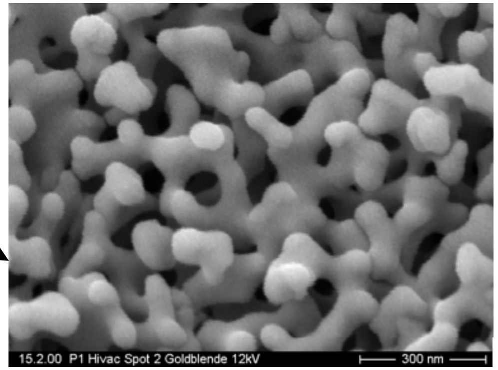
PALS on Controlled Pore Glass – Porosimetry and Phase Transition of Gas in Confinement

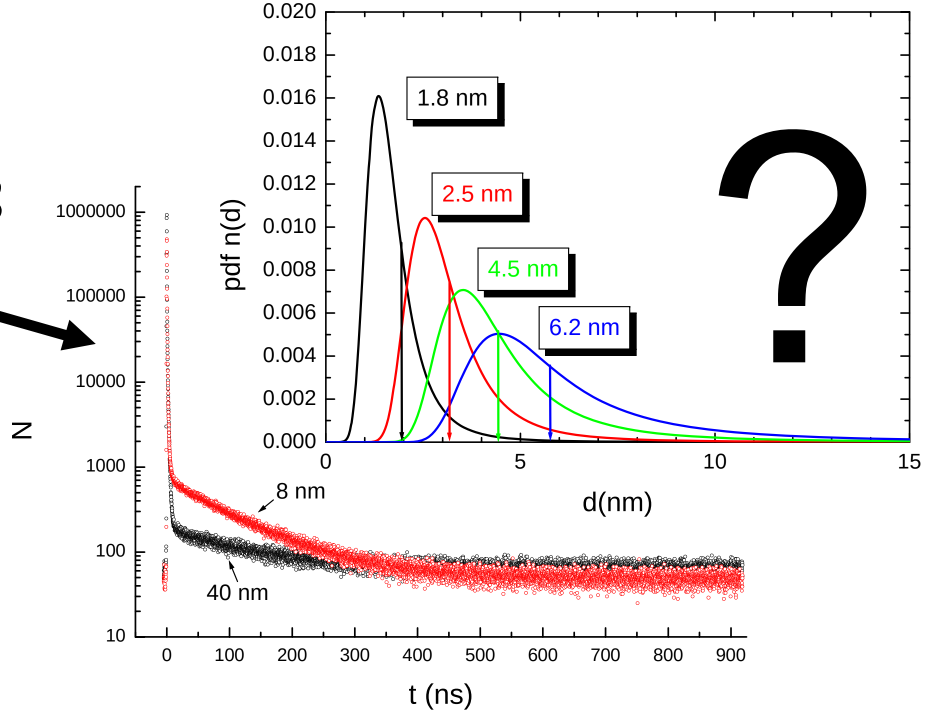
S. Thraenert[1], D. Enke[2],
R. Krause-Rehberg[1]

Martin-Luther-Universität
Halle-Wittenberg
Naturwissenschaftliche Fakultät II
[1]Institut für Physik
[2]Institut für Chemie

Outline

- **Porous glass - CPG**
  - synthesis
  - properties
- **From τ_4 to d**
  - o-Ps and pick off
  - ETE (diff. geometries)
- **Experimental results**
  - relation to ETE
  - pore size distribution
  - phase trans. of gas
- **Summary**

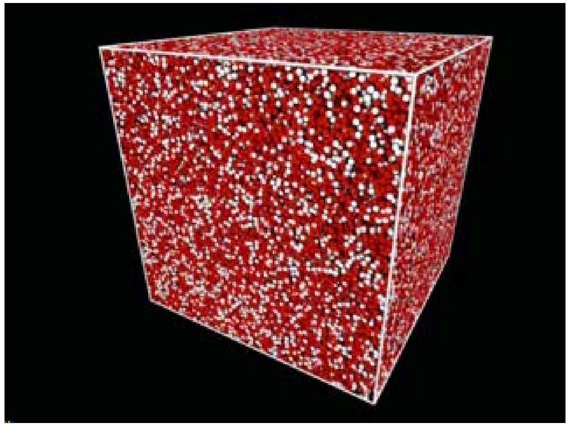




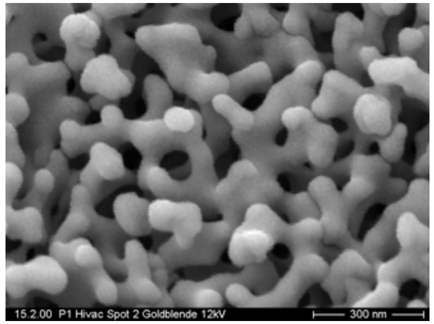
Controlled pore glass - CPG

VYCOR-Process

alkali borosilicate glass → **T** (*530 - 710°C*) →



→ **Extraction** (*HCl/NaOH*) →

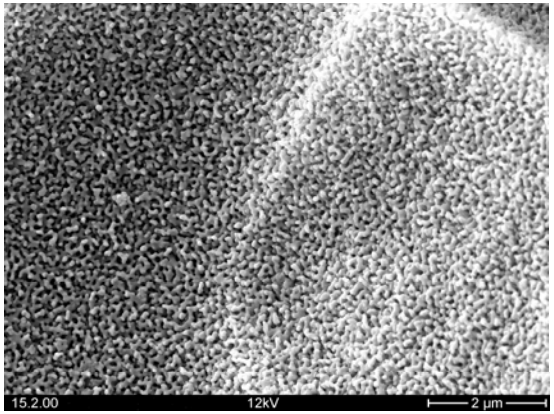


d_p 1 to 110 nm

- spinodal phase separation
- decomposition is initiated by heat treatment
- alkali rich borate phase <-> pure silica
- alkali phase soluble in acid -> silica network
- pore size depends on basic material
- porosity of 50 %

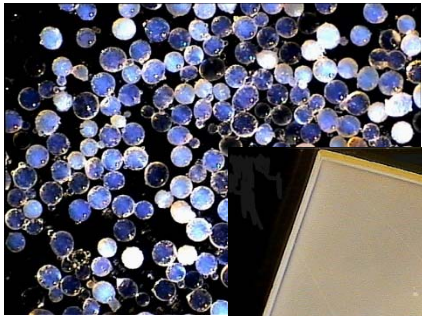
F. Janowski, D. Enke in F. Schüth, K.S.W. Sing, J. Weitkamp (Eds.), *Handbook of Porous Solids*, WILEY-VCH, Weinheim, **2002**, 1432-1542.

