Adsorption and Phase Behavior of Fluids in Advanced Micro/Mesoporous Materials and their Structural Characterization

Matthias Thommes

Quantachrome Instruments
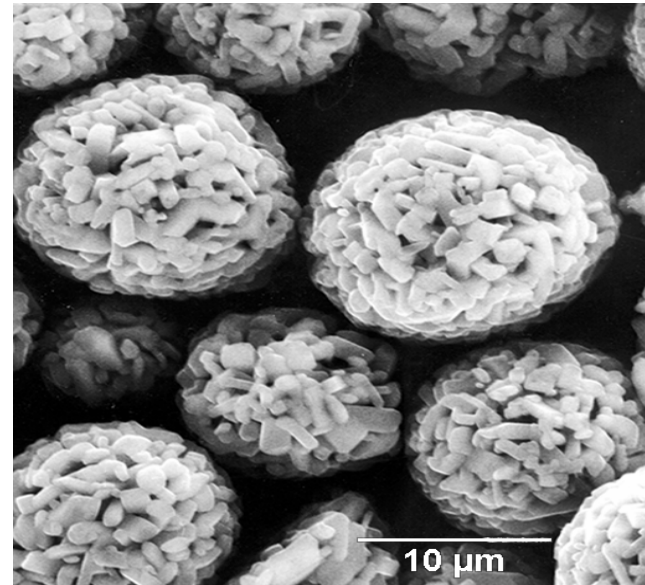
Boynton Beach, FL, USA

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Quantachrome Instruments Corporate Headquarters, Boynton Beach, Florida

CONTENT

Structural Characterization of Nanoporous Materials

- Surface Area

- Pore Size/Volume Distribution

- Pore geometry, Structure of
  Pore Network

- Surface Properties

- Particle Size distribution

Particle and Porosity Analysis :

- Special Issue of: Particle & Particle Systems Characterization, Vol. 21, No. 2, (2004) *Title: Characterization of Porous Systems*
  Guest Editors: Matthias Thommes & Alex Neimark

- Special Issue of: Particle & Particle Systems Characterization, Vol. 23 No. 7 (2006) *Title: Analysis of Meso- and Macroporous Systems*
  Guest Editors: Renaud Denoyel & Matthias Thommes

Some Experimental Techniques for Structural Analysis

- Gas adsorption

- Liquid Intrusion/Mercury porosimetry

- Thermoporometry (by DCS, and NMR based techniques)

- Scattering techniques (x-ray and neutron scattering techniques such as SAXS, SANS, XRD)

- Microscopy, (e.g.SEM, TEM)

- **Combining gas adsorption with mercury porosimetry allows to assess a pore size range from ca. 0.3 nm up to 400 μm!**

Structural Characterization 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) 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 to describe the configuration of adsorbed molecules in pores on a molecular level.

(iii) *Carefully performed experiments (by combining various experimental techniques)*
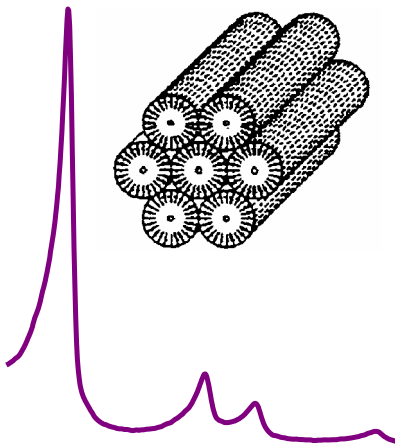
Mesoporous Silica Molecular Sieves

Synthesis Conditions
- *Tetraethylorthosilicate, Na-silicates*
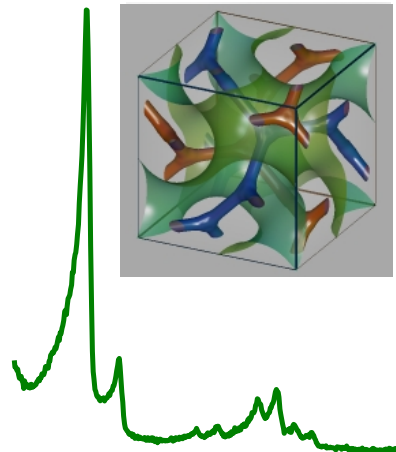- *Acidic, basic, neutral conditions*
- *cationic, non-ionic, anionic surfactants*
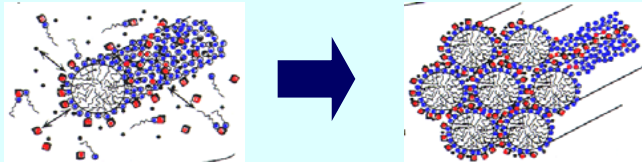
- *Controllable pore sizes between 2-15 nm*
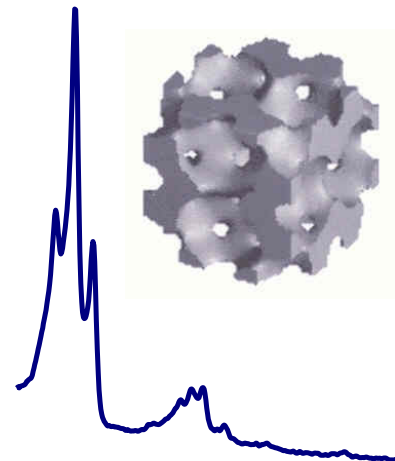- *Various channel structures*
- *Easily removable template*

Hexagonal *p6mm*
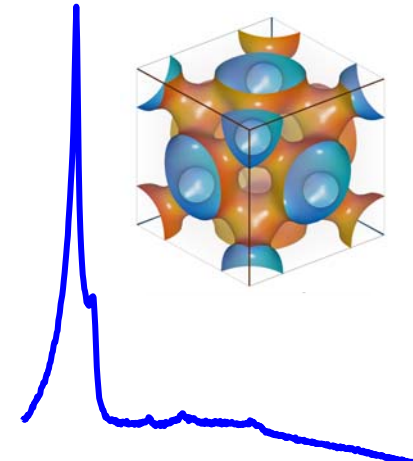**MCM-41, SBA-15**

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

Cubic *Pm-3n*
SBA-1

Cubic Fm-3m
KIT-5

Courtesy of Freddy Kleitz

Results of sorption studies on ordered mesoporous materials in combination with advanced theoretical and molecular simulation approaches :

- The thermodynamic state and the 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…)-

  ⇒ *Sorption isotherms are affected by this and theories and methods for pore size analysis have to take this into account in order to allow for a reliable pore size analysis !*

Problem: Conventional, macroscopic, thermodynamic methods (e.g, methods based on the Kelvin equation such as BJH, BdB) assume bulk-fluid like behavior for pore fluid and neglect details of the fluid-wall interactions

  ⇒ Errors of 25 % and more in pore size analysis!!

Solution:

- *(1) Application of microscopic methods based on statistical mechanics (e.g., NLDFT, GCMC) which describe the configuration of the adsorbed phase on a molecular level*

⇒ *Pore size analysis over complete micro/mesopore size range*

  (2) Correction, and/or proper calibration of classical methods (e.g, KJS method):.

 ⇒ *Pore size analysis over calibrated pore size range*

Effect of thermodynamic state of adsorptive on Adsorptionisotherm: Methane and Hydrogen at 107 K in socMOF (Me080)
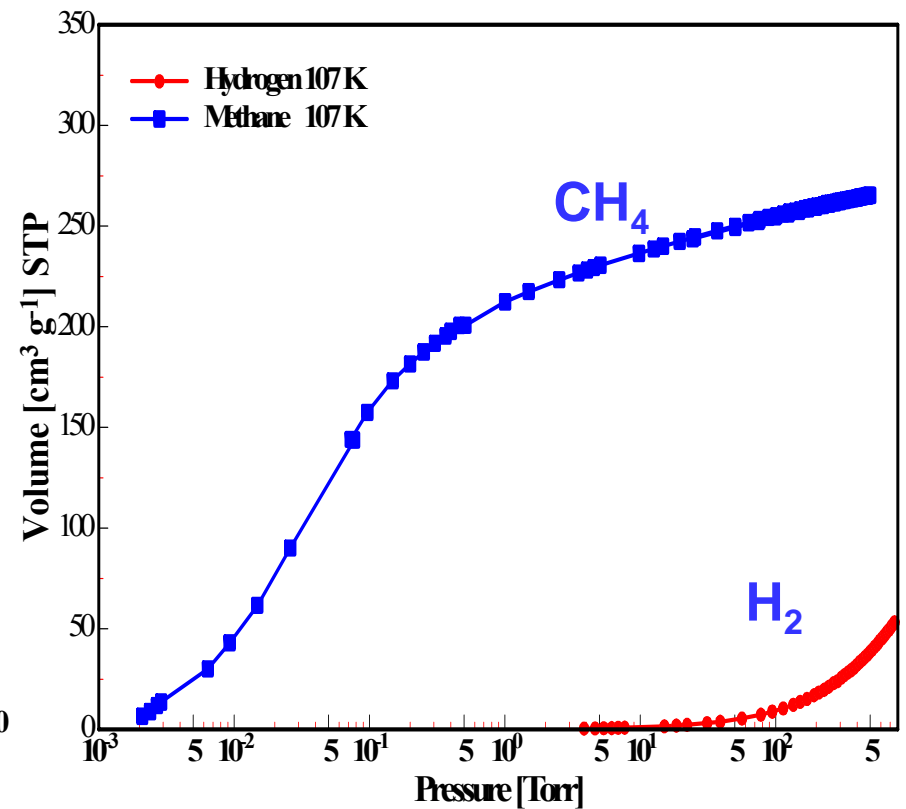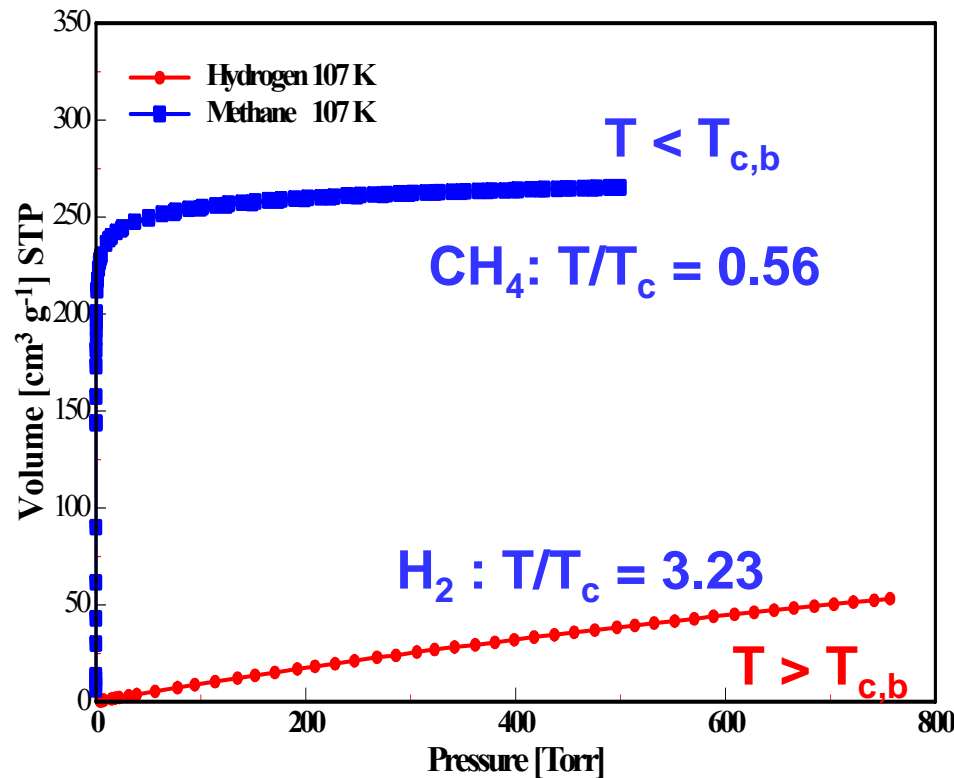
Differences in adsorbed amount of H2 an CH₄ at 107 K are due to differences in thermodynamic state!

M. Thommes , E. Celer, M. Eddaoudi (2008)

Adsorption in Mesopores: Adsorption, Phase Behavior and Hysteresis
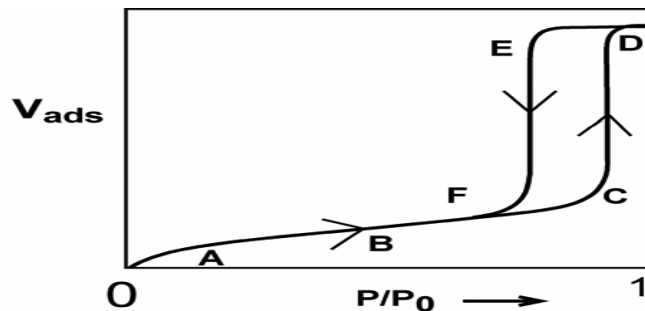
Classical description of pore condensation by Kelvin equation:

$$\ln(P/P_0) = -2\gamma\cos\theta / RT\Delta\rho(r_p - t_c)$$
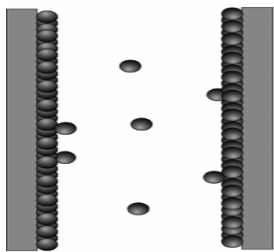
r_p: pore radius

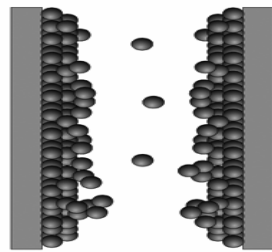t_c : adsorbed multilayer film prior to condensation
γ: surface tension

$\Delta\rho$: densities of the coexistent liquid (ρl) and gas (ρg) ($\Delta\rho = \rho l - \rho g$)
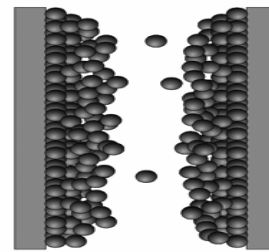
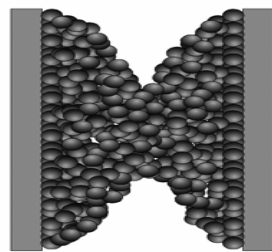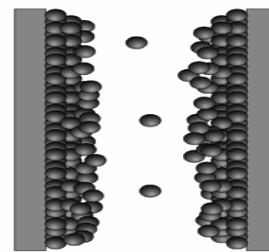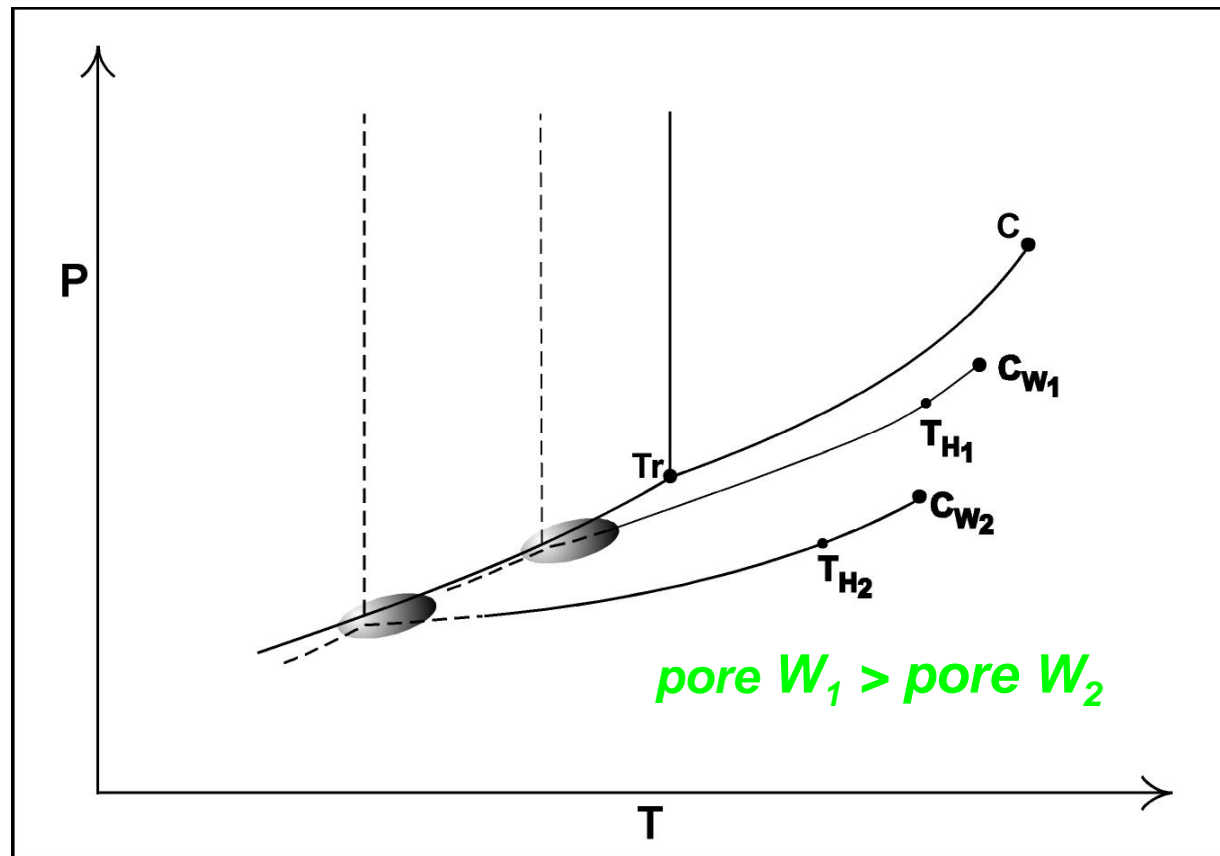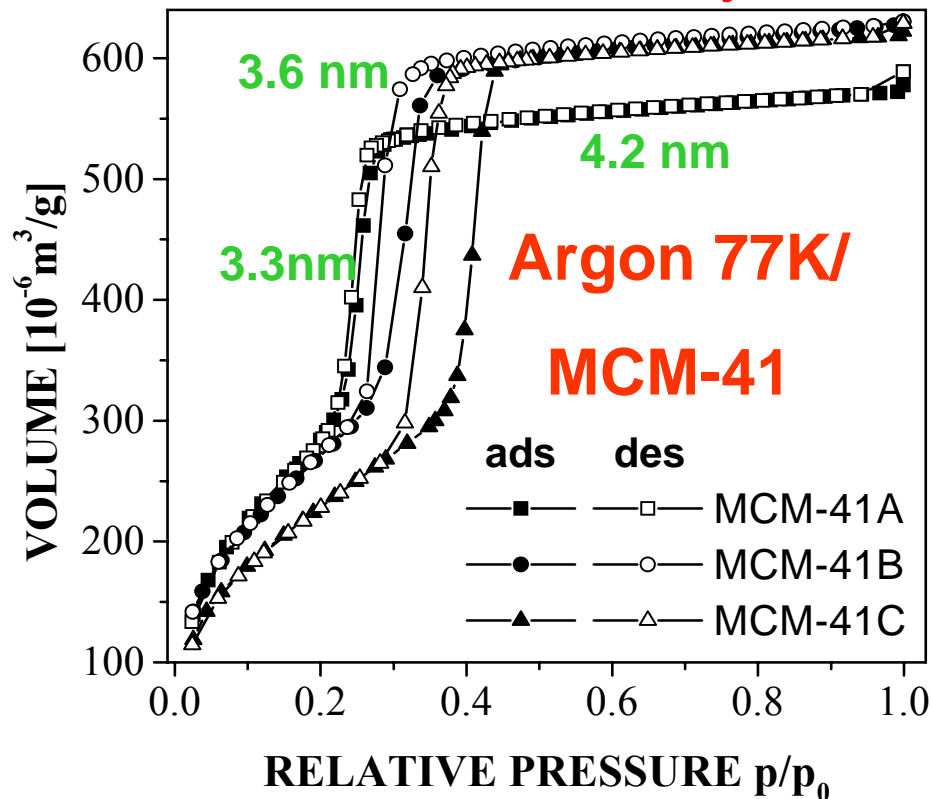θ : contact angle of the liquid meniscus against the pore wall
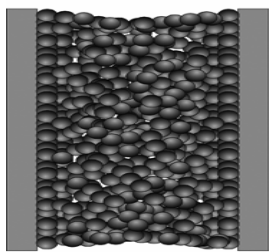
Schematic phase diagram of pore fluid and bulk fluid

M. Thommes, In Nanoporous Materials Science and Engineering, (edited by Max Lu and X.S Zhao, eds.), Imperial College Press, Chapter 11, 317 –364, (2004)

Effect of Pore size and Temperature on Pore Condensation and Hysteresis

Effect of Pore Size on Hysteresis

Effect of Pore Size on Hysteresis

3.6 nm
3.3nm
4.2 nm

Argon 77K/

MCM-41

ads   des
- ■ — □   MCM-41A
- ● — ○   MCM-41B
- ▲ — △   MCM-41C

VOLUME [10^{-6} m^3/g]

