Nano-scale porosimetry using ortho-Positronium lifetime measurement

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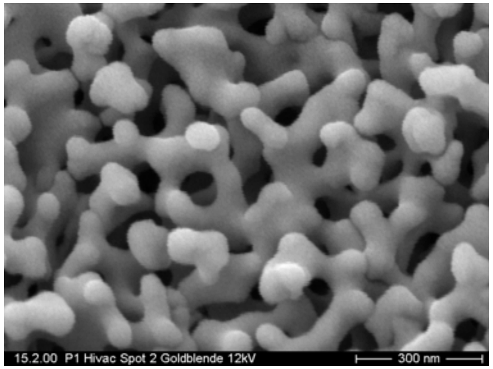
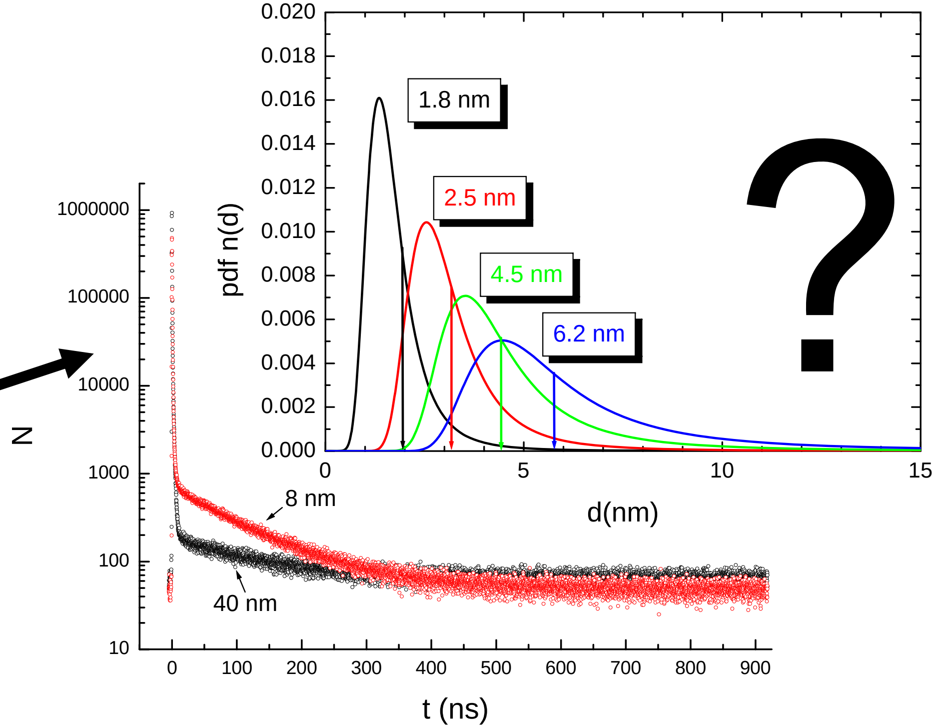
Outline

- **Principles of PALS**
  - positron and positronium
  - lifetime measurement
  - the spectrum
- **Porous glass - CPG**
  - synthesis
  - properties
- **From τ_4 to pore size d**
  - the model
- **Experimental results**
  - calibration curve
  - pore size distribution
- **Summary**

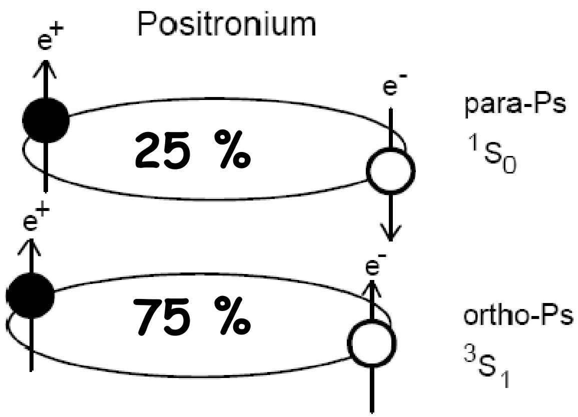




Principles of PALS: pick-off annihilation

positrons from ^{22}Na:

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

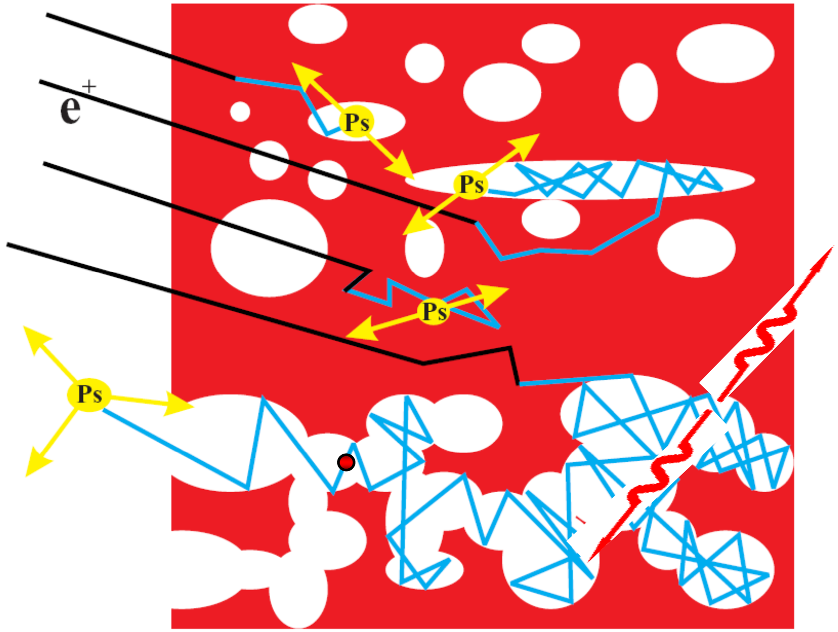


positronium:

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

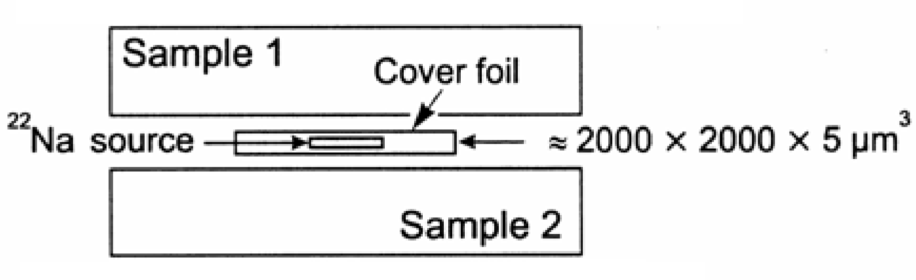
pick-off annihilation:

