Multiscale Materials Modeling

Lecture 07

Development of Coarse-Grained Potentials

Fundamentals of Sustainable Technology

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Development of Coarse-Grained Potentials

I. Introduction
II. Techniques
  II.A. Direct Potential Fitting
  II.B. Iterative Boltzmann Inversion
  II.C. Integral Equation Theory
III. Applications
  III.A. Small Molecules
  III.B. Nanoparticles
  III.C. Polymers
IV. Conclusions

Introduction

The purpose of coarse-grained simulations is to provide computationally tractable simulations of materials with a broad spectrum of dynamic modes that eliminate degrees of freedom, which are not crucial to understanding the particular physics of interest.

These coarse-grained (CG) simulations require potentials to describe the interaction between the CG particles.

The topic of this module is the procedures by which these CG interaction potentials are generated.

Techniques: Define Beads

polystyrene

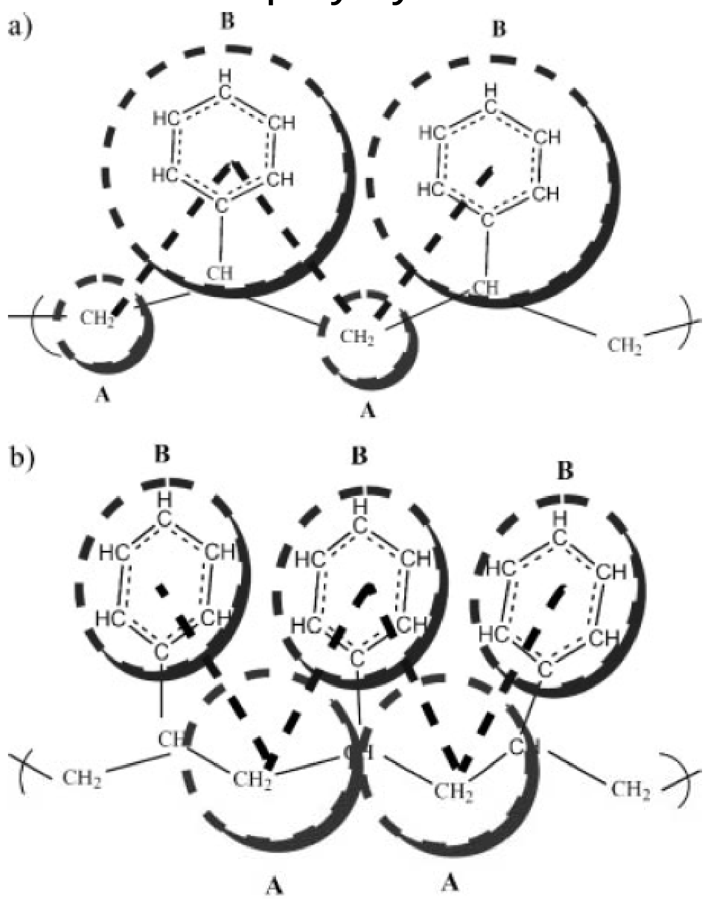
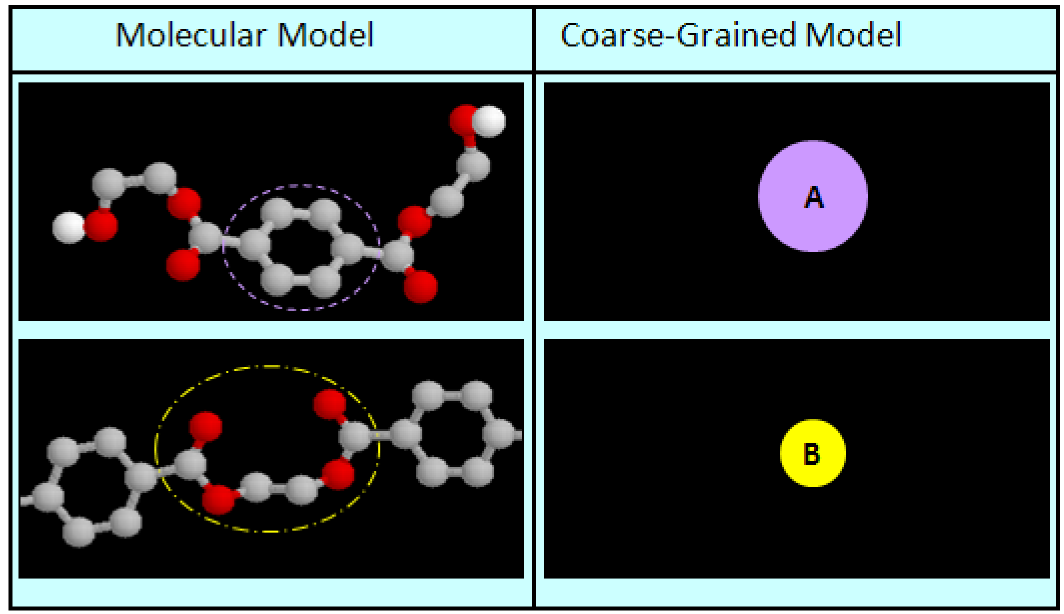


Figure 1. Two different coarse-graining mapping schemes of PS: (a) M1 model: mass ratio 1:6.5. (b) M2 model: mass ratio 1:2.8. Dashed lines show CG bonds between CG beads A and B.

Harmandaris et al., Macromolecular Chem. Phys., 2007.

PET



Wang, Q., et al. J.Phys.Chem.B, 2010.

Techniques: Direct Potential Generation

To generate the interaction potential between a CG bead of type A and a CG bead of type B:

1.Take an isolated fragment of the molecule corresponding to A and an isolated molecule corresponding to B and separate their center-of-masses by a distance r.
2. Compute the energy for each possible orientation and configuration, where the orientation must be averaged over all possible rotations and the configuration over all internal degrees of freedom (bending, stretching, torsion).
3. Compute the average A-A interaction energy as the potential of mean force.

$$\beta\, U_{\mathrm{PMF}}(r, T) = -\ln\langle \exp(-\beta U(r,\Gamma))\rangle_r.$$

4. Repeat for the next separation r.
5. This must be done again for each temperature.

Harmandaris et al., Macromolecules, 2006.

Techniques: CG Potential Functional Forms

Sometimes the CG potentials are left in tabular form as a function of separation, r.
Sometimes, they are fit to a given functional form.

$$U_{\mathrm{NB}}^{\mathrm{CG}}(r) = 4 \times \varepsilon[(\sigma_i/r)^{n_i} - (\sigma_i/r)^{m_i}] + U^{\mathrm{shift}}$$

Table 1. Values for the nonbonded parameters of Lennard–Jones-type potentials of model M2. The functional form is stated in Equation 6.

Interaction type	σ (Å)	n	m
A–A	4.10	7.0	6.0
A–B	4.65	7.0	5.0
B–B	5.20	7.0	4.0

Harmandaris et al., Macromolecular Chem. Phys., 2007.

Techniques: Iterative Boltzmann Inversion

To generate the interaction potential between a CG bead of type A and a CG bead of type B:

1.Perform an atomistic simulation of a small system or short chain system and generate the pair correlation function (PCF) for the center-of-mass of molecules or molecule fragments corresponding to CG beads.
2. Estimate the CG potential as

$$U_{\alpha\beta,0}(r) = -k_B T \ln\left(g_{\alpha\beta}(r)\right)$$

3. Perform CG simulations and generate PCFs.

4. Compare PCFs from atomistic and CG simulations. If they are the same, then you are done. If not, improve the potential estimate iteratively by

$$U_{\alpha\beta,i+1}(r) = U_{\alpha\beta,i}(r) + k_B T \ln\left(\frac{g_{\alpha\beta,i}(r)}{g_{\alpha\beta}(r)}\right)$$

Techniques: Iterative Boltzmann Inversion

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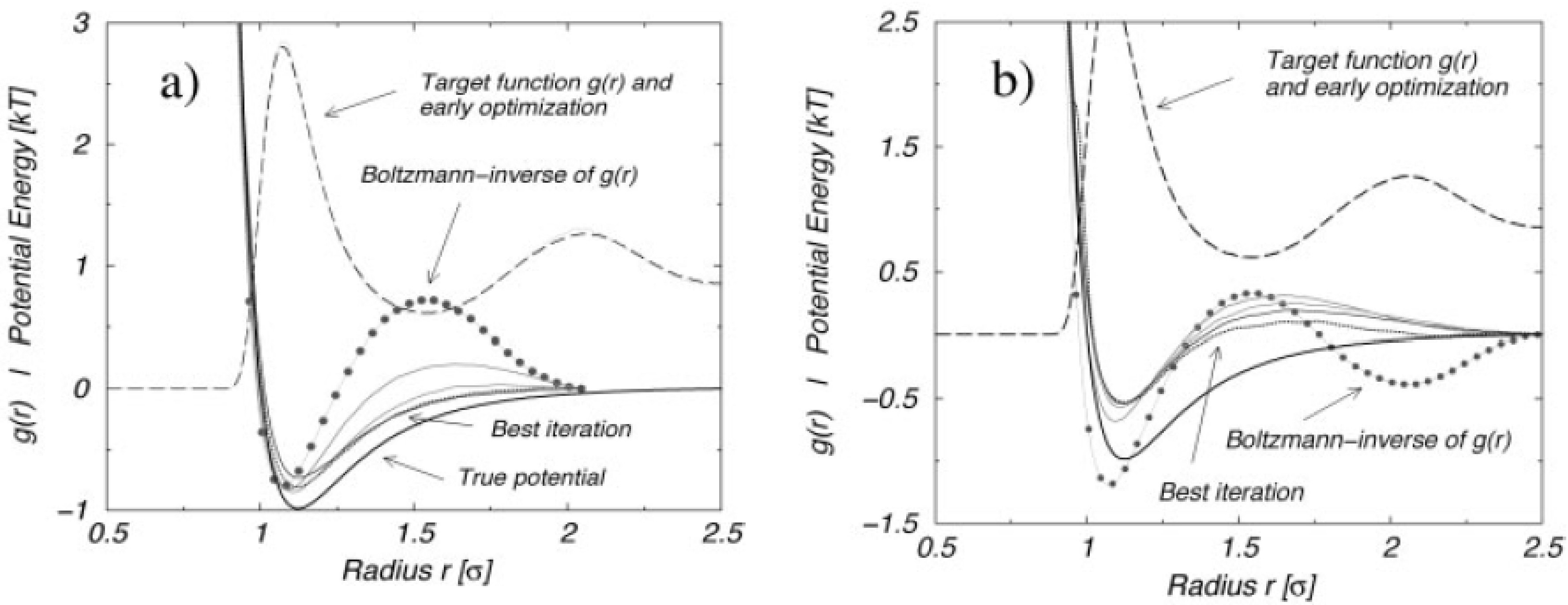


Figure 4. Potential reproduction test for a dense liquid of LJ model particles. In both cases, the optimization starts from the Boltzmann-inverted potential of the target RDF. The range of optimization is (a) 2.05σ, (b) 2.5σ. The latter equals the cut-off range of the original LJ system. For reasons of clarity, graphs from only some iteration steps are drawn. In every case, the target RDF can be quickly reproduced, however, the best iterative potentials do not exactly match the original function. By watching the slope note that the derivatives (i.e., the forces) match very well up to $r \approx 1.5\sigma$.

The IBI method cannot reproduce the LJ potential in a simple test of self-consistency, due to cut-off and statistical noise problems and poor sensitivity of the PCF to the potential.

Reith et al., J. Comput. Chemistry, 2003.

