Characterization of Micropore Structure of Porous Materials Using DFT Models Applied to Ar, N_2 and H_2 Adsorption Data.

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Outline of the presentation

- Objective
- Earlier results
- Experimental
- Assumptions of model calculations
- Method of the PSD calculation
- Calculation of carbon PSDs using multiple adsorbates: Examples
- Fundamental and practical advantages of using more than one adsorbate for PSD analysis
- DFT based prediction of high-pressure H_2 adsorption at ambient temperature from H_2 measurements at 77 K
- PSD analysis for zeolites
  - Effect of pore sizes and materials chemistry
- Conclusions

Objective

Discussion of the micropore structure analysis of porous

{nanoporous, microporous}

materials based on adsorption measurements of standard adsorbates N_2 and Ar, and H_2 isotherms

at cryogenic temperatures .

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Earlier results

Comparison of PSDs calculated from different adsorbates

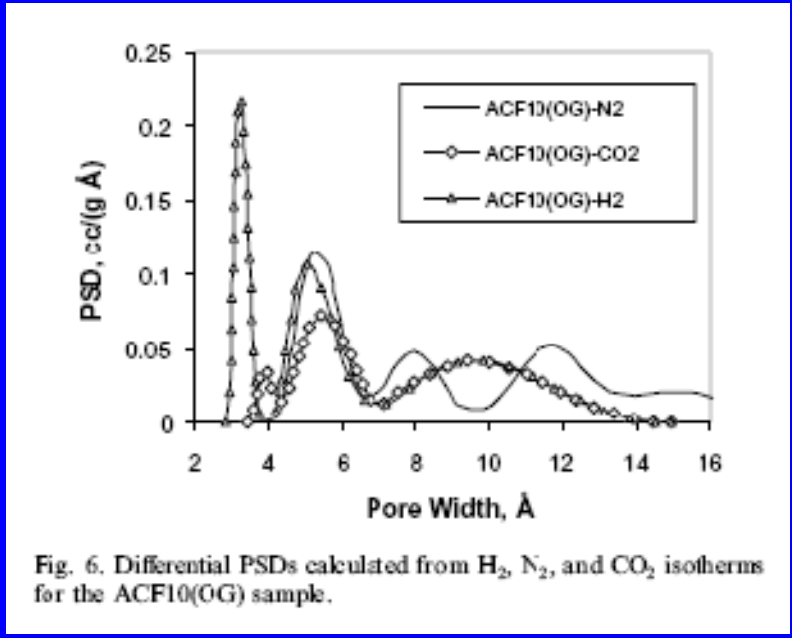

Fig. 6. Differential PSDs calculated from H_2, N_2, and CO_2 isotherms for the ACF10(OG) sample.

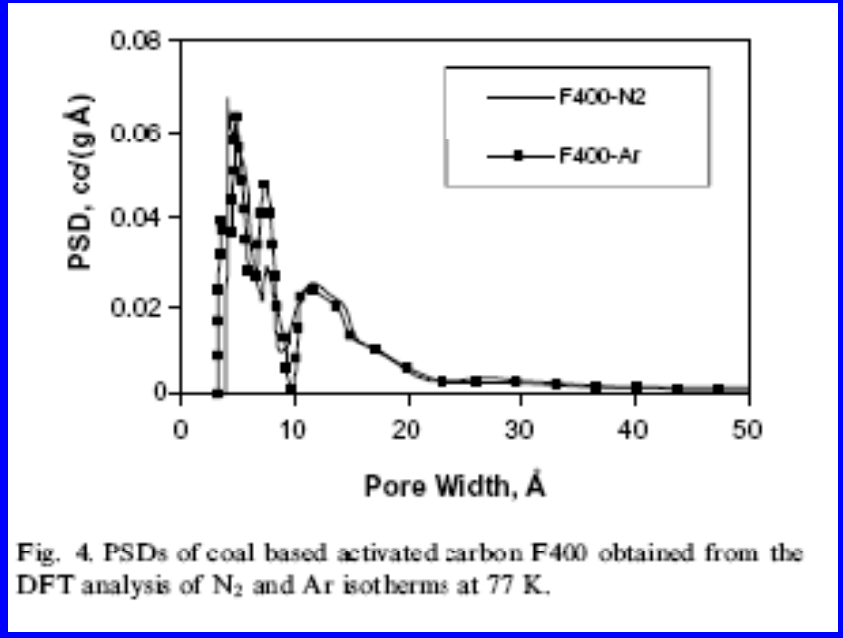

Fig. 4. PSDs of coal based activated carbon F400 obtained from the DFT analysis of N_2 and Ar isotherms at 77 K.

J. Jagiello, M. Thommes, Carbon Conference, Oviedo (2003)
Carbon 42,1227–1232 (2004)

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Earlier results

H_2 Adsorption on Takeda 3A Carbon Molecular Sieve

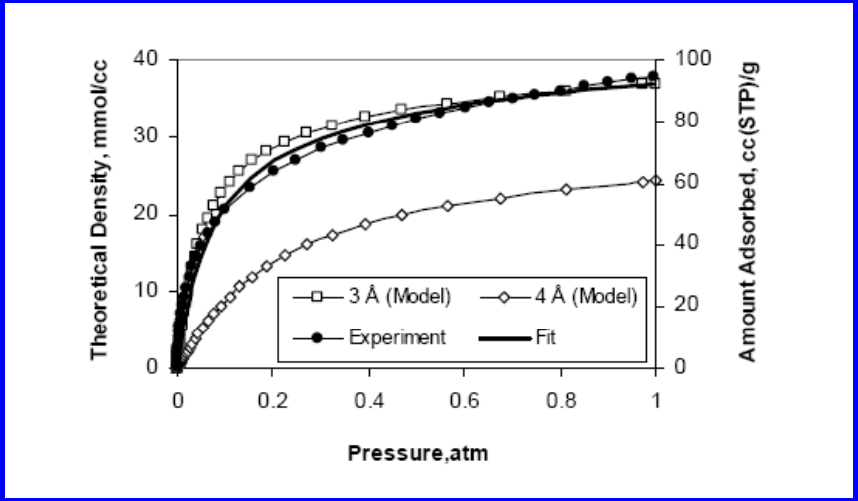

Figure 1. Experimental H_2 isotherm measured at 87 K for the Takeda 3A sample compared with the NLDFT isotherms calculated for the 3 and 4 Å pores and with the curve fitted by SAIEUS.

Jagiello, J.; Thommes M.; Linares-Solano, A.; Cazorla-Amorós, D.; Lozano-Castelló, D., Extended Abstracts, Carbon 2004

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Experimental

Materials

Set 1:

- Carbons derived from poly(ethylene terephthalate), PET
- Sample PC obtained by pyrolysis of PET.
- Samples PC12, PC35, PC58, and PC76 obtained from PC by CO_2 activation with increasing burn-off (12, 35, 58, 76 %)
- Details: Parra JB, Ania CO, Arenillas A, Rubiera F, Palacios JM, Pis JJ., J Alloys Compd, 379: 280–89 (2004)

Set 2:

- Commercial CMSs from Supelco obtained from polymeric precursors
- Details: Jagiello, J., Betz, W. Microporous and Mesoporous Materials, **108,** 117–122 (2008)

Sample ACF10, Activated carbon fiber (Kynol)

- Details: Jagiello, J., Thommes, M. Carbon 42,1227–1232 (2004)

Commercial Zeolite Samples (Aldrich)

Outline of model calculations

- Model **NLDFT** isotherms (kernels) are calculated using **Tarazona** approach [1, 2].
- **Slit pore model** for carbon pores.
- Carbon-gas interactions described by the **Steele potential** [3].
- LJ parameters for N_2 and Ar taken from **Ravikovitch** et al. [4].
- **Weeks-Chandler-Andersen** attractive potential [2].
- H_2-H_2 interactions: **Silvera-Goldman** [5] potential modeled by LJ potential [6]
  $e_{ff}/k = 34.3$ K, $s_{ff} = 3.04$ Å
- Gas-solid interaction parameters for H_2–carbon derived from the fit to experimental isotherm measured on graphitized carbon black [7]
- Quantum corrections for H_2 model applied by using **Feynman** "Effective Potential."
- The **cylindrical** pore model is assumed for zeolite pores.

1. Tarazona P, Marini Bettolo Marconi U, Evans R. *Mol Phys* 1987;60:573.
2. Lastoskie C, Gubbins KE, Quirke N. *J Phys Chem* 1993;97:4786-96.
3. Steele WA. *The Interactions of Gases with Solid Surfaces* Pergamon, Oxford, 1974.
4. Ravikovitch PI, Vishnyakov A, Russo R, Neimark AV. *Langmuir* 2000;16:2311-2320.
5. Silvera IF, Goldman VV. J Chem Phys 1978; 69: 4209
6. Stan G, Cole MW. *J. Low Temp. Phys.* 1998; 110:539-544.
7. J. Jagiello, A. Anson, M.T. Martinez, *J. Phys. Chem.*, 110 (2006) 4531

Outline of the PSD calculation method

Multi Adsorbate Integral Equation [1]:

$$\min \sum_{m}^{M} \sum_{i}^{N_m} \left[V_m(p_i) - \int_{\alpha_m}^{\beta_m} K_m(p_i, w) f(w) dw \right]^2 \qquad (1)$$

p_i - experimental pressure of i-th adsorption point
V_m - measured adsorption isotherm for m-th adsorbate
K_m - set of theoretical DFT isotherms (Kernel) for m-th adsorbate model
f(w) - PSD
w - effective pore width
M - number of adsorbates/models
N_m - number of points of m-th experimental isotherm

f(w) is obtained by conditional minimization of (1) using regularization, SAIEUS [2], nonnegativity constraints [3], L-curve [4].

[1] Jagiello, J.; Thommes M.; Linares-Solano, A.; Cazorla-Amorós, D.; Lozano-Castelló, D., Extended Abstract, Carbon 2004
[2] Jagiello, J. Langmuir 1994, 10, 2778
[3] Lawson, C. L.; Hanson, R. J. Solving Least Squares Problems; Prentice-Hall: Englewood Cliffs, New Jersey, 1974
[4] Hansen, P. C.; O'Leary, D. P. SIAM J. Sci. Comput. 1993, 14, 1487

Effect of regularization

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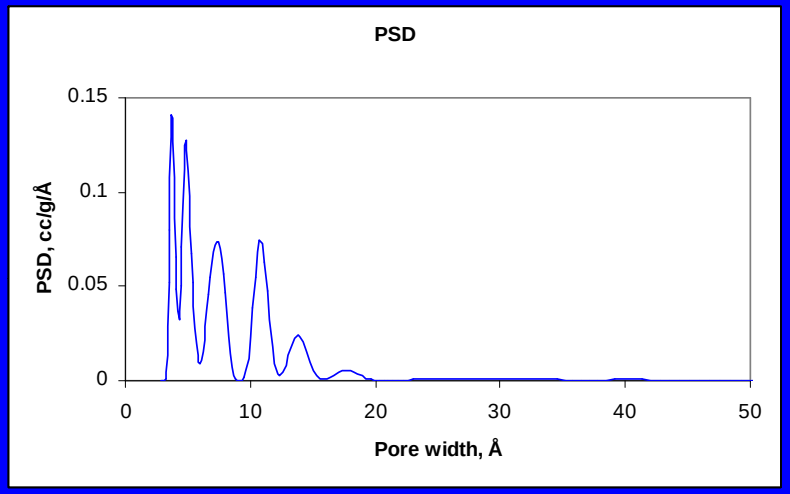

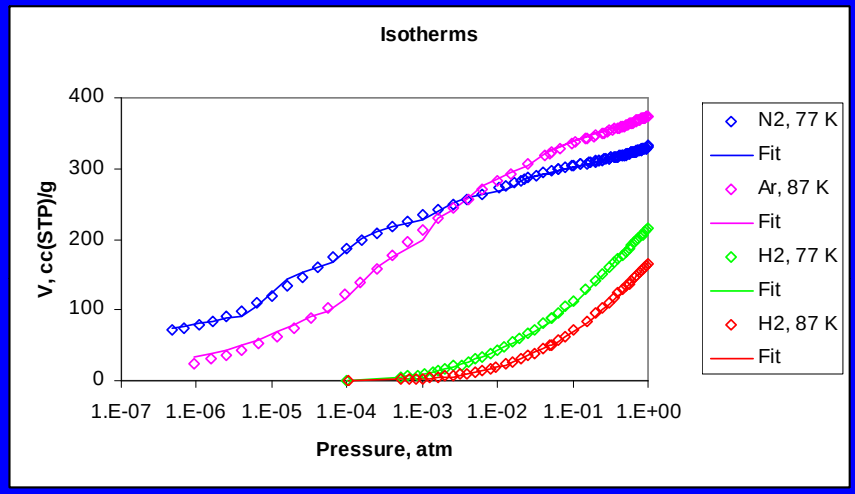

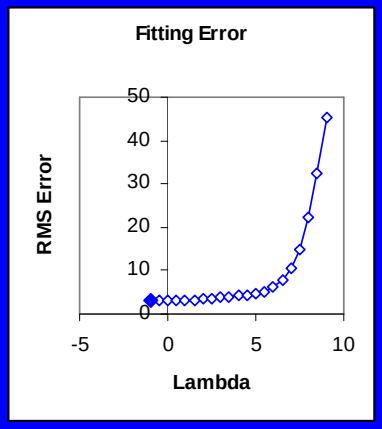

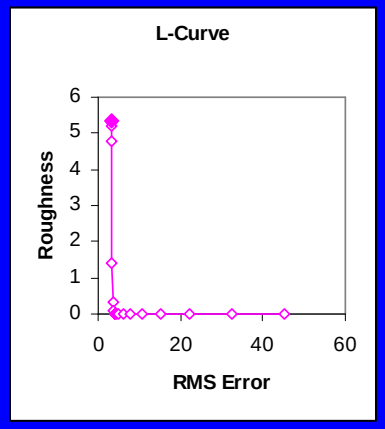

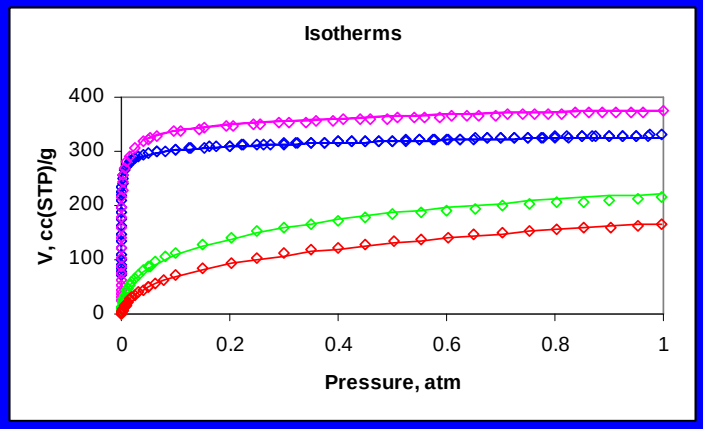

J. T. Duda, L. Jagiello, J. Jagiello, J. Milewska-Duda, Appl. Surface Sci., **253**, 5616–5621 (2007)

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Effect of regularization

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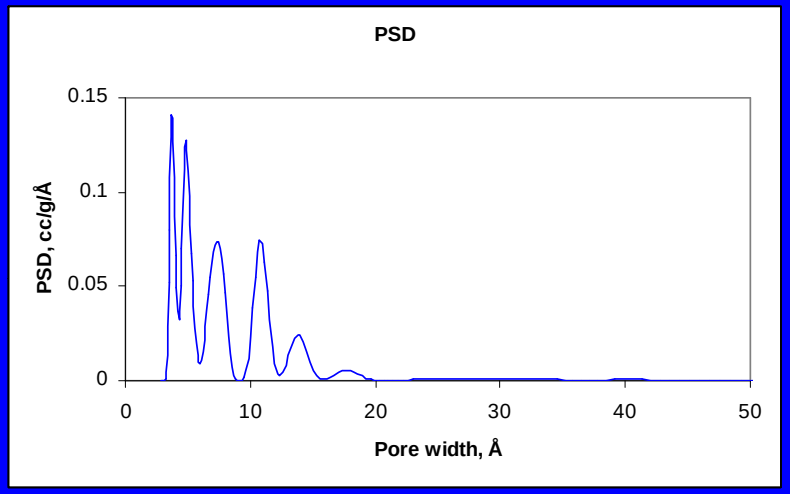

