# 2-Molecule RISM: Validating RISM Theory With MD Simulation

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Introduction

Molecular modeling has progressed in leaps and bounds in the last few decades, largely due to exponential improvements in computer hardware, but also due to new theory-based approaches, specifically reference interaction site module, or RISM theory. The goal of this new approach is to combine the accuracy of molecular dynamics simulations and the speed of theory-based simulations. Unfortunately, there are still limitations to RISM theory, such as poor closure equations that cause errors in systems with attractive forces. Luckily, Chandler and Weeks were able to decompose the equation for intermolecular potential, the Lennard-Jones equation, into just the repulsive term, which is optimal for high density systems that are chiefly described by repulsive interactions. With this repulsive only function, RISM simulation results can be more appropriately cross-referenced with accurate molecular dynamics simulations.
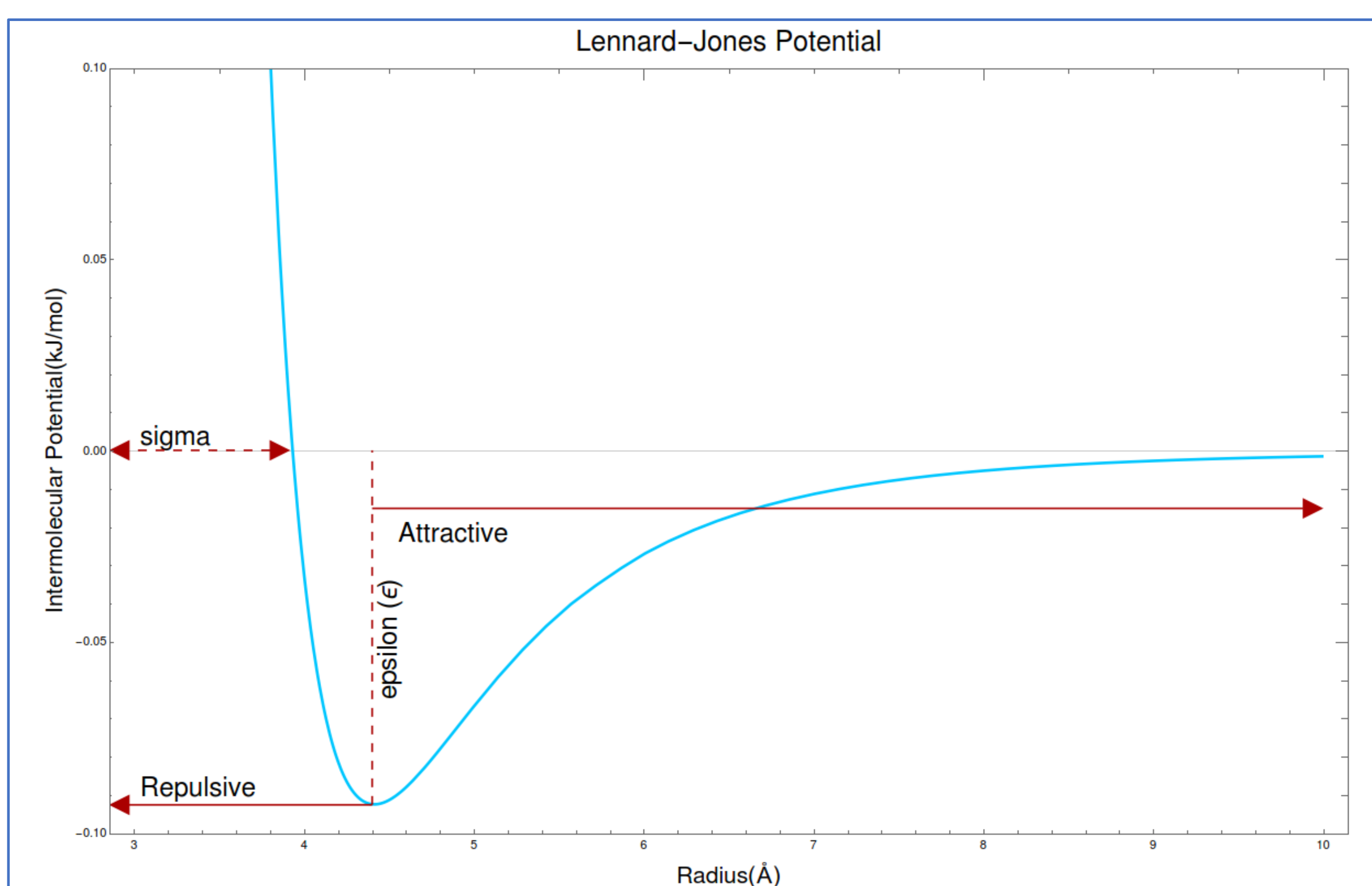
A standard graph of the Lennard-Jones potential with labeled components.

