A New Reactive Molecular Dynamics Model for Polymer Pyrolysis

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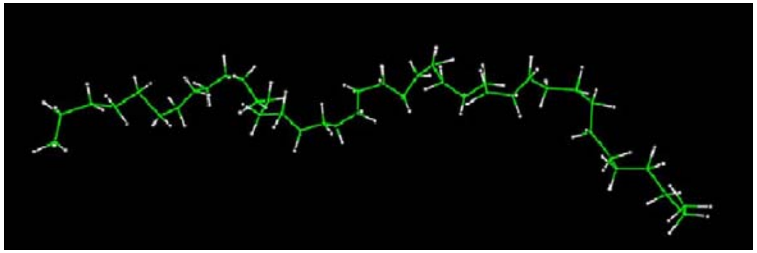
Pyrolysis kinetics are key to understanding flammability.

www.iafna.org.uk/links.php

- Commercial aircraft are estimated to have 2 tons of flammable materials.
- Generally, only a few minutes are available for escape prior to the flashover point.
- Development of fire-safe polymers is a time-consuming task.

Even for relatively small polymer systems,



$$H\Psi(\vec{q},t)=E\Psi=i\hbar\frac{\partial\Psi(\vec{q},t)}{\partial t}$$

Ab initio calculations of the kinetics become impractical.

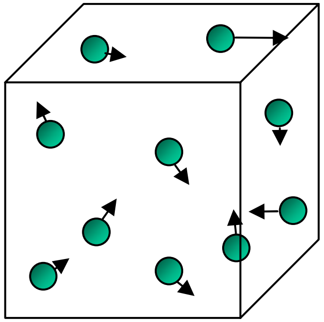
Need a tool to investigate the mechanisms of polymer decomposition for the development of new, fire-safe polymers.

What is Reactive Molecular Dynamics?

Solve Hamilton's Classical Equations of Motion

$$\frac{\partial H}{\partial p_i} = \frac{dq_i}{dt}, \quad \frac{\partial H}{\partial q_i} = -\frac{dp_i}{dt},$$

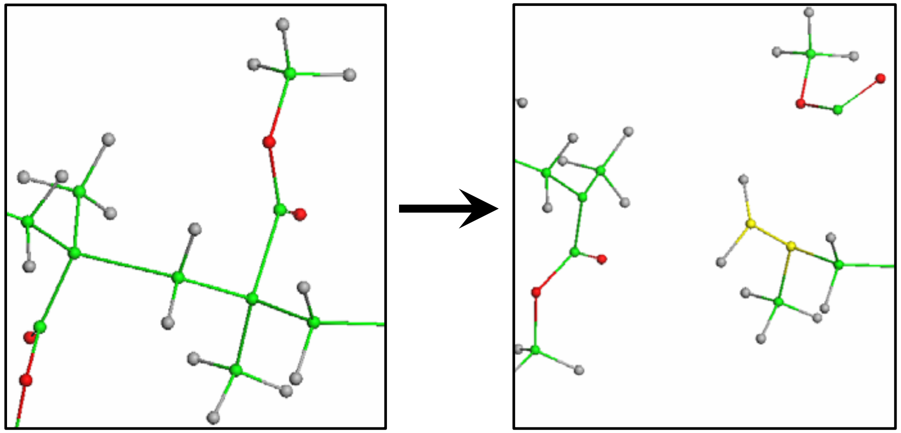
$$H = \sum_{i}^{N} \frac{\mathbf{p}_i^2}{2m_i} + V(q_1, q_2, \ldots, q_{3N})$$



$$V = \sum^{n_{bonds}} V_{bond}^{\text{Morse}} + \sum^{n_{angles}} V_{angle}^{\text{harmonic}} + \sum^{n_{torsions}} V_{torsion}^{\text{sinusoidal}} + \sum^{n_{pairs}} V_{nonbond}^{\text{Lennard-Jones+Coulombic}}$$

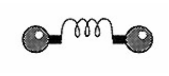
Coupled with a chemical bond-breaking and -making routine

Allow dynamics to progress into non-equilibrium conformations that will eventually lead to a reactive event.

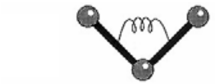


MM3 Forcefield is used to represent equilibrium structures.

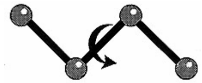
Terms associated with MM3



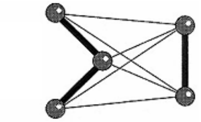
quartic



Sextuple corrected-harmonic



3-term Fourier series



van der Waals & dipoles

Errors associated with MM3 in kcal/mole

Hydrocarbons	0.35
Rotational Barriers	1.25
Oxygen Compounds	0.65
Haloalkanes	0.80

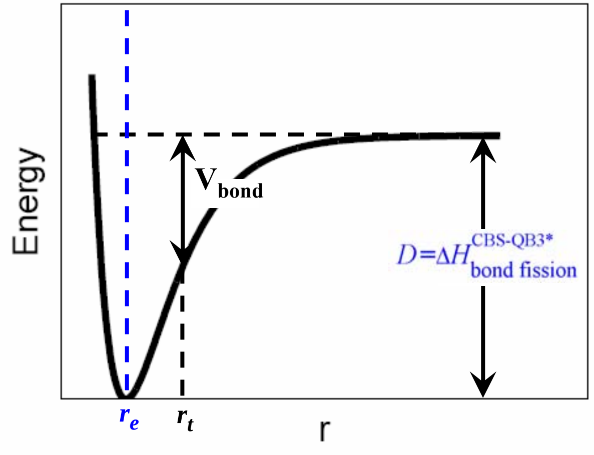
MM3 represents equilibrium structures reasonably well and has widespread use.

Allinger *et al.*, *J Am Chem Soc* **111**, 8551 (1989)

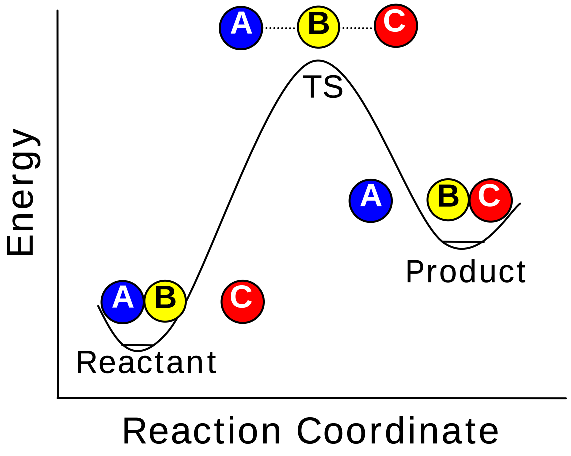
Gundertofte *et al.*, *J Comput Chem* **17**, 429 (1996)

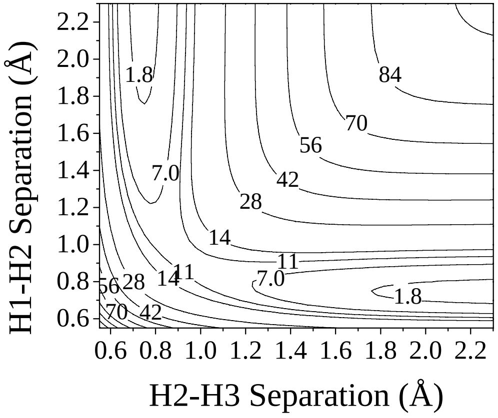
How can we describe a reactive event?

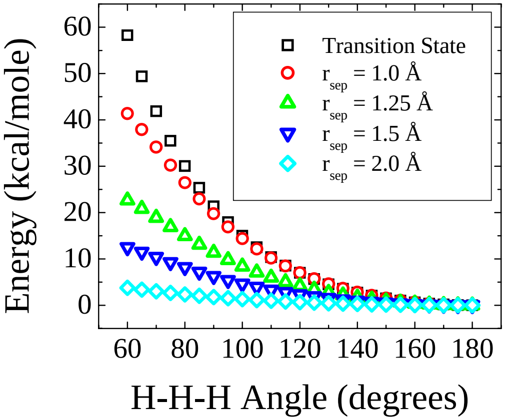
For homolytic scissions & recombinations, its easy.



But other reactions must consider a more complicated potential energy surface.

