Giorgio Zgrablich School, San Luis, February 17 -19, 2013

Surface and pore structure characterization of nanoporous materials

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INSTRUMENTS

Life in South Florida

Outline

(1) Introduction, comments to the application of the BET method for surface area analysis

(2) Choice of Adsorptive for Pore Size Analysis

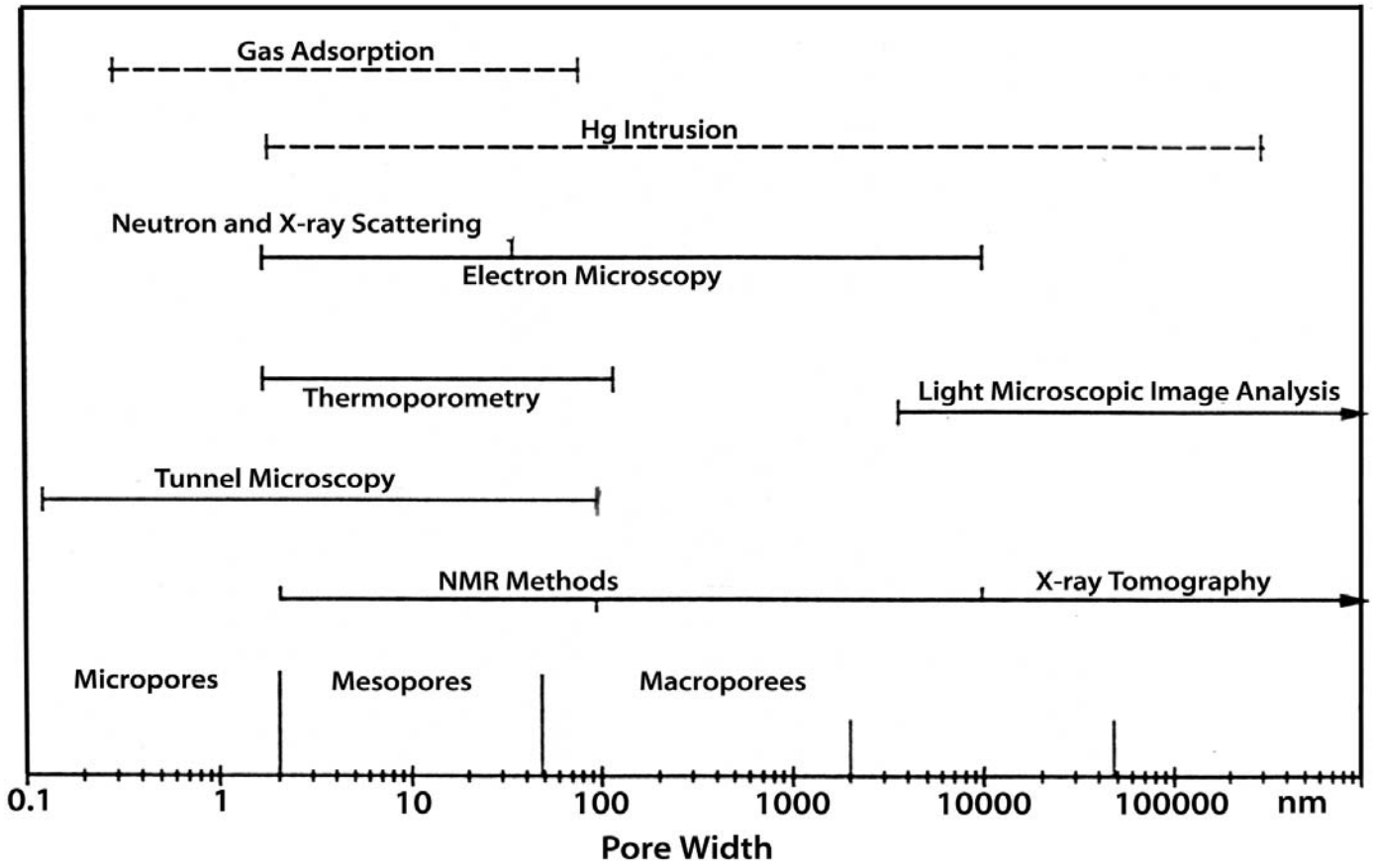
(3) Pore Size Analysis

Comparison of classical, macroscopic thermodynamic methods with microscopic approaches such as DFT, MC

(4) Pore Condensation and Hysteresis

(5) Recommendations & Conclusions

Some Methods for Pore Size Characterization and their Range of Application



According to : P. Klobes, and K. Meyer (BAM, Germany)

Physical Adsorption: IUPAC Classification of Adsorptionisotherms (1985)

IUPAC(1985)

Micropores: < 2 nm

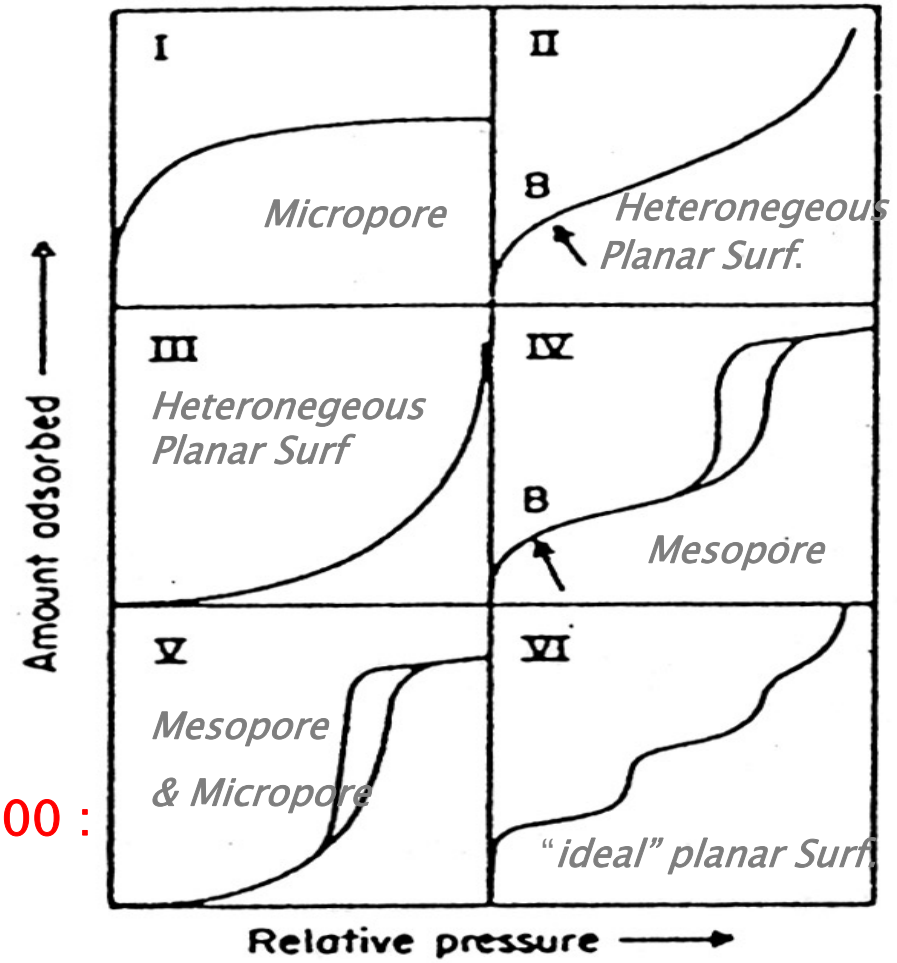
Mesopores: 2- 50 nm

Macropores: > 50 nm

New IUPAC Project – update of Recommendation from 1985:

http://www.iupac.org/web/ins/2010-009-1-100

SAASA-Symposium: Feb 20, at 12:00 : Report on new IUPAC recommendations



This isotherm classification is valid for adsorption of subcritical adsorptives on rigid solids

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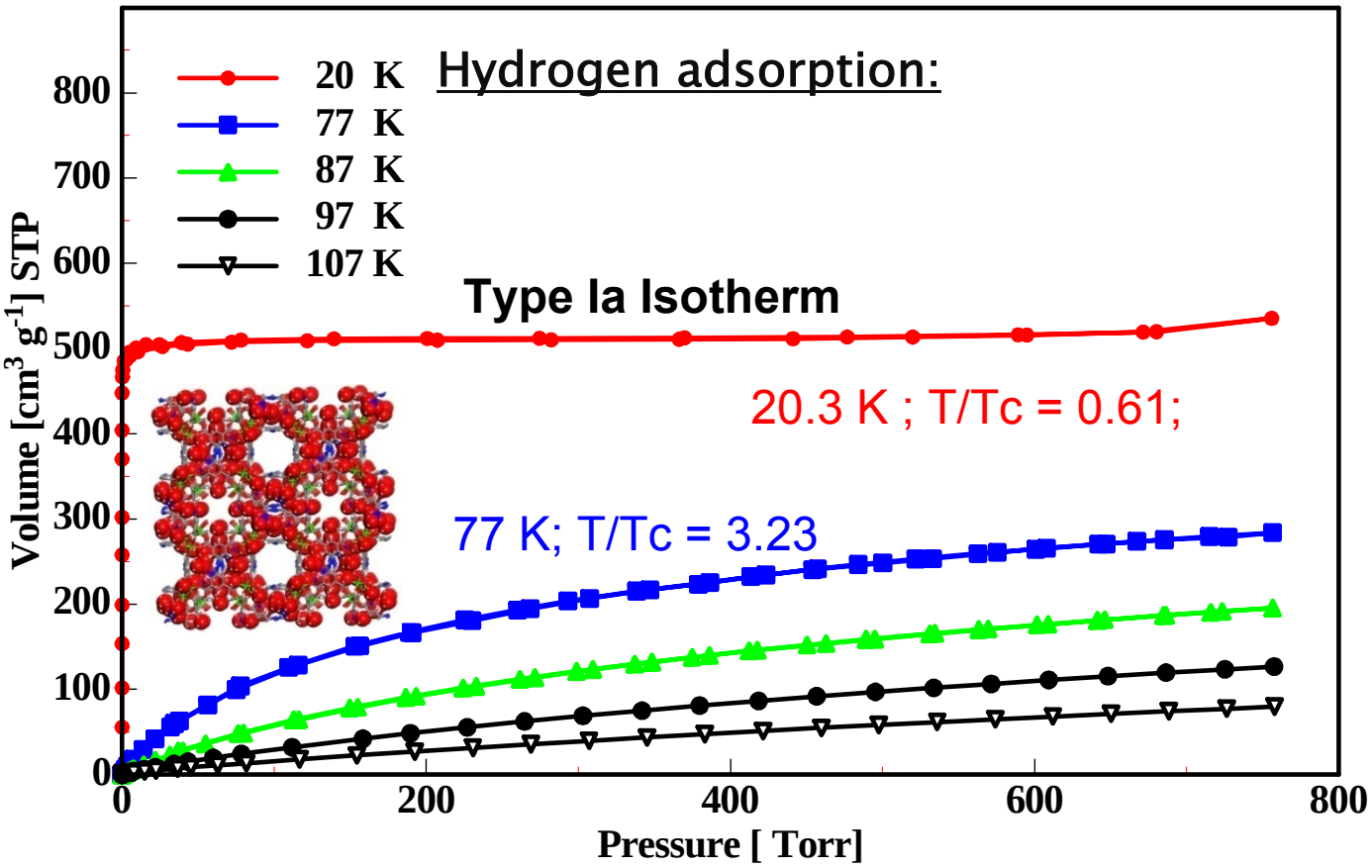
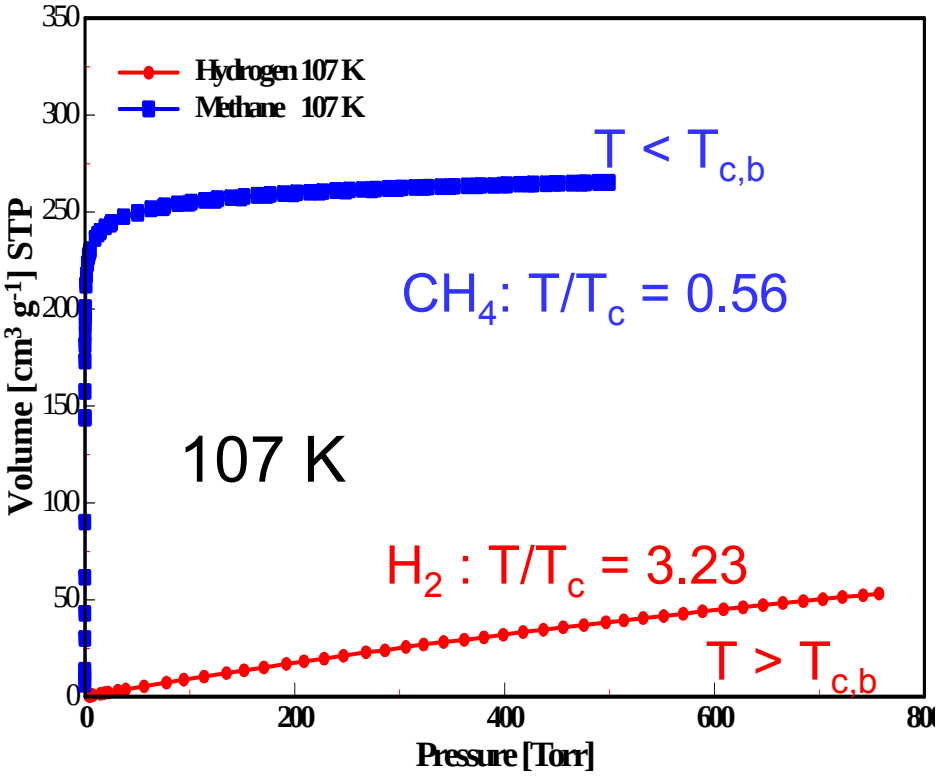
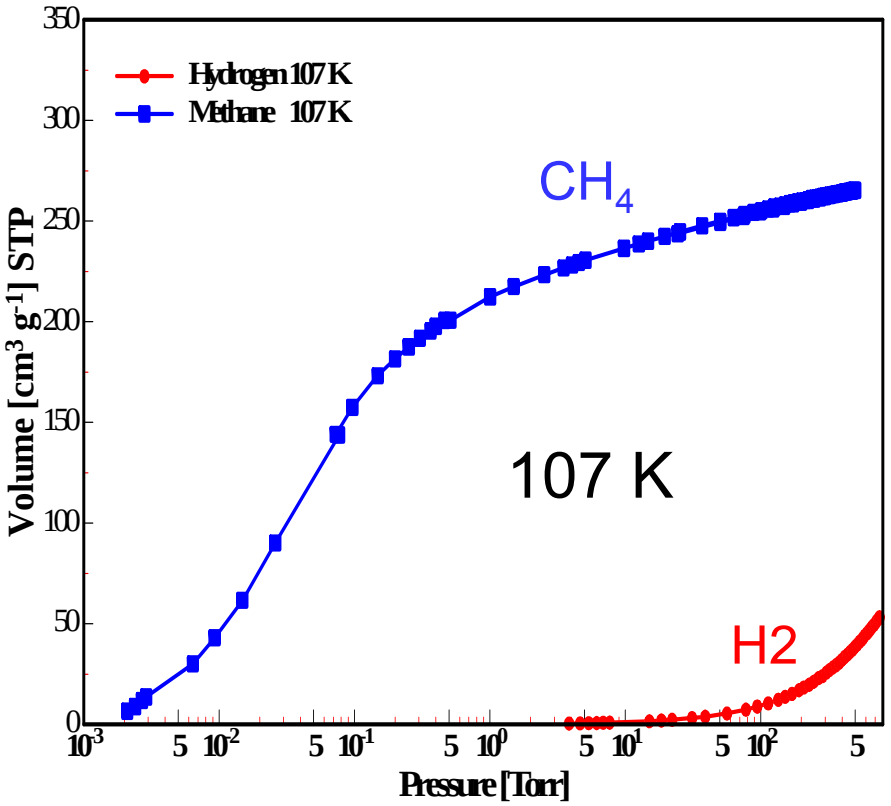
Hydrogen Adsorption in Fe socMOF as a function of temperature below and above the bulk critical temperature



A Cairns, M. Eddaoudi, M. Thommes , D. Wallacher to be published, 2011

Methane and Hydrogen Adsorption at 107 K Indium socMOF





Significant Differences in adsorbed amount of H_2 an CH_4 at 107 K are mainly due to differences in thermodynamic state of adsorptive

Moellmer, E.B. Celer, R. Luebke, A.J. Cairns, R. Staudt, M. Eddaoudi, M. Thommes, Microporous and Mesoporous Materials 129 (2010) 345

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Aspects of Surface Area Analysis

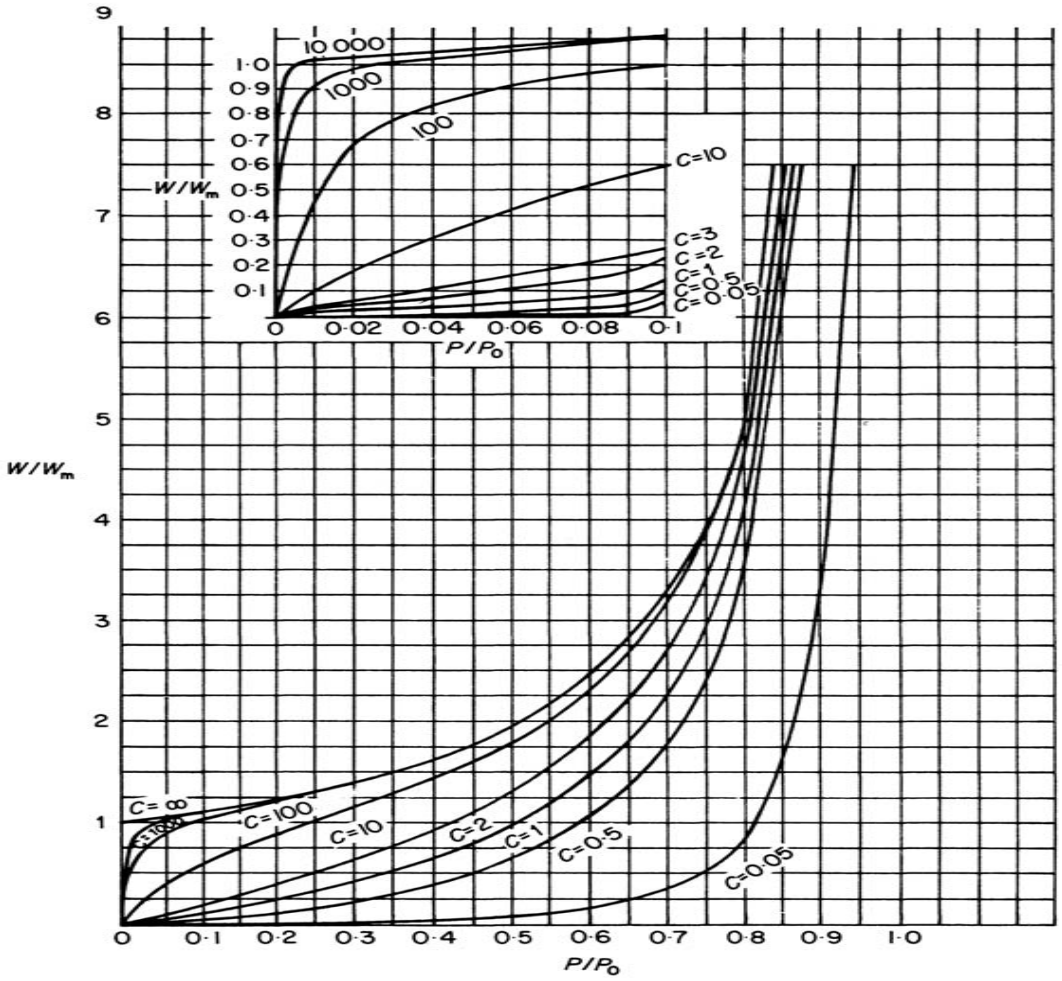
Brunauer, Emmett and Teller Isotherm (1938): Expands the Langmuir Theory from Mono- to Multilayer Adsorption

- Main Assumptions:

- All adsorption sites on the surface are energetically identical
- Lateral interactions (i.e. forces between the adsorbate molecules have been neglected
- The heat of adsorption of the second and each higher adsorbed layer equals the heat of liquefaction

$$\frac{1}{V\left[\left(P/P_0\right)-1\right]} = \frac{1}{V_m C} + \frac{C-1}{V_m C}\left(\frac{P}{P_0}\right)$$

Effect of BET-C onstant on Isotherm Shape

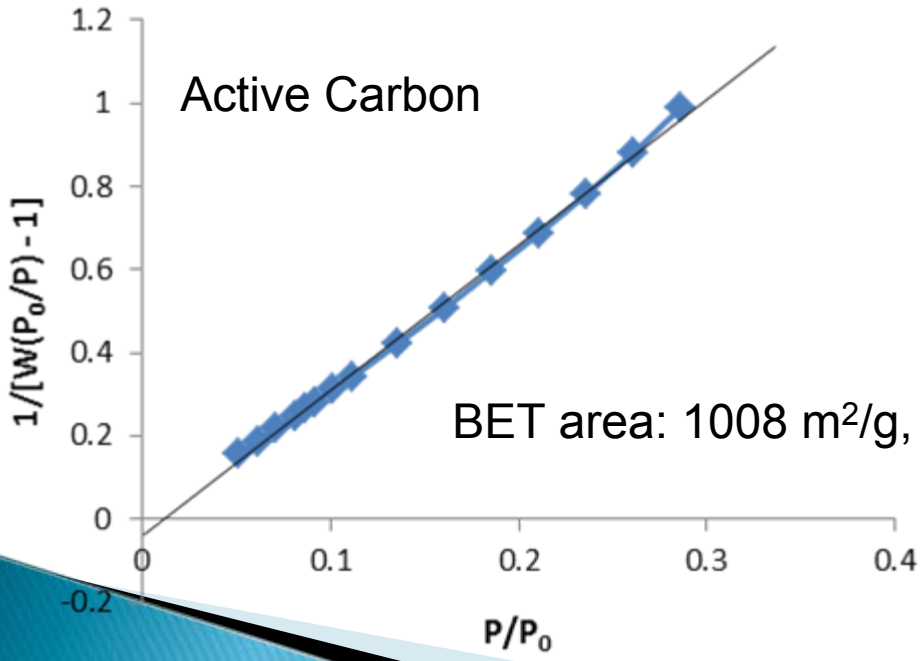


Classical BET range: $P/P_0 = 0.05 - 0.3$

Application of BET method for the Determination of Apparent Surface Area of Microporous Materials

Problem: BET equation is in a strict sense not applicable to microporous materials ⇒ BET Area (equivalent surface area)

$$\frac{p/p_0}{n_a[1-(p/p_0)]} = \frac{1}{n_m C} + \frac{C-1}{n_m C}\cdot\frac{p}{p_0}$$



Application of BET equation in "classical range", i.e. rel pressure range 0.05 to 0.3 :

⇒ Negative Intercept, i.e. neg. C-constant

⇒ Less than optimal correlation coefficient

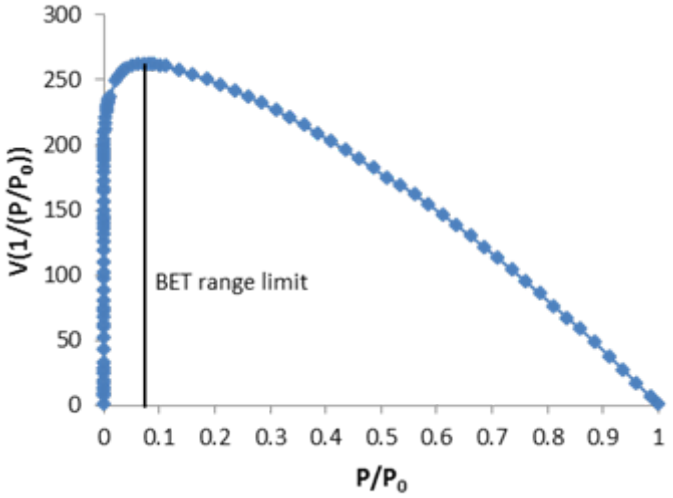
Determination of BET area of microporous materials

How to find the linear range of the BET plot for microporous materials in a way that it reduces any subjectivity

J. Rouquerol et al. (Studies in Surface Science and Catalysis, 160 2007 pp. 49-56) suggest to apply the following criteria:

- The quantity of C must be positive (i.e. any negative intercept on the ordinate of the BET plot is an indication that one is outside the valid range of the BET equation)
- The application of the BET equation should be limited to the pressure range where the term $n (P_0 – P)$ or alternatively $n(1– P/P_0)$ continuously increases with P/P_0; all data points above the maximum in the plot should be eliminated
- The pressure finally corresponding to the monolayer capacity n_m should necessarily enter the pressure range for the calculation

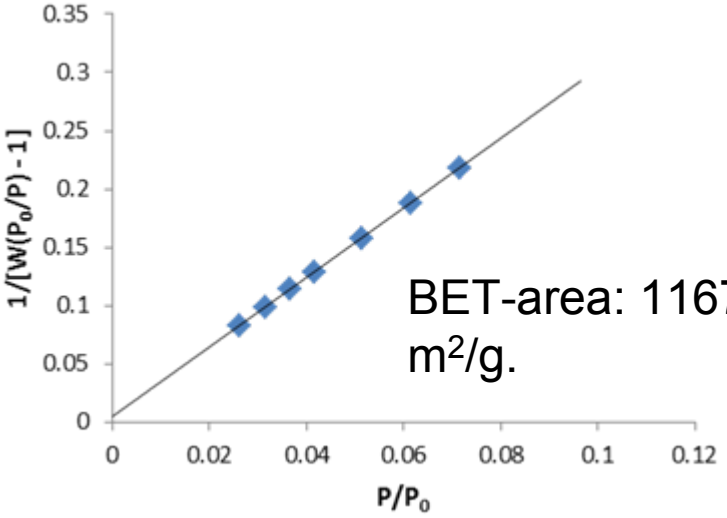
Procedure to find "linear range" for application of the BET equation for microporous materials



Maximum at $P/P_0 = 0.07$,

⇒ Applying BET equation for data points < 0.04!

Activated carbon



BET-area: 1167 m^2/g.

⇒positive C constant

⇒Good correlation coefficent

Application of this procedure: (meanwhile featured in ISO 9200 and ASTM C1274)

- **improves reproducibility of BET area (apparent surface) determination of microporous materials**

-improves the comparison of BET area data between labs.

