Modeling Chemical Reactions in Classical Molecular Dynamics Simulations

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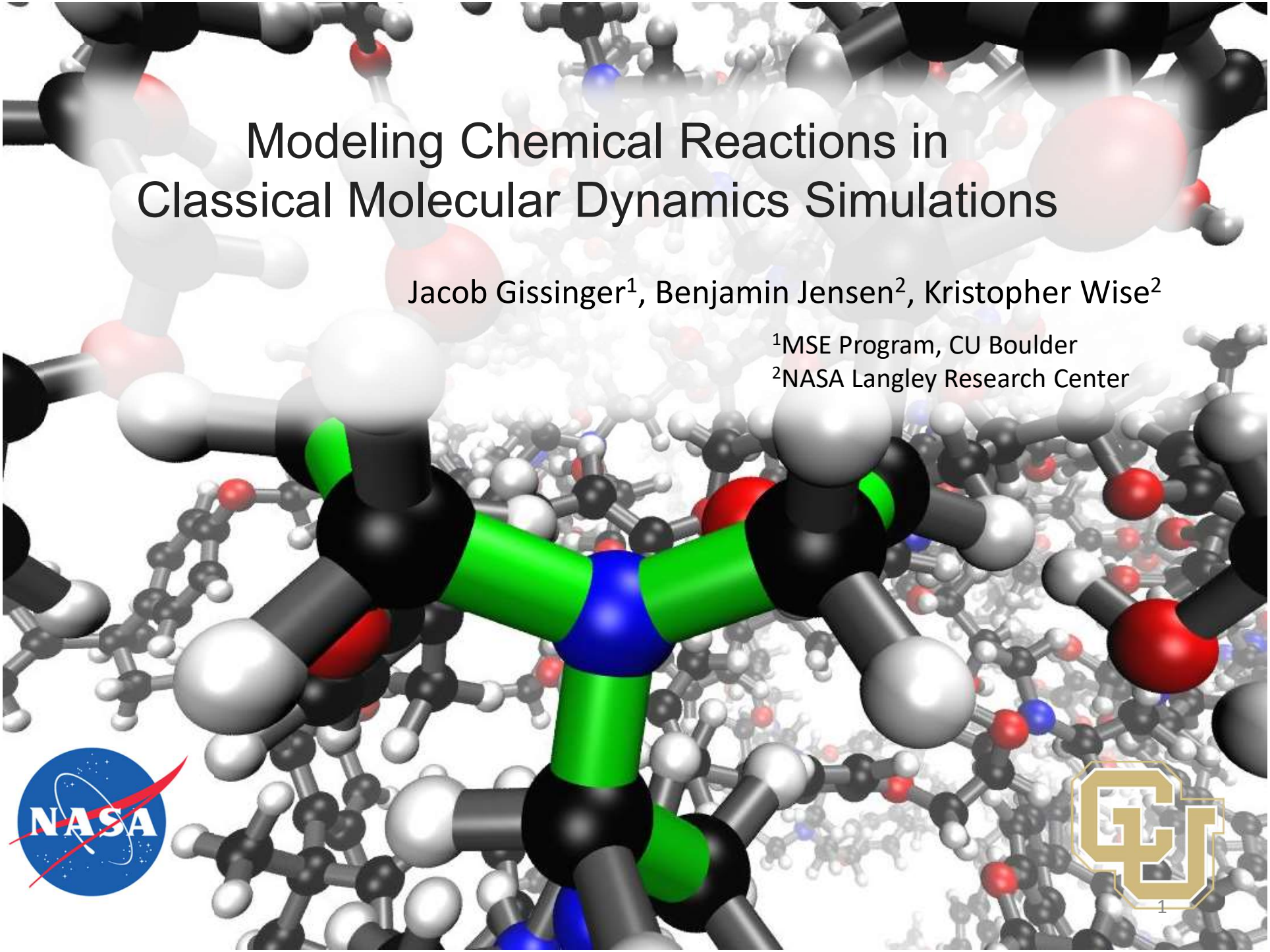
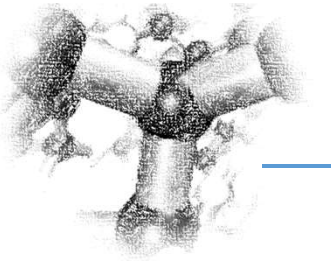
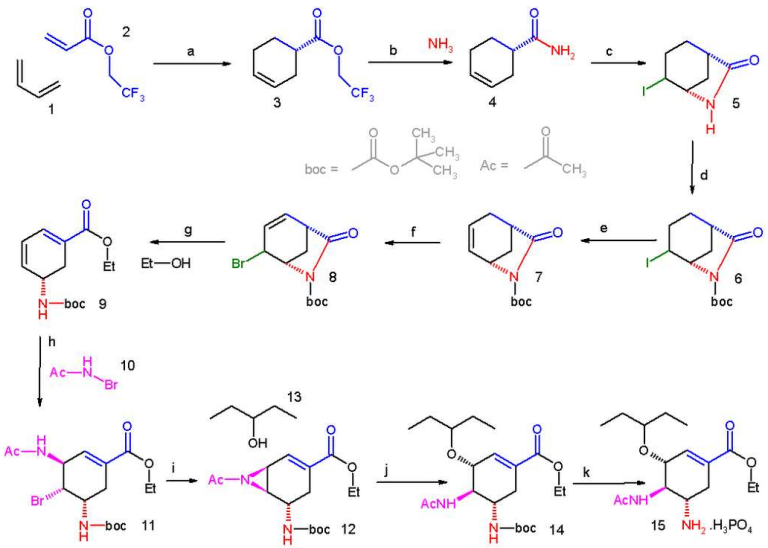