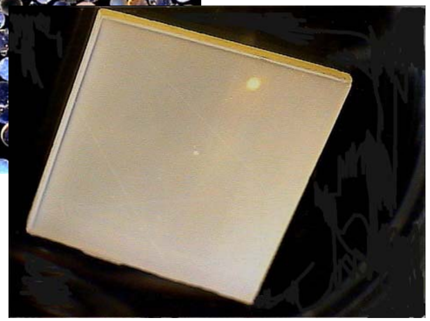
Controlled pore glass - CPG

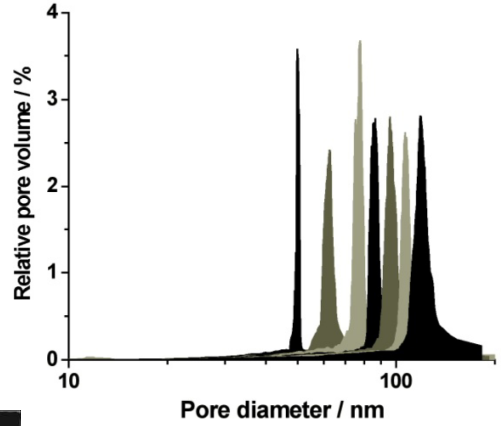


- homogenous microstructure
- uniform pore size

- different geometries possible







- controlled pore size
- we can choose d (!)

D. Enke, F. Janowski, W. Schwieger, *Microporous and Mesoporous Materials* **2003**, *60*, 19-30.

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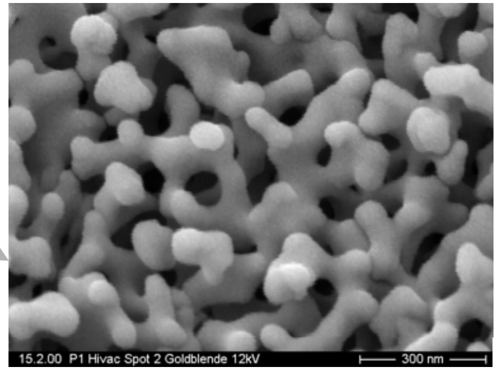
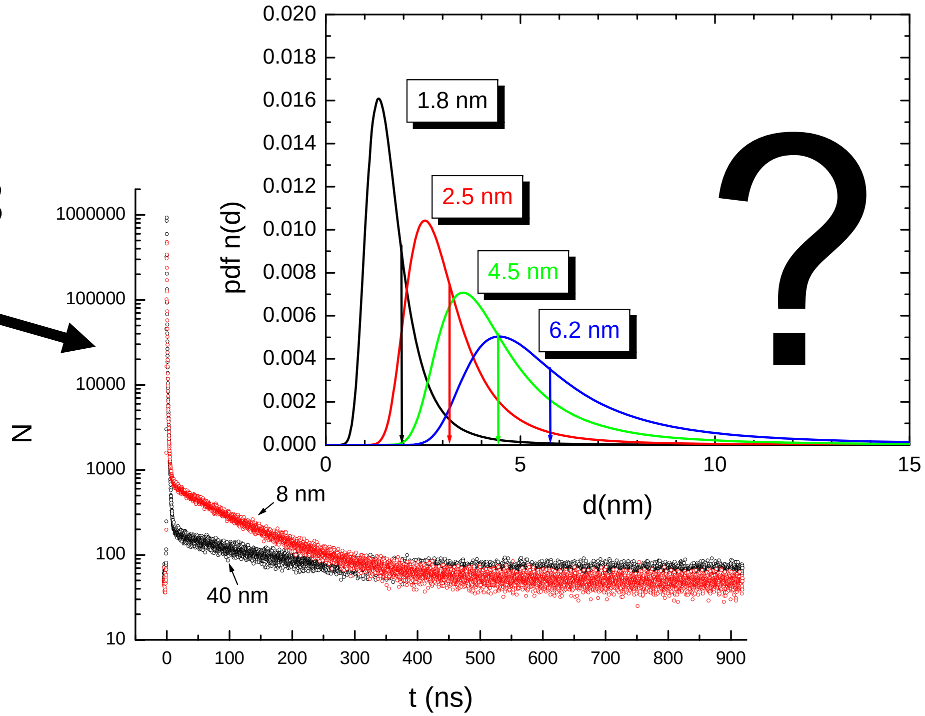
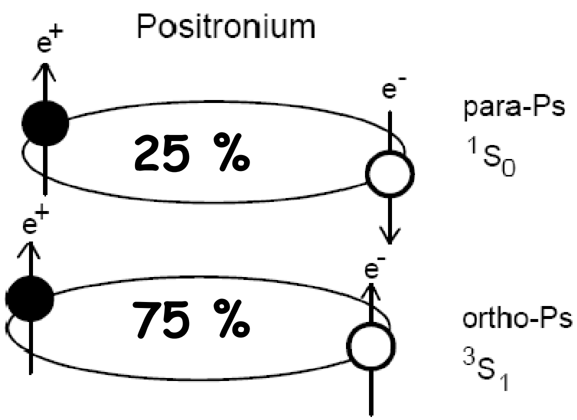




Principles of PALS: pick-off annihilation

positrons from ^{22}Na:

- thermalize, diffuse, being trapped and annihilate
- *OR*: **positrons form Ps**

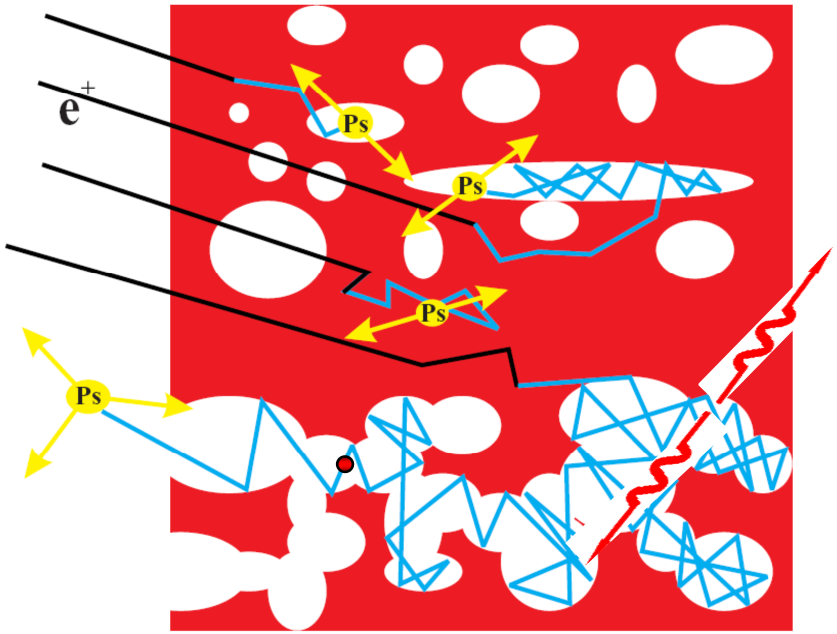


positronium:

- **p-Ps** -> short self annihilation lifetime of 0.125 ns
- **o-Ps** -> long self annihilation lifetime of 142 ns (3γ)
  -> pick off annihilation (2γ)

