Measurements of contact angles at subzero temperatures and implications for ice formation

Golrokh Heydari[1], Mikael Järn[2], Per Claesson[1,2]

[1]Department of Chemistry, Surface and Corrosion Science, Royal Institute of Technology, KTH

[2]SP Technical Research Institute of Sweden, Chemistry Materials and Surfaces

SP Technical Research Institute of Sweden

Outline

- Introduction to SP
- TopNANO project
- Theoretical background
- Contact angles
- Superhydrophobic surfaces
- Experiments
- Results
- Summary

YKI, Institute for Surface Chemistry

Your R&I Partner
in Applied Surface Chemistry

YKI your Science Partner

1 Jan 2013 →

SP your Science Partner

SP Chemistry, Materials and Surfaces

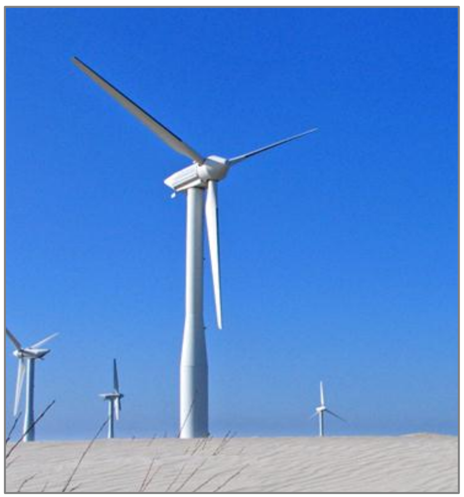
About SP

The SP Group	is wholly owned by RISE
Subsidiaries	7
Employees	1 200
Revenues	Euro 120 million
Customers	> 10 000
Ph.D. and Lic. Eng.	approx. 300
Ph.D. students	approx. 80
Degree projects	approx. 70
Adjunct professors	26

TOPNANO – Nordic project with funding from industry and the Top-level Research Initiative

www.topnano.se

- Keep aircraft, wind turbine blades and heat exchanger surfaces free from ice and contaminants using nanotechnology surface coatings
- Focus on passive anti-icing



Duration 2010-2014
Grant from Top-level Research Initiative. Total project budget 35 MSEK

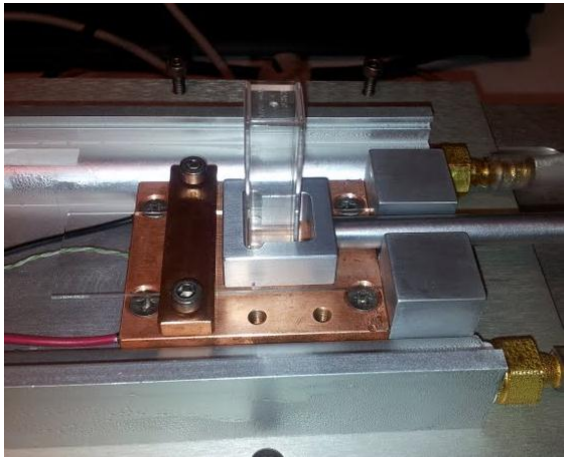
Research partners in the TopNano project

Industrial partners in the TopNano project

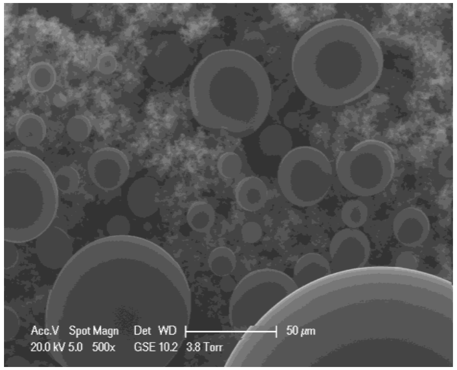
- Companies from aircraft, wind power, heat-exchanger industry and coating companies

