



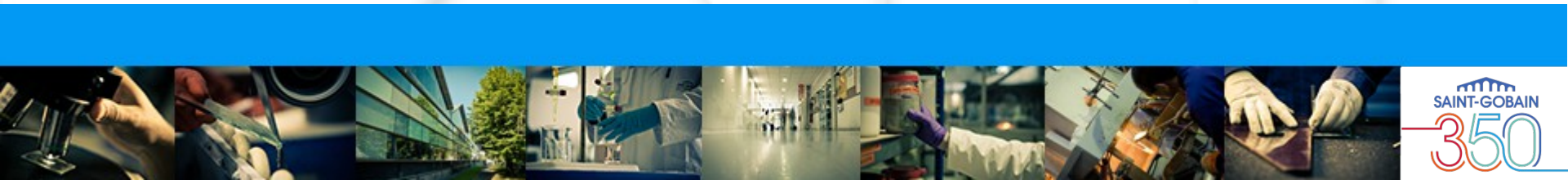
Démouillage sur surfaces hétérogènes - comment relier approche locale et réponse macroscopique ?

A. Gauthier, E. Contraire, M. Rivetti, P. Hayoun, J. Teisseire

Surface du Verre et Interfaces, CNRS/Saint-Gobain

*and E. Verneuil, F. Lequeux and E. Barthel**

SIMM ESPCI



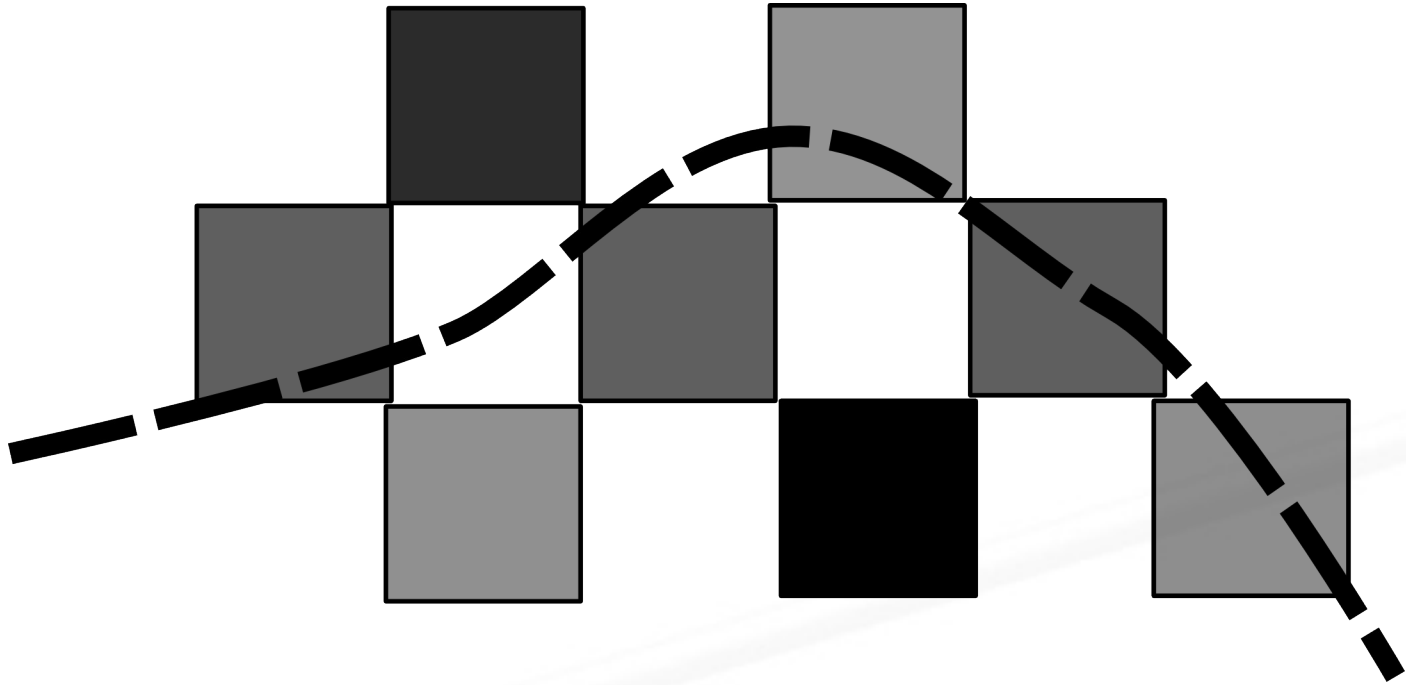
Hydrophobic surfaces



standard glass
without coating

SGS AQUACONTROL[®]
hydrophobic coated





Pomeau JCIS 1985

III. *An Essay on the Cohesion of Fluids.* By Thomas Young,
M. D. For. Sec. R.S.

Young's Young's equation

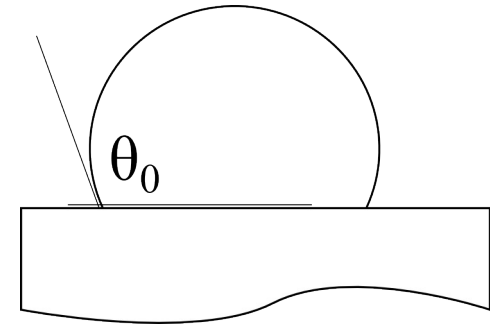
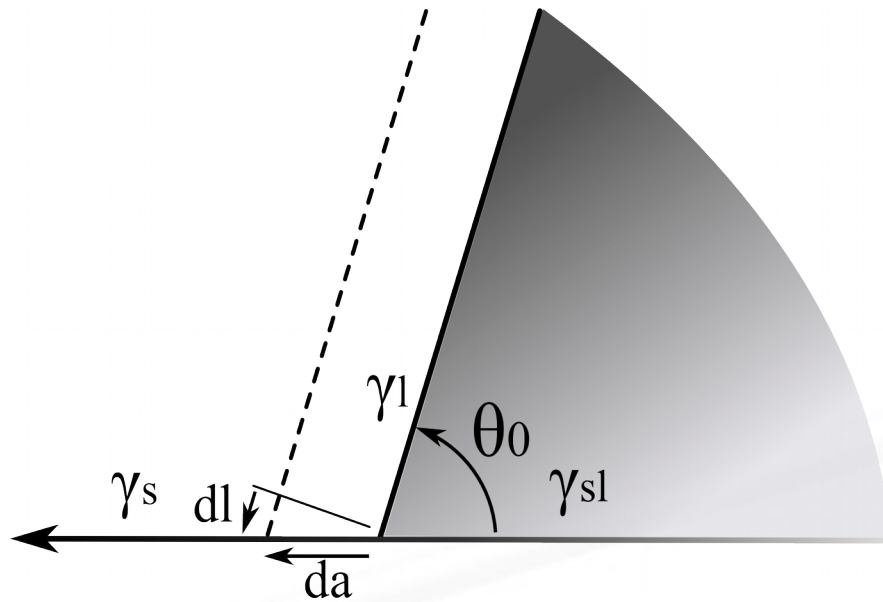
Read December 20, 1804.

I. *General Principles.*

IT has already been asserted, by Mr. MONGE and others, that the phenomena of capillary attraction of the surface of a fluid, employed, and that the surface of a fluid, into curves of the natural curvature, the results of a unit pressure of a fluid, €

Now, supposing the angle of the fluid to be obtuse, the whole superficial cohesion of the fluid being represented by the radius, the part which acts in the direction of the surface of the solid will be proportional to the cosine of the inclination; and this force, added to the force of the solid, will be equal to the force of the common surface of the solid and fluid, or to the differences of their forces; consequently, the cosine added to twice the force of the solid, will be equal to the whole force of the fluid, or to the radius: hence the force of the solid is represented by half the difference between the cosine and the radius, or by half the versed sine; or, if the force of the fluid be represented by the diameter, the whole versed sine will indicate the force of the solid. And the same result follows when the angle of the fluid is acute. Hence we may infer, that if the solid have half

Contact angle – Young's equation



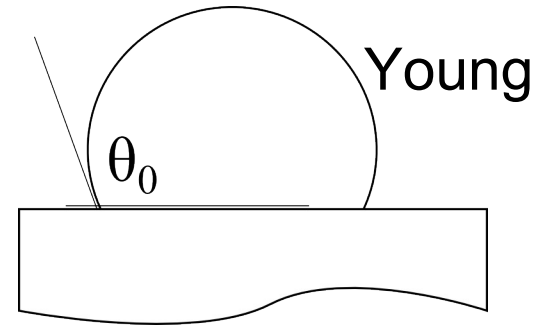
$$\gamma_l dl + (\gamma_{sl} - \gamma_s) da = 0$$

$$da \cos \theta_0 = dl$$

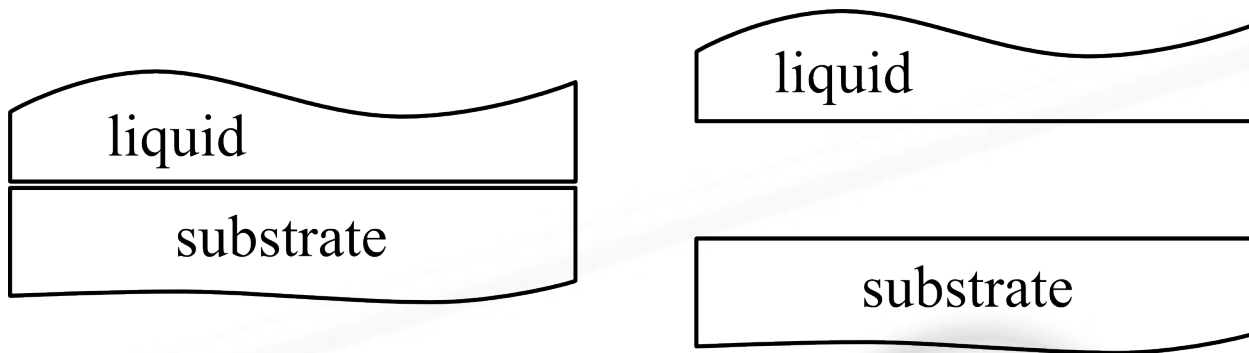
$$\gamma_s - \gamma_{sl} = \gamma_l \cos \theta_0$$

Contact angle and adhesion

Young-Dupré equation



$$\gamma_s - \gamma_{sl} = \gamma_l \cos \theta_0$$



$$w_{eff} = \gamma_s + \gamma_l - \gamma_{sl} = \gamma_l (1 + \cos \theta_0)$$

CONTACT ANGLES

By A. B. D. CASSIE

Received 27th January, 1948

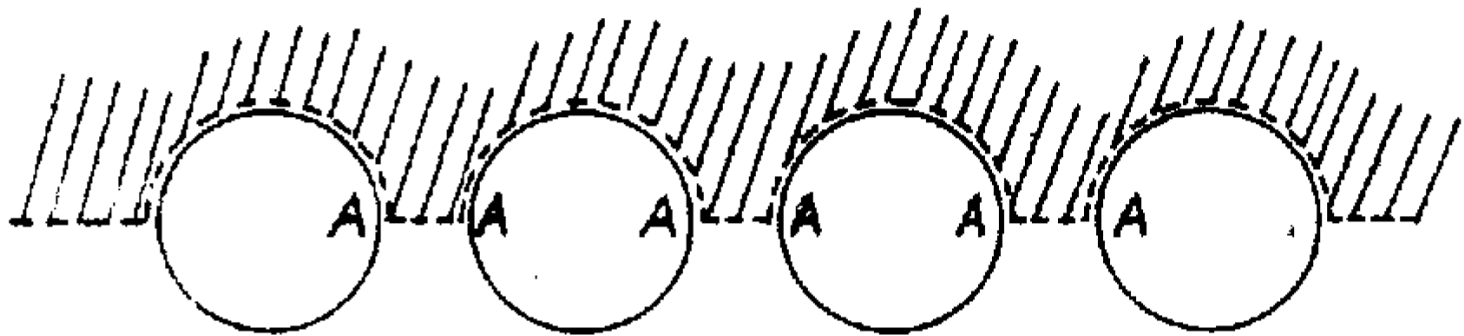
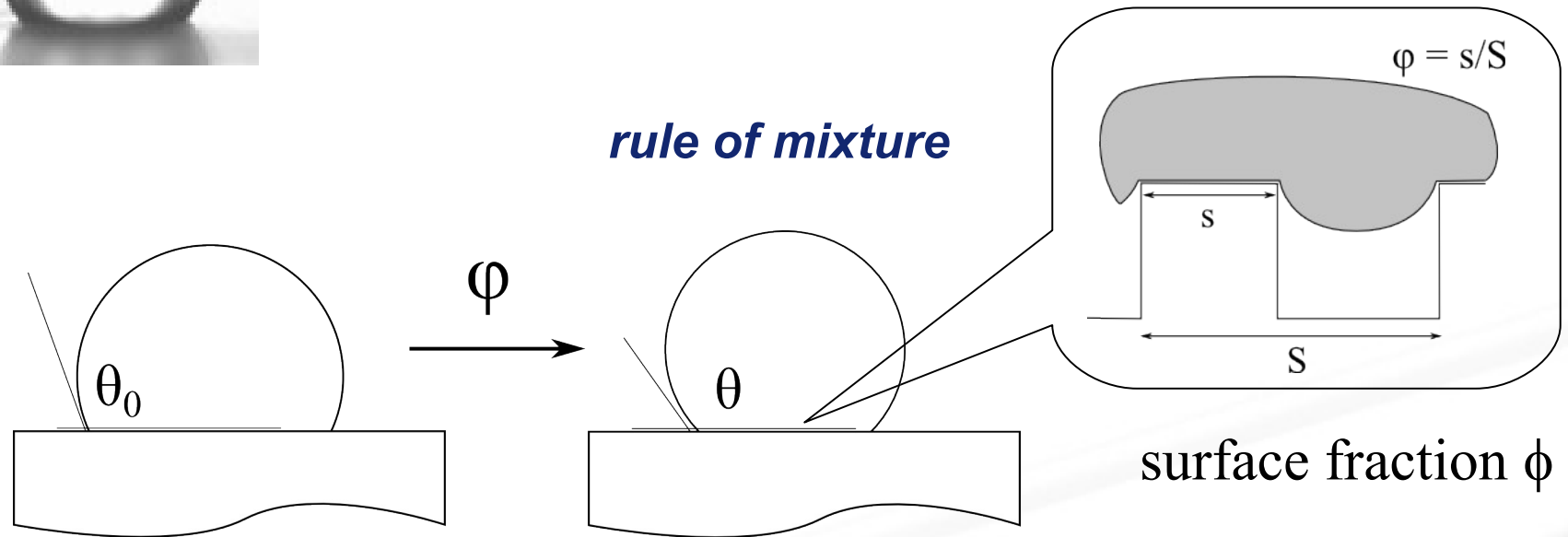
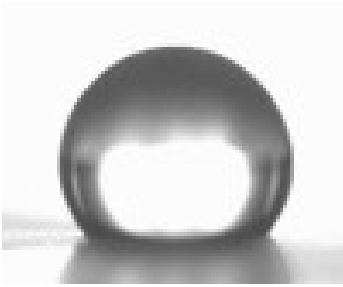


FIG. 1.—Water on cylinders.

