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Kinetics and Mechanisms of Elementary Reactive Processes in Polymer Pyrolysis

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- Pyrolysis of polymers is directly related to flammability and thermal stability of plastics.
- Combustion of polymers is, generally, a gas-phase process with gaseous fuel supplied by the decomposing solid or liquid polymer. Understanding of polymer pyrolysis is key to understanding and controlling the chemistry and physics of polymer combustion and flammability.
- Existing abundant experimental data on polymer pyrolysis stimulate development of microscopic models based on the chemistry of the elementary reactions involved.
- Kinetic modeling has become a valuable and widely used tool for design and control of a multitude of different chemical processes.
- Over the past decade, considerable efforts have been directed at kinetic modeling of decomposition of polymers.

However...

- Fundamental knowledge of rate constants of elementary reactions is of key importance to the success of such modeling. This information is largely unavailable for the reactions involved in polymer decomposition.

Backbone C-C scission

- **Gas phase rate:** $k = (10^{16} – 10^{17})\times\exp(-348\ \text{kJ mol}^{-1}/RT)\ \text{s}^{-1}$

  This rate expression requires unrealistically high temperatures for initiation of polymer decomposition.

  $k = 1.0\ \text{s}^{-1}$ at T = 1069 – 1136 K

- At typical temperatures of experiments on polyethylene pyrolysis this gives very low values of rate constants:

  $k = 10^{-11} - 10^{-10}\ \text{s}^{-1}$ per C-C bond, at T = 400 ^{o}C (673 K)

  (or $10^{-8} - 10^{-7}\ \text{s}^{-1}$ per a C_{1000} PE chain)

- To explain low-temperature (350 – 450 ^{o}C) pyrolysis of polyethylene and similar polymers, one needs to assume that initial C-C bond scission occurs with rates that are significantly higher than the rates of the gas phase alkane decomposition.

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Backbone C-C scission

Recent work by Nyden, Stoliarov, and coworkers (2004):

- Thermal decomposition of polyethylene, polypropylene, and polyisobutylene was studied using Reactive Molecular Dynamics (RMD). Bulk polymer melt conditions were used in the model.
- Several reaction types were included in these simulations, including C-C bond scission.
- These authors reported activation energies for polymer C-C scission (40 – 190 kJ mol^{-1}) that are significantly lower that those of alkanes in the gas phase (~ 350 kJ mol^{-1}).
- In-depth analysis of polyisobutylene decomposition demonstrated that C-C scission activation energy decreases with the polymer chain length, from 240 kJ mol^{-1} for PIB4 to 170 kJ mol^{-1} for PIB150.
- Authors' explanation:
  - nonbonding interactions induce torsional and angular stresses; these stresses are larger in larger polymer molecules.
  - These stresses are partially relaxed when the polymer chain is broken, thus reducing the barrier for C-C backbone scission.

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Backbone C-C scission

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Current work:

- C-C backbone scission in polyethylene was chosen as the model system.
- Reactions were studied in the gas phase and in polymer melt (periodic boundary conditions).
- Software: GROMACS, version 3.2. MD integration step time 0.2 – 1.0 fs.
- Force field: OPLS-AA all-atom force field with Morse function for C-C bonds (348 kJ mol^{-1} bond energy).
- Temperature control methods: Nose-Hoover (shorter chains) and Berendsen et al. (longer chains).
- Reaction rates were studied as functions of temperature, polymer chain length (PE-1 – PE-1000), and polymer melt density.

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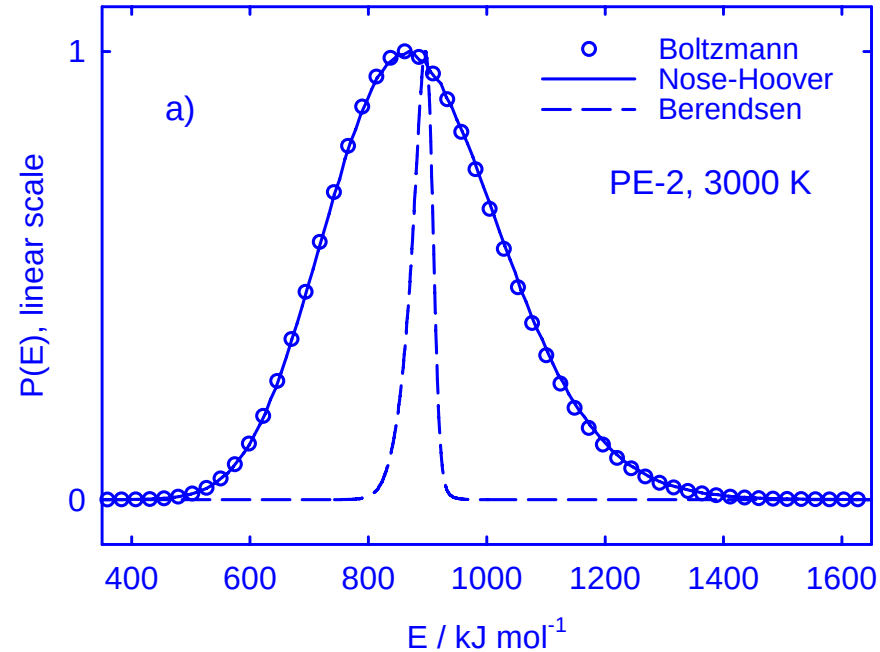
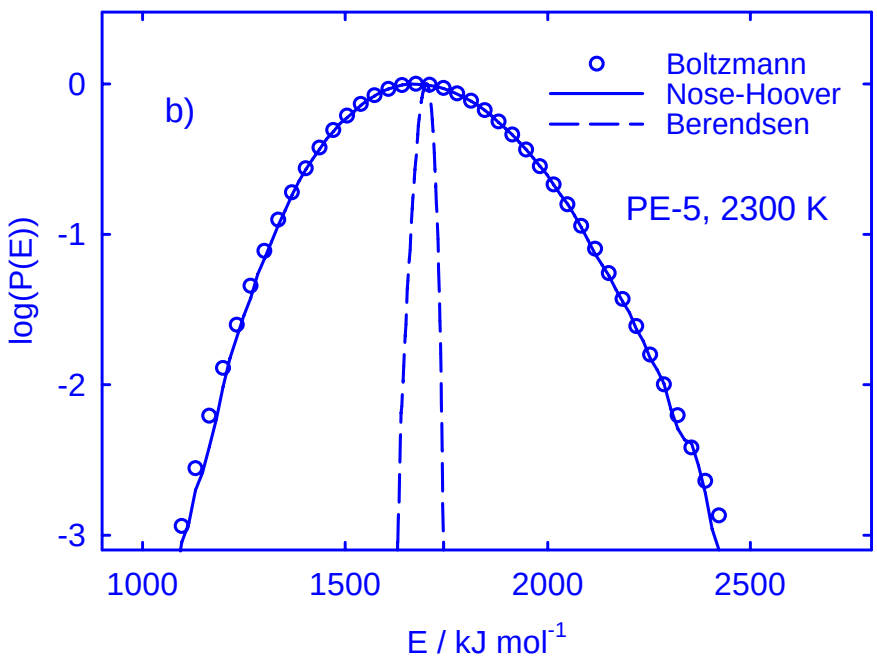