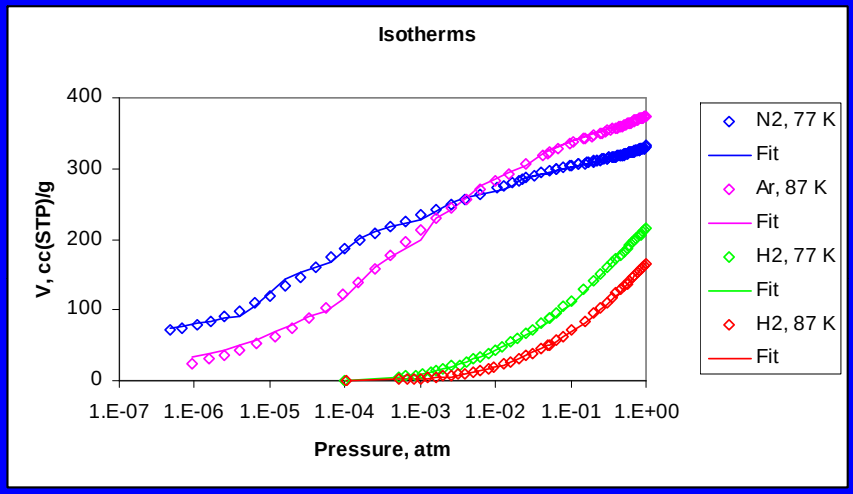

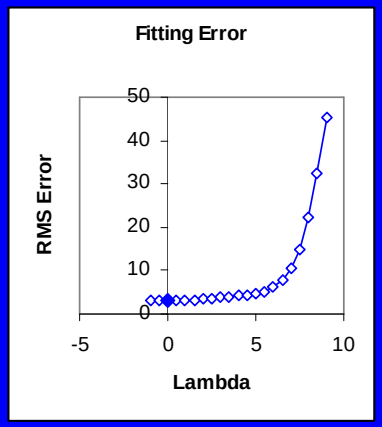

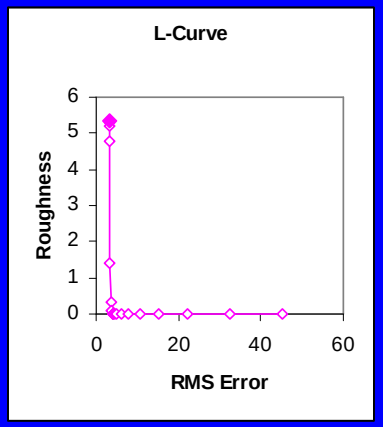

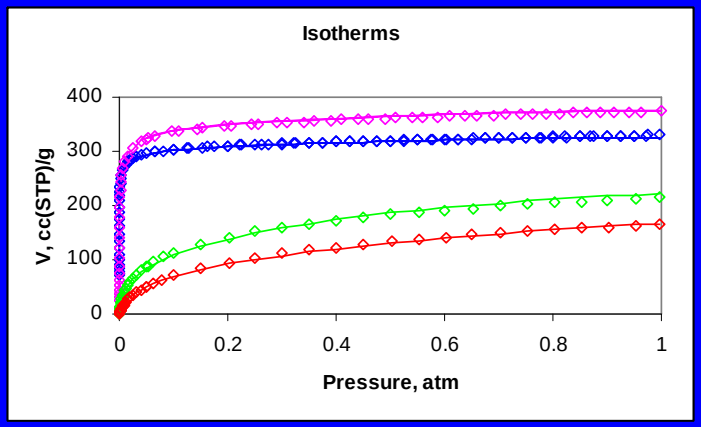

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Effect of regularization

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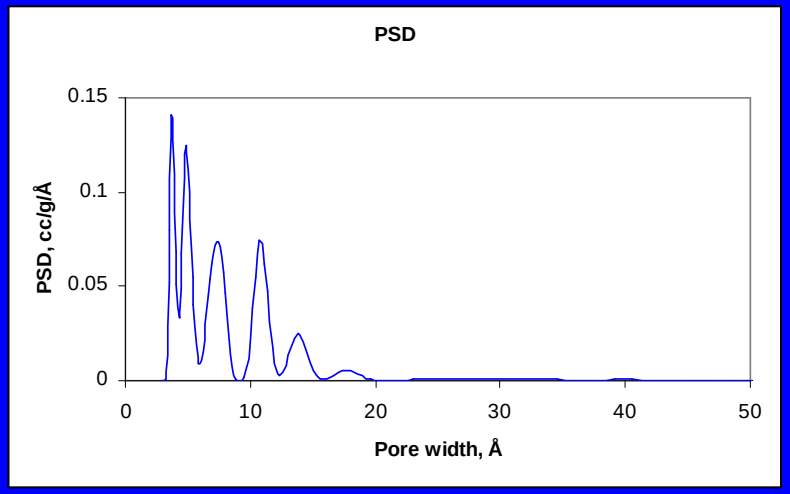

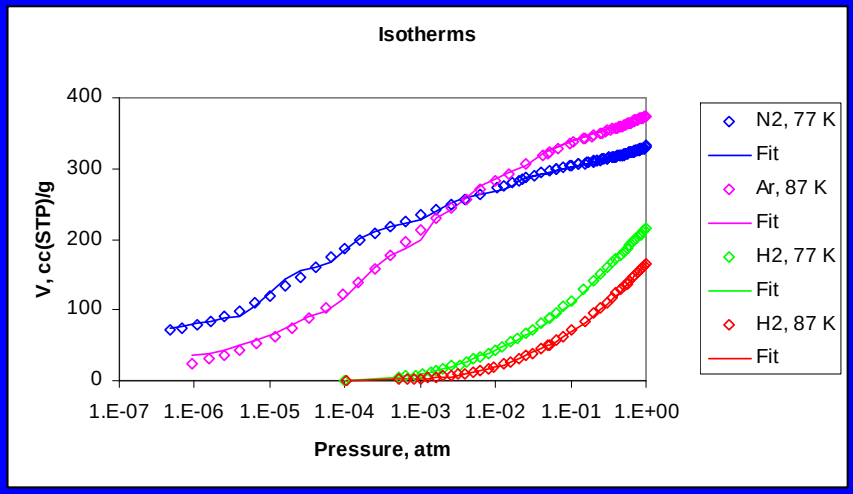

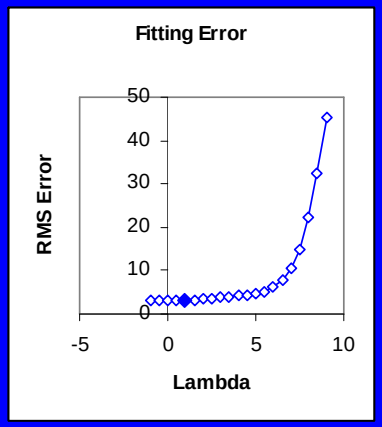

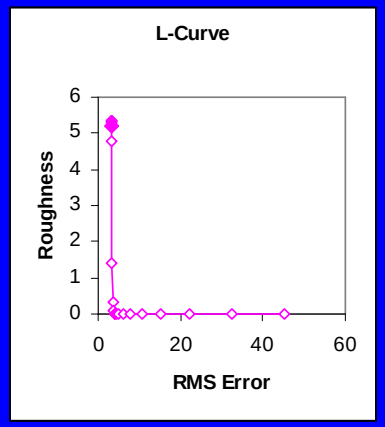

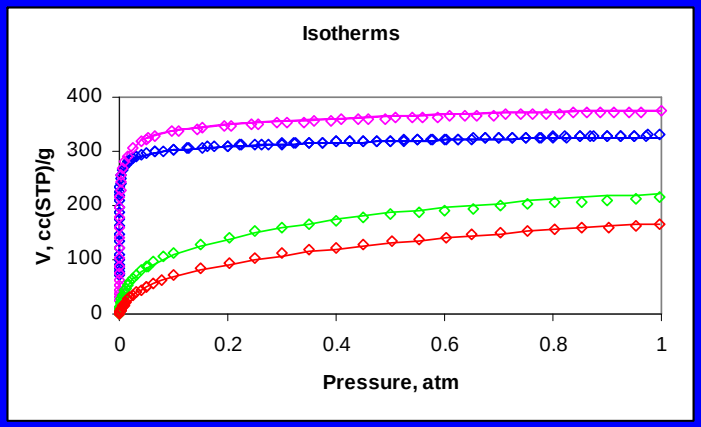

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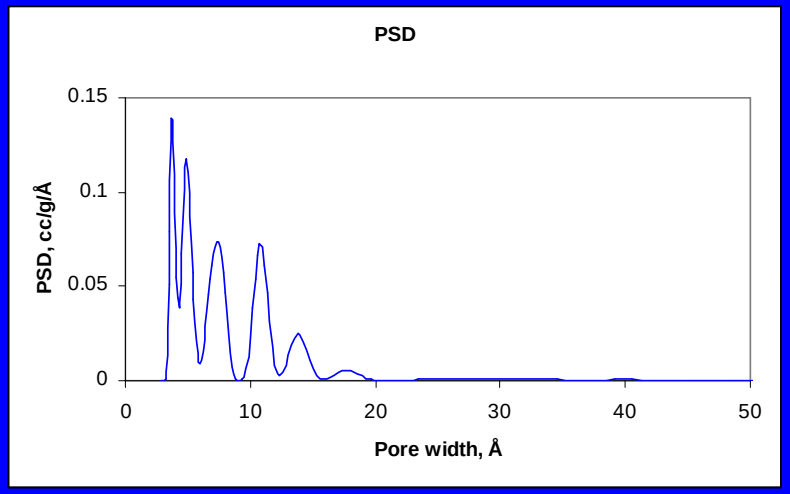
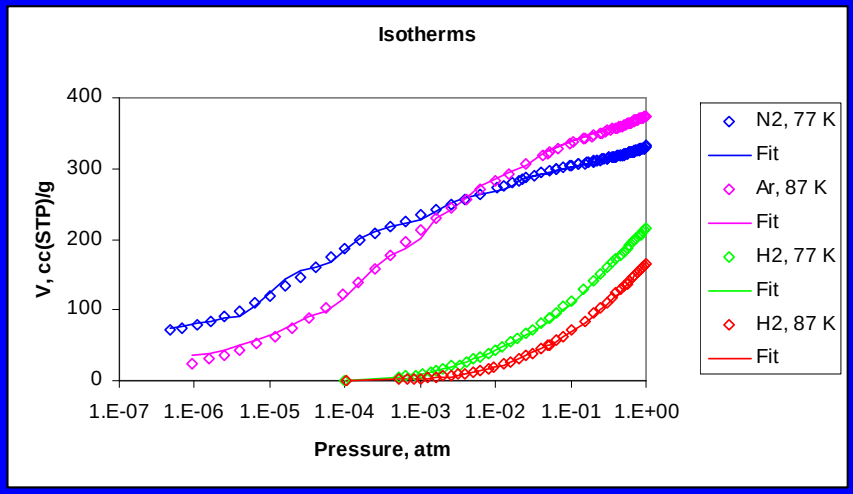
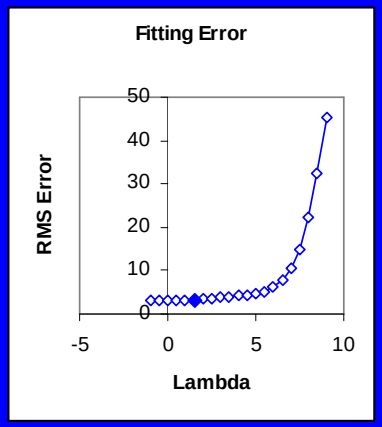
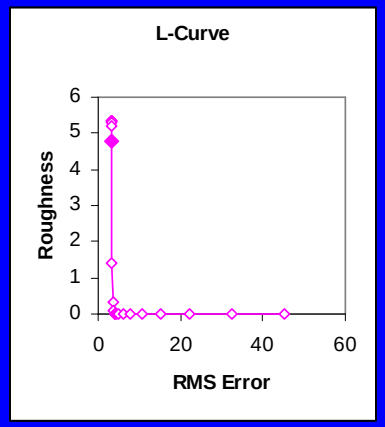
Effect of regularization

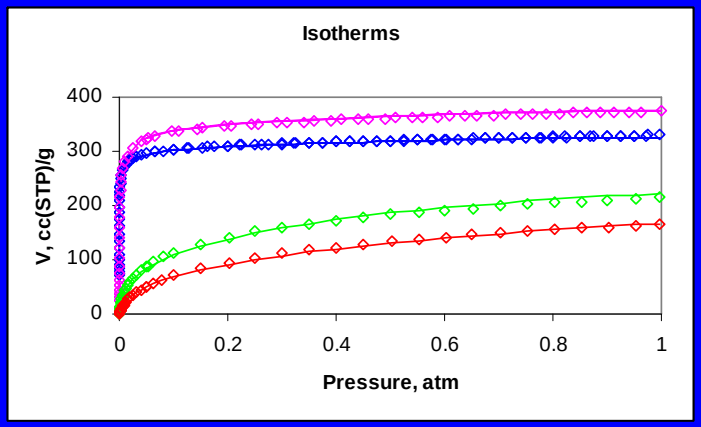
$\lambda = 1.5$











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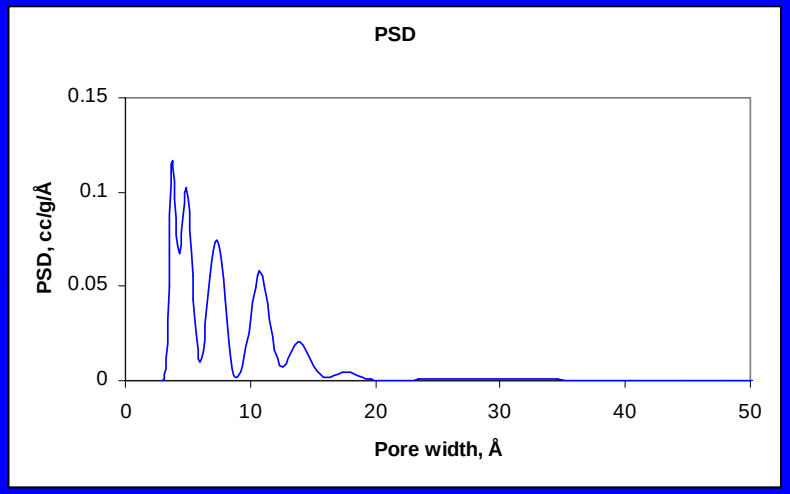
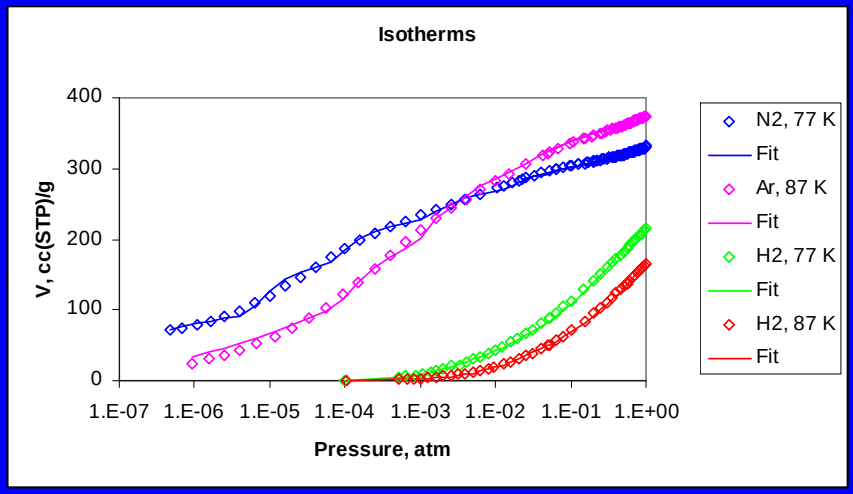
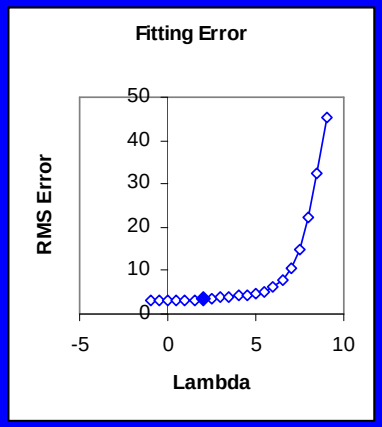
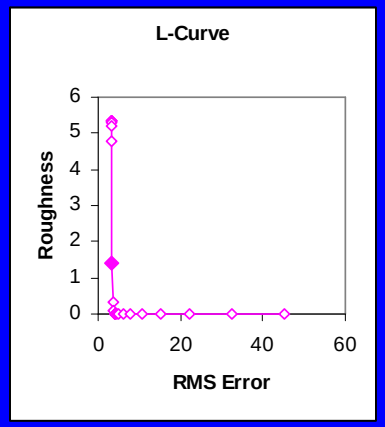
Effect of regularization

