Investigating the State Point Dependence of Coarse Grained Potentials Across a Glass Transition

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Abstract

The application of coarse grained (CG) models are becoming more common to model systems unattainable by molecular dynamics. The effective potentials that are used to govern the CG interactions are state-point dependent, which limits the transferability of models to state points at which they were not parameterized. Force-matching and pressure-matching were employed to determine the effective potentials across the glass transition temperature of OTP. The pair potentials become increasingly attractive with increasing temperature at constant pressure, however at the constant liquid density, the pair potentials become increasingly repulsive with increasing temperature. At constant glass density, the pair potentials do not display monotonic trends with temperature and thus do not behave as a molecular liquid.

Introduction

Coarse grained models that utilize a potential of mean force (PMF) parameterized from an atomistic model often struggle with both a transferability and representability problem. The transferability problem appears when a model parameterized at a given state point does not be reflect the effective potential at a different state point.[2] Previous studies have investigated both the density and temperature dependence of CG effective potentials in molecular liquids, revealing monotonic trends with temperature and density. More interestingly, the density dependence has been shown to dominate over the temperature dependence.[4]

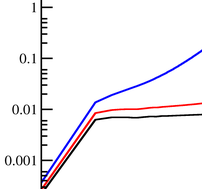


Figure 1: Ortho terphenyl (OTP) in atomistic (ball and stick) representation.

OTP is a small glass forming molecule that has been studied intensely in attempts to better understand both the dynamic and structural anomalies that occur at a glass transition.[1] Typically, simulation models of glassy state points struggle to obtain the necessary statistics to be confident in calculations. Structure based coarse grained models can provide a valuable tool to overcome the problems with traditional MD simulations, however the parameterization of a model that can reproduce both the liquid and glassy state is non trivial. A better understanding in how the effective potential across the glass transition varies will help build models that can help uncover the intricate nature of a glass transition. The goal of this study is to determine the temperature and density dependence of the PMF across the glass transition of OTP.

Atomistic Simulations

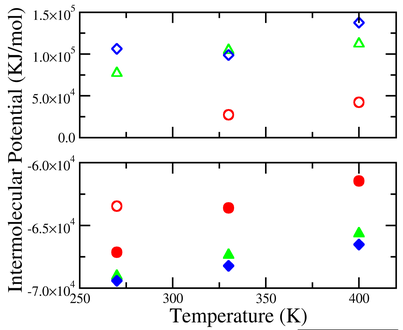


Figure 2: Average intermolecular potential vs temperature. The solid symbols represent atomistic simulations and the hollow symbols represent the corresponding CG simulation.

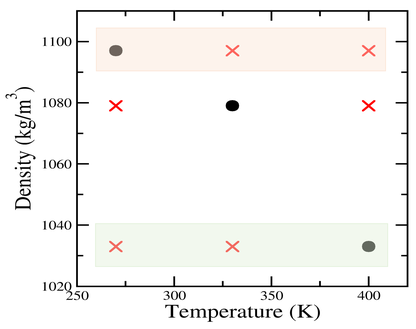


Figure 3: State points for atomistic simulations. Black circles signify state points simulated in the NPT ensemble, while red crosses signify state points simulated in the NVT ensemble..

Figure 4: Mean square displacement vs. time on a logarithmic scale

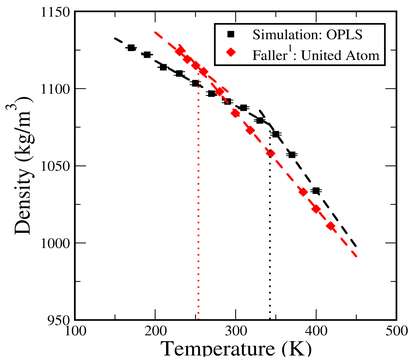


Figure 5: Density vs. temperature. The dashed lines represent linear fits to the two density regimes and the dotted vertical lines represent the calculated glass transition temperature

Coarse Grained Models

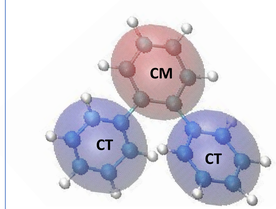


Figure 6: Ortho terphenyl (OTP) in atomistic (ball and stick) and coarse-grained (blue and red spheres) representations.

