Introduction to molecular dynamics

nano101 Lectures – Network for Computational Nanotechnology
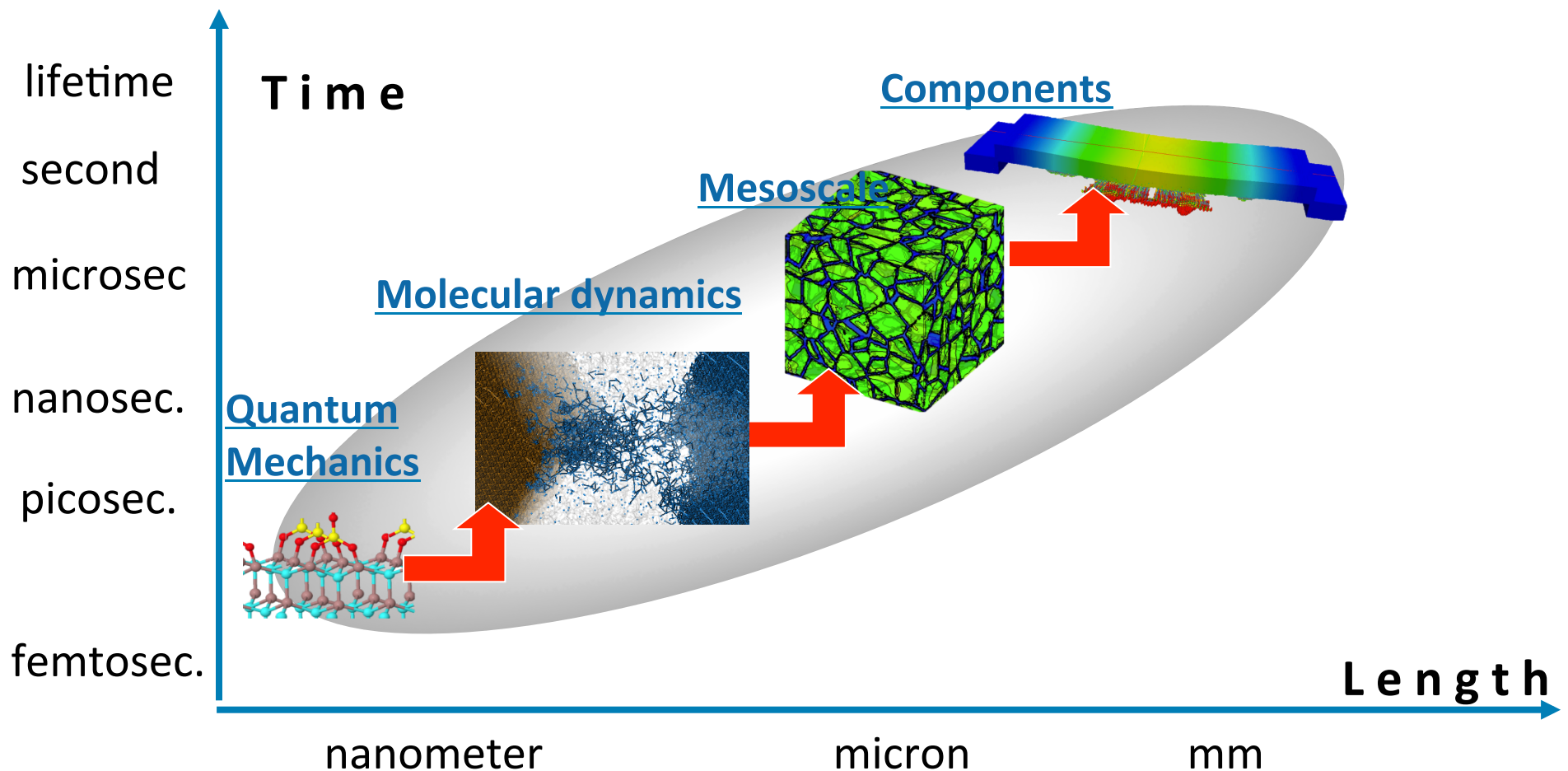
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Predictive science & materials modeling

- Predict materials performance from first principles
- Design and optimize new materials, understand their behavior under conditions where experiments are difficult to perform
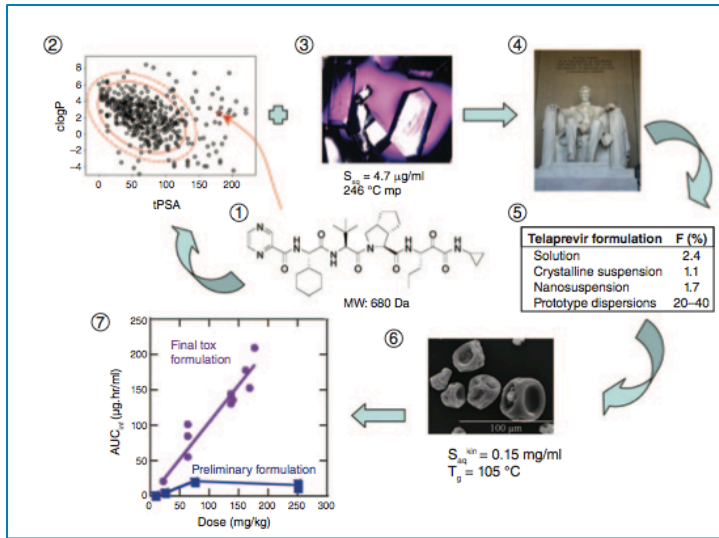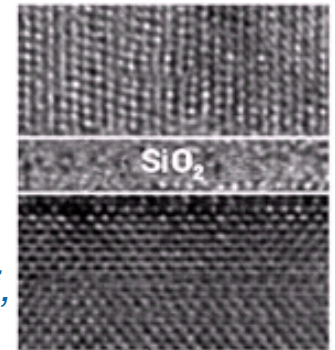

Time

lifetime

second

microsec

nanosec.

picosec.

femtosec.

Quantum Mechanics

Molecular dynamics

Mesoscale

Components

nanometer   micron   mm

Length

Materials are everywhere

Structural materials
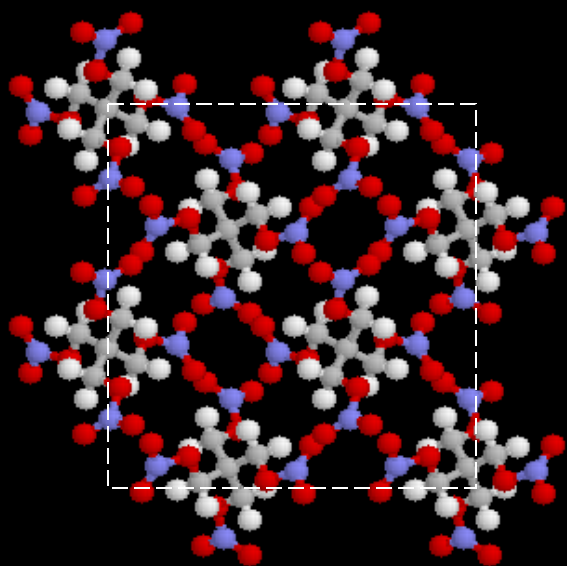*http://www.boeing.com/commercial/787family/*
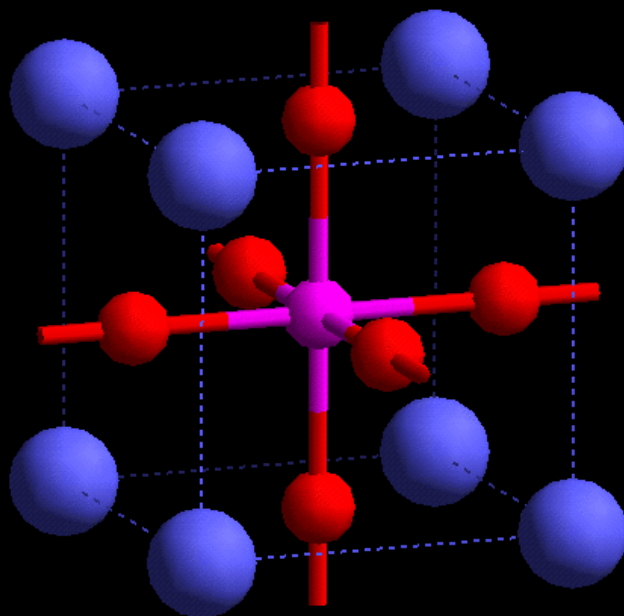

Pharmaceuticals
Kwong, Kauffman, Hurter & Mueller
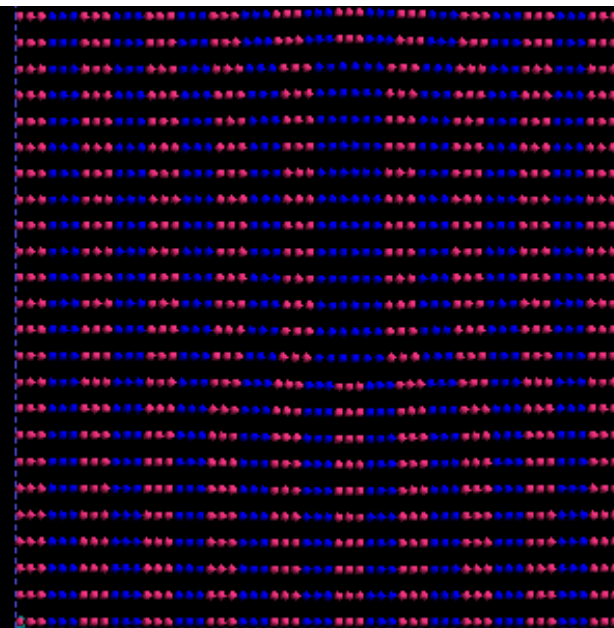*Nature Biotechnology, 29, 993 (2011)*

Nanoelectronics *"The High-k Solution", Bohr, Chau, Ghani, and Mistry* http://www.spectrum.ieee.org/oct07/5553
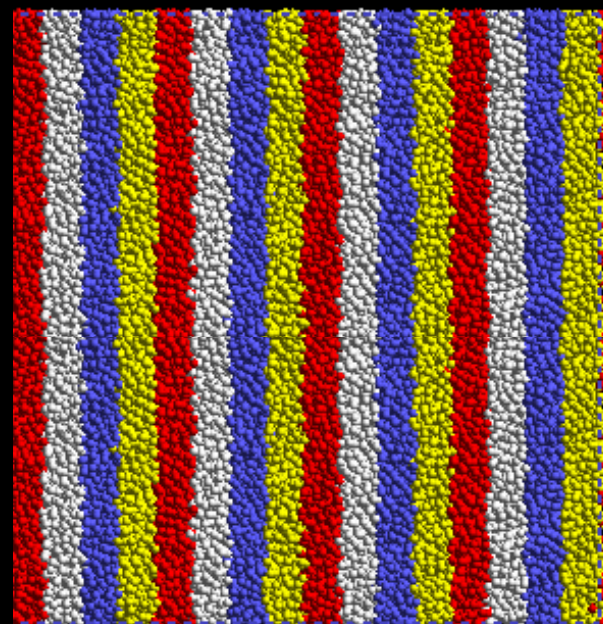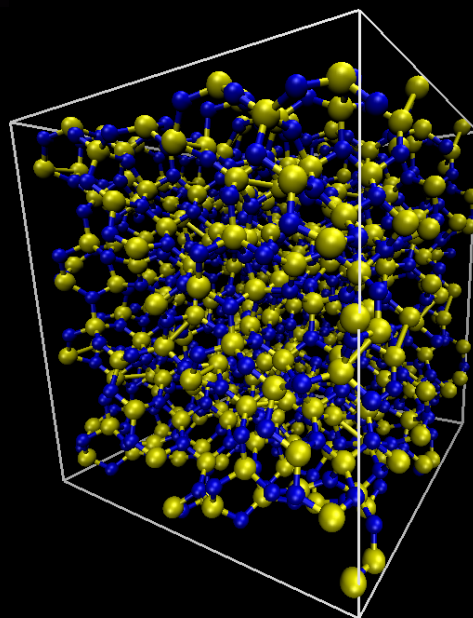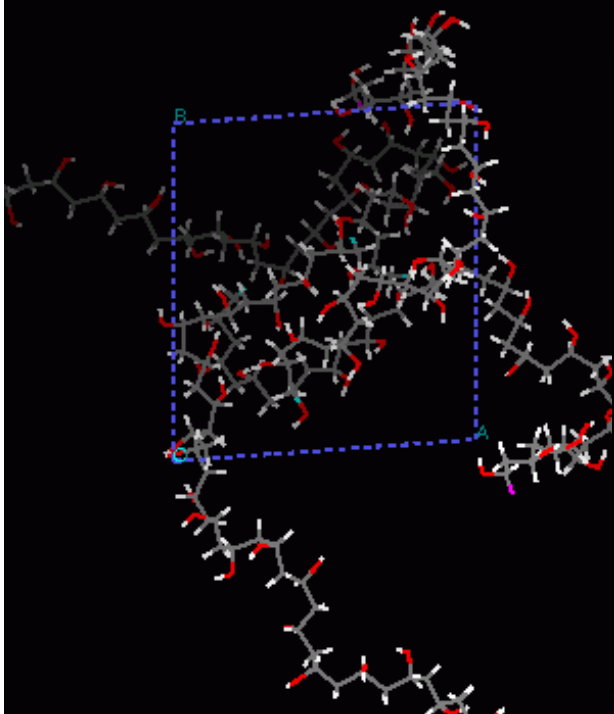
Molecular materials

