Modeling Dynamics (*and Thermodynamics*)
of Fluids Confined in Mesoporous Materials

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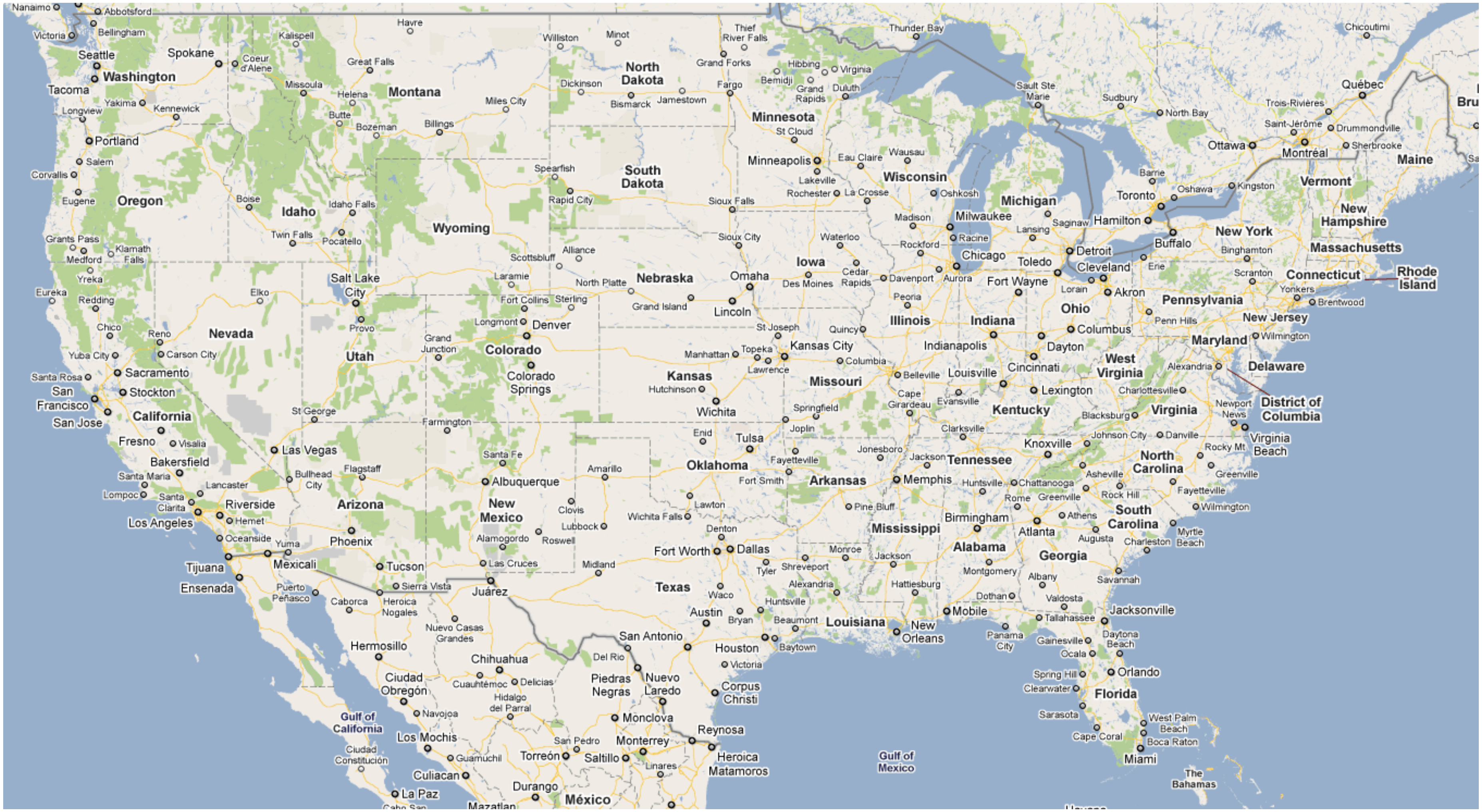
February 17th-19th, 2013

Acknowledgements: John Edison

Funding: National Science Foundation (CBET)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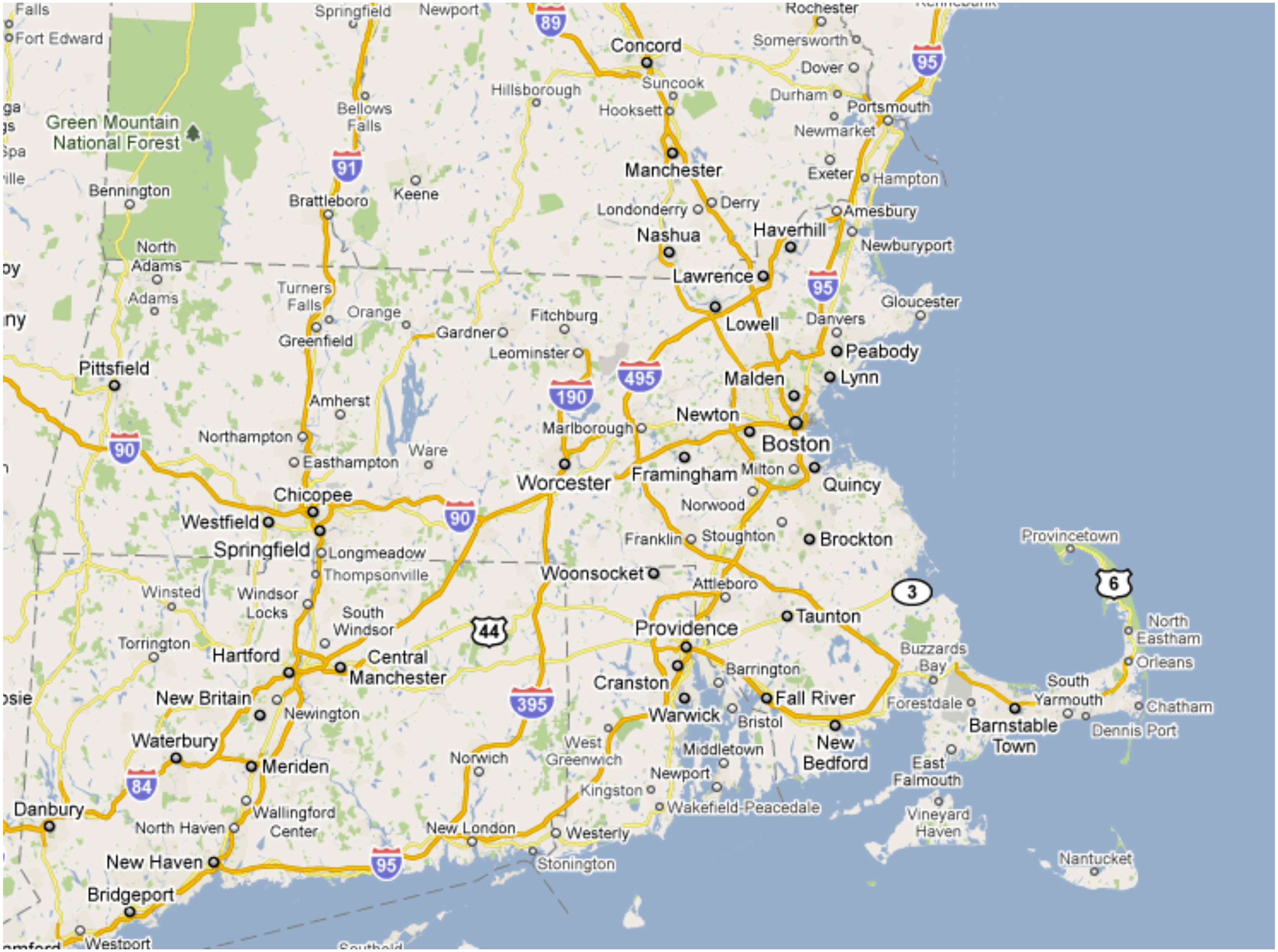
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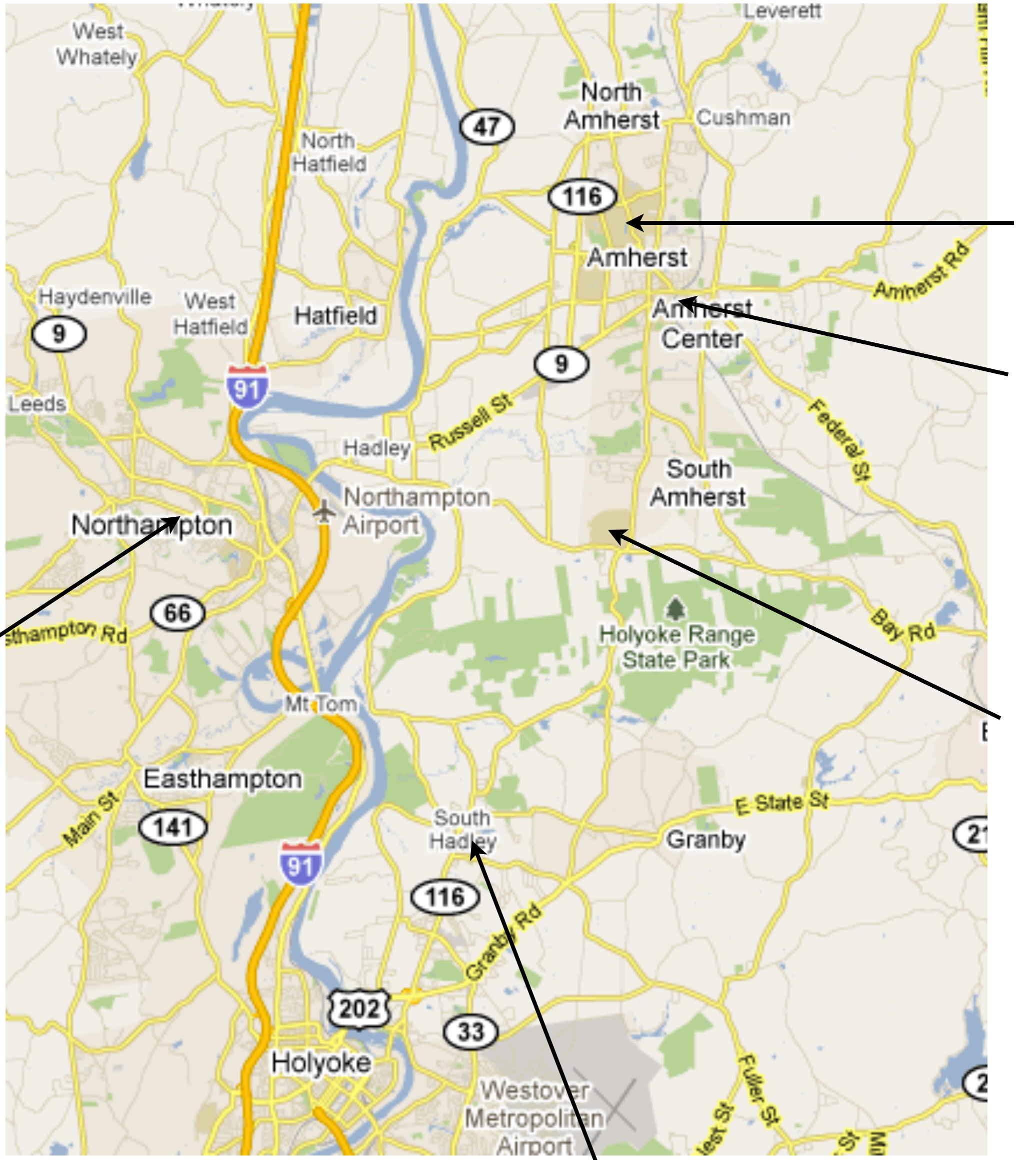

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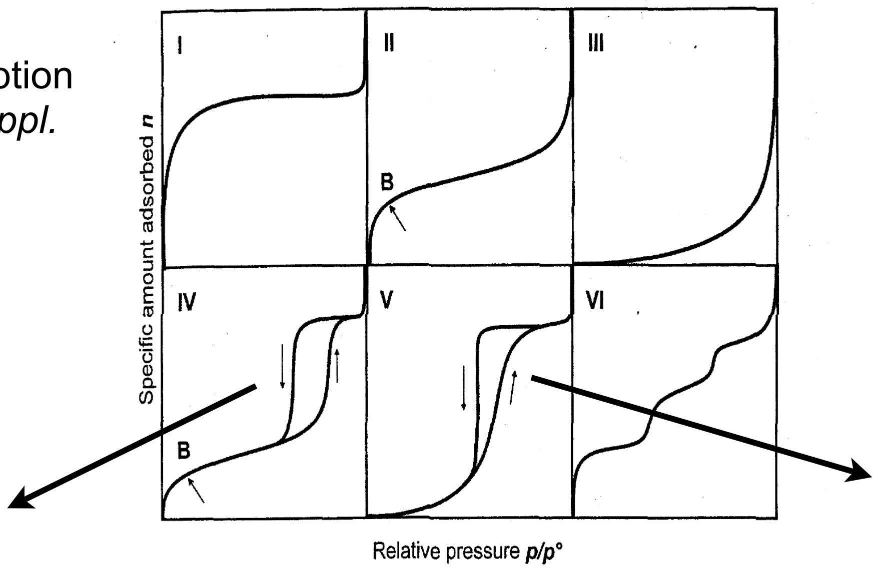
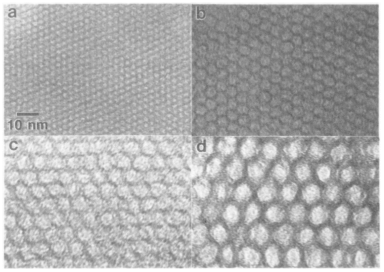
Impact of Classical Density Functional Theory in Modeling Confined Fluid Properties

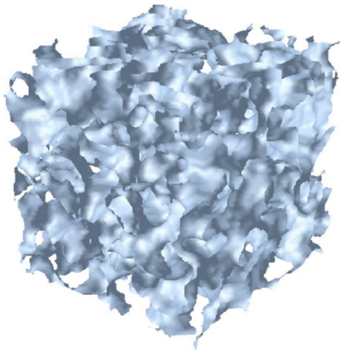
DFT allows calculation of the density distribution and thermodynamics for confined fluids from a model of pore structure and molecular interactions

- 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)

- *Metastability and mass transfer limitations to equilibration motivate studies of the dynamics*

- *Can we develop a theory of relaxation dynamics for fluids in mesoporous materials that complements the thermodynamic picture from classical density functional theory ?*

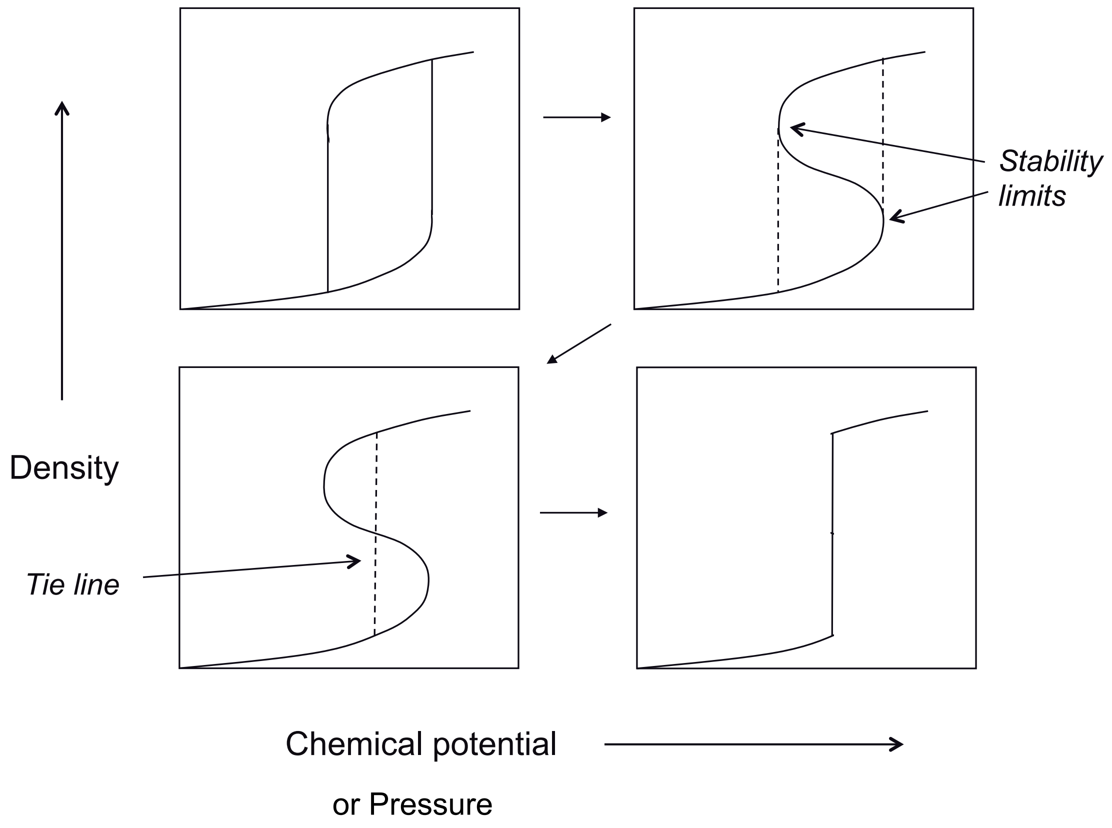
Outline

- Introduction to Classical Density Functional Theory (DFT)
- Lattice gas models of fluids in porous materials and static mean field DFT
  - *density distributions and thermodynamics*
- Dynamic mean field theory (DMFT)
  - *formulation*
  - *applications: single pores and pore networks, mixtures, partial wetting, partial drying and drying*
  - *visualizations of condensation and evaporation processes in porous materials*

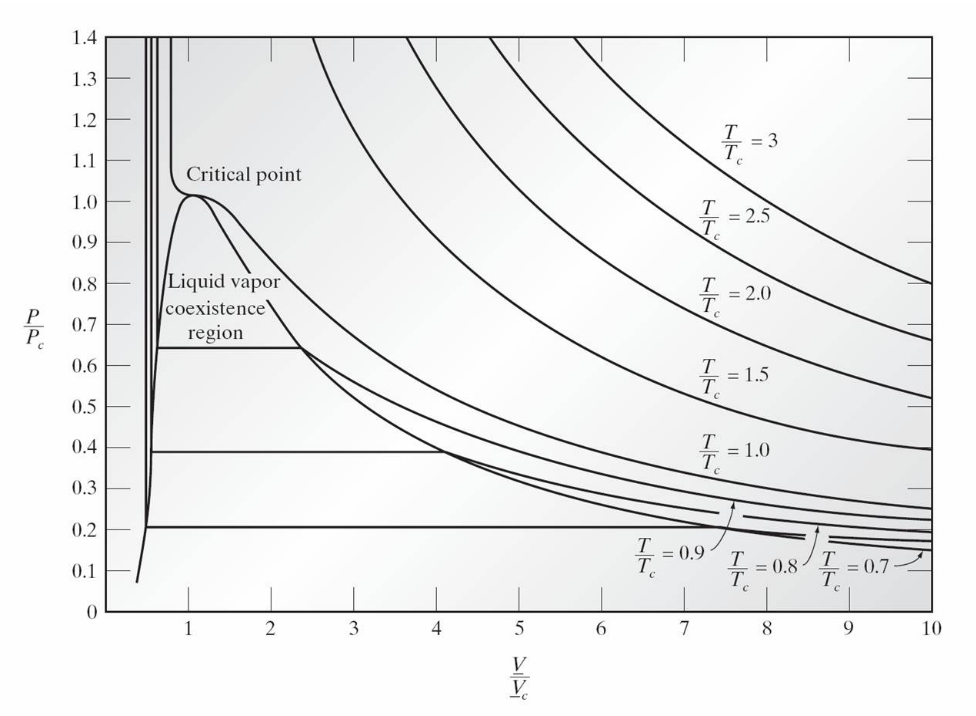
Classical Density Functional Theory I

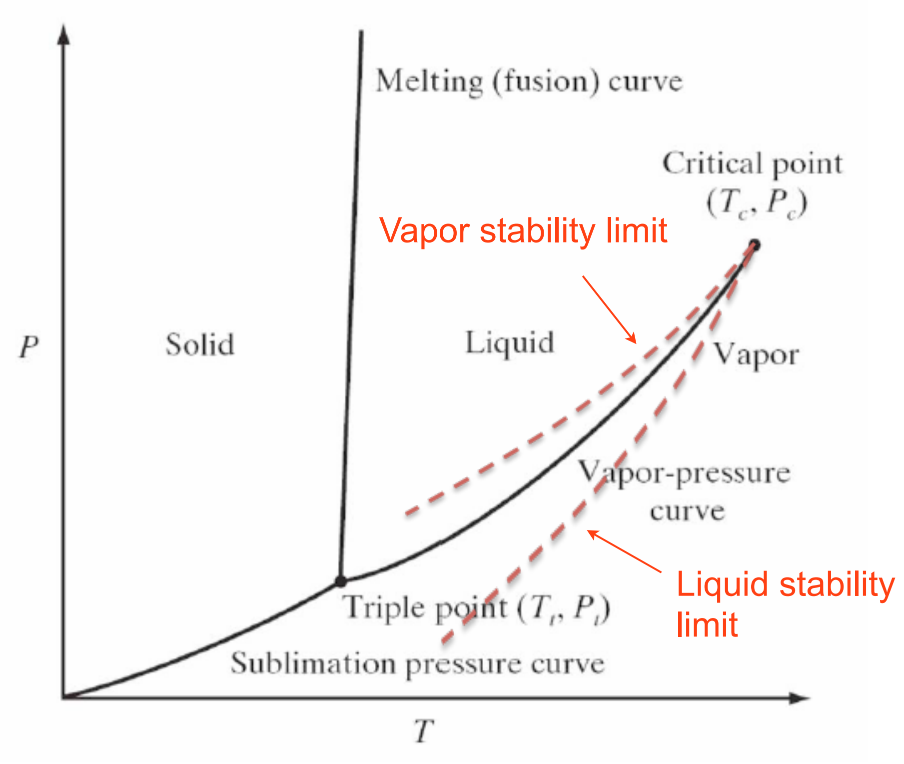
For bulk fluids calculations of phase equilibrium start with knowledge of Helmholtz free energy, $F(\rho,T)$, from which we can determine the pressure, $P(\rho,T)$, and the chemical potential $\mu(\rho,T)$.

