PoreLab
NTNU-UiO Porous Media Laboratory

Norwegian Centre of Excellence
The Research Council of Norway

NTNU

UiO : University of Oslo

Power and Clean Water from Thermal Energy (PoreWatt)

Michael Rauter, Dick Bedeaux, Sondre Schnell and Signe Kjelstrup

Outline

- Motivation
- Objects of the PhD
- Equilibrium Pressures in Hydrophobic Pores
- Thermal Transport in Hydrophobic Pores

Motivation


[1]

Waiting for water in Cape-Town

Cape Town delayed Day Zero but South Africa's water woes aren't over [2]

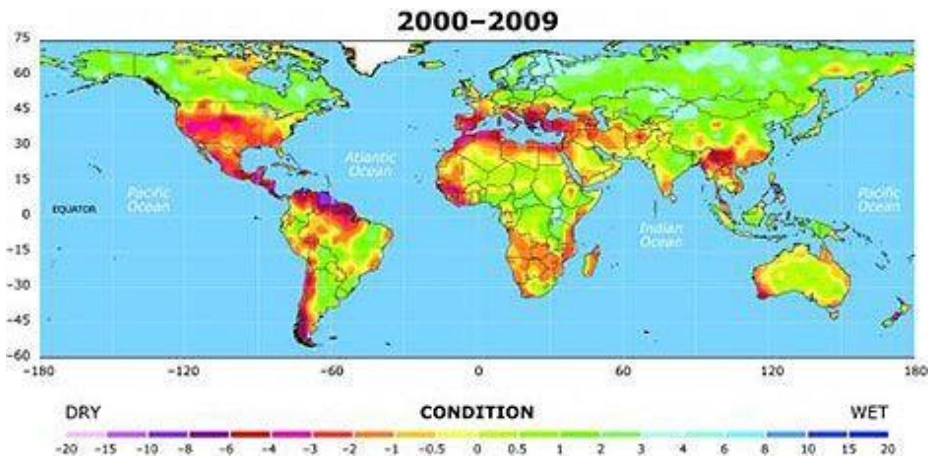
Severe water restrictions to bite as drought could cost over $100 million [3]

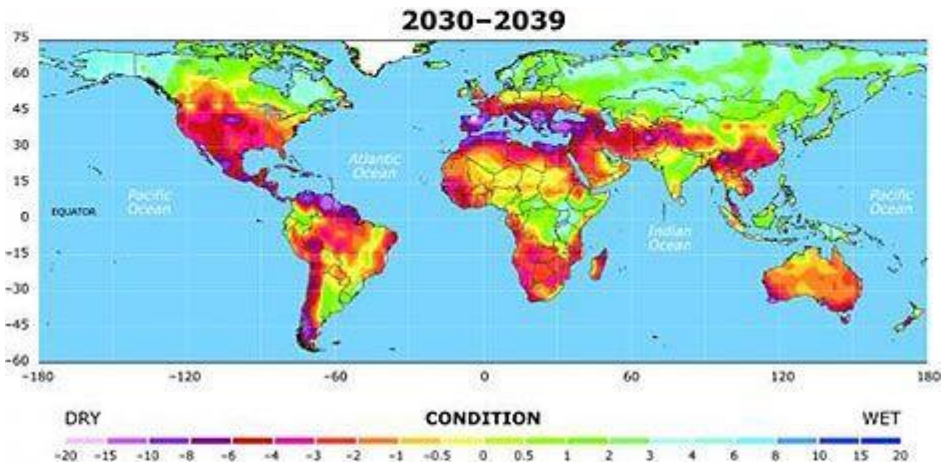
New Zealand

In Search Of A Solution For Water Scarcity In The Caribbean [4]

Caribbean

Motivation





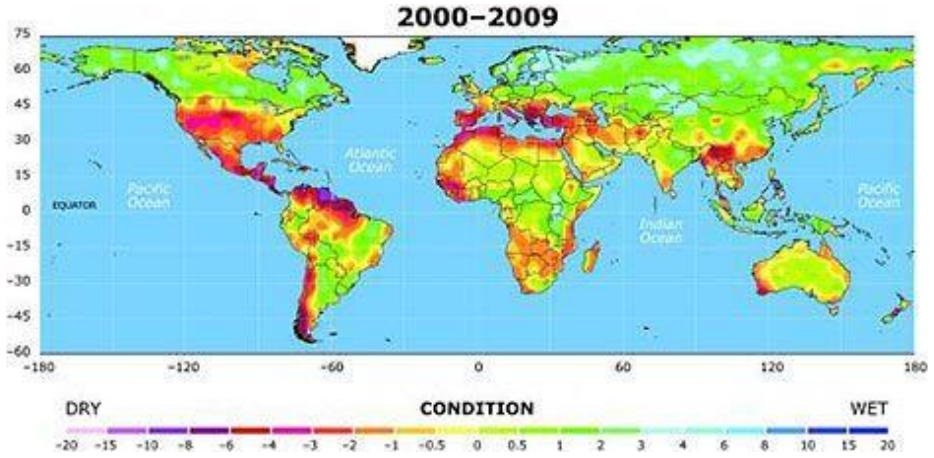
[5]

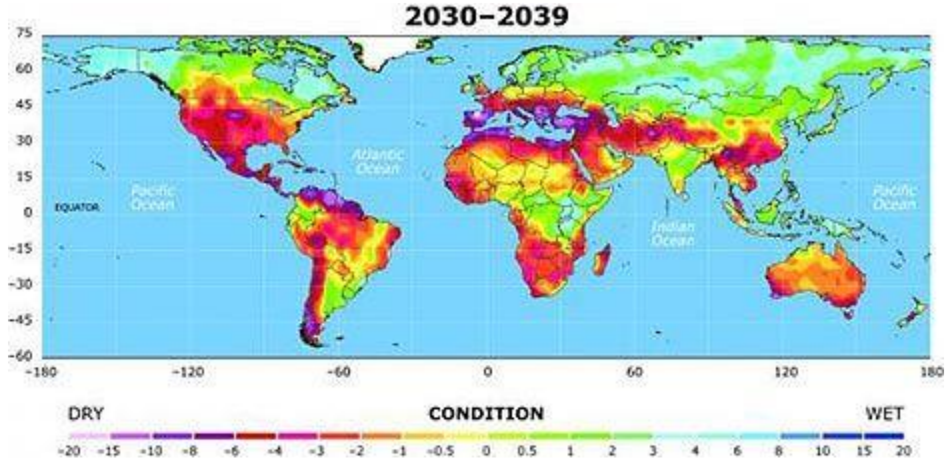
United Nations

United Nations: Decade 2018 – 2028 to be used to "Avert a global water crisis"

➡ **Solutions Needed! Urgently!**

Motivation





[5]

United Nations: Decade 2018 – 2028 to be used to "Avert a global water crisis"

➡ **Solutions Needed! Urgently!**

- Drinking water mostly produced by reverse osmosis at a cost of 0.45 – 0.66 $\$/m^3$
- Alternative methods more expensive
- 2016: CO_2 emission of 70 mio tonnes/year by reverse osmosis
    - Expected to increase above 200 mio tonnes/year in 2040

Thermal Osmosis

Recent proposal:

Use of low temperature waste heat to produce water

With use of a hydrophobic vapor gap membrane

N. Kuipers et al. Desalination and Water Treatment, 55 (2015) 2766

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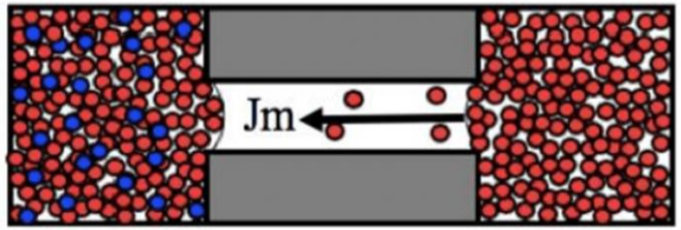
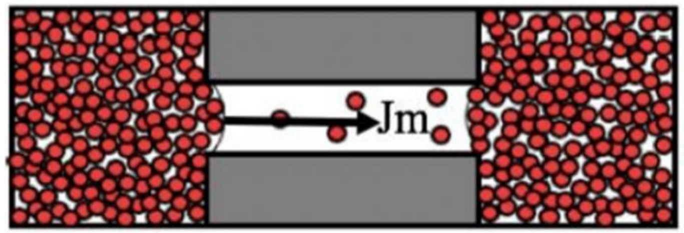
Chemical driving force



Water flows from a pure state to a contaminated state down the gradient in chemical potential.

Thermal driving force



Water flows against a concentration-or pressure difference, driven by a temperature difference

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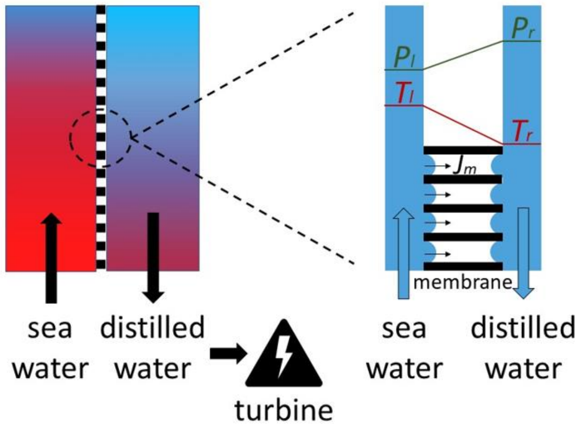
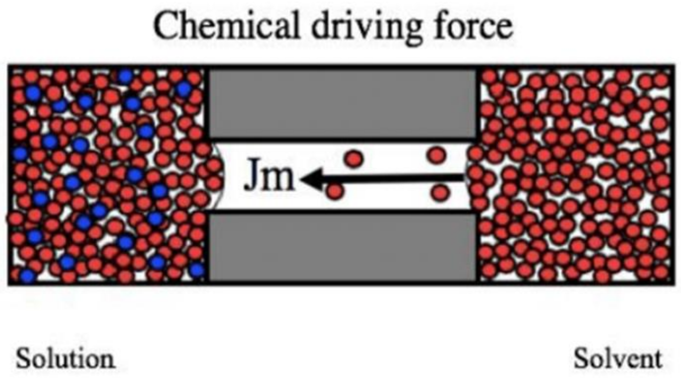


Clean water vapor flows from the hot seawater (left) through the membrane (stippled line) to a water reservoir, which can be used in a turbine.



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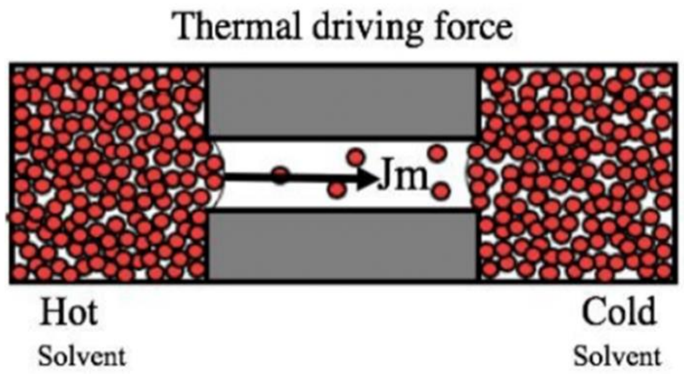
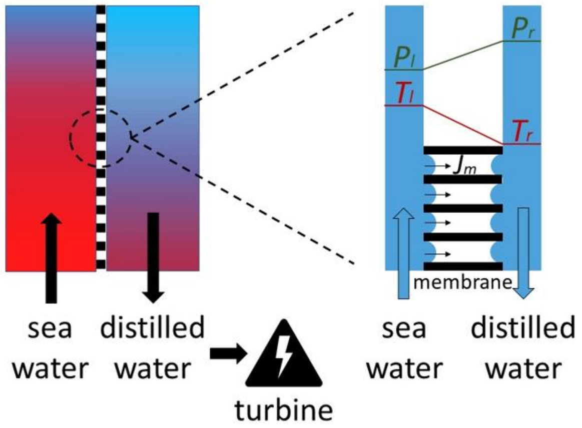


Water flows against a concentration-or pressure difference, driven by a temperature difference

Objects of the PhD



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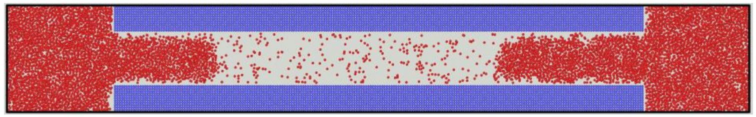
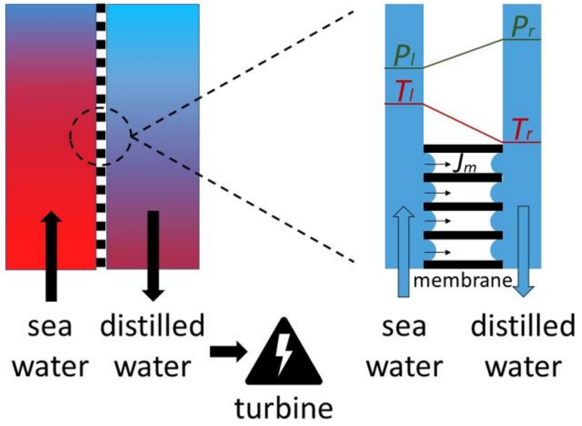
Objects of the PhD

Molecular Dynamic Simulation



- Determination of most important factors for mass transport
- Determination of key transport coefficients



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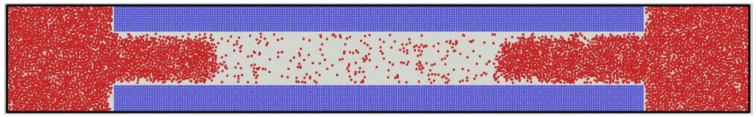

