NANOENERGETICS AND HIGH HYDROGEN CONTENT MATERIALS FOR SPACE PROPULSION

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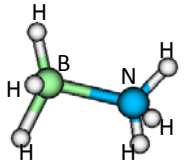
Accomplishments

- Thermochemical behavior of Ni-coated Al particles
- Particle size effects on melting, diffusion, and reactions
- Pyrophoricity of nano-aluminum particles
- Micron Al with nanoscale inclusions of fluorocarbons
- Encapsulation of nanoscale particles in AP
- Thermal decomposition and high temperature oxidation studies of ammonia borane (NH_3BH_3) as an energetic fuel/additive
- High speed OH PLIF analysis of ammonium perchlorate combustion at high pressures
- Investigation of solid oxidizer and gaseous fuel combustion performance using counterflow burner and reverse hybrid motor

Ammonia Borane (NH_3BH_3) as a Energetic Fuel/Additive

Why study ammonia borane (AB)?



- 20% hydrogen by mass – hydrogen leads to decreased MW of combustion products → increased I_{sp}.
- High energy boron is available for oxidation.
- Solid at room temp → high density hydrogen storage; other liquid fuels also of interest – methyl AB.
- Unlike old borane fuels (B_2H_6, B_5H_9), AB is not toxic or pyrophoric.

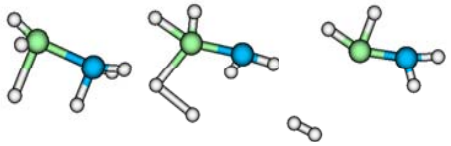
Lab scale hybrid motor tests performed.

- AB added to hybrid fuel (paraffin).
- $I_{sp,exp}$ increased ~10% with 20% mass addition.
- Significant AB addition led to condensed phase product accumulation on fuel grain.
- Fundamental studies performed to understand chemistry of AB combustion.

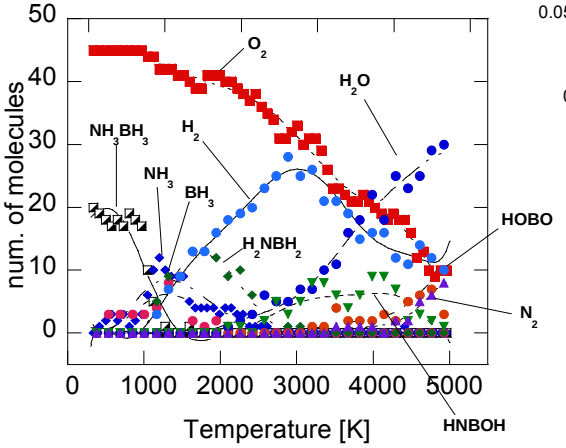
Accomplishments (in collaboration with Stefan Thynell and Adri van Duin at PSU).

- Kinetic experiments performed to determine AB decomposition products.
- Molecular dynamics simulations performed with ReaxFF reactive force field to gain atomistic understanding of AB decomposition, polymerization, and oxidation reactions.
- Intermediate species identified, and thermo-chemical properties calculated using density functional theory.
- First high temperature kinetic mechanism for AB oxidation developed.

