Gary Leal

Chemical Engineering at UCSB (also Materials and ME)

My group does theoretical and experimental work on fluid mechanics, and the dynamics of complex fluids (polymeric liquids, suspensions, colloids, emulsions/blends, surfactant systems etc.)

Our approach is typically from the continuum point of view, but various problems of interest have motivated us in the past few years to begin to try to engage multiscale and/or hybrid methods

TODAY

1) An idea of the type of problems that started us thinking about multiscale methods

2) A summary of our work on one aspect – namely coarse graining methods applied to MD (Chia-Chun Fu)

We work on a number of problems that might benefit from multiscale or hybrid computational analysis

•Polymer rheology: Rheological models for branching effects in non-linear flow conditions. Coupling between flow and concentration fields in polymer solutions.

We have already heard about "coarse graining" efforts to achieve mesoscopic and continuum descriptions of polymeric liquids, but our work has been strictly at the level of kinetic theory (e.g. reptation theory) and continuum models derived from these theories.

•Vesicle dynamics; adhesion; line tension effects in hole dynamics; stability and roll-up of bilayer sheets; via Continuum models that treat the bilayer as a somewhat complicated elastic membrane

Many of the parameters in these models can be measured experimentally and some can be explored directly via mesoscale models, but there is an obvious role for direct molecular predictions too (and there is, of course, work in this direction via many people including Frank Brown here at UCSB)

Our FOCUS for Multiscale Methods :
problems that (likely) require molecular resolution in some localized part of a macroscopic flow domain where we can otherwise use continuum mechanics.

Two **motivating** problems:

- Drop Coalescence; rupture process for thin films

- Nanobubble stability (focused on transport contributions, i.e. the continuum-based transport model of Detlef Lohse and Michael Brenner)

Next; a few words about these problems

Coalescence involves the rupture of the thin film between a pair of colliding drops: preceded by a complex process of film drainage and evolution of shape until a configuration is reached where van der Waals attraction across the film leads to rapid rupture and coalescence.

There is no hydrodynamic instability and in the case of fluids with relatively weak van der Waals effects (e.g. polymeric fluids) continuum based calculations indicate that the film can thin locally to a few nanometers before it finally ruptures.

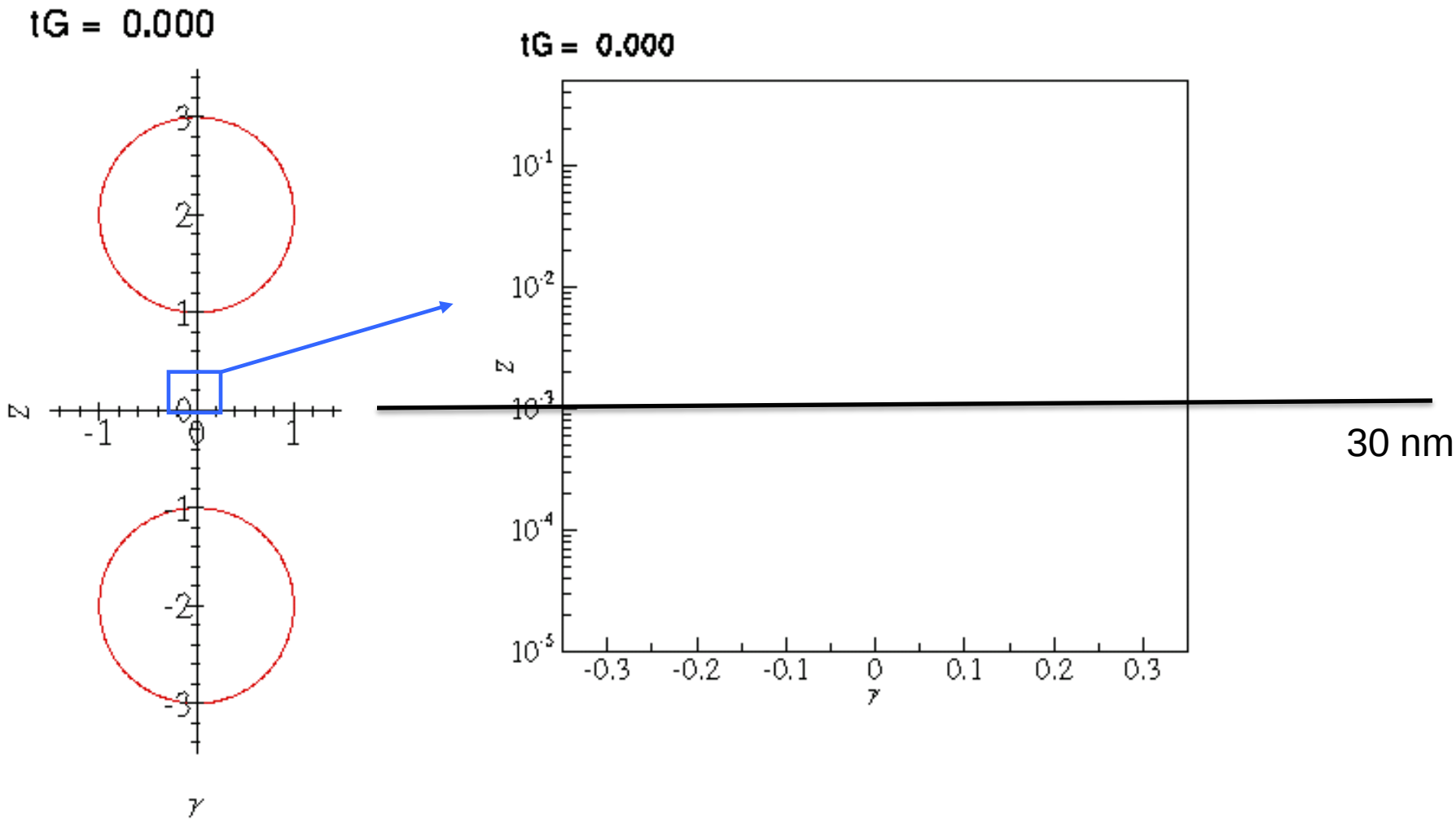
Not surprisingly, there is a problem when the continuum based description of this phenomena is compared with experiments

Incompressible Newtonian fluids; van der Waals forces included via a disjoining pressure approximation; multiscale via boundary integral methods with systematic local grid resolution

Ref: Yoon, Baldessari, Ceniceros & Leal, *Physics of Fluids*,**19** (2007)

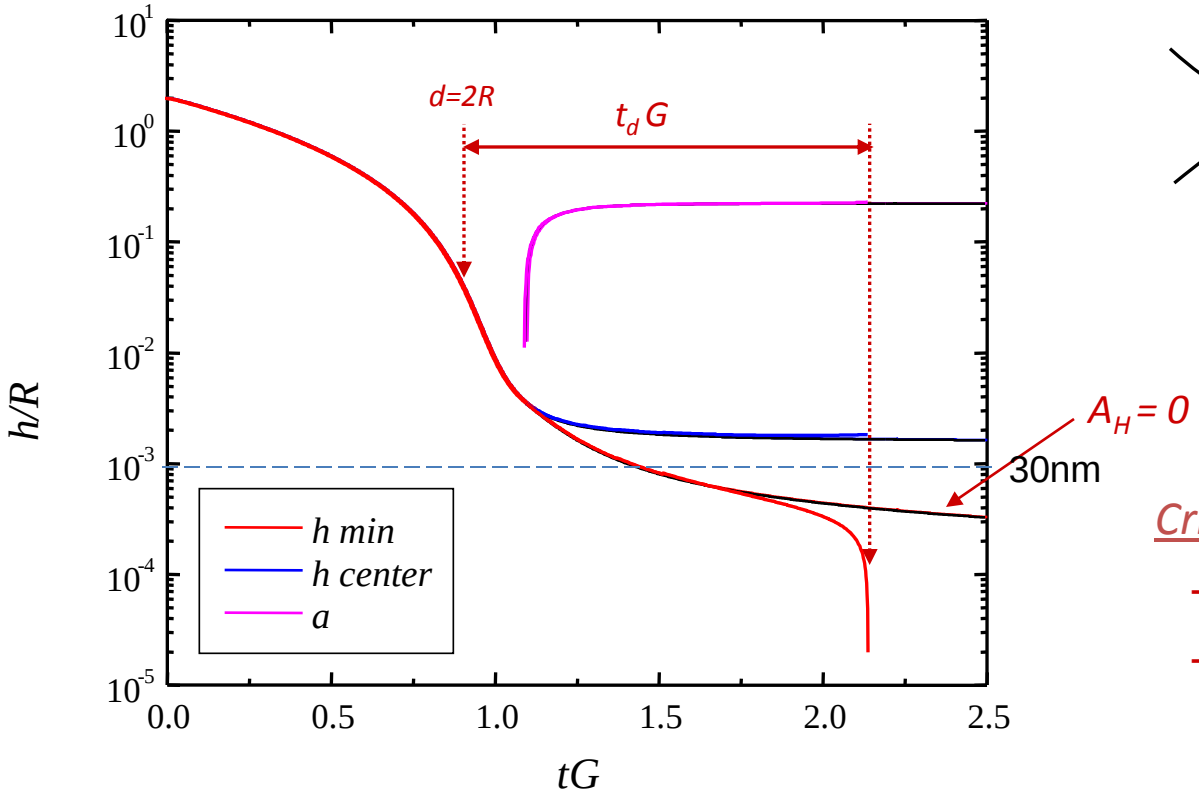
Predicted evolution of the thin film shape (head-on)

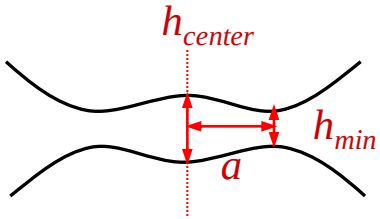
- λ=0.19, Ca=0.015, R=27μm, A_H=3.2$\times$10^{-21}J
(PBd drops in PDMS)



Film thickness vs. time : *Ca = 0.015*

λ=0.19, Ca=0.015, R=27μm, A_H=3.2$\times$10^{-21}J





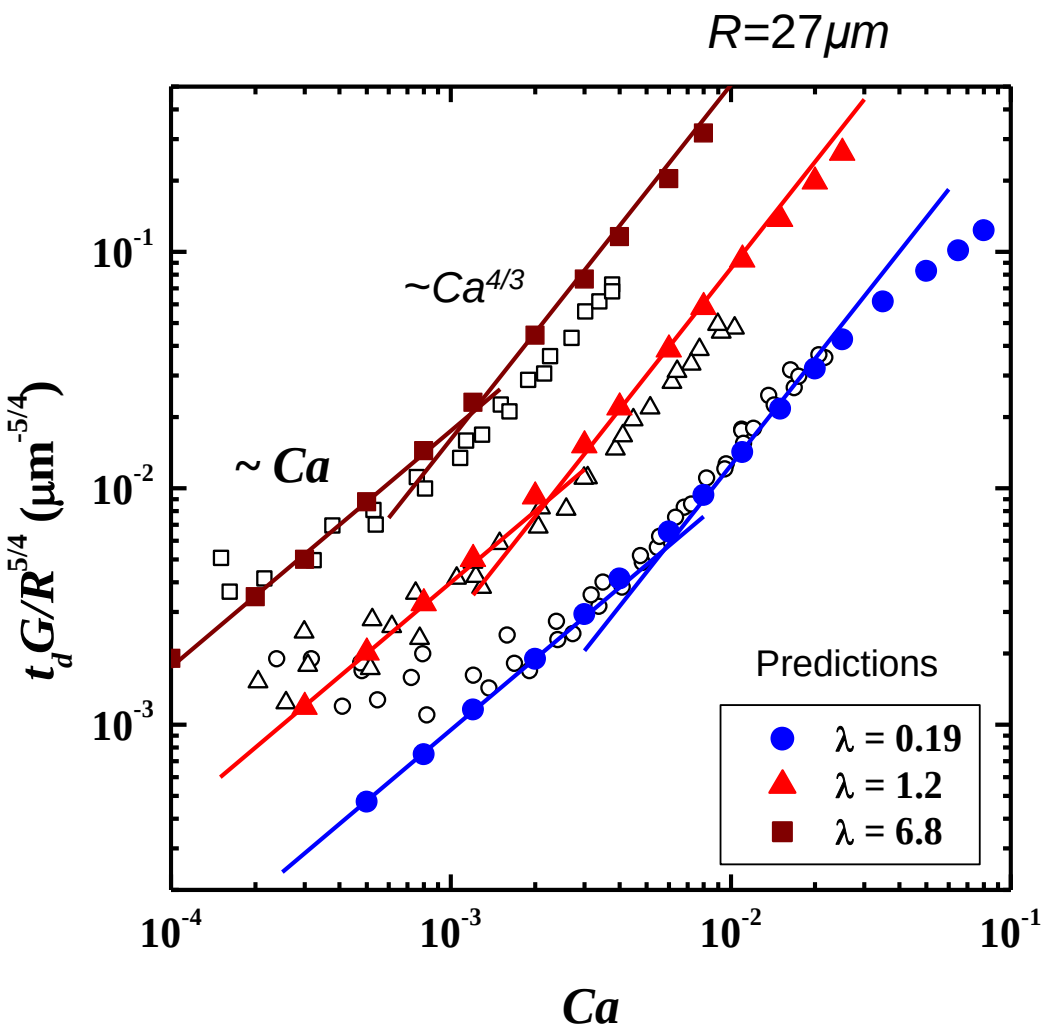
Critical film thickness

- $h_c/R \approx 0.00034$
- $h_c \approx 10$ nm

Can the continuum treatment be extended this far?

Drainage time for head-on collision

Data for PBd drops in PDMS (but identical for inverted system)



Scaling with capillary number

-Experiment and theory (both numeric and scaling)

$$t_d G \sim Ca^{4/3}$$

Scaling with viscosity ratio

- Experiment

$$t_d G_{exp} \sim \lambda^{0.8}$$

- Simulation & scaling theory

$$t_d G_{sim} \sim \lambda^{1}$$

(mainly implicated in film thinning process while film is still macroscopic)

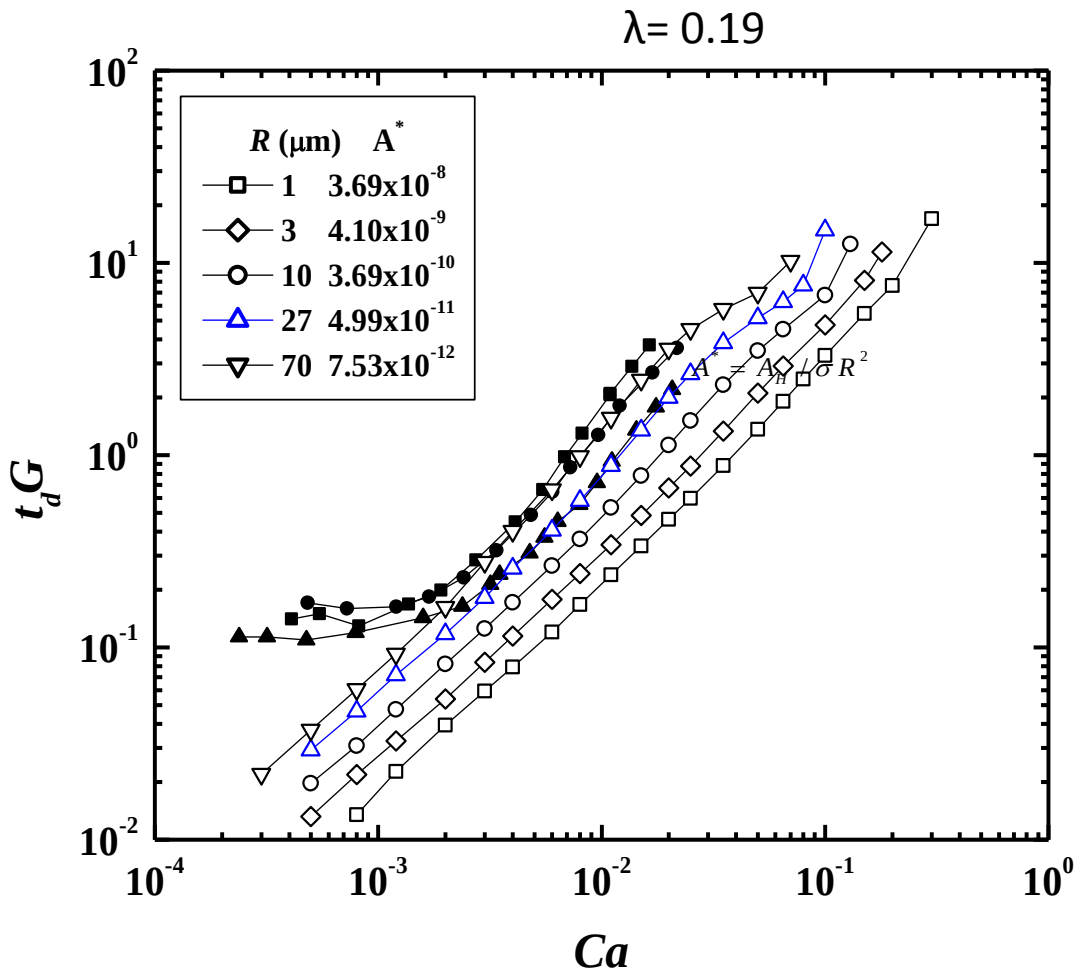


Figure 15. The experimental data are represented by:
solid triangles for R= 27.2 μm,
solid circles for R= 40.1 μm,
solid squares for R= 45.4 μm.