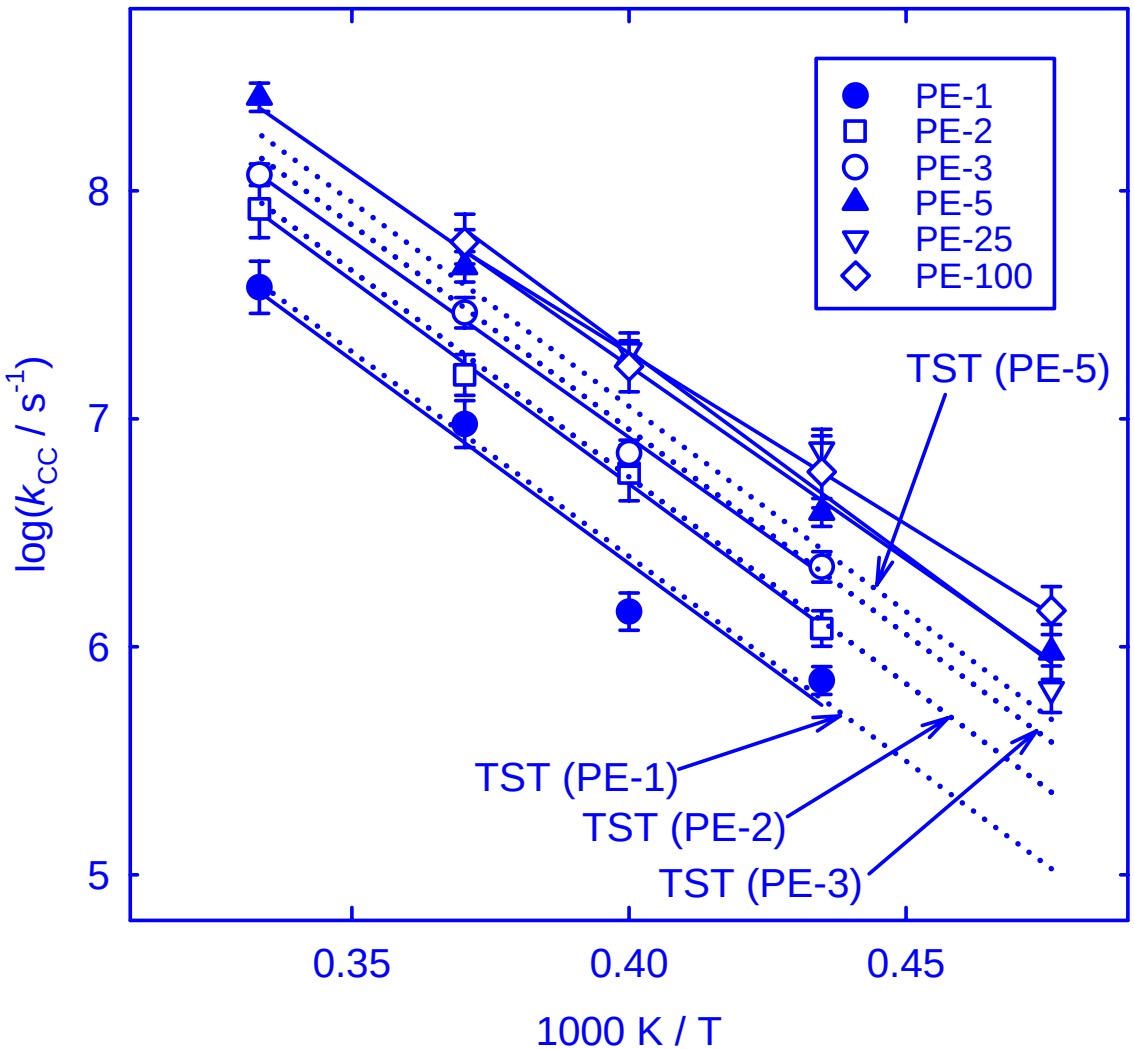


Energy distributions obtained using two methods of temperature control:

- Two different methods of temperature control (lines).
- Classical (non-quantum) Boltzmann energy distributions (symbols).
- Rate constants obtained in simulations did not depend on the method of temperature control for chains of PE-25 and larger.
- For shorter chains, Berendsen temperature control method resulted in too low rates of decomposition, as expected.

Rate constants dependence on the chain length

- Rate constants (per C-C bond) increase with the chain length
- Activation energy is similar to the bond energy (348 kJ mol^{-1}).



