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Scientific Impacts and Opportunities in Computing

"Science-Based Model for Soot Formation from Novel Fuels"

Angela Violi

Departments of Mechanical, Chemical and Biomedical Engineering

University of Michigan

Maui, HI

Current Needs

Novel Fuels / Novel Engine Designs

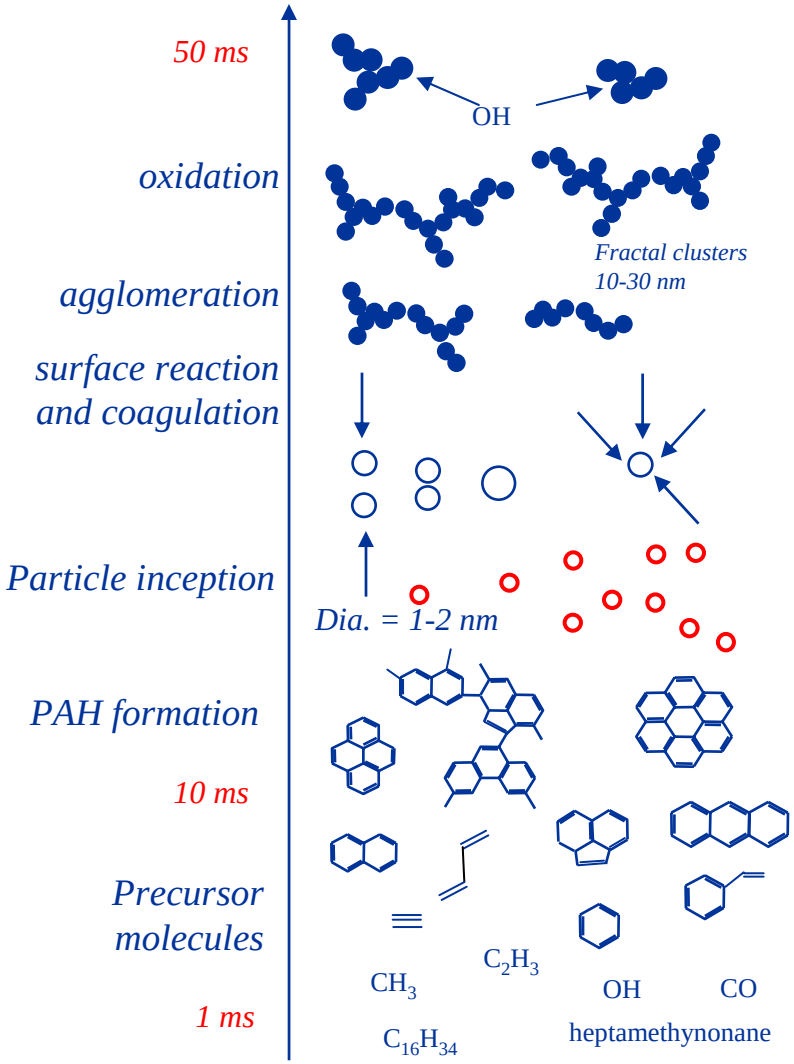
- Choice of current renewable fuels is dictated by considerations that relate to availability - not result of an optimization process that has considered physical and chemical properties as well as the intricacies of automotive use.
- Optimization of fuels needs to relate to efficient energy conversion and emissions.

Current Needs in Science

1. Advanced engine strategies rely on chemistry to initiate ignition; the relevant <u>chemistry and physics for alternative fuels</u> is poorly known.

2. <u>Soot formation</u> is one of the major constraints in engine performance. The underlying mechanisms for its inception, growth, and oxidation and emissions are poorly known. Quantitative understanding of soot processes will allow better strategies for its control.