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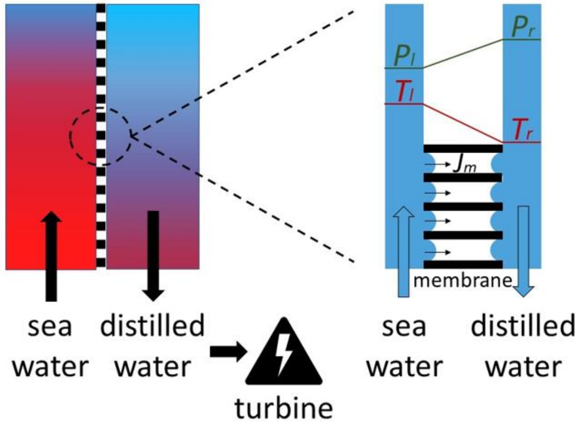

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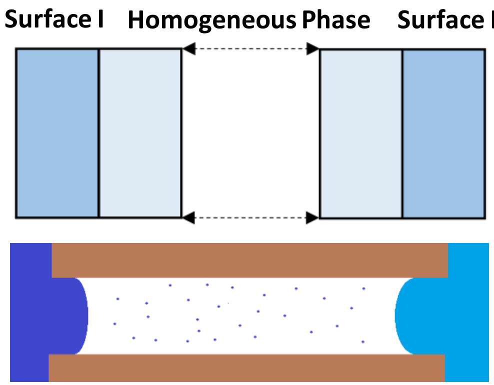
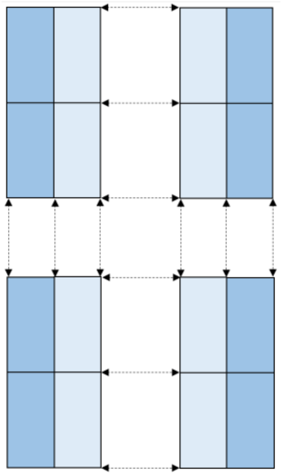
Numerical Pore Simulation



$$\Delta_{1n}\frac{1}{T} = r_{qq}^{tot} J'_{q,n} + r_{qw}^{tot} J_w$$

$$-\frac{\Delta_{1n}\mu_w(T_1)}{T_1} = r_{wq}^{tot} J'_{q,n} + r_{ww}^{tot} J_w$$

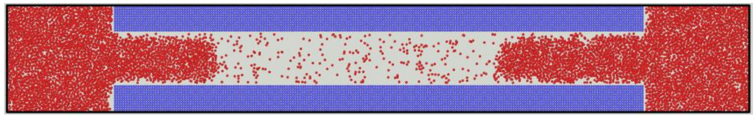
Numerical Process Simulation



- For optimization of process parameters (Δp, ΔT,$\dot{m}$)
- Link to experiments (Kim)
- 2D / 3D

Objects of the PhD

Molecular Dynamic Simulation



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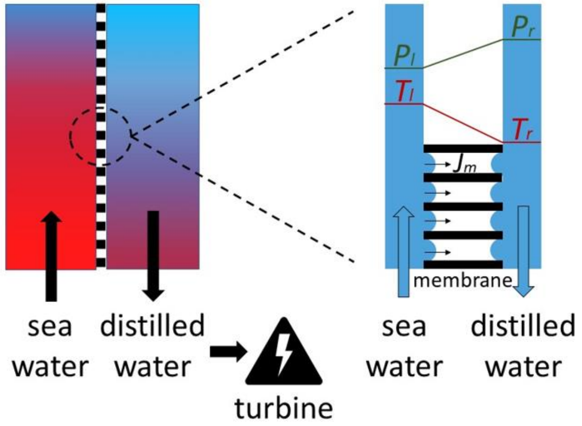

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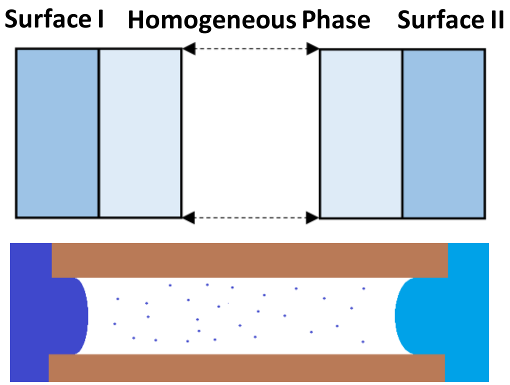

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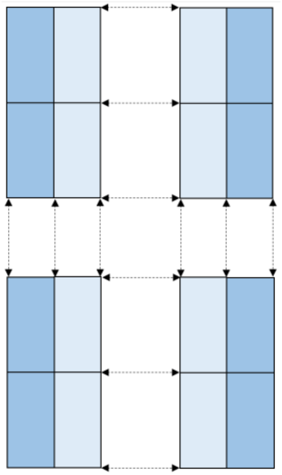

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Molecular Dynamic Simulation

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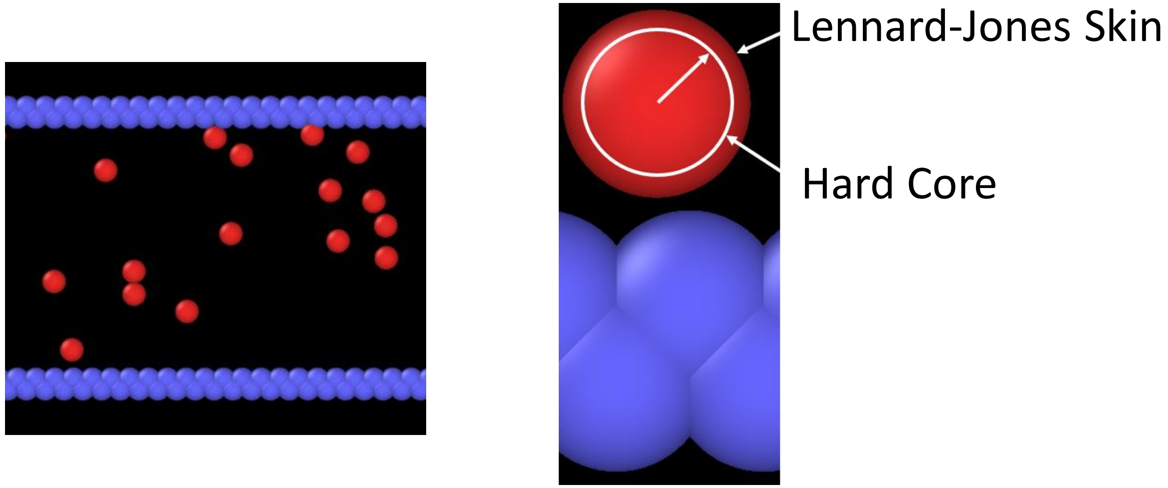
Solving Newtons equation of motion

$$f_i = m_i \frac{\mathrm{d}v_i}{\mathrm{d}t} = m \frac{\mathrm{d}^2 r_i}{\mathrm{d}t^2} = \sum_{j=1}^{N} \frac{\mathrm{d}u_{ij}}{\mathrm{d}r_{ij}}$$



Lennard-Jones/spline Potential

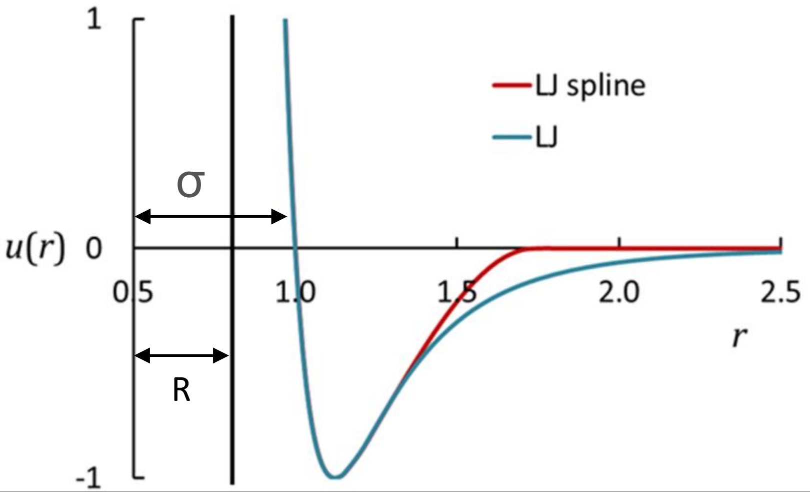
$$u_{ij} = \begin{cases} \infty & \text{if } r < R_{ij} \\ 4\epsilon_{ij}[(\frac{\sigma_{ij}-R_{ij}}{r-R_{ij}})^{12} - \alpha_{ij}(\frac{\sigma_{ij}-R_{ij}}{r-R_{ij}})^{6}] & \text{if } R_{ij} \leq r < r_s \\ a_{ij}(r-r_c)^2 + b_{ij}(r-r_c)^3 & \text{if } r_s \leq r \leq r_c \\ 0 & \text{if } r > r_c \end{cases}$$

σ_{ij} is the particle radius

α_{ij} is the wetting parameter

R_{ij} is the hard core radius

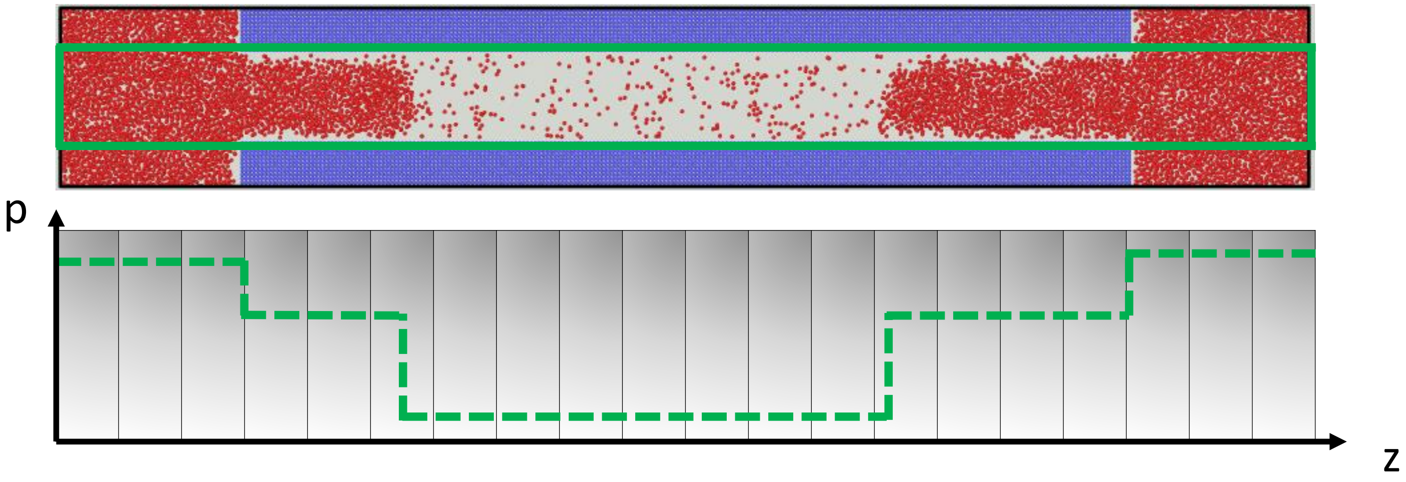
ϵ_{ij} is the interaction strength



Equilibrium Pressures in Hydrophobic Pores

Pressure in a Nanopore

System in Equilibrium!



Pressure in a Nanopore

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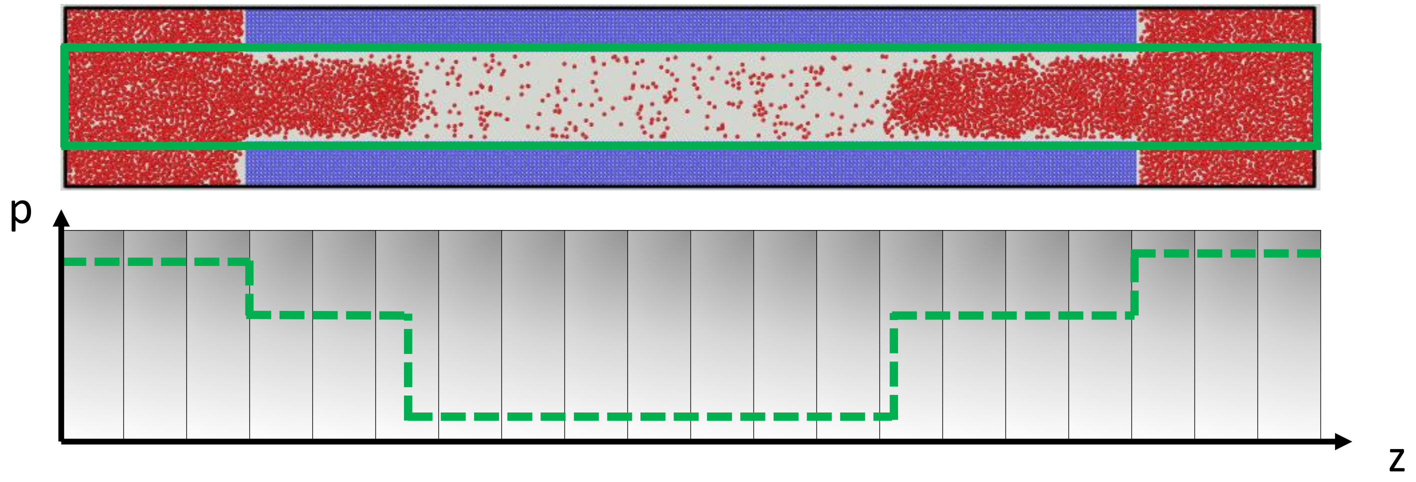


