Molecular Modeling of Interfacial Phenomena

SAND2009-1953C

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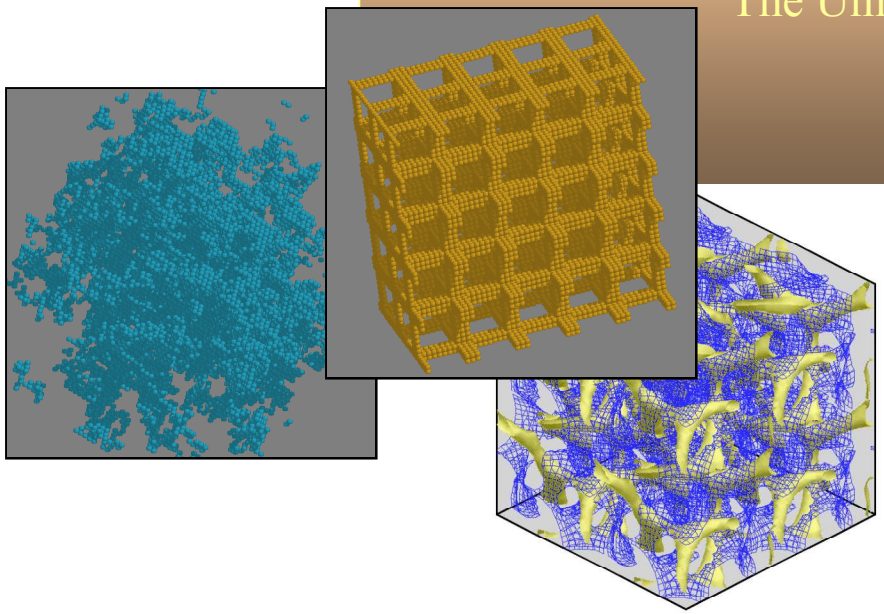
The University of New Mexico



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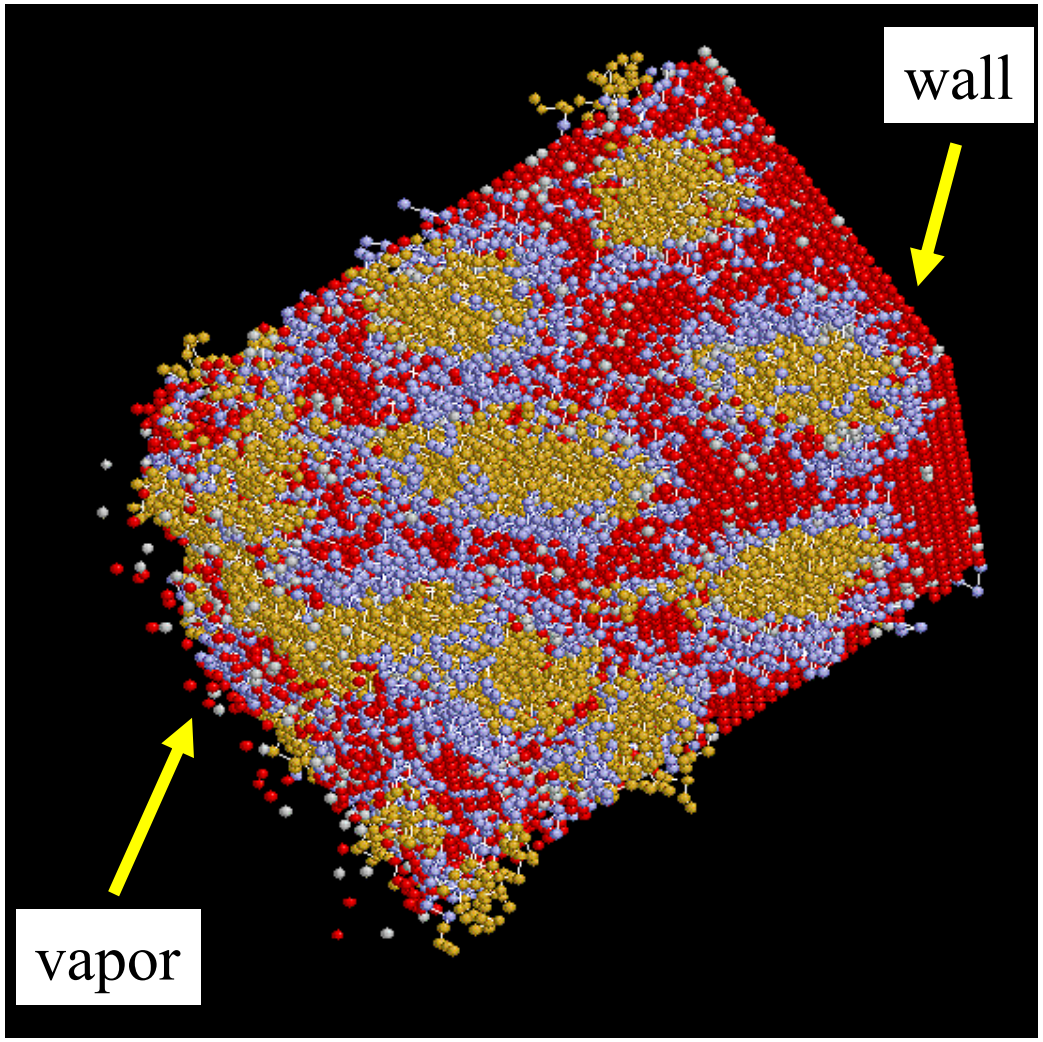
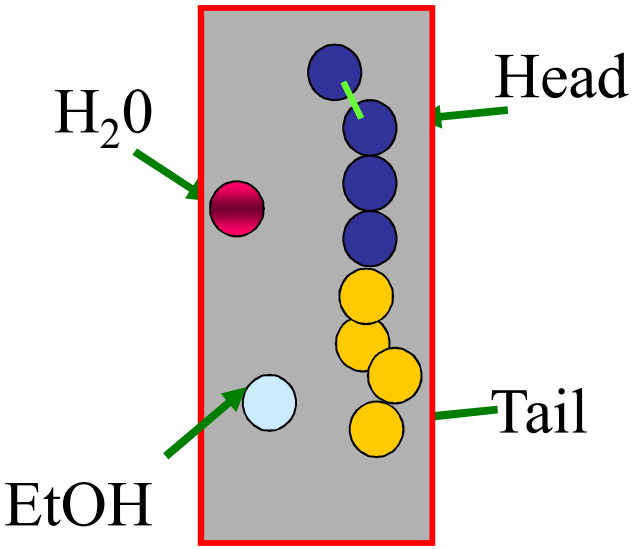
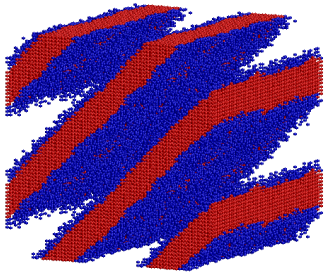
Snapshot of vapor-liquid system

