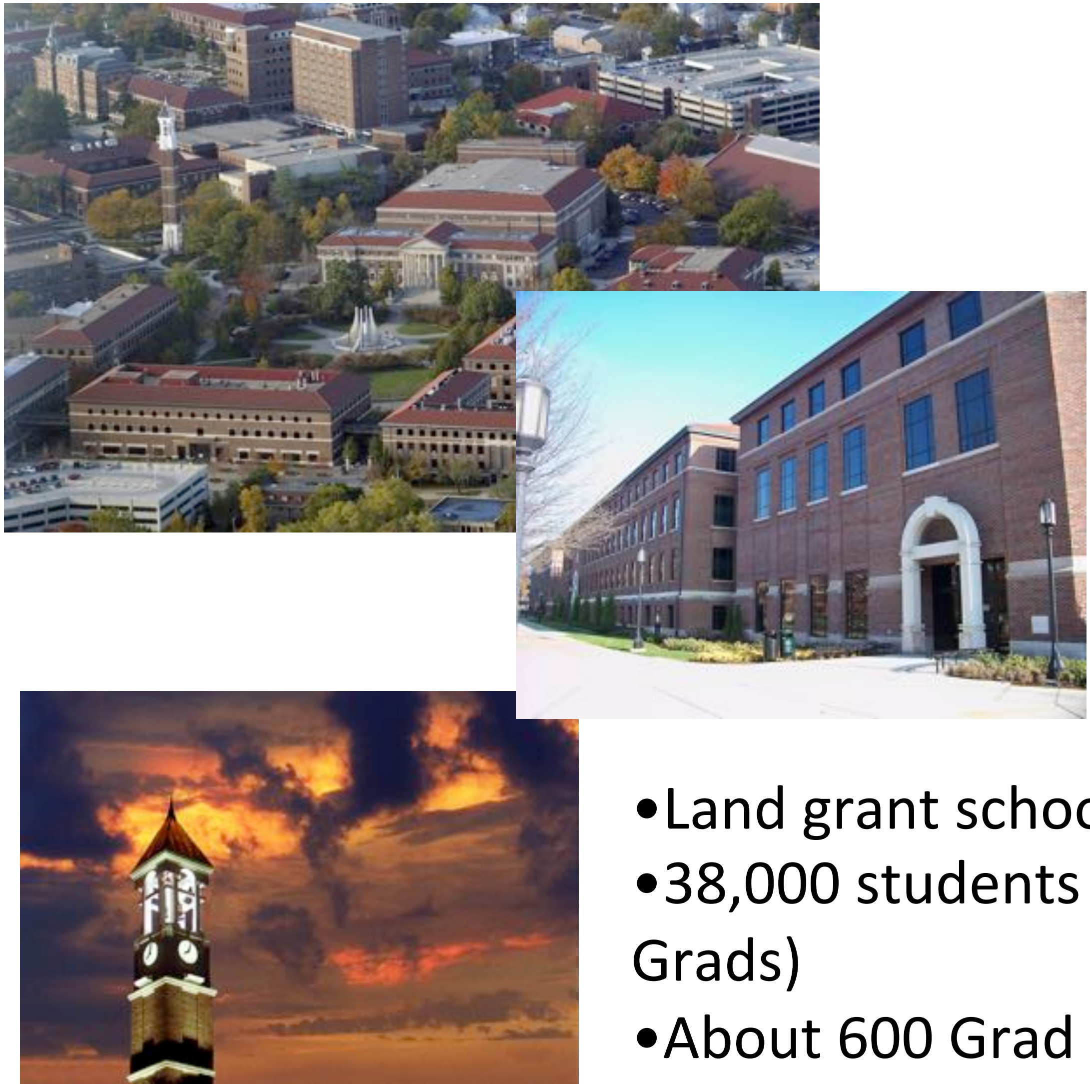
An Overview of Energetic Materials Research at Purdue University

S.F. Son

School of Mechanical Engineering, Purdue University, West Lafayette, IN, USA

Purdue University



- Land grant school
- 38,000 students (29,000 UGs, 9000 Grads)
- About 600 Grad students in ME

Facilities: Zucrow Labs

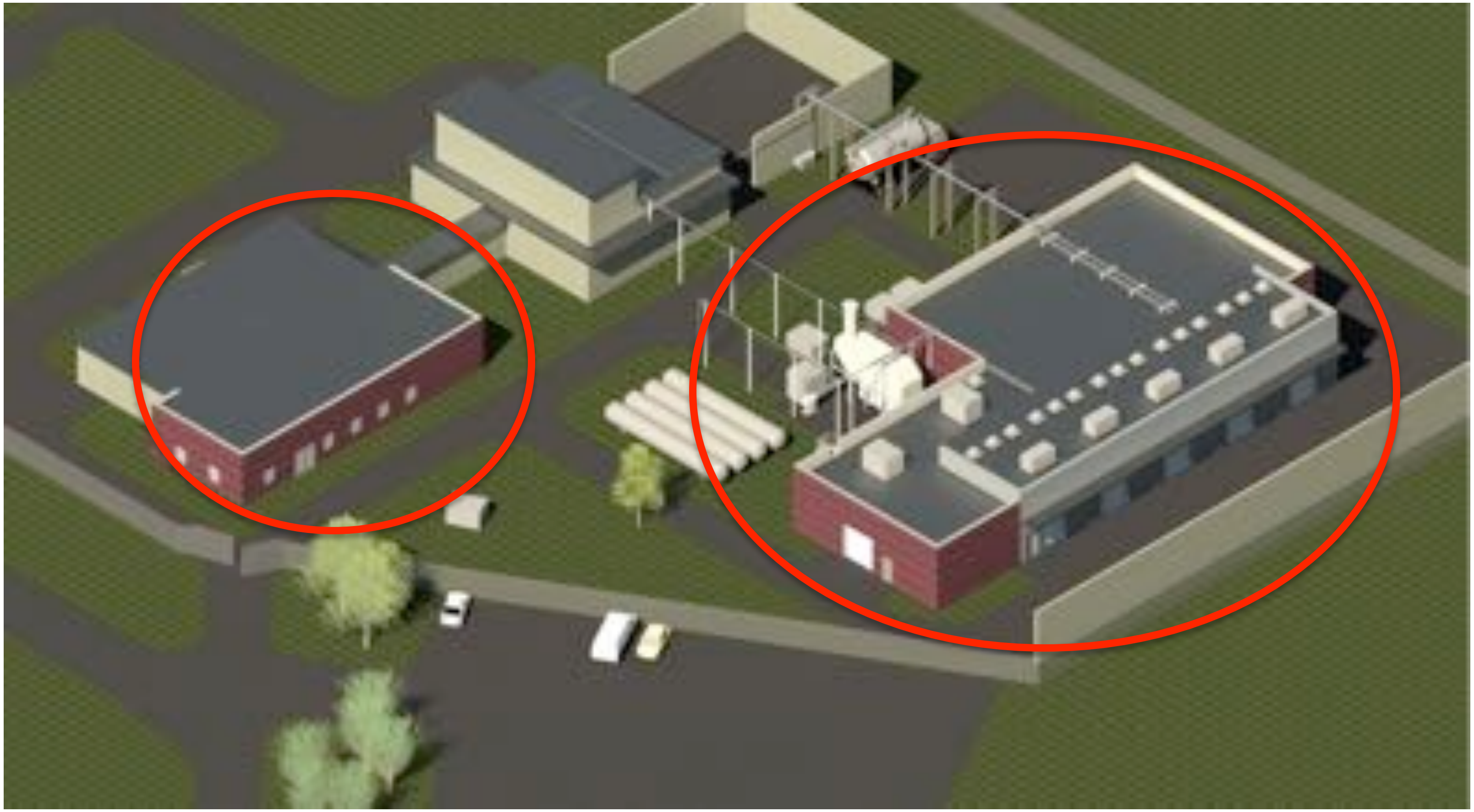
- 70 year history
  - Solid, hybrid and liquid rockets
  - Jet engines
- About $9M/yr research expenditures
  - Rocket and air-breathing propulsion
  - Energetic materials
  - Energy
- About 90 current students, 15 faculty

Dr. Wernher von Braun visits with Doc Zucrow at Propulsion Lab (1953)

MAURICE ZUCROW LABORATORIES

PURDUE UNIVERSITY
ZUCROW LABS
ENERGETICS LABORATORY

High Pressure Lab Expansion



- $8.2 M Expansion and remodeling.
- Construction to begin early 2016.
- Features five additional test cells.
- Integrated laser lab

Aerospace Industrial Research Park

- 980-acre aerospace research park approved
- Local related small businesses include INSpace (rocket propulsion), Adranos (new EM company), En'Urga (diagnostics)

- PRF plans to build a 44,000-square-foot facility where Rolls-Royce will develop and test jet engines
- Additional space available for others.

Other Facilities

- Birck Nanotechnology Center
  - 186,000 square feet, 25,000 sq. ft. Class 1-10-100 nanofabrication cleanroom
  - Optical Photolithography (resolution to ~ 2 µm)
  - Electron-Beam Lithography (resolution to ~ 10 nm)
  - Reactive Ion Etching (RIE)
  - Plasma etching
- Herrick Labs
  - Noise and Vibration Control
  - Electromechanical Systems
  - Diagnostics and Prognostics
  - Energetic materials printing
  - 20 faculty
- Laser Diagnostics Labs
  - Profs. Bob Lucht, Terry Meyer (arrived this summer), and Chris Goldstein (new in March)

Energetic Materials Team

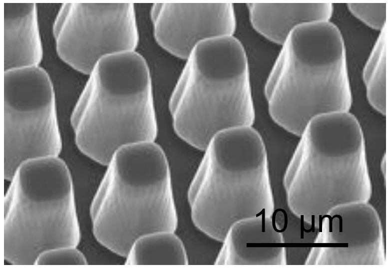
- Capabilities in experiments (fabrication and diagnostics), simulation (multiple scales), explosives detection, etc.
  - **M. Koppes, Director of Fire Protection Engineering-head of county bomb squad**
  - **S. Meyer, Zucrow Lab Manager, testing**
  - S. Son, combustion of EMs
  - R. Lucht, laser diagnostics of propellants
  - T. Meyer, laser and x-ray diagnostics of explosives
  - W. Chen, high rate mechanics of EMs and xray diagnostics
  - A. Varma, Combustion synthesis
  - A. Raman, AFM, dynamics and vibration applied to EMs
  - J. Rhoads, Explosives sensing, thermomechanics of EMs
  - G. Chiu, Printing of EMs
  - A. Strachan, atomistic and molecular simulations of EMs
  - M. Gonzales, mesoscale simulation of EMs
  - M. Koslowski, multiscale modeling of EMs
  - S. Beaudoin, detection of explosives (adhesion of explosives at the nanoscale)
  - B. Boudouris, advance polymers
  - G. Cooks, Explosives detection
  - C. Goldenstein (new), diode-based laser diagnostics applied to EMs

https://www.purdue.edu/energetics/

Molecules to Application

AFOSR, DHS, ARO, ONR, DTRA, NASA, & MDA funding

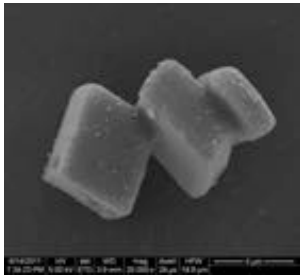
Plus Industrial funding



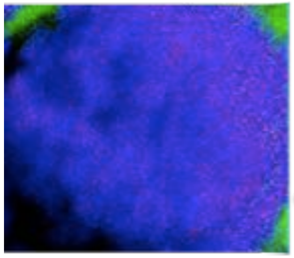
Explosives detection

Novel nitrate ester (SMX)
Hiring chemist!

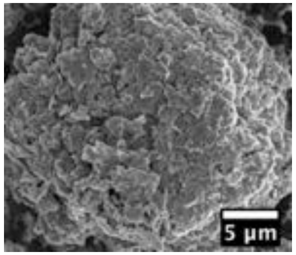
Encapsulated nanocatalysts



Tailored Al

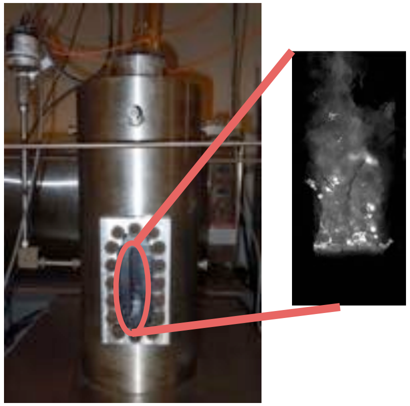


Al=blue, F=red, C=green.

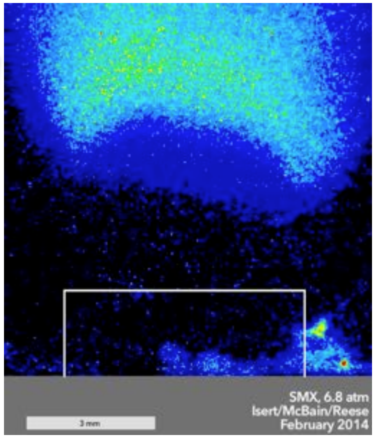


Tailoring ingredients & Propellants

Windowed combustion vessel



In situ high speed OH PLIF



Characterizing and performing unique dynamic

Rocket motor testing

Some Current Projects

- **Hypergolic hybrids**
- **Impact initiated reactives**
- Energy localization (**hot-spots**) in explosives & detection
- Coupled **acoustic** and electromagnetic energy insult
- Characterization of energetic **cocrystals**
- Small-scale Characterization of **Homemade Explosives**
- **Core-shell** reactives
- Integration of **printed energetic materials** and MEMs
- Characterization of fuels containing **in situ** grown aluminum nanoparticles for ramjets
- **Nanoscale propellant ingredients**
  - High speed OH PLIF, modified metal fuels, encapsulated catalysts
- **Explosives detection**, including adhesion of explosives
- **Wide collaborations with Energetic Materials team!**

EXAMPLE: Real-Time Dynamic Measurements and Characterization of Mesoscale Deformation and Temperature Fields in Reacting Energetic Materials under Impact and Periodic Loading

PURDUE
UNIVERSITY

Research Program Areas

- ***Mesostructure identification (Chen)***: 3-D X-ray computed tomography determines initial sample internal structures at the mesoscale.
- ***Deformation field (Chen)***: Impact experiments with high-speed X-ray imaging record *in-situ* dynamic deformation at the mesoscale.
- ***Property distribution (Rhoads/Son)***: Scanning laser Doppler vibrometry and infrared thermography characterize the dynamic interactions that occur at the crystal/crystal and crystal/binder interfaces.
- ***Temperature distribution (Son/Meyer)***: Laser-induced phosphorescence methods and infrared imaging measure the temperature field evolution.
- ***Micro-,Mesoscale modeling (Gonzalez/Koslowski)***: A predictive modeling and simulation capability is developed.

Research Team

Wayne
Chen

Marcial
Gonzalez

Marisol
Koslowski

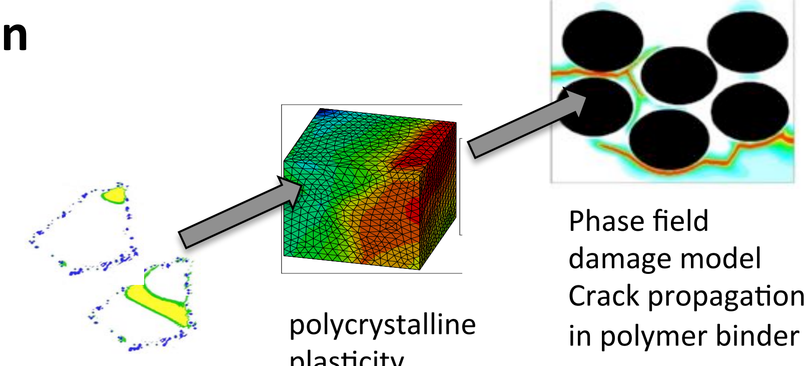
Jeff
Rhoads

Steve
Son

Terry
Meyer

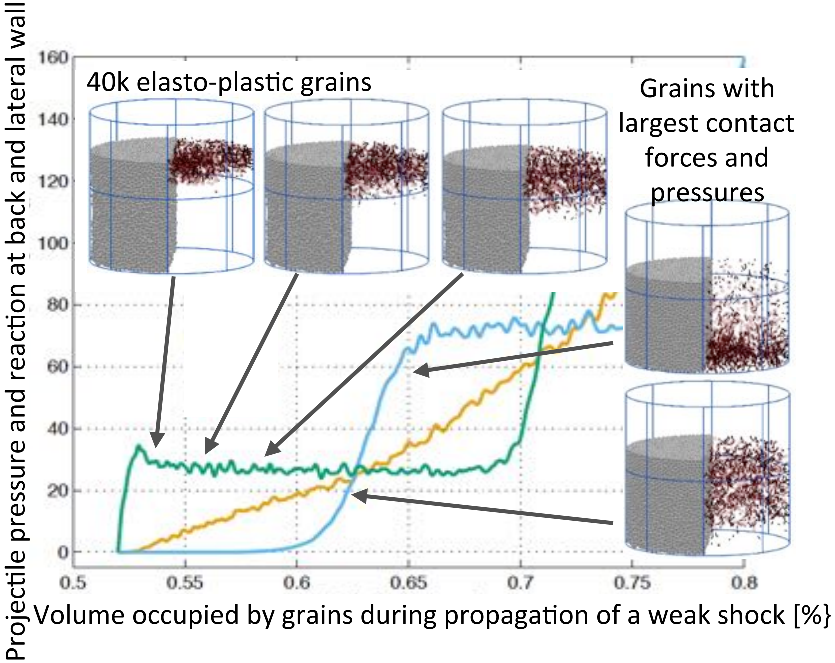
Mesoscale predicting modeling and simulation

- Mesoscale multi-physics model based on a particle mechanics approach.
  The model individually describes each grain in the specimen and the multi-physics is accounted by complex contact mechanics laws)
- Informed by proposed lower scale models.
- Calibrated and validated with proposed in-situ experimental capabilities.



