

# Positron Annihilation as a Method to Characterize Porous Materials

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# Abstract:

- **Beam-based Positron Annihilation Spectroscopy (PAS)**
- nondestructively pore-size determination and distribution of 0.3nm-30nm pores
- Depth profiling:
  - interconnection length of pores
  - depth-dependent inhomogenities
  - damage in pore-structure
  - hidden porosity (dense layers, diffusion barriers)

# Main spectroscopies:

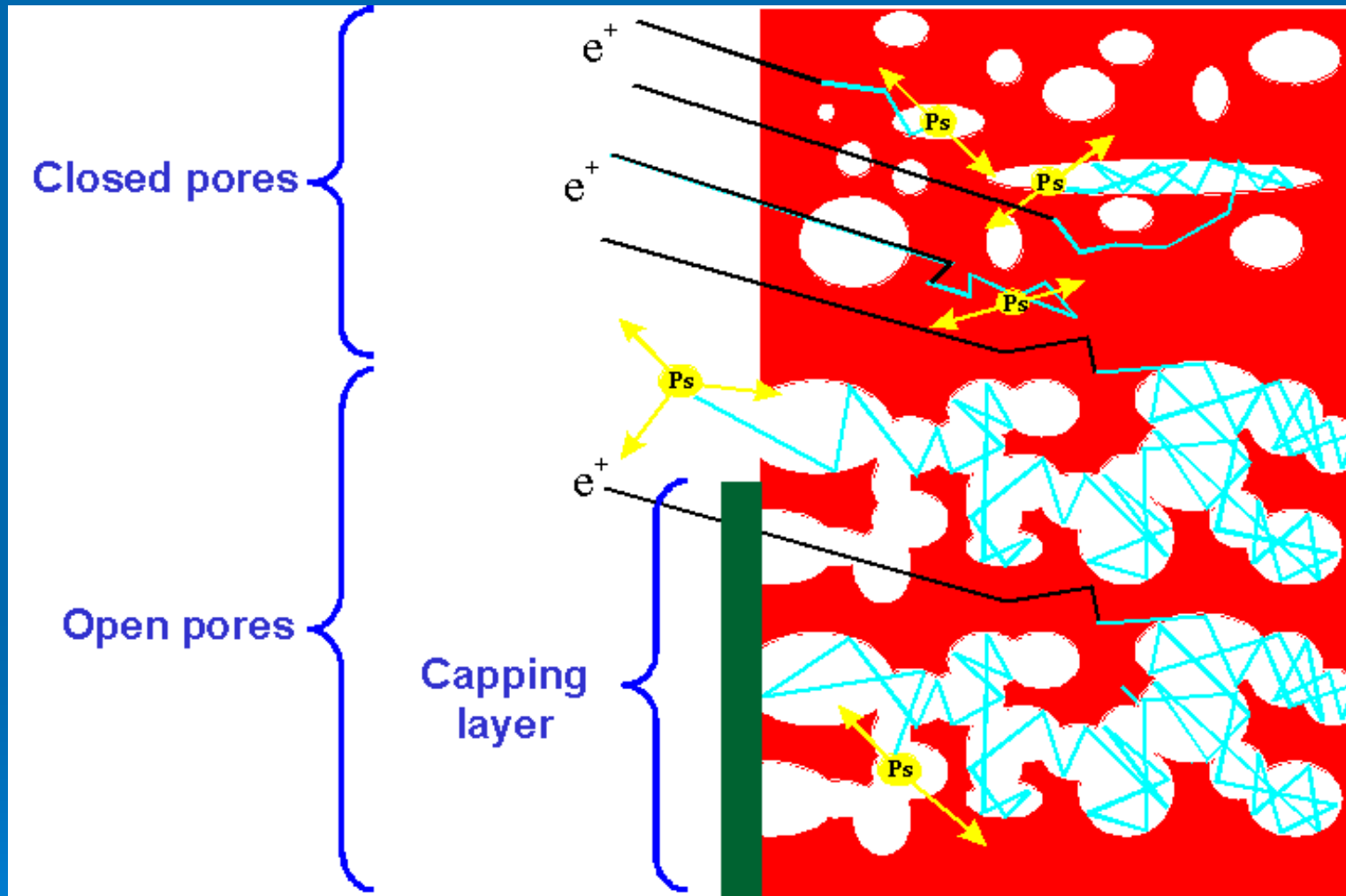
- time domain
- energy of annihilation gamma rays
- momentum of gamma rays:
  - doppler Energy shifts
  - Angular distribution



# Most interesting parameters:

- pore size
- pore size distribution (PSD)
- Pore interconnection length  $L_{int}$ 
  - Scale length over which pores are connected to each other

# Ps in nanoporous films:



# Ps in nanoporous films:

➤ Positrons (50 eV-15keV):

- scatters of atoms and electrons
- slows down to atomic scale energy (several eV) in pico-seconds

➤ **Typically 10%-50%:**

➤ Capture bound molecular electron (**Ore-model**)

➤ Recombines with „spur“  $e^-$  from  $e^+$  ionizing collisions (**Spur-model**)

➤ Forming Ps

Note:

Relationship between these formation mechanisms and contribution of material to them are largely unknown





# Ps



## ➤ p-Ps

- singlet (para-) Ps
- $S=0$
- $LT=125$  ps
- $2\gamma$ -annihilation  
conserving momentum  
and energy
- narrow peak at 511 keV

## ➤ $\sigma$ -Ps

- triplet (ortho-)
- $S=1$
- $LT=142$  ns
- $3\gamma$ -annihilation
- $\gamma$ -ray energy distribution  
increases linear
- cutoff at 511 keV
- Annihilation strongly  
perturbed by interaction  
with surrounding  $e^-$ 
  - reduces  $\sigma$ -Ps  
lifetime while  
localized in pores

➤ inside potential well of void Ps is trapped with small loss of energy

➤ singlet interaction of  $e^+$  in  $\sigma$ -Ps with surrounding molecular  $e^-$  of opposite spin SHORTENS Ps-lt. Mixing in fast  $2\gamma$  decay during wall collisions

➤ “pick-off” annihilation decreases lifetime from

142ns  $\longrightarrow$  ~1ns

↙  
annihilation with Ps-bound  $e^-$

➔ most useful property to find out: **PORESIZE**

- Micropores ( $R \leq 2\text{nm}$ ) ➔ good correlation to QM-Tao-Eldrup model (RTE: extension to mesopores ( $R > 2\text{nm}$ ))
- if pores closed ➔ Ps trapped (“bounces like gas-atom”)
  - smaller pores ➔ faster pickoff  
➔ more  $2\gamma$ -annihilation
- if PSD ➔ distribution of Ps-lifetime

# Connected pores:

- Length scale of connection  $L_{\text{int}}$
- Ps light and mobile
  - Can diffuse over great distances (greater than film thickness)
  - $\sim 10^6$  pore-wall collisions before annihilation
  - Ps escaping into vacuum:  $LT=142$  ns
    - indicates connection
- but only part of Ps escapes
  - Profiling into various depths

- profiling into various depths
  - average pore size by mean free path of Ps  
(material must be capped by thin film)

$$\text{mean free path} = 4 \frac{V}{S}$$

V-pore volume; S-pore surface area

# PAS-techniques:

- Doppler-broadening spectroscopy (DBS)
- Angular correlation of annihilation radiation (ACAR)
- Ps-time of flight (PS-TOF)
- $3\gamma$  annihilation spectroscopy ( $3\gamma/2\gamma$  branching ratio)
- Positronium annihilation lifetime spectroscopy (PALS)
- Implantation directly from  $\beta^+$  source in sample (bulk-PAS)

➤ **Bulk-PAS:** unsuitable for thin films

- high energies
- broad energy range

➤ **Positron beam:**

- focused, mono energetic  $e^+$ , defined energy
- vacuum system
- depth profiling (varying energies)