$$F(\rho,T)/N = F_{HS}/N - a\rho$$ van der Waals / mean field theory



Phase diagram in vapor-liquid coexistence region





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

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

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

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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

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

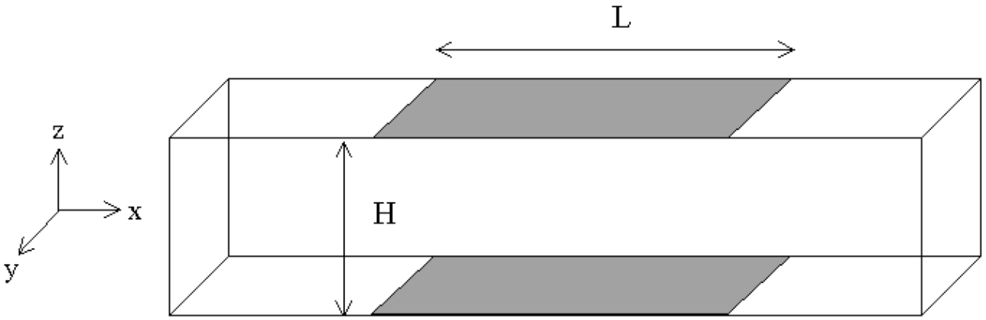
Can also solve for $\rho(\mathbf{r})$ at fixed N,ϕ,T by minimizing F, with μ as a Lagrange multiplier for the fixed N constraint

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*

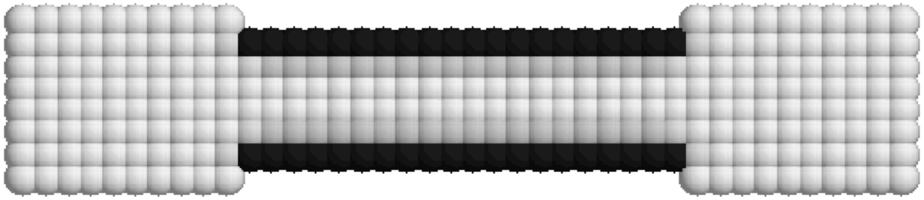
Lattice Gas Model of a Fluid in an Open Slit Pore



- 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

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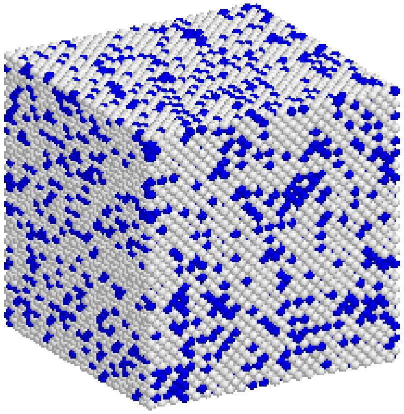
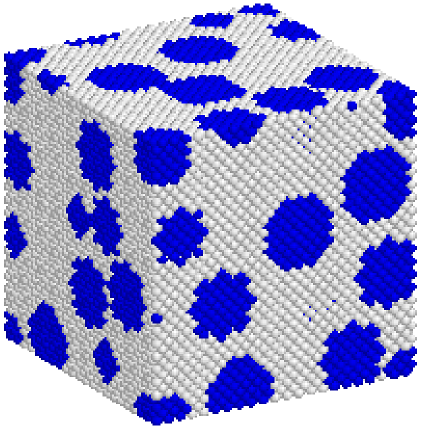
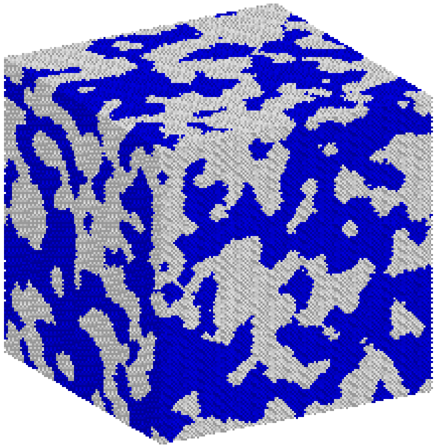
Lattice models of 3-D mesoporous structures



Random distribution of solid



Silica xerogel



Porous glass

See also Kierlik, Rosinberg, Tarjus, Donohue, Aranovich, Gelb ....

Lattice Gas Hamiltonian for a Confined Fluid

$$H = -\frac{\epsilon}{2}\sum_{\mathbf{i}}\sum_{\mathbf{a}} n_{\mathbf{i}} n_{\mathbf{i}+\mathbf{a}} + \sum_{\mathbf{i}} n_{\mathbf{i}}\phi_{\mathbf{i}}$$

ϵ - nearest neighbor interaction strength

$n_{\mathbf{i}}$ - occupancy (0 or 1) at site $\mathbf{i}$

$\phi_{\mathbf{i}}$ - external field at site $\mathbf{i}$

$\mathbf{i}$ - set of lattice coordinates

$\mathbf{a}$ - vector to nearest neighbor site

Mean Field DFT I

Helmholtz free energy

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

Free energy of single occupancy lattice gas (c.f. hard sphere system)

Nearest neighbor attractions in mean field

Contribution from external field (fluid interaction with pore walls)

Bulk limit

$$F = MkT\left[(1-\rho)\ln(1-\rho) + \rho \ln \rho\right] - \frac{cM}{2}\epsilon\rho^2$$

$$P = -kT \ln(1-\rho) - c/2\epsilon\rho^2$$

Mean Field DFT II

Grand free energy

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

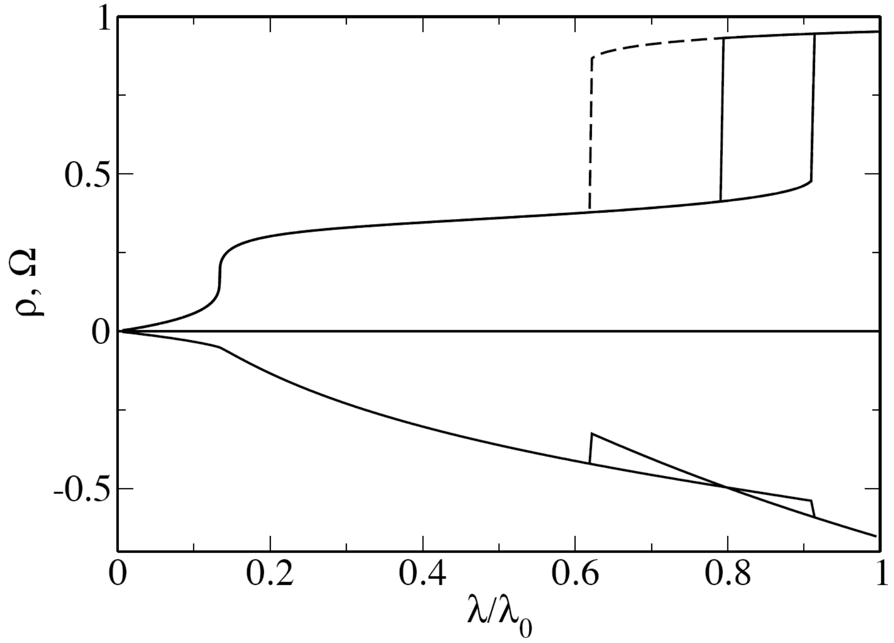
Necessary condition for minimum of Ω $\left(\frac{\partial\Omega}{\partial\rho_{\mathbf{i}}}\right)_{T,\mu} = 0 \qquad \forall \quad \mathbf{i}$

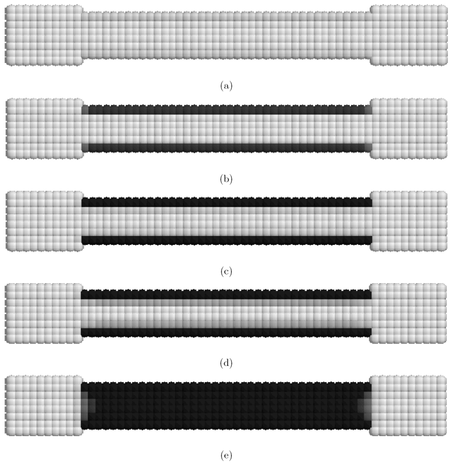
$$kT\ln\left[\frac{\rho_{\mathbf{i}}}{1-\rho_{\mathbf{i}}}\right] - \epsilon\sum_{\mathbf{a}}\rho_{\mathbf{i}+\mathbf{a}} + \phi_{\mathbf{i}} - \mu = 0 \qquad \forall \quad \mathbf{i}$$

Solve for $\{\rho_{\mathbf{i}}\}$ at fixed μ, V, T

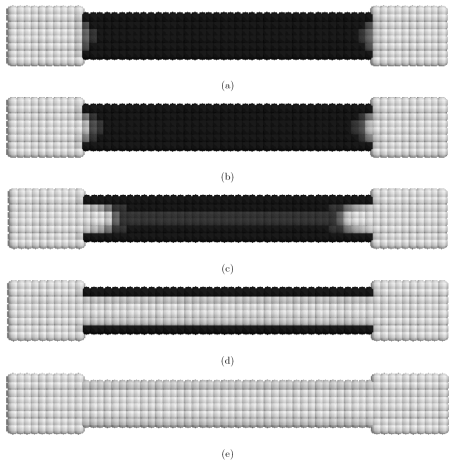
Can also solve for $\{\rho_{\mathbf{i}}\}$ at fixed N, V, T by minimizing F, with μ as a Lagrange multiplier for the fixed N constraint.

Results from static MFT (μ, V, T)





Adsorption



Desorption

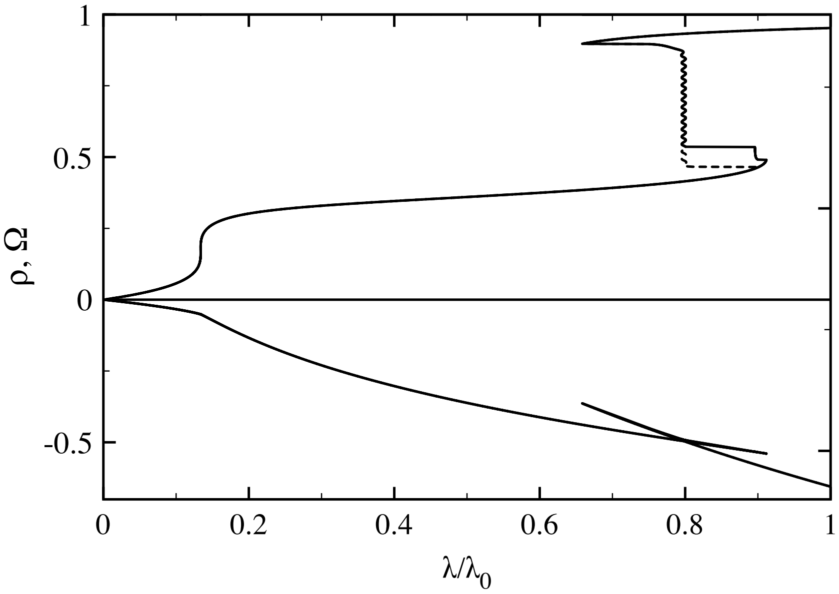
dashed curve shows desorption branch for infinite pore

vapor-liquid transition almost coincides with desorption step for open pore

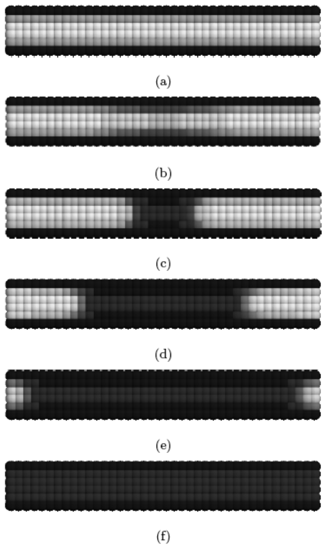
c.f. U. Marconi and F. van Swol, Phys. Rev. A, 39, 4109 (1989)

Results from static MFT (N, V, T)

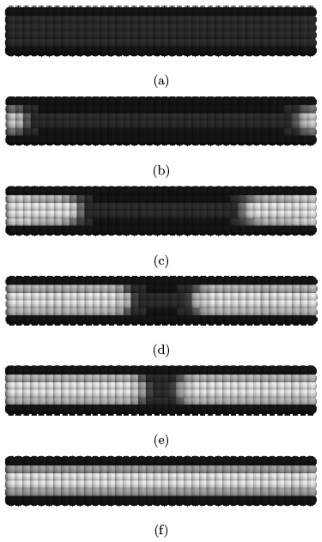
infinite pore - periodic boundaries in x-direction



dashed curve shows decreasing density branch branch



Increasing density



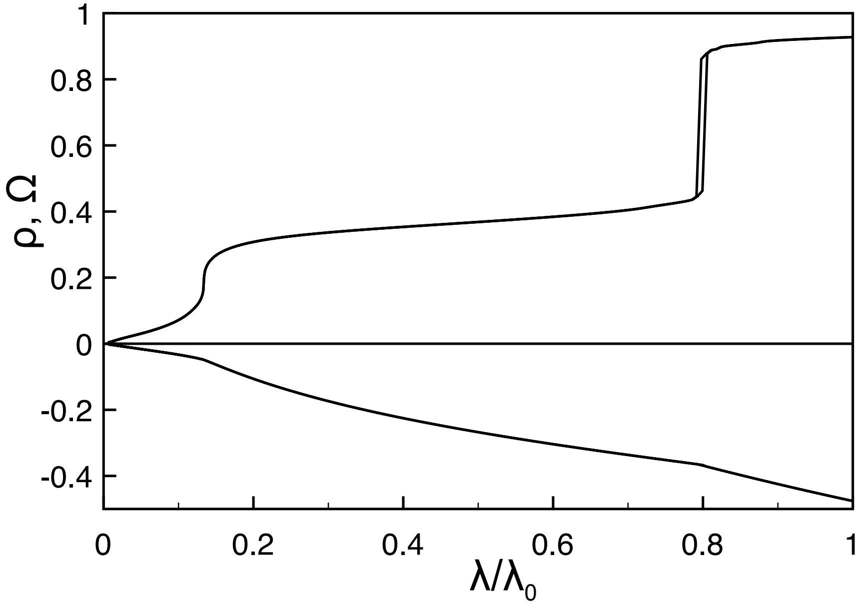
Decreasing density

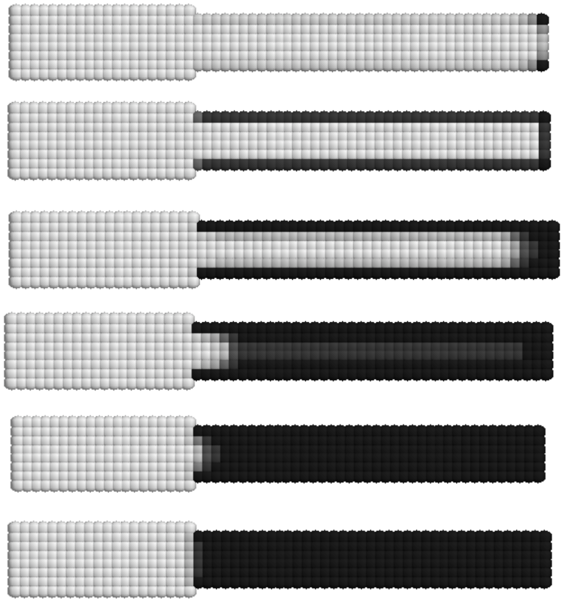
Density distributions show formation of undulates, liquid bridges and bubbles

(c.f. Everett and Haynes, 1972, Vishnyakov and Neimark, 2003)

Results from static MFT (μ, V, T)

Slit pore closed at one end

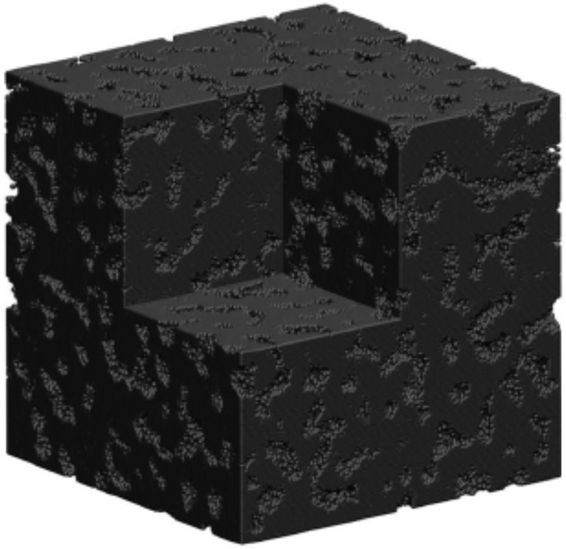




Almost no hysteresis in this case. Condensation initiated at pore end

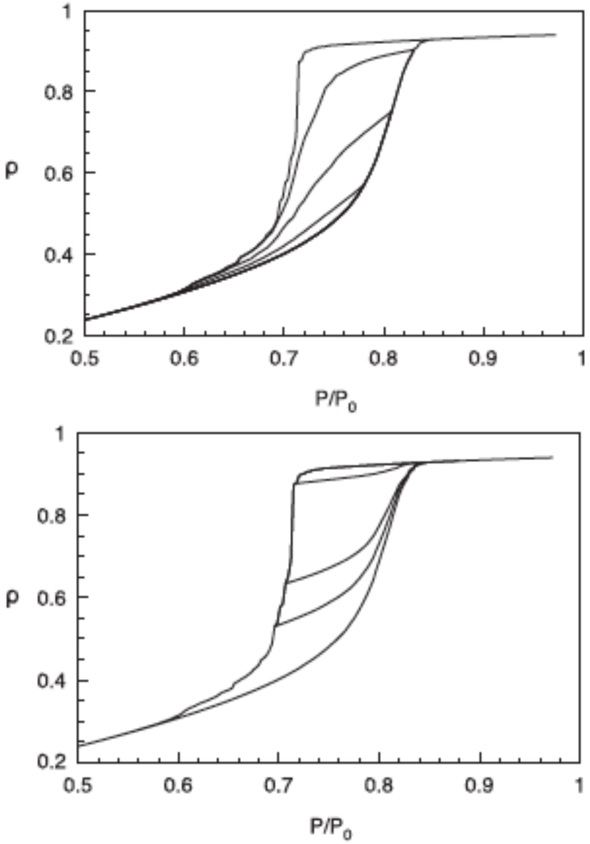
c.f. Cohan (1938)

Application to Fluids in Porous Vycor Glass



Lattice model of Vycor

Lattice DFT



Edison, 2011

Xenon in Vycor

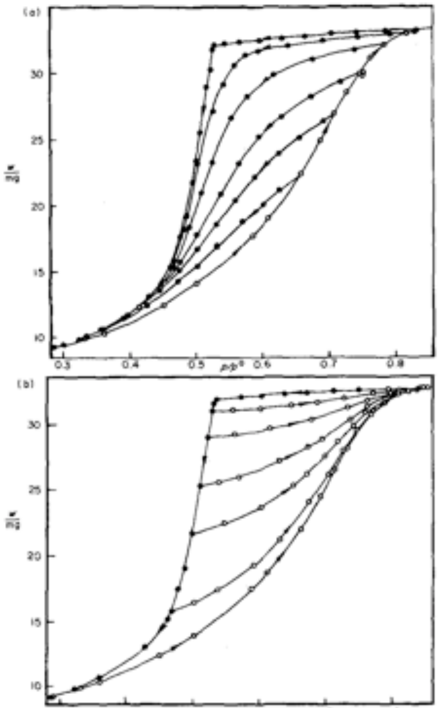


FIG. 36-12. Xenon on porous glass at 151.0°K (13). (a) Primary desorption scanning curves. (b) Primary adsorption scanning curves. Weight of sample, 61.60 mg.