Methodologies

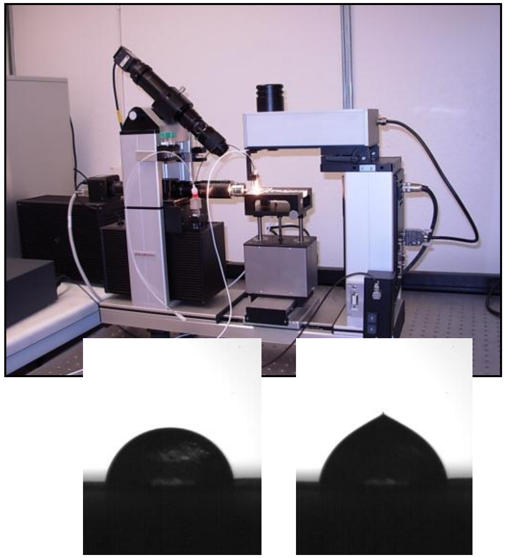
Ice adhesion



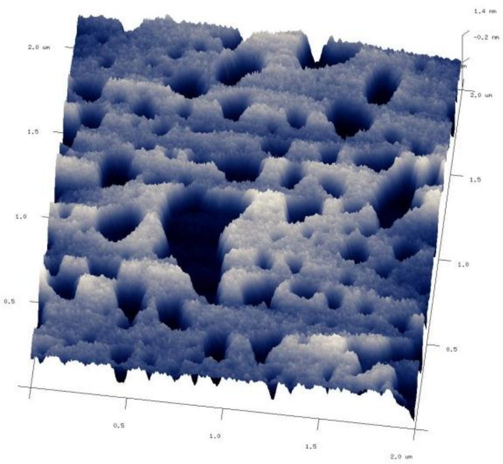
E-SEM



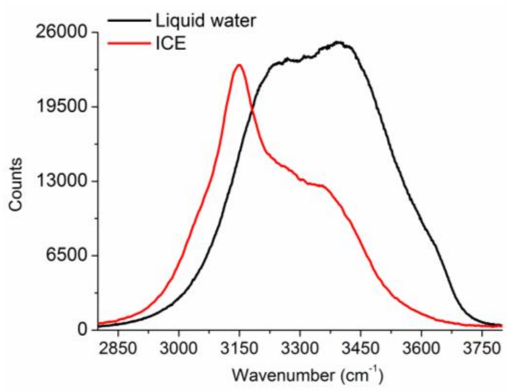
Contact angle device



AFM

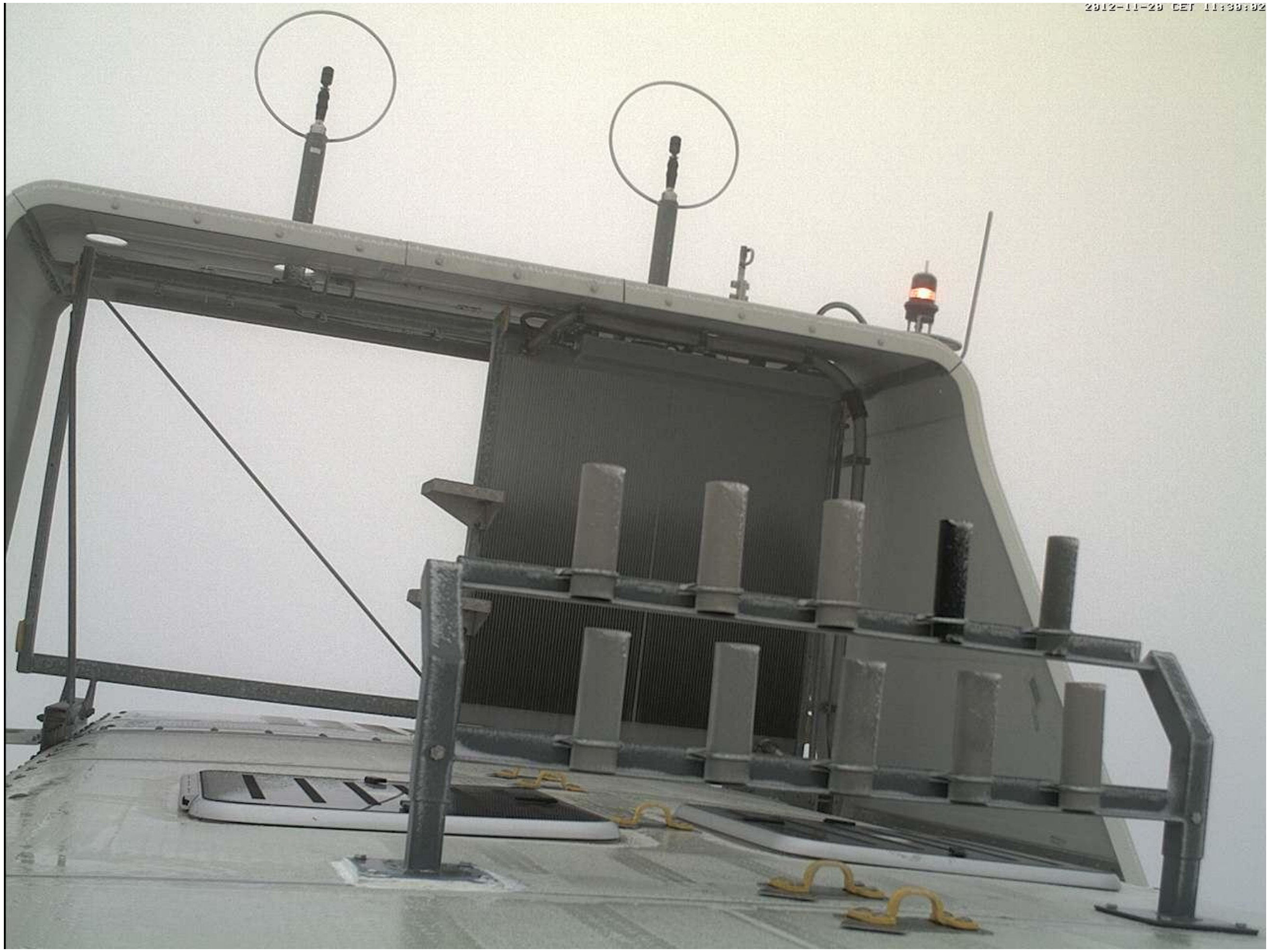


Spectroscopic methods

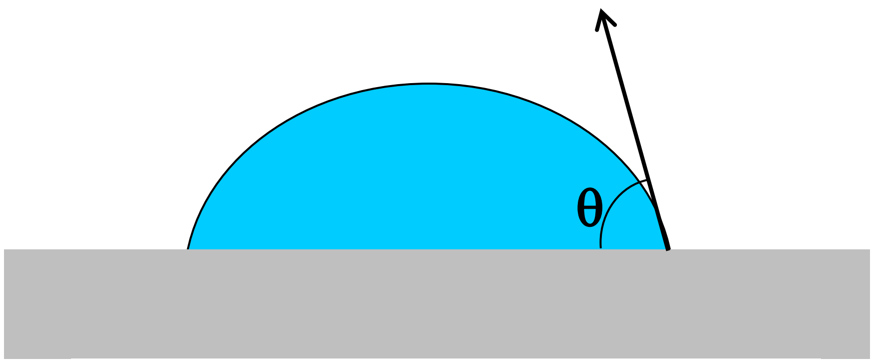


Field tests (on-going)

- Test site: Stor-Rotliden Wind Power Plant (Vattenfall)

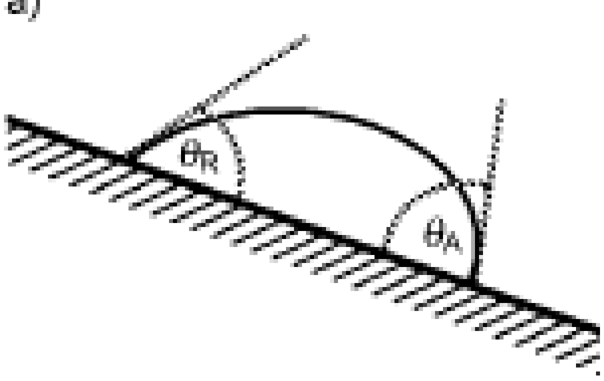


Theoretical background – Contact angle



θ < 90° hydrophilic

θ > 90° hydrophobic



θ_A = Advancing contact angle

θ_R = Receding contact angle

$\theta_A - \theta_R$ = contact angle hysteresis

Large hysteresis = high friction

Low hysteresis = low friction

Superhydrophobic surfaces

