SAND2008-3534C

Numerical methods for fluids-DFTs

(Why advanced solver and bifurcation methods are important)

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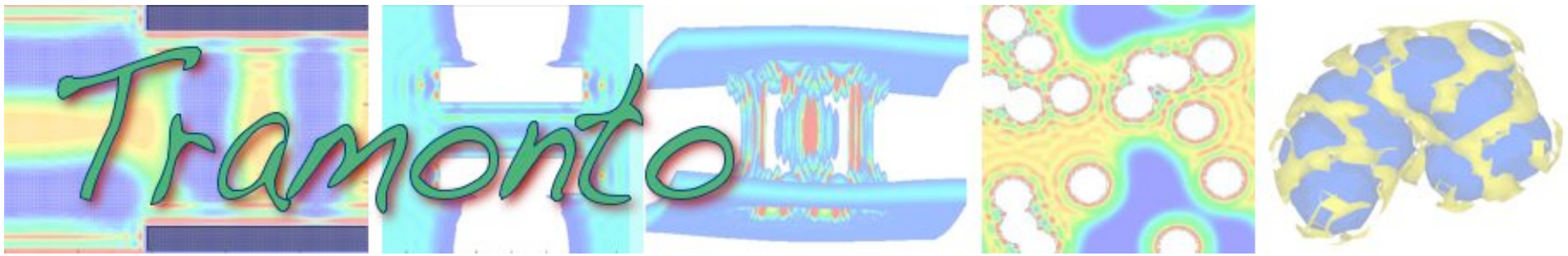
June 24, 2008

Imperial College, London, UK

An overview of Tramonto

(current capabilities, future directions)



http://www.software.sandia.gov/tramonto

Colder Insights Corp

Sandia National Laboratories

Albuquerque, New Mexico USA

Andrew Salinger – software development

Mike Heroux – solver algorithms

Amalie Frischknecht – physics of polymers and membranes

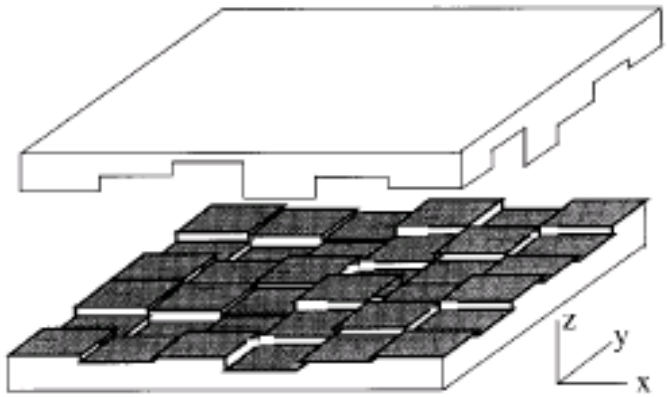
Frank van Swol – physics of surfaces and fluids

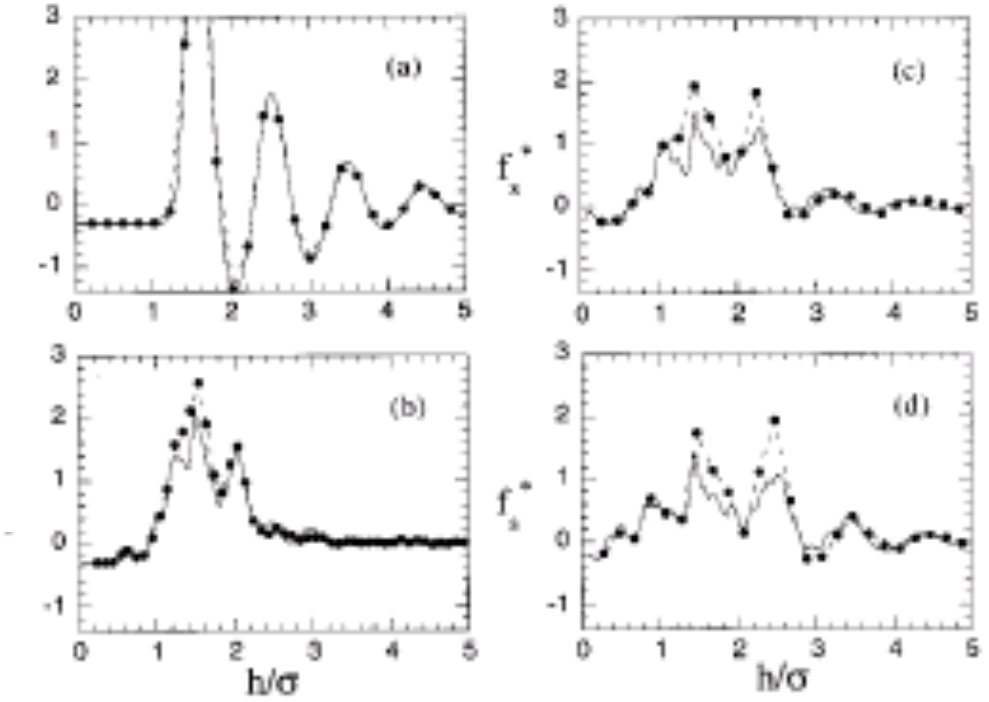
Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000.

NNSA National Nuclear Security Administration

Sandia National Laboratories

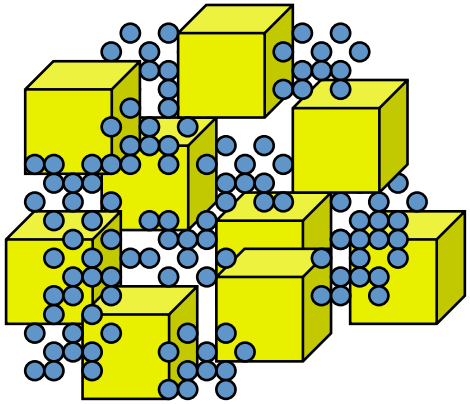
1993-1998





Frink and van Swol, J.Chem. Phys., 1998
Frink and van Swol, Colloids and Surf. A 2000
SFA/AFM/OS Device/BB Device…

1993-1998



$$Z_{NV\mu T} = \int dr^N e^{-\beta U_N(r^N)} \times \left\{ \sum_{n=0}^{\infty} \frac{z^n}{n!} \int dr^n e^{-\beta u_n(r^N, r^n)} \right\}$$

Grand canonical partition function for a fluid in an external field; X.

$$\Omega(r^N; \mu, T) = -\beta^{-1} \ln \Xi_{\mu VT}$$

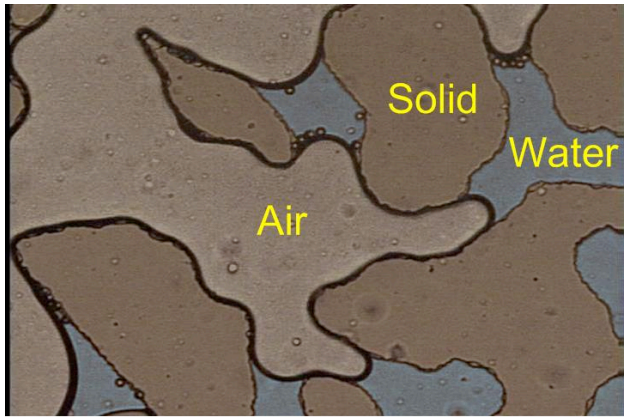
$$Z_{NV\mu T} = \int dr^N e^{-\beta U_N(r^N)} e^{-\beta \Omega(r^N; \mu, T)}$$

$$w(r_N) = U_N + [\Omega_s(r_N) - \Omega_s(\infty)]$$

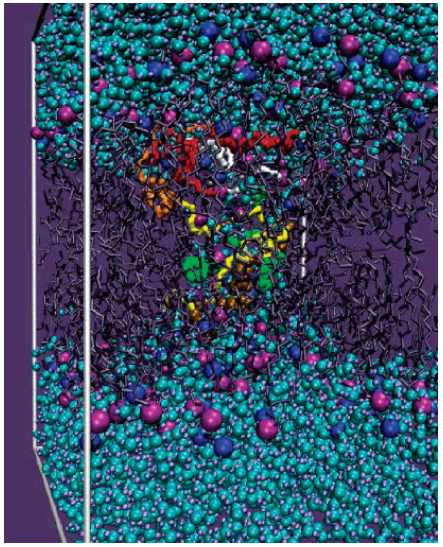
Implicit Solvent method = Compute grand free energy, Ω !!

Frink and van Swol, J.Chem. Phys., 1994

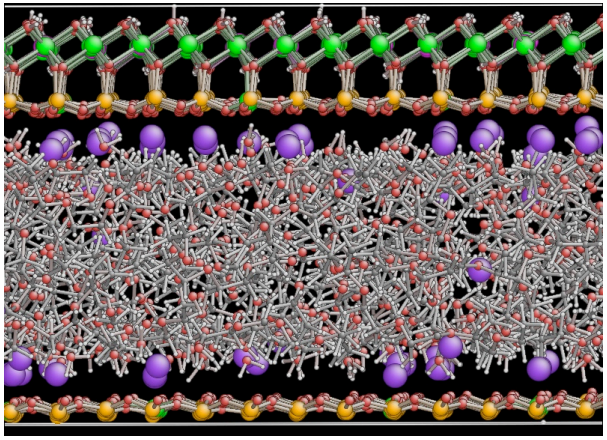
Complexity



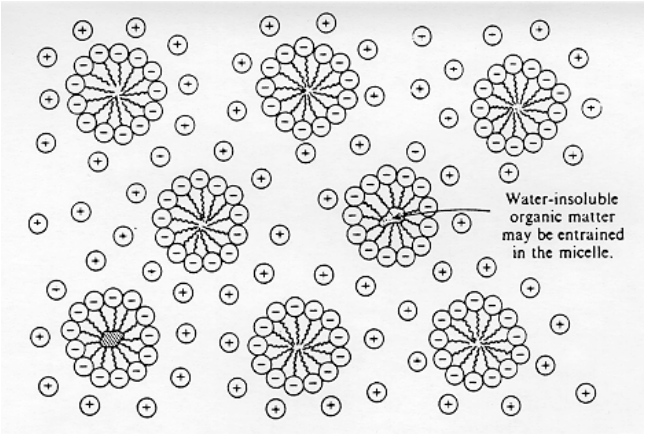
Porous Media
(www2.bren.ucsb.edu/~keller/micromodels.html)



