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THE STATE UNIVERSITY OF NEW JERSEY

Quenched Solid Density Functional Theory (QSDFT) of Adsorption on Hetererogenoues Solids and Pore Structure Characterization

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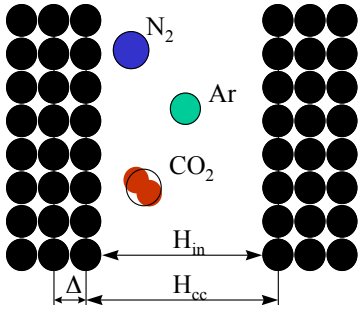
Workshop on Measurement Needs in the Adsorption Sciences, NIST, Nov.5, 2014

OUTLINE

- Introduction: Non-Local Density Functional Theory (NLDFT) of adsorption is the most popular method for pore size characterization, recommended by ISA as a replacement of classical methods based on Laplace-Kelvin equation, like BJH
  - Many advantages; one major deficiency – does not account for molecular level surface roughness inherent for most of practical systems
- Quenched Solid density Functional Theory (QSDFT), in which the solid enters the model as a quenched component with given density distribution rather than a source of an external potential
  - Systematic account for the surface roughness and microporosity
  - Solid density profile can be taken from independent XRD data
- QSDFT provides a unified approach to interpreting adsorption and XRD
  - Good agreement with in situ XRD measurements
- QSDFT method for pore size distribution calculations eliminates artifacts of NLDFT and other conventional theories, which are based on smooth wall pore models
- Library of QSDFT kernels for micro- and mesoporous carbons of various morphology based on N_2 and Ar low temperature isotherms
- New development – CO_2 high pressure isotherms for pore size characterization in the whole rage of micro- and mesopores, 0.36 – 50 nm

DFT for Inhomogeneous Fluids



- Grand Canonical μ-V-T ensemble:
  an open system of volume V within solid walls
  at constant temperature T *and* chemical potential μ

- fluid-solid interactions are modeled by an external potential, $U_{sf}(r)$

- fluid-fluid interactions are modeled by a pair-wise potential, $U_{ff}(r_1,r_2)$

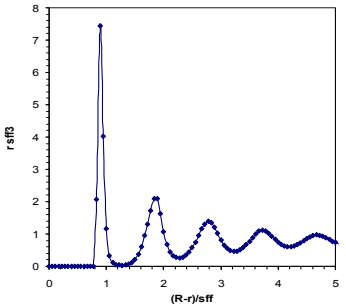
- equilibrium states are defined by minimization of the
  Grand Thermodynamic Potential,

$$\Omega[\rho(r)] = F[\rho(r)] - \mu\int_v \rho(r)dr \Rightarrow \min$$

Helmholtz free energy $F[\rho(r)]$ is a functional of the local density $\rho(r)$

- equilibrium density profile $\rho(r,\mu,V,T)$

is a solution of Euler equation $\mu = \dfrac{\partial F}{\partial \rho}$



Non-Local Density Functional Theory (NLDFT)

Grand potential functional:

$$\Omega(\rho(\mathbf{r})) = F(\rho(\mathbf{r})) - \int d\mathbf{r}\rho(\mathbf{r})[\mu - V_{ext}(\mathbf{r})]$$

Helmholtz free energy functional:

$$F(\rho(\mathbf{r})) = kT\int d\mathbf{r}\rho(\mathbf{r})\left[\left(\ln\left(\Lambda^3\rho(\mathbf{r})\right)-1\right) + f\left(\bar{\rho}(\mathbf{r})\right)\right] + \frac{1}{2}\iint d\mathbf{r}d\mathbf{r}'\,\rho(\mathbf{r})\rho(\mathbf{r}')\Phi_{attr}(|\mathbf{r}-\mathbf{r}'|)$$

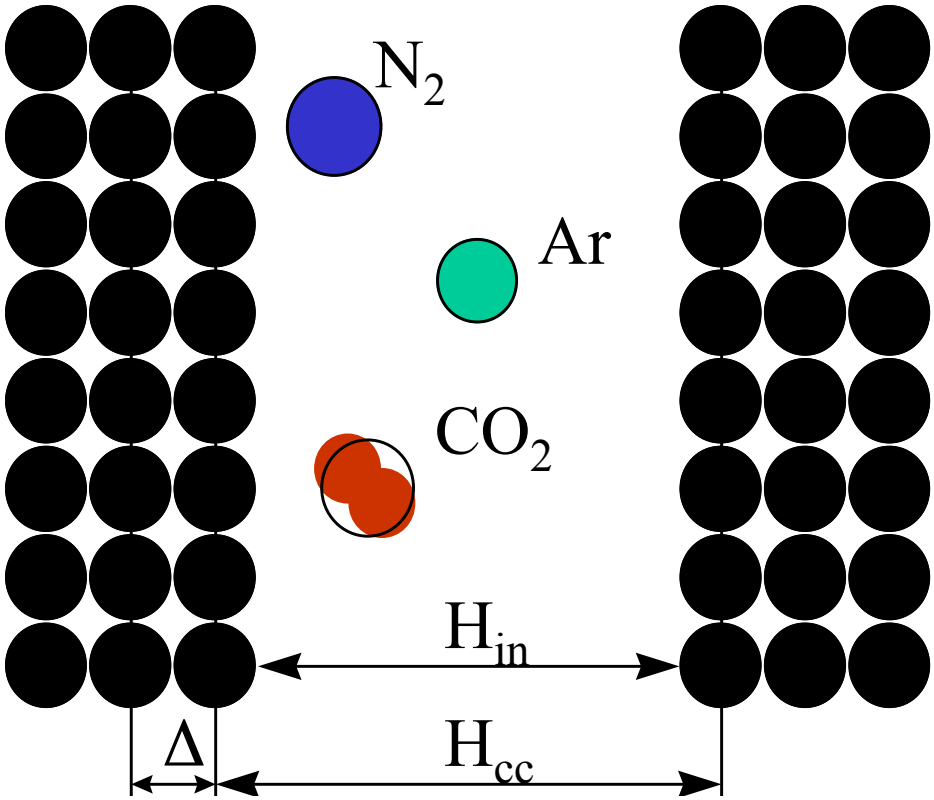
Repulsive part — **Mean field attractive contributions**

NLDFT: Instead of local fluid density employ smoothed density

Smoothed density:

$$\bar{\rho}(\mathbf{r}) = \int d\mathbf{r}'\rho(\mathbf{r}')\left[w_0(|\mathbf{r}-\mathbf{r}'|) + w_1(|\mathbf{r}-\mathbf{r}'|)\bar{\rho}(\mathbf{r}) + w_2(|\mathbf{r}-\mathbf{r}'|)\bar{\rho}(\mathbf{r})^2\right]$$

Modeling adsorption in pores with smooth walls



Reservoir
(bulk phase)

μ, T

Solid-fluid interactions (e.g, Steele):

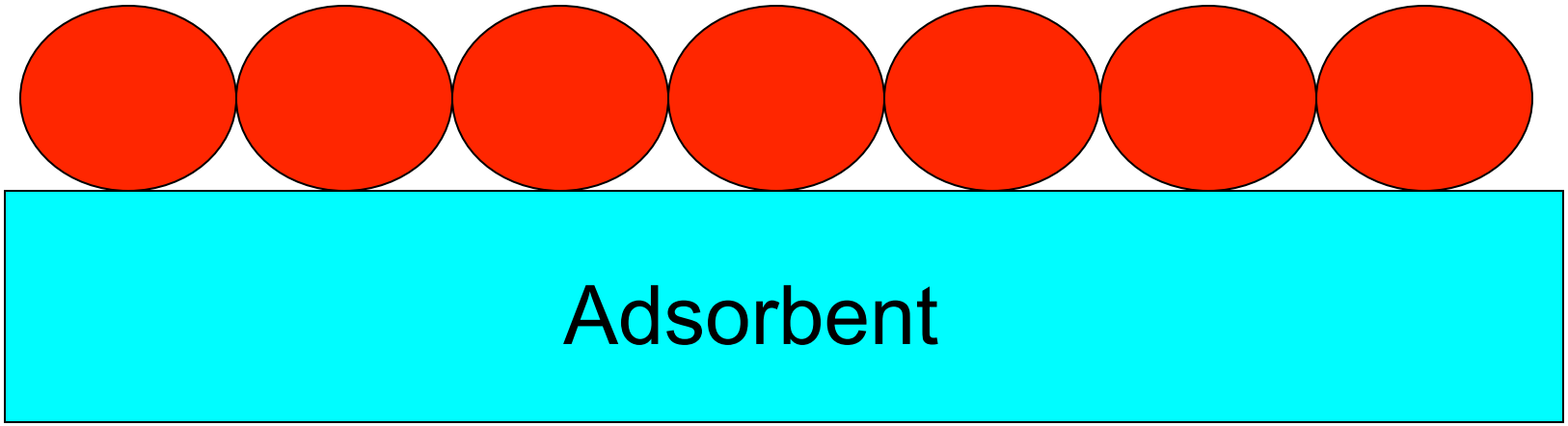
$$U_{sf}(z) = 2\pi\rho_s\varepsilon_{sf}\sigma_{sf}^2\Delta\left[\frac{2}{5}\left(\frac{\sigma_{sf}}{z}\right)^{10} - \left(\frac{\sigma_{sf}}{z}\right)^{4} - \frac{\sigma_{sf}^4}{3\Delta(0.61\,\Delta + z)^3}\right]$$

$$U_{sf,pore}(z) = U_{sf}(z) + U_{sf}(H_{cc} - z)$$

Fluid-fluid interactions
(e.g., Lennard-Jones):

$$U_{ff}(r) = 4\varepsilon_{ff}\left[\left(\frac{\sigma_{ff}}{r}\right)^{12} - \left(\frac{\sigma_{ff}}{r}\right)^{6}\right]$$

Adsorption Process on a Molecularly Smooth Surface implies Formation of Adsorbed Layers – Major Artifact of Traditional Models



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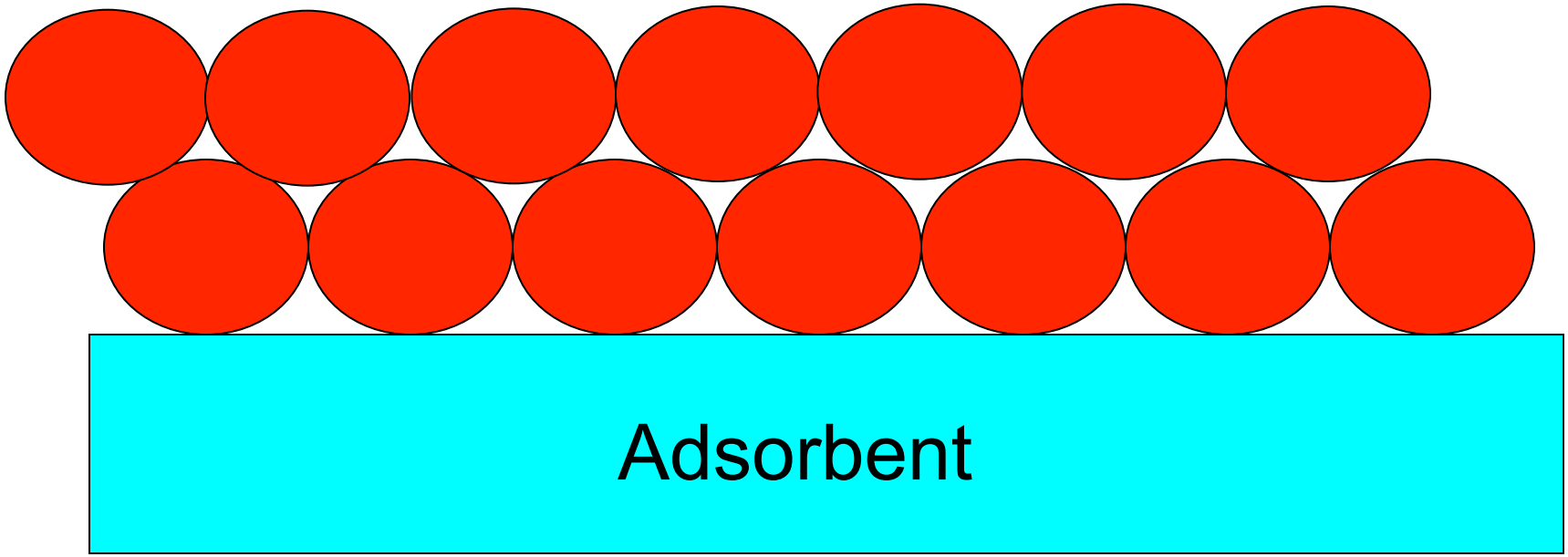

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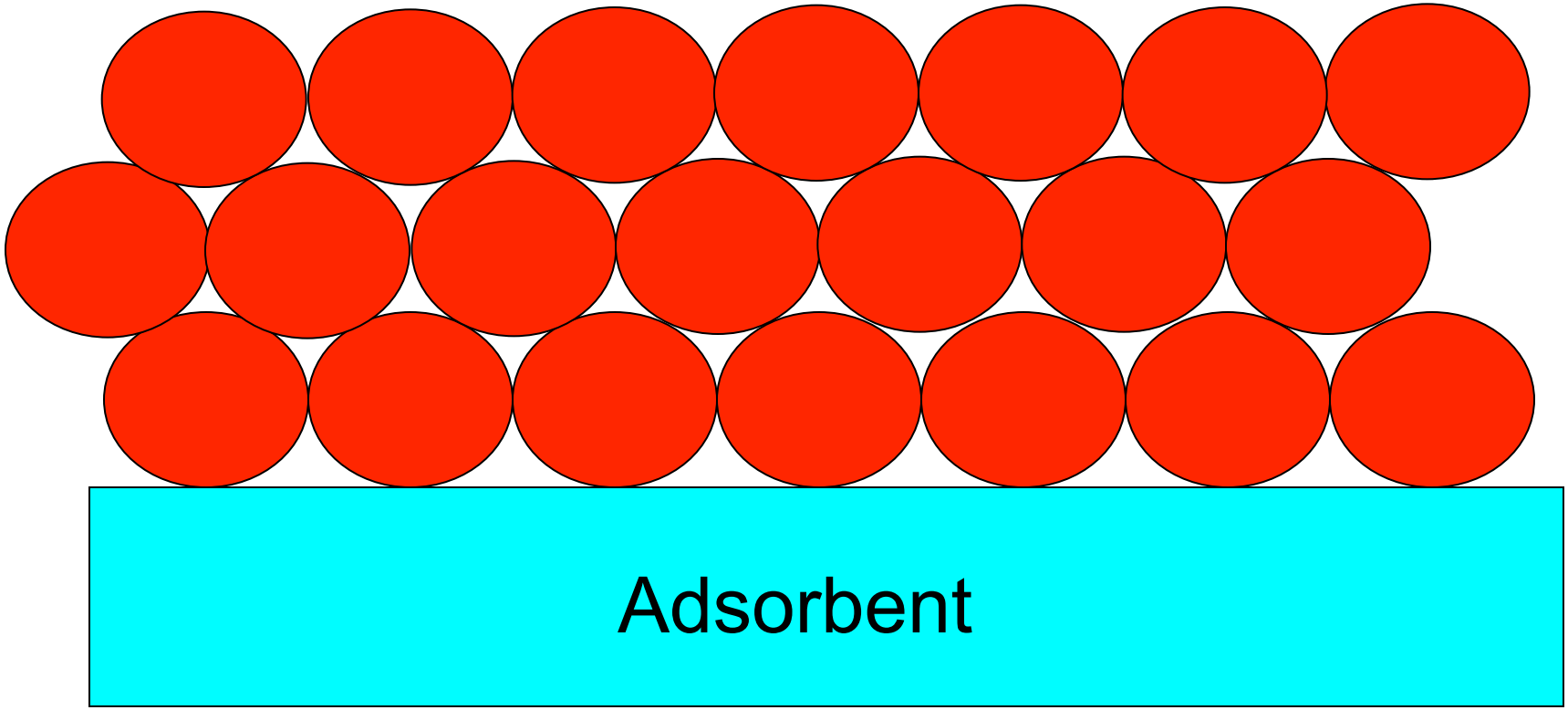
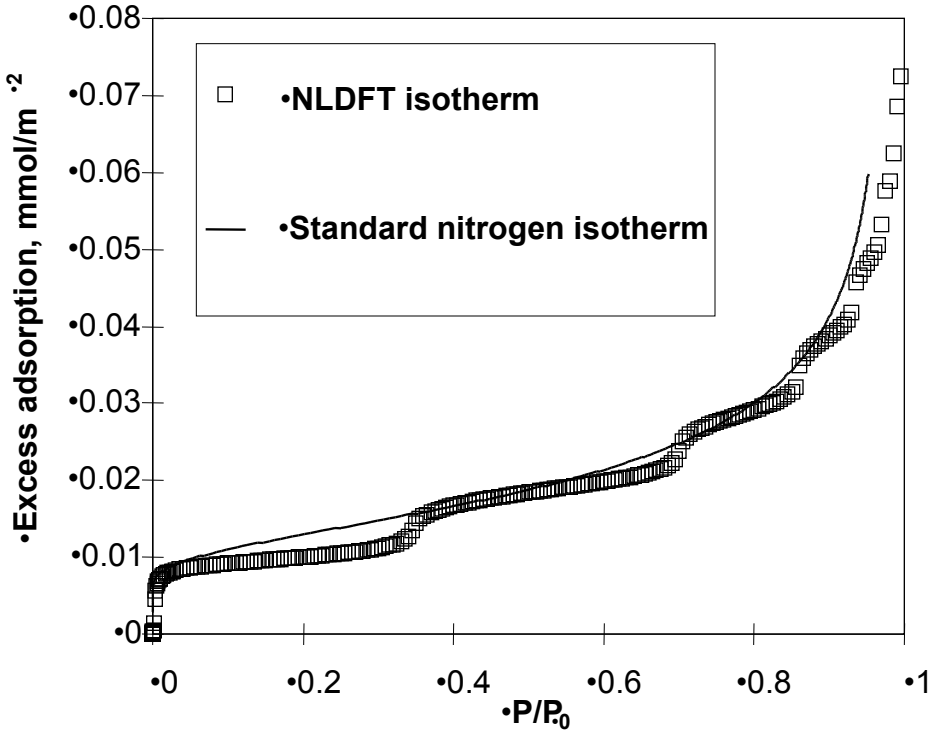
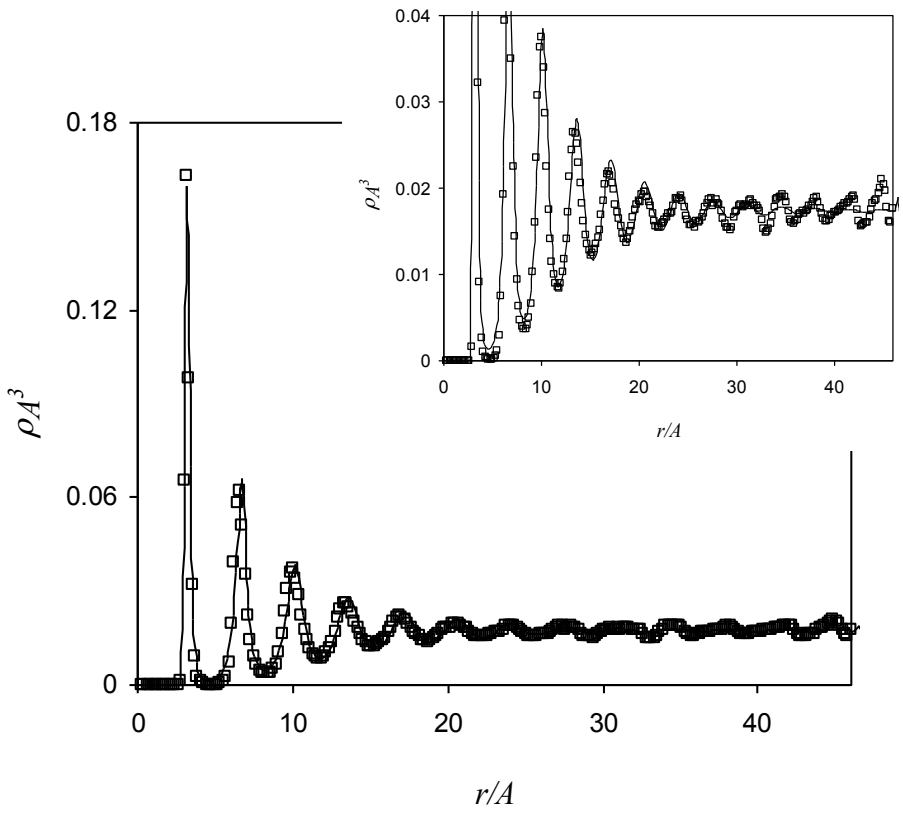


Adsorption Isotherms: Theory vs Experiment
Layering is Artificial!

