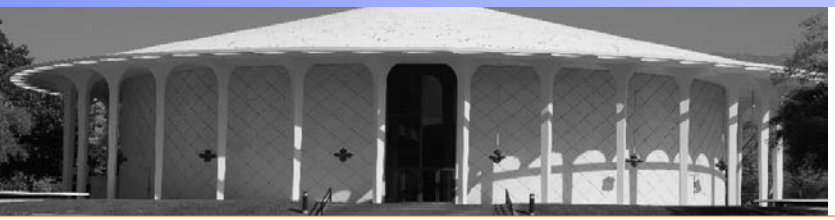


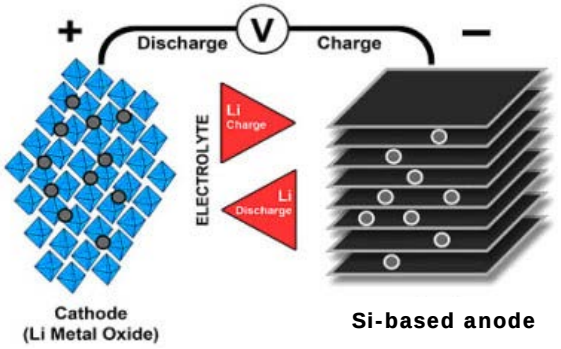
Atomistic Simulation of hydrogen storage in Pd nanoparticles

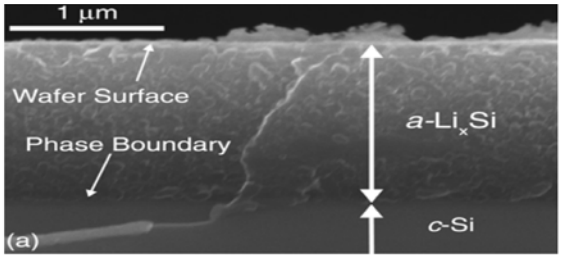
Michael Ortiz
California Institute of Technology

Collaborators: M.P. Ariza (Seville), J.P. Mendez (Caltech), X. Sun (Caltech), M. Ponga (UBC), K.G. Wang (VPI&SU),

USACM Workshop on Mechanics of Nanoscale Materials
University of Pennsylvania, Philadelphia
August 21-23, 2019

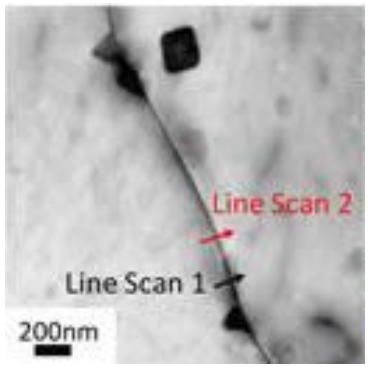
Motivation – Diffusive time scale

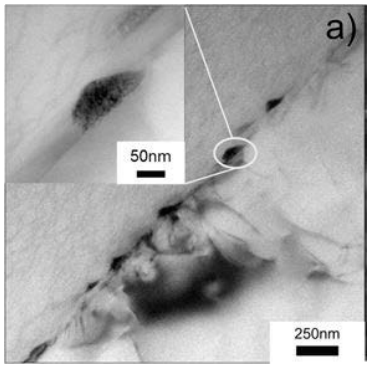




M. J. Chon *et al., Phys. Rev. Lett.*, **107** (2011) 045503.

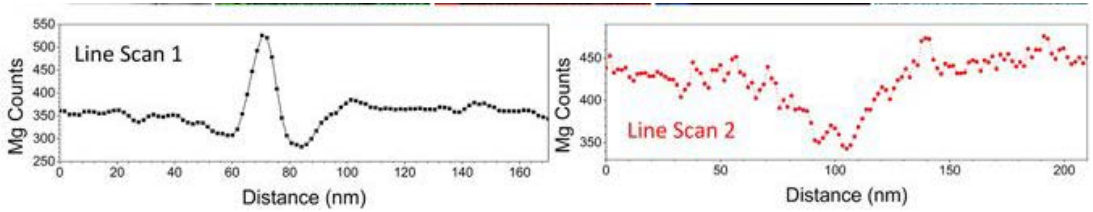
- Si-based anodes in Li-ion batteries
- Silicon loses crystalline structure upon lithiation and amorphizes
- Volume increase of 300%
- Loss of structure integrity and function after a few charge cycles





- Al-Mg 5xxxx series alloys
- Sensitization due to GBs
- Formation of β phase (Mg_2Al_3)
- Stress corrosion cracking

R. Zhang *et al., Scientific Reports*, **7** (2017) 2961.



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The spatial and temporal gaps

- The essential difficulty: ***Multiple scales***
  - *Atomic level rate-limiting processes: Thermal activation, transport, defects, grain boundaries…*
  - *But macroscopic processes of interest:*
    - *Microstructure evolution in alloys*
    - *Long-term transport phenomena: Heat, mass…*
    - *Full chemistry: Corrosion, combustion…*
- ***Time-scale gap***: From molecular dynamics (femtosecond) to macroscopic (seconds-years)
- ***Spatial-scale gap***: From lattice defects (Angstroms) to macroscopic (mm-m)
- Problem intractable by brute force (even with exascale computing ☺), *ergo* must think…

Diffusive Molecular Dynamics (DMD)

- *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***
  - *Append Onsager-like **empirical atomic-level kinetic laws** (heat and mass transport)*
  - ***Quasicontinuum** spatial coarse-graining*
- Implementation:
  - *Meanfield approximation of phase integrals*
  - *Quasistatic, forward integration of transport equations*

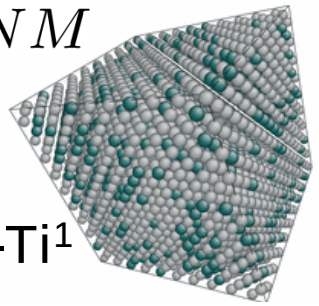
[1]Y. Kulkarni, J. Knap & MO, *J. Mech. Phys. Solids*, **56** (2008) 1417.

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

Anyone for a little theory?

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: $\{\boldsymbol{p}\} = \{\boldsymbol{p}_1, \ldots, \boldsymbol{p}_N\}$
  - Occupancy: $n_{ik} = \begin{cases} 1, & \text{site } i \text{ occupied by species } k, \\ 0, & \text{otherwise.} \end{cases}$



Al-Ti[1]

- 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.

Max-Ent Non-Equilibrium SM

- Gran-canonical free entropy:

$$\Phi(\{\bar{\boldsymbol{q}}\},\{\bar{\boldsymbol{p}}\},\{\beta\},\{\gamma\}) = k_B \log \Xi$$

- Local equilibrium relations:

$$-\frac{1}{k_B}\frac{\partial \Phi}{\partial \beta_i} = e_i$$

Local internal energy vs. temperature relation

$$\frac{1}{k_B}\frac{\partial \Phi}{\partial \gamma_{ik}} = x_{ik}$$

Local chemical potential vs. atomic fraction relation

$$\frac{1}{k_B}\frac{\partial \Phi}{\partial \bar{\boldsymbol{q}}_i} = 0$$

Force equilibrium (quasistatic)

- Equilibrium SM recovered when $\beta_i = \beta$, $\gamma_{ik} = \gamma_k$

Non-equilibrium SM – Meanfield theory

- Trial Hamiltonian: $\mathcal{H}_0 \equiv$ local harmonic oscillators,

$$h_{0i} = \frac{1}{2m(\boldsymbol{n}_i)}|\boldsymbol{p}_i - \bar{\boldsymbol{p}}_i|^2 + \frac{m(\boldsymbol{n}_i)\omega_i^2}{2}|\boldsymbol{q}_i - \bar{\boldsymbol{q}}_i|^2$$

- Entropy function (parameterized by $\{\omega\}$):

$$\Phi_{\mathsf{MF}} = \sum_{i=1}^{N} k_B \left(\frac{\beta_i}{2m_i}|\bar{\boldsymbol{p}}_i|^2 + \beta_i \langle V_i \rangle_0 + 3\log(\hbar\beta_i\omega_i) - 3 \right)$$

Gaussian integrals!
Hermite quadrature!

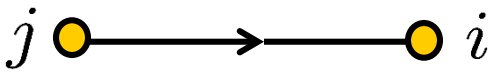
- Meanfield mesoscopic dynamics:

$$-\frac{1}{k_B}\frac{\partial \Phi_{\mathsf{MF}}}{\partial \beta_i} = e_i, \quad \frac{1}{k_B}\frac{\partial \Phi_{\mathsf{MF}}}{\partial \gamma_{ik}} = x_{ik}, \quad \frac{1}{k_B}\frac{\partial \Phi_{\mathsf{MF}}}{\partial \bar{\boldsymbol{q}}_i} = 0$$

- Meanfield optimality: $\dfrac{\partial}{\partial \omega_i} \displaystyle\sum_{j=1}^{N} \beta_j \langle V_j \rangle_0 + \frac{3}{\omega_i} = 0$

Non-equilibrium SM – Onsager kinetics

- Closure: Need evolution equations for $\{\beta\}$ and $\{\gamma\}$
- Local conservation equations:



$$\underbrace{\dot{e}_i = \dot{w}_i + \boldsymbol{\mu}_i^T \dot{\boldsymbol{x}}_i + \sum_{j \neq i} R_{ij},}_{\text{energy}} \qquad \underbrace{\dot{\boldsymbol{x}}_i = \sum_{j \neq i} \boldsymbol{J}_{ij}}_{\text{mass}}$$

- Local dissipation inequality:

$$\Sigma_{ij} = k_B(\beta_i - \beta_j)R_{ij} + k_B(\boldsymbol{\gamma}_i - \boldsymbol{\gamma}_j) \cdot \boldsymbol{J}_{ij} \geq 0$$

- General kinetic relations: calibrate from exp. data!

$$\underbrace{R_{ij} = f(\beta_i - \beta_j),}_{\text{Discrete Fourier law}} \qquad \underbrace{\boldsymbol{J}_{ij} = g(\boldsymbol{\gamma}_i - \boldsymbol{\gamma}_j)}_{\text{Discrete Fick's law}}$$

Non-equilibrium SM – Sample potentials

- Structure of typical multispecies EAM potential:

$$V = \sum_{i=1}^{N} \left[n_i F_i(\rho_i) + \frac{1}{2} \sum_{j \neq i} n_i n_j S_{ij}(n_i, n_j) \phi_{ij}(r_{ij}) \right]$$

- Meanfield equilibrium: $\mu_i = \dfrac{k_B T}{2} \log \dfrac{x_i}{1 - x_i}$

- Master equation: $\dfrac{\partial x_i}{\partial t} = \sum_{\langle i,j \rangle} (\psi_{j \to i} - \psi_{i \to j})$

- Transition probabilities:

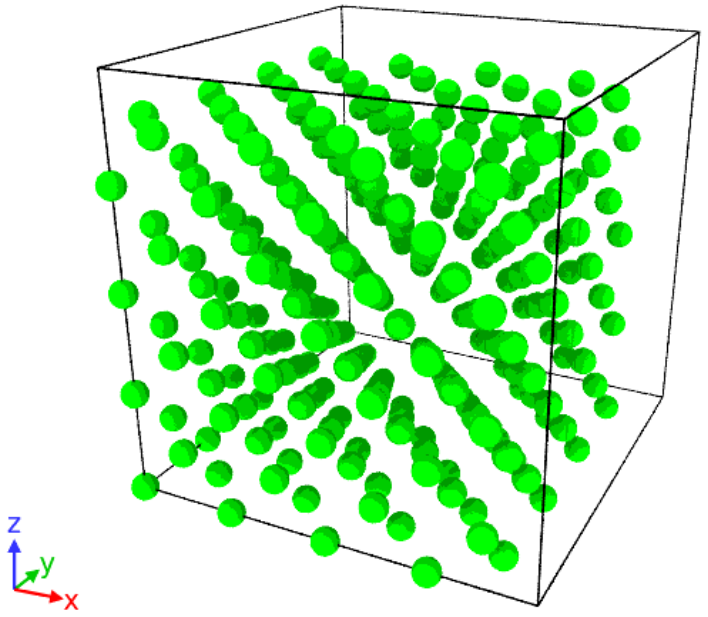
$$\psi_{i \to j} = \nu_i \, x_j (1 - x_i) \, e^{-\beta \left(E_{i \to j} + (\mu_i - \mu_j)/2 \right)}$$

attempt frequency

energy barrier

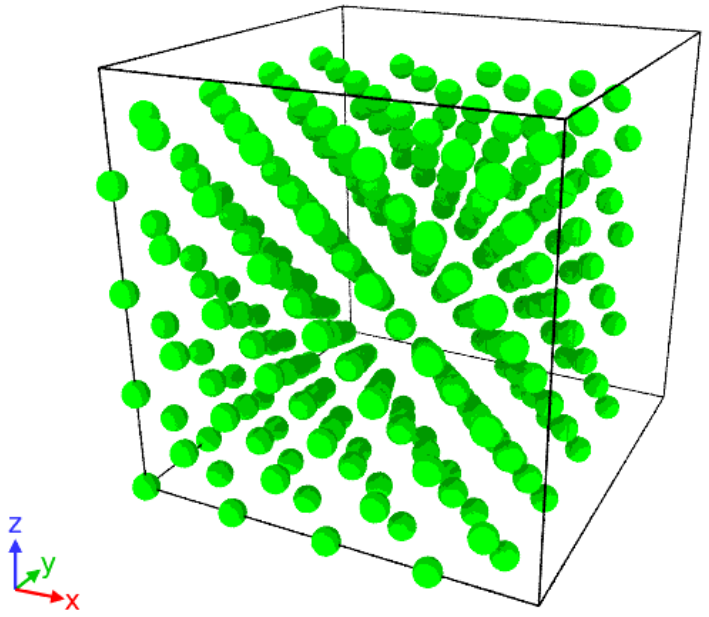
MD *vs*. DMD in pictures

MD: must track thermal vibrations of the atoms



FCC-Al
T=900K
NVT ensemble

DMD: atoms are quiescent but hot (mean flow)



FCC-Al
T=900K
NVT ensemble

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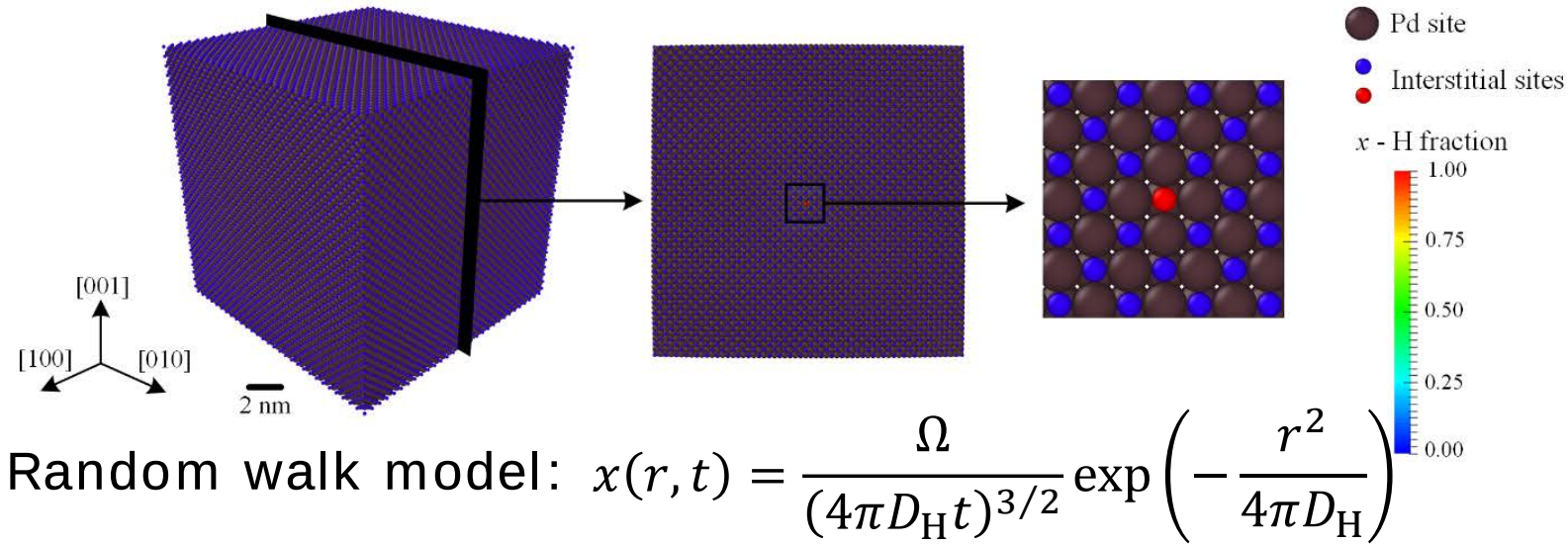
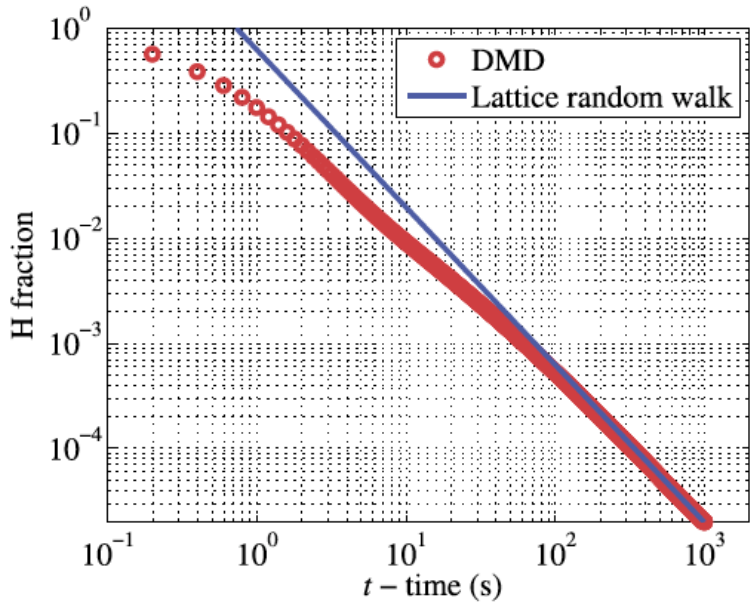
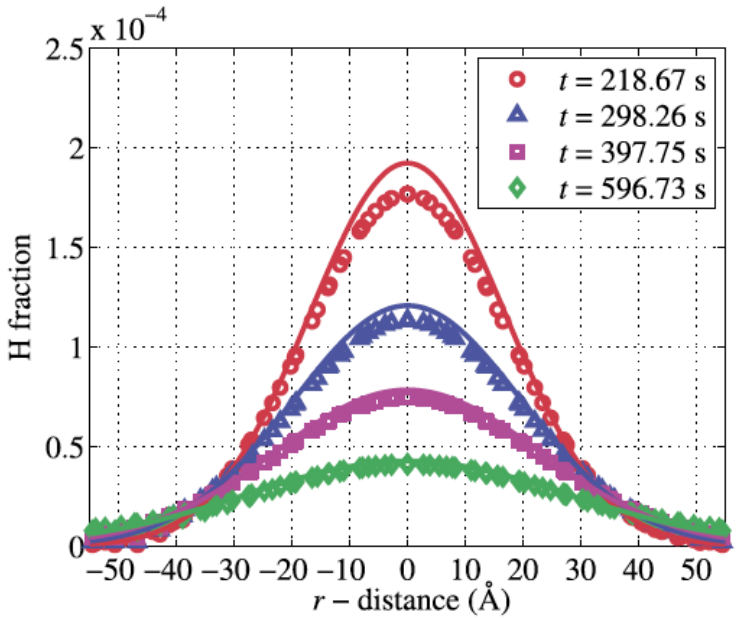
MD *vs*. DMD in pictures



Random walk model: $x(r,t) = \dfrac{\Omega}{(4\pi D_{\mathrm{H}} t)^{3/2}} \exp\left(-\dfrac{r^2}{4\pi D_{\mathrm{H}}}\right)$





X. Sun, M. P. Ariza, M. Ortiz, K. G. Wang, J Comput Phys, **350**:470-492, 2017.

Liouville equation

- Liouville equation: $\partial_t \rho + \mathrm{div}\,(\rho\, X_H) = 0$
- Weak form: $\int \left(\partial_t \rho + \mathrm{div}\,(\rho\, X_H) \right) \pi \, dz = 0$
- Non-equilibrium Bolzmann: $H = \sum_{i=1}^{N} h_i,$

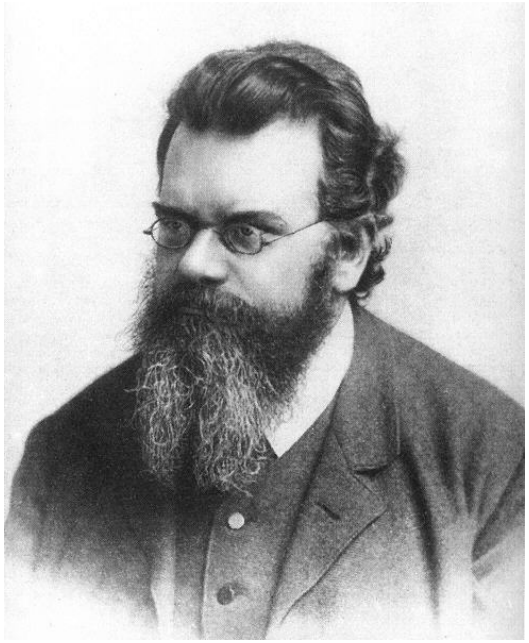
$$\rho = \frac{1}{Z} \exp\left(-\alpha \cdot z - \beta \cdot h\right), \qquad \pi = \xi \cdot z + \eta \cdot h$$

