



Long-term mass transport: Application to H storage in Pd

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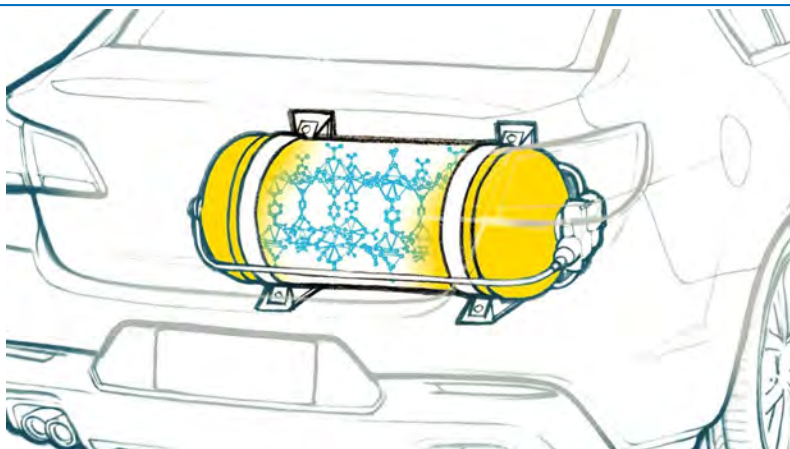
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(Virginia Tech)

MS Math. and Numerical Approaches to Energy Science
SIAM Conf. Mathematical Aspects of Materials Science
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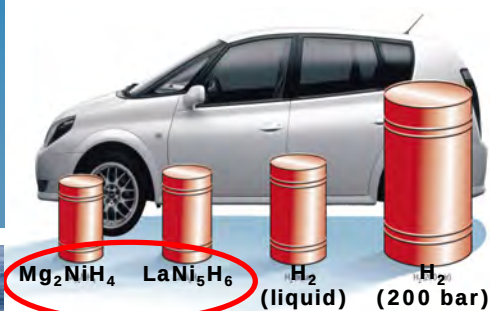
The hydrogen economy



From: JM Crow, Hydrogen Storage Gets Real, Chemistry World, 2019

- A **hydrogen economy** is one potential approach toward lowering carbon emissions while maintaining standard of living...
- **Fuel cells** are electrochemical cells that convert the chemical energy of a fuel (hydrogen) and an oxidizing agent (oxygen) into electricity through a pair of redox reactions
- Hydrogen storage? **Metal hydrides** (PdH , MgH_2 ...) offer high storage capacity, stability, safety...

Hydrogen fuel cells



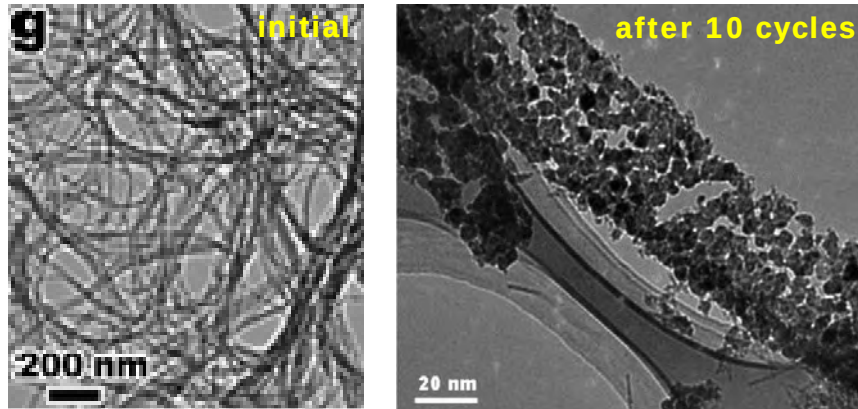
Metal hydrides

33rd Tokyo Motor Show



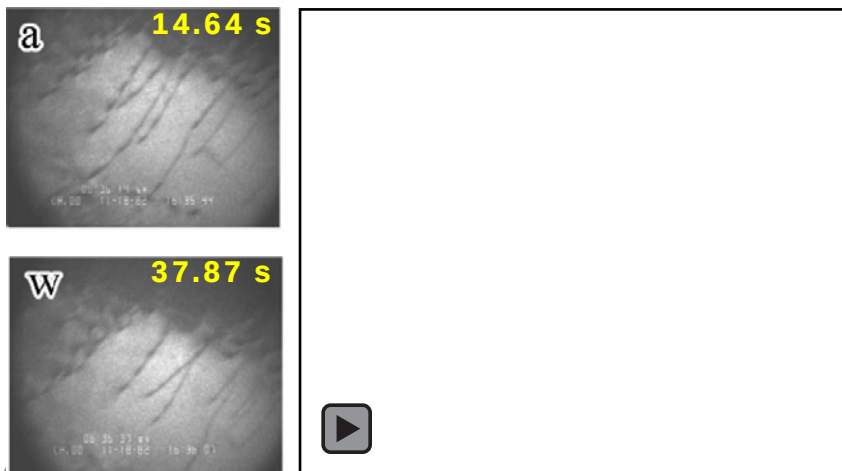
H storage – Nanomaterials

H-induced collapse in Mg nanowires



Li et al., J Am Chem Soc, 2007

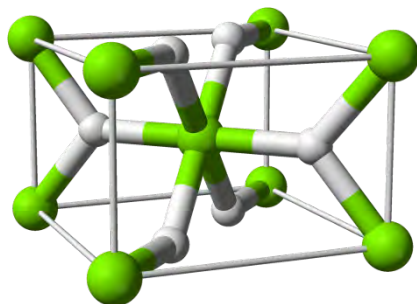
H-induced dislocation motion in Fe



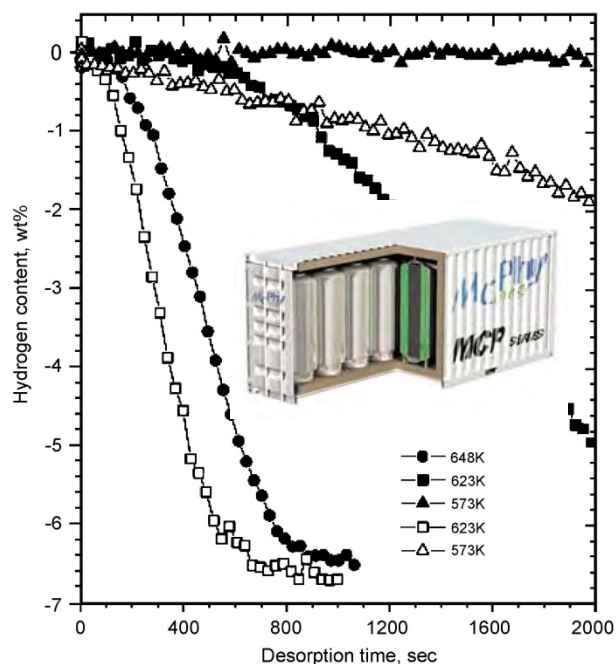
Robertson et al., Metall Mater Trans A, 2015

