

Cavitation in nanopores

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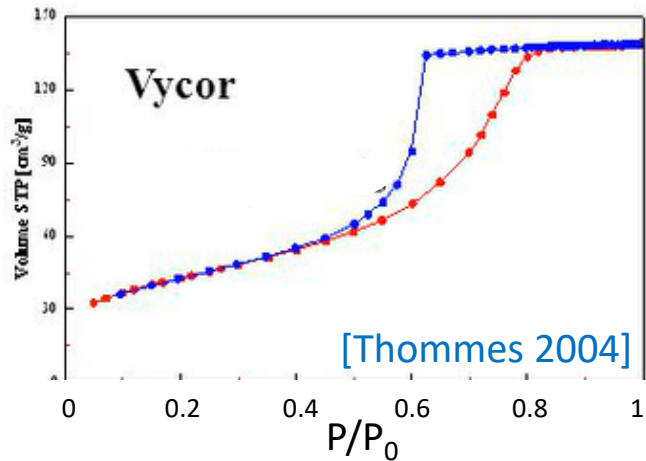
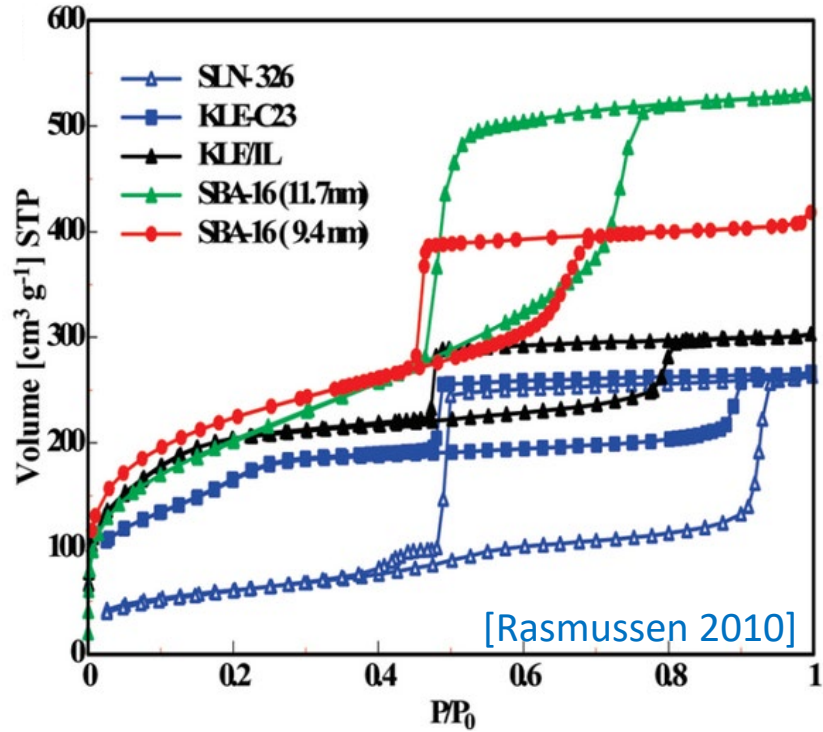
Institut Néel – *P. Coutin, P. Spathis*

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ANR project NanoCav

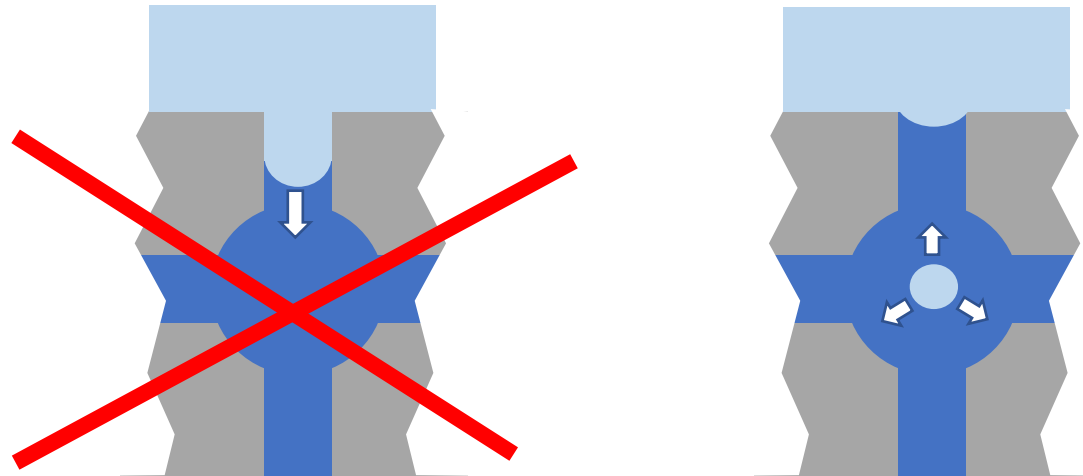


Evaporation in ordered mesoporous silica

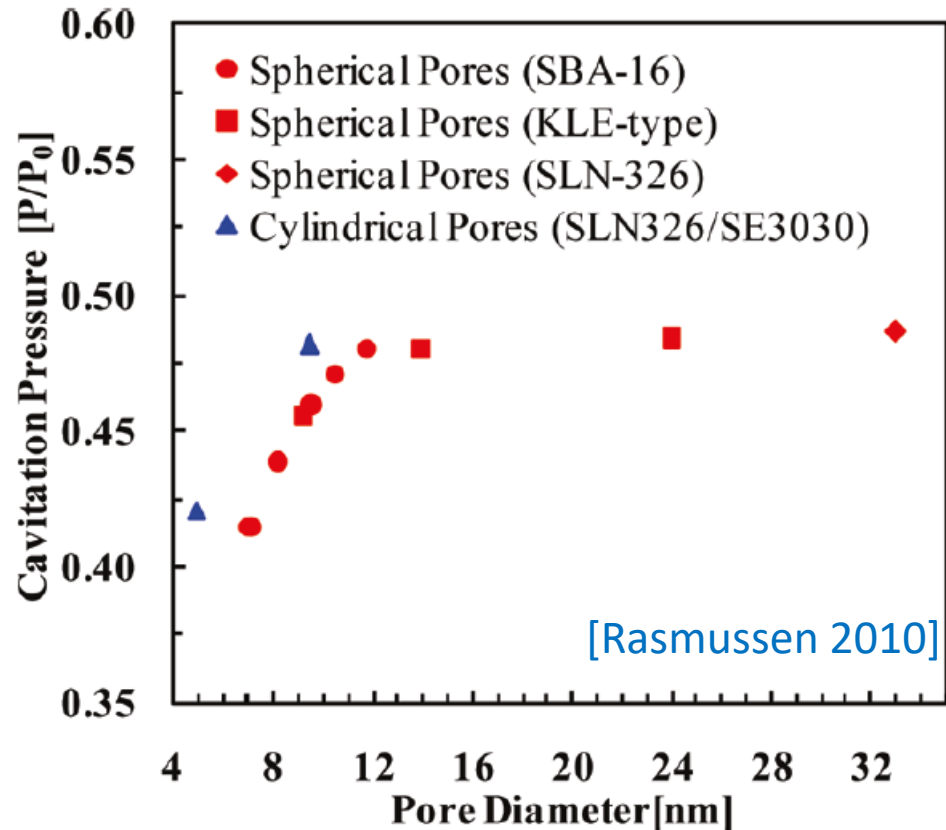


Sharp drop of V_{ads}
 +
 Evaporation pressure $P^* \sim 0.45 P_{sat}$
 (N₂ @ 77 K)

} *signature of cavitation*



Evaporation in ordered mesoporous silica



Evaporation pressure P^*/P_0 lies in the range 0.42 – 0.46

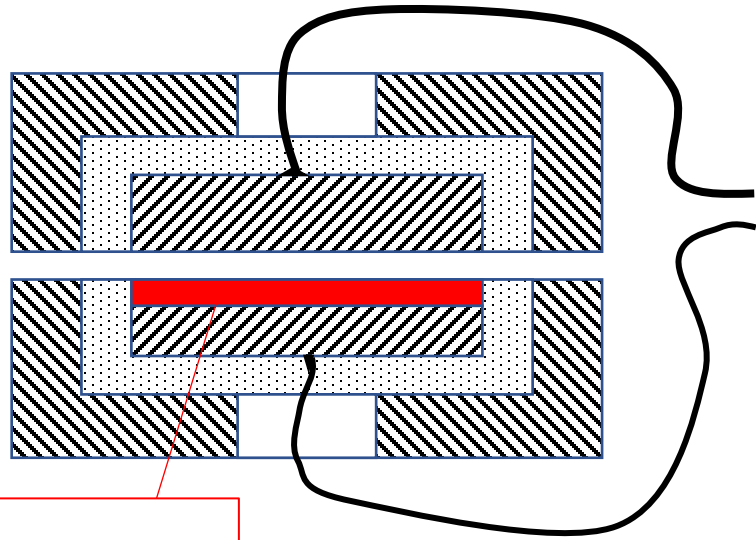
depends on pore size (cavitation more difficult in confined liquid)

→ How to identify cavitation unambiguously ?