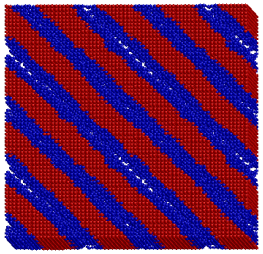


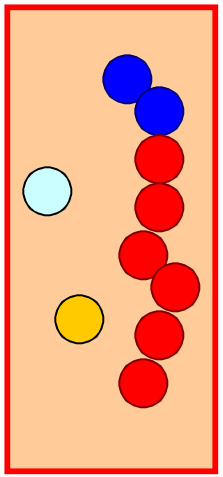


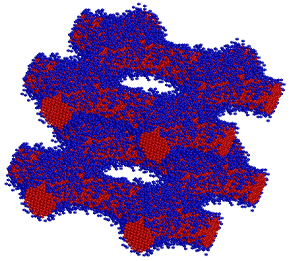
Phase-diagram for linear chains

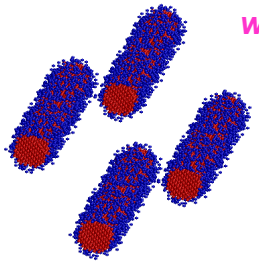
Water/ethanol mixtures: H_2T_6

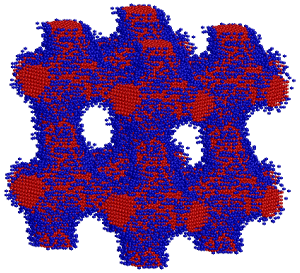


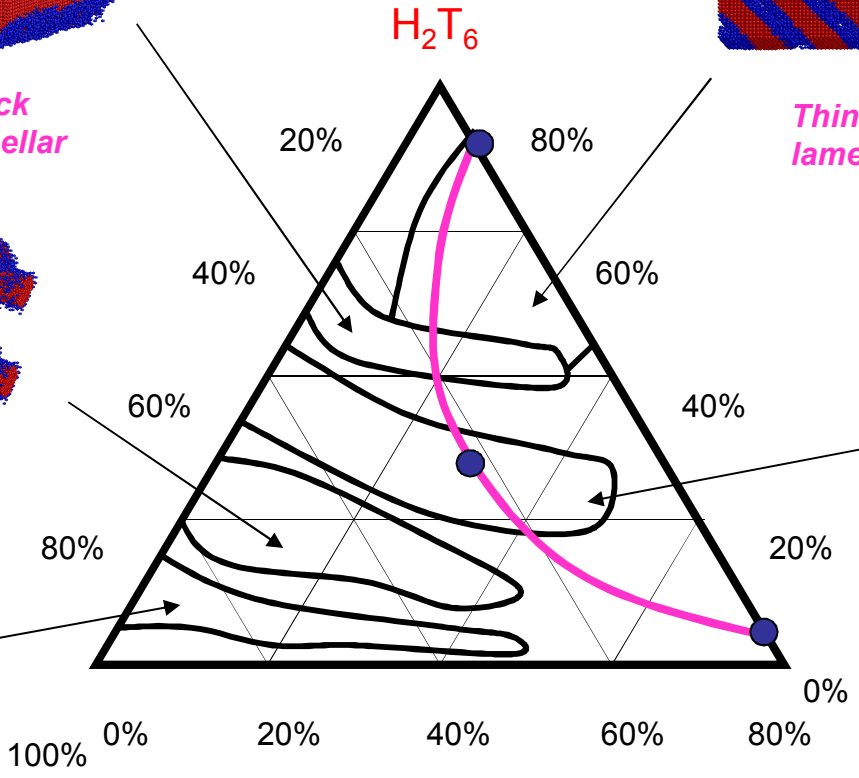












Thick lamellar

Thin lamellar

layers with holes

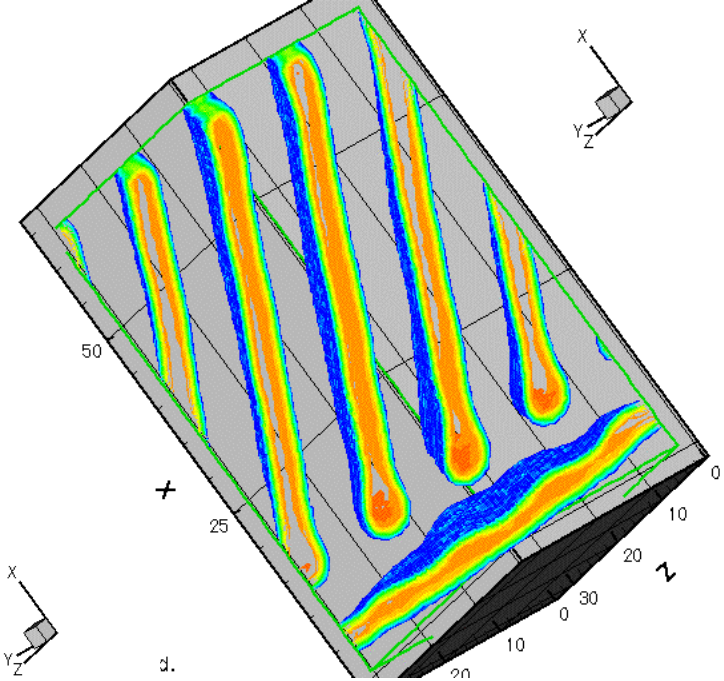
simple cubic

cylindrical micelles

Systems with interfaces:

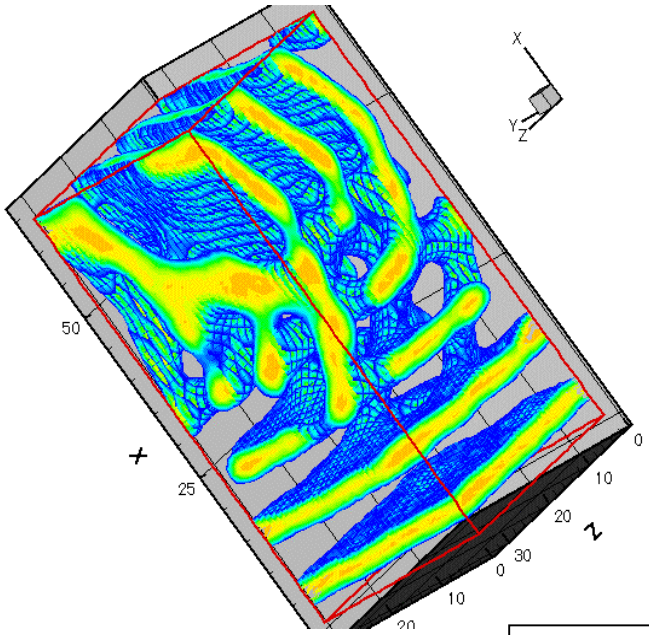
one hydrophilic wall

one noninteracting wall

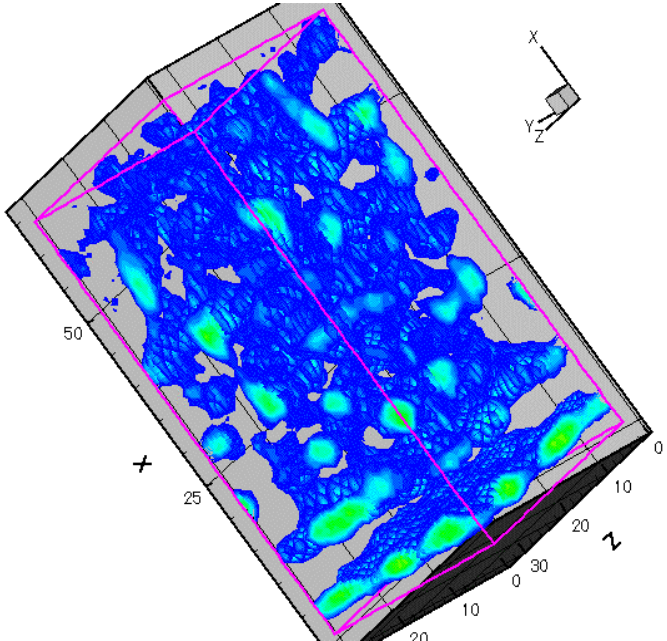


T=4

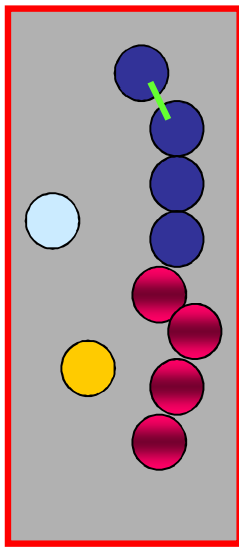
T=6



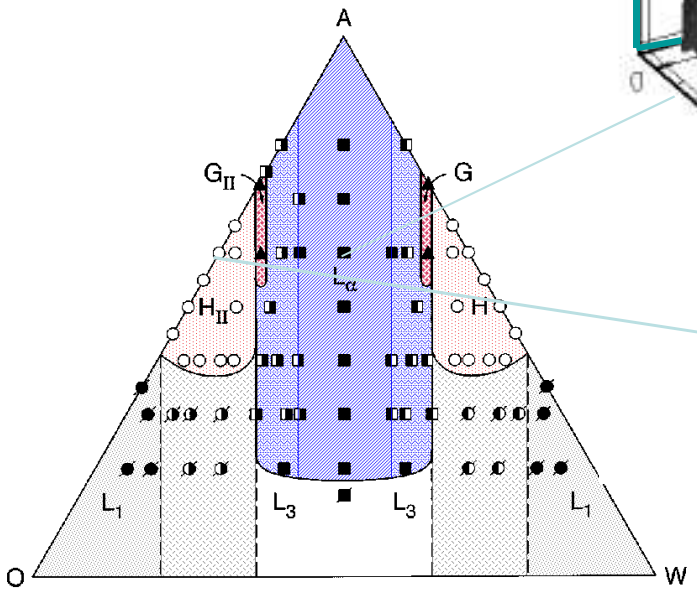
T=9.5