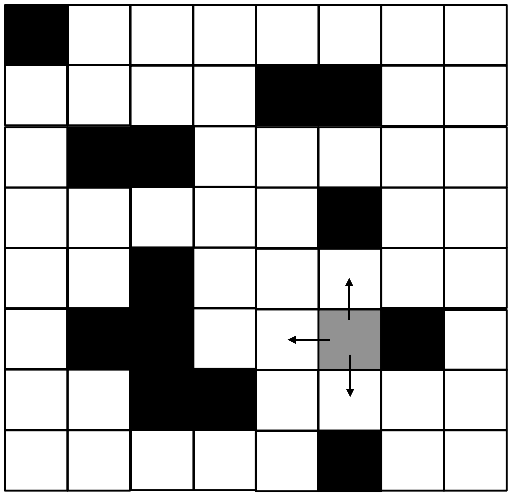
Everett, 1967

Dynamic Mean Field Theory

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 -)

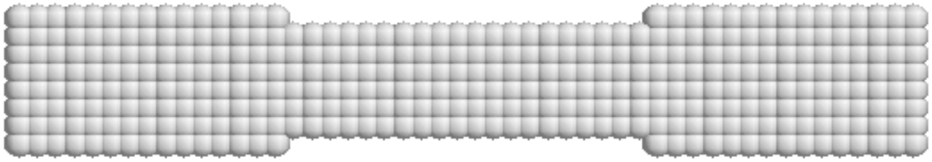
Can be viewed as a mean field approximation to Kawasaki dynamics for the lattice model



Dynamics generated by transitions of molecules to neighboring sites

Metropolis transition probabilities

Kawasaki Dynamics of Pore Filling for a Slit Pore



Dynamic Mean Field Theory (contd.)

$$\rho_{\mathbf{i}}(t) =< n_{\mathbf{i}} >_t= \sum_{\{n\}} n_{\mathbf{i}} P(\{n\},t)$$ - mean density for site **i** at time t

P(*{n},t*) - probability of observing a given ocupancy configuration, {n}, at time t

Evolution equation for local density in mean field approximation

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

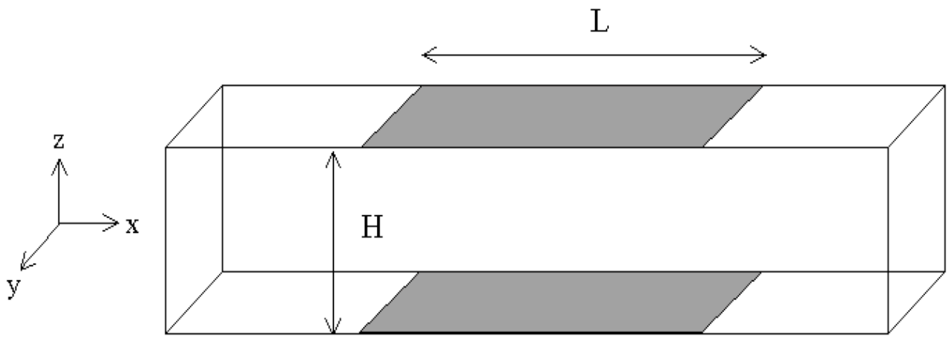
Metropolis transition probabilities (Matuszak et al., 2004)

$$w_{\mathbf{ij}} = w_o \exp(-E_{\mathbf{ij}}/kT) \qquad E_{\mathbf{ij}} = \begin{cases} 0 & E_{\mathbf{j}} < E_{\mathbf{i}} \\ E_{\mathbf{j}} - E_{\mathbf{i}} & E_{\mathbf{j}} > E_{\mathbf{i}} \end{cases} \qquad E_{\mathbf{i}} = -\epsilon \sum_{\mathbf{a}} \rho_{\mathbf{i}+\mathbf{a}} + \phi_{\mathbf{i}}$$

w_0 - jump rate in the absence of interactions
(sets the time scale)

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

Application to Adsorption/desorption in an Open Slit Pore

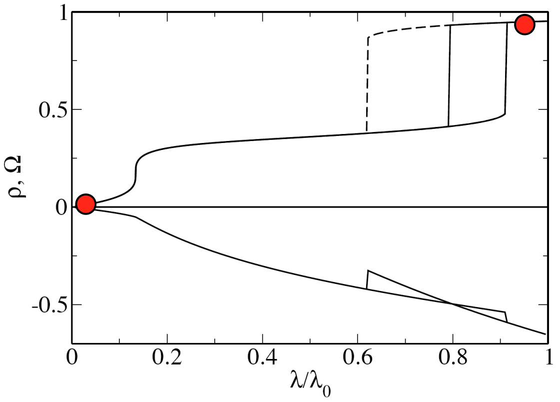


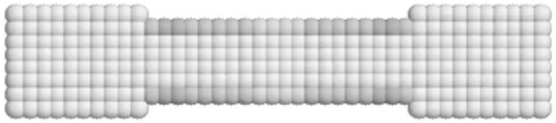
Initialize the system using density distribution from static MFT for starting value of chemical potential

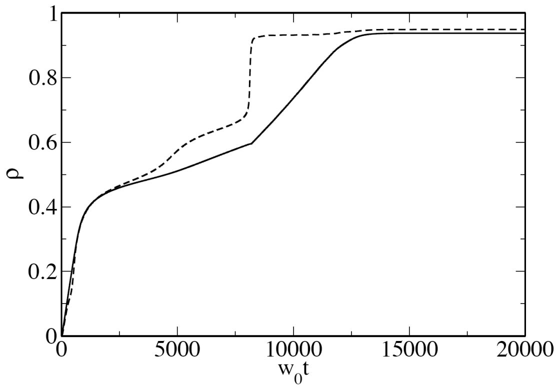
Add layer of sites at end of bulk region maintained at fixed density associated with final value of chemical potential

Integrate evolution equation using Euler’s method

Dynamic uptake for an L = 20 pore for quench from dilute gas state to condensed state







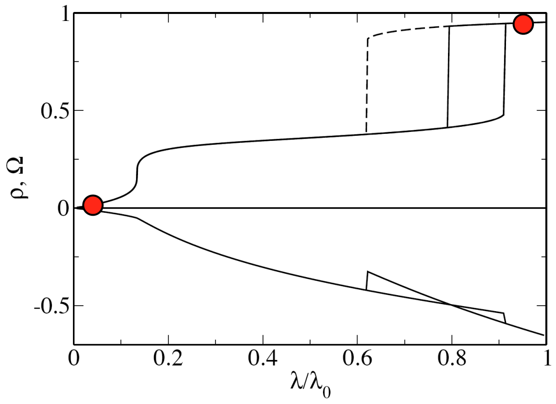
Note formation of undulates and liquid bridge.

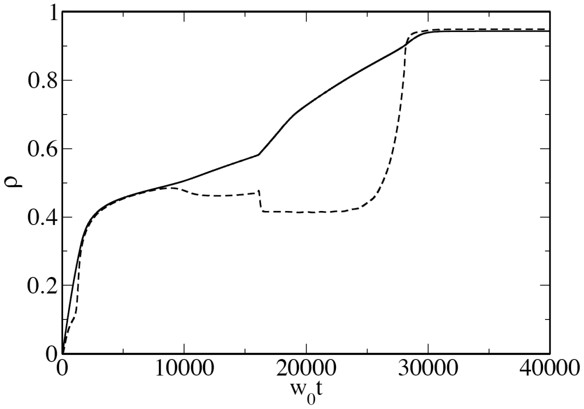
These states do not appear in μ,V,T static MFT but do appear in N,V,T static MFT for infinite pore

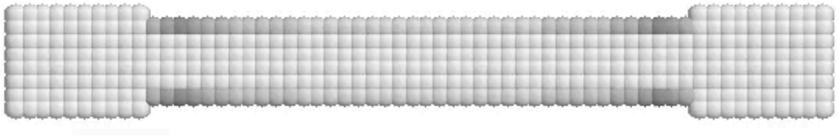
Full line: density averaged throughout pore

Dashed line: density averaged over plane at pore center

Dynamic uptake for an L = 40 pore for quench from dilute gas state to condensed state

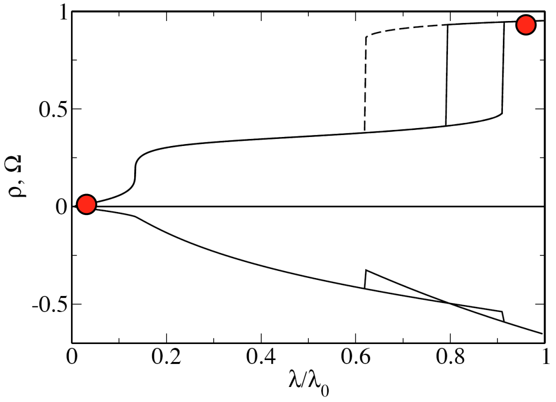


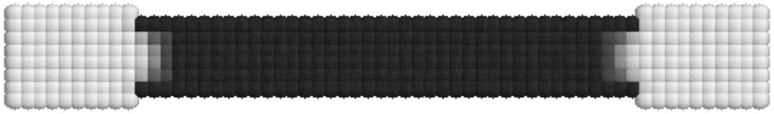


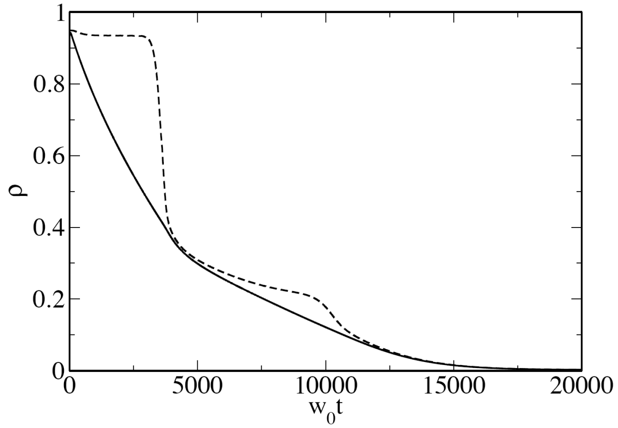


Full line: density averaged throughout pore
Dashed line: density averaged over plane at pore center

Dynamic desorption from an L = 40 pore for quench between condensed state and dilute gas state



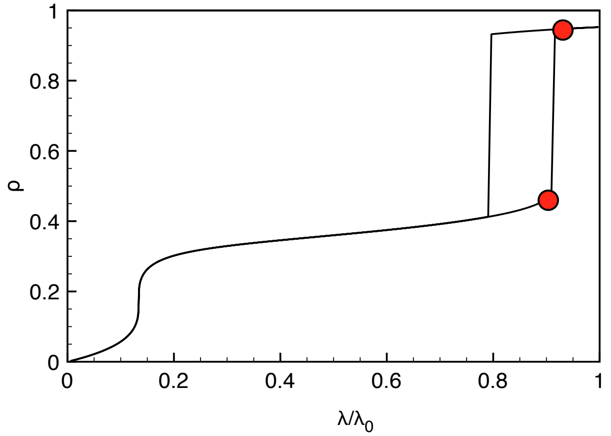


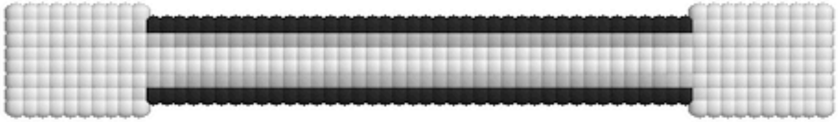


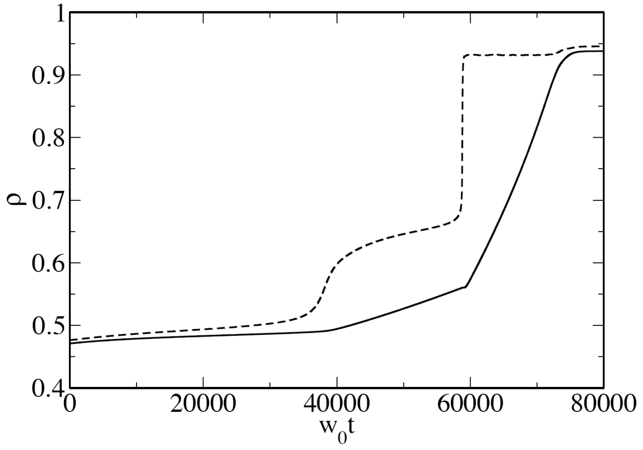
No undulate state on desorption

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

Dynamic uptake for an L = 40 pore for quench between states either side of condensation transition







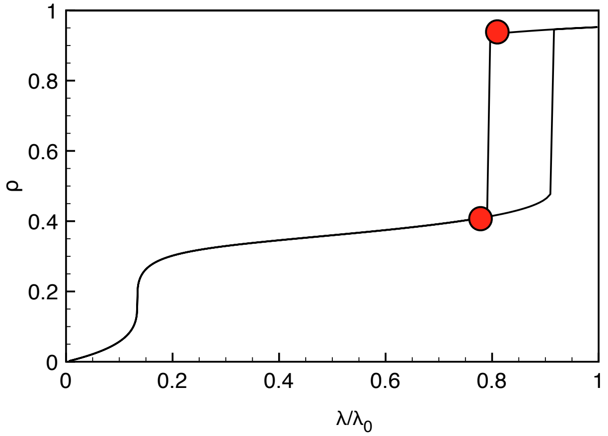
Note formation of undulates and liquid bridge.

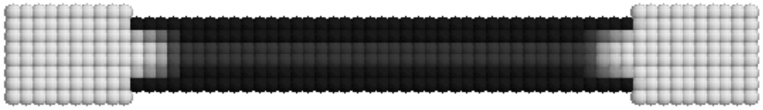
These states do not appear in μ*,V,T static MFT but do appear in N,V,T static MFT for infinite pore*

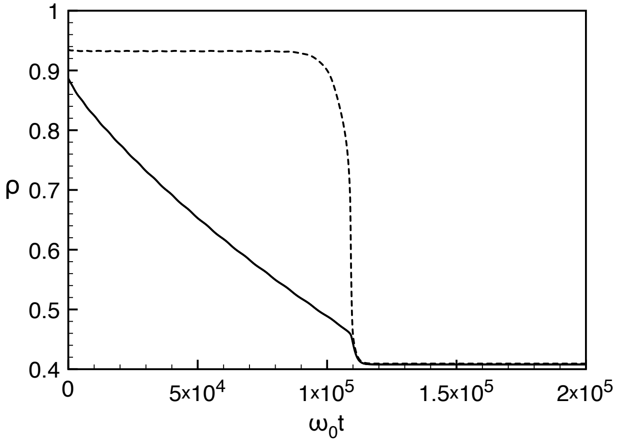
Full line: density averaged throughout pore

Dashed line: density averaged over plane at pore center

Dynamic desorption from an L = 40 pore for quench between states either side of evaporation transition







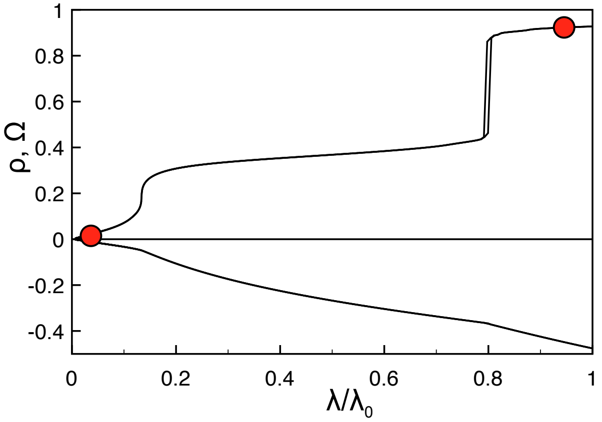
No undulate state on desorption

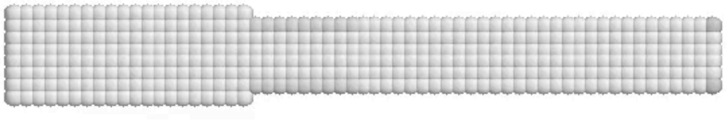
Full line: density averaged throughout pore
Dashed line: density averaged over plane at pore center

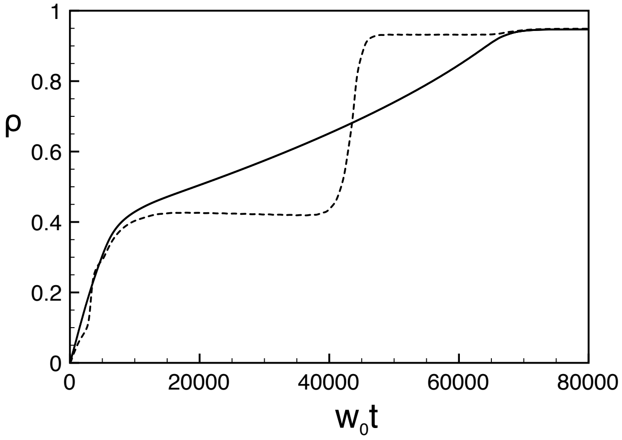
“In order that condensation may occur in a capillary, it is essential that the meniscus shall be formed. This process, however, cannot take place until there is sufficient liquid present to block the pore at its narrowest point. In seeking an explanation for hysteresis it is therefore necessary to enquire whether the phenomenon may not be due to some delay in the appearance of capillary condensation, after the completion of the adsorbed layer, owing to the lack of reversibility associated with the formation and breaking of the meniscus.”

A. G. Foster, *Trans. Faraday Soc.*, 28, 645 (1932)

Dynamic uptake for an L = 40 closed end pore for quench between dilute gas state and condensed state

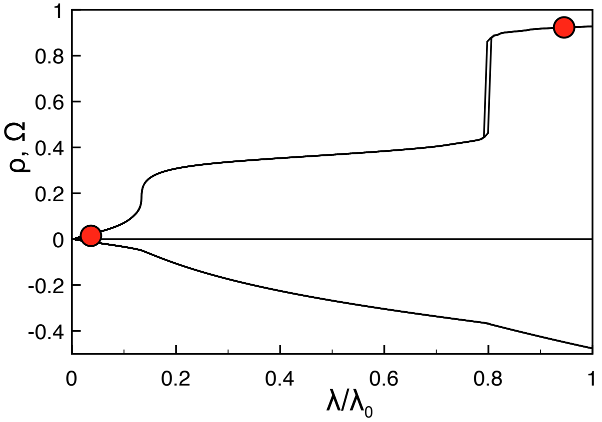


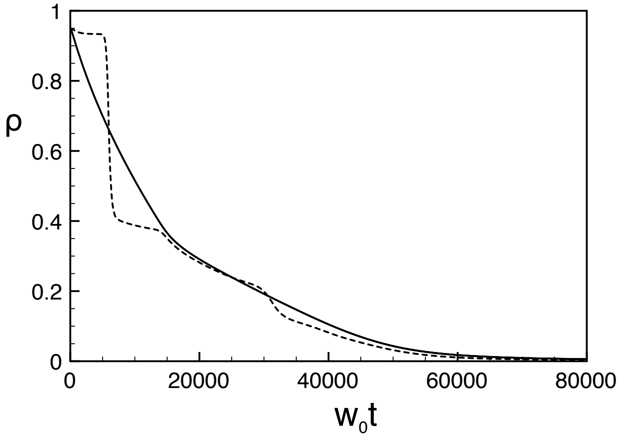




Full line: density averaged throughout pore
Dashed line: density averaged over plane at pore center

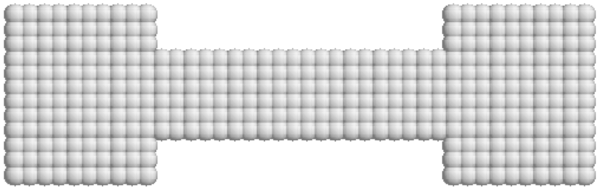
Dynamic desorption from an L = 40 closed end pore for quench between condensed state and dilute gas state



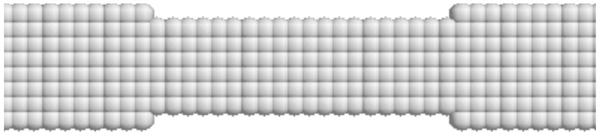


Full line: density averaged throughout pore
Dashed line: density averaged over plane at pore center

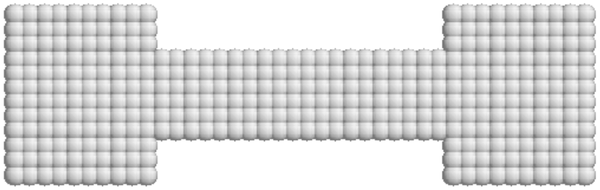
Comparison with Dynamic Monte Carlo Simulations



DMFT



A single Monte Carlo trajectory

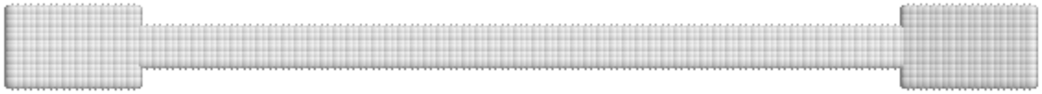


Average of 1536 statistically independent DMC trajectories

L=20 H=6 slit pore

Comparison with Dynamic Monte Carlo Simulations

DMFT

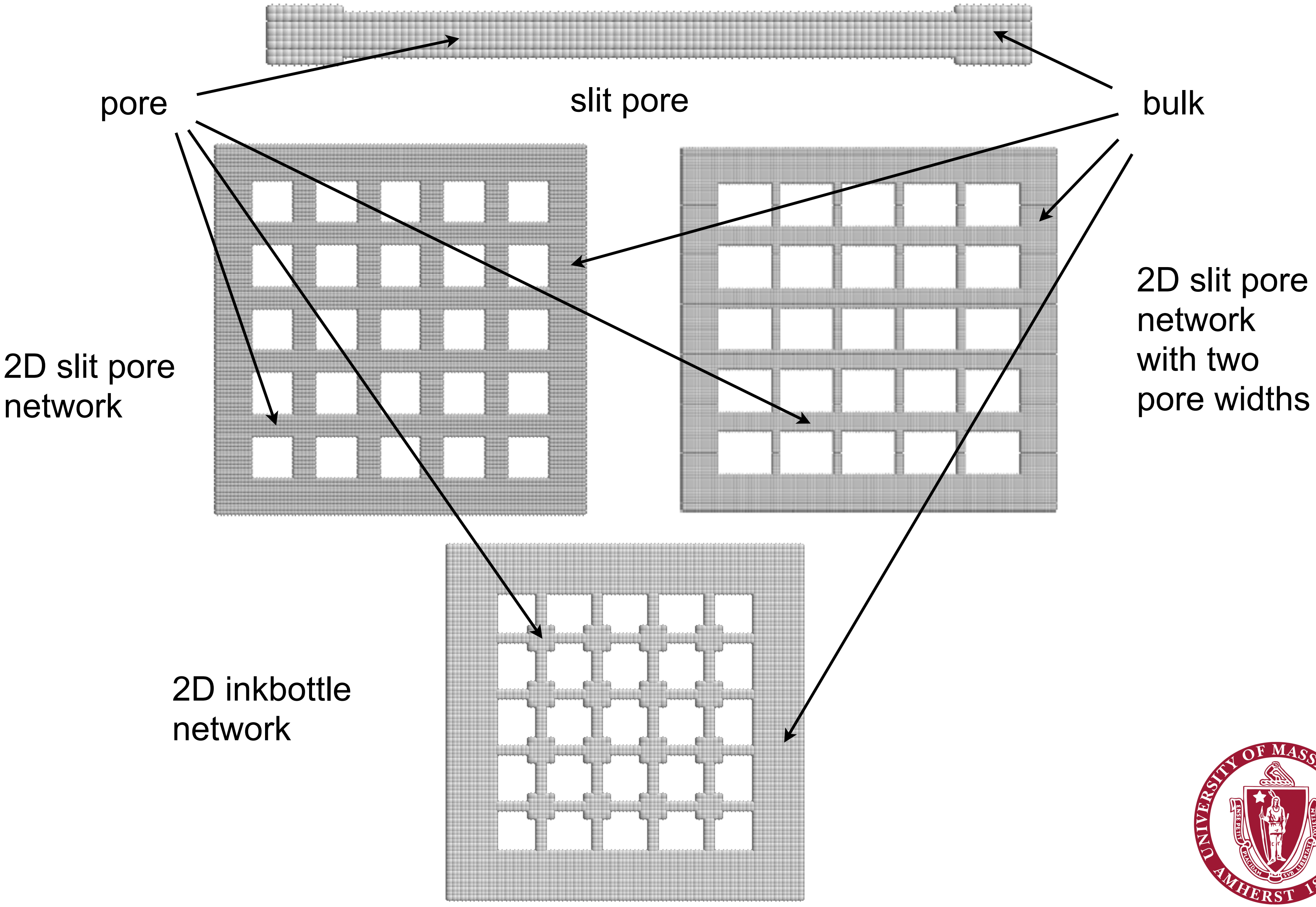


Average of 1536 statistically independent DMC trajectories

L=120 H=6 slit pore

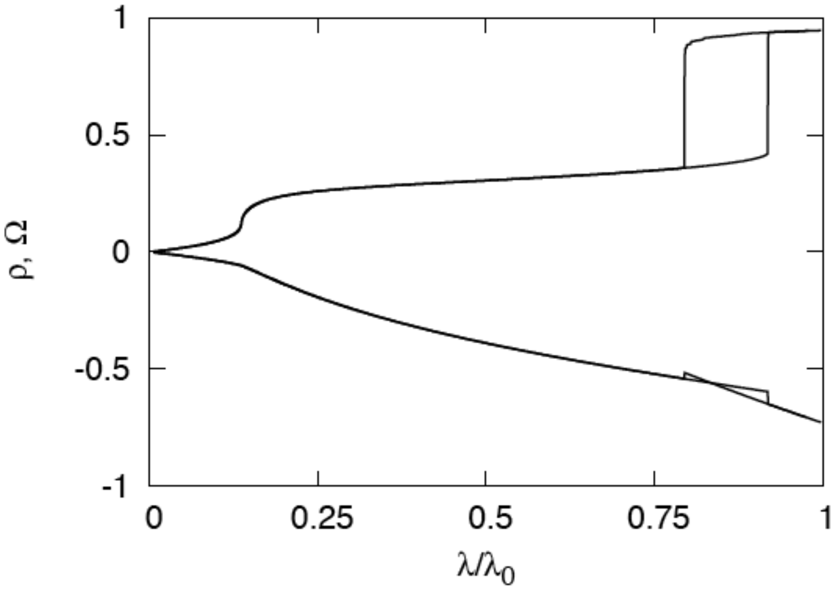
Pore Networks

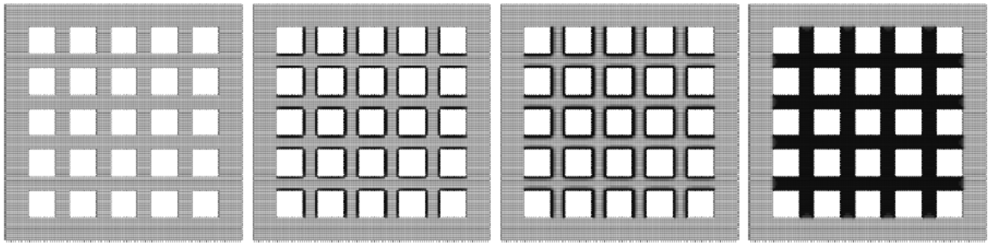
Lattice Gas Models of Fluids Confined in Porous Networks