# DBS and ACAR:

➤ Sensitive to momentum

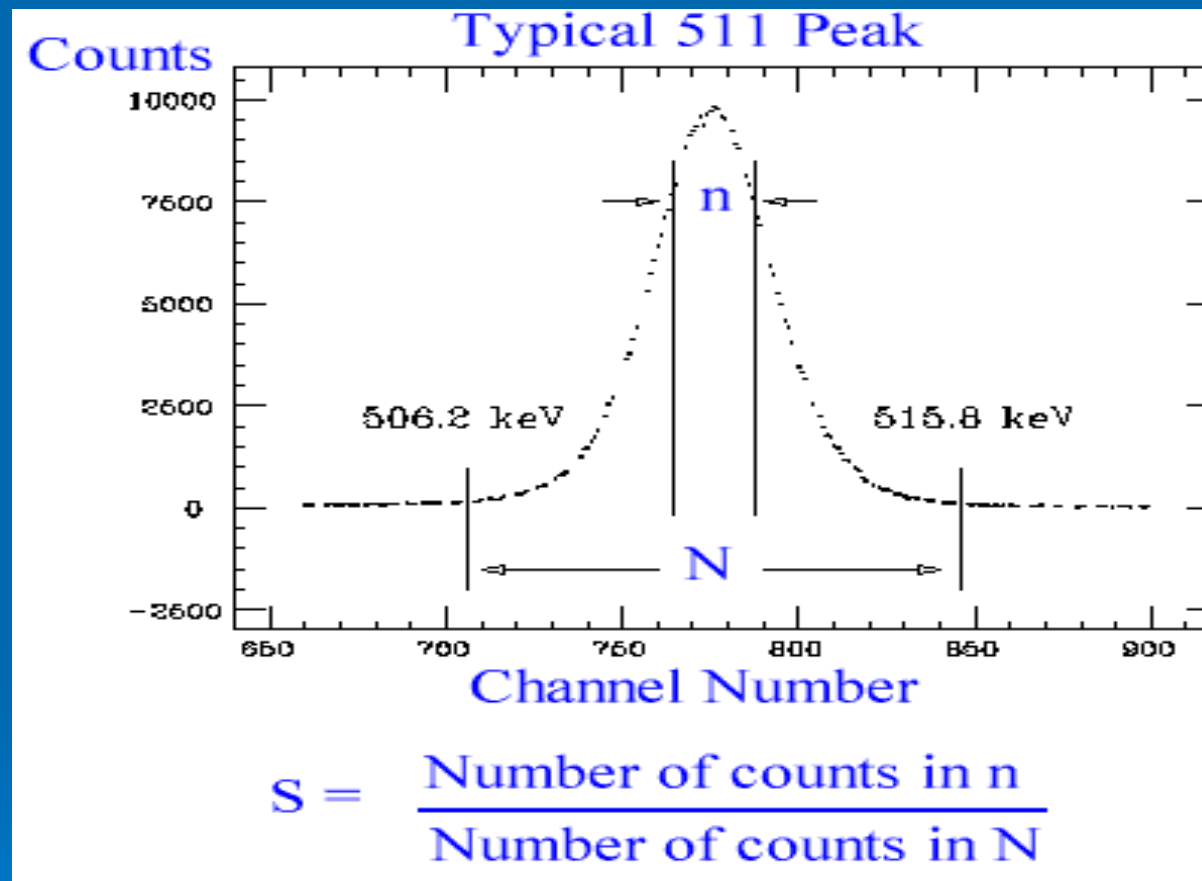


- determined by momentum of  $e^-$  in Ps and free  $e^+$  annihilation
- probe electronical and physical environment



# DBS:

- high energy resolution  $\gamma$ -detectors (germanium)



- needs sufficient calibration
- no pore size

# Coincidence DBS:

- 2  $\gamma$ -detectors (germanium) simultaneously
- better energy resolution
- useful probing pore surface chemistry



# ACAR:

- measures not energy broadening of 511 keV  $\gamma$ -rays but relative angle between them
- component of pair momentum in transverse to  $\gamma$ -ray direction
- at rest: p-Ps, Ps quenching
  - deviation angle  $\theta$  from  $180^\circ$  of the back to back gamma rays
  - $\Theta$  typically  $\sim 10$  mrad
  - $\Theta$  larger for high momentum annihilations

# ACAR Setup:

- 2 positron sensitive detectors (ACAR cameras)
- 5 meters apart → angular resolution ~mrad
- $\Theta$  calculated from 2 coincident 511 keV gamma rays
  
- difference to DBS: only p-Ps annihilation contributes
- needs intense positron beam for beam based depth-profiling

# Ps-TOF:

- porous media with highly interconnected pores
- beam forms Ps near surface of film
- narrow collimated gamma shield placed in front of one detector near front of the film
- Ps escaping film annihilates in collimator  
→ TOF recorded
- Time histogram can be converted to energy distribution

# Ps TOF:

- beam energy varies:

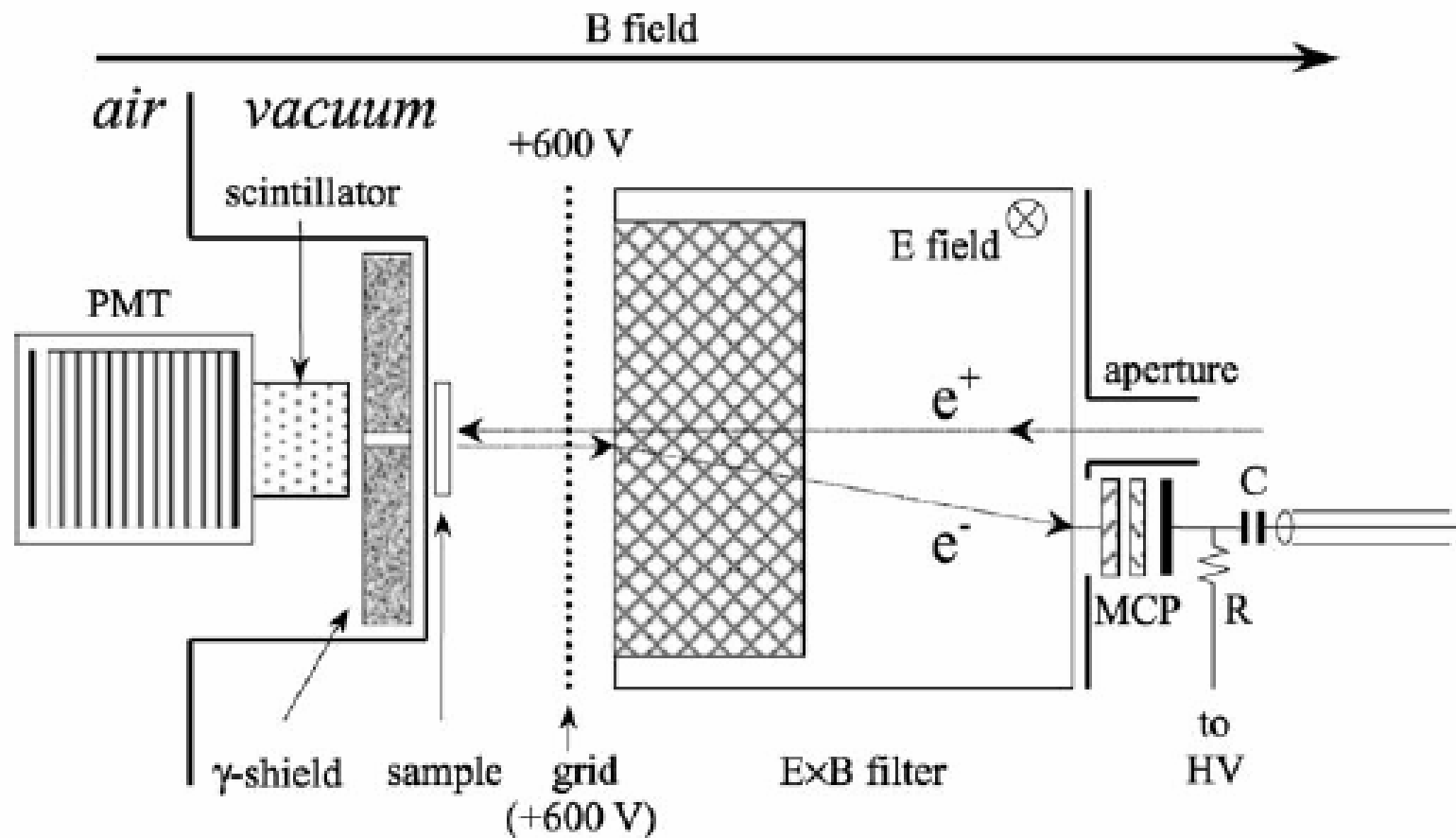


- degree of Ps than can thermalize and its escape-energy varies
- useful to understand thermalisation and diffusion in pores
  - check interconnection
- no pore size, not suitable for closed pores

