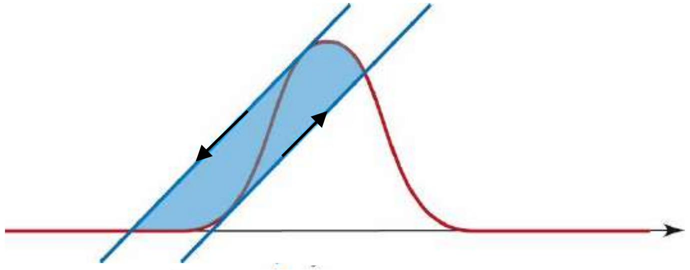
For localized defect: $F = k.y$ with

$$k = \frac{\pi\gamma \sin^2\theta_e}{\ln(L/a)}$$

➢ Balance of forces



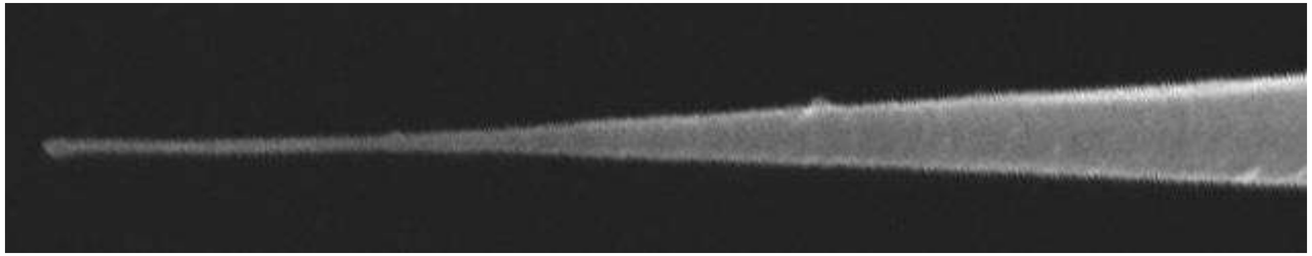
Weak defect

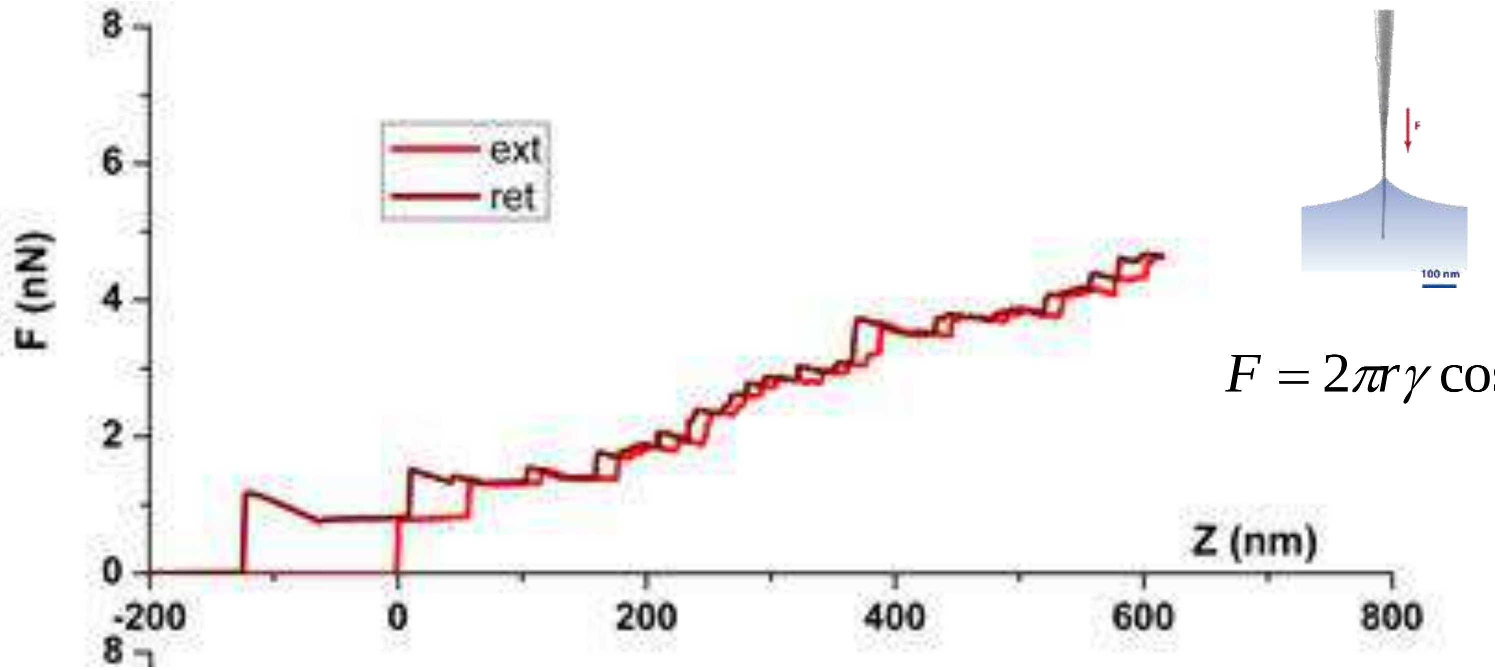


Strong defect

Contact angle hysteresis: individual defect

Ø = 11 nm



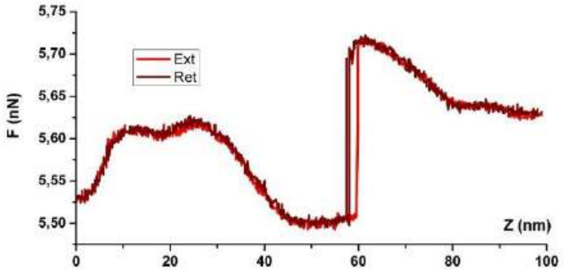


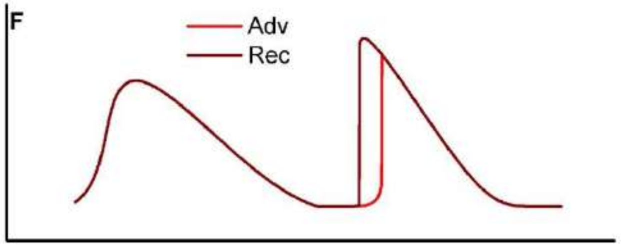
$$F = 2\pi r\gamma\cos\theta$$

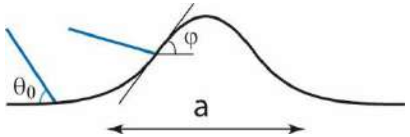
Delmas *et al. PRL* 2011

Weak defect

Strong defect



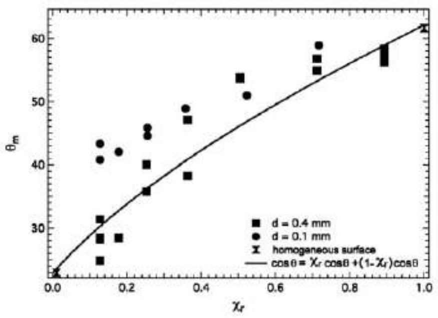


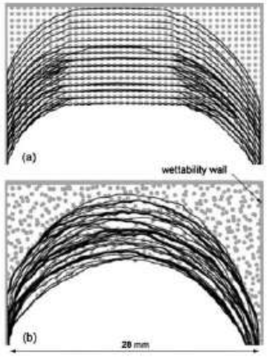


$$W = \frac{F_0^{\ 2}}{2k} > kT \Longrightarrow a_C = \left(\frac{4\pi}{Ln(L/a)\sin^2\varphi}\right)^{1/2} b \approx 1{,}5\ b$$

Contact angle hysteresis: collective effects

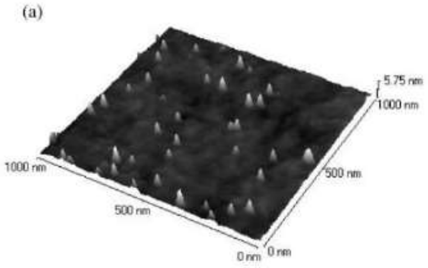
- Patterned substrates (> 10 µm)

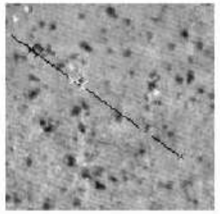




Cubaud, Fermigier *JCIS* 2004

- Nanometric defects



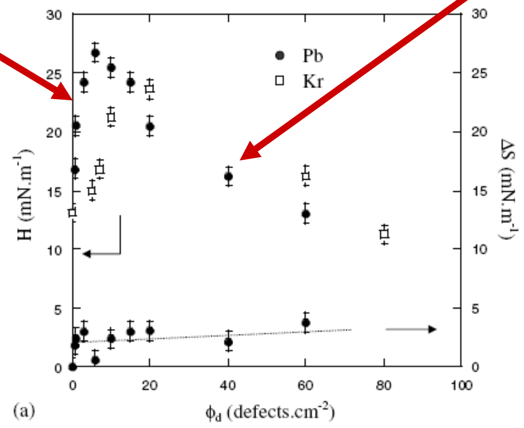


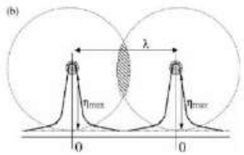
Ø ~ 20-200 nm

Ramos et al *Surf. Sci.* 2003
Eur. Phys. J E 2006

Individual pinning

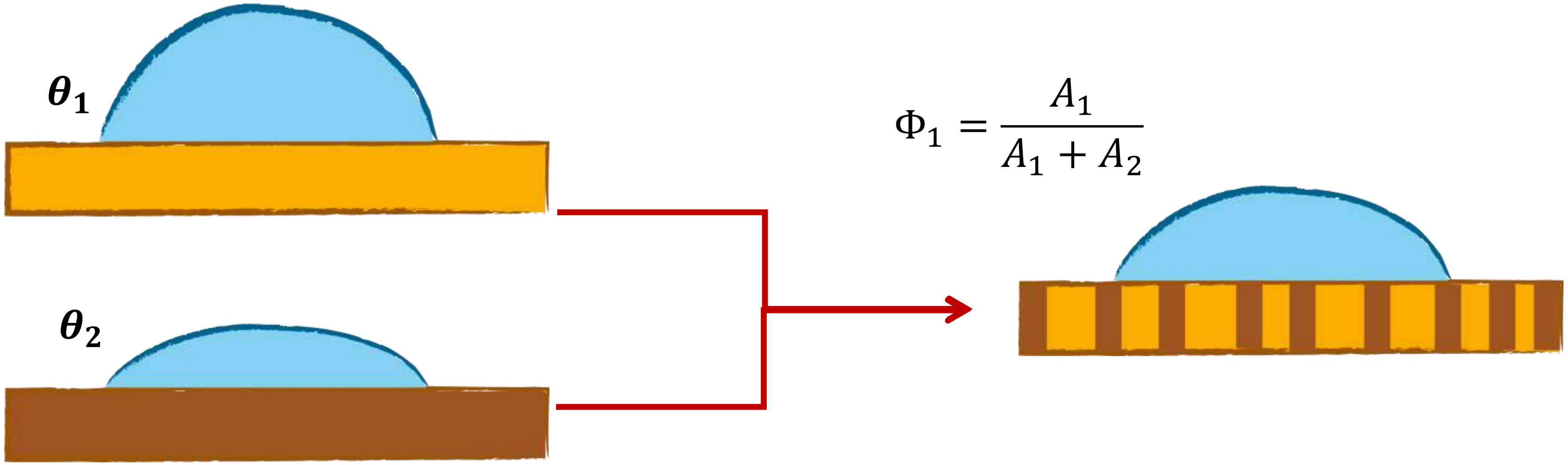
Collective pinning





- **Pb : reference surface without hysteresis**

Chemical heterogeneity: Cassie-Baxter model



$$\Phi_1 = \frac{A_1}{A_1 + A_2}$$

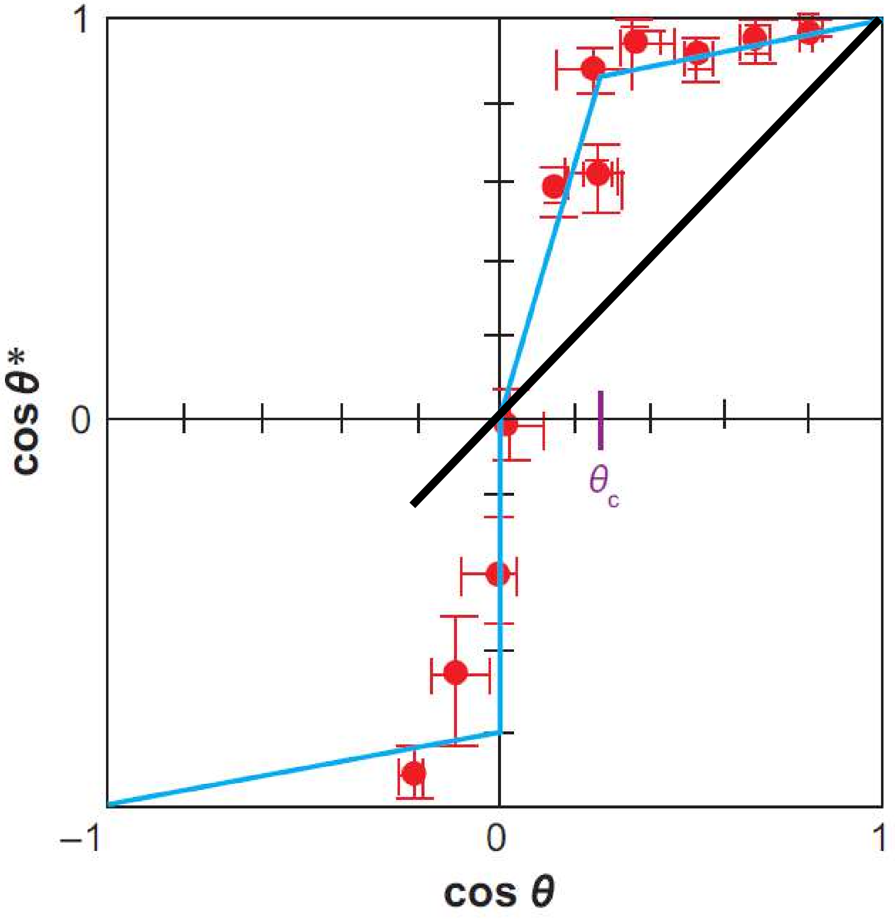
$$dE = [\Phi_1(\gamma_{1L} - \gamma_{1G}) + \Phi_2(\gamma_{2L} - \gamma_{2G})].dx + \gamma.\cos\theta.dx$$

$$\cos\theta^* = \Phi_1 \cos\theta_1 + (1 - \Phi_1)\cos\theta_2$$

Cassie and Baxter *Trans. Farad. Soc.* 1944

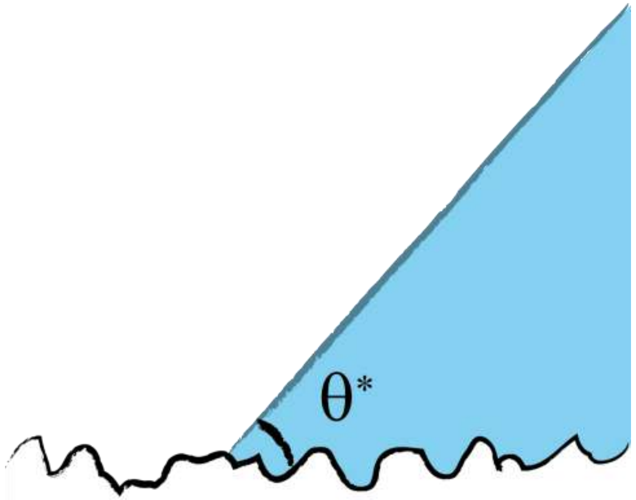
Rough substrates

Quéré, *Ann. Rev. Mat. Res*. 2009



Onda *et al.*, *Langmuir* 1996

Rough substrates: Wenzel state

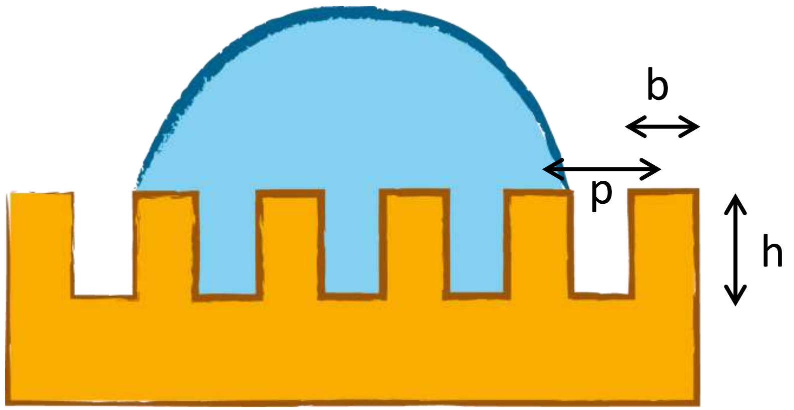


$$dE = r(\gamma_{SL} - \gamma_{SV})dx + \gamma.\cos\theta.dx$$

$$\boldsymbol{\cos\theta^* = r.\cos\theta_e}$$

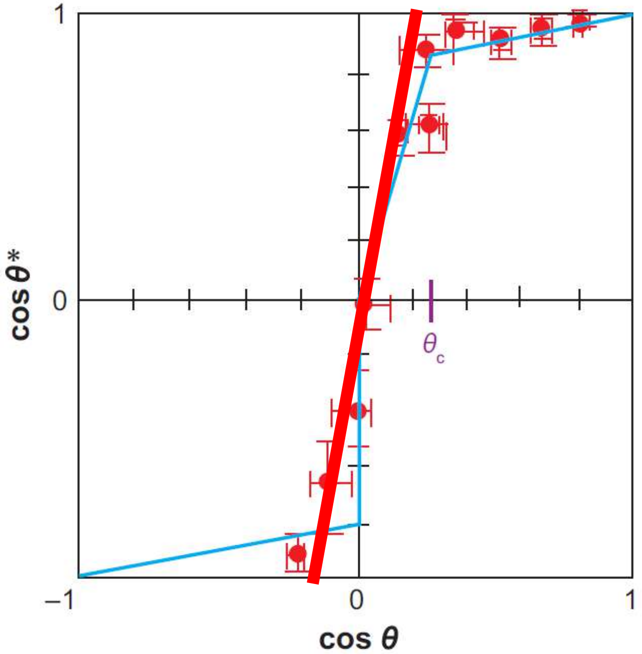
Wenzel, *Ind. Eng. Chem.* 1936

$$r = \frac{actual\ surface\ area}{projected\ surface\ area}$$ = roughness factor

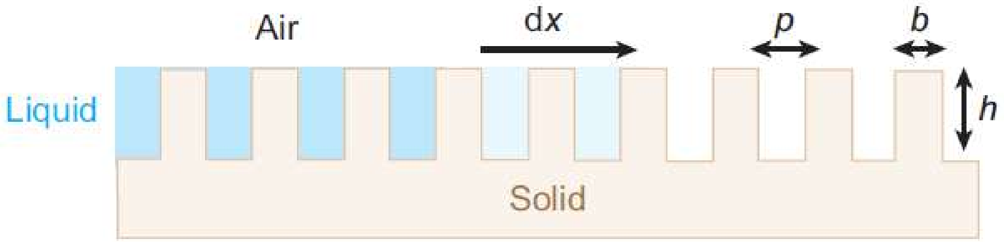


$$r = \frac{p + 2h}{p} = 1 + 2\frac{h}{p}$$

$$\Phi_s = \frac{b}{p}$$

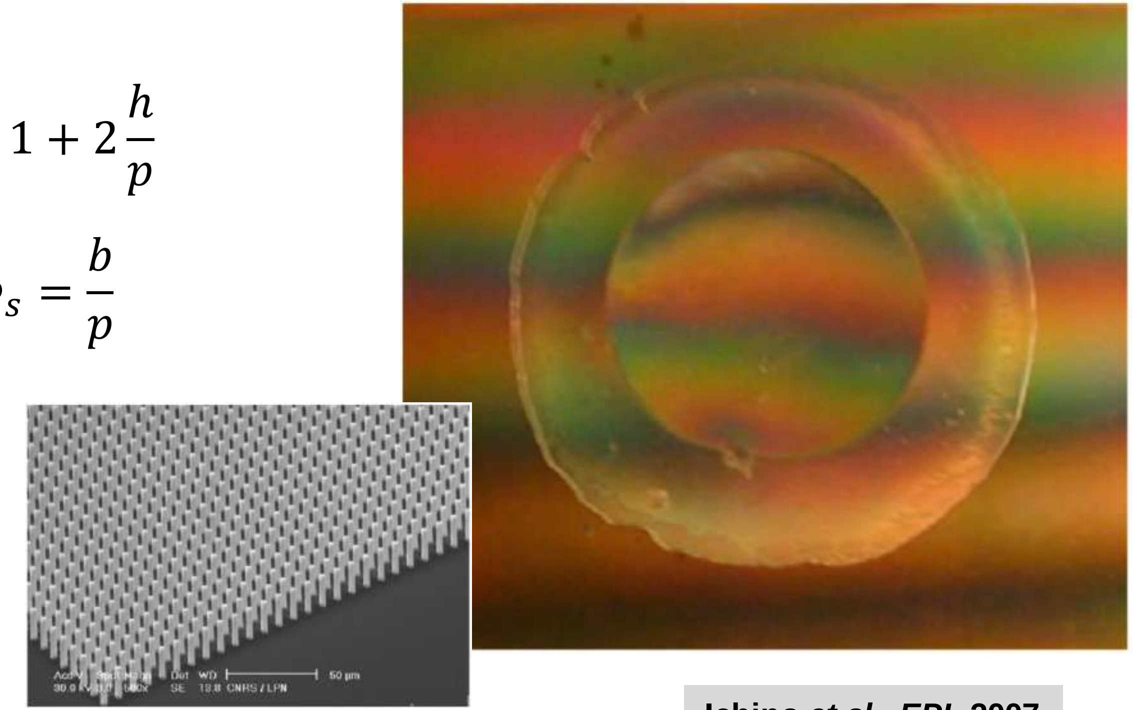


Rough hydrophilic: superhydrophilicity



$$r = 1 + 2\frac{h}{p}$$

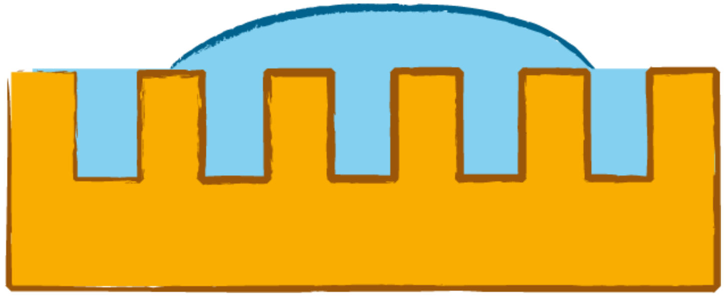
$$\Phi_s = \frac{b}{p}$$



Ichino *et al.*, *EPL* 2007

$$dE = (\gamma_{SL} - \gamma_{SG})(r - \Phi_S) + \gamma(1 - \Phi_S)$$

$$\cos\theta_c = \frac{1 - \phi_S}{r - \phi_S}$$



$$\theta_1 = \theta_e$$
$$\theta_2 = 0°$$

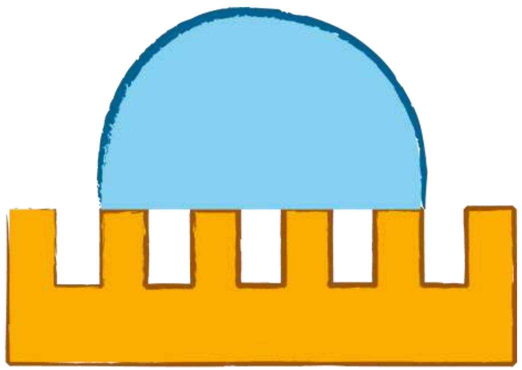
$$\cos\theta^* = \phi_S \cos\theta_e + (1 - \phi_S)$$

$$\cos\theta^* = 1 - \phi_S(1 - \cos\theta_e)$$

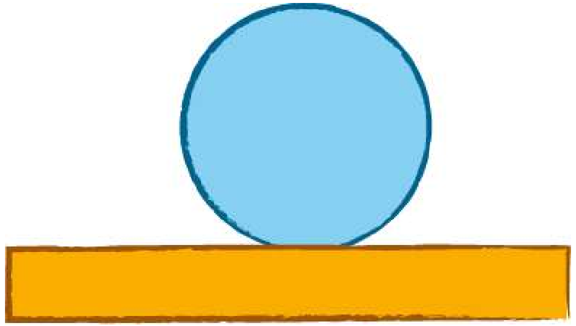
Rough hydrophobic: superhydrophobicity

$$\cos\theta_c = -\frac{1-\Phi_S}{r-\Phi_S}$$

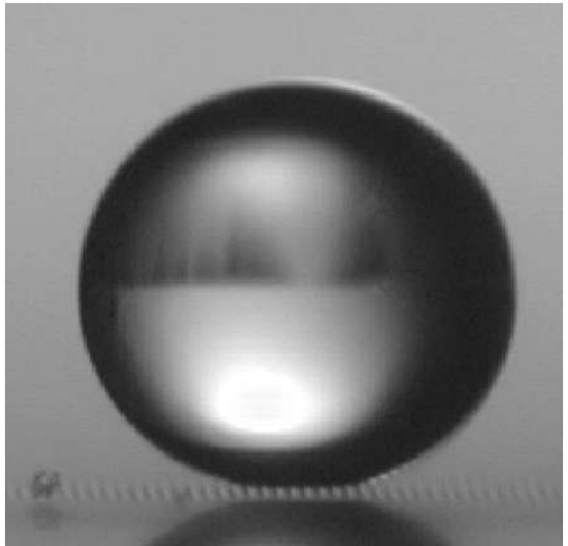
$$\cos\theta^* = -1 + \phi_S(1-\cos\theta_e)$$

