Hydrophobicity under Condensation

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International Workshop on Surface Icing and Assessment of De-Icing / Anti-Icing Technologies
24. - 25. January 2017, Bremen, Germany

Supported by the European Union
through the Horizon 2020 project
"MATChING" (www.matching-project.eu)
Grant Agreement no. 686031

Hydrophobicity under condensation

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1. **More efficient surface condensers for thermal power plants**

2. How to achieve and exploit retarded frost spreading

MATChING: Materials technologies for Performance Improvement of Cooling Systems in Power Plants

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Technology overview

RECOVER EVAPORATION

Water recovery from plume through **membrane condenser** (MC)

EVAPORATION

:
REDUCE EVAPORATION

Advanced Hybrid Systems

ALTERNATIVE WATER SOURCES

INTAKE WATER

Novel membrane based technologies for intake water pretreatment

Special materials/coatings to handle "dirty" fluids

CONDENSER

ENHANCE HEAT TRANSFER AND EQUIPMENT ROBUSTNESS

Coating to promote drop-wise condensation

Special materials/coatings to handle "dirty" fluids

Recirculating water

RECOVER BLOWDOWN

Novel membrane based technologies for blowdown recovery

BLOWDOWN WATER

REDUCE BLOWDOWN

Special materials/coatings to handle "dirty" fluids in CT and condenser

Novel membrane based technologies to enhance intake water quality

Novel Circulating water conditioning systems

Surface condensers of thermal power plants

Tube bundle in a shell (Picture: Old museum condenser)

Outer diameter: Condensing steam
Inner diameter: Cooling water

Surface condensers of thermal power plants

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Rapid condensation

- Continuous water film on the tubes
- Water condenses on top of the water film
- Constrains heat transfer

MATChING project target

- Dropwise condensation
- Water condenses directly on the coated tube surface
- Higher efficiency

In the future, suitable hydrophobic surfaces shall **save energy & cooling water**

Theoretical background for improved drainage

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Indicator for improved drainage: Low critical diameter d_{crit}
Diameter that a growing water drop has to reach to start sliding down a surface

A low d_{crit} is expected to be relevant to achieve both improved heat transfer for surface condensers and retarded frost spreading.
(Kim et al., ACSNano 6 (2012), 6569)

d_{crit} can be calculated from advancing and receding contact angles.

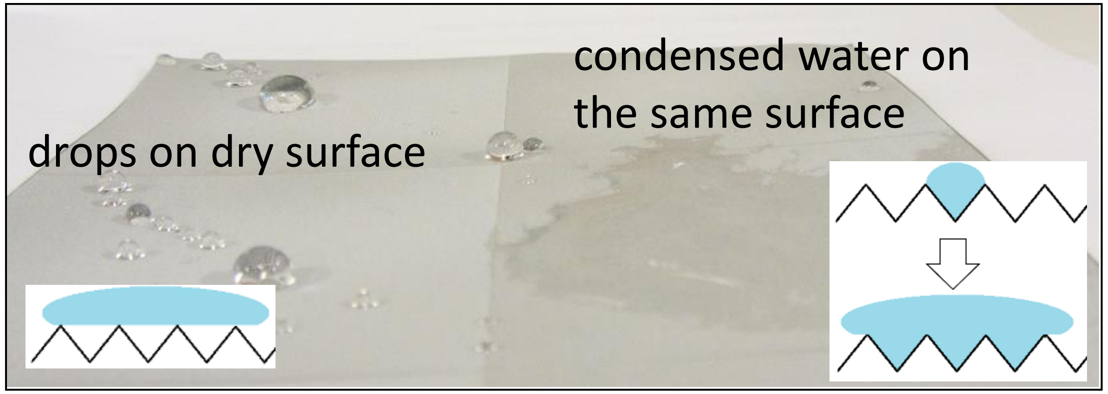
$$d_{crit} = \sqrt{\left(\frac{24 \, sin^3\theta adv \, \gamma(cos\theta rec - cos\theta adv)}{\pi\rho(1 - cos\theta adv)^2(2 + cos\theta adv) g sin\alpha}\right)}$$

Optimal surface for low d_{crit}:
High receding contact angle and **low contact angle hysteresis**

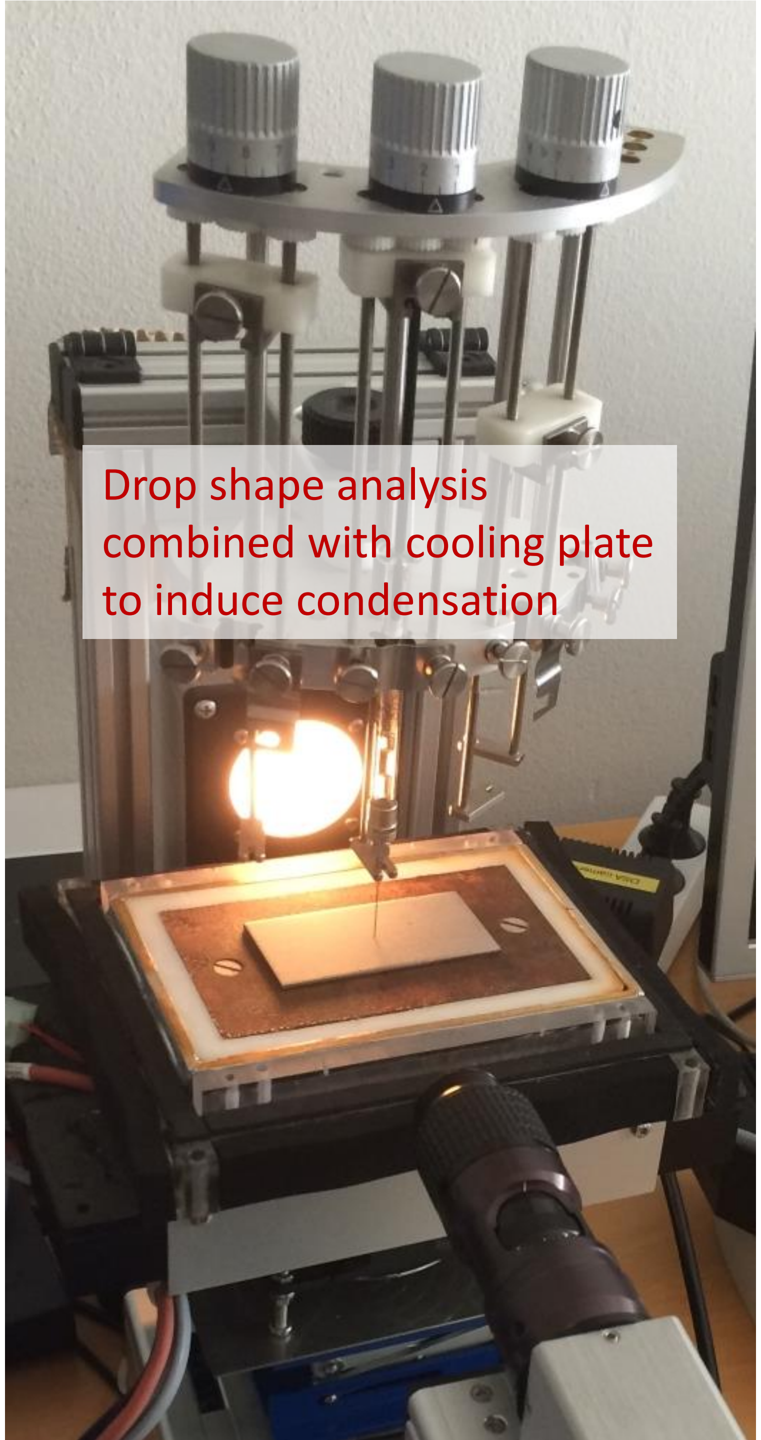
Investigation of receding water contact angles under condensation

