

Understanding Adsorption/Desorption Hysteresis for Fluids in Mesoporous Materials using Simple Molecular Models and Classical Density Functional Theory

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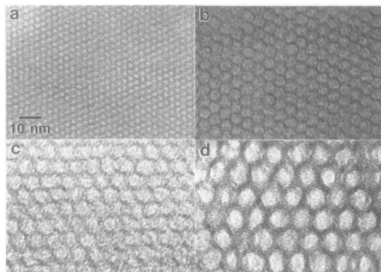


Impact of Classical Density Functional Theory in Modeling Confined Fluid Properties

DFT allows calculation of the density distribution and thermodynamics for confined fluids from a model of pore structure and molecular interactions

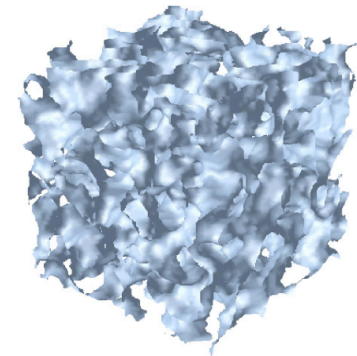
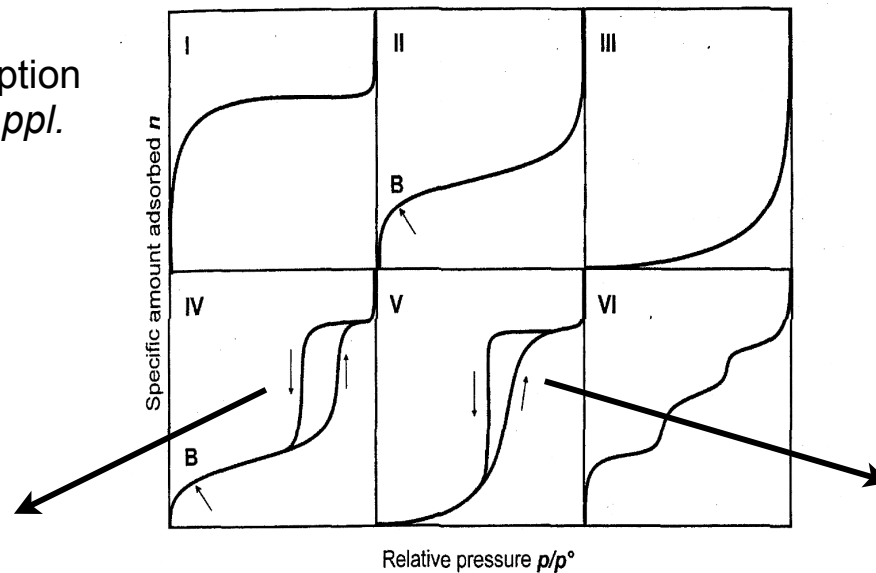
- a powerful complement to experimental characterization methods

IUPAC classification of adsorption isotherms (Sing et al., *Pure Appl. Chem.*, 57, 603 (1985))



Independent pores
(e.g. ordered mesoporous materials)

Beck et al., *J. Am. Chem. Soc.*, 114, 10834 (1992)



Complex pore networks
(e.g. porous glasses and other disordered materials)

Woo and Monson, *Phys. Rev. E*, 67, 041207 (2003)



Outline

- Classical density functional theory of fluids in porous materials
 - *basics*
 - *lattice gas models*
- Understanding Hysteresis
 - *single pore*
 - *inkbottle*
 - *distribution of independent pores*
 - *porous Vycor glass*
- Dynamic Mean Field Theory
 - *a theory of dynamics consistent with DFT*