FY15 – Research plan

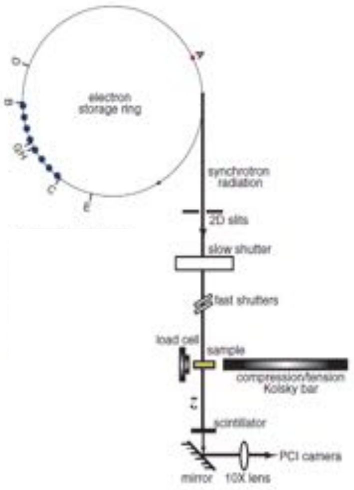
- Development of 3D elasto-plastic contact laws for grain/grain, grain/binder, grain/wall, and binder/wall interfaces.
- Study of weak shock propagation for different mixtures fractions, polydispercity, and impact velocities.
- Extension of nonlocal contact mechanics formulations to elasto-plastic grains.



Real-time Deformation, Damage, and Temperature Measurements

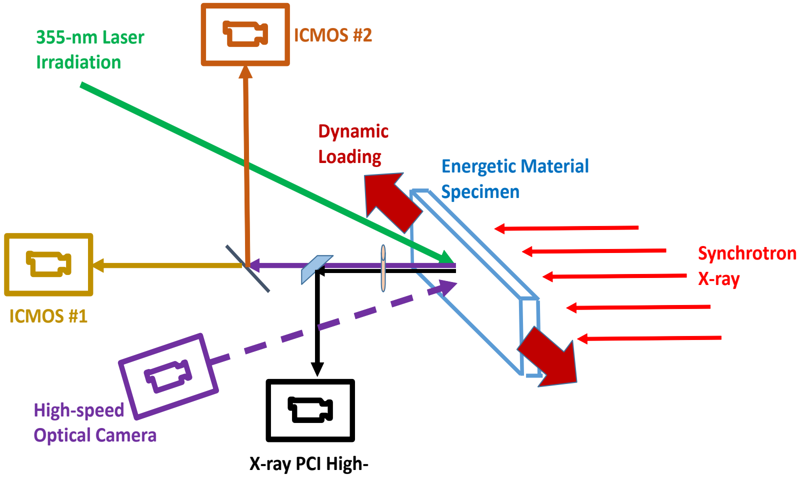
Chen/Son/Meyers

- ***Need for Real-time Visualization***: Impact deformation, damage evolution, and temperature measurements are critical physical quantities at meso-scale to understand the response of energetic materials but are currently unavailable.
- ***Experimental Approach***: We will conduct impact experiments with high-speed X-ray imaging to record *in-situ* dynamic deformation and damage at mesoscale, and laser-induced phosphorescence method and IR imaging to measure the temperature field evolution.
- ***Expected Outcome***: Meso-scale measurements of time evolutions of deformation field, damage status, and temperature field.



(A)

(B)



355-nm Laser Irradiation

ICMOS #2

Dynamic Loading

Energetic Material Specimen

Synchrotron X-ray

ICMOS #1

High-speed Optical Camera

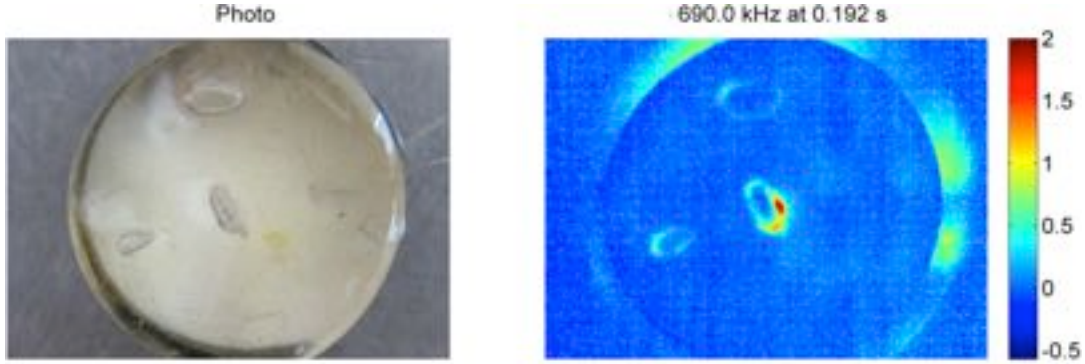
X-ray PCI High-speed Camera

Particle-Scale Thermomechanical Interactions in Energetic Materials

Jeff Rhodes and Steve Son

Project Overview:

- The thermomechanics underlying hot-spot formation and growth are poorly understood.
- Preliminary experimental results [1,2] have demonstrated that hot spots can be generated locally, even by weak periodic excitations.
- The present effort seeks to address the fundamental questions of “Why?” and “How?” hot-spot formation takes place, through a joint analytical and experimental study.



[1] Mares, et al. Journal of Applied Physics, 2013.

[2] Mares, et al. Journal of Applied Physics 2014.

Example 2: Nanoscale Propellants MURI

Solid propellants are commonly used in space launch vehicles and military missiles

- The most common oxidizer (ammonium perchlorate, AP) contains:
  - ✓ 54.5 wt.% oxygen
  - X 30.2 wt.% chlorine

  As much as 98% of the chlorine is converted to HCl (hydrochloric acid)
- The most common fuel (aluminum) forms large molten products (**two phase flow losses**)
- Also, **high surface area catalysts or metals** can lead to rheology and mechanical issues
  - Catalysts in binder accelerate aging too!

HCl Formation Issues

- Corrodes the launch area
- Deteriorates the ozone layer

Two-Phase Flow Losses

- Molten particles agglomerate
- Up to 10% loss in motor I_{sp}

Image: http://commons.wikimedia.org/wiki/File:Peacekeeper_launch.jpg

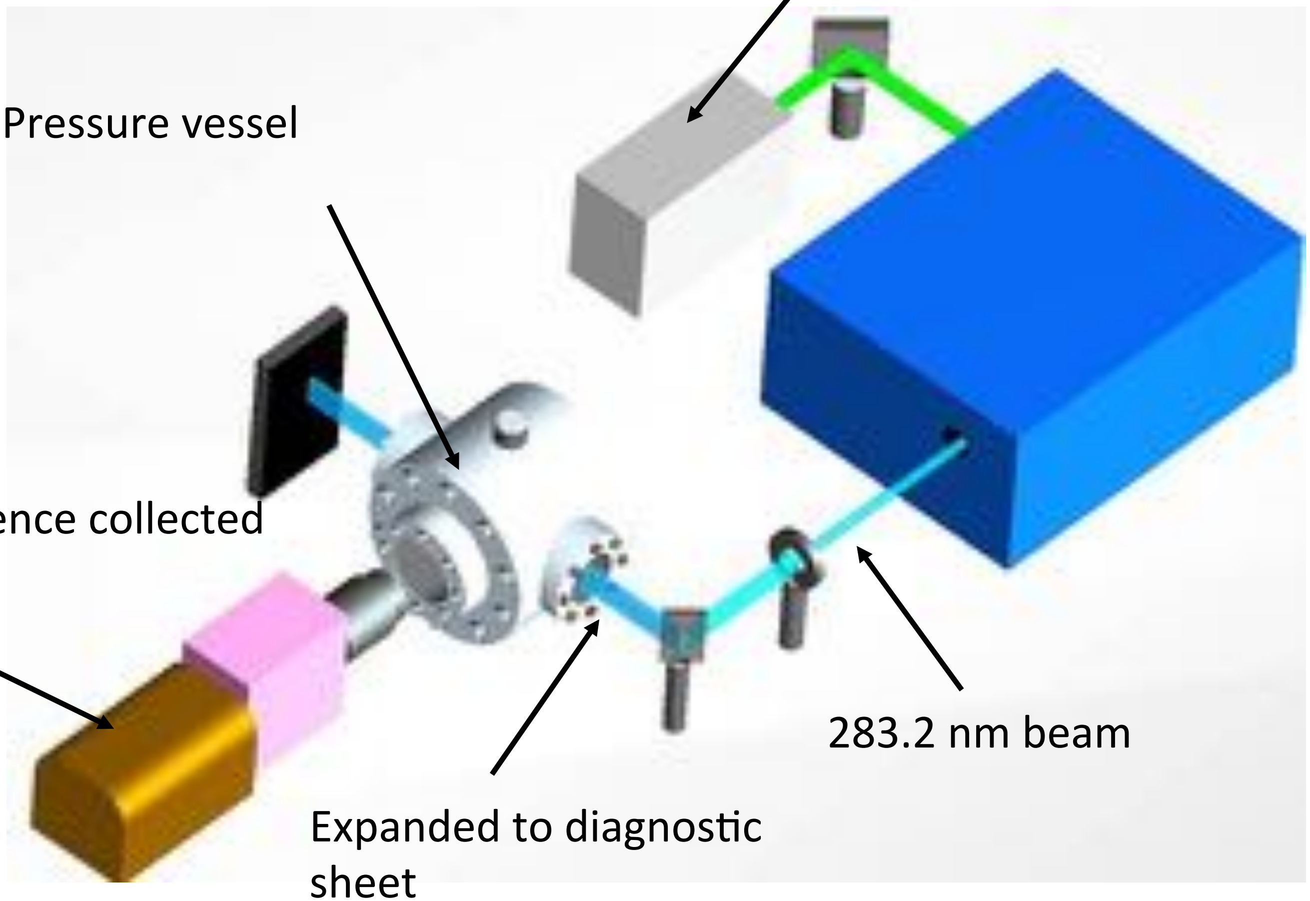
Approach: Tailored Particles

- **Encapsulated Catalysts:**
- Catalysts often used in solid propellants
- Catalysts work best when in contact with oxidizer
  - So, let's fabricate catalysts INSIDE oxidizer crystals!

- **Alloys and "Inclusion Fuels"**
- An example of an "inclusion fuel" is aluminum with nanoscale features of another component
- Alloys such as Al-Li are also being studied

We also need improved diagnostics

Planar Laser-Induced Fluorescence



532 nm pump laser

Pressure vessel

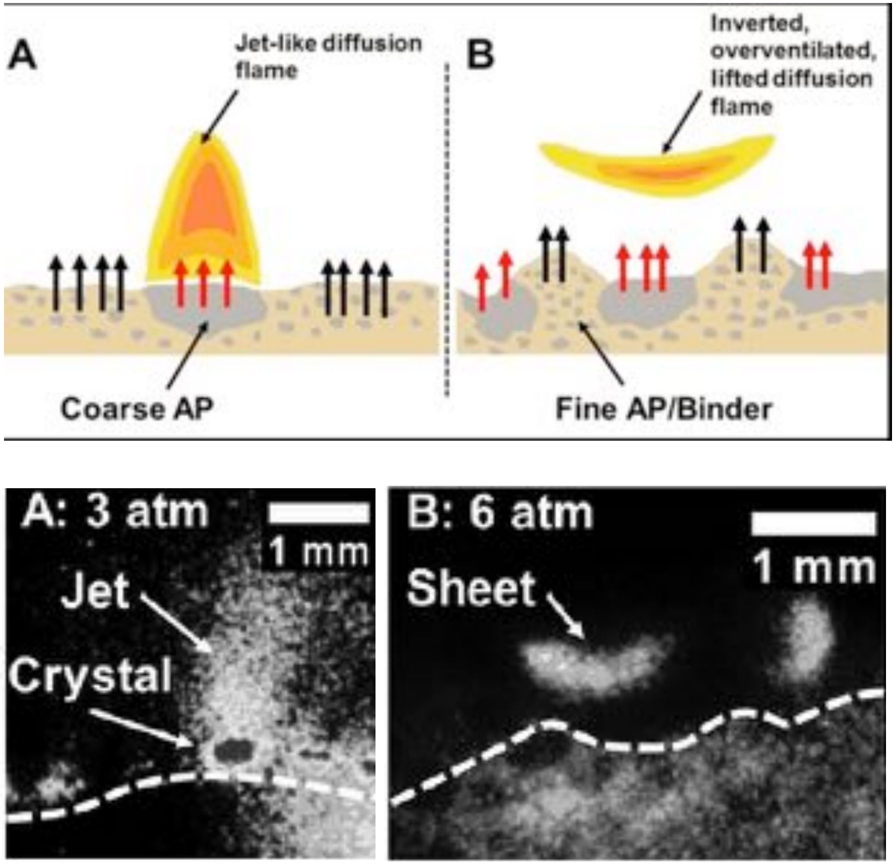
310 nm fluorescence collected at 5 kHz

283.2 nm beam

Expanded to diagnostic sheet

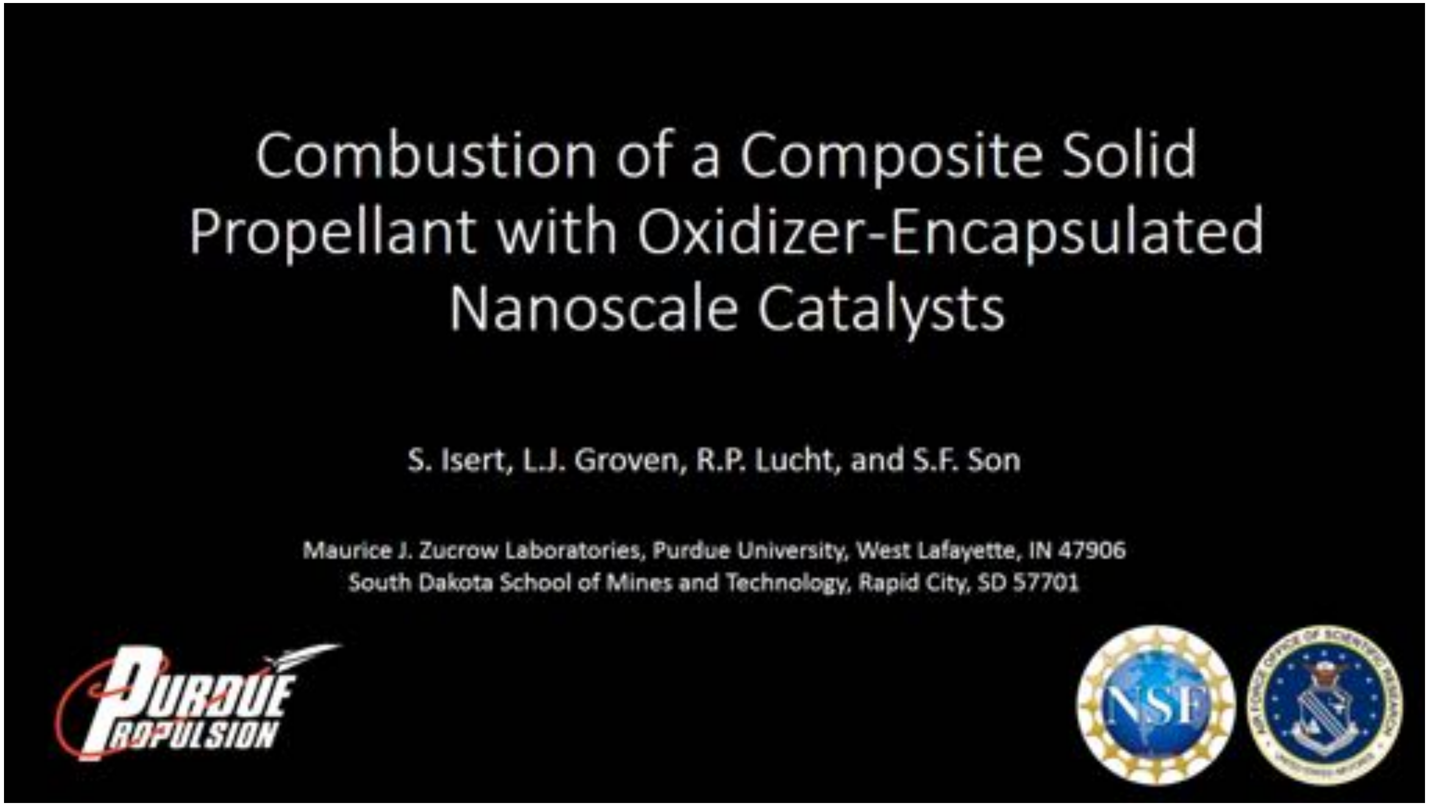
In Situ Flame Visualization

- OH PLIF has recently been applied in situ to propellants in our group (Bob Lucht collaborator)
- **We can now image the flame structures!**



A: Oxidizer released into a fuel-rich gas phase
B: Recessed AP burning faster than surrounding mixture. Result is lifted, overventilated flame.