Magainin pore
Leontiadou et al.,
JACS, 128, 12156 (2006)



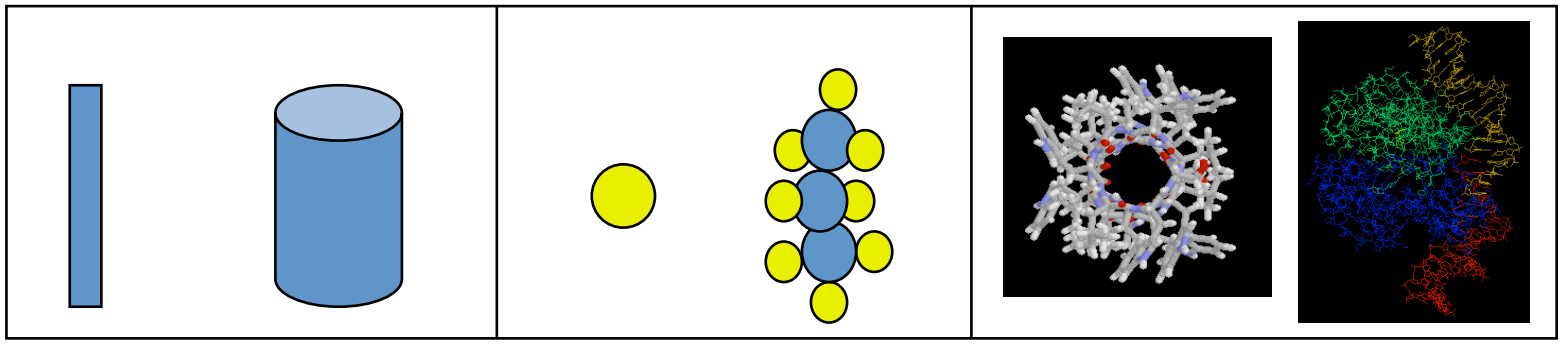
Clay-polymer nanocomposites
(Univ. College London exclaim.org.uk)



Colloidal/Amphiphilic systems
(www.science.duq.edu)

Problem classes

Surfaces

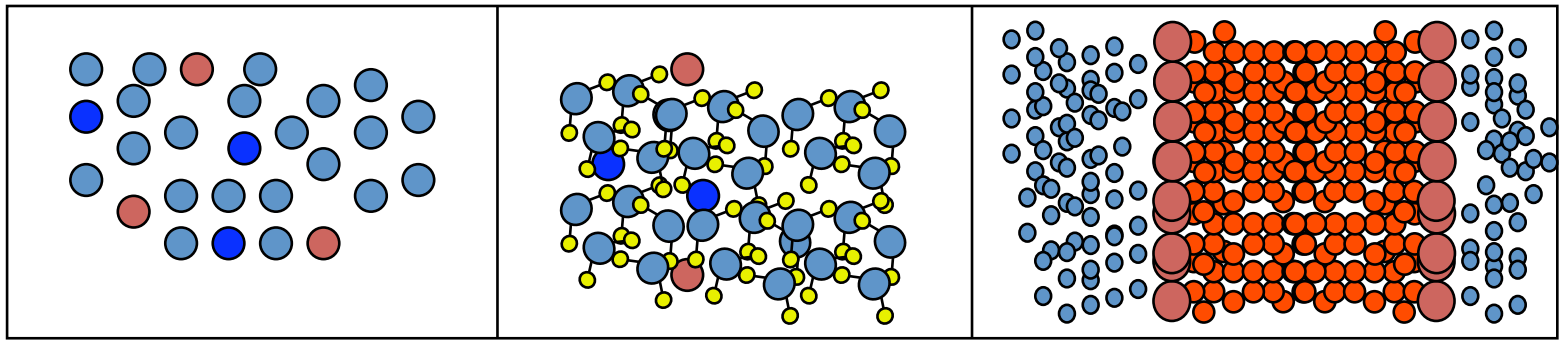


Simple extended surfaces (SFA)

atoms & molecules

Complex extended surfaces

Fluids



Atomic fluids

Molecular fluids

Polymer Chain fluids

Equilibrium, Dynamic, Reacting Systems

State of the Art

1995

- 1D applications.
- Picard iterative schemes [one or two FE/Newton's method codes (Sabeur and Henderson, H.T. Davis)].
- Fundamental Measures (FMT) approach for atomistic systems emerging.
- Rich phase transitions, but time consuming to study.
- Theoretical and apps work focused on fluids at surfaces.

2008

- Theories more mature (FMT), and still improving (bonded systems).
- 3D applications are possible.
- State complexity can be studied efficiently with continuation/ bifurcation algorithms.
- Specialized solver algorithms for DFTs developed.
- Self-assembled systems more accessible for investigation.
- Dynamic-DFTs developed.
- 3D-MC-DFT calculations possible (still emerging).

I. Math and algorithms (in Tramonto)

II. A sampling of applications

III. Current activities and directions

Some physics…

Coulomb interactions — Associations (H-bonding) — [Applied field]

$$\Omega[\rho(r)] = F_{id} + F_{hs} + F_{vdW} + F_c + F_{assoc} + \int \rho(r)[V(r) - \mu]$$

Ideal gas — Hard sphere — Dispersion attractions

Legendre Transform from Canonical to Grand canonical ensemble

HS – volume exclusions
- FMT / Rosenfeld 19xx
- FMT / Rosenfeld and xxx
- FMT - White Bear 2002

Pair interactions (strict mean field)
- LJ interactions
- Coulomb interactions
- Yukawa potentials

Bonded systems
- iSAFT(1) Tripathi/Chapman
- iSAFT(2) Jain/Dominik/Chapman

Other implementations
- Coupled Poisson approach for electrostatics (PDE form)
- Steady State Diffusion (PDE)
- Chandler-McCoy-Singer polymer-DFT

Limiting Cases
- Ideal gas
- Poisson-Boltzmann electrolyte
- (SCFT – not yet)

numerical methods…

Picard –

- Derive Euler-Lagrange equation
- Set up an initial guess
- iterate by successive substitution
- mix update with “old” solution
- updates of <1% in some cases
- O(100s-1000s) of iterations 1D

$$\frac{\delta\Omega}{\delta\rho_i(r)}_{\mu,T} = 0$$

Newton-Rhapson -

- Euler-Lagrange is the “residual” equation to solve
- Need gradients of residual (aka second functional derivative)
- opportunity for “numerical methods” research –
  - solvers, preconditioners, parallel computing etc.
  - engineering analysis and optimization
- partial updates ~20% sometimes needed
- O(10s) of iterations (1D-3D)

FMT

$$\frac{\delta\Omega}{\delta\rho_i(r)} = \int \sum_\gamma \frac{\partial\Phi}{\partial n_\gamma}(r')\frac{\delta n_\gamma(r')}{\delta\rho_i(r)}dr'$$

$$n_\gamma[\{\rho_i(r)\}] = \sum_i \int dr'\,\rho_i(r')w_i^{(\gamma)}(r-r';R_i)$$

$$w_i^{(\gamma)}(|r-r'|) = C_\gamma\delta(|r-r'|-R_i)$$

$$w_i^{(\gamma)}(|r-r'|) = C_\gamma\theta(|r-r'|-R_i)$$

Integral Eqns
Of Finite Range!

Residual $$\frac{\delta\Omega}{\delta\rho_i(r)} = \ldots + \int \sum_\gamma \frac{\partial\Phi}{\partial n_\gamma}(r')w_i^{(\gamma)}(r-r')dr' + \ldots$$

Jacobian

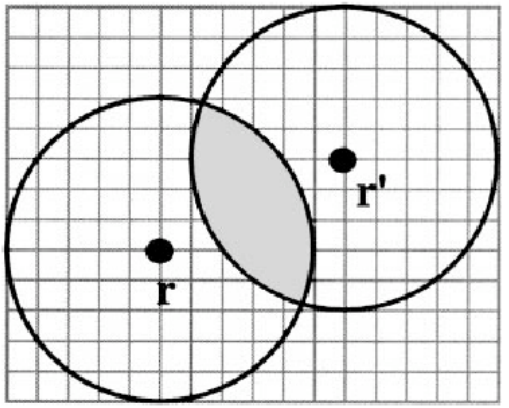
$$A_{ij}(r,r') = \frac{\delta^2\Omega}{\delta\rho_i(r)\delta\rho_j(r')} = \ldots + \int \sum_\varepsilon \sum_\gamma \frac{\partial^2\Phi}{\partial n_\gamma \partial n_\varepsilon}(r'')w_i^{(\gamma)}(r-r'')w_j^{(\varepsilon)}(r'-r'')dr'' + \ldots$$

Two ways to form the matrix problem…

(1) "second order" in complexity in forming the system of equations.

$$[A][\Delta\rho] = [b]$$

$$A_{ij}(r,r') = \frac{\delta^2\Omega}{\delta\rho_i(r)\delta\rho_j(r')} = \ldots + \int\sum_{\varepsilon}\sum_{\gamma}\frac{\partial^2\Phi}{\partial n_\gamma \partial n_\varepsilon}(r'')w_i^{(\gamma)}(r-r'')w_j^{(\varepsilon)}(r'-r'')dr'' + \ldots$$



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(2) Reduced fill complexity.

$$R_1 = 0 = n(r) - \int w(r-r')\rho(r')dr'$$

$$R_2 = 0 = \ldots + \int \frac{\partial\Phi}{\partial n}(r')w(r-r')dr' + \ldots$$

$$\begin{bmatrix} A_{11} & A_{12} \\ A_{21} & A_{22} \end{bmatrix}\begin{pmatrix} \Delta n(r) \\ \Delta\rho(r) \end{pmatrix} = \begin{bmatrix} b_1 \\ b_2 \end{bmatrix}$$