- For small systems: Thermodynamic properties are not proportional to the volume any more
- No consensus at all about the pressure computation
- Ordinary thermodynamic functions are defined for macroscopic systems only

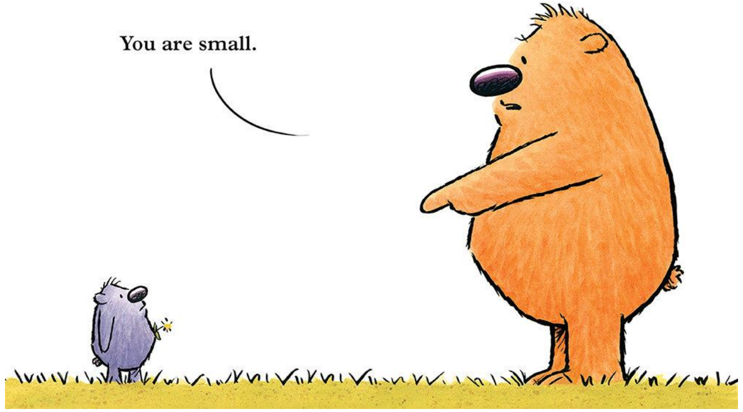
➡ Need to be adapted for small systems

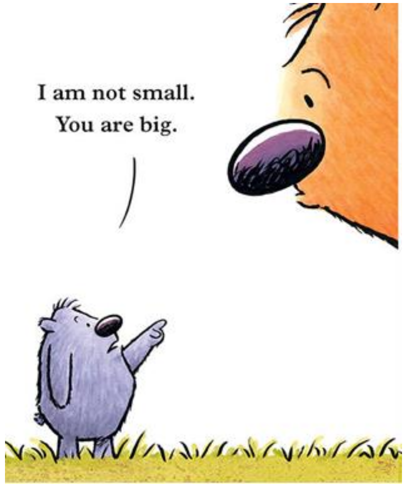
Thermodynamic of Small Systems (Hill)

What is Small?

[6]

What is Small?





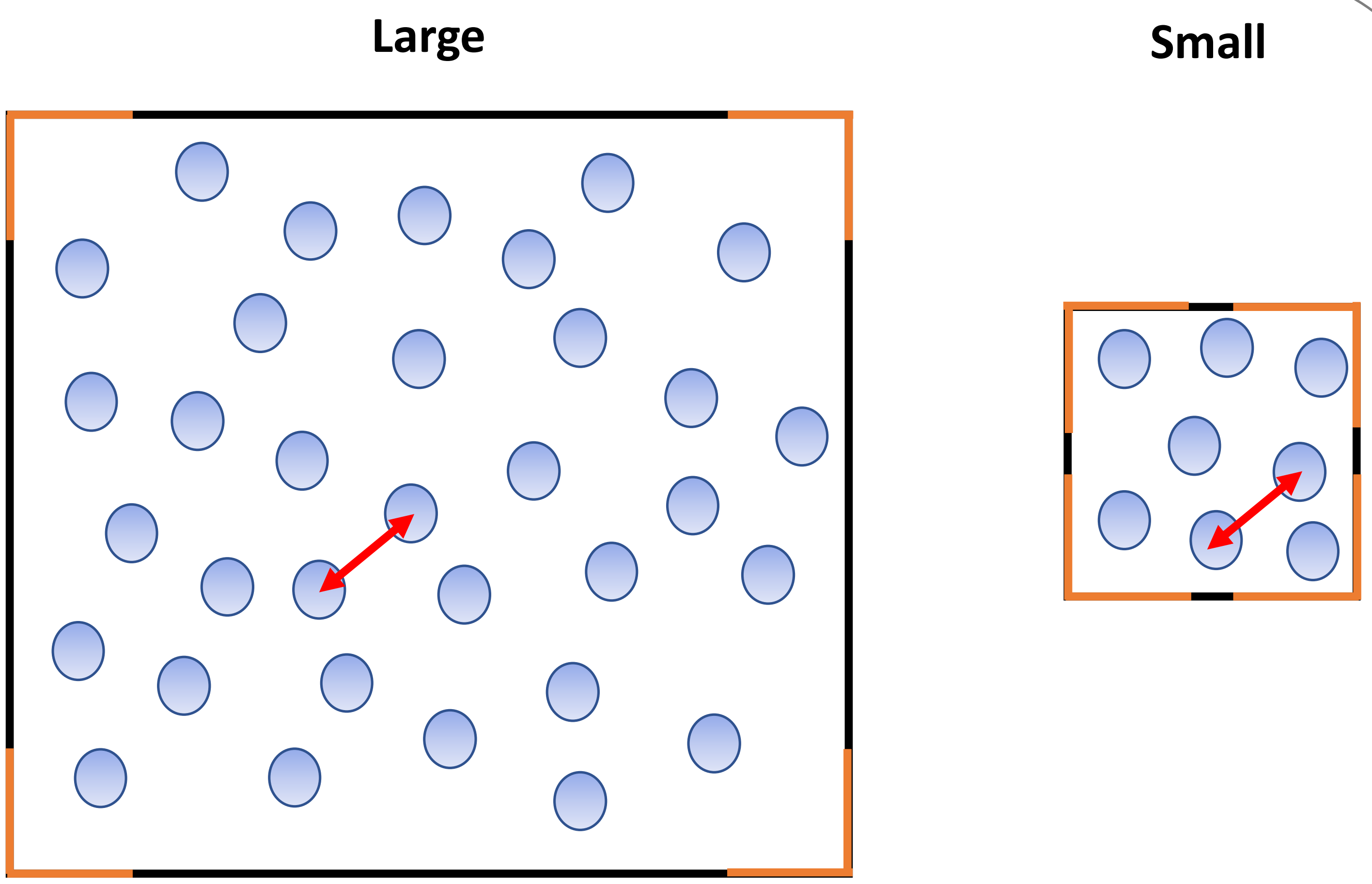
[6]

A system is large when the thermodynamic variables U, S and N are proportional to the systems volume

➡ The total energy of two large systems combined into one system is then equal to the sum of the separate energies.

A system is small when the thermodynamic variables U, S and N are **NOT** proportional to the systems volume

What is Small?



Large
Wall distance **IS NOT** in the range of distance between particles

Small
Wall distance **IS** in the range of distance between particles

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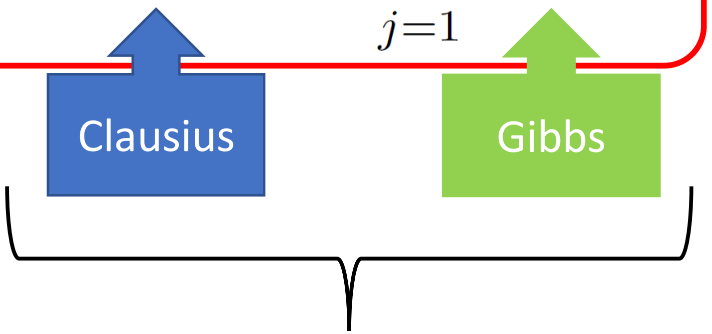
Hill's Nanothermodynamics

$$\mathrm{d}U = T\mathrm{d}S - p\mathrm{d}V + \sum_{j=1}^{n} \mu_j \mathrm{d}N_j$$



extensive variables

➡ proportional to the systems volume

Not suitable for small systems!

Hill's Nanothermodynamics

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$$dU = TdS - pdV + \sum_{j=1}^{n} \mu_j dN_j$$

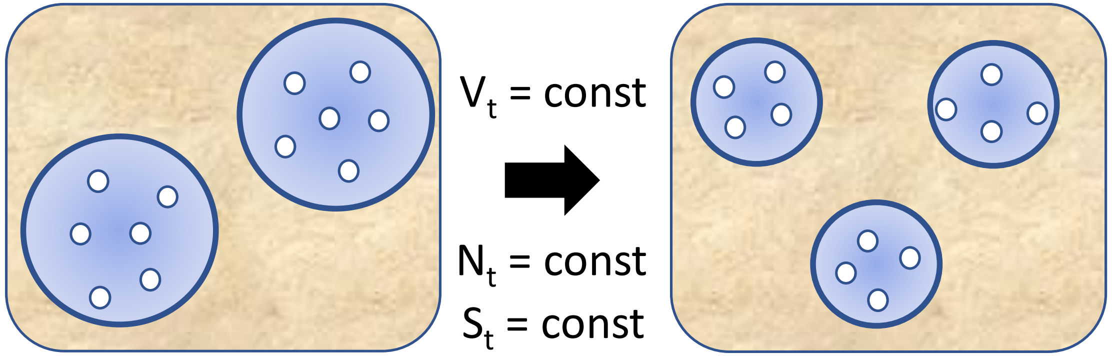
Clausius — Gibbs

extensive variables

➡ proportional to the systems volume

Not suitable for small systems!

Hill



$$dU_t = TdS_t - pdV_t + \sum_{j=1}^{n} \mu_j dN_{j,t} + \varepsilon d\mathcal{N}$$

Hill

Replica Energy ε - for change of energy, when adding one replica keeping S_t, V_t and N_t constant

$\mathcal{N}$ = Number of Replicas

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Replica Energy ε

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Replica energy ε is dependent on the set of variables that are controlled!

$$\mathrm{d}U_t = T\mathrm{d}S_t - p\mathrm{d}V_t + \sum_{j=1}^{n} \mu_j \mathrm{d}N_{j,t} + \varepsilon \mathrm{d}\mathcal{N}$$

with

$$V_t = \mathcal{N} V$$ V = Volume of 1 Replica

becomes

$$\mathrm{d}U_t = T\mathrm{d}S_t - p\mathcal{N}\mathrm{d}V + \sum_{j=1}^{n} \mu_j \mathrm{d}N_{j,t} + \underbrace{(\varepsilon - pV)}_{-\hat{p}V} \mathrm{d}\mathcal{N}$$

Here, the replica energy is a compressional energy and was denoted $-\hat{p}V$ by Hill

Replica Energy ε

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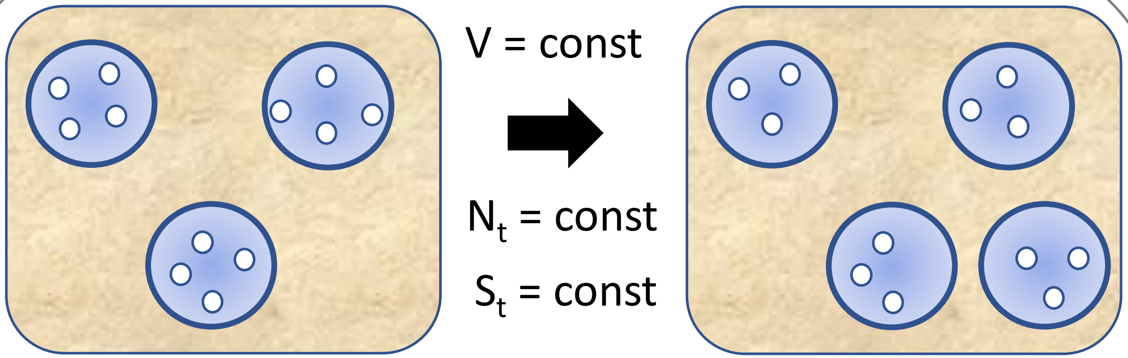
Here, the replica energy is a compressional energy and was denoted $-\hat{p}V$ by Hill



- Total Volume increases by 1 more replica ($\mathcal{N}$ increases)
- For small systems ($\hat{p}V \neq pV$) the last term comes into account
- For macroscopic systems ($\hat{p}V = pV$) the last term disappears

New Pressure Definition

A couple of thermodynamic tricks lead to the definition of a new pressure

$$p = \left(\frac{\partial \hat{p} V}{\partial V}\right)_{T,\mu} = \hat{p} + V\left(\frac{\partial \hat{p}}{\partial V}\right)_{T,\mu}$$

1) Integral pressure $\hat{p}$
2) Differential pressure p

If the pressure is not dependent on the volume (large systems):

$$p = \hat{p}$$

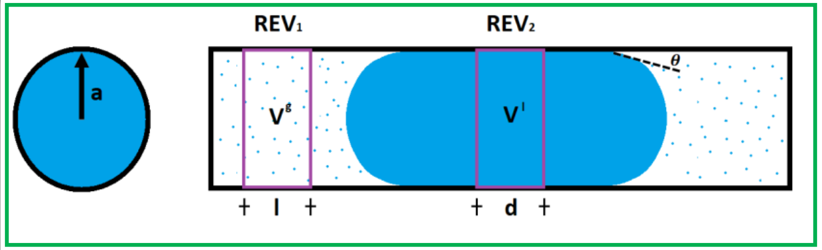
Two Phase System Within a Pore

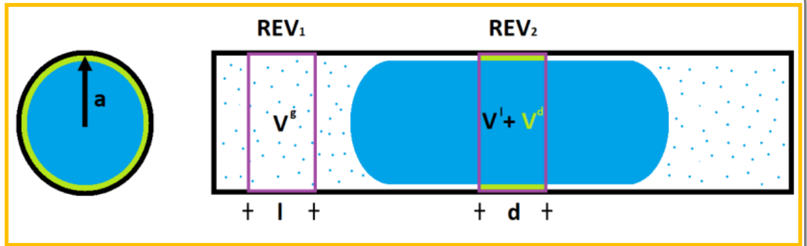
Liquid droplet inside pore in equilibrium with vapor phase

