

Condensation and Evaporation of Hexane in Nanoporous Alumina Membranes

Hermann Böttcher¹ Victor Doebele² Pierre-Etienne Wolf²
Panayotis Sphatis² Fabien Souris²

¹University of Constance

²Institut Néel, Centre national de la recherche scientifique

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Overview

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- 3 Theoretical background
 - 1 Condensation and evaporation in cylindrical pores
 - 2 Membrane production
- 4 Experimental
 - 1 Pore defects
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Context

Grand scheme

- Condensation and evaporation of fluids in confinement

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Plan

- Anodized alumina membranes (AAM)
- Test setup using Hexane → working at room temperature permits much faster executable experiments
- Transfer to **helium** experiment

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- Comparing the pore diameters extracted from the volumetric measurements those from scanning electron microscopy (SEM) images

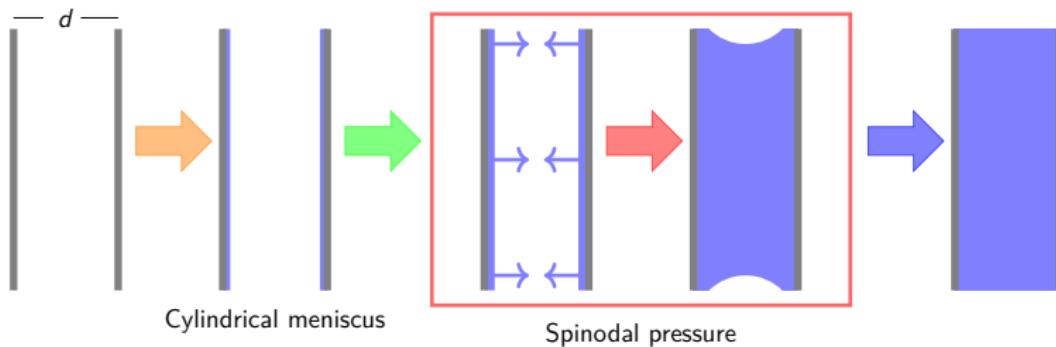
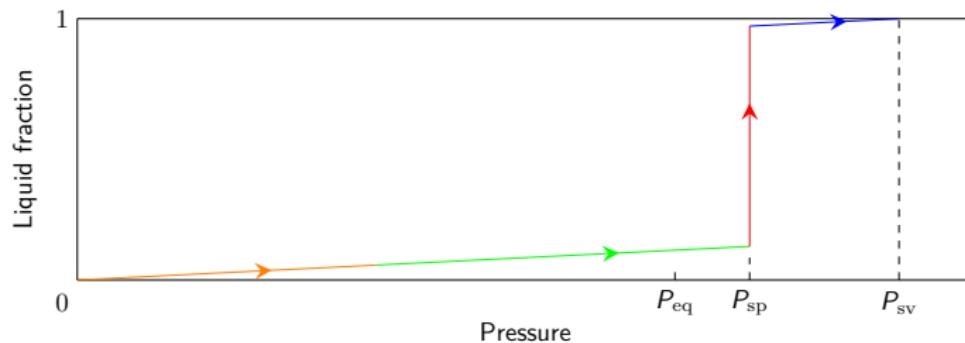
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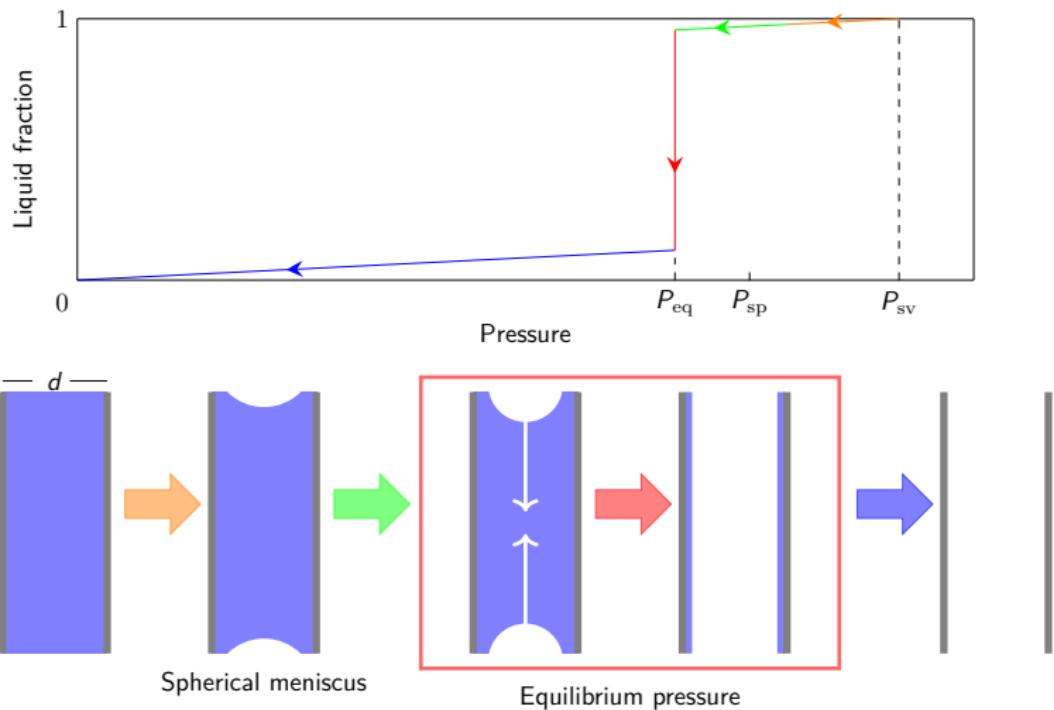
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- Performing isotherm measurements on many membranes for **statistics**
- Comparing the pore diameters extracted from the volumetric measurements those from scanning electron microscopy (SEM) images
- Improving the fabrication process to reduce the dispersion
- Testing the efficiency of the ALD process as a means to reduce the pore diameters

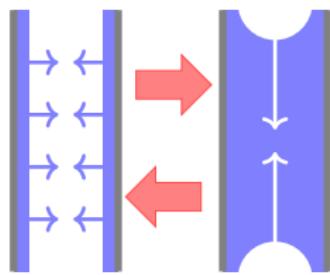
Condensation in a cylindrical open pore



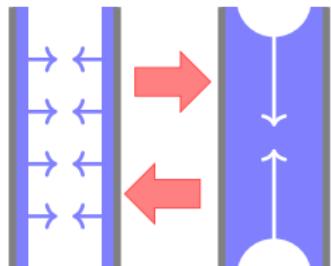
Evaporation in a cylindrical open pore



Condensation and evaporation in a cylindrical open pore



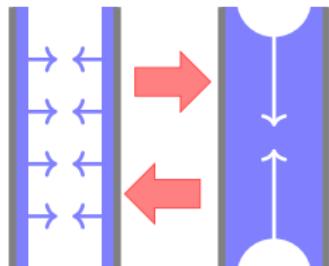
Condensation and evaporation in a cylindrical open pore



Open cylindrical pore

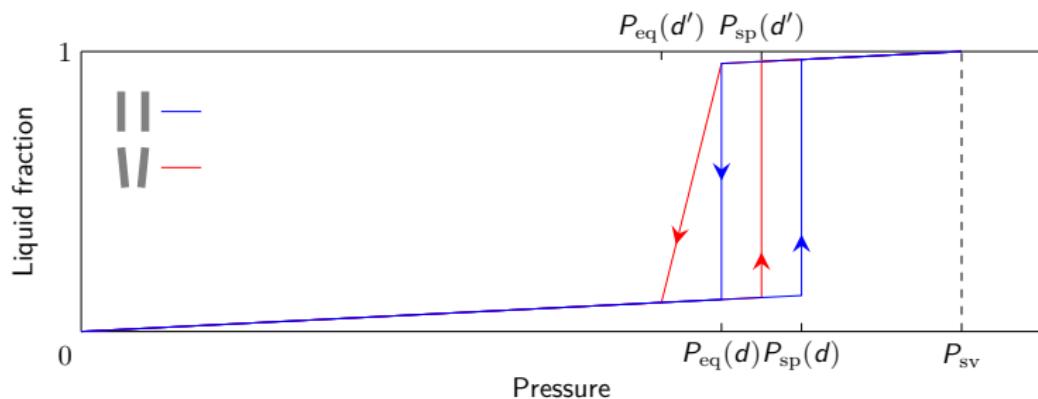
Condensation at spinodal pressure and
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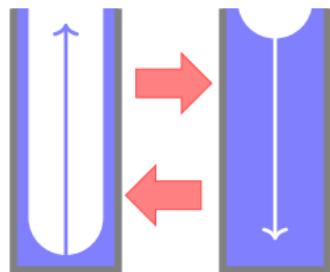


Open cylindrical pore

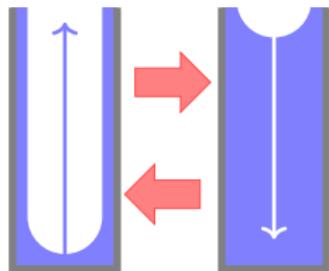
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Condensation and evaporation in a cylindrical closed pore



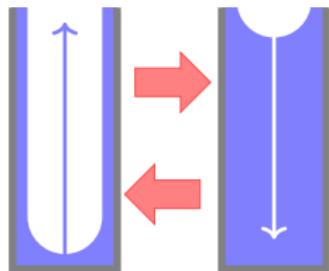
Condensation and evaporation in a cylindrical closed pore



Closed cylindrical pore

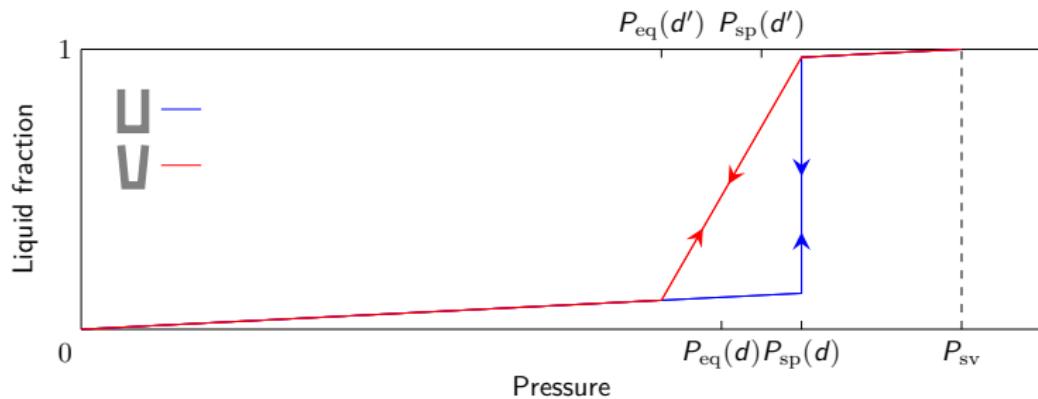
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Condensation and evaporation in a cylindrical closed pore



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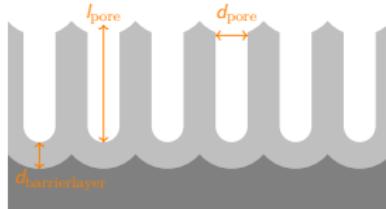
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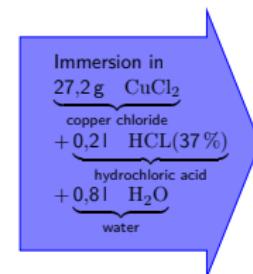
Membrane production



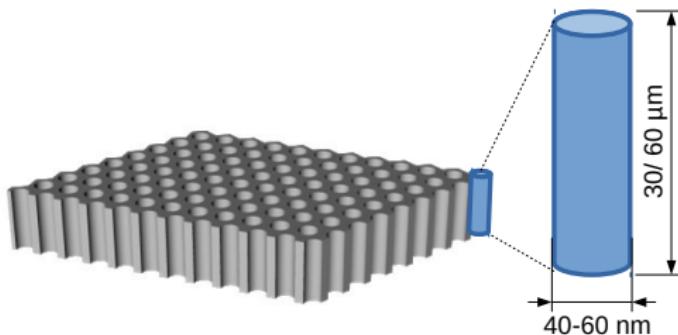
Two step anodizing
in oxalic acid
($\text{C}_2\text{H}_2\text{O}_4$) at 0°C



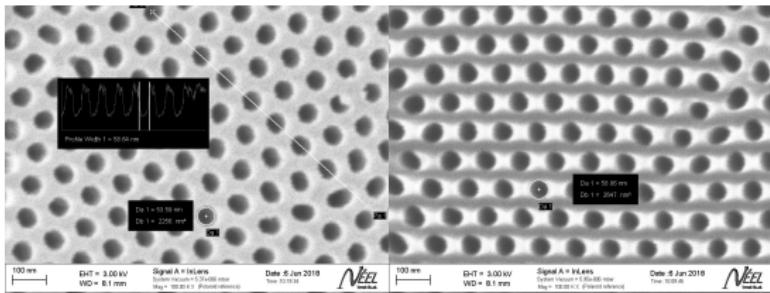
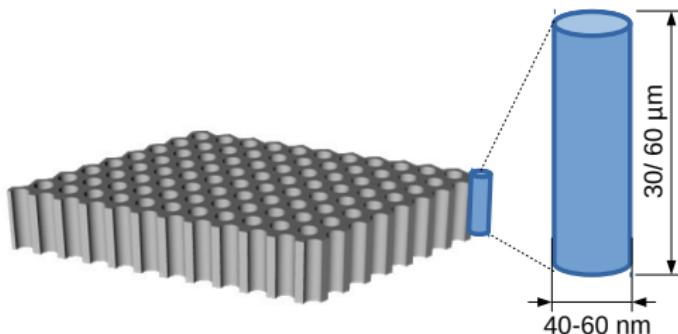
Floating on
phosphoric acid
($\text{H}_3\text{O}_4\text{P}$) till milky
aspects appear
plus 15 min



