
A Novel Algorithm for Creating Coarse-Grained, Implicit Solvent Models for the Simulation of Surfactant Systems

DOE CSGF Conference

June 18, 2008

Erik Allen

Advisors: Prof. G.C. Rutledge and K.J. Beers

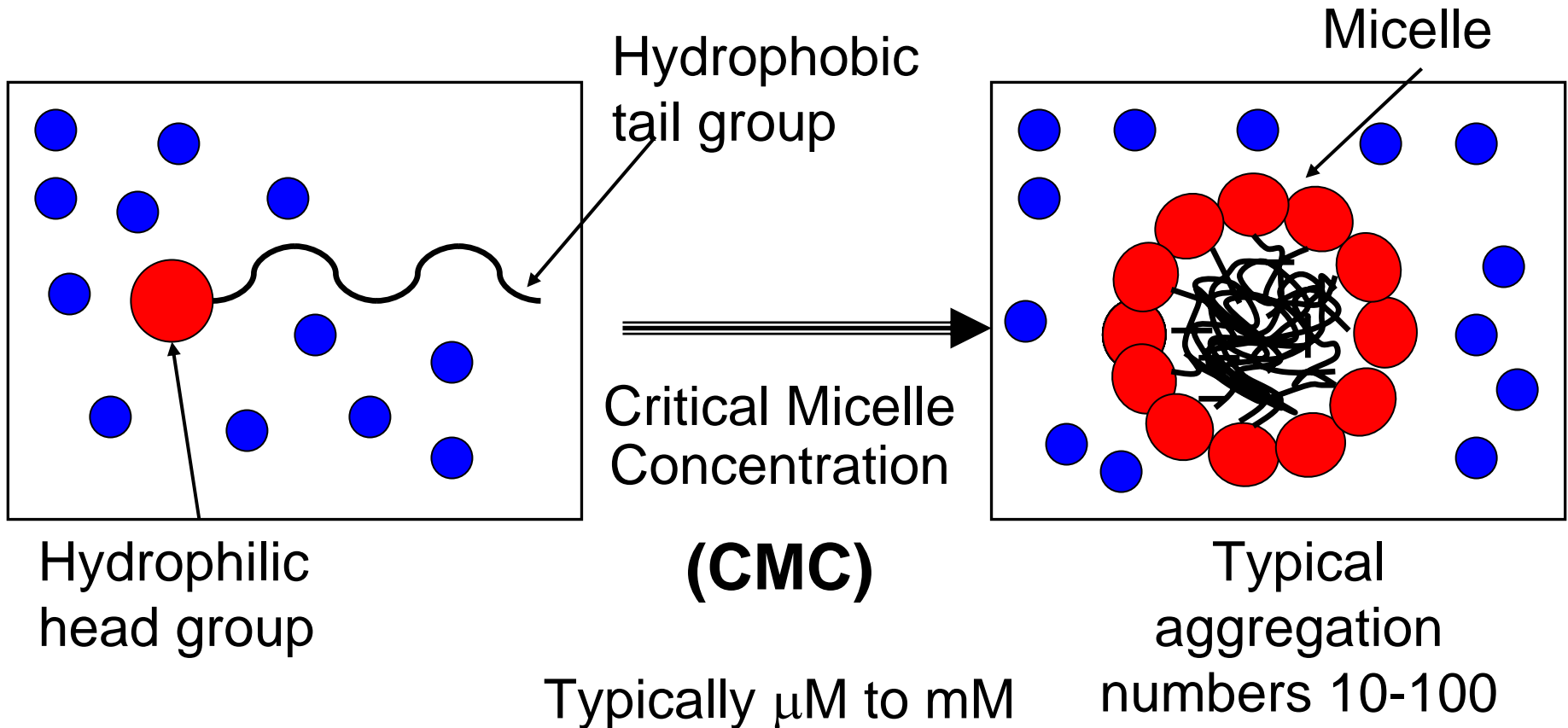


Outline

- The importance of surfactants
- Our Coarse-graining algorithm
- Coarse-graining applied to surfactant systems

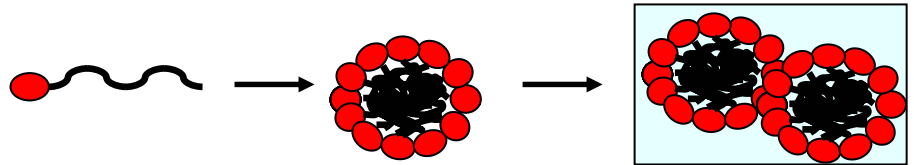


Surfactant Background



Why Surfactants?