Smooth surfaces
Contact angles on dry surfaces and during condensation are identical

Micro-/nanostructured surfaces, including superhydrophobic surfaces:
Contact angles on dry surfaces and during condensation may vary
→ Required testing under condensation



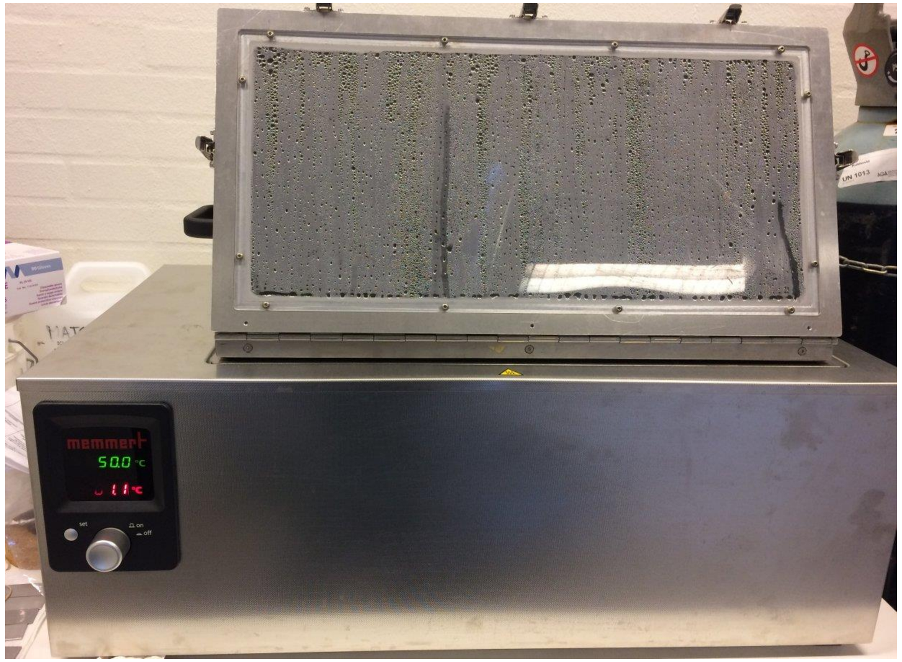
Example of a surface providing superhydrophobicity (air-pockets, "Cassie Baxter state"), that collapses under condensation when small droplets nucleate inside the air-pocket structure



Durability of surface hydrophobicity under condensation

Exposure to condensation for month or years at ~40 °C (Real power plant: 25-40 °C)

Simple laboratory test: Water bath + modified lid with sample holder, passive cooling through backside



Front view, lid closed

Transverse view, lid opened

Further power plant related challenge: Biofouling

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Cooling water is typically from the sea, from rivers or lakes

- Bio-fouling
- Lower heat transfer
- Higher pressure drop

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MATChING project target

- Anti-fouling coating
- Effective
- Non-toxic
- Thin enough to assure heat transfer

Future coating development shall

- Save energy
- Save cooling water
- Allow unusual water sources (low quality water)

Further power plant related challenge: Corrosion in geothermal power plants

Corrosive brine (high salt concentrations)

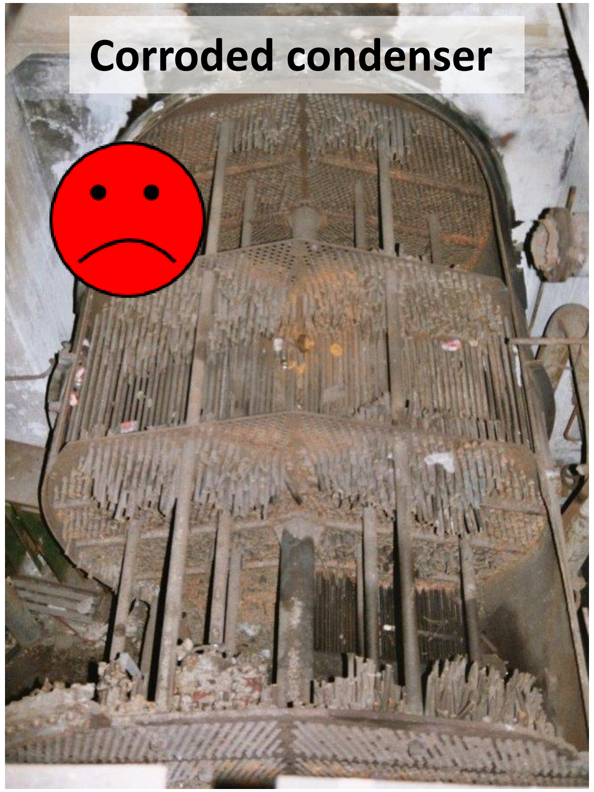
- Either regular replacement
- Or expensive, resistant materials such as titanium

Target (MATChING project)

- Economic material such as carbon steel
- Economic coating with outstanding corrosion protection

Future coating development shall

- Reduce costs of geothermal power plants
- Support the development of geothermal energy as **regenerative energy source**



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Hydrophobicity under condensation

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1. More efficient surface condensers for thermal power plants

2. **How to achieve and exploit retarded frost spreading**

Passive anti-ice surfaces (no heating, no leaching agents)

Icing problems (examples)

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Options for passive anti-ice surfaces

Low ice adhesion

- Frost forms, but easy removal
- Promising, we consider it for future development

Temporarily avoid freezing or delay freezing

- Especially for refrigeration, heat pumps and HRV
- For wind turbines/aircraft?
- Requires periodic defrosting (e.g. by heating)
- A **coating saves energy** by allowing longer time between defrosting intervals

Ice tester (Both for freezing and frost propagation tests)