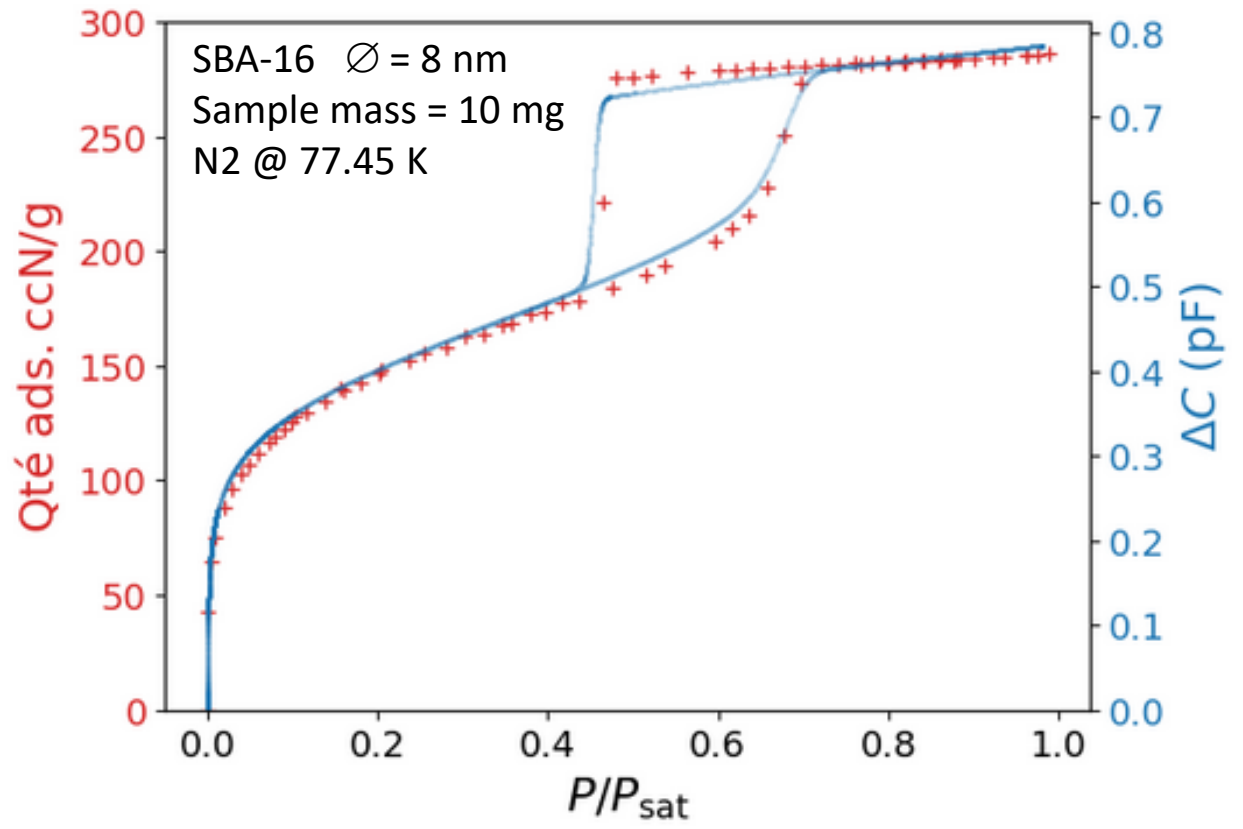
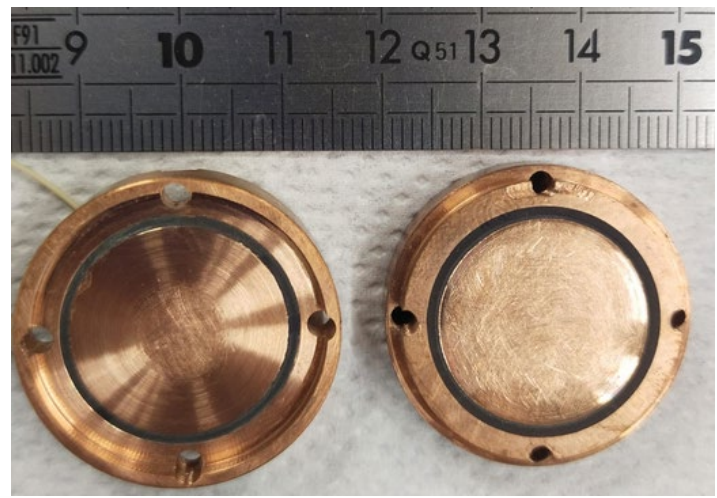
→ Impact of confinement ?

P^* dependance on pore radius, temperature...

Capacitive measurements



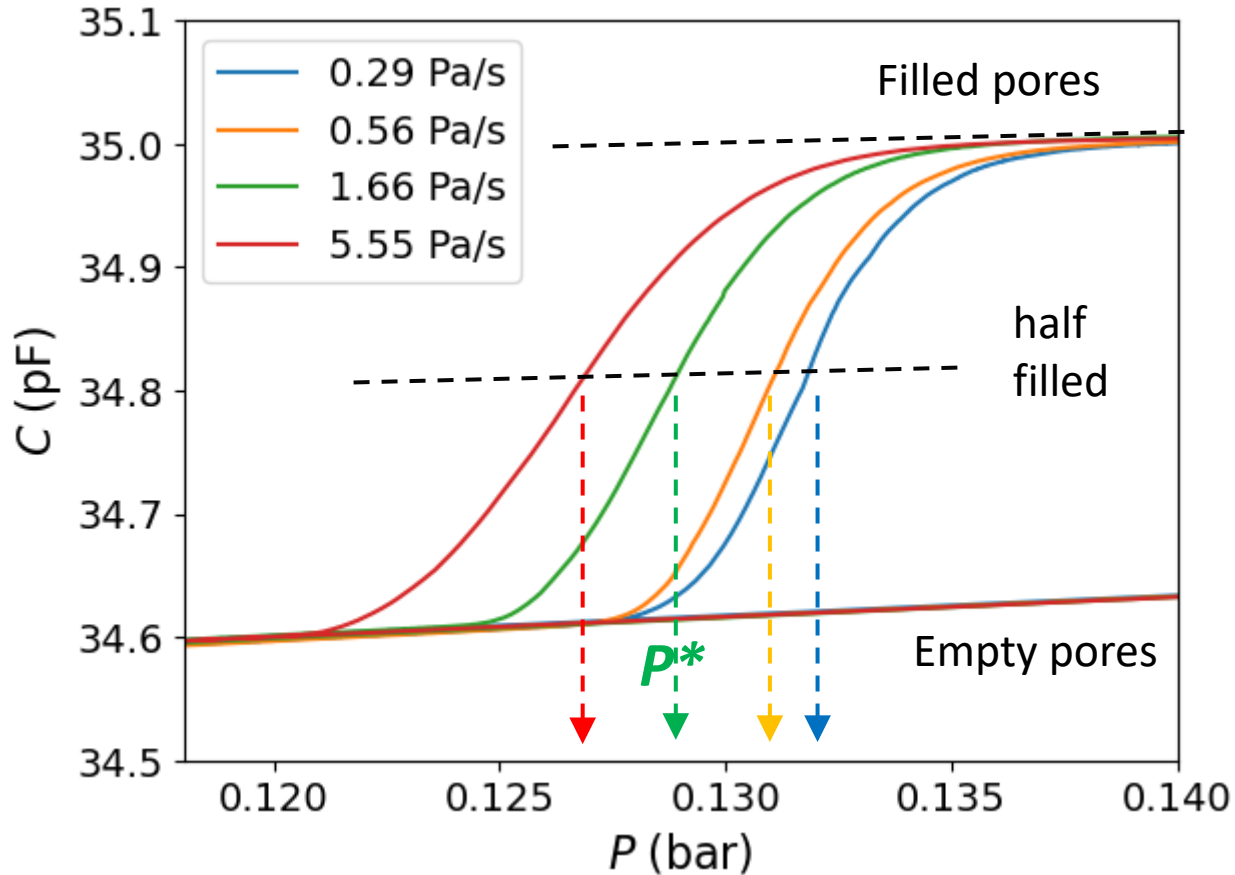
$\varnothing = 20 \text{ mm}$
Espacement = 0.1 mm