Techniques: Integral Equation Theory

The Ornstein-Zernike (OZ) Integral Equation is an exact relation between energy, u(r), and structure, g(r), because it introduces a new unkonwn, c(r).

$$g_{\alpha\beta}(r,r')-1=c_{\alpha\beta}(r,r')+\sum_{\gamma}\int c_{\alpha\gamma}(r,r'')n_{\gamma}(r'')\left[g_{\gamma\beta}(r'',r')-1\right]d^3r''$$

The Percus-Yevick approximation expresses the direct correlation function as

$$c_{\alpha\beta}(r,r')=g_{\alpha\beta}(r,r')\left[1-\exp\left(\frac{u_{\alpha\beta}(r,r')}{k_BT}\right)\right]$$

Cavity correlation function defined as

$$y_{\alpha\beta}(r,r')=g_{\alpha\beta}(r,r')\exp\left(\frac{u_{\alpha\beta}(r,r')}{k_BT}\right)$$

Total correlation function defined as

$$h_{\alpha\beta}(r,r')=g_{\alpha\beta}(r,r')-1$$

OZPY

$$y_{\alpha\beta}(r,r')=1+\sum_{\gamma}\int c_{\alpha\gamma}(r,r'')n_{\gamma}(r'')h_{\gamma\beta}(r'',r')d^3r''$$

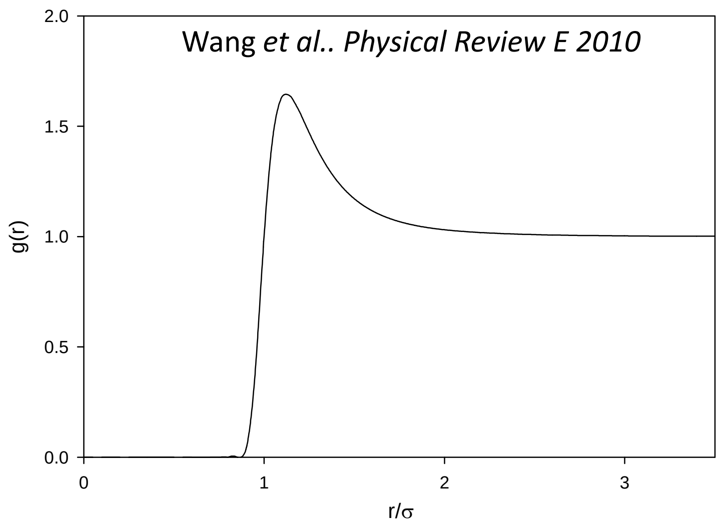
Techniques: Integral Equation Theory

The Ornstein-Zernike (OZ) Integral Equation

$$g(r)-1=c(r)+n\int c(s)h(t)\,\mathrm{d}V$$

- exact relationship between the pair correlation function (PCF) and the interaction potential.
- splits PCF into direct and indirect parts

PCF: probability of finding an neighboring particle at distance r, as shown right typical PCF of Argon from MD simulation at $T^* = 2.0$, $\rho^* = 0.005$.



The Percus-Yevick (PY) approximation

$$c(r) = g(r)\left[1-\exp\left(\frac{u(r)}{k_B T}\right)\right]$$

- estimation of direct correlation function so that the OZ equation can be solved.

Outline

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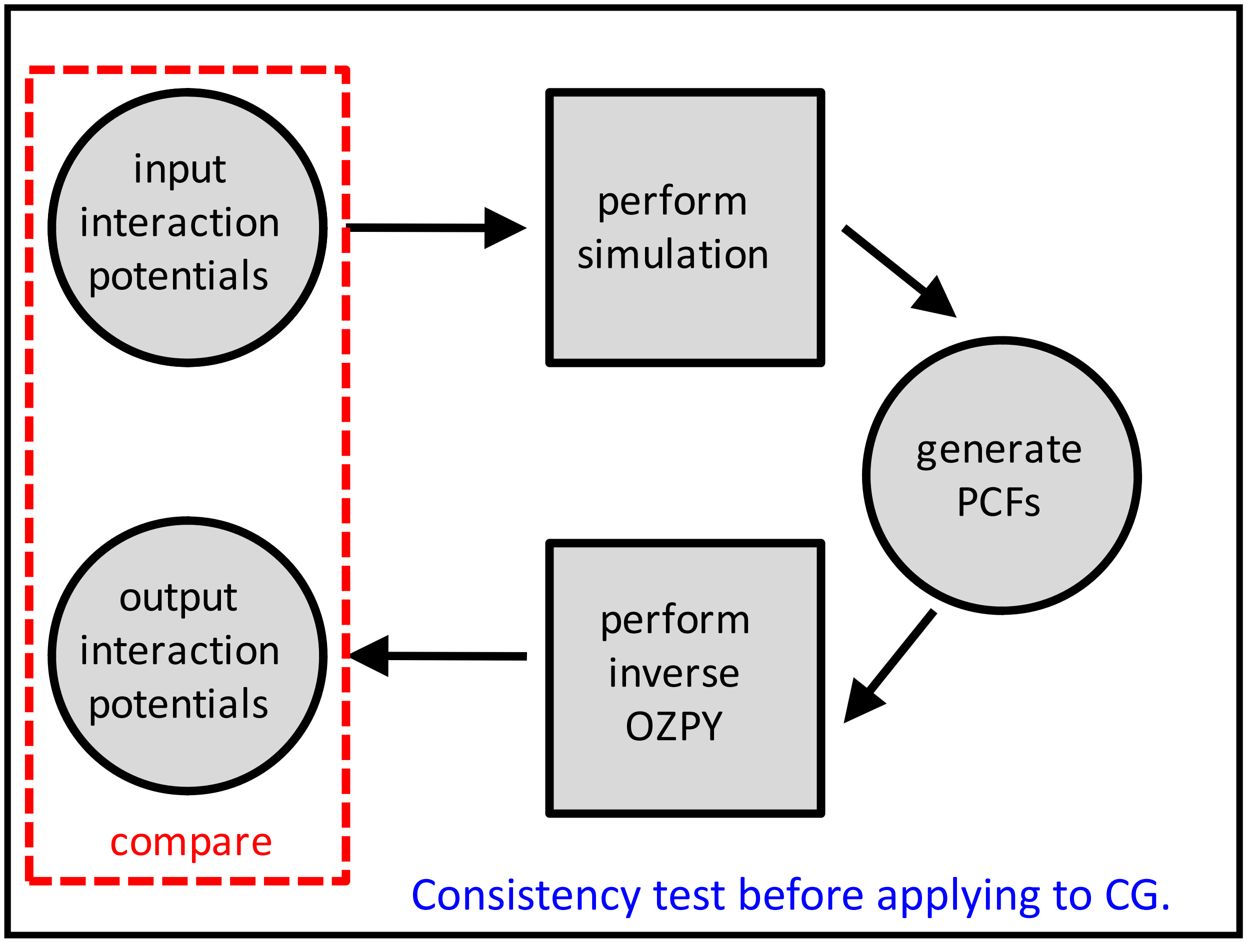
OZPY: Consistency Test

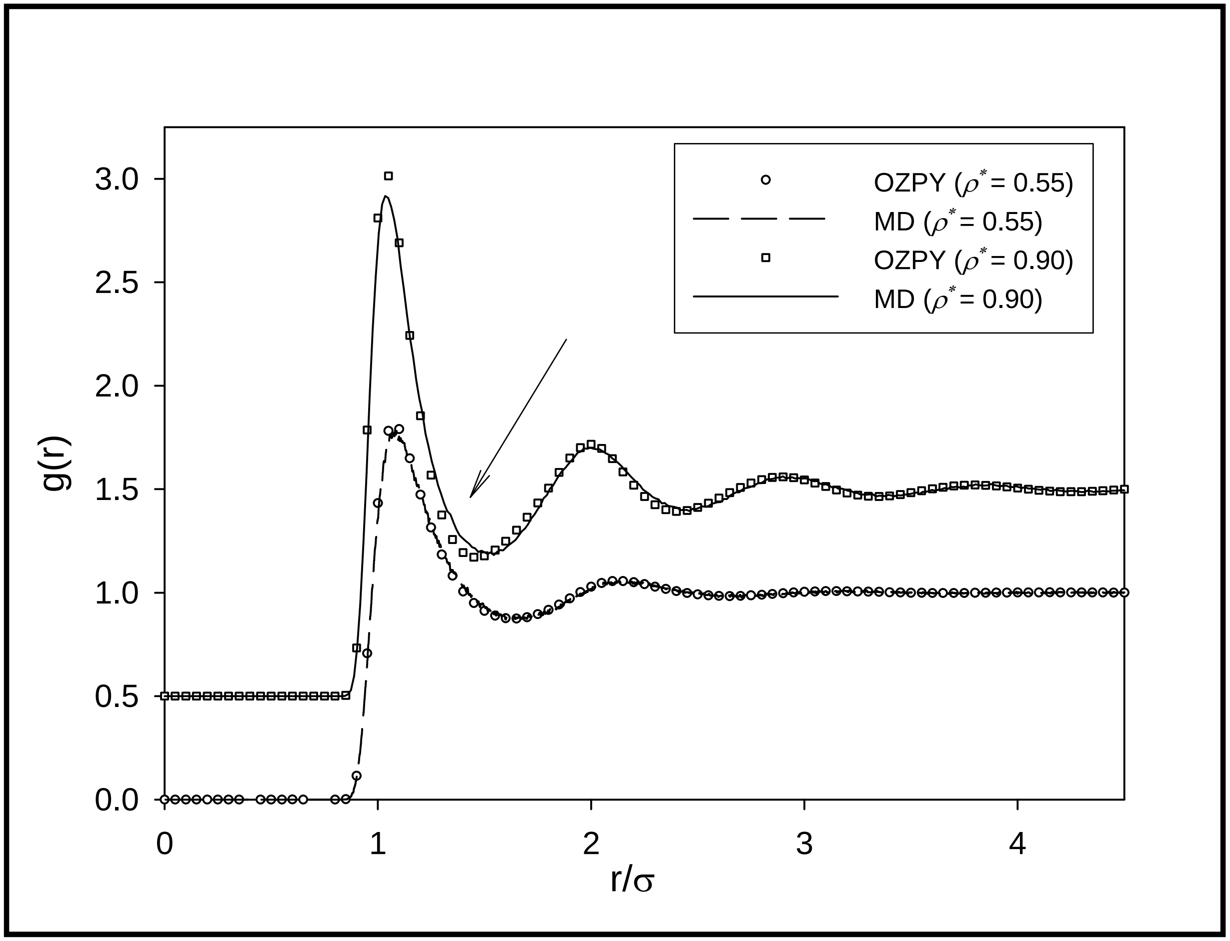
An alternative method that we develop and investigate here is to use the Ornstein-Zernike (OZ) equation with the Percus-Yevick approximation (OZPY) to extract the non-bonded potential from the PCFs.



OZPY: Typical Application

Given U, find PCF.

Comparison of PCFs from OZPY with MD simulation for monatomic fluid.



