

Condensation and Evaporation of Hexane in Nanoporous Alumina Membranes

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Overview

1 Context

2 Goals

3 Theoretical background

- Condensation and evaporation in cylindrical pores
- Membrane production

4 Experimental setup

5 Experimental results

- Data evaluation
-

6 Conclusions and prospects

Context

Grand scheme

- Condensation and evaporation of fluids in confinement

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- Dependency on
 - pore diameter
 - temperature (relative to the critical temperature)

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Grand scheme

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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

Goals

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

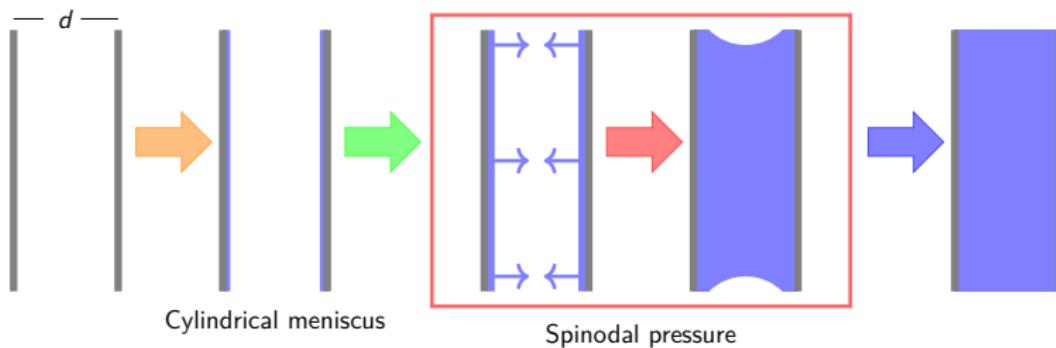
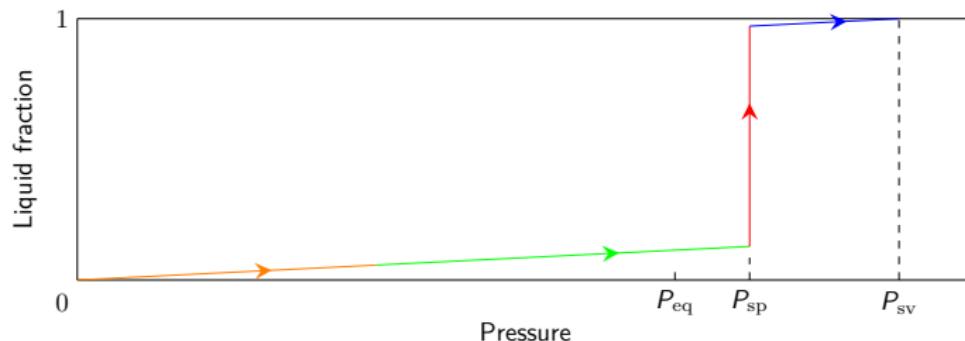
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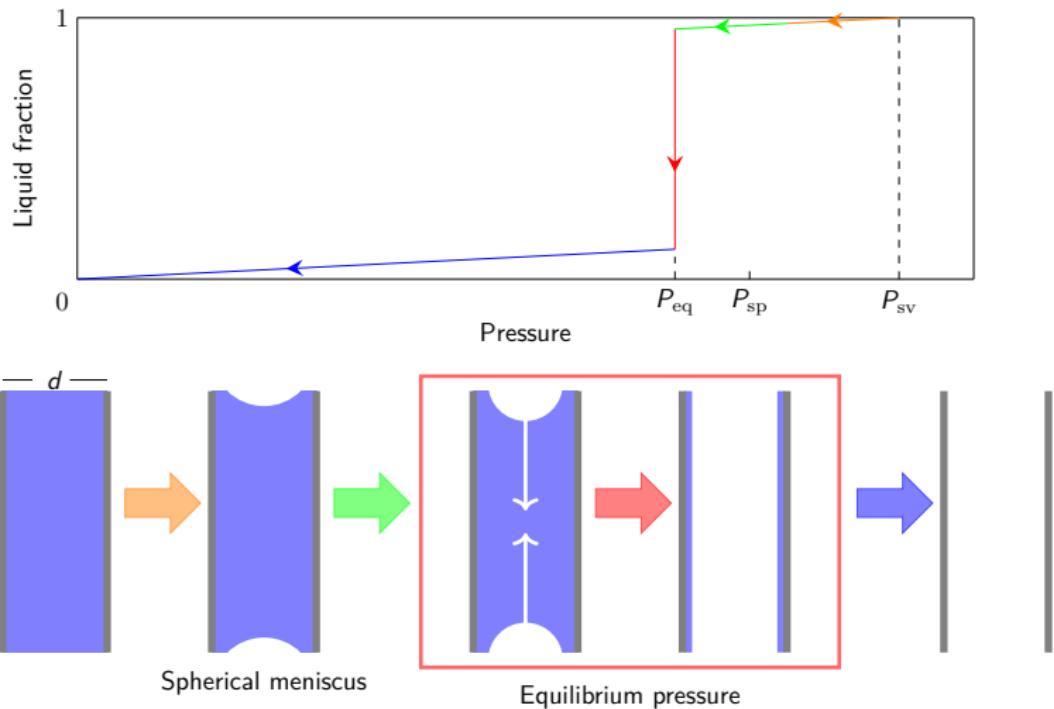
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- Performing isotherm measurements on many membranes for **statistics**
- Comparing the pore diameters extracted from the volumetric measurements those from scanning electron microscopy (SEM) images
- Improving the fabrication process to reduce the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

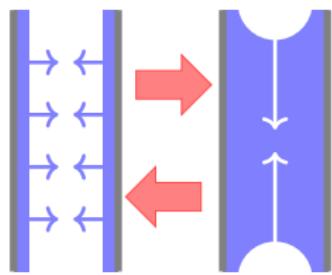
Condensation in a cylindrical open pore



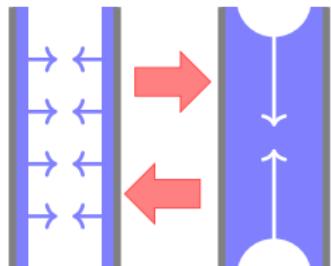
Evaporation in a cylindrical open pore



Condensation and evaporation in a cylindrical open pore



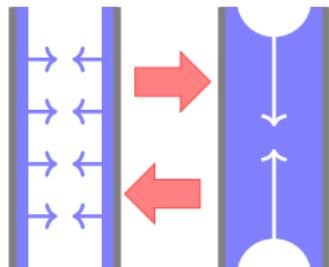
Condensation and evaporation in a cylindrical open pore



Open cylindrical pore

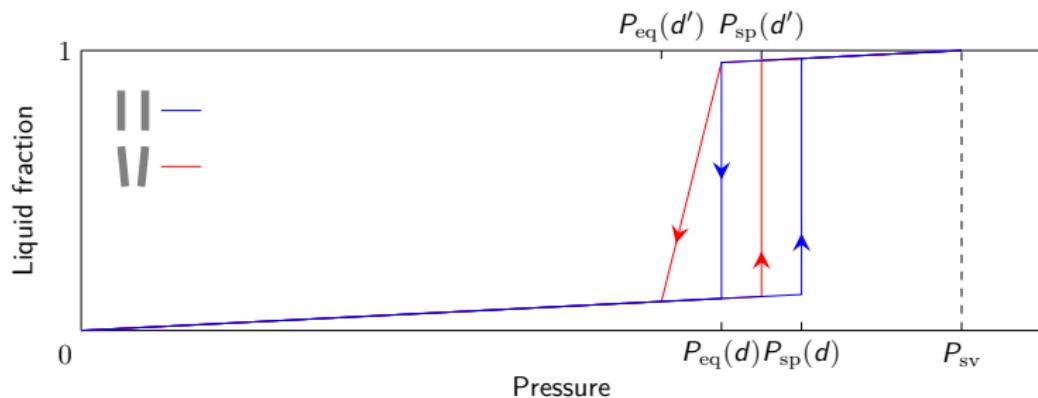
Condensation at spinodal pressure and
evaporation at equilibrium pressure
yield a **hysteresis**.

Condensation and evaporation in a cylindrical open pore

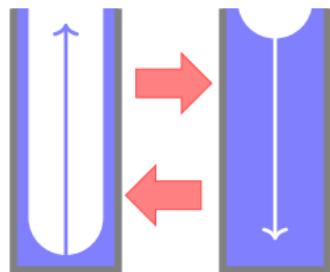


Open cylindrical pore

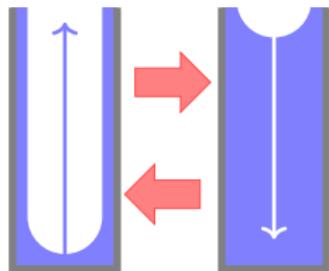
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Condensation and evaporation in a cylindrical closed pore



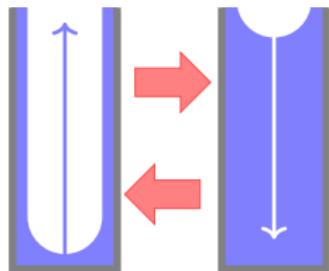
Condensation and evaporation in a cylindrical closed pore



Closed cylindrical pore

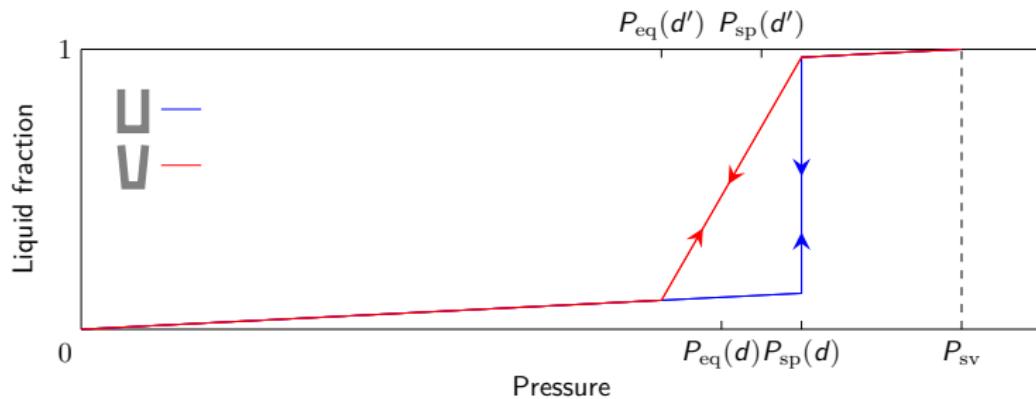
Condensation at equilibrium pressure and
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Condensation and evaporation in a cylindrical closed pore



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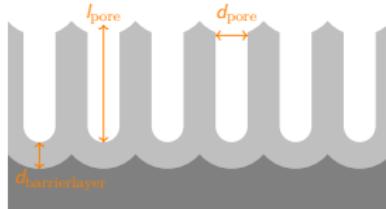
Condensation at equilibrium pressure and evaporation at equilibrium pressure leads to **disappearance of the hysteresis**.



Membrane production



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

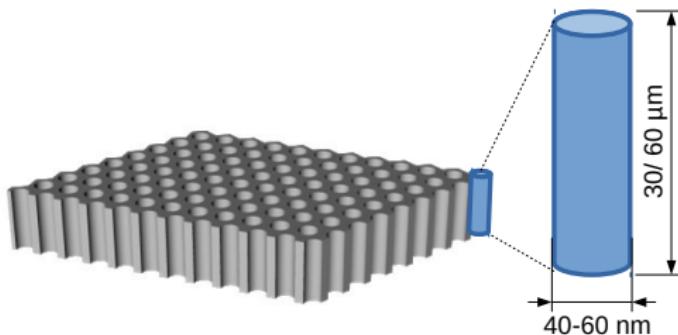


Floating on
phosphoric acid
($\text{H}_3\text{O}_4\text{P}$) till milky
aspects appear
plus 15 min

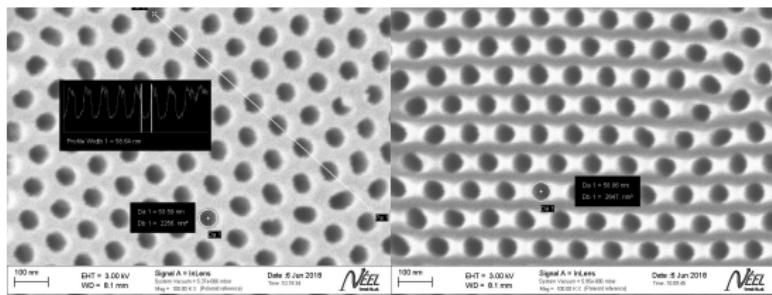
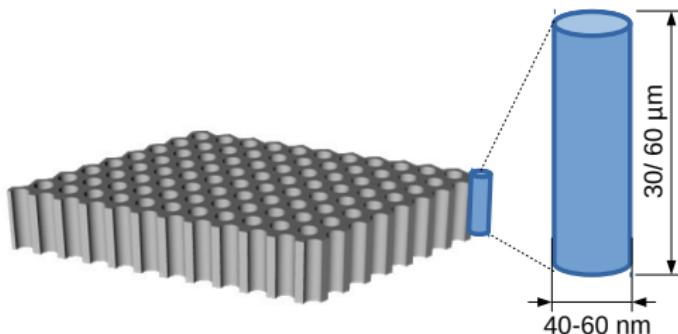
Immersion in
27,2 g CuCl_2
copper chloride
+ 0,21 HCl(37 %)
hydrochloric acid
+ 0,81 H_2O
water