Catalyzed Propellant

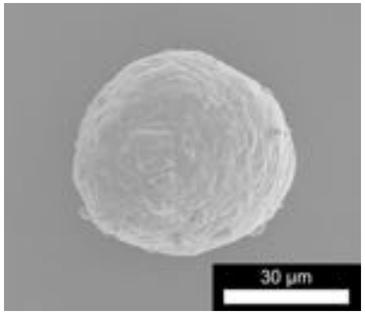


Combustion of a Composite Solid Propellant with Oxidizer-Encapsulated Nanoscale Catalysts

S. Isert, L.J. Groven, R.P. Lucht, and S.F. Son

Maurice J. Zucrow Laboratories, Purdue University, West Lafayette, IN 47906
South Dakota School of Mines and Technology, Rapid City, SD 57701

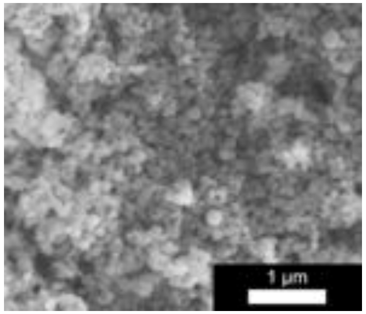
Metallized Fuels



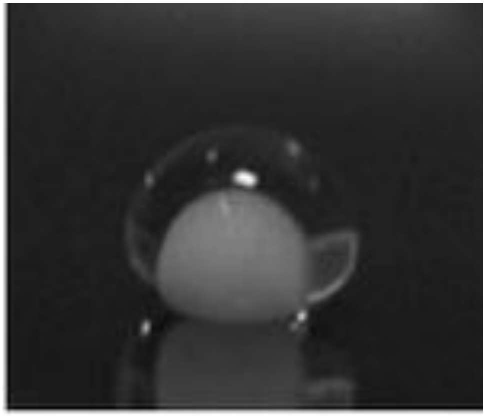
- Metals and metalloids have been widely used as neat elemental fuels
- Modifying and tuning the combustion characteristics of these fuels remains challenging
- Can modify reactivity through particle size reduction or surface modification/functionalization (drawbacks)
- **How one can obtain the advantages of nanoscale fuels without the drawbacks?**

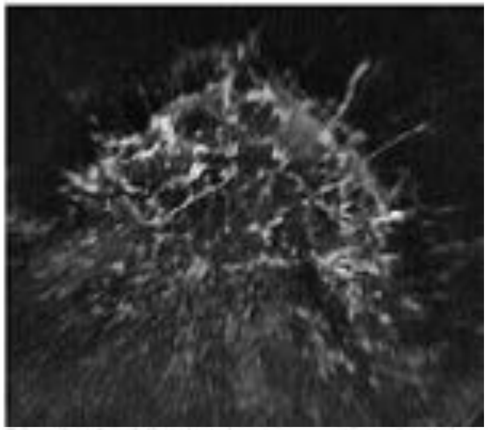
Major Drawbacks to nanoscale and nanoporous materials

- High Cost
- Difficulty of synthesis (e.g., strong acids, scalability)
- High specific surface area (SSA)
  - Processing issues (unfavorable rheology)
  - Rapid oxidation and aging

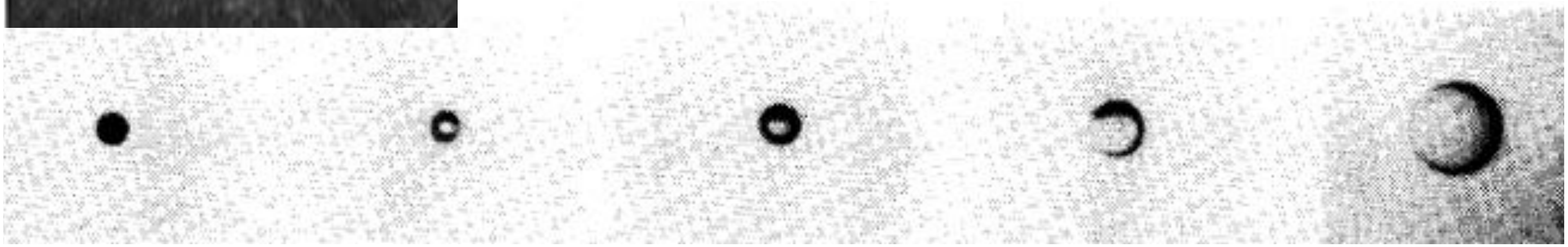


Lessons from Liquid Microexplosive Liquids





- Microexplosive liquid fuels have been investigated since the early 1960's
- Mixtures of high/low volatility constituents
- The multicomponent fuels can be either emulsions (oil/water, left) or missive (heptane/hexadecane, bottom)
- Has been shown to:
  - **Promote fuel atomization**
  - **Reduce residence times**
  - **Increase completeness of combustion**



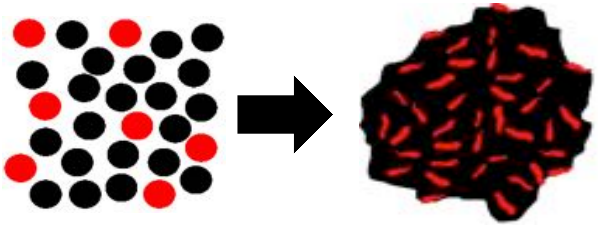
Images: Wang, C.H., X.Q. Liu, and C.K. Law, *Combustion and microexplosion of freely falling multicomponent droplets.* Combustion and Flame, 1984. **56**(2): p. 175-197.; Kadota, T., et al., *Microexplosion of an emulsion droplet during Leidenfrost burning.* Proceedings of the Combustion Institute, 2007. **31**(2): p. 2125-2131.

Analogies to Metallized Microexplosive Fuels

We have been researching micron-scale metallized fuel particles/droplets can have similar properties to liquid fuel droplets that microexplode

Emulsion Fuels

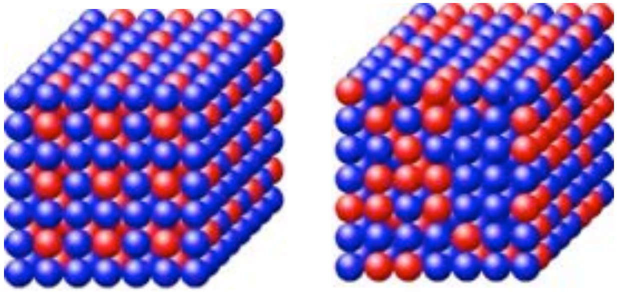
- **Mechanical activation** (MA, ball milling) can create composite particles with nanometric inclusion material (e.g., polymer)



Constituents Nanocomposite Particle

Missive Fuels

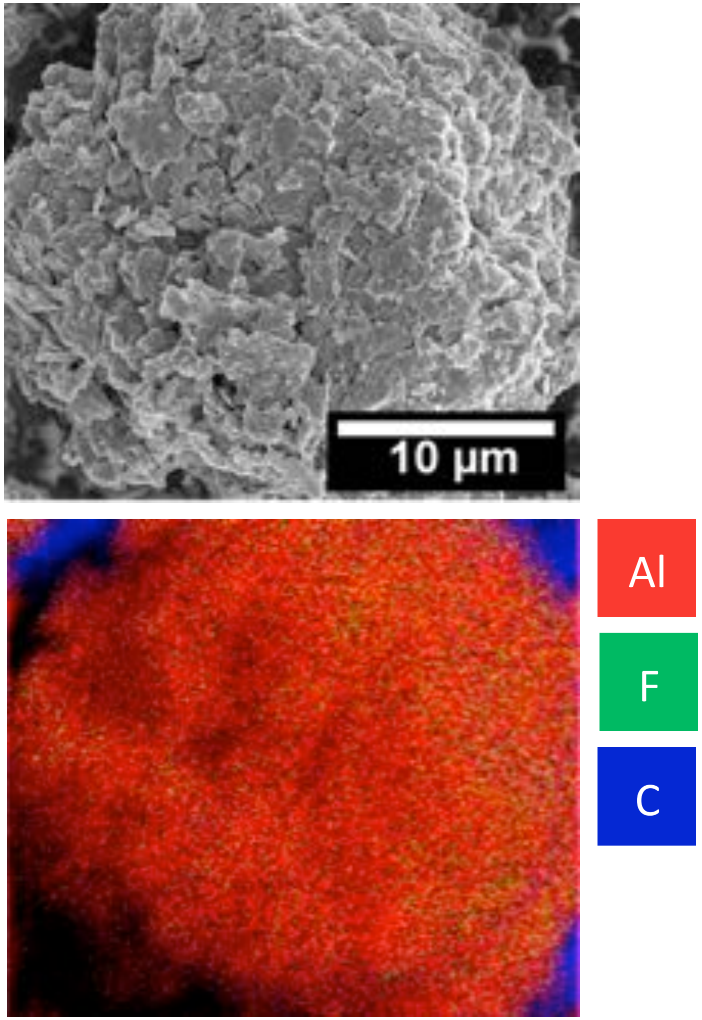
- **Metal alloys** can yield particles that have constituents mixed at the molecular scale



New Phase Solid Solution

Right Images: http://www.spaceflight.esa.int/impress/text/education/Images/Solidification/Intermetallics/Intermetallic%20versus%20alloy.jpg

Mechanical Activation

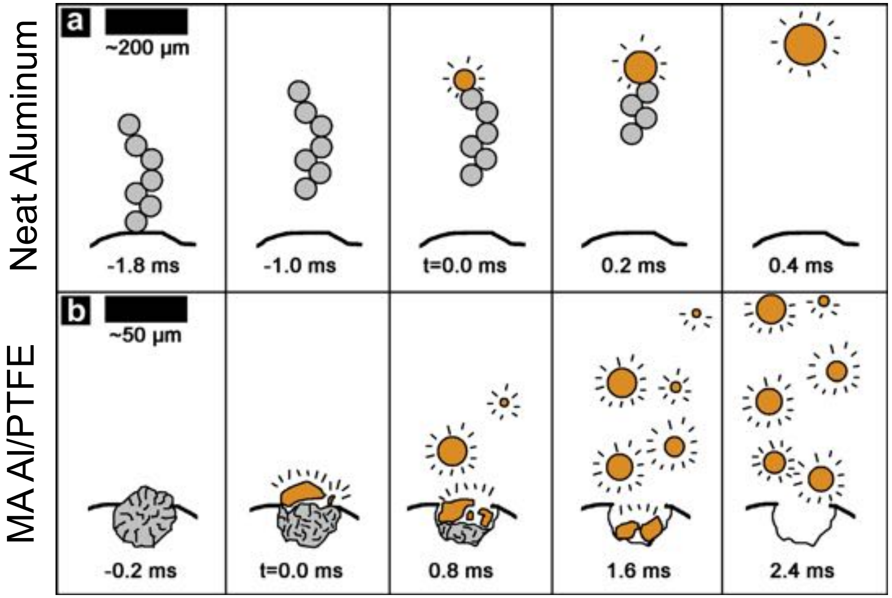


- Have been shown to:
    - Modify reactivity
    - Alter combustion products (e.g., morphology, composition, etc.)
    - Affect the completeness of combustion
- Micron-scale morphologies (moderate SSA)
- Can be tailored to achieve desired material properties and combustion characteristics

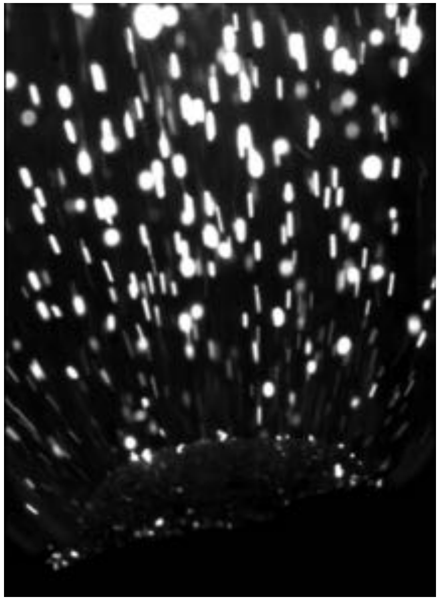
Inclusion materials can be *interacting* or *non-interacting*

Images modified from: Sippel, T.R., S.F. Son, and L.J. Groven, *Modifying Aluminum Reactivity with Poly(Carbon Monofluoride) via Mechanical Activation.* Propellants Explosives Pyrotechnics, 2013. **38**(3): p. 321-326.

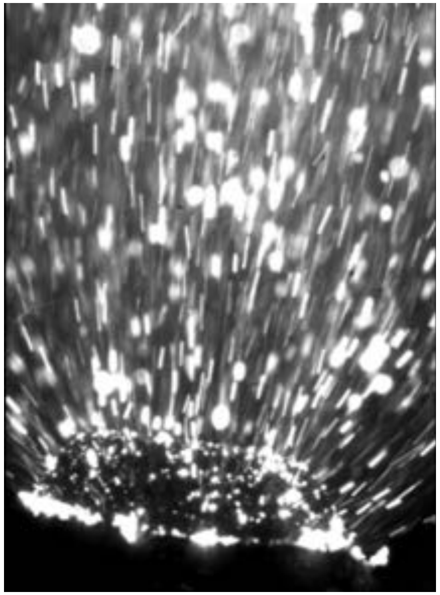
MA Powders – Solid Propellant

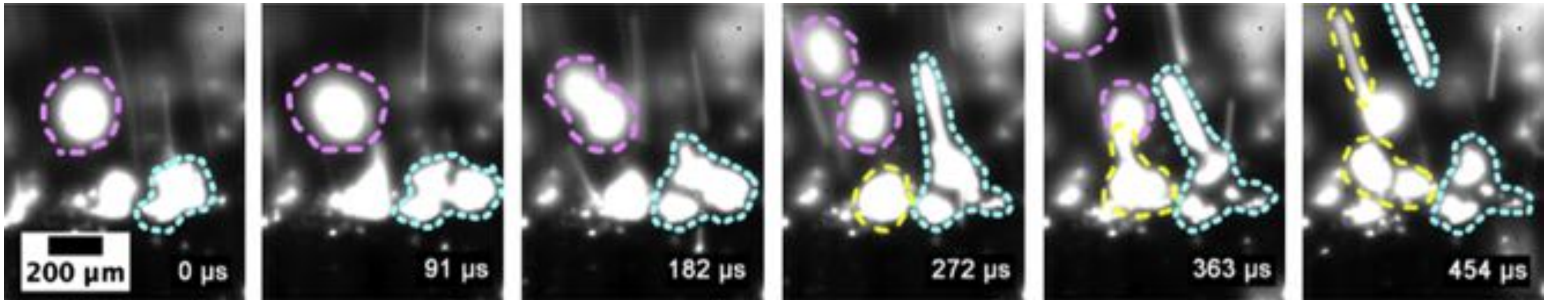


Neat Aluminum



MA 70/30 Al/PTFE

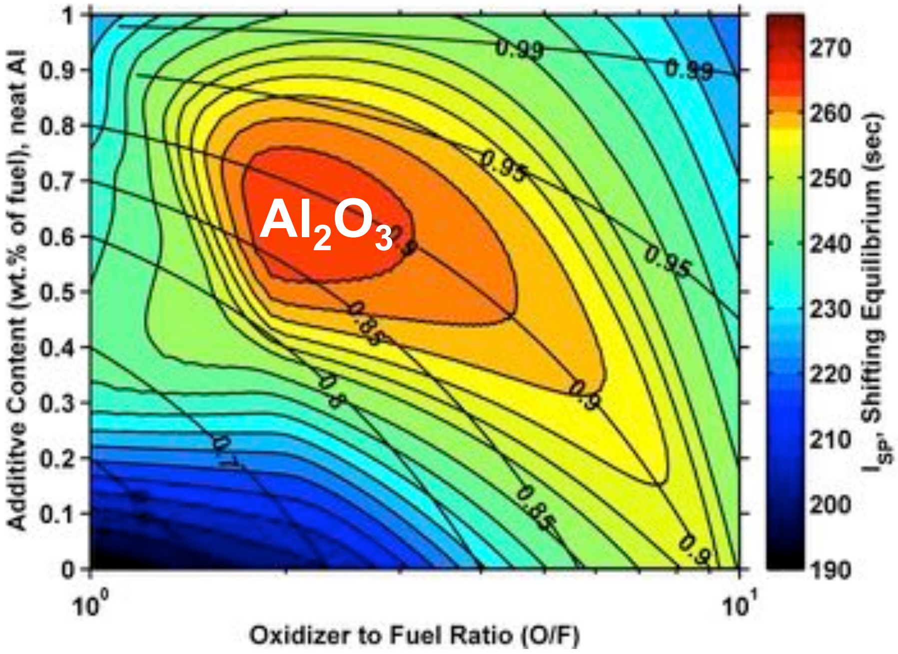




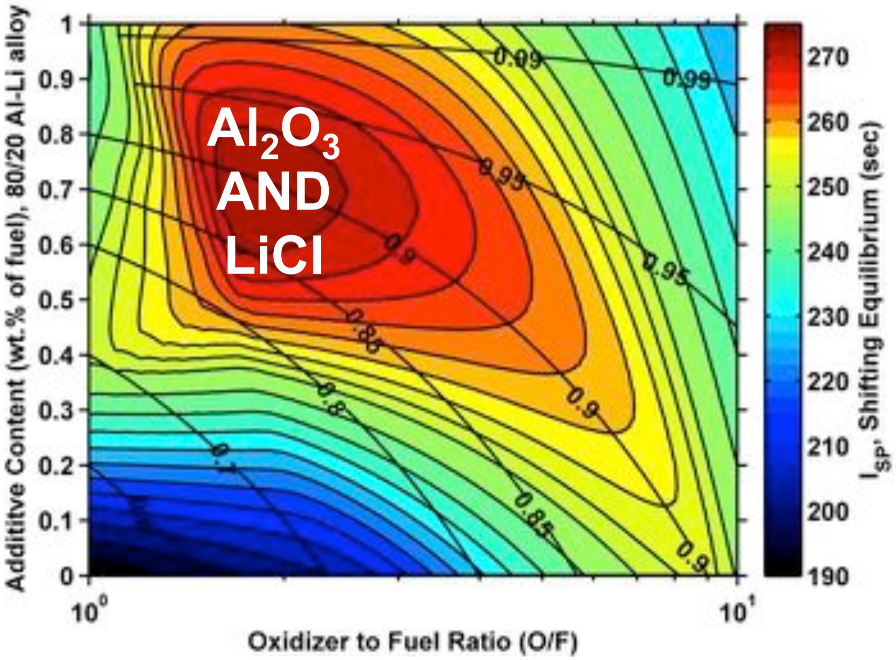
Images: Sippel, T.R., S.F. Son, and L.J. Groven, *Aluminum agglomeration reduction in a composite propellant using tailored Al/PTFE particles.* Combustion and Flame, 2013(0).