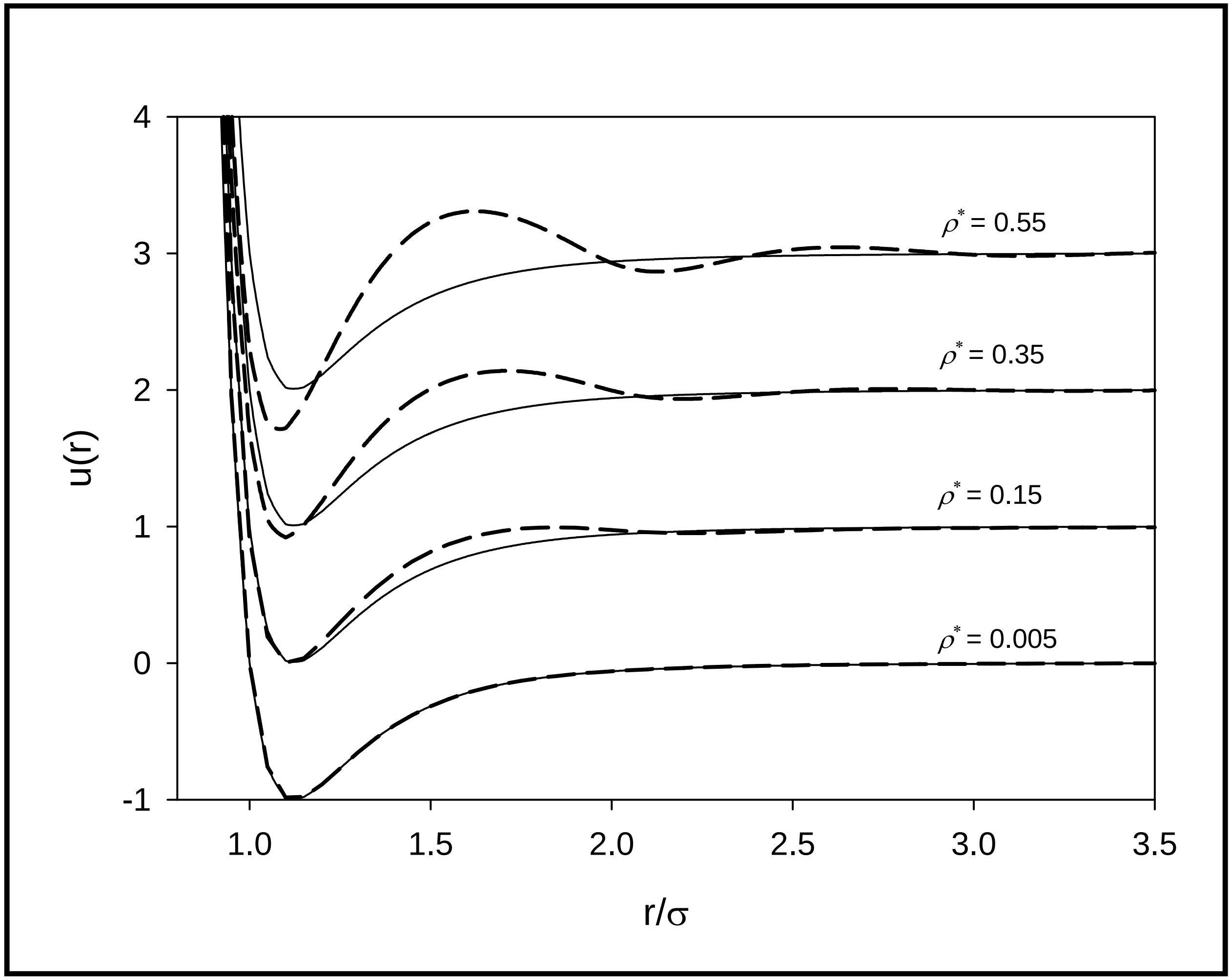
monatomic Lennard-Jones fluid

➢ **Good agreement in PCFs from OZPY and MD at low density, deviation at high density**

OZPY: Consistency Test

Simple inversion : only works at very low density of simple fluids

$$U_{\alpha\beta}(r) = -k_B T \ln\left(g_{\alpha\beta}(r)\right)$$



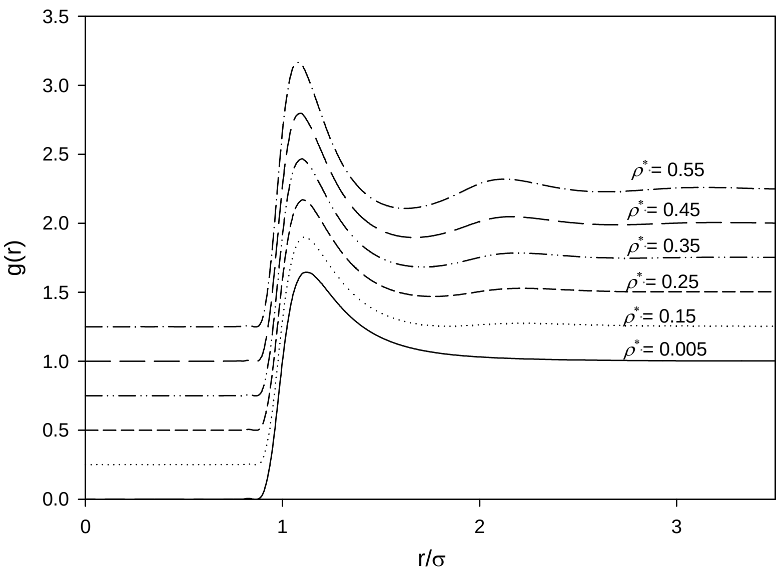
monatomic Lennard-Jones

only able to reproduce the correct potential at very low density.

OZPY: Consistency Test with Simple Fluid

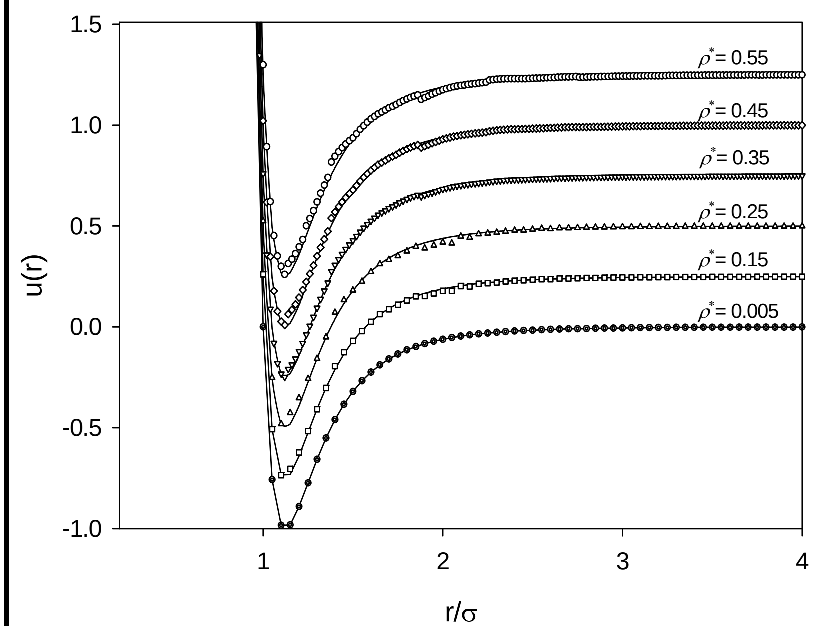
OZPY^{-1}: test of consistency on monatomic Lennard-Jones fluid

OZPY: Given U, find PCF



Pair Correlation Functions (PCFs) obtained by solving OZPY equation directly, under T^* =2.0, ρ^* from 0.005 to 0.55, here $T^* = T/\varepsilon$; $\rho^* = r\,\sigma^3$, the data has been shifted in vertical direction for clarity.

OZPY^{-1}: Given PCF, find U



Comparison of non-bonded interaction potential obtained by solving the OZPY equation inversely (symbol) and potential predicted by Lennard-Jones model (line), under the same conditions

- **The OZPY^{-1} is capable of reproducing the potentials in the density range studied here.**

OZPY: Consistency Test: Diatomic Fluids

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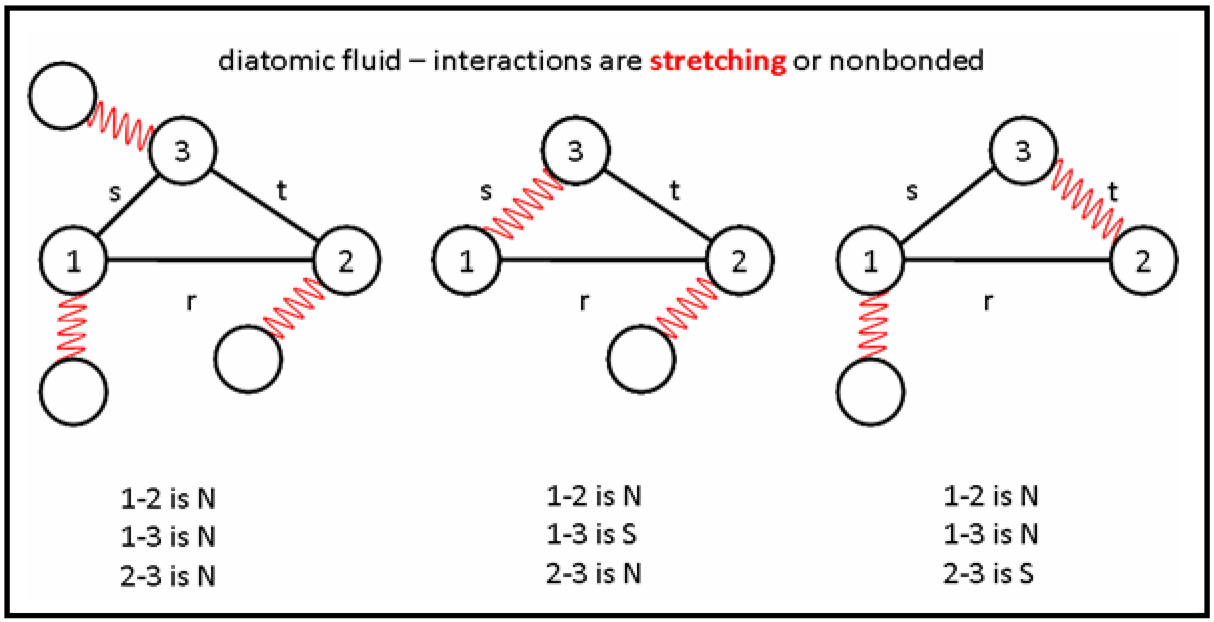
The OZPY equation for multi-component is

$$y_{\alpha\beta}(r) = 1 + \sum_{\gamma} \frac{2\pi n_{\gamma}}{r} \int_0^{\infty} \mathrm{d}s\, s \left[h_{\alpha\gamma}(s) - y_{\alpha\gamma}(s) + 1 \right] \int_{|r-s|}^{r+s} \mathrm{d}t\, t\, h_{\gamma\beta}(t)$$

$$h_{\alpha\beta}(r) = g_{\alpha\beta}(r) - 1 \qquad y_{\alpha\beta}(r) = g_{\alpha\beta}(r) \exp\left(\frac{u_{\alpha\beta}(r)}{k_B T} \right)$$

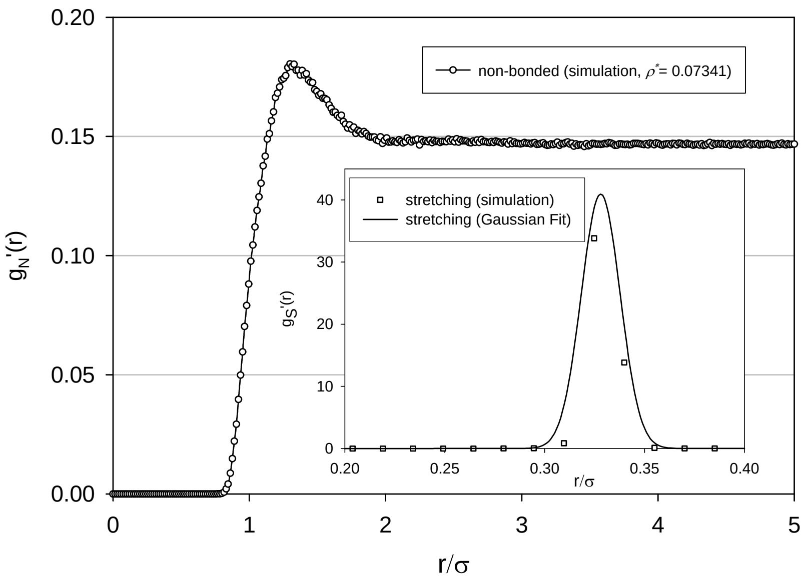
α, β, γ are the particles' relative possible positions, assume we have three particles, we fix particle 1 and 2 at positions α and β, particle 1 and 2 interact via non-bonded. The summation over γ counts all the possible particles that could sit at γ.