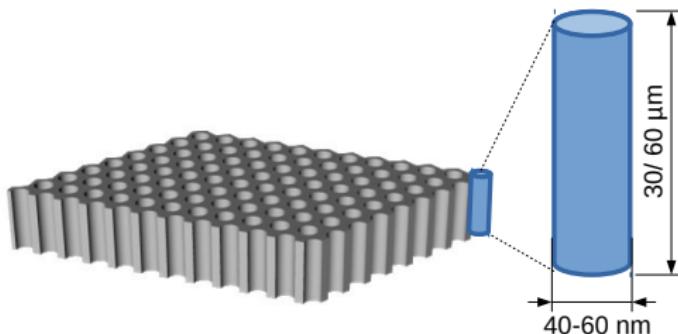
Alumina membranes - funnelling



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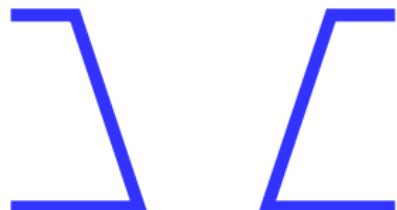
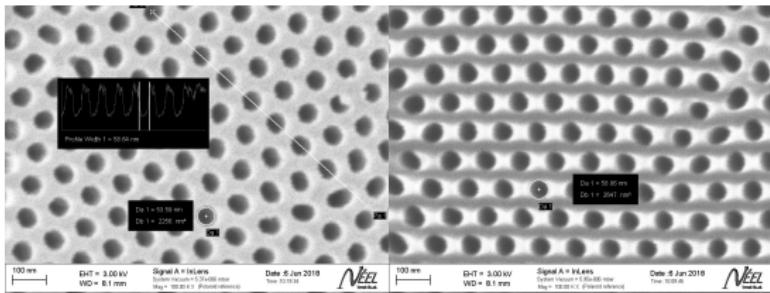


Alumina membranes - funnelling

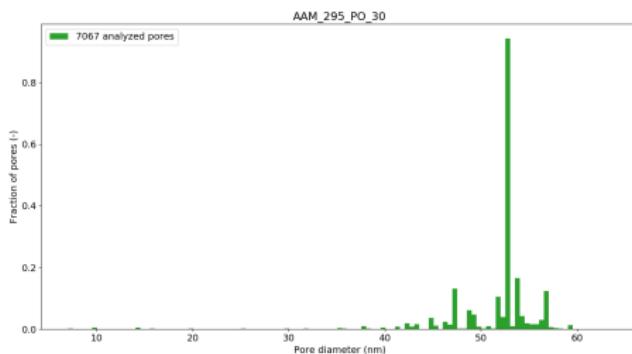


Funnelling

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



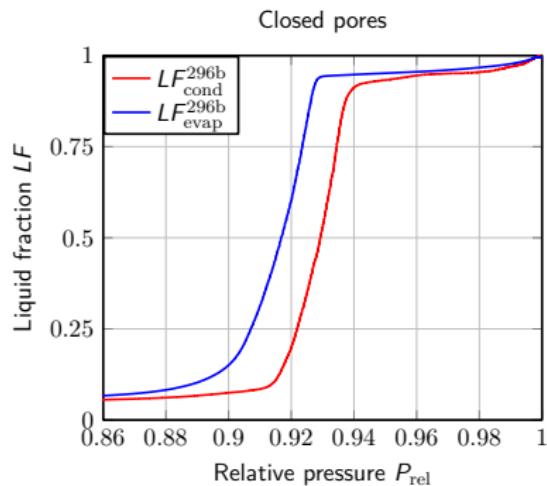
Alumina membranes - pore size distribution



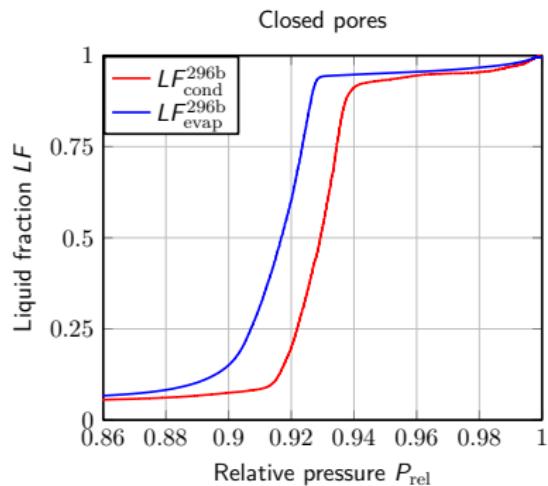
Pore size distribution

SEM analysis shows pore size distribution on a given membrane.

Alumina membranes - corrugations

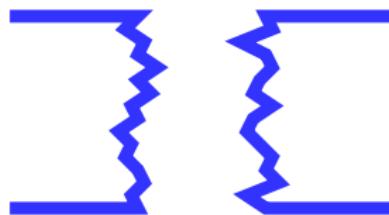


Alumina membranes - corrugations



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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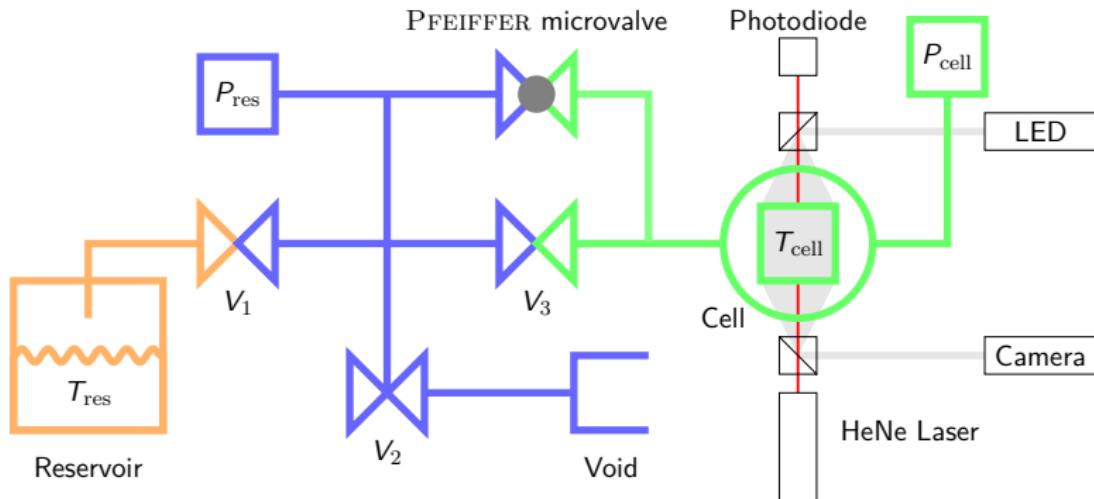
Problem

No simple ways to characterize these defects!

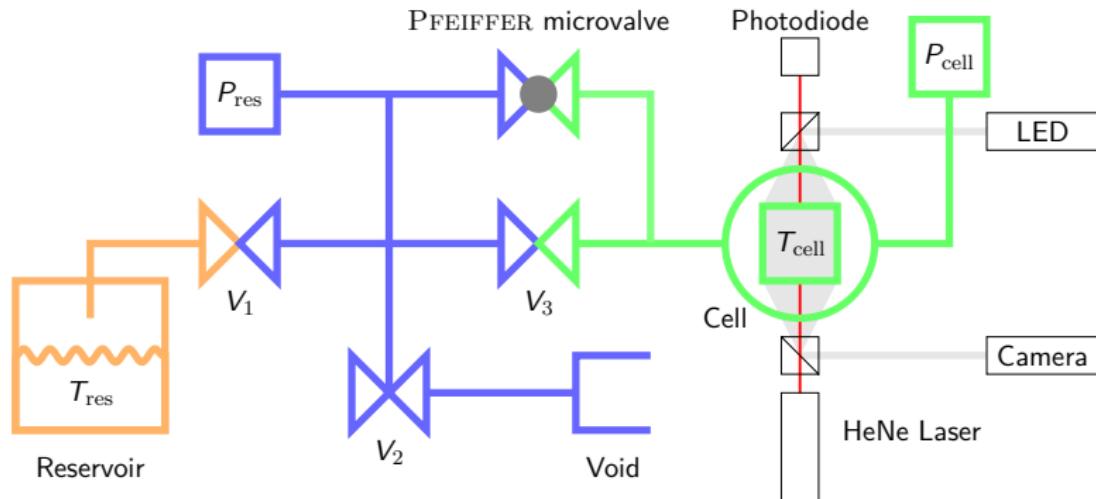
SEM images only give an impression of the surfaces of the membrane (factor between pore diameter and pore length is 1000!).

→ Need of **monodisperse membranes**

Final experimental setup



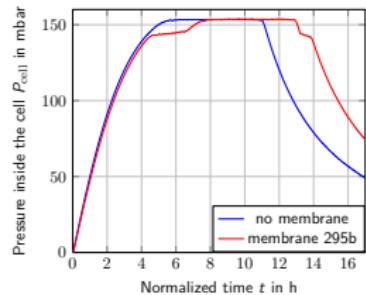
Final experimental setup



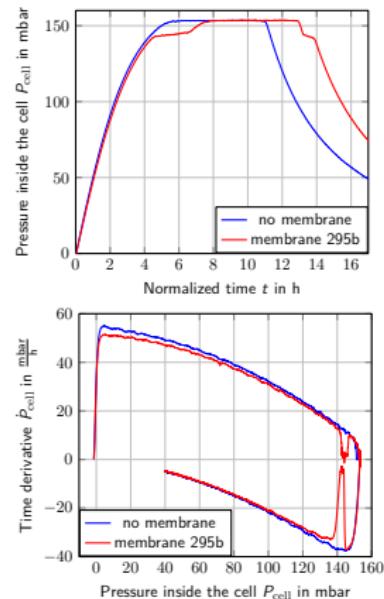
Volumetric and optical measurements

Volumetric and optical setups work independently.

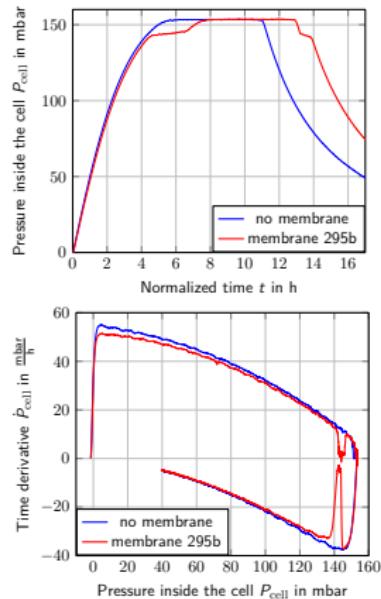
Data evaluation - volumetrics



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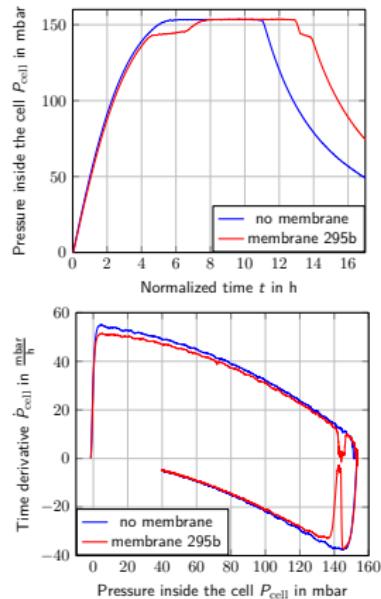
Data evaluation - volumetrics



Computation

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

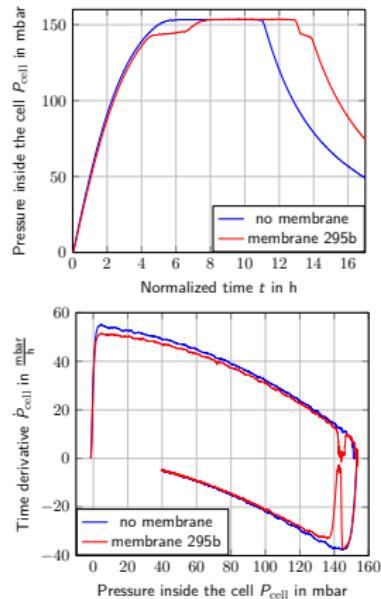
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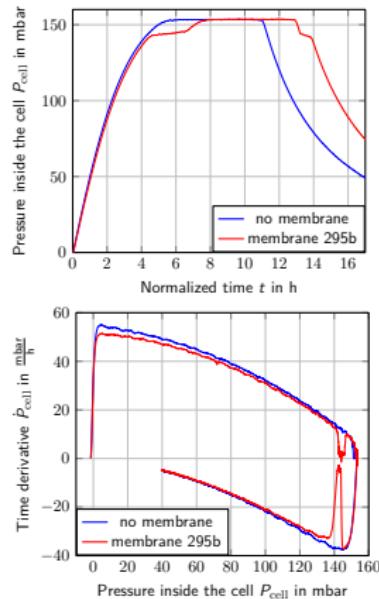
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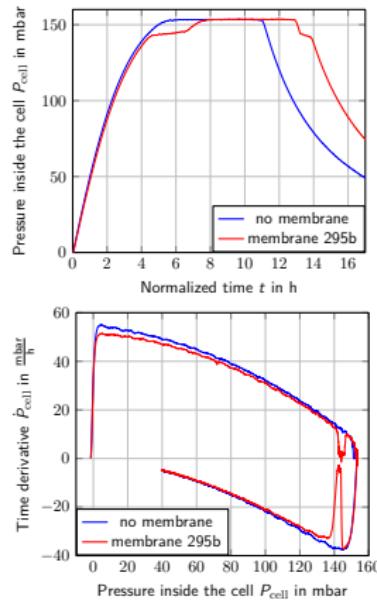
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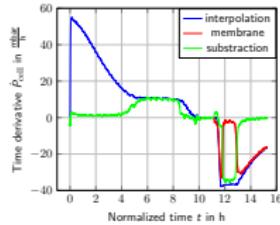
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Data evaluation - volumetrics