- Properties Over Multiple Length Scales (hierarchical)



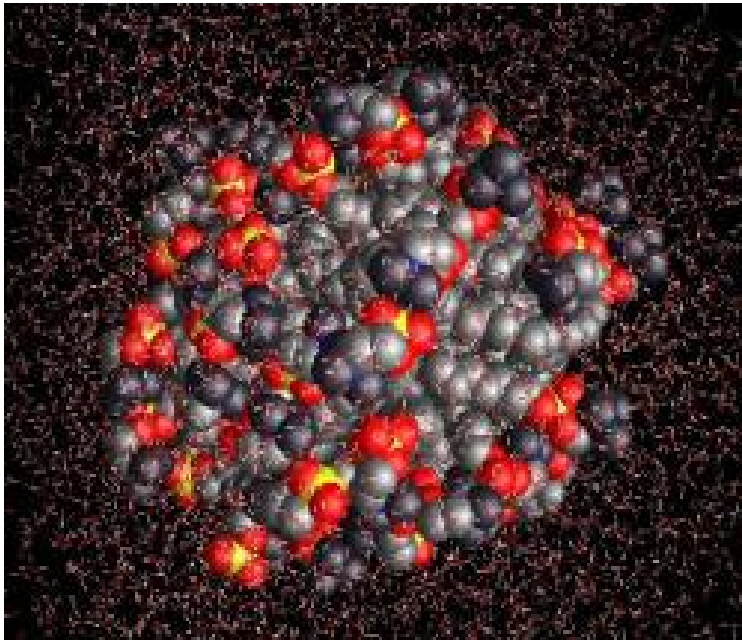
- Complex Behavior from simple molecules
- Similar physics to protein folding, other biological systems

QuickTime™ and a TIFF (Uncompressed) decompressor are needed to see this picture.