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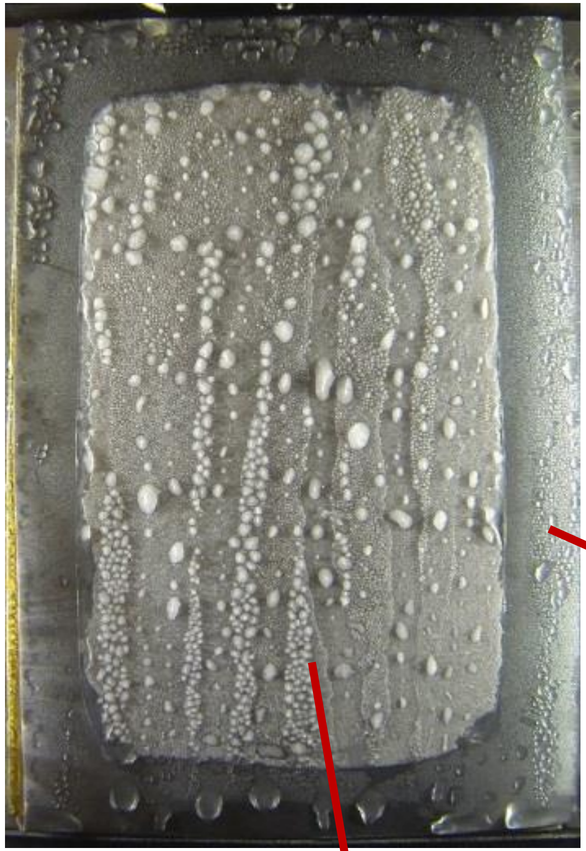
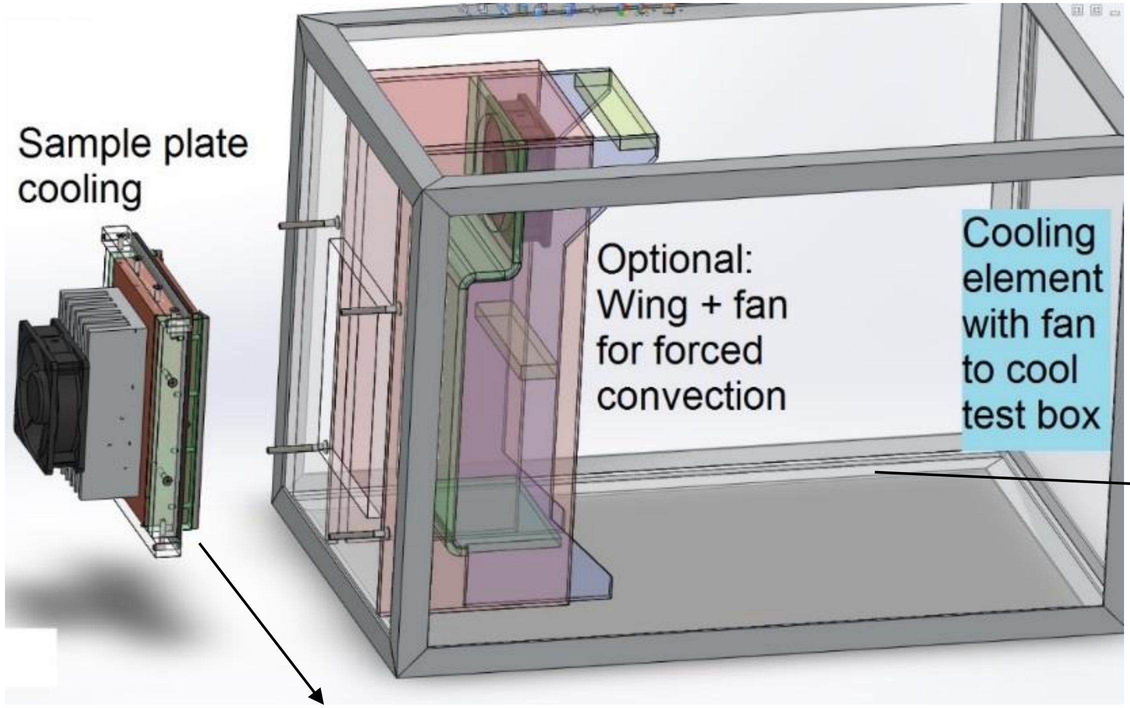
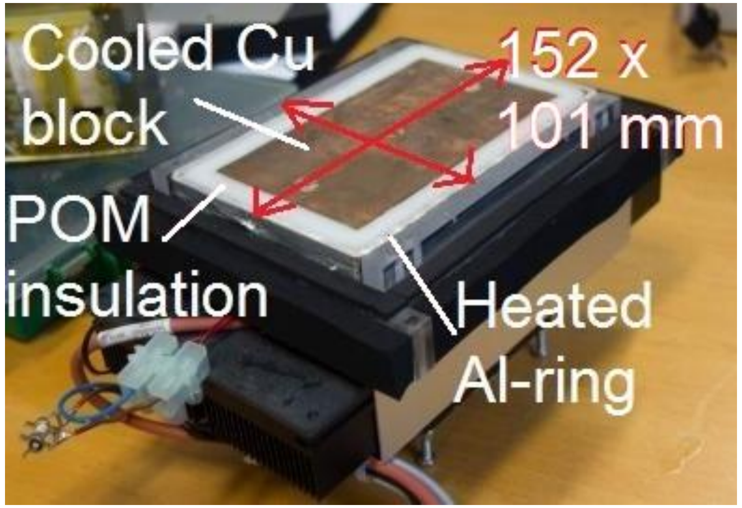


central area (100 cm^2) with practically constant temperature

heated edge prevents contact freezing from the backside



Humid atmosphere to continuously induce condensation on the sample surface



Freezing (ice nucleation)

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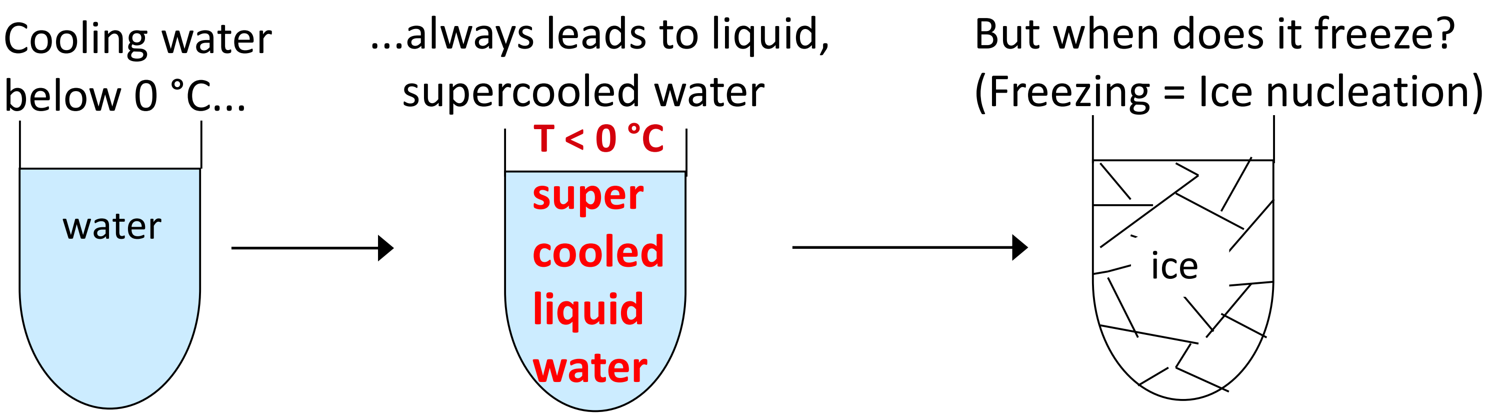
Common knowledge: Water freezes just below 0 °C? → Only true for large structures



- Ice nucleation happens at random (you cannot predict time or temperature of a single experiment)
- Ice nucleation happens with a distinct probability

Excursus: Yatzee/Kniffel game.