Choice of Adsorptive

Choice of Adsorptive

- **Pore Size/Volume Characterization of microporous materials with polar surfaces, e.g. zeolites, MOFs**

  ⇒ ***Argon 87 K***

- **Pore Size/Volume Characterization of nanoporous carbons**

  ⇒ ***Combination of Nitrogen/Argon (at 77 K/87K) with Carbon Dioxide (273K)***

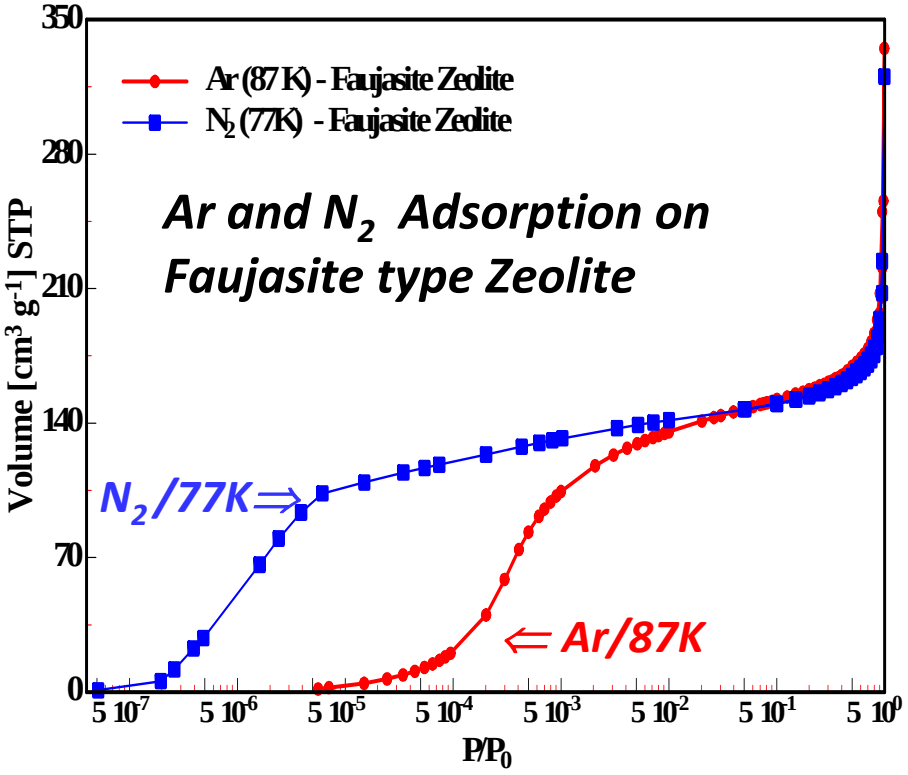
- ***Pore Volume of ultramicroporous materials***

  ⇒ ***Carbon Dioxide (273K)***

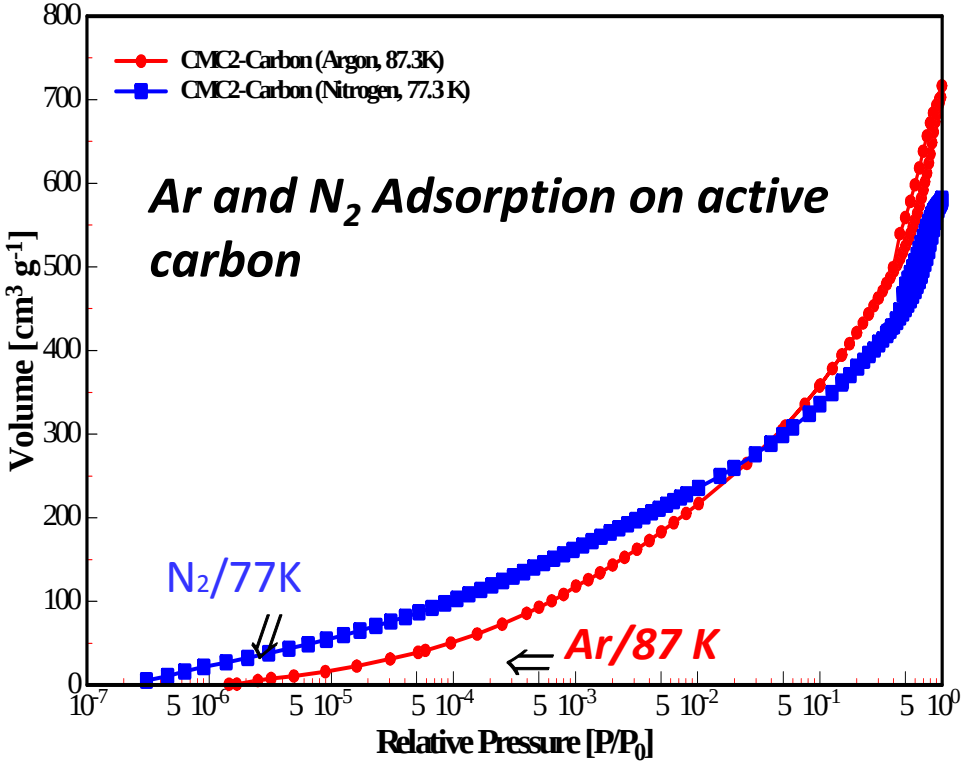
- **Surface and Pore Size Analysis of materials with ultra-low surface area (e.g. thin films)**

  ⇒ ***Krypton adsorption at 87 K and 77 K***

Choice of Adsorptive for Pore Size Analysis by Gas Adsorption: *Nitrogen (77.35 K) or Argon (87.27 K) ?*



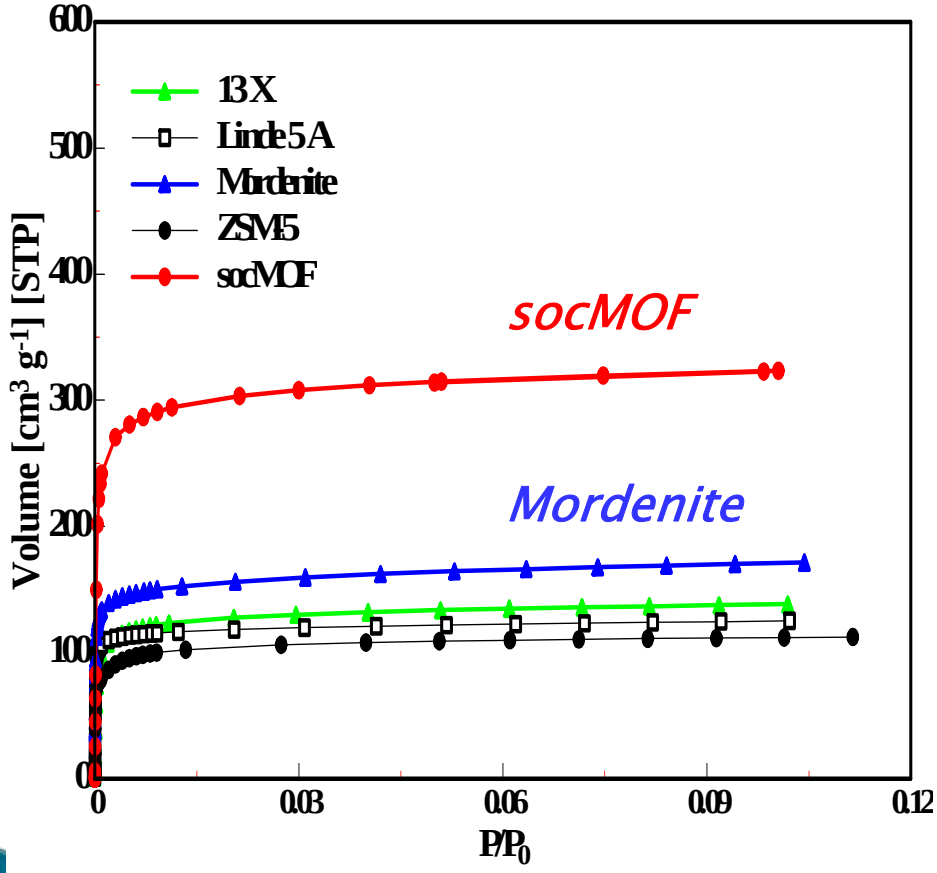
Zeolites: N_2- quadrupole interactions important!

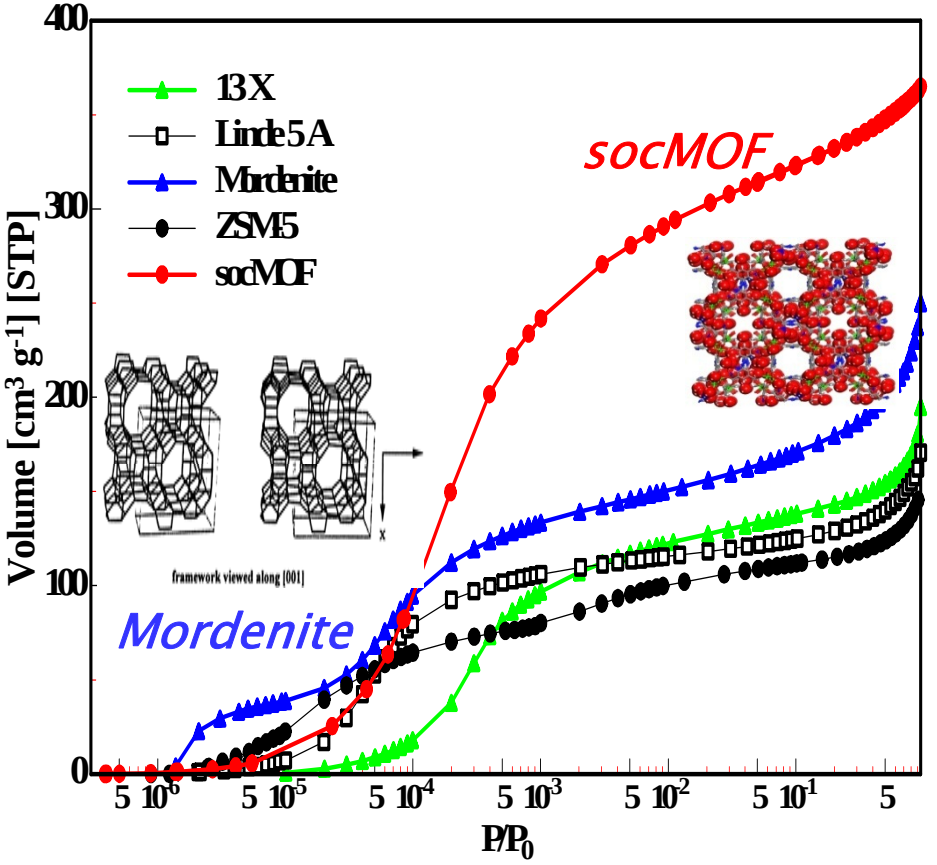


Many Carbons: N_2 –quadrupole interactions not so important

Problem: Below 100 mTorr(P/P0 = 10-5): Regime of extremely slow kinetics , the selection of proper equilibrium parameters is essential for obtaining accurate adsorption isotherm data

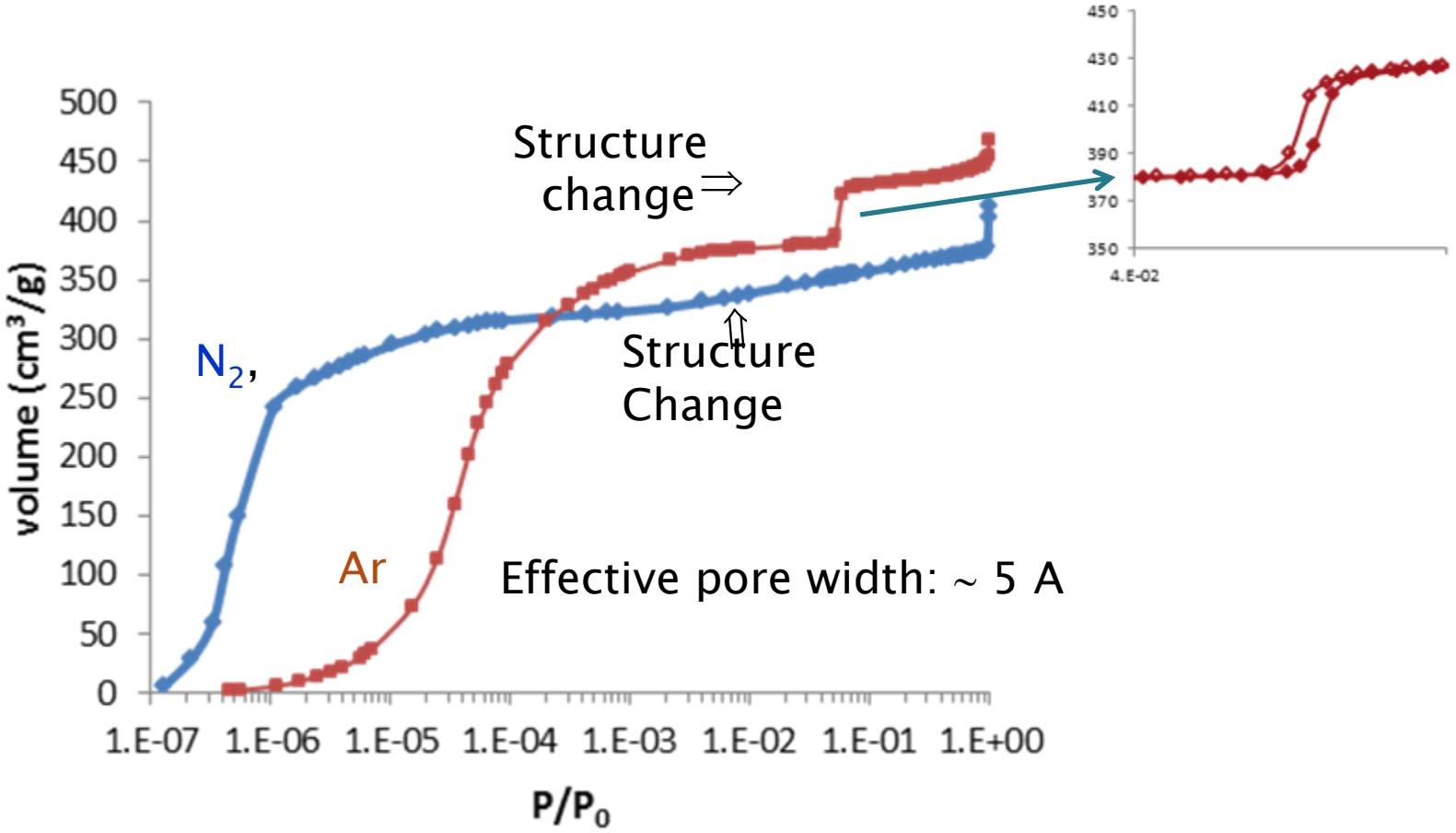
Argon (87 K) Adsorption in Zeolites and MOFs





Zeolite data: M. Thommes, in "Introduction to Zeolite Science, 3rd Revision, Chapter 15, Studies in Surface Science and Catalysis 168 , Elsevier 2007 pp.495 -525

Nitrogen(77.4K) and Argon (87.3K) in a novel Copper-MOF



D. Lässig, J. Lincke, J. Moellmer, C. Reichenbach, A. Moeller, R. Gläser, G. Kalies, K. A. Cychosz, M. Thommes, R. Staudt and H. Krautscheid*, ***Angew. Chem. Int. Ed. 50 (2011),***

Argon Adsorption at 87.27 K for Zeolite/MOF Pore Size Analysis

- Due to weaker attractive fluid-wall interactions (and the lack of a quadrupole moment), Argon fills micropores of dimensions 0.45 nm – 0.8 nm (and with polar surface functionality) at much higher relative pressures, (.i.e., at least 1.5 decades higher in relative pressures) as compared to nitrogen.
- $\Rightarrow$ High resolution adsorption isotherms of high accuracy can be measured over the complete micro-mesopore range!

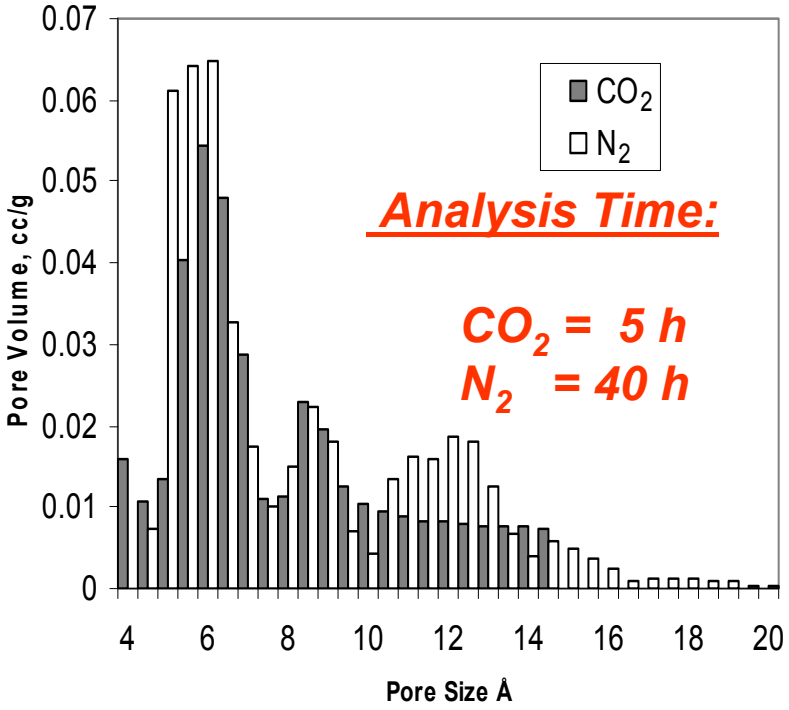
- The application of advanced theoretical approaches based on statistical mechanics is facilitated for argon adsorption as compared to the complex situation of the nitrogen molecule

In contrast: no clear correlation between pore filling pressure and pore size in case of nitrogen adsorption in zeolites and MOF (for instance)

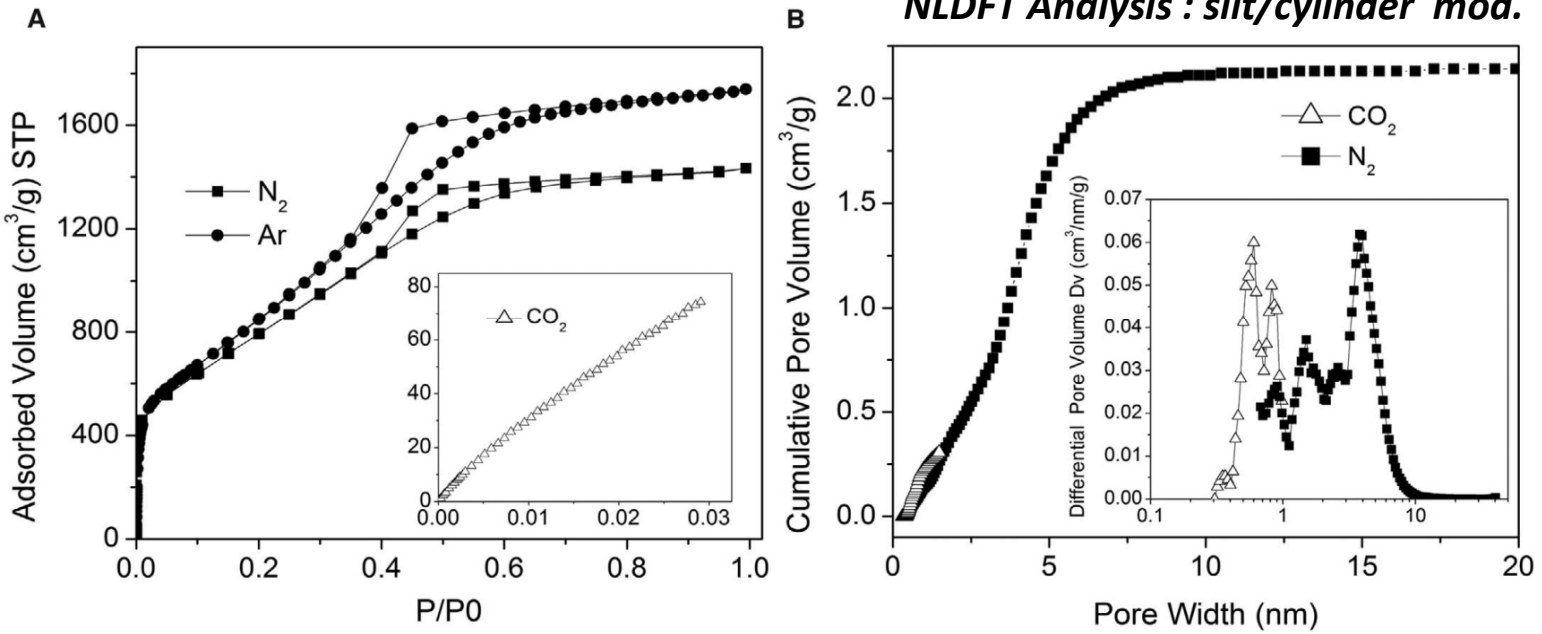
CO_2 Micropore Analysis of active carbons at 273.15 K

- At elevated temperatures and higher absolute pressure (P_0 = 26200 Torr)) CO_2 can access micropores, which are not accessible for nitrogen at 77 K
- Fast analysis: due to higher diffusion rate equilibrium is achieved faster as compared to nitrogen adsorption at 77 K $\Rightarrow$ dramatic decrease in analysis time i.e., 3-5 h for CO_2 versus 30-50 h N_2
- No need for high vacuum system
- No need for a low-pressure transducer 1000 Torr transducer is sufficient

Rodriguez-Reinoso and Linares et al 1986, 1987

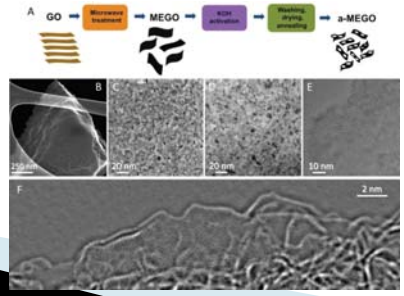


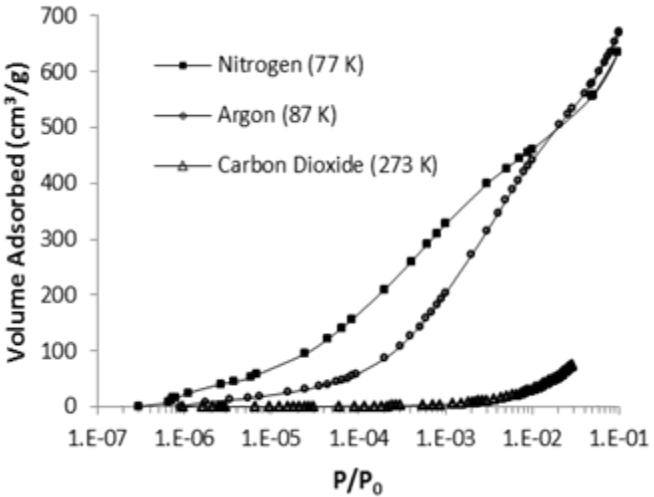
Characterization of novel porous carbon obtained by chemical activation of graphene



Yanwu Zhu, Shanthi Murali, Meryl D. Stoller, K. J. Ganesh, Weiwei Cai, Paulo J. Ferreira, Adam Pirkle, Robert M. Wallace, Katie A. Cychosz, Matthias Thommes, Dong Su, Eric A. Stach and Rodney S. Ruoff.

Science 2011, 332, 1537-1541





Krypton Adsorption at 77 K – Low surface area analysis

- Krypton at 77K is frequently used for low surface area measurements

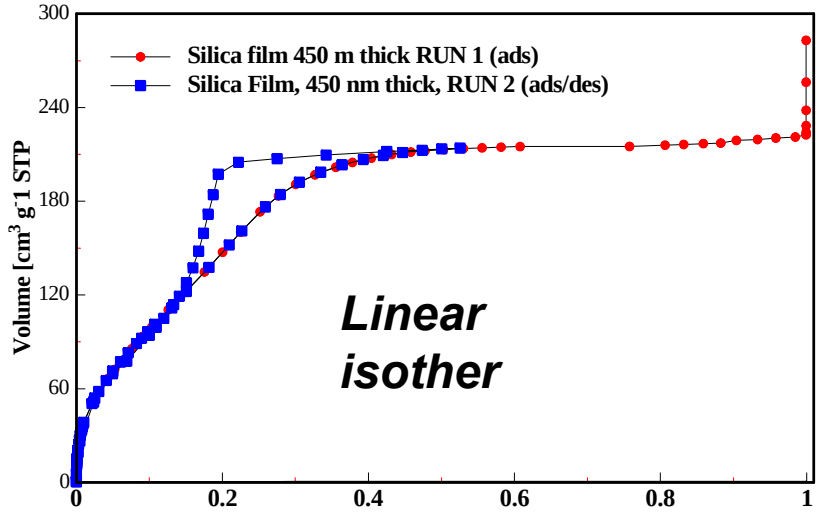
- The saturation pressure is 2.63 Torr (assuming supercooled liquid) at 77K, which means (compared to nitrogen 77K and argon 87 K) by far fewer molecules in the void volume and therefore a smaller void volume error.

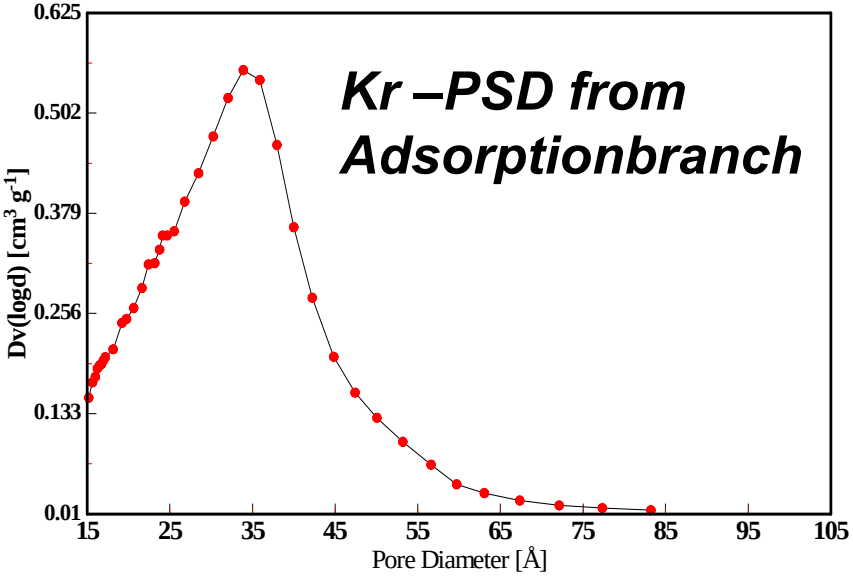
⇒***Total surface areas down to at least 0.05 m^2 can be determined with Kr adsorption at 77 K***

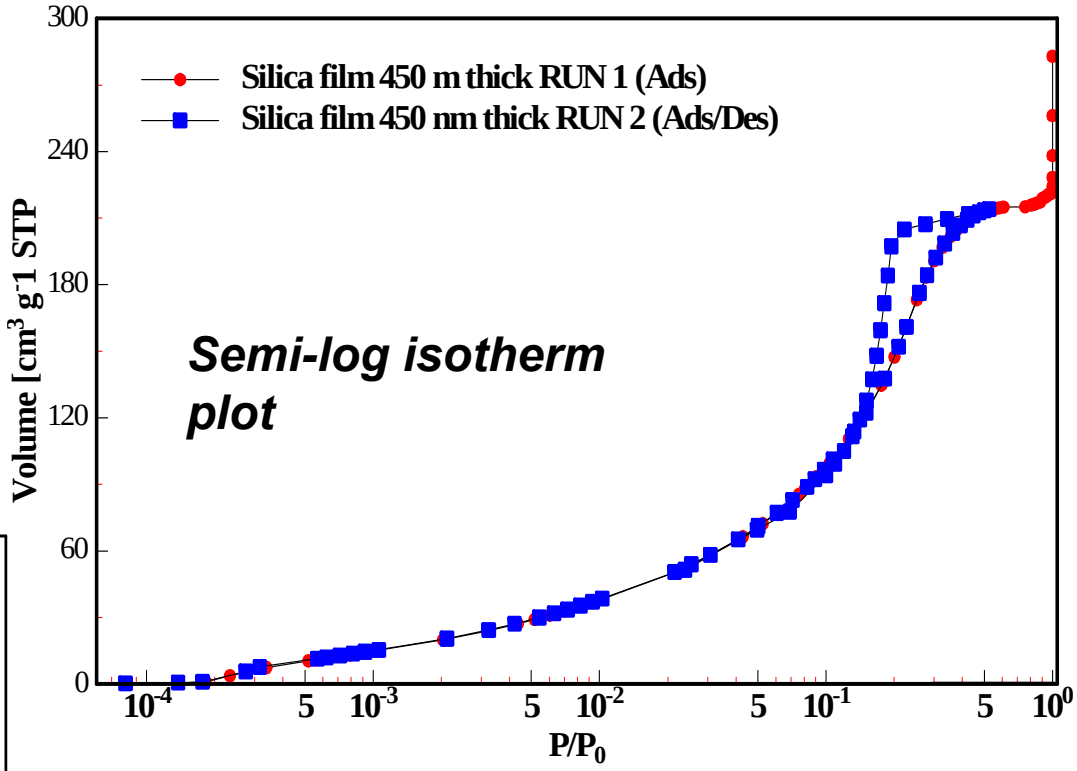
- Due to details of the phase diagram of confined Krypton application for pore size analysis at 77 K is very limited

⇒***however, Kr adsorption at 87 K provides option of pore size analysis of thin films of pore widh up to ca 10 nm***

Characterization of thin porous silica film (thickness 450 nm) deposited on a Si-wafer by a novel method based on Krypton adsorption at 87K





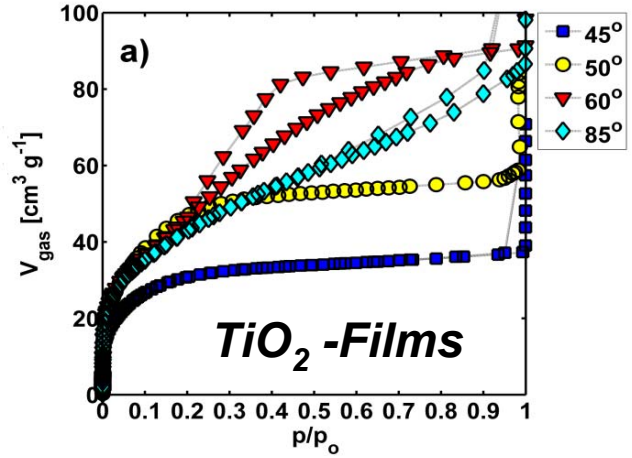


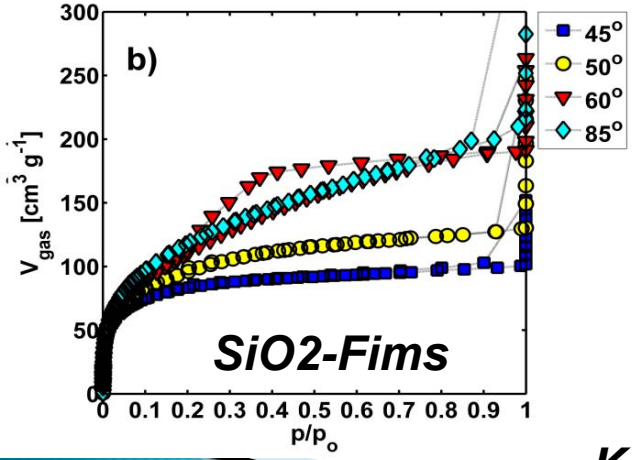
M.Thommes, N. Nishiyama,

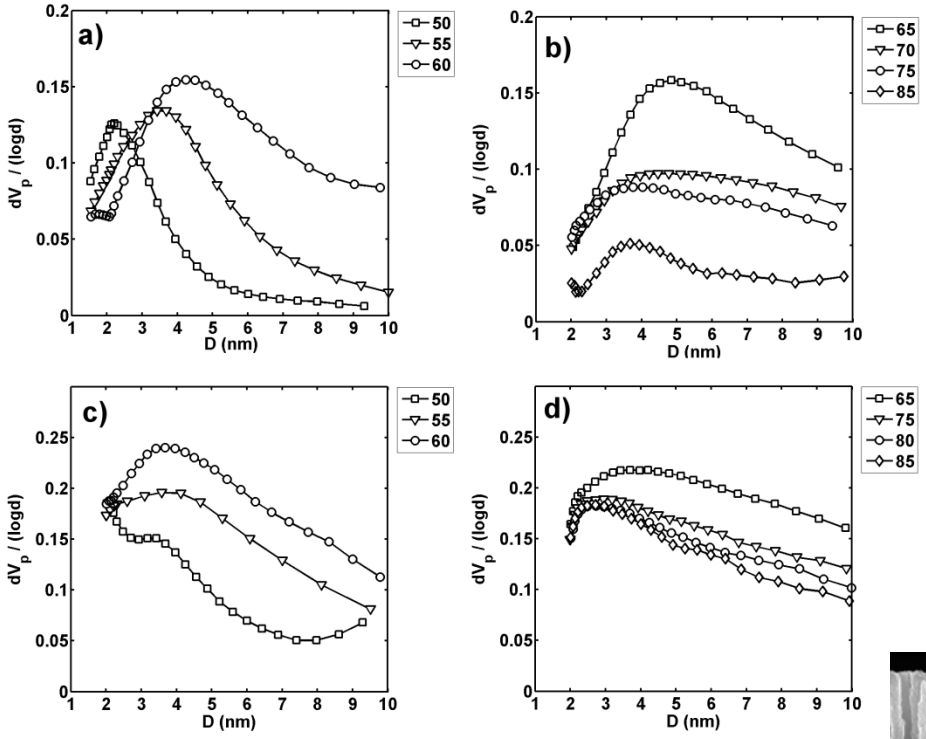
Studies in Surface Science and Catalysis, 2007

Thin Film Pore Size Analysis with a Novel Method based on Kr 87K Adsorption:

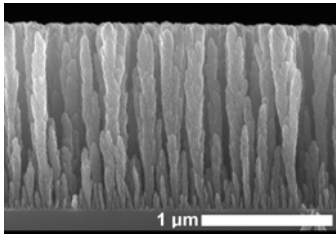
Pore analysis of obliquely deposited GLAD nanofilms







Kr- PSD



K. M. Krause, M. Thommes, M. J.Brett, Microporous & Mesoporous Materials, 43(1), 166-173 (2011).

Water as adsorptive for characterization?