From few C to agglomerates of millions of C atoms



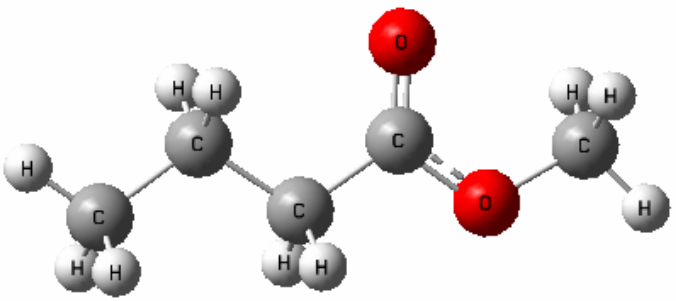
Particle – particle interactions

Particle inception

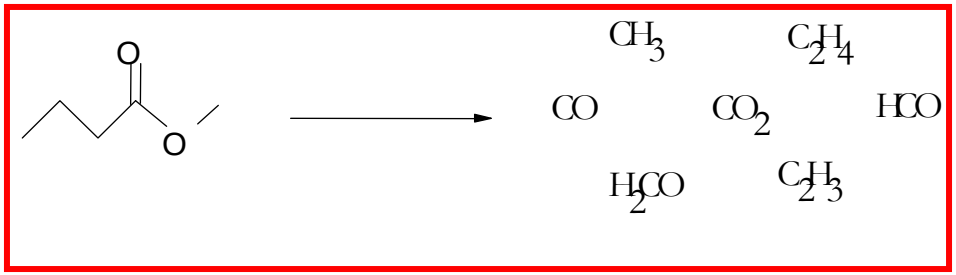
Gas-phase chemistry

Gas-Phase: Chemical and Physical properties of Novel Fuels

1. Kinetic Pathways and Thermochemical properties



Biodiesel surrogate
Methyl butanoate



New kinetic mechanism for MB breakdown
Hyuhn and Violi, J. Org. Chem 2007

Chemical and Physical properties of Novel Fuels

2. Transport Properties

Binary diffusion coefficients using molecular dynamic simulations with the Green-Kubo formula.

Chapman-Enskog equation fails to produce accurate values especially in high density conditions.

Science in the next 18 months with increased computing capabilities

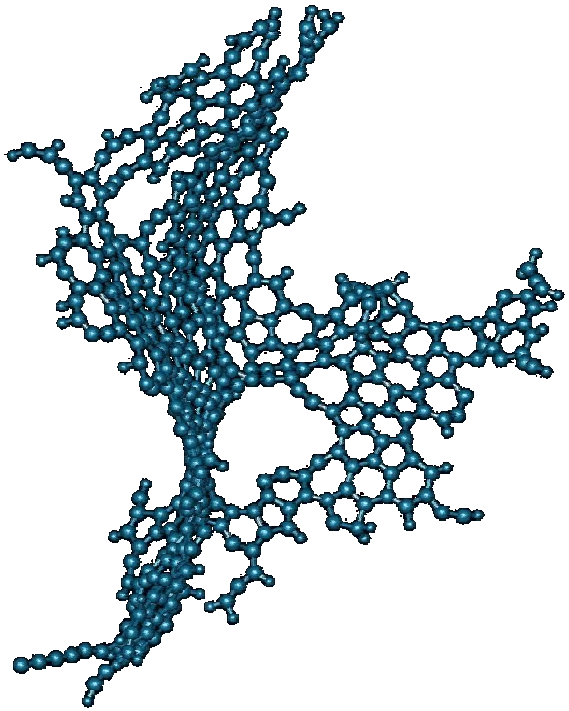
1. **Reaction pathways and Thermochemical Properties of more complex biofuel molecules** with the goal of identifying information that is dependent on the functional groups and conditions. *Expected outcome: ability to generate kinetics based on reaction classes.*