"Yatzee": All five dices show the same number

→ It can be your next cast, but it can also take (annoyingly) long

(Happens at random, but with a distinct probability)

Freezing (ice nucleation)

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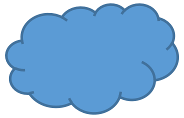
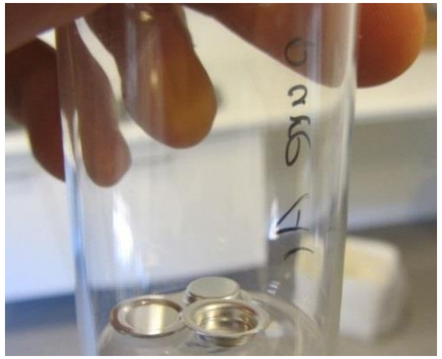
Ice nucleation probability depends on

- Temperature: Lower T → higher freezing probability → faster freezing (by average)
- Availability of a solid surface
  → Kind of surface (practically all solid surfaces induce freezing to some extend)
  → Surface area!



Drops in clouds can be liquid below -30°C

"Yatzee" in one single roll.
Chance by average: One success for every 1296 rolls

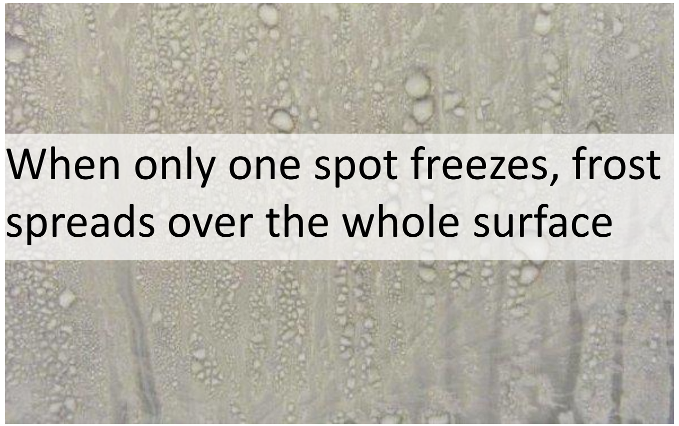


We observed liquid drops in DSC-pans (A ~0.03 cm^2) at -20°C for 1 h.

We observed liquid water on test plates (A=100 cm^2) at -7°C for several hours

Real object (e.g. heat exchanger, A ~1 to 500 m^2, at least 300.000 times larger than a DSC-pan)

Rolling the dices 300.000 times, hoping for at least one "Yatzee" → very easy



When only one spot freezes, frost spreads over the whole surface

Freezing (ice nucleation)

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Simplified conclusion for temperatures just below 0°C, for example 0 to -5°C, maybe to -10°C

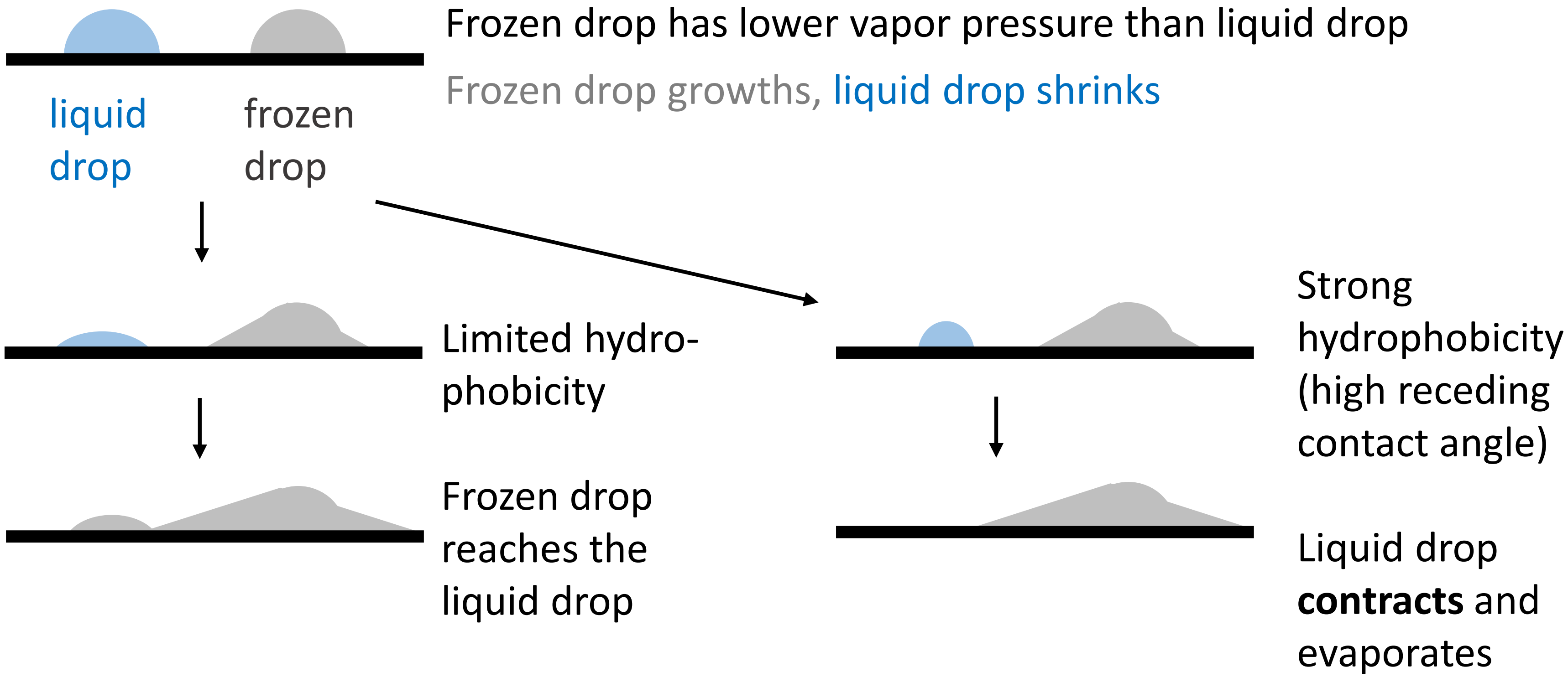
- The freezing probability of liquid water is considerably low
- Real devices freeze fast, as the large areas counteracts the low freezing probability
- When one spot freezes, frost propagates fast on most technical surfaces
- When reading results on "Freezing point depressing surfaces" or "Surfaces inhibiting ice nucleation" obtained on microscopic or small-size equipment:
  These surfaces usually show a negligible effect on full size devices ☹.

