# Positron Annihilation as a Method to Characterize Porous Materials

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by

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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)

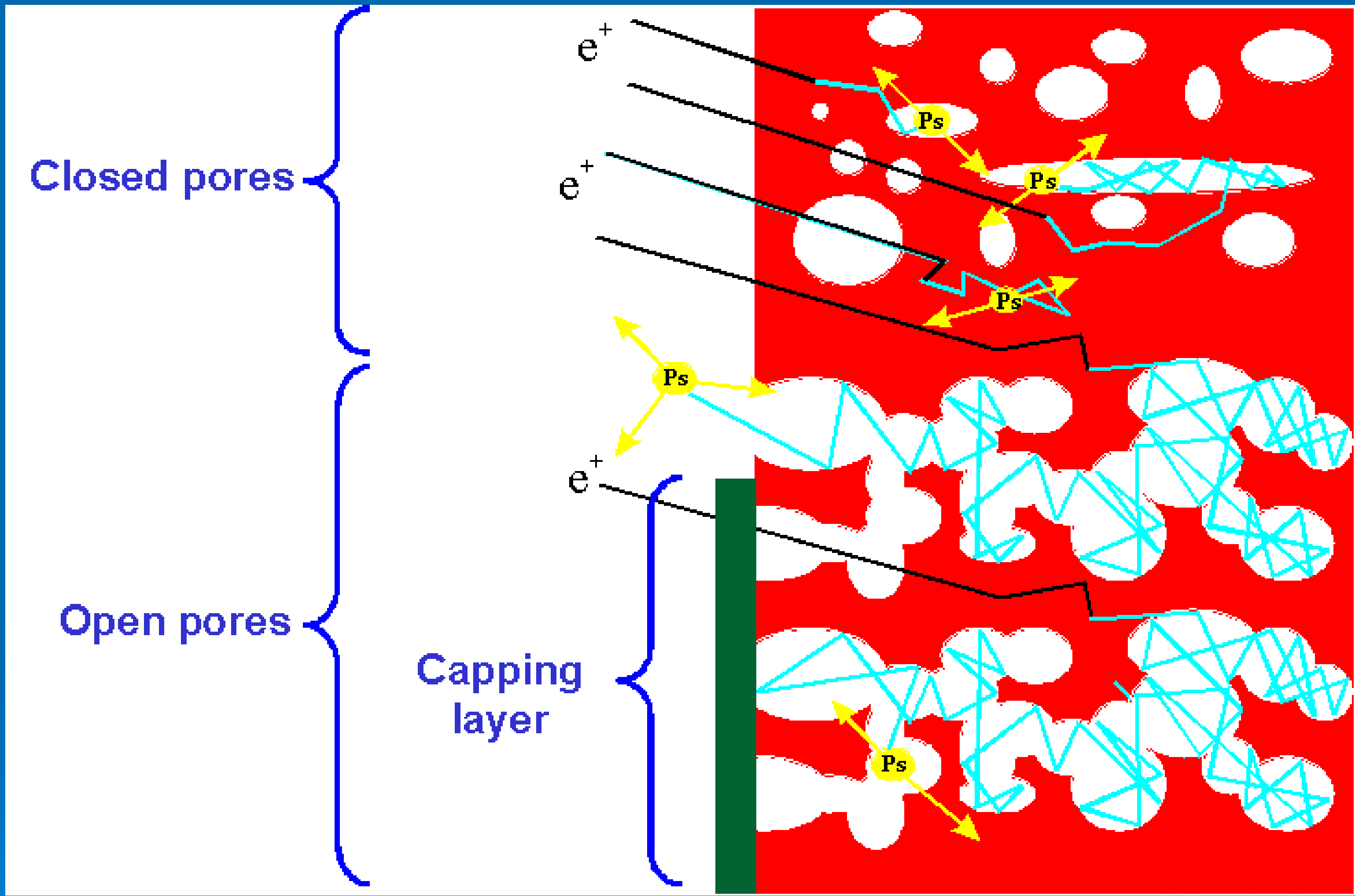
# Main spectroscopies:

- 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)**
- **<u>Forming Ps</u>**

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

- **σ-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 σ-Ps lifetime while localized in pores

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

- singlet interaction of $e^+$ in σ-Ps with surrounding molecular $e^-$ of <u>opposite spin</u> SHORTENS Ps-lt. Mixing in fast 2γ 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 ($R \leq 2$nm) → good correlation to QM-Tao-Eldrup model (RTE:extension to mesopores ($R > 2$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 $\mathbf{L_{int}}$
- Ps light and mobile
  - Can diffuse over great distances (greater than film thickness)
  - ~ $10^6$ 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)

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

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

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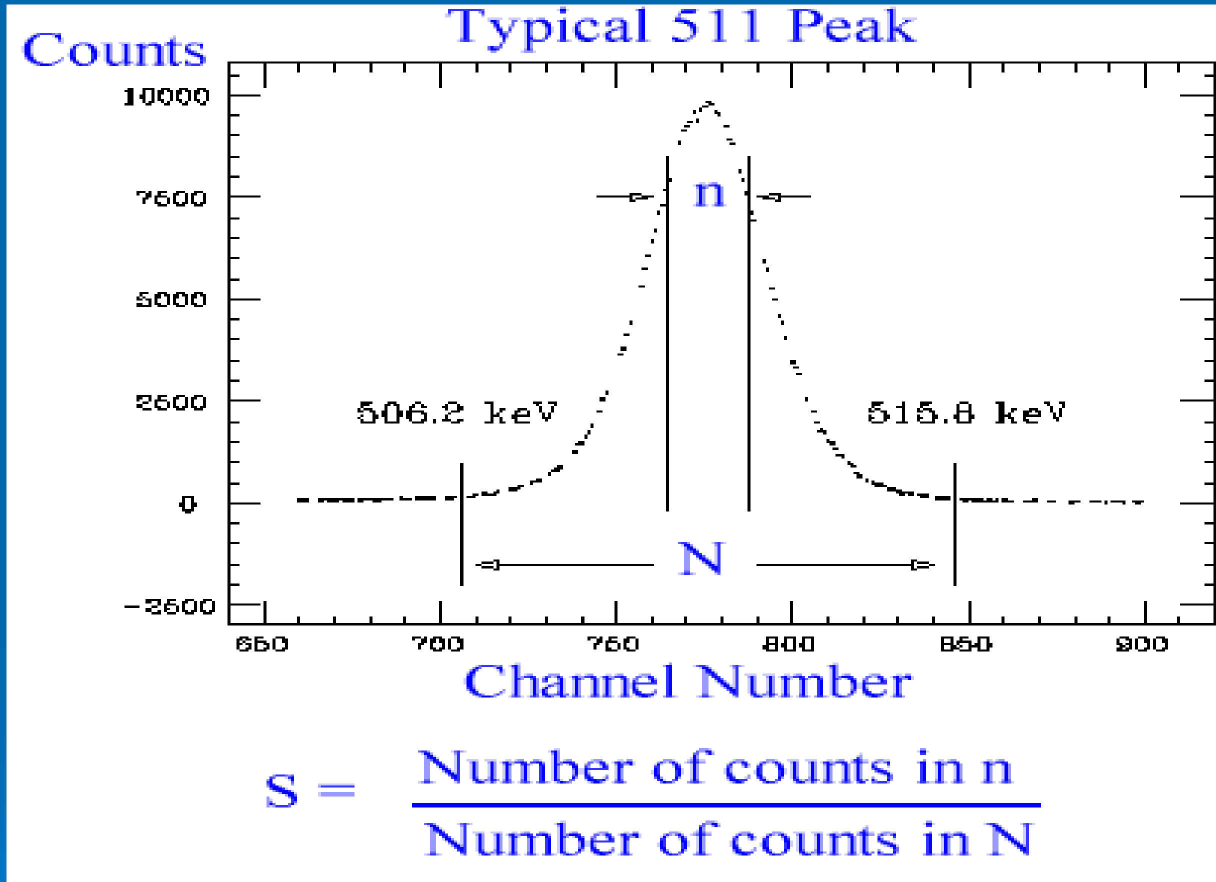
  - determined by momentum of $e^-$ in Ps and free $e^+$ annihilation
  - probe electronical and physical environment