Scaling with drop size

(i.e. with $A^* = A_H / \sigma R^2$)

theory

$t_d G \sim R^{2/3}$

experiment

$t_d G \sim R^{5/4}$

(Mainly controls final stages of film thinning and rupture when film is very thin)

Maybe multiscale simulations could help?

Nanobubbles

Nanobubbles form spontaneously on hydrophobic surfaces in the presence of water (or water based fluids) containing an adsorbed gas (could be air). Expectation is that they should have a lifetime of a few microseconds, but they are observed to last for days.

The Lohse-Brenner picture of nanobubble stability is that it is established as a quasi-steady state with an active transport of gas into the surrounding fluid, and back via a recirculation mechanism into the bubble in the vicinity of the contact line.

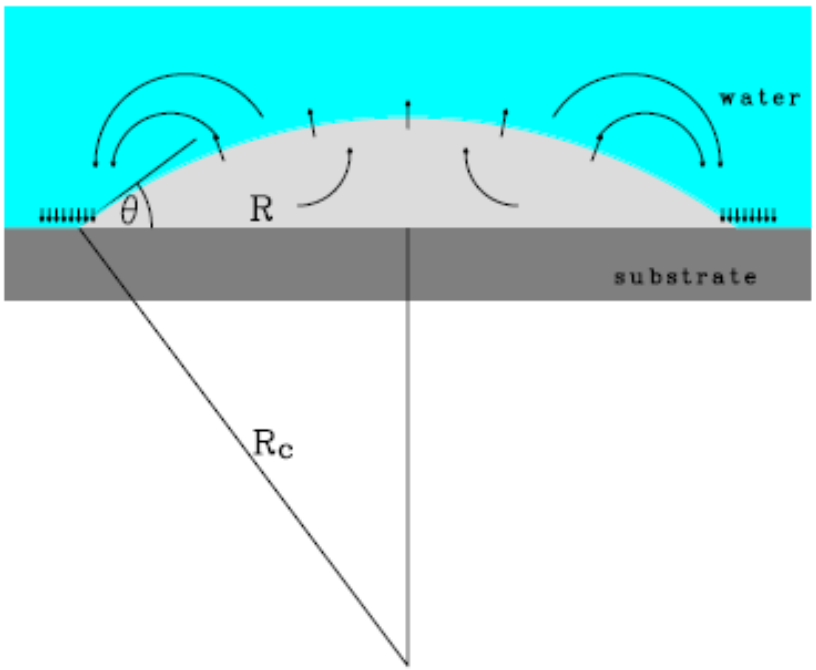


FIG. 1 (color online). Sketch of gas outflux and influx into a surface nanobubble and definition of the contact angle θ, the surface nanobubble radius R, and the radius of curvature R_c.

Dynamic equilibrium mechanism for surface nanobubble stabilization, D. Lohse and M. P. Brenner, PRL (2008)

Exit velocity: measured and predicted via scaling theory to be 3-4 m/s

Height of the jet in the water required to lose momentum and turn around is several microns

A simulation “model” of this process would require an MD simulation of the bubble and a continuum description of the fluid domain

Our focus (in joint work with Scott Shell) has thus been on the development of methods to cope with systems that combine the need for molecular (or possibly mesoscopic) resolution in localized regions of a macroscopic (continuum) fluid domain.

3 Project areas:

1) An adaption of the methods developed by Robbins for **direct coupling** between MD and continuum (for viscous flow systems where the macroscale problem can be solved via BI methods) with a few modest wrinkles; applied to steady flow problems such as shear flows with slip/no-slip boundaries.

Coupling of MD and Continuum via a mesoscale transition region

<u>"Top-down"</u>

2) Progress toward the development of a computational algorithm with MD coupled to continuum via an intermediate mesoscale fluctuating SPH description (SDPD).

<u>"Bottom up"</u>

3) Coarse grain MD **(Chia-Chun Fu)**

A Systematic Coarse-Graining of Molecular Dynamics Simulation

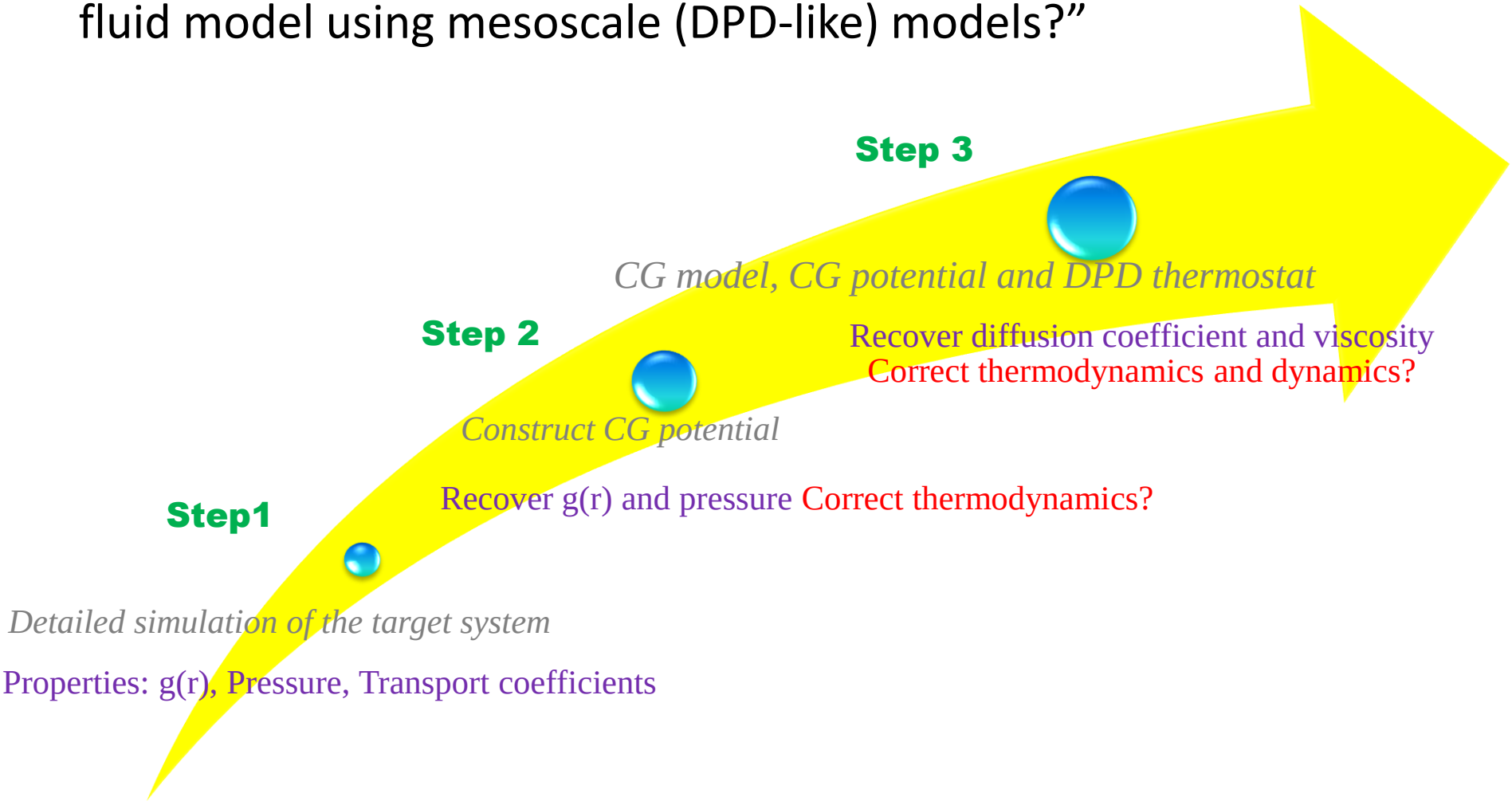
KITP Physical Principles of Multiscale Modeling

2012, May 10

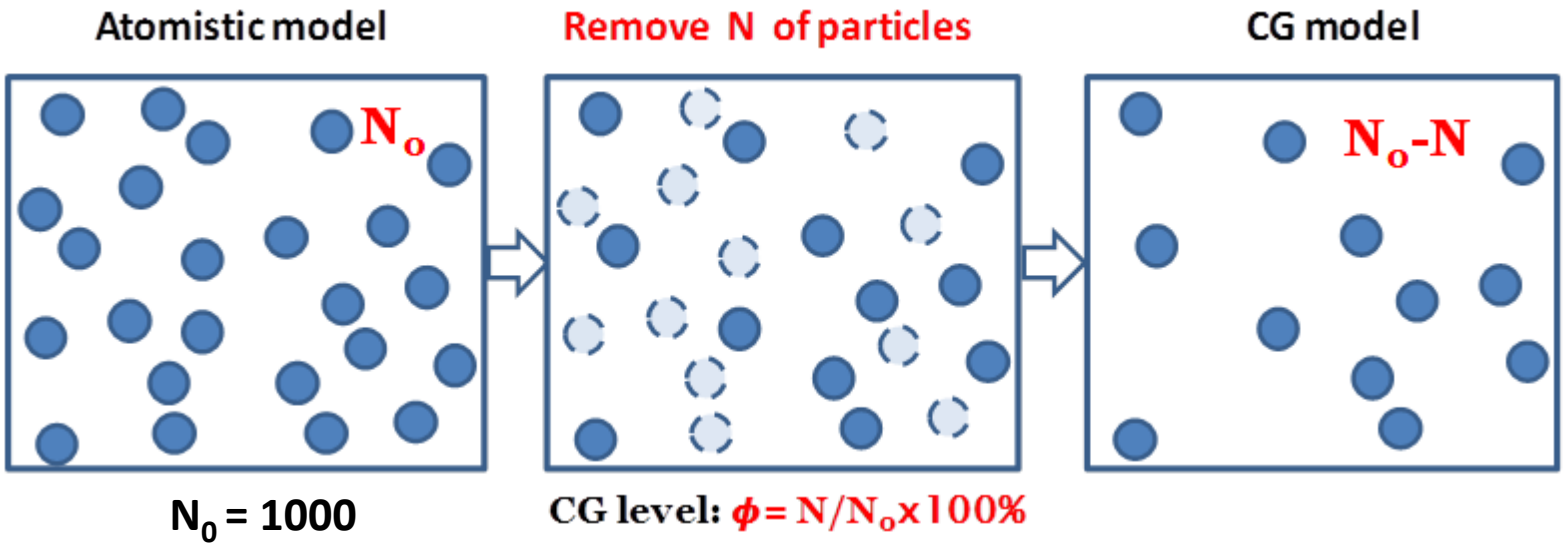
Chia-Chun Fu, Pandurang Kulkarni, Scott Shell and Gary Leal
University of California, Santa Barbara

Systematic Coarse-graining

"To what extent can we systematically match a simple Lennard-Jones fluid model using mesoscale (DPD-like) models?"



Coarse-grained MD - Model



- Target system: Lennard-Jones liquid @ T^*=1.0 and ρ^*=0.8

  (Ar @ T = 120K and ρ = 1344 kg/m^3)

- CG system@ T^*=1.0 and reduced number density

CG = 10% → ρ_{CG} = 0.72 CG = 30% → ρ_{CG} = 0.56
CG = 50% → ρ_{CG} = 0.40 CG = 70% → ρ_{CG} = 0.24
CG = 90% → ρ_{CG} = 0.08

From Prof. Lyubertsev's talk on last Wednesday

- To construct the effective interaction from a reference atomistic system:

1. Select $R=\theta(r_i)$
2. Find effective interactions for R by integrating out remaining DOFs

$$W(R) = -kT \ln \int dr_i \delta\big(R - \theta(r_i)\big) e^{-\beta H(r_i)}$$

3. Practically, $W(R_1 \ldots R_N) \approx \sum_i V_{eff}(R_{ij})$
   (1) force matching
   (2) match averages: **RDF** or other averages.