Ceramics & semiconductors

Metals

Fundamental theory

- Late 1500's to early 1800's: Classical mechanics
  Galileo, Newton, Legendre, Hamilton, …

- Second half of 1800's: Statistical mechanics
  Gibbs, Maxwell, Boltzmann, …

- 1905-1926: Quantum mechanics
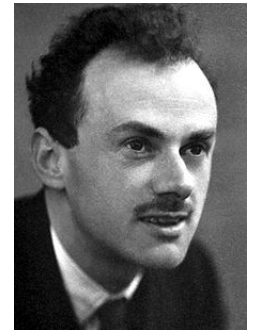 Plank, Bohr, Dirac, Schrödinger, Dirac, …

Hamilton   *Maxwell*   *Boltzmann*   *Schrödinger*   *Dirac*

Predictive simulations

- 1957: Molecular dynamics
  Alder and Wainwright

- 1964-1965: Density functional theory
  Kohn, Hohenberg, Sham: density functional theory

- 1980's-present: Predictive simulations
  Extensions to classical mechanics
  Accurate approximations for DFT
  Accurate interatomic potentials for large-scale MD
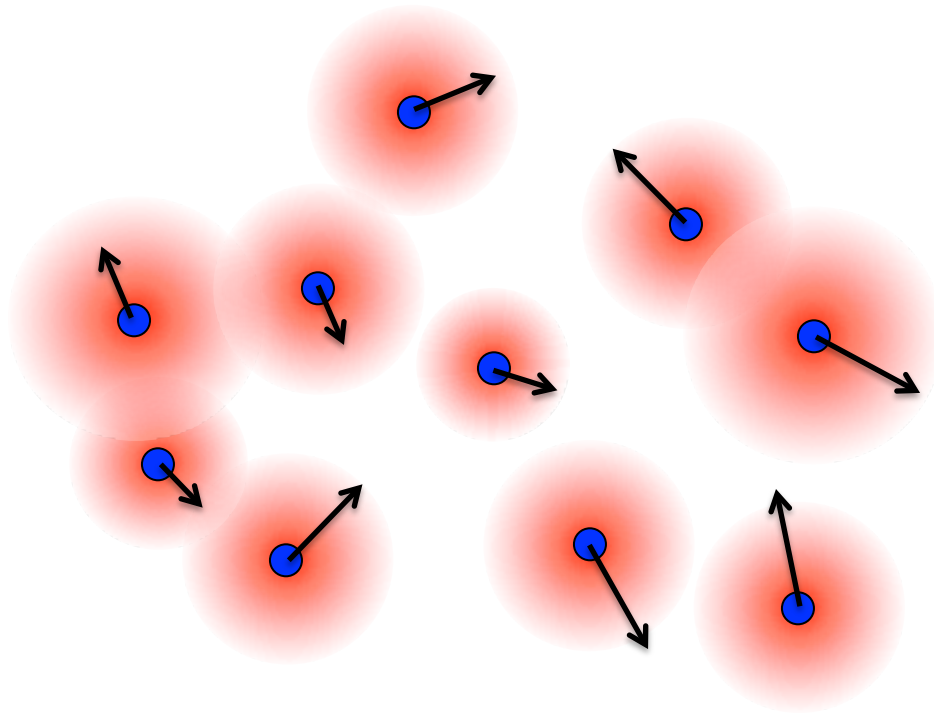
Basic physics & approximations

Dynamics of atoms:
Classical (Newton's) mechanics

$$F_i = m_i a_i$$

Force between atoms originates from the electronic structure
Time independent Schrodinger Eq.

$$H\psi = E\psi$$

Electronic and atomic processes

Initial condition

$$\{R_i\} \quad \{V_i\}$$
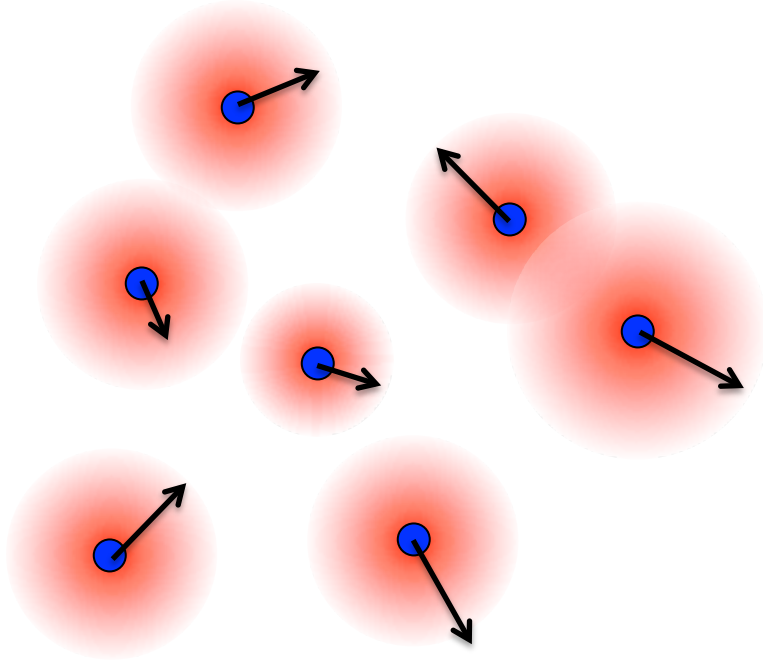
Time evolution

$$\dot{R}_i = V_i$$

$$\dot{V}_i = \frac{F_i}{M_i}$$

Energy & forces

$$H\psi = E\psi$$

$$F_i = -\nabla_{R_i} E\left(\{R_i\}\right)$$

Molecular dynamics

Initial conditions

$$\{R_i\} \quad \{V_i\}$$

Compute energy & forces

$$H\psi = E\psi$$

$$F_i = -\nabla_{R_i} E\left(\{R_i\}\right)$$

Integrate Eqs. of Motion

$$R_i(t) \rightarrow R_i(t + \Delta t)$$

$$V_i(t) \rightarrow V_i(t + \Delta t)$$

So … what is MD?

Follow the dynamics (motion) of all the atoms in your material

Numerically solve classical equations of motion (Newton's):

Approximation

$$\vec{F}_i = m_i \vec{A}_i \qquad \text{or} \qquad \begin{cases} \dot{\vec{R}}_i = V_i \\ \dot{\vec{V}}_i = \dfrac{\vec{F}_i}{M_i} \end{cases}$$

Forces on atoms come from the interaction with other atoms:

$$\vec{F}_i = -\vec{\nabla}_{R_i} V\left(\{R_j\}\right)$$

Approximated
(in almost all cases)

Total potential energy
- Eigenvalue in the time-independent Schrodinger Eq.
- An empirical potential energy function

Predicting the future with MD

$$\dot{\vec{R}}_i = \dot{\vec{V}}_i = \frac{\vec{R}_i(t+\Delta t) - \vec{R}_i(t)}{\Delta t}$$

$$\dot{\vec{V}}_i = \frac{\vec{F}_i}{M_i} = \frac{\vec{V}_i(t+\Delta t) - \vec{V}_i(t)}{\Delta t}$$

$$\begin{cases} R_i\left(t+\Delta\right) = R_i\left(t\right) + V_i\left(t\right)\Delta t \\[3mm] V_i\left(t+\Delta t\right) = V_i\left(t\right) + \dfrac{F_i\left(t\right)}{M_i}\cdot\Delta t \end{cases}$$

Euler method

Verlet algorithm: Taylor expansion of positions with time

$$R_i\left(t+\Delta t\right) = R_i\left(t\right) + \dot{R}_i\left(t\right)\Delta t + \frac{1}{2}\ddot{R}_i\left(t\right)\Delta t^2 + \frac{1}{6}\dddot{R}_i\left(t\right)\Delta t^3 + O\left(\Delta t^4\right)$$

$$R_i\left(t-\Delta t\right) = R_i\left(t\right) - \dot{R}_i\left(t\right)\Delta t + \frac{1}{2}\ddot{R}_i\left(t\right)\Delta t^2 - \frac{1}{6}\dddot{R}_i\left(t\right)\Delta t^3 + O\left(\Delta t^4\right)$$

Sum two equations:

$$R_i\left(t+\Delta t\right) = 2R_i\left(t\right) - R_i\left(t-\Delta t\right) + \ddot{R}_i\left(t\right)\Delta t^2 + O\left(\Delta t^4\right)$$
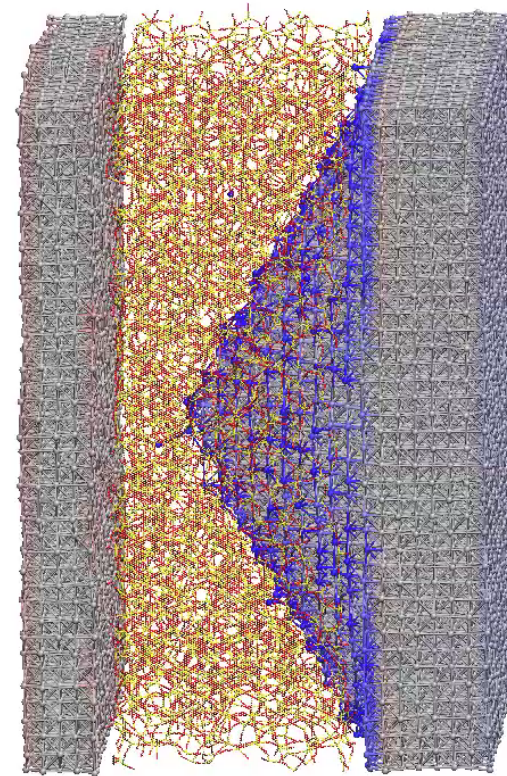
Simple MD simulations