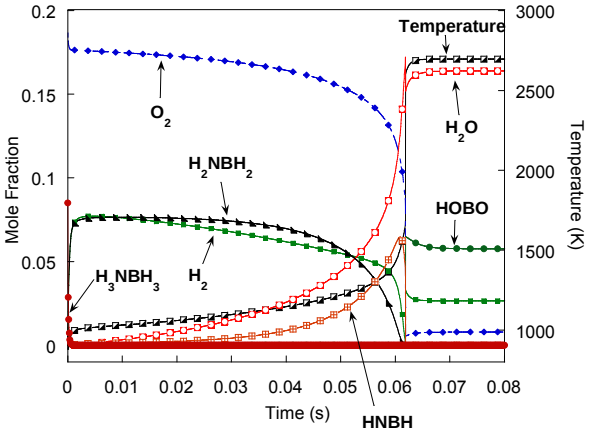
Hydrogen elimination

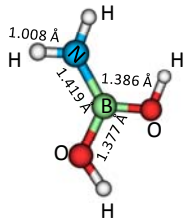


MD Temperature Ramp Simulation

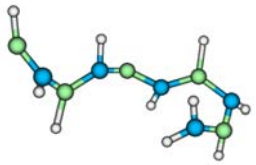


Constant Pressure Kinetics Calculation





$H_2NB(OH)_2$



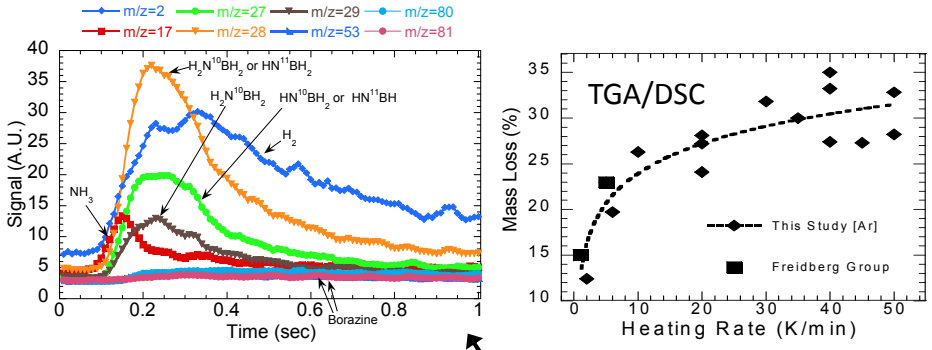
BNH polymer

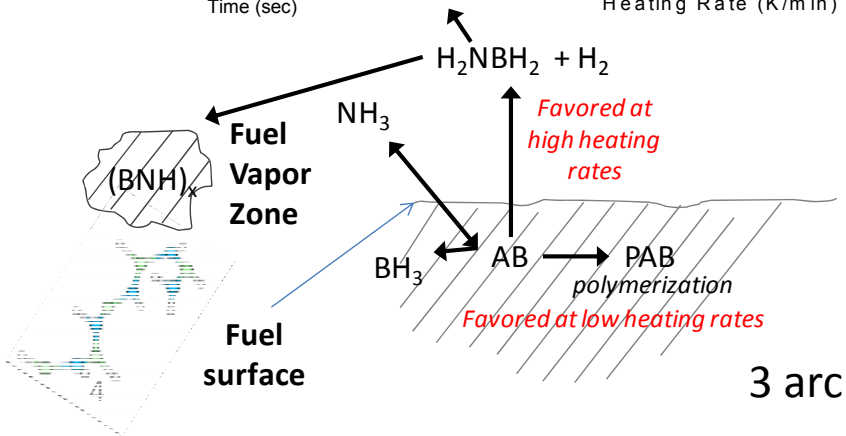
Ammonia Borane Decomposition and Oxidation

(collaboration with Stefan Thynell and Adri van Duin at PSU)

Confined Rapid Thermolysis of Ammonia Borane with TOF-MS and gas/solid phase FTIR

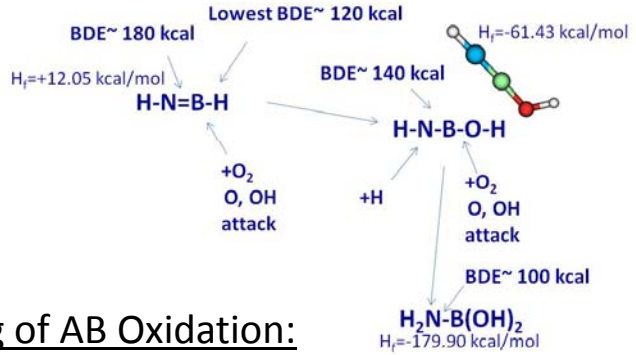
- TGA/DSC studies show with increased external heating rates→ increased gaseous H_2NBH_2 and decreased polymerization
- ToF-MS and gas phase FTIR analysis of rapid thermolysis products show NH_3, followed by H_2 and H_2NBH_2
- Solid phase FTIR of residue shows that H_2NBH_2 will readily condense and polymerize on cool surfaces
- Borazine [c-($N_3B_3H_6$)] produced at later times, as polymers decompose





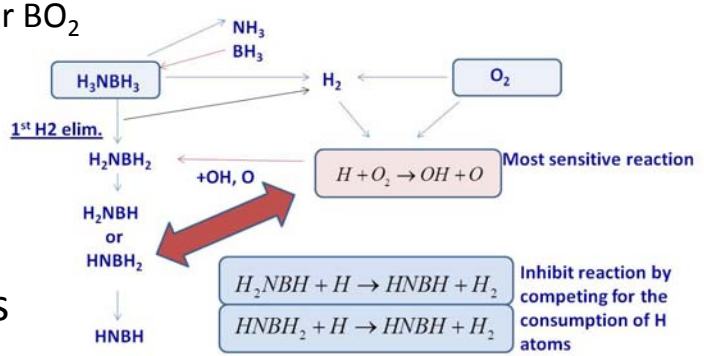
MD Simulations :

- ReaxFF force field developed for B/N/H/O
- Simulations show hydrogen elimination from AB, then H_2 reacting with O_2
- Oxygen attack of boron in HNBH and subsequently HNBOH leads to large oxidized compounds with weak B-N bonding.



