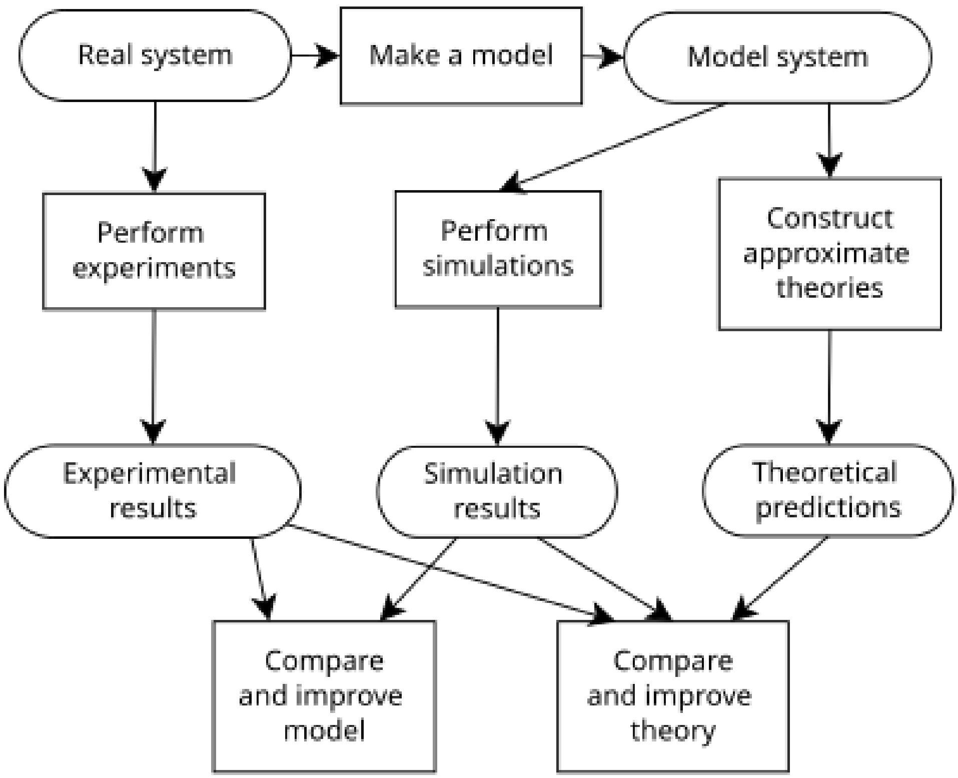
11th i-CoMSE Workshop: Mesoscale Particle-Based Modeling

Mississippi State University
July 21–25, 2025

Session 2: Top-down coarse graining

Top-down coarse graining

- **Objective:** use macroscopic/mesoscale information to parameterize a simplistic model or build simplistic model to match theory



Top-down coarse graining

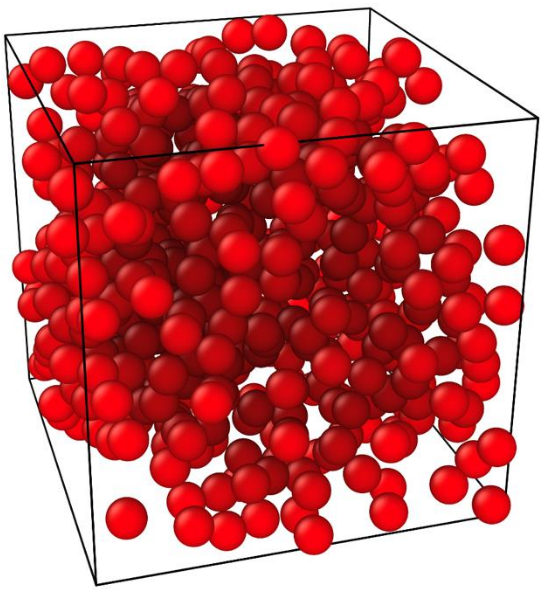
- **Objective:** use macroscopic/mesoscale information to parameterize a simplistic model or build simplistic model to match theory