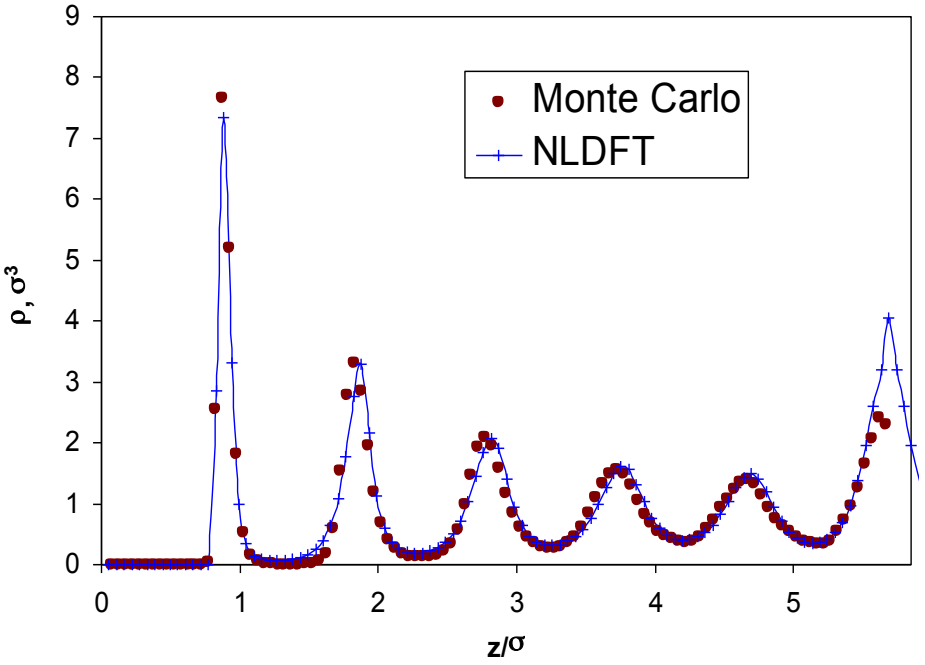


Comparison of the NLDFT isotherm on a smooth surface with the standard nitrogen isotherm [J.H. de Boer, B.G. Linsen, Th.J. Osinga, *J. Catalysis* 4 (1965) 643.] and corresponding statistical film thickness plot.

Layering in Smooth Surface Models: MC and DFT

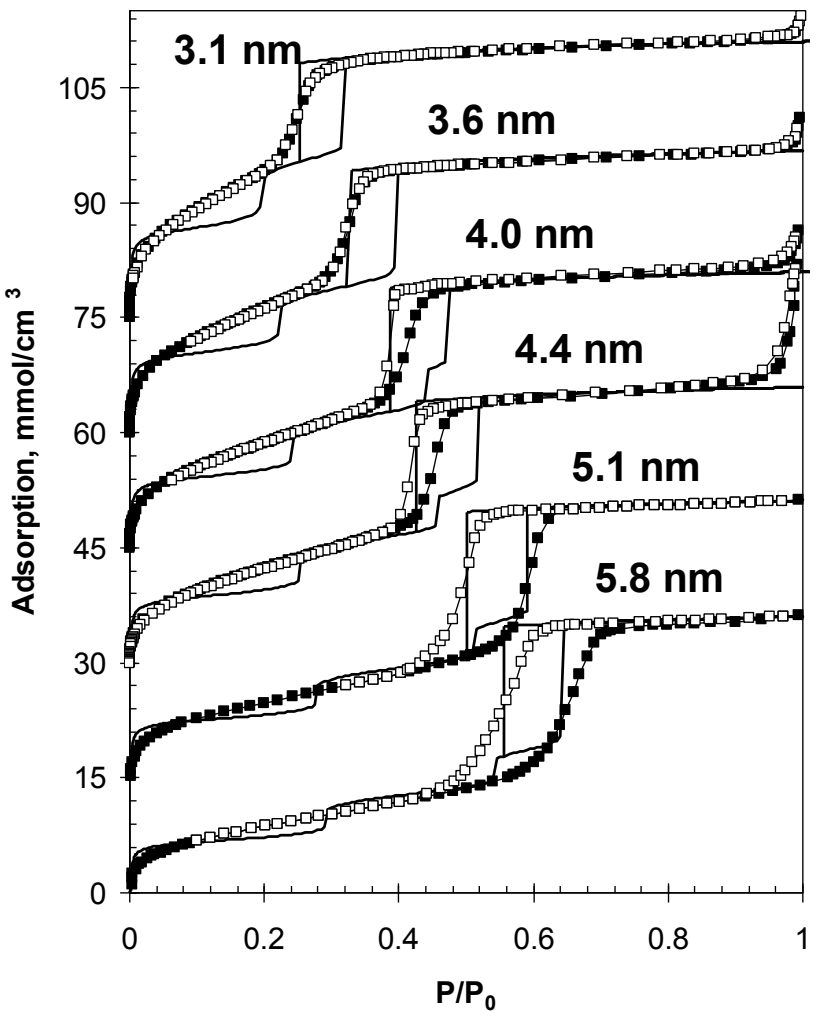


9 nm pore, N_2@77K

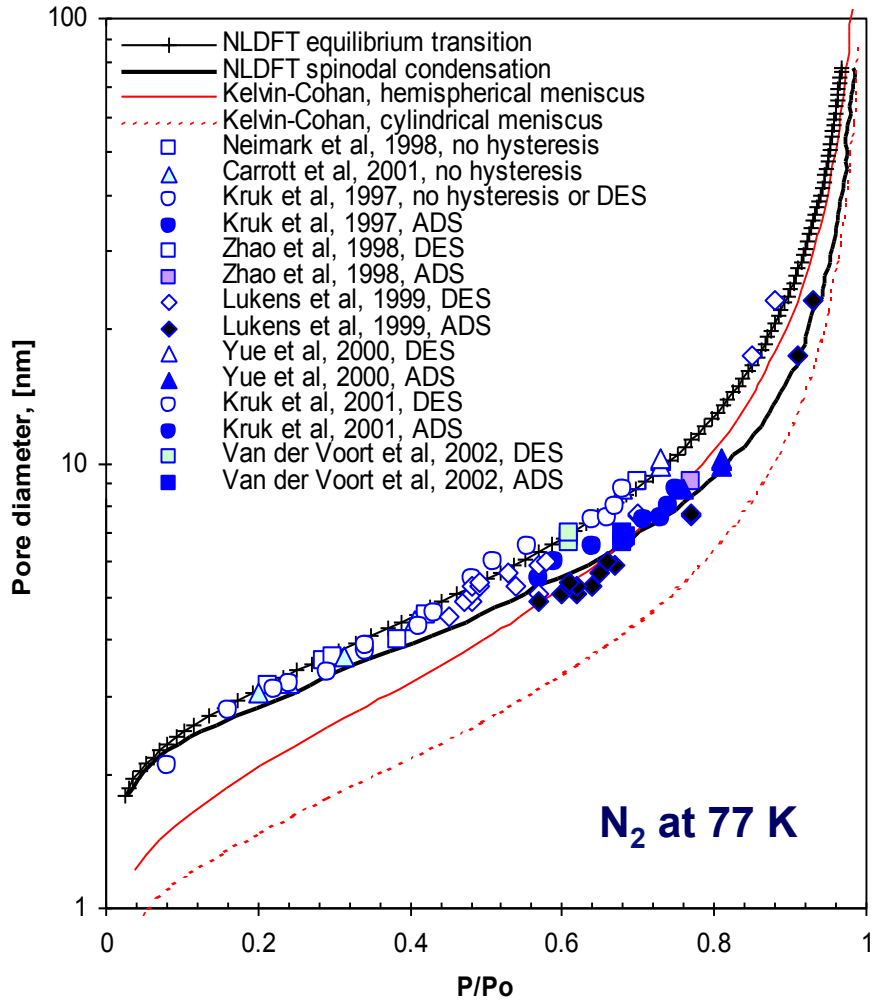


3.4 nm pore, Ar@87K

Adsorption on MCM-41 and SBA-15: NLDFT and Experiment

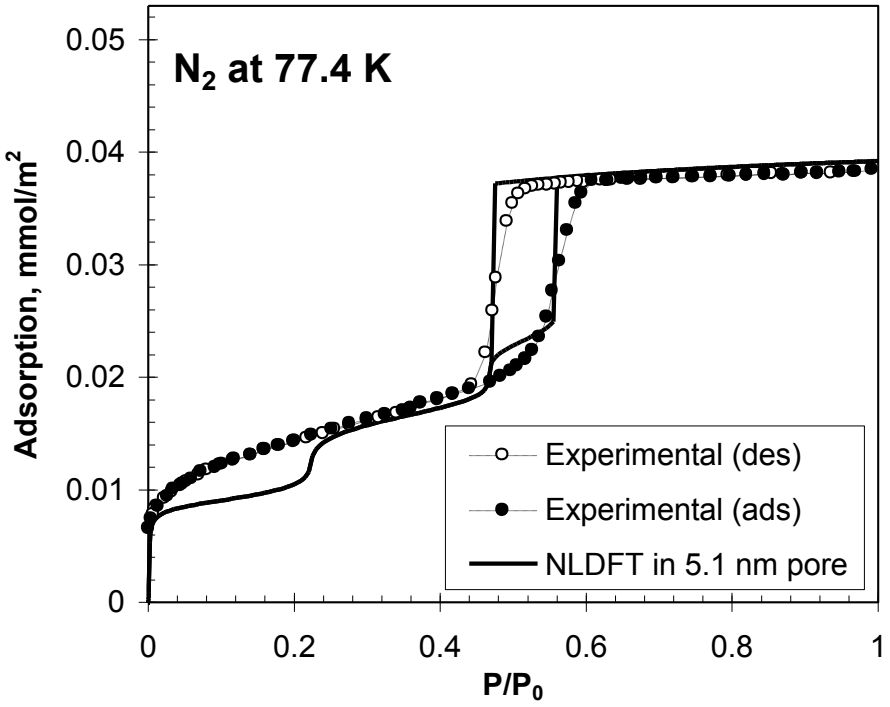


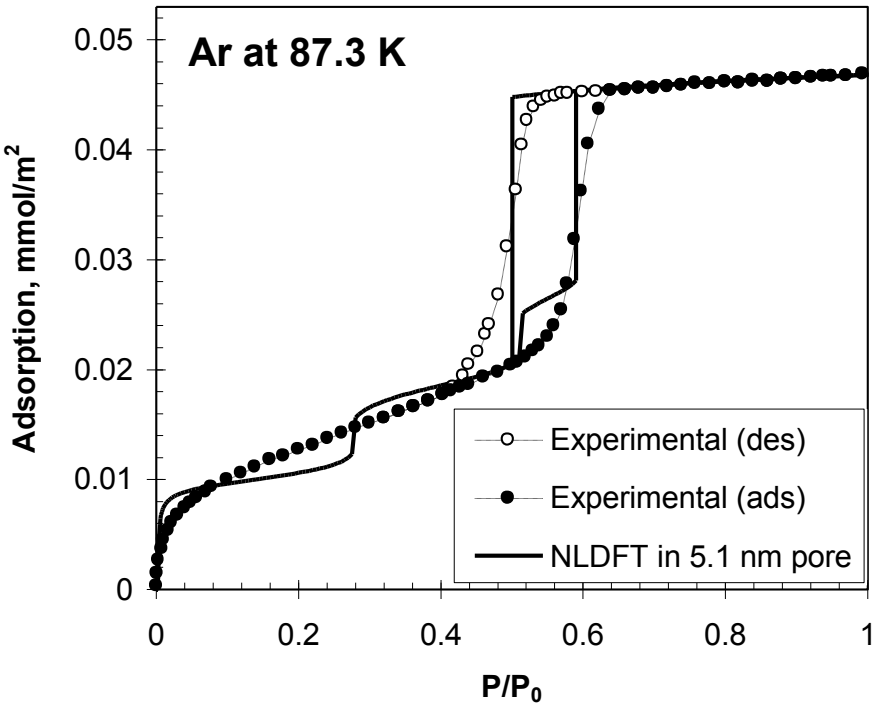
Ar at 87 K



Neimark et al, J. Phys.: Cond. Matt. 15, 347-365 (2003)

Comparison of the NLDFT model with the experimental data on regular MCM-41 type materials





Experimental data from M. Kruk, M. Jaroniec, *Chem. Mater.* 12 (2000) 222

AVN & Ravikovitch, *Microp. Mesopor. Mater.*, **2001**, 44-45, 697

Calculation of Pore Size Distributions from Adsorption and Desorption Isotherms

Solution of Integral Adsorption Equation

Kernel of theoretical **equilibrium** isotherms in individual pores

Experimental **equilibrium** branch

$$N_{eq}^{exp}(P) = \int_{D_{min}}^{D_{max}} N_{equilibrium}^{theory}(P,D) f_{eq}(D) dD$$

$f_{eq}(D)$

Experimental **adsorption** isotherm

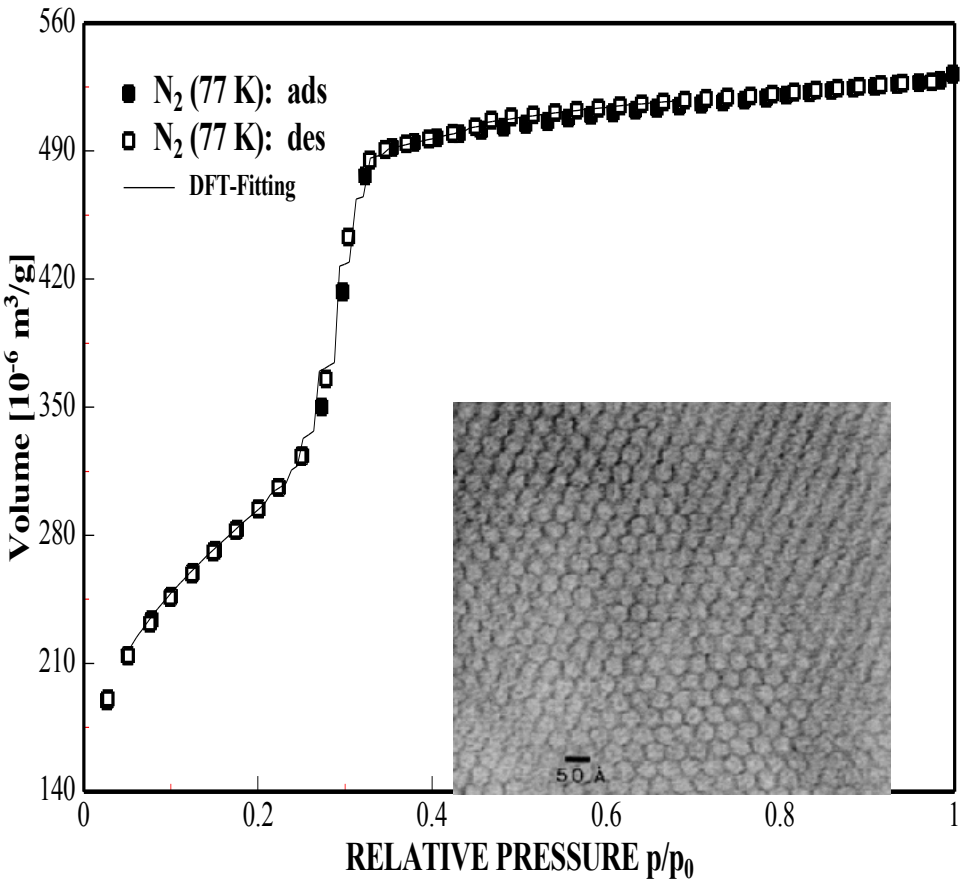
$$N_{ads}^{exp}(P) = \int_{D_{min}}^{D_{max}} N_{metastable}^{theory}(P,D) f_{ads}(D) dD$$