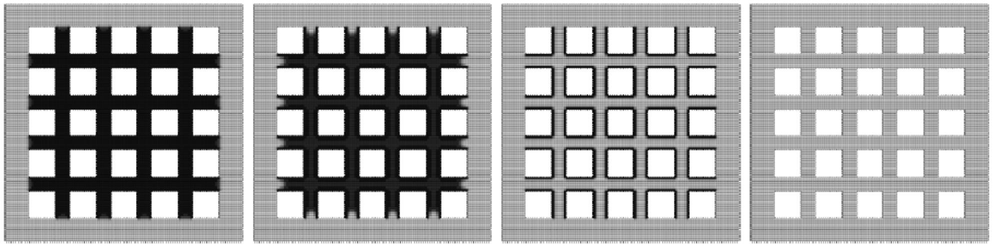
Results from static MFT - 2D Slit Network

(kT/ε = 1.0; T/Tc = 0.67)



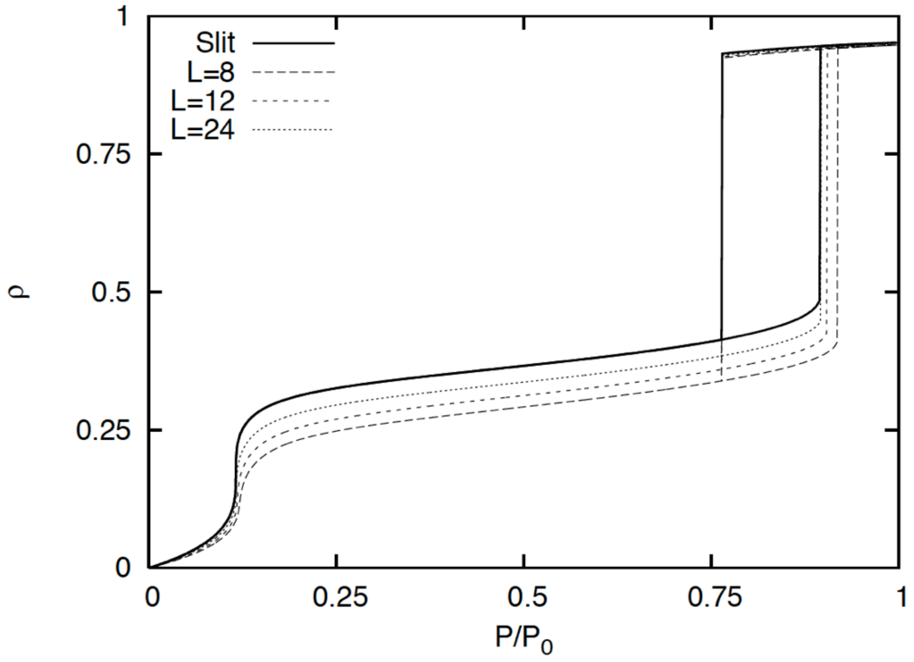


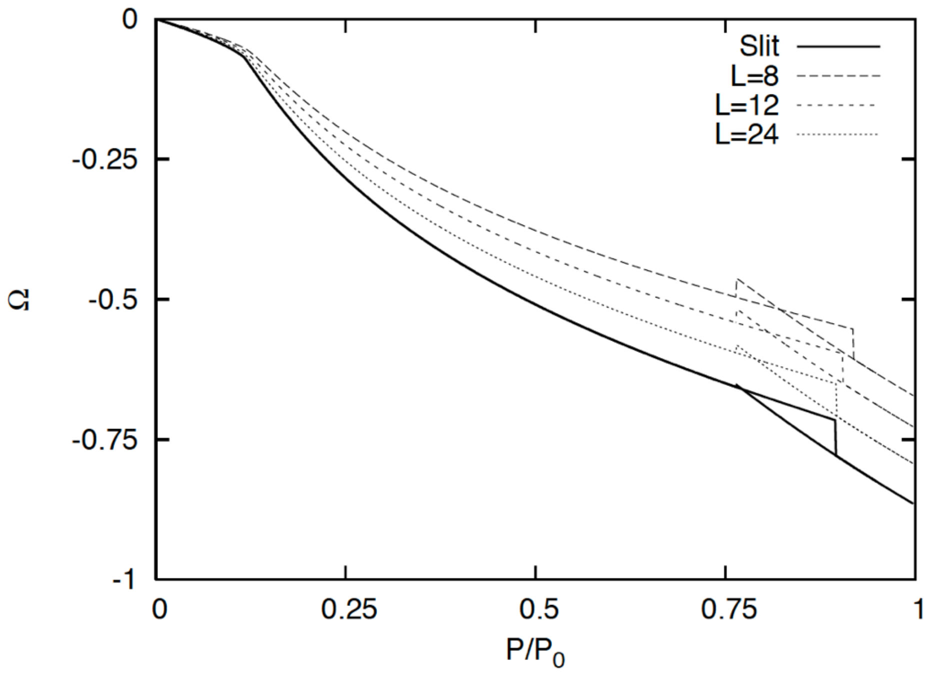
Adsorption

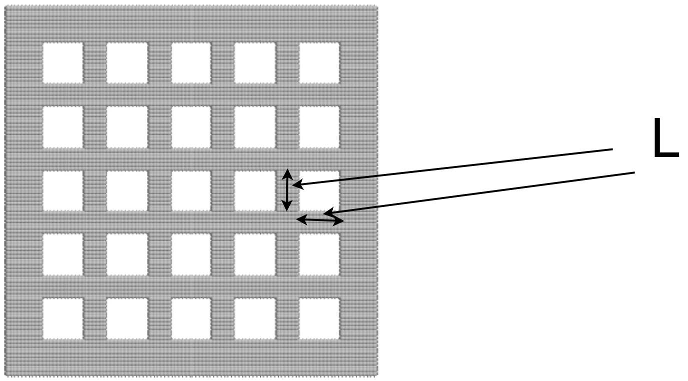


Desorption

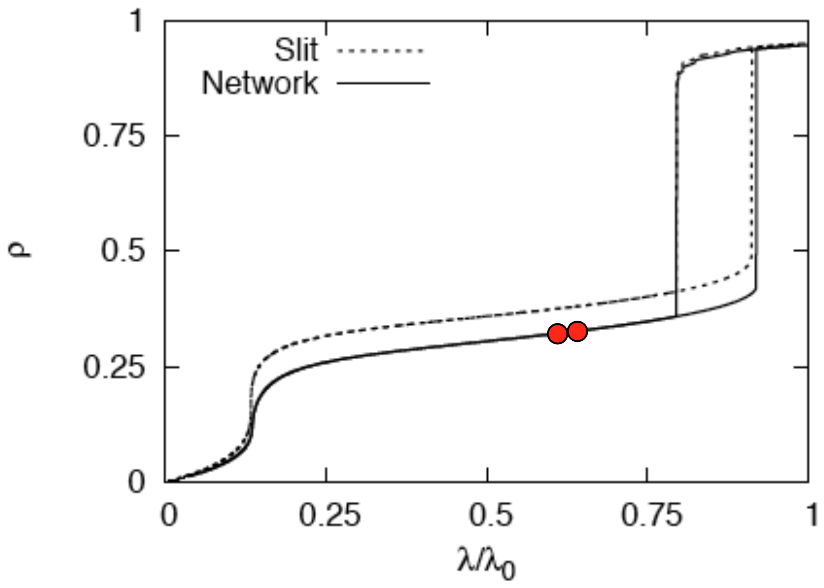
Comparison with single slit and effect of segment length

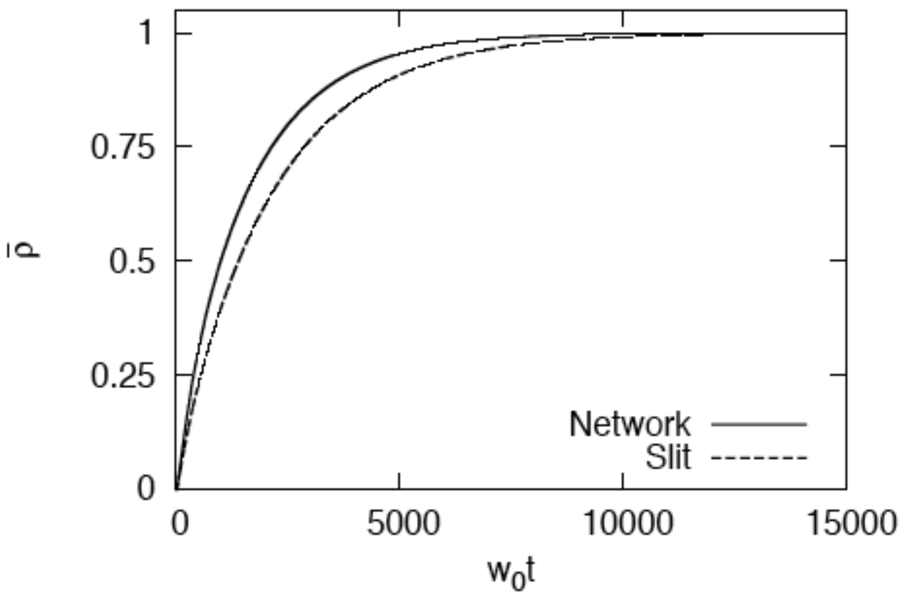






Dynamic uptake for a narrow quench between medium density states. Single pore vs. network.



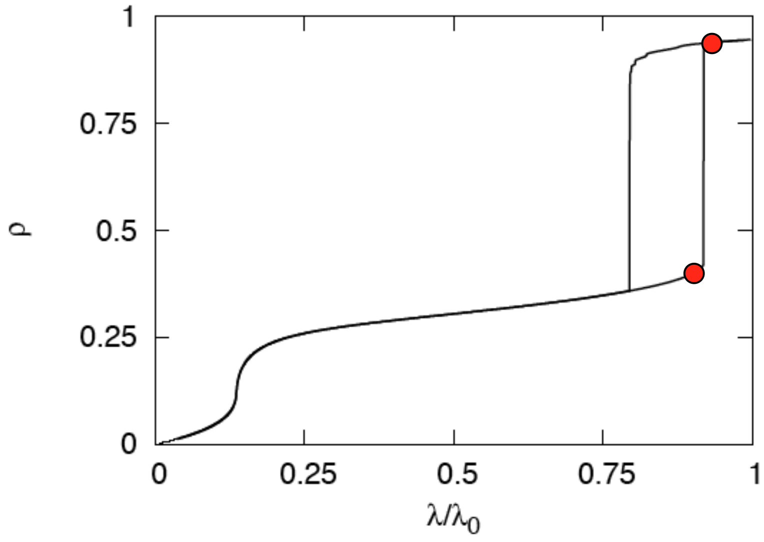


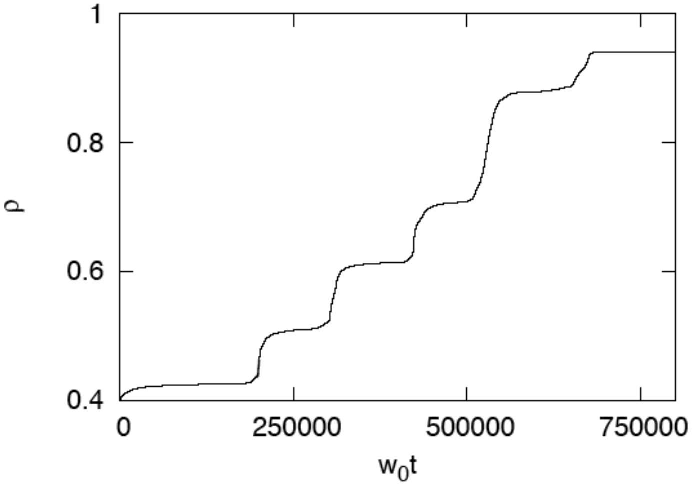
$$\bar{\rho} = \frac{\rho - \rho_0}{\rho_f - \rho_0}$$

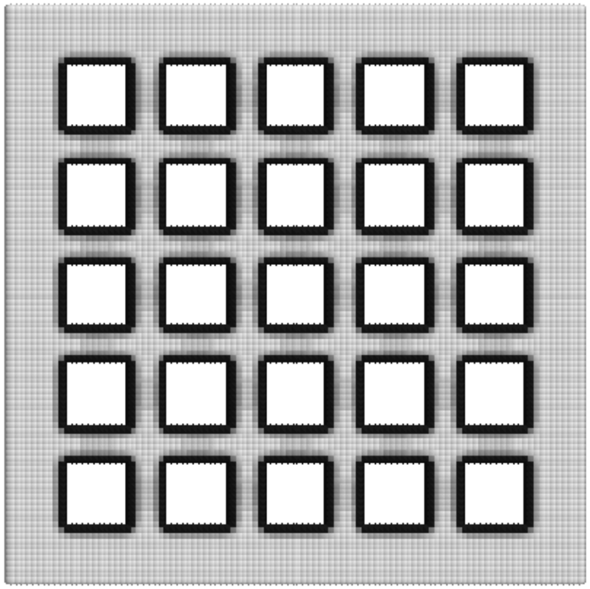
Network equilibrates faster due to greater access to bulk

- 2D vs. 1D

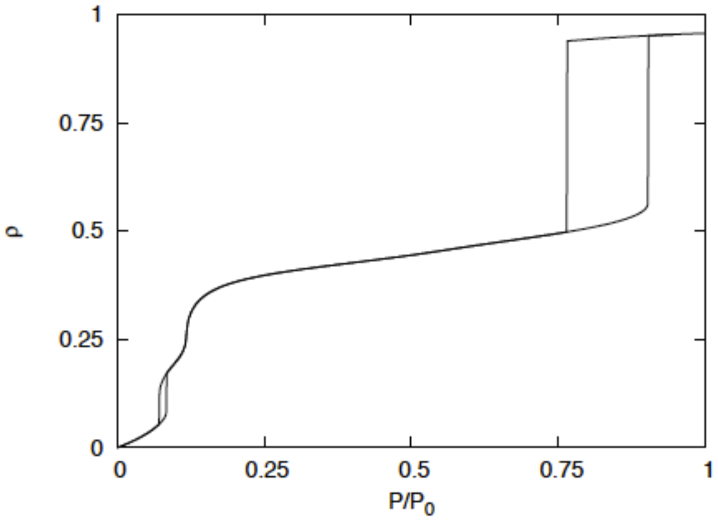
Dynamic uptake for a slit pore network for quench between states either side of condensation transition (kT/ε = 1.0; T/Tc = 0.67)

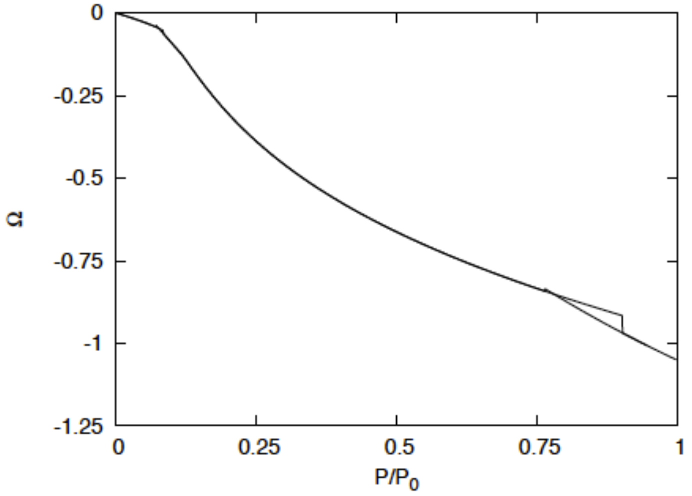


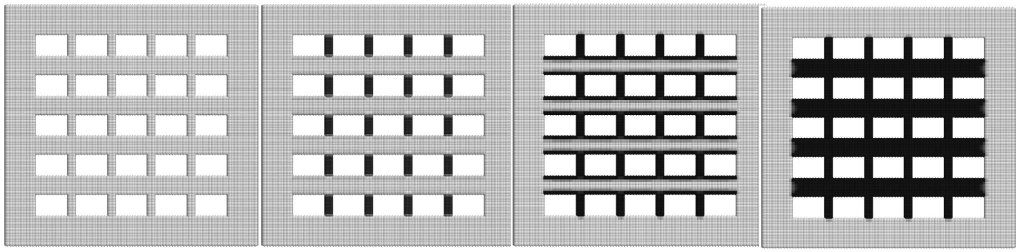




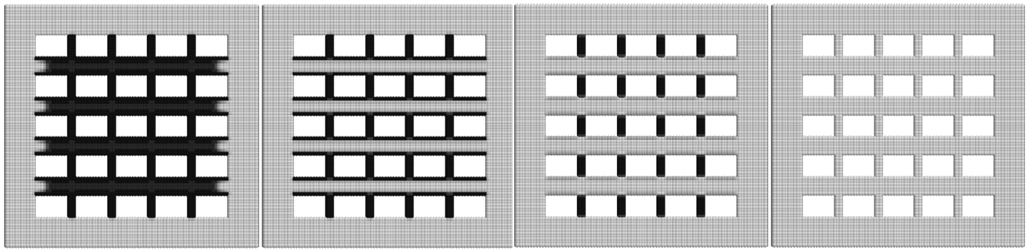
Results from static MFT - 2D Slit Network with two pore sizes (kT/ε = 1.0; T/Tc = 0.67)





