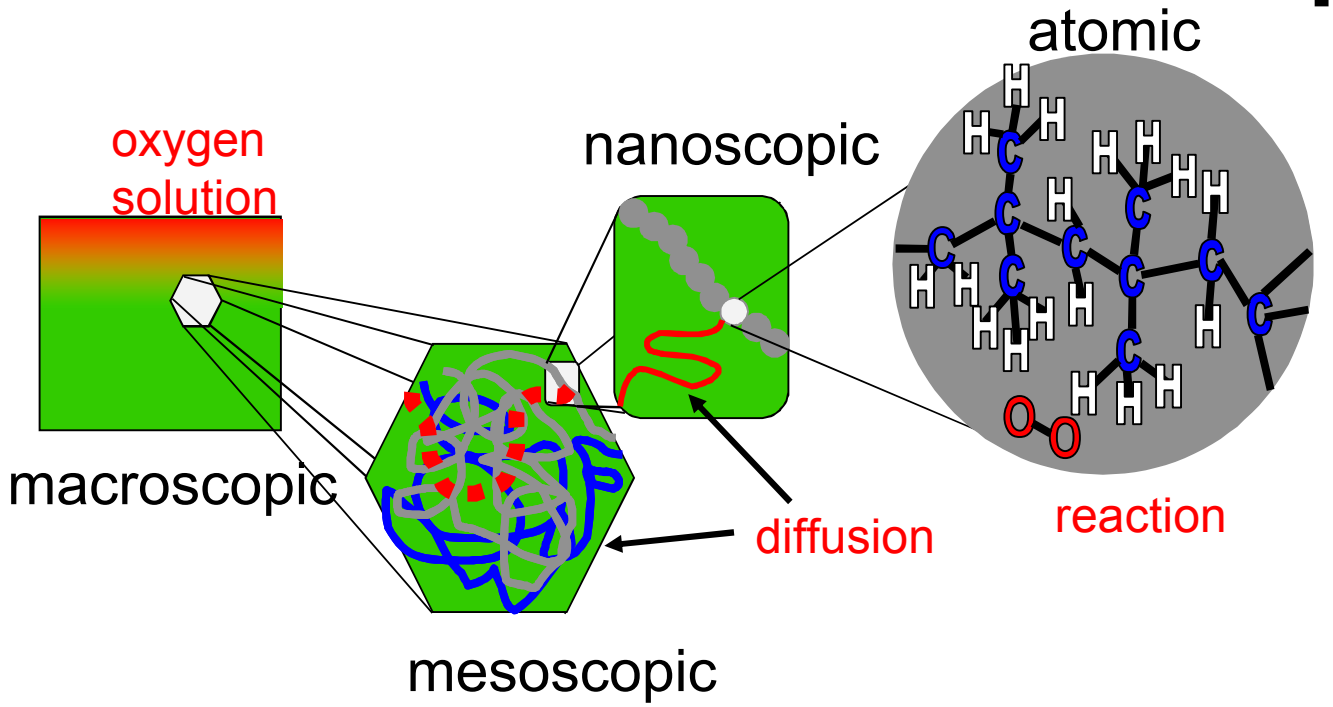
SAND2008-3459P

Simulating Polymer Degradation from Atomistic to Continuum Properties



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Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000.

