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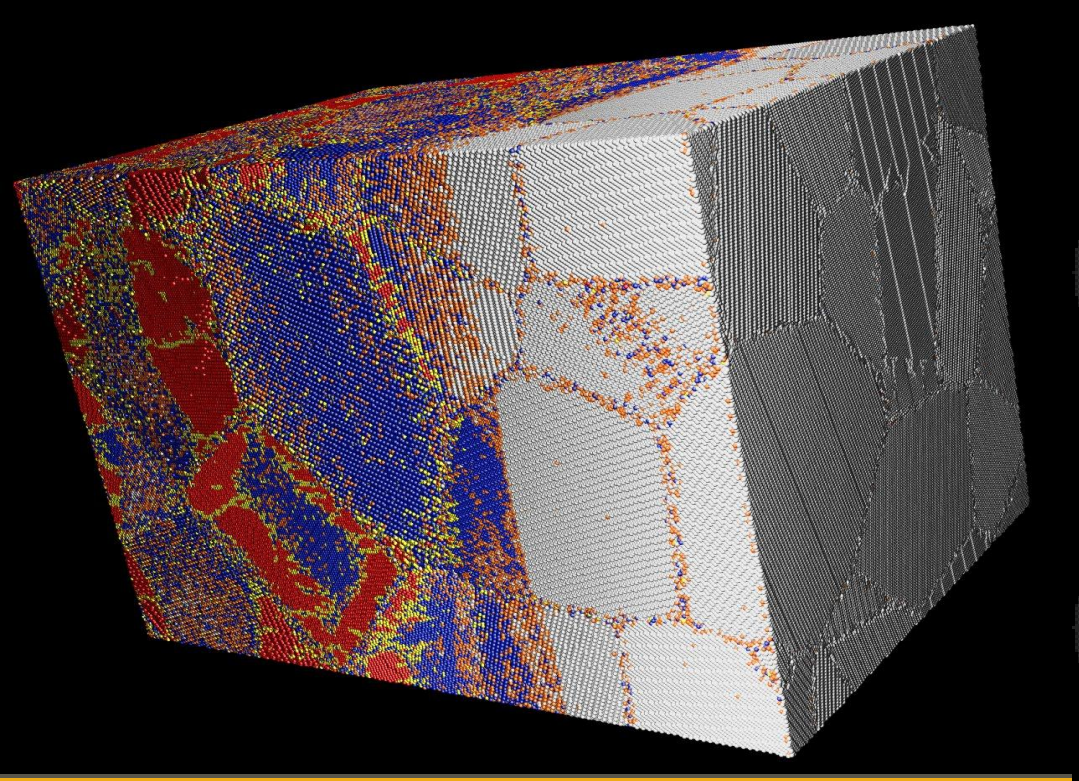
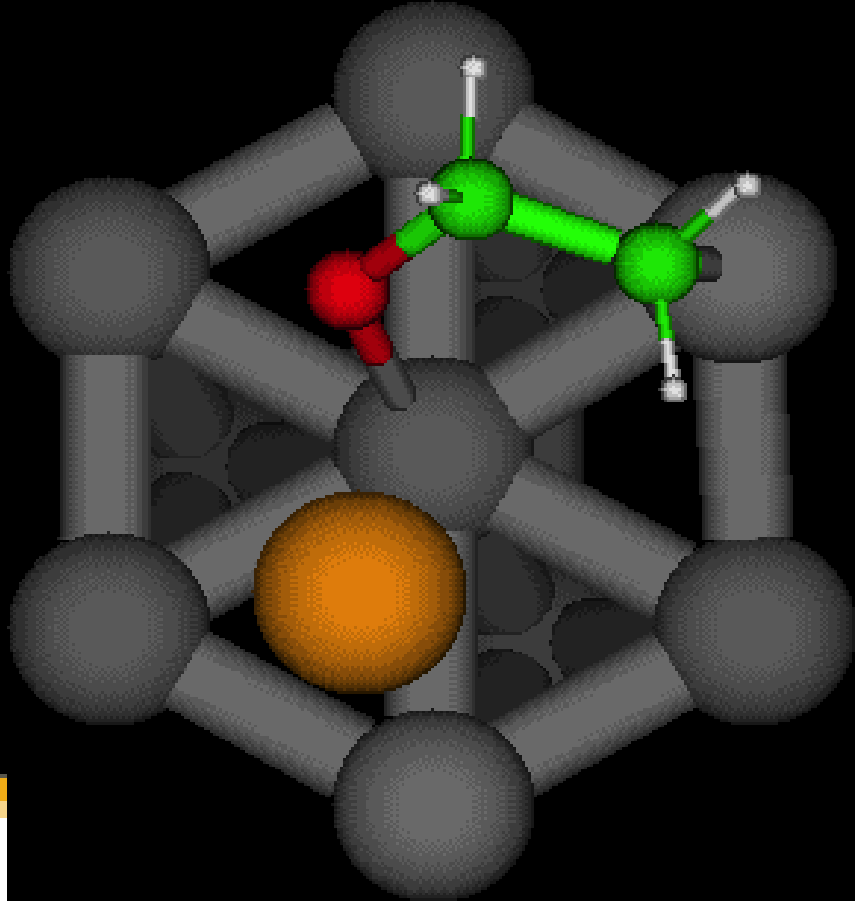
Title:	Theory Modeling and Simulation
Author(s):	Shlachter, Jack
Intended for:	Initiating a BASF collaboration





Jack Shlachter
Los Alamos National Laboratory
Theoretical Division

Presentation to
BASF
August 20, 2012

Theory Modeling and Simulation

Los Alamos
NATIONAL LABORATORY
EST. 1943

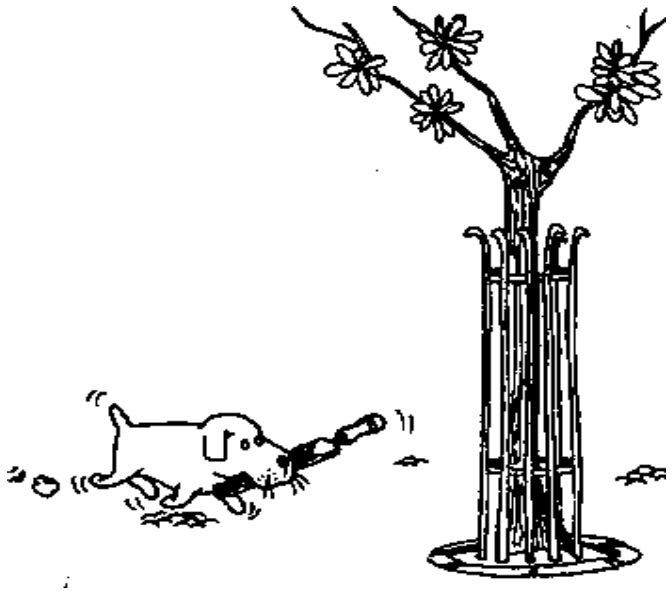
General philosophy

- We focus on multidisciplinary teams that tackle complex problems

- We have extensive collaborations with academia, industry and other national laboratories
  - Procter & Gamble
  - Chevron
  - Dow Chemical
  - DuPont
  - Many others

Approach to problem-solving

- We focus on the solution of the problem
  - We do not have a technique in search of applications
- Use appropriate theory and simulation tools
  - Use tools in our present toolbox
  - Modify previous tools
  - Develop new tools



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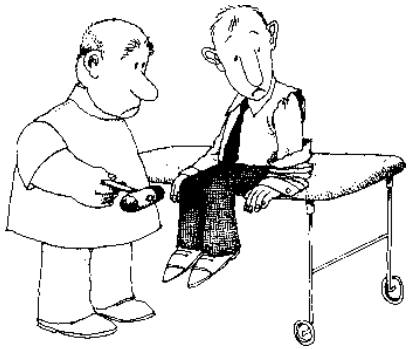
Los Alamos has a long history in theory, modeling and simulation

- The Monte Carlo method was invented at LANL
- Some of the very first molecular dynamics simulations were done at Los Alamos
- The particle-in-cell (PIC) method to do computational fluid dynamics was invented at LANL
- The nuclear weapons program at LANL has some of the most sophisticated multiscale-multiphysics simulation tools in the world
- The Laboratory has been at the forefront in the use of state-of-the-art hardware and software to push the frontiers of modeling and simulation

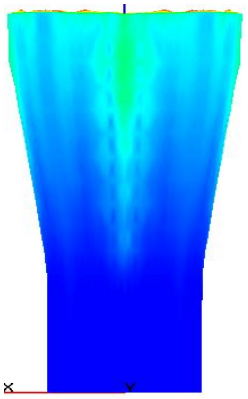
Role of theory, modeling and simulation

- Fundamental understanding
  - Produce new concepts
  - Lead to new experiments
- Reduce parameter space for experiments
  - Simple models first
  - Refine models as needed
- As an additional tool to solve problems
  - Some calculations can give detailed information about phenomena not accessible by experiments
  - To understand complex experiments
- Predictive modeling
  - Mature models used as production tools

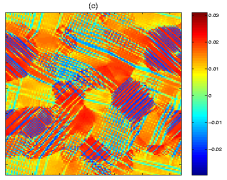


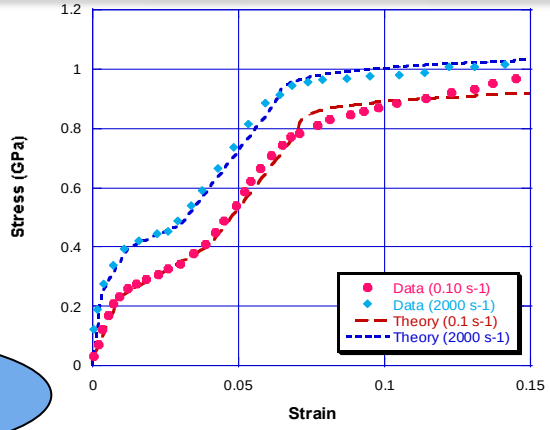
Multiscale materials modeling

Macro-Mechanical

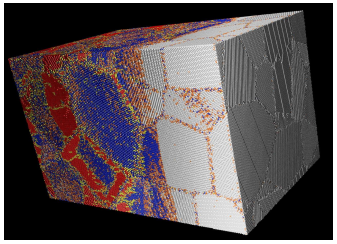


Polycrystal

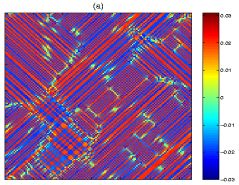




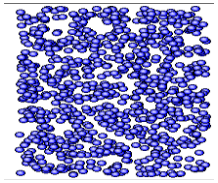
Experiment



Single Crystal



Molecular Dynamics



Quantum Mechanics

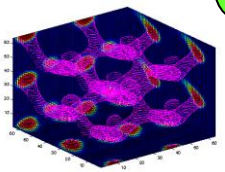
Time / Length Scales

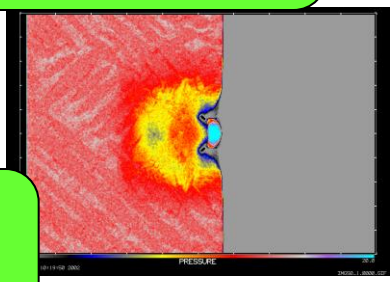
We are staffed to meet complex materials problems with interdisciplinary approaches: taking theory to models to numerical implementation to production codes