2. **Transport Properties**

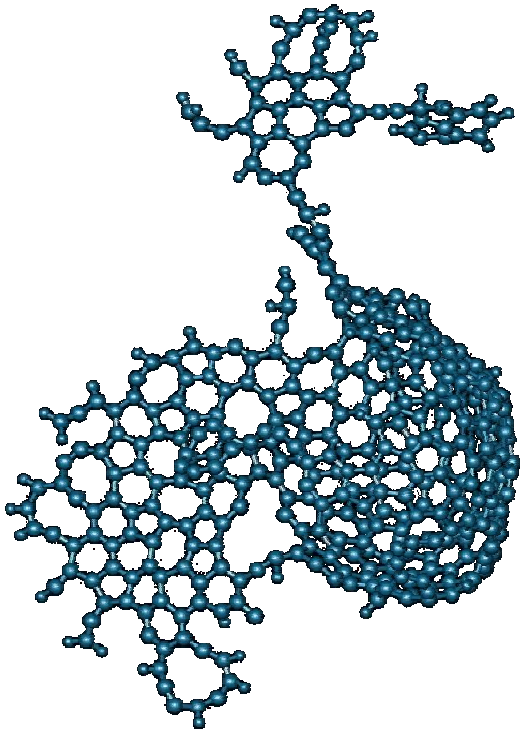
Complex molecules for binary and multi-component systems. Expected outcome: Molecules up to hundreds atoms in high T and P

Overarching Goal: develop accurate kinetic models for novel fuels

AMPI code: Influence of reaction pathways



Aliphatic Fuel



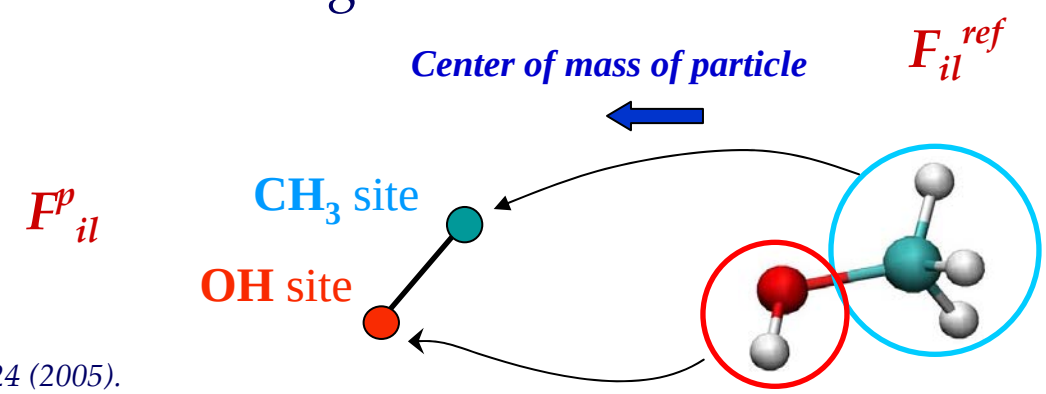
Aromatic Fuel

Violi, Venkanathan J.C.P. 2006
Chung, Violi CARBON 2007

The Intermolecular Scale: Multiscale Coarse-Grained Approach

A detailed atomistic model is transformed into a lower resolution Multiscale-CG model via a systematic and thermodynamically consistent procedure.