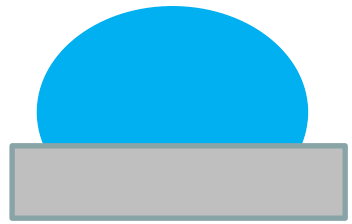
- Superhydrophobic surfaces = surfaces that repel water ($\theta > 150°$)

- Inspired by nature:

Lotus leaf

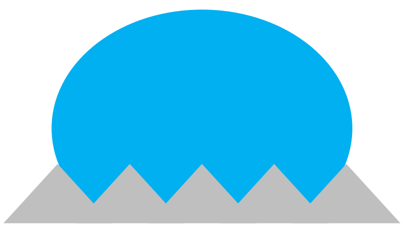
R. Blossey, Nature Mater. **2003**, *2, 301.*

Superhydrophobic surfaces



Smooth hydrophobic surface
-maximum water contact angle ~ 120° (CF_3)

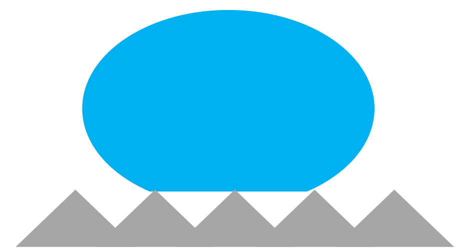
Wenzel state



-liquid wets the surface texture

Rough hydrophobic surfaces

Cassie state



-droplet rests on a solid-air composite surface

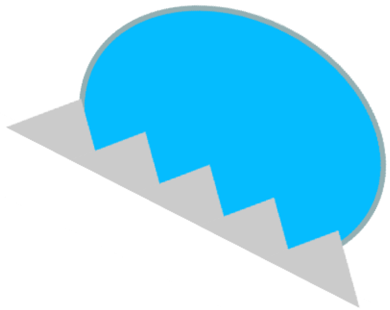
R. N. Wenzel, *Ind. Eng. Chem.*, **1936**, *28*, 988.

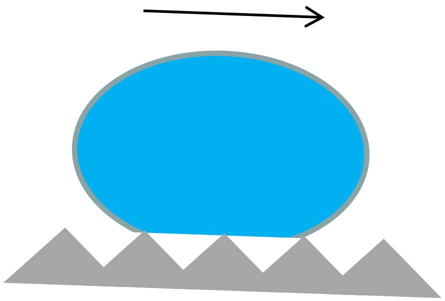
A. B. D. Cassie, S. Baxter, *Trans. Faraday Soc*. **1944**, *40*, 546.