RELATIVE PRESSURE p/p$_0$

Ar / 77 K and 87 K

77 K
87 K

ads   des
- ○ — ●   77 K
- □ — ■   87 K

Argon/ MCM-48 (dp= 4.01nm)

volume [10^{-6}m^3/g]

relative pressure p/p$_0$

In : S. Lowell, J. Shields, M. Thomas, M. Thommes, *Characterization of porous solids and Powders: Surface Area, Pore Size and Density*, **Kluwer Academic Publ, 2004**.
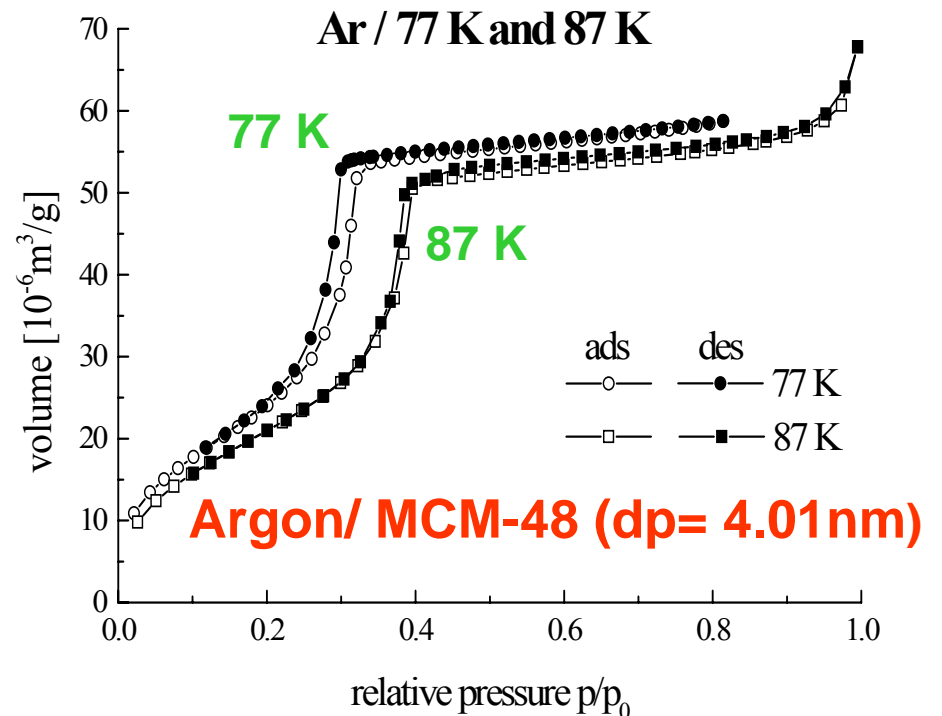
M. Thommes,, R. Koehn and M. Froeba et al. J. Phys. Chem B 104, (2000), 7933

Pore Size Analysis by Gas Adsorption

Macroscopic, thermodynamic methods

Micropores *(< 2 mn***):** e.g**.,** *Dubinin-Radushkevitch*
or more advanced methods such as *Horvath-Kawazoe*
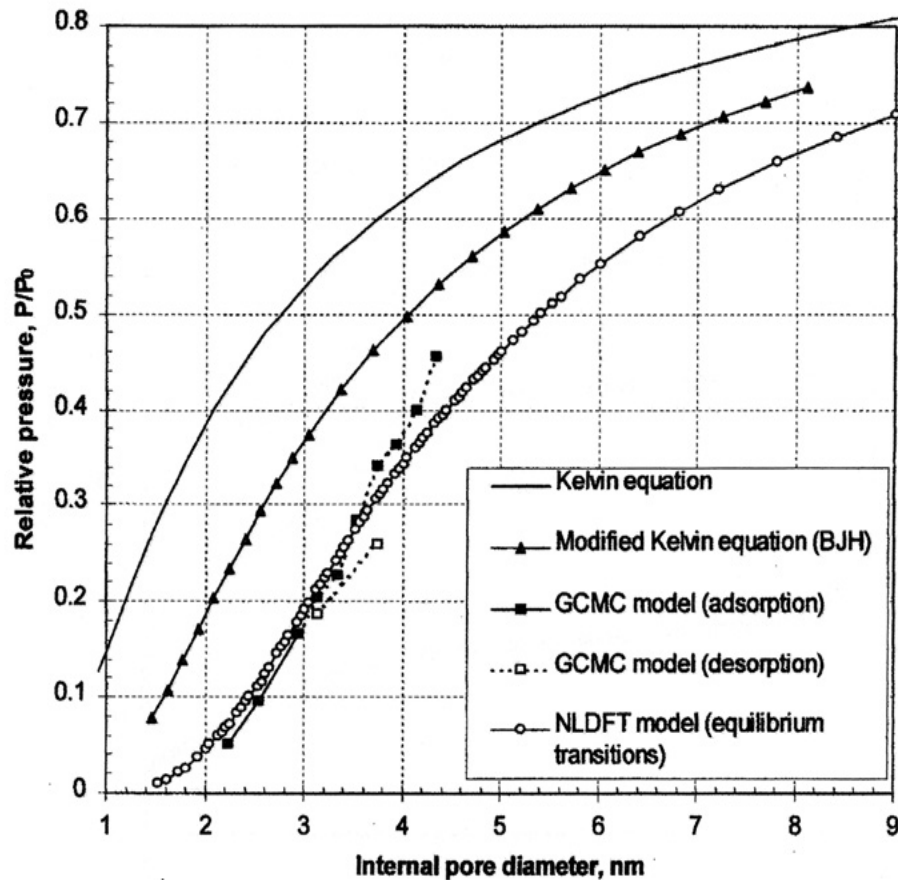(HK) and *Saito-Foley* (SF) , t-method, alpha-s method
Meso/Macropores *(2-100 nm):* e.g., Kelvin equation based methods such
    as BJH (Barrett,Joyner, Halenda)

**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

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

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

Legend:
- Kelvin equation
- Modified Kelvin equation (BJH)
- GCMC model (adsorption)
- GCMC model (desorption)
- NLDFT model (equilibrium transitions)

Axes: Relative pressure, P/P$_0$ vs Internal pore diameter, nm

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

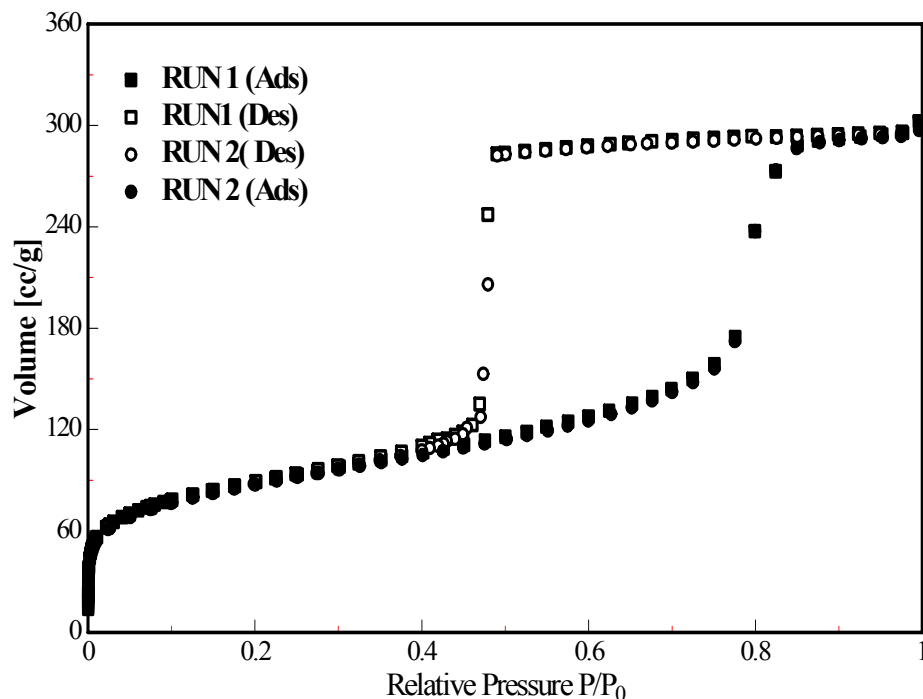# N₂ sorption (77 K) in MCM-41 and Pore Size Analysis by Modified Kelvin eq. (BJH method) and Nonlocal-Density Functional Theory (NLDFT)
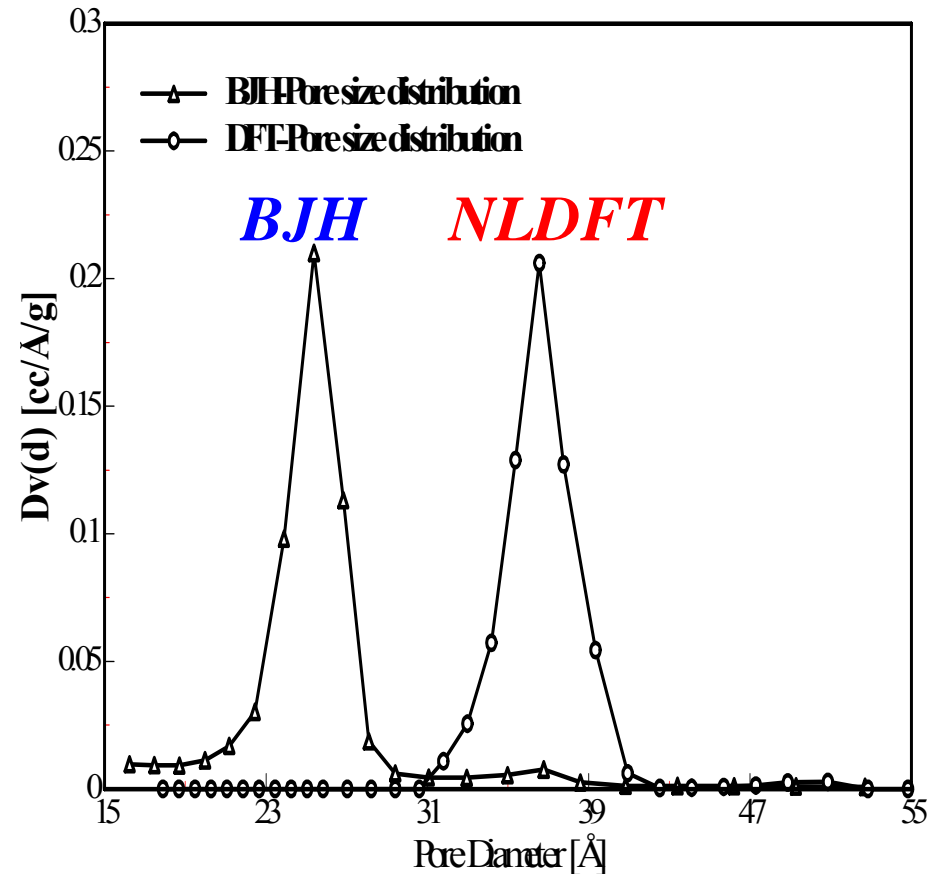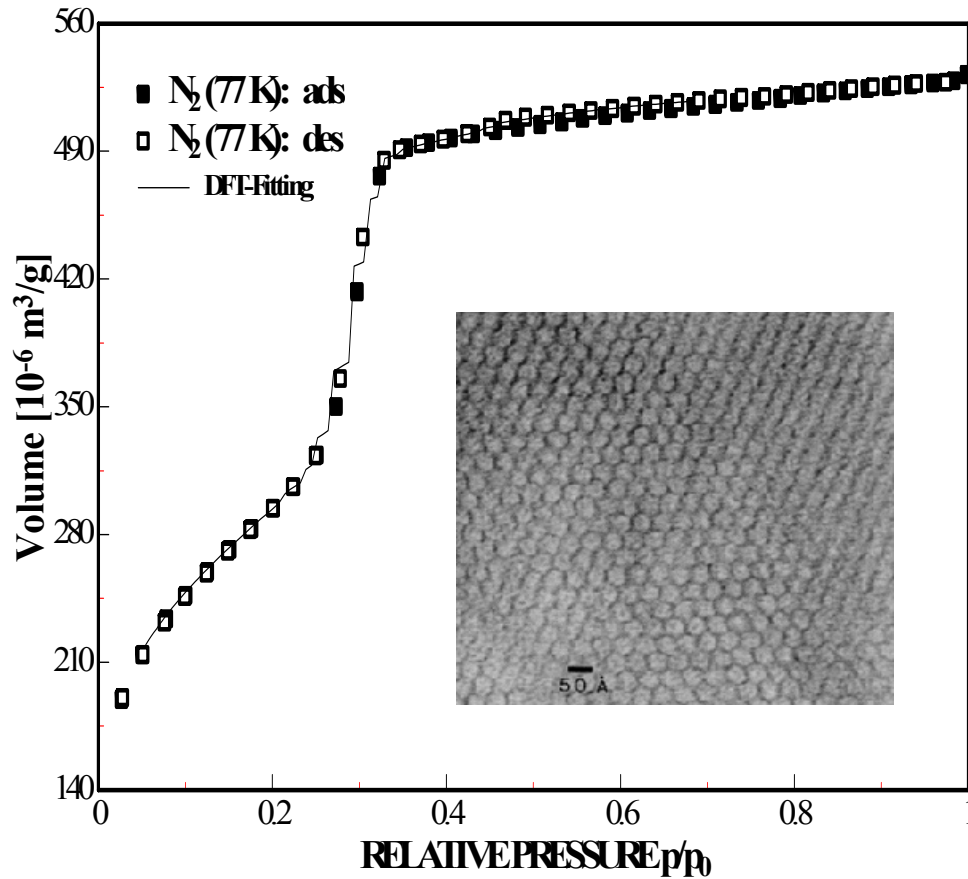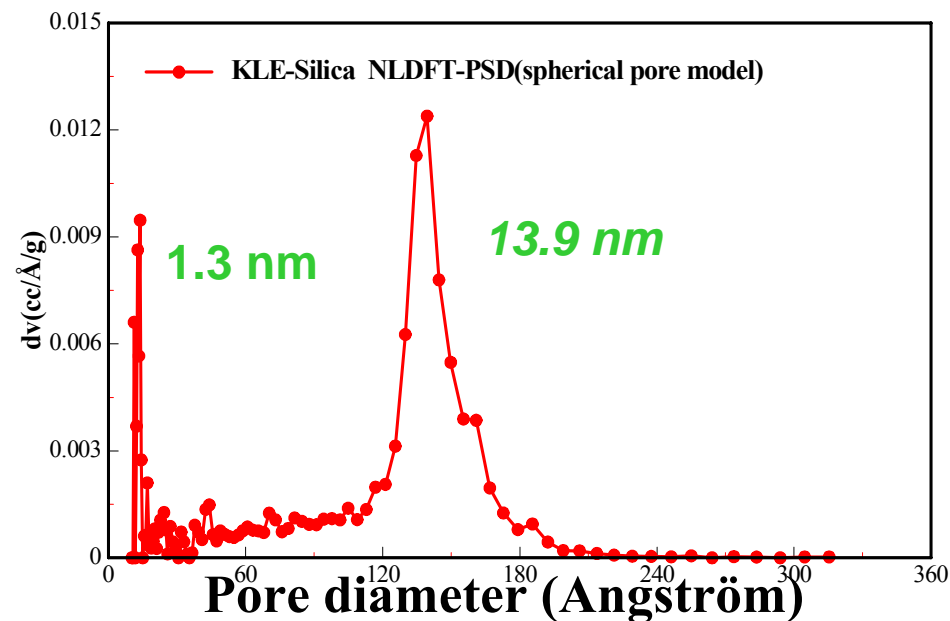

- *Classical methods (i.e. BJH, based on Kelvin equation) underestimate the pore diameter up to ca. 25 % !*
- *NLDFT allows to calculate an accurate pore size distribution*

Nitrogen sorption of "KLE silica" at 77K and NLDFT analysis
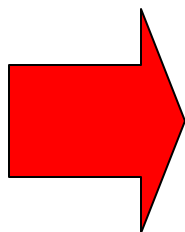
N$_2$ sorption isotherm

- ■ RUN 1 (Ads)
- □ RUN1 (Des)
- ○ RUN 2(Des)
- ● RUN 2 (Ads)

Volume [cc/g]

Relative Pressure P/P$_0$

Pore size distribution

— KLE-Silica NLDFT-PSD(spherical pore model)

1.3 nm

13.9 nm

dv(cc/Å/g)

Pore diameter (Angström)

NLDFT analysis (spherical mesopores, cylindrical micropores)
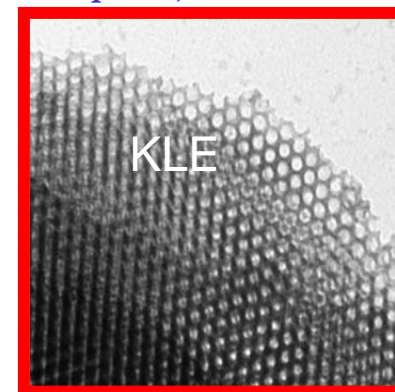
Mesopore Size:

N$_2$-sorption: 13.9 nm
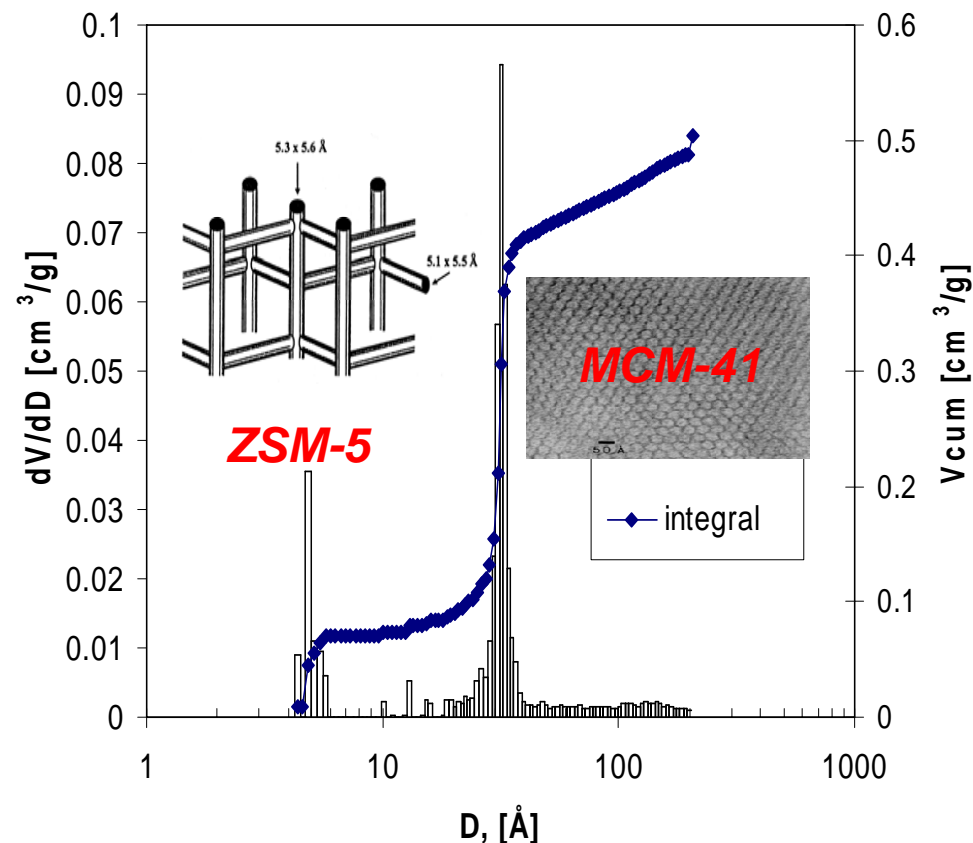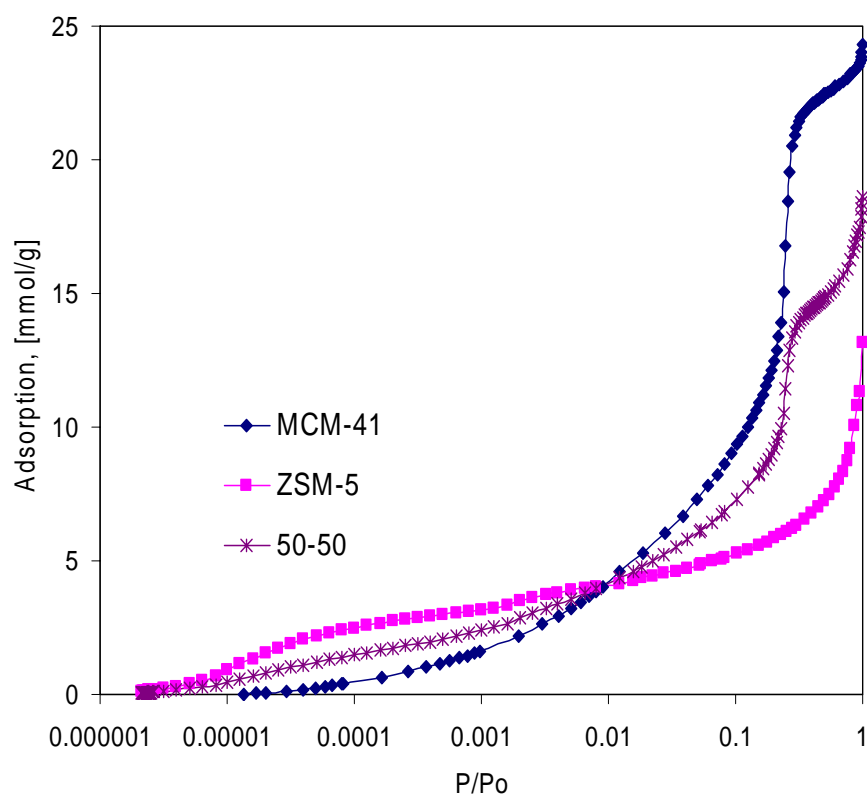
TEM: Ca. 13 nm

SAXS: 13.8 nm

Excellent agreement between SAXS and new NLDFT approach!