Kinetic Modeling of AB Oxidation:

- Constant pressure/energy simulations (P=1 atm, T_0=1000 K) show after the first H_2 elim, H_2NBH_2 is dehydrogenation through H abstraction by radicals (OH)
- BNH oxidized to form HNBO, oxidation of HNBO molecule results in the breaking of B-N bond; formation of HOBO or BO_2



3 archival publications

Investigation of Solid Oxidizer and Gaseous Fuel Combustion Performance Using Counterflow Burner and Reverse Hybrid Motor

Objectives:

Investigate feasibility and characterization of reverse hybrid motor using AP with gaseous fuels as a reference system.

Approach:

Conduct pressurized counterflow experiments and lab-scale static rocket motor firings.

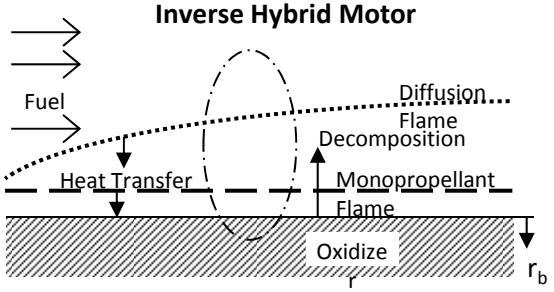
Results:

- Three burning regimes observed as a function of pressure ranging from diffusion flame control at low pressure to monopropellant flame control at high pressures. These findings represent infinite AP particle diameter behavior of a composite propellant.
- Linear burning rate has slight dependence on flame strain rate at low pressures and is independent of strain rate at high pressures.
- Reverse hybrid motors require high pressure operation to produce significant thrust.

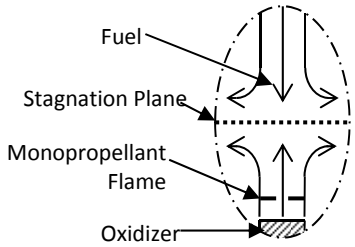
Examples of Theoretical Performance

	HTPB/LOX	C_2H_4/AP	HTPB/AP
$V_{fuel,i}/V_{HTPB}$	1	0.517	0.299
$V_{ox,i}/V_{LOX}$	1	0.784	0.789
T_c [K] [13]	3576	3077	3032
I_{sp} [s] [13]	294.3	256.7	252.1
ρI_{sp} [kg-s/m^3]	312386	397570	442152

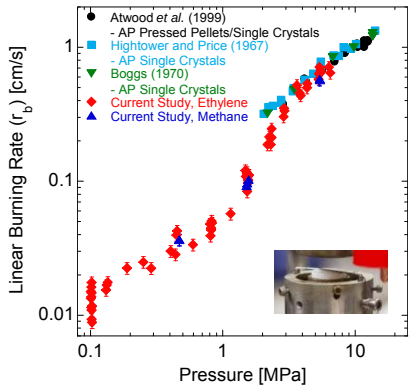
Inverse Hybrid Motor

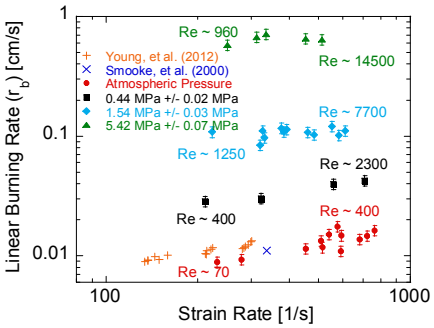


Simplified 1-D Analysis

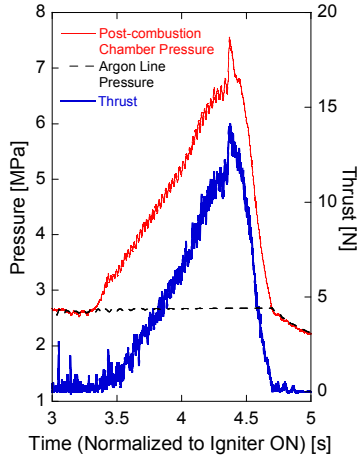


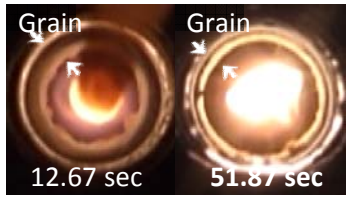
Variable Pressure Opposed Flow Experiments
AP-Ethylene and AP-Methane