- The introduction of *nanomaterials* in onboard hydrogen storage systems is a major turning point in the automotive industry
- *Enhanced performance* due to improved hydrogen splitting kinetics and catalytic activity of the nanoparticles
- *Improved rate of sorption* at nanoscale due to short diffusion distance
- Issues: Storage capacity? Charge/discharge rate? Reversibility? *Structural integrity?*

H storage – Modeling challenges



MgH₂ unit cell¹



MgH₂ desorption curves²

- *Fundamental understanding requires atomistic fidelity*
- *Absorption/desorption* rates controlled at atomic level
- *Transport* tightly coupled to atomic level mechanisms (defects, phase transitions...)
- But: Device charge/discharge times temperature-pressure dependent and in *hour range*
- *Outside range of straight MD!*

¹W. H. Zachariasen, C. E. Holley and J. F. Stamper, *J. Acta Cryst*, **16** (5):352-353.

²B. Sakintuna, F. Darkrim and M. Hirscher, *Int.J. Hydrogen Energy*, **32** (2007) 1121– 1140.

H storage – Modeling challenges

- The essential difficulty: *Scale separation, gap...*
 - *Atomic level rate-limiting processes: Thermal activation, transport, point defects, dislocations...*
 - *But processes of interest are macroscopic: Long-term transport phenomena (storage, charge/discharge...)*
- *Temporal-scale gap*: From molecular dynamics (femtosecond) to device scale (hours)
- *Spatial-scale gap*: From atoms, lattice defects (Angstroms) to device scale (meters, moles)
- *Problem intractable by brute force* (even with exascale computing ☺), ergo must think...
- Our approach: *Mixed statistical/deterministic analysis*
 - Fast (thermal) component of the motion *statistical*
 - Slow (diffusion) component of the motion *deterministic*



Hamiltonian systems – Liouville

- Molecular dynamics: $H(q, p) = \sum_{i=1}^N \frac{|p_i|^2}{2m_i} + V(q)$
- Hamilton's equations: $\frac{dq_i}{dt} = \frac{\partial H}{\partial p_i}, \quad \frac{dp_i}{dt} = -\frac{\partial H}{\partial q_i}$
- Paradigm shift: Deterministic $\rightarrow$ statistical!
- $\rho(q, p, t) \equiv$ probability of state (q, p) at time t
- Liouville transport equation:

$$\frac{\partial \rho}{\partial t} + \sum_{i=1}^N \left(\frac{\partial \rho}{\partial q_i} \cdot \frac{\partial H}{\partial p_i} - \frac{\partial \rho}{\partial p_i} \cdot \frac{\partial H}{\partial q_i} \right) = 0$$



Approximation – Mesodynamics

- Approximation: Restrict to special densities!
- Assume: $H = \sum_{i=1}^N h_i$, non-equilibrium Boltzmann

(max-ent¹)

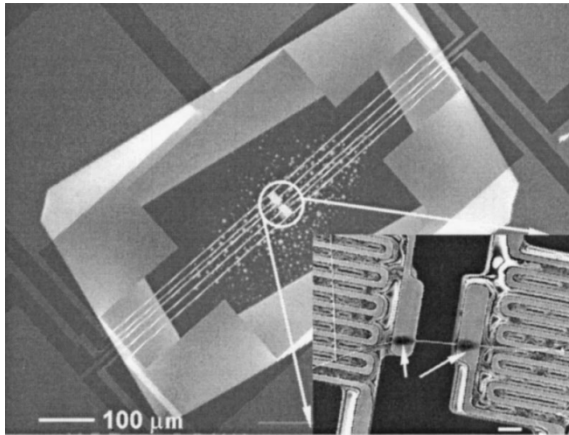
- *Mesodynamics*: Insert into Liouville,

$$\left\{ \begin{array}{l} \dot{\bar{q}}_i = \frac{\bar{p}_i}{m_i}, \quad \dot{\bar{p}}_i = -\left\langle \frac{\partial V}{\partial q_i} \right\rangle, \\ \dot{\bar{h}}_i = \sum_{j=1}^N \left\langle \frac{\partial V_i}{\partial q_j} \right\rangle \cdot \frac{\bar{p}_j}{m_j} - \left\langle \frac{\partial V}{\partial q_i} \right\rangle \cdot \frac{\bar{p}_i}{m_i} + \langle \partial_t V_i \rangle \end{array} \right. \quad \begin{array}{l} \text{(mean-flow!)} \\ \text{(energy!)} \end{array}$$

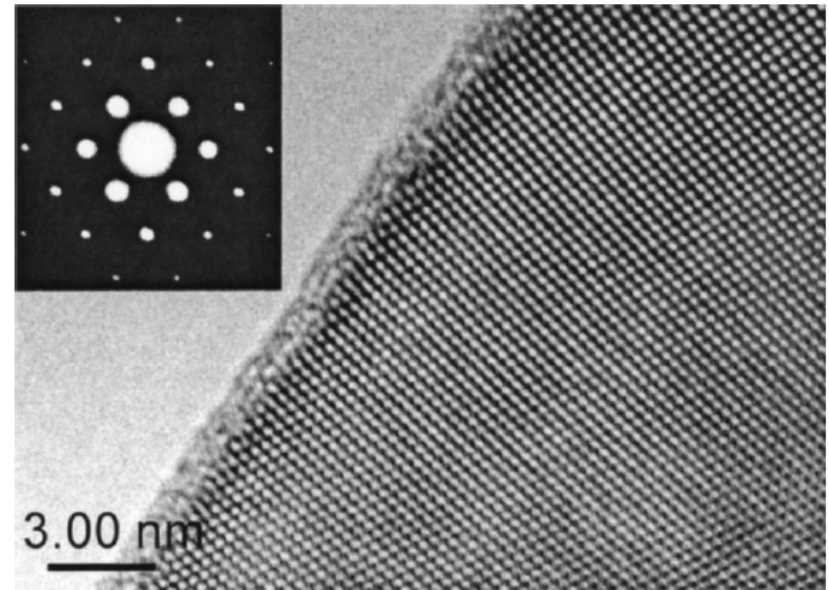
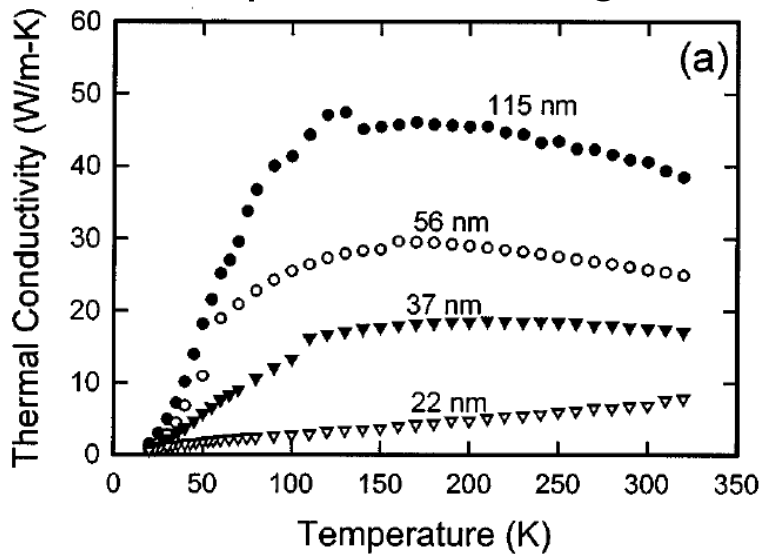