Nanoelectronics: electrometallization cells

- Resistance switching devices
  - Creation and dissolution of conductive metallic bridges
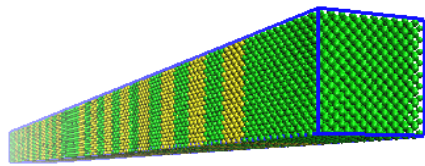 - Ultrafast switching & miniaturization to the nanoscale
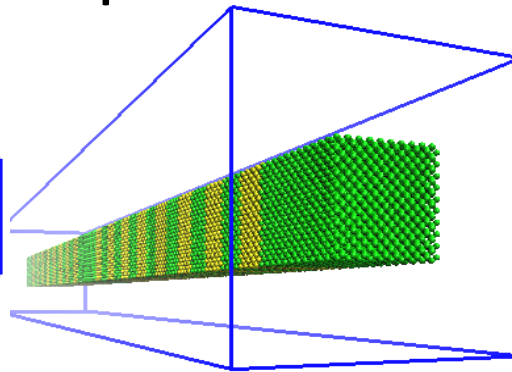

Tappertzhofen et al. ACS Nano (2013)

Onofrio, Guzman, Strachan, Nature Materials 14, 440–446 (2015)

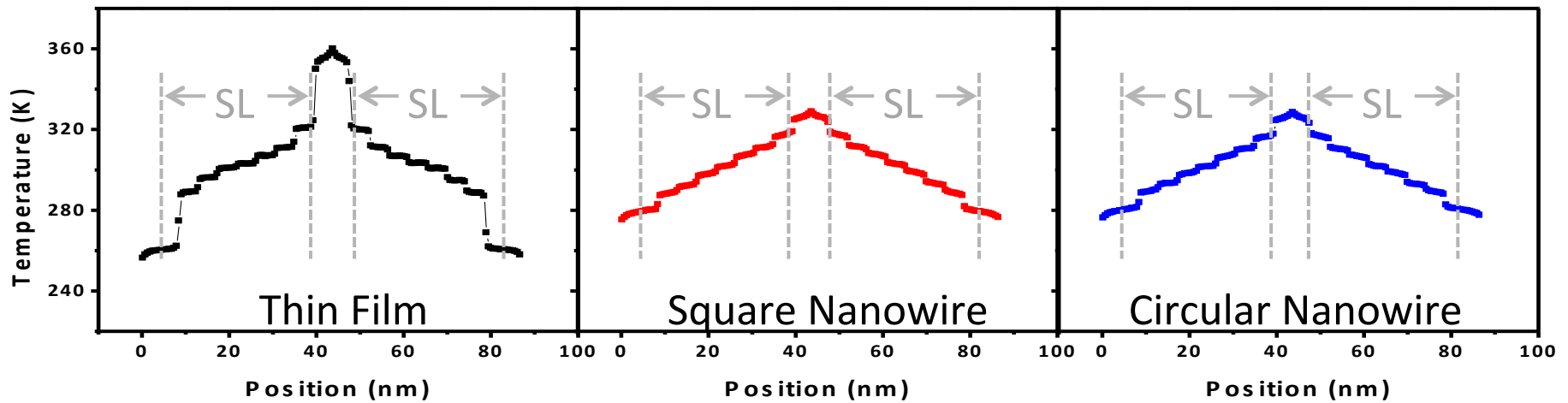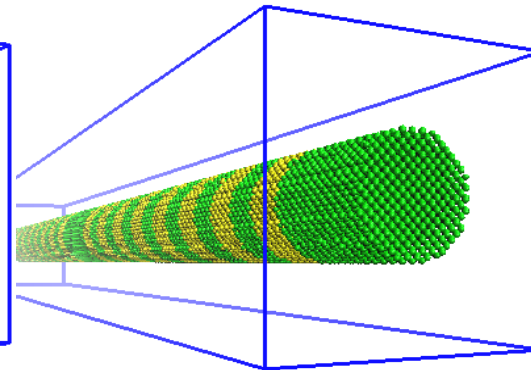# Nano-engineering to control thermal transport
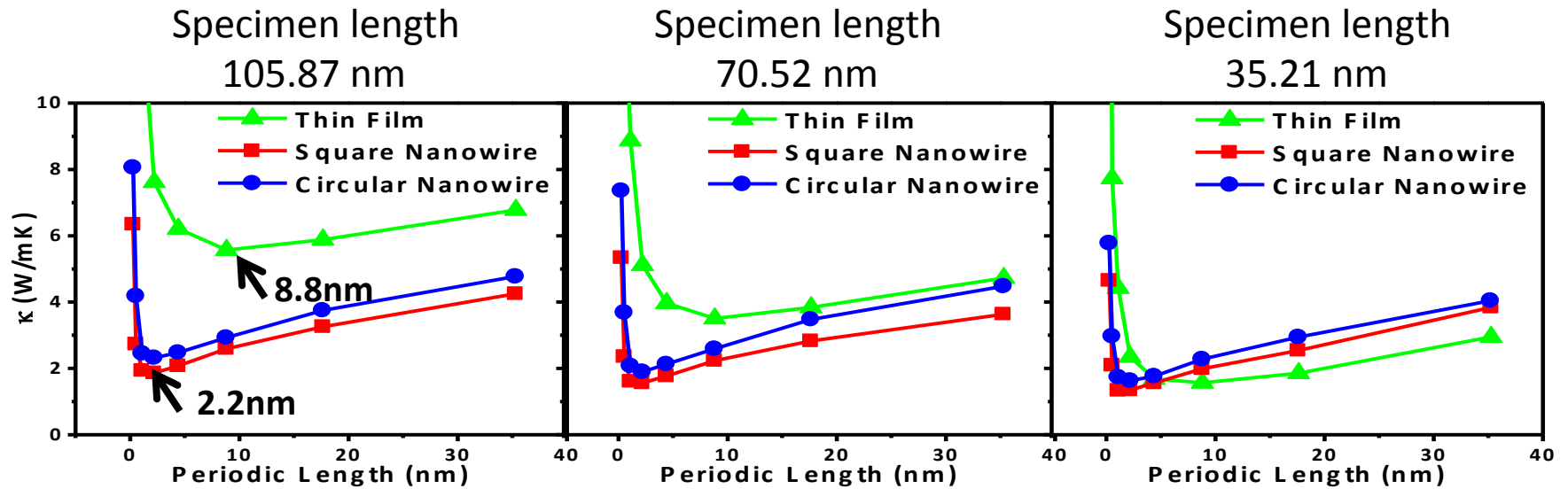

SL Thin film   SL Square Nanowire   SL Circular Nanowire

Keng-Hua Lin and A. Strachan, Physical Review B, **87**, 115302 (2013).

Role of size and interfaces

Specimen length
105.87 nm

Specimen length
70.52 nm

Specimen length
35.21 nm

Role of superlattice period

- Decreasing SL period reduced thermal conductivity up to a minimum size
- Further reduction increases k (phonons *see* material as homogeneous)

Role of specimen length

- Reducing specimen length affects the thin film SL's more dramatically
- For small specimens thin film SL's can have lower thermal conductivity of their nanowire counterparts

Keng-Hua Lin and A. Strachan, Physical Review B, **87**, 115302 (2013).

Thermal transport at the nanoscale

Corrugated Si nanowires

- Conductance smaller than straight wires with inner core diameter

S. Sullivan, K. Lin, S. Avdoshenko, and A.S. Applied Physics Letters, 103 243107 (2013).

Nano-engineering for mechanical response
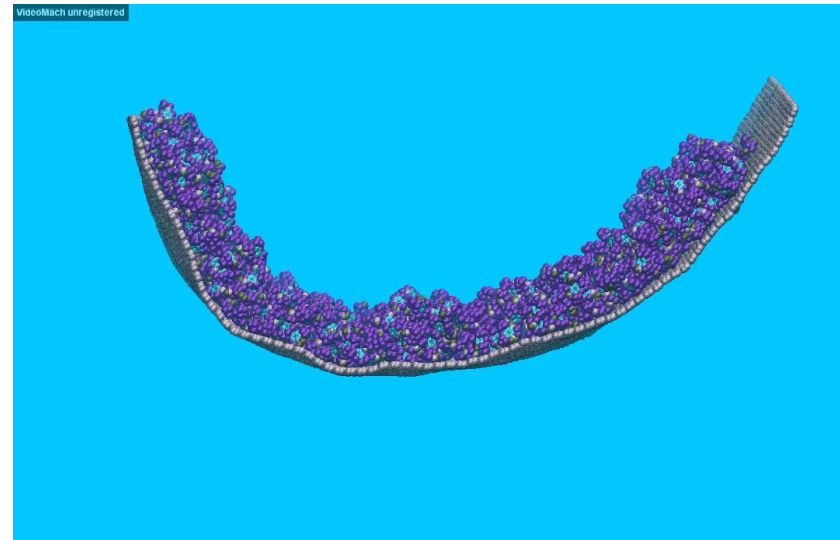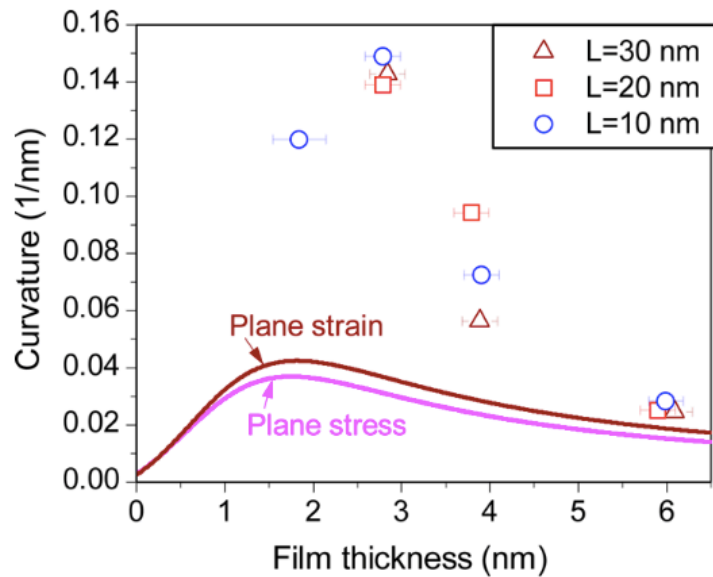
Deformation of a polycrystalline metal
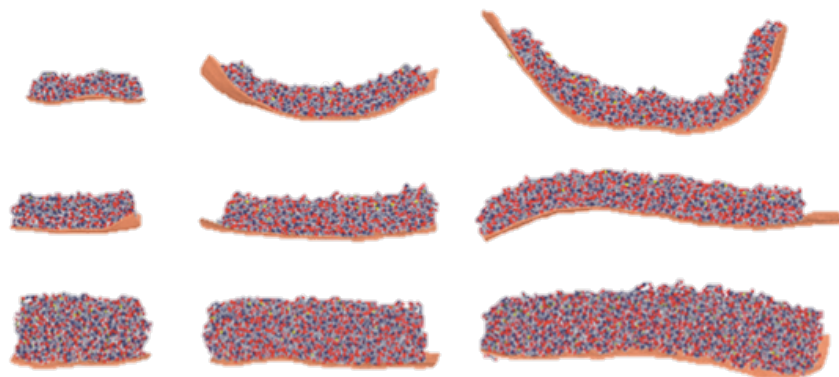
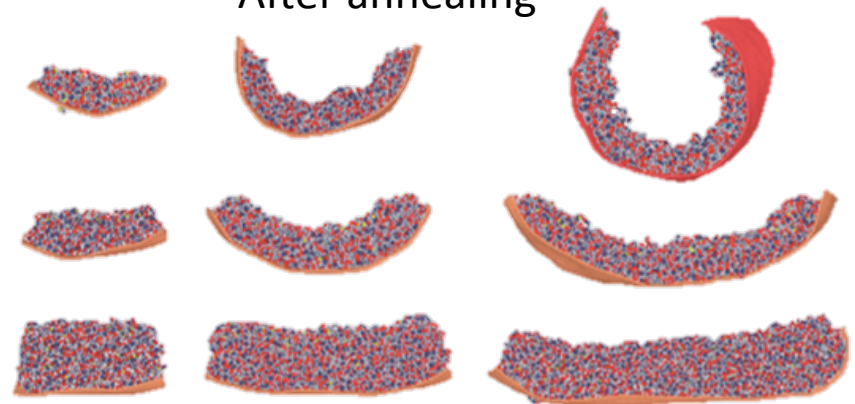Platinum yield stress vs. grain size