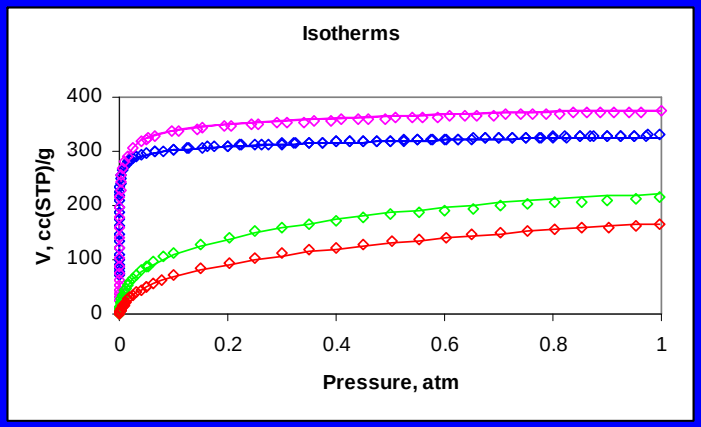
$\lambda = 2$











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Effect of regularization

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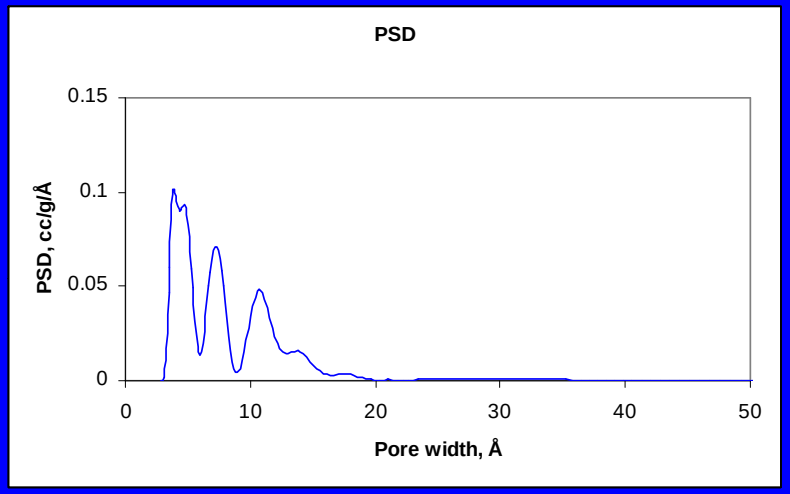

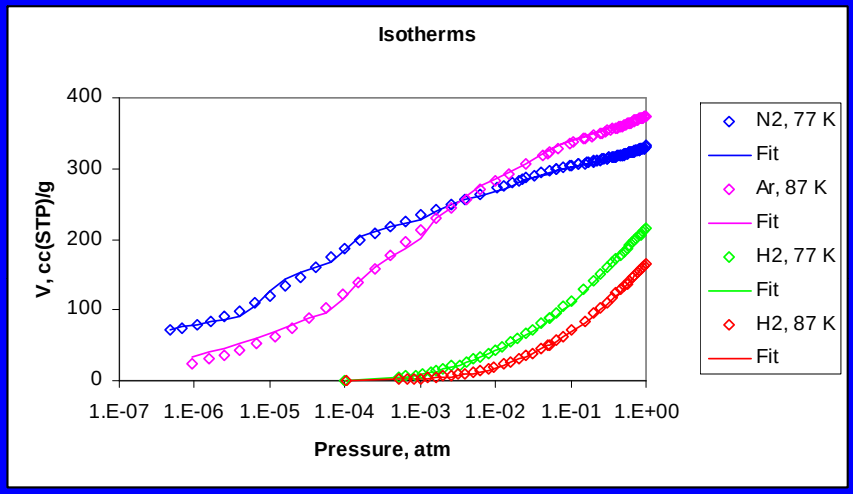

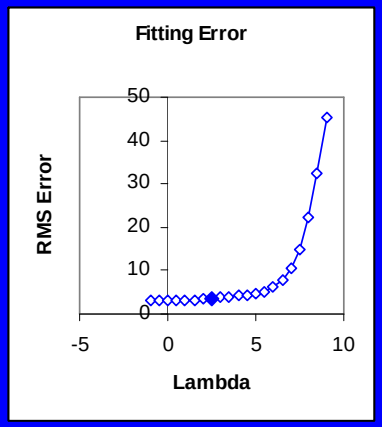

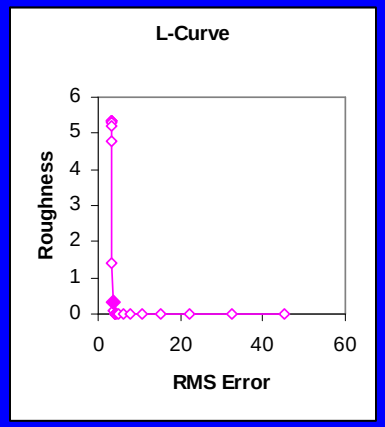

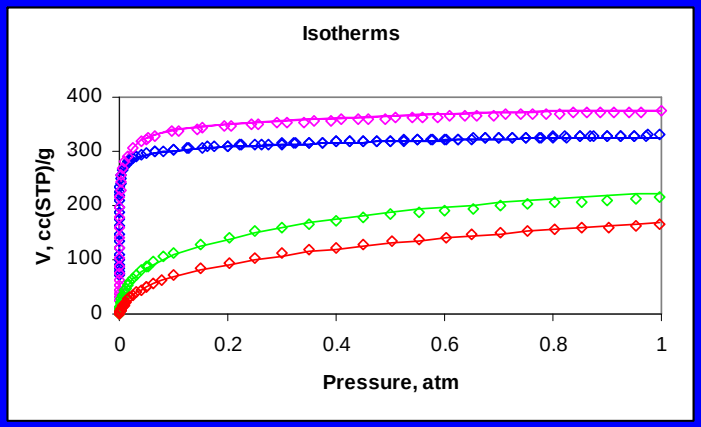

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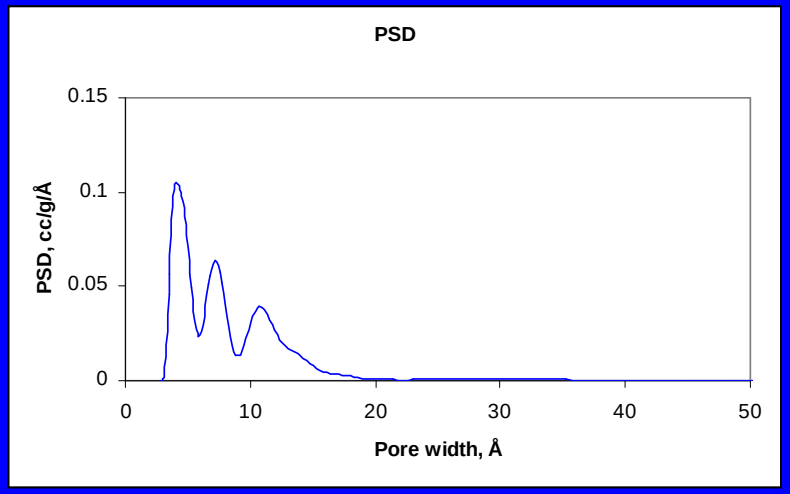
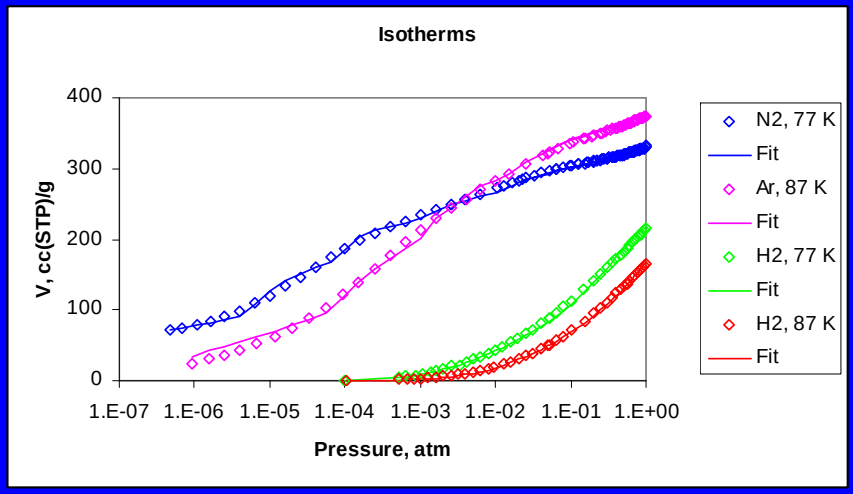
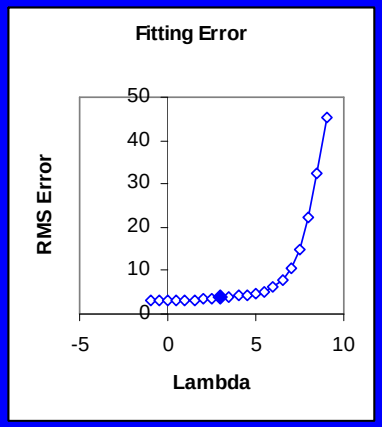
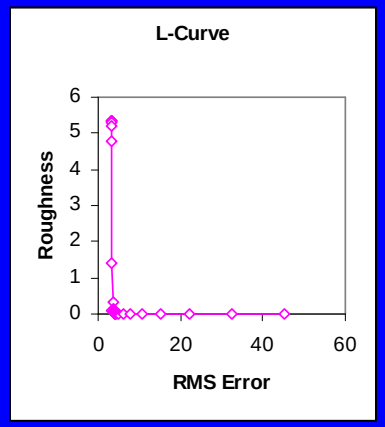
Effect of regularization

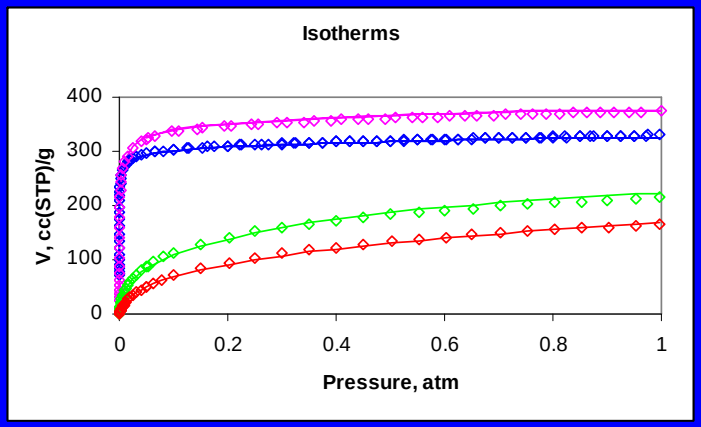
$\lambda = 3$











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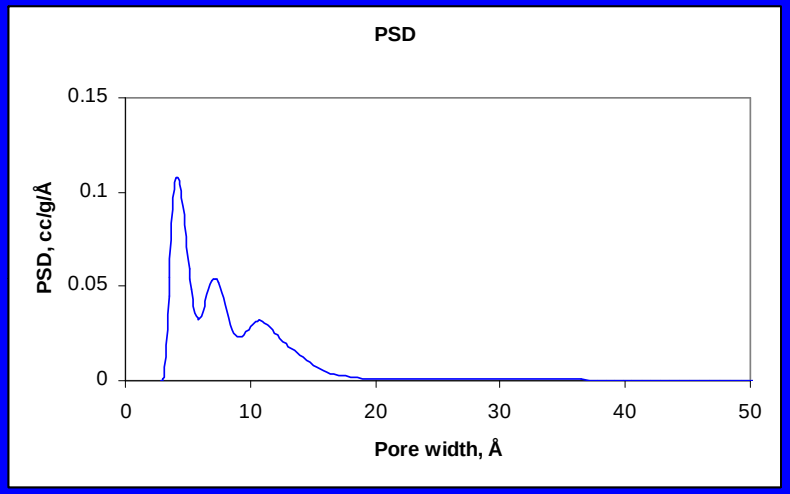
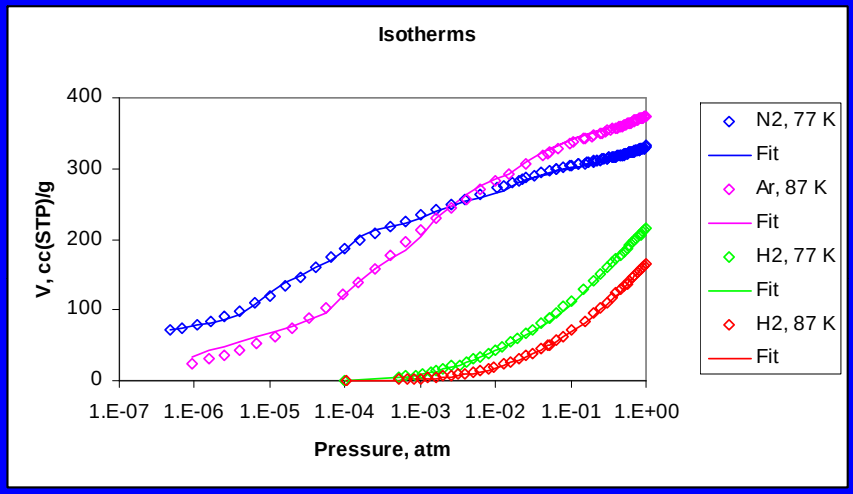
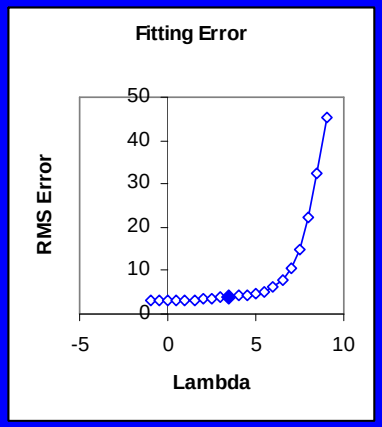
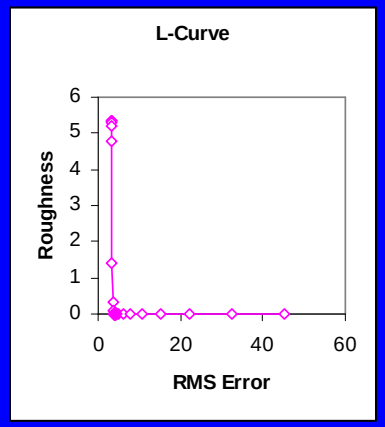
Effect of regularization

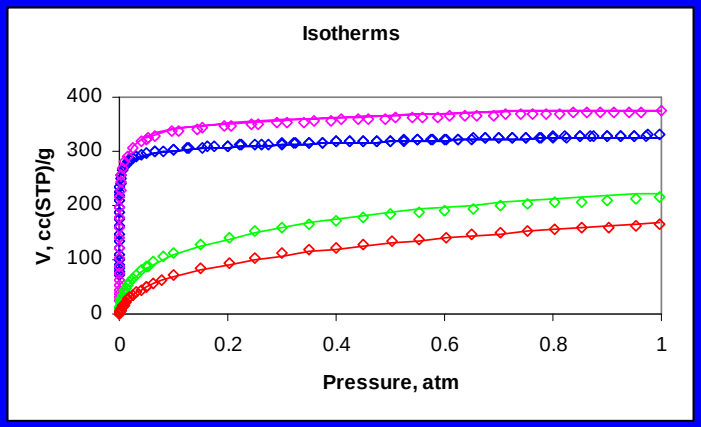
$\lambda = 3.5$











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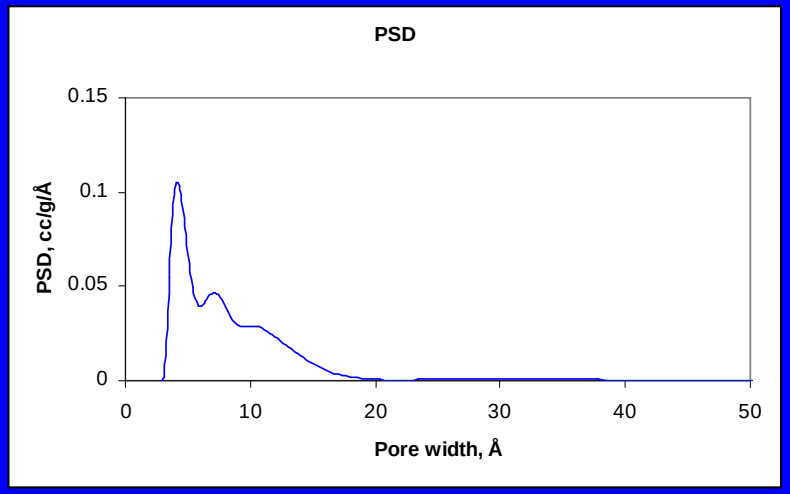
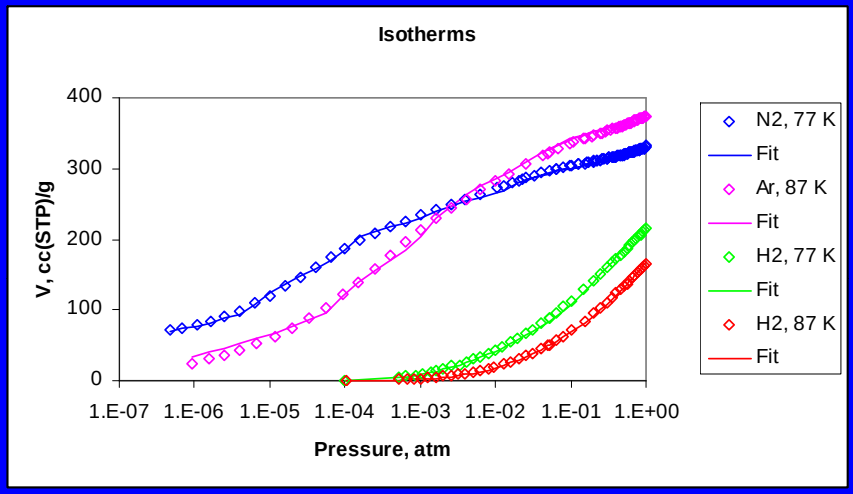
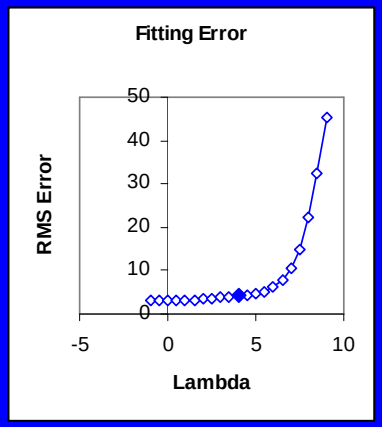
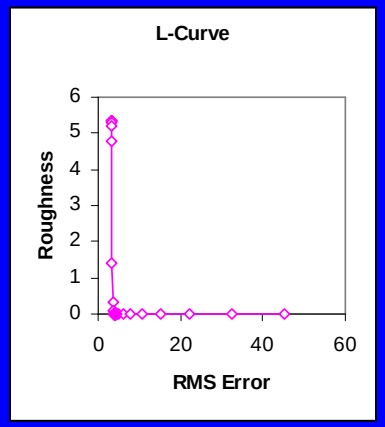
Effect of regularization