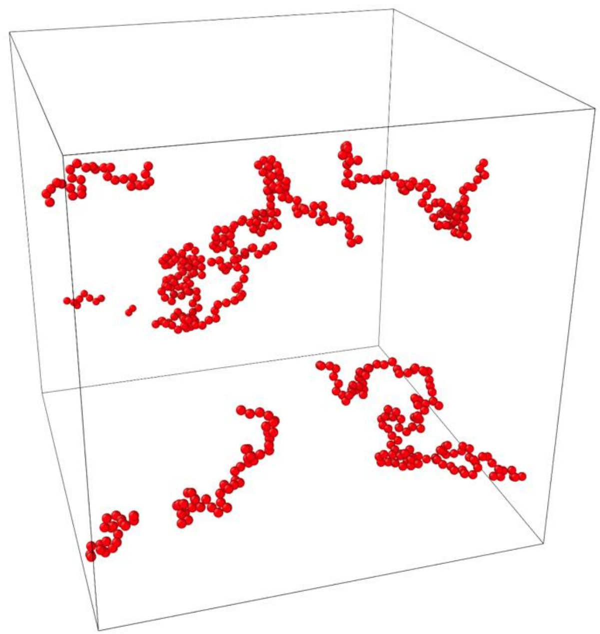
- Macroscopic/mesoscale information:
  - Experimental measurements
  - Thermodynamic quantities (densities, concentrations, liquid–liquid partitioning,.., critical temperatures, interfacial tensions, radius of gyration, system free energies, ..)

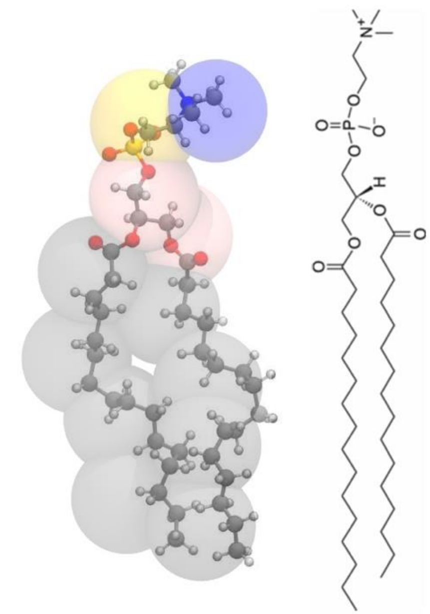
- Use coarse-grained “beads” to express the general character of molecular structure, de-emphasizing specific chemical features
- Remove solvent

Top-down coarse graining

- Examples of top-down models:
  - Martini force field for lipids and biomolecules (non-bonded interactions based on experimental partitioning free energies, four-to-one mapping)
  - Kremer-Grest and Bead-Spring models for polymers
  - LJ for fluids, …

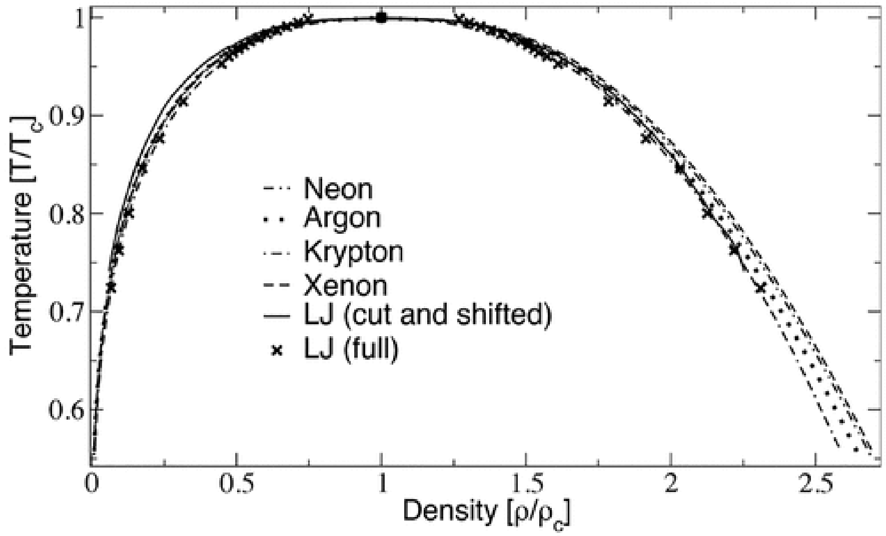






Toy Models: Generic Top-down models

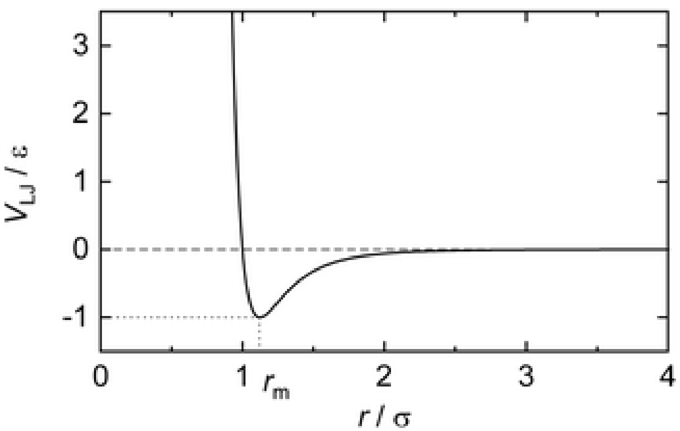
- Phenomenological with relatively low resolution with few/no chemical detail
- Do not describe any particular system
- Used for investigation of generic consequences of basic physical principles (systematic variation of parameters)
- Simple potentials with relatively few parameters