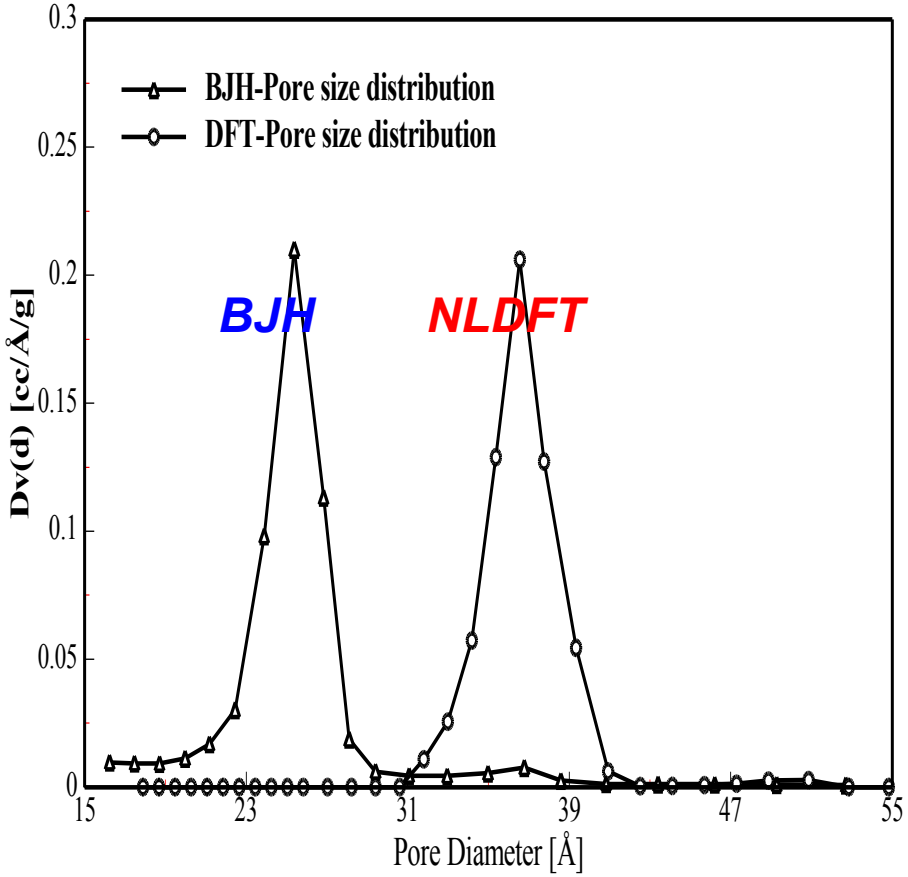
$f_{ads}(D)$

Kernel of theoretical **metastable adsorption** isotherms in individual pores

Pore size distributions, $f_{ads}(D)=f_{des}(D)$ for ideal cylindrical structures with H1 hysteresis loop

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

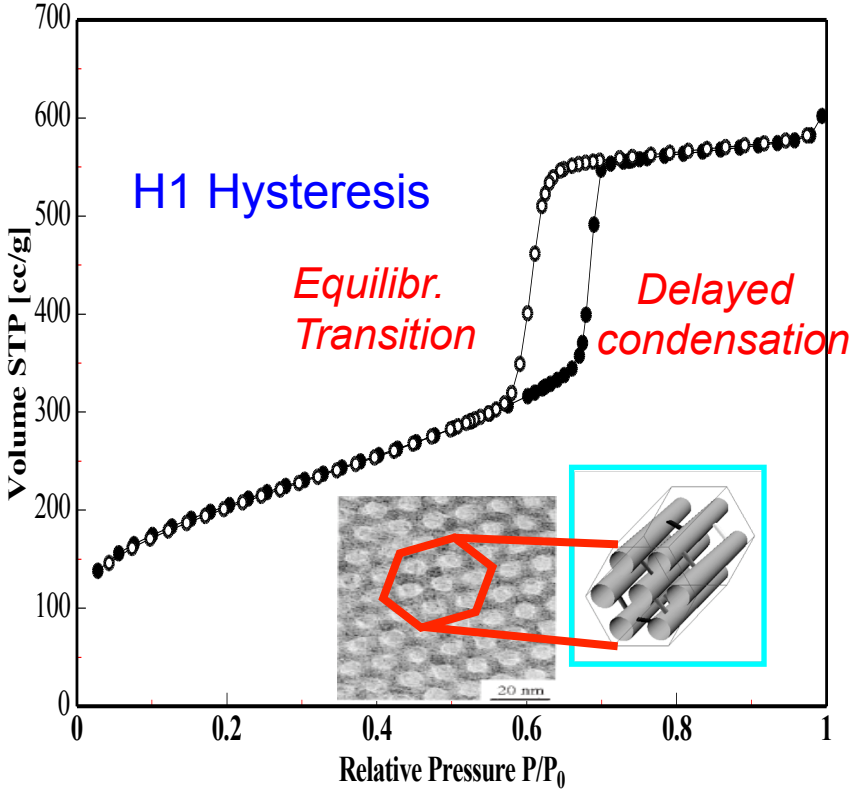


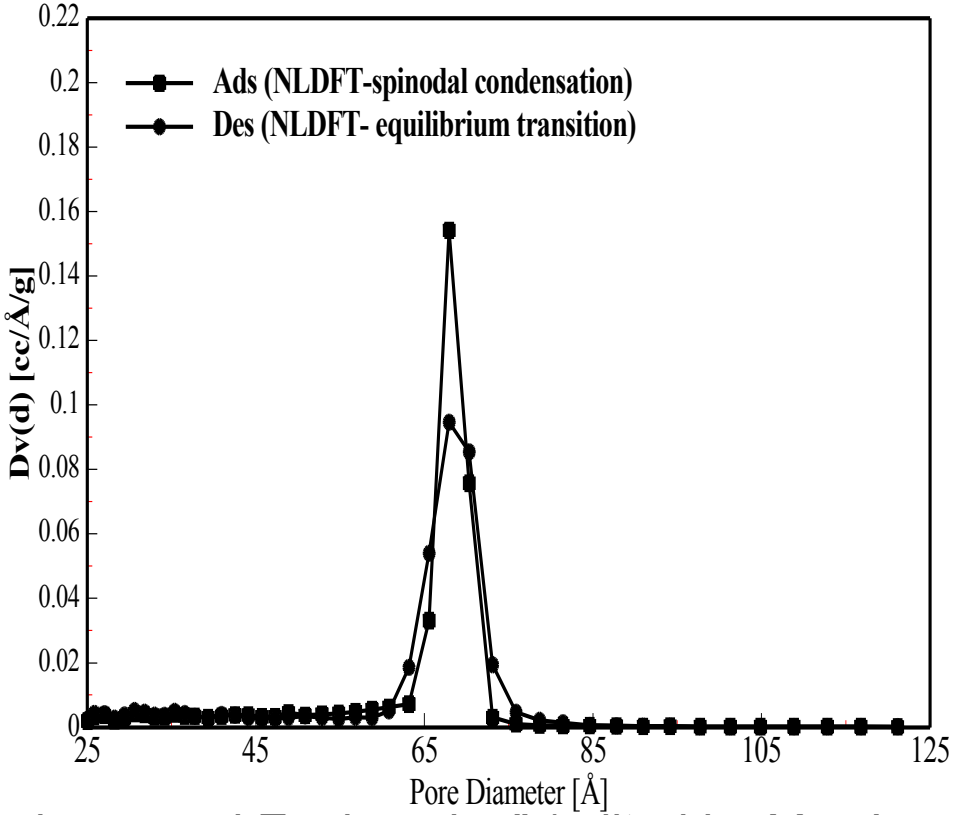


- ***Classical methods (i.e. BJH, based on Kelvin equation) underestimate the pore diameter up to ca. 25 % !***
- ***NLDFT allows to calculate an accurate pore size distribution***

Courtesy of Matthias Thommes

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*)

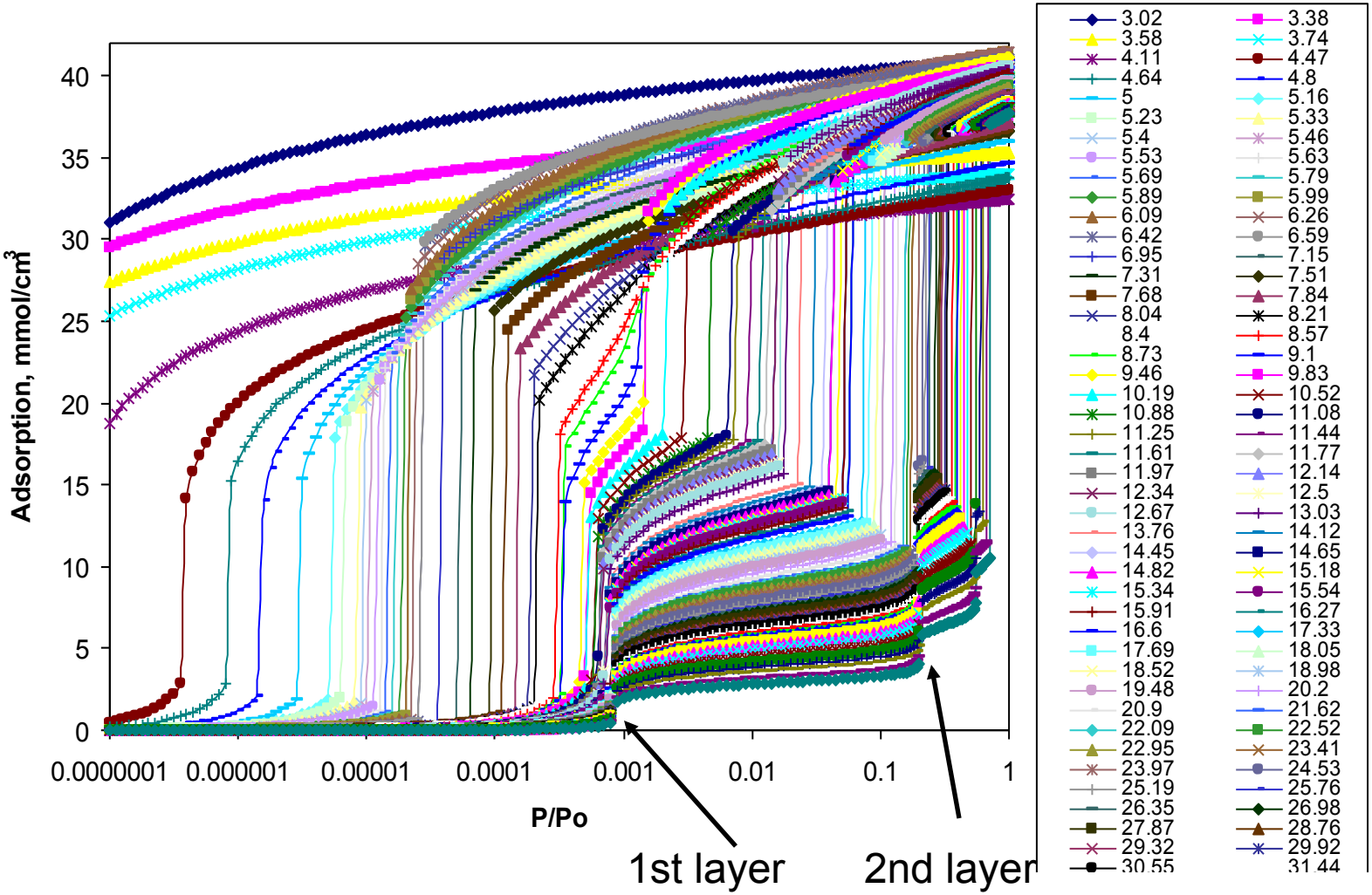




M. Thommes, In Nanoporous Materials- Science and Engineering" (edited by Max Lu and G. Zhao), Imperial College Press, Chapter 11 p. 317 - 364 (2004)

Courtesy of Matthias Thommes

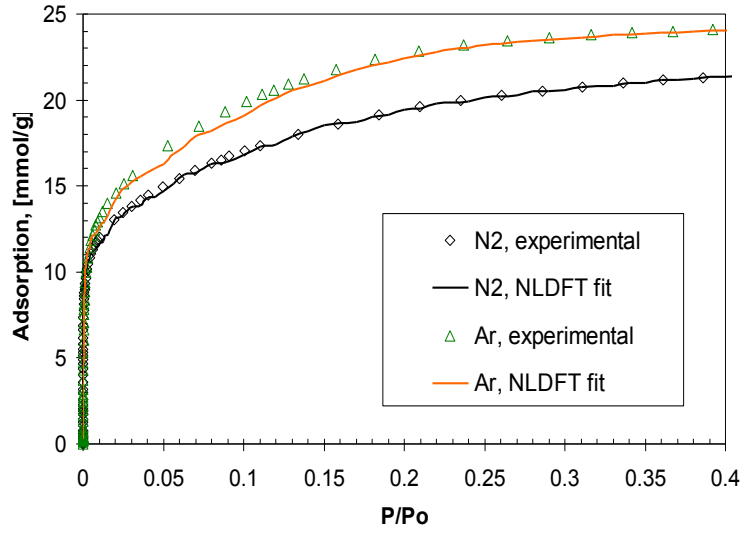
Adsorption Isotherms in Slit Pores
Argon on Carbon @ 77.4 K (NLDFT kernel)

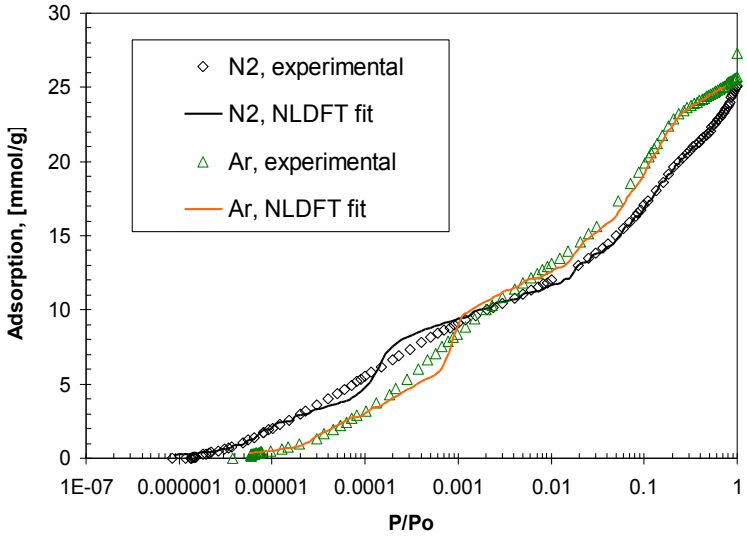


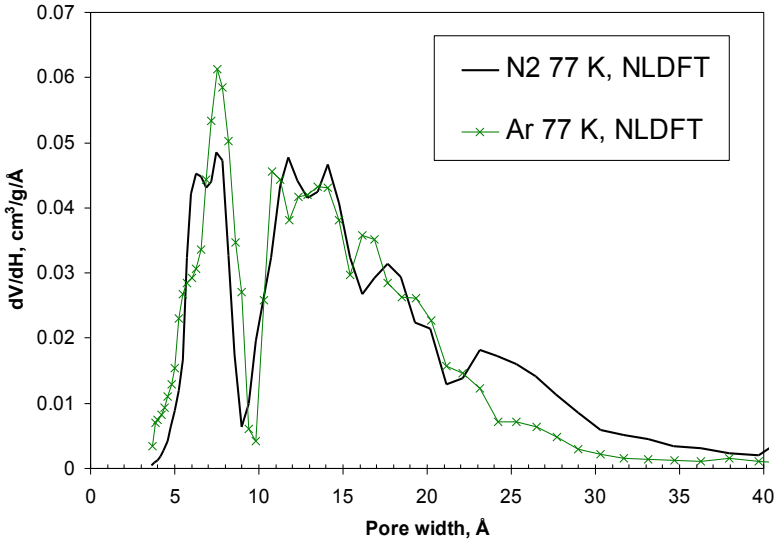
Layering transitions prior to capillary condensation

Ravikovitch, Vishnyakov, Russo, & AVN, Langmuir, 2000, 16, 2311

Pore volume distribution of P15 carbon fiber



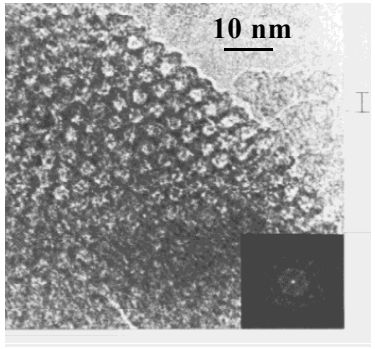


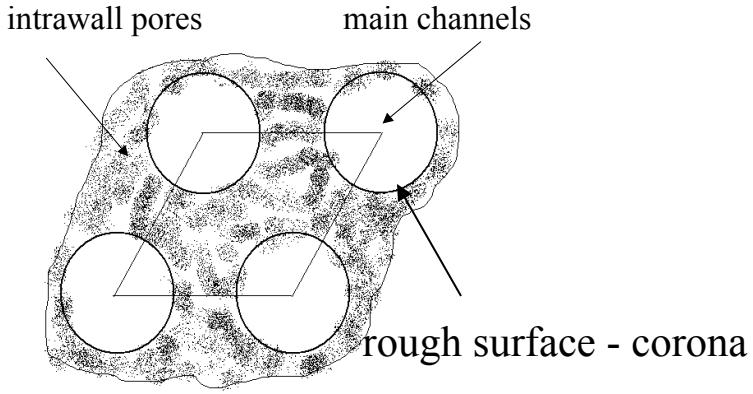


Artificial layering transition implied by the smooth surface model at $p/p_0 \sim 10^{-4}$ (monolayer formation for N_2 @ 77K) causes artificial gap around 9-10 A in NLDFT pore size distributions observed for microporous carbons.

