At the interface of thermofluidics and rational materials engineering: *The case of intrinsically icephobic surfaces*

Thomas M. Schutzius

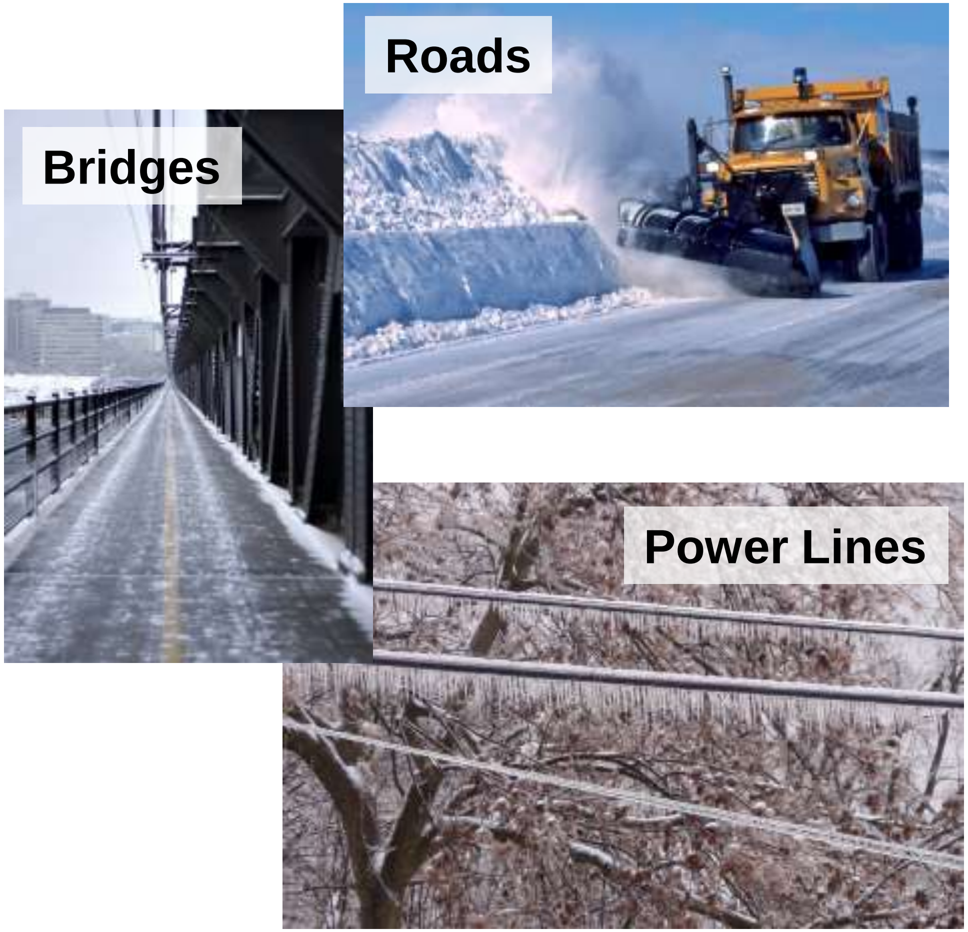
Key talking points: The case of intrinsically icephobic surfaces

- Fundamental aspects of thermodynamics and related fluidics that pertain to icing.
- Materials engineering: The surfaces we created.
- Using engineered surfaces to develop design rules.
- For applications where the design rules are clear: Large-area fabrication of engineered surfaces.

Surface icing: Energy, safety, infrastructure

Aircraft

Wind Turbines



Roads

Bridges

Power Lines

Surface icing: Energy, safety, infrastructure

55.8k likes 2w

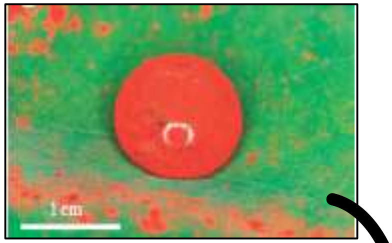
elonmusk Falcon lands on droneship, but the lockout collet doesn't latch on one the four legs, causing it to tip over post landing. Root cause may have been ice buildup due to condensation from heavy fog at liftoff.

roneship,
't latch on
to tip over
y have been
ition from

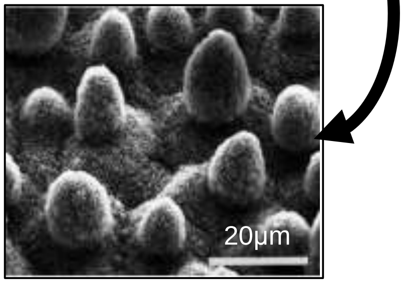
Background: *Wettability engineering*

- How does nature handle water? Some approaches may be useful for ***phase change problems.***

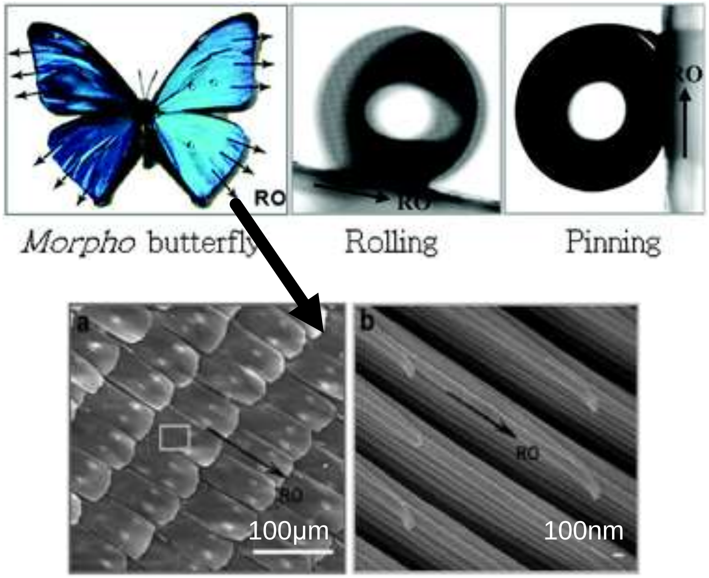
Self-cleaning



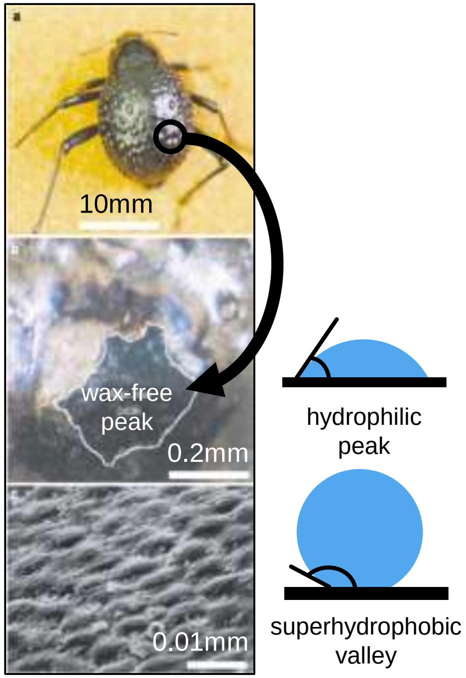
Lotus leaf contaminated with Sudan red. Water drop *cleans* it.



Directional dependency



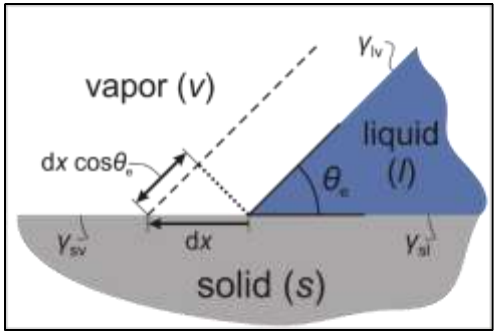
Site-selective



Koch et al. Phil. Trans. Roy. Soc A, 2009, 367 1487-1509;
Barthlott et al. Planta, 1997, 202, 1-8;
Zheng et al. Soft Matter, 2007, 3, 178-182;
Parker et al. 2001, 414, 33-34; BBC

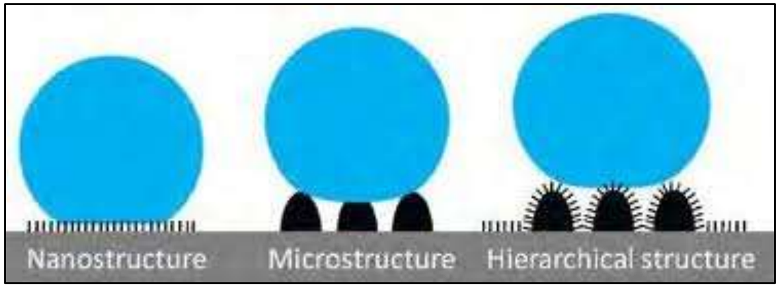
Superhydrophobicity

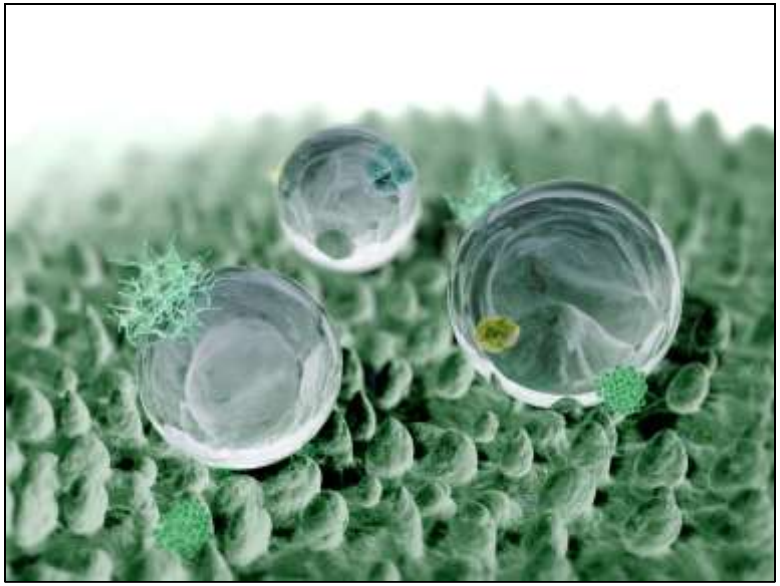
Wettability of surfaces:
Intrinsic contact angle



Young-Dupré:

$$\cos\theta_{\mathrm{e}} = \frac{(\gamma_{\mathrm{sv}} - \gamma_{\mathrm{sl}})}{\gamma_{\mathrm{lv}}}, \quad \gamma = \left(\frac{\partial G}{\partial A}\right)_{T,V,n}$$





The combination of ***hydrophobic chemistry*** and ***hierarchical structure*** produces the self-cleaning property of the Lotus leaf (computer graphic).

Credit: Ask Nature

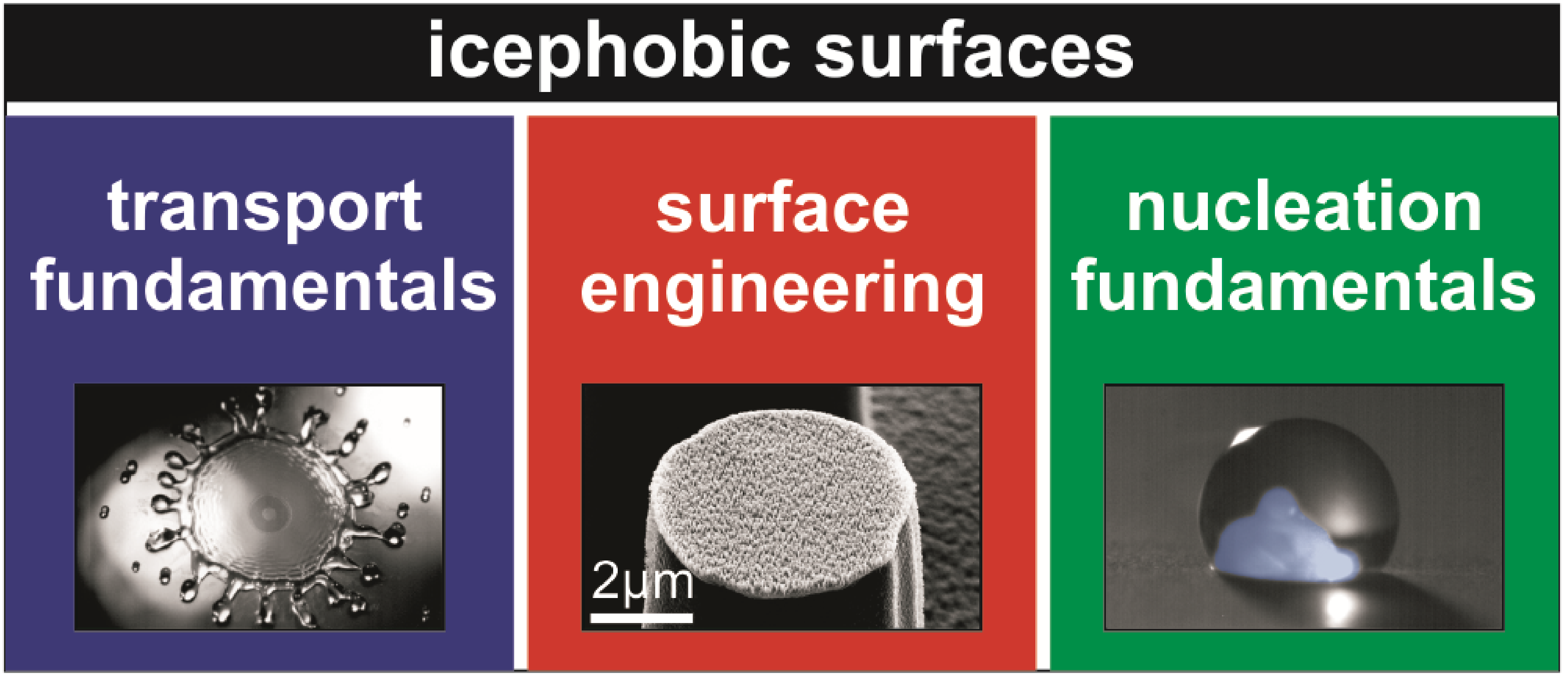
Superhydrophobicity: *Departing from ambient conditions*

Droplet impacting onto a cooled superhydrophobic surface.

