



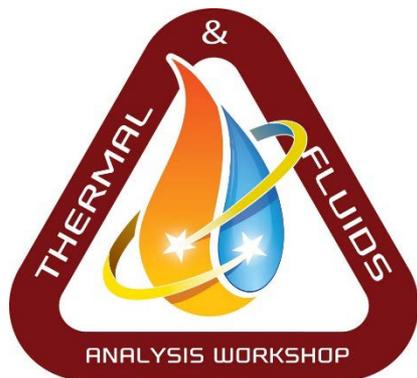
## Computational Tools for Modeling Chemical Degradation in Extreme Environments

Srujan K. Rokkam, *Advanced Cooling Technologies, Inc.*

John W. Lawson, *NASA Ames Research Center*

Peter Cross, Richard Burns, *NAVAIR-China Lakes*

Presented By  
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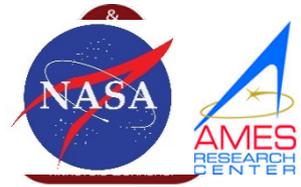


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*Advanced Cooling Technologies, Inc.*

Thermal & Fluids Analysis Workshop  
**TFAWS 2016**  
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NASA Ames Research Center  
Mountain View, CA



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- ◆ Peter Cross, Richard Burnes (NAVAIR-WD, China Lake, CA)
- ◆ Dr. John Lawson (NASA Ames)
- ◆ Prof. Don Brenner (NCSU)
- ◆ Raghavan Ranganathan, Kiran Sasikumar (ACT/RPI)
- ◆ Tapan Desai (formerly ACT)
- ◆ Prof. Pawel Keblinski (RPI)



# Outline



- ◆ Background
- ◆ Studies capturing thermo-chemical response of materials and Material chemistry.
  - Understanding Pyrolysis process through Reactive Molecular Dynamics Simulations
  - ‘Resin-to-char’ process in ablative phenolic resins
  - Thermal degradation and reaction chemistry of EPDM rubber
- ◆ Extraction of Chemical Kinetics Data from Reactive MD data
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- ◆ Summary

# Background: Need for modeling chemical degradation

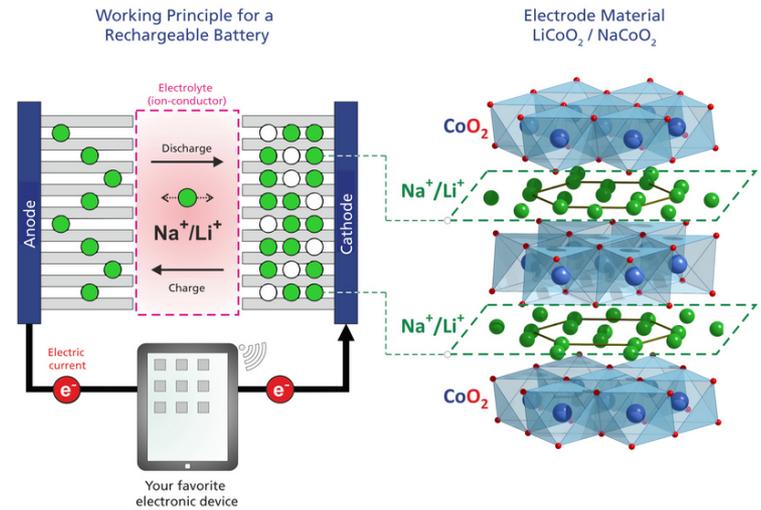
- ◆ Several applications of NASA and DoD involve the need to understand and model the behavior of chemical, thermo-chemical degradation of materials.
- ◆ Examples include:
  - Ablative heatshield materials
  - Energetic explosives
  - Batteries and energy storage devices
  - H-storage, fuel cells
  - Combustion, Hypersonic response



**Re-entry vehicles**



**Energetic materials**



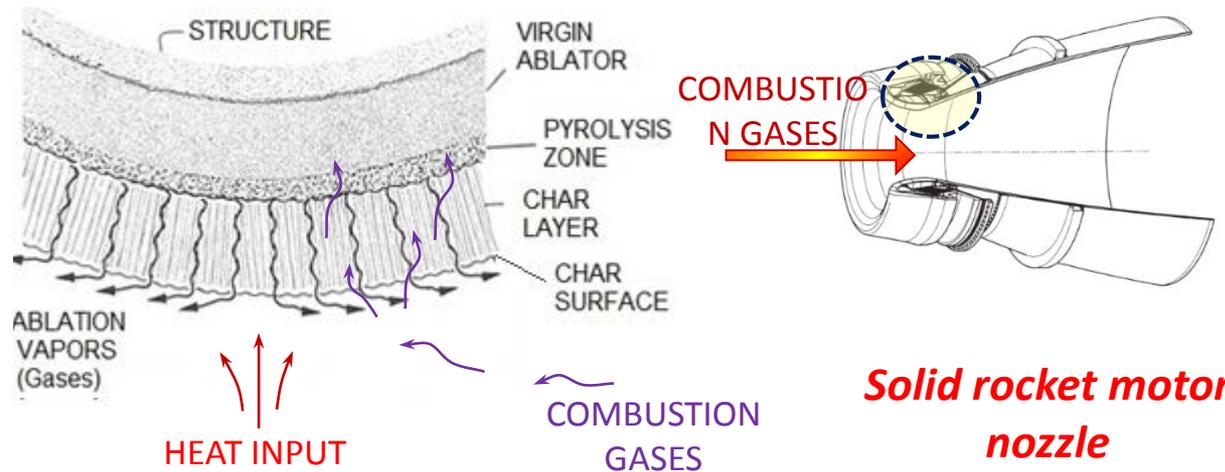
**Energy storage devices**

- ◆ What do all these applications have in common ?
  - Chemical degradation of materials → which changes their performance and functionality
- ☞ There is a need to **develop tools for investigating material chemistry and response in these (multi-specie, multi-physics) environments.**

- ◆ Ablative materials used in TPS remove heat by undergoing pyrolysis (thermal degradation) to form a foamy char.
- ◆ Thermal insulation layer = Char layer + decomposing layer + virgin composite



**Re-entry vehicles**



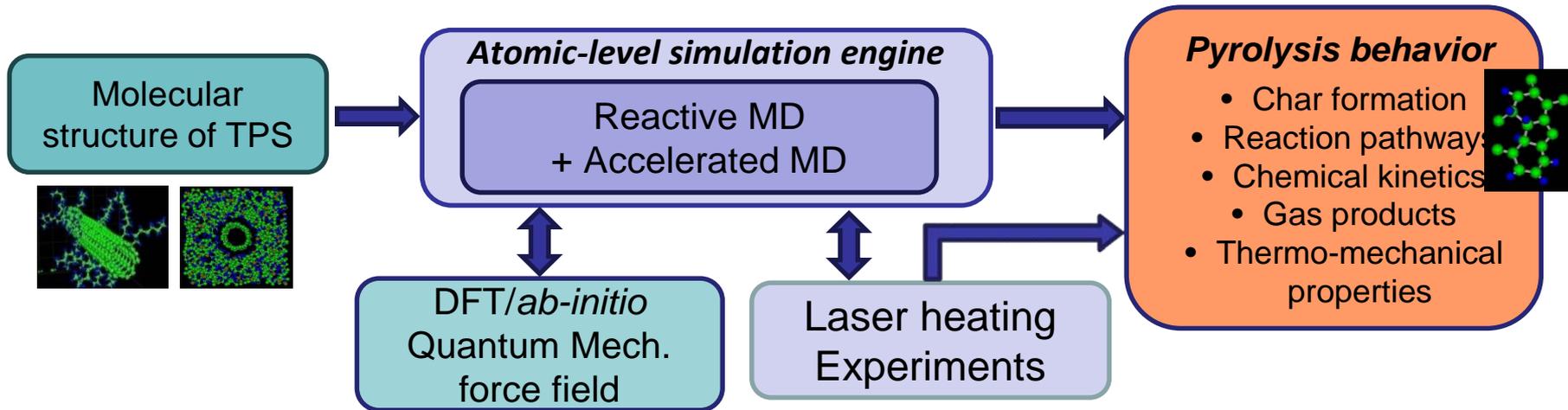
**Solid rocket motor nozzle**

- ◆ Strong and stable char is needed to retain insulation.
  - ◆ Optimal design needed to reduce payload.
  - ◆ Current tools and methods cannot accurately predict material response of ablative composites under extreme conditions.
- ☞ **Need to develop tools to understand the complex phenomenon.**

To obtain detailed understanding of complex reactions mechanisms leading to formation of char and chemical interactions at the surface of the TPS (due to combustion gases), under extreme conditions.