Hojin Kim and A. Strachan, unpublished

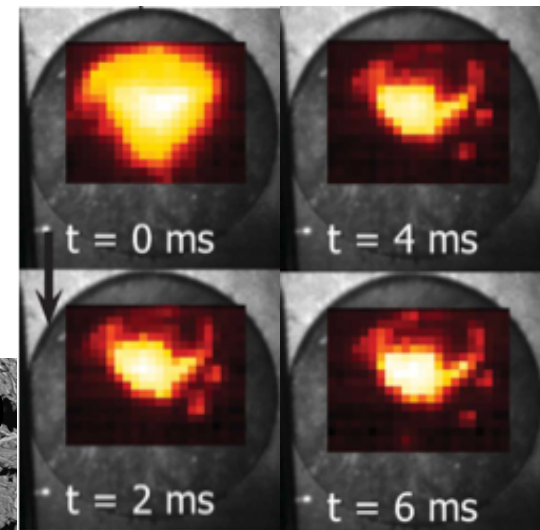# Engineering curvature in graphene

After polymer curing
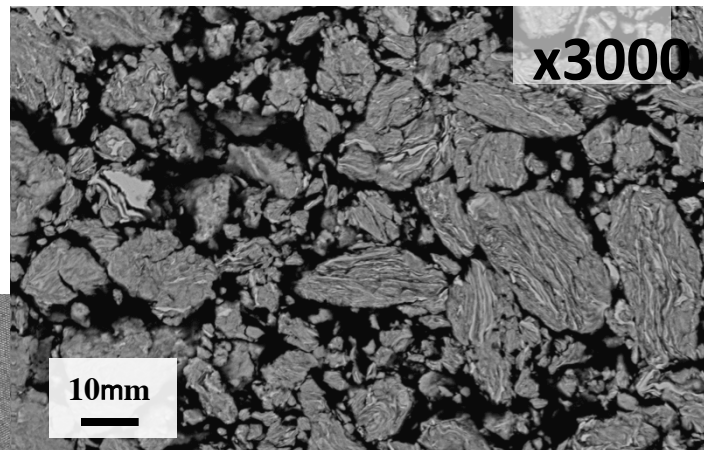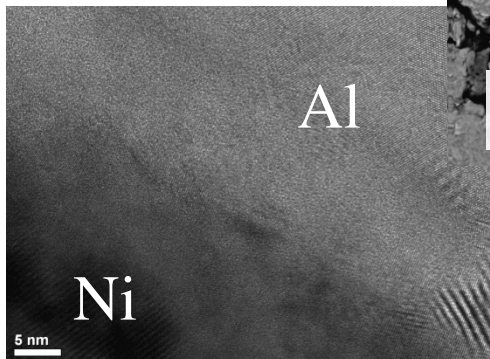
After annealing

Nano-engineering energetic materials

Highly reactive composite materials

Attractive properties
- High-energy density
- Significant ability to tune properties via micro-nano-structure
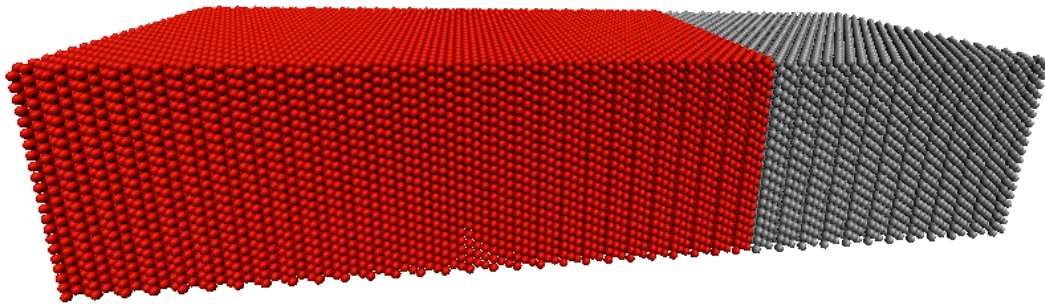- Potential for multifunctionalty

Co-PIs: Son, Cuitiño, Mukasyan

x3000

t = 0 ms
t = 4 ms
t = 2 ms
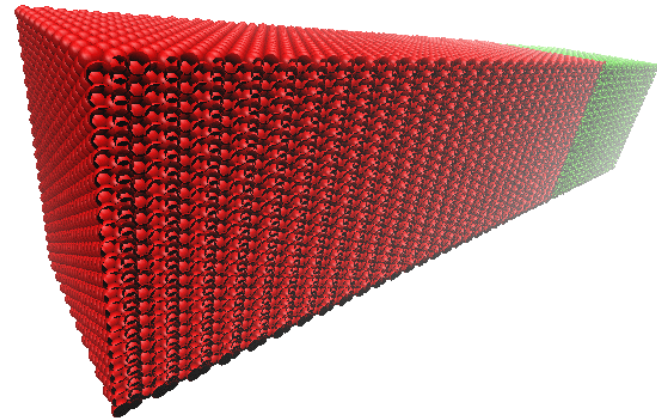t = 6 ms

Al

Ni

10mm

5 nm

Challenges
- Role of nano- and micro-structure on sensitivity, exorthemicity under different insults
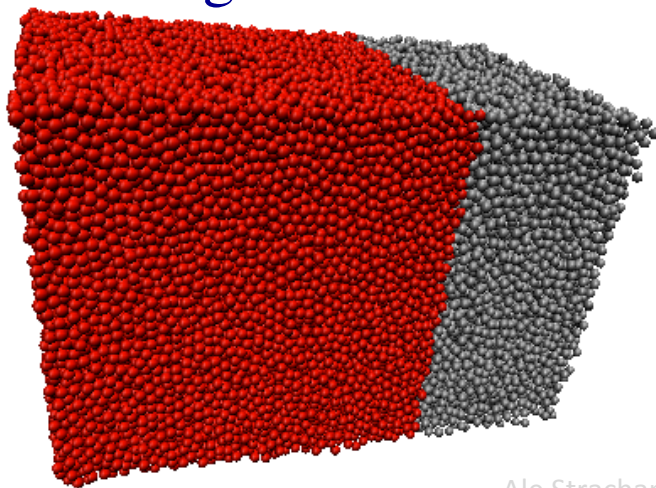- Processing routes to tune performance

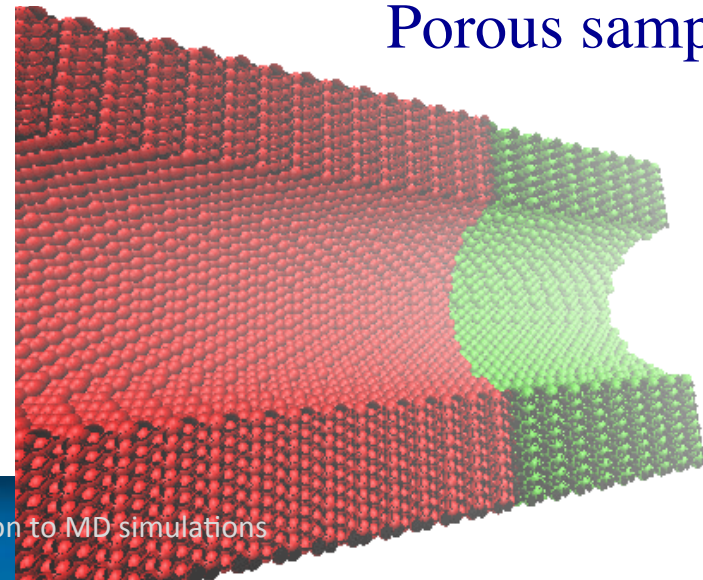# Nanostructure role on chemical reactions

Nanolaminates

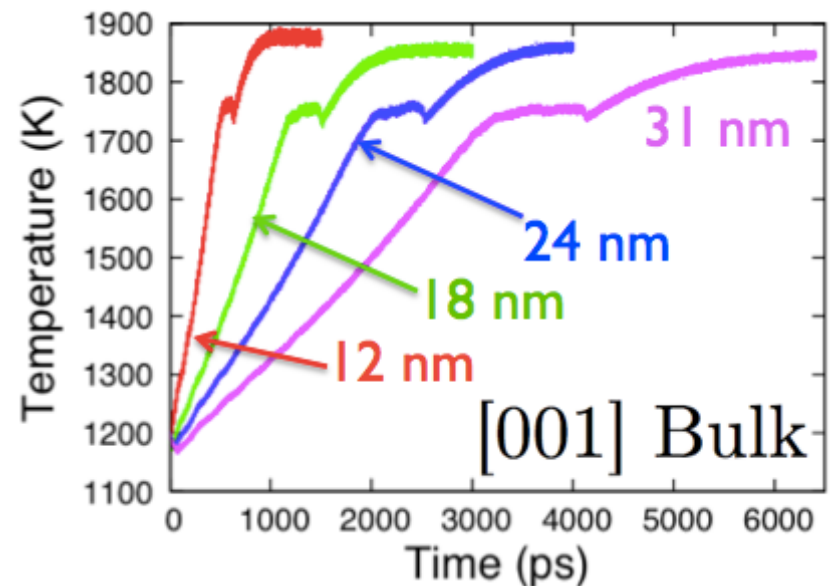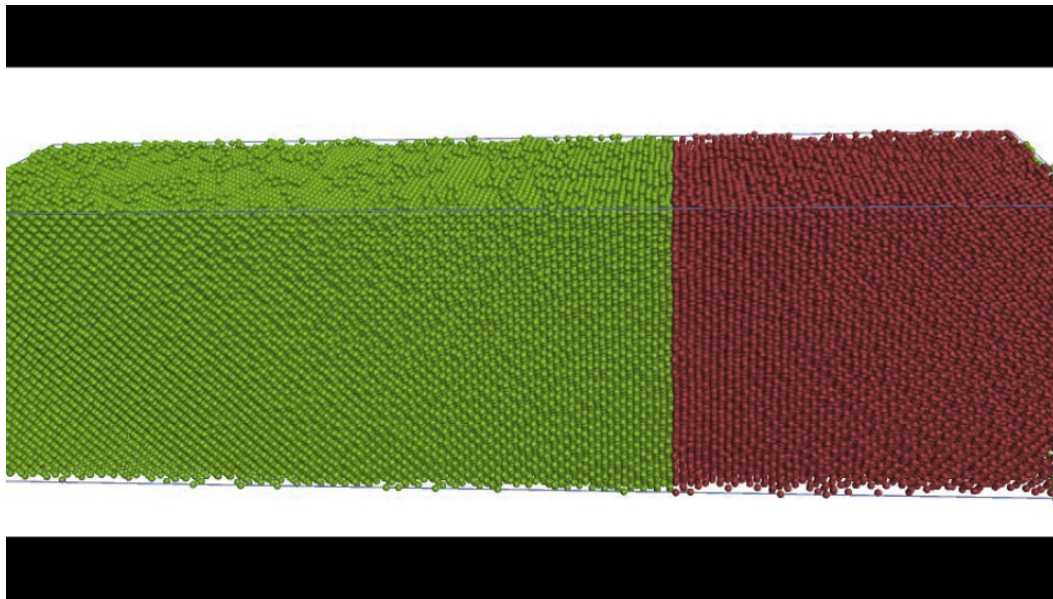Free surfaces