¹E.T. Jaynes, *Physical Review Series II*,
106(4) (1957) 620–630; **108**(2) (1957) 171–190.

Validation – Si nanowires



Experimental rig¹



Amorphous layer in SiNW!

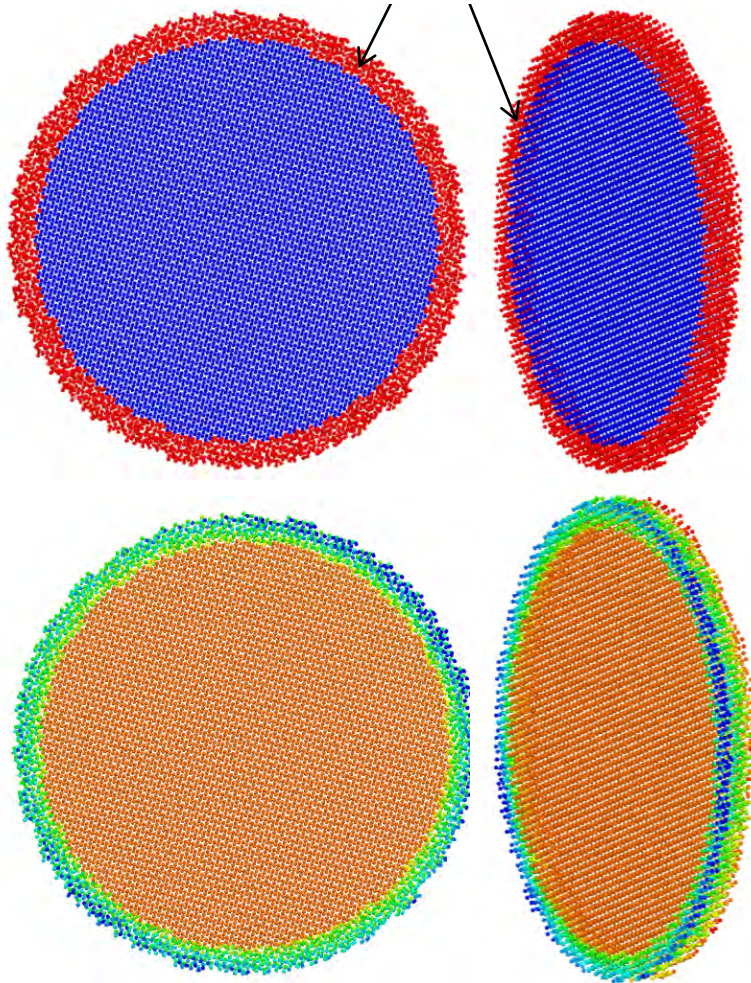


¹D. Li, Y. Yu, P. Kim, L. Shi, P. Yang and A. Majumdar, *Appl. Phys. Lett.*, **83** (2003) 2934.

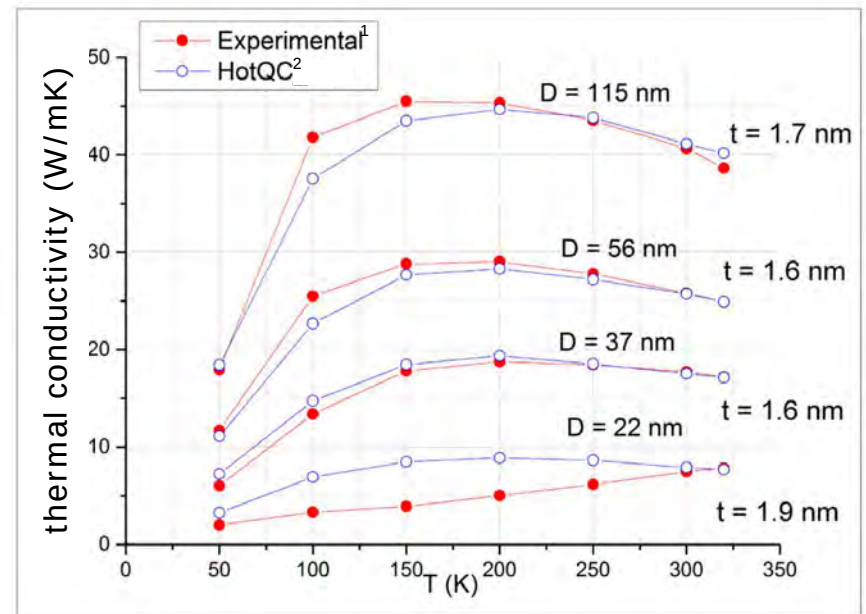
Michael Ortiz
SIAM/MS 2021

Validation – Si nanowires

amorphous layer



- Rigid-limit approximation
- Discrete heat equation
- Prescribed temperature gradient
- Output: Average axial heat flux



Temperature



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

²C.S. Martin, M.P. Ariza, M. Ortiz, *GAMM-Mitt.*, **38**(2) (2015) 201-212.