Without drying layer between liquid and pore wall

With drying layer between liquid and pore wall

Cylindrical Pore





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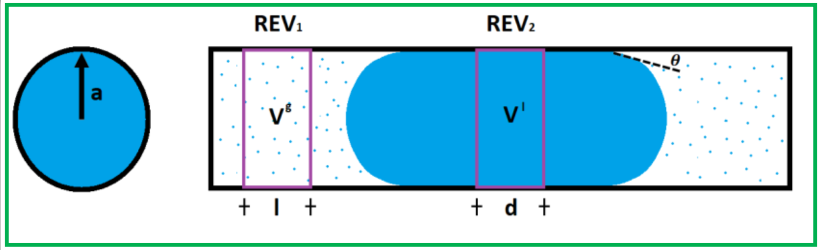

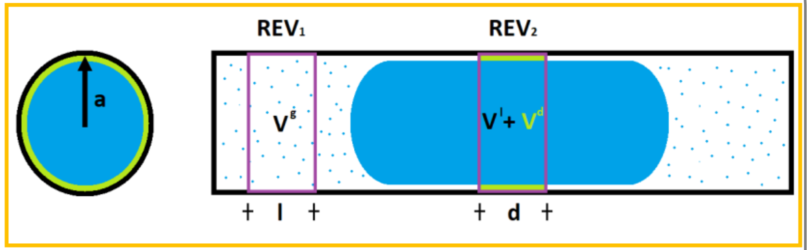

- In Equilibrium the compressional energy must be the same in both REV's*
- The internal compressional energy is an additive variable [7]

* REV = Representative Elementary Volume

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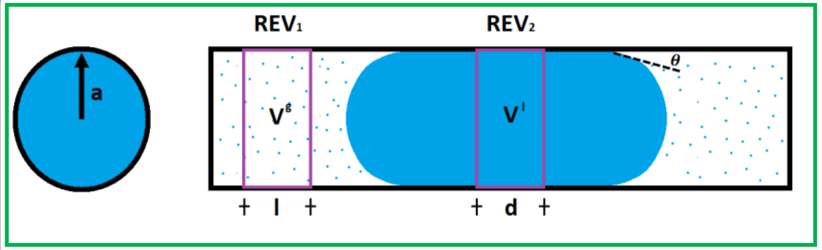
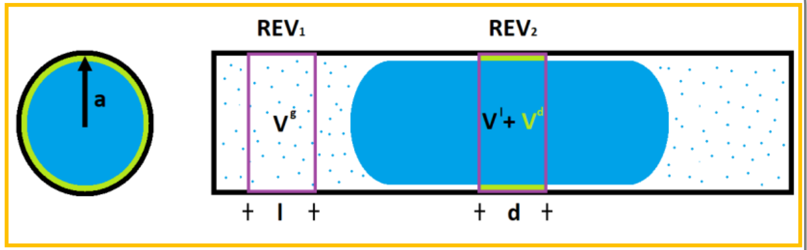
Cylindrical Pore



$$\hat{p}V = p^l V^l - \gamma^{ls}\Omega^{ls}$$



$$\hat{p}V = p^l V^l + p^d V^d - \gamma^{ls}\Omega^{ls}$$

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Two Phase System Within a Pore

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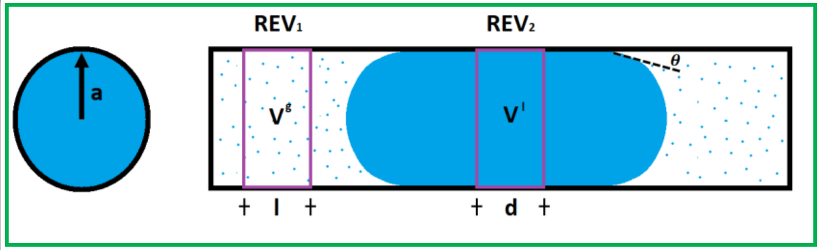

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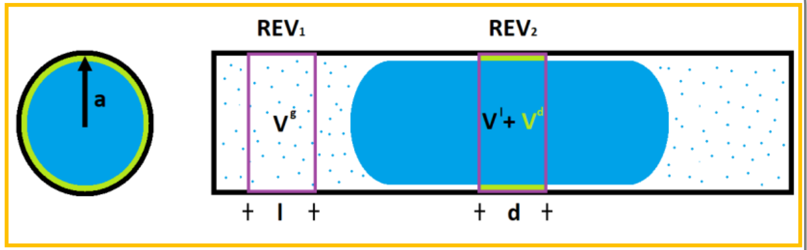

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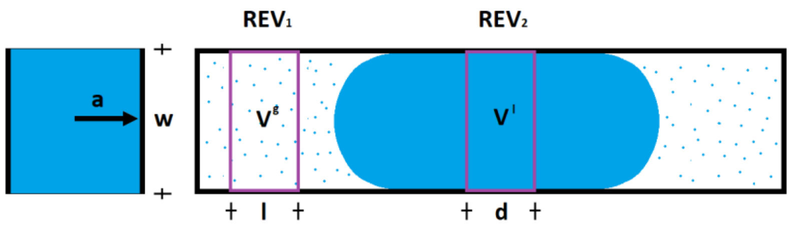
Slit Pore



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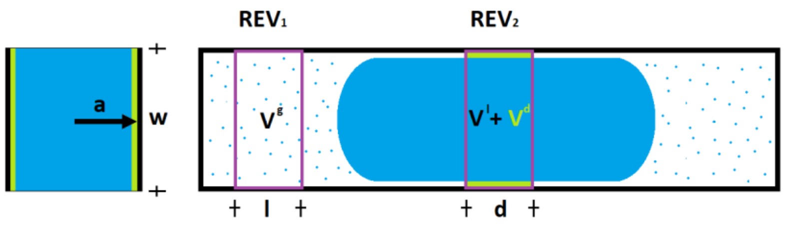

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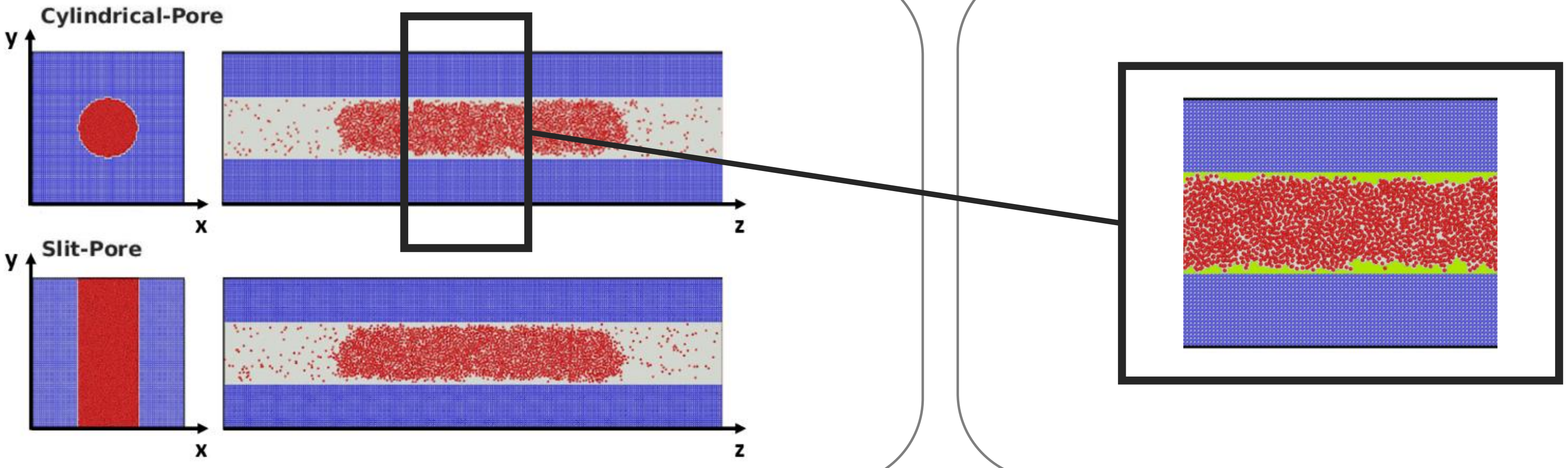
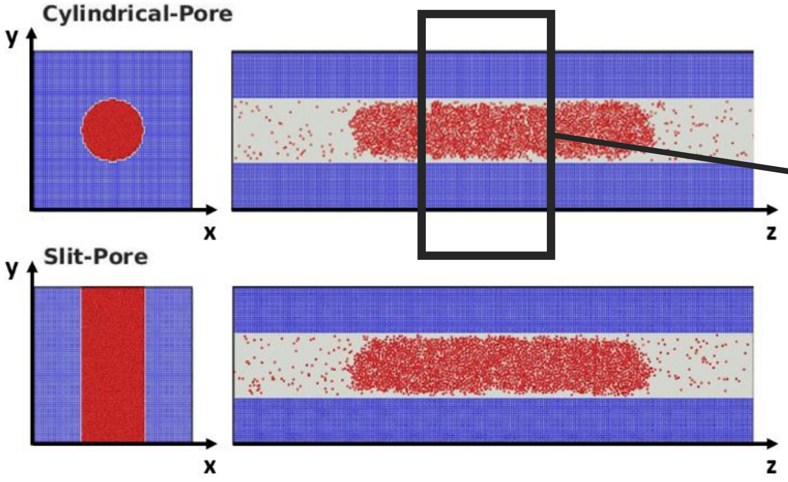
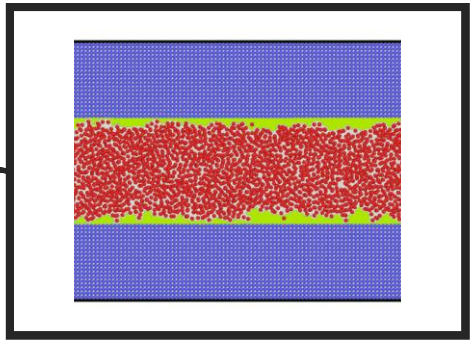
Pressure Computation via Onion-Technique



Layer between liquid and pore wall

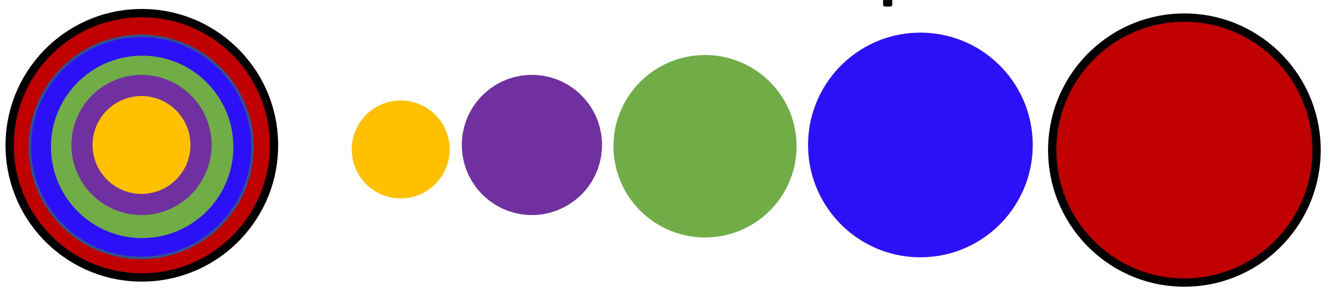
Pressure Computation via Onion-Technique





Layer between liquid and pore wall

The Onion-Technique

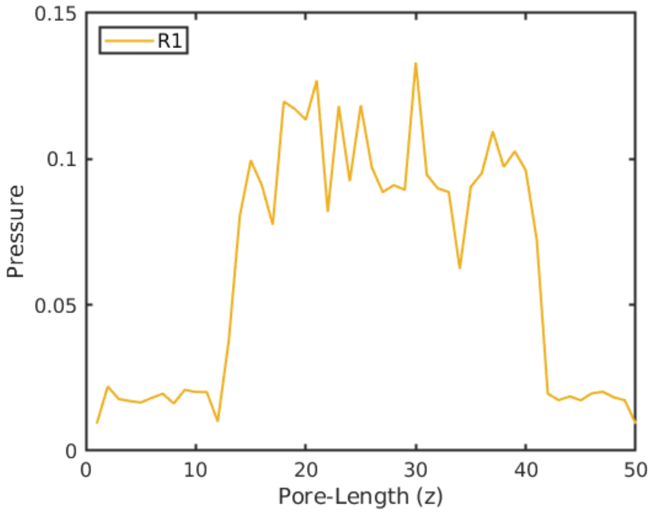


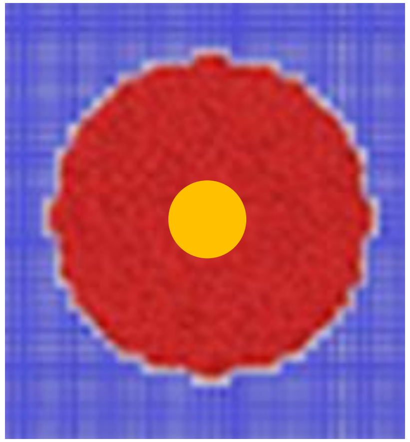
$$p_s^f V_s^f = \frac{1}{3}\Big[\sum_{i\epsilon l} m_i(v_i v_i)\Big] - \frac{1}{6}\Big[\sum_{i\epsilon l}\sum_{j=1}^{N}(r_{ij} f_{ij})\Big]$$