KLE

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

Argon adsorption at 87 K on a 50:50 mixture of ZSM-5 +MCM-41: Combined micro/mesopore analysis by NLDFT

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

- DFT is 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)

  ISO- 15901: Pore size distribution and porosity of solid materials by mercury porosimetry and gas adsorption –
  Part 2 Analysis of mesopores bas adsortion
  Part 3: Analysis of micropores by gas adsorption

$\Rightarrow$ *Facilitates the application/use of DFT methods for pore size analysis in industry*

- However:

  NLDFT does not take into account surface heterogeneity

Accounting for surface roughness/heterogeneities

Molecular Simulation

- Tremendous progress in modeling reaistic 3D structures (***Gubbins, Monson*** and   others …) of porous solids

Non-local Density Functional Theory

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

Ustinov&Do, 2004-06

Quenched Solid Density Functional Theory

- 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 in **2006**; QSDFT for carbons in **2007**)

Oral presentation 22: by Alex Neimark et al.

QSDFT vs. NLDFT: Nitrogen adsorption (77.4 K) on activated carbon fiber
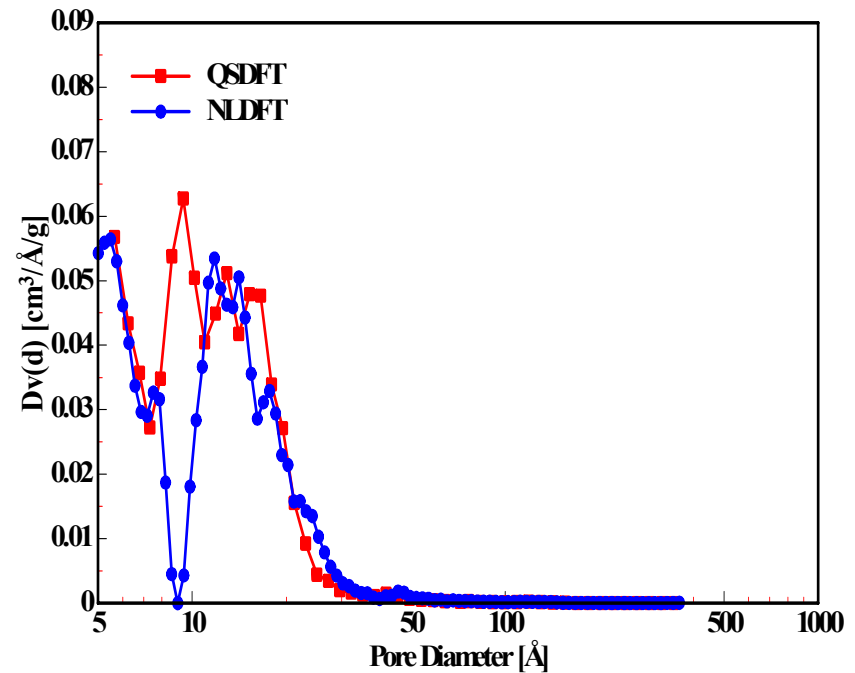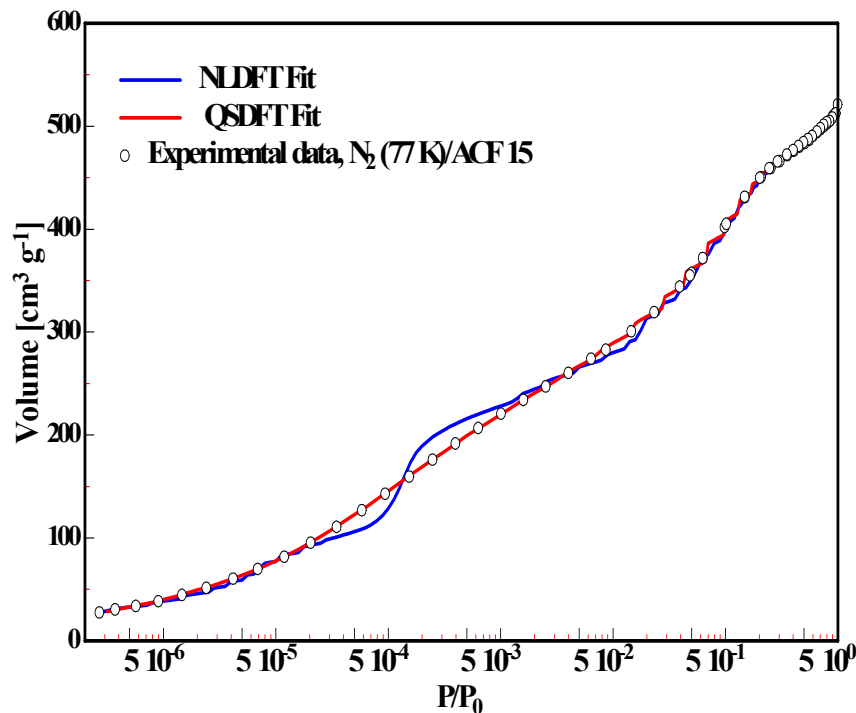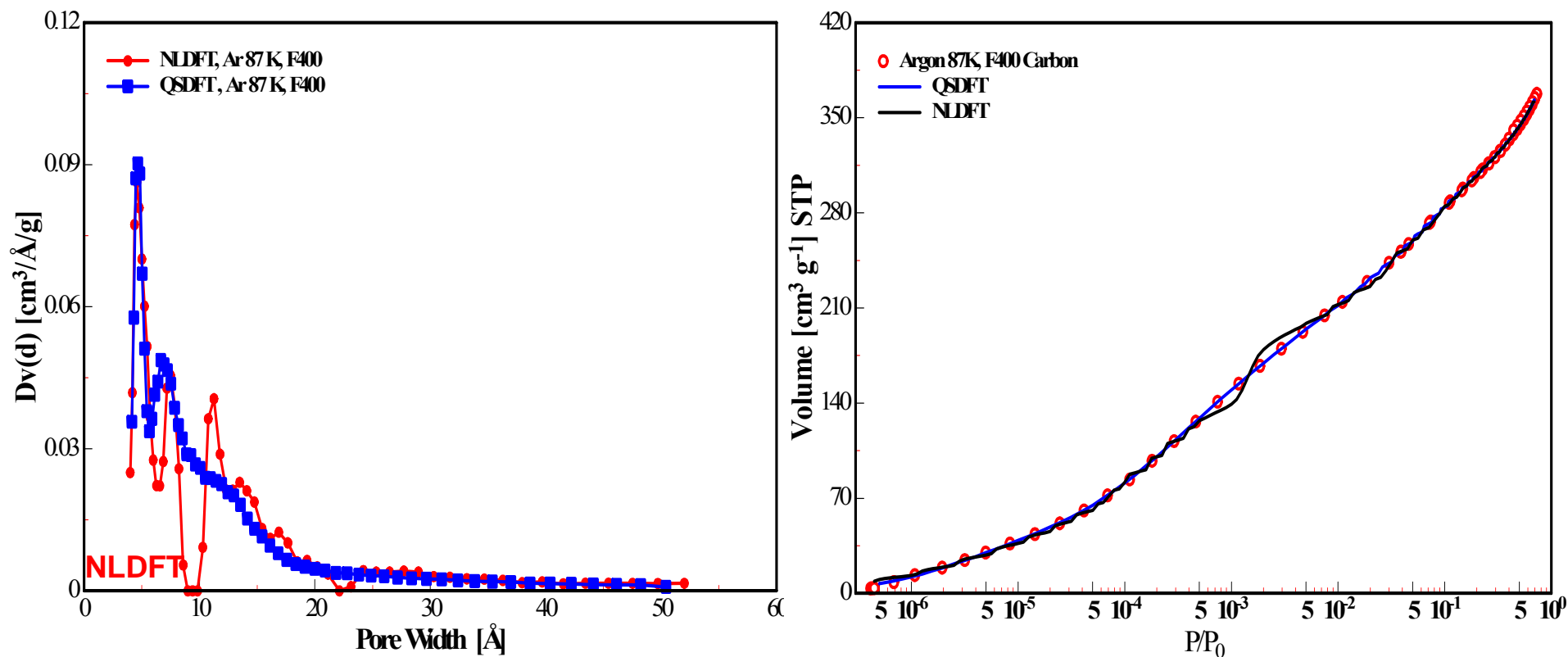

Activated carbon fiber ACF-15
(sample from Osaka Gas, Japan,).

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

⇒ *QSDFT provides a much more realistic approach for the pore size analysis of heterogeneous activated carbon!*
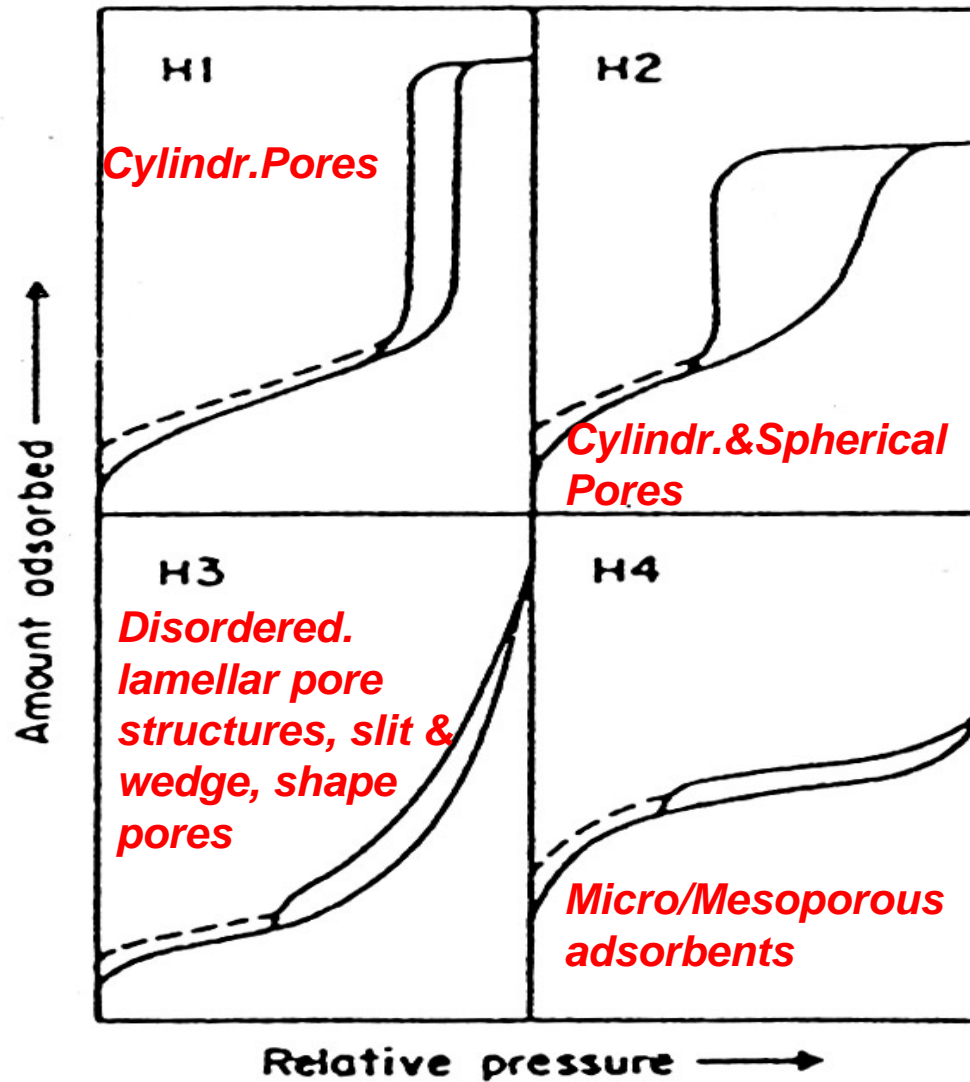
NLDFT and QSDFT Pore Size Analayis of F400 from Argon 87 K Adsorption

A.V Neimark, P.I Ravikovitch, Y. Lin, M. Thommes,

Carbon, in press (2009)

Pore Condensation and Hysteresis in ordered pore networks and hierarchically structured micro/mesoporous materials

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

Origin of Hysteresis

Single Pore Model:

Cylindrical/slit like pores:

  - Delayed condensation due to metastable pore fluid

  - Desorption Branch reflects equilibrium transition

$\Rightarrow$ *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

$\Rightarrow$ *H2,H3, H4 Hysteresis*

Hysteresis in Disordered Porous Materials :

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

$\Rightarrow$ *H2,H3, H4 Hysteresis*

Type H1 Hysteresis: Hysteresis due to "delayed" pore condensation
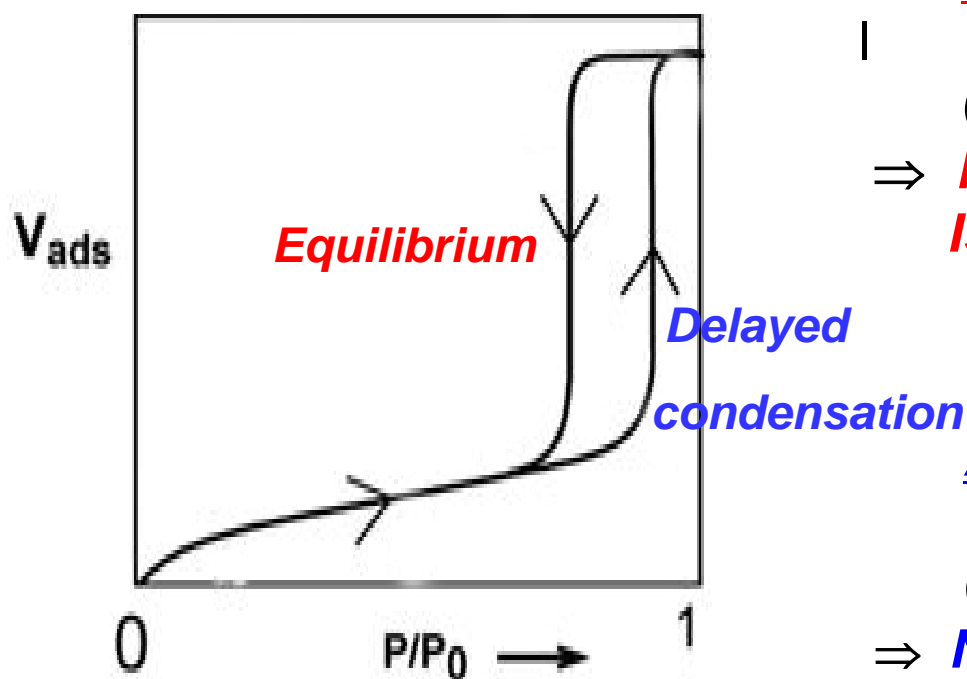

***Desorption Branch*:** Equilibrium liquid-gas phase transition (evaporation

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

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

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*)

H1 Hysteresis

Equilibr. Transition

Delayed condensation

Legend (right plot):
- Ads (NLDFT-spinodal condensation)
- Des (NLDFT- equilibrium transition)
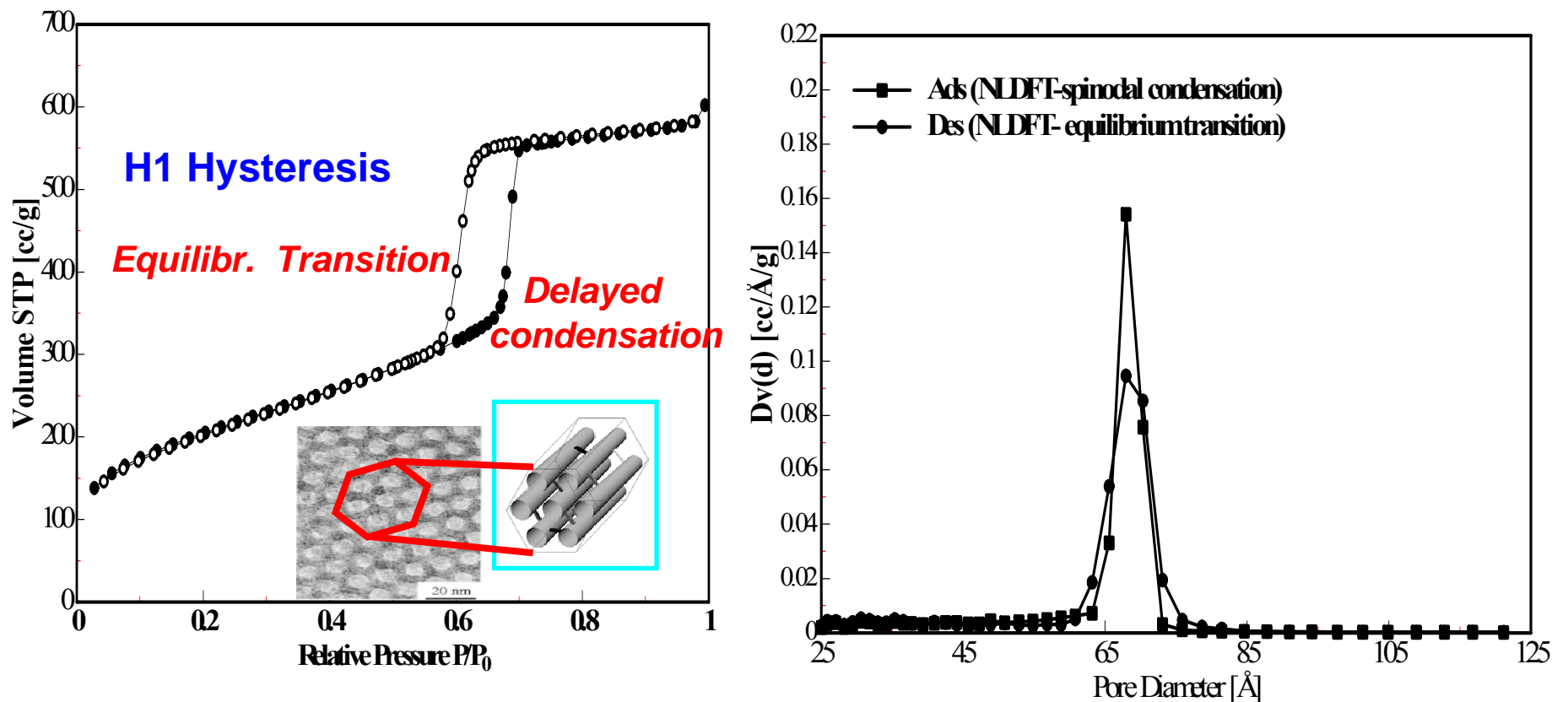
M. Thommes, In Nanoporous Materials- Science and Engineering" (edited by Max Lu and G. Zhao), Imperial College Press, Chapter 11 p. 317 - 364   (2004)

Two interrelated Open Questions:

(i) Is the adsorption, pore condensation and hysteresis behavior of fluids into pseudo-one dimensional systems comparable with the behavior in ordered three dimensional systems ?