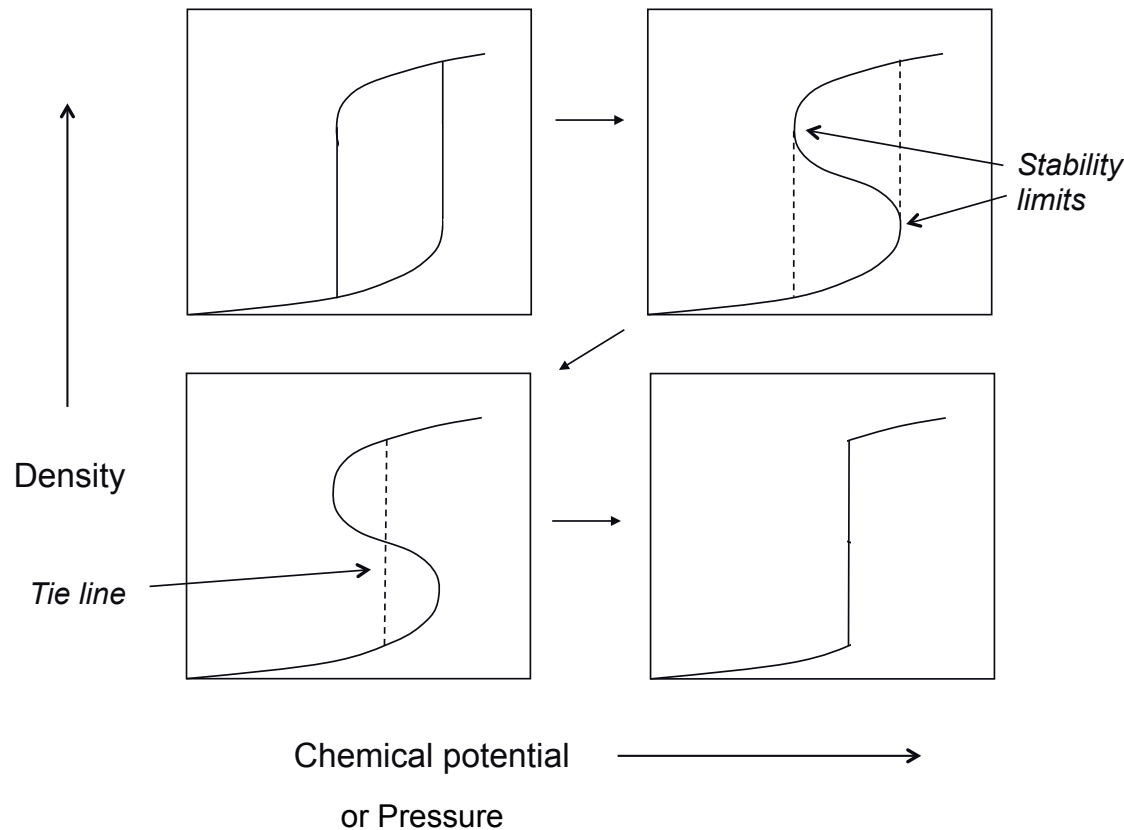


Classical Density Functional Theory I

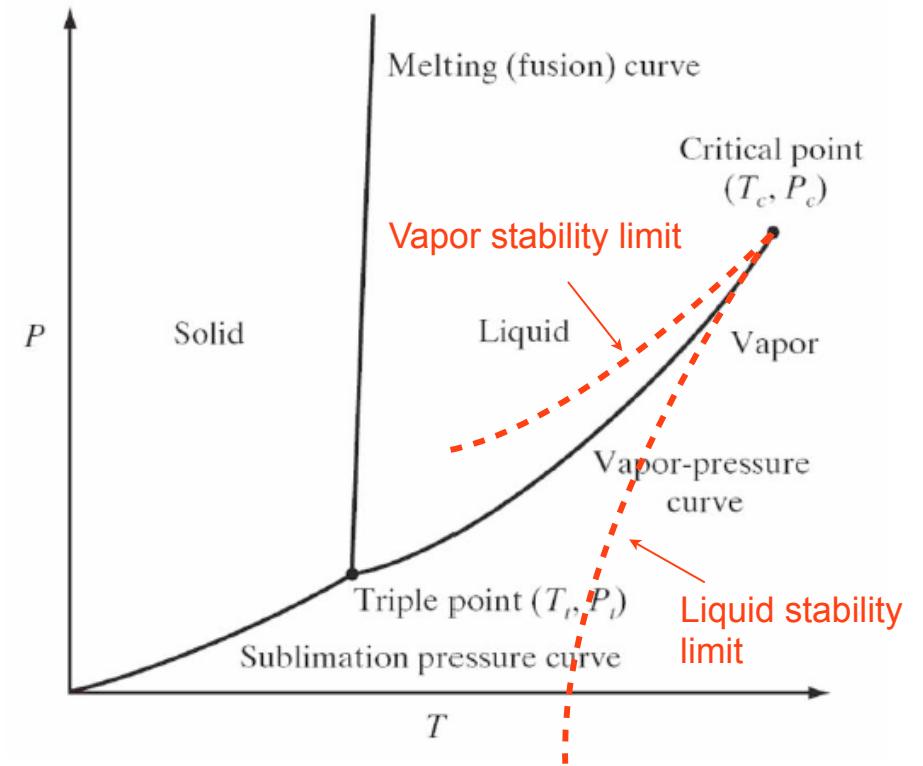
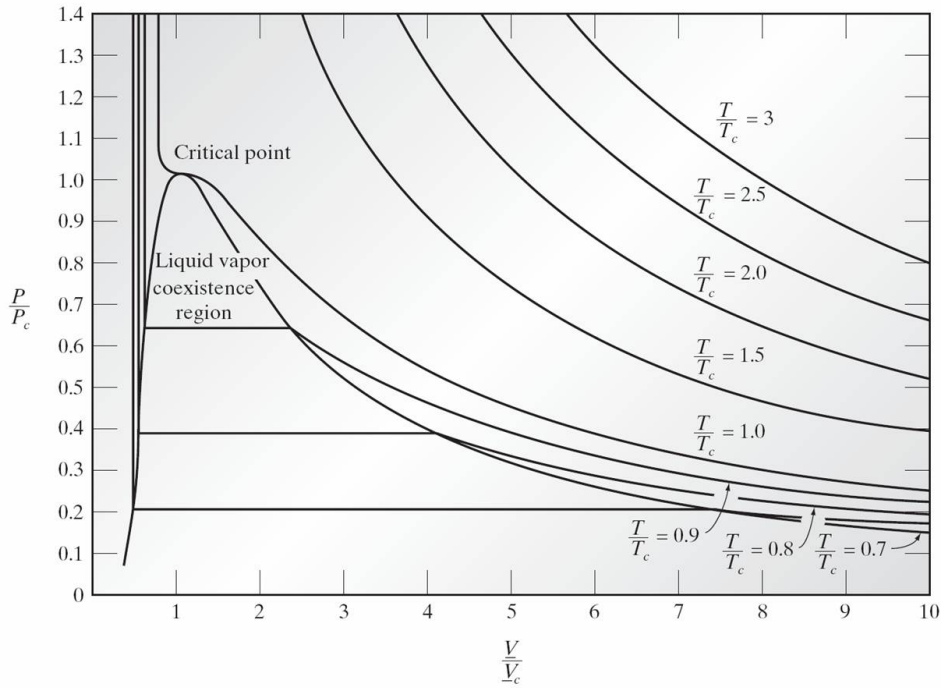
For bulk fluids calculations of phase equilibrium start with knowledge of Helmholtz free energy, $F(\rho, T)$, from which we can determine the pressure, $P(\rho, T)$, and the chemical potential $\mu(\rho, T)$.

$$F(\rho, T) / N = F_{HS} / N - a\rho$$

van der Waals / mean field theory



Bulk phase diagram in vapor-liquid coexistence region in mean field theory



From S. I. Sandler, Chemical, Biochemical and Engineering Thermodynamics, Wiley, 2006



Classical Density Functional Theory II

For a system with interfaces (solid-fluid, vapor-liquid, etc.) the density is inhomogeneous so we focus on the Helmholtz energy functional, $F[\rho]$.

$$F[\rho] = F^{int}[\rho] + \int d\mathbf{r} \rho(\mathbf{r}) \phi(\mathbf{r})$$

$F^{int}[\rho]$ is the intrinsic Helmholtz free energy functional.

In mean field theory

$$F^{int}[\rho] = F_{hs}^{int}[\rho] + \frac{1}{2} \int \int d\mathbf{r}' d\mathbf{r}'' \rho(\mathbf{r}') \rho(\mathbf{r}'') u(|\mathbf{r}' - \mathbf{r}''|)$$

$F_{hs}^{int}[\rho]$ is the intrinsic Helmholtz free energy functional for a system of hard spheres (Tarazona, Rosenfeld ...)



