Modeling Nonequilibrium Reactive Systems with REACTER

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Chemical Reactions are Everywhere
There was a Missing Scale for Reaction Modeling

- Quantum mechanics can model reactions from first principles
- Levels of abstraction come with a tradeoff: accuracy vs. speed
- Reactive force fields can achieve near-DFT accuracy
  - Much faster than DFT, much slower than classical MD
- Can a heuristic description of reactions allow for reactive modeling at much greater scales?

DFT: Density Functional Theory
Many relevant reaction pathways are already well characterized
- Polymer chemistry, organic chemistry, materials science
- Reaction pathways available in literature, textbooks, and online databases

Dynamic modeling of products forming from reactants allows:
- Creation of realistic initial configurations for further study
- Large-scale, computationally-efficient simulations of reactive systems

Example of a sequence with complex but well-characterized reactions (artificial synthesis of caffeine).

What is REACTER?

- A protocol for modeling reactions during classical MD
  - Add/remove specific bonds, angles, dihedrals, etc.
  - Modify all force field types as well as atomic charges
  - Supports any fixed-valence force field (PCFF, OPLS, etc.)
  - Reaction stabilization

- Parallel implementation in LAMMPS as fix bond/react
  - User inputs: molecule templates of pre- and post-reaction topology
  - A map file relating atoms before and after the reaction


www.reacter.org
Epoxy Crosslinking

Simple cross-linking mechanism of an amine to two epoxy molecules
Delete Atoms Based on Topology

1) Delete unwanted reaction by-products
2) Remove specific molecules based on topology (such as small rings)

nylon polycondensation

deletion of condensed water molecule
Create Atoms (and their Bonds)

Example:
• Dynamic growth of polystyrene by creating monomers

Features:
• Place new atoms using best-fit between template and reaction site
• Prevent created atoms from overlapping with existing atoms
Bond-Breaking Reaction Trigger

- Simple criterion for mechanically-induced chain scission
- Or, if using custom criteria, REACTER can be used to reorganize topology
REACTER has Applications in a Variety of Fields

- **Polymerization**
  - Large-scale polyamide polymerization
  - Functionalization of nanotube surface

- **Degradation and Healing**
  - Mechanically induced scission
  - Reconfigurable, self-healing materials

- **Interfacial Reactions**
  - Growth of the solid electrolyte interphase in a lithium-ion battery
  - Competing multispecies reactions

- **Dynamic Equilibrium Reactions**
  - REACTER coupled with grand canonical Monte Carlo

- **Coarse-grained Dynamics**
  - Decreasing cross interaction strength

- **Structural transitions of biopolymers**
  - Protein crowded environment

- **Biological Systems**

References:

- Song et al. *Composites Science and Technology* 2021, 209, 108790.
- Yeganeh et al. *Science Advances* 2022, 8.6, eabm0144.

Supplementary Information

Stilbene linkage can undergo photoisomerization.

A hydrazone exchange completes the molecular walker's journey.

Z-E stilbene transition
Step 1: Sample the Committor Function with Quantum Accuracy

Step 2: Learn the Committor Function using a Deep Neural Net

Step 3: Interface the Neural Net with Large-Scale Reactive MD
Step 1: Sampling the Committor Function

- DFTB with spin polarization and solvation model (toluene)
- Swarm of trajectories approach used to generate a probability of reaction for a given configuration
- 50 trajectories (500 fs) launched from a given configuration (temperature = 530 K)
- Bond-forming trajectories were identified if bonding atoms were separated by < 1.8 Å at end of run
- Khuong et al.: Reaction barrier: 6.0 - 7.7 kcal/mol, Transition State (TS) bond length: 2.276 - 2.351 Å

Step 2: Learning the Committor Function

- Fully-connected deep neural net used to learn committor using reaction coordinates as input
- Three hidden layers (shown to right)
- Key optimizations of the model:
  - Using reduced reaction coordinates
  - Normalizing and centering input values
  - Continuous representation of rotations
    E.g., rather than Euler angles, use 2D coordinates on unit circle (adds one dimension)
- Mean Absolute Error of Predicted Reaction Probabilities: 0.087
Step 3: Using the Committor Function

- Chain growth of polystyrene governed by Python-enabled reaction constraint
- Before every reaction attempt, reaction site coordinates exported to TensorFlow for evaluation of committor
- Soft Lennard-Jones potentials used to increase sampling of $r < 2.5 \, \text{Å}$
- Large-scale simulated polymerization completed (200K atoms)
- Simulated polymerization reaction rate agrees with previous distance-based reactive MD results

Extent of Reaction: 95%
A Framework for Modeling Organic Reactions at Scale

• REACTER is a versatile tool for reactive molecular dynamics simulations
  • Nonequilibrium reactive systems from battery interfaces to biomolecules

• A committor function was incorporated into classical molecular dynamics:
  1. Sampling the committor - DFTB and swarm of trajectories method
  2. Learning the committor - deep neural network using reduced reaction coordinates
  3. Using the committor - REACTER with Python-enabled reaction constraint

• Future work: Improve REACTER-ML interface; automatic typing of new interactions
Thank You!

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