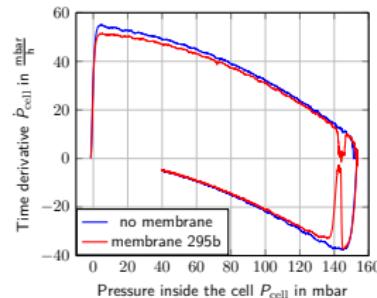
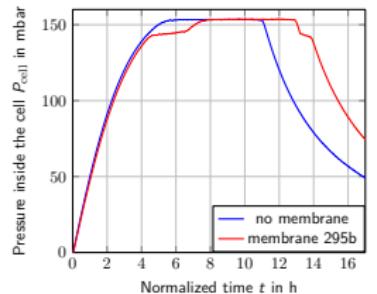


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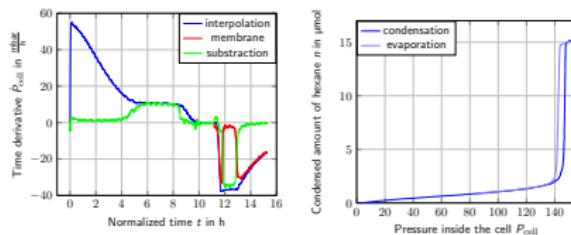


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Kelvin equation

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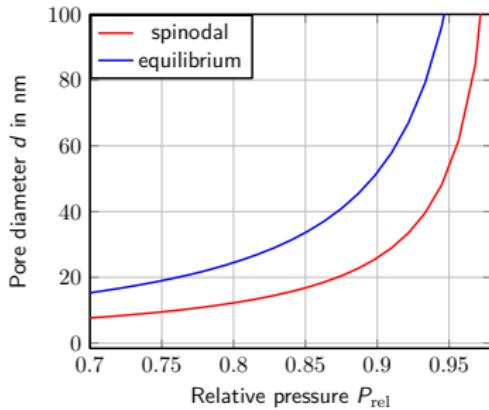
$$P_{\text{eq}} = P_{\text{sv}} \cdot \exp\left(-\frac{2 \cdot \gamma V_{\text{mol}}^l}{R_0 \cdot RT}\right) < P_{\text{sp}} < P_{\text{sv}}$$

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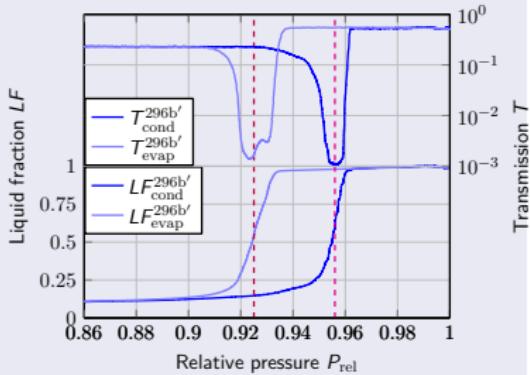
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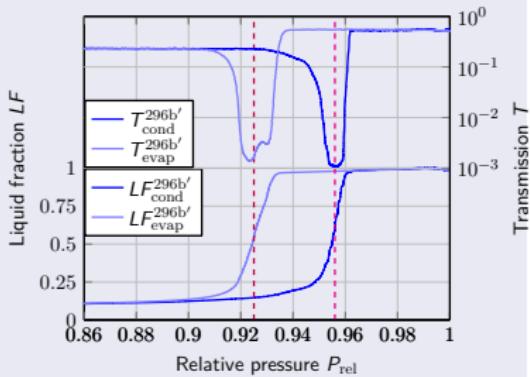
Easy example isotherms

Open pores



Easy example isotherms

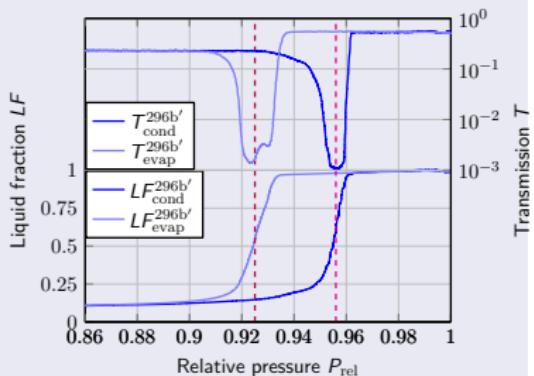
Open pores



- Hysteresis expected from theory

Easy example isotherms

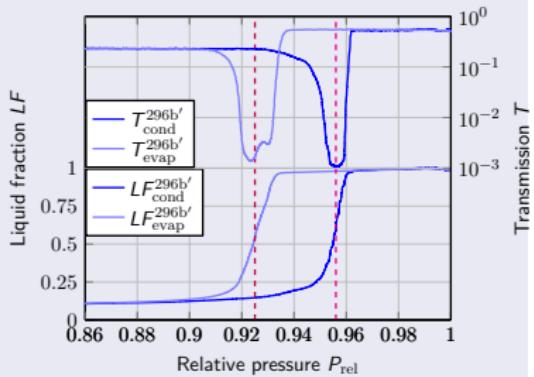
Open pores



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

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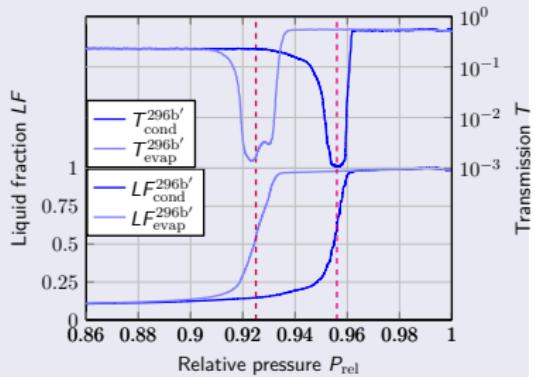
Open pores



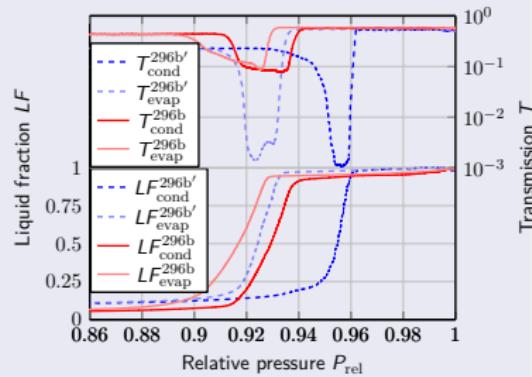
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- KELVIN conversion makes for diameters of 44,4 nm and 51,3 nm

Easy example isotherms

Open pores



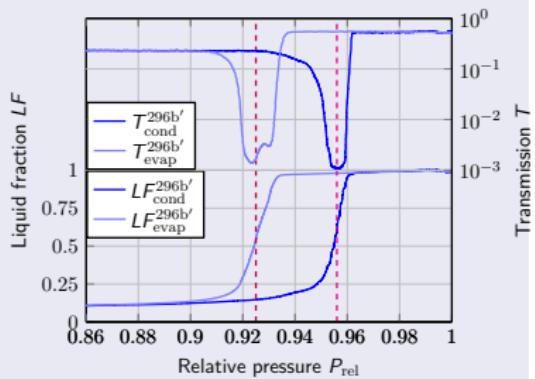
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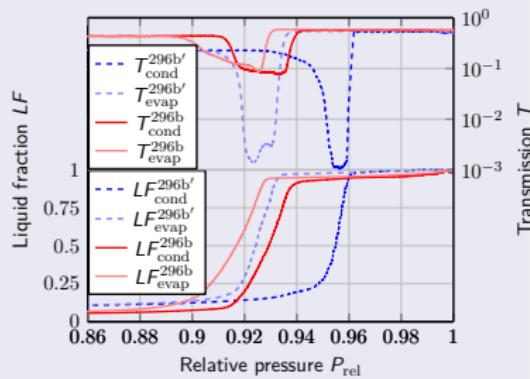
Easy example isotherms

Open pores



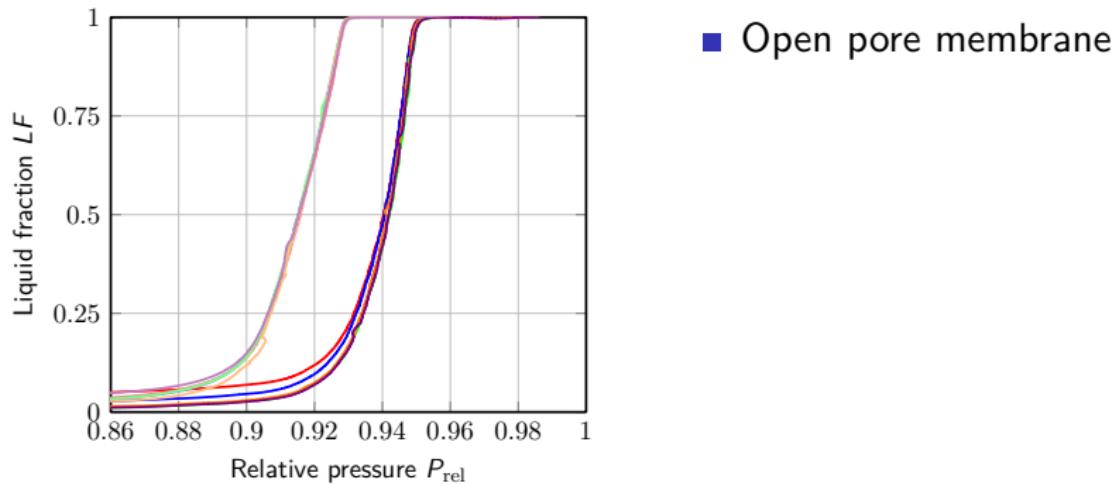
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Closed pores

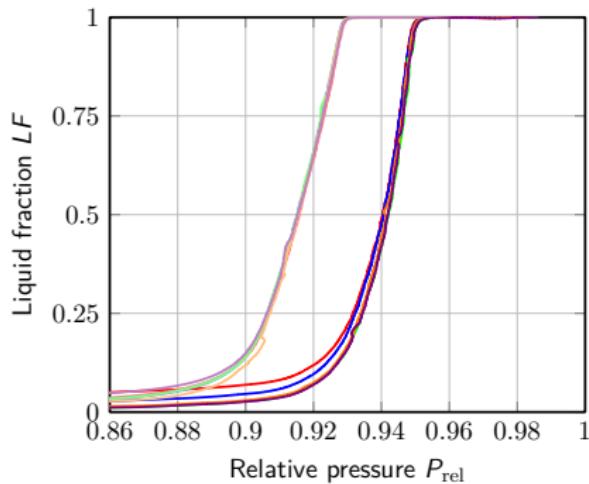


- Hysteresis grows smaller
- Hysteresis does not disappear though

Volumetric measurement reproducibility

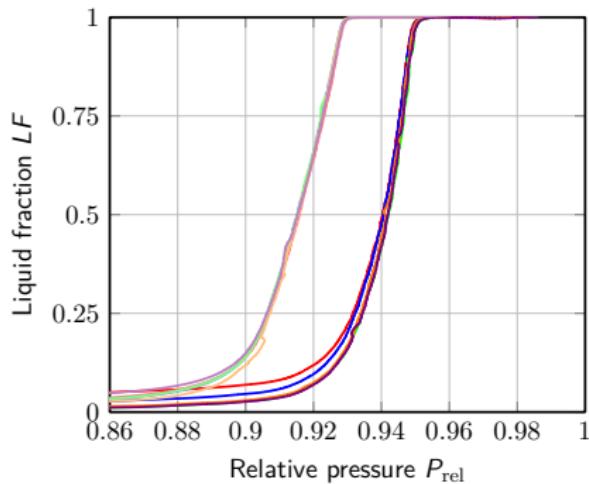


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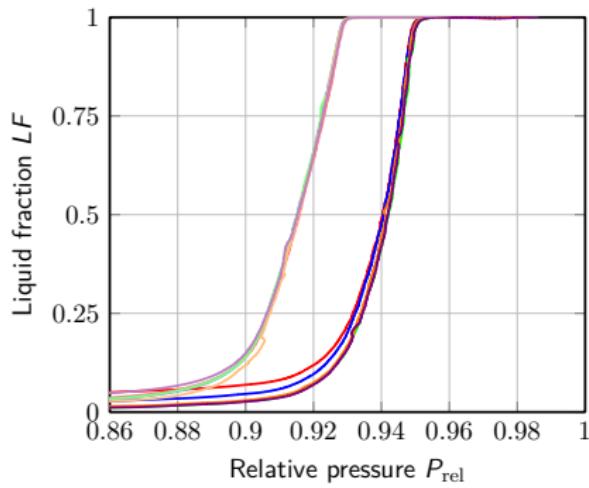
- Open pore membrane
- Slight variations of the height of the condensation branch

Volumetric measurement reproducibility



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→ combination of measurement noise and liquid film thickness