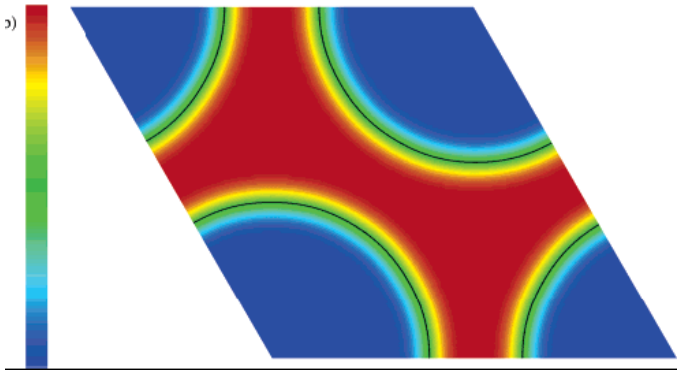
All non-crystalline adsorbents have rough pore walls, even most ordered porous solids like MCM-41 and SBA-15

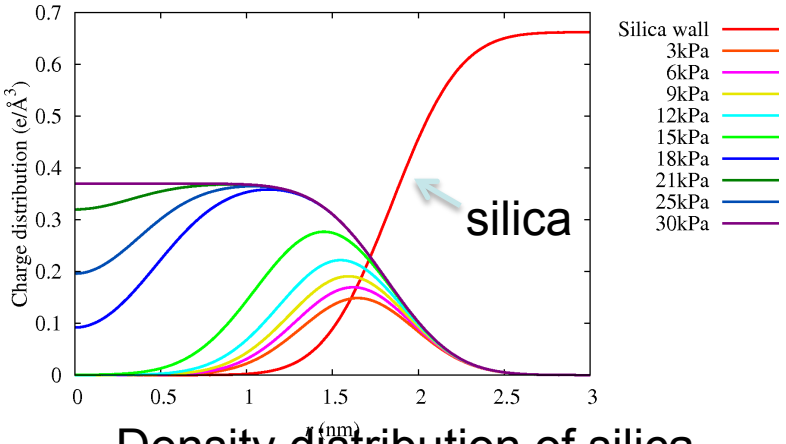
TEM





XRD



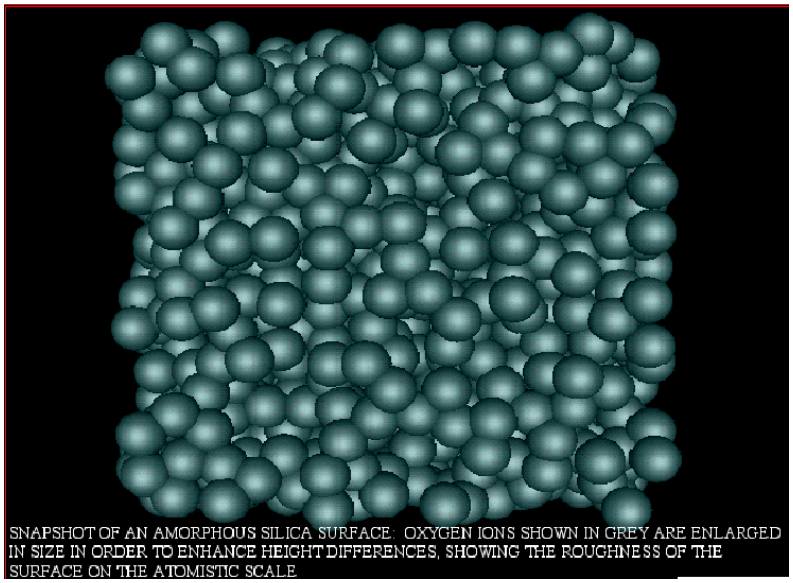


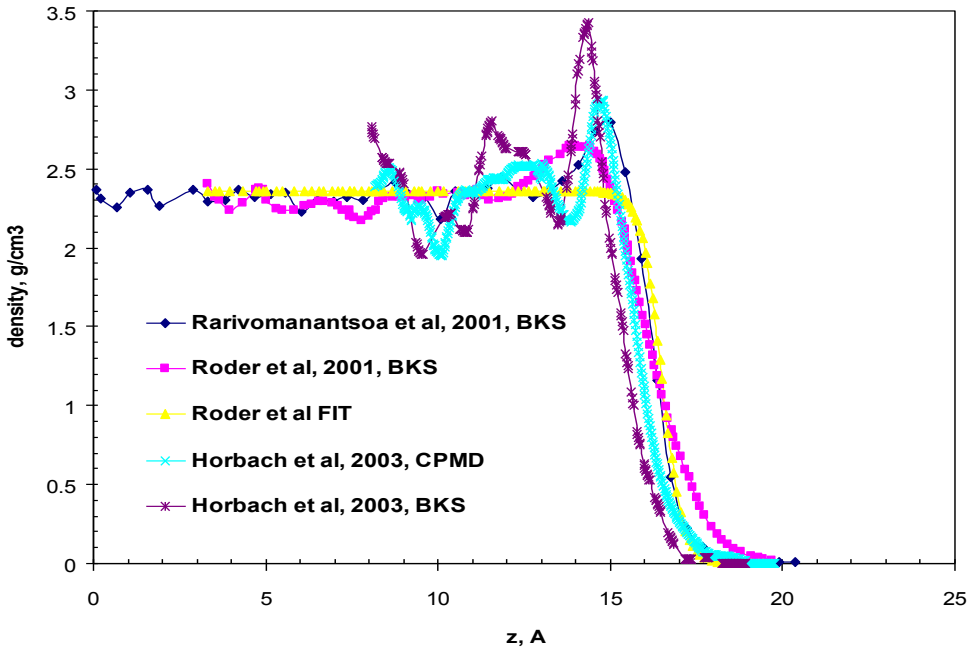
In situ XRD: Ar on MCM-41 - 2D *p6mm* crystal, pore size *D*=3.68 nm, corona thickness, *d*=0.4 nm

Density distribution of silica and Ar at various gas pressures

Miyasaka, AVN, & Terasaki, - JPCC, 2009, 113, 791

Amorphous silica surface





From S. Garofalini (Rutgers) and co-workers

Density from simulations

(amorphous silica from Roder et al, 2000)

$$\rho_S(z) = \frac{\rho_0}{2}\left(1 - \tanh\left(\frac{(z - z_0)}{\delta}\right)\right)$$

surface roughness parameter δ – semi-width of the density profile

Quenched Solid DFT (QSDFT)

Multicomponent DFT –
solid is considered as a component of the adsorbent-adsorbate system

Helmholtz free energy is a functional of both the solid and fluid densities

$$F\left[\rho_{fluid}(r), \rho_{solid}(r)\right]$$

fluid-solid interactions are modeled by a pairwise solid-fluid potential, $U_{sf}(r_s,r_f)$,
similarly to fluid-fluid interactions modeled by fluid-fluid potential, $U_{ff}(r_1,r_2)$

equilibrium states are defined by minimization of the Grand Thermodynamic Potential,

$$\Omega\left[\rho_{fluid}(r), \rho_{solid}(r)\right] = F\left[\rho_{fluid}(r), \rho_{solid}(r)\right] - \mu\int_v \rho_{fluid}(r)dr \Rightarrow \min$$

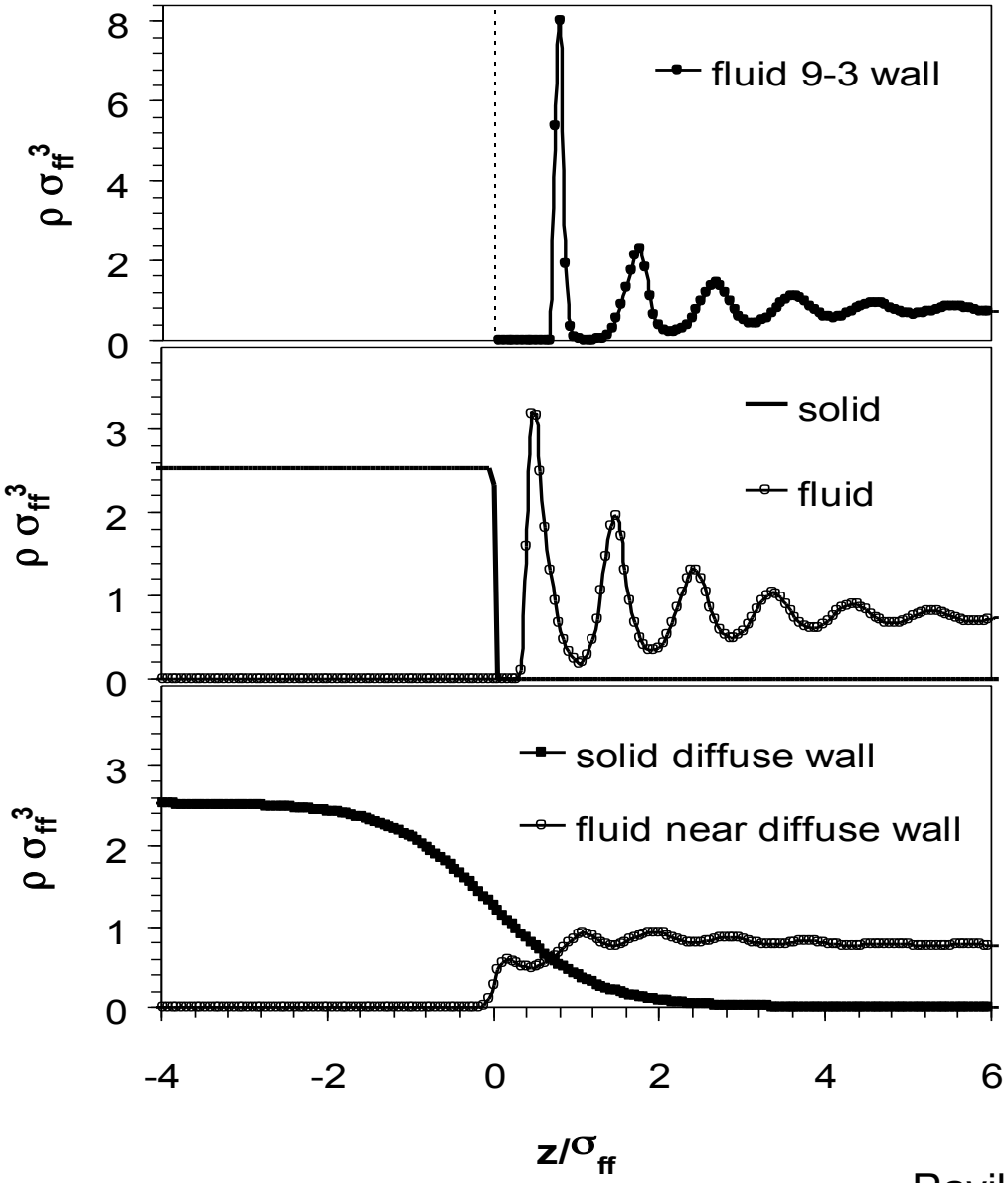
provided that the solid density $\rho_{solid}(r)$ is fixed (quenched)

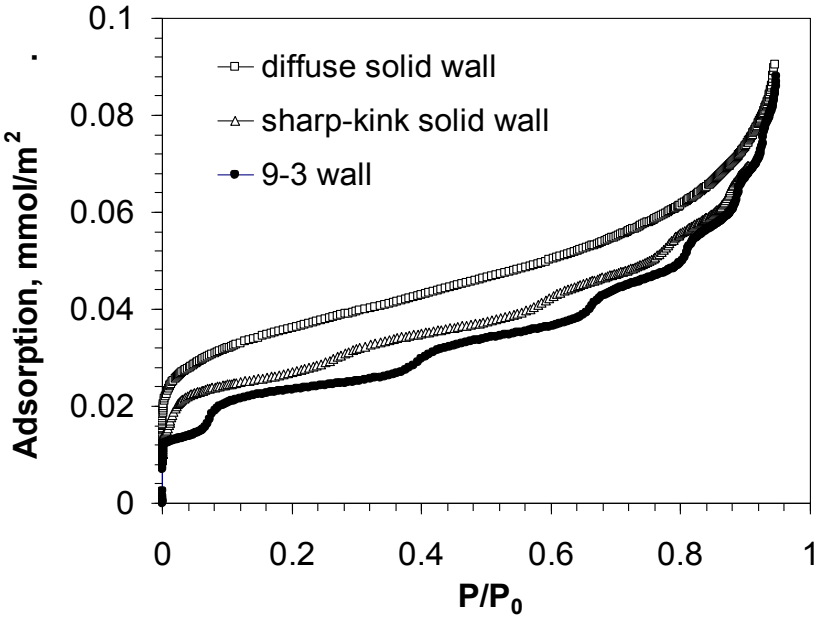
equilibrium density profile $\rho_{fluid}(r)$ at given μ and T is a solution of Euler equation

$$\mu = \left.\frac{\partial F\left[\rho_{fluid}, \rho_{solid}\right]}{\partial \rho_{fluid}}\right|_{\rho_{solid}}$$

Ravikovitch and AVN,
Langmuir, **2006,** *22*, 10864

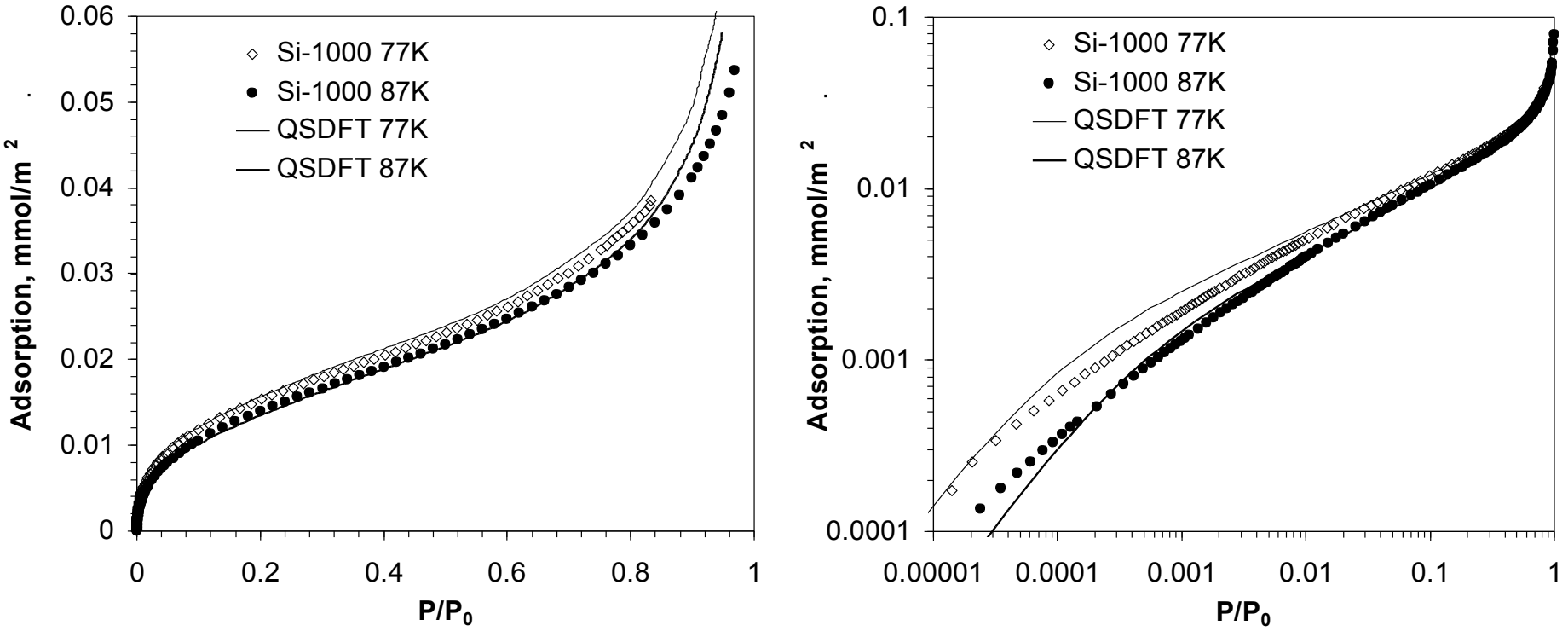
Density profiles: LJ fluid near 9-3 and amorphous walls





Ravikovitch and AVN, Langmuir, **22, 10864 (2006)**

Ar on nonporous silica Si-1000 at 87 and 77 K

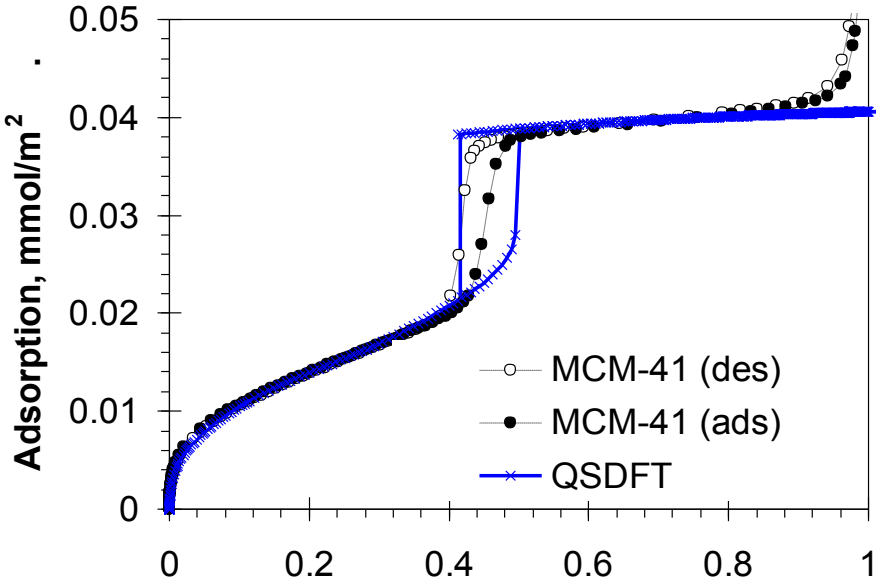


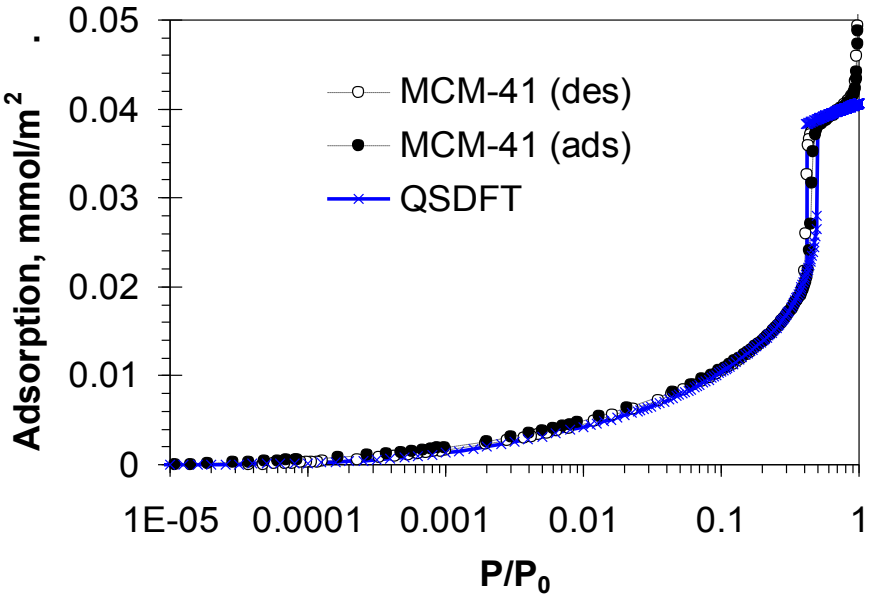
Roughness parameter δ=0.4 nm. No additional adjustable parameters!