Theoretical Calculations

Neat Al

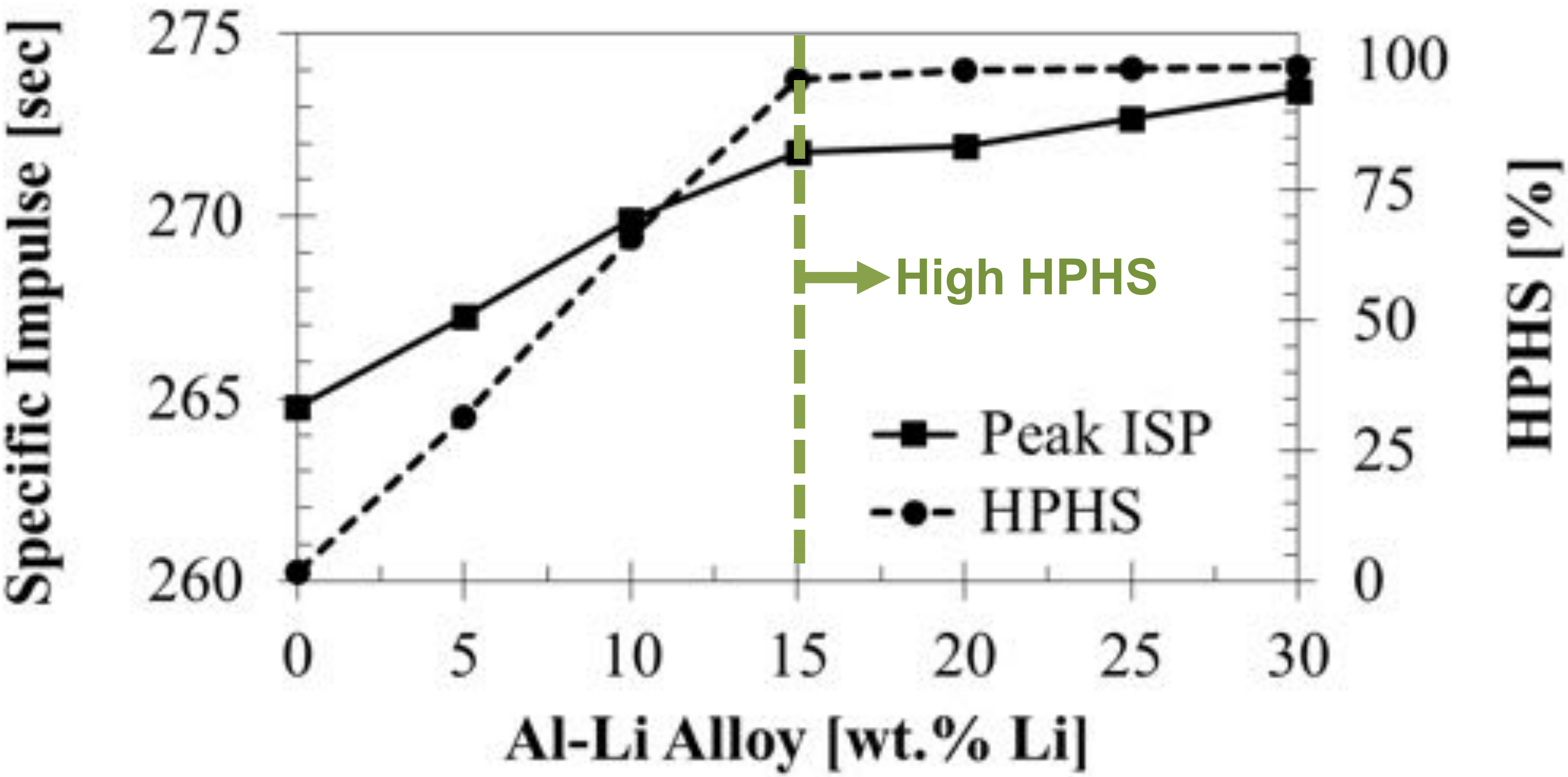


80/20 Al-Li Alloy



Additive	Max I_{SP} [sec]	$\Delta h_{Chamber\text{-}Exit}$ [kJ g^{-1}]	Temperature [K]	Molecular Weight [kg $kmol^{-1}$]	Cl → HCl [%]
Neat Al	264.8	3.4	3614	27.9	98.3
Neat Li	263.4	3.3	3204	27.3	1.8
80/20 Al-Li	271.9	3.6	3553	26.2	1.9

Al-Li Alloy: Theoretical Performance



- **Ideal: 16.9% Li (at 85% Solids Loading)**
- **20% Li powder is ~stable and commercially available**

Alloy Powders – Solid Propellant (1000 fps)

26.80/61.48/11.72 Metal/AP/HTPB

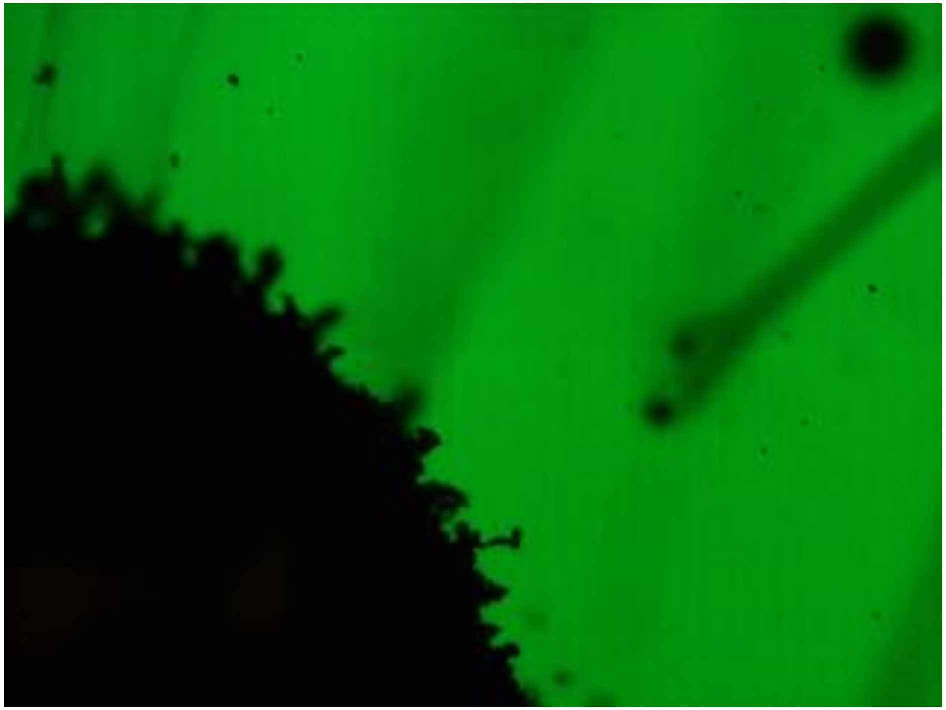
Neat Al

80/20 Al-Li Alloy

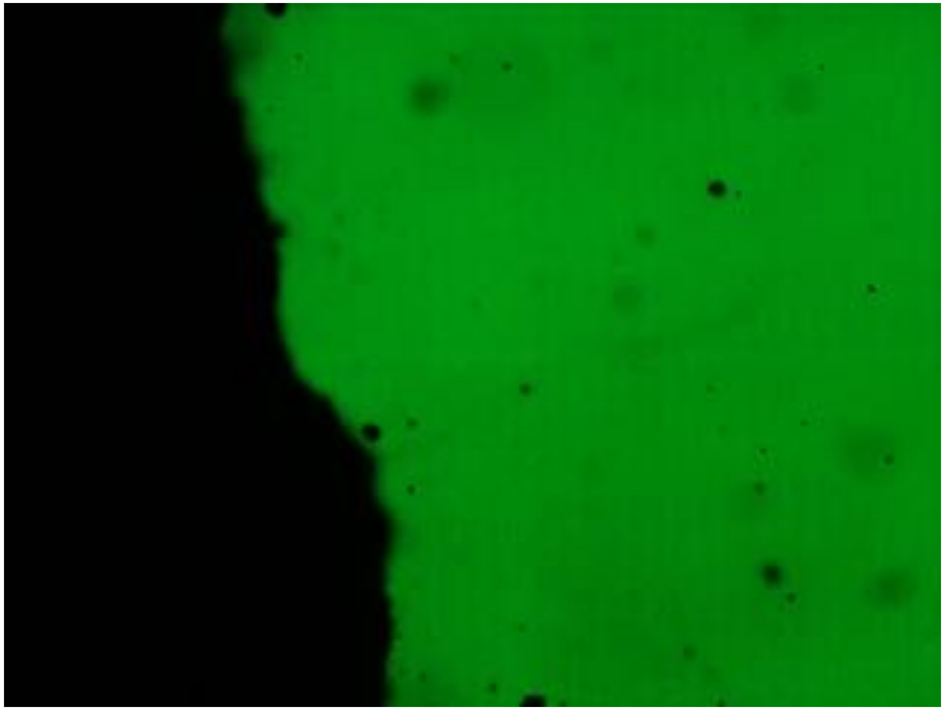
Appears to be less coarse product agglomeration from the Al-Li propellant

Alloy Powders – Propellant Surface (9900 fps)

Neat Al



80/20 Al-Li Alloy

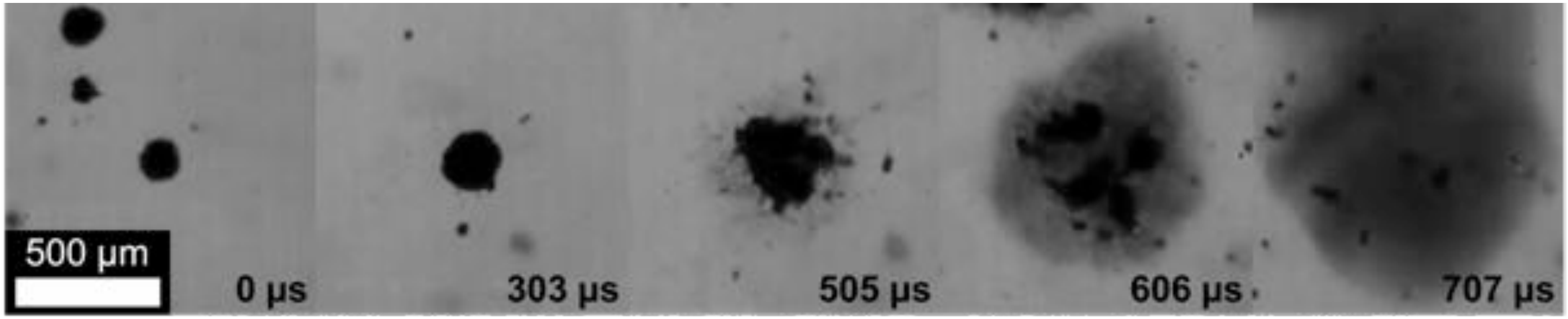


Aluminum sinters and agglomerates on the propellant surface

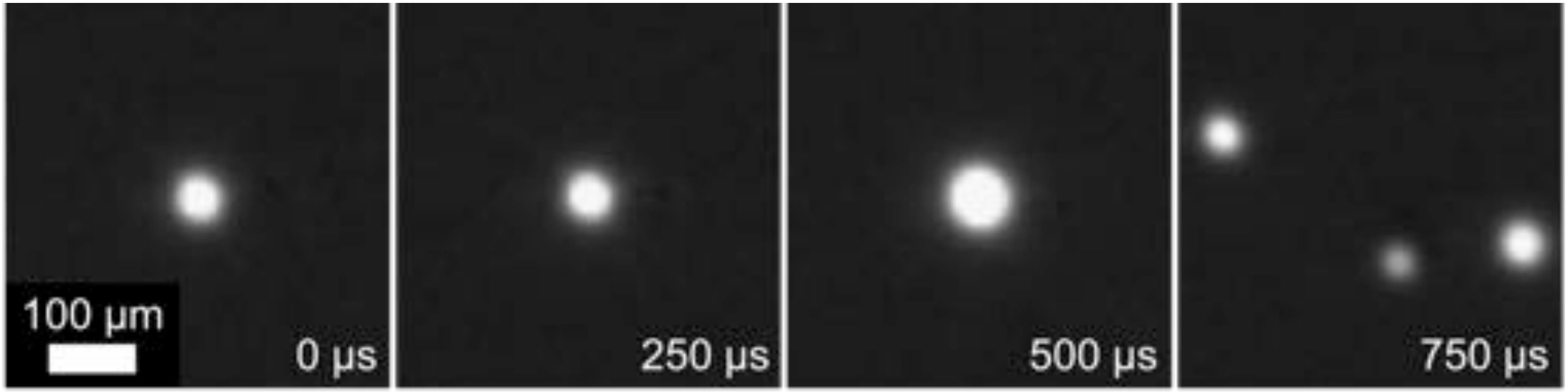
Al-Li forms a surface melt layer, and the Al-Li droplets appear to microexplode