Cassie and Baxter, Trans. Farad. Soc. 1944

Superhydrophobic surfaces

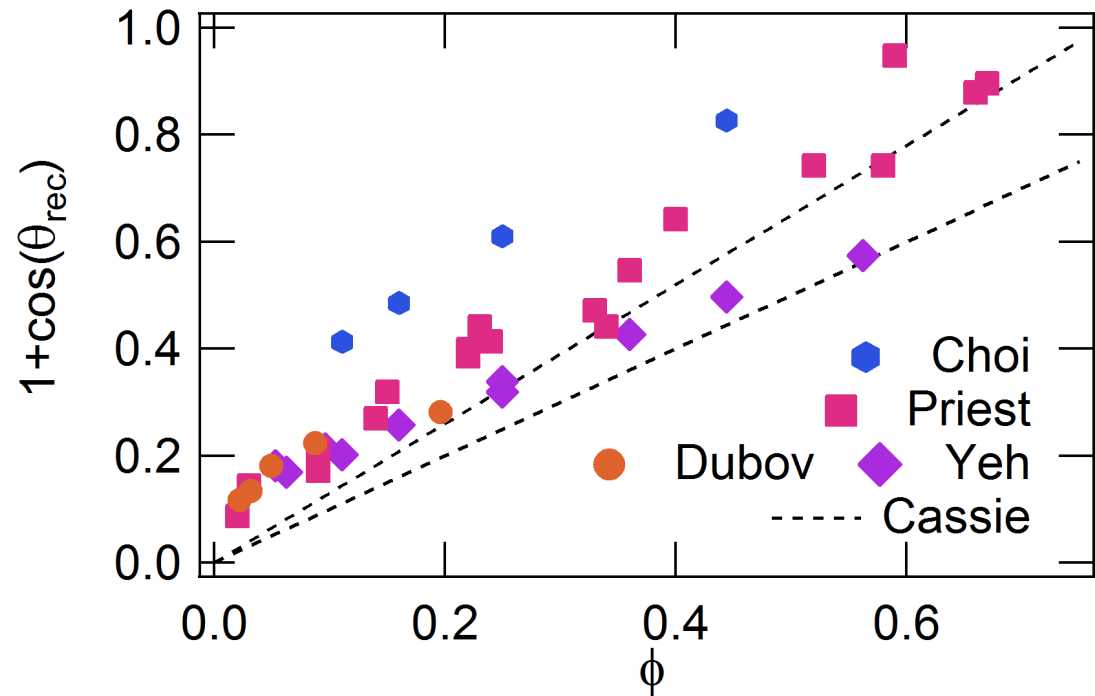
Cassie model



$$\frac{w}{\gamma l} = 1 + \cos \theta = \phi(1 + \cos \theta_0)$$

Cassie and Baxter, Trans. Farad. Soc. 1944
Bico et al. EPL 1998

Does scale with surface fraction **but**
not really proportional



Yeh et al Langmuir 2008

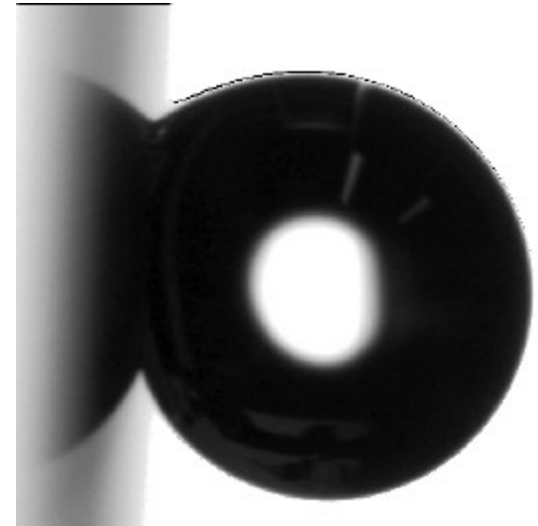
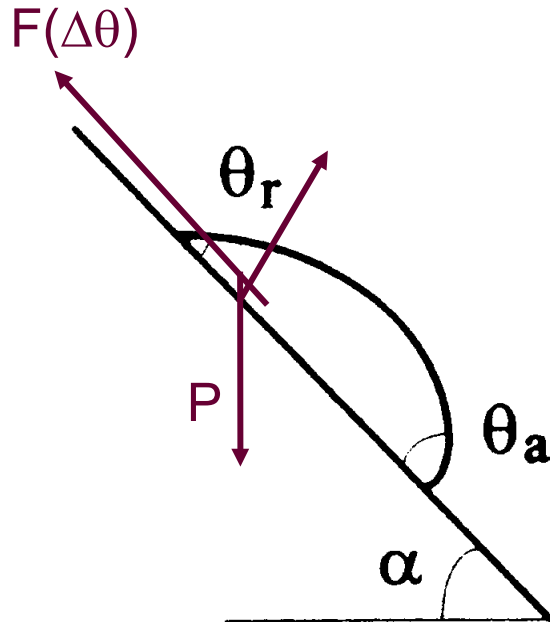
Priest et al Langmuir 2009

Choi et al JCIS 2009

Dubov et al EPL 2011

see Erbil Surf Sci Rep 2014 for a review

Contact angle hysteresis



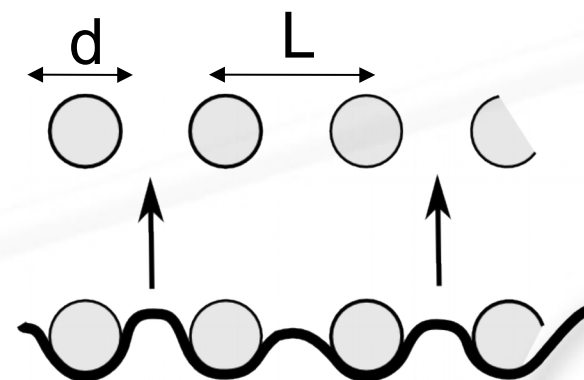
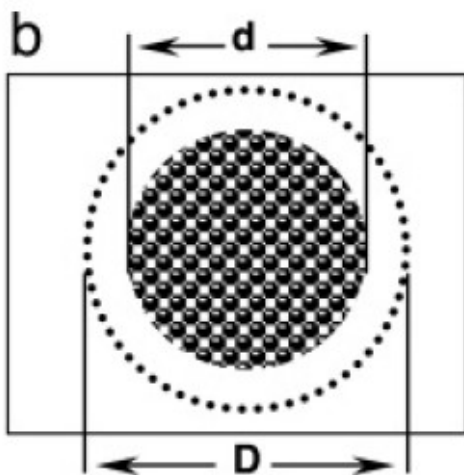
*Dorrer and Rhe,
Beilstein J. Nanotechnol. 2011*

$$\pi r \gamma (\cos \theta_r - \cos \theta_a) < \rho g V \sin \alpha$$

Qur et al. Langmuir 1998

How Wenzel and Cassie Were Wrong

Lichao Gao and Thomas J. McCarthy*



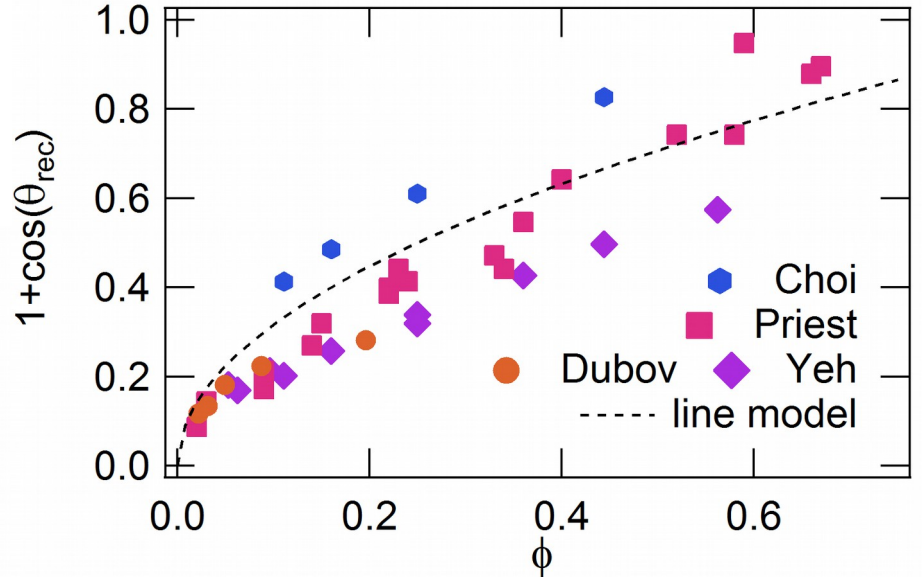
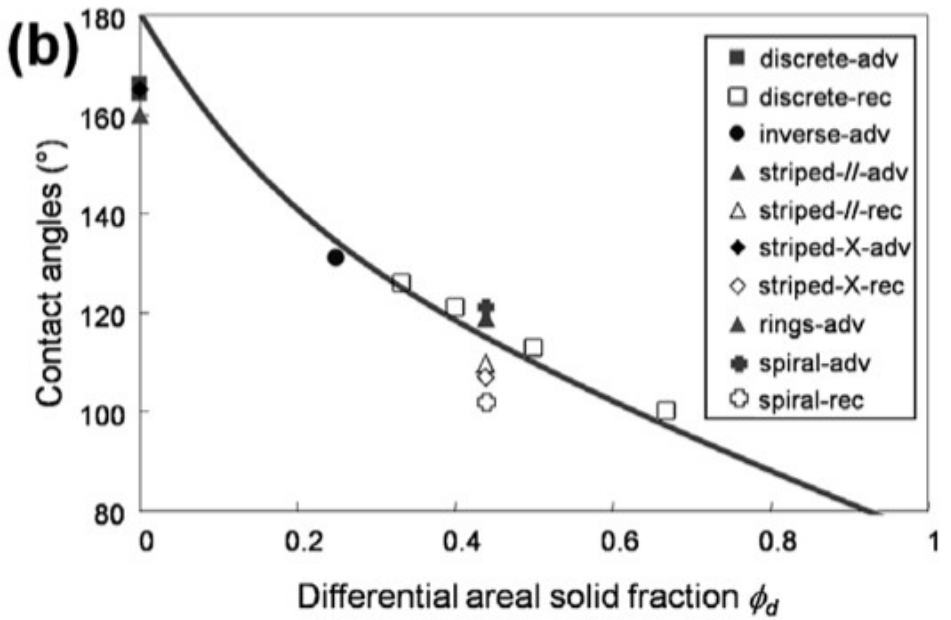
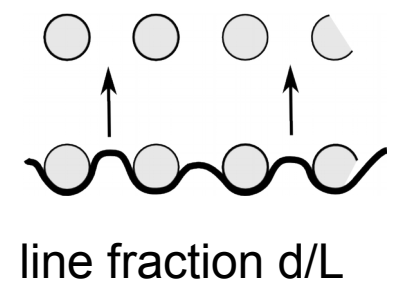
line fraction $\phi_d = d/L$

Gao and McCarthy Langmuir 2007
Extrand Langmuir 2004

Choi et al. JCIS 2009

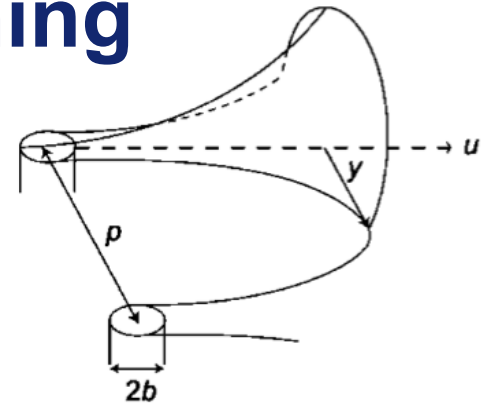
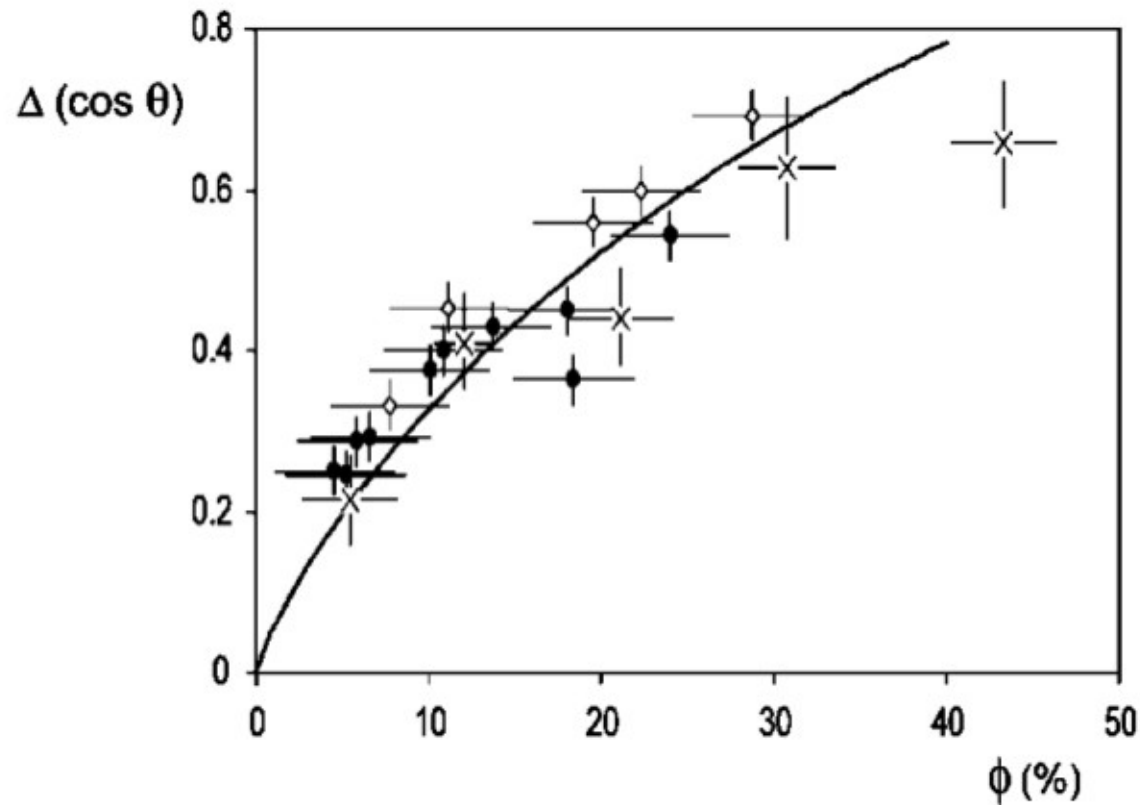
Look at the line...