Frost spreading (frost propagation)

Hydrophilic surface, continuous water film → instant frost spreading

Hydrophobic surface:

- Water drops are not connected
- Frost propagation according to "ice bridging" mechanism (c.f. Chen et al., Sci. Rep. 3 (2013), 2515)



Frost spreading: Practical example of a hydrophobic (water repellent) coating

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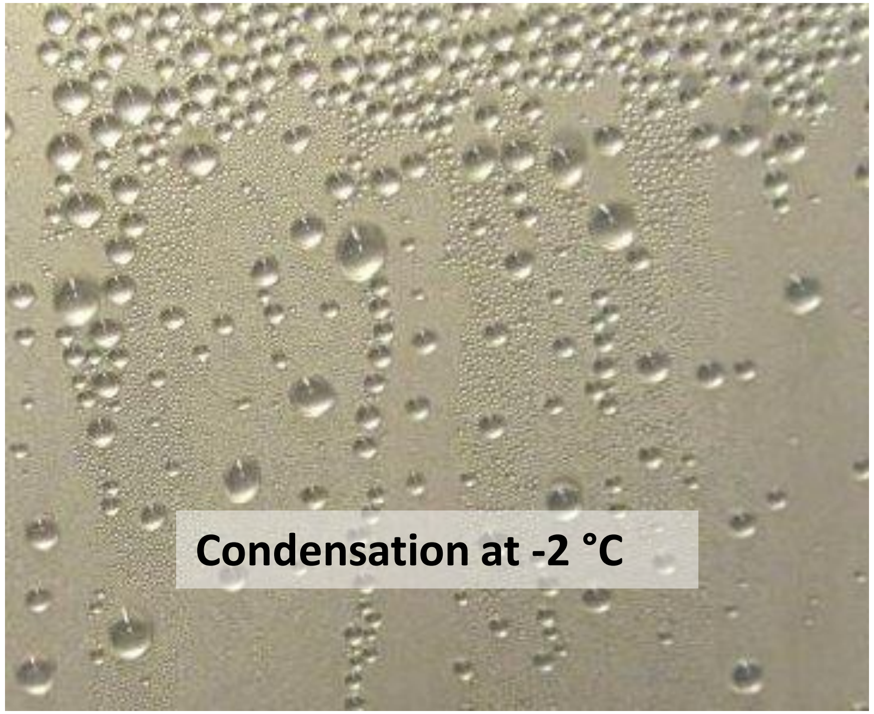
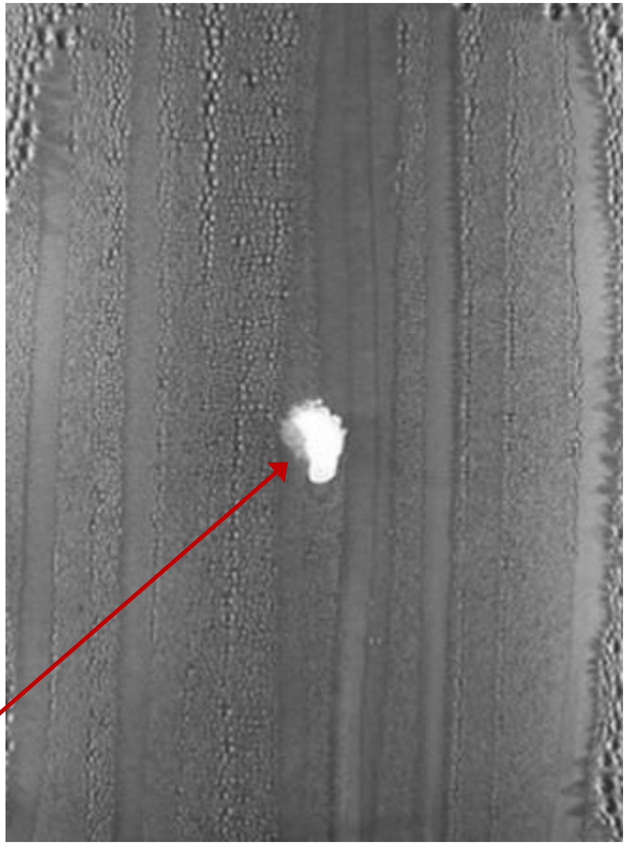


If a single drop would freeze, the surrounding drops would stay liquid...

...but we did not want to wait and put ice in the centre a 10 x 15 cm plate



30 min at -4 °C with ice in the centre
Continuous condensation and drainage of liquid water

At temperatures below ~-10 °C, independent ice nucleation would interfere with slow frost spreading

Frost propagation quantified

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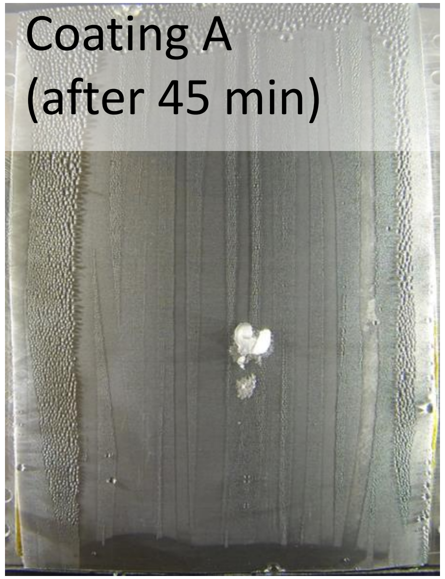
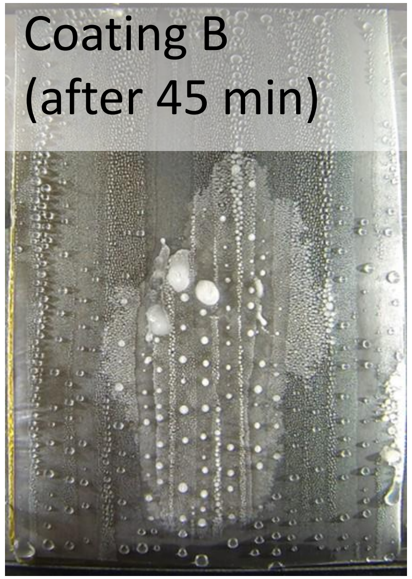
Tests with the ice tester (plates at -4°C, environment +12°C / 90% rel. humidity)

Surface	Water contact angle		Frost spreading rate at -4°C in first 30 min
	adv.	rec.	
Coating A (with PDMS (silicone))	**106°**	**96°**	**2±1 µm/s**
Coating B (like A, but no PDMS)	89°	73°	21 µm/s
Bare Aluminum	96°	50°	3000 µm/s

Slow frost spreading

High receding water contact angle required





Drawback with forced air flow

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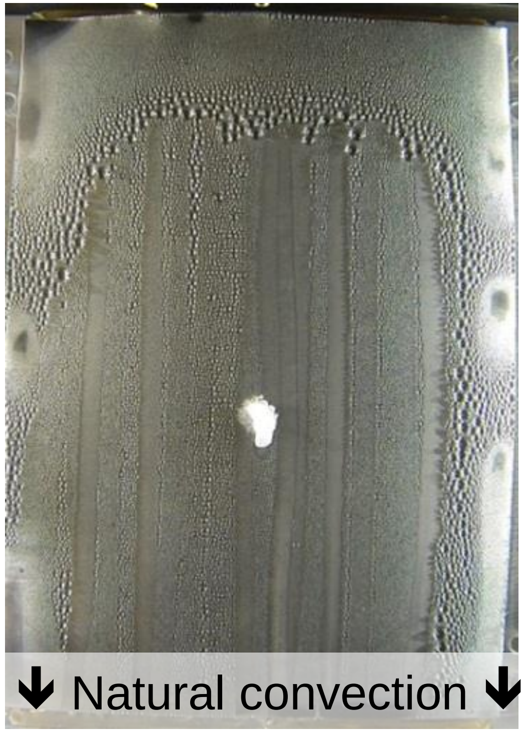