- Mesodynamical equations:

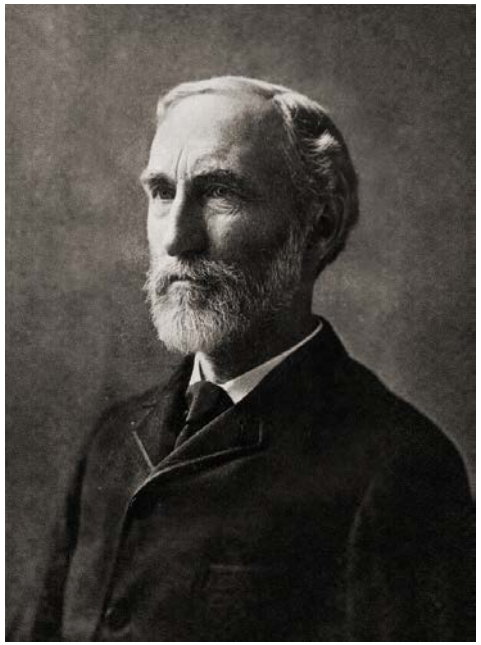
$$\dot{\bar{q}}_i = \frac{\bar{p}_i}{m_i}, \qquad \dot{\bar{p}}_i = -\langle \frac{\partial V}{\partial q_i} \rangle,$$

$$\dot{\bar{h}}_i = \sum_{j=1}^{N} \langle \frac{\partial V_i}{\partial q_j} \rangle \cdot \frac{\bar{p}_j}{m_j} - \langle \frac{\partial V}{\partial q_i} \rangle \cdot \frac{\bar{p}_i}{m_i} + \langle \partial_t V_i \rangle.$$

Statistical mechanics (beating the Avogadro and fs curses)



Ludwig Bolzmann
(1844-1906)



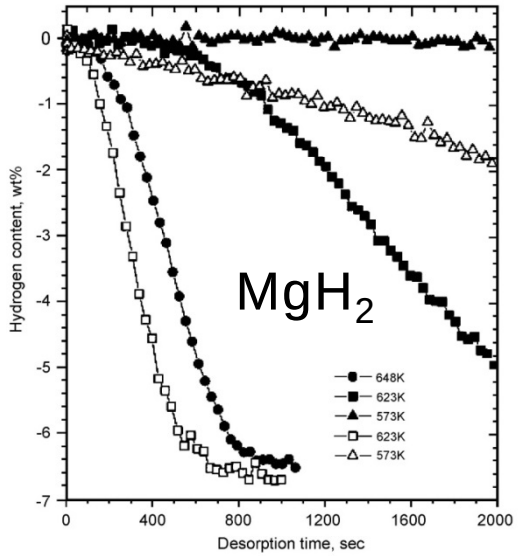
Josiah Willard Gibbs
(1839-1903)

- Gibbs canonical distribution:

$$P(X = x) = \frac{1}{Z(\beta)} \exp(-\beta E(x))$$

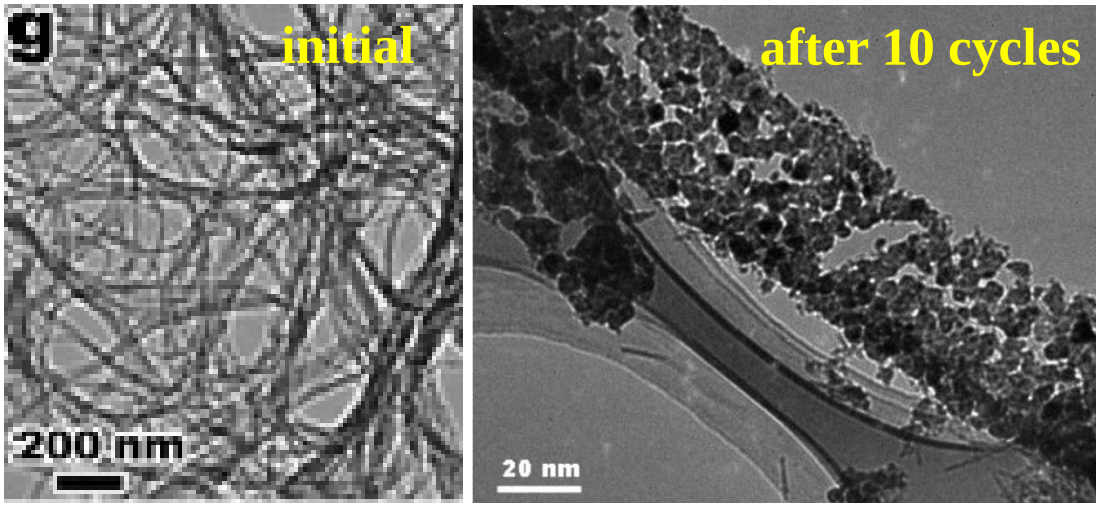
Theory is fun but applications pay the bills

Application: Hydrogen storage in Pd



- Hydrogen storage is a key element of the hydrogen economy…
- Typical absorption/desorption times are temperature/pressure dependent and in hour range[1]
- Outlook: Store hydrogen in nanostructured metals (particles, nanowires)

- But: Structural effects,
  - *Volume expansion*
  - *Pulverization*
- Mg disintegrates after 10 hydration cycles[2]
- Predictive capability:
  - *Atomistic realism*
  - *Long-time behavior…*

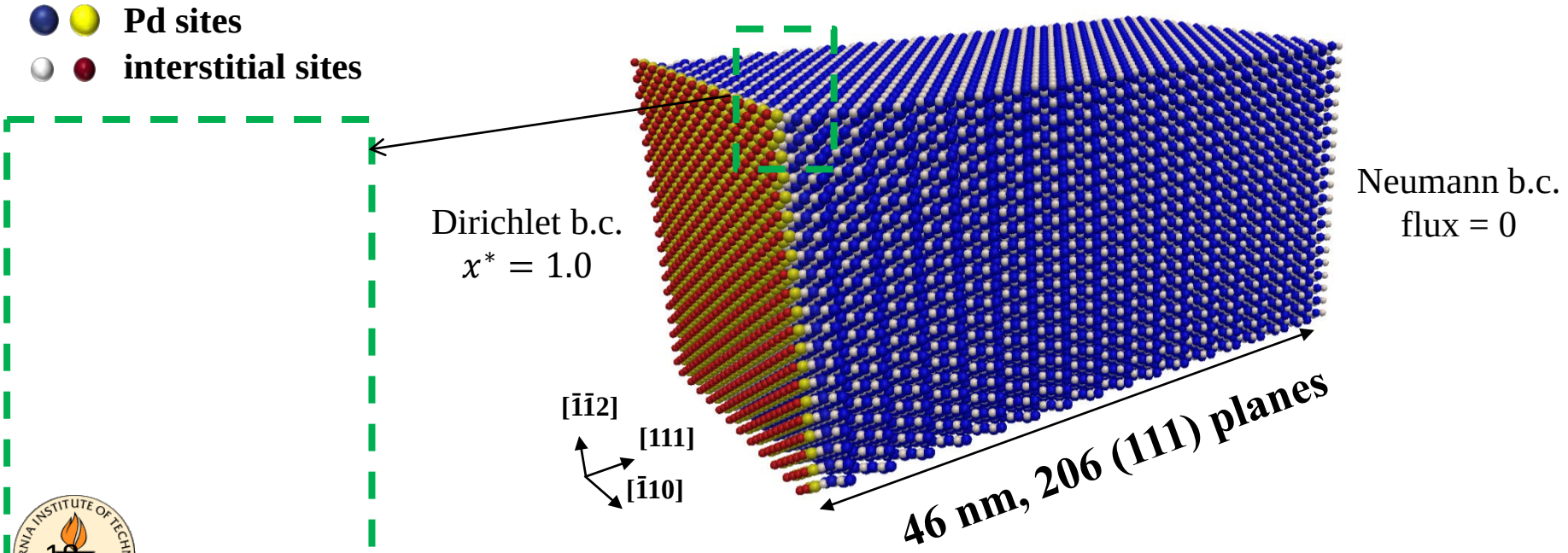


[1]B. Sakintuna, F. Darkrim and M. Hirscher, *Int.J. Hydrogen Energy*, **32** (2007) 1121– 1140.

[2]W. Li, C. Li et al., J. Am. Chem. Soc., 2007

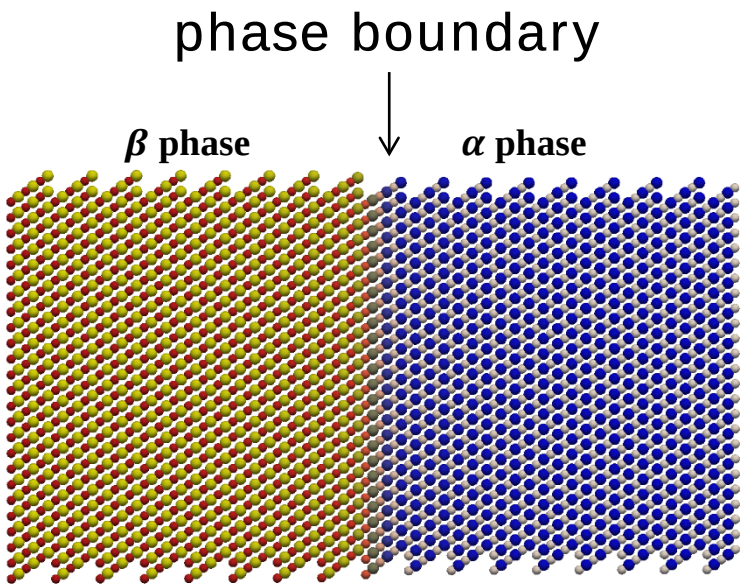
H storage in Pd NW – α–β interface

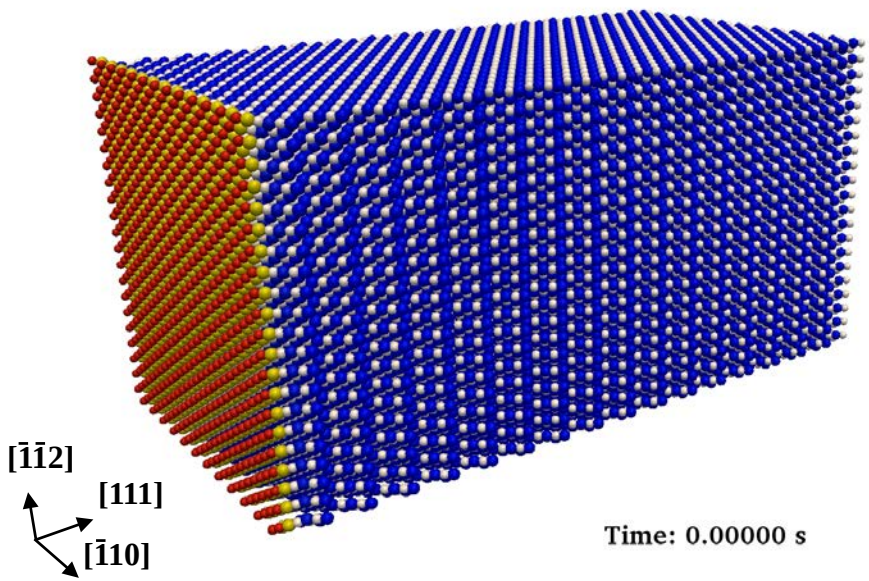
- PdH_x exists in two phases at room temperature:
  - α phase: $0 < x \leq 0.03$
  - β phase: $0.608 \leq x \leq 1$
- In both phases: H occupies octahedral sites of FCC Pd lattice
- Phase transition ($\alpha \rightarrow \beta$): 10.4% volume expansion
- Computational setup: EAM potential[1], NN transport kinetics