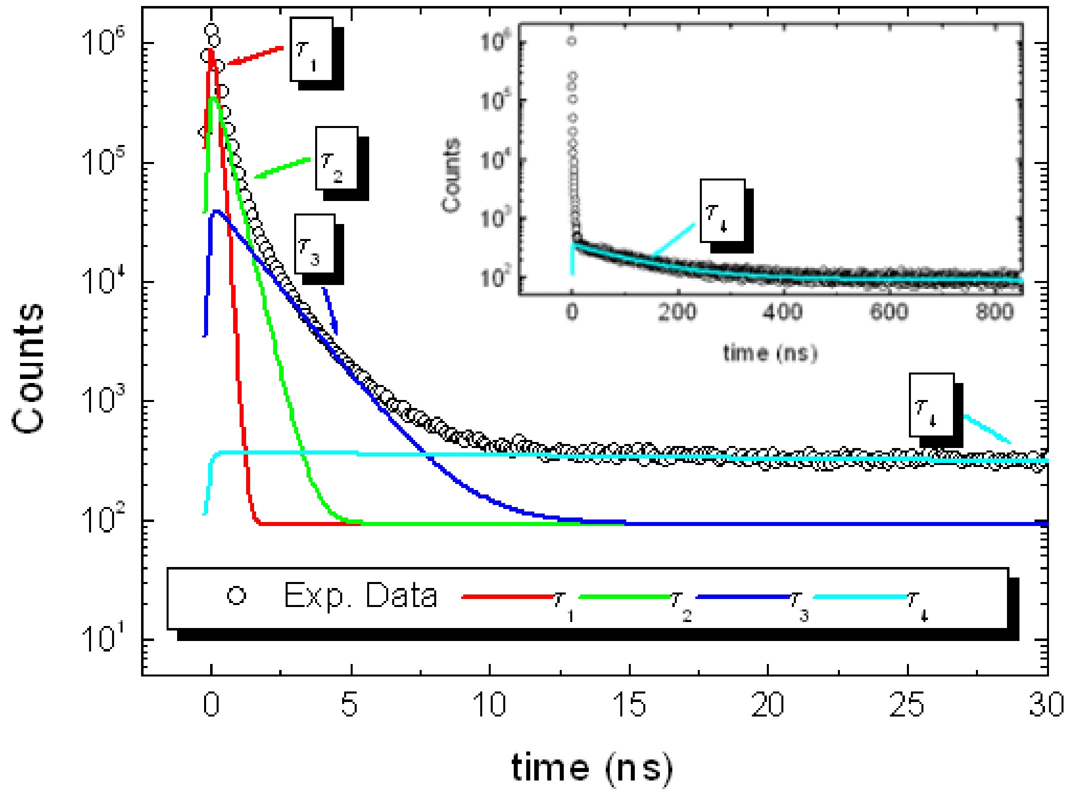
pick-off annihilation:

- o-Ps captures e^- with anti-parallel spin
- happens during collisions at walls of pore
- lifetime (τ) decreases rapidly
- **τ is function of pore size: 1.5 - 142 ns**
- **also for <u>closed</u> pore systems**



Principles of PALS: typical spectrum

typical lifetime spectrum for CPG (here d = 20 nm):

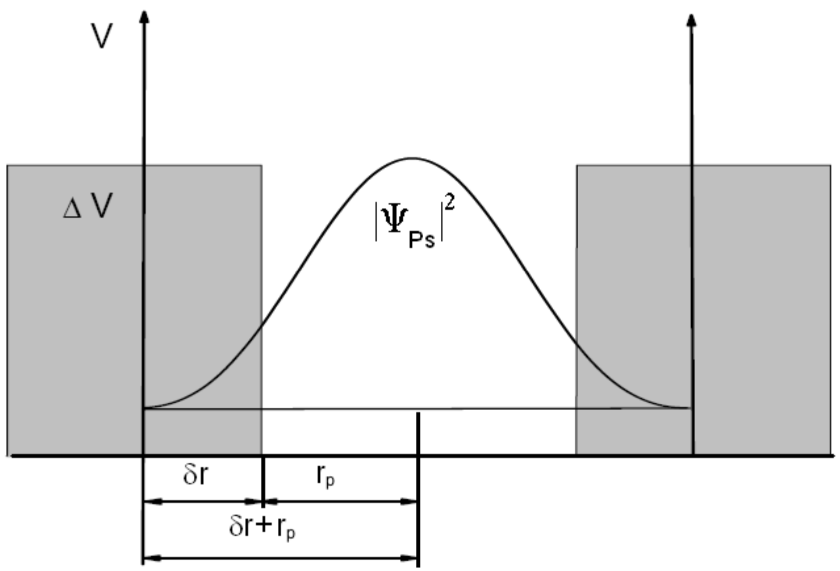


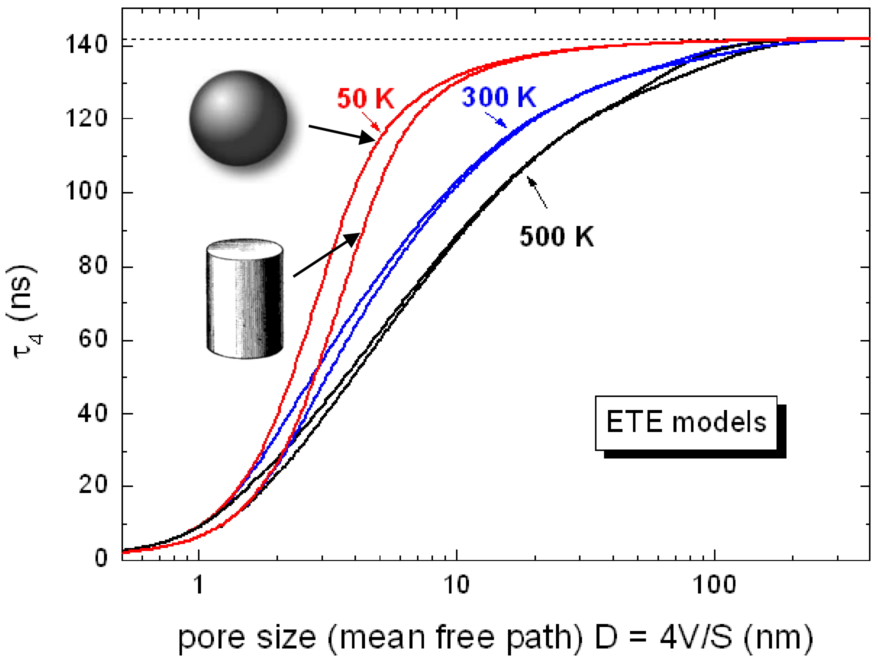
- 4 exponential decay components
- p-Ps -> 0.125 ns
- free positrons ~ 0.5 ns
- o-Ps in disordered structure ~ 1.5 ns
- o-Ps in pores
- analysis with LT9 (LifeTime)

$$N(t) = \sum_{i=1}^{k+1} \frac{I_i}{\tau_i} \exp\left(-\frac{t}{\tau_i}\right)$$