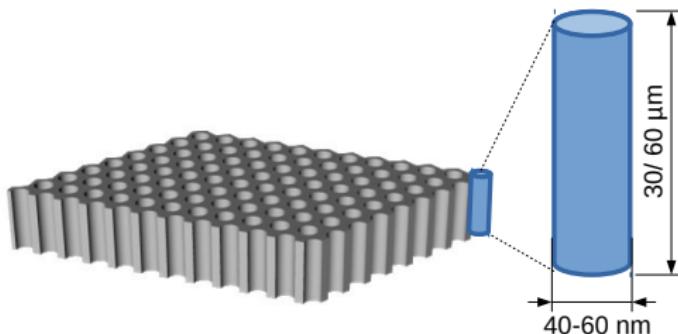
Alumina membranes - funnelling



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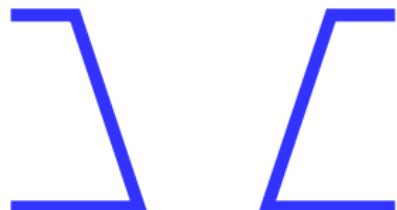
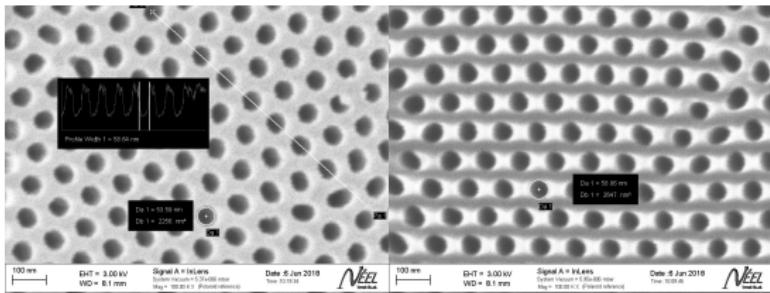


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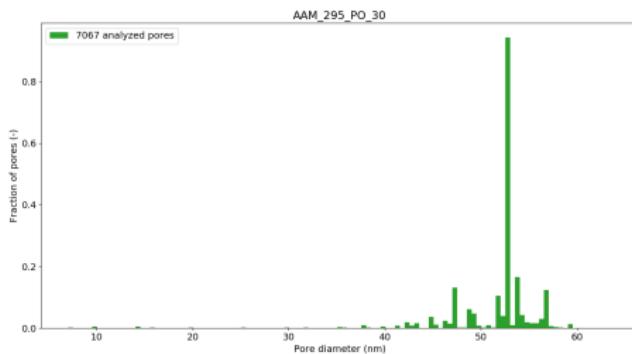


Funnelling

Funnelling suspected due to different pore diameters on top and bottom side.



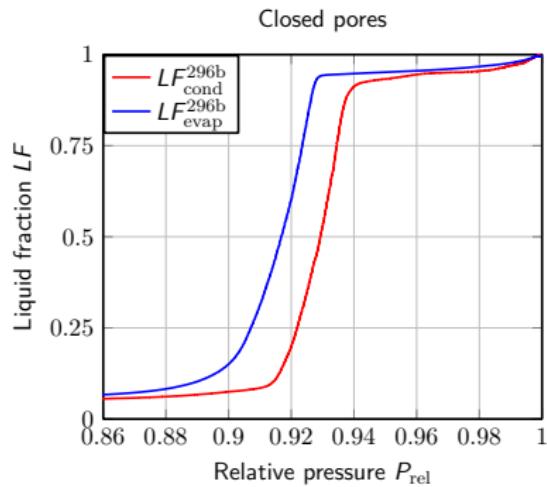
Alumina membranes - pore size distribution



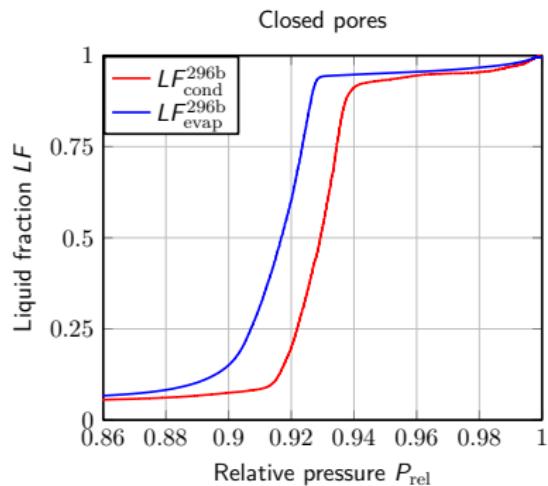
Pore size distribution

SEM analysis shows pore size distribution on a given membrane.

Alumina membranes - corrugations

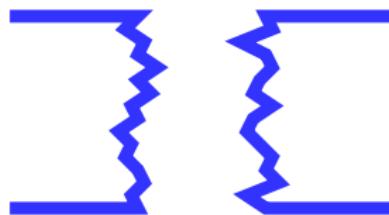


Alumina membranes - corrugations



Corrugations

The appearance of the hysteresis is assumed to be due to **intra pore corrugations**.



Alumina membrane defects

Isotherms are affected by

- Pore size distribution
- Funnellization
- Corrugations

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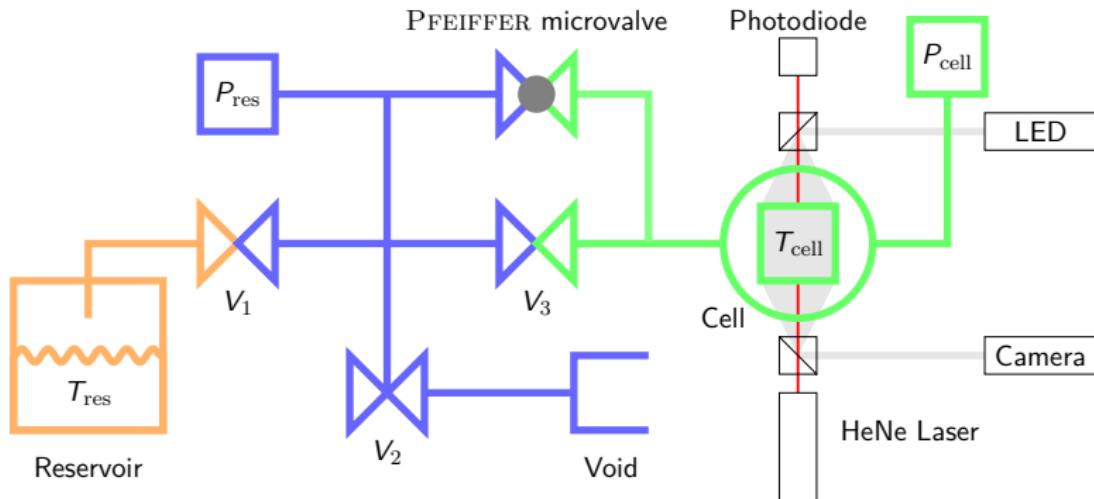
Problem

No simple ways to characterize these defects!

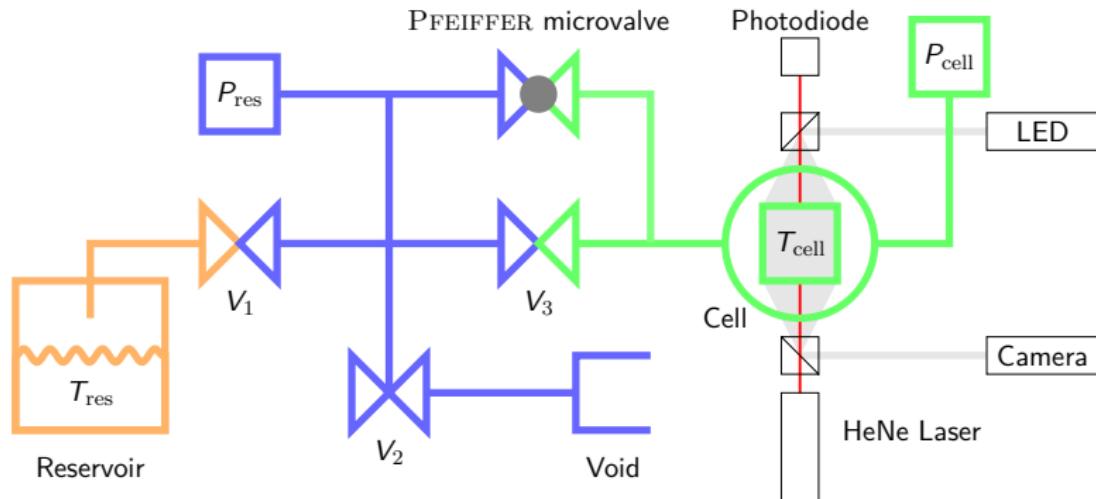
SEM images only give an impression of the surfaces of the membrane (factor between pore diameter and pore length is 1000!).

→ Need of **monodisperse membranes**

Final experimental setup



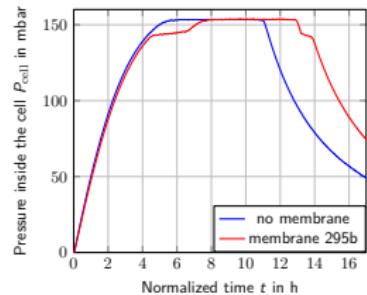
Final experimental setup



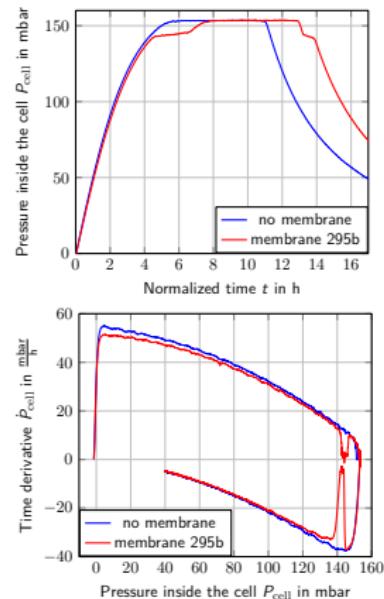
Volumetric and optical measurements

Volumetric and optical setups work independently.

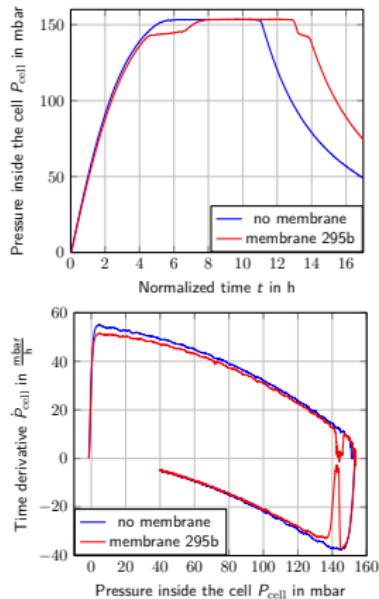
Data evaluation - volumetrics



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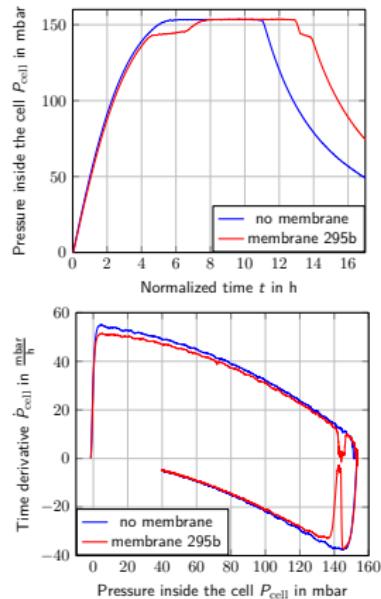
Data evaluation - volumetrics



Computation

- The flow rate depends on the opening of the PFEIFFER microvalve

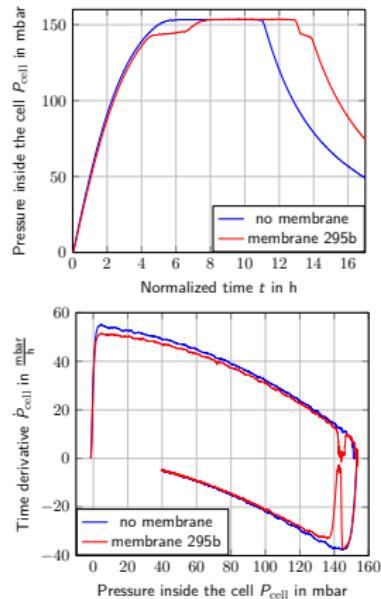
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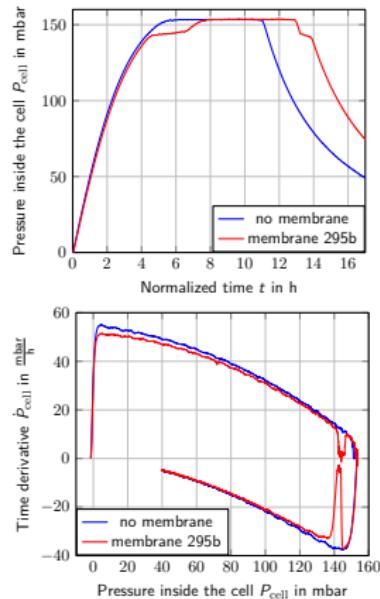
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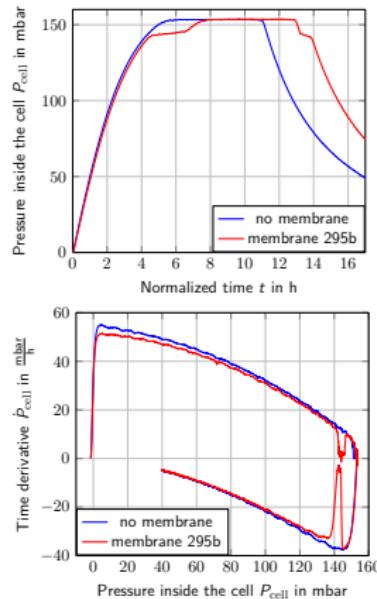
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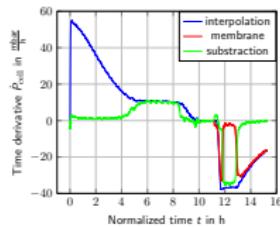
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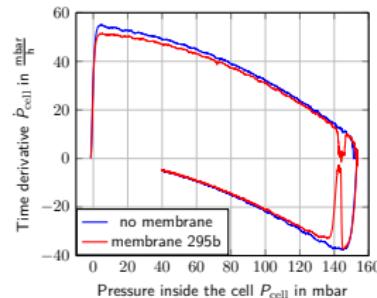
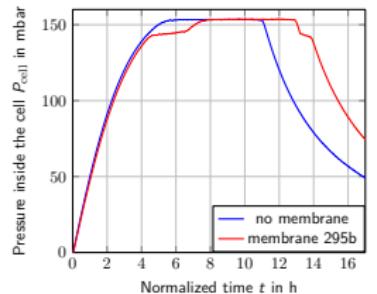