A 'Reaction' Option in Classical MD is Overdue



Previous Options (in LAMMPS):

1) Create or break a single bond
   - based on interatomic distance
2) Run at constant topology



Alternatives: ReaxFF (or QM/MM)

1) Needed for probing mechanisms
2) Requires around 80 parameters
3) Slower and less mature than classical MD

Many researchers still use ad hoc scripts to adjust bond connectivity between MD runs

Current Functionality of 'fix bond/react'

1) Complete arbitrarily complex bond topology changes
   a. model reaction formulas out of e.g. organic chemistry

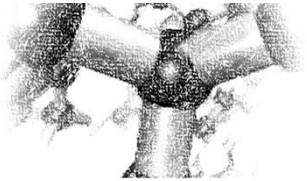
2) Support atomistic, charged, class2 force fields with possibly customized dihedrals, impropers, etc.

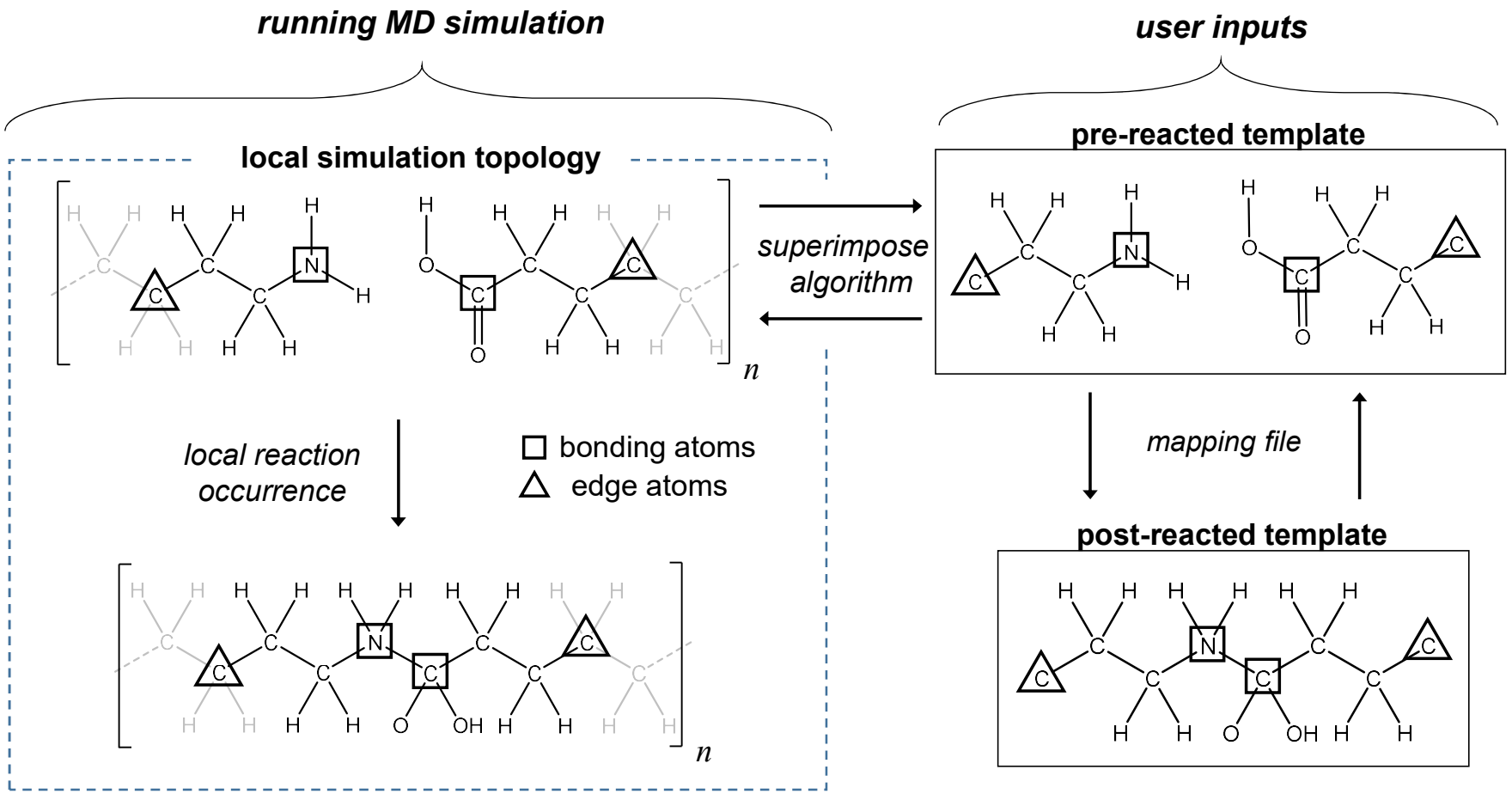
3) Relax high-energy sites on-the-fly
   a. uses nve/limit, dynamic groups via per-atom properties

4) Scalable
   a. scaling up a working *bond/react* = copy/paste coords

5) Parallelized

The Superimpose Algorithm: power of ID

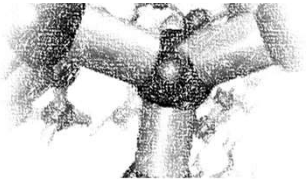




The Superimpose Algorithm locates all instances of local reaction site

Local site is related atom-by-atom and updated to reacted template

How it Works in Parallel



How to correctly assign and unassign atoms to nve/limit?