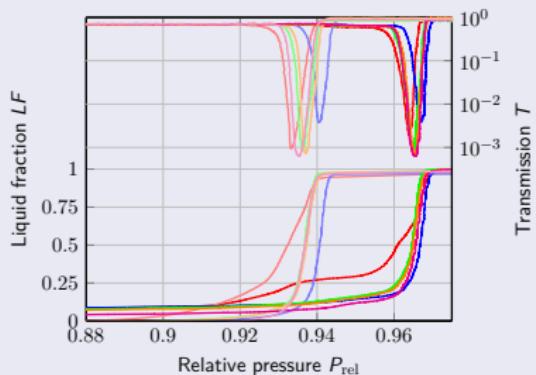
Volumetric measurement reproducibility



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

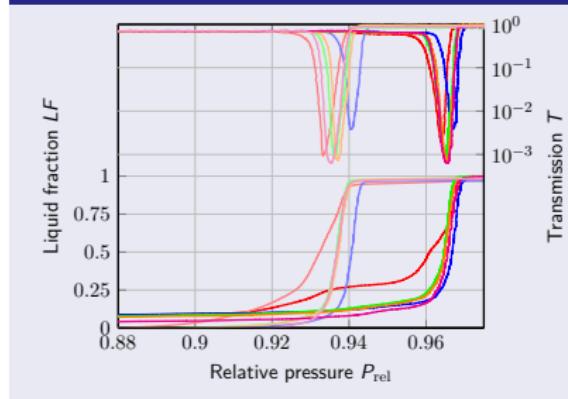
Wafer inhomogeneity - open pore membranes wafer 295

Isotherms

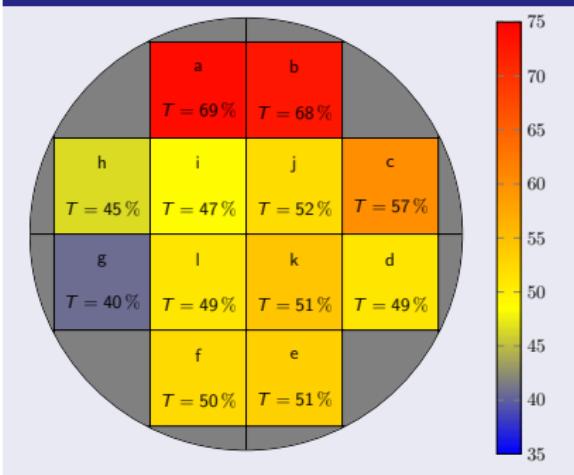


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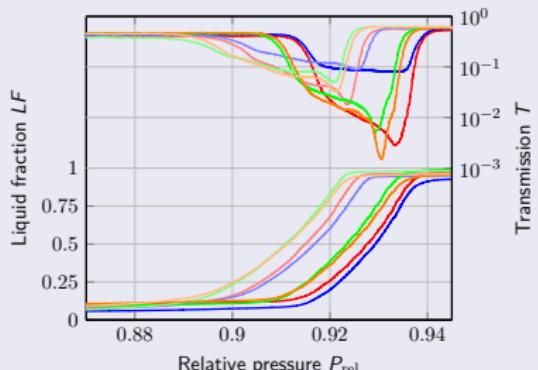


Dry transmission measurements



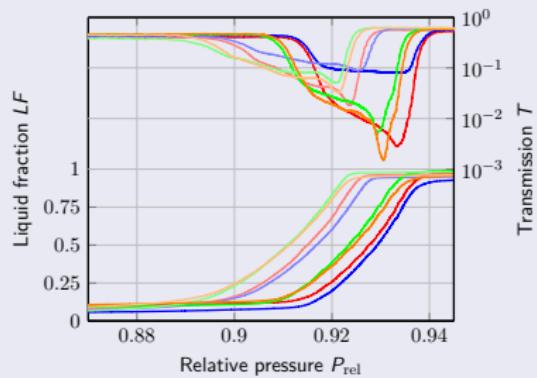
Wafer inhomogeneity - closed pore membranes wafer 296

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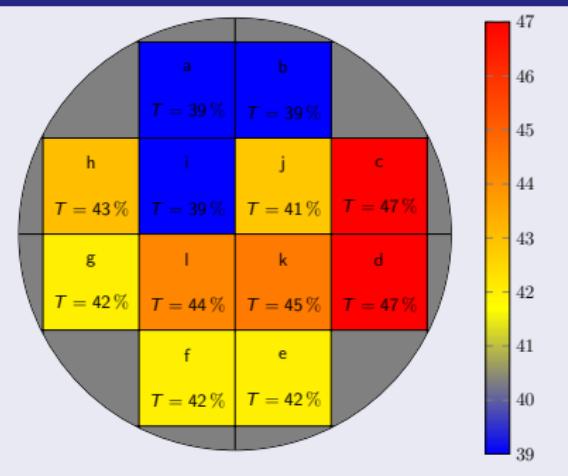


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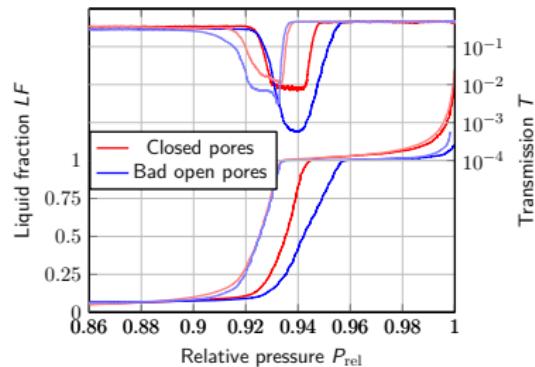
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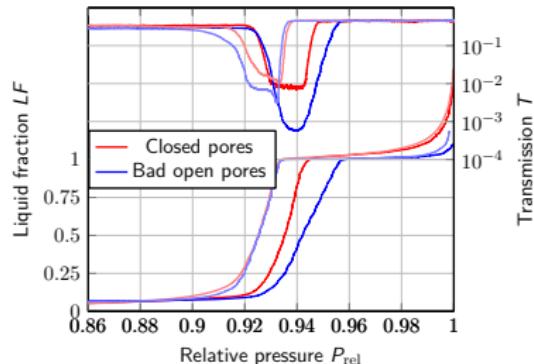
Dry transmission measurements



Bad pore opening



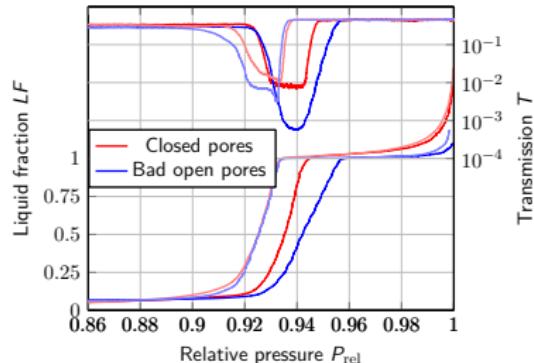
Bad pore opening



Condensation branch

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

Bad pore opening



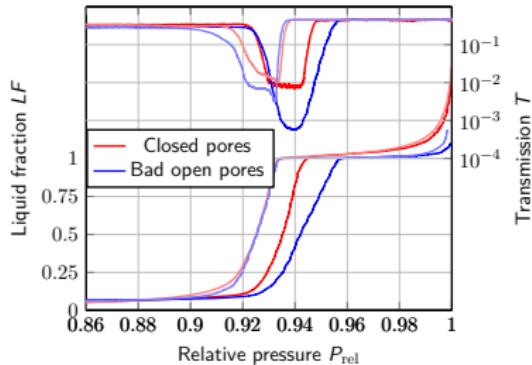
Evaporation branch

- Superimposed with closed pores

Condensation branch

- Starts at equilibrium pressure
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Bad pore opening

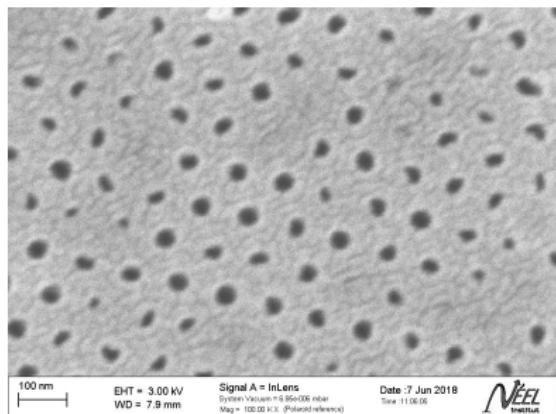


Condensation branch

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

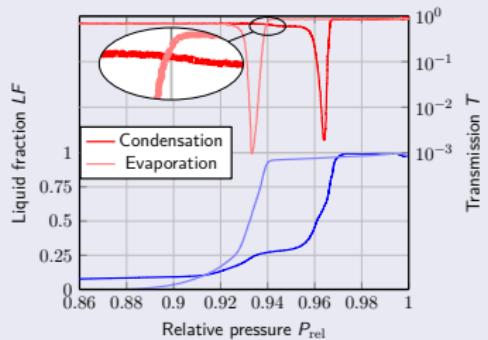
Evaporation branch

- Superimposed with closed pores



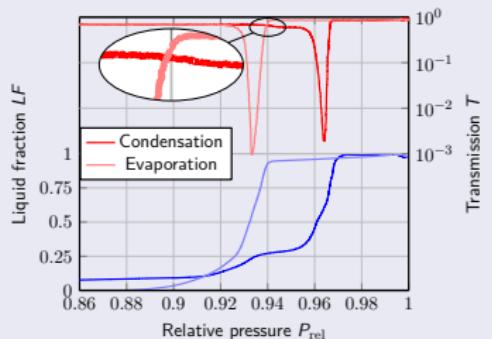
Unexpected closed pores I

Suspicion of closed pores



Unexpected closed pores I

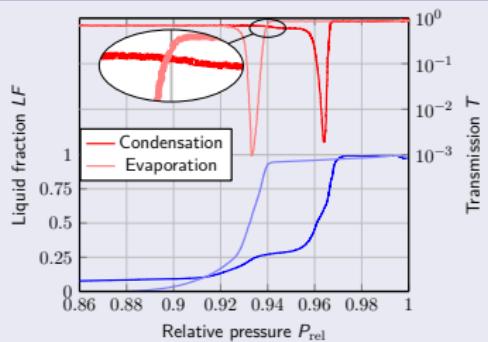
Suspicion of closed pores



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

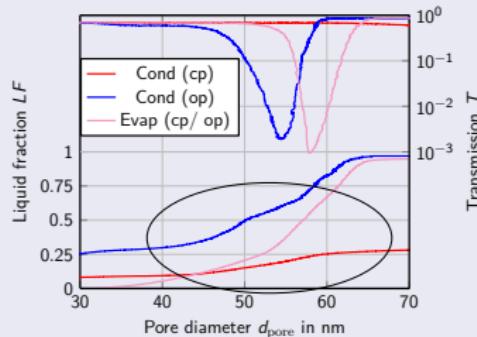
Unexpected closed pores I

Suspicion of closed pores



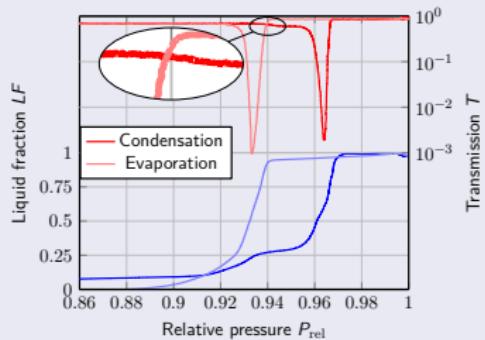
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KELVIN conversion for cp/ op



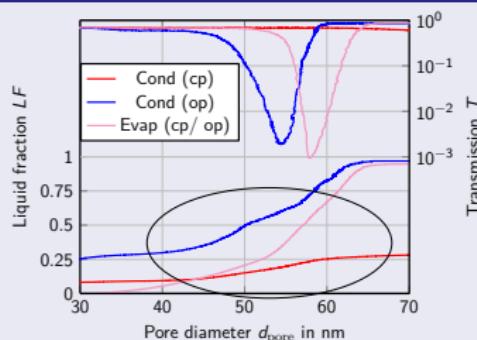
Unexpected closed pores I

Suspicion of closed pores



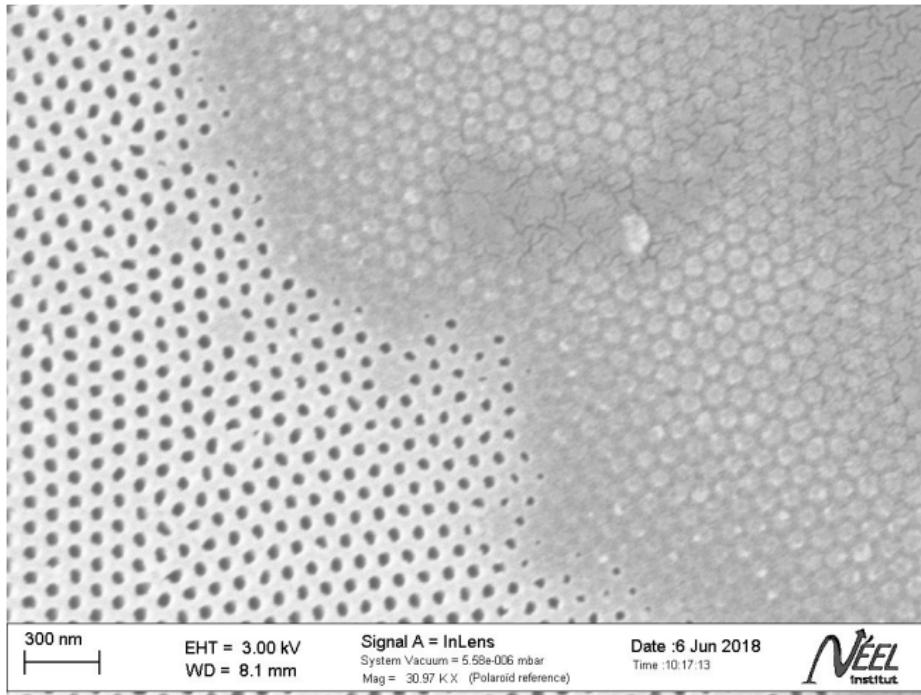
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KELVIN conversion for cp/ op

