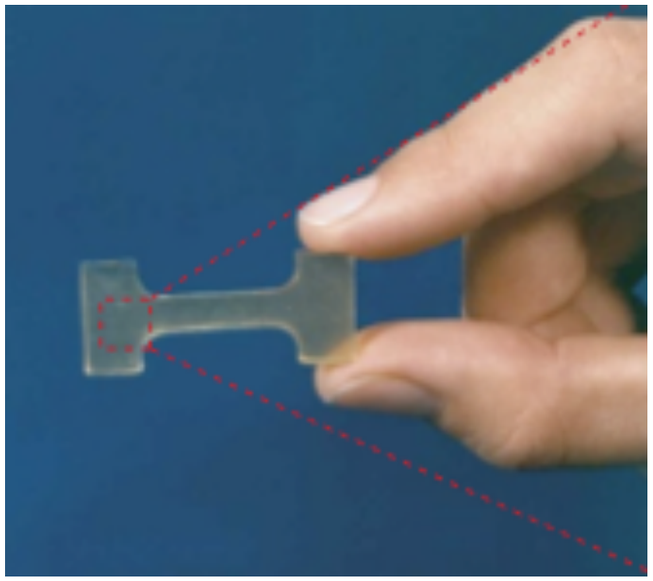
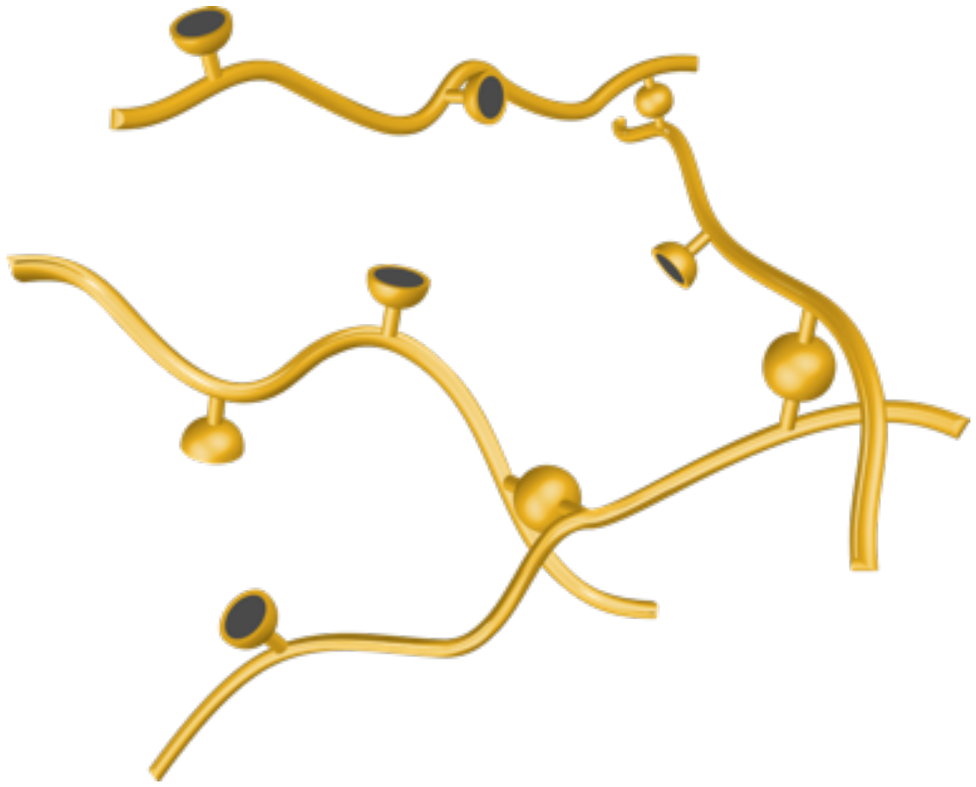
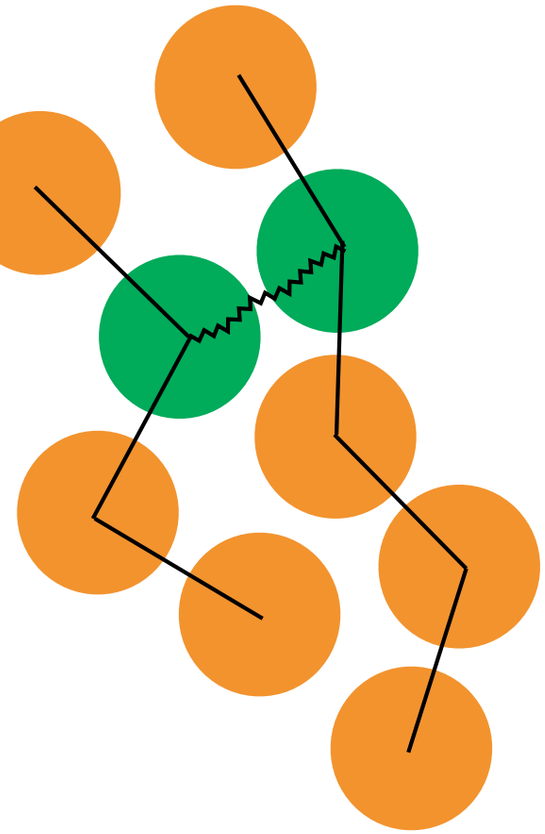
Integrating Monte Carlo for simulation of reversible chemical bonding