Extended Tao Eldrup model

- **extended TE model (calculations by EELViS):**
  - **quantum well of infinite height, but: overlap of o-Ps wave function and wall of pore -> δ**
  - **Boltzmann statistics ascribes explicit temperature dependence to the lifetime**
  - **integrals of spherical / cylindrical Bessel functions**
  - **δ = 0.19 nm**
  - **mean free path D = 4V/S = d_{cyl}, diameter of cylinder**
  - **mean free path D = 4V/S = 2/3 d_{sphere}, diameter of sphere**





R. Zaleski, *Excited Energy Levels and Various Shapes (EELViS)*, Institute of Physics, Maria Curie-Sklodowska University, Lublin, Poland

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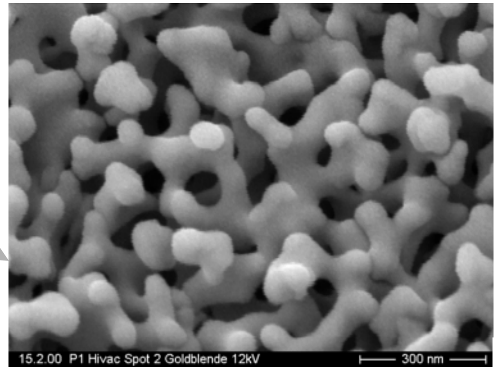
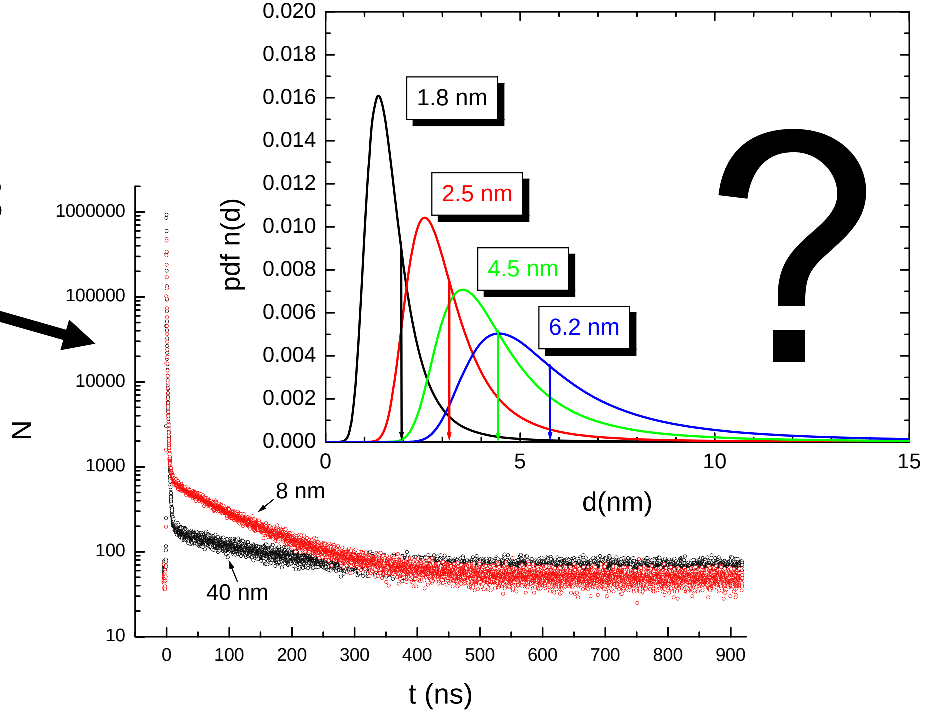
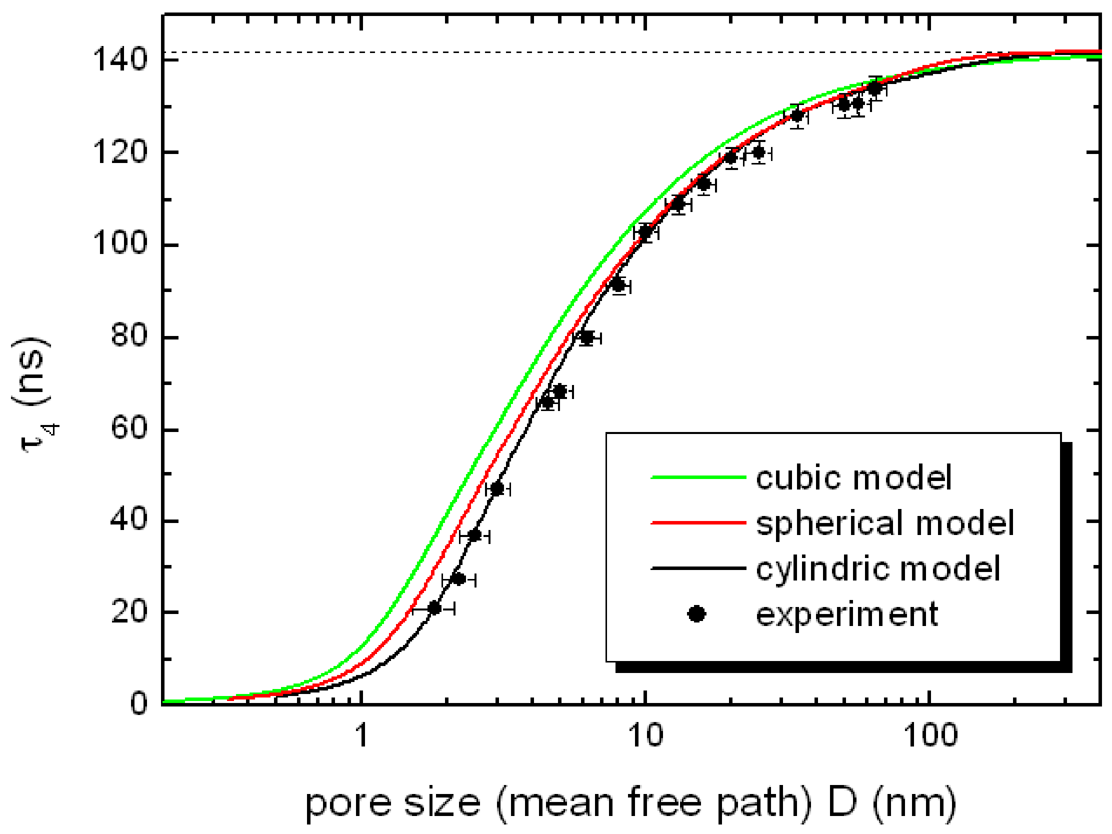