We use a hierarchical approach to simulation

Engineering Predictions

macroscopic properties

Finite Element

physics of mesostructures

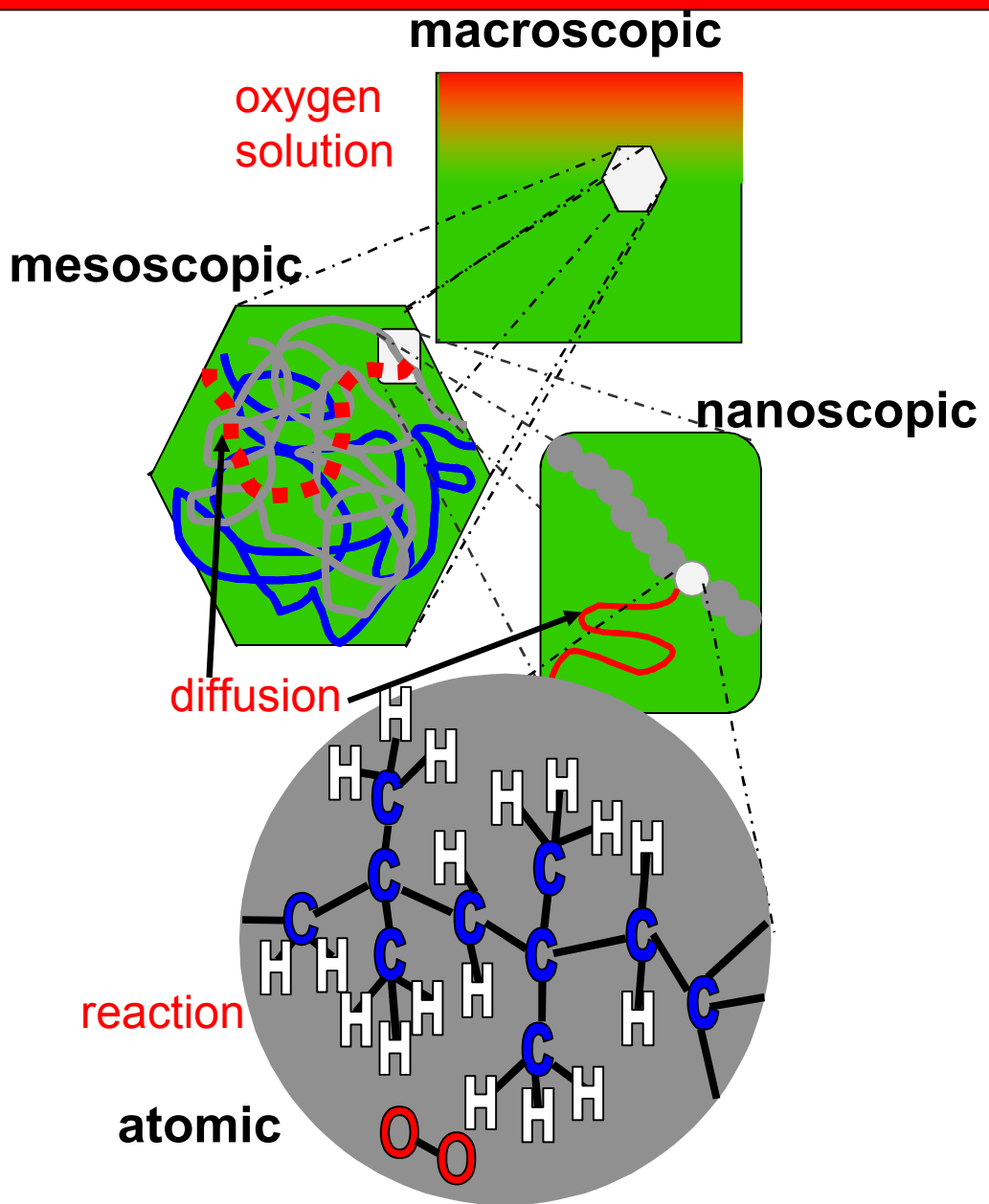
Bead-Spring

physics with chemical details

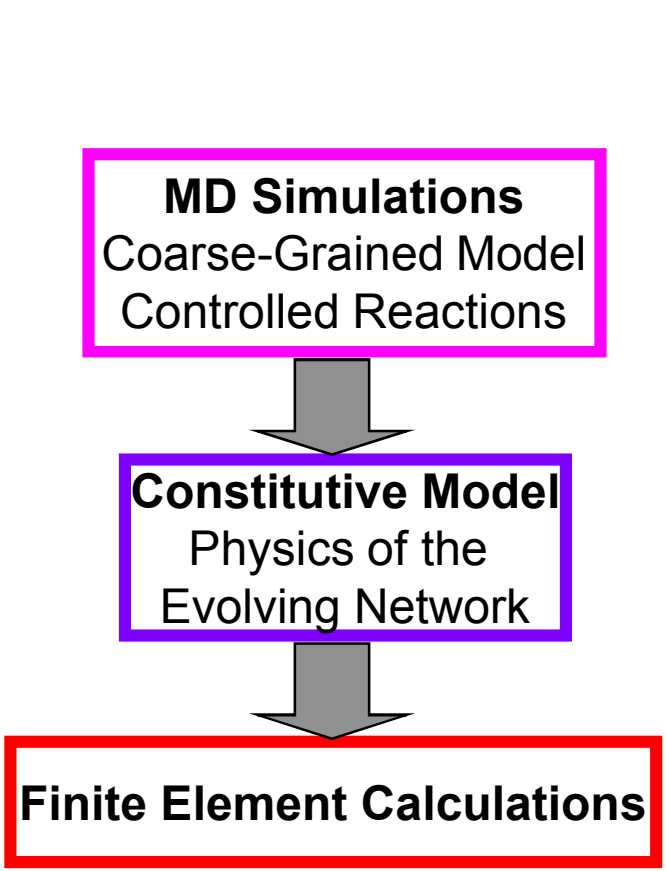
United Atom

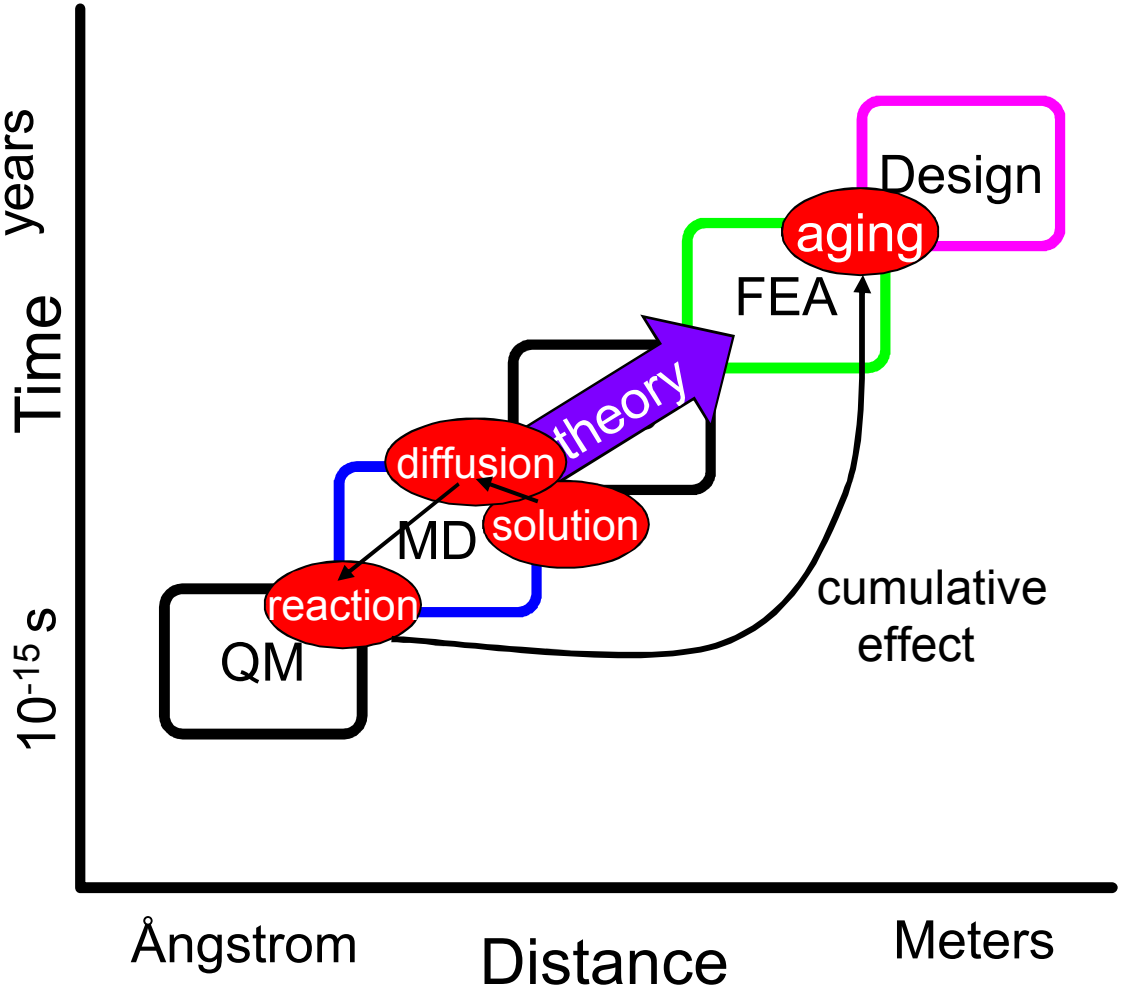
