LPENS
LABORATOIRE DE PHYSIQUE
DE L'ÉCOLE NORMALE SUPÉRIEURE

# Cavitation in nanopores


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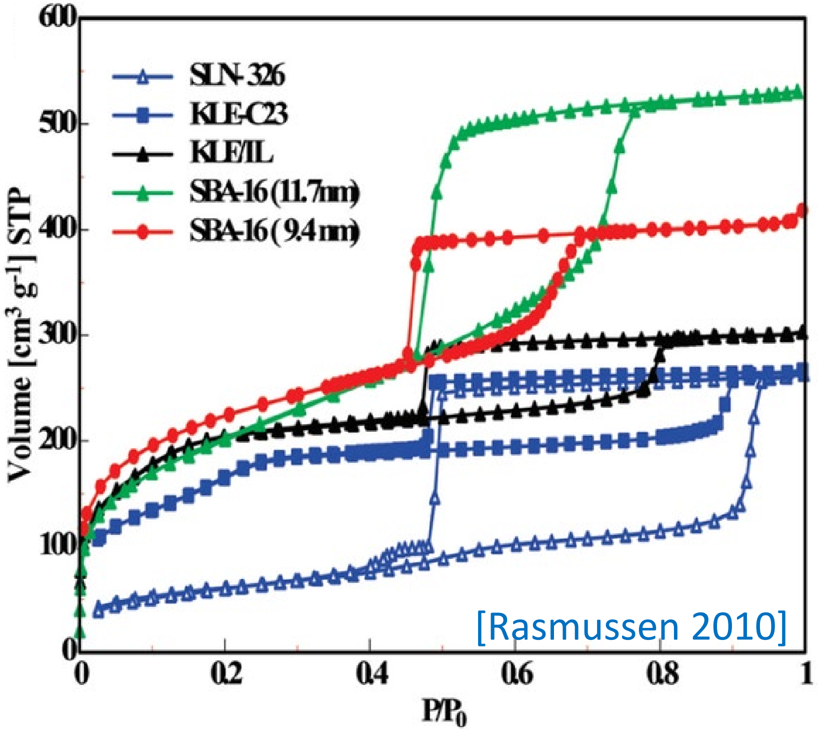
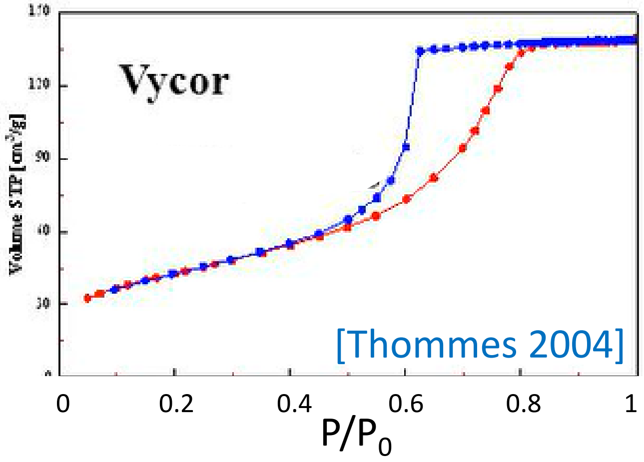
**ANR project NanoCav**

# Evaporation in ordered mesoporous silica



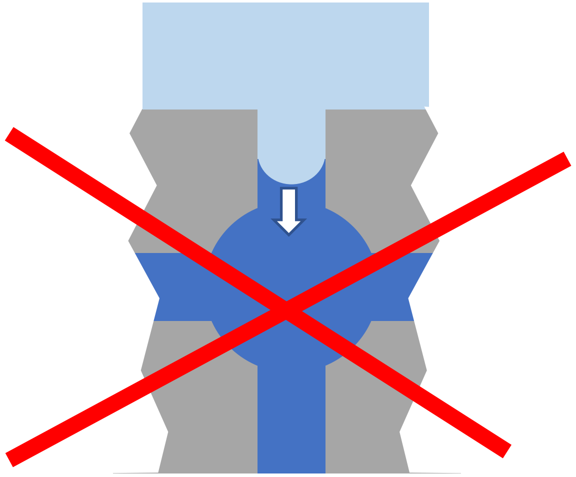



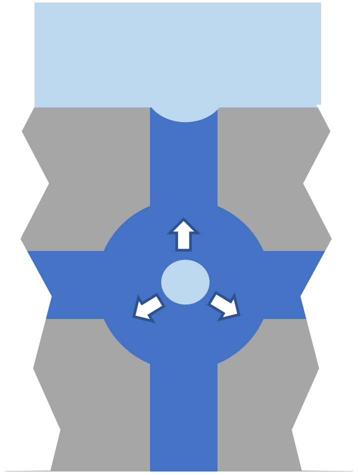

Sharp drop of $V_{ads}$

+

Evaporation pressure P* ~ 0.45 Psat (N2 @ 77 K)

} *signature of cavitation*





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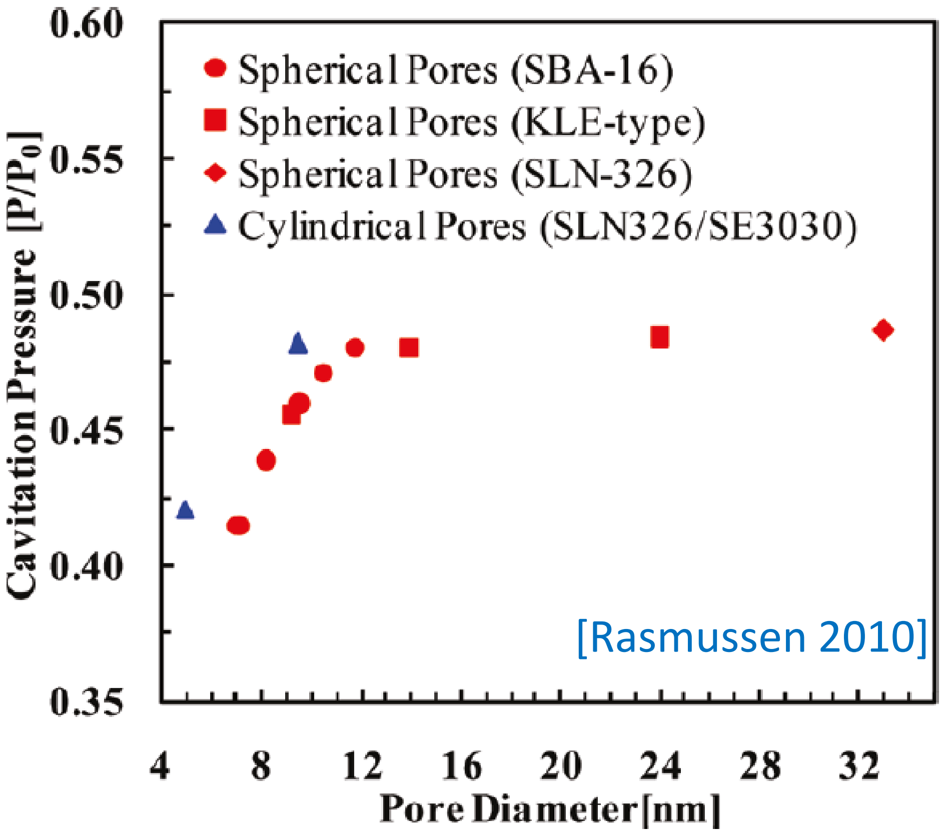