Characteristics for Wenzel and Cassie states

Wenzel
High hysteresis (”high friction”)

Cassie
Low hysteresis (”low friction”)





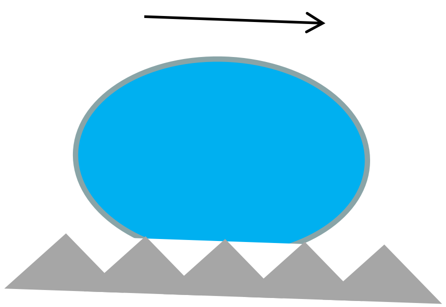
•Superhydrophobicity is achieved by a combination of low surface energy and roughness!
•Cassie state is required for superhydrophobicity

Superhydrophobic coatings as anti-icing surfaces

- General hypothesis: Superhydrophobic = Icephobic

- Water droplets roll off the surface before freezing → no or little ice build up

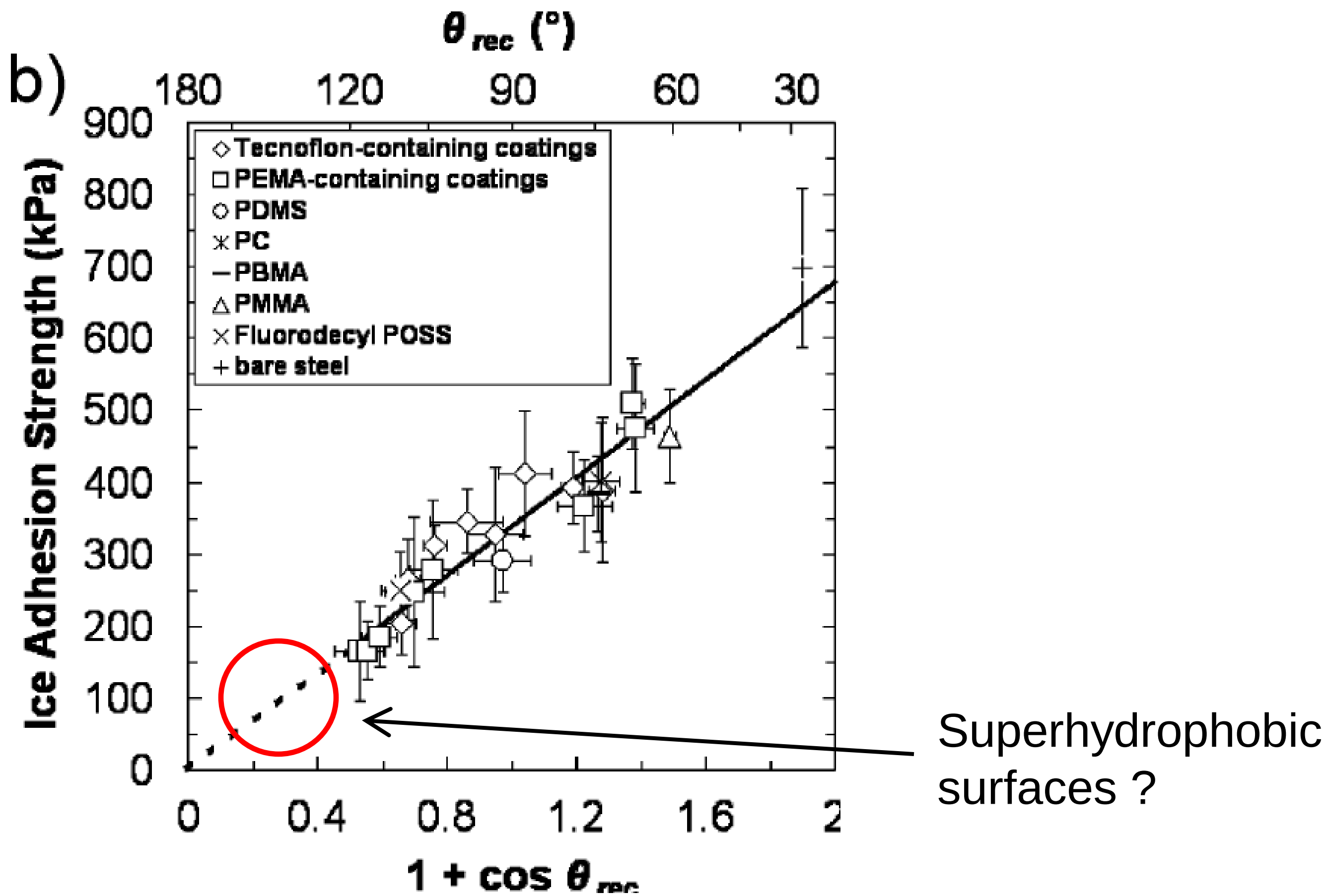
- Water freezes in the Cassie state → delayed freezing due to an insulating air layer and easier removal of ice because of lower adhesion



Cassie
Low hysteresis (”low friction”)

Ice adhesion strength vs. Contact angle

•Good correlation between ice adhesion strength and receding water contact angle at ambient temperature for a series of coatings