# DBS:

- high energy resolution γ-detectors (germanium)




- needs sufficient calibration
- no pore size

# Coincidence DBS:

- 2 γ-detectors (germanium) simultaneously
- better energy resolution
- useful probing pore surface chemistry

# ACAR:

- measures not energy broading of 511 keV γ-rays but relative angle between them
- component of pair momentum in transverse to γ-ray direction
- at rest: p-Ps, Ps quenching
  - deviation angle θ from $180^0$ of the back to back gamma rays
  - Θ typically ~10mrad
  - Θ larger for high momentum annihilations

# ACAR Setup:

- 2 positron sensitive detectors (ACAR cameras)
- 5 meters apart ⇨ angular resolution ~mrads
- Θ 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 collominated gamma shield placed in front of one detector near front of the film
- Ps escaping film annihilates in collominator
  → TOF recorded

- Time histogram can be converted to energy distribution

# Ps TOF:

- beam energy varies:

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- 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 3γ/2γ:

- most used and useful methods
- determine pore size, interconnectivity, depth-dependent film inhomogeneities
- use of positron beam
- **Lifetime measurement:**
- <u>Start Signal:</u> 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.)
- <u>Stop signal:</u> Ps annihilates into gamma-rays, which stops the timing clock

# Lifetime setup for Beam

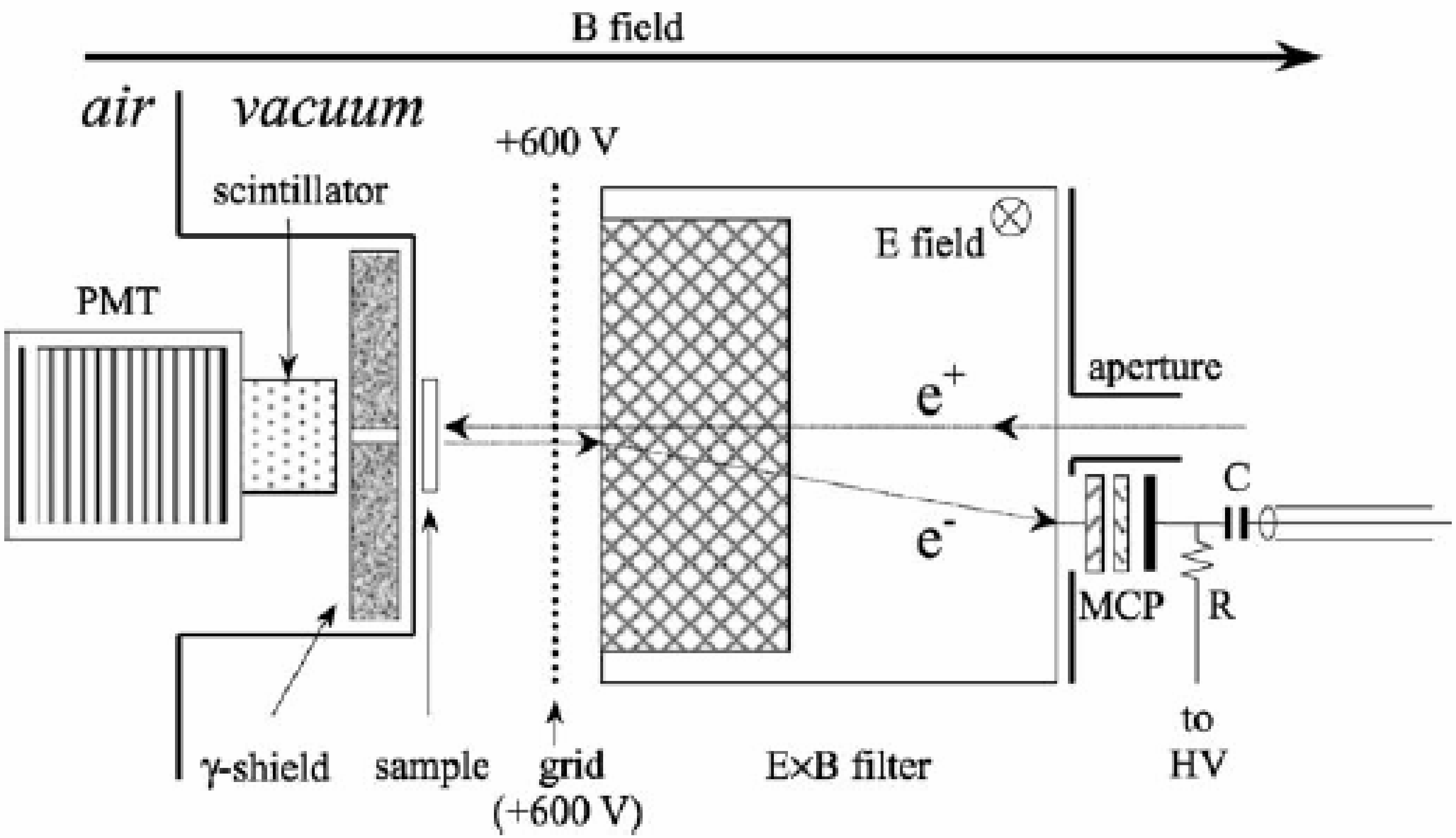
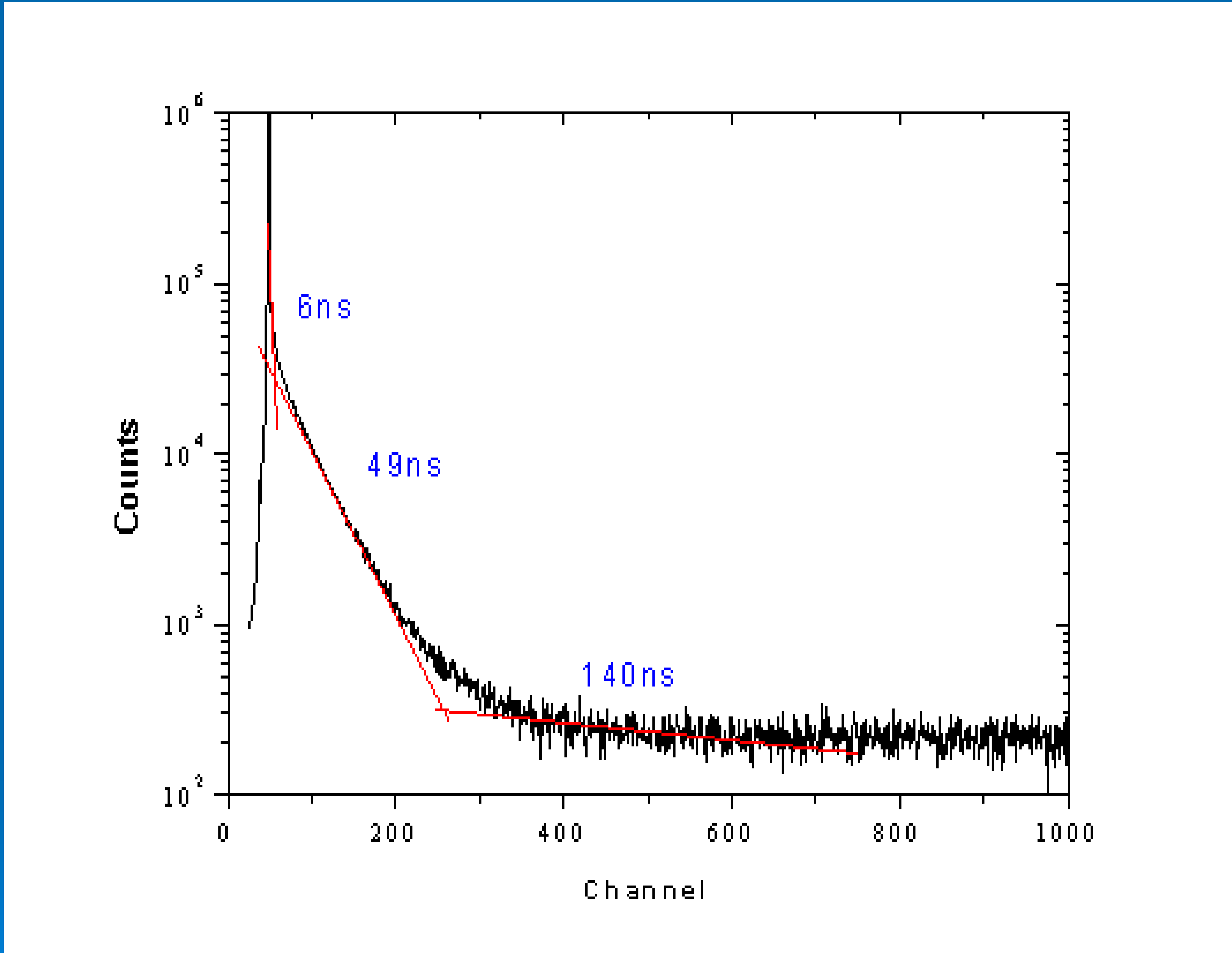