1) Dynamic groups extended to support per-atom properties
   a. the property in this case being ‘recently-reacted’
   b. this may be useful for other advanced functionalities

2) This property is set to store the timestep it was assigned
   a. atoms can therefore be unassigned by any processor

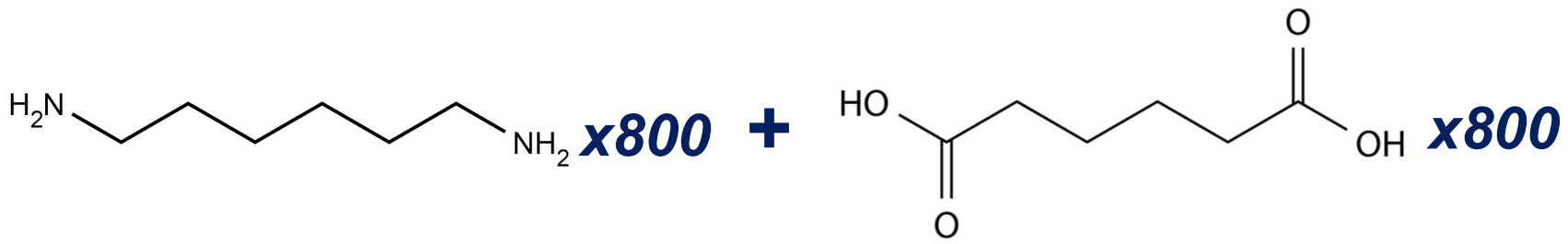
3) Ghost atom updates already supported by per-atom props

How to correctly update topology information across procs?

1) All procs already have post-reacted topology
   a. only one array must be sent (size = natoms in reaction)

Linear Nylon Polymerization: a case study

Simulation box:



Simulation Parameters:

Box size: 75x75x75 Å

Density: .8 g/cm^3

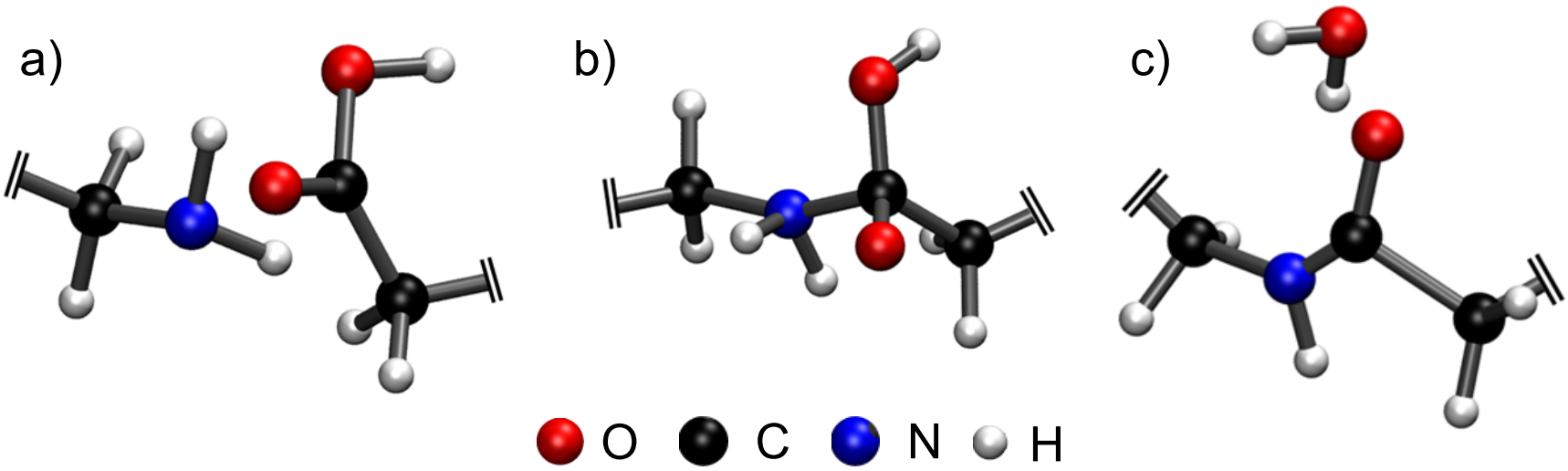
Ensemble: NVT

Temperature: 800 K

Duration: 200 ps

Stabilization Time: 60 fs

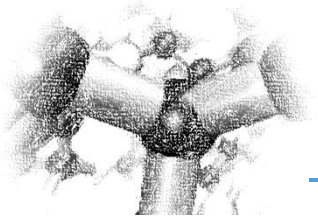
Polycondensation Mechanism

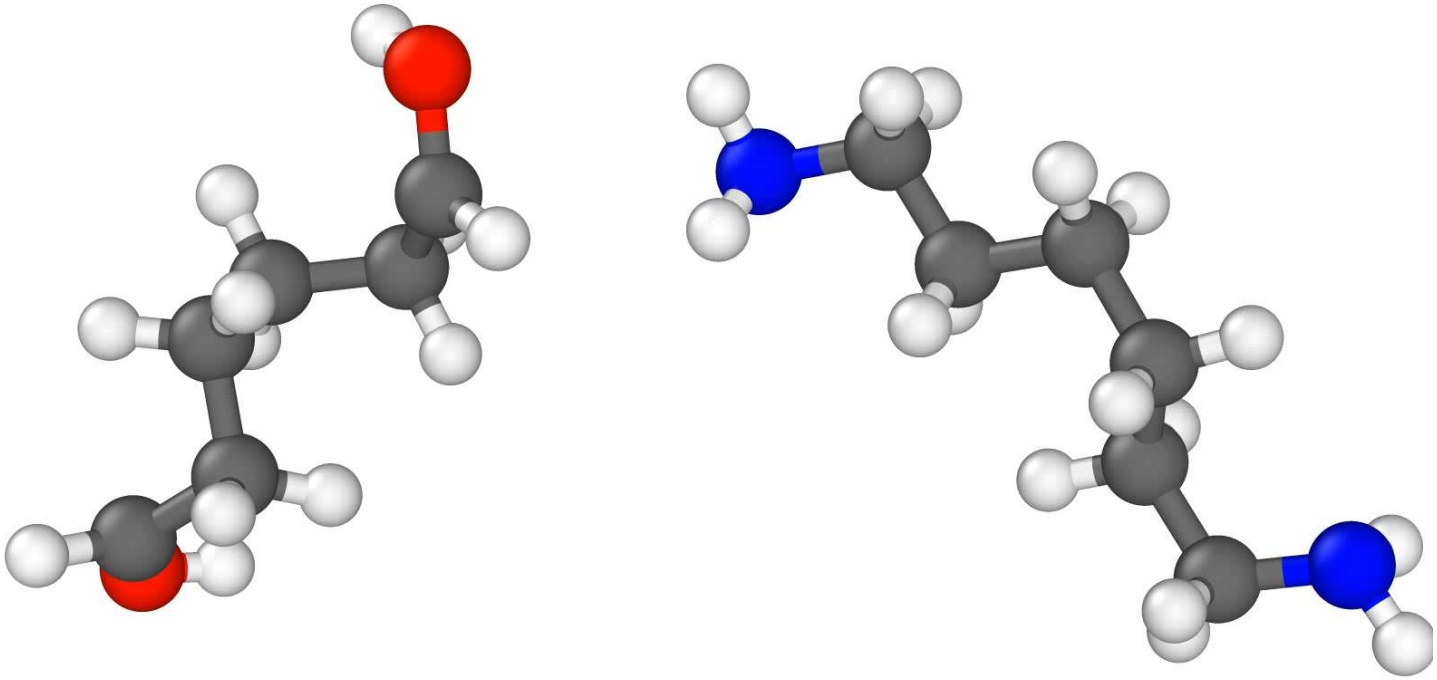


Polycondensation of nylon 6,6

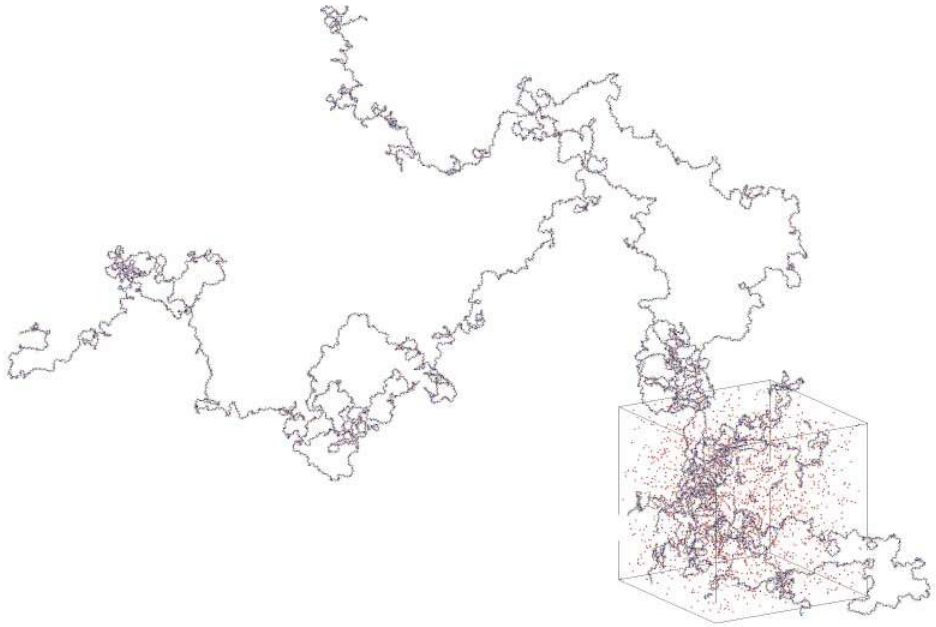
Transition structures stabilized for given number of time steps
'Reactions' dynamically relaxed using *fix nve/limit*