Evaporation pressure $P^*/P_0$ lies in the range 0.42 – 0.46

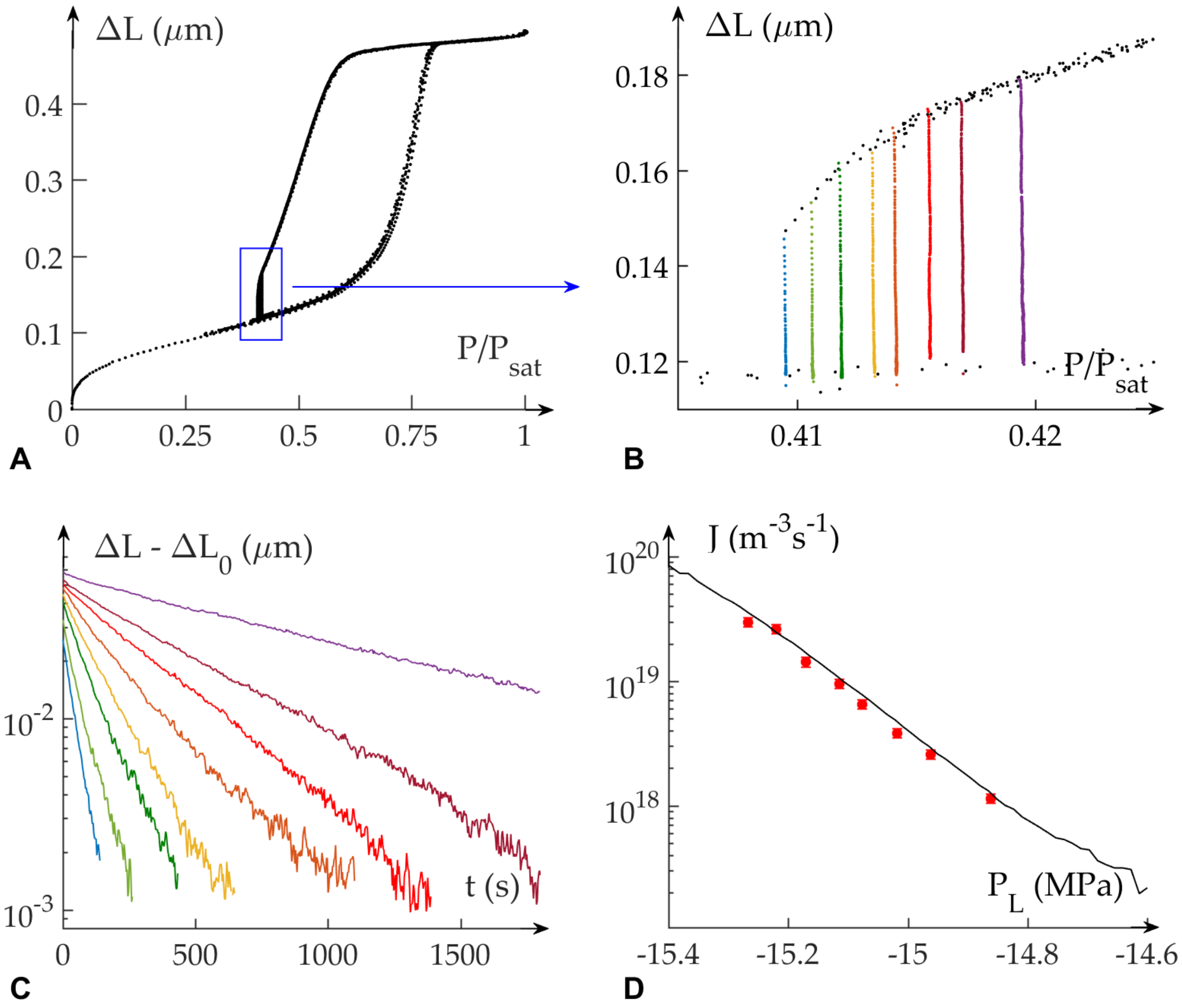
depends on pore size (cavitation more difficult in confined liquid)

→ **How to identify cavitation unambiguously ?**

→ **Impact of confinement ?**
***P**** **dependance on pore radius, temperature…**

# *Continuous* sorption isotherms

[optical isotherms - porous alumina - Bossert 2023]

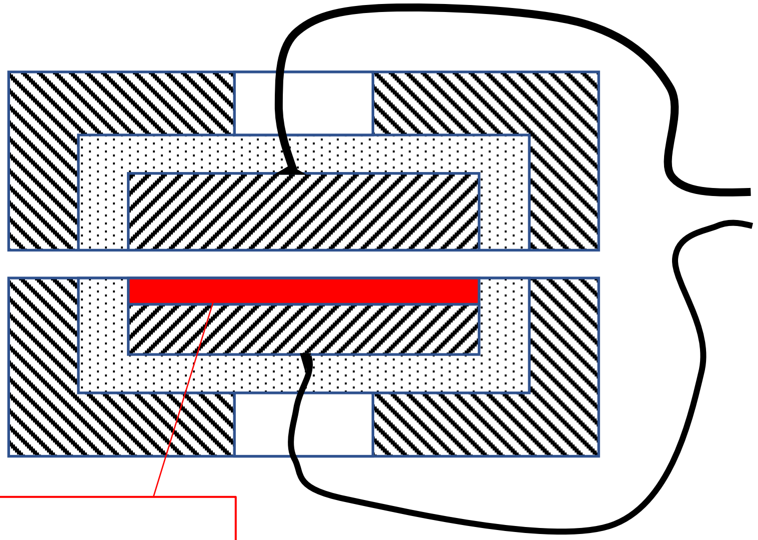



Cavitation is a stochastic process, characterized by a nucleation rate *J*

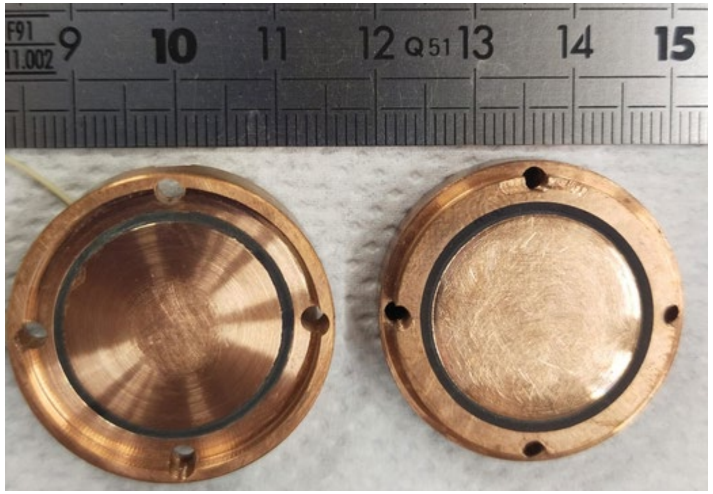
**→ cavitation pressure *P** is an ill-defined quantity** ☹

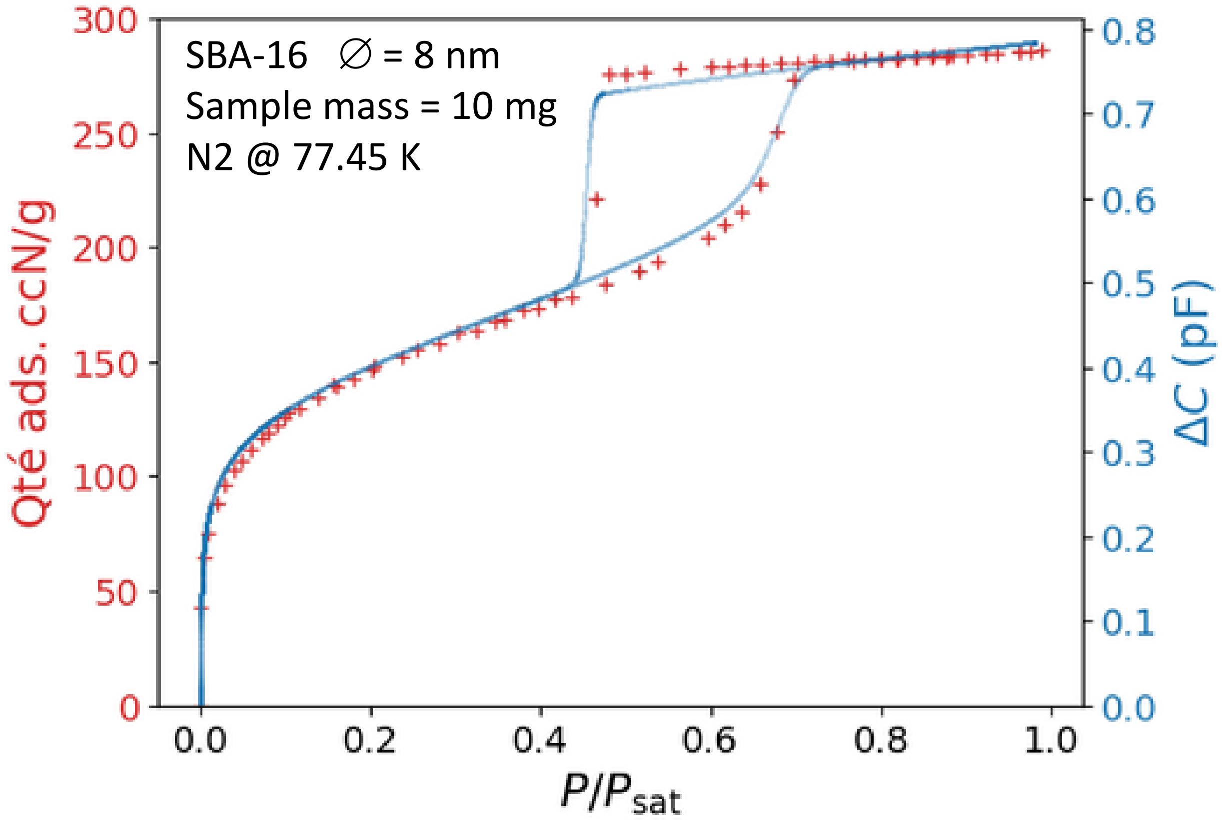
**→ monitoring the adsorbed mass (hence the fraction of pores which have not yet cavitated) brings a lot of information** ☺