- Viscosity of ***supercooled*** water is ~4x higher compared to its room temperature case.
- Recovery very difficult.
- Freezing will result.

Maitra, T.; et a. Langmuir, 2014, 30, 10855-10861

Icephobicity



Schutzius, T. M.; et al. Langmuir, 2015, 31, 4807-4821

Outline

1. **Background: Freezing of sessile supercooled water droplets**

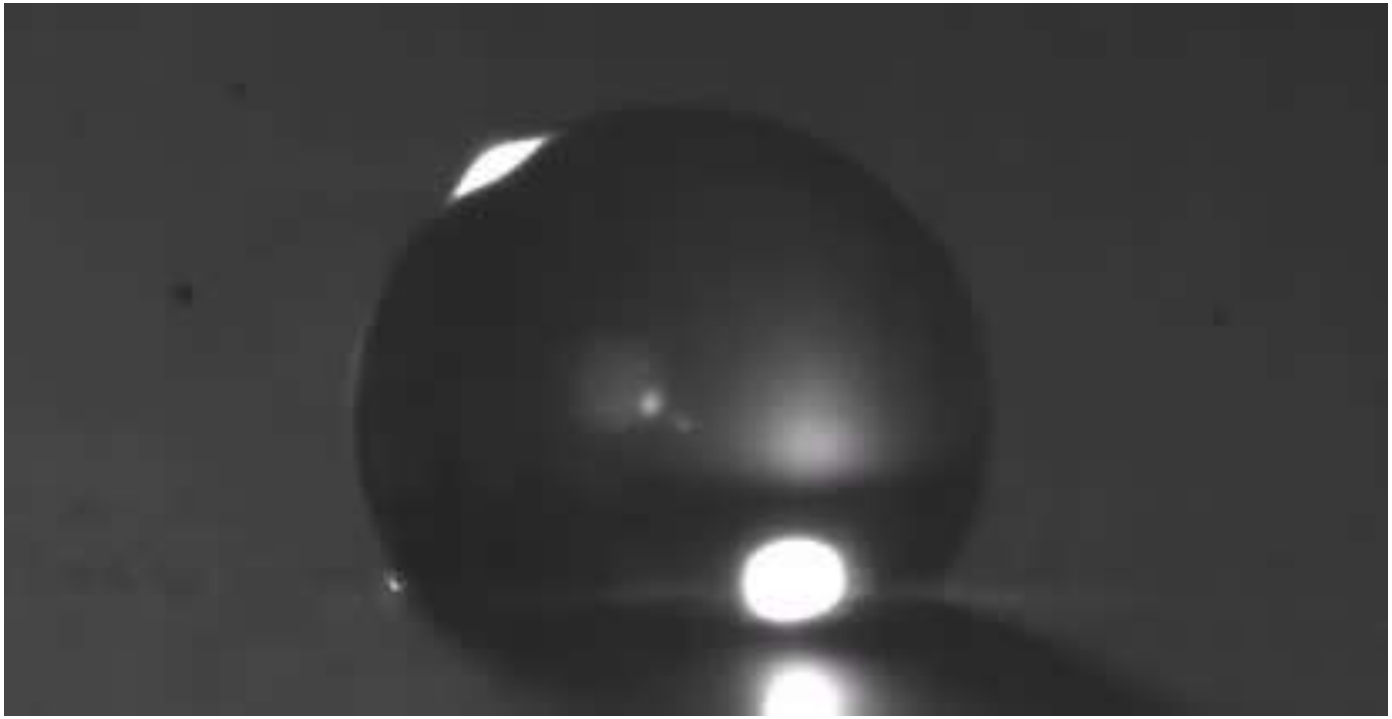
2. Spontaneous droplet trampolining on rigid superhydrophobic surfaces

3. Evaporative droplet freezing and design of surfaces with intrinsic ice-shedding properties

4. Materials considerations: Surface fabrication by large-area techniques

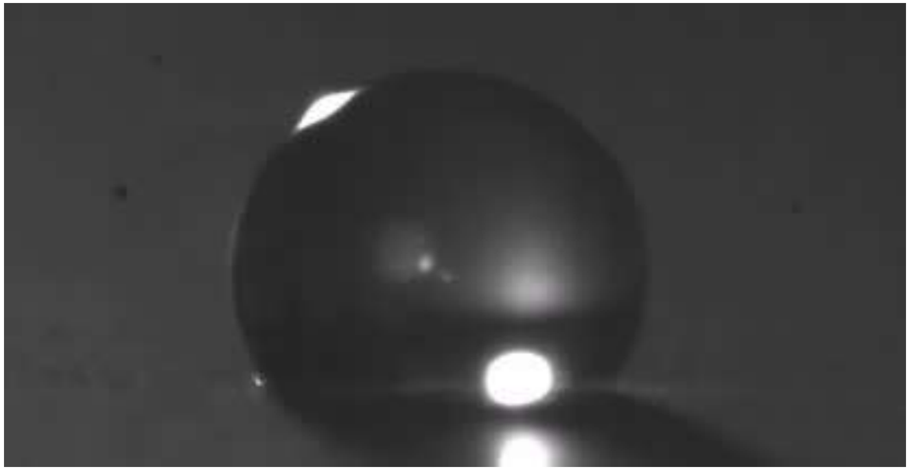
Supercooled droplet freezing: Two stages

- Droplet and environment initially at ~-15°C and dry conditions.



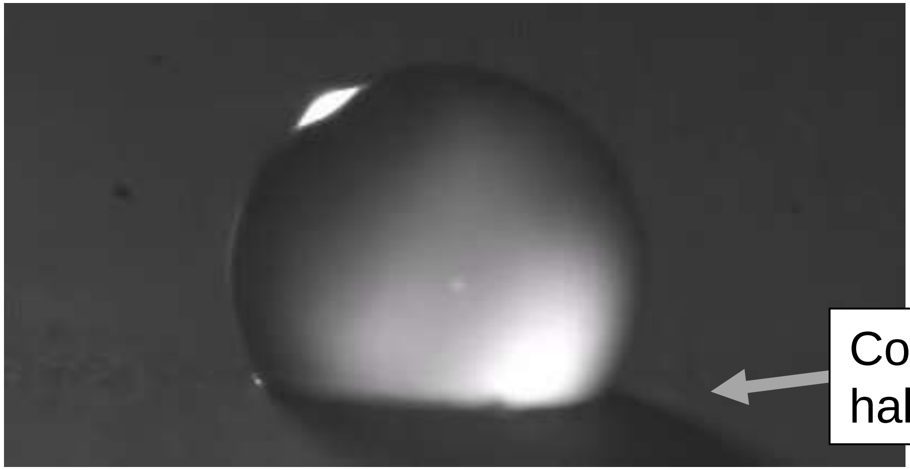
Jung, S.; et al. PNAS, 2012, 109, 16073-16078

Supercooled droplet freezing: Two stages



Stage 1: ~0.02 s
Rapid recalescence freezing.

Counterintuitive:
Droplet freezes and is getting hot (-15 to 0°C).



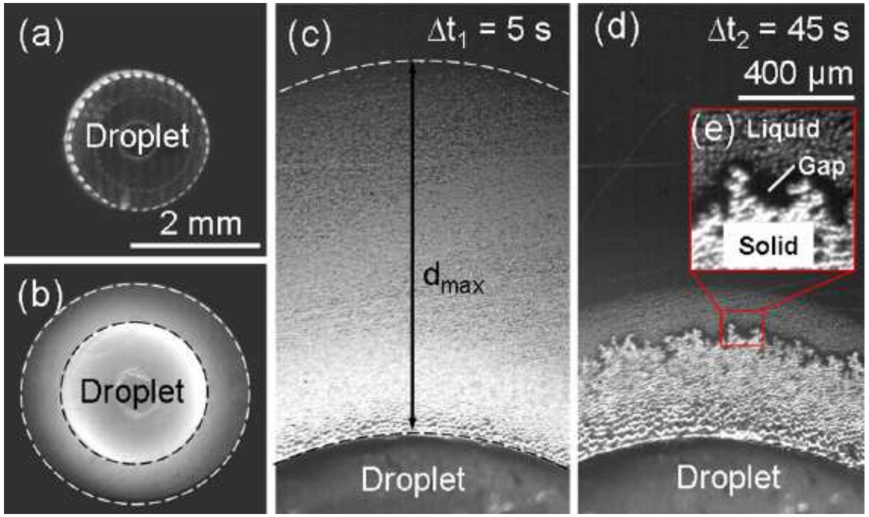
Stage 2: ~10 s
Isothermal freezing

Phase change:
solidification, vaporization, condensation…

Condensate halo

Jung, S.; et al. PNAS, 2012, 109, 16073-16078

Condensate freezing on PMMA

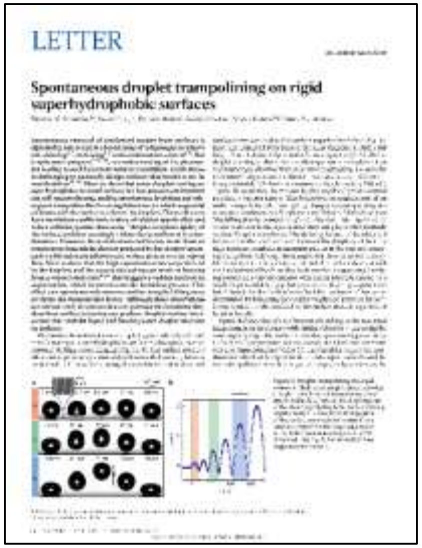


- Non-equilibrium freezing in a dry environment can lead to ***explosive vaporization***.
- Due to the sudden latent heat released upon recalescent freezing.
- This manifests itself through condensation.

Jung, S.; et al. PNAS, 2012, 109, 16073-16078

Outline

1. Background: Freezing of sessile supercooled water droplets
2. **Spontaneous droplet trampolining on rigid superhydrophobic surfaces**
3. Evaporative droplet freezing and design of surfaces with intrinsic ice-shedding properties
4. Materials considerations: Surface fabrication by large-area techniques



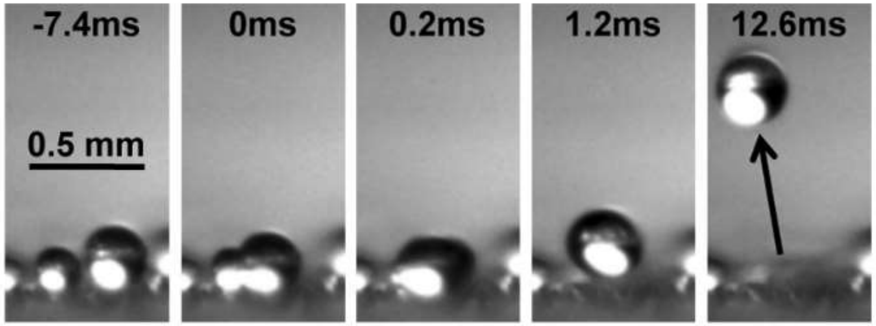
LETTER

Spontaneous droplet trampolining on rigid superhydrophobic surfaces

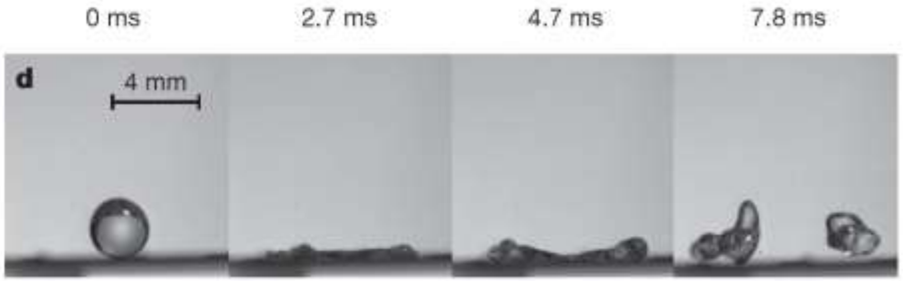
Schutzius, T. M.; Jung, S.; et al. Nature, 2015, 527, 82-85

