Studying phase transitions of DFT models of confined fluids using nonlinear analysis tools

or

why one might want to calculate unstable solutions

or

Tramonto + LOCA

Andy Salinger (9233)
Laurie Frink (9235)

CSCM Seminar, September 6, 2000

Density Functional Theory can be used to study phase transition of fluids near surfaces

DFT: An approximate liquid state theory to deterministically find equilibrium density distributions in inhomogeneous fluids.

Tramonto is a parallel code for solving DFT in 1D, 2D, or 3D geometries. It is based on the Rosenfeld functionals for hard-sphere repulsions, and can also treat Lennard-Jones attractions and Coulombic interactions.

Finding the equilibrium is an energy minimization problem.

$$\frac{\delta\Omega}{\delta\rho(\vec{r})} = 0$$

$$0 = \log(\rho_i/\rho^b{}_i) - \mu^{HS}(\rho^b{}_i) + V_i^{ext} + \sum_j \int [\rho_j(1) - \rho^b{}_j] u^{att}{}_{LJ}(1,2)\, d2 + \int \sum_\gamma w_i{}^\gamma(1,2) \frac{\partial \Phi_{SPT}(2)}{\partial \bar{\rho}_\gamma(2)}\, d2$$

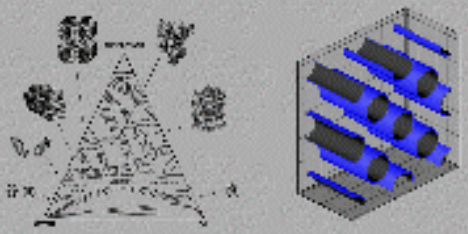
Molecular Theory for Nanotechnology

Overview of Tramonto Code

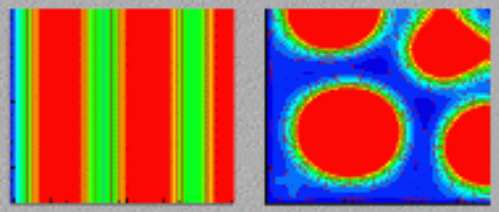
- 3D-DFT for inhomogeneous fluids.
- Memory intensive coupled integral equations.
- Multi-platform code - PC to MP computers (ASCI-Red & Cplant).
- Can treat equilibrium systems, steady-state transport, small molecules fluids, charged systems, and polymers.
- Applications include nanoporous materials, self-assembly, biophysics, heterogeneous surface, colloidal forces, and aggregation.

Self-Assembly

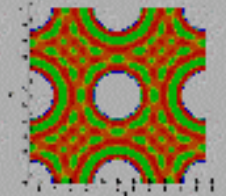
Cylindrical micelles from a bulk tri-ck-copolymer



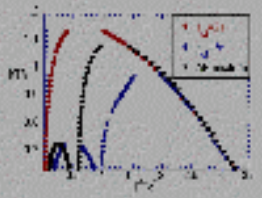
Surface mediated assembly of either lamella (slit pores) or cylindrical micelles (square channel)



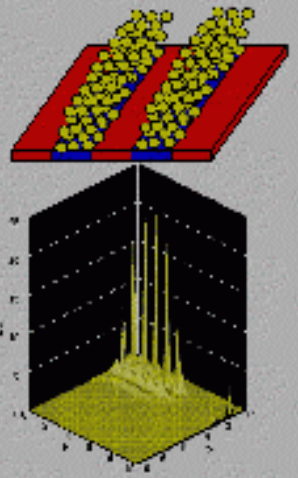
Capillary condensation in nanoporous materials (e.g. zeolites)



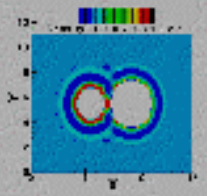
DFT produces fluid adsorption and phase transitions for different molecular properties of nanoporous media.



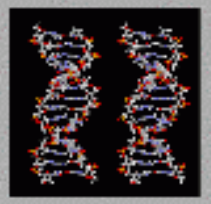
Adsorption at heterogeneous surfaces is critical for soft-lithography



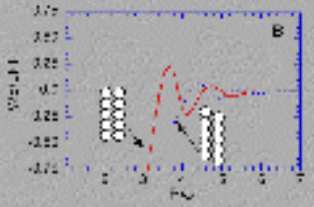
Interaction of biological macromolecules



Solvation of model DNA

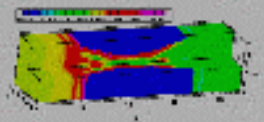


2 DNA strands

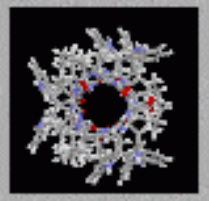


Interaction potentials between model DNA

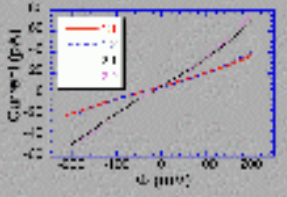
Transport through ion channel proteins



Ion distribution in model channel



Gramicidin



Current voltage response of model channel

Contact: L.J.D Frink, A.G. Salinger, J.D. Weinhold

Stability Analysis Project

Mission: To develop linear and nonlinear stability analysis algorithms to enable sophisticated design and analysis of large-scale nonlinear models.

Motivation: Nonlinear systems can exhibit:

- Multiple Steady States
- Pitchfork Bifurcations from symmetry breaking
- Hopf Bifurcations to oscillating states
- Turning Points signifying Ignition/Extinction phenomenon
- Phase Transitions

Methodology:

- LOCA library for tracking steady-state solutions and bifurcation points.
- Linear Stability analysis capability to determine the stability of a solution (ARPACK, Anasazi libraries).

Status of LOCA Library Of Continuation Algorithms

Codes: MPSalsa; Tramonto; GOMA

Interface Requirements:

• Residual Calculation	• Matrix Vector Multiply
• Jacobian Calculation	• Linear Solve of Jacobian

Current Capabilities:

• Simple Parameter Continuation	• Arc-length Continuation
• Turning Point Tracking	• Phase Equilibrium Tracking
• Pitchfork Bifurcation Tracking	• rSQP Optimization

Future Capabilities:

• Hopf Bifurcation Tracking	• Periodic Orbit Tracking
• Constraint Enforcement	• Bifurcation Analysis of MC

Phase Transition Algorithm Solves Directly for Equilibrium Point

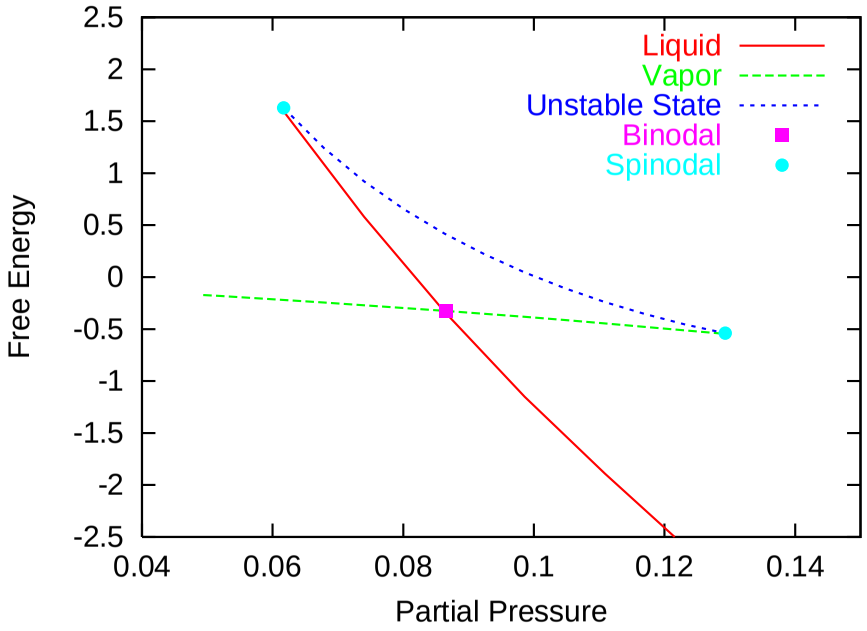
Phase Transition Calculation for x_1, x_2, λ:

$$R(x_1, \lambda) = 0$$

$$R(x_2, \lambda) = 0$$

$$\Omega(x_1) - \Omega(x_2) = 0$$

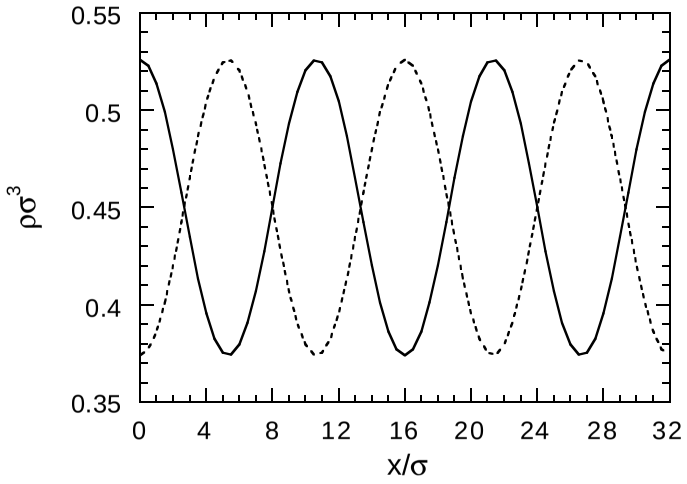
Phase Transition Algorithms Solves for 2N+1 Unknowns