SP Technical Research Institute of Sweden

A. J. Meuler et al. ACS *Appl. Mater. Interfaces* **2010**, *2*, 3100

Aim of the study

To investigate how different surface properties affect

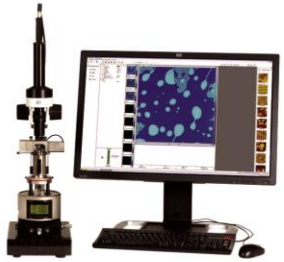
1. contact angles at subzero temperatures
2. freezing of supercooled water droplets

Two model surfaces were chosen with similar chemistry but different roughness

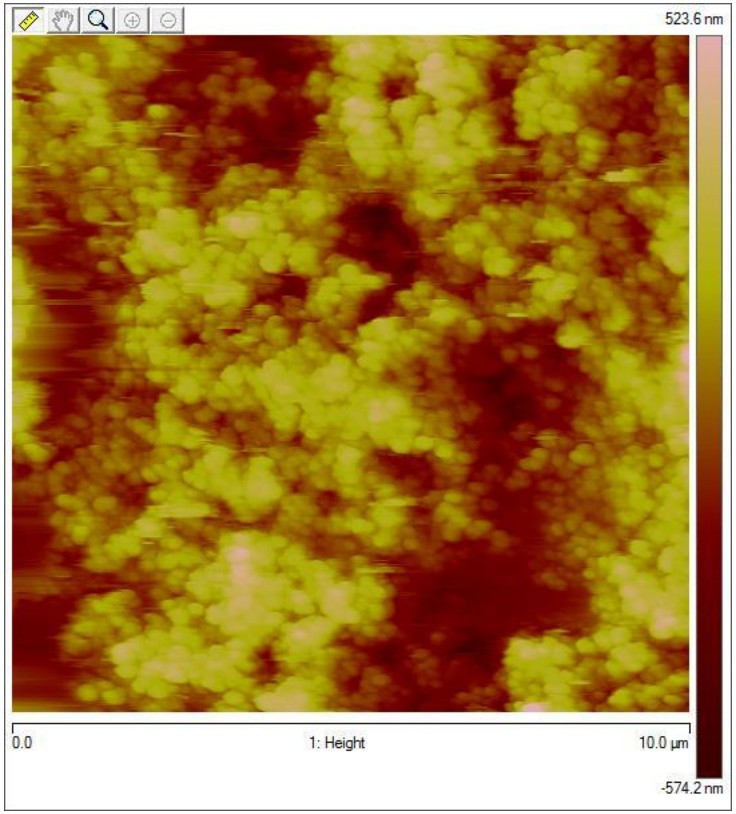
1. Superhydrophobic surface (SiO_2 nanoparticles coated with fluorosilane)
2. Smooth hydrophobic surface (Silicon wafer coated with fluorosilane)

Material Characterization

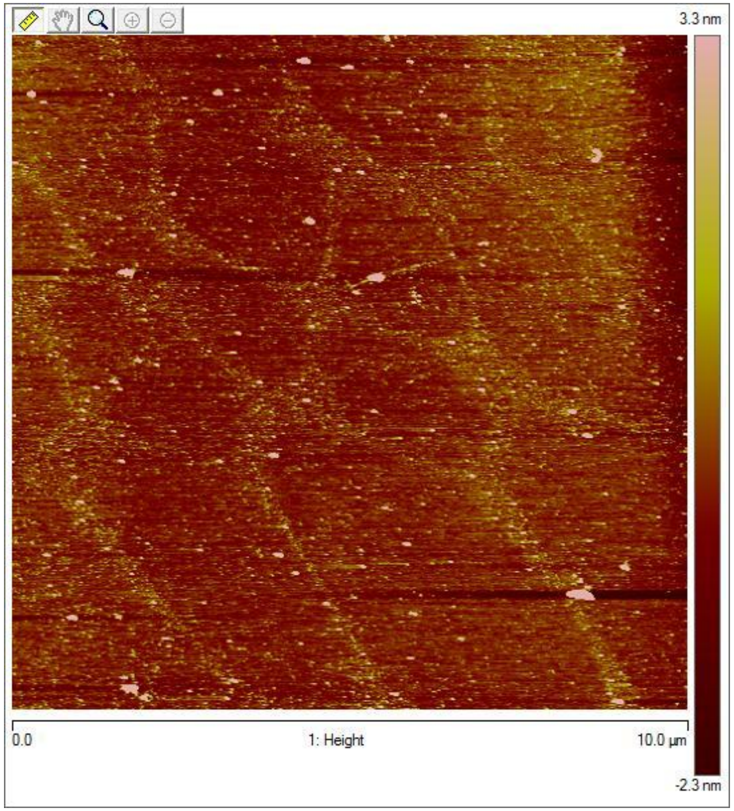
AFM imaging



Superhydrophobic (RMS: 164 nm)