**ACT have been developing multi-scale computational tools to:**

- Develop atomistic level understanding on methodology of char formation (complete carbonization)
- Analyzing effect of reinforcements on char formation and structure
- Obtain detail chemical pathways for reactions between char, pyrolysis gases and combustion edge gases, at high temperature, pressure.
- Predict the thermal and mechanical properties of the ablative TPS.



**ACT's Computational framework for atomistic level modeling of ablative TPS chemistry in extreme environments**



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# Background: Reactive Force Fields



- ◆ Reactive force fields, ReaxFF, allows for bond-order based bond breaking and formation to simulate chemical reactions.
  - Parameters are derived solely from Quantum Mechanics, providing accurate unbiased reaction chemistry.
  - No need to predefine reactive sites or reaction pathways; potential functions automatically handle coordination changes associated with chemical reactions.
  - Smooth transition from non-bonded to single, double and triple bonded systems based on a bond length/bond order relationship.
  - All connectivity-dependent interactions (torsion, valence) are made bond-order dependent

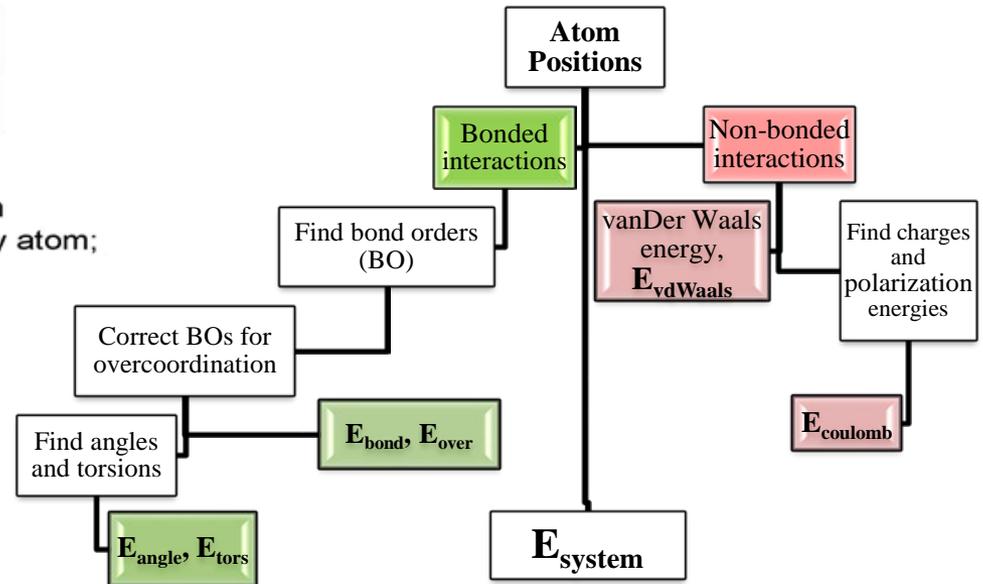
*(Chenoweth et.al., J. Phys. Chem. A, 112, 1040, 2008)*

- ◆ Method successfully applied to study a variety of chemical problems:
  - Thermal degradation of polymers
  - Hydrocarbon Oxidation
  - Pyrolysis of Phenolic resins
  - Transition metal catalyzed reactions
  - H<sub>2</sub> adsorption in Mg-hydrides
  - Segregation and diffusivity estimation

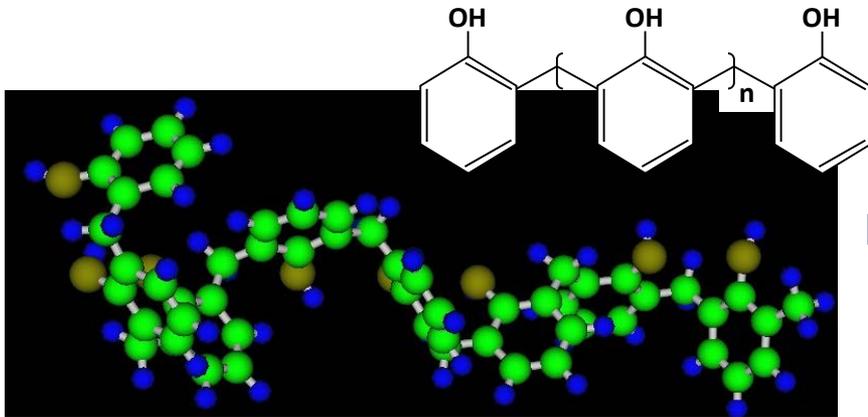
- ◆ System energy obtained from various partial energy contributions,

$$E_{\text{system}} = E_{\text{bond}} + E_{\text{over}} + E_{\text{under}} + E_{\text{val}} + E_{\text{pen}} + E_{\text{coa}} + E_{\text{c2}} \\ + E_{\text{lp}} + E_{\text{tors}} + E_{\text{conj}} + E_{\text{H-bond}} + E_{\text{vdWaals}} + E_{\text{coulomb}}$$

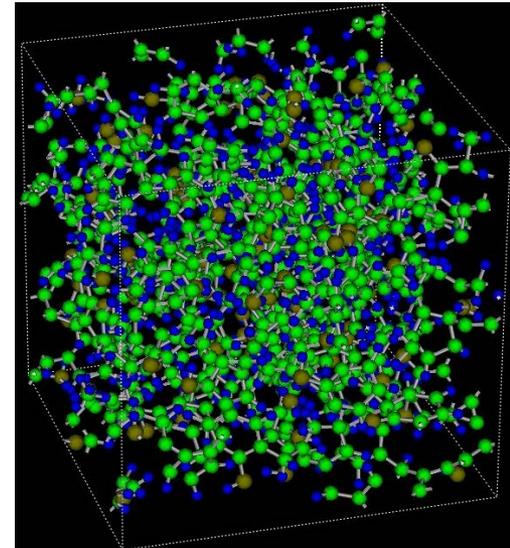
- $E_{\text{bond}}$ : bond energy; attractive term, directly derived from bond orders
- $E_{\text{lp}}$ : Lone pair energy; penalty for breaking up lone pairs in O, N
- $E_{\text{over}}$ : Overcoordination energy: penalty for overcoordinating atoms
- $E_{\text{under}}$ : Undercoordination energy: stabilizes undercoordinated atoms
- $E_{\text{val}}$ : Angle strain; equilibrium angle depends on bond order central atom
- $E_{\text{pen}}$ : Penalty for 'allene'-type molecules ( $\text{H}_2\text{C}=\text{C}=\text{CH}_2$ )
- $E_{\text{coa}}$ : Angle conjugation; stabilizes  $-\text{NO}_2$  groups
- $E_{\text{C}_2}$ :  $\text{C}_2$  correction: destabilizes  $\text{C}=\text{C}$
- $E_{\text{tors}}$ : Torsion energy: bond-order dependent  $V_2$ -term
- $E_{\text{conj}}$ : Torsion conjugation: general conjugation stability
- $E_{\text{H-bond}}$ : Hydrogen bond
- $E_{\text{vdWaals}}$ : van der Waals: calculated between every atom
- $E_{\text{Coulomb}}$ : Coulomb interaction: calculated between every atom;