Mass transport – Grand-canonical

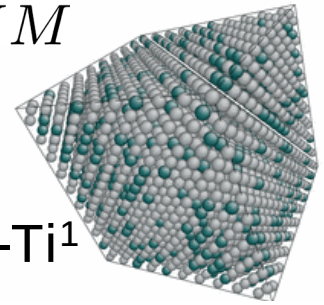
- Grand-canonical ensemble, N atoms, M species:

- State: $(\{q\}, \{p\}, \{n\}) \in \mathbb{R}^{3N} \times \mathbb{R}^{3N} \times \mathcal{O}_{NM}$

- Atomic positions: $\{q\} = \{q_1, \dots, q_N\}$

- Atomic momenta: $\{p\} = \{p_1, \dots, p_N\}$

Al-Ti¹



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

- Structure of typical multispecies EAM potential:

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



Approximation – GC-Mesodynamics

- Assume: $H = \sum_{i=1}^N h_i$, non-equilibrium Boltzmann

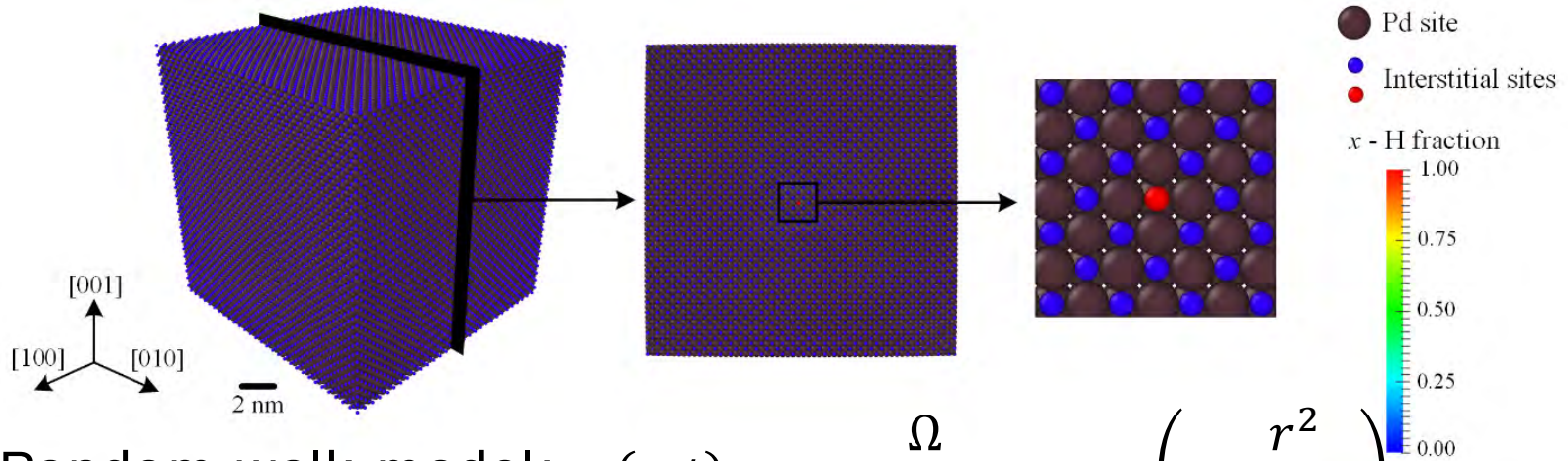
$$\rho(z, t) = \frac{1}{\Xi} \exp(-\alpha(t) \cdot z - \beta(t) \cdot h - \gamma(t) \cdot n)$$

- *Mesodynamics*: Insert into Liouville,

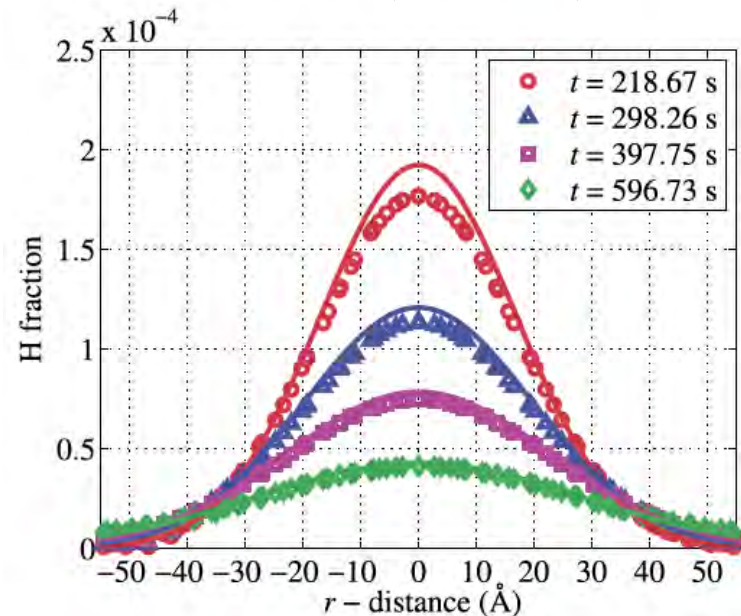
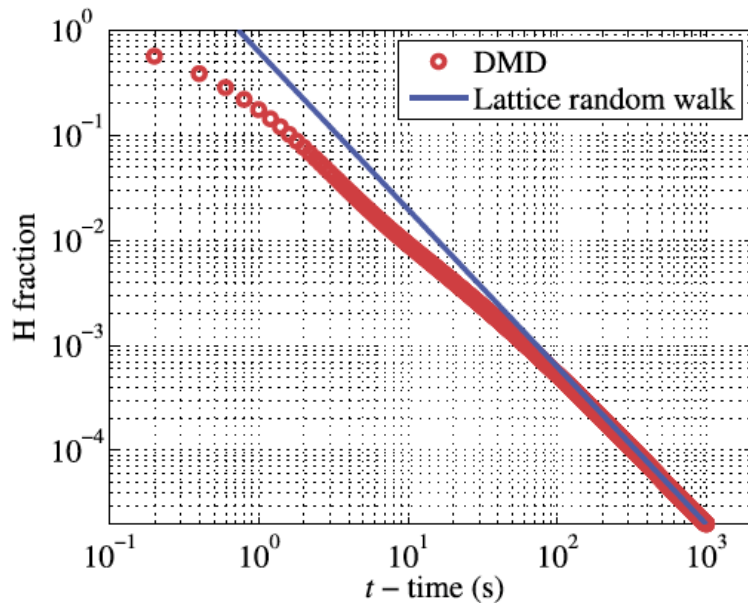
$$\begin{aligned} \dot{\bar{n}}_k = & \left\langle \sum_{i=1}^N \left\{ \sum_{j=1}^N \beta_j \left(\frac{\partial V_j}{\partial q_i} - \left\langle \frac{\partial V_j}{\partial q_i} \right\rangle \right) \cdot \frac{p_i}{m_i} \right. \right. \\ & \left. \left. - \beta_i \left(\frac{p_i}{m_i} - \left\langle \frac{p_i}{m_i} \right\rangle \right) \cdot \sum_{j=1}^N \frac{\partial V_j}{\partial q_i} \right\} (n_k - \bar{n}_k) \right\rangle \quad (\text{transport!}) \end{aligned}$$