Nitrogen (77.4K)
Argon (87.3 K)
Carbon Dioxide (e.g. at 273K)

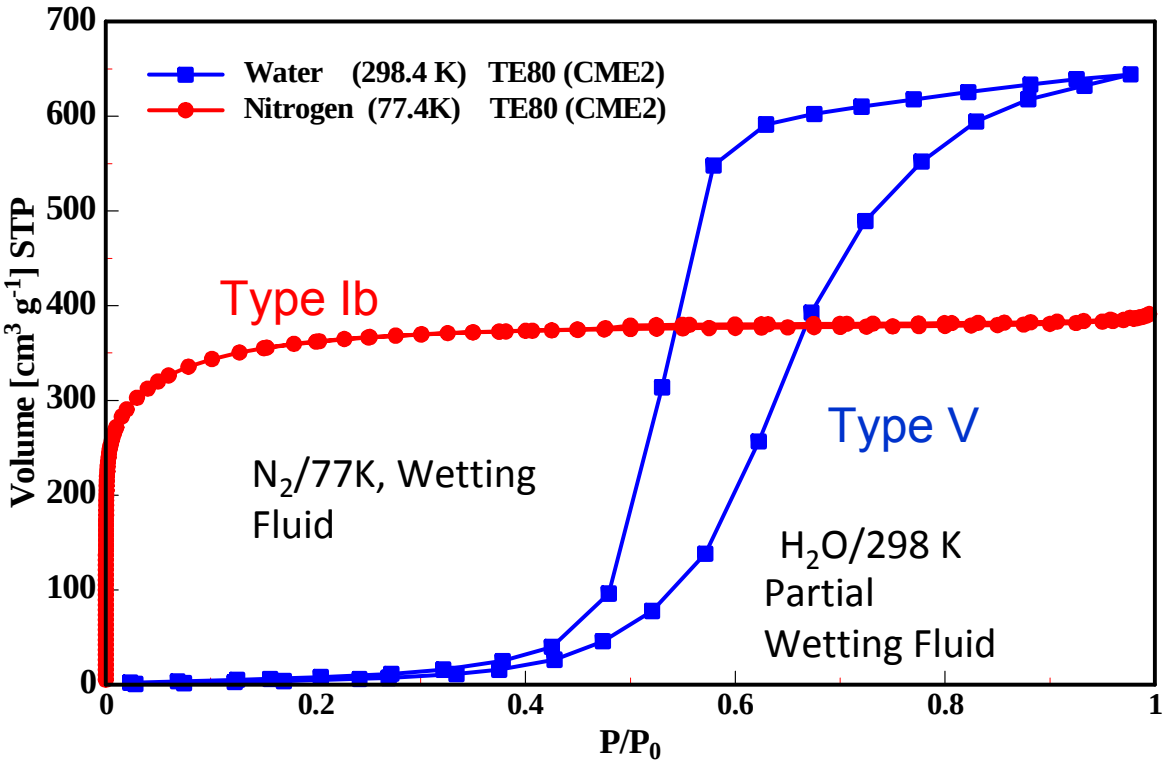
Water?

- Water adsorption can be performed at room temperature, with favorable kinetics. The small kinetic diameter of water (0.28 nm) permits entry into pores that are not accessible to carbon dioxide or nitrogen.

Water adsorption is affected by both pore structure and surface chemistry!

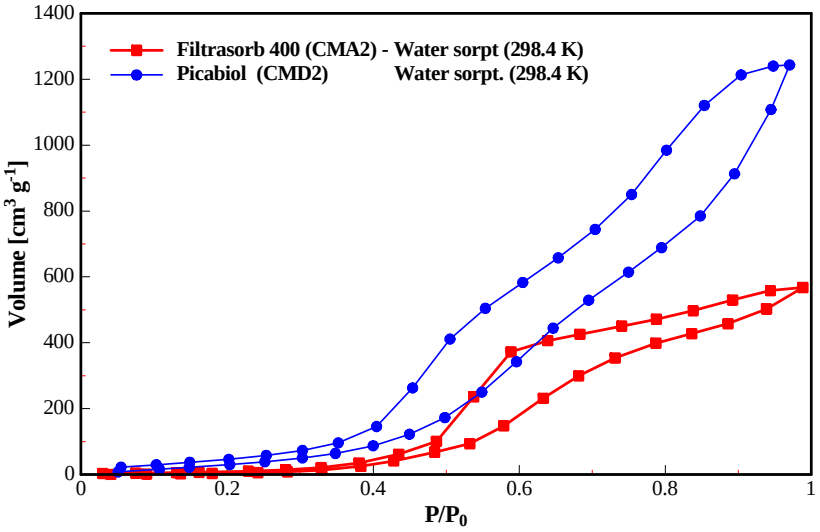
Pioneering Work by: ***K. Kaneko et.al, P. Lodewyckx et al.***
K. Laszlo et al., F. Stoeckli et al.; K. Gubbins et. al.
D.D. Do et al.

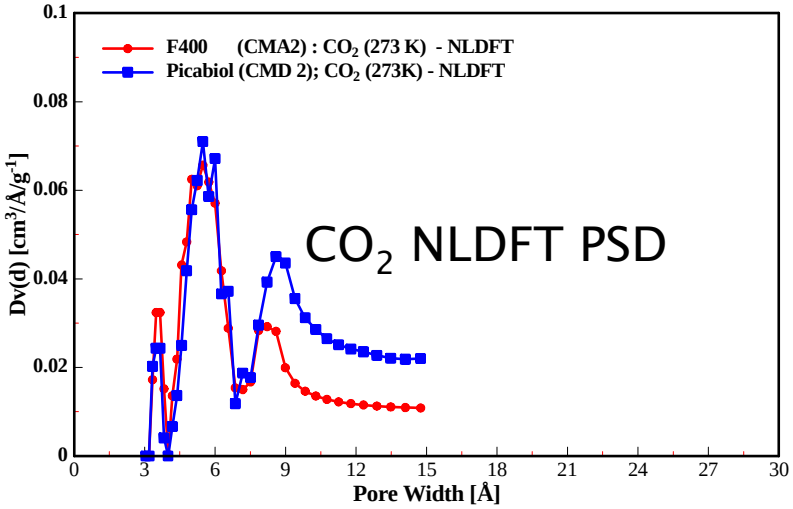
Water (298.5K) and nitrogen (77.4 K) adsorption in purely microporous active carbon with low oxygen content (Picatif ,TE80)

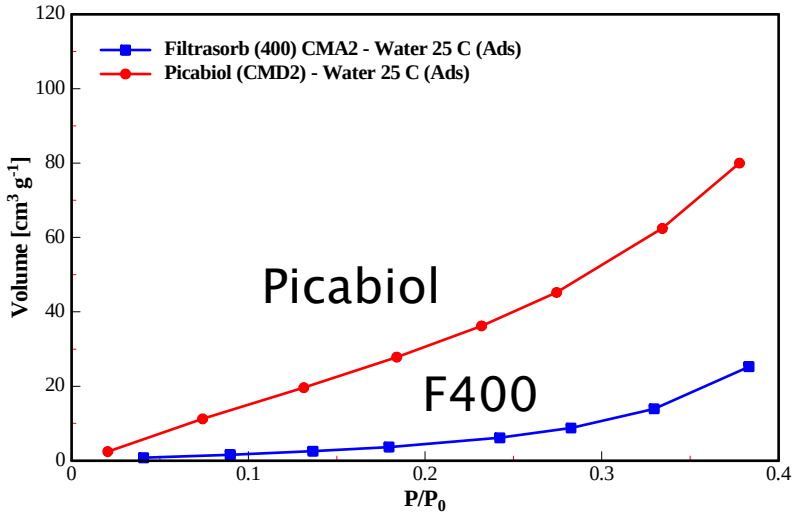


From: M. Thommes, K.A. Cychosz, A.V. Neimark, - "Advanced Physical Adsorption Characterization of Nanoporous Carbons", in: J.M.D. Tascon, Novel Carbon Adsorbents, Elsevier Ltd, 2012, p. 107-145.

Effect of Surface Chemistry: Water adsorption in chemically (Picabiol) and pysically activated (Filtrasorb 400) Carbon with equivalent micropore structure







-⇒ water adsorption suggests that Picabi is more hydrophilic than F400
-this is in agreement with XPS and TPD-MS Analysis

M. Thommes, C. Morlay, R. Ahmad, *Adsorption* 17 (2011) 653

Pore Size Analysis of Porous Materials by Gas Adsorption

Significant progress was achieved mainly because of the following reasons:

i. **The discovery of novel ordered mesoporous molecular sieves (since ca. 1990, e.g. M41S, SBA, KIT, CMK) which were used as model adsorbents to test theories of gas adsorption** (pore size can be obtained by methods independent of gas adsorption)

ii. **The development of microscopic methods (since ca. 1985) such as the Density Functional Theory or computer simulation methods** (e.g. **Monte-Carlo – and Molecular-Dynamic simulations**), **which allow one to describe the configuration of adsorbed molecules in pores on a molecular level.**

iii. **Carefully performed experiments** (by combining various experimental techniques)

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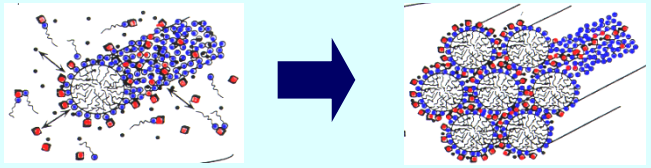
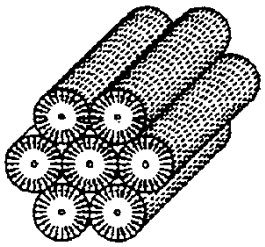
Mesoporous Silica Molecular Sieves

Synthesis Conditions
- Tetraethylorthosilicate, Na-silicates
- Acidic, basic, neutral conditions
- cationic, non-ionic, anionic surfactants

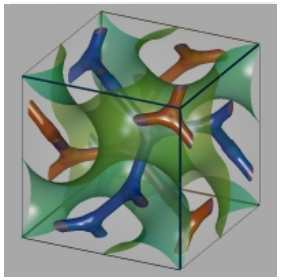


- Controllable pore sizes between 2-15 nm
- Various channel structures
- Easily removable template

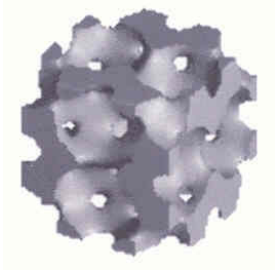
Hexagonal p6mm
MCM-41, SBA-15



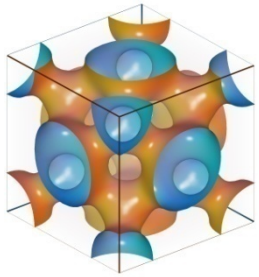
Cubic Ia-3d
MCM-48, KIT-6



Cubic Pm-3n
SBA-1

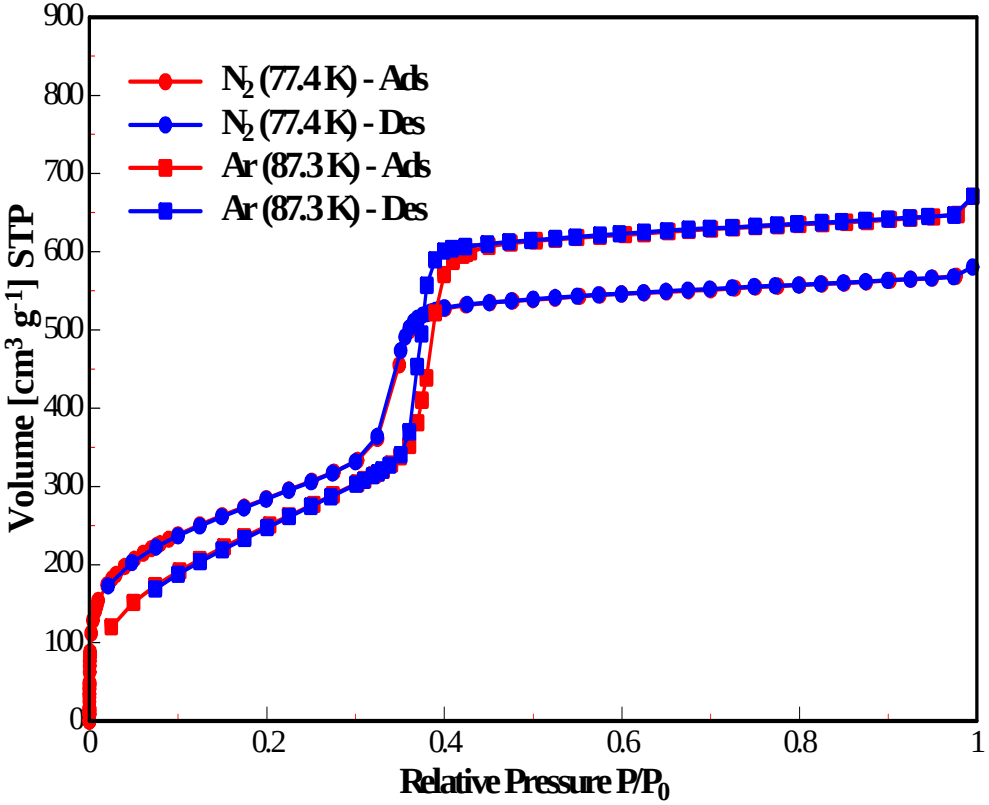


Cubic Fm-3m
KIT-5

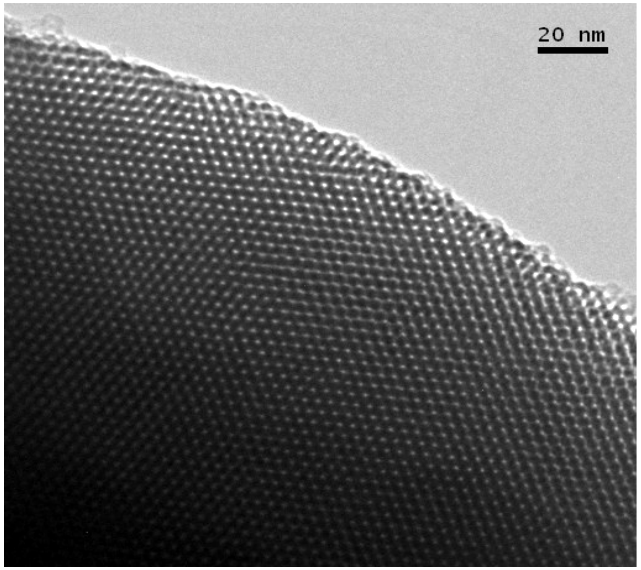


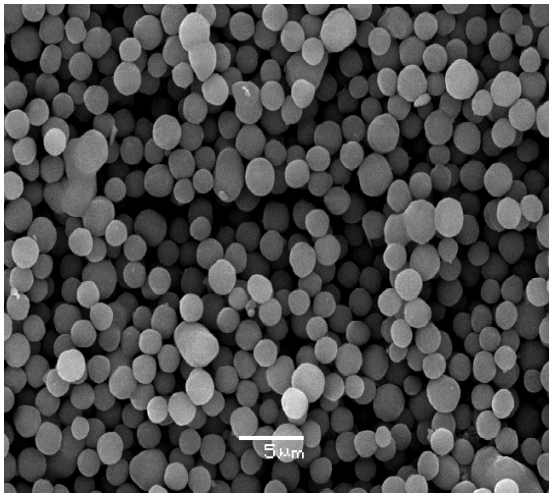
Courtesy of Freddy Kleitz

Nitrogen (77 K) and Argon Adsorption (87 K) in Highly Ordered MCM-41 Silica with Spherical Particles



From: A. Zukal, M.Thommes, J. Cejka, Microporous and Mesoporous Materials Vol. 104 (2007) 52 - 58





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Pore Size Analysis by Gas Adsorption

Macroscopic, thermodynamic methods

Micropores *(< 2 mn)*: e.g., *Dubinin-Radushkevitch , Horvath-Kawazoe* (HK), *Saito-Foley* (SF) , comparison plot methods (t-method, alpha-s method)

Meso/Macropores *(2-100 nm):* e.g., *Kelvin equation* based methods such as *BJH (Barrett,Joyner, Halenda), or BDB (Brockhoff & de Boer)*

Modern, microscopic methods, based on statistical mechanics describe configuration of adsorbed molecules on a molecular level : e.g., *Density Functional Theory* (DFT), *Molecular Simulation* these methods are applicable for pore size analysis of both the micro-and mesopore size range.

- **An accurate pore size analysis over the complete pore size range can be performed by a single method.**

Quantachrome INSTRUMENTS

General problems of macroscopic, thermodyamic and empirical approaches :

- Do not describe structure of adsorbed phase in realistic way, i.e. instead of realistic, microscopic density profiles, it is assumed that even in narrowest micropores the adsorbed phase is considered to be equivalent to a bulk-liquid like state

- Do not take into account that thermophysical properties of the adsorbed pore fluids differs significantly from the bulk fluid (i.e., critical point shifts, freezing point and triple point shifts, etc…)-

- Dubinin related methods, as well Kelvin equation based methods do not take into account details of adsorptive/adsorbent interactions

- $\Rightarrow$ Classical methods underestimate true pore size (of micro and narrow
- mesopores) up to 25 %

$\Rightarrow$ Only valid over limited pore size range

Pore Filling Pressures for Nitrogen in Slit-Pore Carbons at 77 K

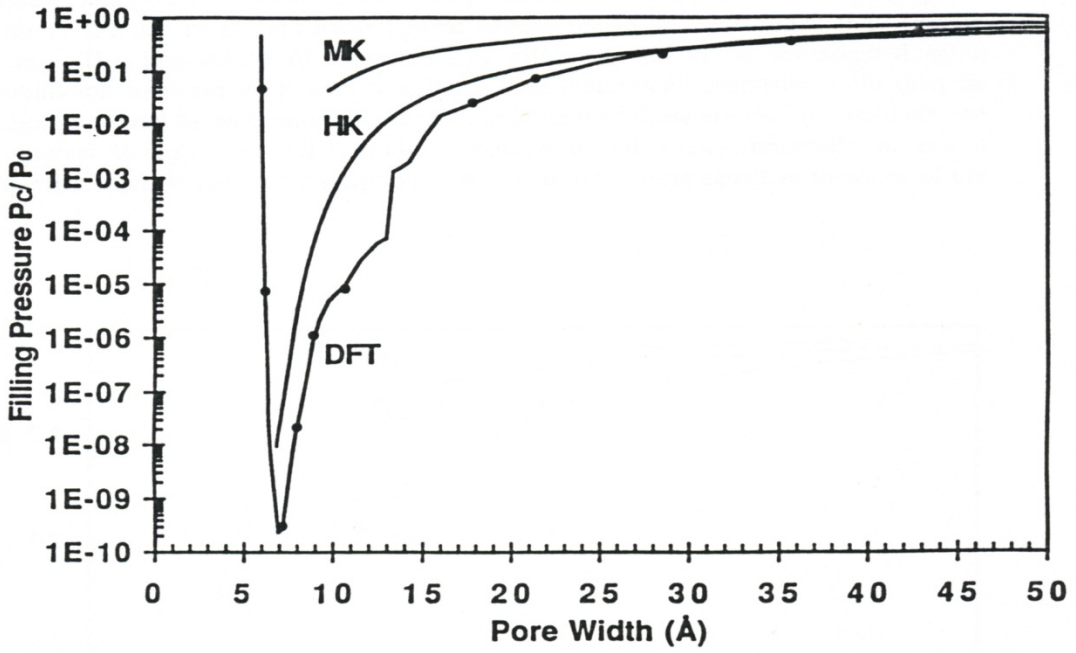
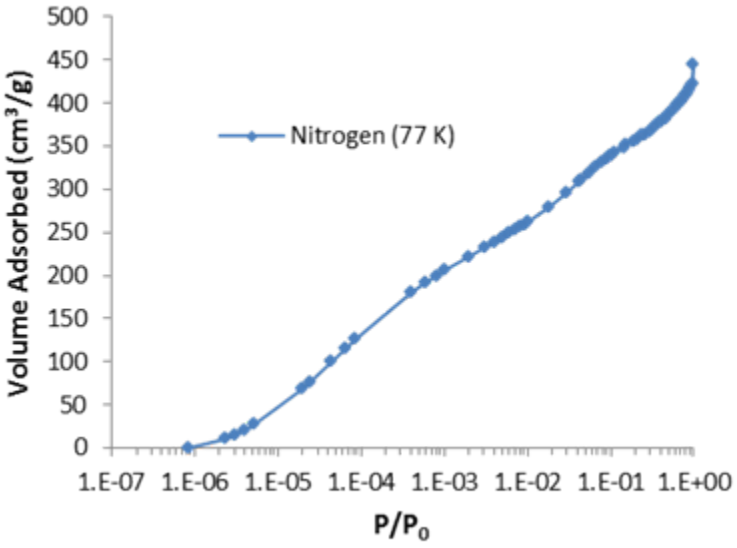


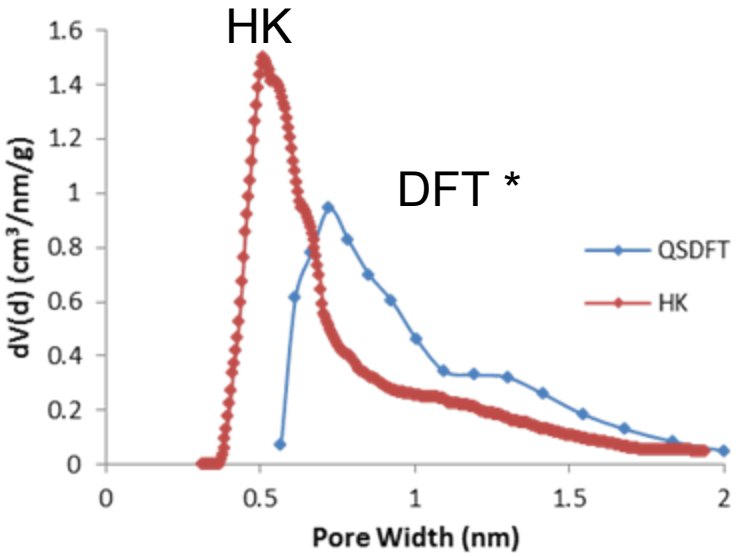
Figure 7. Pore filling pressures P_c for nitrogen in slit pore carbons at 77 K, as predicted by the Tarazona theory (DFT), Horvath-Kawazoe equation (HK), modified Kelvin equation (MK), and from Gibbs Ensemble Monte Carlo simulations (points). [From Lastoskie et al., ref. 24].

C. Lastoskie and K.E.Gubbins, J. Phys. Chem 77, 9786 (1997)

Quantachrome INSTRUMENTS

Micropore size analysis of an activated carbon sample

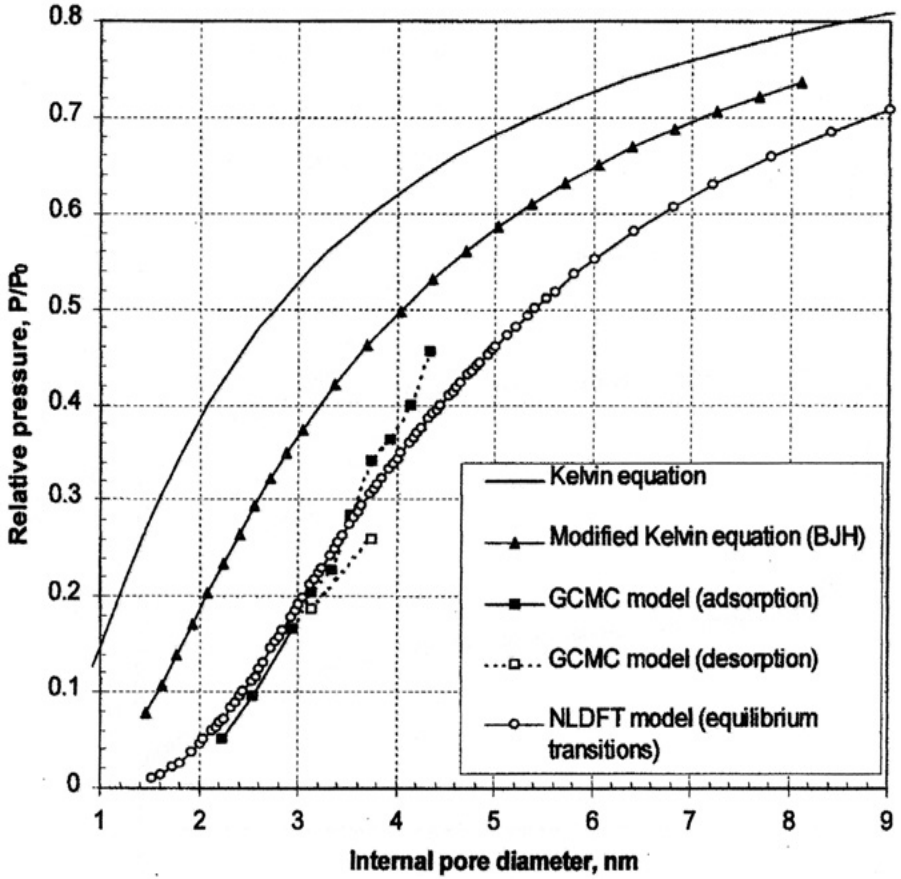




From: M. Thommes, K.A. Cychosz, A.V. Neimark, – "Advanced Physical Adsorption Characterization of Nanoporous Carbons", in: J.M.D. Tascon, Novel Carbon Adsorbents, Elsevier Ltd, 2012, p. 107–145.