To get 1-2 non-bonded Interaction, we have to Integrate over all the possible particle 3.

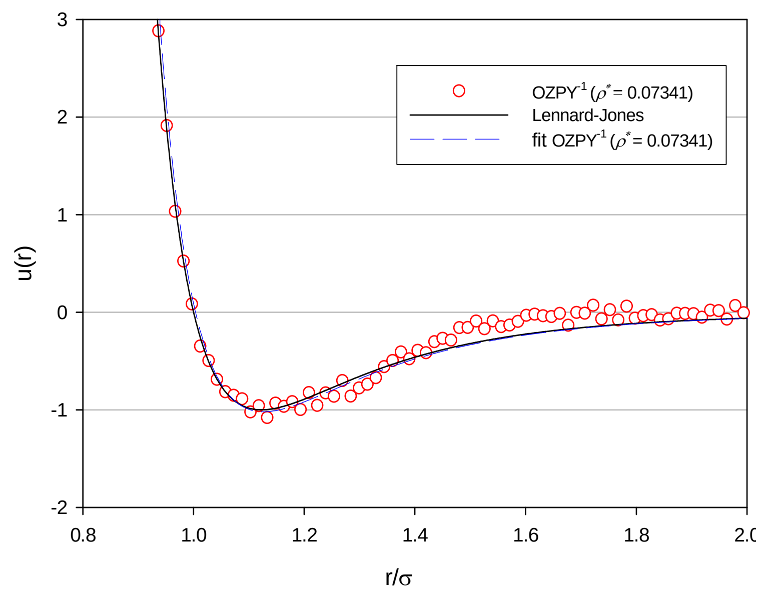
OZPY: Consistency Test: Diatomic Fluids

MD simulation



Bonded and non-bonded PCFs obtained from MD simulation of N_2 under T^* = 8.3333, ρ^* = 0.07341.

OZPY^{-1}



Raw data has some deviation
Fit of short-range data to LJ potential yields original parameters within 1%

- **The OZPY^{-1} is generally able to reproduce the non-bonded potential in the presence of a bonded potential at low density.**

OZPY: Consistency Test: Diatomic Fluids

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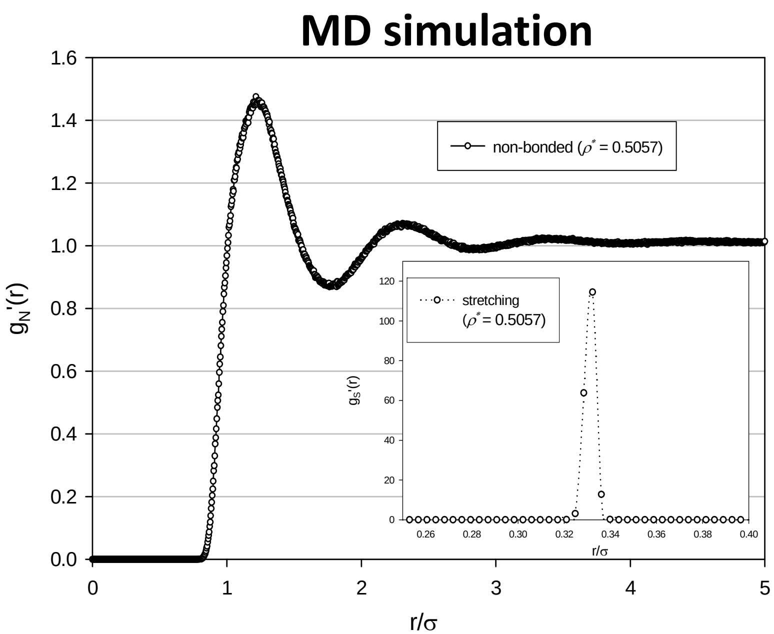
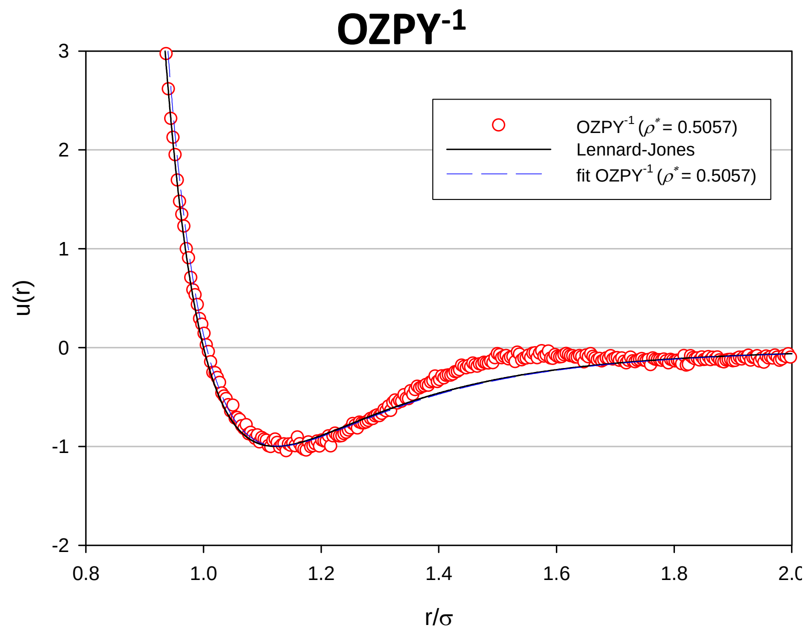


Bonded and non-bonded PCFs obtained from MD simulation of N_2 under T^* = 5.5556, ρ^* = 0.5057.



Raw data has some deviation
Fit of short-range data to LJ potential yields original parameters within 1%

➢ **The $OZPY^{-1}$ is generally able to reproduce the non-bonded potential in the presence of a bonded potential at high density.**

Applications: Nanoparticles

Nanoparticles: a uniform distribution of particles interacting with a Lennard-Jones interaction

$$U_{\mathrm{LJ}}(r) = 4\varepsilon_{\mathrm{nn}}\left[\left(\frac{\sigma_{\mathrm{n}}}{r}\right)^{12} - \left(\frac{\sigma_{\mathrm{n}}}{r}\right)^{6}\right]$$

Total interaction between two nanoparticles includes attractive and repulsive parts.

Total: $$U_{\mathrm{nn}}(r) = U^{\mathrm{A}}_{\mathrm{nn}}(r) + U^{\mathrm{R}}_{\mathrm{nn}}(r)$$

Attractive: $$U^{\mathrm{A}}_{\mathrm{nn}}(r) = -\frac{A_{\mathrm{nn}}}{6}\left[\frac{2a^2}{r^2-4a^2} + \frac{2a^2}{r^2} + \ln\left(\frac{\mathrm{r}^2-4\mathrm{a}^2}{\mathrm{r}^2}\right)\right]$$

Repulsive: $$U^{\mathrm{R}}_{\mathrm{nn}}(r) = \frac{A_{\mathrm{nn}}}{37800}\frac{\sigma_{\mathrm{n}}^6}{r}\left[\frac{r^2-14ra+54a^2}{(r-2a)^7} + \frac{r^2+14ra+54a^2}{(r+2a)^7} - \frac{2(r^2-30a^2)}{r^7}\right]$$

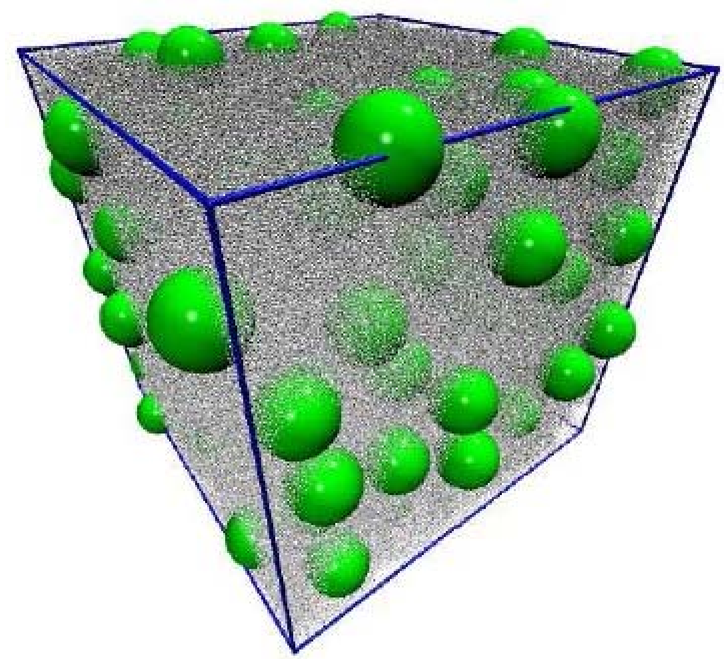


FIG. 1. Sample simulation cell for 167 nanoparticles of radii $a = 10\sigma$ for $\phi_{\mathrm{v}} = 0.20$ in an explicit solvent with $A_{\mathrm{ns}} = 100\varepsilon$. The 1 771 400 solvent atoms are shown as points.

Applications: Nanoparticles

Each nanoparticle is now a bead. The solvent is now implicit. It only exists in the interaction potential.

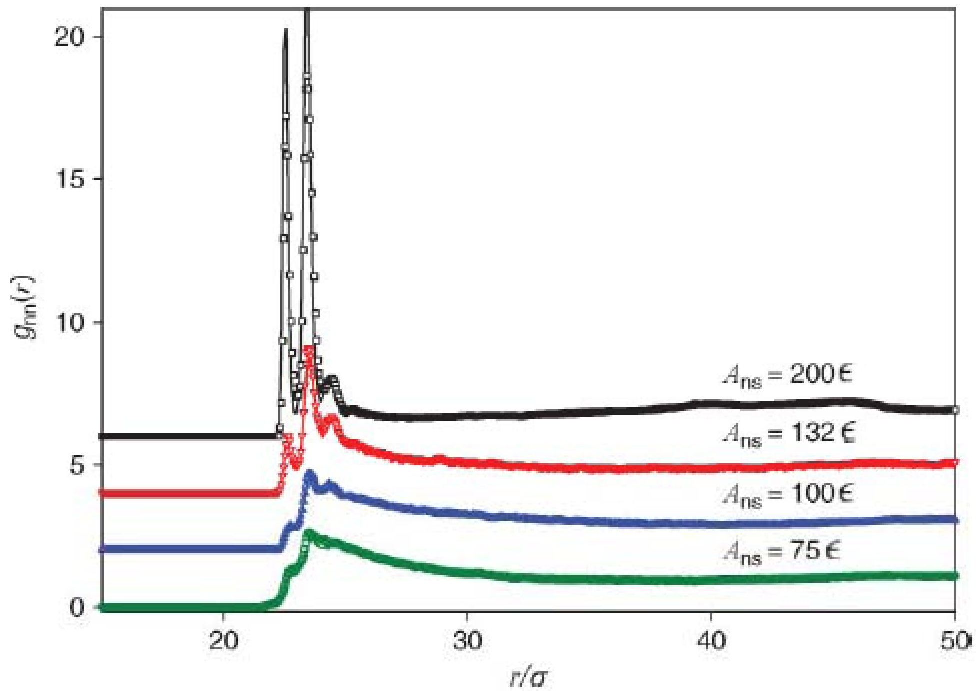


FIG. 3. Nanoparticle–nanoparticle pair correlation functions $g_{nn}(r)$ for nanoparticles of radii $a = 10\sigma$ for volume fraction $\phi_V = 0.20$ and $A_{ns} = 75$, 100, 132, and 200ε. The solid lines are the original PDF's while the points are from the MD simulation using the effective nanoparticle interaction potential $U_{nn}^{eff}(r)$. The curves have been shifted vertically for clarity.