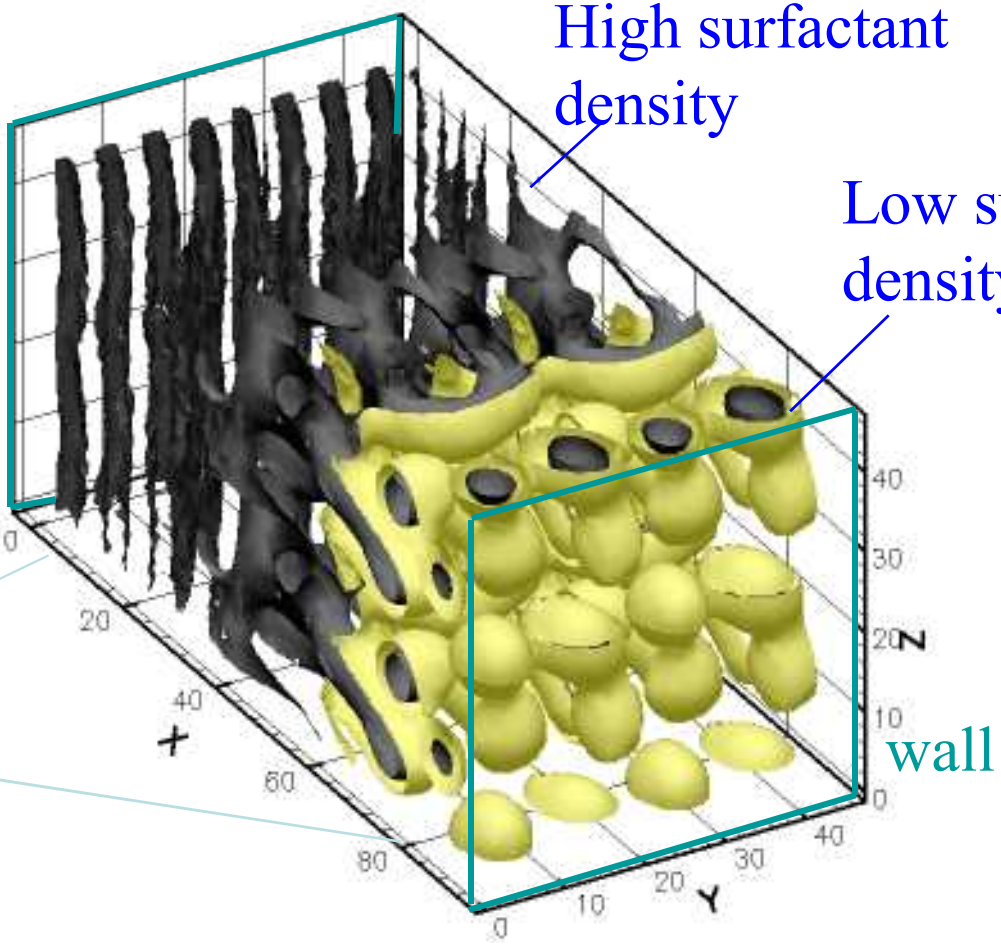
80% H_4T_4
10% EtOH



Effect of Gradient on Mesophase



Lamellae

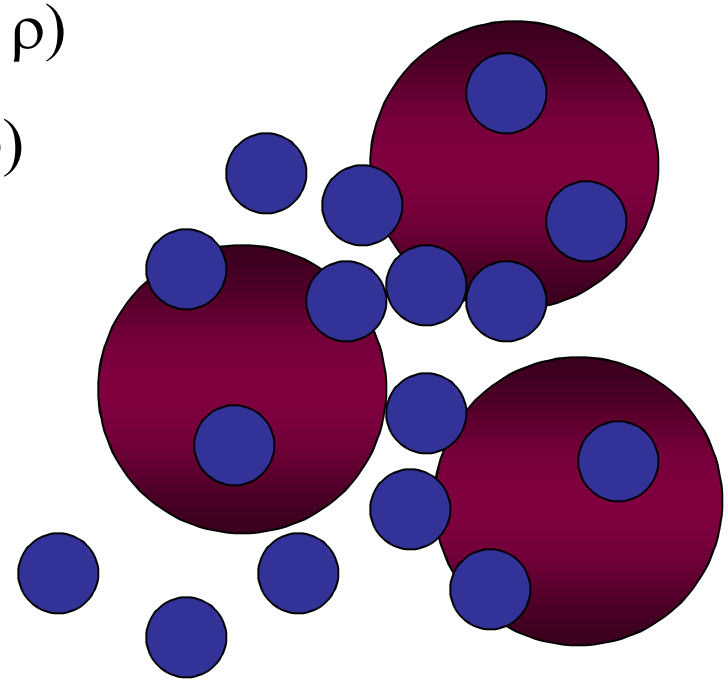


Elongated Spheres

The Challenge

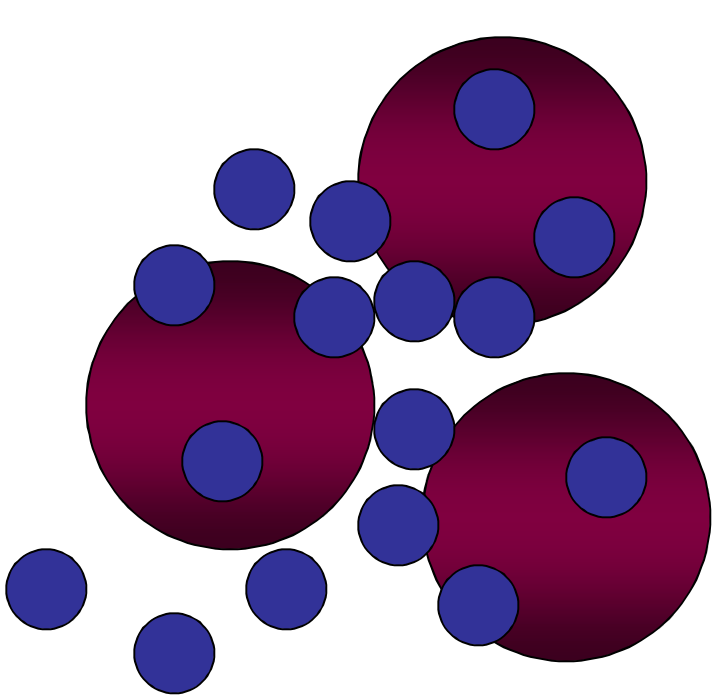
Capture:

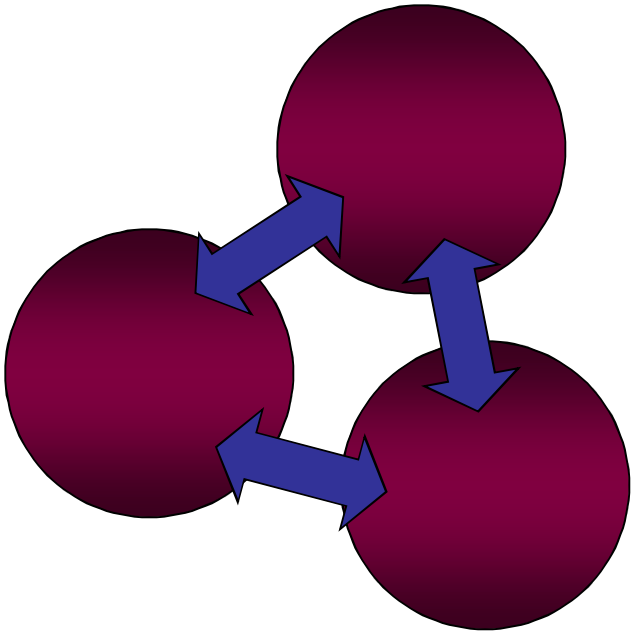
1. thermodynamics (e.g Π vs ρ)
2. hydrodynamics (e.g η vs ρ)
3. fluctuations



Thermodynamics

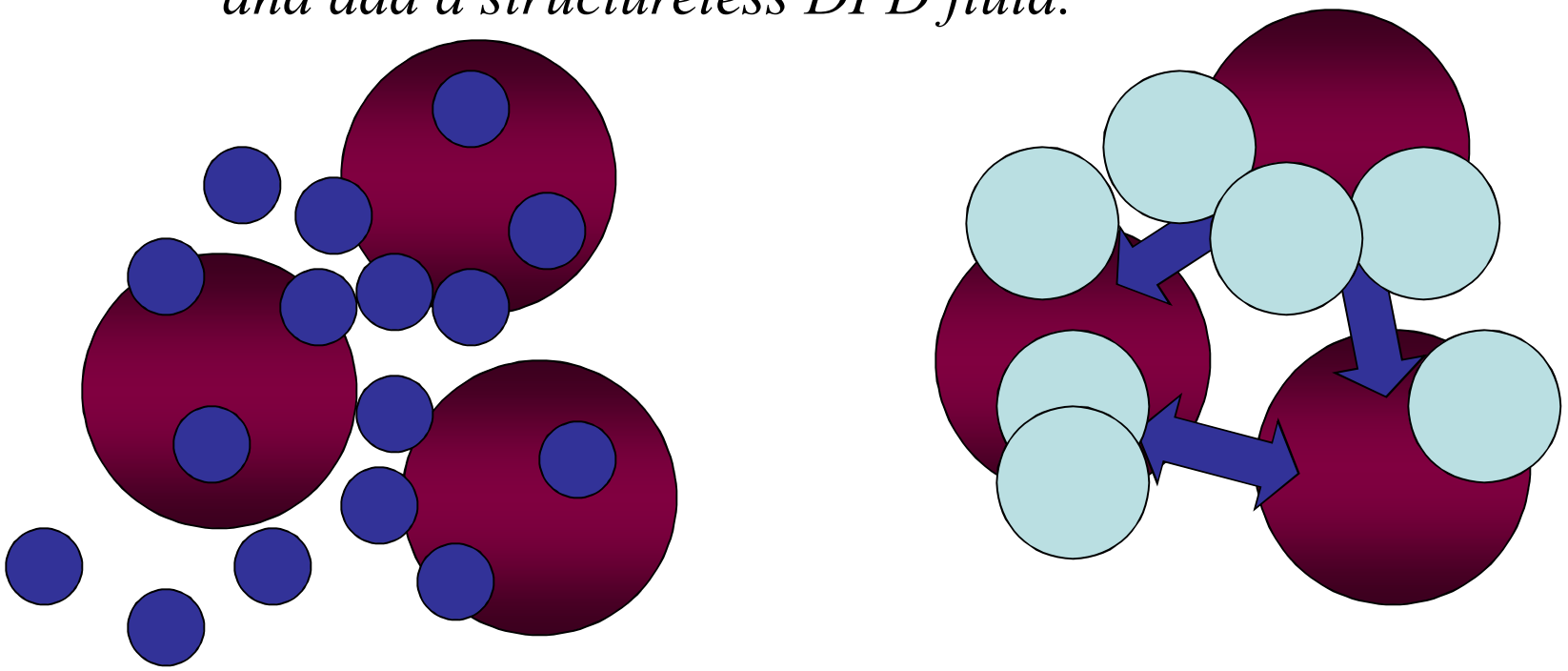
Replace solvent *molecules* by solvation *forces*