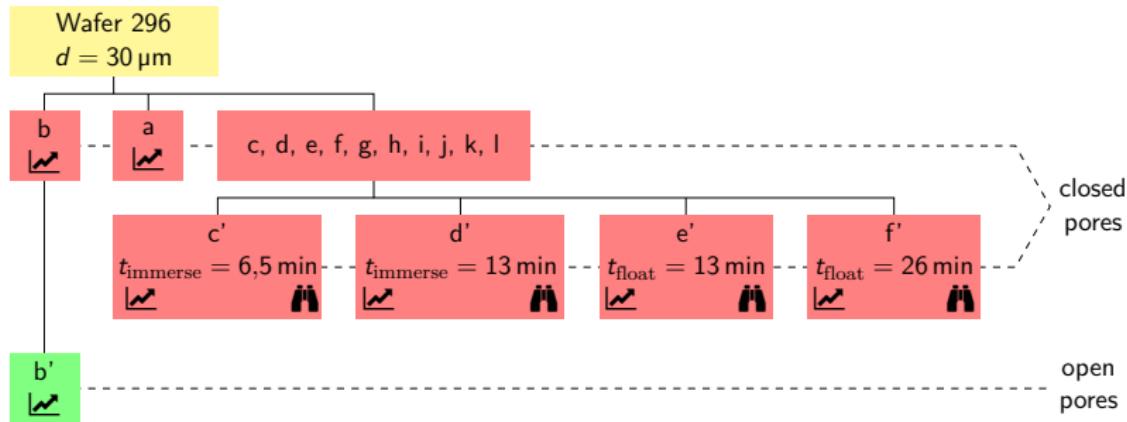


- Evaporation superimposed (appears at P_{eq} for cp/ op)
- Step 1 and the steps 2,3 appear on the same diameter range
- Distinct steps 2 and 3 unclear

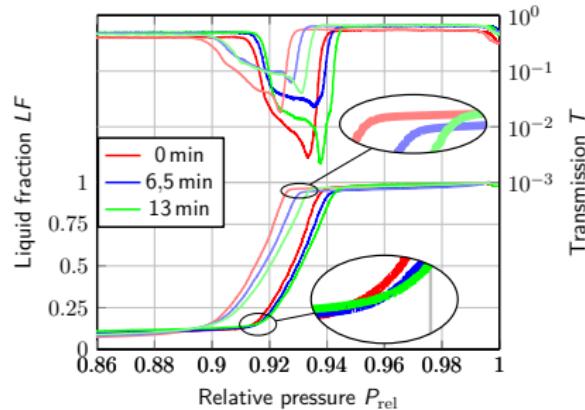
Unexpected closed pores II



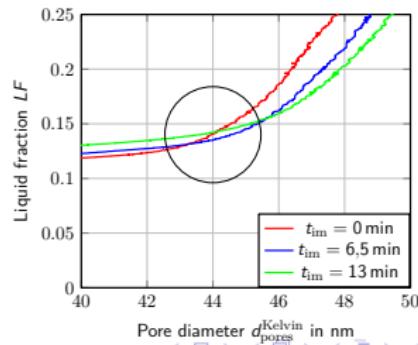
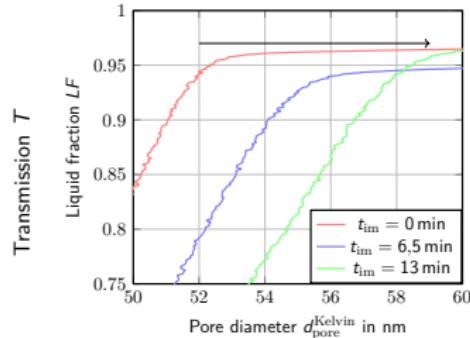
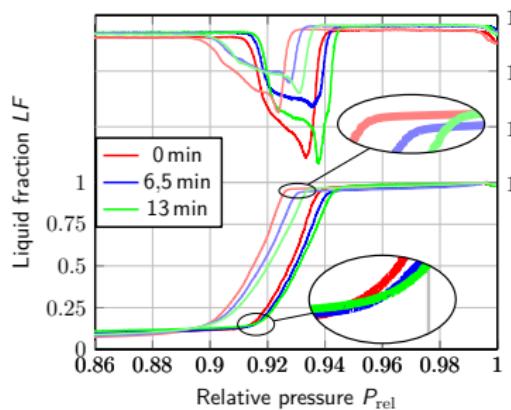
Testing the pore opening process



Funnellization due to immersion in phosphoric acid

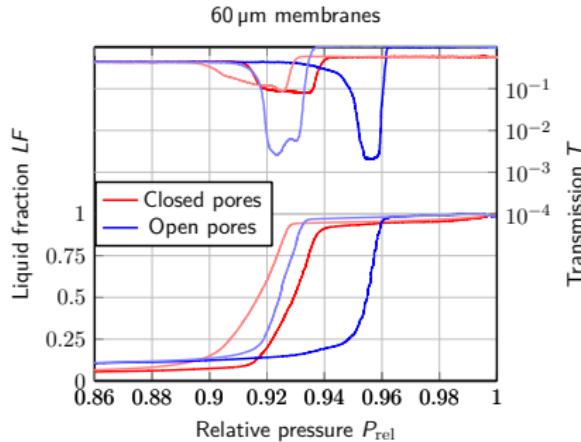


Funnellization due to immersion in phosphoric acid

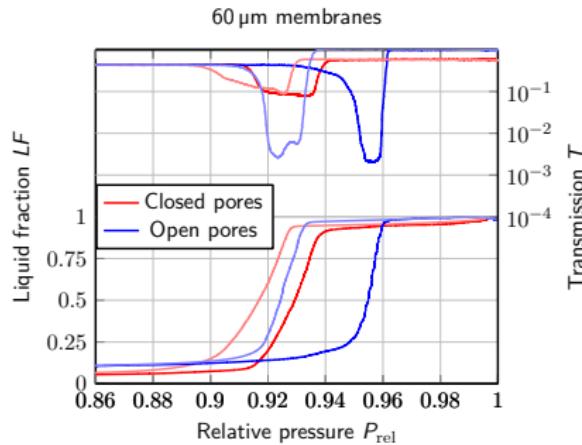


- Continuous shift to larger pressures with increasing immersion times
- Slope increasing with liquid fraction leading to a linear rise upon KELVIN conversion
- Shift seemingly increasing from bottom to top side

Inverse funnelling and thinner membranes

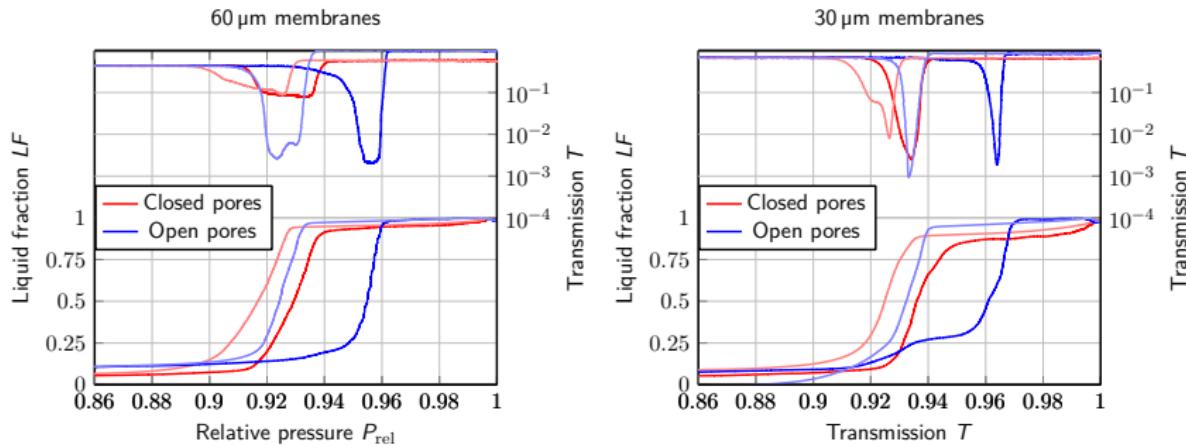


Inverse funnelling and thinner membranes



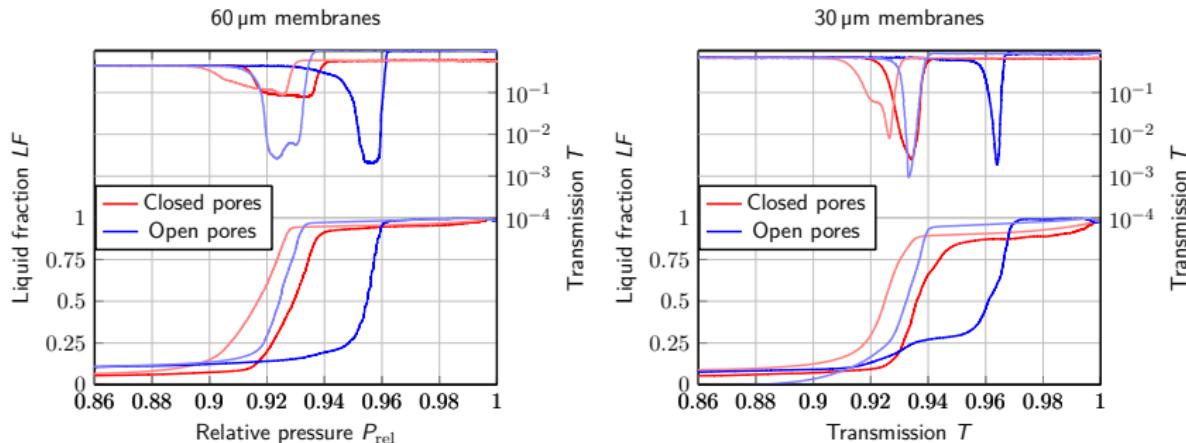
- Sharpening of the isotherm branches upon pore opening
- Shape does not change - same as for inverse funnelling

Inverse funnelling and thinner membranes



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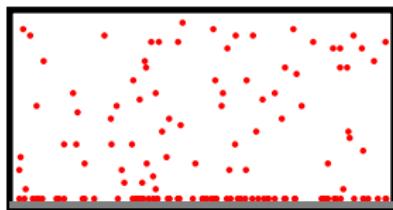
Inverse funnelling and thinner membranes



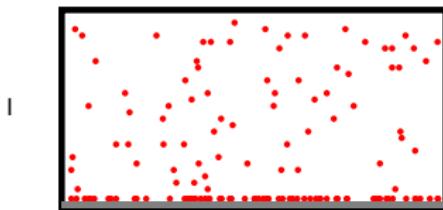
- Sharpening of the isotherm branches upon pore opening
- Shape does not change - same as for inverse funnelling

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

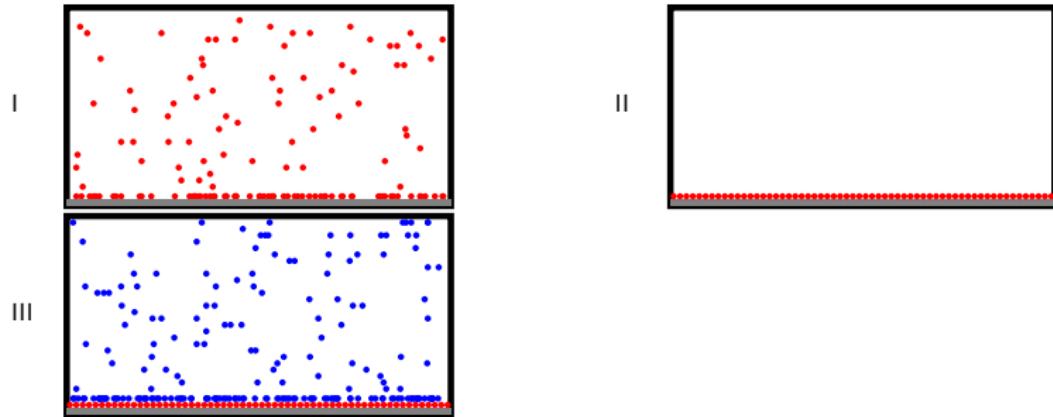
Atomic layer deposition (ALD)



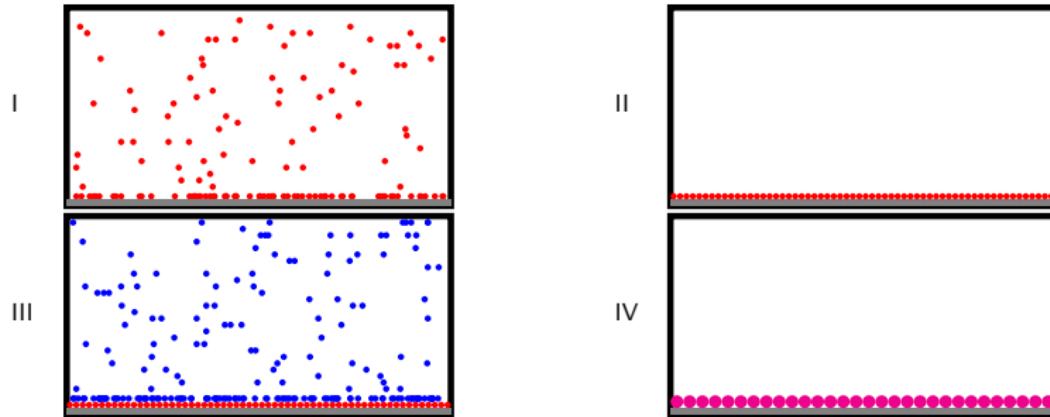
Atomic layer deposition (ALD)