Multiscale modeling of polymers

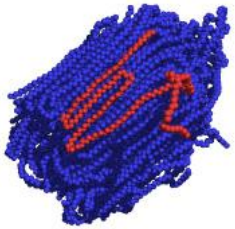
- Polymers present inherently multiscale modeling issues
  - Long relaxation times and physical / chemical aging
  - Entangled / frustrated systems
  - Complex phase diagrams for multiblock systems

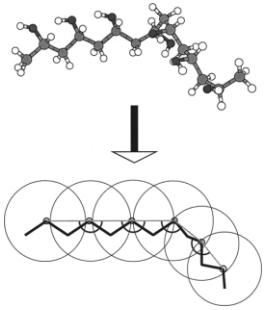
Continuum simulations



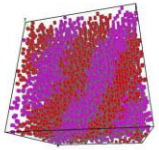


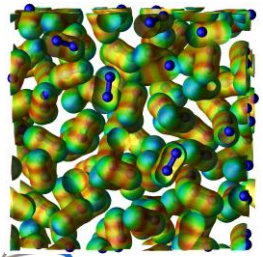
Mean-field computations



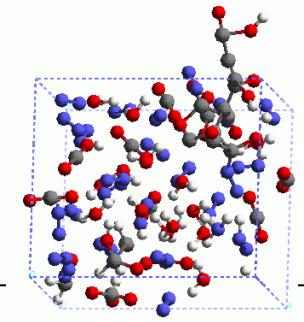


Coarse grained particle-based simulations





Quantum, MD & MC simulations



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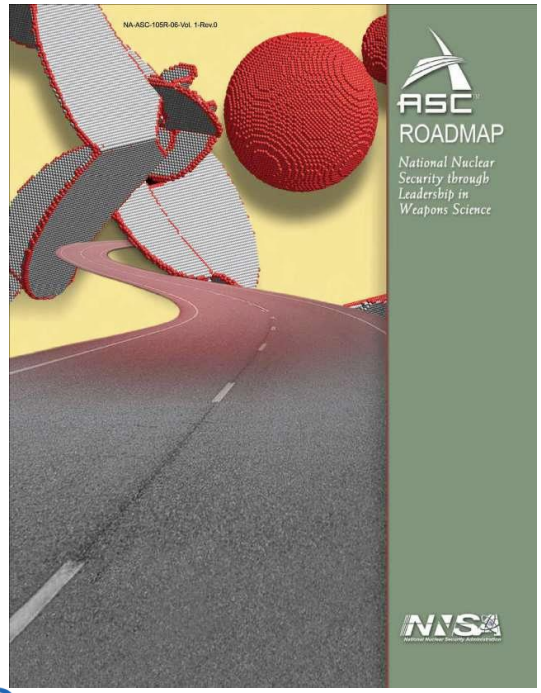
Large-scale molecular dynamics simulations

Fundamental probe of collective effects arising from large numbers of interacting particles or agents in a wide variety of systems

1) Plasticity and phase transitions in materials subjected to high strain-rate loading (e.g. shock)
2) Fluid instabilities (e.g. Rayleigh-Taylor, Richtmyer-Meshkov)
3) Agent-based modeling of disease spread, crowd dynamics, …



Large-scale molecular dynamics techniques for simulation of mesoscale systems using the high-performance SPaSM (Scalable Parallel Short-range Molecular dynamics) code.

SPaSM has exhibited linear scaling and high performance (4-time finalist, 2-time winner of the IEEE/ACM Gordon Bell Prize) up to 10^{12} atoms on platforms including BlueGene/L and Roadrunner.

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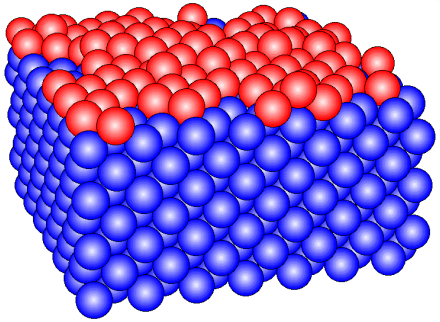
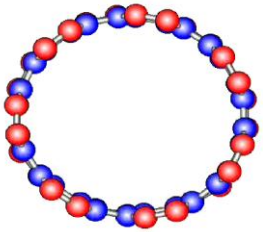
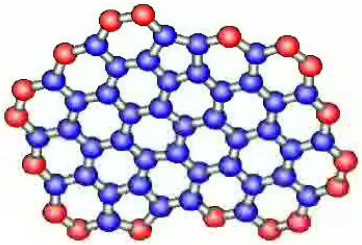
A wide range of problems can be studied with accelerated molecular dynamics

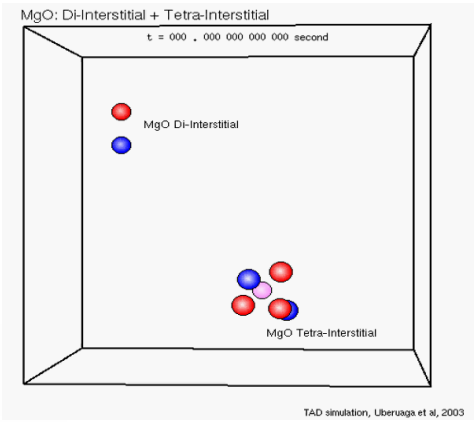


Cu/Ag(100), 1 ML/25 s
T=77K, Sprague et al, 2002.

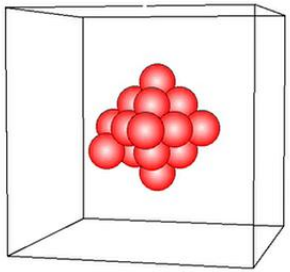


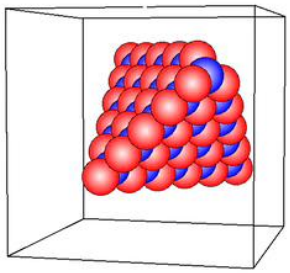


Annealing nanotube slices,
μs, Uberuaga et al, 2011.

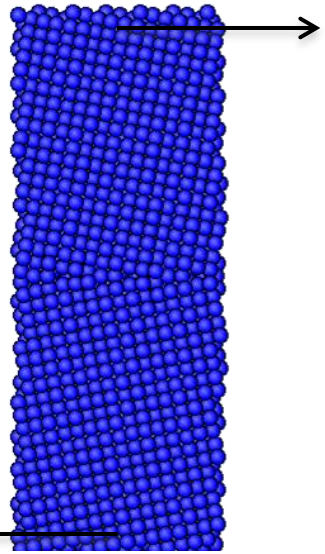


Interstitial defects in MgO,
ps – s, Uberuaga et al, 2004.



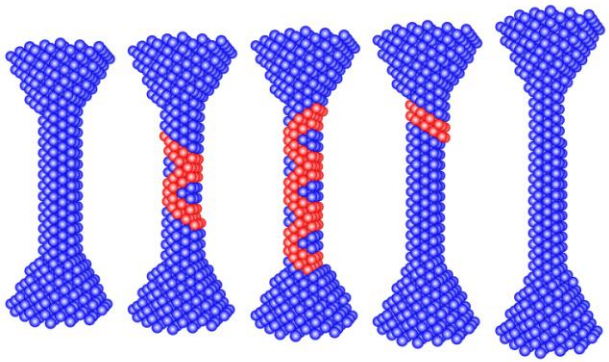


Cu void collapse, μs,
Uberuaga et al, 2007.



Driven Cu GB
sliding, 500 μm/s
Mishin et al, 2007.

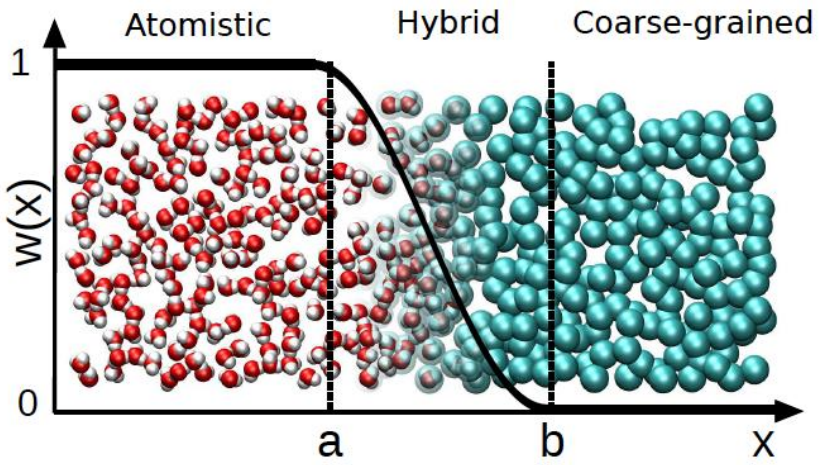
Hexadecane pyrolysis,
μs, Kum et al, 2004.



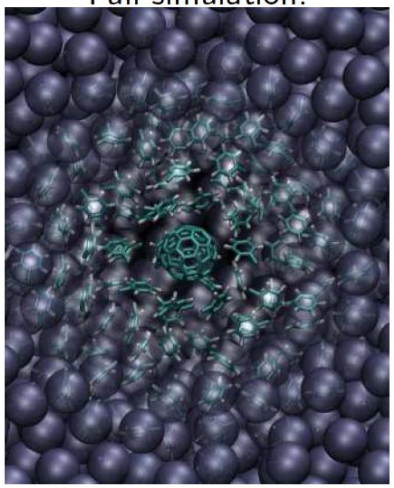
Ag nanowire stretch, μs - ms, Perez et al, 2010.

Recent brief review: Perez et al, Ann. Rep. Comp. Chem. **5**, 79 (2009).