- 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**

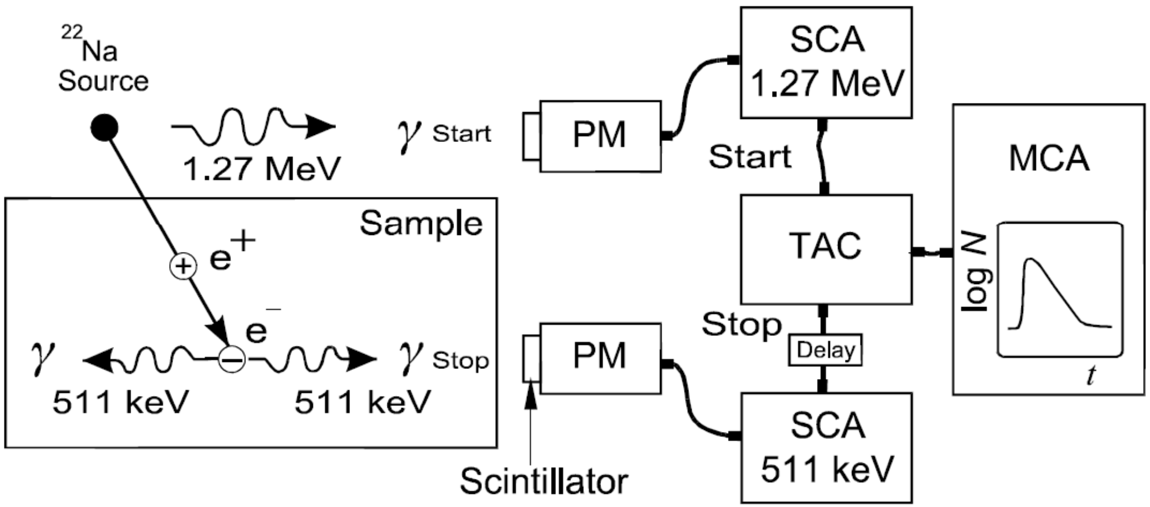


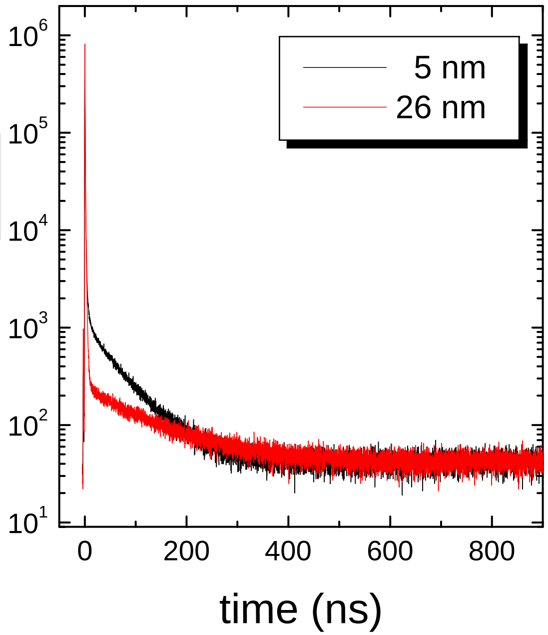
Principles of PALS

- **sample preparation:** "sandwich"



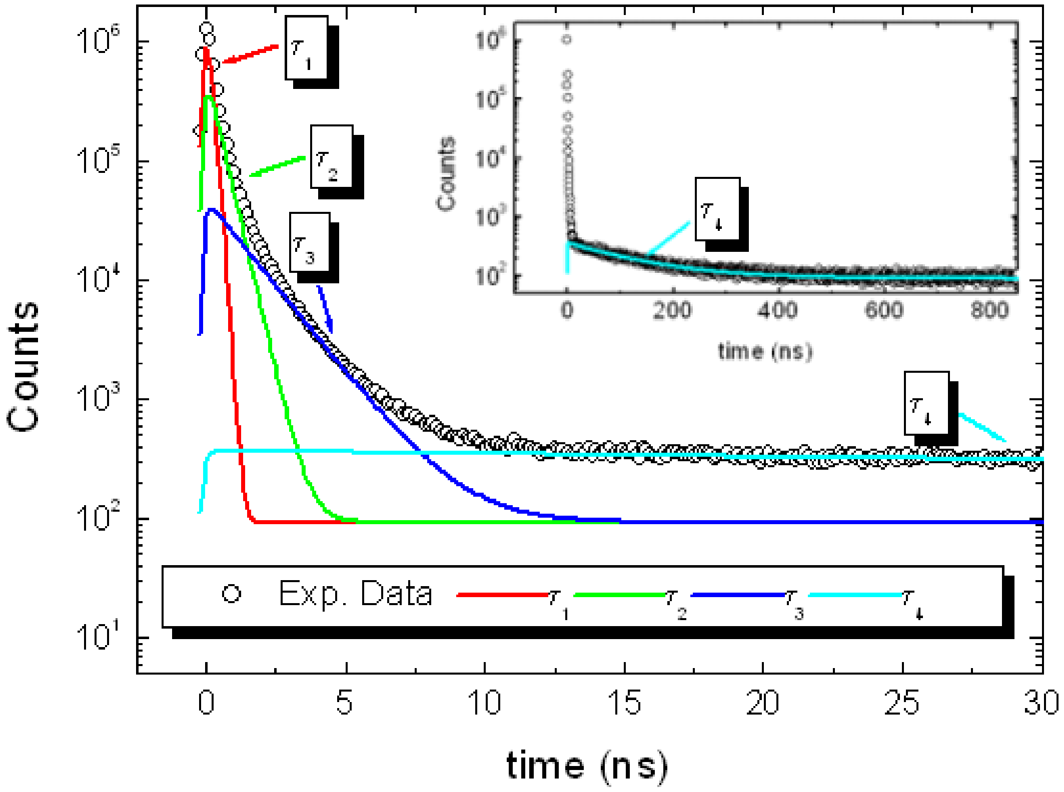
- **positron(ium) lifetime:** time between "birth" (1,27 MeV) and "death" (511 keV)





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)