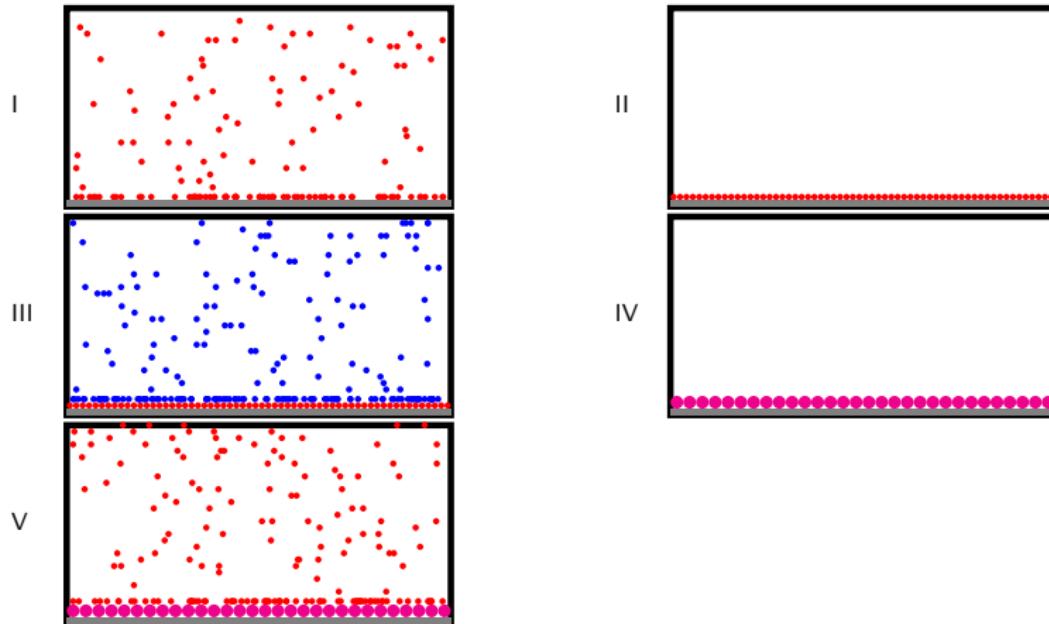
Atomic layer deposition (ALD)



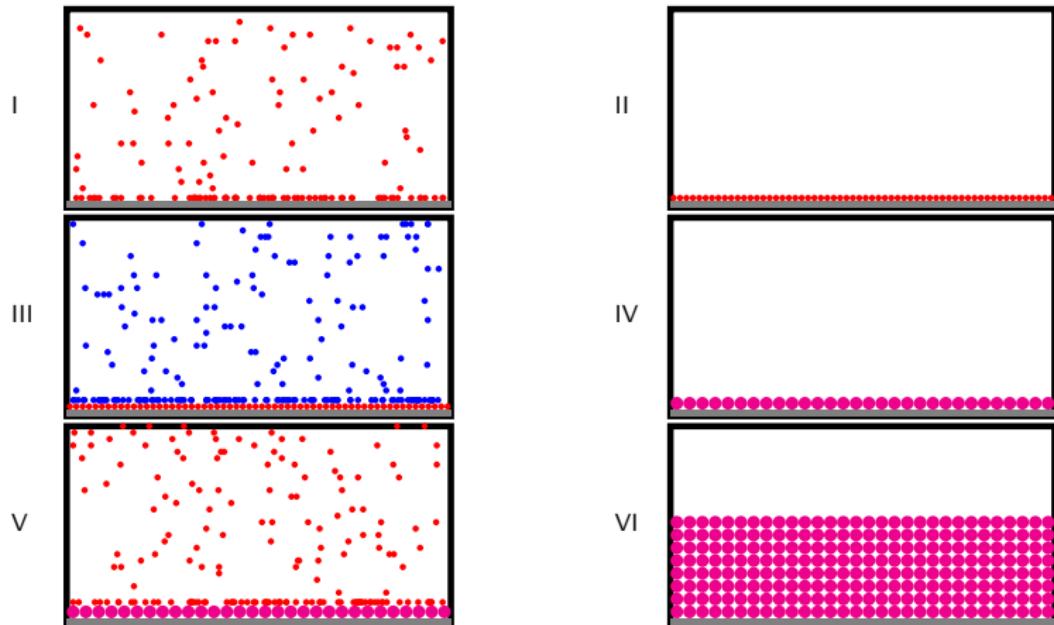
Atomic layer deposition (ALD)



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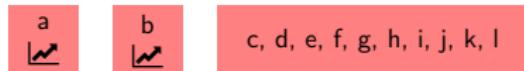


Atomic layer deposition (ALD)



Testing the ALD process

Wafer 295
 $d = 30 \mu\text{m}$



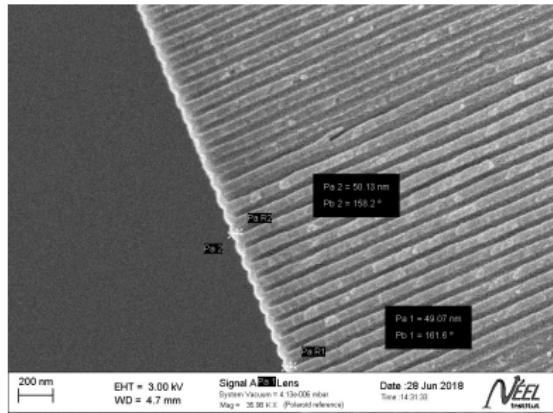
e''
100 ALD

e'''
200 ALD

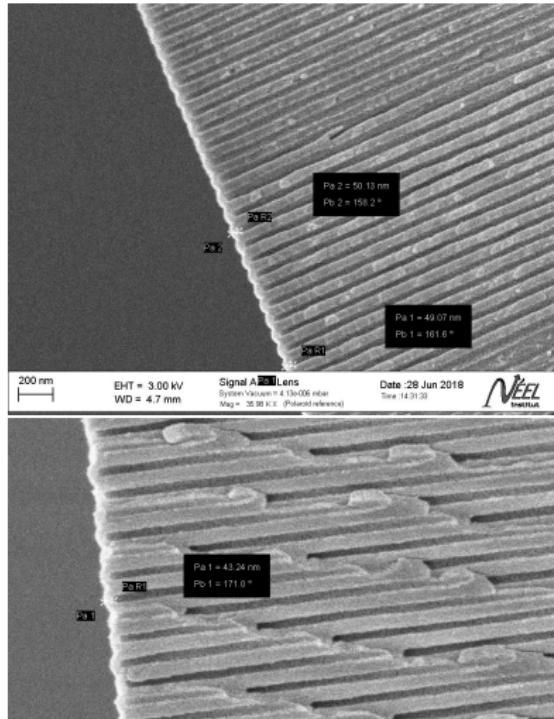
f''
200 ALD

d''
250 ALD

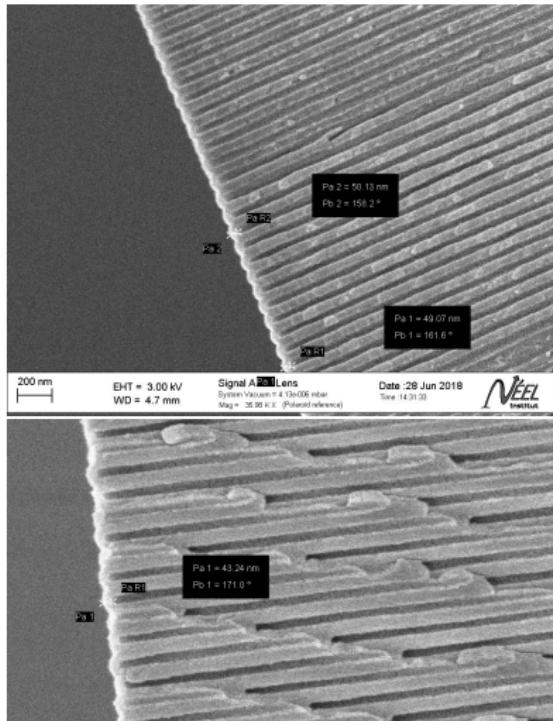
Barrier layer thickness - nonisotrope etch rate



Barrier layer thickness - nonisotrope etch rate



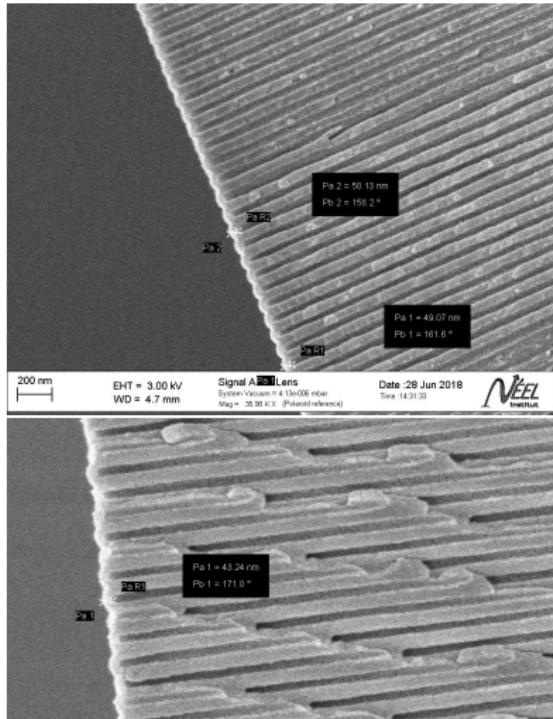
Barrier layer thickness - nonisotrope etch rate



Barrier layer thickness

- Assumed to always be 30 nm

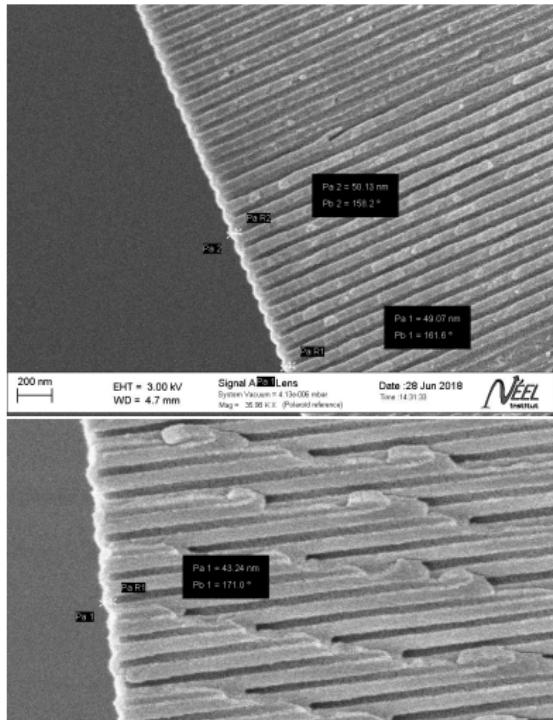
Barrier layer thickness - nonisotrope etch rate



Barrier layer thickness

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

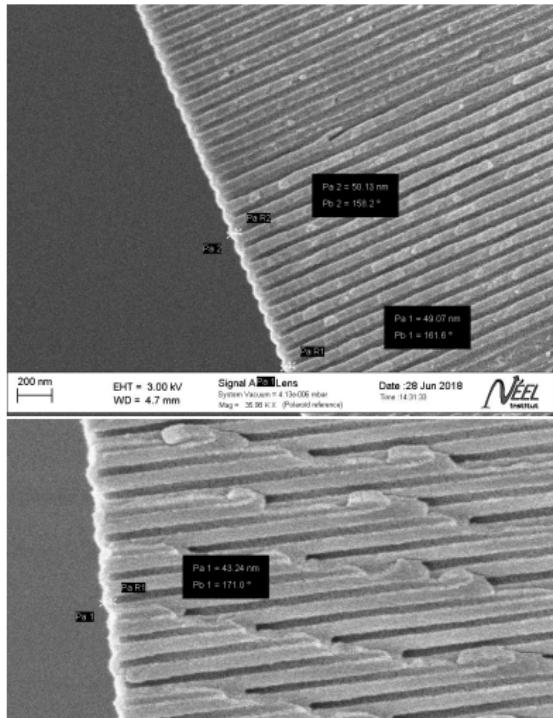
Barrier layer thickness - nonisotrope etch rate



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- Has not been probed before the treatments
- Much too large AFTER floating

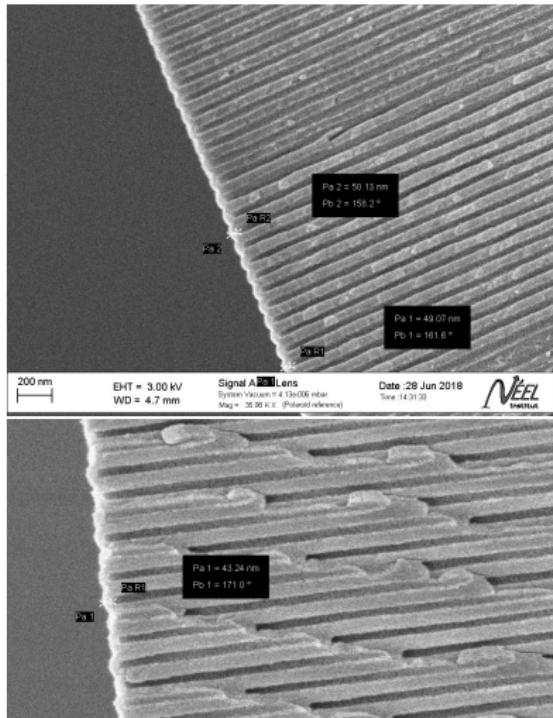
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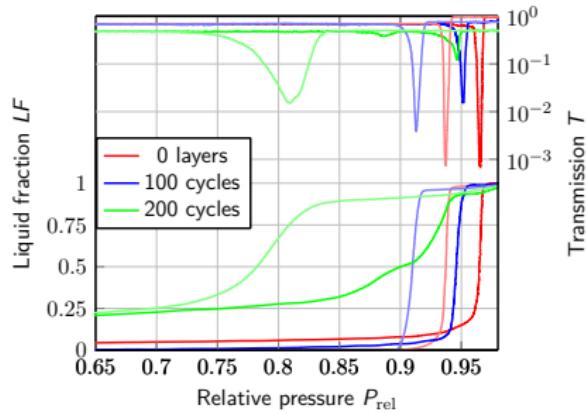
Barrier layer thickness - nonisotrope etch rate