Alloy Powders – Shattering Microexplosion

The lithium boils within the molten Al-Li, shattering the liquid droplets

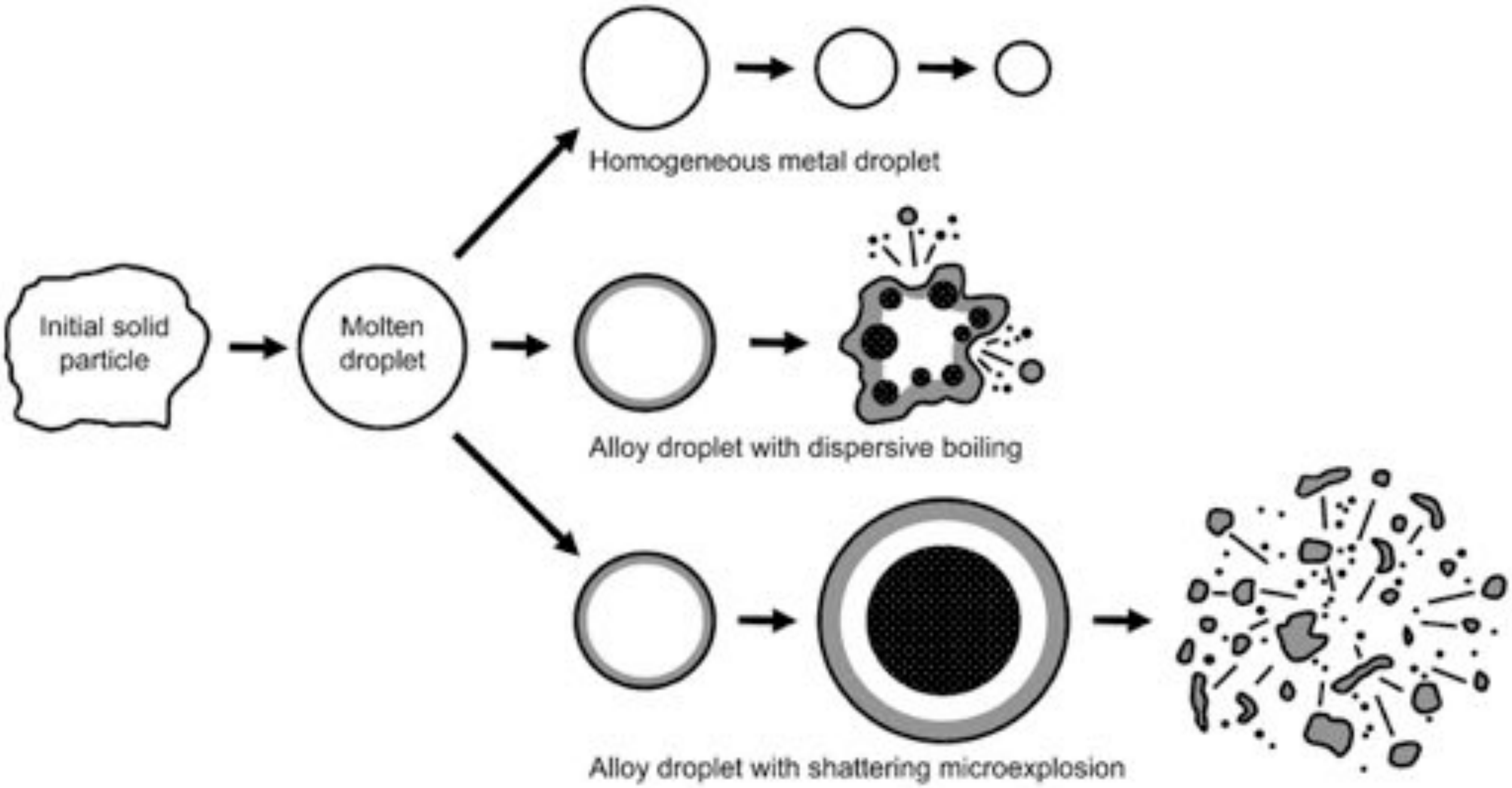


AP Propellant

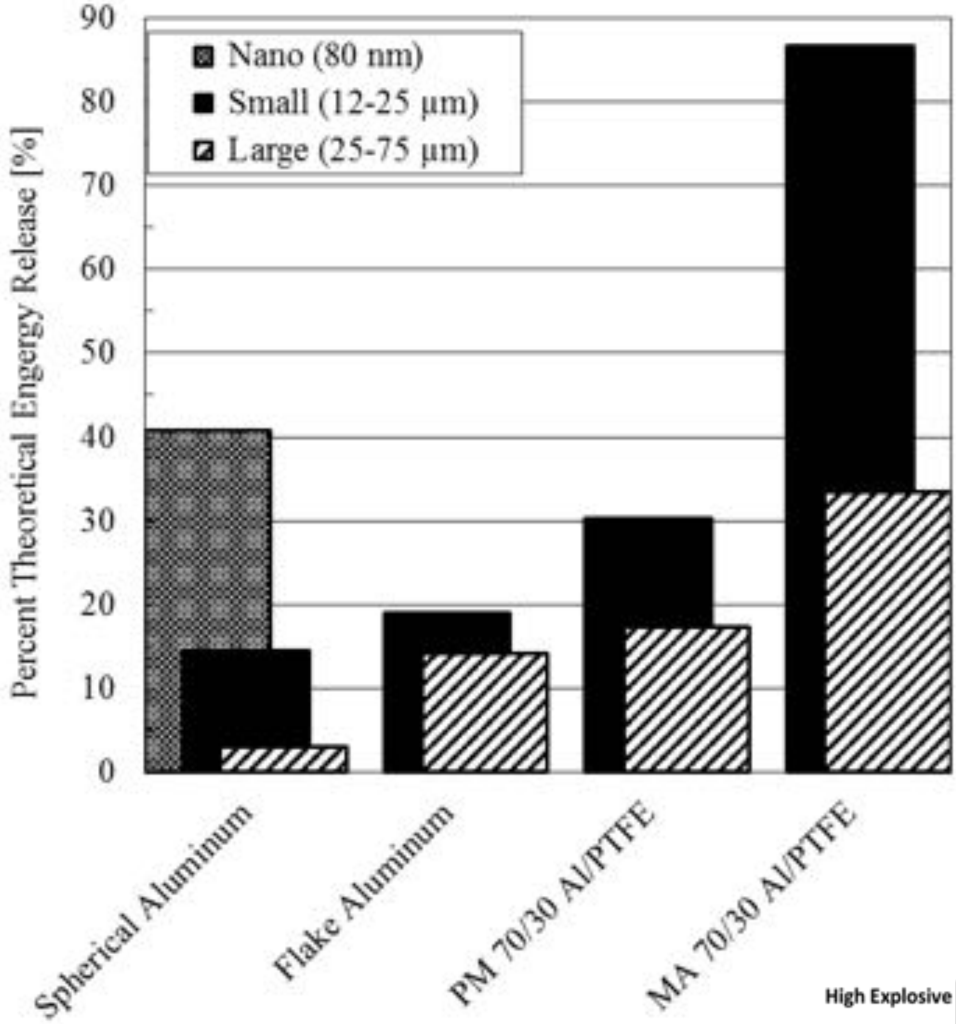


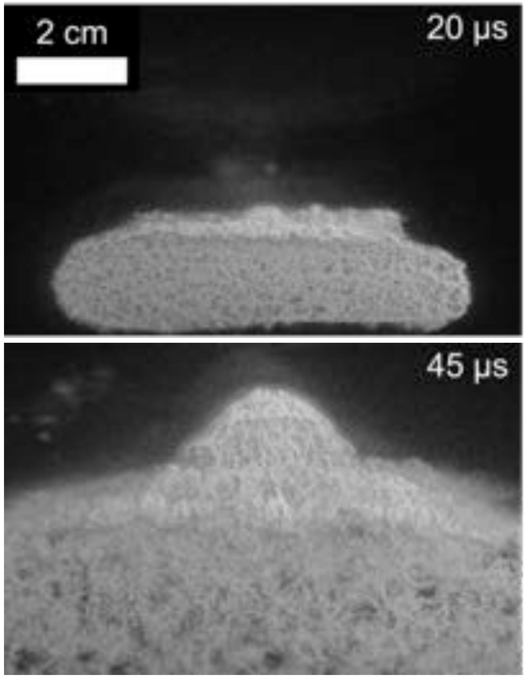
CO_2 Laser in Air (213 W cm^{-2})

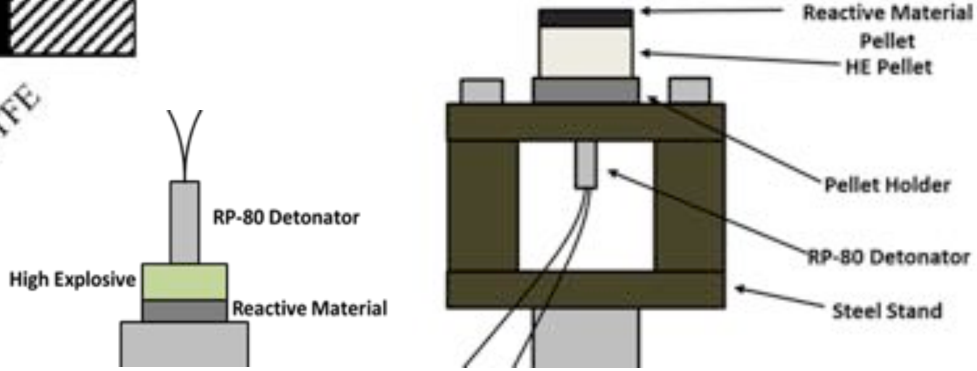
MA Powders – Microexplosion Mechanism



MA Powders - Explosive Shock Ignition



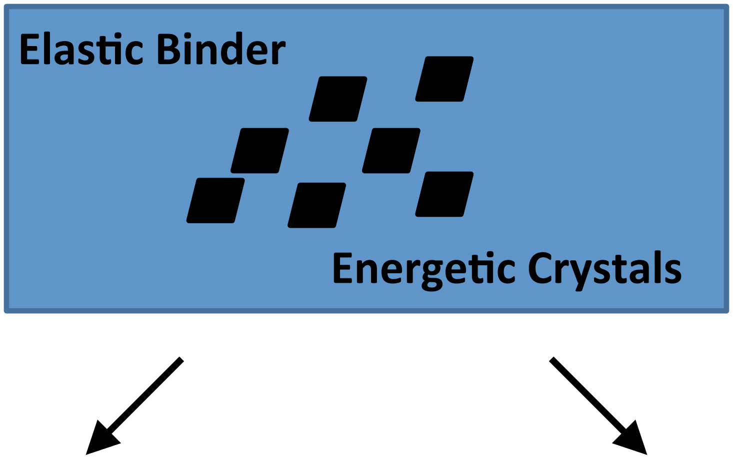




Explosive Shock Ignition Experiment – MA 70/30 Al/PTFE

Example 3: Thermomechanics

- Emphasis on *pre-reaction mechanics* in plastic-bonded explosives



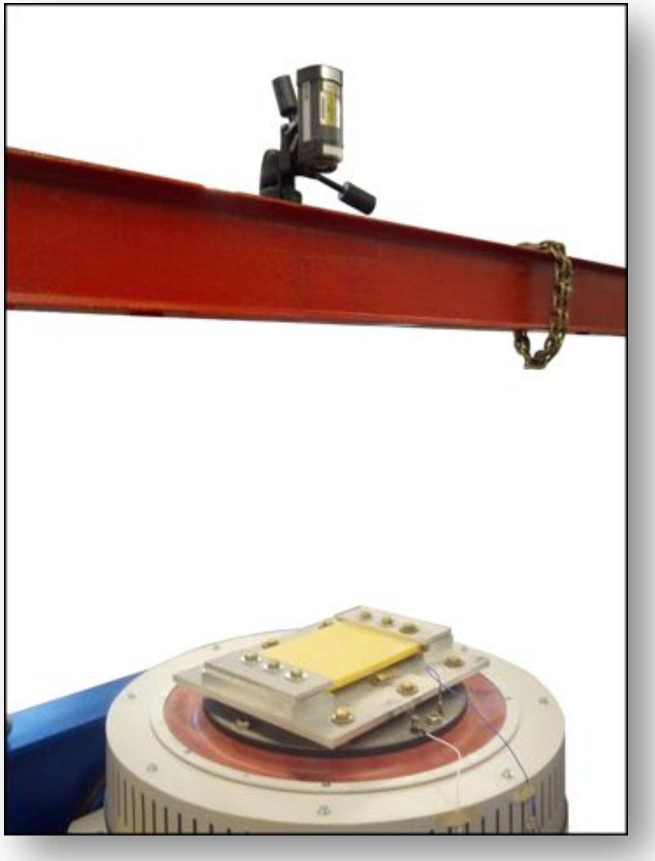
Bulk-scale
(*Low-frequency*)

Particle-scale
(*High frequency*)

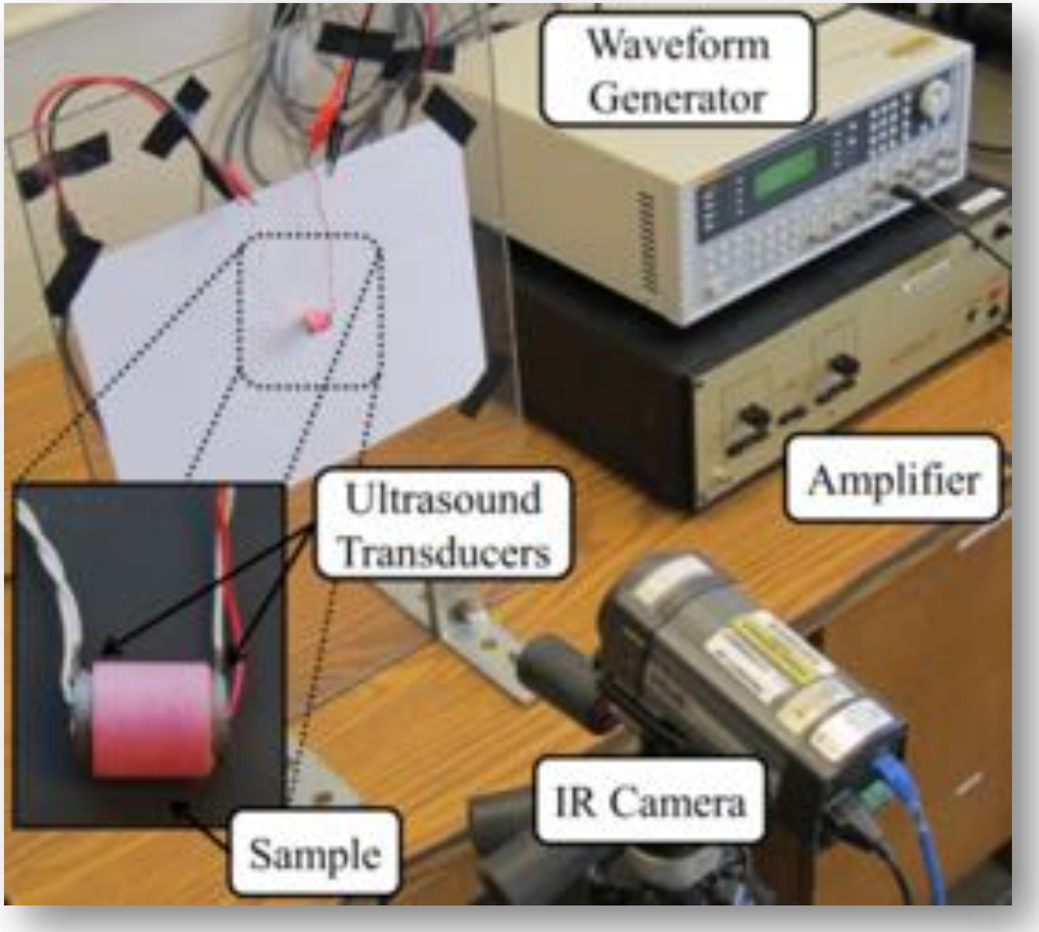
- At the *bulk-scale*:
  - Homogenized material models appear to suffice
  - The thermomechanics appear to be classical
  - Aging and damage appear to dominate the response

- At the *particle-scale*:
  - Detailed particle-scale models necessary
  - *Hot-spot* thermomechanics relevant
  - Weak excitations can have dramatic effects due to *energy concentration*

- Fabricated surrogate materials
  - HTPB/NH4Cl for HTPB/AP
  - Varied volume fractions
  - Varied geometry
- Excited structural resonances
- Measured
  - Mechanical response
  - Thermal response
- Correlated responses