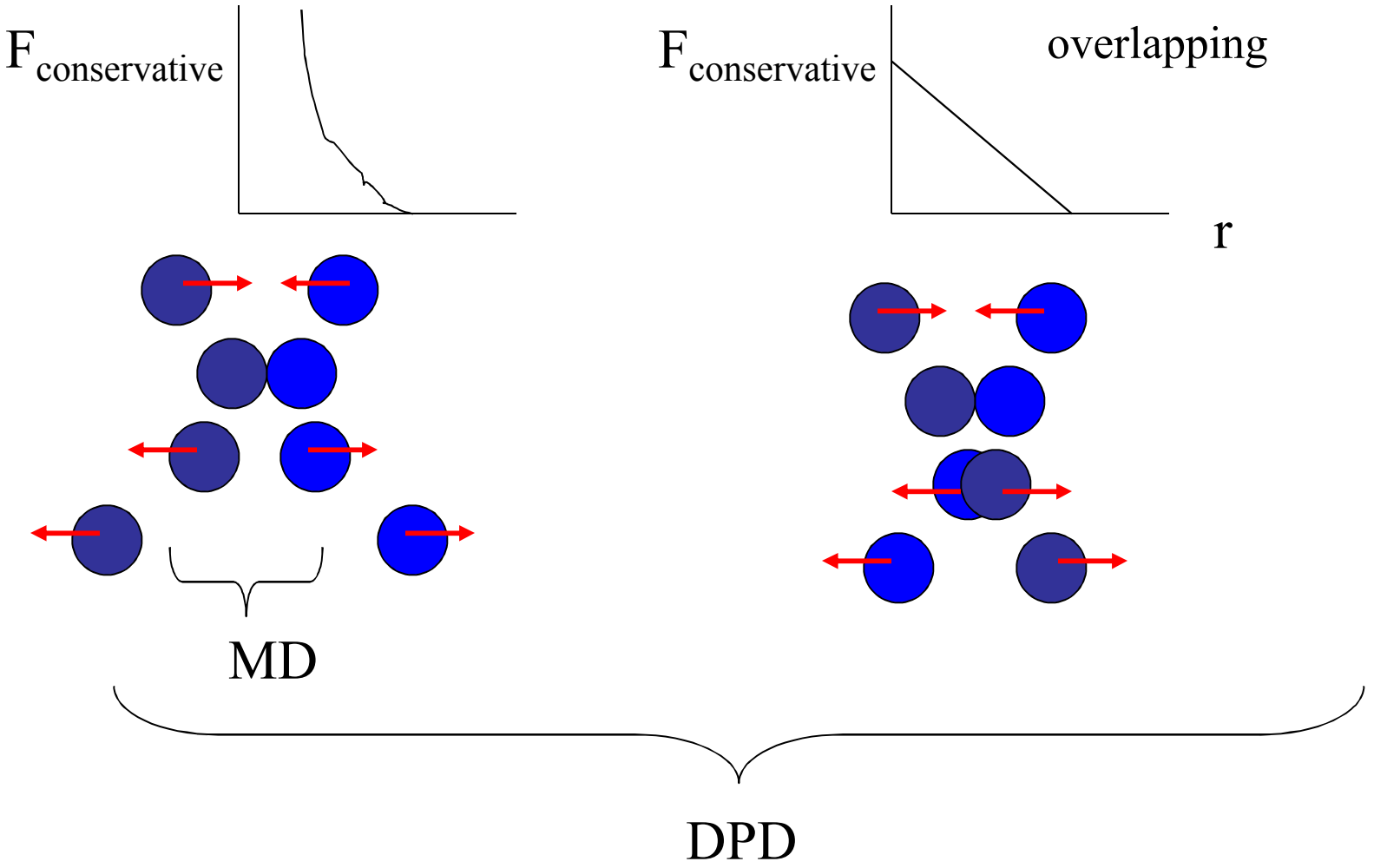


Suspensions

Replace solvent *molecules* by solvation *forces*
and add a structureless DPD fluid.