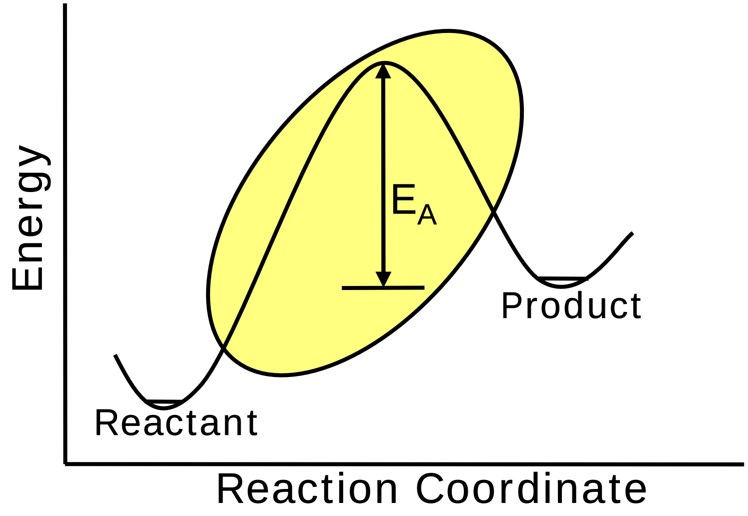


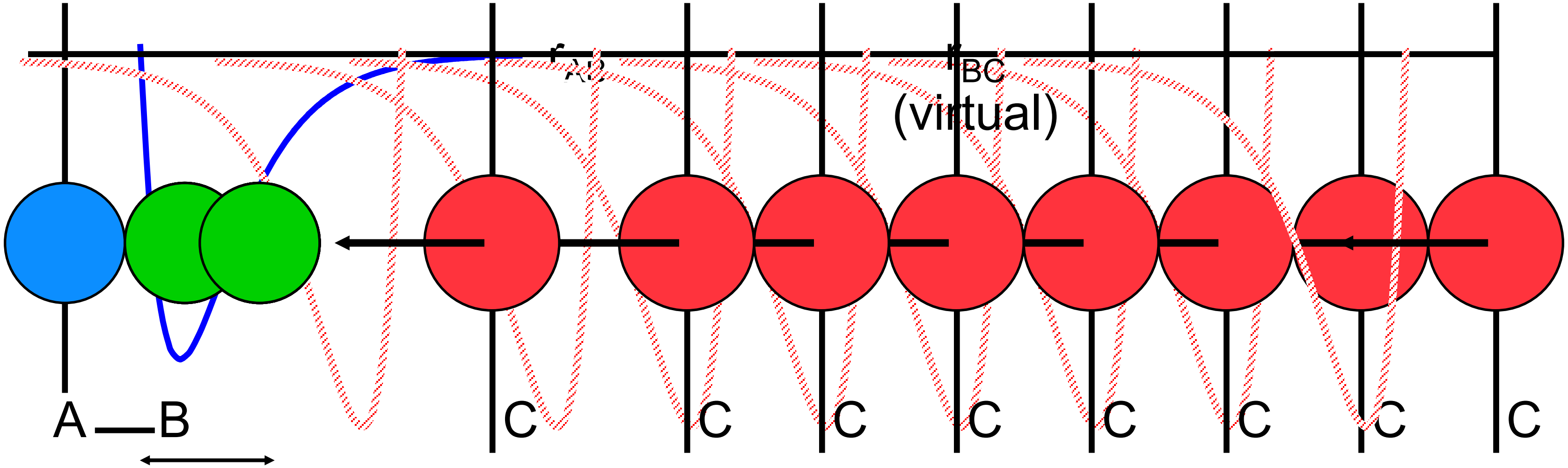




Forcefield Development: Conventional Forcefield Potentials

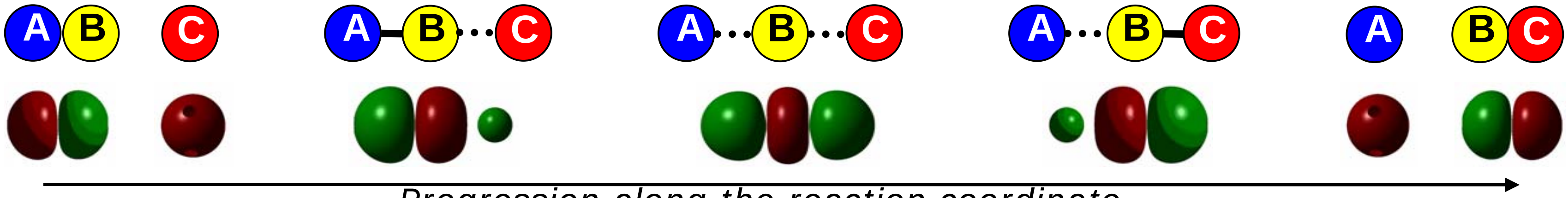
- Conventional forcefields already provide accurate descriptions of the reactants and products.
- Need to combine the interactions of the molecules to represent the reactive path, including transition state during a chemical reaction.





Making the switch smooth.

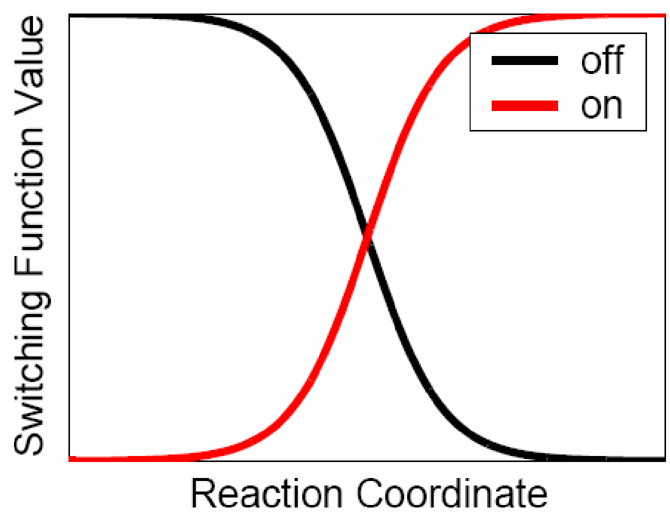
The composite energy is represented as a combination of the energy from the reactant and product structures, as well as transition state if necessary.



Progression along the reaction coordinate

For smoothing, introduce switching functions, f_i, for reactant and product:

$$E = f_1 E_{react} + f_3 E_{prod}$$



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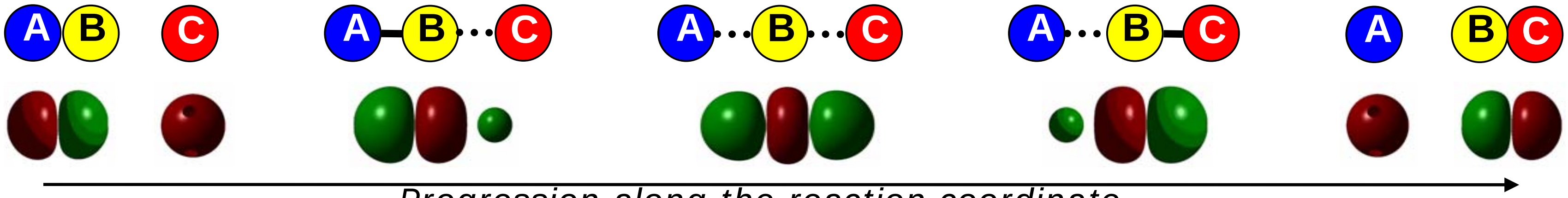
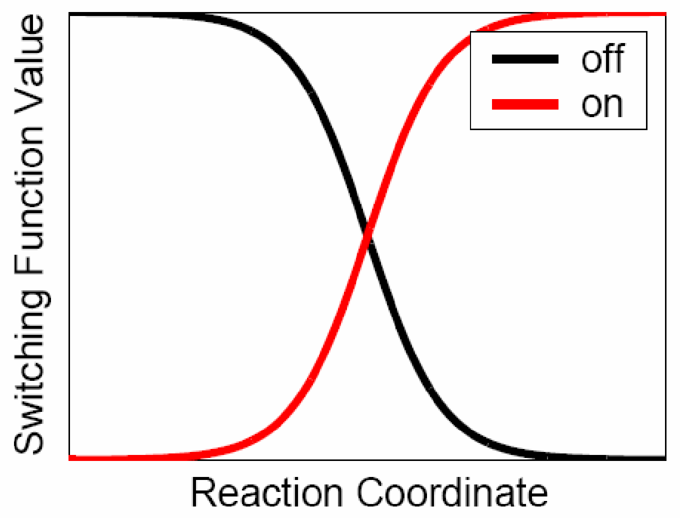


Progression along the reaction coordinate

For smoothing, introduce switching functions, f_i, for reactant and product:

$$E = f_1 E_{react} + (f_2 E_{TS}) + f_3 E_{prod}$$

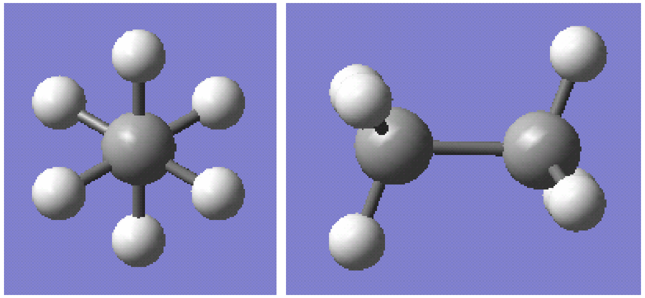


Dissociation in simple molecules involves more complex changes.

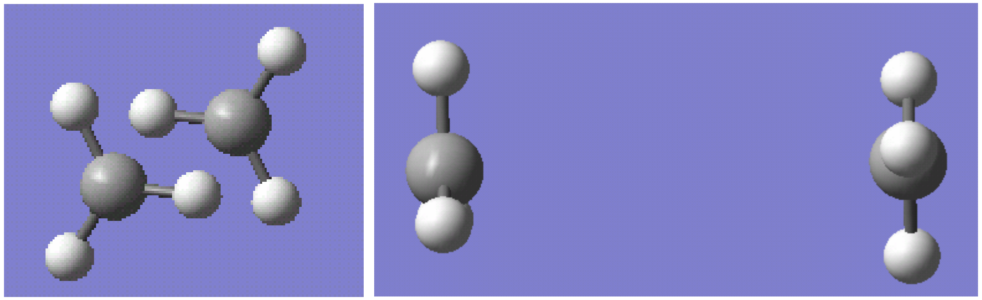
- Consider C-C dissociation in ethane.