Coating A at -4 °C, 20 min after placing ice in the centre of the plates

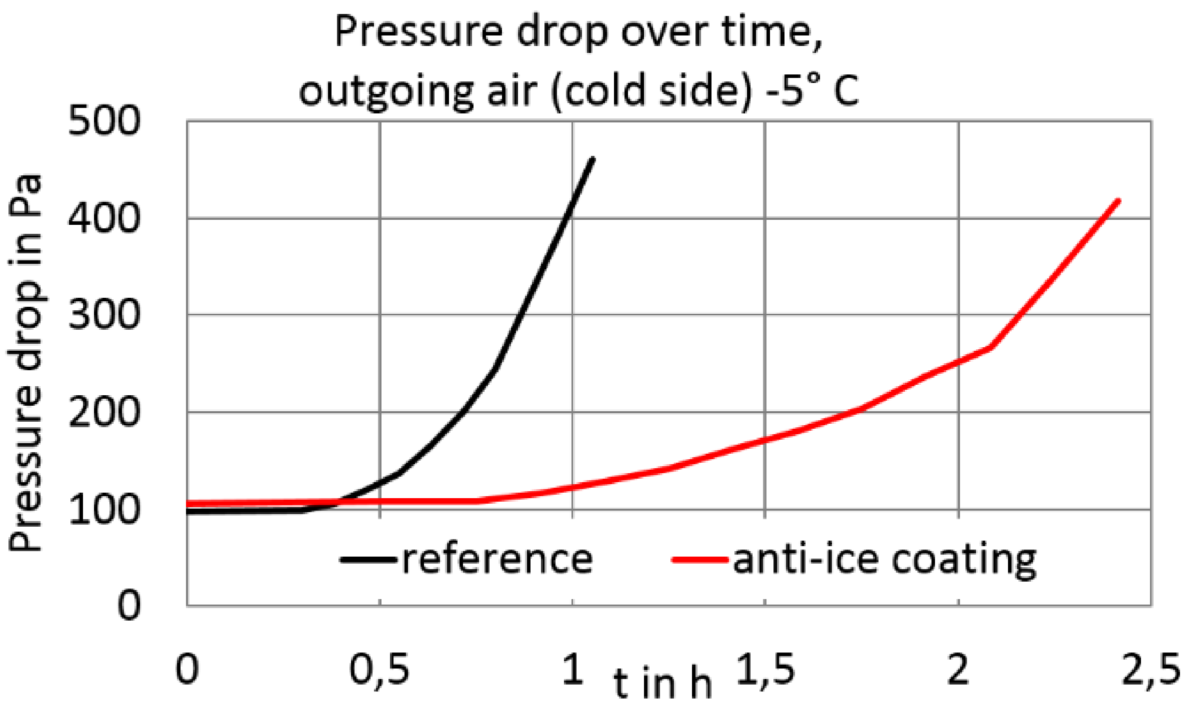
- Realistic ventilation air flow (1 m/s)
  → Fast frost spreading in flow direction
- Direction of lowest humidity, not explainable by ice bridging model
- In other direction, spreading is still retarded
- No flying ice crystals were observed, but this the only plausible explanation

Validation on Heat Recovery Ventilation unit

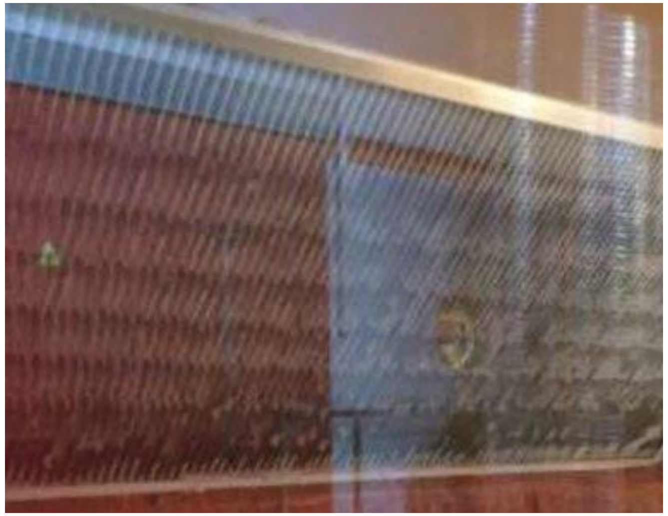
Monitoring according EN 308

Frost blocks the flow → Increased pressure drop → Defrosting

Coating increases time between defrosting by a factor of 2.3



No coating:
Frost inside the heat exchanger

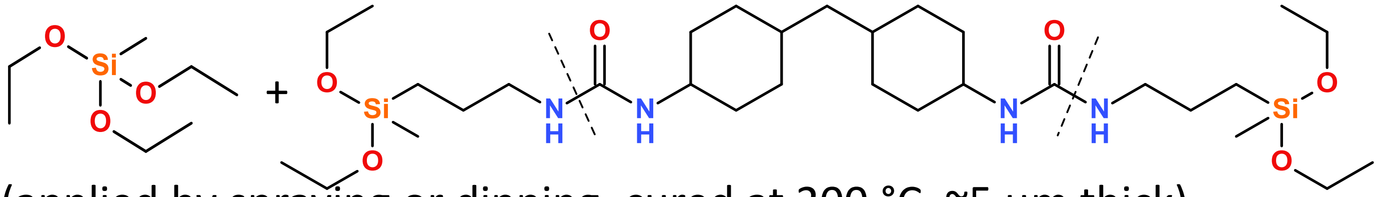


Coating:
Icicles outside the heat exchanger

Coatings A & B

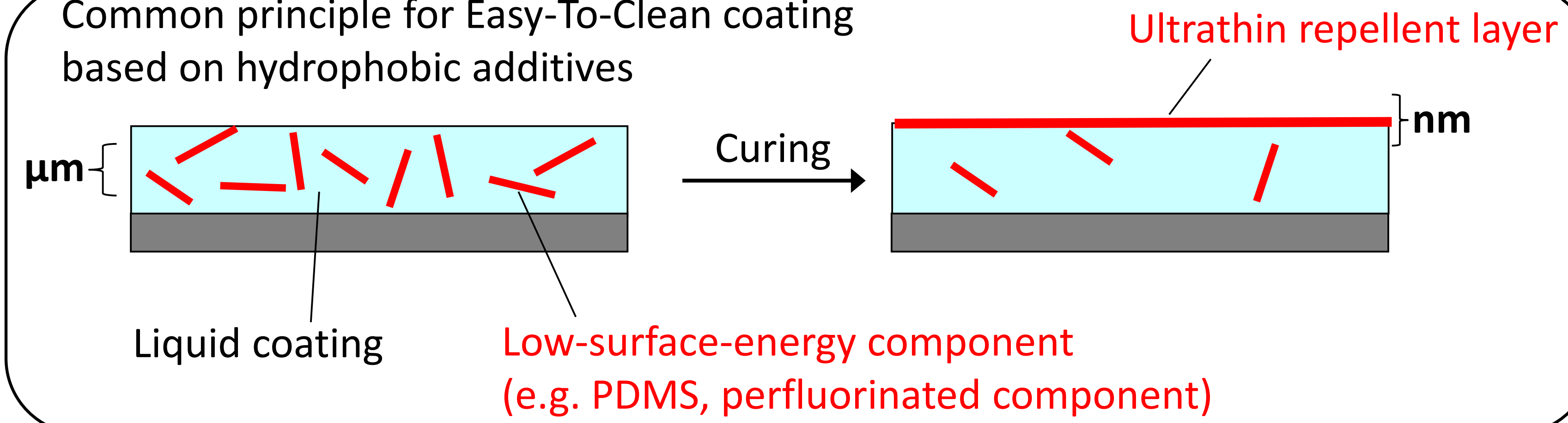
Organic-inorganic hybrid coatings similar to published oil-repellent coatings
(Bischoff & Holberg, Patent US 9029491 / Holberg & Bischoff, Prog. Org. Coat. 77 (2014), 1591))