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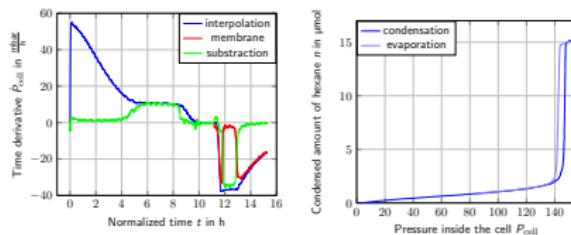


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Kelvin equation

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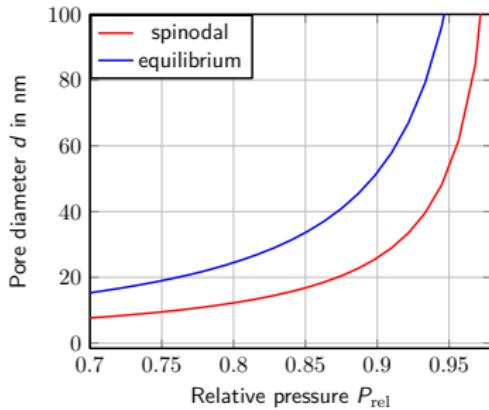
$$P_{\text{eq}} = P_{\text{sv}} \cdot \exp\left(-\frac{2 \cdot \gamma V_{\text{mol}}^l}{R_0 \cdot RT}\right) < P_{\text{sp}} < P_{\text{sv}}$$

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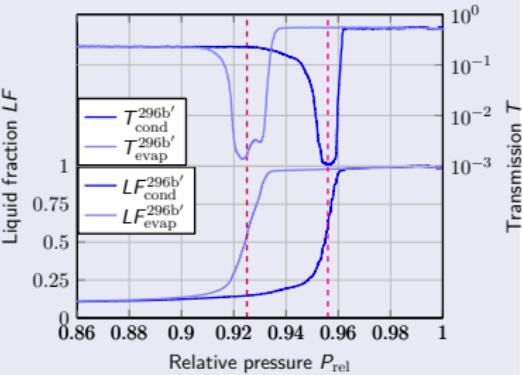
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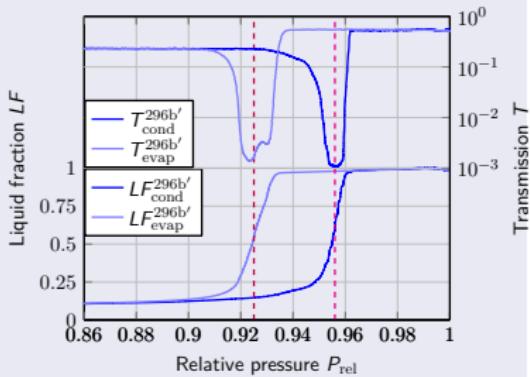
Easy example isotherms

Open pores



Easy example isotherms

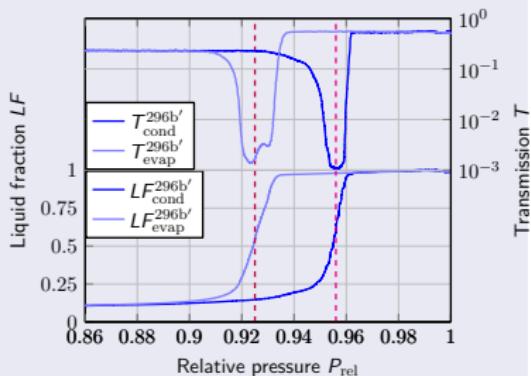
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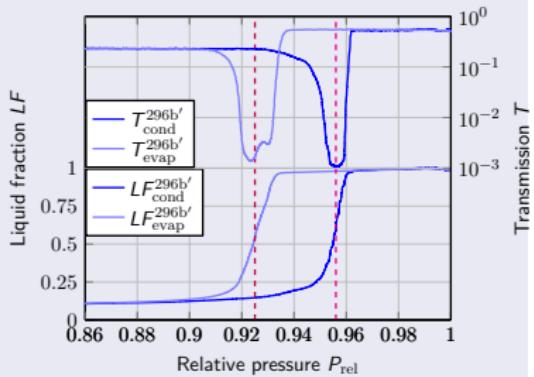
Open pores



- Hysteresis expected from theory
- Inclination of the condensation and evaporation branches

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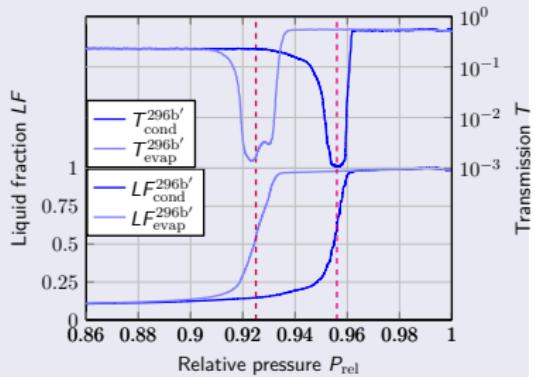
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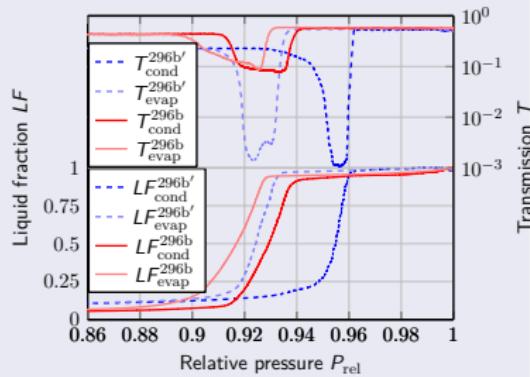
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Easy example isotherms

Open pores



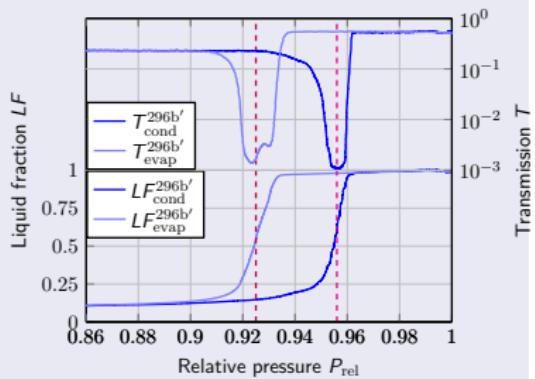
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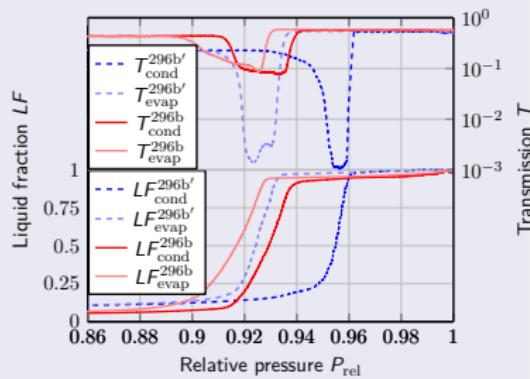
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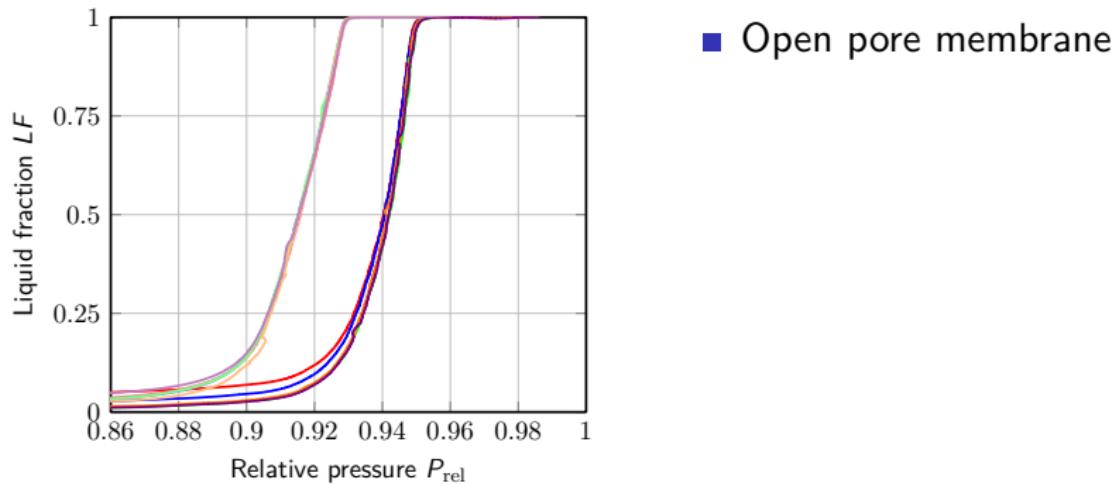
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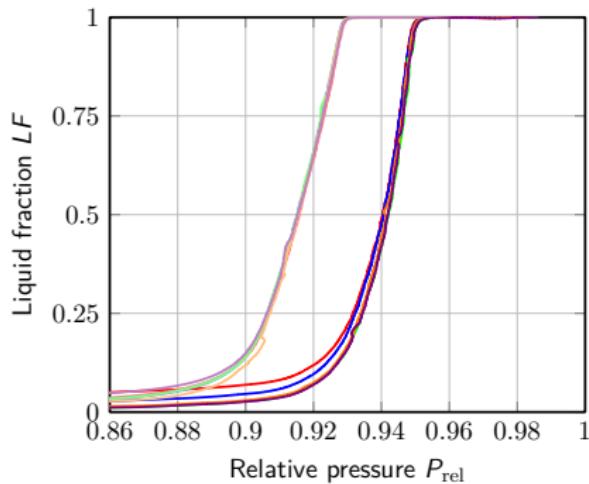


- Hysteresis grows smaller
- Hysteresis does not disappear though

Volumetric measurement reproducibility

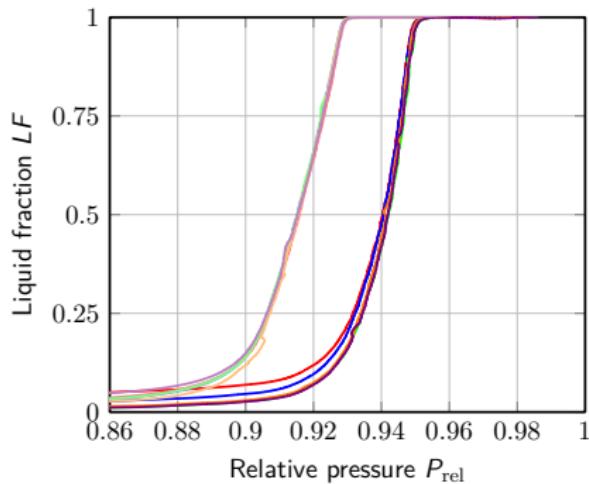


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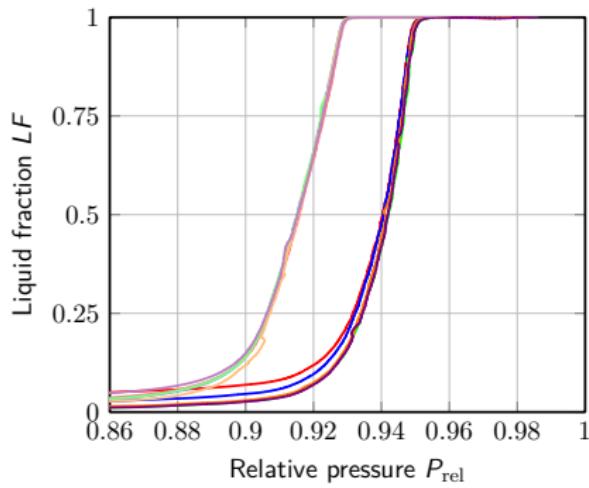
- Open pore membrane
- Slight variations of the height of the condensation branch

Volumetric measurement reproducibility



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→ combination of measurement noise and liquid film thickness

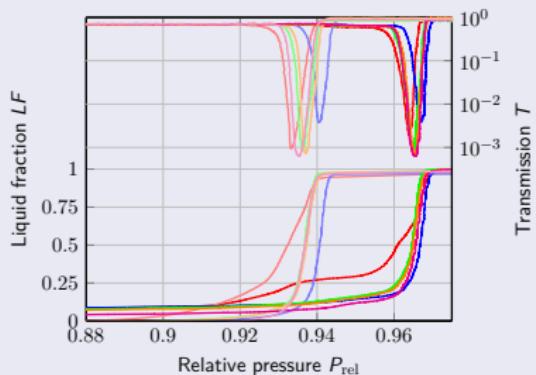
Volumetric measurement reproducibility



- Open pore membrane
- Slight variations of the height of the condensation branch
→ combination of measurement noise and liquid film thickness
- Generally sufficiently superimposed isotherms

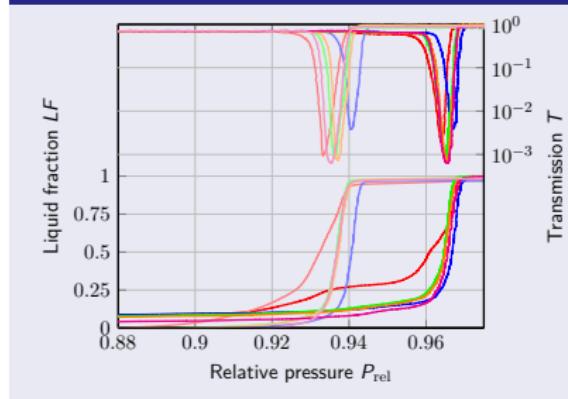
Wafer inhomogeneity - open pore membranes wafer 295