Classical Density Functional Theory III

For fluids in porous materials at fixed chemical potential, μ , we focus on the grand free energy

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

We determine the grand free energy and by minimizing with respect to functional variations in the density distribution

$$\left(\frac{\delta \Omega}{\delta \rho(\mathbf{r})} \right)_{\mu, \phi, T} = 0$$

Can also solve for $\rho(\mathbf{r})$ at fixed N, ϕ, T by minimizing F , with μ as a Lagrange multiplier for the fixed N constraint

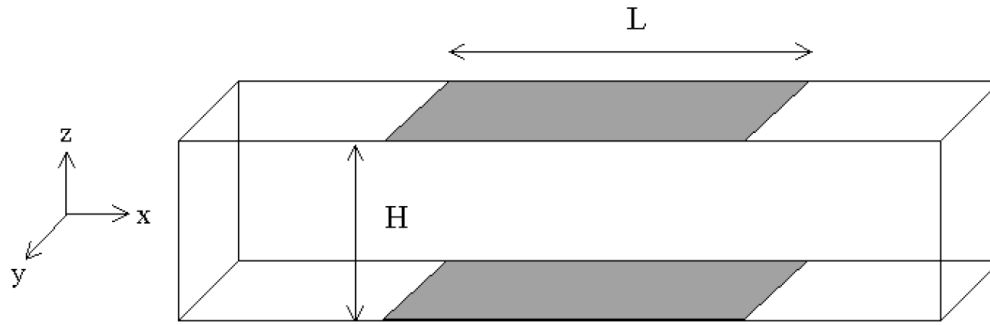
Very efficient for problems with 1-D density distribution, e.g. a fluid in an infinite cylinder

Calculations become expensive in 2-D and 3-D

– *motivates the use of lattice gas models*

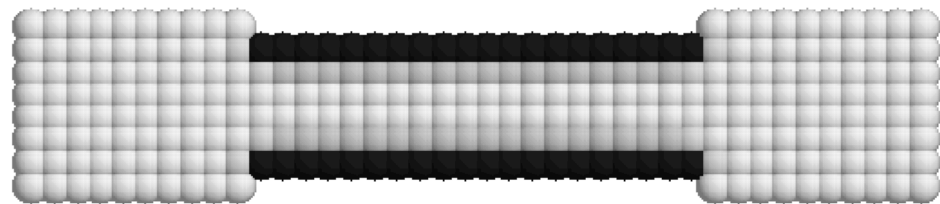


Lattice Gas Model of a Fluid in an Open Slit Pore



- System infinite in y - direction
- Nearest neighbor surface field

Visualization of density distribution for lattice gas model for state with monolayers on the pore walls



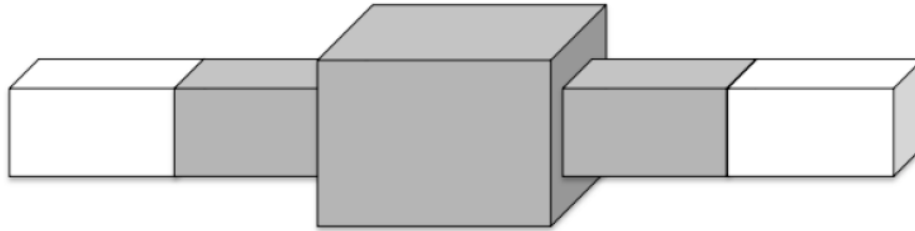
Lattice gas models 2-D and 3-D problems much more accessible computationally



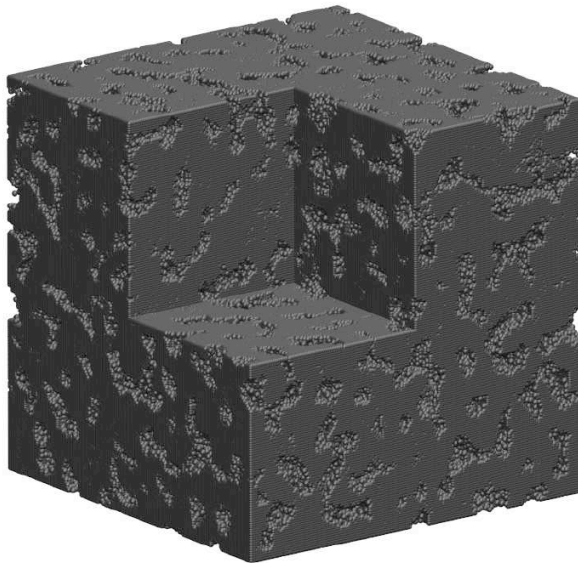
Model Systems



Duct Pore



Inkbottle Pore



Porous Vycor glass



Mean Field DFT

Grand free energy

$$\Omega = kT \sum_{\mathbf{i}} [\rho_{\mathbf{i}} \ln \rho_{\mathbf{i}} + (1 - \rho_{\mathbf{i}}) \ln(1 - \rho_{\mathbf{i}})] - \frac{\epsilon}{2} \sum_{\mathbf{i}} \sum_{\mathbf{a}} \rho_{\mathbf{i}} \rho_{\mathbf{i}+\mathbf{a}} + \sum_{\mathbf{i}} \rho_{\mathbf{i}} [\phi_{\mathbf{i}} - \mu]$$

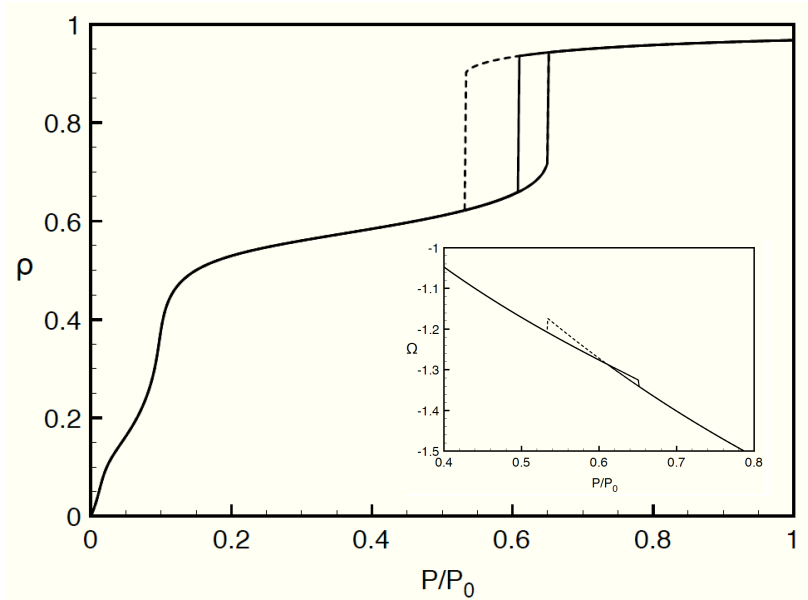
Necessary condition for minimum of Ω $\left(\frac{\partial \Omega}{\partial \rho_{\mathbf{i}}} \right)_{T, \mu} = 0 \quad \forall \mathbf{i}$