High accuracy capacitance bridge – resolution 10^{-5} pF

Relation capacitance – adsorbed mass:
see you at poster session Thursday 10:05

Continuous measurements at controlled pressure rate



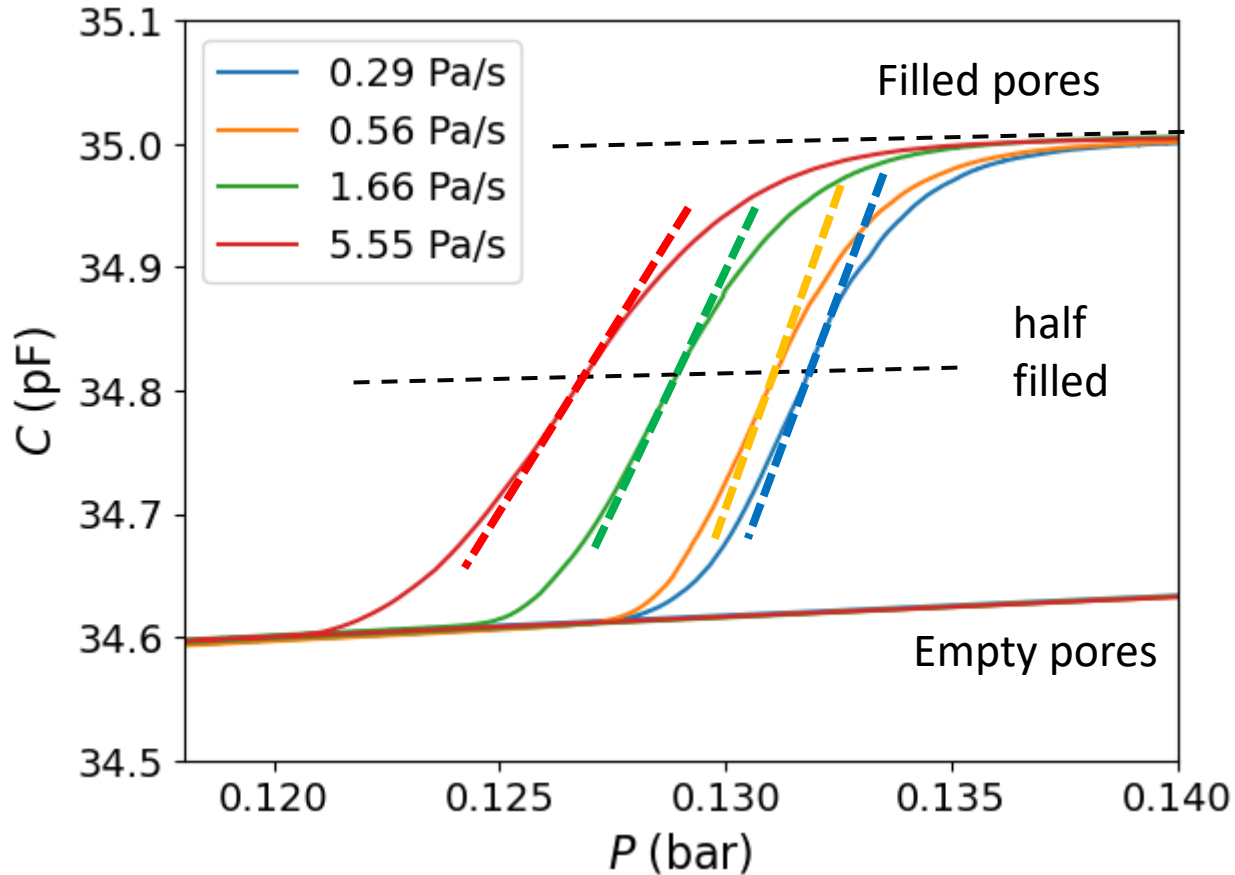
SBA-16 $\varnothing = 7.6$ nm
 N2 @ 70.07 K

assuming ΔC is proportional to the amount of adsorbed fluid,
 normalization gives the fraction Ψ of filled pores
 as a function of P

→ precise determination of cavitation threshold
 P^* as a function of $A = \left| \frac{dP}{dt} \right|$

$$\rightarrow \alpha = - \frac{d(\ln A)}{dP^*} = \frac{1}{k_B T} \frac{dE_b}{dP}$$

Continuous measurement at controlled pressure rate



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N₂ @ 70.07 K

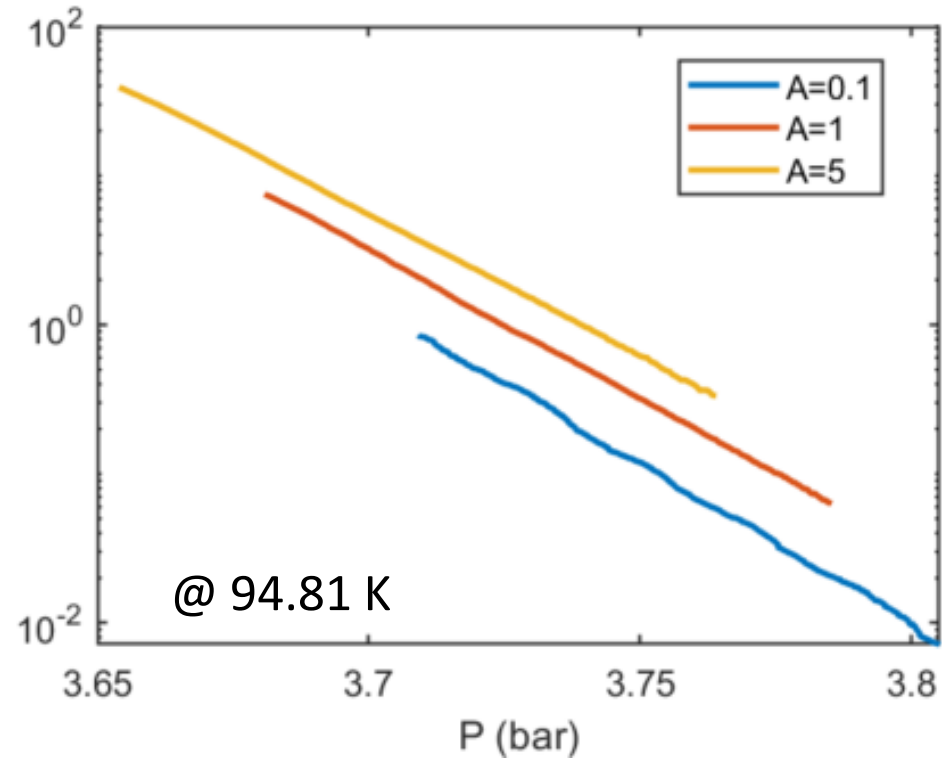
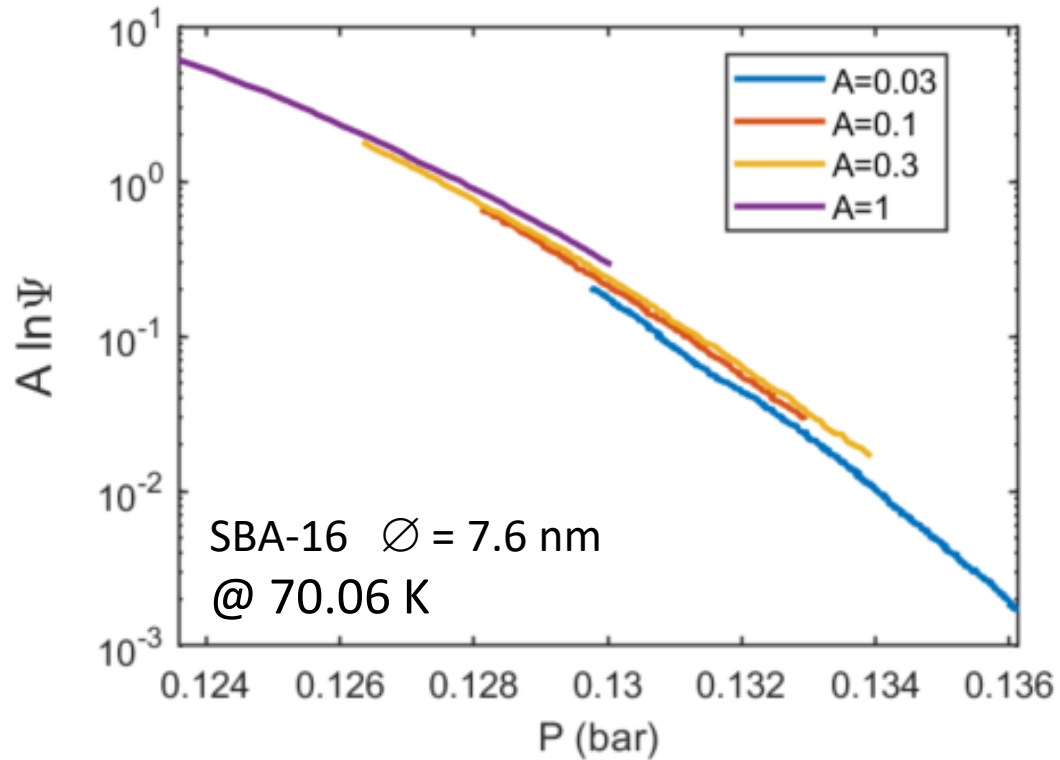
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→ $\beta = \frac{\left. \frac{d\Psi}{dP} \right|_{P^*}}{\alpha}$ depends of the pore size
distribution (= 1 for homogeneous nucleation or
heterogeneous with monodisperses pores)