# PALS and $3\gamma/2\gamma$ :

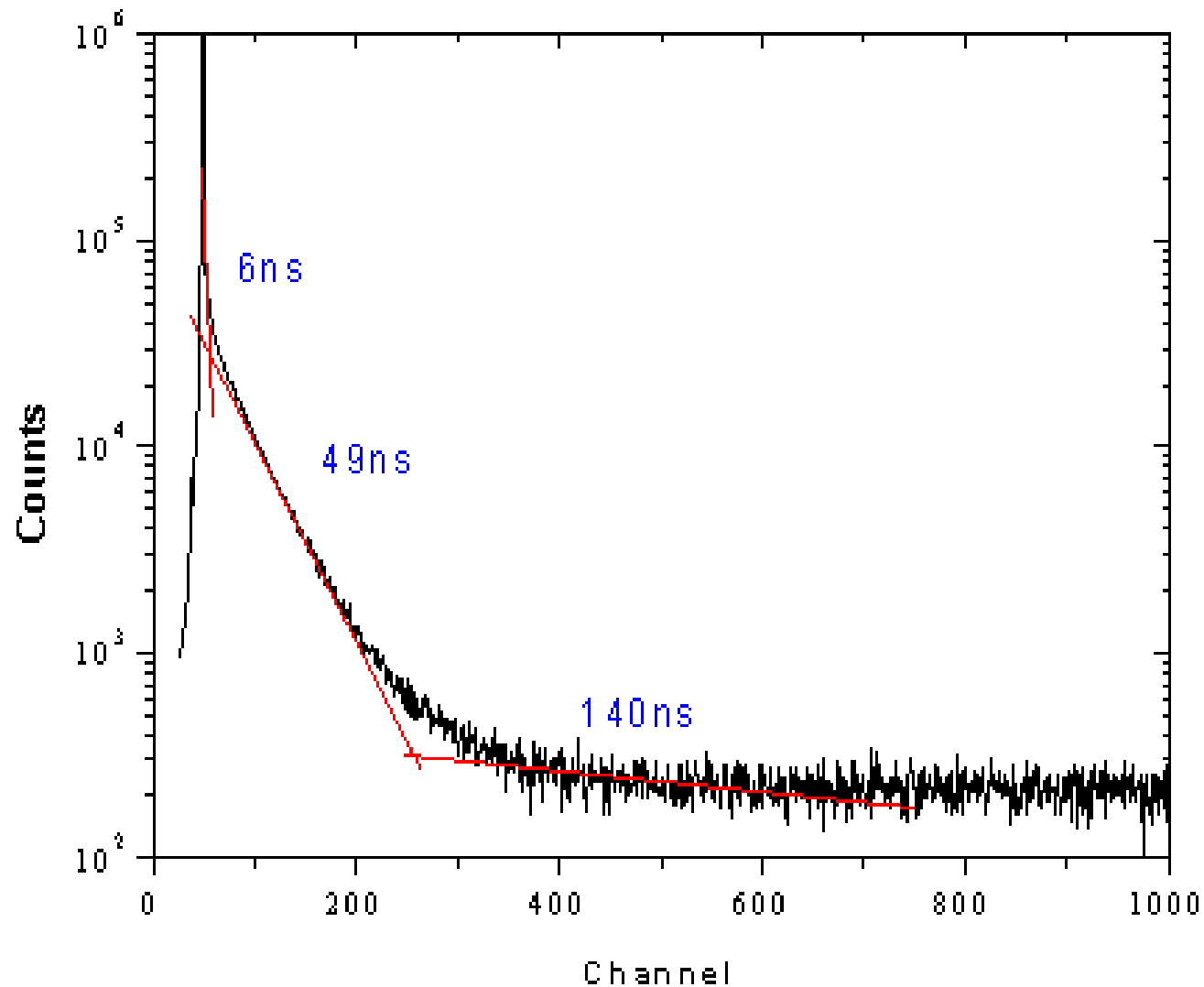
- most used and useful methods
- determine pore size, interconnectivity, depth-dependent film inhomogeneities
- use of positron beam
- **Lifetime measurement:**
- Start Signal: While being implanted into the film, positrons knock off secondary electrons which starts the timing clock. (The time for positrons to form Ps is on the order of picosecond, i.e.,  $10^{-12}$  sec, which can be neglected compared to Ps lifetime on the order of nanosecond.)
- Stop signal: Ps annihilates into gamma-rays, which stops the timing clock

# Lifetime setup for Beam



**Figure 2** The magnetically guided PAS beam/spectrometer at Washington State University. From Reference 4.





A typical PALS spectrum with three film Ps lifetimes fitted using POSFIT. The points for each channel have been connected with a line for visual clarity. Each channel corresponds to 1.25 ns

$3\gamma/2\gamma:$

➤ Energy spectrum

3 $\gamma$  spectra

2 $\gamma$  spectra

➤ Calculation of  $3\gamma/\gamma^2$  ratio

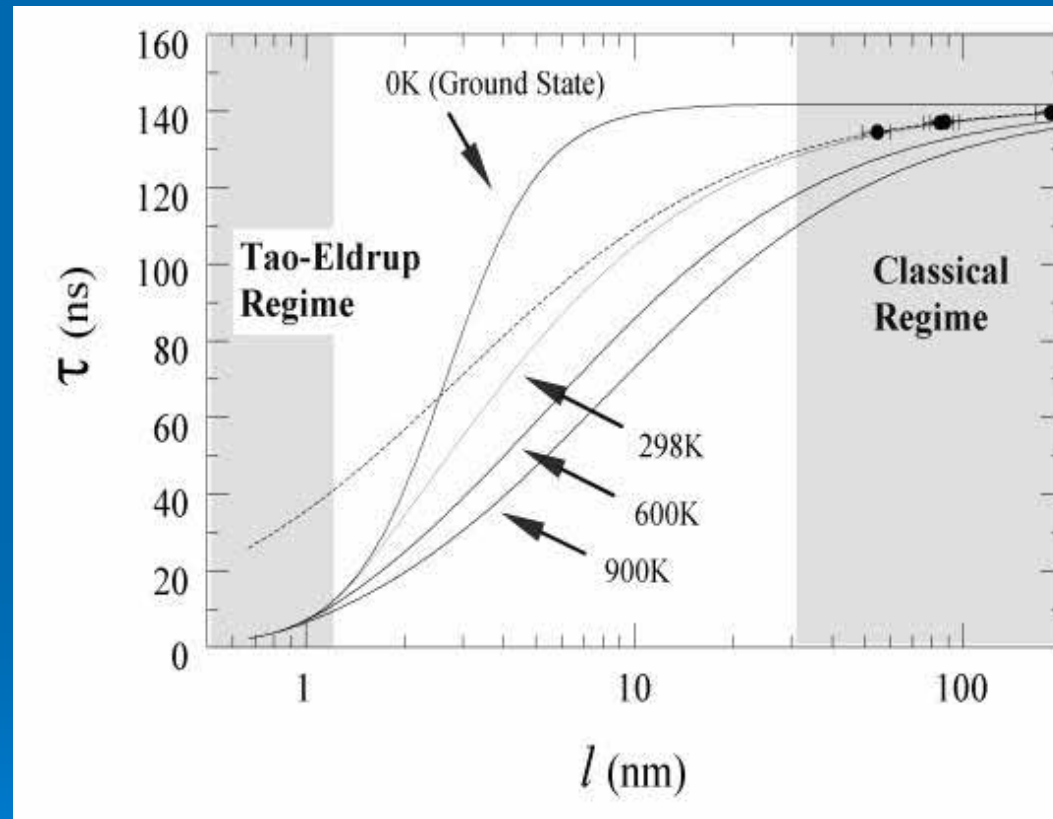
➤ increasing in larger pores

## ➤ Tao-Eldrup:

- unuseful for pore sizes approaching thermal De Broglie wavelength of Ps

~ 6 nm

## ➤ extension for larger pores: RTE



- Pore-size calibration calculated at different temperatures using a cubical pore shape model. The 0K (ground state) curve given by the Tao-Eldrup model and the dashed curve given by the classical model are presented for comparison

