Connectivity-Based Parallel Replica Dynamics For Simulating Chemically Reactive Systems Using ReaxFF

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Panel 1 — Modeling Must Address Questions Spanning from Atomic to Macroscopic Scale

Thermal Cracking/Combustion
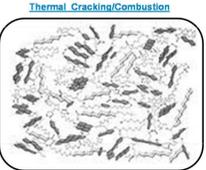
Adsorption and Diffusion in Catalysis

1, 3, 7, 9 = Diffusion; 2, 4, 6, 8 = ads./des.
5 = reaction
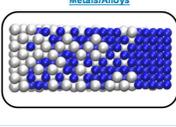
Metals/Alloys   Supported catalysts   Polymer membranes
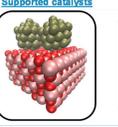
Panel 2 — Currently Adopted Hierarchical Strategy Relies on Chemical Intuition
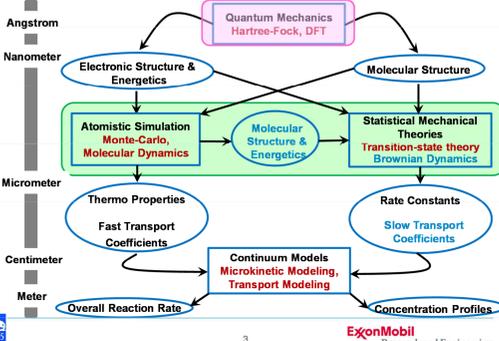
Quantum Mechanics Hartree-Fock, DFT

Angstrom → Electronic Structure & Energetics — Molecular Structure

Nanometer

Atomistic Simulation Monte-Carlo, Molecular Dynamics — Molecular Structure & Energetics — Statistical Mechanical Theories Transition-state theory Brownian Dynamics

Micrometer

Thermo Properties — Fast Transport Coefficients

Rate Constants — Slow Transport Coefficients

Continuum Models Microkinetic Modeling, Transport Modeling

Centimeter

Meter → Overall Reaction Rate — Concentration Profiles

Panel 3 — Hierarchical Approach and ReaxFF Paradigm
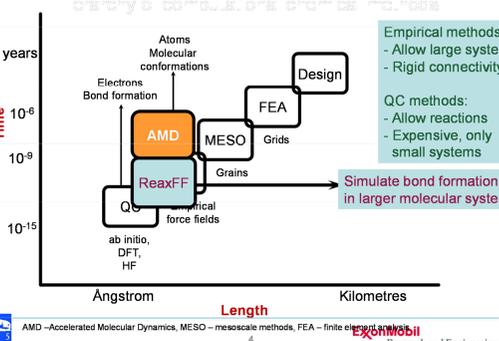
Empirical methods:
- Allow large systems
- Rigid connectivity

QC methods:
- Allow reactions
- Expensive, only small systems

Simulate bond formation in larger molecular systems

AMD –Accelerated Molecular Dynamics, MESO – mesoscale methods, FEA – finite element methods

Panel 4 — Reactive Molecular Dynamics*

- Parameterized exclusively from QM calculations
- Transferable FF requiring info on element type.
- Bond-order dependent valence, vdW and electrostatic terms

$$E_{system} = E_{bond} + E_{vdW} + E_{Coul} + E_{val} + E_{tors} + E_{over} + E_{under}$$

- Environmentally dependent charge distribution on atoms accounting for polarization effects
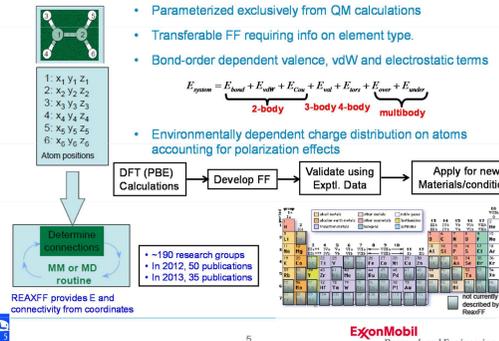
DFT (PBE) Calculations → Develop FF → Validate using Exptl. Data → Apply for new Materials/conditions

Determine connections → MM or MD routine

REAXFF provides E and connectivity from coordinates

- ~190 research groups
- In 2012, 50 publications
- In 2013, 35 publications

Panel 5 — RMD Enables Estimation of Kinetic Parameters of Kerogen Cracking
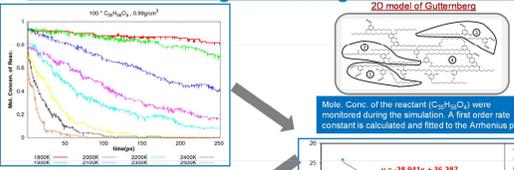
2D model of Guttenberg