Impressive droplet removal mechanisms

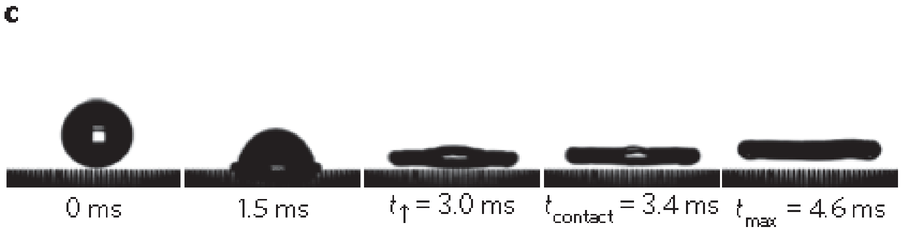
Boreyko
(Chen) 2009
PRL, 103,
184501



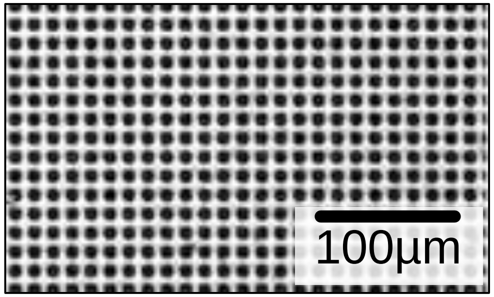
Bird et al.
(Varanasi) 2013
Nature, 503,
385-388



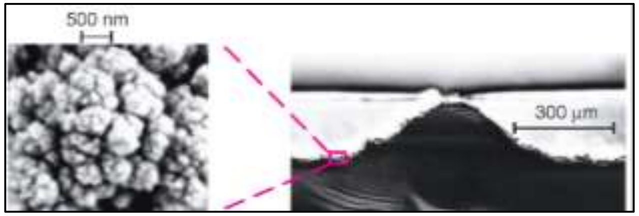
Liu et al.
(Z. Wang) 2014
Nat. Phys., 10,
515-519



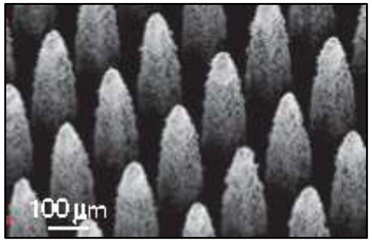
micropillars



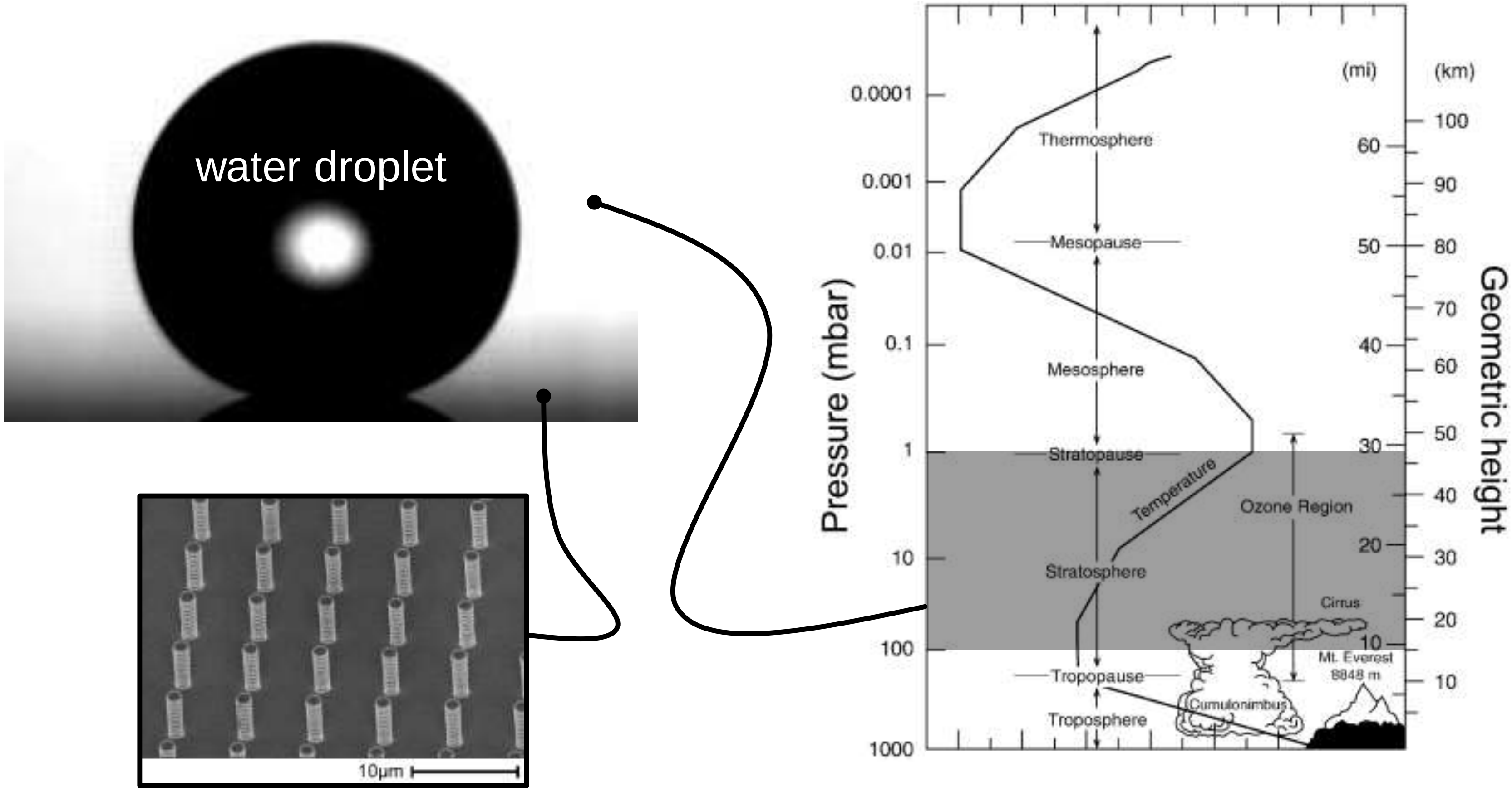
knife-like macrotexture



tapered posts



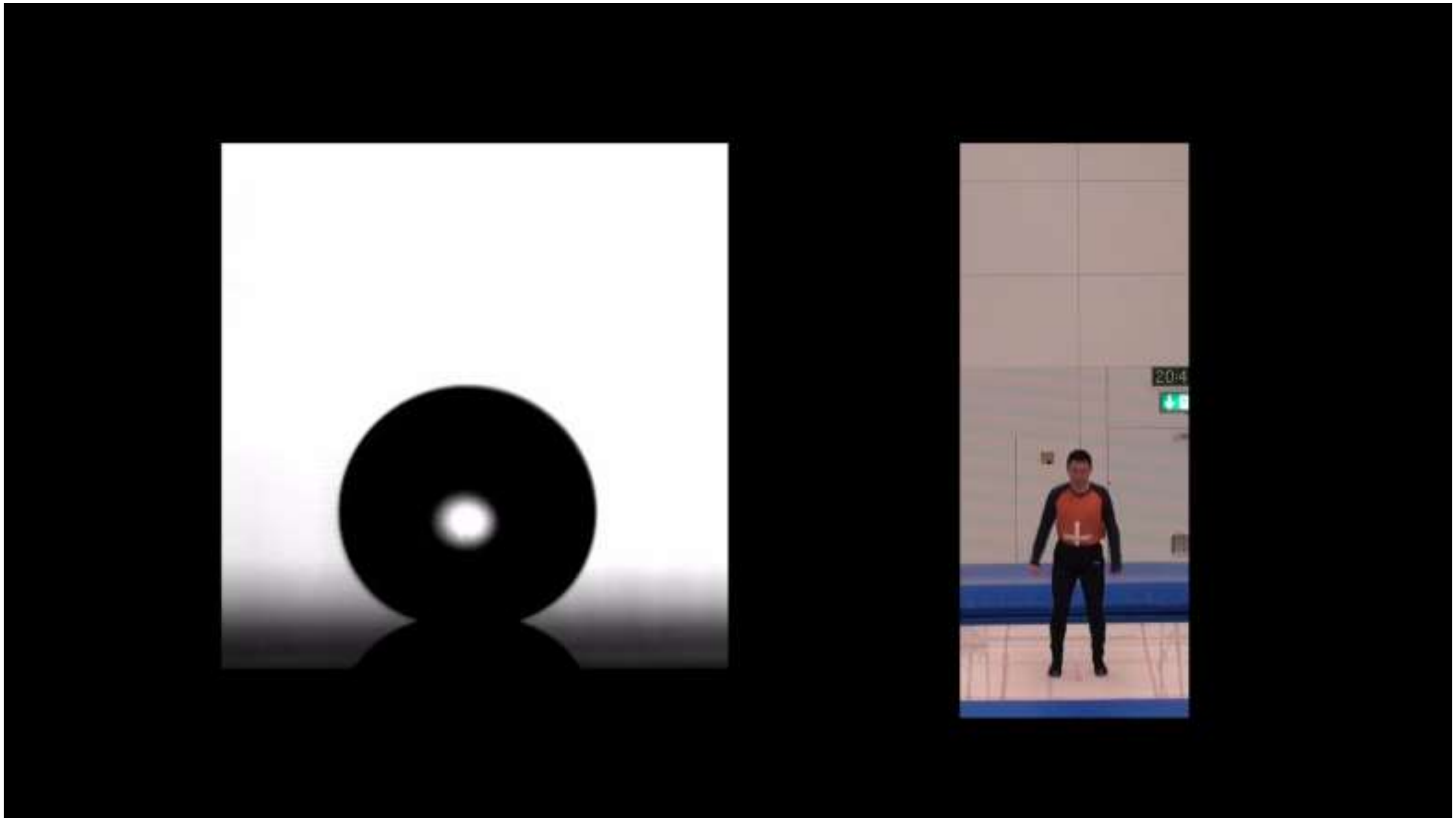
Behavior at low-pressure: Vacuum vs. vaporization



superhydrophobic

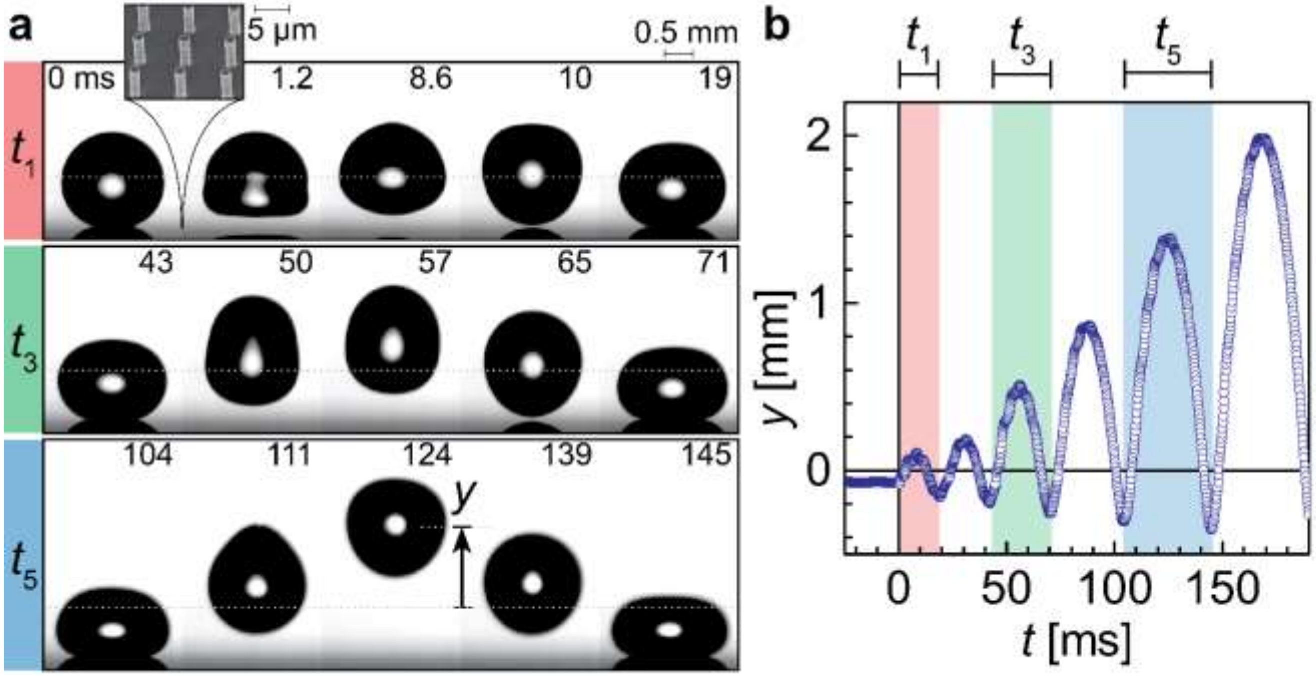
Brasseur, G. P. & Solomon, S. Aeronomy of the middle atmosphere Springer, 2005
Schutzius, T. M.; Jung, S.; et al. Nature, 2015, 527, 82-85