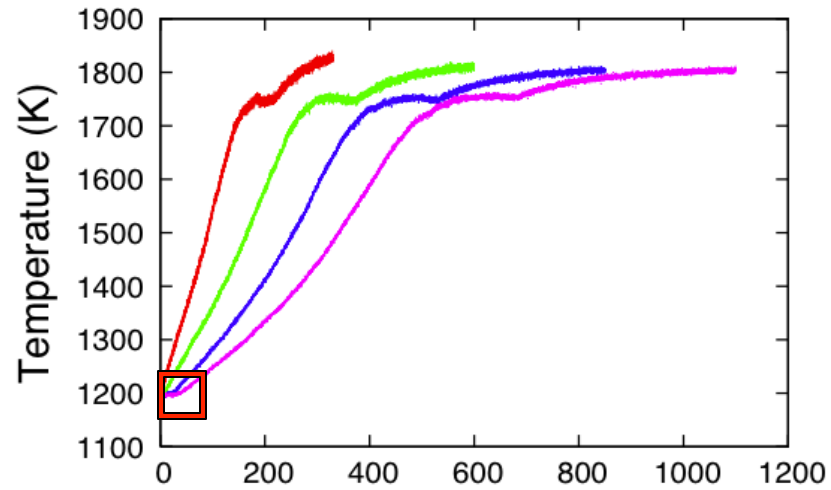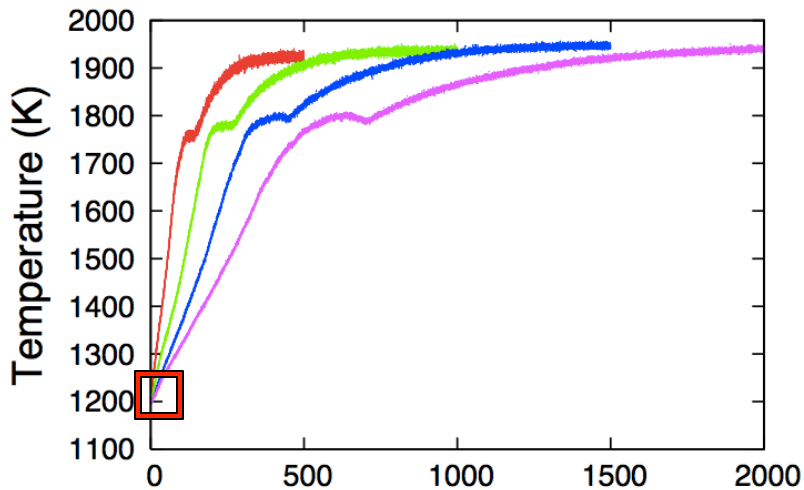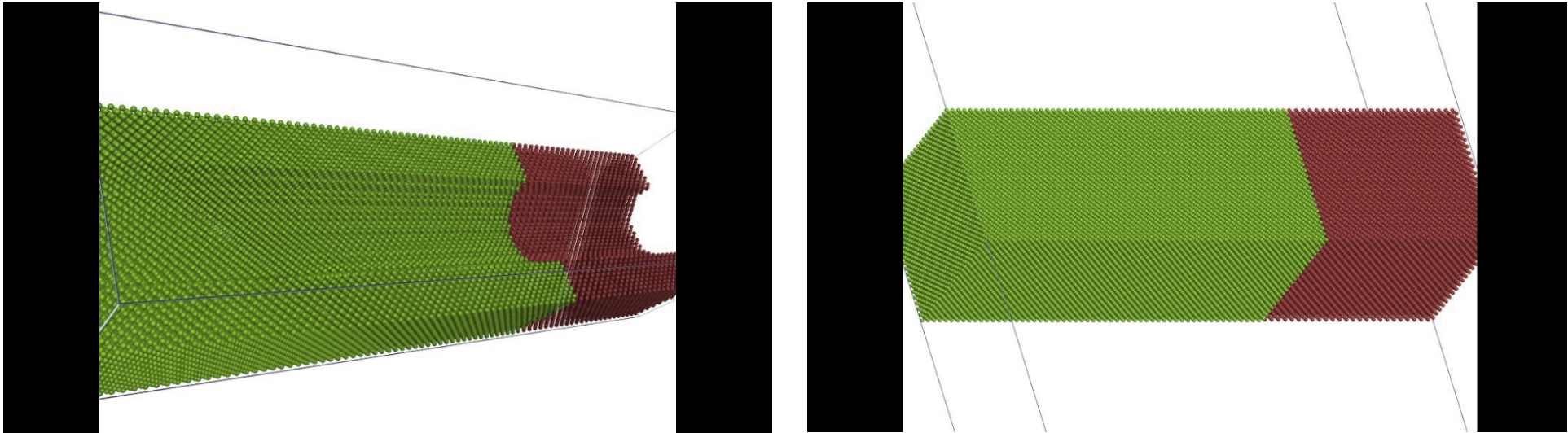Metallic glass laminates

Porous samples

Reactions in bulk nanolaminates

- Rapid heating of samples to ignition temperature (900 to 1400 K)
- Constant enthalpy simulations of chemical reaction
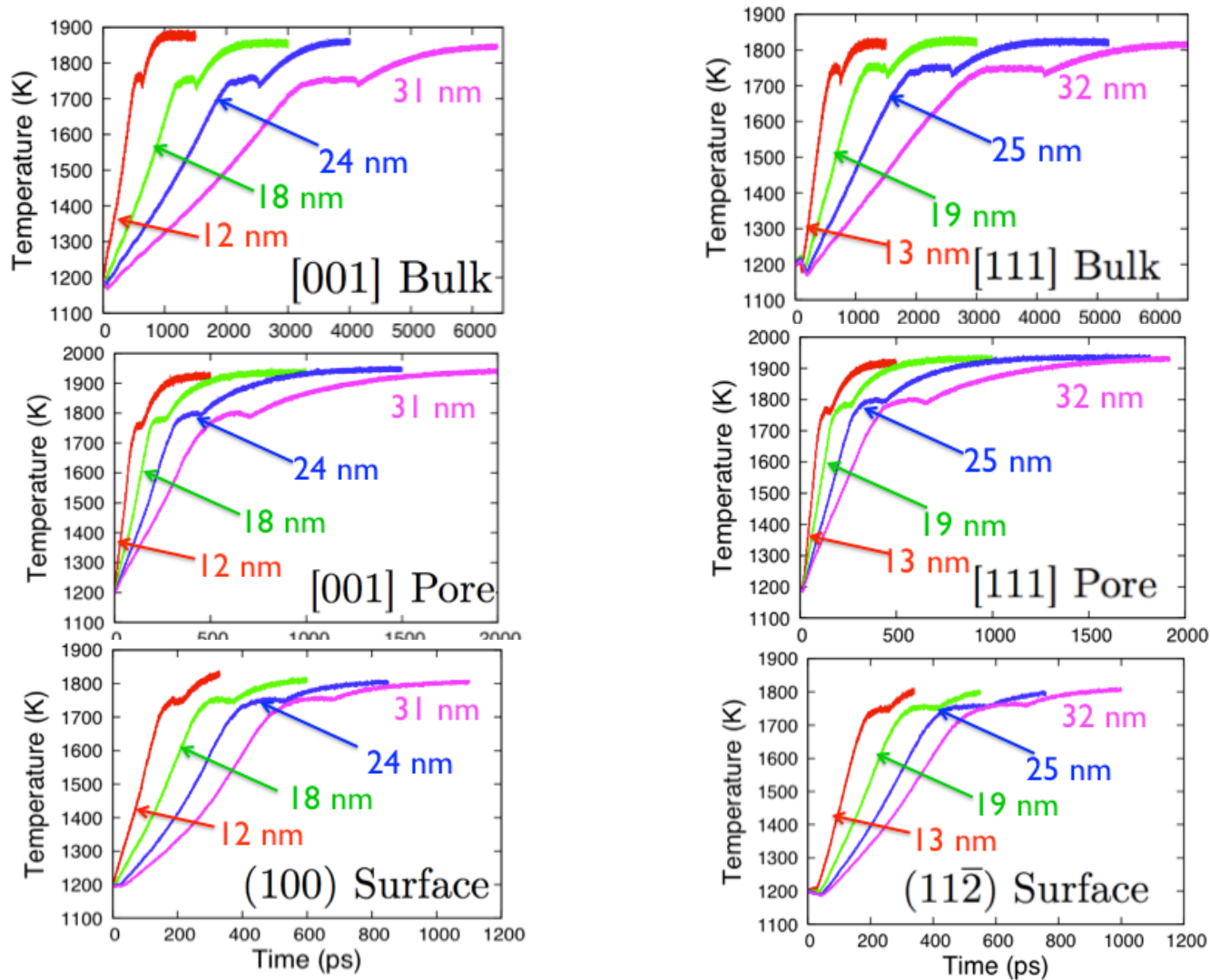- Ni/Al EAM potential from Mishin et al. Phil. Mag. 89, 3245 (2009)

Cherukara, Guda & Strachan, Phys. Rev. B (2012)
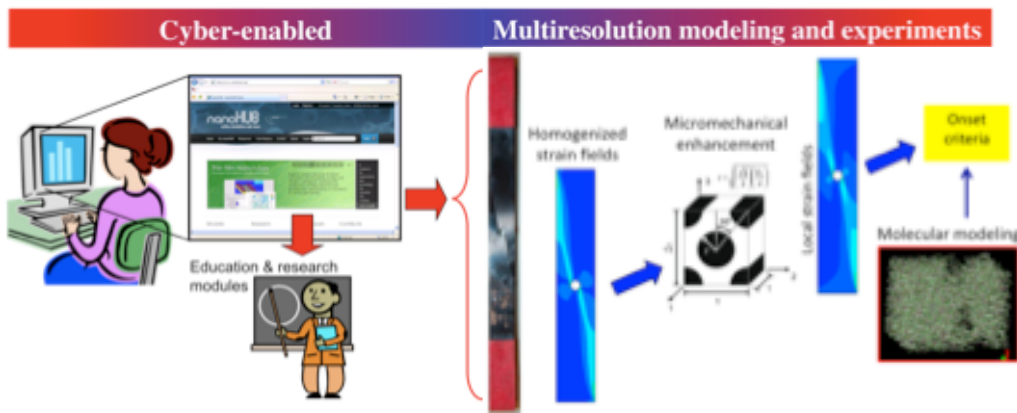
Role of extended defects

Cherukara, Guda and Strachan, Phys. Rev. B (2012)

Role of extended free-volume defects

Polymer composite projects

NSF: cyber-enabled predictive models for polymer nanocomposites: multiresolution simulations and experiments

- Ultimate mechanical properties of nanocomposites
- Poly-imides and PMMA with CNTs and graphne

