Hierarchical theoretical methods for understanding and predicting anisotropic thermal transport and energy release in rocket propellant formulations

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Overview

- Research designed to yield understanding and predictive capability regarding ***anisotropic thermal transport*** and ***energy release*** in ***advanced rocket propellants***:
  - *Practical capability for a priori propellant design*
  - *Polymer nanocomposite formulations augmented by non-traditional additives or passivation agents*
- Study and exploit ***anisotropy*** at three levels:
  - ***Intrinsic*** *anisotropy at the molecular up to the continuum microscale for pure constituents*
  - ***Manufactured*** *nano- and microscale anisotropy that is induced by manufacture specifications of the composition*
  - ***Mesoscale*** *anisotropy persistence during the physico-chemical structural decomposition, mixing, and reaction*

ATTENTION!

(Caltech focus!)

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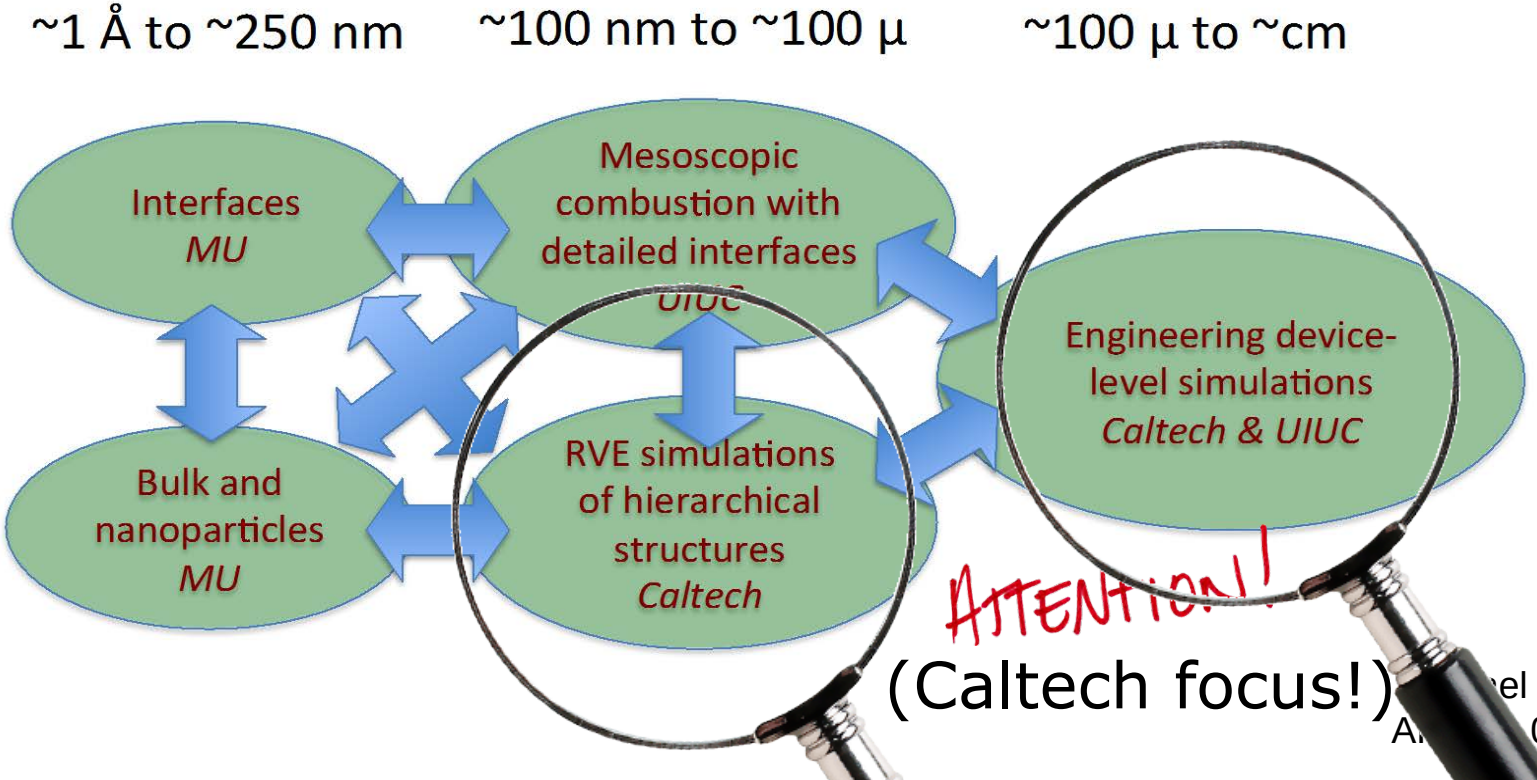
Approach

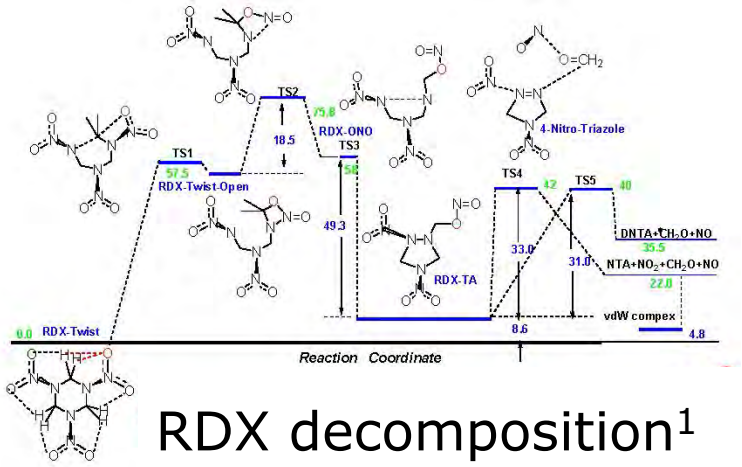
- Fundamental information from atomic-scale simulations
- Detailed mesoscopic models of interfaces and reaction fronts
- Microstructure-resolved RVE-simulations to generate homogenized models
- Engineering-scale models for propellant combustion



The fundamental challenge

10^{-15} s, 1 nm

10^{3} s, 10 m



RDX decomposition[1]

Space Shuttle Atlantis[2]

- Energetic materials undergo complex chemistry coupled to temperature and deformation
- Reactions take place at atomic scale, involve bond breaking and creation of new bonds
- Reaction paths are extremely complex, defy reduce modeling
- Full chemistry, reaction-front speeds on the order of seconds
- Outside scope of straight MD…

[1]R. Asatryan, G. da Silva, J.W. Bozzelli (2008), 20th Intern. Symp. on Gas-Kinetics, Manchester, UK.

[2]http://www1.nasa.gov/images/

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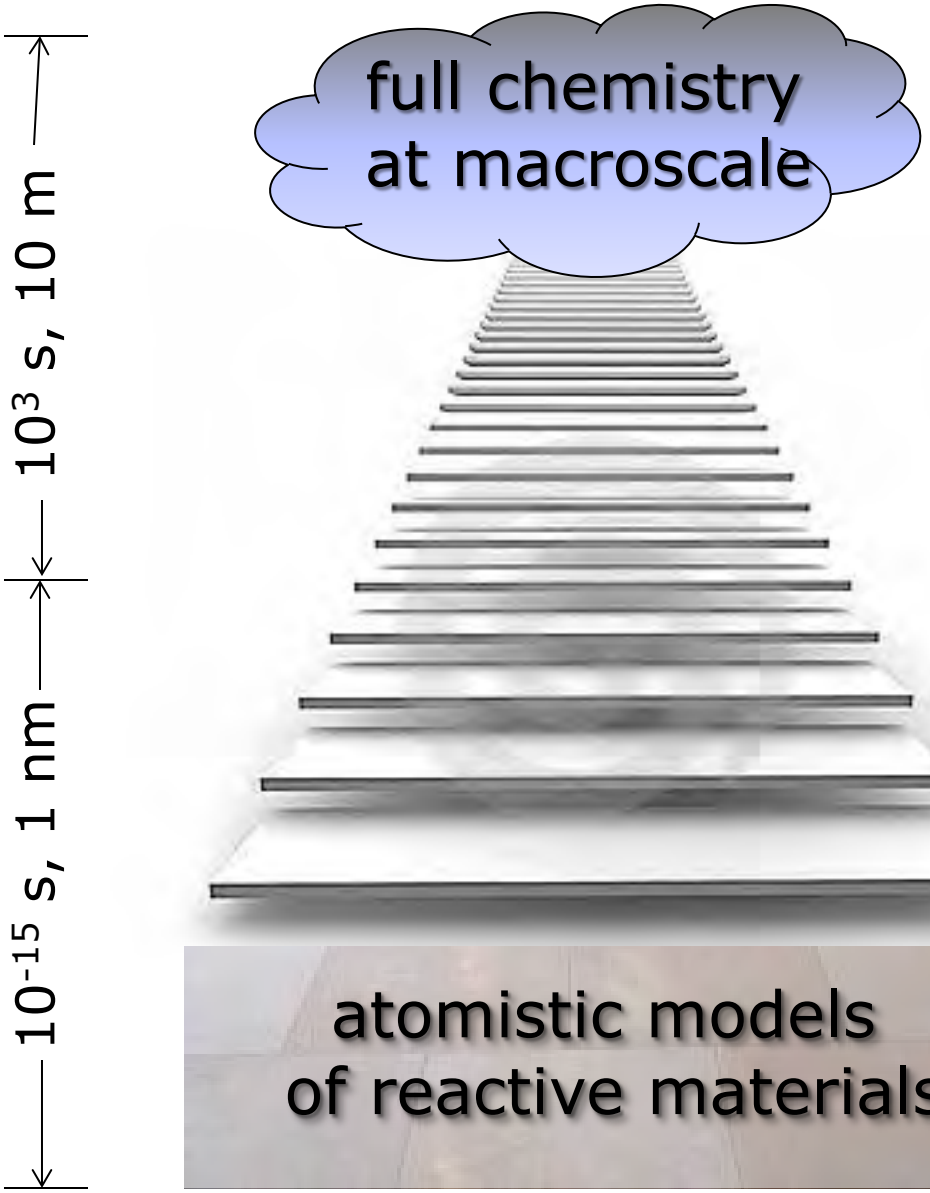
The fundamental challenge



femtosecond
and Angstrom
curse!