kinetic energy contribution

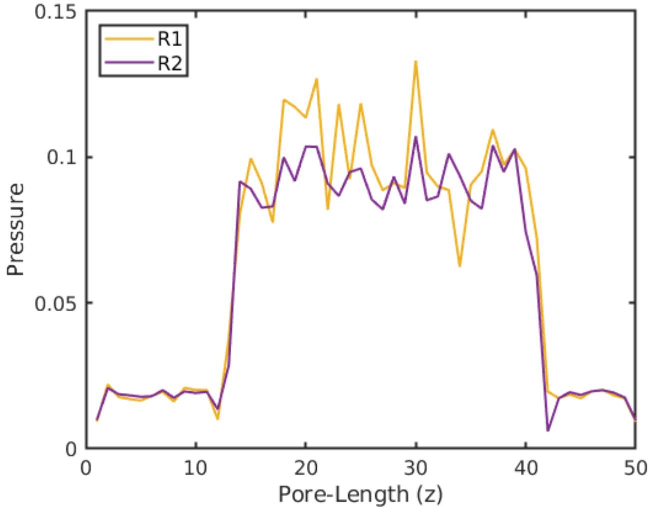
pairwise energy contribution

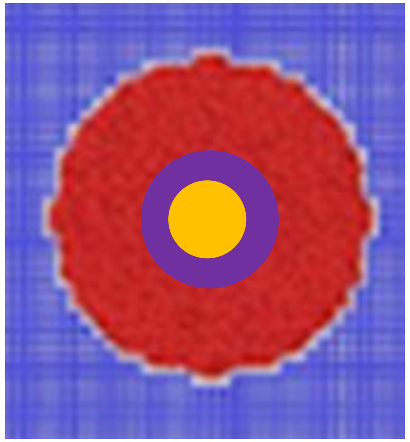
Pressure Variations Across the Pore



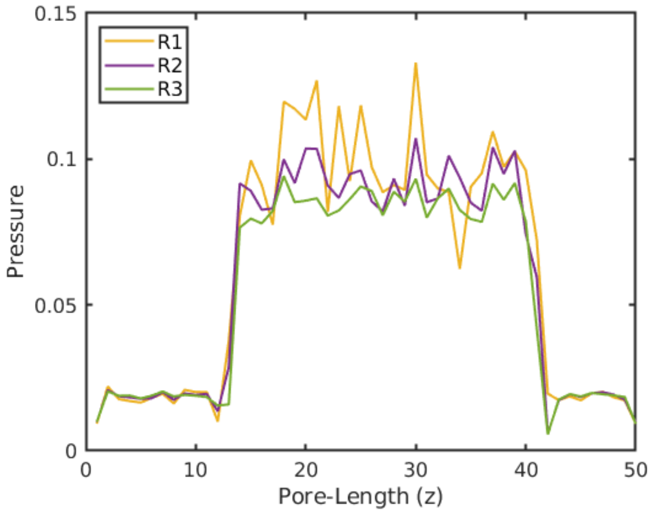


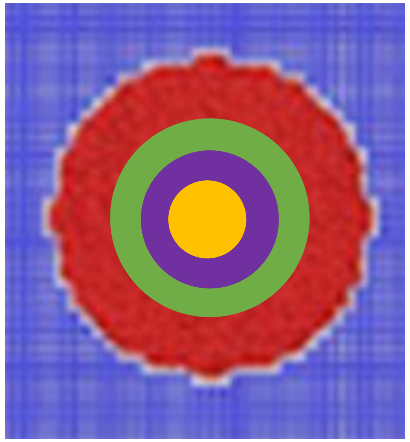
Pressure Variations Across the Pore



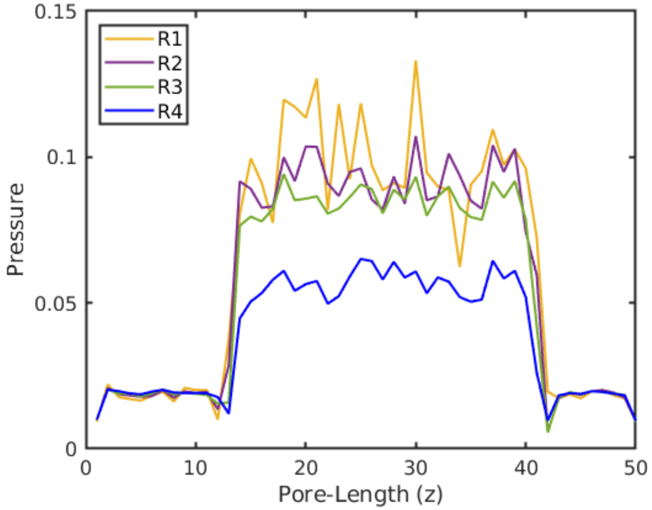


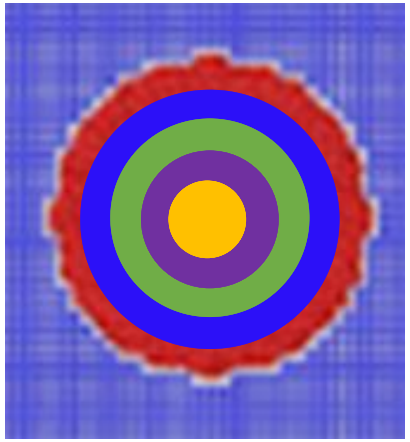
Pressure Variations Across the Pore



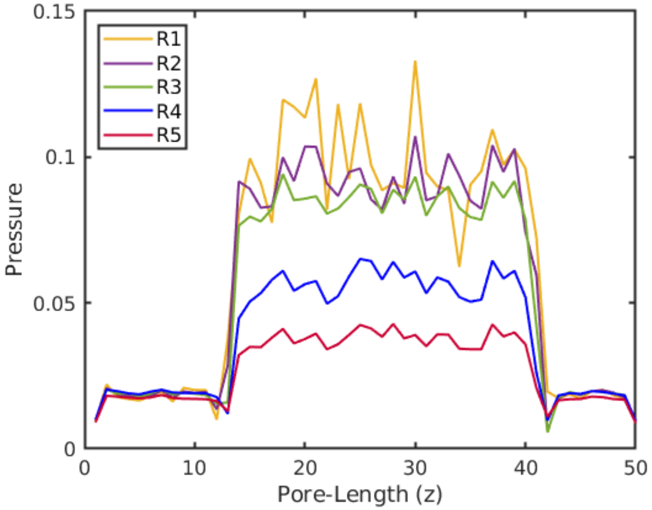


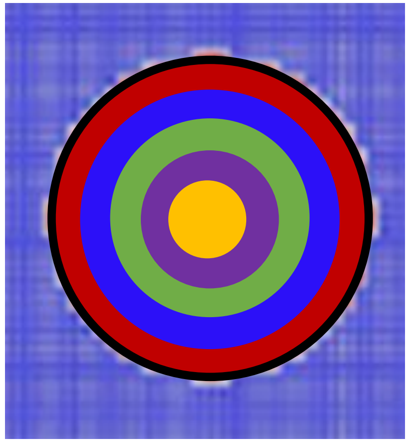
Pressure Variations Across the Pore



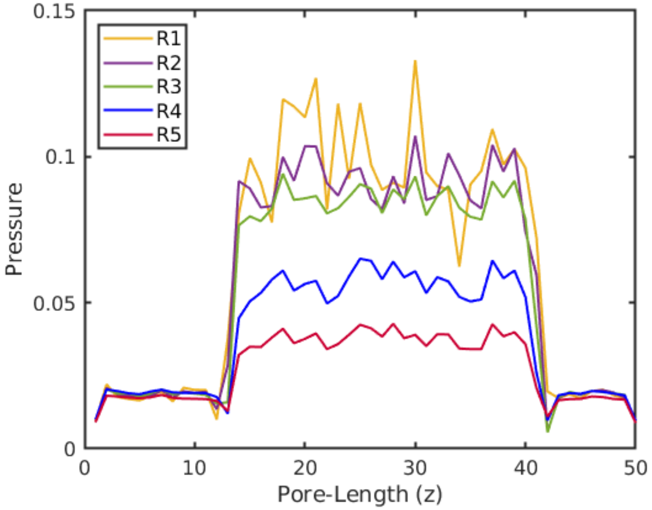


Pressure Variations Across the Pore





Pressure Variations Across the Pore



Δp_{bulk}

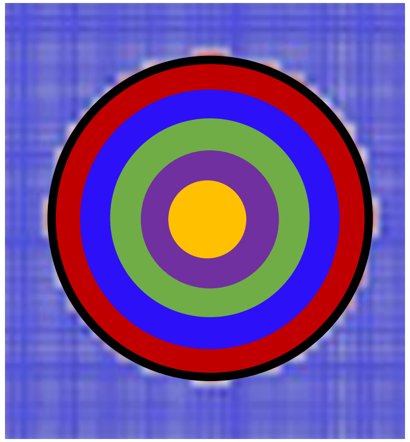
$$p^l \frac{V^l}{V} - \frac{\gamma^{ls}\Omega^{ls}}{V}$$

$$p^d \frac{V^d}{V}$$

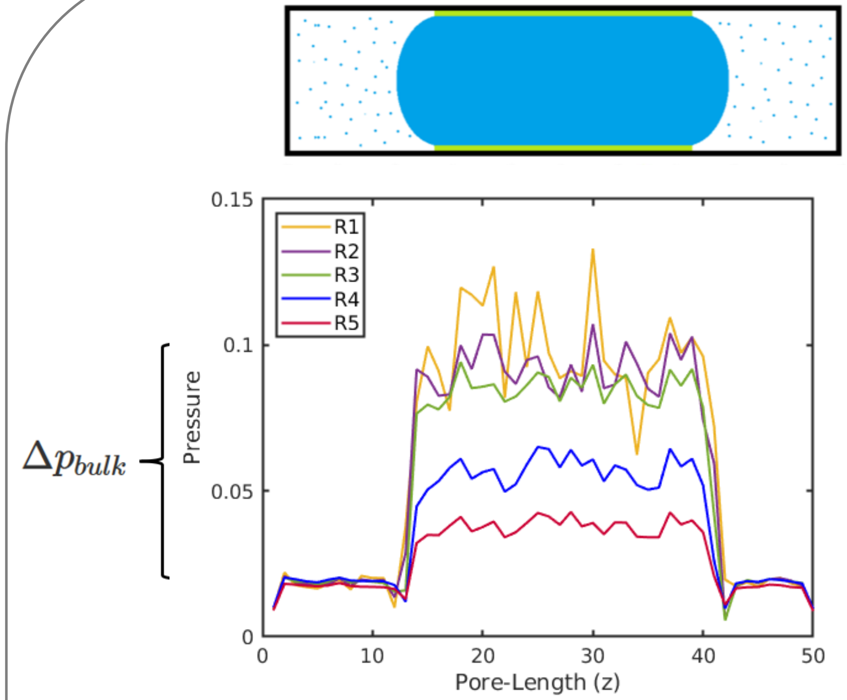
$$\hat{p}V = p^l V^l + p^d V^d - \gamma^{ls}\Omega^{ls}$$

↓

Compute V^d via equimolar surface



Pressure Variations Across the Pore



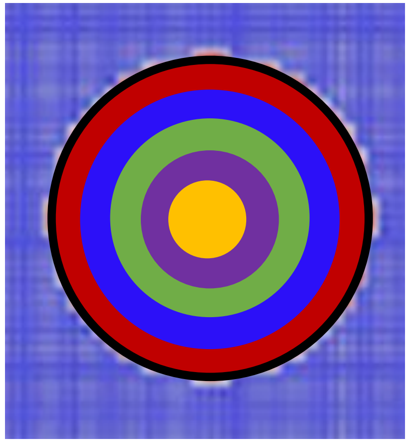
$$p^l \frac{V^l}{V} - \frac{\gamma^{ls}\Omega^{ls}}{V}$$

$$p^d \frac{V^d}{V}$$

$$\hat{p}V = p^l V^l + p^d V^d - \gamma^{ls}\Omega^{ls}$$

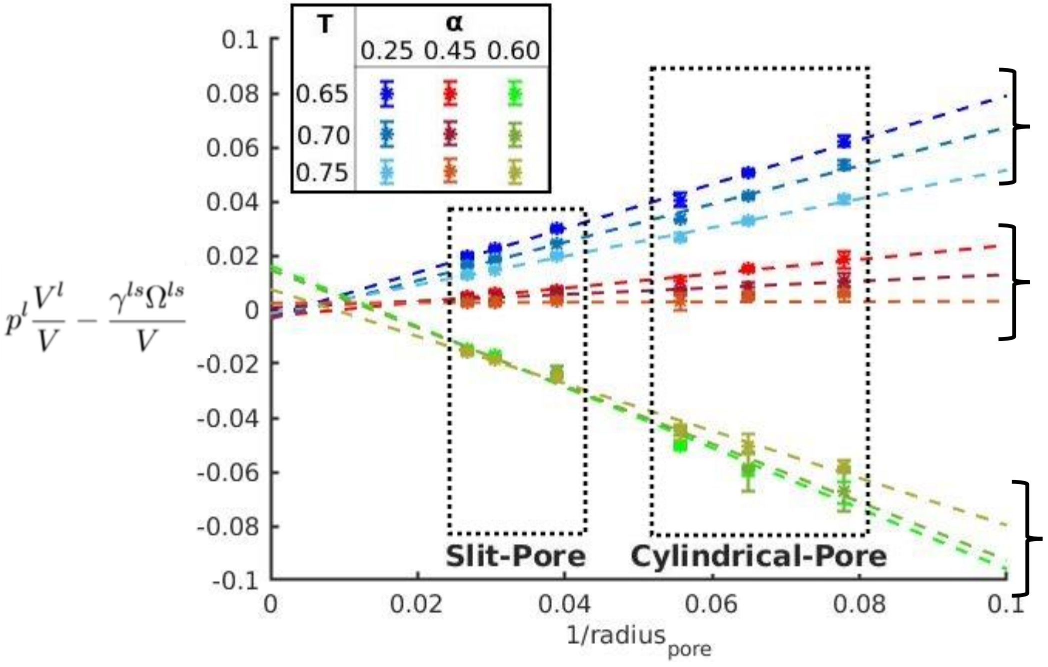
↓

Compute V^d via equimolar surface



- Pressure constant in the centrum of the pore
- Pressure decreases close to pore wall
- Difference between $\text{REV}_{\text{liquid}}$ and $\text{REV}_{\text{vapor}}$ assigned to the compressional energy of the layer (not included in the pressure calculation)