## Capacitive measurements



∅ = 20 mm
Espacement = 0.1 mm

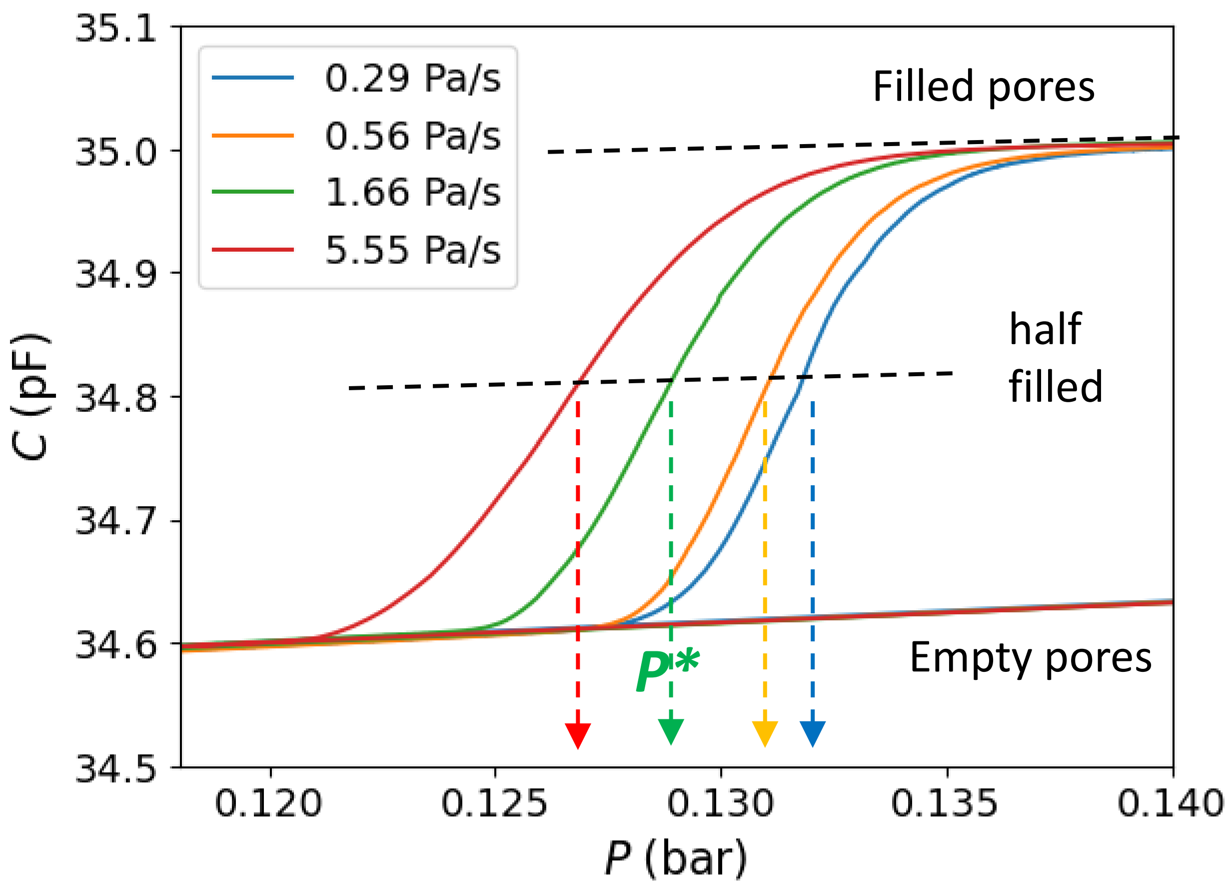



High accuracy capacitance bridge – resolution $10^{-5}$ pF

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

# Continuous measurements at controlled pressure rate




SBA-16 ∅ = 7.6 nm
N2 @ 70.07 K

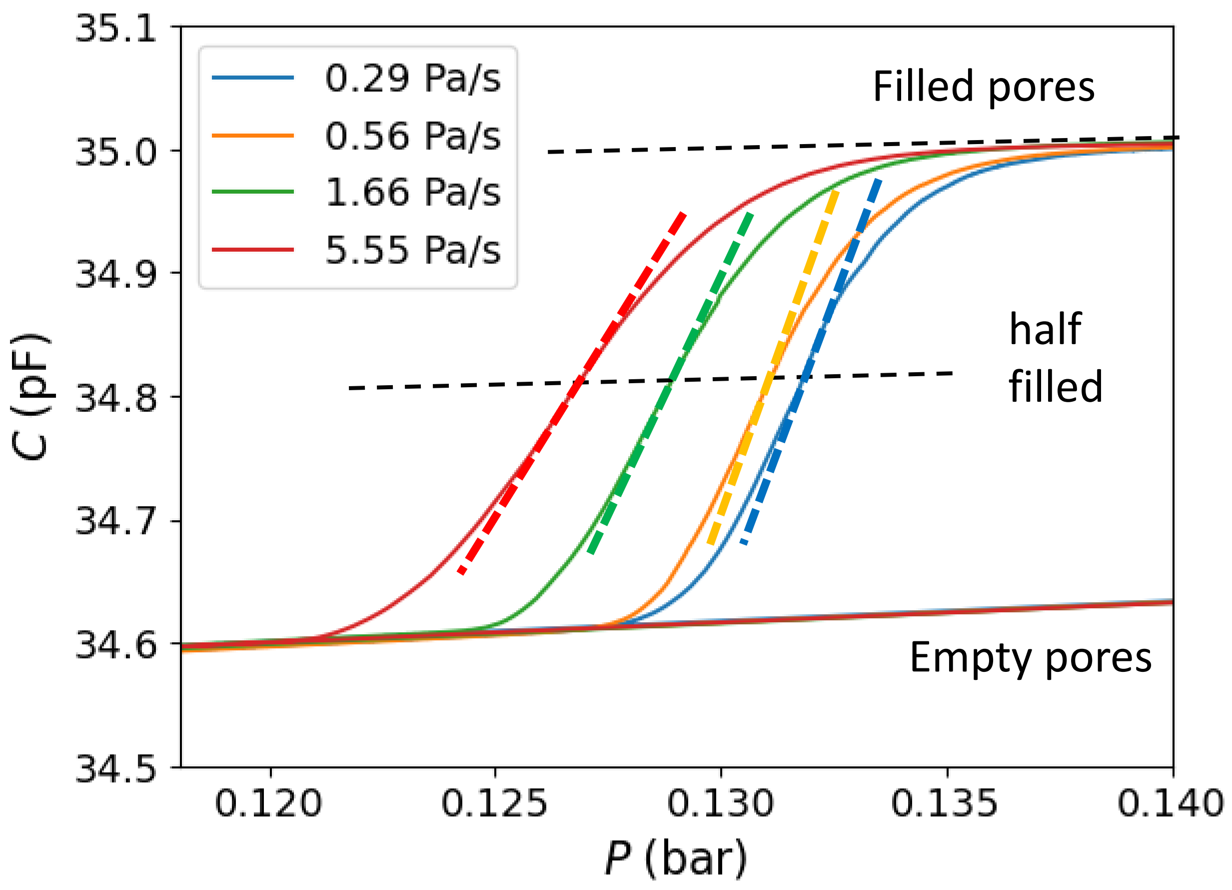
assuming $\Delta C$ is proportional to the amount of adorbed fluid,
normalization gives the fraction $\Psi$ of filled pores as a function of $P$