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Atomistic-to-continuum methods

- The essential difficulty: Multiple scales,
  - *Atomic level rate-limiting processes: Thermal vibrations, bond breaking, collisions, atomic hops…*
  - *Macroscopic processes of interest: Burn rates, kinetics, effect of microstructure, anisotropy, specific impulse…*
- Time-scale gap: From thermal vibrations (femtosecond) to device operation (seconds)
- Spatial-scale gap: From atomic lattice scale (Angstroms) to device dimensions (m)
- Application to solid propellants:
  - *Wish atomistic realism within reaction zone…*
  - *But reaction kinetics is too slow for MD*
  - ***Question**: How to effect space-time coarse-graining (atoms to device) without introducing spurious physics and without essential loss of information?*

Spacetime atomistic-to-continuum

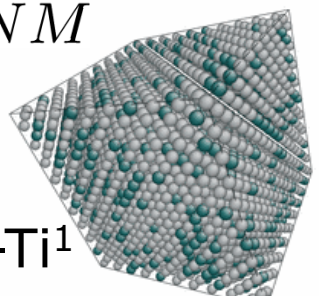
- *Objectives*: Thermodynamics without all the thermal vibrations; mass transport without all the hops; atomistics without all the atoms…
- Our approach[1,2] (max-ent+kinetics+QC):
  - *Treat atomic-level fluctuations statistically (away from equilibrium) through **maximum-entropy principle***
  - *Approximate grand-canonical free entropy using **variational meanfield theory***
  - *Append Onsager-like **empirical atomic-level kinetic laws** (heat and mass transport)*
  - *Treat (smooth) **mesodynamics** by implicit integration (large time steps >> MD!)*
  - ***Quasicontinuum** spatial coarse-graining*

[1]Y. Kulkarni, J. Knap & MO, *J. Mech. Phys. Solids*, **56** (2008) 1417.

[2]G. Venturini, K. Wang, I. Romero, M.P. Ariza & MO, *J. Mech. Phys. Solids*, **73** (2014) 242-268.

Max-Ent Non-Equilibrium SM

- Grand-canonical ensemble, N atoms, M species:
  - State: $(\{\boldsymbol{q}\},\{\boldsymbol{p}\},\{\boldsymbol{n}\}) \in \mathbb{R}^{3N} \times \mathbb{R}^{3N} \times \mathcal{O}_{NM}$
  - Atomic positions: $\{\boldsymbol{q}\} = \{\boldsymbol{q}_1,\ldots,\boldsymbol{q}_N\}$
  - Atomic momenta: $\{\boldsymbol{p}\} = \{\boldsymbol{p}_1,\ldots,\boldsymbol{p}_N\}$



Al-Ti[1]

  - Occupancy: $n_{ik} = \begin{cases} 1, & \text{site } i \text{ occupied by species } k, \\ 0, & \text{otherwise.} \end{cases}$

- Ensemble average of observable: $\langle A \rangle =$

$$\sum_{\{\boldsymbol{n}\}\in\mathcal{O}_{NM}} \int A(\{\boldsymbol{q}\},\{\boldsymbol{p}\},\{\boldsymbol{n}\})\ \rho(\{\boldsymbol{q}\},\{\boldsymbol{p}\},\{\boldsymbol{n}\})\, dq\, dp$$

grand-canonical pdf

J. von Pezold, A. Dick, M. Friak and J. Negebauer, Phys. Rev. B, 81 (2010) 094203.

Max-Ent Non-Equilibrium SM

- Assume $H = \sum_{i=1}^{N} h_i$, (e. g., EAM, TB...)
- Principle of max-ent[1]: $\mathcal{S}[p] = -k_B \langle \log \rho \rangle \rightarrow$ max!

  subject to: $\left.\begin{aligned} \langle \boldsymbol{q}_i \rangle = \bar{\boldsymbol{q}}_i, \;\; \langle \boldsymbol{p}_i \rangle = \bar{\boldsymbol{p}}_i, \\ \langle h_i \rangle = e_i, \;\; \langle n_{ik} \rangle = x_{ik} \end{aligned}\right\}$ local constraints!

- Lagrangian: reciprocal temperatures ↓ β, chemical potentials ↓ γ

$$\mathcal{L}[p, \{\beta\}, \{\gamma\}] = \mathcal{S}[p] - k_B \{\beta\}^T \{\langle h \rangle\} - k_B \{\gamma\}^T \{\langle \boldsymbol{n} \rangle\}$$

- Gran-canonical pdf: $\rho = \frac{1}{\Xi} \mathrm{e}^{-\{\beta\}^T \{h\} - \{\gamma\}^T \{\boldsymbol{n}\}}$,

on affine subspace $\left\{ \langle \{\boldsymbol{q}\} \rangle = \{\bar{\boldsymbol{q}}\}, \langle \{\boldsymbol{p}\} \rangle = \{\bar{\boldsymbol{p}}\} \right\}$

[1]E.T. Jaynes, *Physical Review Series* II, **106**(4) (1957) 620–630; **108**(2) (1957) 171–190.

Non-Equilibrium Statistical Mechanics

- From max-ent principle, free entropy:

$$\Phi(\{\beta\}) = k_B \log \int \mathrm{e}^{-\{\beta\}^T \{h(q,p)\}}\, dq\, dp$$

reciprocal atomic temperatures

local atomic Hamiltonians

- Mesoscopic dynamics:

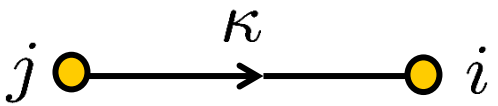
$$\frac{d\bar{\boldsymbol{q}}_i}{dt} = \frac{1}{k_B}\frac{\partial^2 \Phi}{\partial \beta_i \partial \bar{\boldsymbol{p}}_i}, \qquad \frac{d\bar{\boldsymbol{p}}_i}{dt} = -\frac{1}{k_B}\frac{\partial^2 \Phi}{\partial \beta_i \partial \bar{\boldsymbol{q}}_i}$$

- Temperature field evolution, discrete heat equation:

$$\frac{d}{dt}\underbrace{\frac{1}{k_B}\frac{\partial \Phi}{\partial \beta_i}}(\{\beta\}) = \sum_{j \neq i} \underbrace{\partial \psi(\beta_i - \beta_j)}$$

internal energy of atom *i*

heat flux into atom *i*



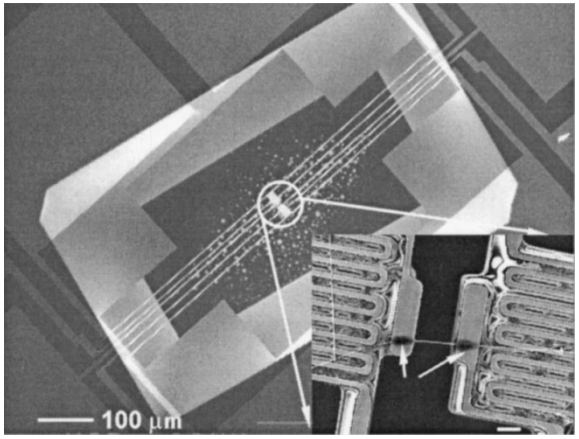
Non-Equilibrium Statistical Mechanics

	Molecular dynamics	N.E. Stat. Mech.
Configuration space	Phase space *(q,p)*	•Temperature field •Atomic-fraction field
Governing equations	ΣF=ma	•Diffusive transport •Mesodynamics
Spatial resolution	Atomic lattice	•Temperature grads. •Concentration grads.
Temporal resolution	•Thermal vibrations •Transition states	•Mesoscopic dynamics •Diffusional transients
Time-scale bridging	Non-equilibrium statistical mechanics	
Spatial-scale bridging	Quasicontinuum method	

- Paradigm shift: From Newtonian dynamics to diffusional transport (heat and mass)
- Time step limited by diffusional time scale!