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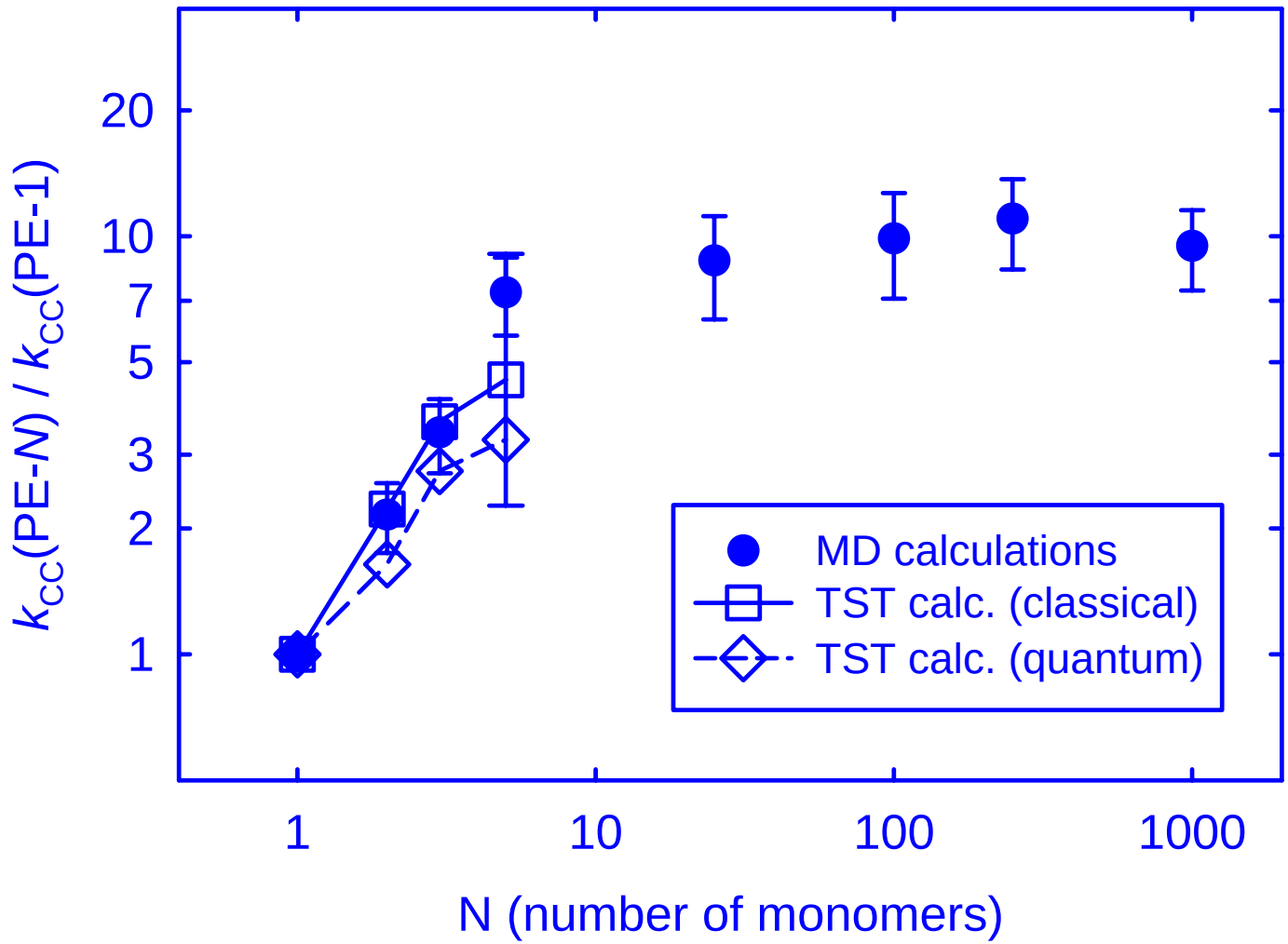
Rate constants dependence on the chain length

- Factor of acceleration of the C-C bond scission reactions vs. alkane or polyethylene chain length.
- Uncertainties in VTST rate constants dramatically increase for $N > 5$.



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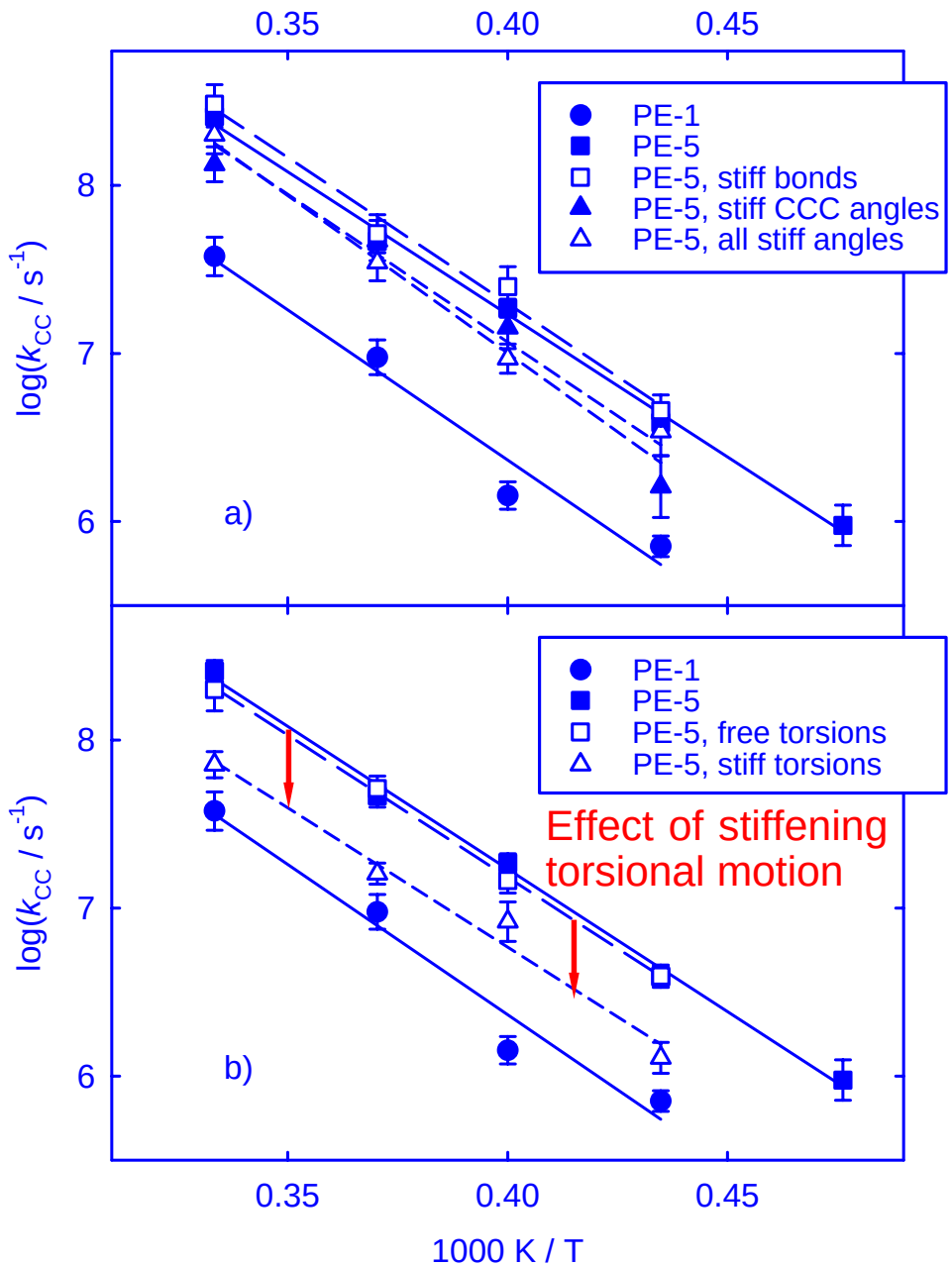