Newman Projection

3-D Projection



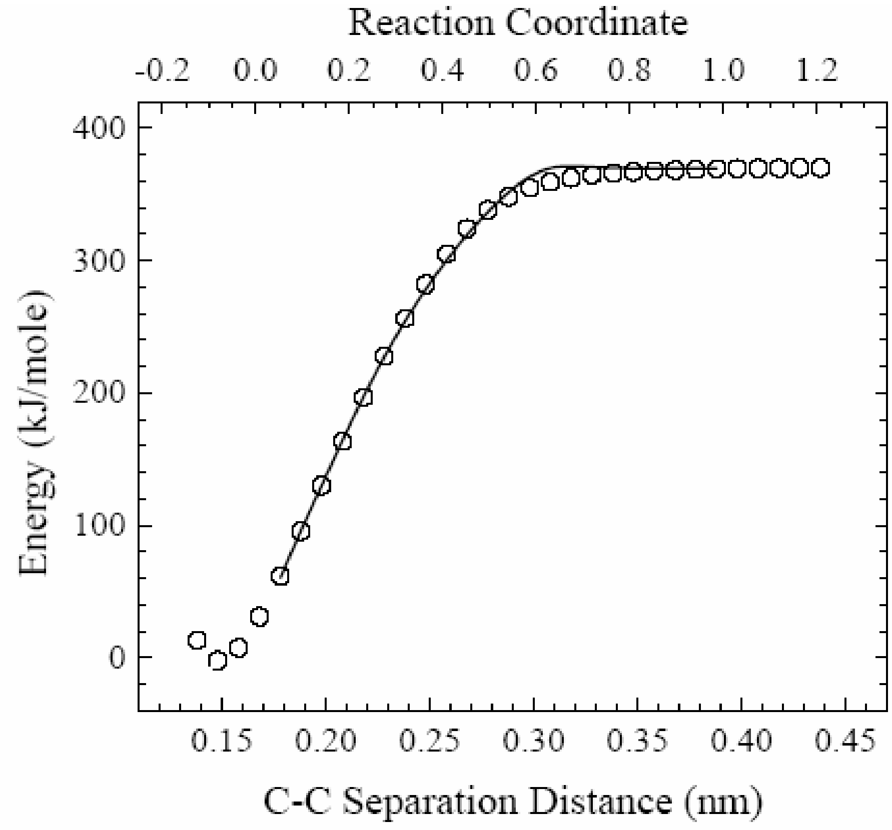
3-D Projection

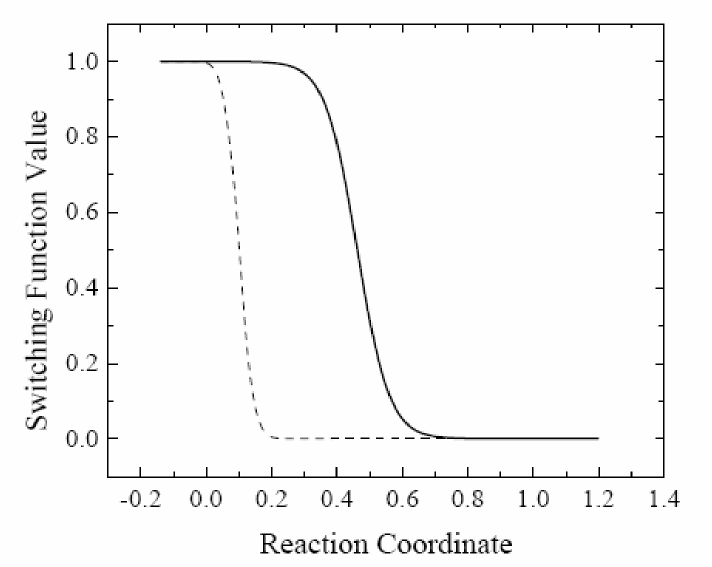


1 sp^3 C – sp^3 C bond →	No C – C bond
6 sp^3 C – H bonds →	6 sp^2 C – H bonds
6 H – sp^3 C – H angles →	6 H – sp^2 C – H angles
6 H – sp^3 C – sp^3 C angles →	No H – C – C angles
9 H – sp^3 C – sp^3 C – H torsions →	No H – C – C – H torsions
and	C – C vdW interaction
	C – H vdW interaction
	H – H vdW interaction

Homolytic scission was modelled with two switching functions.

- Two separate switching functions were used.
- The same RC parameters were used in each switching function.



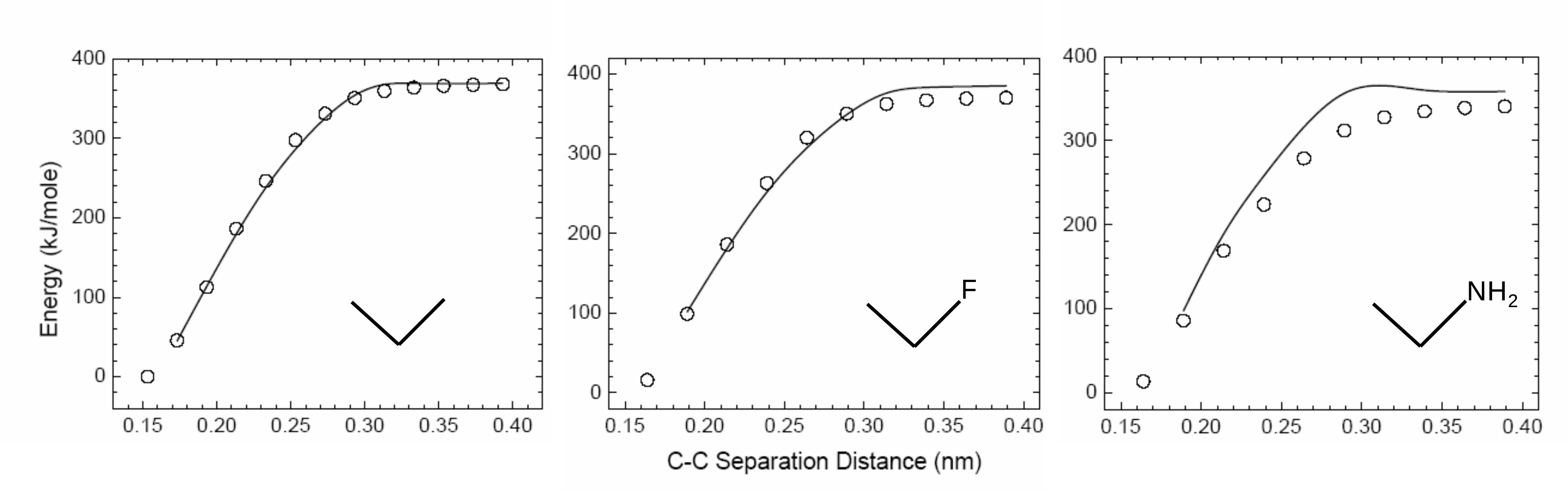


Energy data are from UCCSD(T)/cc-pVTZ calculations shown as points.
The fitted model is the solid line.

Smith, Stoliarov, Nyden, Westmoreland, *Mol. Sim.*, **4-5**, 361 (2007)

C-C switching function from ethane usefully transferrable.

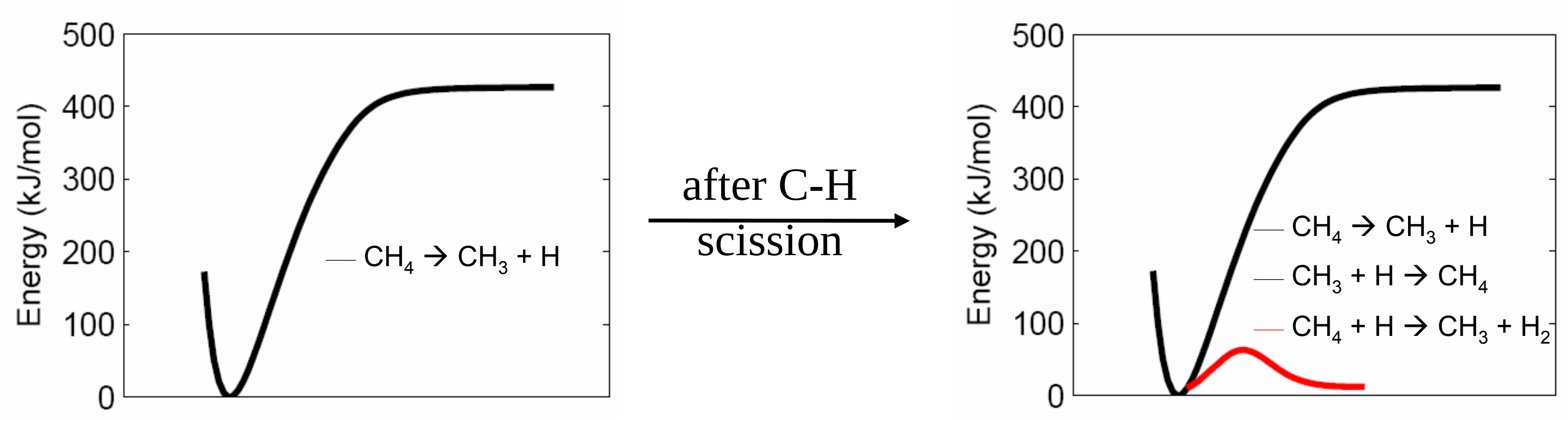
- Used the same C-C switching function parameters derived from ethane.



The main limitation to the forcefield description lies within the ability of the equilibrium forcefield to describe the components correctly.

RxnMD: Unbiased selection of possible reactive events

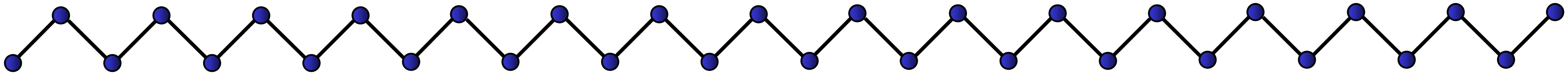
RxnMD is written in C++ and couples the solution of Newton's classical equations of motion with our new reactive forcefield, RMDff.



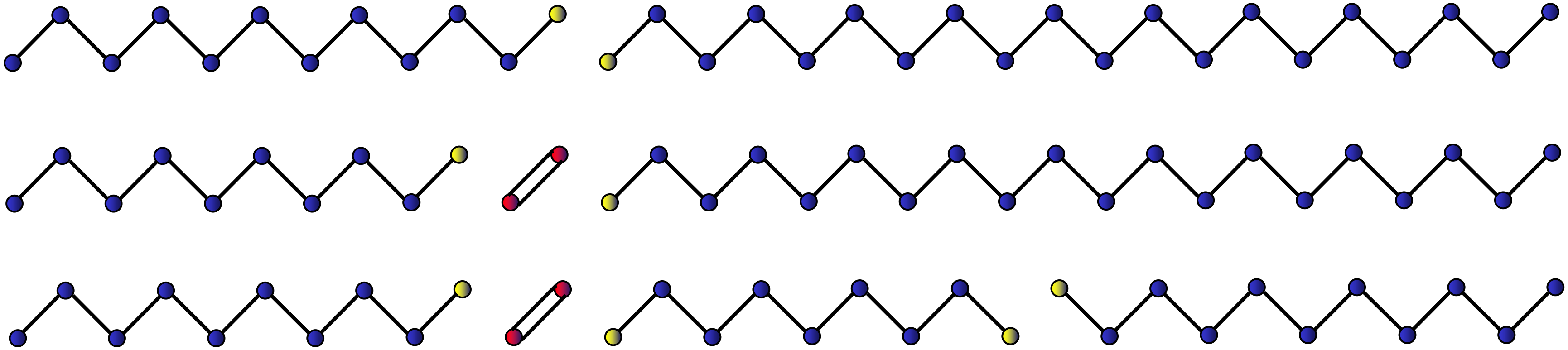
1. For a system of methane molecules, initially the only available reaction is the C-H bond scission.
2. Once scission occurs, the potential energy surface has different reactions available because of the presence of radicals, such as H abstraction and radical combination.

Transferring models to larger structures

From a long polymer chain …

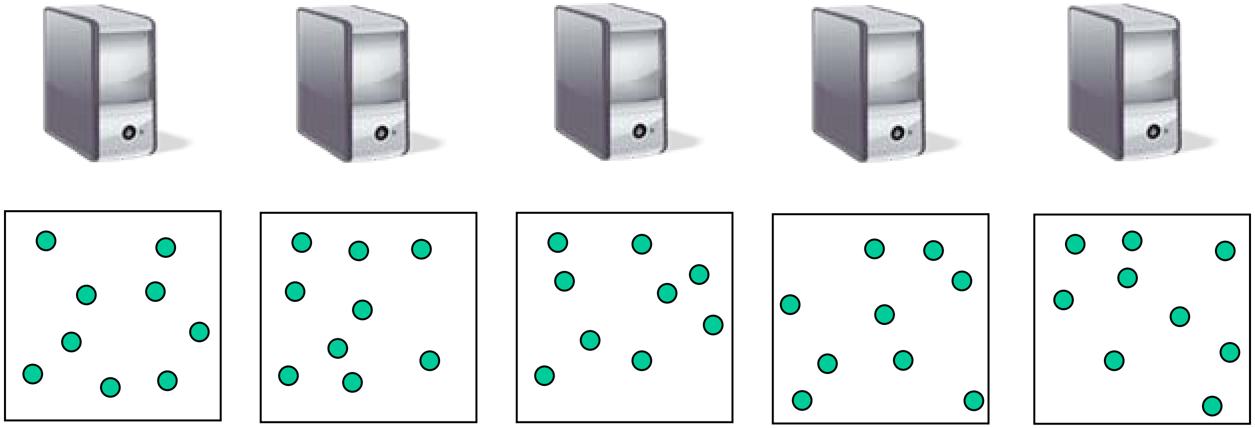


Now the system progresses, allowing each possible reaction to proceed.