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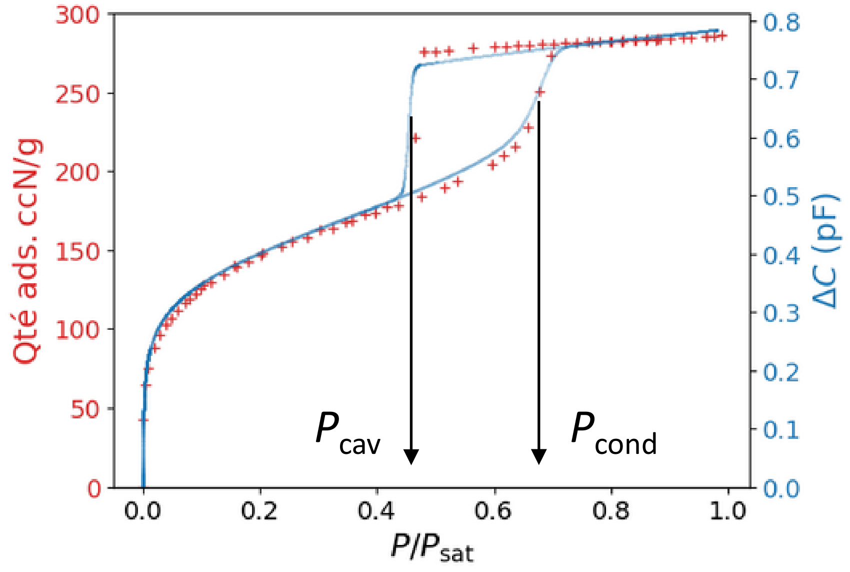
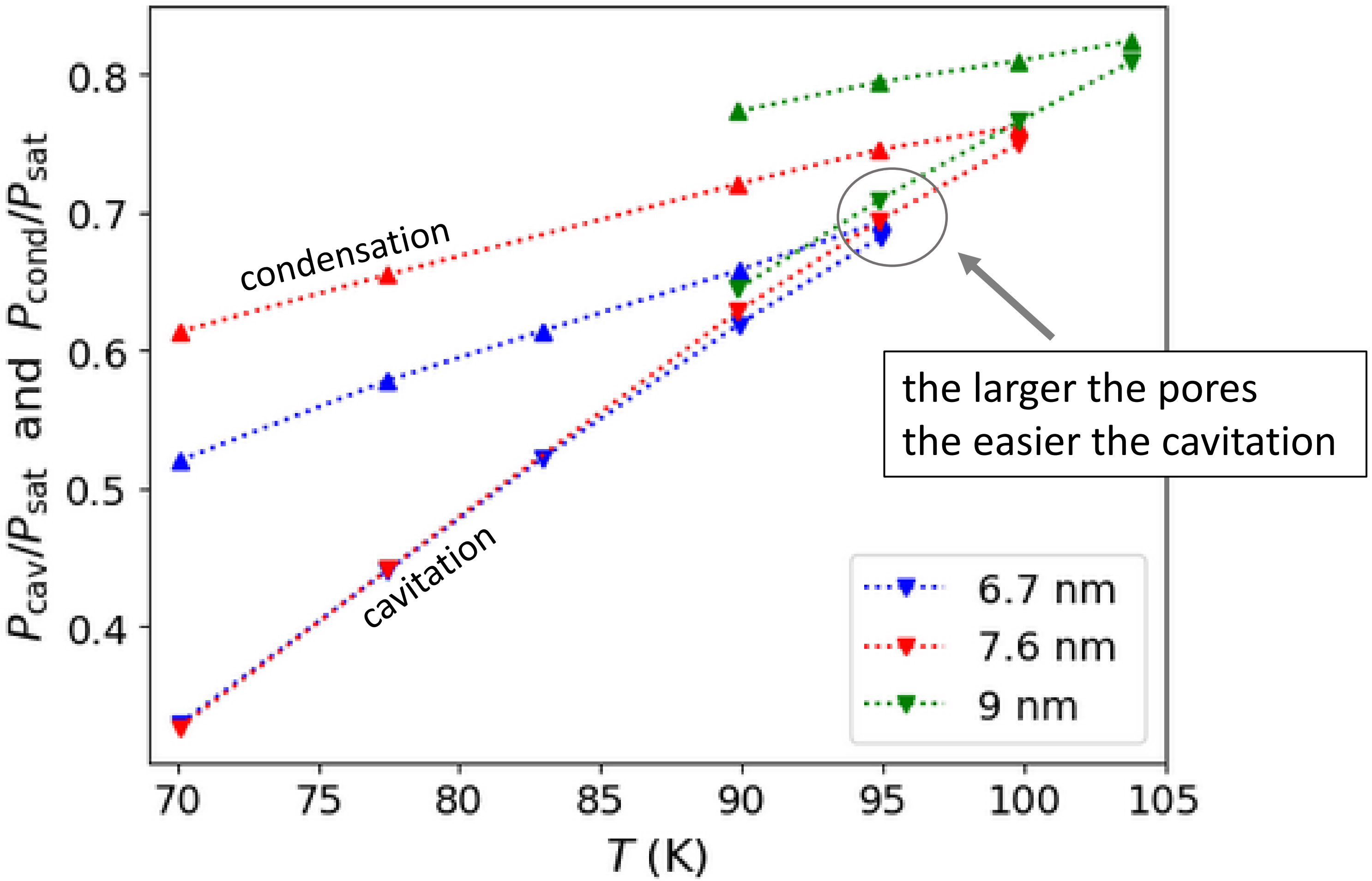
$$\rightarrow \beta = \frac{\left.\frac{d\Psi}{dP}\right|_{P^*}}{\alpha}$$ depends of the pore size distribution (= 1 for homogeneous nucleation or heterogeneous with monodiperses pores)