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Computing Challenges

Need model with

- realistic dynamics
- variable "chemical" kinetics
- controllable bonding topology (~ typical real systems)
- ability to treat inhomogeneous systems

Must be coarse-grained to access relevant length, time scales

Limitations of Previous Work

- early attempts used lattice MC; can't apply stress, strain
- standard "pure" MD sims use deterministic bond breaking/formation; *traditionally* no control of kinetics/binding topology
- MC sims difficult to capture realistic dynamics, esp. correlated relaxations

Bead-Spring Polymer Model

Kremer & Grest, 1980s-present

$$U_{LJ}(r) = 4u_0\left(\left(\left(\frac{a}{r}\right)^{12} - \left(\frac{a}{r_c}\right)^{12}\right) - \left(\left(\frac{a}{r}\right)^{6} - \left(\frac{a}{r_c}\right)^{6}\right)\right)$$

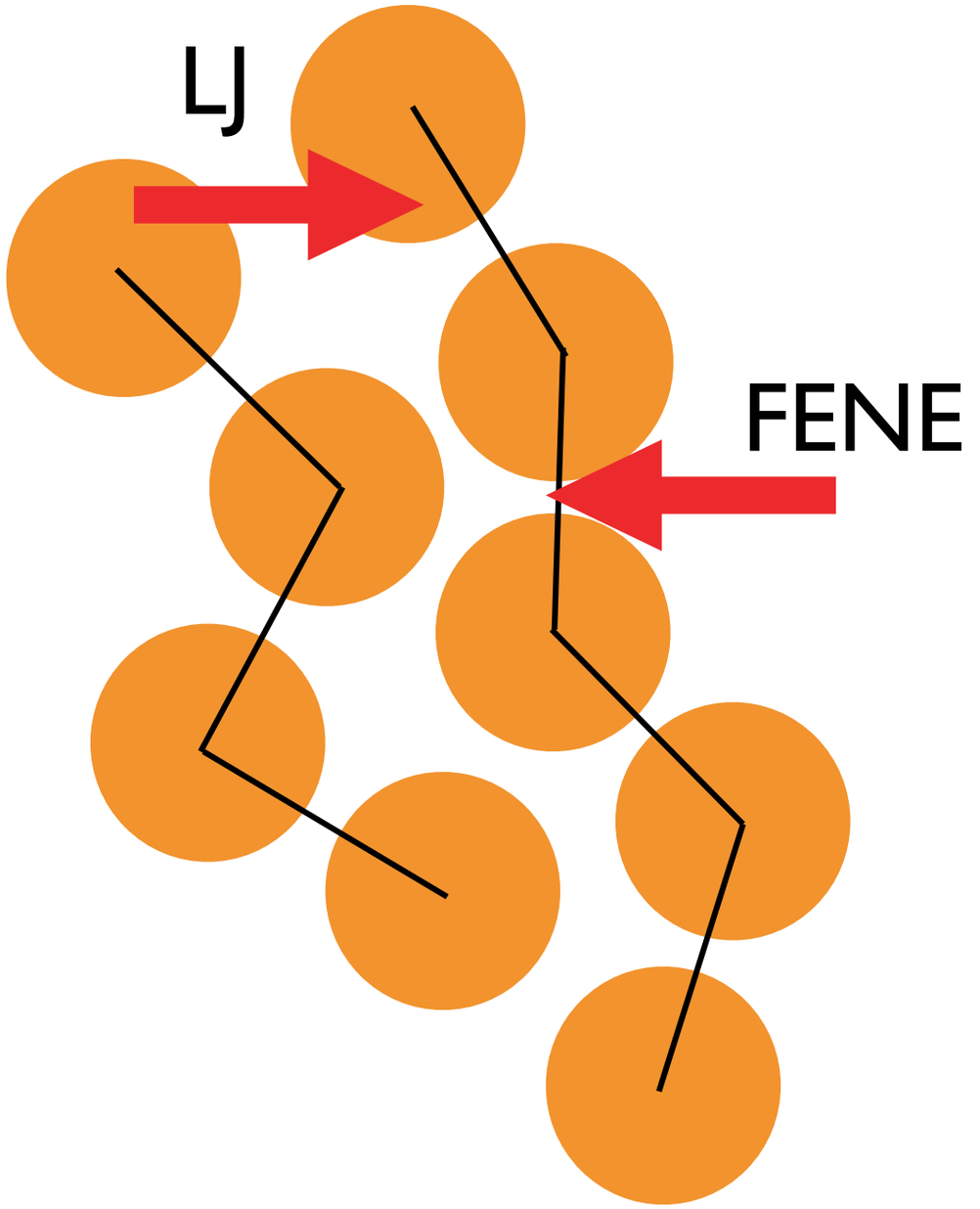
$$U_{FENE}(r) = -\frac{1}{2}kR_0^2\log(1-(r/R_0)^2)$$