* QSDFT

Theoretical predictions of the pore size dependence of the relative pressure of the equilibrium condensation/evaporation transition

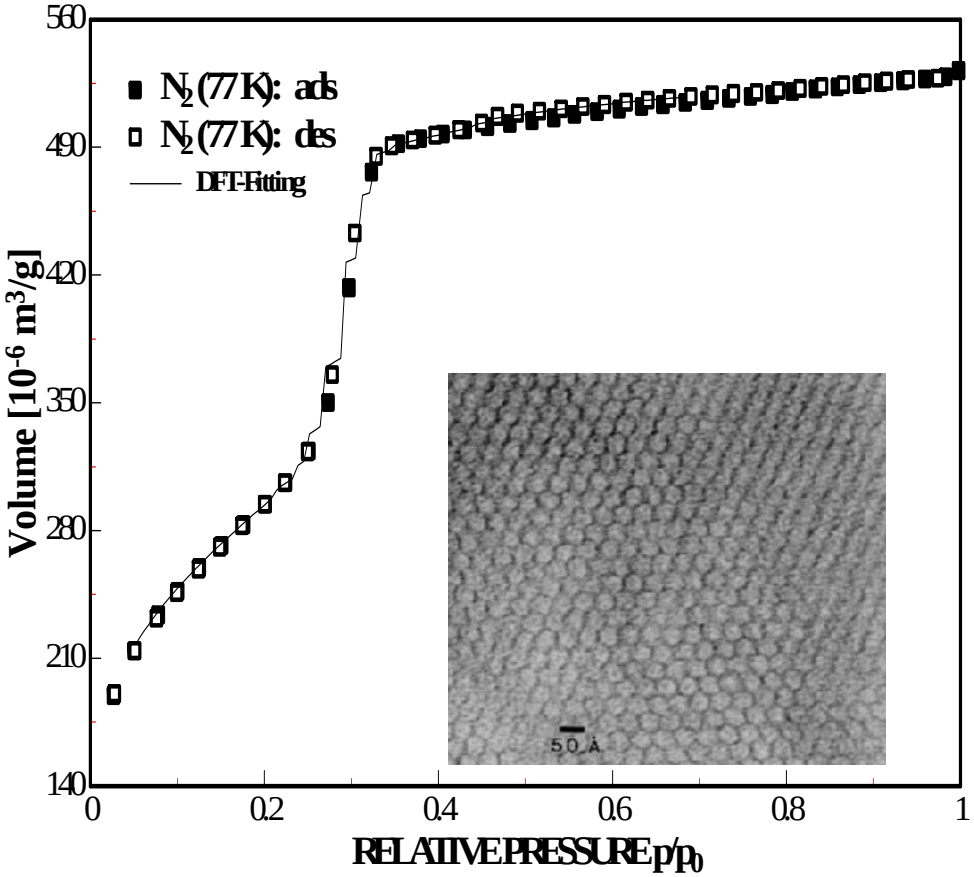


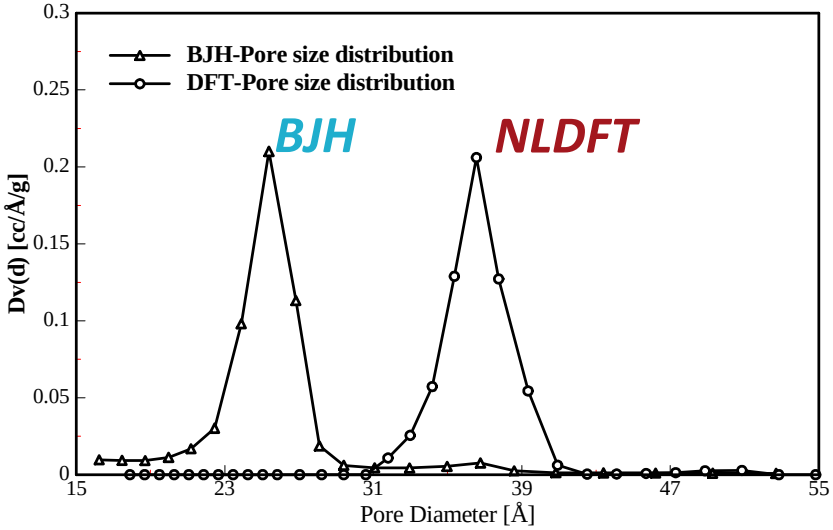
N_2/77 K in cylindrical silica pores

Neimark AV, Ravikovitch P.I., Grün M., Schüth F., Unger K.K, (1998) J. Coll. Interface Sci. 207,159

Quantachrome INSTRUMENTS

N_2 sorption (77 K) in MCM-41 and Pore Size Analysis by Modified Kelvin eq. (BJH method) and Nonlocal-Density Functional Theory (NLDFT)

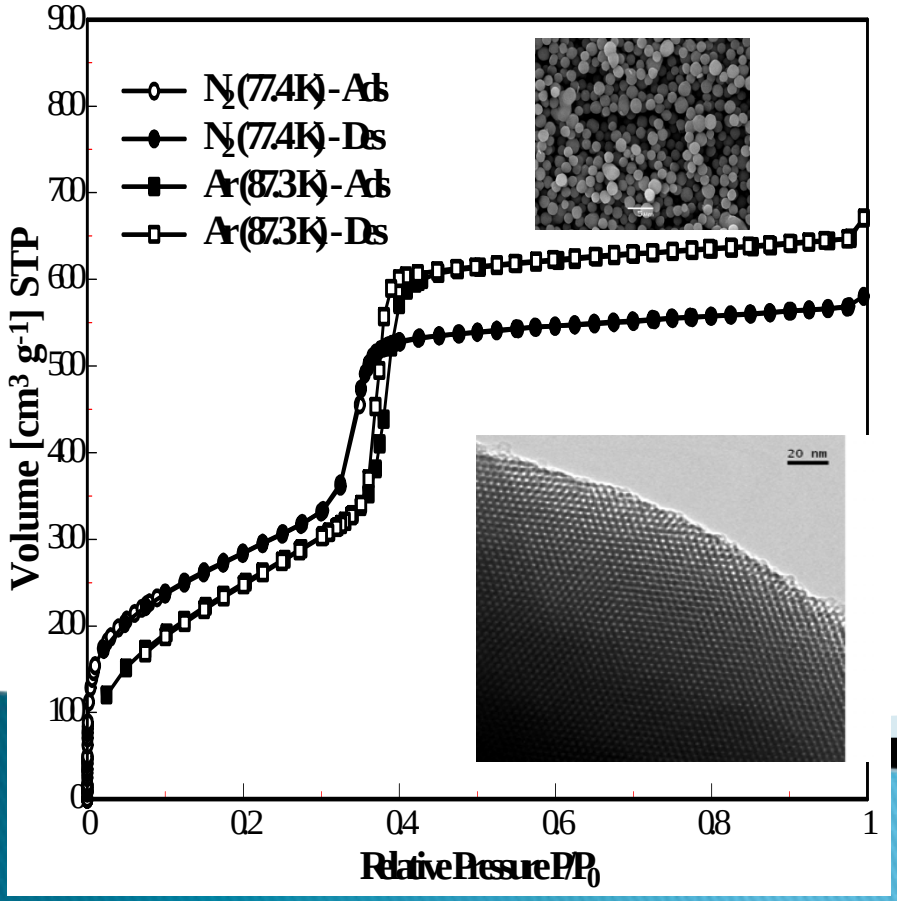


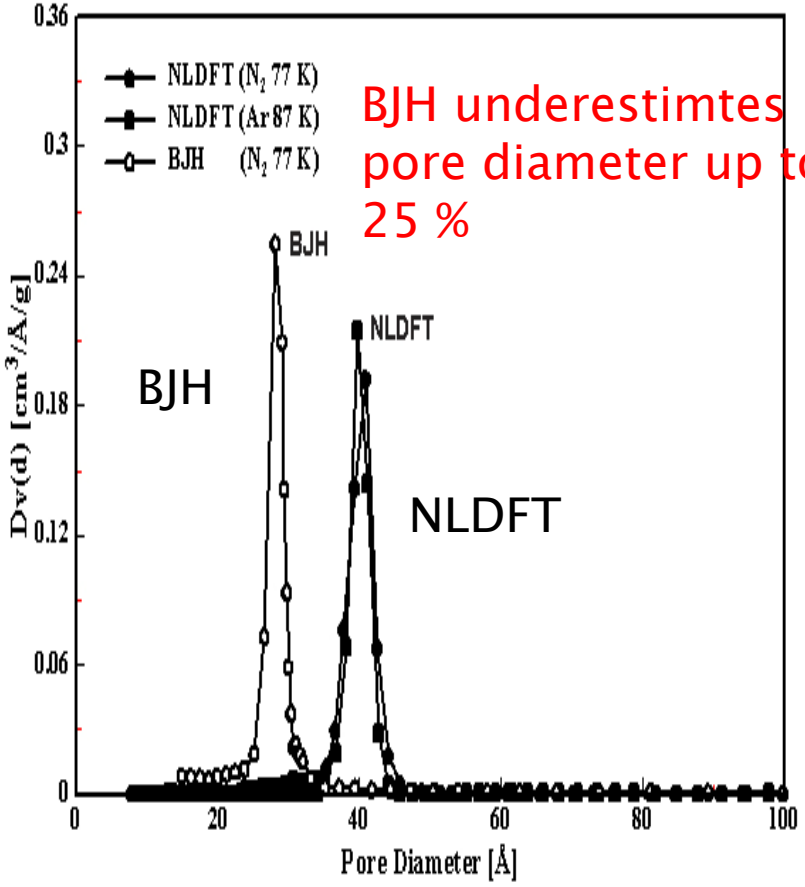


- *Classical methods (i.e. BJH, based on Kelvin equation) underestimate the pore diameter up to ca. 25 % !*
- *NLDFT allows to calculate an accurate pore size distribution*

Quantachrome INSTRUMENTS

Nitrogen (77 K) and Argon Sorption (87 K) in MCM-41 and Pore Size Analysis

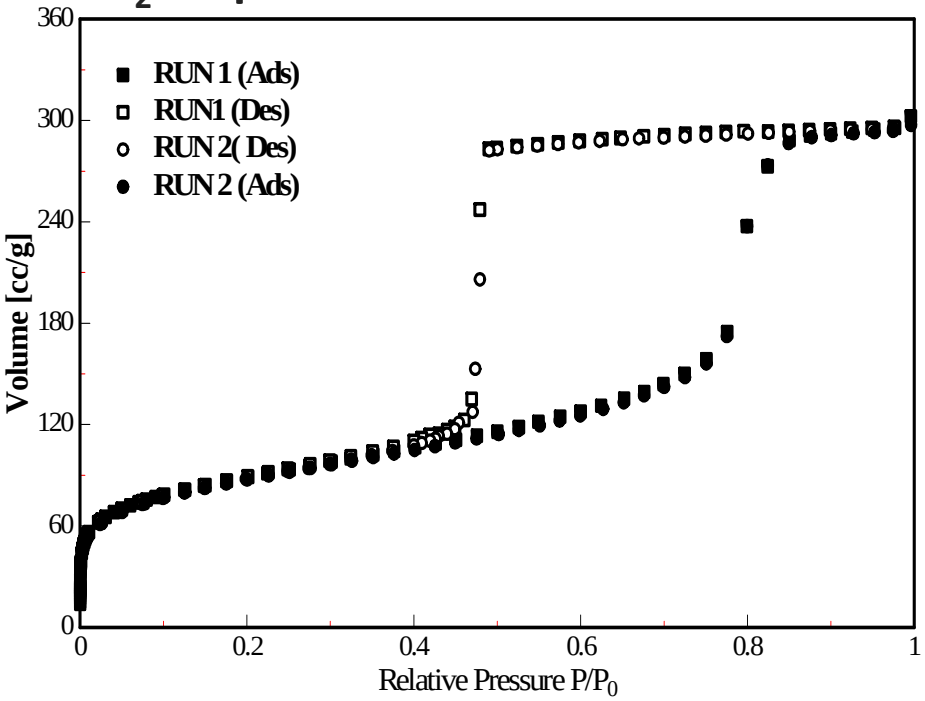




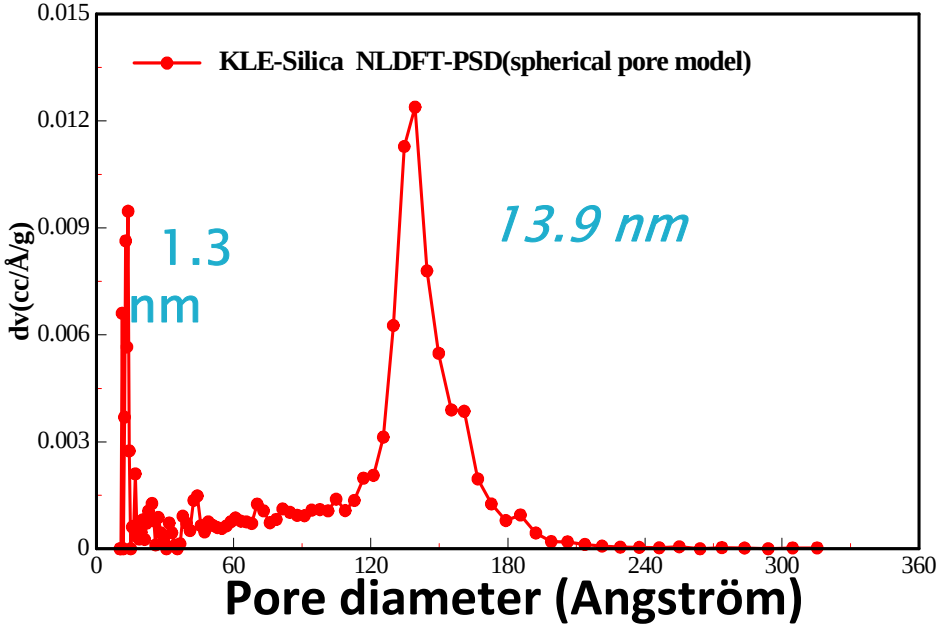
Data from: A. Zukal, M.Thommes, J. Cejka, Microporous and Mesoporous Materials Vol. 104 (2007) 52 – 58

Nitrogen sorption in hierarchically structured Silica (KLE)

N_2 sorption isotherm



Pore size distribution



NLDFT analysis (spherical mesopores, cylindrical micropores)

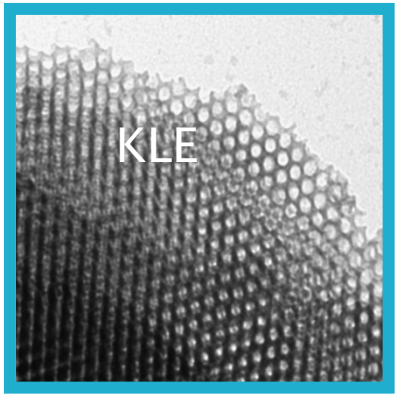
Mesopore Size:

N_2-sorption: 13.9 nm

TEM: Ca. 13 nm

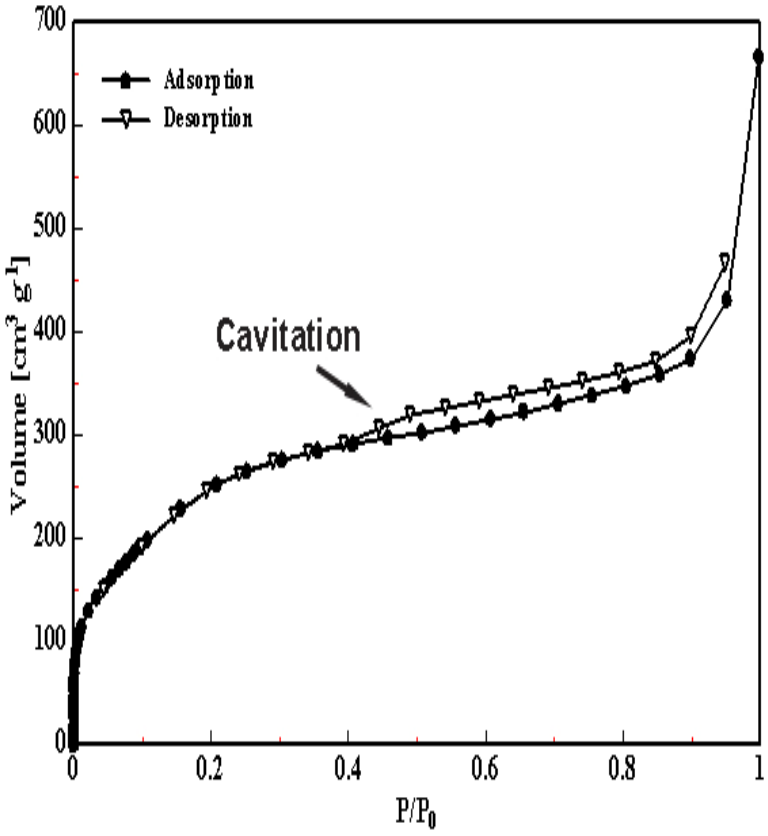
SAXS: 13.8 nm

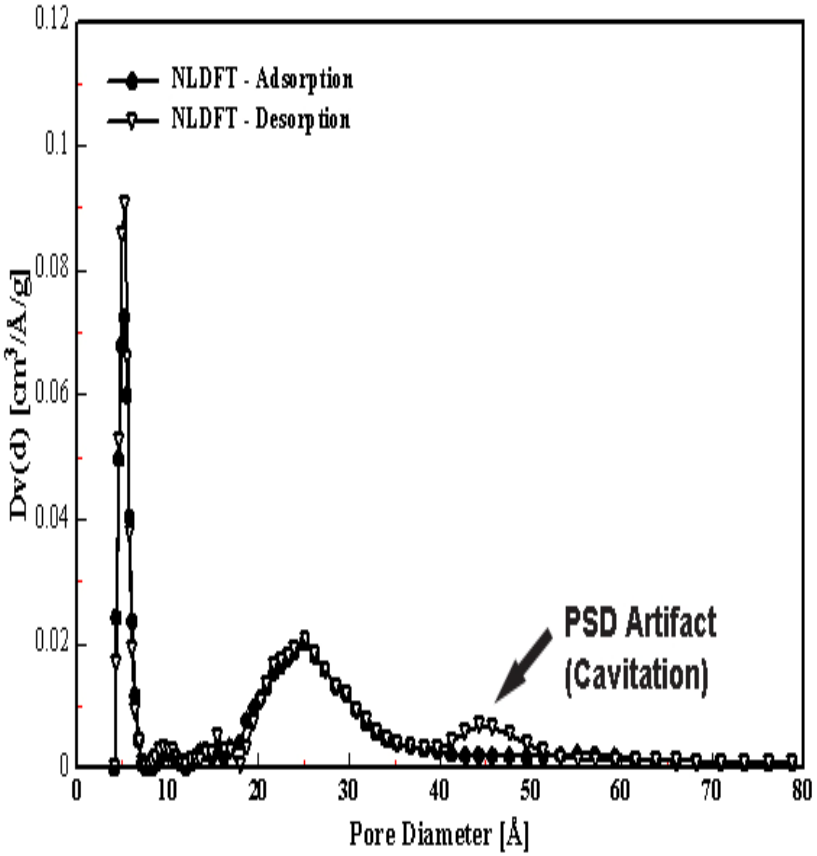
→ **Excellent agreement between SAXS and new NLDFT approach!**



M. Thommes, B. Smarsly, M. Groenewolt, P.I. Ravikovitch, A.V. Neimark,Langmuir, 22,756 (2006)

Argon Sorption at 87 K in Mesoporous ZSM-5 and NLDFT Pore Size Analysis

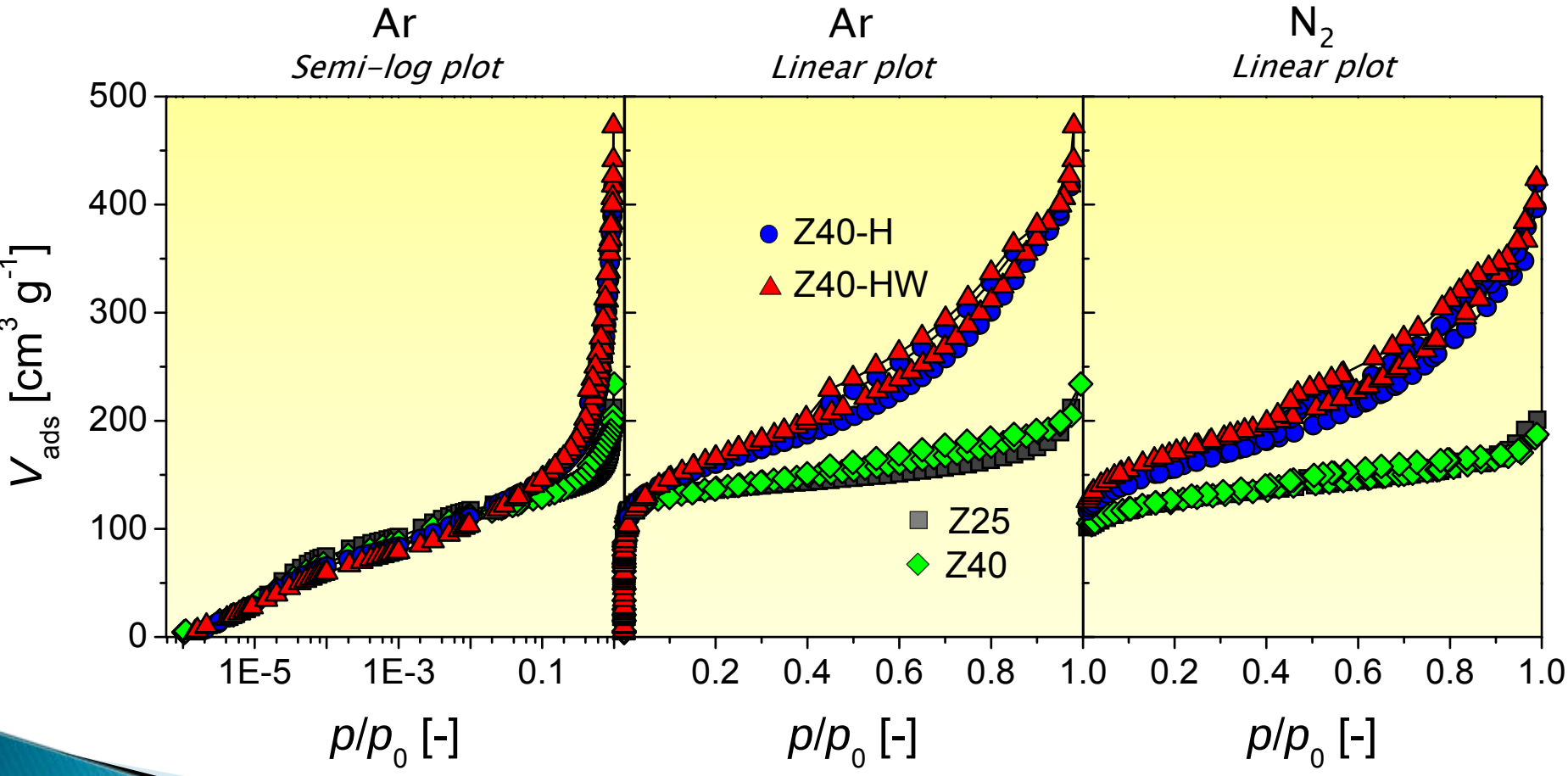




ZSM-5 data from: D. Serrano, J. Aguado, G. Morales, J. Rodriguez, A. Peral, M. Thommes, J.D. Epping, B.F. Chmelka, Chemistry of Materials Vol. 21 641 (2009)

Quantachrome INSTRUMENTS

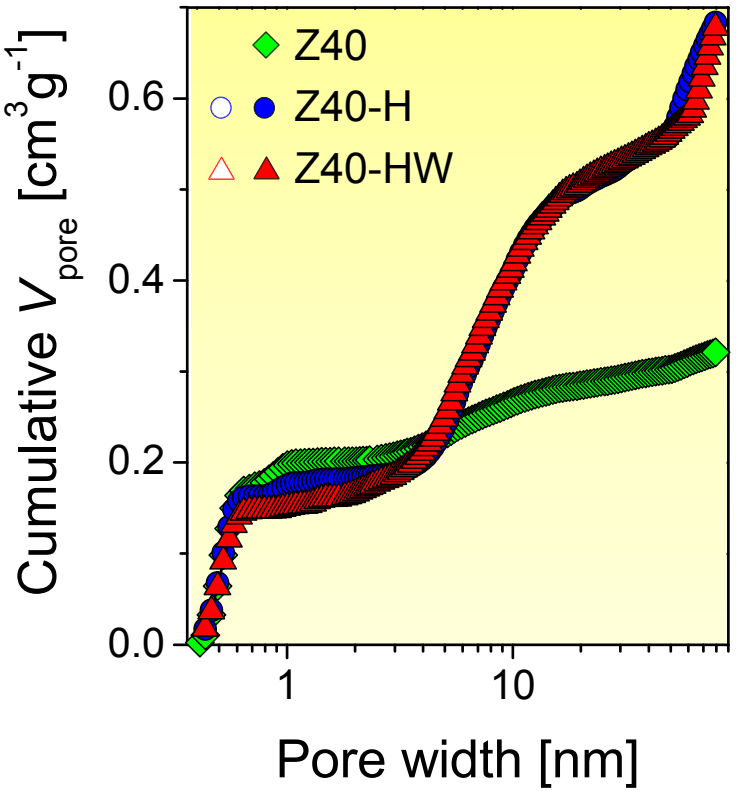
Adsorption and Characterization of conventional and hierarchical ZSM-5with different Si/AL ratios



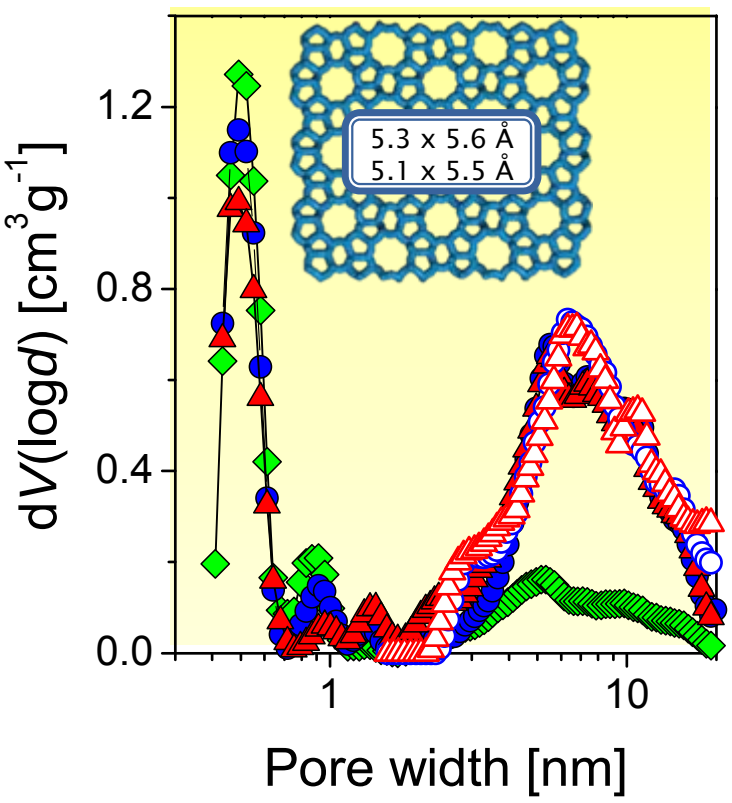
M. Thommes, S. Mitchell, Javier Perez-Ramirez,
J. Phys. Chem C 2012, 1886-18823

NLDFT pore size analysis of conventional and mesoporous ZSM-5

Cumulative pore volume (Ar)



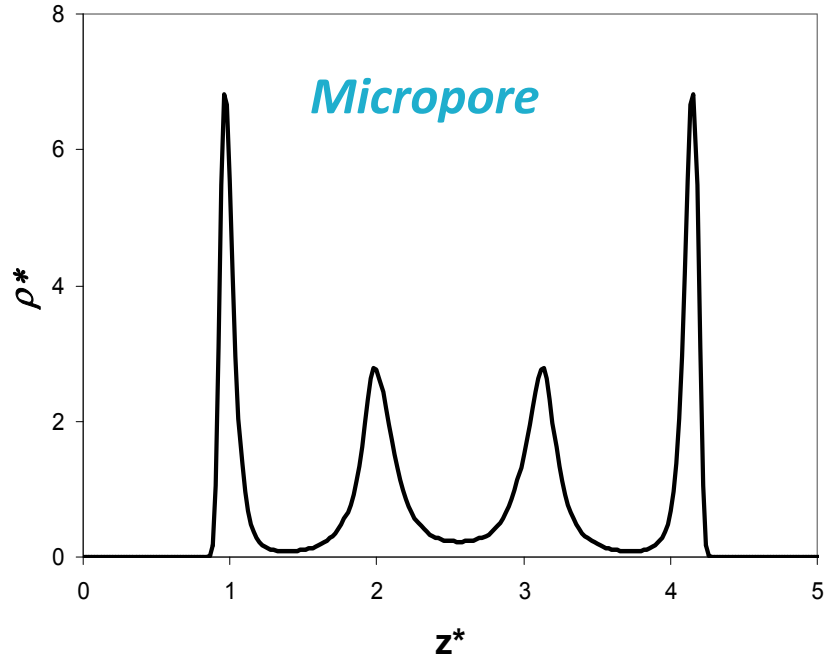
Differential PSD (Ar and N_2)

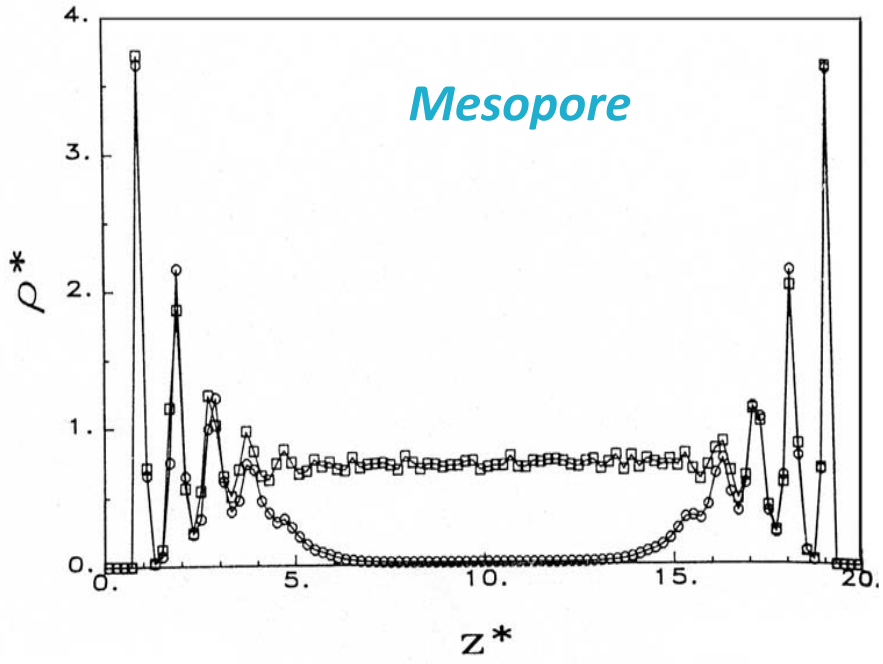


M. Thommes, S. Mitchell, Javier Perez-Ramirez,
J. Phys. Chem C 2012, 1886-18823

Calculation of the DFT Pore Size distribution ?