Comparison of the atomistic and CG PCFs for nanoparticles.

Applications: Nanoparticles

The CG interaction potential between nanoparticles can capture effects of the strength of the solvent for the nanoparticle.

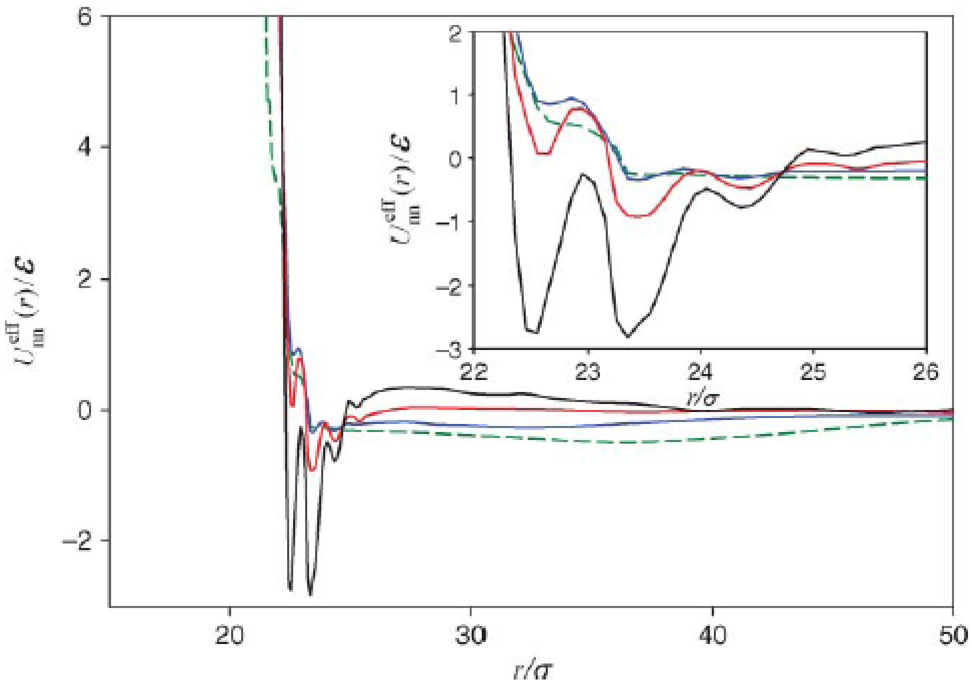


FIG. 7. Effective pair potential $U_{nn}^{eff}(r)$ between nanoparticles in an explicit LJ solvent for nanoparticles of radii $a = 10\sigma$ and volume fraction $\phi_v = 0.20$ for $A_{ns} = 75, 100, 132$, and 200ε. The inset shows an expansion of the region near contact.

Applications: Polymers

Direct Potential Fitting: Polystyrene

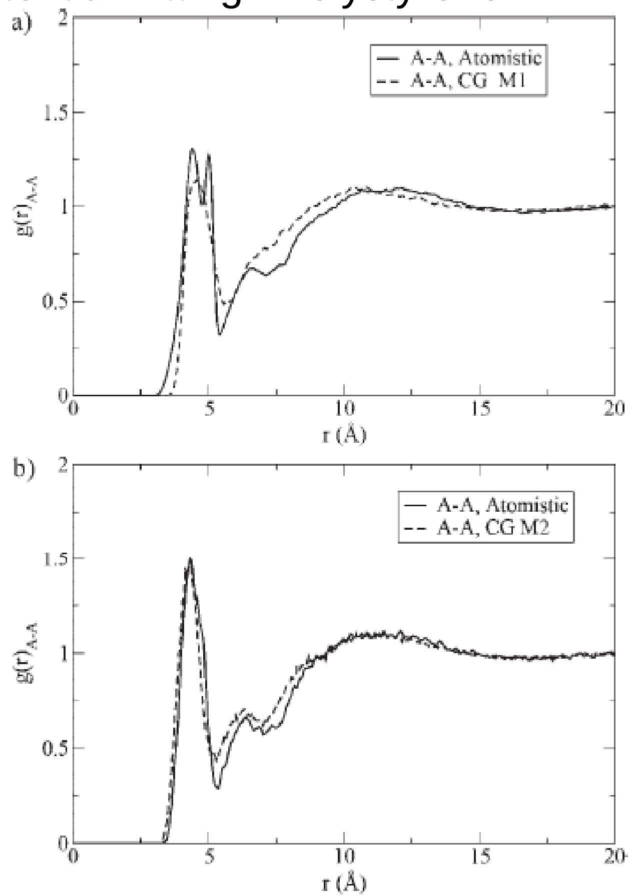


Figure 6. Nonbonded A–A pair distribution function for a PS melt (MW = 1 kDa, T = 463 K), obtained from atomistic MD (full lines) and CG simulations, analyzed in the two CG mapping schemes: (a) CG M1 and (b) CG M2.

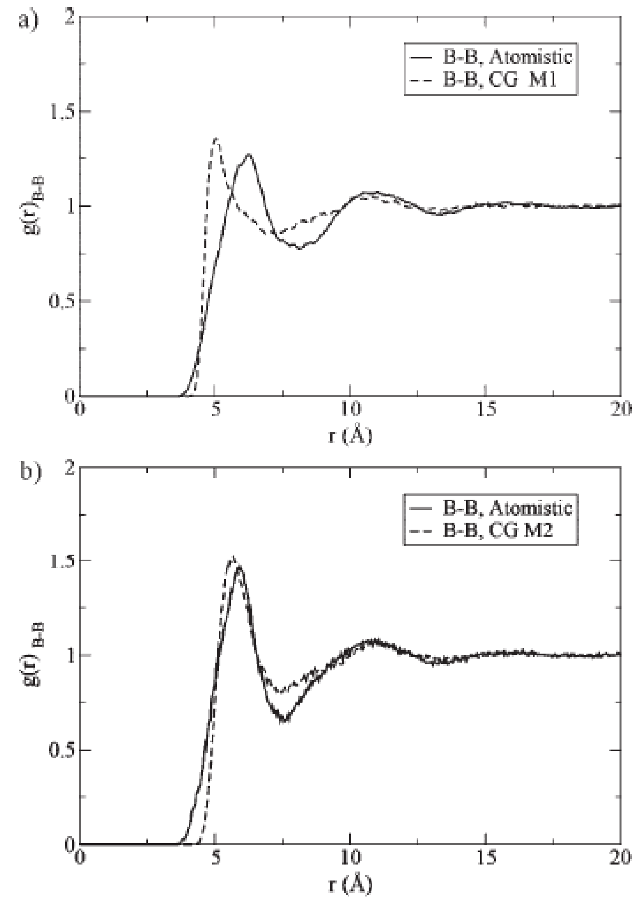
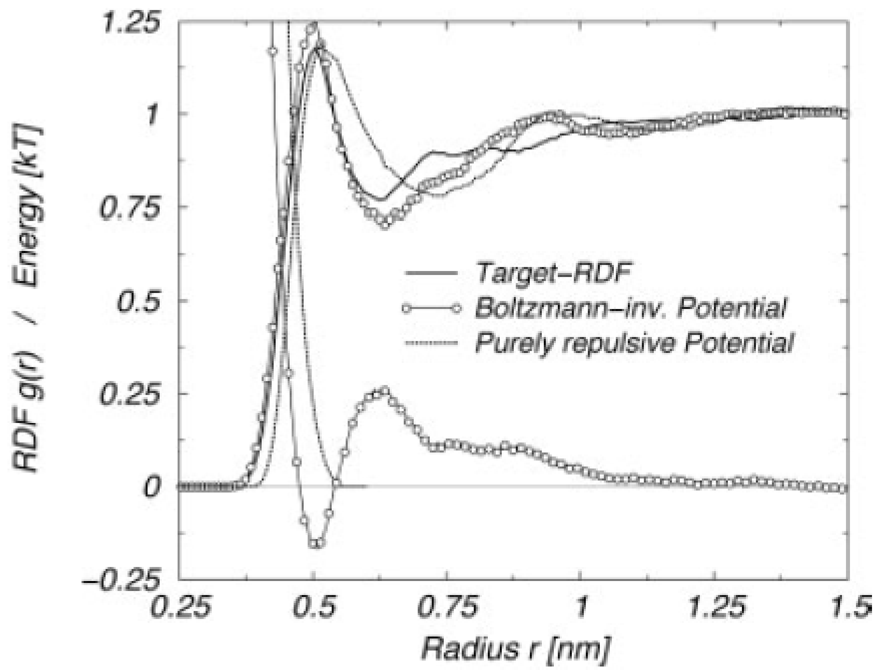


Figure 7. Nonbonded B–B pair distribution function for a PS melt (MW = 1 kDa, T = 463 K), obtained from atomistic MD (full lines) and CG simulations, analyzed in the two CG mapping schemes: (a) CG M1 and (b) CG M2.

Harmandaris et al., Macromolecular Chem. Phys., 2007.

Applications: Polymers

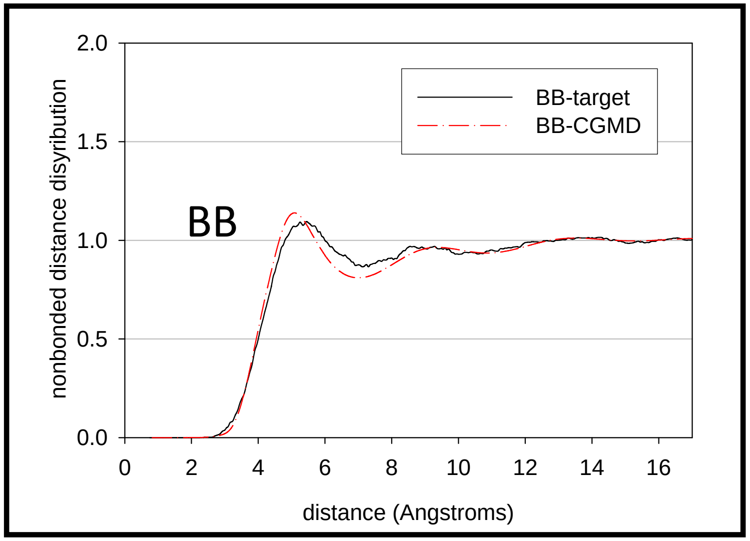
Inverse Boltzmann Inversion: Polyisoprene