$$kT \ln \left[\frac{\rho_{\mathbf{i}}}{1 - \rho_{\mathbf{i}}} \right] - \epsilon \sum_{\mathbf{a}} \rho_{\mathbf{i}+\mathbf{a}} + \phi_{\mathbf{i}} - \mu = 0 \quad \forall \mathbf{i} \quad \text{Solve for } \{\rho_{\mathbf{i}}\} \text{ at fixed } \mu, V, T$$

Can also solve for $\{\rho_{\mathbf{i}}\}$ at fixed N, V, T by minimizing F , with μ as a Lagrange multiplier for the fixed N constraint.

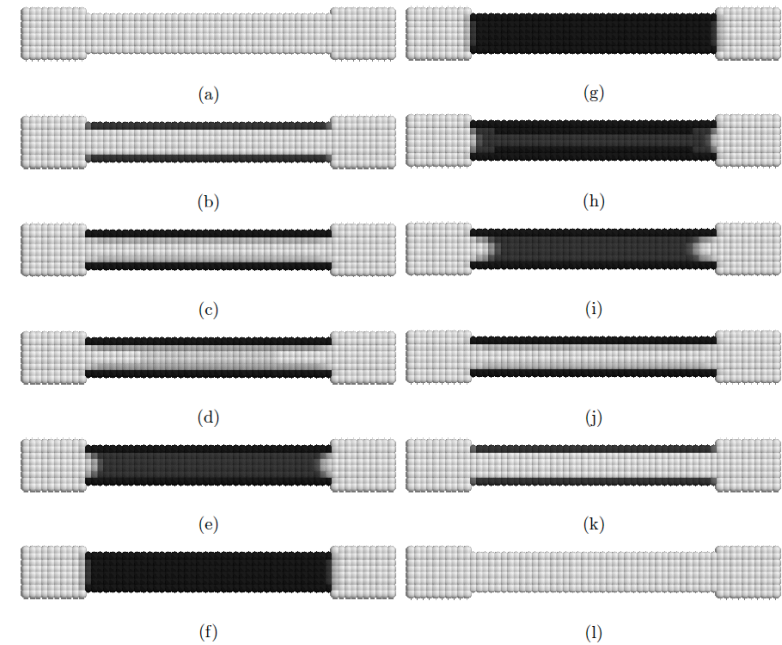


DFT for duct pore



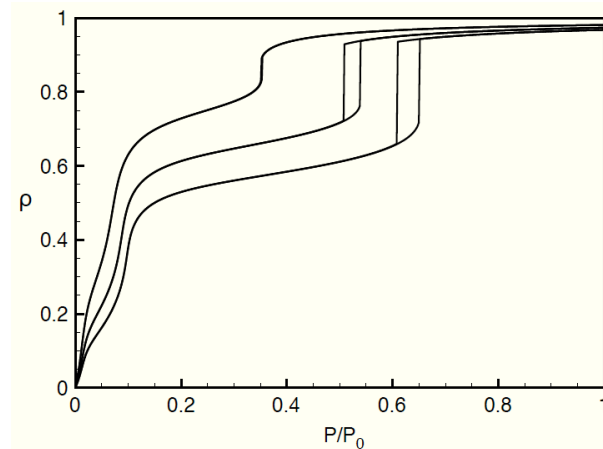
dashed curve shows desorption branch for infinite pore

Effect of changing pore size

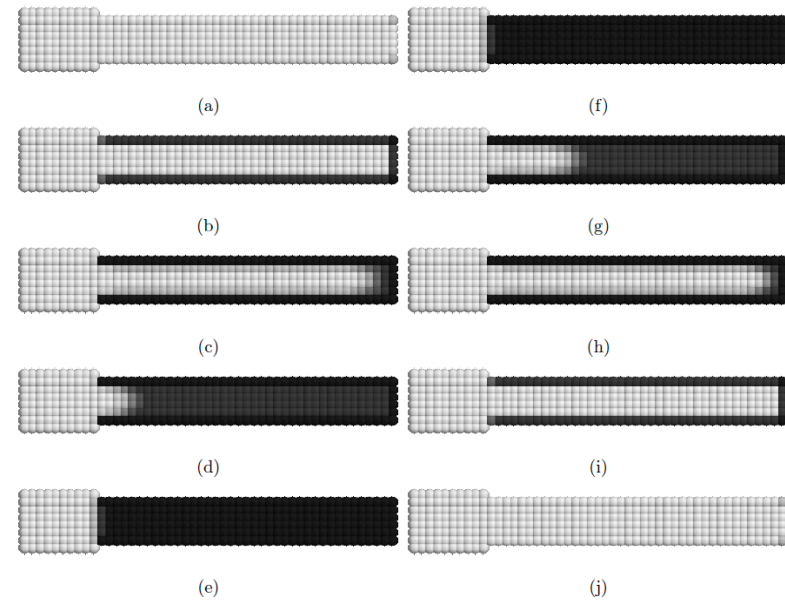
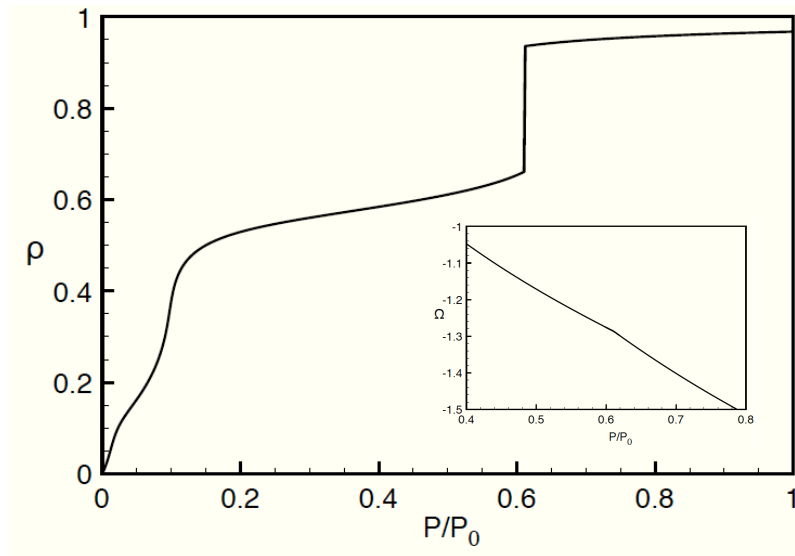


