

A Coarse-Grained Model for Capturing the Helical Behavior of Isotactic Polypropylene

Nikolaos I. Sigalas ^{1,*}, Stefanos D. Anogiannakis², Doros N.
Theodorou², and Alexey V. Lyulin^{1,3}

¹Soft Matter and Biological Physics Group, Department of
Applied Physics, Technische Universiteit Eindhoven, 5600,
MB, Eindhoven, The Netherlands

²Computational Materials Science and Engineering Group,
School of Chemical Engineering, National Technical University
of Athens (NTUA), GR-15780 Athens, Greece

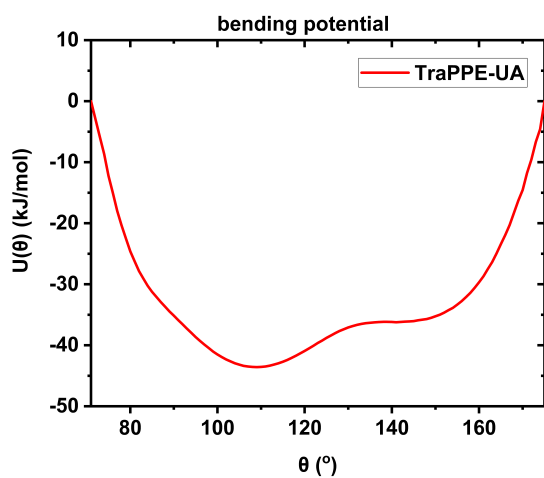
³Center for Computational Energy Research (CCER), P.O.
Box 513, 5600 MB Eindhoven, The Netherlands

*Corresponding author: n.sigalas@tue.nl

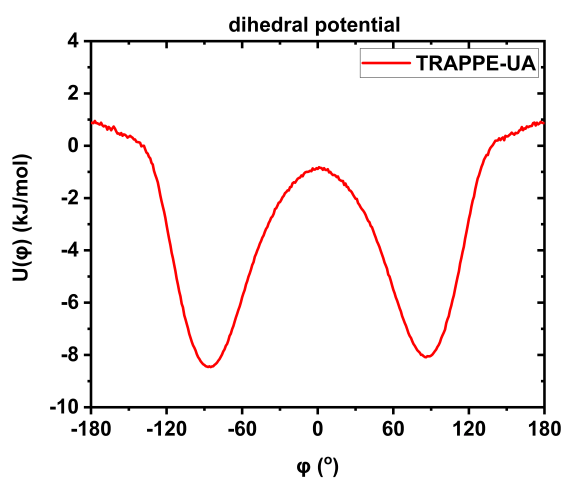
March 22, 2022

Implementation of Tabulated Potentials

The purpose of using tabulated potentials is to improve the overlap of the probability densities of the effective valence θ and dihedral angles ϕ between TraPPE-UA and HELIPP. The first step was to map the UA trajectory produced by single unperturbed chain Monte Carlo simulation using TraPPE-UA onto the CG level. From this mapped CG trajectory the probability density functions (PDF) of effective valence $P(\theta)$ and dihedral angles $P(\phi)$ were extracted and, subsequently, were converted to the bending, $U(\theta) = -RT\ln(c_\theta P(\theta))$, and dihedral effective potential, $U(\phi) = -RT\ln(c_\phi P(\phi))$. The constants $c_\theta = 10^6$ ° and $c_\phi = 10^3$ ° were selected arbitrarily, as they do not have any effect on the simulation. The bending and dihedral potentials are plotted in Figure S1. All the figures were constructed using Origin version 2020 [1].



(a)



(b)

Figure S1: Monte Carlo simulations performed for a single unperturbed chain of 2000 UA monomers at 500K using the TraPPE-UA force field: (a) Bending free energy $U(\theta)$ vs CG valence angles (b) Dihedral free energy $U(\phi)$ vs CG dihedral angles. The single unperturbed chain configurations were initially sampled at the UA level using TraPPE-UA and then mapped onto the CG level to obtain the potential of mean force of CG valence and torsion angles.