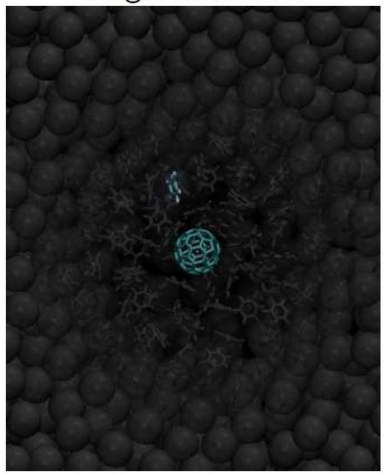
Hybrid atomistic/coarse-grained/continuum methods



Full simulation:



Single molecule:



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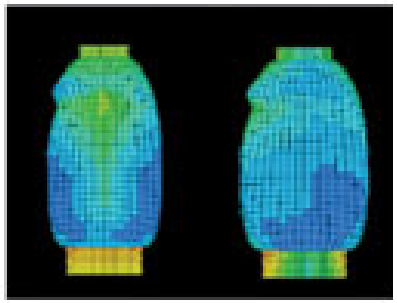
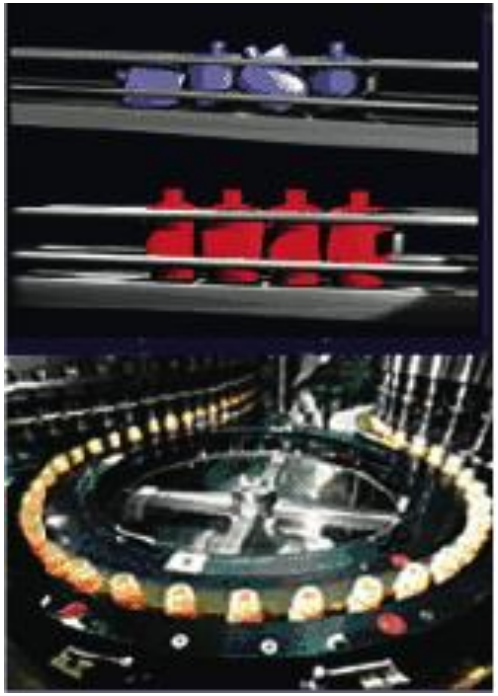
Capabilities for industrial process modeling

Capabilities:

- Breadth of materials modeling skills across all multiple length, time, and materials scales from atomistic to continuum
- State-of-the-art models and algorithms coupled with up to petascale computers
- Cross-disciplinary systems-level approach including strong coupling of experiment and theory
- Successes/Impacts
  - Enabled cost savings in the billion dollar range
  - Enabled waste reduction

PowerFactoRE, a suite of reliability engineering tools designed to optimize materials manufacturing processes.





Applications

- Predicting, reducing and preventing manufacturing equipment failures
- Improving product quality and increasing throughput
- Improving bottom-line results through higher reliability
- Reducing operating and capital expenses

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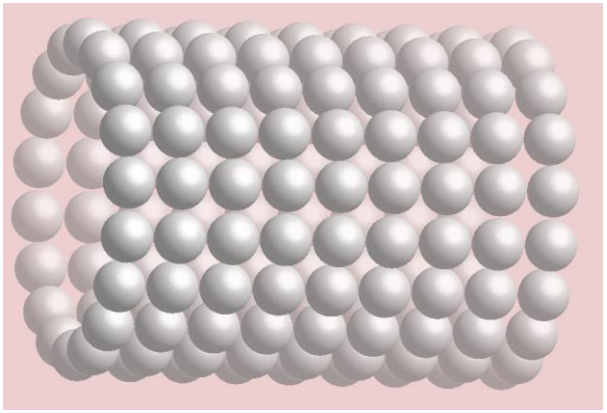
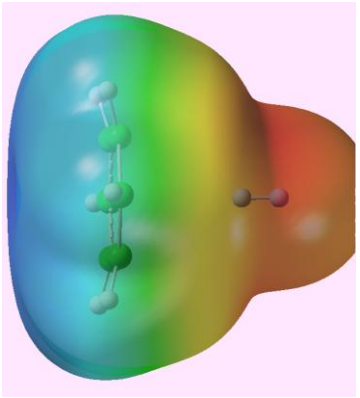
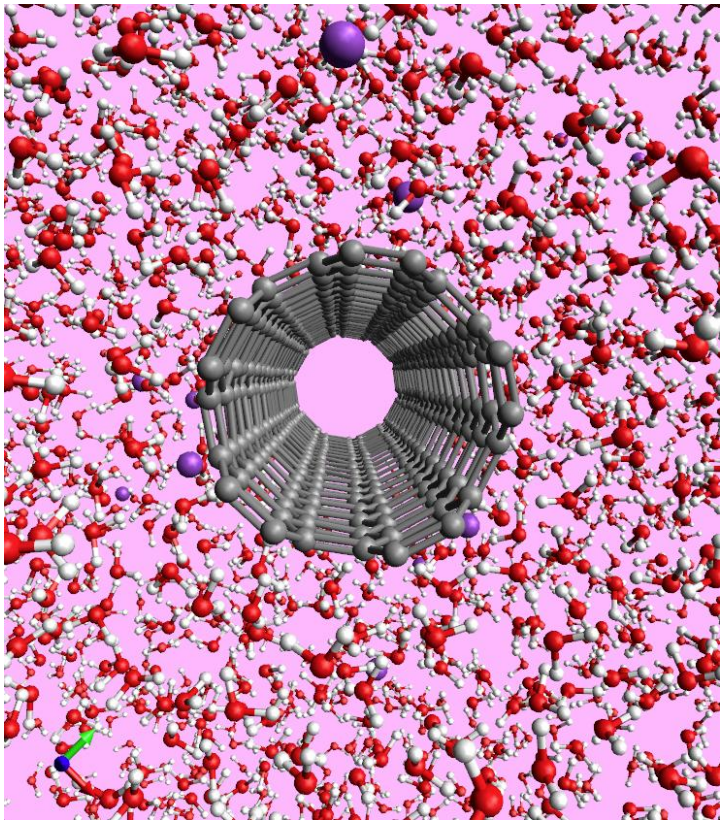
Electrical energy storage

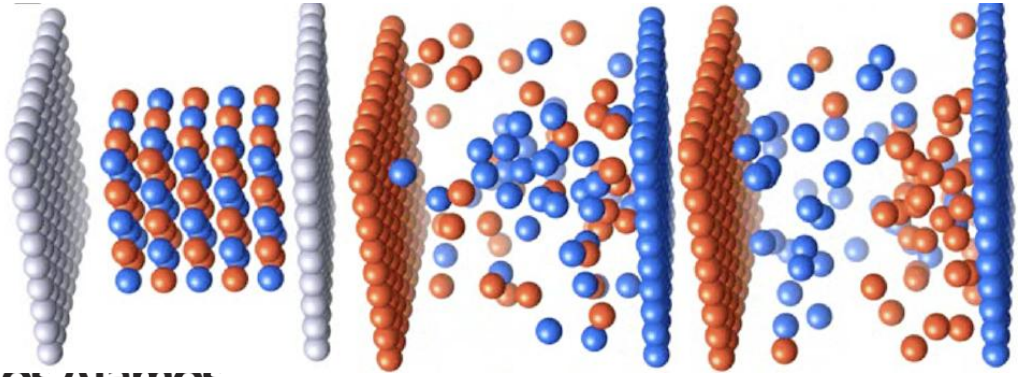




using the electric field gradient around nanoscale electrodes to initiate chemical transformations



simulating the formation of the electrical double layer in a supercapacitor



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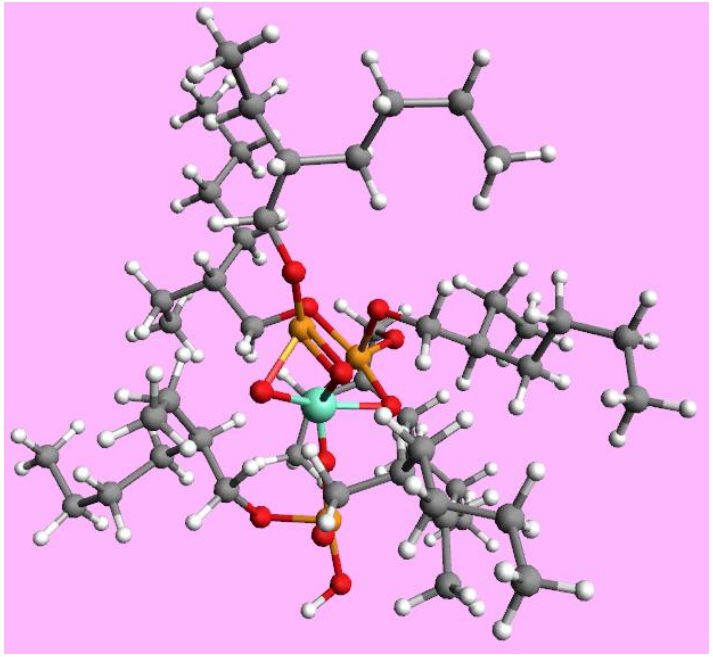
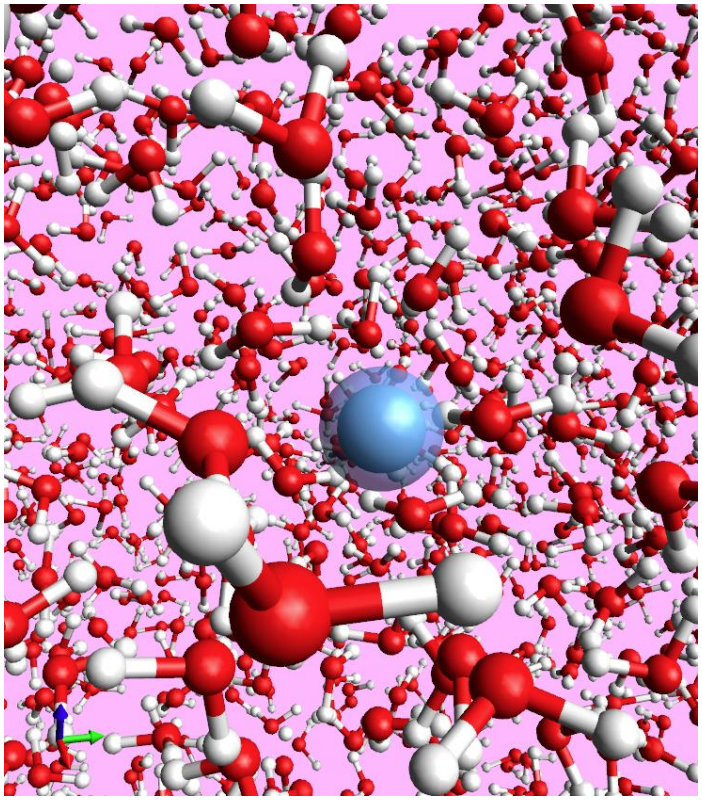
Lanthanide and actinide separations



accurate quantum chemical predictions of binding constants for new separation ligands