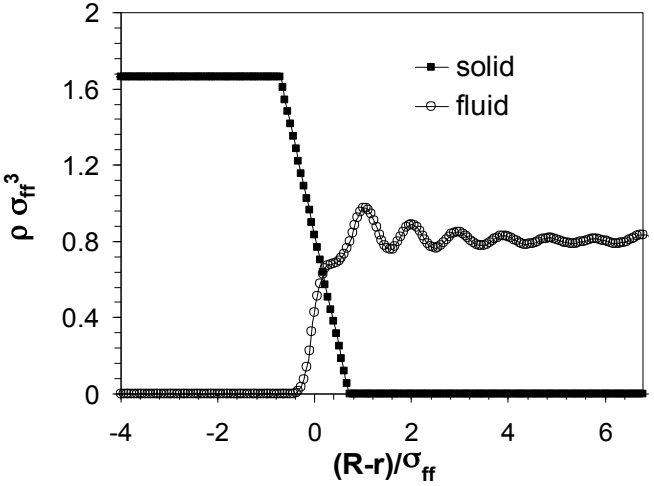
P_0 of supercooled Ar at 77K. From QSDFT: S_{BET}=18.3 m^2/g, C=34, a_m=0.119 nm^2

Experimental data from Kruk, M.; Jaroniec, M. *Chem. Mat.* **2000**, *12*, 222-230; *J. Phys. Chem. B* **2002**, *106*, 4732-4739

Ar on 4.5 nm MCM-41 at 87 K

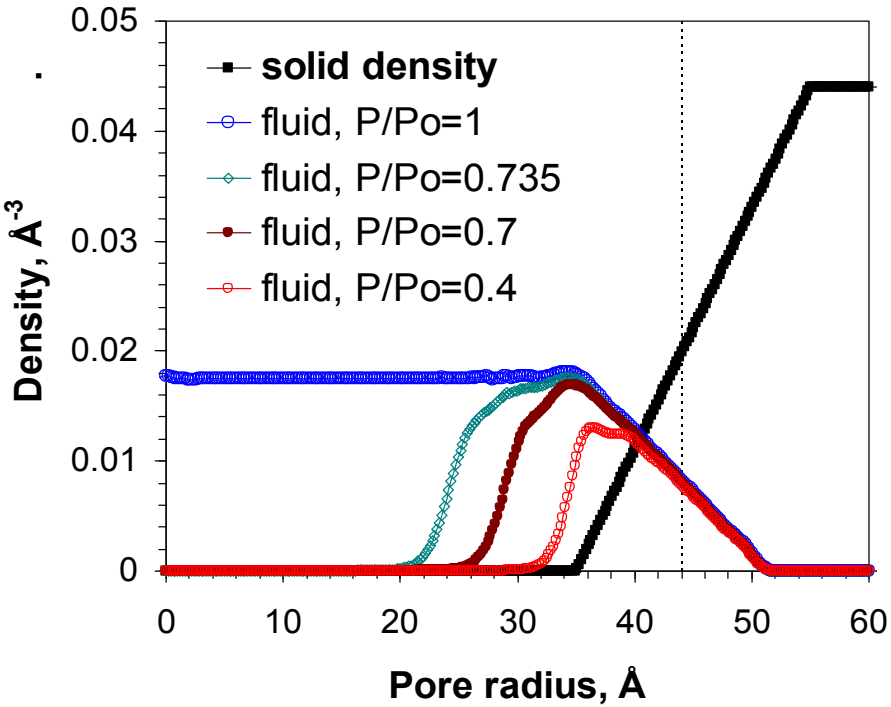


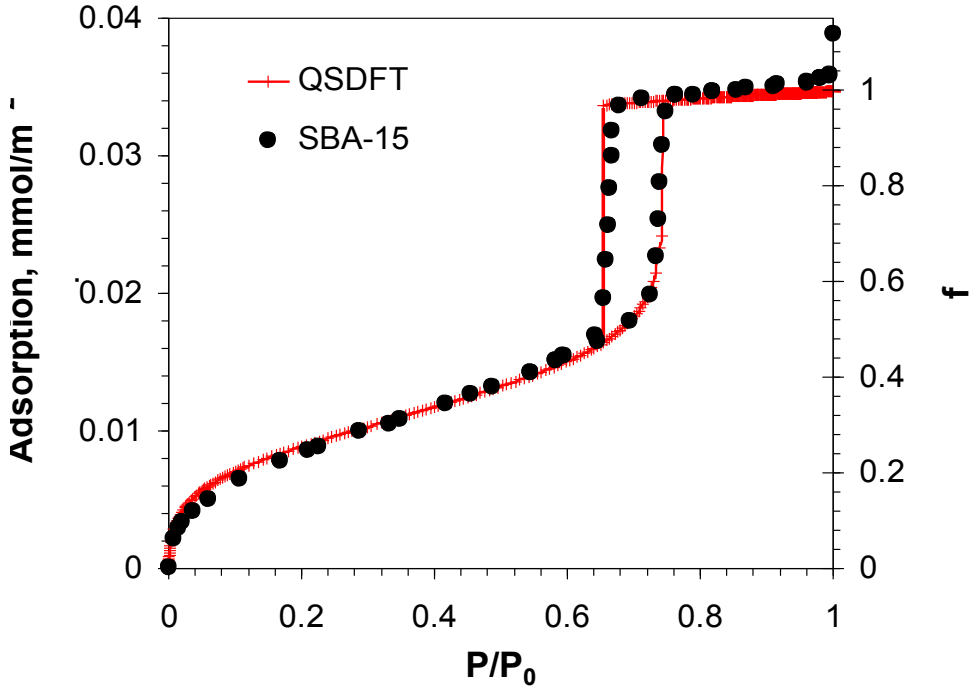




Roughness parameter δ=0.24 nm.
No additional adjustable parameters!

Prediction of Kr adsorption on SBA-15@119K from XRD data





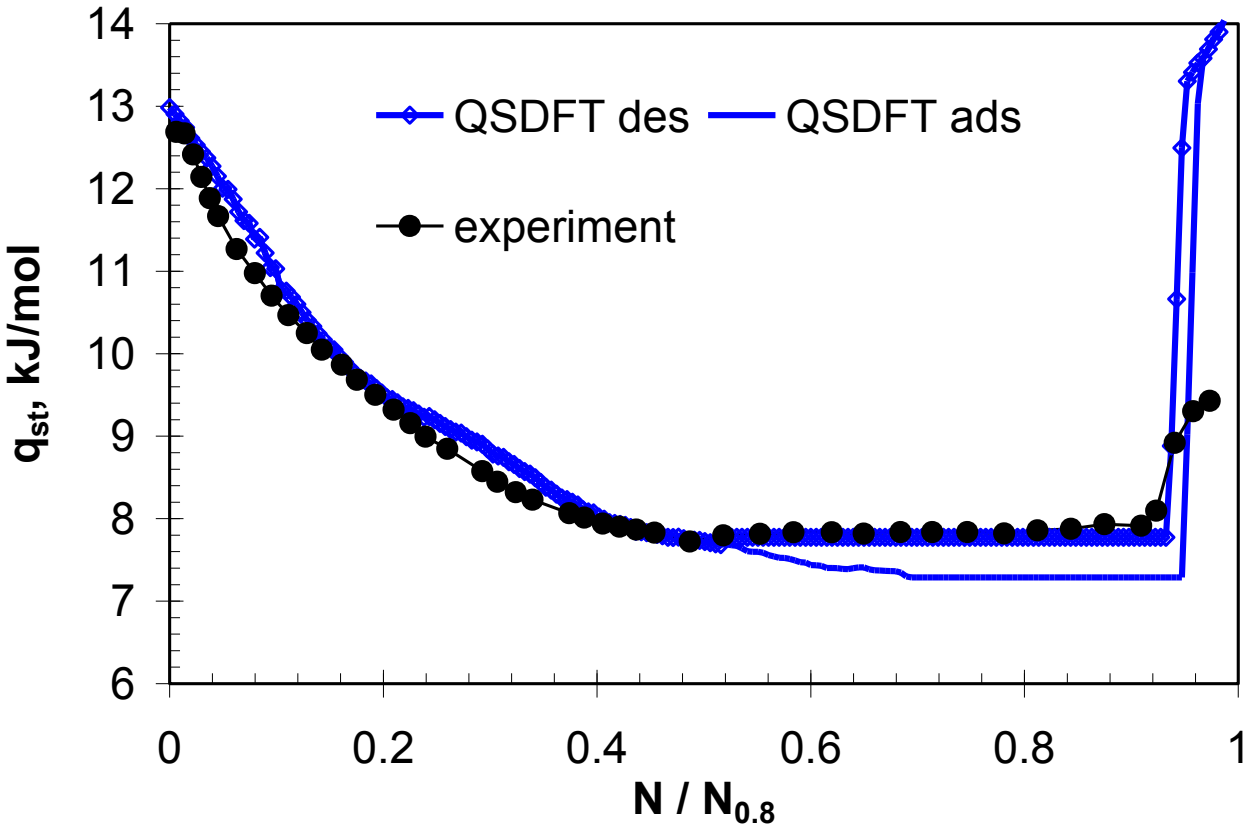
Roughness parameter δ=1 nm (from XRD) – semi-width of the corona

Pore radius 4.5 nm.

No adjustable parameters!

Experimental data: Hofmann et al, *Phys. Rev. B* **2005**, *72*, 064122
QSDFT calculations: Ravikovitch and AVN, Langmuir, **2006,** *22*, 10864

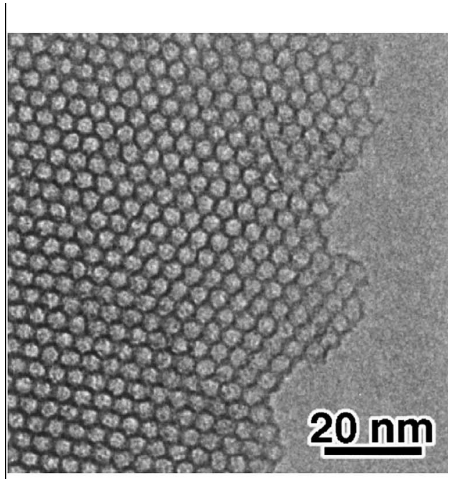
Isosteric Heat of Adsorption

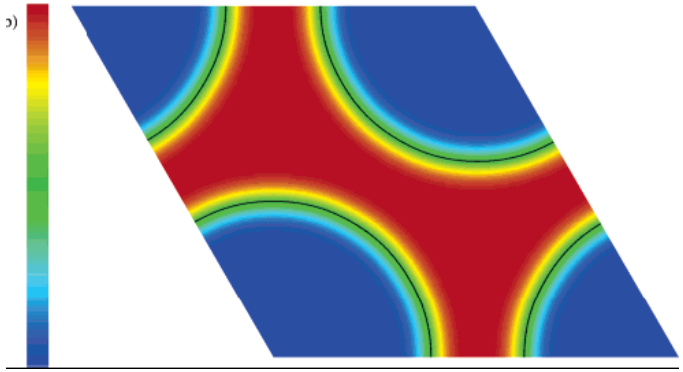


$$q_{st} = \frac{RT_1T_2}{T_2 - T_1}(\ln P_2 - \ln P_1)_N.$$

Ar adsorption on MCM-41. Experiment from J. Olivier, 2000

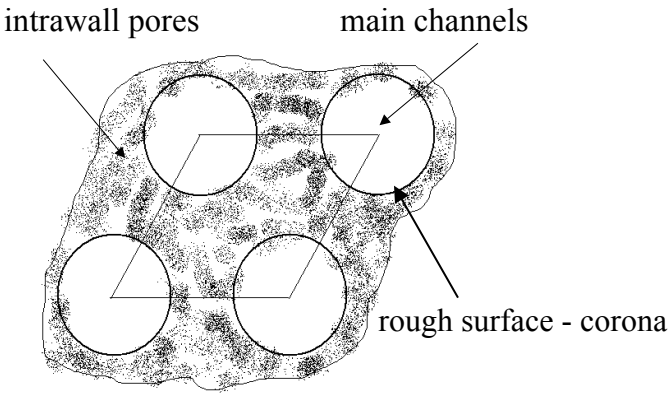
QSDFT prediction of situ XRD: Ar on MCM-41 - 2D *p6mm* crystal

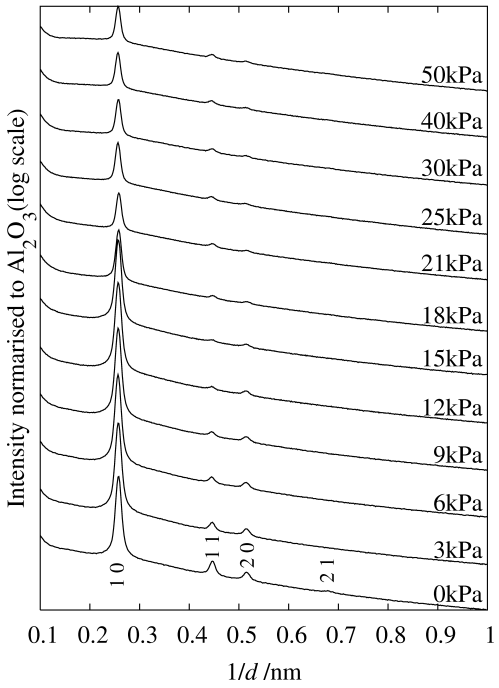




Density map for dry sample:
pore diameter D=3.68 nm
roughness parameter, δ=0.4 nm

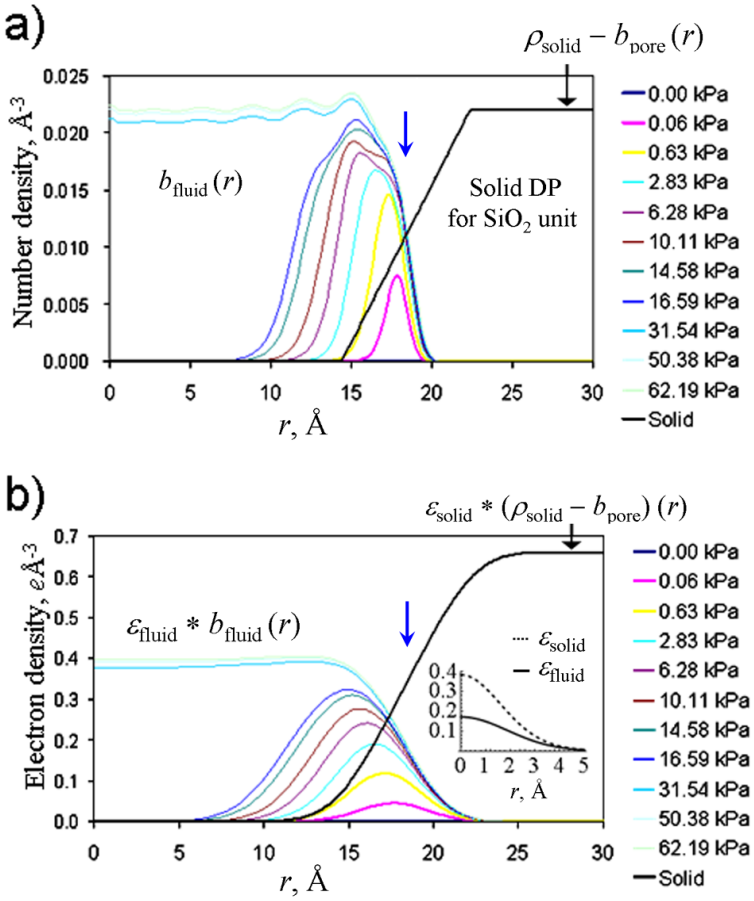
Miyasaka, Neimark, & Terasaki, - JPCC, 2009, 113, 791

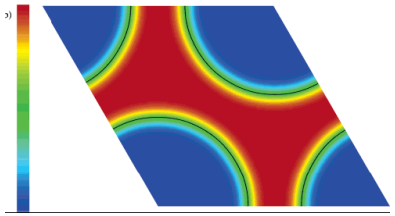




XRD patterns

QSDFT prediction of in-situ XDR data



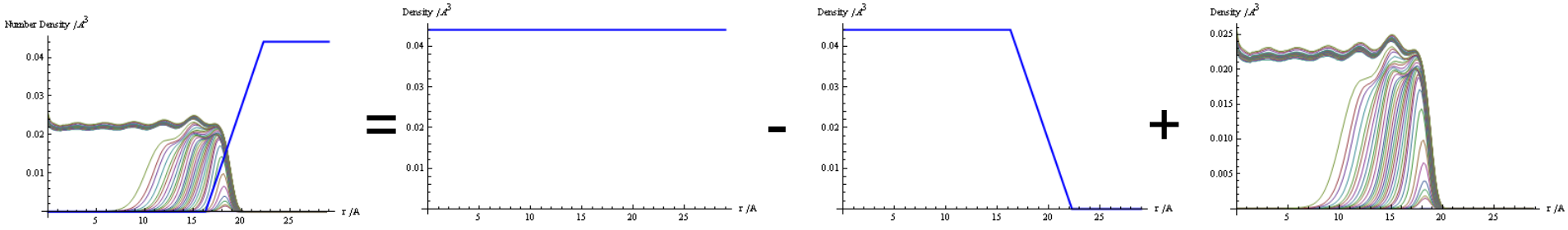


Ar@MCM-41

(a) QSDFT Ar density profiles (b) electron density profiles.
Inset: kernel for the electron spread of solid and fluid
Pore diameter D=36.8A; roughness parameter, δ=4A; temperature T= 83K.
Blue arrows indicate the position of the mean pore radius, 18.4 Å.