- ◆ Polymer chain of non-crosslinked phenol formaldehyde resin with 8 repeating units in ortho-ortho sequence (methyl terminated at one end)

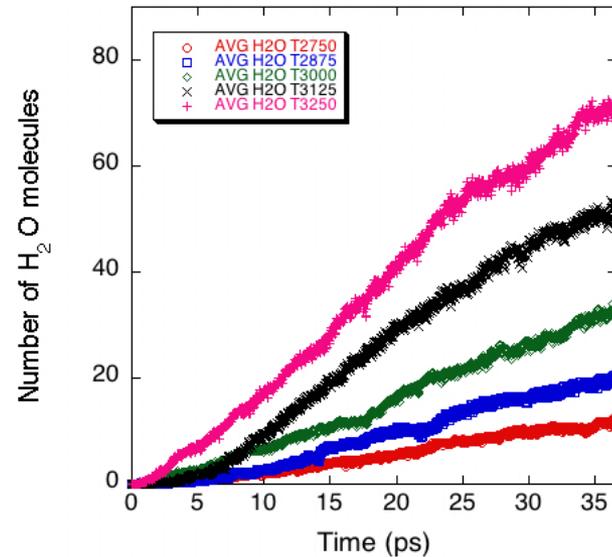
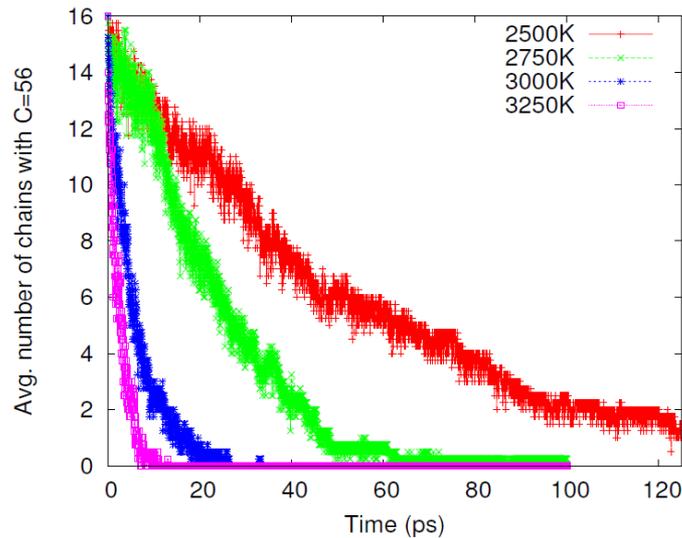


C: Green, H: Blue, O: Brown



- ◆ Simulation cell adjusted to match experimental density 1.25gm/cc.
- ◆ Sequence of annealing steps performed to relax the chains. Followed by long equilibration at 2000K for 250ps (no reactions were found during these steps)

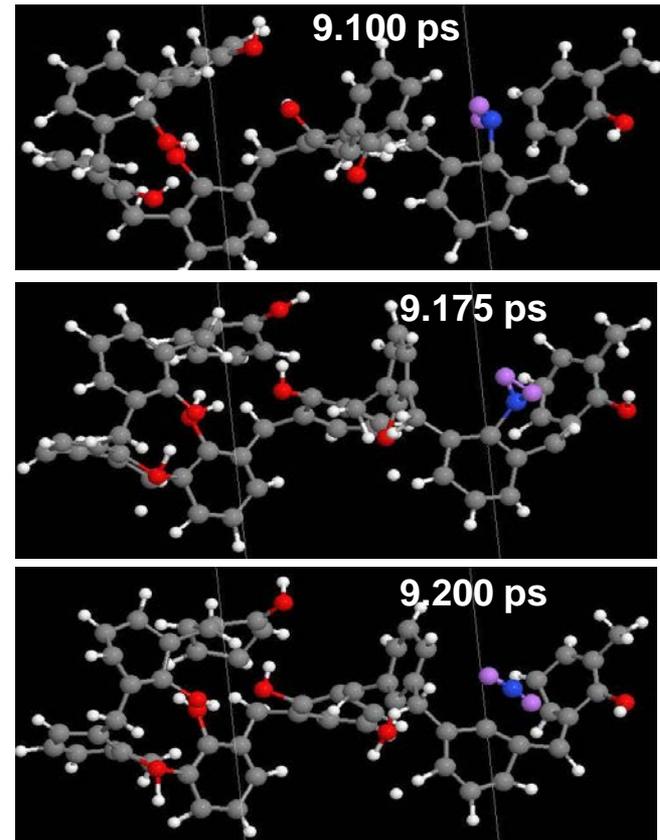
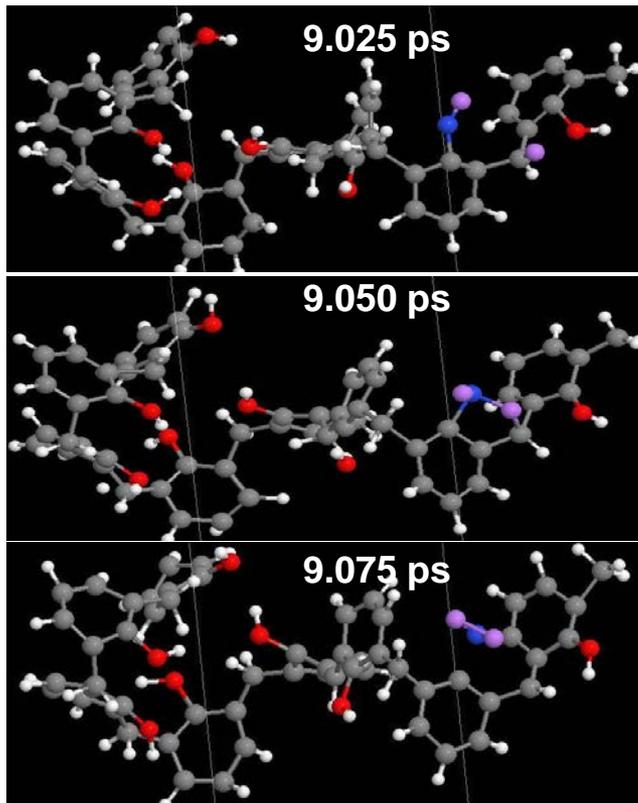
- ◆ Thermal degradation study on equilibrated phenolic resin system
  - Isothermal NVT reactive MD simulations at temperature 2500K to 3250K
- ◆ Degradation rate, products formed and chemical reaction pathways were analyzed



- ◆ Degradation rate increases with temperature. At 2500K, degradation of all chains doesn't set in until ~200ps (not shown)
- ◆ Water (H<sub>2</sub>O) is the most dominant product of pyrolysis simulations. Other products found include H<sub>2</sub>, C<sub>2</sub>H<sub>2</sub>, CO, C<sub>2</sub>H<sub>4</sub>, CO<sub>2</sub>, CH<sub>3</sub>OH