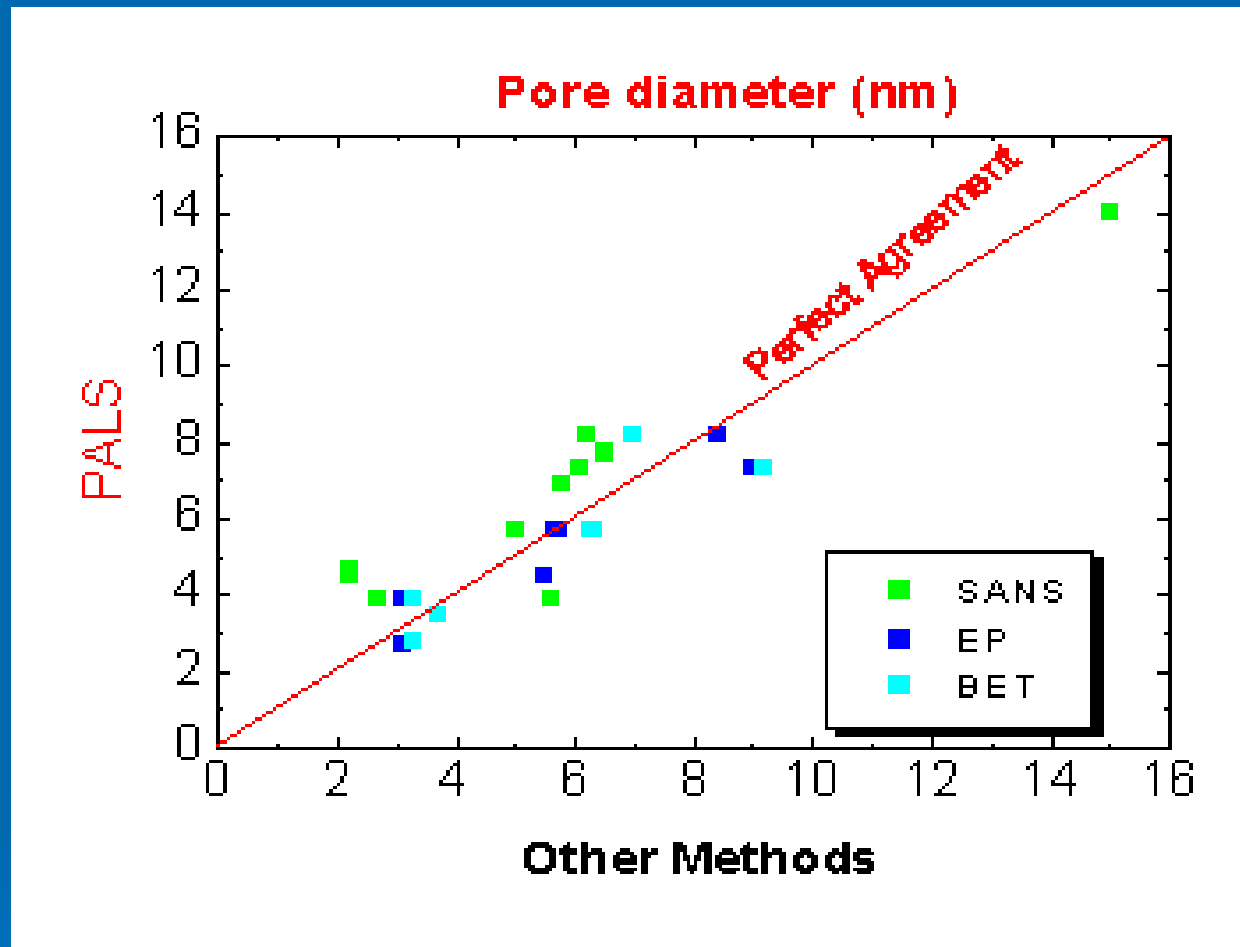
# Tao-Eldrup:

$$\lambda = \frac{1}{\tau} = \lambda_{pickoff} + \lambda_{vac}$$

$$\lambda_{vac} = \frac{1}{142ns}$$

- RTE: at given temperature and assumed pore shape → curve measuring lifetime versus pore dimension can be calculated
- conversion to classical mean free path → mean distance between P's pore wall collisions → pore size
- not specific to pore geometry

# round-robin:



SANS: small angle neutron scattering

EP: ellipso-metric porosimetry

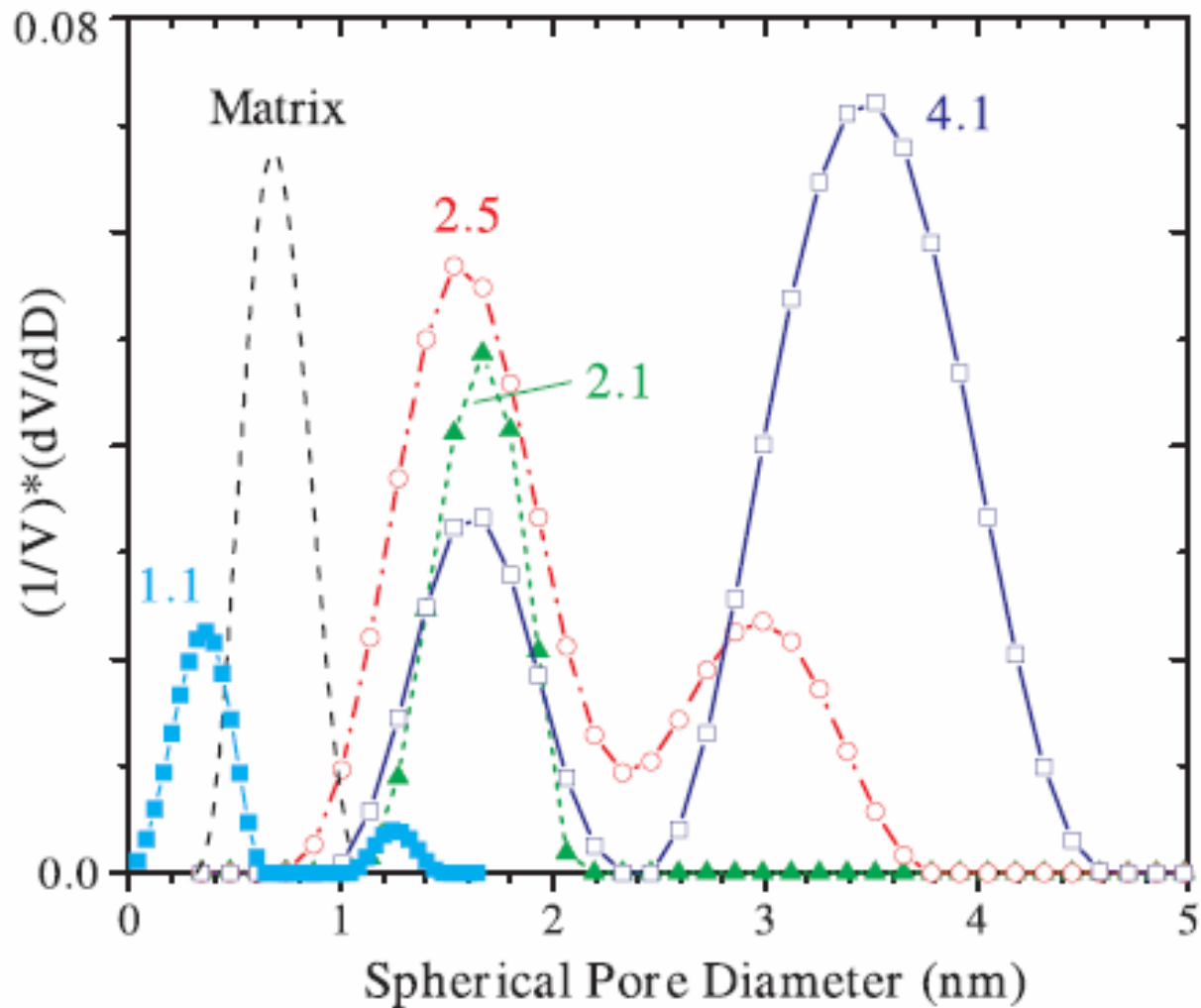
BET: gas absorption

# PSD:

- Fitting of decay spectrum to a continuum of lifetimes using CONTIN or MELT
- Converted into fractional pore volume as a function of a f. e. spherical pore diameter