**Figure 2** The magnetically guided PAS beam/spectrometer at Washington State University. From Reference 4.




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

# 3γ/2γ:

- Energy spectrum

3γ spectra

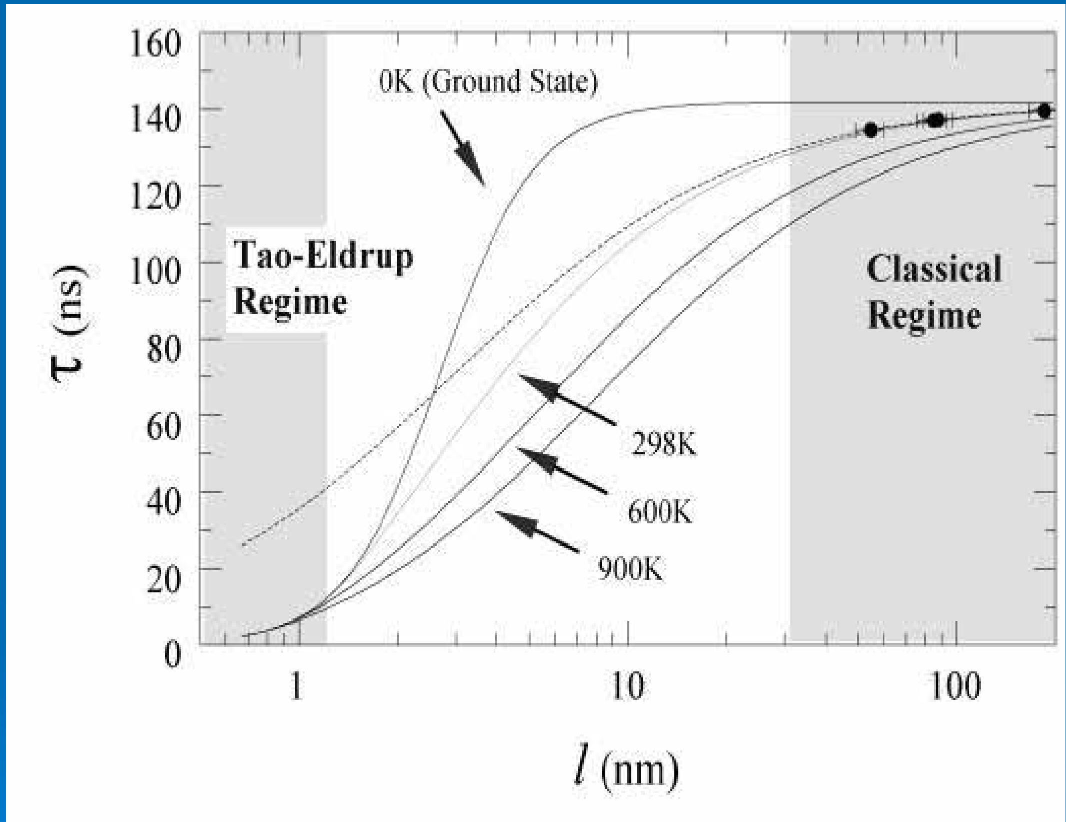
2γ spectra

- Calculation of 3γ/γ2 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**

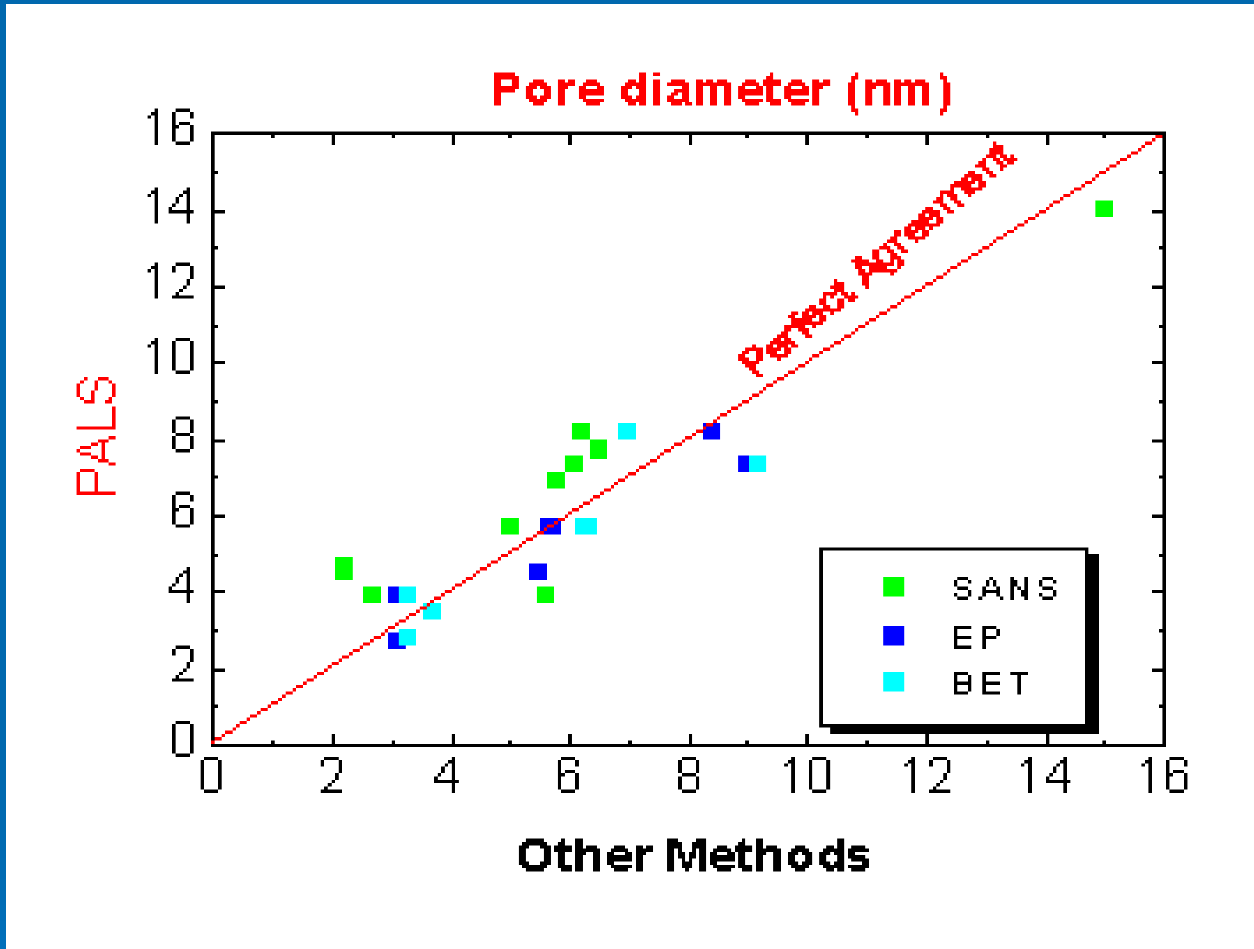
# Tao-Eldrup:

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

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

- RTE: at given temperature and assumed pore shape $\longrightarrow$ curve measuring lifetime versus pore dimension can be calculated
- conversion to classical mean free path $\longrightarrow$ mean distance between Ps pore wall collusions $\longrightarrow$ 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:

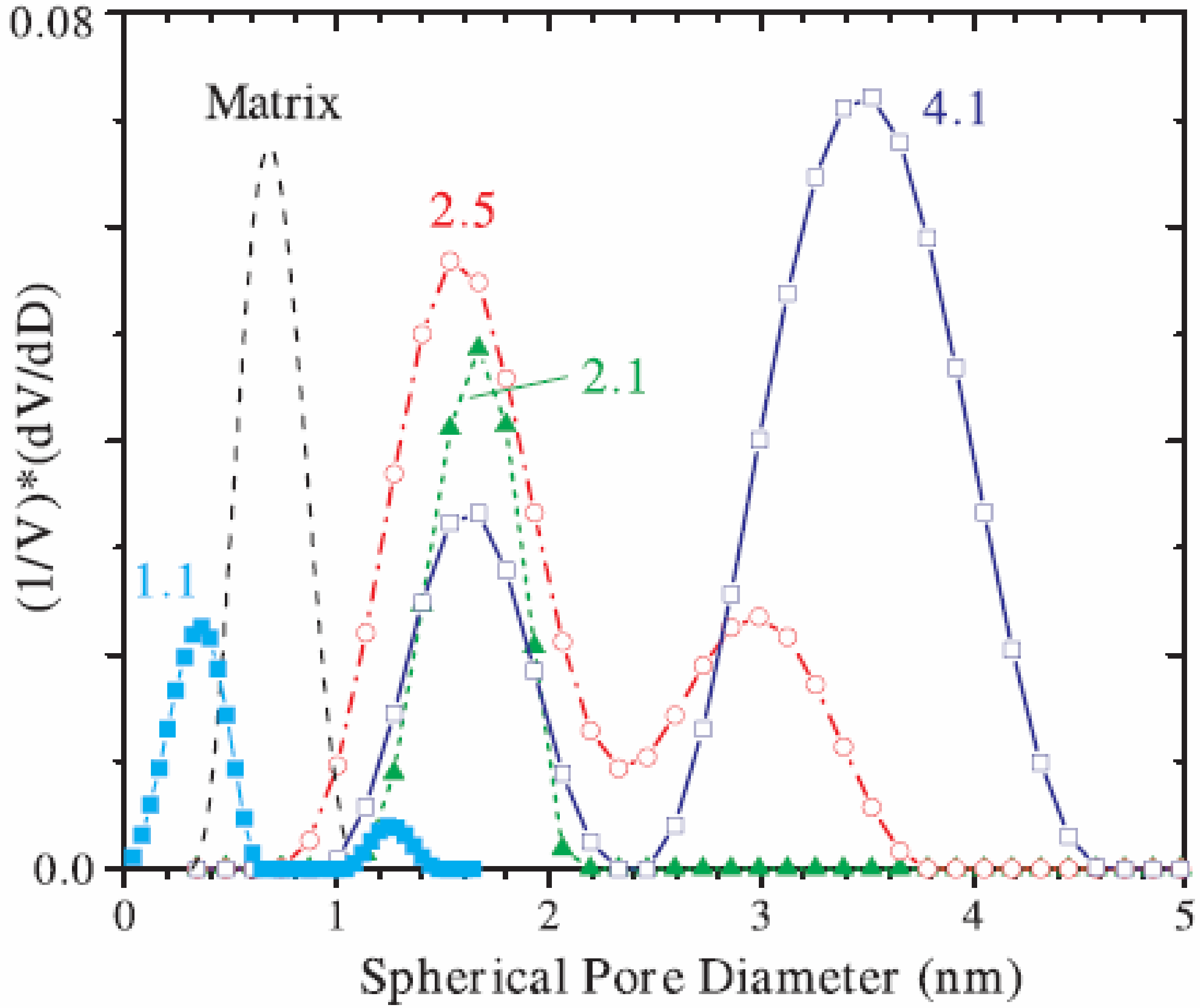
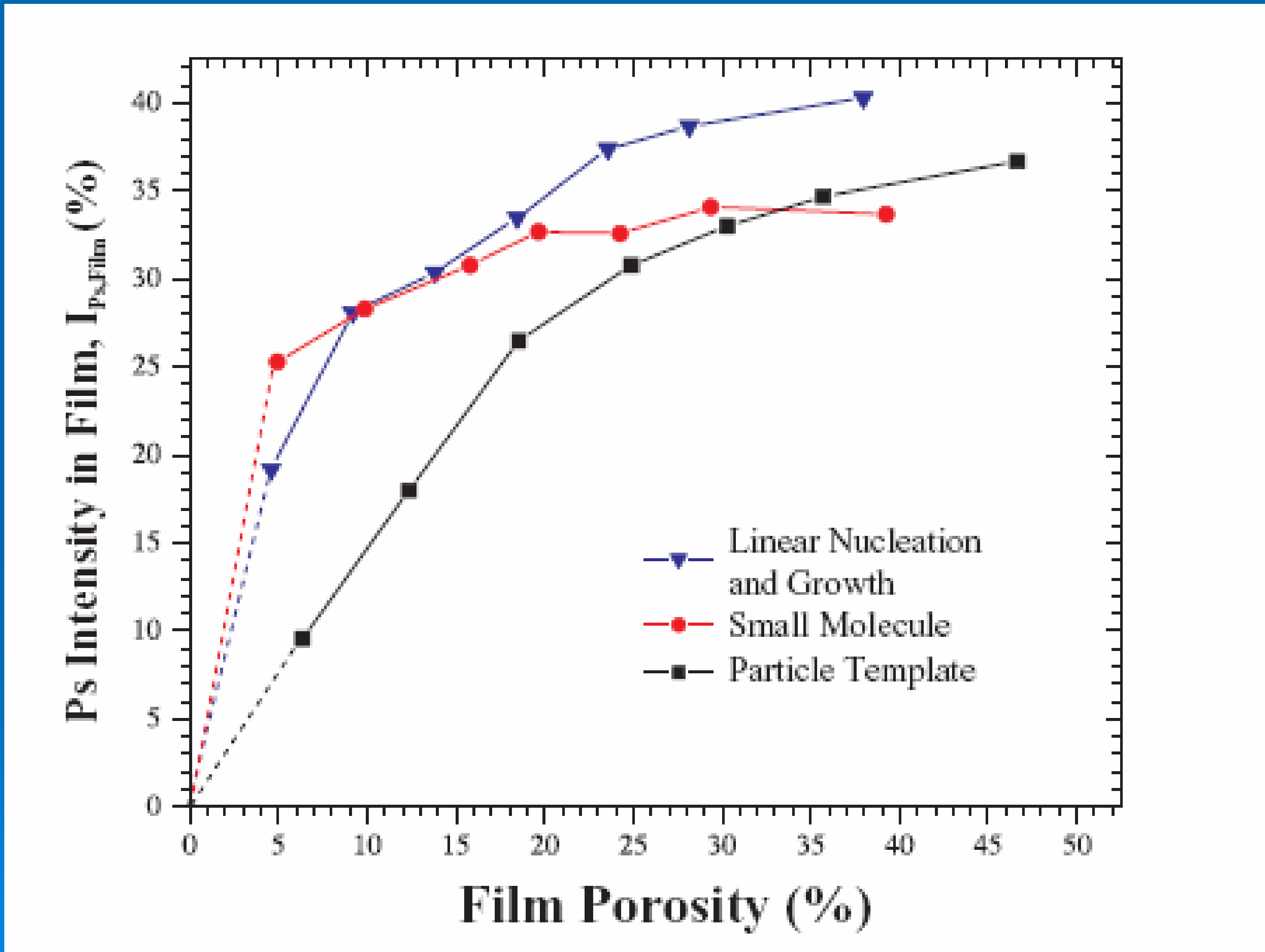