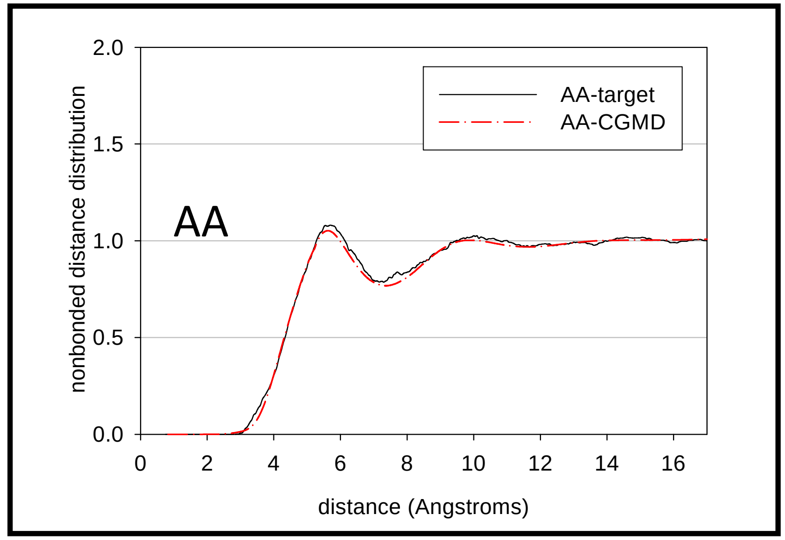


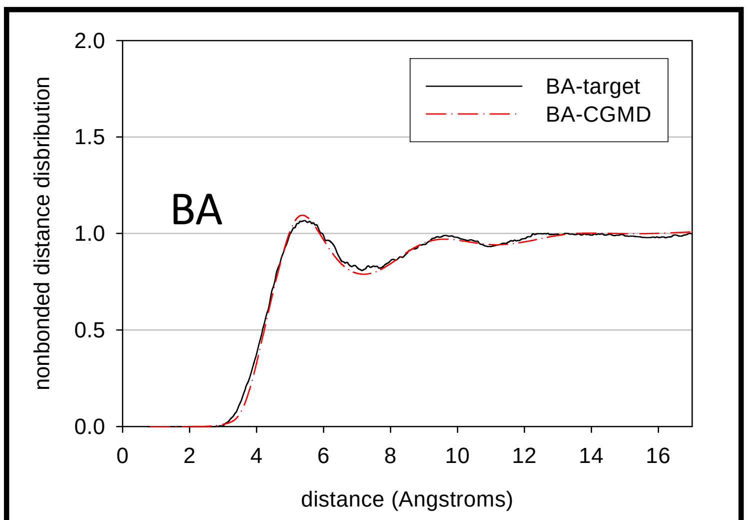
Reith et al., J. Comput. Chemistry, 2003.

Applications: Polymers

Ornstein-Zernike Percus-Yevick Integral Equation Theory: PET







Wang et al., Macromolecules, 2010.

Applications: Polymers

OZPY Integral Equation Theory: PEG

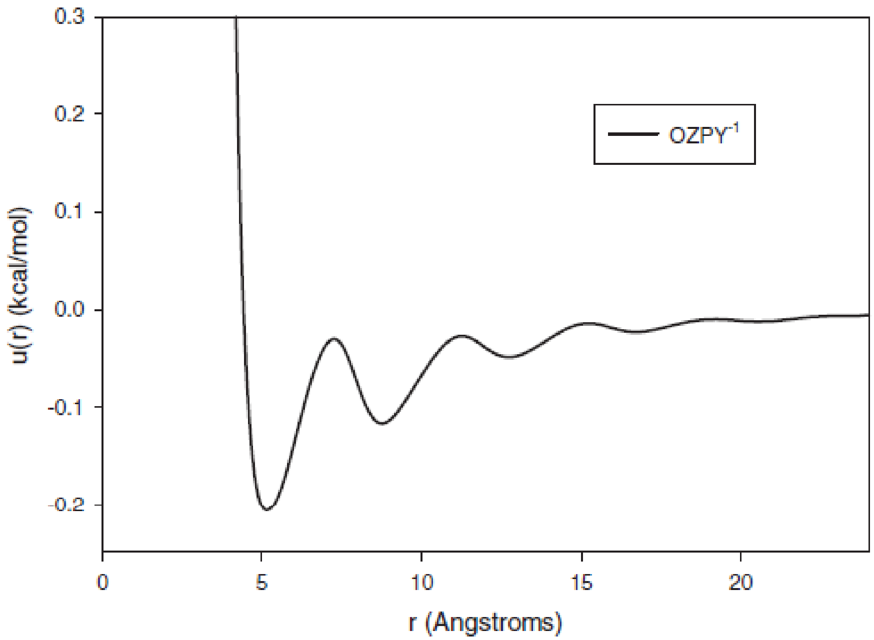


FIG. 4. Coarse-grained nonbonded potential from the OZPY^{-1} method.

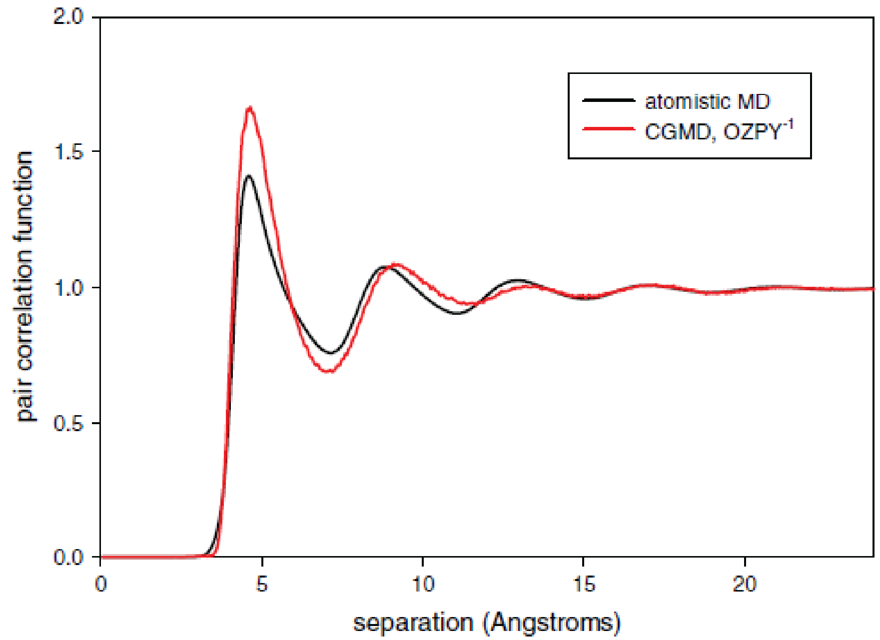


FIG. 5. Comparison of CG nonbonded pair correlation functions for PEG (DP = 20) from atomistic and CGMD simulations using the potential from the OZPY^{-1} method.

Wang et al., J. Chem. Phys., 2011.

Applications: Polymers

IBI initialized by OZPY Integral Equation Theory: PEG

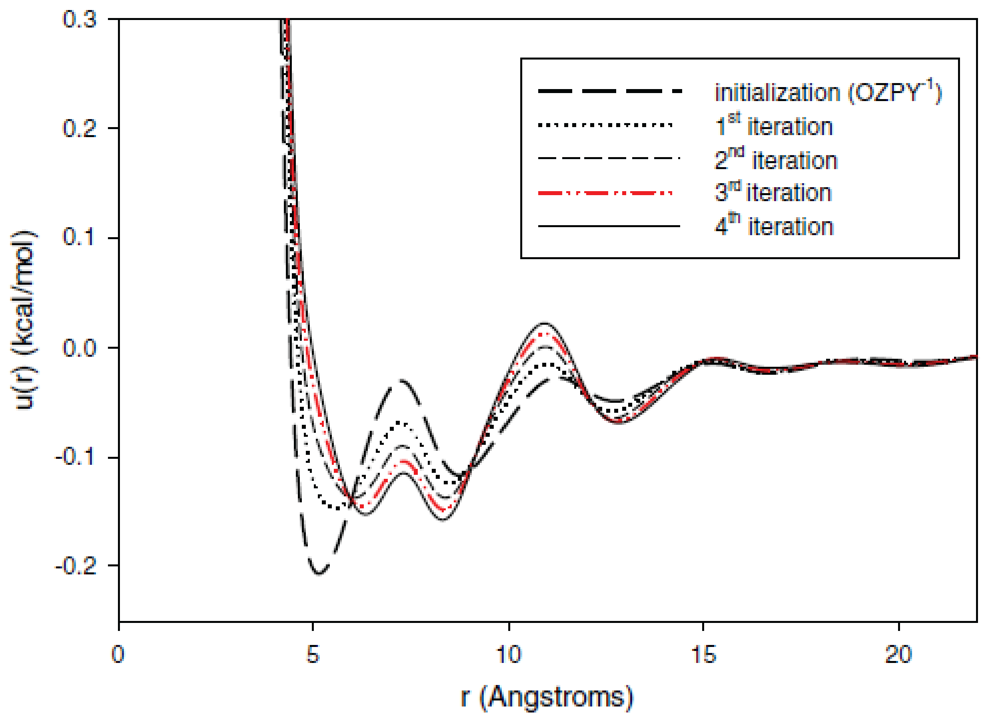
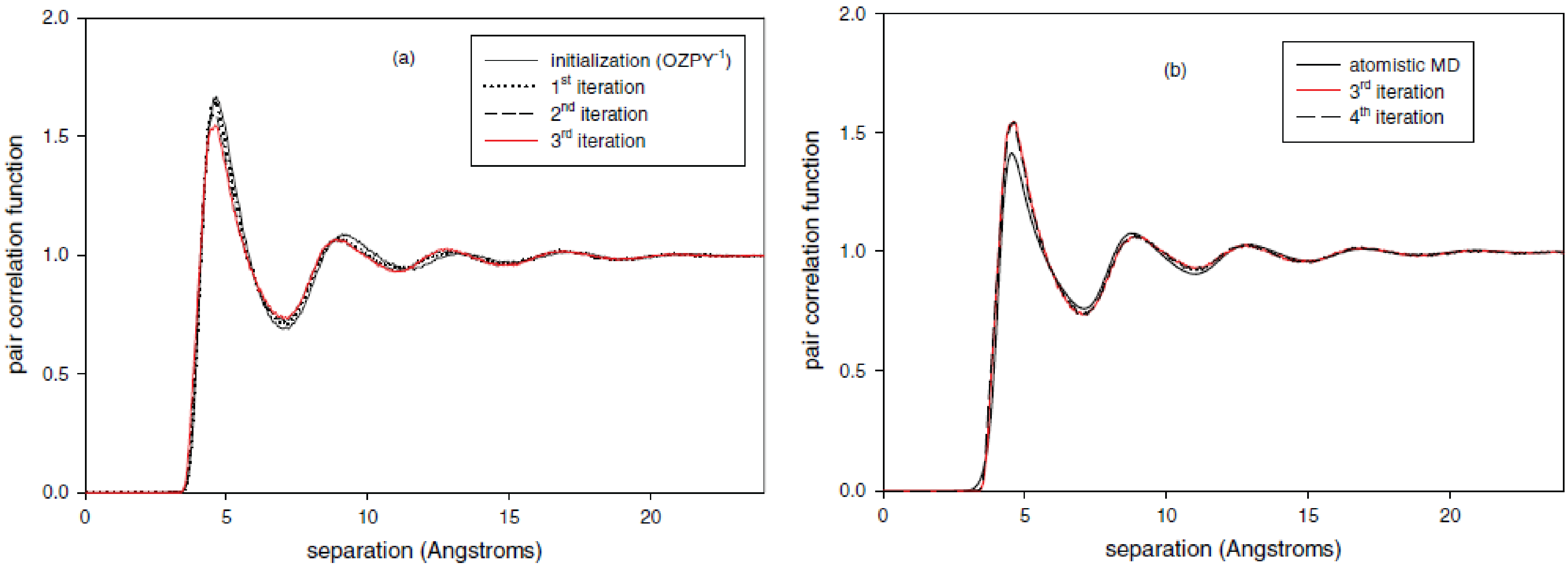


FIG. 6. Coarse-grained nonbonded potentials for PEG (DP = 20) from the $OZPY^{-1}$+IBI method. The potential from $OZPY^{-1}$ (Figure 4) serves as initial guess for the IBI method.

Wang et al., J. Chem. Phys., 2011.