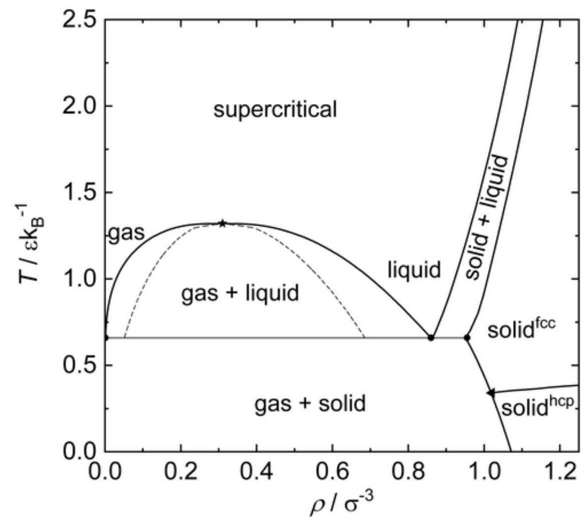


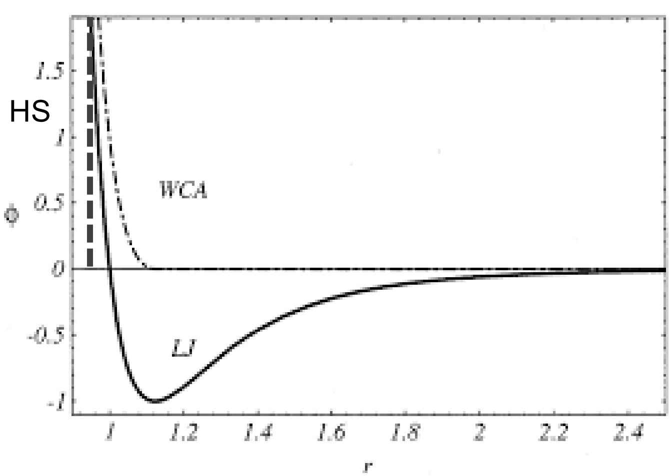
100 Years of the Lennard-Jones Potential
Peter Schwerdtfeger and David J. Wales
Journal of Chemical Theory and Computation 2024 20 (9), 3379-3405
DOI: 10.1021/acs.jctc.4c00135

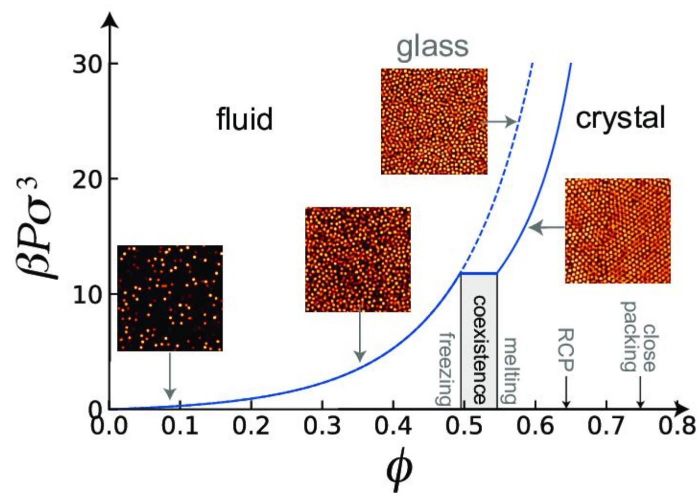
Toy Models: Generic Top-down models

Simple Fluids (Lennard Jones, Hard Spheres/WCA,…)