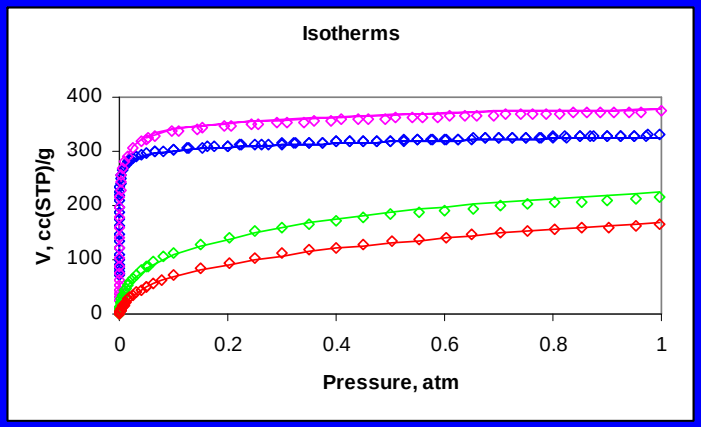
$\lambda = 4$











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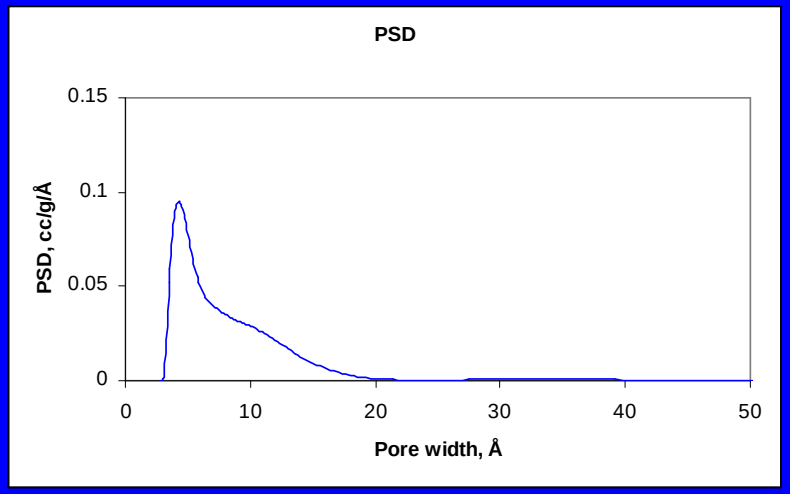
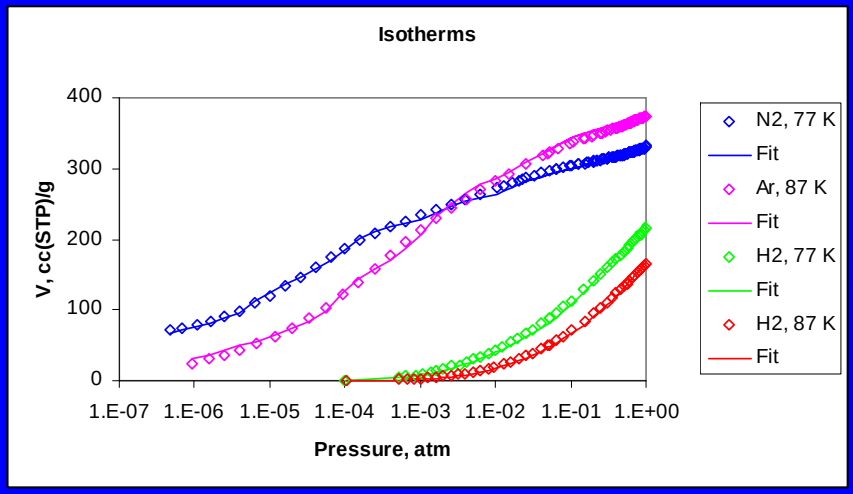
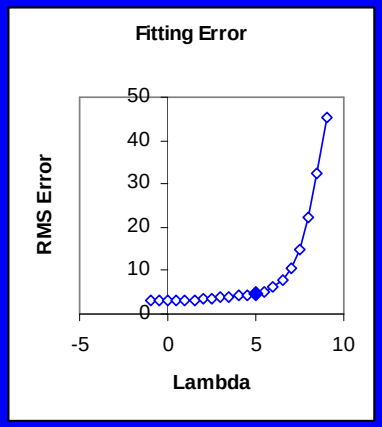
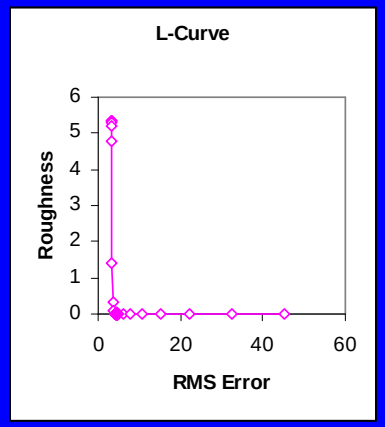
Effect of regularization

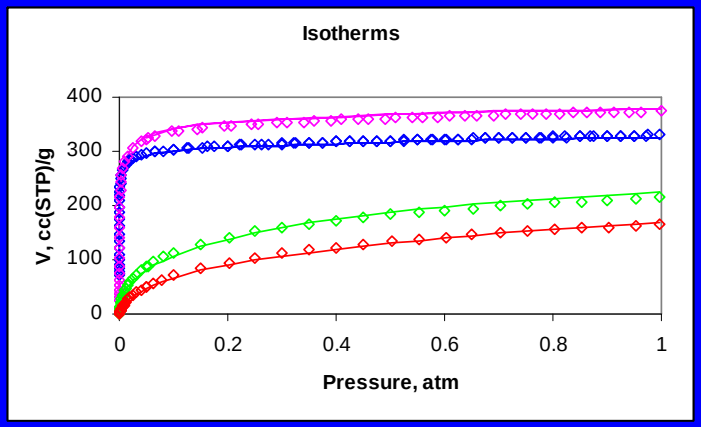
$\lambda = 5$











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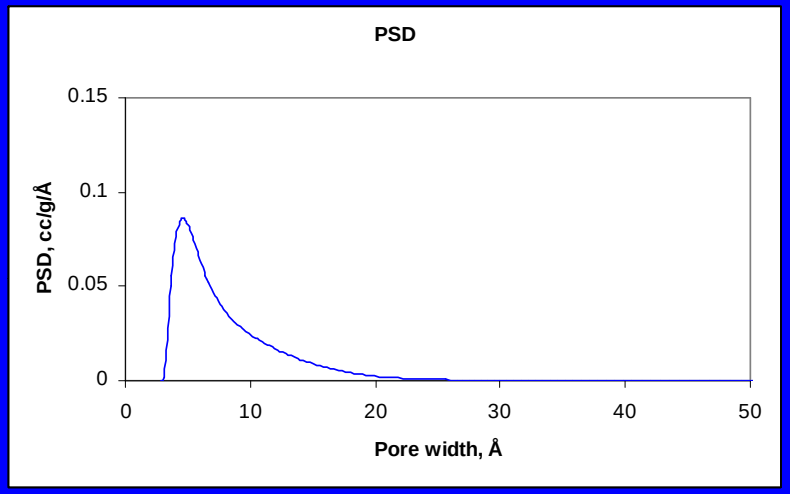
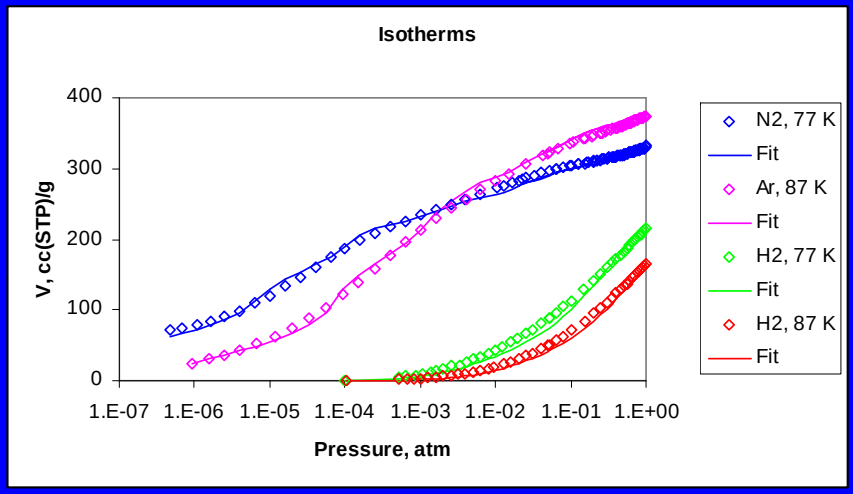
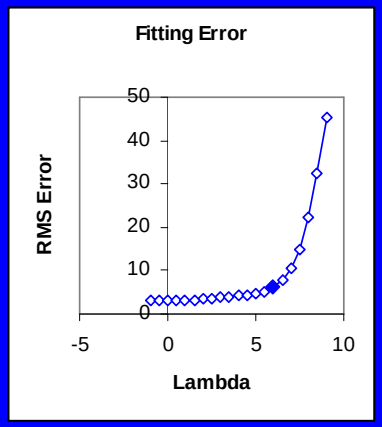
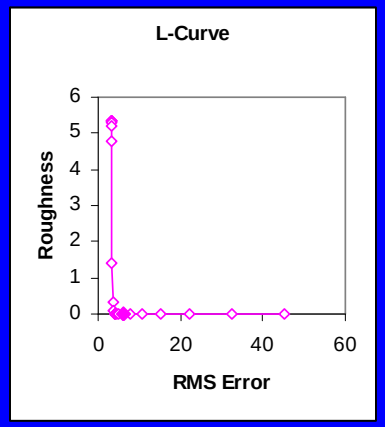
Effect of regularization

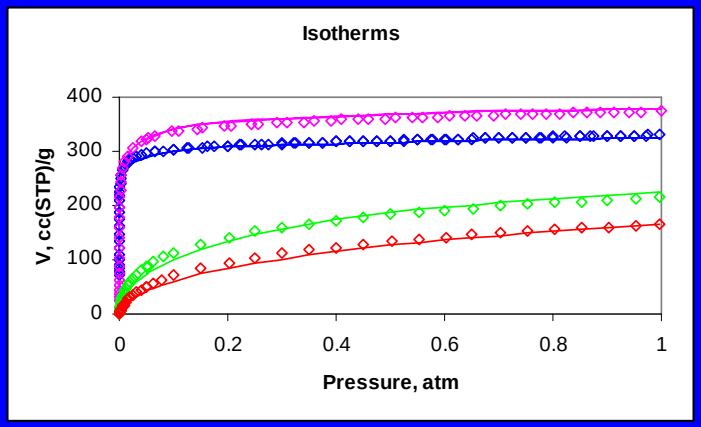
$\lambda = 6$











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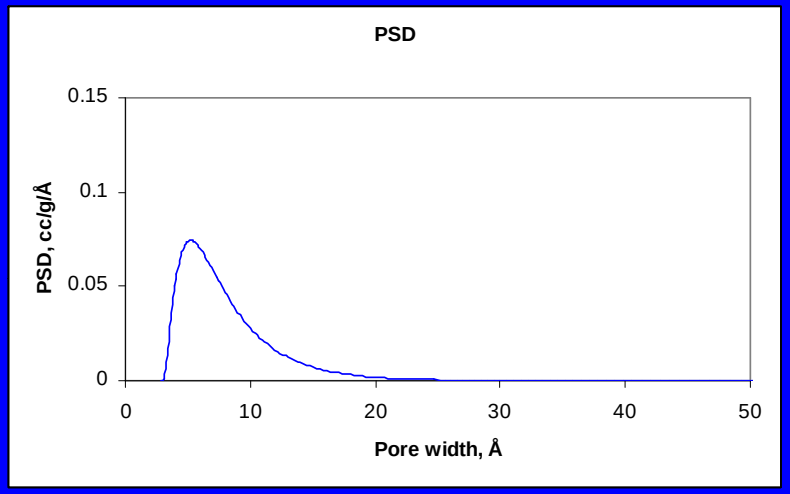
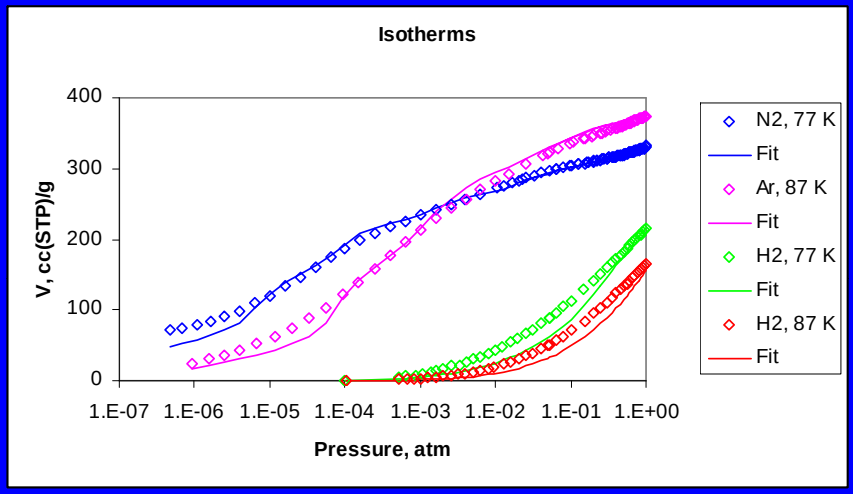
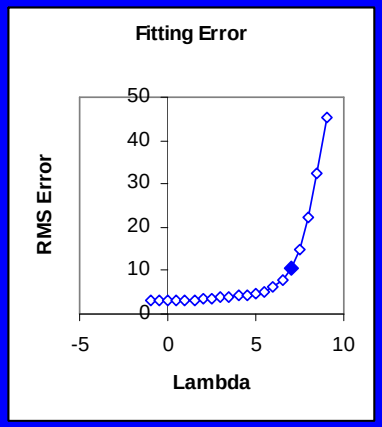
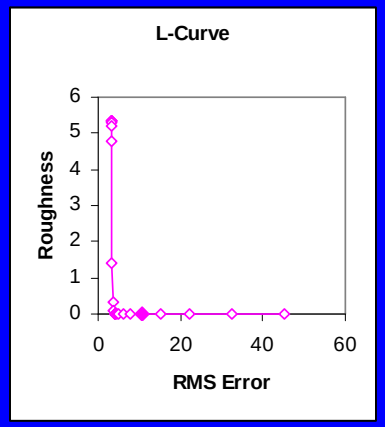
Effect of regularization