Adsorption

Desorption



DFT for closed end duct pore



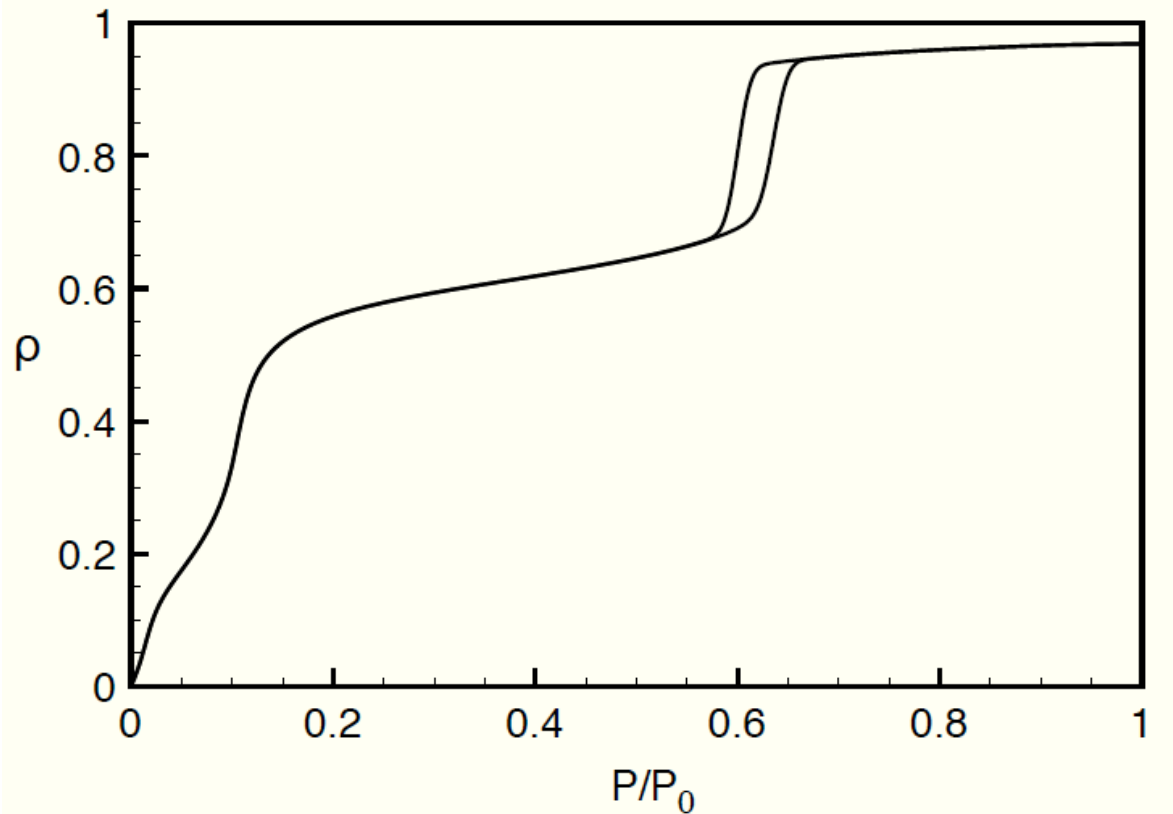
Adsorption

Desorption

c.f. L. Cohan, J. Am. Chem. Soc., 60, 433 (1938).



DFT for duct pore

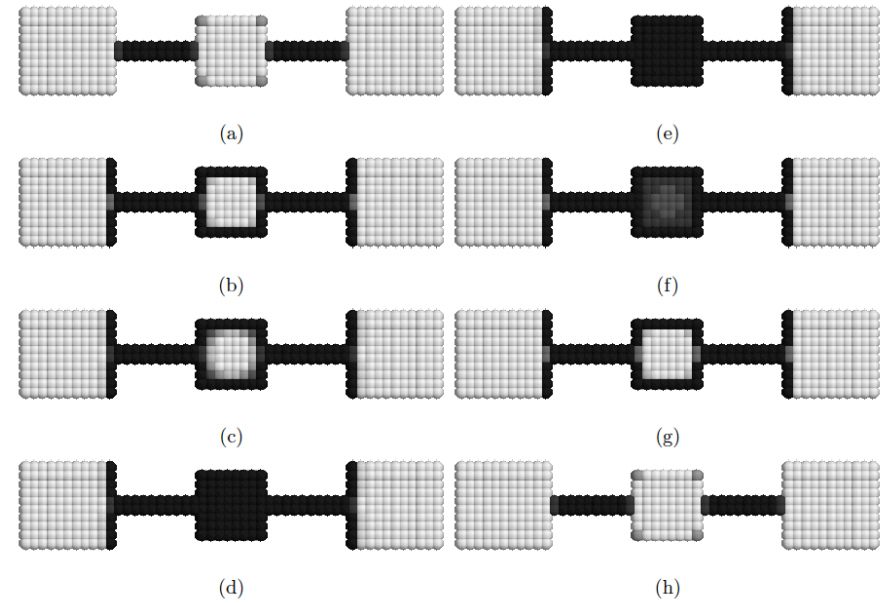
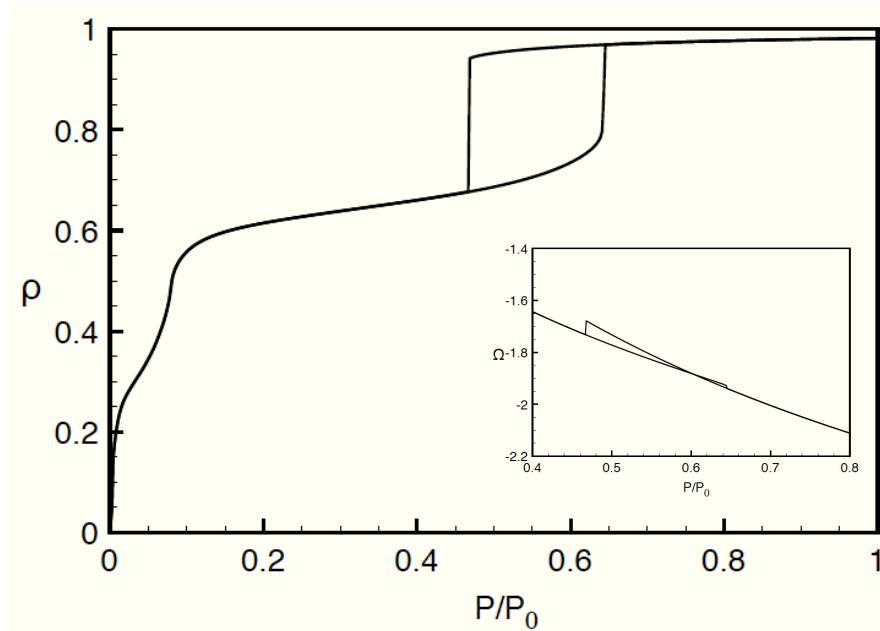