- Sol-gel process: Hydrolysis of two silanes



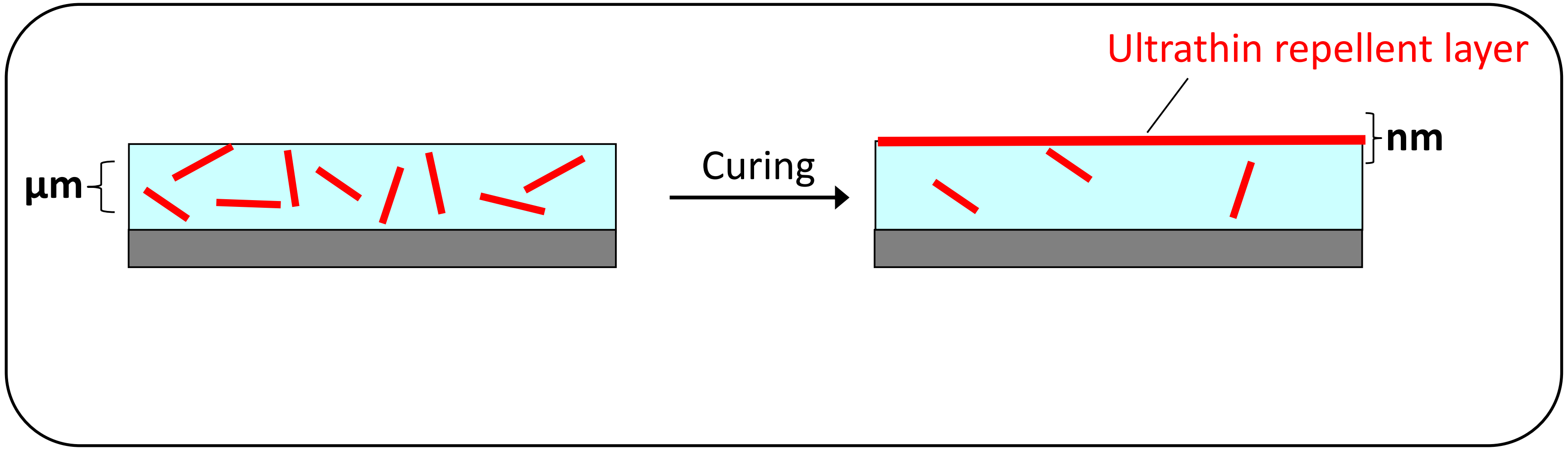
- Smooth surface (applied by spraying or dipping, cured at 200 °C, ~5 µm thick)
- **Solely coating A: 2% silanol-terminated PDMS (silicone)**
  → Hydrophobic (rather low CAH for a technical coating, θ_{adv} = 106°, θ_{rec}=96°)

Common principle for Easy-To-Clean coating based on hydrophobic additives



Phase separation model, surface tension driven
(cf. Majumdar & Webster, Polymer 48 (2007), 7499)

Possible coatings



- We obtained best results with various organic-inorganic hybrid coatings, including curing at 60°C (ambient cure possible)
- Pure organic coatings were not tested, but might might work as well with suitable hydrophobic additives
- Hydrophobic bulk polymers like bulk-PDMS (silicone rubber) or FEP (fluoropolymer) were tested. Slightly outperformed by our best hybrid coatings, but still promising, especially for applications with wear/erosion

What makes a "good" coating? / Physical properties

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Simplified: High receding water contact angle

- High static contact angles are insufficient

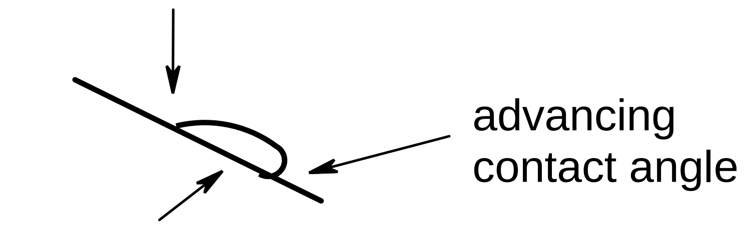
More precise parameter for improved drainage:
Critical diameter d_{crit} (similar to sliding angle)
Diameter that a growing water drop has to reach to start sliding down a surface

A low d_{crit} is relevant for slow frost spreading
(Kim et al., ACSNano 6 (2012), 6569)

d_{crit} can be calculated from advancing and receding contact angles.

$$d_{crit} = \sqrt{\left(\frac{24\,sin^3\theta adv\,\gamma(cos\theta rec - cos\theta adv)}{\pi\rho(1-cos\theta adv)^2(2+cos\theta adv)gsin\alpha}\right)}$$

Optimal surface for low d_{crit}:
High receding contact angle and **low contact angle hysteresis**