R. Pool and P.G. Bolhuis, J. Phys. Chem. B **109** (2005), 6650.



Surfactants in All-Atom Simulation

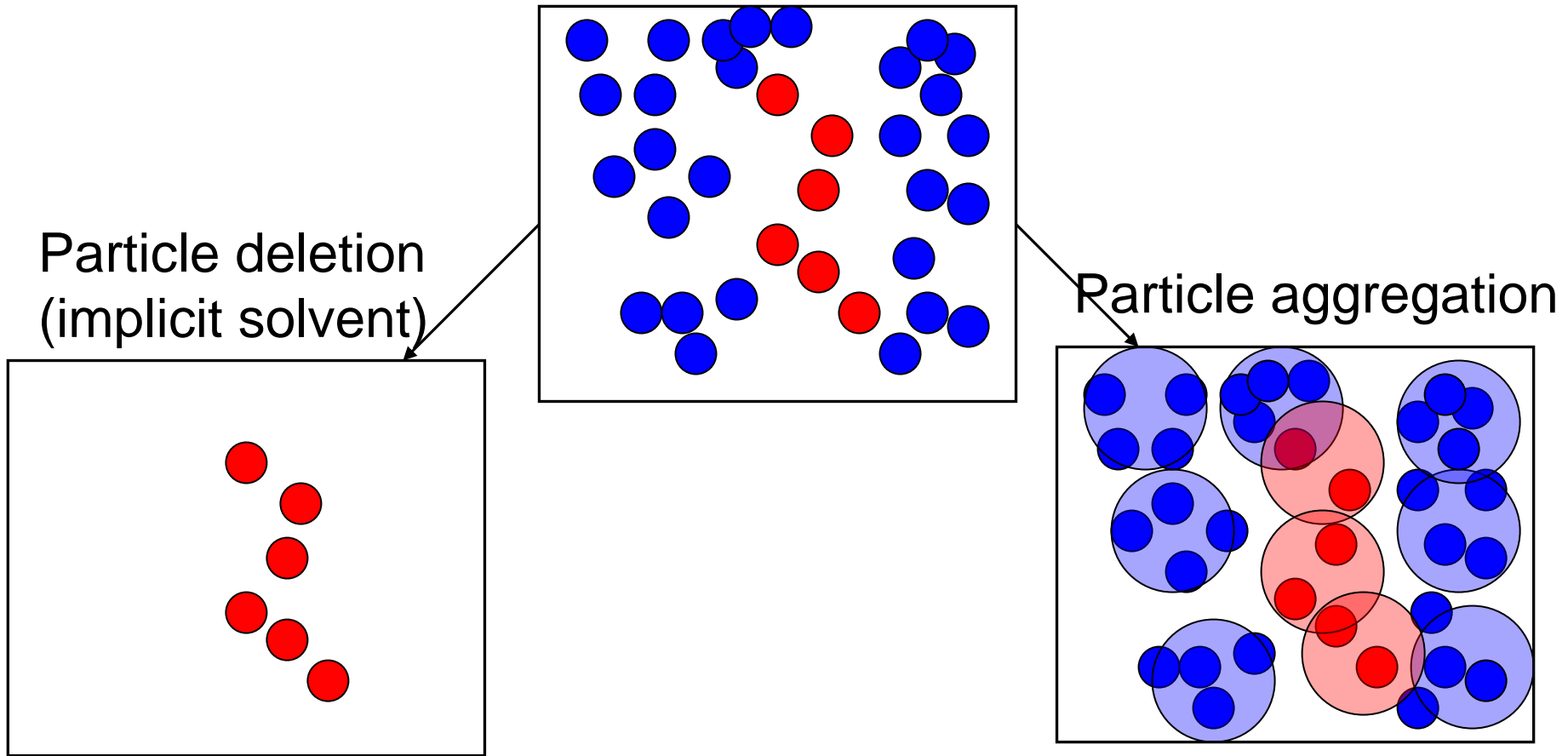


D. P. Tieleman, D. van der Spoel, H.J.C. Berendsen, J. Phys. Chem. B 104, 2000

- Simulation size limited to one micelle
- Simulation times limited to <100 ns
 - >1 μ s needed to study aggregation properties
- Solvent is the main culprit!!



def Coarse-graining: the systematic removal of degrees of freedom (i.e. particles) from an all-atom representation in order to speed computation, while “conserving” some property or properties of the underlying all-atom system.



Coarse-Graining Approach

1. **What** property or properties to conserve?
2. **What** form of potential will best conserve these properties?
3. **How** to fit the potential?
4. **What** are the limits of transferability of the potential?



Step 1: What Property or Properties to Conserve?

- Create an implicit solvent model that replicates both a free energy metric ($\mu^{ex}(\rho_S)$) and a local structure metric ($g(r, \rho_S)$)
 - Based on statistical thermodynamic model of micelle formation
 - Across the entire range of solute concentrations/densities, ρ_S
- Other implicit solvent approaches
 - μ^{ex} : Effective Energy Function (Lazaridis and Karplus, *Proteins* 35)
 - $g(r, \rho_S)$: Radial distribution function inversion (Lyubartsev, *Phys. Rev. E* 52)
- Only fit potentials to monomeric solute data



Step 2: What Form of Potential?