Results – shape of $\psi_A(P)$



Homogeneous nucleation : curves $A \ln \Psi$ collapse on a single master curve

Critical nucleation radius $R^* = \frac{2\gamma}{\Delta P}$

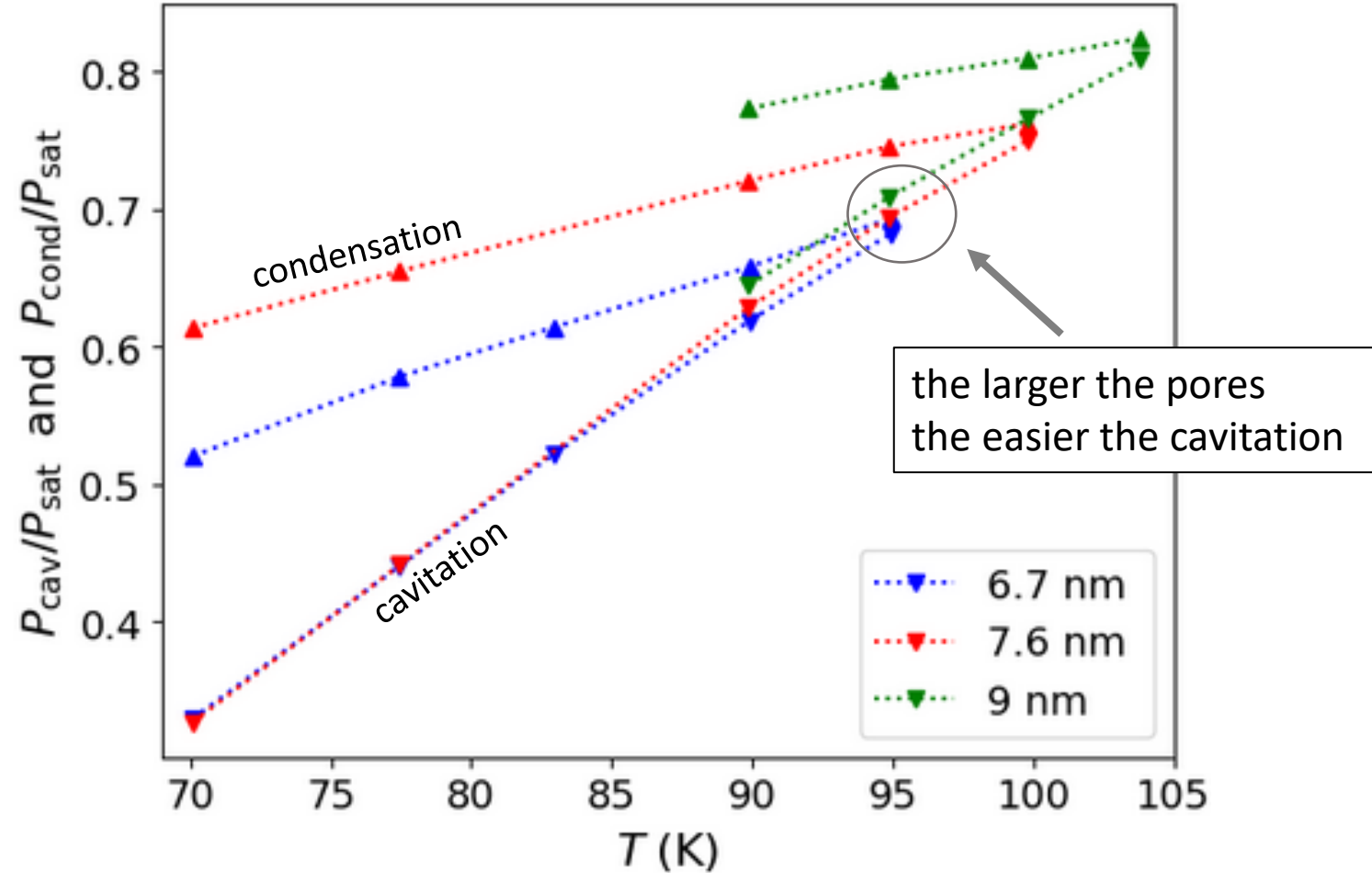
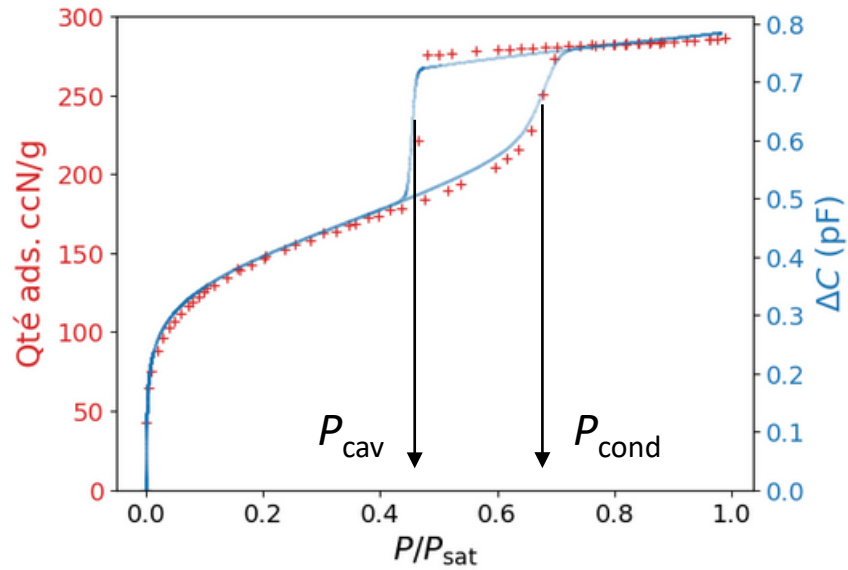
1.0 nm @ 70 K