Applications: Polymers

IBI initialized by OZPY Integral Equation Theory: PEG

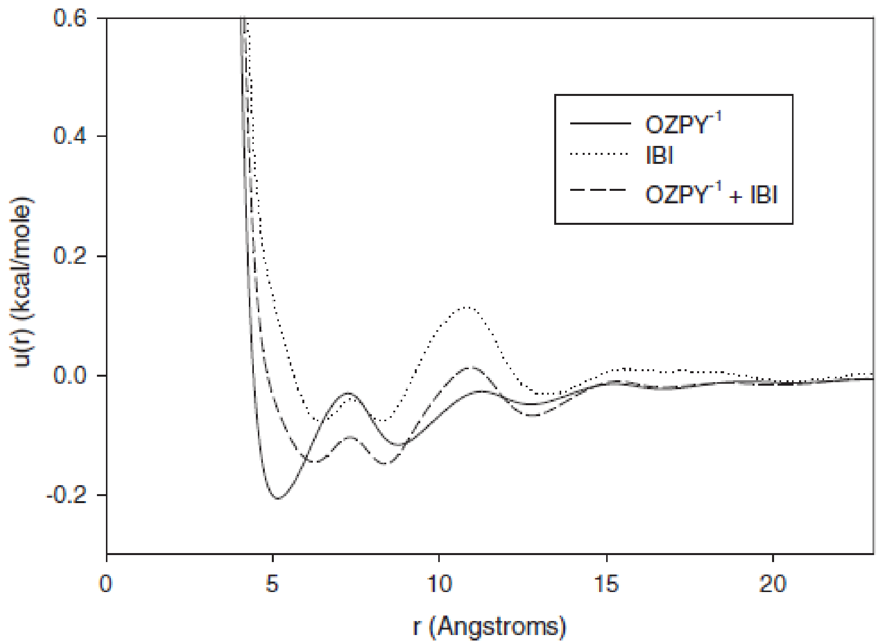


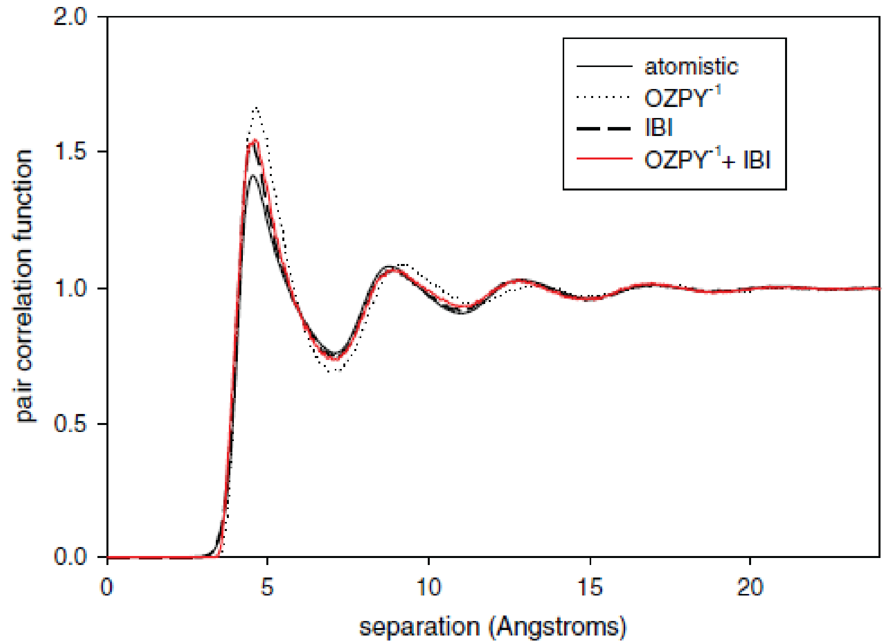
Subsequent conversions do not get first peak height correct.
There are limitations in the convergence of the iterative method due to sensitivity to noise and long range interactions.

Wang et al., J. Chem. Phys., 2011.

Applications: Polymers

IBI initialized by OZPY Integral Equation Theory: PEG





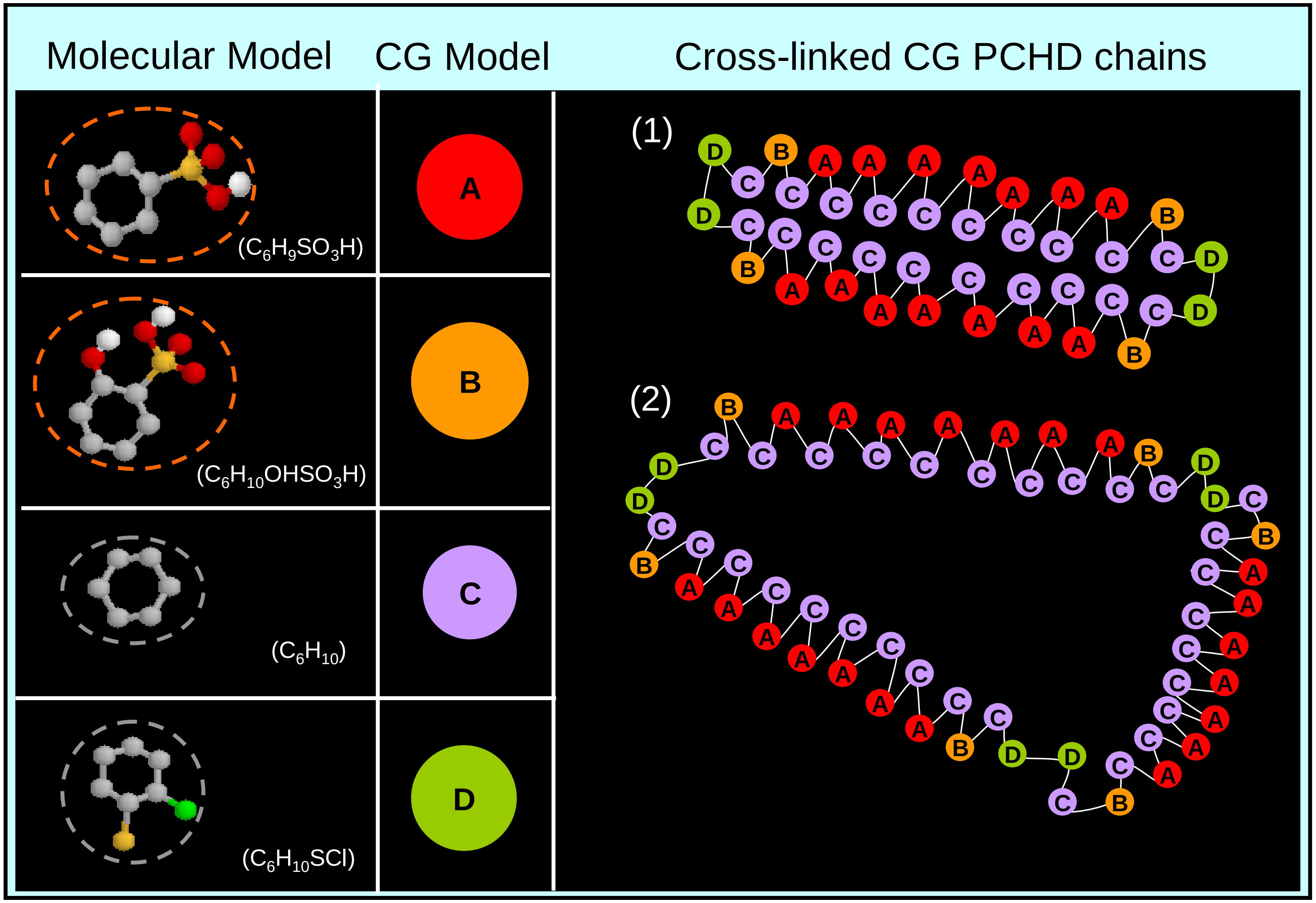
In comparing the different methods, the structures look very similar but the potentials are very different.

The PCF has poor sensitivity to the shape of the potential.

Wang et al., J. Chem. Phys., 2011.

Applications: Polymers

IBI: PCHD



This complex polymer has different types of A and C beads.

Wang et al., polymer, 2012.

Applications: Polymers

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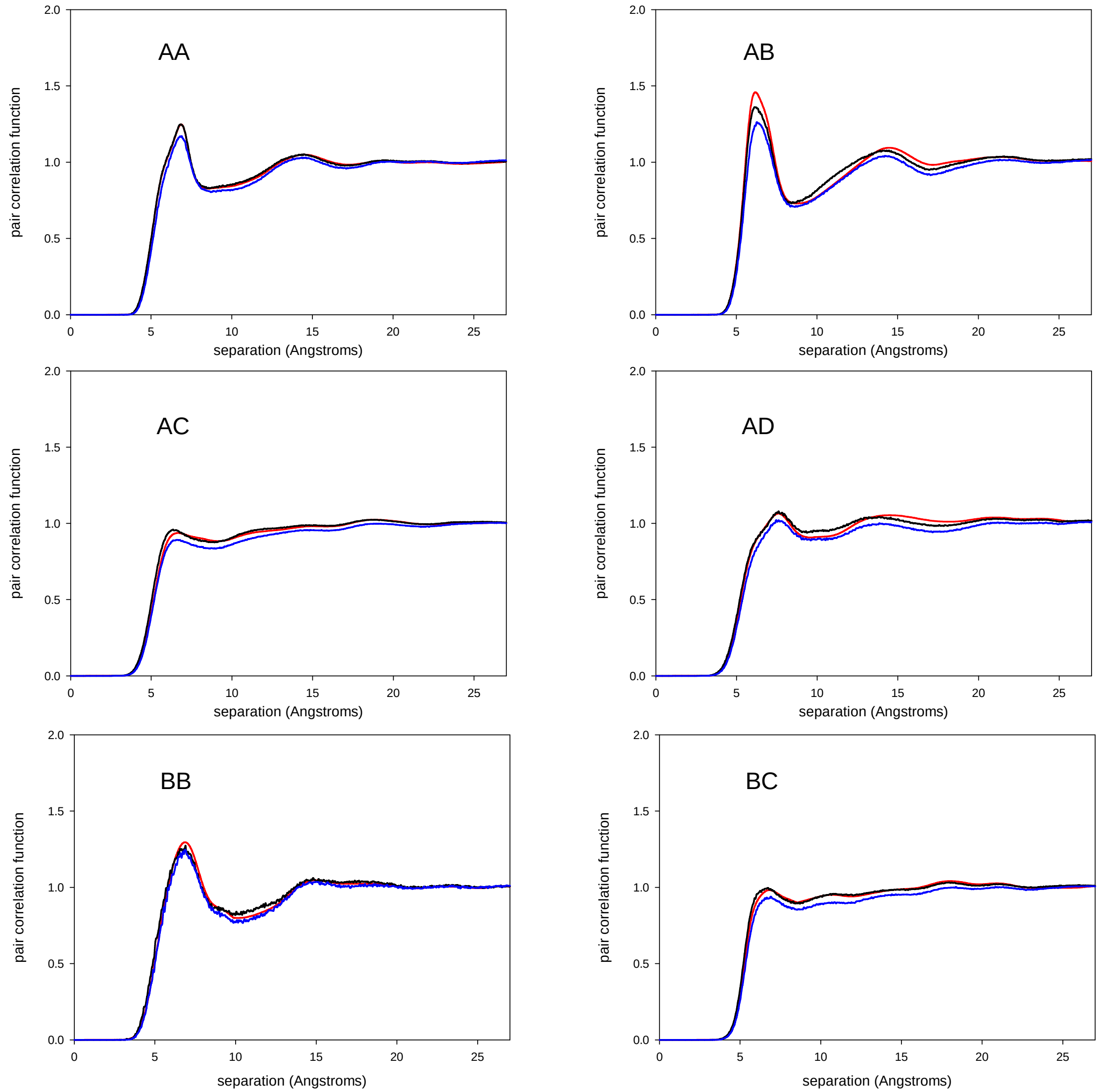
IBI:
PCHD



Red line:
Atomistic-
two chains
cross-linked

Black line:
CG-
two chains
cross-linked

Blue line:
CG-
three chains
cross-linked

The OZPY method failed due to complex nature of polymer. Results for IBI for 6 of 10 modes.