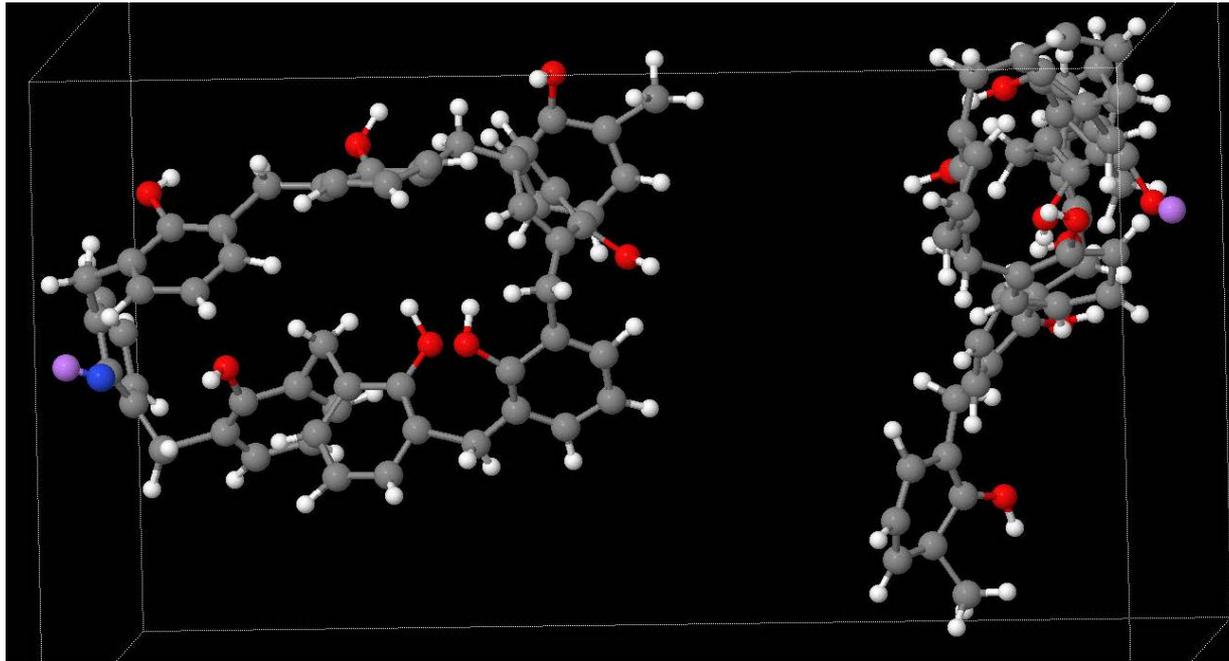
C: Grey  
H: White  
O: Red

H<sub>2</sub>O forming  
atoms in blue  
(O) & violet(H)



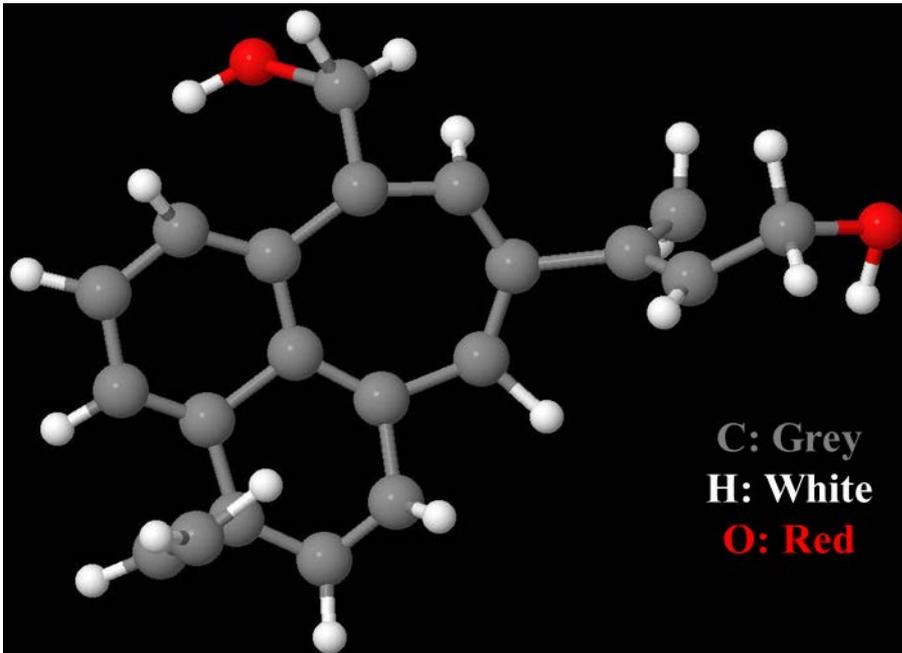
- ◆ Hydroxyl unit abstracts an H from its neighborhood
- ◆ H<sub>2</sub>O unit breaks away from the chain

C: Grey  
H: White  
O: Red

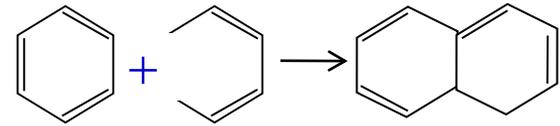


- ◆ The mechanisms for dehydration are:
  - -OH group and hydrogen from –CH<sub>2</sub>- group
  - Between two –OH groups
  - Dissociated hydrogen and –OH group
  - H on a carbon ring and –OH group

- ◆ At high temperatures ( $\sim 3000\text{K}$ ), fused ring structures are observed

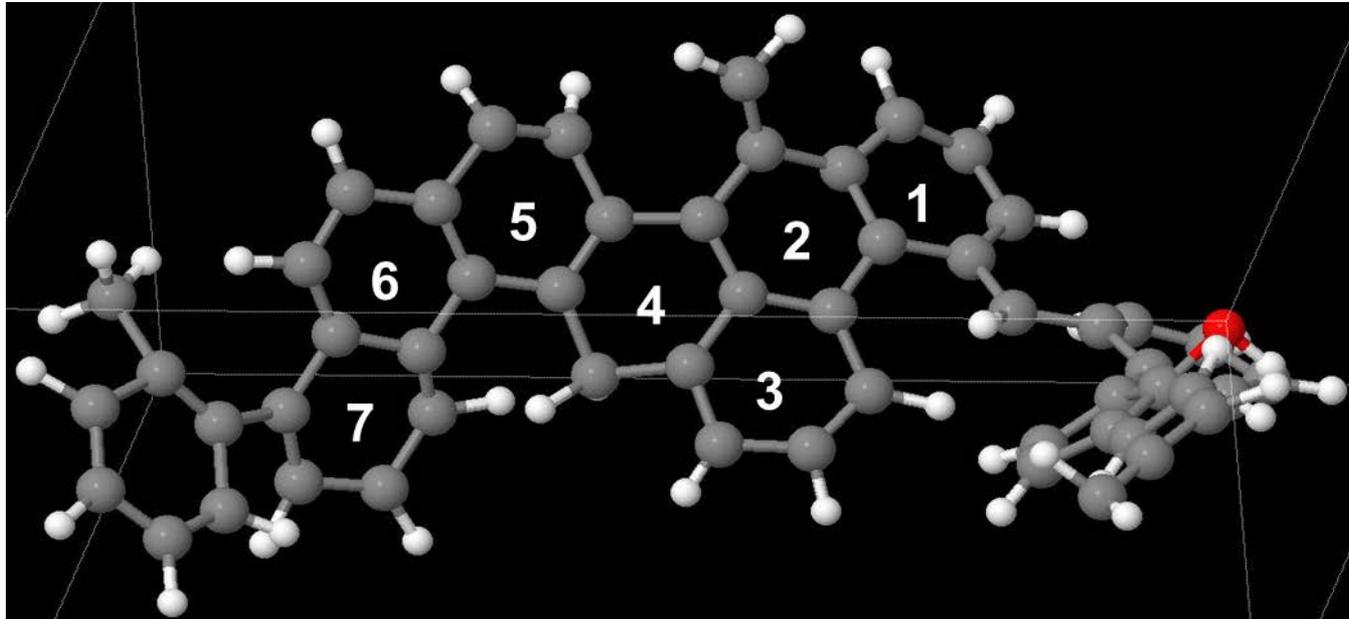


## Conventional Mechanism



Fused rings are precursor for large graphene fragments

- ◆ Fused-ring structures grow to yield precursor of char at low temperature



- ◆ Polymer chains (two) containing at least 7 fused rings were found.
- ☞ Essential to run simulations at low temperature to capture accurate physics