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

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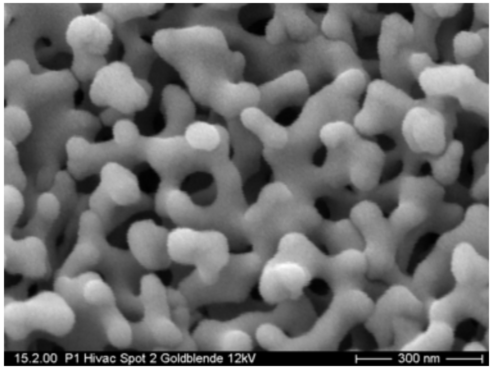
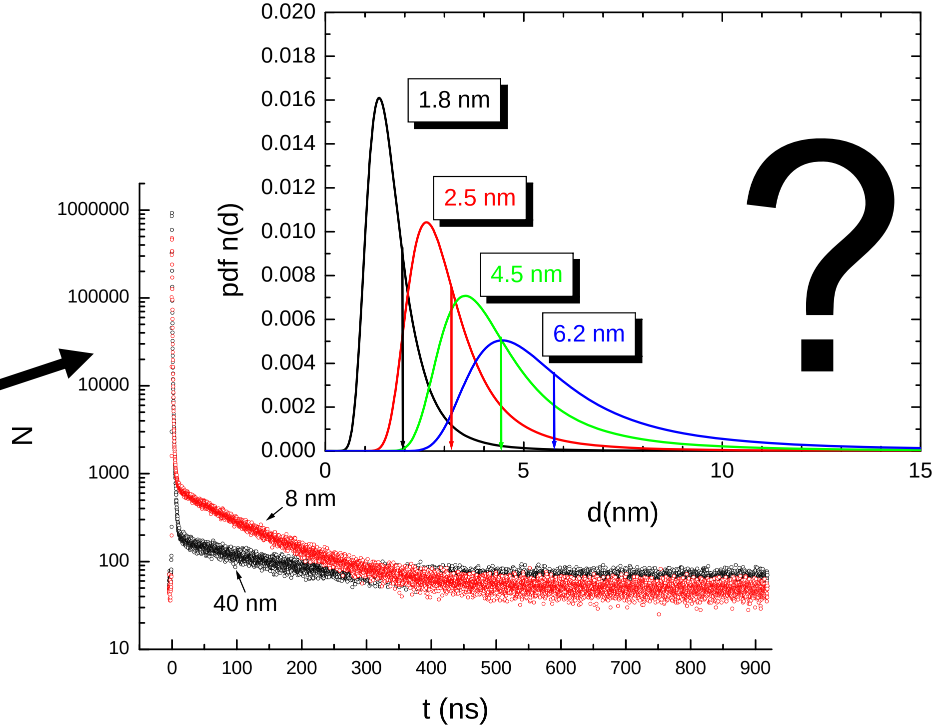
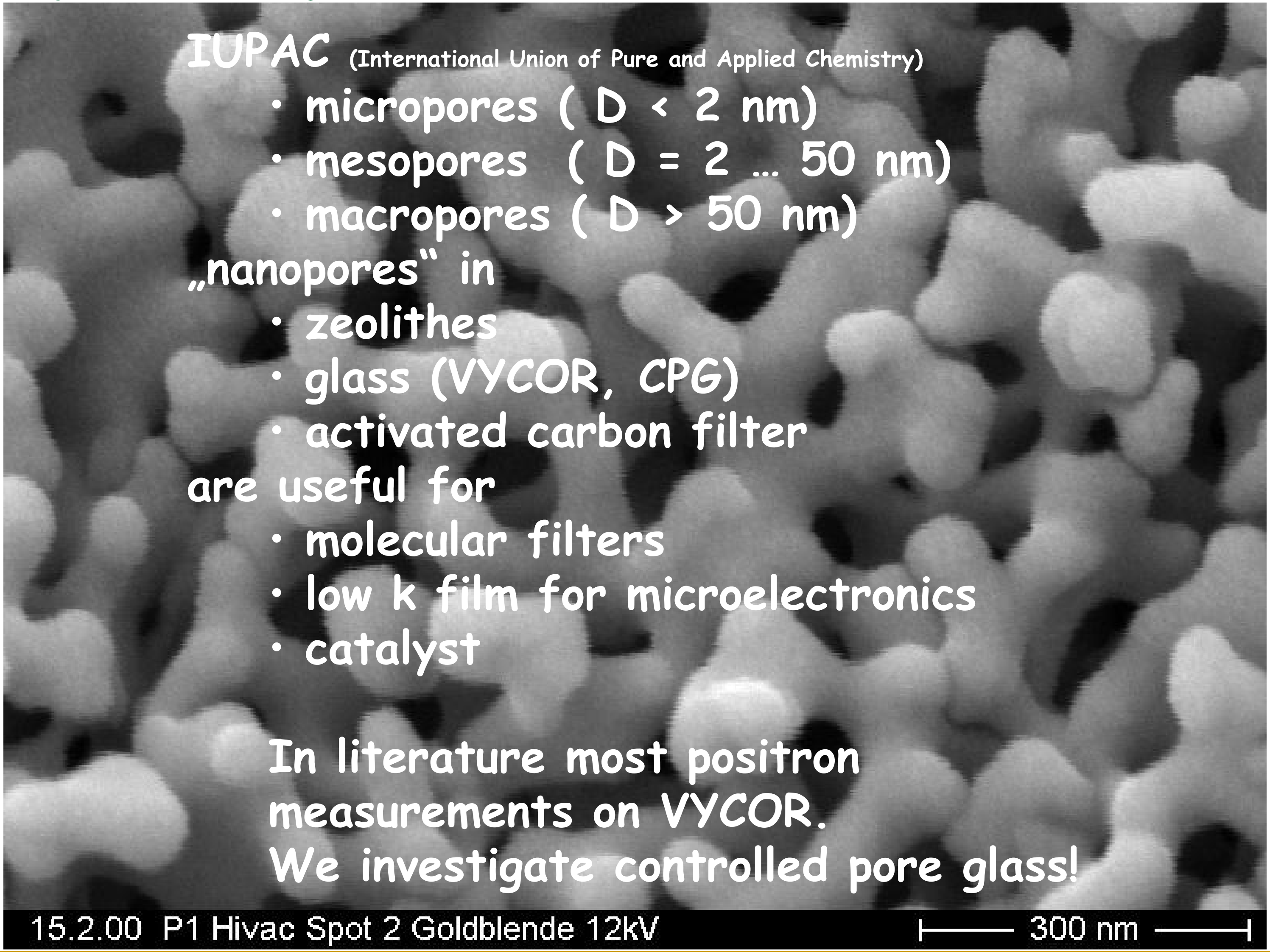




Why „nanopores"?



IUPAC (International Union of Pure and Applied Chemistry)

- micropores (D < 2 nm)
- mesopores (D = 2 … 50 nm)
- macropores (D > 50 nm)

„nanopores" in

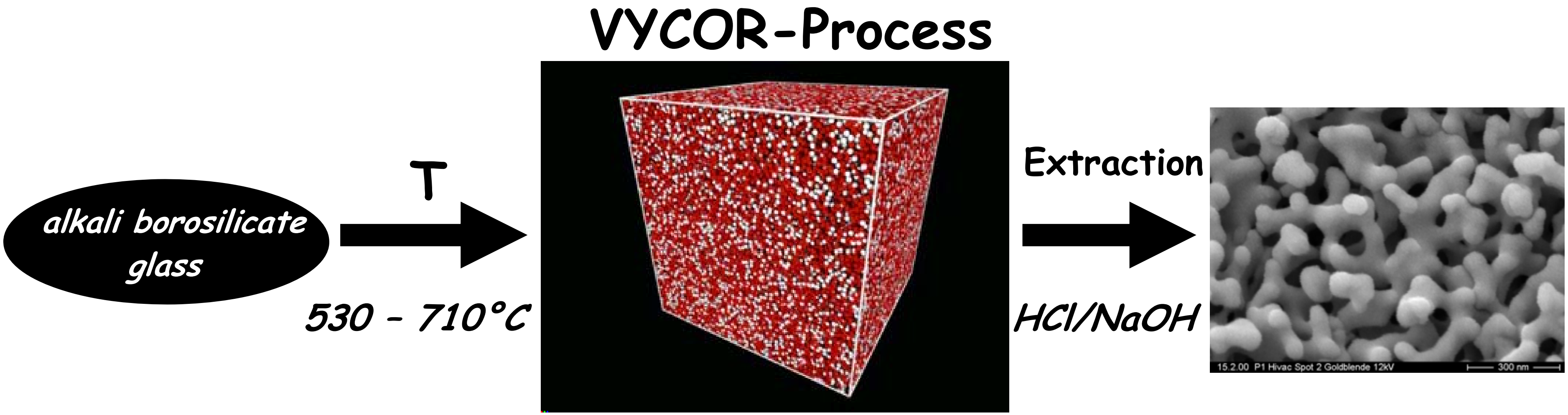
- zeolithes
- glass (VYCOR, CPG)
- activated carbon filter

are useful for

- molecular filters
- low k film for microelectronics
- catalyst

In literature most positron measurements on VYCOR.
We investigate controlled pore glass!