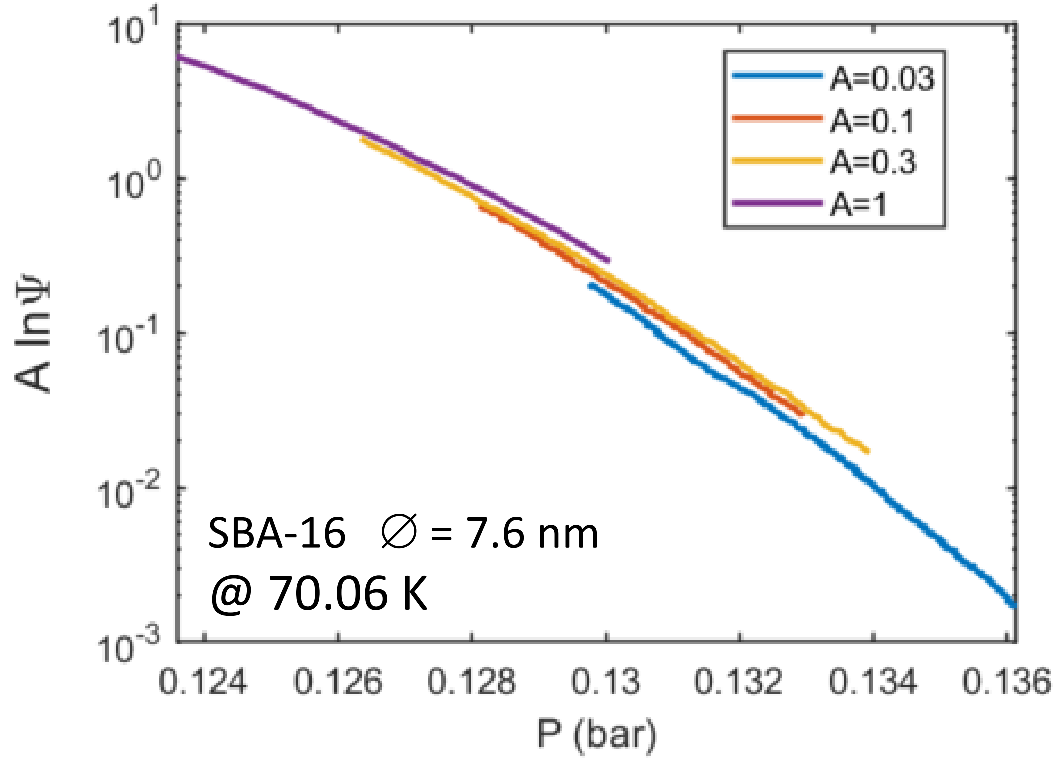
# Experimental results – phase diagram

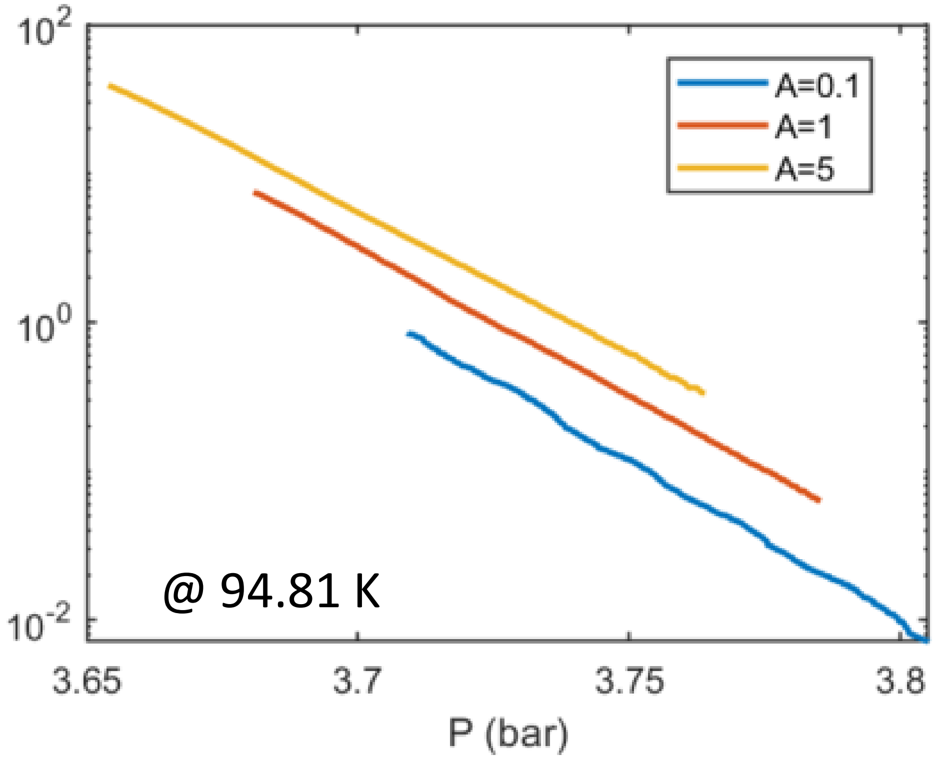
3 SBA-16 samples
with dif. pore diameter



# Results – shape of $\psi_A(P)$




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

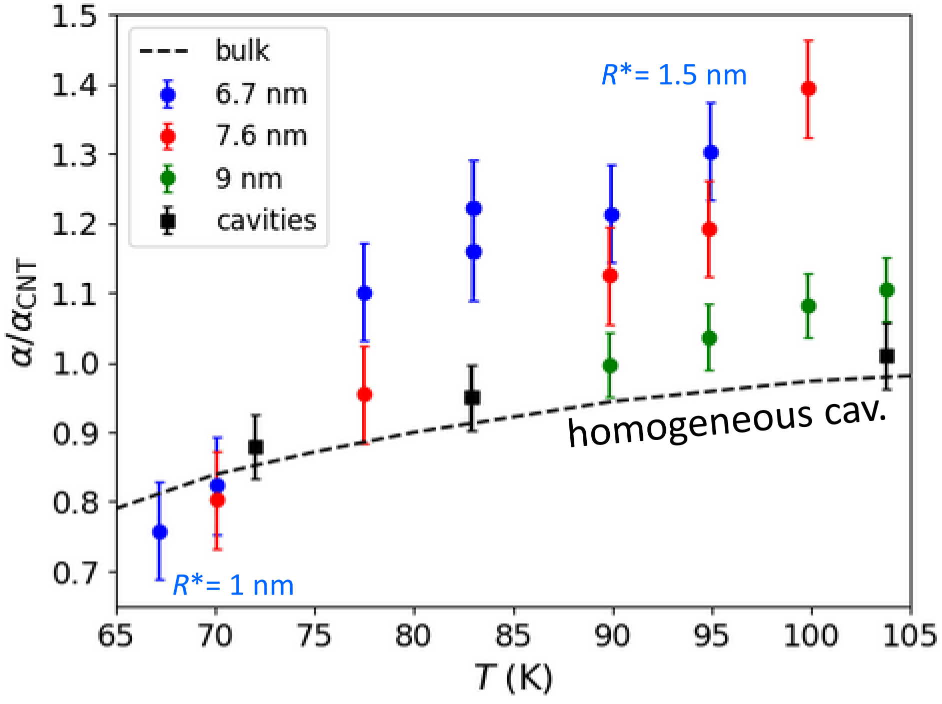
Critical nucleation radius $R^* = \dfrac{2\gamma}{\Delta P}$ 1.0 nm @ 70 K

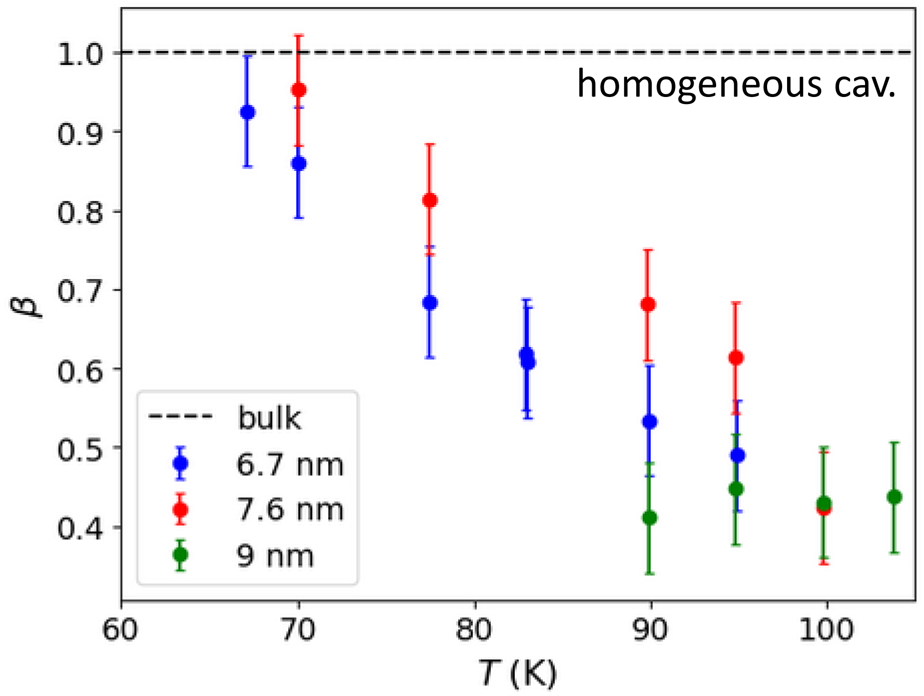
1.8 nm @ 95 K

pore radius $R_p$ = 3.8 nm

# Experimental results – coefficients α and β

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

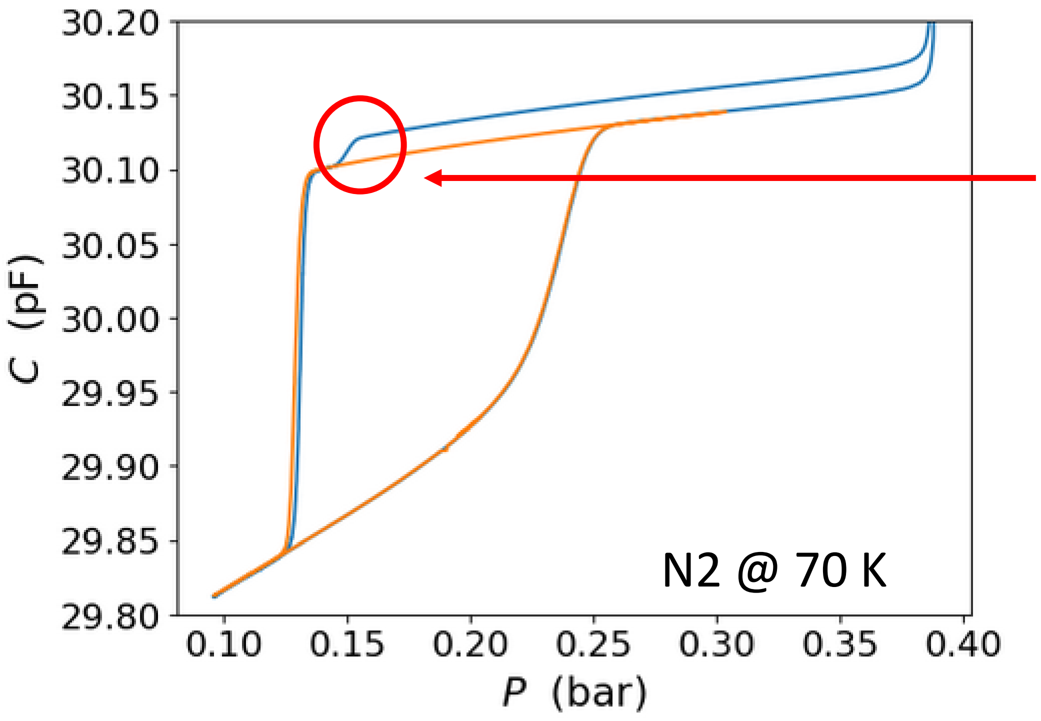



- The smaller the pore radius $R_P$
- the larger T (hence critical radius $R^*$)