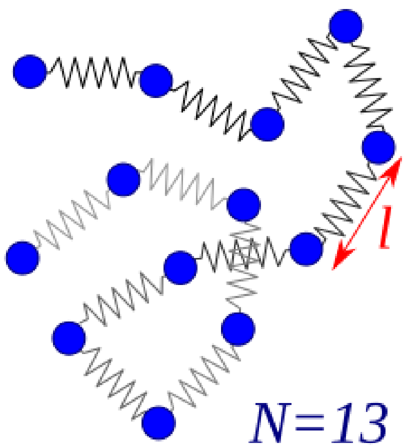




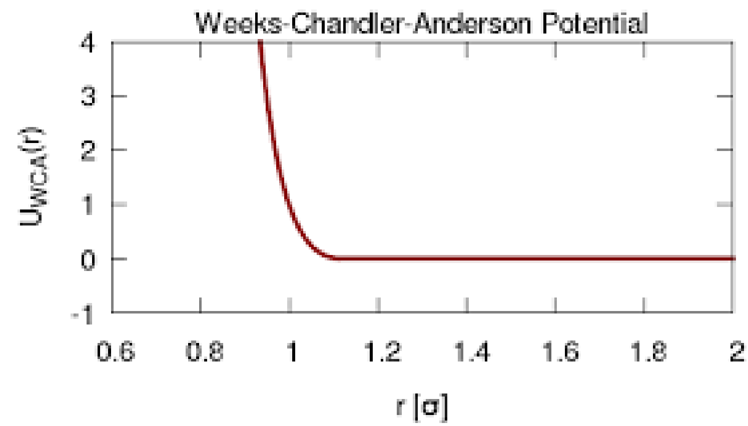


Toy Models: Generic Top-down models

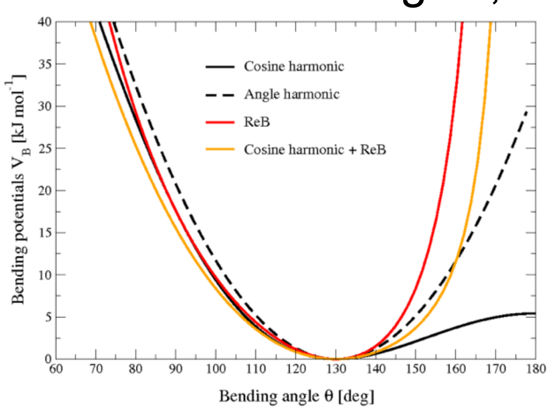
Bead-Spring models (Kremer-Grest,…)



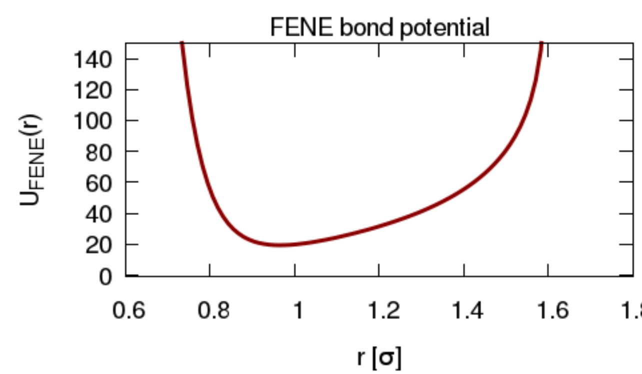
Non-bonded pair interactions:



Sometimes also: angles, dihedrals



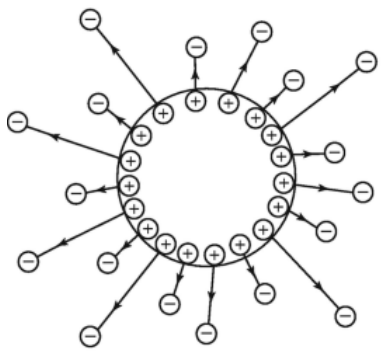
Bonded interactions:

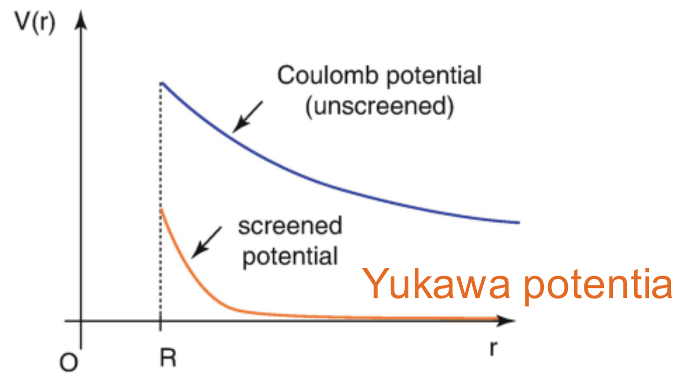


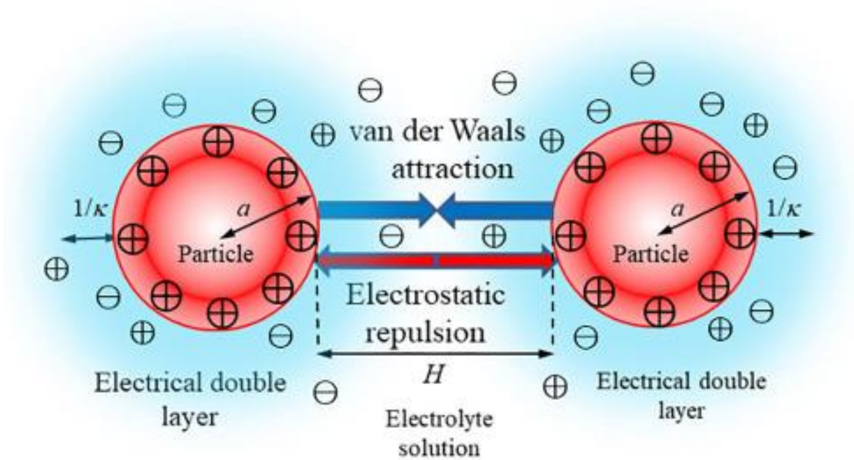
$$E = -0.5KR_0^2 \ln\left[1-\left(\frac{r}{R_0}\right)^2\right] + 4\epsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^6\right] + \epsilon$$