Boeing – Purdue: atoms to aircraft

- Prediction of onset of irreversible deformation and damage propagation in epoxy formulations
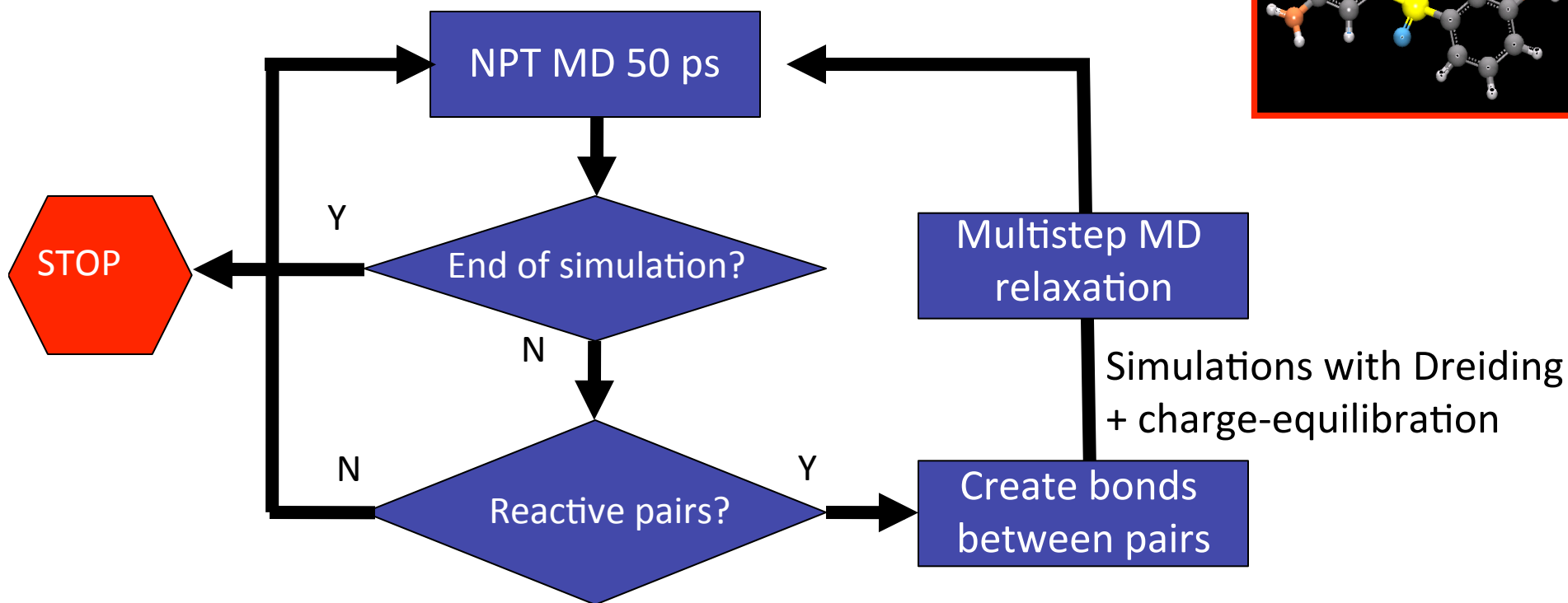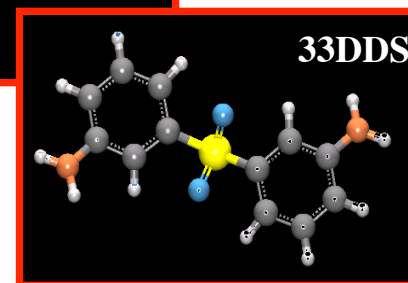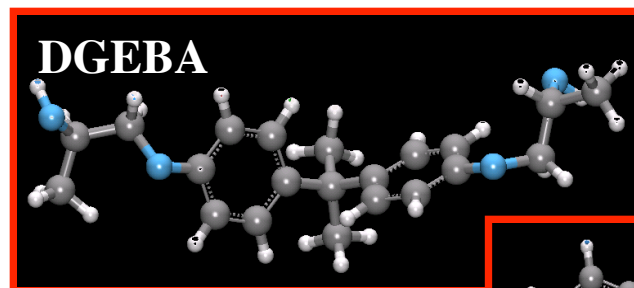- Continuous carbon fiber reinforced composites

Co-PIs: Pipes, Koslowski, Raman, Caruthers

www.newairplane.com

Molecular structure of thermoset polymers

Create simulation cell with desired number
of epoxy and curing agent molecules
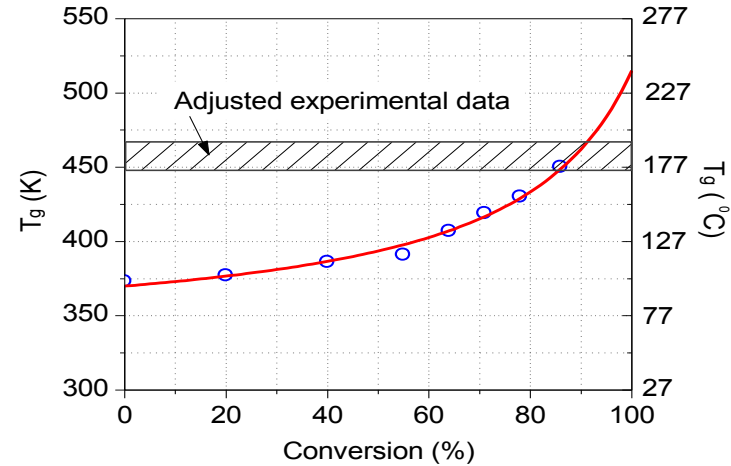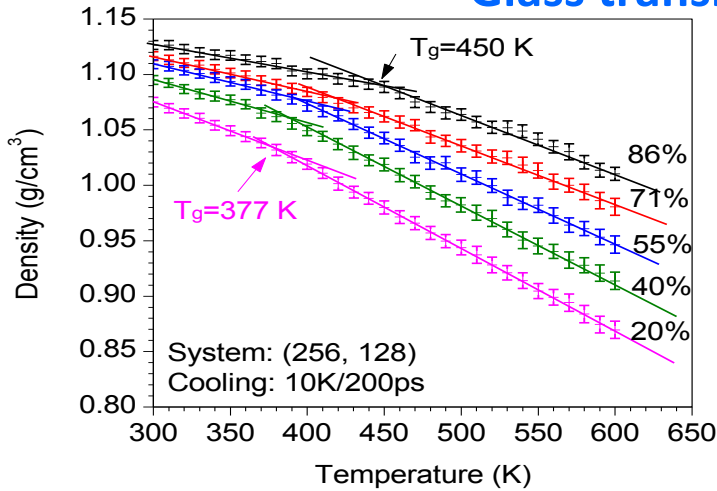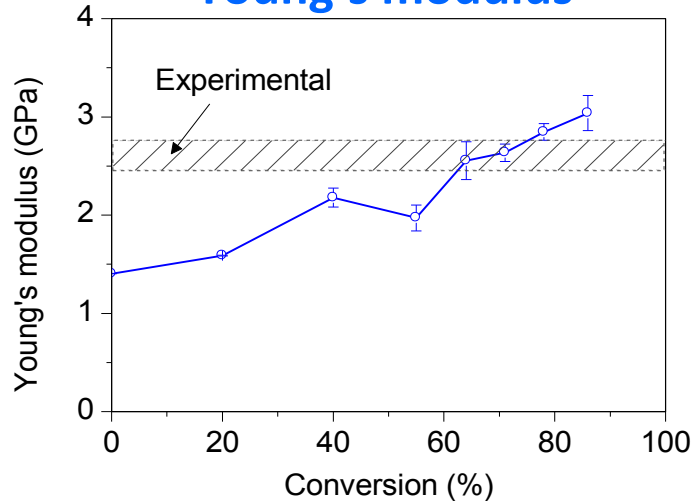
MD procedure to mimic the curing process

DGEBA

33DDS

```
        ┌──────────────────┐
  ┌────▶│  NPT MD 50 ps    │◀────┐
  │     └──────────────────┘     │
  │              │               │
  │              ▼               │
  │        ◇──────────◇     ┌──────────────┐
  │   Y   ╱            ╲     │ Multistep MD │
┌─────┐◀──  End of simulation?  │  relaxation  │
│STOP │   ╲            ╱     └──────────────┘
└─────┘    ◇──────────◇           │
  ▲              │ N              │
  │              ▼               │
  │        ◇──────────◇     ┌──────────────┐
  │   N   ╱            ╲  Y  │ Create bonds │
  └──────  Reactive pairs?  ──▶│ between pairs │
           ╲            ╱     └──────────────┘
            ◇──────────◇
```

Simulations with Dreiding
+ charge-equilibration

Li & Strachan, Polymer (2010)

Properties vs. conversion degree

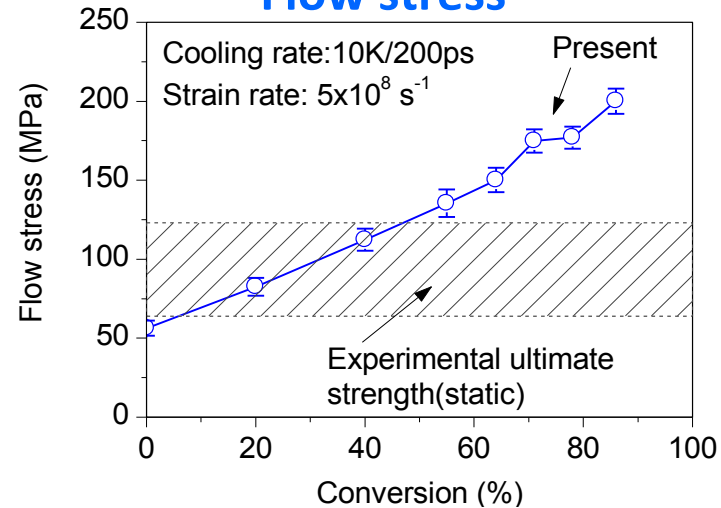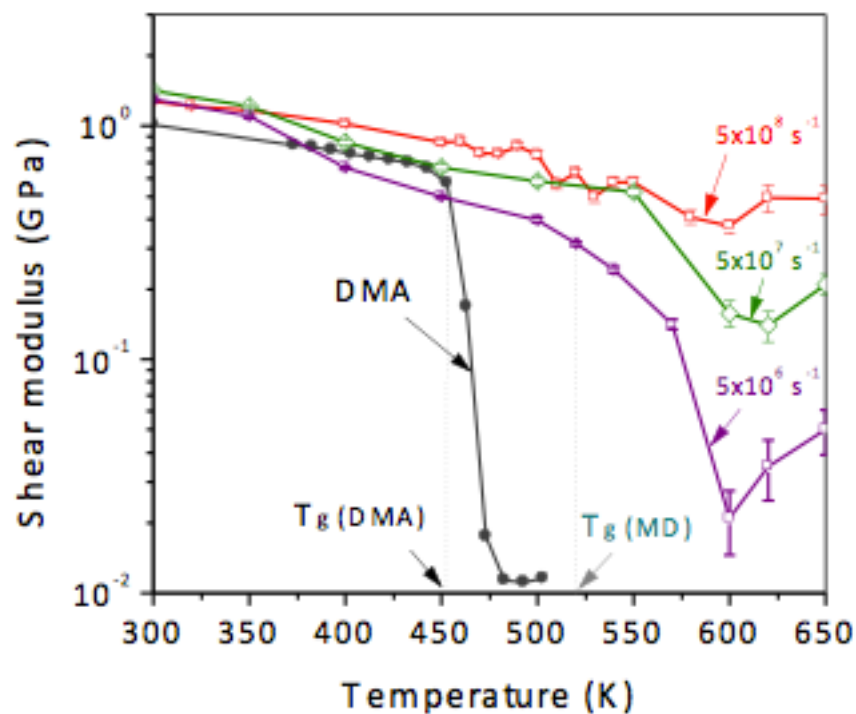**Glass transition temperature**
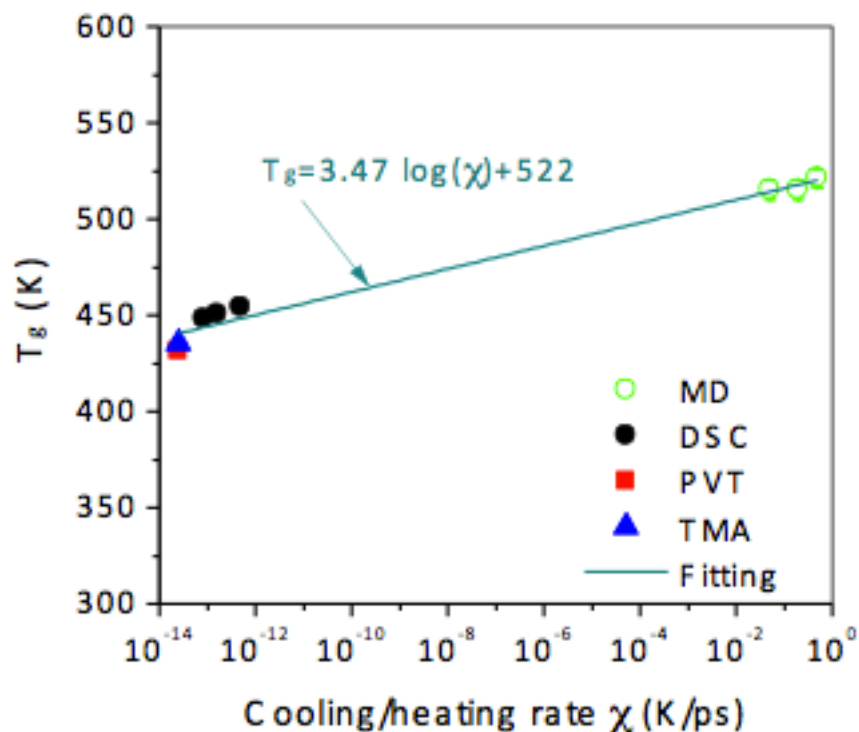
EPON862/DETDA
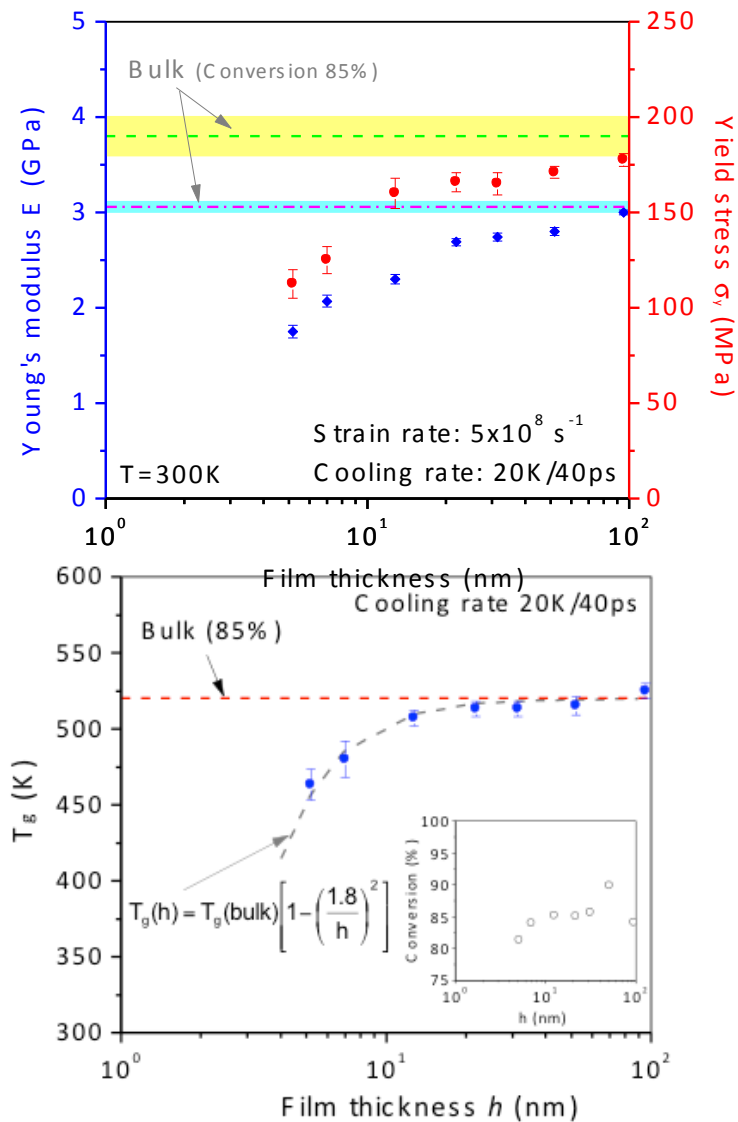