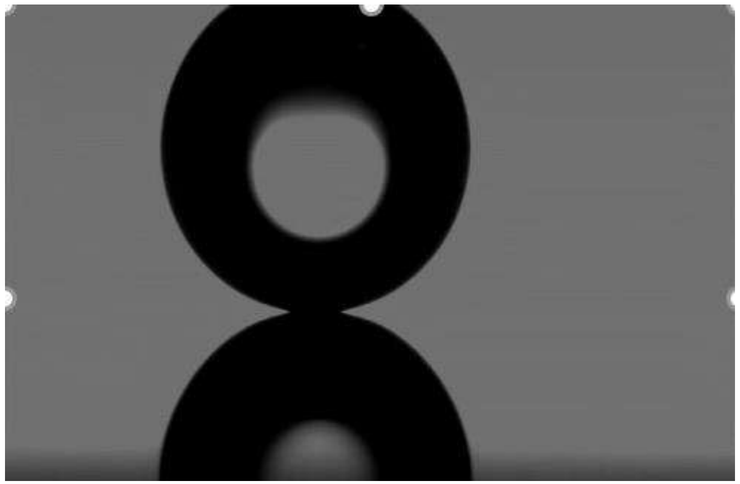


$\theta_1 = \theta_e$
$\theta_2 = 180°$

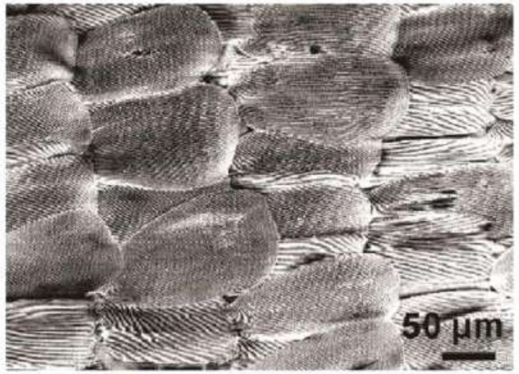


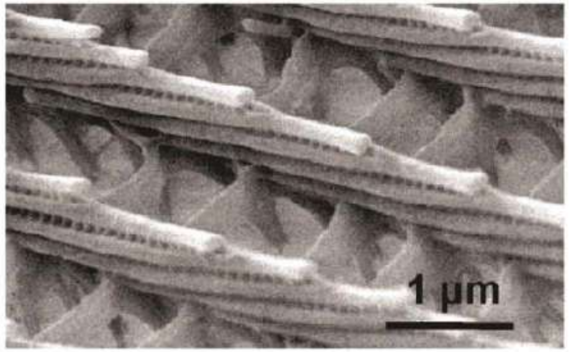
$\theta > 160\,°$

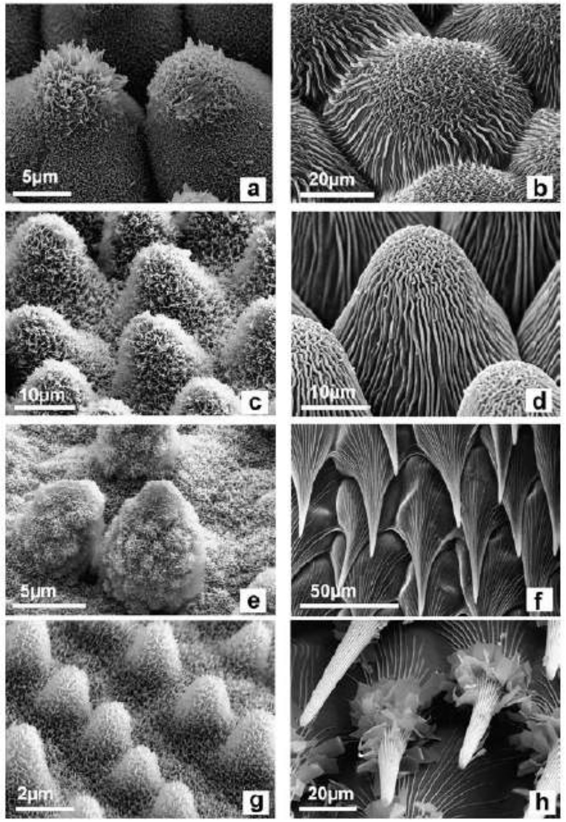




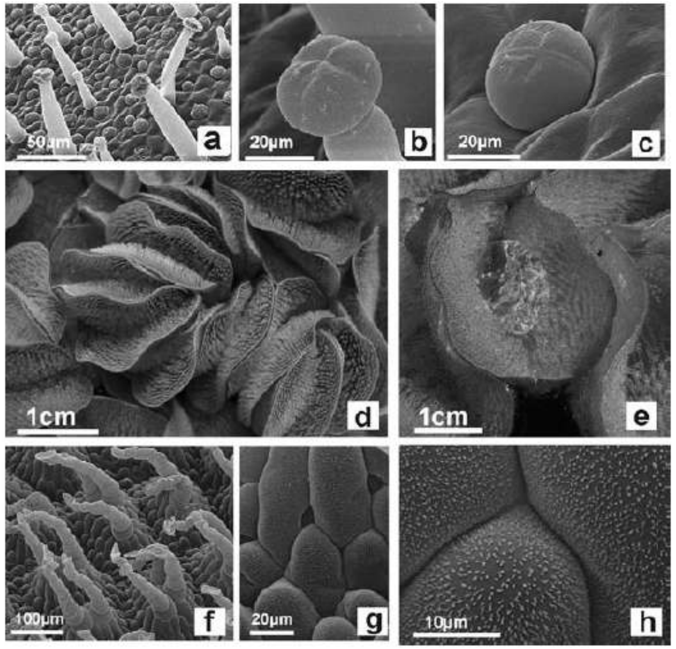
Superhydrophobicity in nature

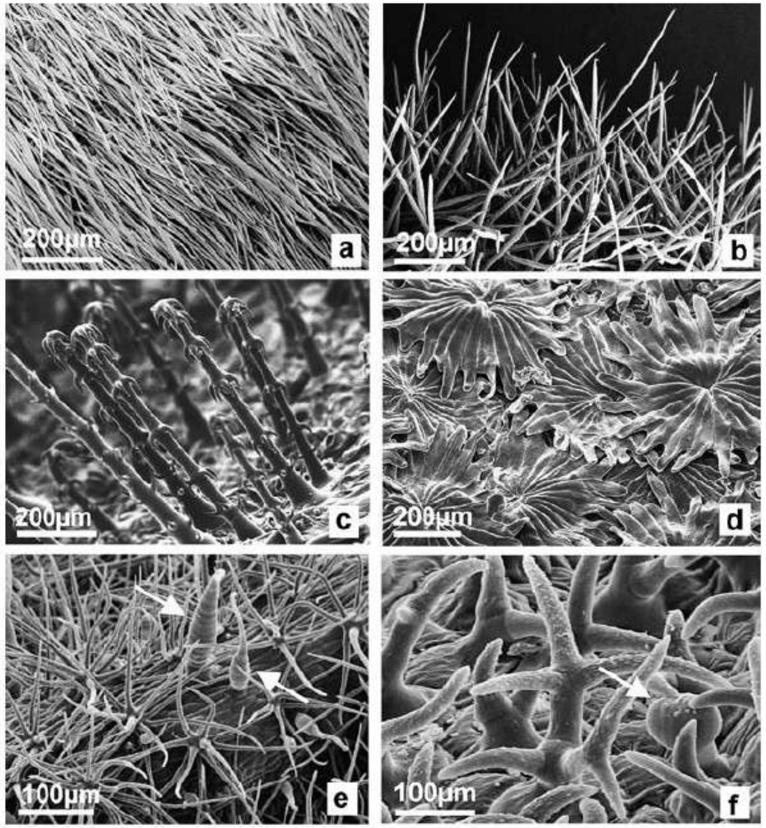




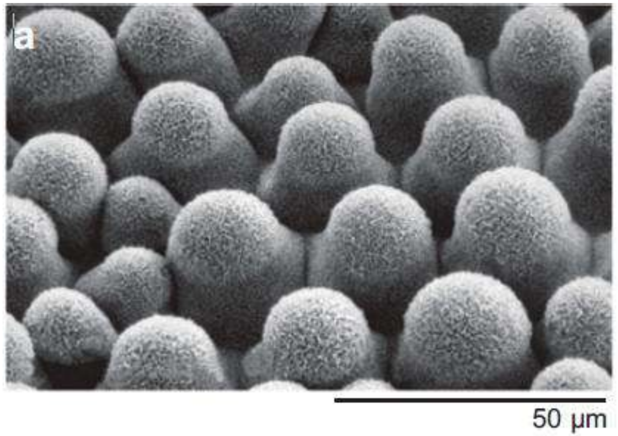


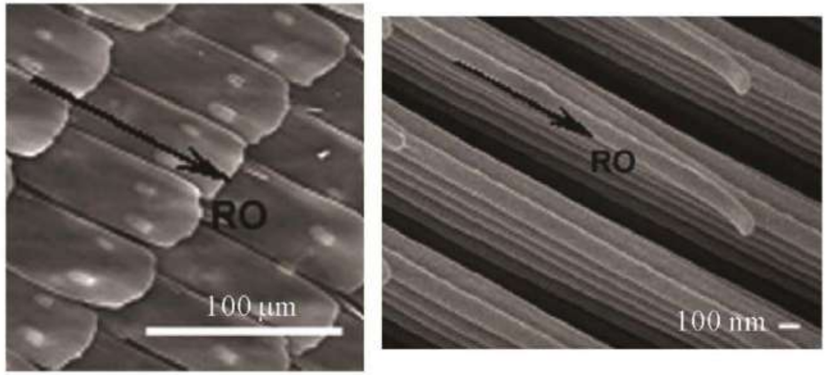
Koch *et al.*, *Soft Matt.* 2008





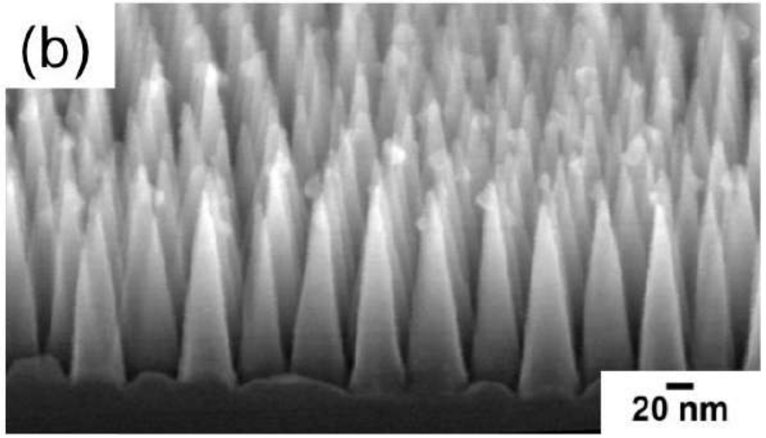
Micro + nano

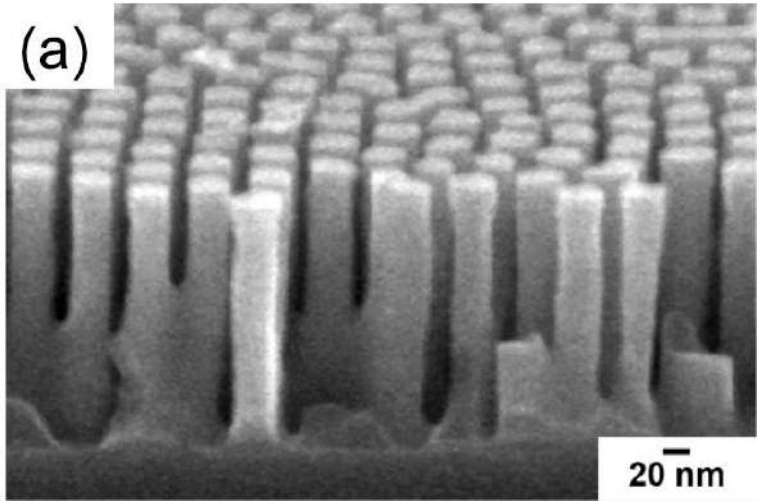


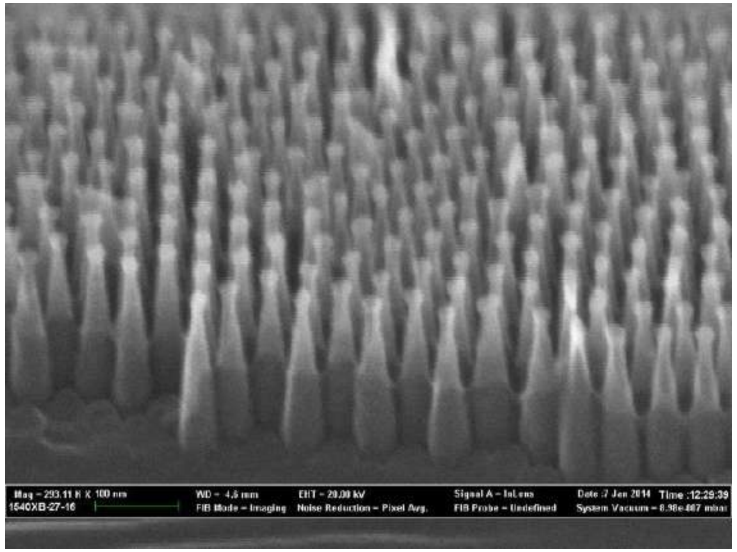


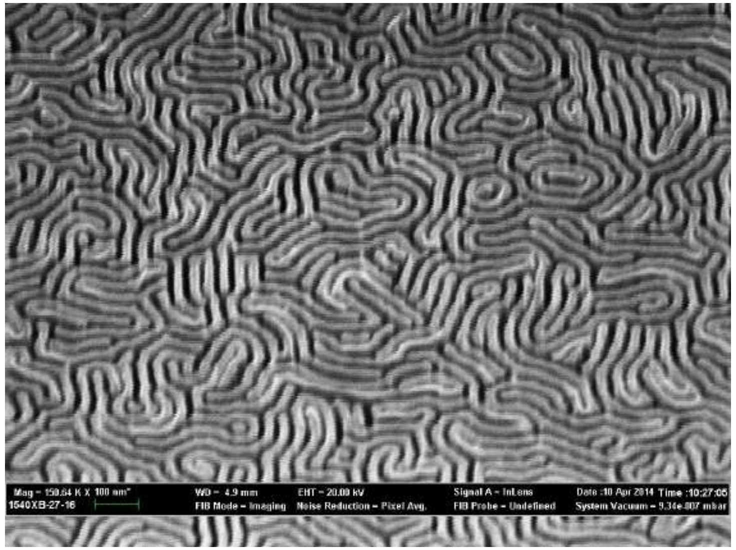
Artificial superhydro-phobic (philic) surfaces

Checco *et al.*, Adv. Mat. 2014



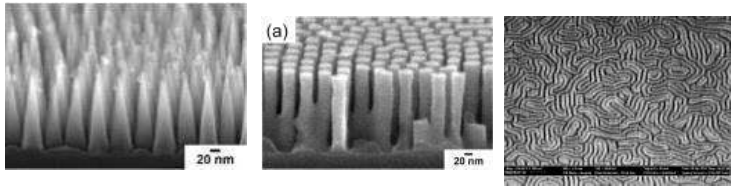


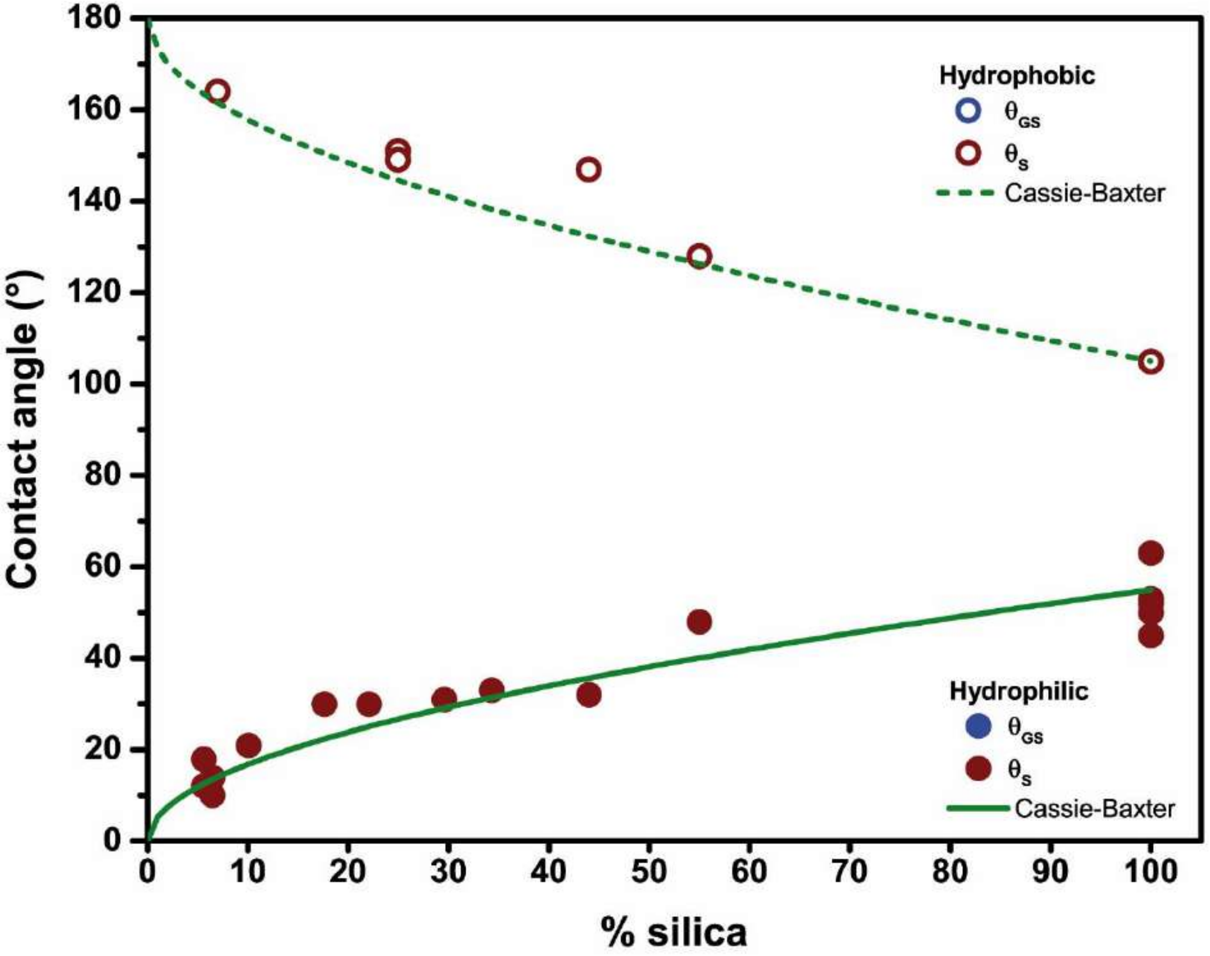




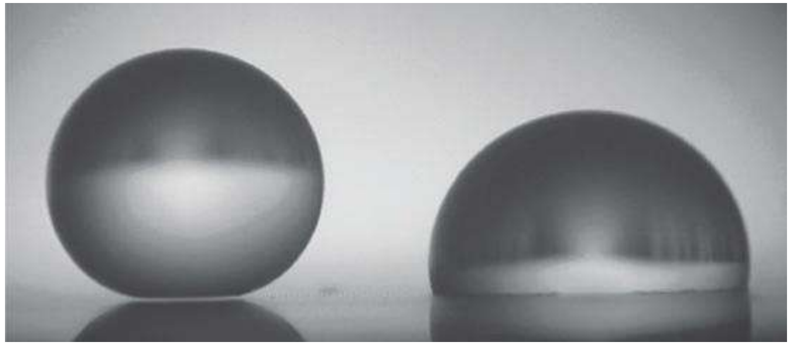
Superhydrophilicity - superhydrophobicity

Ondarçuhu *et al.*, Sci. Rep. 2016



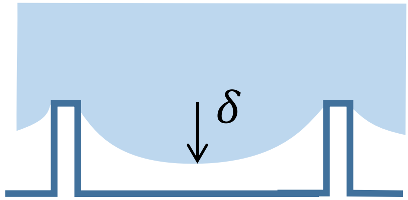


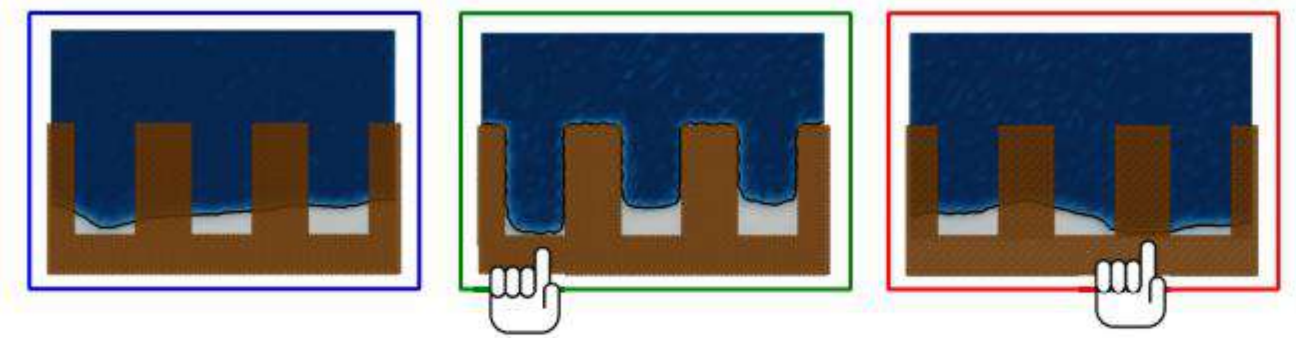
Metastability of Cassie state



Cassie Wenzel

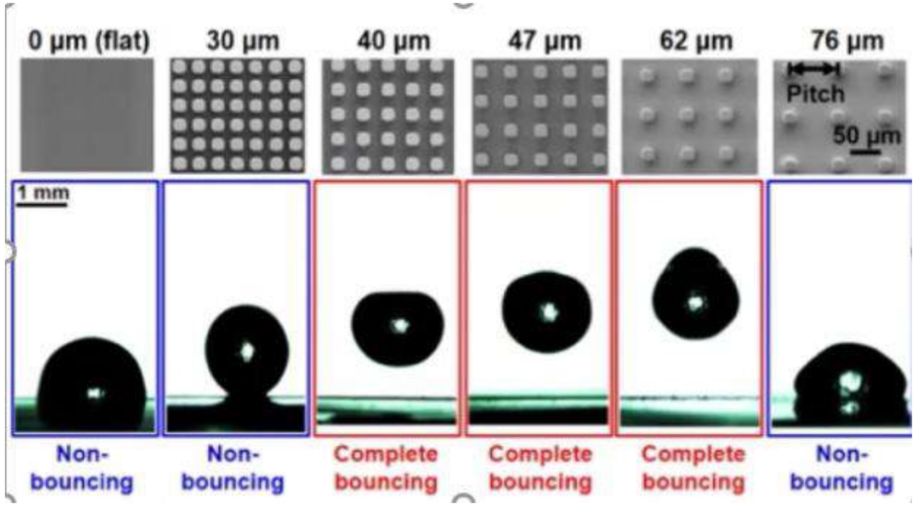
$$\Delta E \approx 2\pi bh/p^2\gamma \cos\theta$$