Controlled pore glass - CPG

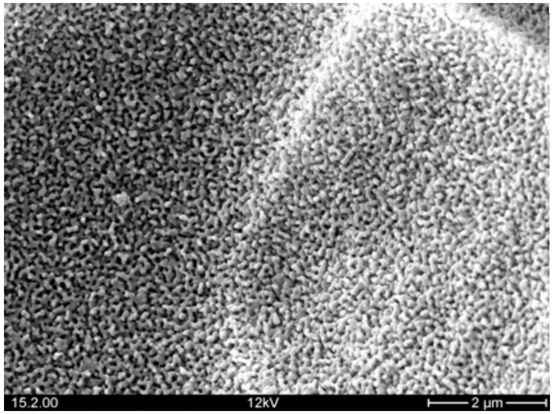


d_P 1 to 110 nm

- 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 %

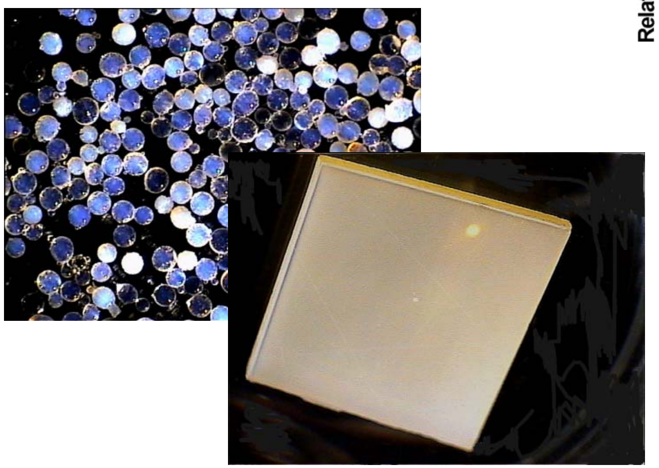
F. Janowski, D. Enke in F. Schüth, K.S.W. Sing, J. Weitkamp (Eds.), *Handbook of Porous Solids*, WILEY-VCH, Weinheim, **2002**, 1432-1542.

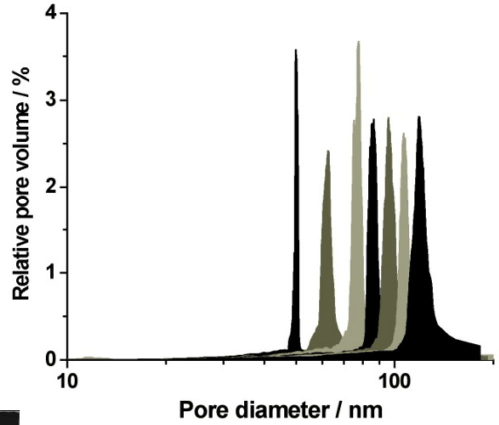
Controlled pore glass - CPG



- 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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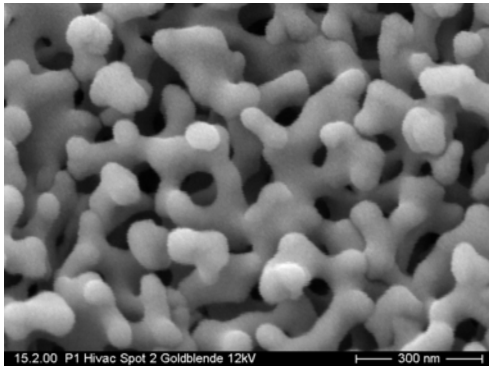
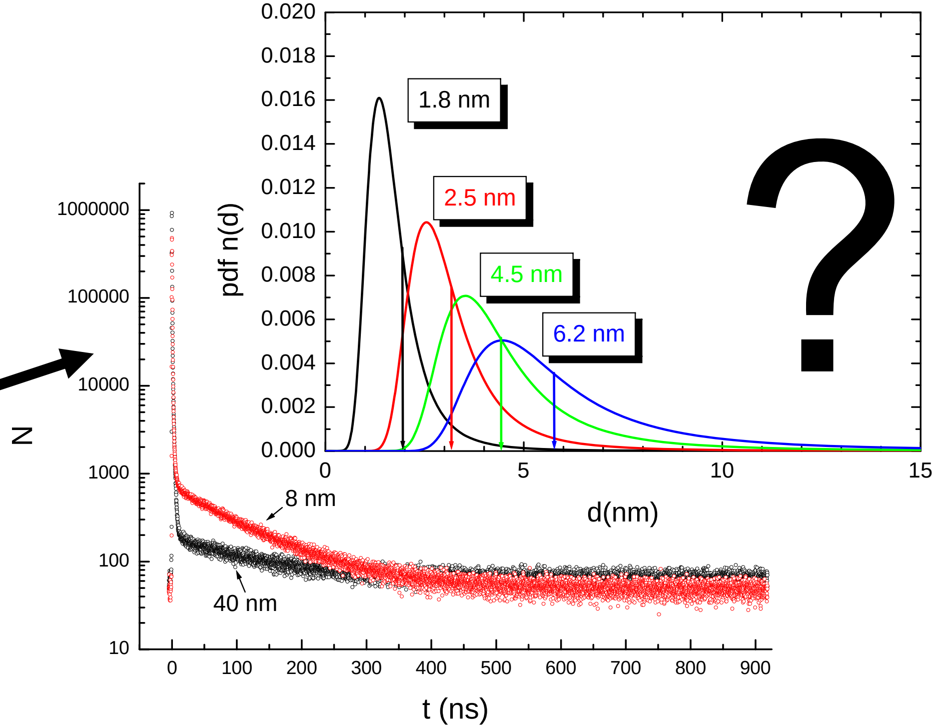
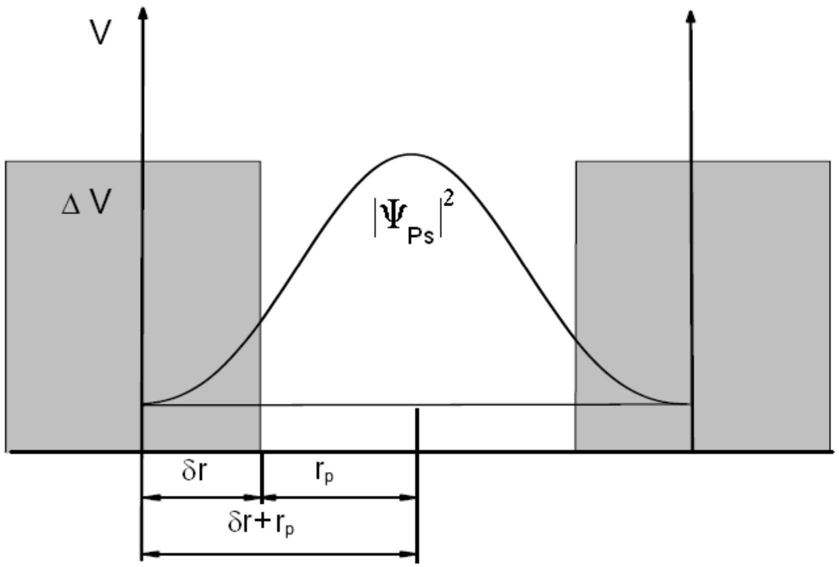
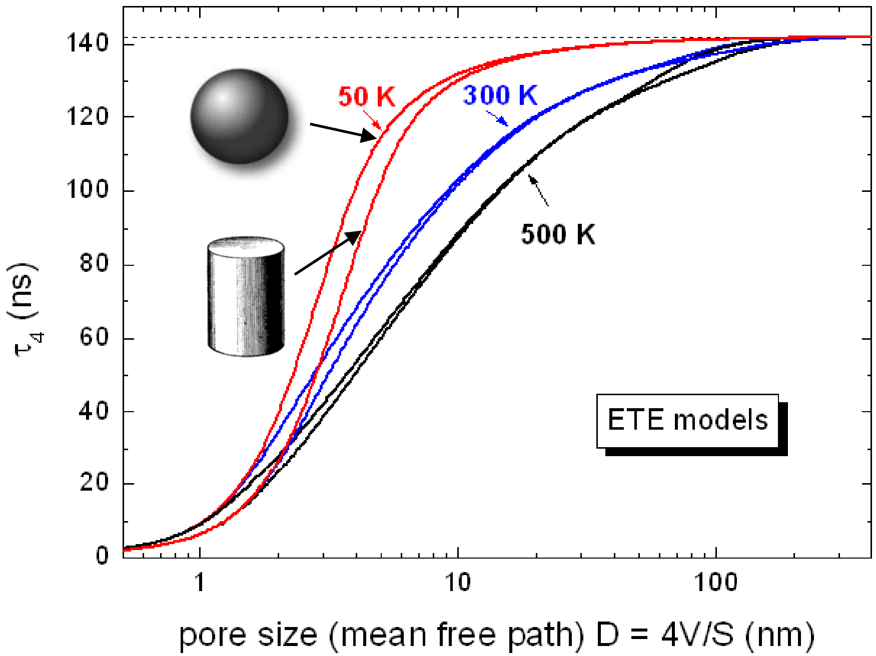