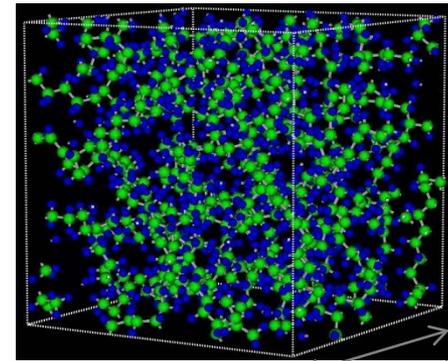
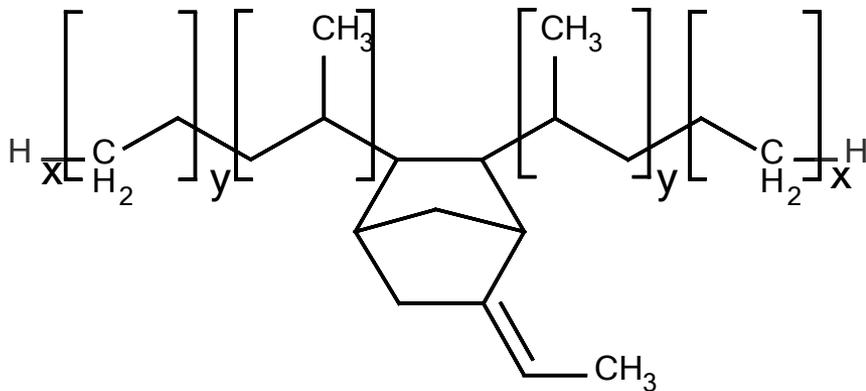


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- ◆ *Ethylene Propylene Diene Monomer* (EPDM) based rubber composites are commonly used for insulation of case-bonded solid rocket motor engine.
- ◆ EPDM molecules comprising of 54% ethylene, 40% propylene and 6% ENB (by weight).

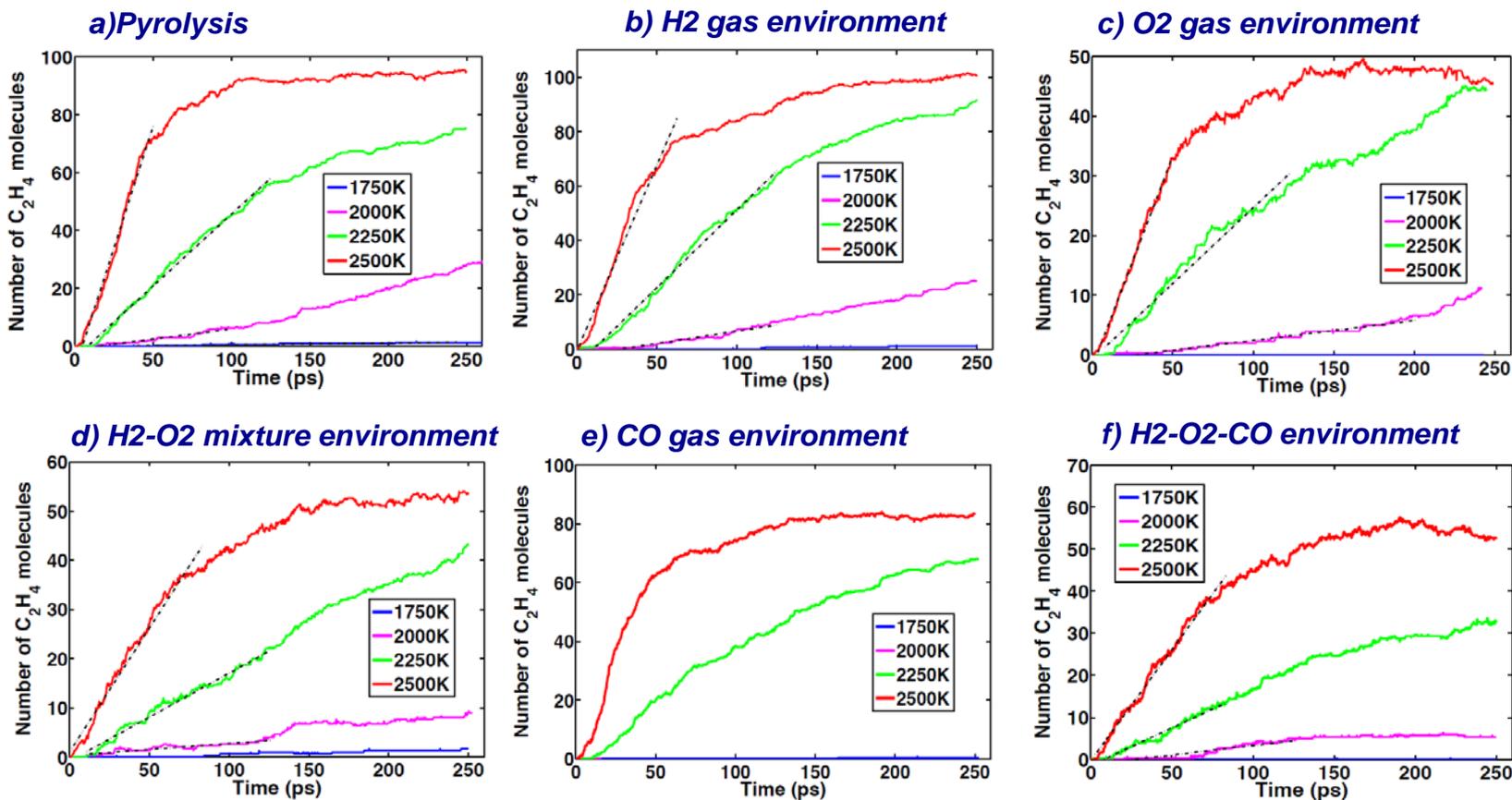


C : green atom  
H : blue atom

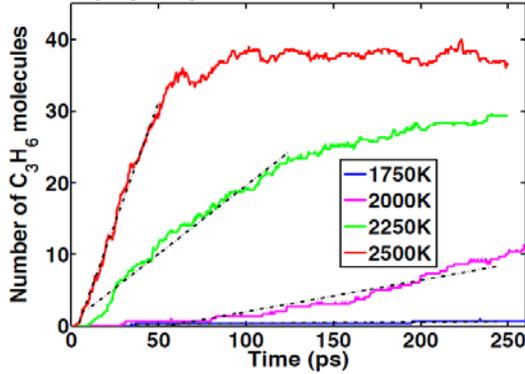
25.487 Å

- ◆ Simulation cell: 4 EPDM molecules (422 atoms each) → 1688 atom system
  - Packed to experimental density of 0.87 gm/cc
  - Sequence of equilibration and annealing cycles performed (at 300K ↔ 1500K) to relax chains.