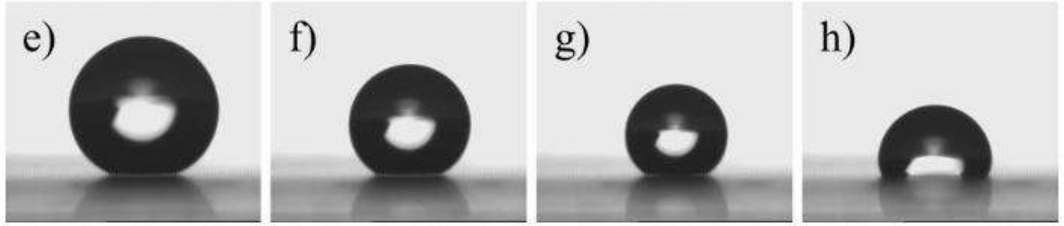


Amabili *et al.*, PRF 2017

Impact



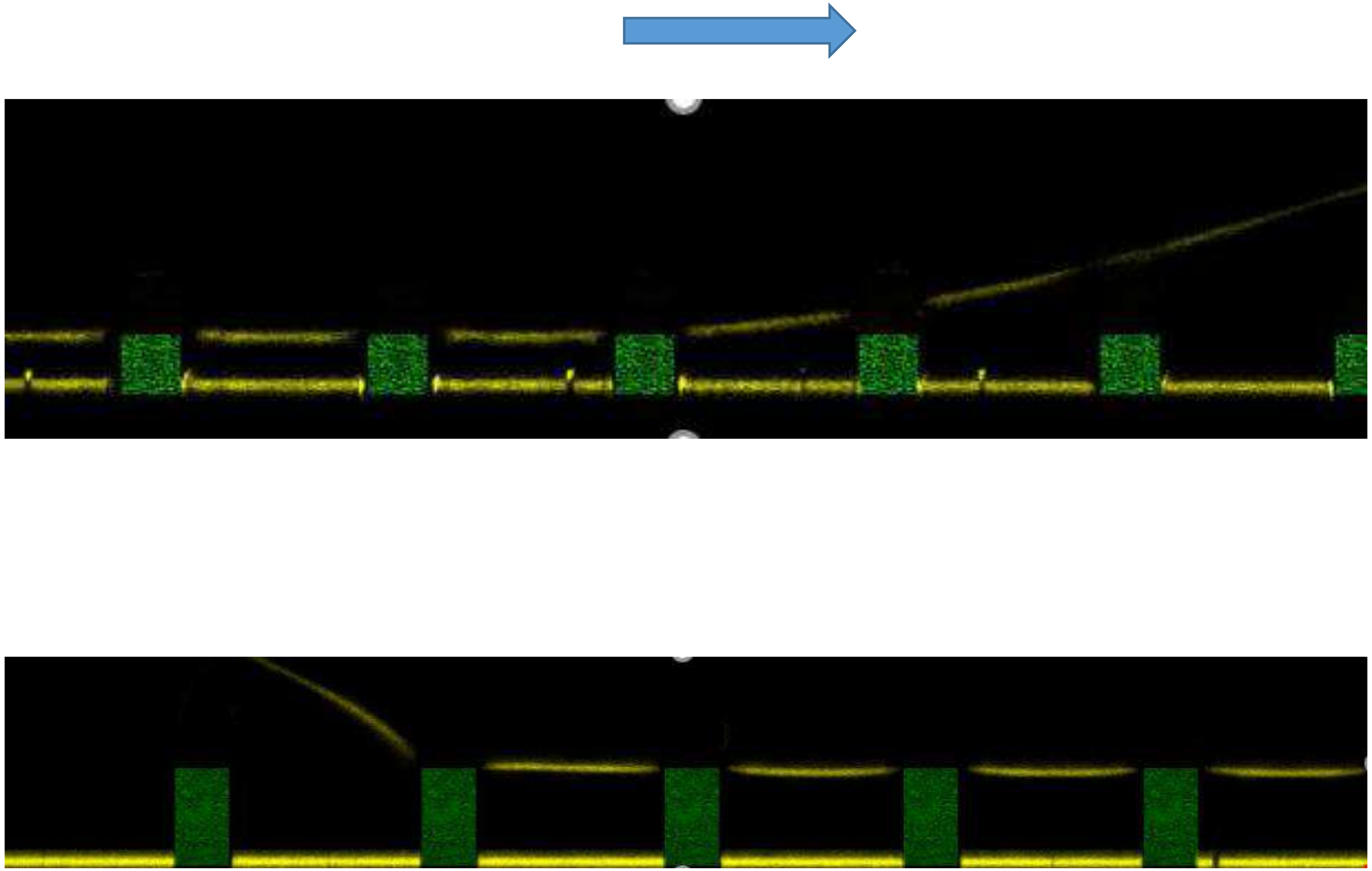
Evaporation



Mc Hale *et al.*, Langmuir 2004

At microscopic scale

Schellenberger *et al.*, Sci. Rep. 2016



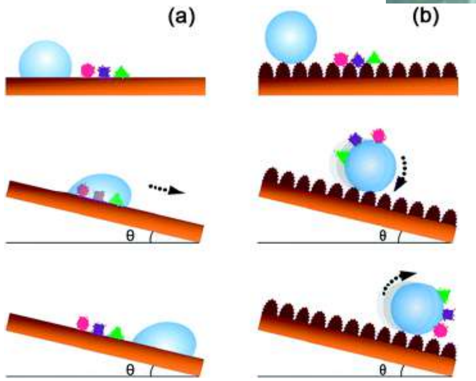
$\theta_{av} \sim 180°$

$\theta_{rec} \ll 180°$

Applications

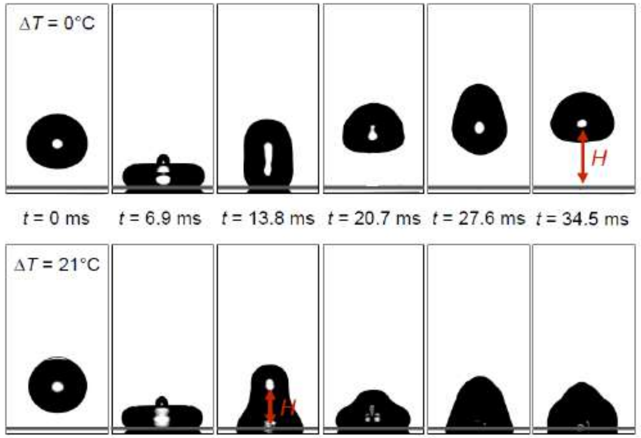
- Water repellency

- Self Cleaning

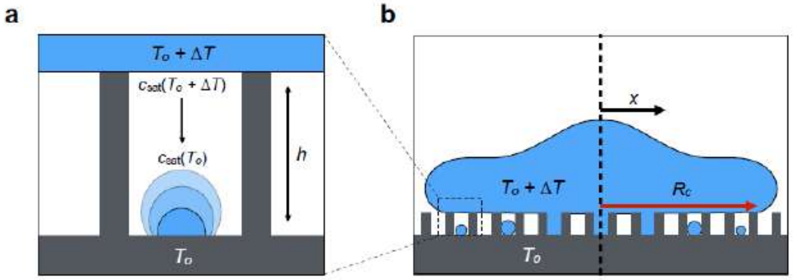


Nishimoto *et al.*, RSCAdv 2015

- Issues
  - ✓ Robustness
  - ✓ Contamination
  - ✓ Hot water

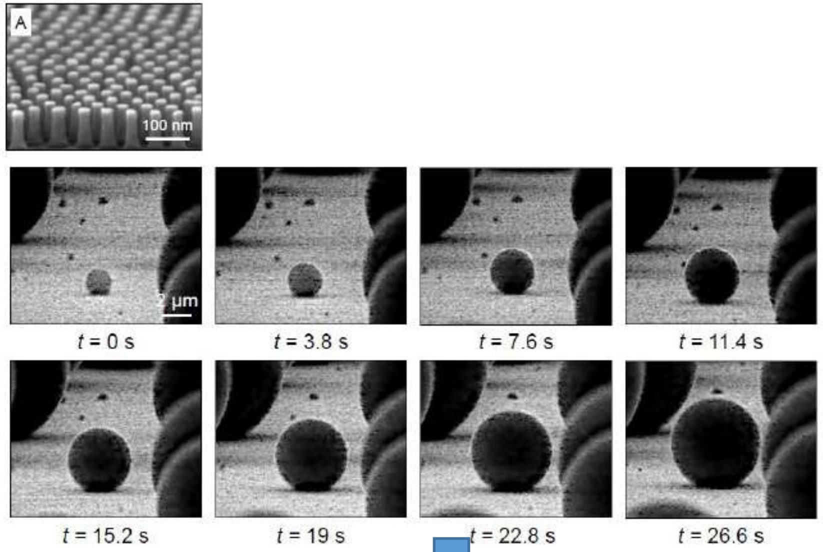


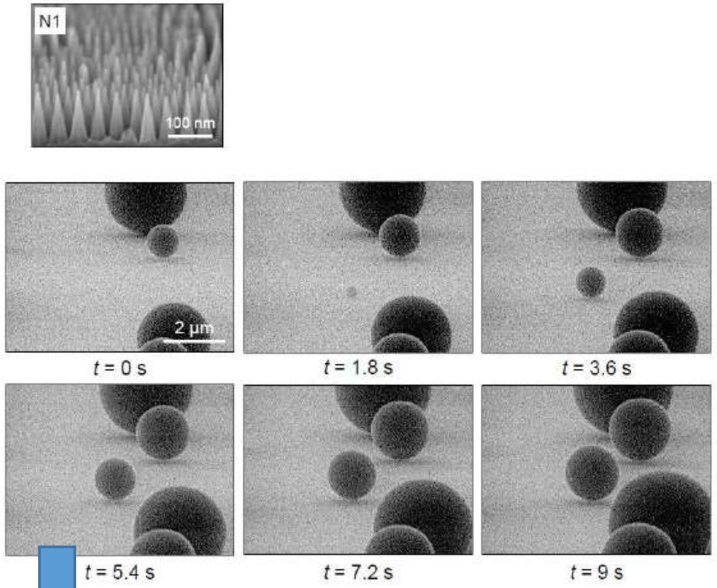
Mouterde *et al.*, *Nature Comm.* 2019

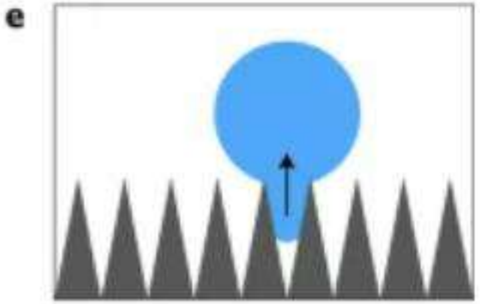


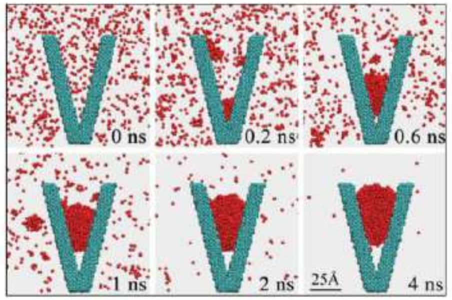
Anti-fogging

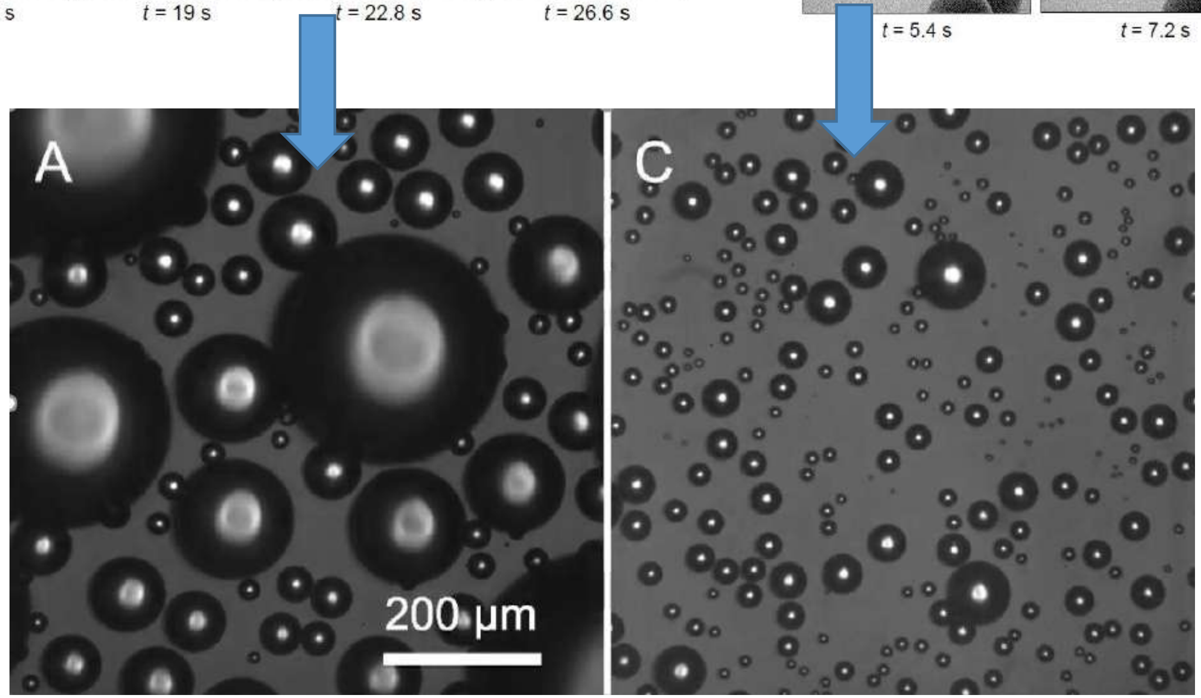
Lecointre *et al.*, *Nature Comm.* 2021

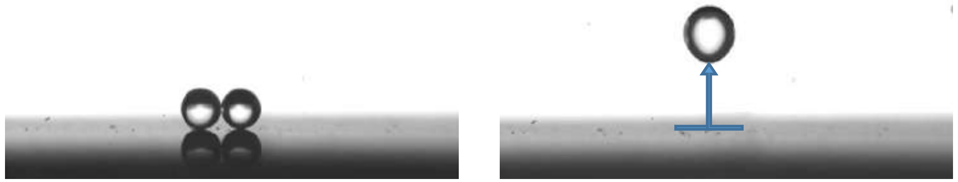






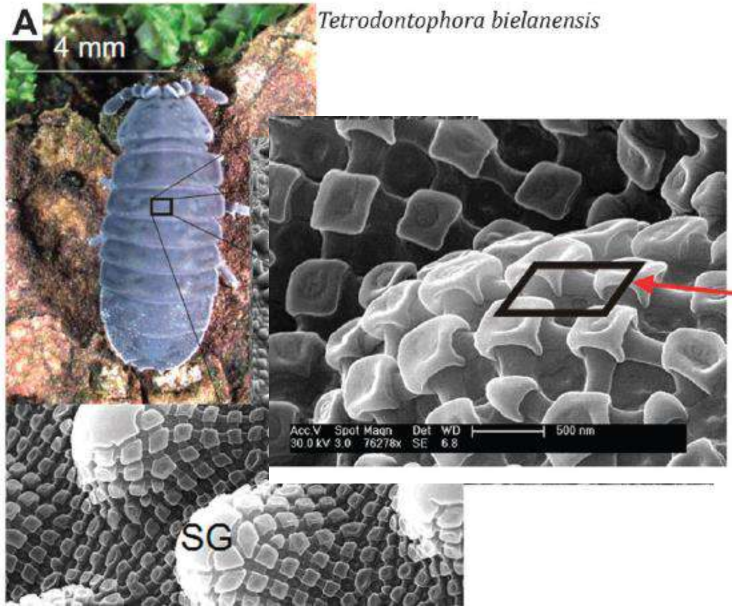


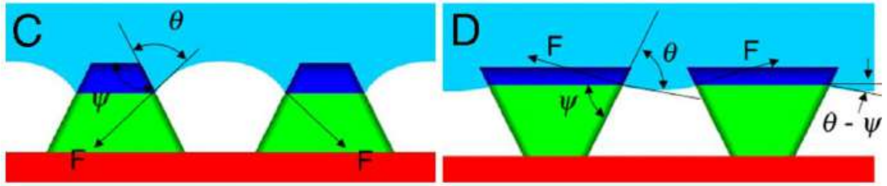




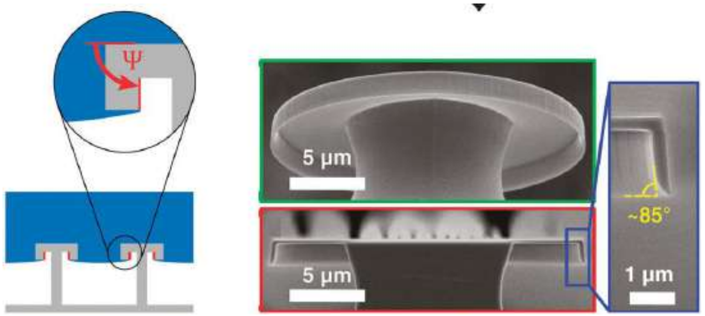
Omniphobic surfaces

- Contact angle of oil on hydrophobic surface < 90°

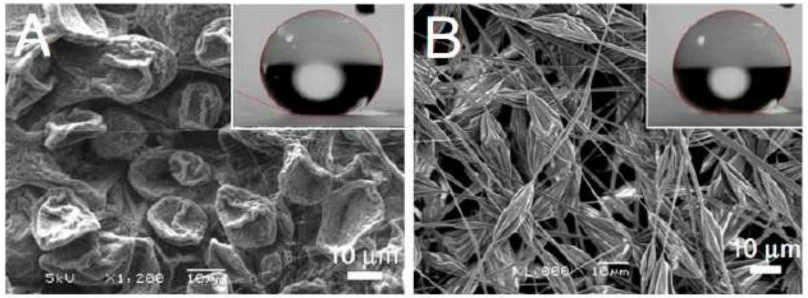




Tuteja *et al.*, *PNAS* 2008



Hensel *et al.*, *Chem. Soc. Rev.* 2016



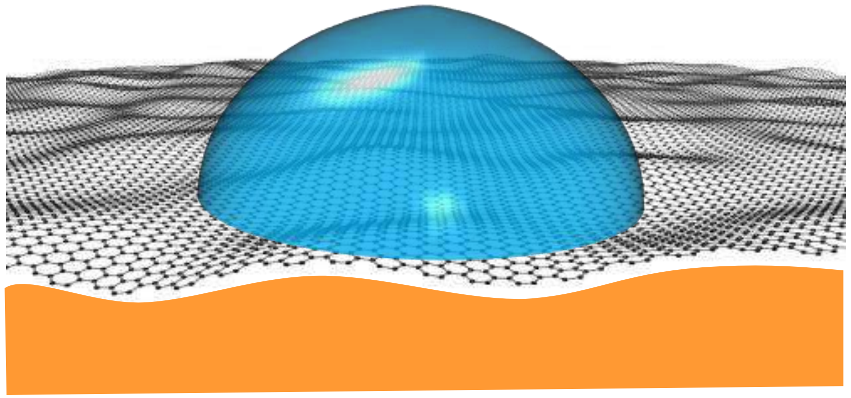
Tuteja *et al.*, *PNAS* 2008

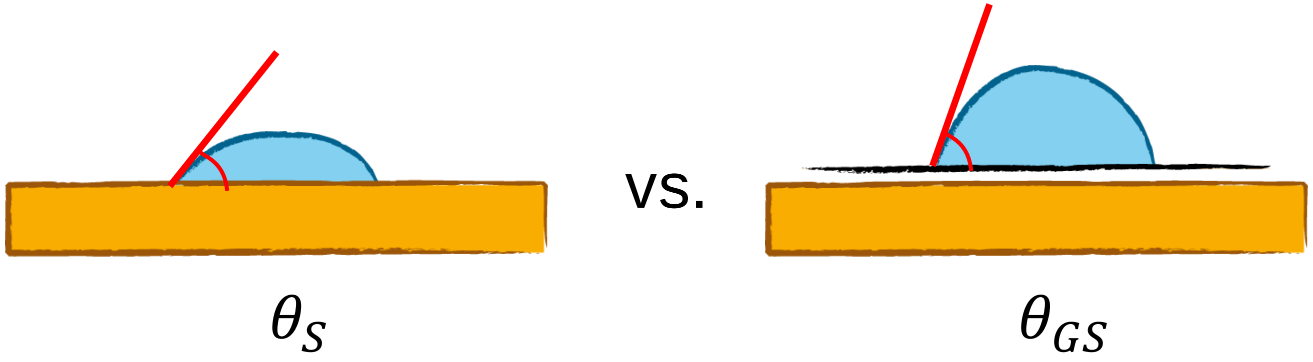
Nano-wetting

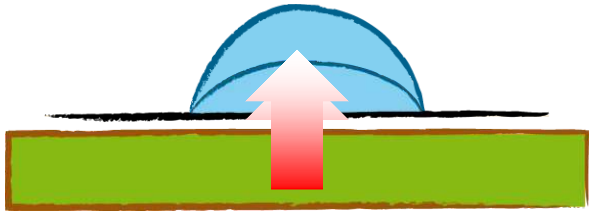
- Long range forces (vdW)

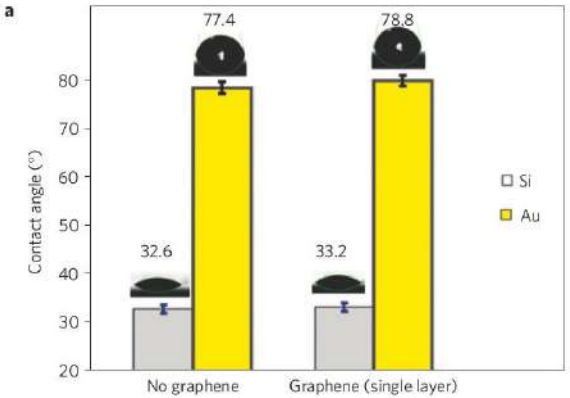
  - Which interaction determines contact angle?
  - How does it affect spreading regimes?
  - How does it affect thin film stability?
  - Shape of nanodroplets?

Wetting of graphene

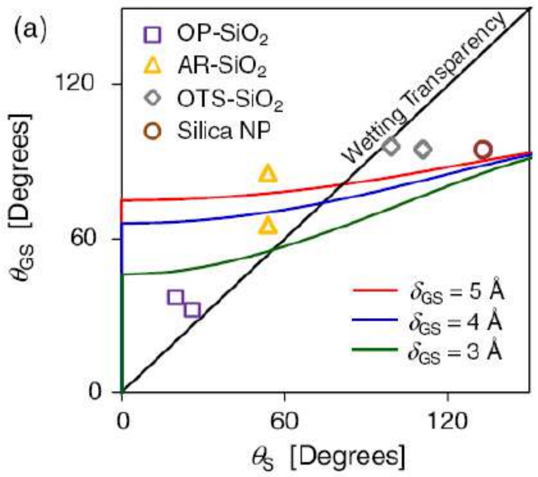






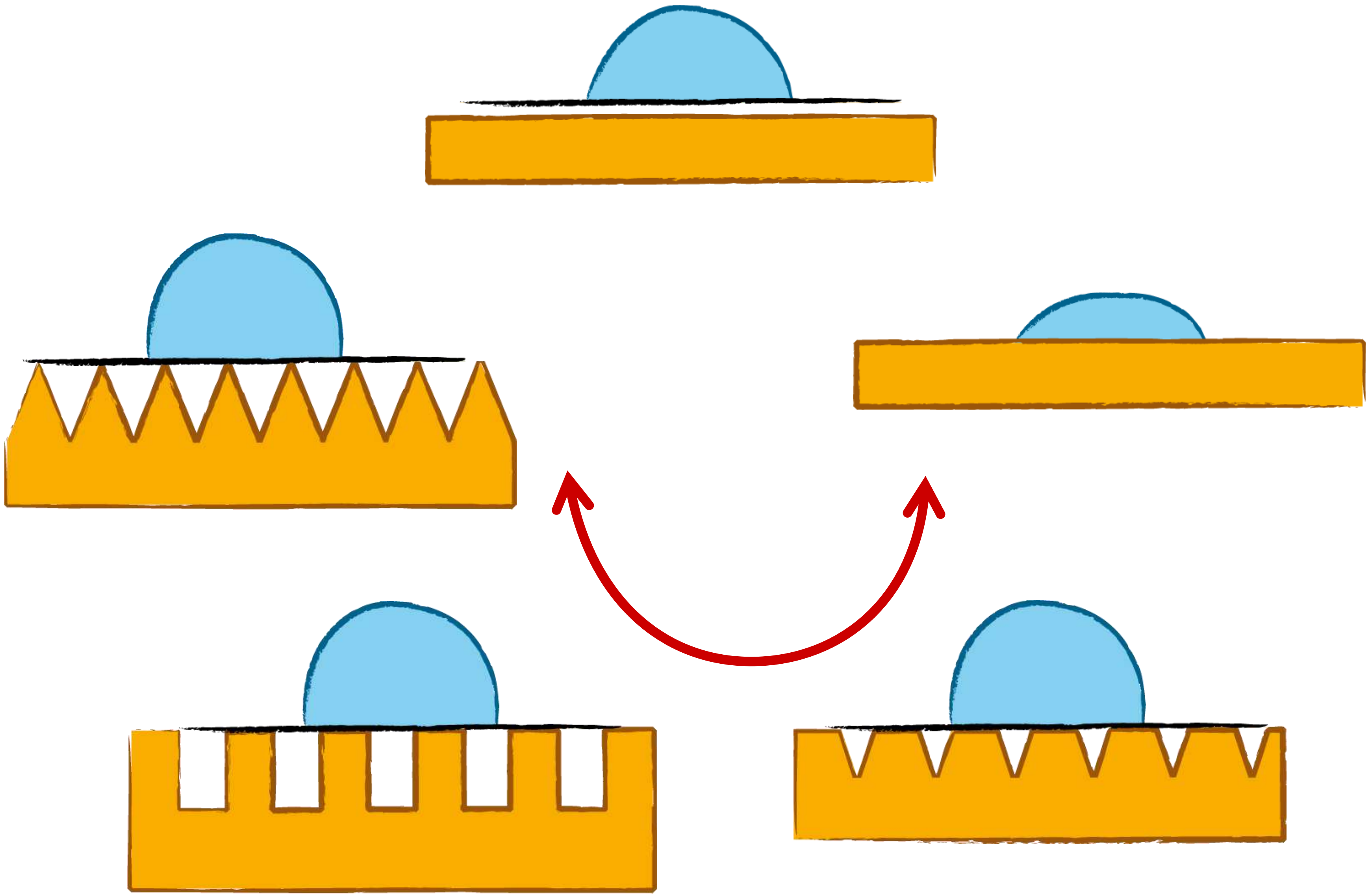


Rafee *et al. Nature Mat.* 2012

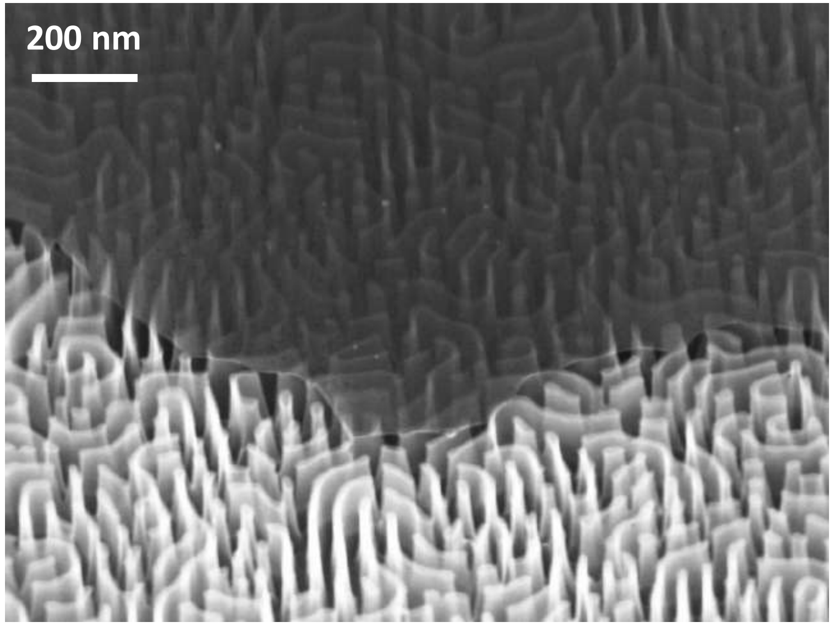


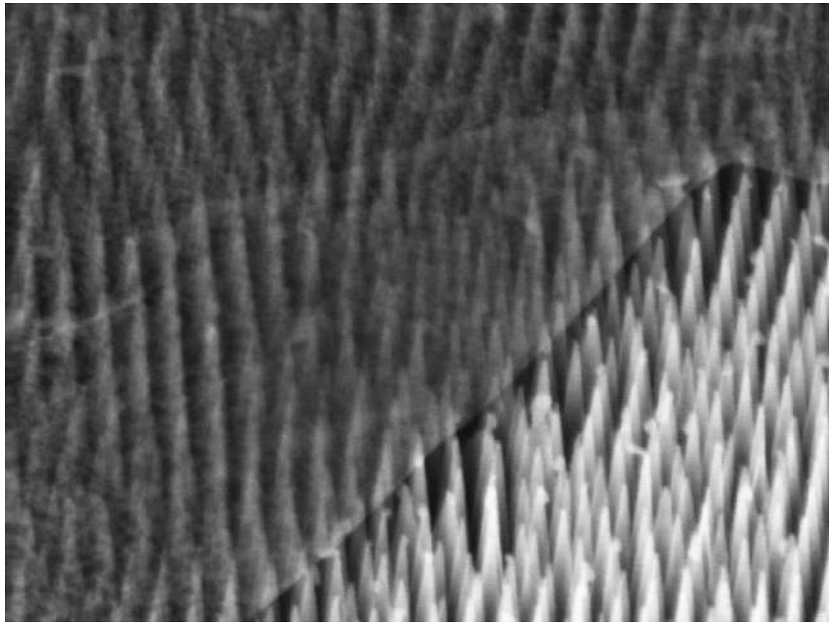
Shih *et al. PRL* 2012

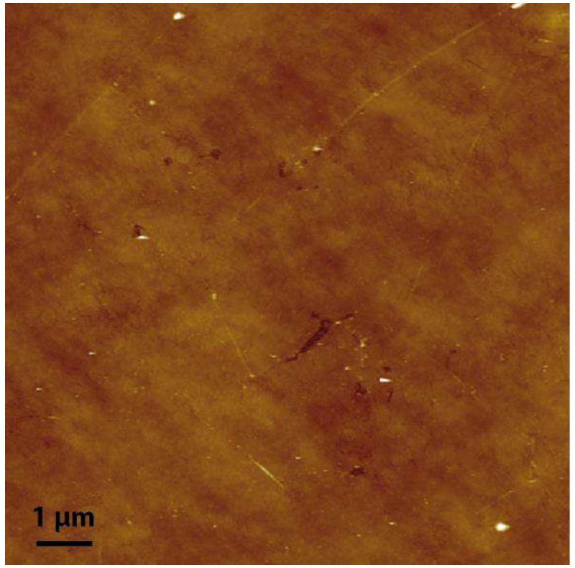
Wetting of graphene

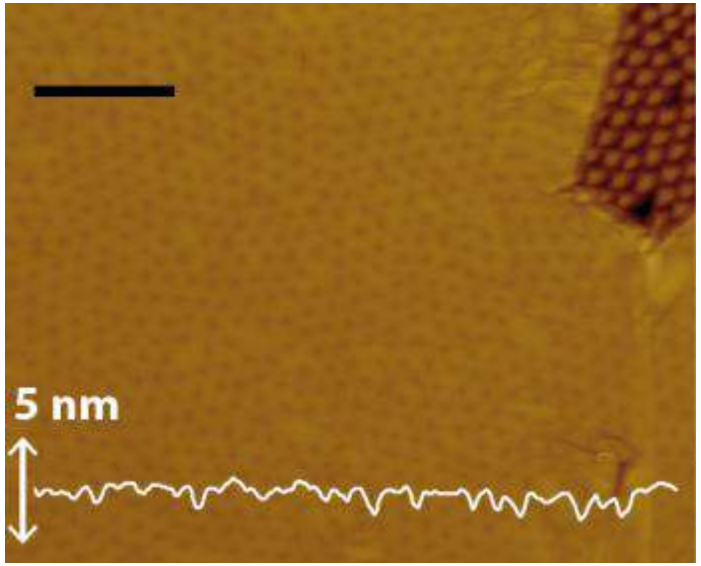


Wetting of graphene



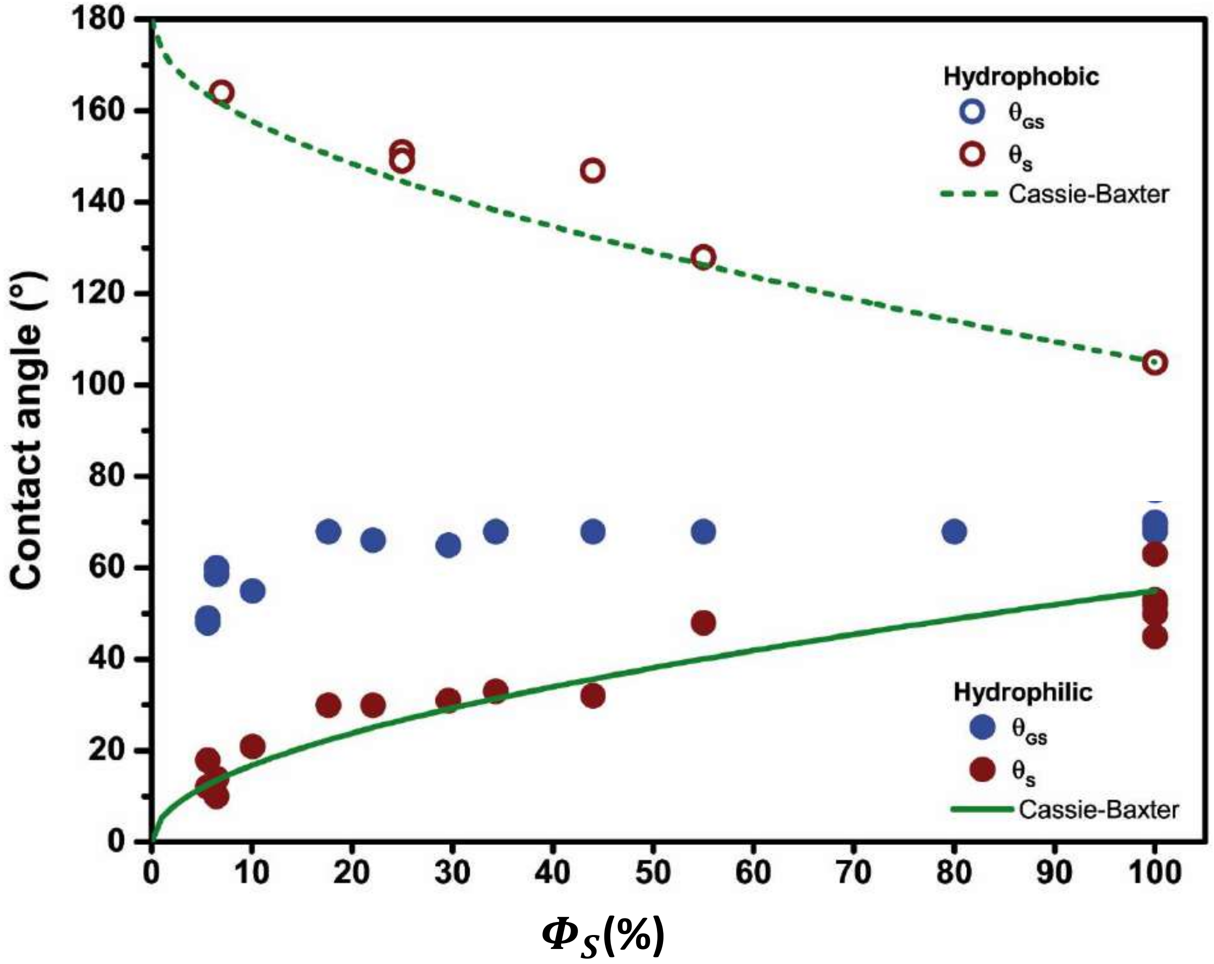


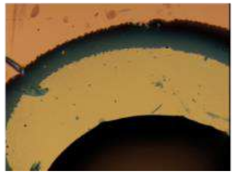


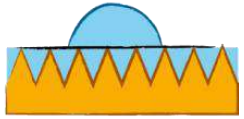


Rms roughness
0,4 nm

Wetting of graphene



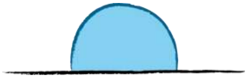




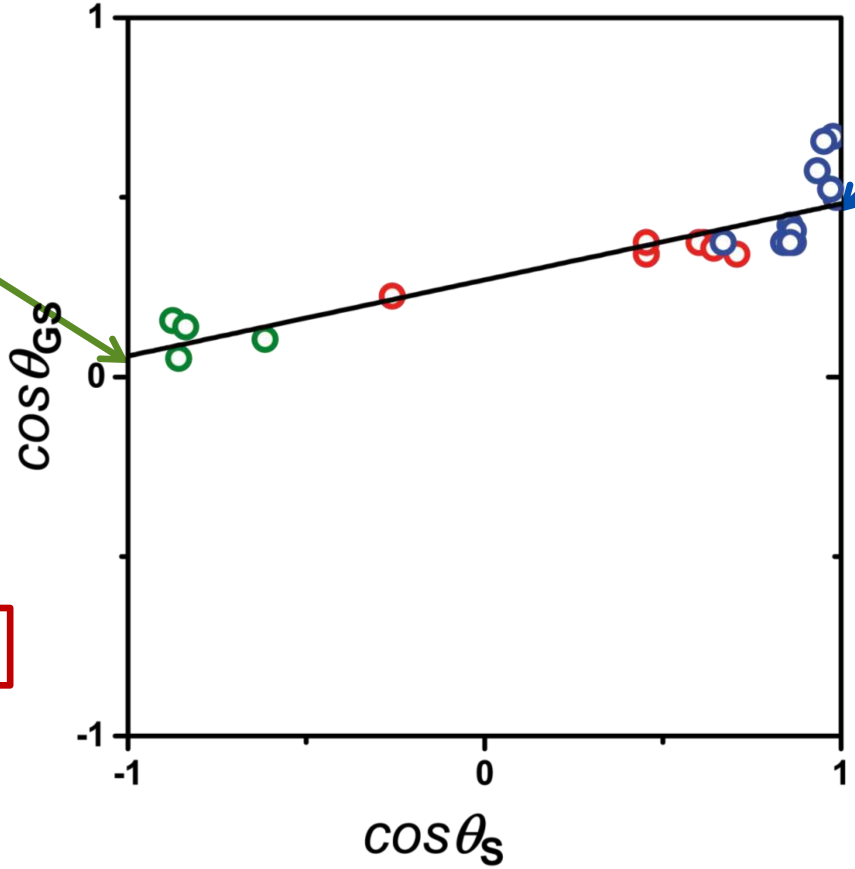
➢ **No wetting transparency**

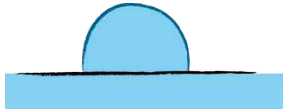
Ondarçuhu *et al. Sci Rep* 2016

Wetting of graphene



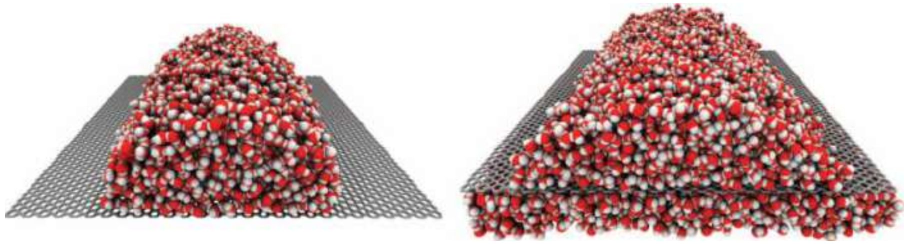
$\theta_G = 85° \pm 5°$





$\theta_{GW} = 61° \pm 5°$

$\Delta\theta_W \cong -21° \pm 5°$

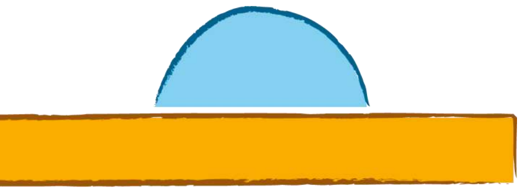


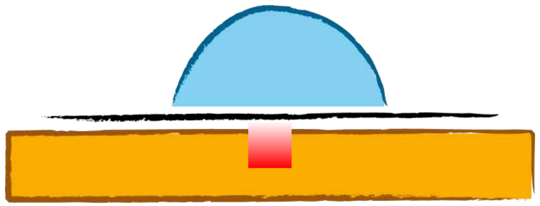
$\Delta\theta_W \cong -10°$

Driskill *et al.*, *J. Chem. Phys.* 2014

80 % of the interaction comes from the graphene
20 % from underlying substrate

$$W(h) = -\frac{A}{3\pi h^2}$$





Nano-wetting: effect of long range forces

➢ Effective interaction potential

Brochard *et al.*, Langmuir 1991

van der Waals interaction :

$$W(h) = \frac{A}{3\pi h^2}$$

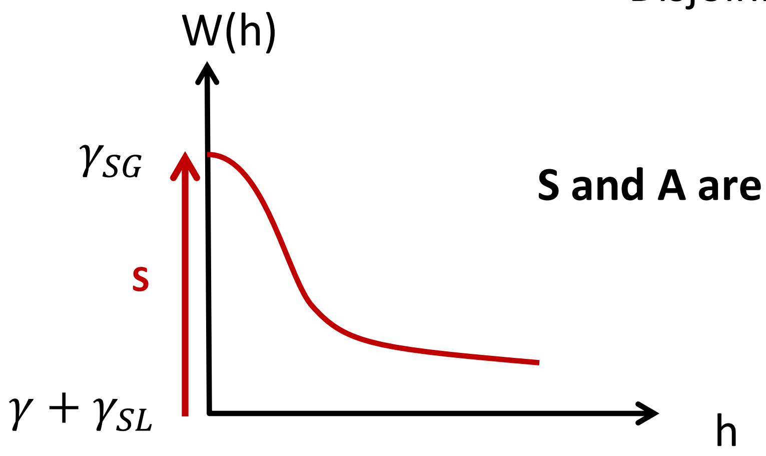
Hamaker constant

$$A = \pi^2 k \bar{\alpha}_L (\bar{\alpha}_S - \bar{\alpha}_L)$$

Disjoining pressure : $\Pi(h) = -\frac{dW}{dh} = \frac{A}{6\pi h^3}$

$$E(h) = \gamma + \gamma_{SL} + W(h)$$

$$E(0) = \gamma_{SG} \Rightarrow W(0) = S$$

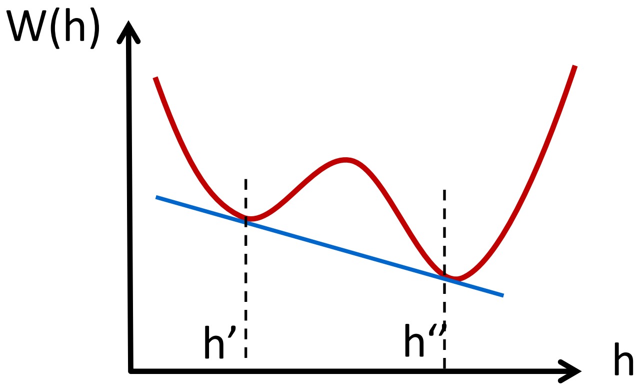


S and A are rather independant

$$\mathcal{E}(h) = \mathcal{A}\big(\gamma + \gamma_{SL} + W(h)\big)$$

At constant volume : $\frac{d\mathcal{A}}{\mathcal{A}} + \frac{dh}{h} = 0$

$$\frac{d\mathcal{E}}{d\mathcal{A}} = \gamma_{film} = \gamma + \gamma_{SL} + W(h) + h\Pi(h)$$