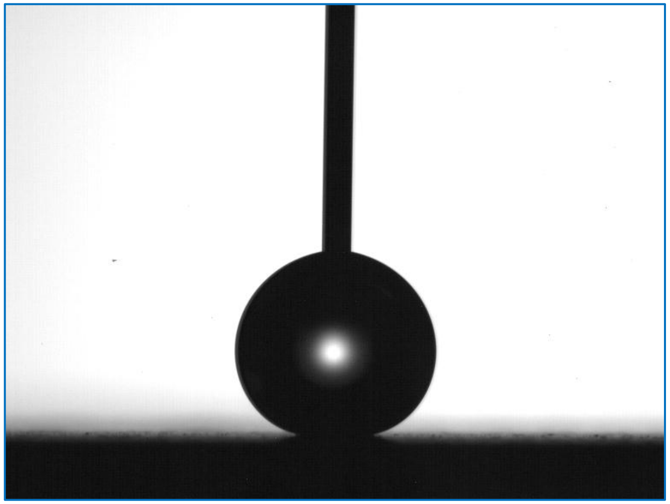


Hydrophobic (RMS: 1 nm)

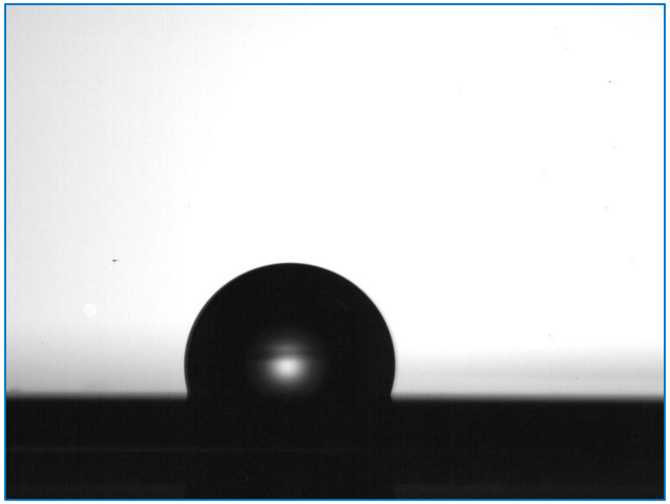


Material characterization
Contact angles

Superhydrophobic



Hydrophobic



Surface	ACA(º)	RCA(º)	Hysteresis(º)
Hydrophobic	107	94	13
Superhydrophobic	161	161	0

Experiments

1. Contact angle measurements at subzero temperatures

2. Freezing temperature of supercooled water droplets

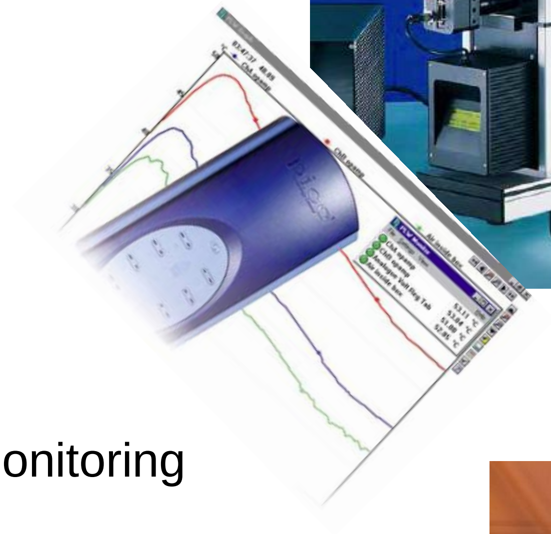
3. Freezing delay of supercooled water droplets

Temperature Controlled Measurements

www.dataphysics.de

DataPhysics OCA40 micro instrument

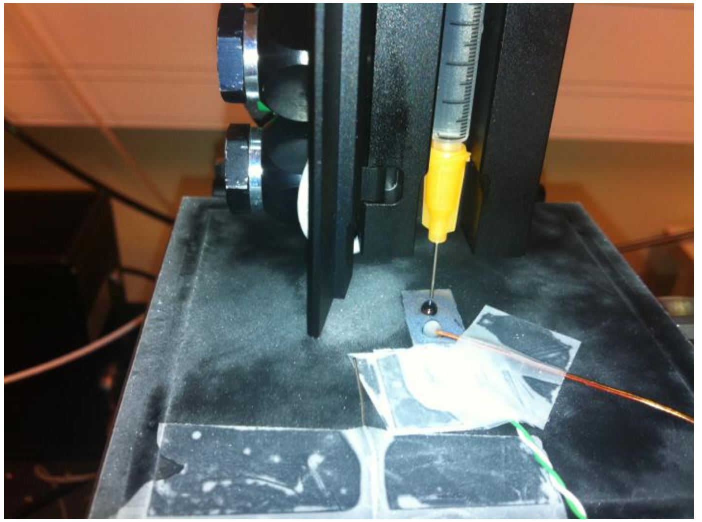
- high speed CCD camera (2200 image s^{-1})
- 20X magnification
- Peltier cooling stage
- tilting to 90°