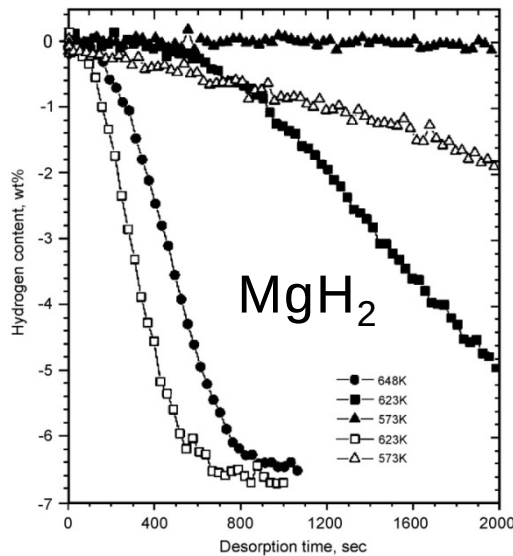
MD vs. GC-Mesodynamics



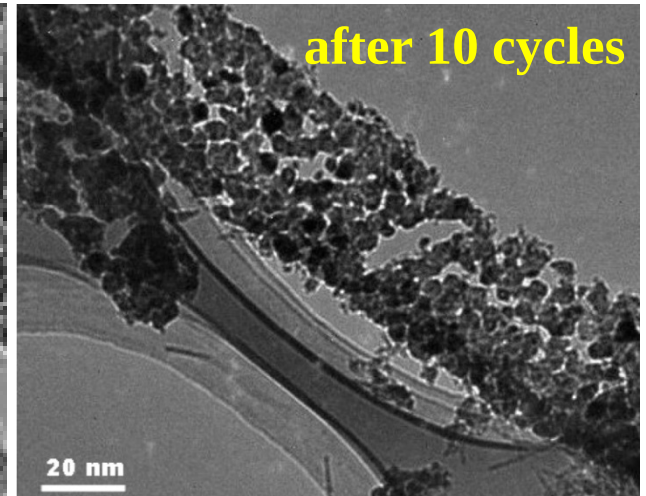
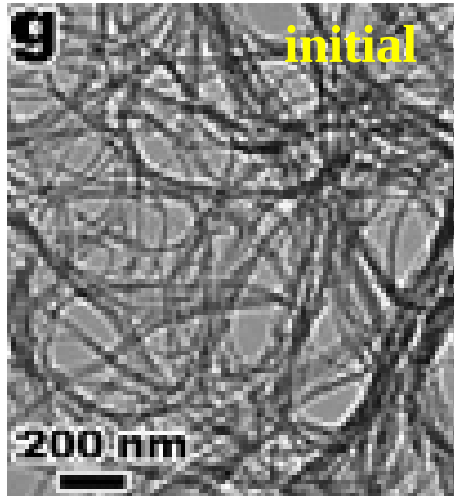
Random walk model:
$$x(r, t) = \frac{\Omega}{(4\pi D_H t)^{3/2}} \exp\left(-\frac{r^2}{4\pi D_H t}\right)$$



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 range¹
- Outlook: Store hydrogen in nanostructured metals (particles, nanowires)
- But: Structural effects,
 - Volume expansion
 - Pulverization
- Mg disintegrates after 10 hydration cycles²
- Predictive capability:
 - Atomistic realism
 - Long-time behavior...



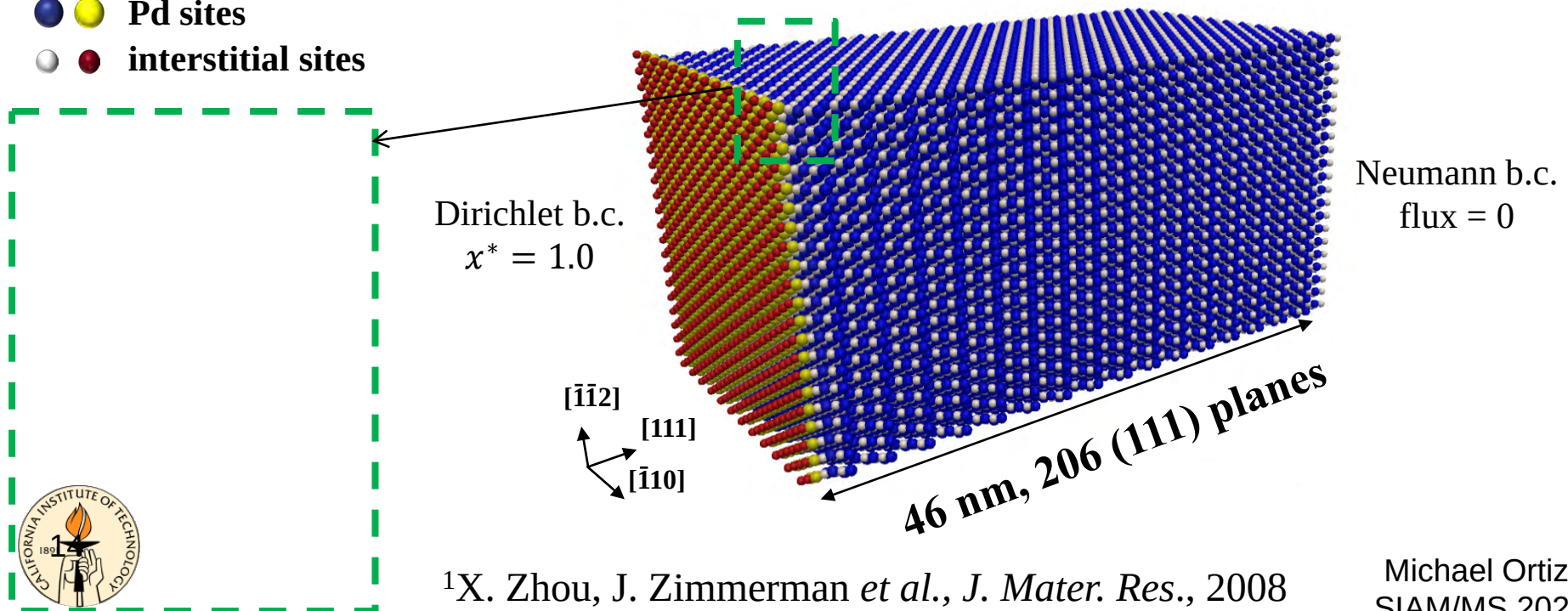
¹B. Sakintuna, F. Darkrim and M. Hirscher, *Int.J. Hydrogen Energy*, **32** (2007) 1121– 1140.