The Lennard-Jones potential is a two-part piecewise function that describes the intermolecular potential between molecules at a radius r. The first of the two terms describes the steep repulsive forces that exist between atoms at close distances due to the Pauli exclusion principle. The second term describes the attractive forces that exist due to Van der Waals forces.

$$V(r)=4\epsilon\left[\left(\frac{\sigma}{r}\right)^{12}-\left(\frac{\sigma}{r}\right)^{6}\right]$$

The repulsive Lennard-Jones potential appears to be quite similar to the full Lennard-Jones potential, but crucially cuts off at $r \geq 2^{\frac{1}{6}}\sigma$. This is because the bottom of the well (where epsilon defines the depth) will always be at $r = 2^{\frac{1}{6}}\sigma$ so the equation defines only repulsive forces.

$$V(r)=4\epsilon\left[\left(\frac{\sigma}{r}\right)^{12}-\left(\frac{\sigma}{r}\right)^{6}+\frac{1}{4}\right]$$
$$r \geq 2^{\frac{1}{6}}\sigma$$

Methods

GROMACS, a molecular dynamics software, has a feature that allows the user to supply his or her own functions to describe intermolecular potentials. This feature was attempted to be used to define intermolecular potentials according to the repulsive Lennard-Jones potential by supplying a table values defined by the equation for the repulsive potential.
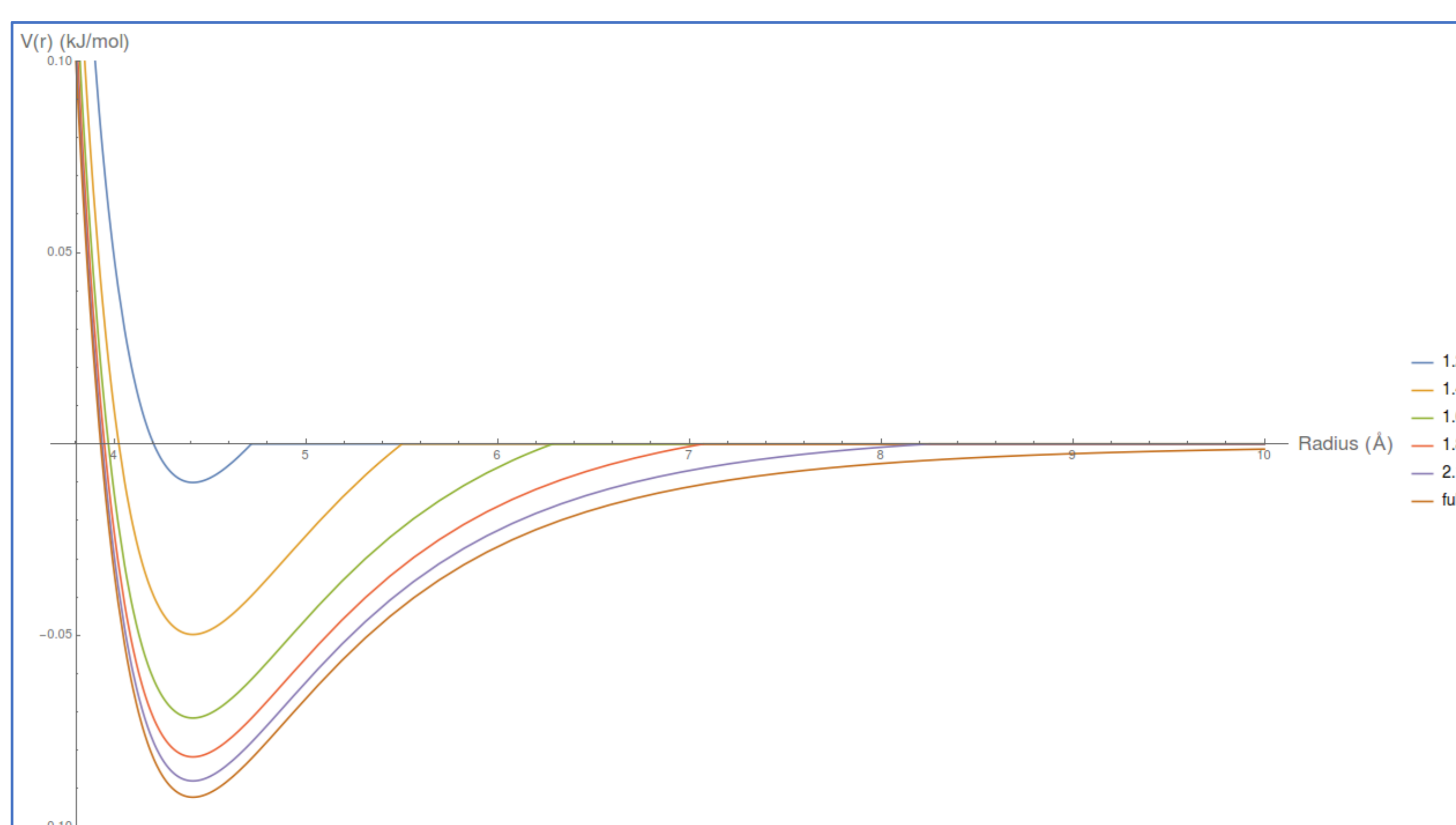
A graph of the Lennard-Jones potential at varying sigma values