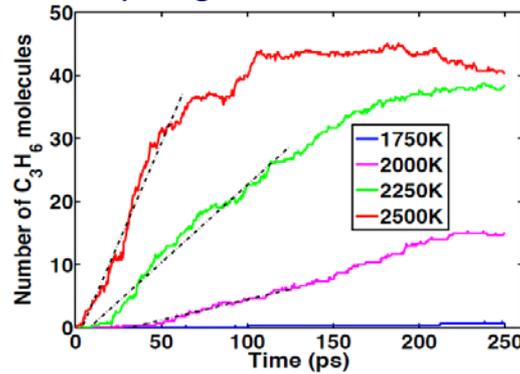
- ◆ EPDM degradation behavior in 6 environments was simulated using reactive MD.
  - Post processing reveals major products formed, formation rates, reaction pathways and chemical kinetics data (obtained using custom developed analysis codes)



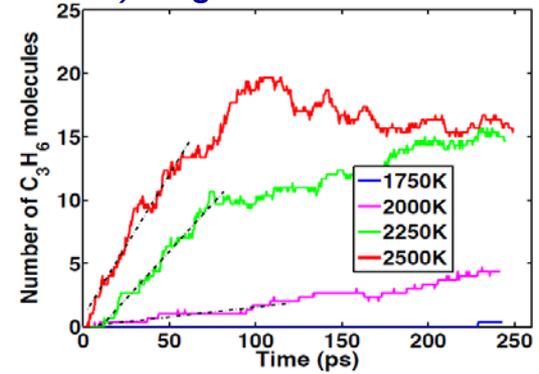
a) Pyrolysis



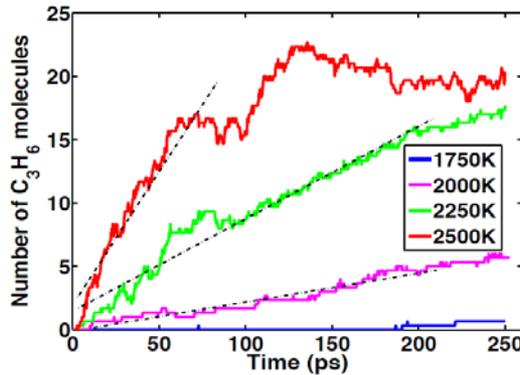
b) H<sub>2</sub> gas environment



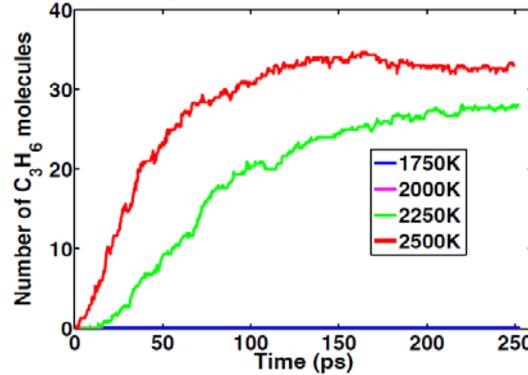
c) O<sub>2</sub> gas environment



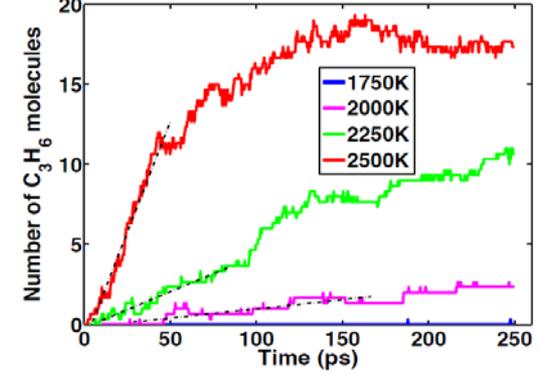
d) H<sub>2</sub>-O<sub>2</sub> mixture environment



e) CO gas environment



f) H<sub>2</sub>-O<sub>2</sub>-CO environment



- ◆ Maximum formation of ethylene and propylene were observed for pyrolysis (case a) and H<sub>2</sub> gas (case b)
- ◆ Presence of O<sub>2</sub> is seen to suppress ethylene, propylene formation, indicating other products could be formed through competing pathways → information will aid *reduced kinetic model development*.

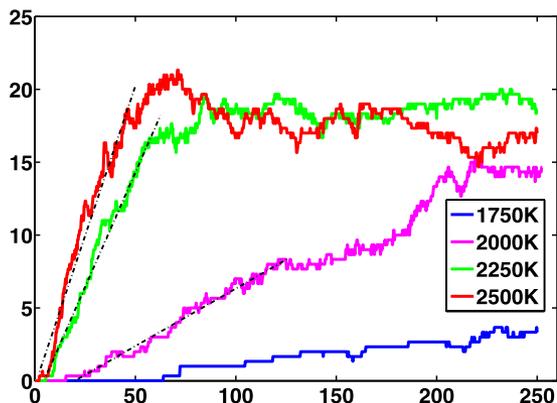


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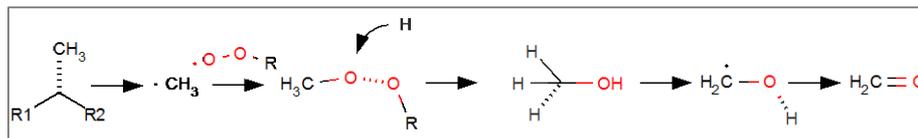
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- ◆ Analyzing reactive MD simulation results, all the information necessary to build both detailed and reduced chemical kinetics model can be obtained.
- ◆ Ingredients for building chemical kinetics model in multi-species environment:
  - Reaction pathways
  - Energy barriers for reaction
  - Specie formed and formation rates



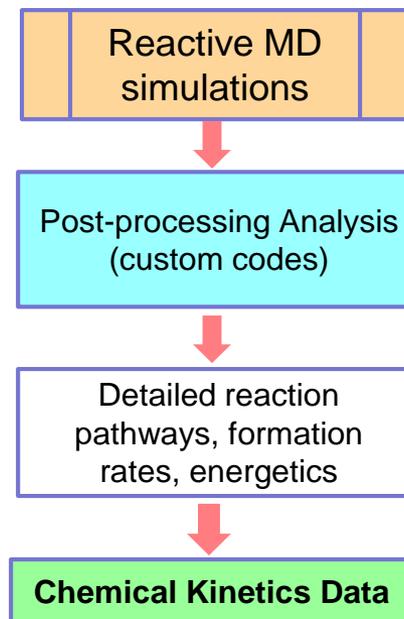
Formation rate,

$$k_f = Ae^{-\frac{E_a}{k_B T}}$$



Reaction rate,

$$k_r = Ae^{-\frac{E_a}{k_B T}}$$



*MD based Reaction analysis to obtain (detailed) chemical kinetics*



# Arrhenius parameters for major reaction products



Based on the product evolution (average) behavior the activation energy  $E_a$  and pre-exponent factor (A) according to the Arrhenius equation,  $k_f = Ae^{-\frac{E_a}{k_B T}}$  for various molecules can be estimated from reactive MD simulations of EPDM degradation in presence of various edge-gas constituents

Molecule	$E_a$ (KJ/mol)	$\ln(A)$
<i>Reaction with O<sub>2</sub></i>		
H <sub>2</sub> O	275.46	12.25
C <sub>2</sub> H <sub>4</sub>	256.34	12.11
C <sub>3</sub> H <sub>6</sub>	228.0	9.76
HCHO	190.19	8.801

Molecule	$E_a$ (KJ/mol)	$\ln(A)$
<i>Reaction with H<sub>2</sub>-O<sub>2</sub> mixture</i>		
H <sub>2</sub> O	87.77	5.09
C <sub>2</sub> H <sub>4</sub>	254.34	11.67
C <sub>3</sub> H <sub>6</sub>	184.36	7.28
HCHO	139.93	6.01