Methods for matching selected thermodynamic properties

- Iterative Boltzmann inversion (Reith, 2003)

$$U_0 = -k_B T \ln g_{\text{target}}(r)$$ "potential of mean force" U_{PMF}

$$U_{i+1}(r) = U_i(r) + \xi k_B T \ln\left[\frac{g_i(r)}{g_{\text{target}}(r)}\right]$$

1. converges based on uniqueness theorem
   -- one to one relationship between pair potential and RDF.
2. qualitative convergence argument given in Soper, 1996.
3. state-point dependence

- Pressure correction (our work)

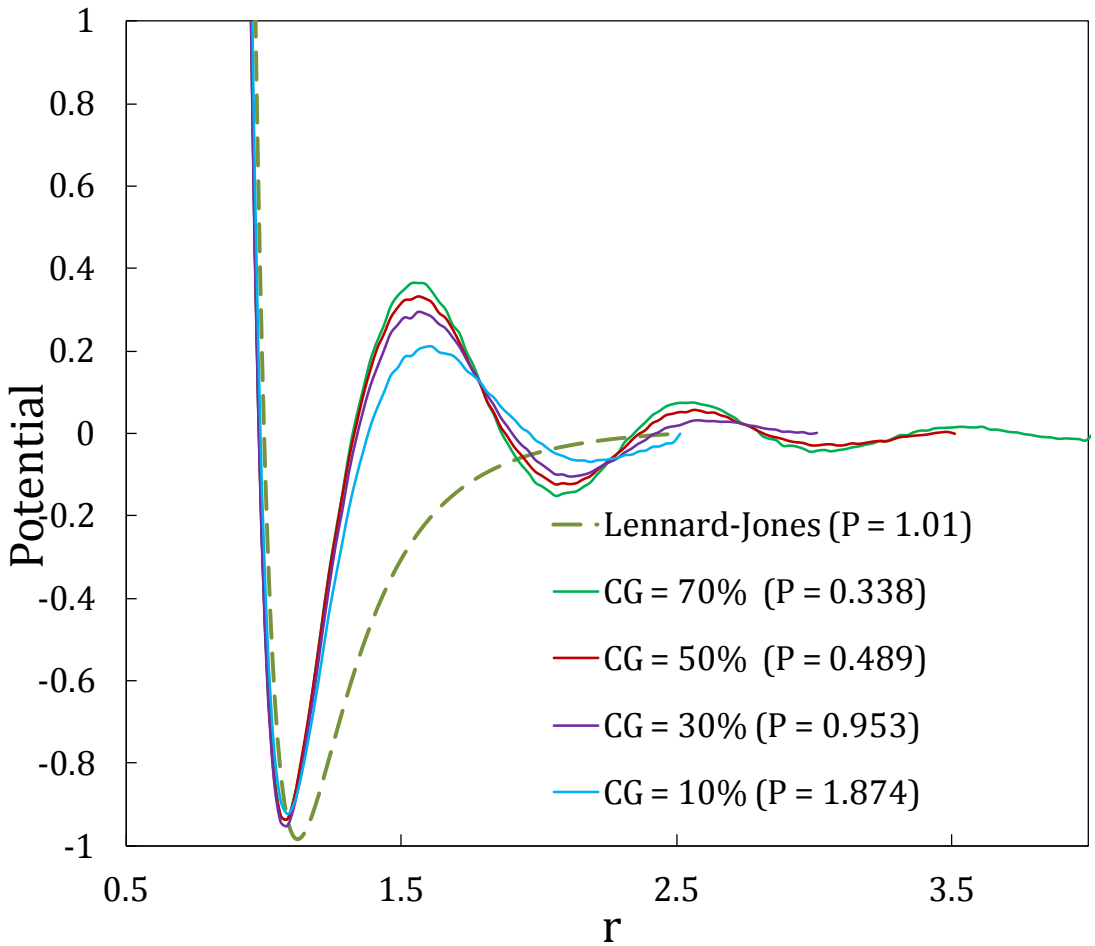
$$P_{CG} = \frac{N_{CG} k_B T}{V} - \frac{W_{CG}}{3V} \qquad W_{CG} \equiv \sum_{i<j} \frac{d\mathrm{U}_{CG}(r_{ij})}{dr} r_{ij}$$

$$f[U] = \frac{1}{2} \int_0^{cutoff} \left[\ln \frac{g(r,U)}{g_{\text{target}}(r)} \right]^2 dr + \frac{1}{2} \alpha \left(\frac{P_{CG}}{P_{AA}} - 1 \right)^2$$

$$u_j^{k+1} = u_j^k - \frac{\partial f^k}{\partial u_j^k} \chi$$

-steepest descent
-nonlinear optimization
-adaptive time step χ
-adaptive penalty parameter α

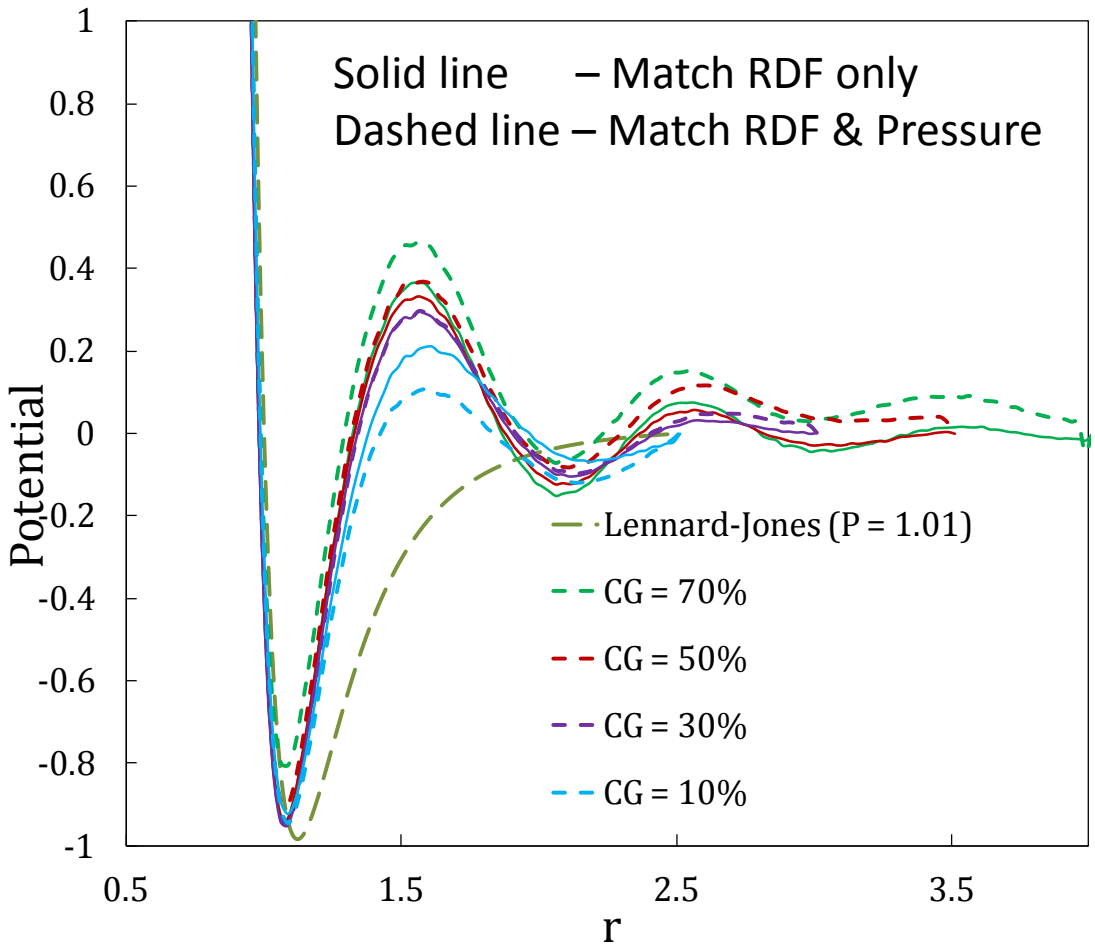
Match structure (RDF) only



- RDF is mostly determined by the repulsive core of potential.

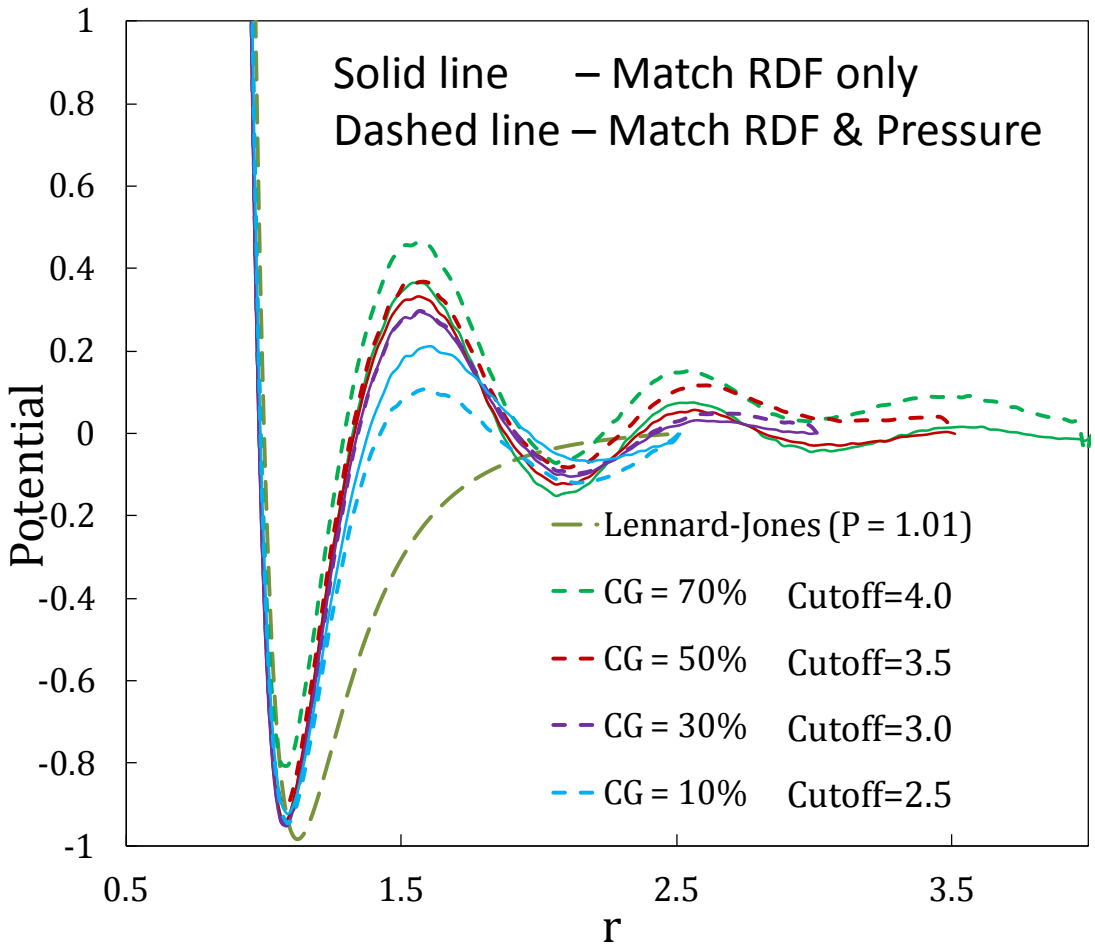
(Weeks and Chandler, 1971)

Match RDF & Pressure



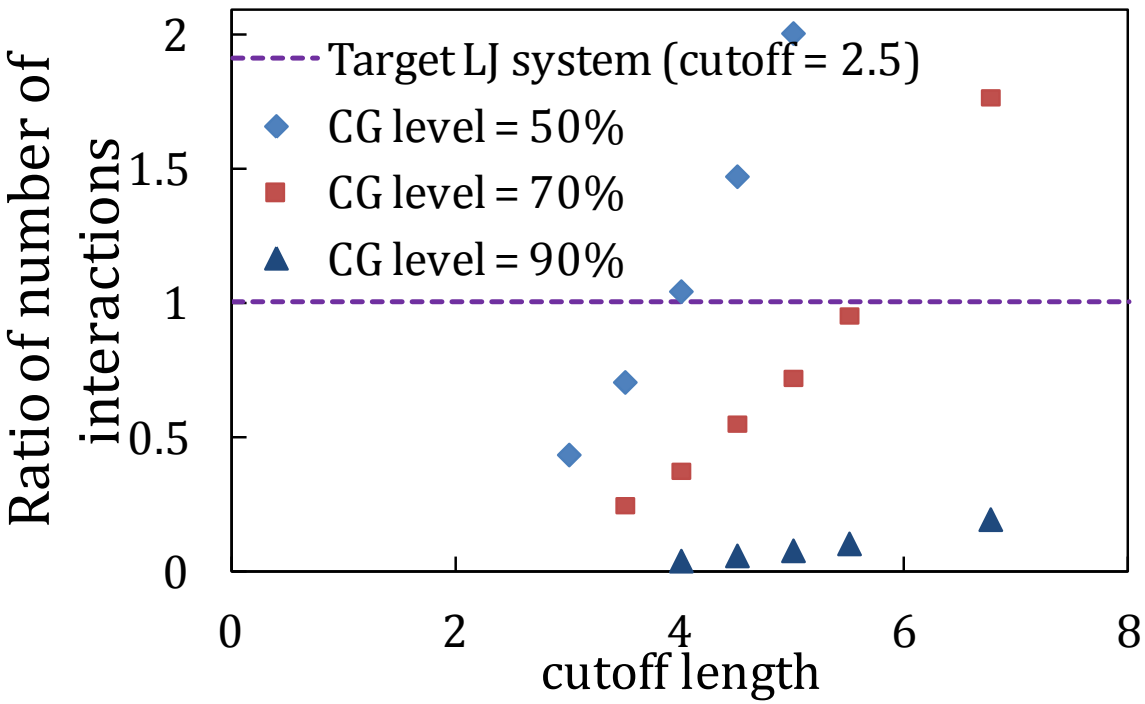
- Pressure correction acts at the tail.

Match RDF & Pressure



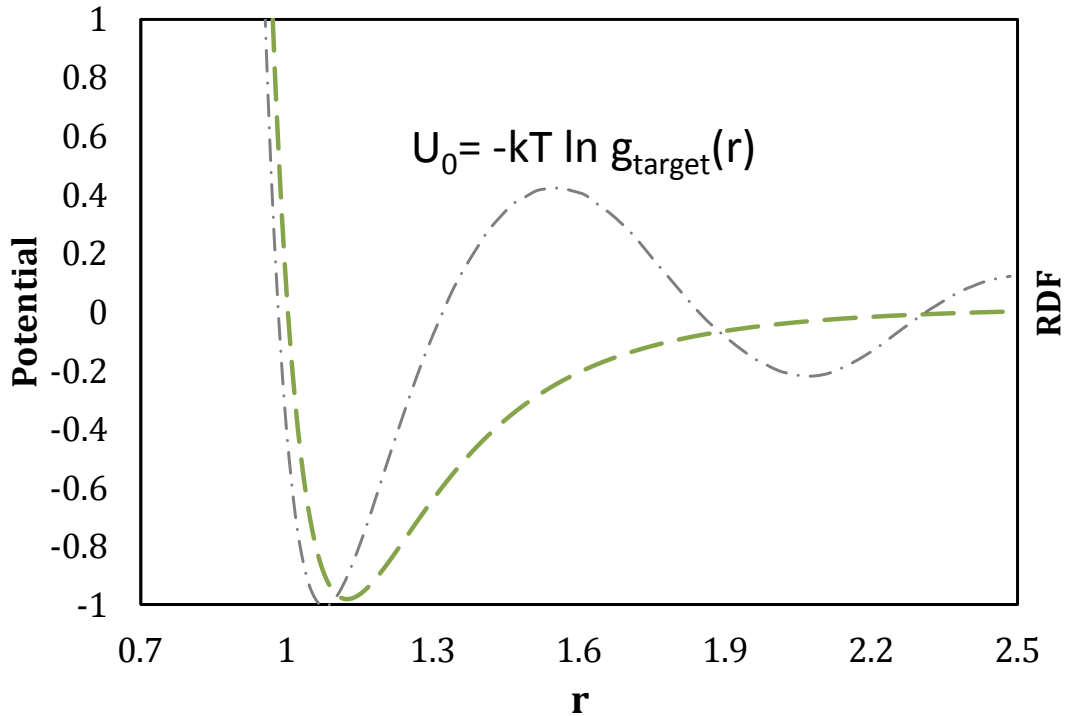
- Pressure correction acts at the tail.