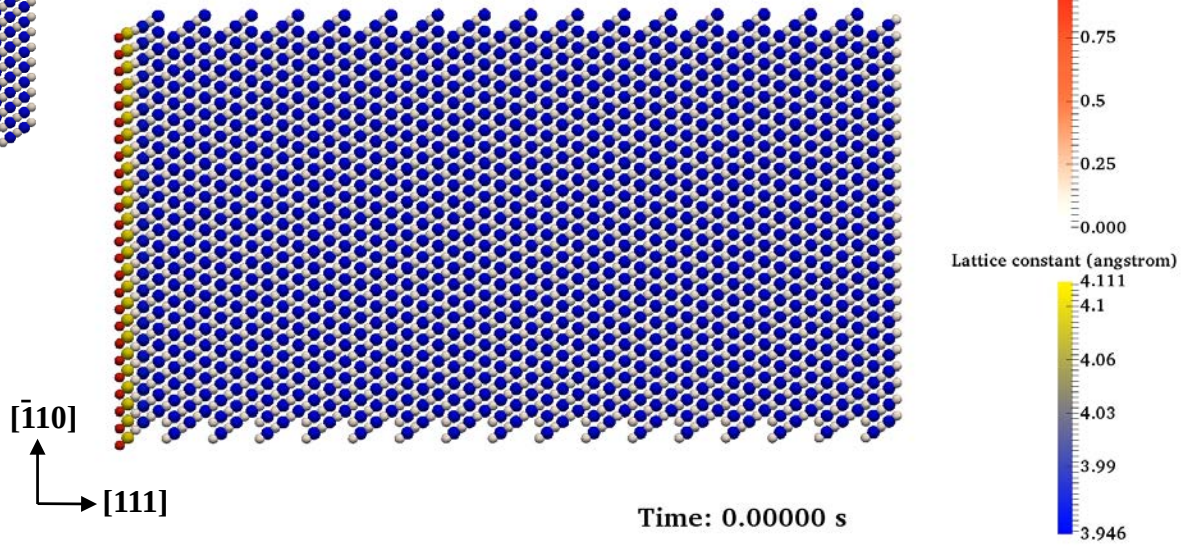


[1]X. Zhou, J. Zimmerman *et al.*, *J. Mater. Res.*, 2008

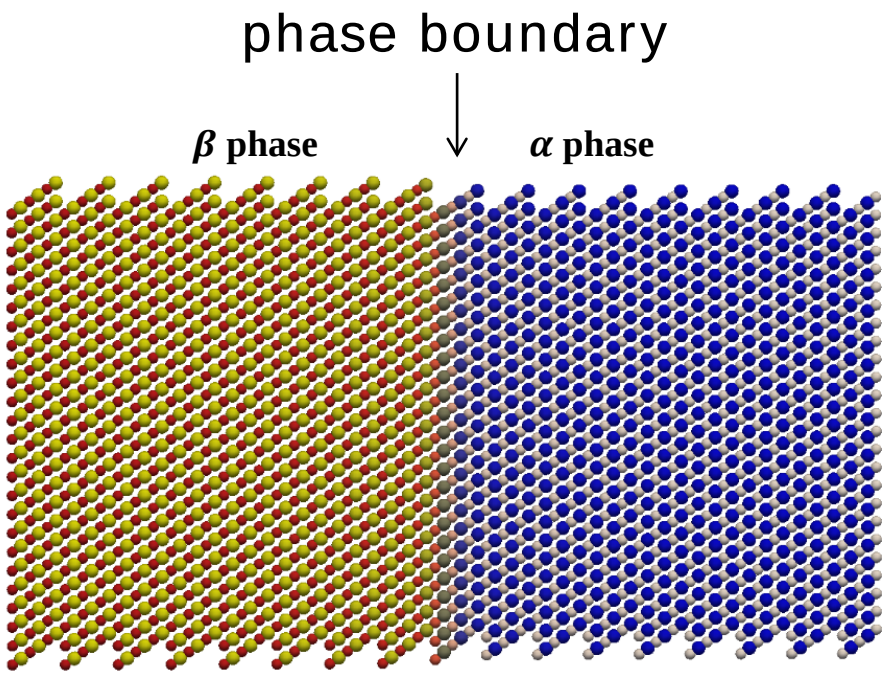
H storage in Pd NW – α–β interface

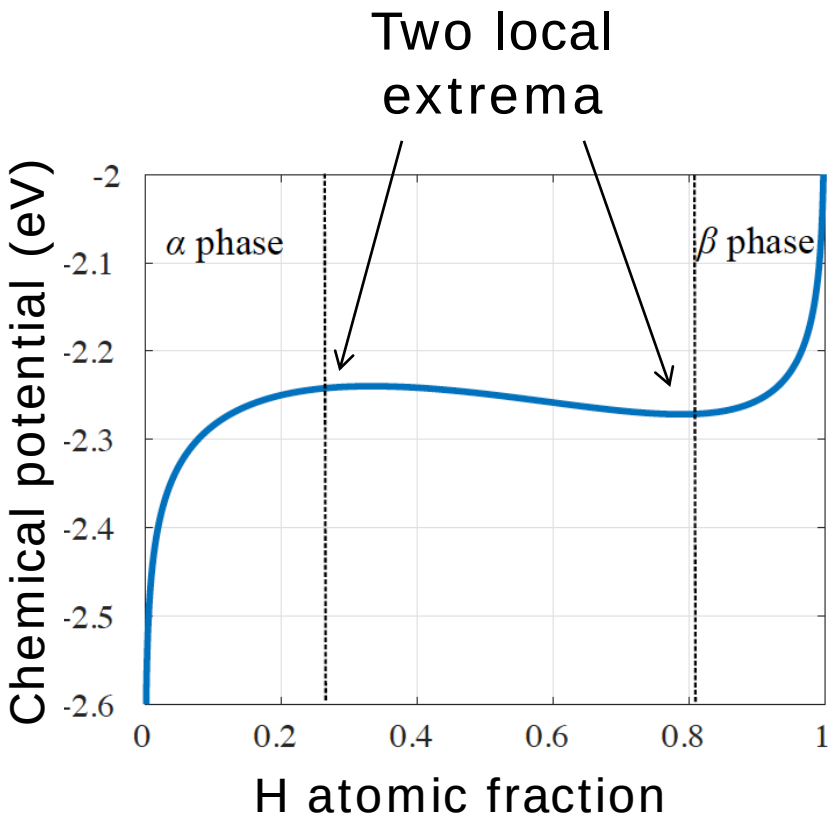






H storage in Pd NW – α–β interface





- Double-well (bistable, non-convex) free entropy

Each well corresponds to a stable phase (α and β)

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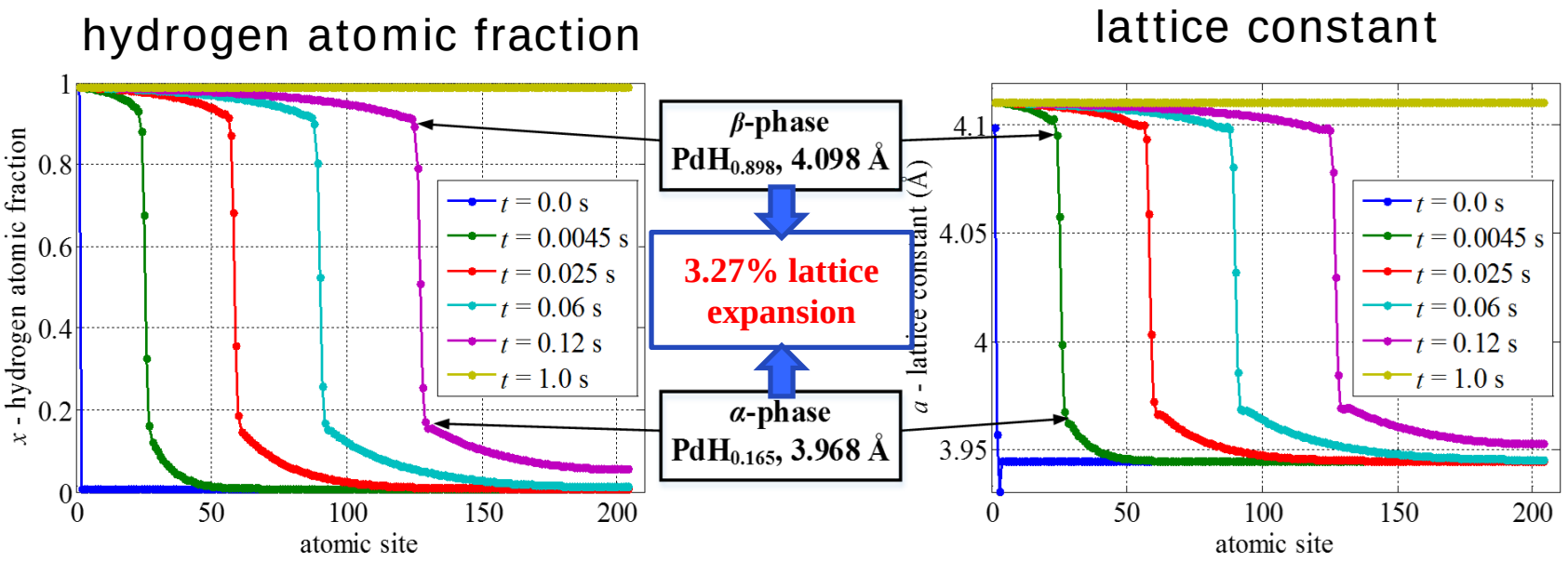
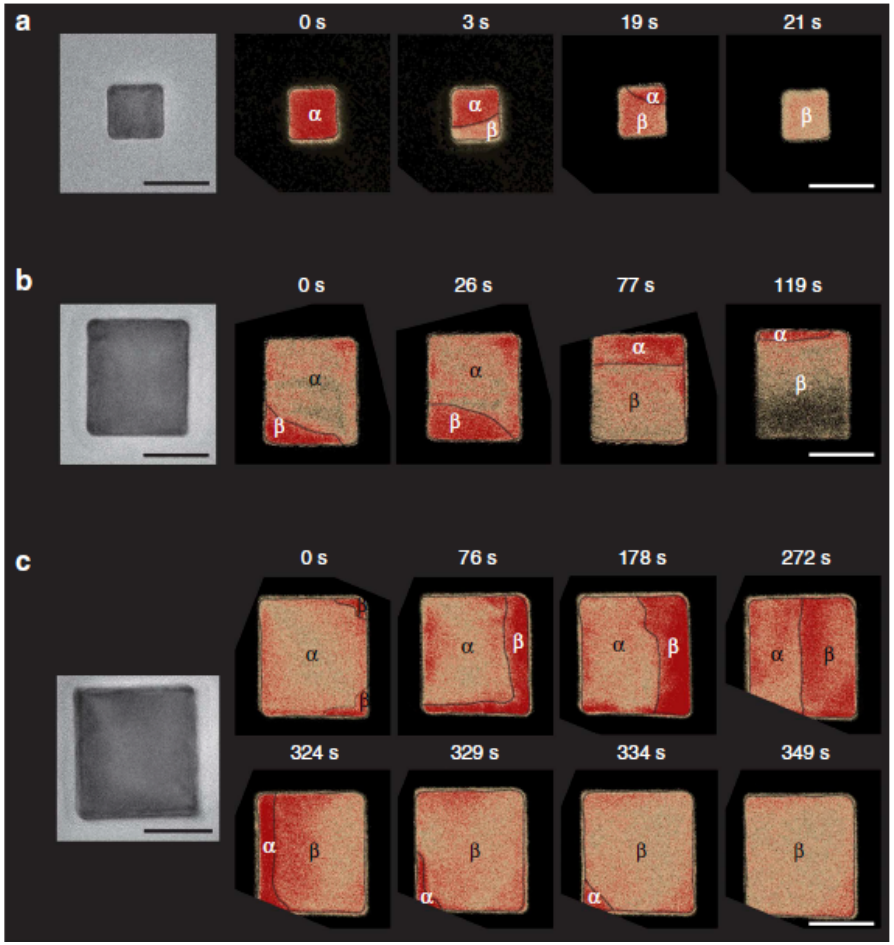
H storage in Pd NW – α–β interface