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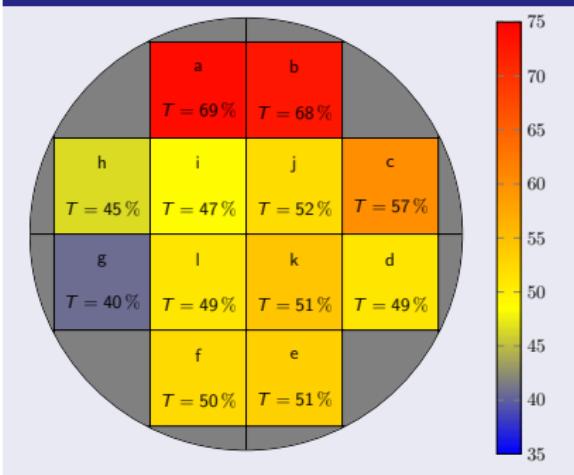


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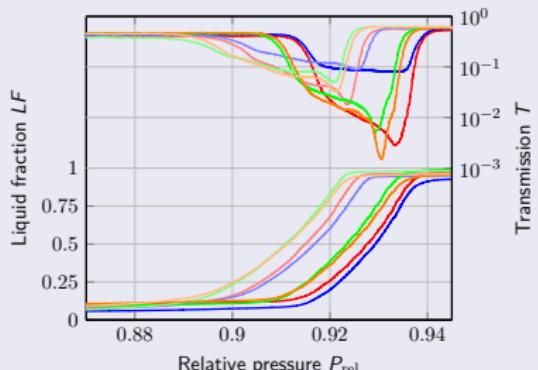


Dry transmission measurements



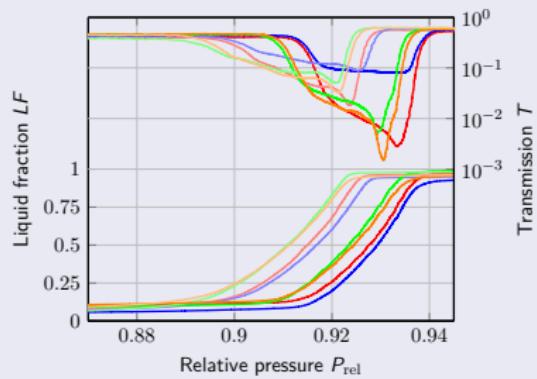
Wafer inhomogeneity - closed pore membranes wafer 296

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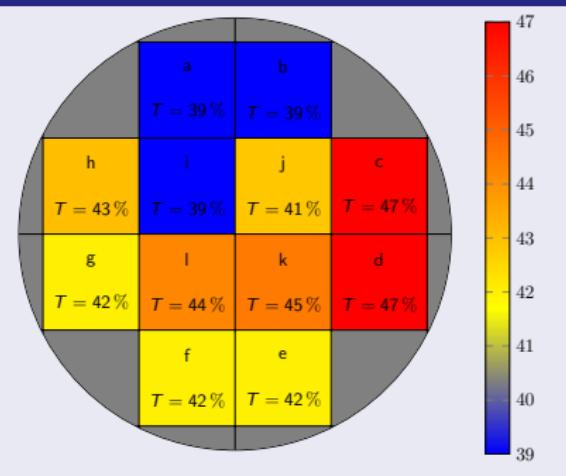


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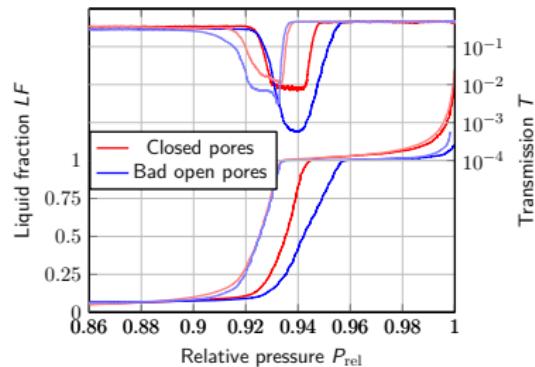
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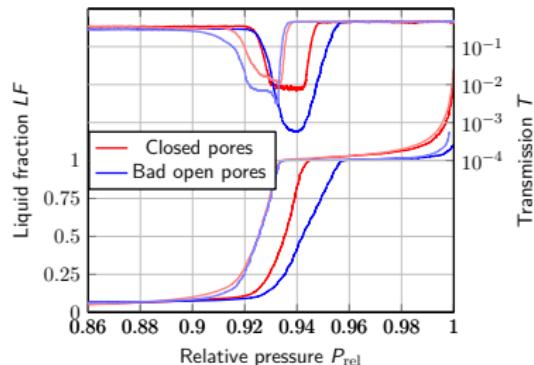
Dry transmission measurements



Bad pore opening



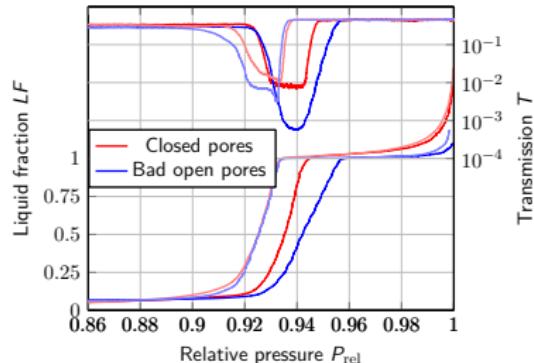
Bad pore opening



Condensation branch

- Starts at equilibrium pressure
- Slope more inclined than for closed pores

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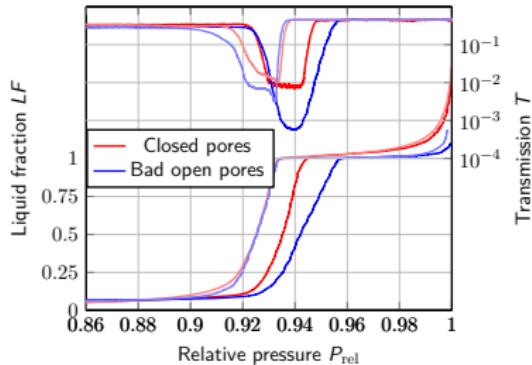
Evaporation branch

- Superimposed with closed pores

Condensation branch

- Starts at equilibrium pressure
- Slope more inclined than for closed pores

Bad pore opening

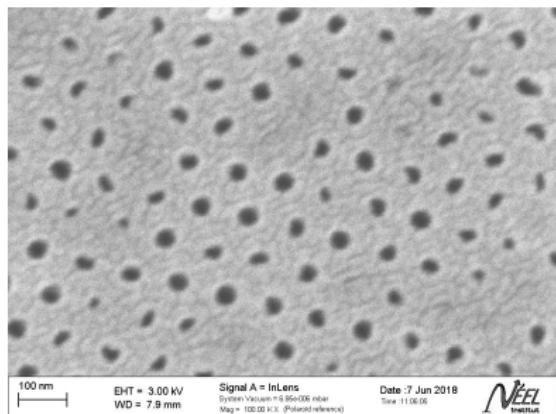


Condensation branch

- Starts at equilibrium pressure
- Slope more inclined than for closed pores

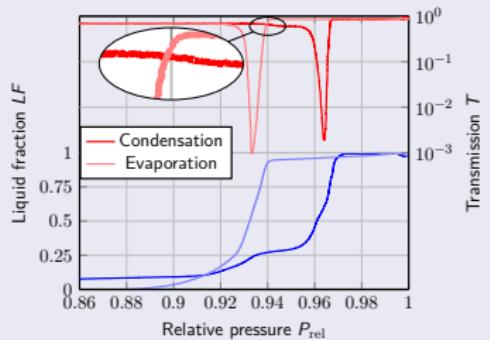
Evaporation branch

- Superimposed with closed pores



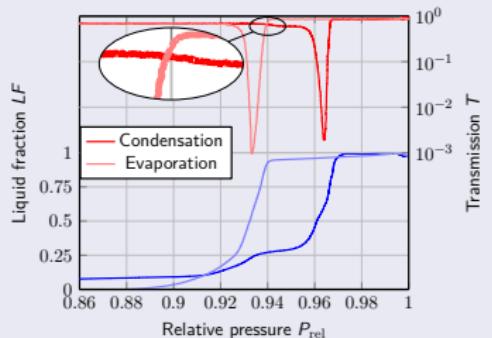
Unexpected closed pores I

Suspicion of closed pores



Unexpected closed pores I

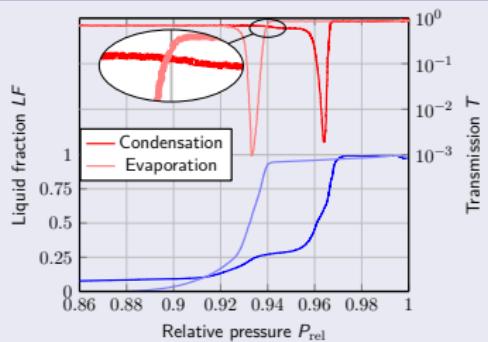
Suspicion of closed pores



- Condensation rises in three steps
- Transmission drops along with step 1
- Transmission does not rerise before step 2

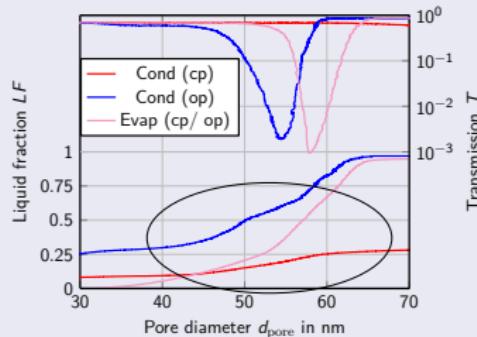
Unexpected closed pores I

Suspicion of closed pores



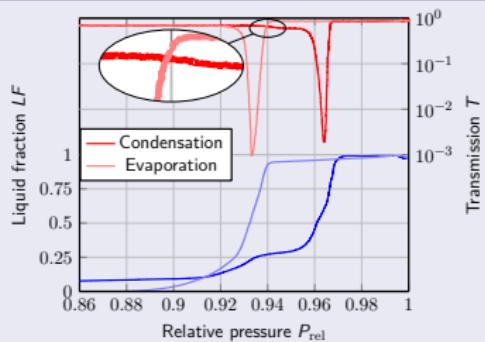
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KELVIN conversion for cp/ op



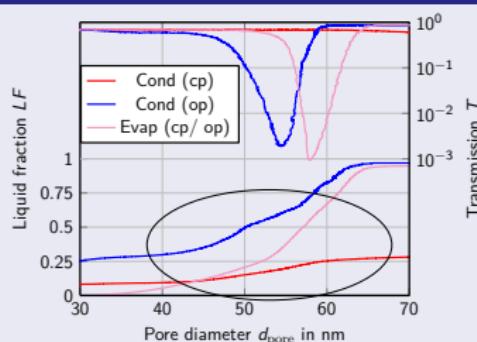
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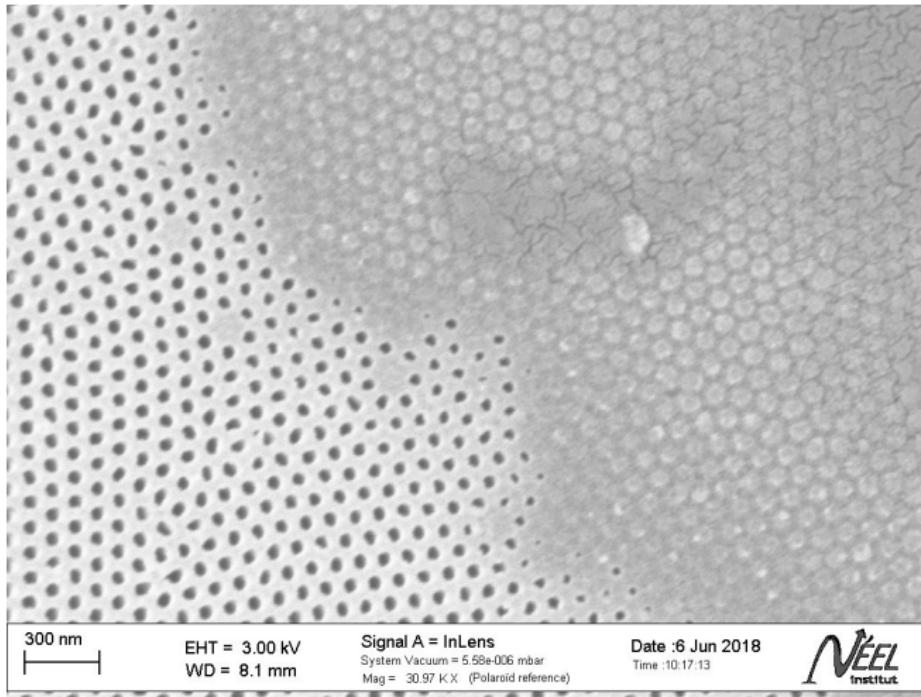
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KELVIN conversion for cp/ op

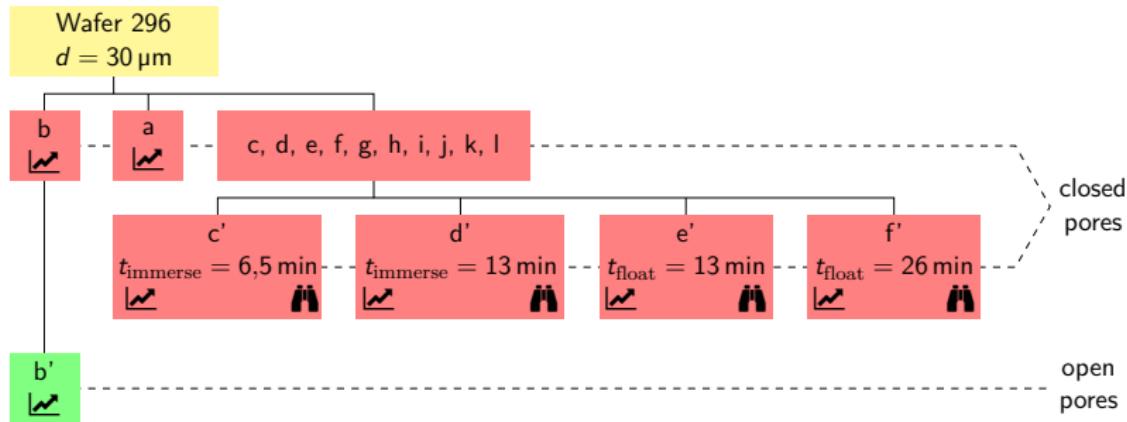


- Evaporation superimposed (appears at P_{eq} for cp/ op)
- Step 1 and the steps 2,3 appear on the same diameter range
- Distinct steps 2 and 3 unclear