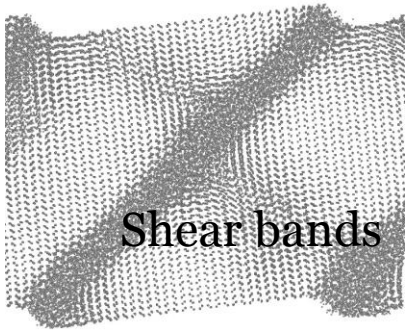


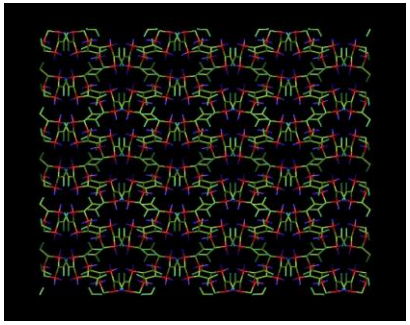
fitting new molecular mechanics forcefields for metal ion solution chemistry

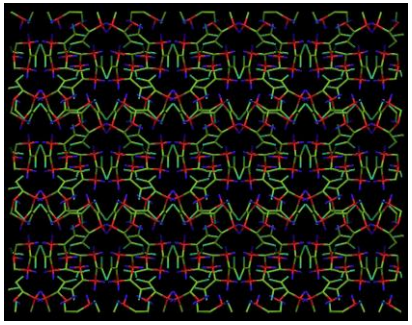
Static and dynamic deformation of organic crystals

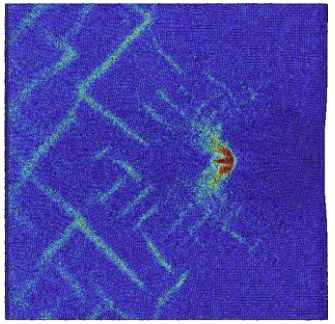
Large-scale MD simulations of the shock compression of oriented organic single crystals are now routine

Phase transformations

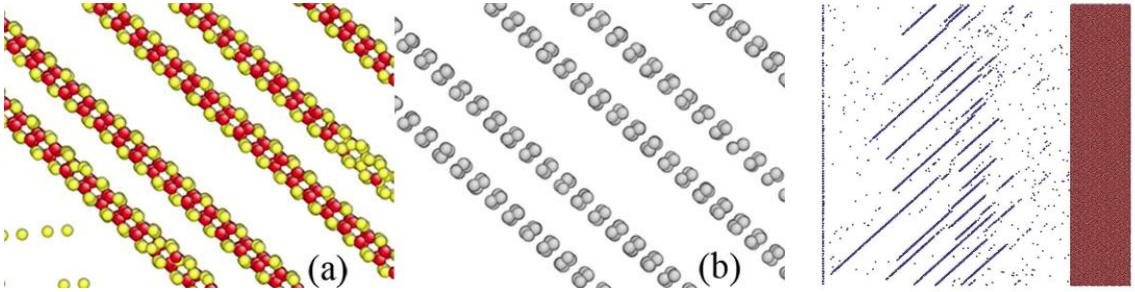


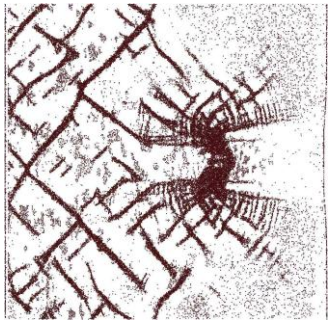






Void collapse





Homogeneous dislocation nucleation

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MaRIE builds on the LANSCE facility to provide unique experimental tools to develop predictive control of materials

First x-ray scattering capability at high energy and high repetition frequency with simultaneous charged particle dynamic imaging

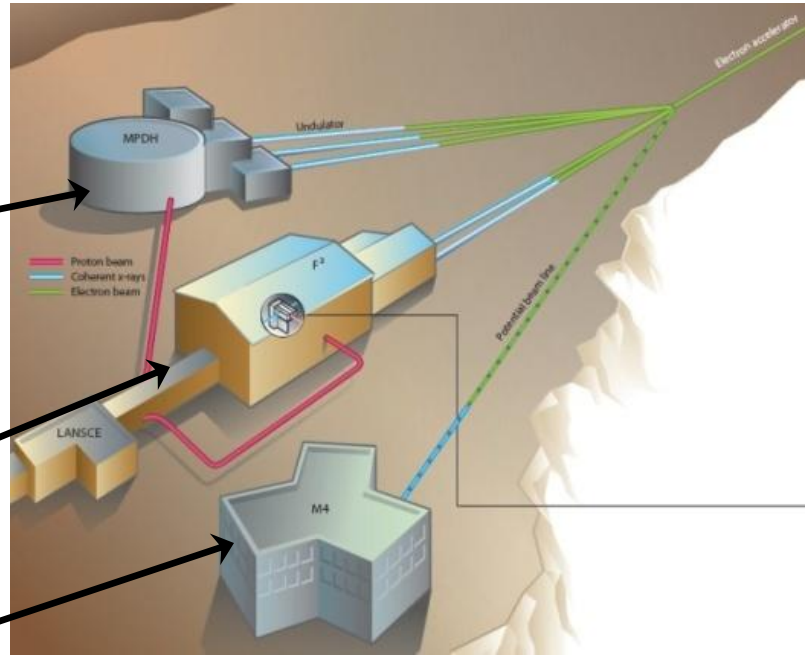
(**MPDH**: Multi-Probe Diagnostic Hall)

Unique in-situ diagnostics and irradiation environments beyond best planned facilities

(**F³**: Fission and Fusion Materials Facility)

Comprehensive, integrated resource for materials synthesis and control, with national security infrastructure

(**M4**: Making, Measuring & Modeling Materials Facility)



Unique very hard x-ray XFEL

Unique simultaneous photon-proton imaging measurements

Unique spallation neutron-based irradiation capability

Unique in-situ, transient radiation damage measurements

Unique materials design and discovery capability

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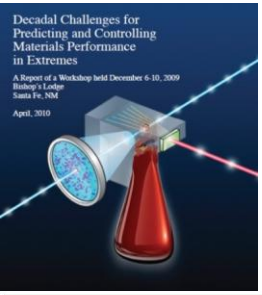
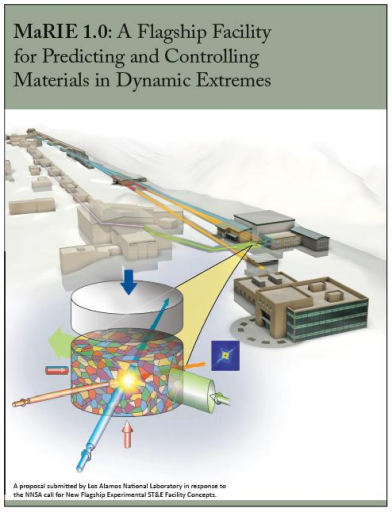
MaRIE will provide unprecedented international user resources

We have not yet achieved a predictive, process-aware understanding of materials performance

Materials research is on the brink of a new era – from observation of performance to control of properties

- **The confluence of unprecedented experimental capabilities (e.g. 4th generation light sources, controlled synthesis and characterization, …) and simulation advances are providing remarkable insights at length and time scales previously inaccessible**





New capabilities will be needed to realize this vision:

In situ, dynamic measurements

simultaneous scattering & imaging

of well-controlled and characterized materials

advanced synthesis and characterization

in extreme environments

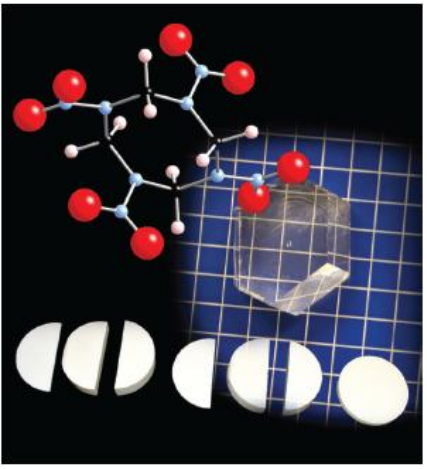
dynamic loading, irradiation

coupled with predictive modeling and simulation

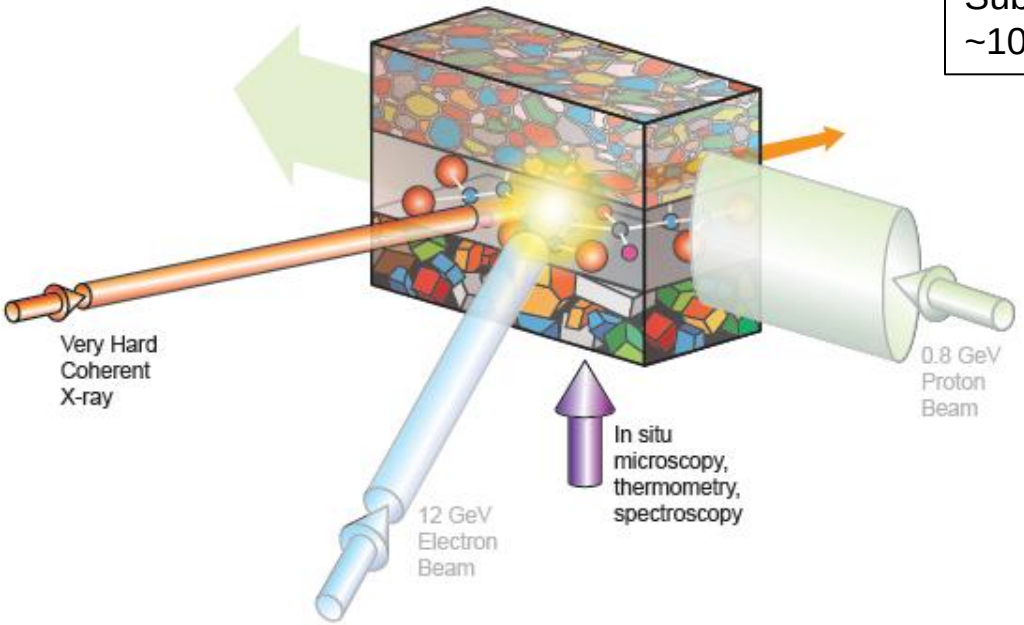
materials design & discovery

MaRIE is a key step towards this vision

The challenge is to quantify and ultimately control key mesoscale features during the dynamic conditions of materials synthesis from crystallization through component manufacture