Video: Droplet trampolining



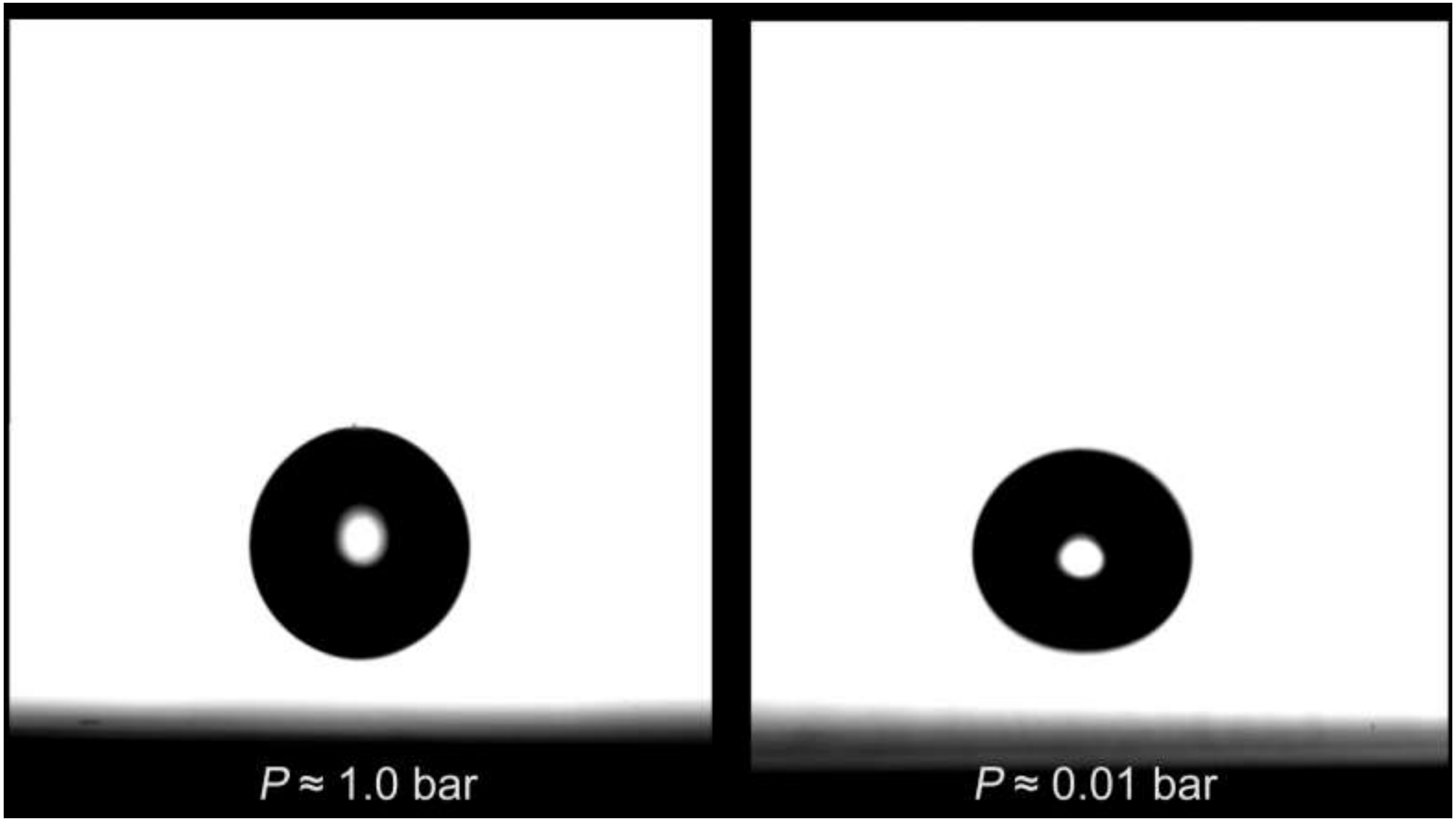
Schutzius, T. M.; Jung, S.; et al. Nature, 2015, 527, 82-85

Droplet behavior at low-pressure



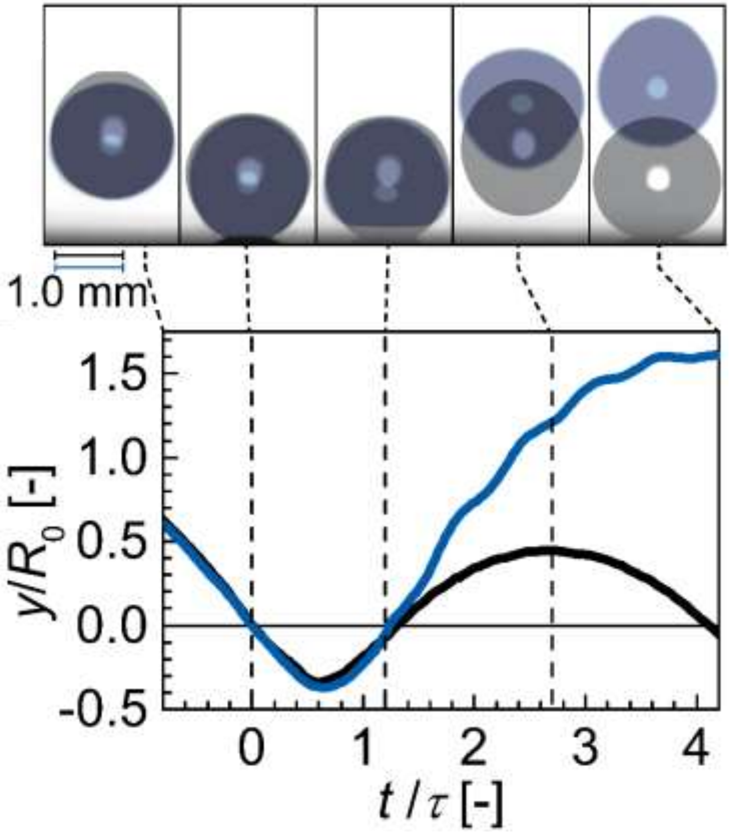
Schutzius, T. M.; Jung, S.; et al. Nature, 2015, 527, 82-85

Video: Droplet impact, varying environmental pressure



Schutzius, T. M.; Jung, S.; et al. Nature, 2015, 527, 82-85

Droplet impact, varying environmental pressure, $v_1 = -0.9 R_0 / \tau$



time scale

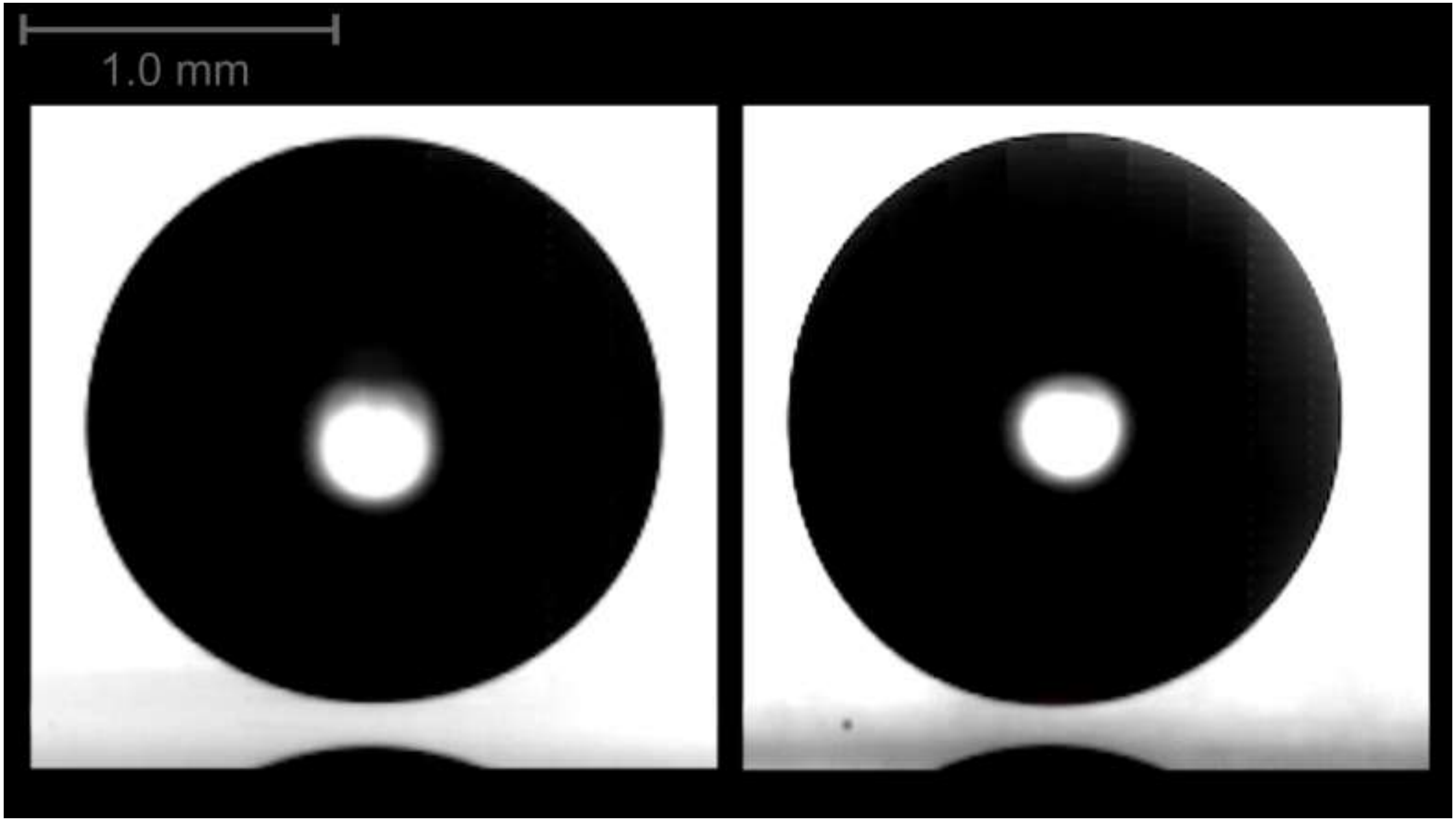
$$\tau = \sqrt{m/\sigma}$$

length scale

$$R_0$$

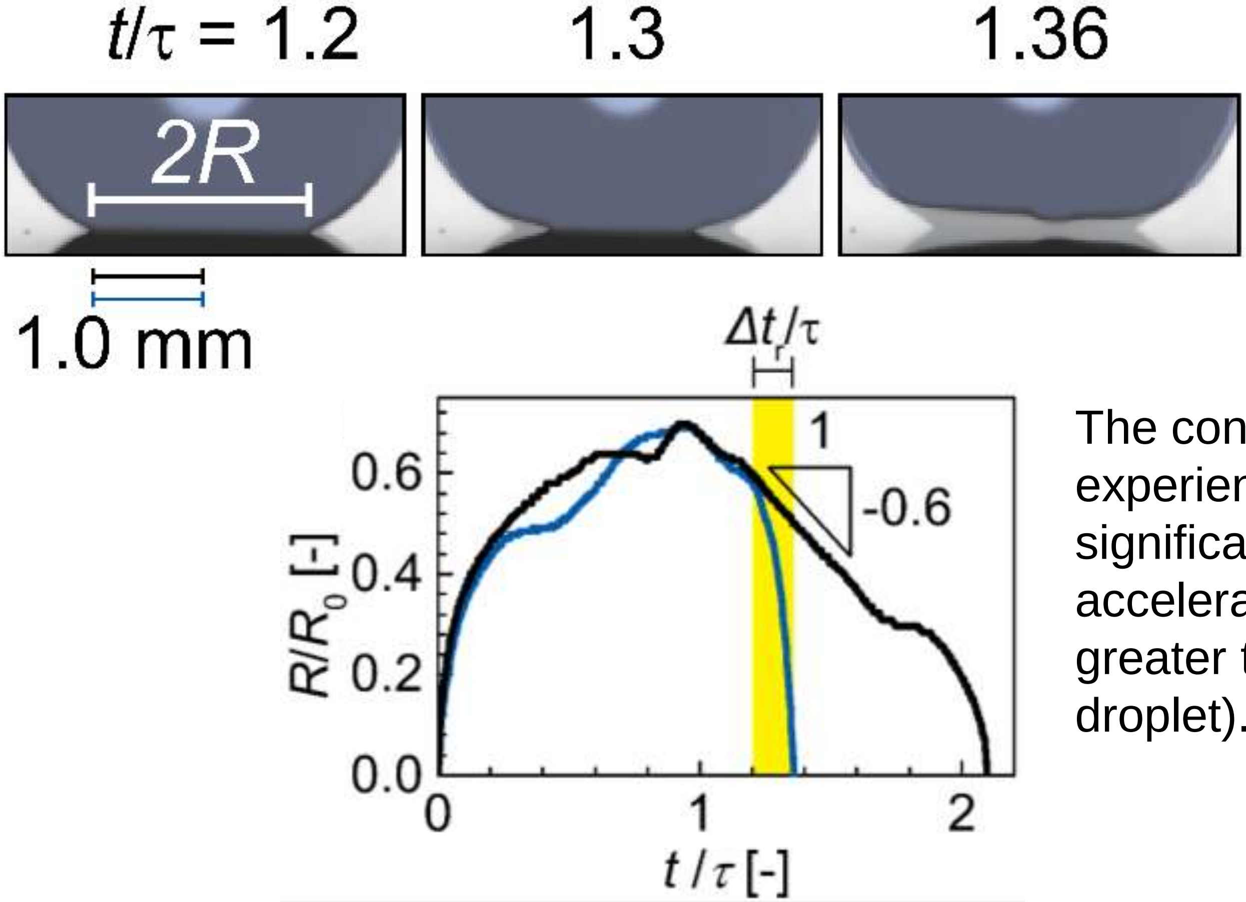
Schutzius, T. M.; Jung, S.; et al. Nature, 2015, 527, 82-85