Line model – Results



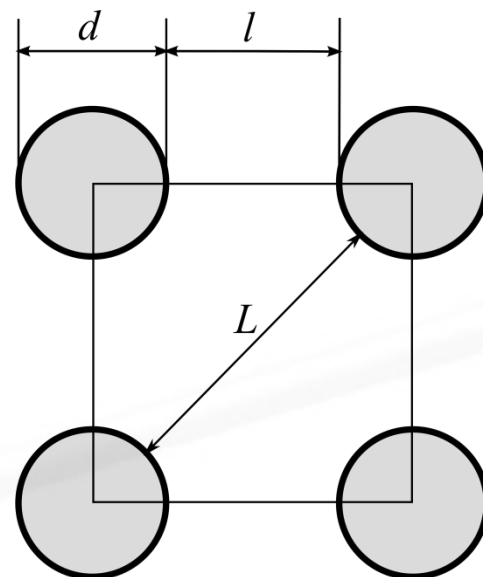
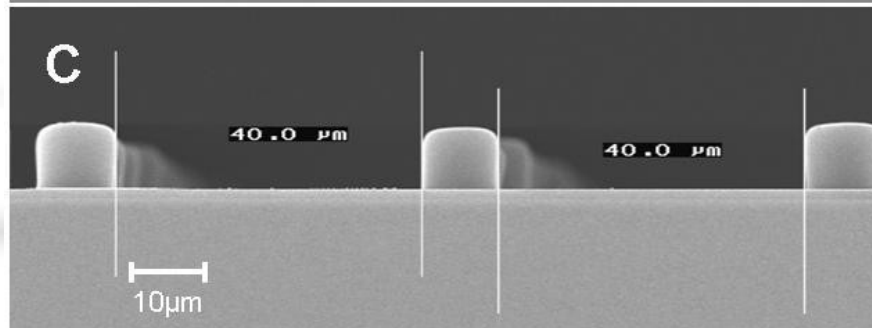
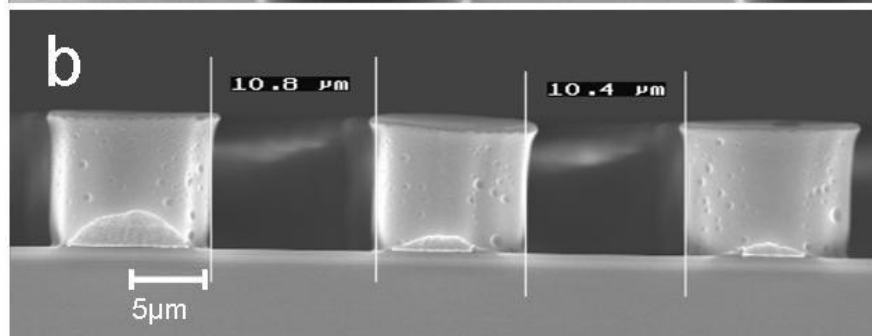
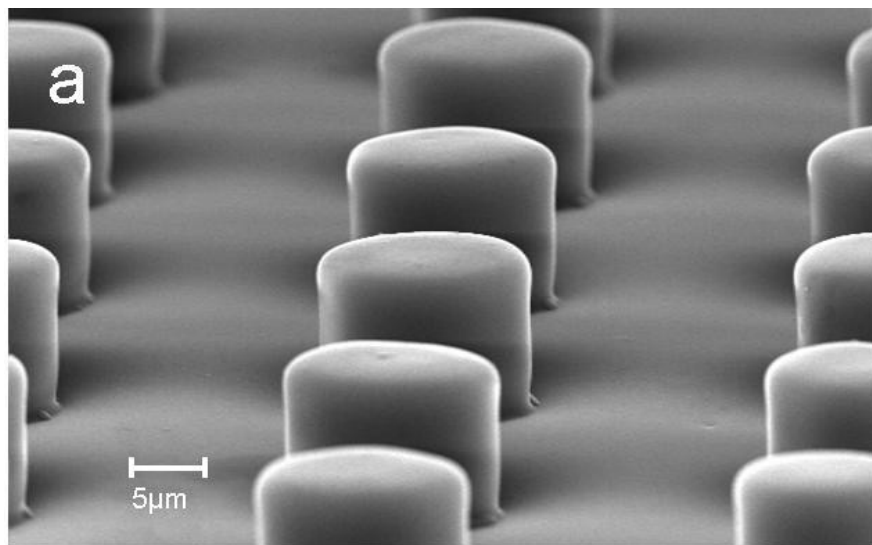
Choi et al. *JCIS* (2009)

Contact angle hysteresis – Pinning



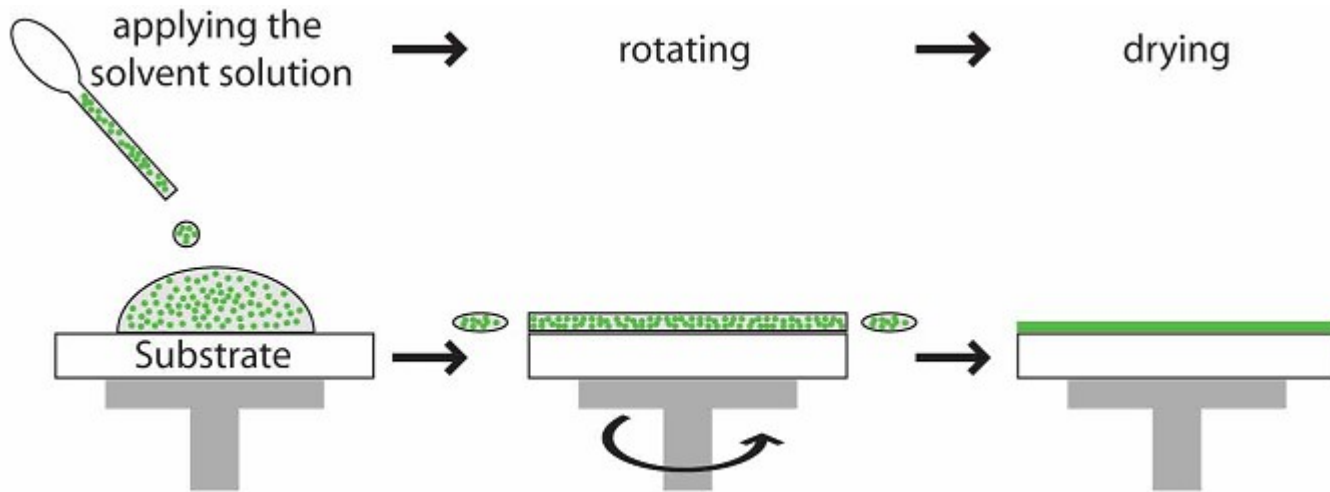
Joanny and de Gennes *J. Phys Chem* (1984)
Paterson and Fermigier *Phys. Fluids* 9 (1997) 2210
Reyssat and Quéré *J. Phys Chem B* (2009)

Imprinted surfaces

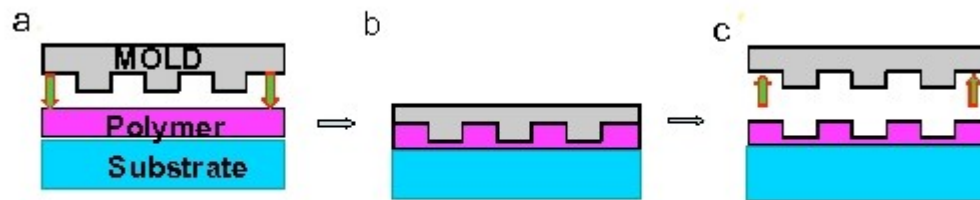


Film deposition

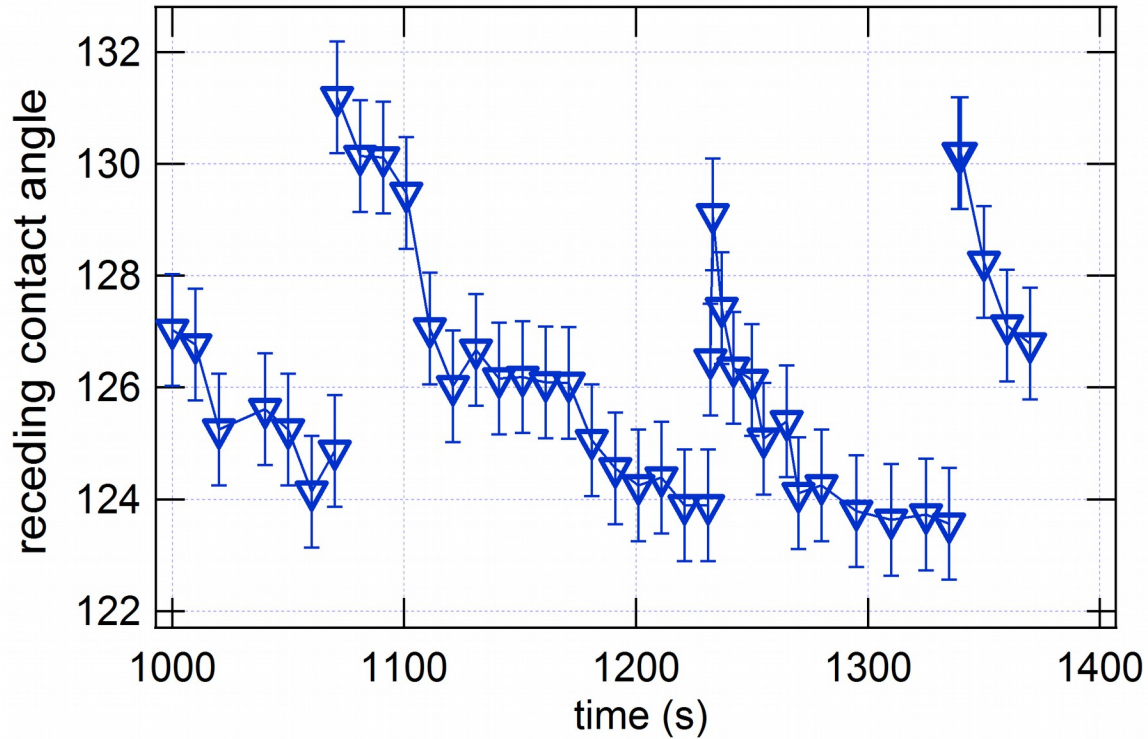
spin coating



Embossing



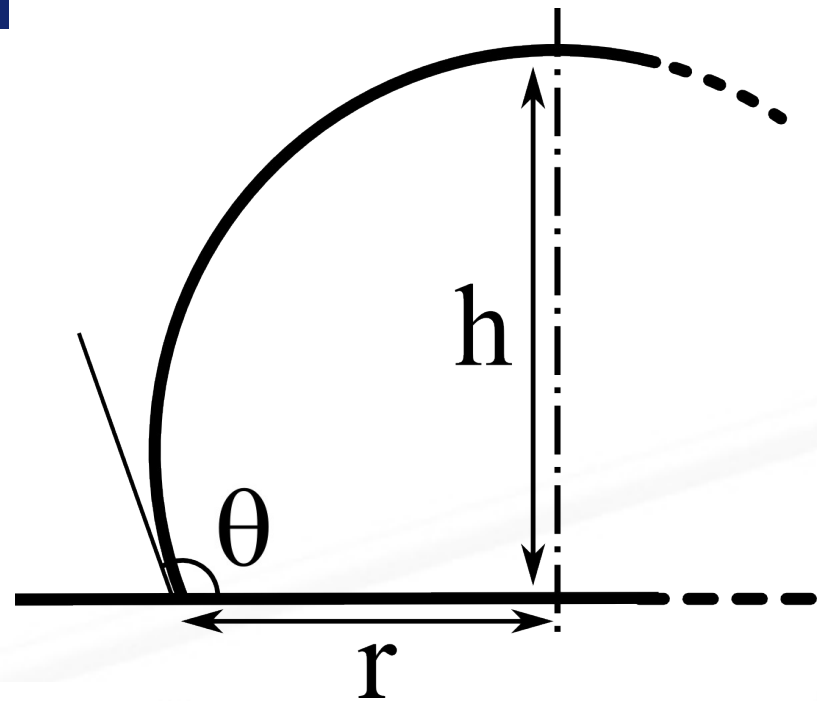
Receding contact angle square lattice



McHale et al. Langmuir (2005)