The goal
Design of energetic materials with specific function

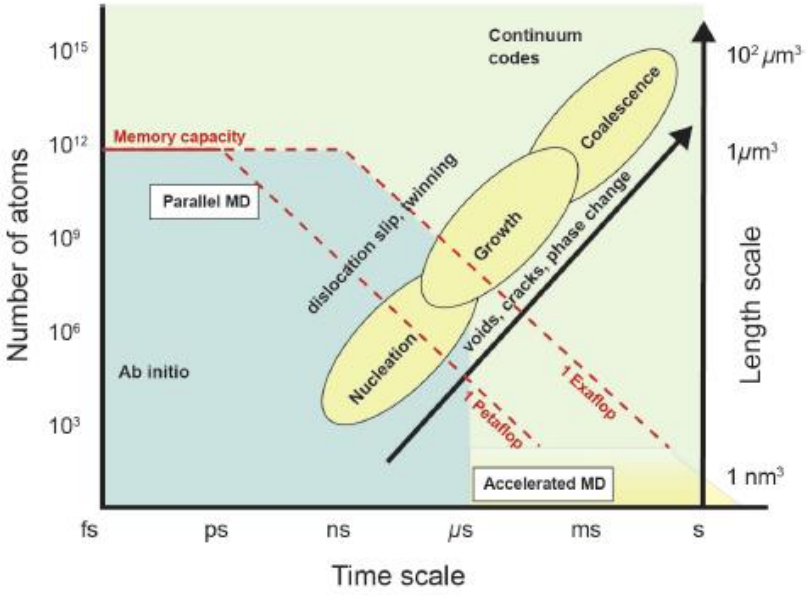


Sub-μm resolution
100's – 1000's μm samples
Sub-ns resolution,
~100 fs spectroscopy

The first experiment : Multi-probe, real-time characterization of HE fabrication "from molecules to microstructure," including dynamic response

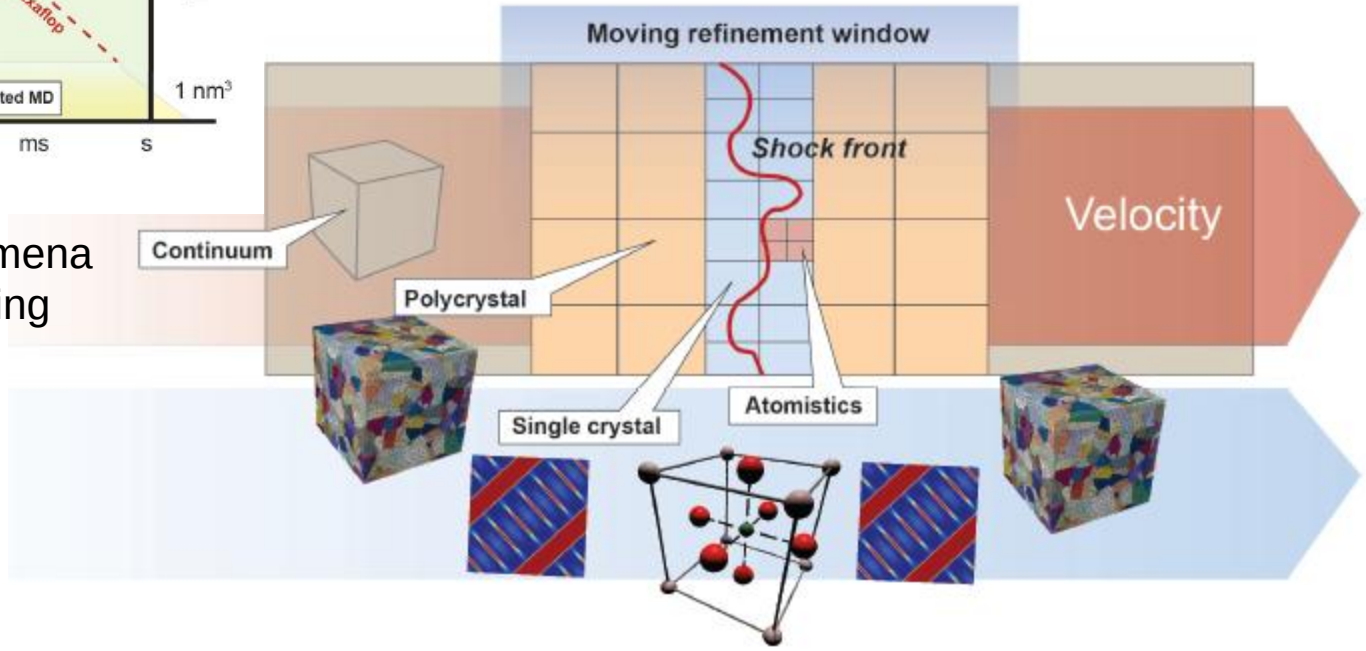
The model : Prediction of heterogeneity-induced dynamic response of explosives

MaRIE 1.0 with LANL's integrated co-design approach will couple multi-scale theory and multi-probe experiment on next-generation computing architectures



Mesoscale materials phenomena need extreme-scale computing

Variable-resolution models are synergistic with multi-probe, in-situ, transient measurements



Example from catalysis: ethylene epoxidation

- Highly selective oxidation of olefins to epoxides on Ag surfaces:
  - Commercial process
- Promoters are very important:
  - Cs
  - Cl
- Will discuss results of theoretical calculations on:
  - O and O_2 adsorption on Ag(111) surface with and without Cs
  - Oxymetallocycles on Ag(111)
- Collaboration with Eastman Chemical Company

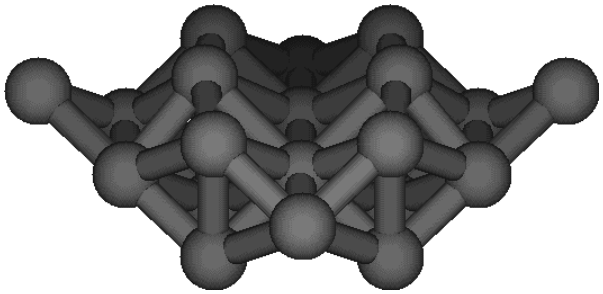
Objectives

- Qualitative and quantitative models for various species on silver surfaces
- Develop theories to explain experimental results
- Use these models and theories to generate concepts for experiments
- Predict effect of modifications to catalysts and reactants

Understand and improve olefin epoxidation catalysis

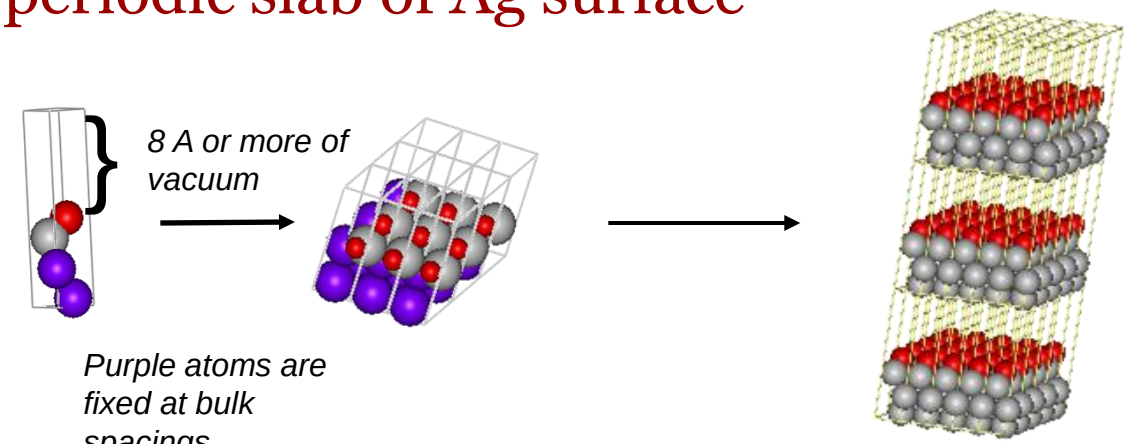
Theoretical techniques

- Cluster calculations
  - (111) Surface
    - Ag_n n = 9, 10, 13, 15, 23
  - (110) Surface
    - Ag_n n = 10, 22



Ag_{22} (110)

- Slab models (will not discuss this here)
  - Infinite, periodic slab of Ag surface



Purple atoms are fixed at bulk spacings

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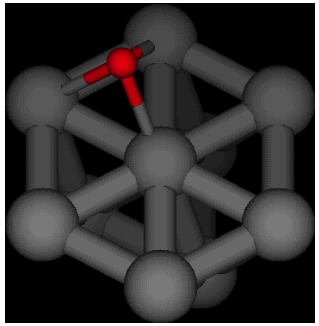
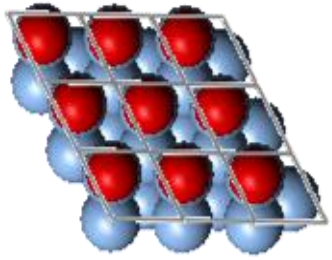
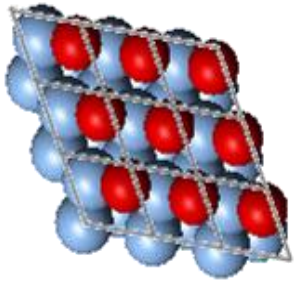
Ag (111) binding sites



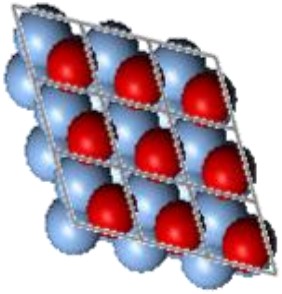
3-fold hollow



atop



2-fold or bridge



3-fold

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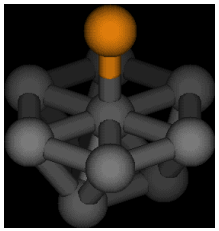
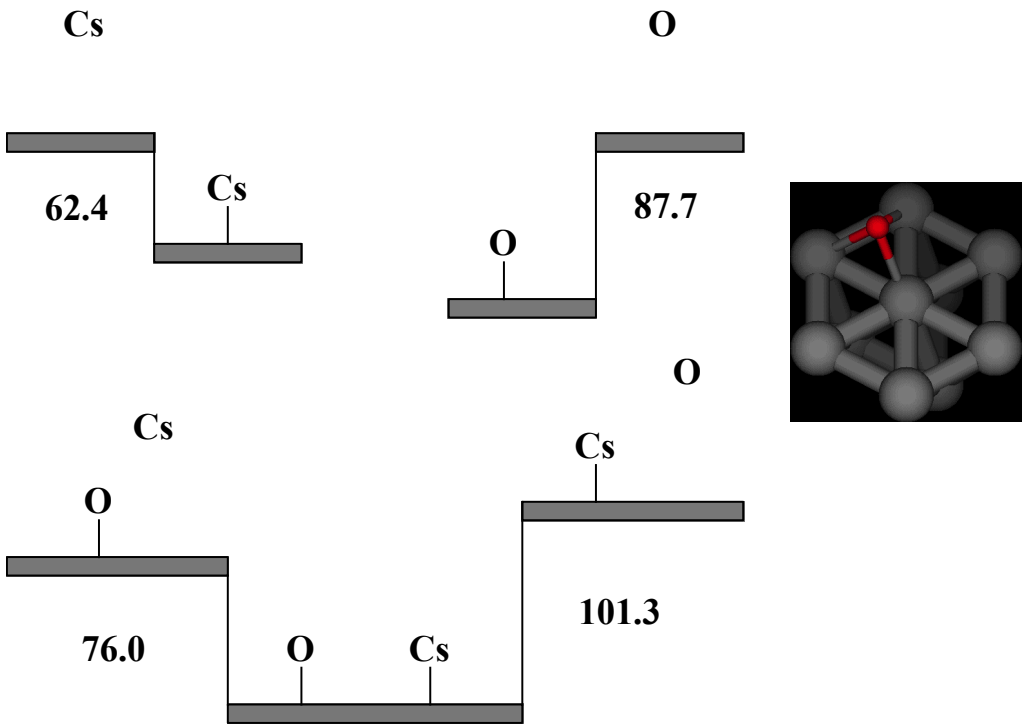
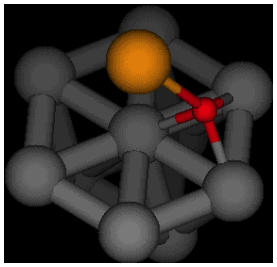
Cs - O interactions - Ag(111)