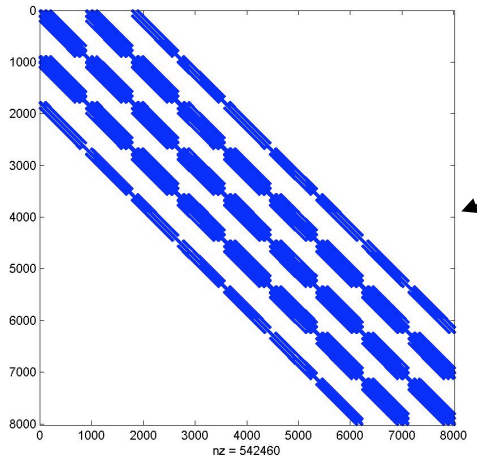
$$A_{11} = I$$

$$A_{12} = -\omega(r-r')$$

$$A_{21} = \frac{\partial^2\Phi}{\partial n^2}\omega(r-r')$$

$$A_{21} = \frac{\delta(r,r')}{\rho(r)}$$

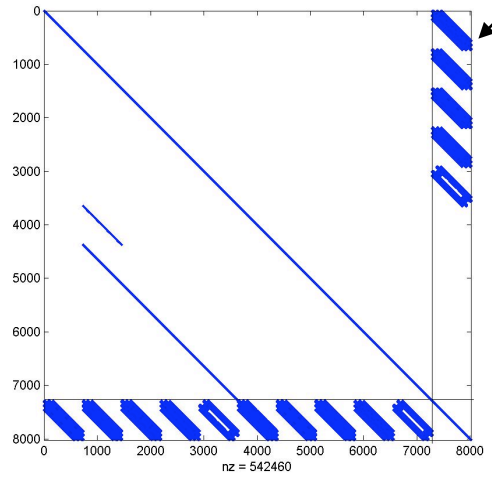
Two ways to order the matrix…



Nodal Ordering

Example:
Hard-sphere problem

Physics Block Ordering



Block Matrix Nonzeros

Subblock	Nonzeros
A11	10,935
A12	176,932
A21	353,864
A22	729

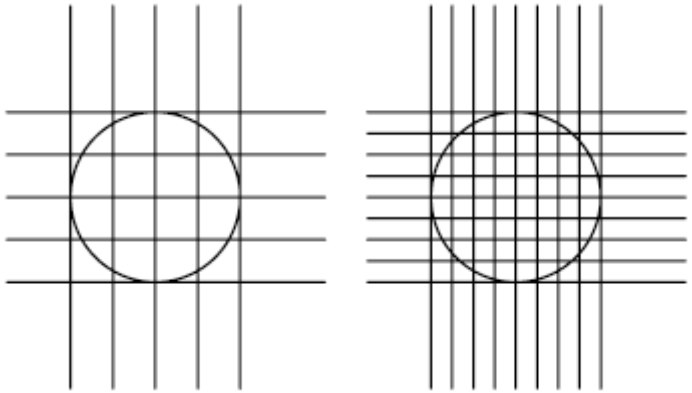
A numerical perspective

DFT - Integral equations of finite range
(smaller systems have higher density)
PDE - matrix density independent of system size.

DFT- Inter-physics coupling dominates
PDE - Inter-nodal coupling dominates

DFT - Stencils based on physical constants
PDE - Stencils based on nearest neighbors

DFT - May have large numbers of DOF per node
HS (3D) 10+
Polymer (20 beads) 42+
PDE - Usually a few DOFs per node



Two solution strategies

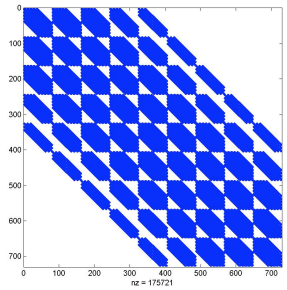
DFT optimized solver

- Construct A_{11} so it is easy to invert.
  - $A_{11} = I \qquad then \quad A_{11}^{-1} = I$
  - $A_{11} = L - I \quad then \quad A_{11}^{-1} = -L - I$
- Schur complement on 2-by-2 block system.
  - At each iteration apply: $\boldsymbol{S} = (\boldsymbol{A}_{22} - \boldsymbol{A}_{21}\boldsymbol{A}_{11}^{-1}\boldsymbol{A}_{12})$.
  - Solve: $\boldsymbol{S}x_2 = (b_2 - \boldsymbol{A}_{21}\boldsymbol{A}_{11}^{-1}b_1)$.
  - Apply preconditioning (e.g. ILU) to $\boldsymbol{S}$

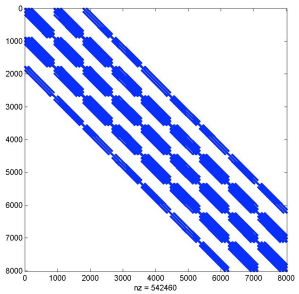
Out of the box PDE solvers (AztecOO)

- Solve $\boldsymbol{A}x = b$
- Apply preconditioning to $\boldsymbol{A}$

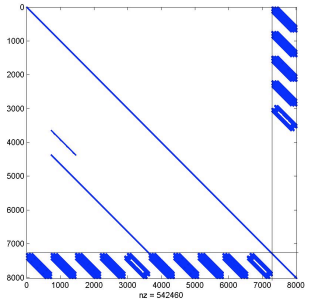
Methods - results



EXP(ρ): GMRES: A



IMP1(ρ,n): GMRES: A

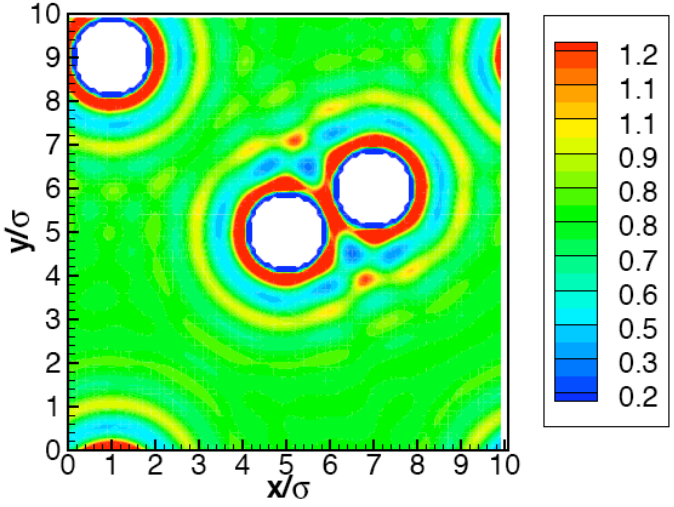


IMP2(ρ,n): Schur/GMRES A_{22}

Stats \Form Phase Cost \	EXP	IMP1	IMP2	IMP2 has cost of
System Dimension	4,913	54,043	4,913	EXP
Matrix nonzero cnt	5M	15M	15M	IMP1
Condition Number	6E2	1E4	6E2	EXP
Matrix Preprocessing	105.4	10.8	10.8	IMP1
Matrix Fill	118.0	4.0	4.0	IMP1
Solve Time	12.2	145.9	38.4	Both
Linear Solve Iterations	46	124	45	EXP
Total Time (4 Newton Steps)	628.3	616.9	186.9	Both

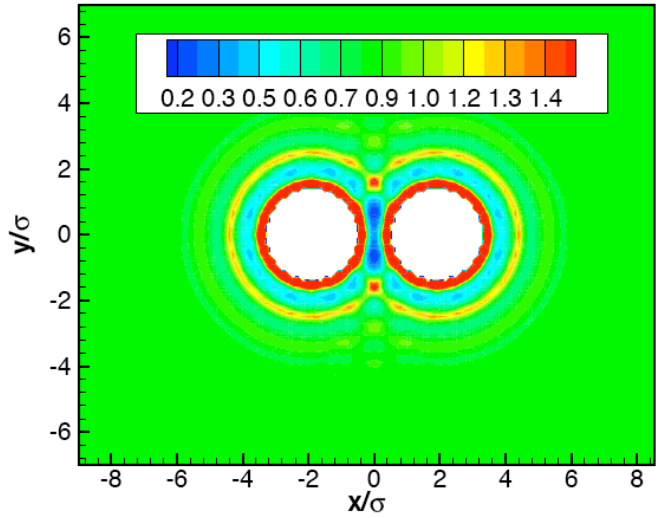
**note no preconditioner was used for these studies.*

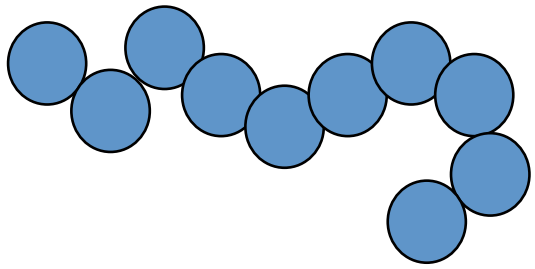
Parallel scaling – 2D



#Procs	<# Lin iters>		Time/N_{iter}		T_{1Proc}/T	T_{old}/T_{new}
	Old	New	Old	New	(New)	
1	8	22	495.1	14.7	1	33.8
2	10	22	148.7	8.5	1.7	17.5
4	11	22	47.4	4.2	3.5	11.3
8	12	22	16.1	2.1	6.9	7.6
16	13	22	6.3	1.1	13.3	5.7
32	15	22	2.1	0.6	24.8	3.6
64	18	22	1.1	0.3	43.1	3.2

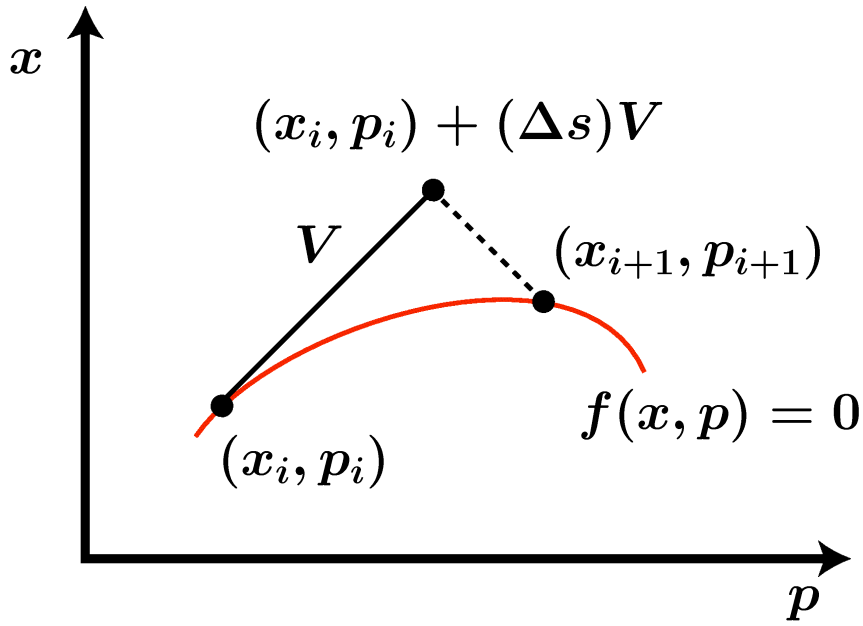
Scaling with Chain Length





N_{seg}	N_{iter}	<# Lin iters>		Time/N_{iter}		$T/T_{N_{seg}=10}$	T_{FullA}/T_{SA22}
		FullA	*SA22*	*FullA*	*SA22*	(*SA22*)	
10	8	40	70	7.1	3.7	1	1.9
20	8	48	69	21.7	8.9	2.4	2.4
40	8	62	70	58.7	15.1	4.1	3.9
80	7	93	68	257.4	30.9	8.4	8.3