Reverse Hybrid Motor Experiments

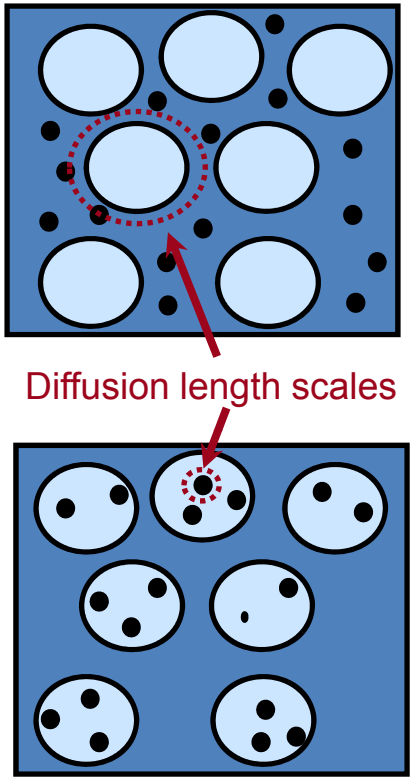




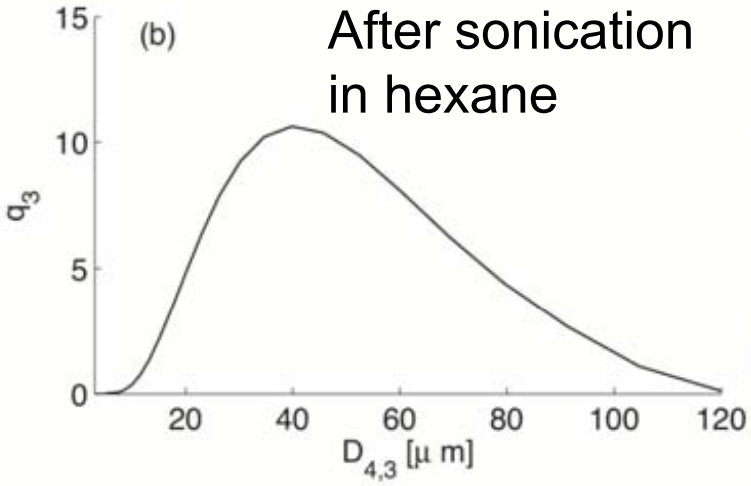
1 archival publication

Encapsulation of Nanoscale Particles in AP

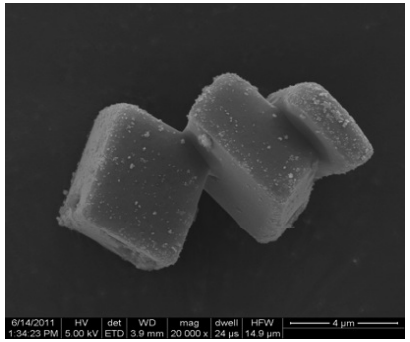
- Replacing nanoscale particles for micron powders results in rheology and mechanical issues
- If nanoscale particles are captured (encapsulated) WITHIN micron scale crystalline ingredients formulation issues could be avoided
  - More intimate & uniform mixing could improve catalytic and combustion rate
  - Dramatic decrease of diffusion scale
- 90% capture and ~5x decrease in surface area with addition of nanoscale catalysts!
  - Particle morphology improved



Collaboration with Prof. L. J. Groven



After sonication in hexane

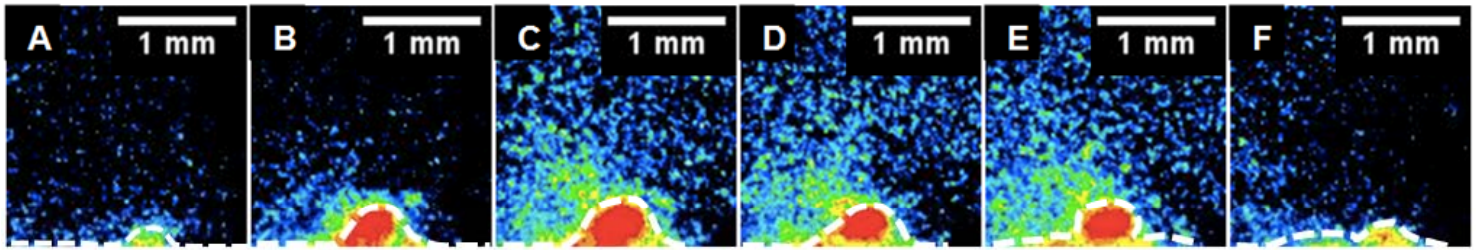


Paper submitted to PEP, 2012

High speed OH PLIF reveals that coarse ammonium perchlorate burns much faster at high pressures