Self Interaction
Energy

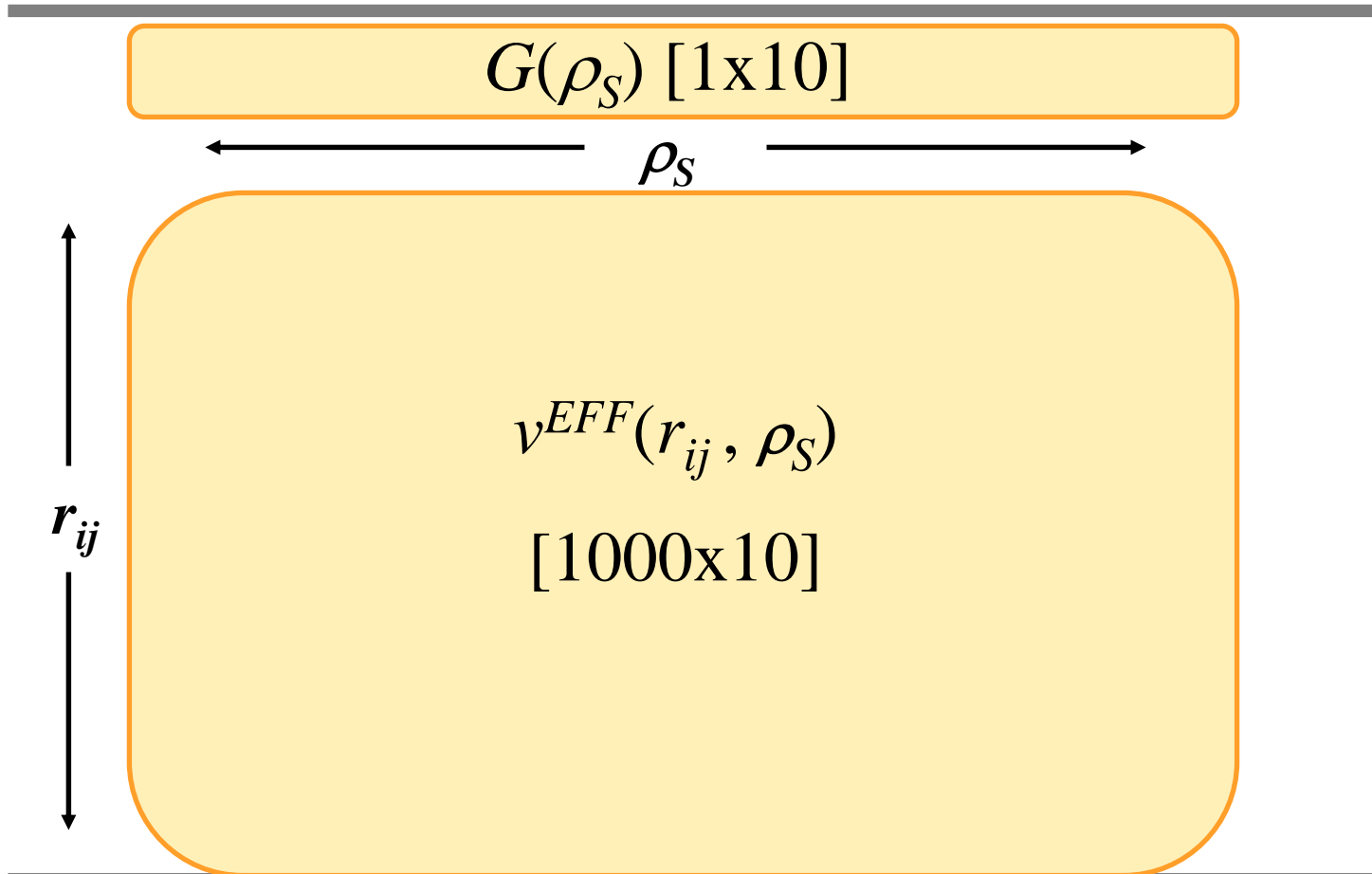
$$E_i(r_i, \rho_S) = G_i(\rho_S) + \frac{1}{2} \sum_j v^{EFF}(r_{ij}, \rho_S)$$