Surface Contribution (Liquid – Pore Wall)



- inverse radius of the pore was multiplied with the pre-factors derived in the theory
- Slope is the surface tension γ^{ls} between liquid and pore wall

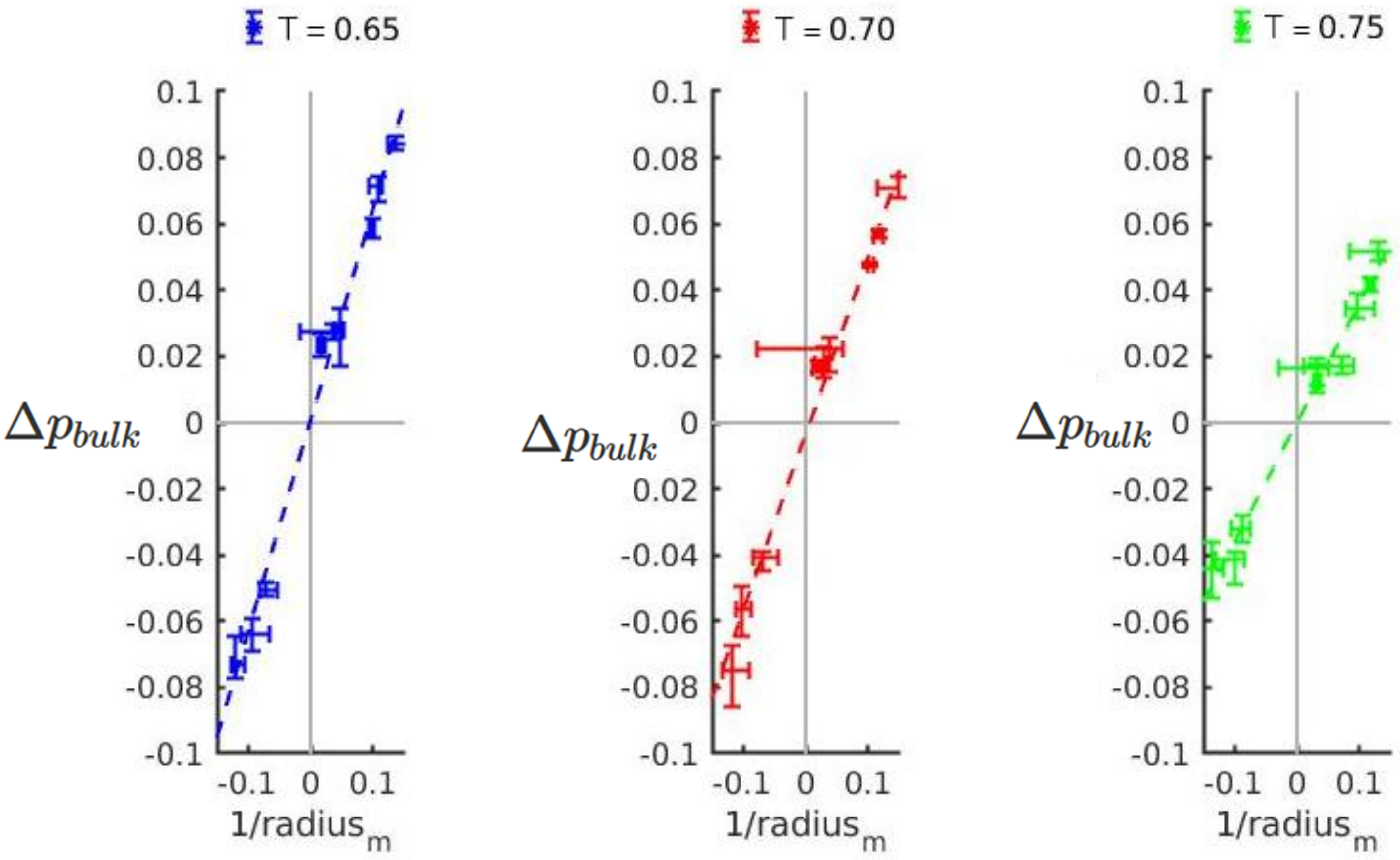
➡ Surface tension independent of geometry

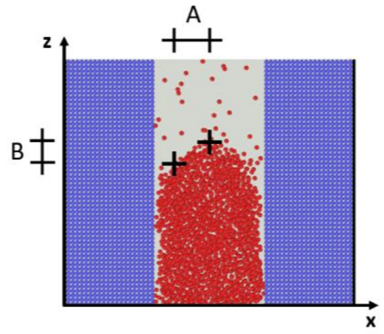
- Extension goes nicely through x = 0 / y = 0
- the surface tension decreases with increasing temperature
- No statement about the hydrophilic case

Gives us confidence that we attributed this pressure contribution in a right way

Surface Contribution (Liquid – Vapor)

Cylindrical Pore





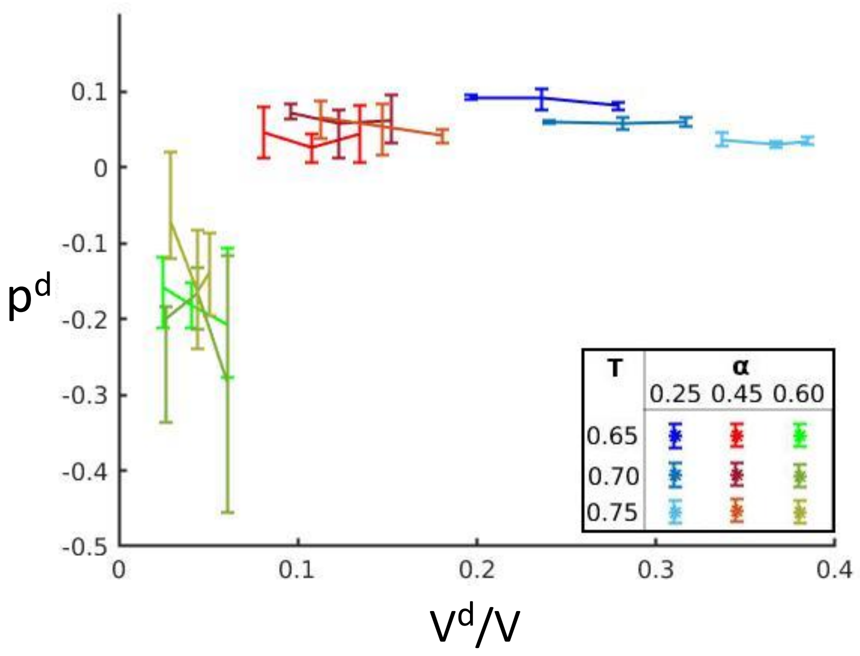
radius$_m$ = measured radius of meniscus

- Slope is the surface tension γ^{lv} between liquid and vapor
- Extension of the linear fit goes nicely through x = 0 / y = 0

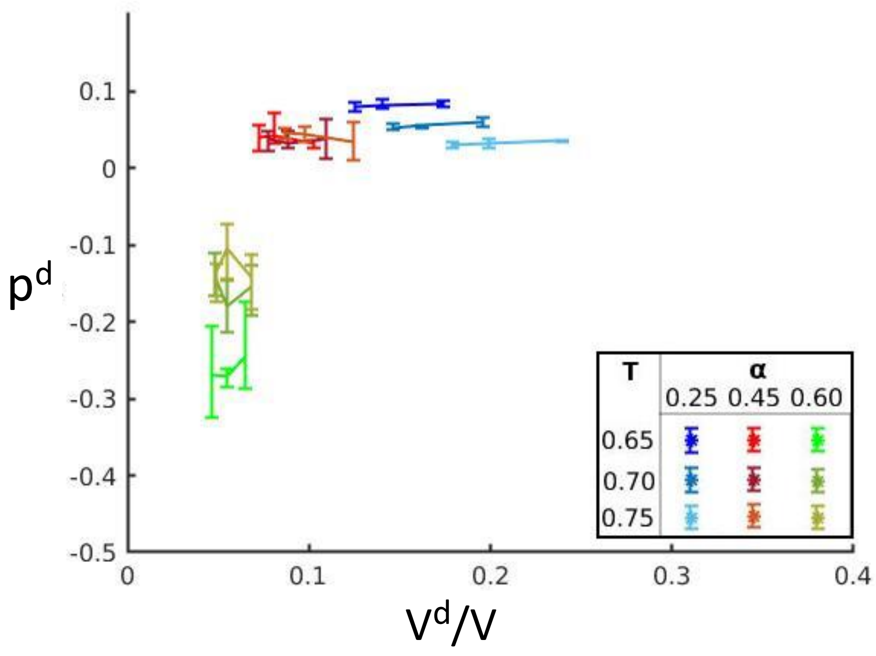
Gives us confidence that we attributed this pressure contribution in a right way

Disjoining Pressure

Cylindrical Pore



Slit Pore

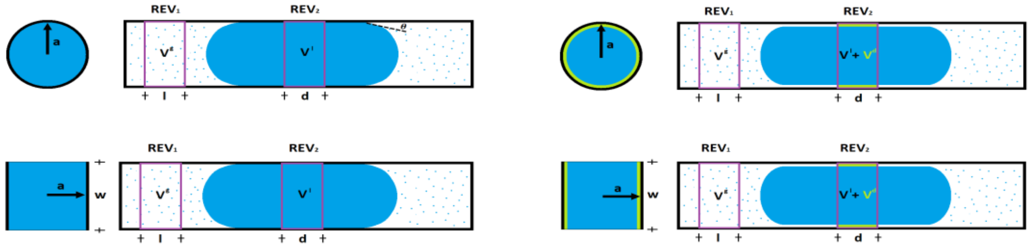


p^d = disjoining pressure V^d = volume of drying layer V = volume of pore

- Disjoining pressure independent of geometry
- Disjoining pressure appears to be constant
- Disjoining pressure dependent on temperature
- Negative disjoining pressure in hydrophilic pore

Summary

- Defined the pressures in a two-phase confined system in terms of the compressional energy



- The differential and integral pressures are defined following Hill

- Assisted by a new procedure, the onion-technique, we obtained the disjoining pressure which is characteristic and possible to determine for hydrophobic systems

- We found a procedure to find this pressure using molecular dynamics simulations

Thank you for your attention!

Thanks to the Norwegian Research Council for their center of excellence funding scheme and UNINETT Sigma2 - the National Infrastructure for High Performance Computing and Data Storage in Norway

Sources

[1] - https://www.hindustantimes.com/world-news/cape-town-faces-day-zero-water-crisis-highlights-city-s-rich-poor-divide/story-M9e5lOjXhXYYLt4M8hYzAN.html

[2] - https://qz.com/africa/1525526/cape-towns-day-zero-water-shortage-fear-spreads-in-south-africa/

[3] - https://www.stuff.co.nz/nelson-mail/news/110556228/severe-water-restrictions-to-bite-as-drought-could-cost-over-100-million

[4] - https://www.stuff.co.nz/nelson-mail/news/110556228/severe-water-restrictions-to-bite-as-drought-could-cost-over-100-million

[5] - https://onlinelibrary.wiley.com/doi/abs/10.1002/wcc.81

[6] - Anna Kang & Christopher Weyant - You Are Not Small

[7] - Kjelstrup, S., Bedeaux, D., Hansen, A., Hafskjold, B., & Galteland, O. (2018). Non-isothermal transport of multi-phase fluids in porous media. Constitutive equations. *Frontiers in Physics*, *6*, 150.

Thermal Transport Inside Nanopores

State of the Art

NTNU-UiO Porous Media Laboratory

Simultaneous production of high-quality water and electrical power from aqueous feedstock's and waste heat by high-pressure membrane distillation

Norbert Kuipers[a,*], Jan Henk Hanemaaijer[a], Hans Brouwer[a], Jolanda van Medevoort[a], Albert Jansen[a], Frank Altena[b], Peter van der Vleuten[b], Henk Bak[c]

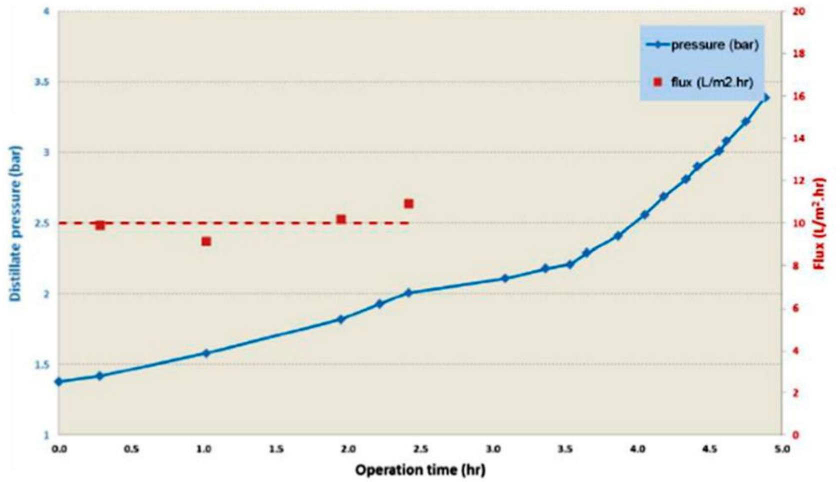
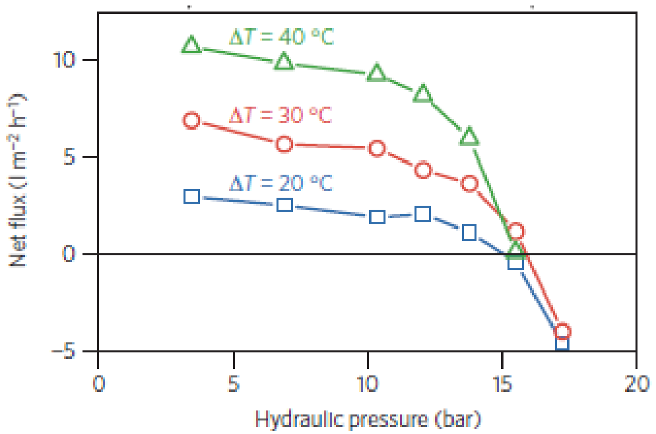


Fig. 7. First MemPower experiment, proving the existence of a positive distillate flux at a negative hydraulic pressure difference across a membrane.