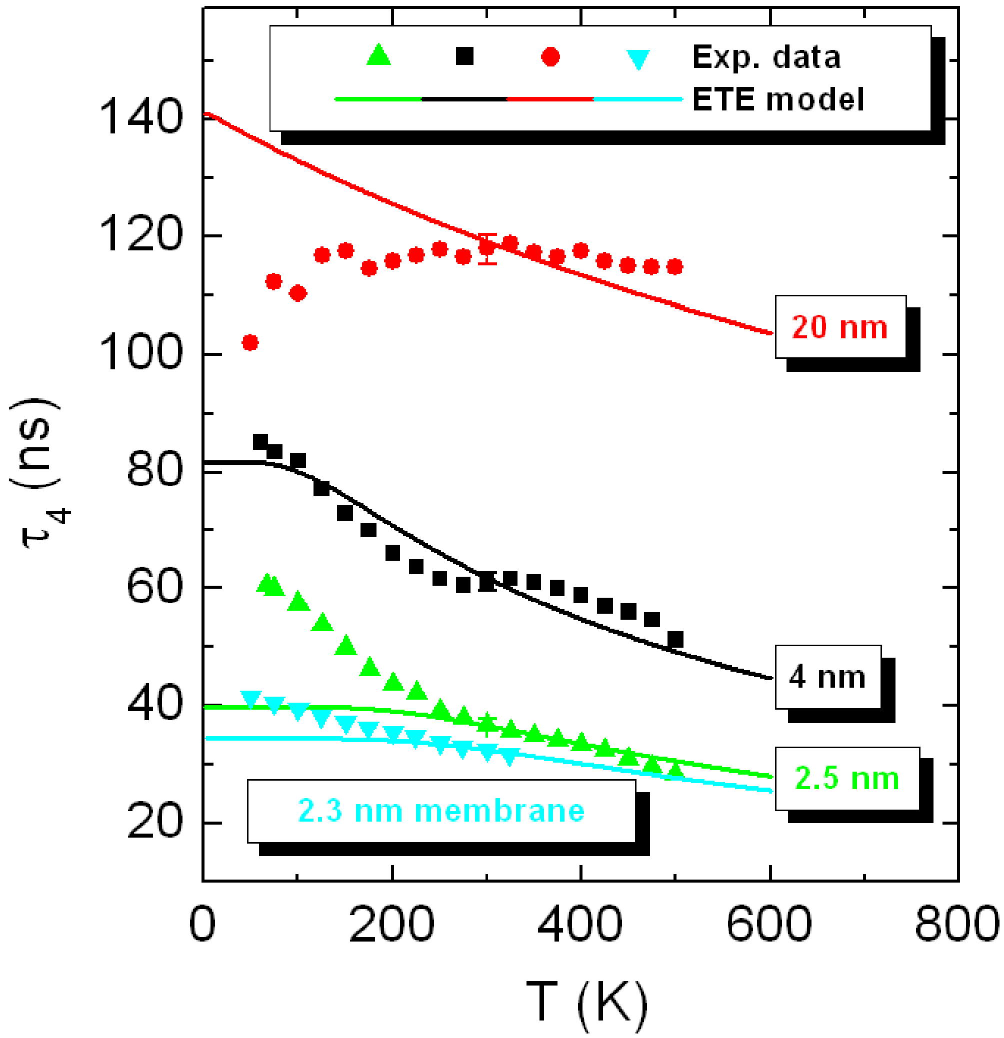
The experiments at T = 300 K



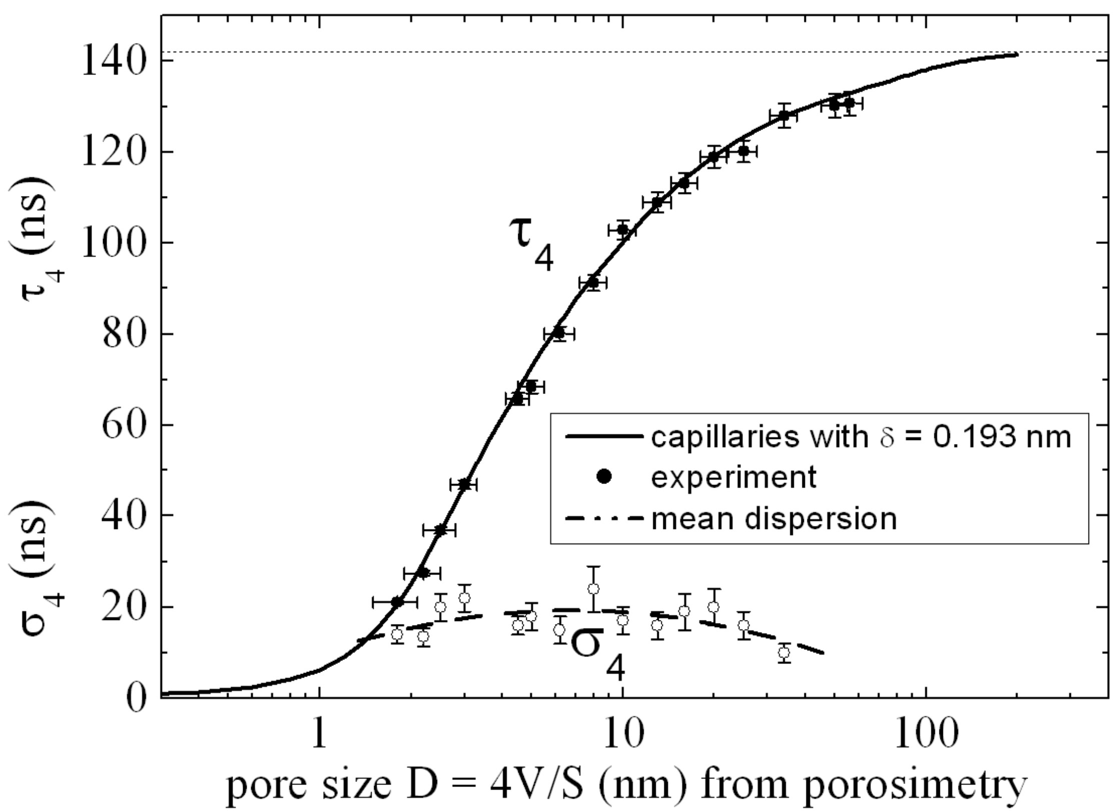
- we measured CPG in a broad pore size range
- given pore sizes obtained by N_2-adsorption or Hg-intrusion
- cubic and spherical model not sufficient for small pores
- **cylindric model with δ = 0.193 nm best fit for our CPG -> calibration curve for calculating pore size**
- works well for RT, other T ?