} the larger the departure from homogeneous cavitation

# Large cavities (inter-grains ?) cavitation

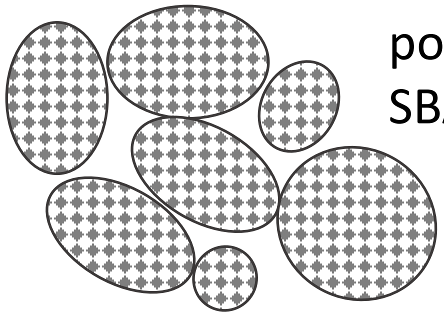



additionnal evaporation step at $P_{ac}^{*}$

observed only if pressure is ramped up to $P_{sat}$

$T$-dependence of $P_{ac}^{*} \rightarrow$ cavitation event

position of $P_{ac}^{*}$ $\rightarrow$ cavitation in large cavities



possibly voids between SBA grains ?

Cavities (≡ bulk liquid) provide a reference for cavitation features

# Thermodynamic approach – the energy barrier $E_B$

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

$$\Delta\Omega = \frac{4\pi}{3} R^3 \Delta\rho\, k_B T \ln\left(\frac{f(P)}{f_{\text{sat}}}\right) - \Delta\rho \int_0^R U(r) d^3r + 4\pi R^2 \sigma$$

gain in chemical potential: *known*

correction due to substrate-fluid interaction potential

cost of the interface

***Surface tension*** $\alpha$ 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 dispertion forces ( Saam & Cole, Neimark and co-workers …)
- empirical exponential dependance (Celtini, Pellenq, Morishige…)

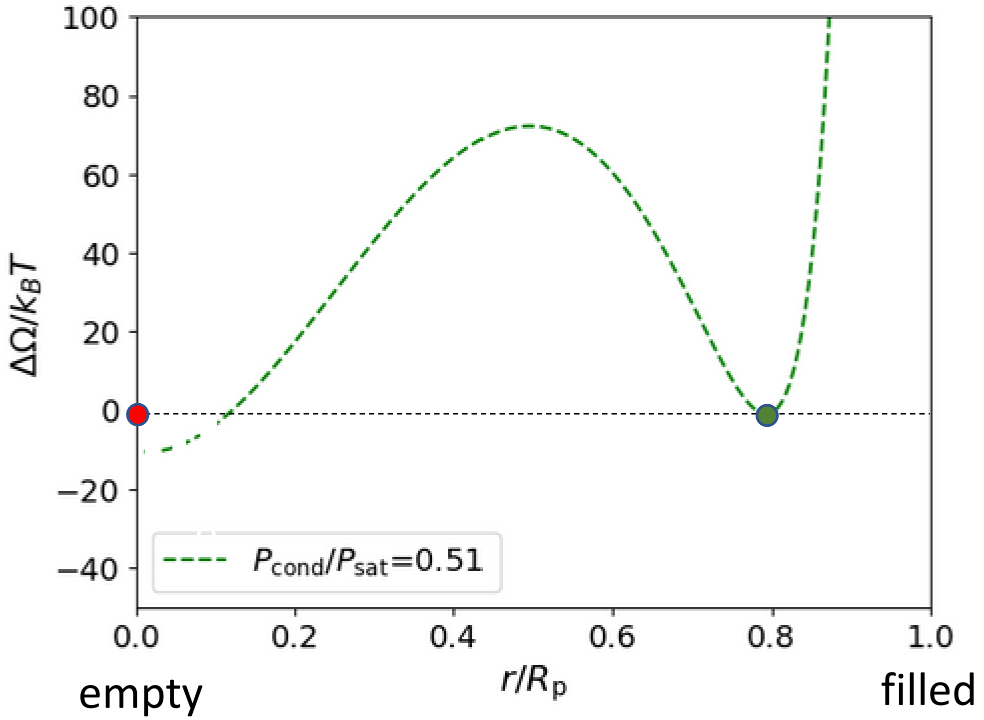
1 or 2 adjustable parameters / adjusted on the critical point for confined fluid (point where hysteresis disappears)

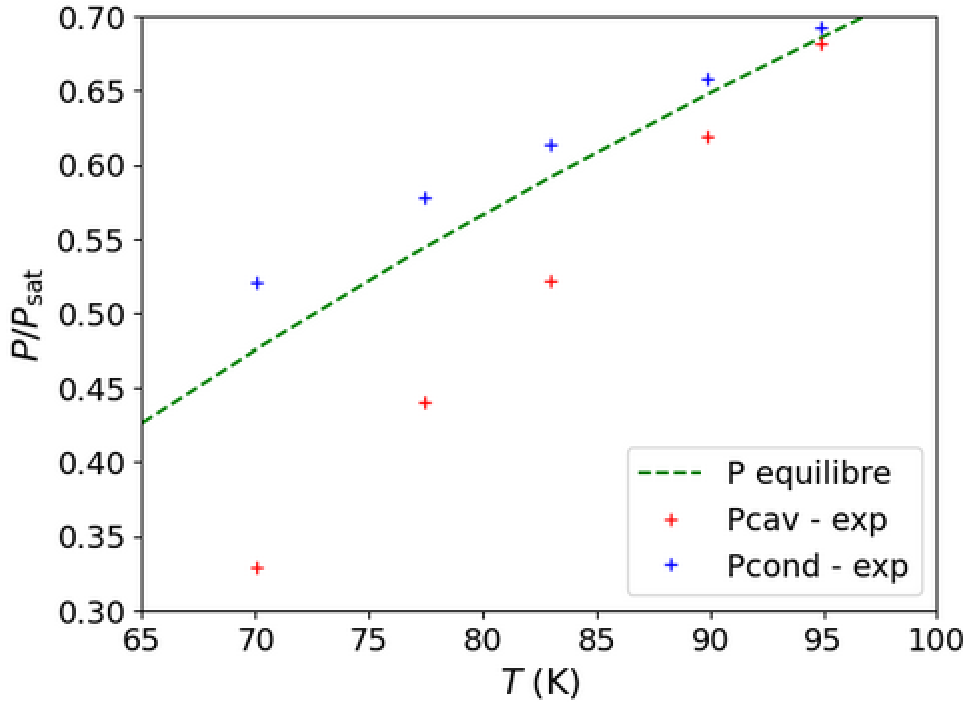
# Thermodynamic approach – substrate-fluid potential

***Substrate-fluid potential*** - derivation from dispertion forces ( Saam & Cole, Neimark and co-workers …)

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

$\rightarrow$ 1 adjustable parameter: pore radius 6.7 nm (NLDFT-type potential: 7.6 nm)