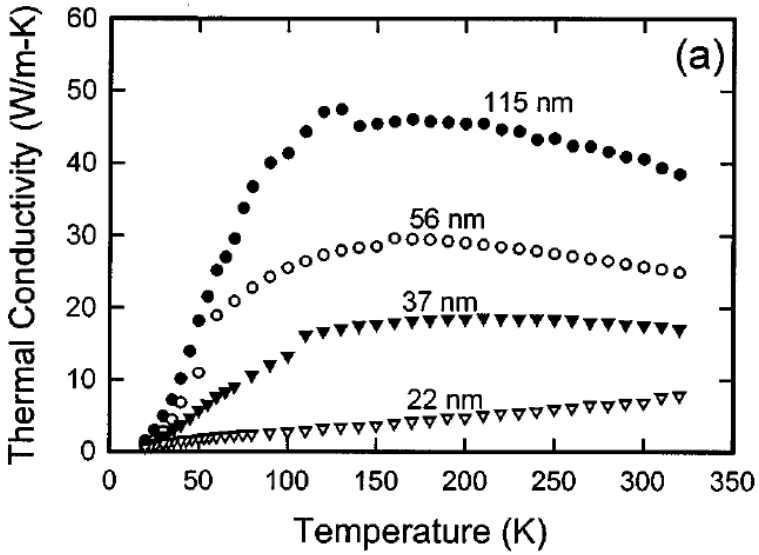
Y. Kulkarni *et al.*, *J. Mech. Phys. Solids*, **56**:1417-1449, 2008

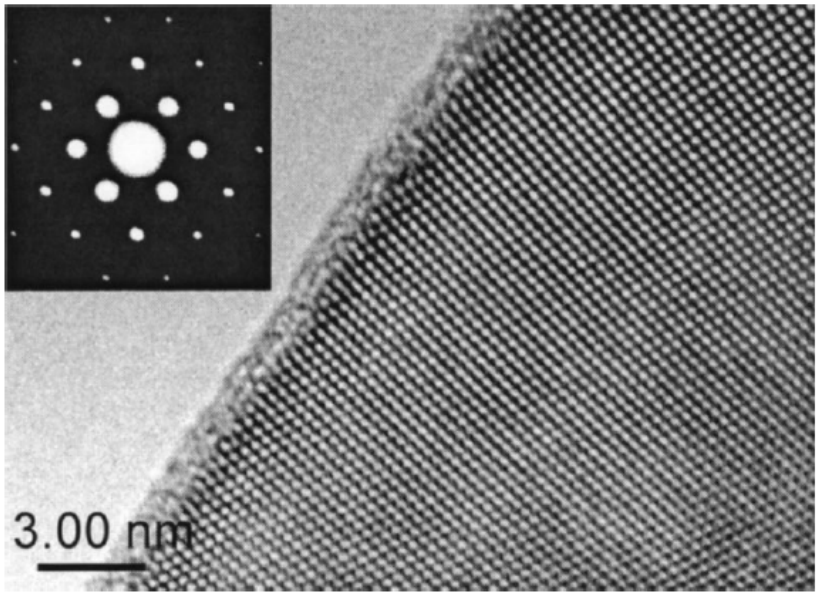
Kinetic validation – Si nanowires



Experimental rig[1]

- Si (111) nanowires[1]
- Radius = 11, 18.5, 28, 57.5 nm
- Data: Thermal conductivity
- Predictive challenge: Size effect!

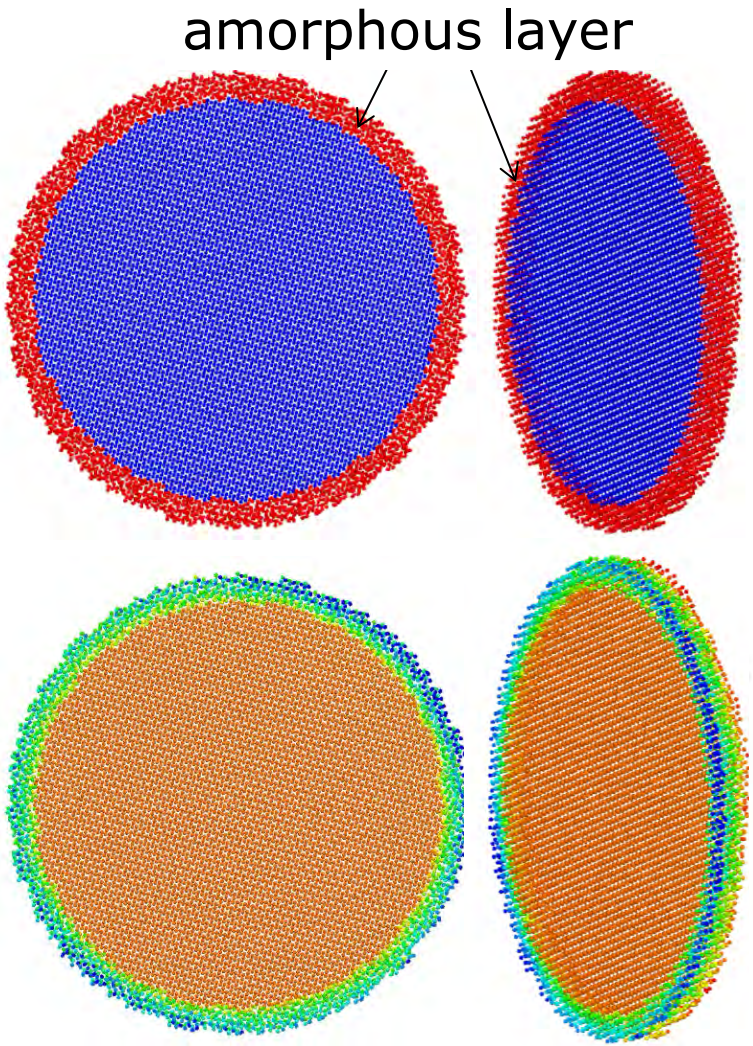




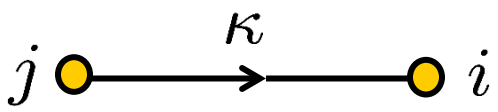
Amorphous layer in SiNW!

[1]D. Li, Y. Yu, P. Kim, L. Shi, P. Yang and A. Majumdar, *Appl. Phys. Let.*,**83** (2003) 2934.

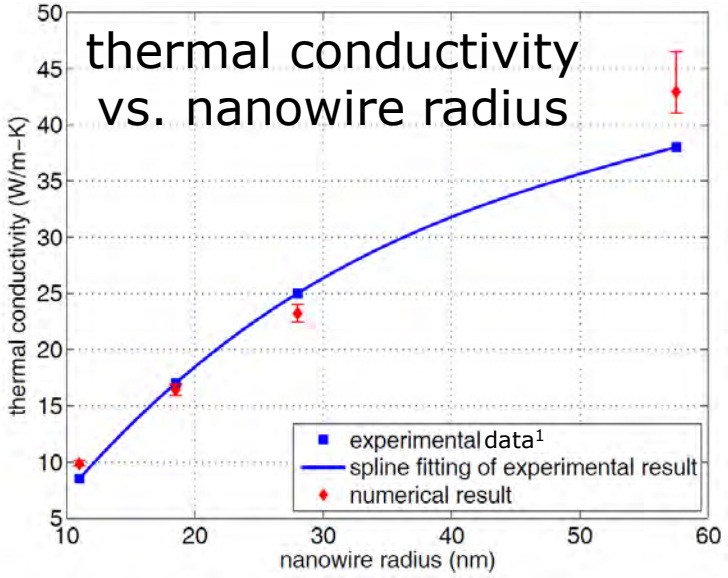
Kinetic validation – Si nanowires



Temperature distribution



- Rigid model, linear kinetics
- κ_{xal} = 0.09 nW/K, κ_{amo} = 16 nW/K
- Prescribed temperature gradient
- Output: Average axial heat flux