Isotherm averaged over gaussian distribution of pore widths for independent pores

$$\rho(P, T) = \int_0^{\infty} dH p(H) \rho_H(p, T)$$



DFT for inkbottle pore

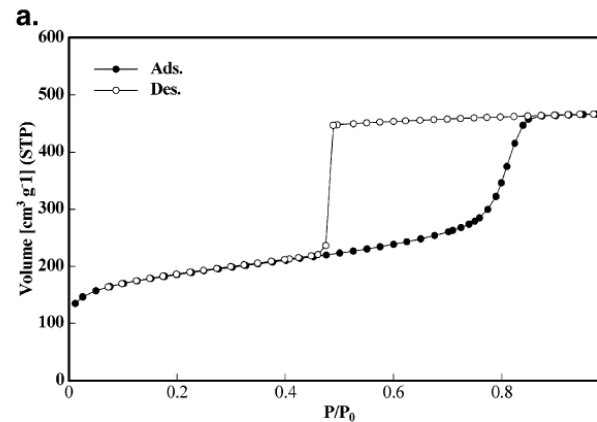


Adsorption

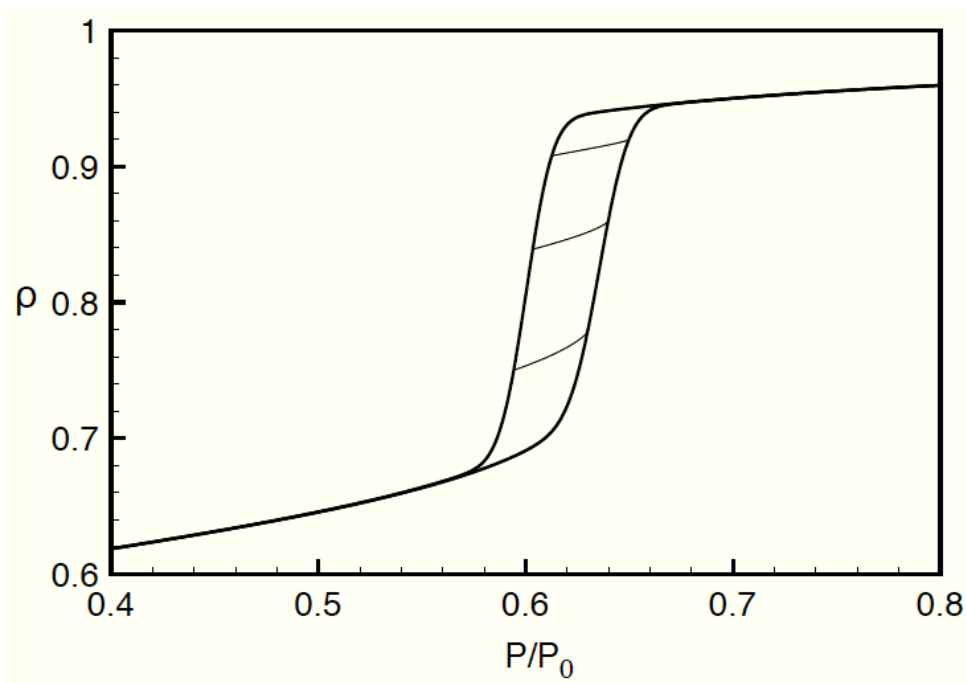
Desorption

Nitrogen adsorption in hierarchically ordered mesoporous silica materials

Thommes et al., *Langmuir*, 22, 756 (2006)
Rasmussen et al., *Langmuir*, 26, 10147 (2010)



DFT for duct pore - Scanning curves for distribution of independent pores



Hysteresis boundary curves are loci of pore filling and pore emptying pressures for points in the pore size distribution.

Scanning curves are reversible and no filling or emptying transitions occur along these curves

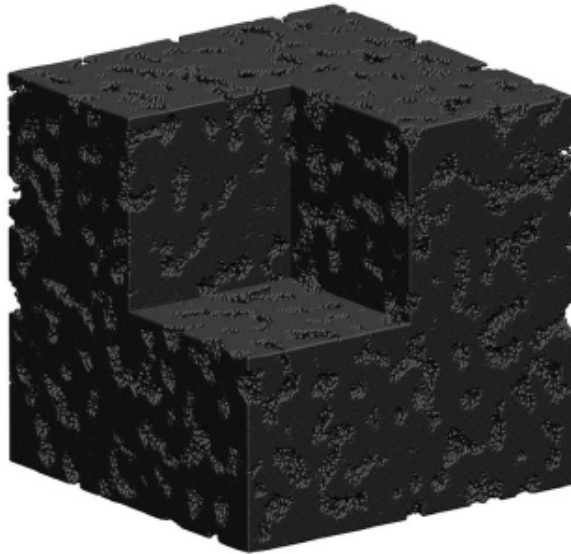
Shapes of scanning curves change if emptying and filling pressures are nonmonotonic with pore size