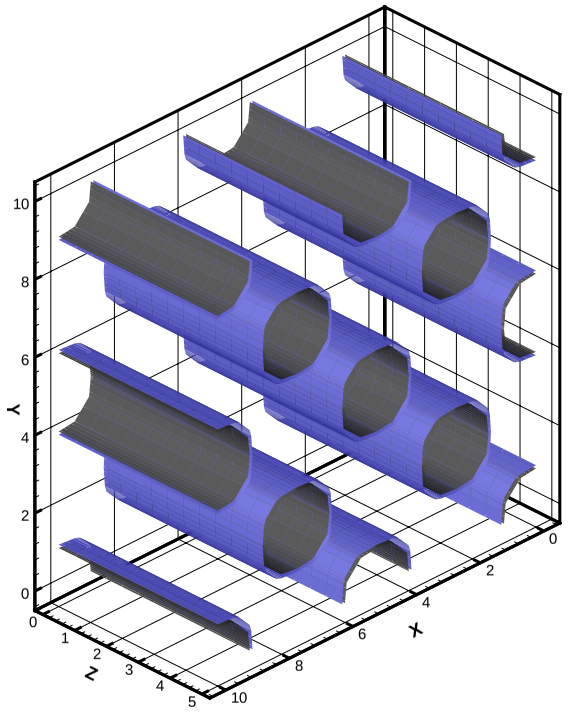


Arc-length continuation traces out entire loop.

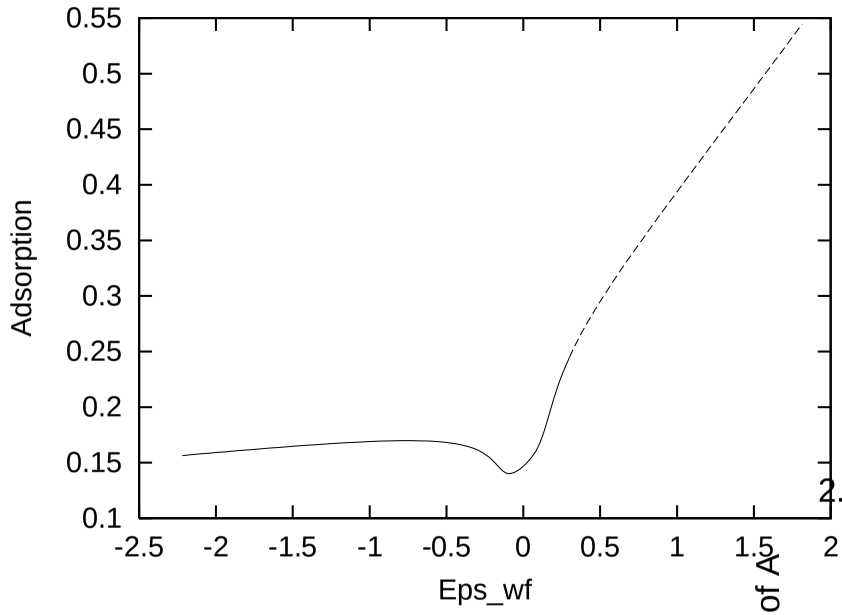
Self-assembly of block-copolymers near surfaces can also be studied using DFT

Weinhold, Frink, Salinger: Freely jointed chain model using bulk interactions from Prism (Curro, Weinhold)

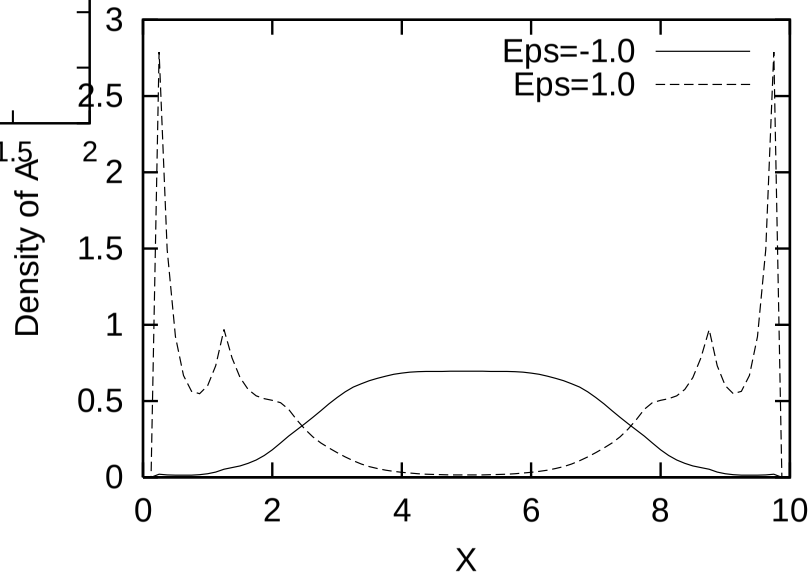




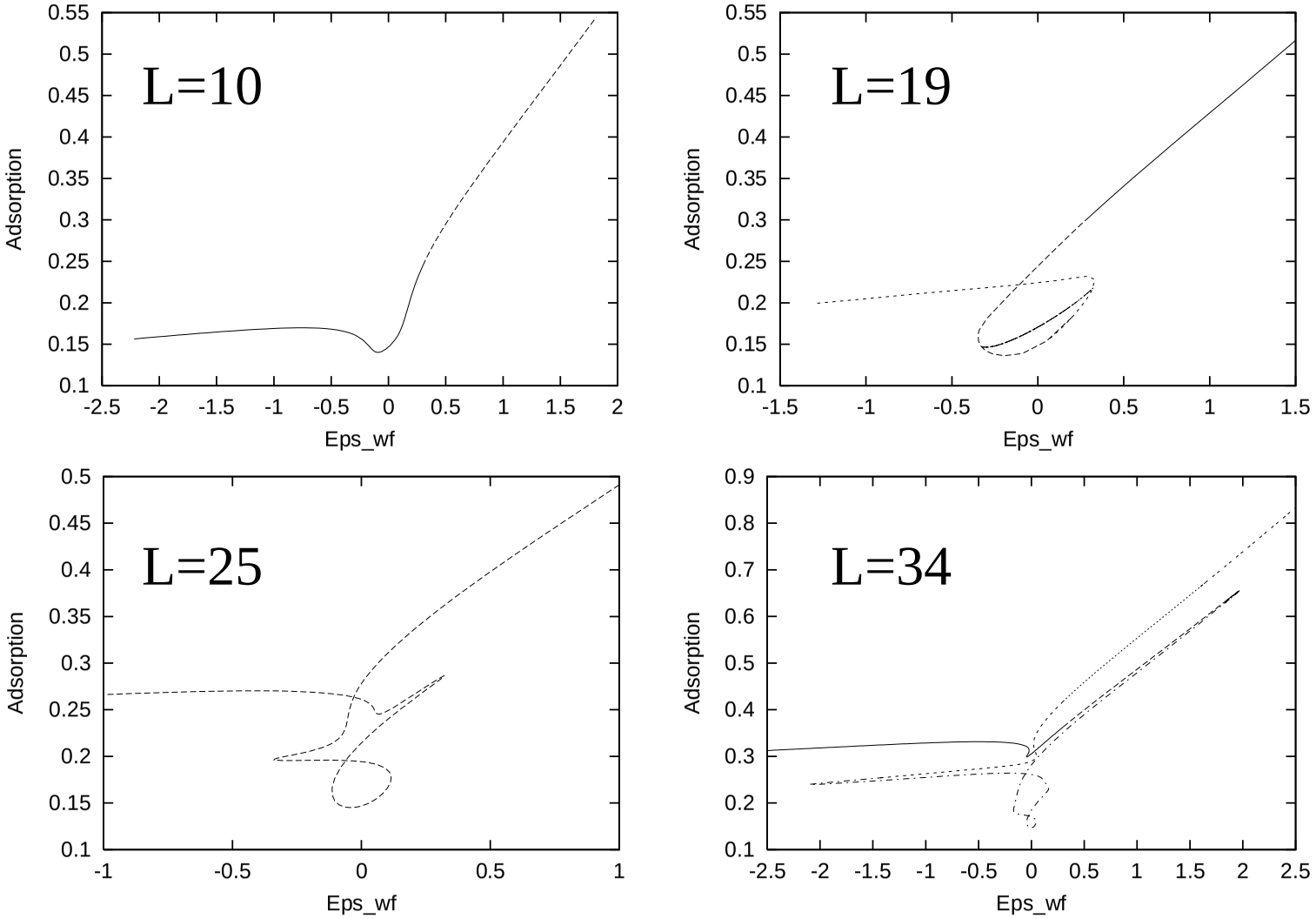
Self-assembly of 8-8 block copolymer is complicated even when restricted to 1D solutions in a slit pore