²W. 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 potential¹, NN transport kinetics

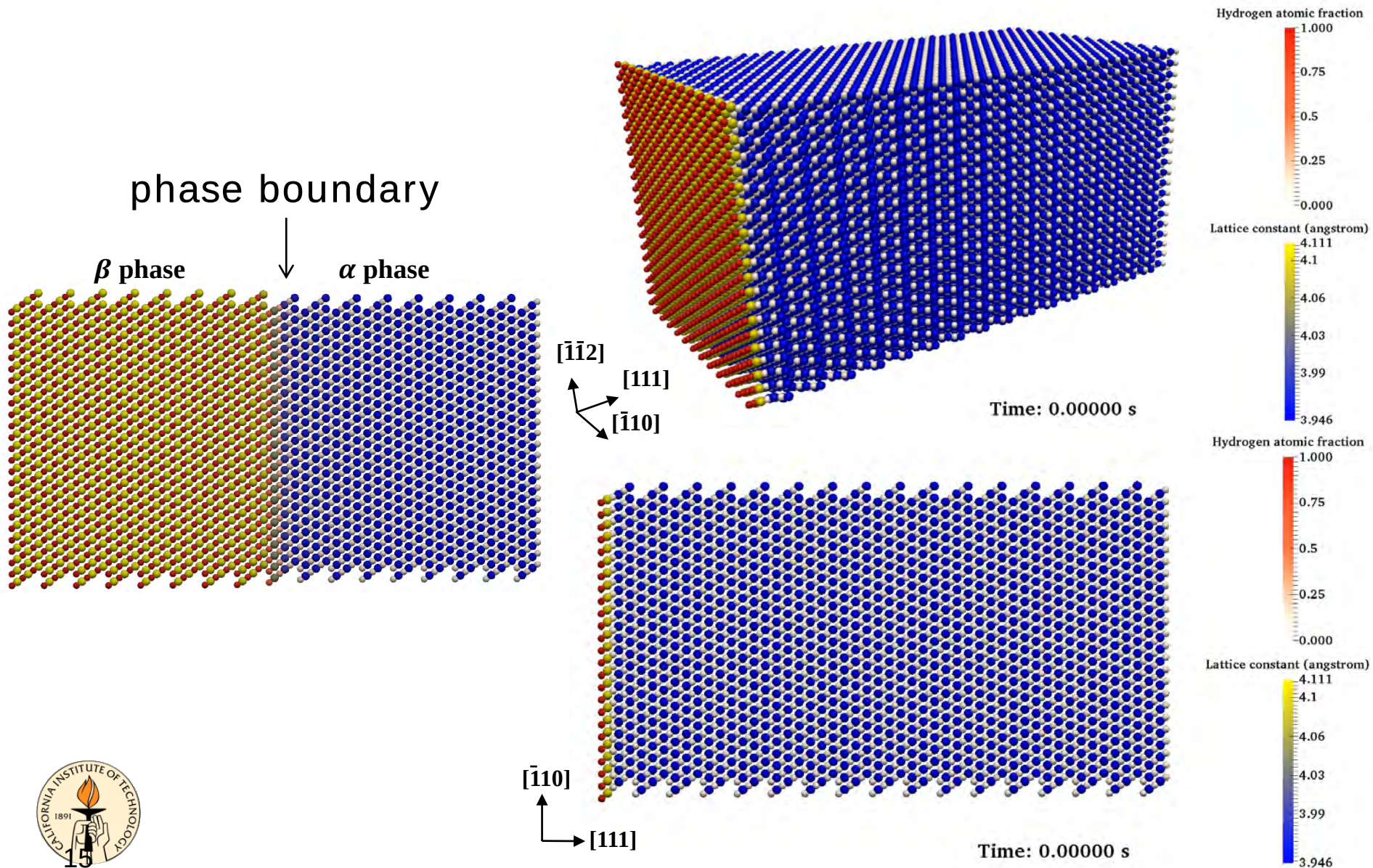
● ● Pd sites
● ● interstitial sites



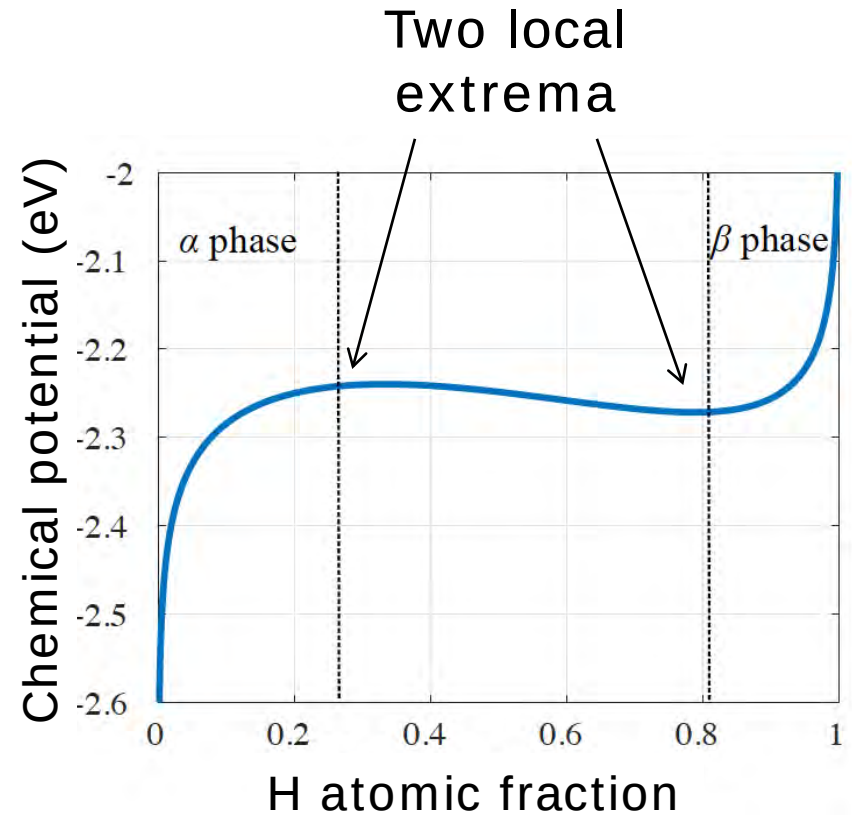
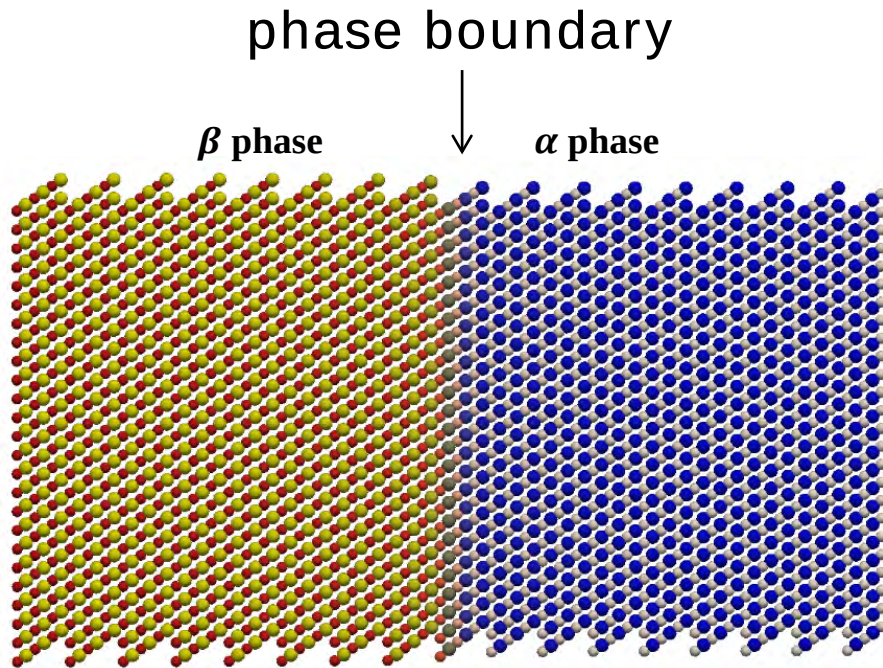
¹X. Zhou, J. Zimmerman *et al.*, *J. Mater. Res.*, 2008