Young's modulus

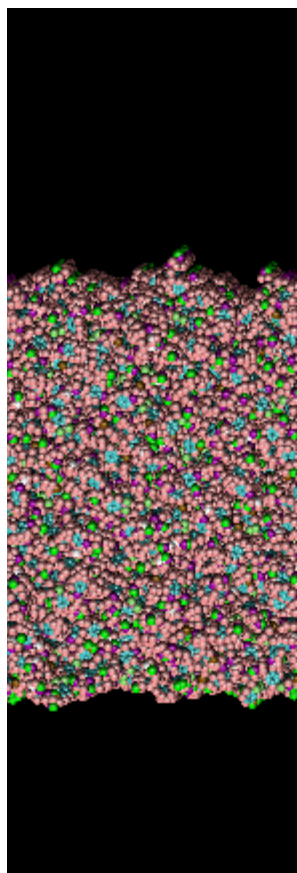**Flow stress**

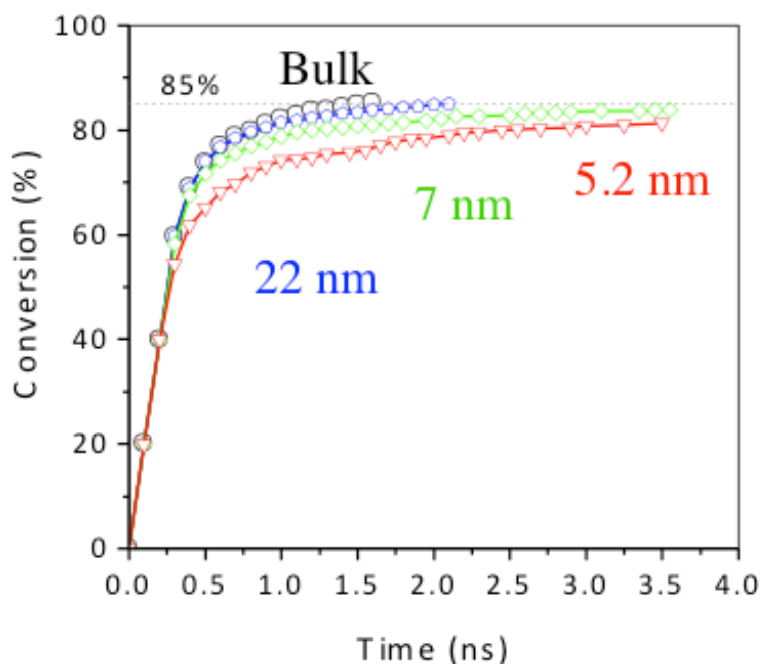

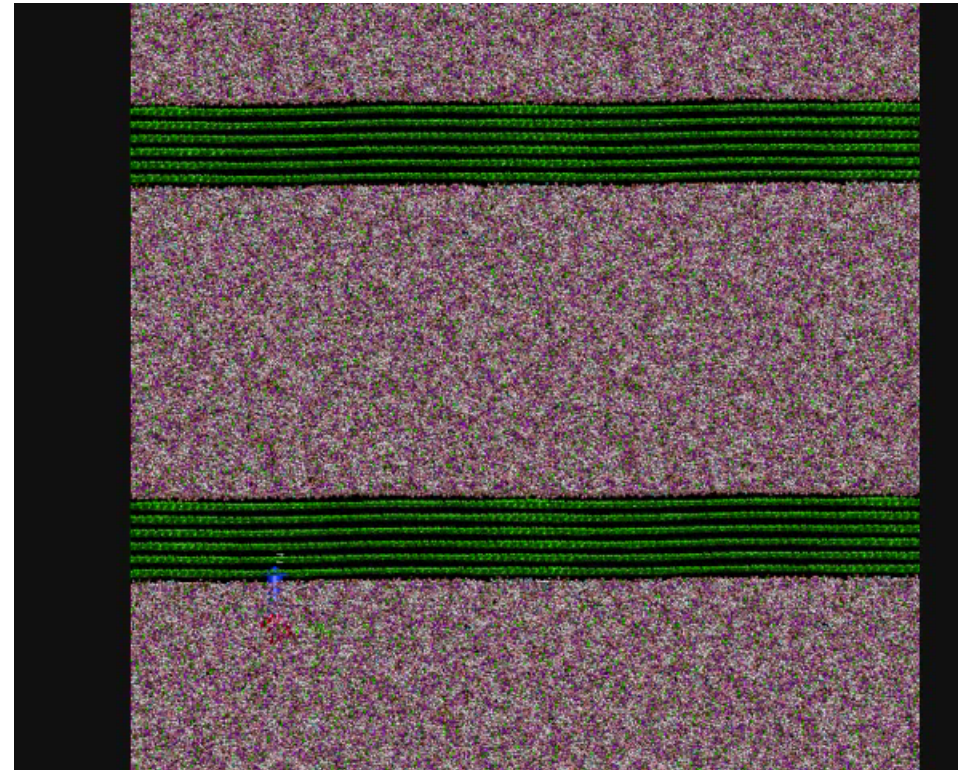Li and Strachan, Polymer 2010, 2011

Rate effects in polymer properties
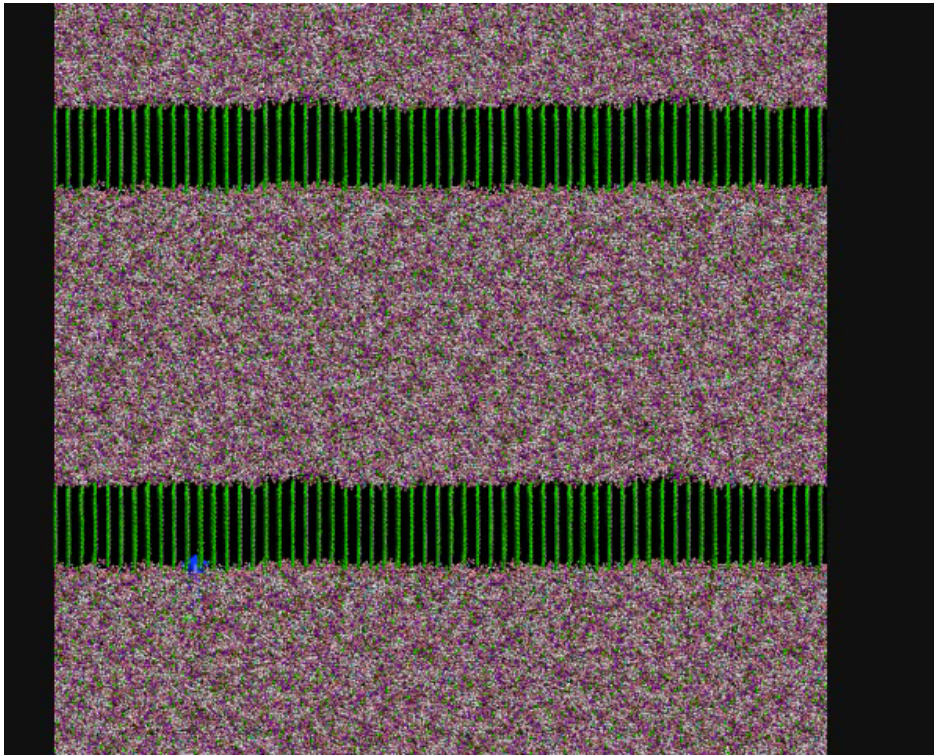
BGEBA/3,3DDS