# PSD:



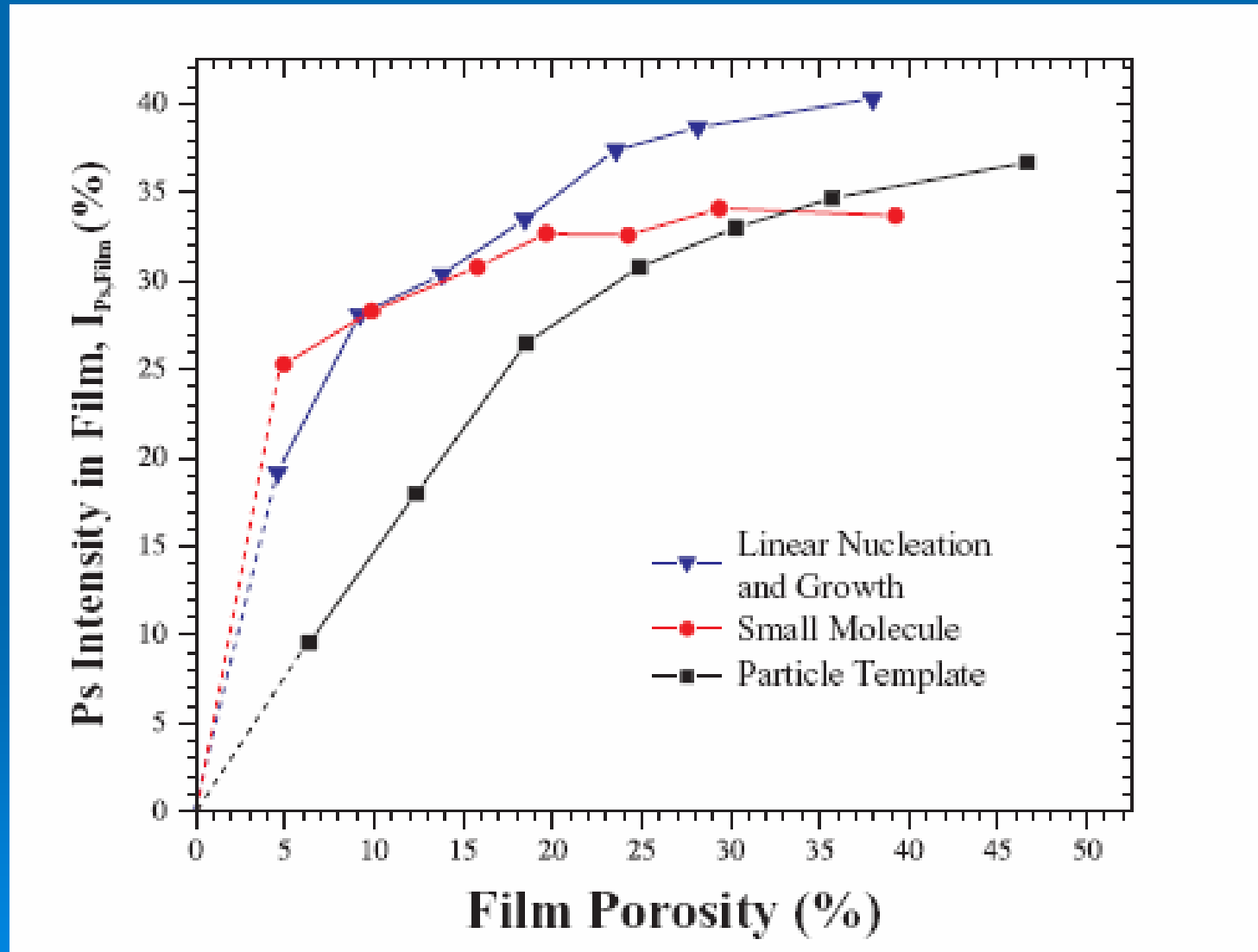
**Figure 6** Plausible PSDs in a low-k film for a variety of positron beam energies (in keV) determined from continuum lifetime fitting. This film has a complicated depth dependence to porosity. The curve labeled “matrix” has no engineered pores.

# Determination of Film Porosity:

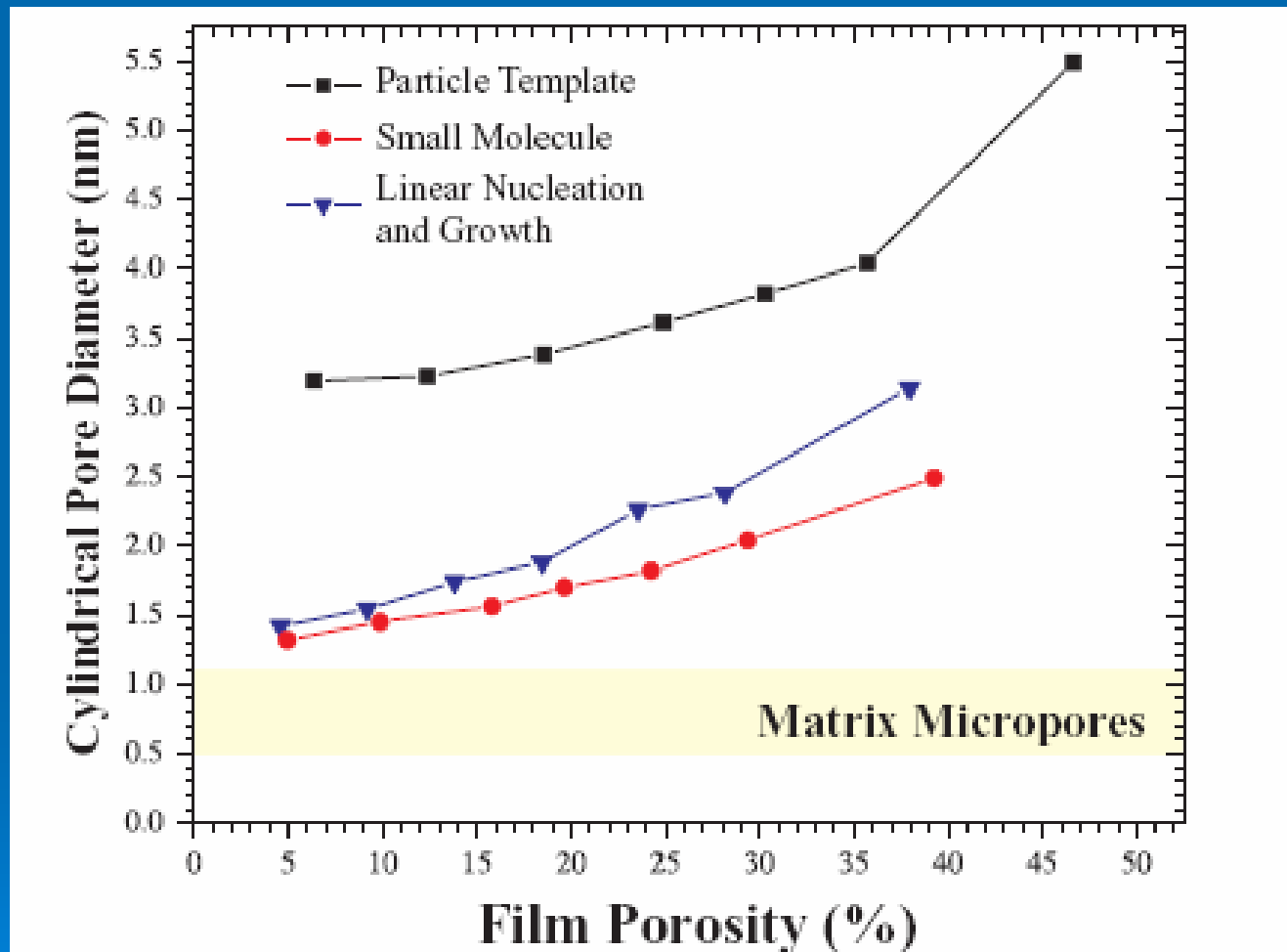
- complicated dependence of Ps-annihilation intensity on pore size and porosity
- no unique correspondence from fitted Ps-intensity or  $3\gamma/2\gamma$  to porosity
- independent measures of porosity required