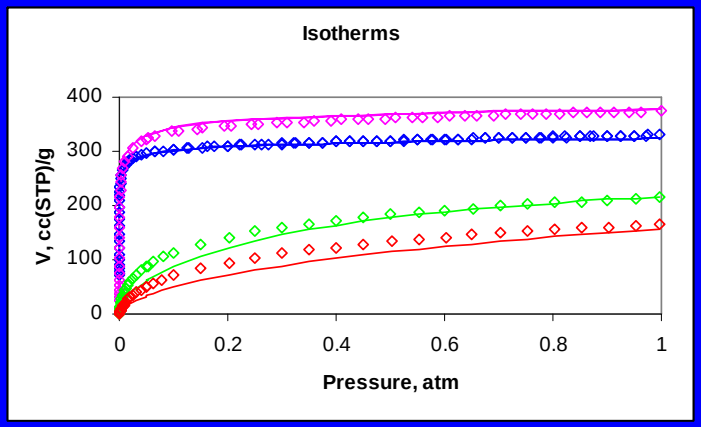
$\lambda = 7$











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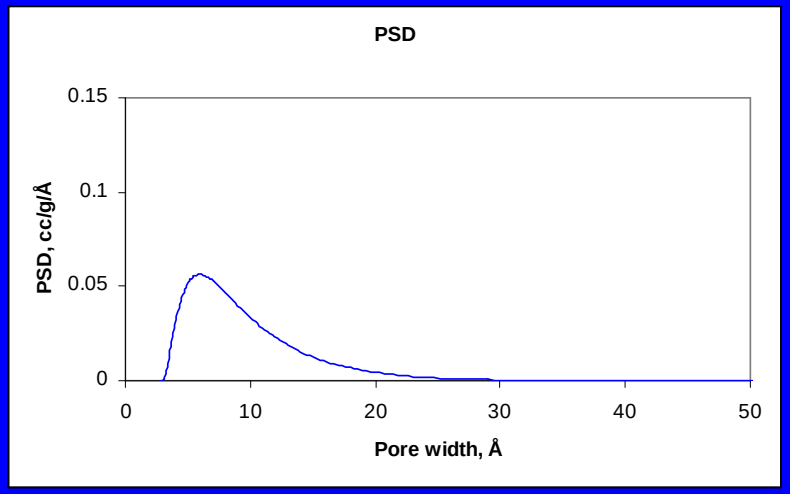
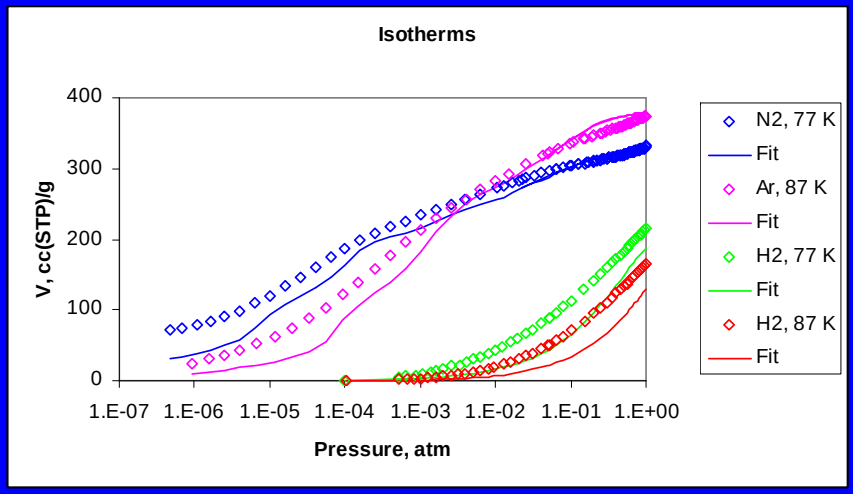
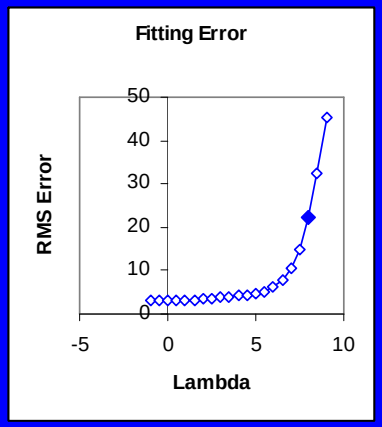
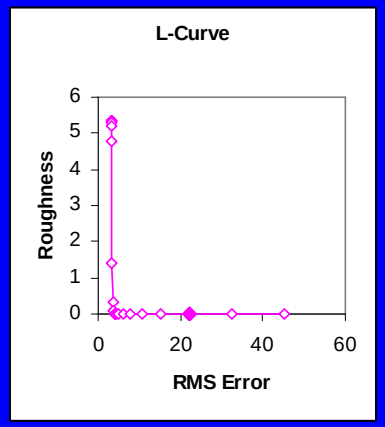
Effect of regularization

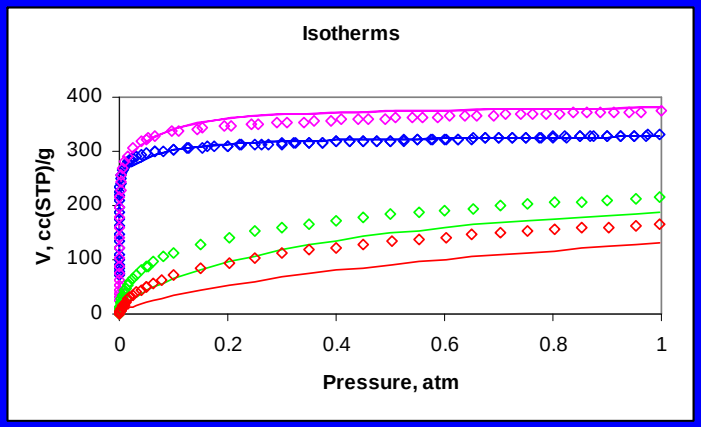
$\lambda = 7.5$











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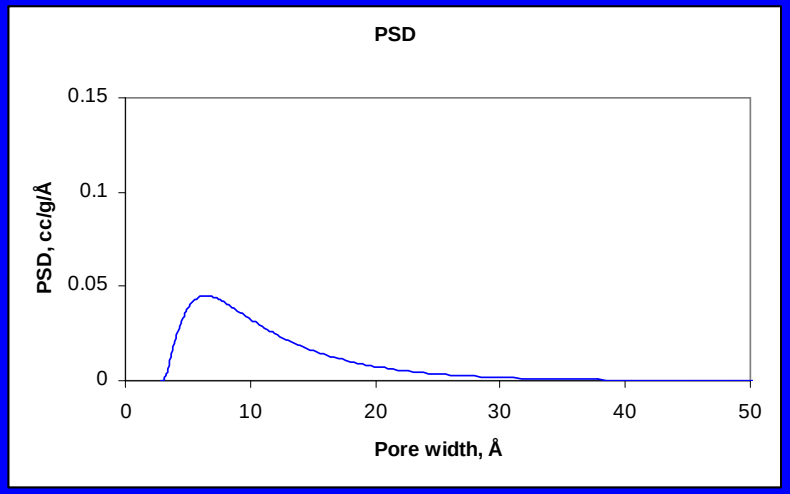
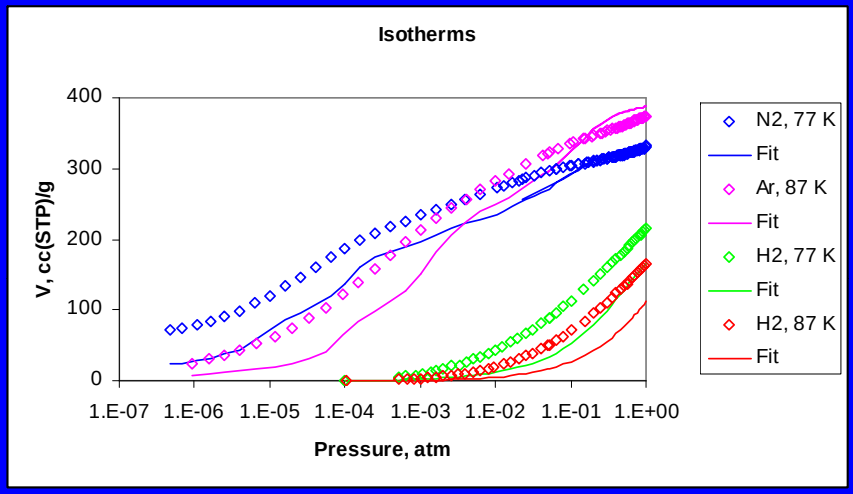
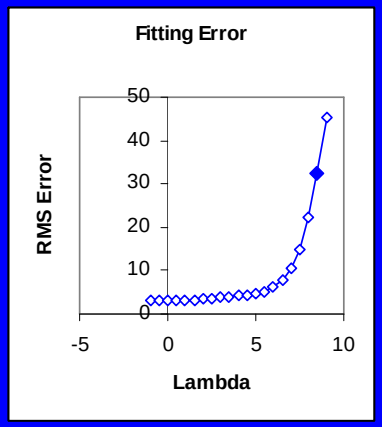
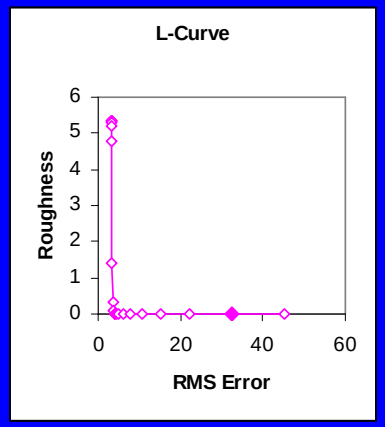
Effect of regularization

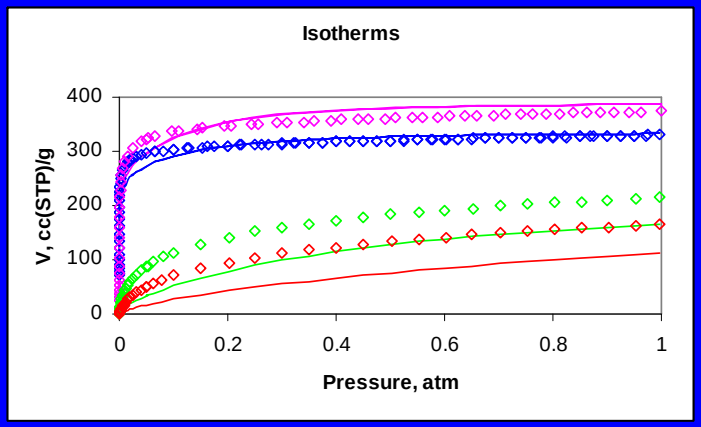
$\lambda = 9$











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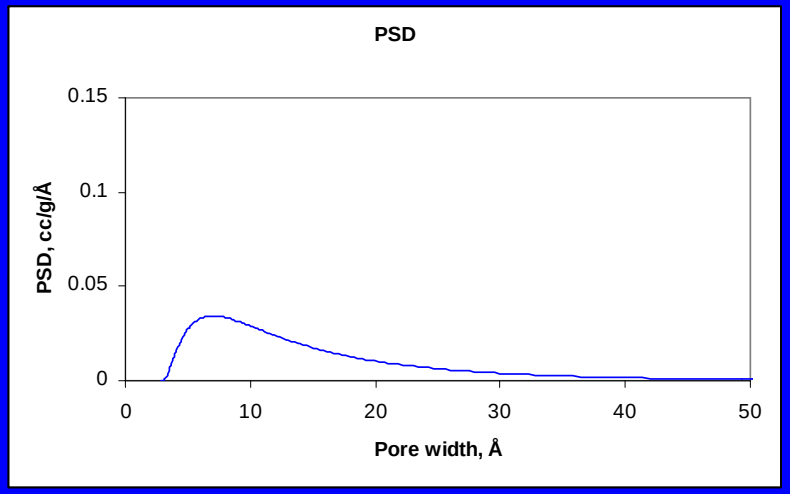
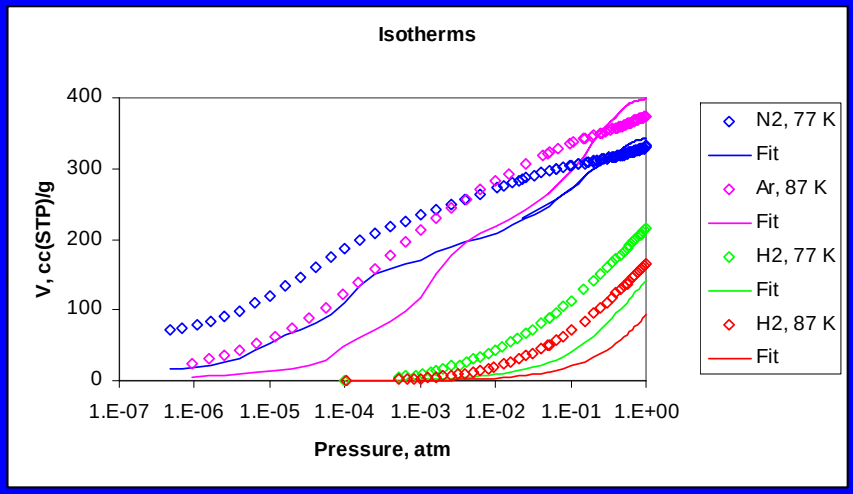
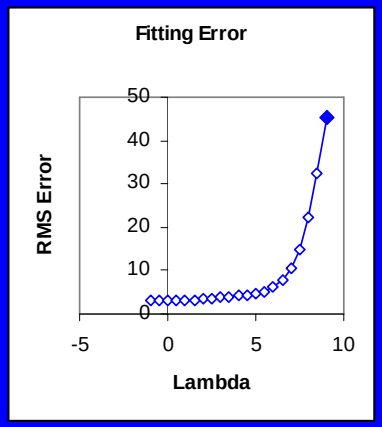
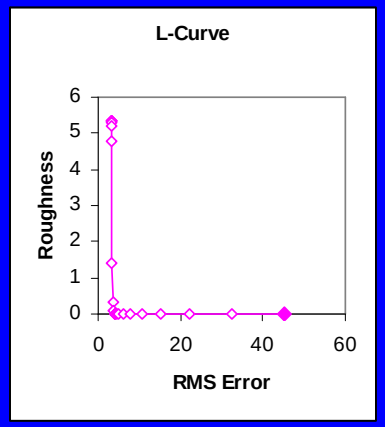
Effect of regularization

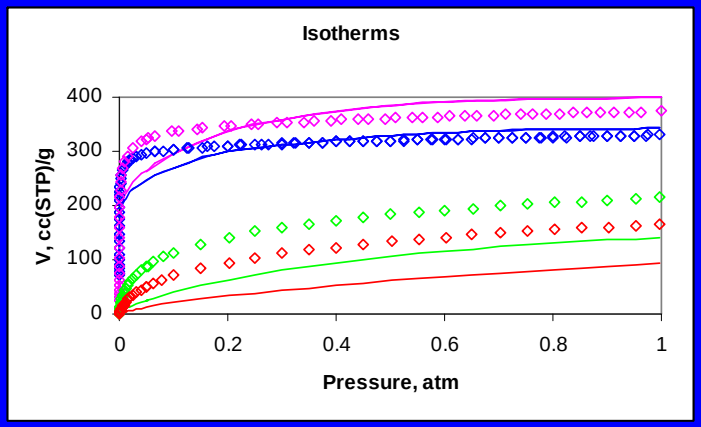
$\lambda = 9$











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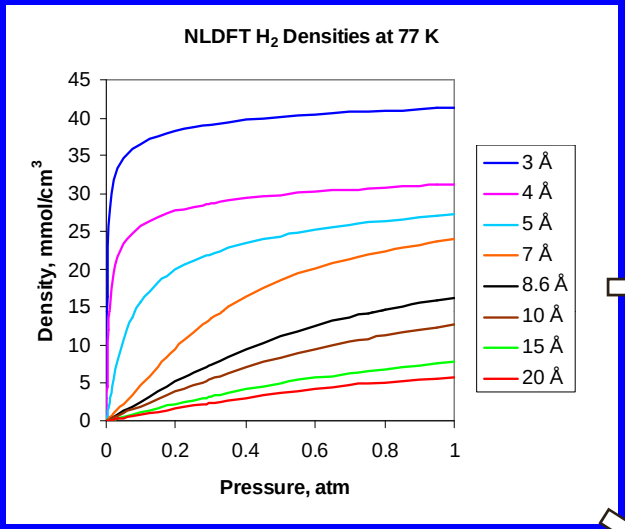
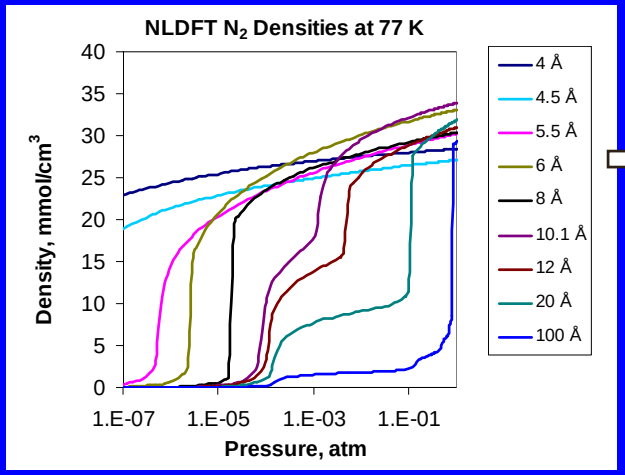
Using Isotherms at Sub and Super Critical Temperatures