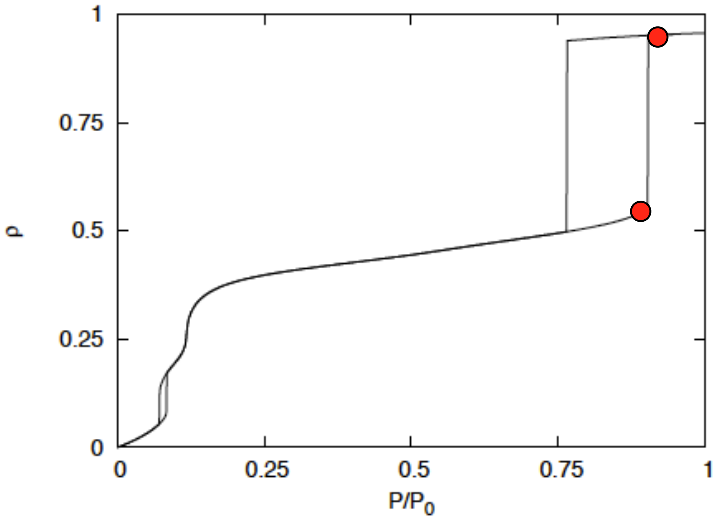


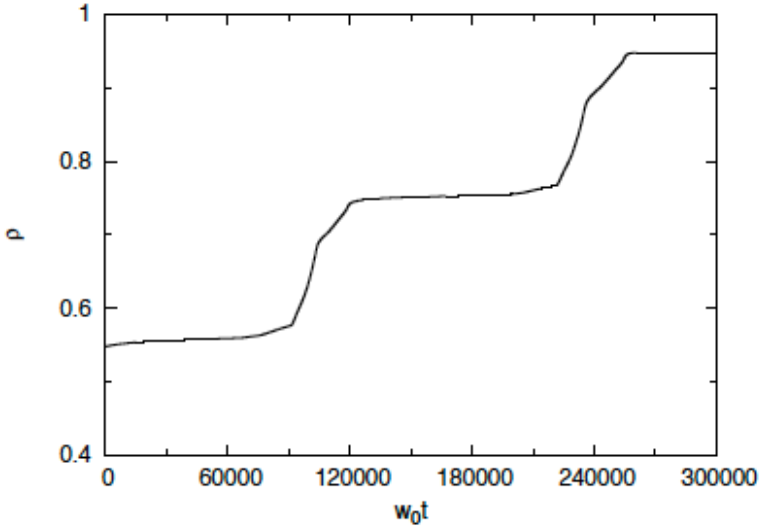
Adsorption

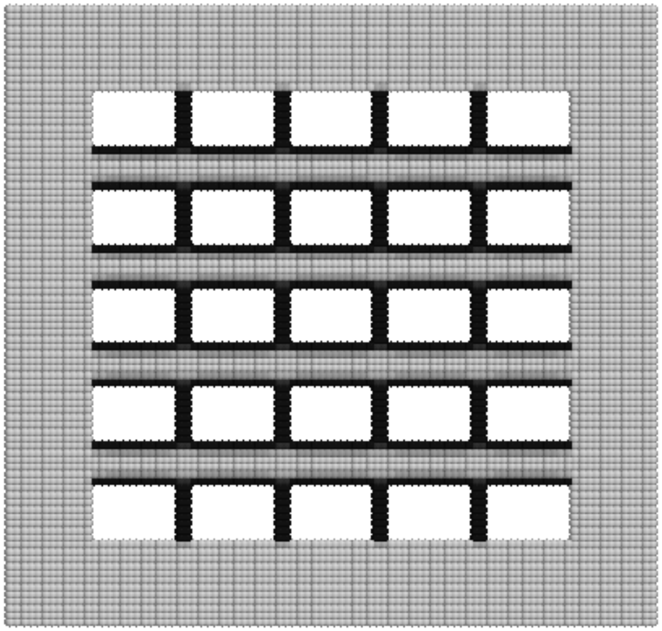


Desorption

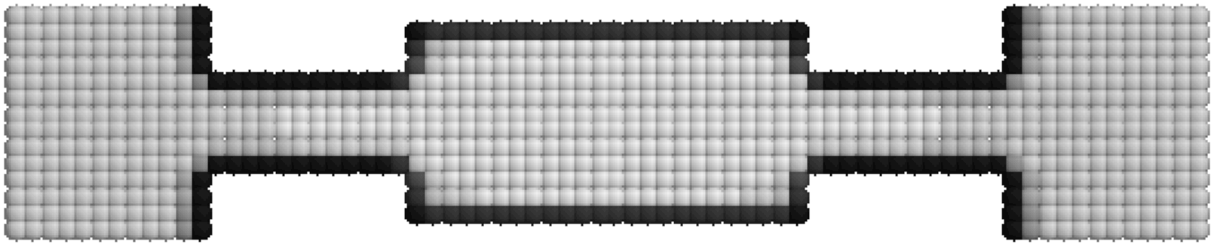
Dynamic uptake for a slit pore network with two pore sizes for quench between states either side of condensation transition (kT/ε = 1.0; T/Tc = 0.67)







The Inkbottle: Stretching Liquids in Pores



- on adsorption “necks” fill first, then the “bottle”

- on desorption different emptying mechanisms are possible

  - *bottle and necks empty simultaneously (pore blocking)*

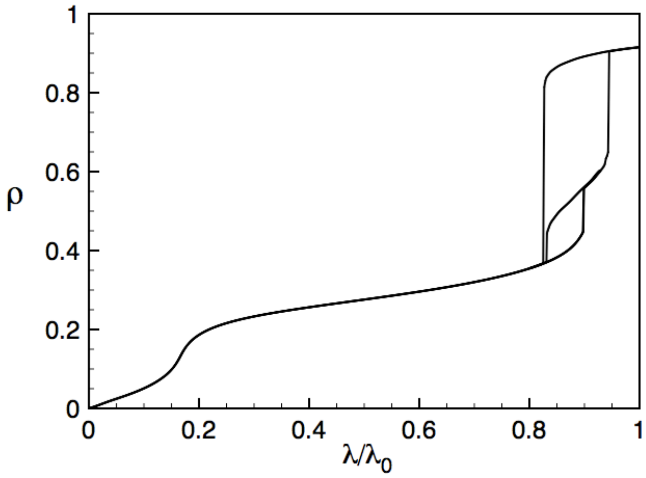
  - *bottle may empty while necks remain filled (Sarkisov and Monson, 2001)*

see also Ravikovitch and Neimark, 2002,Vishnyakov and Neimark, 2003, Libby and Monson, 2004

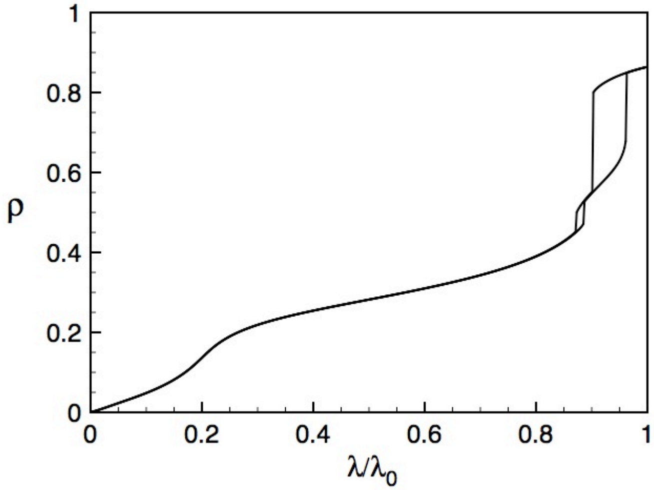
Static MFT for inkbottle at two temperatures

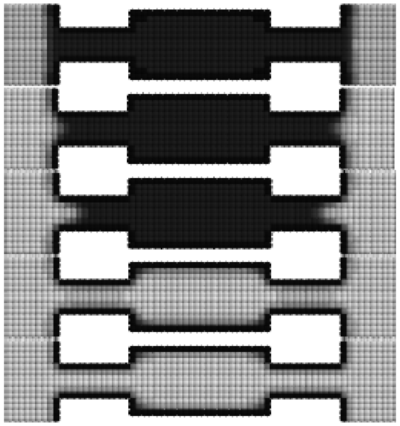
(Libby and Monson, 2004)

kT/ε = 1.125 (T/Tc = 0.75)

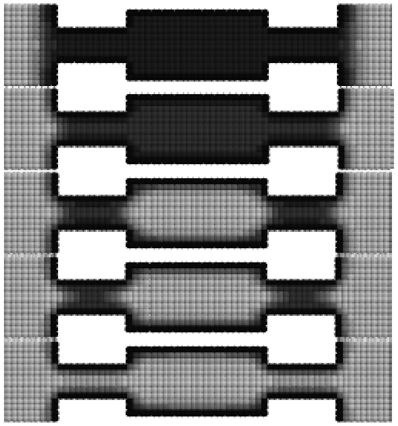


kT/ε = 1.275 (T/Tc = 0.85)



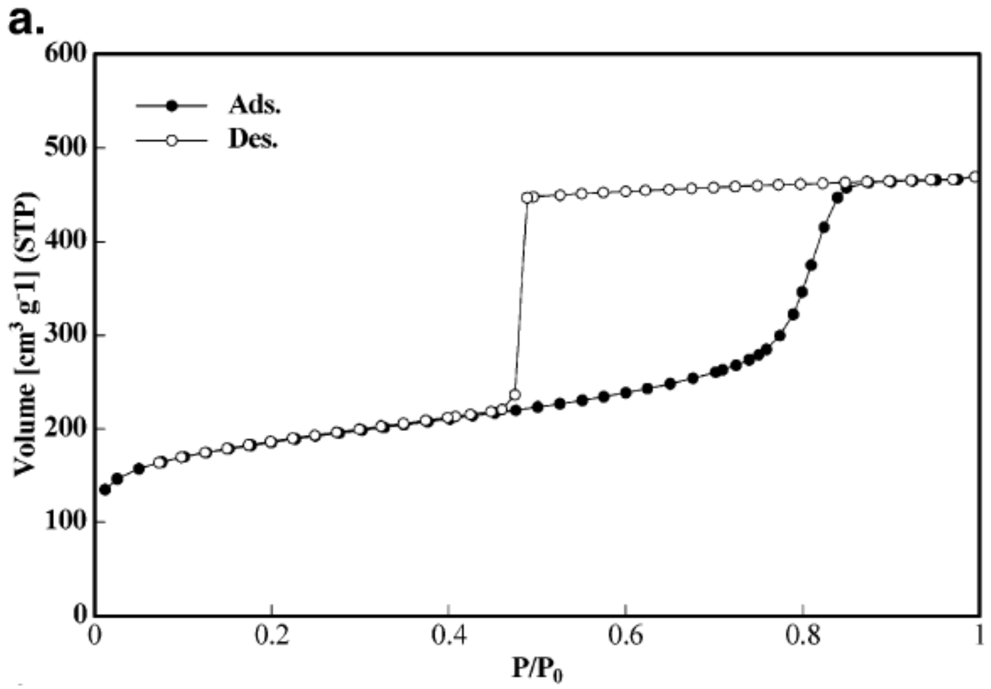


Visualizations of states on desorption



Nitrogen adsorption in hierarchically ordered mesoporous silica materials

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

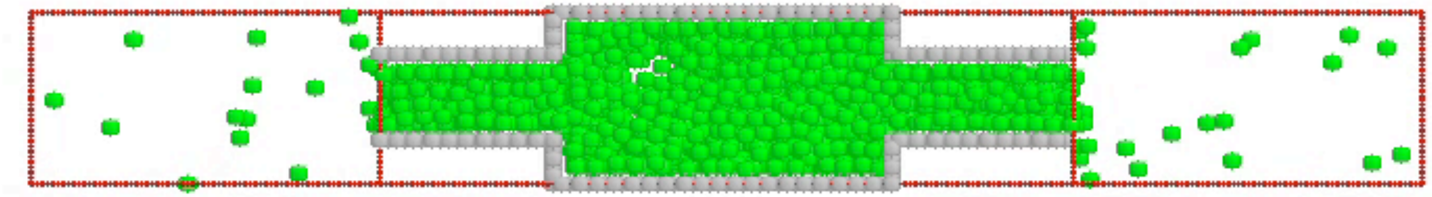


SE3030, a network of mesopores interconnected via micropores

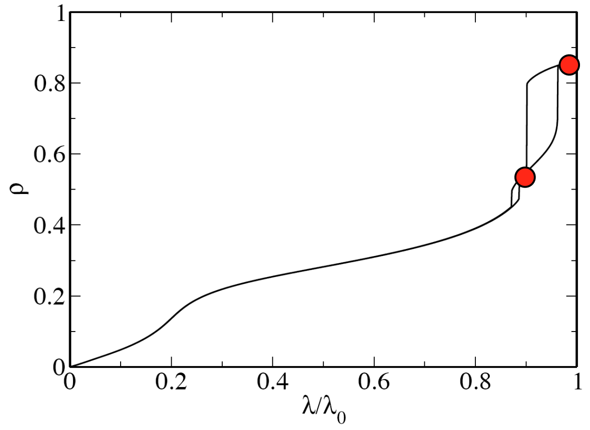
Can generate extremely overexpanded (metastable) states of the liquid in the spherical mesopores

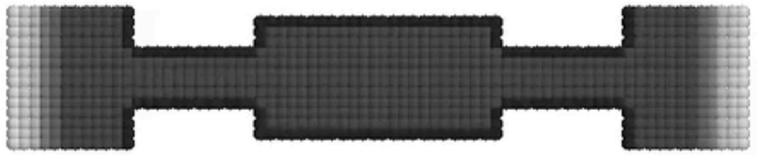
Grand Canonical Molecular Dynamics simulation of cavitation in an inkbottle pore

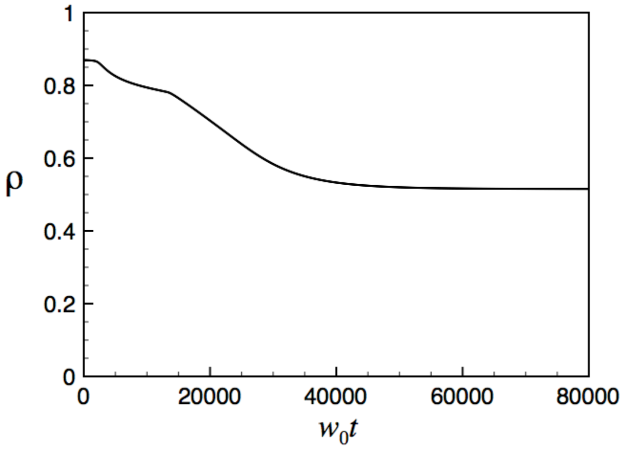
Sarkisov and Monson, *Langmuir*, 17, 7600 (2001)



Dynamic desorption for an inkbottle showing cavitation in the large pore. $kT/\varepsilon = 1.275$ ($T/T_c = 0.85$)





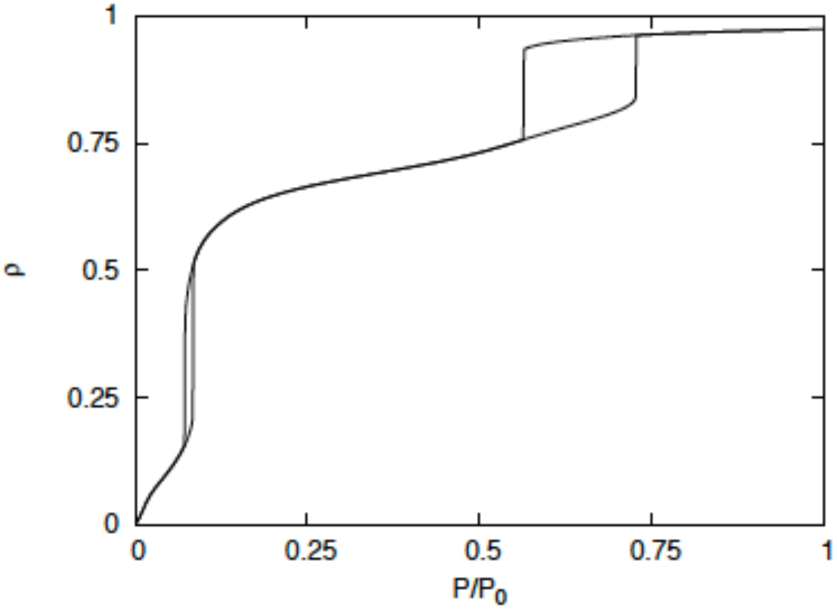


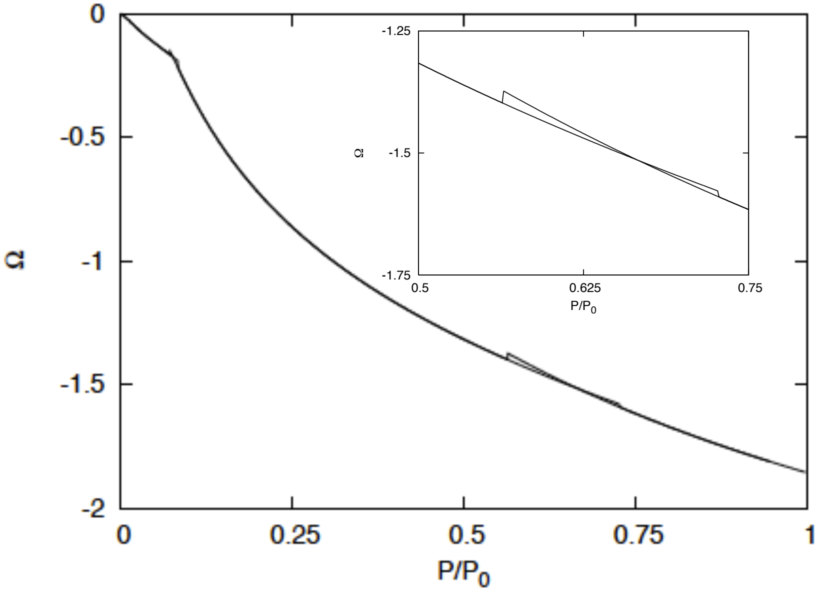
Cavitation process in large pore

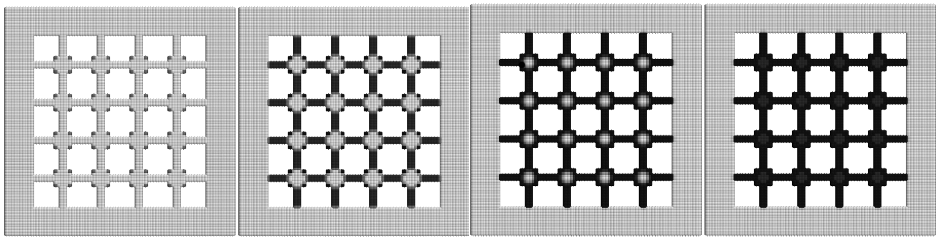
Liquid in pore behaves like an elastic material

Results from static MFT - 2D inkbottle network

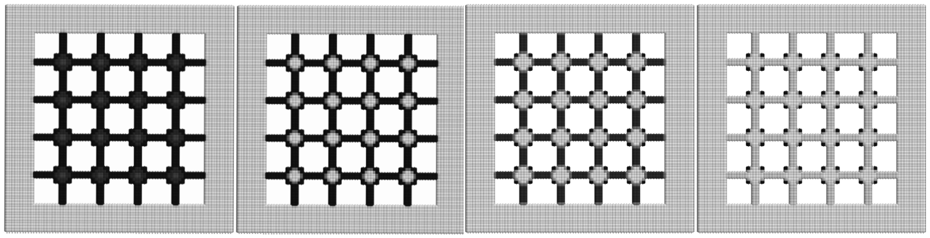
(kT/ε = 1.0; T/Tc = 0.67)





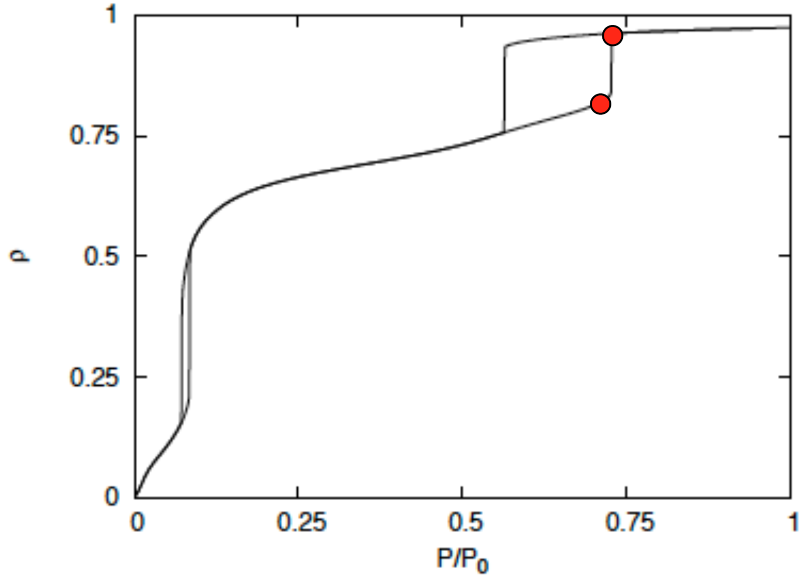


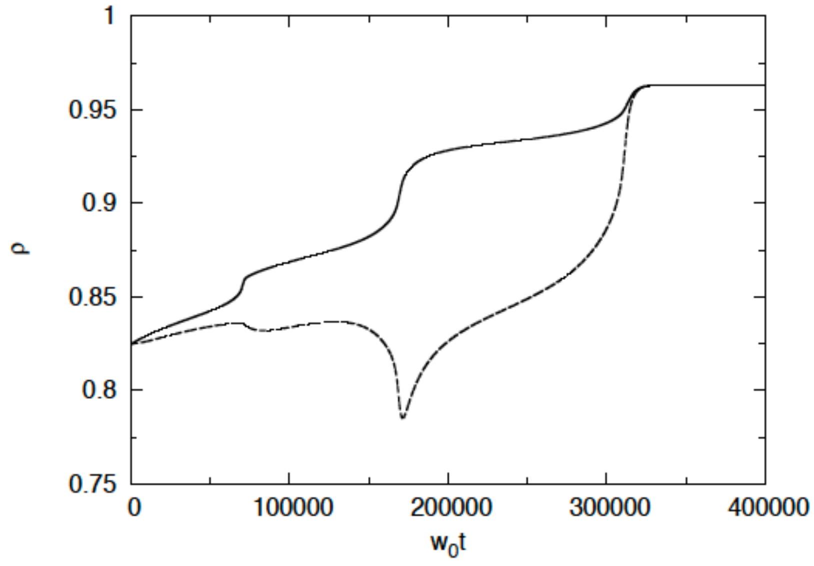
Adsorption

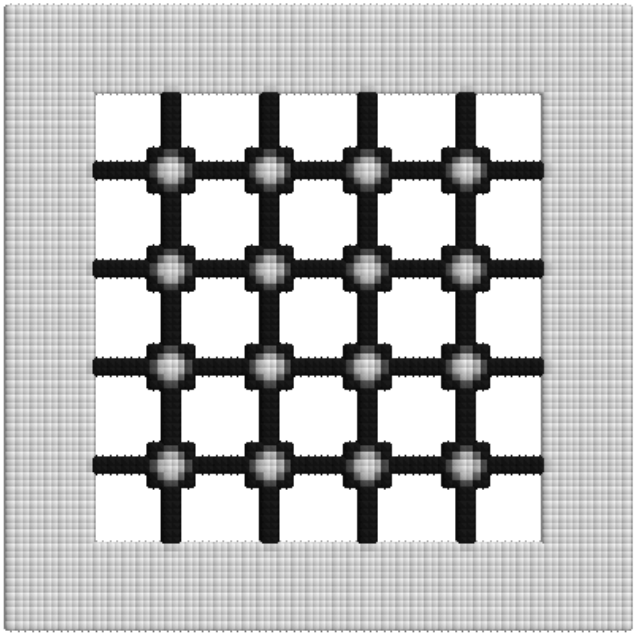


Desorption

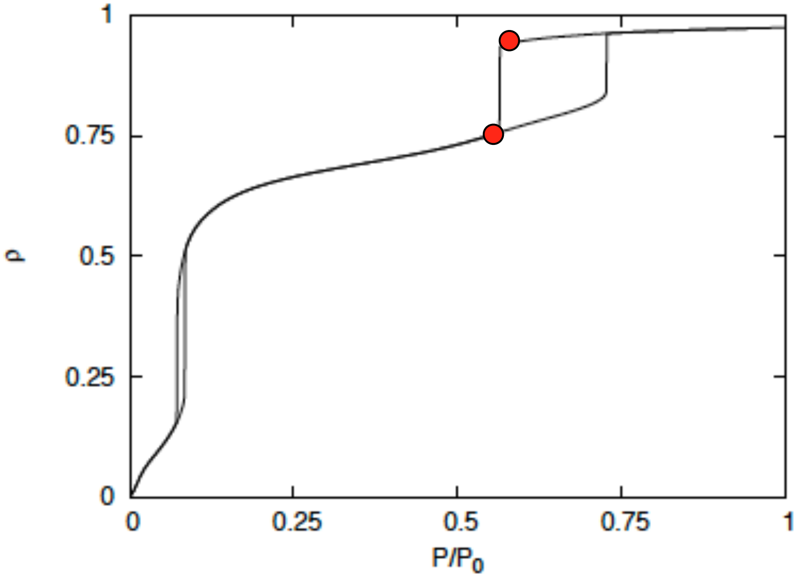
Dynamic uptake for a 2D inkbottle during condensation step (kT/ε = 1.0; T/Tc = 0.67)