reactions and chemical realism

All Atom

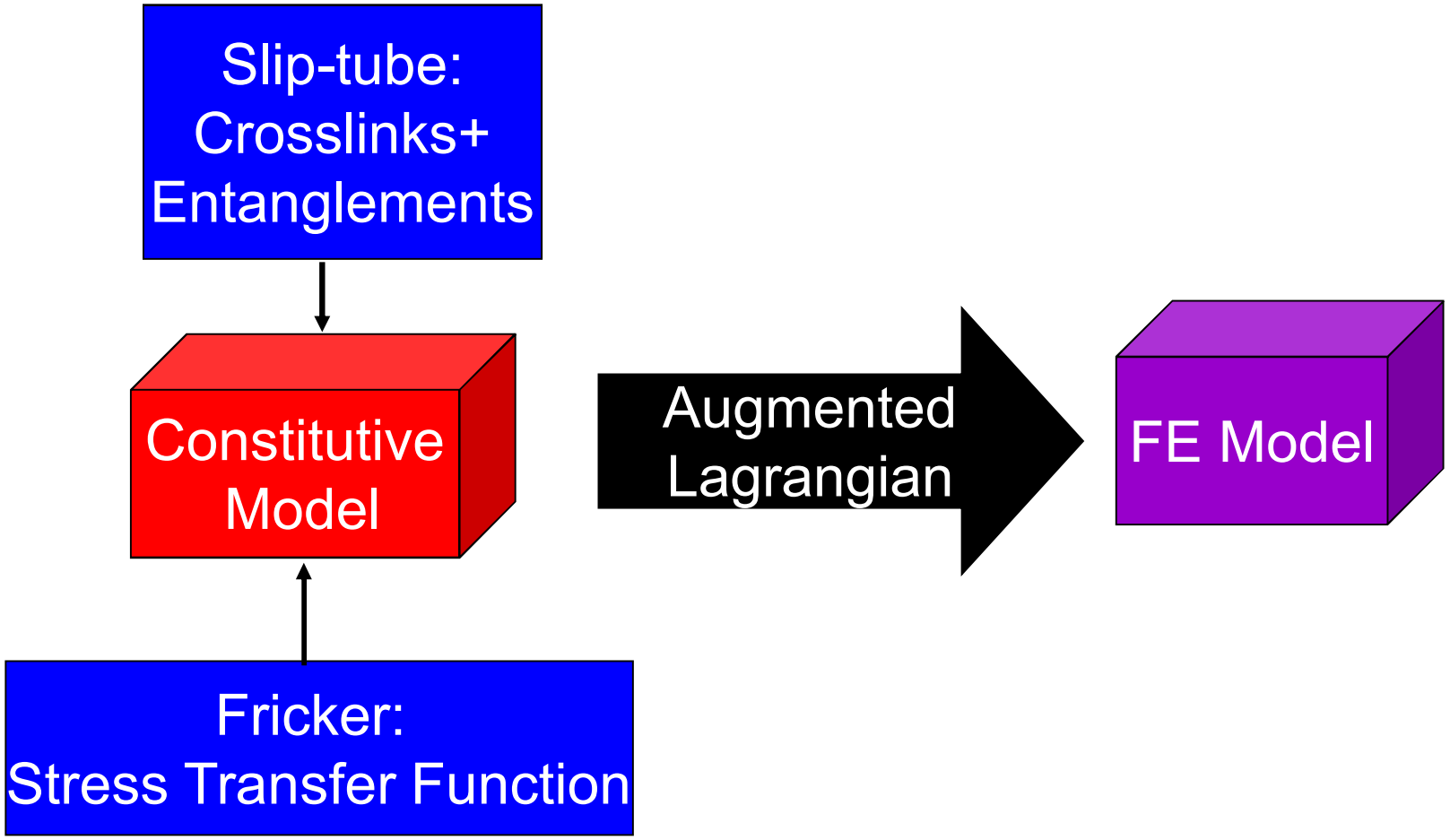


The relevant physical processes occur on different time and length scales



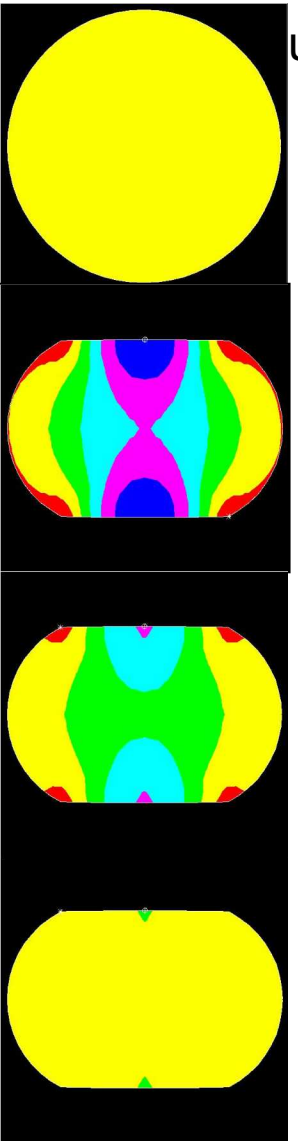


By concentrating on the physics of the evolving network, we developed a useful constitutive model