(ii) To which extend can the single pore model (which is mostly used in pore size characterization) be used for the pore size analysis of ordered pore networks?
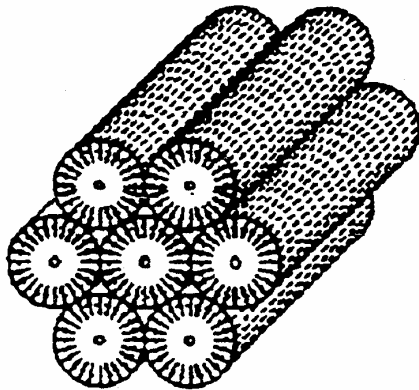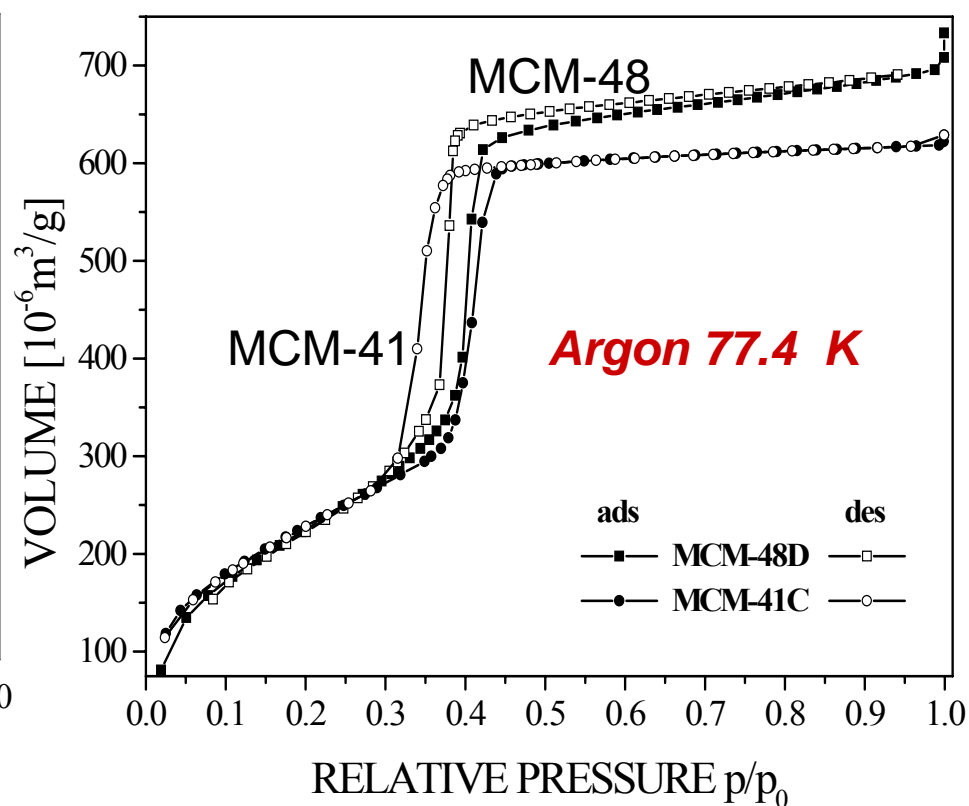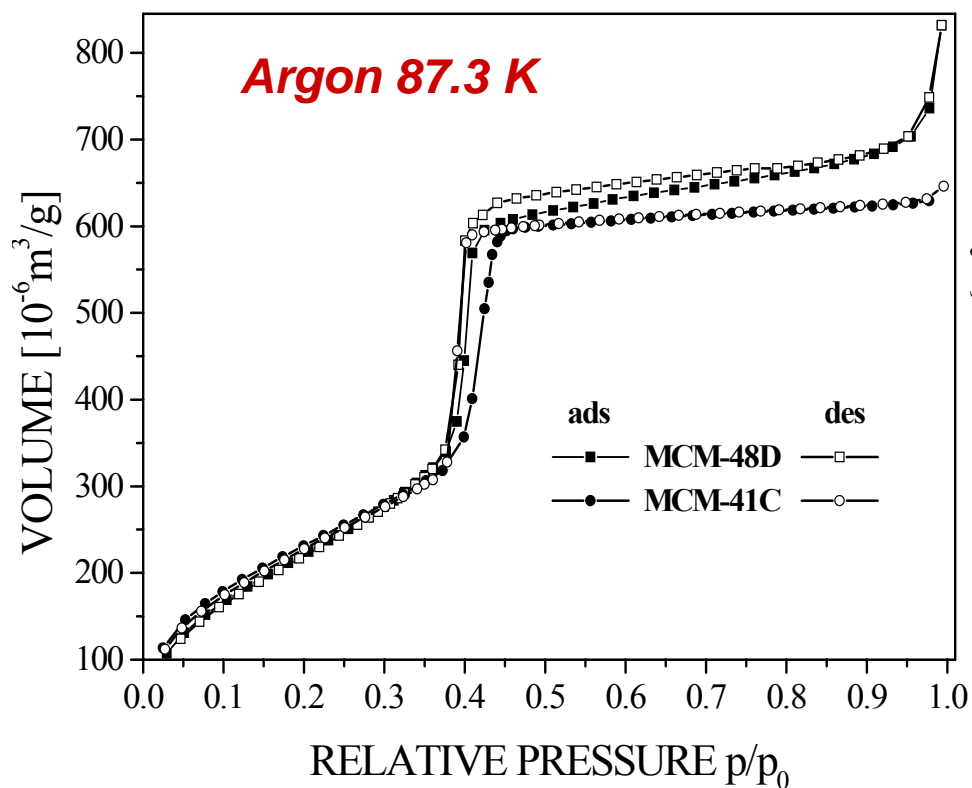

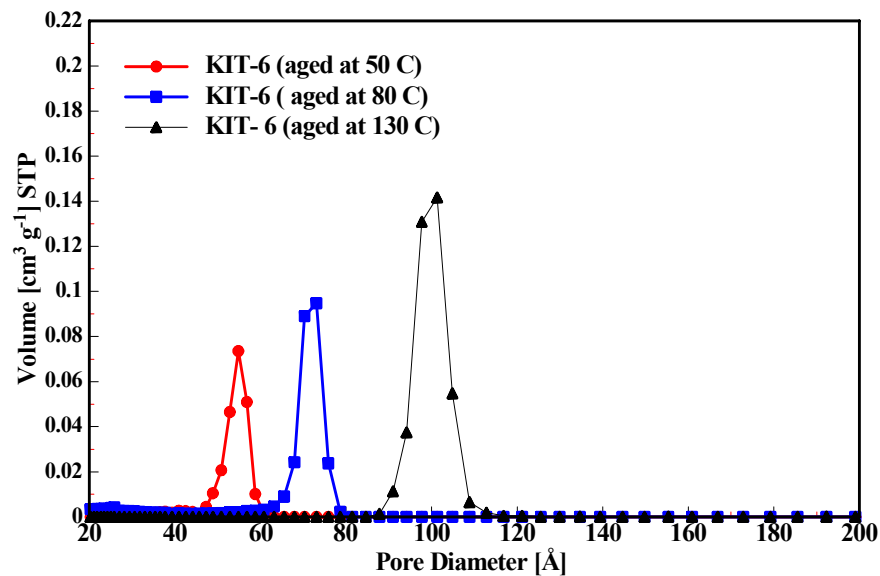**MCM-41, SBA-15**
Hexagonal, *p6mm*
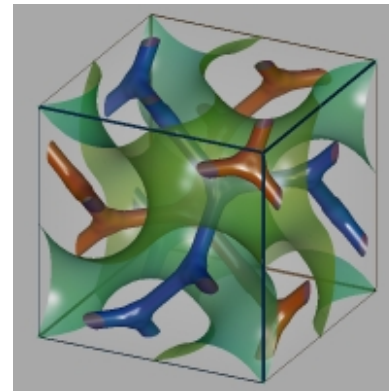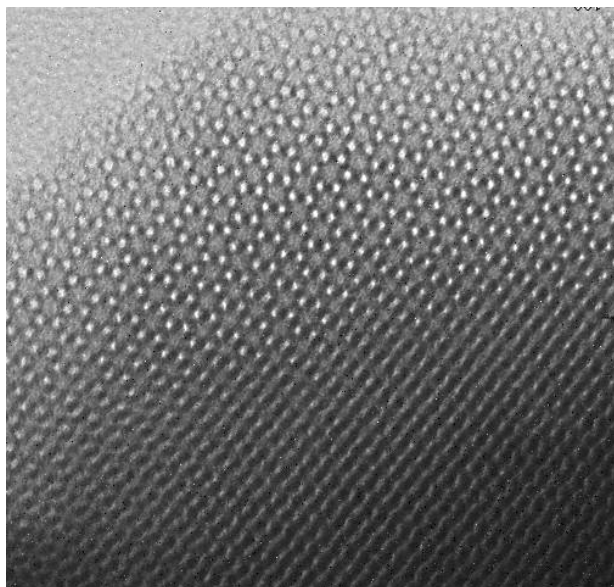

MCM-48, KIT-6
Cubic *Ia-3d*

Freddy Kleitz and M. Thommes, (2006 - 2008)

Comparison of Argon Adsorption Behavior in MCM-41 and MCM-48 Silica

M. Thommes, R. Koehn, M. Froeba, Stud. Surf. Sci. Catal. 142, 2002 1695
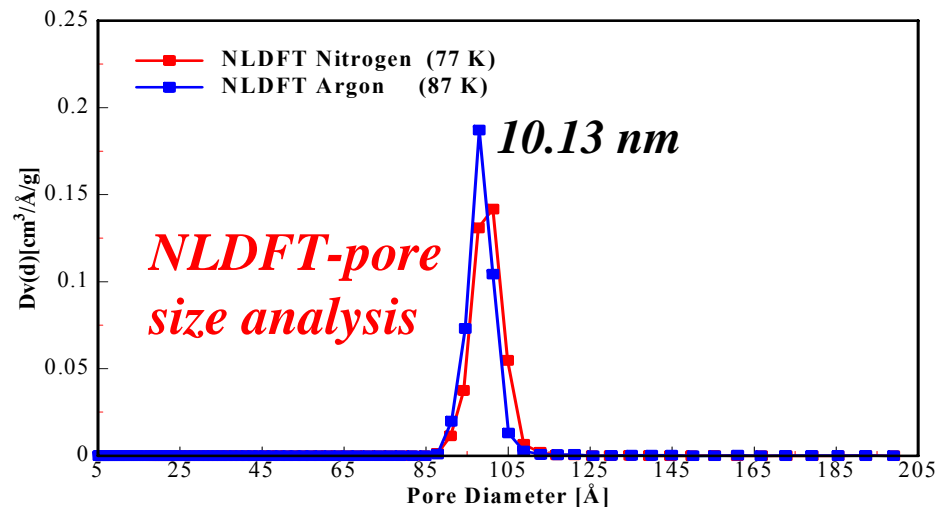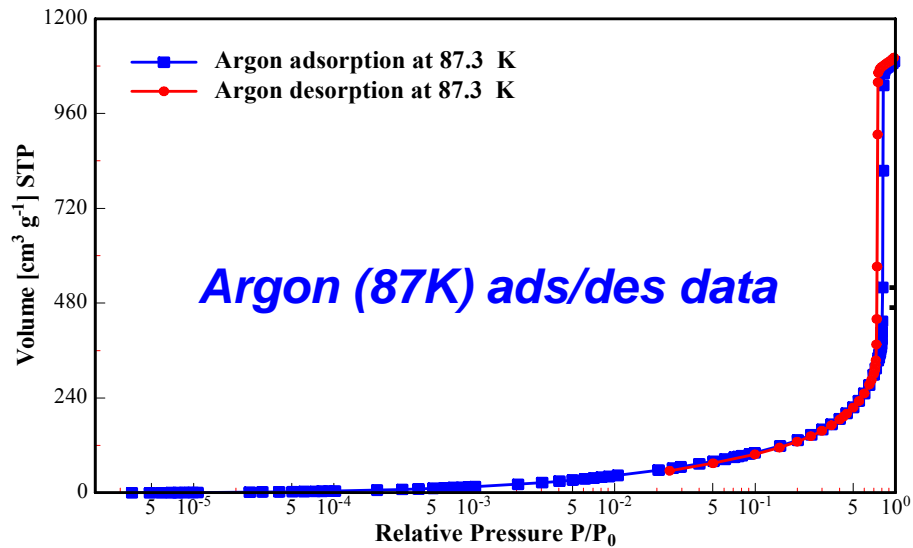
Large Pore Cubic *Ia*-3d Silica (KIT-6)
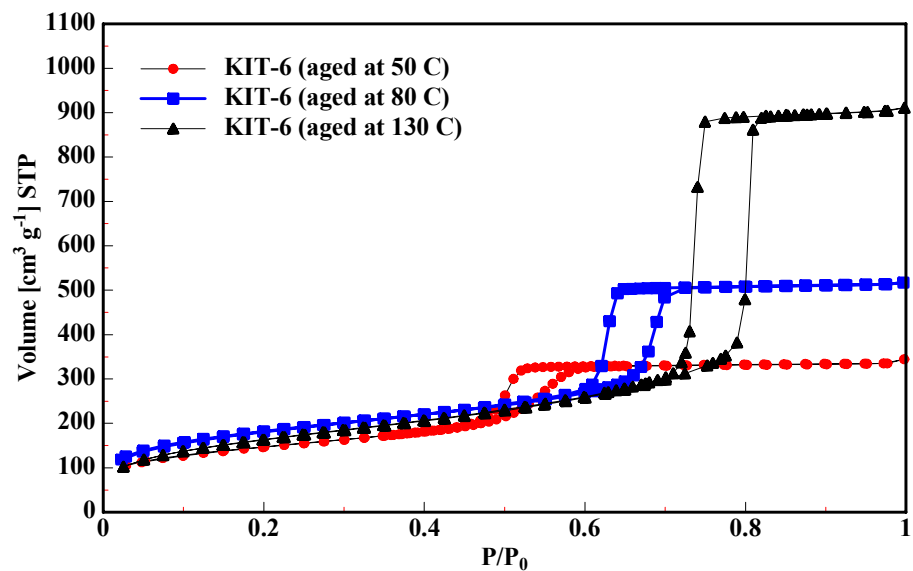
Cubic Ia-3d Phase by Transmission Electron Microscopy

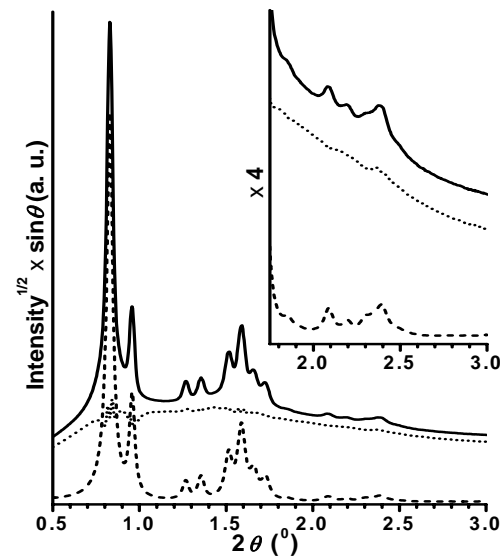**Details:** Kleitz, F., Choi, S. H., Ryoo, R.

Chem. Commun. 2003, 2136

Pore Size Evaluation of KIT-6 silica aged at 130 ° C

Argon (87K) ads/des data

Argon adsorption at 87.3 K
Argon desorption at 87.3 K

Volume [cm³ g⁻¹] STP

Relative Pressure P/P₀

NLDFT-pore size analysis

NLDFT Nitrogen (77 K)
NLDFT Argon (87 K)

10.13 nm

Dv(d)[cm³/Å/g]

Pore Diameter [Å]

XRD analysis (Solovyov J. Phys. Chem B 2005, 109, 3233)

Lattice Param.: a= 23.85nm

Intensity$^{1/2}$ x sinθ (a. u.)

x 4

2 θ (°)

Mesoporosity from N_2 and Ar ads.: 75.4%

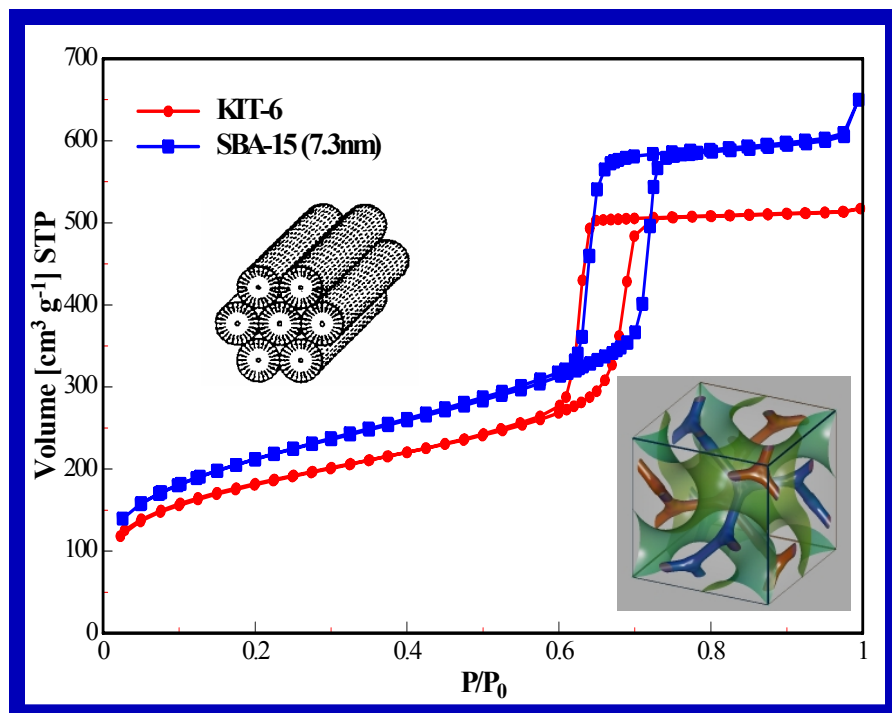$\Rightarrow$ Wall Thickness t= 1.9 nm

$\Rightarrow$ Cylindr. Pore segment diameter, d

$$d = a/2 - t = \textbf{10.025 nm}$$

Effect of Connectivity on pore condensation and hysteresis: Comparison of Nitrogen adsorption into SBA-15 (7.3 nm) and KIT-6 (aged at 80 C)

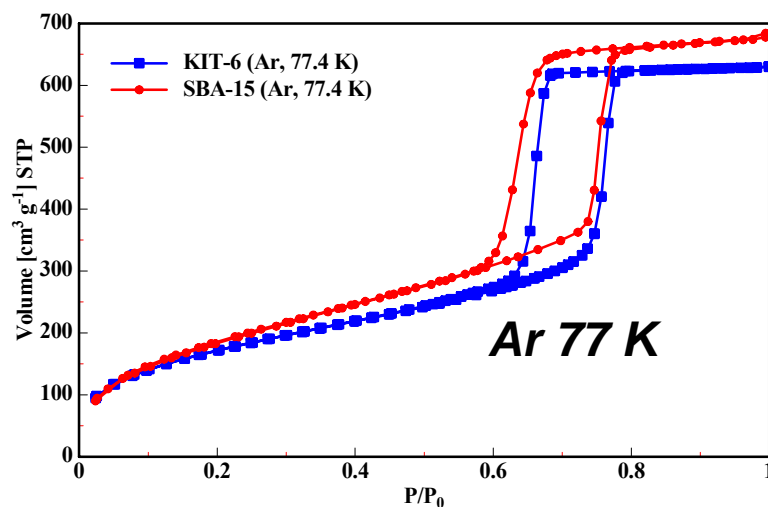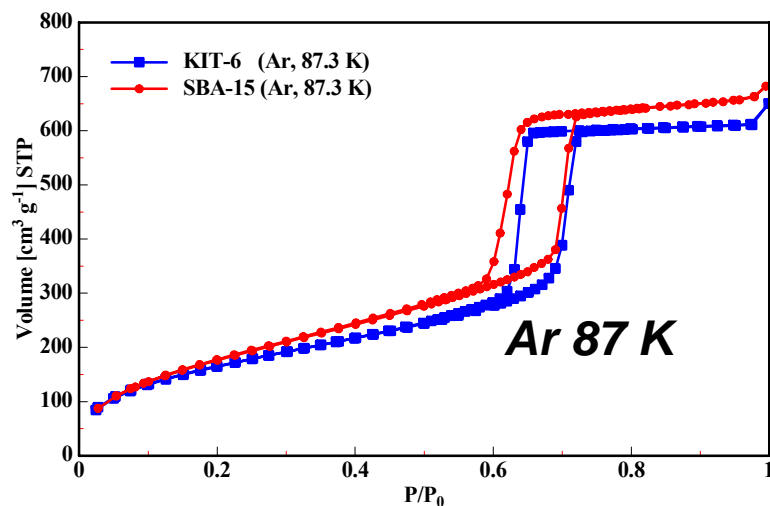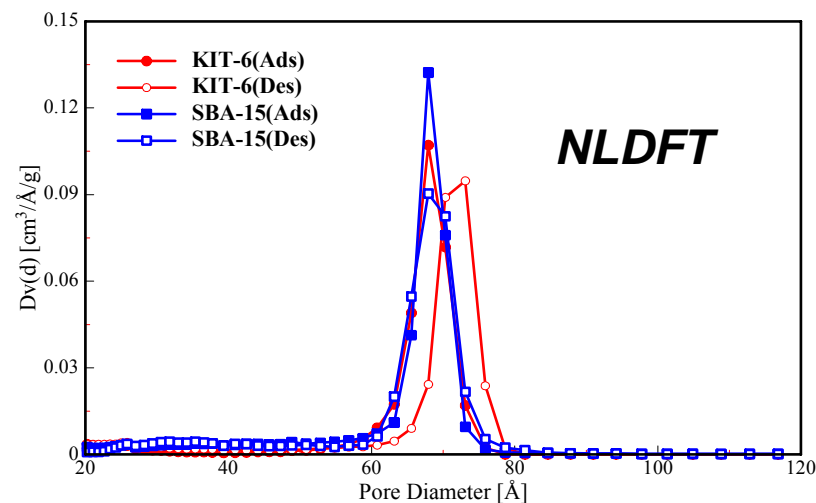**N_2 (77.4 K)**