Extended Tao Eldrup model

- 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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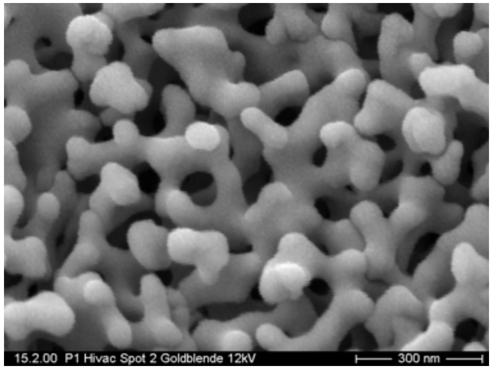
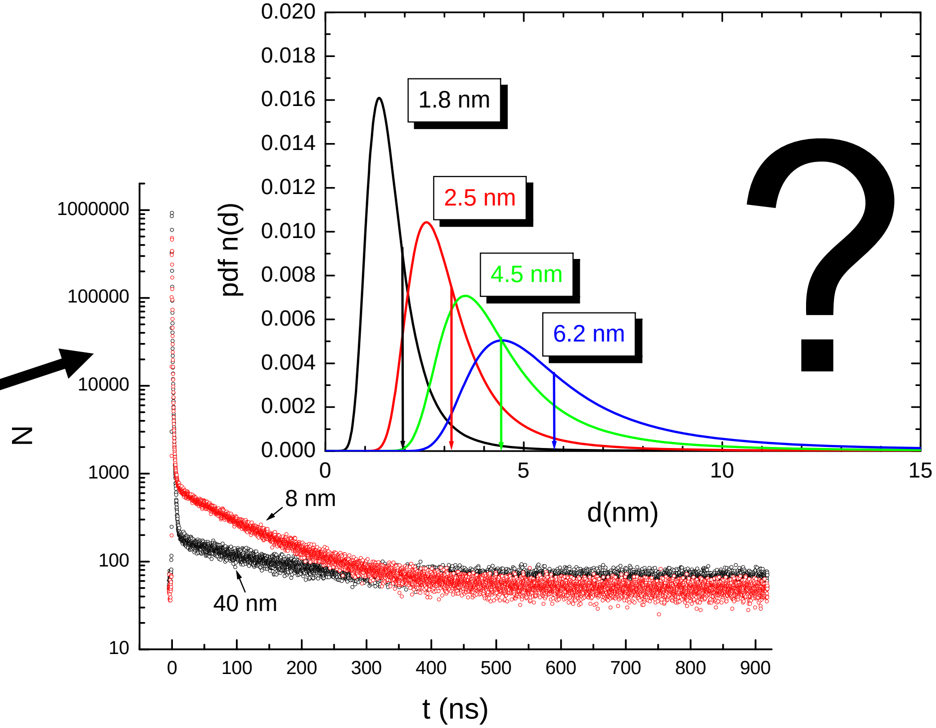
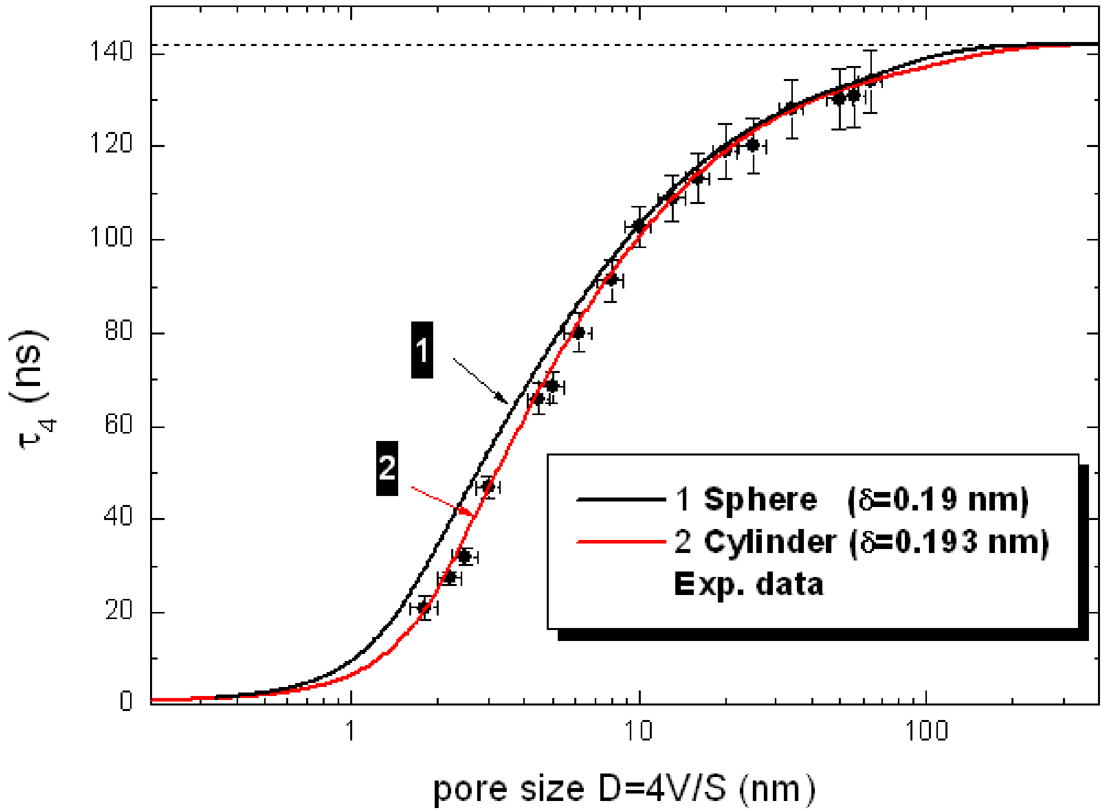