- Phase transition predicted (3.27% *vs.* 3.35%)
- Phase boundary velocity predicted (~100 nm/s)
- In progress: MgH_2 (hcp α-phase, rutile β-phase)

Sun, X., Ariza, M.P., Ortiz, M. and Wang, K., *Int J Hydrogen Energy*, 2018;**43**(11):5657-67.

Application: H storage in Pd nanoparticles



20 nm

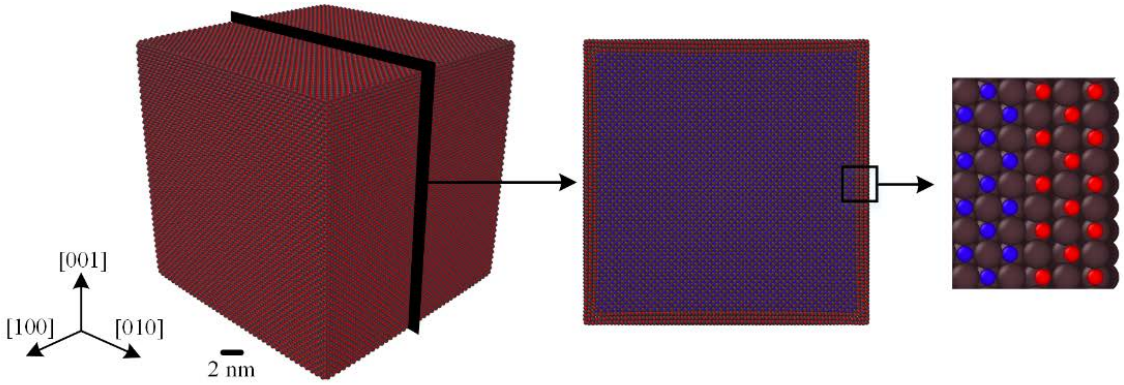
36 nm

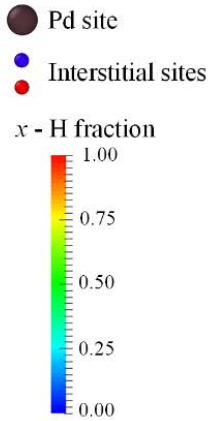
43 nm

STEM frames showing α to β phase evolution

Narayan *et al.*, *Nature Comm.* (2017)| DOI: 10.1038/ncomms14020)

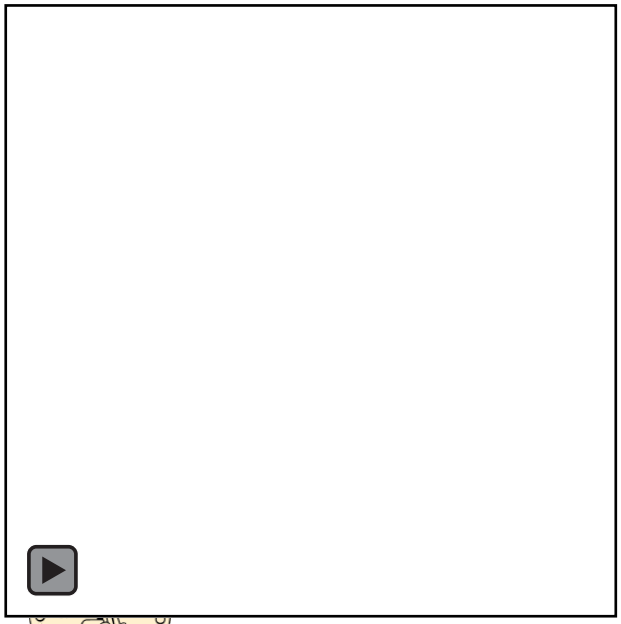
H storage in Pd NP – Problem setup

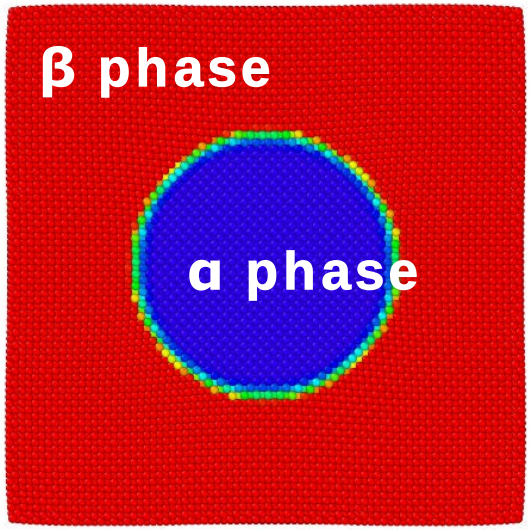




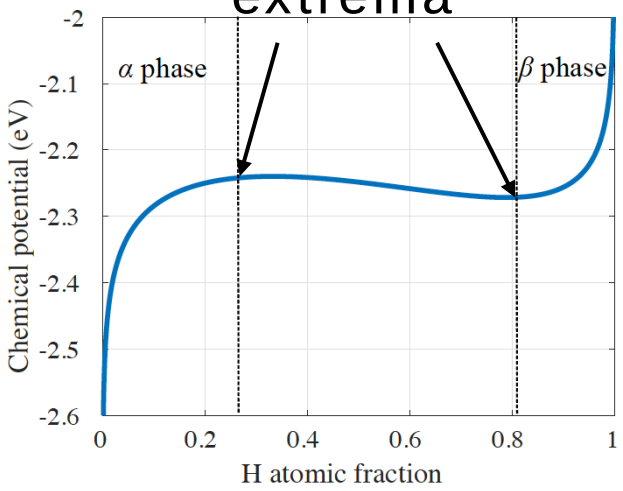
Nanocube (edge length: 16 nm), with faces on {100} planes.

α–β interphase

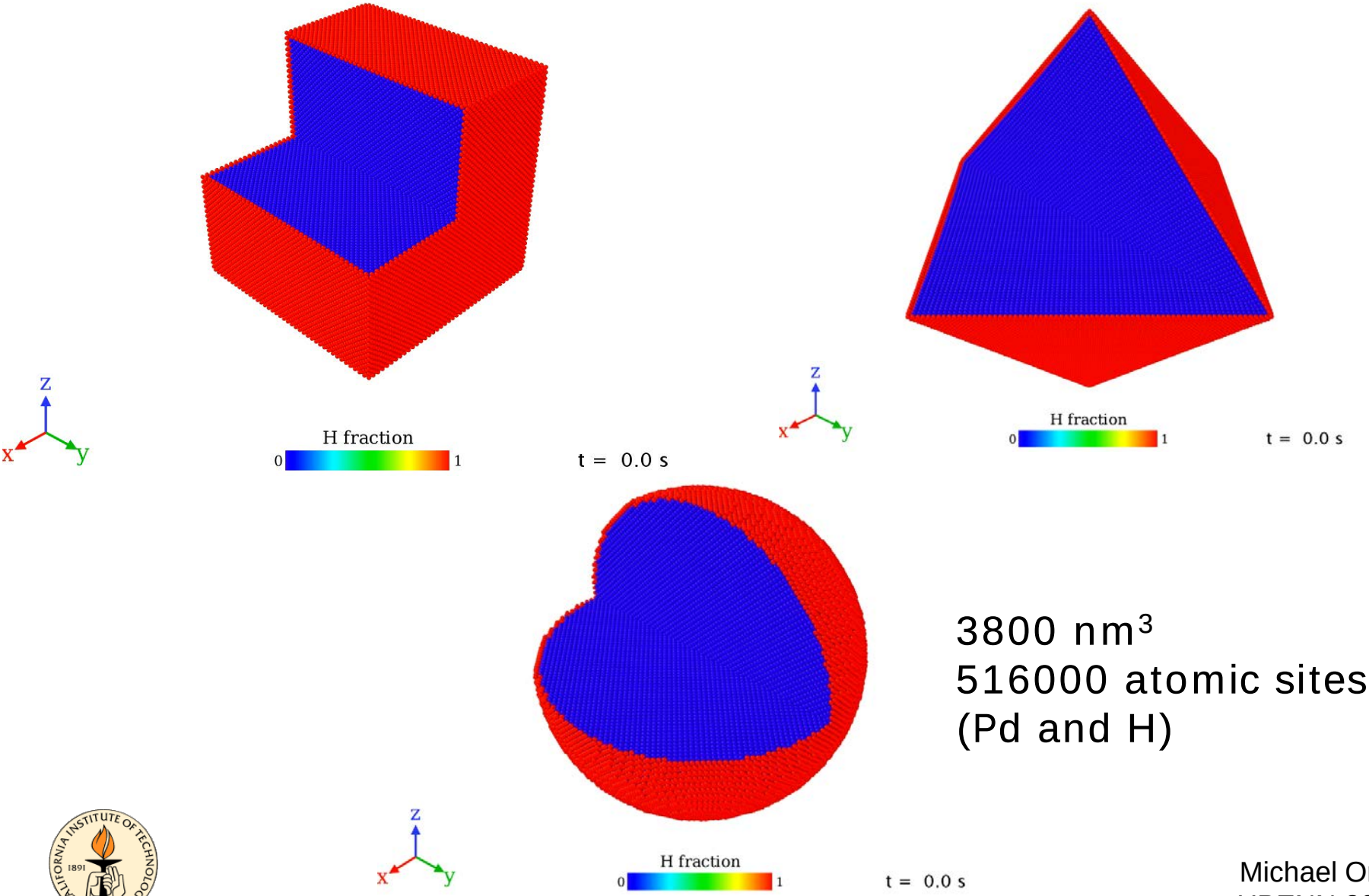




Two local extrema



H storage in Pd NP – Interface evolution



3800 nm³
516000 atomic sites
(Pd and H)