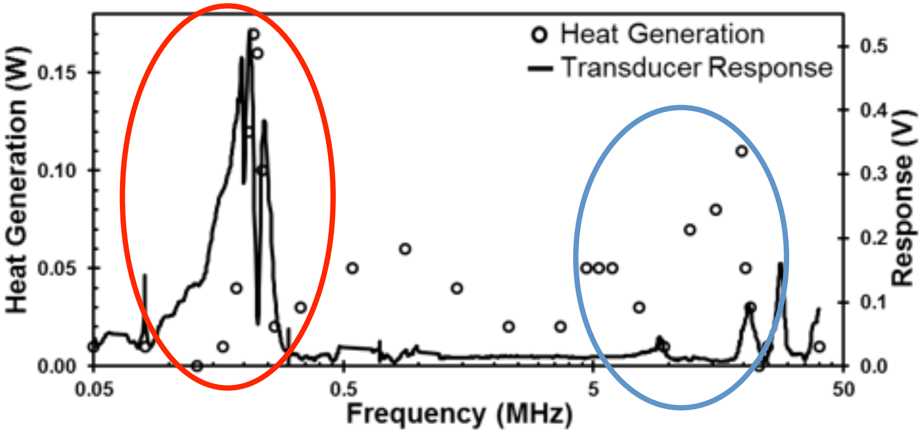


Particle-Scale Thermomechanics

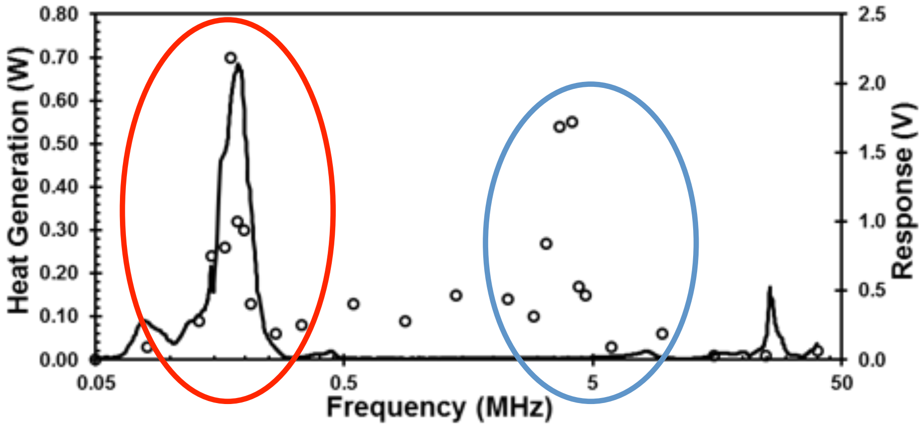


Particle-Scale Thermomechanics

PBX 9501, 215R

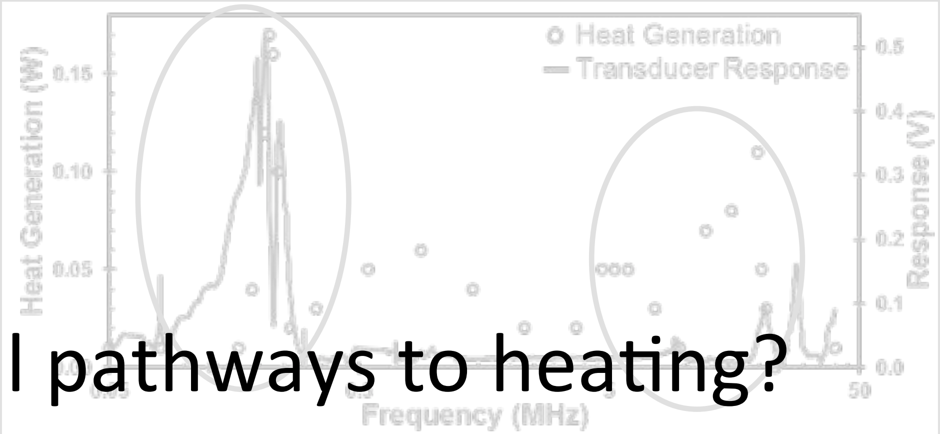


PBX 9501, 3400A



Particle-Scale Thermomechanics

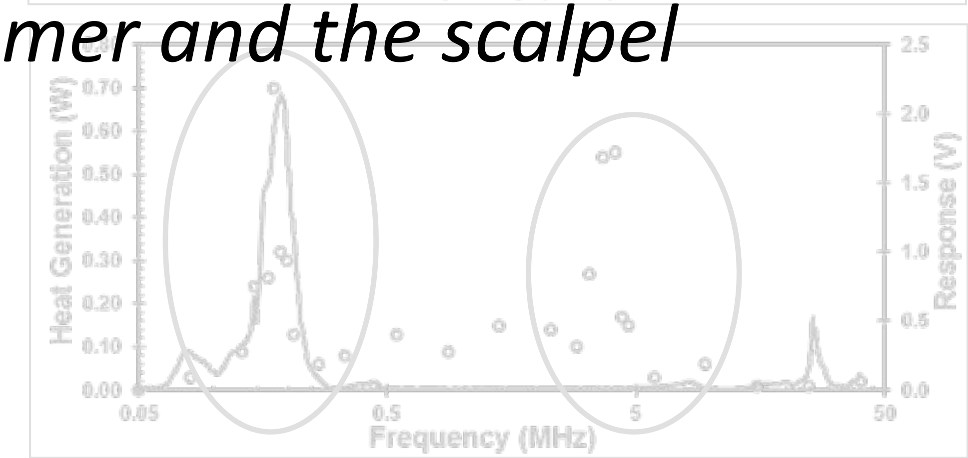
PBX 9501, 215R



Two potential pathways to heating?

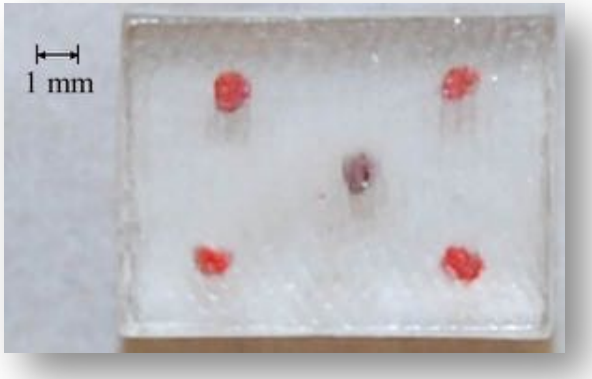
The hammer and the scalpel

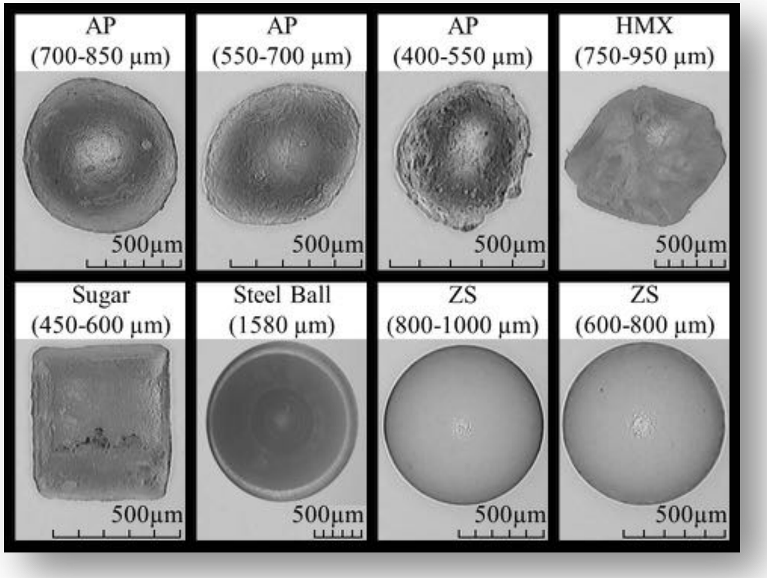
PBX 9501, 3400A



Particle-Scale Thermomechanics

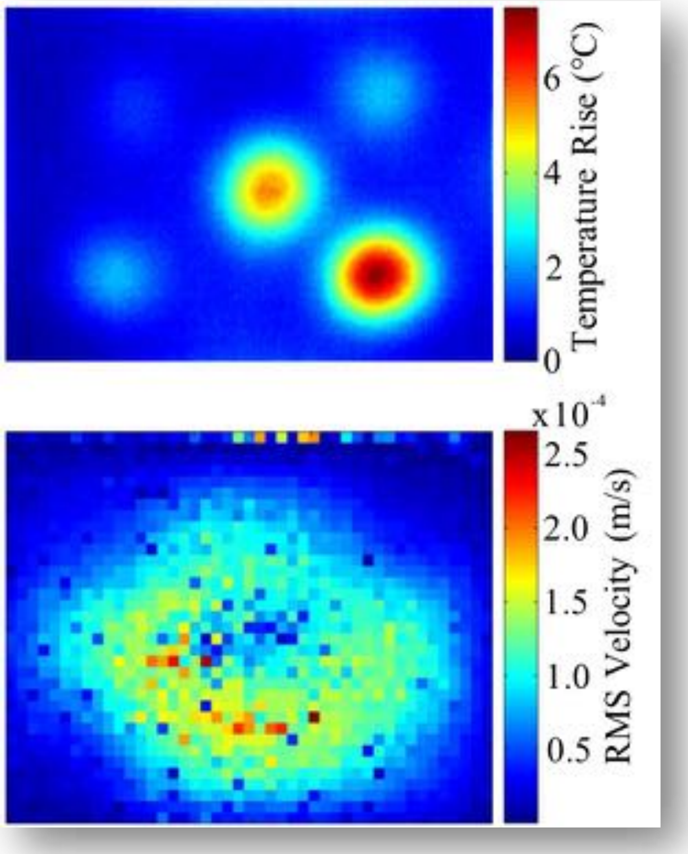
- Sylgard 184 embedded with various energetic and inert particles
  - 4.0 x 6.7 x 9.0 mm
  - Particles ~1.0 mm beneath surface
- Piezoelectric ultrasonic transducers epoxied to each sample
  - Radial excitation
  - 215 kHz resonance