Gauthier et al. Langmuir 2014

Receding contact angle axisymmetric model

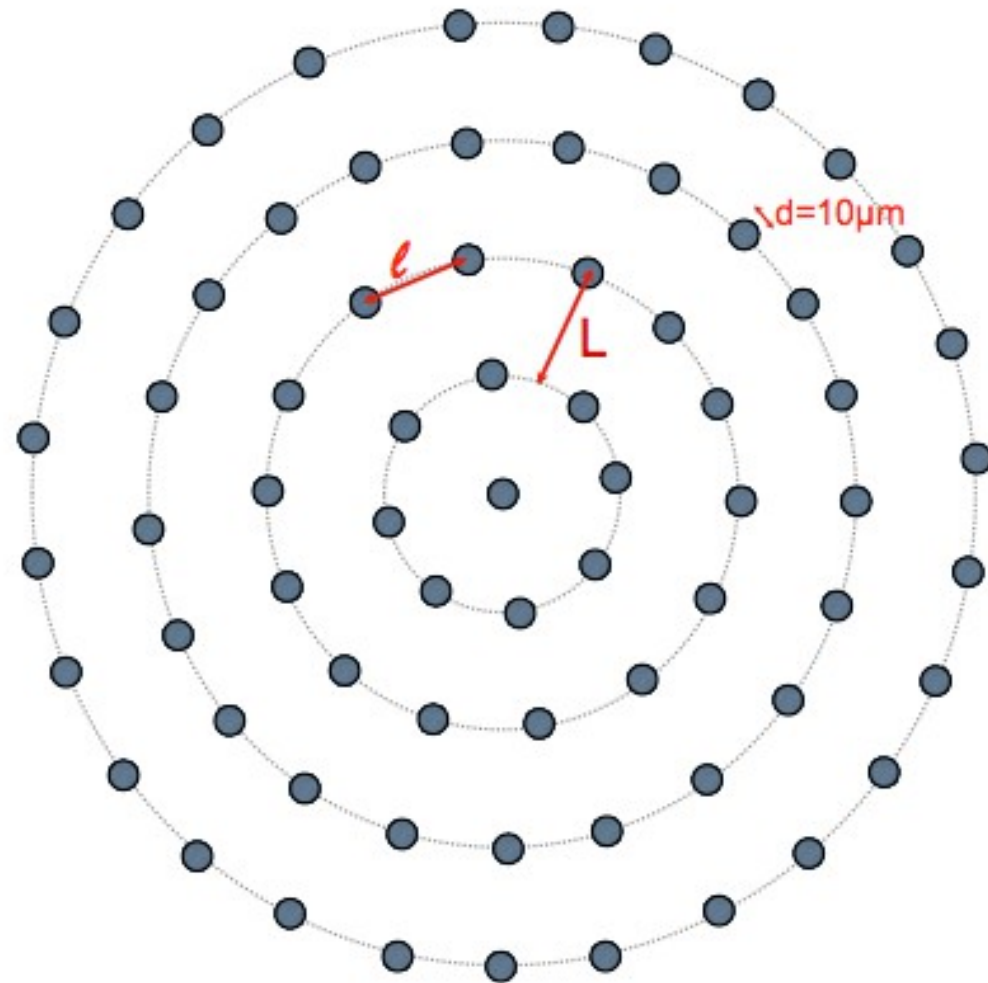


$$\delta\theta = \sin\theta(2 + \cos\theta)\frac{\delta r}{r}$$

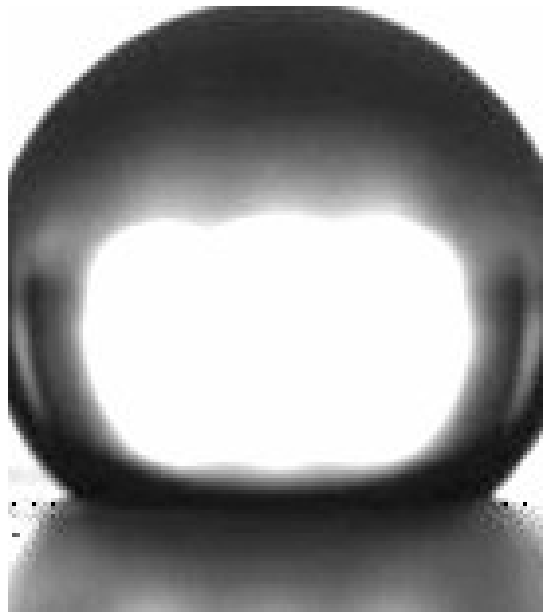
Shanahan Langmuir 1995

McHale et al. Langmuir 2005

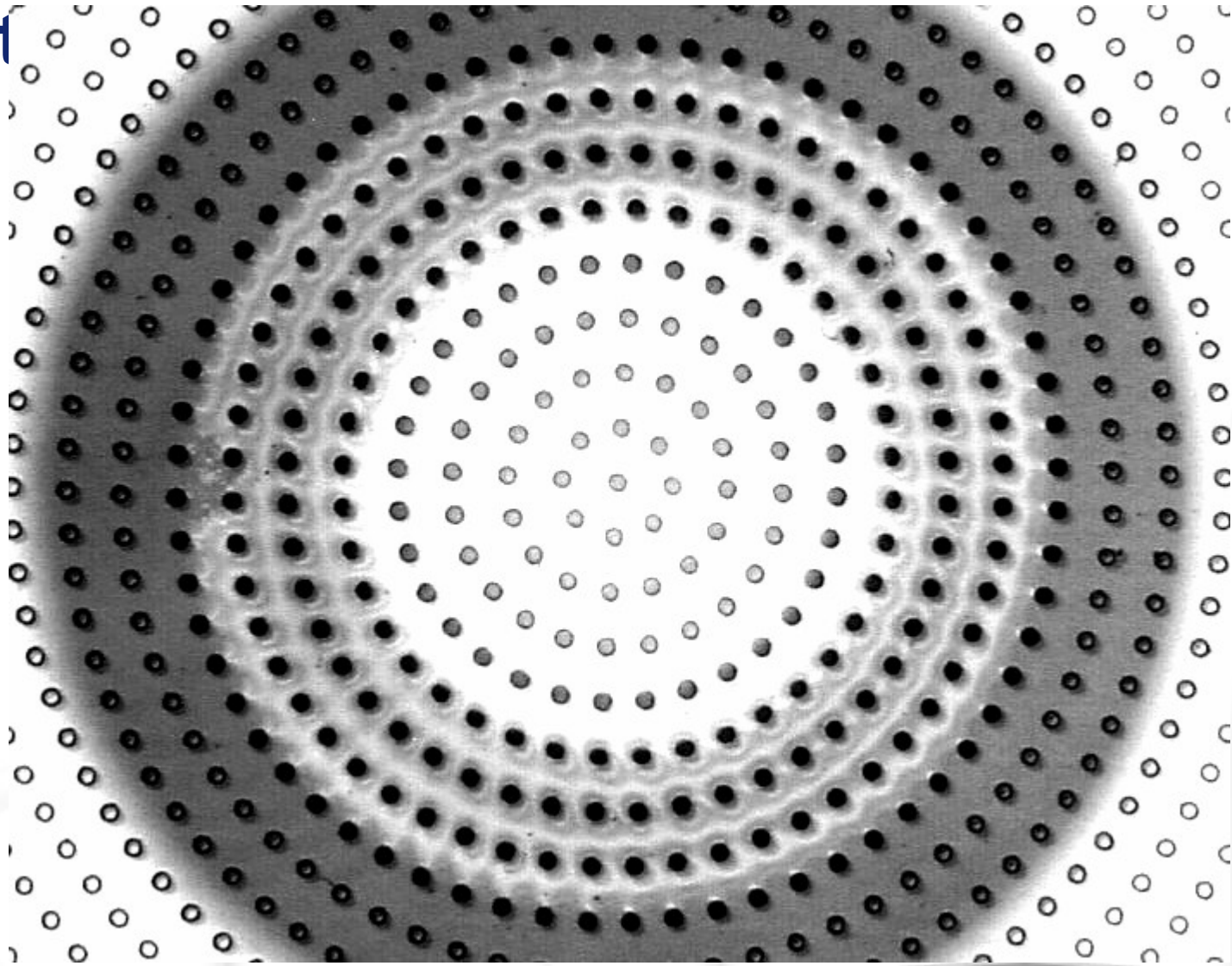
An axisymmetric texture



Evaporation on axisymmetric surface – side view

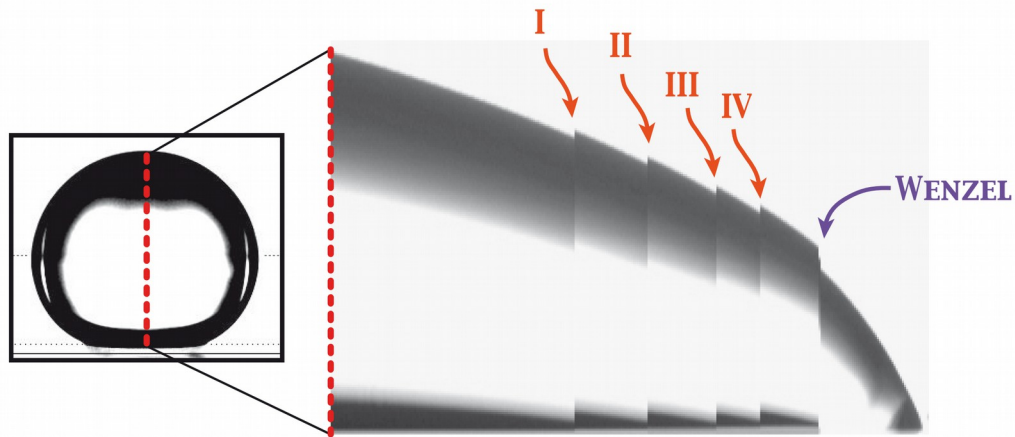
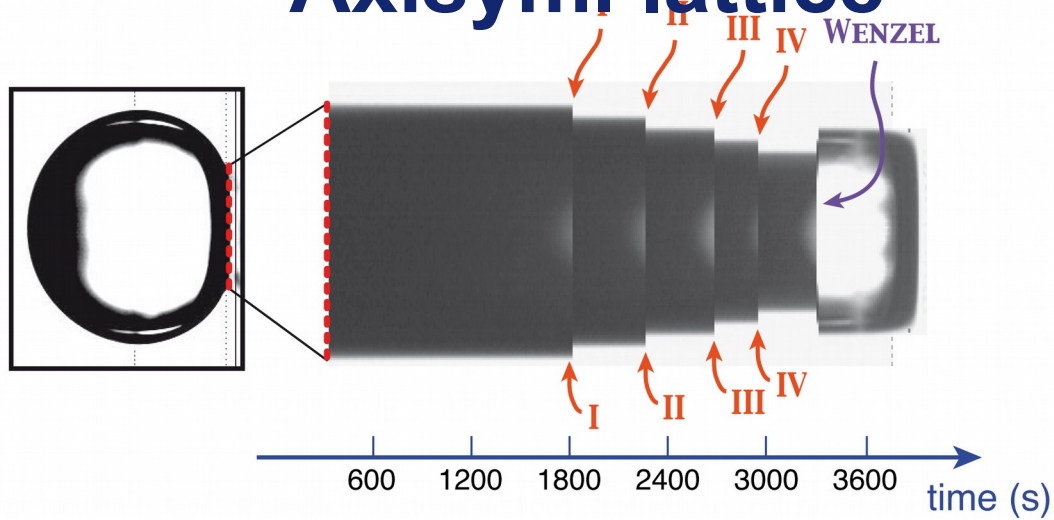


Evaporation on axisymmetric surface – both

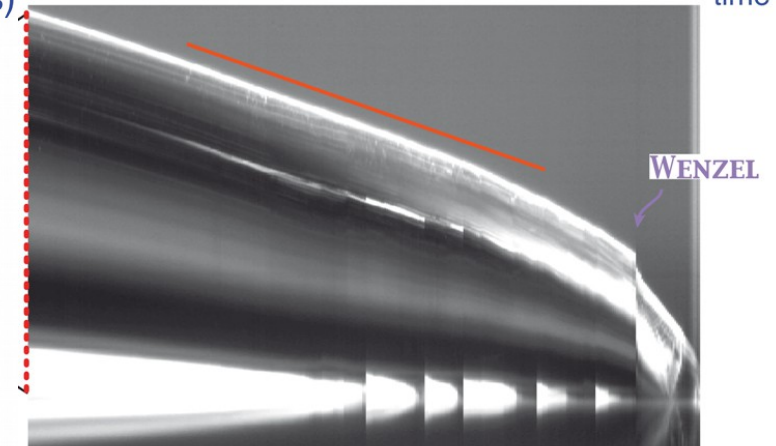
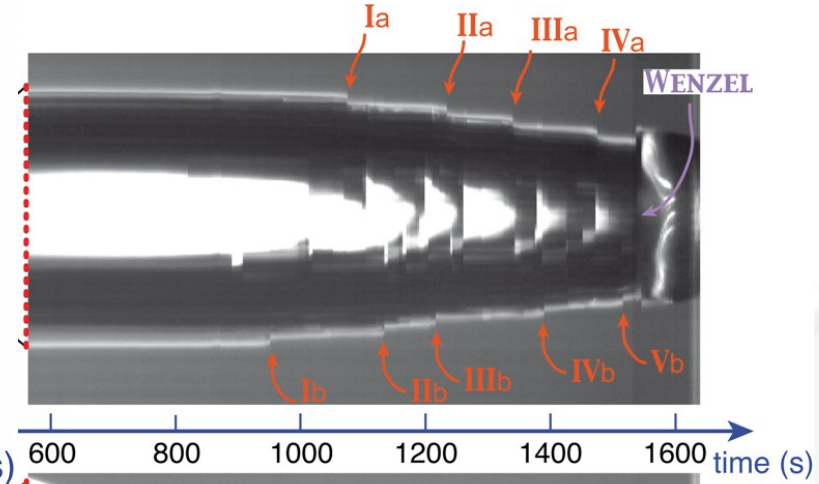