Two helpful algorithms



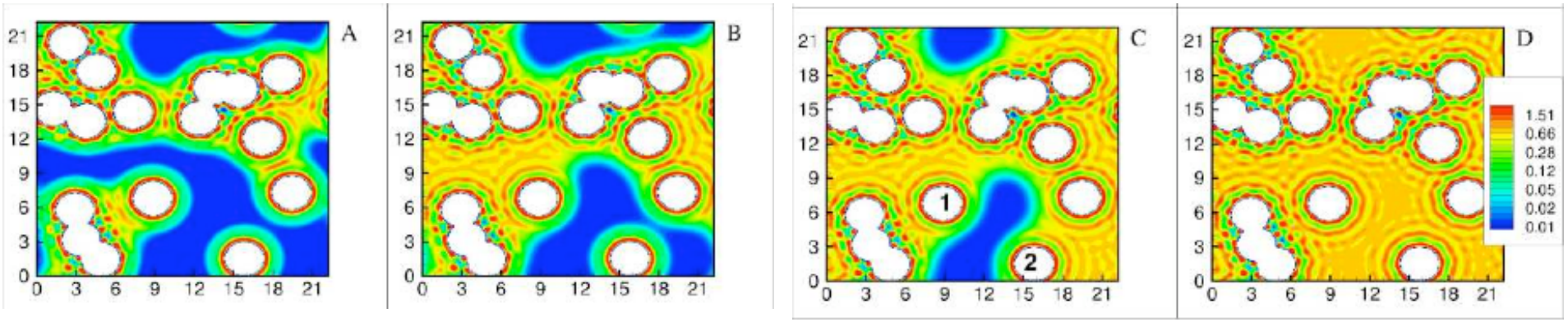
$$f(x,p) = 0$$

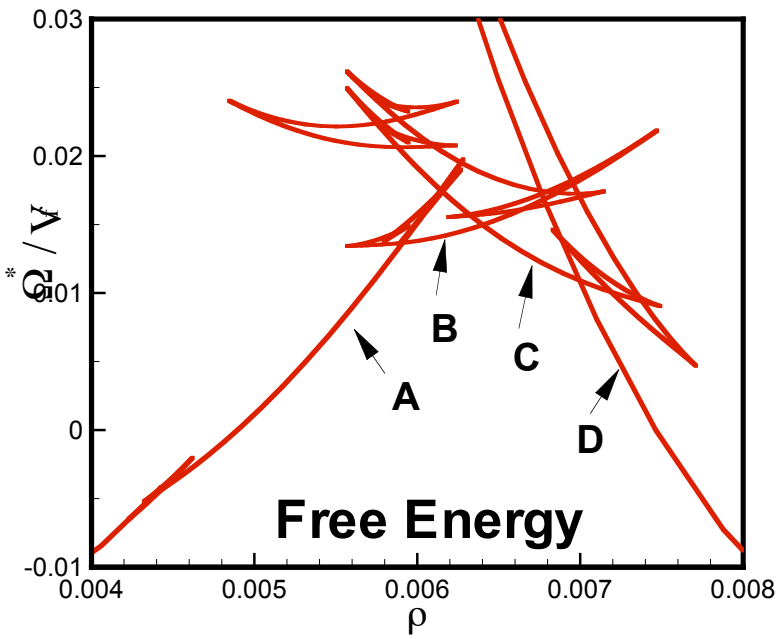
$$V_x^T(x - x_i) + V_p(p - p_i) = \Delta s$$