H storage in Pd NW – α - β interface



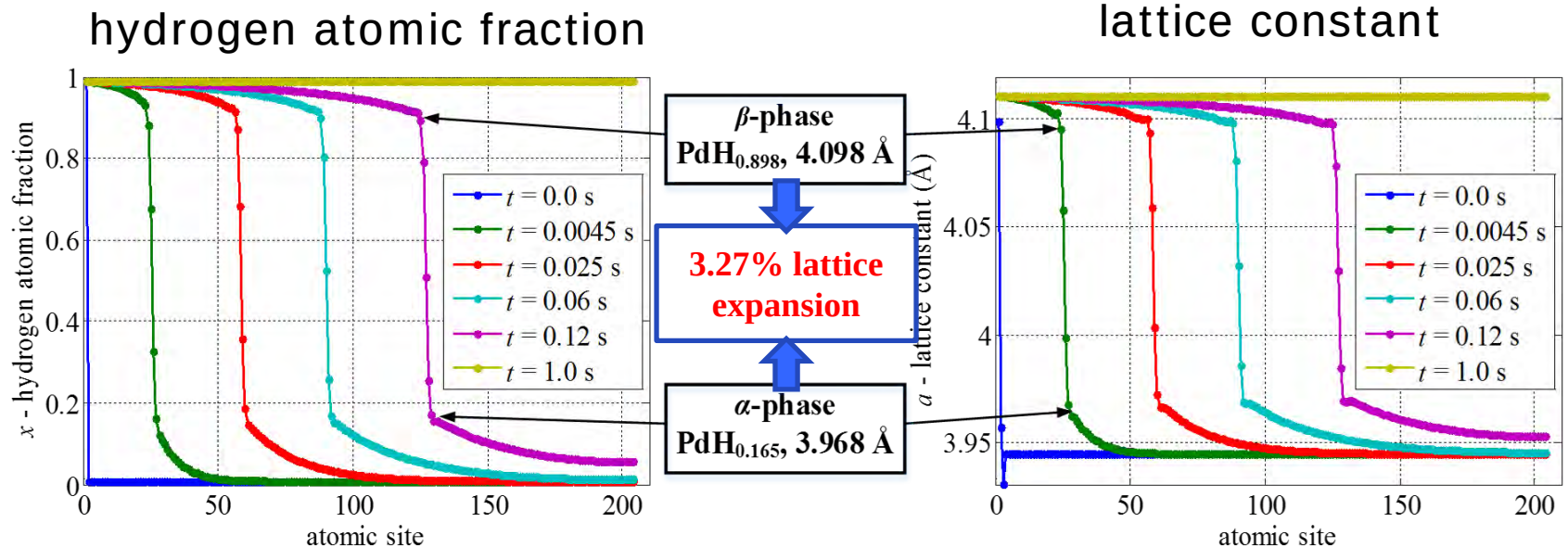
H storage in Pd NW – α - β interface



- Double-well (bistable, non-convex) free entropy
- Each well corresponds to a stable phase (α and β)



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.

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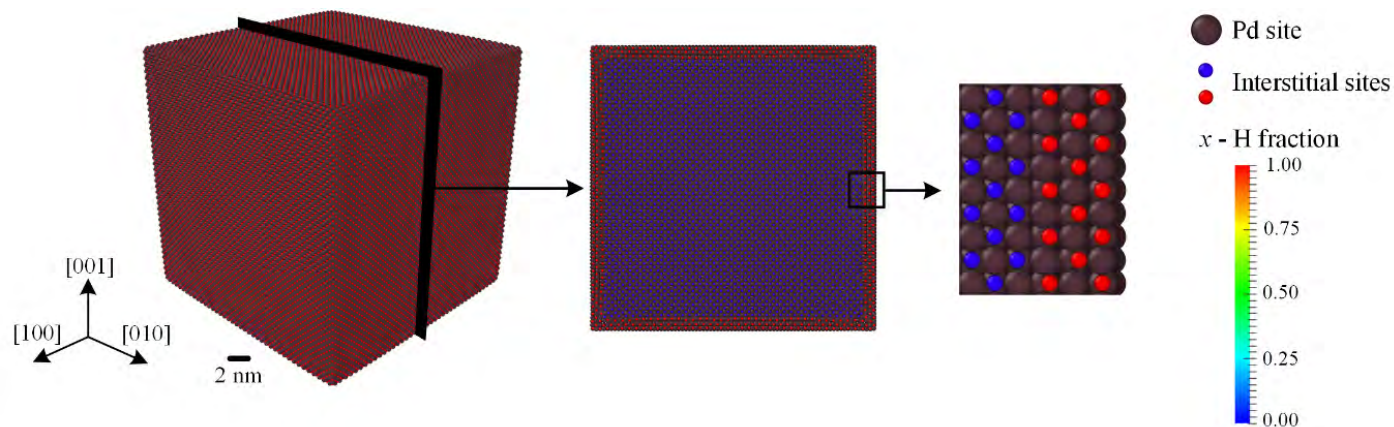
Application: H storage in Pd nanoparticles