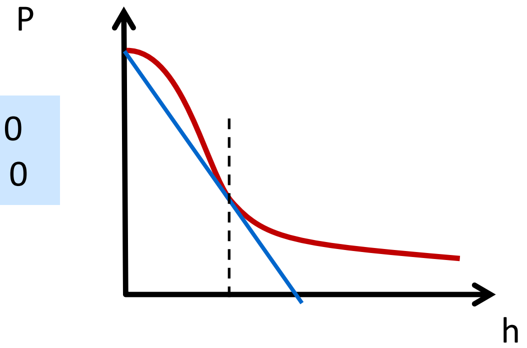


Nano-wetting: effect of long range forces

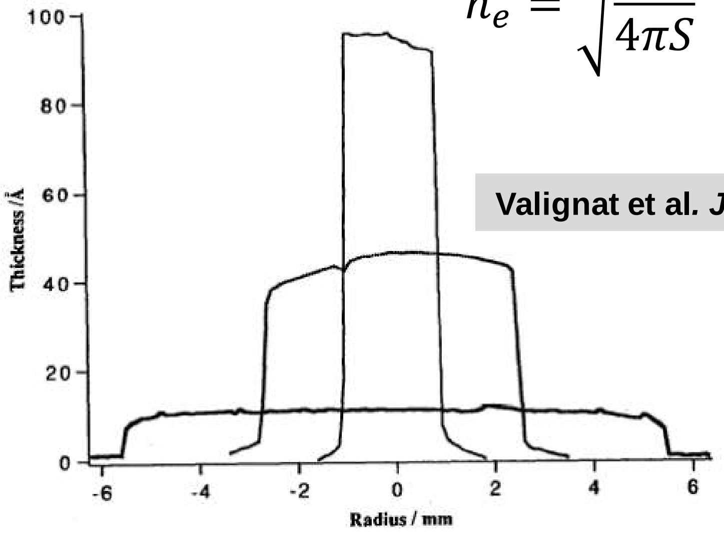
➢

Total wetting

S > 0
A > 0



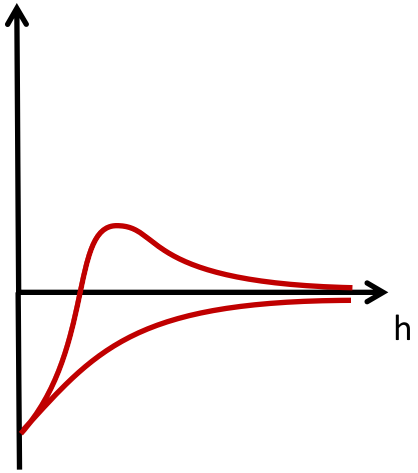
$$h_e = \sqrt{\frac{A}{4\pi S}}$$



Valignat et al. *JCIS* 1994

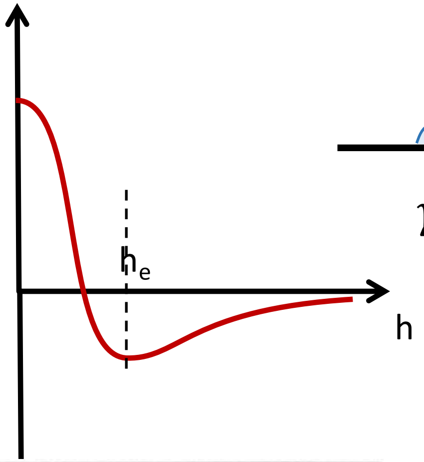
Partial wetting

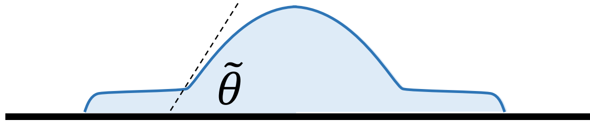
S < 0



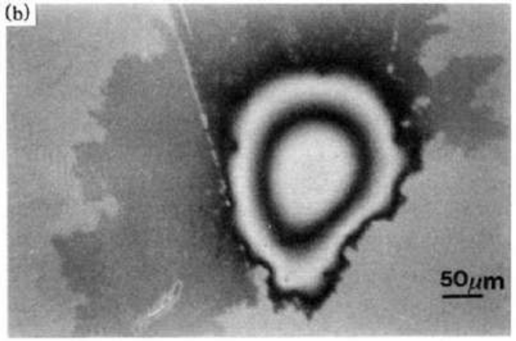
Pseudo-partial wetting

S > 0
A < 0





$$\gamma(1 + \cos\tilde{\theta}) = -W(h_e)$$



Silberzan, Léger, PRL 1991

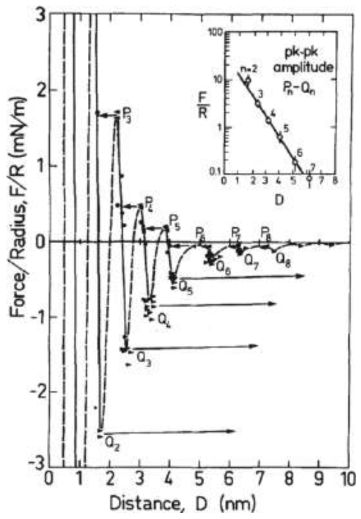
More frequent in L/L

Du *et al.*,
Chem Eng. Process. 2013

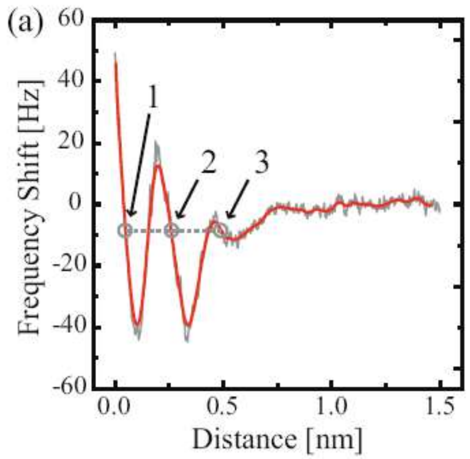
➢ **Wetting criterion depends on : - sign of spreading coefficient**
- sign of Hamaker constant

Nano-wetting: effect of long range forces

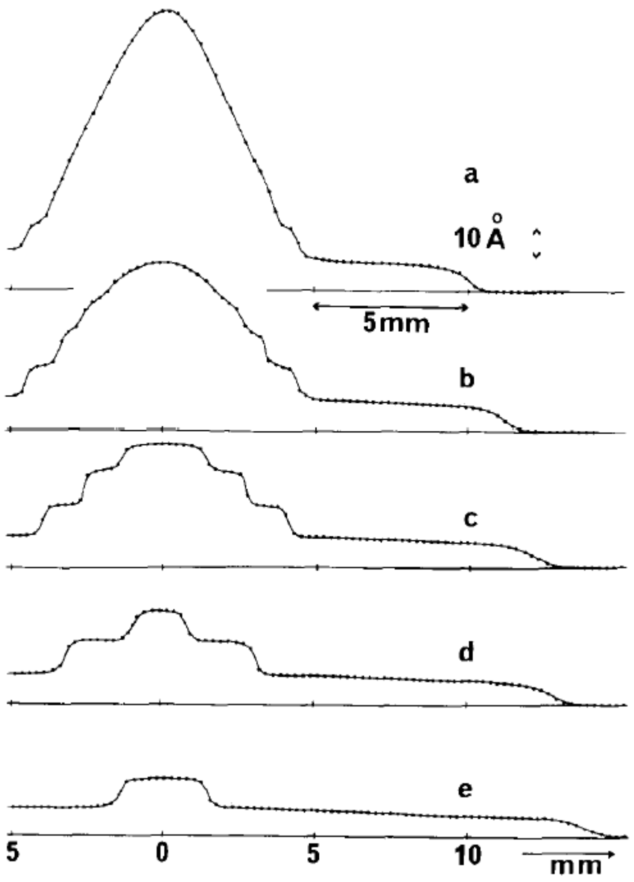
➢ **Structural forces**



Tabor, Israelachvili (1968-1970)



T. Ando



Heslot *et al.*, Nature 1989

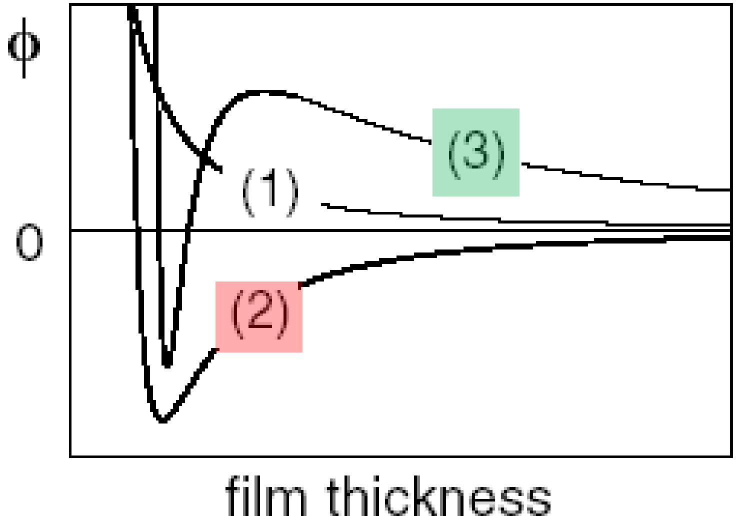
tetrakis(2-ethylhexoxy)-silane (TK)

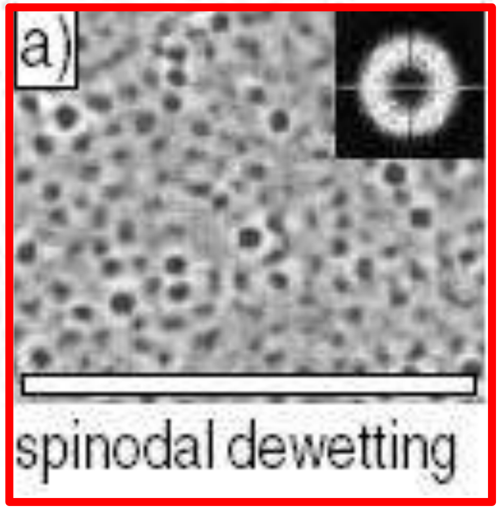
➢ **Wetting criterion depends on : - sign of spreading coefficient**
- sign of Hamaker constant

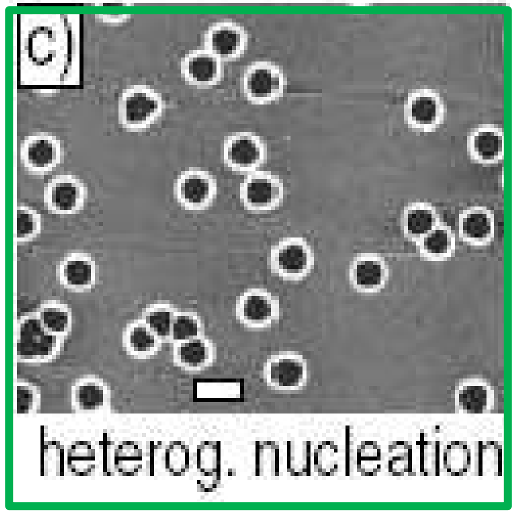
Effect on wetting films

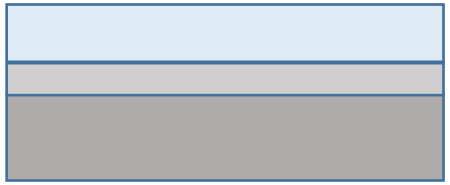
- Dewetting

$\Phi''(h) < 0$ unstable



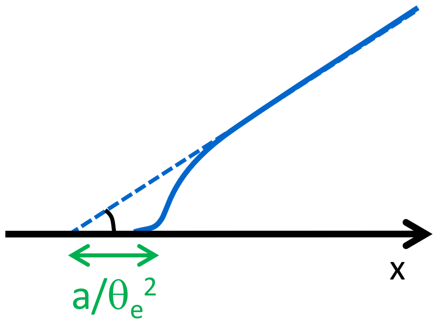






Seemann *et al.*, Phys. Rev. Lett. 2001

Influence on drops

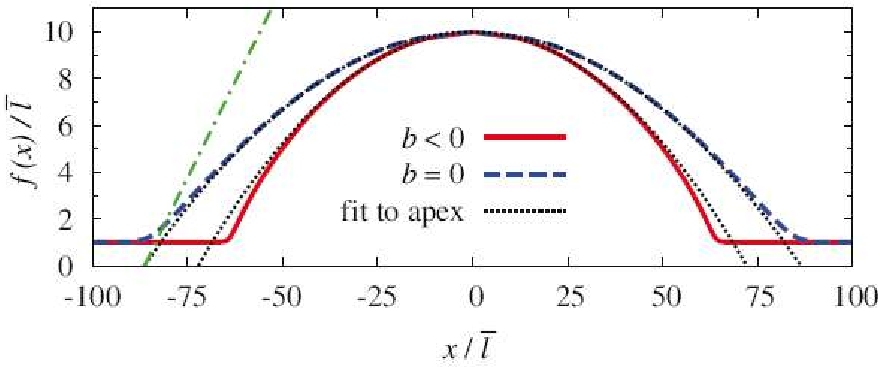


$$\gamma \frac{d^2 h}{dx^2} + \Pi(h) = 0$$

$$\frac{1}{2}\gamma\left(\frac{dh}{dx}\right)^2 - W(h) = \frac{1}{2}\gamma\theta_e^2$$

$$h^2 = \theta_e^2 x^2 \pm \frac{a^2}{\theta_e^2}$$ with $$a^2 = \frac{|A|}{6\pi\gamma}$$

$$\mathcal{H}[f] = \int dx \int dy \left[\frac{1}{2}\sigma_{lv}(\nabla f)^2 + \omega(f)\right]$$

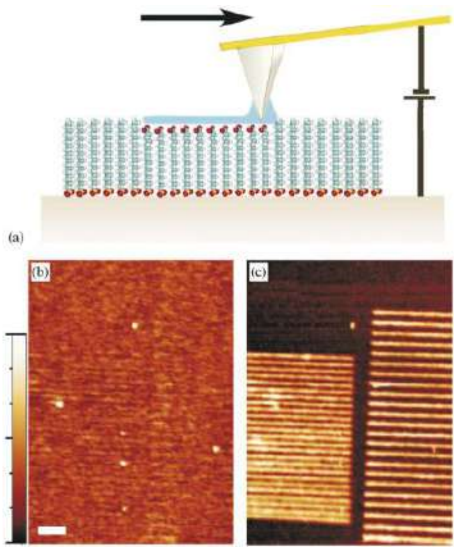


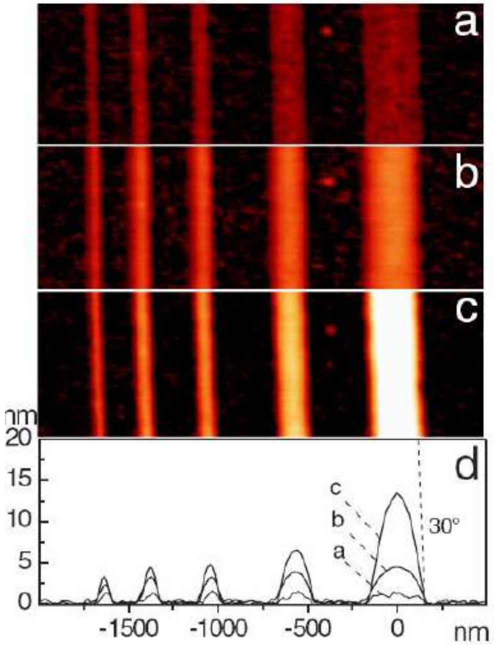
Getta *and Dietrich.* Phys. Rev. E 1998

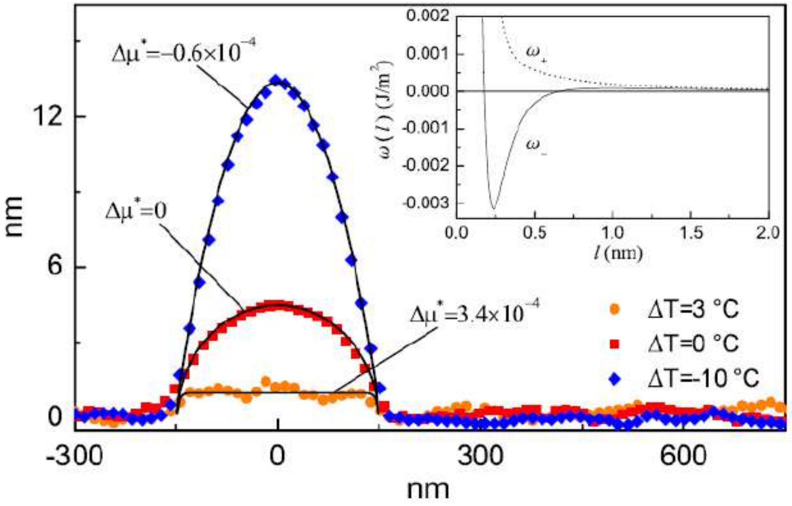
Influence on drops

➢ Condensation on hydrophilic nanostripes

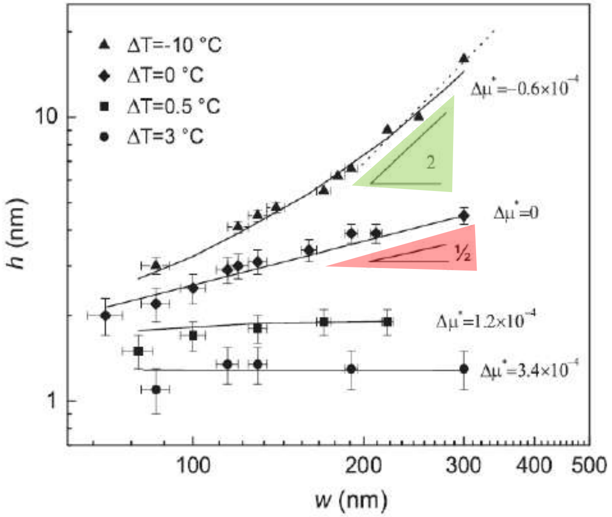
Checco *et al.*, Phys. Rev. Lett. 2003
Phys. Rev. E 2008







$$\gamma \frac{l''(x)}{\sqrt{(1 + l'^2(x))^3}} = \rho \Delta\mu + \frac{\partial \omega_{CS}(x, l(x))}{\partial l}.$$



- Δμ = 0 (saturation)

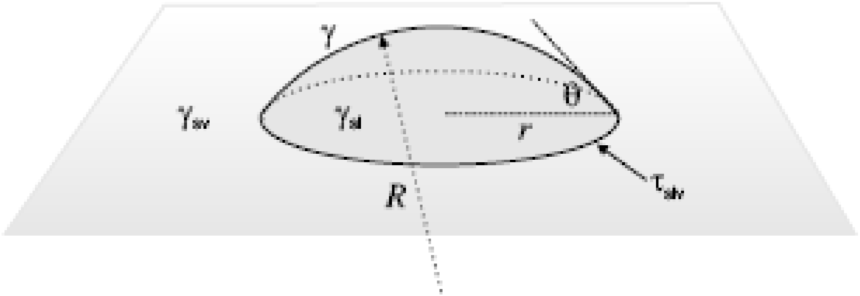
$$\gamma \frac{d^2h}{dx^2} = \frac{-2A}{h^3} \Rightarrow \frac{h}{w^2} \propto \frac{1}{h^3} \Rightarrow h \propto w^{1/2}$$

- Spherical cap

$$h \propto w^2$$

Line tension

➢ Phenomenological description



$$dE = \gamma dA_{LV} + \gamma_{SL} dA_{SL} + \gamma_{LV} dA_{LV} + \tau dL$$
$$= \left(\gamma \cos\theta + \gamma_{SL} - \gamma_{LV} + \frac{\tau}{r} \right) dA_{LV}$$

$$\cos\theta = \cos\theta_e - \frac{\tau}{\gamma \; r}$$

$$\gamma \approx \frac{kT}{a^2} = 10^{-2} N/m$$

$$\tau \approx \frac{kT}{a} = 10^{-12} N$$

➡ $\frac{\tau}{\gamma} \approx a$

$\tau > 0$ or $\tau < 0$

➢ Theoretical description

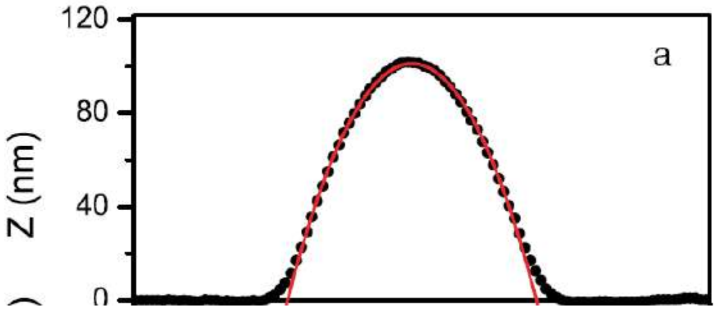
Multiples contributions

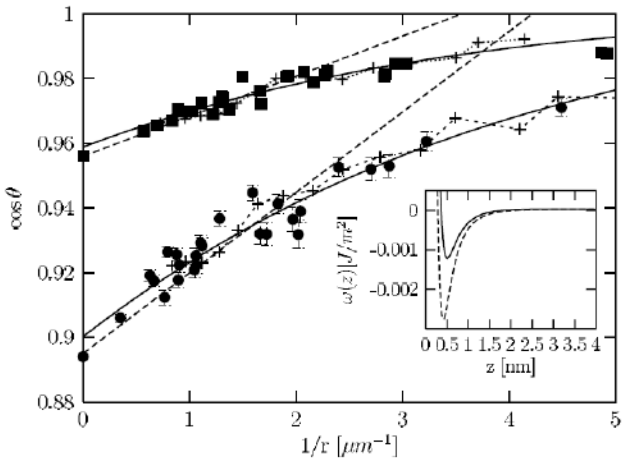
$$\tau_{lvs} = \sqrt{2}\,\sigma_{lv} \int_{\bar{\ell}}^{\infty} \left[\sqrt{\omega(\ell) - \omega(\bar{\ell})} - \sqrt{-\omega(\bar{\ell})} \right] d\ell,$$

+ Tolman length + line rigidity…

Schimmele *et al.*, *J. Chem. Phys.* 2007

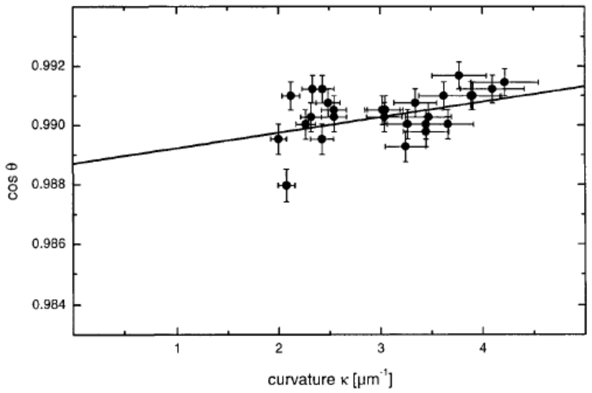
Line tension: experimental determination

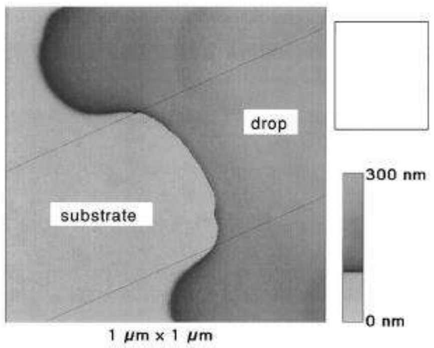




Checco et al Phys. Rev.Lett. 2001

$$\tau = -500\ \mathrm{pN}$$





Pompe, Herminghaus Phys. Rev.Lett. 2000

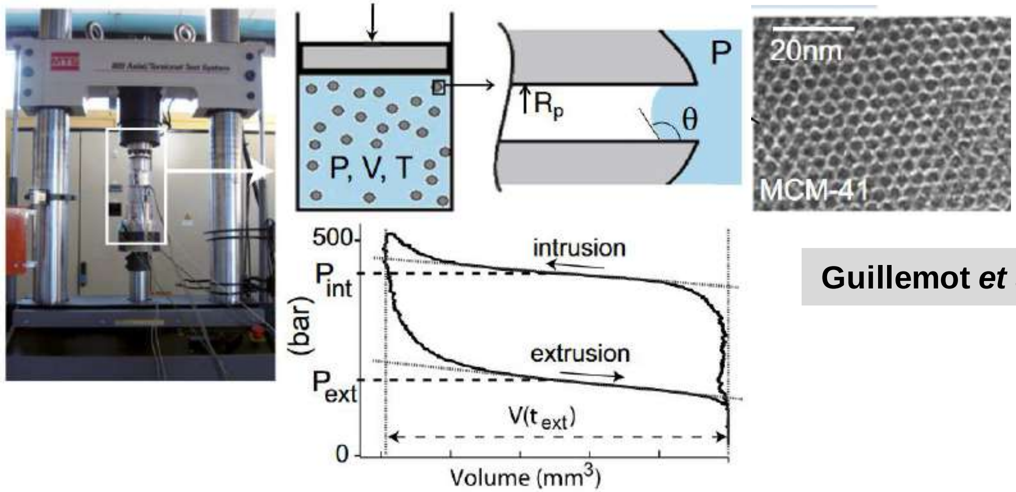
$$\tau = -300\ \mathrm{pN}$$

Line tension: experimental determination

➢ Nucleation of vapor bubble

Critical nucleus energy :

$$\Delta\Omega_c \simeq P_L K_1(\theta)\, R_p^3 + \gamma_{lv} K_2(\theta)\, R_p^2 + \tau K_3(\theta)\, R_p$$



Guillemot *et al. PNAS* 2012

$$P^o_{ext} = \frac{k_B T}{V_c} \ln \frac{L \nu t_o}{b} - \frac{K_2(\theta)}{K_1(\theta)} \frac{\gamma_{lv}}{R_p} - \frac{\tau}{R_p^2} \frac{K_3(\theta)}{K_1(\theta)}.$$

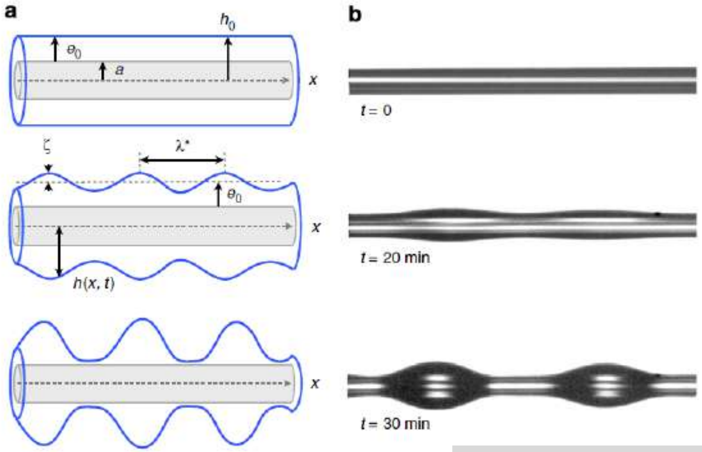
$$\tau = -23 \text{ to } -35 \text{ pN}$$

P_{ext} = -200 bars → 80 bars

Huge impact on bubble nucleation (energy barrier)