Wang et al., polymer, 2012.

Transferability

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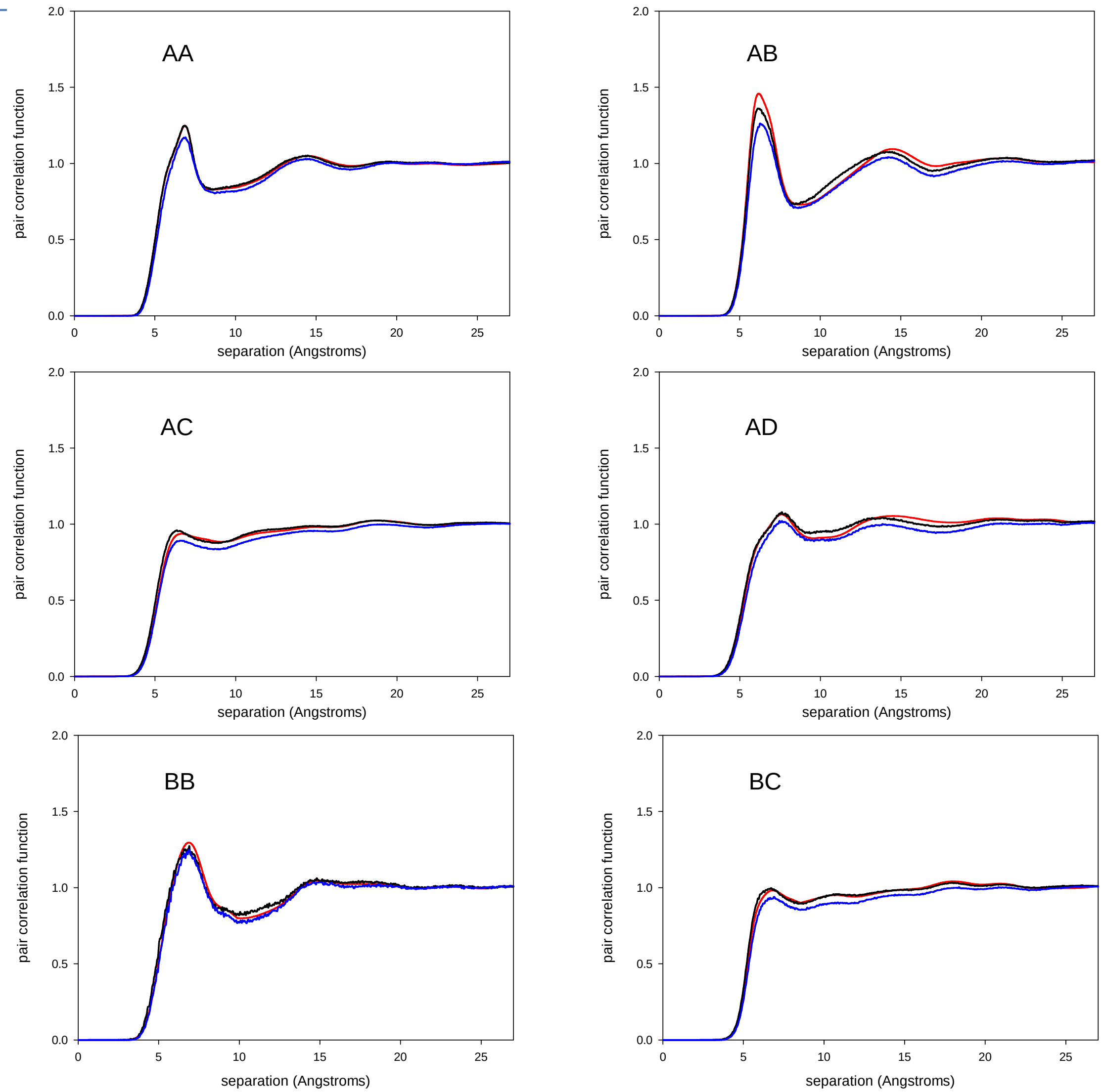
IBI:
PCHD



Red line:
Atomistic-
two chains
cross-linked

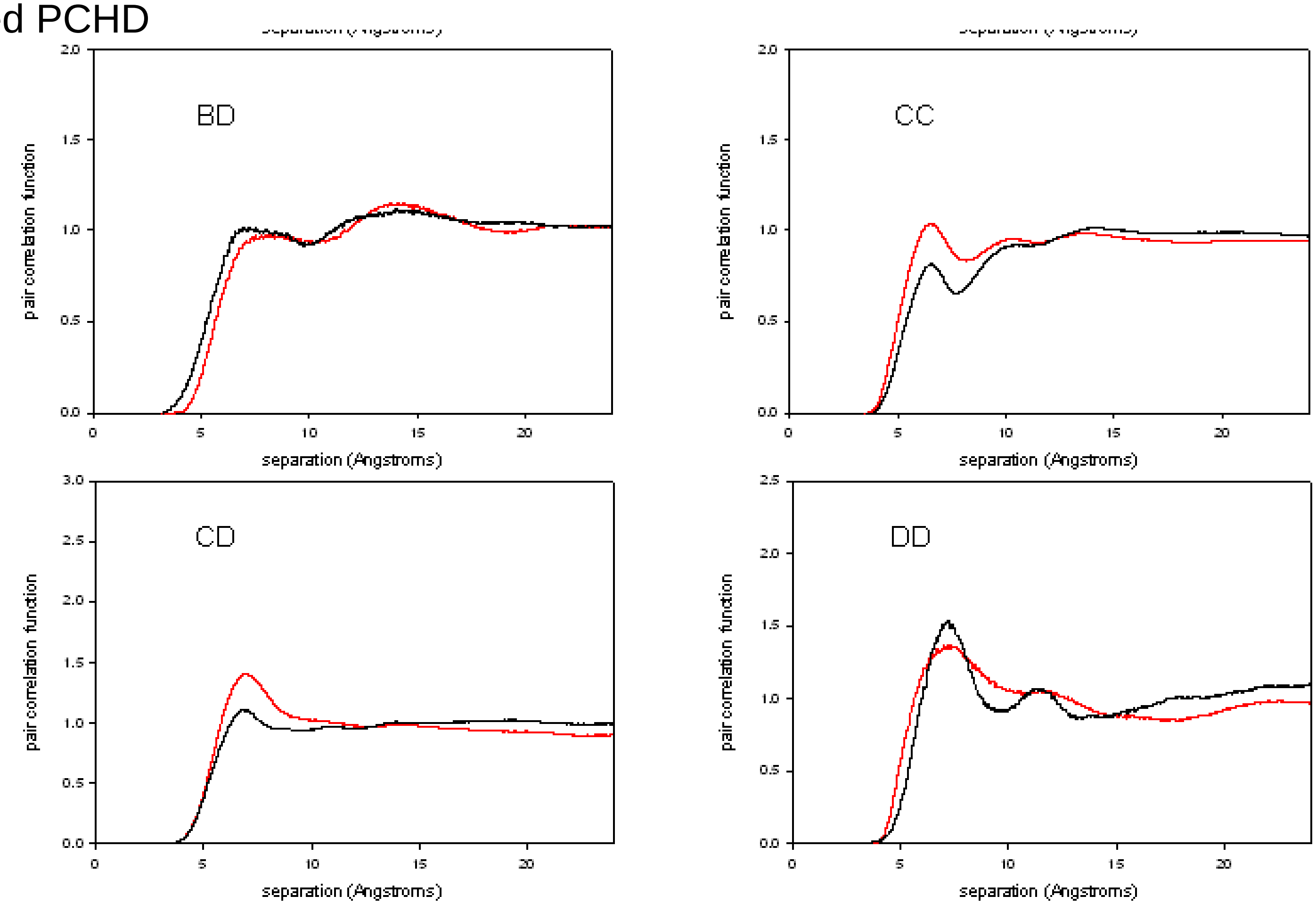
Black line:
CG-
two chains
cross-linked

Blue line:
CG-
three chains
cross-linked

CG potentials are generally transferable aross chaing lengths, so parameterization to short chains is okay..

Transferability

IBI: hydrated PCHD

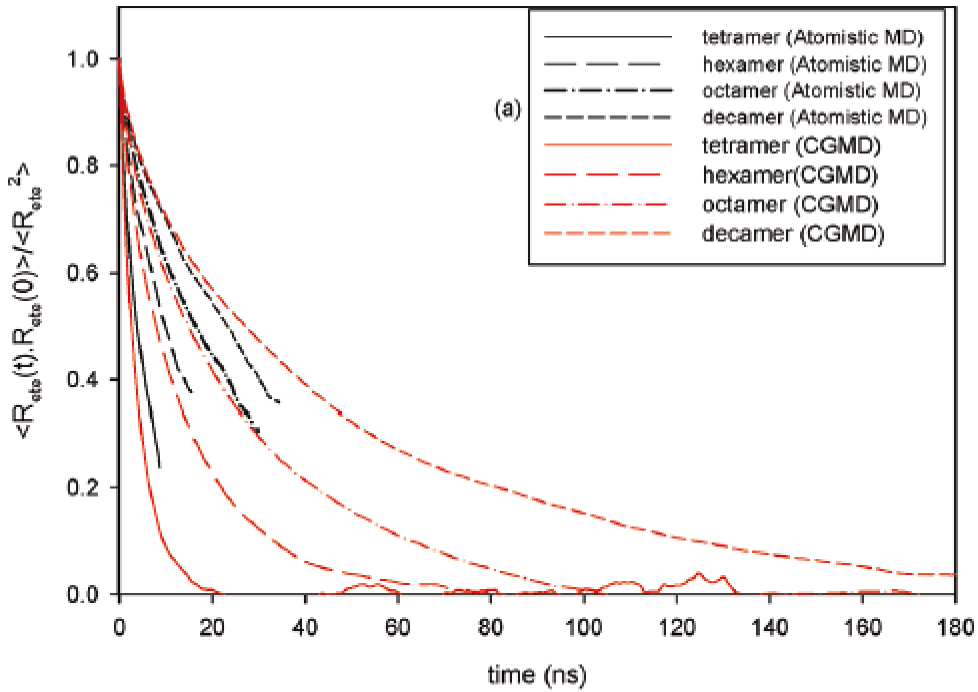


Here we look at a CG hydrated PCHD membrane at (λ = 15 H_2O/HSO_3) using CG potentials parameterized at (λ = 10 H_2O/HSO_3) and (λ = 20 H_2O/HSO_3) . The structure is different so the results are not transferable across different water contents.

Wang et al., under review, 2012.

Dynamics

When one uses structure to validate CG potentials, other features like dynamics may not match.



In order to get a good comparison for relaxation times, time was scaled in the CG simulation by an empirically determined factor of 7.5. 1 CG fs = 7.5 atomistic fs. Why? CG molecules are smoother and thus generate less friction, allowing them to move more quickly. All dynamic properties, relaxation times, diffusivities, viscosities, thermal conductivities are impacted by this.

Conclusions

Before one can perform coarse-grained simulations, one must generate course-grained interaction potentials.

There are several different methods for generating these potentials. No one method is perfect. Work still needs to be done.

The CG potentials can be solvent explicit (solvent molecules treated as CG beads) or solvent implicit (solvent incorporated in the CG potential).

The CG potentials are in general not transferable to other temperatures, densities and compositions. This must be validated.

The dynamics of CG simulations are skewed. Currently, empirical scaling factors are used to correct the dynamics.