Density Functional Theory (DFT): Characteristic density profile of a Lennard-Jones fluid in micro-and mesopores



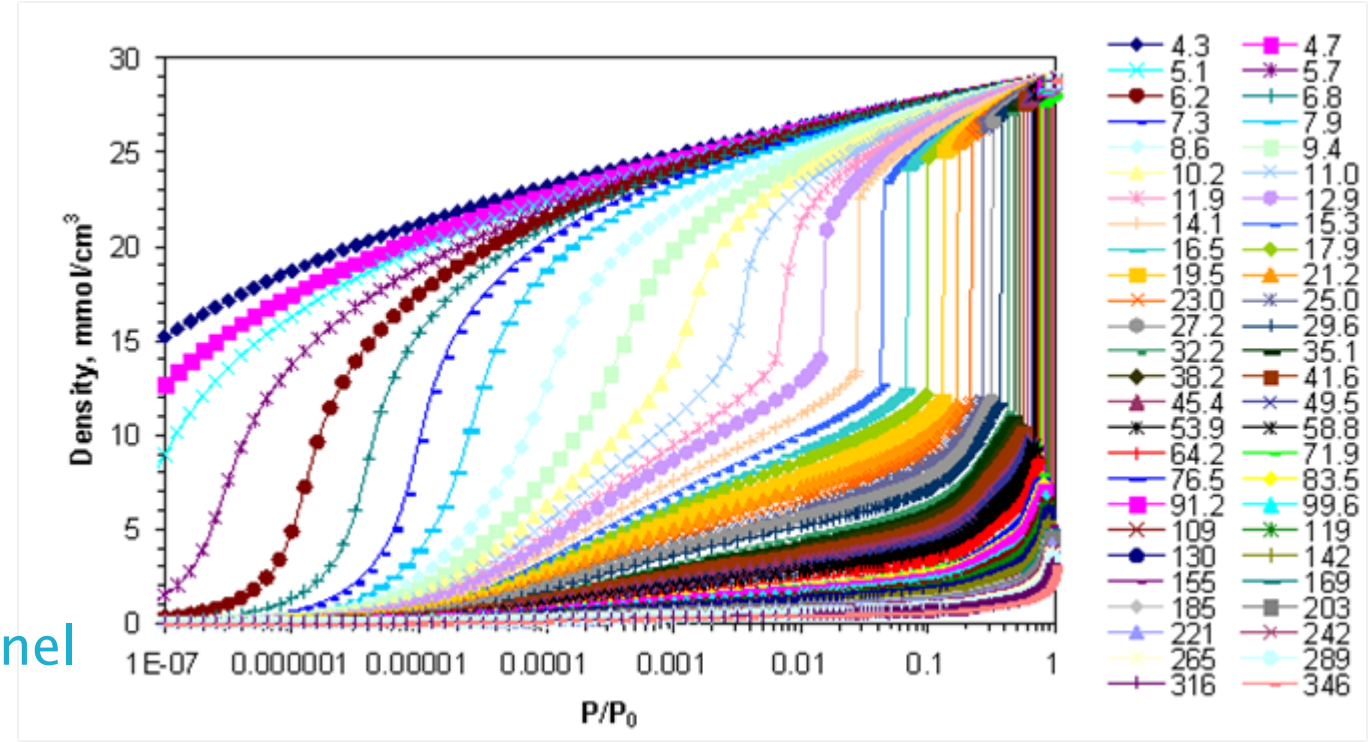


From: *S. Lowell, J. Shields, M. Thomas, M. Thommes, Characterization of porous solids and Powders: Surface Area, Pore Size and Density, Kluwer Academic Publ, 2004,*

J.P.R.B. Walton and N. Quirke, Mol. Sim. 2 361 (1989)

Quantachrome INSTRUMENTS

Kernels of Theoretical Isotherms for N_2 adsorption in carbon

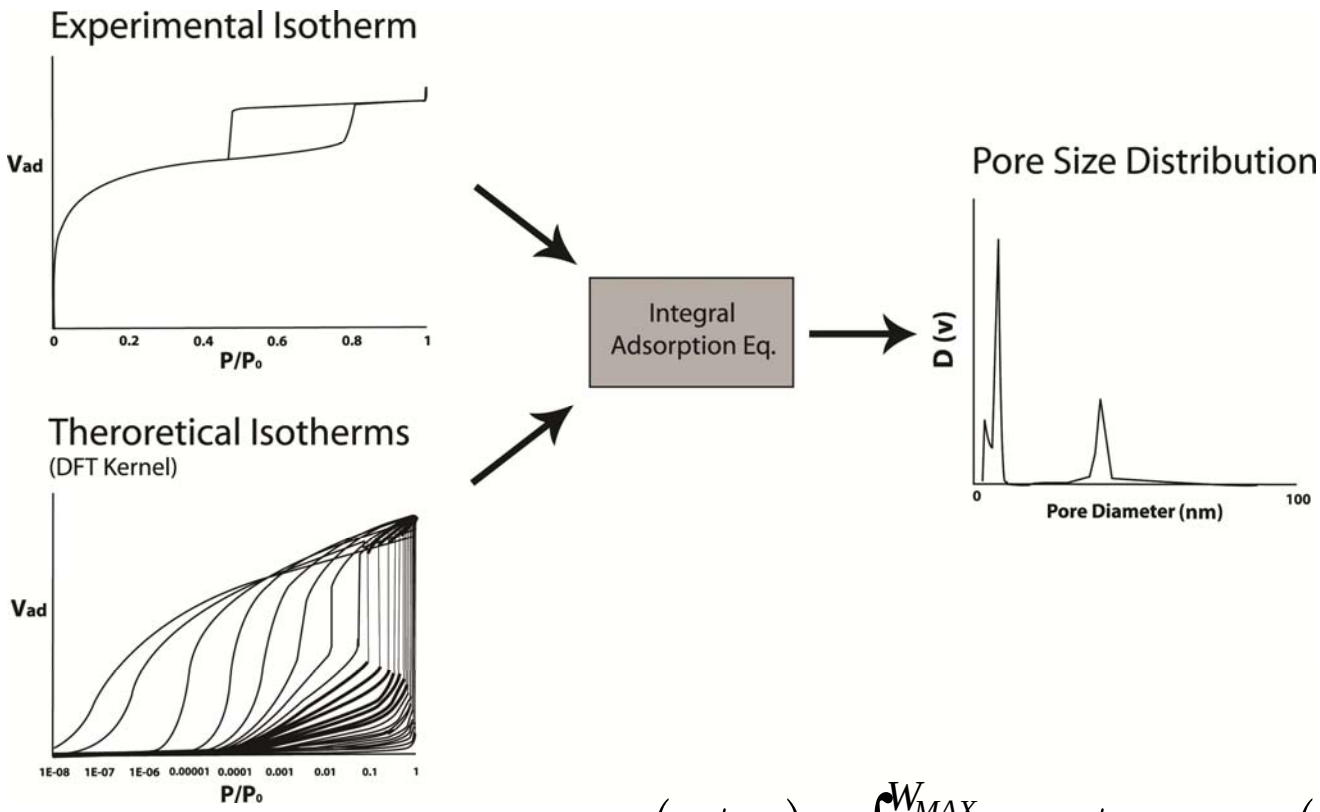


QSDFT Kernel

A.V Neimark, P.I Ravikovitch, Y. Lin, M. Thommes, Carbon, 47, 1617 (2009).

Quantachrome INSTRUMENTS

Calculation of DFT Pore Size Distribution Curves from Experimental Adsorption/Desorption Isotherms



$$N(P/P_0) = \int_{W_{MIN}}^{W_{MAX}} N(P/P_0, W) f(W) dW$$

Quantachrome INSTRUMENTS

Application of methods based on DFT and molecular simulation for pore size analysis in industry and academia

- DFT is meanwhile widely used for micro/mesopore analysis
- Comprehensive library of DFT methods for various adsorptive/adsorbent pairs is available
- Since 2007: NLDFT methods for pore size analysis are featured/recommended in standards of the International Standard Organization (ISO, i.e. ISO-15901-3)

⇒ ***Facilitates the application/use of DFT methods for pore size analysis in industry***

- ***However:***
  NLDFT does not take into account surface heterogeneity /roughness

Quantachrome INSTRUMENTS

Accounting for heterogeneities

Molecular Simulation

- Tremendous progress in modeling realistic 3D structures (*Gubbins, Monson* and others …) of porous solids; *Zgrablich and co-workers 2010 (mixed geometry model)*

Non-local Density Functional Theory

Various efforts to account for heterogeneity in NLDFT/DFT (*Olivier, 1997; Ravikovitch, Jagiello, Neimark, 1989; Bhatia, 2002;*

Ustinov&Do, 2004-06, Jagiello, Olivier 2010,

Quenched Solid Density Functional Theory (QSDFT)

•Solid enters the model as a quenched component with a fixed density distribution rather than a source of an external potential (*Neimark and Ravikovitch: QSDFT* for silica (2006);

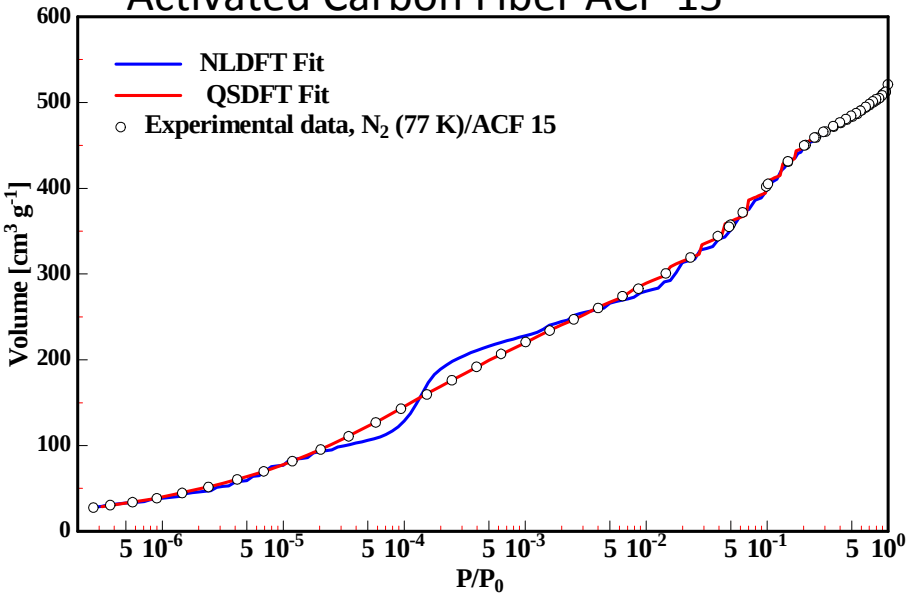
QSDFT for carbons: Neimark, Lin,Thommes Carbon (2009),

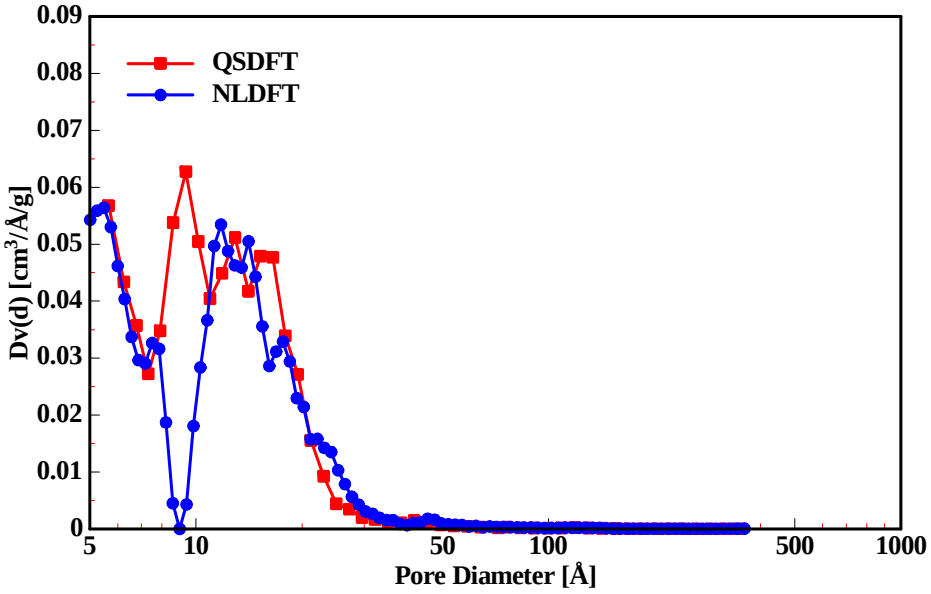
Gor, Thommes,Cychosz, Neimark, Carbon (2012)

Carbon Pore Size Analysis: QSDFT vs. NLDFT

Nitrogen adsorption (77.4 K) on activated carbon fiber ACF-15

Activated Carbon Fiber ACF-15

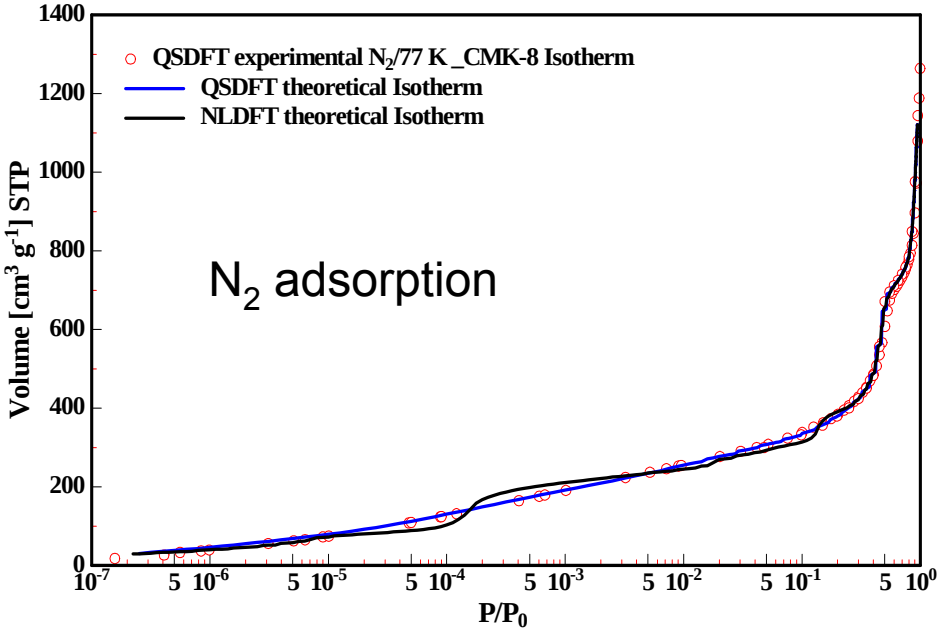


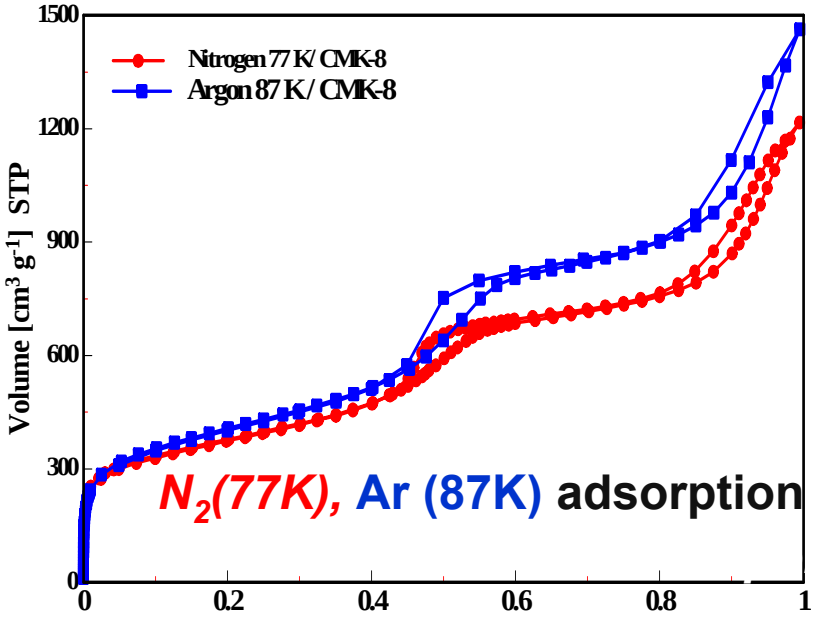


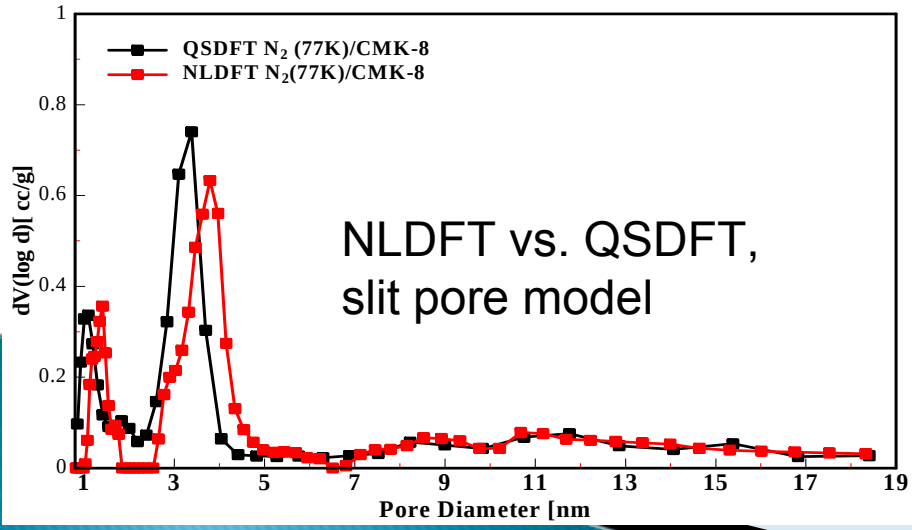
Neimark, A.V.; Ravikovitch, P.I.; Lin, Y.; Thommes, M. *Carbon* **2009**, *47*, 1617

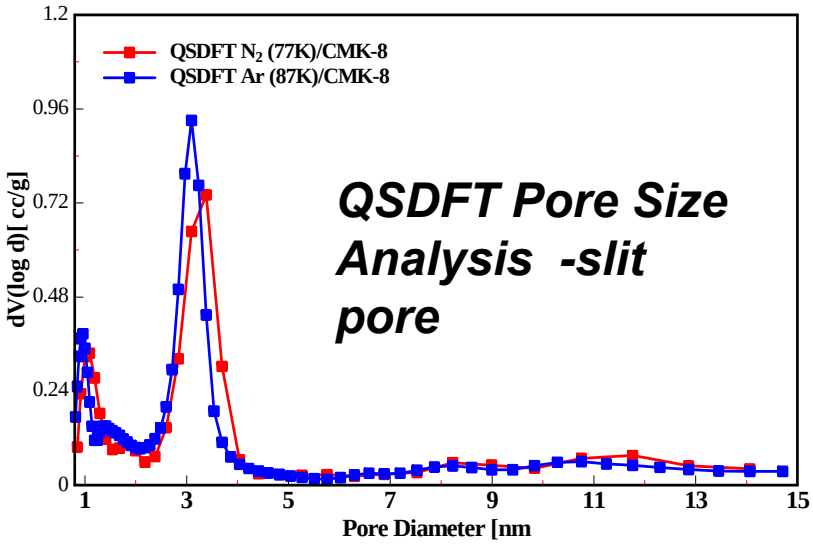
- QSDFT provides a much more realistic approach for the pore size analysis of heterogeneous activated carbon!

Characterization of ordered mesoporous CMK-8 Carbon









Application of Methods Based on DFT and Molecular Simulation for Carbon Pore Size Analysis

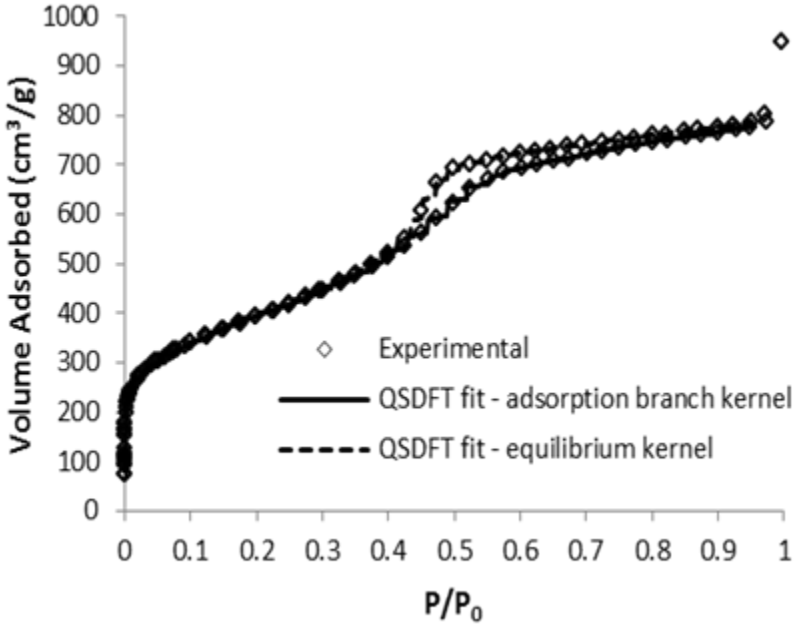
- QSDFT method for carbons has been originally developed assuming slit-shaped pores which are typically found in activated microporous carbons.

- Emergence of novel materials with pre-designed pore morphology (obtained by synthesis routes which make use of structure directing agents or hard templates) requires the development of new methods.

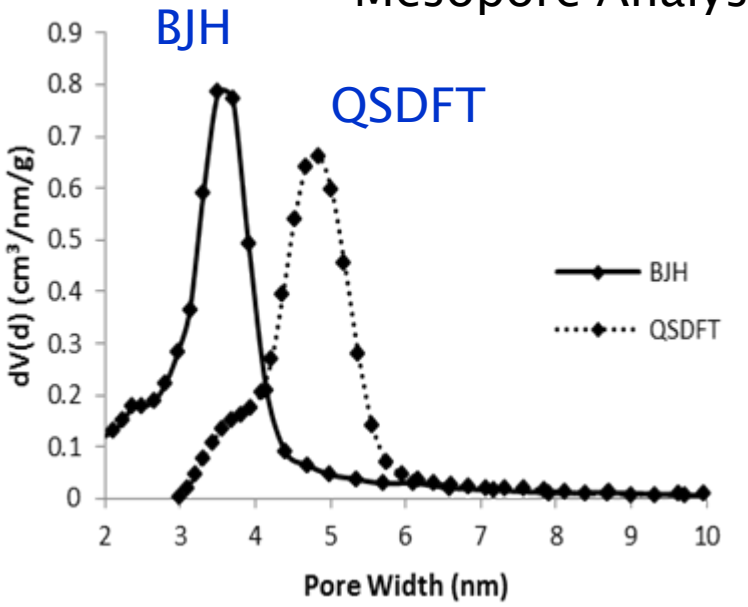
- We extend the QSDFT method to micro- and mesoporous carbons with cage-like (e.g. 3DOM carbons) and channel-like pore geometries (e.g. CMK 3, CMK5) .