The experiments at T = 300 K

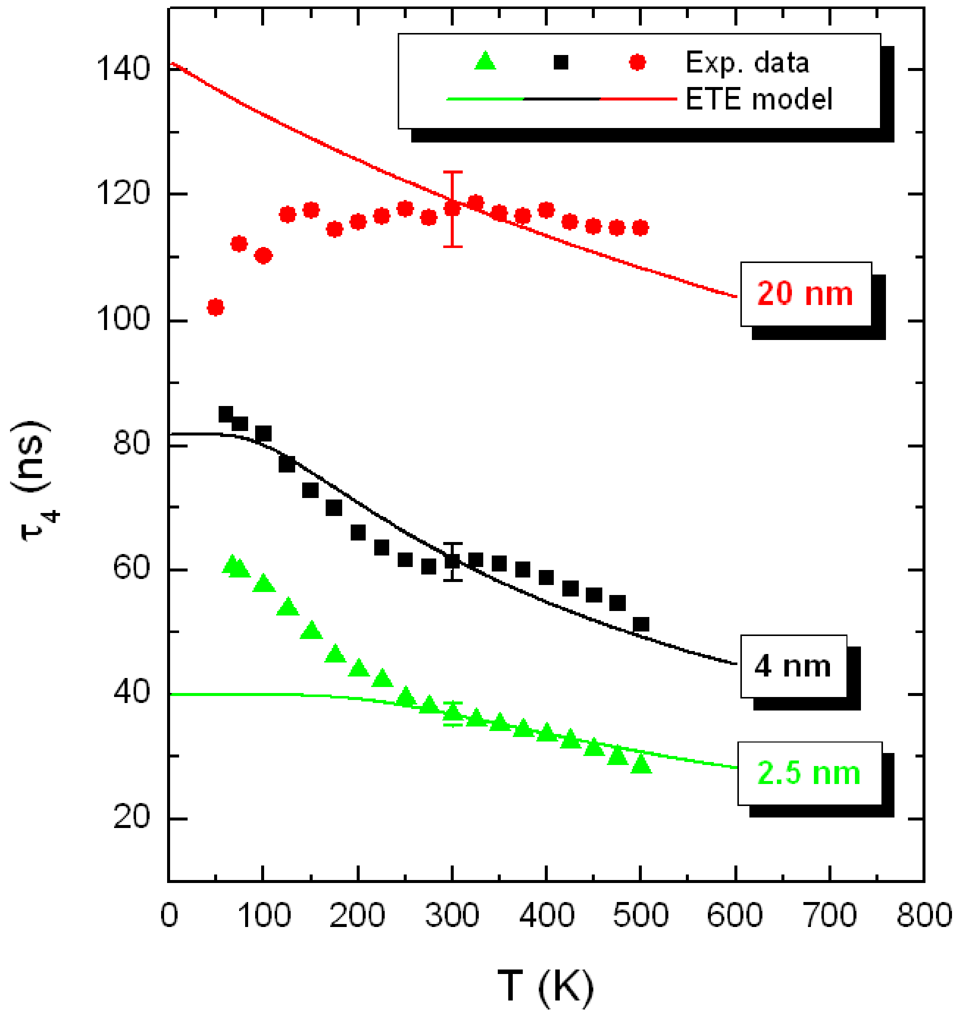


- we measured CPG in a broad pore size range
- given pore sizes obtained by N_2-adsorption or Hg-intrusion
- **δ = 0.193 nm best fit for our CPG -> calibration curve for calculating pore size**
- good model for T = 300 K, also good model for temperature dependence of lifetime?