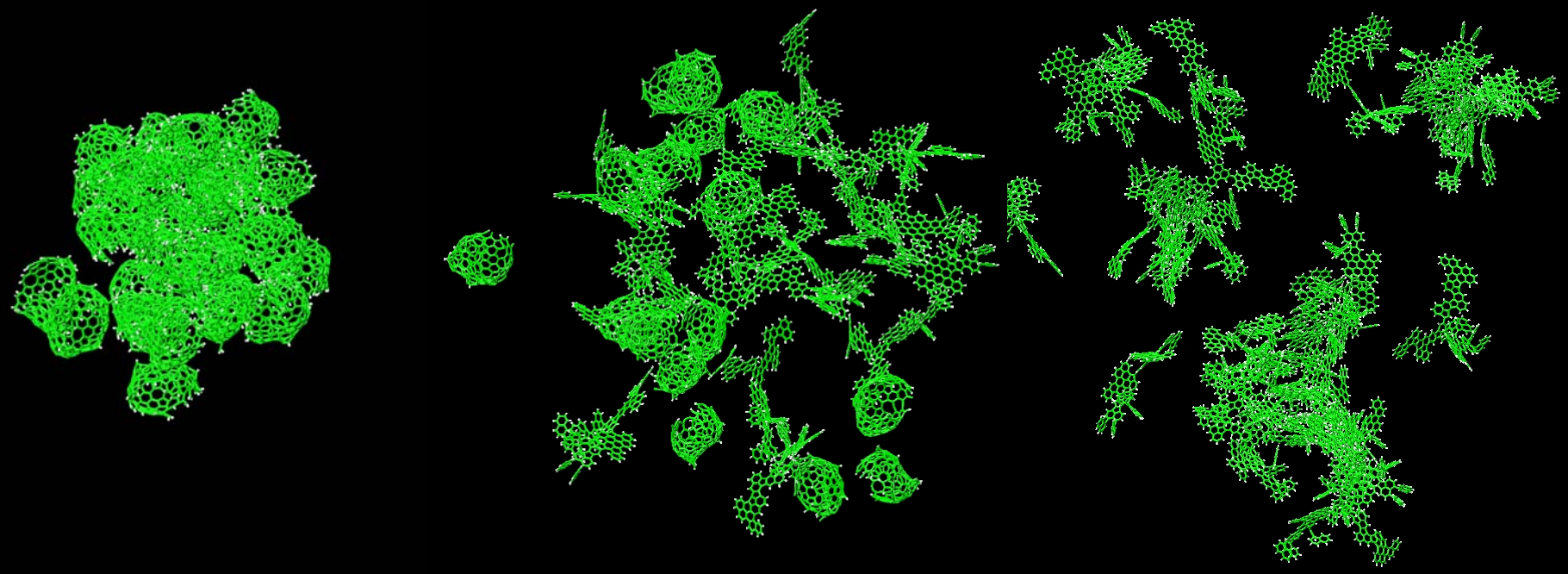
1. partitioning of the system into the larger structural units – CG units
2. construction of an effective force field for CG unit interactions (Force Matching algorithm)



Izvekov, Violi *J. Phys. Chem. B 109(36): 17019-17024 (2005).*

Violi, Voth *Lecture Notes in Computer Sci. 3726: 938-947 (2005).*

IMPORTANCE OF MORPHOLOGY



Izvekov, Violi *J. Chem. Theory Comput. 2(3), 504-512 (2006).*

Currently

This is *the first attempt* to describe the formation of large collections of primary soot particles of ~20 nm in size, using coarse-grained MD simulations of effectively 2 million carbon atoms at flame temperature conditions for microsecond timescales, complete with chemical and structural information bridged upward from the atomistic-scale.

This work has the potential to reduce much of the empiricism presently associated with soot modeling.

Current Findings

1. Gas-phase species and combustion conditions influence particle morphology

2. chemical changes and transformation can propagate upward in scale to help define the function of the particle structures.

3. Morphology of the nano-particles is critical in determining the overall growth and agglomeration behavior of larger scale molecular structures and compounds (soot).

Needs for Advanced Computing Capabilities

Current levels of computing allow for roughly 10^4 nanoparticles to be formed using approximately $2x10^6$ atoms over nanosecond time scales. These calculations currently take about 30 days running on 16 processors. At this level of simulation, soot precursor clusters of approximately 20nm can be formed and studied numerically.

For realistic predictions of soot formation, soot clusters of size approaching 1μm are needed, resulting in a factor of 50 increase in computational requirements. Furthermore, the physical dimensions will also be increased accordingly, resulting in a factor of 125,000 more atoms, or roughly 10^{11} atoms in total.

Science in the next 18 months with advanced computing capabilities

Microscale

- Need to produce at least 1,000 simulations per condition to generate statistical ensemble (AMPI code)

Mesoscale

- Parameterize the coarse-grained model of nanoparticles at the mesoscale: The CG model can be improved to take into account different geometries with orientational degrees of freedom with additional computational power.

- Simulations of realistic size of carbon aggregates – reaching 1μm

Scientific Discovery by Computing

Soot Formation Model:
multi-scale interactions, emergent behavior, pattern formation, and self-organization; Nonlinear couplings and feedbacks across multiple processes and scales.

High value results could be expected at the end of a focused 5-year effort

Predictive model for soot formation

Predictive models of soot processes responsive to blends of alternative fuels and the broad pressure ranges of new engines. (soot formation, growth, oxidation, surface chemistry, and size distributions).