1.8 nm @ 95 K

pore radius $R_p = 3.8$ nm

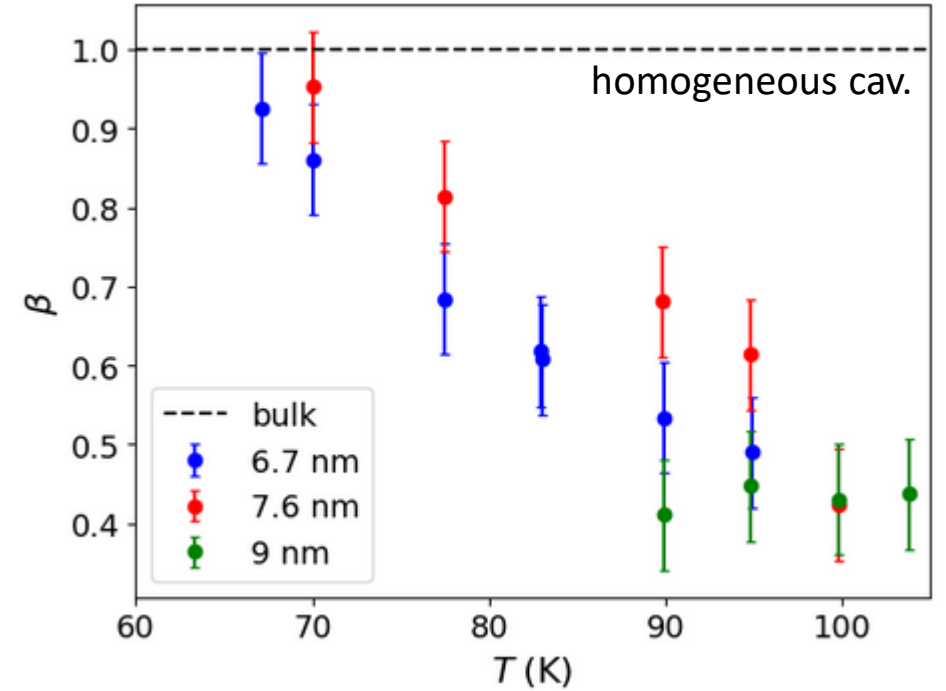
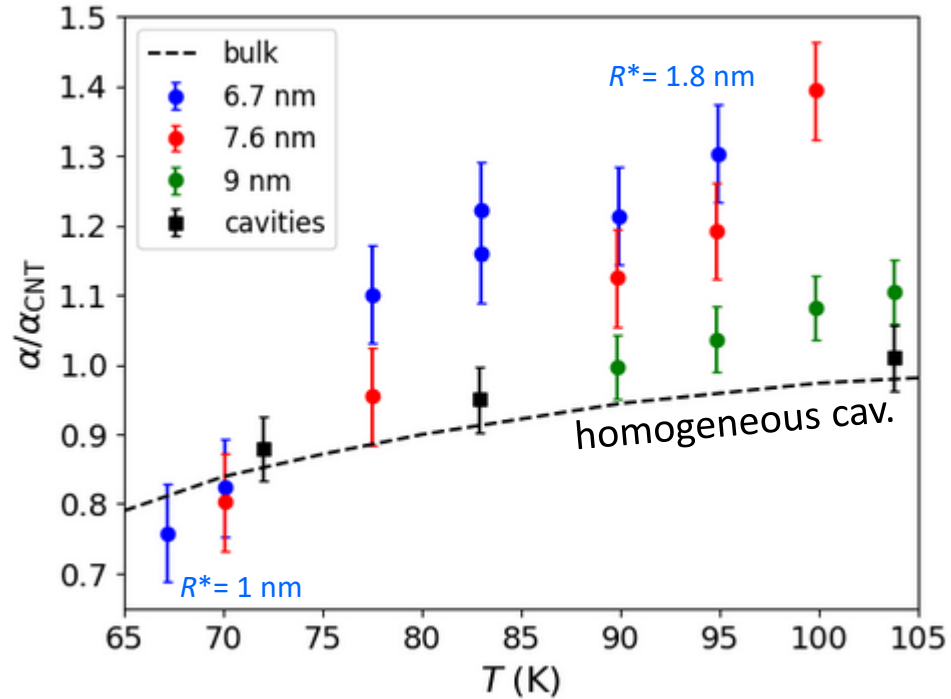
Experimental results – phase diagram

3 SBA-16 samples
with dif. pore diameter



Experimental results – coefficients α and β

$$\alpha = \frac{1}{k_B T} \frac{dE_b}{dP}$$

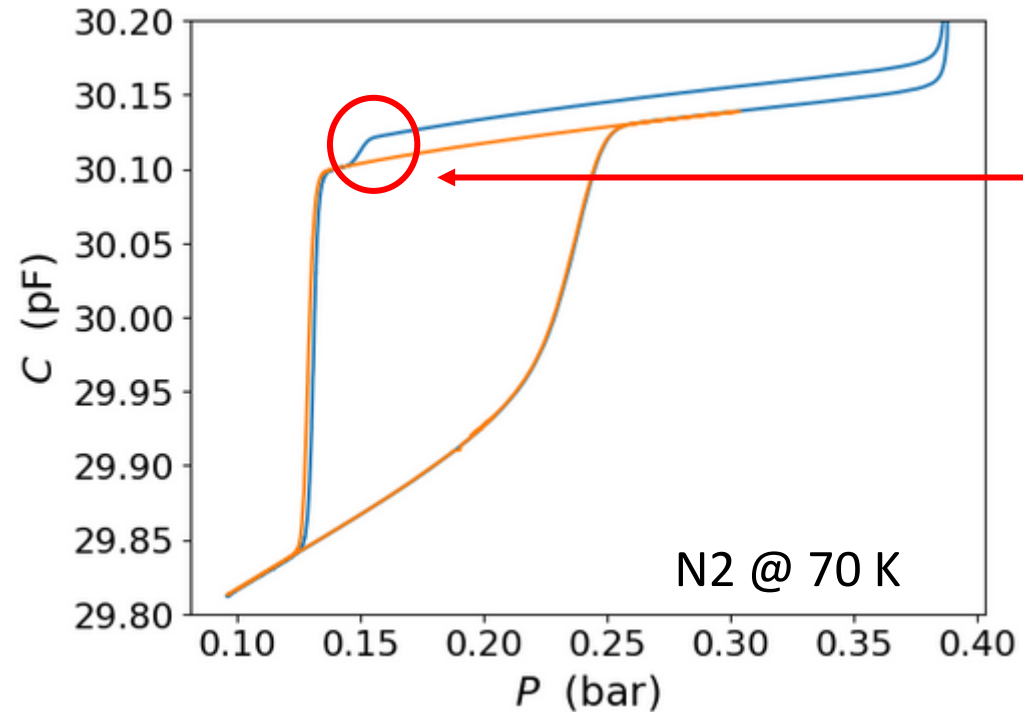


- The smaller the pore radius R_p
- the larger T (hence critical radius R^*)



the larger the departure from homogeneous cavitation

Large cavities (inter-grains ?) cavitation

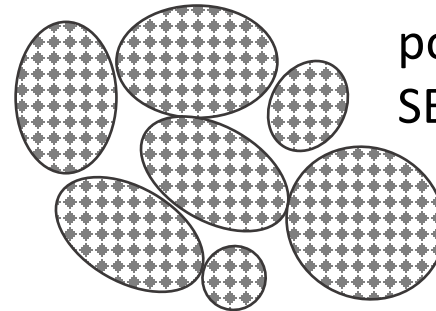


additional evaporation step at P_{ac}^*
observed only if pressure is ramped up to P_{sat}

T -dependence of P_{ac}^* → cavitation event

position of P_{ac}^* → cavitation in large cavities

Cavities (\equiv bulk liquid) provide a reference for cavitation features



possibly voids between
SBA grains ?

Thermodynamic approach – the energy barrier E_B

Grand potential for bubble formation in the metastable liquid [*Sharp interface* - Bonnet & Wolf

$$\Delta\Omega = \underbrace{\frac{4\pi}{3} R^3 \Delta\rho k_B T \ln \left(\frac{f(P)}{f_{\text{sat}}} \right)}_{\text{gain in chemical potential: } \textit{known}} - \underbrace{\Delta\rho \int_0^R U(r) d^3r}_{\text{correction due to substrate-fluid interaction potential}} + \underbrace{4\pi R^2 \sigma}_{\text{cost of the interface}}$$

Surface tension α corrected for bubble curvature $\sigma = \sigma_0 \left(1 + \frac{a}{R} + \frac{b}{R^2} \right)$

Measured for N2 *homogeneous* cavitation in large pores [Bossert 2023]

- Substrate-fluid potential**
- derivation from dispersion forces (Saam & Cole, Neimark and co-workers ...)
 - empirical exponential dependance (Celtini, Pellenq, Morishige...)