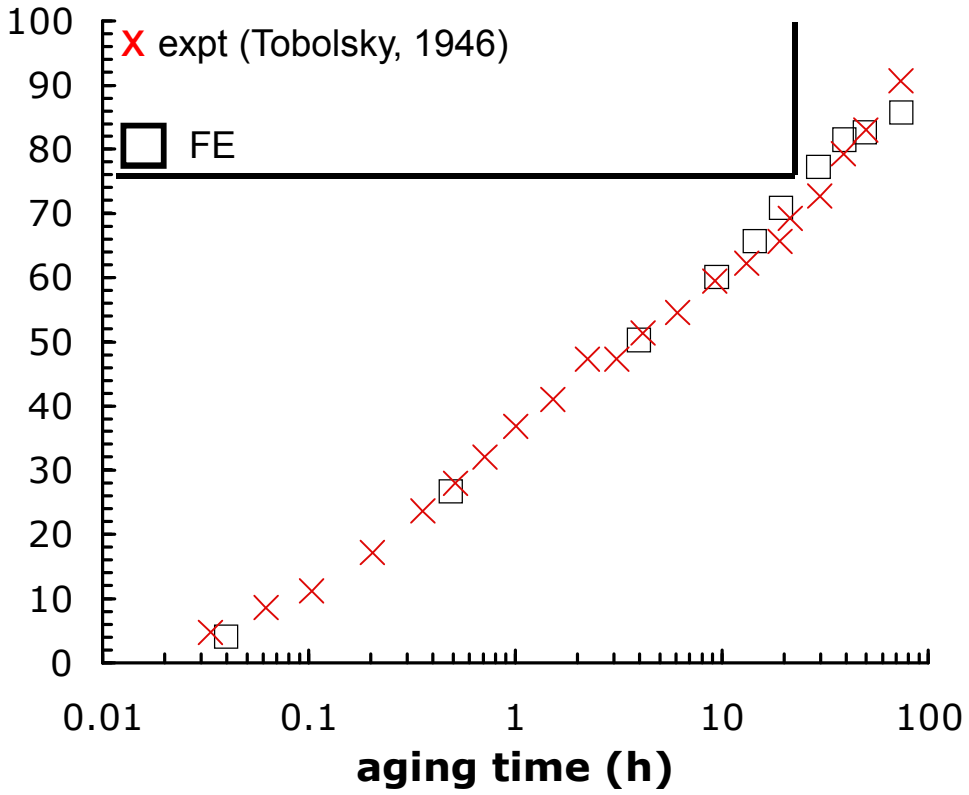


The constitutive model gave predictions in quantitative agreement with experiment