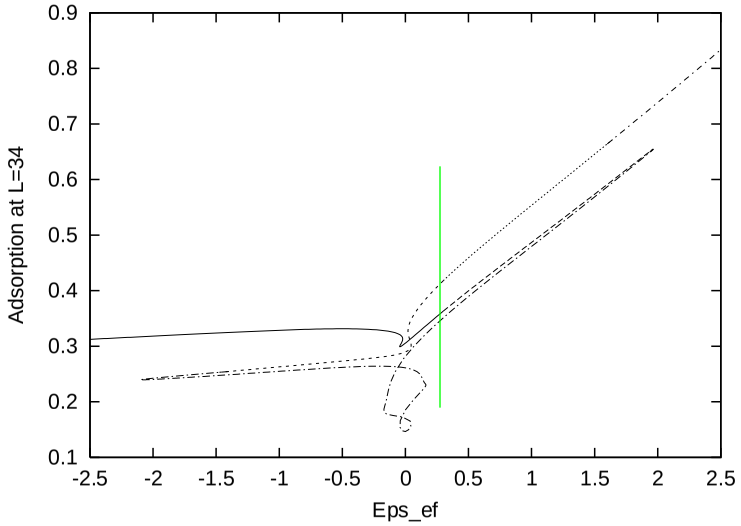
Pore size of L=10 is relatively simple:

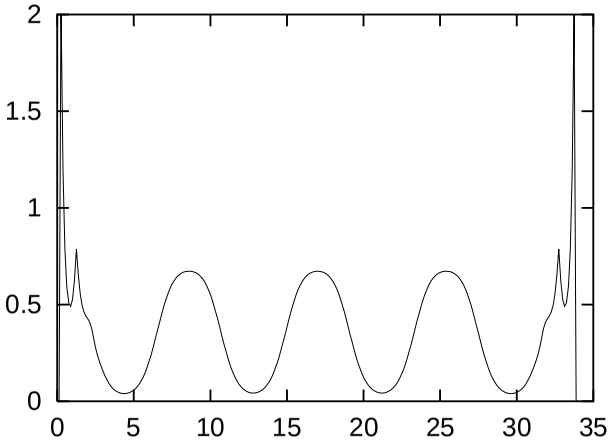


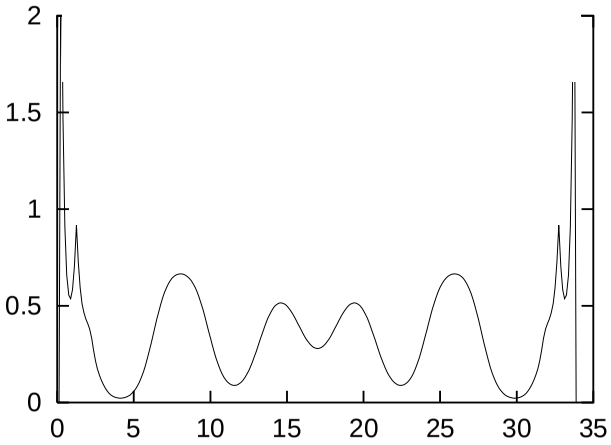
As pore size increases, so does solution multiplicity

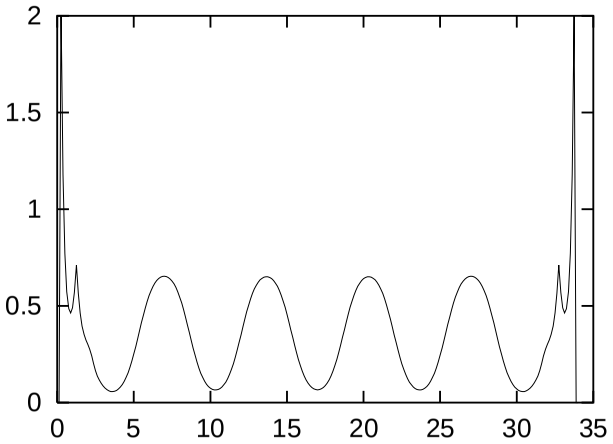


For a slit pore of size L=34, up to 9 solutions (5 stable) solutions coexist at the same conditions

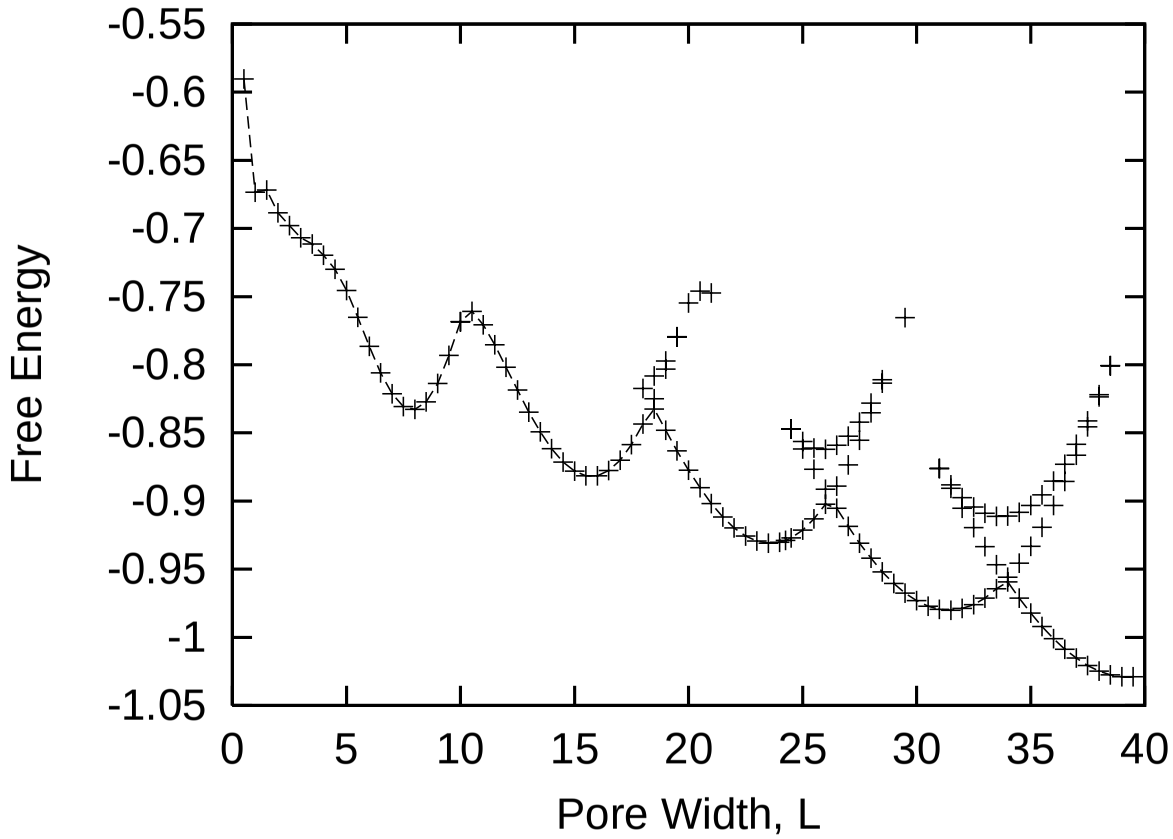








Solution space as a function of pore width for fixed Eps_wf=0.3 shows increasing complexity



Tramonto-LOCA used to study phase transitions

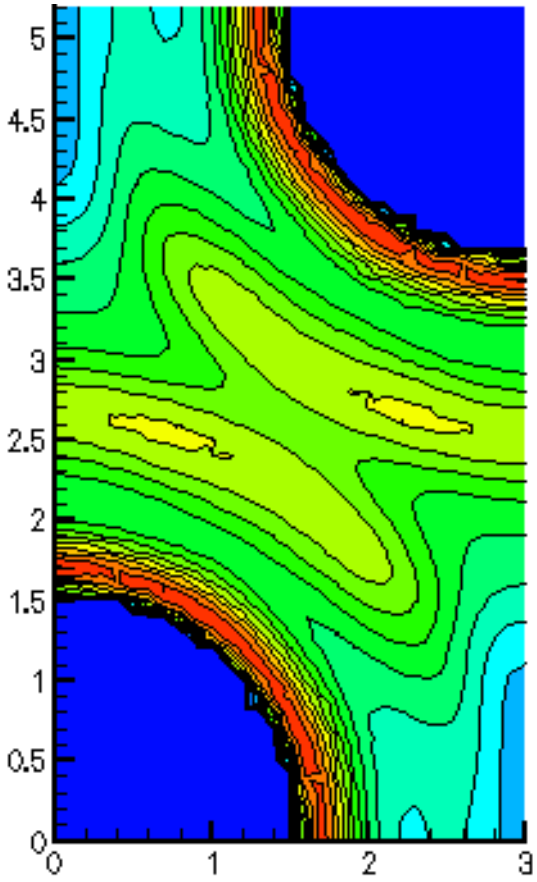
Three model systems: Slit Pore, HCP Cylinders, Random Cylinders

