DisARMMD: Distance-Actuated Reaction Mechanisms in Molecular Dynamics

Jacob Gissinger\textsuperscript{1}, Benjamin Jensen\textsuperscript{2}, Kristopher Wise\textsuperscript{2}

\textsuperscript{1}MSE Program, CU Boulder
\textsuperscript{2}NASA Langley Research Center

newly polymerized
What is the DisARMMD protocol?

- A general, user-friendly method for adjusting topology during classical MD
  - Add and remove specific bonds, angles, dihedrals, and impropers
  - Modify all force field types as well as atomic charges
  - Supports any fixed-valence force field
  - Reaction stabilization options

- 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

*Molecule templates are simple! And quite similar to data files!*

www.disarmmd.org
What’s new?

• Recently-Added Options/Extensions to *fix bond/react*:
  • Support for coarse-grained systems (Mark Stevens, Amulya Pervaje)
  • Limit on total occurrences of a given reaction (Wolfgang Verestek)
    Use case: Halt reactions after a certain percentage of crosslinking
  • Customizable behavior of edge atoms (Wolfgang Verestek)
    For example, specify which atomic charges are updated
  • Thanks to Axel Kohlmeyer for multiple bug fixes
  • Thanks to Yoshiaki Kawagoe, Doug Pratt, etc. for additional testing

• Major updates:
  • Delete user-specified atoms based on topology
  • Reactions triggered by bond-breaking
  • Reaction constraints
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
Bond-breaking reaction trigger

- Simple bond-length criterion for mechanically-induced chain scission

grab chain ends and pull...
Reaction constraints

- Currently one option: distance constraints between any two atoms
  - Can be used to enforce a relative orientation between reacting molecules
- Other ideas: angle constraint, energy criteria, others?
Large-scale Nylon 6,6 Demo

Setup: 5,000x adipic acid
5,000x hexamethylenediamine

220,000 atoms
Temperature: 530 K
(actual synthesis temp)
Final density: 0.9 g/cm$^3$
Side length: 13.3 nm
3-5 Å reaction cutoff

>99% polymerized

condensed water molecules removed
Chain PDI $\approx 2$  Overall PDI (with cycles) $\approx 3.9^*$

( nylon 6,6 )

265 repeat units
>7,400 backbone atoms

*Experimental PDI $\approx 4$.

>99% polymerized Nylon 6,6: Chains vs. Cycles

weight % cycles:
simulation: 3.7%
experiment: 1-5%\(^1\)

>250 repeat units
(>500 reactant molecules)

Nylon 6,6: chain morphology

\[ \langle r^2 \rangle^{1/2} \approx 10 \text{ nm} \]

end-to-end distance

\[ \langle R_g^2 \rangle^{1/2} \approx 4 \text{ nm} \]

radius of gyration

\[ \left\langle \frac{r^2}{R_g^2} \right\rangle = 6.07 \]

Value for a Gaussian chain: 6

Nylon 6,6: chain radii of gyration

\[ R_g \sim N^{1.1} \]

# repeat units
Chain growth vs. ring formation

Nylon 6,6

Single topologically-constrained cycle

Cycle constraining two chains: physical ‘slip-link’
Uniaxial extension with chain scission:

- **Uniaxial strain**
  - Highly entangled system
  - Craze formation

- **Chain scission reaction**
  - Relieve topological constraints
  - Activated if C-N bond > 1.67Å
    - Chosen empirically
  - Only 6 chain scissions occurred

(nylon 6,6)
Polystyrene demo

>99% polymerized polystyrene
200,000 atoms (12,500x styrene)

>98.5% polymerized with 3.0 Å distance cutoff, before switching to 3.5 Å

Conclusion: DisARMMMD can handle small monomers with bulky side groups

530 K
13.7 nm box
Epoxy Cross-linking

Simple cross-linking mechanism of an amine to two epoxy molecules

Modeling chemical reactions in classical molecular dynamics simulations.
Summary and Outlook

• The DisARMMD protocol scales well
  • 10,000 nylon precursors \{ \text{true temp. (≈260 C)} \}
  • 12,500 styrene molecules \{ \text{low cutoff 3-5 Å} \}
  \{ >99\% polymerization \}

• Correctly predicts cyclic content, dispersity and chain morphology

• What’s next?
  • More predictive reaction constraints
    • Potential energy surfaces?
  • Large-scale bio applications
    • See Andrew Jewett’s talk tomorrow
  • Features in progress
    • Additional reaction constraints
    • Option to create atoms
Thank you!

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