Gor, G.; Thommes, M.; Cychosz, K.A.; Neimark, A.V.
Carbon 2012, 50, 1583-1590

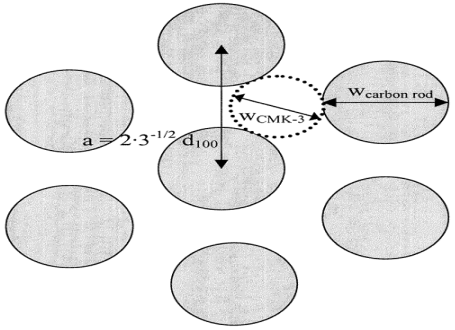
Advanced Analysis of ordered CMK 3 Carbon with QSDFT cylindrical carbon pore model



Mesopore Analysis



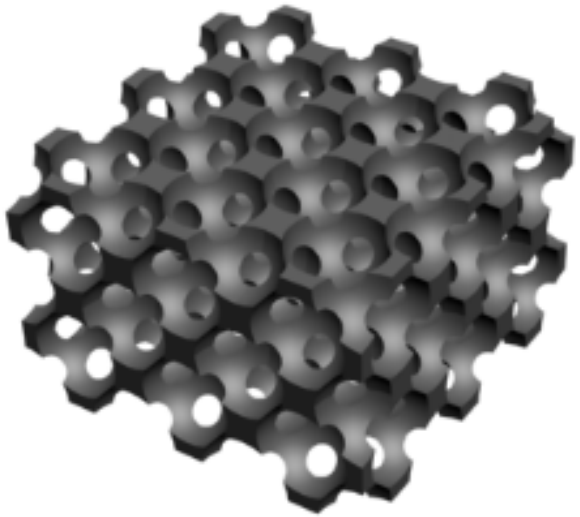
The obtained QSDFT pore size agrees well with the pore size derived from XRD (49.97 Å) by using the geometrical model of hexagonally arranged carbon rods described in the paper by Joo, Ryoo, Kruk and Jaroniec, J. Phys. Chem 2002 (106), 4640- 4646)

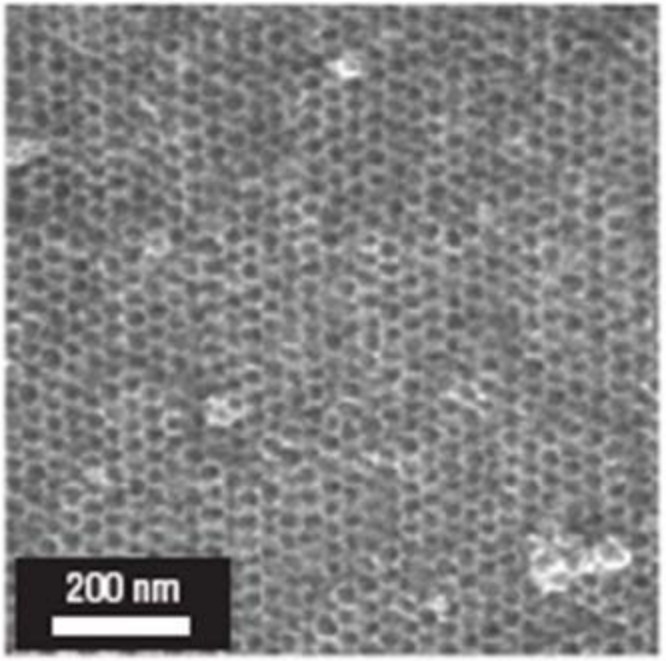


G. Gor, M. Thommes, K.A. Cychosz, A.V. Neimark, *Carbon* (2011)

Three-Dimensional Ordered Mesoporous (3DOm) Carbons (Spherical Pores)

- Template: 3D colloidal crystals formed from lysine-silica nanoparticles
- High degree of control over nanoparticle size
- Pore size of 3DOm carbon verified using SEM, TEM, SAXS

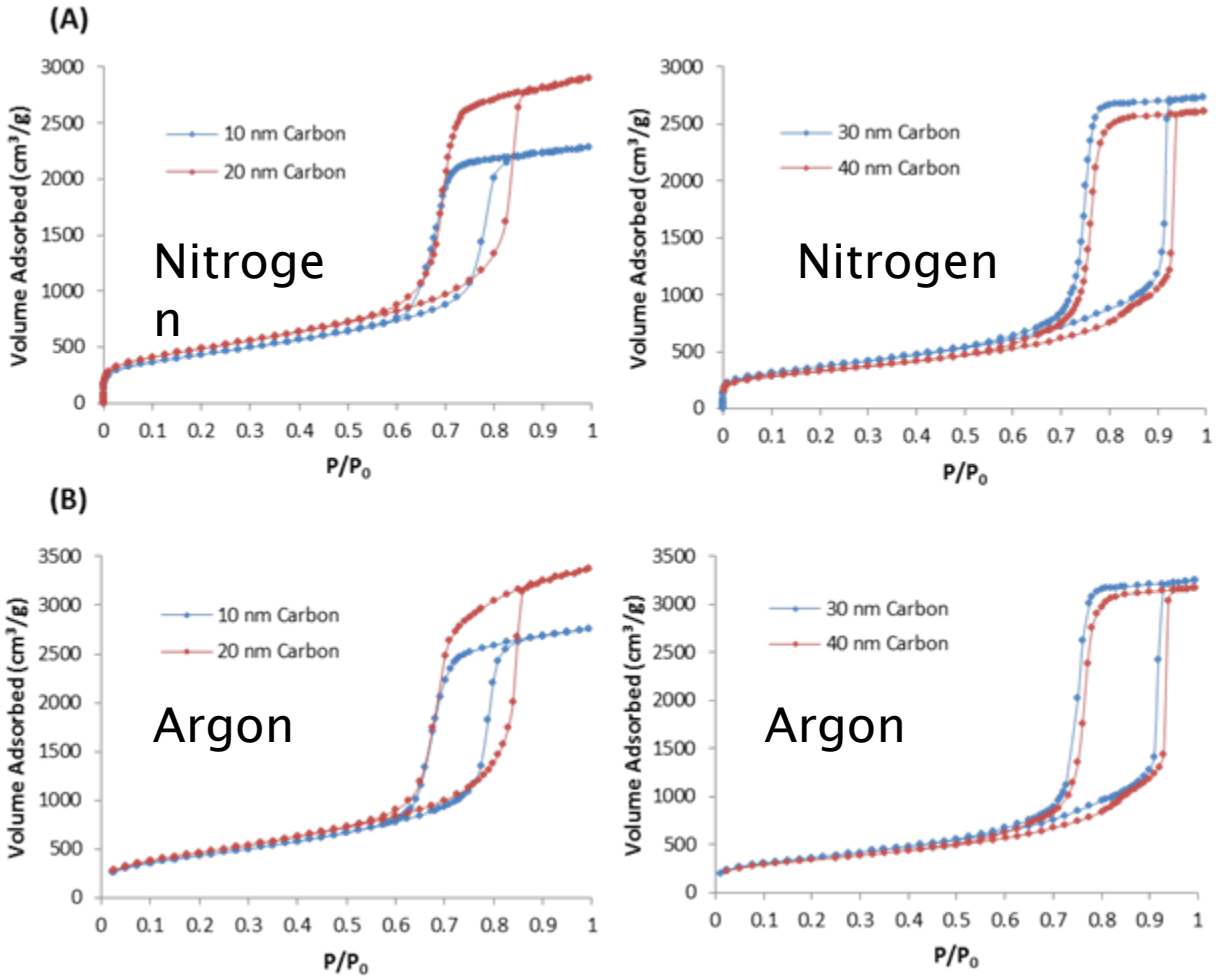




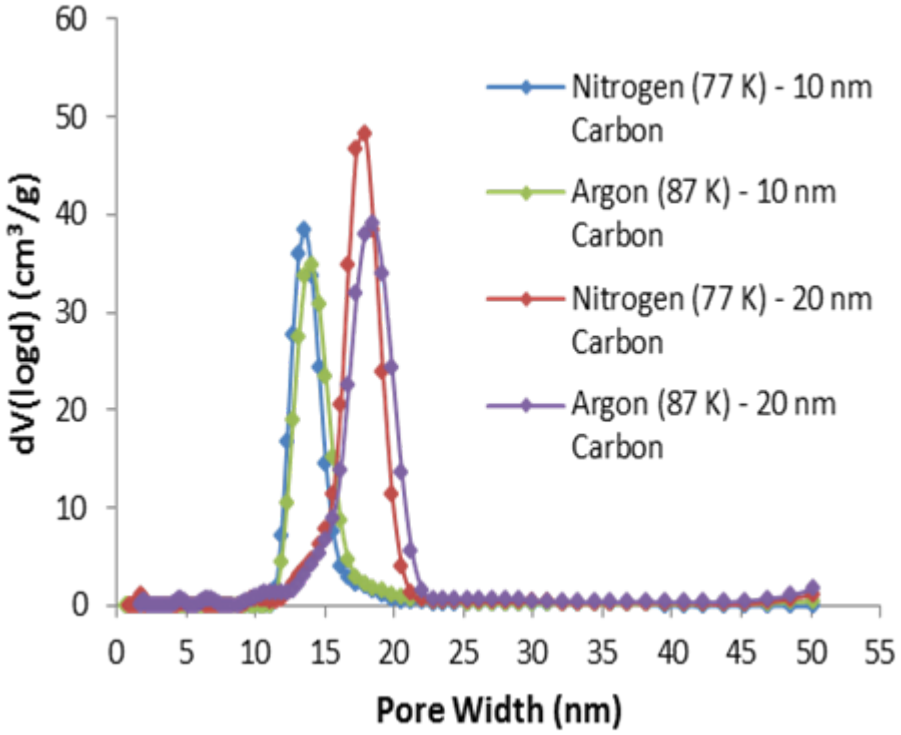
Fan, W.; Snyder, M.A.; Kumar, S.; Lee, P-S.; Yoo, W.C.; McCormick, A.V.; Penn, R.L.; Stein, A.; Tsapatsis, M. *Nature Materials* **2008**, *7*, 984-991

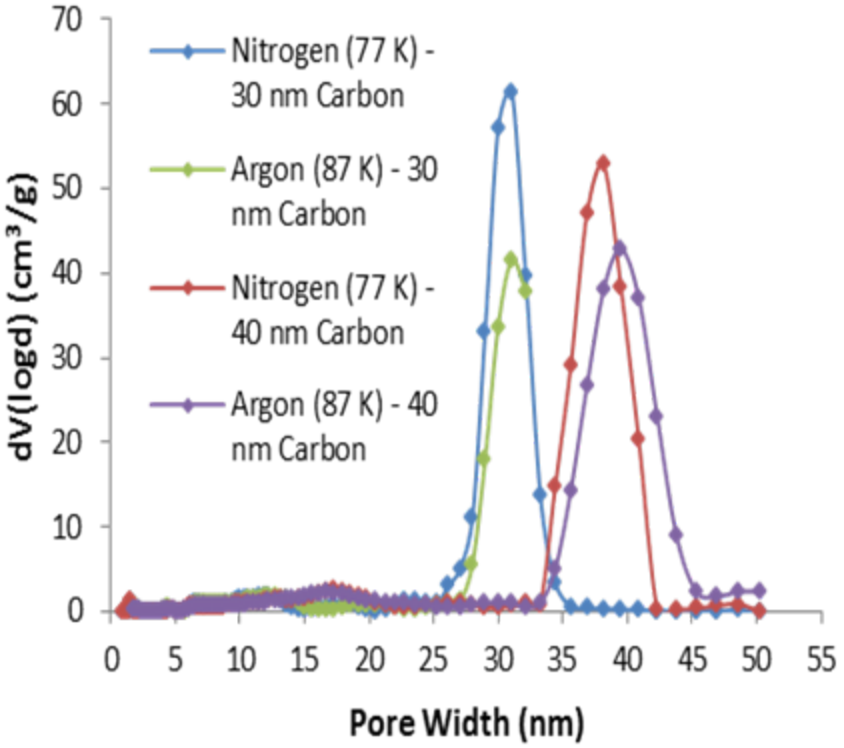
Nitrogen 77 K and Argon 87K Adsorption in 3DOM Carbons

- .



QSDFT Pore Size Distribution from N2(77K) and Ar (87K0 adsorption isotherms





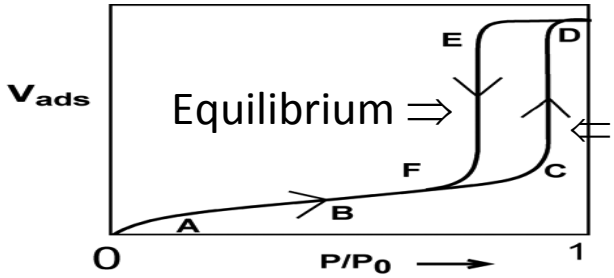
QSDFT method: assuming spherical mesopores and taking into account delay in

condensation due to metastable pore fluid

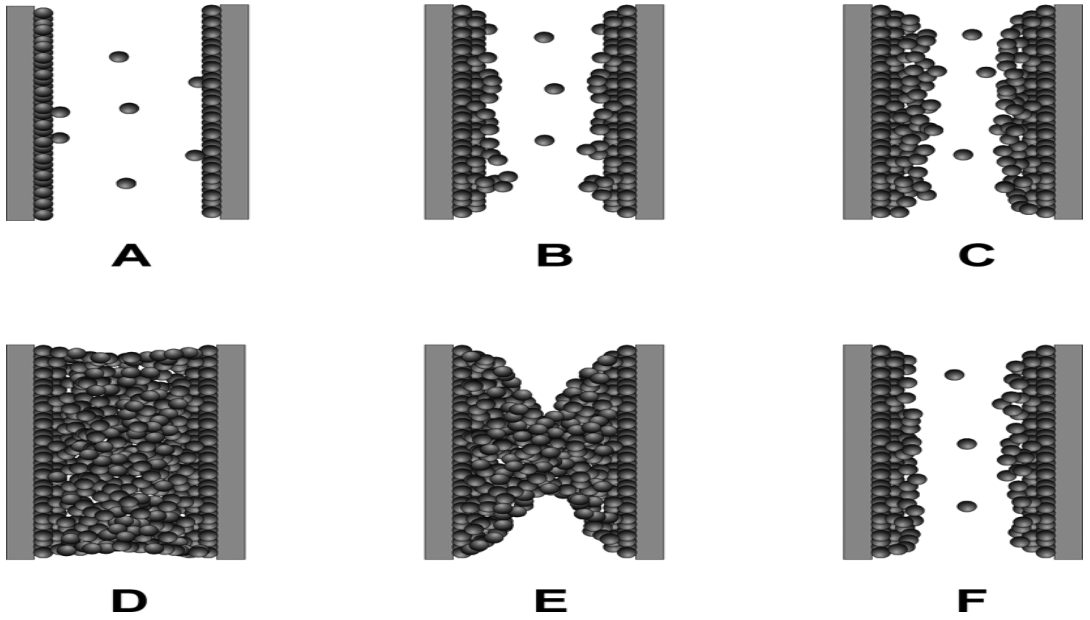
⇒ Pore/Cavity Size of materials with cage-like pore structure from adsorption branch by applying advanced QSDFT

Aspects of Pore Condensation and Hysteresis in Advanced Mesoporous Materials

Adsorption in Mesopores
Adsorption, Phase Behavior and Hysteresis



⇐ Delayed condensation due to metastable pore fluid



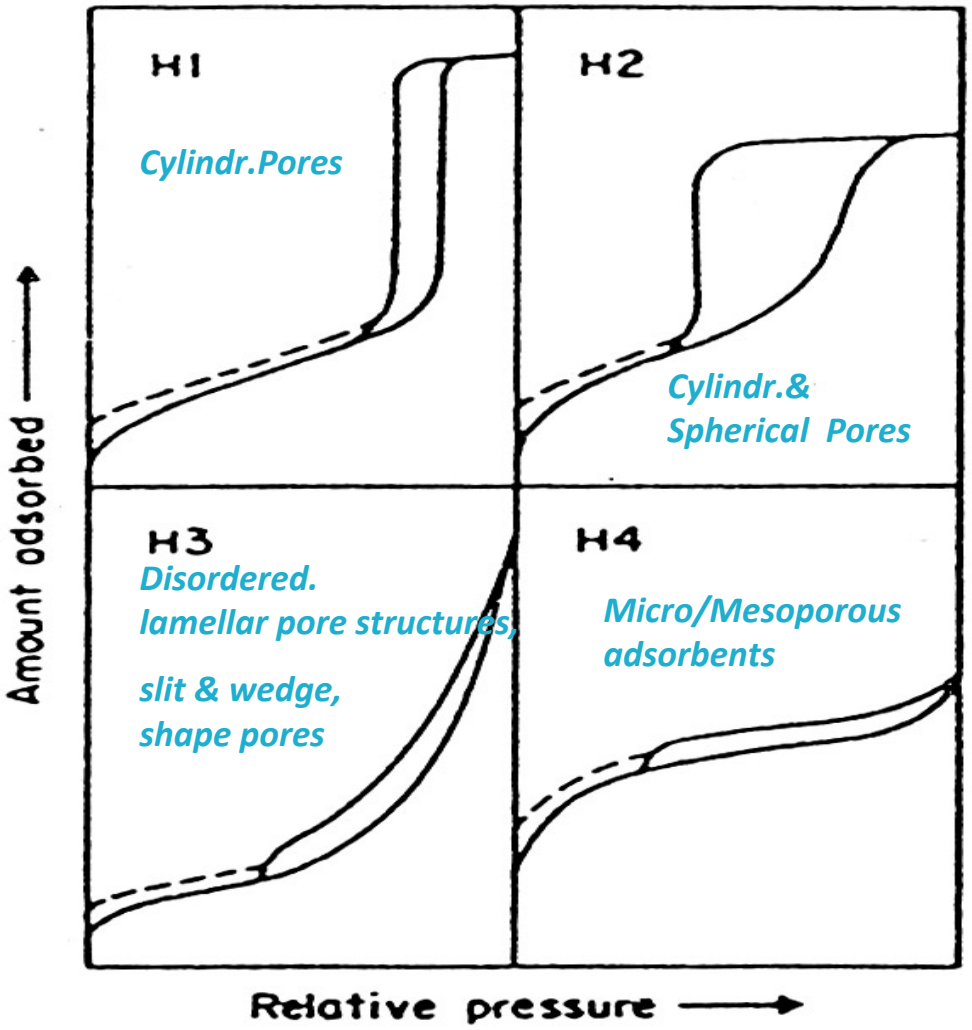
Quantachrome INSTRUMENTS

Pore Condensation in Mesopores: IUPAC Classification of Hysteresis(1985)

New IUPAC Project – Revision of Recommendation from 1985:

http://www.iupac.org/

SAASA-Symposium: Feb 20, at 12:00 : Report on new IUPAC recommendations



Origin of Hysteresis

Single Pore Model:

Cylindrical/slit like pores:

- Delayed condensation due to metastable pore fluid
- Desorption Branch reflects equilibrium transition

⇒ ***H1 Hysteresis***

Pore Networks and Ink-bottle pores,

- Delay in condensation, but also delay in evaporation potentially due to pore blocking , cavitation and percolation phenomena

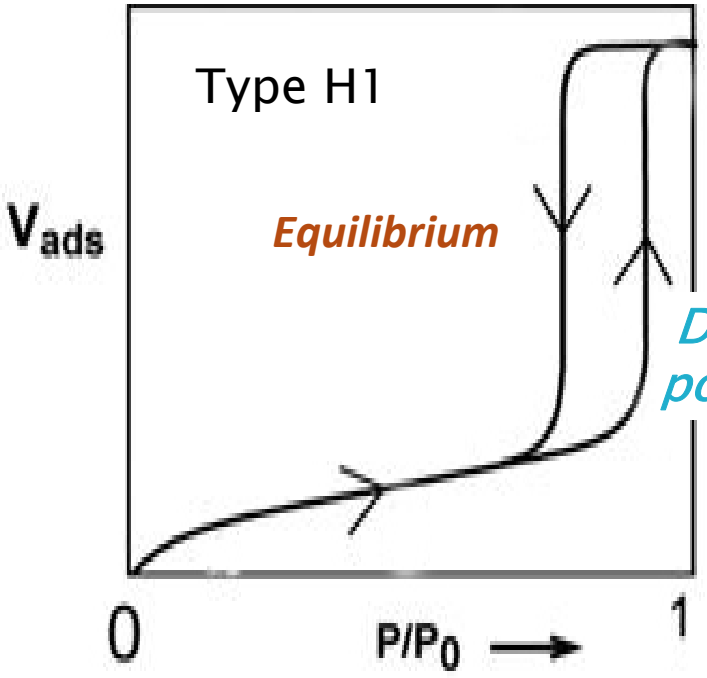
⇒ ***H2,H3, H4 Hysteresis***

Hysteresis in Disordered Porous Materials :

- Combination of kinetic and thermodynamic effects spanning the complete disordered pore system

⇒ ***H2,H3, H4 Hysteresis***

Pore condensation in single cylindrical and slit-pore: Hysteresis due to metastable pore fluid



Desorption Branch: Equilibrium liquid-gas phase transition (evaporation)

⇒ ***NLDFT-Kernel of Equilibrium Isotherms***

Delayed condensation due to metastable pore fluid

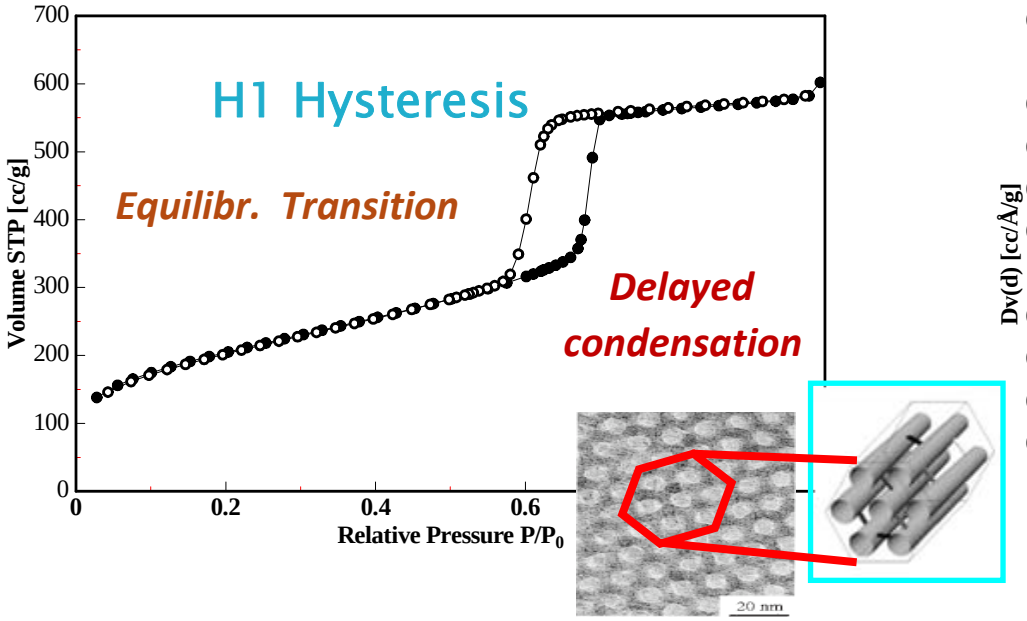
Adsorption Branch: NLDFT-spinodal- gas-liquid phase transition (condensation)

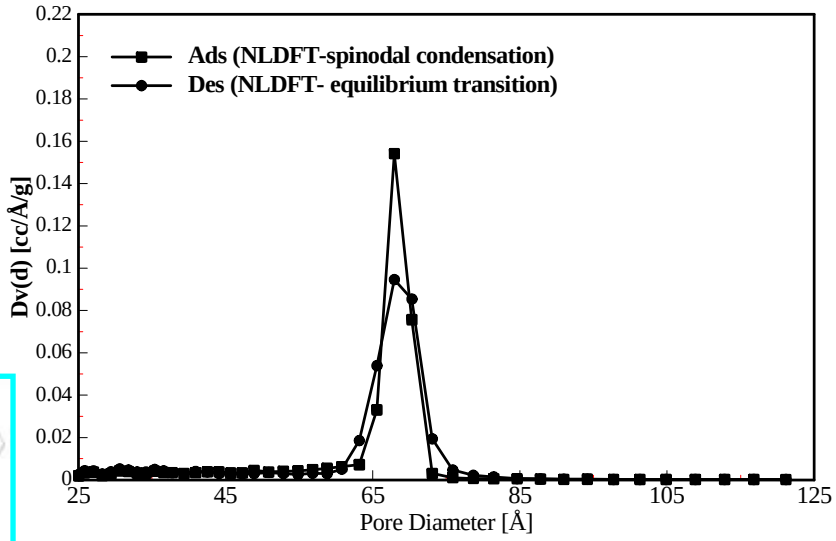
⇒ ***NLDFT- Kernel of (Metastable) Adsorption Isotherms***

A.V. Neimark and P.I.Ravikovitch,
Microporous and Mesoporous Materials, 44-56 (2001) 697

Quantachrome INSTRUMENTS

H1 Hysteresis: Nitrogen adsorption/desorption at 77.35 K in SBA-15 and pore size distributions from adsorption- (*NLDFT metastable adsorption branch kernel*) and desorption (*NLDFT equilibrium transition kernel*)



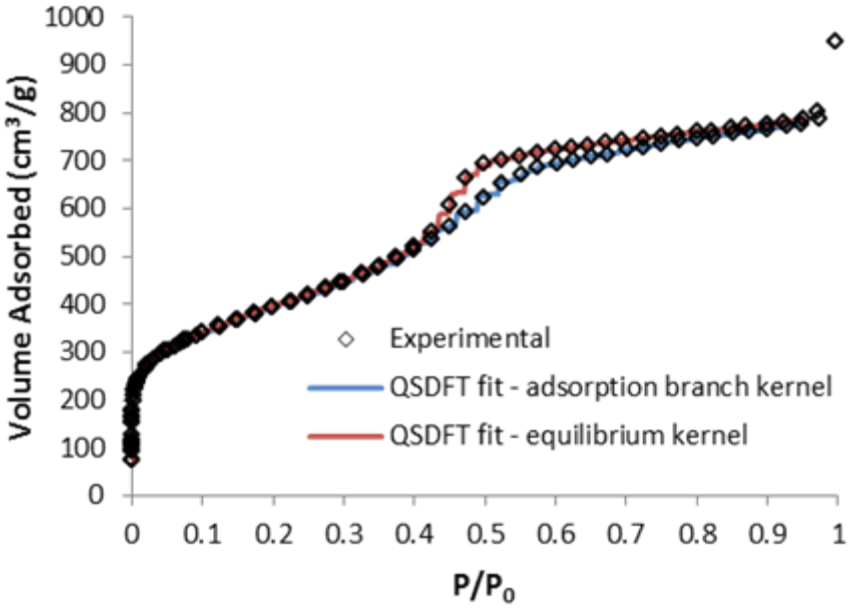


M. Thommes, In Nanoporous Materials- Science and Engineering" (edited by Max Lu and G. Zhao), Imperial College Press, Chapter 11 p. 317 - 364 (2004)

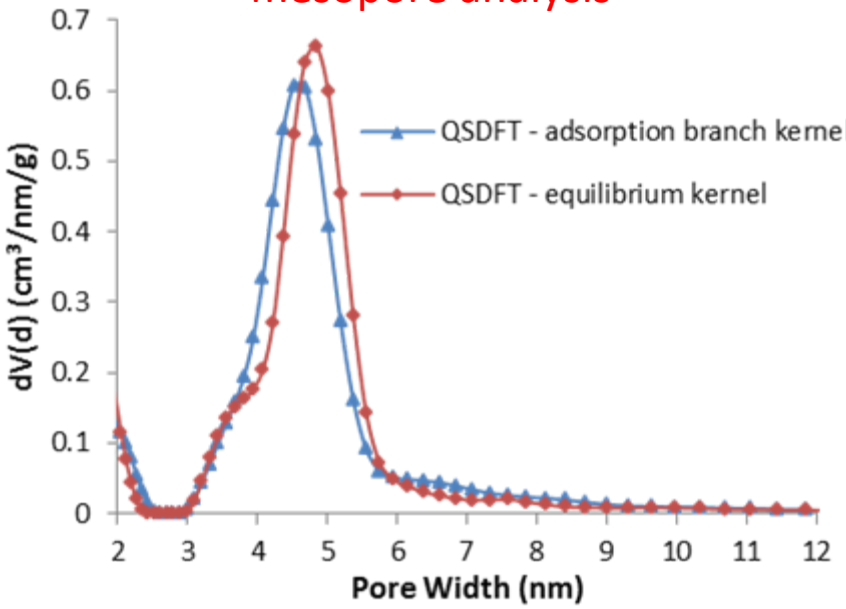
Quantachrome INSTRUMENTS

Advanced Analysis of CMK-3 Carbon

N_2 (77 K) adsorption



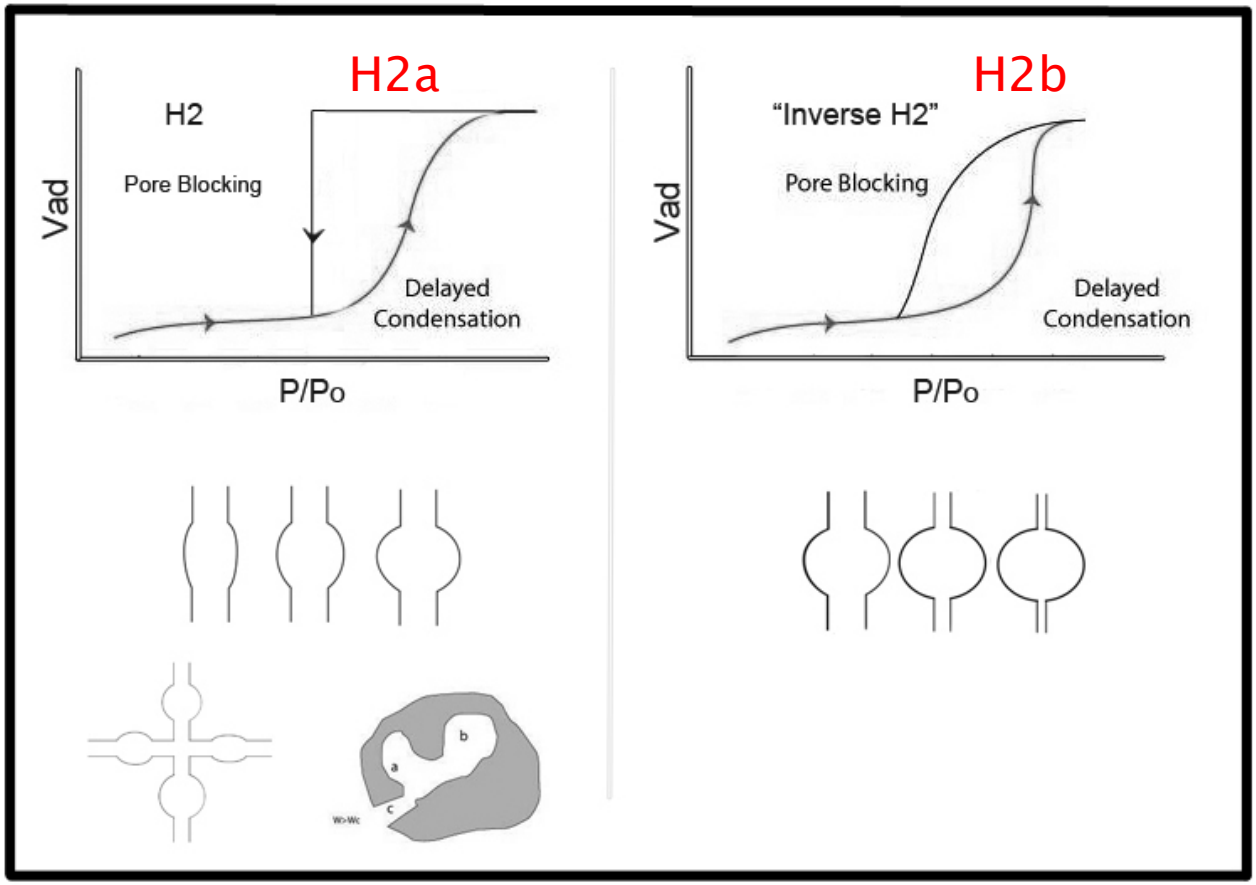
QSDFT (cylindrical carbon pore) mesopore analysis



- Agreement between pore size distribution obtained from adsorption (condensation) and desorption suggests that hysteresis in this CMK-3 is caused by a delay in (pore) condensation due to metastable pore fluid