Wetting of fibers

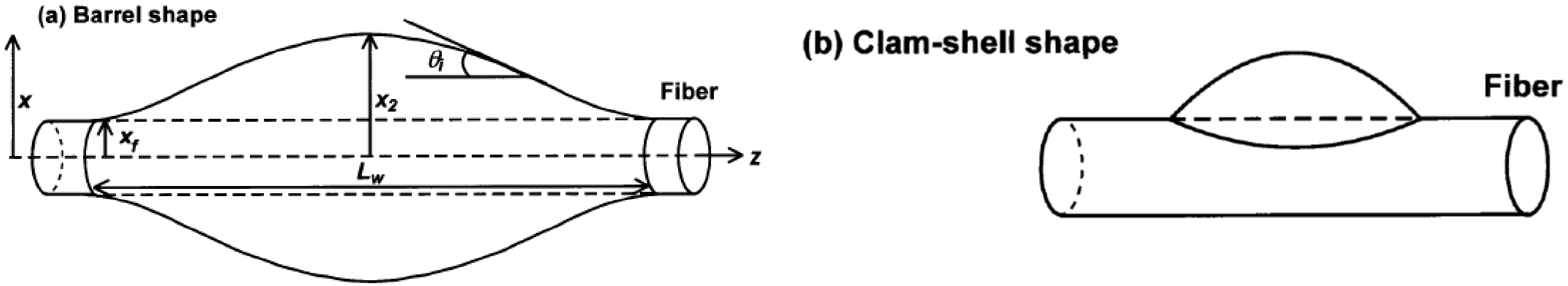
- Rayleigh-Plateau instability



Haefner *Nature Comm.* 2015

$$\lambda^* = 2\sqrt{2}a$$

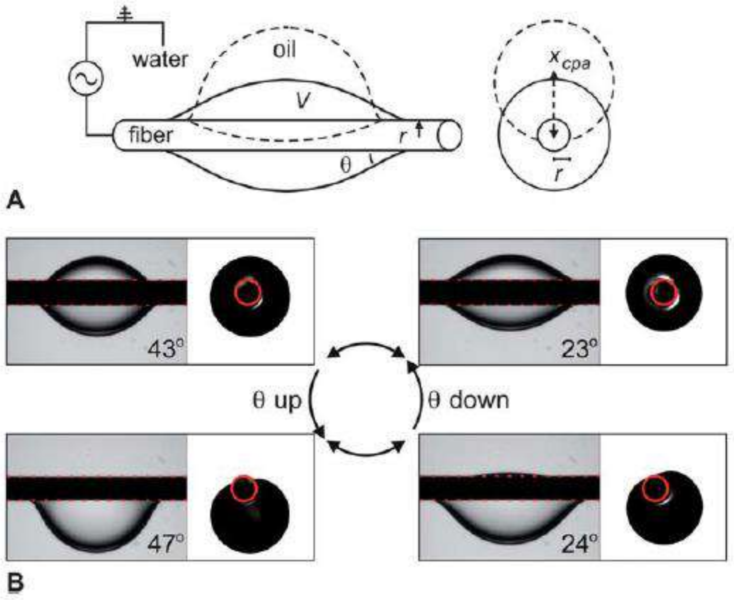
- Clampshell/barrel shapes

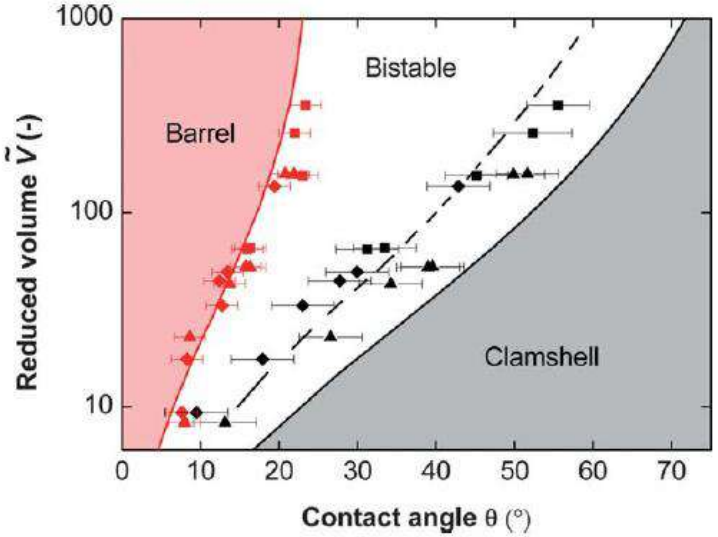


Mc Hale *et al. Coll. Surf. A.* 2002

Wetting of fibers

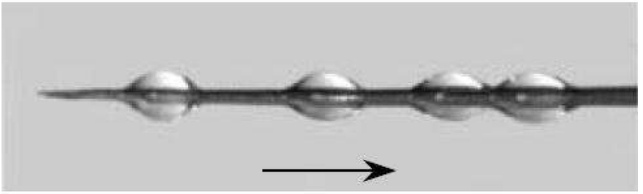
➢ Barrell-clamshell transition



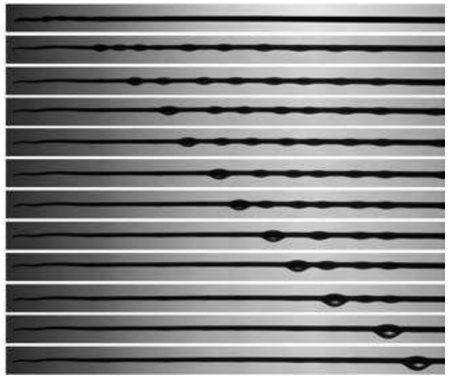


Eral *et al. Soft. Matt* 2011

➢ Tapered fibers

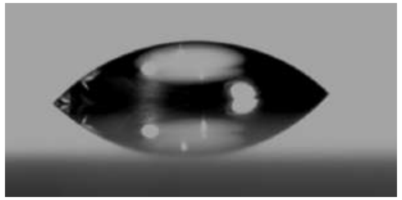


Lorenceau *et al. JFM* 2004



Coalescence filters, water collection, fog harvesting…

Wetting dynamics



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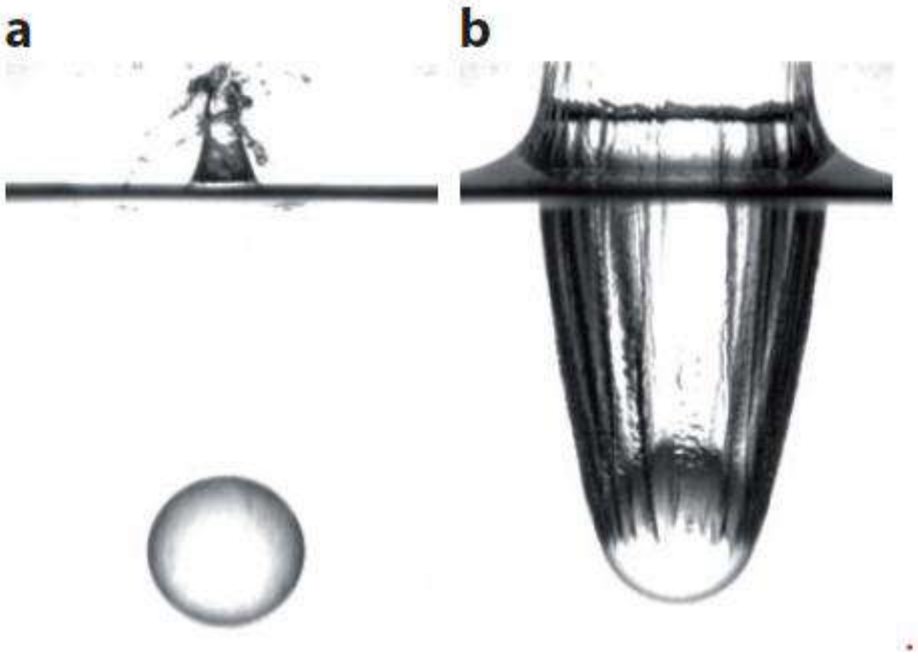


Duez *et al. Nature Phys.* 2007

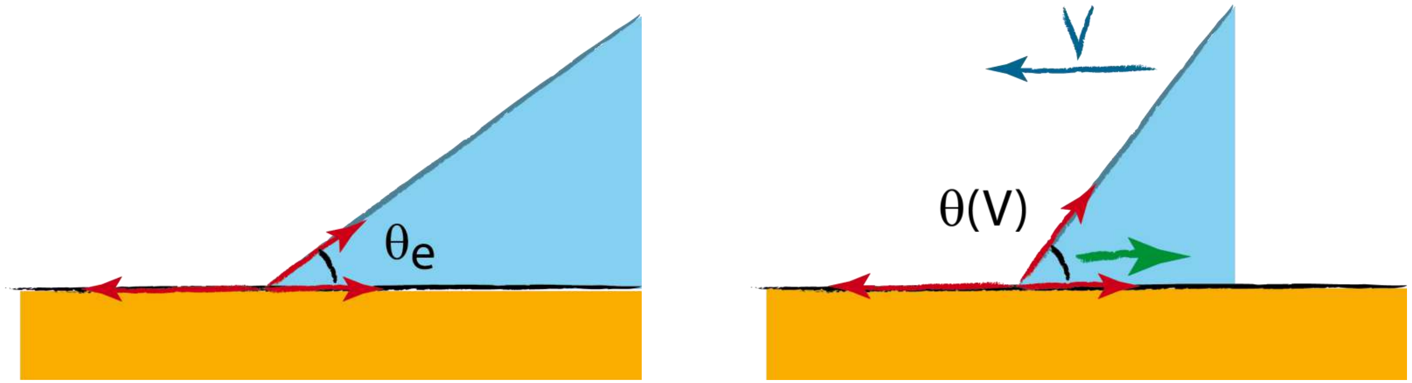
Wetting dynamics

- Dynamic contact angle
  - ✓ Dissipation at the contact line
  - ✓ Dynamic instabilities
- Spreading regimes
  - ✓ Droplet spreading
  - ✓ Film dewetting

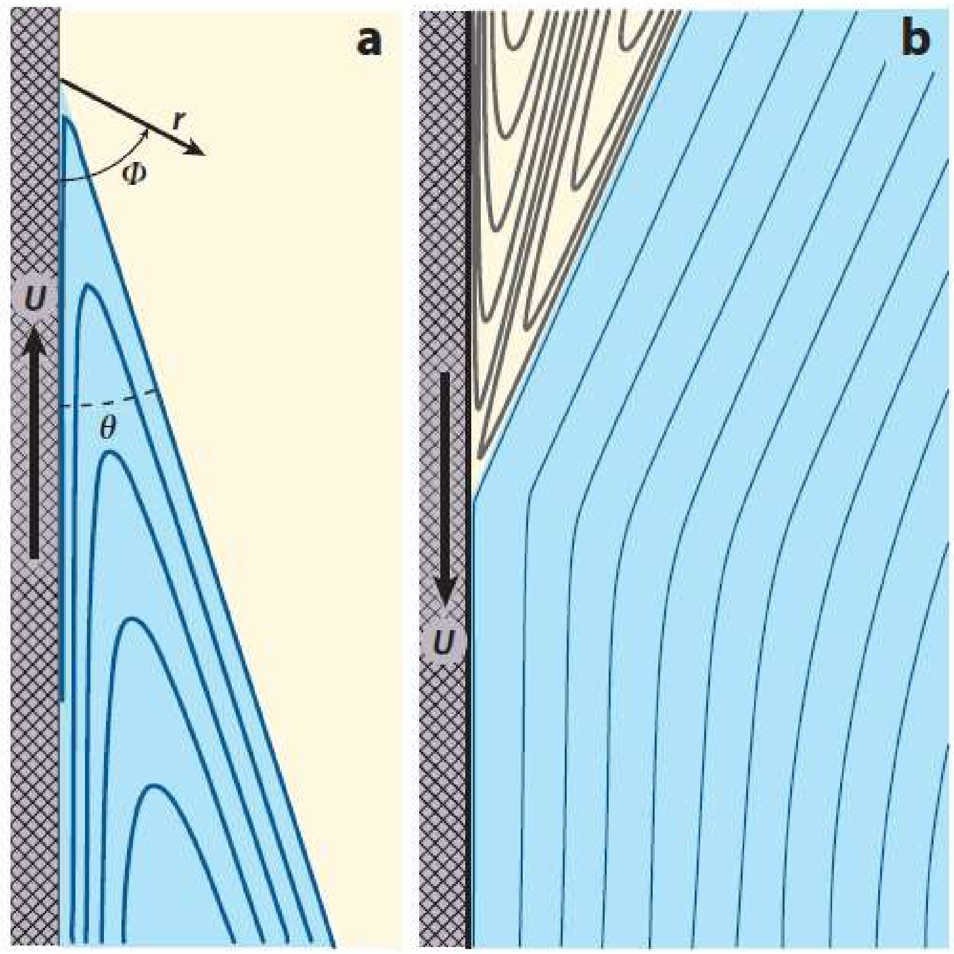
Wetting dynamics

Snoeijer *et al.* *ARFM* 2013

- Dynamic contact angle



Wetting dynamics



Huh, Scriven *JCIS* 1971

$$\sigma_{vis} \approx \eta \frac{U}{r}$$

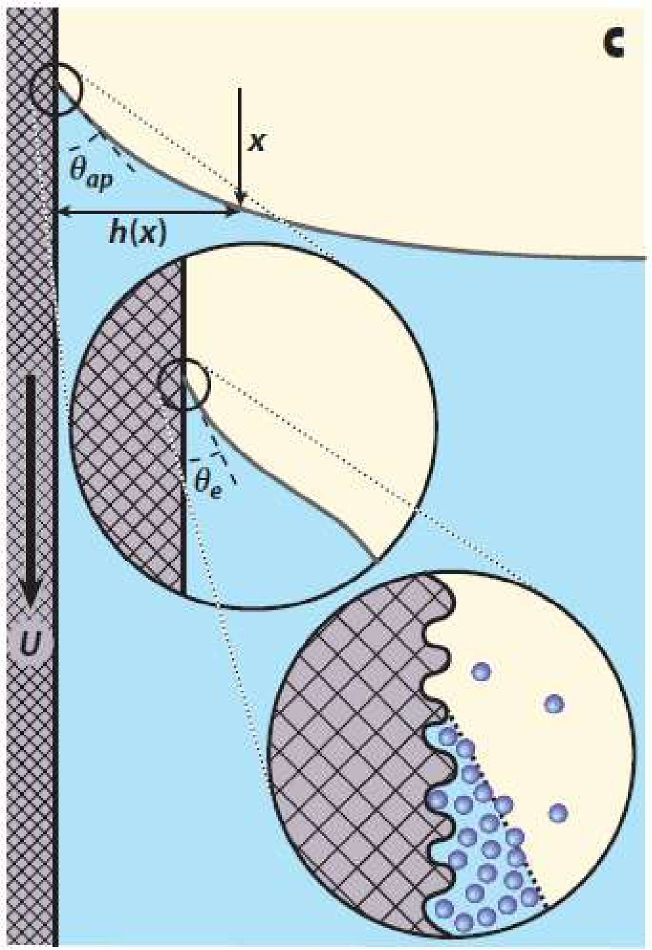
diverges at CL

Three regions:

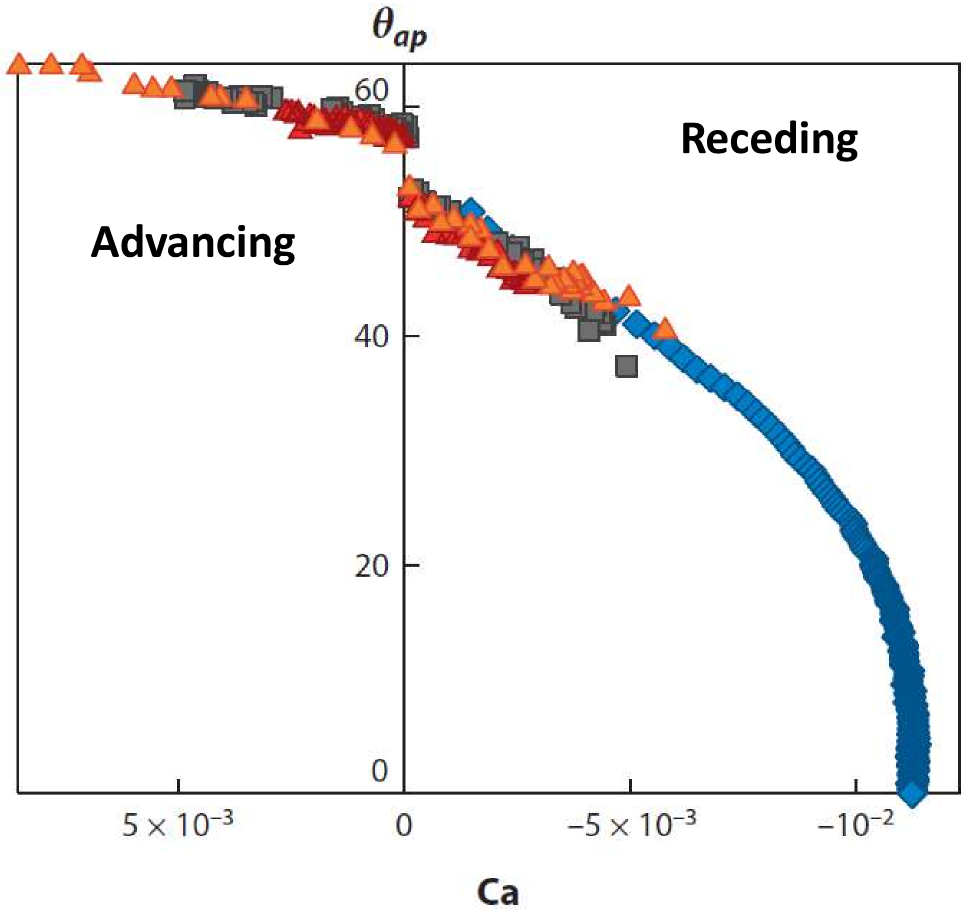
macroscopic,

mesoscopic,

Molecular



Wetting dynamics: macroscopic scale

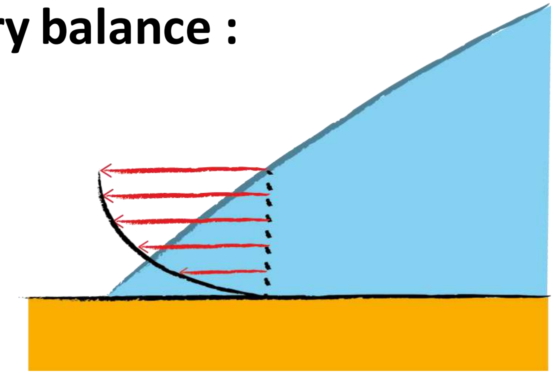


Capillary number

$$Ca = \frac{\eta U}{\gamma}$$

Wetting dynamics: mesoscopic scale

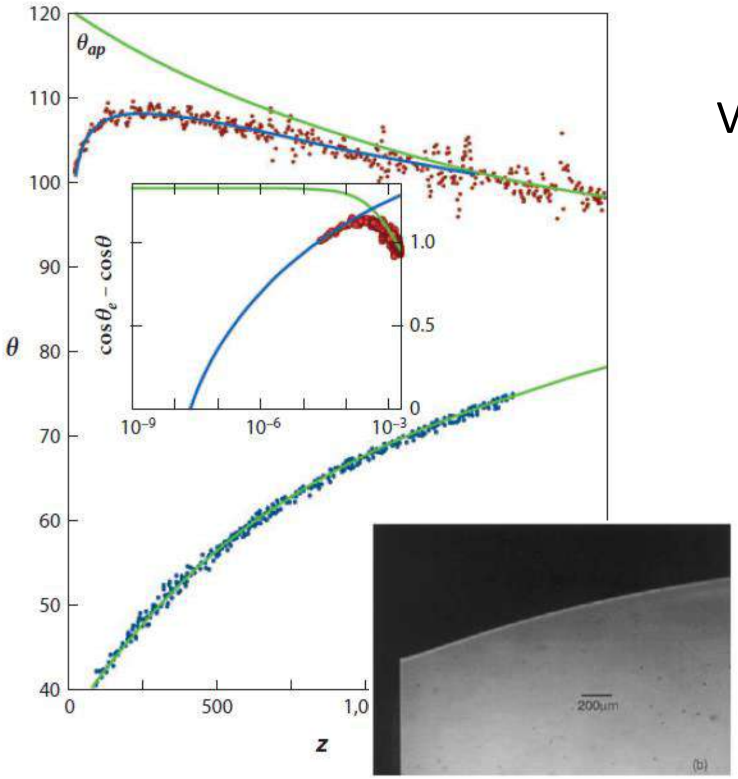
Visco-capillary balance :



Viscous stress *vs.* Capillary pressure

$$\frac{\partial P_{vis}}{\partial x} = \gamma(h_{xx})_x$$

$$h_{xxx} = -\frac{\pm 3Ca}{h^2}$$



Voinov solution: $h_x \approx \theta(x) \cong \left[9Ca.\,ln\left(\frac{x}{l}\right)\right]^{1/3}$

Voinov *Fluid Dyn.* (1976)

Matching :

Cox-Voinov equation:

$$\theta_{ap}^3 = \theta_e{}^3 \pm 9Ca.\,ln\left(\frac{L}{l}\right)$$

Cox *J. Fluid. Mech* (1986)

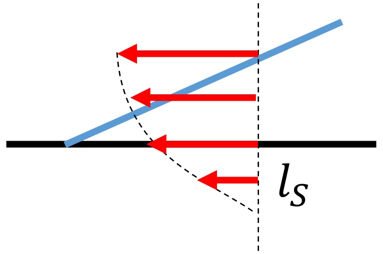
Ramé *et al. JCIS* (1971)

Wetting dynamics: microscopic scale

- Regularization of contact line singularity

mechanism	reference
mesoscopic precursor film	Hervet and de Gennes (1984)
molecular film	Eres *et al.* (2000)
Navier slip	Huh and Scriven (1971)
nonlinear slip	Thompson and Troian (1997)
surface roughness	Hocking (1976)
shear thinning	Weidner and Schwartz (1993)
evaporation/condensation	Wayner (1993)
diffuse interface	Seppecher (1996)
normal stresses	Boudaoud (2007)

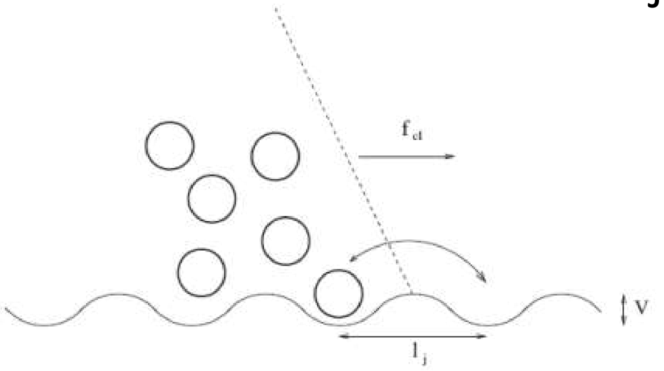
$$\sigma_{vis} \approx \frac{3\eta U}{h + 3l_s}$$



Wetting dynamics: Molecular Kinetic Theory

Thermally activated process

T.D. Blake, J.M. Haynes, JCIS (1969)



Jump frequency

$$\nu_{\pm} = \nu_0 exp\left(\frac{-V \pm F l_j/2}{kT}\right)$$

with $\nu_0 \sim \frac{kT}{h} \sim 10^{13} Hz$ $\quad V \sim \gamma {l_j}^2 (1 + \cos\theta_e)$

$$F \sim \gamma l_j (\cos\theta_e - \cos\theta)$$

$$U = l_j(\nu_+ - \nu_-) = 2\nu_0 l_j exp\left(-\frac{V}{kT}\right) sinh\left(\frac{\gamma {l_j}^2 (\cos\theta_e - \cos\theta)}{2kT}\right)$$

Eyring model $\quad \eta = \frac{kT}{\nu_0 {l_j}^3} exp\left(-\frac{V_l}{kT}\right)$ $\quad$ with $\quad V_l \sim 2\gamma {l_j}^2$

$$U = \frac{\gamma}{\eta} exp\left(-\frac{V - V_l}{kT}\right)(\cos\theta_e - \cos\theta)$$

$$\theta^2 - {\theta_e}^2 \sim Ca$$

= line friction

l_j, V as adjustable parameter

Values from 0,1 to 10 nm

Wetting dynamics

➢ Mixed models

- ✓ spatial scales

MKT → $\theta_\mu(U)$ introduced in Cox-Voinov

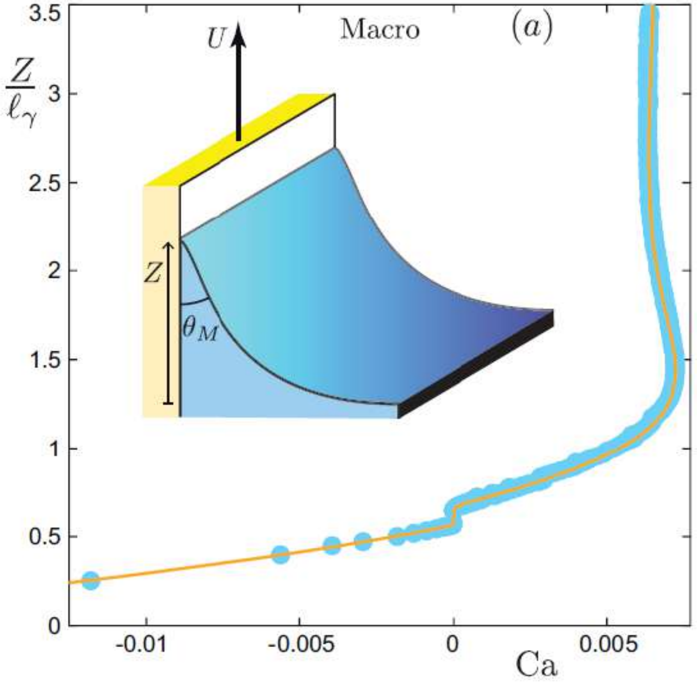
- ✓ Velocity

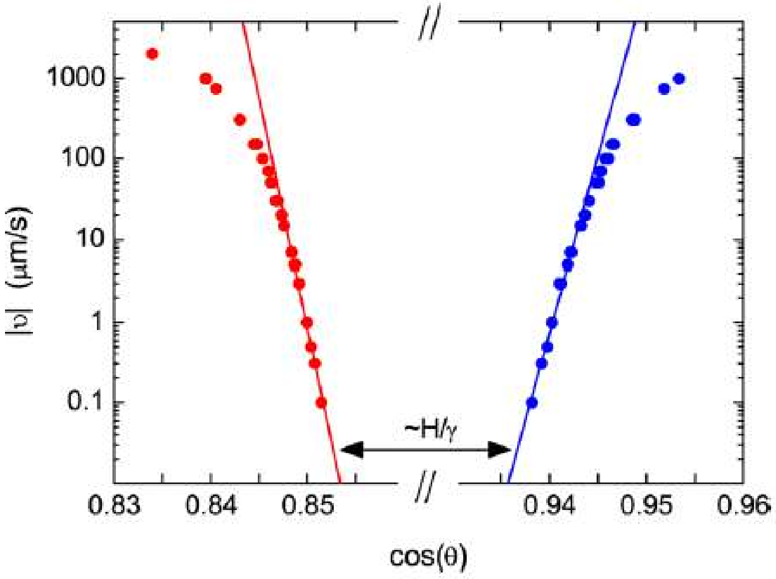
Small velocities: MKT
Large velocities: Cox-Voinov

Wetting dynamics on heterogeneous surfaces

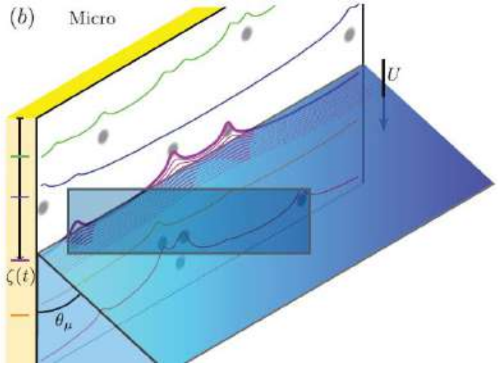
- Use of Cox-Voinov with static advancing or receding contact angles

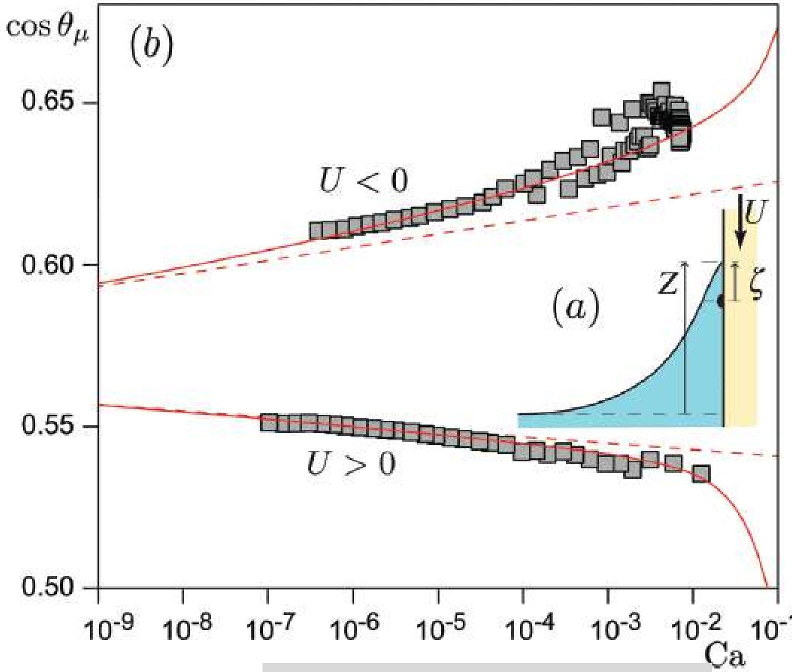
- MKT with defects





Davitt *et al. Langmuir* 2013

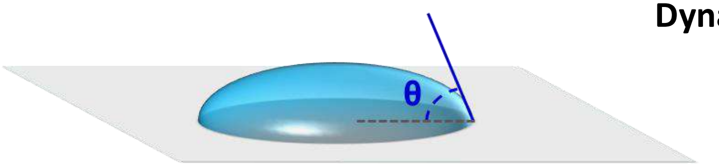




Perrin *et al. PRL* 2013

✓ Link with surface defect energy and size

Spreading dynamics: Tanner's law



Dynamics $$\theta^3 = \frac{9\dot{R}\eta}{\gamma}\ln(L/l)$$

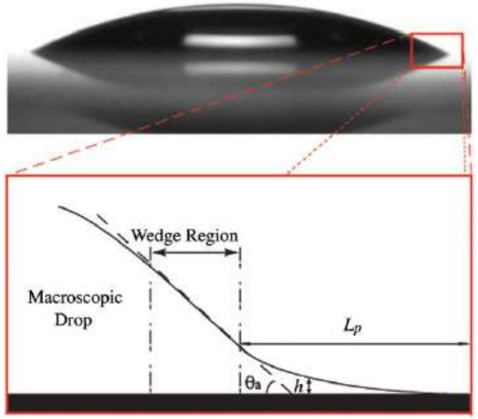
Geometry $$\theta \propto \frac{1}{R^3}$$