Drop shape

Axisym. lattice

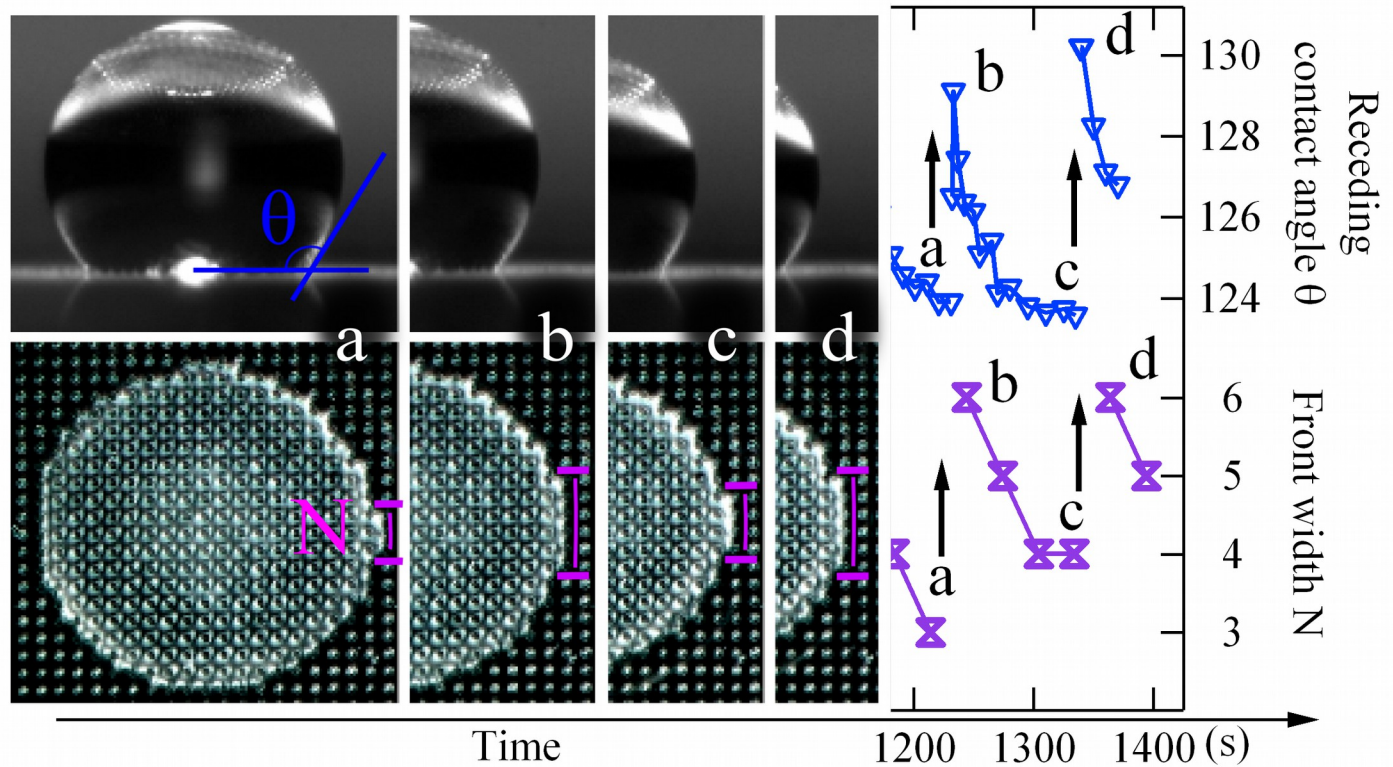


Square lattice



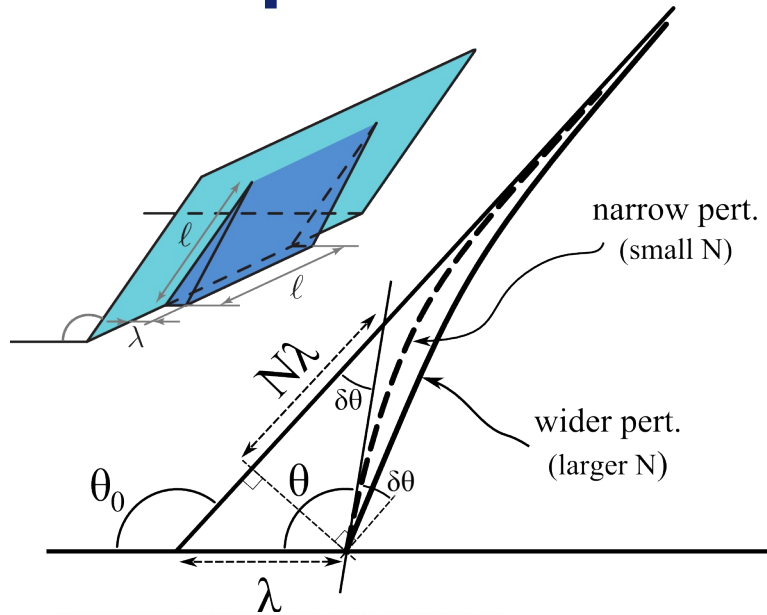
Gauthier et al. Langmuir 2014

Drop shape – square lattice

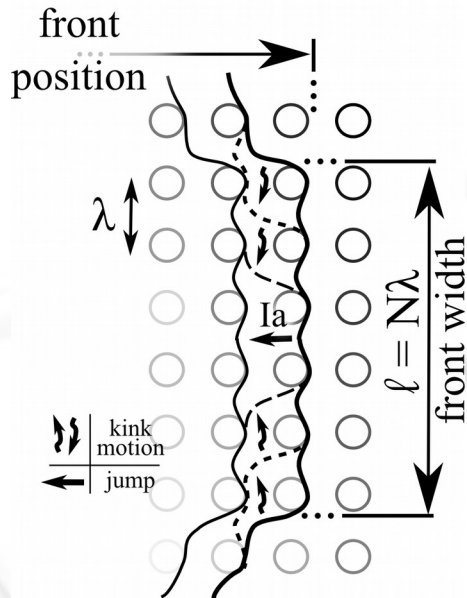


Gauthier et al. Langmuir 2014

Macroscopic contact angle – square lattice

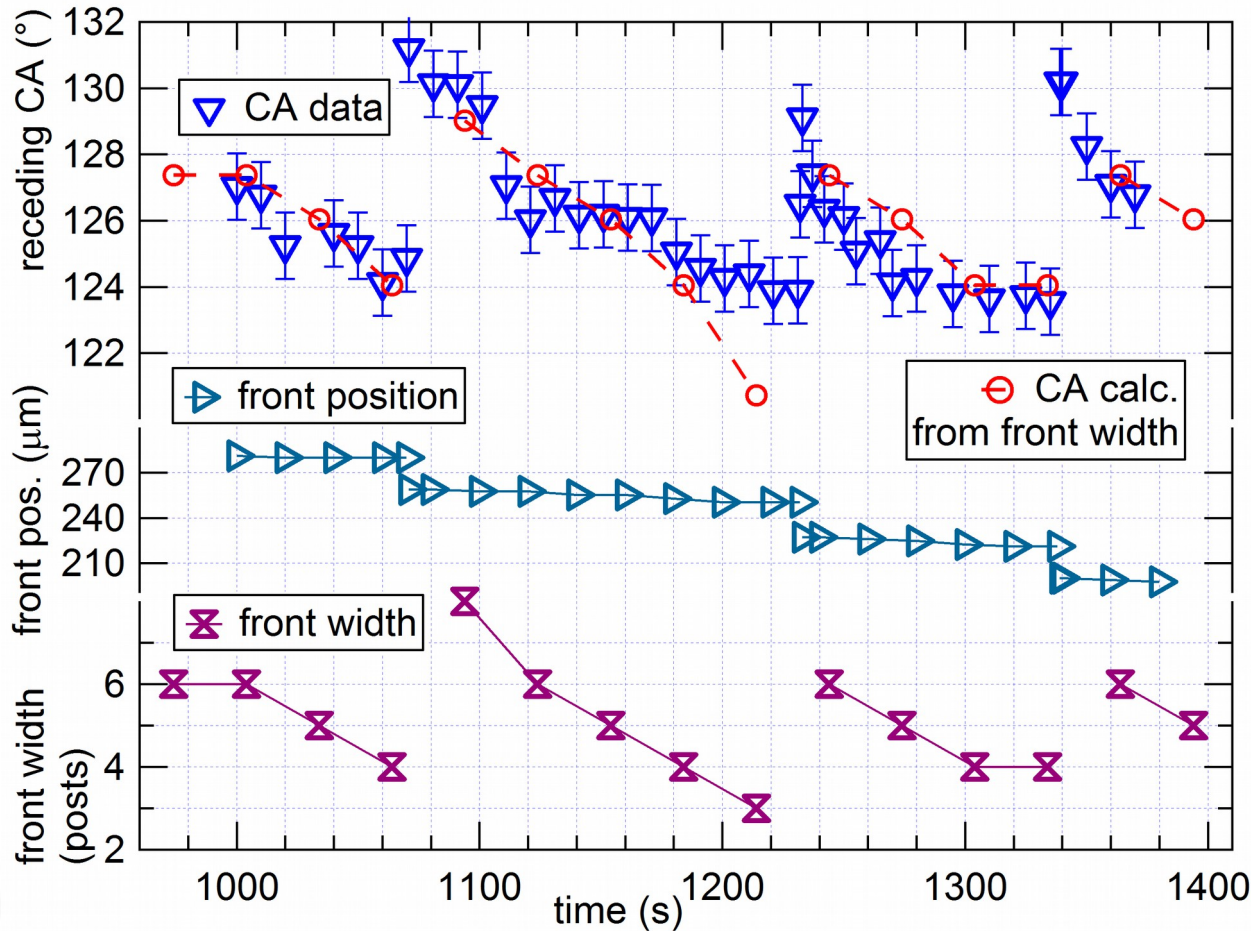


$$\theta = \theta_0 - \frac{\sin \theta_0}{N}$$



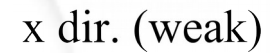
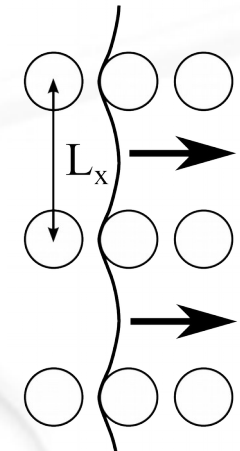
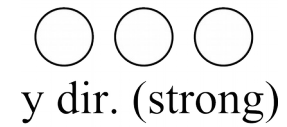
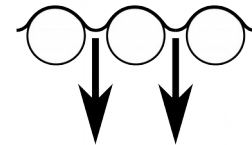
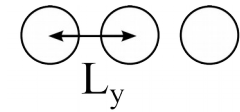
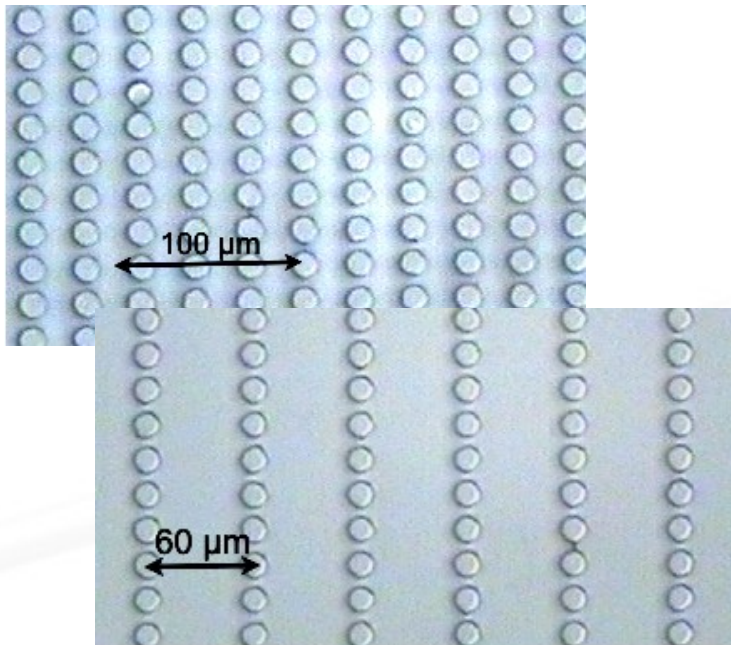
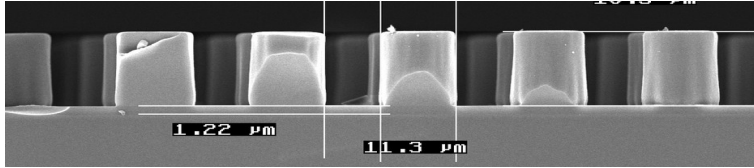
Gauthier et al. Langmuir 2014

Macroscopic contact angle – square lattice



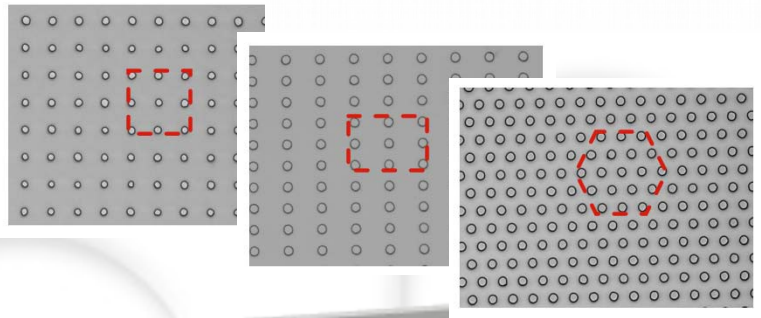
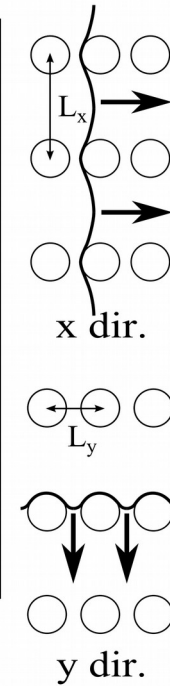
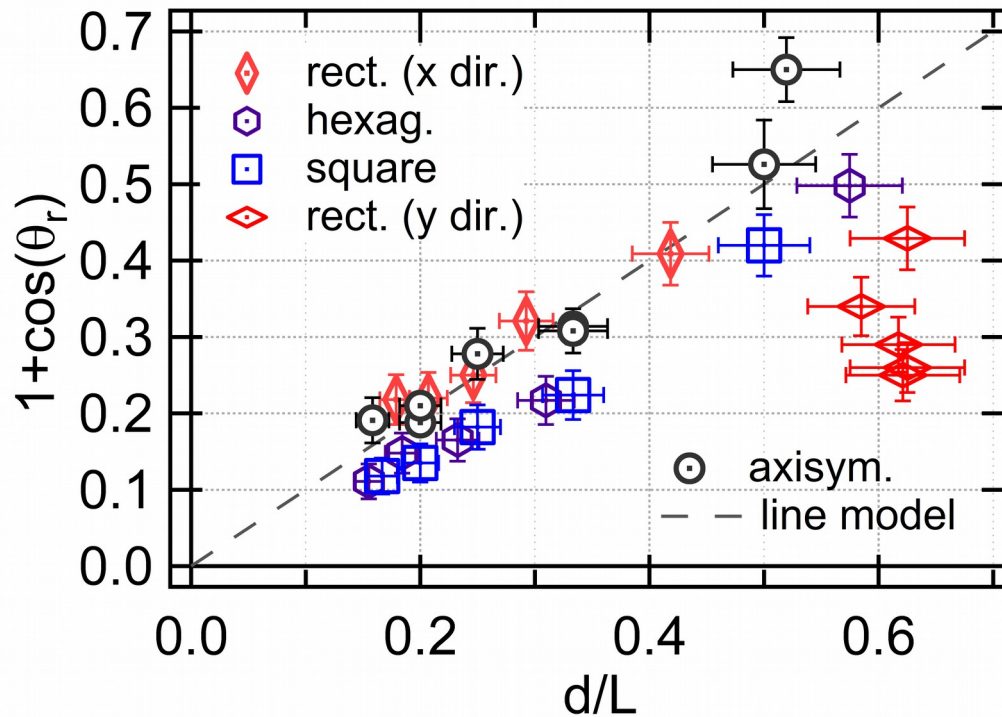
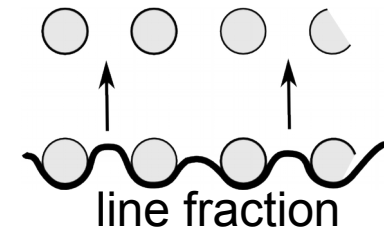
$$\theta = \theta_0 - \frac{\sin \theta_0}{N}$$

Rectangular arrays

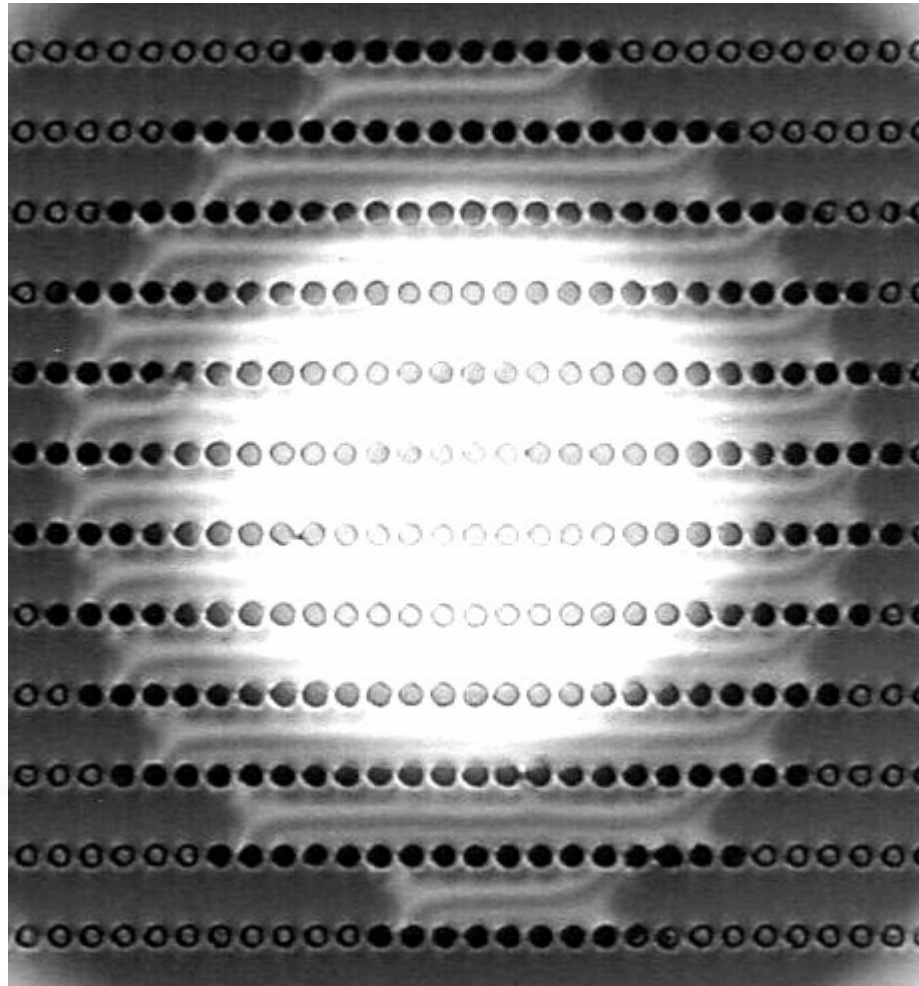
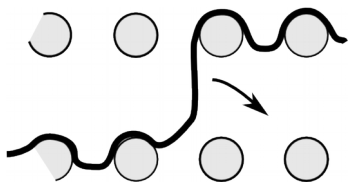