Ag_{10} cluster, Cs-atop, O-3-fold-hollow







Combined effect leads to stronger adsorption than O and Cs separately.

Energies in kcal/mol

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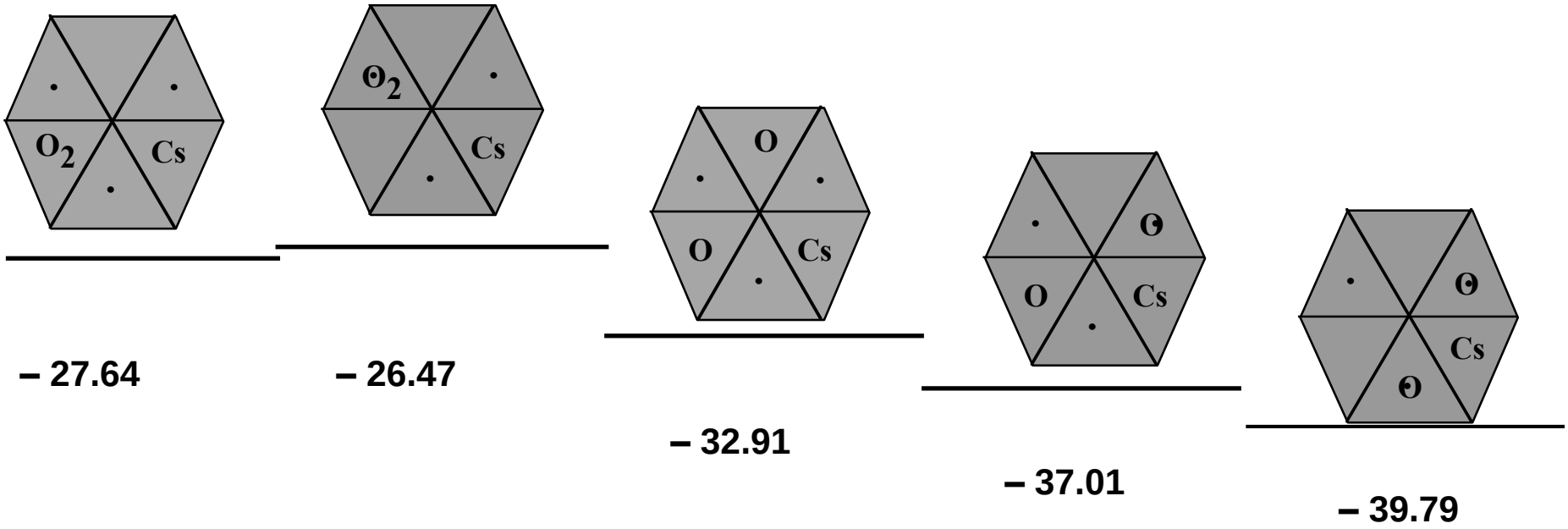
O_2/Cs interactions on Ag (111)

Ag_{10}/ Cs (3-fold-hollow)/O_2



- O_2 dissociation favored for all combinations
  - This is true if the Cs is on any of the other binding sites

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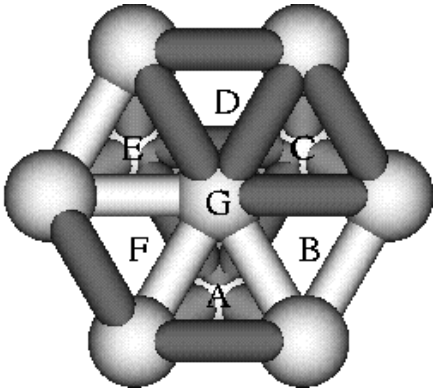
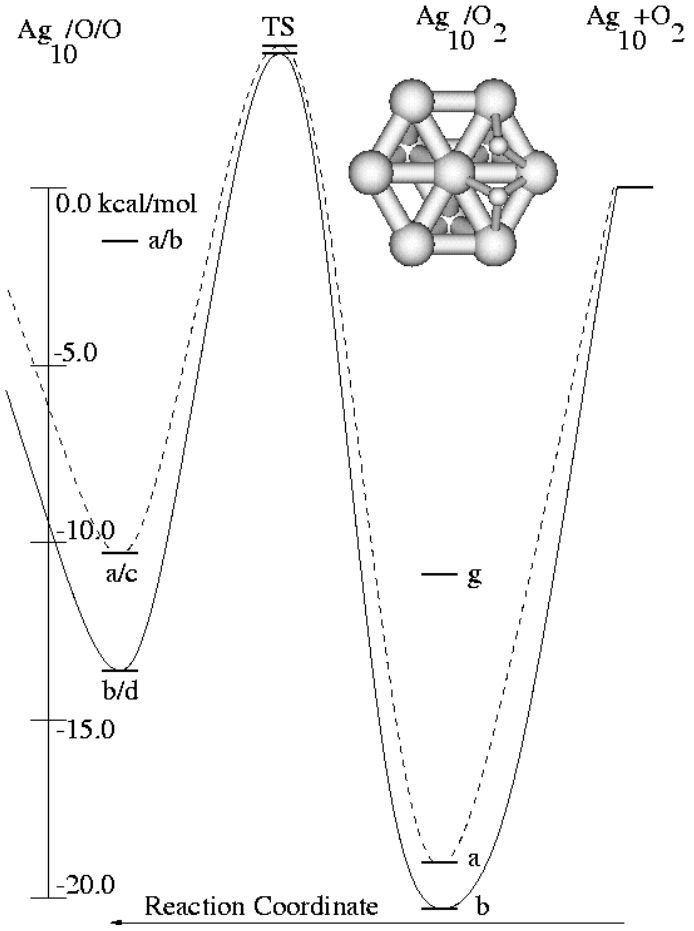
Dissociation of O_2 on unpromoted Ag_{10} cluster

- O_2 molecule more stable than dissociated atoms on unpromoted surface
- Barrier ~ 25 kcal/mol





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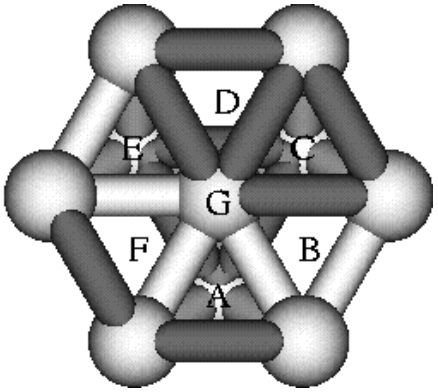
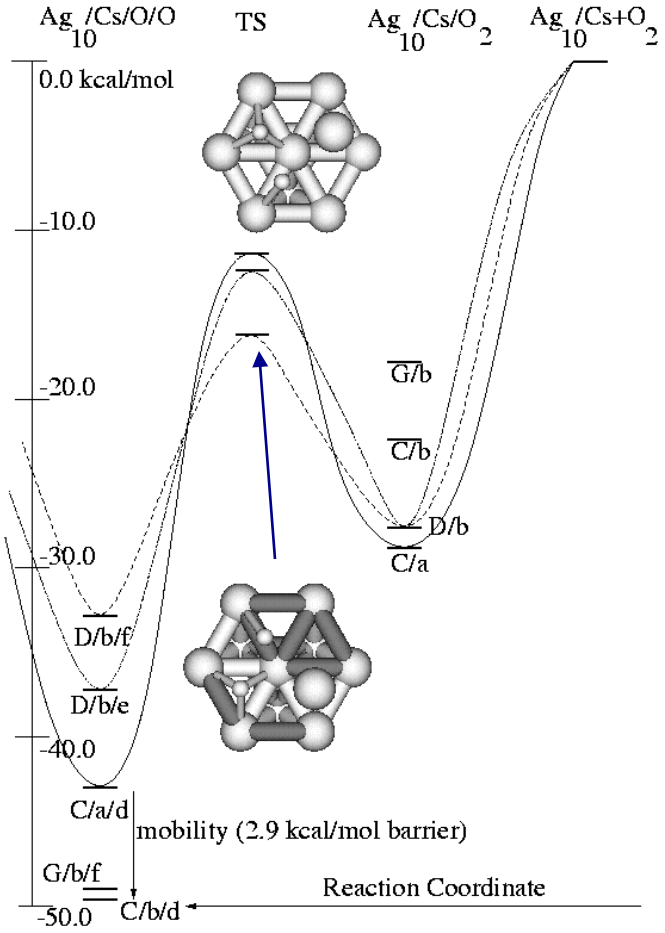
Dissociation of O_2 on promoted Ag_{10} cluster
(with single Cs atom)

- Dissociated atoms are more stable than O_2 molecule
- Barrier ~ 17 kcal/mol but desorbed O_2 is ~ 12 kcal/mol above transition state