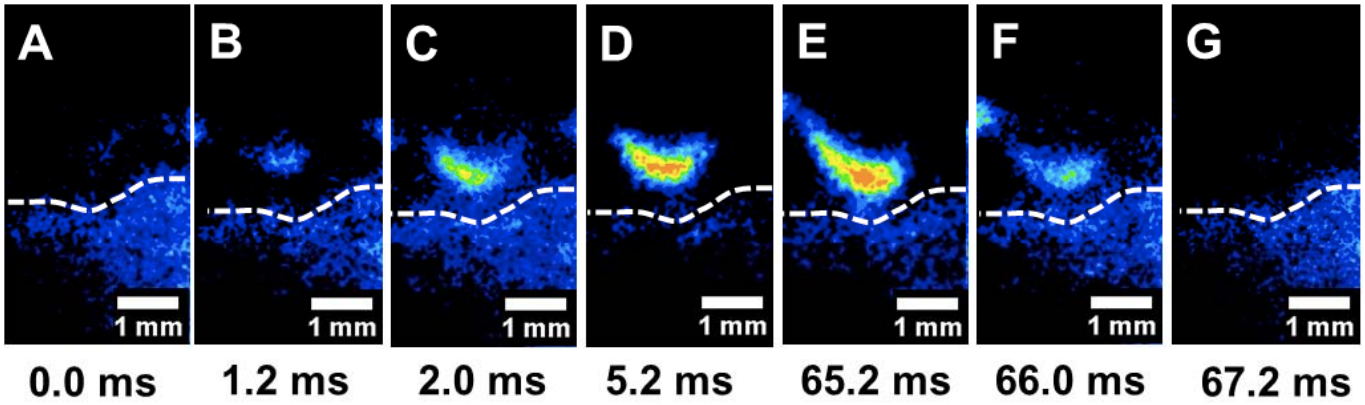
- The diffusion flame structure changes from a jet-like to a lifted sheet-like diffusion flame as pressure is increased because of the relatively high local burning rate of the coarse AP

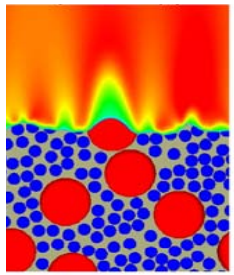
1 atm: Fluorescing coarse AP crystal is shown in red. Dashed line is the surface



Collaboration with Prof. L. J. Groven & R. Lucht

6 Atm: The relatively fast burning crystal cannot be seen because it is below the surface.





State-of-the-Art 3-D simulation at high pressure (6 atm)

•High speed OH PLIF also reveals that: Coarse AP is not affected by catalyst (Fe_2O_3 and CuO) addition. New flame structure quantified and flaws in modeling identified.

Three archival papers papers published, 2 in preparation

Tailored nano-scale features can affect meso-scale behavior: Micron Al with nanoscale inclusions of fluorocarbons

- Fluorinated graphite encapsulated inside aluminum at nanoscales can provide increased combustion efficiency, reduced ignition temperature and agglomeration

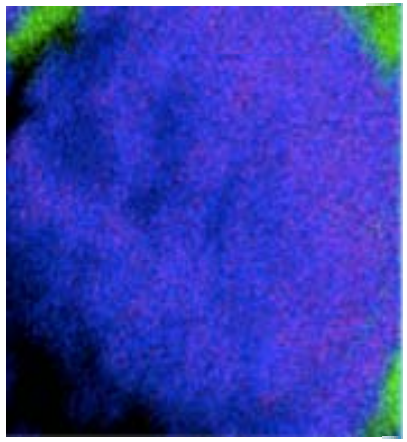
Al + polycarbon monofluoride Powder Mixture