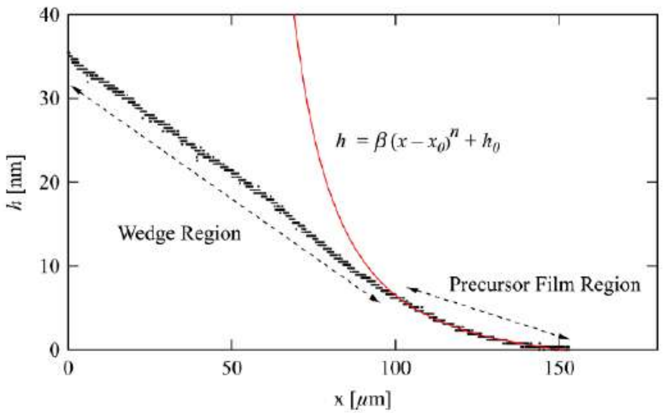
$$R \propto t^{1/10}$$

L. Tanner, J. *Phys. D* (1979)

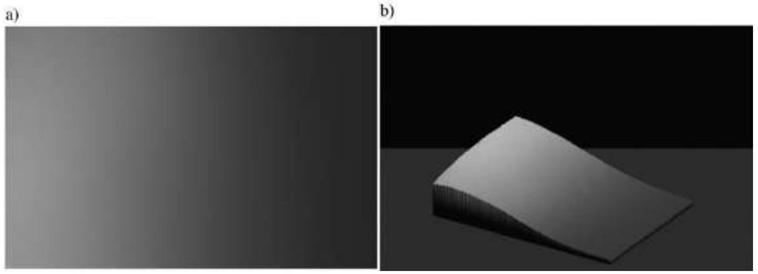
- **Precursor film**

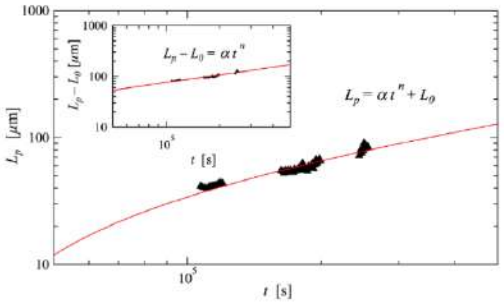
Huang *et al.*, Phys. Rev. Lett. 2011





$$L_p = \sqrt{\frac{A}{3\pi\eta h_c}}t^{1/2},$$





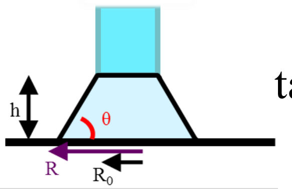
$$h(x,t) = \frac{A}{6\pi\eta}t\frac{1}{x^2}$$

Spreading dynamics: nanodispensing

L. Fabié, T.O. Soft Matt. 2012

$$\theta^3 - \theta_m^3 = 9\frac{\eta V}{\gamma}\ln\left(\frac{L}{l}\right)$$

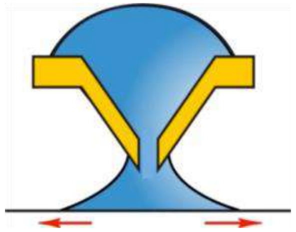
Spreading at constant pressure



$$\tan\theta \approx \theta \approx \frac{h}{R-R_0}$$

$$\left(\frac{h}{R-R_0}\right)^3 = \theta_m^3 + 9\alpha\frac{dR}{dt}$$

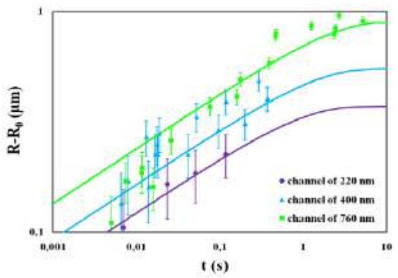
L. Fabié, T.O. Langmuir 2011

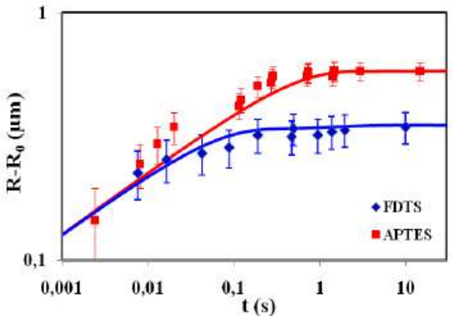


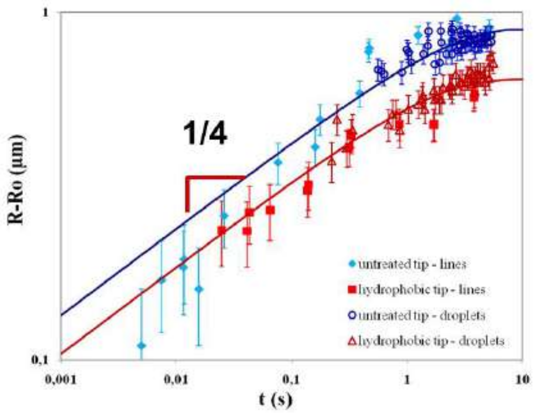
For $\vartheta_m = 0$, analytical solution :
$R\text{-}R_0 = At^{1/4}$

For $\vartheta_m \neq 0$, numerical solution

Ln(L/l) = 10



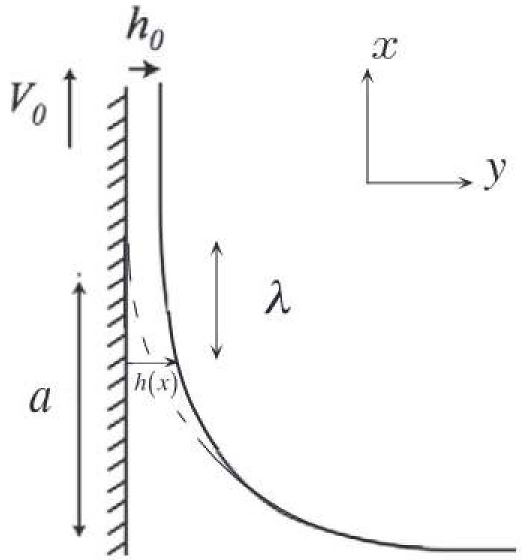


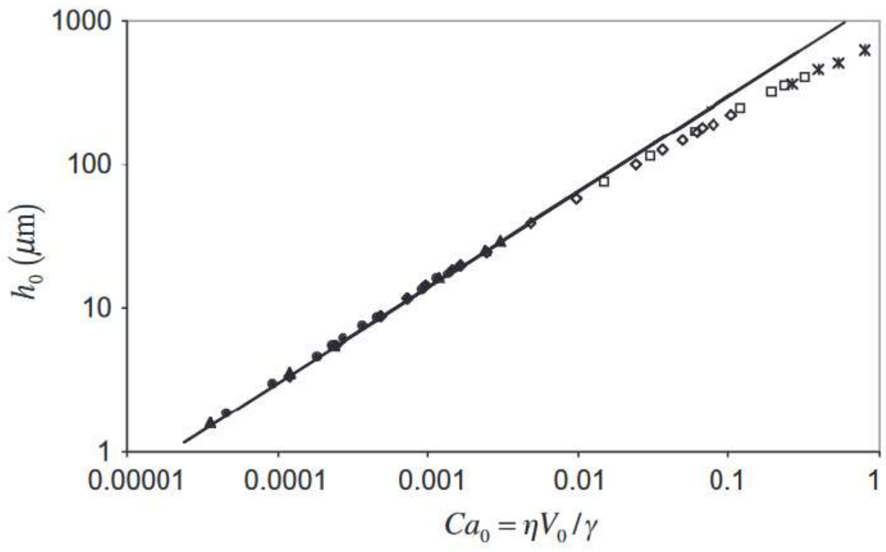


Coating: liquid entrainment

- The Landau-Levich film (mouillage total)

$$h_0 \approx 0.94 a Ca^{2/3}$$

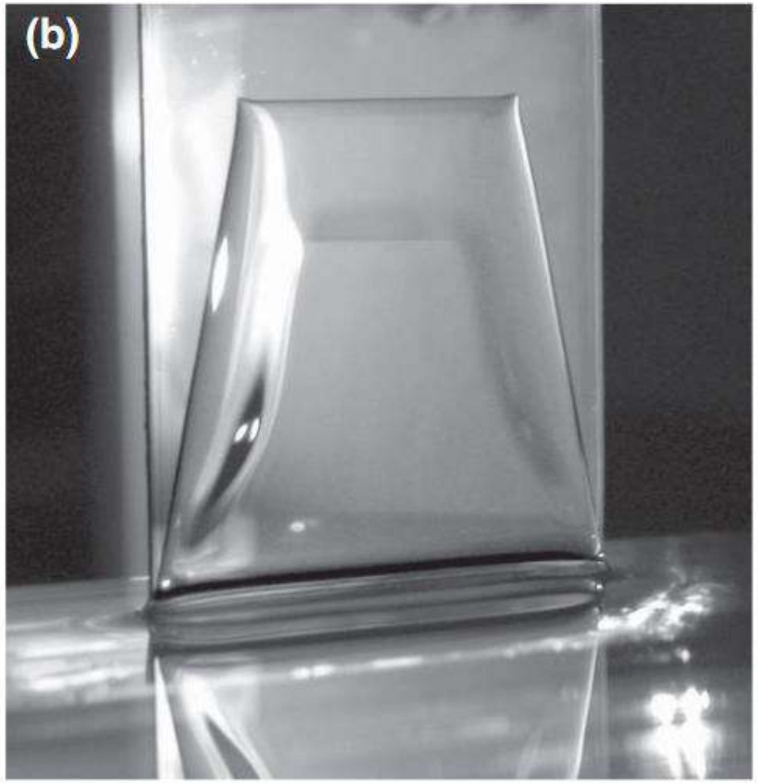




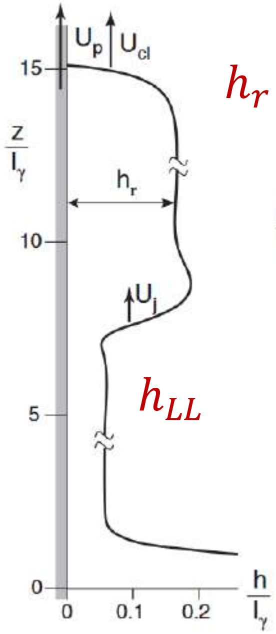
Maleki *et al.*, *JCIS* 2011

Dynamical instability

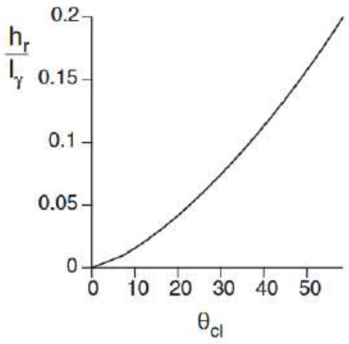
➢ Partial wetting

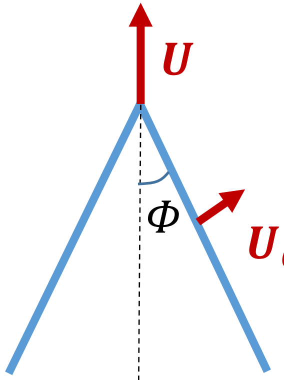


Snoeijer *et al.*, *PRL* 2006

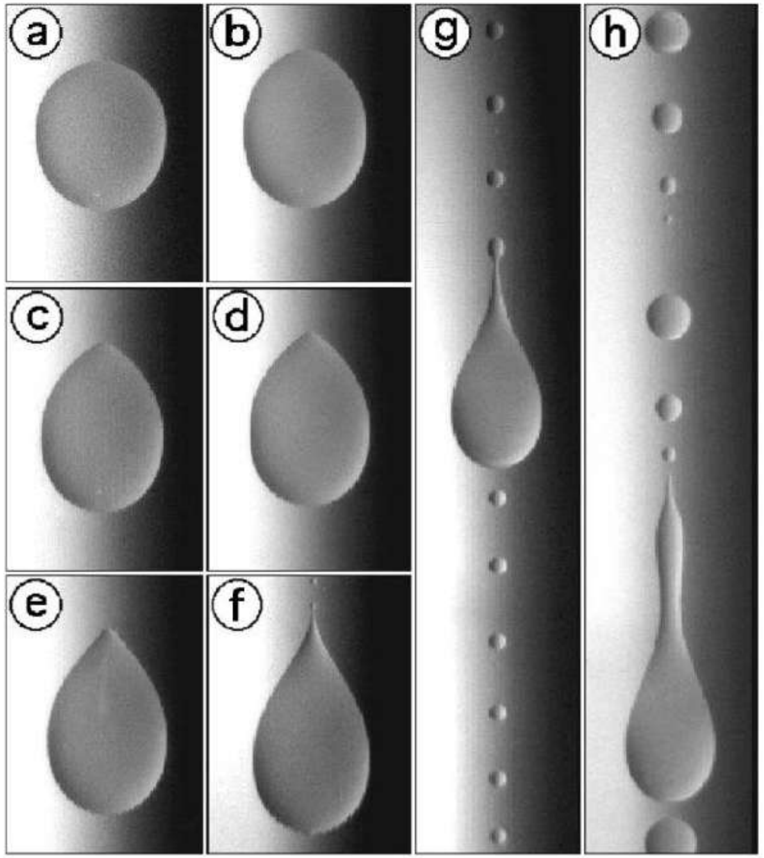


h_r determined by contact line dynamics





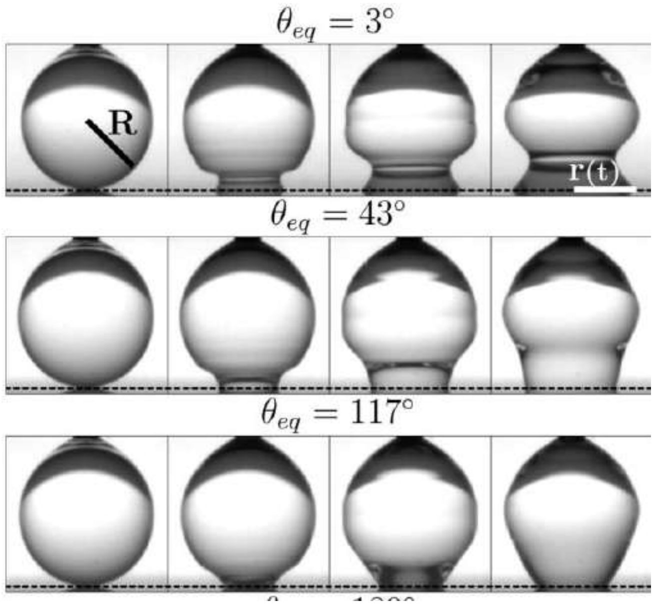
$U_{CL} = U \sin \Phi$



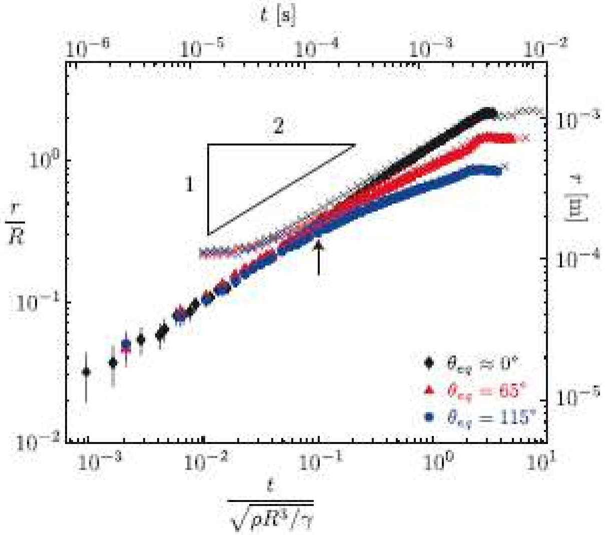
Le Grand *et al.*, *JFM* (2005)

Snoeijer *et al.*, *Phys. Fluids* 2007

Short time dynamics: inertial spreading



Bird, *et al. Phys. Rev. Lett* (2008)



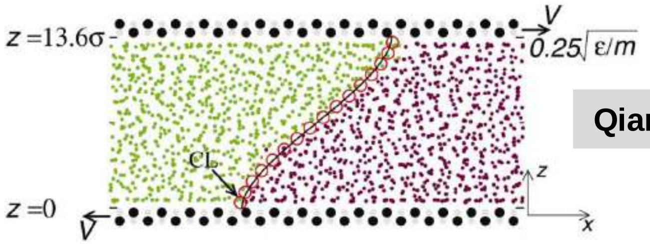
Winkels *et al.*, *Phys. Rev. E* (2012)

$$\rho\left(\frac{dr}{dt}\right)^2 \sim \gamma\frac{R}{r^2} \Rightarrow r \sim t^{1/2}$$

Inertia capillarity

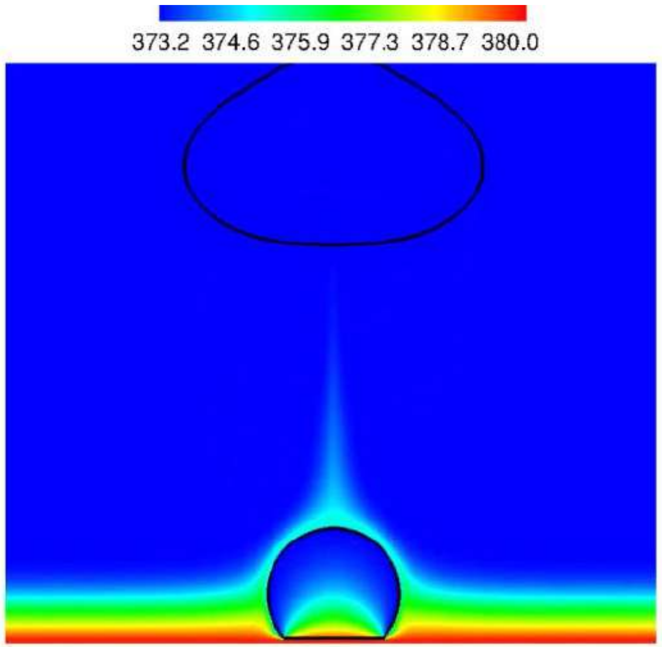
Simulations

- Molecular dynamics



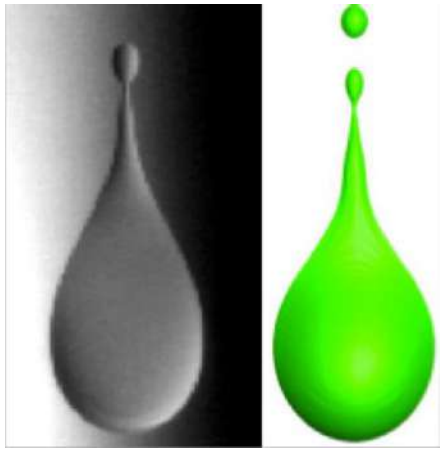
Qian *et al.*, *Phys. Rev. E* (2003)

Sui *et al.*, *ARFM 2014*



- Direct numerical simulations
  - ✓ **DNS solver with sub-grid model (slip or dynamics contact angle)**

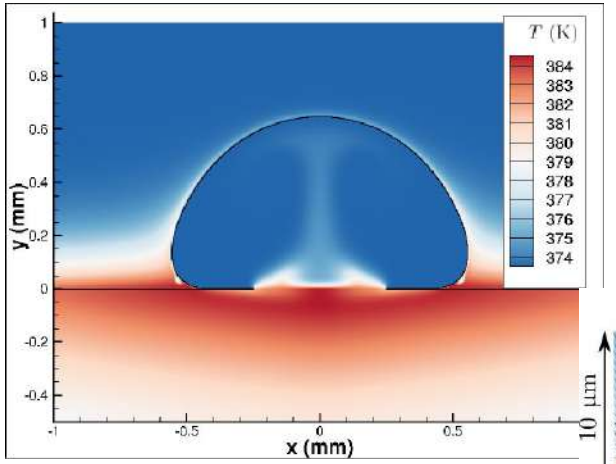
Code JADIM (IMFT)

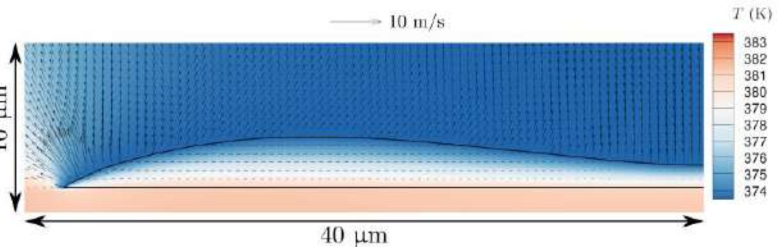


Maglio, Legendre, Comp. *Exp. Fluid Mech.* (2014)

Le Grand *et al.*, *JFM* (2005)

Code DIVA (IMFT)

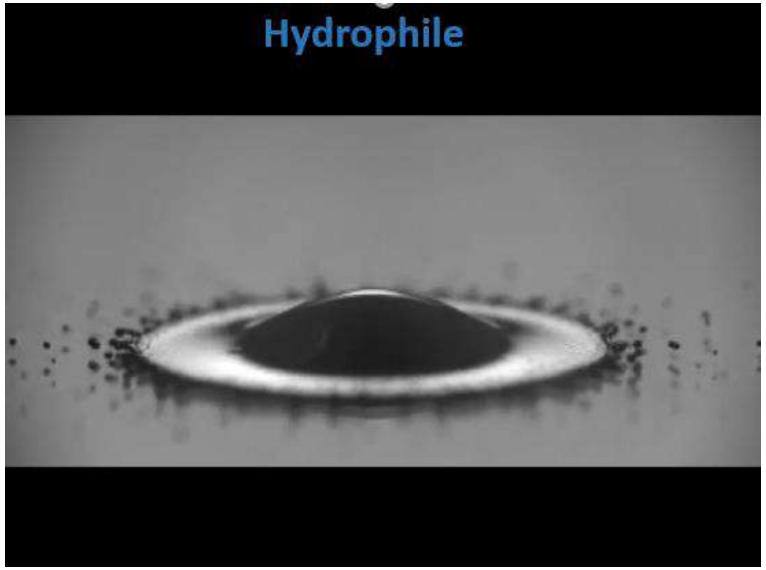


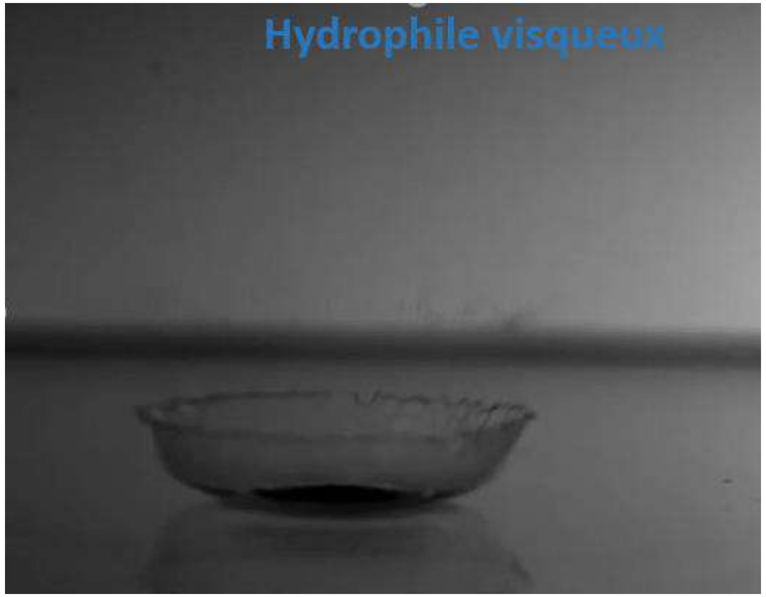


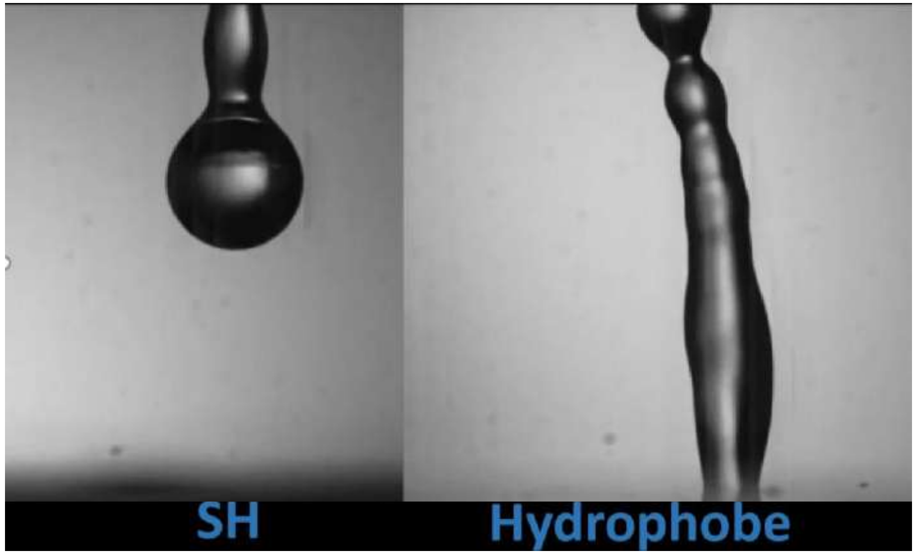
Microlayer regime

Urbano *et al.*, *IJHMT* (2018)

Impact



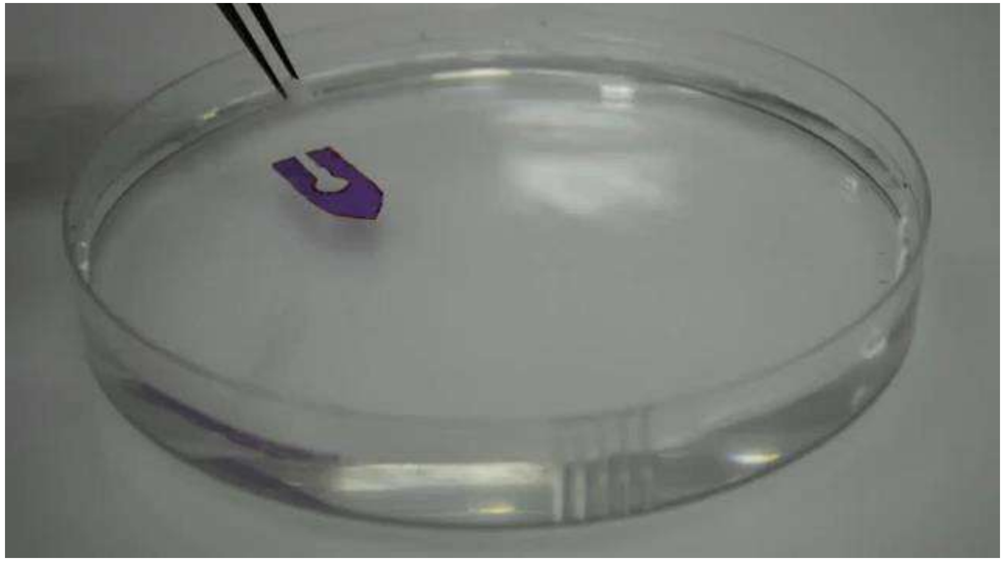




Wetting with complex liquids

- Marangoni effect
- Wetting with volatile liquids
- Reactive wetting
- Wetting with surfactants solutions

Marangoni effect



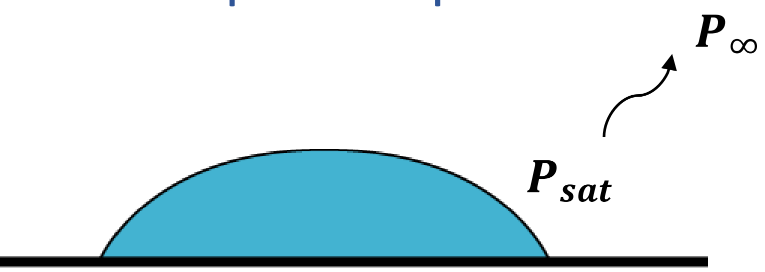
Ex : camphor boat

Solutal Marangoni effect $\gamma(C)$: surfactants $\gamma(C)\downarrow$, binary solutions

Thermal Marangoni effect $\gamma(T)\downarrow$

Wetting with volatile liquids

- Droplet evaporation



$$m = \frac{1}{3}\pi r^3 \rho (1-\cos\theta)^2 (2+\cos\theta)$$

Diffusion controlled

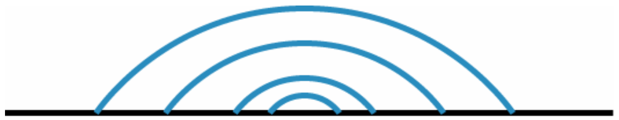
$$\frac{dm}{dt} = -4\pi r^2 D\left(\frac{dc}{dr}\right) = -4\pi r D(c_0 - c_\infty)$$

$$\frac{dm}{dt} \propto r$$

Picknett, Bexon *J.C.I.S.* 1977

Tapez une équation ici.