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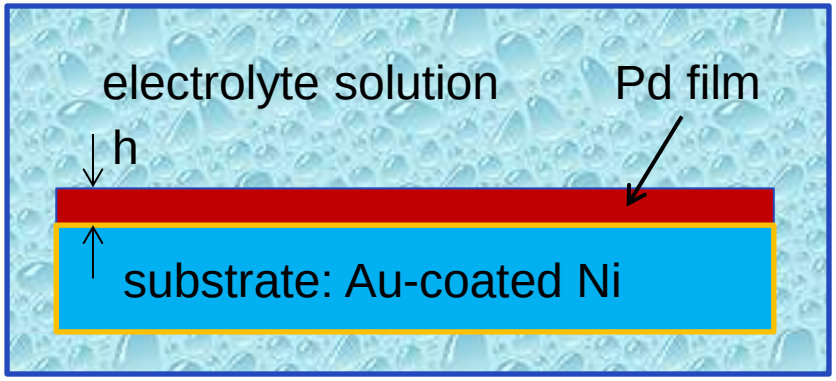
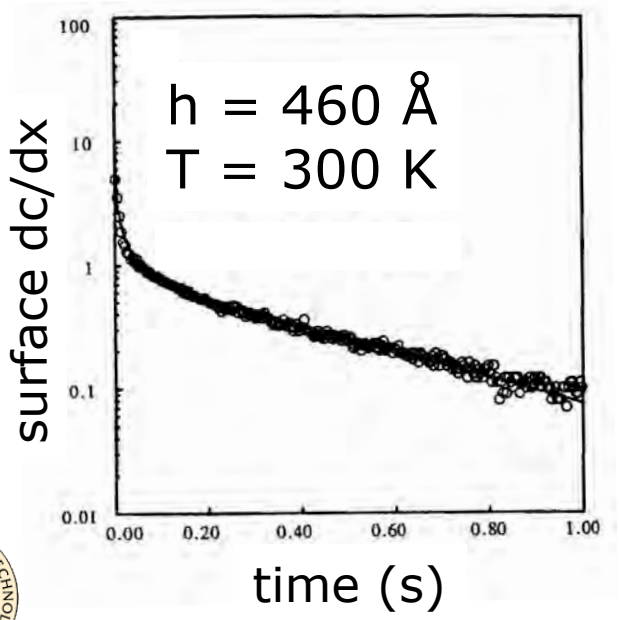
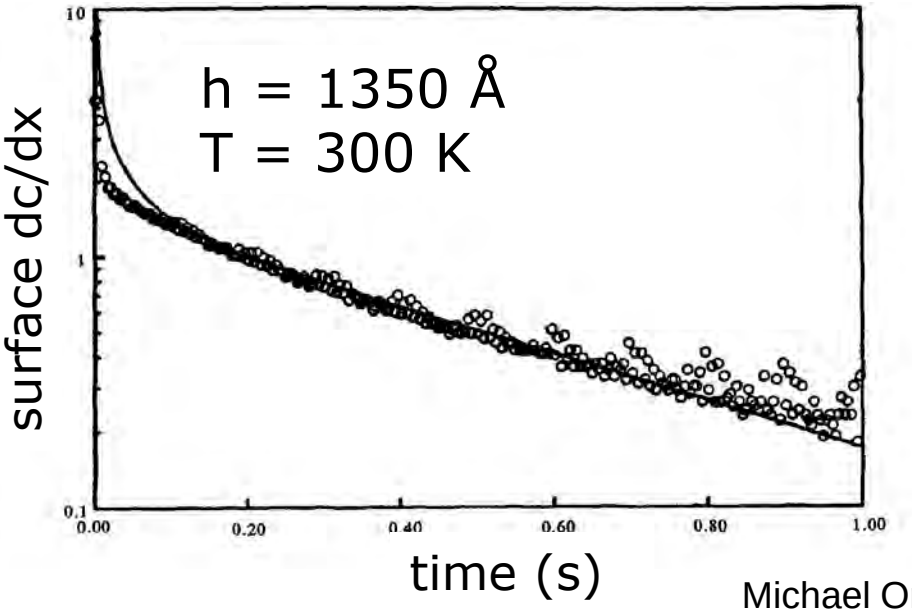
Kinetic validation – H absorption in Pd



- H absorption into (111) Pd foil[1]
- Foil thickness = 460, 1350 Å
- Temperature = 300K
- Measurement: Surface concentration gradient vs. time

Experimental configuration[1]





[1]Y. Li and Y.-T. Cheng,, *Int. J. Hydrogen Energy*, **21** (1996) 281-291.

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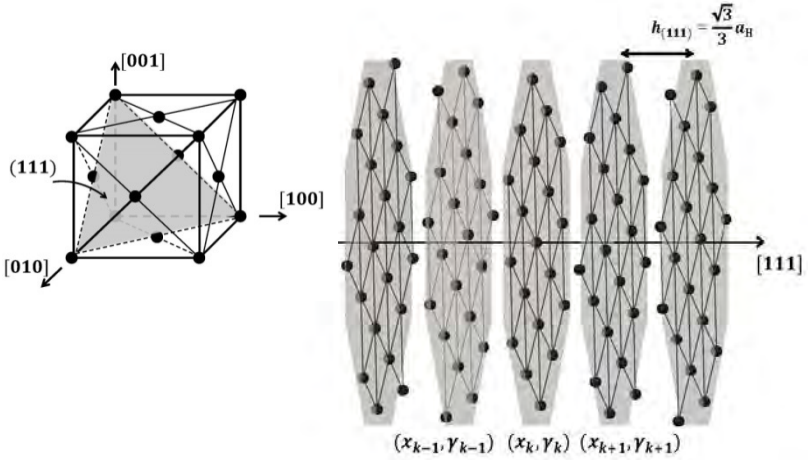
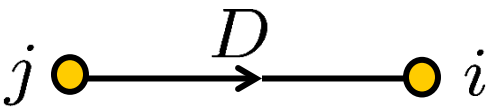
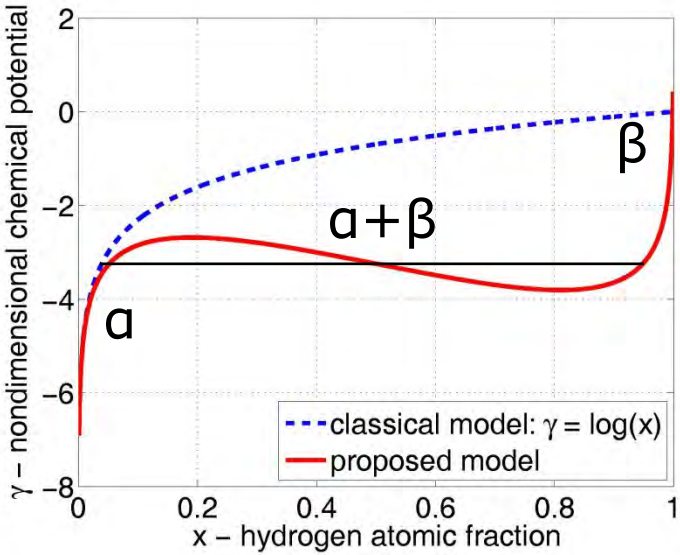
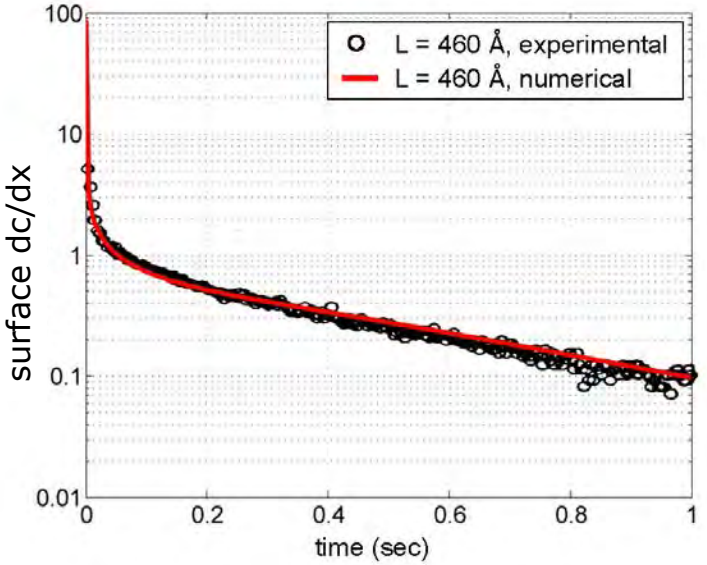


Pd foil crystallography



- Linear kinetics, D = 2.1x10^5 Å^2/s
- Ising-type meanfield model
- Johnson EAM potential[1]
- Prescribed surface concentration
- Output: Surface dc/dx vs. time





[1]R. Johnson, *Phys. Rev. B*, **39**(17):12554, 1989

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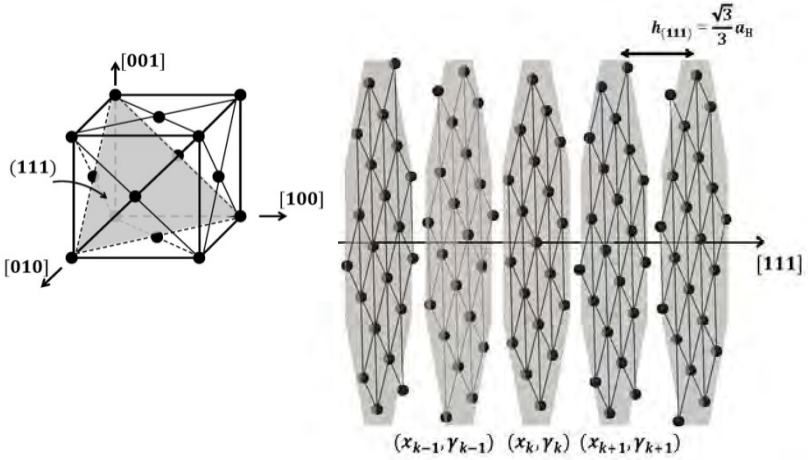

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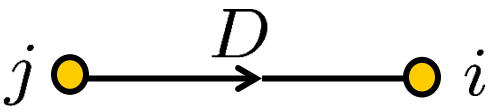

