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

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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\textsubscript{2} and Ar low temperature isotherms
• New development – CO\textsubscript{2} high pressure isotherms for pore size characterization in the whole range of micro- and mesopores, 0.36 – 50 nm
DFT for Inhomogeneous Fluids

• Grand Canonical $\mu$-V-$T$ ensemble: an open system of volume $V$ within solid walls at constant temperature $T$ and chemical potential $\mu$

• 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,

$$
\Omega[\rho(r)] = F[\rho(r)] - \mu \int \rho(r) dr \Rightarrow \text{min}
$$

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

$$
\mu = \frac{\partial F}{\partial \rho}
$$
Non-Local Density Functional Theory (NLDFT)

Grand potential functional:

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

Helmholtz free energy functional:

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

- Repulsive part
- Mean field attractive contributions

NLDFT: Instead of local fluid density employ smoothed density

Smoothed density:

$$\bar{\rho}(r) = \int d\mathbf{r}' \rho(r') \left[ w_0(|r-r'|) + w_1(|r-r'|) \bar{\rho}(r) + w_2(|r-r'|) \bar{\rho}(r)^2 \right]$$
Modeling adsorption in pores with smooth walls

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

\[ U_{sf}(z) = 2\pi \rho_s \epsilon_{sf} \sigma_{sf}^2 \Delta \left[ \frac{2}{5} \left( \frac{\sigma_{sf}}{z} \right)^{10} - \left( \frac{\sigma_{sf}}{z} \right)^4 \right] \]  

\[ U_{sf, pore}(z) = U_{sf}(z) + U_{sf}(H_{cc} - z) \]

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

\[ U_{ff}(r) = 4\epsilon_{ff} \left[ \left( \frac{\sigma_{ff}}{r} \right)^{12} - \left( \frac{\sigma_{ff}}{r} \right)^6 \right] \]
Adsorption Process on a Molecularly Smooth Surface implies Formation of Adsorbed Layers – Major Artifact of Traditional Models
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Layering in Smooth Surface Models: MC and DFT

9 nm pore, N\textsubscript{2}@77K

3.4 nm pore, Ar@87K
Adsorption on MCM-41 and SBA-15: NLDFT and Experiment

Ar at 87 K

N₂ at 77 K

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


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

Experimental adsorption isotherm

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
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)


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 Å 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 \( \delta \) – semi-width of the density profile
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

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

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,

$$\Omega[\rho_{\text{fluid}}(r), \rho_{\text{solid}}(r)] = F[\rho_{\text{fluid}}(r), \rho_{\text{solid}}(r)] - \mu \int_\nu \rho_{\text{fluid}}(r) dr \Rightarrow \text{min}$$

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

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

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

Ravikovitch and AVN, Langmuir, 2006, 22, 10864
Density profiles: LJ fluid near 9-3 and amorphous walls

Roughness parameter $\delta=0.4$ 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$^2$

Roughness parameter $\delta=0.24$ nm. No additional adjustable parameters!
Prediction of Kr adsorption on SBA-15@119K from XRD data

Roughness parameter $\delta$ = 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

\[ q_{st}^{\text{des}} = \frac{RT_1 T_2}{T_2 - T_1} (\ln P_2 - \ln P_1)_N. \]

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, $\delta=0.4$ nm
Miyasaka, Neimark, & Terasaki, - JPCC, 2009, 113, 791
QSDFT prediction of in-situ XDR data

(a) QSDFT Ar density profiles   (b) electron density profiles.
Inset: kernel for the electron spread of solid and fluid
Pore diameter $D=36.8\,\text{Å}$; roughness parameter, $\delta=4\,\text{Å}$; temperature $T=83\,\text{K}$.
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:

\[ FT \left[ \rho_{\text{obj}}(r) \right](q) = \int_0^\infty dr \ 2\pi r \cdot \rho_{\text{obj}}(r) \cdot J_0(2\pi qr) \]

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

Miyasaka, Neimark, & Terasaki, - JPCC, 2009, 113, 791
QSDFT prediction of XRD intensities

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

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

QSDFT method for pore size characterization

QSDFT kernel in slit-shaped pores
AVN, Lin, Ravikovitch, & Thommes, Carbon, 2009, 47, 161

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

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

QSDFT model for spheroidal pores: 3DOm carbons

QSDFT for cylindrical pores: micro-mesoporous CMK-3

Gor, Thommes, Cychosz, and AVN, Carbon, 2012, 50, 583.
CO₂ 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

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References


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)
7th International Workshop
“Characterization of Porous Materials: From Angstroms to Millimeters”

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

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.

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