Video: Droplet impact, recoil behavior, v_1=-0.6R_0/τ



Schutzius, T. M.; Jung, S.; et al. Nature, 2015, 527, 82-85

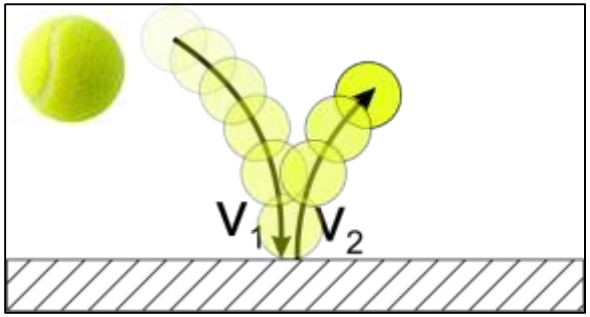
Droplet impact, recoil behavior, v_1=-0.6R_0/τ



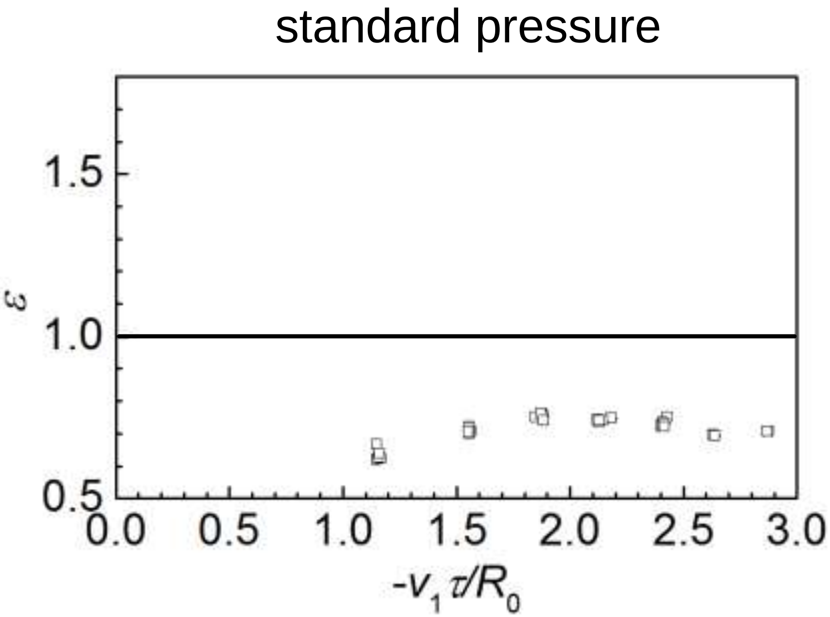
The contact line is experiencing significant acceleration (22x greater than the bulk droplet).

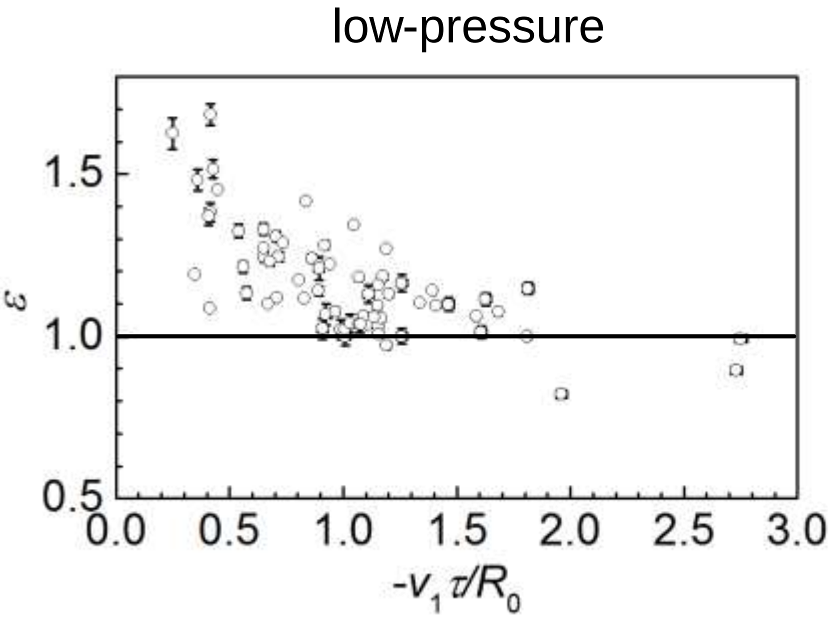
Schutzius, T. M.; Jung, S.; et al. Nature, 2015, 527, 82-85

Restitution coefficients



$$\boxed{\varepsilon = -v_2 / v_1}$$

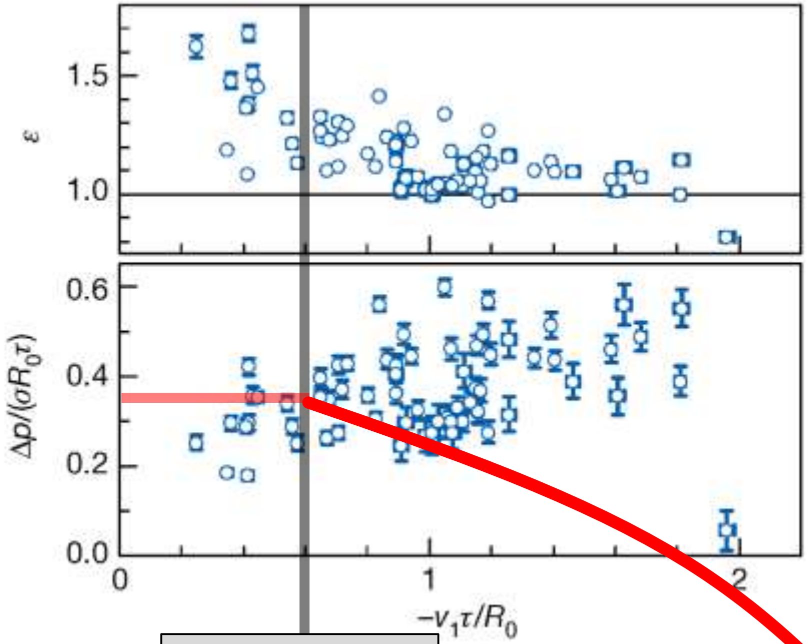




Schutzius, T. M.; Jung, S.; et al. Nature, 2015, 527, 82-85

Restitution coefficients: Change in momentum

low-pressure



$-v_1=0.6R_0/\tau$

experimental value

experimental value

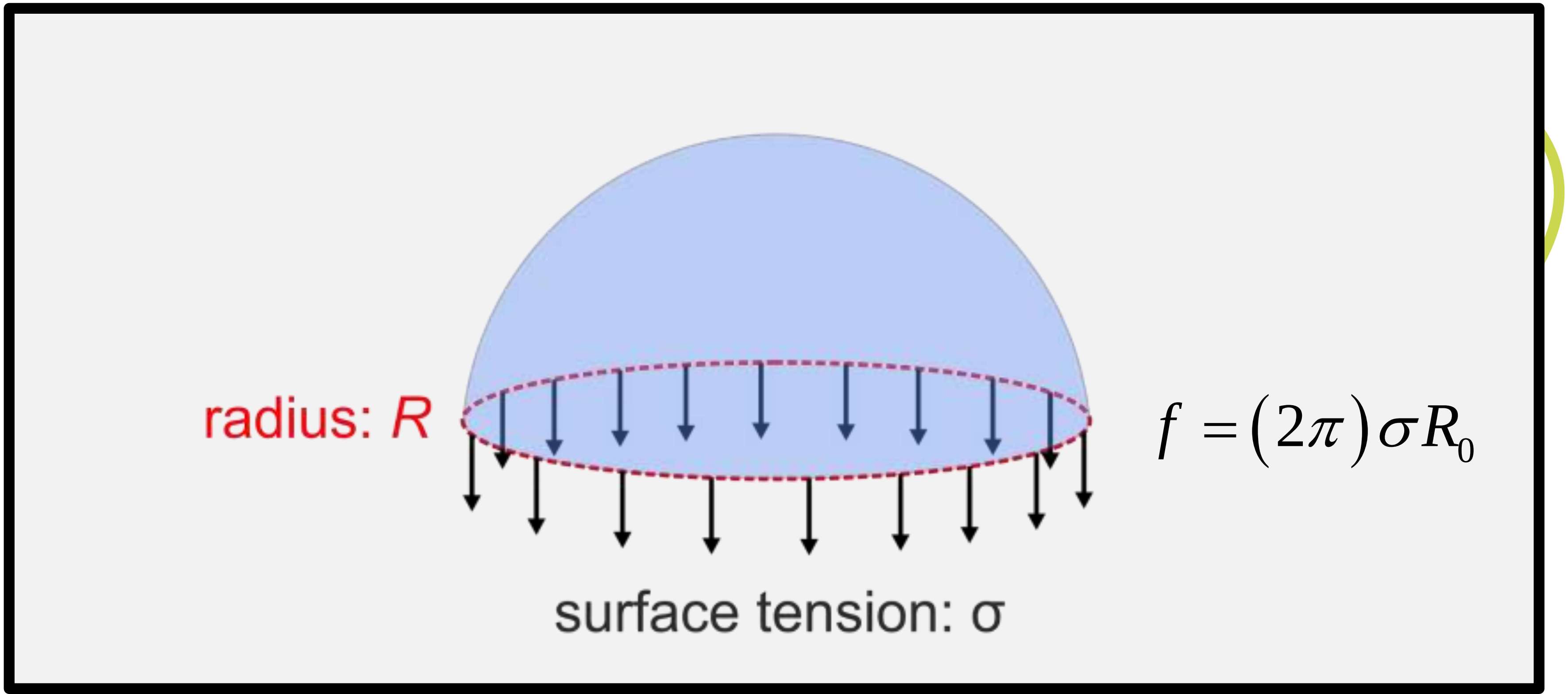
$$\Delta p = \int_0^{\Delta t_r} f\,dt \approx \bar{f}\,\Delta t_r$$

unknown

$$\Rightarrow \quad \frac{\bar{f}}{\sigma R_0} \approx \frac{\Delta p}{\sigma R_0 \tau}\,\frac{\tau}{\Delta t_r}$$