Mechanical Activation

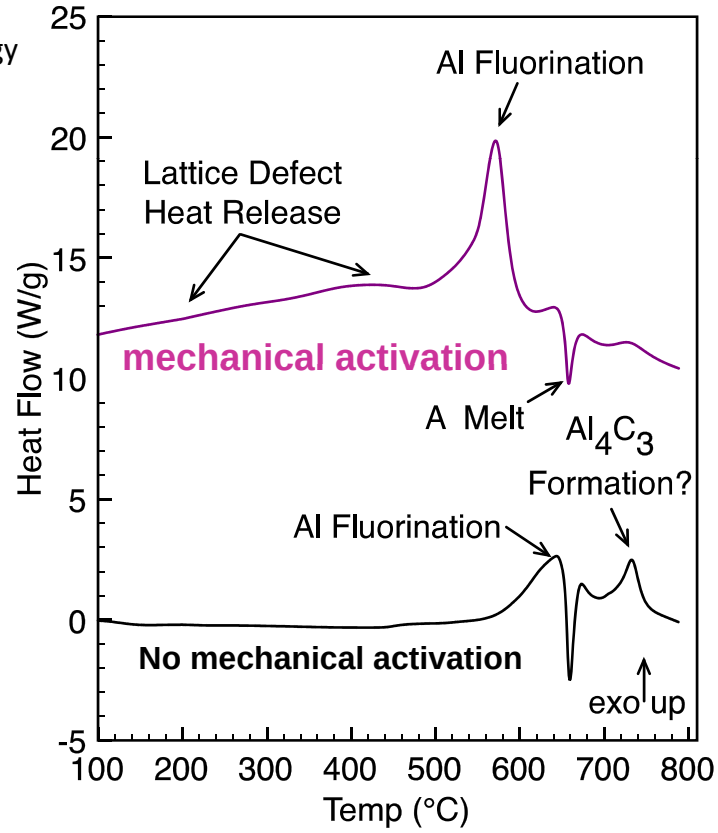
Uniform composition and induced lattice defects (stored energy)

SEM/EDX (Scanning Electron Microscopy/Energy DIspersive X-ray Spectroscopy)
Activated energetic particles

Aluminum=blue, Fluorine=red
Carbon=green



DSC analysis of Al + polycarbon monofluoride



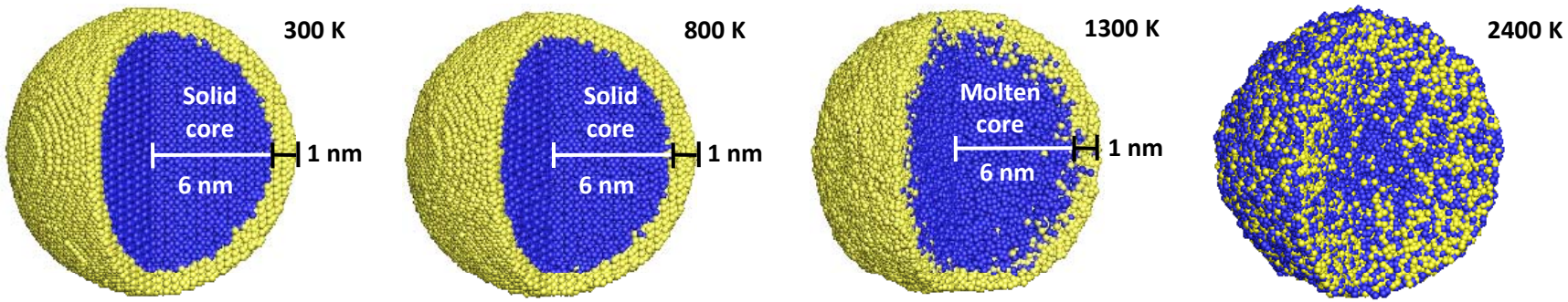
Collaboration with Prof. L. J. Groven

Thermochemical Behavior of Ni-Coated Al Particles

- Beneficial to replace aluminum oxide (Al_2O_3) layer on aluminum (Al) particle with nickel (Ni) coating
  - Ni can react with aluminum and oxygen, while the aluminum oxide layer is an inert substance
    - Ni + Al$\rightarrow$ NiAl, $\Delta H = -4.38$ kJ/g (Inter-metallic reactions)
    - Ni + 1.5 $O_2\rightarrow$ NiO, $\Delta H = -3.27$ kJ/g (Oxidizing reactions)
  - Ni-coated Al particles (d = 2 mm) ignite at 1300 K, while oxide coated particles ignite at 2350 K in air*
  - Nano-Al particles ignite at 933 K; oxide content greater at nano-scale (47.5 wt. % oxide at d = 38 nm)
  - Nickel coated nano-aluminum particles are promising candidates for next-generation energetic materials

MD simulations performed to analyze thermochemical behavior of Ni-coated Al particles