**Pore size distribution from NLDFT**
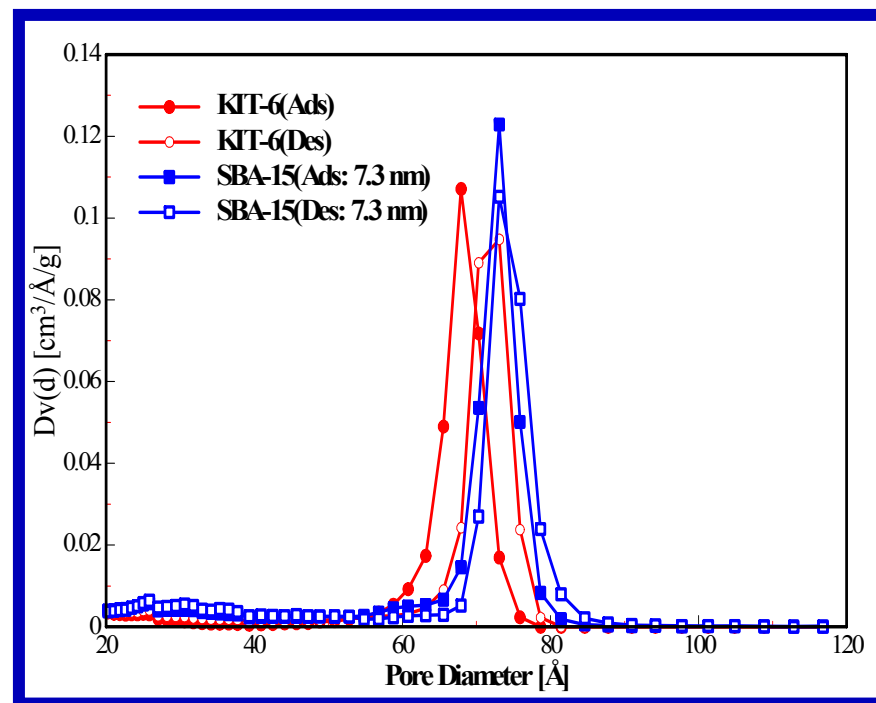
Connectivity in the 3D system(KIT-6) may help to reduce the nucleation barriers associated with capillary condensation

$\Rightarrow$ reduces the width of the hysteresis loop

Application of NLDFT equilibrium Trans. kernel on the desorpt. branch
Application of metastable adsorption branch kernel on the adsorption branch

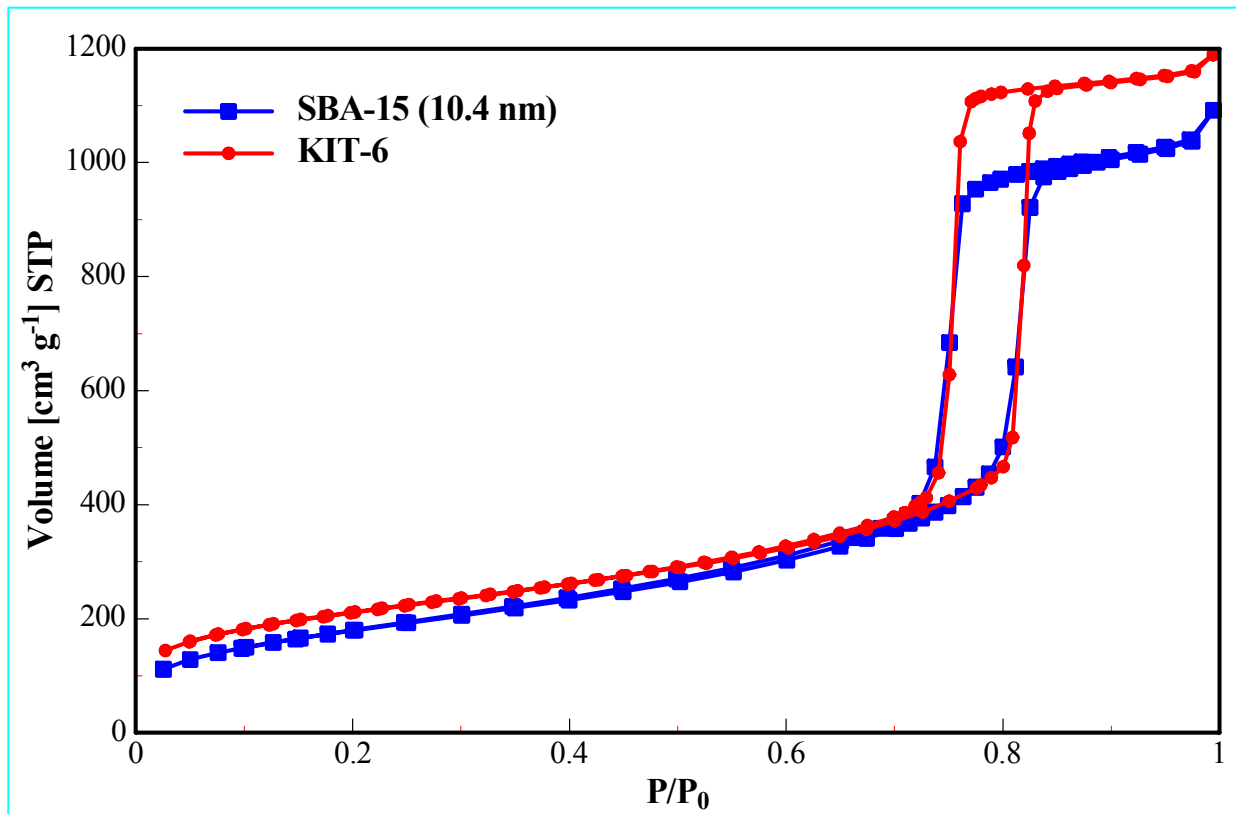**F. Kleitz, C.M-Yang , M. Thommes,** *Stud. Surf. Sci. & Cat., 170*, **1843,(2007)**

Pore condensation and hysteresis in pseudo-one-dimensional and three dimensional pore systems:
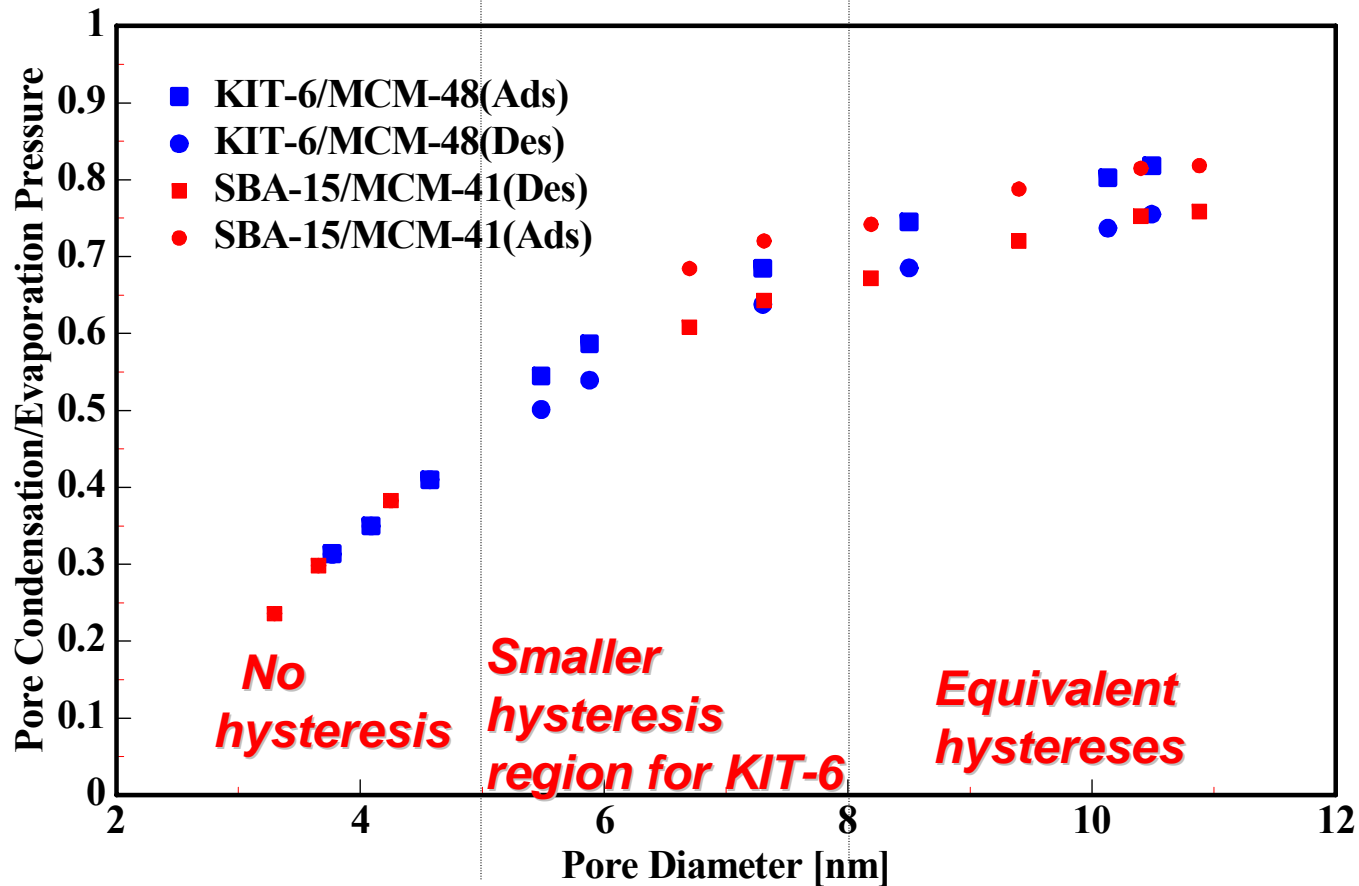## N_2 and Ar adsorption SBA-15 (6.7 nm) and KIT-6
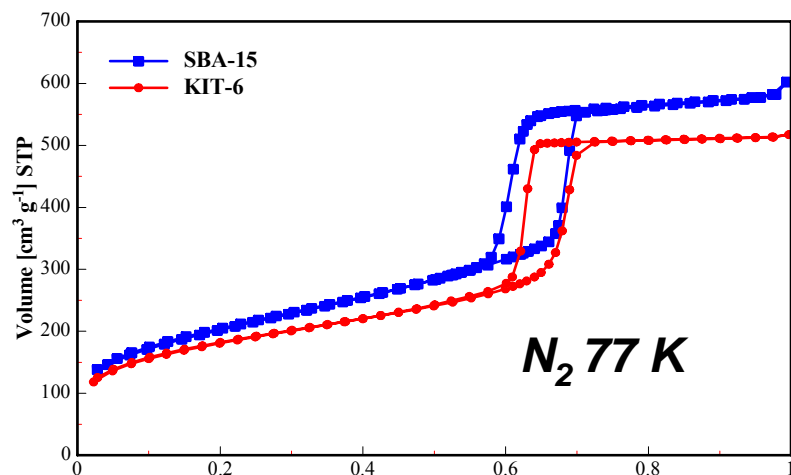
Comparison of Nitrogen adsorption into SBA-15 (7.9 nm, aged at 100 C) and KIT-6
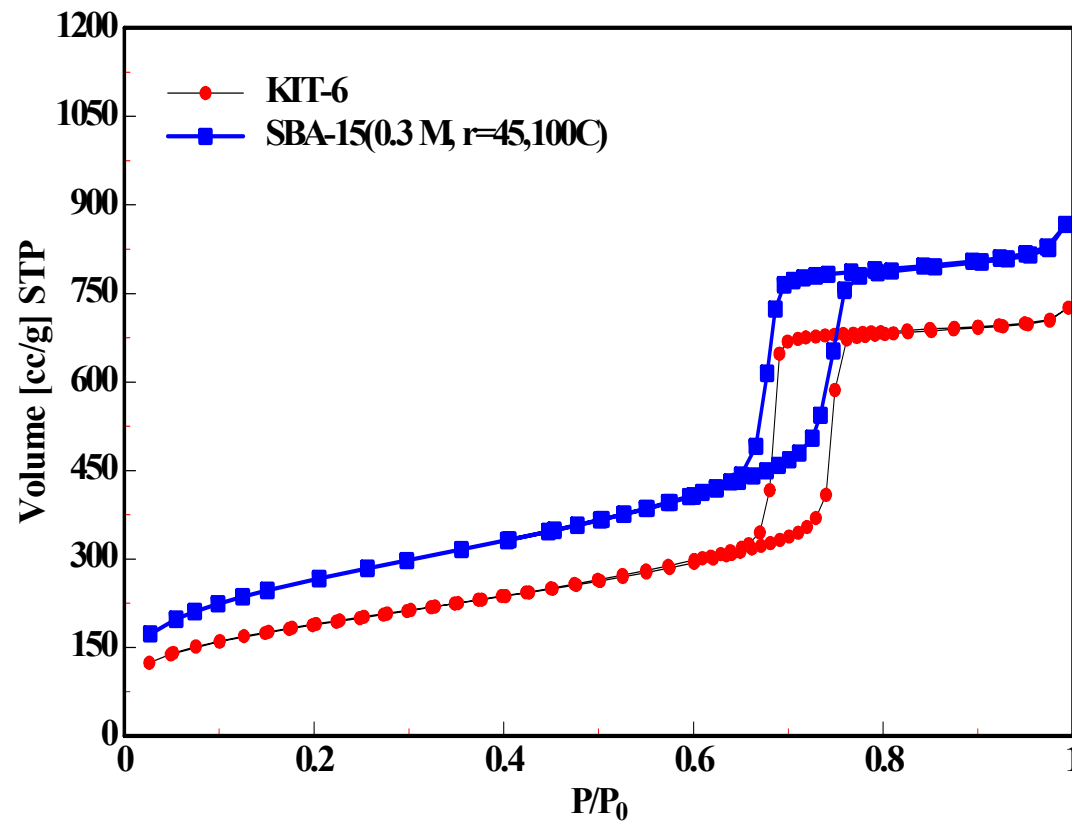
Nitrogen Adsorption (at 77.4 K) in SBA-15 (10.4 nm, aged at 130 C) and KIT-6
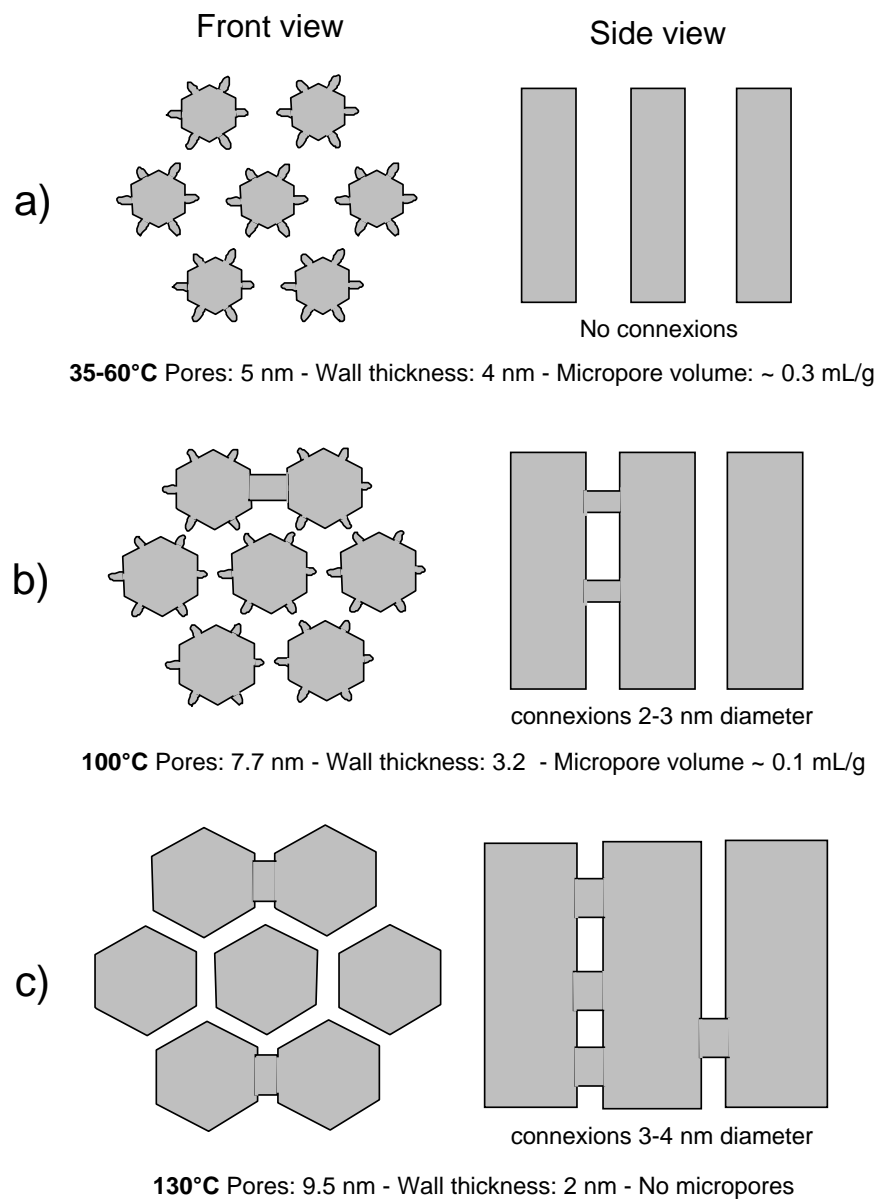
Pore Condensation/Evaporation of N_2 (77.4 K) in pseudo-one dimensional systems (MCM-41 and SBA-15) and three-dimensional systems (MCM-48 and KIT-6)
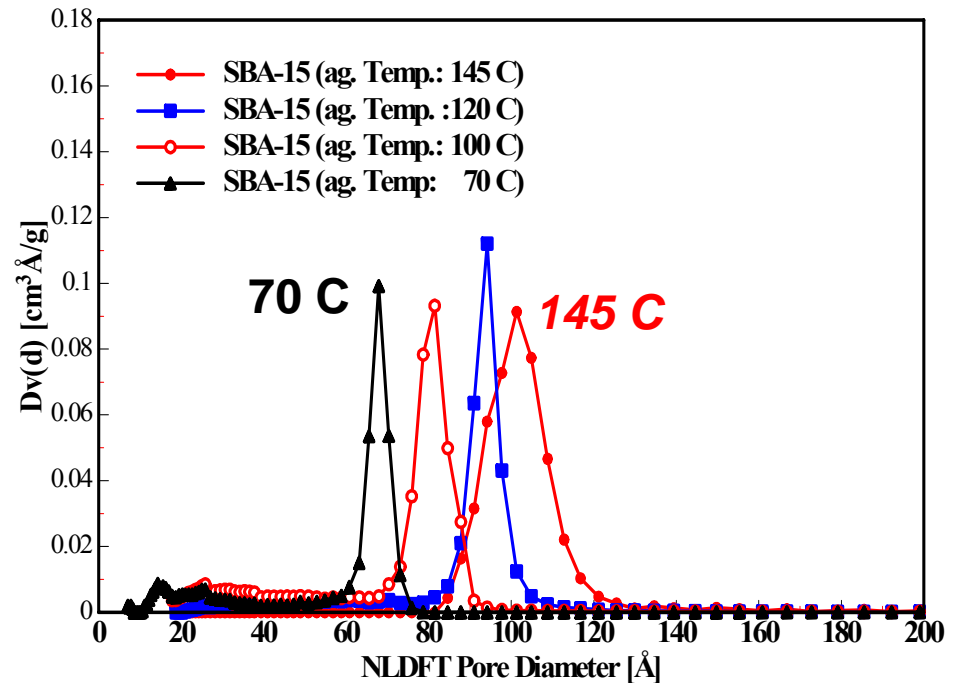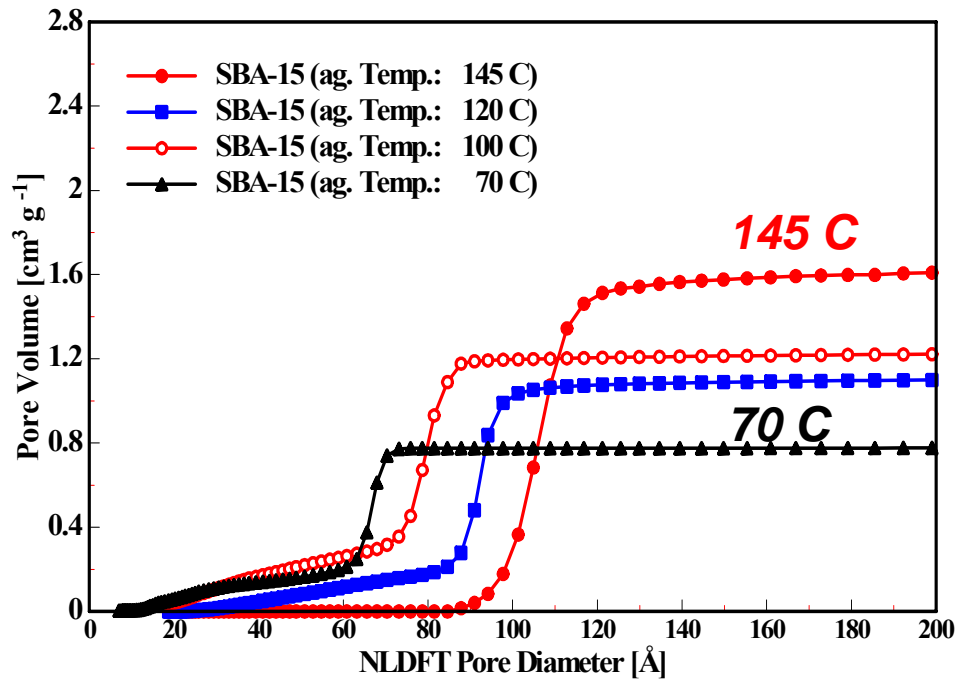