The T-dependence

- **calculations:** cylindric model with δ = 0.193 nm
- **although we found good agreement for T > 300 K temperature behavior can not be explained very well at low temperatures**
- for 20 nm catching effect of o-Ps at low temperatures (v. d. Waals power, “capill. cond.”), o-Ps bonds at the wall
- for small pores -> thermal activated surface atoms -> low T causes larger effective pore size (Ganguly et al. PPC8)
- model still too simple but works well for room temperature



Pore size distribution



D	τ_4	σ_4
1.8 nm	21.1 ns	14.8 ns
2.5 nm	46.9 ns	17.6 ns
4.5 nm	65.9 ns	18.9 ns
6.2 nm	80.0 ns	19.3 ns

- τ_4 and its distribution σ_4 by analysis of truncated spectra starting from 20 ns
- **problem of LT: limit of 142 ns is not taken into account, for large pores unphysically large σ_4**
- distribution for 4 smaller selected pores

Pore size distribution

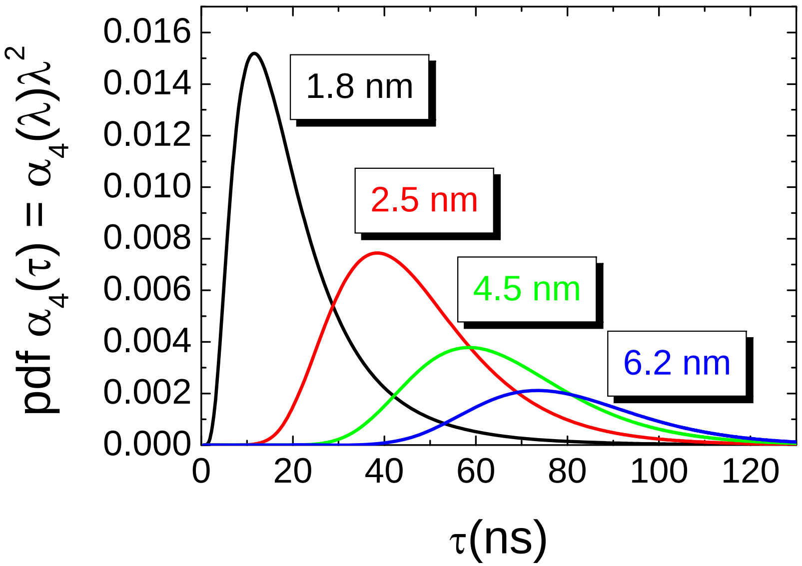
- **distribution of τ_4: $\alpha_4(\tau) = \alpha_4(\lambda)\lambda^2$,**
  $\alpha_4(\lambda)$ is probability density function (pdf) of o-Ps annihilation rate, assumed by LT to be a log. Gaussian

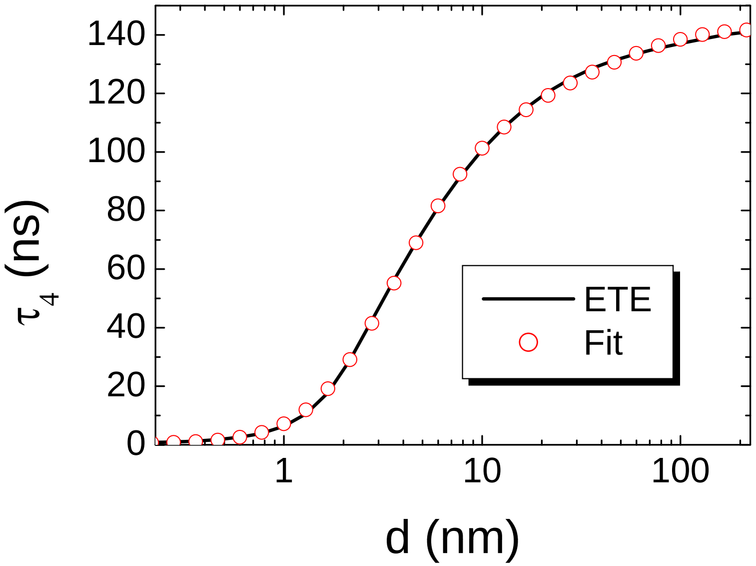
- **from distr. $\alpha_4(\tau)$ it is possible to calc. distribution of diameters of the pore:**

$$n(d_{cyl}) = \alpha_4(\tau)\left(\frac{d\tau_4}{dd_{cyl}}\right)$$

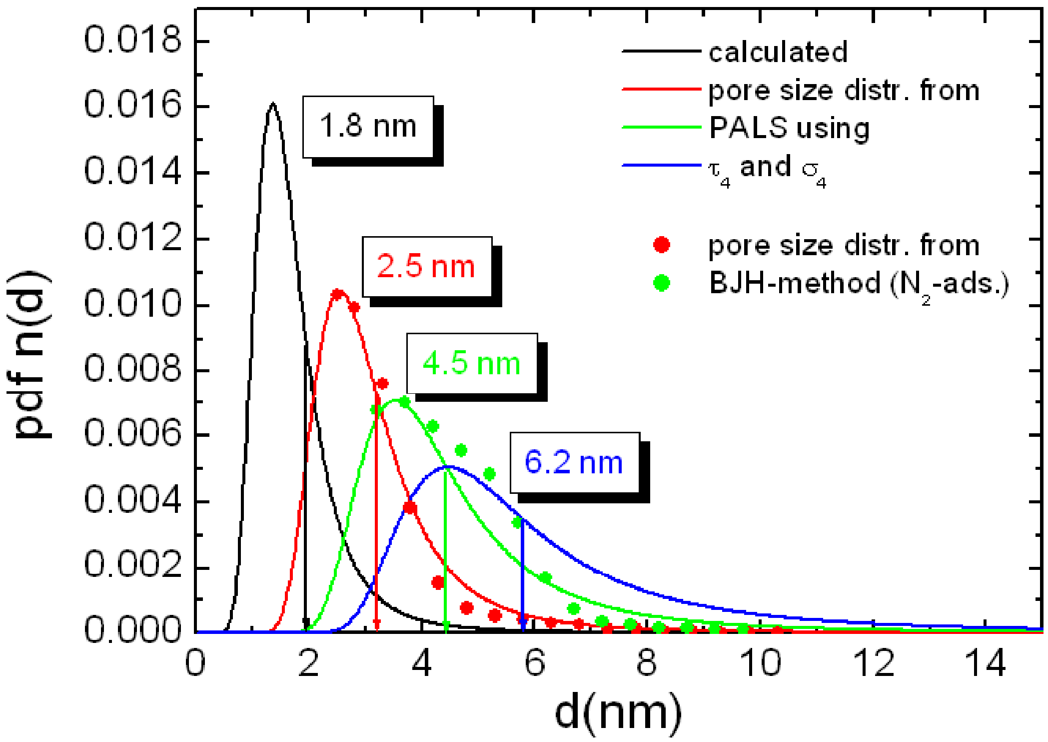
- **all we need is a differentiable analytical function $\tau_4 = \tau_4(d_{cyl})$:**