Colliding “lumps of fluid”



DPD: fluctuating hydrodynamics

- **mesoscopic lumps of fluid**
- **displays truly hydrodynamic behavior**
- **includes fluctuations consistent with statistical mechanics.**

Hoogerbrugge and Koelman, Europhys. Lett, **19**, 155 (1992) and **21**,369 (1993)

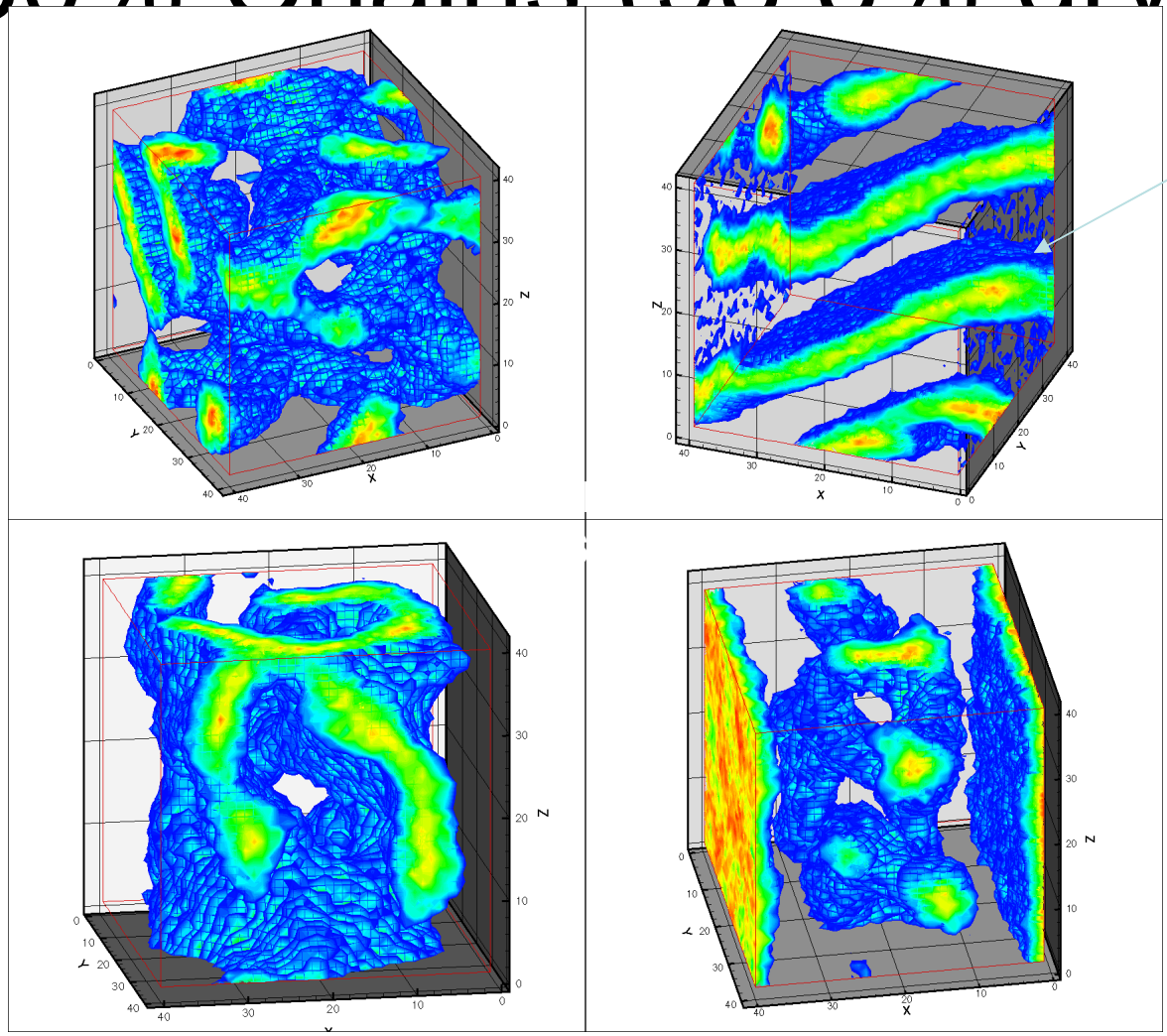
Espanol and Warren, Europhys. Lett, **30**, 191 (1995)

Espanol Phys Rev E **52**, 1734 (1995)

30% Chains (98.3% dry)

NO WALL (BICONT)

INERT WALLS (LAMELLAE ⊥ WALLS)

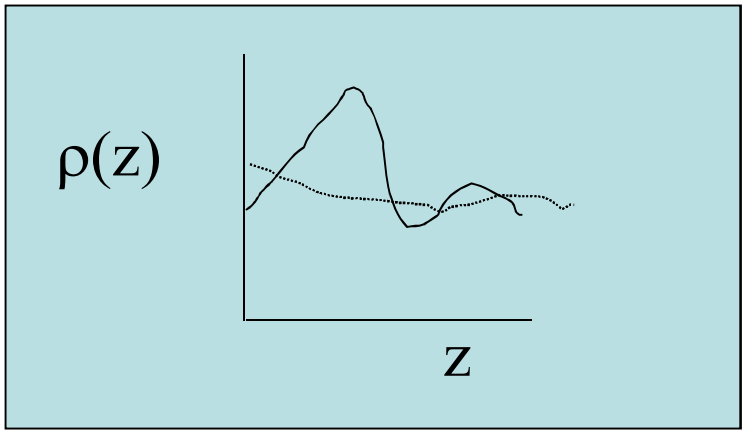


HYDRO-PHILIC (COM-PRESSED)