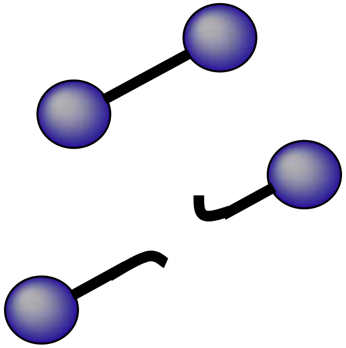


Localized reaction descriptions allows for accurate reaction models developed in small, representative molecules to be transferable to larger molecules.

RxnMD is ideally suited for parallel computation.



- Parallel simulations via temporal decomposition.
- Decoupled, infrequent events are exploited to amass necessary statistics.
- Each path is independent and annealed of any previous reactive path.
- For high-pressure-limit bond dissociation, use first-order kinetics.



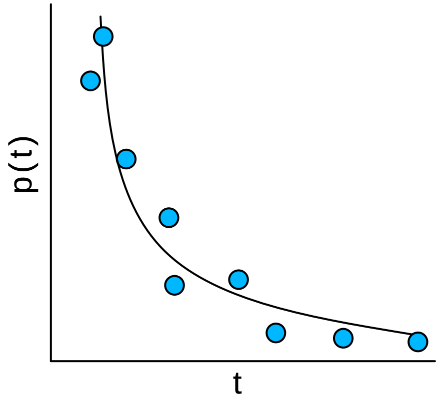
Voter, *PRB*, **52**, R13985 (1998)

Getting quantitative kinetics from RxnMD.

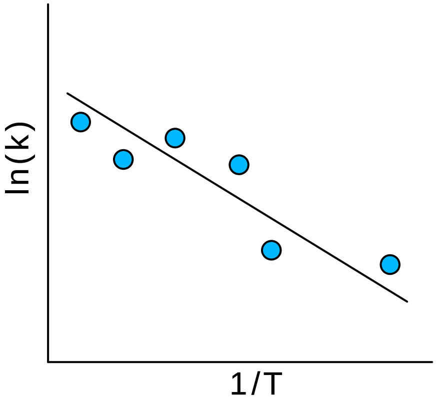
First-order processes have exponential-decay statistics.

$$p(t) = k_{total} \exp\left[-k_{total} t\right]$$

Accumulation of time for kinetic events at a particular temperature yields the kinetic rate constant.



$$\langle \Delta t \rangle = \frac{1}{k_{TST}}$$

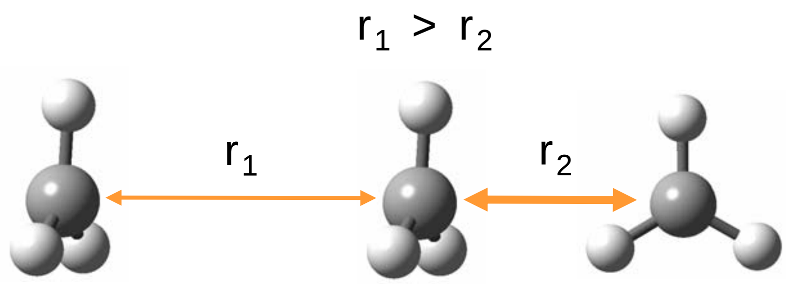


Analyze many simulations at different temperatures to yield the Arrhenius kinetic parameters.

Selecting between reaction possibilities.

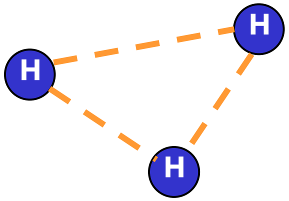
How do you select between the recombination of the methyl radicals?

- Based on a distance criteria alone, the r_2 bond would be formed.
- Energetically, r_1 is more favored than r_2.



Select the reaction by probabilistically weighting each structure with its energy and randomly implement one reaction each time step.

$$P_i = \frac{e^{\frac{-E_i}{kT}}}{\sum e^{\frac{-E_i}{kT}}}$$

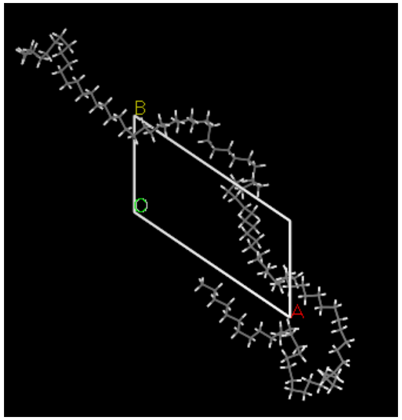


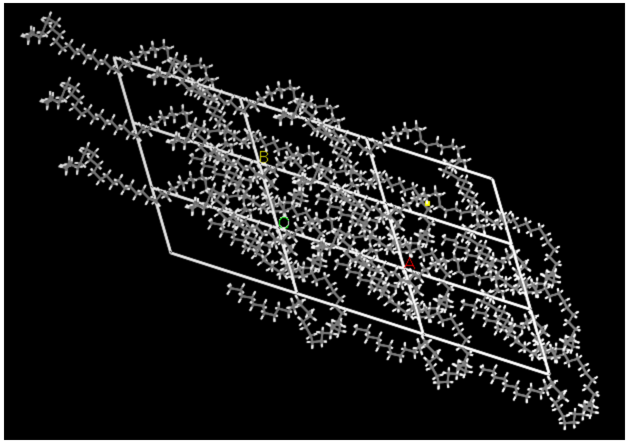
As the integrated time step approaches zero, a natural, stochastic selection of the chemistry is implemented, including both structure and dynamics.

A test on HDPE: Simulation Conditions

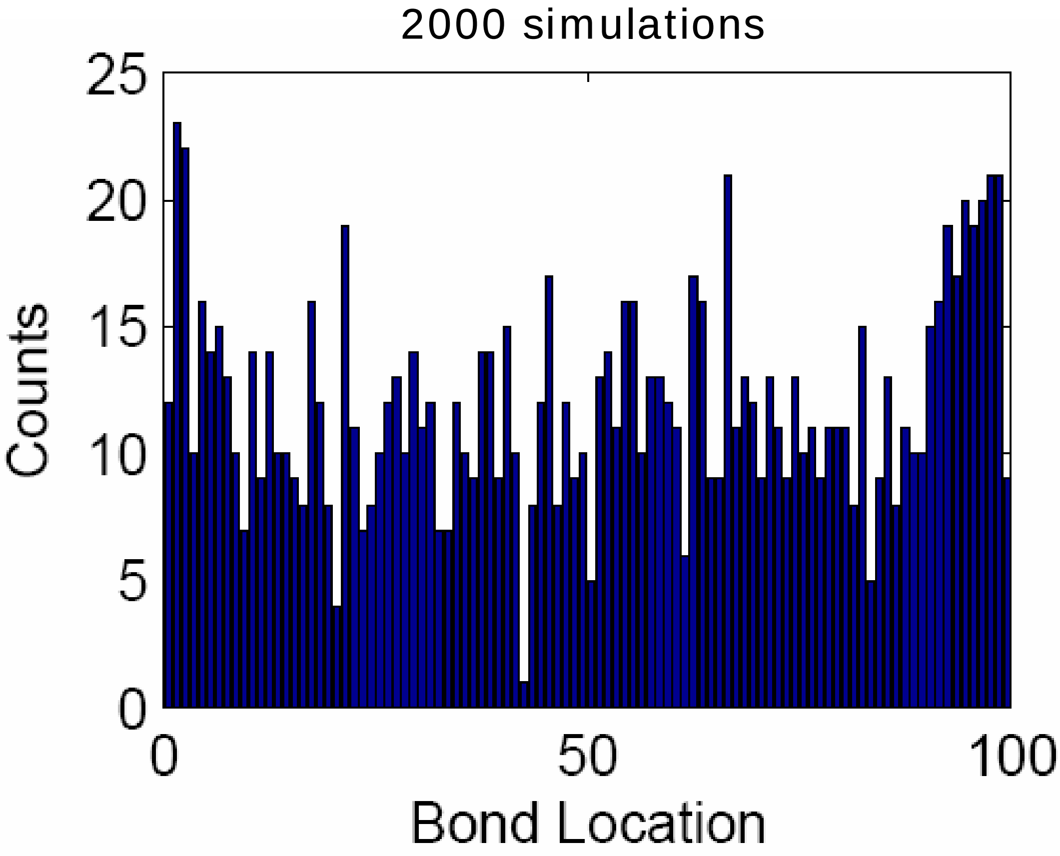
- Single chain polymers are used with periodic boundary conditions to approximate condensed-phase chain interactions.
- High temperatures allow reactions to be observed within realistic time scales. (1700-2050 K)
- Simulations use NVT-ensemble.

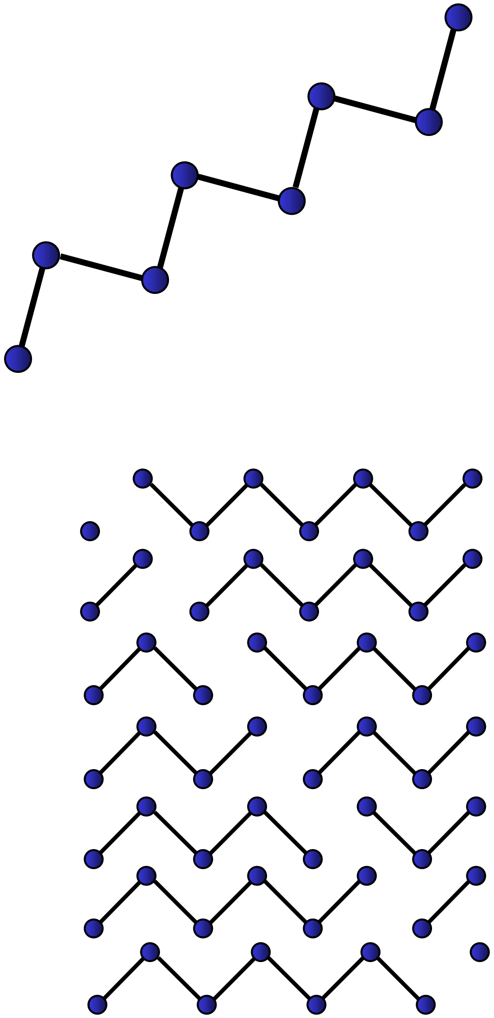
50-repeat unit HDPE





HDPE: The scission location is random like experiments.