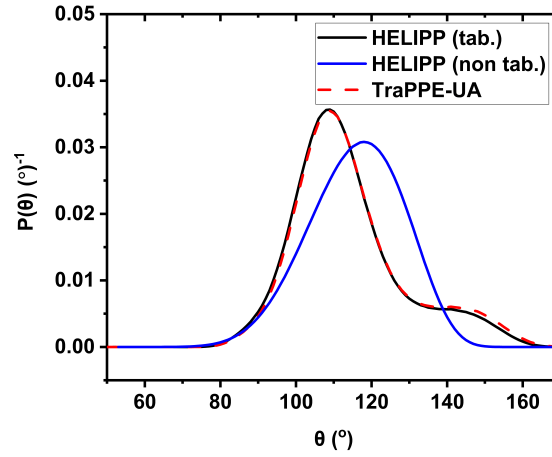
Next, both bending and dihedral effective potential curves were smoothed using the Analysis/Signal Processing/Smooth tool in Origin so as to decrease

noise as much as possible. Then, a cubic spline interpolation was implemented. For the bending potential, $\theta_{min} = 0^\circ$ and $\theta_{max} = 180^\circ$, while the number of the interpolation points were equal to 181. For the dihedral potential, $\phi_{min} = -180^\circ$ and $\phi_{max} = 180^\circ$, while the number of the interpolation points were equal to 361. In order to run a simulation with tabulated potentials, Gromacs version 2019.6 was needed. Two files were used as input, `table_a0.xvg` and `table_d0.xvg`, for valence and dihedral angles, respectively,

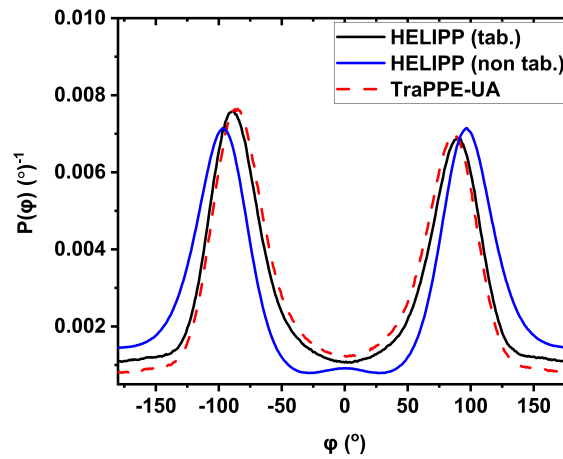
```
gmx mdrun -deffnm npt -tableb table_a0.xvg table_d0.xvg
```

Using the tabulated potentials, we performed an MD simulation starting from an iPP CG melt of 40 chains of 500 monomers per chain. The iPP melt was first energy-minimized using the steepest descent algorithm for 10^4 steps. Subsequently, a NVT simulation followed for 50 ps and, finally, a NPT simulation was carried out for 1000 ns. The last 800ns were used for production. For both equilibration and production stage, a timestep of 5 fs was used. The Nosé-Hoover thermostat and the Parrinello-Rahman barostat were chosen. In Figure S2, the PDF of CG valence and dihedral angles are plotted. In each graph, results from the TraPPE-UA curve and the HELIPP with tabulated potentials are in really good agreement. Furthermore the characteristic ratio was calculated equal to 5.4, slightly underestimated in comparison to the value 5.9 calculated by HELIPP without tabulated potentials. The main reasons we did not use these tabulated potentials for the production simulations were: 1) Tabulated potentials can not be easily used in different simulation packages 2) The maximum timestep with the tabulated potentials was 5 fs,

while without tabulated potentials the timestep was 20 fs.



(a)



(b)

Figure S2: PDF of (a) CG valence angles θ and (b) CG dihedral angles ϕ for a CG melt of 40 chains of 500 beads per chain simulated by molecular dynamics using TRaPPE-UA (red dash curve), HELIPP with tabulated potentials (black curve) and HELIPP without tabulated potentials (blue curve) at 500 K.

References

- [1] Origin(Pro). Version 2020. *OriginLab Corporation, Northampton, MA, USA.*