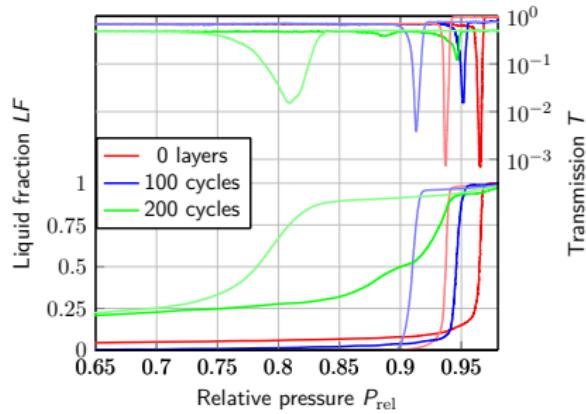
Barrier layer thickness

- Assumed to always be 30 nm
- 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

ALD membranes

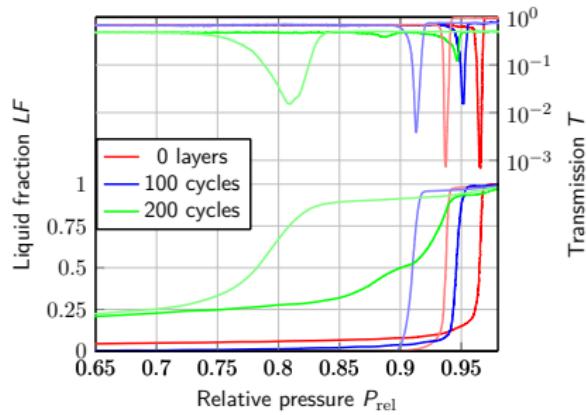


ALD membranes



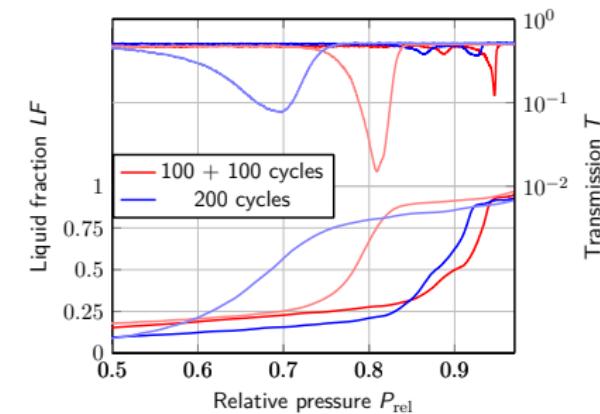
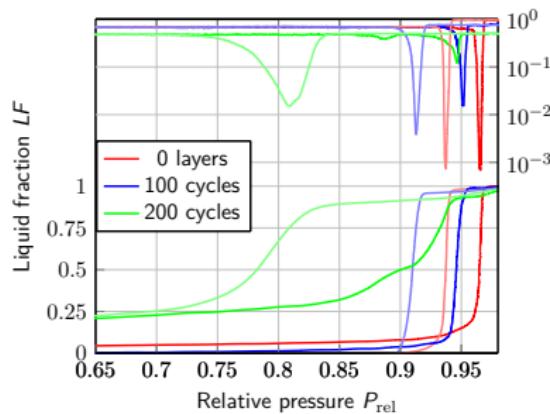
- ALD effectively reduces pore diameters of large pores

ALD membranes



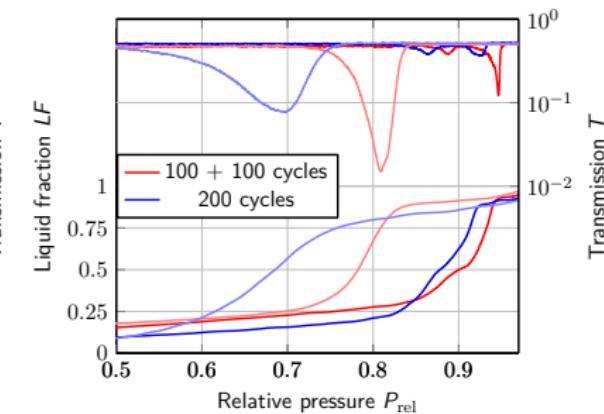
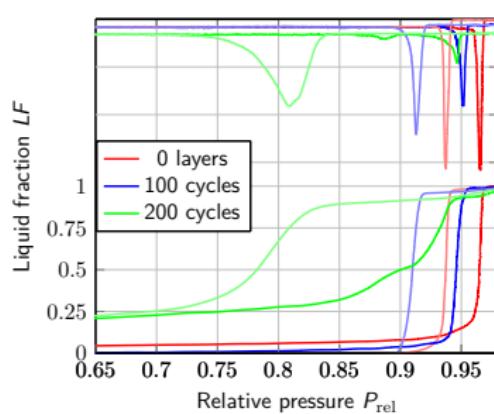
- ALD effectively reduces pore diameters of large pores
- defects appear for smaller pore diameters

ALD membranes



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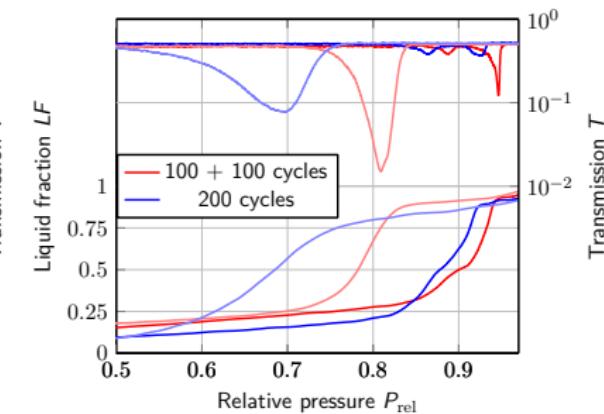
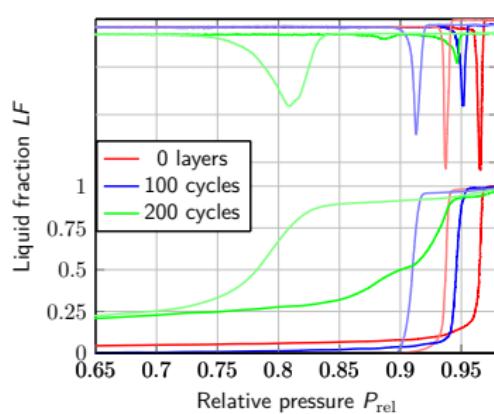
ALD membranes



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- Evaporations at low pressures

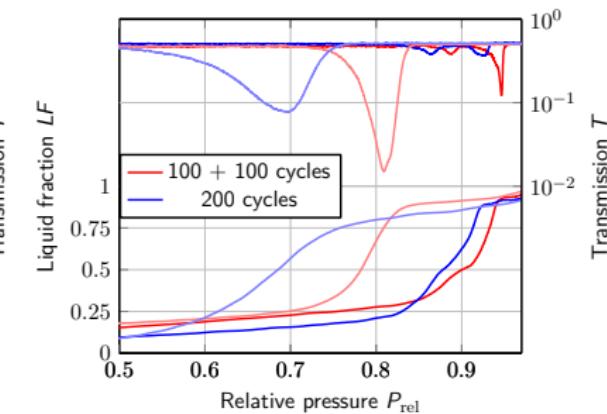
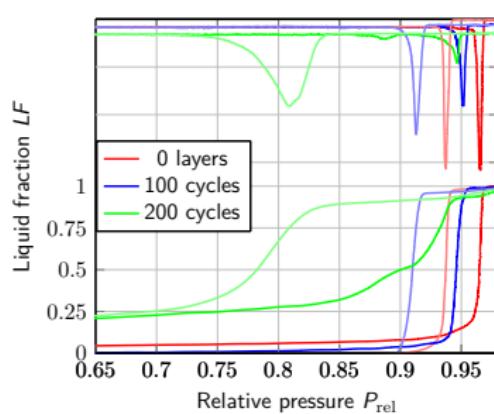
ALD membranes



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- defects appear for smaller pore diameters

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

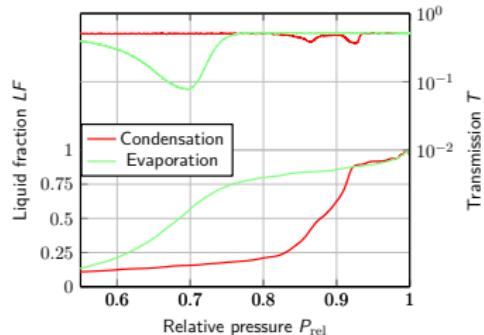
ALD membranes



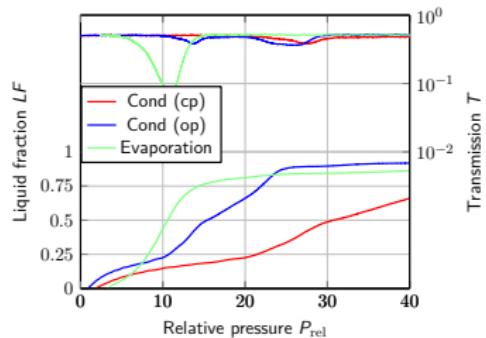
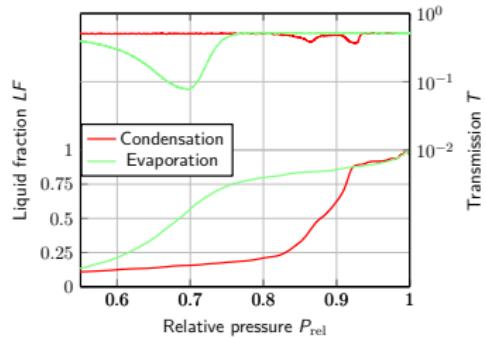
- ALD effectively reduces pore diameters of large pores
- defects appear for smaller pore diameters

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

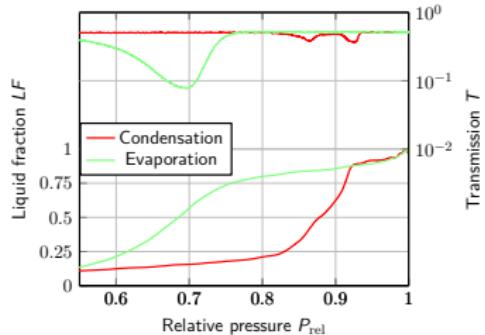
ALD for smaller pore diameters I



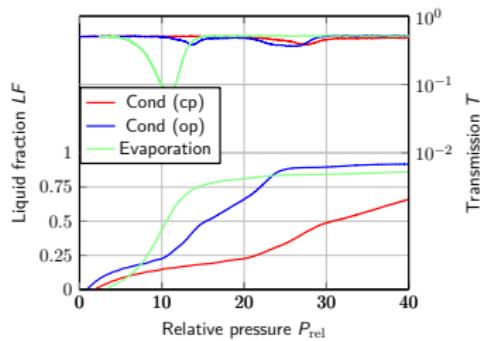
ALD for smaller pore diameters I



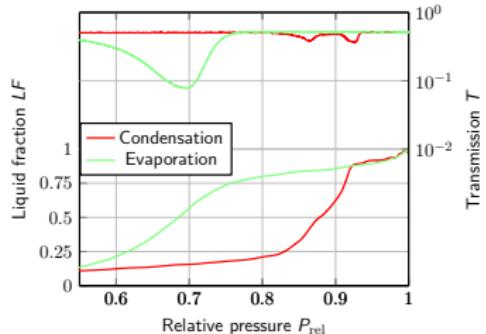
ALD for smaller pore diameters I



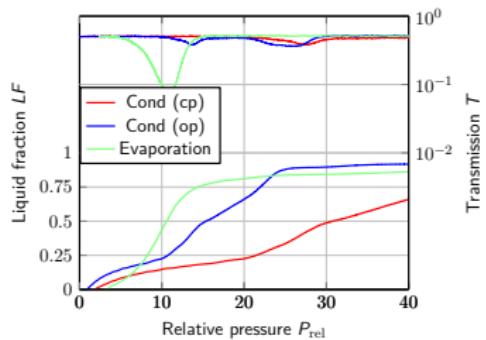
- Closed and open pore KELVIN conversion yields branches covering the same diameter ranges



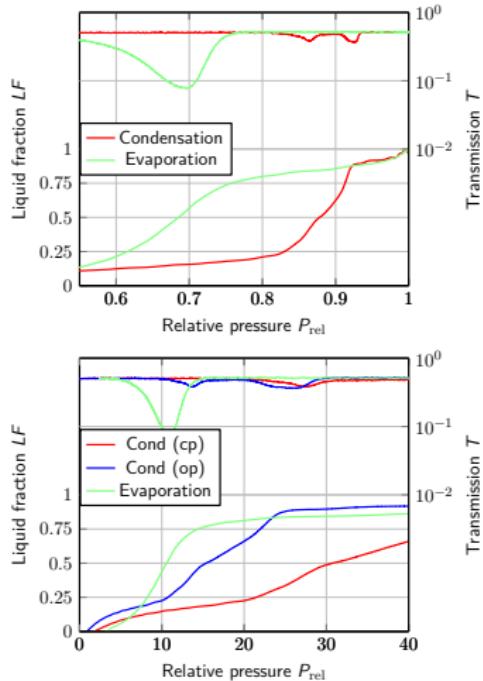
ALD for smaller pore diameters I



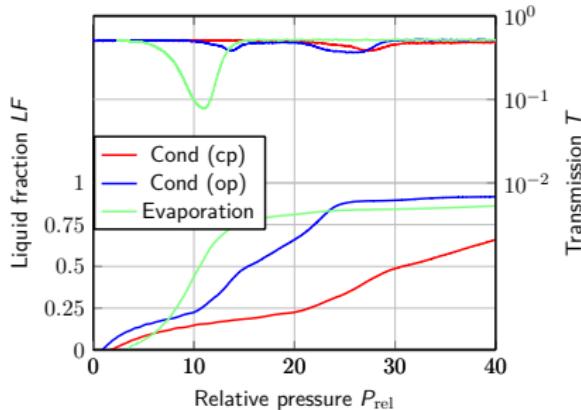
- Closed and open pore KELVIN conversion yields branches covering the same diameter ranges
- Expected to work on the membrane with 100 + 100 cycles of ALD too