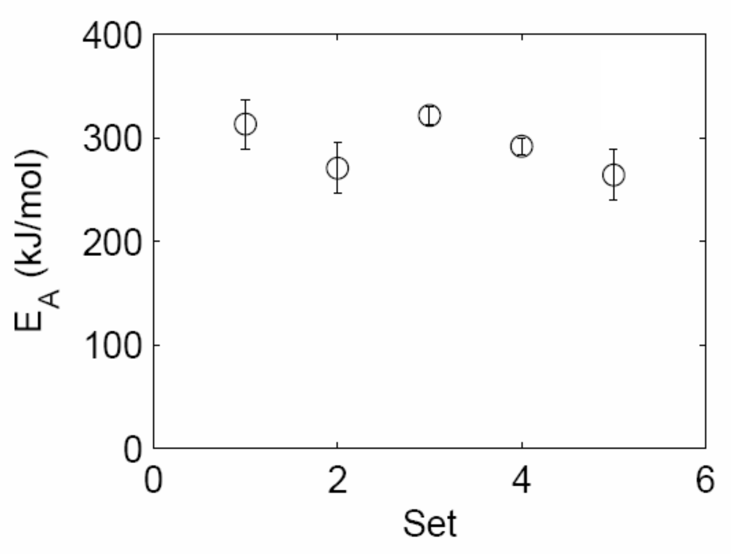




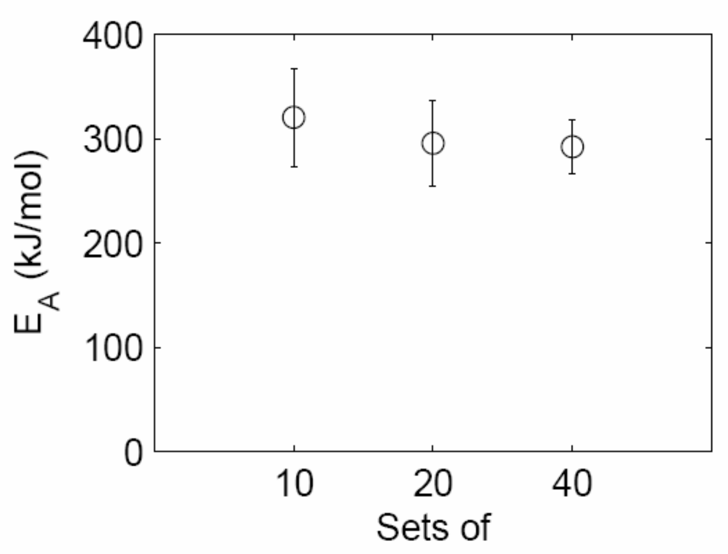
Quantitative kinetics depend on the number of simulations.

Determine the number of simulations necessary for a single structure of PE50.

Simulations completed on different sets, which contain 40 simulations per temperature.



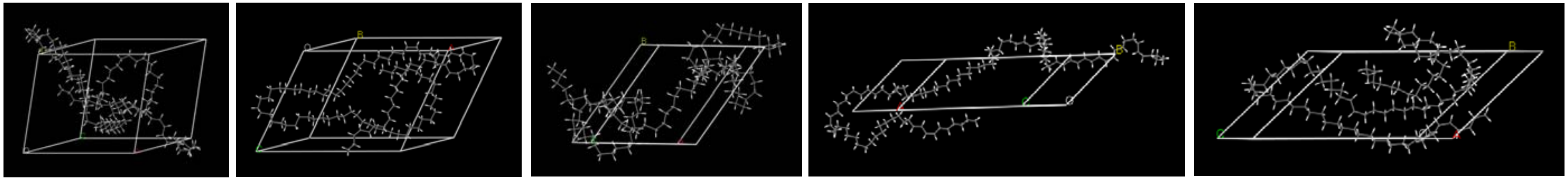
Averages of E_A from 5 sets of simulations, which contained either 10, 20, or 40 simulations per temperature.

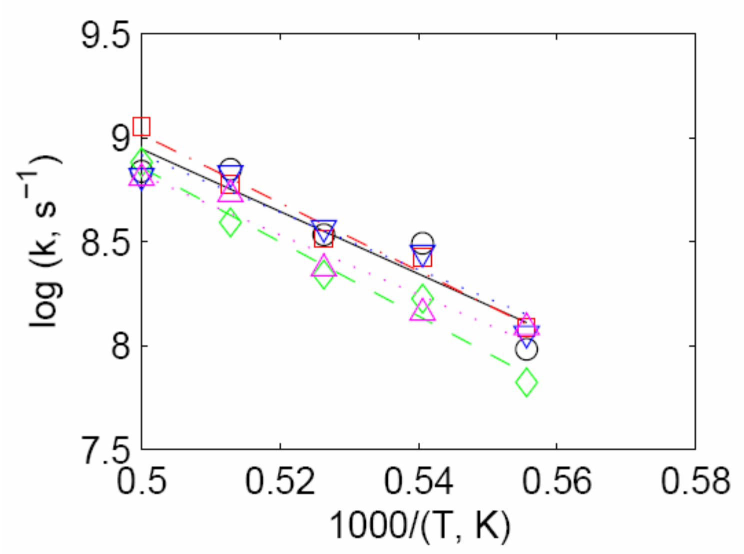


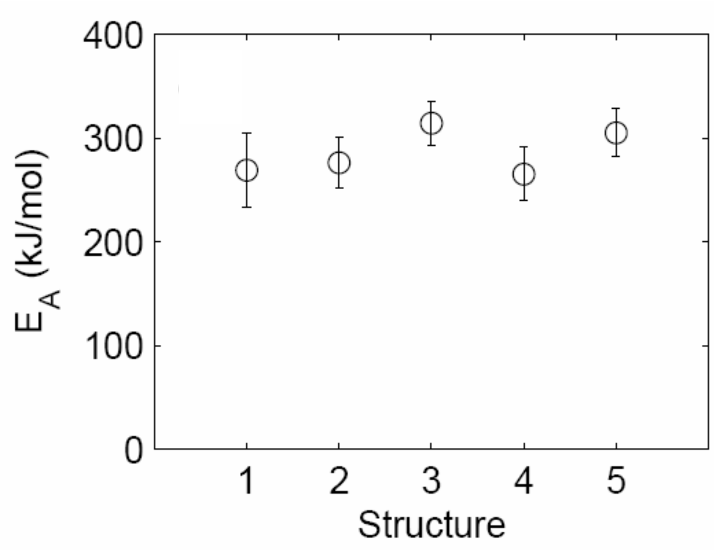
ANOVA shows the kinetic parameters to not be statistically significant with respect to the number of simulations.

Kinetics are independent of polymer structural effects.

Determine the effect of different, annealed structures on kinetic parameters.



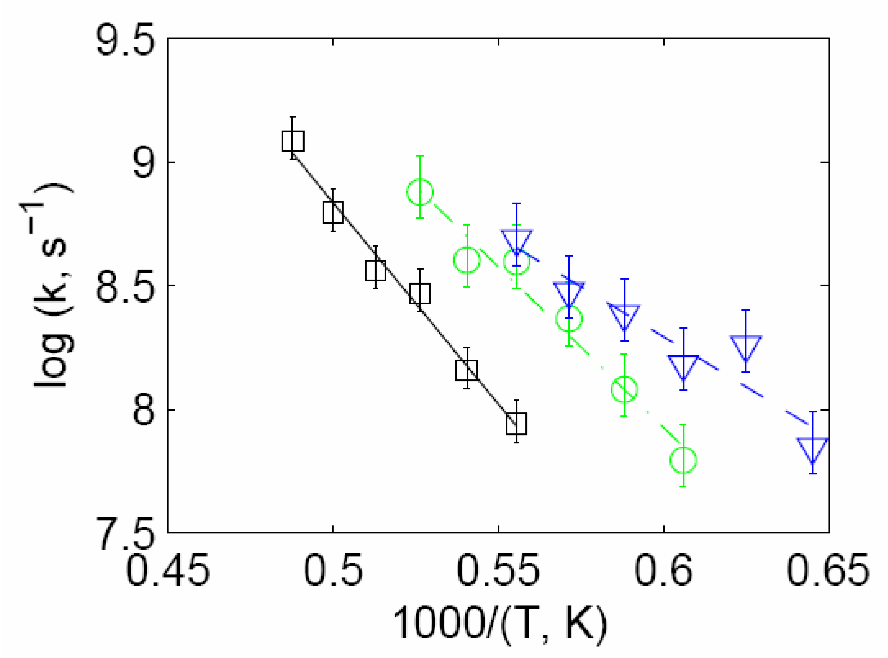




Student's t-test comparisons demonstrate the kinetic parameters to not be statistically significant with respect different structures.

Longer chain length results in decreased activation energy.

- NVT-ensemble decomposition of HDPE chains.
- Simulated chains in a periodic box in order to obtain condensed-phase decomposition kinetics.