Schutzius, T. M.; Jung, S.; et al. Nature, 2015, 527, 82-85

Restitution coefficients: Change in momentum



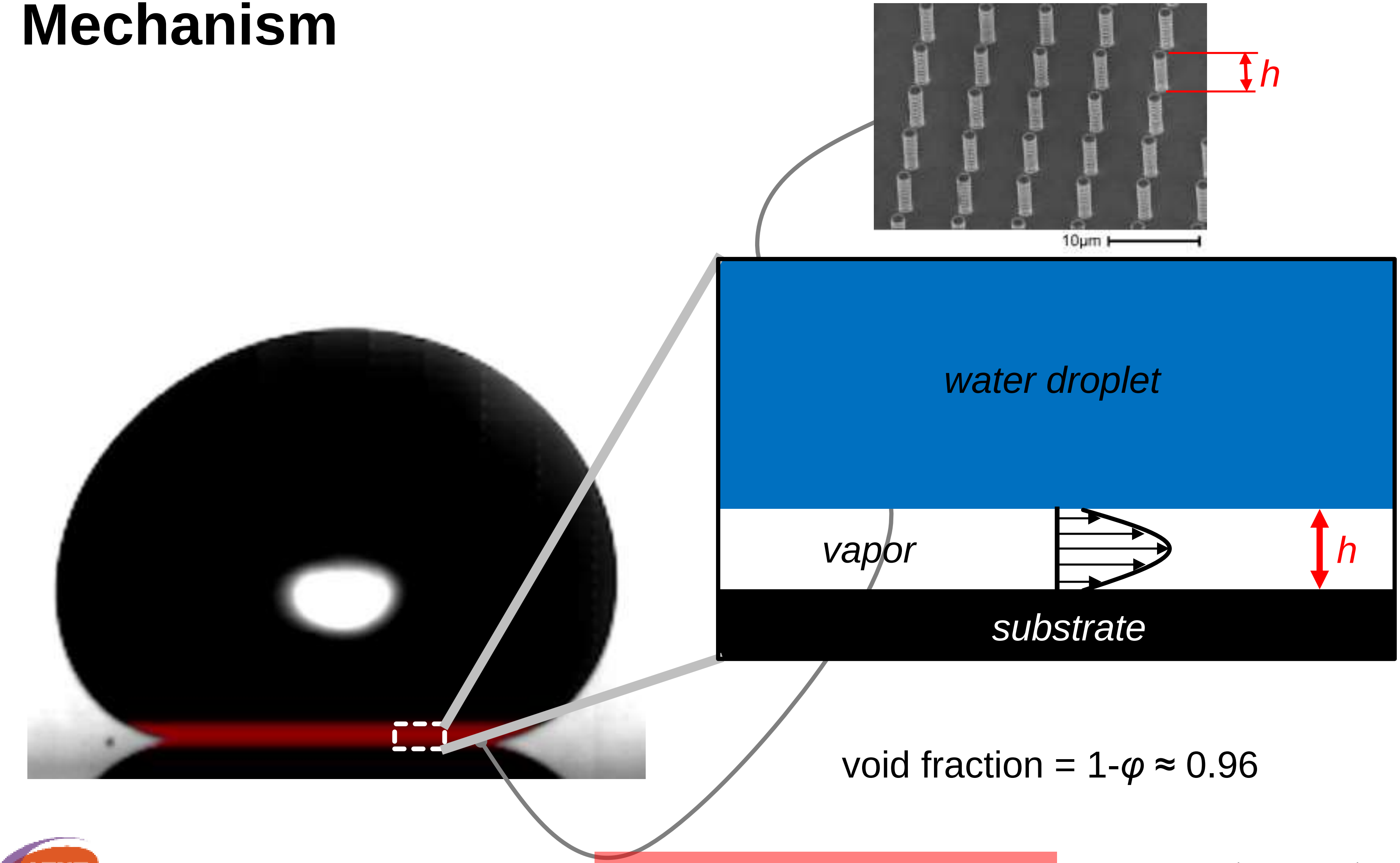
$$f = (2\pi)\sigma R_0$$

$$\Delta p = \int_0^{\Delta t_r} f dt \approx \bar{f}\,\Delta t_r$$

$$\frac{\bar{f}}{\sigma R_0} \approx \frac{\Delta p}{\sigma R_0 \tau}\frac{\tau}{\Delta t_r} = (0.35)(1/0.16) = 2.2$$

Schutzius, T. M.; Jung, S.; et al. Nature, 2015, 527, 82-85

Mechanism

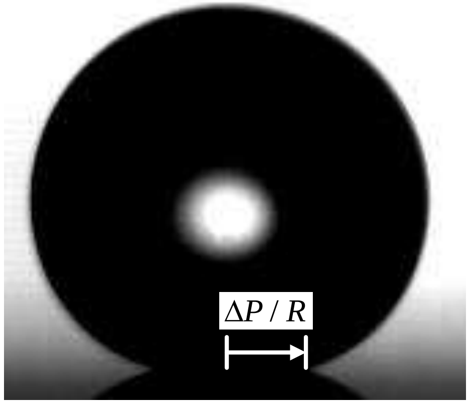


void fraction = $1-\varphi \approx 0.96$

Schutzius, T. M.; Jung, S.; et al. Nature, 2015, 527, 82-85

Forces

Vaporization:



Pressure differential along parallel plates:

$$\Delta P \approx \frac{12Q\mu R}{h^3 F} \approx \frac{3\mu R^2 J}{h^3 F \rho_\mathrm{v}}$$

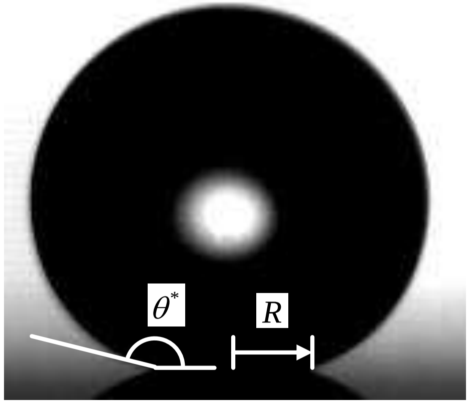
Variables:

Q: flow rate
μ: Vapor viscosity
R: Droplet contact radius
h: Pillar height
F: Slip factor
J: Vaporization flux
ρ: Vapor density

Force acting on the droplet :

$$f_\mathrm{v} = \Delta \bar{P} \pi R^2 \approx \frac{3\pi\mu R^4 J}{2h^3 F \rho_\mathrm{v}}$$

Surface tension:



Force due to adhesion:

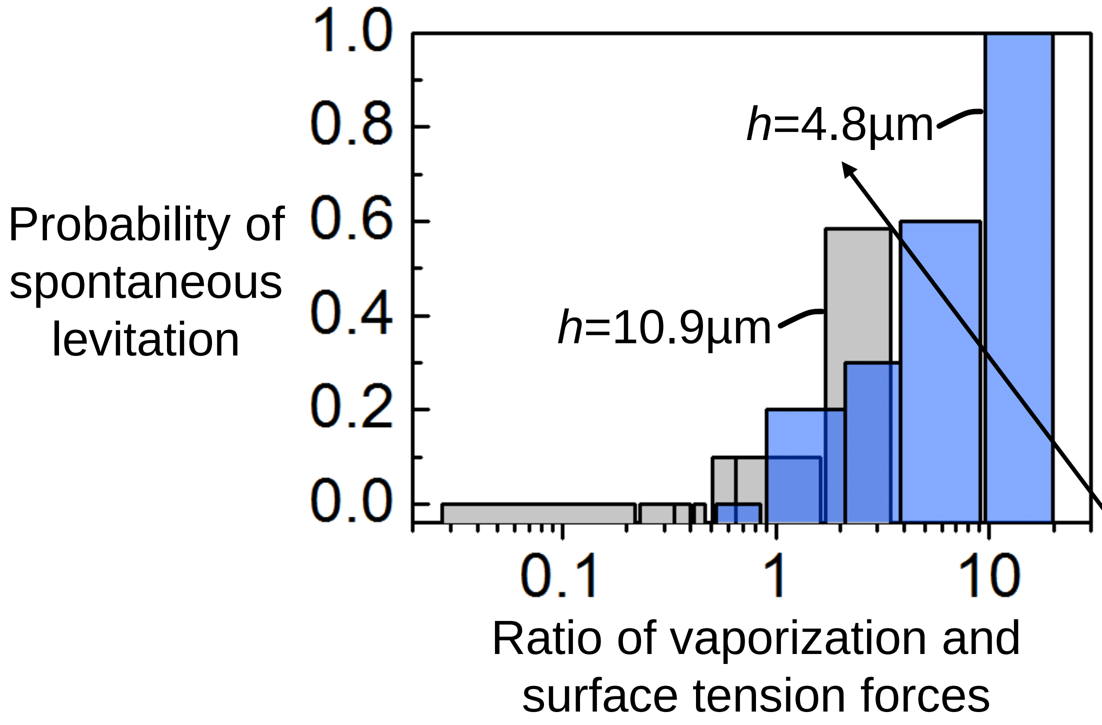
$$f_\mathrm{c} = 2\pi R\sigma \sin(\theta_\mathrm{r}^*)$$

Variables:

θ^*_r: Receding contact angle
σ: Surface tension

Schutzius, T. M.; Jung, S.; et al. Nature, 2015, 527, 82-85

Designing the surface



Property of the flow and droplet

$$Ca^* = J\mu/(4F\rho_v\sigma)$$

J: Vaporization flux

μ: Vapor viscosity

F: Slip factor

ρ: Vapor density

σ: Surface tension

Property of the surface and droplet

$$(R/h)^3/\sin\theta_r^*$$

R: Droplet contact radius

h: Pillar height

θ_r^*: Receding contact angle

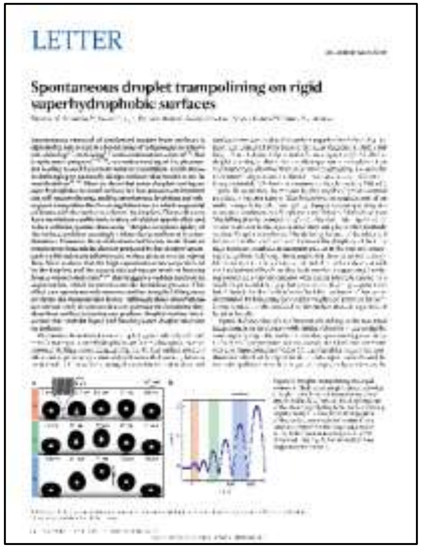
Maximize the ratio of *R*/*h*

h is a tunable parameter

Schutzius, T. M.; Jung, S.; et al. Nature, 2015, 527, 82-85

Outline

1. Background: Freezing of sessile supercooled water droplets
2. Spontaneous droplet trampolining on rigid superhydrophobic surfaces
3. **Evaporative droplet freezing and design of surfaces with intrinsic ice-shedding properties**
4. Materials considerations: Surface fabrication by large-area techniques



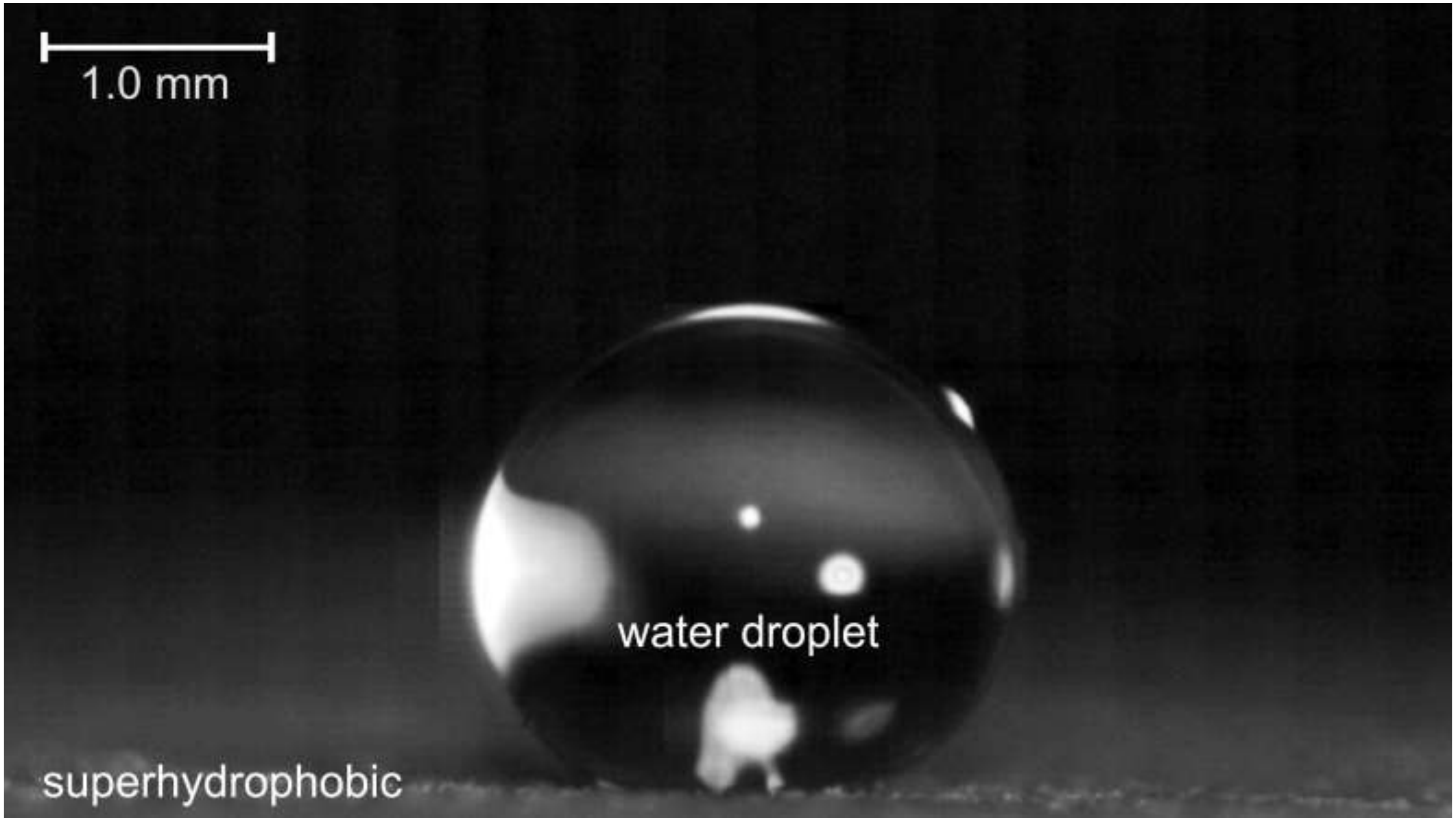
LETTER

Spontaneous droplet trampolining on rigid superhydrophobic surfaces

Evaporative droplet freezing and design of surfaces with intrinsic ice-shedding properties