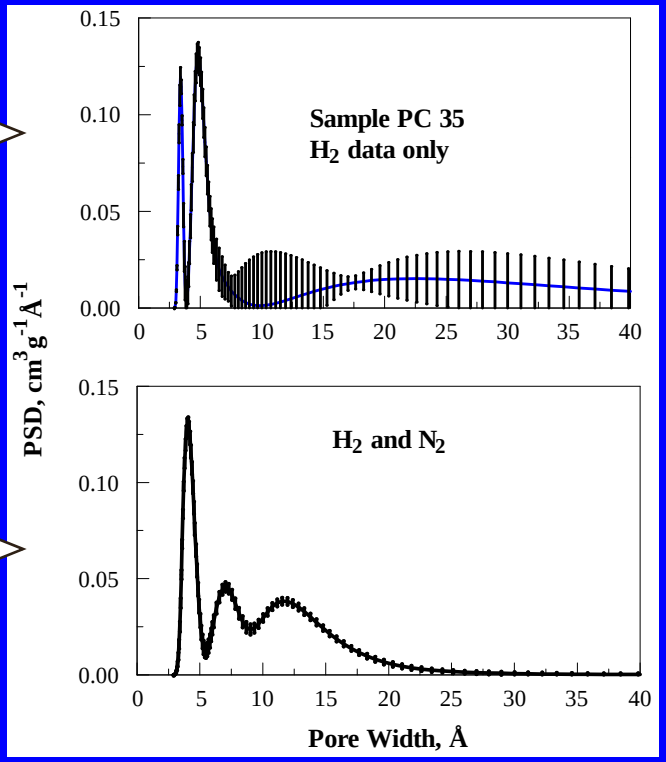
H_2 at 77 K
(Super Critical)

N_2 at 77 K
(Sub Critical)





Multi Adsorbate Fit
reduces uncertainty of calculated PSD



Error bars from the covariance matrix

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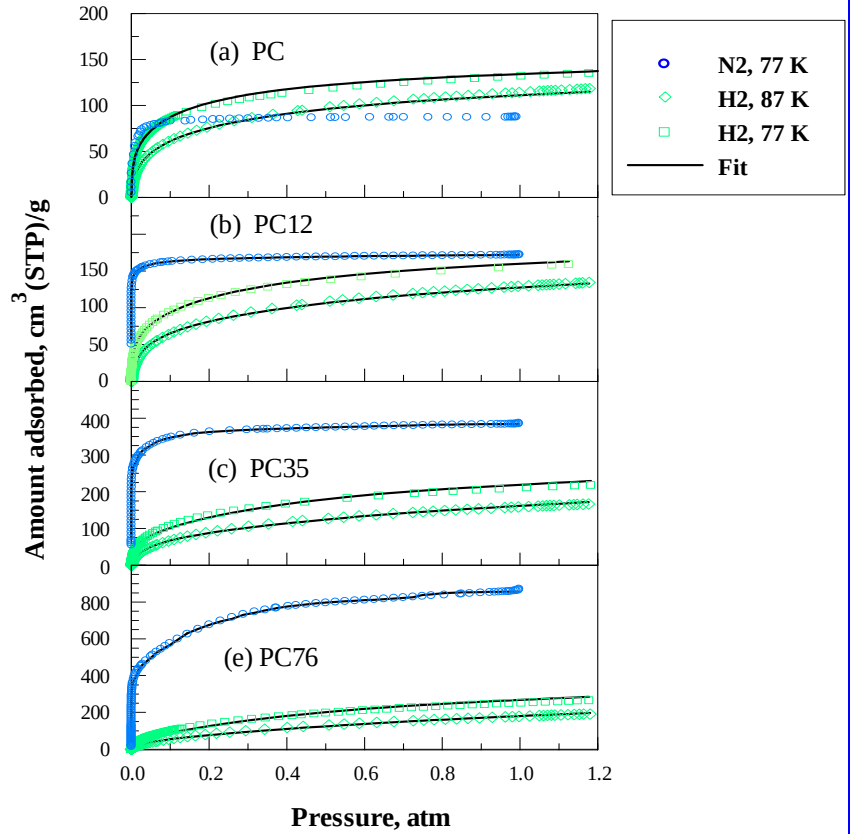
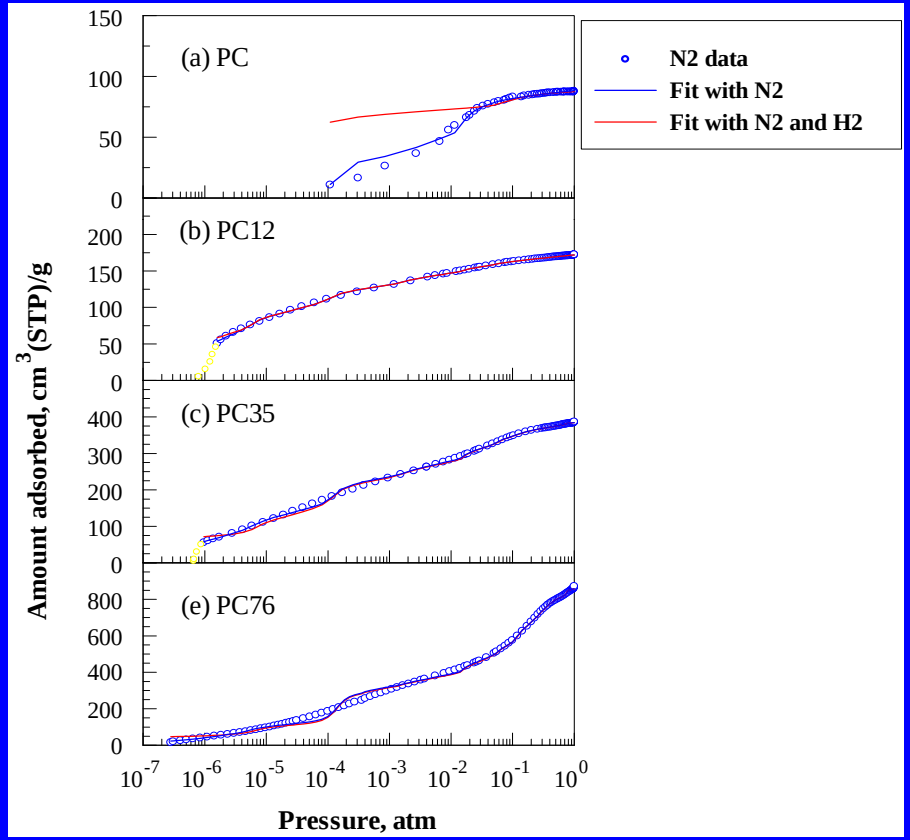
Analysis of adsorption isotherms for series of PC carbons

Multi versus single adsorbate fit





J. Jagiello, C. O. Ania, J. B. Parra, L. Jagiello, J. J. Pis, Carbon 45, 1066-1077 (2007)

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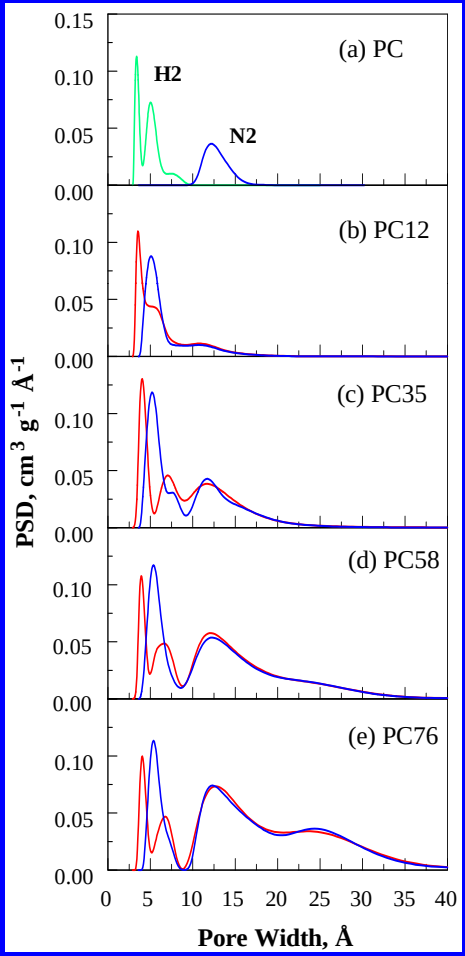
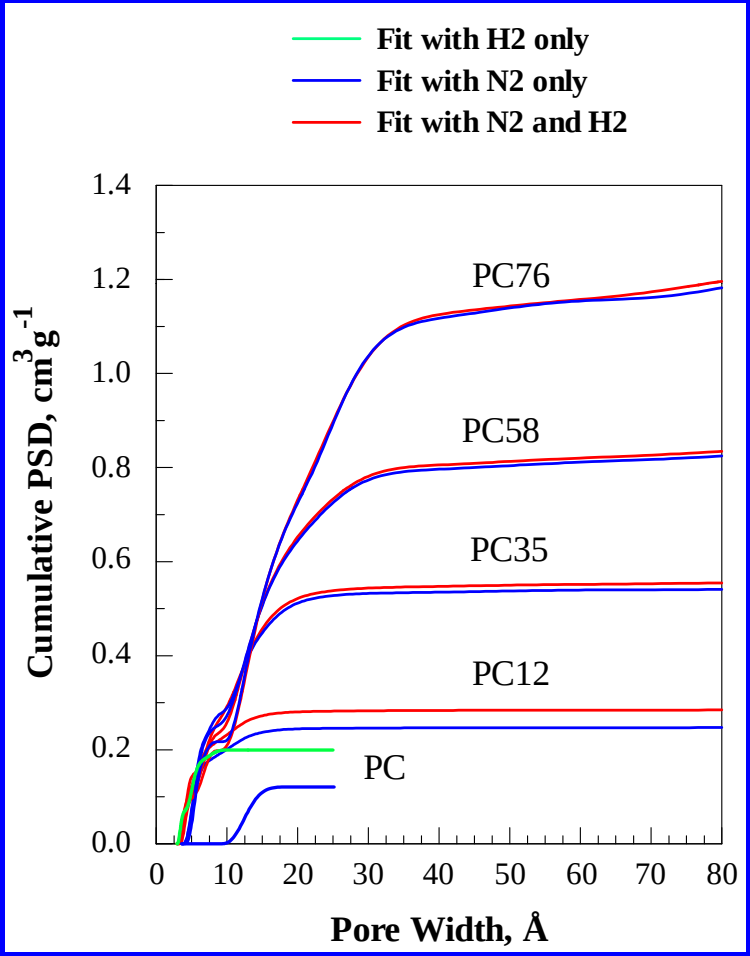
Calculated PSDs for PC samples

Differential



Cumulative



J. Jagiello, C. O. Ania, J. B. Parra, L. Jagiello, J. J. Pis, Carbon 45, 1066-1077 (2007)

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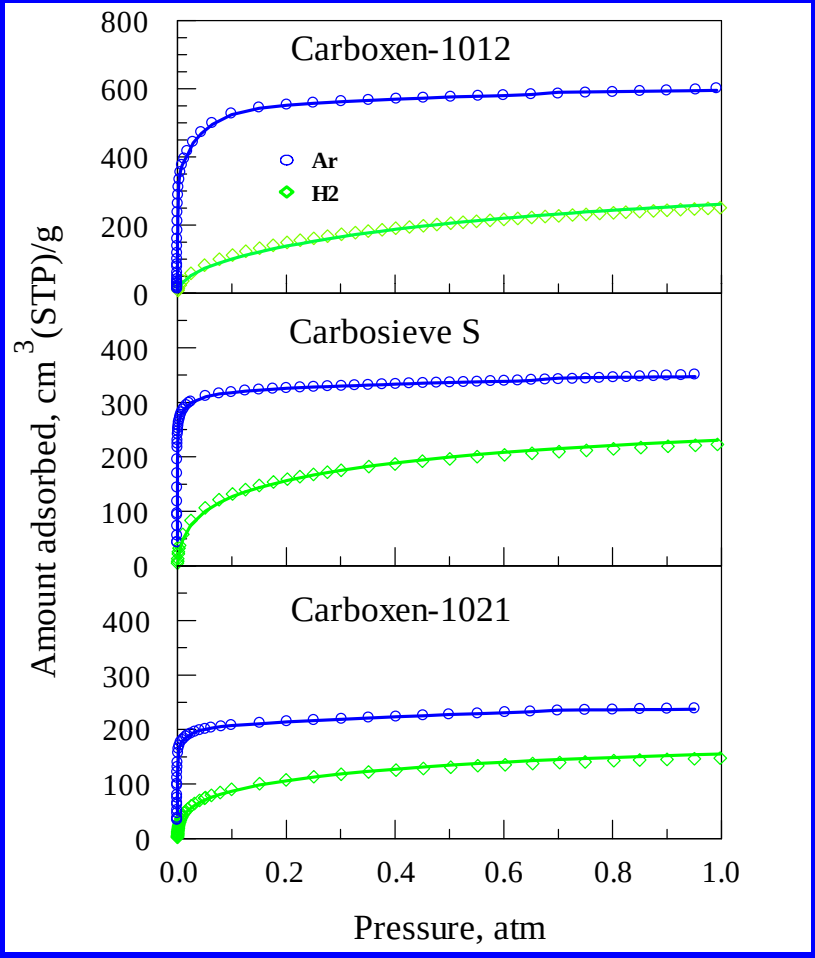
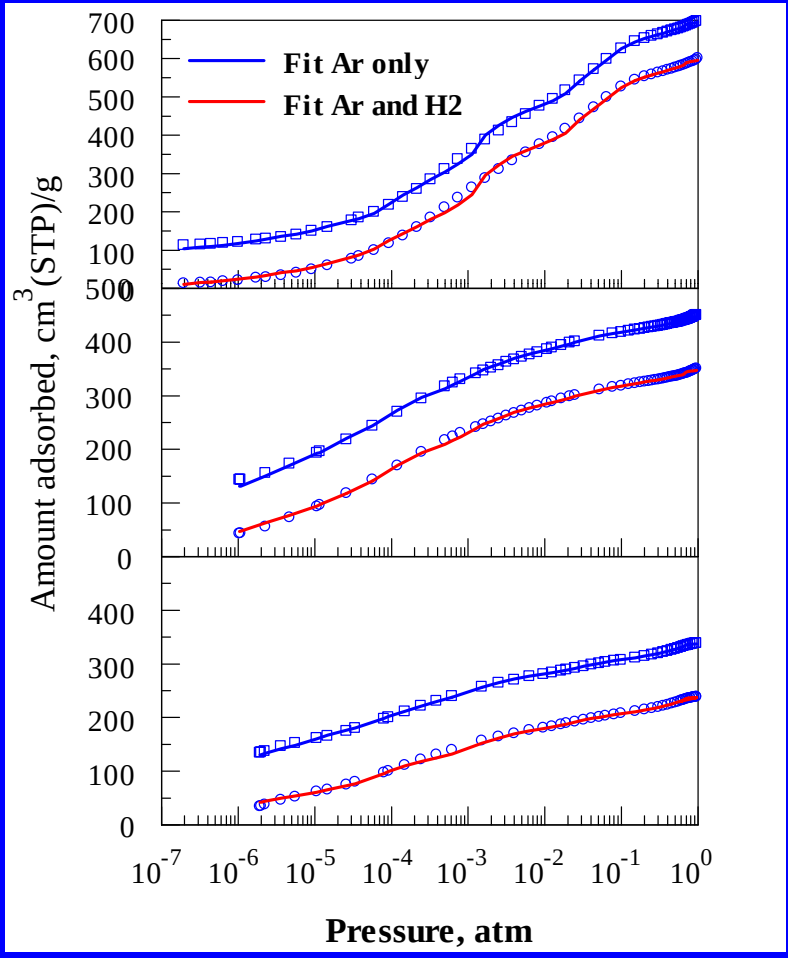
Fitting Ar and H_2 isotherms measured on CMS samples