captures RW structure, chain stiffness and uncrossability, excluded volume & adhesion, but no "chemistry"

N spherical monomers per chain, all interact via LJ, covalently bonded also have FENE

strength, range of adhesive interactions varied by changing r_c

Simulate with MD: integrate Newton's eqns for all monomers



Hybrid MD/MC Model for Associating Polymers

Fraction c_{st} of monomers are "sticky" (green)

Use Metropolis Monte Carlo to form/break reversible bonds between SMs with potential

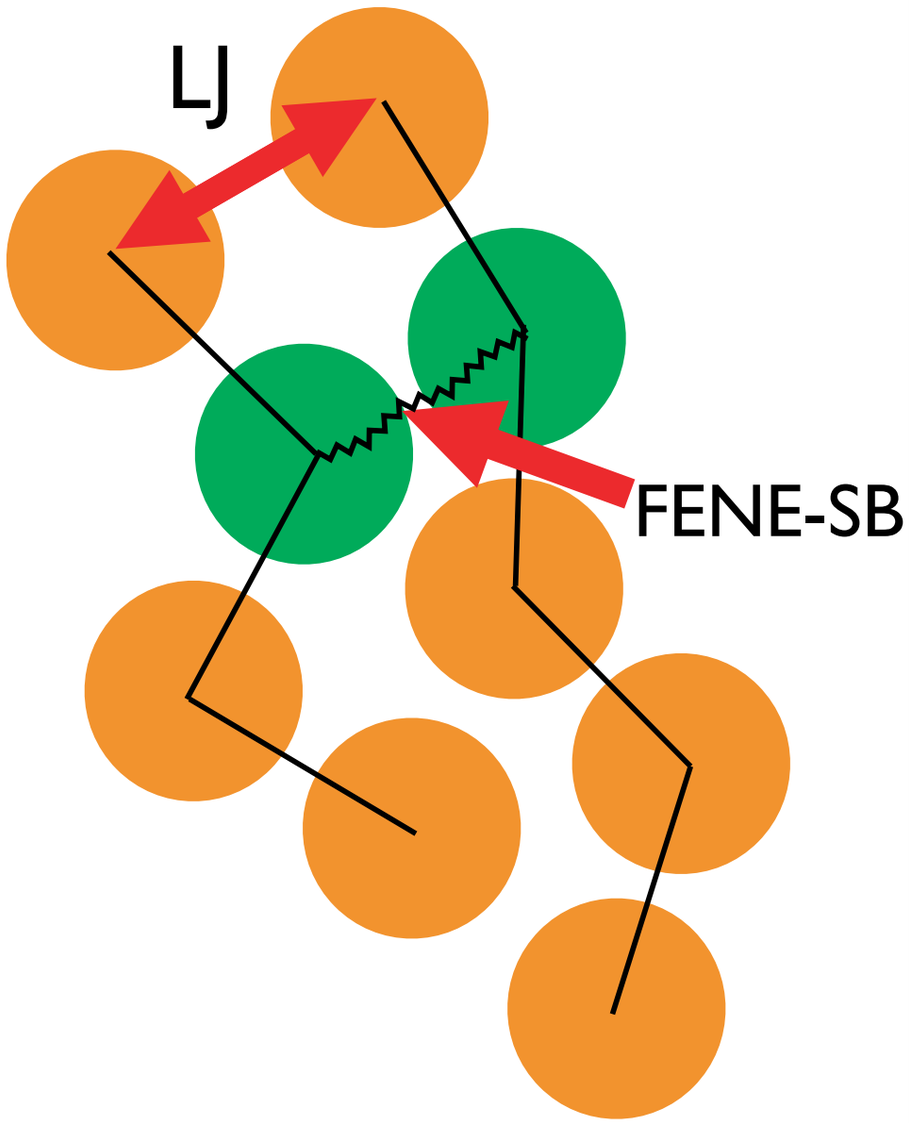