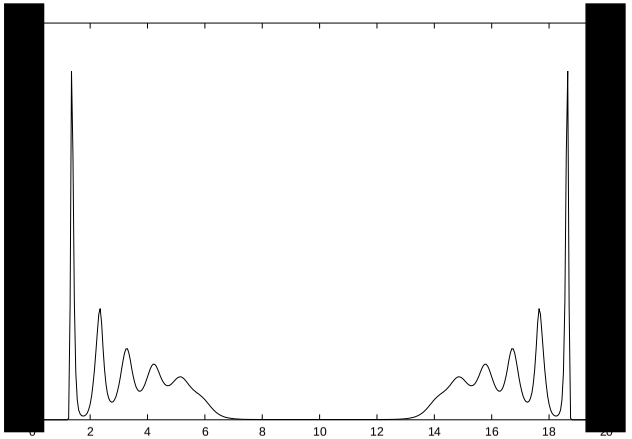
LJ Fluid

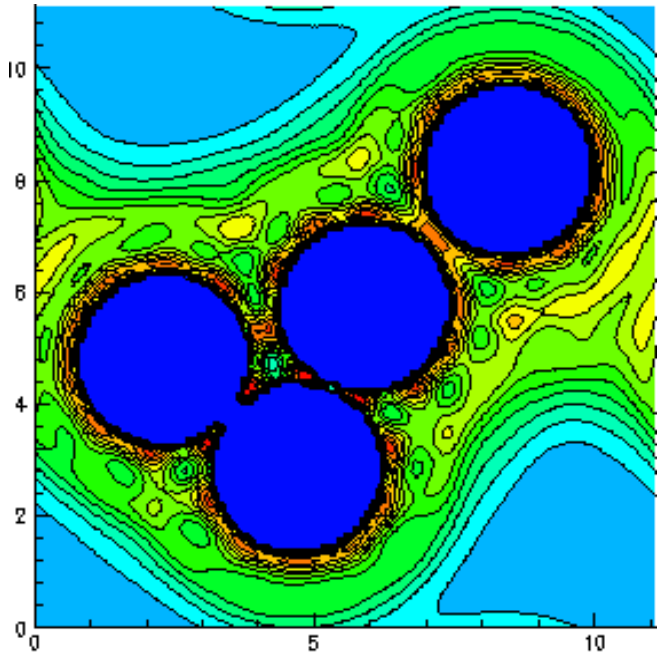
Hard Core

$\varepsilon_{ff}=1$

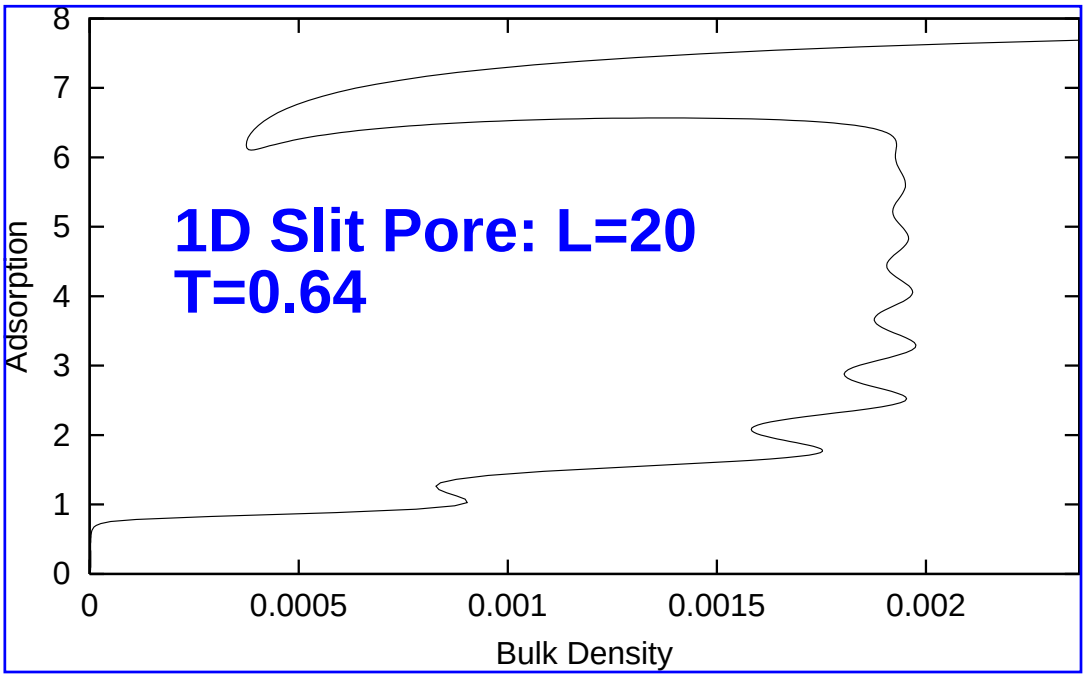
$\varepsilon_{wf}=5$

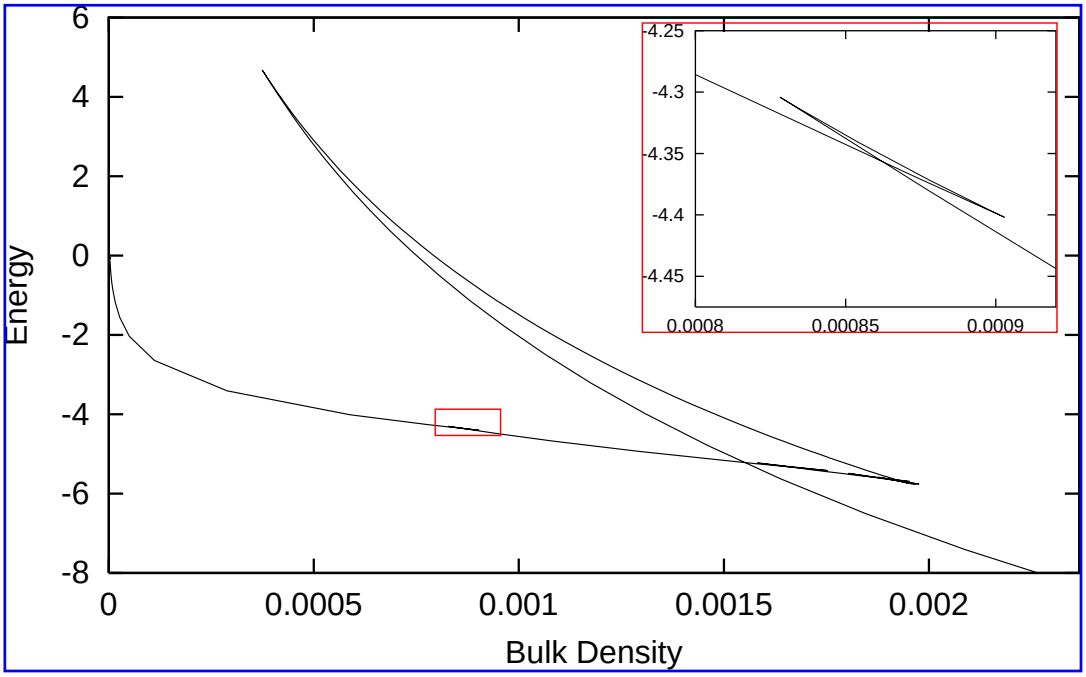


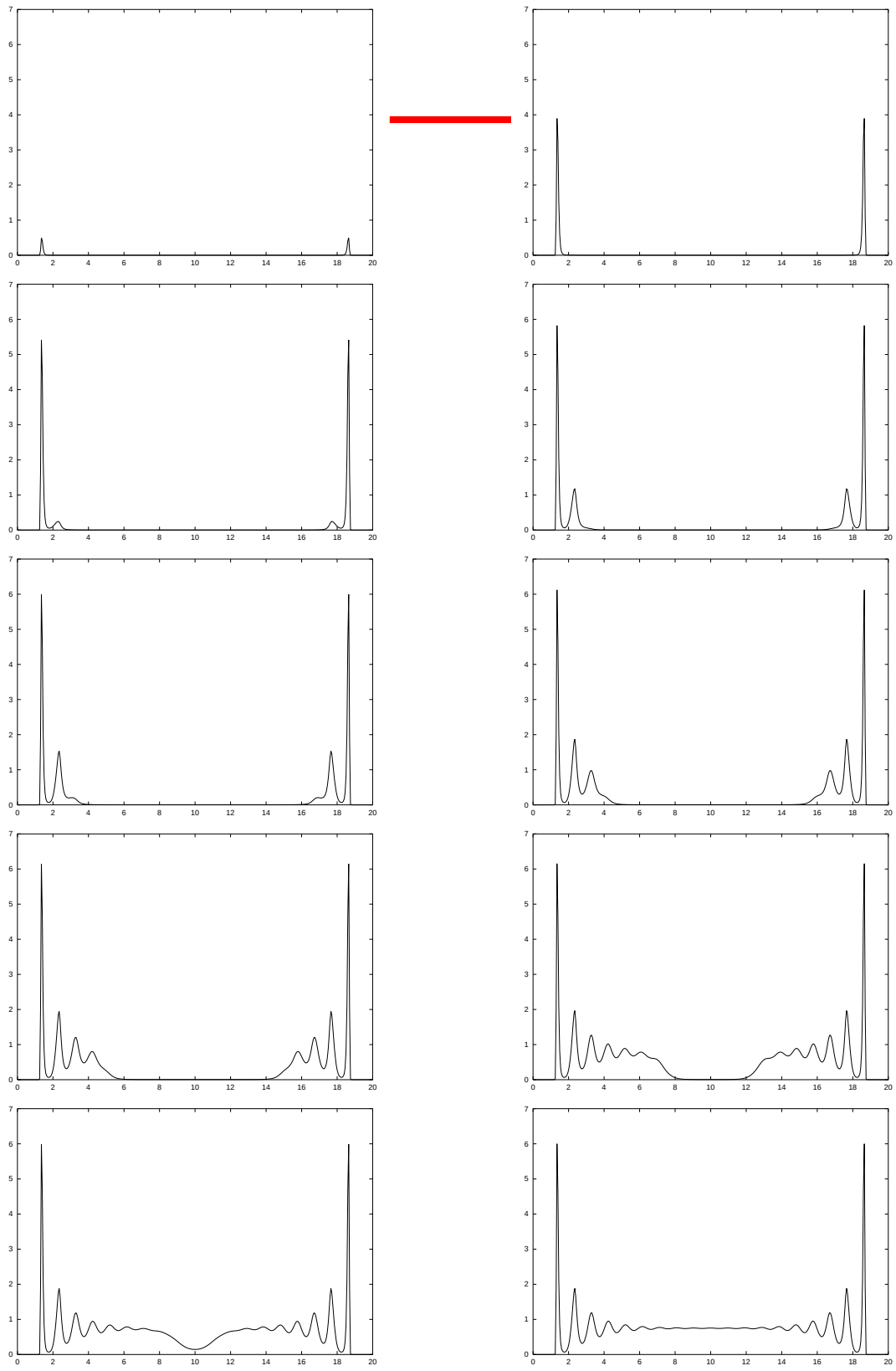




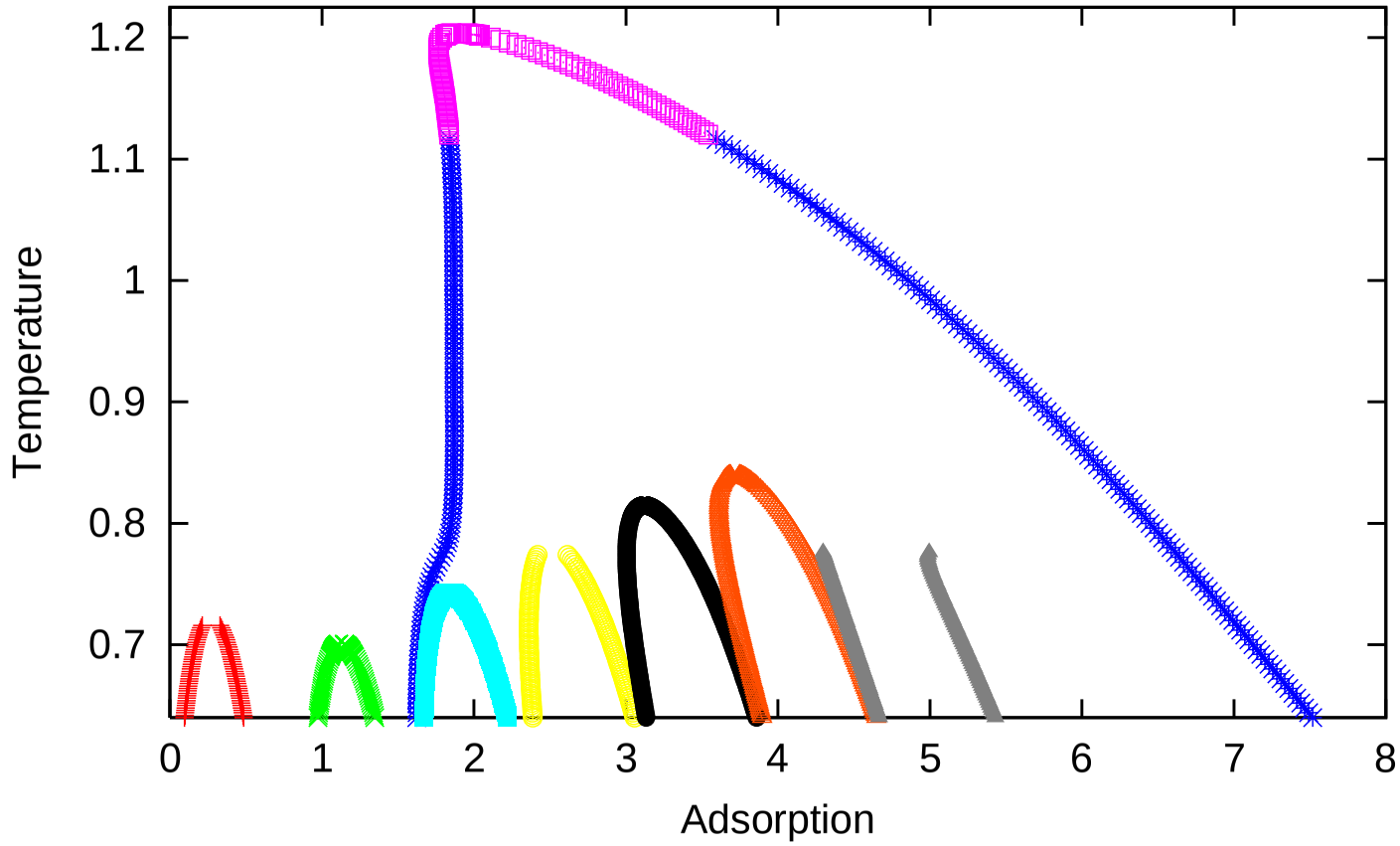