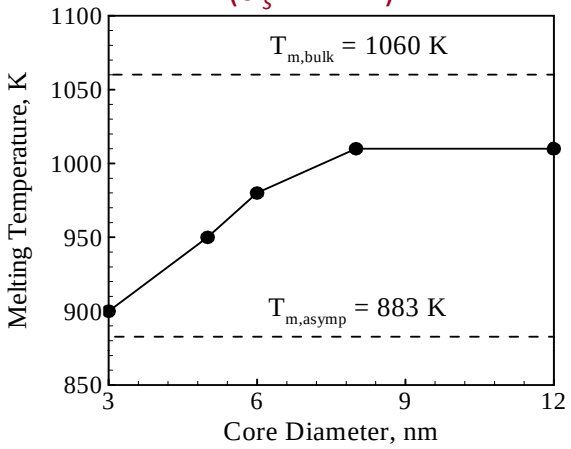
Snapshots of 14 nm particle (d_c = 12 nm, δ_s = 1 nm)



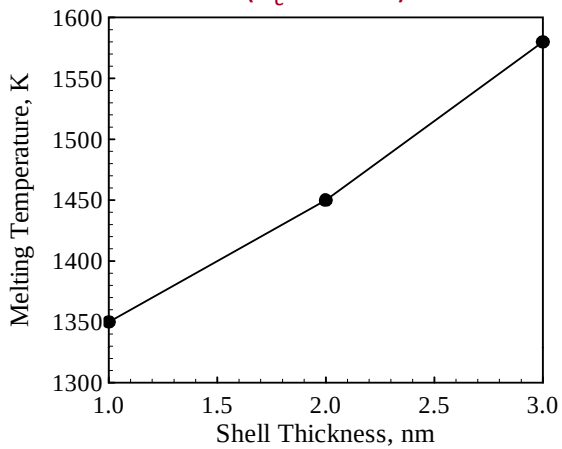
- The core melts at 1010 K and loses its crystal structure as seen by the random distribution of melted atoms
- The Al atoms begins to diffuse out into the shell, initiating the Ni-Al inter-metallic reactions at interface
- The shell melts at a temperature of 1200 K, which is lower than the bulk melting of Ni, 1728 K
- Melting of the shell is followed by sudden increase in the diffusion rate of core and shell atoms
- Inter-metallic reactions transform core-shell structure into homogenous alloyed (NiAl) particle by 2400 K

Particle Size Effect on Melting, Diffusion, and Reactions

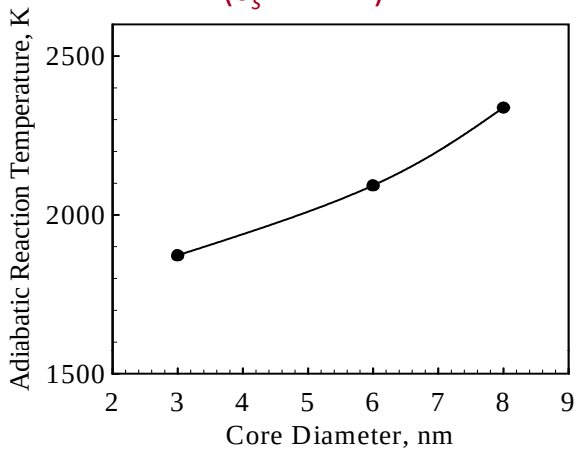
Core melting point vs. core diameter (δ_s = 1 nm)



Shell melting point vs. shell thickness (d_c = 3 nm)

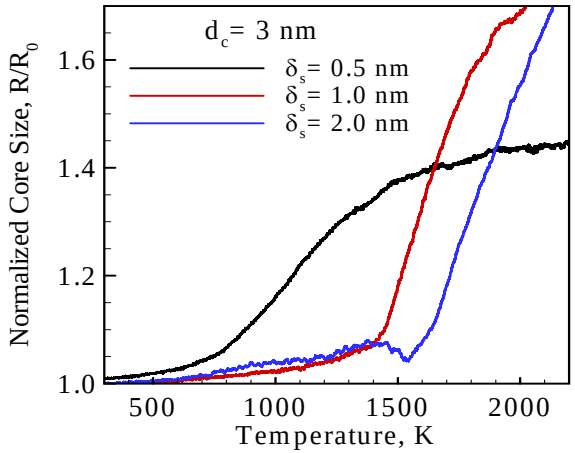


Equilibrium temperature vs. core size (δ_s = 1 nm)