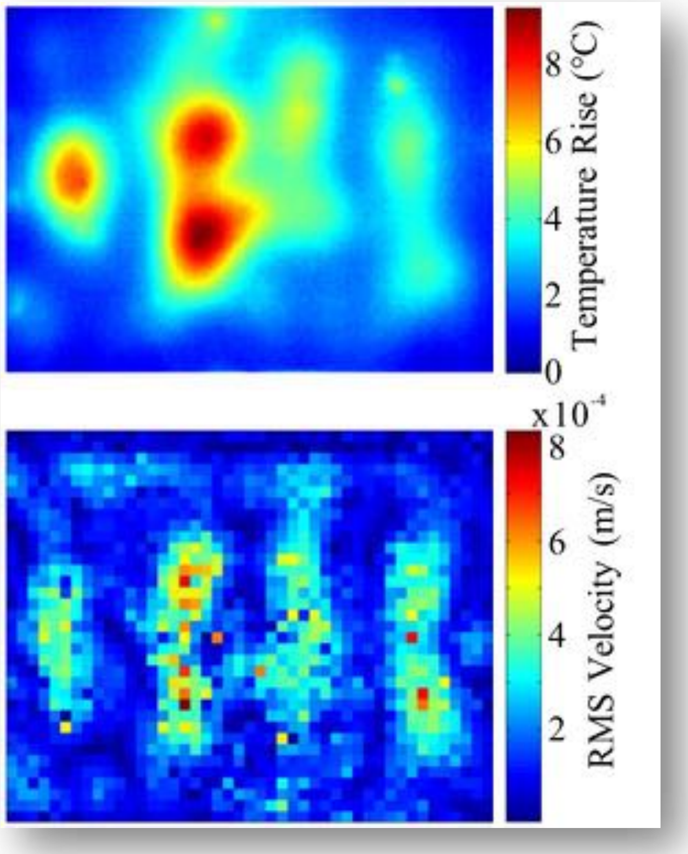


Particle-Scale Thermomechanics

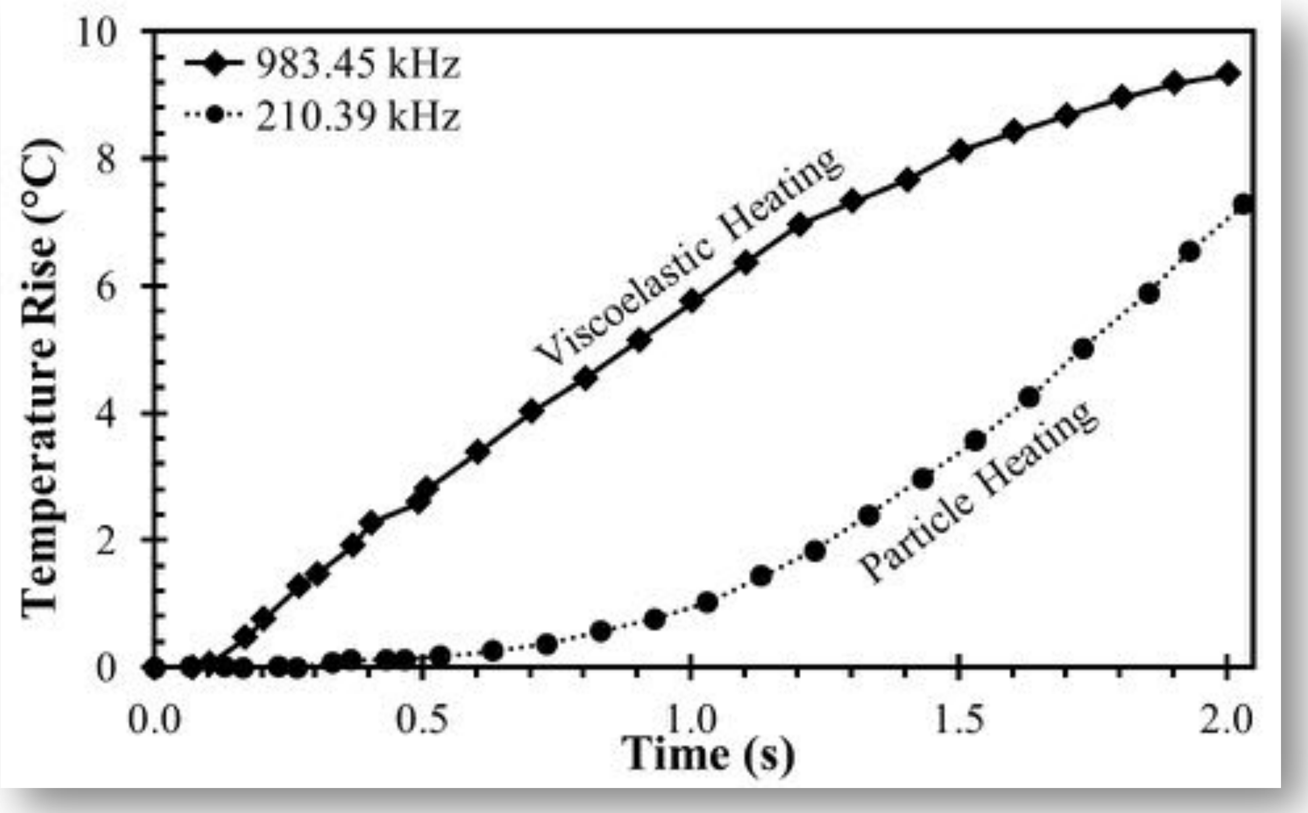
210.39 kHz



983.45 kHz

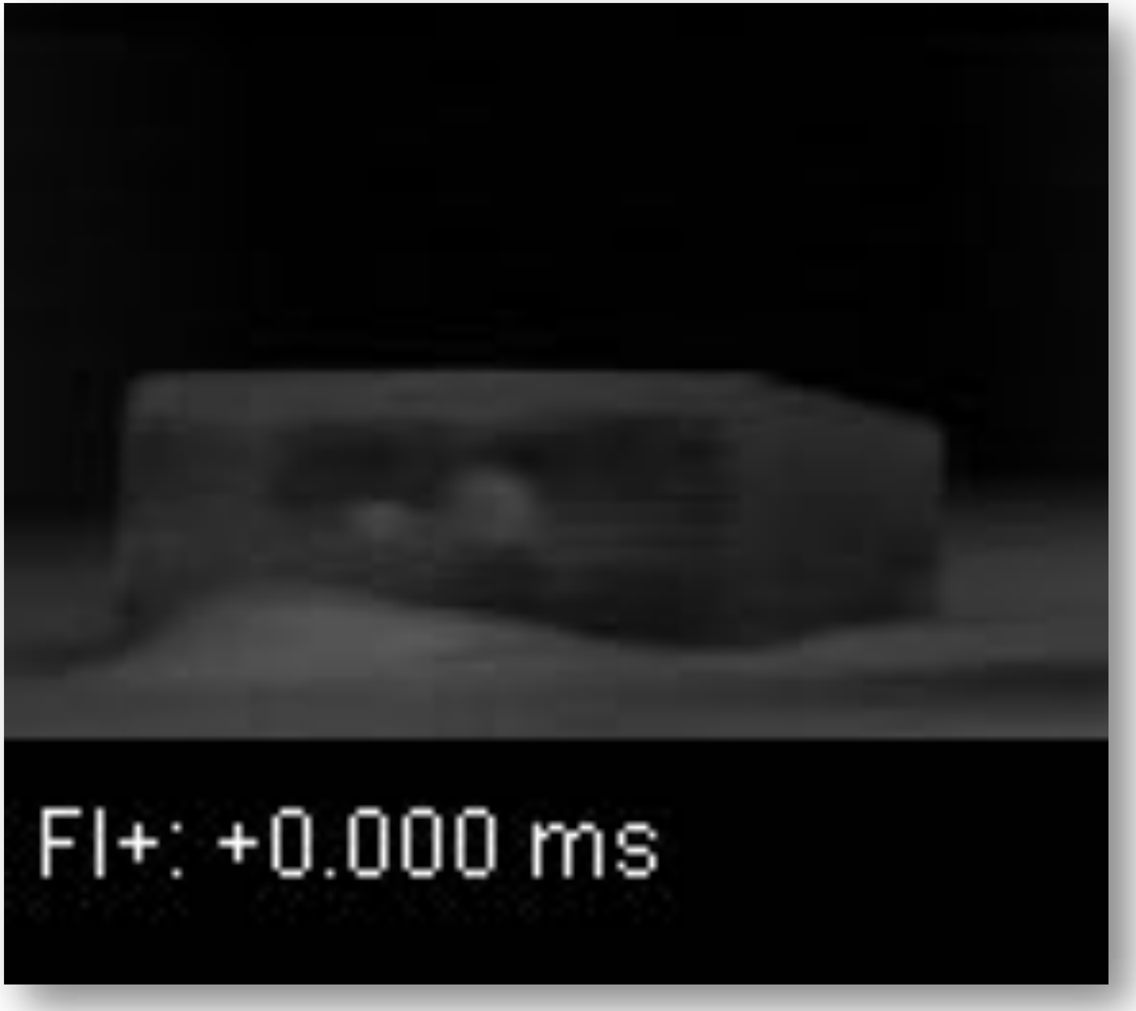


Particle-Scale Thermomechanics

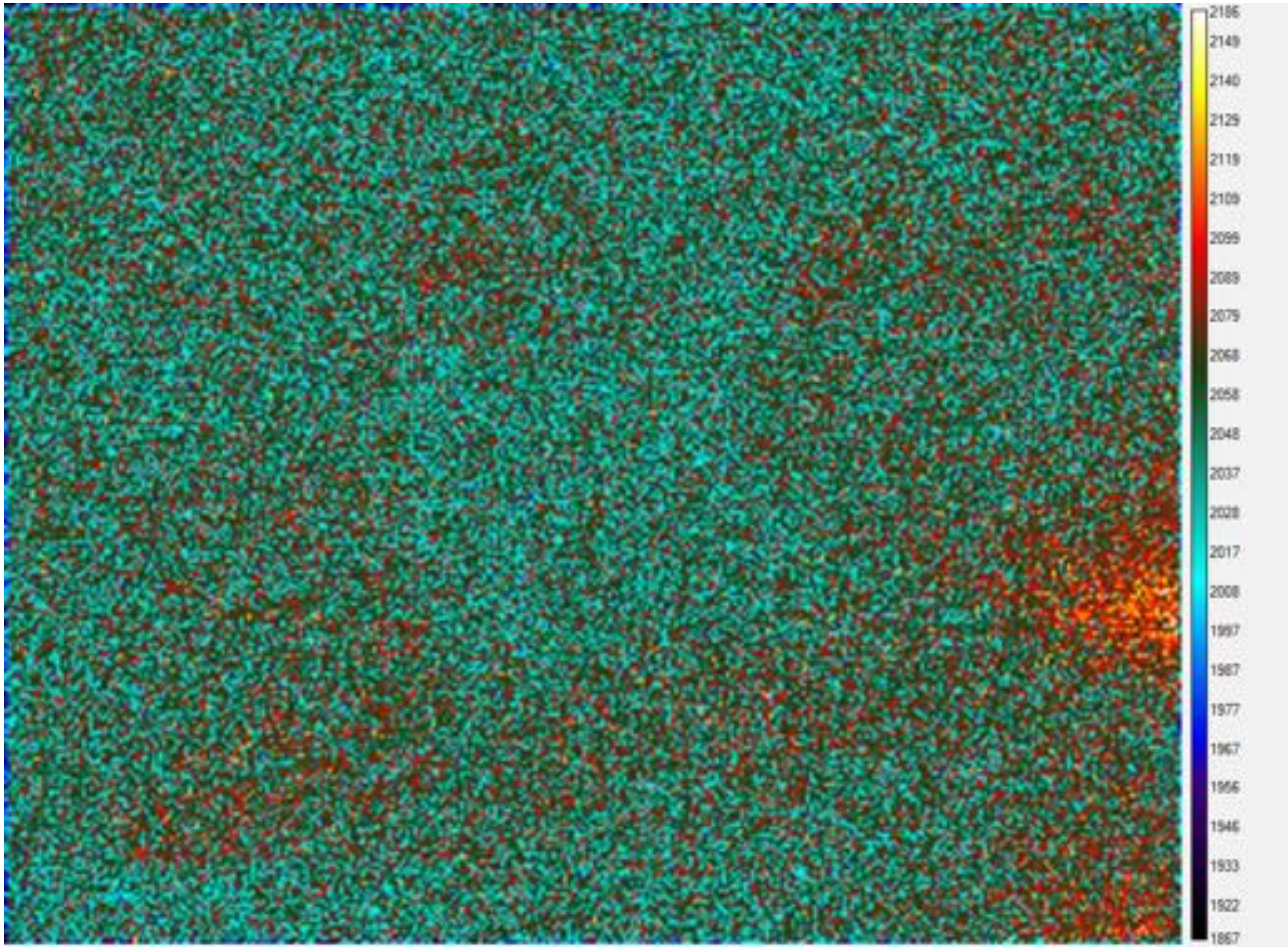


Particle-Scale Thermomechanics

AP (550-700 μm) sample at 10 Watts of supplied electrical power at 215 kHz. Total time to ignition ~8 seconds.



Particle-Scale Thermomechanical Interactions

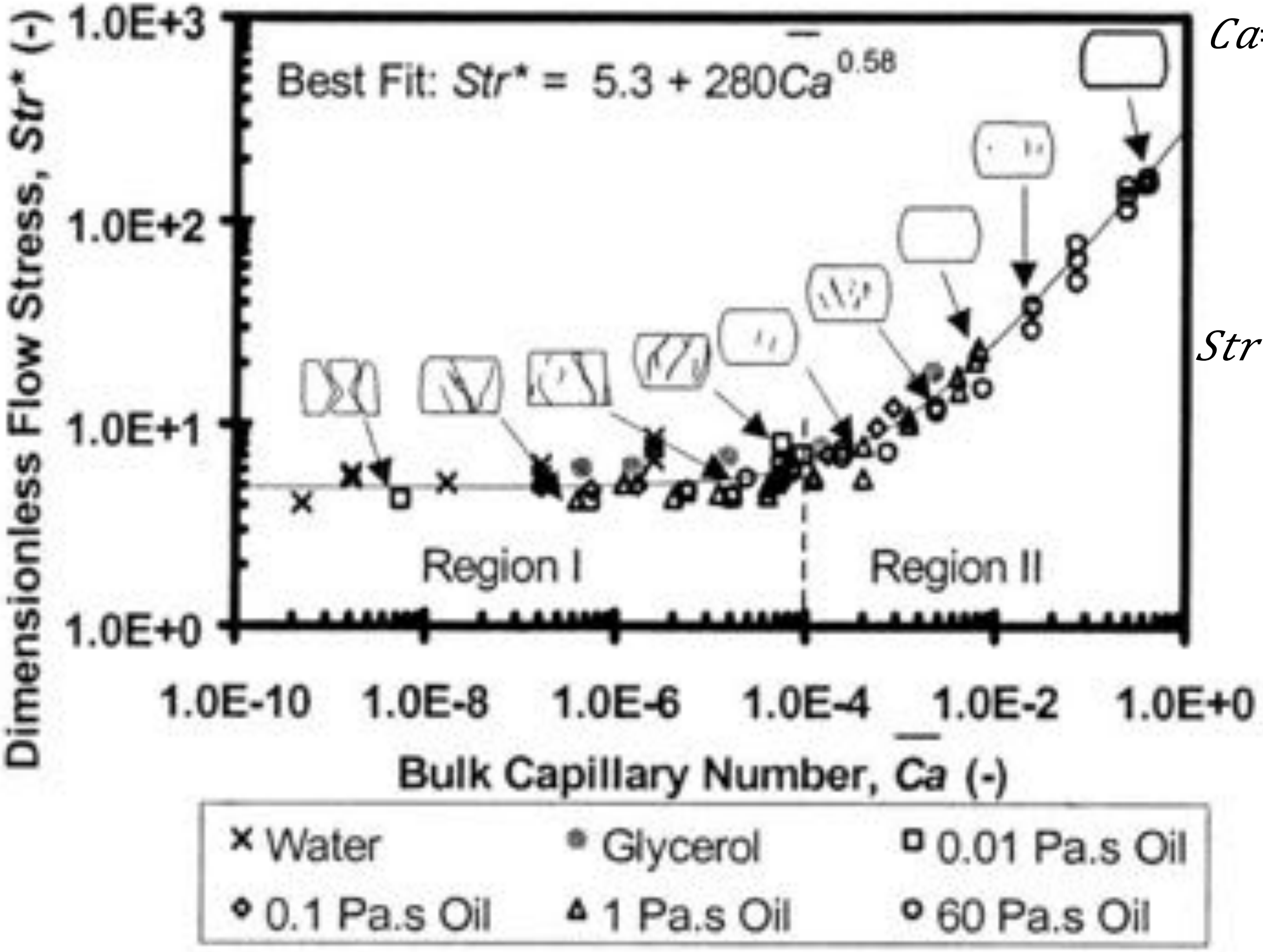


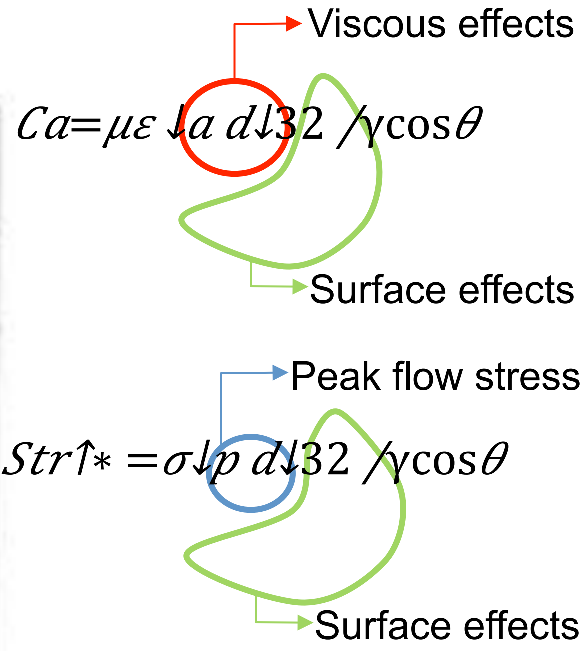
Trace Explosives Detection
Research at Purdue

Steve Beaudoin

Professor of Chemical Engineering
Academic Director ,Teaching and Learning Technology
Purdue University
West Lafayette, IN 47907
sbeaudoi@purdue.edu

- Measure adhesion between explosives residues and representative substrates
- Model observed adhesion
  - Quantify effects
    - Residue and substrate mechanical properties
    - Residue and substrate topography
    - Environmental conditions (humidity)
- Relate adhesion behavior to residue removal during contact sampling
  - Optimize composition and structure of swabs
  - Optimize swabbing protocols
- Develop benign surrogates for live explosives





Viscous effects

$Ca = \mu\varepsilon_a d_{32} / \gamma\cos\theta$

Surface effects

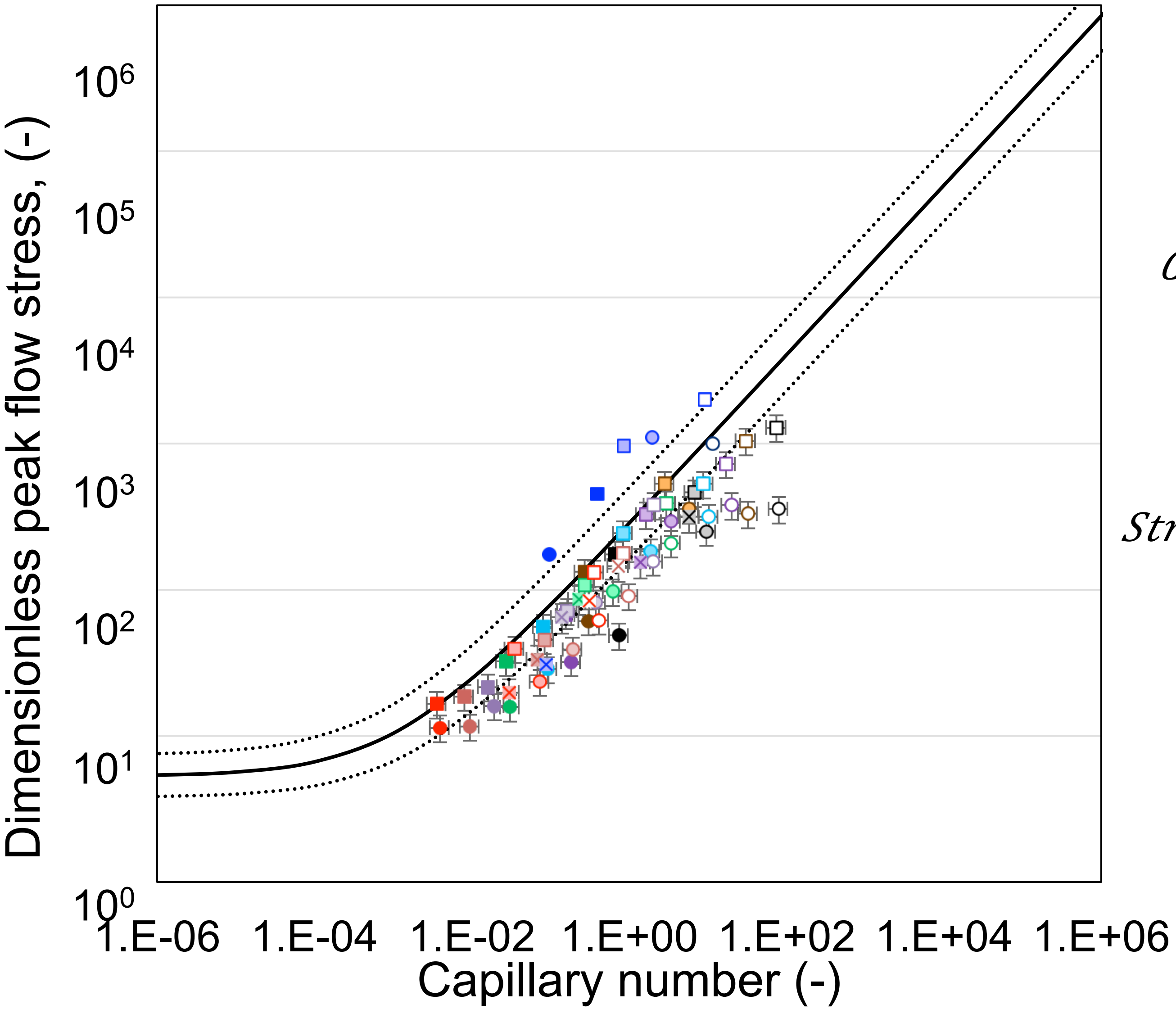
Peak flow stress

$Str^* = \sigma_p d_{32} / \gamma\cos\theta$

Surface effects

$Str^* = k_1 + k_2 Ca^n$

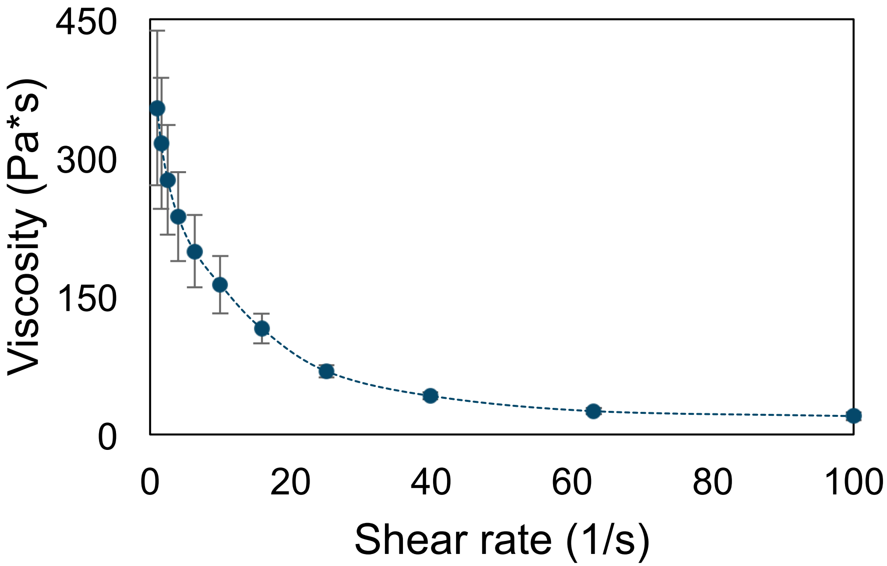
Iveson, S. M., & Page, N. W. (2004). Brittle to Plastic Transition in the Dynamic Mechanical Behavior of Partially Saturated Granular