Arclength continuation enables automatic calculation of adsorption isotherm







Phase Transition Algorithm used to Directly Calculate Phase Diagram for 1D Slit Pore



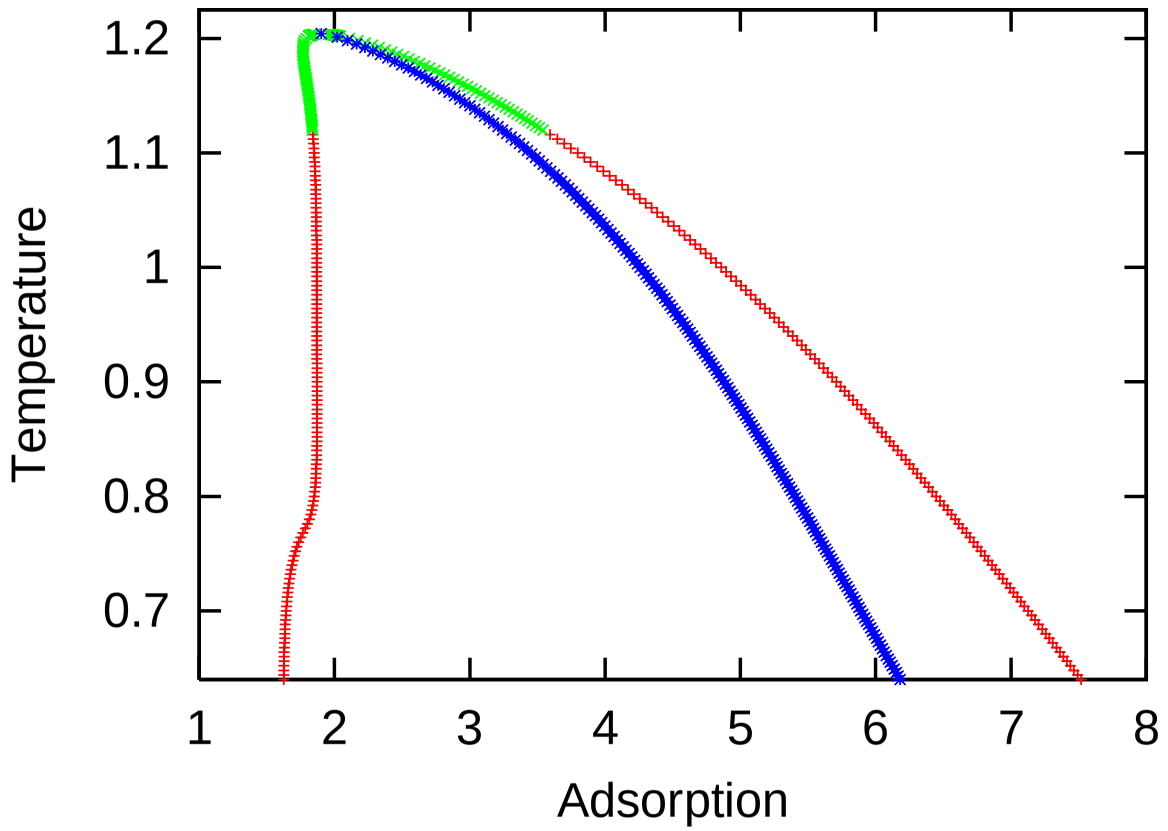
Spinodal curve can also be calculated directly using Turning Point Tracking Algorithm

Turning Point Calculation for x, n, λ given l^t:

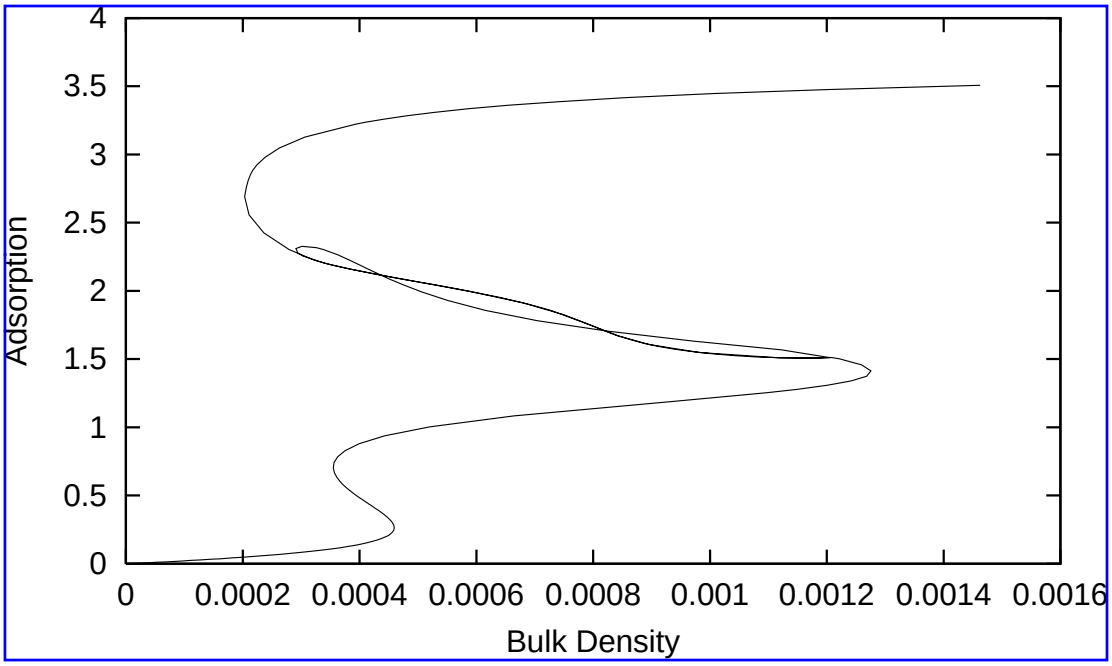
$R = 0$

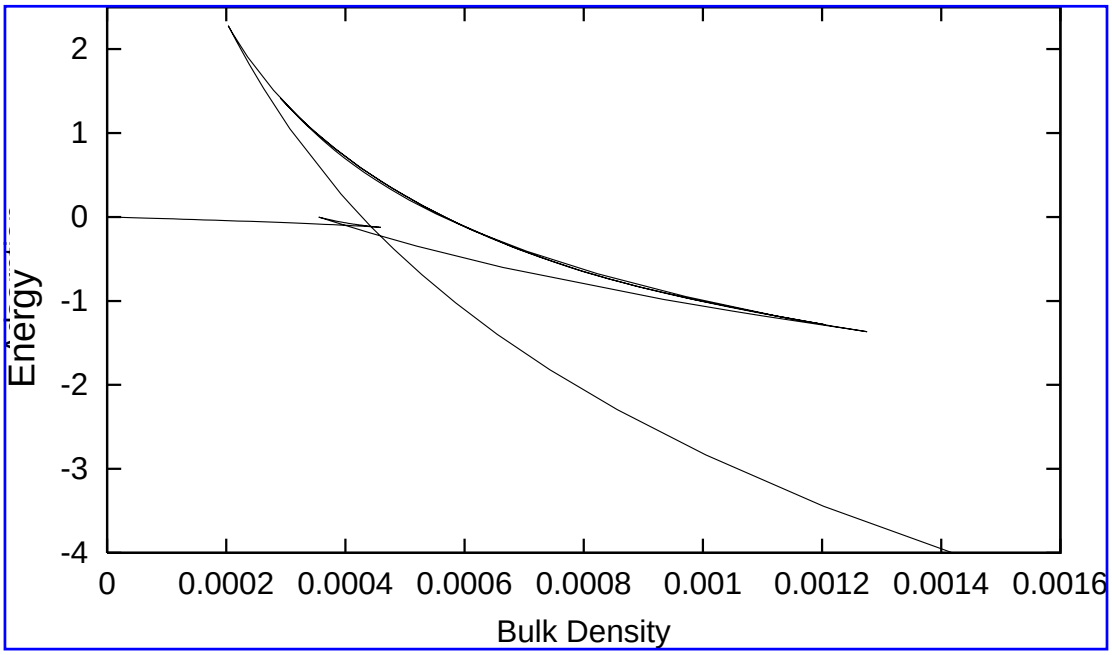
$\boldsymbol{J}n = 0$

$l^t n = 1$

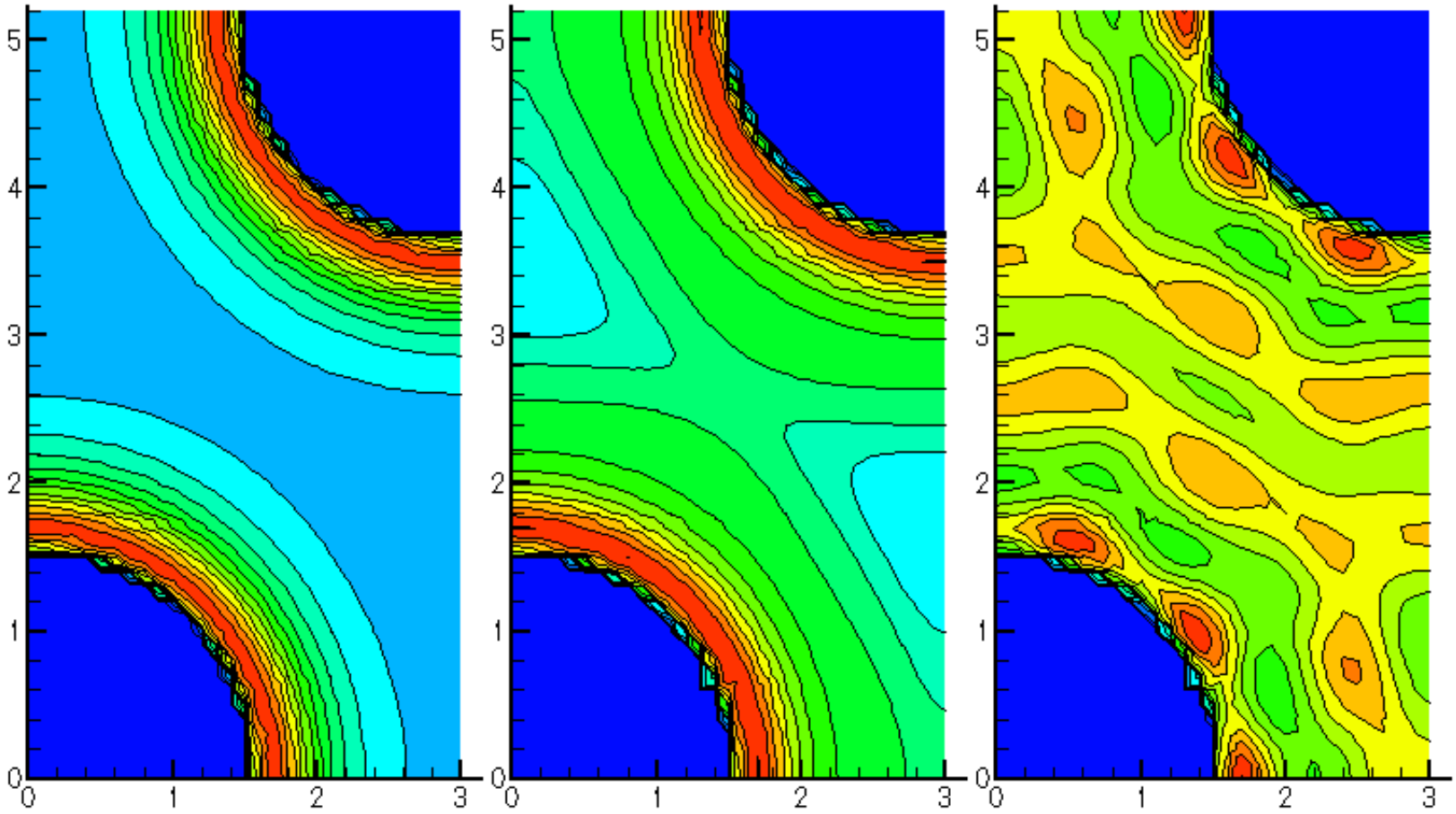


2D ordered porous media model (HCP)