$$\tau_4 = A_2 + \left(\frac{A_1 - A_2}{1 + (d_{cyl}/d_{cyl0})^p}\right)$$





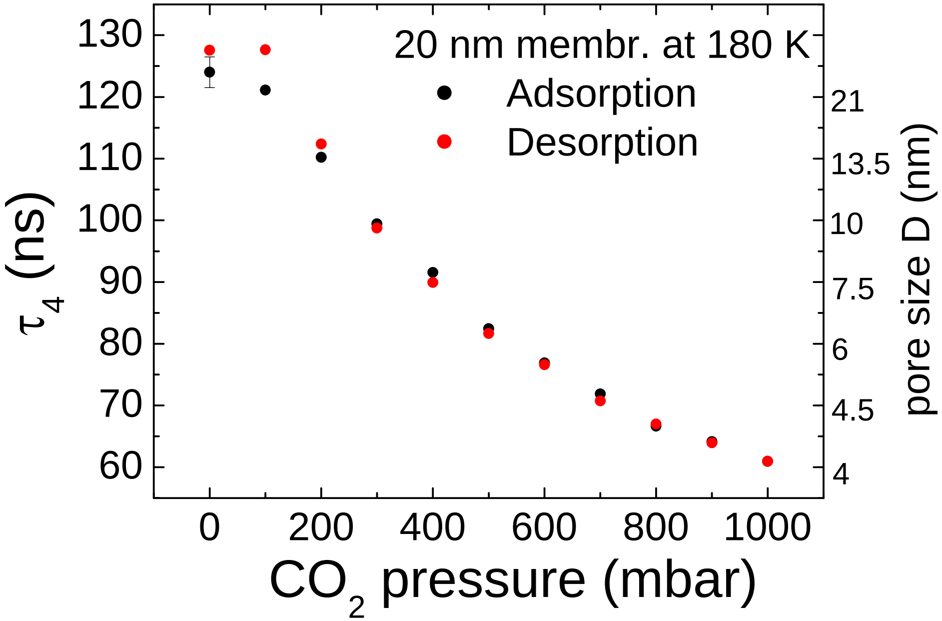
Pore size distribution

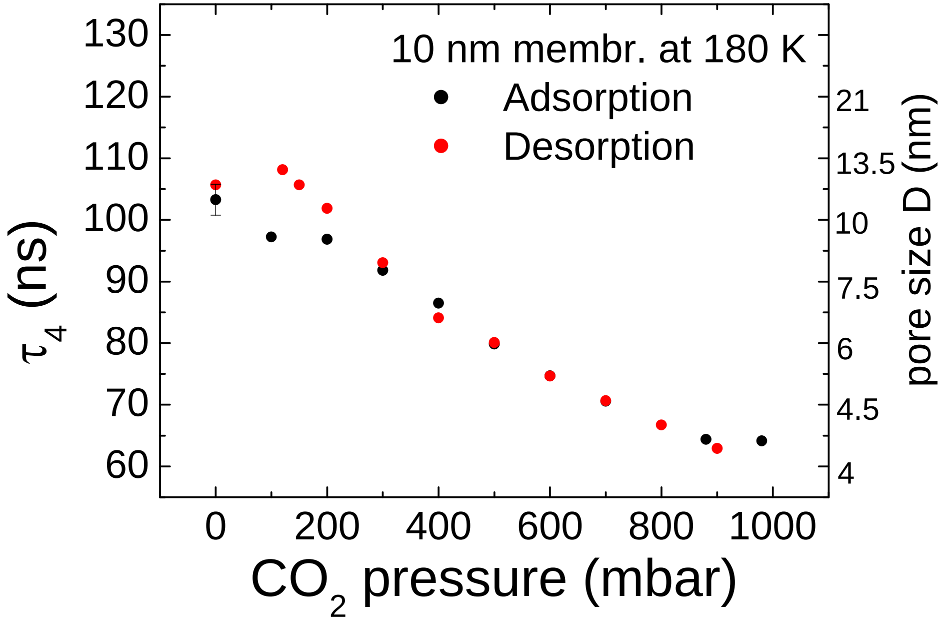


- distribution norm. to 1
- arrows show d directly calculated from mean o-Ps lifetime using cylindric model (1.77 nm, 3.09 nm, 4.38 nm and 5.80 nm)
- **this distribution contains the true variation of pore sizes but also the effect of irregular not linear character of pores**
- **long tail for larger pores:**
  - **overestimation of $\alpha_4(\tau)$**
  - **nonlinear char. τ_4 vs. d**

to be published

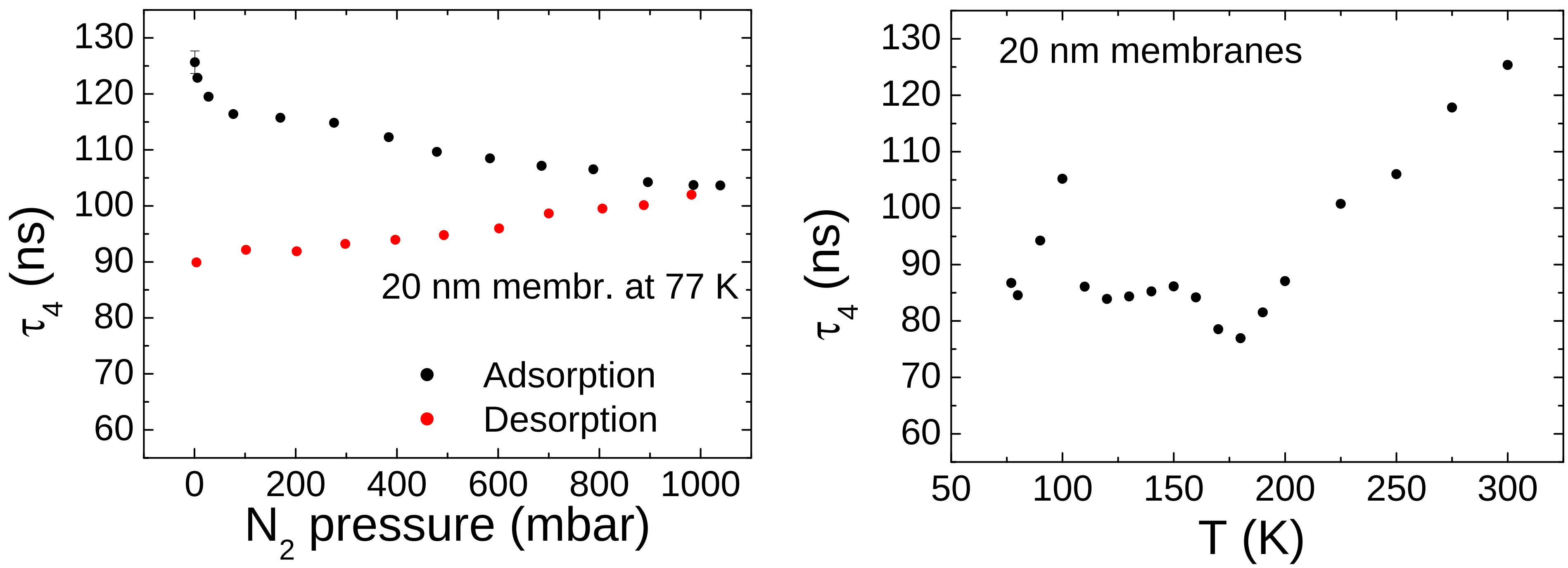
Phase transition of CO_2





- we fill / degas in steps of 100 mbar
- phase transition from gas to solid, p_0 ~ 300 mbar at 180 K
- **we observe nearly no difference between adsorption and desorption curves for p > p_0, small hysteresis in the end -> desorption of CO_2 very easy**
- **no complete pore filling because of pore blocking effect**