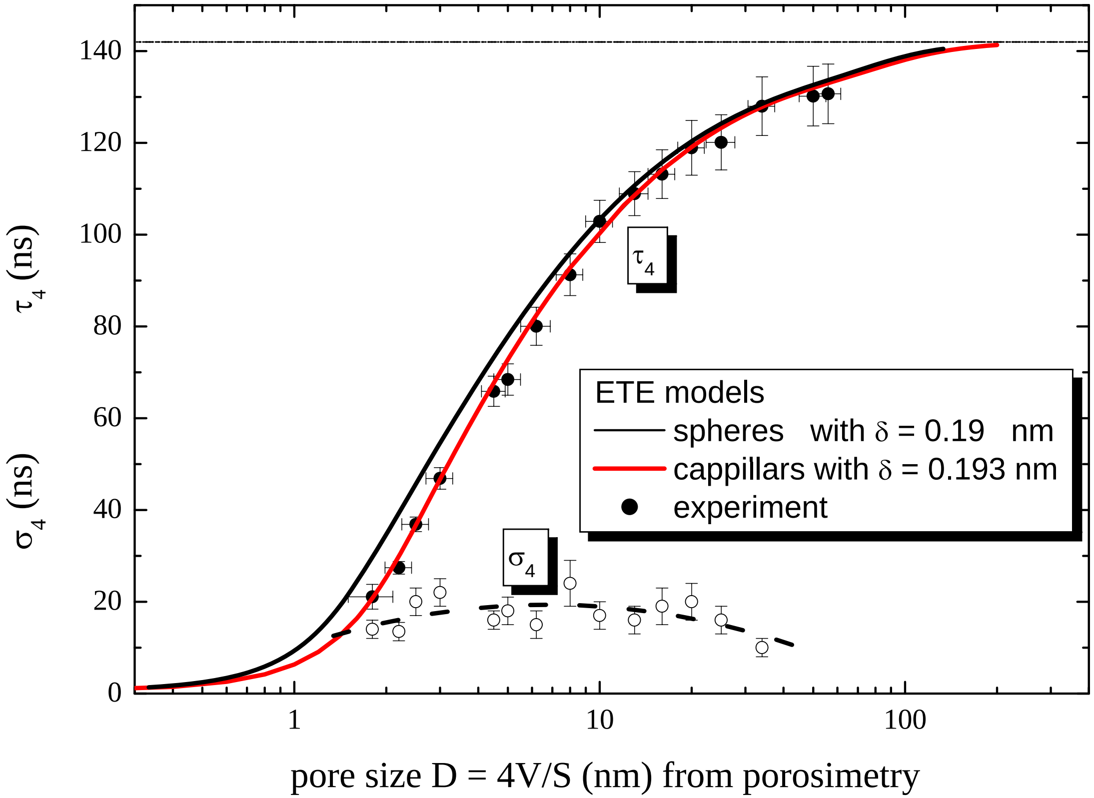
The T-dependence

- **calculations:** cylindric model with δ = 0.193 nm
- **although we found good agreement for T > 300 K temperature behavior cannot be explained very well at low temperatures**
- for 20 nm a catching effect of o-Ps at low temperatures may occur (van-der-waals power, “capillary condensation”)

  and o-Ps bonds at the wall
- 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

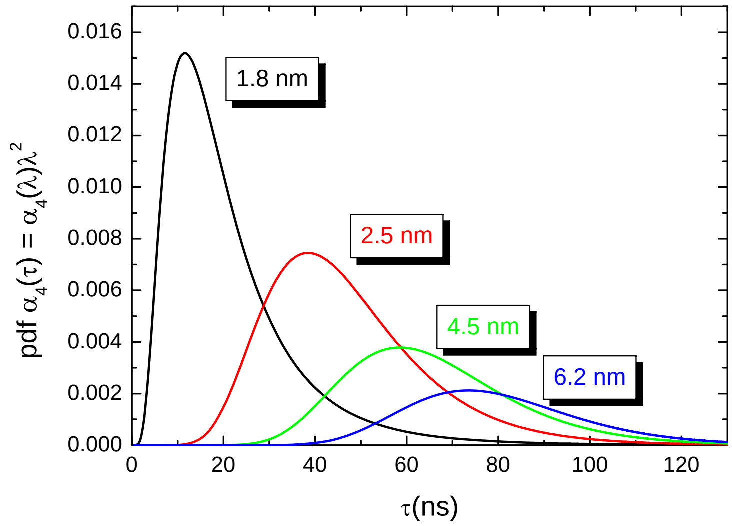
- **distribution of τ_4: $\alpha_4(\tau) = \alpha_4(\lambda)\lambda^2$,**
  $\alpha_4(\lambda)$ is probability density function (pdf) of o-Ps annihilation rate, assumed by LT to be a log. Gaussian

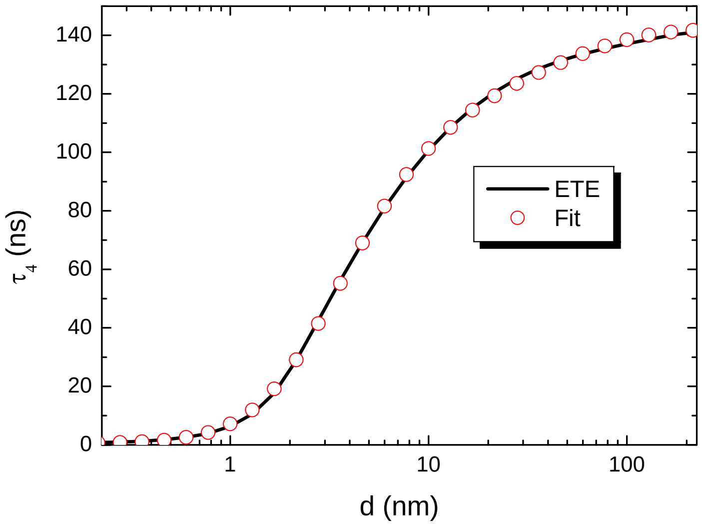
- **from distr. $\alpha_4(\tau)$ it is possible to calc. distribution of diameters of the pore:**

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

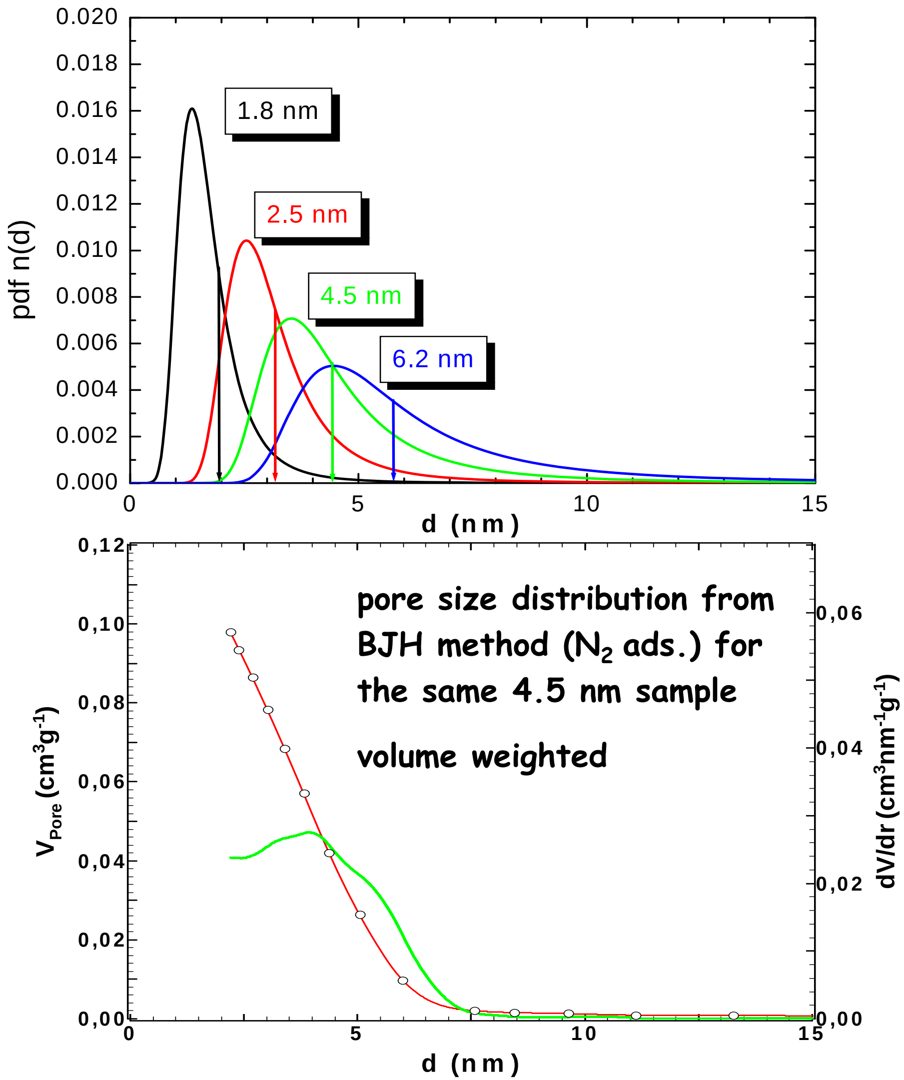
- **all we need is a differentiable analytical function $\tau_4 = \tau_4(d_{cyl})$:**