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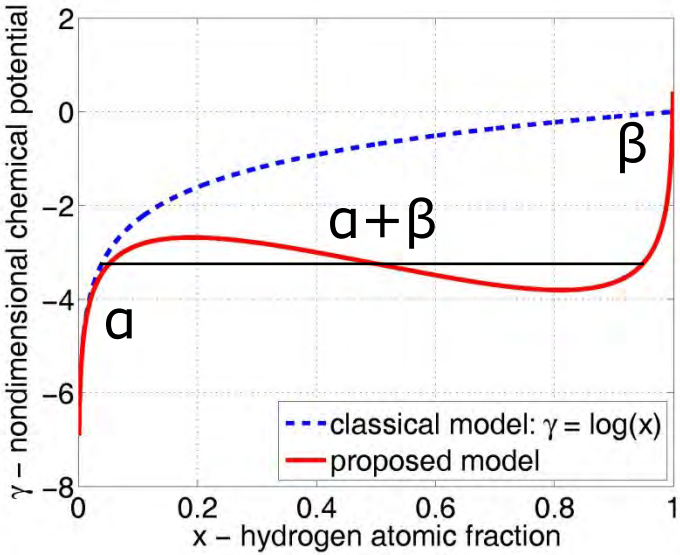

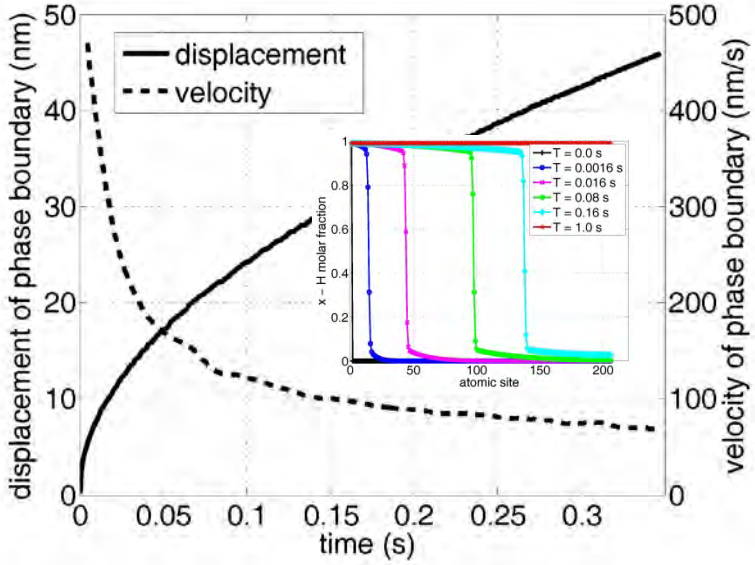

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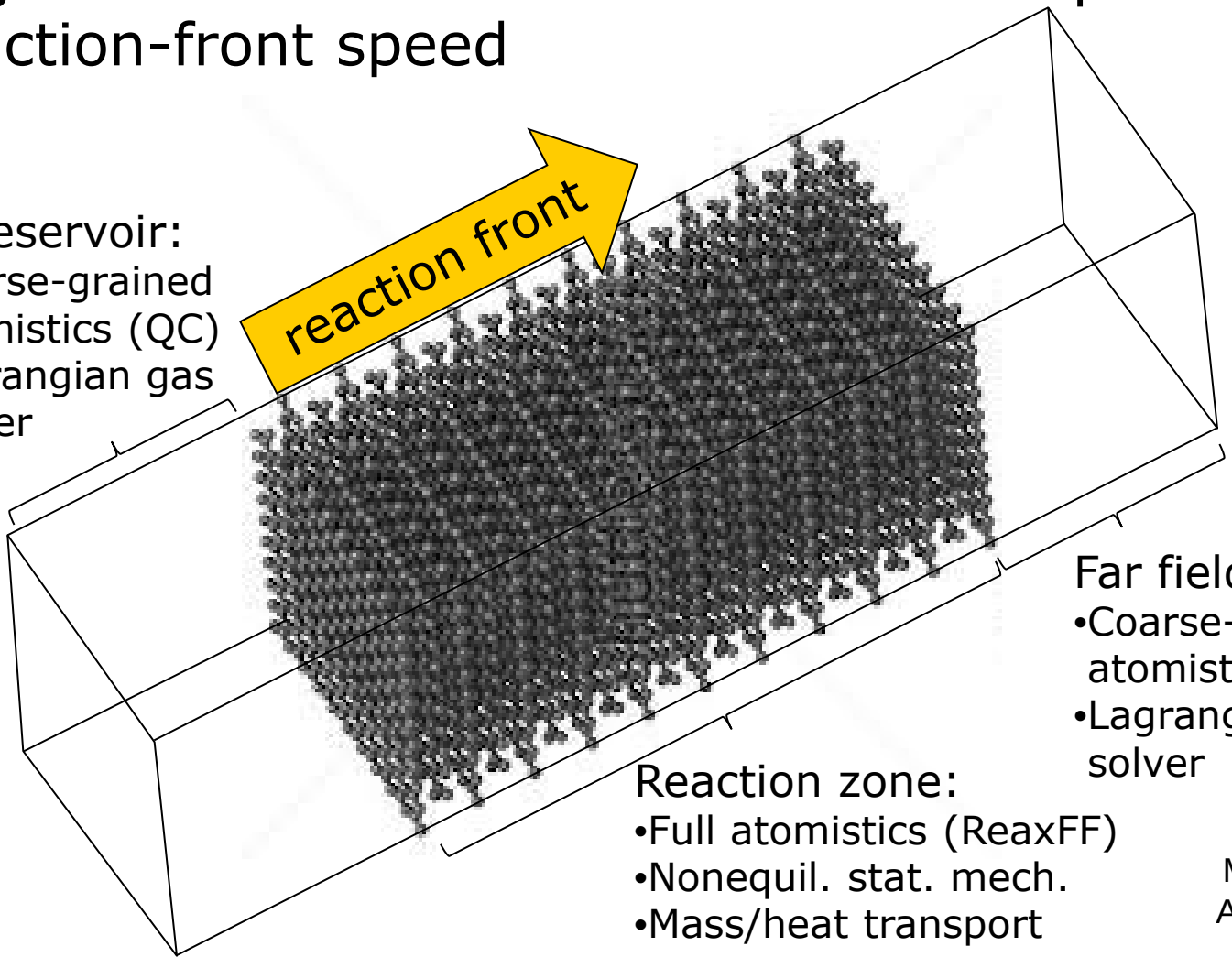
Non-Equilibrium Statistical Mechanics

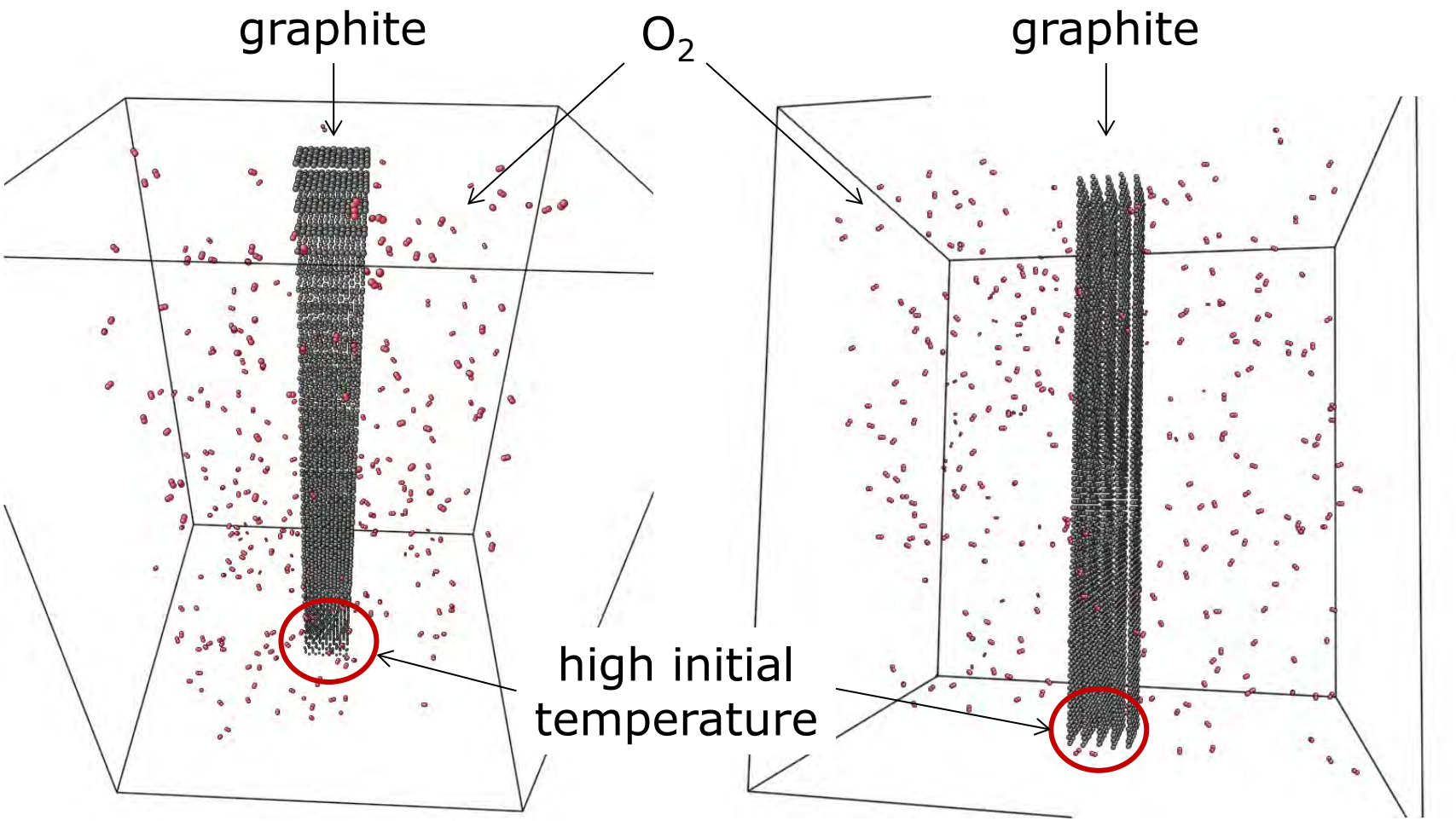
- N.E. Stat. Mech. (max-ent + kinetics) provides atomistic realism without the femtosecond curse
- Time step is limited by diffusive scale
- N.E. Stat. Mech. is built on arbitrary interatomic potentials + kinetic models
- ***Challenge***: Applications involving chemical reactions (modeled through reactive force fields, e.g., ReaxFF)
- Expect chemical reaction rates to be controlled by heat transport/anisotroy