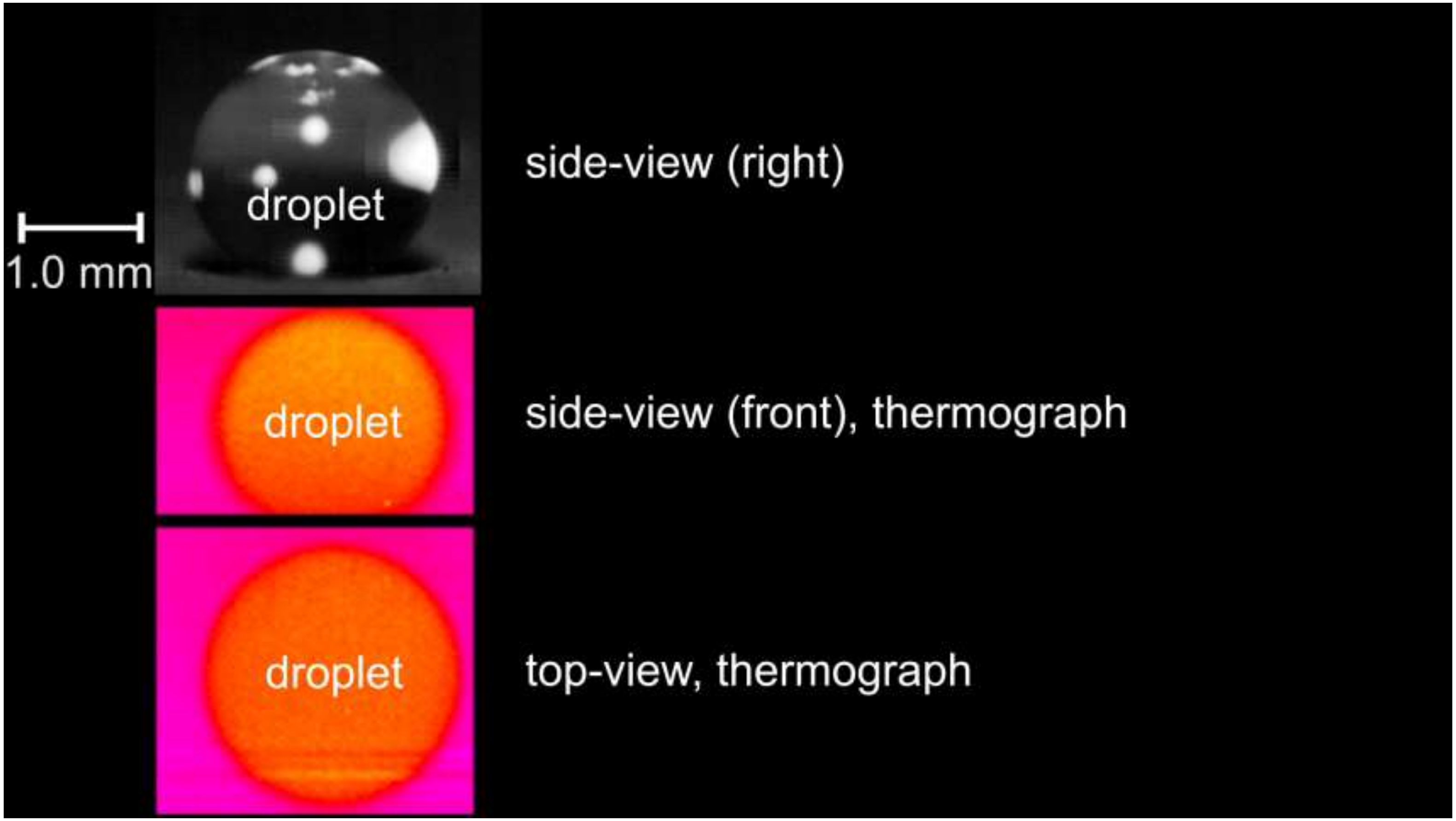
Schutzius, T. M.; Jung, S.; et al. Nature, 2015, 527, 82-85

Evaporative droplet freezing and design of surfaces with intrinsic ice-shedding properties



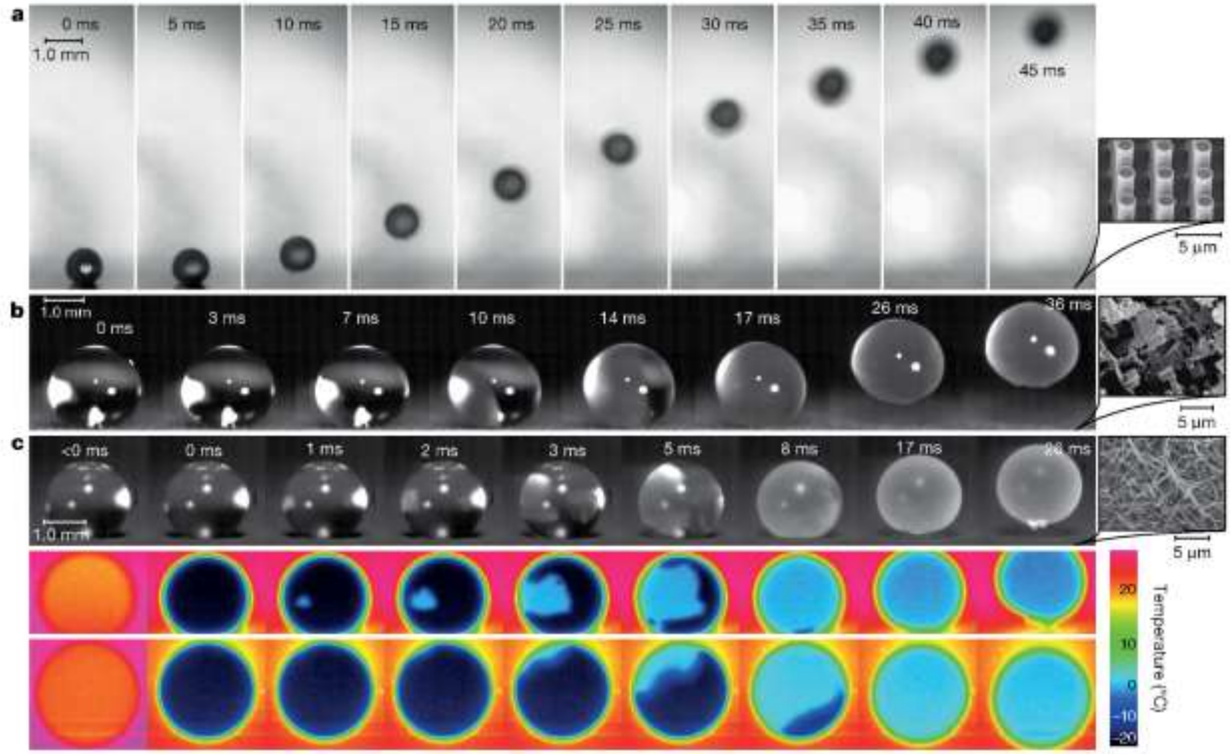
Schutzius, T. M.; Jung, S.; et al. Nature, 2015, 527, 82-85

Recalescence



Schutzius, T. M.; Jung, S.; et al. Nature, 2015, 527, 82-85

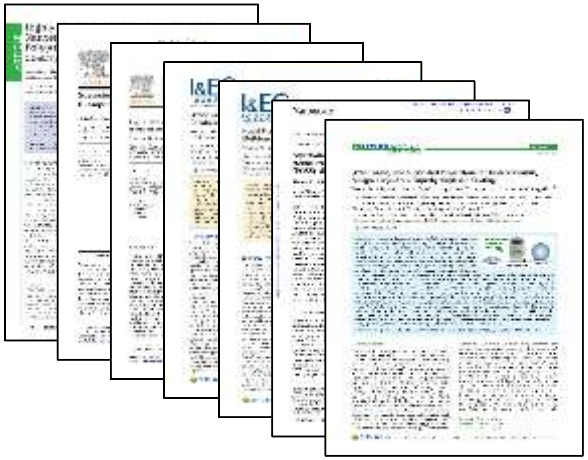
Ice Levitation



Schutzius, T. M.; Jung, S.; et al. Nature, 2015, 527, 82-85

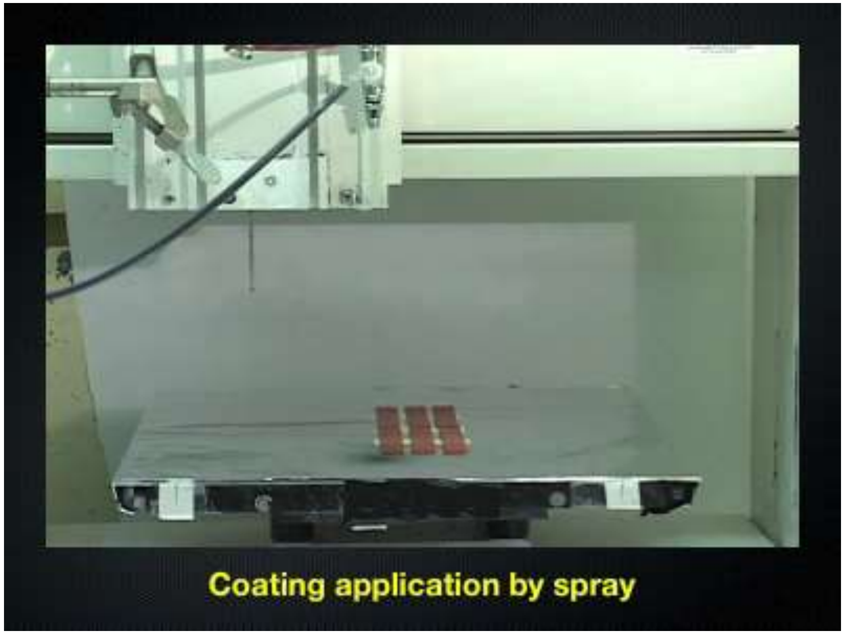
Outline

1. Background: Freezing of sessile supercooled water droplets
2. Spontaneous droplet trampolining on rigid superhydrophobic surfaces
3. Evaporative droplet freezing and design of surfaces with intrinsic ice-shedding properties
4. **Materials considerations: Surface fabrication by large-area techniques**



Materials considerations: Surface fabrication by large-area techniques

- For some applications, particularly isothermal ones, ***the design rules are clear***.
- Therefore, we can focus on large-area fabrication to bring the technology to market.



Schutzius, T. M.; et al. *Composites Part A.* **2011**, *42*, 979-985

Environment and safety: Are engineered surfaces scalable?

Organic solvents

Fluorochemistry

The Lawyer Who Became DuPont's Worst Nightmare

Rob Bilott was a corporate defense attorney for eight years. Then he took on an environmental suit that would upend his entire career — and expose a brazen, decades-long history of chemical pollution.

By NATHANIEL RICH JAN. 6, 2016

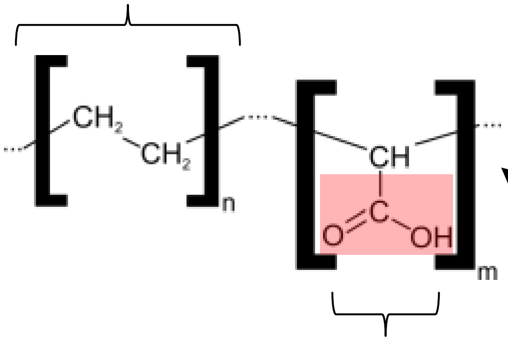
The paradox: A superhydrophobic coating from a water-based (non-fluorinated) dispersion?

Schutzius, T. M.; et al. ACS Appl. Mat. & Int., 2013, 5, 13419-25
Mates, J. E.; et al. I&ECr, 2014, 53, 222-227
Megaridis, C. M.; et al., US Patent Appl.13/193,145. 2013
Megaridis, C. M.; et al.,, US Patent Appl. 13/873,663. 2013

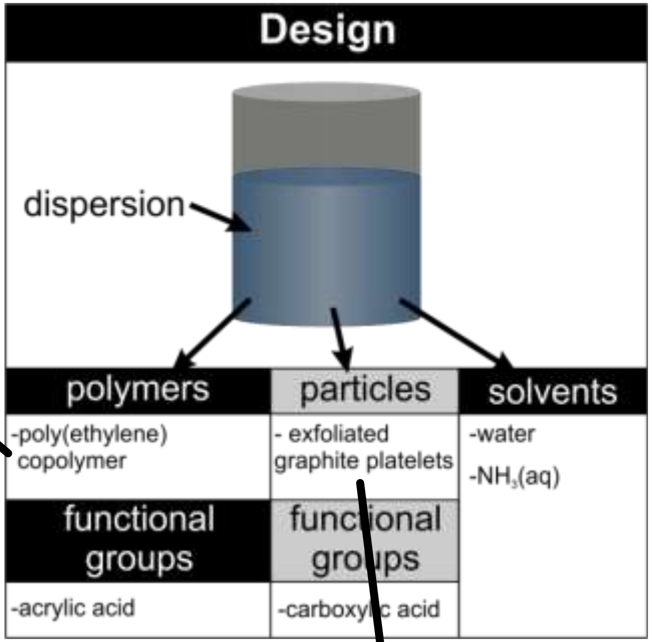
Water-based, non-fluoro paints…

- Utilize materials that are ***hydrophobic*** and also ***water dispersible***.

hydrophobic



pendant functional group

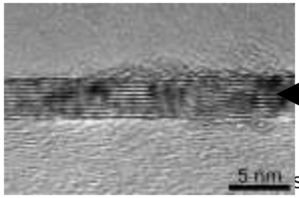


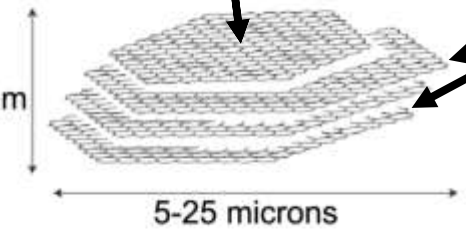
polymers	particles	solvents
-poly(ethylene) copolymer	- exfoliated graphite platelets	-water -NH$_3$(aq)
functional groups	**functional groups**	
-acrylic acid	-carboxylic acid	

- The materials—polyethylene and graphite—are ***inherently hydrophobic***

- They can become ***water-dispersible*** by increasing the pH of the dispersion. ***Functional groups*** become charged.