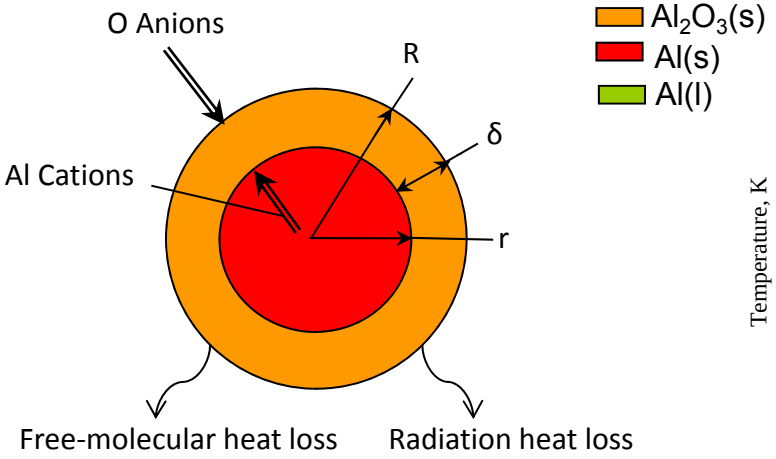
- Melting temperature of the core higher than that of nascent particle but lower that that of surface-free bulk aluminum
  - Shell imposes "cage-like" mechanical effect on the core
- Core melting point increases from 900 K at 3 nm to 1010 K at12 nm
  - liquid phase nucleation begins at the core-shell interface
- Shell melting point increases with thickness, from 1350 at 1 nm to 1580 K at 3 nm
- Shell thickness affects the onset of diffusion and chemical reactions
  - δ_s = 0.5 nm, diffusion/reactions upon melting of the core
  - δ_s = 1- 2 nm, diffusion/reactions upon melting of the shell
- Equilibrium temperature increases with core size, from 1850 K at 3 nm to 2350 K at 8 nm
  - more Al atoms to react exothermically with Ni atoms

Core radius vs. temperature (d_c = 3 nm)

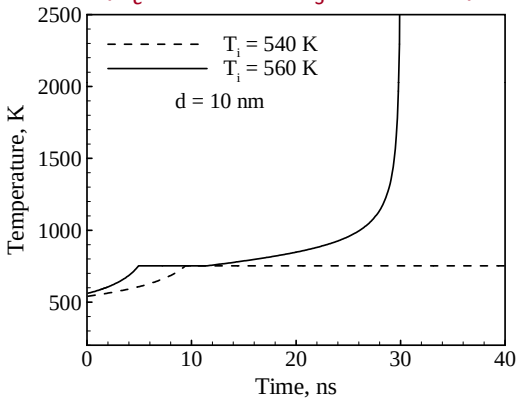


Pyrophoricity of Nano-Aluminum Particles

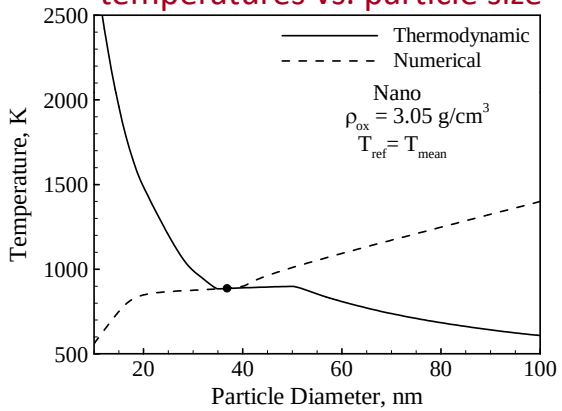
- Enhanced reactivity of aluminum particles at nano-scales poses significant safety hazards
- Nano-Al particles may ignite spontaneously when exposed to air at room temperature (pyrophoricity)
- Need reliable estimates of the critical particle size at which particles become pyrophoric
- Glassman et al.'s model (steady state energy balance, with no heat losses): 27 nm
- Dreizin's model (unsteady energy balance with heat losses): 68 nm



Temperature vs. time (d_c = 10 nm, δ_s = 0.3 nm)



Final and minimum ignition temperatures vs. particle size



- Present work uses unsteady energy balance, Mott-Cabrera oxidation kinetics, size-dependent properties
- Formation of 0.3 nm oxide layer on nascent particle approximated as an adiabatic process
- Thermodynamic energy balance to compute final temperature upon growth of 0.3 nm oxide layer
- Numerical analysis to find minimum ignition temperature for particles with 0.3 nm oxide layer
- Example: It is 560 K for a core diameter of 10 nm
- Analysis indicate critical size of 37 nm, lower than the previous prediction of 68 nm
- For particles with 0.3 nm oxide layer, the critical particle size is predicted to be 3.8 nm
- Nano-sized particles with thicker oxide layers (δ_s > 0.3 nm) are non-pyrophoric