Results

Radial distribution functions are a key piece of analysis in the field of molecular modeling and liquid state theory. As part of a larger project to develop new RISM theory-based software, comparing radial distribution functions (RDF) from the developing software to a known RDF using GROMACS was critical to ensure that the new software is accurate. To confirm that the RDFs composed from GROMACS simulations were accurate, work was to verify results from work that John Curro published concerning high density polyethylene melts. Curro not only ran simulations using the full Lennard-Jones potential, but also using the repulsive potential. Only results using the full Lennard-Jones potential were successful, which matched what Curro produced. Simulations attempted with the repulsive function, but errors caused these simulations to fail before completion.
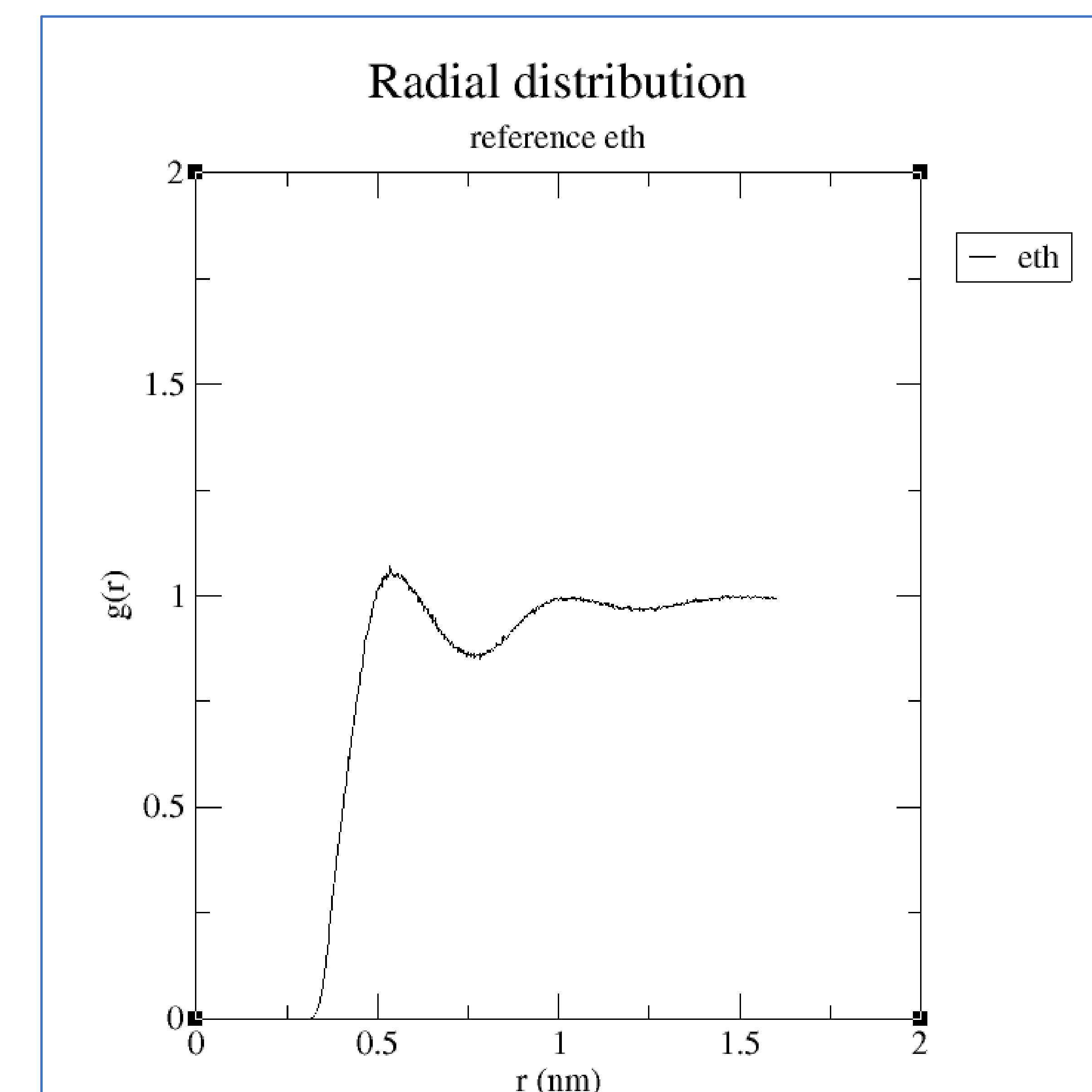
A graph of the radial distribution function of a polyethylene melt

Conclusion

Success was achieved in using Assemble! to build polymer chains as we well as simulating polyethylene melts using the full Lennard-Jones potential. The resulting radial distribution function from the generated polymer melt systems matched those produced by Curro. Attempting to add a repulsive Lennard-Jones potential to GROMACS proved unsuccessful, though the success with the full Lennard-Jones potential provides a frame of reference to pursue further work on the repulsive function.

Future Work

As software is being developed that would attempt to combine the accuracy of molecular dynamics simulations with the speed of RISM theory simulations, it's necessary to have a means of verifying the results. Future work is planned that would utilize the repulsive Lennard-Jones potential in GROMACS to use as a reference to verify results for newly developing software. At the moment, it's necessary to use the repulsive potential in GROMACS so as to stay consistent with the new software that isn't able to use the full potential as was mentioned in the introduction.

References and Acknowledgements

- M.J. Abraham, D. can der Spoel, E. Lindahl, B. Hess, and the GROMACS development team, GROMACS User Manual version 2019, http://www.gromacs.org