$$\exp[\beta W(\boldsymbol{R};V,T)] = V^{N-n}\int \exp[\beta u(\boldsymbol{r})]\,\delta(M(\boldsymbol{r})-\boldsymbol{R})$$

$$W(\boldsymbol{R};V,T) \sim U(\boldsymbol{R},V)$$

$$U(\boldsymbol{R},V) = U_R(\boldsymbol{R}) + U_V(V)$$

$$U_{R,}(\boldsymbol{R}) = \sum_{(I,J)} U_2(R_{IJ})$$

$$U_V(V) = N\left(\psi_1\frac{V}{\bar{v}} + \psi_2\left(\frac{V}{\bar{v}}-1\right)^2\right)$$

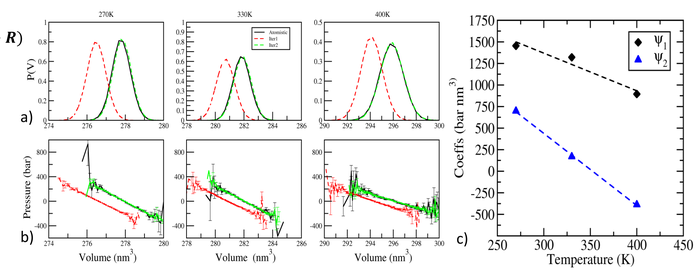


Figure 7: a) Volume distributions of the atomistic model and subsequent pressure matching iterations. b) Pressure-Volume equation of state obtained from iterations of pressure matching to reproduce the atomistic PV equation of state. c) Final volume correction coefficients determined from pressure matching.

CG NPT Simulations

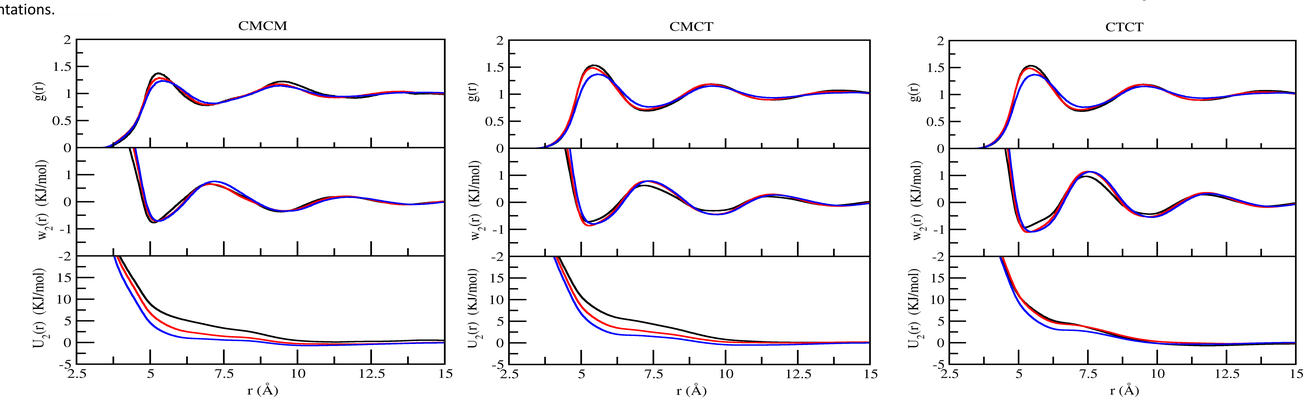
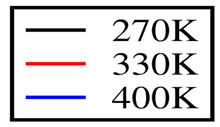


Figure 8: Pair potentials obtained from coarse grained simulations of 800 OTP molecules at a constant external pressure of 1 bar. (Top) radial distribution function. (Middle) pair potential of mean force. (Bottom) site pair interaction potentials from MS-CG