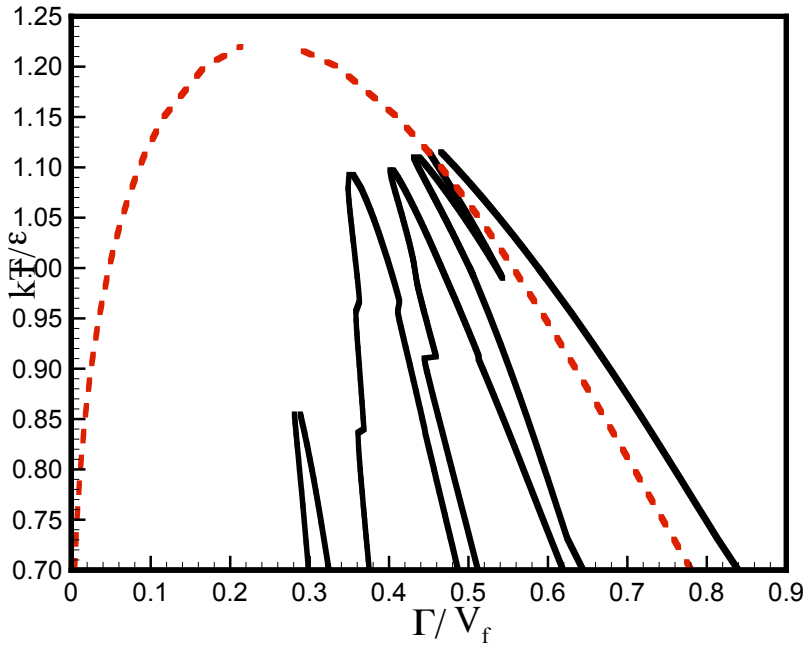
Arc Length Continuation

Multistate Tracking

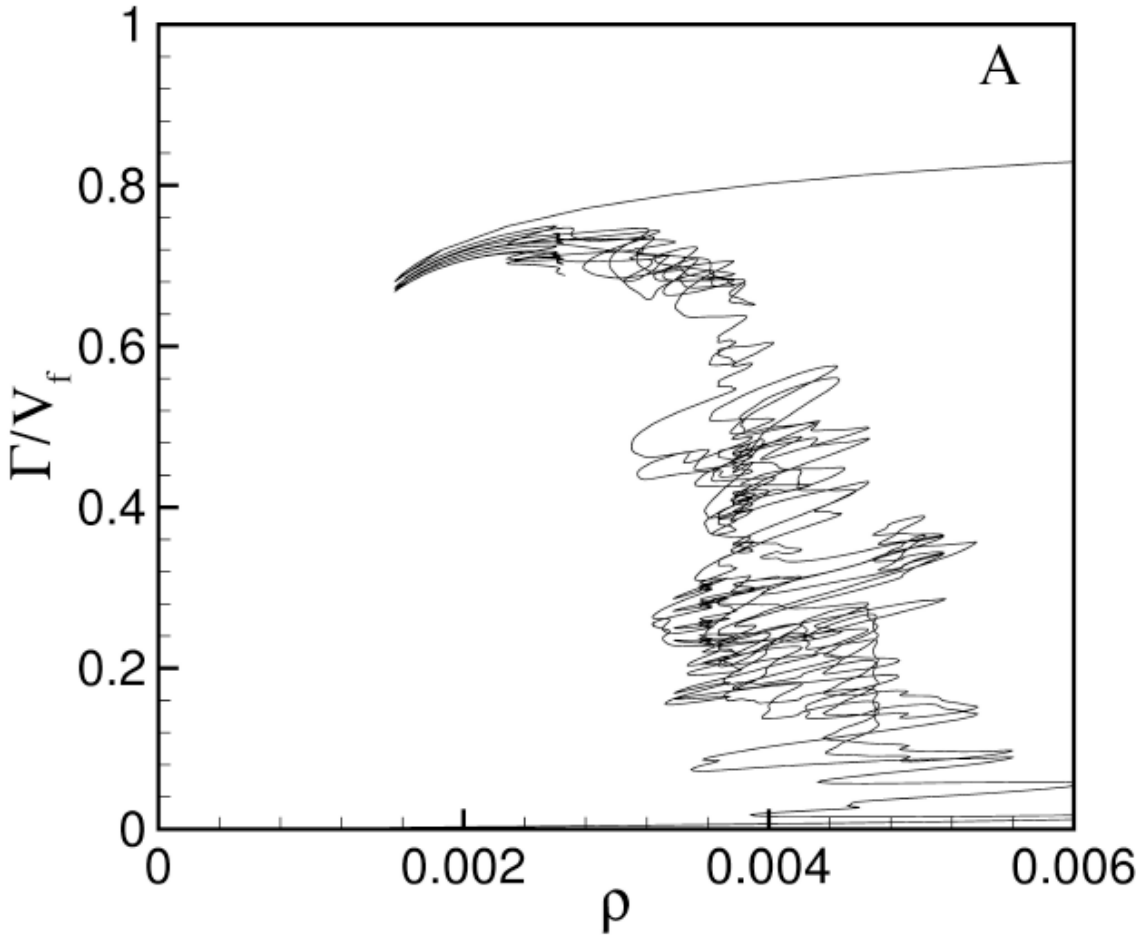
Porous Media



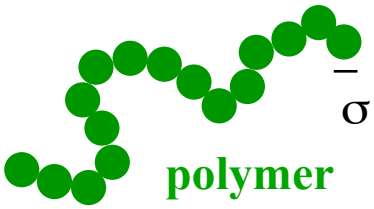


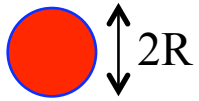


Porous Media



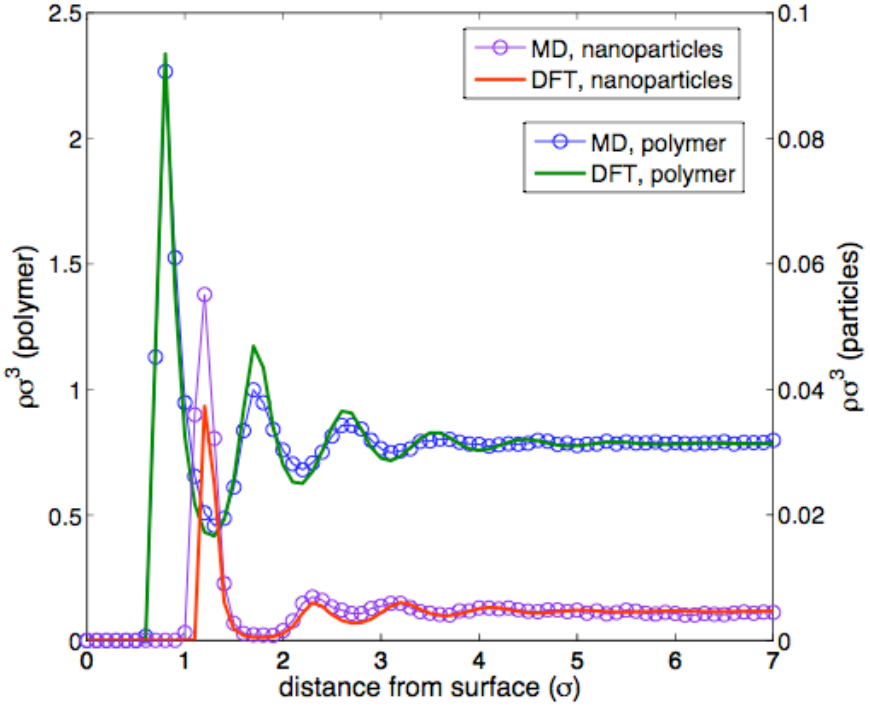
Nanocomposite thin films



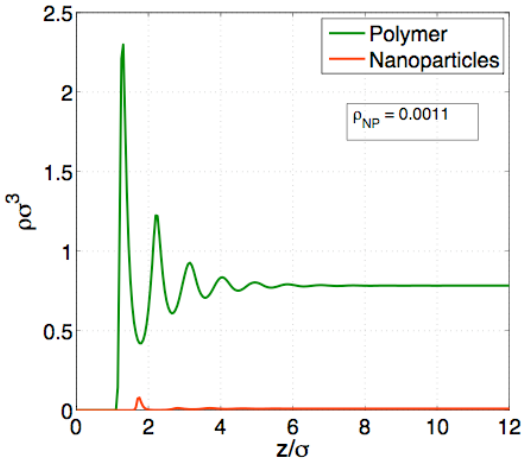


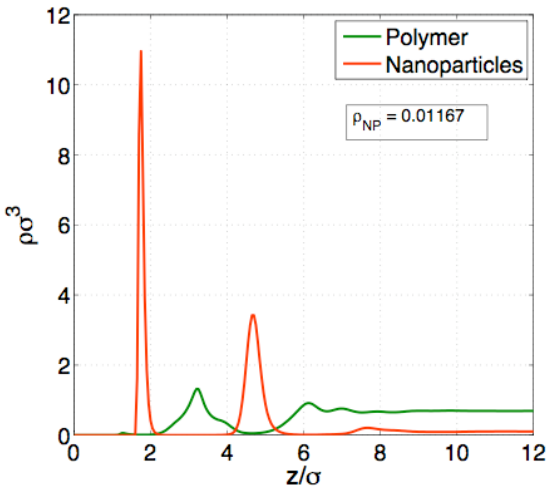
Experiment:
PS nanoparticles go to the surface
(Krishnan et al., Langmuir, 2005)

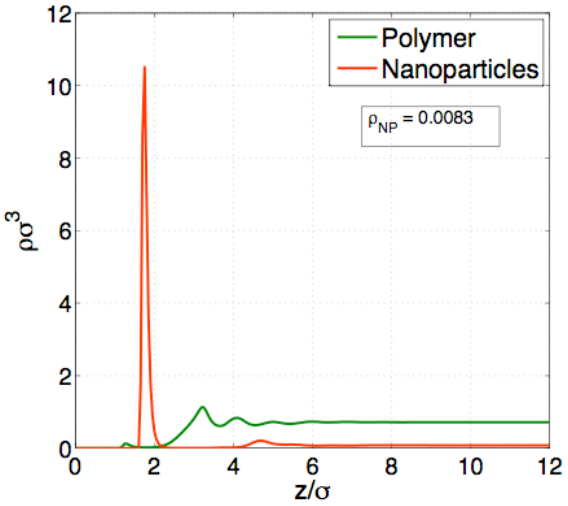
DFT/MD:
McGarrity, Mackay (MSU),
Frischknecht (Sandia)

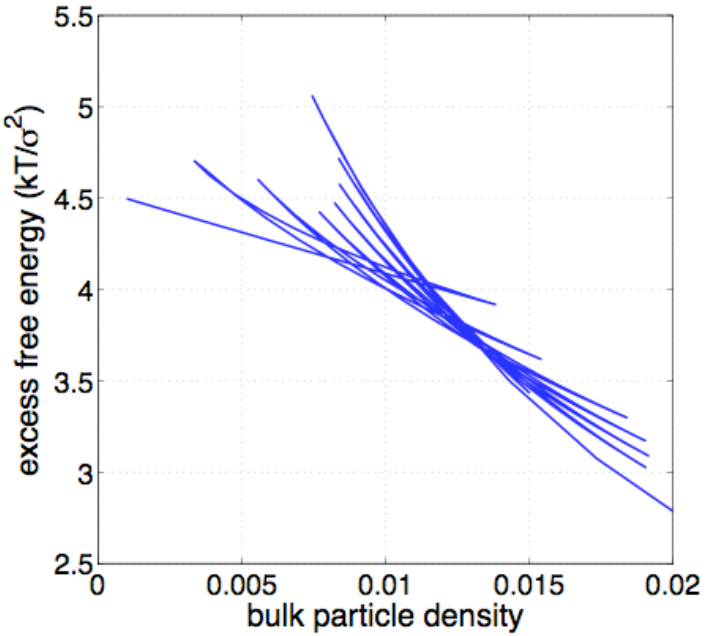


Nanocomposites

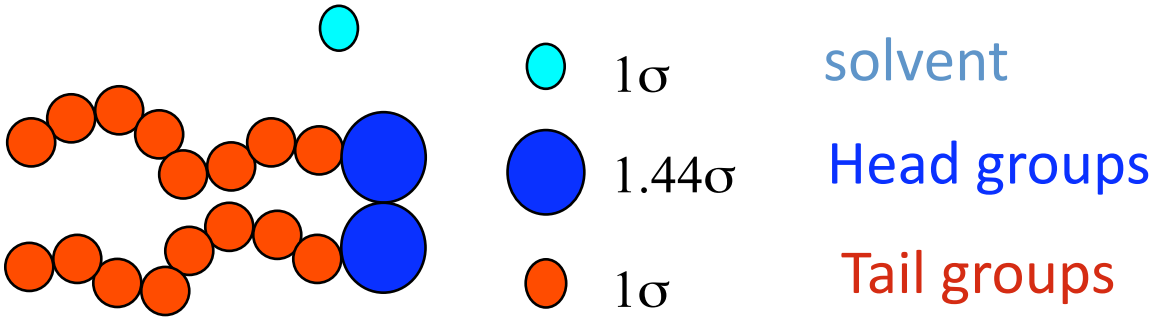








Lipid Bilayers



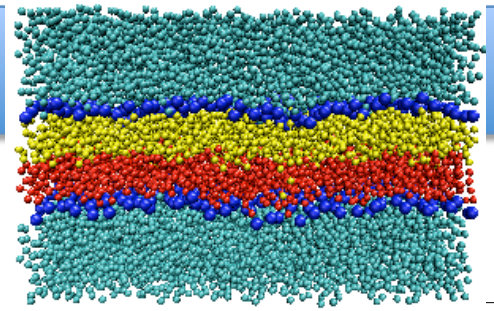
$$u = \frac{4\varepsilon}{k_B T}\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right]$$

Cut and shifted Lennard-Jones potentials … *cutoffs = 3.5σ*

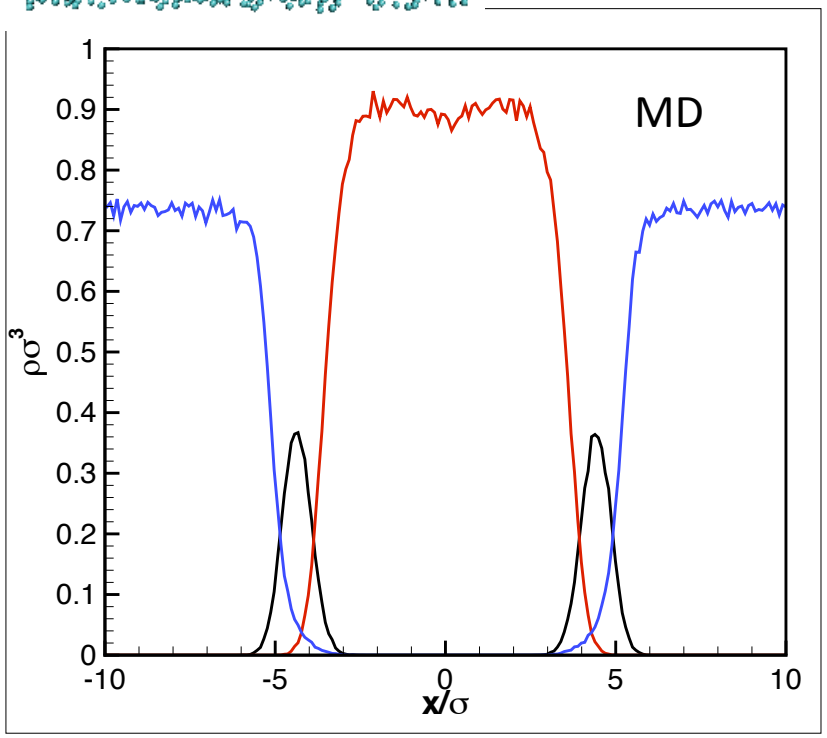
Define:

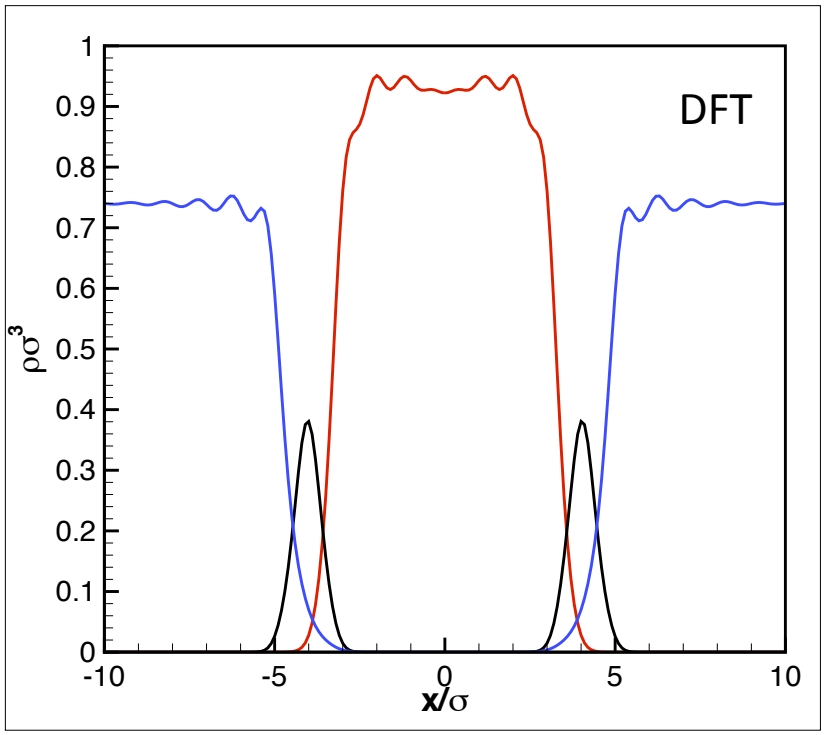
state point and

energy parameters, ε



Comparing MD and DFT





$kT/\varepsilon=1.0$

$P\sigma^3/kT=0.5$

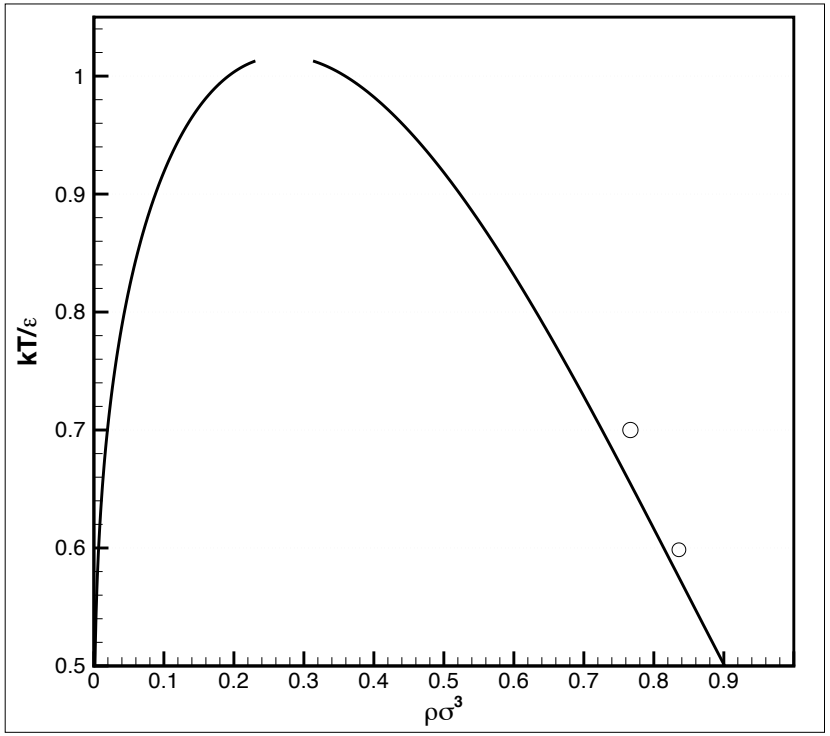
	Head	Tail	Solvent
Head	1	0	1
Tail	0	1	0
Solvent	1	0	1

State Point

Biological membranes are zero tension membranes. The temperature and pressure are set by the bulk solvent (water / physiological electrolyte).

	$T_{critical}$	T_{triple}	T
H_20 (°C)	374	0.01	37
Model (k_BT/ε)	1.015	~0.55	0.6-0.7

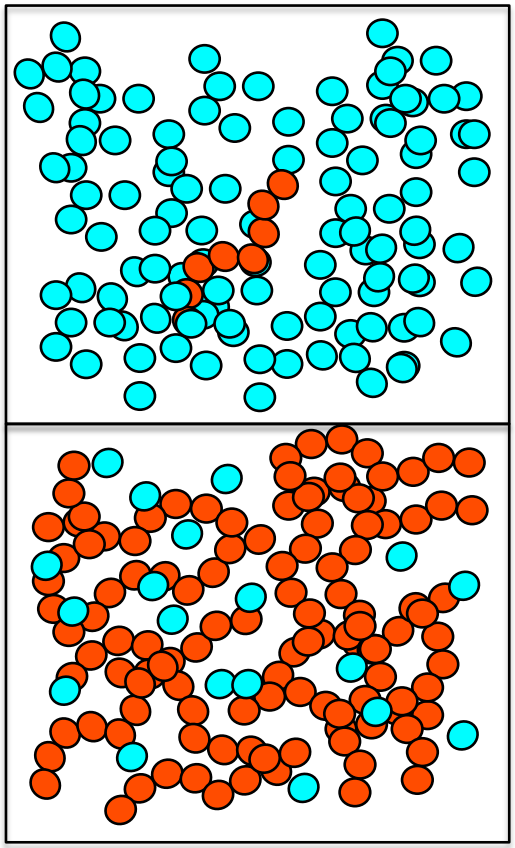
	P	$P_{vap}(T)$	P/Pvap
H_20 (atm)	1	0.0619	16.2
Model ($P\sigma^3/kT$)	0.279	0.00334	16.2



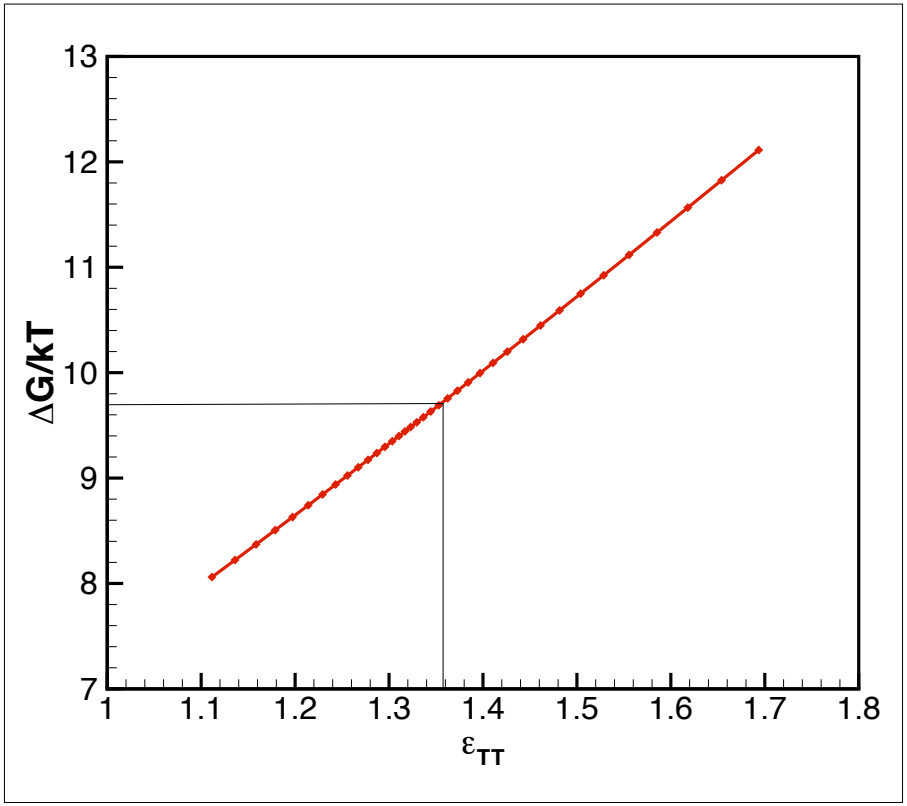
The mappings are not unique because the ***law of corresponding states*** is not true for a comparison of LJ fluids and water.

Partitioning Calculations

Energy parameters are set to mimic the interactions of water with hydrocarbon tails of lipid chains. Partitioning studies of the model system were done on water and hexadecane (= 8 "tail" beads). *ΔG/kT=9.69 for water/hexadecane at 40°C*



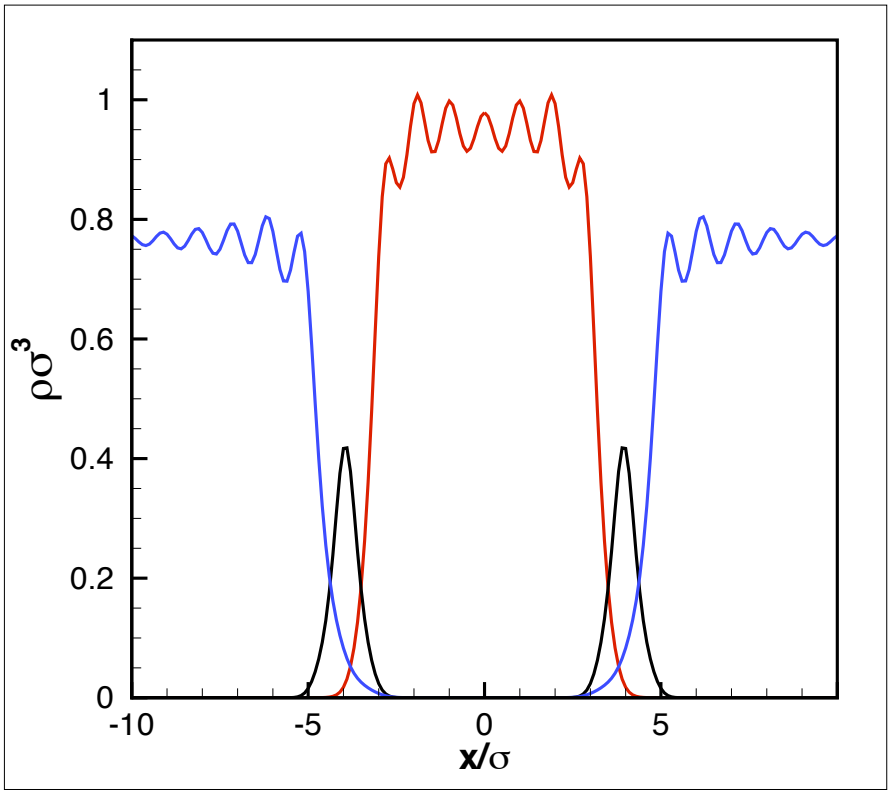
$$\Delta G / kT = -\ln(\rho_w^{oil} / \rho_w^{aq})$$