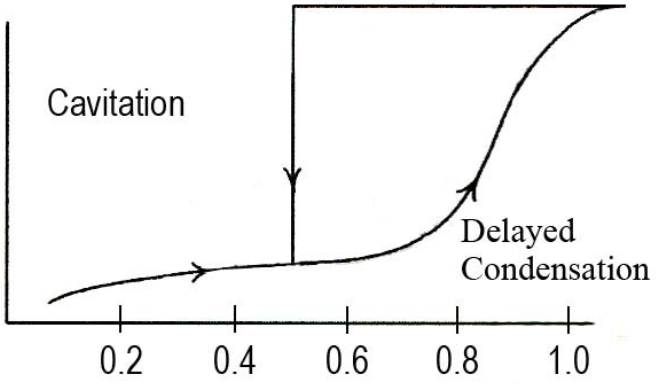
Pore Condensation and Hysteresis in complex and disordered pore networks

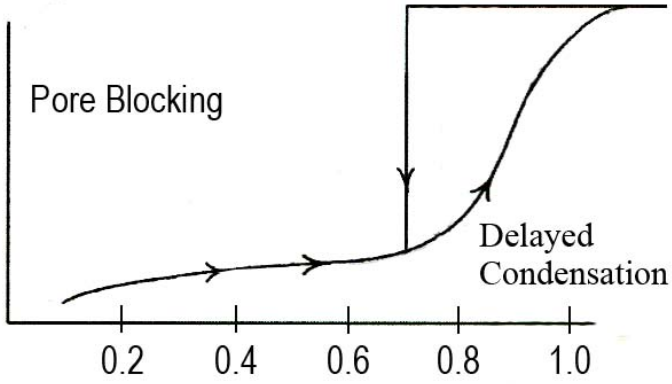
H2 Hysteresis: Pore Blocking /Percolation Phenomena



"Inverse type H2 " Hysteresis Seen for hydrothermally treated SBA-16, KIT-5 silica

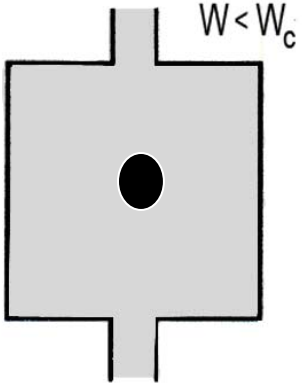
Pore Blocking/Percolation and Cavitation Phenomena

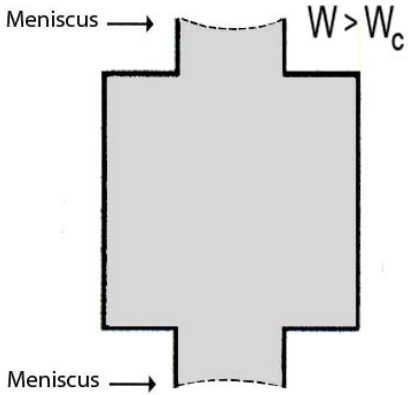




Wc = critical "neck" diameter;

≈ 5-6 nm for N_2(77 K)

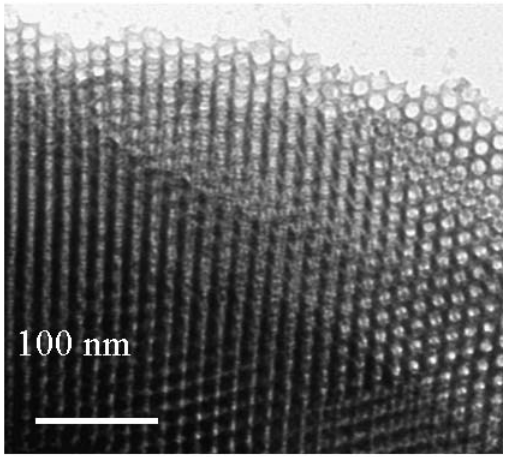




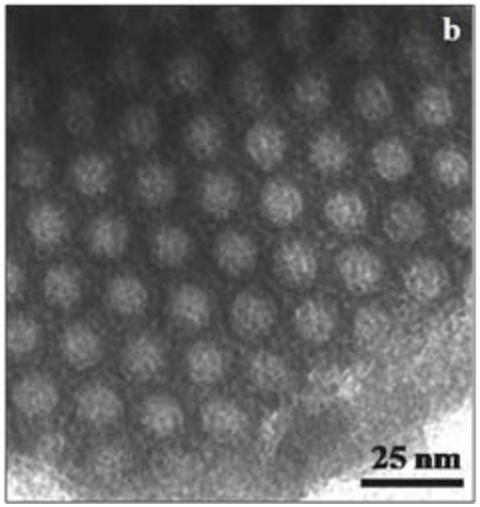
***Theoretical and molecular simulation work on Cavitation*: L.D. Sarkisov, P.A. Monson, Langmuir 17, 7600 (2001);**

P.I Ravikovitch, A.V. Neimark, Langmuir 18, 9830(2002); A. Vishnyakov, A.V. Neimark, Langmuir. 2003,19, 3240; Experiments: M. Thommes, B. Smarsly, M. Groenewolt, P. Ravikovitch A.V. Neimark, Langmuir, 22,756 (2006); O. Sel, A.Brandt, D. Wallacher, M.

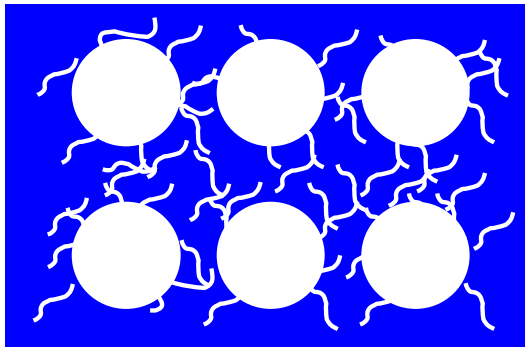
Materials with Hierarchical Pore Structures



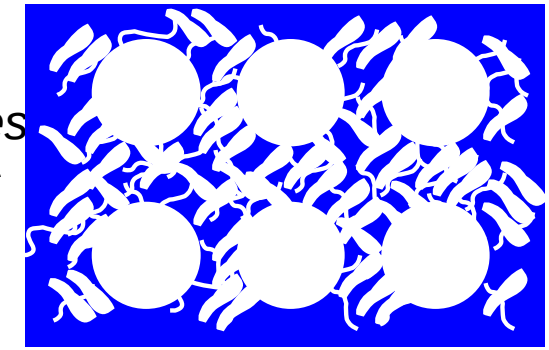
"KLE" silica



"KLE"/ IL silica



14 nm mesopores
1 nm micropores



14 nm mesopores
1 nm micropores
3 nm mesopores

Structure directing agent: KLE-type amphiphilic block copolymer

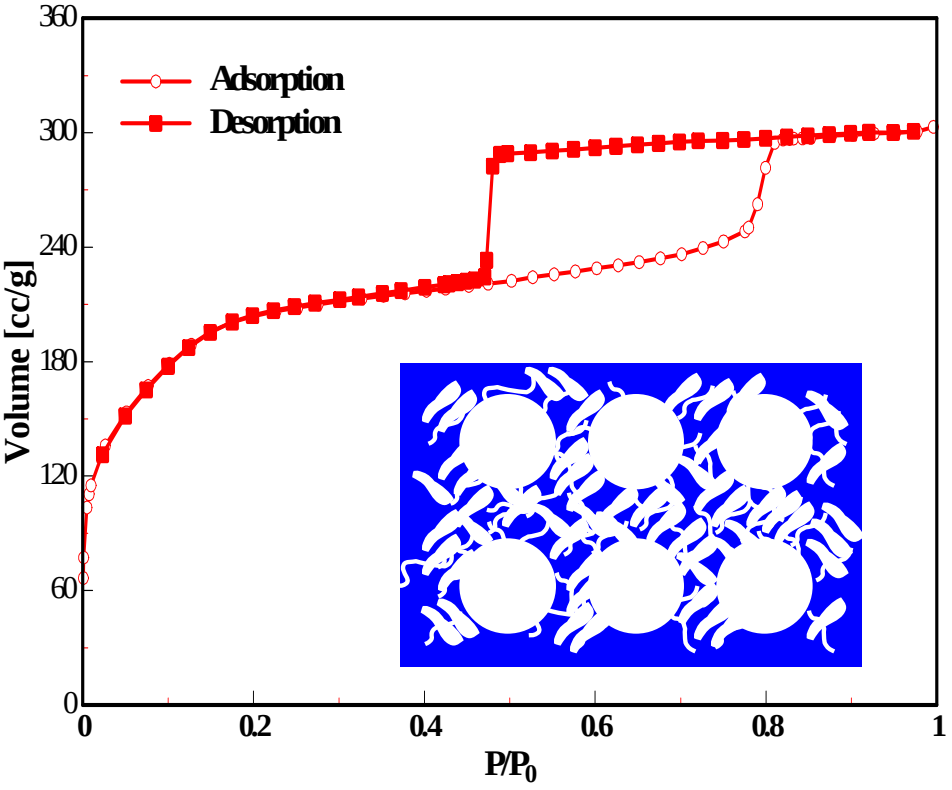
A.Thomas, H. Schladt, B. Smarsly et al., Langmuir 19, (2003

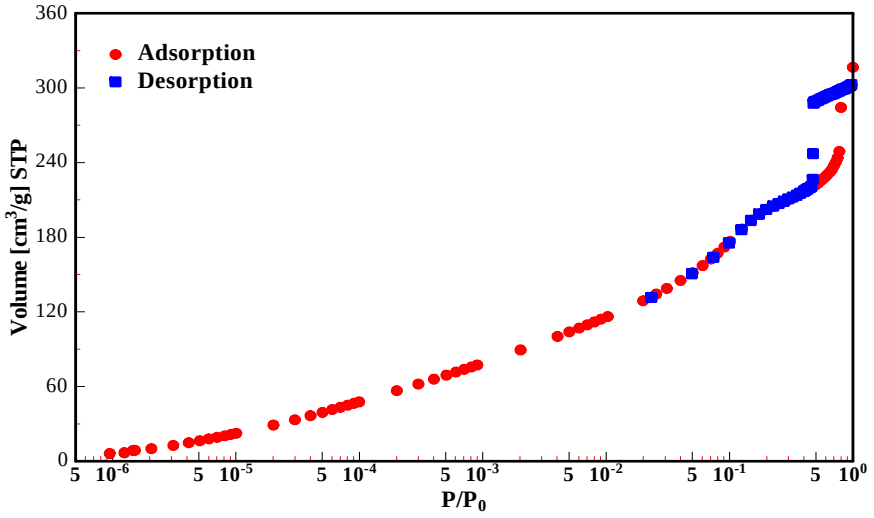
O. Sel, D. Kuang, M. Thommes, B. Smarsly, Langmuir 22, (2006) 2311

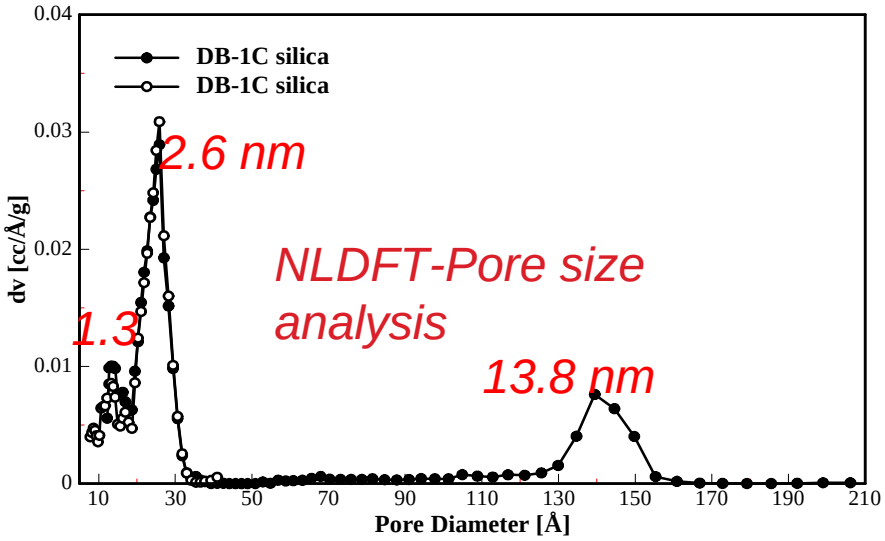
Structure directing agent: KLE-type amphiphilic block copolymer and ionic liquid

O. Sel, A.Brandt, D. Wallacher, M. Thommes B. Smarsly, Langmuir 23, (2007) 4724

Nitrogen Sorption at 77.27 K in Micro/Mesoporous KLE/IL Silica



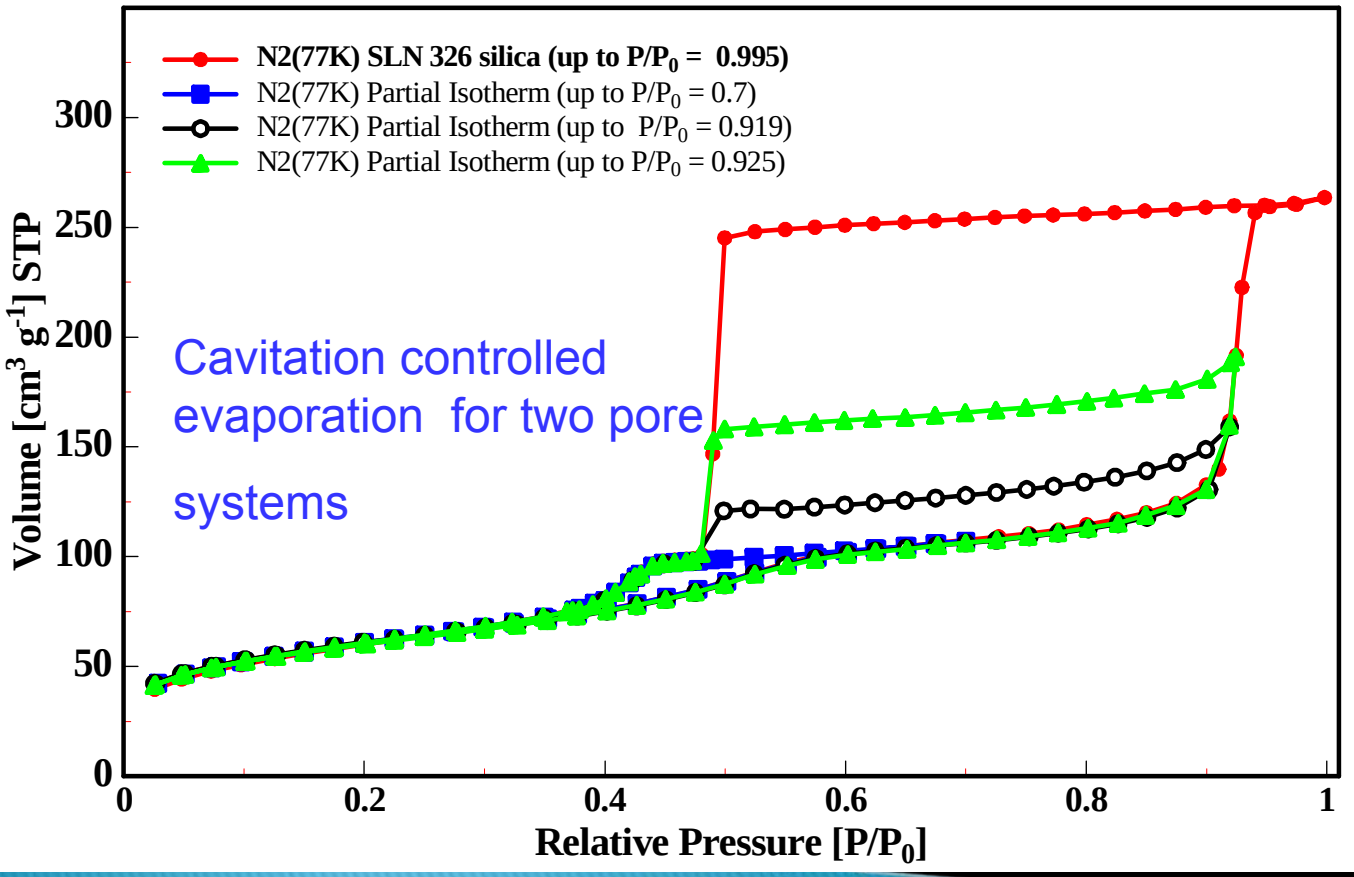




M. Thommes, B. Smarsly, M. Groenewolt, P.I Ravilkovich, A.V. Neimark, Langmuir 22,756 (2006)

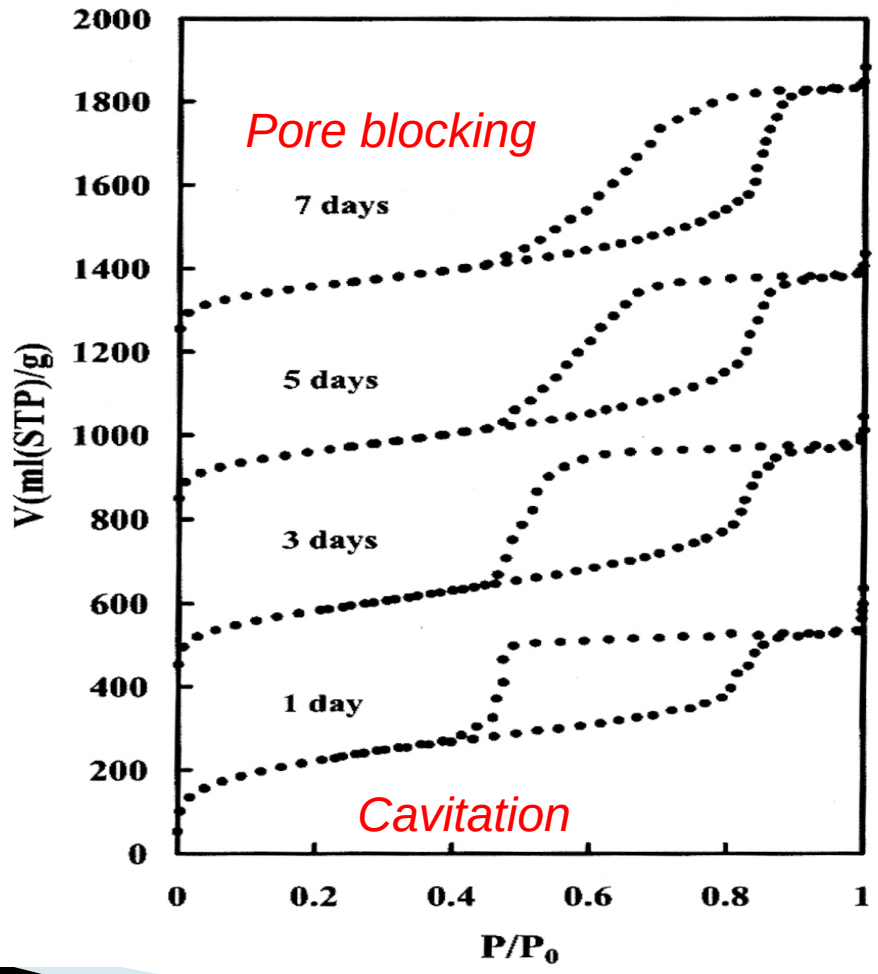
Nitrogen adsorption at 77.4 K in material with hierarchical pore structure

~ 30 nm spherical mesopores are connected through ~5 nı worm-like mesopores and micropores



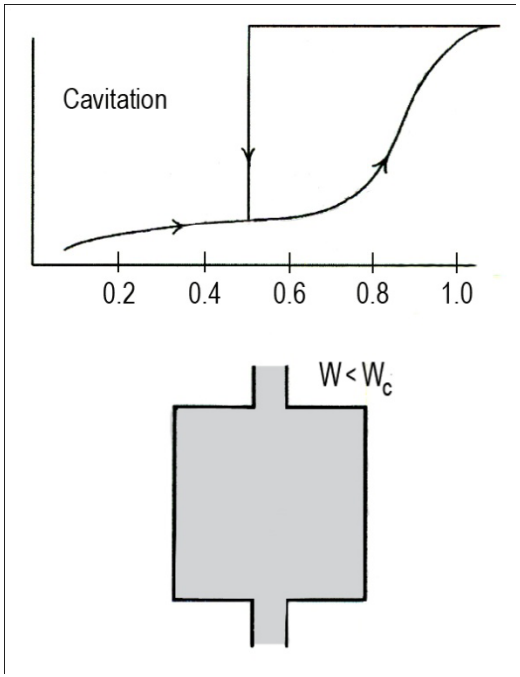
CC.J. Rasmussen, A.Vishnyakov, M. Thommes*, B.M. Smarsly, F. Kleitz, A.V. Neimark,* Langmuir (2010)

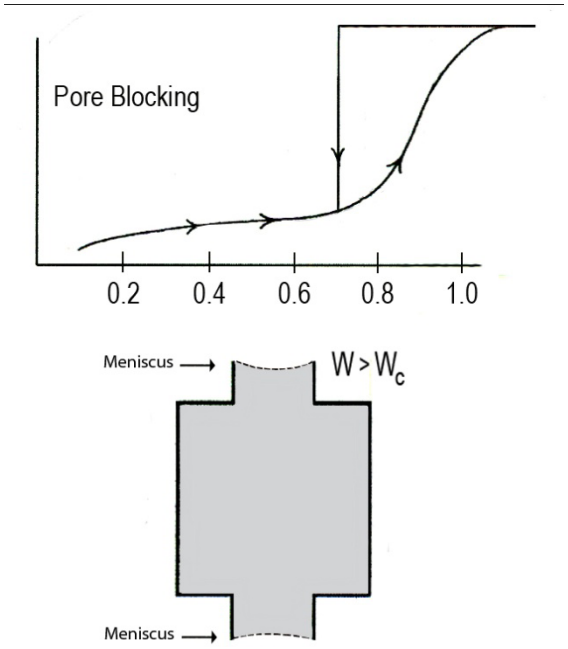
Transition from Cavitation to Pore Blocking in KIT-5 silica by changing neck-size (hydrothermal treatment)



K. Morishige , 2006

1. How to differentiate pore emptying mechanisms?





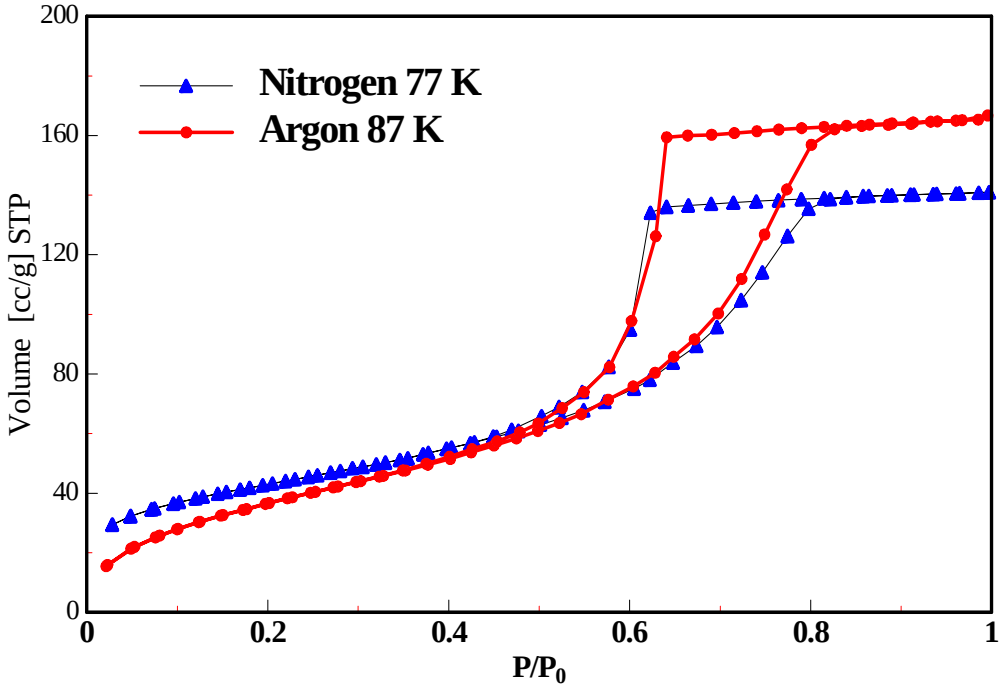
Cavitation formation depends on the thermophysical properties of the adsorptive

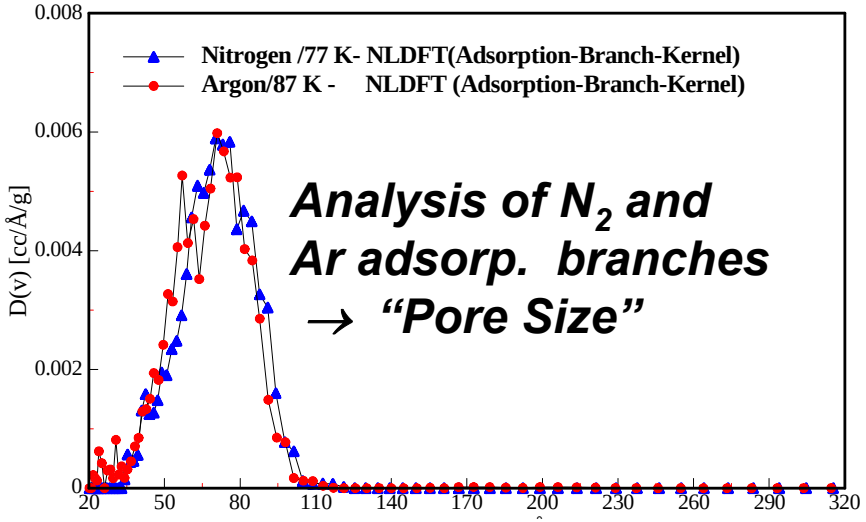
PSD determined from desorption branch does depend on adsorptive or temperature

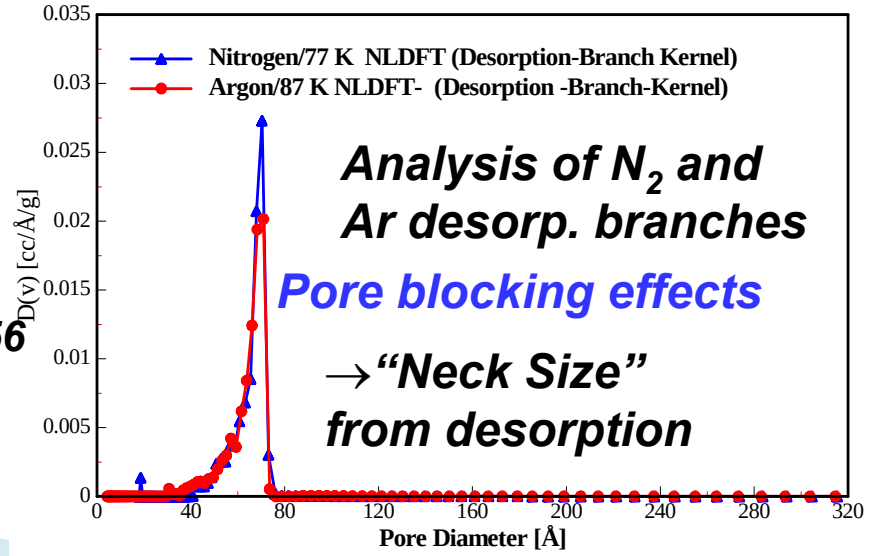
Pore blocking/percolation controlled desorption depends on on the neck size, but NOT on the adsorptive

PSD determined from desorption branch does not depend on choice of adsorptive or temperature

Pore-blocking/percolation as dominant evaporation mechanism: Nitrogen and argon sorption in porous vycor glass