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





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

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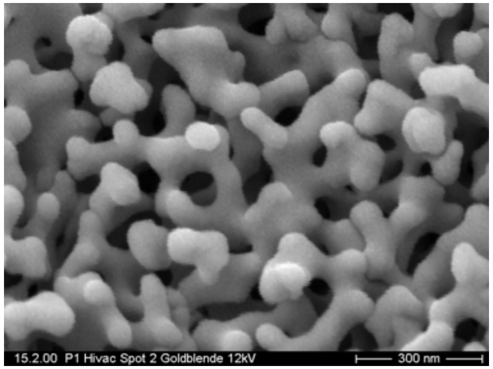
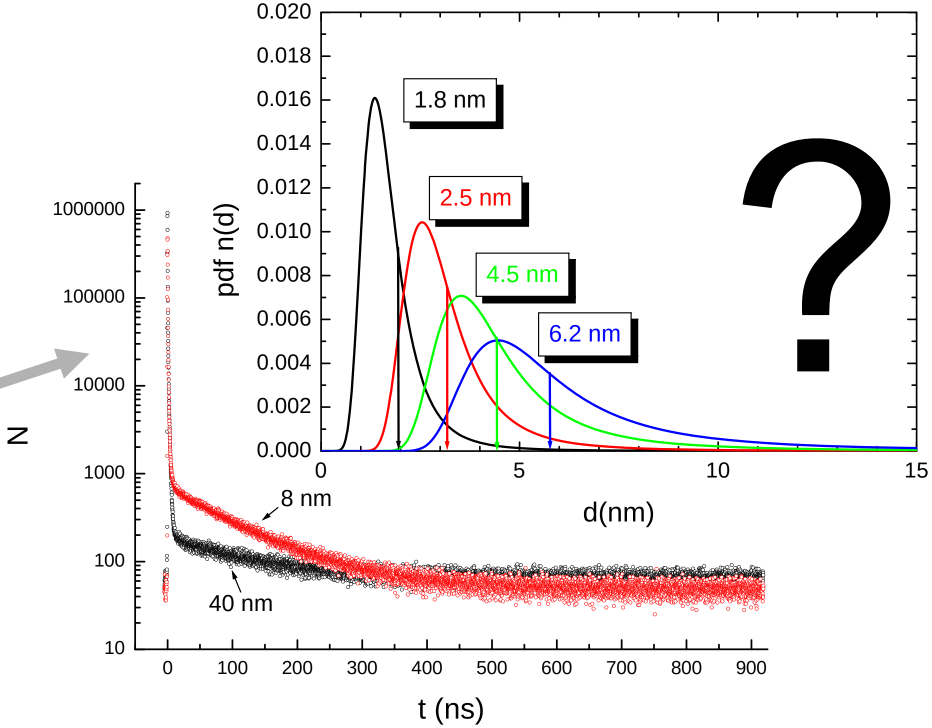
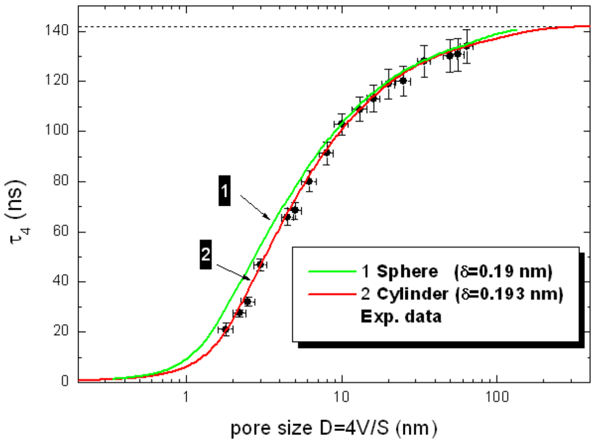
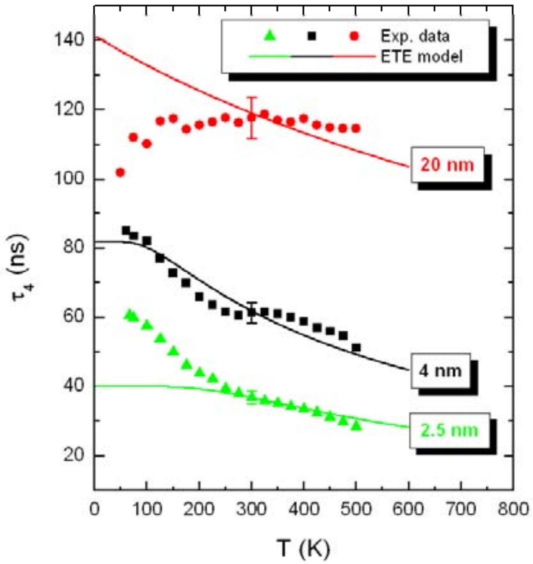


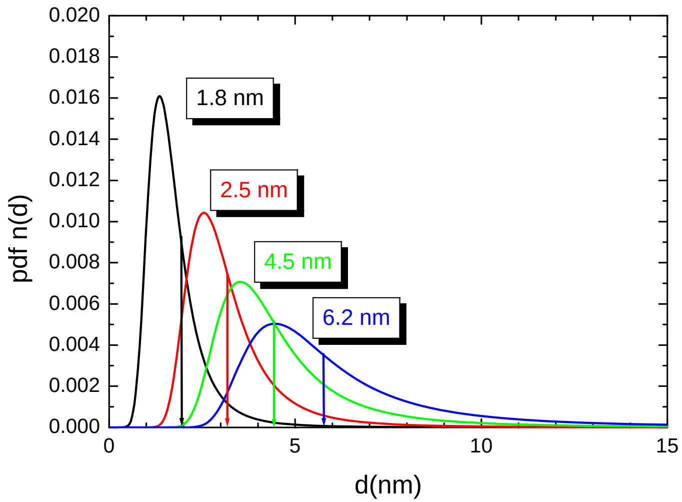


Summary

- for T = 300 K we found a calibration curve for CPG
  - non destructive porosimetry tool for opened <u>and</u> closed pore-systems
  - most sensitive for d = 0.5 … 10 nm
- for other temperatures the measurements show disagreement to the ETE model -> model still too simple
- for pores d < 10 nm we can calculate a pore size distribution
- near future:
  - phase transition of gas in CPG (to be presented @ PPC9 Wuhan / China, May 2008)
  - SBA-15 (to be presented @ COPS VIII Edinburgh / Scotland, June 2008)







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- R. Zaleski and his group (Lublin/Poland) for EELViS
- G. Dlubek (Halle/Germany) for fruitful discussions
- FZD

- Thanks for your patience!
- This talk as pdf?
- http://positron.physik.uni-halle.de