Energy Per Particle

Pairwise Potential

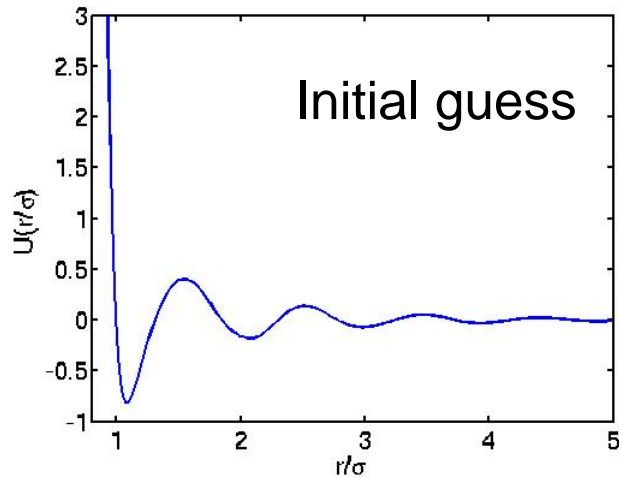


Simulation input

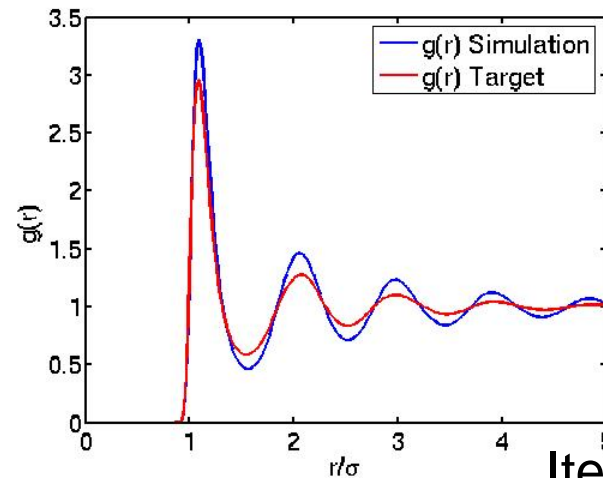


$v^{EFF}(r)$ Solution Procedure

Schommers, *Phys. Rev. A* **28**,3559 (1983)

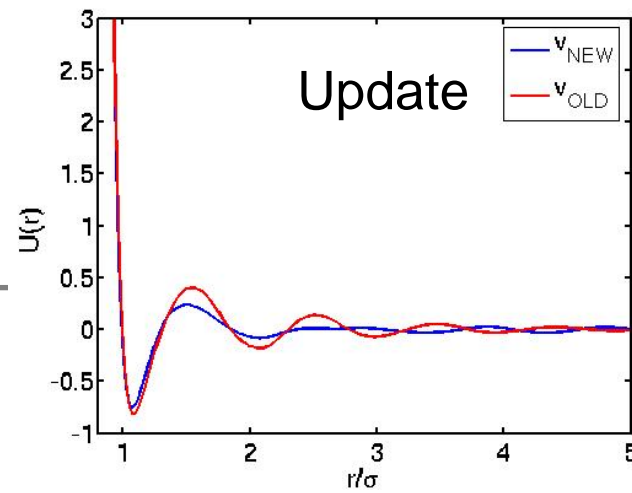


MD sim



Iterate to convergence

$$v^{EFF}(r) = v^{OLD}(r) - kT \log \left(\frac{g(r)_{TARGET}}{g(r)_{SIMULATION}} \right)$$



Massachusetts Institute of Technology

Adding the density dependence

- Stitch together $v^{EFF}(r)$ across a range of densities to form $v^{EFF}(r, \rho_S)$
- Make an initial guess for $G(\rho_S)$ based on a physically motivated equation:

$$G(\rho_S) + \rho_S \frac{\partial G(\rho_S)}{\partial \rho_S} = \mu^{ex}(\rho_S)_{TARGET} - \mu^{ex}(\rho_S)_{MEASURED}$$

- Iterate based on this equation above until:

$$\left| \mu^{ex}(\rho_S)_{TARGET} - \mu^{ex}(\rho_S)_{MEASURED} \right| \leq \varepsilon$$



Local Density Test System

Solute A in Solvent Z

System Specs:

$$\varepsilon_A=1, \sigma_A=1$$

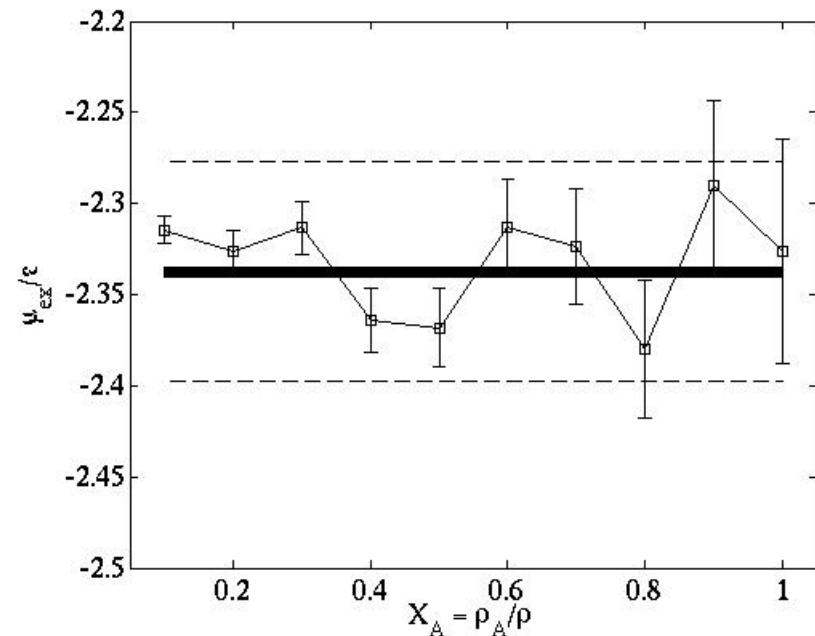
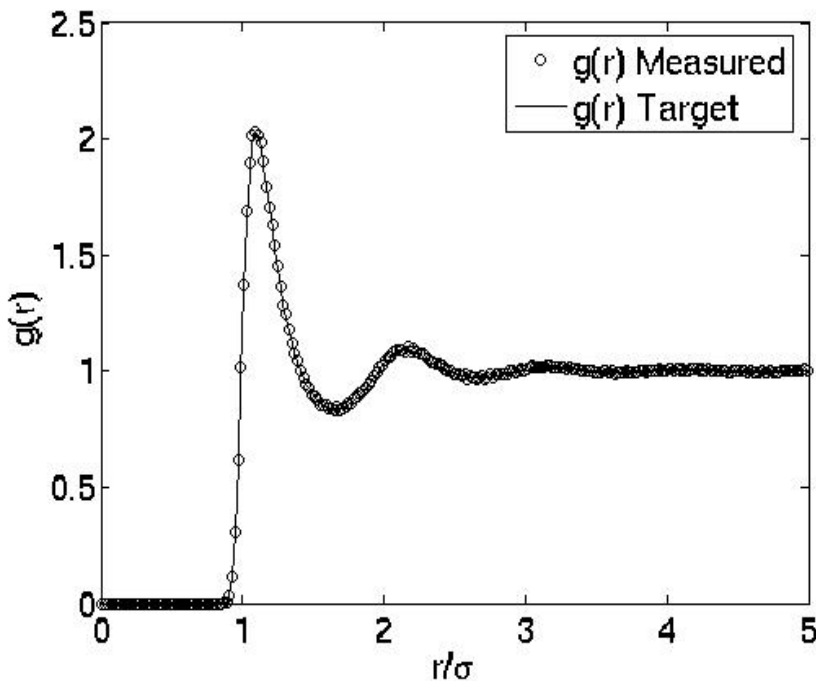
$$\varepsilon_Z=1, \sigma_Z=1$$

$$T^* = 1.35$$

$$\rho^* = 0.55$$

Left: Worst-fit RDF

Right: Excess Chemical Potential



E.C. Allen and G.C. Rutledge, J. Chem. Phys **128** (2008), 154115.



More Fitting Results

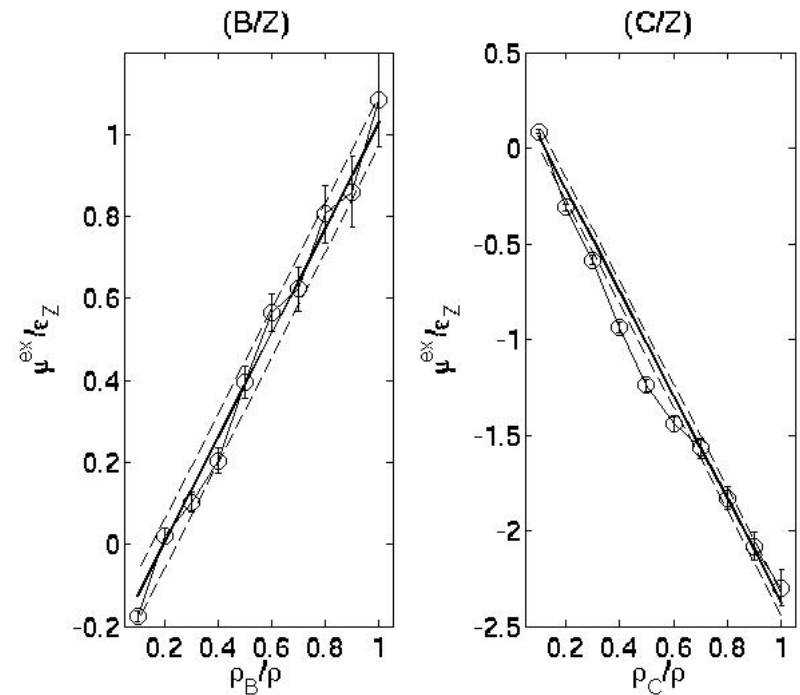
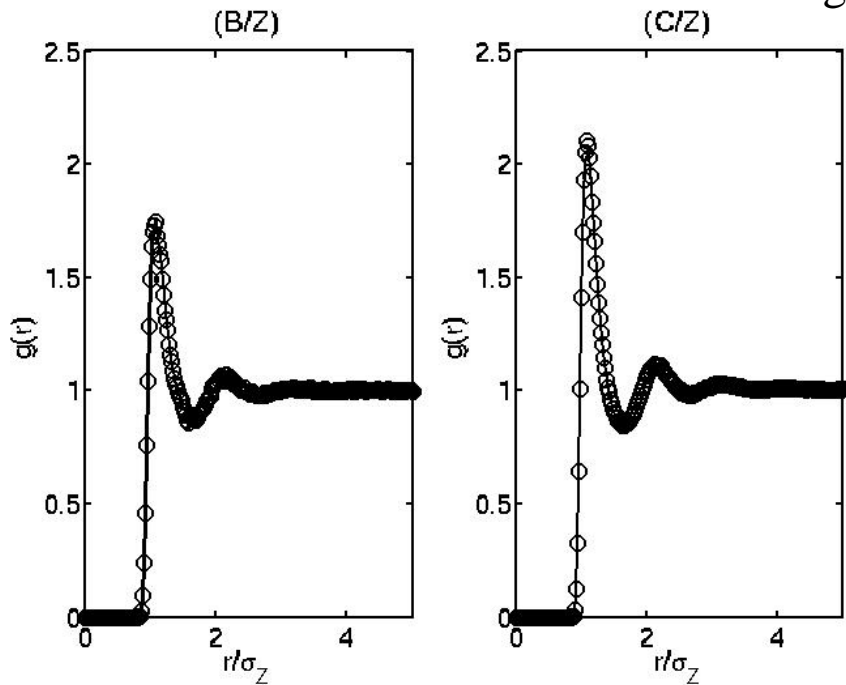
B = Solvent-philic