# Determination of Film Porosity:



# Determination of Film Porosity:



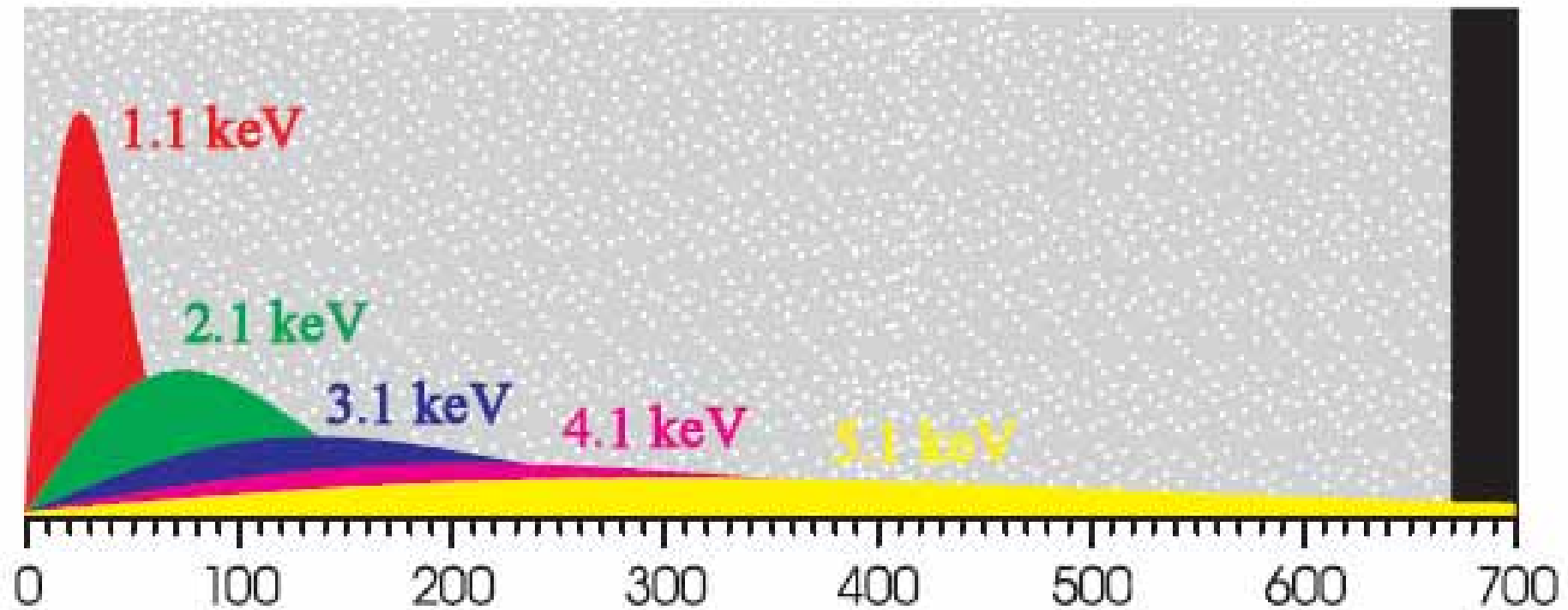
# Depth-profiling of films:

- powerful feature of beam-based PAS
- Mean positron implantation depth:  $\bar{Z} = \frac{40}{\rho} E^{1,6}$

E - beam energy;  $\rho$  – film density in g/cm<sup>3</sup>

- corresponds well to Ps-forming profile but not to annihilation profile (connected pores)
- Depth-dependent variations of Ps-intensity reflect changes in porosity
- Lifetime indicates pore size variations (closed pores)

# Depth-profiling of films:

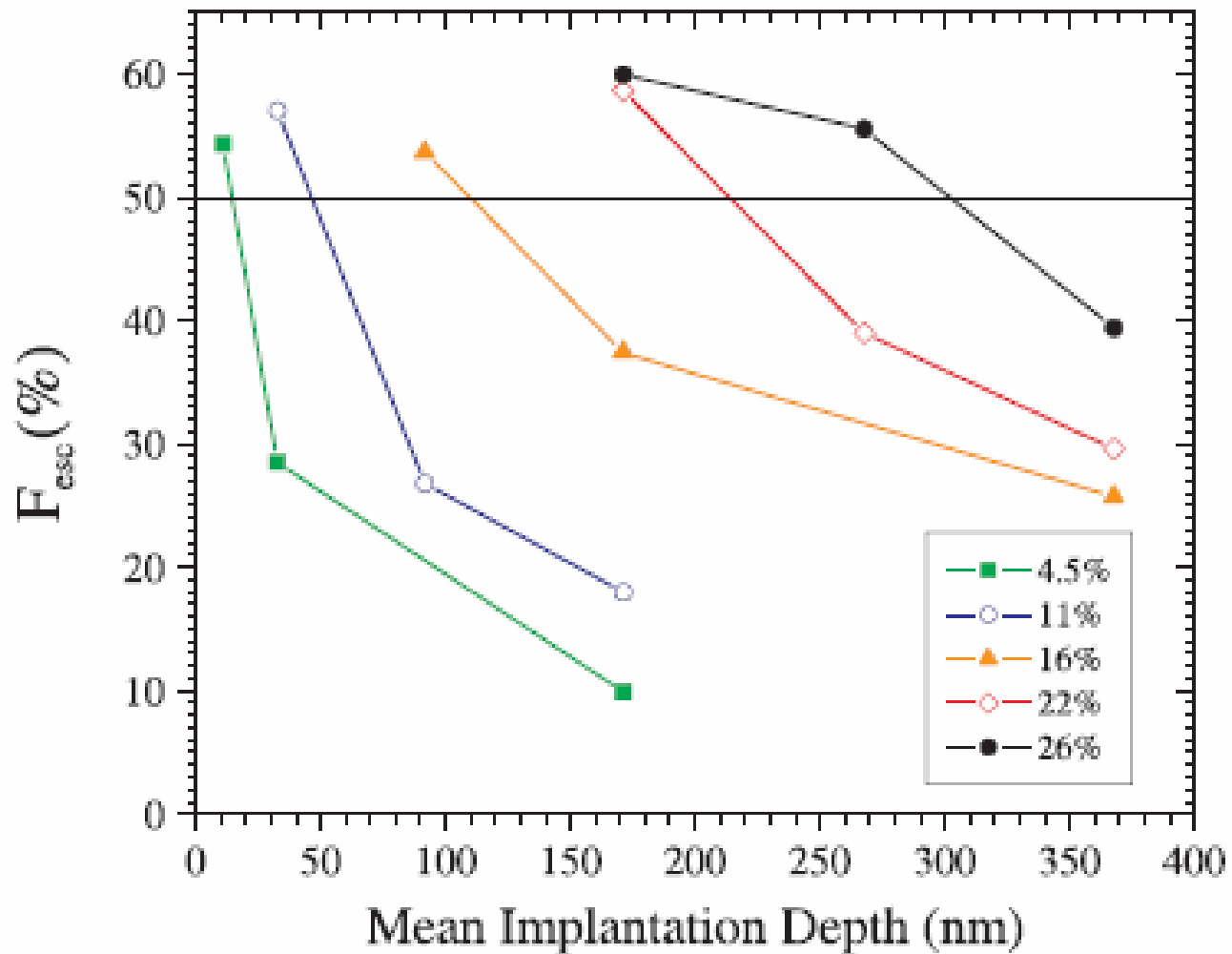


**Figure 8** Positron implantation profiles for several beam energies calculated for  $\sim 45^\circ$  incidence on a film of density  $1 \text{ g cm}^{-3}$ .