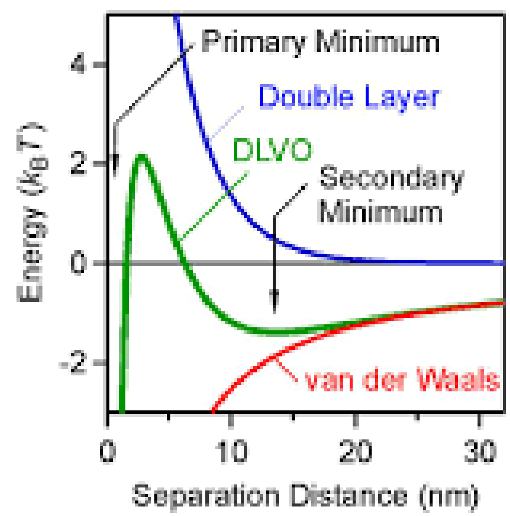
Other Interactions

Screened electrostatics, Van der Waals, DLVO theory





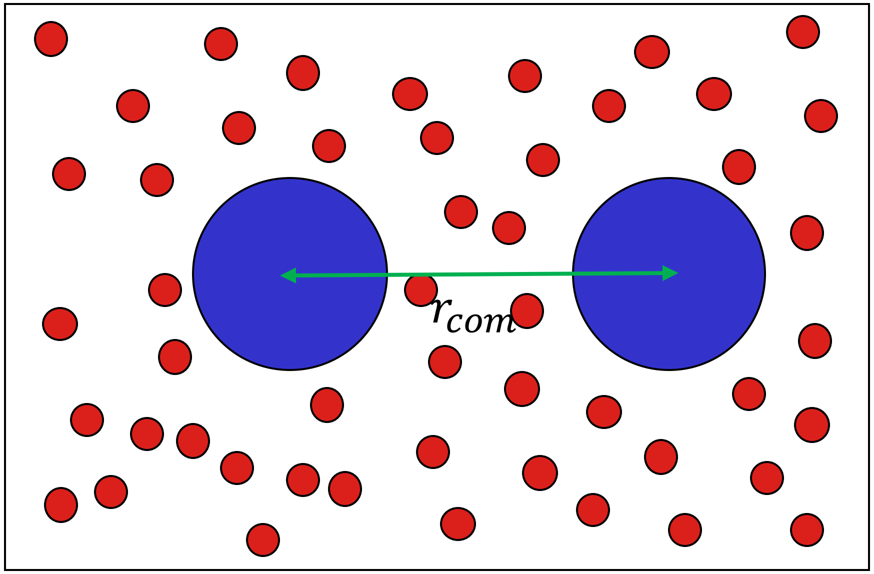




Example: NP in Solvent

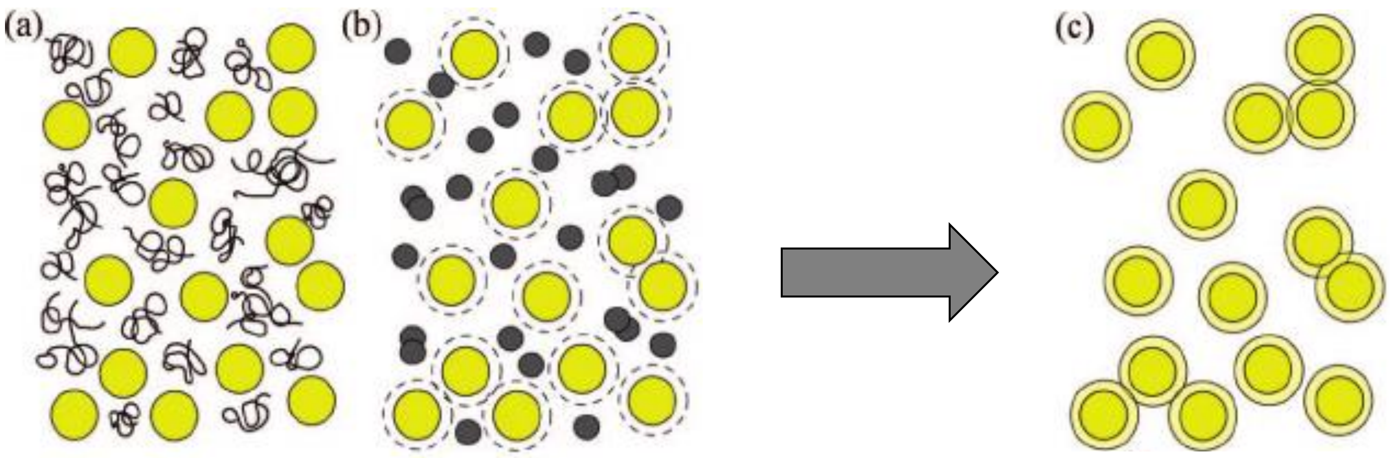
- CG nanoparticles (NP) or colloids in a bath of N solvent (or depletant) particles