Stress in O-ring decreases with time



Permanent set in butyl rubber



Reactive forcefields provide QM information at MD speed

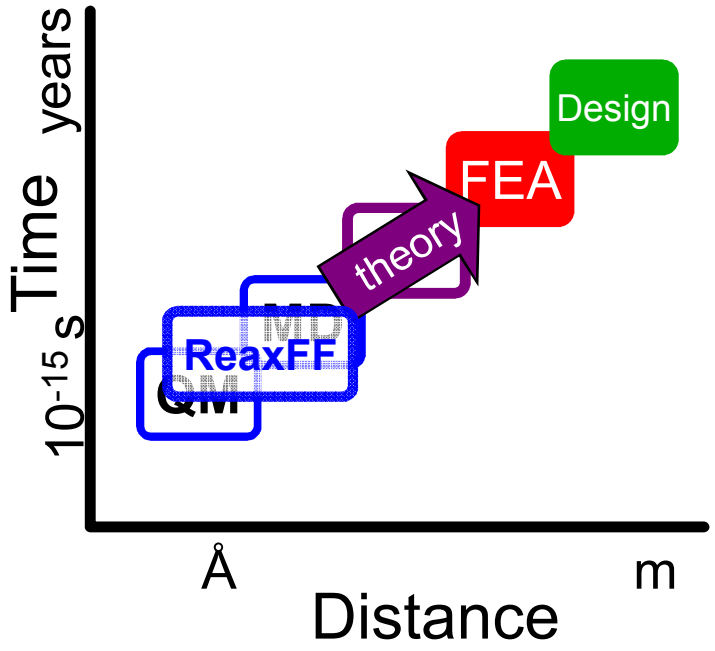
ReaxFF

GRASP

full atomic trajectories

Analysis

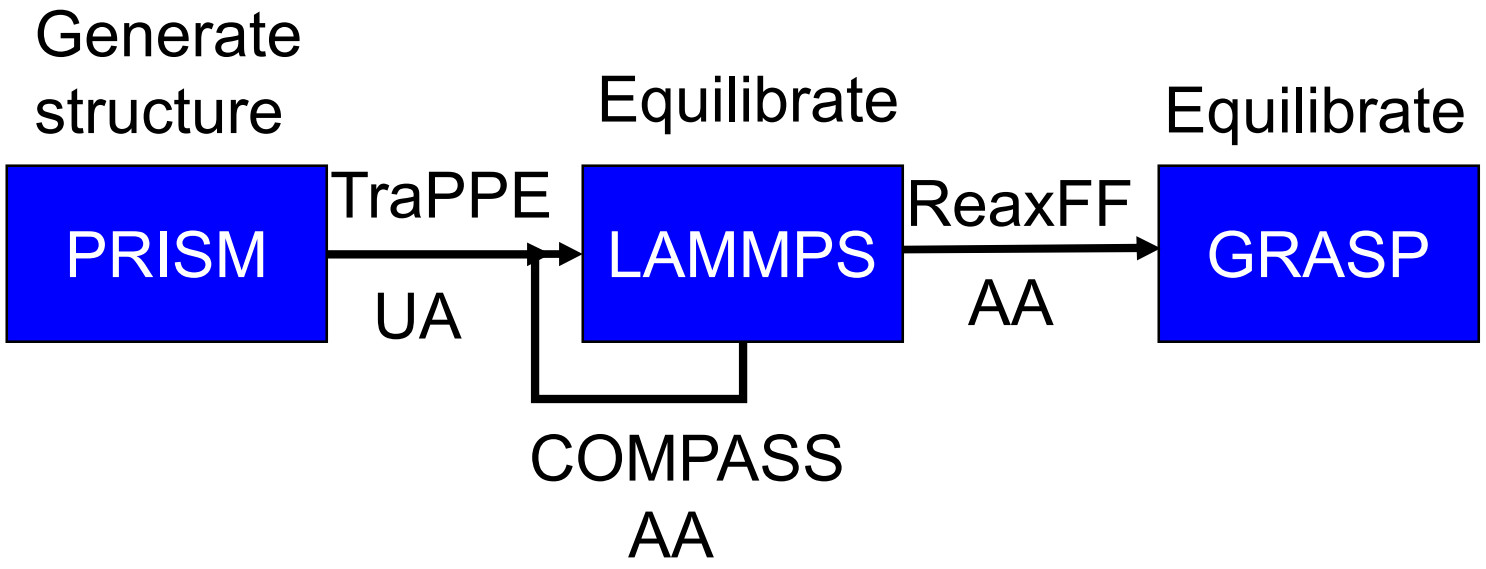
Chemical Insight



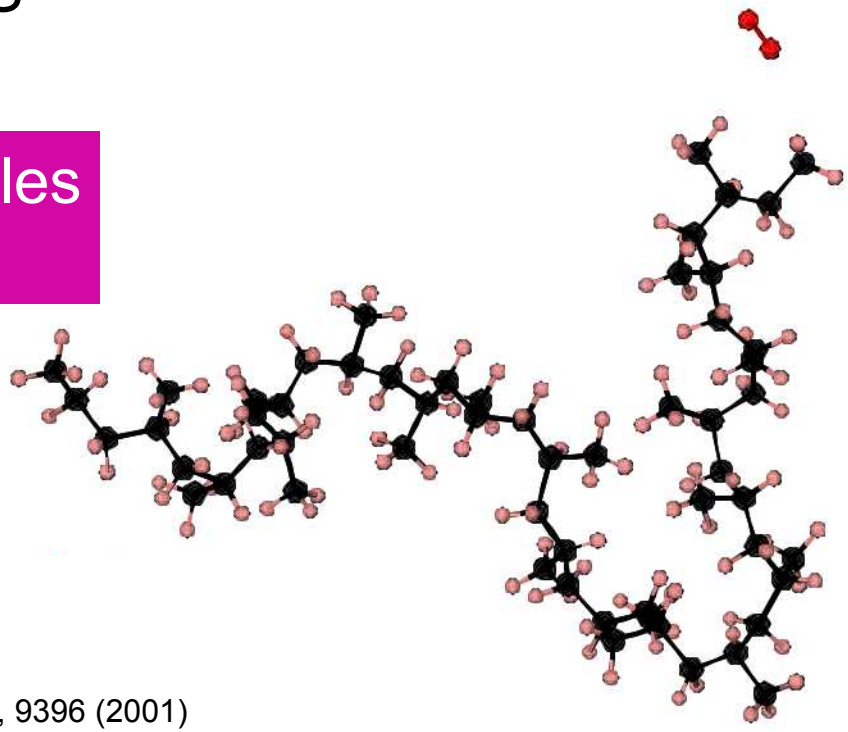
Bonds and charges are calculated self-consistently at every step

ReaxFF: van Duin, Dasgupta, Lorant, Goddard J. Phys. Chem. A 105, 9396 (2001)
GRASP: A. P. Thompson, SNL

Isotactic polypropylene was chosen as the test case

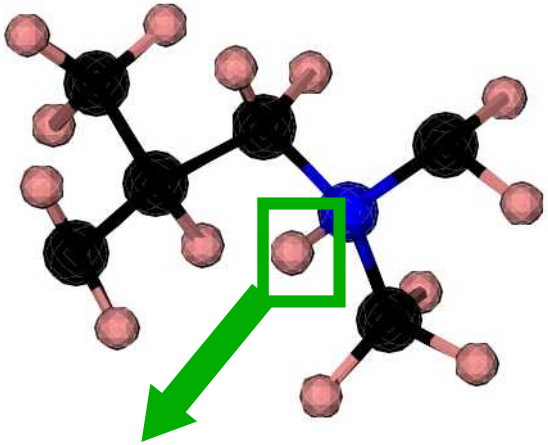


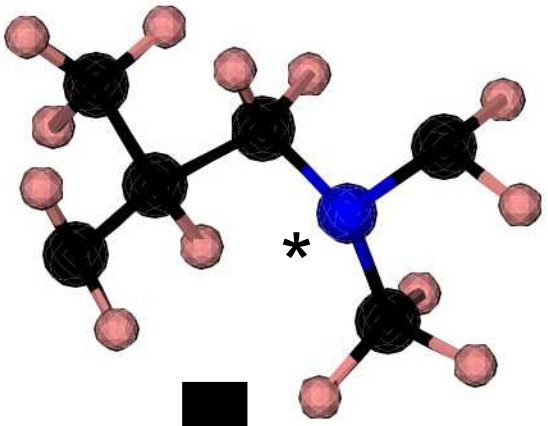
19 mers, 5 chains, oxygen molecules
T=453K, density=0.76 g/cc