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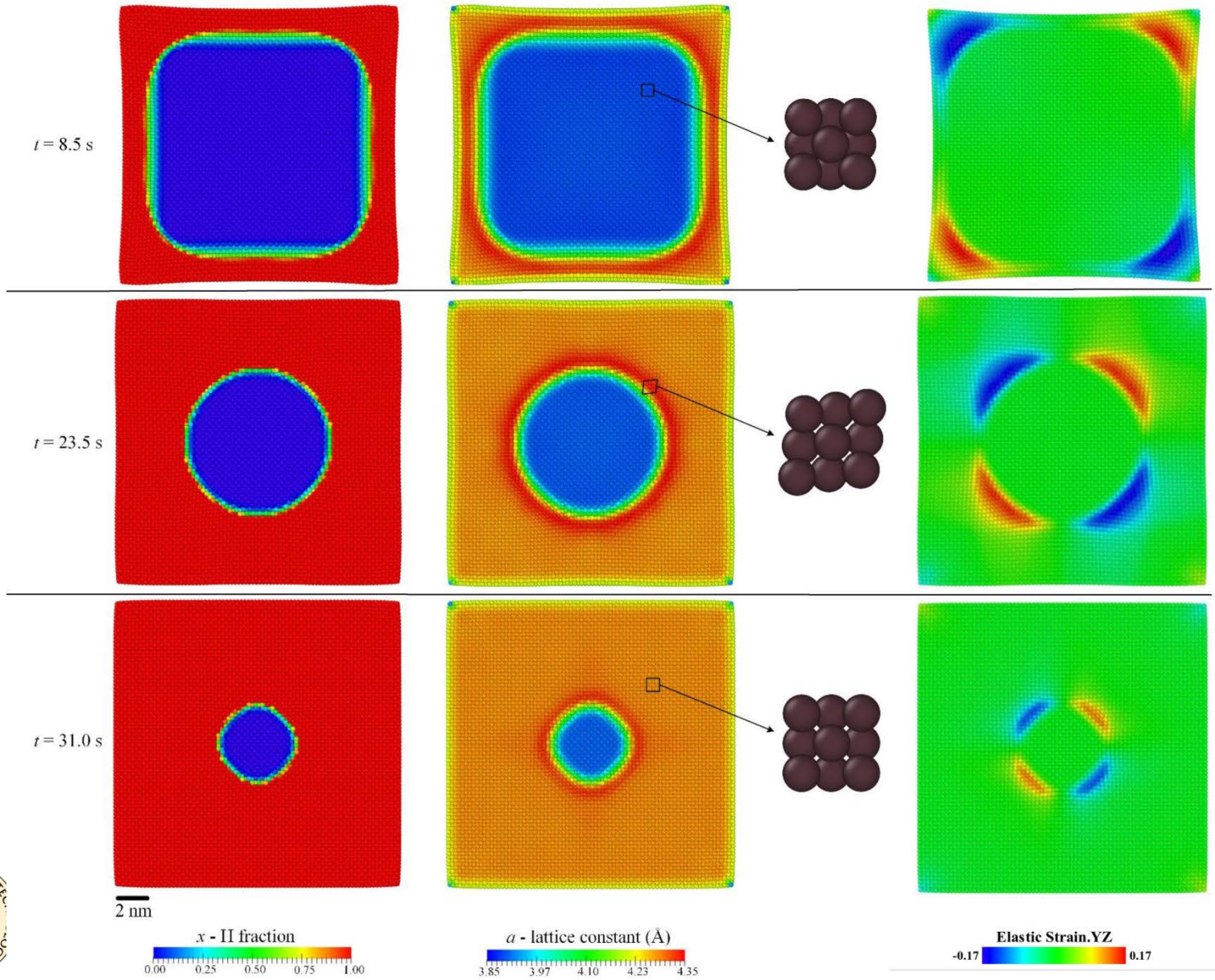
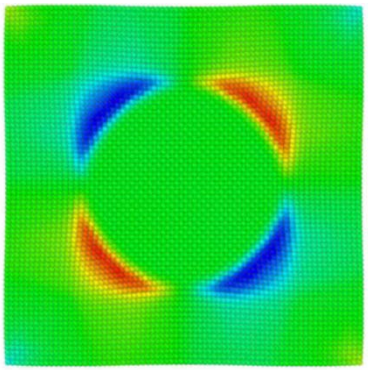
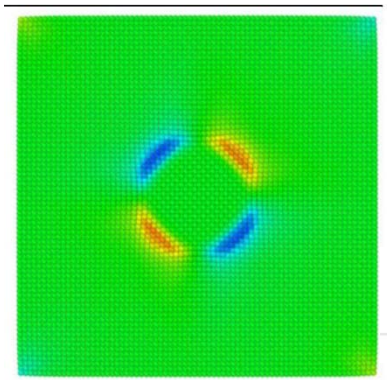
H storage in Pd NP – Interfacial strain

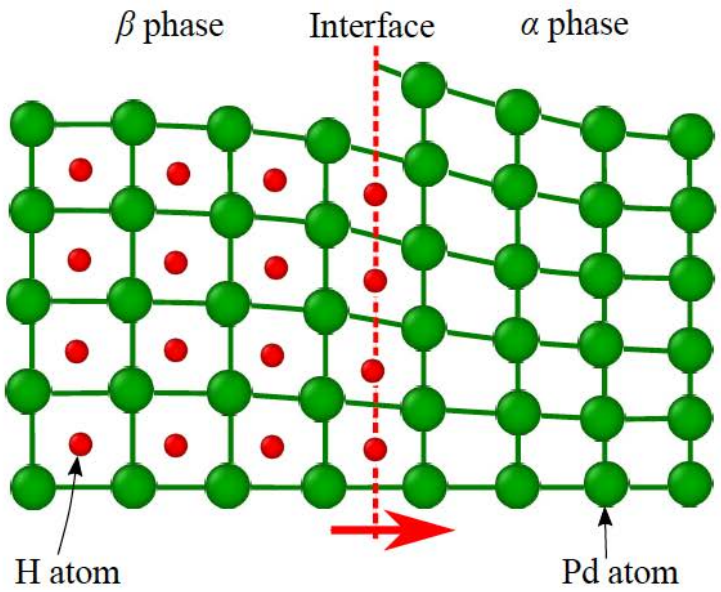


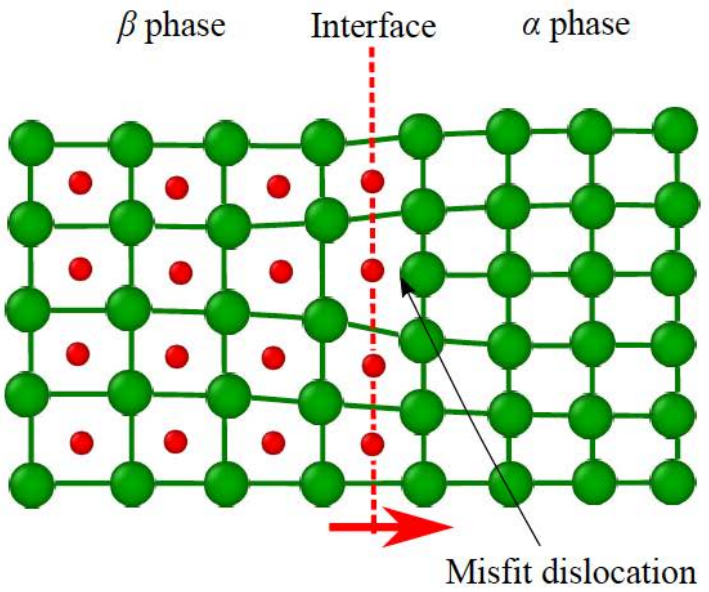
Interfacial dislocations





misfit
strain
evolution





Misfit strain is relieved by misfit dislocations

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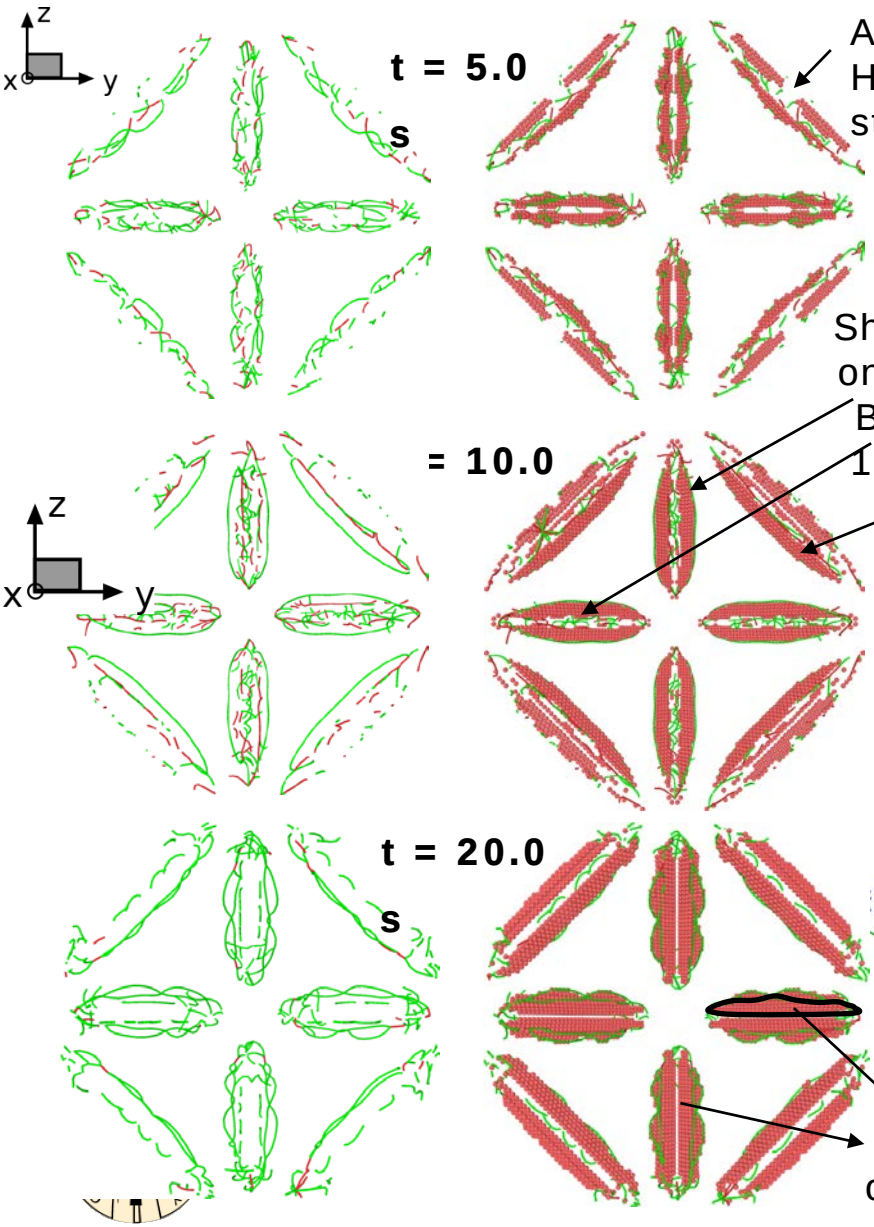
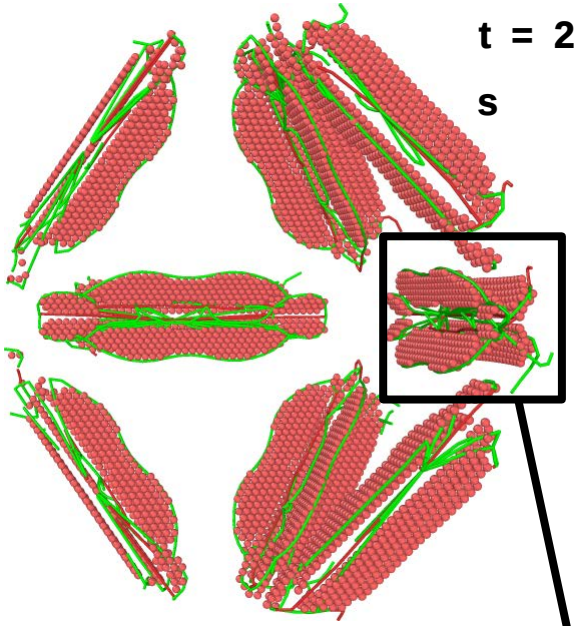
PdH: Interfacial misfit dislocations