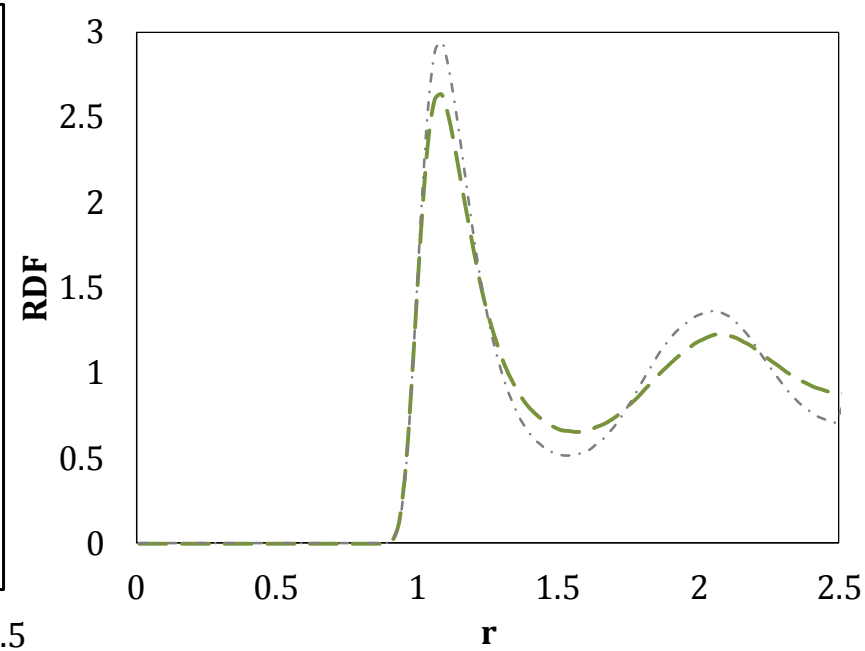
- Cutoff length should be chosen carefully depending on the CG level or the CG simulation will not give any speedup.



Are the CG potentials unique?

A test with no coarse-graining to recover LJ potential





Matching RDF

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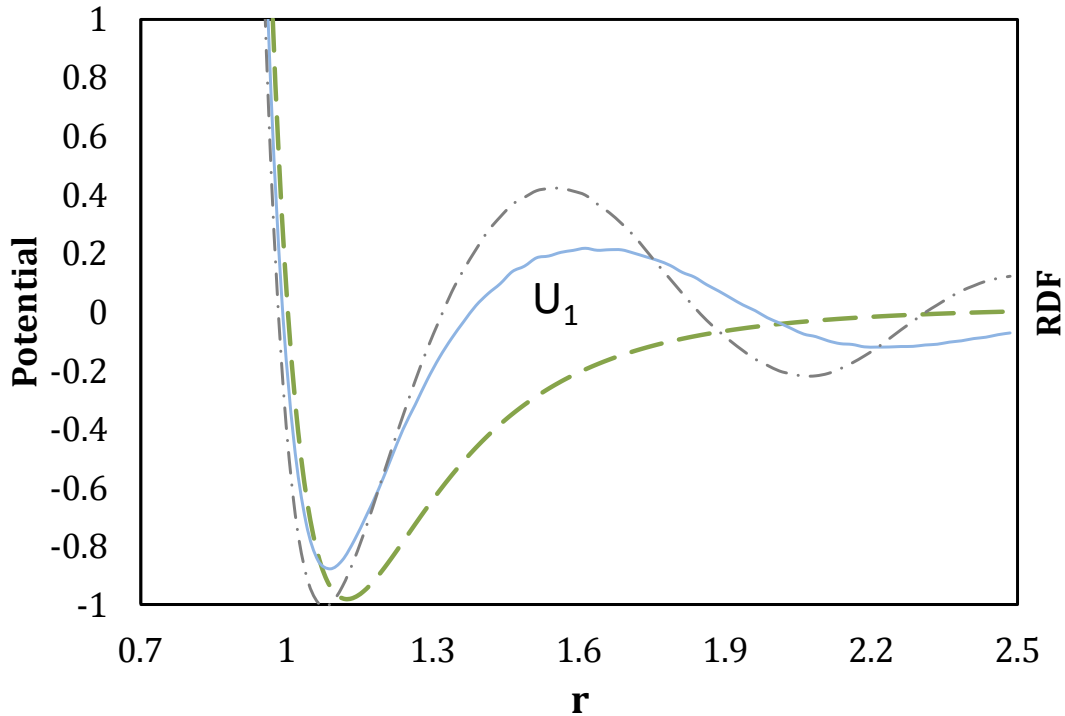

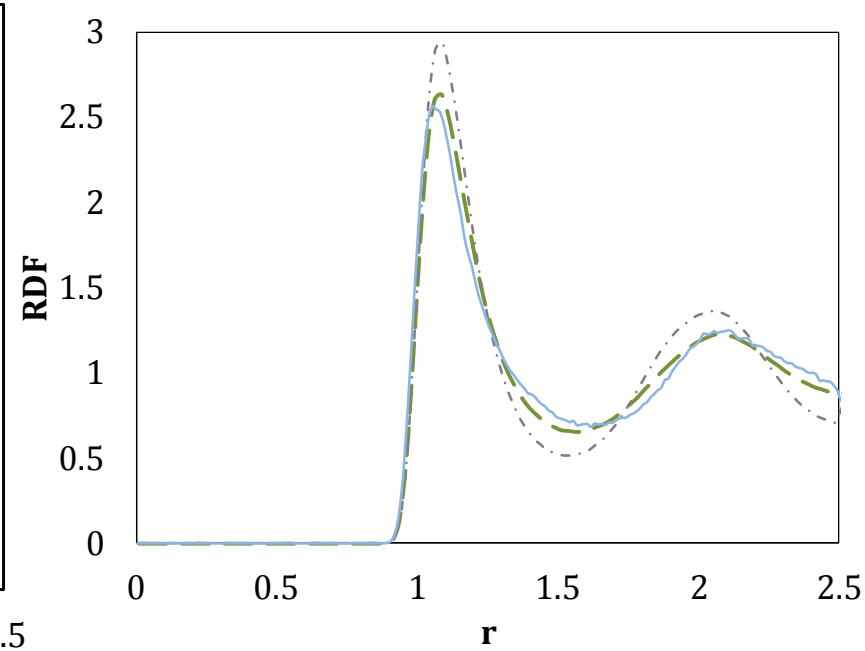

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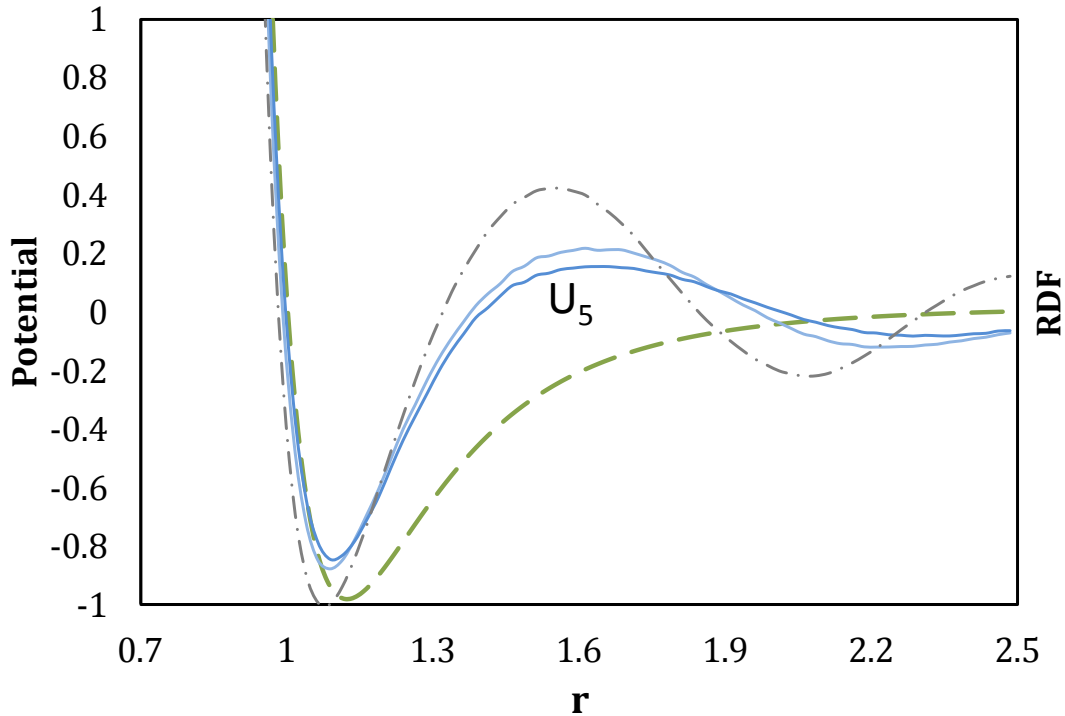
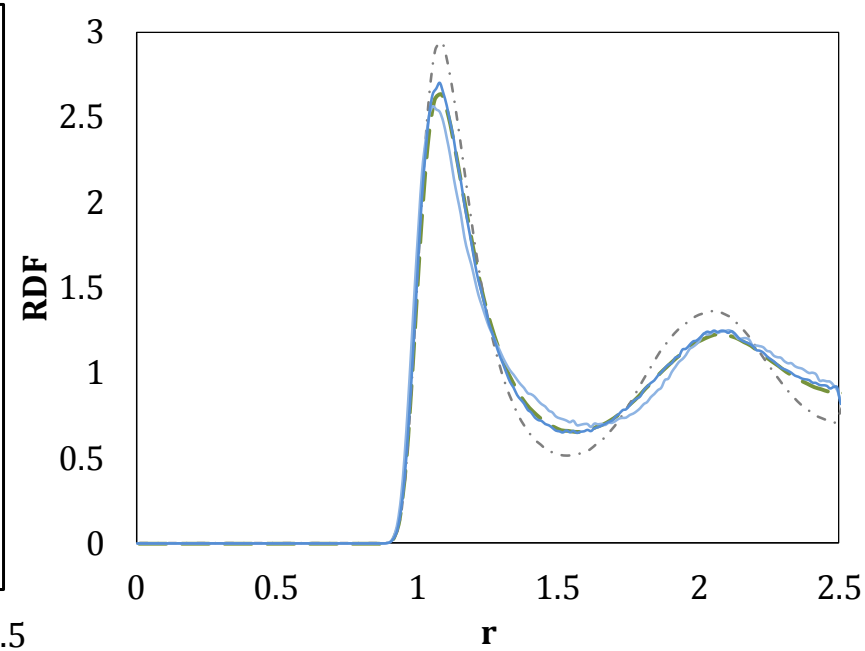
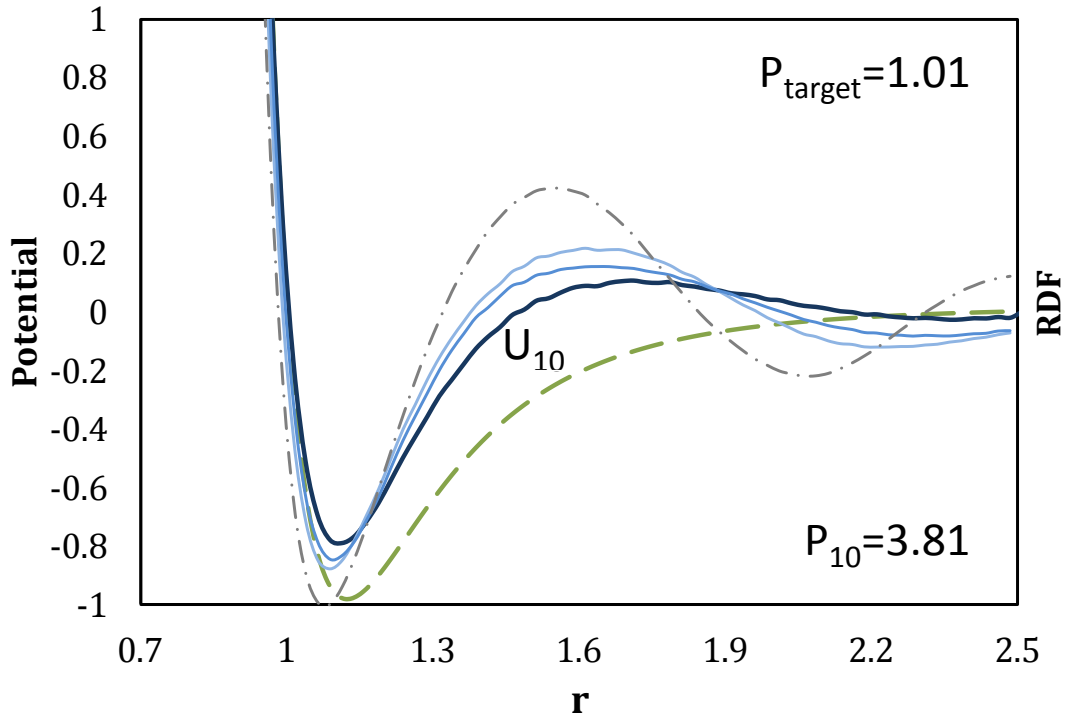


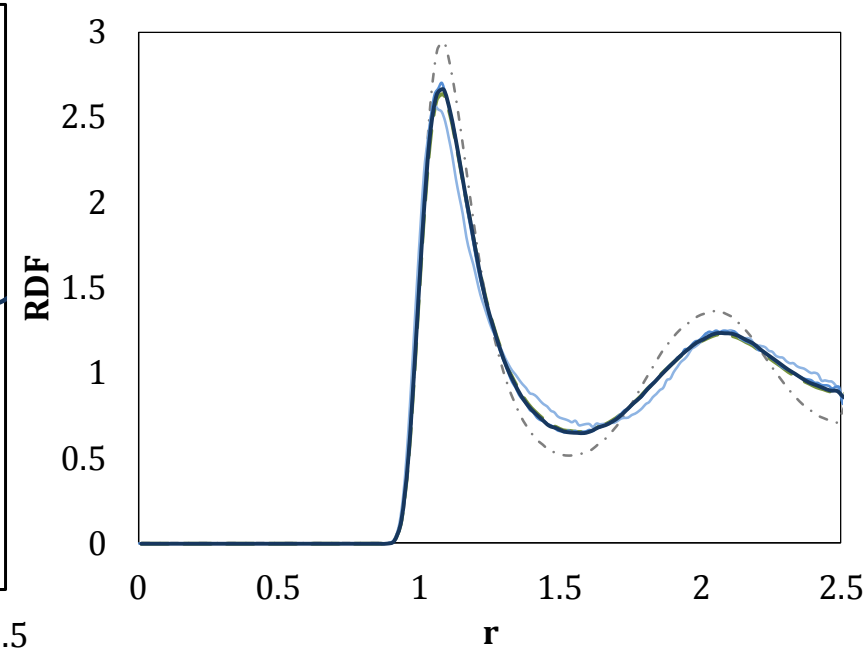


Matching RDF

Are the CG potentials unique?