J. Jagiello, W. Betz, Microporous and Mesoporous Materials **108,** 117–122 (2008)

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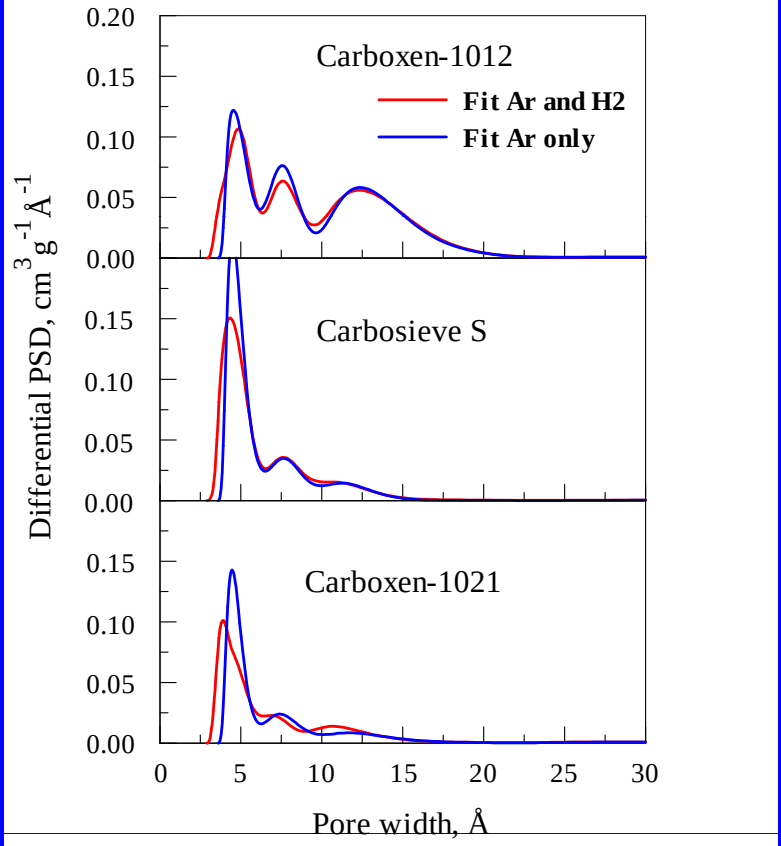
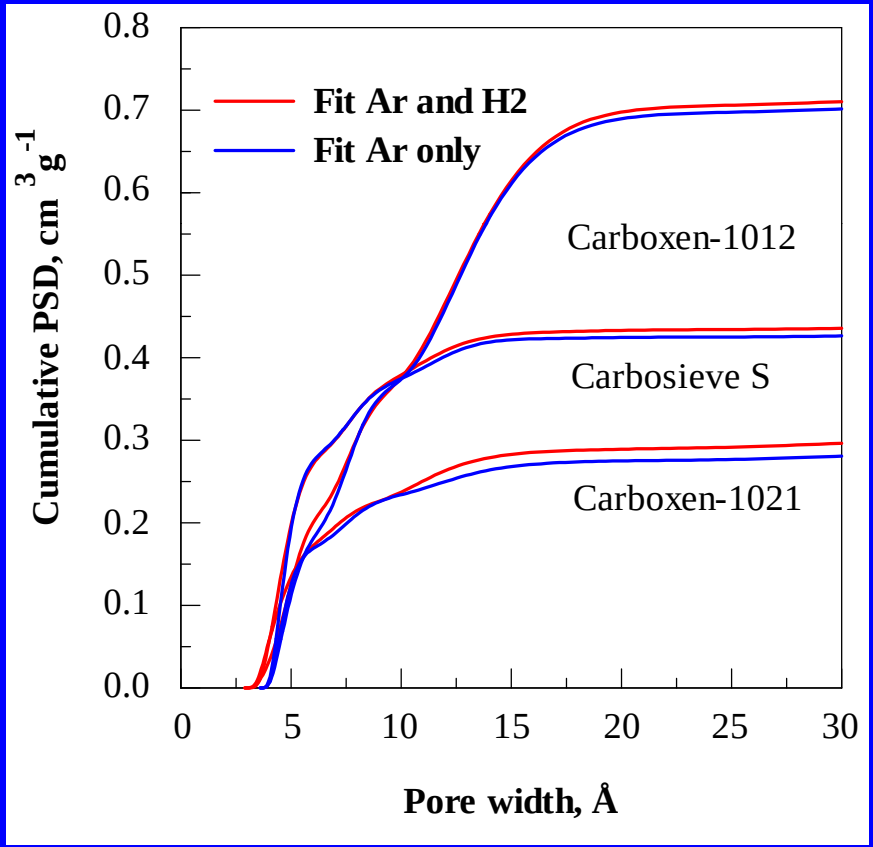
Calculated PSDs for CMS samples

Differential



Cumulative



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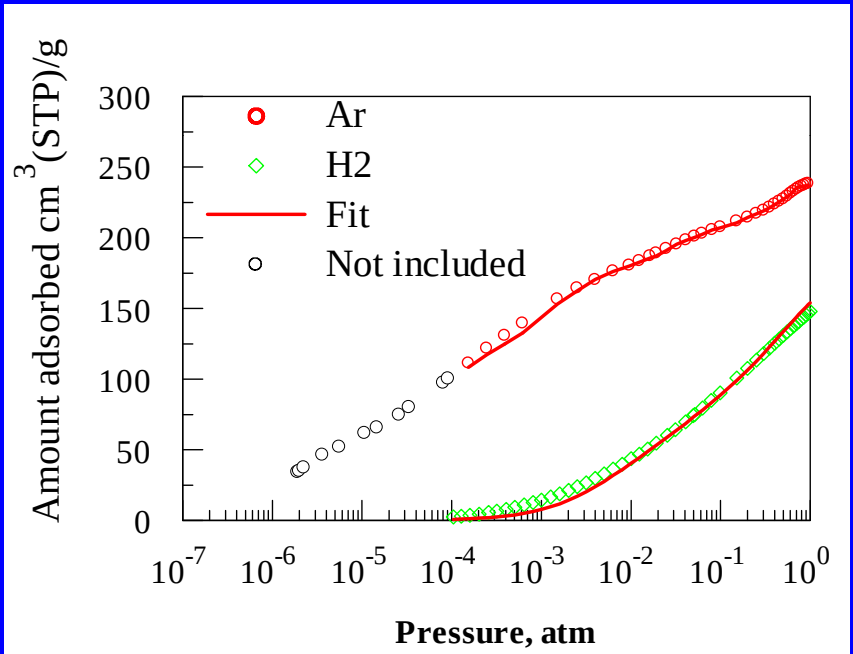
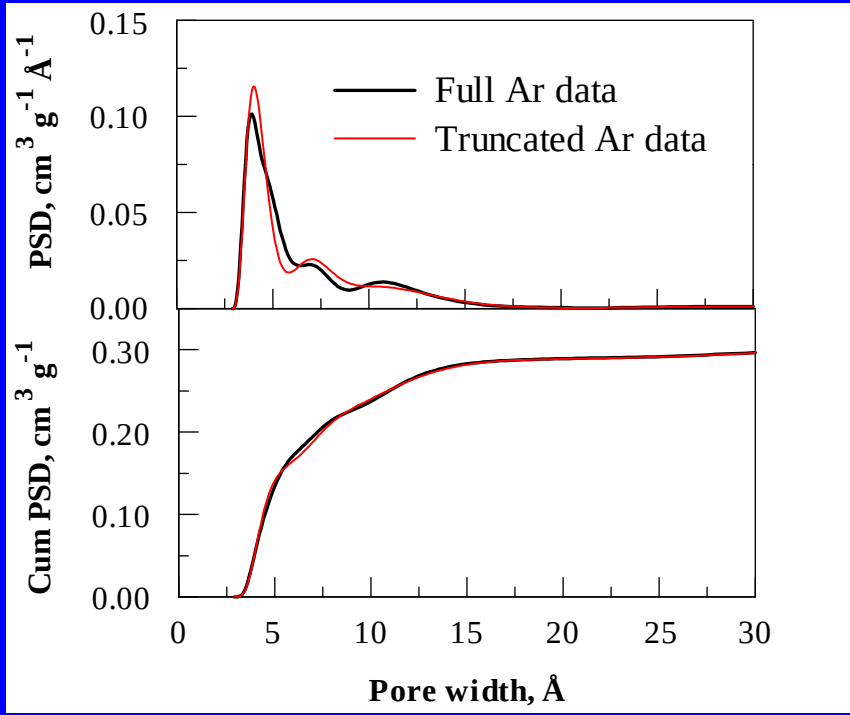
Effect of using truncated Ar data

(Carboxen-1021)

Isotherm data used



Calculated PSD



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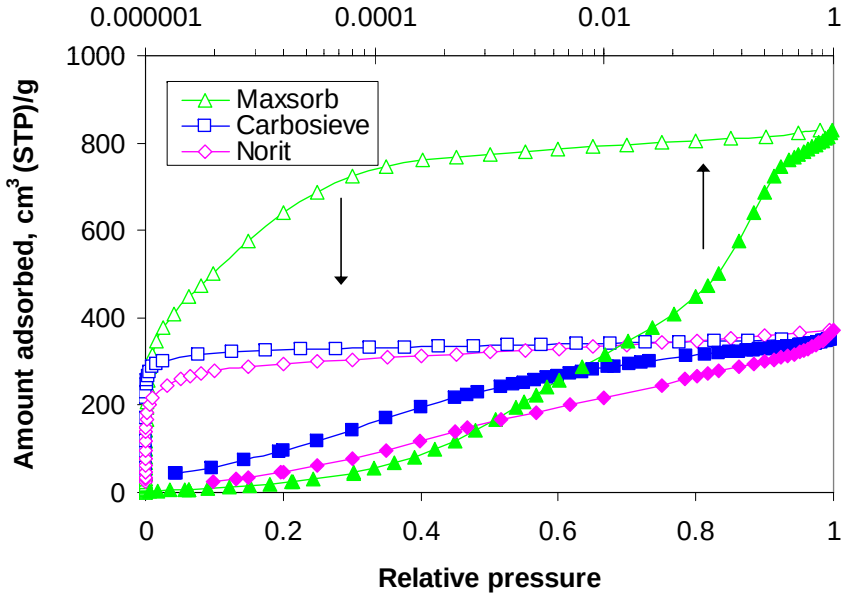
Prediction of High-Pressure H_2 Adsorption

Standard Adsorption Properties Derived from Ar Isotherms (87 K)



Sample	S(BET) m^2/g	V_m(DR) cm^3/g
Maxsorb	2100	0.69
Carbosieve	1120	0.42
Norit	970	0.37

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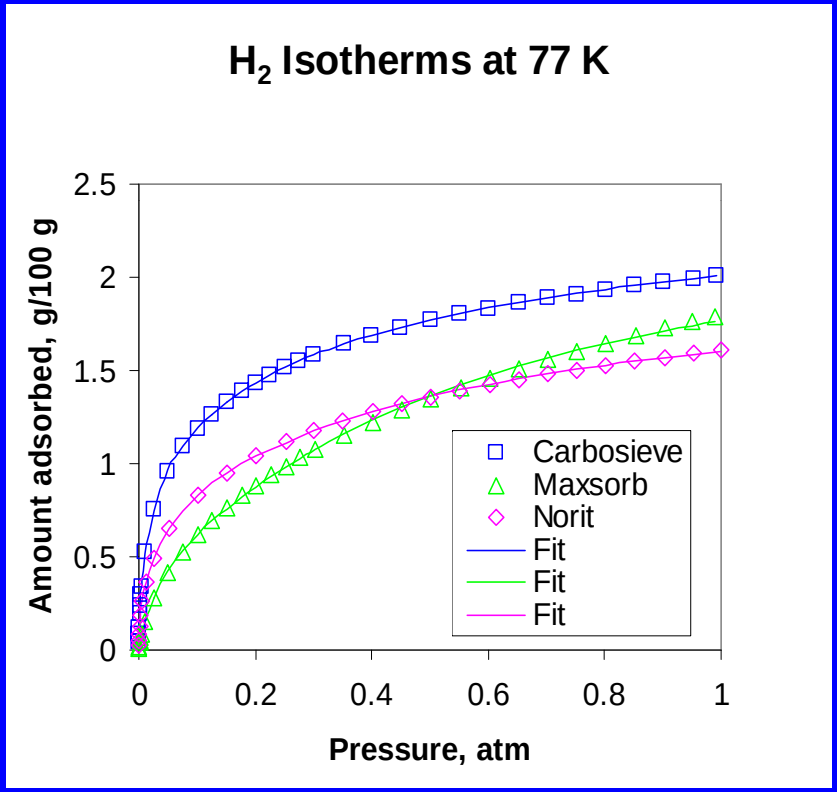
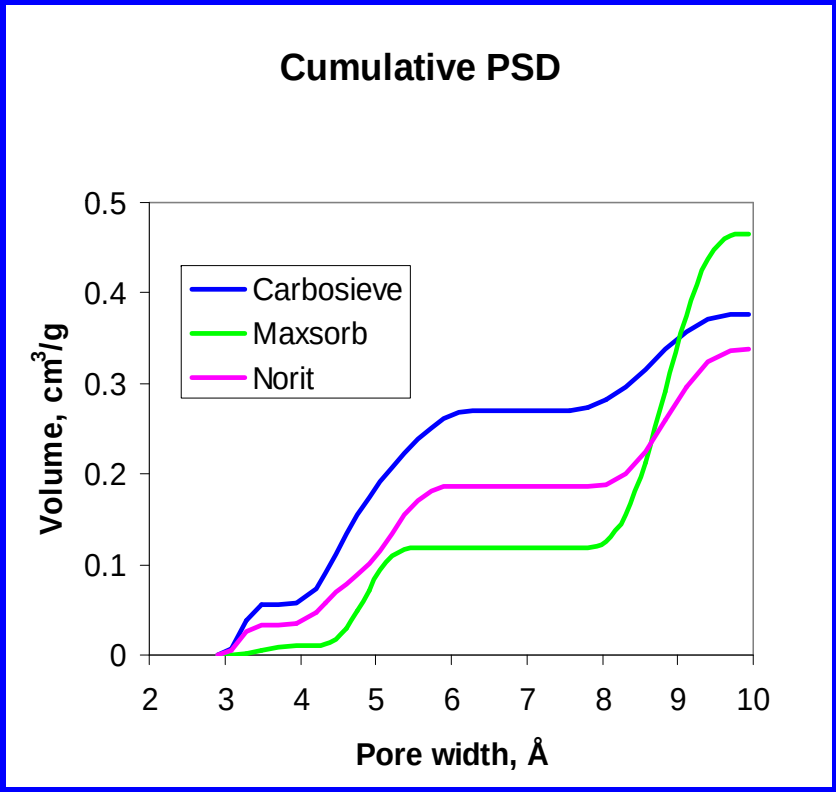
Micro pore Analysis Using H_2 Adsorption





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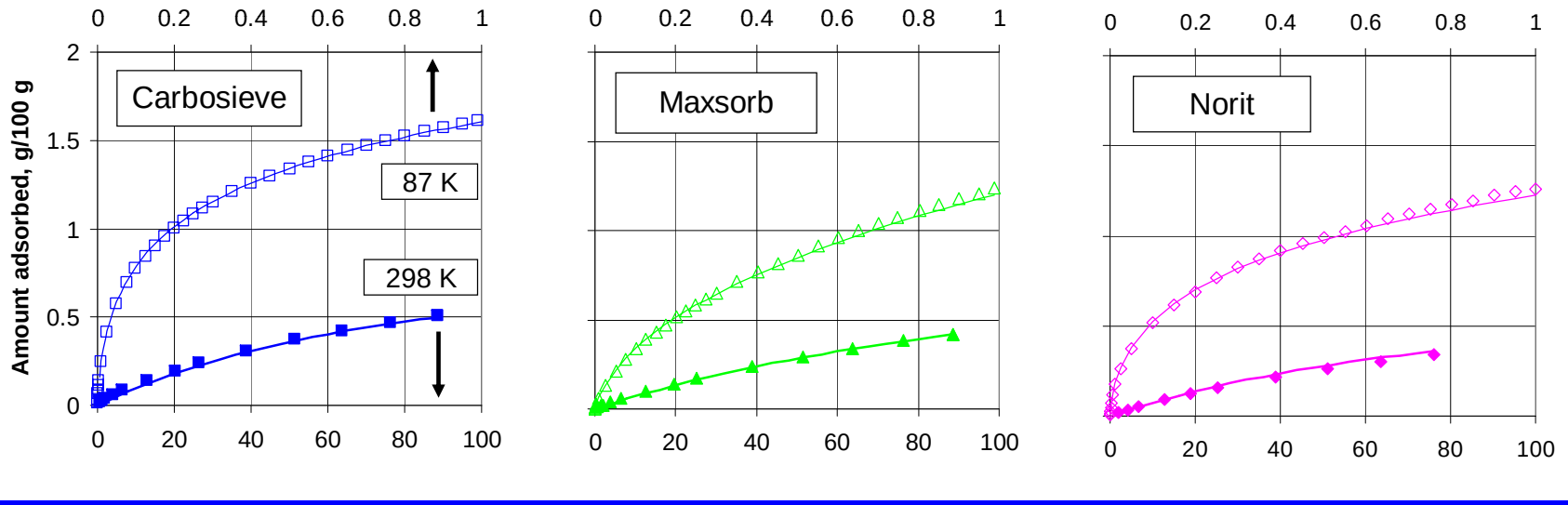
Prediction of H_2 Adsorption at 87 and 298 K from Adsorption Isotherms at 77 K Based on DFT Model



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Effects of pore size and chemistry in analysis of zeolite pore structure

Cylindrical pore model is assumed for zeolite pores.