$$U_{FENE-SB}(h,r) = -h + U_{FENE}(r) - U_{FENE}(r_{min})$$

Sticky bonds intended to be "reversible equivalent of the covalent bond" *(Sijbesma et al, Science 1997)*

Monte Carlo attempt frequency $1/\tau_{MC}$

Restrict SMs to binary, "one at a time" bonding: reflect SMs used in many recent experiments

Vary two parameters:
h = binding energy ~ thermodynamics
τ_{MC} ~ kinetics



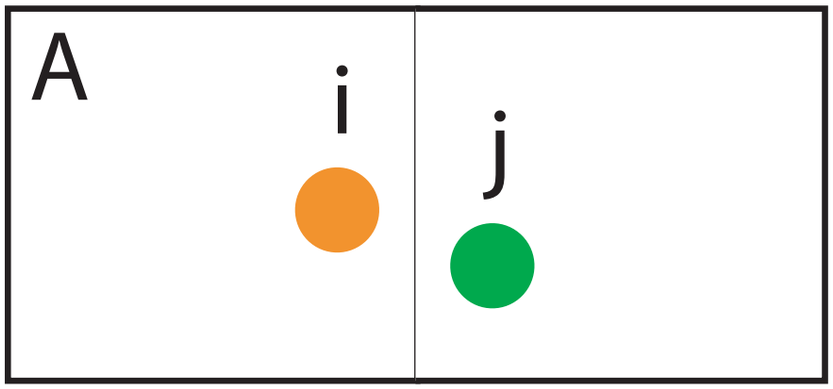
Model thoroughly validated, has 2nd-order kinetics with Arrhenius activation

Similar method applied to linear equilbrium polymers by Ryckaert et al, 2006-2009