Receding contact angle

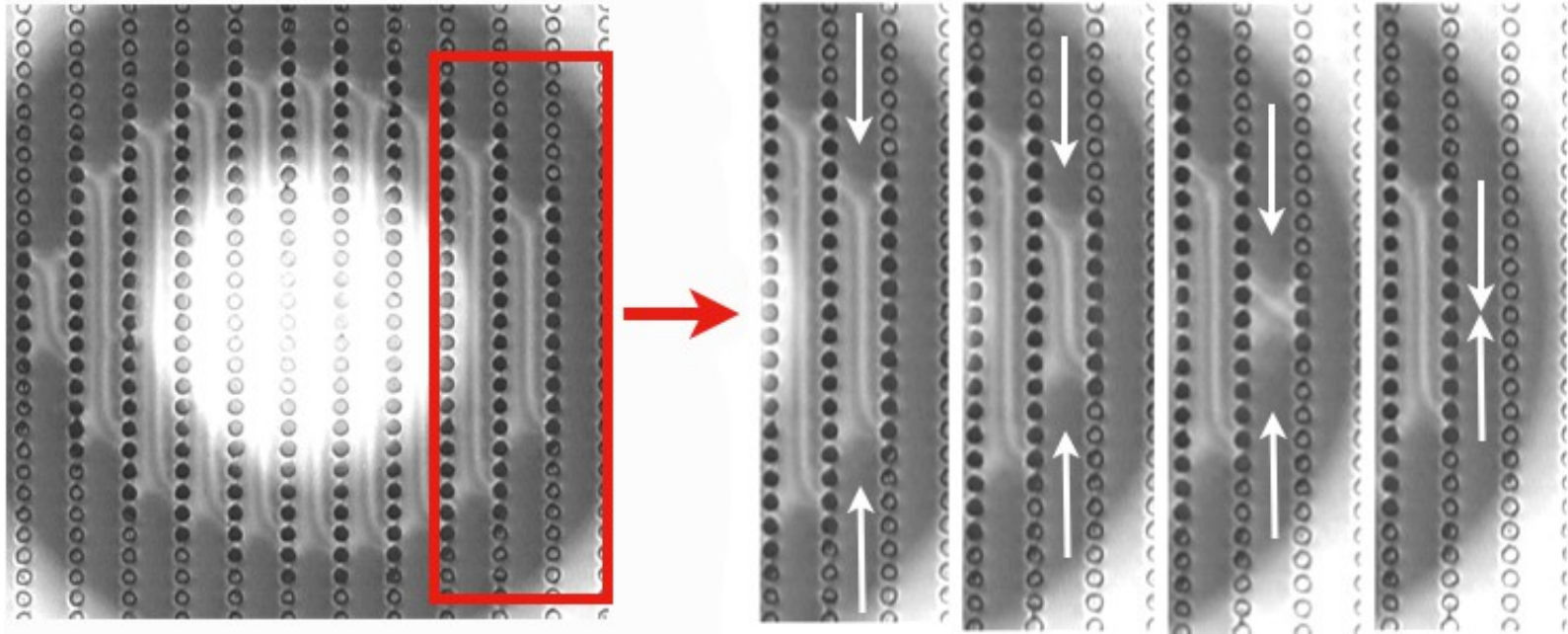
Impact of lattice



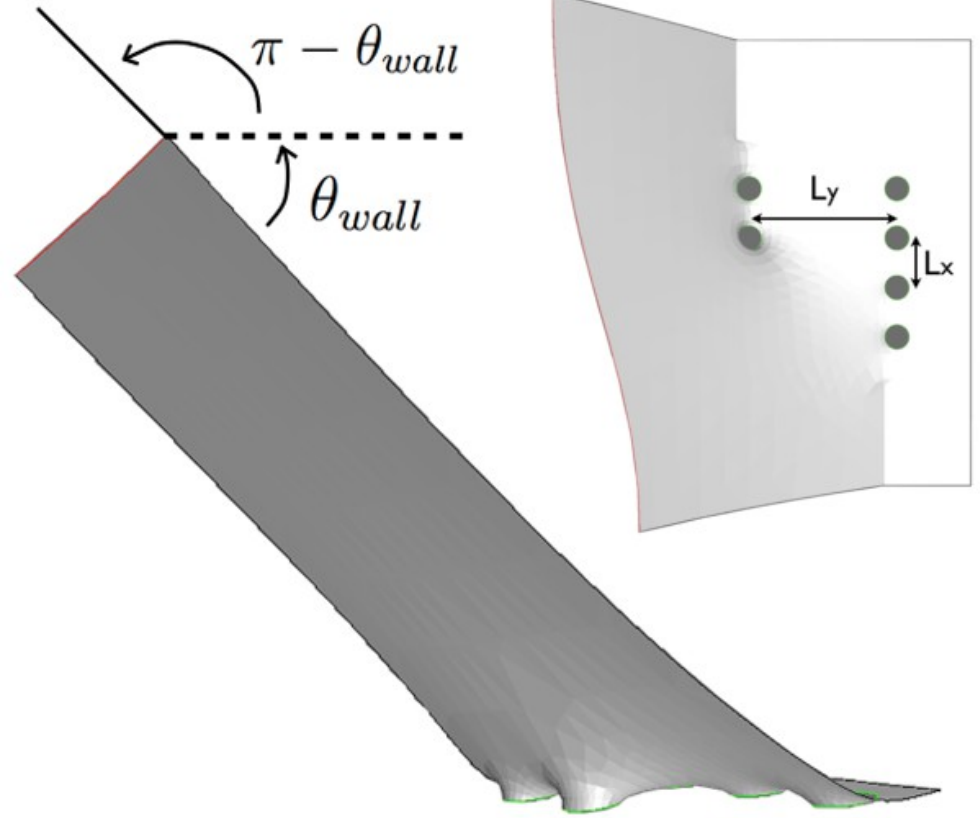
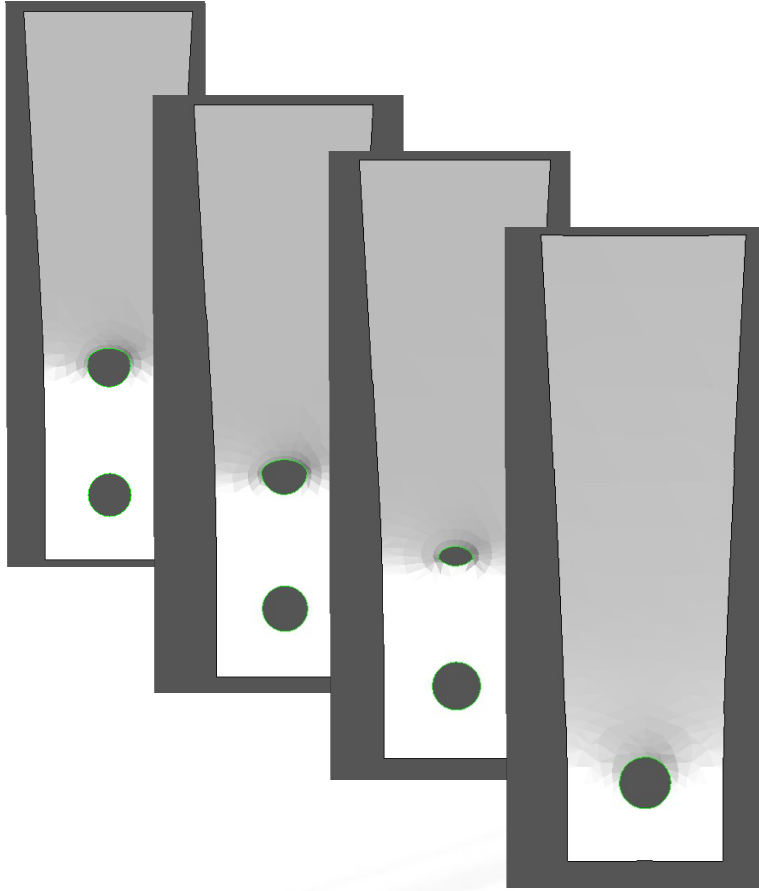
Rivetti et al. PRL 2015



Front Propagation Mechanism

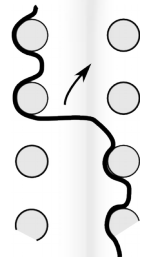


Numerical simulations

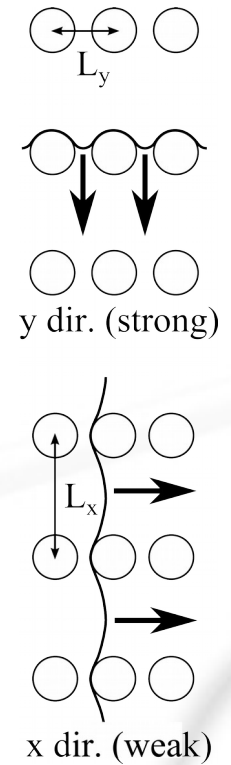
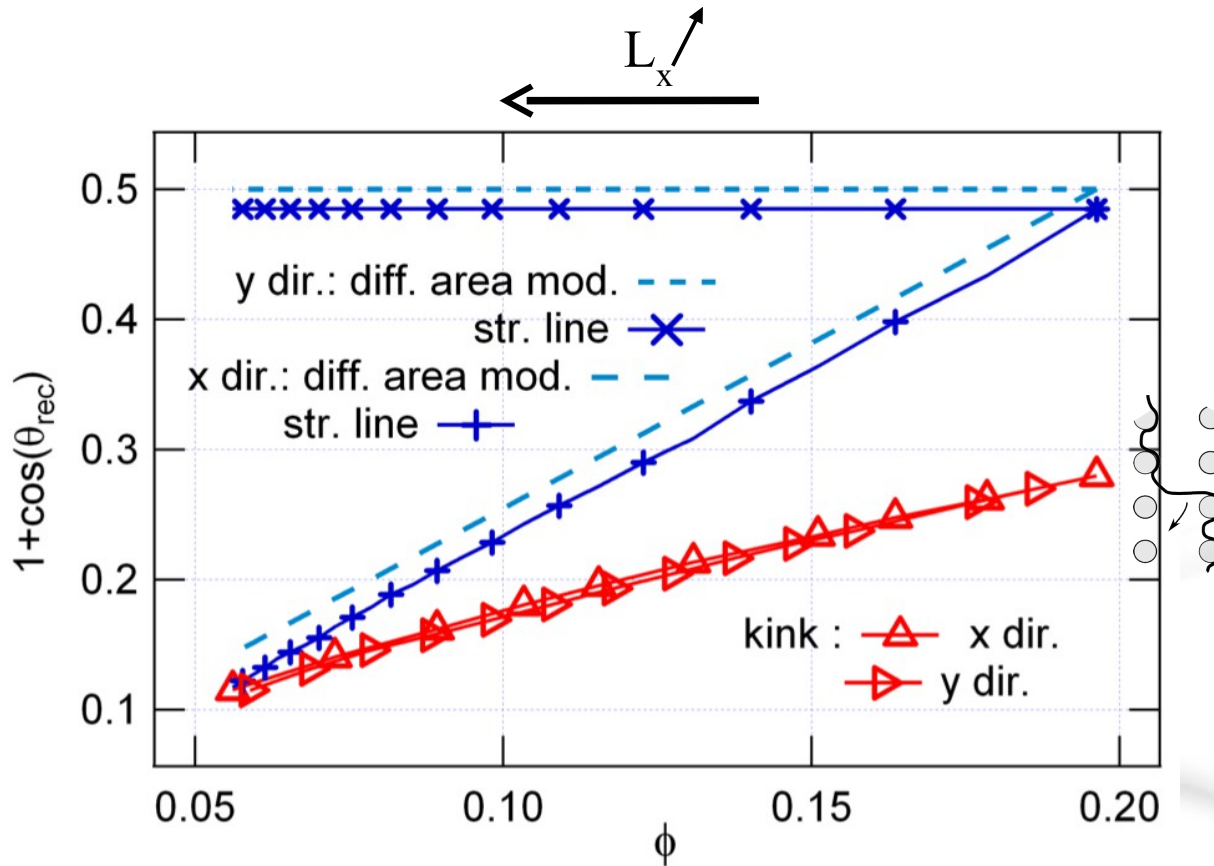


straight

kinked



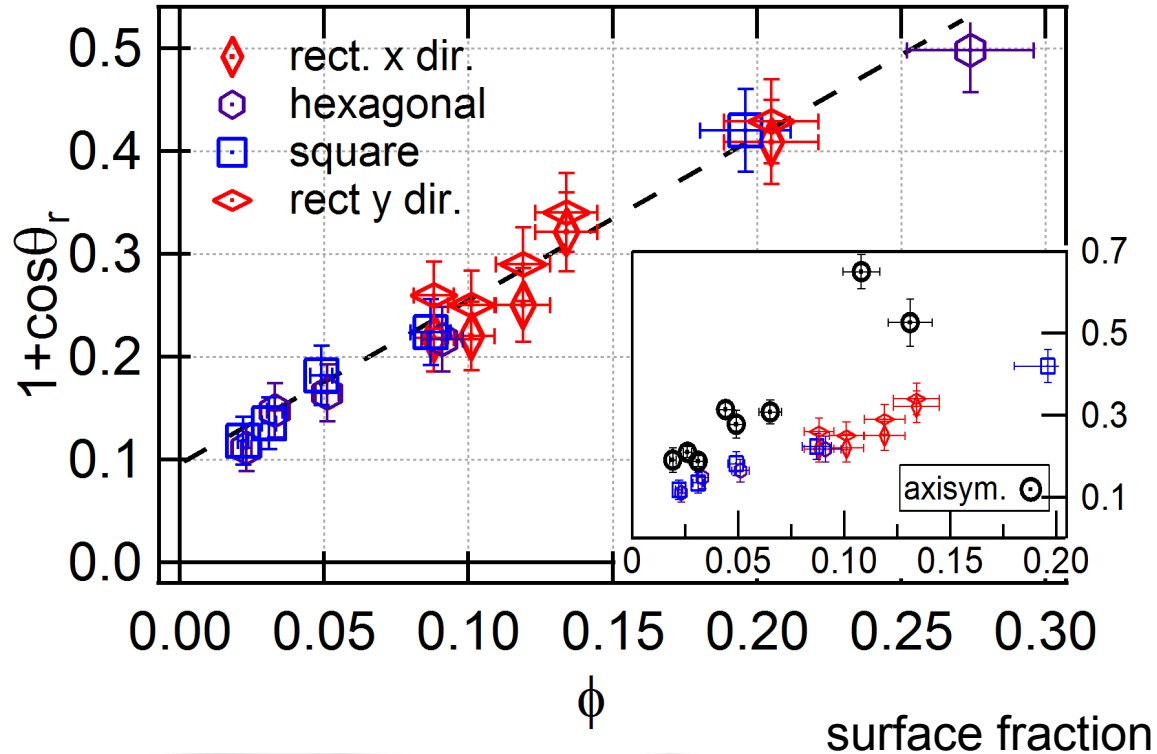
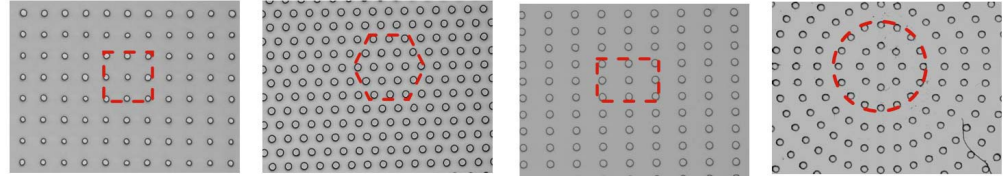
Model – Impact of the kink