A test with no coarse-graining to recover LJ potential

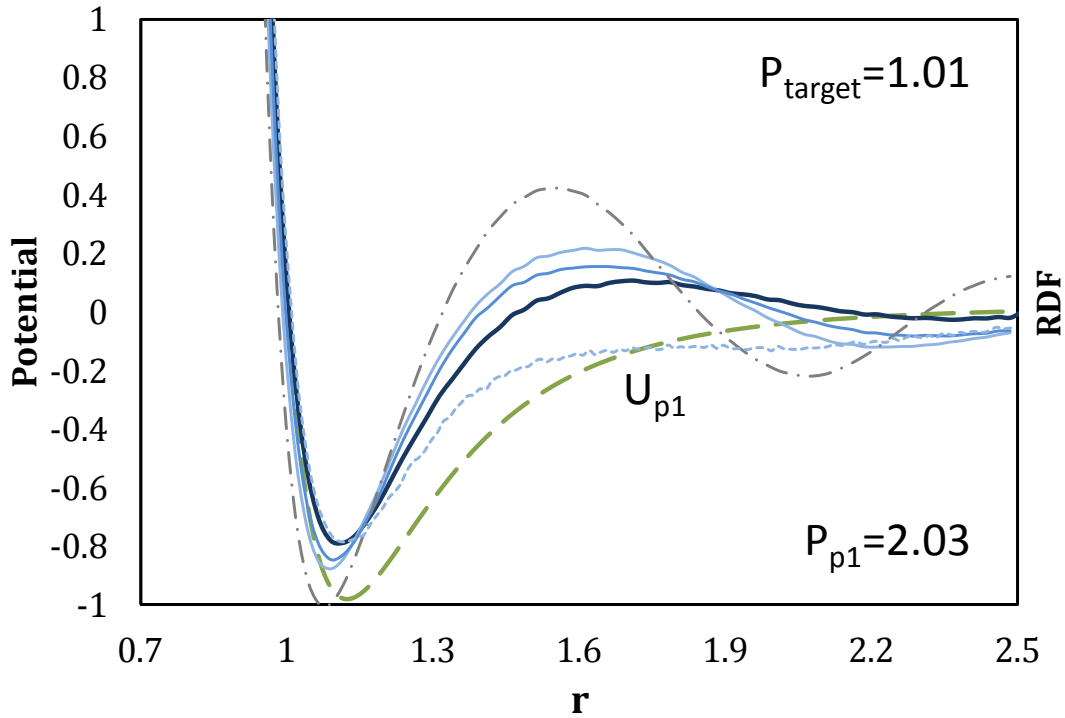


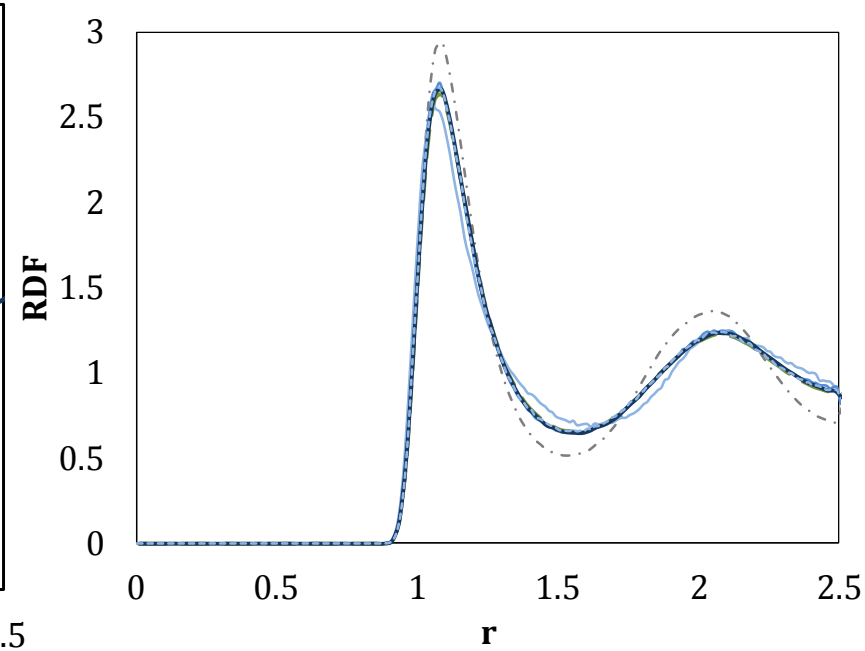


Matching RDF

- After 10 iteration, the RDFs are virtually indistinguishable but the potential differs from the original LJ potential.
- No further changes with more iterations.

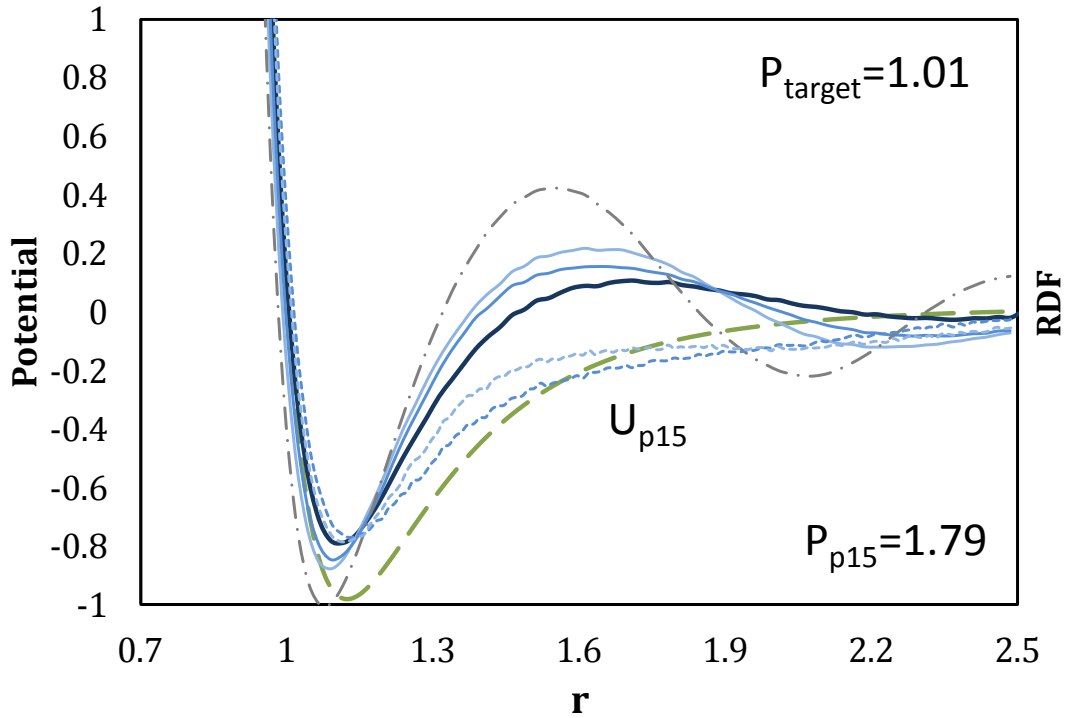
What happens if we add the pressure correction?

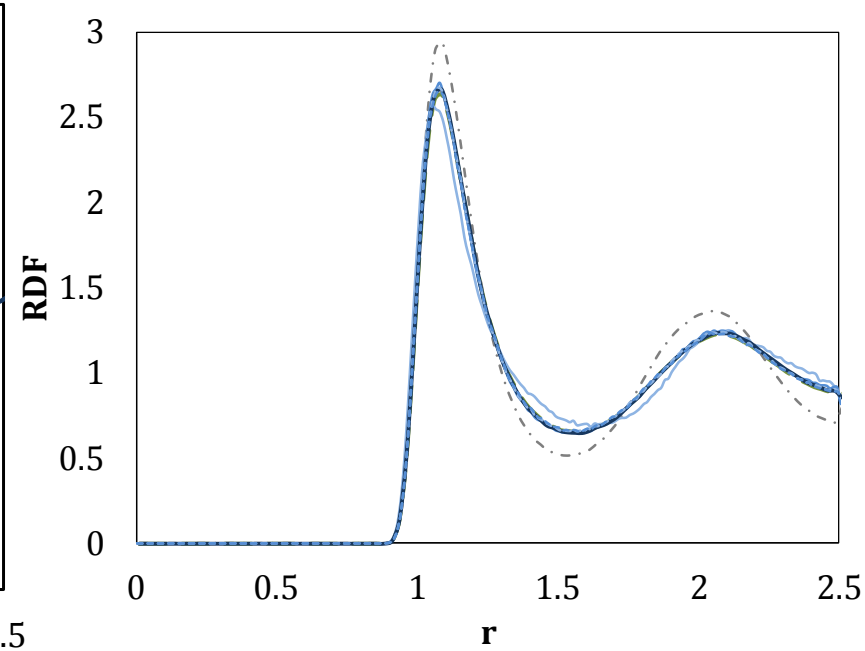




Matching RDF and pressure

What happens if we add the pressure correction?





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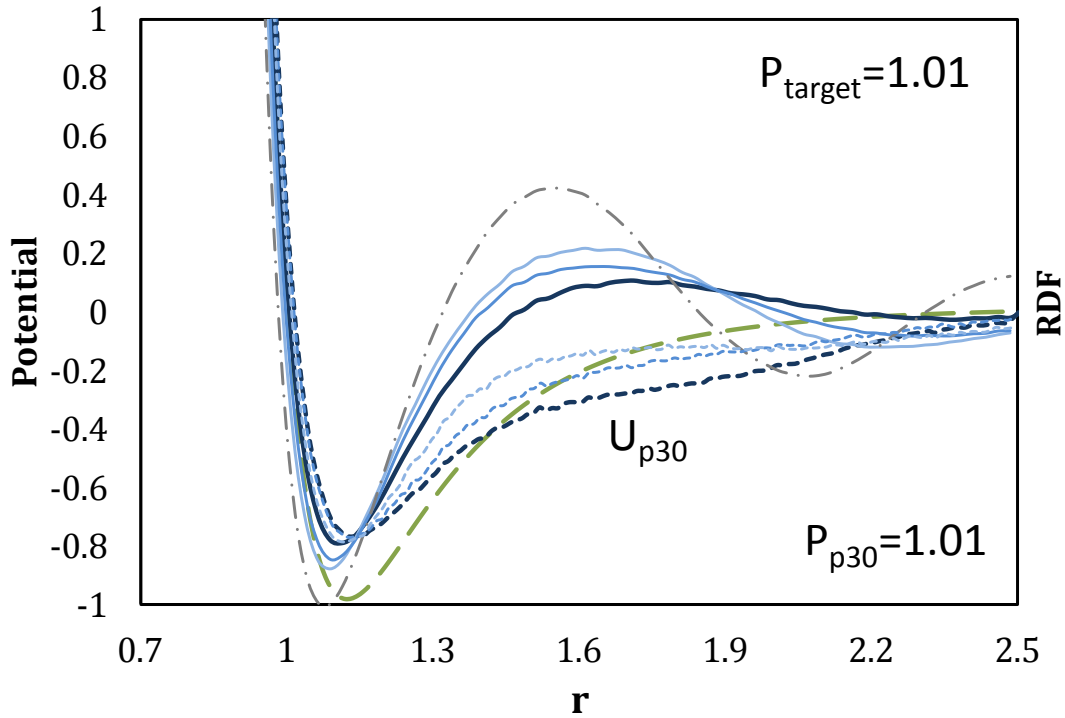
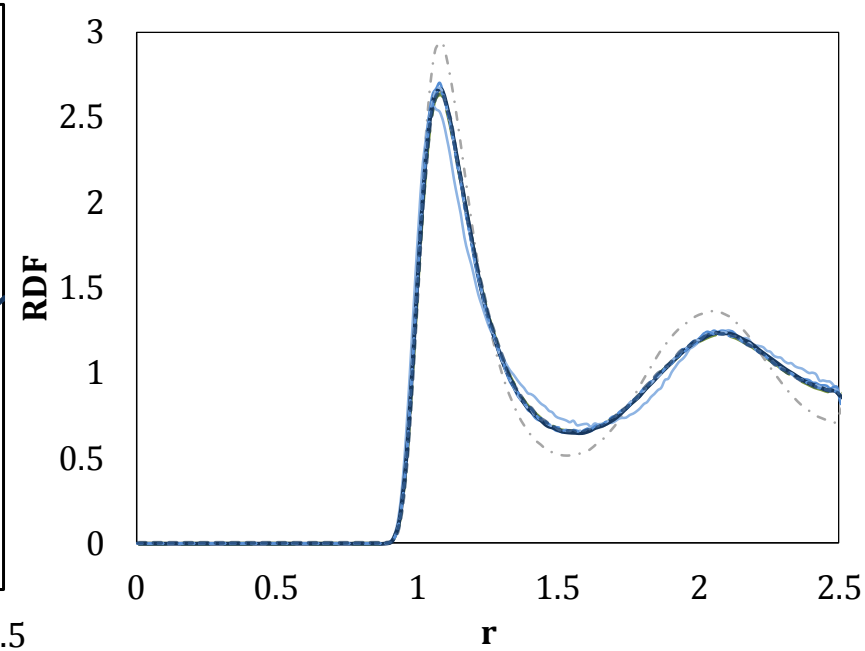
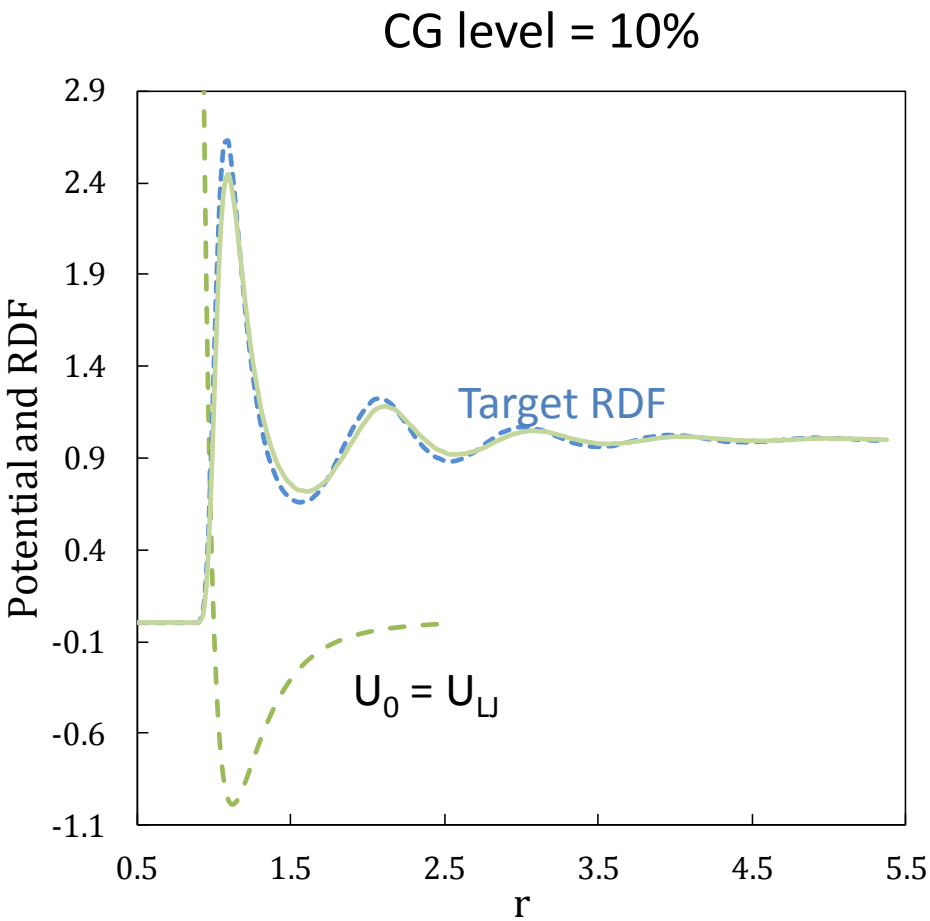
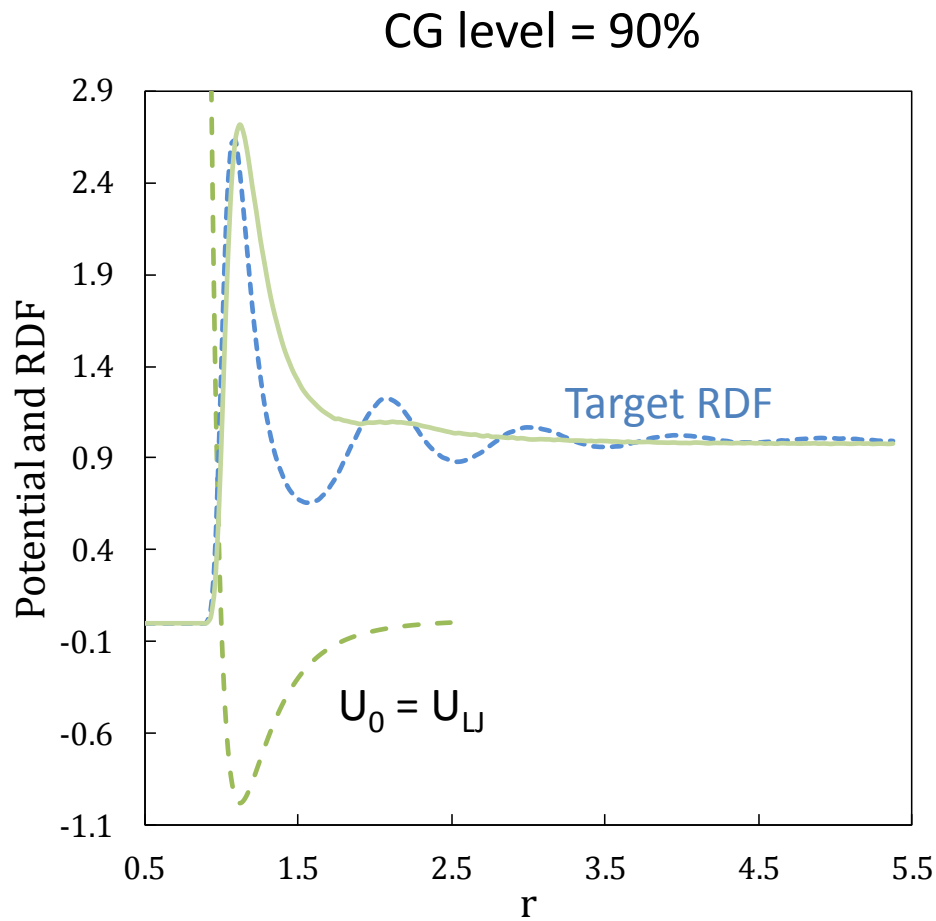