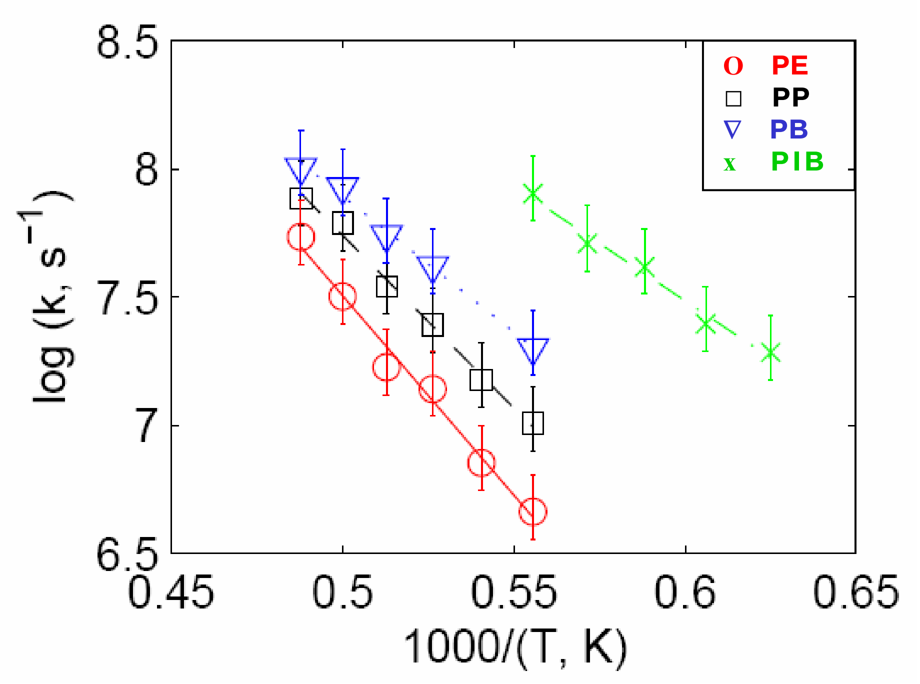


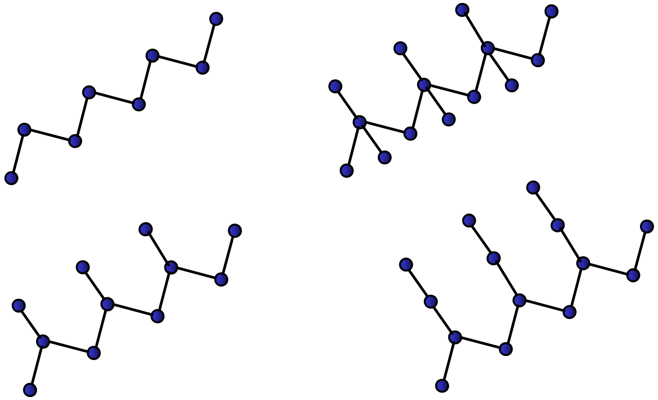
N	$A \times 10^{15} (s^{-1})$	E_A (kJ/mol)
50	27.3	292
100	5.24	248
200	0.037	169

The increased length allows for decreased chain mobility, which in turn results in the polymer pulling apart more easily.

The side-group further effects the initial backbone scission.

- NVT-ensemble decomposition of 50-repeat-unit, periodic chains.

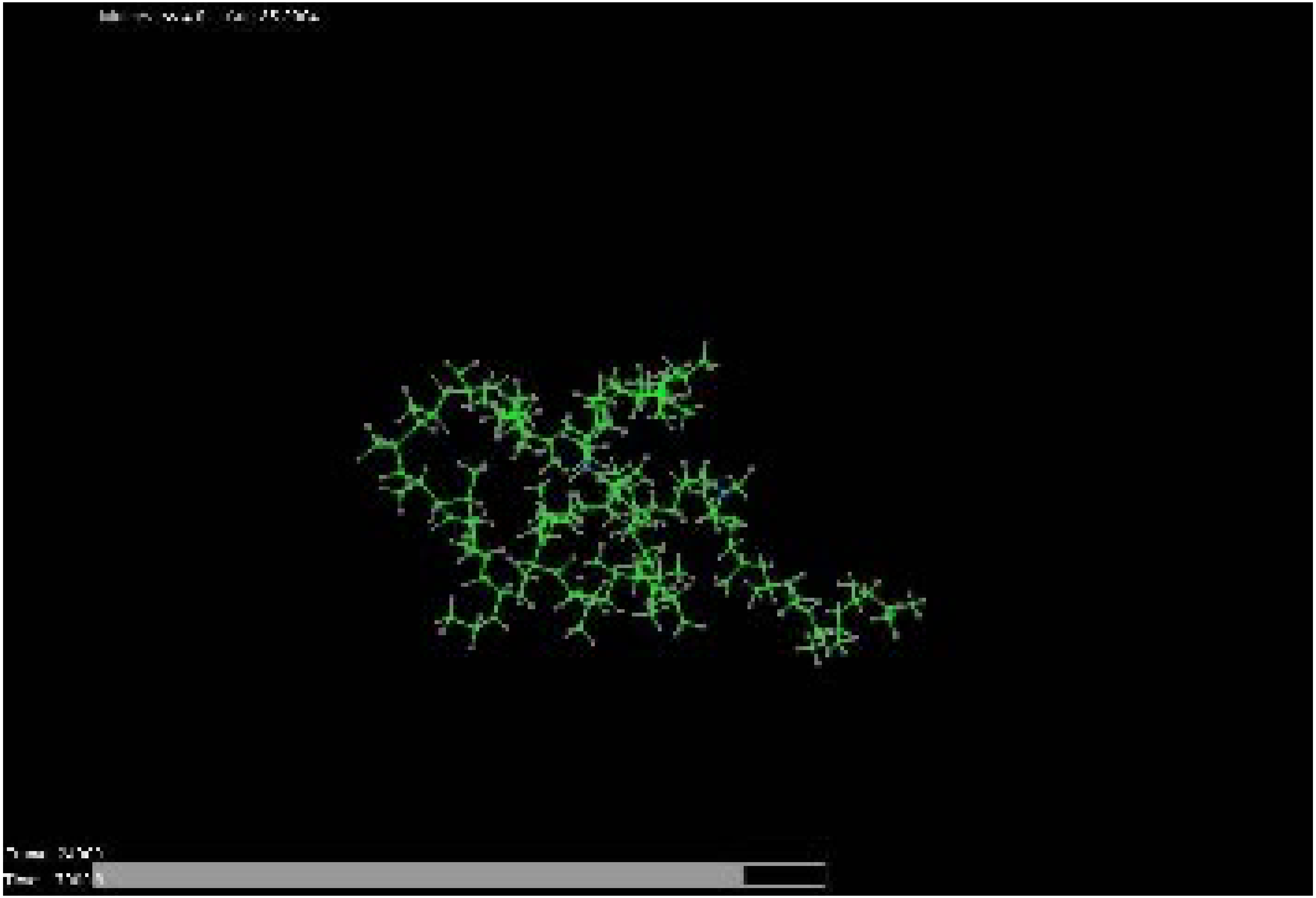




Polymer	A × 10^{14} (s^{-1})	E_A (kJ/mol)
PE	273	292
PP	2.9	257
PB	0.16	203
PIB	0.0694	171

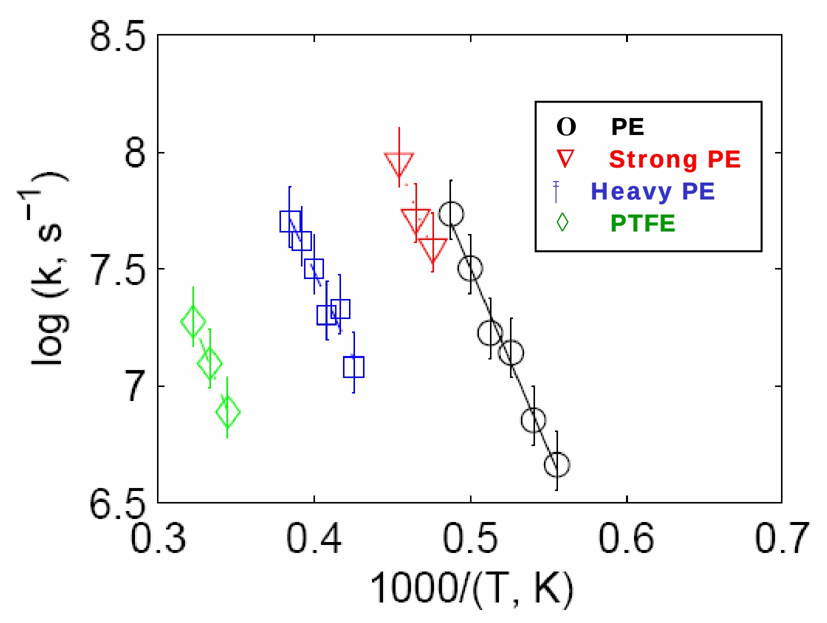
HDPE can easily diffuse through the melt with less chain hindrance than other polymers that have methyl and ethyl side-groups.

Polypropylene backbone decomposition



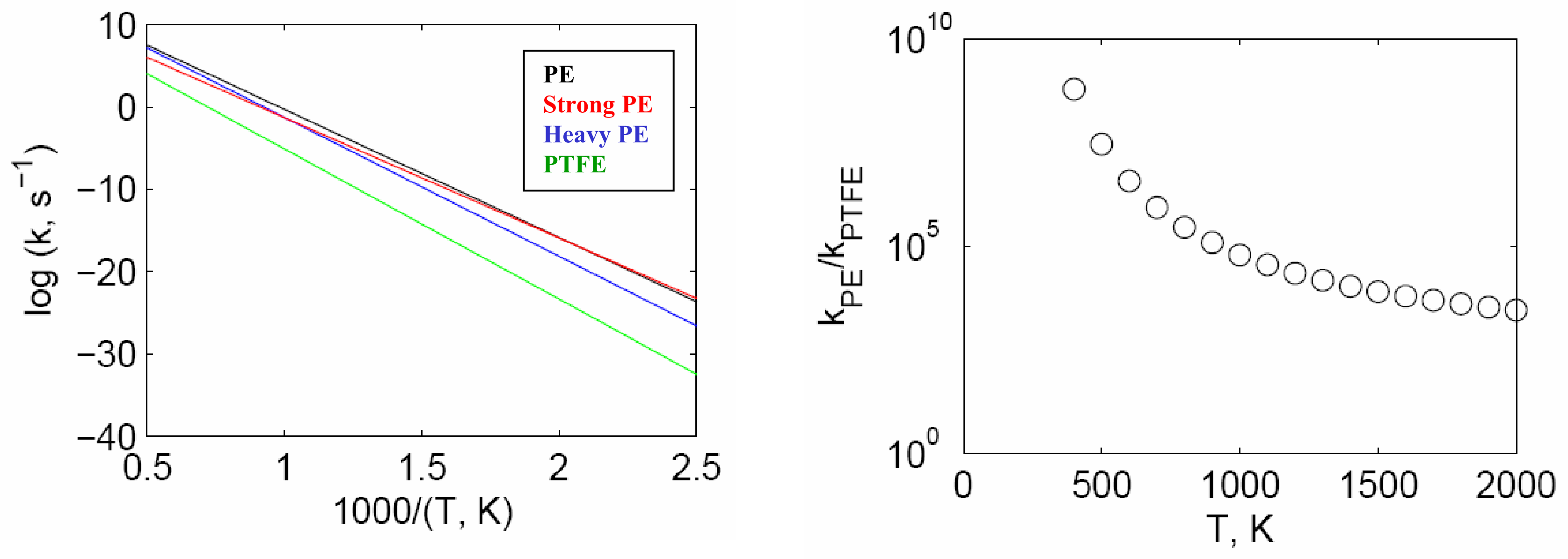
Pushing further: Test on PTFE and comparison to HDPE.