M. Thommes , F. Kleitz, 2008

SBA-15

Increase in connectivity and pore size
with increasing aging temperature

Front view   Side view

a)

No connexions

35-60°C Pores: 5 nm - Wall thickness: 4 nm - Micropore volume: ~ 0.3 mL/g

b)

connexions 2-3 nm diameter

100°C Pores: 7.7 nm - Wall thickness: 3.2 - Micropore volume ~ 0.1 mL/g

c)

connexions 3-4 nm diameter

130°C Pores: 9.5 nm - Wall thickness: 2 nm - No micropores
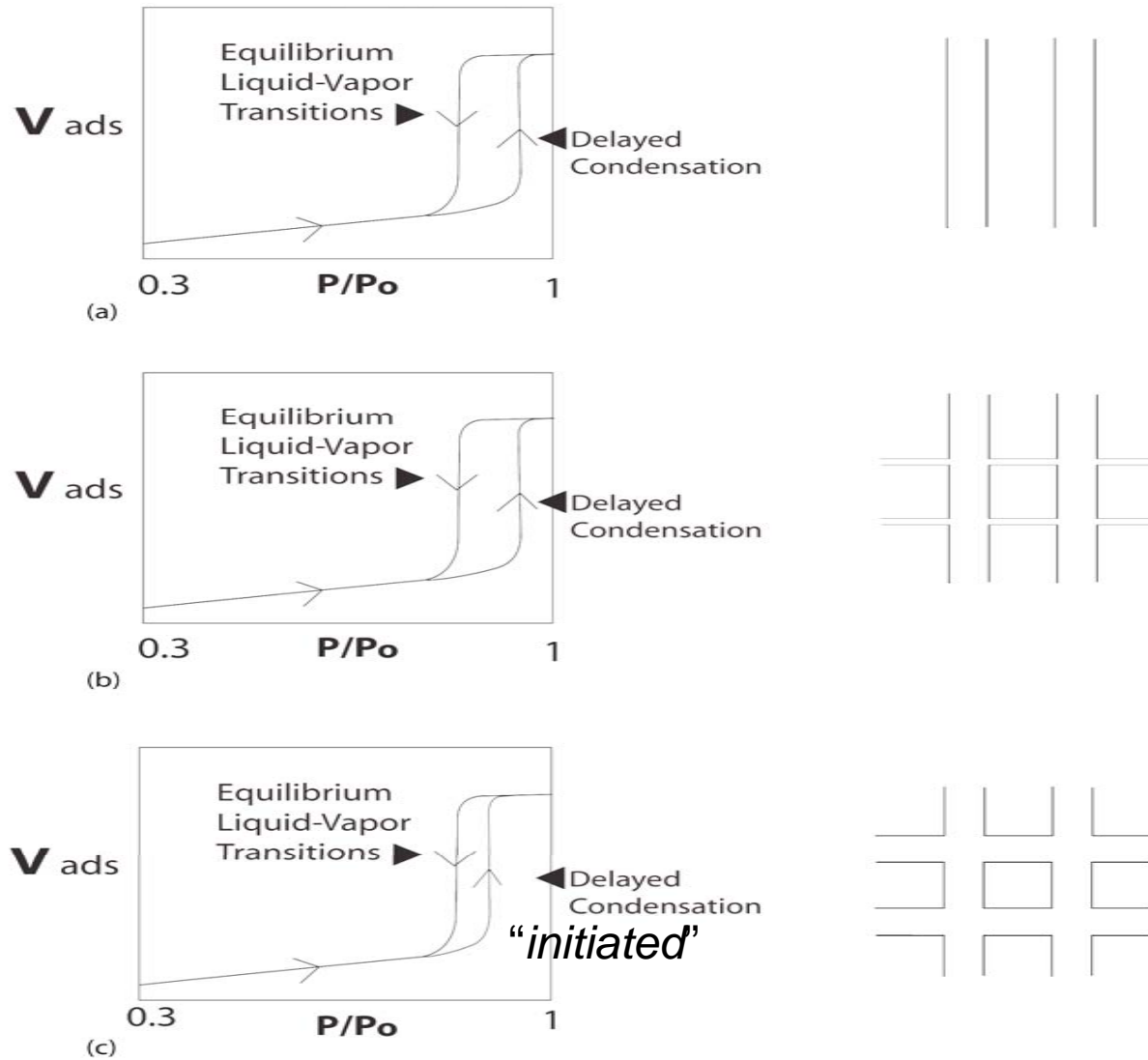
A.   Galarneau, H. Cambon, F. DiRenzo, R. Ryoo, M. Choi, F. Fajula,
New J. Chem. **2003**, *27*, 73.

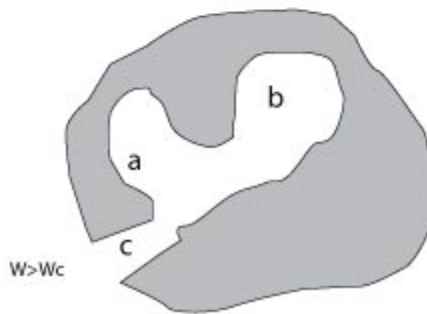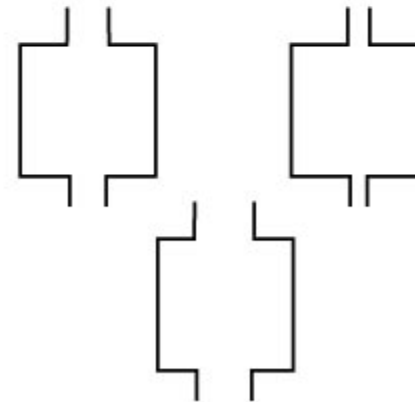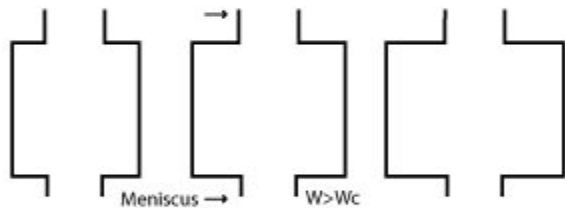# Effect of Aging Temperature on Pore Structure of SBA-15 Silica
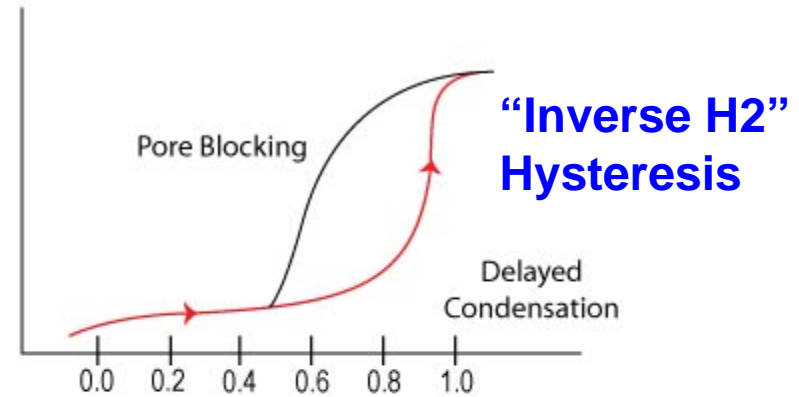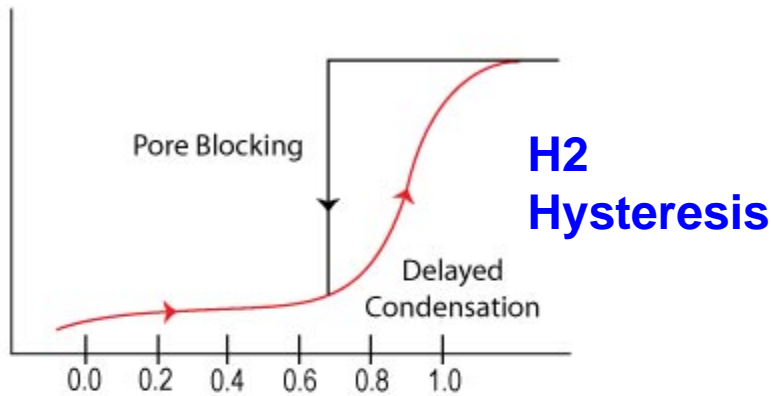

F. Kleitz, R Guillet-Nicolas, F, Berube, M. Thommes , 2008

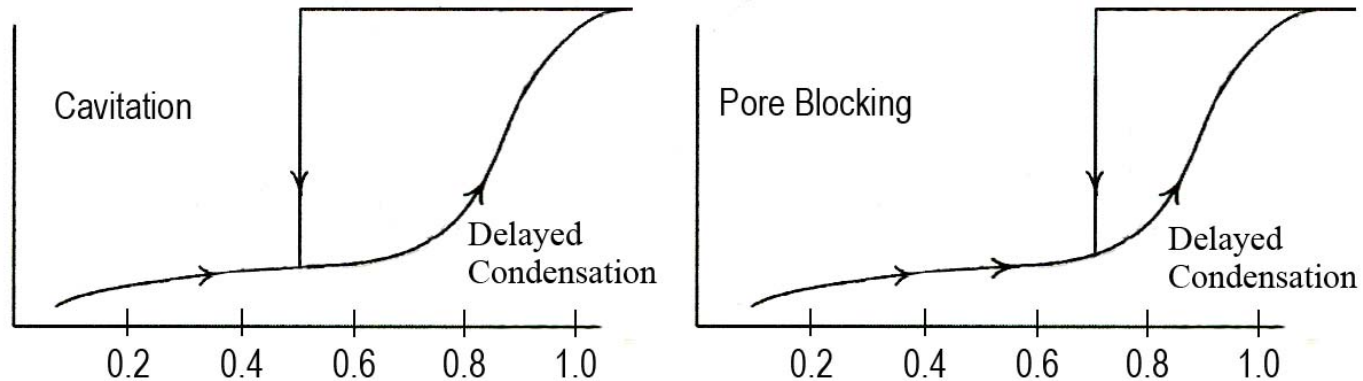# Pore condensation and hysteresis in single pores and ordered threedimensional systems (3D)
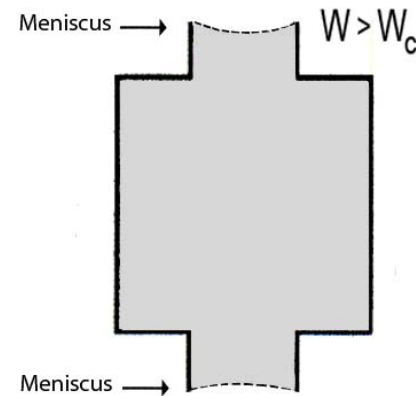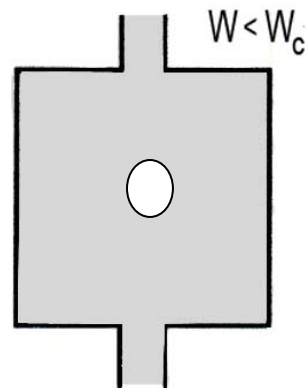
H2 Hysteresis: Pore Blocking /Percolation Phenomena

H2 Hysteresis

"Inverse H2" Hysteresis

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

Pore Blocking/Percolation and Cavitation Phenomena

Wc = critical "neck" diameter;

≈ 5 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. Thommes B. Smarsly, Langmuir 23, (2007) 4724

Pore fluid as van-der Waals fluid confined in ink-bottle pore

Pneck(evap) > Ppore_spin. ⇒ **Pore Blocking**

Pneck(evap) < Ppore_spin. ⇒ **Cavitation**

Materials with Hierarchical Pore Structures
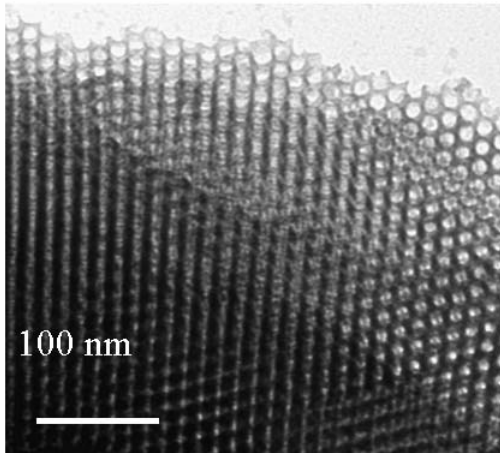
"**KLE**" silica
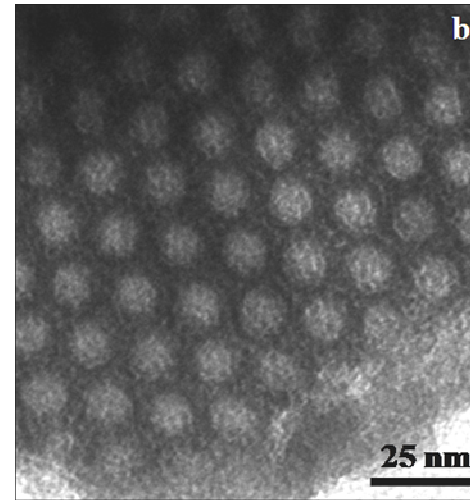
"**KLE**"/ IL silica

14 nm mesopores
1 nm micropores

14 nm mesopores
1 nm micropores
3 nm mesopores

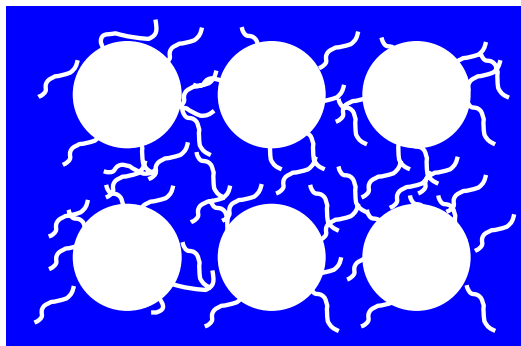**_Structure directing agent_**: *KLE-type amphiphilic block copolymer*

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

A.Thomas, H. Schladt, B. Smarsly et al., Langmuir _19_, (2003

O. Sel, D. Kuang, M. Thommes, B. Smarsly, Langmuir _22_, (2006) 2311

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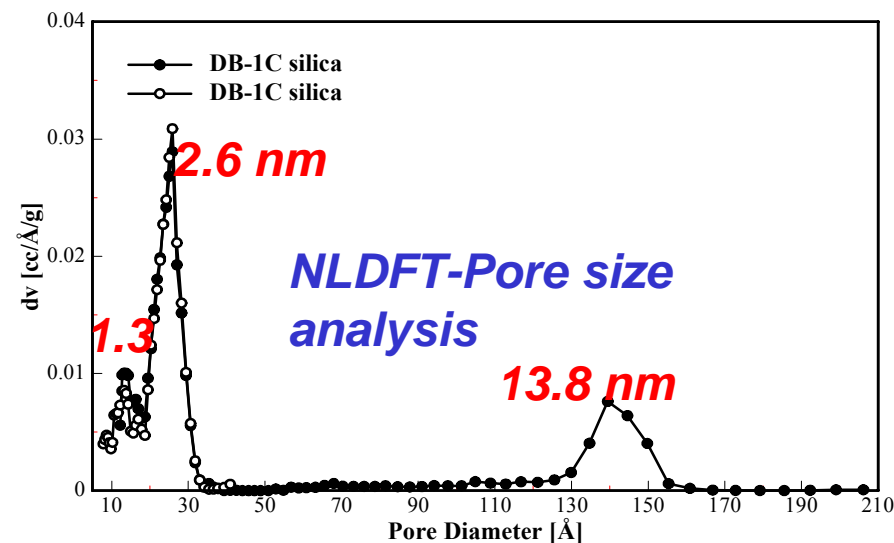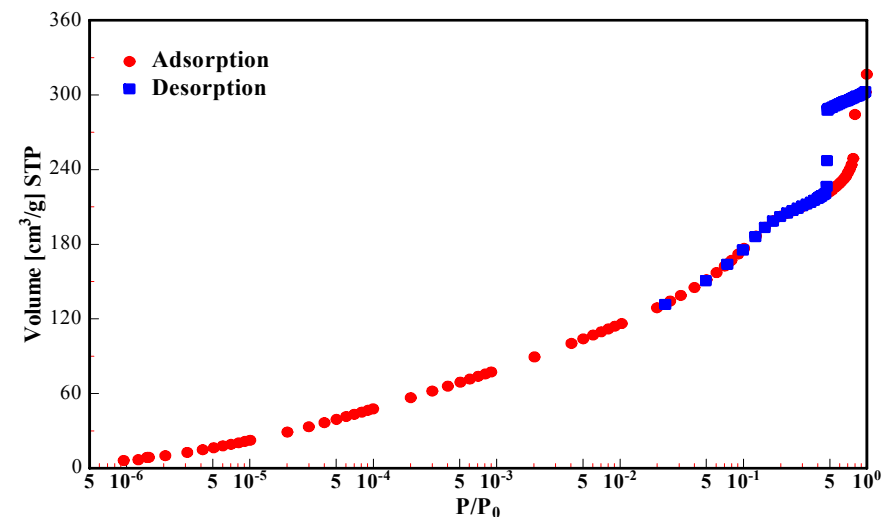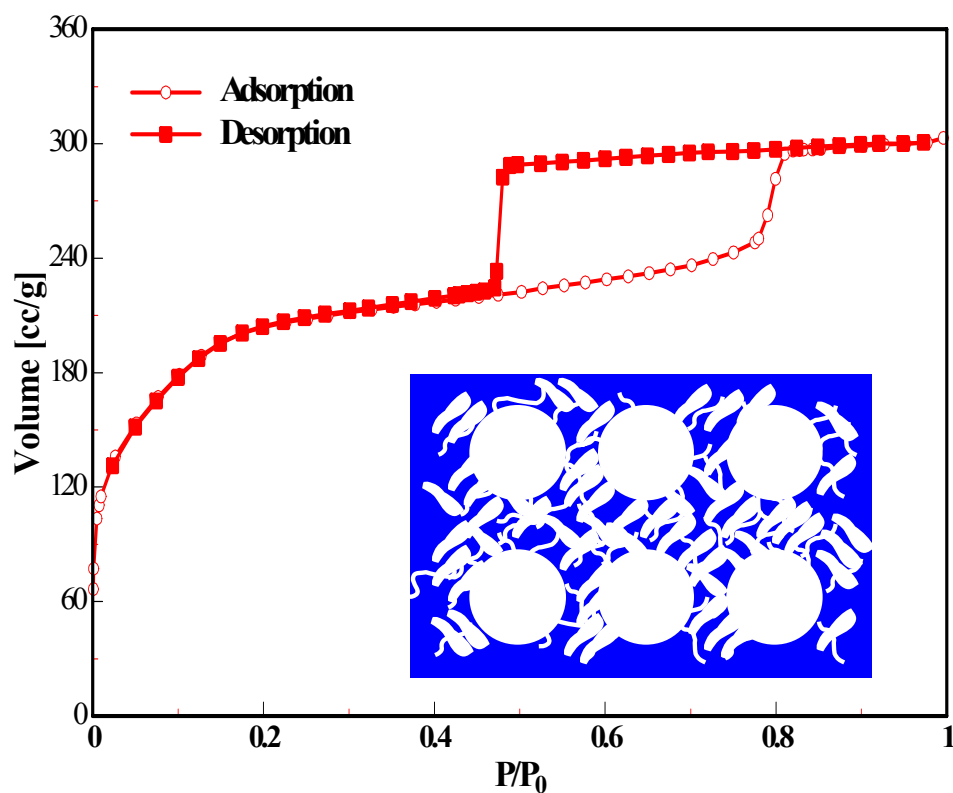
M. Thommes, B. Smarsly, M. Groenewolt, P.I Ravilkovich, A.V. Neimark, Langmuir 22,756 (2006)