A. Wootters and R. Hallock, *Journal of Low Temperature Physics* 121, 549 (2000)

R. Cimino, K. Cychoz, M. Thommes, A. V. Neimark, *Colloids and Surfaces A*, 437, 76-89 (2013)

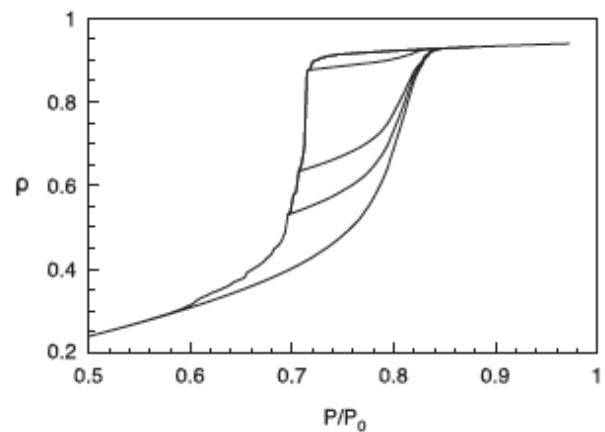
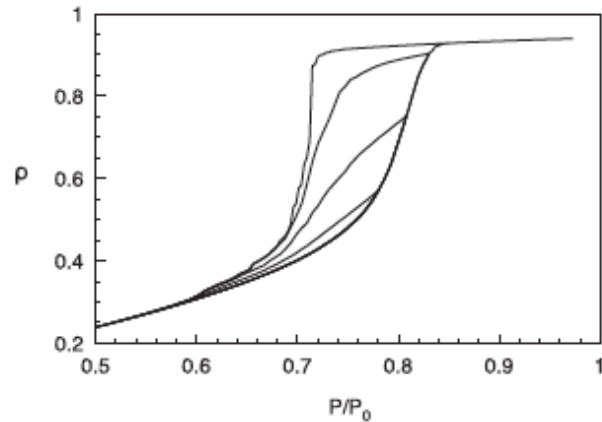


Application to Fluids in Porous Vycor Glass



Lattice model of Vycor

Lattice DFT



Edison, 2011

Xenon in Vycor

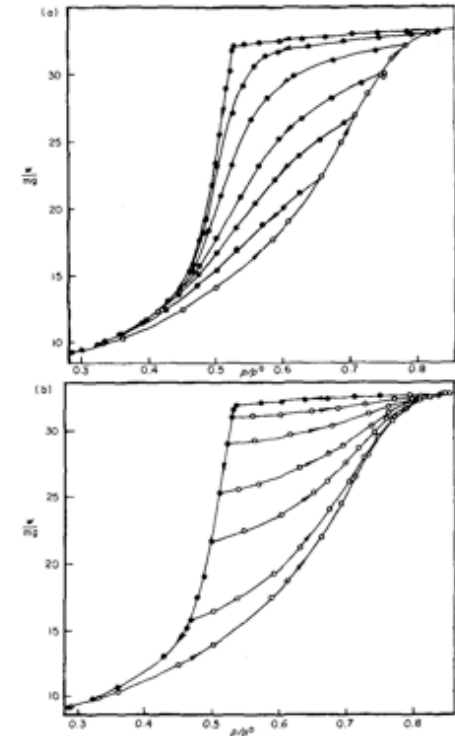


FIG. 36-12. Xenon on porous glass at 151.0°K (13). (a) Primary desorption scanning curves. (b) Primary adsorption scanning curves. Weight of sample, 61.60 mg.

Everett, 1967

See also Kierlik, Rosinberg, Tarjus, Gelb, Siderius,

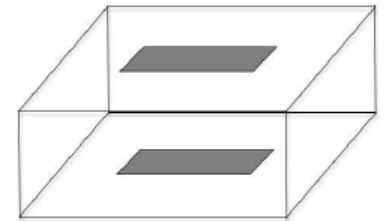


Dynamic Mean Field Theory

Based on previous work on Ising and binary alloy models

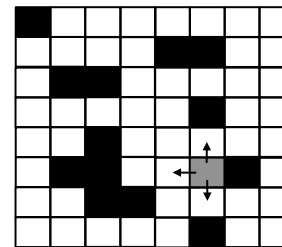
(Martin, 1990; Penrose, 1991; Gouyet et al. 2003;
see also Matuszak, Aranovich & Donohue, 2004 -)

Describes relaxation dynamics for a lattice gas model of a fluid in a step change in the bulk chemical potential



- *visualization of density distribution in pore after change in bulk state*

Can be viewed as a mean field approximation to Kawasaki dynamics



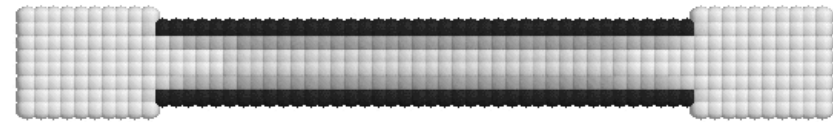
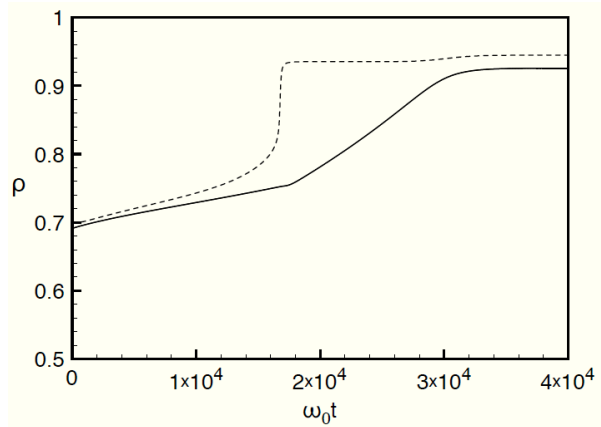
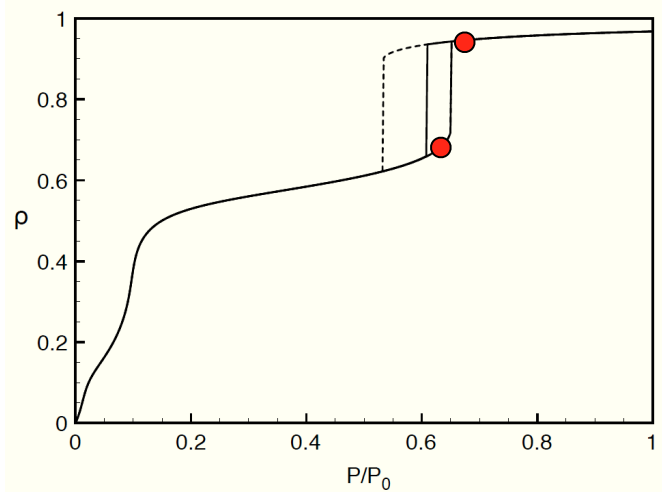
$$\frac{\partial \rho_i}{\partial t} = - \sum_{\mathbf{a}} w_{\mathbf{i}, \mathbf{i}+\mathbf{a}}(\{\rho\}) \rho_i (1 - \rho_{\mathbf{i}+\mathbf{a}}) - w_{\mathbf{i}+\mathbf{a}, \mathbf{i}}(\{\rho\}) \rho_{\mathbf{i}+\mathbf{a}} (1 - \rho_i)$$