Phase transition of N_2



- we fill / degas in steps of 100 mbar
- phase transition from gas to a liquid, p_0 ~ 1000 mbar at 77 K
- **we observe a huge difference between adsorption and desorption curves, at 0 mbar shortest lifetime -> desorption of N_2 not possible at 77 K**
- **T-dep. desorption shows interesting behavior, also for other pore sizes**

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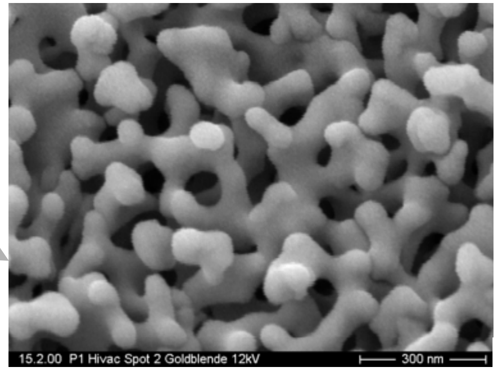
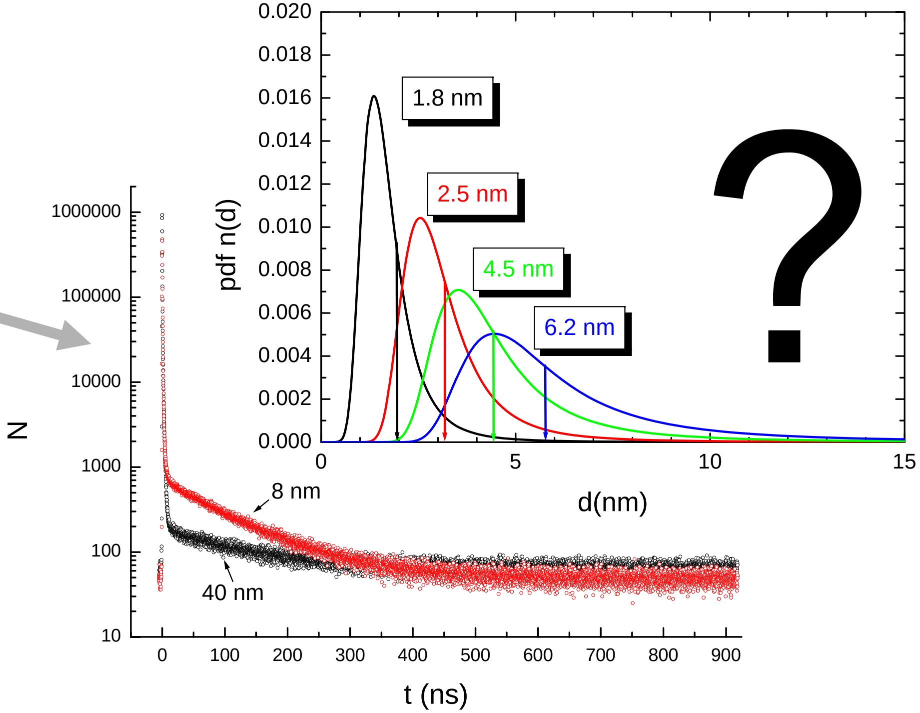
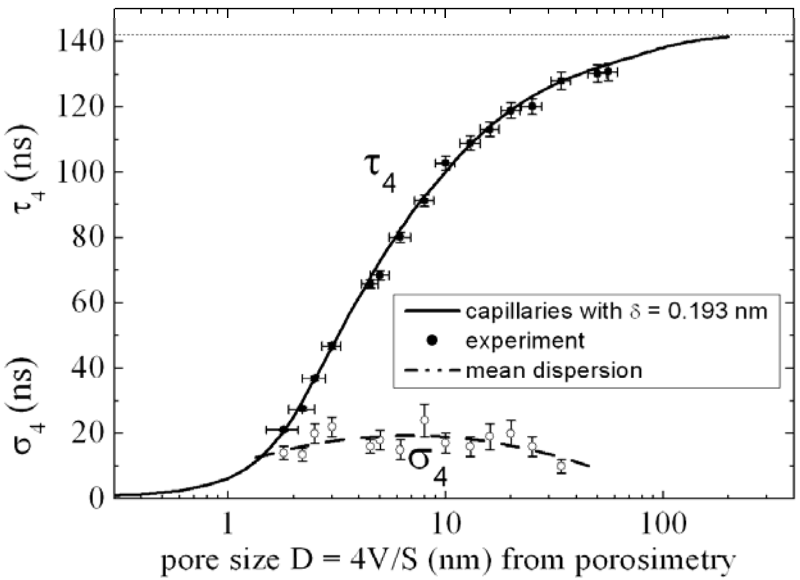
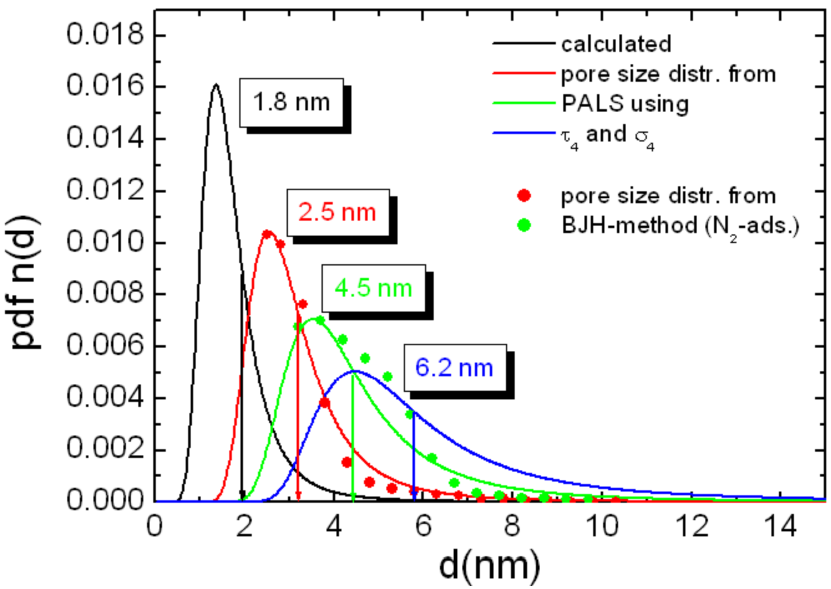




Summary

- for T = 300 K we found a calibration curve for CPG
  - non-destructive porosimetry tool for open and closed pore-systems
  - most sensitive for d = 0.5 … 10 nm
- for pores d < 10 nm we can calculate a pore size distribution
- first measurements on phase transition of gas in CPG
- near future:
  - SBA-15 (to be presented @ COPS VIII Edinburgh / Scotland, June 2008)





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- G. Dlubek (Halle/Germany) for fruitful discussions
- all organizers of PPC9

- 谢谢 for your patience!

- this talk as pdf?

- http://positron.physik.uni-halle.de