CG NVT Simulations

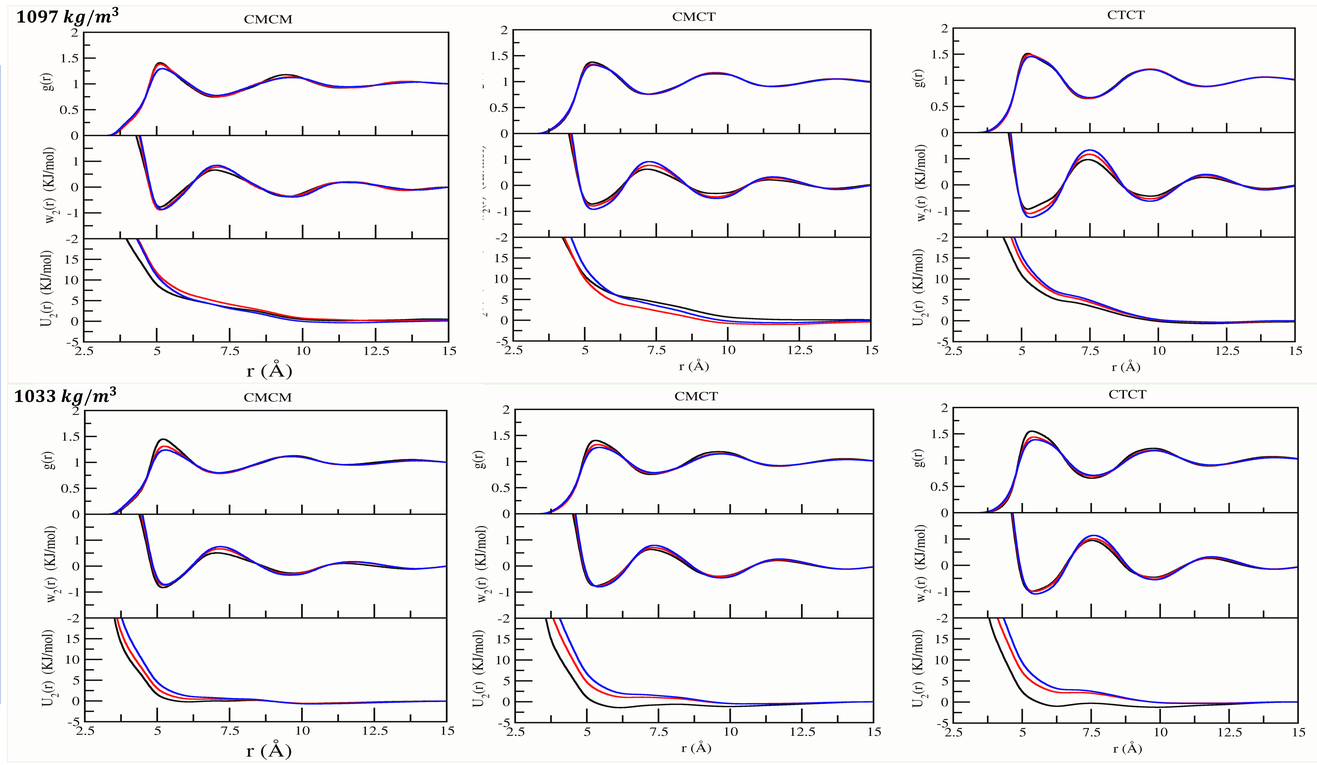


Figure 9: Pair potentials obtained from coarse grained simulations of 800 OTP molecules at constant density across the temperature range. Average volume was calculated from the NPT simulation and then used to simulate the corresponding density at the other temperatures (Top) radial distribution function. (Middle) pair potential of mean force. (Bottom) site pair interaction potentials from MS-CG

Conclusions:

- At the glass density, the pair potentials do not exhibit monotonic trends with temperature
- The MS-CG pair potential trends calculated at constant external pressure are opposite in direction as the trend at constant density in the liquid state
- The glass density NVT calculations show very small differences across the temperature range studied, with different features observed for the different interaction types

BOCS
https://github.com/noid-group/BOCS

References:

1. Ghosh, Jayeeta, and Roland Faller. *Molecular Simulation* 33.9-10 (2007): 759-767.
2. Noid, William George. " *The Journal of chemical physics*139.9 (2013): 09B201_1.
3. Dunn, Nicholas JH, and William George Noid. *The Journal of chemical physics* 143.24 (2015): 243148.
4. Lebold, Kathryn M., and William George Noid. *The Journal of chemical physics* 150.1 (2019): 014104.

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