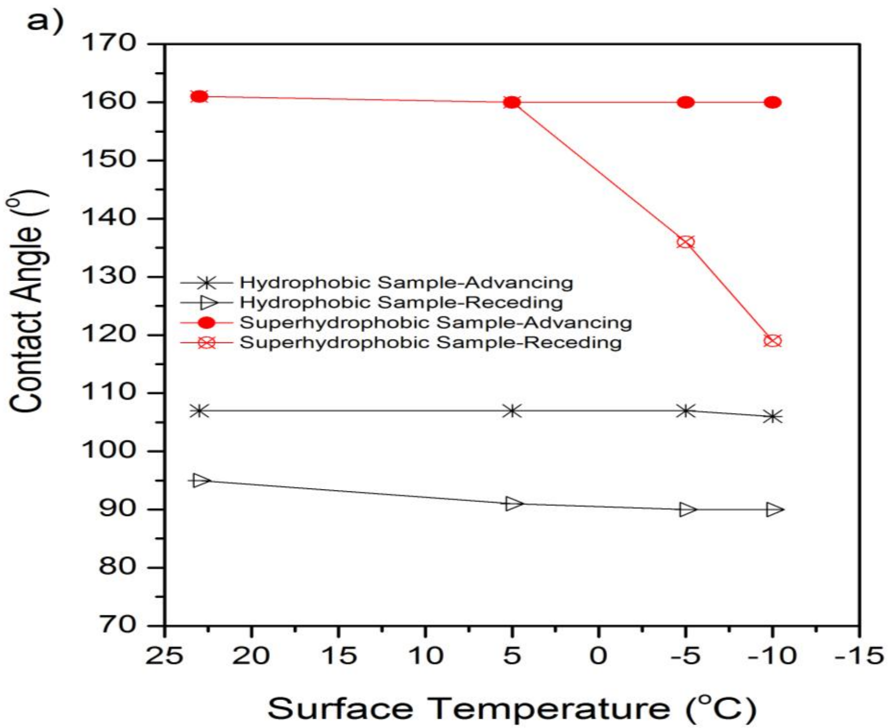
- controlled climate room
- dry N_2 atmosphere
- Milli-Q water (18.2 MΩ cm)

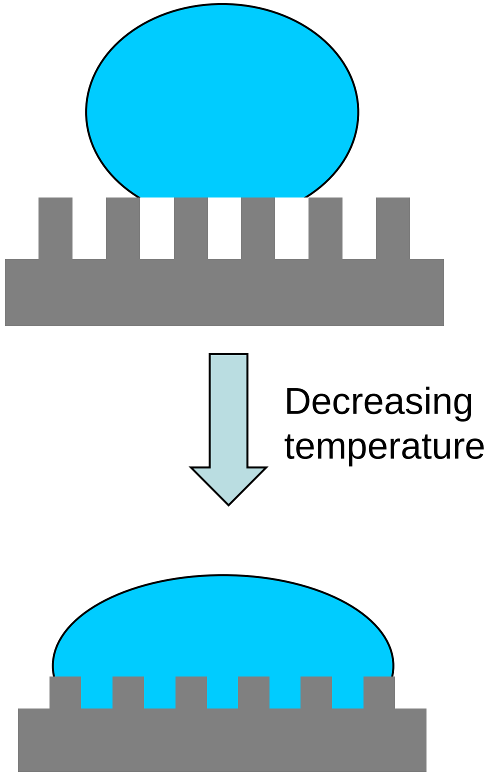
Equipment for temperature monitoring

- thermo-sensors for monitoring of the air, droplet and surface temperature
- high resolution temperature logger



Contact angle as a function of temperature





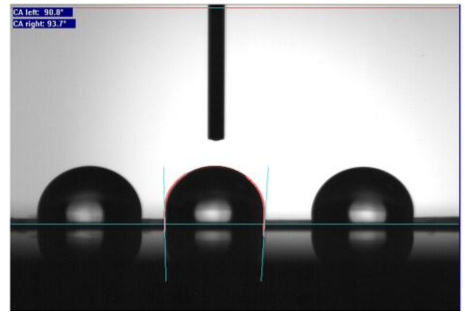
Superhydrophobic sample: Cassie to Wenzel transition at subzero temperatures → increased hysteresis that implicates higher ice adhesion

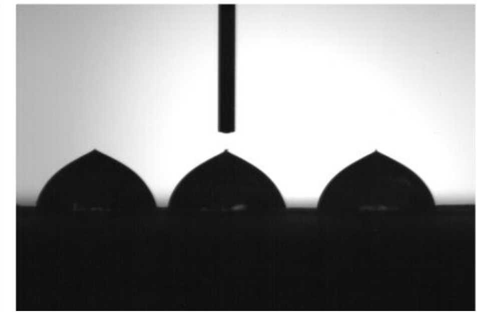
The contact angle on the smooth hydrophobic surface is unaffected by temperature