In an attempt to investigate the causes of the observed accelerating effects of molecular chain length, several series of MD simulations were performed using modified Hamiltonians in which certain types of degrees of freedom were constrained or impeded.

The plot shows the effect of restrictions imposed on different types of motion in decomposition of PE-5 (see text). MD-based rate constants for PE-1 (no reaction acceleration) are shown for comparison.

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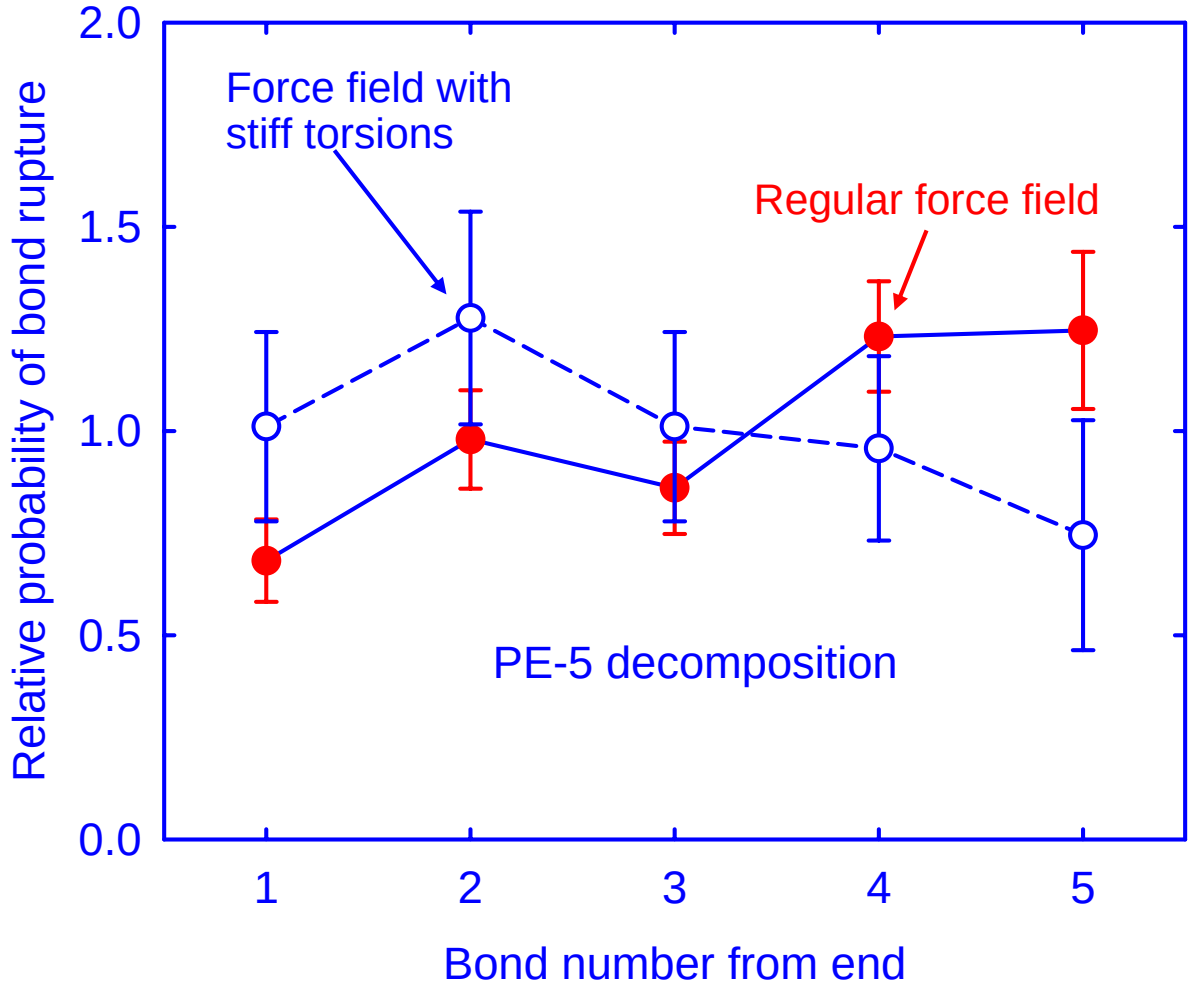

Dependences of the relative probability of bond scission on the bond position in the chain obtained in MD simulations of PE-5 (decane) decomposition using the “regular” force field (filled circles) and that with impeded torsions (open circles).