**Figure 6** Plausible PSDs in a low-k film for a variety of positron beam energies (in keV) determined from continuum lifetime fitting. This film has a complicated depth dependence to porosity. The curve labeled "matrix" has no engineered pores.

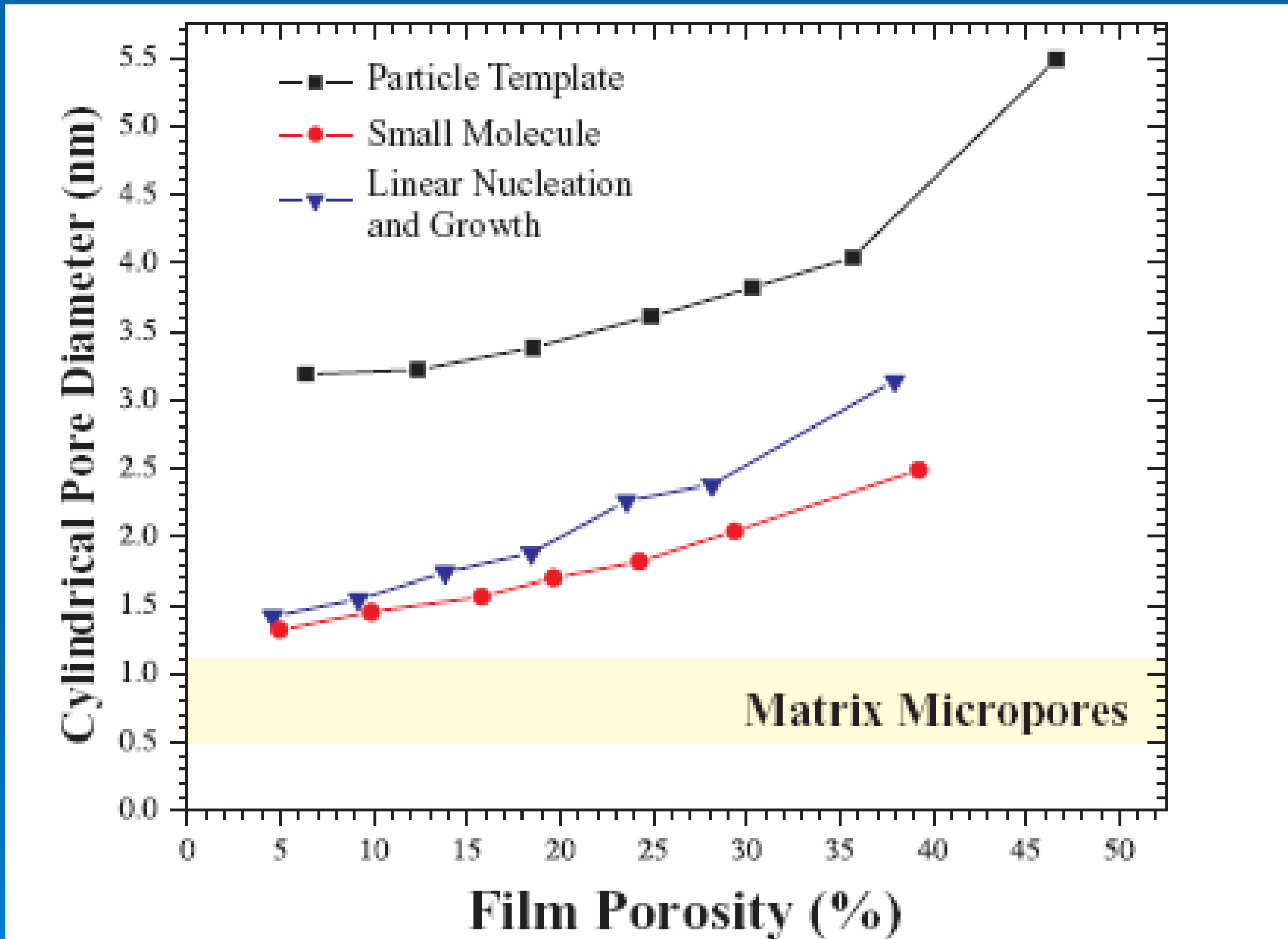
# Determination of Film Porosity:

- 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 implatation depth: $\overrightarrow{Z} = \frac{40}{\rho} E^{1,6}$