Constant contact angle mode:

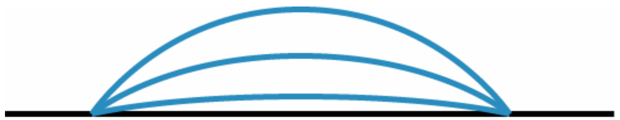


$$\frac{dm}{dt} = -\alpha . m^{1/3}$$

$$m^{2/3} = m_0^{\ 2/3} - \frac{2}{3}\alpha t$$

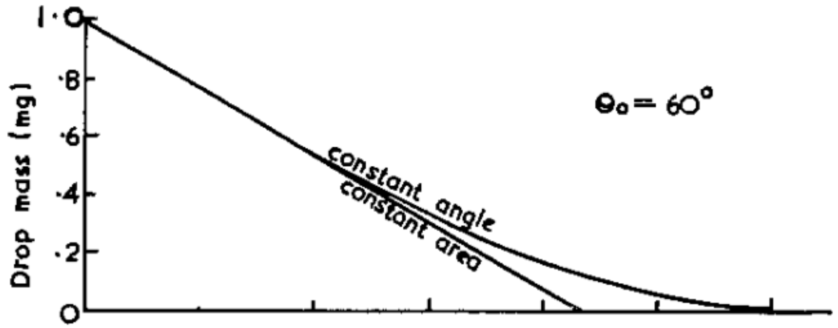
- $m^{2/3}$ (t) linear
- $t_{evap} \propto m_0^{\ 2/3}$

Constant radius R mode:



$r \sin\theta = R$

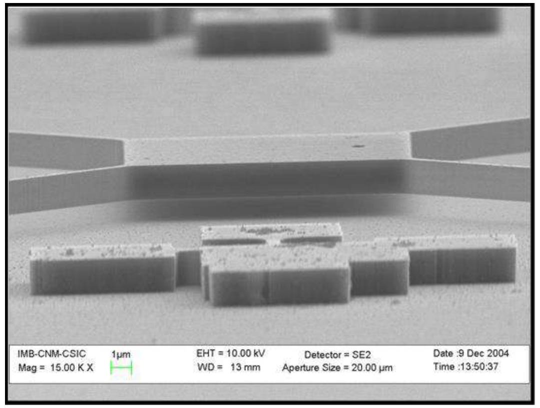
$$\frac{dm}{dt} = -Cte$$

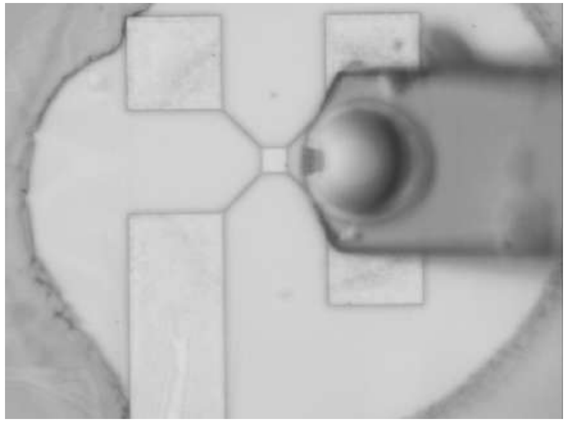


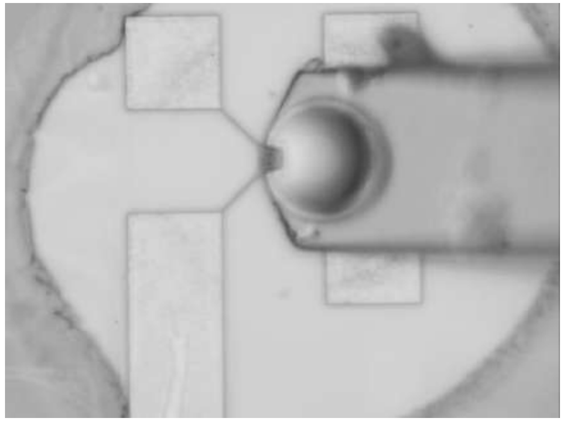
Wetting with volatile liquids

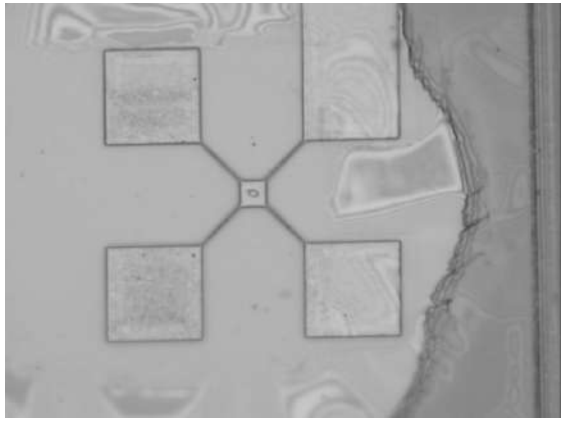
Arcamone, *J.Phys. Chem. B* 2007

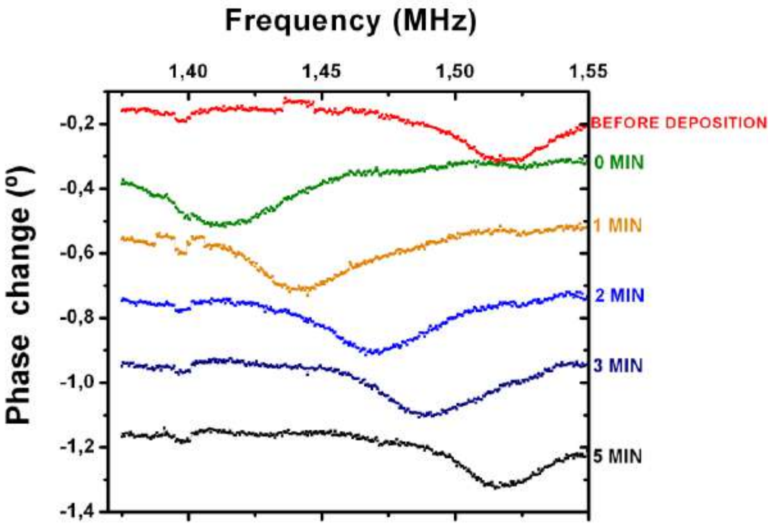
- Evaporation of femtoliter ($10^{-15} l$) droplets

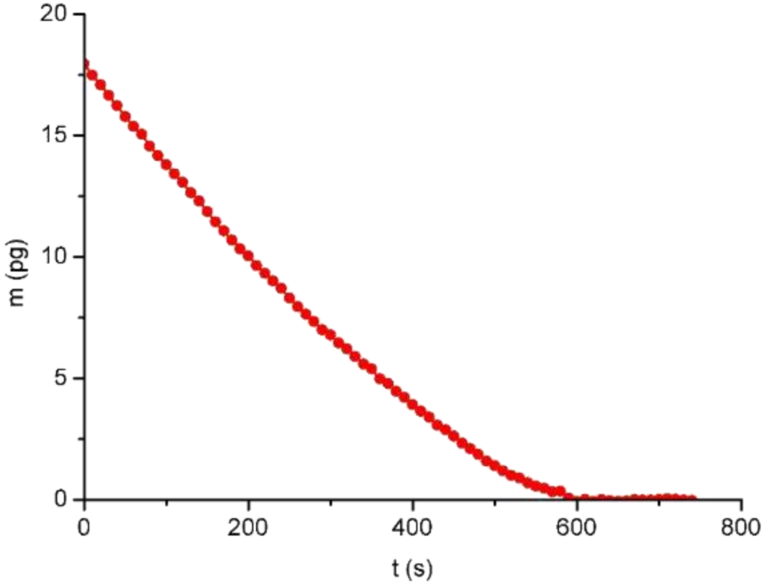


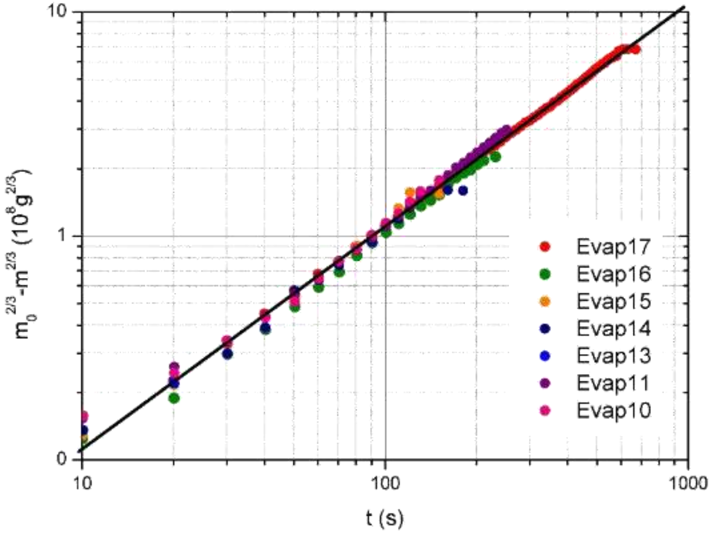








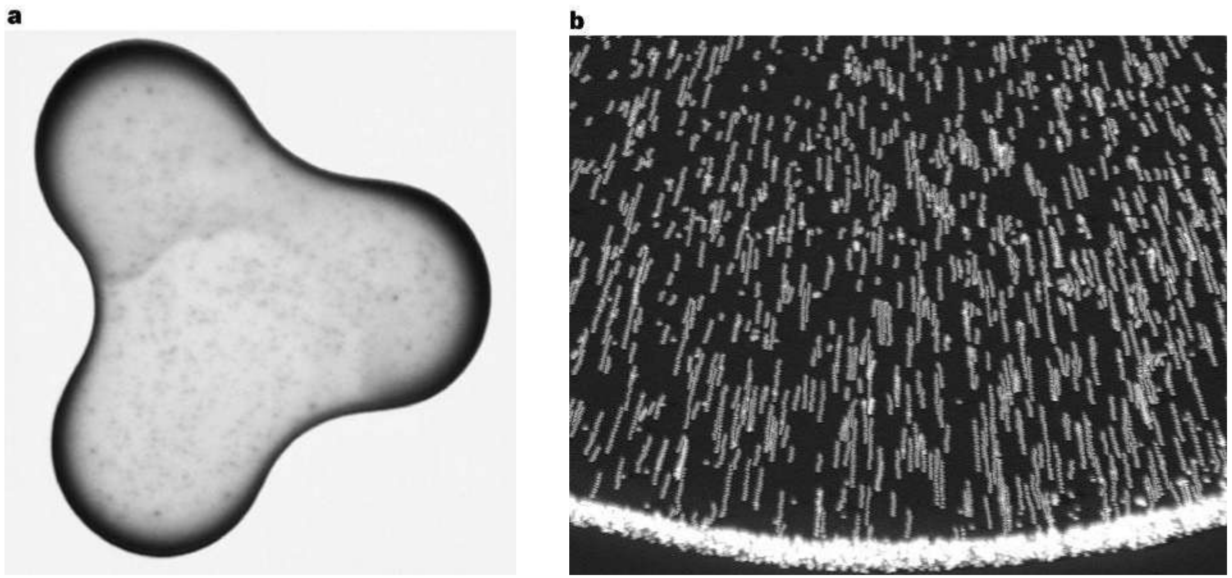


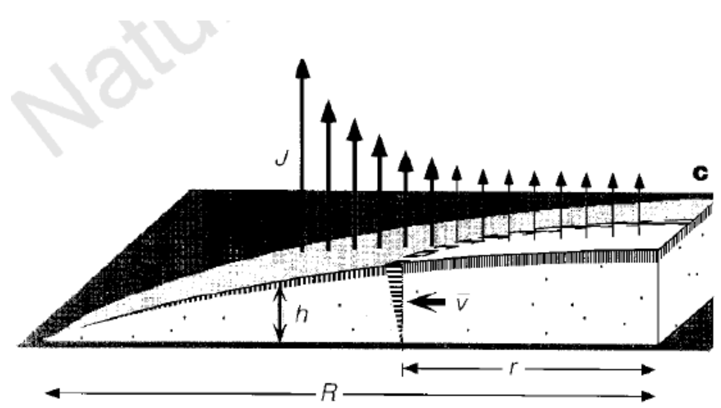


Wetting with volatile liquids

- Deposition pattern: the coffee stain

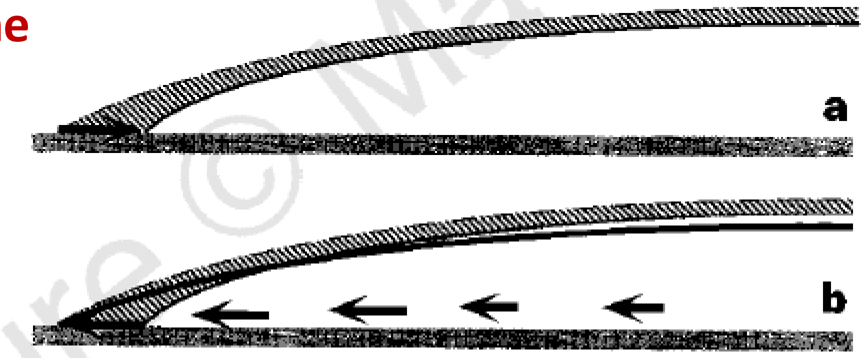
Deegan *et al.*, *Nature* 1994





$$J(r) \propto (R-r)^{-\lambda} \quad \text{with} \quad \lambda = (\pi - 2\theta)/(2\pi - 2\theta)$$

Pinned contact line

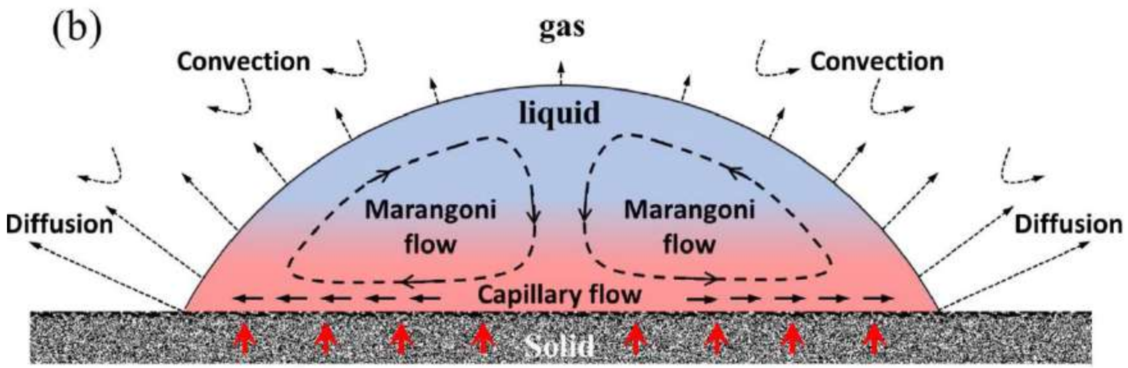


Capillary flow

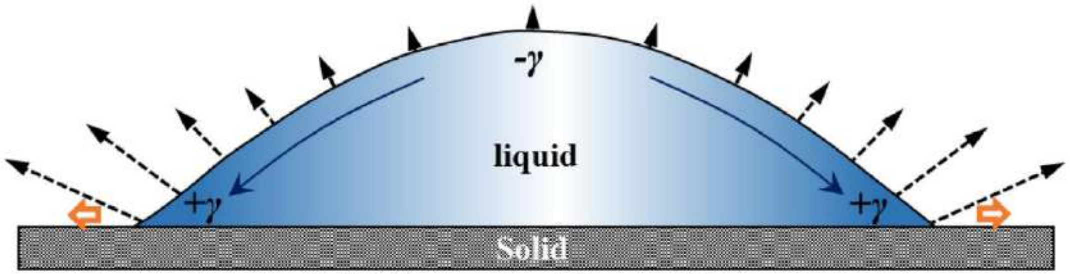
towards the contact line

Wetting with volatile liquids

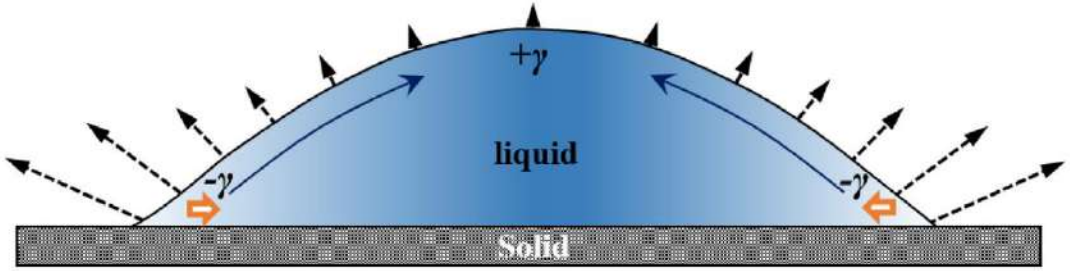
Wang *et al.*, *Phys. Rep.* 2022



- Binary mixture

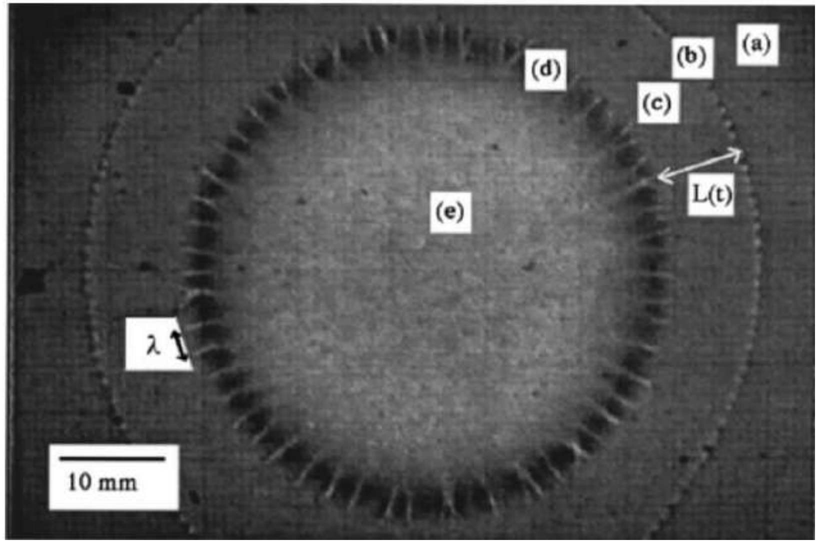


(a) Marangoni Spreading



(b) Marangoni Contraction

Water/alcohol mixture



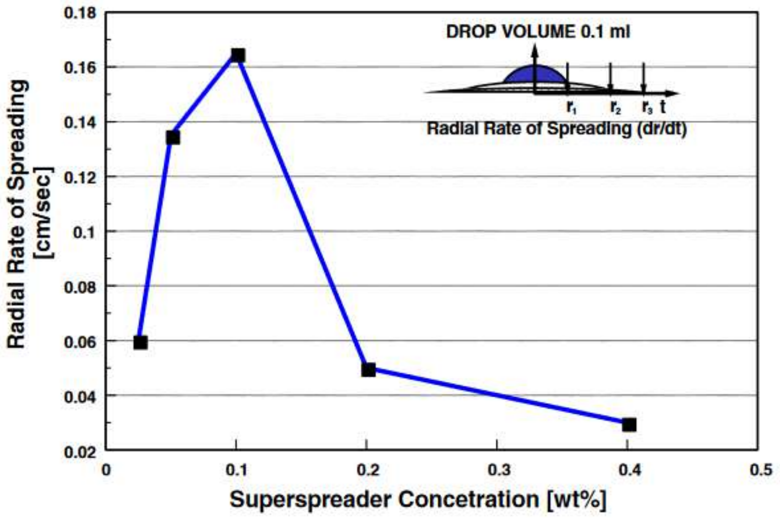
Fanton *et al.*, *Langmuir* 1998

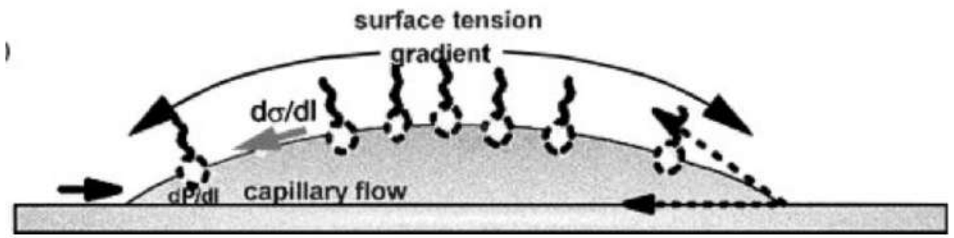
Wetting with complex liquids: surfactants

➢ A particular case: superspreading on hydrophobic surfaces

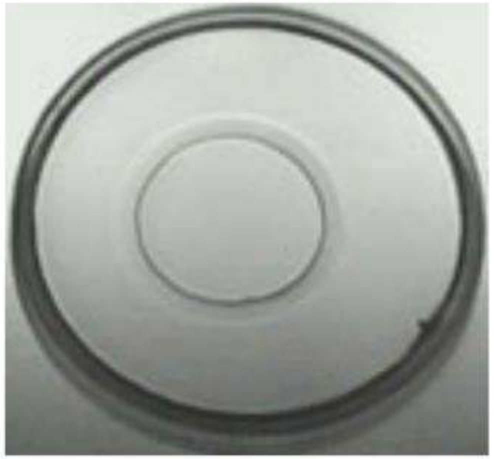
Nikolov *et al.*, *Current Opinion Coll Interf Sci.* 2020
EPJST 2011

1. Initial spreading

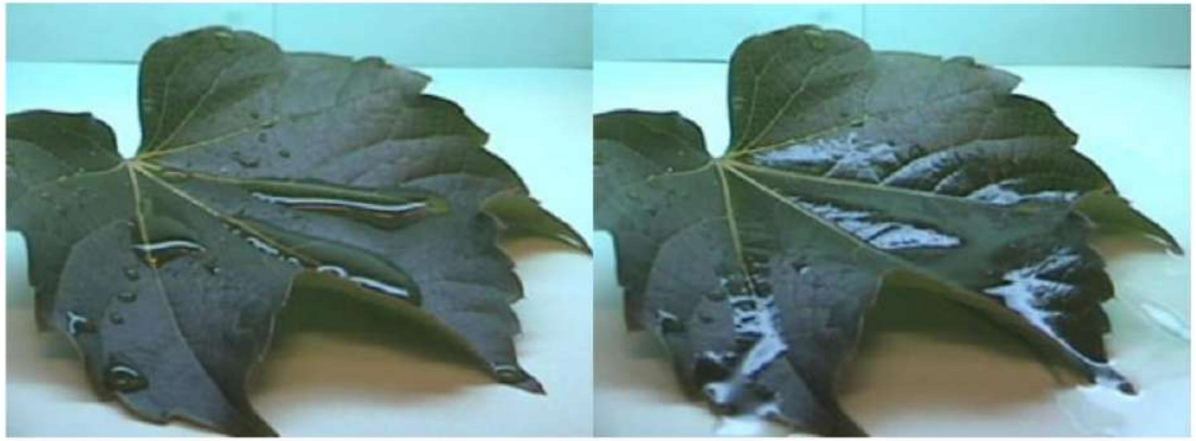




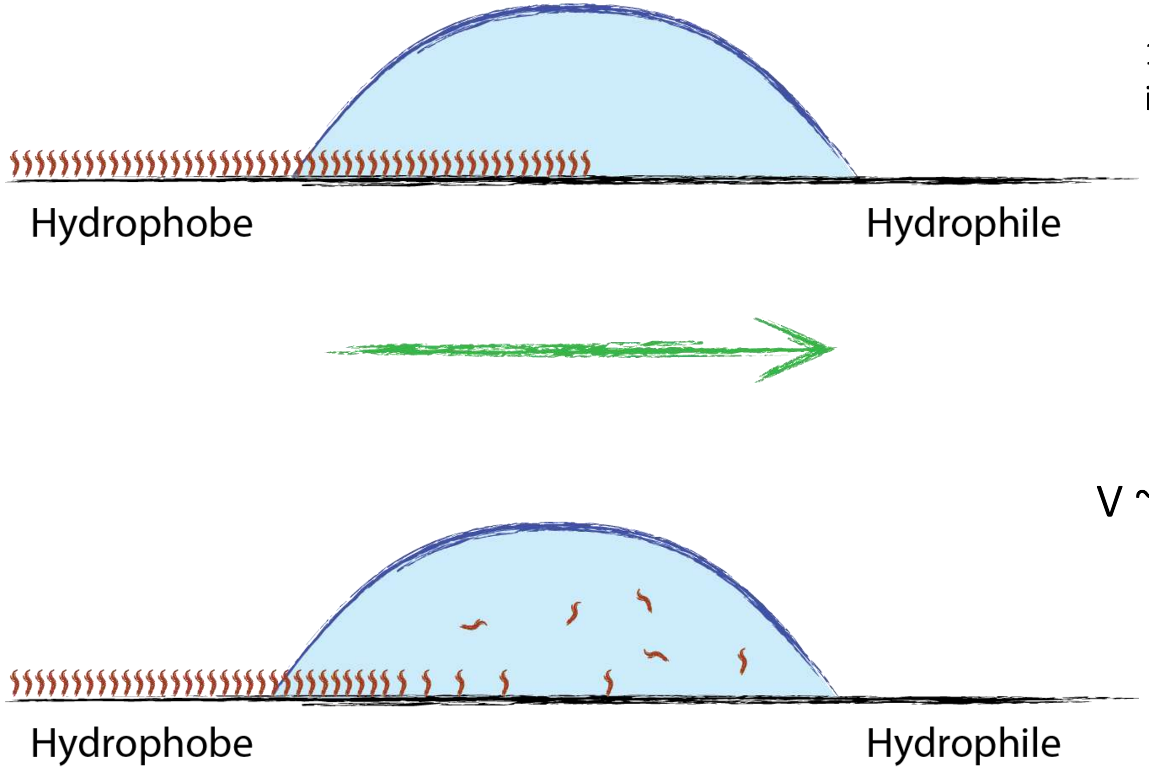
2. Bump



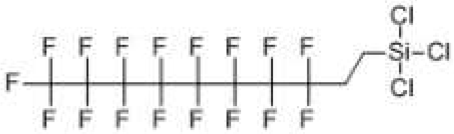
3. Instability



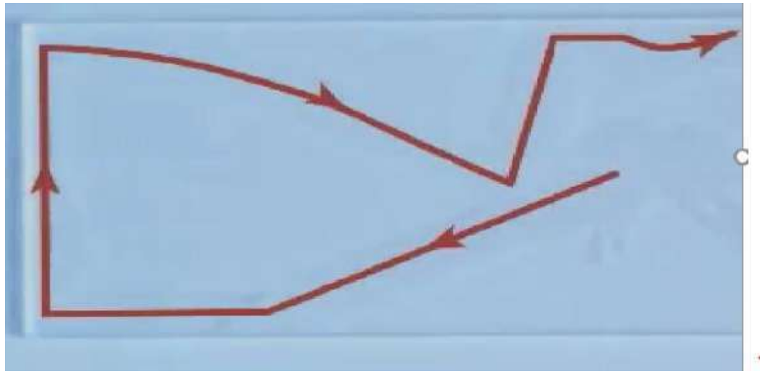
Reactive wetting: self-propelled droplets



1H,1H,2H,2H, perfluorodecyltrichlorosilane in octane

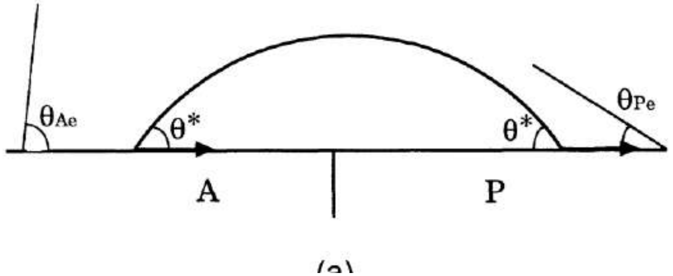


V ~ 10 cm/s



Domingues dos Santos, Ondarçuhu, *PRL.* 1995

Reactive wetting: self-propelled droplets



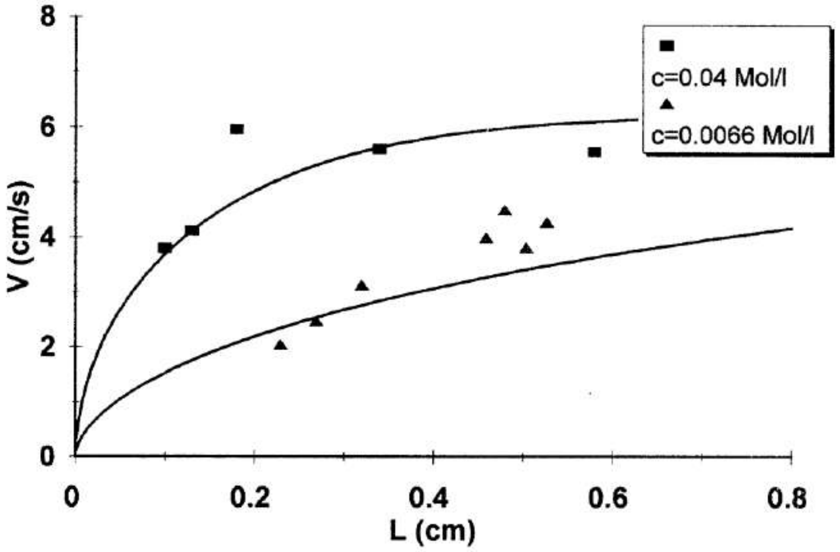
$$\begin{cases} V_A(\theta^*) = \dfrac{\gamma}{9\eta l}\left(\theta_A^3 - \theta^{*3}\right) \\ V_P(\theta^*) = \dfrac{\gamma}{9\eta l}\left(\theta^{*3} - \theta_P^3\right) \end{cases}$$