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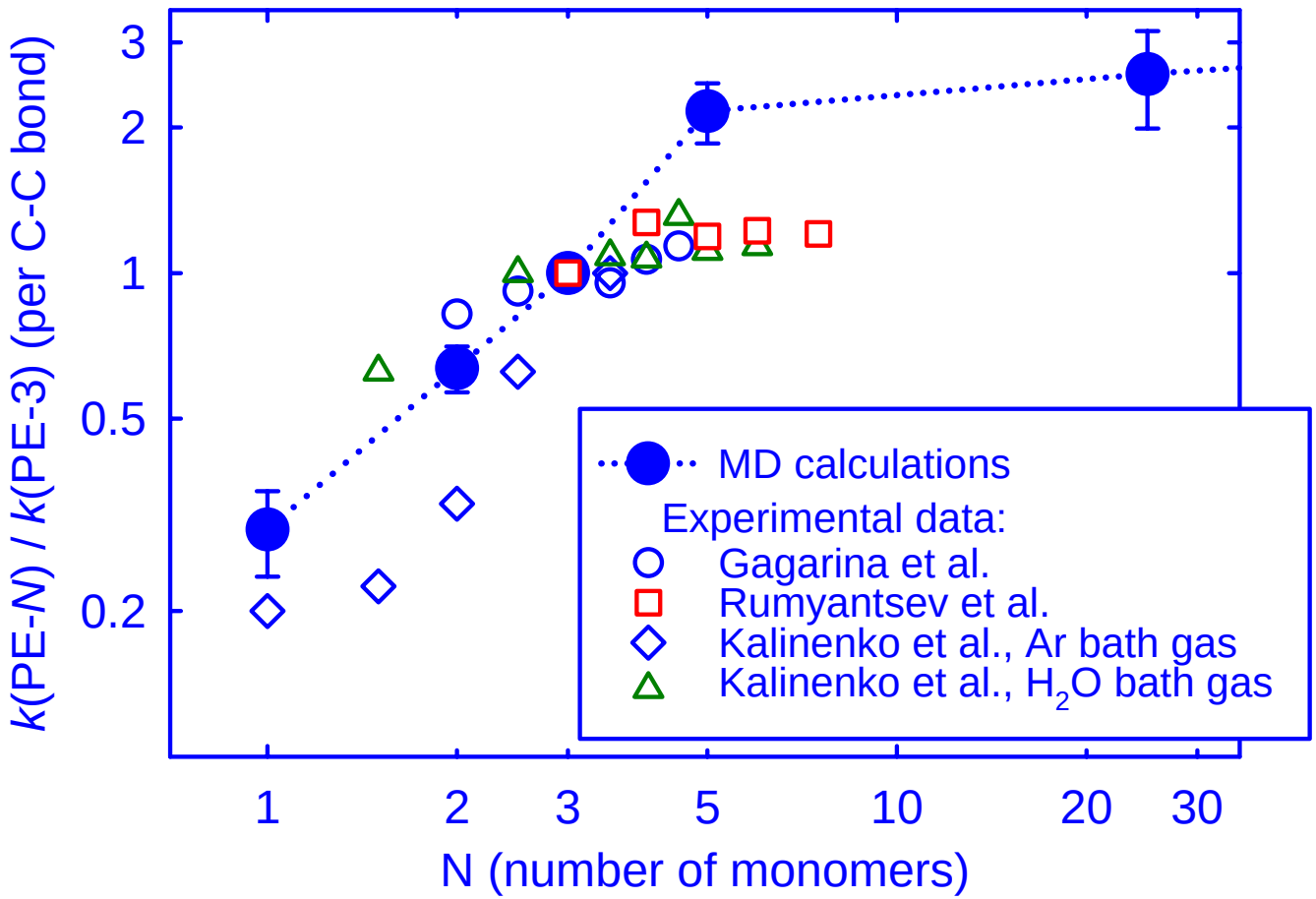
Reaction acceleration in longer chains: attempt at explanation

- Torsional motions in the chain produce centrifugal forces that act on adjacent C-C bonds.
- These centrifugal forces result in quasiperiodic effective reductions or increases of the potential barriers for C-C bond dissociation.
- The averaged effect of these centrifugal forces is the increase in the rate constant.
- Longer chains $\rightarrow$ larger numbers of torsions $\rightarrow$ increase in the rate constant with the chain length.
- Longer chains tend to coil, which results in randomization of the directions of centrifugal forces. This explains the saturation of the rate constant vs chain length dependence.
- Lower probability of dissociation of terminal bonds is thus explained.
- Excitation of torsions increases with temperature, which in turn results in larger effective barrier lowering at higher temperatures; thus, the reaction accelerating effects of chain length do not decrease with temperature.

Reaction acceleration in longer chains: comparison with experiment



- Experimental dependences of the rates of thermal PE-N decomposition on N are from Gagarina et al. (903 – 1010 K), Rumyantsev et al. (873 – 993 K), and Kalinenko et al. (913 – 1170 K).
- Reaction rates for PE-N are given relative to those of PE-3 (n-hexane).