Recover the attractive tail

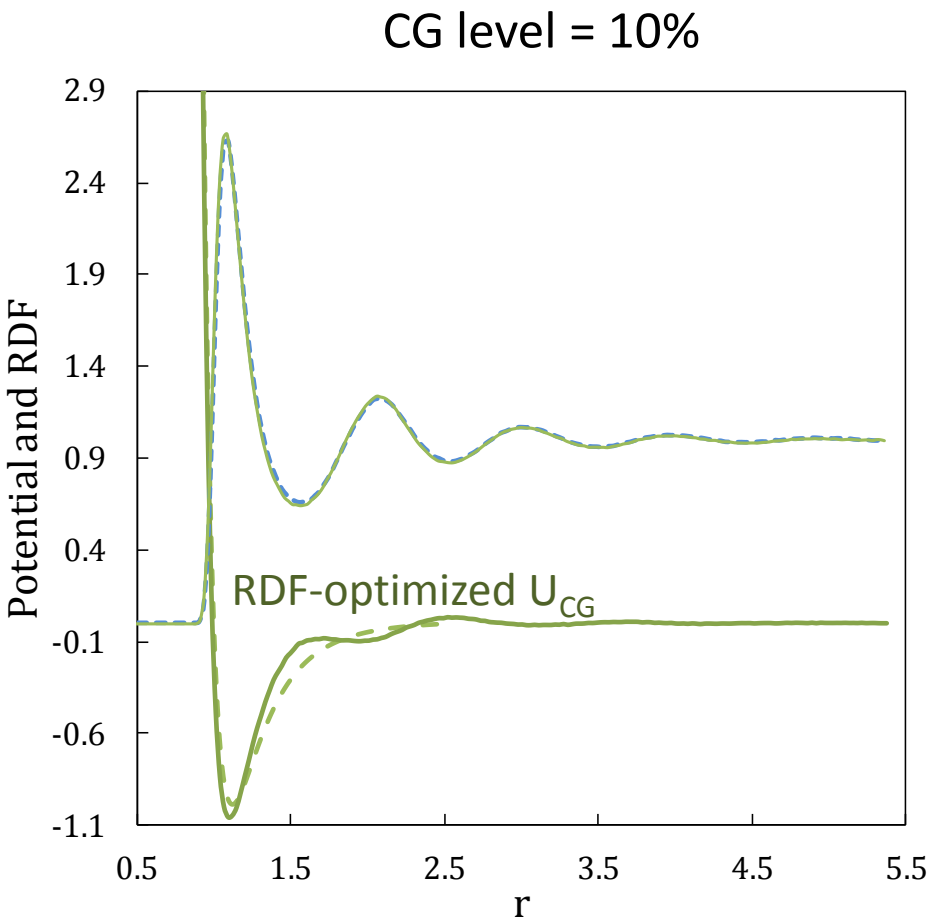
CG potential depends upon the initial guess for potential U_0

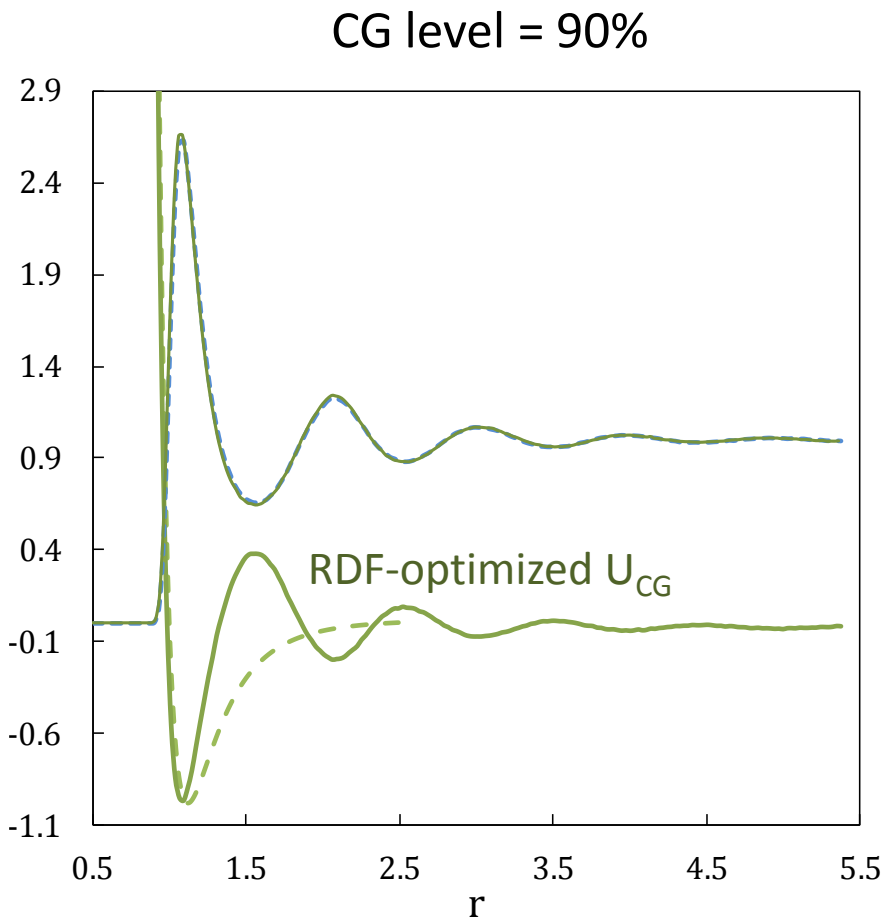




- Initial RDFs due to U_0 reflect original LJ system at reduced densities.

CG potential depends upon the initial guess for potential U_0





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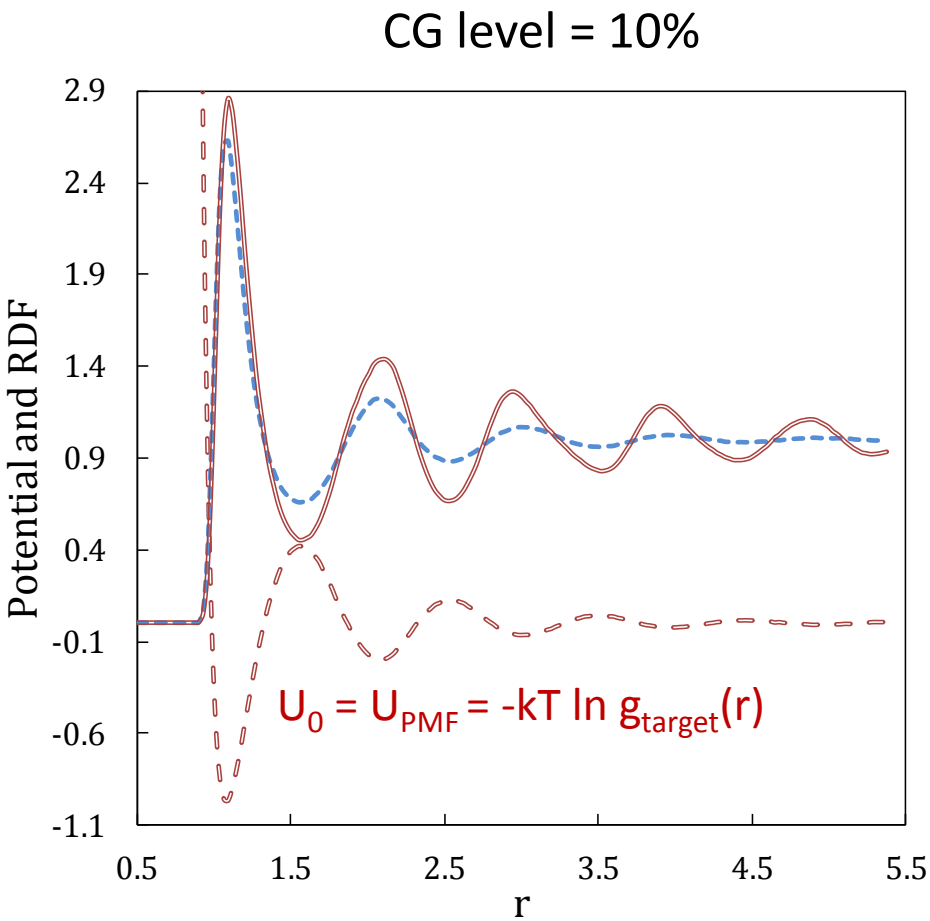

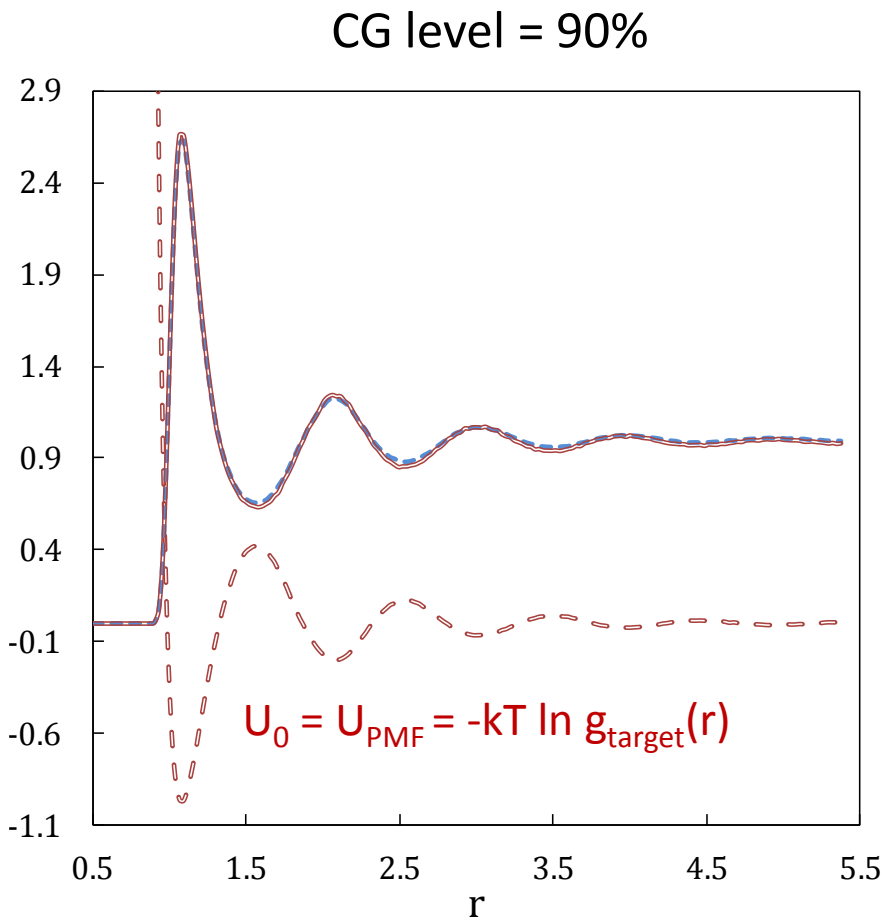

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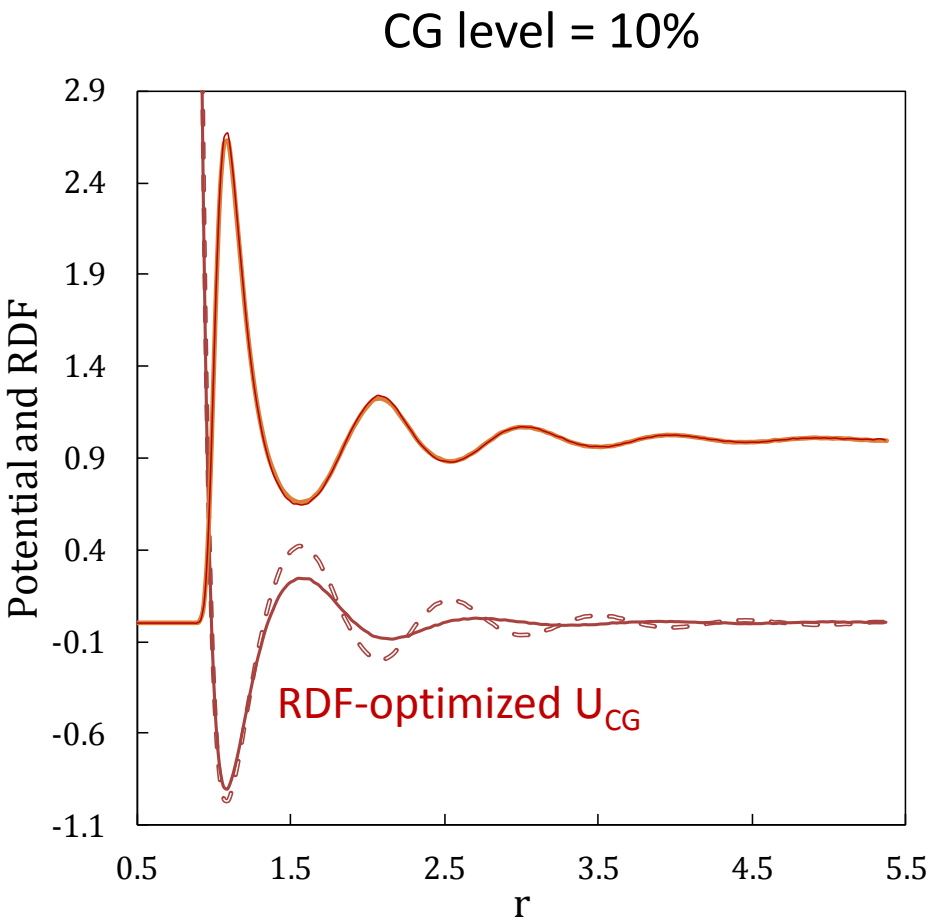