- Typical experimental system: each 10 nm diameter nanoparticle is surrounded by > 10^6 solvent molecules under dilute conditions (0.1 volume fraction)



Solvent coarse graining

Asakura–Oosawa theory

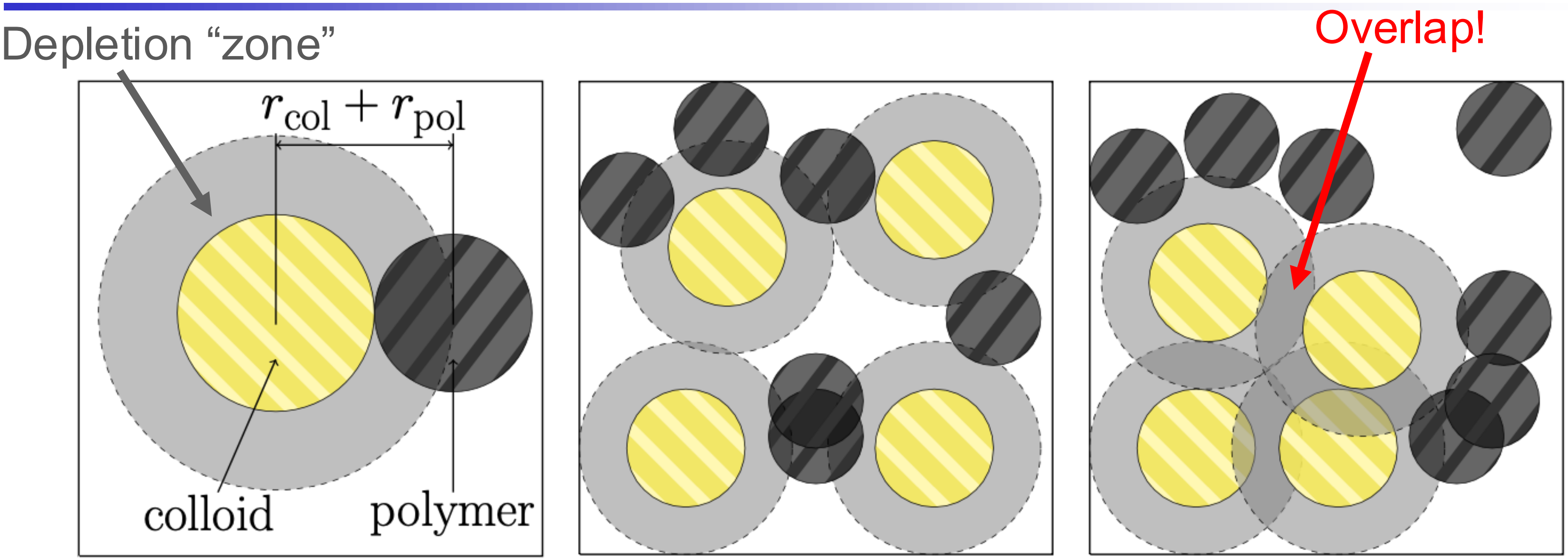


Explicit solvent (small other particles, polymers,…)

Implicit solvent with modified interactions

Kurt Binder, Peter Virnau, Antonia Statt; Perspective: The Asakura Oosawa model: A colloid prototype for bulk and interfacial phase behavior. J. Chem. Phys. 14 2014; 141 (14): 140901. DOI: 10.1063/1.4896943

Asakura-Oosawa Theory



Dispersed colloids

Aggregated colloids

Small depletants (solvent, polymers,..) can cause effective attraction between NP/Colloids due to free volume and entropy arguments.

Asakura, Sho; Oosawa, F. (1 January 1954). "On Interaction between Two Bodies Immersed in a Solution of Macromolecules". The Journal of Chemical Physics. 22 (7): 1255. doi:10.1063/1.1740347.

Asakura, Sho; Oosawa, F. (1958). "Interaction between Particles Suspended in Solutions of Macromolecules". Journal of Polymer Science. 33 (126): 183–192. doi:10.1002/pol.1958.1203312618.