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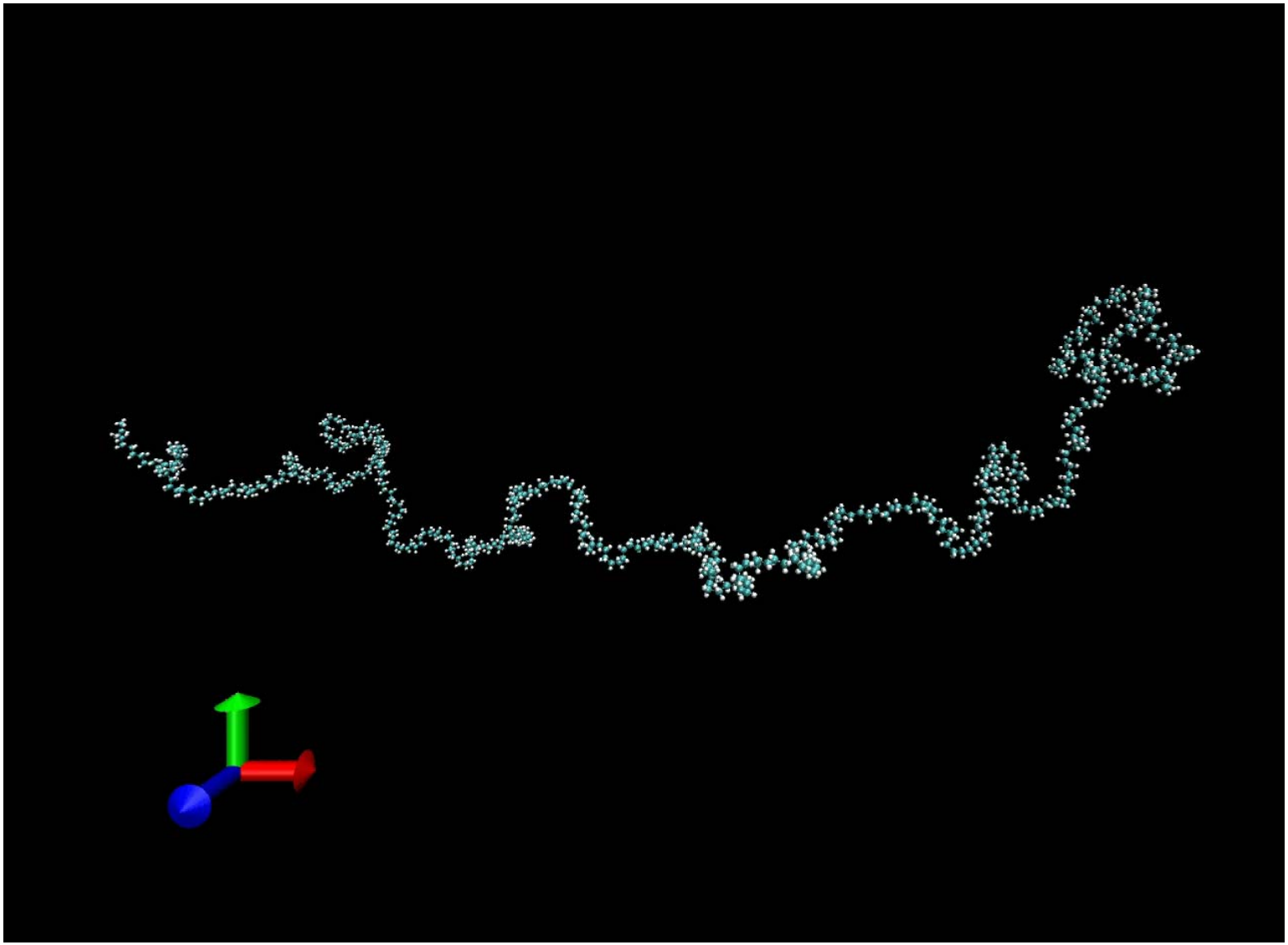
Backbone C-C scission

- Example of MD run with C-C bond dissociation in the gas phase:



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- Example of MD run in the liquid phase (PBC):

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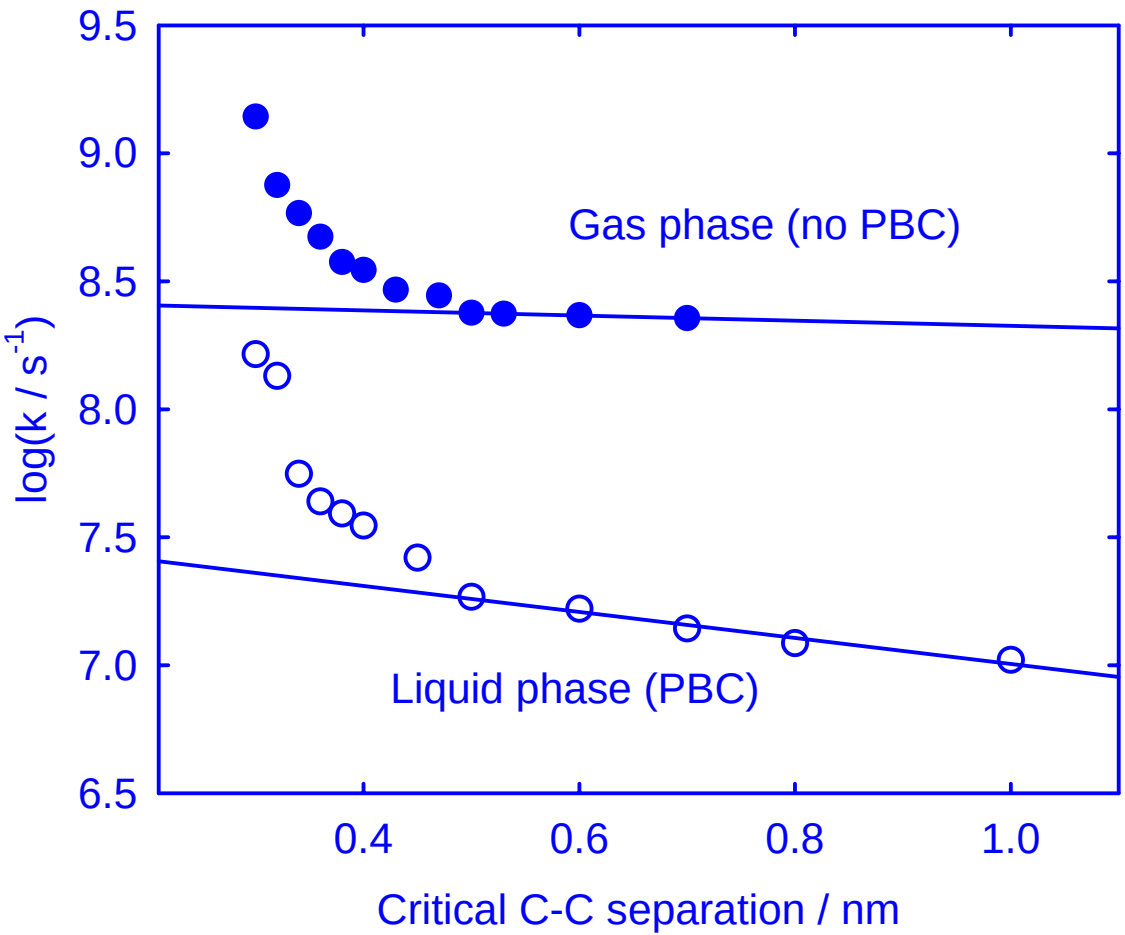
Differences between gas phase and liquid phase