$Ca = viscous\ effects/surface\ e$

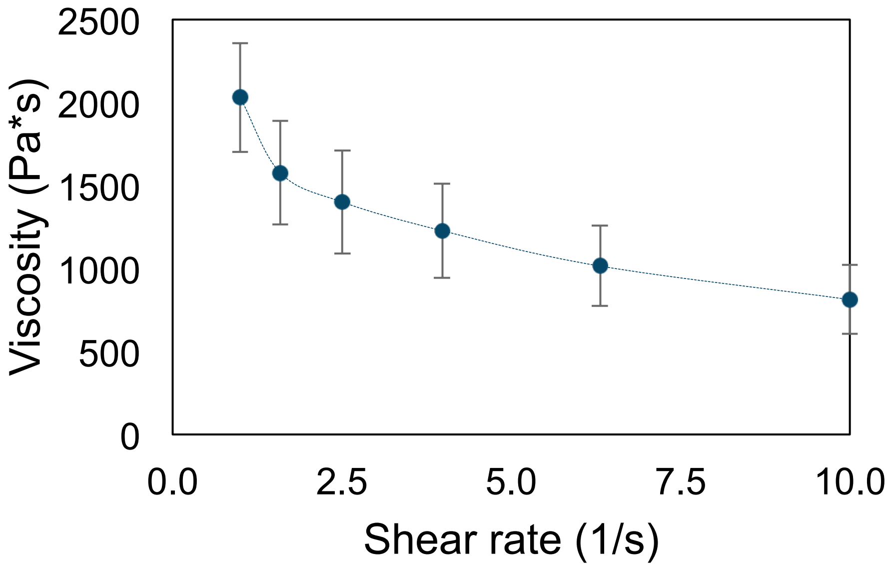
$Str^{*} = peak\ flow\ stress/surfac$

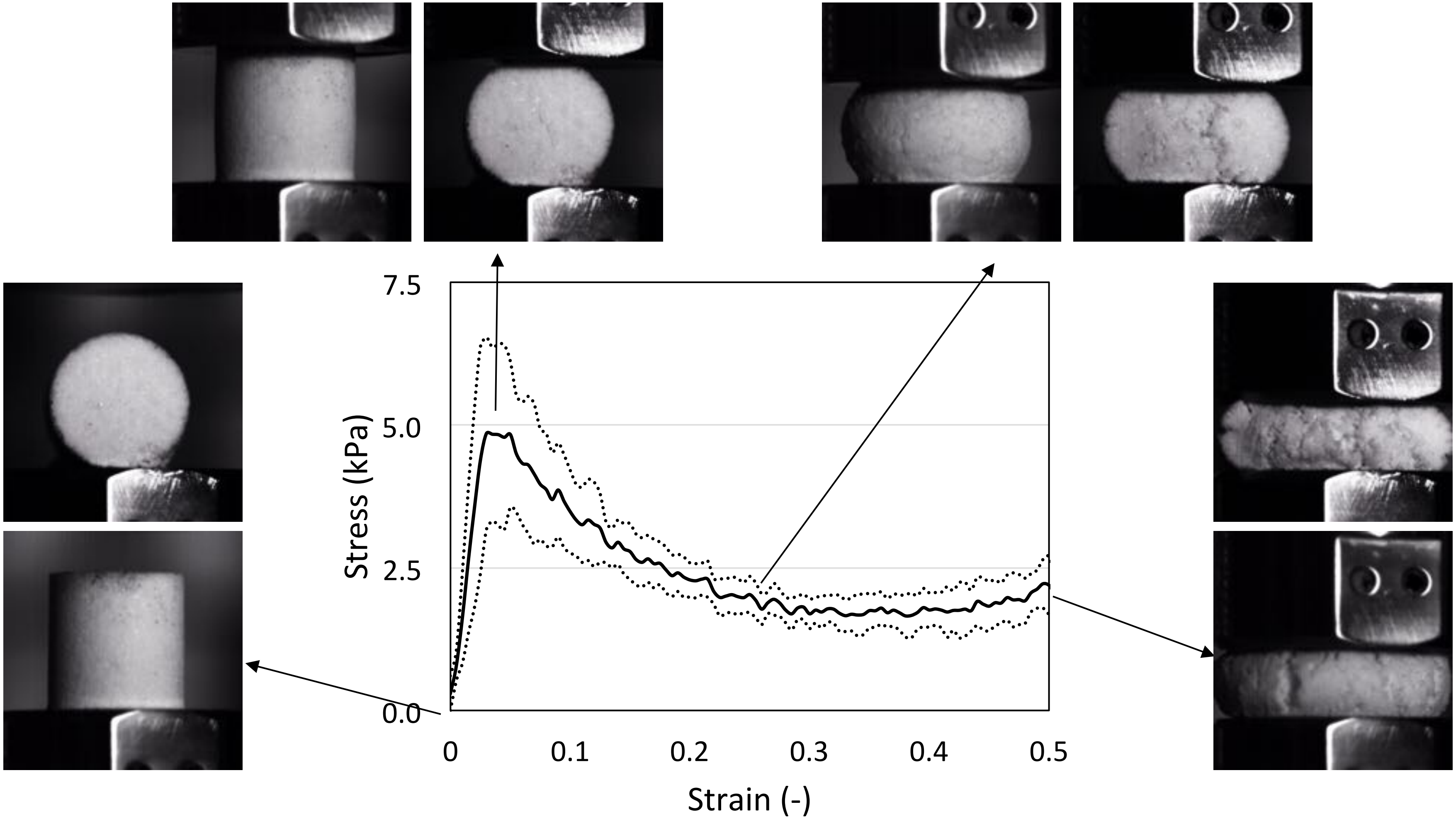
Behavior consistent with existing theory



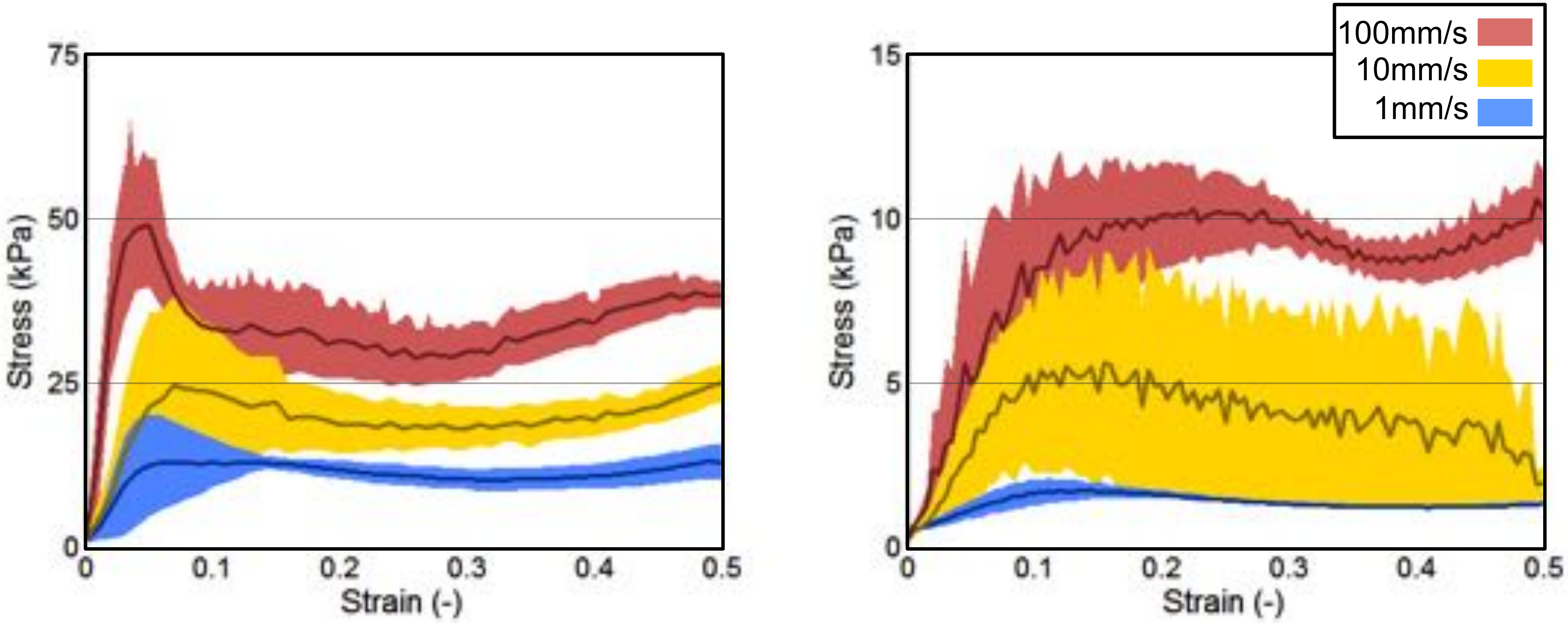
C-4 binder

Semtex H binder



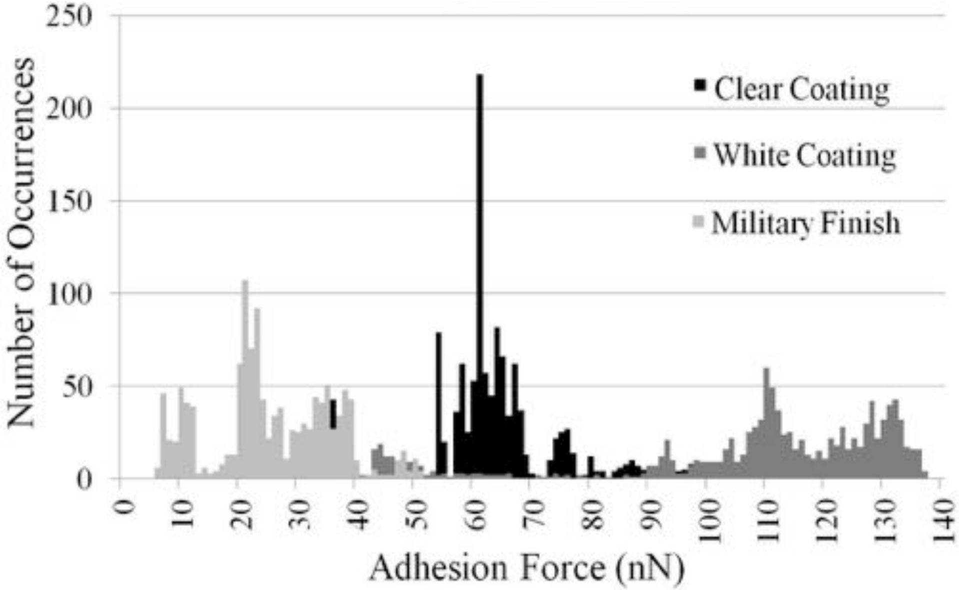


Stress-strain curve (with error regions) for silica particles (40-150mesh) in PDMS (60 Pa·s viscosity) at 10mm/s compression rate. Axial images shown bottom and left; diametrical are top and right.



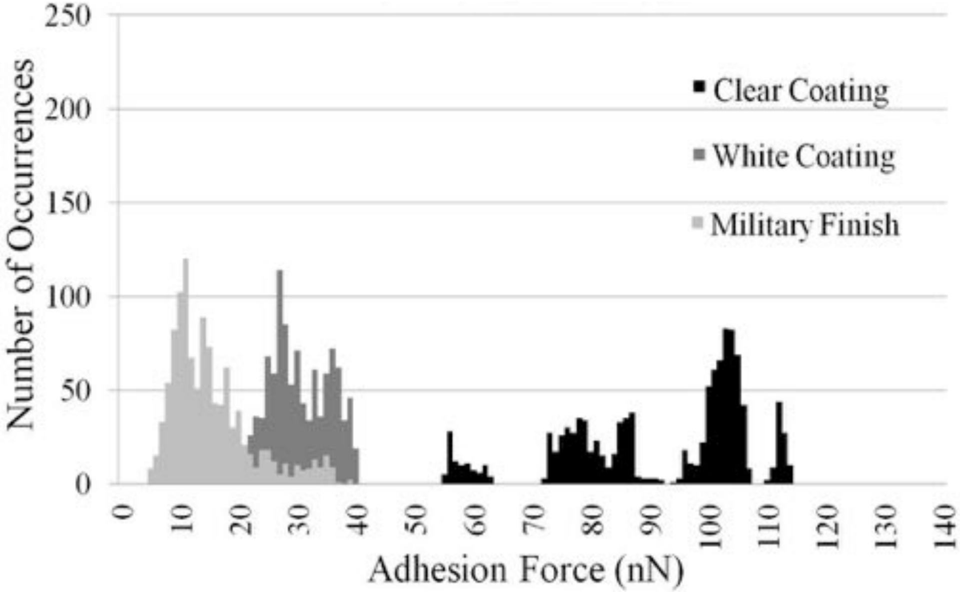
Stress-strain curves (with error regions) for live C-4 (left) and silica particles in simulated C-4 binder (right) at 1mm/s, 10mm/s, and 100mm/s compression rates.

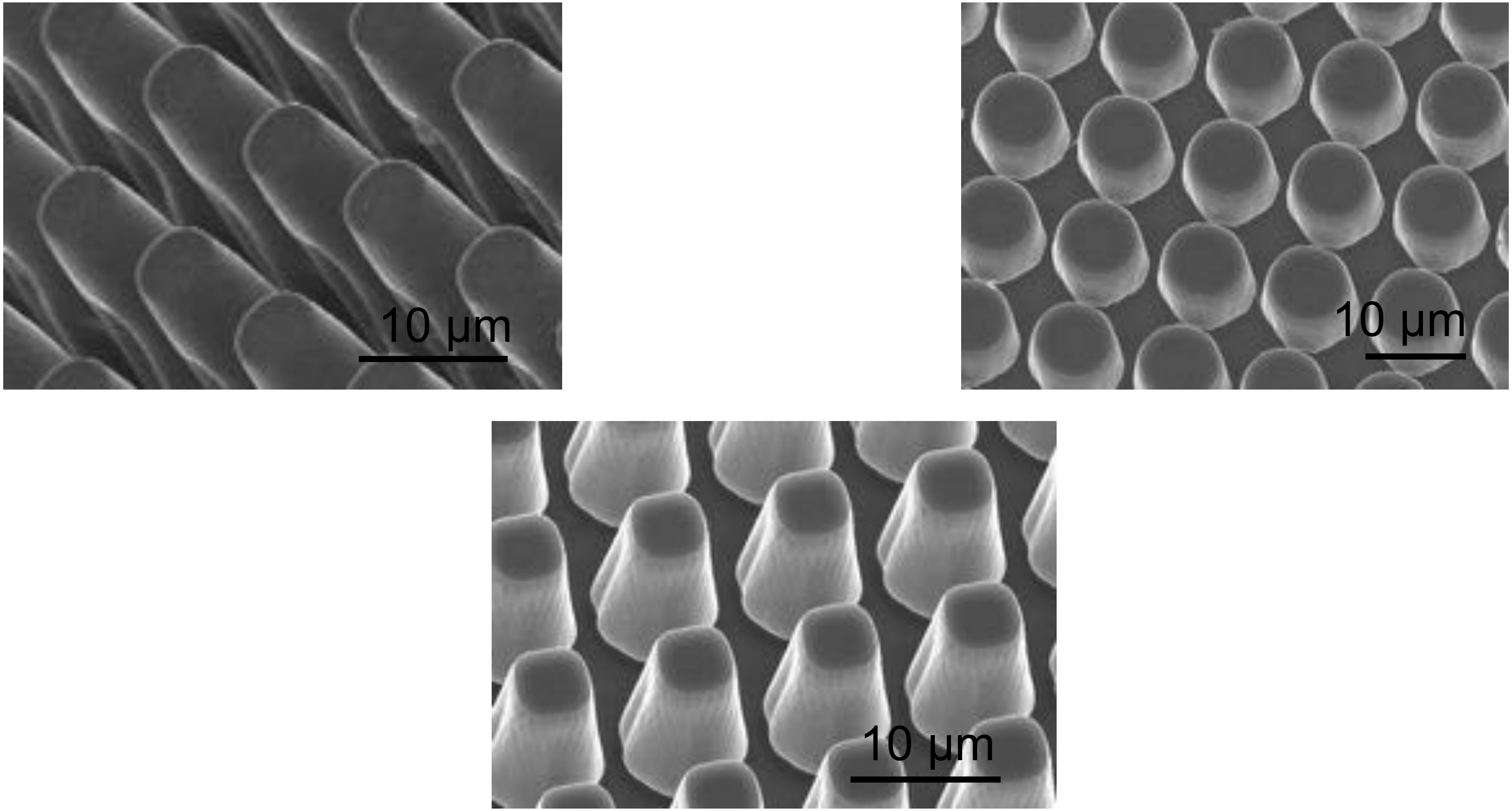
- Shape of profile for simulant matches that of live material
- Ongoing work: Vary particle size distribution in simulant to match magnitude of stress response



Adhesion between RDX and coated aluminum substrates

Adhesion between TNT and coated aluminum substrates





SEM images of polypyrrole pillars of varying aspect ratio. The dimensions of the pillars can be easily tuned by changing the photolithographic template.

Circled:
- Melissa Sweat
  - Dec. 2015
- Aaron Harrison
  - Dec. 2015

Not pictured:
- Johanna Smith
  - Grad. May 2014
  - Employed at General Mills
- Andrew Parker
  - Grad. May 2016
- Chris Browne
  - Grad. May 2017
- Alyssa Bass
  - Grad. May 2017

This material is based upon work supported by the U.S. Department of Homeland Security, Science and Technology Directorate, Office of University Programs, under Grant Award 2013-ST-061-ED0001. The views and conclusions contained in this document are those of the authors and should not be interpreted as necessarily representing the official policies, either expressed or implied, of the U.S. Department o

The Future?

- **Performance**
  - Room for improvement - NOT 10x, probably not even 5x
  - That's OK – a few inches of extra reach can determine the outcome of a boxing match
  - Tailored particles, tunability, microenergetics, and switchability also
- **Sensitivity**
  - IHE requirements will continue to drive research
- **Life cycle**
  - Environmental & toxicity drivers
  - Additive manufacturing
  - Aging

AFOSR, DHS, ARO, ONR, DTRA, NASA, & MDA funding

NSF, NDSEG, SMART, NASA Fellowships

Purdue University Zucrow Labs
Energetics Laboratory

Questions?

Purdue Propulsion