HYDRO-PHOBIC (LAYERS + WEAK ORDER)

- Order gained in neutral case, lost for ‘philic

DFT: inhomogeneous fluids



Ideal gas: $\rho(z)=\rho_b \exp(-U(z)/kT)$ (trivial)

Nonideal gas: minimize $\Omega[\rho(z)]$

Equilibrium DFT: Canonical and Grand Canonical Ensembles

For μVT systems, the grand potential is the associated energy and can be written as a functional of density as

$$\beta\Omega[\rho] = \sum_{i}^{l}\left[(1-\sum_{k}^{lspe}\rho_i^k)\ln(1-\sum_{k}^{lspe}\rho_i^k)+\sum_{k}^{lspe}\left(\rho_i^k\ln\rho_i^k+\rho_i^k\beta V_i^k-\rho_i^k\beta\mu_i^k+\frac{\beta}{2}\sum_{m}^{Ne}\sum_{n}^{lspe}\epsilon_{d(i,m)}^{kn}\rho_i^k\rho_{I(i,m)}^n\right)\right]$$

For NVT systems, the Helmholtz free energy is the associated energy and can be written as a functional of density as subject to constraints

$$\beta F[\rho] = \sum_{i}^{l}\left[(1-\sum_{k}^{lspe}\rho_i^k)\ln(1-\sum_{k}^{lspe}\rho_i^k)+\sum_{k}^{lspe}\left(\rho_i^k\ln\rho_i^k+\rho_i^k\beta V_i^k+\frac{\beta}{2}\sum_{m}^{Ne}\sum_{n}^{lspe}\epsilon_{d(i,m)}^{kn}\rho_i^k\rho_{I(i,m)}^n\right)\right.$$

$$N^k = \sum_{i}^{l}\rho_i^k$$

ρ_i^k is the density of component ***k*** at site ***i***.

l is the total number of lattice sites.

$lspe$ is the total number of species.

Ne is the number of neighboring lattice sites which contribute to attractive energy.

βV_i^k is the external potential applied to component ***k*** at site ***i***.

$\beta\mu_i^k$ is the chemical potential for component ***k*** at site ***i***.

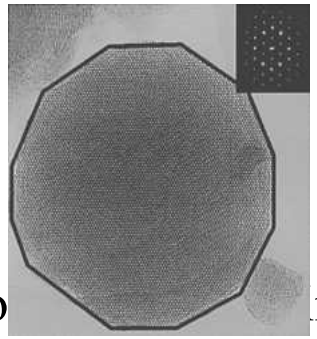
$d(i,m)$ is a function to determine interaction energy based on site ***i*** and neighbor ***m.***

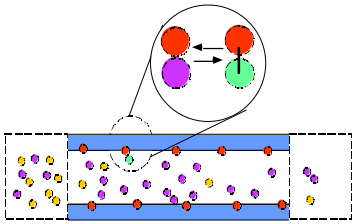
$I(i,m)$ is a function to give real lattice site of neighbor based on site ***i*** and neighbor ***m***.

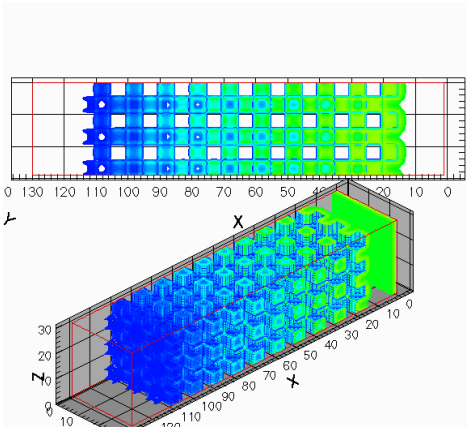
$\epsilon_{d(i,m)}^{kn}$ is the interaction energy between species ***k*** and ***n*** at a distance from ***d(i,m)***.

Focus: address multiple length scales

- Design Separation Membranes with facilitated transport

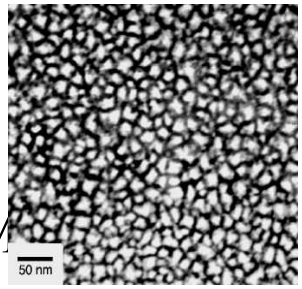


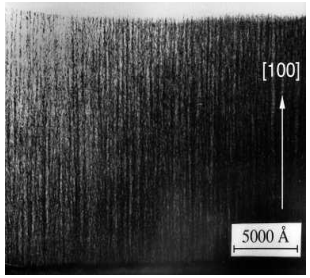


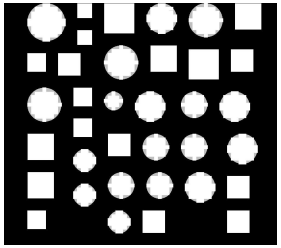


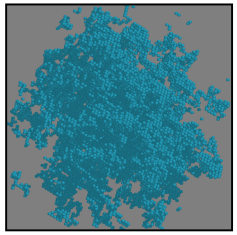
- Adso ng of in nanostructures

- M









Example:Non equilibrium Density Functional Theory(DFT) on a lattice