$kT/\varepsilon=0.7$

$P\sigma^3/kT=0.28$

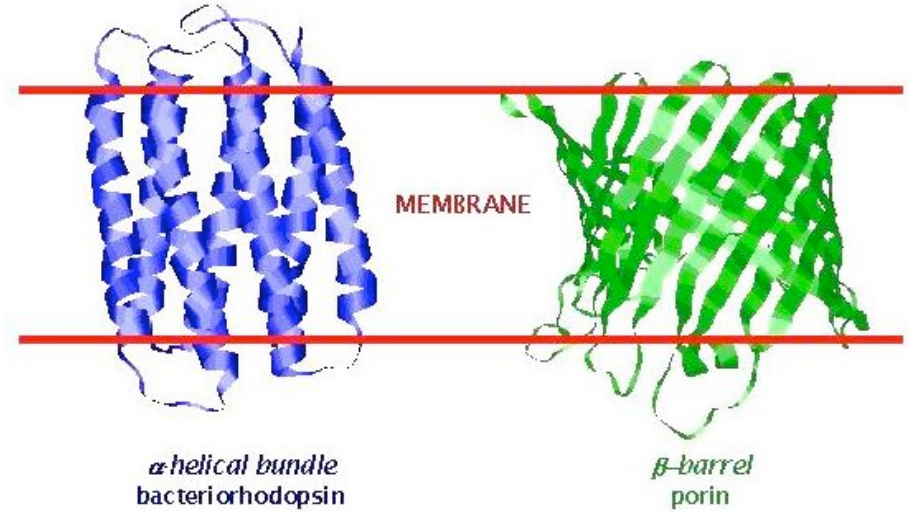
	Head	Tail	Solvent
Head	1.42	0.51	1.42
Tail	0.51	1.38	0.51
Solvent	1.42	0.51	1.42



Peptide Assemblies

Biology

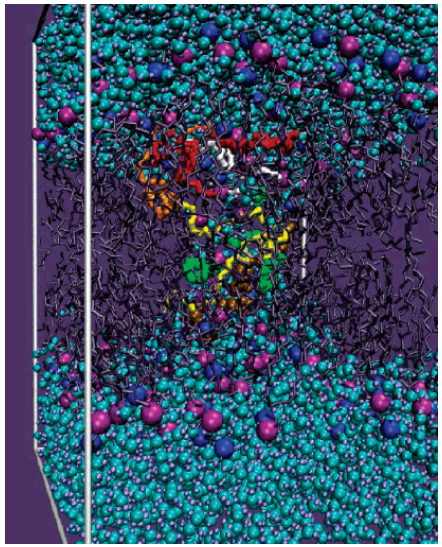
- **Found in bacterial, archaeal, eukaryotic cytoplasmic and organellar membranes**
- **Antibimicrobial peptides**
- **Ion channels**
- **Pore-forming toxins**
- **Viruses**



S. White Lab: http://blanco.biomol.uci.edu/mp_assembly.html

Nanotechnology

- **Sensors**
- **Smart Materials**

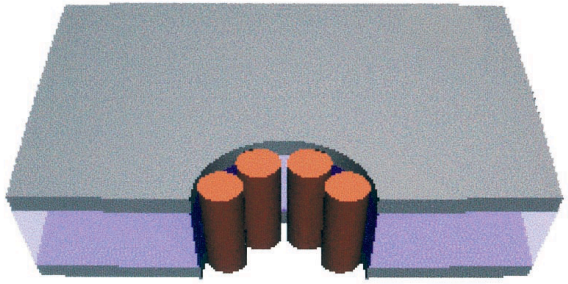


magainin pore

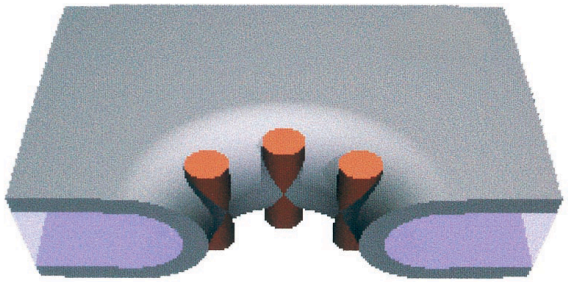
Leontiadou et al., JACS, 128, 12156 (2006)