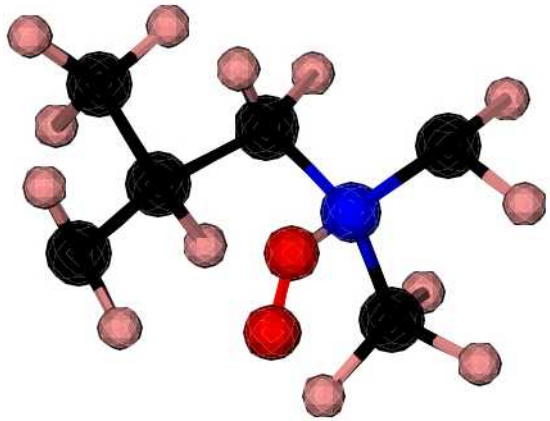


PRISM: Schweizer, Curro Adv. Chem. Phys. 98, 1 (1997)
TraPPE: Martin, Siepmann J. Phys. Chem. B 102, 2569 (1998)
LAMMPS: http://lammps.sandia.gov
COMPASS: Sun J. Phys. Chem. B 102, 7338 (1998)
ReaxFF: van Duin, Dasgupta, Lorant, Goddard J. Phys. Chem. A 105, 9396 (2001)

The reactions were accelerated by hydrogen abstraction





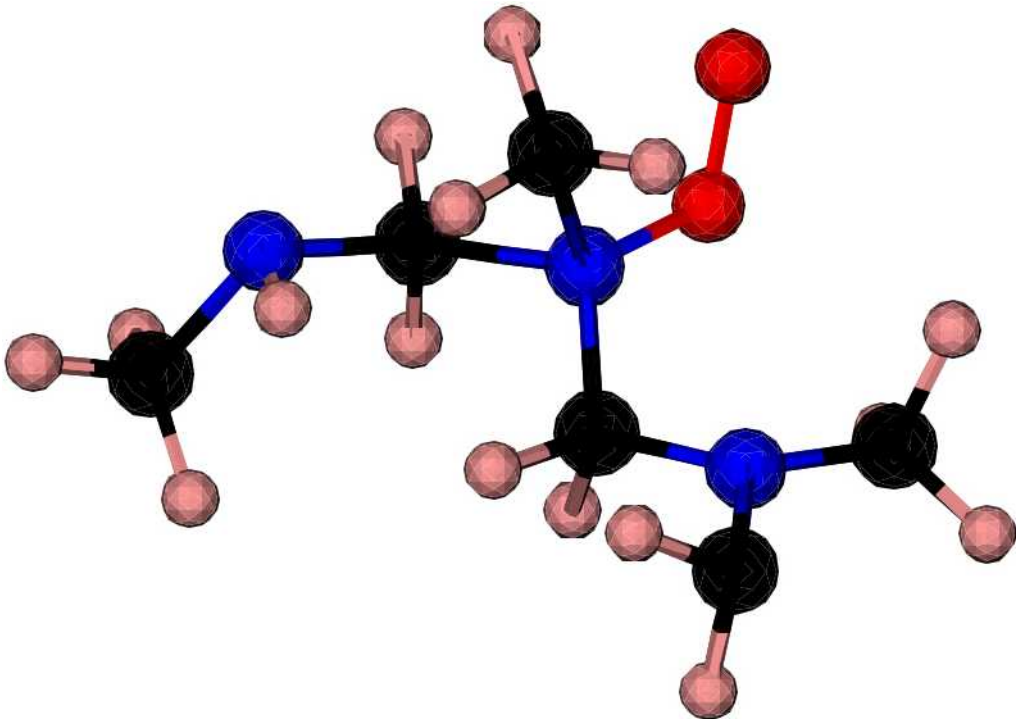


Conventional pathway:

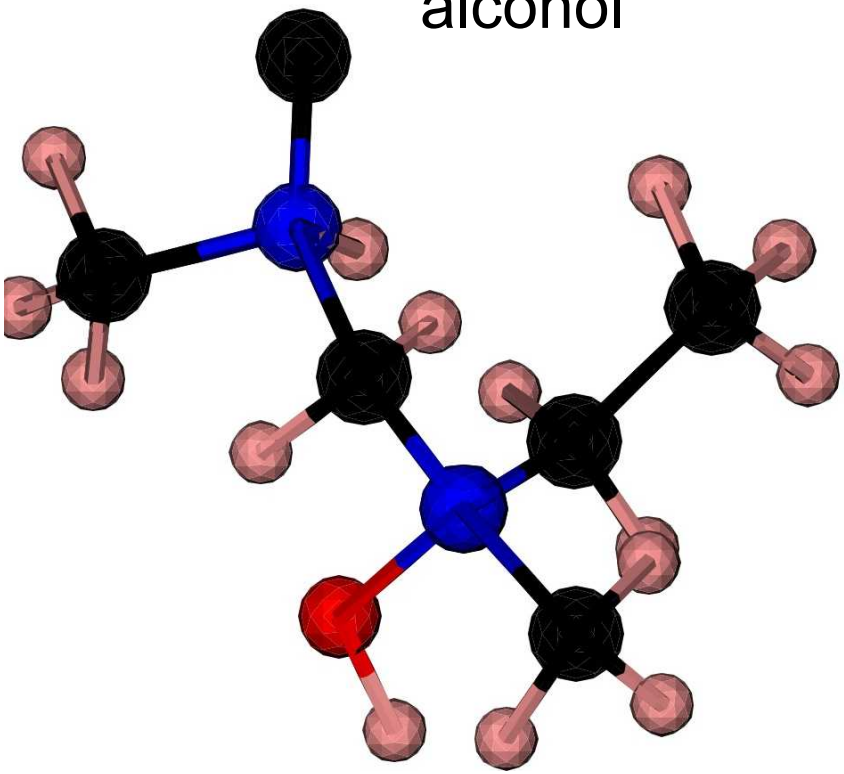
- ❖ slow initiation
- ❖ reactive tertiary carbon