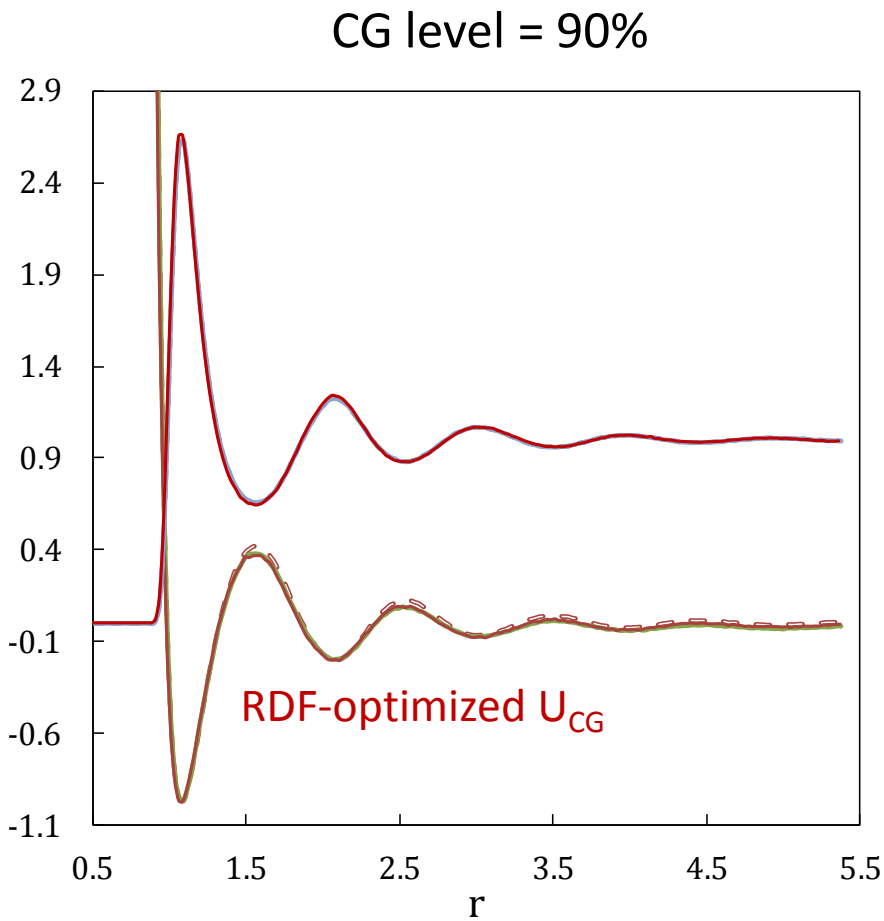

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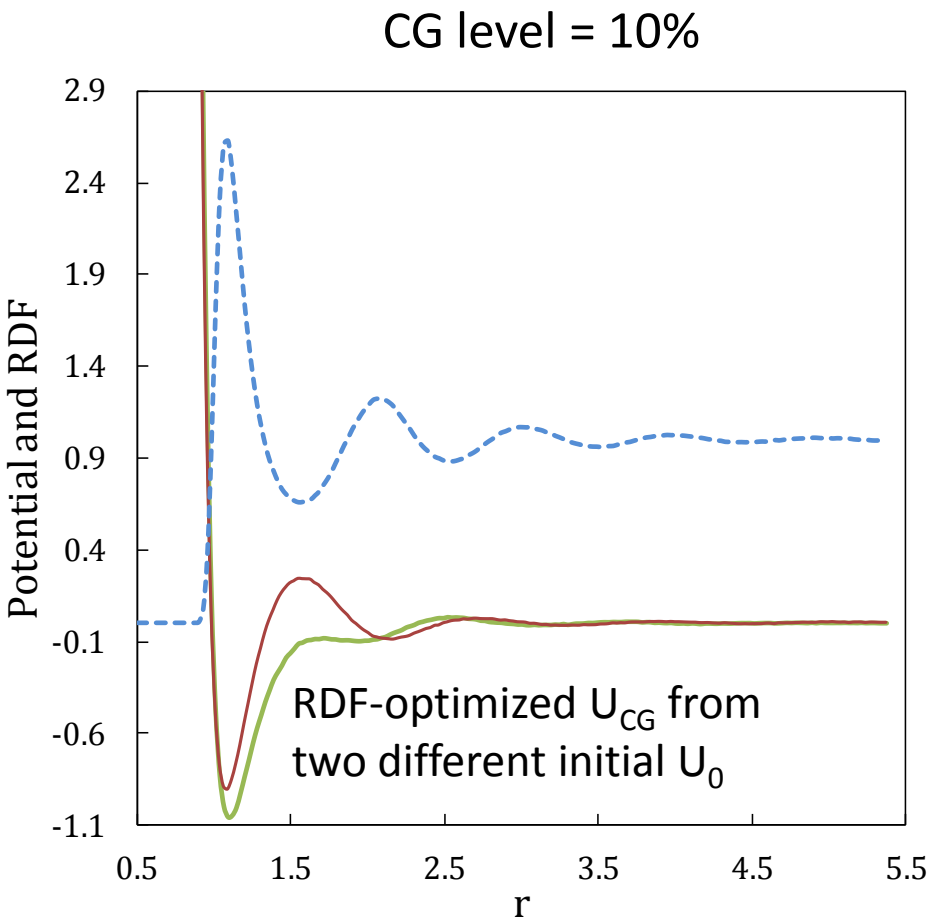
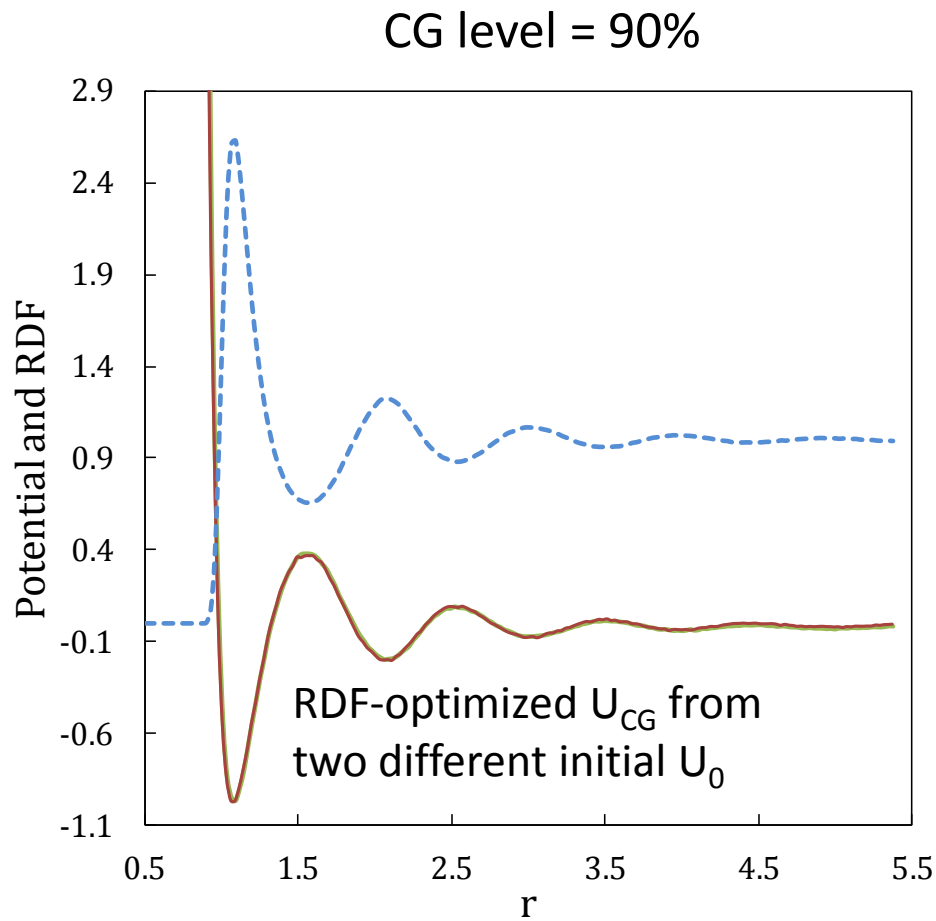
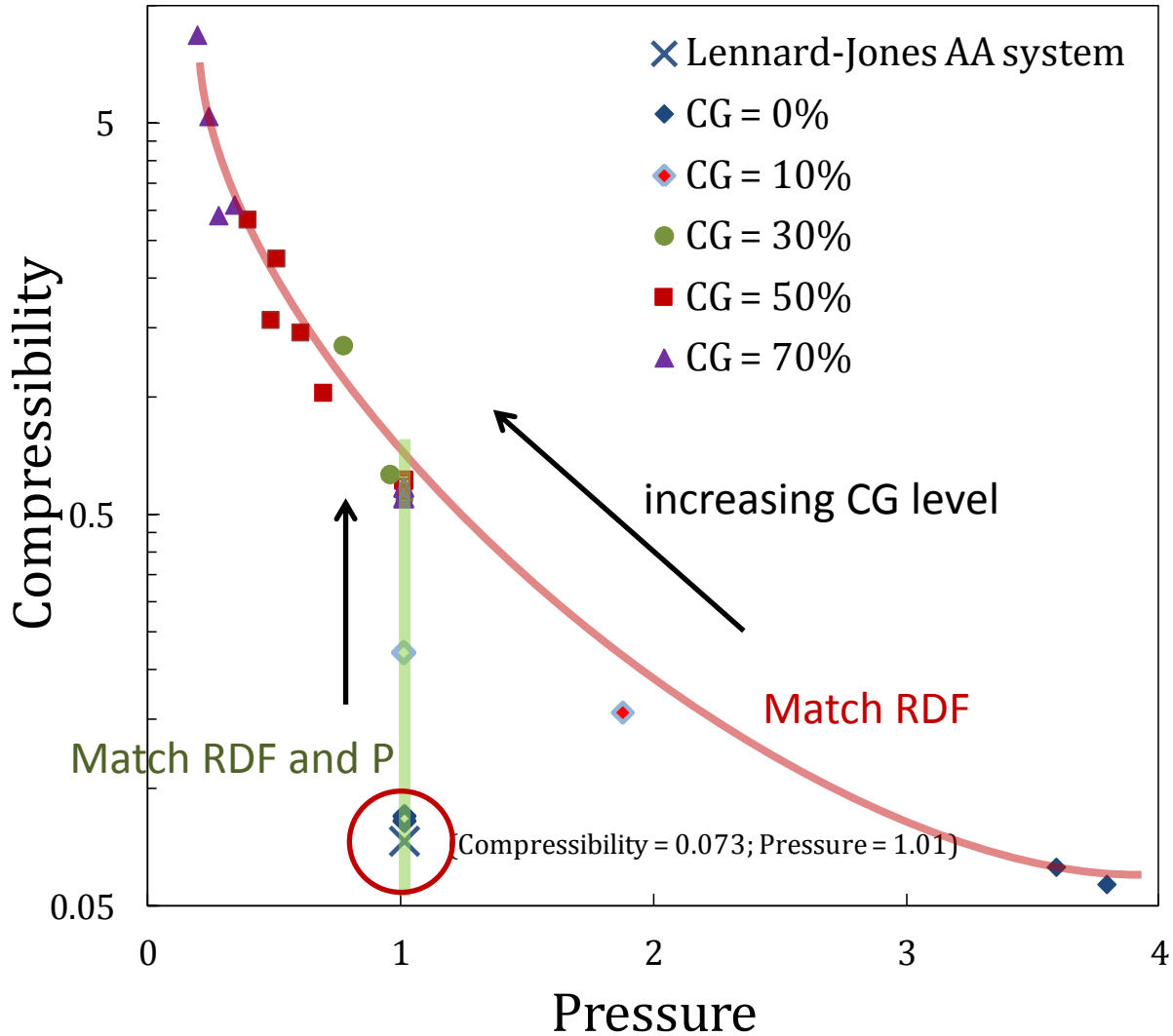




- When ϕ is small (little coarse-graining), U_{CG} depends on U_0.
- When ϕ is large (high coarse-graining), U_{CG} is less sensitive to U_0.

Isothermal compressibility

$$\kappa_T \equiv -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_T = \frac{1}{\rho}\left(\frac{\partial \rho}{\partial p}\right)_T$$



Matching dynamics

- Dissipative particle dynamics (DPD) thermostat

Equations of motion: $\dot{\vec{r}}_i = \frac{\vec{p}_i}{m_i}$ $\qquad \dot{\vec{p}}_i = \vec{F}_i^C + \vec{F}_i^D + \vec{F}_i^R$

Dissipative term

Random force term

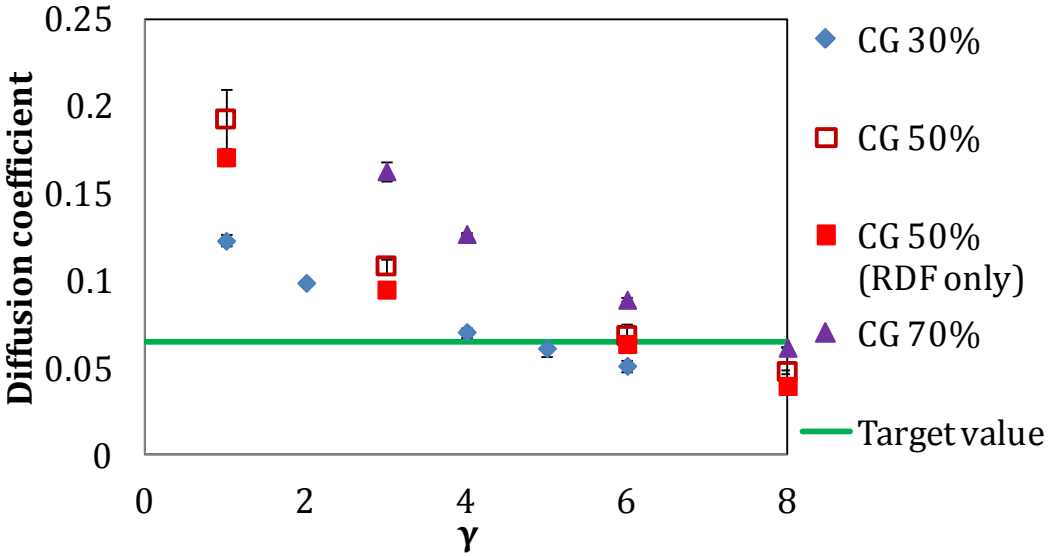
Galilean invariance: F^D, F^R depend on ***relative*** particle velocities and positions.
Balance of F^R and F^D (fluctuation-dissipation) generates canonical ensemble.