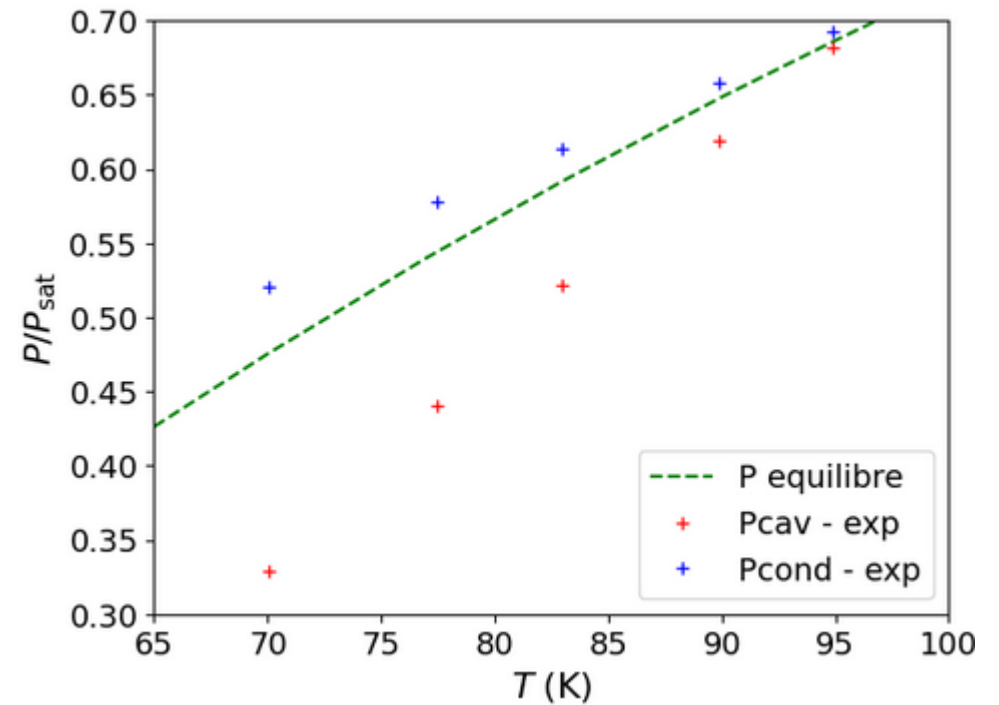
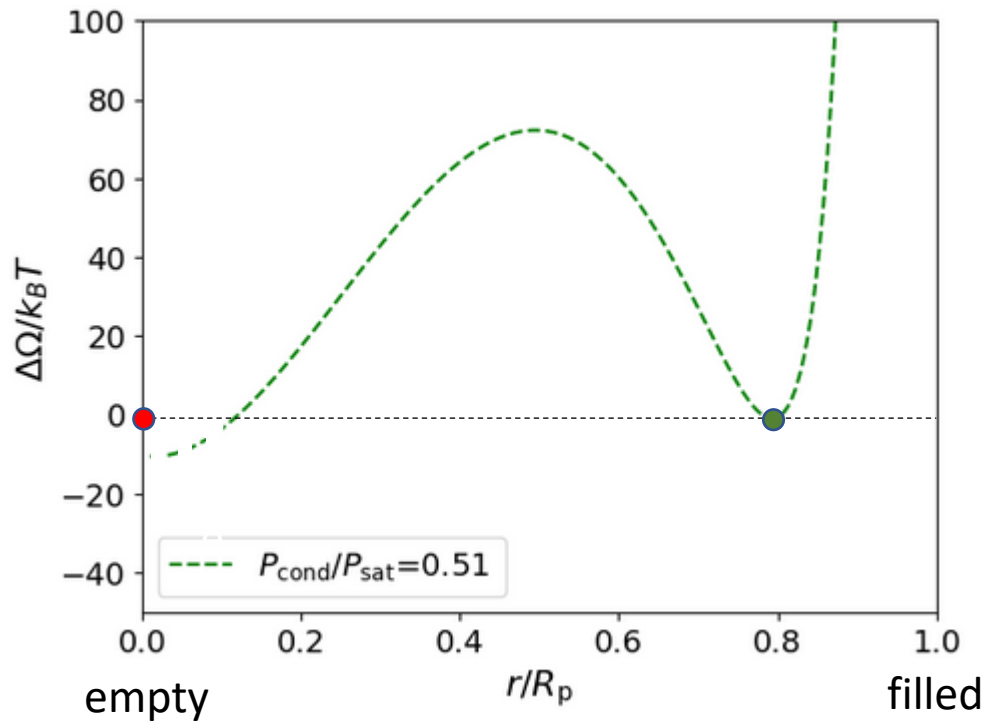
1 or 2 adjustable parameters / adjusted on the critical point for confined fluid (point where hysteresis disappears)

Thermodynamic approach – substrate-fluid potential

Substrate-fluid potential - derivation from dispersion forces (Saam & Cole, Neimark and co-workers ...)

$$U(z) = -\frac{A}{z^3} \quad , \quad \text{with Hamaker constant } A = 4.4 \text{ K} \cdot \text{nm}^3 \quad [\text{Saam\&Cole}]$$

→ 1 adjustable parameter: pore radius 6.7 nm (NLDFT-type potential: 7.0 nm)



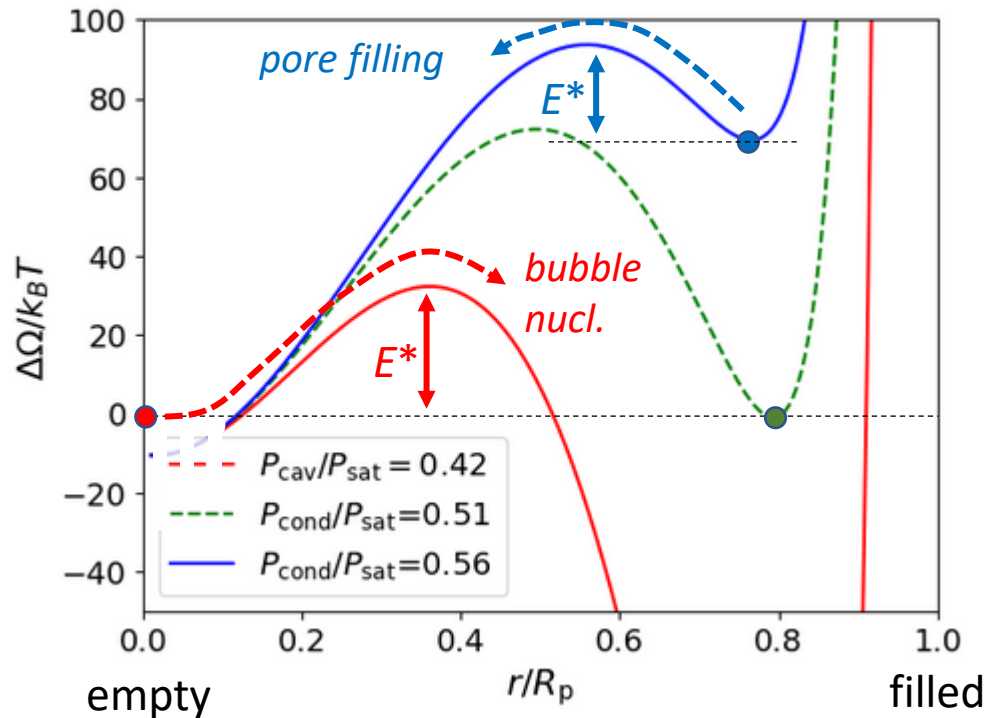
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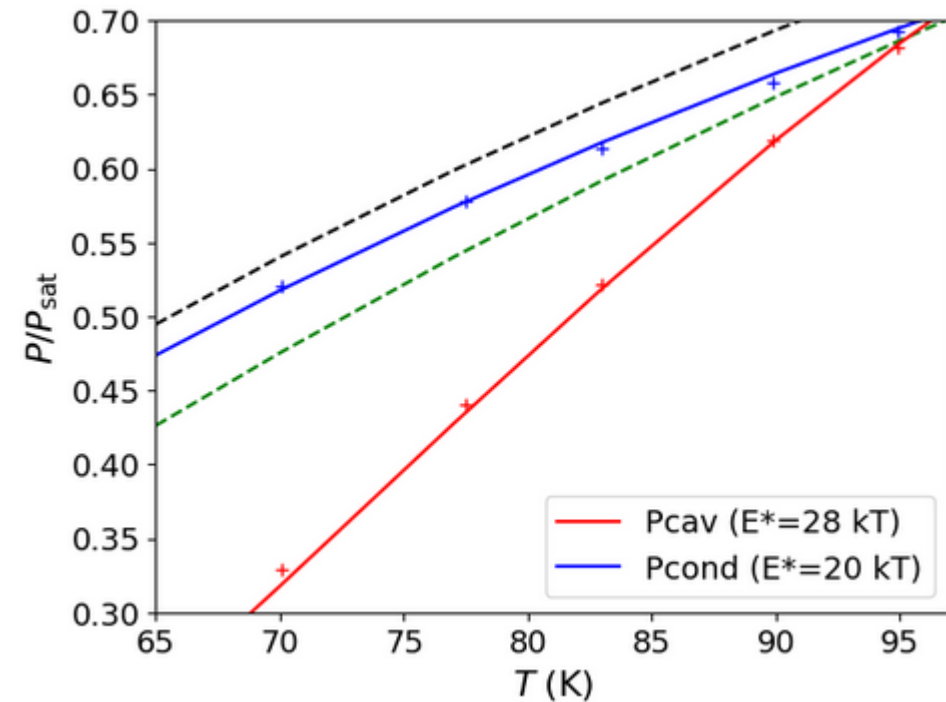
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→ pore radius 6.7 nm (NLDFT potential 7.0 nm)