Asakura–Oosawa Theory

Assumptions:

- low concentrations of macromolecules
- homogeneous, uniform density
- Pairwise interactions

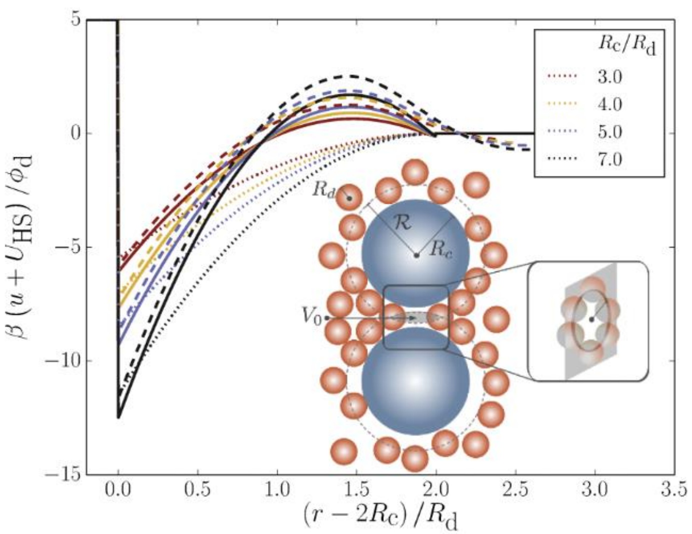
Force between two particles:

$$\mathrm{F} = \Pi \Delta S_{exclusion}$$ → Integrate → Potential Energy U

osmotic pressure

area of the circular cross section of the over-lapping region

Solution is exact when the depletants are small (size ratio $q = \sigma_p/\sigma_c < \ 0.1547$)



$$\beta\phi_{\mathrm{AO}}(r) = \begin{cases} \infty & (r < \sigma_{\mathrm{c}}) \\ -\frac{\pi}{6}\sigma_{\mathrm{p}}^3\rho_{\mathrm{p}}\left(1+\frac{1}{q}\right)^3\left(1-\frac{3r}{2\sigma_{\mathrm{c}}(1+q)}+\frac{r^3}{2\sigma_{\mathrm{c}}^3(1+q)^3}\right) & (\sigma_{\mathrm{c}} \leqslant r \leqslant \sigma_{\mathrm{c}}+\sigma_{\mathrm{p}}) \, . \\ 0 & (\text{otherwise}) \end{cases}$$

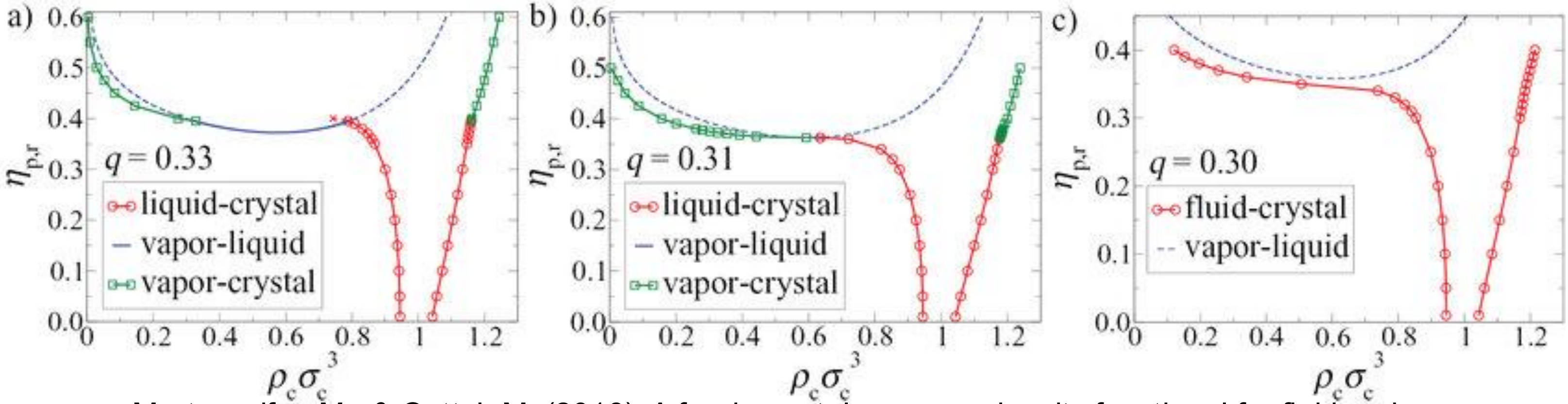
σ_c = colloid size , σ_p = polymer/depletant size

polymer fugacity z_P = " ρ_p, number density ideal polymers"