Molecule	$E_a$ (KJ/mol)	$\ln(A)$
<i>Reaction with H<sub>2</sub>-O<sub>2</sub>-CO mixture</i>		
H <sub>2</sub> O	75.7	4.5
C <sub>2</sub> H <sub>4</sub>	205.29	9.24
C <sub>3</sub> H <sub>6</sub>	262.44	11.19
HCHO	193.61	8.58

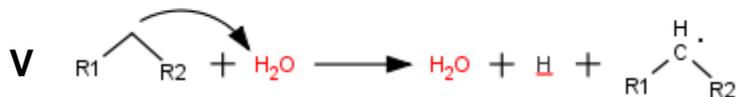
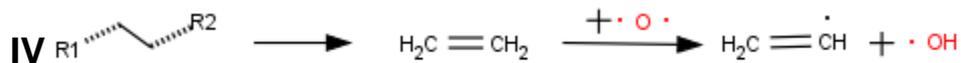
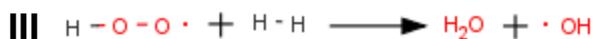
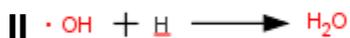


## ACT Custom Toolkits for chemical kinetics extraction



- ◆ ACT developed a custom toolkit to automate reaction extraction process
  - **MolfrACT™** (Molecular Fraction Analysis Custom Toolkit)
  - **KinACT™**, (Kinetic Analysis Custom Toolkit)
- ◆ Both tools are user-menu based (proprietary) programs which simplify the process of extracting chemistry information from reactive MD simulations
- ◆ Based on user-choice during analysis MolfrACT™ can generate:
  - List of species that exist in the reactive MD simulation and their concentration (vs  $t$ ).
  - Chain length variation over time – relevant for C-backbone polymeric systems.
  - List of atom ids belonging to a user-defined species of interest.
  - AtomEye readable color coding for atoms that belong to the species of interest.
  - Chemical reaction pathways: 4 different strategies.
- ◆ Based on user-choice during analysis KinACT™ can generate.
  - Reduced chemical kinetics models and data (which can be input into CFD simulations)
  - Data obtained by analyzing the reaction output from MolfrACT™.

- ◆ For example, using simulation data from EPDM degradation in H<sub>2</sub>/O<sub>2</sub>/CO environment, lets look at H<sub>2</sub>O formation below:



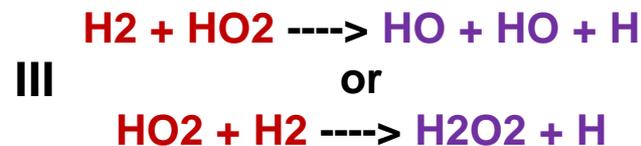
I: Replacement reaction on H<sub>2</sub>O

II: Reduction of OH

III: Reduction of HO<sub>2</sub>

IV: Sequential chain scission + H-abstraction

V: Replacement reaction on H<sub>2</sub>O involving hydrocarbon chain



Comment: Replacement reaction

Not obvious from the reaction since multiple reactions occur in this frame with replacement being one of the steps.



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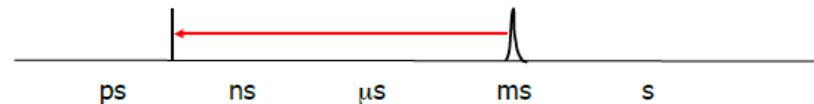
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# Background: Accelerated Molecular Dynamics

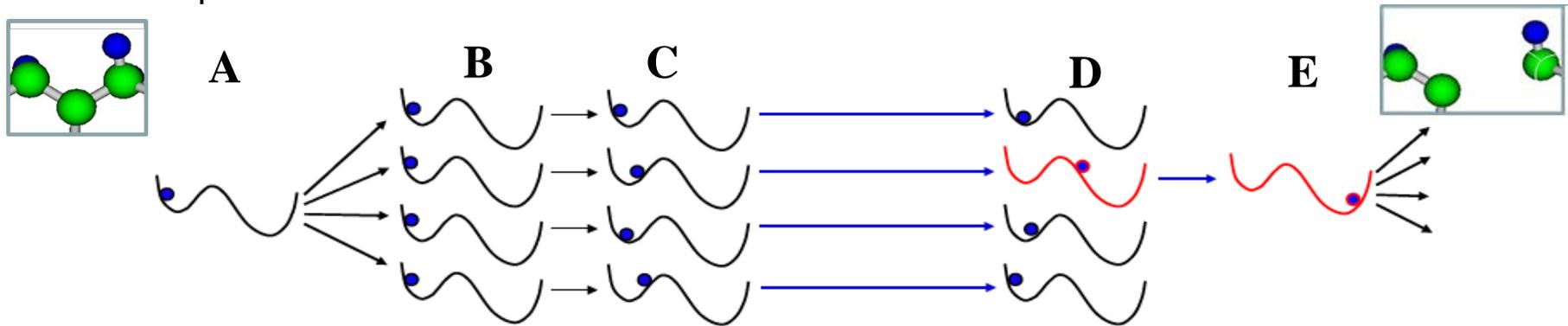


- ◆ *Accelerated Molecular dynamics (AMD)* can extend the accessible timescale by orders of magnitude relative to MD, while retaining full atomistic details.
  - Let the system (trajectories) evolve to find an appropriate way out of each state. But, coax it in doing so more quickly using statistical mechanics concepts .



- ◆ 3 types of AMD methods are most popular:
  - \* Hyperdynamics
  - \* Parallel Replica dynamics (PRD)
  - \* Temperature accelerated dynamics (TAD)
- ◆ Proposed by Arthur F. Voter, LANL
  - Phys. Rev. B, vol. 57 (22), 1998; Annu. Rev. Mater. Res. 2002, 32:321-46.
- ◆ Only couple of AMD study has been reported for reactive hydrocarbon systems
  - J. Chem. Phys., vol.121 (2), 2004.