Polycondensation: the movie



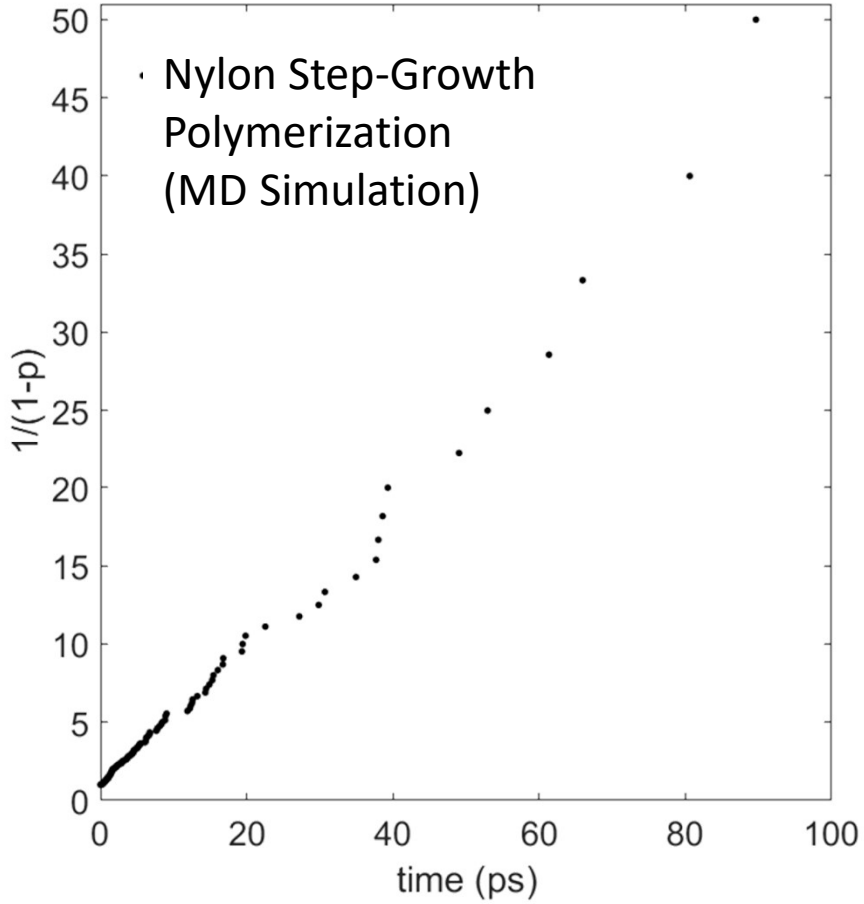


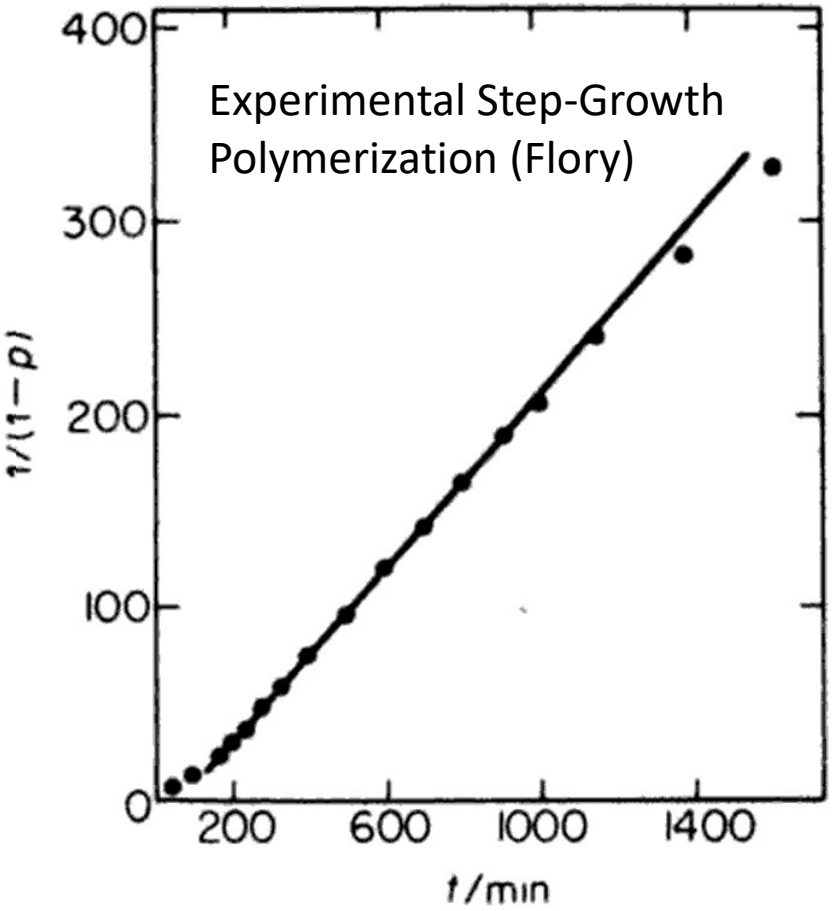
Dynamic Polycondensation of Nylon 6,6



35,200 atoms; 1,600 monomers
> 99.5% conversion
Cutoff: 3.9 Å; Sim. time: 200 ps

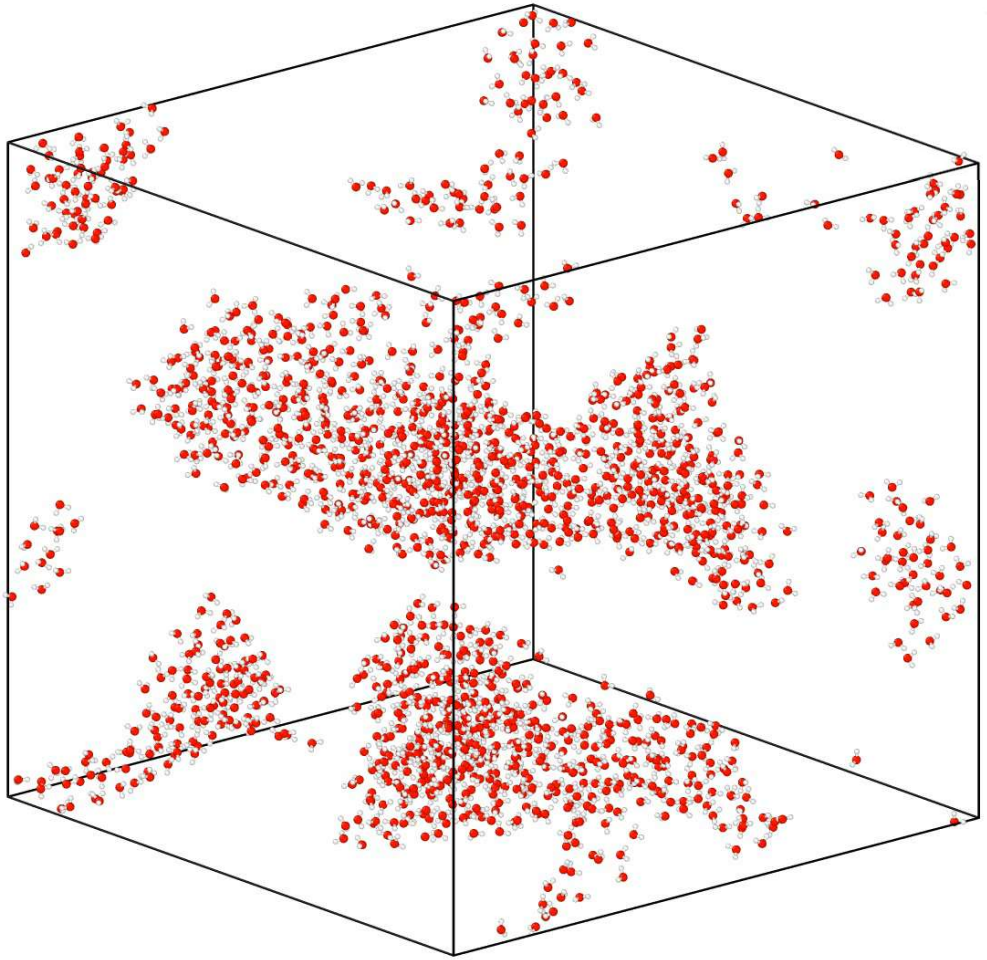
Dynamic Polycondensation of Nylon 6,6