Mole. Conc. of the reactant ($C_{20}H_{32}O_4$) were monitored during the simulation. A first order rate constant is calculated and fitted to the Arrhenius plot

$y = -28.941x + 36.287$, $R^2 = 0.9932$
$y = -31.382x + 37.566$, $R^2 = 0.979$
$y = -32.431x + 37.581$, $R^2 = 0.9732$

Method	System		A(s^{-1})	Ea (kcal/mol)
ReaxFF	$C_{20}H_{32}O_4$	0.6g/cm³	5.74*10⁰·⁵	57.5
		0.99g/cm³	2.06*10⁰·⁶	62.3
		1.38g/cm³	2.09*10⁰·⁶	64.5
Behar et. al(1997)	Type I		7.4*10¹³	54
Tegelaar (1994)	Type I		1.8*10¹⁴	55
Behar et.al(1996)	n-C_{25}		6.1*10¹⁷	68.2

Panel 6 — Mass Fraction Analysis Enables Construction of Lumped Kinetic Model
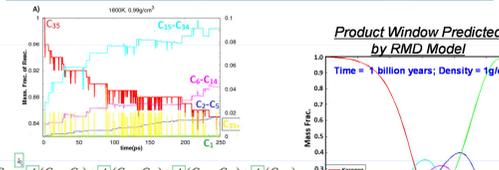
Product Window Predicted by RMD Model

Time = 1 billion years; Density = 1g/cm³

$C_{25} \rightarrow A_1(C_2 - C_5) + A_2(C_6 - C_{14}) + A_3(C_{15} - C_{34}) + A_4(C_{34})$
$C_{34} \rightarrow A_1(C_2 - C_5) + A_2(C_6 - C_{14}) + A_3(C_{15} - C_{34})$
$C_{15} - C_{34} \rightarrow A_1(C_1) + A_2(C_2 - C_5) + A_3(C_6 - C_{14})$
$C_6 - C_{14} \rightarrow A_1(C_1) + A_2(C_2 - C_5)$
$C_2 - C_5 \rightarrow A_1(C_1)$

k_i: first order rate constants
A_i: mass stoichiometry coefficients

High T RMD has difficulty in predicting product selectivity

Panel 7 — Time Scale of RMD Simulation Extended Using Parallel Replica Dynamics[1]

- Parallelizes rare event simulation in time domain

State 1   State 3   State 2

Assumptions:
- Infrequent events
  - Very long vibrational dynamics+ a brief transition
- Transitions can be detected
- Exponential distribution of first-escape times
- Correlation time known

$$p(t) = k_{tot} \exp(-k_{tot}t)$$
$$p(t) = ke^{-kt}$$

- PRD is coupled with REAXFF in LAMMPS by implementing a connectivity-based event detection

[1]Phys. Rev. B, 57, R13985 (1998)

Panel 8 — Event Detection in PRD

- Position-based event detection
  - If any particular atom is displaced by more than certain cutoff distance, then the program tags that instance as a transition event.
  - Works well for crystalline systems
    - Suited for diffusivity studies in crystal structures
      - vacancies
      - adatoms
  - Not a choice for gas phase chemical reactions

- Connectivity-based event detection
  - Implemented new event detection for reactive potential ReaxFF
  - Keep track of the connectivity and number of neighbors surrounding every atom
  - Criteria for identifying transition event
    - Change in number of neighbors surrounding any atom
    - Change in total number of molecules present in the system. This condition allows user to neglect isomerization (optional)

Panel 9 — Evaluation of Exponential Decay Assumption of First Escape Time

P(t) for the initiation step

P(t) for the propagation step

39 C_7H_{14} molecules at 1600K on 192 replicas
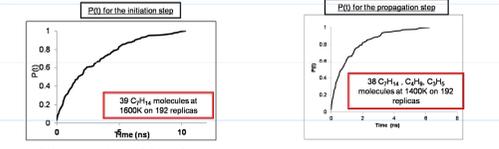
38 C_7H_{14} , C_4H_9, C_3H_5 molecules at 1400K on 192 replicas