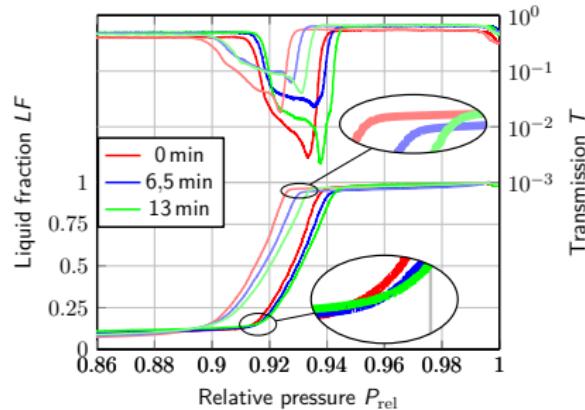
Unexpected closed pores II



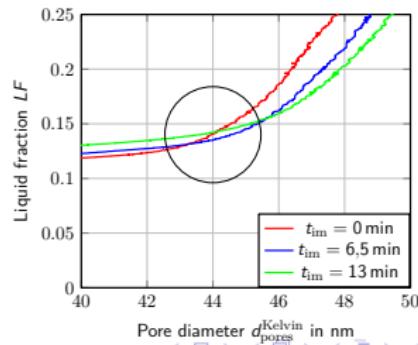
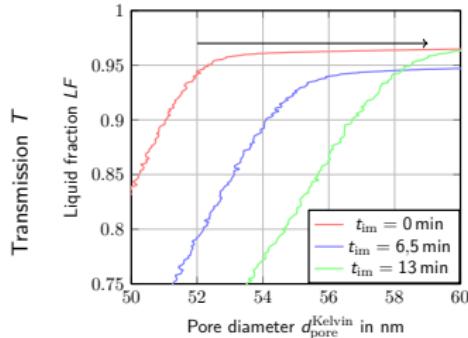
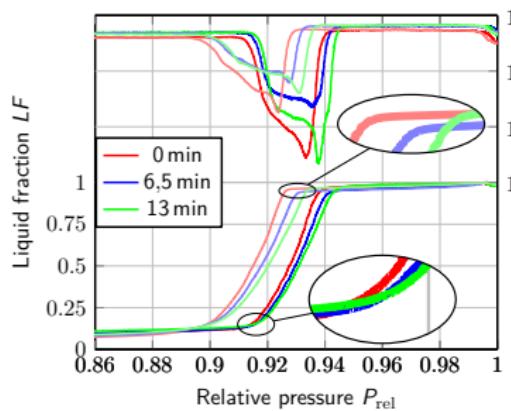
Testing the pore opening process



Funnellization due to immersion in phosphoric acid

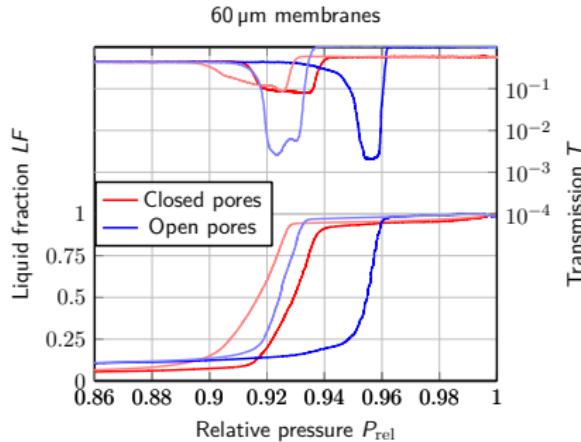


Funnellization due to immersion in phosphoric acid

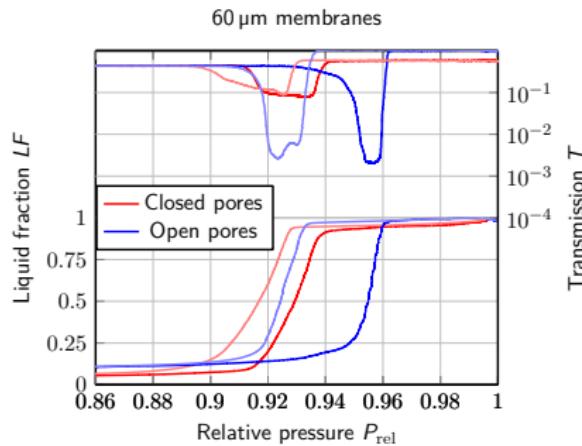


- Continuous shift to larger pressures with increasing immersion times
- Slope increasing with liquid fraction leading to a linear rise upon KELVIN conversion
- Shift seemingly increasing from bottom to top side

Inverse funnelling and thinner membranes

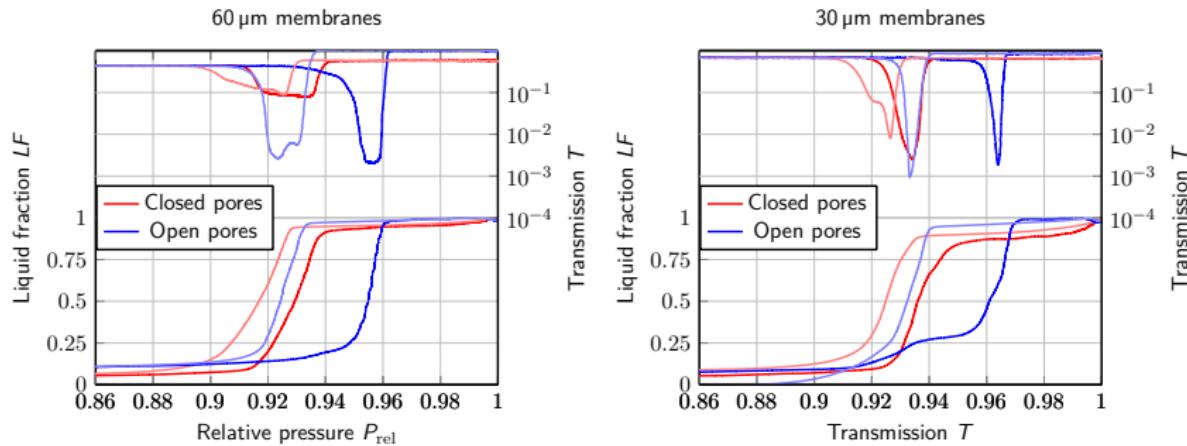


Inverse funnelling and thinner membranes



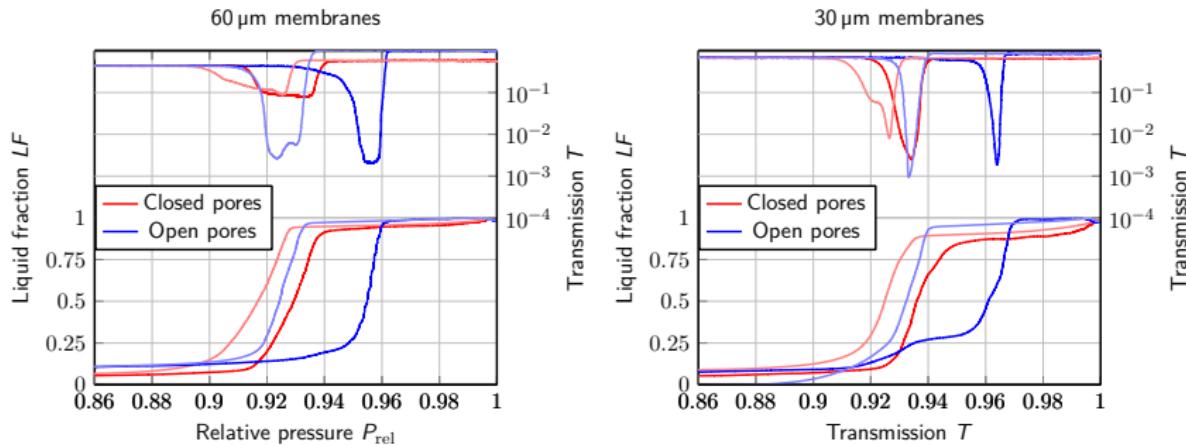
- Sharpening of the isotherm branches upon pore opening
- Shape does not change - same as for inverse funnelling

Inverse funnelling and thinner membranes



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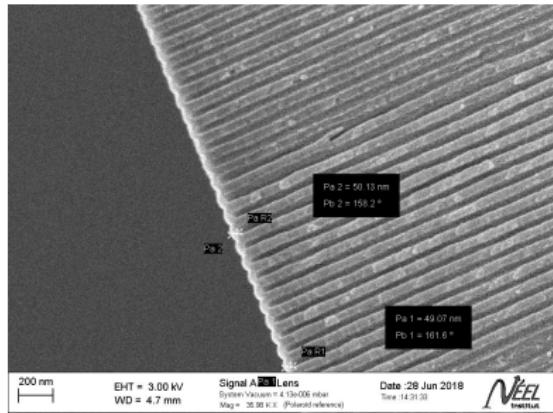
Inverse funnelling and thinner membranes



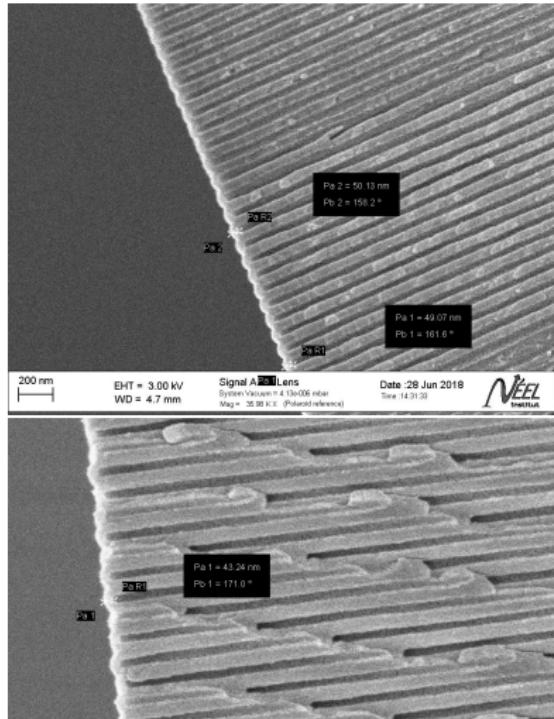
- Sharpening of the isotherm branches upon pore opening
- Shape does not change - same as for inverse funnelling

- Closed pores: Thinner membrane does not reduce funnelling as expected
- Open pores: Thinner membranes do indeed reduce funnelling

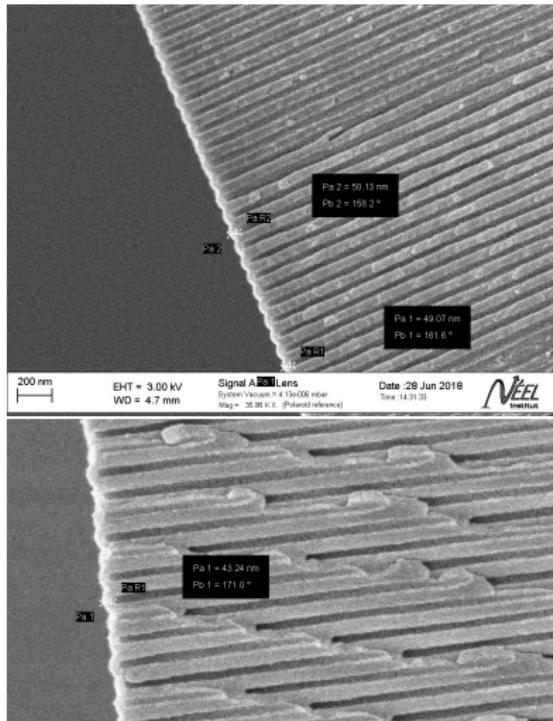
Barrier layer thickness - nonisotrope etch rate



Barrier layer thickness - nonisotrope etch rate



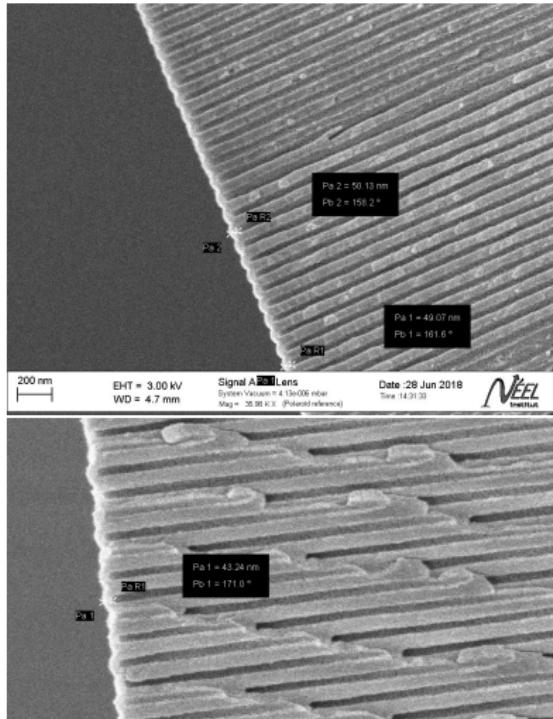
Barrier layer thickness - nonisotrope etch rate