Validation of Pore Structure/Texture for Hierarchically Structured silicas

- **Detailed SAXS analysis**
- **Gas adsorption**
- **TEM**

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

- **In-situ SANS**

O. Sel, A.Brandt, D. Wallacher, M. Thommes , B. Smarsly, Langmuir 23, 4724 (2007); D. Wallacher et al, manuscript in preparation (2008)

In-situ neutron scattering adsorption experiments on KLE/IL silica are being performed at the Hahn-Meitner Institut, Berlin(Dirk Wallacher et al)

(*1) Confirmation of texture:*
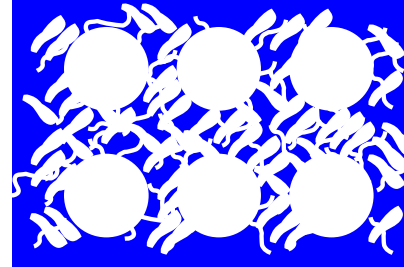
O. Sel, A.Brandt, D. Wallacher, M. Thommes , B. Smarsly, Langmuir 23, 4724 (2007)

(2) *Direct evidence for cavitation* (D. Wallacher et al, to

be published, 2009)
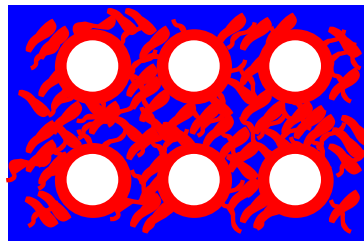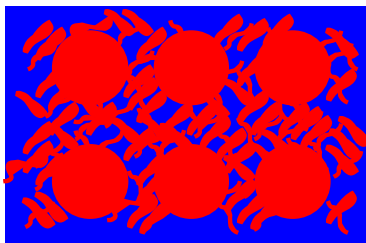
Principle of in-situ neutron scattering experiment

SANS – contrast matching of SiO_2 with N_2 at T = 77 K

$$I(q) \propto (\delta_{SiO_2/N_2} - \delta_{Pore})^2$$

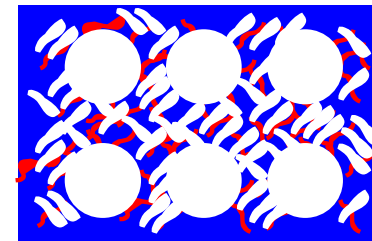*Scattering length density:* $\delta(SiO_2) \approx \delta(N_2)_{liq}$

$\Rightarrow$ **Filled pores do not contribute to the SANS pattern of the mesopore structure**

Pore filling from the point of view of neutrons

$p/p_0 = 0$ $0 < p/p_0 < 1$ $p/p_0 \approx 1$
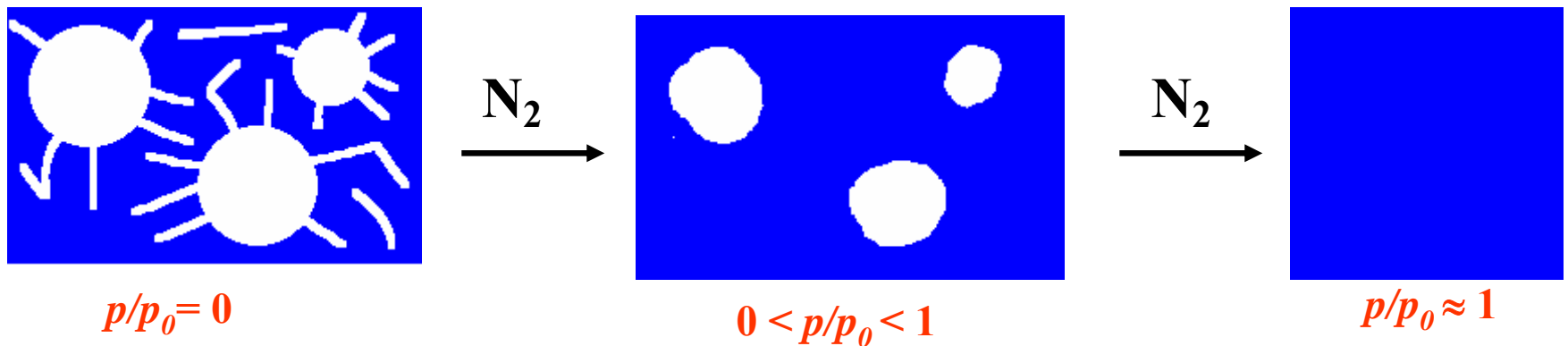
Coutesy: Dirk Wallcher, HMI Berlin

In-Situ Neutron (77K) Adsorption Measurements

- Filled pores do not contribute to the SANS pattern of the Mesopore Structure
- A fully hierarchical, interconnected pore architecture should show a measurable difference in SANS pattern compared to a system where a significant fraction of large mesopores is not being connected through smaller ones.
- A system with completely phase separated domains of pores of different sizes would show a steady decrease in SANS intensity as the relative pressure increases

$\Rightarrow$ ***In-situ sans allows to confirm the hierarchical pore structure as well as gives information about the mechanism of condensation/evaporation***

SANS Results (Adsorption)
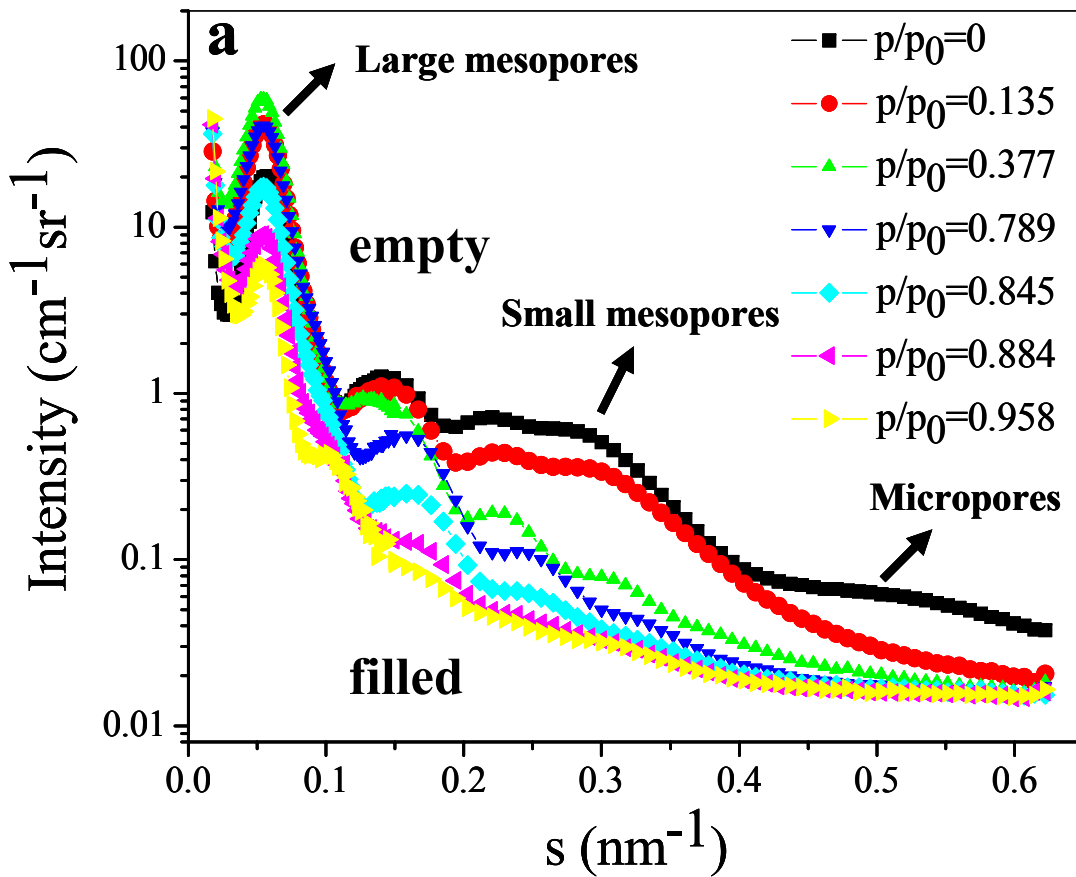
$$s = q/2\pi = 2/\lambda \sin(\theta)$$
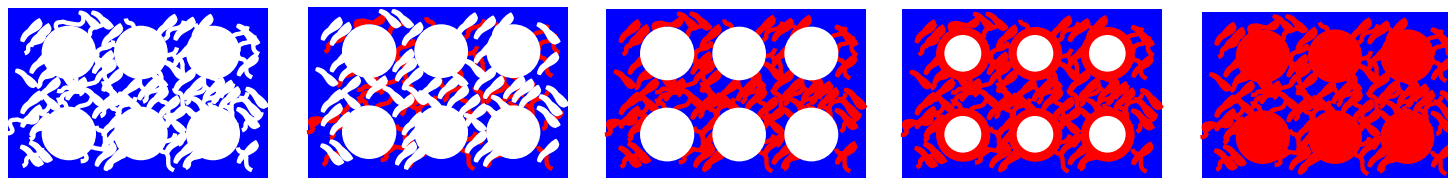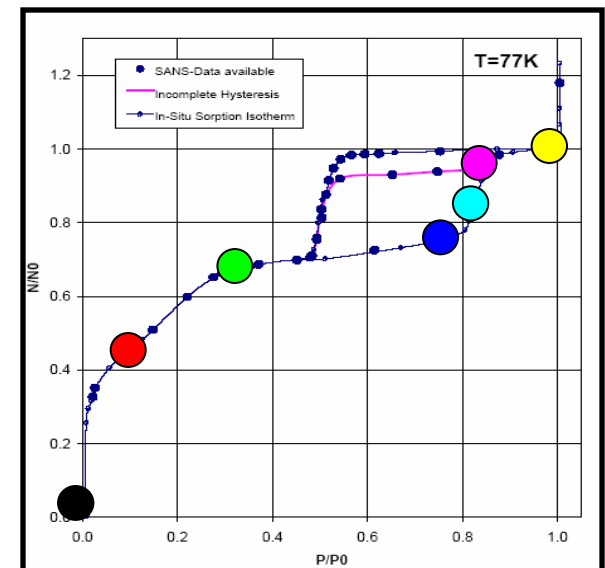
Semi-quantitative evaluation of in-situ SANS data

$$k = \frac{I_{KLE1C16,\,evacuated}(s)}{I_{KLE1C16,\,filled\,IL}(s)}$$

b

$I_{KLE1C16,\,filled\,IL}$

$I_{KLE1C16,\,evacuated}$

I (s)

s (nm^{-1})
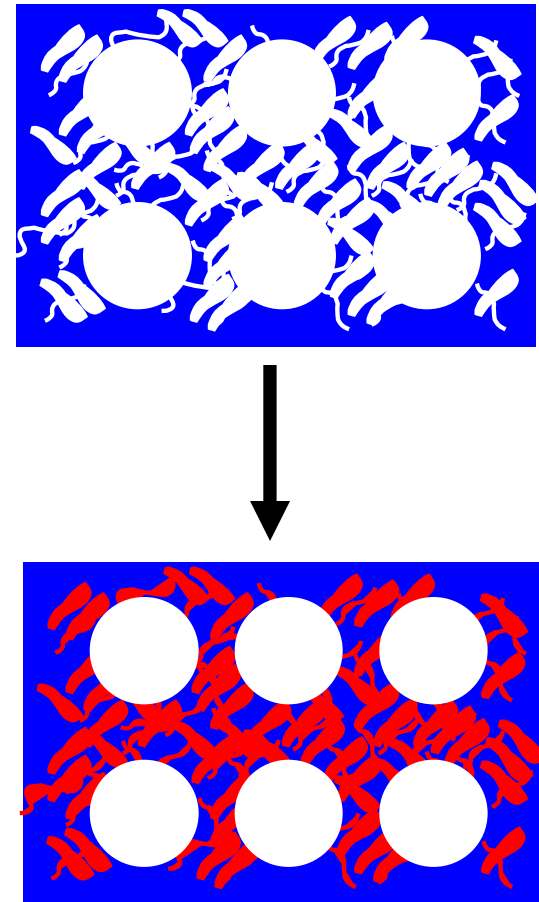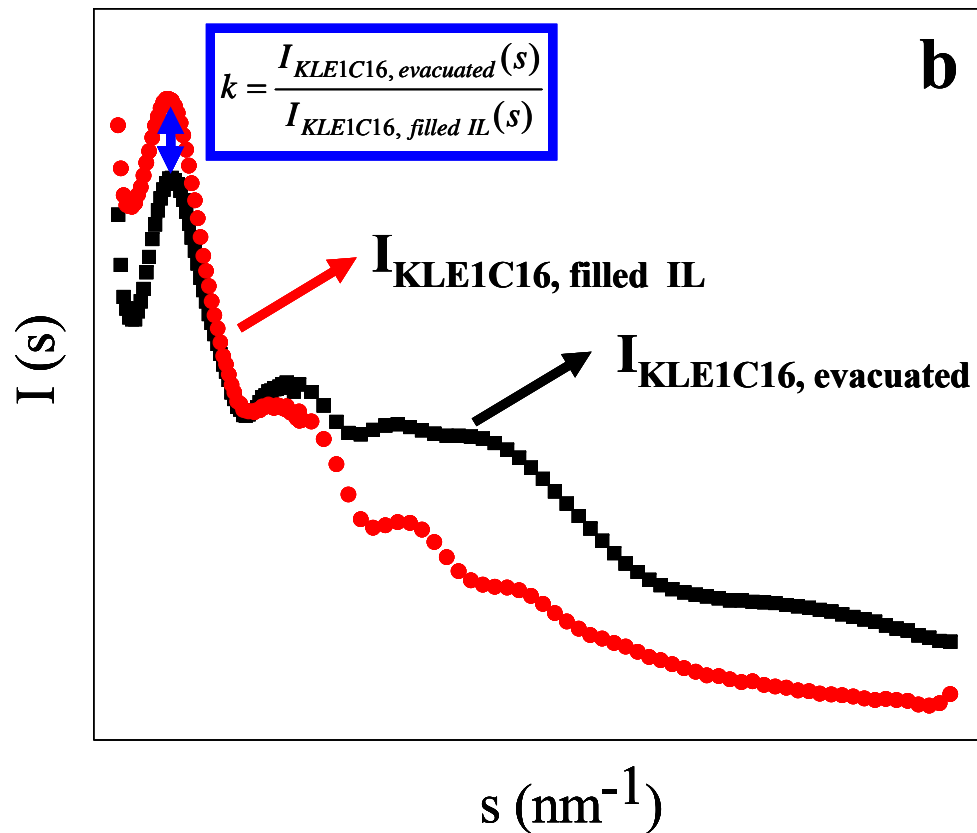
Increase of SANS intensity at small pressures during filling of small mesopores
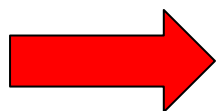
Calculated pore fraction (d < 3 nm) $\quad \phi_{small\,mesopores} = 0.4\,(0.36)$

How to differentiate between pore blocking/percolation and cavitation induced evaporation ?

Gas Adsorption:

(1)   Adsorption measurements with different adsorptives (e.g. argon, nitrogen) and comparison of pore size information obtained from desorption branch (*Thommes et al,* Langmuir 22,756 (2006)*)

(2)   Adsorption measurements with a given adsorptive at different temperatures (*Ravikovitch and Neimark* (2002), *Morishige* (2006))

(3)   Measurement of desorption scanning curves (within the hysteresis loop) provides additional information

Neutron Scattering:

Direct visualization of desorption mechanism by In-Situ Neutron scattering experiments (*D. Wallacher et al, HMI, Berlin*)

Pore Blocking/Percolation and Cavitation

Pore Blocking/Percolation:

"*Pore size" distribution determined from desorption branch should be independent of the choice of the adsorptive or temperature*

Cavitation :

Artificial "Pore" size distribution determined from desorption branch of hysteresis loop should depend on the choice of the adsorptive and temperature

Poreblocking/Percolation as dominant evaporation mechanism: Nitrogen and argon sorption in vycor

Nitrogen 77 K
Argon 87 K
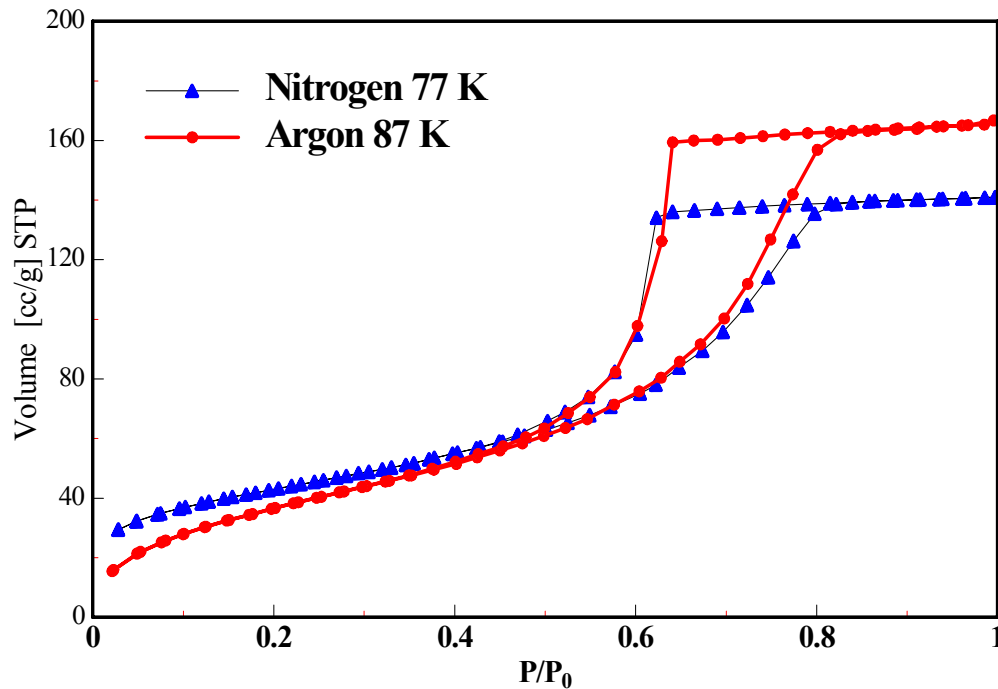
Size of pore constrictions (e.g, "neck" of ink-bottle pores) controls evaporation of pore liquid, i.e. determines the position of desorption branch

Nitrogen /77 K- NLDFT(Adsorption-Branch-Kernel)
Argon/87 K -   NLDFT (Adsorption-Branch-Kernel)

Analysis of N_2 and Ar adsorp. branches → "Pore Size"

Nitrogen/77 K NLDFT (Desorption-Branch Kernel)
Argon/87 K NLDFT- (Desorption -Branch-Kernel)