Schutzius 2013, Megaridis 2013, Megaridis 2013a

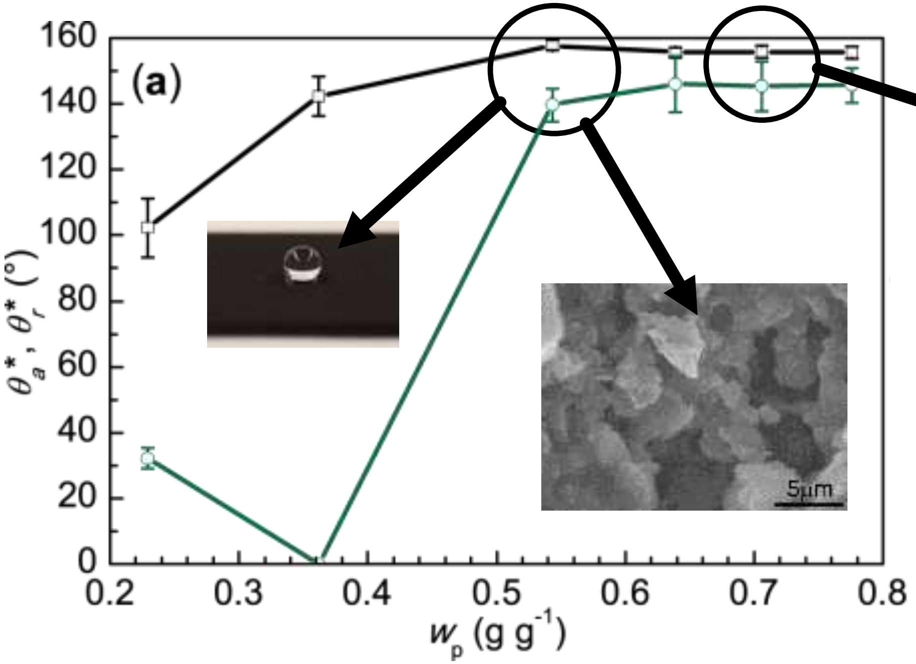




oxygen functional edge groups

Water-based, non-fluoro coatings…

- Taking the stable dispersion, and spray depositing it for varying xGnP concentration we see…

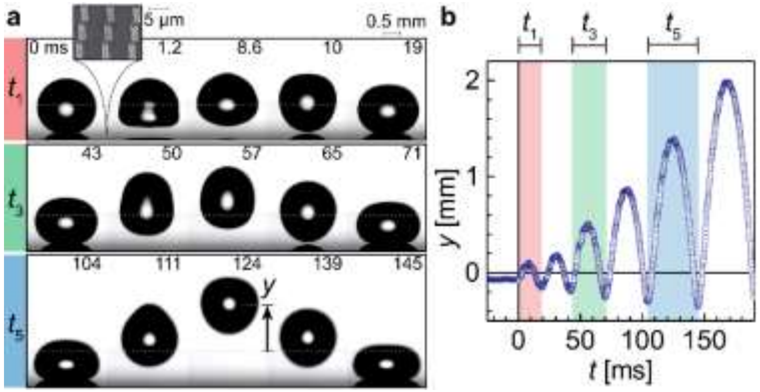


xGnP mass concentration (**w_p**) vs. advancing (**θ_a***) and receding (**θ_r***) contact angles

At **w_p** ≈ 0.7 we see that a ***non-fluorinated***, SHPo coating from a ***water-based*** dispersion has been achieved.

Schutzius, T. M.; et al. ACS Appl. Mat. & Int., 2013, 5, 13419-25
Megaridis, C. M.; et al.,, US Patent Appl. 13/873,663. 2013

Conclusions

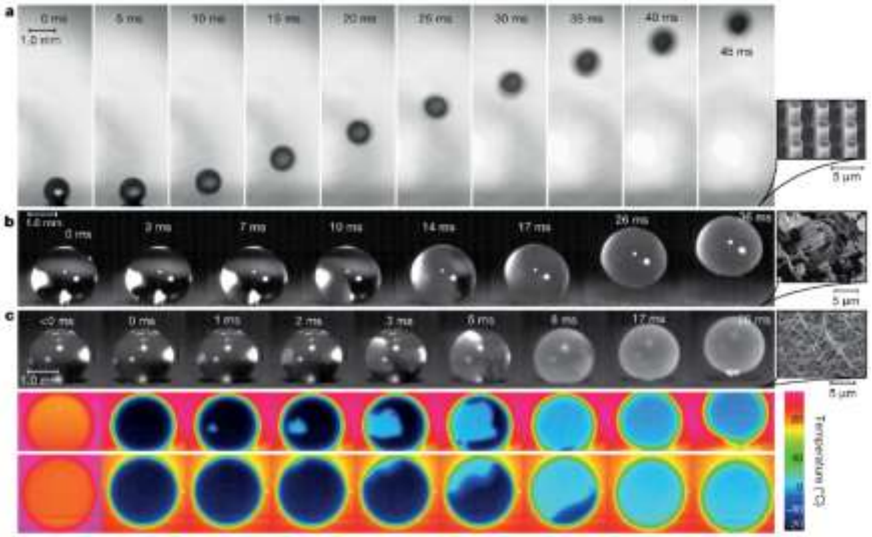


- We showed the role of vaporization in controlling the removal of liquid and as-freezing droplets from superhydrophobic surfaces.

- The thermofluidic behavior was elucidated and surface engineering ***design rules were found***.

- While these observations are only relevant to low-pressure systems, they show how surface texturing can produce ***droplet-surface interactions that prohibit water retention on surfaces***.

Conclusions

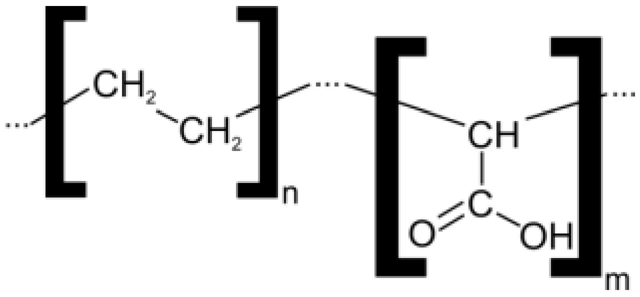


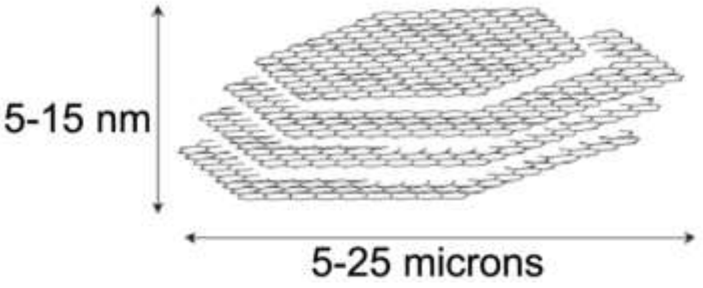
- Explosive vaporization, a natural result of recalescence freezing, was shown to be capable of providing a ***boosting effect***.

- This ice levitation mechanism was demonstrated on a variety of engineered surfaces.

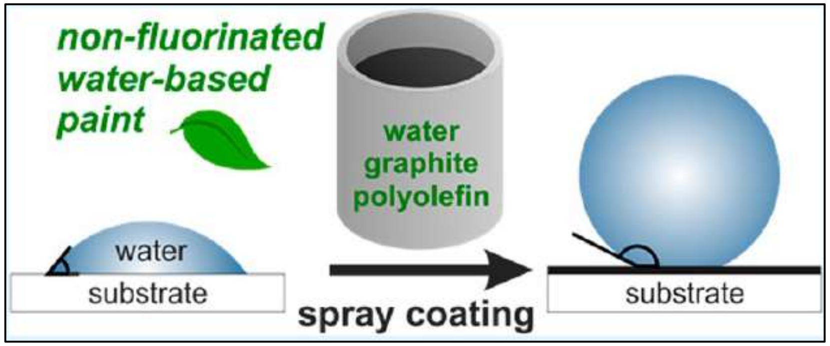
- In general, this work goes towards findings that ***add to our understanding of how droplet–surface interactions can prevent the accumulation of condensed matter on surfaces*** and how these surfaces can be realized in real-world applications.

Outlook





- ***Non-fluorinated***, superhydrophobic coatings from a ***water-based dispersion*** has been achieved.
- Development is ongoing, translating the research back to society.



References

- Barthlott, W. & Neinhuis, C. Purity of the sacred lotus, or escape from contamination in biological surfaces Planta, 1997, 202, 1-8
- Bird, J. C.; Dhiman, R.; Kwon, H.-M. & Varanasi, K. K. Reducing the contact time of a bouncing drop Nature, 2013, 503, 385-388
- Boreyko, J. B. & Chen, C.-H. Self-Propelled Dropwise Condensate on Superhydrophobic Surfaces Physical Review Letters, 2009, 103, 184501
- Brasseur, G. P. & Solomon, S. Aeronomy of the middle atmosphere Springer, 2005
- Jung, S.; Tiwari, M. K. & Poulikakos, D. Frost halos from supercooled water droplets. Proceedings of the National Academy of Sciences of the United States of America, 2012, 109, 16073-16078
- Koch, K. & Barthlott, W. Superhydrophobic and superhydrophilic plant surfaces: an inspiration for biomimetic materials Philosophical Transactions of the Royal Society A: Mathematical, Physical & Engineering Sciences, 2009, 367, 1487-1509
- Liu, Y.; Moevius, L.; Xu, X.; Qian, T.; Yeomans, J. M. & Wang, Z. Pancake bouncing on superhydrophobic surfaces Nat Phys, 2014, 10, 515-519
- Maitra, T.; Antonini, C.; Tiwari, M. K.; Mularczyk, A.; Imeri, Z.; Schoch, P. & Poulikakos, D. Supercooled Water Drops Impacting Superhydrophobic Textures Langmuir, 2014, 30, 10855-10861
- Mates, J. E.; Schutzius, T. M.; Bayer, I. S.; Qin, J.; Waldroup, D. E. & Megaridis, C. M. Water-Based Superhydrophobic Coatings for Nonwoven and Cellulosic Substrates Industrial & Engineering Chemistry Research, 2014, 53, 222-227
- Megaridis, C. M.; Schutzius, T. M.; Bayer, I. S. & Qin, J. Superhydrophobic Compositions, US Patent Application 13/193,145. 2013
- Megaridis, C. M.; Schutzius, T. M.; Bayer, I. S.; Qin, J. & Waldroup, D. E. Non-Fluorinated Water-Based Superhydrophobic Compositions, US Patent Application 13/873,663. 2013
- Parker, A. R. & Lawrence, C. R. Water capture by a desert beetle Nature, 2001, 414, 33-34
- Schutzius, T. M.; Jung, S.; Maitra, T.; Graeber, G.; Köhme, M. & Poulikakos, D. Spontaneous Droplet Trampolining on Rigid Superhydrophobic Surfaces Nature, 2015, 527, 82-85
- Schutzius, T. M.; Bayer, I. S.; Qin, J.; Waldroup, D. & Megaridis, C. M. Water-Based, Nonfluorinated Dispersions for Environmentally Benign, Large-Area, Superhydrophobic Coatings ACS Applied Materials & Interfaces, 2013, 5, 13419-13425
- Zheng, Y.; Gao, X. & Jiang, L. Directional adhesion of superhydrophobic butterfly wings Soft Matter, 2007, 3, 178-182

Acknowledgements

Prof. Poulikakos
ETH

Prof. Megaridis
UIC

Prof. Tiwari
UCL

Dr. Bayer
IIT

Dr. Mates
NRC Postdoc

Dr. Jung

Dr. Eghlidi (ETH)
Dr. Maitra (Stanford)
Gustav Graeber (ETH)

COFUNDED BY
MARIE CURIE ACTIONS

ETH Fellowship

UIC
UNIVERSITY OF ILLINOIS AT CHICAGO

Dean’s Scholar

Schutzius, T. M.; Jung, S.; et al. Nature, 2015, 527, 82-85