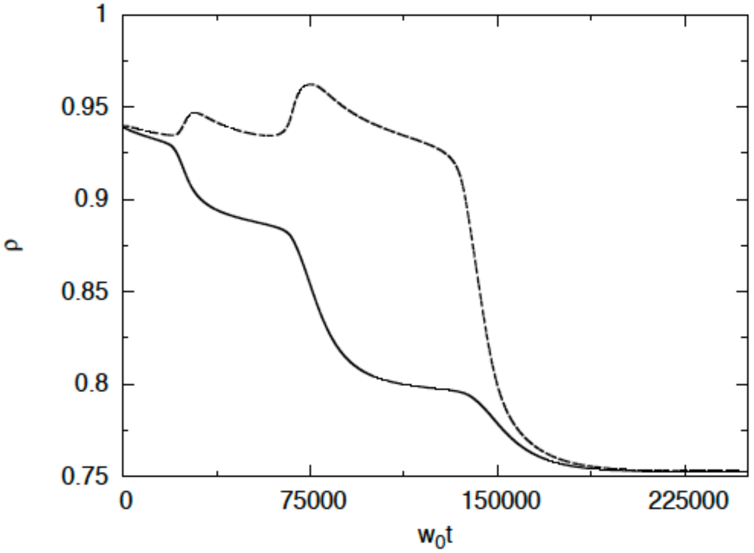


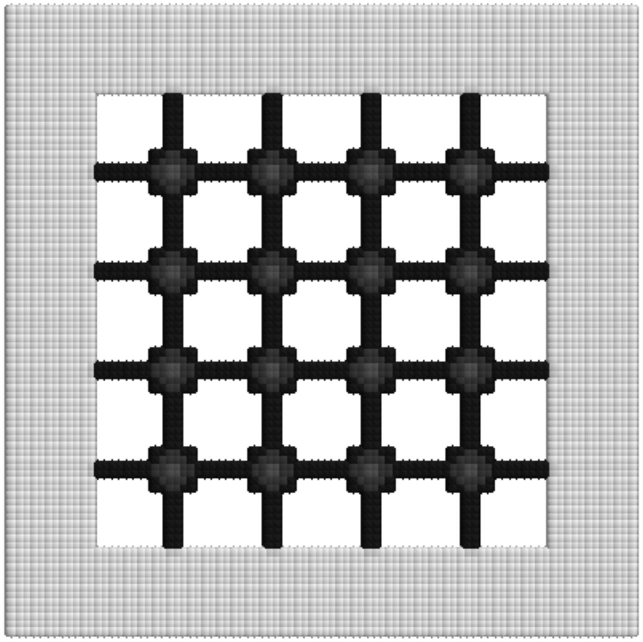




Dynamics of cavitation for a 2D inkbottle
(kT/ε = 1.0; T/Tc = 0.67)







Fluid Mixtures

DFT for Mixtures

Lattice gas Hamiltonian

$$H = -\frac{1}{2}\sum_{\mathbf{i}}\sum_{\mathbf{a}}\sum_{\alpha}\sum_{\gamma} \epsilon_{\alpha\gamma} n_{\mathrm{i}}^{\alpha} n_{\mathrm{i+a}}^{\gamma} + \sum_{\mathbf{i}}\sum_{\alpha} n_{\mathrm{i}}^{\alpha}\phi_{\mathrm{i}}^{\alpha}$$

Grand Free energy

$$\Omega = kT\sum_{\mathrm{i}}\left[\sum_{\alpha}\rho_{\mathrm{i}}^{\alpha}\ln\rho_{\mathrm{i}}^{\alpha} + \left(1-\sum_{\alpha}\rho_{\mathrm{i}}^{\alpha}\right)\ln\left(1-\sum_{\alpha}\rho_{\mathrm{i}}^{\alpha}\right)\right] - \frac{1}{2}\sum_{\mathbf{i}}\sum_{\mathbf{a}}\sum_{\alpha}\sum_{\gamma}\epsilon_{\alpha\gamma}\rho_{\mathrm{i}}^{\alpha}\rho_{\mathrm{i+a}}^{\gamma}$$

$$+\sum_{\mathbf{i}}\sum_{\alpha}\rho_{\mathrm{i}}^{\alpha}(\phi_{\mathrm{i}}^{\alpha} - \mu^{\alpha})$$

DFT for Mixtures

Bulk mixture equations for phase equilibrium calculations

$$P = -\frac{\Omega}{M v_s} = -kT \ln\Big(1 - \sum_{\alpha} \rho_b^{\alpha}\Big) - \frac{z}{2} \sum_{\alpha} \sum_{\gamma} \epsilon_{\alpha\gamma} \rho_b^{\alpha} \rho_b^{\gamma}$$

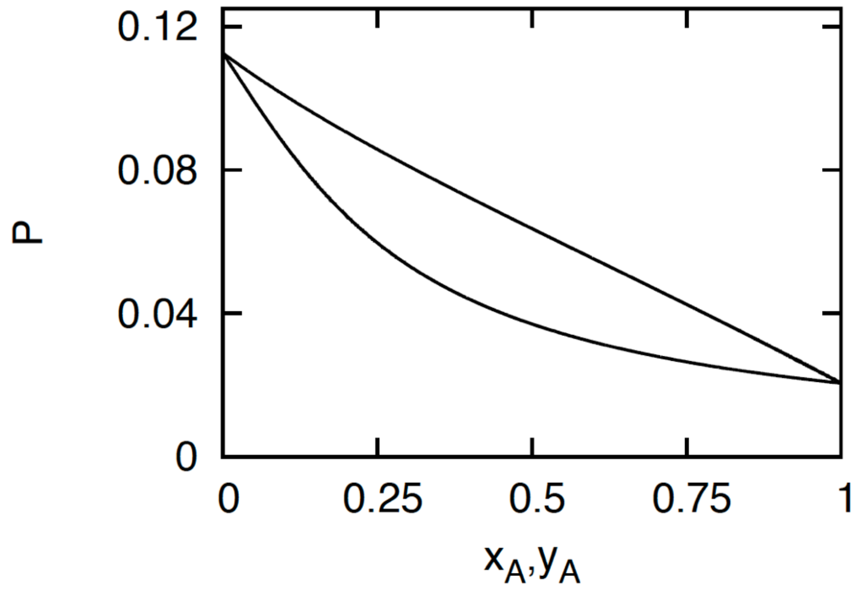
$$\mu^{\alpha} = kT \left[\ln \rho_b^{\alpha} - \ln\Big(1 - \sum_{\gamma} \rho_b^{\gamma}\Big) \right] - z \sum_{\gamma} \epsilon_{\alpha\gamma} \rho_b^{\gamma}$$

Dynamic Mean Field Theory for Mixtures

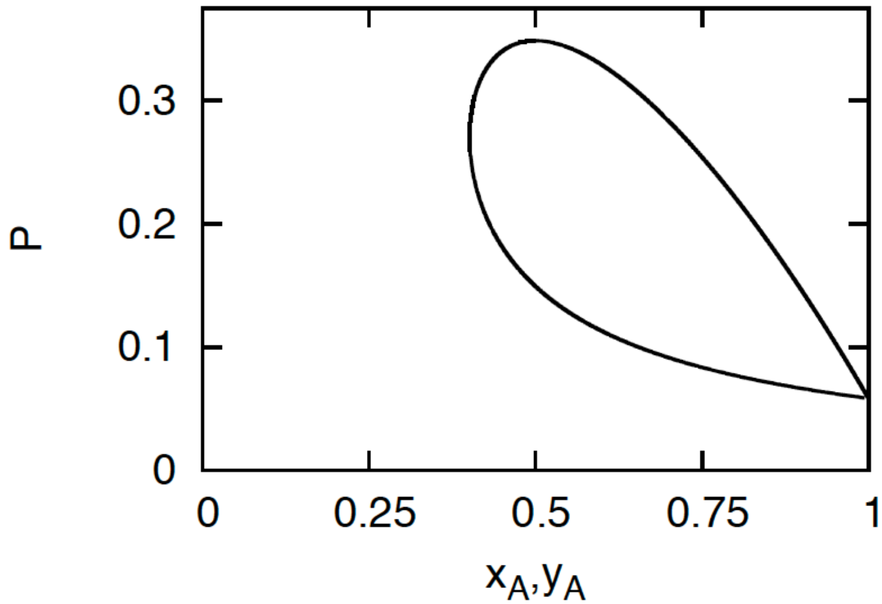
$$\frac{\partial \rho_{\mathbf{i}}^{\alpha}}{\partial t} = -\sum_{\mathbf{a}} J_{\mathbf{i},\ \mathbf{i+a}}^{\alpha}$$

$$J_{\mathbf{ij}}^{\alpha}(t) = w_{\mathbf{ij}}^{\alpha}\rho_{\mathbf{i}}^{\alpha}(1-\sum_{\gamma}\rho_{\mathbf{j}}^{\gamma}) - w_{\mathbf{ji}}^{\alpha}\rho_{\mathbf{j}}^{\alpha}(1-\sum_{\gamma}\rho_{\mathbf{i}}^{\gamma})$$

Application to Binary Mixtures



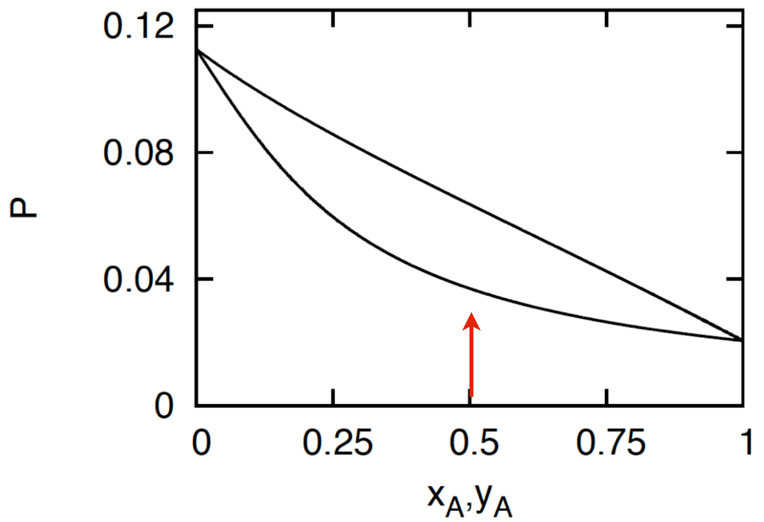
"Ethane-methane"

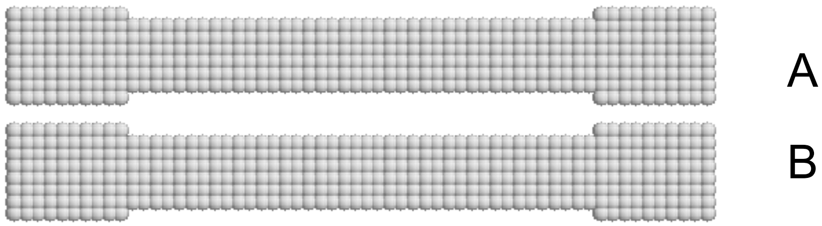


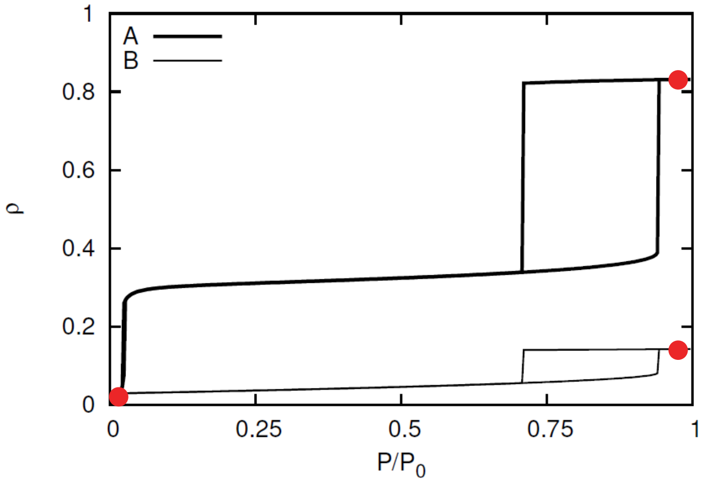
"Butane-methane"

DFT and DMFT calculations for mixtures in "carbon" slit and inkbottle pores

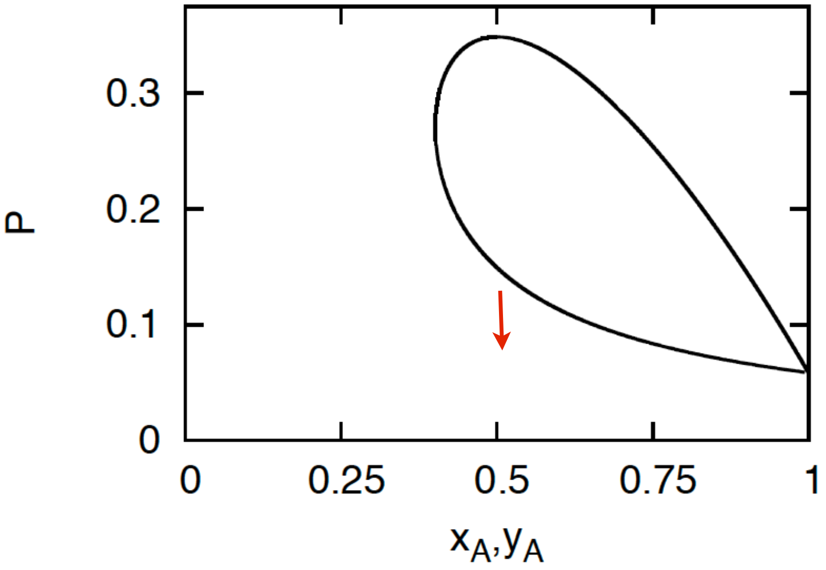
Dynamics of Capillary Condensation for a Binary Mixture in a Slit Pore

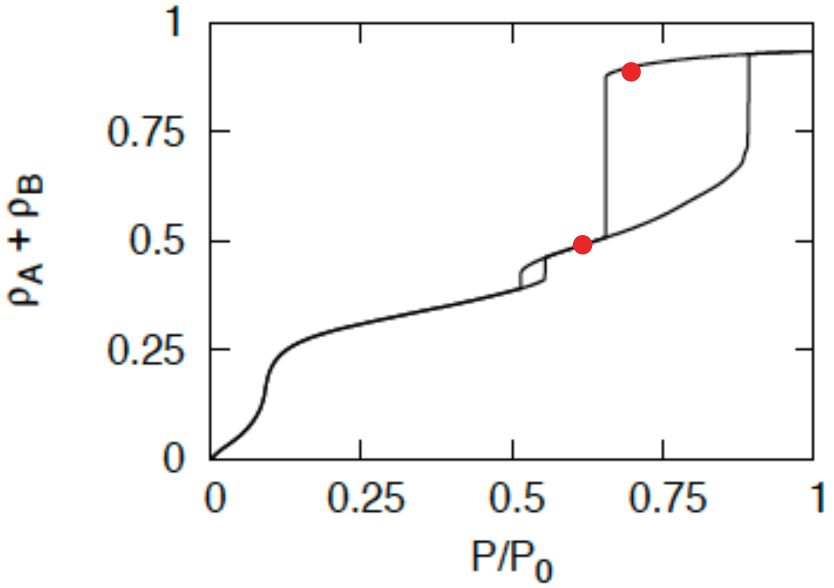


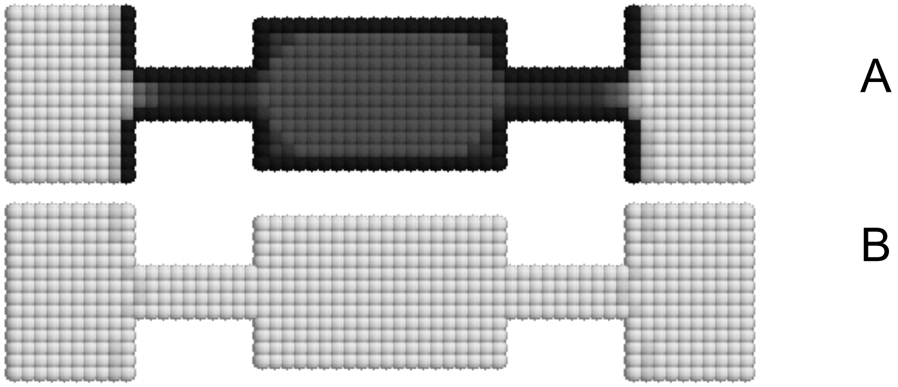




Dynamics of Cavitation for a Binary Mixture in an Inkbottle Pore







Permporometry: a characterization technique for porous membranes

(Eyraud et al., 1984)

- Based on co-permeation of a lighter, non-condensable gas and a heavier, condensable vapor through a porous membrane

- As P_C/P_{C0} increases the condensable component progressively fills pores

  - greatly decreases permeation of light component through those regions

- A plot of steady state flux of the light component through the membrane as a function of P_C/P_{C0} provides information about the membrane pore size distribution

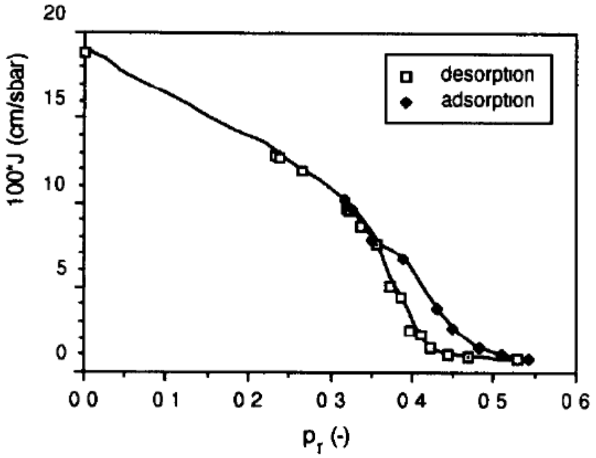


Fig 3 Permporometry adsorption and desorption curve for a γ-alumina membrane with cyclohexane used as adsorbate

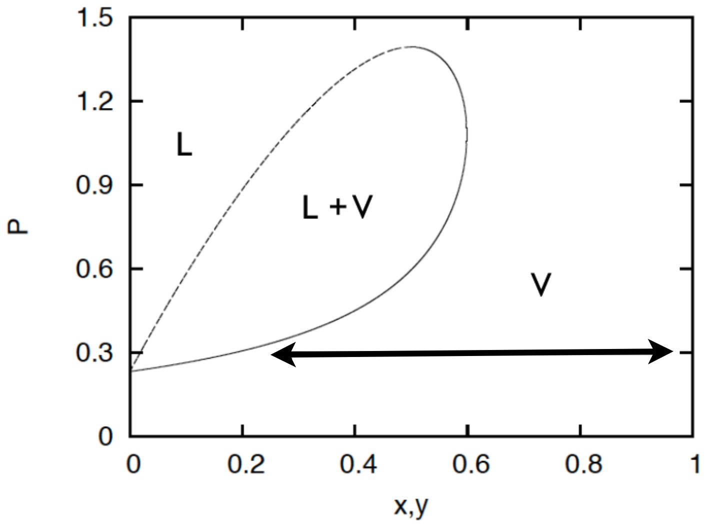
Cuperus et al., *J. Membrane Sci.*, 71, 57 (1992)