Barrier layer thickness

- Assumed to always be 30 nm

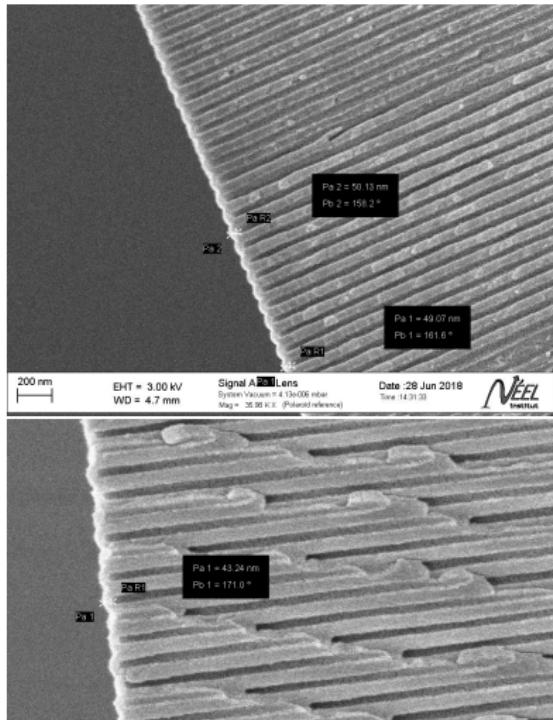
Barrier layer thickness - nonisotrope etch rate



Barrier layer thickness

- Assumed to always be 30 nm
- Has not been probed before the treatments

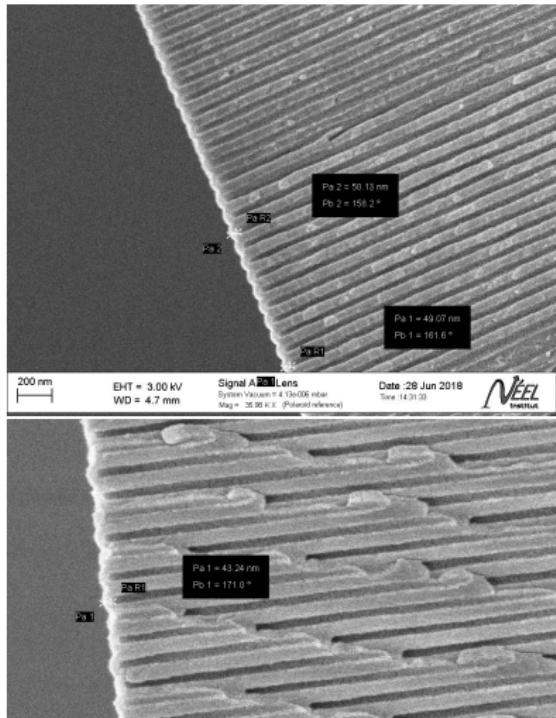
Barrier layer thickness - nonisotrope etch rate



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- Much too large AFTER floating

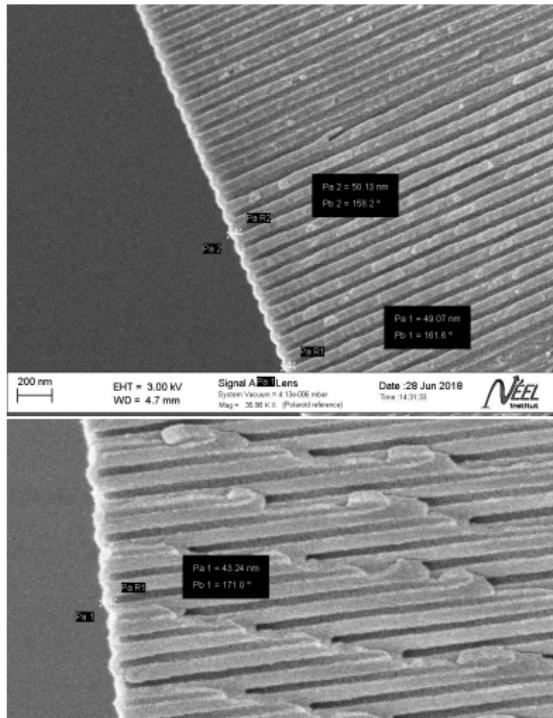
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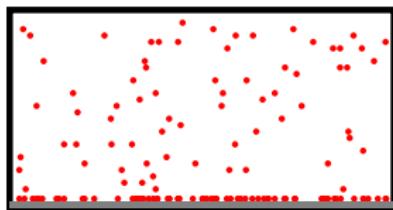
Barrier layer thickness - nonisotrope etch rate



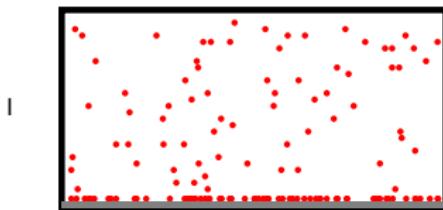
Barrier layer thickness

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- Has not been probed before the treatments
- Much too large AFTER floating
- Not uniform over multiple wafers; uniformity on a given wafer remains to be probed
- Etch rate much stronger than within the pores

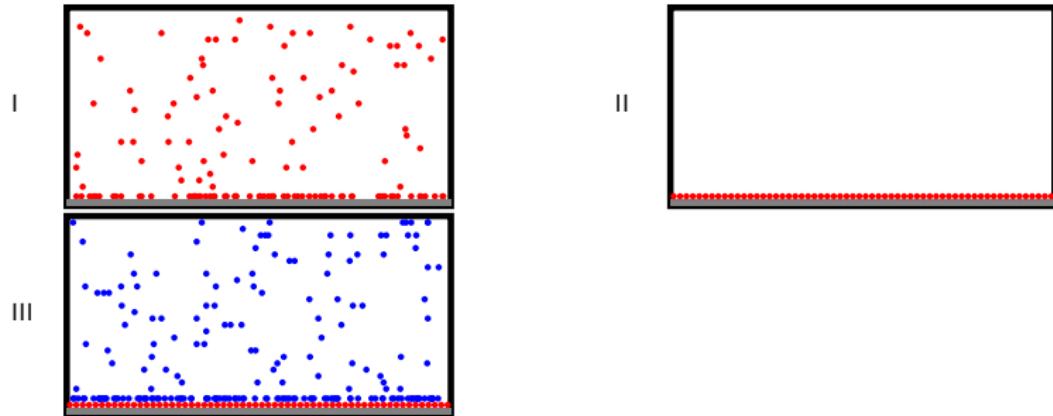
Atomic layer deposition (ALD)



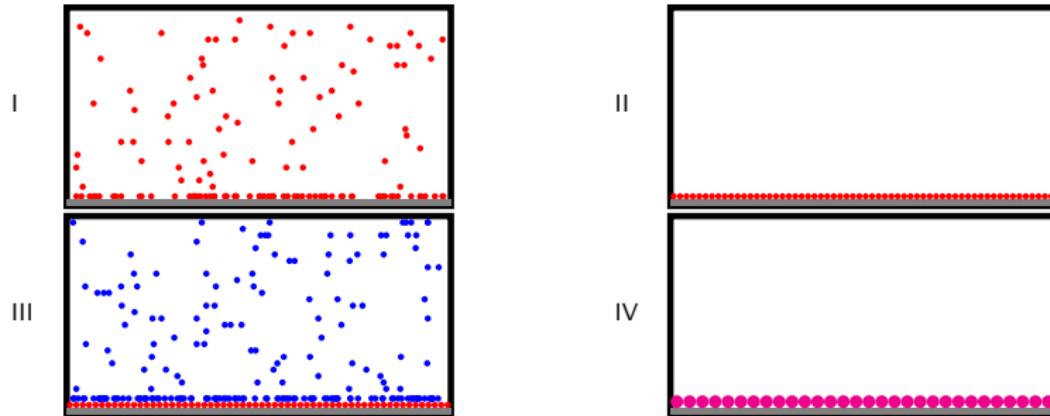
Atomic layer deposition (ALD)



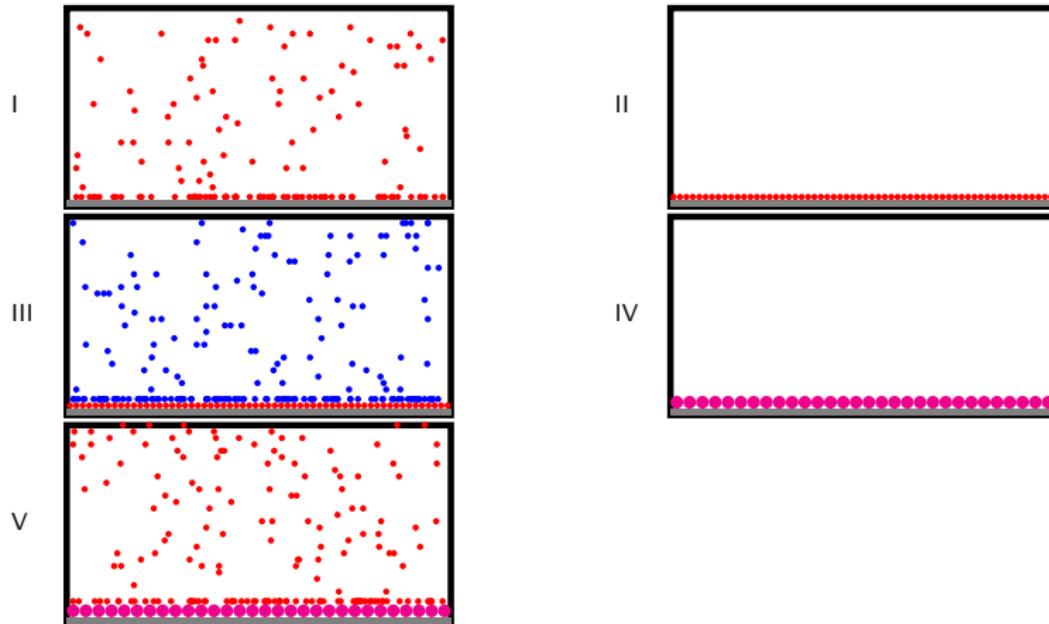
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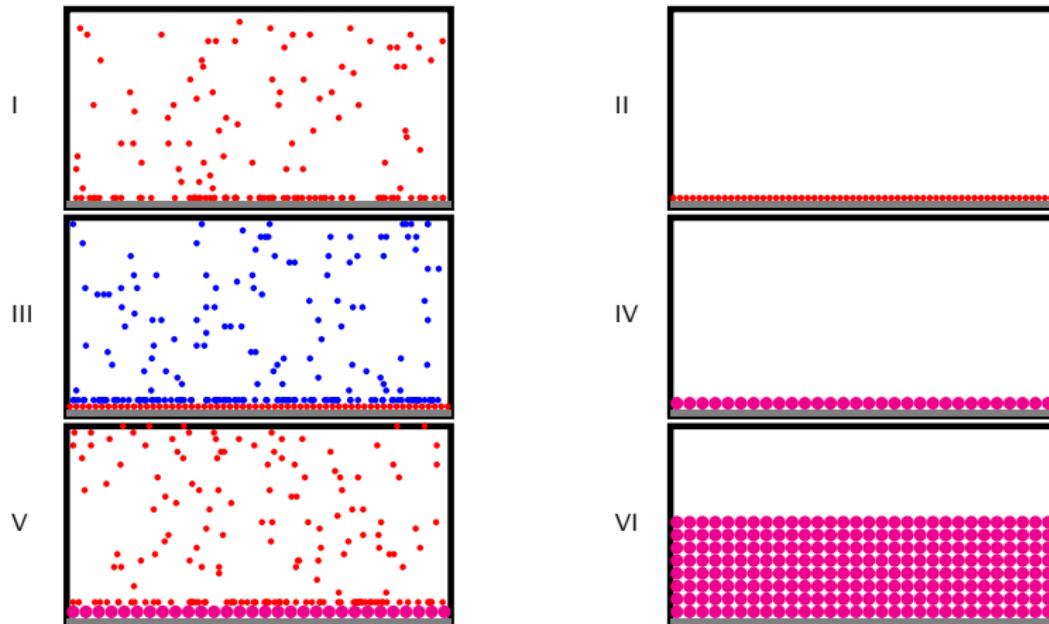
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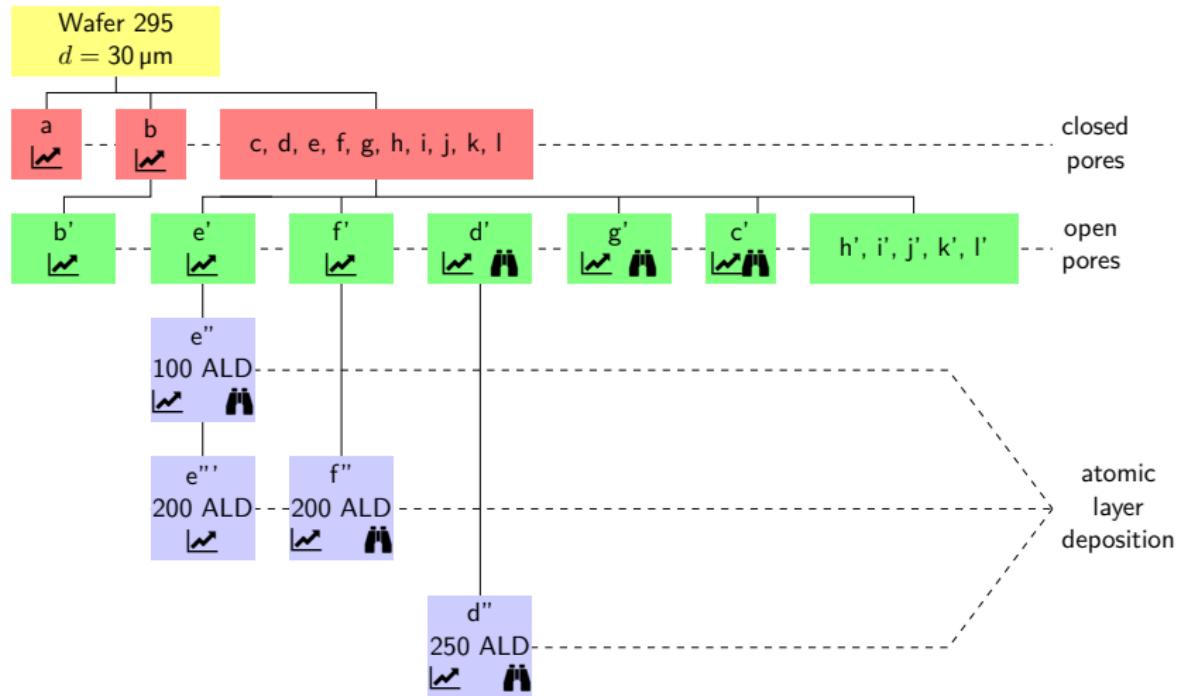
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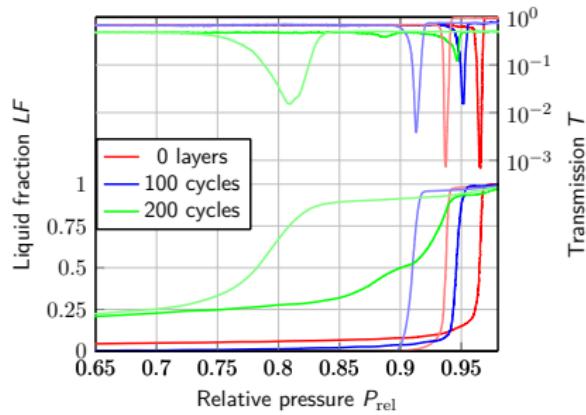
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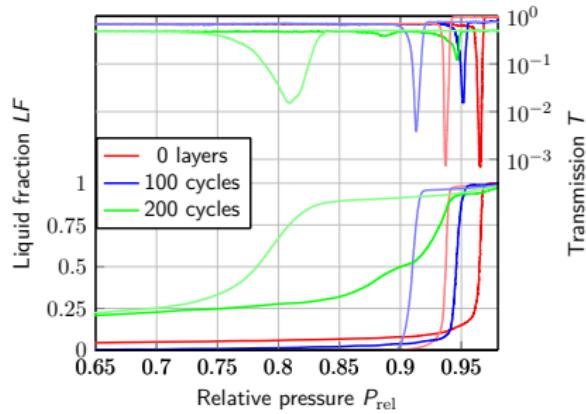
Testing the ALD process