Model NLDFT isotherms (kernels) are calculated using Tarazona approach.

Fluid-pore interaction potential has the following form:

$U_{pore} = E_{wall}(\rho,\varepsilon_{sf})\ U_{cylinder}(w,r)$

where:

ρ - the solid density

ε_{sf} - the adsorbate-solid atom interaction parameter

w - the effective pore width

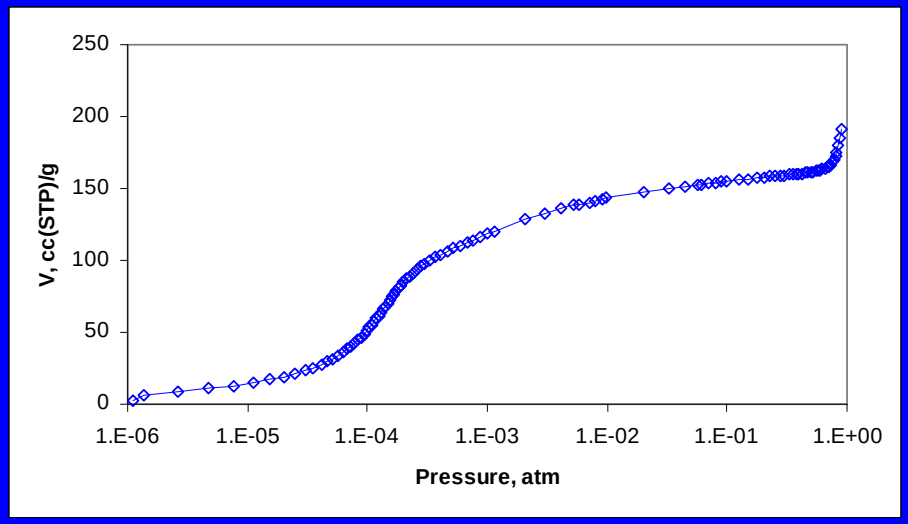
r - the distance of a molecule from the pore wall

E_{wall} – the wall potential interaction parameter

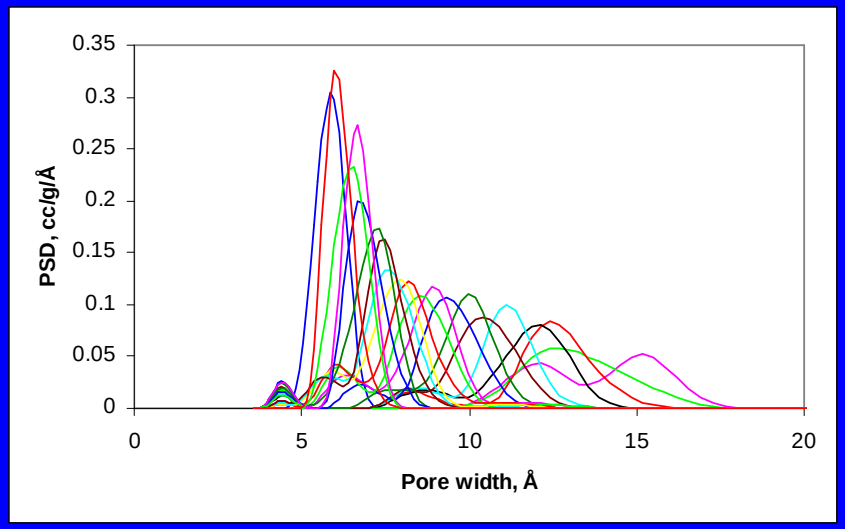
$U_{cylinder}$ - the fluid-cylindrical wall interaction potential

Effects of pore size and chemistry on gas adsorption in zeolites

N_2 Adsorption Isotherm Measured for Zeolite Y Sample



PSDs clculated for Y-N_2 data using different E_{wall} parameters



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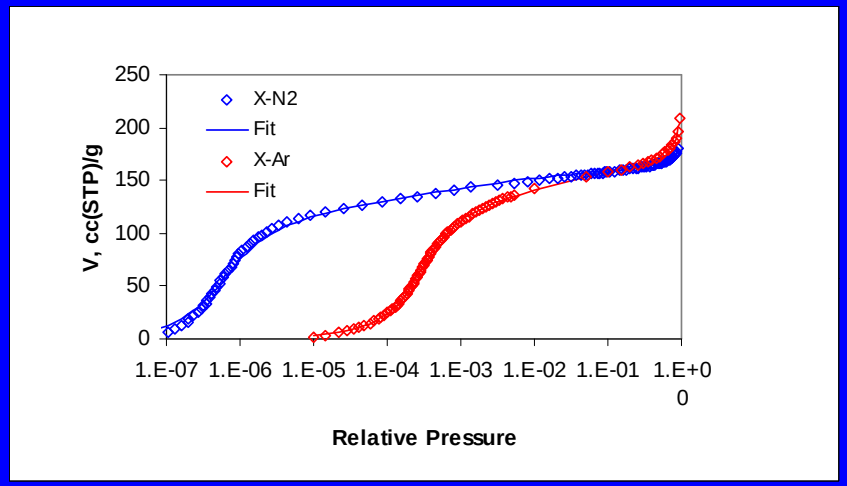
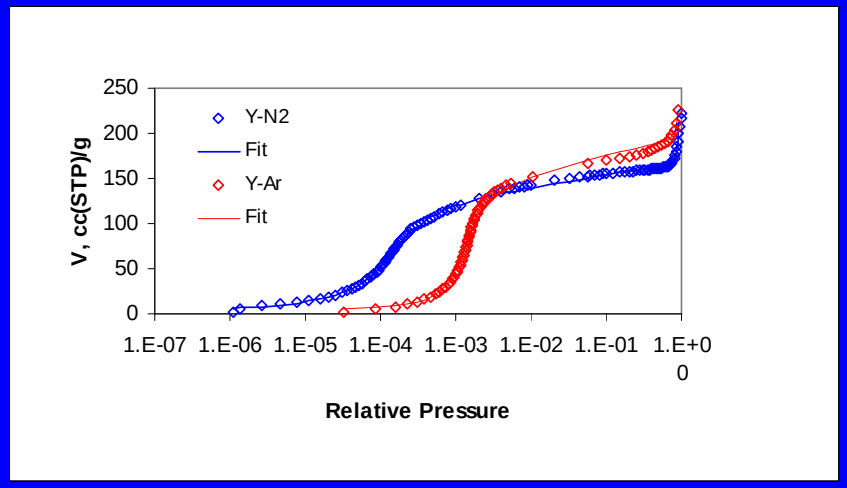
Analysis of N_2 and Ar Adsorption Isotherms for Zeolite X and Y Samples

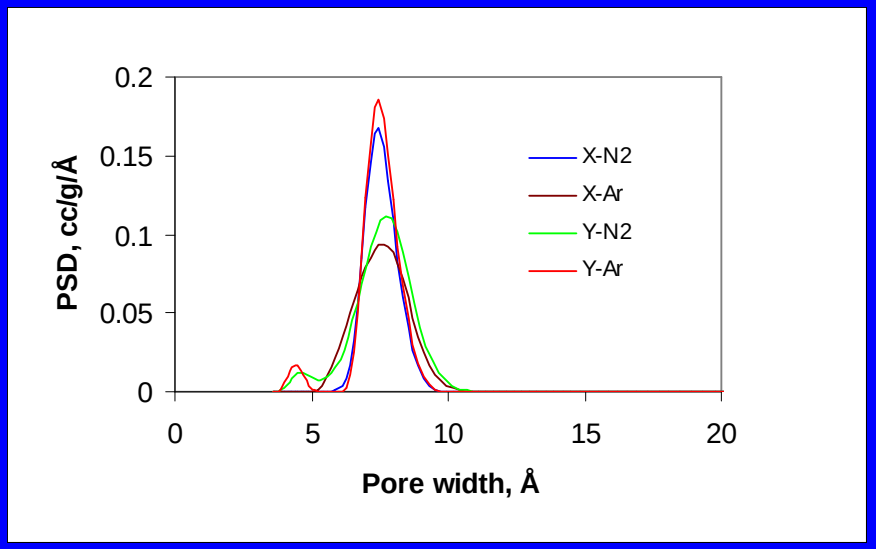
Adsorption Isotherms for Zeolite X



Adsorption Isotherms for Zeolite Y



PSDs Calculated using Optimal E_{wall} parameters



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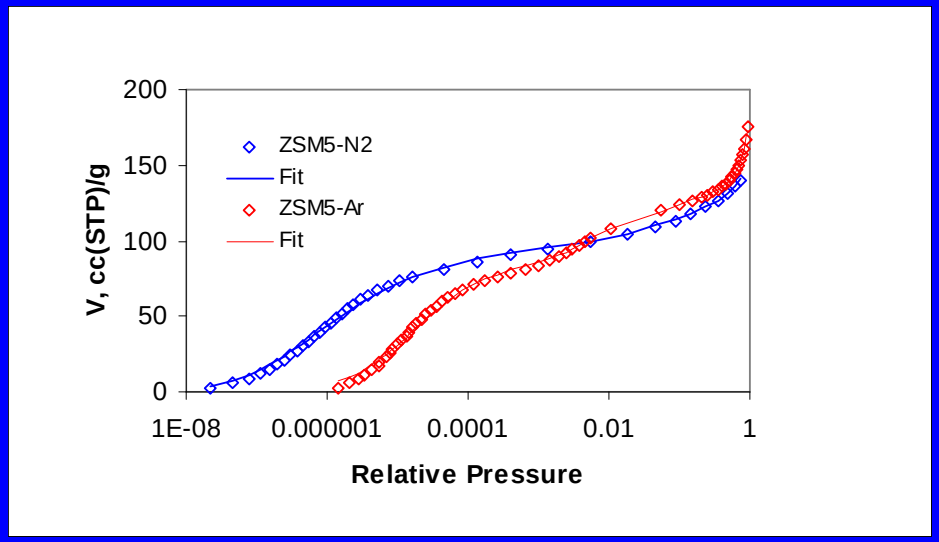
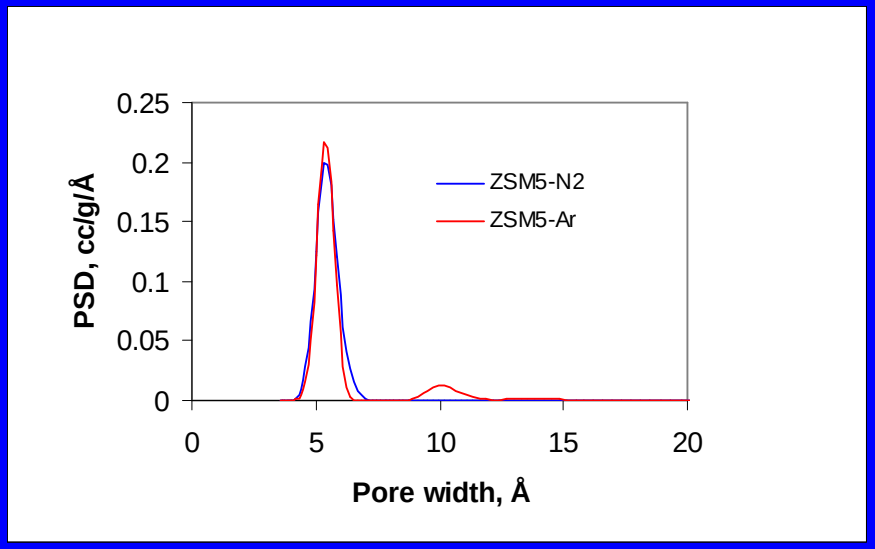
Analysis of N_2 and Ar Adsorption Isotherms for ZSM5 Sample (NH_4 form)

N_2 and Ar Adsorption Isotherms



PSDs Calculated using Optimal E_{wall} parameters



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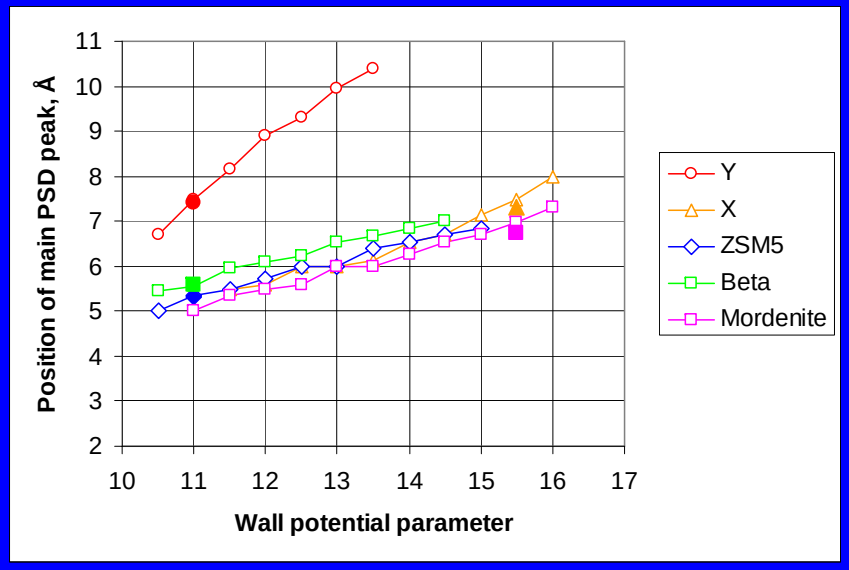
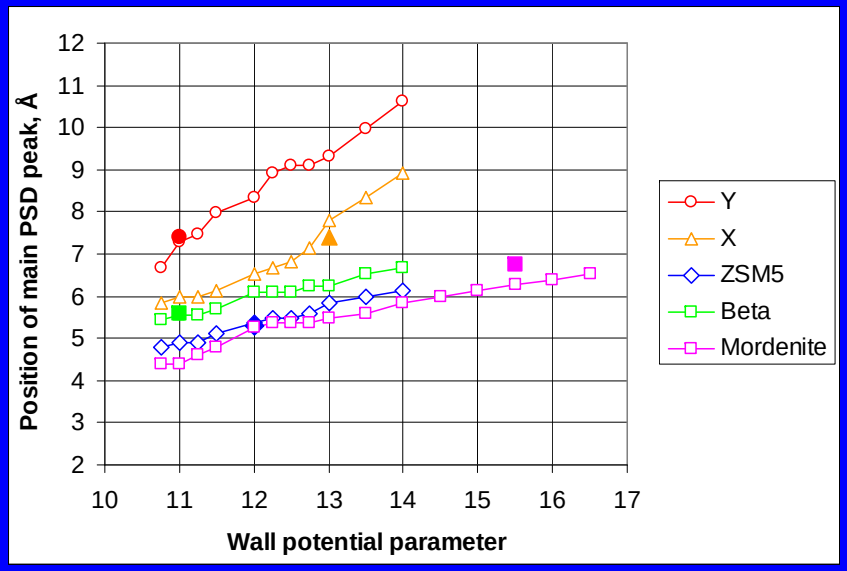
PSD Peak Position as a Function of Wall Potential Parameter, E_{wall}

N_2



Ar



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Conclusions

- Carbon PSDs obtained from the simultaneous analysis of multiple adsorption isotherms are robust and consistent with more than one adsorbate.
- This approach allows detecting experimental points that are not fully equilibrated due to very slow diffusion to narrow micropores.
- The range of pore size analysis is extended to smaller pore sizes compared to the standard nitrogen or argon adsorption analysis.
- Data of the two isotherms provide complementary information about the carbon porosity in the range of micro and mesopores.
- Proposed approach can be considered a useful tool for a comprehensive characterization of activated carbons, and for obtaining detailed and reliable carbon PSDs.
- Effective pore wall potential assumed for zeolites allows separating geometrical and chemical effects in the analysis of zeolite pore structure.

PSDs calculated for Y-N2 data using different Ewall parameters.

N2 and Ar Adsorption Isotherms for Zeolite X Sample

PSDs calculated for Y and X data using
Ewall parameters from Table 1

N_2 and Ar Adsorption Isotherms for Zeolite Y Sample

N2 and Ar Adsorption Isotherms for ZSM5 Sample

PSDs clculated for ZSM5 data using
Ewall parameters from Table 1

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