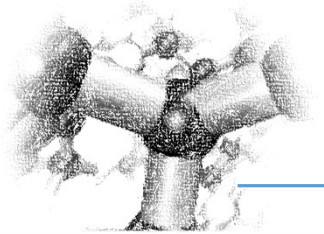
Simulated nylon chain formation obeyed step-growth kinetics

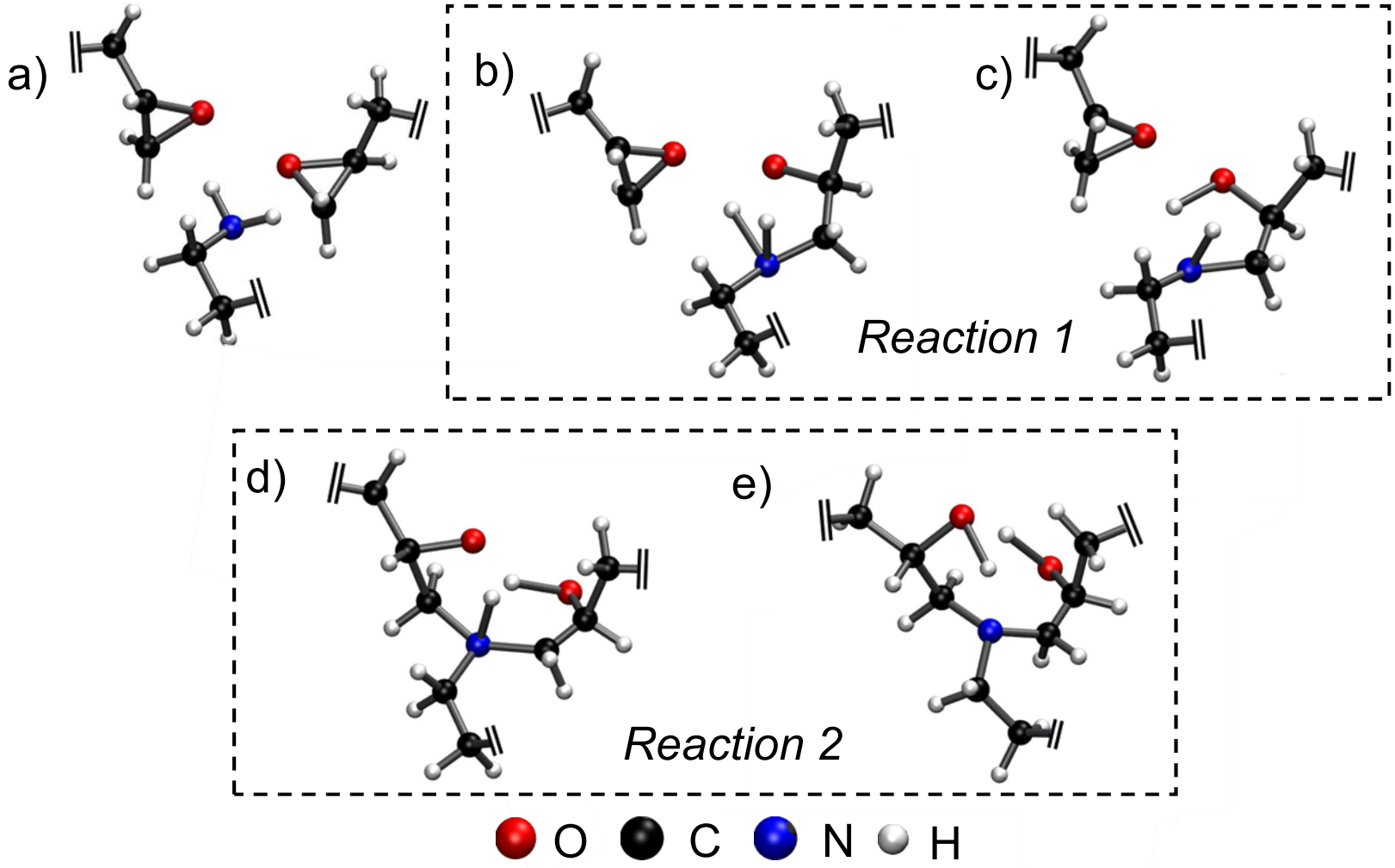
Phase Separation of Condensed Water



Dynamic creation and phase separation of reaction byproducts can provide insight into physical mechanisms and kinetics