E - beam energy; ρ – film density in g/cm$^3$

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

# Depth-profiling of films:

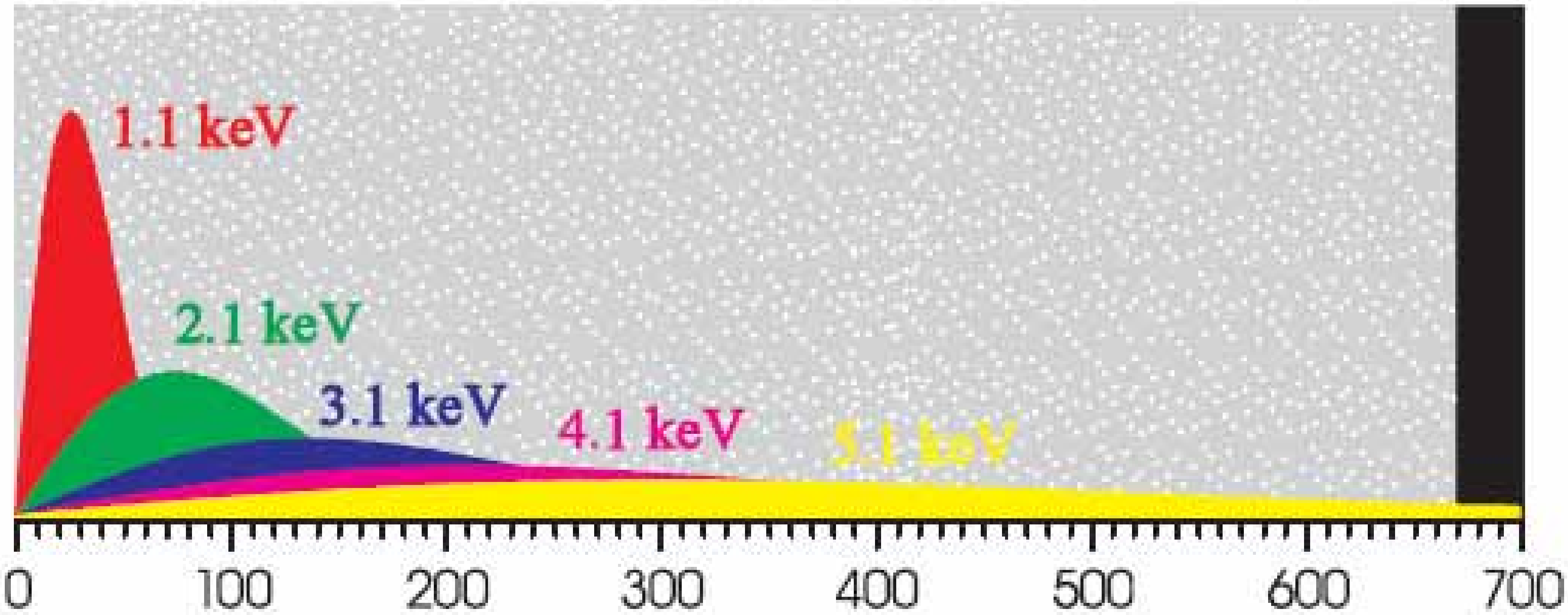
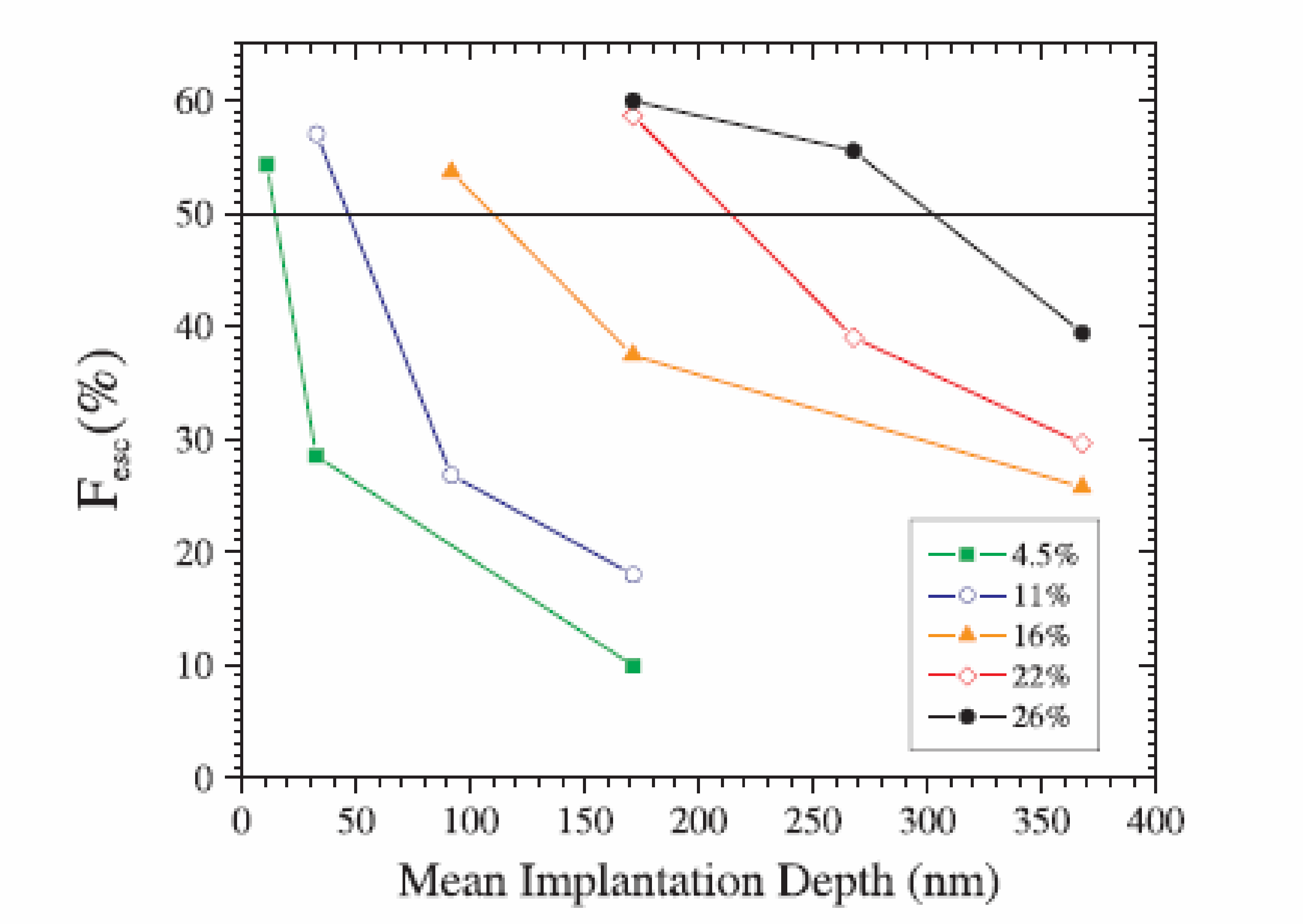



**Figure 8** Positron implantation profiles for several beam energies calculated for ~45° incidence on a film of density 1 g cm$^{-3}$.