- What are the changes from polyethylene to poly(tetrafluoroethylene)?
  - Increase the “H” atom mass from 1 g to 18 g for F.
  - Increase the C-C bond energy from 370 kJ/mol in C_2H_6 to 421 kJ/mol found in C_2F_6.
- Assess the effects of these simple changes between HDPE and PTFE in relation to the initial backbone decomposition.



Polymer	$A \times 10^{14}$ (s^{-1})	E_A (kJ/mol)
PE	19.2	298
Strong PE	41.1	323
Heavy PE	0.22	280
PTFE	0.14	349

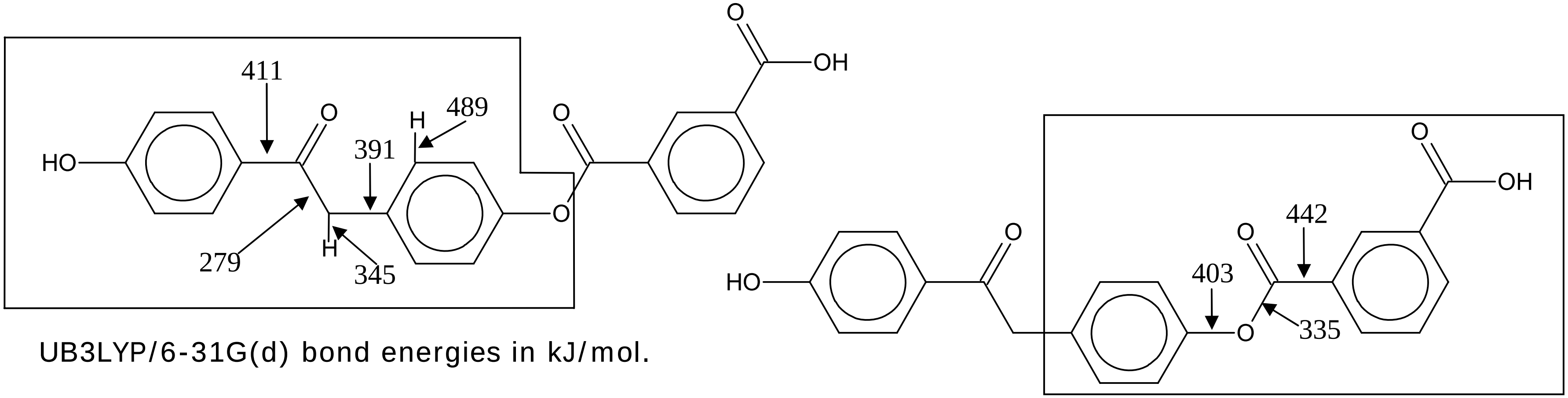
Consistent with observation, decomposition is slowed.



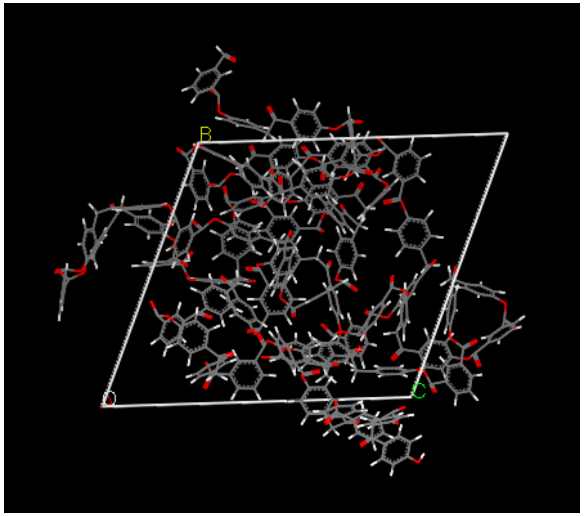
Comparing the RxnMD-derived kinetic parameters shows how much faster PE backbone scission is than PTFE.

Extending RxnMD to novel polymer decomposition.

poly(bishydroxydeoxybenzoin-arylate)



UB3LYP/6-31G(d) bond energies in kJ/mol.



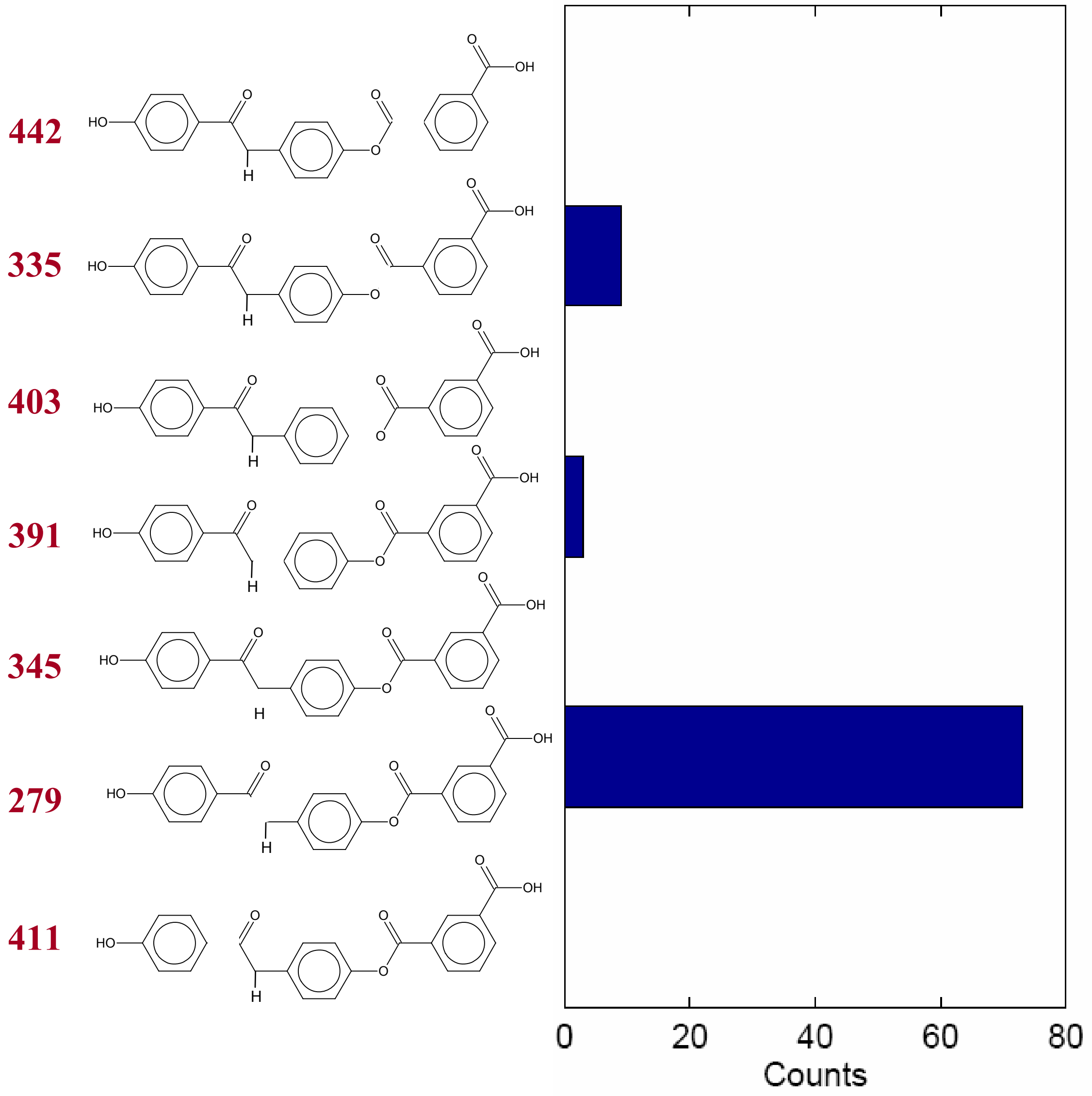
- 20 repeat units (7640 g/mol)
- NVT-ensemble
- Simulations conducted at 2800K
- $\rho = 1.263\ g/cm^3$
- Modeled backbone scissions

K Ellzey, *et al.*, *Macromolecules*, **39**, 3553 (2006)

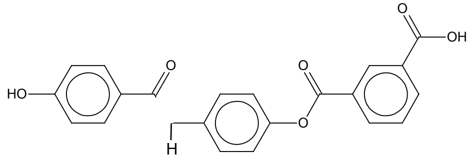
T Ranganathan, *et al.*, *Macromolecules*, **39**, 5974-5975 (2006)

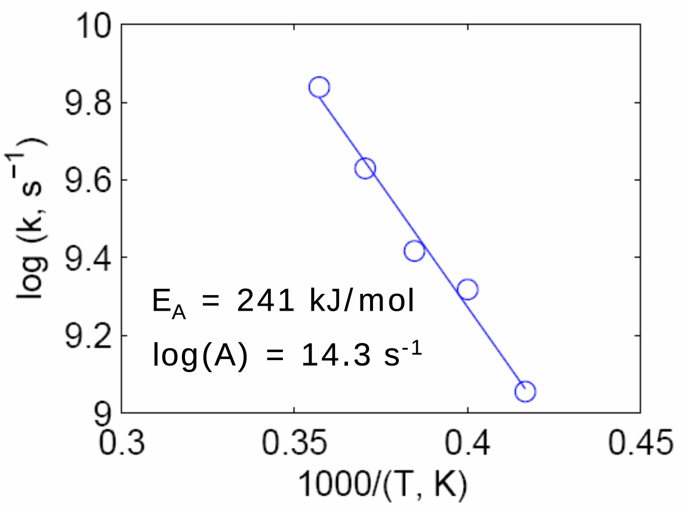
RxnMD captures the effects of the structure in pyrolysis.

20 Simulations Conducted at 2800 K



Kinetics carbonyl-methylene bond scission





RxnMD captures the energetic and structural effects of polymer decomposition.

Conclusions

- RMDff is a reactive forcefield method that uses switching functions to describe localized transitions within reacting systems.

- RxnMD is a tool that uses the system dynamics for predicting chemical kinetics *a priori* by inclusion of the structural and thermal effects.

- For minimum energy structures, the main effect on the kinetic parameters is the number of simulations included in the statistics.

- Increasing chain length decreases the activation energy because of the decreased mobility through the melt.

- The polymer side-group plays a significant role in the initial backbone decomposition by regulating the freedom of the polymer to diffuse through the melt.

- Decomposition effects of novel polymers such as poly(bishydroxydeoxybenzoin-arylate) can be identified, making RxnMD a useful tool for guiding future flame-resistant, polymer synthesis efforts.