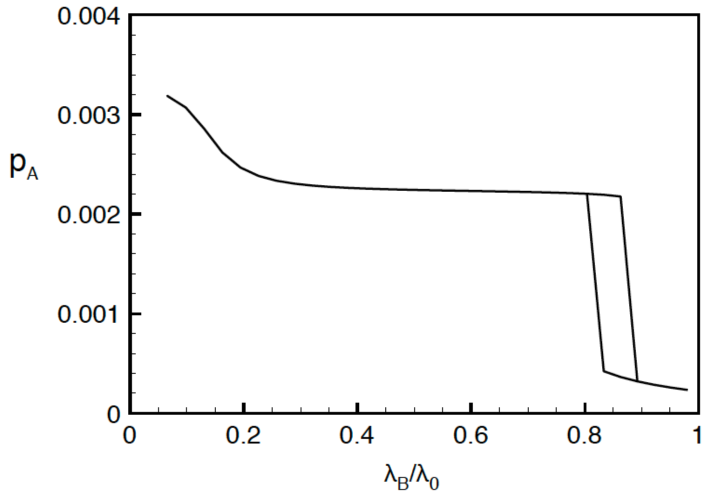
Collaboration with D. M. Ford

Modeling Permporometry with DMFT

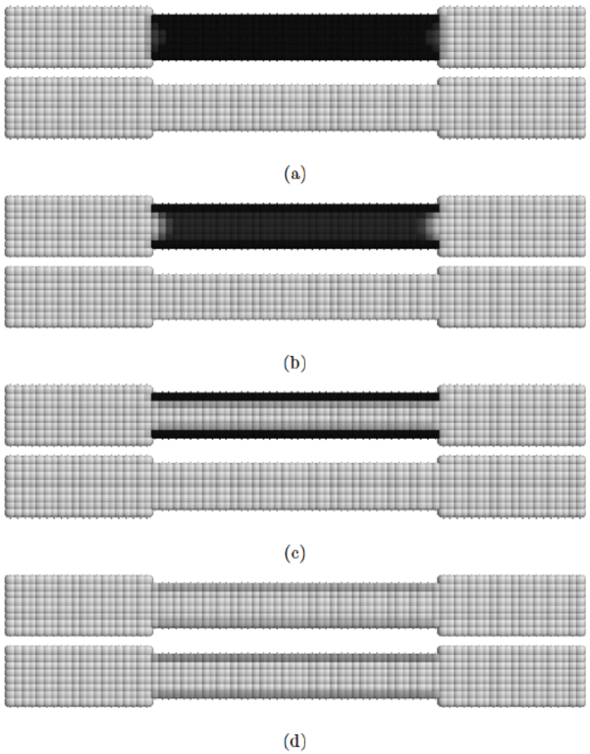
Can apply DMFT by solving for nonequilibrium steady states for given species chemical potential differences across membrane

"nitrogen-cyclohexane" mixture





states on desorption



Partial wetting of the pore walls by fluid

e.g. water in carbon pores

Adsorption of n-hexane and water on graphitized carbon black

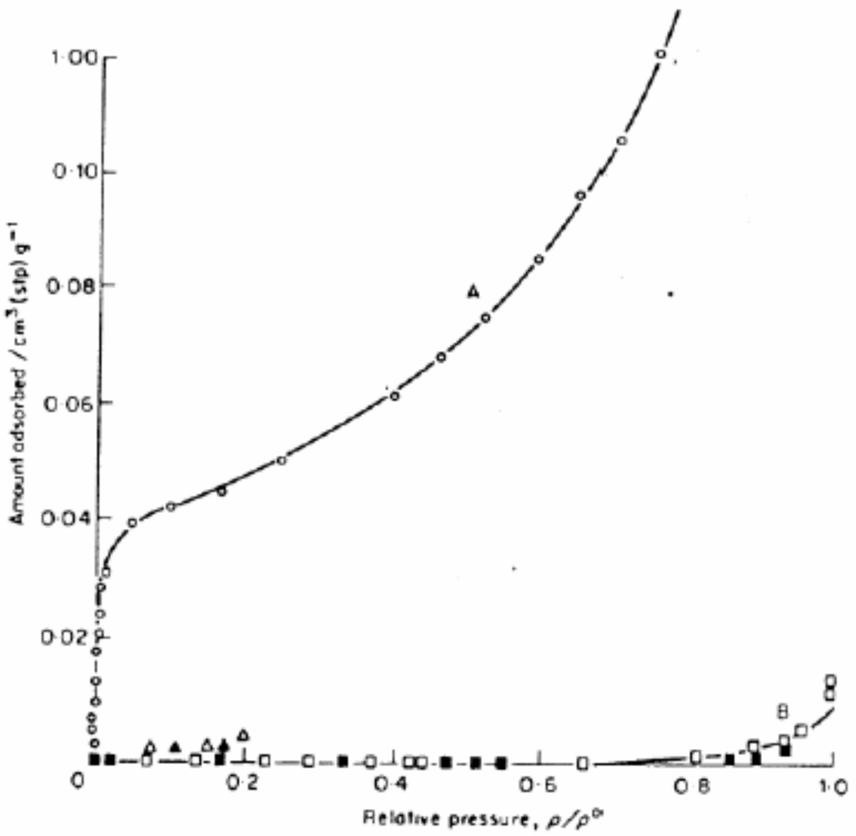
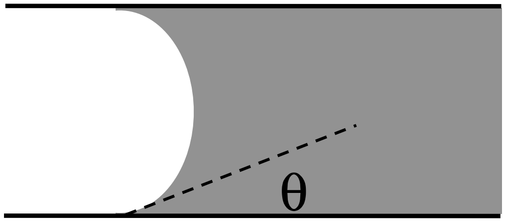


Figure 30: The adsorption isotherms of *n*-hexane (A) and of water (B) on graphitized carbon black. Filled symbols for desorption. (S.J. Gregg, K.S. Sing. Adsorption, Surface Area and Porosity. 2nd ed., Academic Press, New York, 1982.)

From Gregg and Sing, “Adsorption Surface Area and Porosity”, 2nd edition, Academic Press, 1982.

Kelvin Equation Perspective

$$RT \ln\left(\frac{P_v}{P_0}\right) = \frac{-2\sigma_{VL} V^{l} \cos\theta}{r}$$



e.g. Contact angle of water on graphite ~ 85 – 86^0

Fowkes, F. M.; Harkins, W. D.
J. Am. Chem. Soc. **1940**, *62*, *2* (12), 3377-3377

Equilibrium pore condensation for $P < P_0$

(Valid for large H)

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Adsorption of water on graphitized carbon black

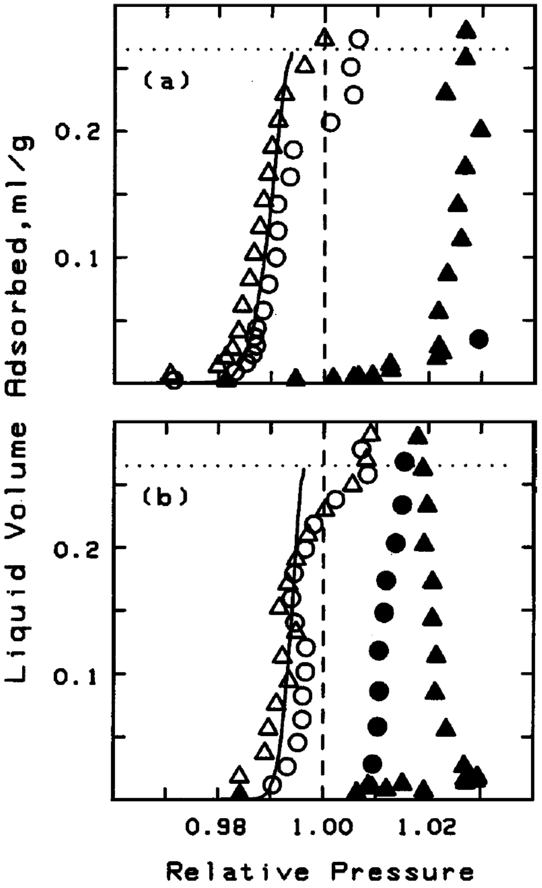


FIG. 1. Adsorption isotherms at high relative pressure for water on Sterling FT-G (2700) at (a) 280.15 K and (b) 295.15 K. Adsorption points are filled; ○, run 1; △, run 2. The horizontal dotted line indicates the pore volume, 0.265 mL g^{-1}. The curved solid line passing through the desorption points indicates the desorption path as calculated from the adsorbent particle size distribution (see

E. B. Easton and W.D. Machin,
J. Colloid Interface Sci., 231, 204 (2000)

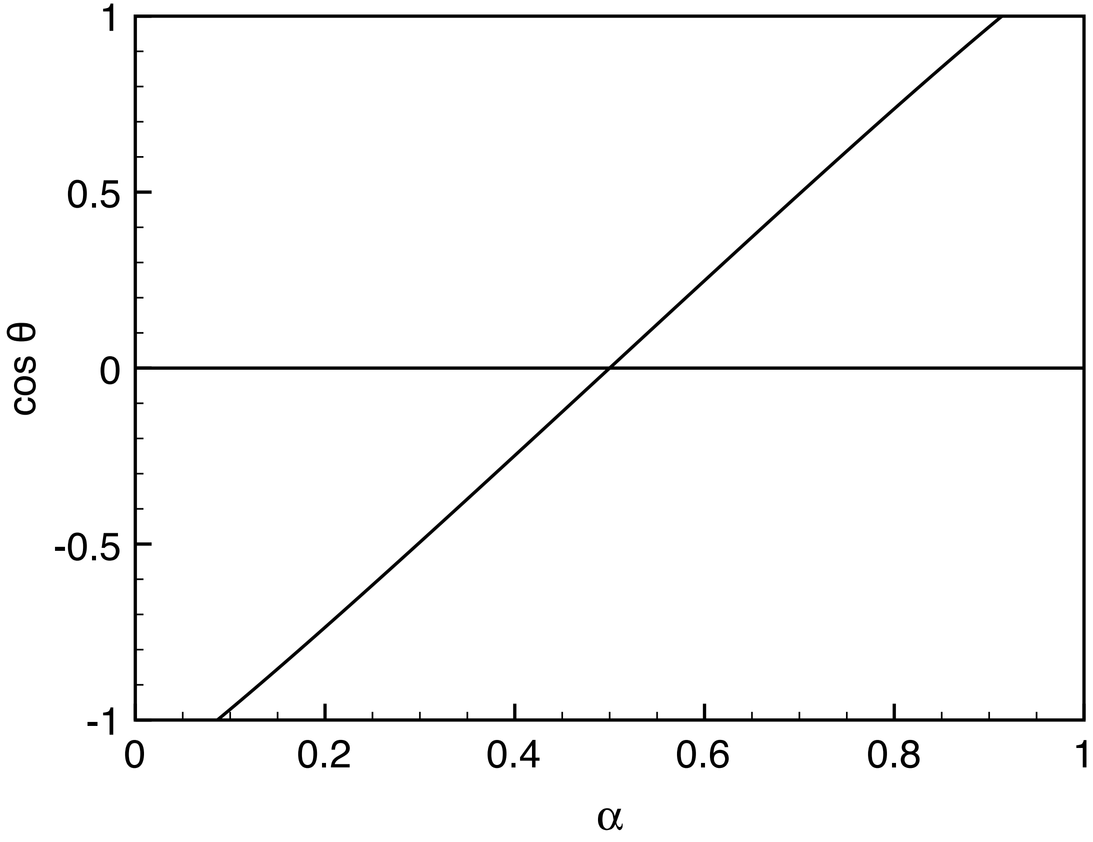
a) 280.25 K
b) 295.15 K

circles - run 1
triangles - run 2

filled symbols - adsorption
open symbols - desorption

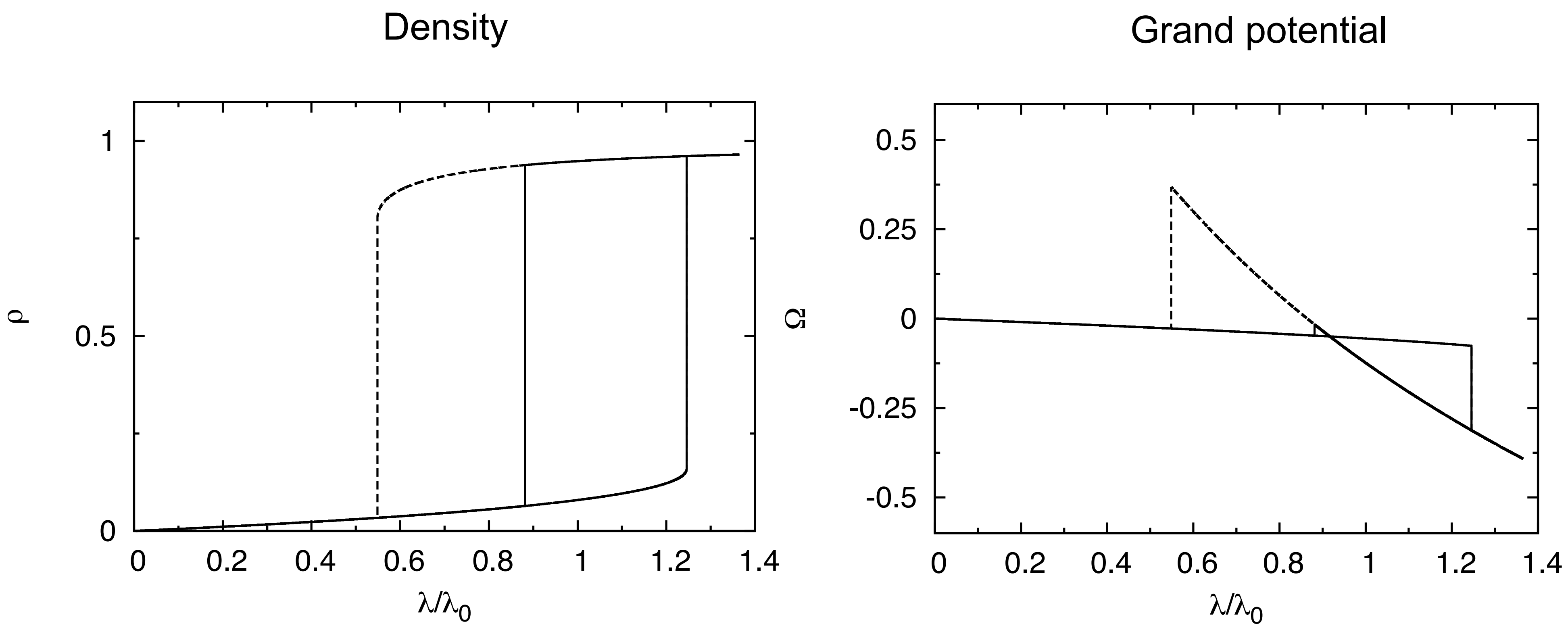
- *Pore condensation for supersaturated bulk states*

Contact angles for nearest neighbor lattice model from Young's equation using MFT for interfacial free energies



$$\sigma_{VL}\cos\theta = \sigma_{SV} - \sigma_{SL}$$

Isotherm from static mean field theory ($\varepsilon_{sf} / \varepsilon_{ff} = 0.75$, $T^* = 0.9$)


Density

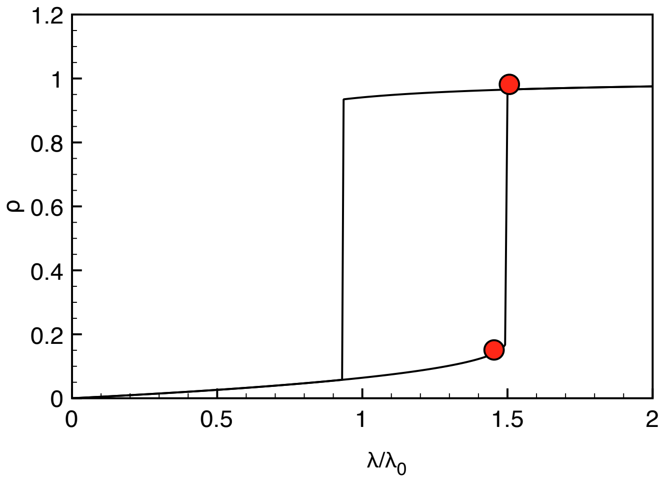
Grand potential

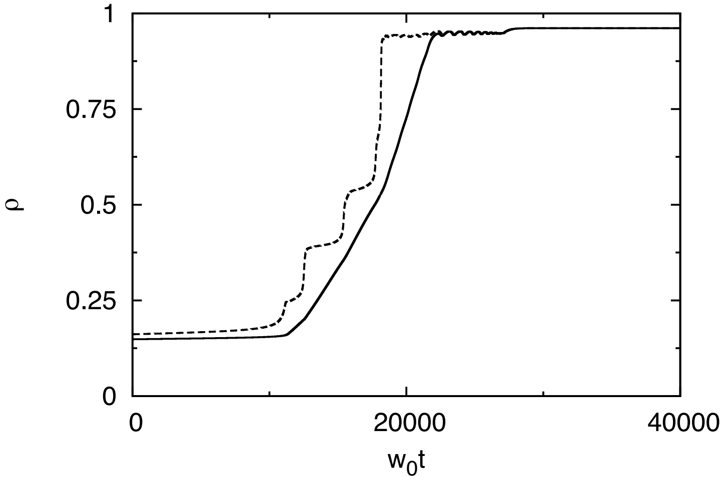
- - - - infinite length pore

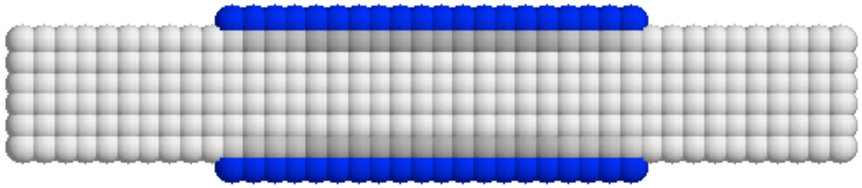
Equilibrium pore condensation below bulk saturation but adsorption branch extends to supersaturated conditions

c.f. water in graphitized carbon black (Easton and Machin, 2000)

Dynamic uptake for an L = 20 pore for quench between states either side of condensation transition (partial wetting case, $\varepsilon_{sf}/\varepsilon_{ff}$ = 0.55, T* = 0.9)



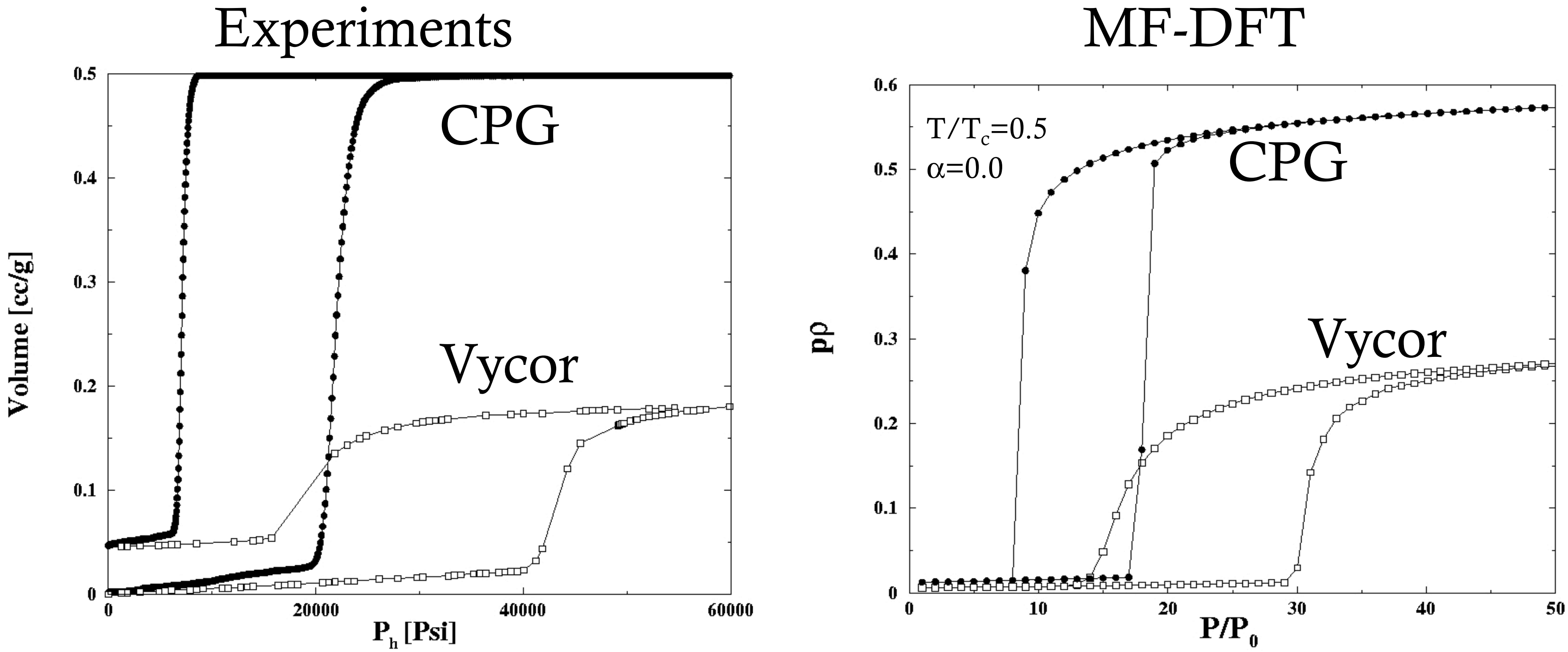




Systems with complete/partial drying pore surfaces

e.g. mercury porosimetry

Mercury Porosimetry in Porous Glasses



Porcheron et al., Langmuir, 23, 3372 (2007)

Acknowledgement: Matthias Thommes

Water in Zeolites

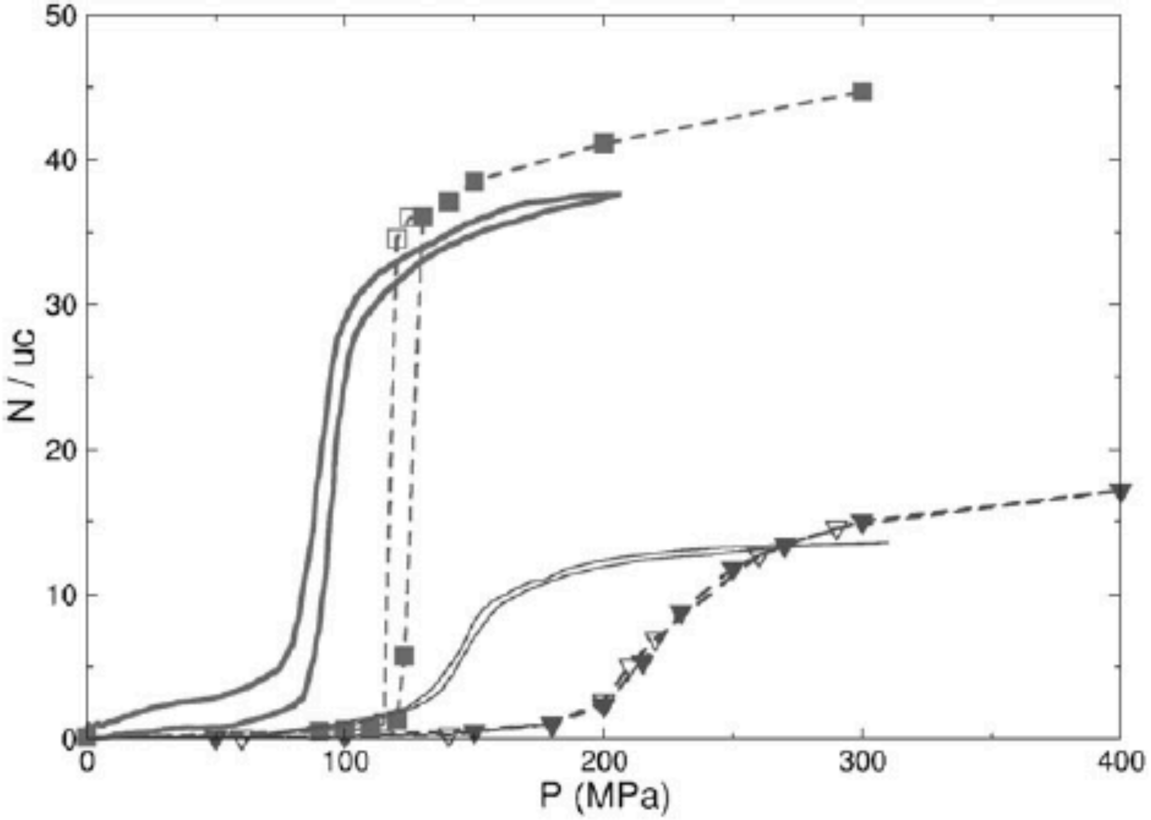


Fig. 3 Water intrusion/extrusion isotherms in silicalite-1 (squares and thick line) and ferrierite (triangles and thin line). Experimental data are shown in solid lines, symbols represent GCMC simulations (filled symbols: intrusion, open symbols: extrusion).