Mean field approximation for conservation equation and Metropolis transition probabilities

Steady state solutions with uniform chemical potential in the long time limit corresponding to static mean field density functional theory



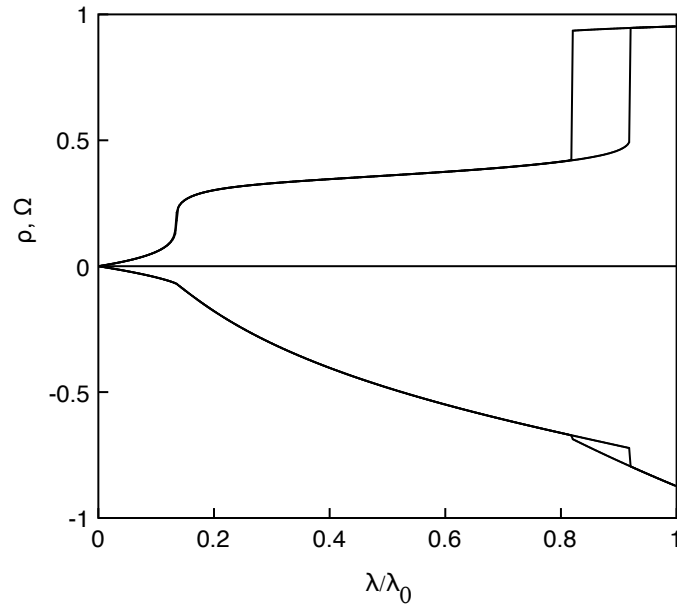
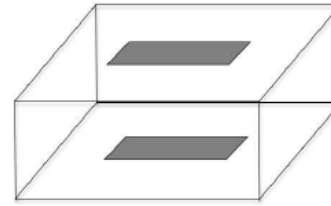
Dynamic uptake for duct pore from DMFT



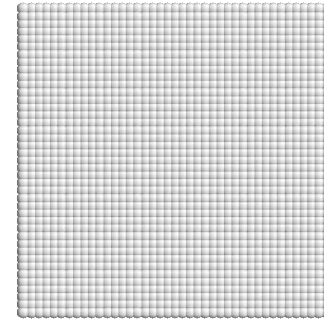
Full line: density averaged throughout pore
Dashed line: density averaged over plane
at pore center



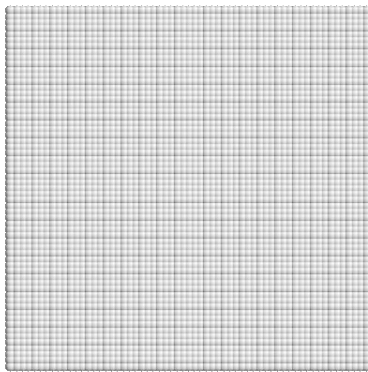
3-D Slit



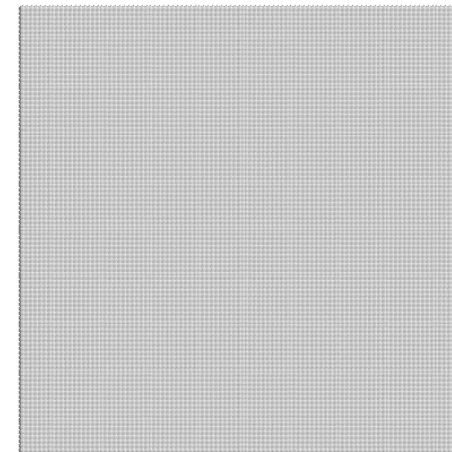
20 x 20



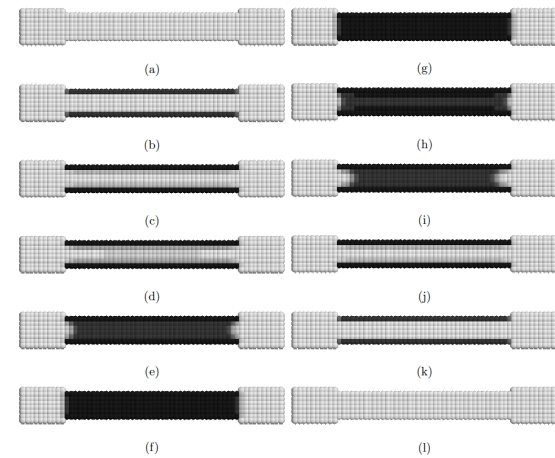
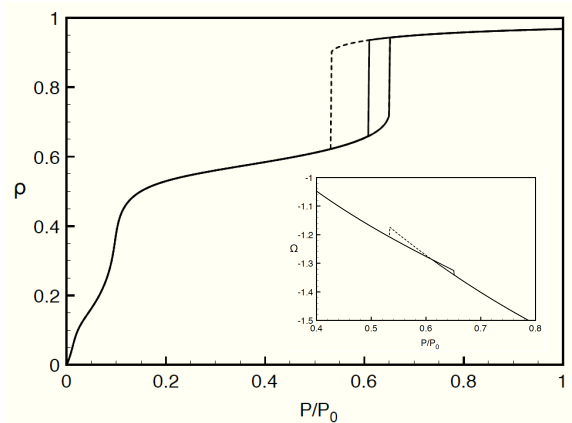
40 x 40



80 x 80



Summary



Adsorption/desorption hysteresis for fluids in mesoporous materials can be understood using simple molecular models and classical density functional theory