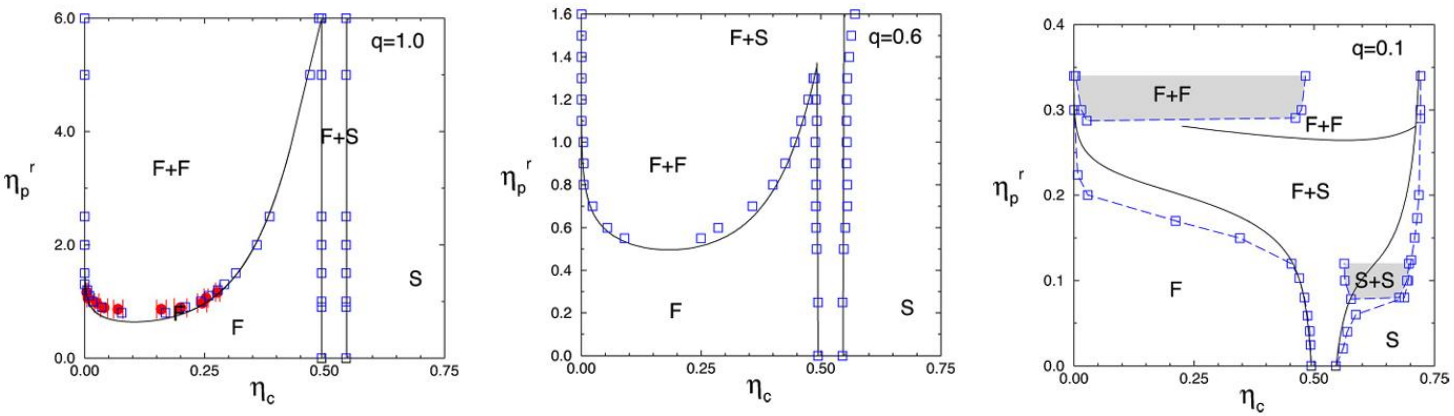
Polymer reservoir packing fraction $\eta_p^r = \dfrac{\pi\sigma_p^3 z_p}{6}$

Asakura–Oosawa Theory

Free Volume Theory, measure density functionals, simulations:



Mortazavifar, M., & Oettel, M. (2016). A fundamental measure density functional for fluid and crystal phases of the Asakura–Oosawa model. Journal of Physics: Condensed Matter, 28(24), 244018.

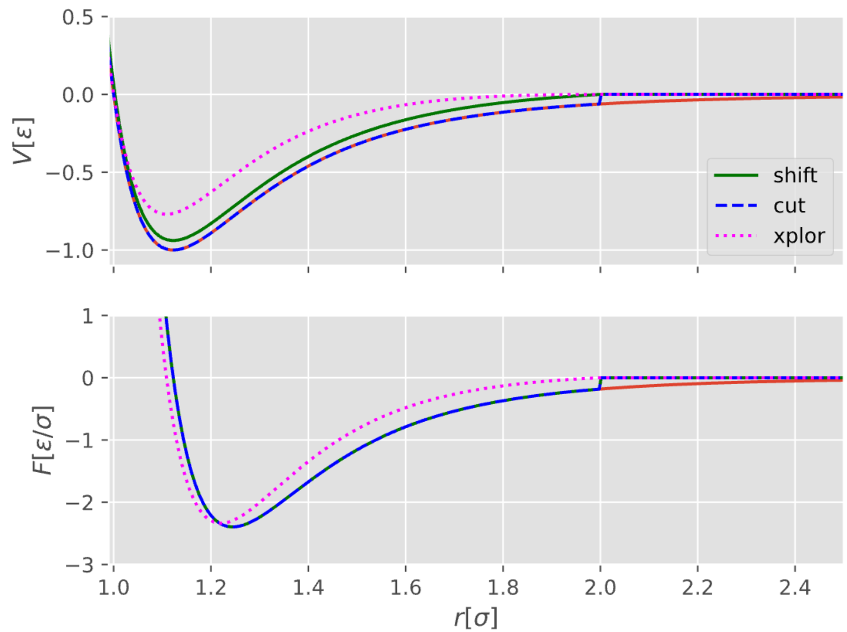


Dijkstra, M., van Roij, R., Roth, R., & Fortini, A. (2006). Effect of many-body interactions on the bulk and interfacial phase behavior of a model colloid-polymer mixture. Physical Review E—Statistical, Nonlinear, and Soft Matter Physics, 73(4), 041404.

Exercise

Objective:

- Plot potentials and forces
- Set up simple HOOMD simulation with two particles
- Run simple AO model simulation



Questions / Common Pitfalls

- How **transferable** and how **representative** is a model?
- Ignoring reduced units
- How many “ad hoc” or other empirical fixes does a model need to describe a particular system?
- Matching experiments is difficult!
- Not comparing with existing models, theory, scaling predictions
- What are the **limitations** of the model?