ReaxFF shows the same products as NMR

peroxide

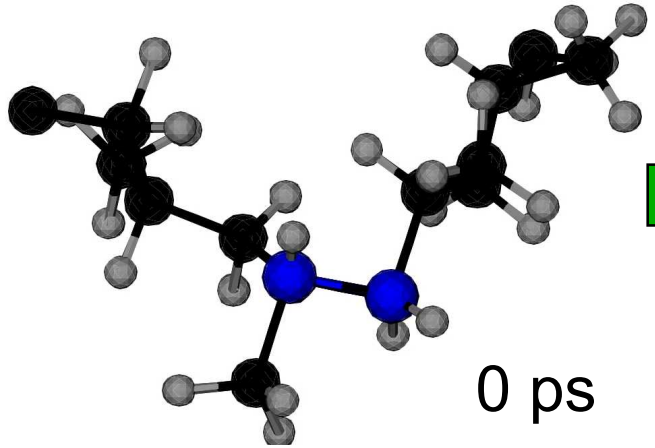


alcohol



NMR results: Mowery et al. Macromolecules 38, 5035 (2005)

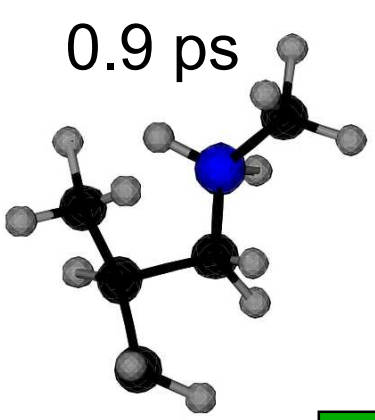
We can follow reaction pathways

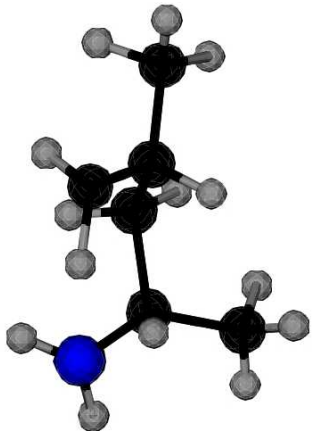


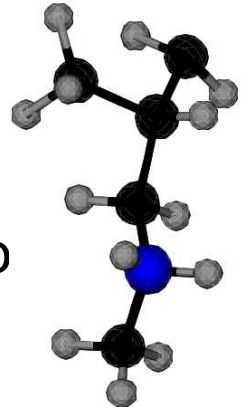
0 ps

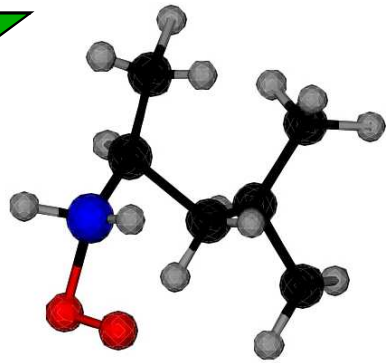
H attaches to tertiary carbon,
C-C bond broken