Caillez et al., PCCP, 10, 4817-4826 (2008)

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Symmetry of lattice gas model

$\alpha = 1/2 + \delta\alpha$ surface field

$\delta\alpha > 0$ wetting or partial wetting (“hydrophilic”)

$\delta\alpha < 0$ drying or partial drying (“hydrophobic”)

$\mu = \mu_0 + \delta\mu$ chemical potential

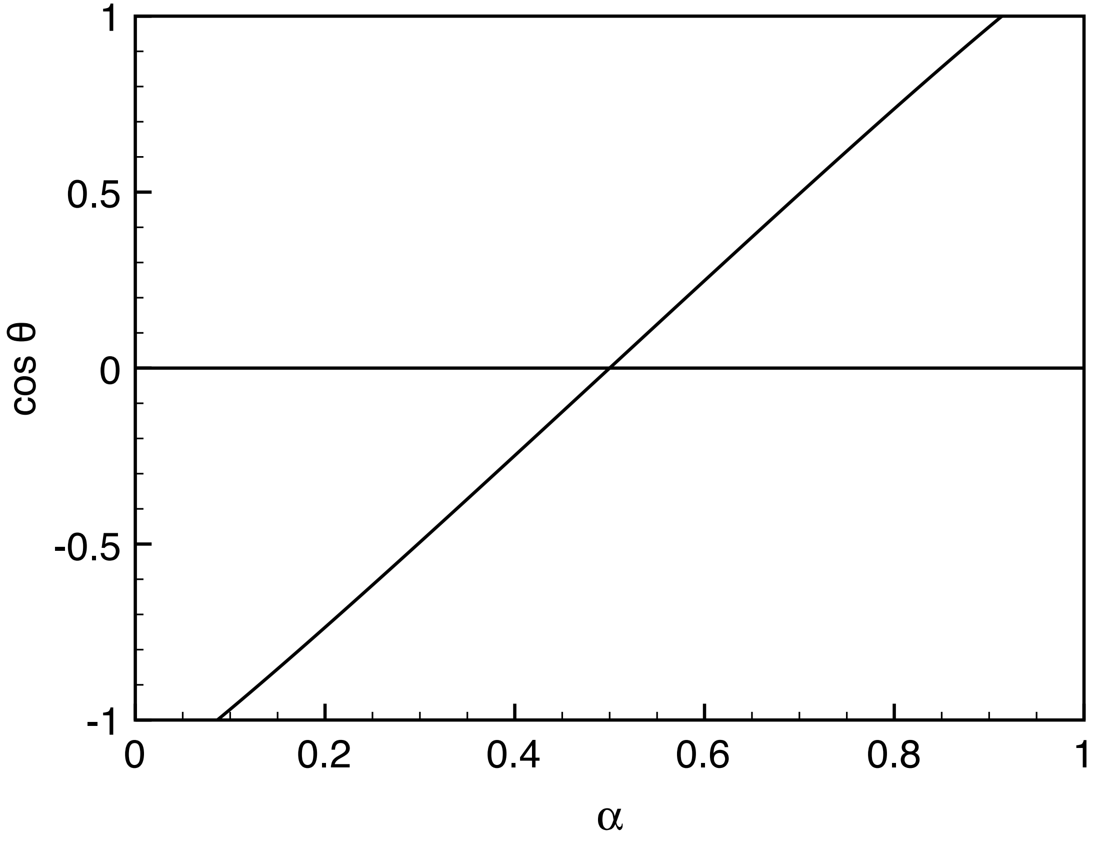
$\mu_0 = -Z\epsilon/2$

$\delta\mu < 0$ bulk vapor state

$\delta\mu > 0$ bulk liquid state

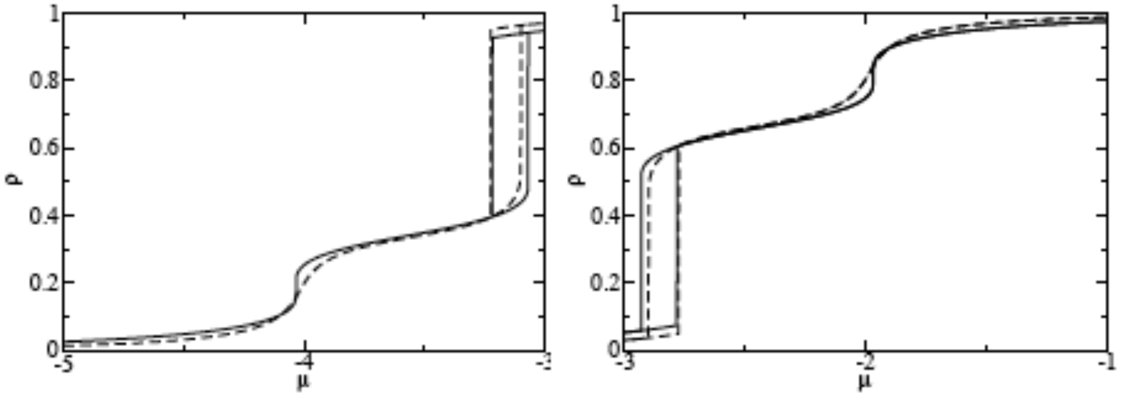
- Intrusion of a liquid with $\delta\alpha < 0$ isomorphic with desorption/evaporation for $\delta\alpha > 0$
- Extrusion of a liquid with $\delta\alpha < 0$ isomorphic with adsorption/condensation of liquid for $\delta\alpha > 0$

Contact angles for nearest neighbor lattice model from Young's equation using MFT for interfacial free energies



$$\sigma_{VL}\cos\theta=\sigma_{SV}-\sigma_{SL}$$

Symmetry of density isotherms

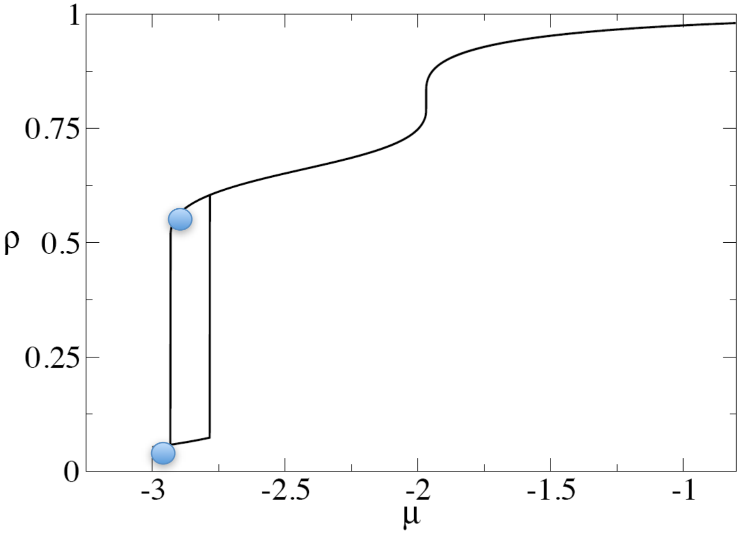


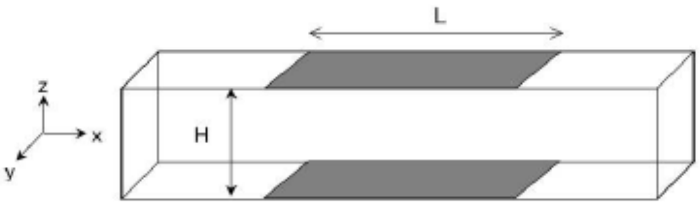
(a)

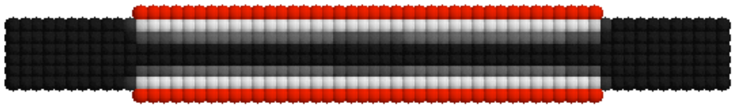
(b)

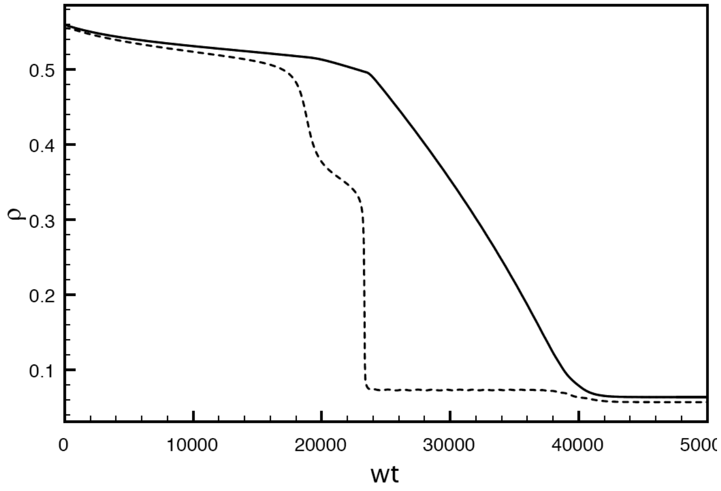
FIG. 3: Adsorption/Desorption isotherms of density vs. the chemical potential μ for (a) a completely wetting $[\alpha = 2]$ and (b) a competely drying $[\alpha = -1]$ slit pore at $T/T_c = 0.667$ computed with the Mean Field (full line) and the Bethe-Peierls Approximations (dashed line)

Dynamics of pore emptying for a complete drying case



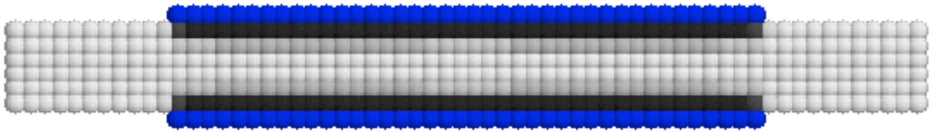




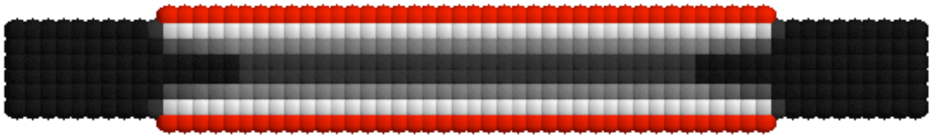


Capillary Condensation / Evaporation

$\alpha = 2.0$



$\alpha = -1.0$



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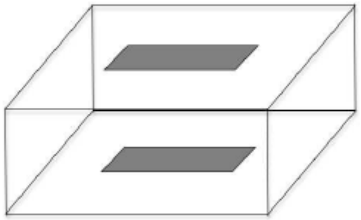
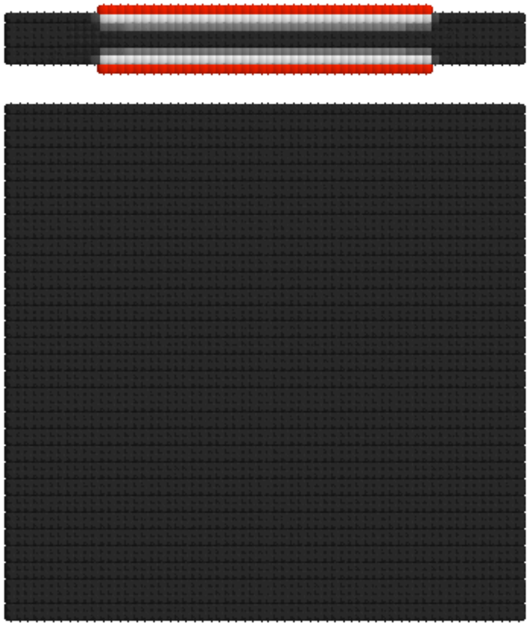
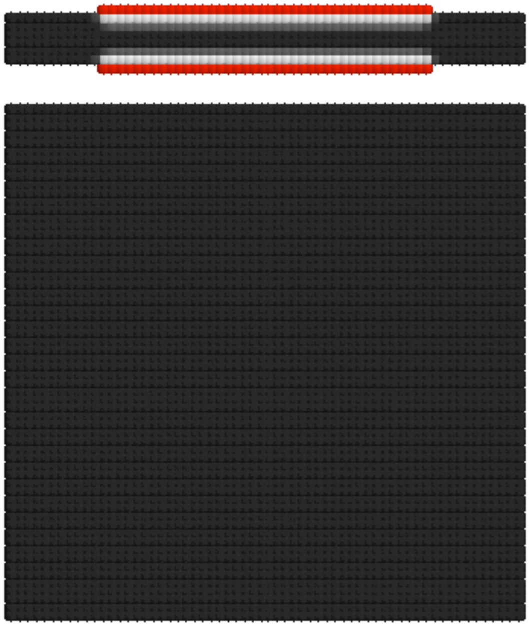
Complete drying in 3-D





Original quench

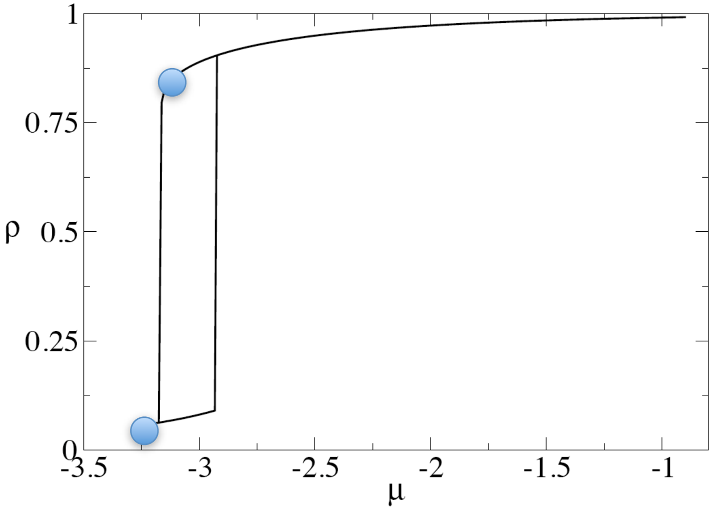


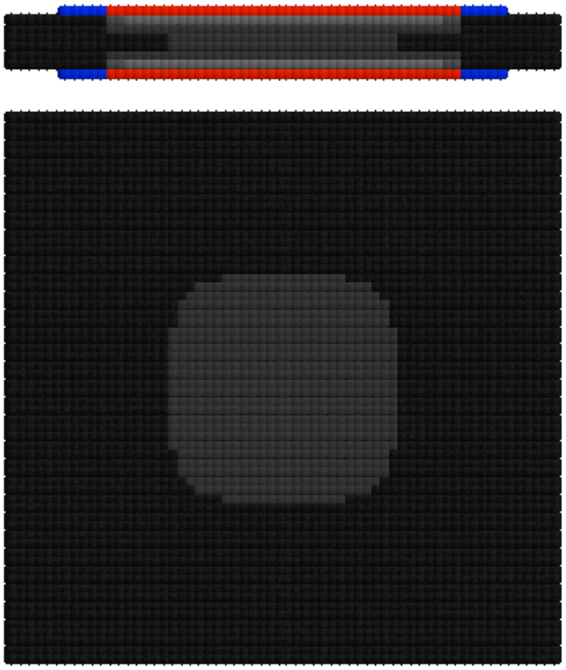
Quench from outside hysteresis loop

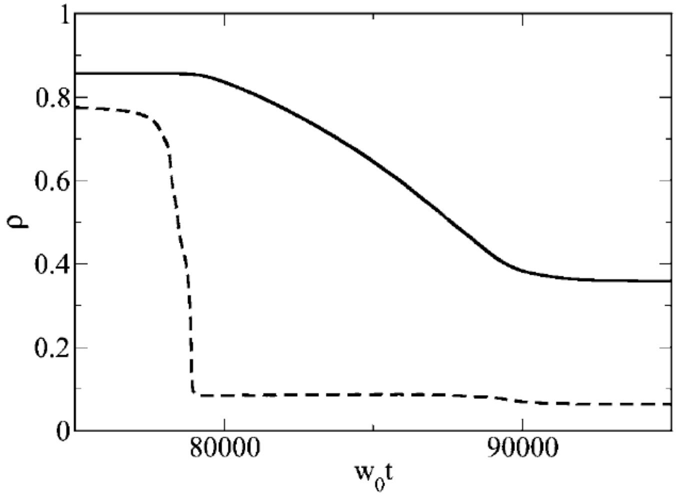
- nucleation via multiple vapor bridges/tubes

Partial drying case in 3-D

$$\theta = 120°$$

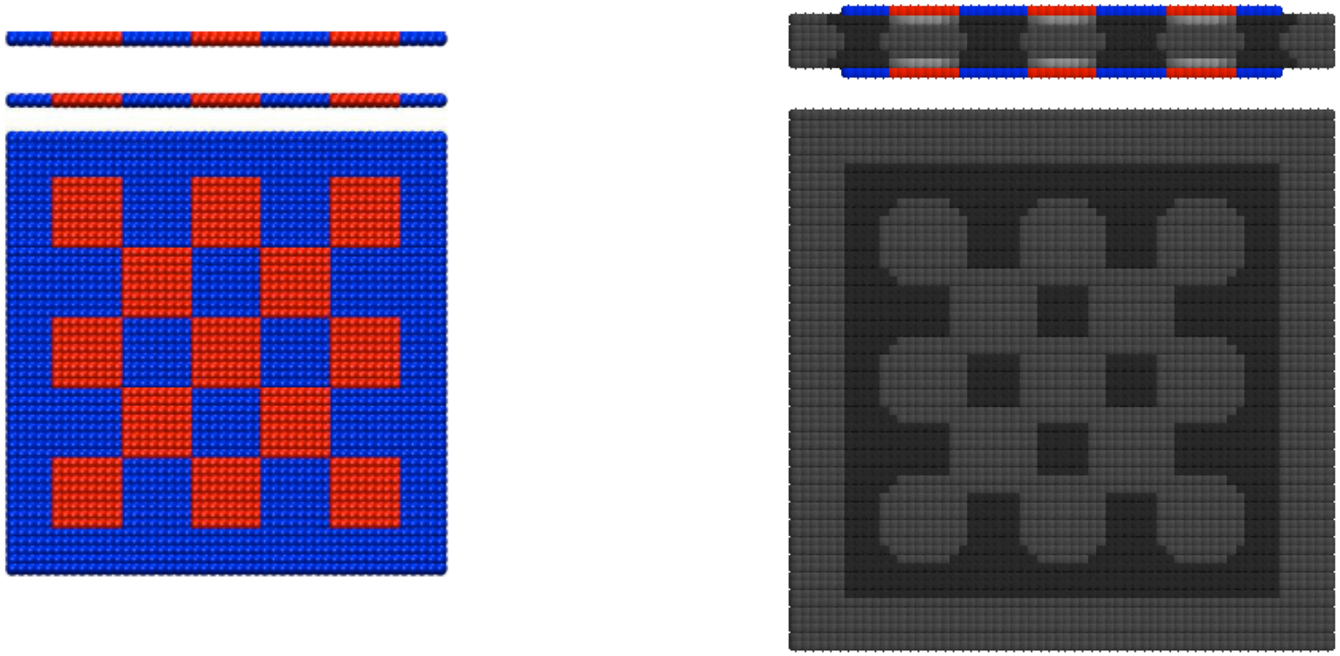






Patterned surfaces 3-D

Checkerboard



Summary

- A dynamic mean field theory for lattice gas model of fluids in porous materials
    - *describes relaxation dynamics in approach to equilibrium*
    - *yields static MFT in the long time limit*

- Application to fluids in pores in contact with bulk
    - *slit pore*
    - *network models (cavitation in inkbottles)*
    - *mixtures*
    - *partial wetting (water in carbon)*
    - *drying/partial drying (mercury porosimetry)*
    - *insights into adsorption and desorption mechanisms*

References

P. A. Monson, “*Mean Field Kinetic Theory for a Lattice Gas Model of Fluids Confined in Porous Materials*”, J. Chem. Phys., **128**, 084701 (2008)

J. Edison and P. A. Monson. “*Dynamic Mean Field theory of Condensation and Evaporation Processes for Fluids in Porous materials: Application to Partial Drying and Drying*”, Faraday Discussions, **146**, 167 (2010)

J. R. Edison and P. A. Monson, “*Dynamic mean field theory of condensation and evaporation in model pore networks with variations in pore size*”, Microporous Mesoporous Materials, 154, 7-15 (2012)

P. A. Monson, “*Understanding Adsorption/Desorption Hysteresis for Fluids in Mesoporous Materials using Simple Molecular Models and Classical Density Functional Theory*”, Microporous Mesoporous Materials, 160, 47-66 (2012).