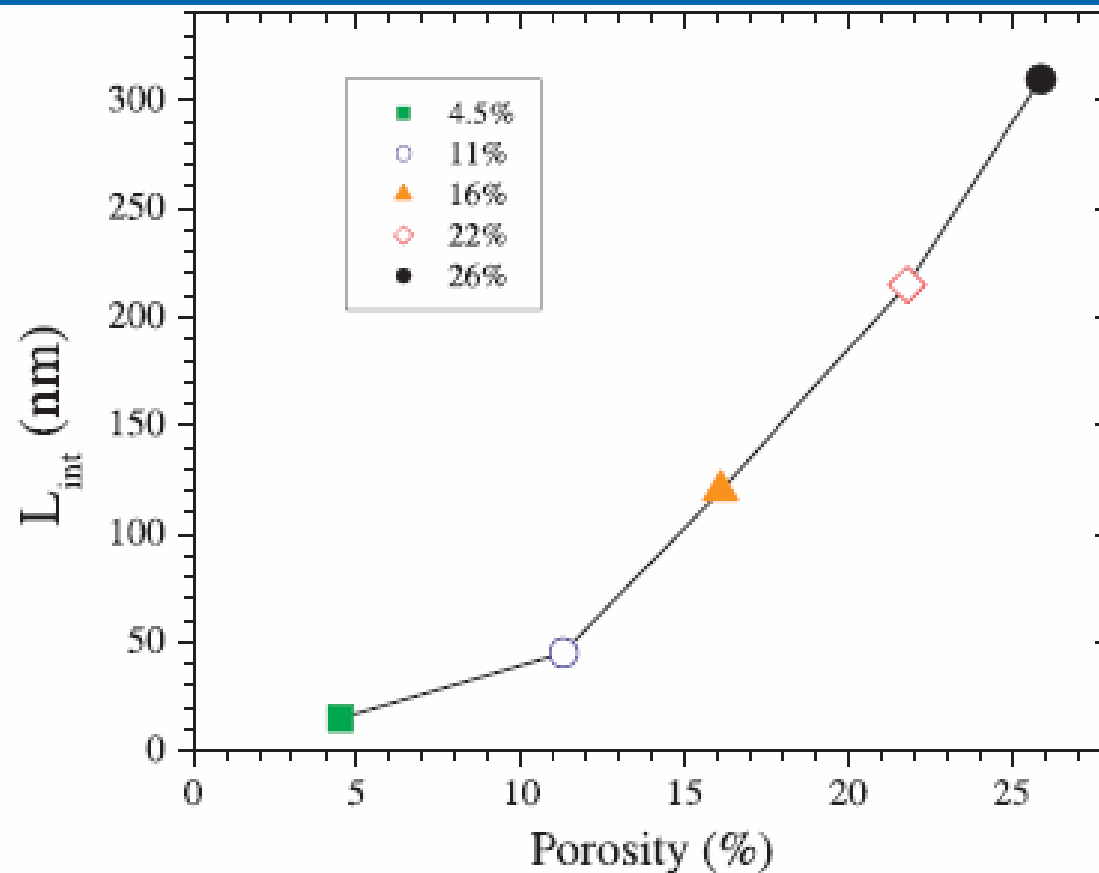
# Depth-profiling of films:

- Reveals  $L_{int}$ :
- Ps-light and mobile - can diffuse 1000nm-thick film (fully interconnected pores)
- Annihilation in vacuum(142 ns, high  $3\gamma/2\gamma$  ratio)
- Measuring escaping-Ps fraction of film as function of implantation length
- calculation of mesopore  $L_{int}$ :
  - mean implantation depth from which 50% Ps escape the film

# Depth-profiling of films:



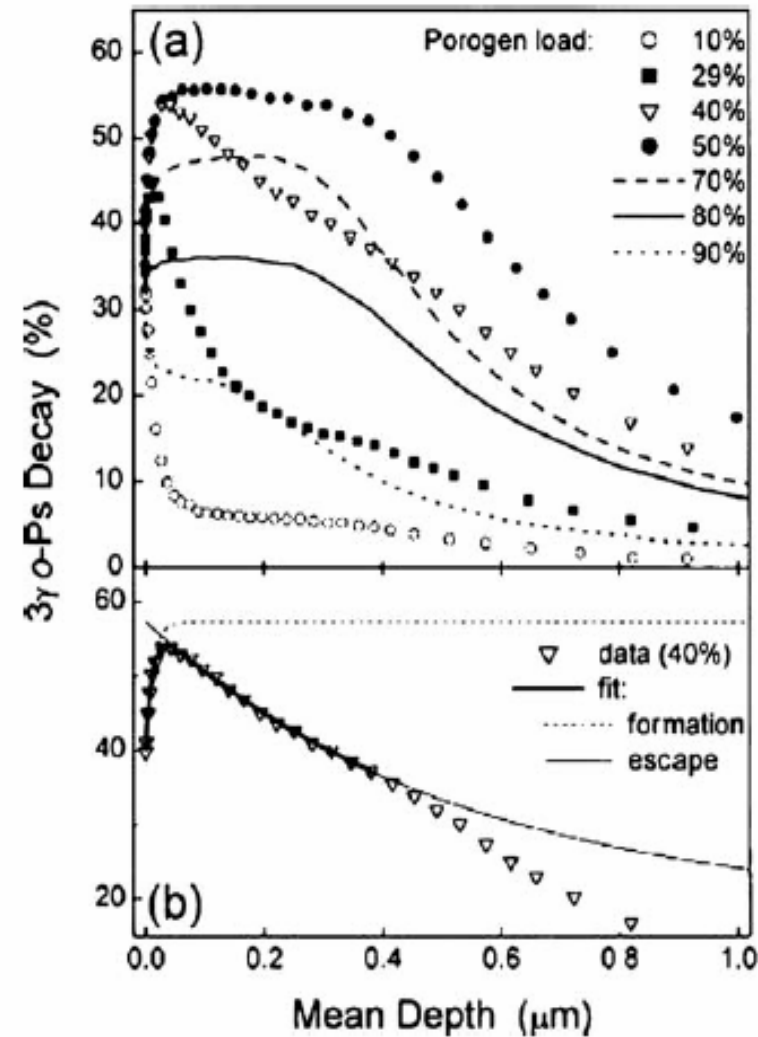
# Depth-profiling of films:



**Figure 9** Plot of the Ps escape fraction ( $F_{esc}$ ) as a function of mean positron implantation depth (*top*) used to calculate the mesopore interconnection length ( $L_{int}$ ) (*bottom*) for films of increasing porosity. This film is a cyclodextrin-based porogen in a MSSQ matrix.

# Depth-profiling of films:

- Information from  $3\gamma/2\gamma$  ratio:

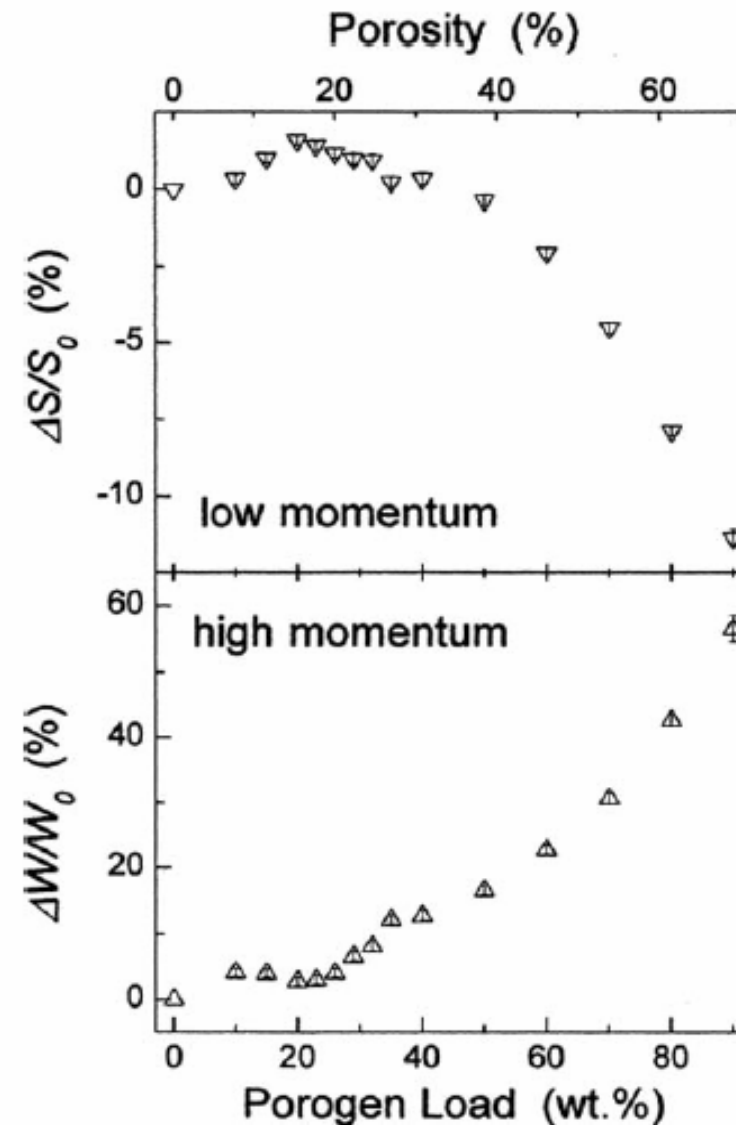


**Figure 10** Typical depth-profile of the  $3\gamma$  fraction for several porogen weight fractions. The lower panel is a fit of the data to a diffusion model to determine  $L_{\text{int}}$ . Reprinted with permission from Reference 28. Copyright 2005, American Institute of Physics.



# Depth-profiling of films:

- DBS parameters  $s, w$  also sensitive:



**Figure 11** Plot of the change in low-momentum (S) and high-momentum (W) parameters as a function of film porosity. Reprinted with permission from Reference 5. Copyright 2003, American Chemical Society.