- No theory
- No information about the membrane

Harvesting low-grade heat energy using thermo-osmotic vapour transport through nanoporous membranes

Anthony P. Straub[1], Ngai Yin Yip[2], Shihong Lin[3], Jongho Lee[1] and Menachem Elimelech[1]*



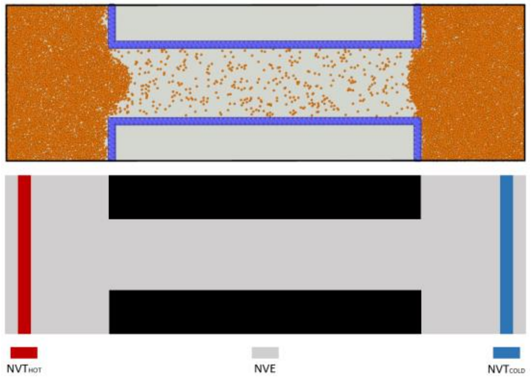
- Theory:

Dependence of the equilibrium vapor pressure on the hydraulic pressure

$$\ln\left(\frac{P_v}{P_{v,0}}\right) = \frac{P_h v_M}{RT_0}$$

Simulation System

System 1

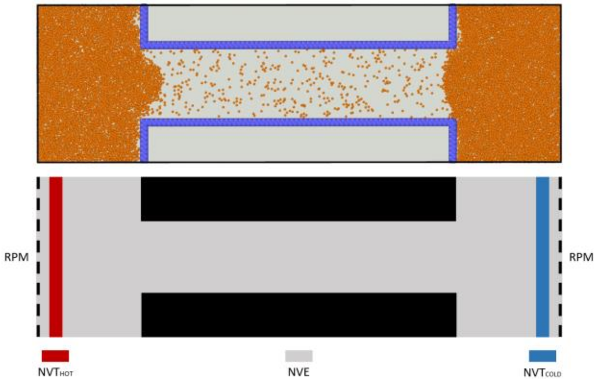


- No pressure difference

$$\Delta p = 0$$

- Temperature difference with two thermostats

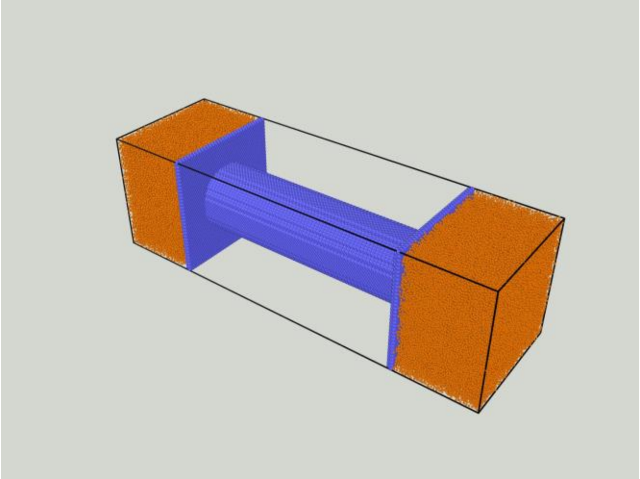
System 2



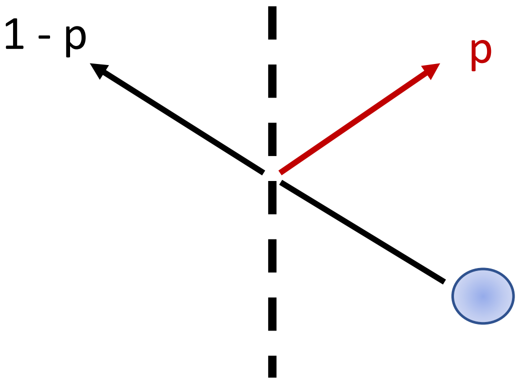
- Pressure difference by reflective membrane

Δp = low Δp = high

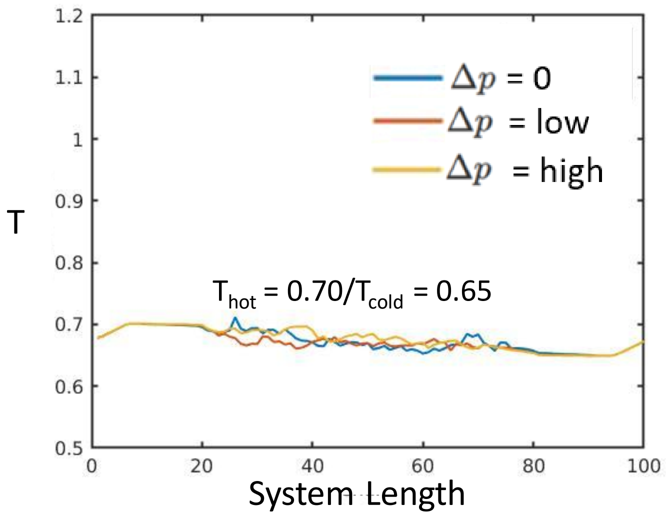
- Temperature difference with two thermostats