Miyasaka, AVN, & Terasaki, - JPCC, 2009, 113, 791

In-situ XRD: Form Factor from QSDFT



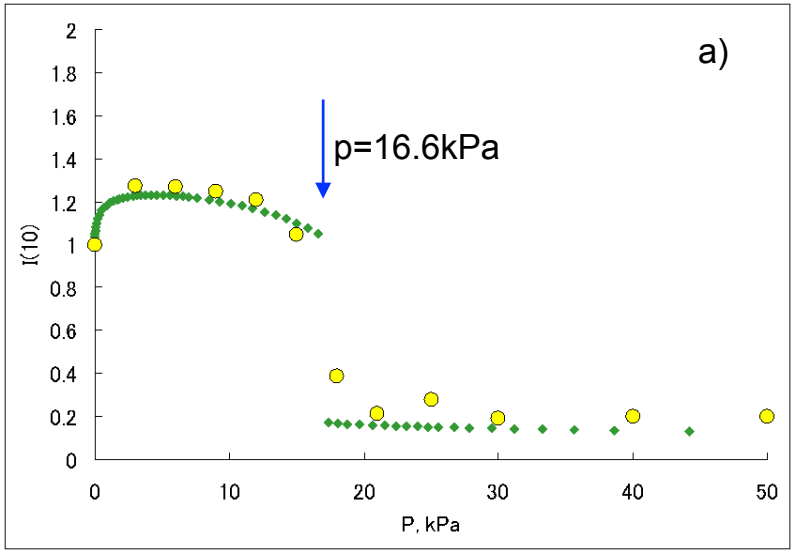
$$f(r) = \rho_{\text{wall}} - b_{\text{pore}}(r) + b_{\text{adsorbate}}(r)$$

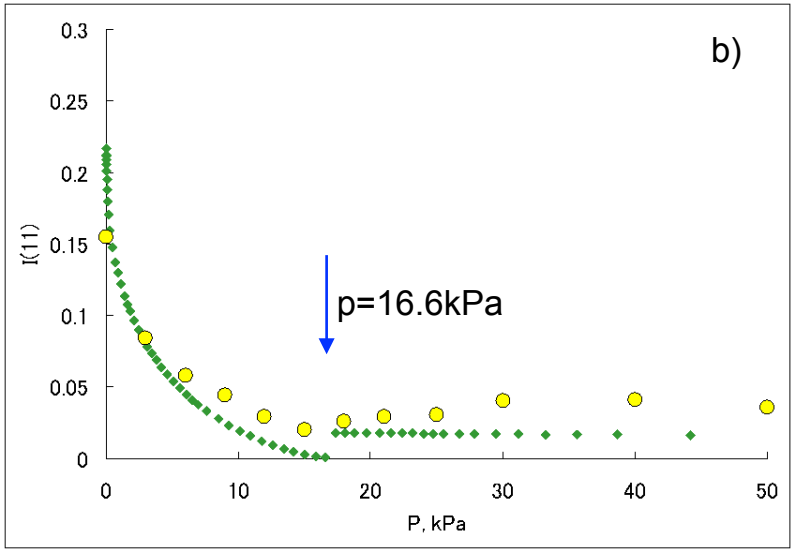
Fourier Transform for cylindrical object : $FT\left[obj(r)\right](q) = \int_0^\infty dr\ 2\pi r \cdot obj(r) \cdot J_0(2\pi q r)$

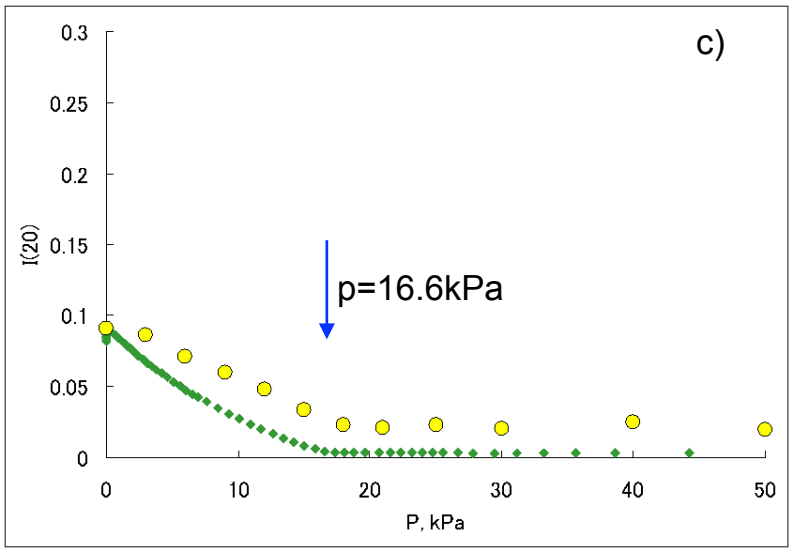
$$F(q) = \rho_{\text{wall}} \cdot \delta_{\text{Dirac}}(q) - B_{\text{pore}}(q) + B_{\text{adsorbate}}(q)$$

Miyasaka, Neimark, & Terasaki, - JPCC, 2009, 113, 791

QSDFT prediction of XRD intensities





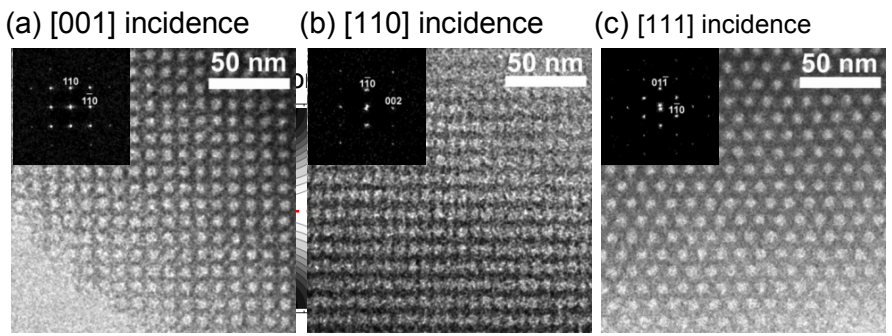


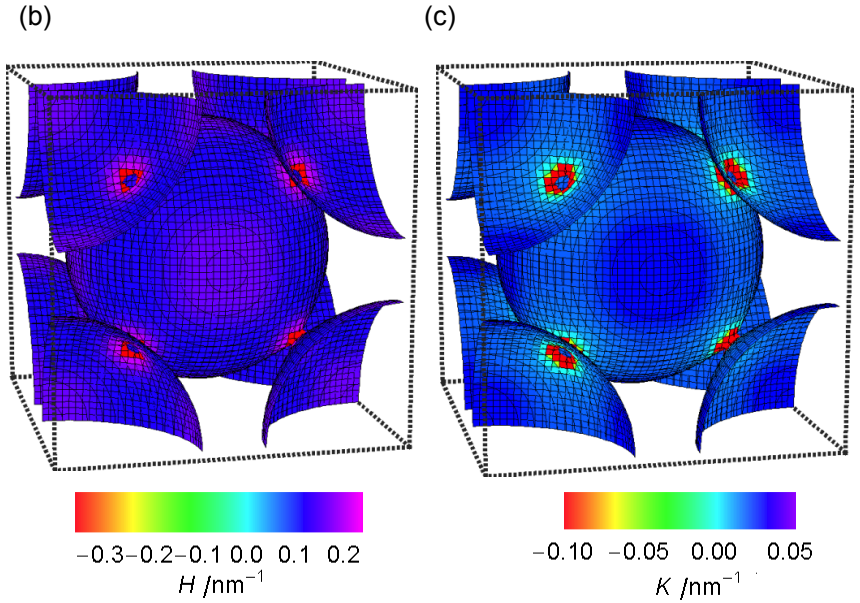
◆ Predicted by QSDFT

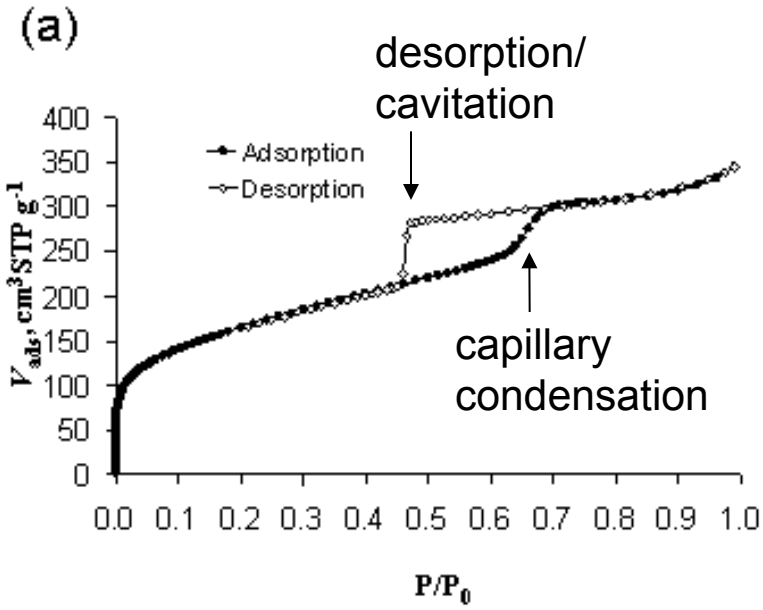
○ Experimental XRD

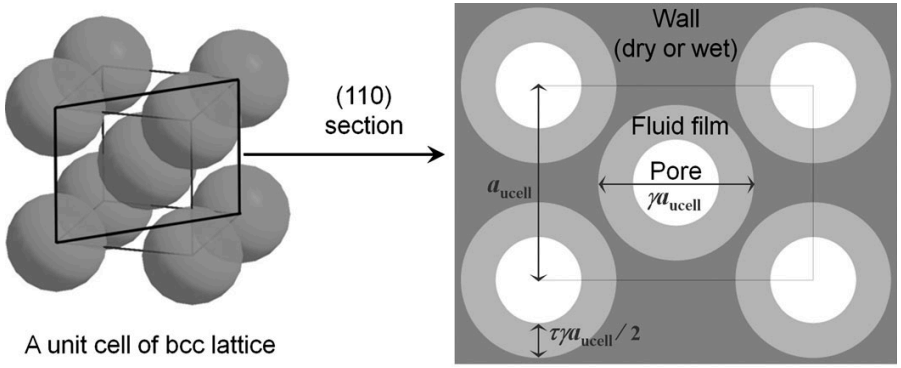
Miyasaka, AVN, & Terasaki, - JPCC, 2009, 113, 791

Adsorption on micro-mesoporous SBA-16 - *Im*-3*m* crystal.





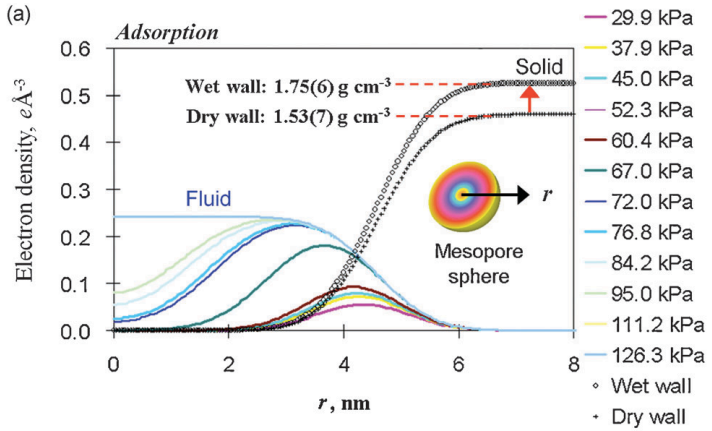


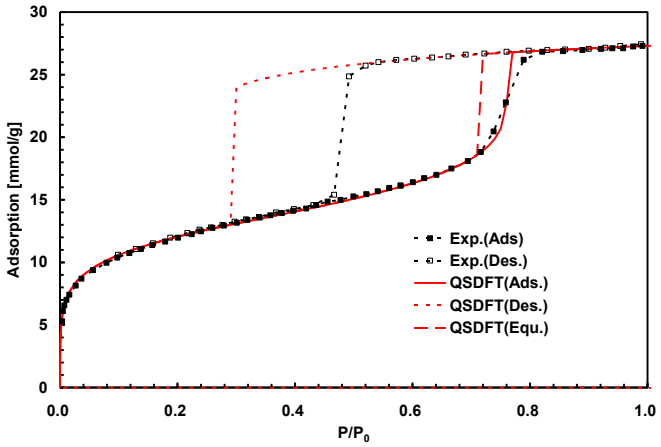


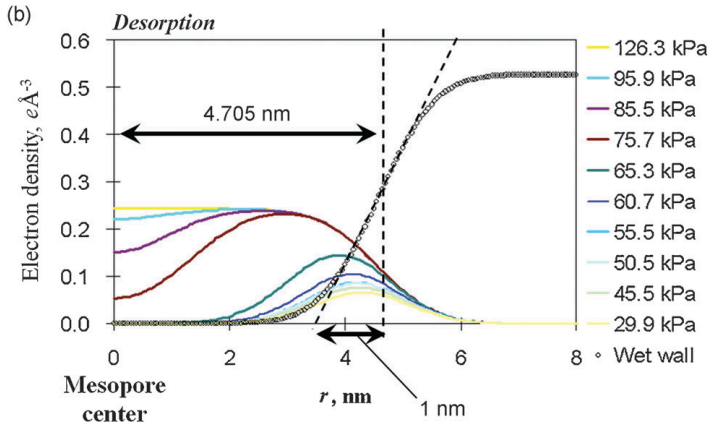
A unit cell of bcc lattice

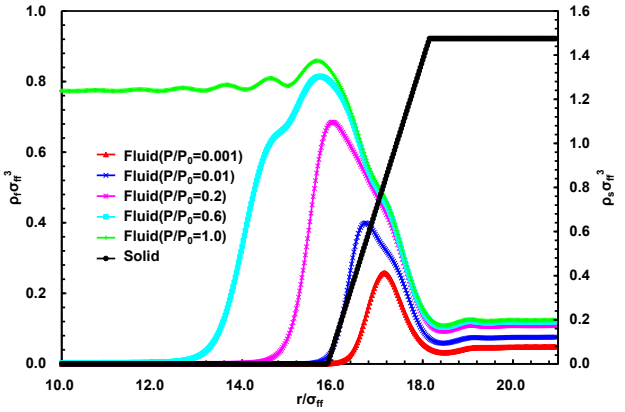
Miyasaka et al, Chem. Eur. J. 2012, 18, 10300 – 10311

Adsorption on micro-mesoporous SBA-16 – QSDFT and experiment









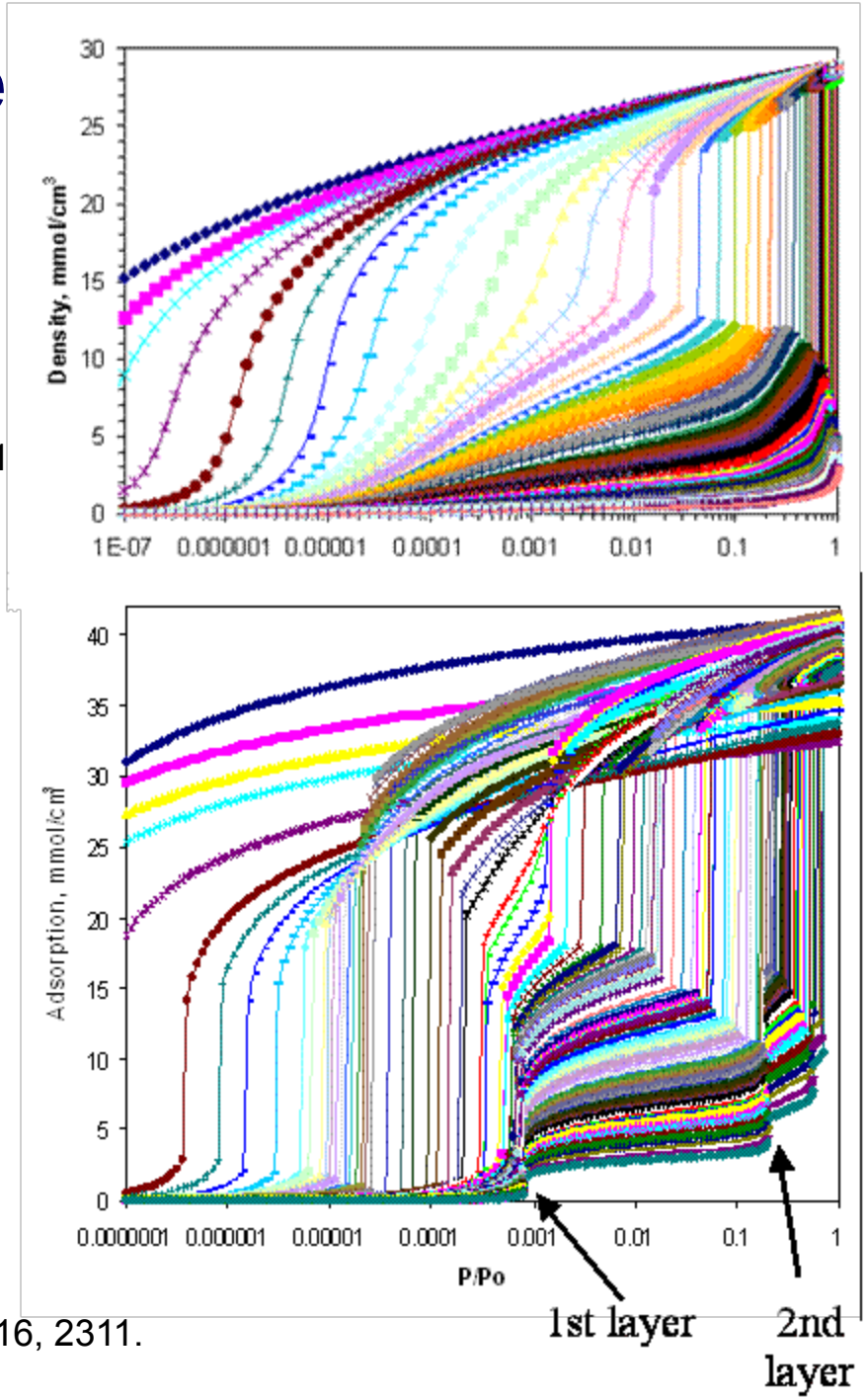
Ar@87.3K – QSDFT with structural parameters taken from XRD predicts adsorption isotherm without adjustable parameters

Miyasaka et al, Chem. Eur. J. 2012, 18, 10300 – 10311

QSDFT method for pore size characterization

QSDFT kernel in slit-shaped pores

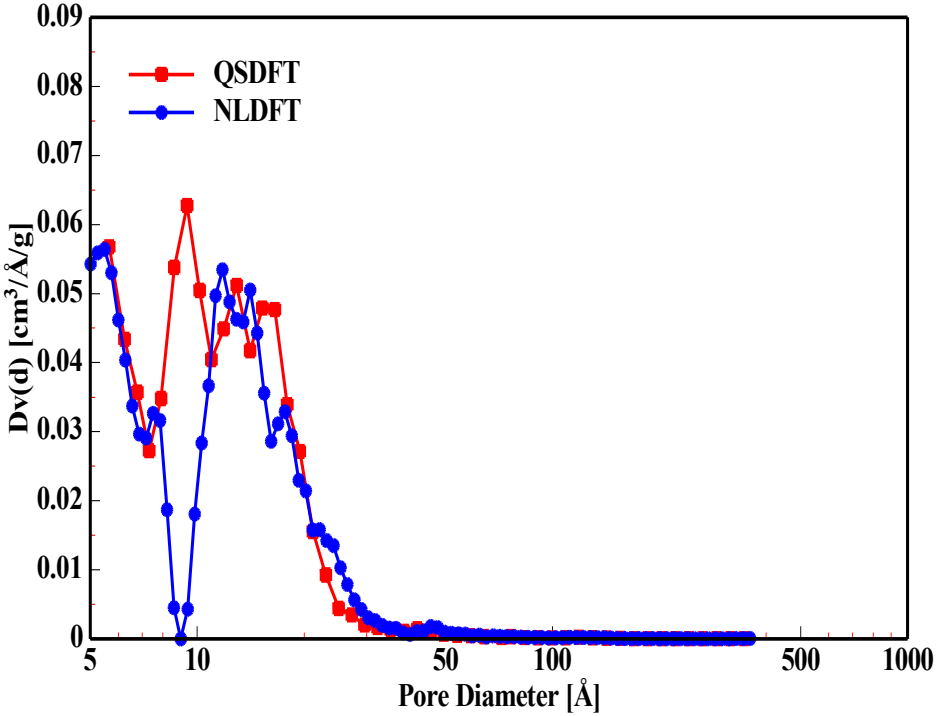
AVN, Lin, Ravikovitch, & Thommes, Carbon, 2009, 47, 161

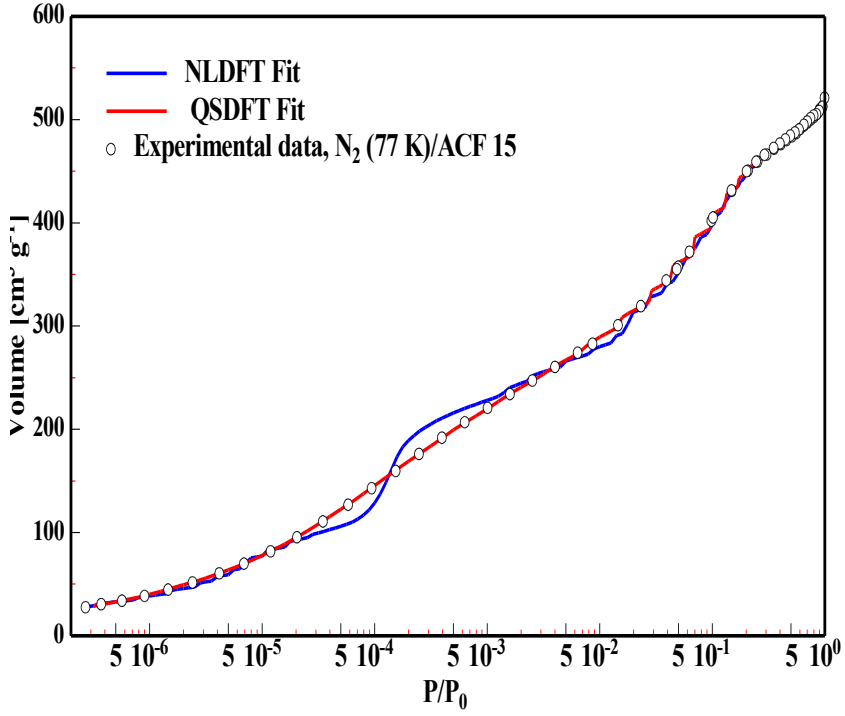


NLDFT kernel

Ravikovitch, Vishnyakov, Russo, & AVN, Langmuir, 2000, 16, 2311.