$P(t) = 1 - e^{-kt}$ with $k = 3.81 \times 10^5 s^{-1}$

Reaction path	Frequency	% Frequency
$C_7H_{14} \rightarrow C_4H_9 + C_3H_5$	144	77.8
$C_7H_{14} \rightarrow C_2H_5 + C_5H_9$	16	8.6
$C_7H_{14} \rightarrow C_4H_7 + C_3H_7$	16	8.6
$C_7H_{14} \rightarrow C_6H_{11} + CH_3$	5	2.7
$C_7H_{14} \rightarrow C_7H_{13} + H$	2	1
$C_4H_9 \rightarrow C_2H_4 + C_2H_5$	1	0.5
$C_3H_5 \rightarrow C_2H_{13} + H$	1	0.5

Reaction Path	Frequency	% Frequency
$C_4H_9 \rightarrow C_2H_4 + C_2H_5$	136	73.1
$C_4H_9 \rightarrow C_3H_6 + CH_3$	32	17.2
$C_3H_5 \rightarrow C_2H_3 + C_2H_4$	3	1.6
$C_7H_{14} \rightarrow C_7H_{13} + H$	3	1.6
$C_7H_{14} \rightarrow C_4H_9 + C_3H_5$	3	1.6
$C_7H_{14} + C_4H_9 \rightarrow C_{11}H_{23}$	3	1.6
$C_7H_{14} \rightarrow C_2H_5 + C_5H_9$	2	1.07
$C_7H_{14} + C_4H_9 \rightarrow C_3H_5 + C_8H_{18}$	2	1.07
$C_7H_{14} + C_3H_5 \rightarrow C_6H_9 + C_4H_9 + C_2H_7$	1	0.53

Panel 10 — PRD Enables Simulation of Heptene Pyrolysis Under Experimental Conditions of Temperatures

Maximum fuel conversion achieved is about 47.5%

Temperature (K)	No of Replicas	Simulated time (ns)
1800	10	7.39
1500	80	174.72
1450	80	386.18
1400	120	650.07
1350	180	992.3 ≈ 1µs

Lowering the simulation temperature resulted in

- efficient utilization of more number of replicas and effective acceleration in time without compromising the parallel efficiency
- intermediate radicals survive longer instead of undergoing only fragmentation reactions
- Amount of (C2+C1) products formed progressively decreased with T, in accordance with shock tube experiments[6] performed at 900 to 1300K and 25 -50 atm

[6]Garner, S. Sivaramakrishnan R., Brezinsky K., (2009) Proceedings of the Combustion Institute 32 461-467.

Panel 11 — Estimation of Apparent Kinetic Parameters from PRD Simulations

1300K 1400K 1450K 1500K
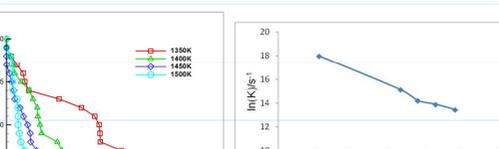
Heptene decay as function of temperature

$$\ln(N_0) - \ln(N_t) = Kt$$
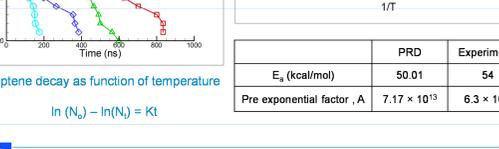
	PRD	Experiment[7]
E_a (kcal/mol)	50.01	54
Pre exponential factor , A	7.17×10^{13}	6.3×10^{11}

[7]Blades A.T., Sandhu H.S. (1971) Int. J. Kin., 3 187-193

Panel 12 — Conclusions

- We have successfully implemented connectivity-based event detector in LAMMPS to perform reactive PRD simulations using ReaxFF reactive force field method.

- For heptene pyrolysis, our calculations indicate that the probability distribution function for the first two phases follows first order kinetics and hence thermal decomposition of heptene (any olefin and paraffin at low density) can be studied using PRD.

- PRD simulations of heptene pyrolysis indicate that
  - Timescales up to microseconds can be achieved
  - Pyrolysis simulations can be performed at much lower temperatures that were previously inaccessible in MD simulations.
  - Lowering simulation temperatures significantly improves the product distribution and overall chemistry description and enables a qualitative comparisons with experiments
  - PRD simulations also enable estimation of kinetic parameters at temperatures that are much closer to experiments
  - PRD efficiency is strongly dependent on "infrequent event" assumption