Chunyu Li et al. Polymer (2012)
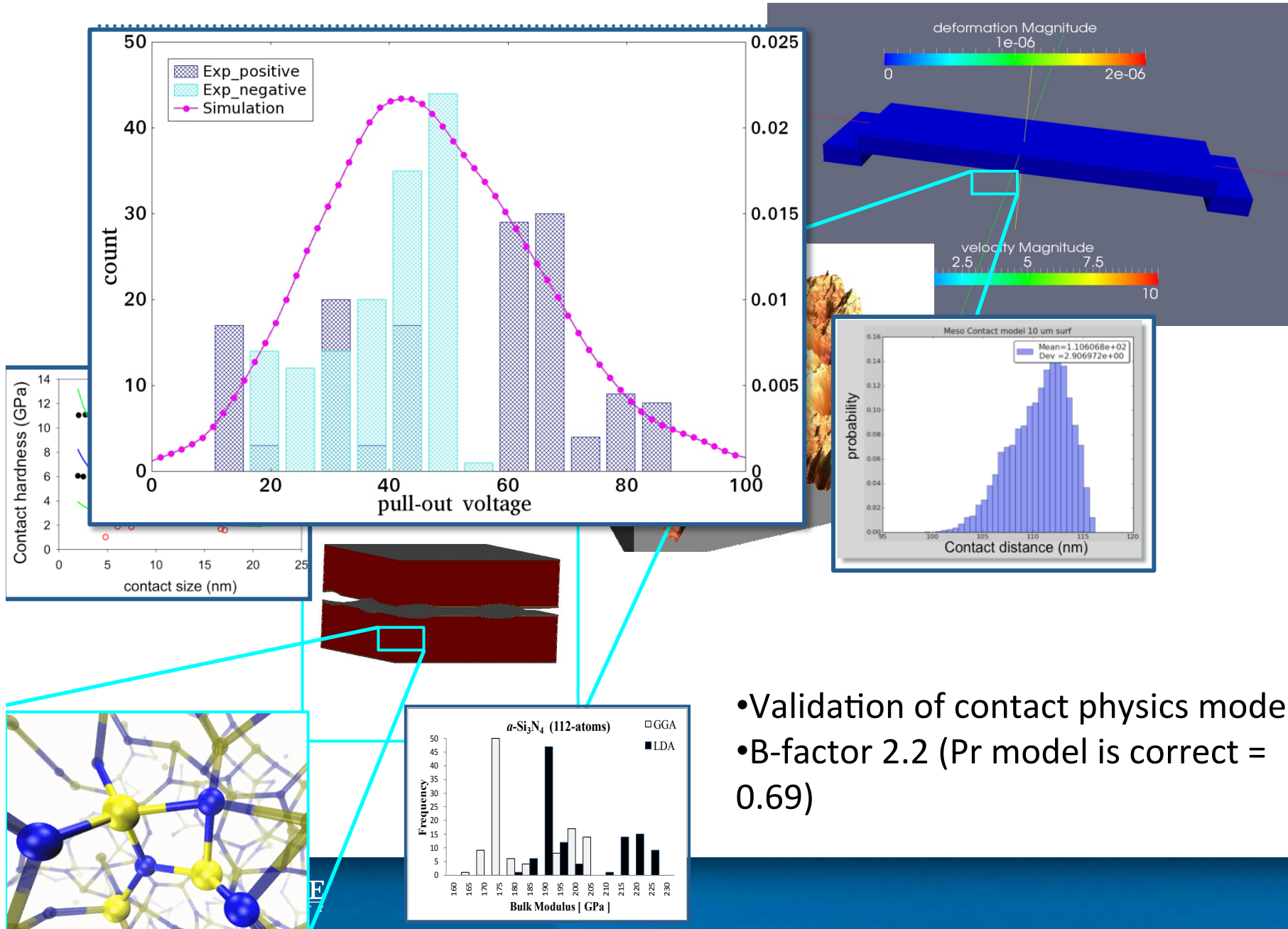
Processing and properties of thin films

Li and Strachan, Macromol. **44**, 9448–9454 (2011).

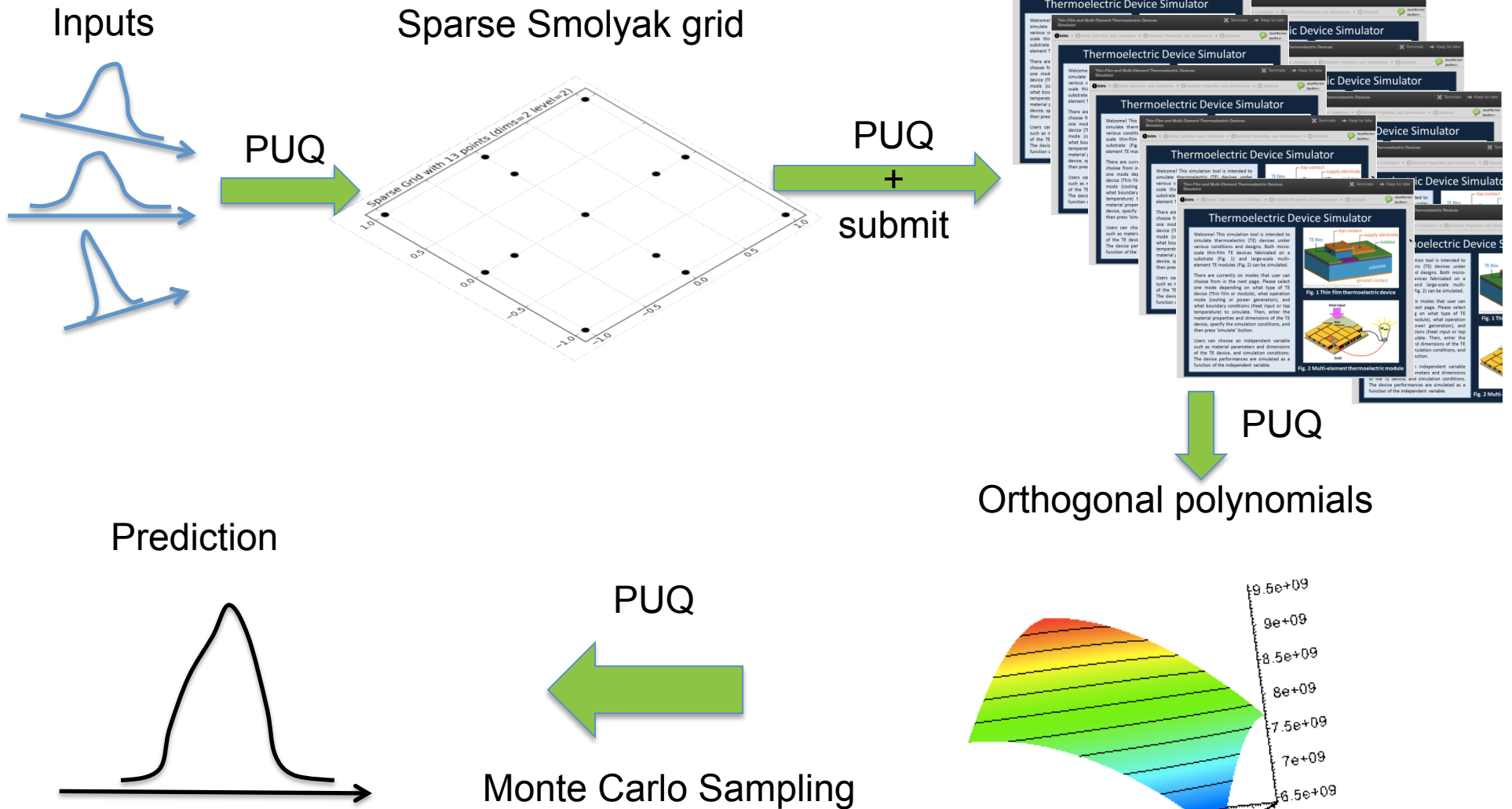# Polymer/graphite nanocomposites

C. Li, A. Browning, S. Christensen, and A. Strachan, Composites Part A (2012)

Multiscale, multiphysics w/ quantified uncertainties

- Validation of contact physics model
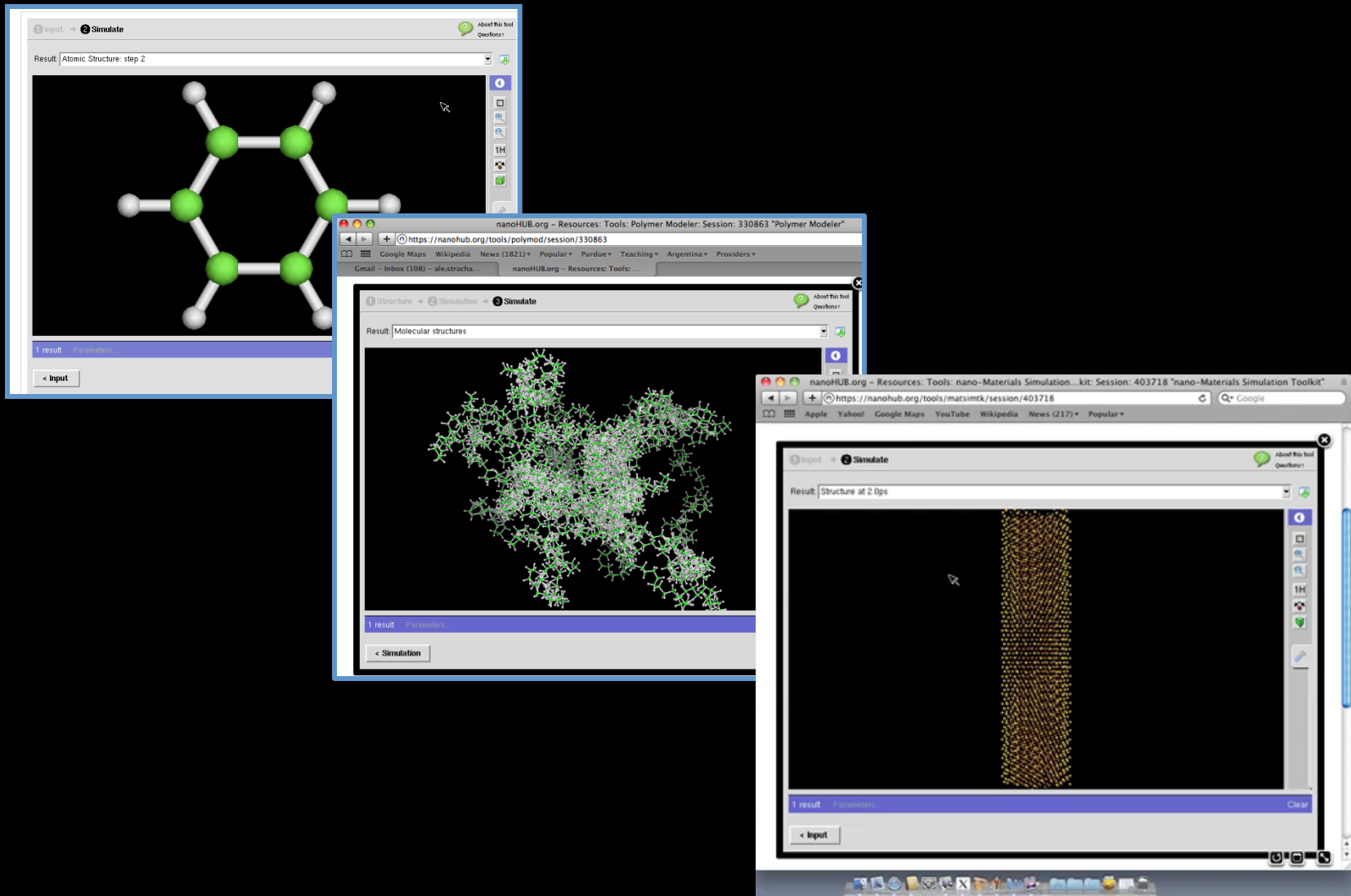- B-factor 2.2 (Pr model is correct = 0.69)

Uncertainty propagation

Inputs

Sparse Smolyak grid

PUQ

PUQ
+
submit

PUQ

Orthogonal polynomials

Prediction

PUQ

Monte Carlo Sampling

Additional resources online

- nanoHUB topics page on MD
  - https://nanohub.org/topics/MD

- Short and full courses on predictive simulations and MD
  - nanoHUB-U course "Atoms to Materials": https://nanohub.org/groups/u
  - Lecture series on MD simulations: http://nanohub.org/resources/5838

- Online MD simulations
  - nanoMATERIALS simulation tool: https://nanohub.org/tools/matsimtk
  - PolymerModeler: https://nanohub.org/tools/polymod
  - nanoMATERIALS nanoscale heat transport: https://nanohub.org/tools/nmstthermal

Online simulations at nanoHUB

Thanks