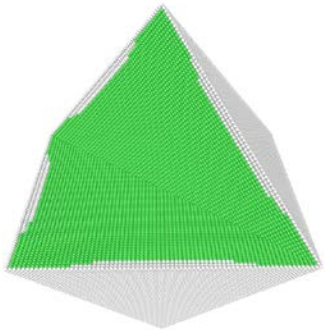


Atoms with HCP crystal structure

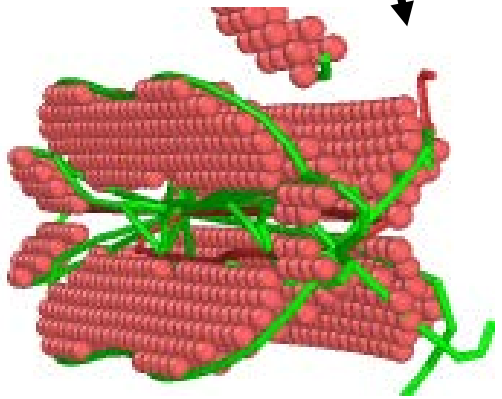
Shockley partials on {111} planes Burgers vector 1/6[112]{111}

Leading Dislocations on {111} plane





t = 0.0 s



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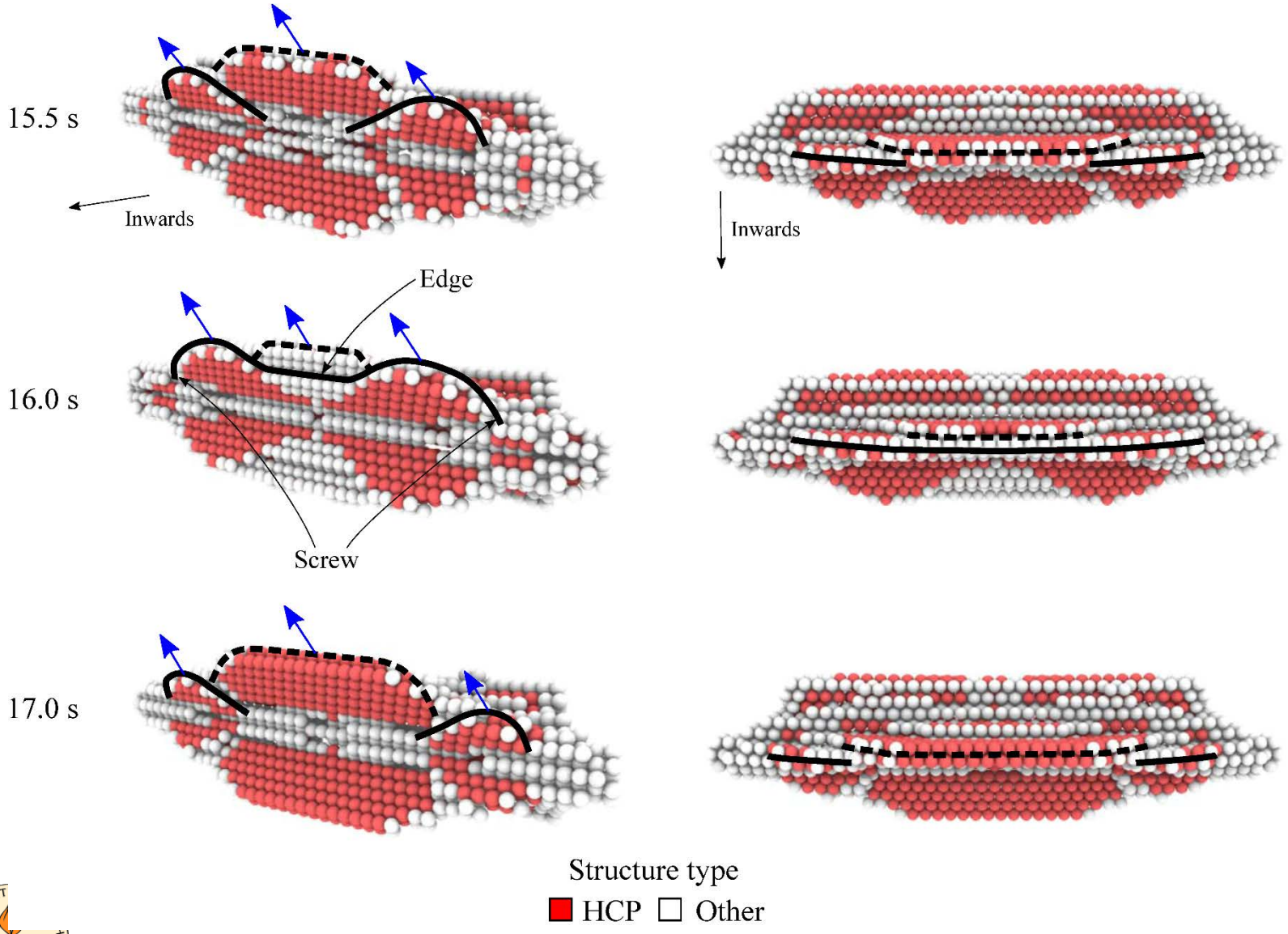
PdH: Interfacial misfit dislocations



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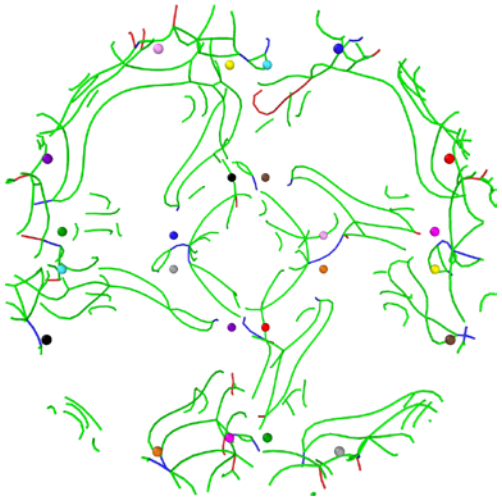
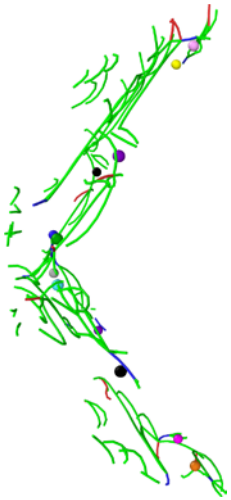
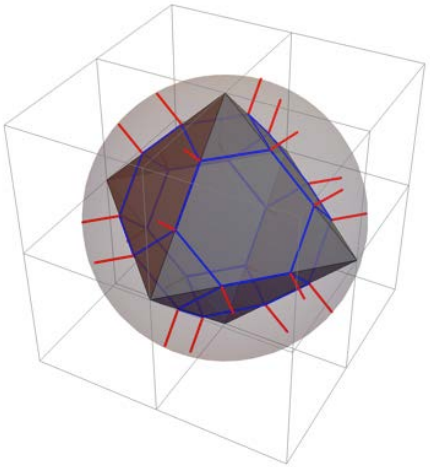
PdH: Interfacial misfit dislocations