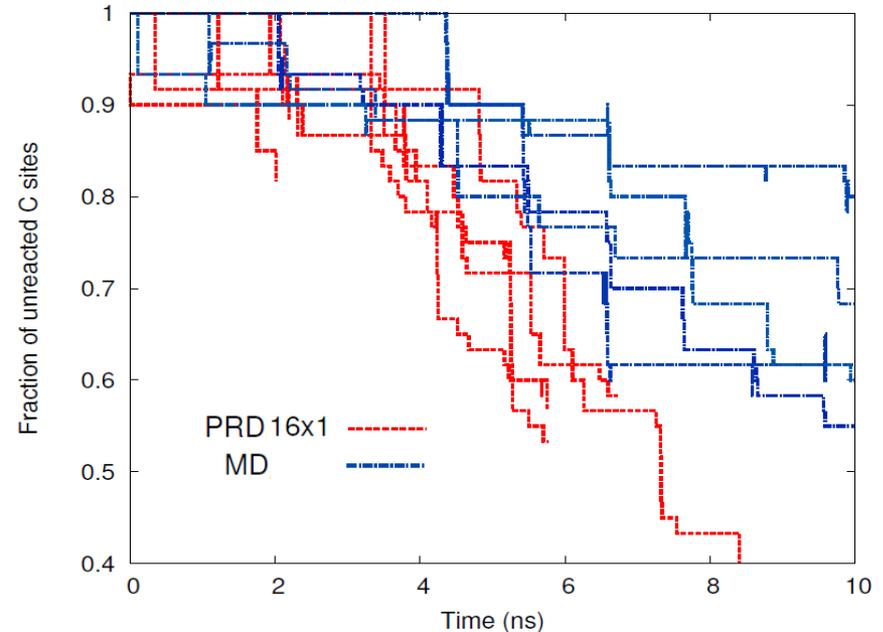
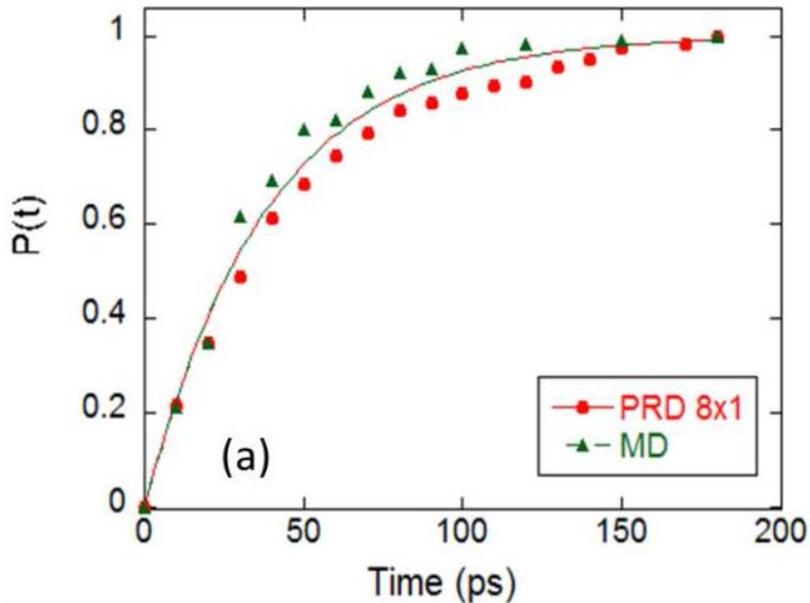
- ◆ ACT developed an AMD framework for reactive systems using parallel replica dynamics.
  - Long term dynamics consisting of infrequent events between different states (activated process) can be modeled by following many replicas of the system in parallel.



- ◆ Only assumption is the system needs to obey first order kinetics,
- ◆ Requires:
  - Event detection scheme
  - Account for correlated time

**Time spend by system in a bonding state,**  
 $t_{sum} = \sum_i^M t_{replica}$  **(time spent on all replicas)**

- Using a polymer system as surrogate, the dynamics obtained from PRD simulations is compared with direct MD simulations

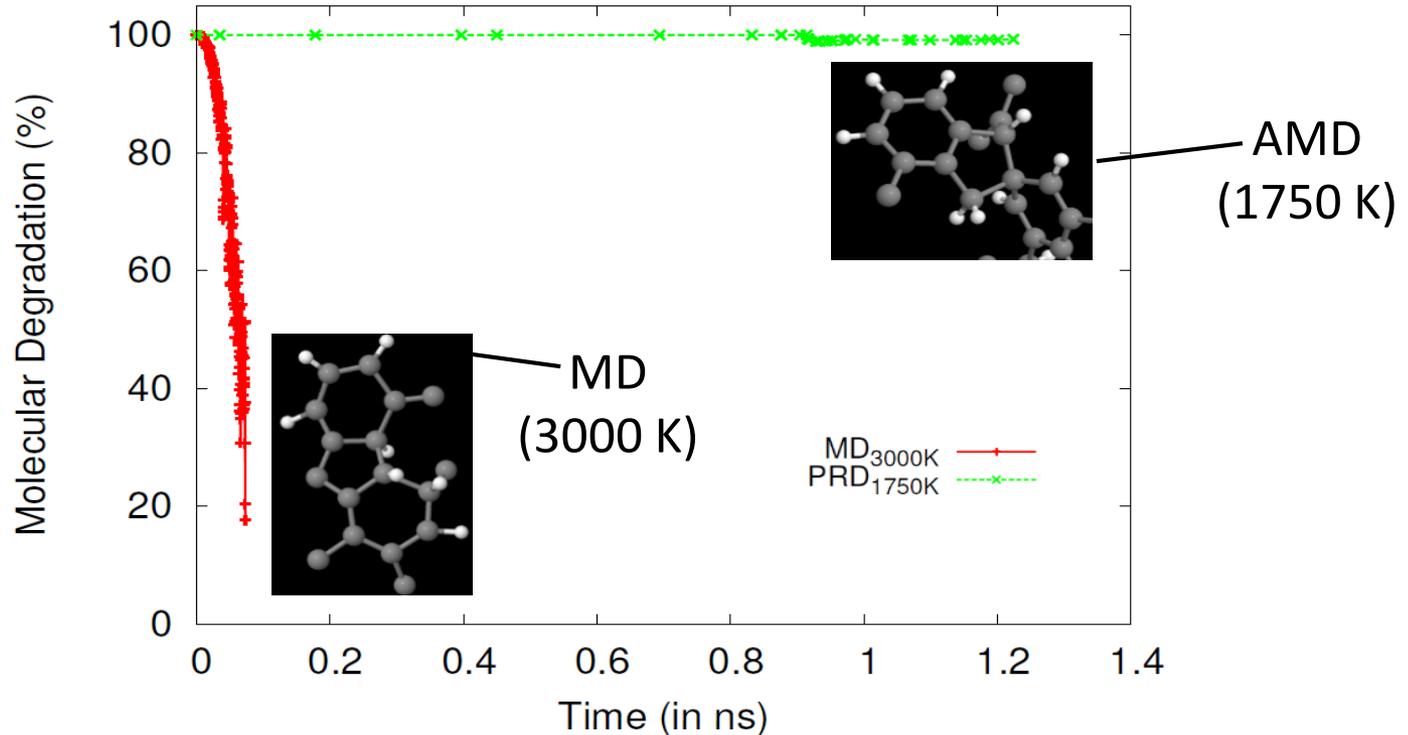


- Good agreement between PRD and direct MD for both reaction initiation and propagation.

ACT developed accelerated MD (AMD) method which allows simulation of pyrolysis reactions at significantly lower temperature than direct MD.

Pyrolysis of PICA heat shield begins at 1000K.

AMD allows us to reach longer timescale



- ◆ There is a need for developing custom tools for investigating material chemistry and response due to thermo-chemical degradation. Currently models over/under-predict in multi-specie, multiphysics environments.
- ◆ We discussed capabilities for ‘atomistics-based’, ‘physics-based’ modeling of chemical degradation phenomena, which can help improve the predictive models at macroscale (CFD based). We illustrate these capabilities using:
  - Ablative (phenolic resin) materials exposed to high temperatures ~2000 K upwards.
  - High temperature pyrolysis behavior of EPDM, materials used in rocket casing insulation
- ◆ Reactive MD simulations were employed on phenolic resins to capture the initial stages of pyrolysis, pyrolysis products and reaction pathways (kinetic models).
  - For the first time in literature, we illustrate formation of stable large graphitic precursors (7-fused rings).
- ◆ Custom tools: MolfrACT™ and KinACT™ developed to extraction chemical reaction data/statistics, their use for chemical kinetics data is discussed.
- ◆ Accelerated MD methodology developed for modeling chemically reactive systems at low temperatures has been discussed.
- ☞ This framework is also **applicable for modeling chemical response of materials** for: battery materials phenomena, energetics/explosive, hydrogen storage materials, combustion chemistry and petroleum processing steps – for fundamental understanding and optimization.

- ◆ We provide/develop custom modeling capabilities for wide range of materials phenomena.
  - Ablative heatshield materials
  - Energetic explosives
  - Batteries and energy storage devices
  - H storage, fuel cells
  - Combustion modeling
  - Modeling hypersonic flow and chemistry
- ◆ If you need to help obtaining fundamental understanding or modeling above applications.

- ◆ Contact us:

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