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- National Center for Supercomputing Applications – TeraGrid access Grant #CTS-060029N

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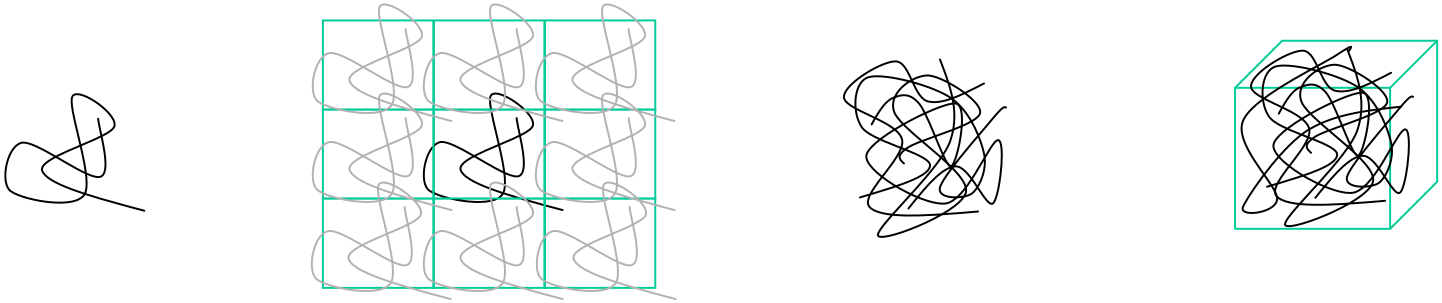
Role of configurational entropy in polymer decomposition

From Transition State theory, the rate constant is $k_{TST} = \frac{kT}{h} e^{\frac{-\Delta S}{R}} e^{\frac{-\Delta H}{RT}}$

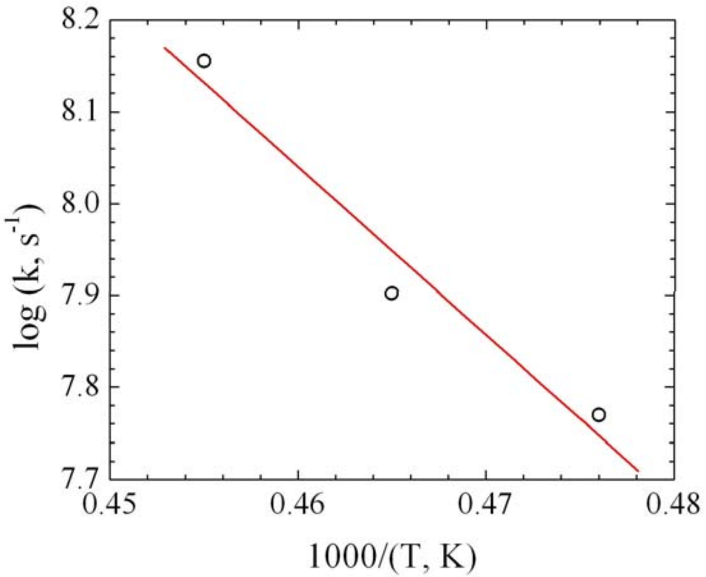
Thus, the traditional Arrhenius pre-exponential factor *A* would be $A = \frac{ekT}{h} e^{\frac{-\Delta S}{R}}$

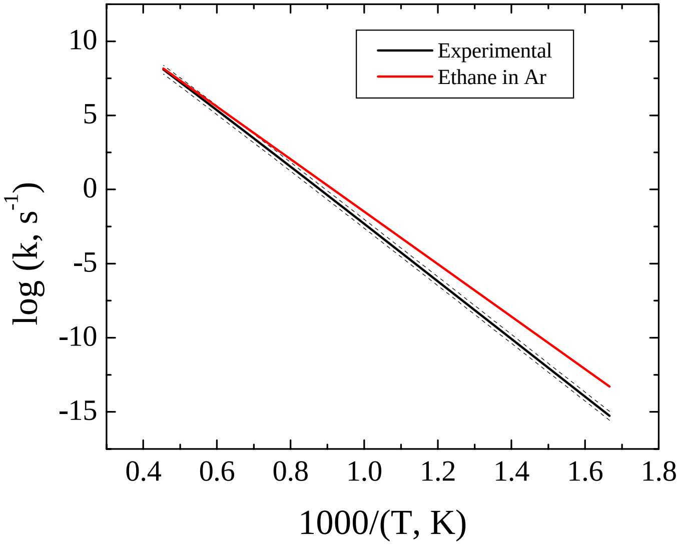
? If entropy contributes the pre-exponential factor, then can we postulate how the density, chain entanglements, and branching are affecting the kinetics of decomposition? ?



Validation thru ethane decomposition.

- Purpose: Test the new RxnMD code against fundamental data.
- Simulated 32 ethane molecules and 1000 Ar atoms in a NVT periodic box at 2100, 2150, and 2200 K. ($\rho = 2.04 \times 10^{20}$ molecules/cm^3; $P \approx 65$ atm)



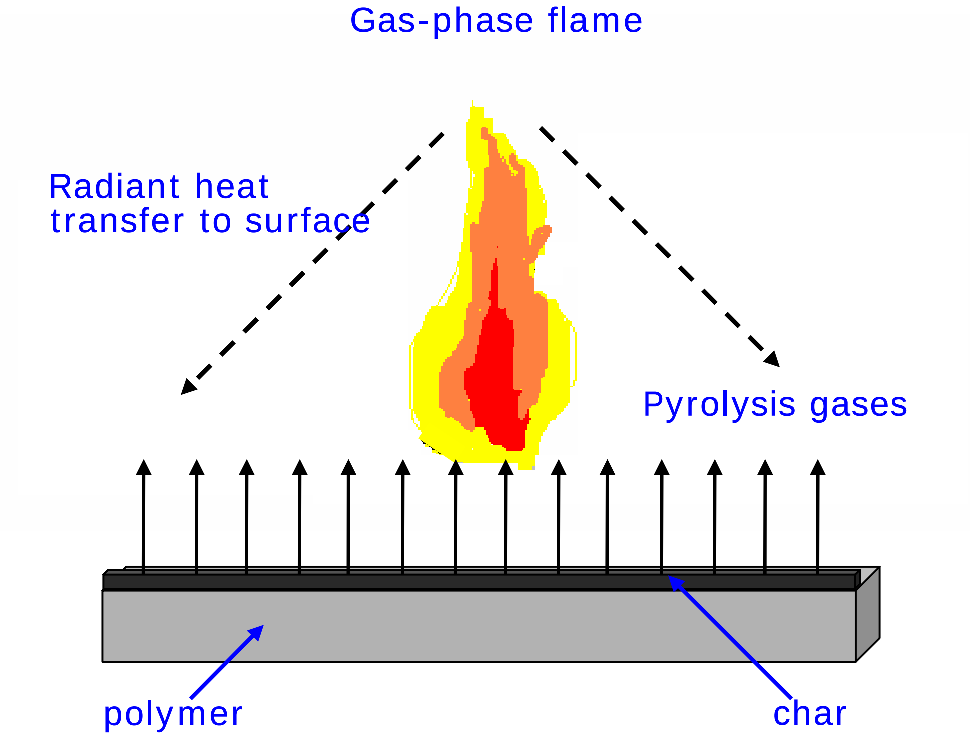


E_A = 340 kJ/mole

A = 1.61×10^{16} s^{-1}

CBS-QB3 C-C Bond Dissociation Energy:
370 kJ/mol

Pyrolysis kinetics are key to understanding flammability.

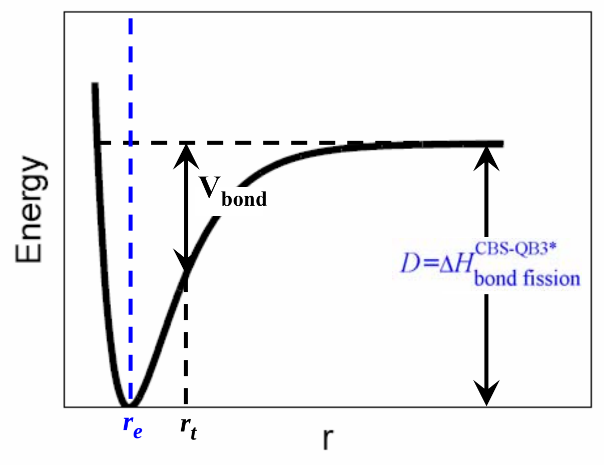


Pyrolysis gases:

- feed the fire
- are also generated by the heat of the fire

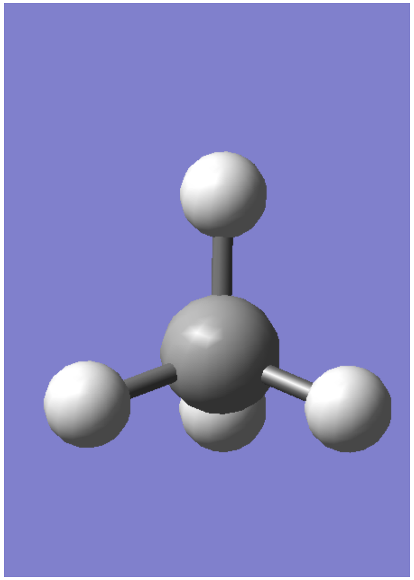
For aircraft safety, the goal is to understand how to slow the spread of the fire in order to provide more time to evacuate.

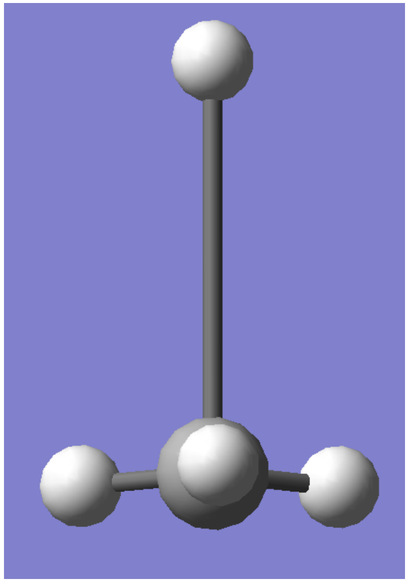
Bond breaking requires significant deviations from equilibrium.


Morse Potential

- Using a Morse bonding potential is not sufficient description for a reactive event.
- Other related motions must be included.

B3LYP/6-311++G(d,p) calculations


Optimized Methane Structure with 1.09 Å bonds and 109° angles


Optimized Methane Structure with one bond of 3.00 Å, with angles distorted from 109°

Title