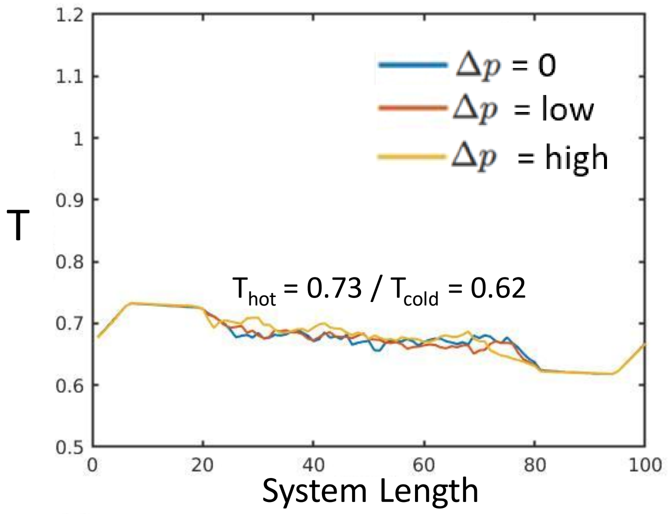


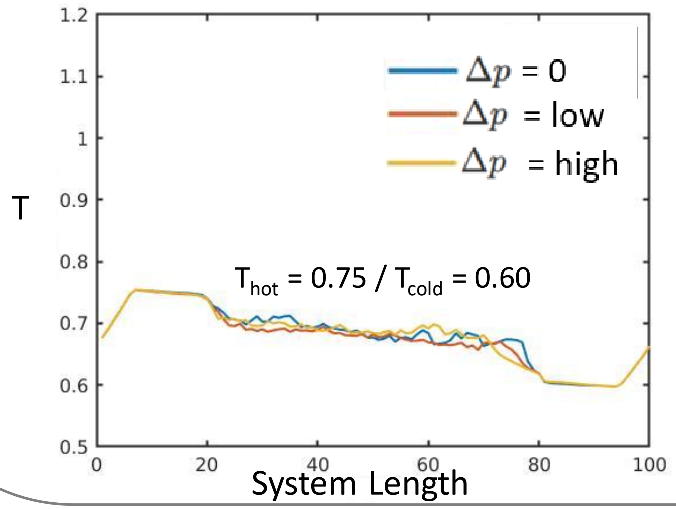
Reflective Membrane

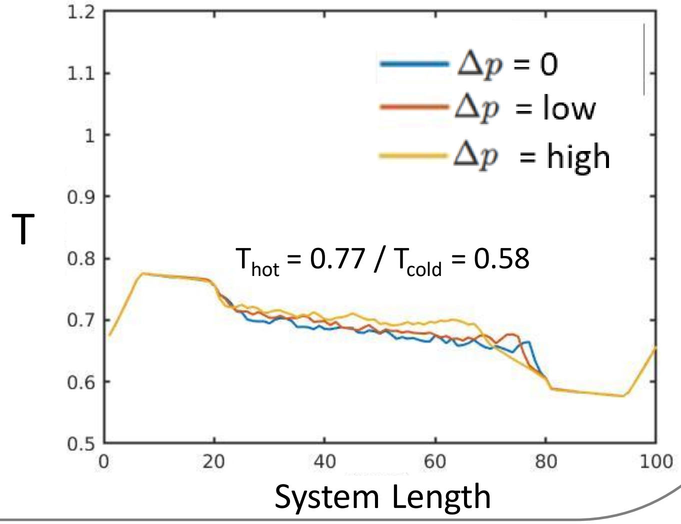


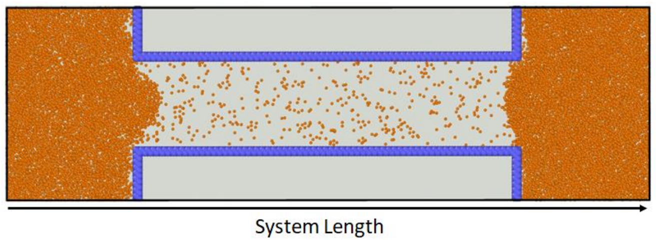
Temperature Along the Pore





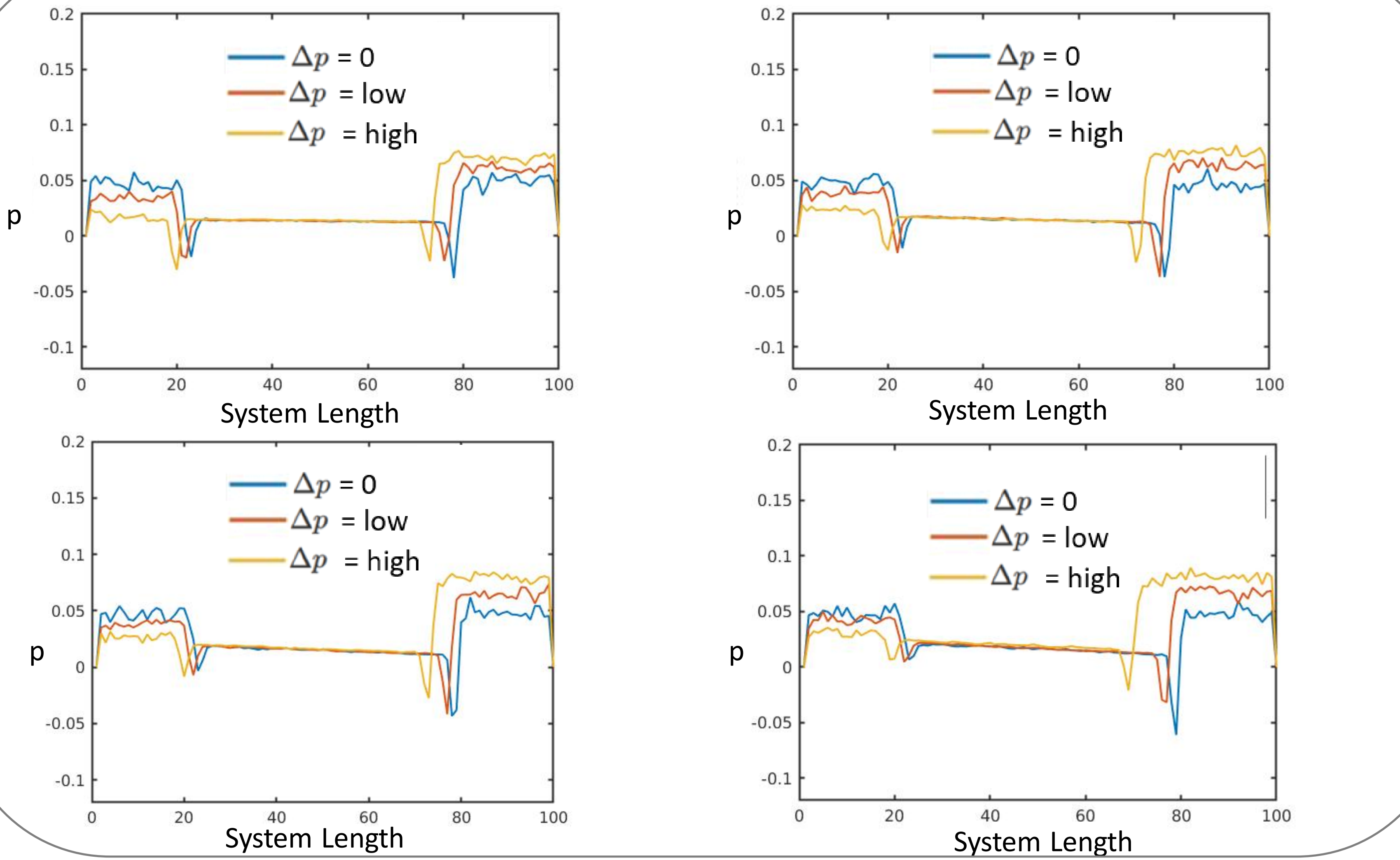


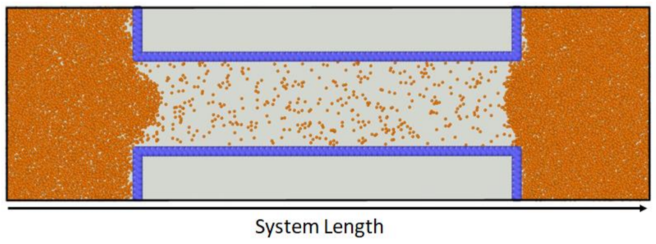




- 4 Different temperature gradients
- Temperature independent of the pressure

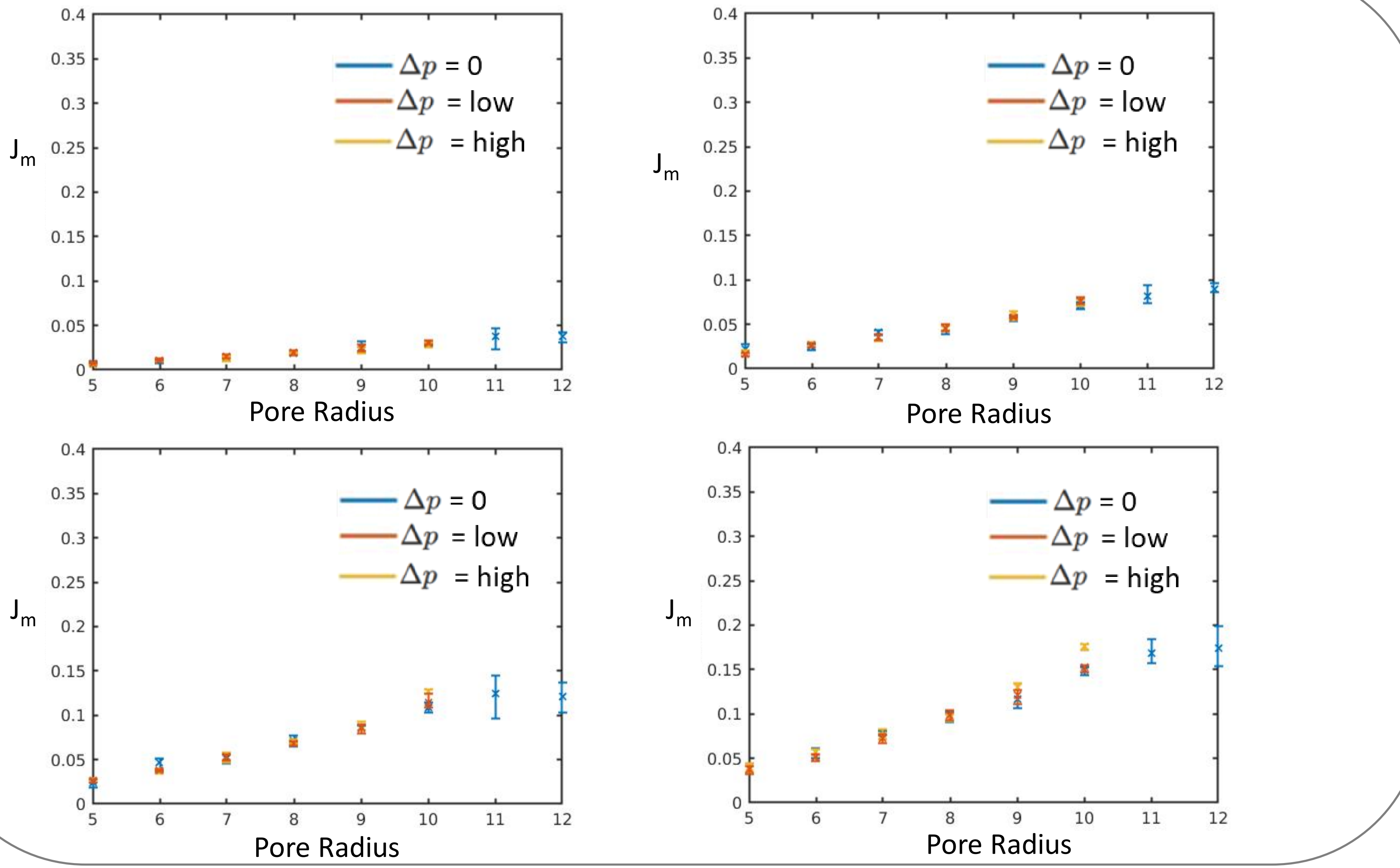
Pressure



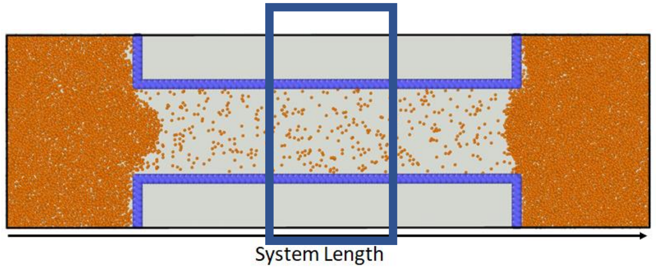


- Vapor pressure independent of hydraulic pressure
- Depending on pressure fluid pushes into pore

Mass flux

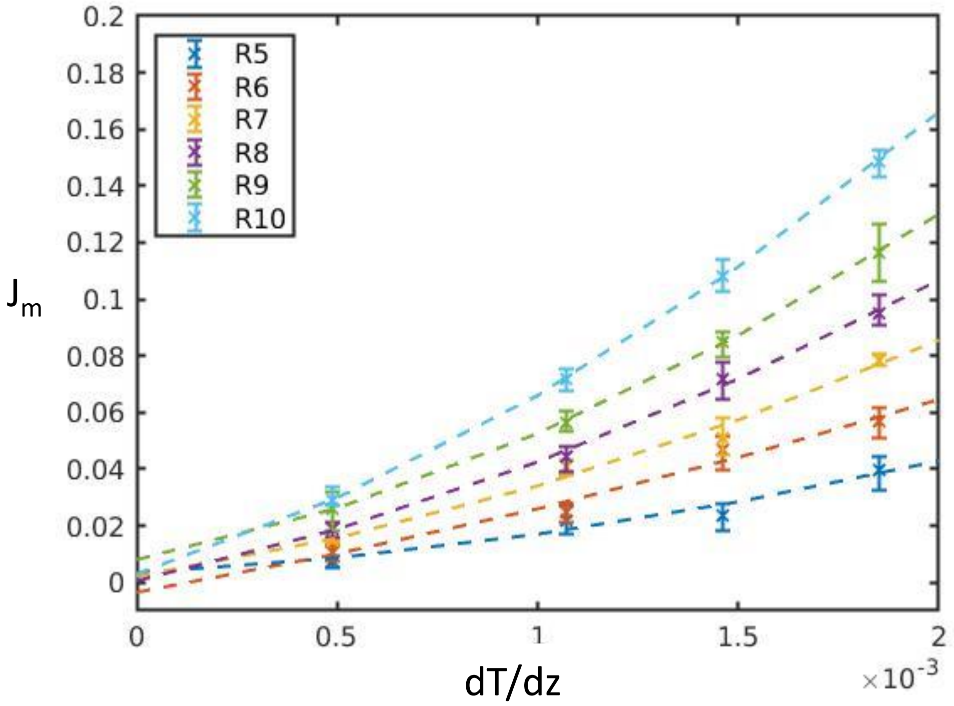


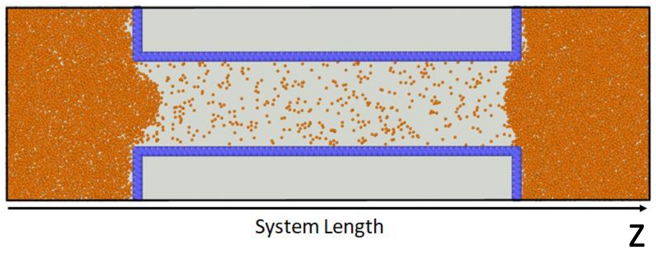
Mass flux in segment



- Mass flux independent of pressure
- Mass flux reaches plateau

Temperature Gradient





- Exponential dependence of mass flux towards temperature gradient

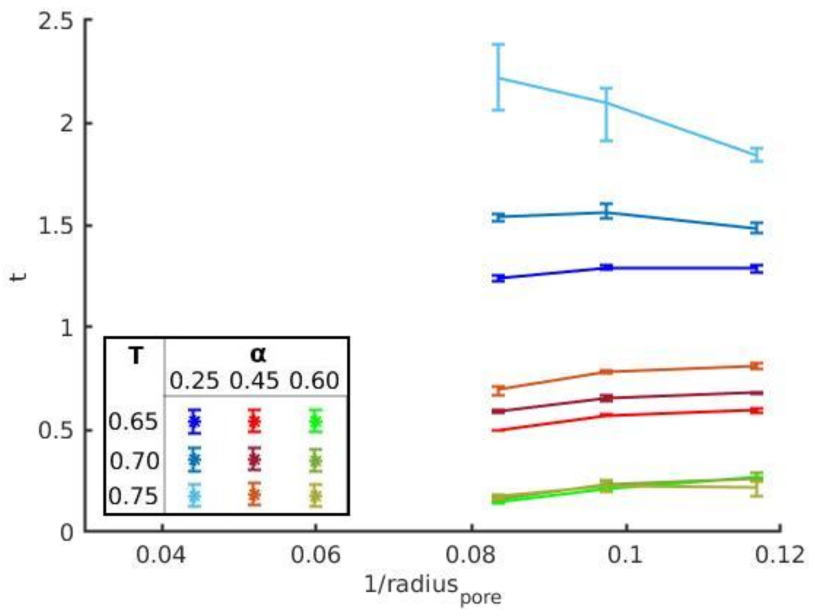
Thank you for your attention!

Thanks to the Norwegian Research Council for their center of excellence funding scheme and UNINETT Sigma2 - the National Infrastructure for High Performance Computing and Data Storage in Norway

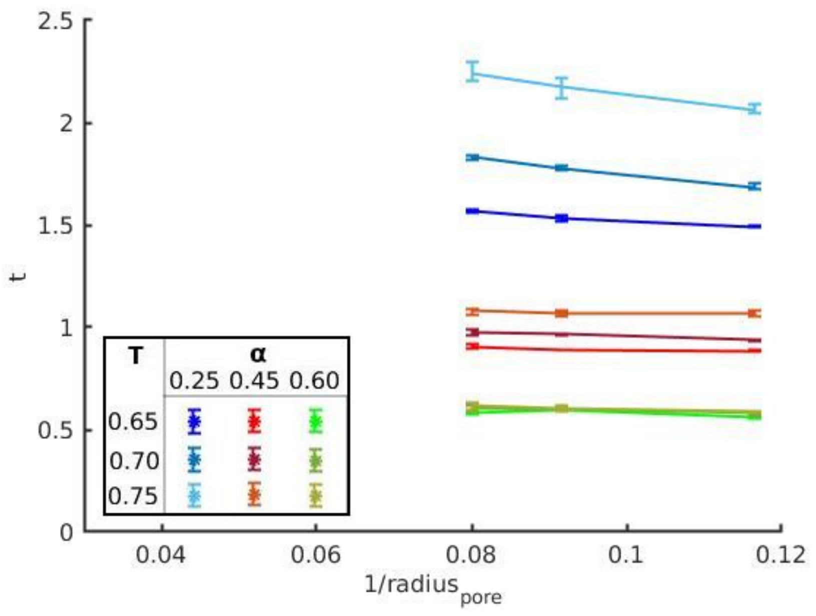
Backup

Drying Layer Thickness

Cylindrical Pore



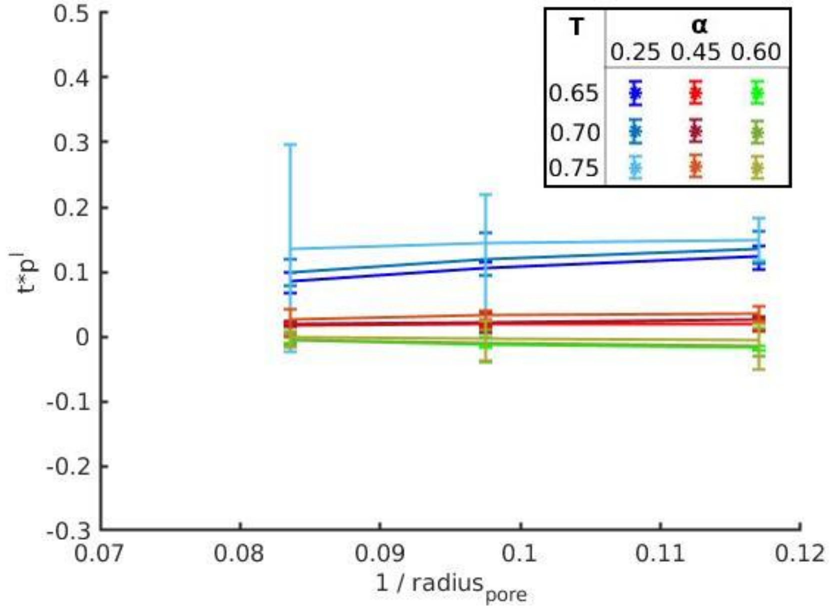
Slit Pore



Drying Layer Thickness with Liquid Pressure

PoreLab
NTNU-UiO Porous Media Laboratory

Cylindrical Pore



Slit Pore