# 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 3γ/2γ 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:

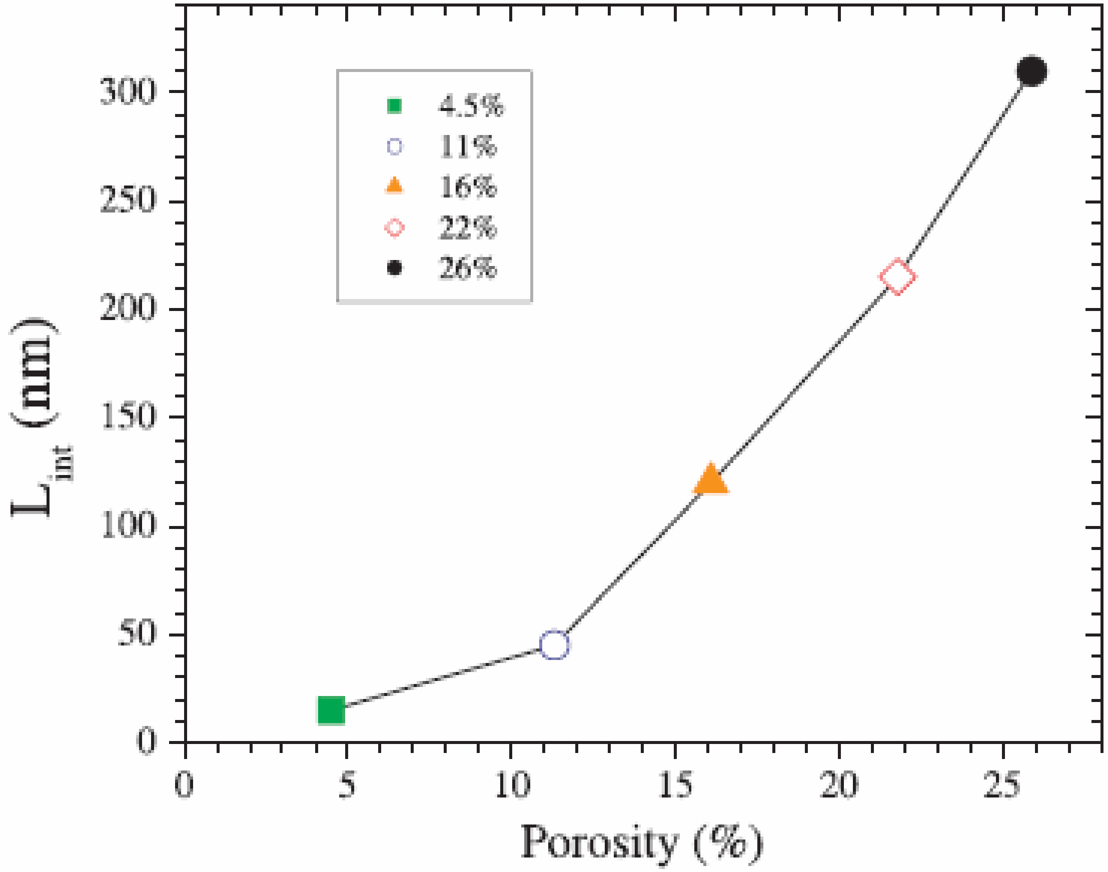



**Figure 9** Plot of the Ps escape fraction ($F_{esc}$) as a function of mean positron implantation depth (*top*) used to calculate the mesopore interconnection length ($L_{int}$) (*bottom*) for films of increasing porosity. This film is a cyclodextrin-based porogen in a MSSQ matrix.

# Depth-profiling of films:

- Information from 3γ/2γ ratio:

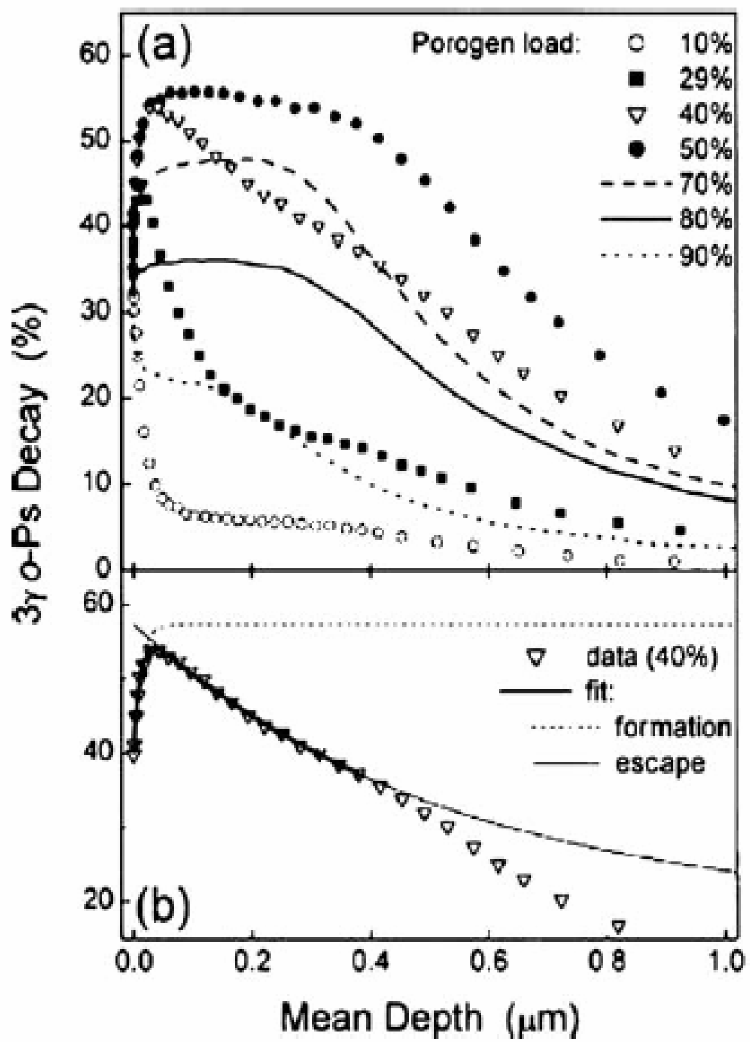



**Figure 10** Typical depth-profile of the 3γ fraction for several porogen weight fractions. The lower panel is a fit of the data to a diffusion model to determine $L_{int}$. Reprinted with permission from Reference 28. Copyright 2005, American Institute of Physics.

# Depth-profiling of films:

- DBS parameters s,w also sensitive:

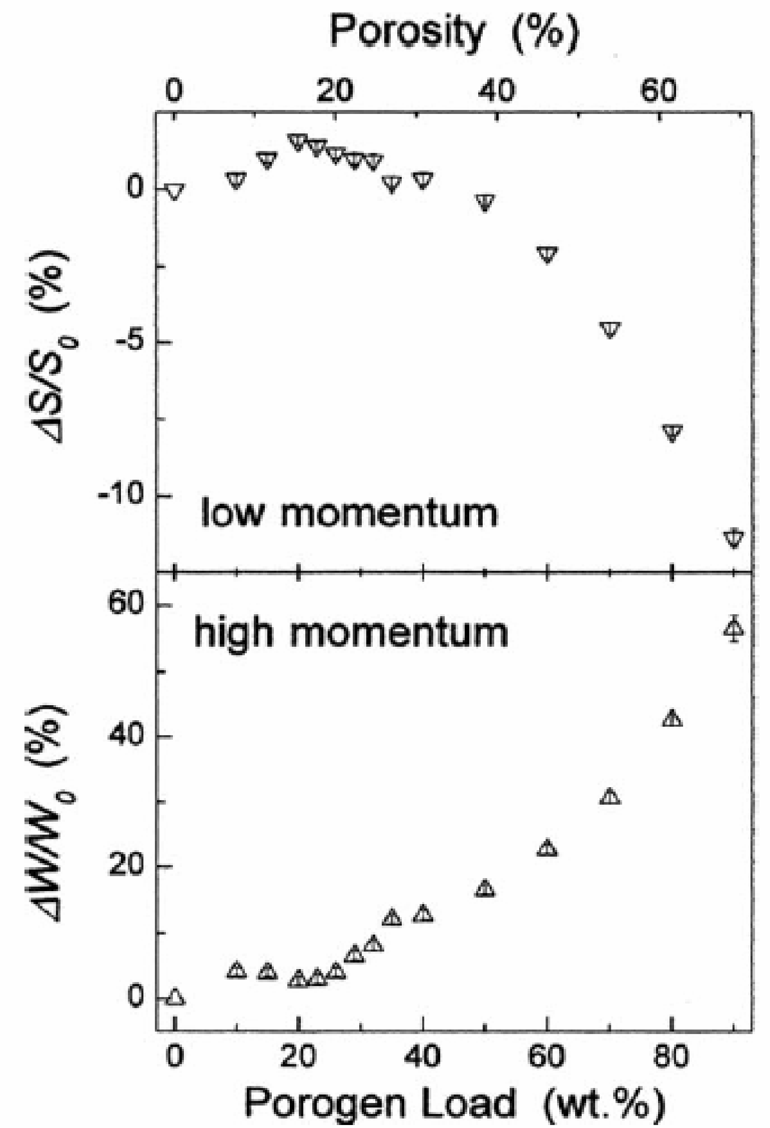



**Figure 11** Plot of the change in low-momentum (S) and high-momentum (W) parameters as a function of film porosity. Reprinted with permission from Reference 5. Copyright 2003, American Chemical Society.