- Cage effect: the fragments produced upon bond dissociation eventually recombine. As a result, bond dissociation is not immediately visible.
- Choice of the criterion of bond dissociation is not obvious.
- Rate constant values depend on the bond dissociation criteria.



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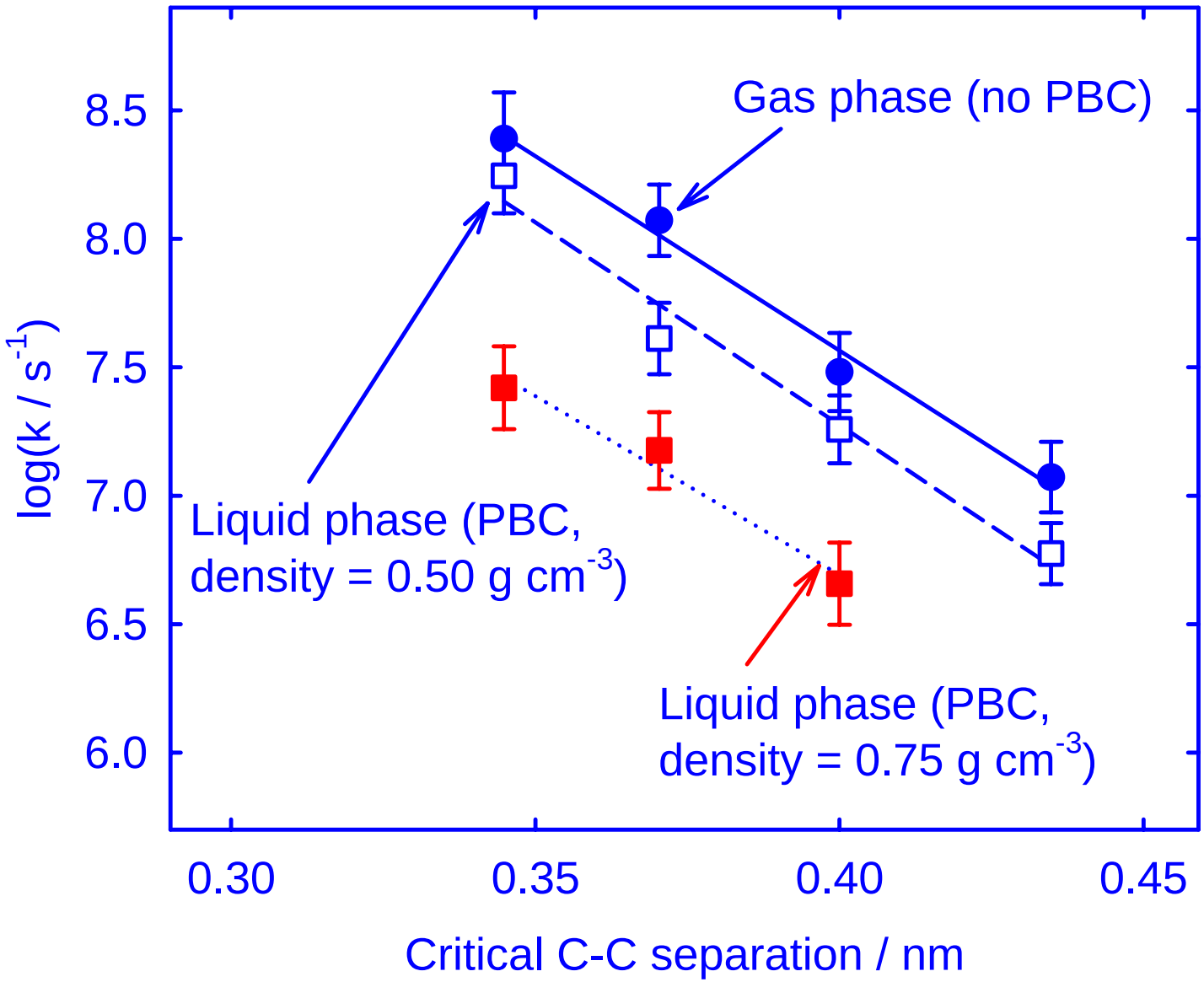
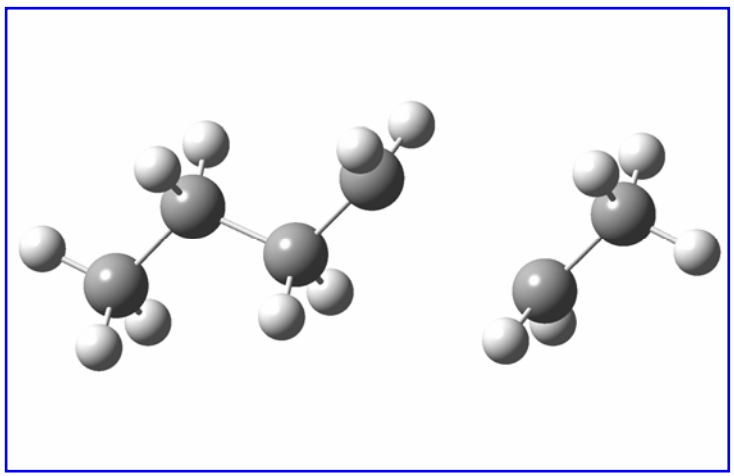
Rate constant Arrhenius dependences for gas and liquid phases