QSDFT vs. NLDFT: ACF-15, N2@77K

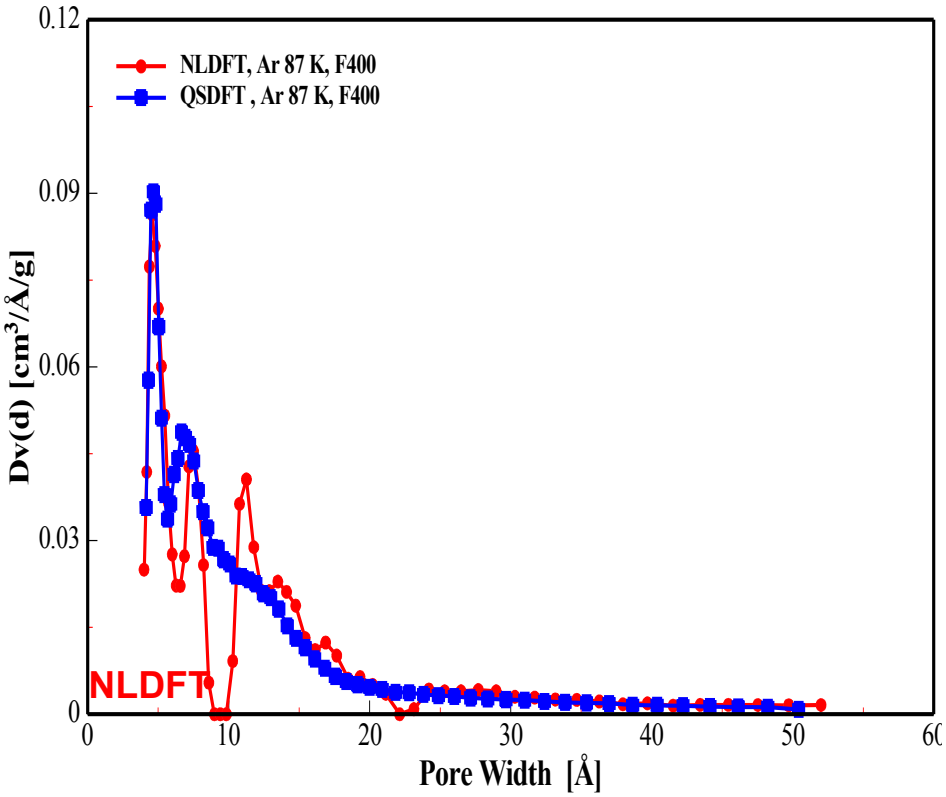


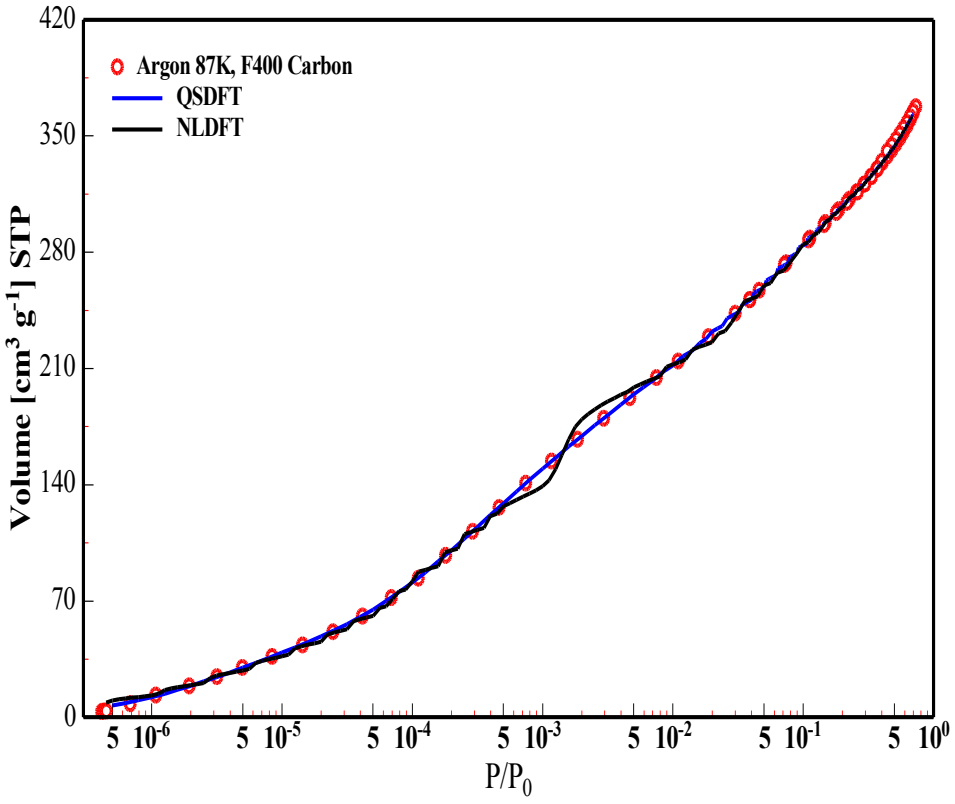


Activated carbon fiber ACF-15
(sample from Osaka Gas, Japan,).

Neimark, Lin, Ravikovitch, Thommes, Carbon, 2009, V.47, 161.

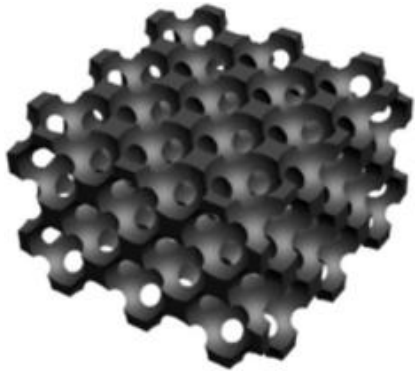
QSDFT vs NLDFT: Filtrasorb carbon F400, Ar @ 87 K

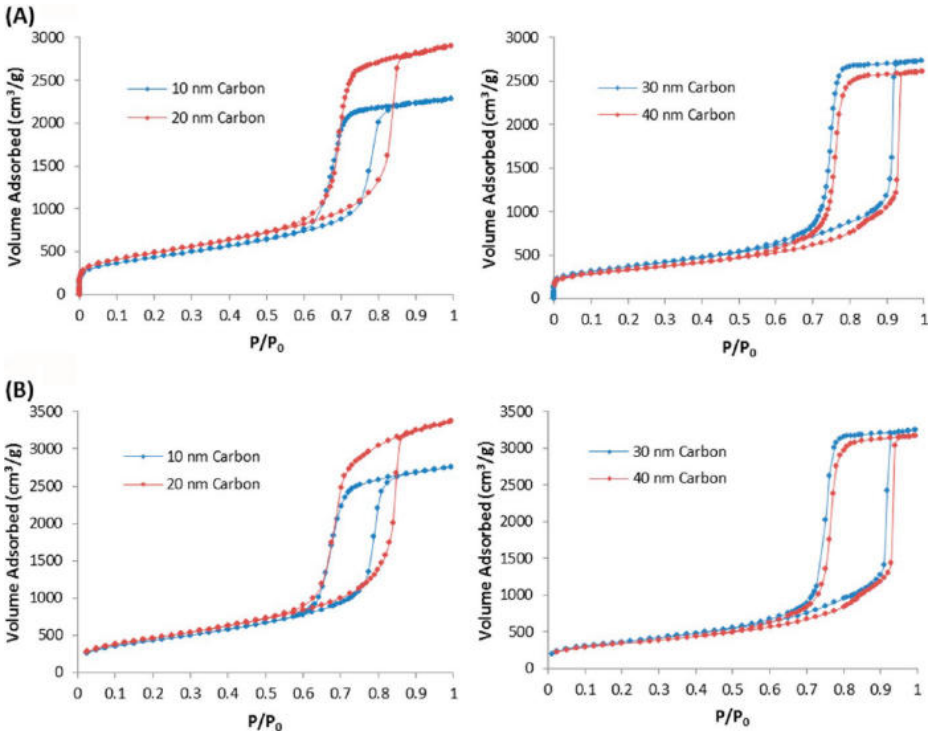


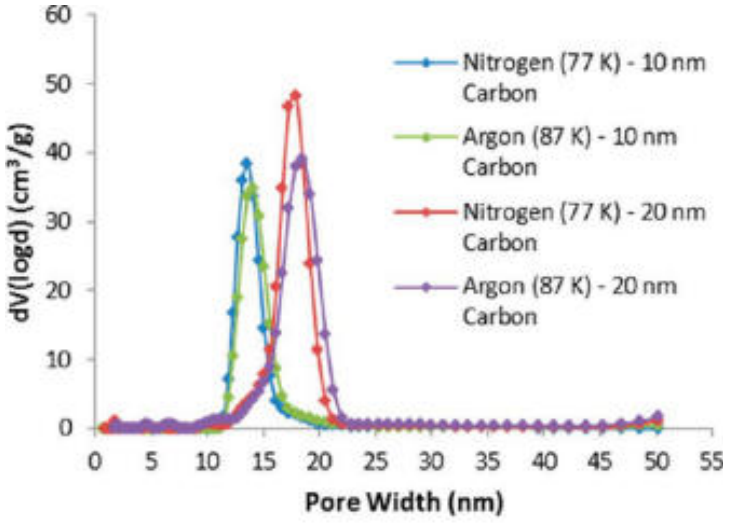


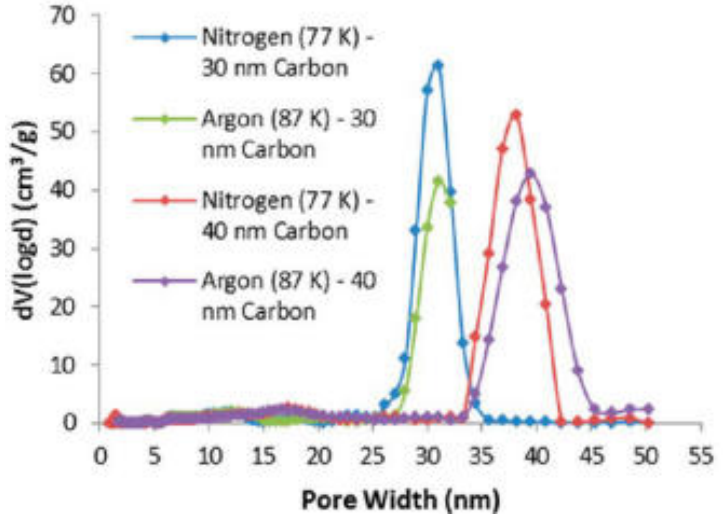
Neimark, Lin, Ravikovitch, Thommes, Carbon, 2009, V.47, 161.