0.9 ps







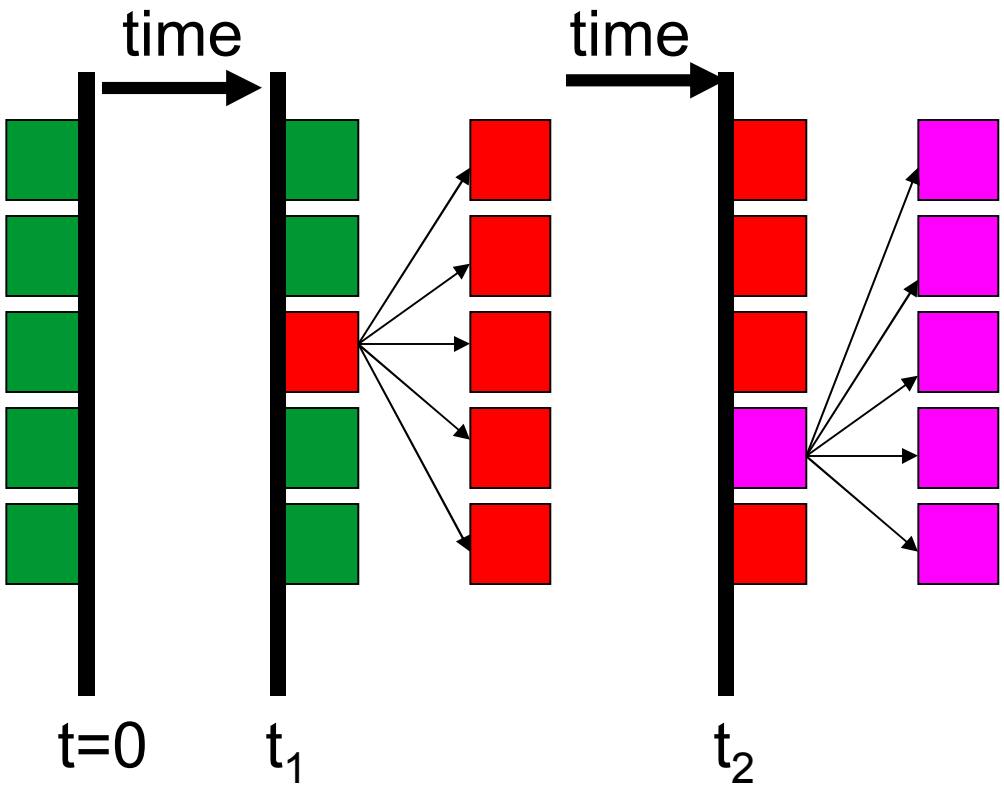


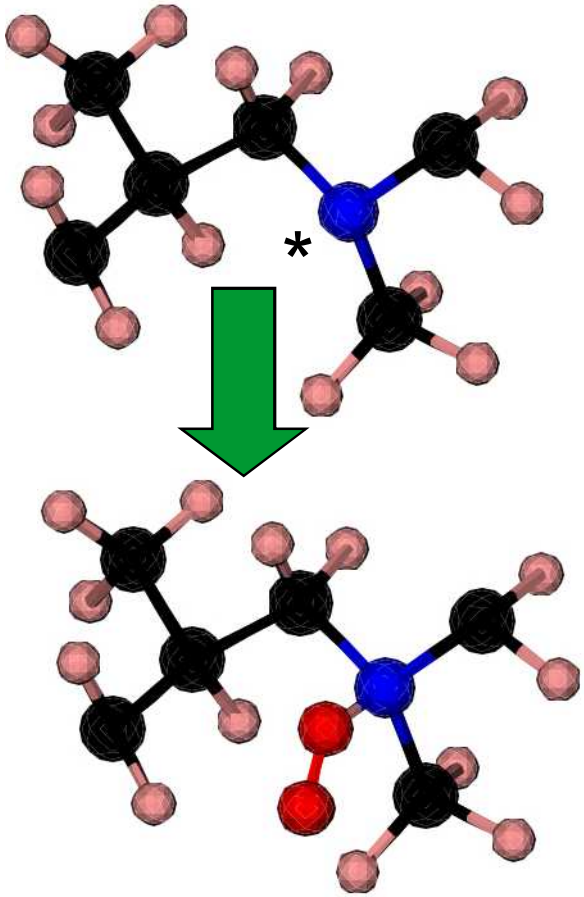
Peroxide attaches to
secondary carbon

23.6 ps

Parallel replicas may help surmount the problem of vastly different diffusion and reaction time scales

Positions identical; velocities vary between replicas

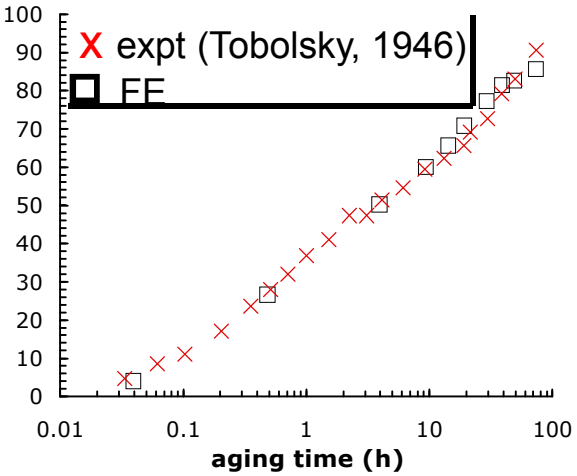


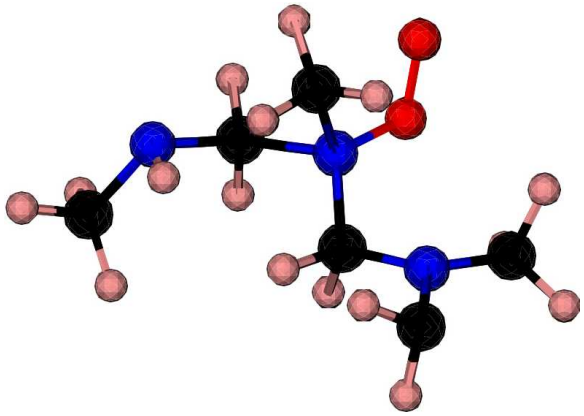


Rare events increased using physically meaningful paths
Correlated reactions directly observed for determining pathways

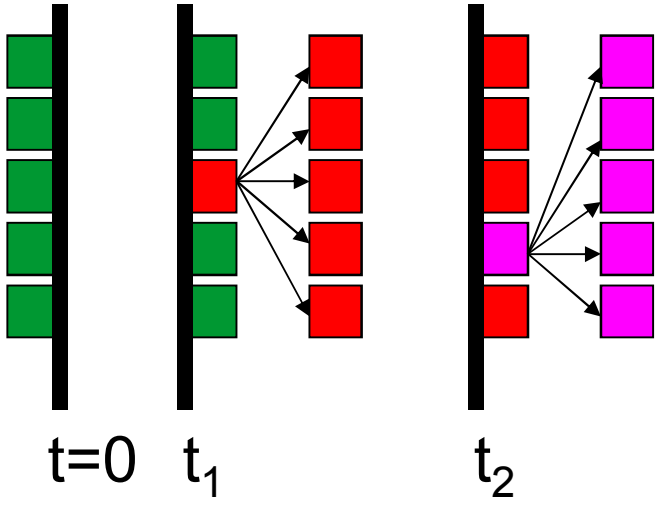
We have made progress on simulating the aging of polymeric systems

Good constitutive model developed from coarse-grained MD, implemented in FEM





Atomistic simulations using ReaxFF give reasonable results



Future Work: accelerating rare events in atomistic systems