N.E. Stat. Mech. + Quasicontinuum

- Test case: Combustion of graphite (anisotropy!)
- Objective: Calculation of orientation-dependent reaction-front speed



Graphite + O_2 – Calculations in progress

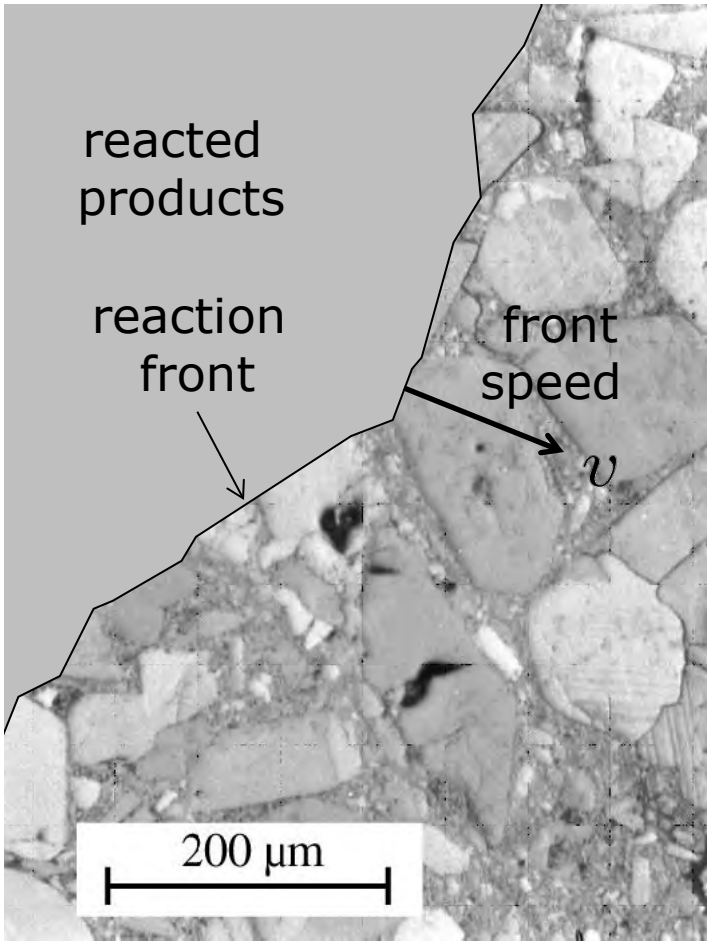


- Interatomic potentials: ReaxFF/LAMMPS
- Calibration *vs.* thermal conductivities

Outlook: Optimal propellant microstructures

- Build on fundamental information from atomic-scale calculations:
  - *Orientation-dependent reaction-front speed*
  - *Anisotropic thermal conductivity tensor*
- Parameterize microstructures of interest:
  - *Composites: Polymer binder + oxidizer granules + additives (e.g., NH_4ClO_4 Composite Propellant, APCP)*
  - *Parameters: volume fractions, texture, morphology…*
- Simulate passage of reaction fronts through representative volume elements (front tracking)
- Determine effective/macroscopic burning rates
- Optimize microstructure for ***maximum specific impulse***

Front-tracking (Hamilton/Jacobi) in heterogeneous/anisotropic media



H. Tan, iMechanica, 2008

- Fermat's principle (rays):

$$T = \min_{\text{paths}} \int_0^L \frac{ds}{v(x(s), x'(s))}$$

propagation speed

propagation direction

- Lagrangian: $L(x, x') = \dfrac{1}{v(x, x')}$
- Ray equations:

$$\dot{x}(s) = \nabla_\xi H(x(s), \xi(s))$$

$$\dot{\xi}(s) = -\nabla_x H(x(s), \xi(s))$$

- Front (eikonal) equation:

$$H(x, \nabla u(x)) = E$$

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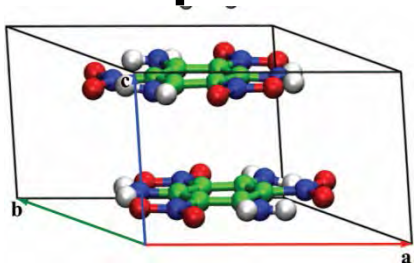
Development of methods to identify optimal propellant microstructures

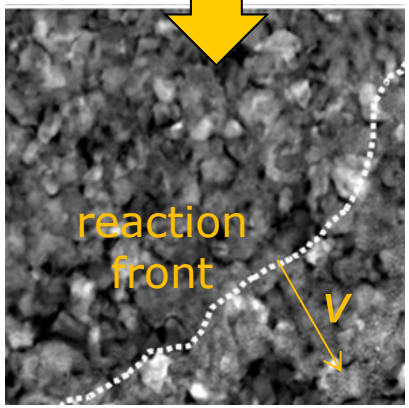


Anisotropic thermal conductivity of TATB
(Kroonblawd & Sewell, *J. Chem. Phys.*, 2013)

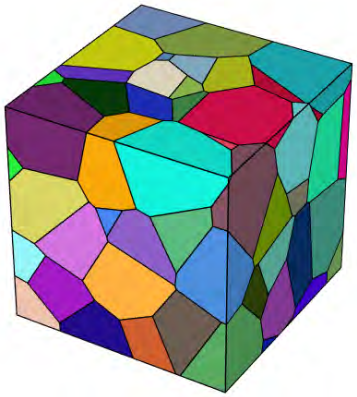
- Microstructure/specific impulse relation?
- Optimal microstructures?

Optimizer (e.g., genetic algorithm)

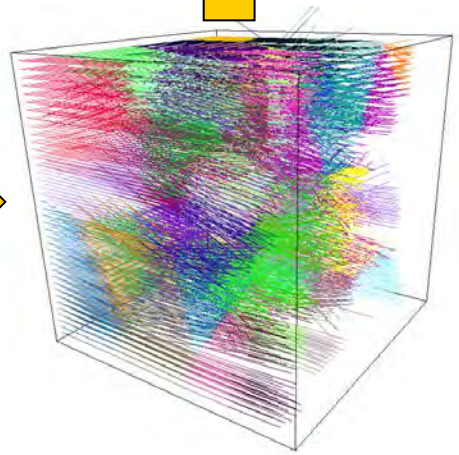
Objective function (e.g., mean reaction front speed)



Anisotropic reaction-front propagation speed



Parameterized microstruture (e.g., Voronoi tessellation)



Reaction front tracking calculation (ray tracing)

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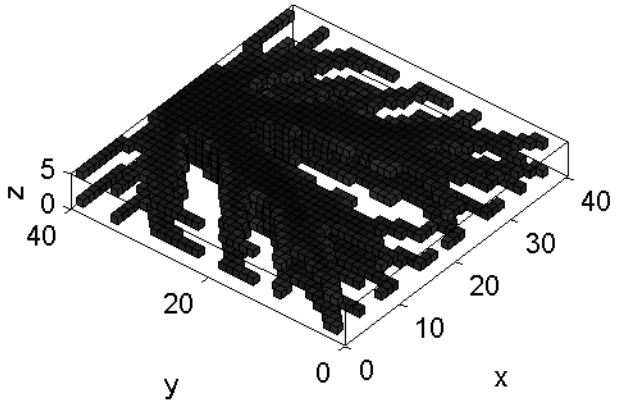
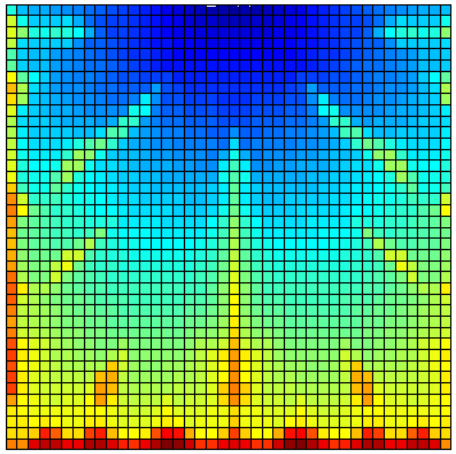
Test case: Heat Conduction