Freezing Temperature of Supercooled Water Droplets

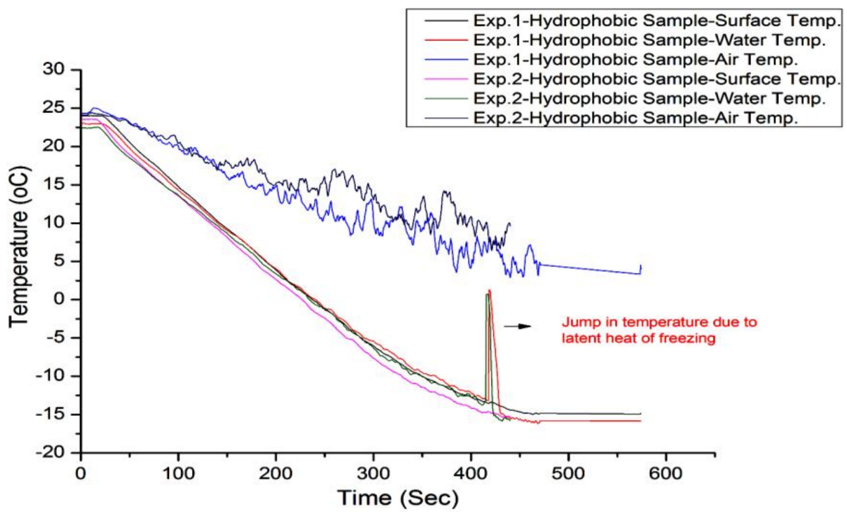
- The freezing point from

- the change in optical appearance of the droplets



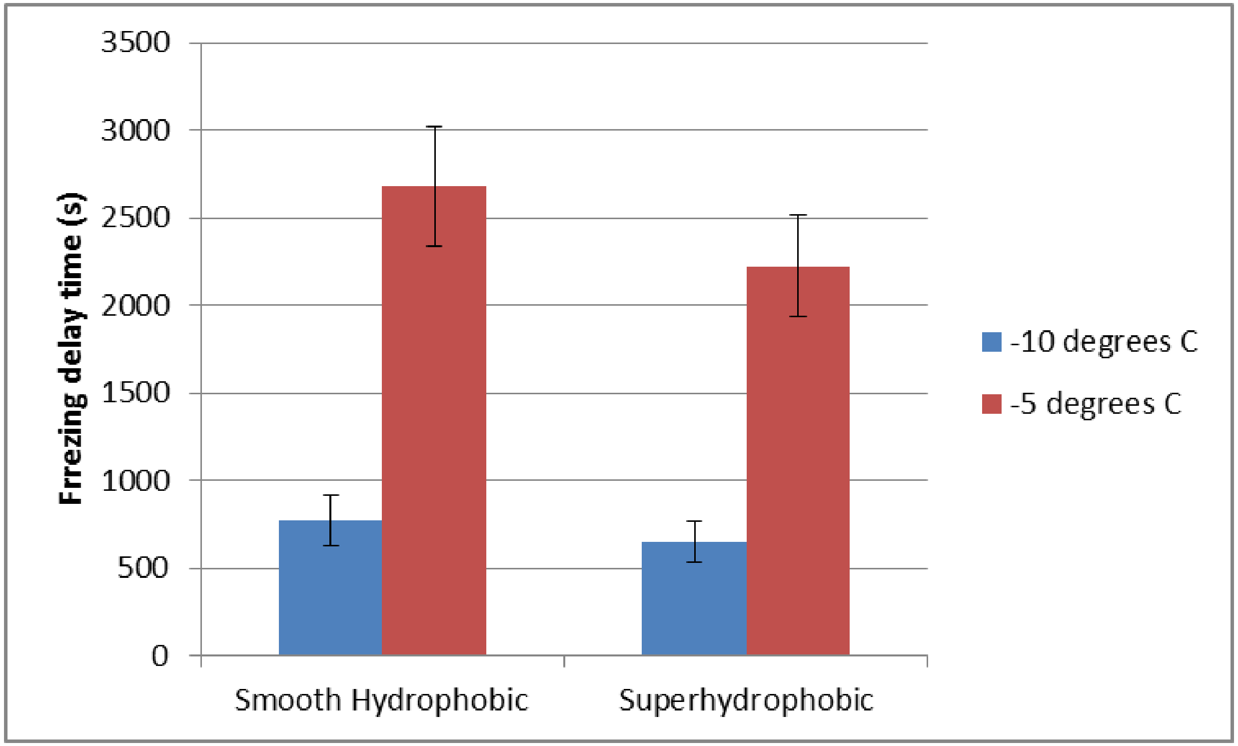


- peak in droplet temperature due to latent heat of freezing



Very similar freezing temperature (-17°C to -22°C) on hydrophobic and superhydrophobic surfaces

Freezing Delay of Supercooled Water Droplets



No improvement in freezing delay time on the superhydrophobic surface!

Summary

- The contact angle on the smooth hydrophobic surface was unaffected by temperature

- The contact angle hysteresis increased on the superhydrophobic surface at subzero temperatures, due to a wetting transition (vapor condensation into the air pockets of the rough surface)

→Higher adhesion of the water droplet which suggests higher ice adhesion

- No delay in freezing time was observed for the superhydrophobic surface as compared to the smooth hydrophobic surface at -5°C and -10°C

- The findings suggest limitations for the use of superhydrophobic coatings as anti-icing materials, but further studies in dynamic conditions are needed