# 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:

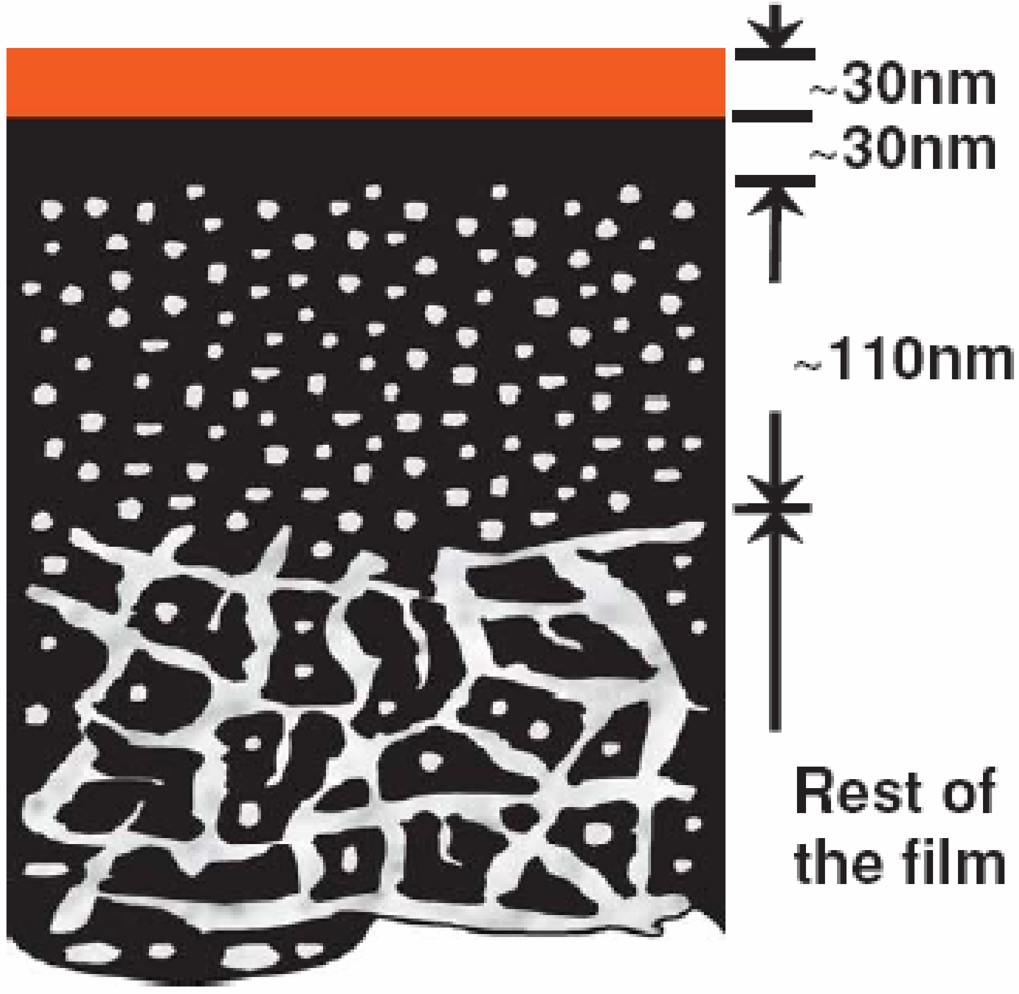



**Figure 12** Schematic of the porosity in a PECVD low-k film derived from depth-profiling with PALS.

1,5 nm

3,5 nm

- PALS depth-profiling must be combined with etching off upper layers (interconnections)

# Pore shape and growth:

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

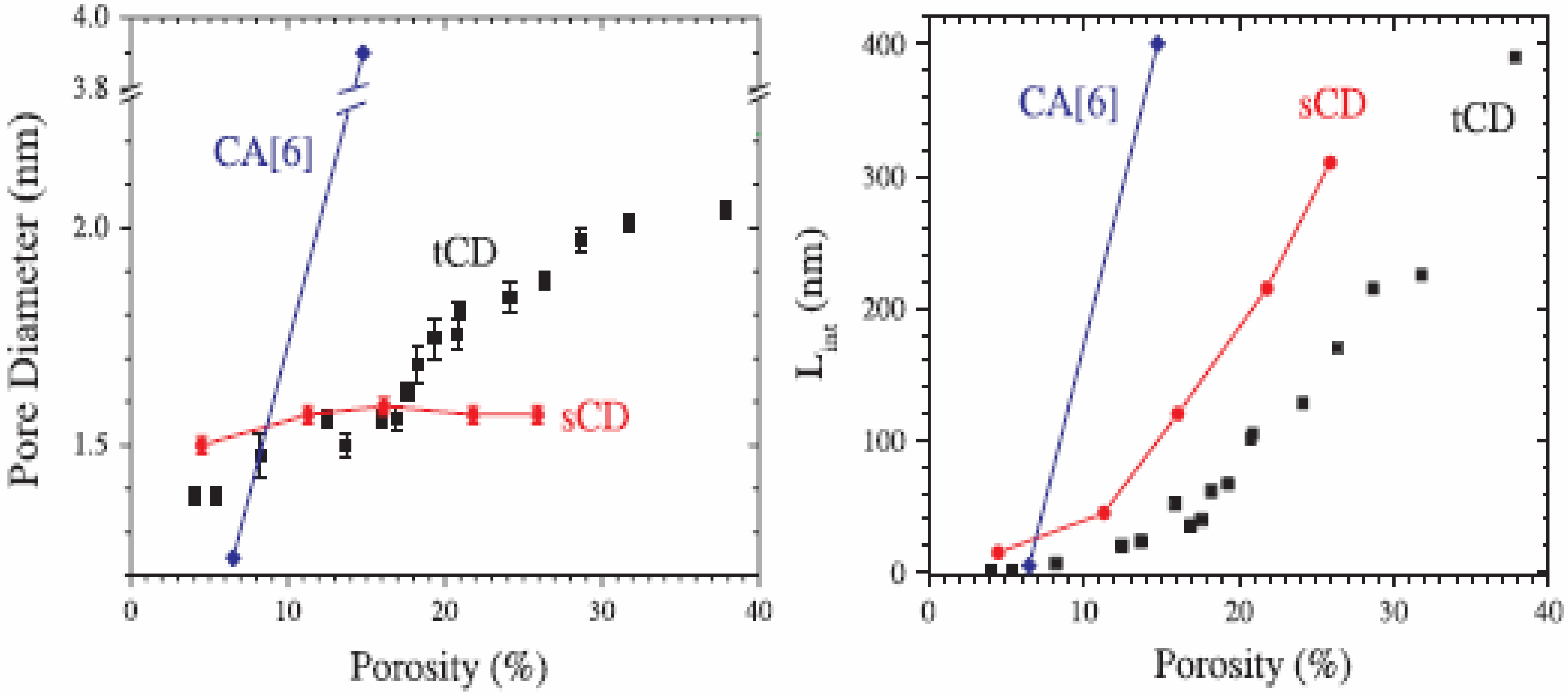



**Figure 13** Plots of pore diameter (*left*) and pore interconnection length (*right*) as a function of porosity for MSSQ films made with three different porogens. The growth modes for the porogens are dramatically different.

# 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