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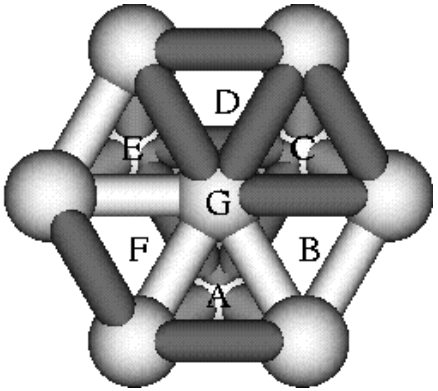
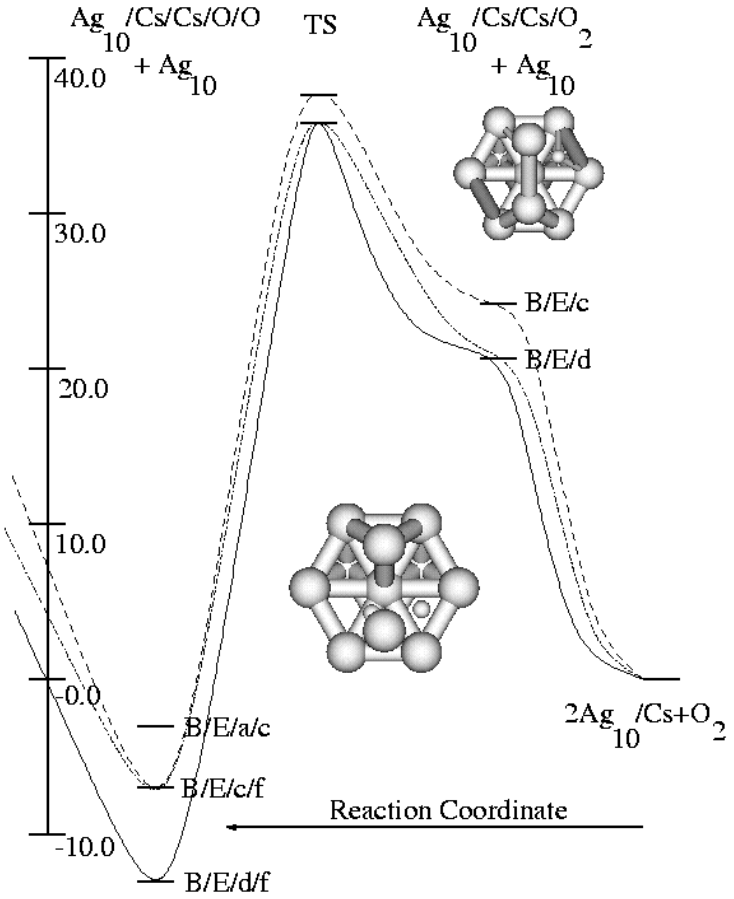
Dissociation of O_2 on promoted Ag_{10} cluster
(with two Cs atoms)

- Dissociated atoms are more stable than O_2 molecule
- Barrier ~ 40 kcal/mol from desorbed





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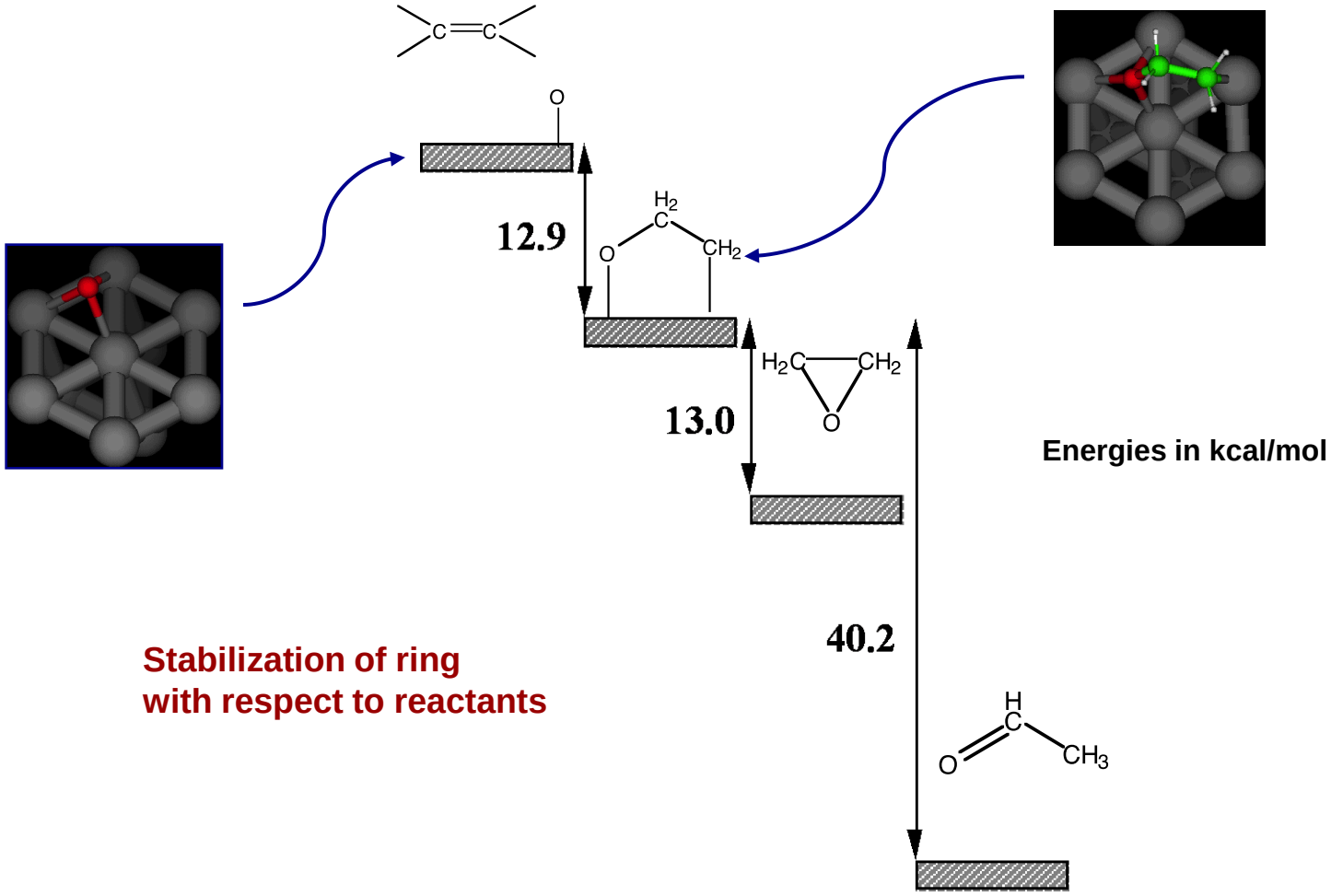
Oxymetallocycle Thermochemistry
Unpromoted – Ethylene on Ag(111)



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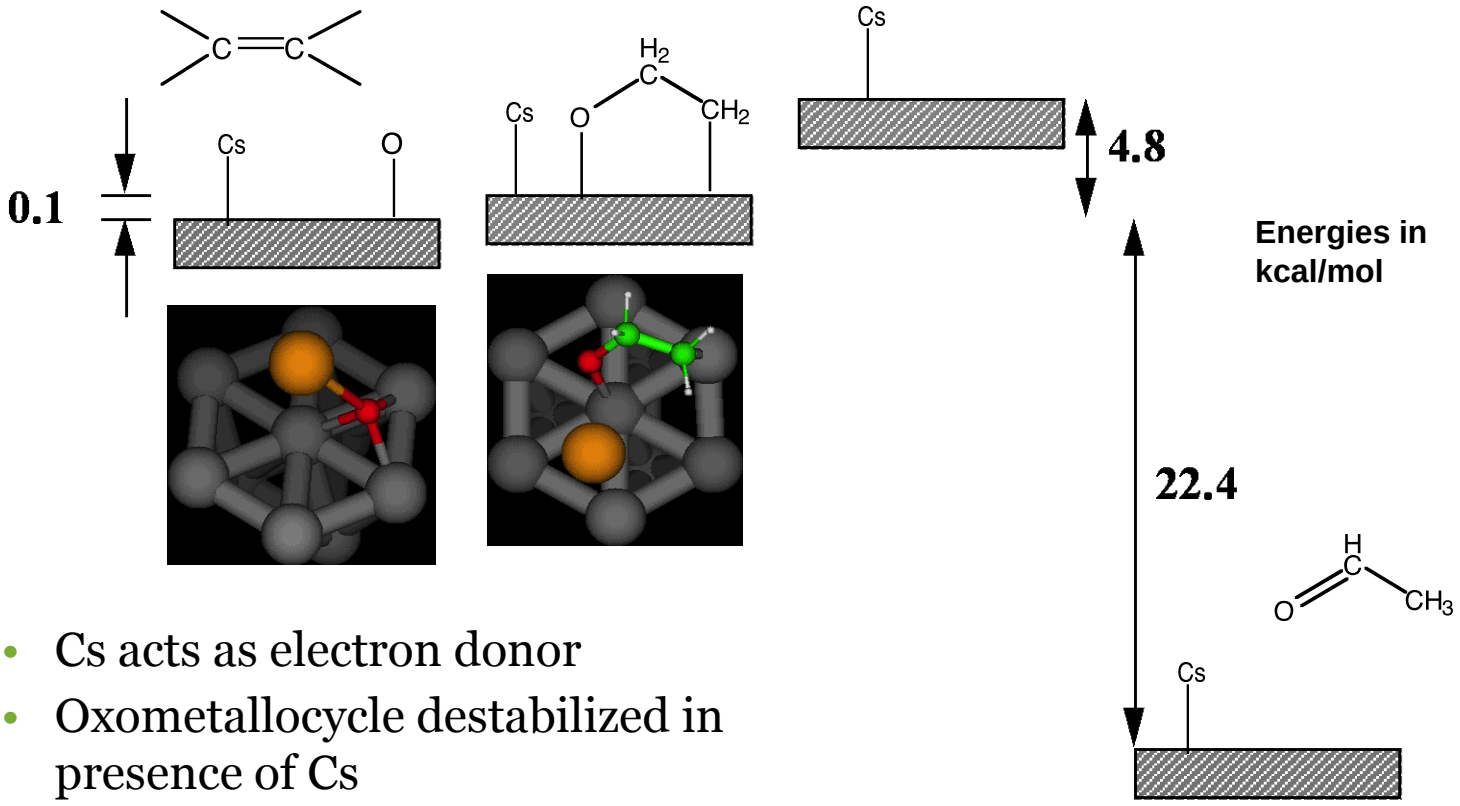
Oxymetallocycle Thermochemistry

Promoted: Cs – Ethylene on Ag(111)



- Cs acts as electron donor
- Oxometallocycle destabilized in presence of Cs
- Carbon atoms move away from Cs