Phase diagram (similar with NLDFT potentials)



Thermodynamic approach – substrate-fluid potential

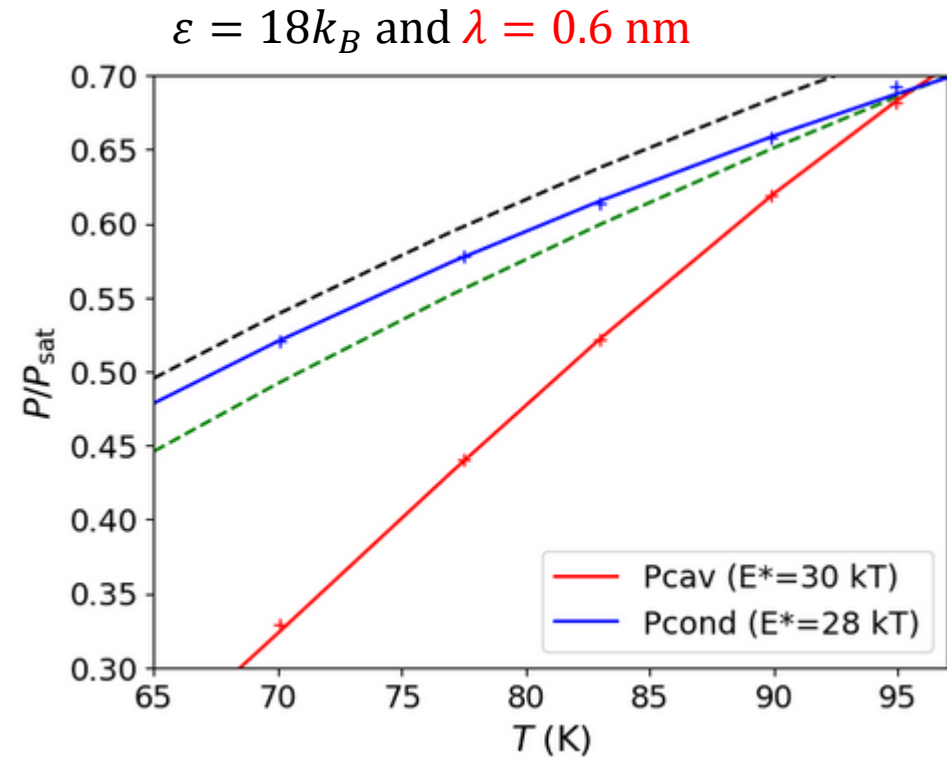
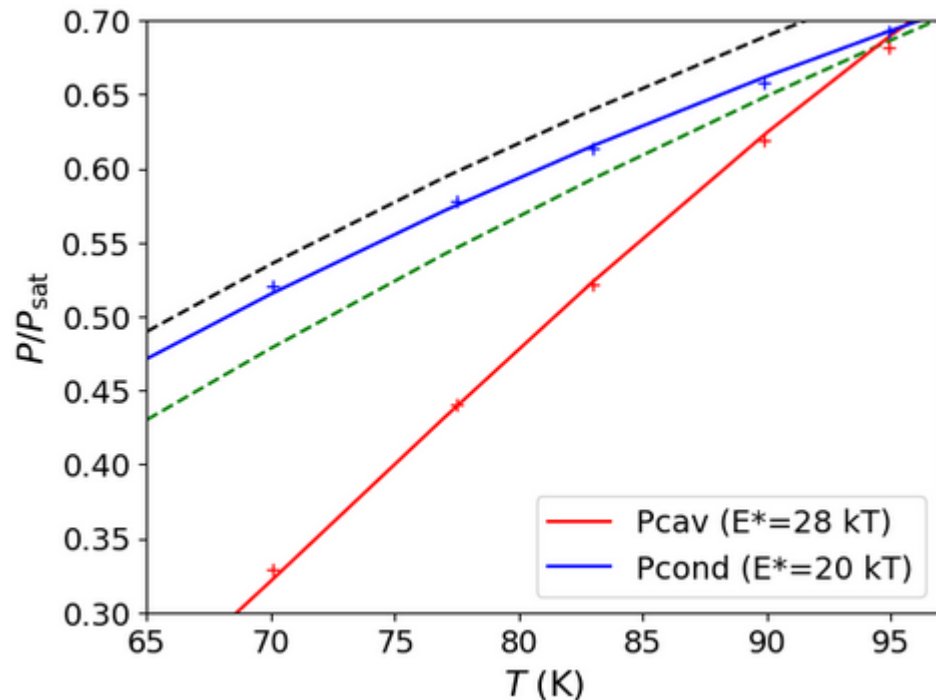
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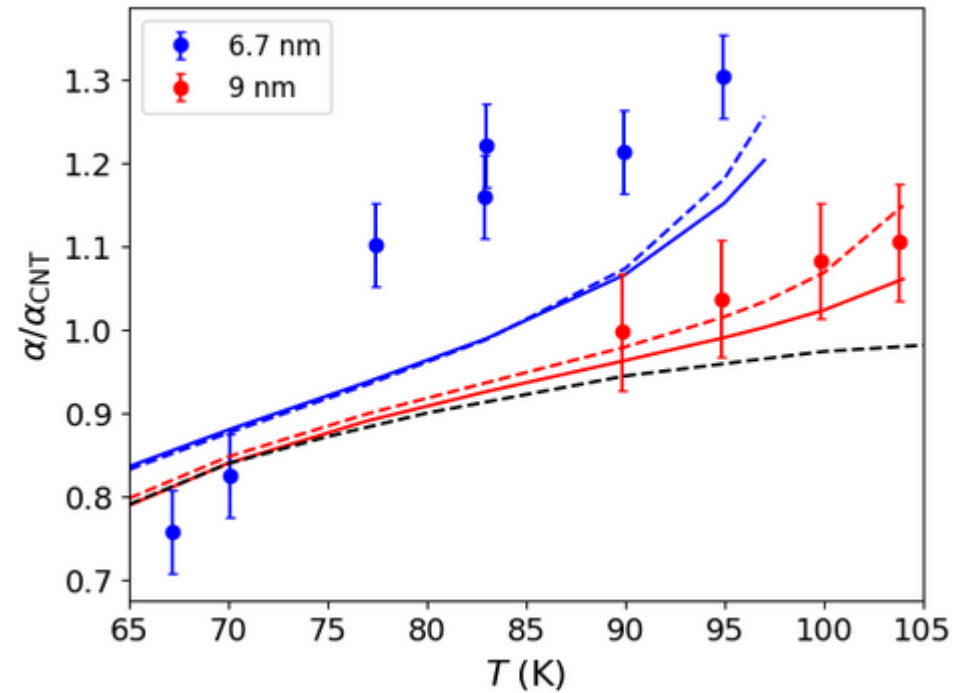
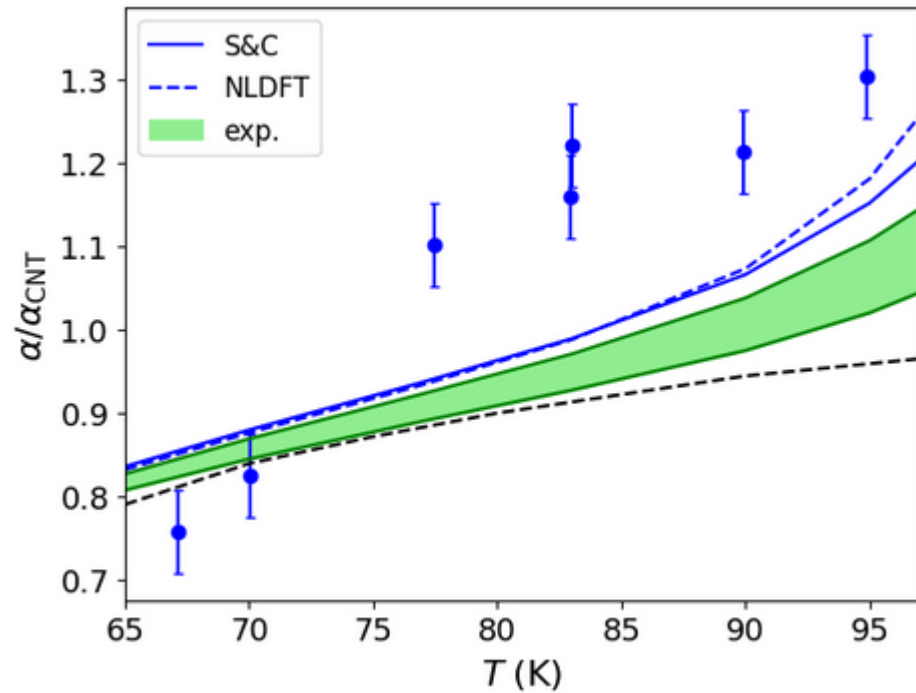
$$U(z) = -\varepsilon e^{-\frac{z}{\lambda}}$$