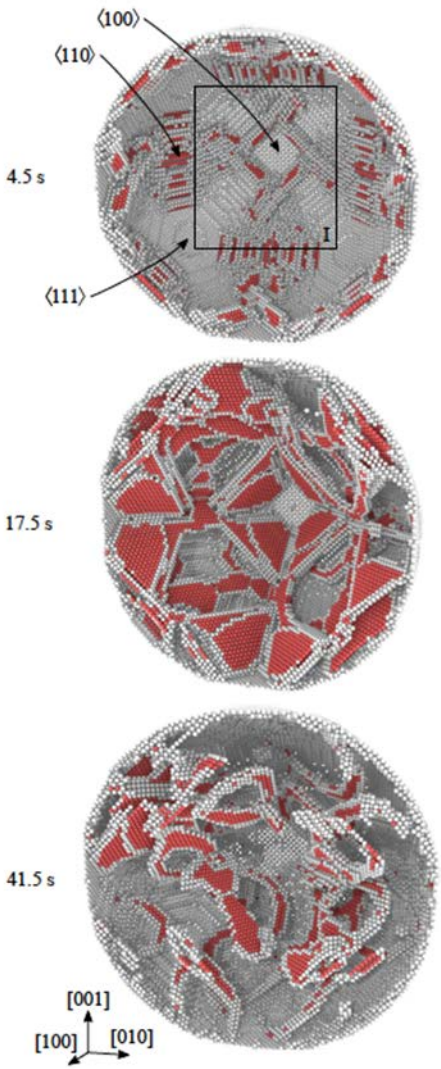


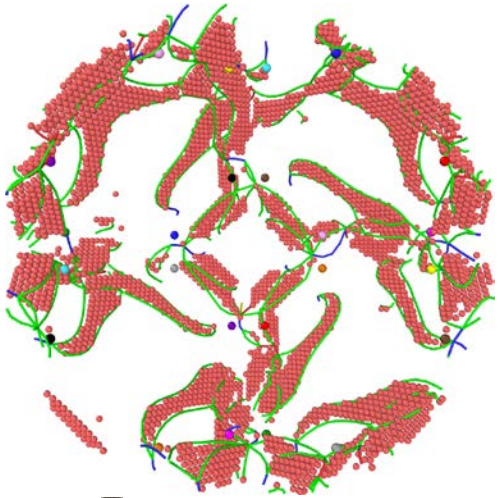
(100) plane



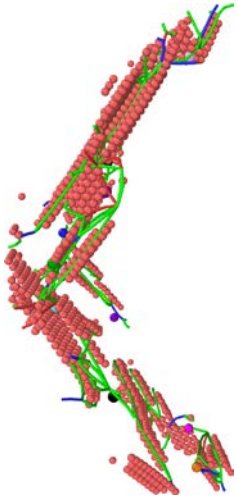
(111) direction



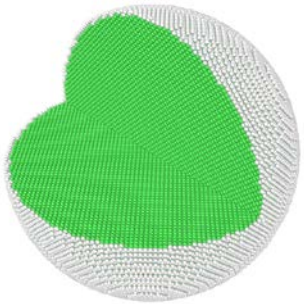




(100) plane



(111) direction



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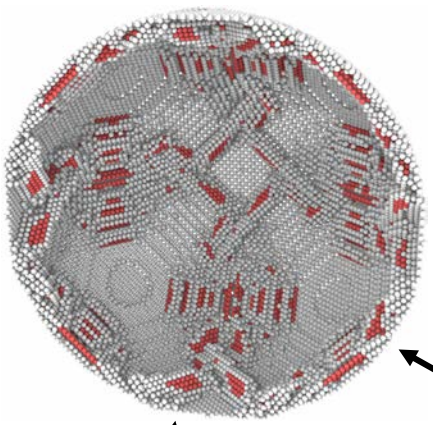
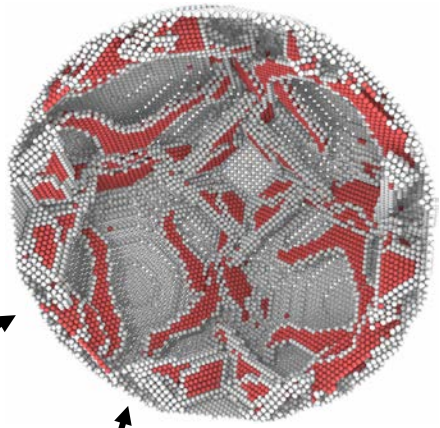
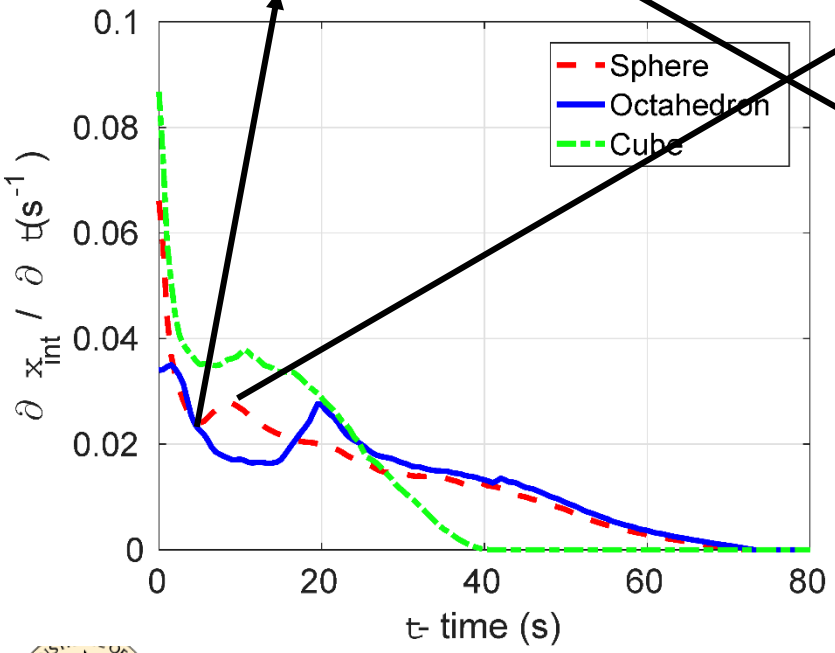
PdH: Dislocations vs. kinetics

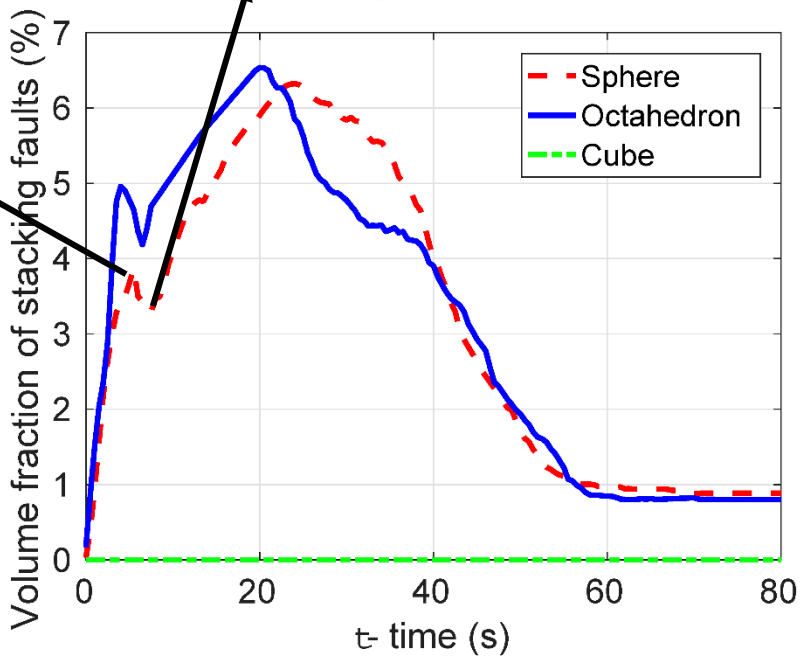


4.5 s



9.0 s





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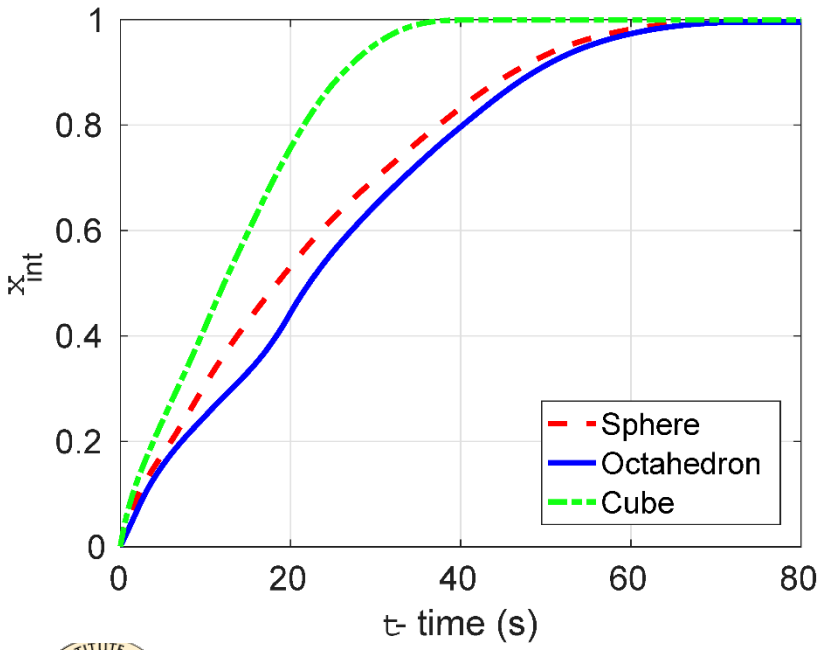
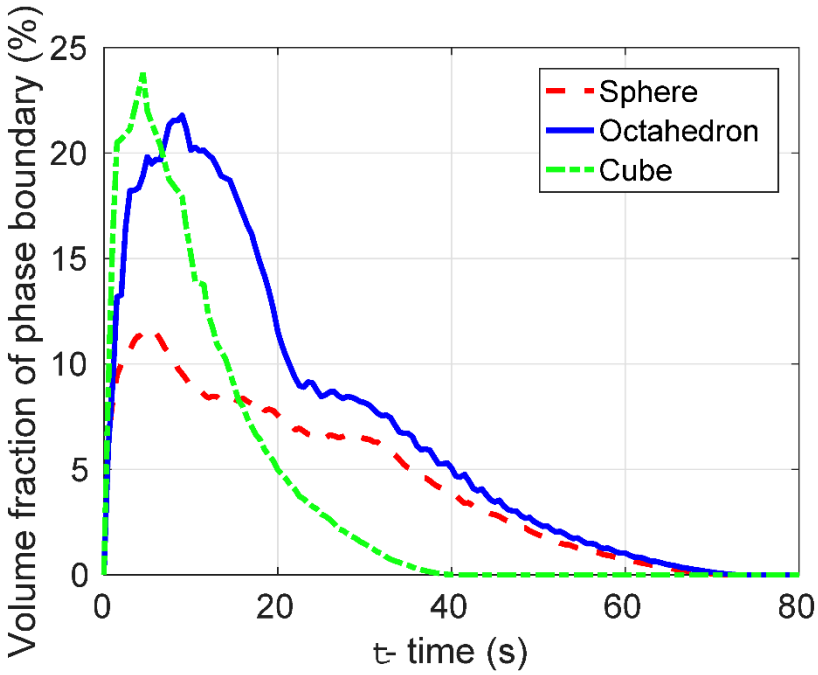
PdH: Morphology vs. kinetics

	$x_{\text{int}} = 0.3$	$x_{\text{int}} = 0.7$	$x_{\text{int}} = 1.0$
Cube	7.0 s	18.5 s	36.5 s
Sphere	9.0 s	26.5 s	59.5 s
Octahedron	12.0 s	27.0 s	60.0 s





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Concluding remarks

- *Diffusive Molecular Dynamics* (DMD) provides a useful paradigm for describing slow/long term transport phenomena with atomistic realism
- Thermodynamics without all the thermal vibrations, mass transport without all the hops
- Other applications of DMD:
  - *Heat conduction in Si nanowires*[1]
  - *Lithiation/amorphization of Si nanowires*[2]
- Work in progress: Microstructure evolution in Al/Mg alloys (work in collaboration with SINTEF/ Norway, NTNU, HZG...)

[1]C.S. Martin, M.P. Ariza and M. Ortiz *GAMM-Mitt*, **38(2)** (2015) 201.
[2]J.P. Mendez, M. Ponga and M. Ortiz, JMPS, 115 (2018) 123.

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