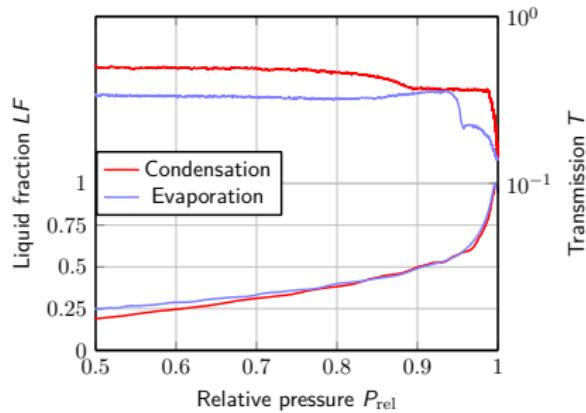
ALD for smaller pore diameters I



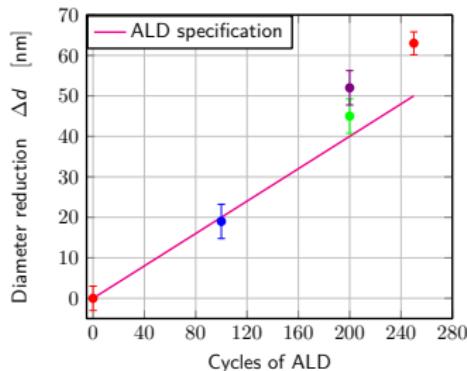
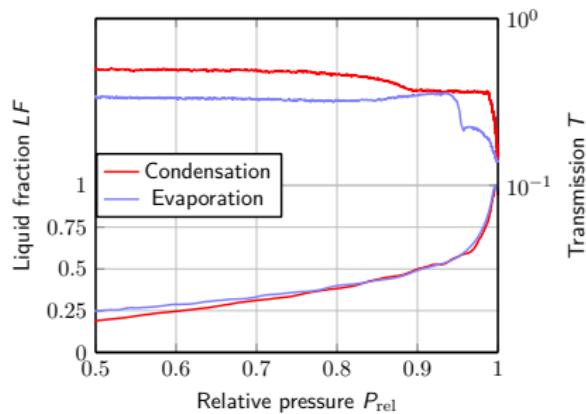
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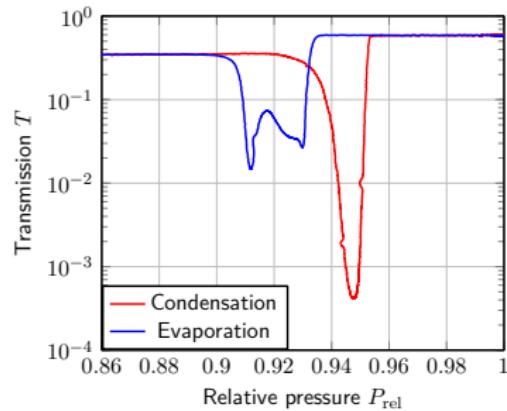
ALD for smaller pore diameters II



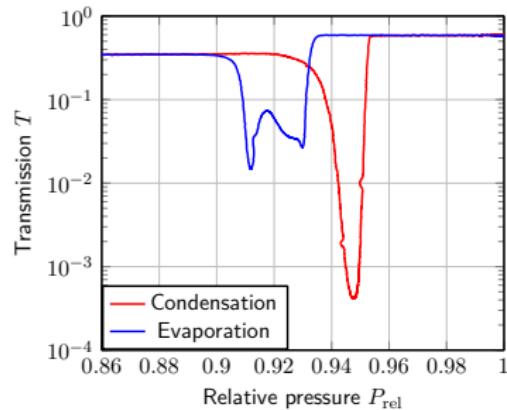
ALD for smaller pore diameters II



Transmission & pore disorder theory

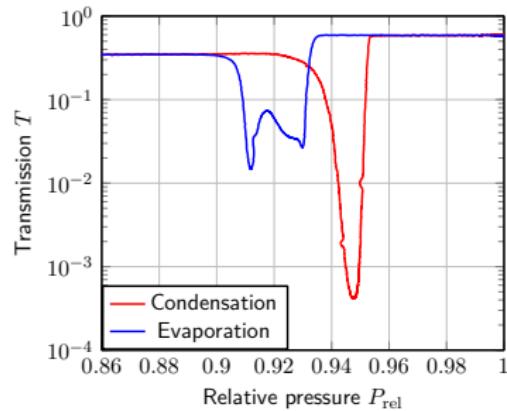


Transmission & pore disorder theory



Transmission drops for membranes of wafer 292 and before

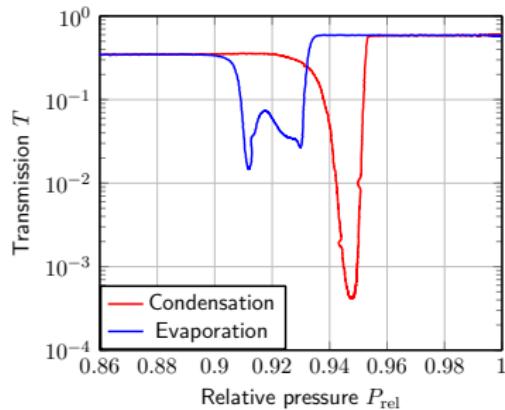
Transmission & pore disorder theory



Transmission drops for membranes of wafer 292 and before

- deeper for condensation,
- shallower for evaporation.

Transmission & pore disorder theory



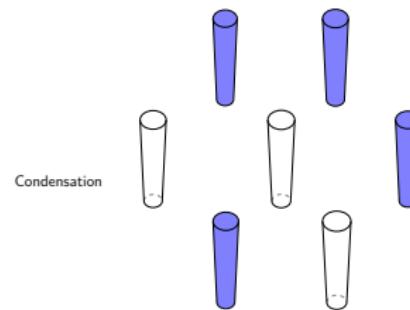
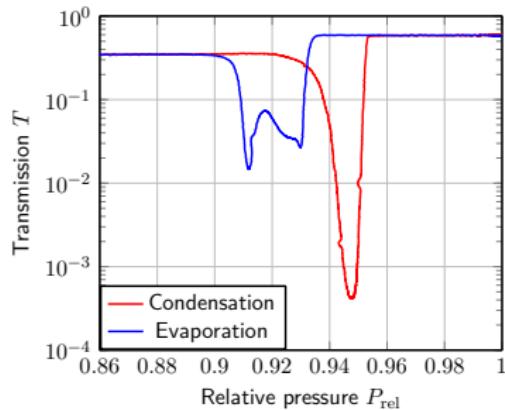
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Same observation made on the measurements made

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Transmission & pore disorder theory



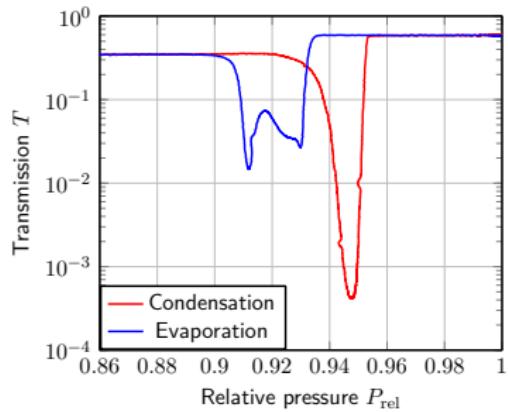
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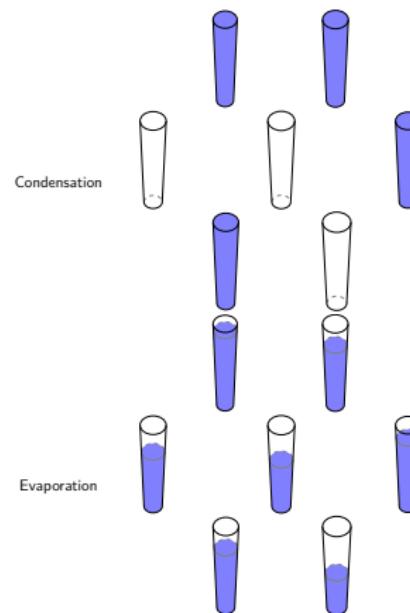
Transmission & pore disorder theory



Transmission drops for membranes of wafer 292 and before

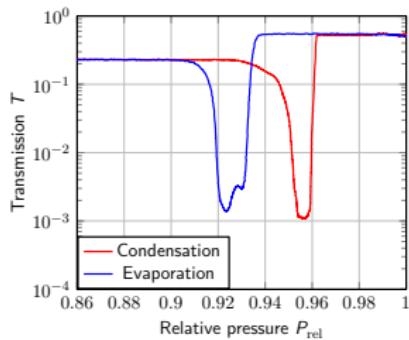
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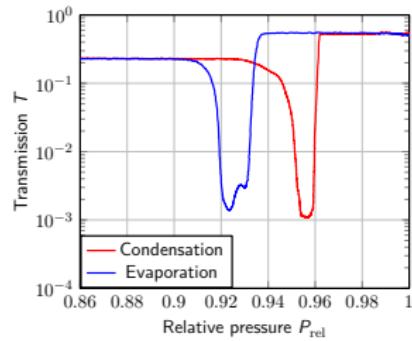
More transmission measurements

60 μm
closed
pores

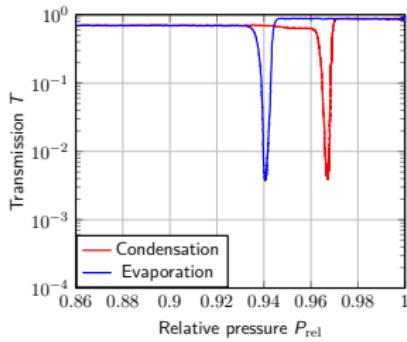


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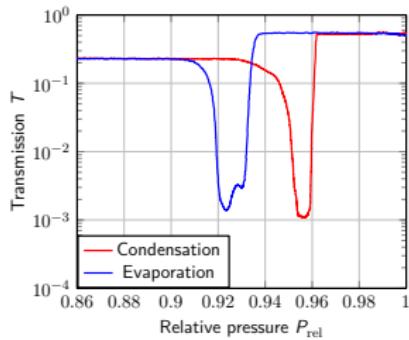


30 μm
open pores

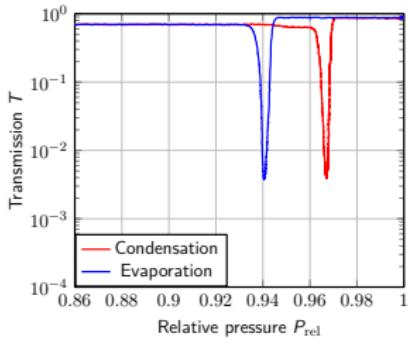


More transmission measurements

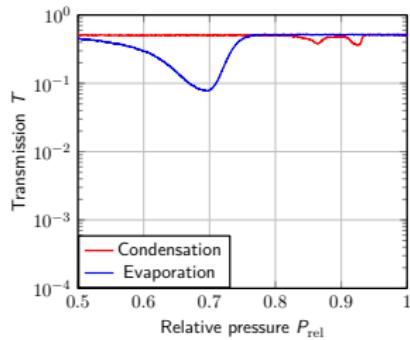
60 μm
closed
pores



30 μm
open pores

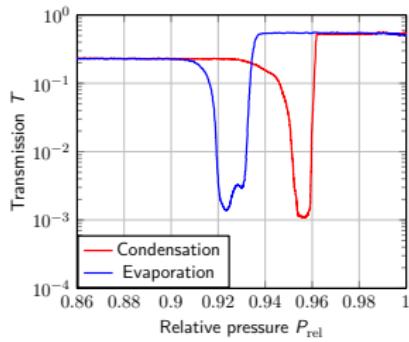


30 μm
open pores
200 ALD

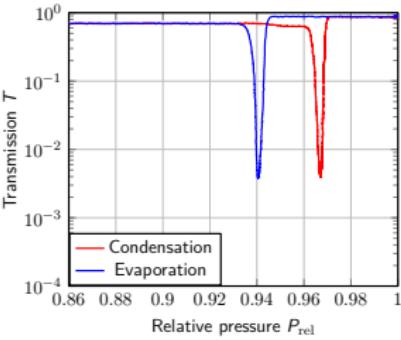


More transmission measurements

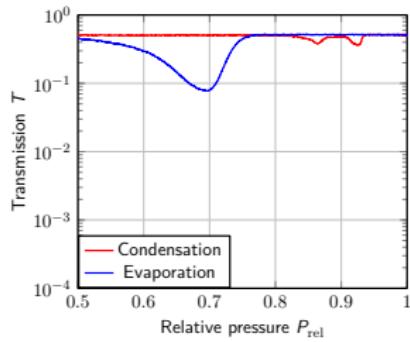
60 μm
closed
pores



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