Analysis of N_2 and Ar desorp. branches → "Neck Size"
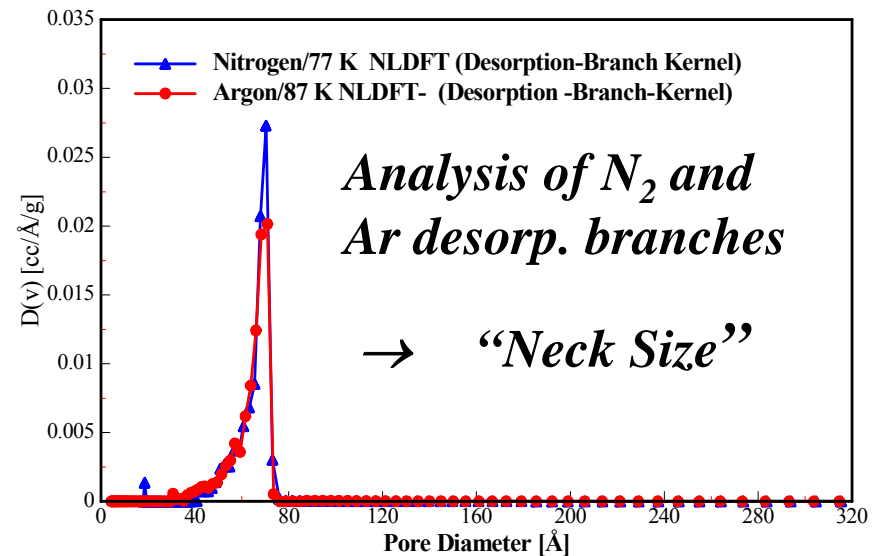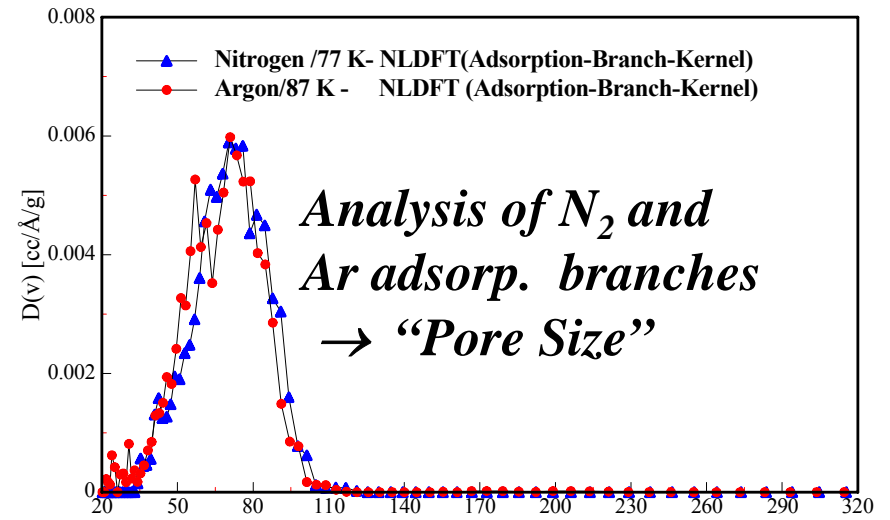
Cavitation as dominant mechanism for pore evaporation:
N_2 and Ar sorption in SE3030 micro/mesoporous silica
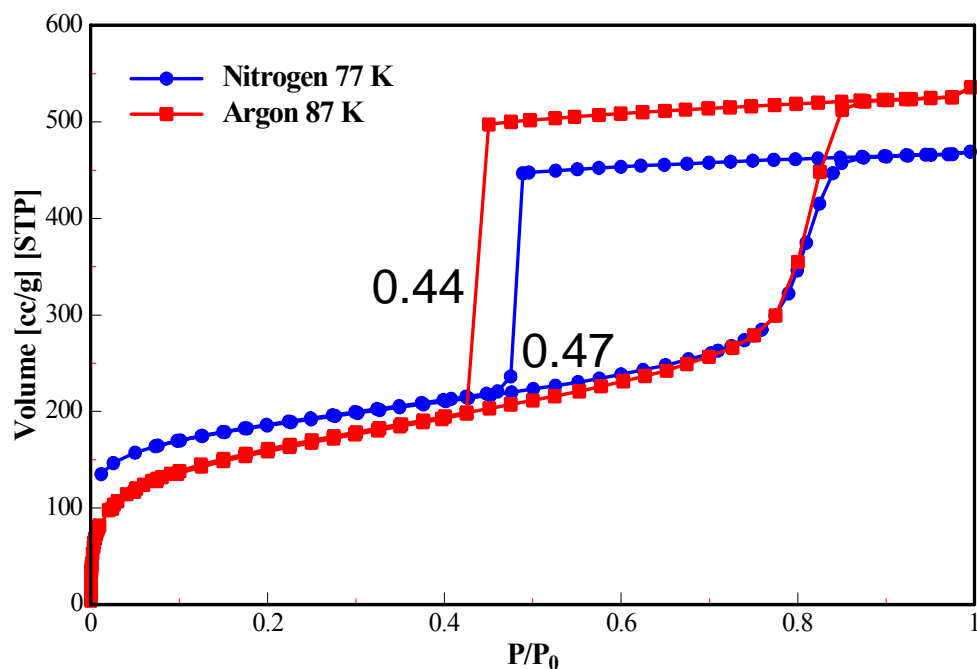
Disagreement between Ar-and N_2 "pseudo" desorption PSD's due to Cavitation transition

$\rightarrow$ *position of cavitation transition depends on properties of confined fluid and not on neck/pore size*
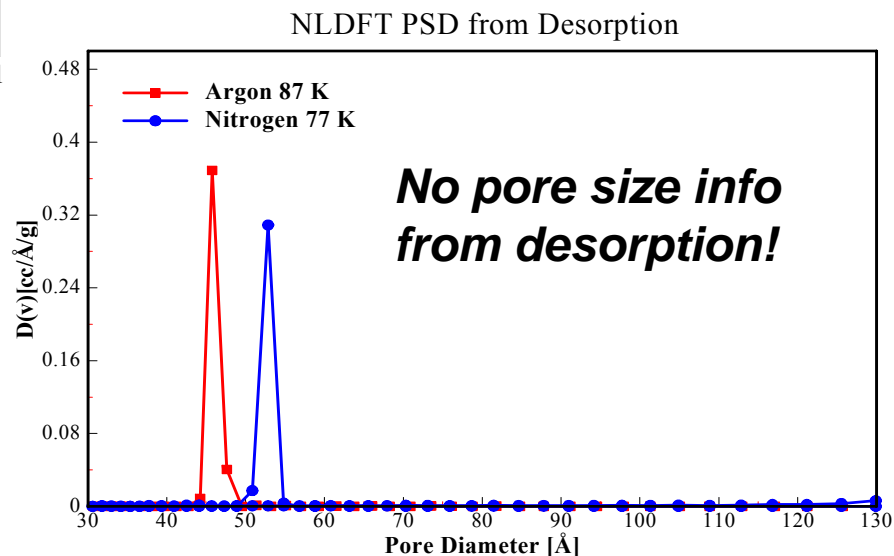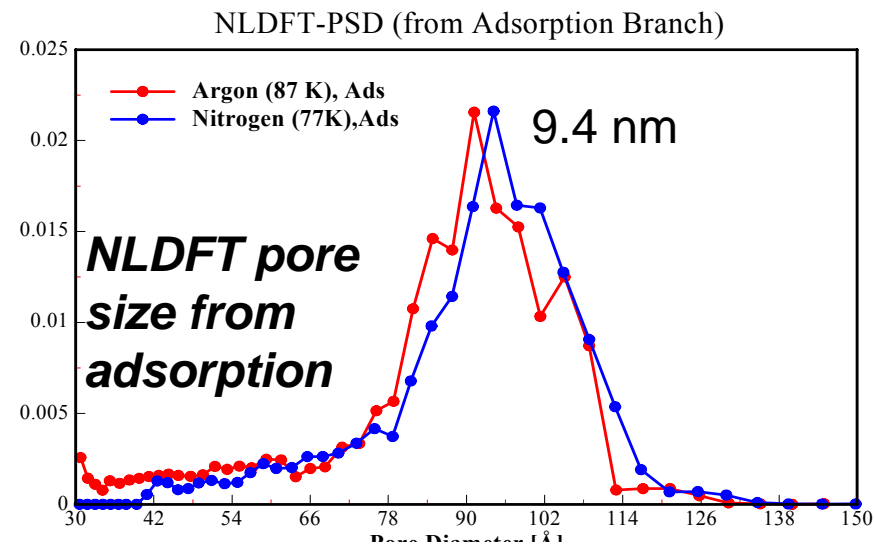
Cavitation in micro-mesoporous materials
and importance for pore structure characterization

H4-Hysteresis: Argon adsorption at 87.3 K in a AL-PILC (AL-P500)
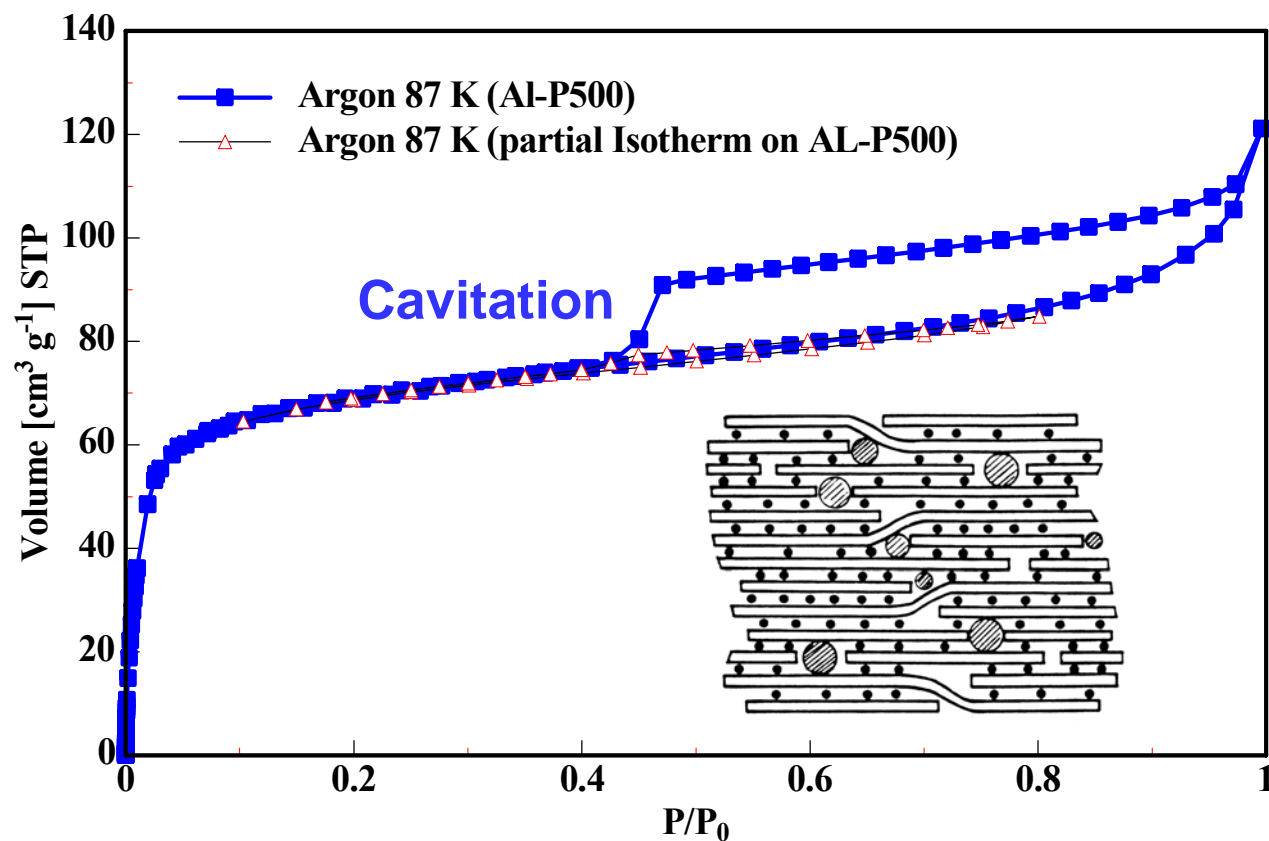
- *Cavitation induced evaporation appears to be important for many micro/mesoporous solids and is responsible for the often observed step down in adsorpton isotherm at rel. 0.4 (i.e. for nitrgoen adsorption at 77.4*

H3 Hysteresis:–Tensile Strength Effect – Cavitation induced Evaporation/Desorption
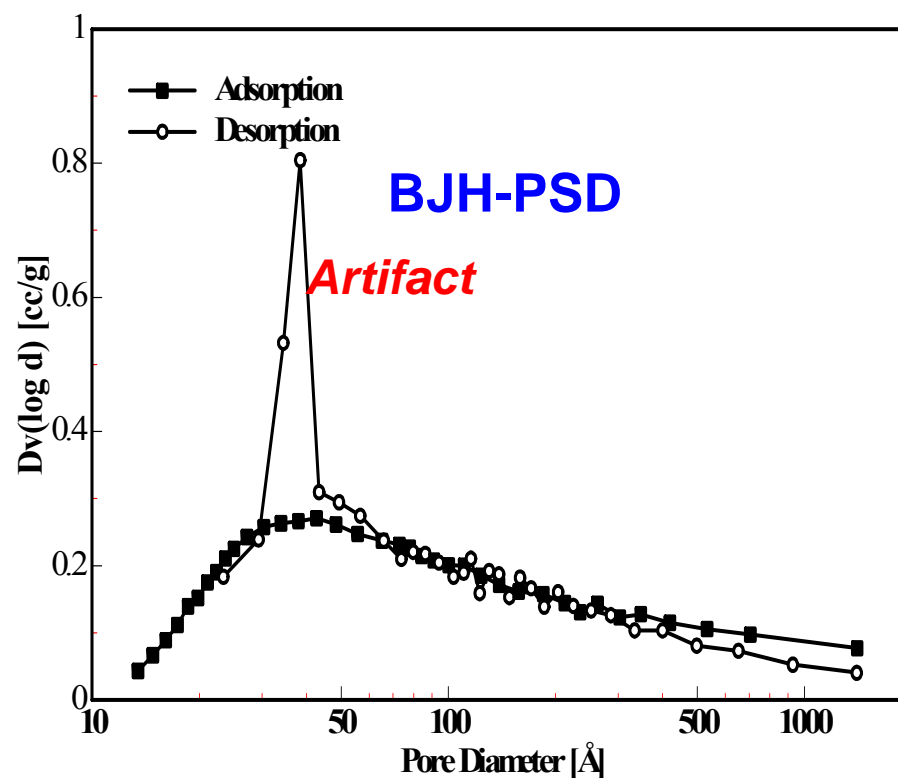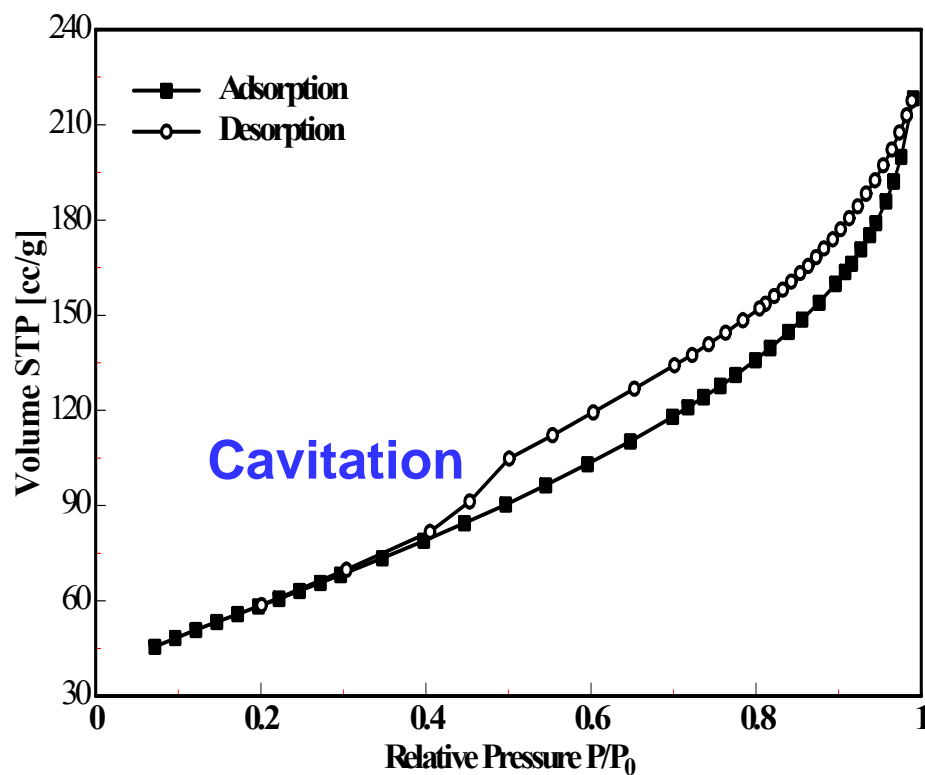
N$_2$/77K sorption on disordered alumina catalyst

Interpretation of Adsorption Hysteresis of Nitrogen, and Argon in Micro/Mesoporous Carbons
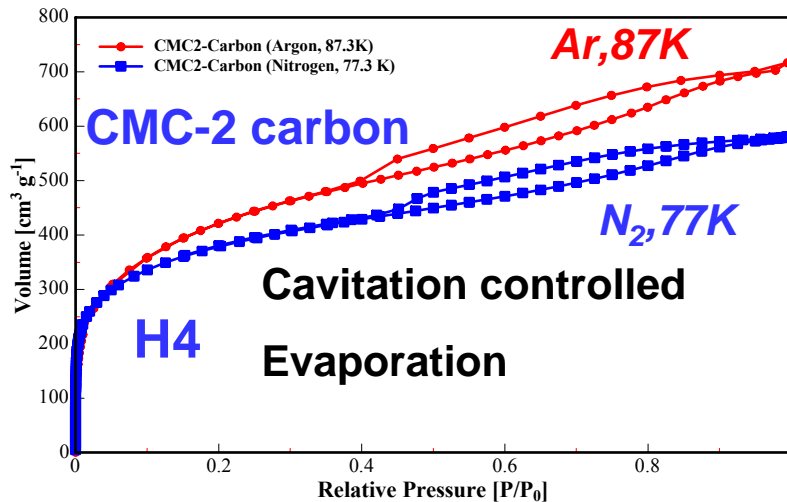
Cavitation

⇒ *Larger Mesopores only accessible through narrow micro/mesoporous constriction,i.e. larger mesopores are embedded into microporous matrix!*

⇒ *No pore size informatiion from desorption branch*
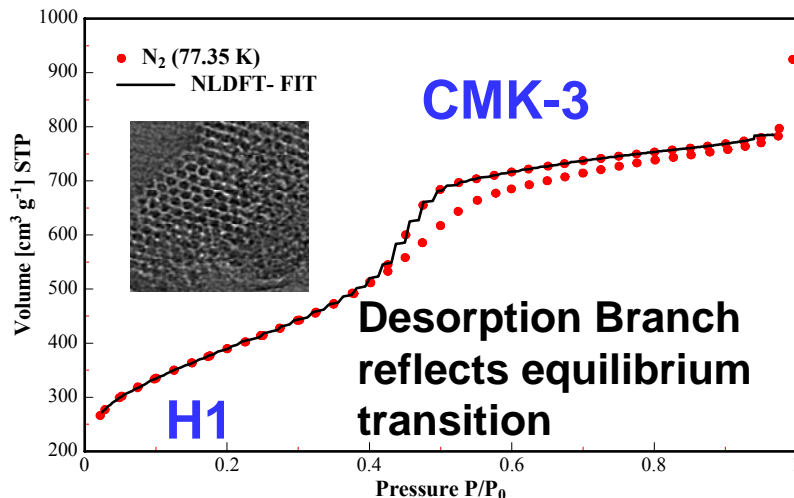
Evaporation at equilibr. (Vapor-liquid) transition:

⇒ *Mesopores are freely accessible, no constrictions!*

⇒ *Pore size information from adsorption and desorption branch*

• *Hysteresis due to delayed condensation*

Summary and Conclusions

- *Taking into account the effect of pore wall heterogeneity*: Quenched solid density functional theory (QSDFT) improves significantly the pore size analysis of nanoporous carbon materials

- *Pore connectivity* appears to decrease nucleation barrier for pore condensation in ordered porous 3D materials (KIT-6, MCM-48, large pore SBA-15) - effects position of adsorption branch (so-called "advanced condensation) $\Rightarrow$ Pore size analysis

- *Micro/mesoporous materials with hierarchical pore structure :* Various phenomena such as spinodal condensation (i.e. delayed condensaton due to metastable pore fluid) pore blocking/percolation and cavitation are contributing to hysteresis

  - *Pore blocking:* $\Rightarrow$ Pore (cavity) size from adsorption branch; Neck size from desorption branch,

  - *Cavitation:* $\Rightarrow$ Pore (Cavity Size) from adsorption branch; <u>No pore size information from desorption branch</u>

- *Pore size dependency on cavitation*: Contrary to classical understanding, we find based on both experiment and molecular simulation that the cavitation pressure depends on pore size up to a critical pore size (of around 12 nm), but no pore size dependence for larger pores- $\Rightarrow$ indicates that for large pores the cavitation pressure correlated with the liquid-vapor spinodal of the bulk fluid?

Recommendations: Hysteresis and Pore Size Analysis

- **H1 Hysteresis:**

  - *Materials with independent pores* (e.g., MCM-41 some MCM-41) : Pore size can in principle be determined from both desorption branch and adsorption branch if proper methods are applied
  - *Materials with ordered pore networks*: Pore size analysis from desorption branch

- **H2 Hysteresis**: caused by pore blocking/percolation or cavitation phenomena in mesoporous and micro/mesoporous pore networks

  Pore blocking: $\Rightarrow$ Pore (cavity) size from adsorption branch; Neck size from desorption branch,

  Cavitation: $\Rightarrow$ Pore (Cavity Size) from adsorption branch; <u>No quantitative pore size distribution information from desorption branch</u>

- **H3/H4 Hysteresis:** observed in very disordered micro/mesoporous pore networks and caused by a combination of various phenomena (incl. cavitation, pore blocking) $\Rightarrow$ Pore Size from adsorption branch

Acknowledgement

Special Thanks to:

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Dr. P. Ravikovitch