surface fraction

A. Gauthier et al. PRL 2013

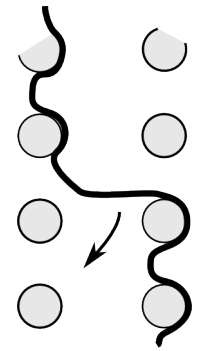
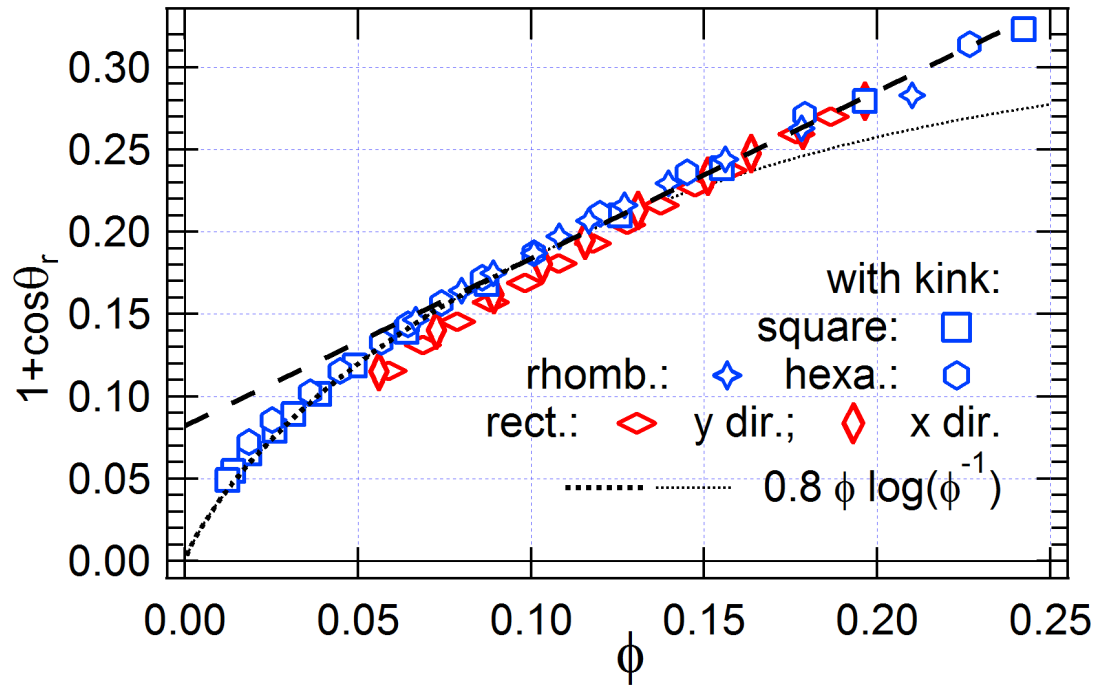
Receding contact angle – impact of texture



Rivetti et al. PRL 2015

Simulations – receding contact angle

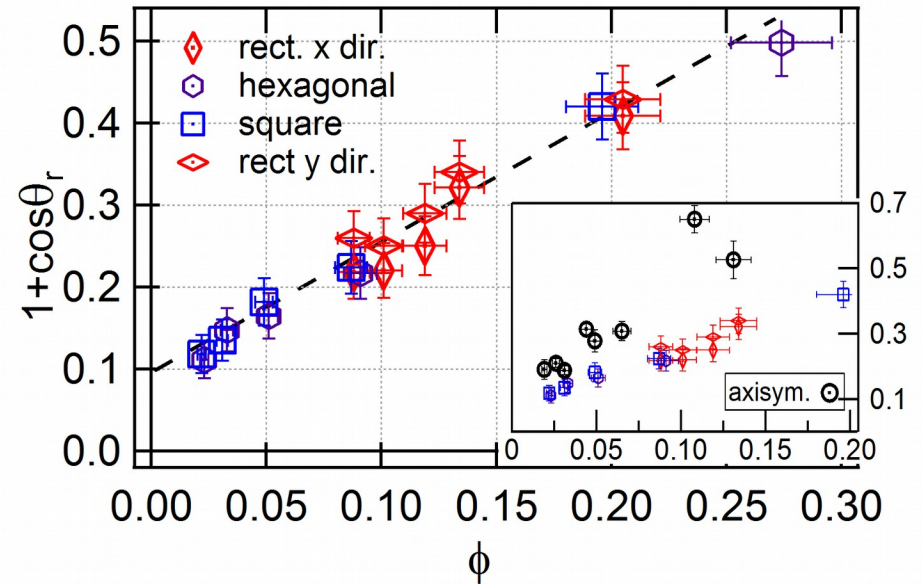
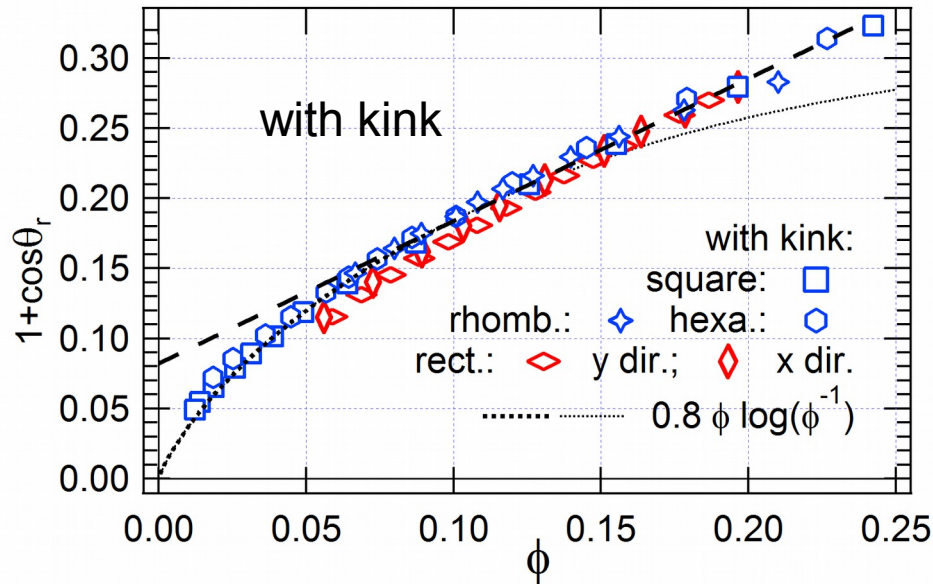
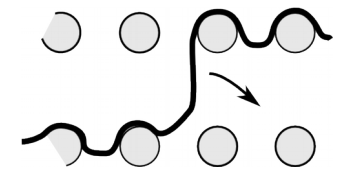
with kink



surface fraction

Rivetti et al. PRL 2015

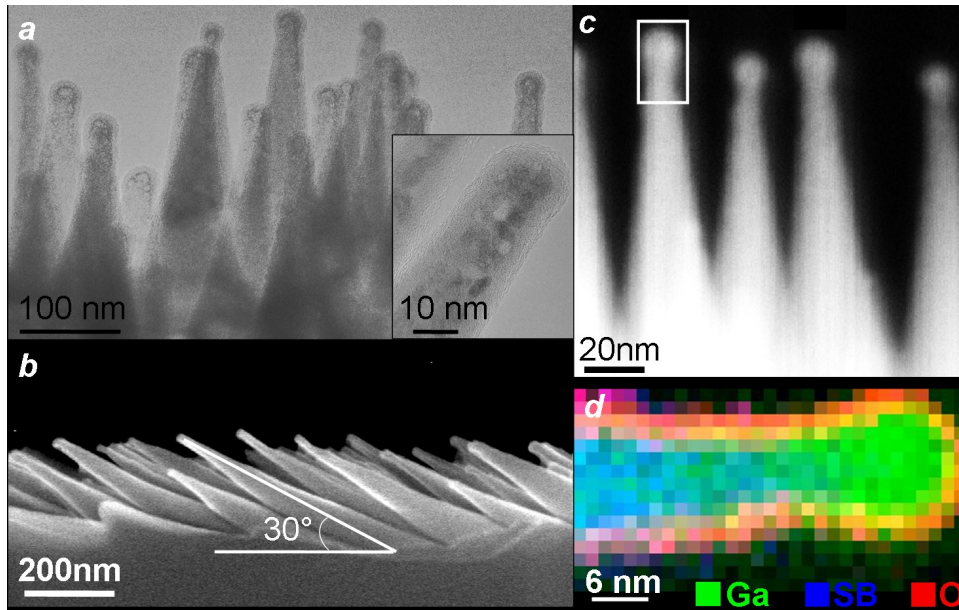
Simulations – data



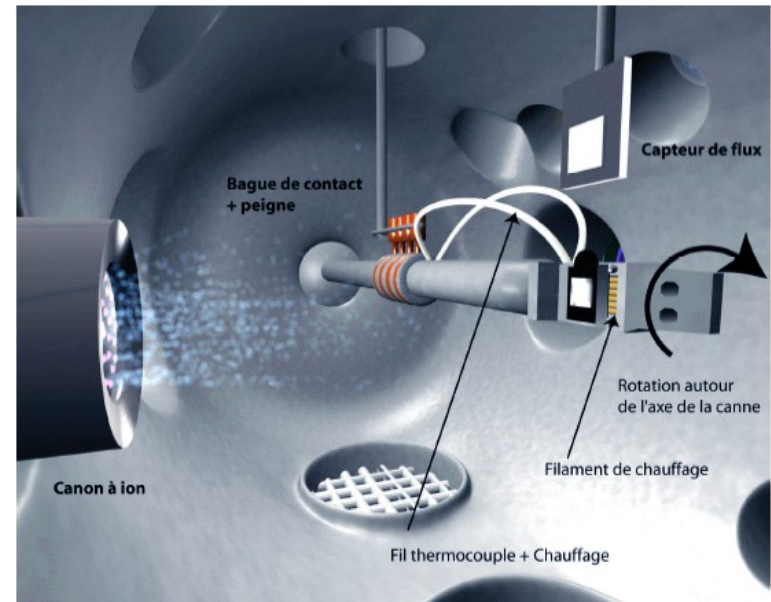
Rivetti et al. PRL 2015

Jansons JFM 1985 (periodic + random)
Joanny & de Gennes J Chem Phys 1984 (random)
Paterson and Fermigier Phys. Fluids 1997
Reyssat and Quéré J. Phys Chem B 2009

Self-organised GaSb structures



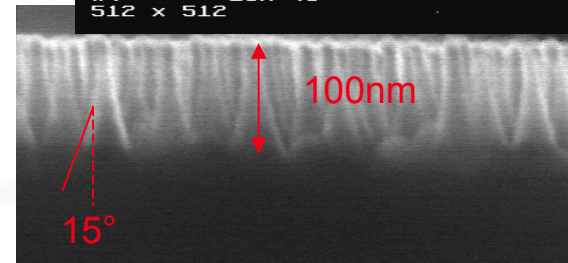
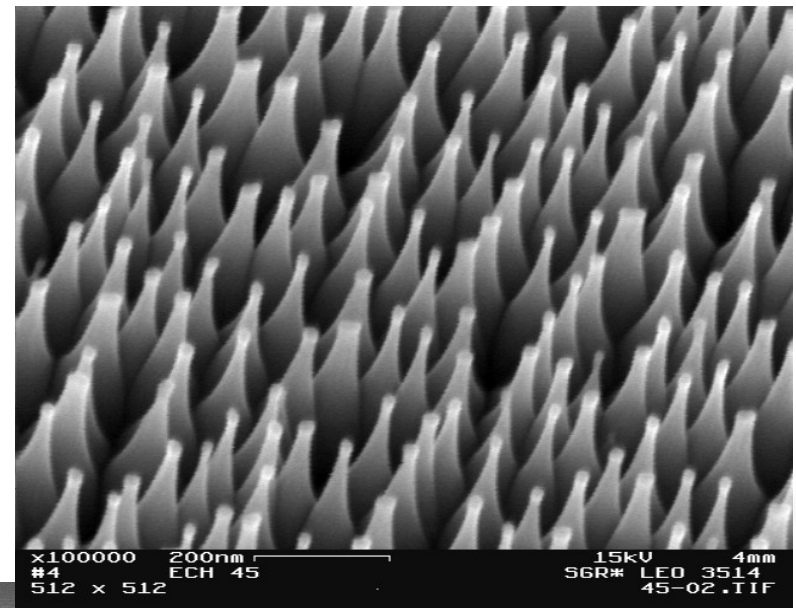
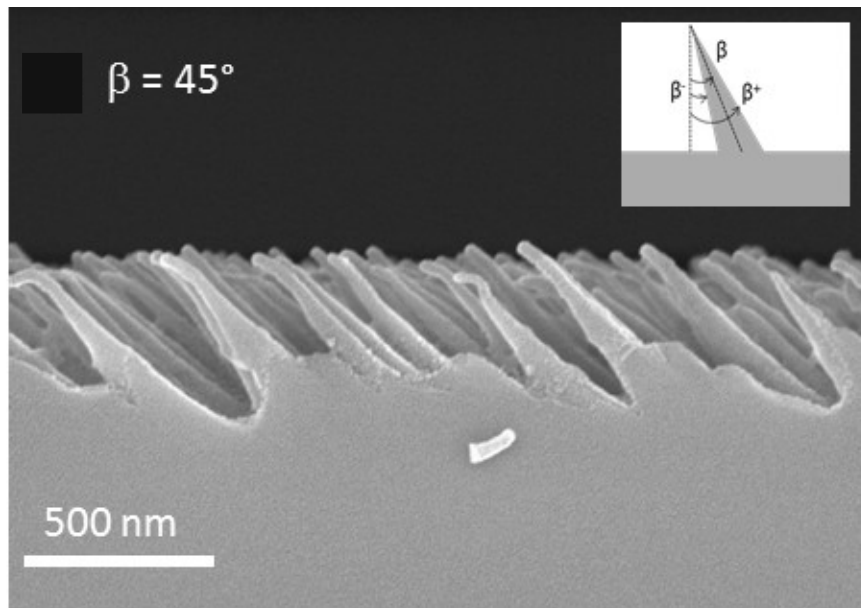
Leroy et al. APL 2009



- GaSb(100) monocrystals
- ion gun
 - Ar⁺ plasma
 - 0.1 - 2KeV
 - divergence of 5°