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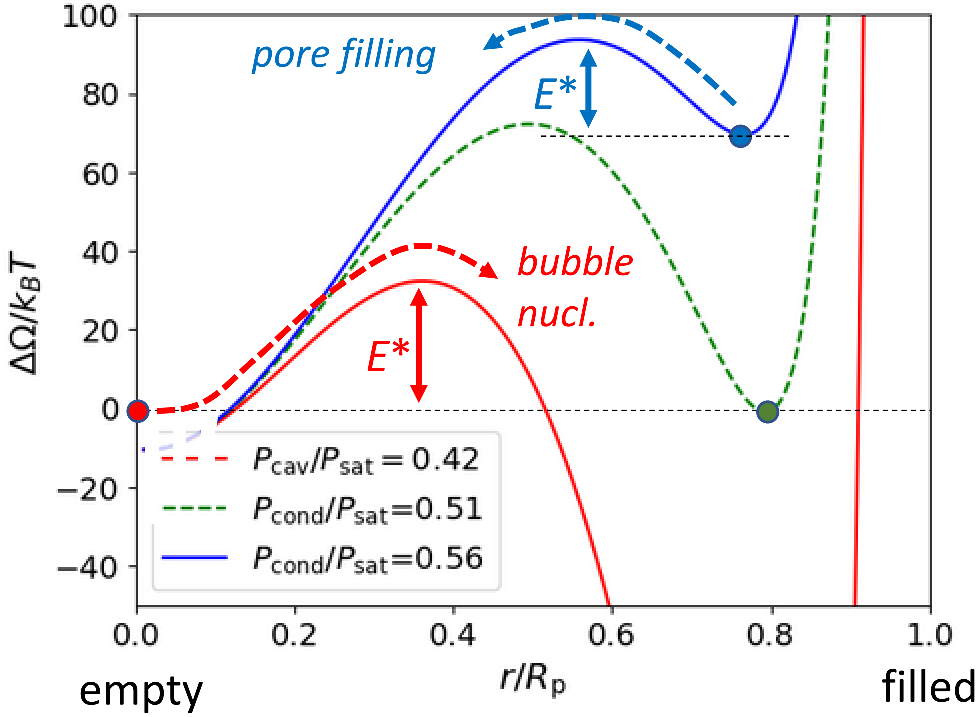
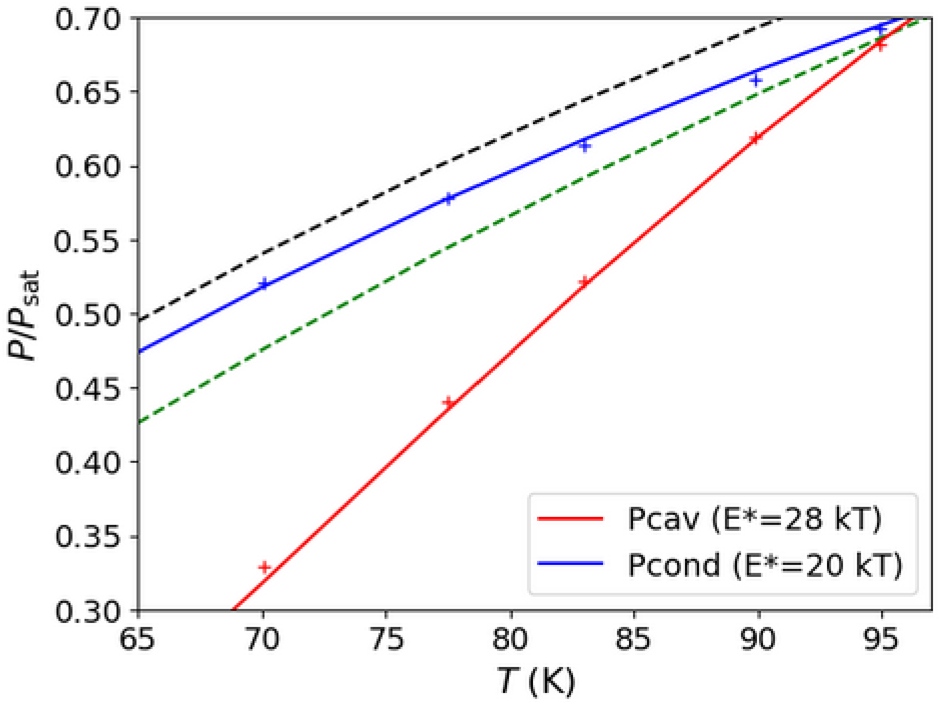



Phase diagram (similar with NLDFT potentials)



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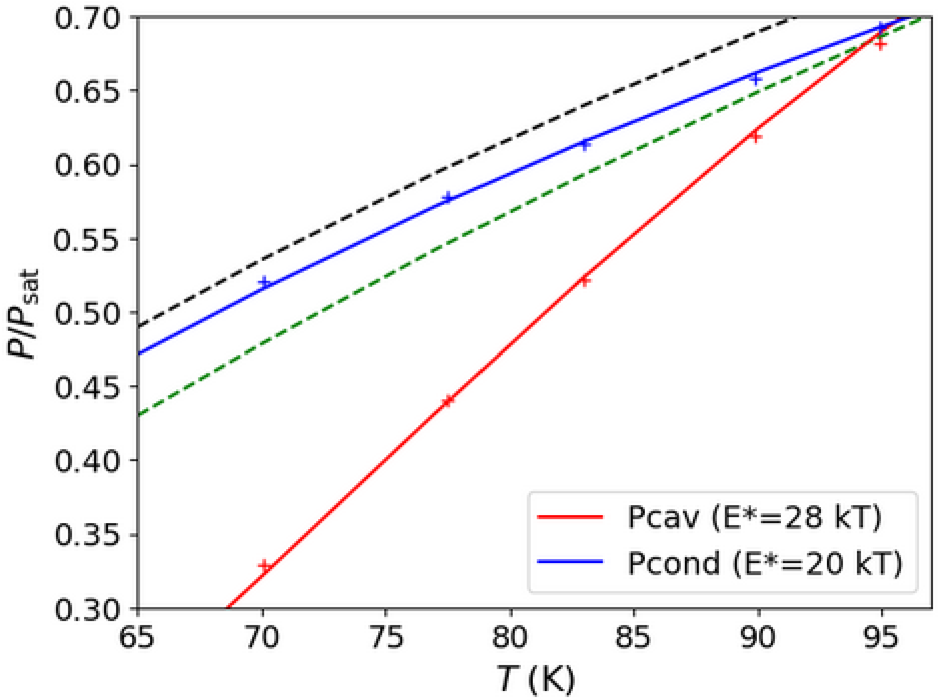
***Substrate-fluid potential*** - derivation from dispertion forces ( Saam & Cole, Neimark and co-workers …)
- empirical exponential dependance (Celtini, Pellenq, Morishige…)

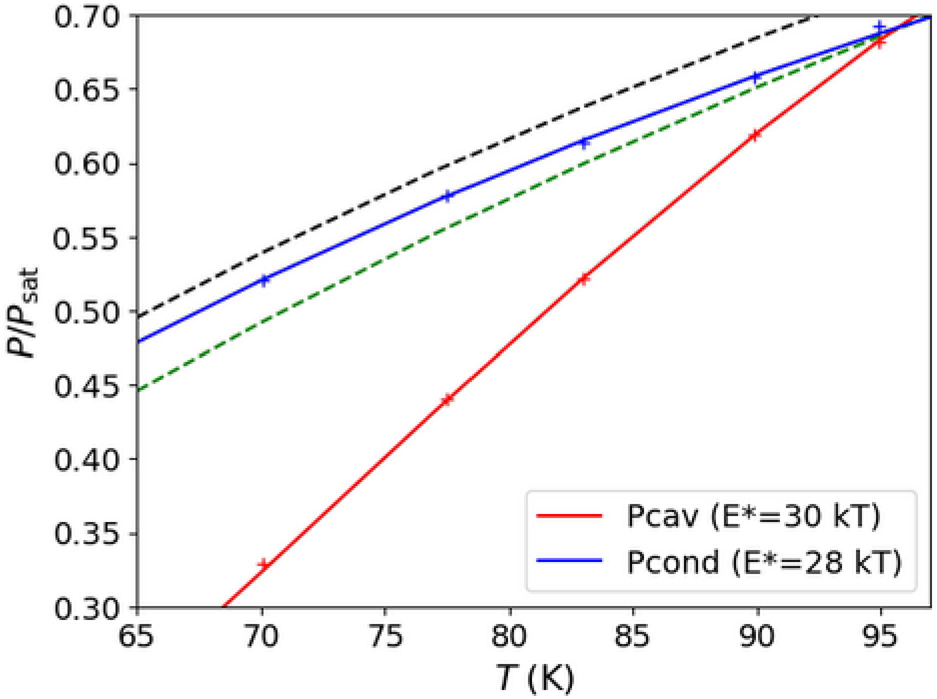
$$U(z) = -\varepsilon\, e^{-\frac{z}{\lambda}}$$