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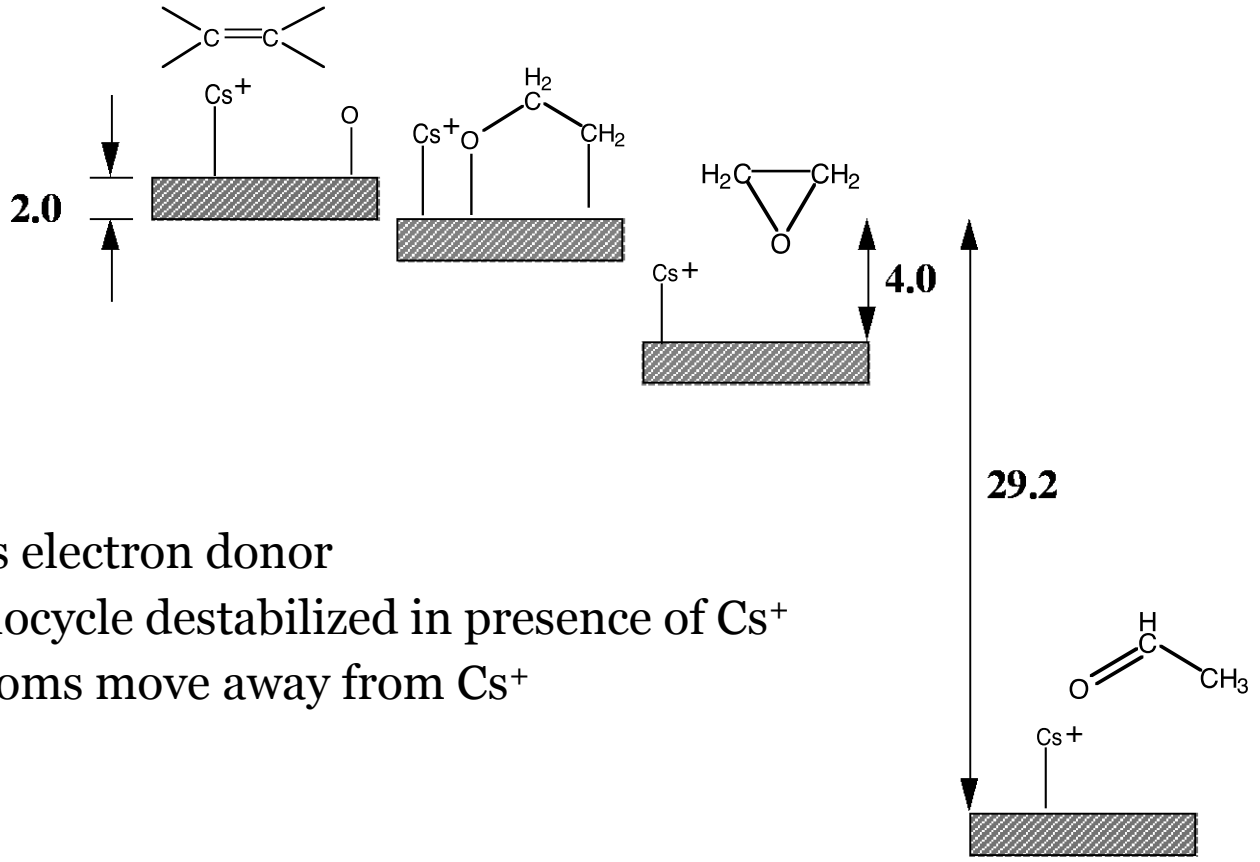
Oxymetallocycle Thermochemistry

Promoted: Cs^+ - Ethylene on Ag(111)



- Cs^+ acts as electron donor
- Oxymetallocycle destabilized in presence of Cs^+
- Carbon atoms move away from Cs^+

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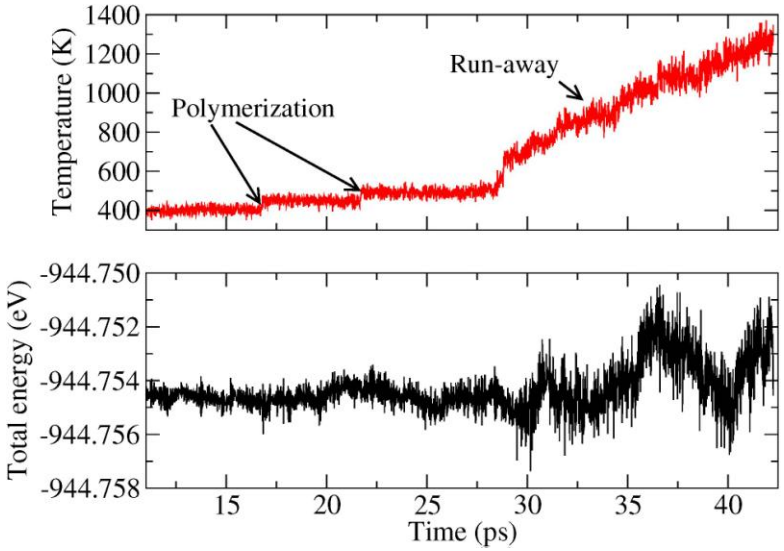
Dynamics and kinetics

- LATTE – large-scale semi-empirical quantum molecular dynamics package

- LATTE is an open-source quantum molecular dynamics code developed in the Theoretical Division at Los Alamos
  - Based on the self-consistent tight binding approximation to density functional theory (a.k.a. density functional tight-binding)
  - Captures the making and breaking of covalent bonds, charge transfer, electrostatics, spin polarization, and van der Waals bonding
  - An accurate parameterization for C, H, N, and O-containing molecules has been developed that yields extremely accurate *predictions* for the gas- and condensed phase structures, heats of formation, vibrational properties, and densities of a huge range of organic molecules (including energetic materials)
  - Other atom parameterizations are being developed

LATTE – microcanonical trajectories with precise energy conservation

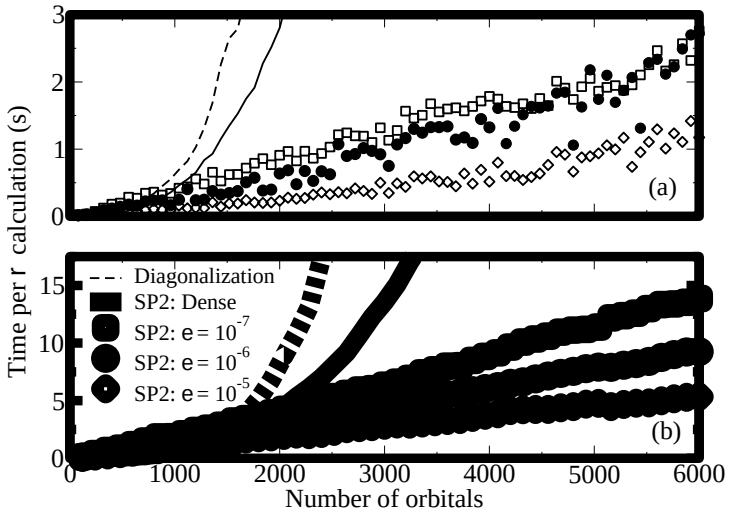


Conservation of the total energy during the exothermic radial chain polymerization of liquid ethylene

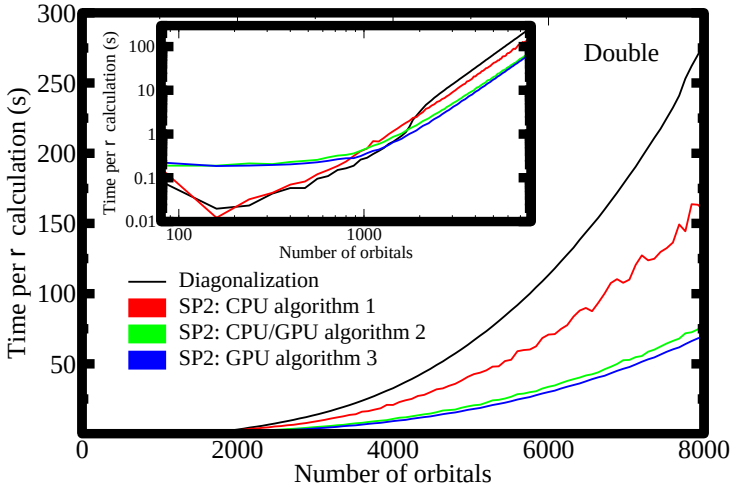
- Many first principles and empirical force fields exhibit poor energy conservation during ‘NVE’ molecular dynamics simulations
- The LANL-invented extended Lagrangian Born-Oppenheimer molecular dynamics formalism enables LATTE to compute NVE trajectories with no systematic drift in the total energy
- These accurate underlying dynamics provide unique capabilities for the computation of accurate vibrational spectra, exothermicity during reactions, heating during dynamic loading etc
- NVE, NVT, NPT, and shock compression simulation tools are standard

LATTE – large-scale, long duration simulations via novel algorithms and advanced architectures

O(N) vs. standard $O(N^3)$ scaling in LATTE



GPUs enable speed-ups compared with even heavily optimized CPU code



- LATTE employs novel algorithms for the computation of the density matrix that enable large-scale calculations
- Sparse matrix methods overcome the $O(N^3)$ bottleneck faced by most quantum-based codes
- LATTE maintains precise energy conservation even in the O(N) limit
- Many of LATTE's most intensive subroutines have been ported to and optimized for Nvidia GPUs
- Work underway on parallel sparse matrix methods and parallel execution on multiple GPUs

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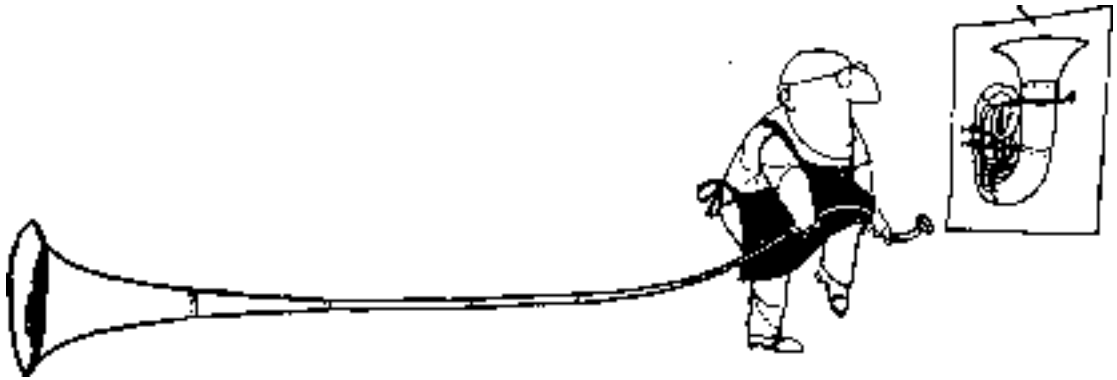
Conclusion

- Theory, modeling and simulation are tools to solve problems just like an NMR spectrometer, a gas chromatograph or an electron microscope.
- Problems should be used to define the theoretical tools needed and not the other way around.
- Best results occur when theory and experiments are working together in a team.



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