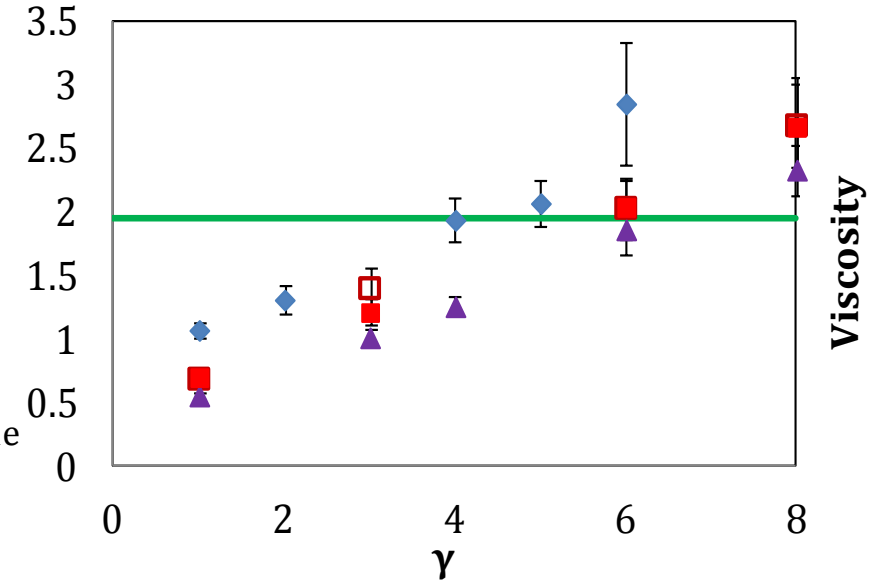
Diffusivity – Mean Square Displacement

$$D = \frac{1}{6t}\sum_{\alpha=1}^{3}\left\langle \left[r_{\alpha i}(t) - r_{\alpha i}(0) \right]^2 \right\rangle$$

Viscosity – Reverse Non Equilibrium MD (Muller-Plathe, 1999)

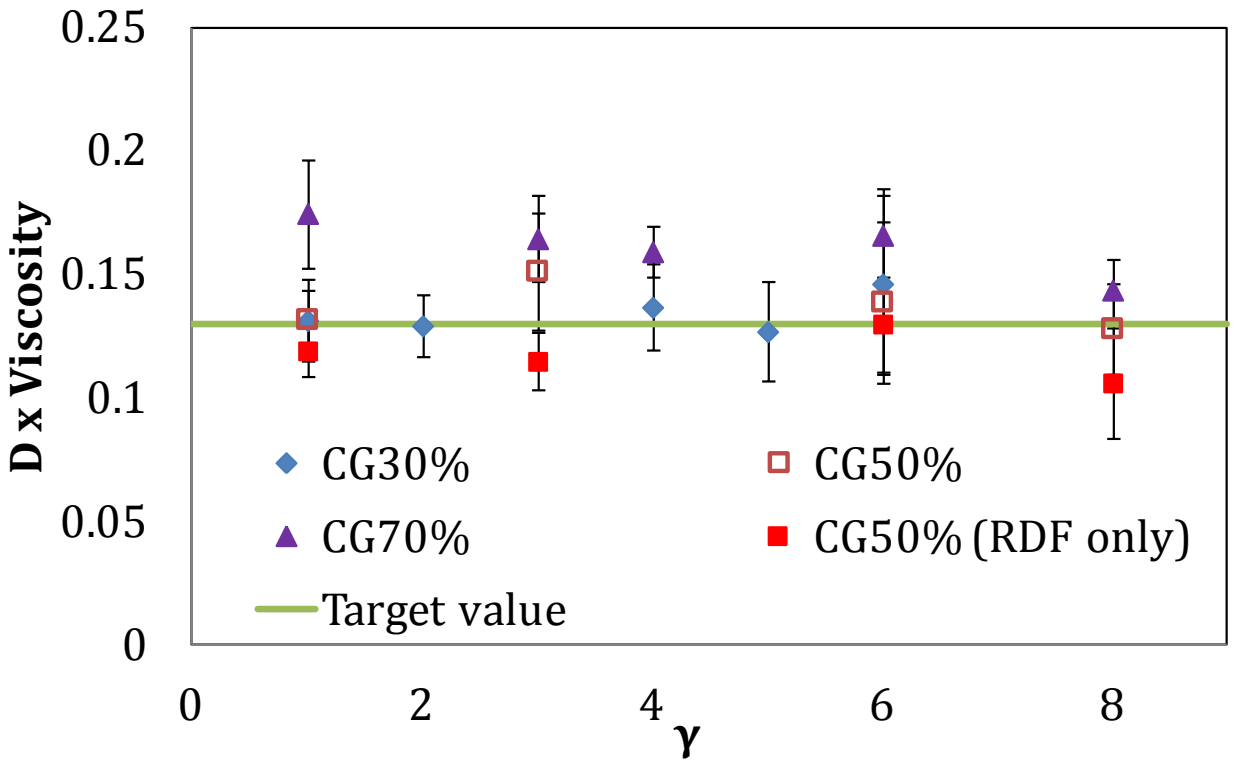
A self consistent friction coefficient can be found using the DPD thermostat.





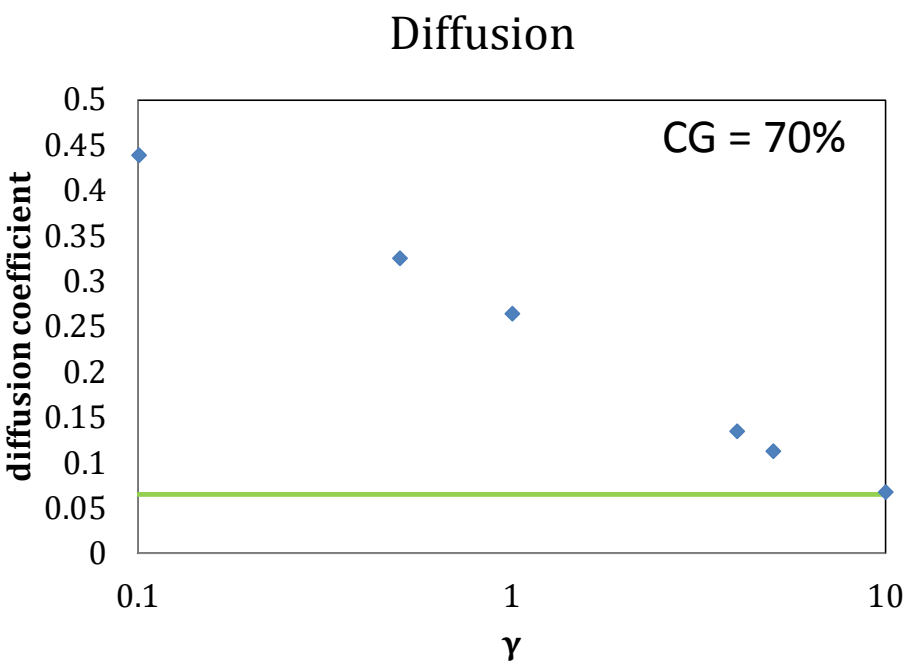
γ is the DPD friction coefficient

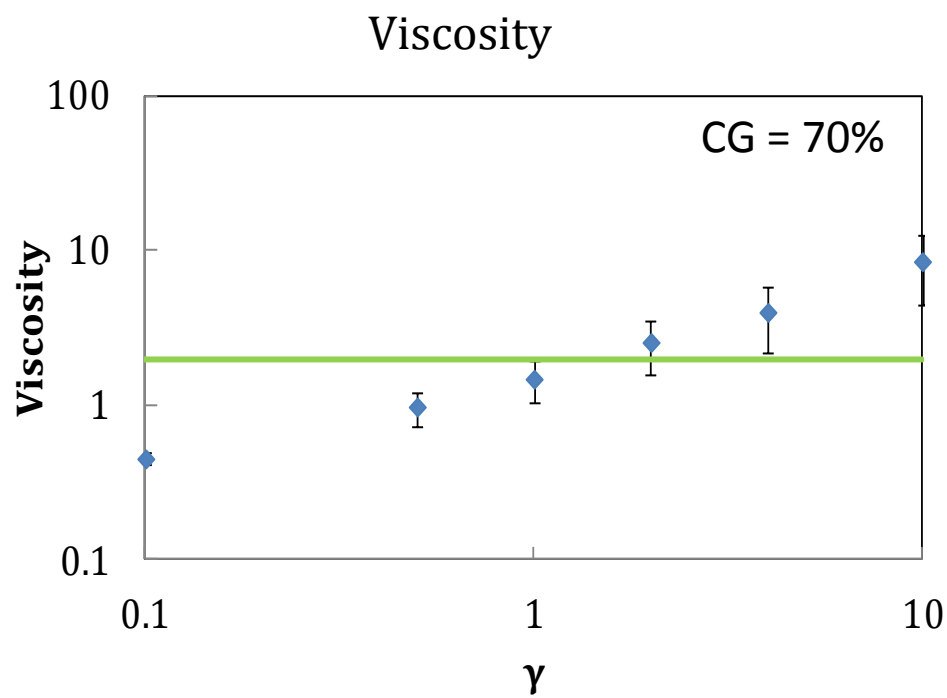
The product of diffusion and viscosity roughly remains constant with various γ, as would be expected from Stokes-Einstein.



What happens if a non-Galilean-invariant thermostat is used, e.g., Langevin dynamics?

$$m\ddot{r}_i = -\nabla_i U - m\gamma\dot{r}_i + \sqrt{2\gamma kTm}R(t)$$

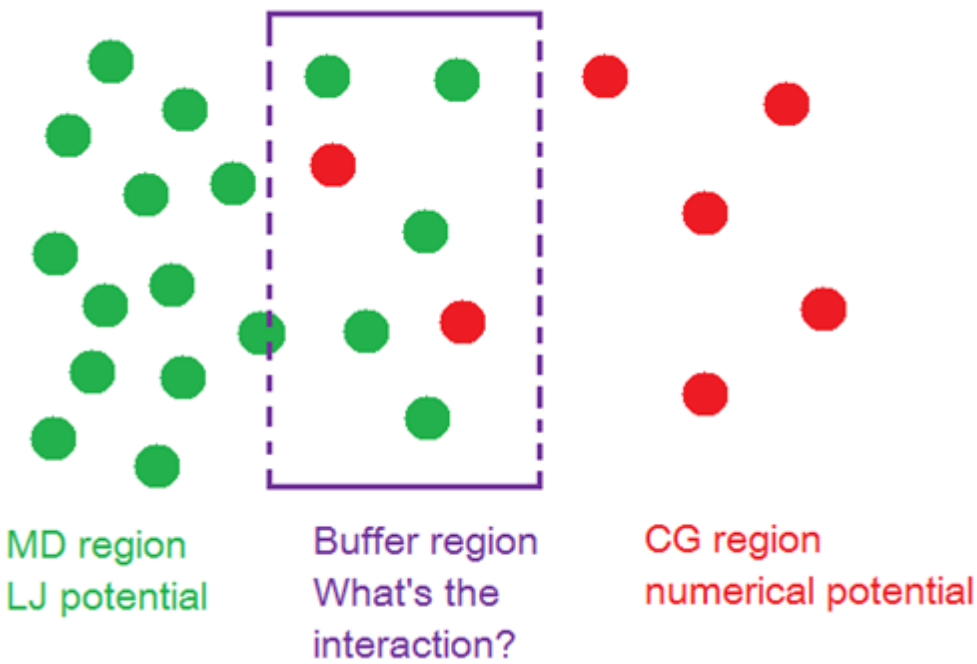




Problems and Future Work

- Are the properties that we chose to match adequate for dynamic multiscale simulation, such that the underlying physics is not undermined?
- Adaptive resolution – connect to MD.

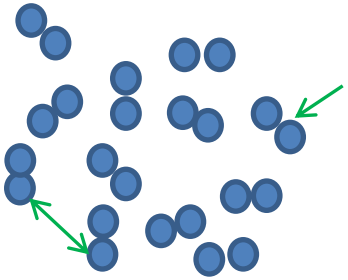
  Need special treatment in the buffer/transition region.



Other system-
Lennard-Jones chain

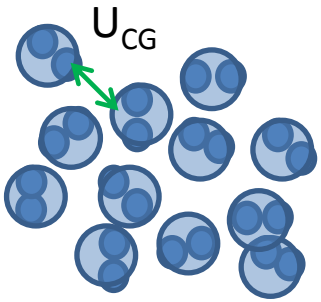
Nonbonded interaction

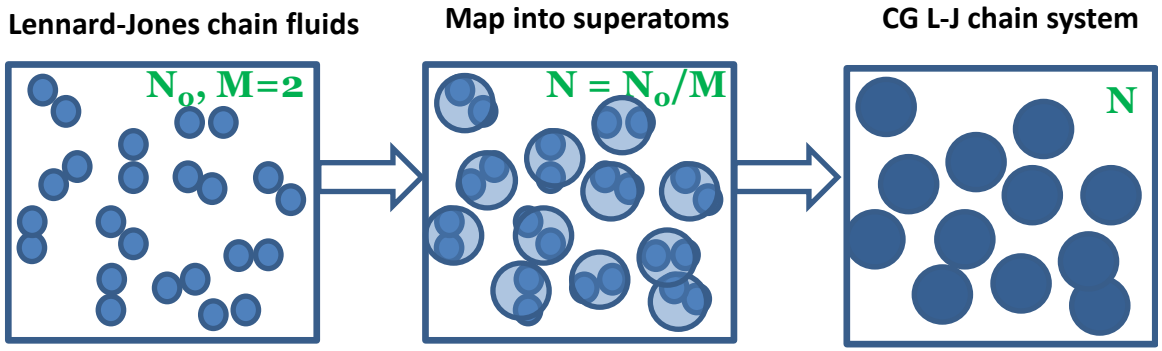
$$U = \sum_{i<j,\, ij \text{ not bonded}} 4\left(r_{ij}^{-12} - r_{ij}^{-6}\right)$$



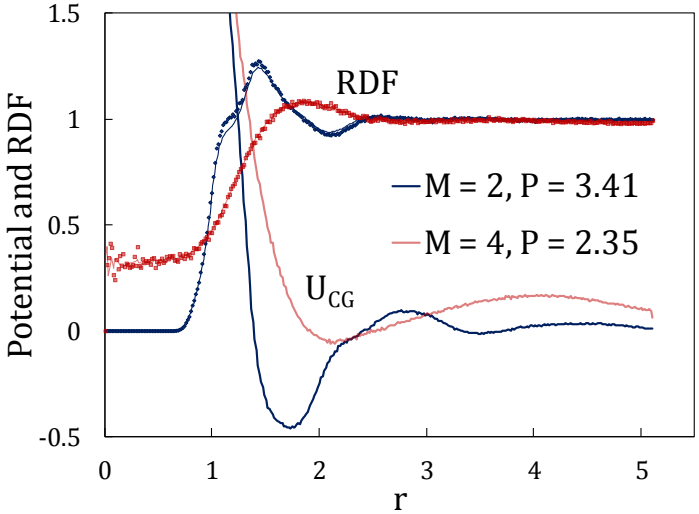
Bonded interaction

$$U = \sum_{i<j,\, ij \text{ bonded}} \frac{k}{2}\left(r_{ij} - r_0\right)^2$$





CG level: ϕ = (1-1/M) x 100%



Dynamics

- Dissipative particle dynamics(DPD) Thermostat

Equation of motion

$$\dot{\vec{r}}_i = \frac{\vec{p}_i}{m_i} \quad , \quad \dot{\vec{p}}_i = \vec{F}_i^C + \vec{F}_i^D + \vec{F}_i^R$$

$$\vec{F}_i^D = \sum_{j \neq i} \vec{F}_{ij}^D \quad , \quad \vec{F}_i^D = -\zeta\, w^{\mathrm{D}}(r_{ij})(\vec{r}_{ij} \cdot \vec{v}_{ij})\hat{r}_{ij}$$

$$\vec{F}_i^R = \sum_{j \neq i} \vec{F}_{ij}^R \quad , \quad \vec{F}_i^R = -\sigma\, w^{\mathrm{R}}(r_{ij})\Theta_{ij}\hat{r}_{ij}$$

Galilean invariance

$$\vec{v}_{ij} = \vec{v}_i - \vec{v}_j \quad , \quad \vec{r}_{ij} = \vec{r}_i - \vec{r}_j$$

Fluctuation-Dissipation theorem

$$\sigma^2 = k_{\mathrm{B}} T \zeta \quad , \quad w^{\mathrm{R}}(r)^2 = w^{\mathrm{D}}(r)$$

Viscosity – Reverse Non Equilibrium MD

$$j_z(p_x) = -\eta \frac{\partial v_x}{\partial z} \qquad j(p_x) = \frac{P_x}{2tA}$$

(Muller-Plathe, 1999)