Assuming $R_p$ = 6.7 nm

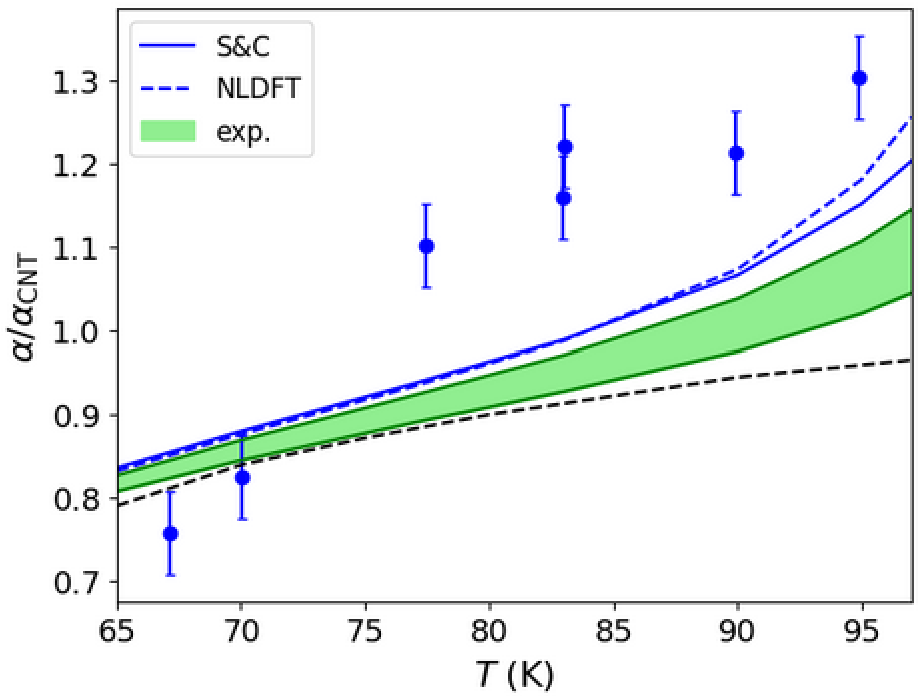
$\varepsilon = 52 k_B$ and $\lambda = 0.375$ nm

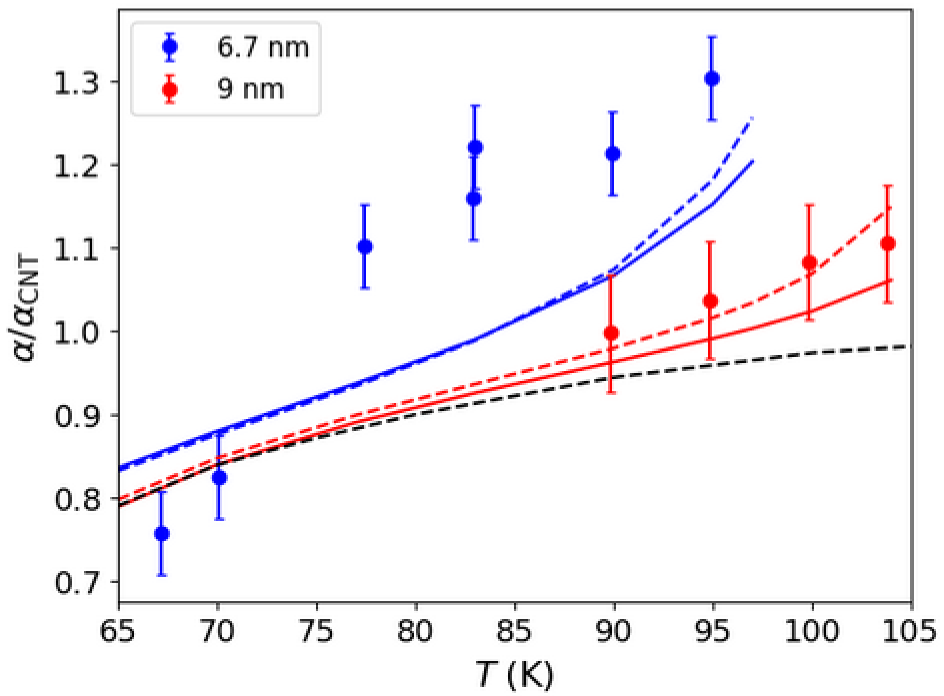



$\varepsilon = 18 k_B$ and $\lambda = 0.6$ nm



# Thermodynamic approach - results



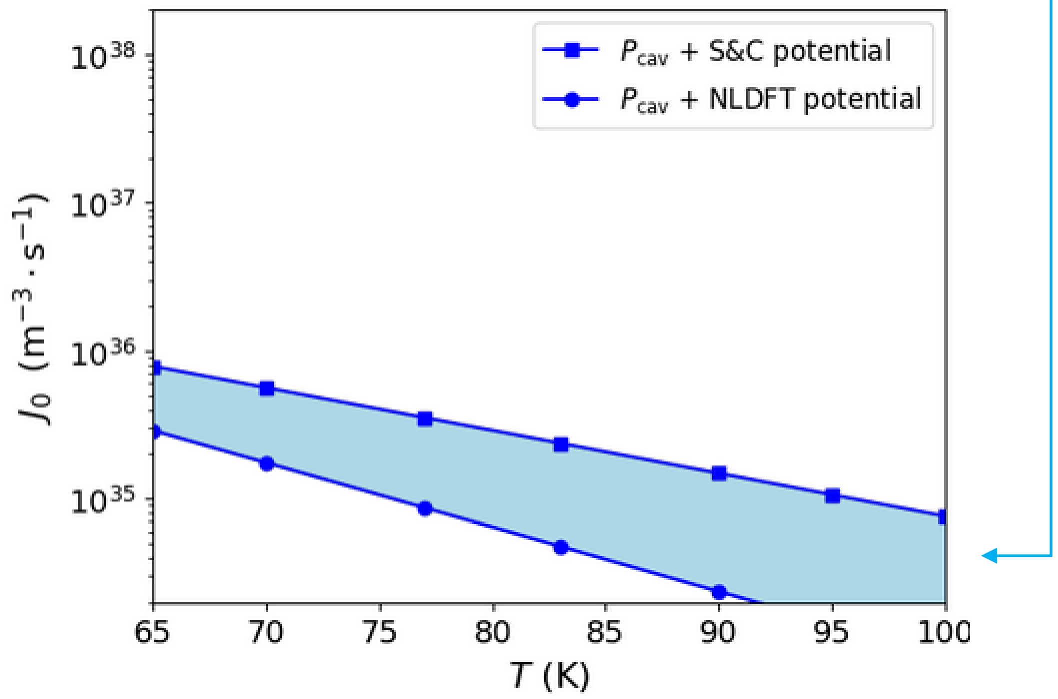

The NLDFT potential does the best job, but predicted $\alpha$ still smaller than measured for small pores
$\rightarrow$ underestimates confinement

# Thermodynamic approach – nucleation rate

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

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

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



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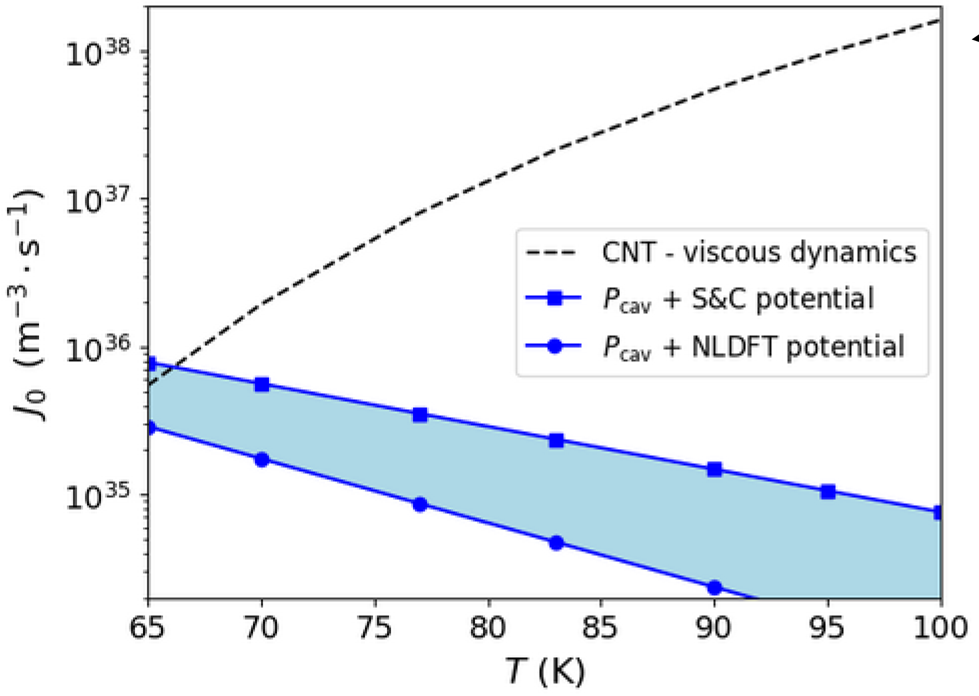
**Measurements** + **model(s)** $\rightarrow$ ( $V_P$ , $\tau$ , $E_B$ ) $\rightarrow J_0$




**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 $10^3$ x $J_0$ at high T
significant ? ($\Delta E_B \sim$ 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
- Reasonnable agreement with simple thermodynamic approach

  $\rightarrow$ 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 $\beta$)

THANKS FOR YOUR ATTENTION !

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