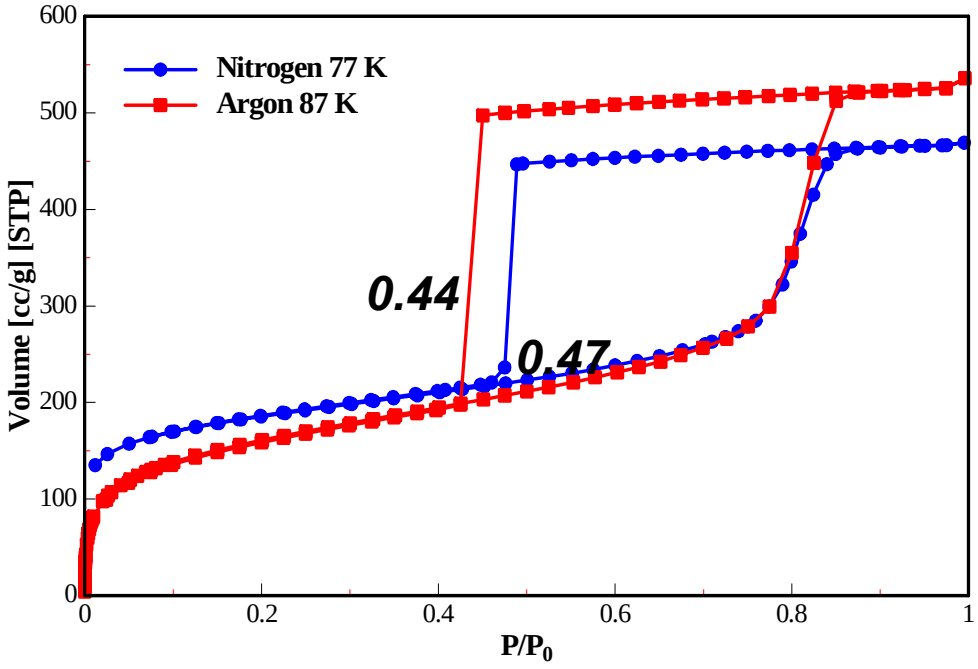




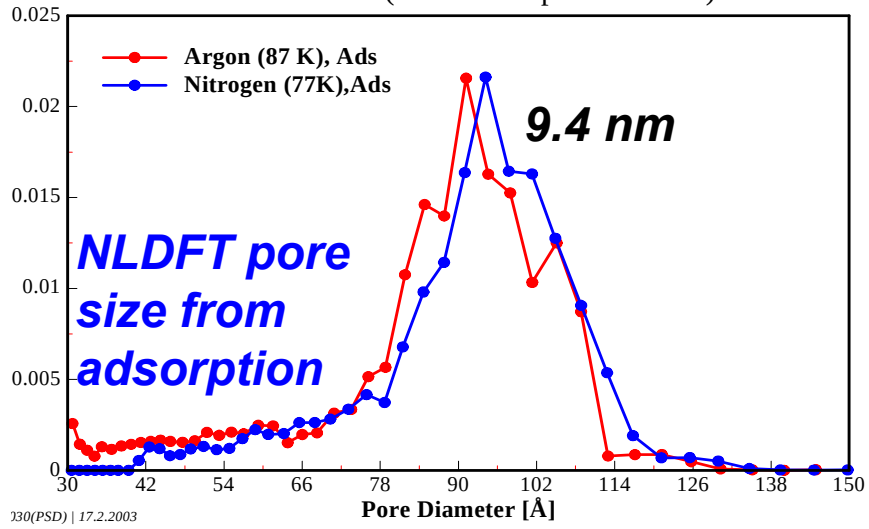


M. Thommes, B. Smarsly, M. Groenewolt, P.I. Ravikovitch, A.V. Neimark,et al .Langmuir, 22,756 (2006)

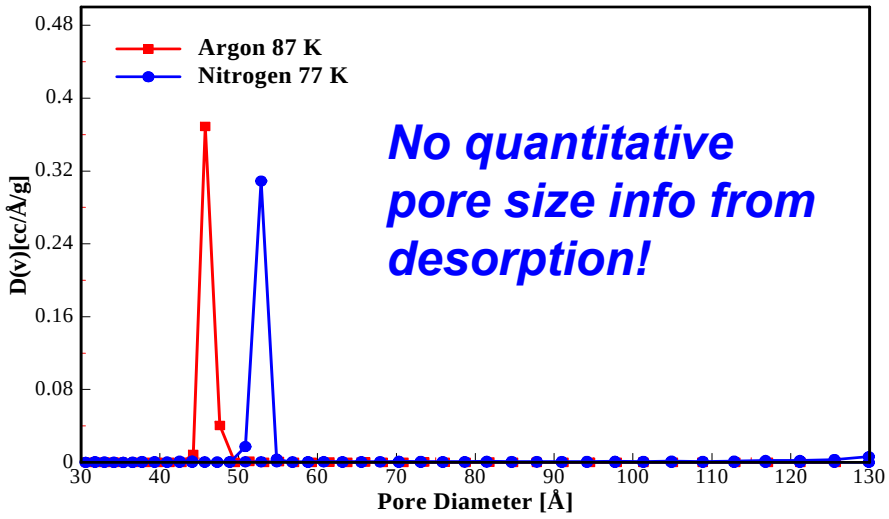
Cavitation as dominant mechanism for pore evaporation: N_2 (77.3K) and Ar(87.3K) sorption in SE3030 silica



NLDFT-PSD (from Adsorption Branch)



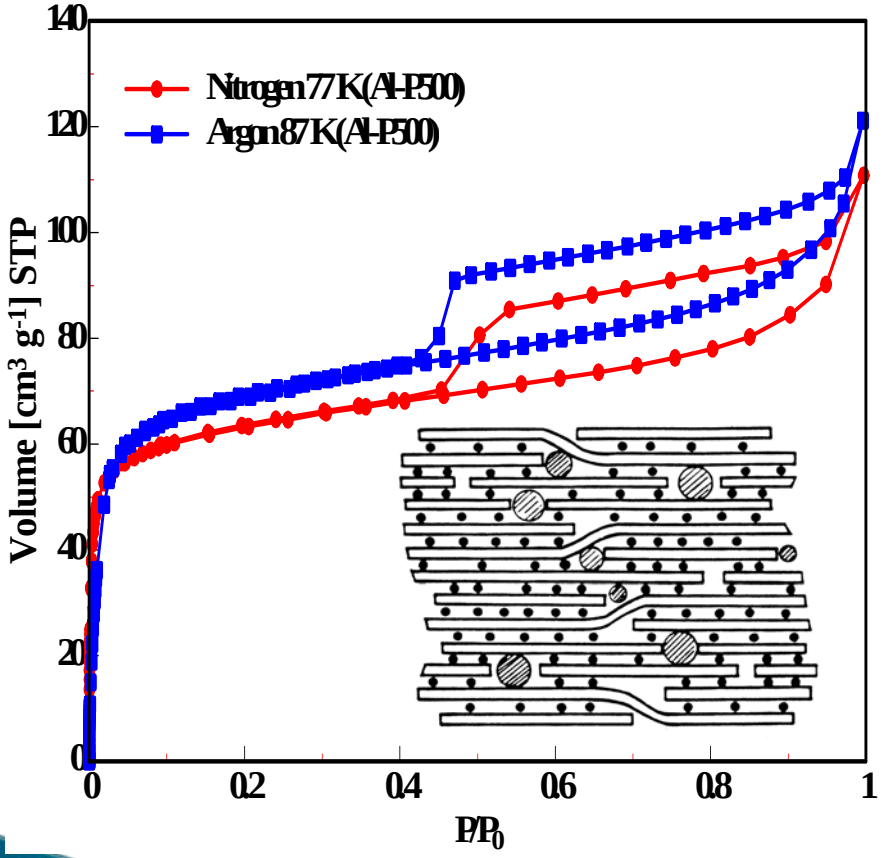
NLDFT PSD from Desorption

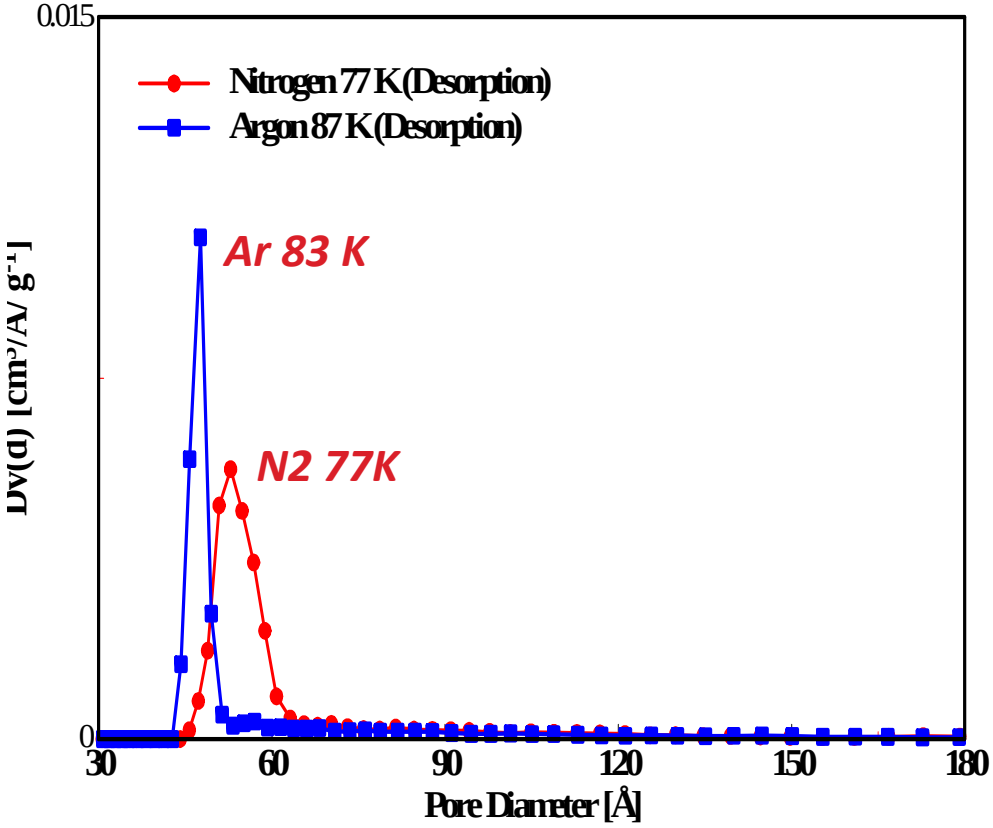


Disagreement between Ar-and N_2 "pseudo" desorption PSD's due to Cavitation transition

M. Thommes, B. Smarsly, M. Groenewolt, P.I. Ravikovitch, A.V. Neimark,et al .Langmuir, 22,756 (2006)

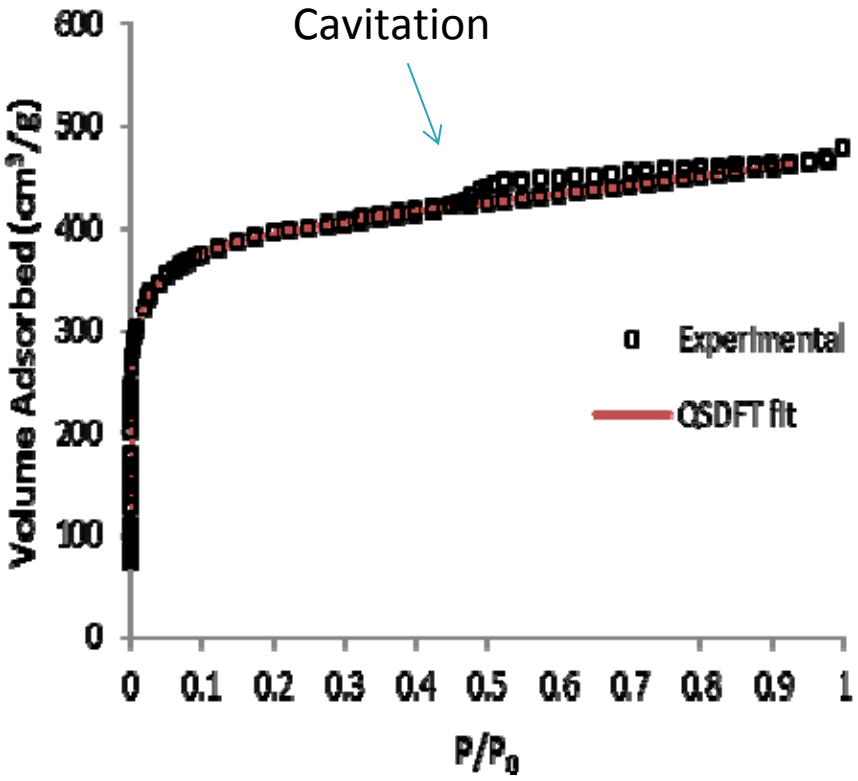
Argon (87.3 K) and Nitrogen (77.4 K) Adsorption into Pillared Clay AL P500

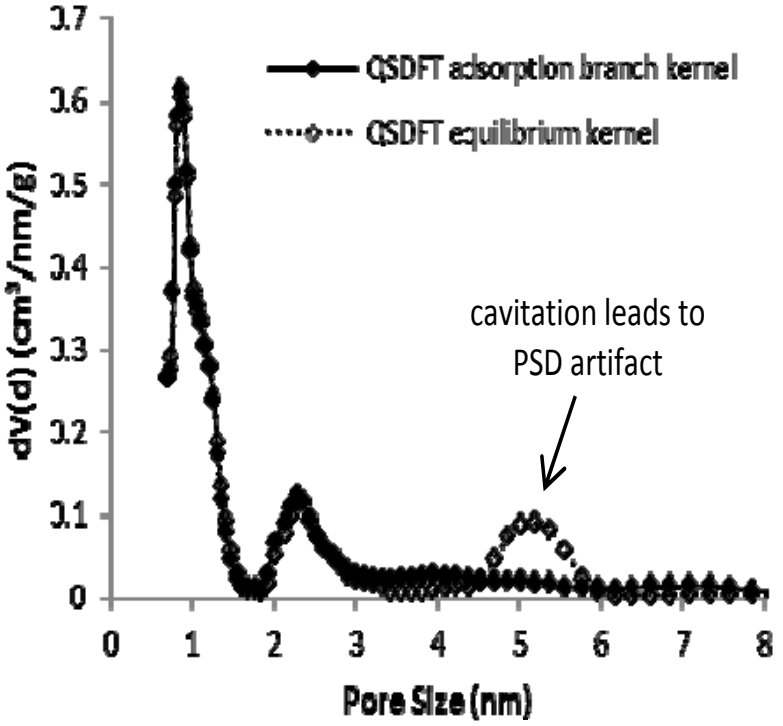




Disagreement between Ar-and N2 "pseudo" desorption PSD's due to cavitation transition (evaporation)

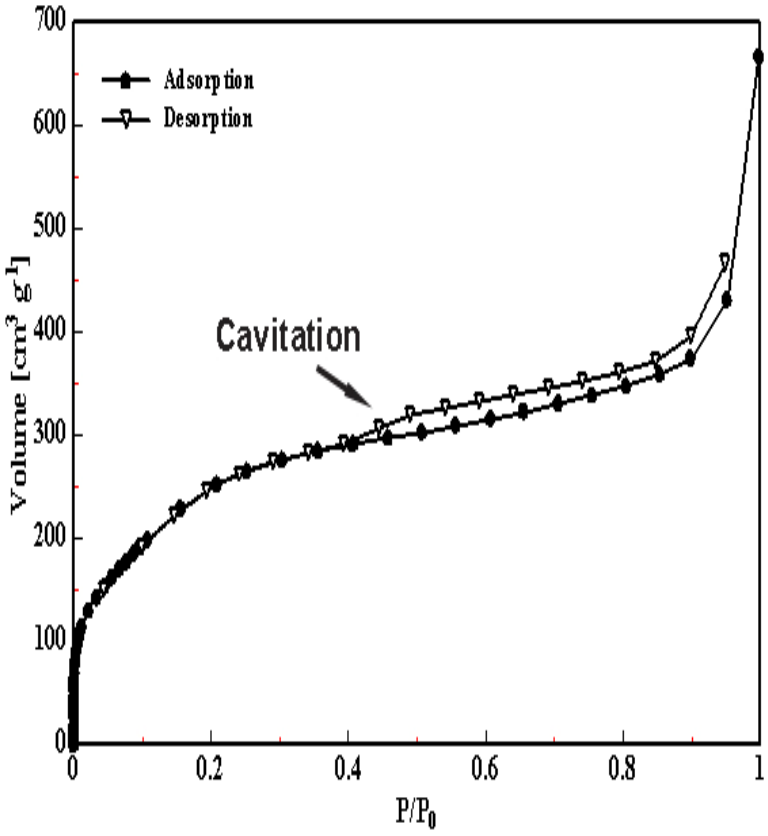
Nitrogen Adsorption and Advanced QSDFT Pore Size Analysis of Carbide-Derived Micro/Mesoporous Carbon

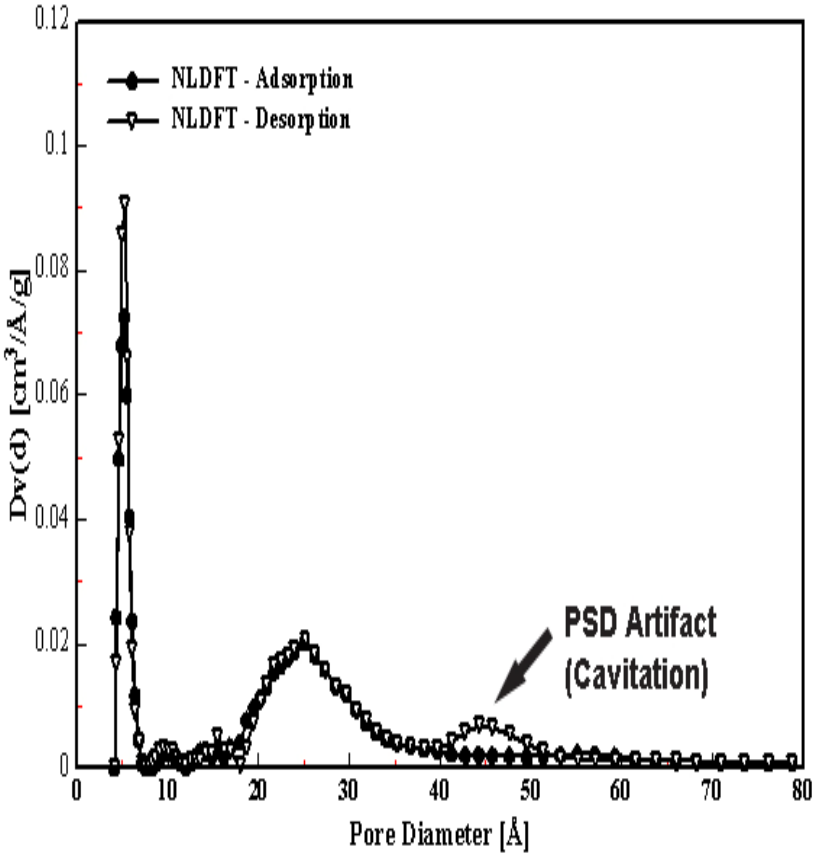




From: M. Thommes, K.A. Cychosz, A.V. Neimark, – "Advanced Physical Adsorption Characterization of Nanoporous Carbons", in: J.M.D. Tascon, Novel Carbon Adsorbents, Elsevier Ltd, 2012, p. 107–145.

Argon Sorption at 87 K in Mesoporous ZSM-5 and NLDFT Pore Size Analysis

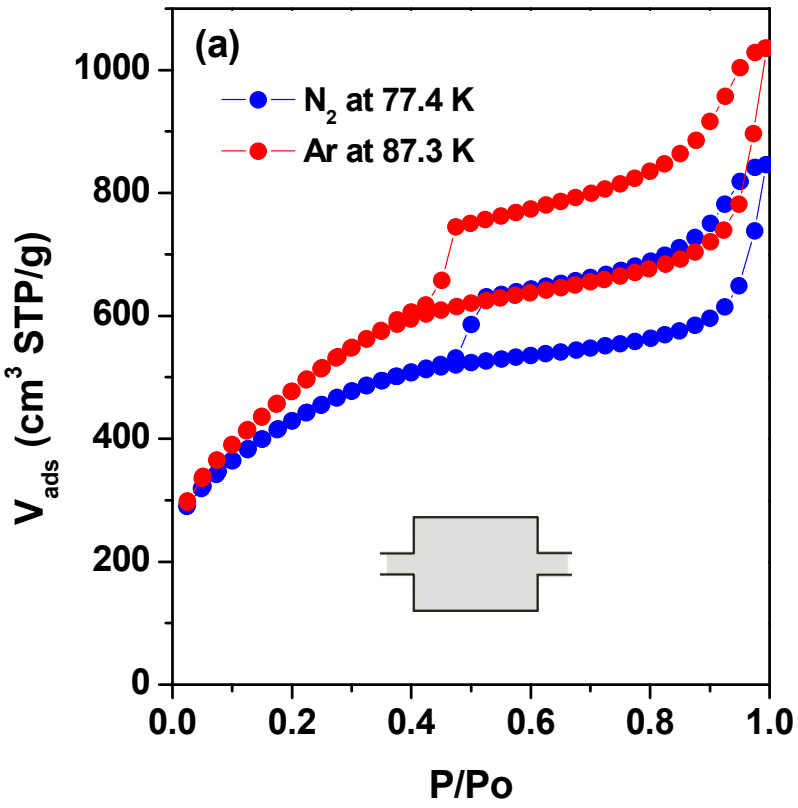


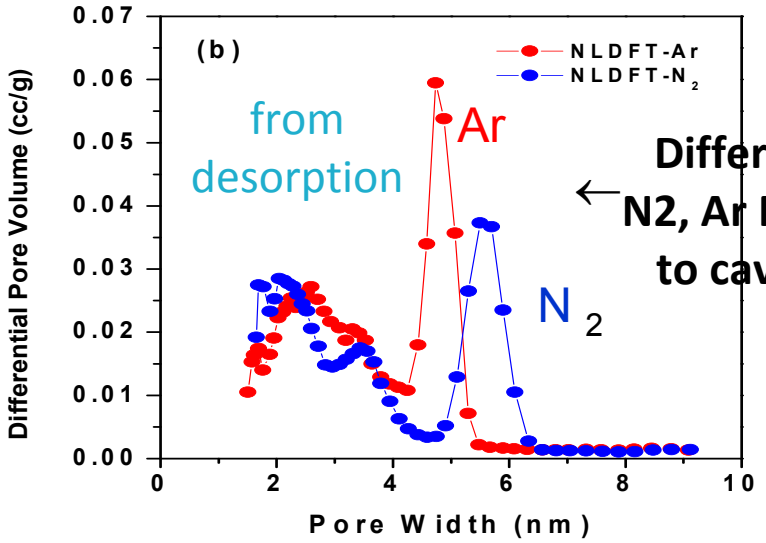


ZSM-5 data from: D. Serrano, J. Aguado, G. Morales, J. Rodriguez, A. Peral, M. Thommes, J.D. Epping, B.F. Chmelka, Chemistry of Materials Vol. 21 641 (2009)

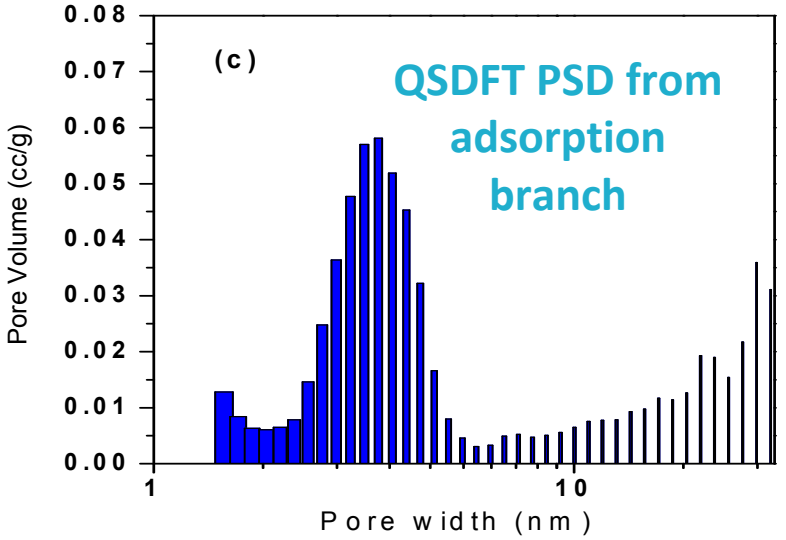
Quantachrome INSTRUMENTS

Adsorption and Pore Size Analysis of Lignocellulosic-Derived Activated Carbons





Difference in N2, Ar PSDs due to cavitation



Silvestre-Albero, A.; Goncalves, M.; Itoh, T; Kaneko, K.; Endo, M.; Thommes, M.; Rodriguez-Reinoso, F.; Silvestre-Albero, J. *Carbon* **2012**, *50*, 66-72

Conclusions

- Microscopic methods (e.g, NLDFT, molecular simulation) allow to obtain a much more accurate and comprehensive pore size analysis compared to macroscopic, thermodynamic methods (e.g. Kelvin equation, BJH, Horvath-Kawazoe, Saito-Foley)
- Various phenomena such as spinodal condensation (i.e. delayed condensation due to metastable pore fluid) pore blocking/percolation and cavitation are contributing to hysteresis in micro/mesoporous materials
- The use of different probe molecules (e.g.Argon 87 K, Nitrogen 77 K) allows not only to check for consistency in the pore size and surface area analysis, but allows also to obtain a much more accurate micro- and mesopore analysis.
- The shape of sorption isotherms is affected by, surface chemistry and the texture of the adsorbent but also by the difference in thermodynamik states of pore and bulk fluid phases
- $\Rightarrow$ This has to be taken into account in order to obtain a correct and comprehensive pore size analysis, but also for gas storage applications .

Assessment of Microporosity

Experiment: Choice of adsorptive is important

- Argon 87 K is recommended for the pore size analysis in microporous materials with polar sites

- For microporous carbons a combination of nitrogen (77K) and/or argon 87 K with carbon dioxide adsorption at 273 K is useful

- Molecular probes

Data reduction

Micropore Volume

-Dubinin based methods works well for routine assessment of micropore volume

-Comparison plot methods: alpha-s method (no need for BET area) is superior compared to t-method

Pore Size Analysis

DFT or molecular simulation based mehods essentially replace methods based on macroscopic, classical assumption for pore size analysis

Assessment of Mesoporosity

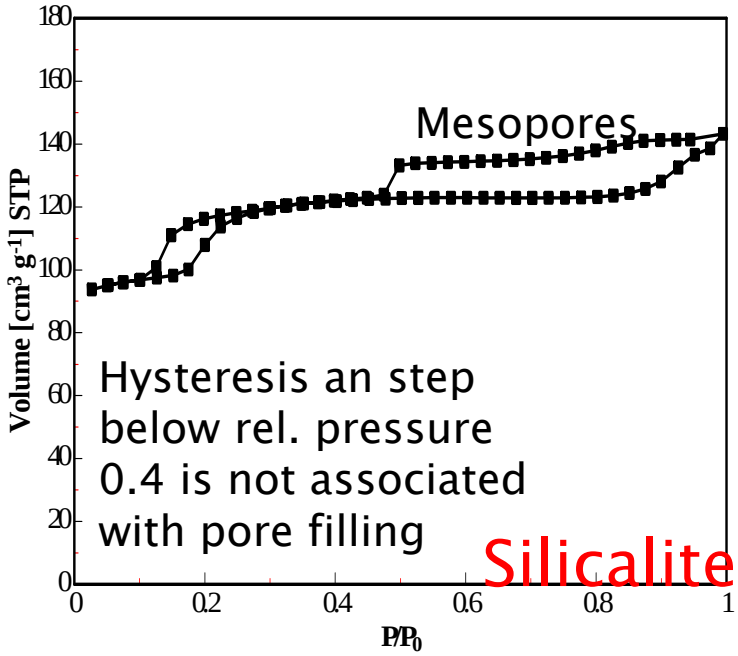
- DFT or molecular simulation based mehods replace methods based on macroscopic, classical assumption (e.g. Kelvin equation based approaches) for narrow mesopores (< ~ 10 nm)

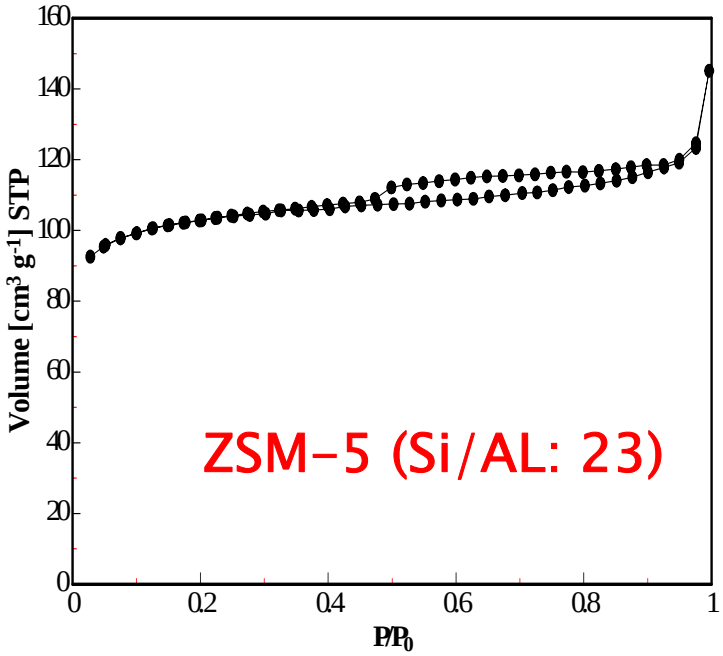
- A proper intepretation of hysteresis loops is required for pore size analysis

- DFT/molecular simulation based methods allow for a description of the mechanisms of hysteresis

- DFT and related methods are the only way to obtain a pore size analysis of the complete micro-and mesopore size analysis with one method

Pitfall: Nitrogen (77 K) adsorption on mesoporous Silicalite I and on a ZSM-5 zeolite (with Si/Al ratio: 23)





Pore condensation related Hysteresis cannot occur below ca. P/P0 0.35 for Nitrogen and Argon adsorption at 77 K and 87 K, respectively

Adsorption in Silicalite and ZSM5 with high Si/Al ratio