C = Solvent-phobic

Z = Solvent

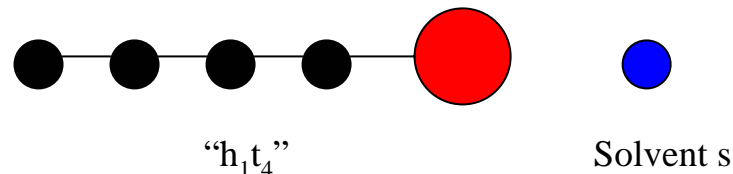
Left: Worst-fit RDF

Right: Excess Chemical Potential



Surfactant System of Interest

- “Smit”¹ surfactant model



- $\epsilon_t = \epsilon_h = \epsilon_s = 1.0$

- $\sigma_t = \sigma_s = 1.0, \sigma_h = 2.0$

- Particles interact via truncated and shifted Lennard-Jones potential

$$V_{ij}^{TS}(r_{ij}; \epsilon_{ij}, \sigma_{ij}, R_{c,ij}) = \begin{cases} V_{ij}^{LJ}(r_{ij}; \epsilon_{ij}, \sigma_{ij}) - V_{ij}^{LJ}(R_{c,ij}; \epsilon_{ij}, \sigma_{ij}) & r_{ij} \leq R_{c,ij} \\ 0 & r_{ij} > R_{c,ij} \end{cases}$$

- Pool and Bolhuis²

– h₁t₄: $\rho^{\text{CMC}} \sim 10^{-6} - 10^{-5}$

– h₁t₅: $\rho^{\text{CMC}} 10^{-7} - 10^{-6}$

R_c/σ_{ij}	s	h	t
s	2.5	2.5	$2^{1/6}$
h	2.5	$2^{1/6}$	$2^{1/6}$
t	$2^{1/6}$	$2^{1/6}$	2.5