AMPs in membranes

Barrel-stave structure

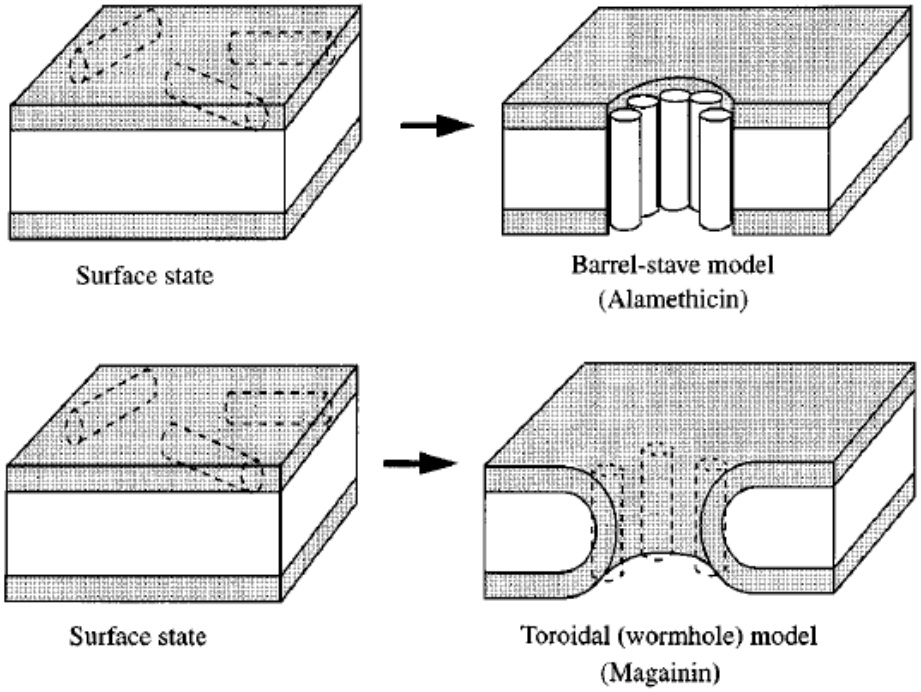


Toroidal structure

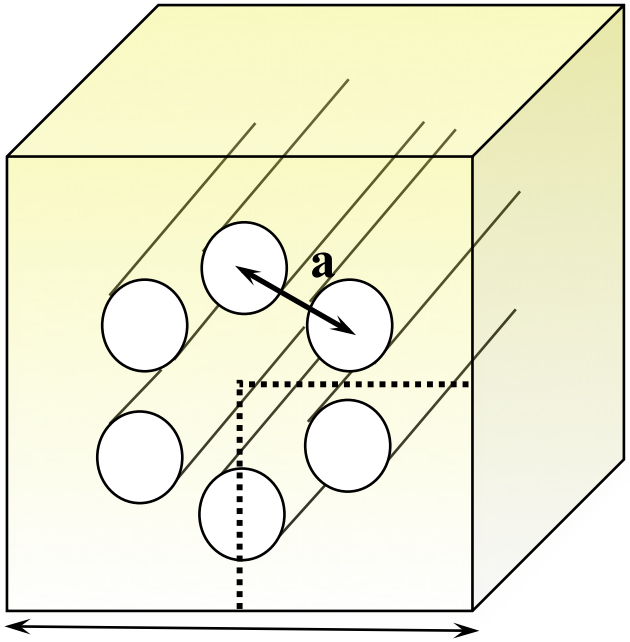


Yang et al., Biophys. J. 2001

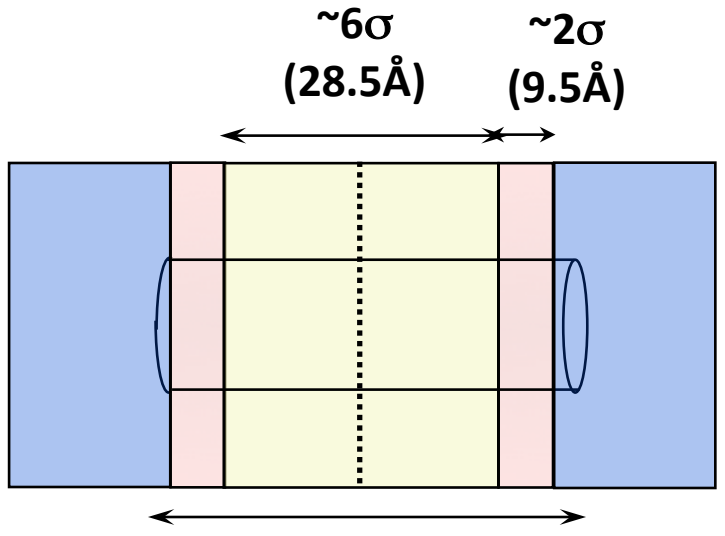
Protein insertion



Ludtke et al, Biochemistry, 1996



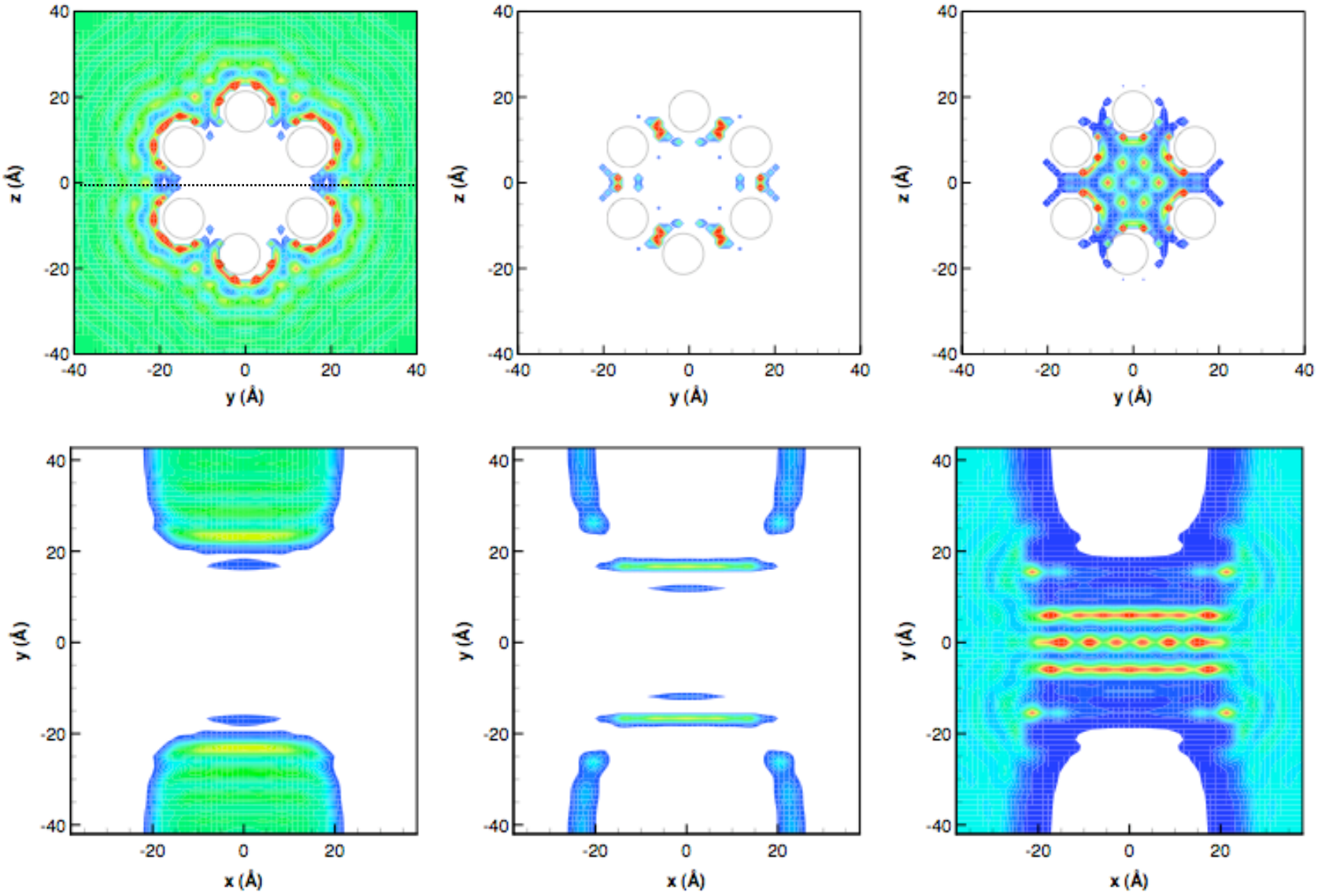
16-22σ (76-105Å)

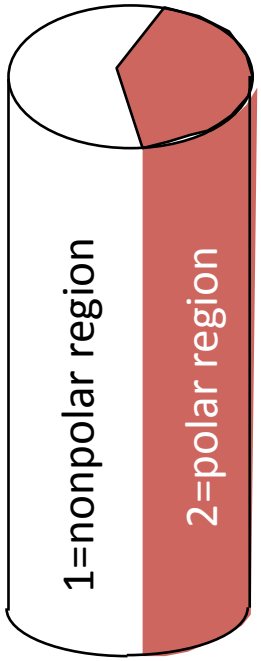


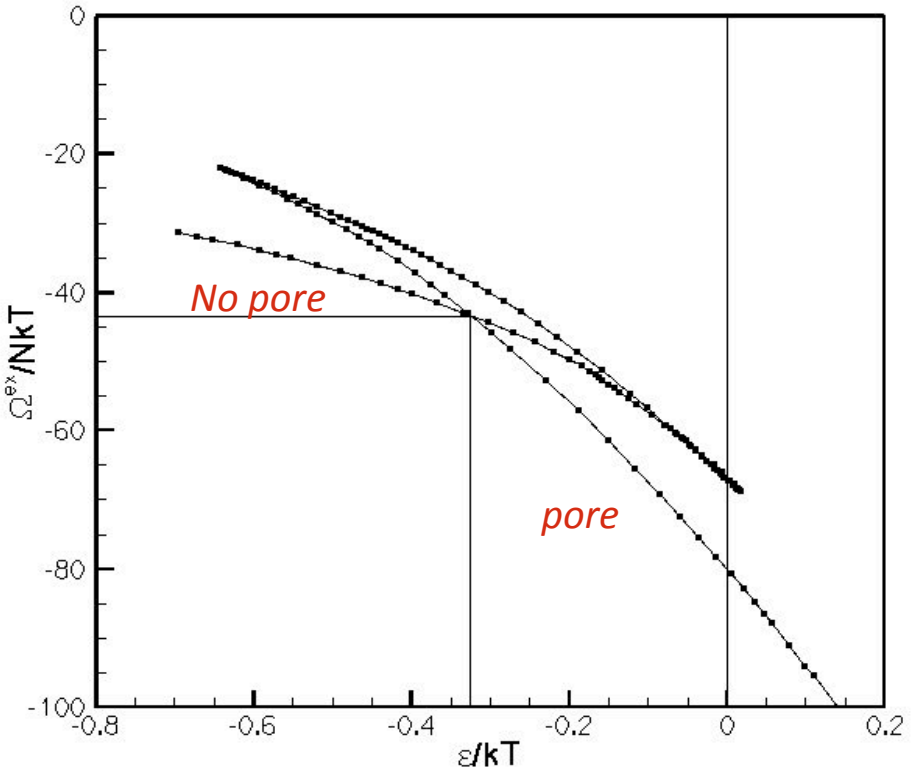
Cylinder-lipid interactions:
- diameter = 2σ = 9.5 Å
- a=lattice constant
- hard (no particular molecular preferences)

3D calculations: Time per solve is ~10-20 minutes on 100 procs

Toroidal Pore (a=16.6 Å) - cut 2



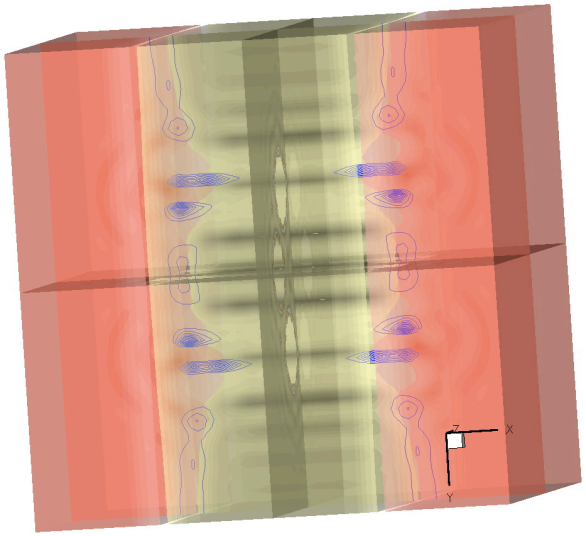


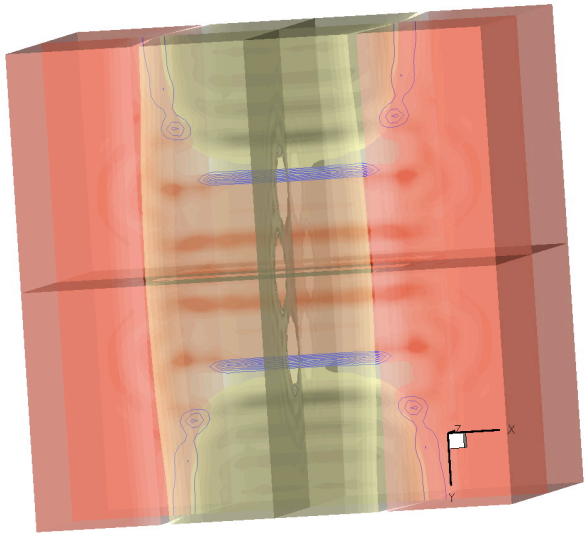


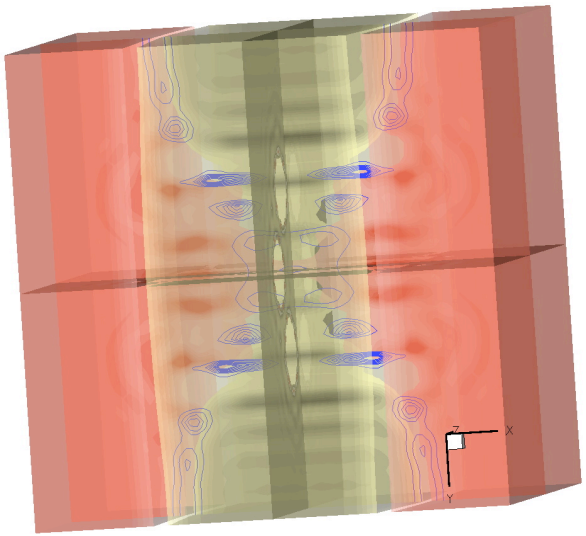
Varying ε_{2s} and ε_{2h}

with ε_{1t}=0

- *a=14.875Å assembly*
- *Found a first order phase transition.*
- *The first converged solution was the metastable solution.*
- *162 data points*


Z
X
Y


Z
X
Y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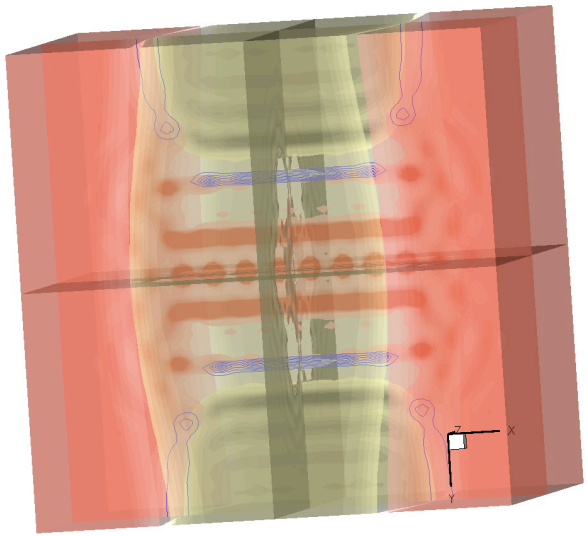
Z
X
Y

Current Efforts

Software Development

- Building New Physics Capabilities
  - Tensor weight functions
  - Dynamics
  - Bond angle constraints
  - …

- Solvers
  - Generalization of Schur Solvers
  - Investigation of optimal solution of coupled PDE / DFTs

- Usefulness and Accessibility
  - Build complexity
  - Parameter input and handling

- Tramonto 2.2 is expected this summer