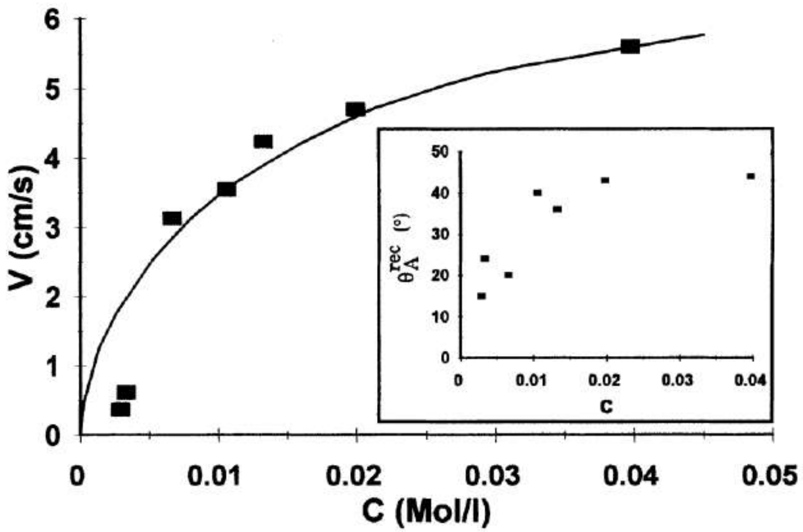
$$V = \frac{\gamma}{18\eta l}\left(\theta_A^3 - \theta_P^3\right)$$

$$\gamma \cos\theta_A = \gamma \cos\theta_P - \gamma_1 \Phi_S$$

$$\Phi_S = 1 - \exp\left(-\frac{t}{\tau}\right) = 1 - \exp\left(-\frac{L}{V\tau}\right)$$

$V(C)$ and $V(L)$



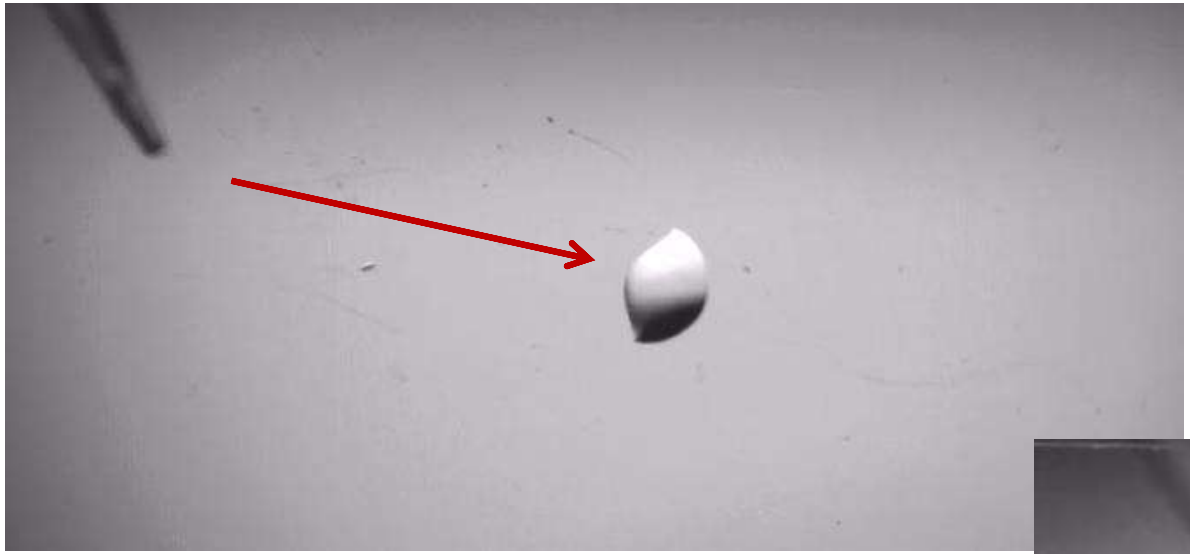


$\tau \in [0{,}01\ \mathrm{s} - 0{,}2\ \mathrm{s}]$

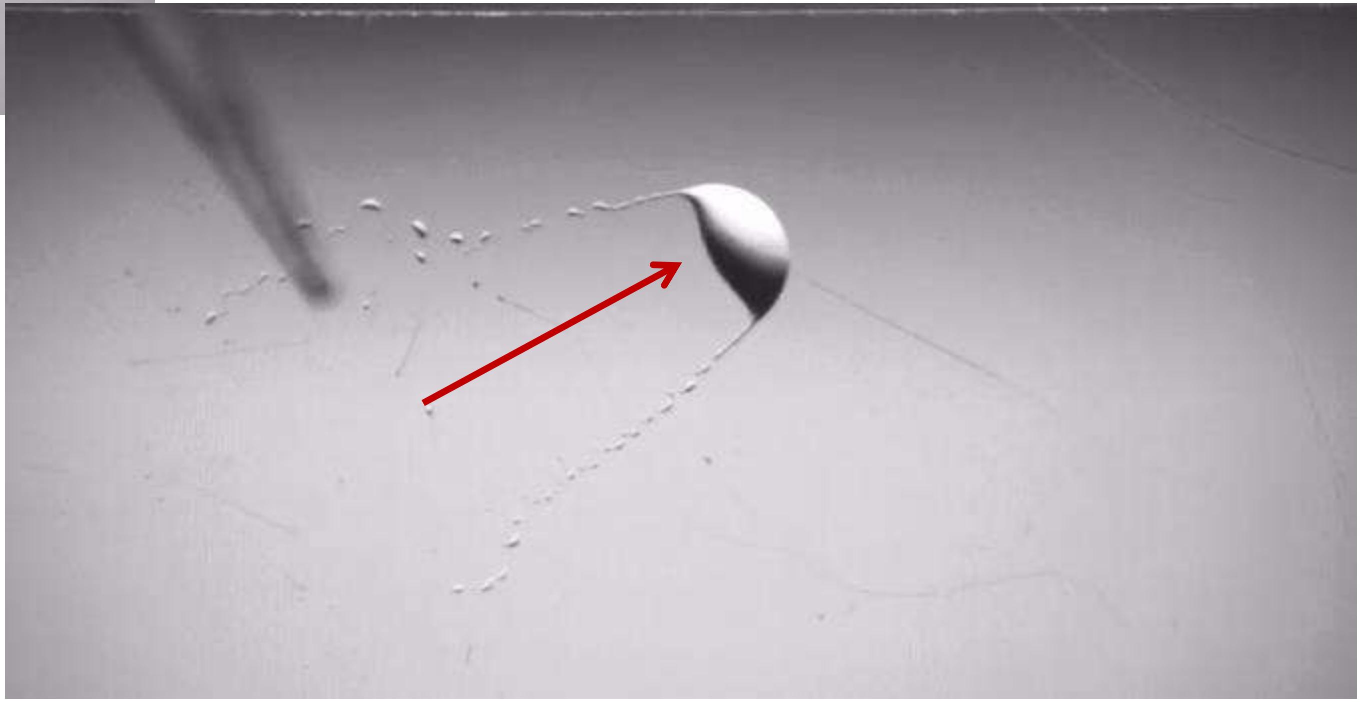
Reactive wetting: self-propelled droplets

Perfluorosilane 0,02 M sur **lame de verre brute**

Beaune *et al.*, *PNAS.* 2018

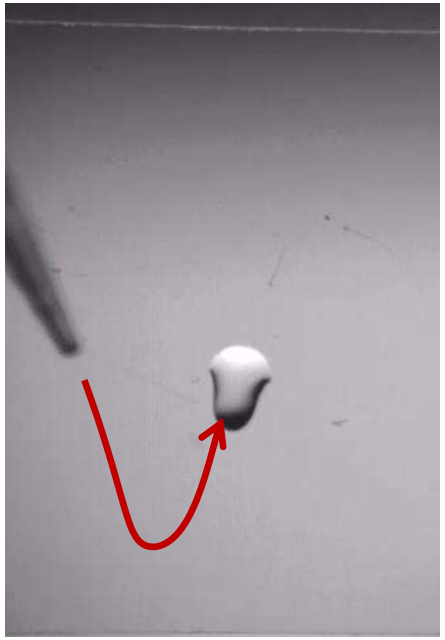


sur **lame de verre traitée corona (mouillage total)**

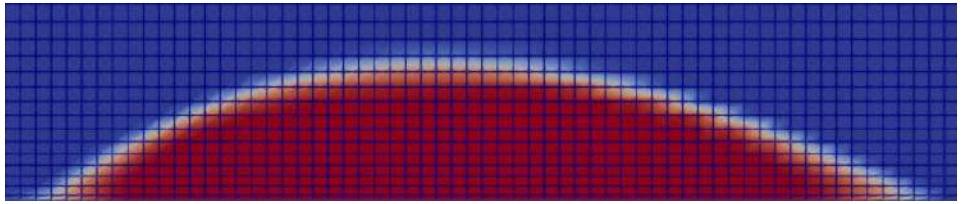


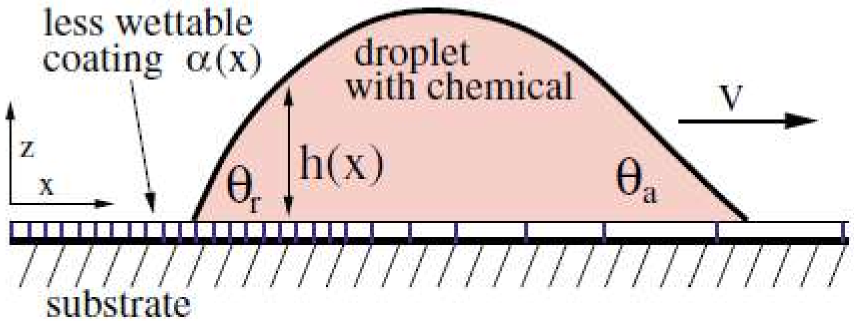
Reactive wetting: self-propelled droplets

Perfluorosilane 0,05 M sur **lame de verre brute**

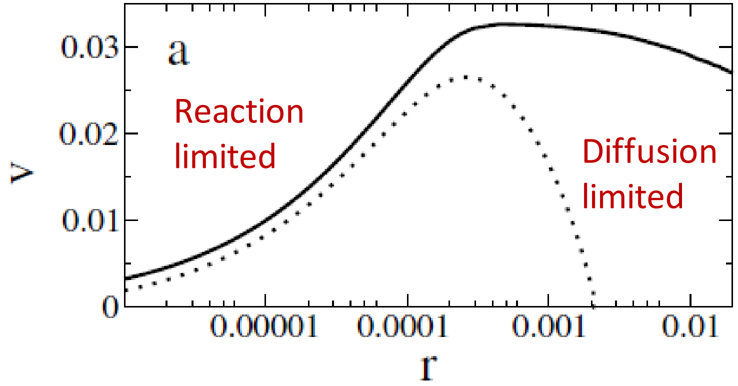


Simulations JADIM





Thiel *et al.*, *PRL* 2004



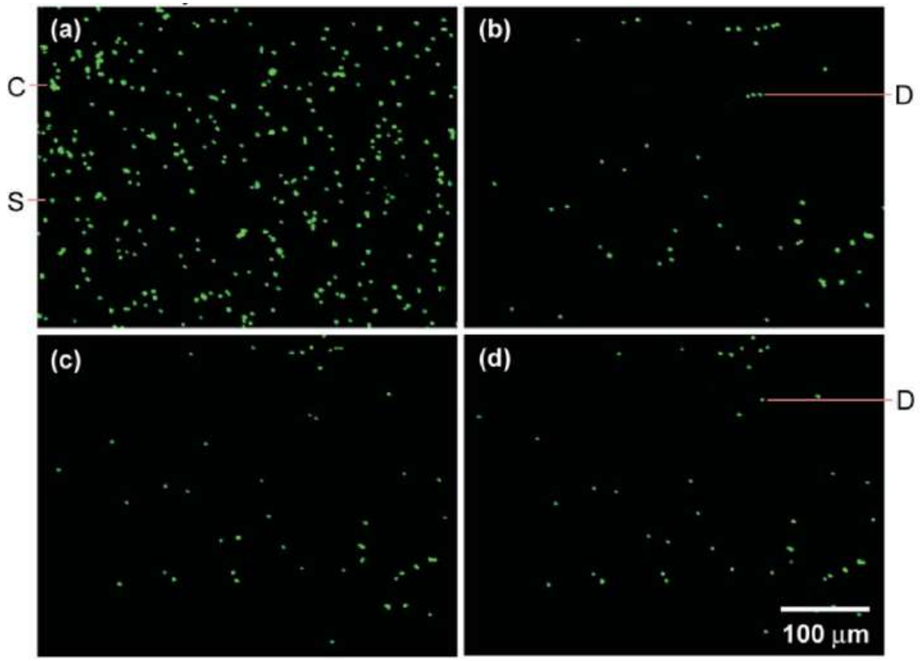
Wetting and adsorption: contamination and cleaning

- Water is totally wetting clean glass surface
  - Cleaning can be achieved by UV/Ozone cleaning, O_2 plasma, piranha solution…
- Left in air, glass becomes hydrophobic due to airborne contaminant adsorption
  - Short hydrocarbons (butane, propane) are the main source of contamination
  - Water contact angle : 30-40 °

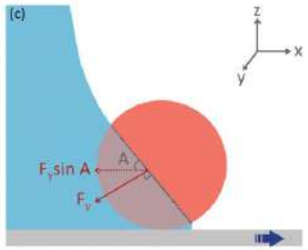
Millet *et al. J. Geophys. Reseach Atm.* 2005

Wetting and adsorption: contamination and cleaning

➢ **Contamination by particles**

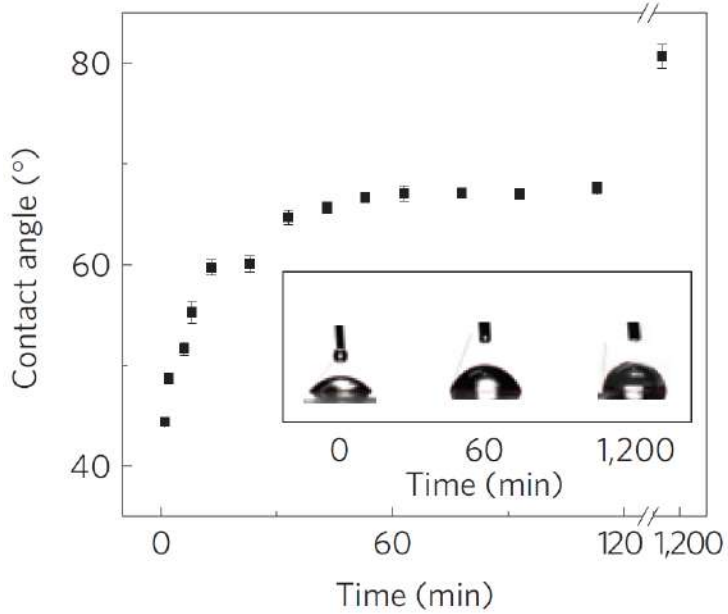


Sharma et al. JCIS 2008



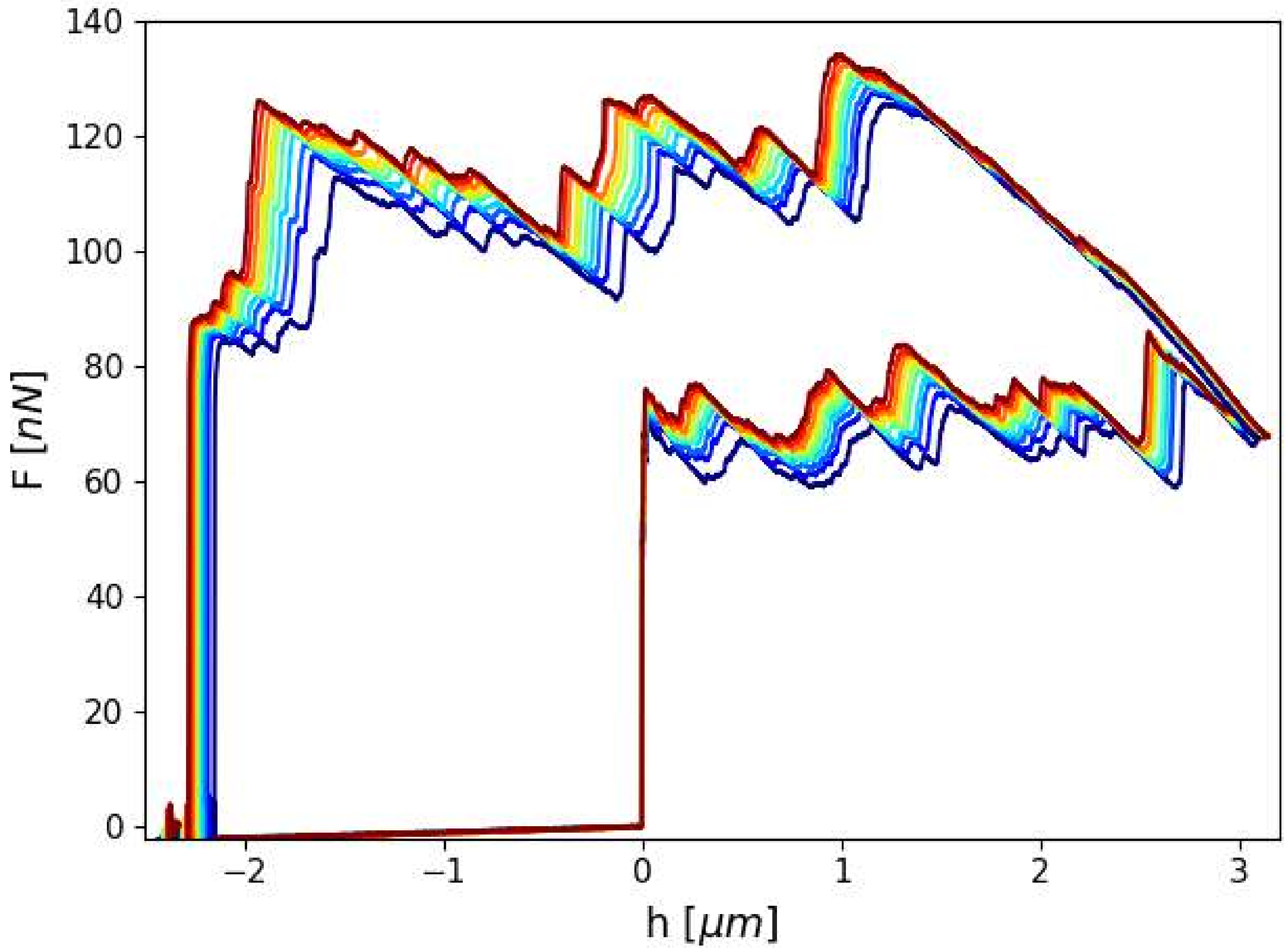
Aramrak et al. Soft Matt 2021

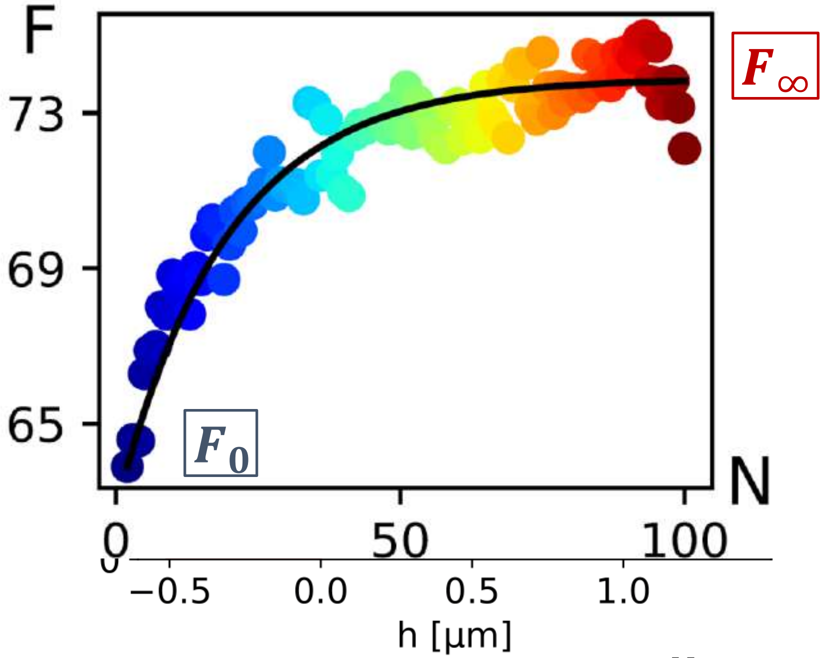
➢ **Chemical contamination by airborne molecules**



Liu *et al. Nature Mat* 2013

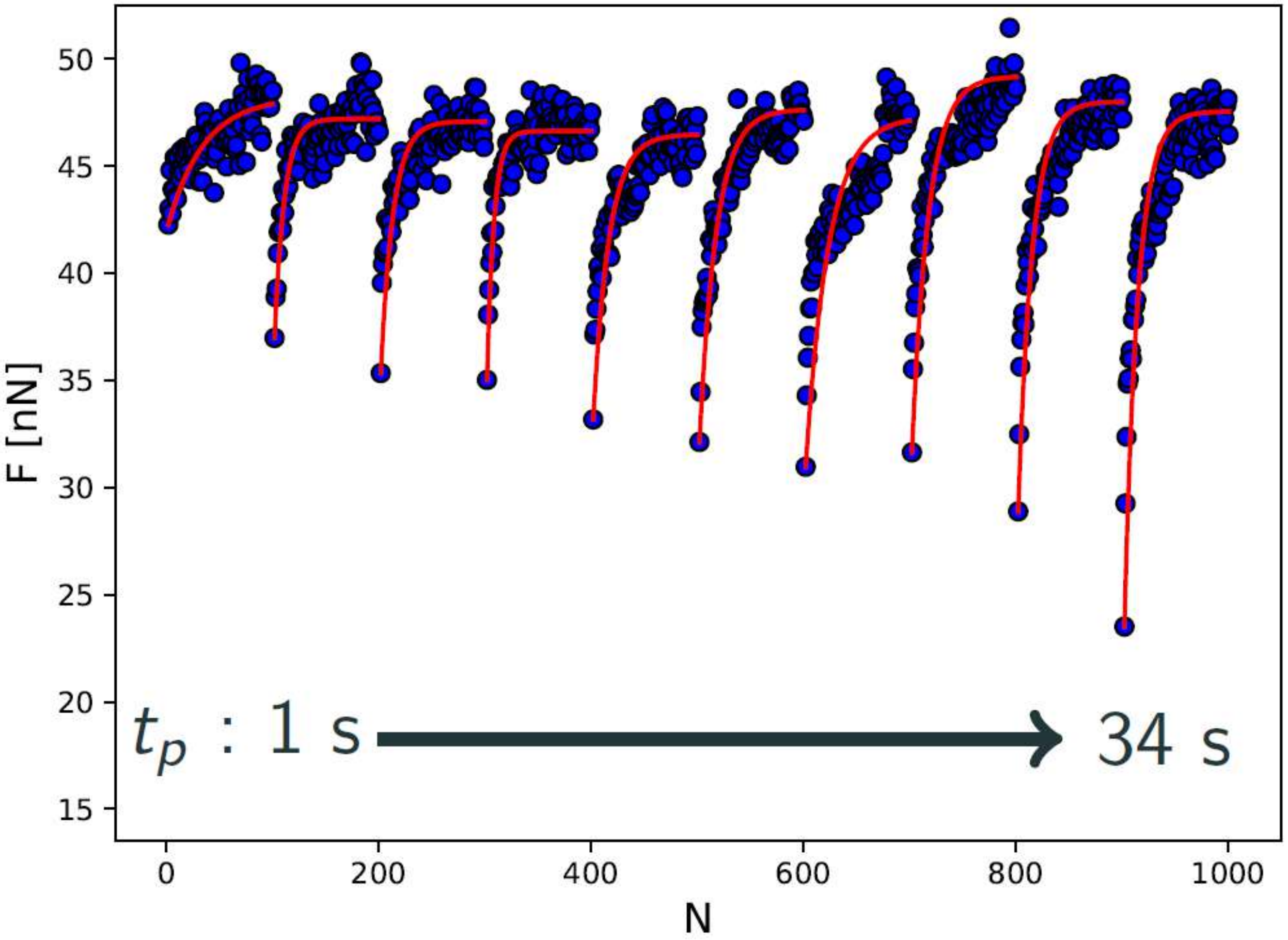
Wetting and adsorption: contamination and cleaning





$$F = F_0 + (F_\infty - F_0)\left(1 - e^{-\frac{N}{N^*}}\right)$$

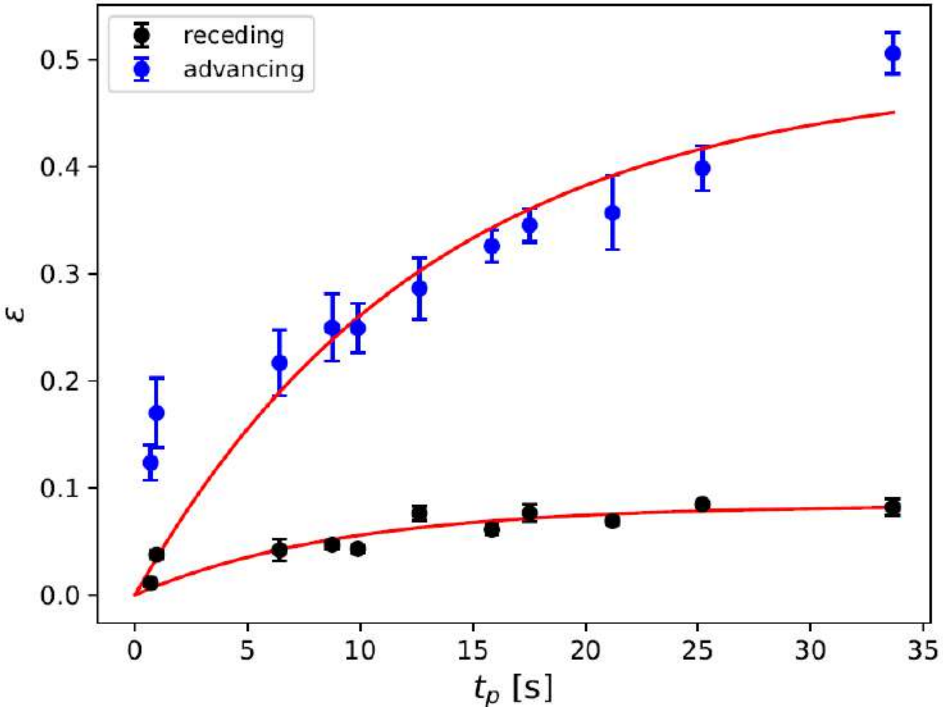
Wetting and adsorption: contamination and cleaning



$$F = F_0 + (F_\infty - F_0)\left(1 - e^{-N/N^*}\right)$$

Desorption

$$\epsilon = \frac{F_\infty - F_0}{F_\infty}$$

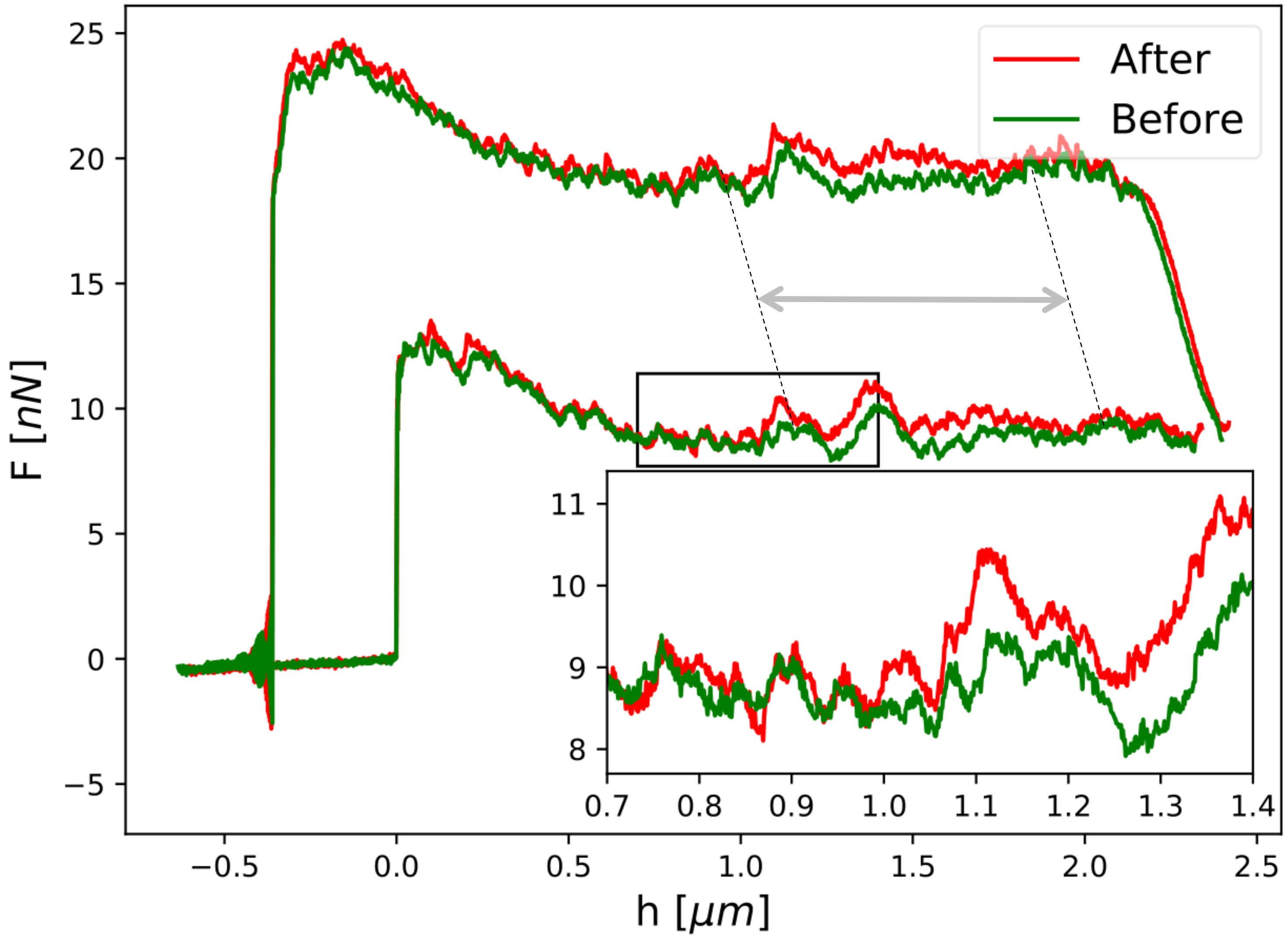


$$\epsilon = \epsilon_{max}\left(1 - e^{-t/\tau}\right)$$

Adsorption

Wetting and adsorption: contamination and cleaning

Franiatte *et al.* *PRL* 2021
Langmuir 2022



- Force curve until h = 2.5 μm
- **1000 cycles between h = 1 μm and 2 μm**
- Force curve until h = 2.5 μm

→ **Desorption at the contact line**