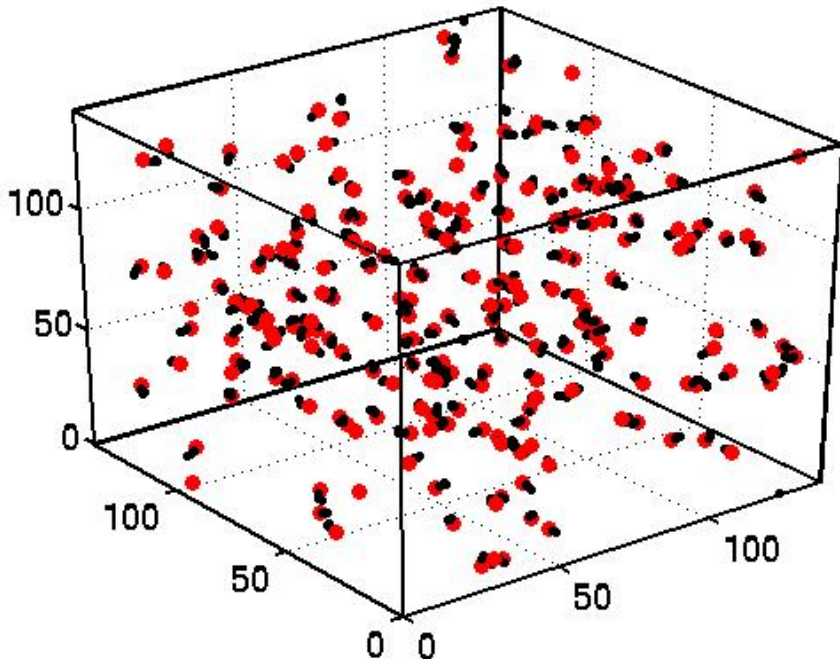


1. B. Smit, Phys. Rev. A. **37** (1988), 343.
 2. R. Pool and P.G. Bolhuis, J. Phys. Chem. B **109** (2005), 6650.

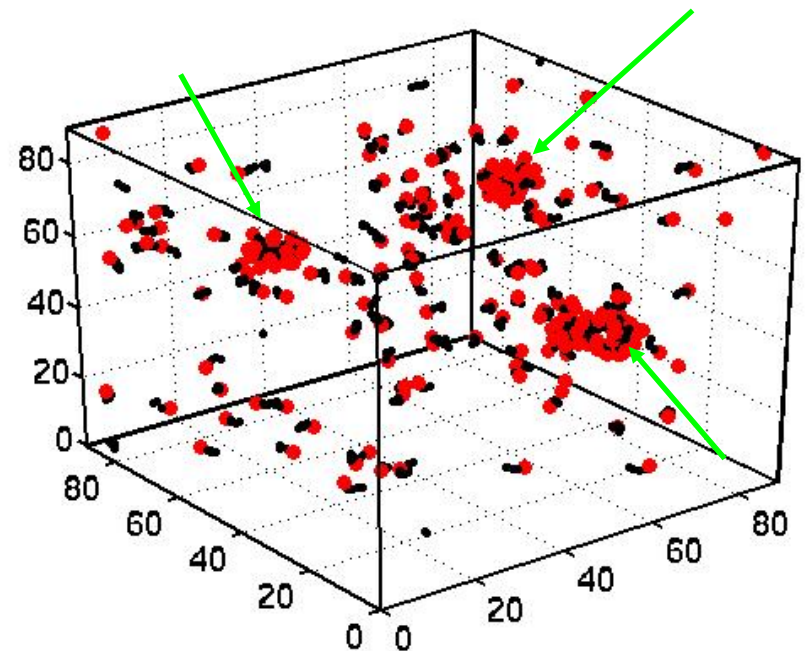
Simulation Screenshots

216 h_1t_4 molecules in implicit solvent

Below CMC



Above CMC



Coarse-grained Accuracy

<i>Simulation</i>	<i>H₁T₄ CMC</i>	<i>H₁T₅ CMC</i>	<i>CMC Ratio</i>
All-Atom	10 ⁻⁶ -10 ⁻⁵	10 ⁻⁷ -10 ⁻⁶	10
Implicit Solvent	2×10 ⁻⁴	2×10 ⁻⁵	10



Computation Performance

<i>Simulation</i>	<i># Atoms</i>	<i>H₁T₅ CMC</i>
All-Atom (est)	2.5×10^8	4.6×10^7
Implicit Solvent	1080	2



Summary and Future Work

- Developed a method to create coarse-grained, density-dependent, implicit solvent potentials that reproduce both $\mu_{ex}(\rho_S)$ and $g(r, \rho_S)$
- Potentials can be used to simulate surfactant systems
- Future work could investigate more effective fitting simulations



Thank You

- Advisor: Professor G.C. Rutledge
- Practicum Advisor: Paul Crozier, Sandia National Labs
- Krell Institute
- Department of Energy Computational Science Graduate Fellowship
- All of you!