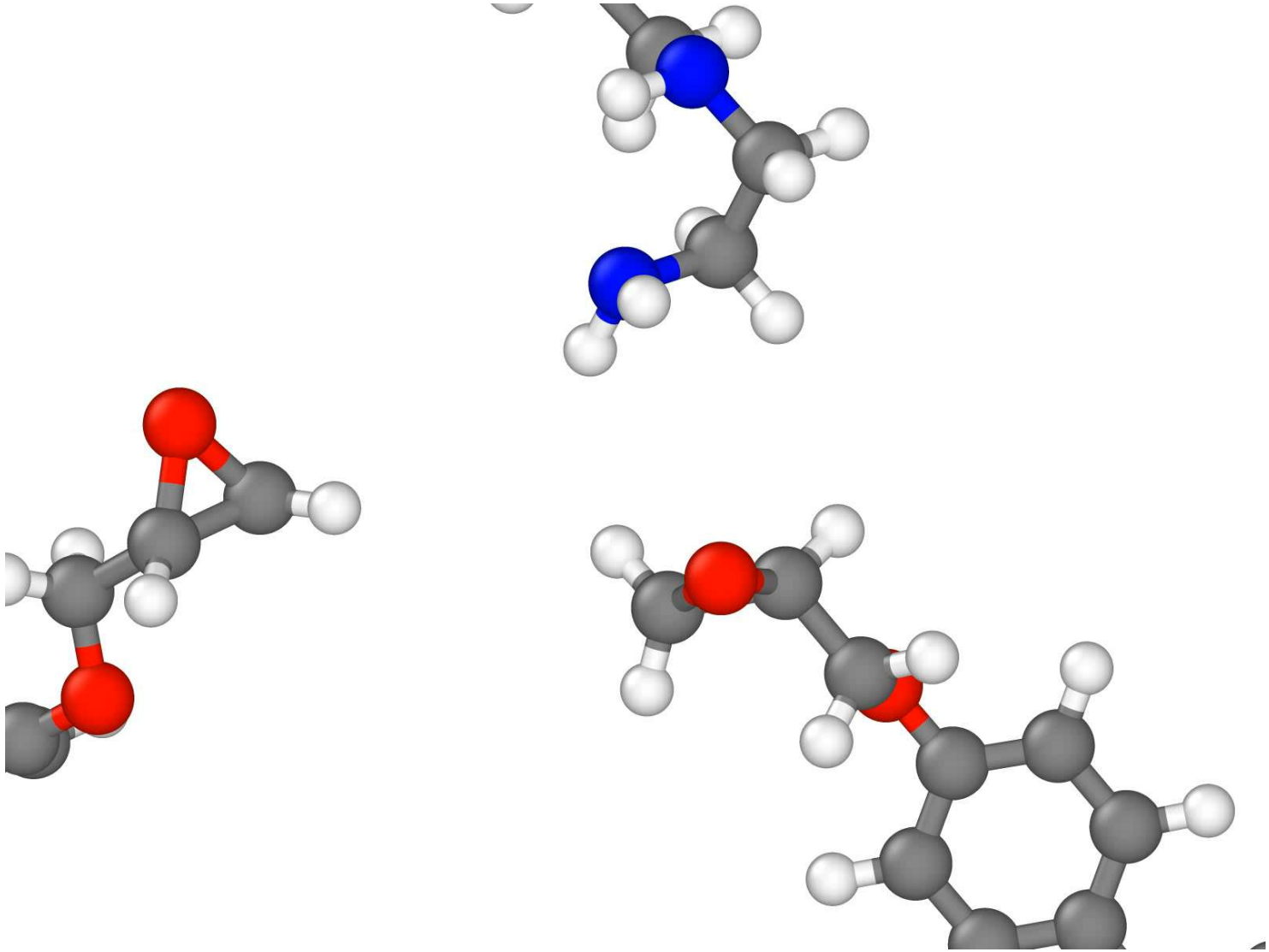
Highly Cross-linked Epoxy: a preview





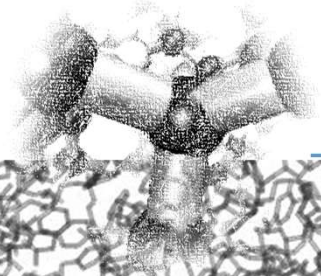
Cross-linking mechanism of an amine to two epoxy molecules