Assuming $R_p = 6.7$ nm

$\varepsilon = 52k_B$ and $\lambda = 0.375$ nm



Thermodynamic approach - results



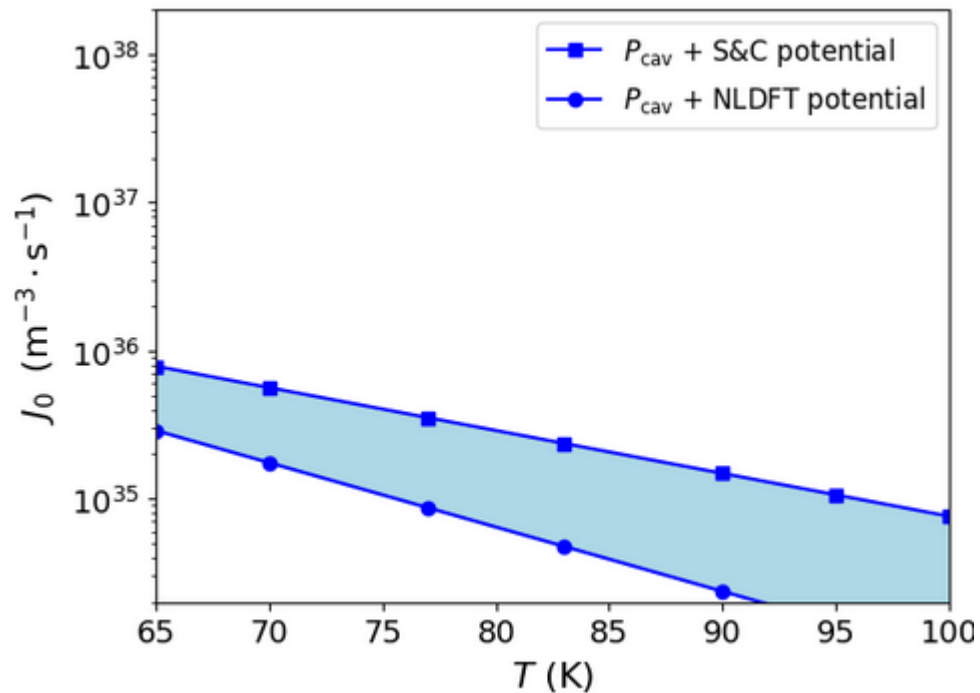
The NLDFT potential does the best job, but predicted α still smaller than measured for small pores
→ underestimates confinement

Thermodynamic approach – nucleation rate

Until now, no assumption on the nucleation rate $J = J_0 \times \exp\left(-\frac{E_B}{kT}\right)$

at nucleation threshold : $J = \ln(2) / (\text{pore volume} \times \text{waiting time})$

Measurements + model(s) $\rightarrow (V_p, \tau, E_B) \rightarrow J_0$

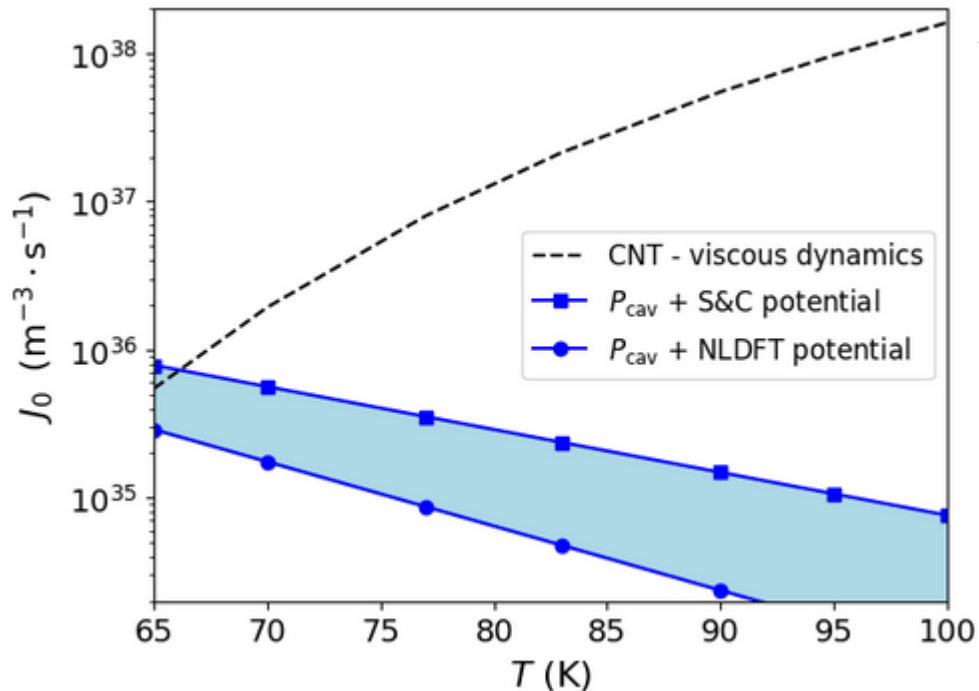


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CNT $J_0 = n_L \frac{\gamma}{\eta} \sqrt{\frac{\gamma}{k_B T}} (1 - P_L^*/P_V^*)^{-1}$ [Bl. & Katz 1975]

- Hyp.
- nucleation site density = liquid number density
 - escape rate controlled by viscous dynamics of the critical bubble.

CNT overestimates $10^3 \times J_0$ at high T
significant? (equiv. to $\Delta E_B \sim 7-8 kT$)

- if yes**
- Effect of confinement on bubble dynamics
 - Number of nucleation sites ?

Conclusion

- New capacitive continuous method for measuring isotherms
- Allows to evidence confinement impact on cavitation
- Reasonable agreement with simple thermodynamic approach
→ indication that the kinetic prefactor J_0 is impacted by confinement

What's next ?

- Go for molecular dynamics?
- Effect of the distributions of pore diameter (parameter β)

THANKS FOR YOUR ATTENTION !