Cone morphologies *straight vs. tilted*

inclination angle β

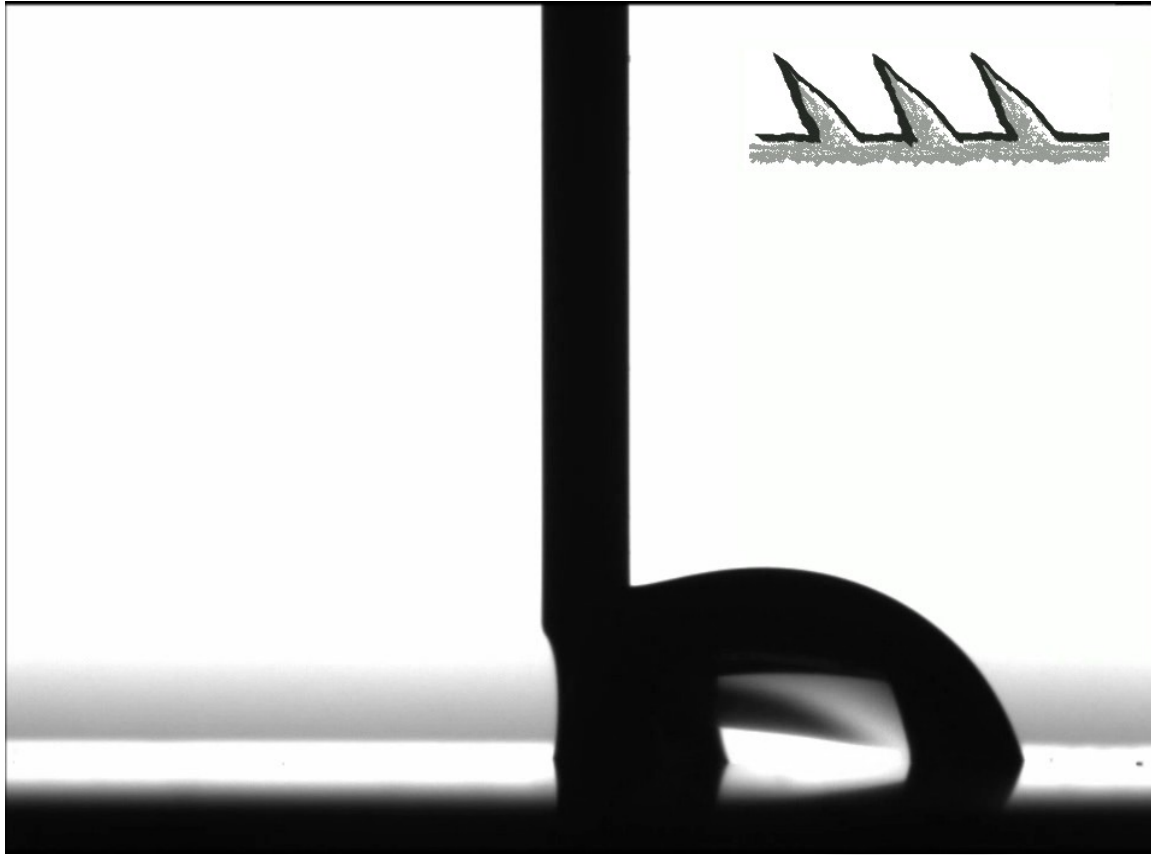


Leroy et al. APL 2009

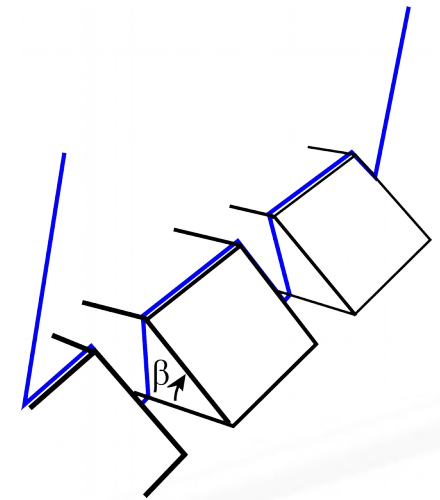
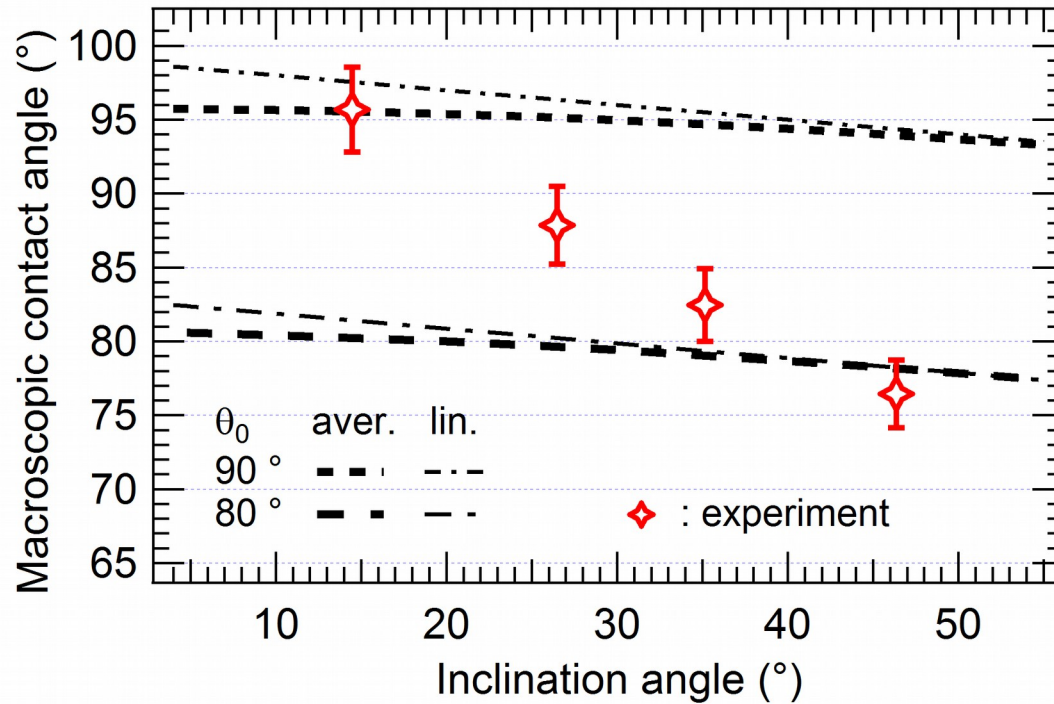
9 min, 500 eV, 0.03mA/s cm²

Advancing contact angle – tilted cones

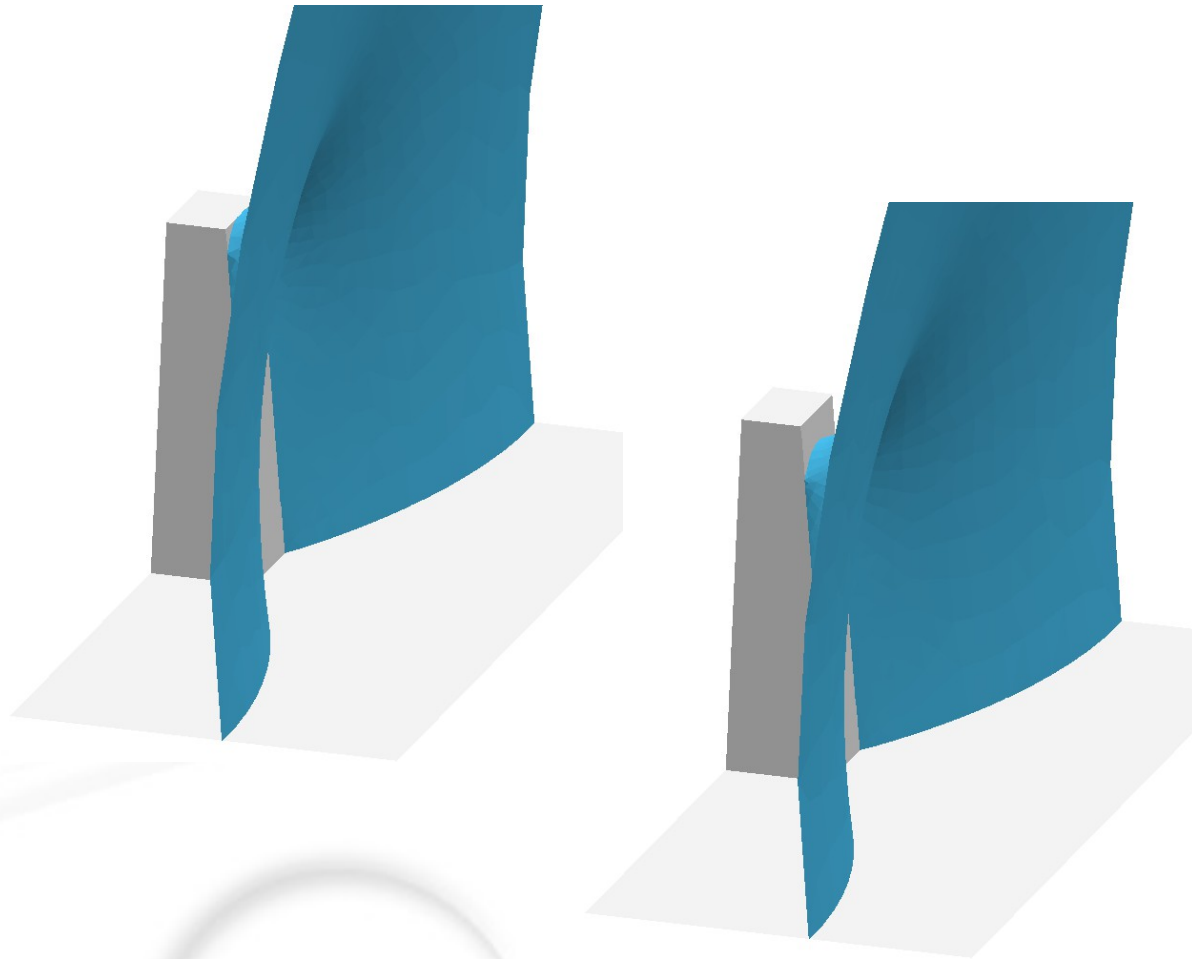




Advancing contact angle vs. inclination

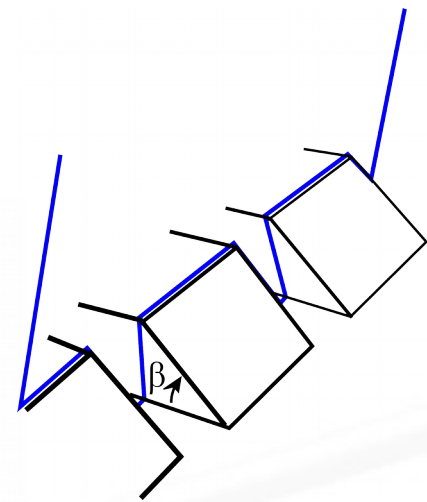
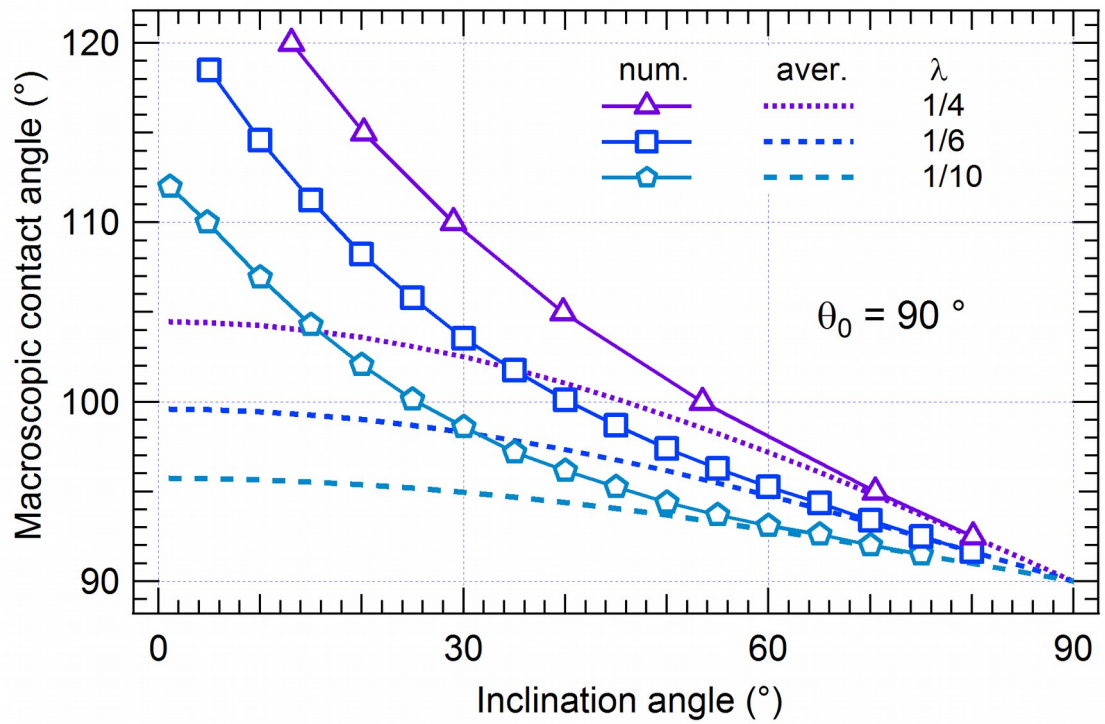


Advancing contact angle as depinning threshold



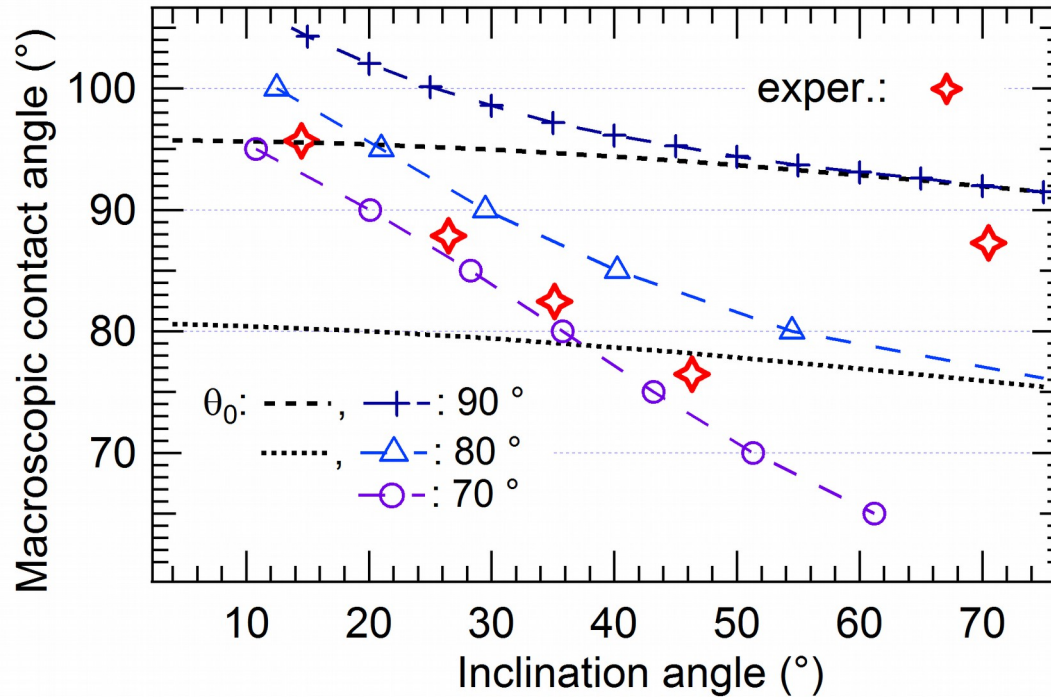
Advancing contact angle - Predictions

Impact of depinning



Advancing contact angle - Data

impact of pinning



E. Contraire et al., Soft Matter 2016

Conclusion

■ Wetting on textured hydrophobic surfaces

- triple line pinning
- elasticity

■ Impact of order

- kink
- reduction of depinning stress