Highly Cross-linked Epoxy: the trailer



Cross-linking mechanism of an amine to two epoxy molecules

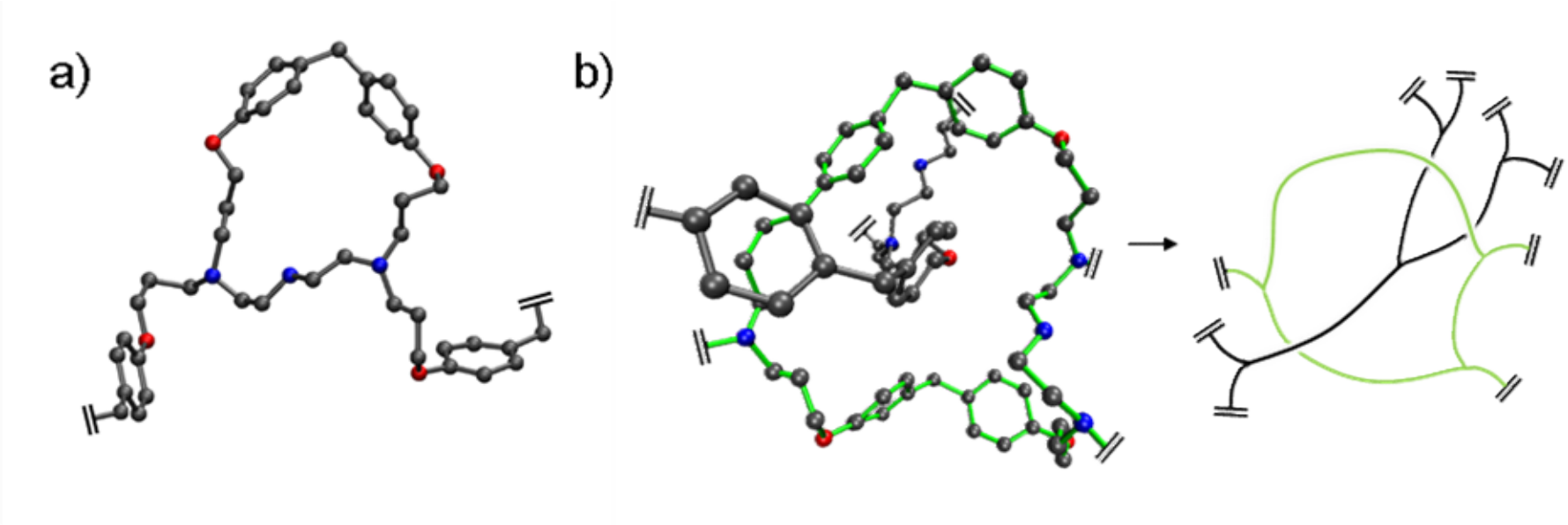
Final Epoxy Morphology



96% cross-linked

Distance cutoffs:
rxn 1: 3.5 Å, rxn 2: 5.0 Å
100 diepoxy molecules,
50 diamine molecules
Run: 200 ps at 800 K

Some Interesting Epoxy Topologies



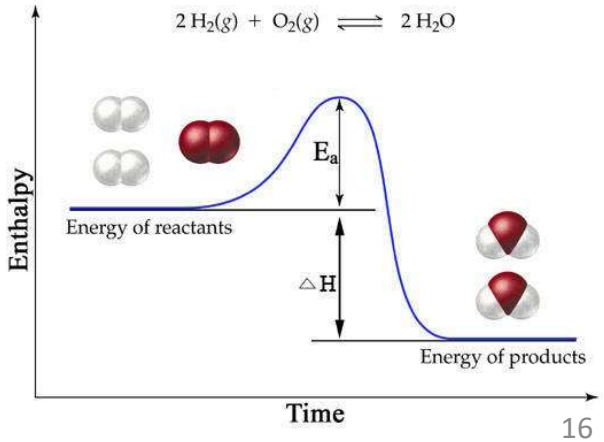
hash marks indicate connectivity with rest of matrix

(a) Small loops detrimental to mechanical properties
(b) Part of matrix passing through larger loop (in green)

Improving Predictive Power

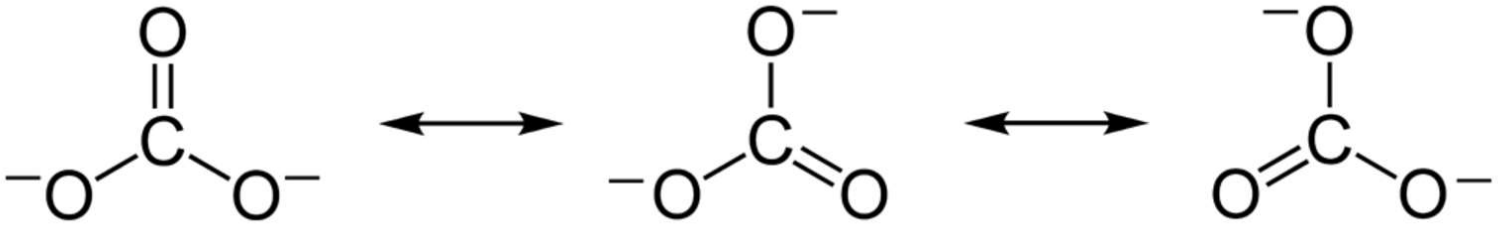
- More advanced reaction trigger options
  - Local scale
    - Require proximity of three or more atoms for reaction
    - Factor relative velocities into initializing reaction
  - Global scale
    - Impose global rate laws (as for DPD)

- Develop a thermostat for ‘reactive’ classical MD
  - enthalpy of reaction added or subtracted from involved atoms



Outlook and Future Directions

- Appears to be a powerful tool for dynamic system setup
- Scheduled to appear in LAMMPS as *fix bond/react*
- Potentially interesting applications:
  - diffusive catalytic systems
  - highly-crosslinked networks such as hydrogels or epoxies
  - high-temperature reactions such as carbonization of carbon fiber
- Advanced possibilities:
    - Resonance Structures
    - Equilibrium Reactions
      - duplicate a reaction with reversed pre- and post-reacted topologies



Acknowledgements

Thanks to Correspondence with:

Steve Plimpton

Thank you