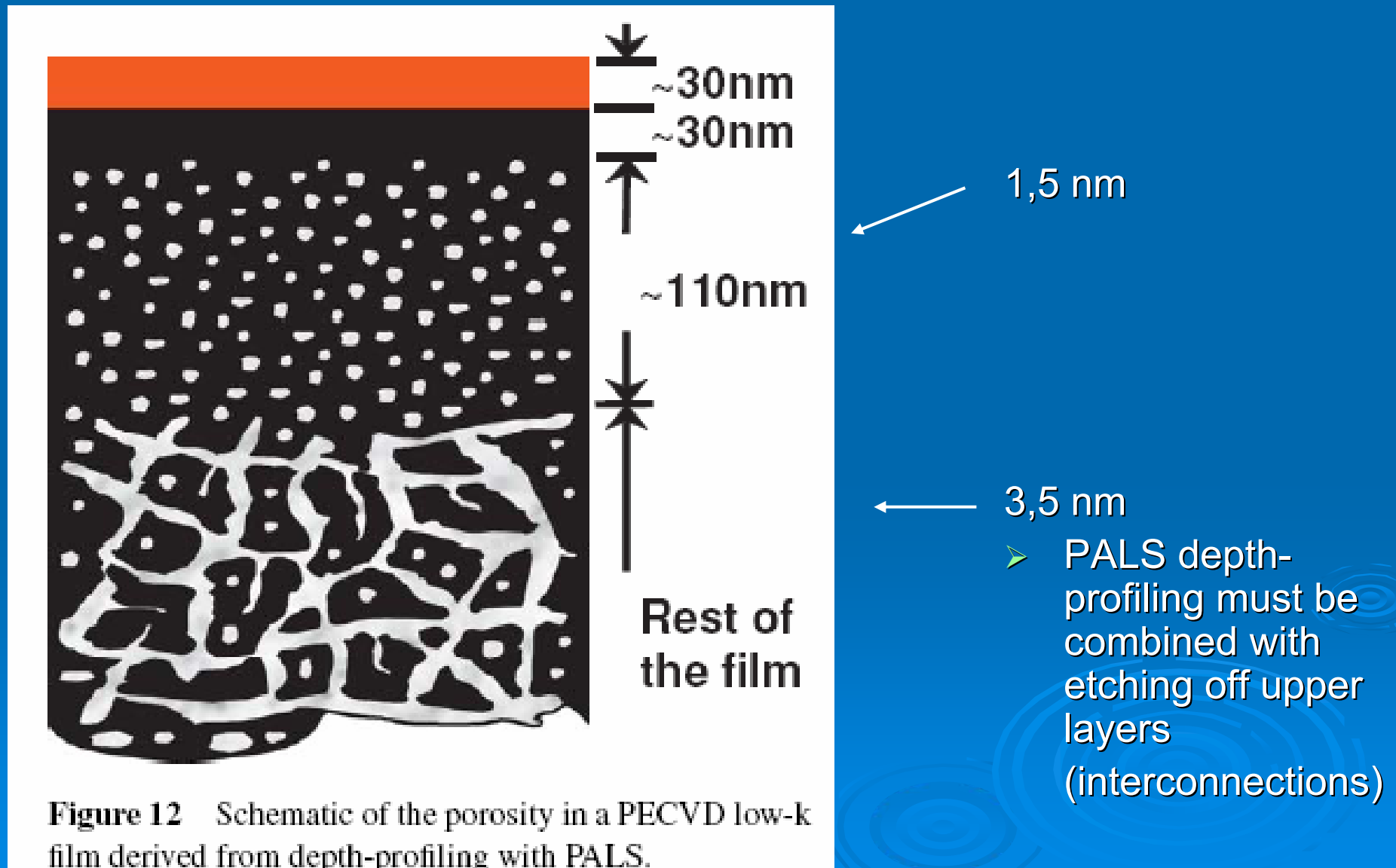
# Porosity variations in film depth:

- What if film not homogeneous?
- Beam-based PAS can study hidden porosity (diffusion barriers, capping layers...)
- diffusion barriers sealing can be tested



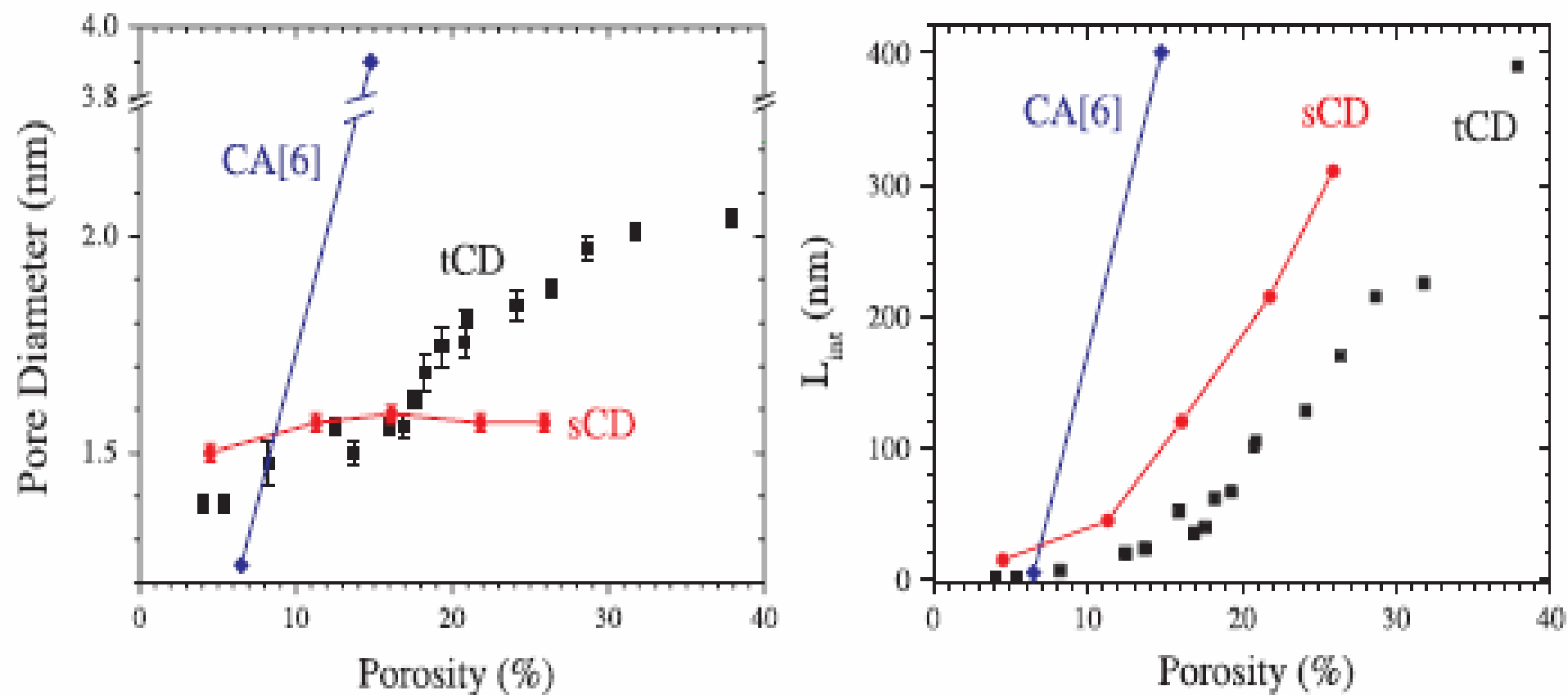
# Porosity variations in film depth:

- multilayer model:



# Pore shape and growth:

- understanding important for controlled pore design (determined pore size and interconnectivity)
- PALS can simultaneously characterize size and interconnection length
- Study nanoporosity from isolated pores to interconnected network
- 3 porogens:
  - CA:calix arene porogens
  - CD:cyclodextrin porogens
    - tCD-methoxyl functional group
    - sCD-trimethoxyl functional group



**Figure 13** Plots of pore diameter (*left*) and pore interconnection length (*right*) as a function of porosity for MSSQ films made with three different porogens. The growth modes for the porogens are dramatically different.

# Pore shape and growth:

- sCD: produces cylindrical growth
- tCD: three-dimensional growth
- CA: explosive growth beyond critical concentration (7%-15% porosity)

# Thanks for listening!

- <http://positron.physik.uni-halle.de>
- <http://positrons.physics.lsa.umich.edu>