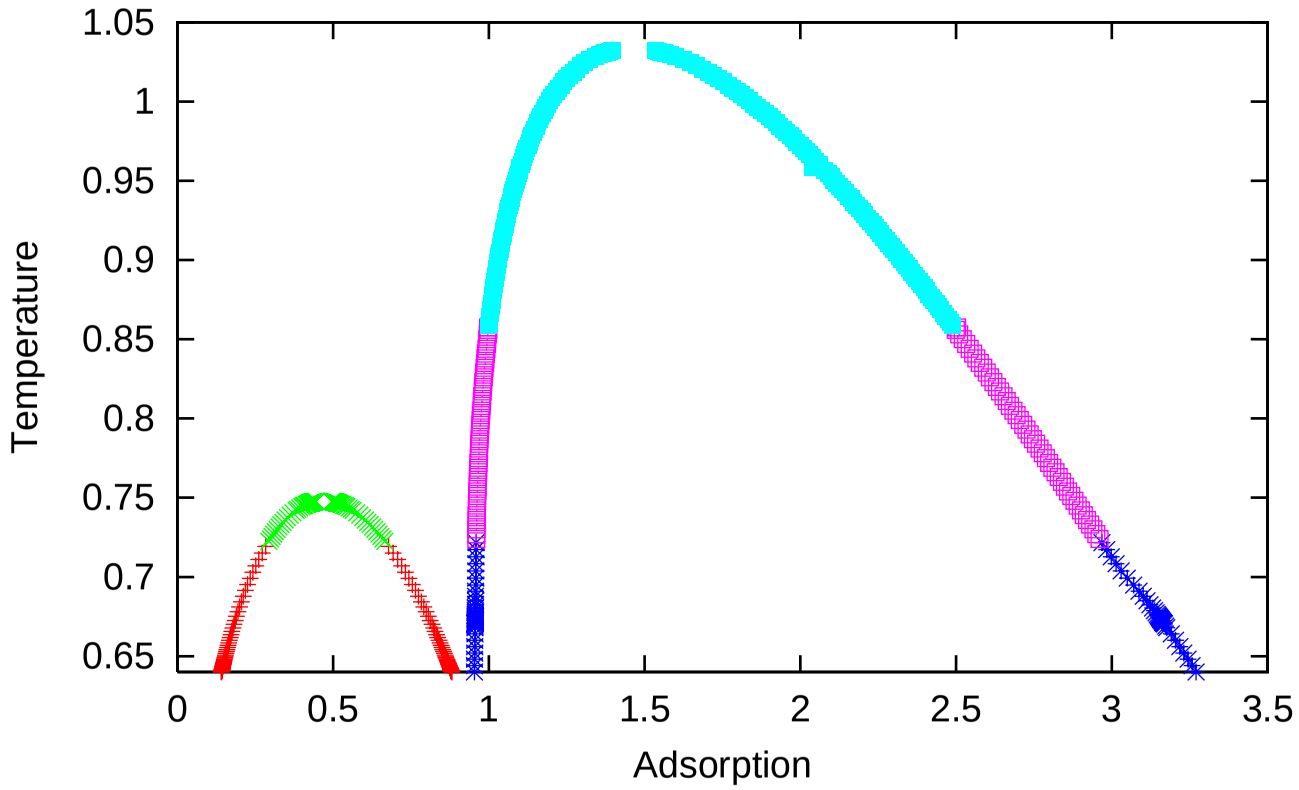




Three Phases Exist for HCP Cylinders at T=0.64

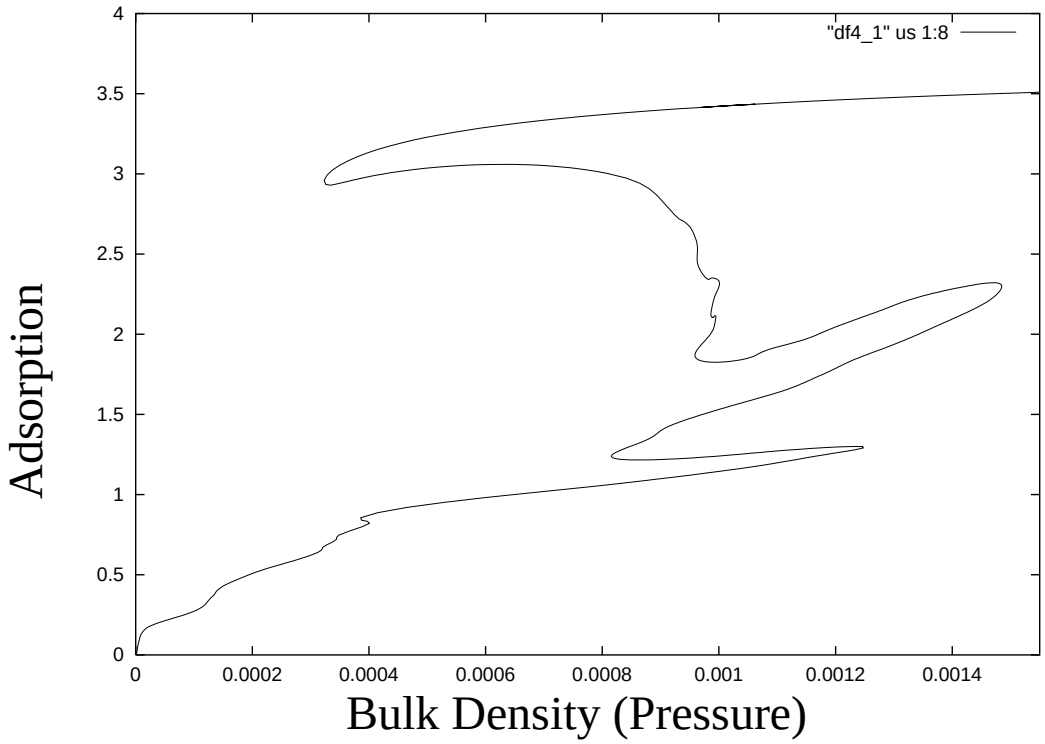


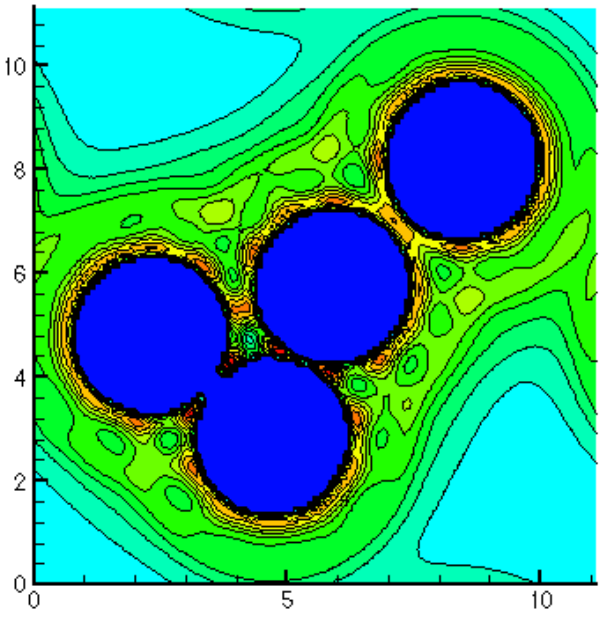
Phase diagram for 2D Ordered Cylinders is relatively simple



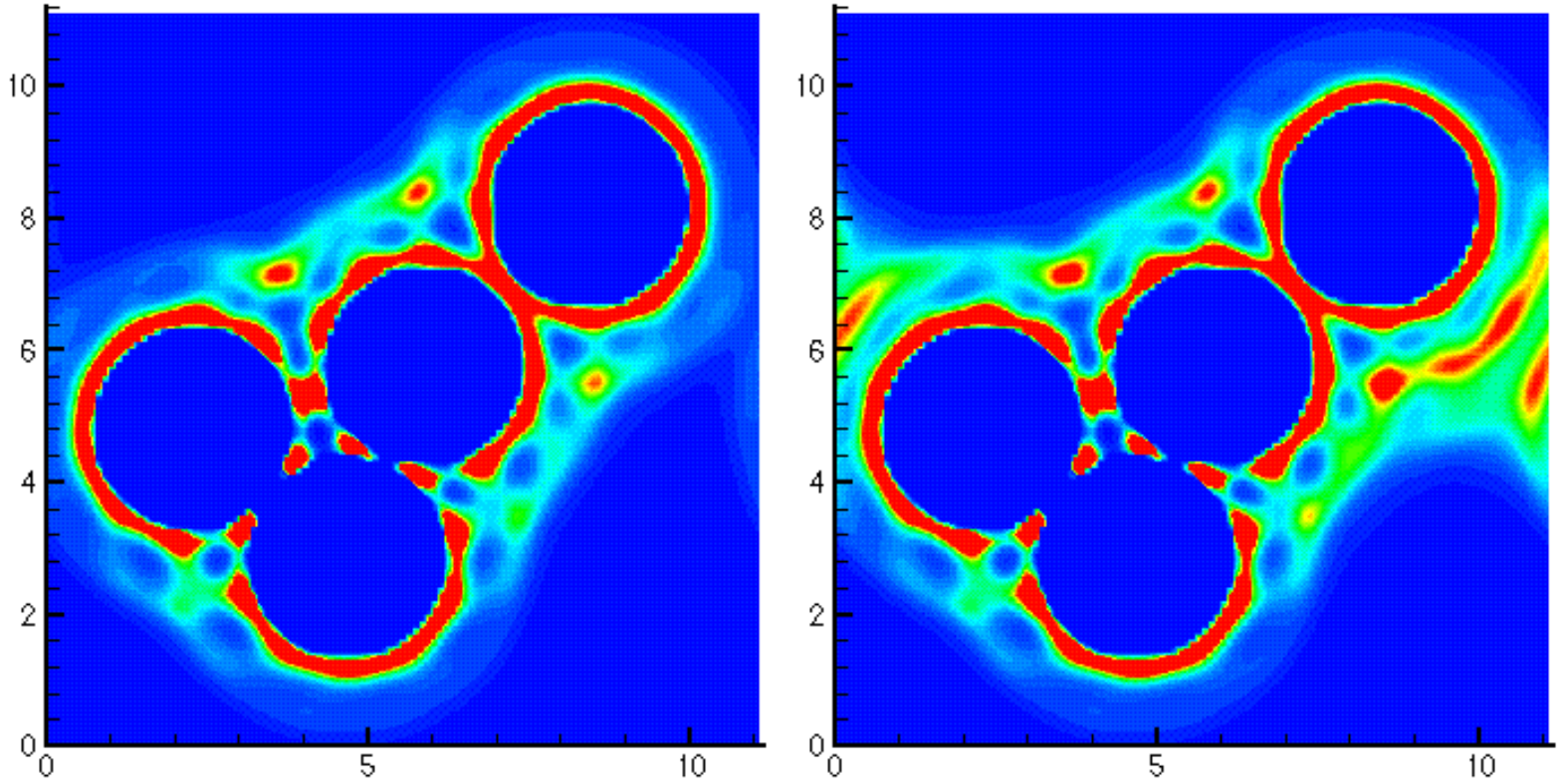
Using 60 processors on janus, the 2D problem required ~3 hrs: 5-10 sec/solution, 20-100 sec per phase transition step