ALD membranes

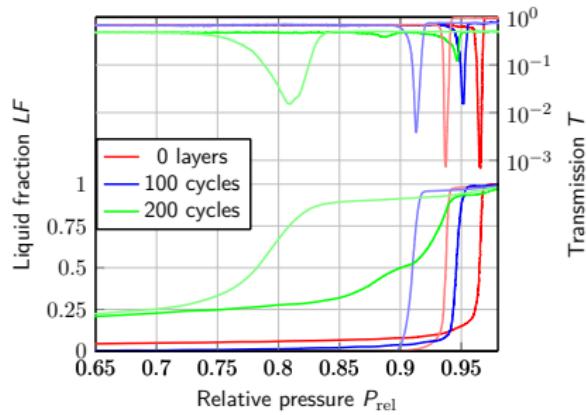


ALD membranes



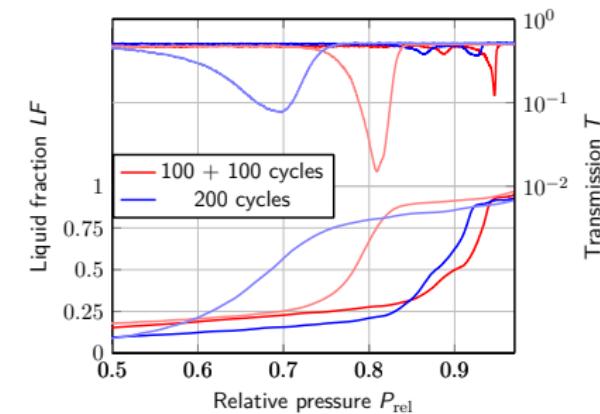
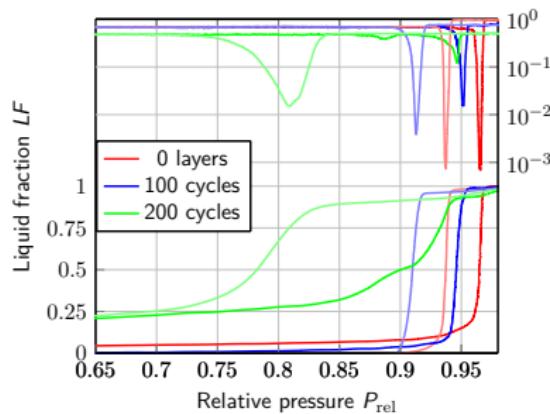
- ALD effectively reduces pore diameters of large pores

ALD membranes



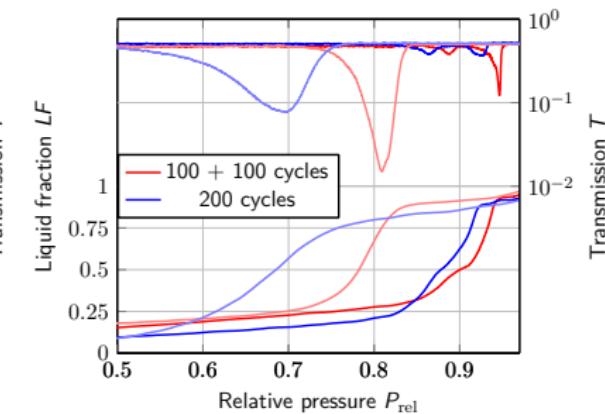
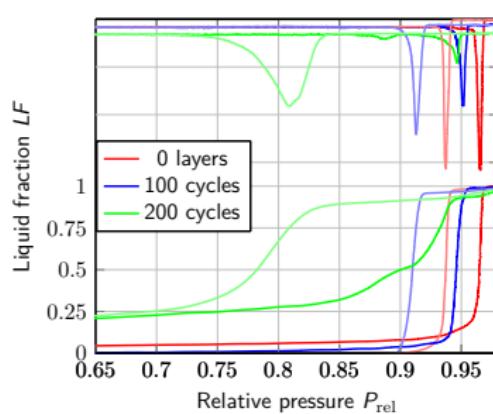
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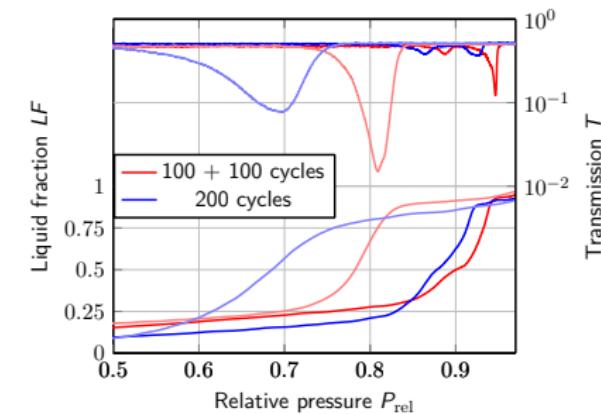
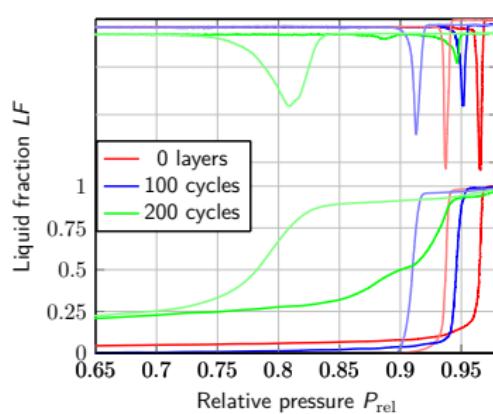
ALD membranes



- ALD effectively reduces pore diameters of large pores
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- Evaporations at low pressures

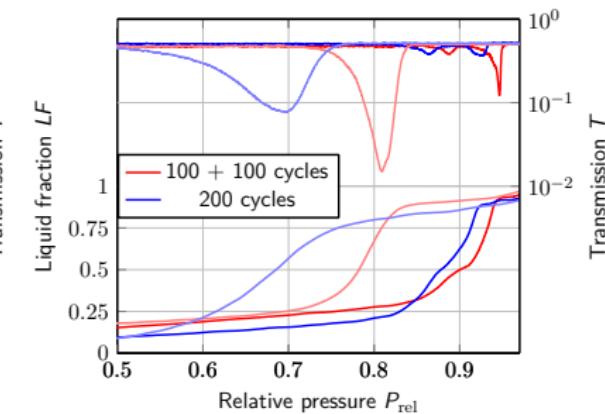
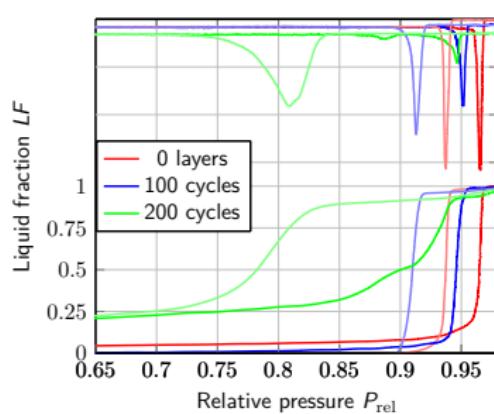
ALD membranes



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- Evaporations at low pressures
- Independent from interruptions of the process?

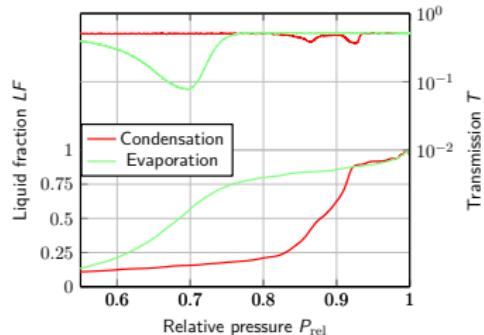
ALD membranes



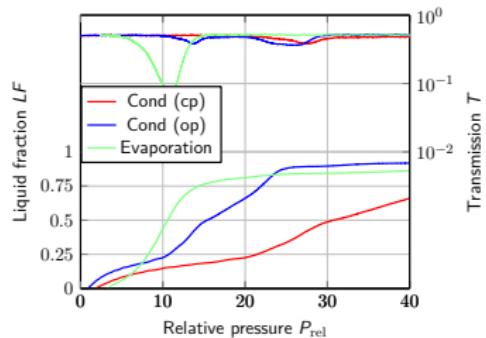
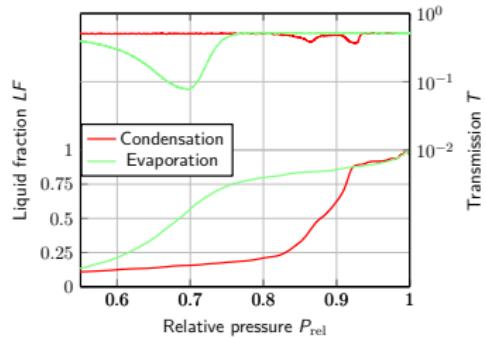
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- Evaporations at low pressures
- Independent from interruptions of the process?
- Result reproducible?

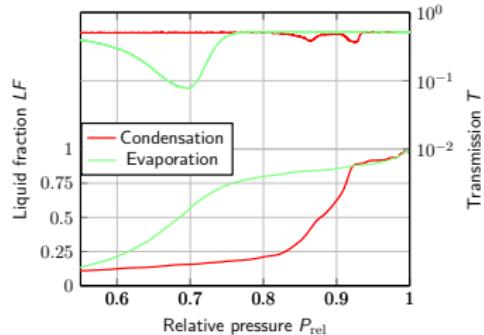
ALD for smaller pore diameters I



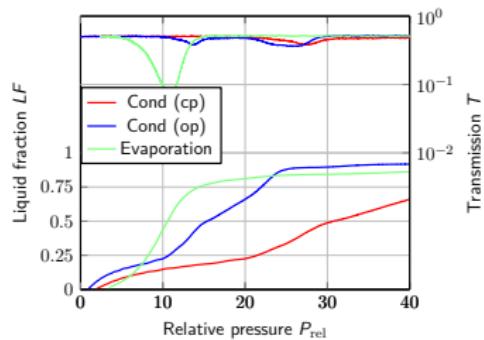
ALD for smaller pore diameters I



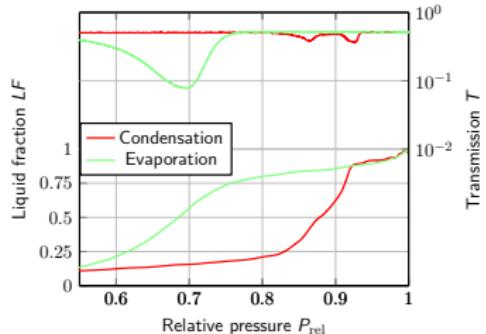
ALD for smaller pore diameters I



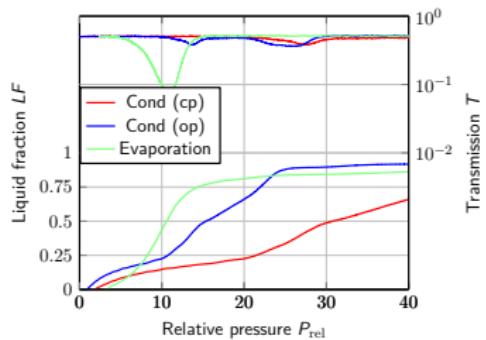
- Closed and open pore KELVIN conversion yields branches covering the same diameter ranges