QSDFT model for spheroidal pores: 3DOm carbons



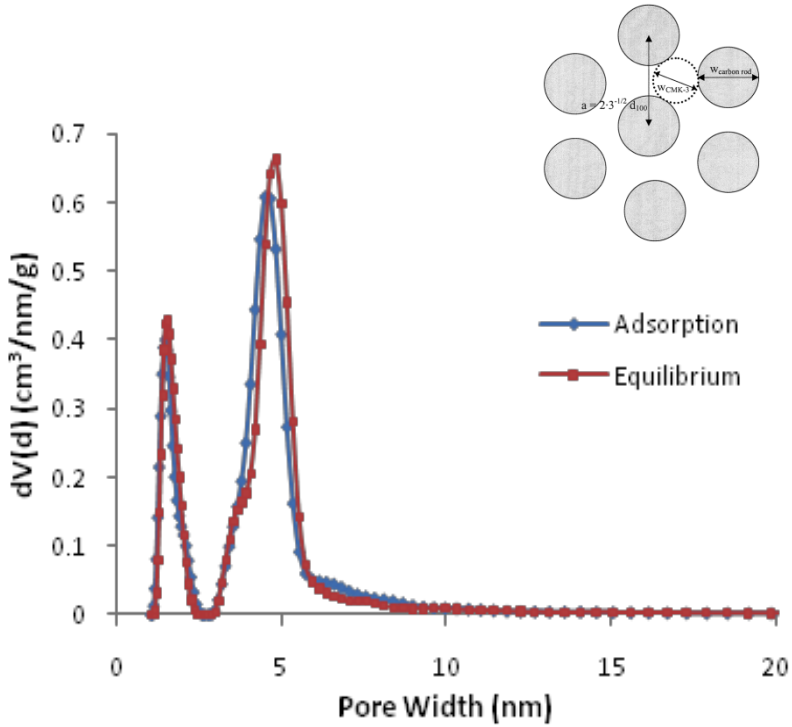


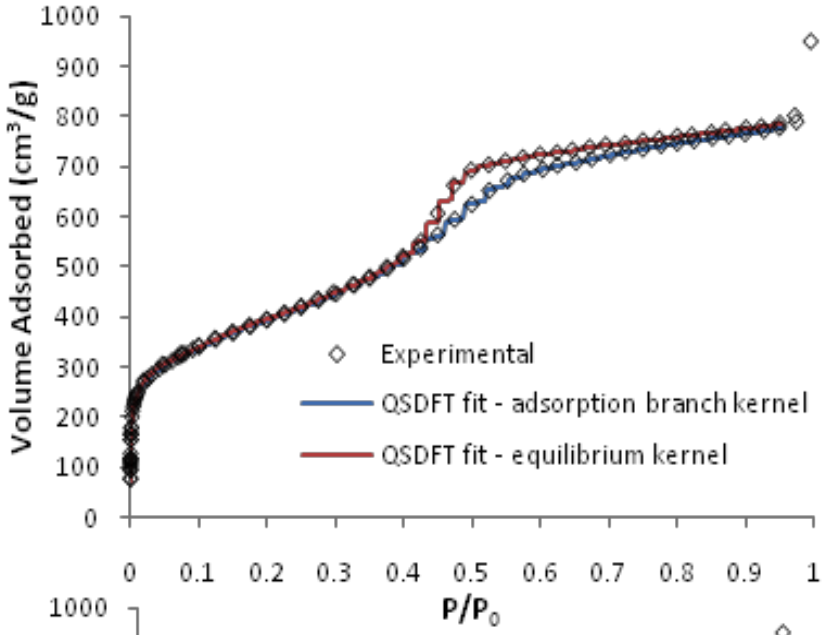


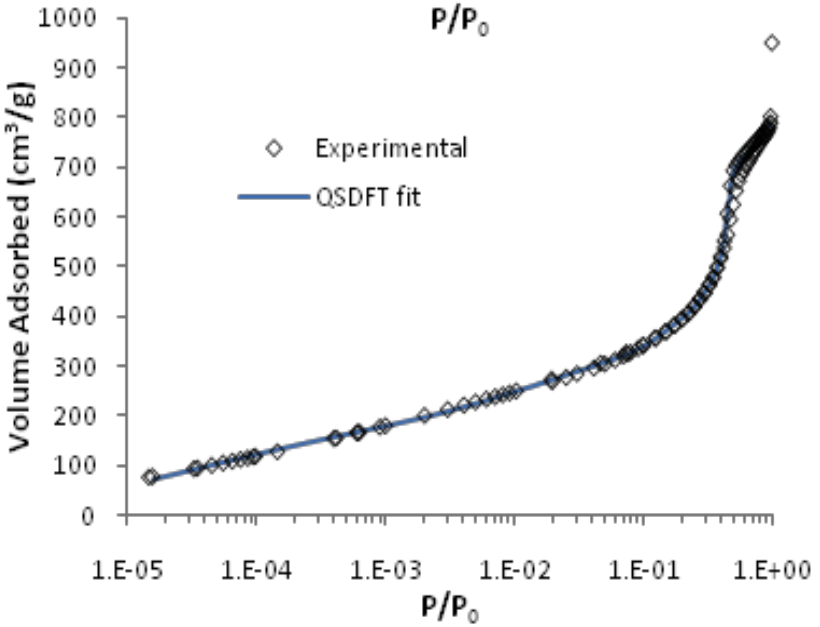


Cychosz et al, Langmuir, 2012. 22, 12647

QSDFT for cylindrical pores: micro-mesoporous CMK-3



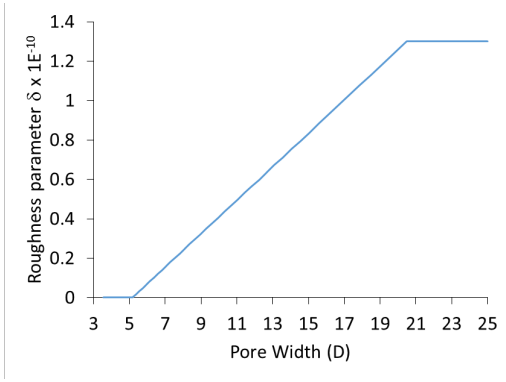


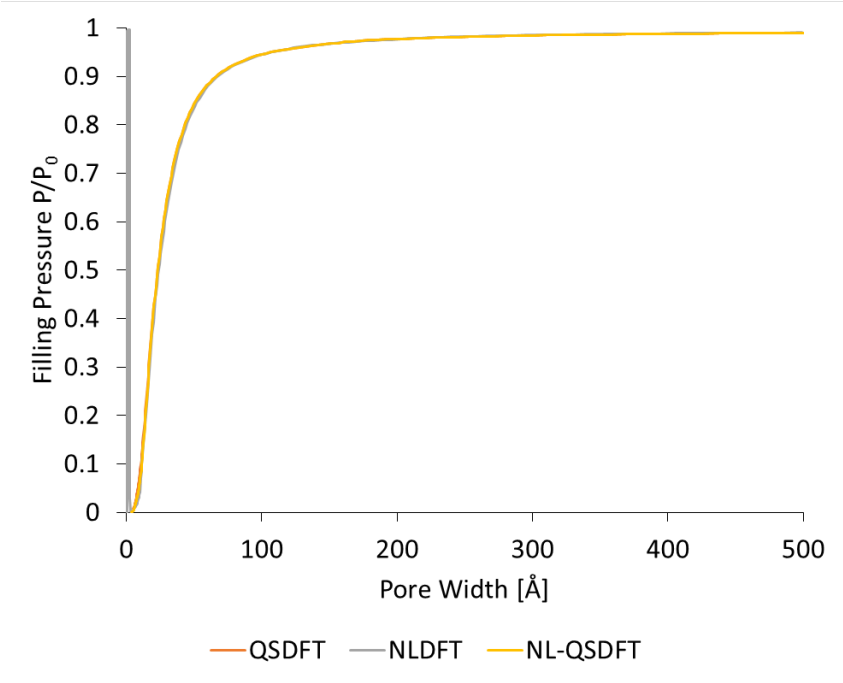


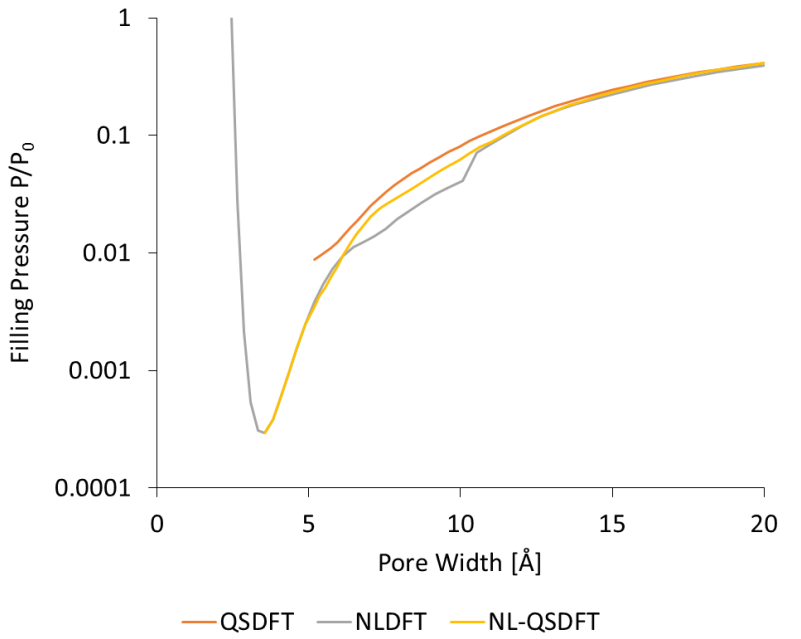
Gor, Thommes, Cychosz, and AVN, Carbon, 2012, 50, 583.

CO_2 High Pressure Isotherms for Carbon Characterization. Pore range from 0.36 to 50 nm: Hybrid kernels – NL-QS-DFT

QSDFT with fixed roughness parameter in mesopores > 2 nm
NLDFT in smallest micropores < 0.5 nm
QSDFT with linear dependence of roughness parameter on the pore size in 0.5-2 nm pores



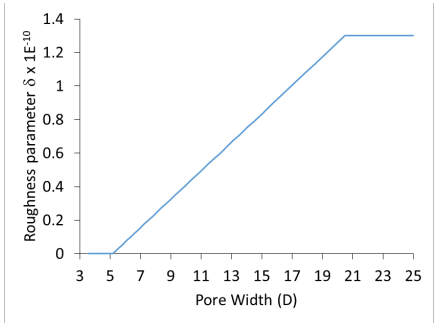




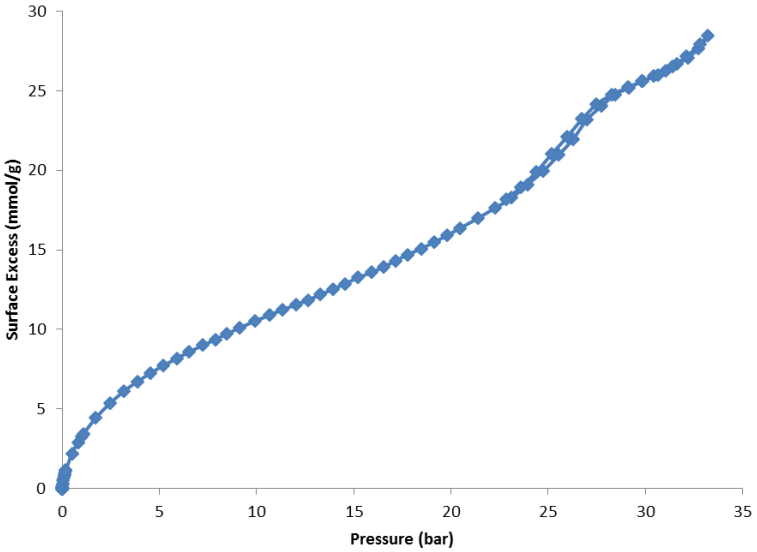
CO_2 High Pressure Isotherms for Carbon Characterization: pore range from 0.36 to 50 nm

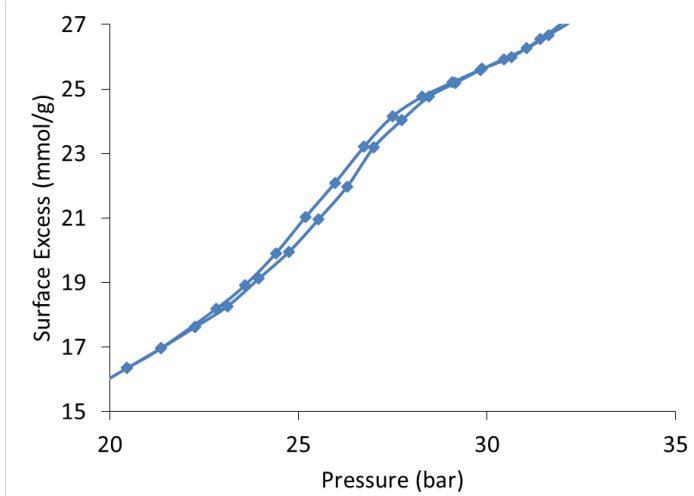
Hybrid NL-QS-DFT Kernels for Slit and Cylindrical Pore Geometries

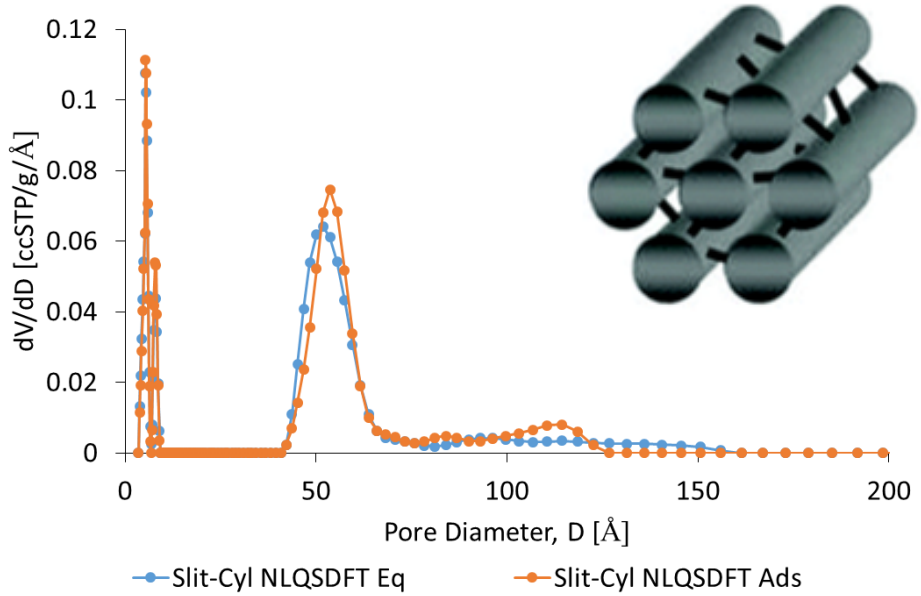
- Slit pores - Equilibrium hybrid NL-QS-DFT
  - 3.56-4.88Å - NLDFT,
    5.17-20.5Å - QSDFT (linear increase of roughness with the pore size), 21.2-502.3Å - QSDFT (constant roughness)
- Cylindrical pores - Equilibrium QSDFT
  - Pore widths: 5.17-502.3Å - QSDFT, constant roughness
- Hybrid Slit-Cylindrical pores - Equilibrium NL-QS-DFT
  - 3.56-4.88Å – NLDFT in slit pores,
    5.17-20.5Å – QSDFT in slit pores (linear increase of roughness with the pore size),
    21.2-502.3Å – QSDFT in cylindrical pores (constant roughness)
- Hybrid Slit-Cylindrical pores - Adsorption NL-QS-DFT
  - 3.56-4.88Å – NLDFT in slit pores,
    5.17-20.5Å – QSDFT in slit pores (linear increase of roughness with the pore size),
    21.2-502.3Å – QSDFT in cylindrical pores (constant roughness)

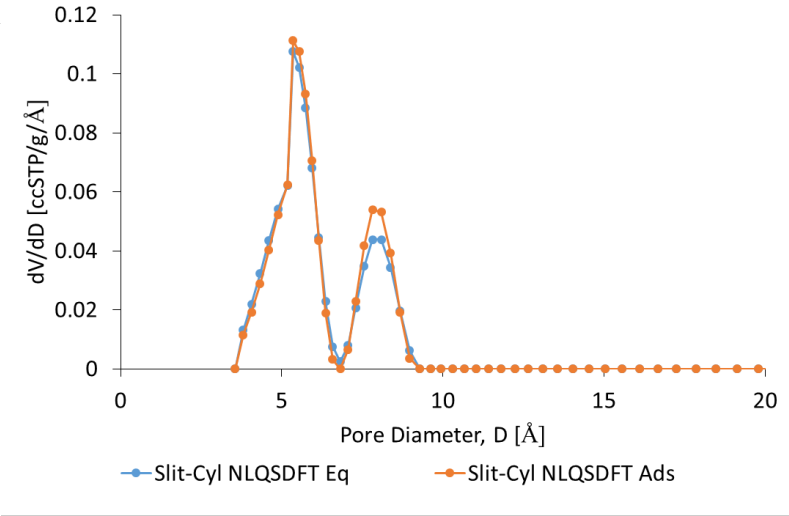


CMK-3: PSDs – Full Pore Range; 0.36 to 50 nm

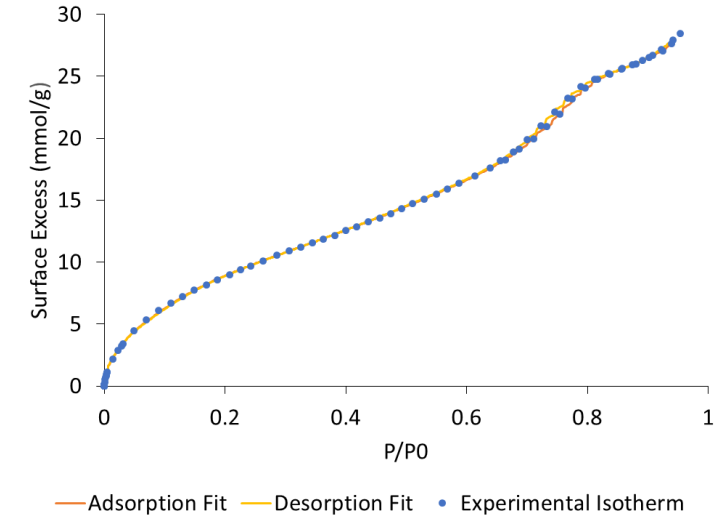


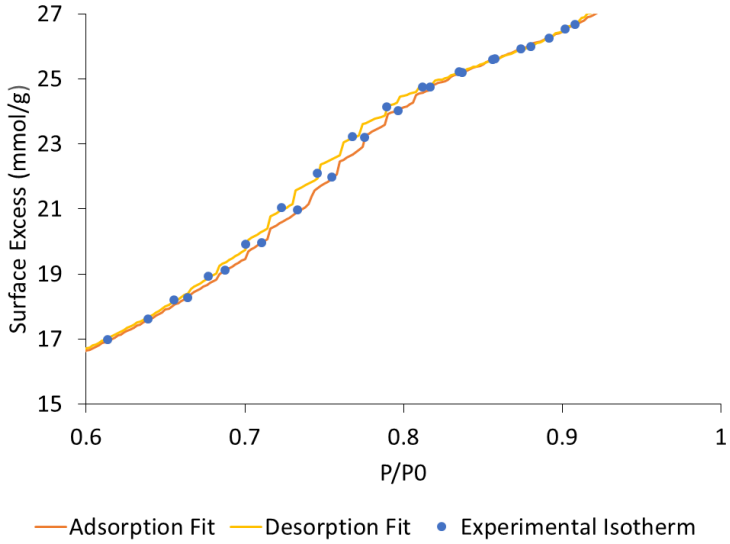


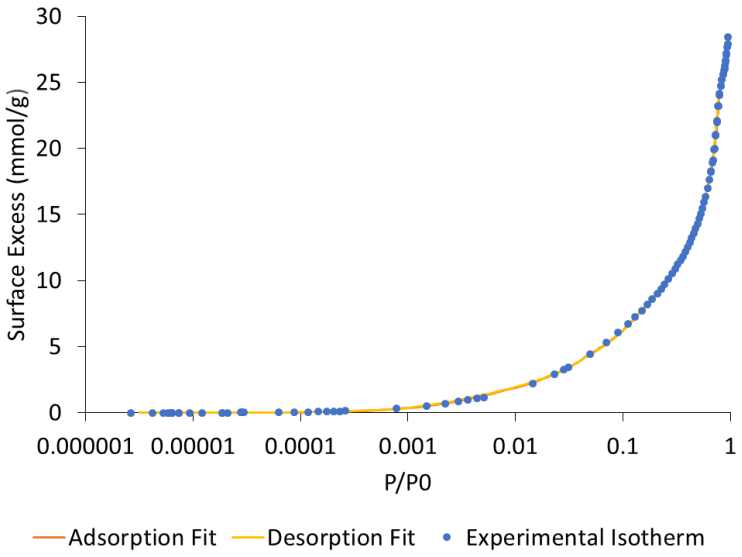




CMK-3: isotherm fitting







Summary

- Quenched Solid Density Functional Theory (QSDFT) of adsorption on heterogeneous and microporous surfaces
  - Solid enters the model as a quenched component with given density distribution rather than a source of an external potential
  - Systematic account for the surface roughness and microporosity
  - Solid density profile can be taken from independent XRD data
- QSDFT provides a unified approach to interpreting adsorption and XRD
  - Good agreement with in situ XRD measurements
- QSDFT provides a qualitative description of adsorption deformation in micro- and mesoporous materials
- QSDFT method for pore size distribution calculations eliminates artifacts of NLDFT and other conventional theories, which are based on smooth wall pore models
- Library of QSDFT kernels for micro- and mesoporous carbons of various morphology based on N_2 and Ar low temperature isotherms
- New development – CO_2 high pressure isotherms for pore size characterization in the whole rage of micro- and mesopores, 0.36 – 50 nm

Acknowledgements

Support: NSF, ARO, Quantachrome Instruments

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P.I. Ravikovitch and A. V. Neimark, - Density Functional Theory Model of Adsorption on Amorphous and Microporous Silica Materials, – Langmuir, 2006, V.22, 10864-10868.

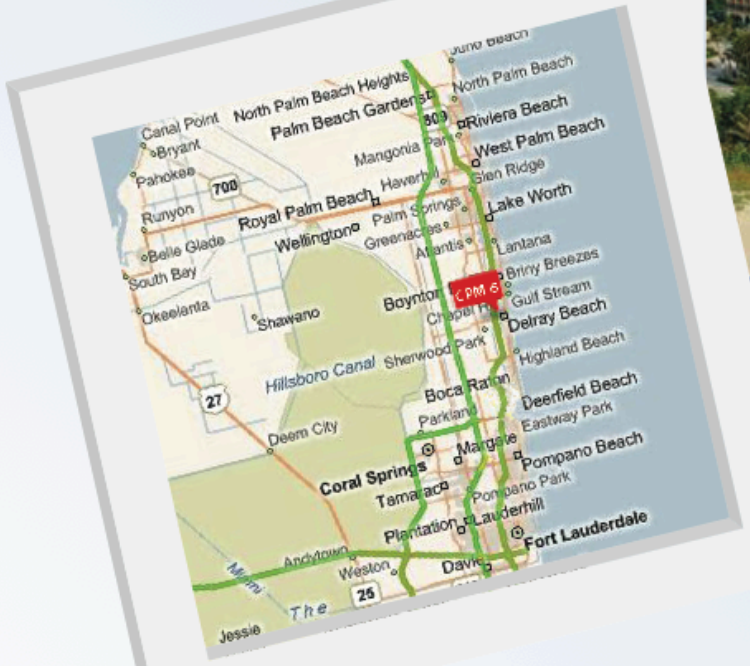
Potential Projects

1. Advanced DFT models for *in-situ* studies of adsorption phenomena with scattering techniques with the focus on the influence of external stimuli on material deformation and adsorption induced phase transformations
2. Development of material-specific methods for pore structure characterization from adsorption data (shale, other geosorbents, new materials, e.g. MOFs)
3. Use non-standard adsorbates (water, toluene, hydrogen, methane) beyond N2, Ar, and CO2 for pore structure characterization
4. Advance the realistic structural models of porous structures (chemical heterogeneity, 3D reconstruction, etc)

CPM 7 7TH International Workshop

"Characterization of Porous Materials: From Angstroms to Millimeters"

May 3 - May 6, 2015
Marriott Hotel, Delray Beach, Florida, USA



Workshop Chair:
Professor Alexander V. Neimark, Rutgers University
aneimark@rutgers.edu

Workshop Vice-Chair:
Dr. Matthias Thommes, Quantachrome Corporation
matthias.thommes@quantachrome.com

Important Deadlines

October 1, 2014 - abstract submission.
December 1, 2014 - notification of acceptance.
February 1, 2015 - discounted early registration.
March 31, 2015 - discounted hotel reservation at the Delray Beach Marriott.
April 10, 2015 - regular registration.
May 3, 2015 - on-site registration and welcome reception.