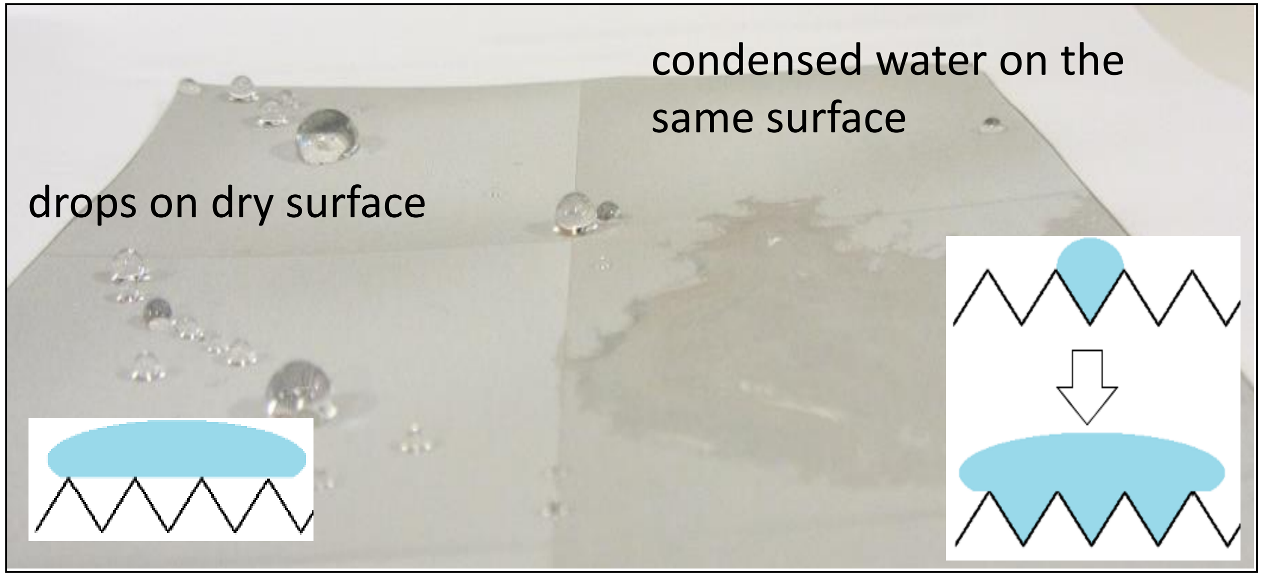


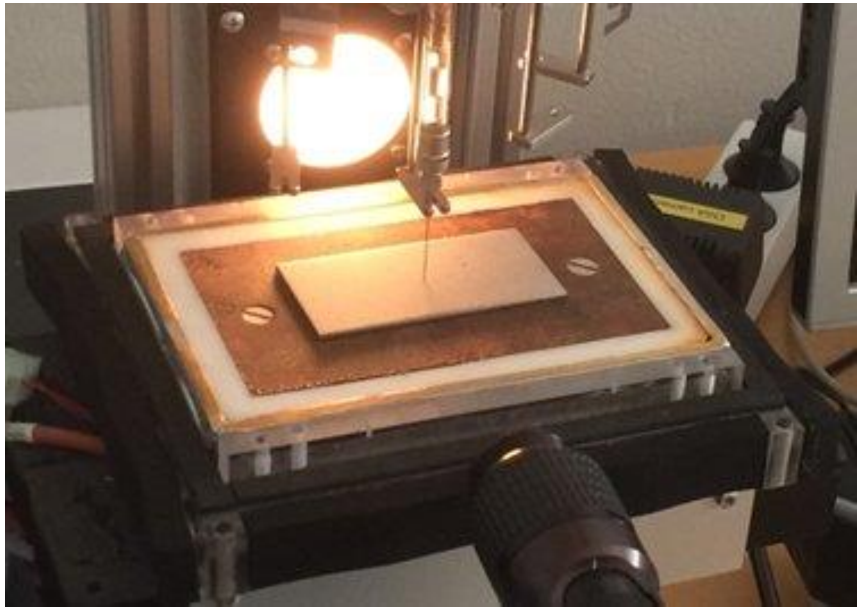
Contact angle hysteresis (CAH)
$CAH = \theta_{adv} - \theta_{rec}$

What makes a "good" coating? / Physical properties

Objects colder than surrounding air?? If yes, coating must work under condensation

- No problem for smooth surfaces
- Challenge for micro-/nanostructured surfaces
  Small water droplets condense inside most nanostructures and void superhydrophobicity.
  If they would work, they would be better...
- Liquid-infused nanostructures ("SLIPS") are suitable (cf. Kim et al. ACSNano 6 (2012), 656)





Drop shape analysis combined with cooling plate to measure receding CA under condensation

Promising superhydrophobic coatings "C" and "D"

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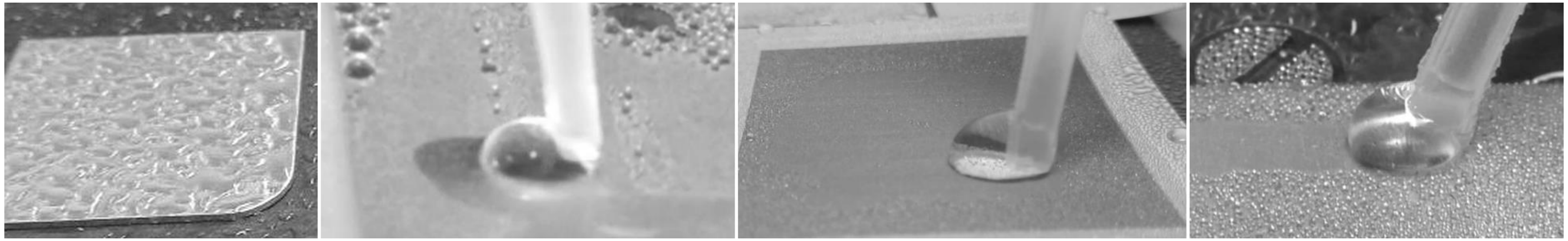
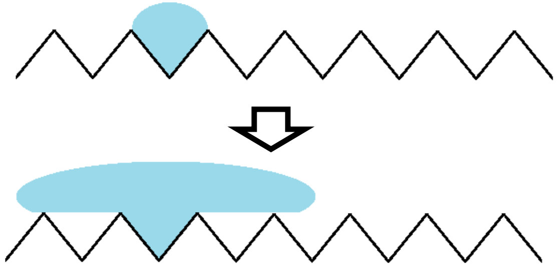
1) Condensation 2) drop moved (left to right) to estimate adv./rec contact angle



bare Al | Coating A (smooth) | **Surface C (laser grid)** | **Surface D (Boehmite)**

- **C** and **D** maintain to a great extent an air pocket state (reflections under the drop)
- Reduced hydrophobicity, **not better than smooth surfaces**
- Improvement promising according to literature
  (e.g. Self propelled condensation, Boryeko & Chen, Phys. Rev. Let. 103 (2009), 184501.)

	Water contact angle dry adv. / rec.		condensation rec.	
Surface C	151°	138°		~90°
Surface D	114°	104°		~90°



Partly air-pocket state expected

What makes a "good" coating? / Physical properties

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Must maintain hydrophobicity under operation conditions

- Ventilation: Long-term contact with humidity (to be investigated in MATChING)
- Wind power/aircraft: Weathering / extreme abrasion (no solution available today)

Conclusion

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- Suitable, technically available surfaces can significantly delay frost formation
- Not freezing (ice nucleation) is delayed, but frost propagation
- Exploitable for devices applying periodic defrosting (ventilation/heat pumps/refrigeration)
- Future exploitation for wind turbines? Maybe in combination to support periodic defrost or other active anti-ice technologies

Additional literature

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Peer-reviewed publications on the content of this presentation with further details

Losada, R., Holberg, S., Bennedsen, J.M.D., Kamuk, K. & Nielsen, F. (2016). Coatings to prevent frost. *Journal of Coatings Technology and Research, 13*, 645-653.

Holberg, S., Losada, R., Kamuk, K. & Nielsen, F. (2016). Coating to prevent frost: less defrosting - more energy efficiency. In P.K. Heiselberg (Ed.). CLIMA 2016 - proceedings of the 12th REHVA World Congress: volume 9. Aalborg, Denmark: Aalborg University, Department of Civil Engineering. (http://vbn.aau.dk/files/233778842/paper_457.pdf)

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