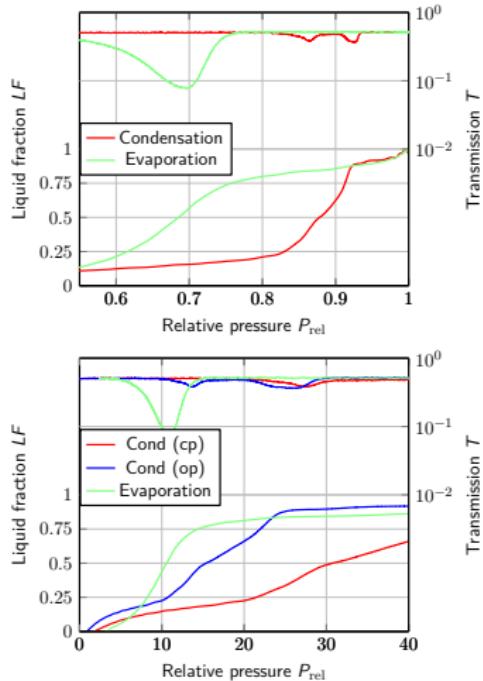
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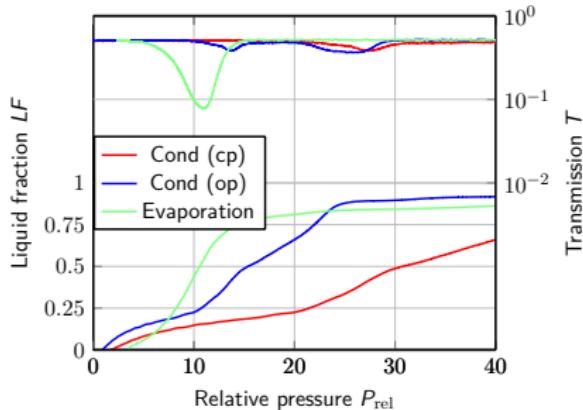
- Closed and open pore KELVIN conversion yields branches covering the same diameter ranges
- Expected to work on the membrane with 100 + 100 cycles of ALD too



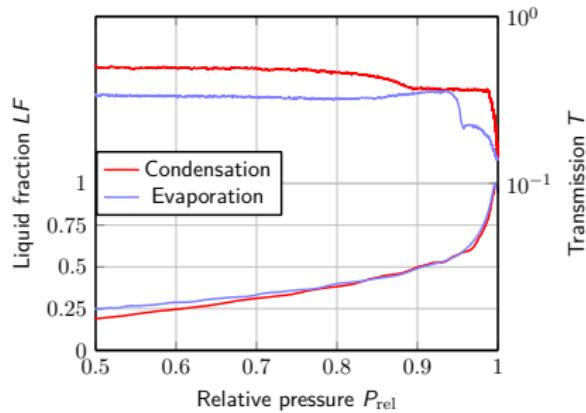
ALD for smaller pore diameters I



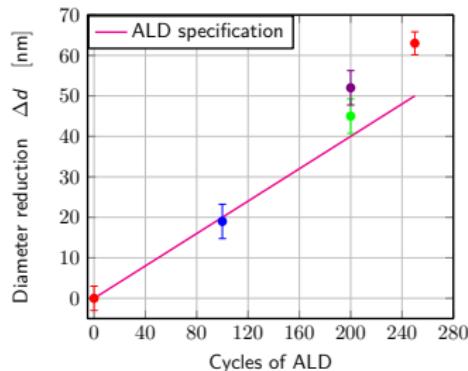
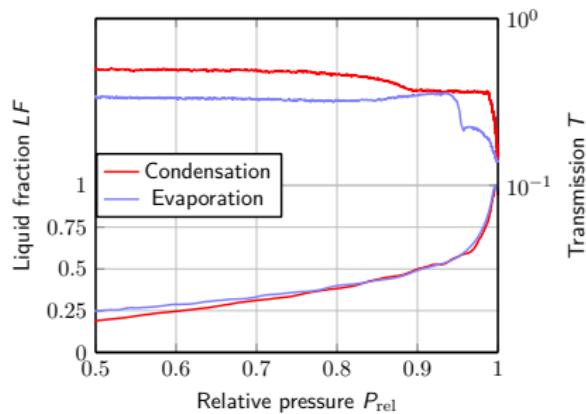
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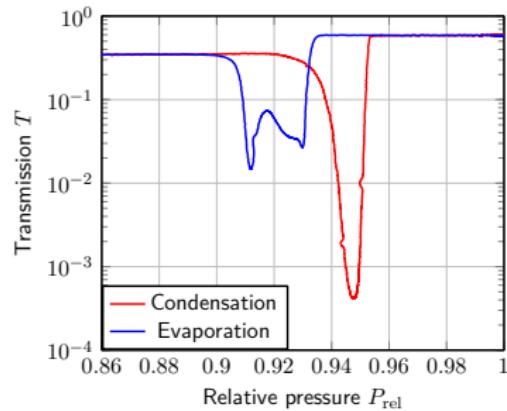
ALD for smaller pore diameters II



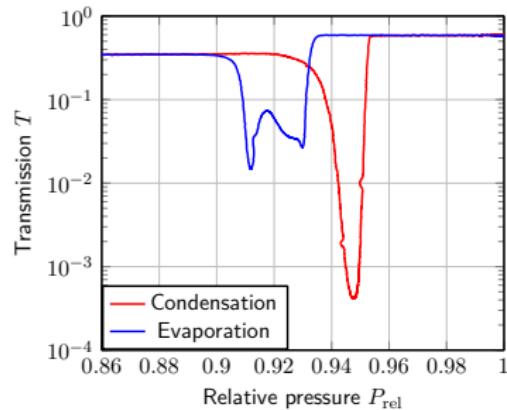
ALD for smaller pore diameters II



Transmission & pore disorder theory

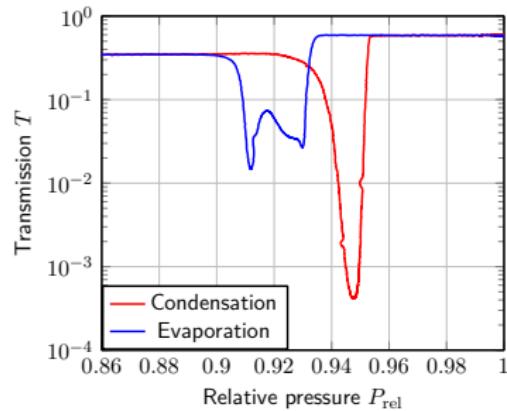


Transmission & pore disorder theory



Transmission drops for membranes of wafer 292 and before

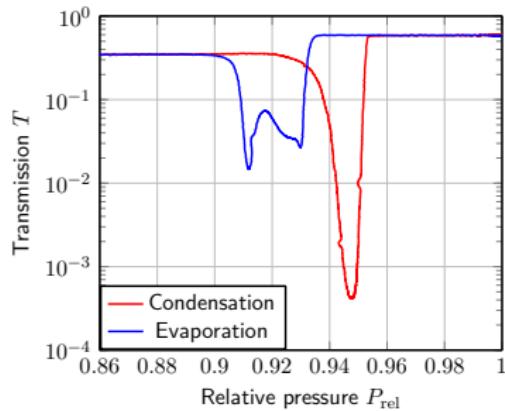
Transmission & pore disorder theory



Transmission drops for membranes of wafer 292 and before

- deeper for condensation,
- shallower for evaporation.

Transmission & pore disorder theory



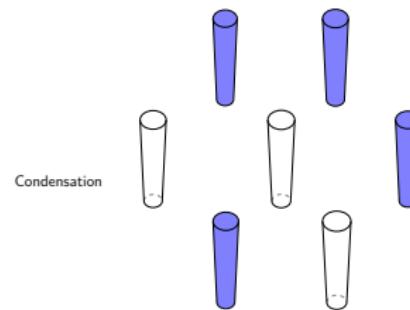
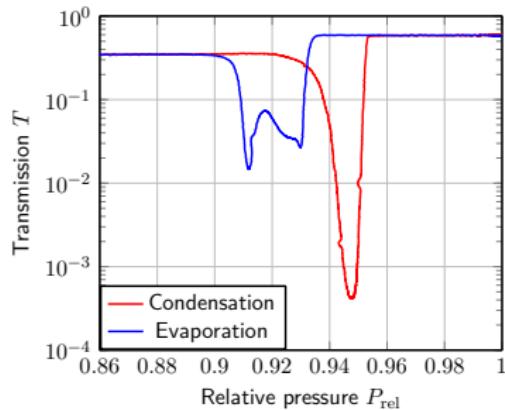
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Same observation made on the measurements made

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Transmission & pore disorder theory



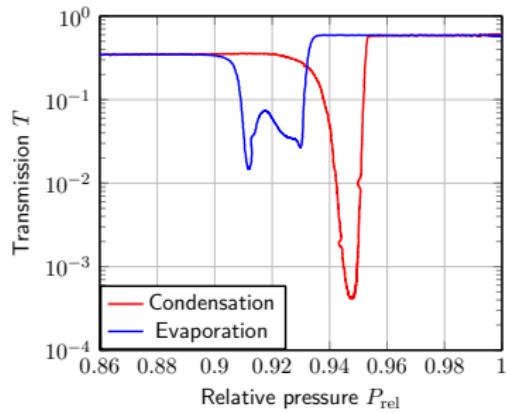
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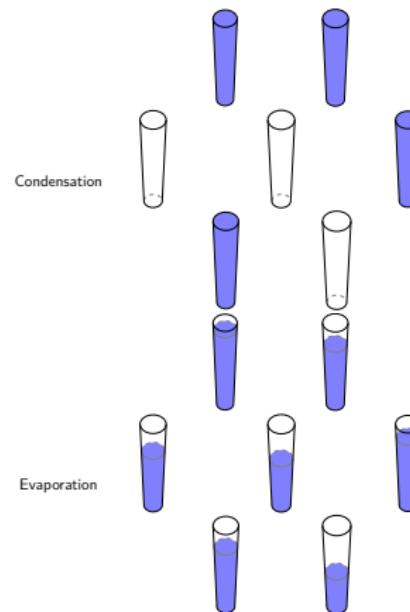
Transmission & pore disorder theory



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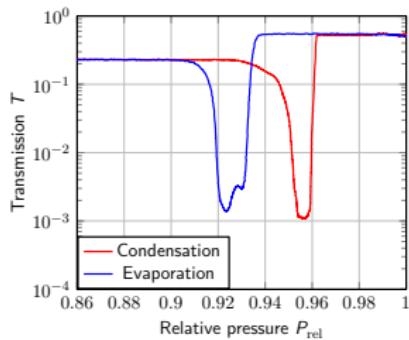
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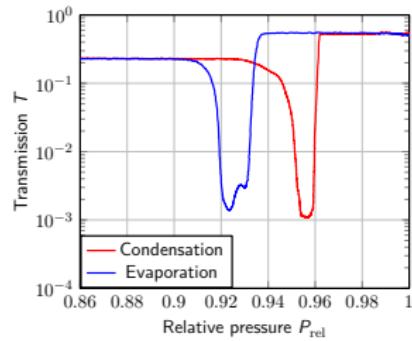
More transmission measurements

60 μm
closed
pores

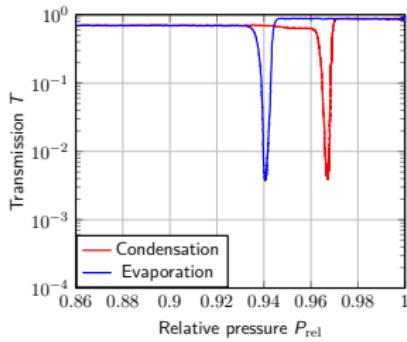


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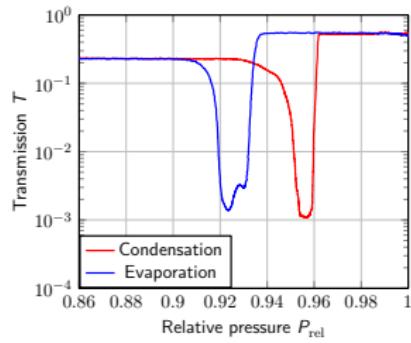


30 μm
open pores

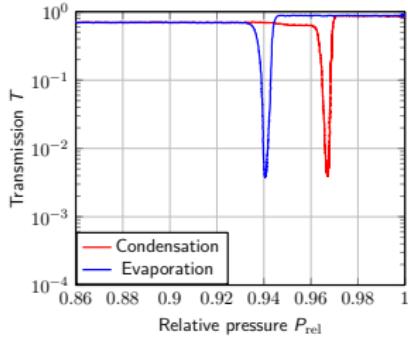


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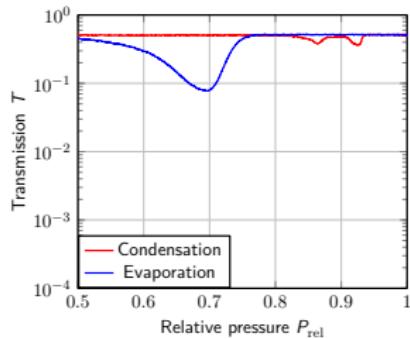
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30 μm
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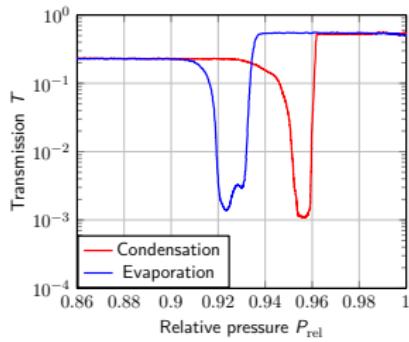


30 μm
open pores
200 ALD

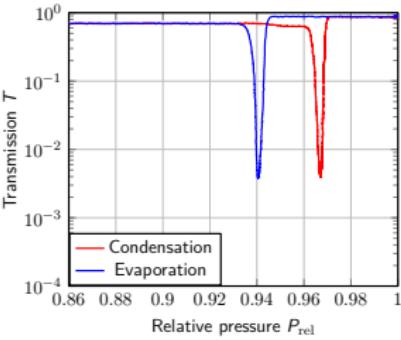


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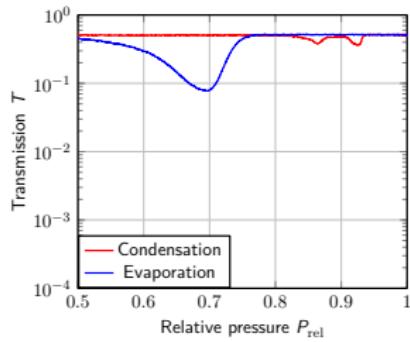
60 μm
closed
pores



30 μm
open pores



30 μm
open pores
200 ALD



Pore disorder theory

- Does not explain observations
- Might be missing something or be incorrect

Conclusions and prospects

- Condensation at spinodal pressure yielding a hysteresis confirmed

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- Inhomogeneity on one single wafer

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- Systemized SEM image analysis possible with porosity from isotherms