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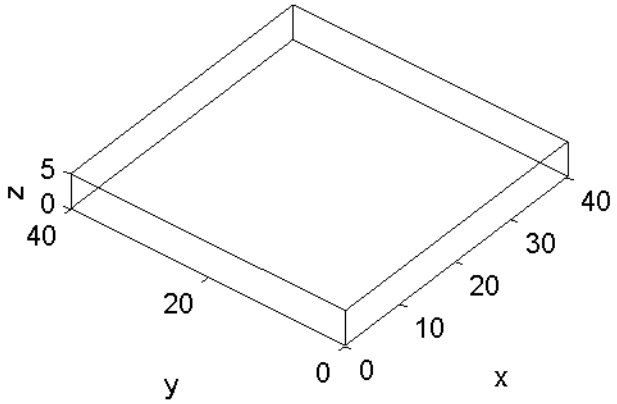
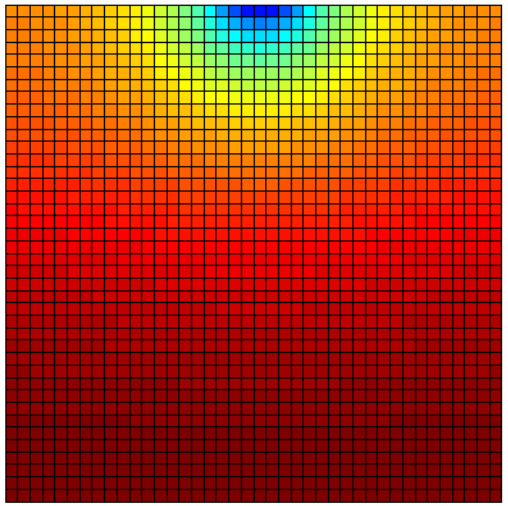
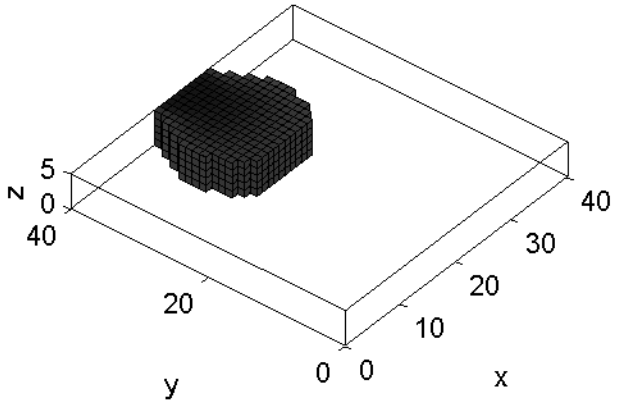
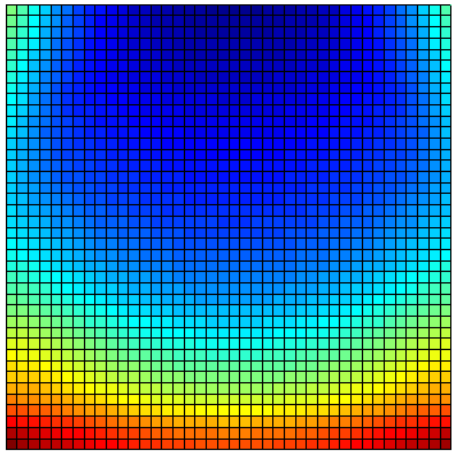