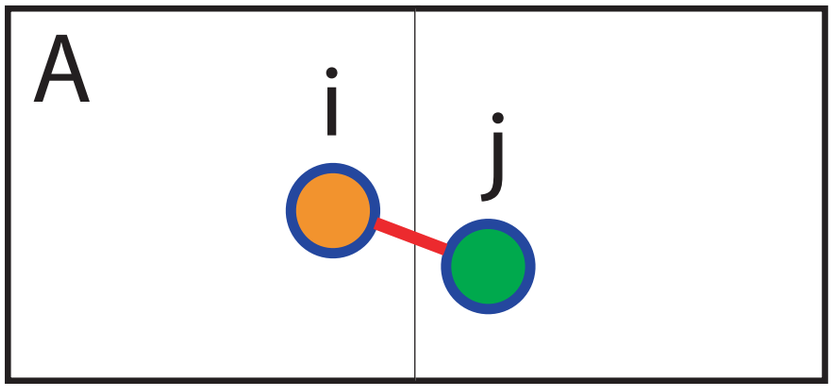
Serial/Parallel Hybrid Method

Serial

Before

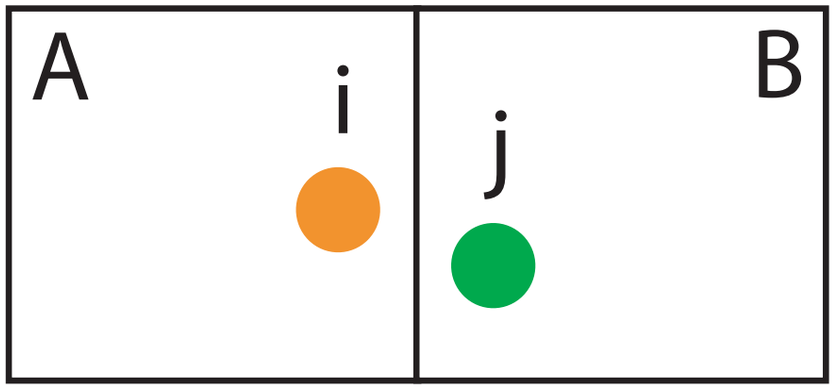


After

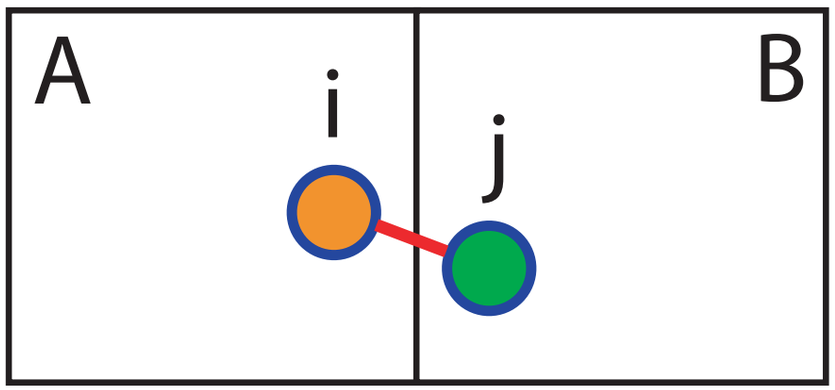


Parallel

Before



After



Parallel MC very difficult!
(changes have to be communicated instantaneously and not interfere)

Added serial MC capability to LAMMPS

Pause (parallel) MD, gather info on sticky monomers, use Metropolis MC to update sticky bonds, redistribute SB topology to all procs, restart MD

parallel-efficiency decrease ~
SM concentration x f_{MC}

f_{MC} = MC steps/ MD steps ~ .01-.1

Differences from Fix Bond Create/Break

(the standard LAMMPS package)

Good:

Uses Metropolis Monte Carlo (bond-potential based ΔE, Boltzmann weighting), satisfies "balance" *(Manousiouthakis & Deem 99)*, modifiable to satisfy detailed balance

Doesn't require special_bonds 011

Bad:

MC part not clearly parallelizable! Had to modify many .cpp files, uses <vector> and <algorithm> classes: - is currently in Steve's "high energy barrier mode" for integration

Question:

Worth integrating into standard LAMMPS dist?

Details, Details

- code implemented by modifying bond_fene.cpp
- Sticky atoms and sticky bonds both different type than nonsticky -- bond and neighbor lists easily accessible
- select sticky neighbors (within distance R_0), gather lists of positions to processor 0
- use dynamical allocation of sticky neighbor list depth to minimize interproc communication
- use std-lib random_shuffle, various flags to impose binary-bonding, improve efficiency

Outlook

- implement as LAMMPS fix so can be used with variety of bonding potentials?
- possible to implement "proper" parallel MC? (big problem: communication); "checkerboard" possible?
- or keep serial but improve efficiency?

Ref: R. S. Hoy and G. H. Fredrickson, J. Chem. Phys. 131, 224902 (2009)

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