Capillary condensation in disordered media studied via random cylinders



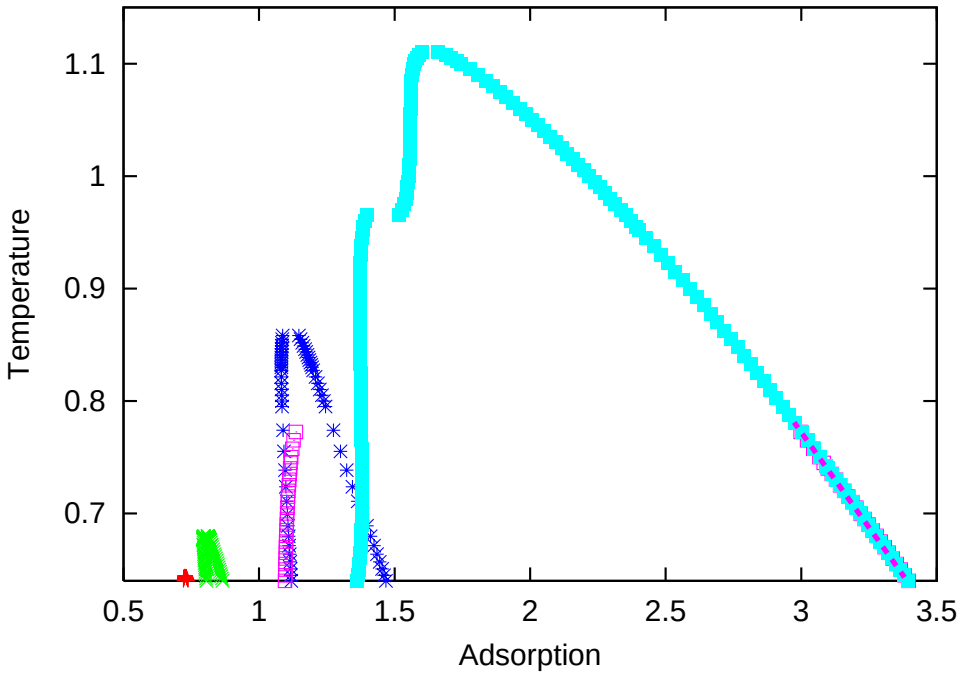


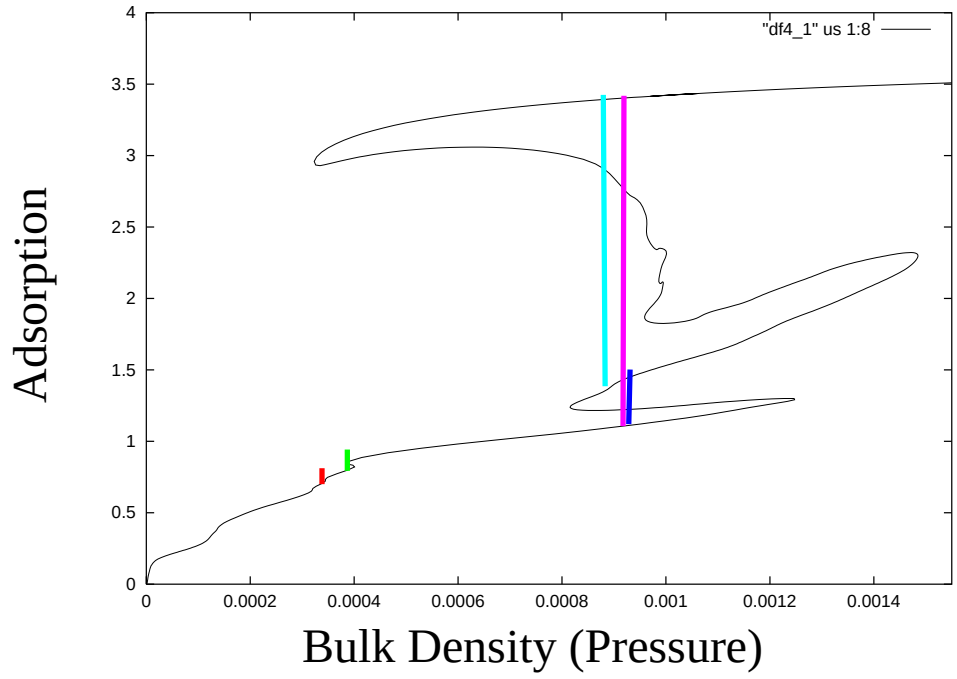
Extra Phase Transition seen in Disordered Cylinders that was not seen in Ordered Cylinders



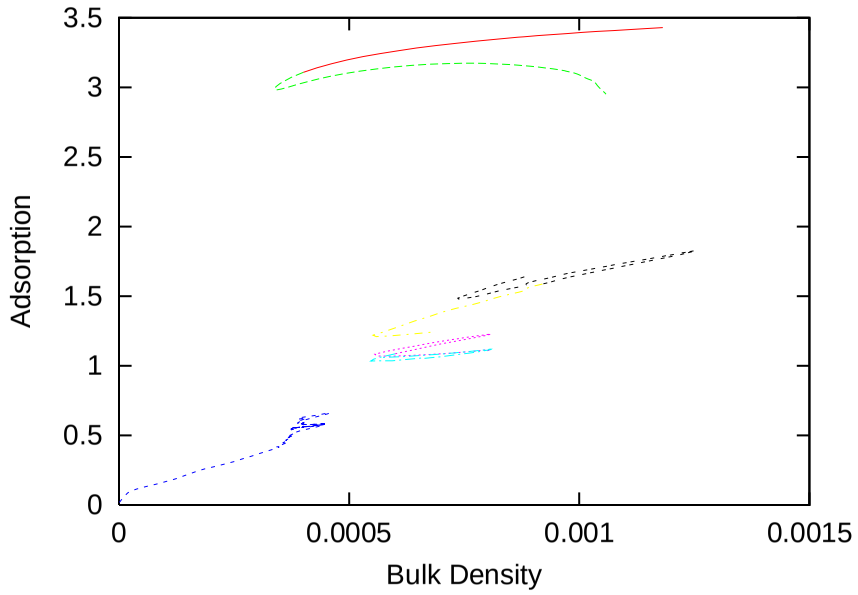
Liquid Bridge formed between adjacent cylinders

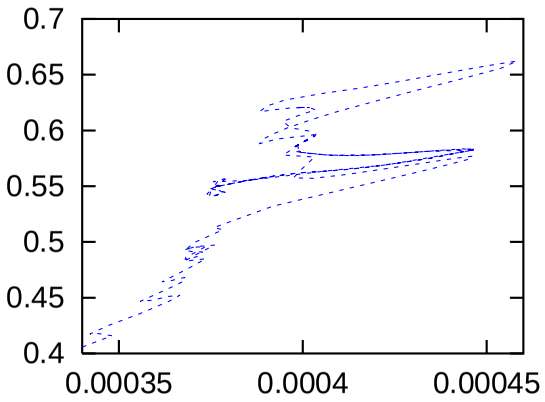
Phase transition algorithm extends results to all temperature (Triple Pt.!)

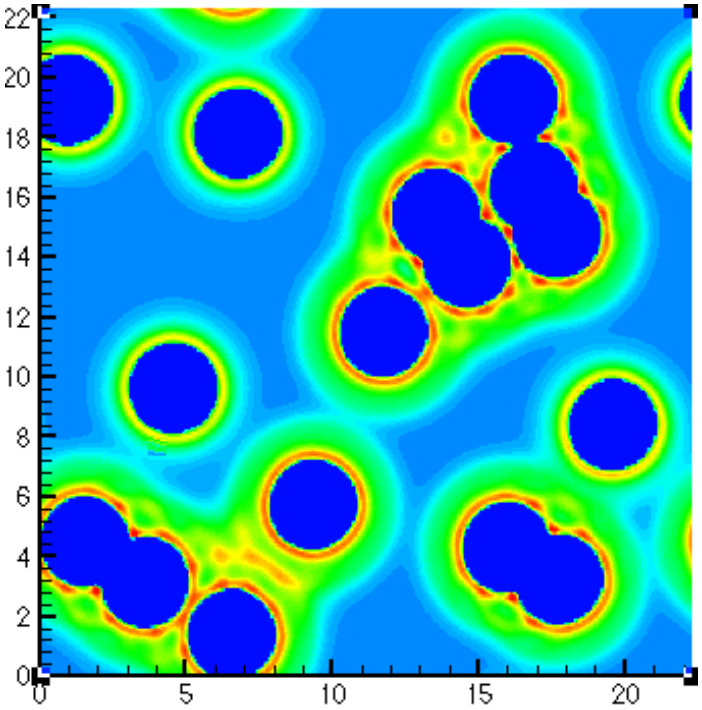




More detailed 16 random cylinder model led to extremely complicated phase behavior







Summary and Conclusions

1. DFT can capture phase transition behavior
2. Locating metastable and even unstable solutions can be advantageous
3. Nonlinear analysis tools (LOCA) can facilitate studying of phase behavior (in deterministic, Newton's method code)

• Arc-length Continuation	• Spinodal Tracking
• Phase Transition Tracking	• Optimization

4. Simple random porous media model shows extra partial-wetting phase transition not seen in ordered systems
5. RPM method might enable similar capabilities to molecular simulations such as Monte Carlo (via collaboration with Kevrekidis at Princeton)

Novel Algorithms for Investigating Capillary Condensation Transitions using Density Functional Theory

or

why one might want to calculate unstable solutions

Andrew G. Salinger and Laura J. D. Frink

Sandia National Laboratories

Albuqerque, NM

Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy under Contract DE-AC04-94AL85000.