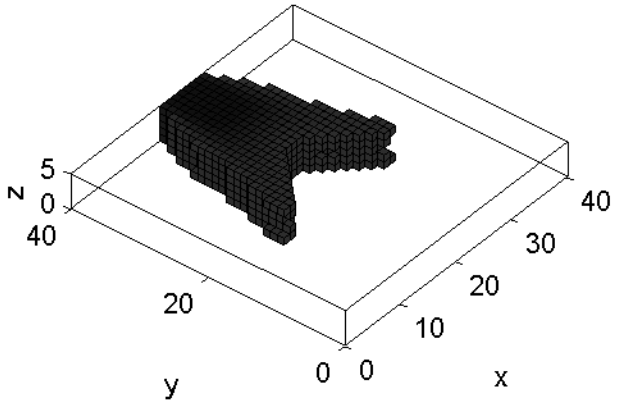


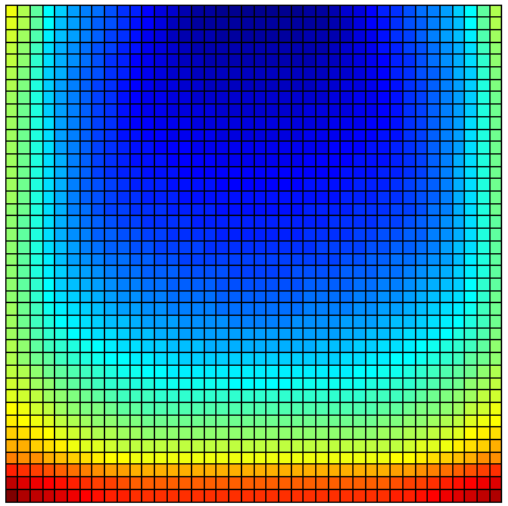
Test case: Heat Conduction



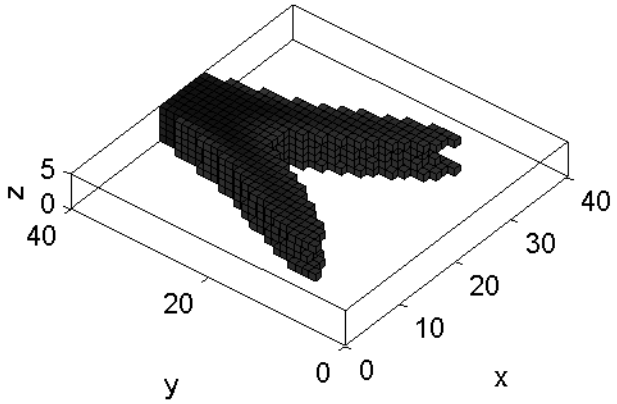


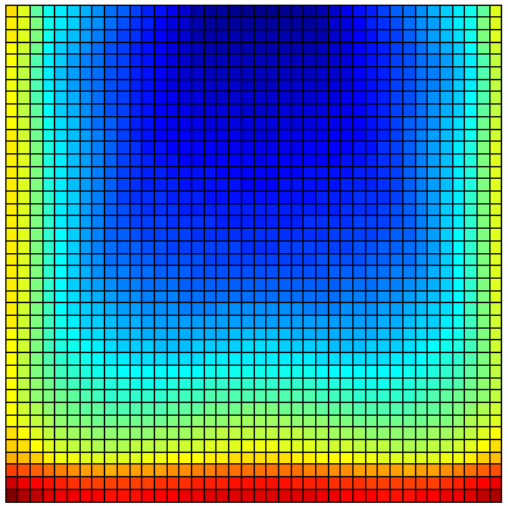
Test case: Heat Conduction



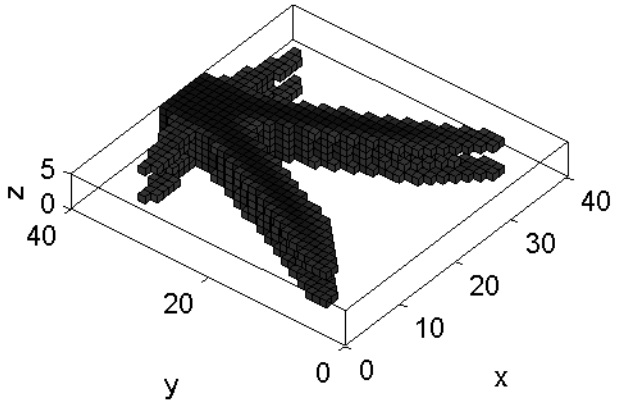


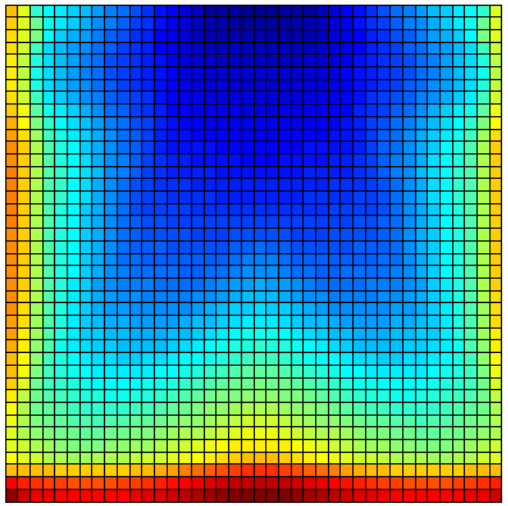
Test case: Heat Conduction



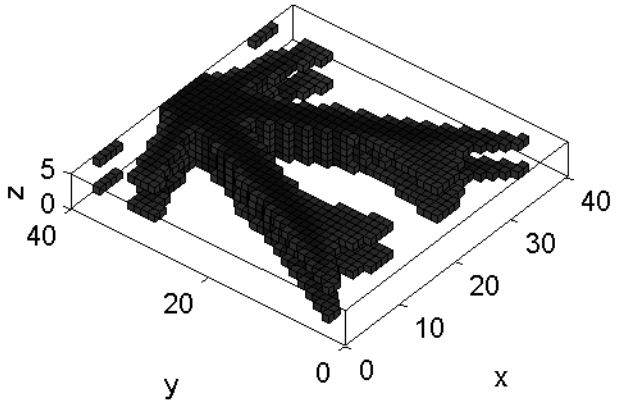


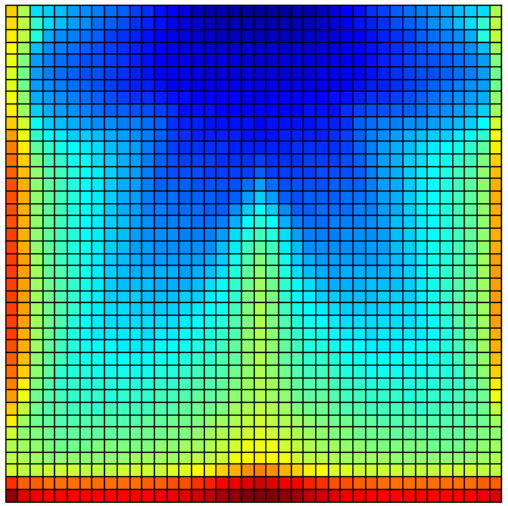
Test case: Heat Conduction





Test case: Heat Conduction





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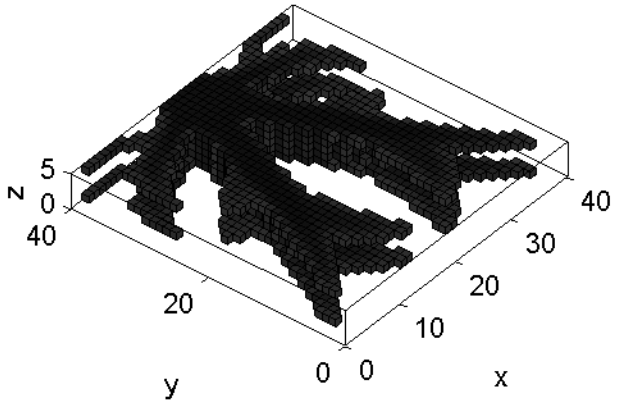

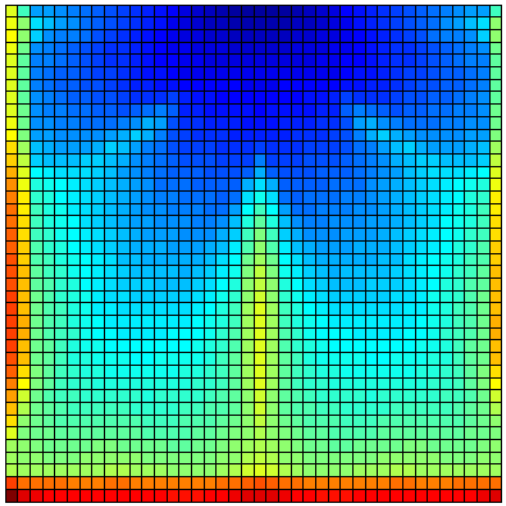

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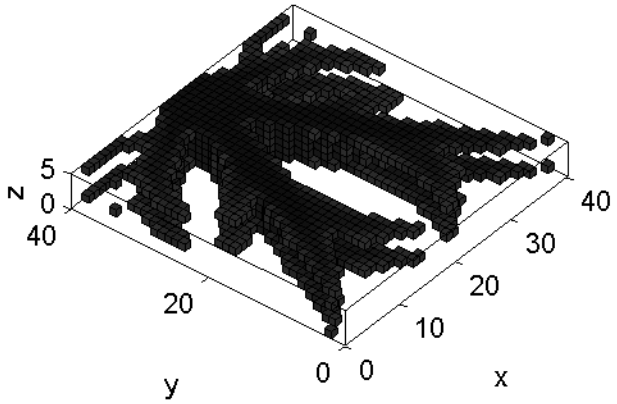
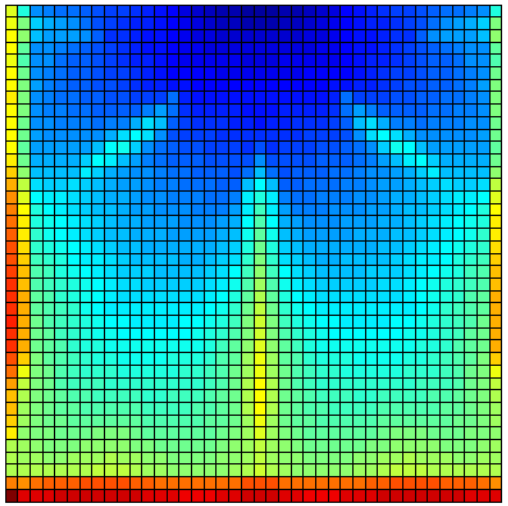
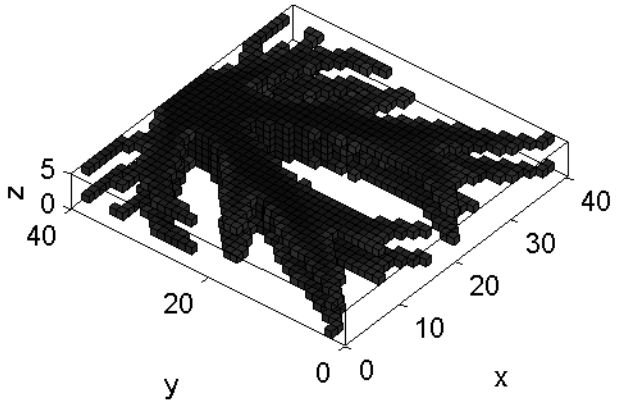
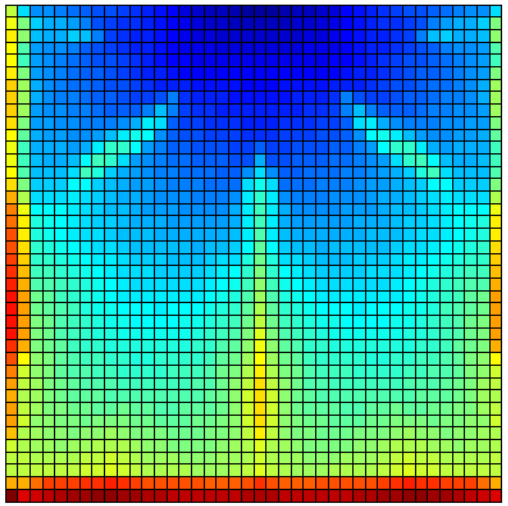


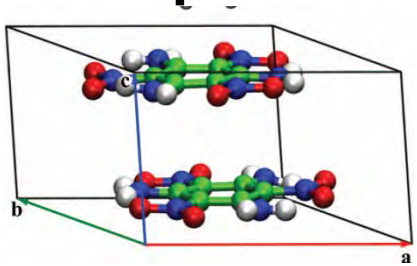


Test case: Heat Conduction





Development of methods to identify optimal propellant microstructures

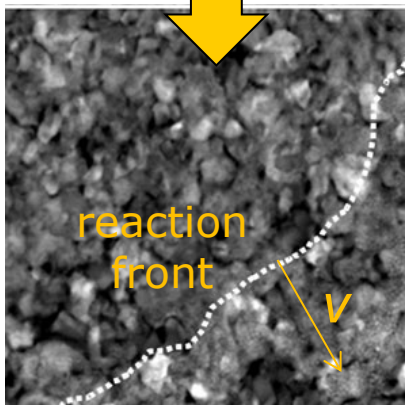


Anisotropic thermal conductivity of TATB
(Kroonblawd & Sewell, *J. Chem. Phys.*, 2013)

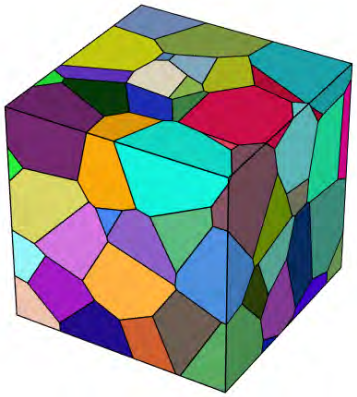
- Microstructure/specific impulse relation?
- Optimal microstructures?

Optimizer (e.g., genetic algorithm)

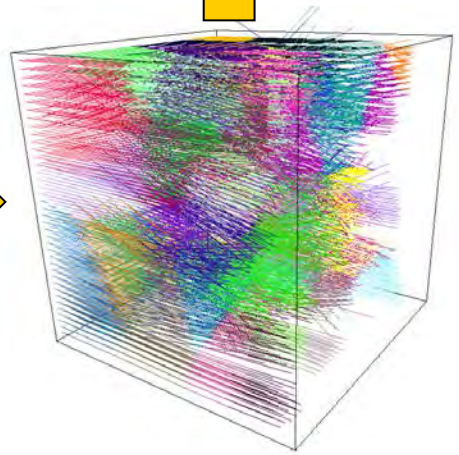
Objective function (e.g., mean reaction front speed)



Anisotropic reaction-front propagation speed



Parameterized microstruture (e.g., Voronoi tessellation)



Reaction front tracking calculation (ray tracing)

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full chemistry
at macroscale

Thank you!

atomistic models
of reactive materials

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