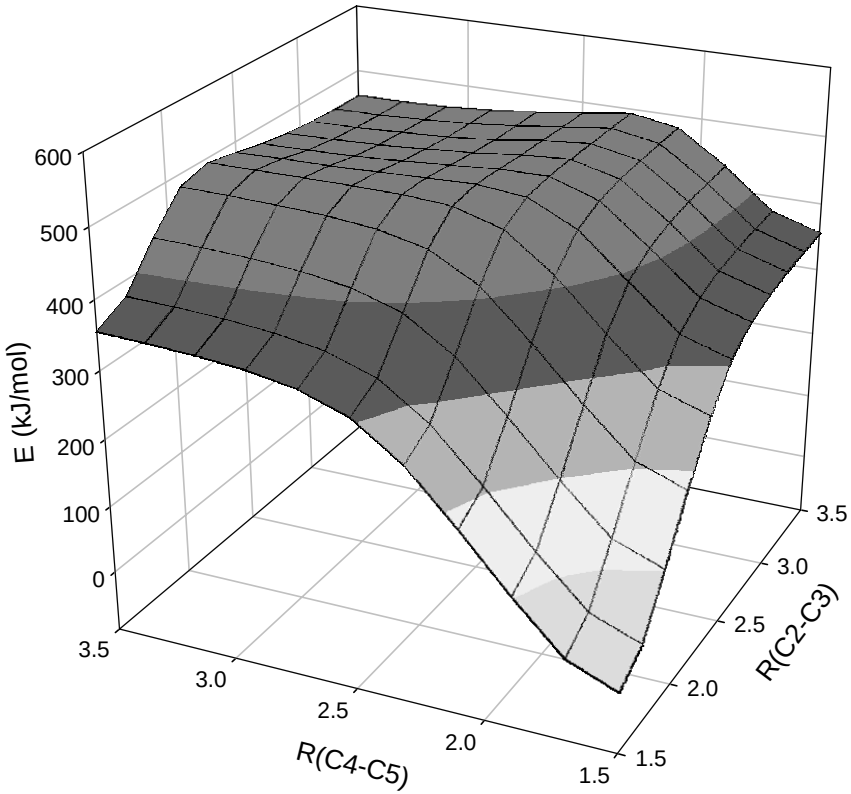


β-Scission of incompletely formed radicals

- C-C bond scission: $R_1\text{-}R_2 \rightarrow R_1 + R_2$
- Subsequent β-scission: $R \rightarrow C_2H_4 + R_3$

- β-Scission can also occur simultaneously with C-C bond scission:





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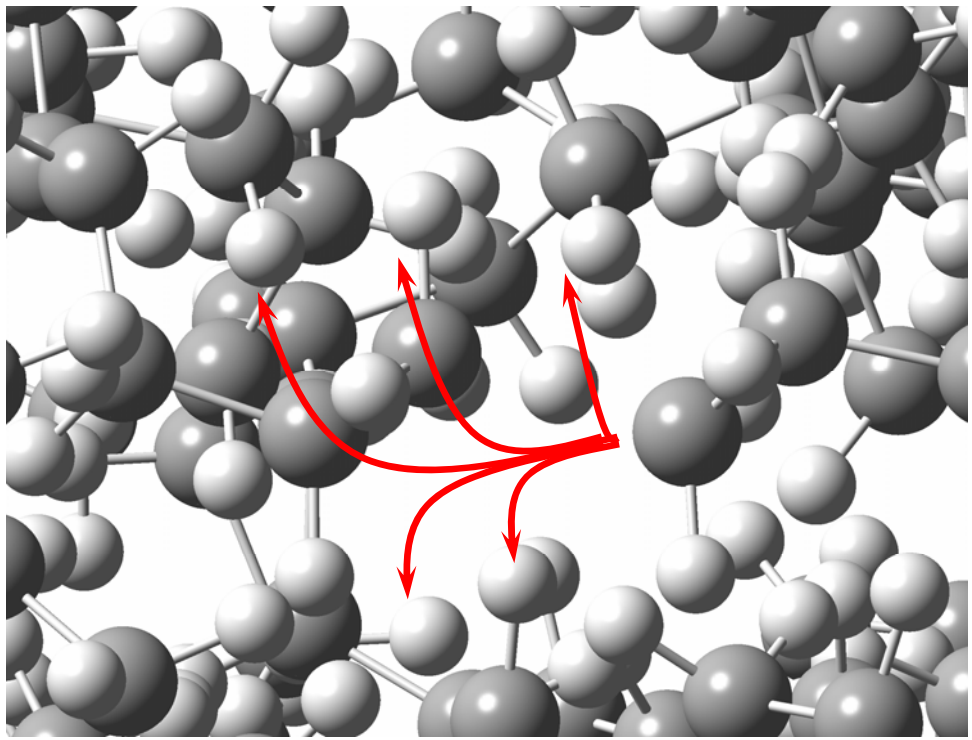
Work in progress: rates of H atom transfer. Comparison of MD and TST rates.

- Rates of reactive encounters between a radical site and H atoms bonded to carbon at various locations along the chain are being evaluated.
- Comparison between MD and TST rates.



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Summary

- Polymer backbone C-C scission reactions were studied computationally using polyethylene as a prototype.
- The results of simulations of gas phase reactions demonstrate significant accelerating effect of chain length on the rates of C-C bond scission. Per-bond rate constant values increase with the increasing chain length, up to an order of magnitude, in the sequence of linear alkanes from PE-1 (ethane) to PE-5 (decane); this dependence becomes saturated for longer chain lengths.
- Stiffening the potentials of bending and especially torsional degrees of freedom diminishes the accelerating effect of chain length, while constraining the bond distances for all C-C bonds except the one undergoing dissociation has no effect.
- Liquid phase environment (polymer melt) results in slower reaction. Rate constants display strong dependence on density.
- Reactions of β-scission occurring simultaneously with C-C bond scission and H atom transfer are currently being studied.

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