STEM frames showing α to β phase evolution

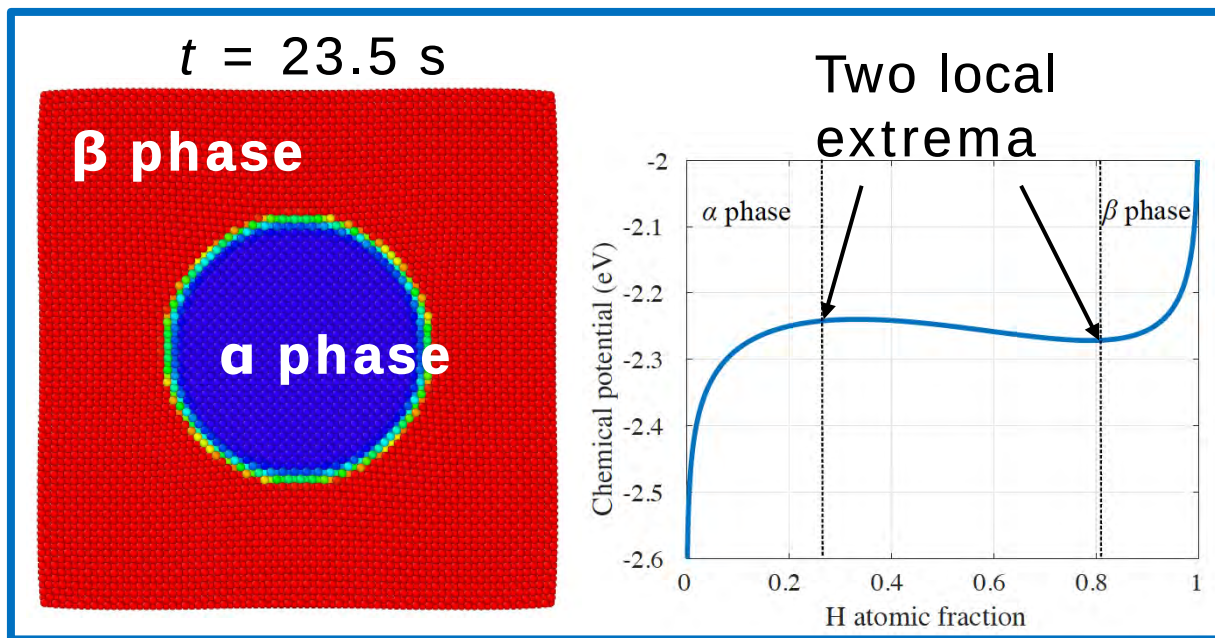
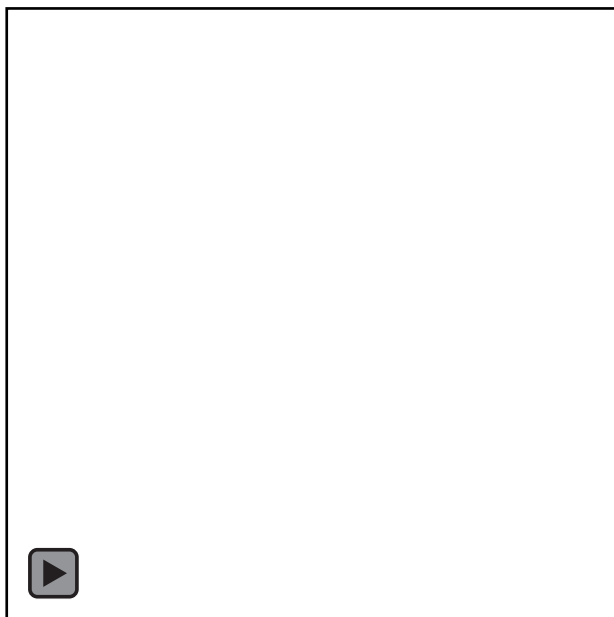


H storage in Pd NP – Problem setup

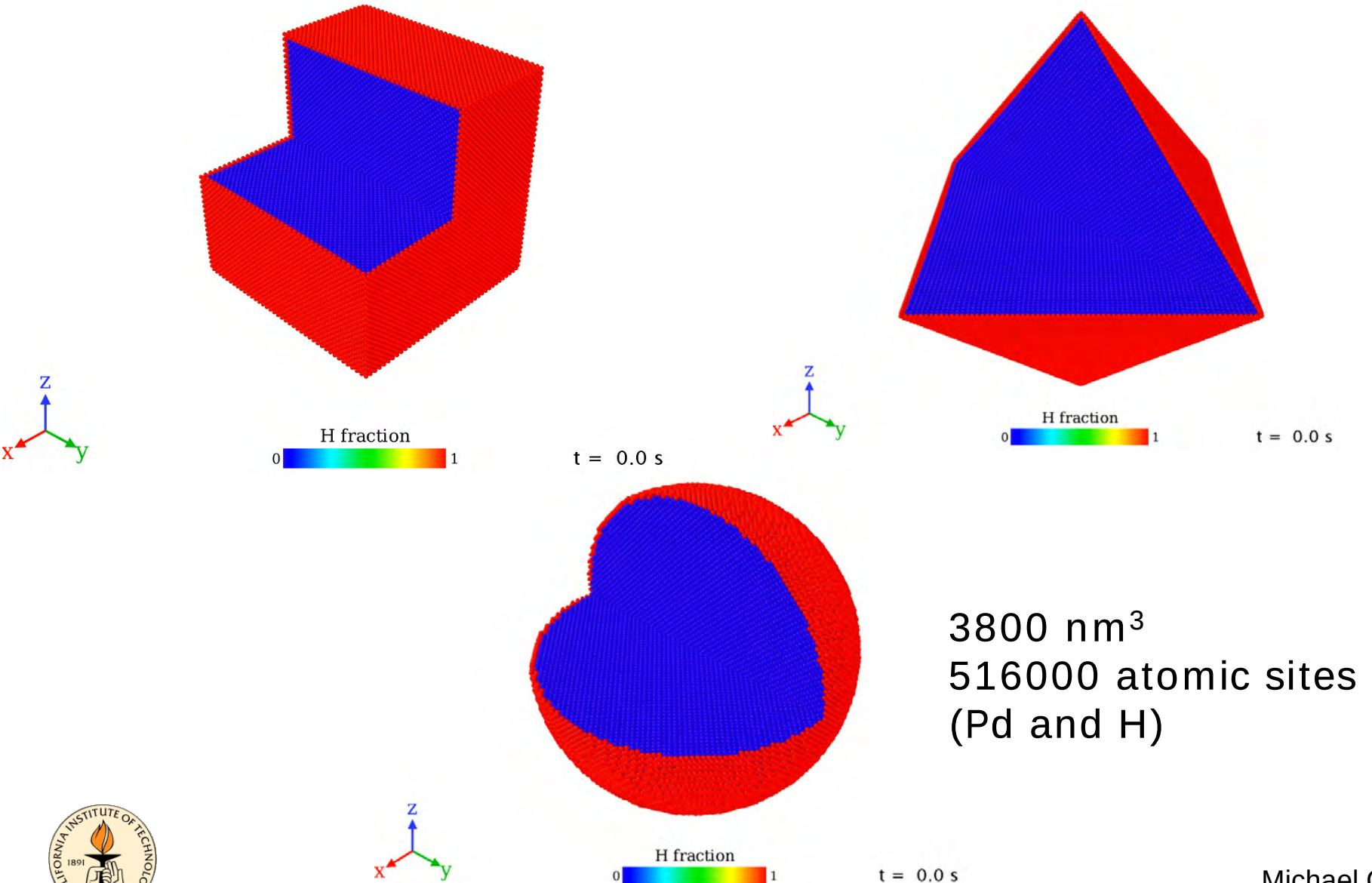


Nanocube (edge length: 16 nm), with faces on $\{100\}$ planes.

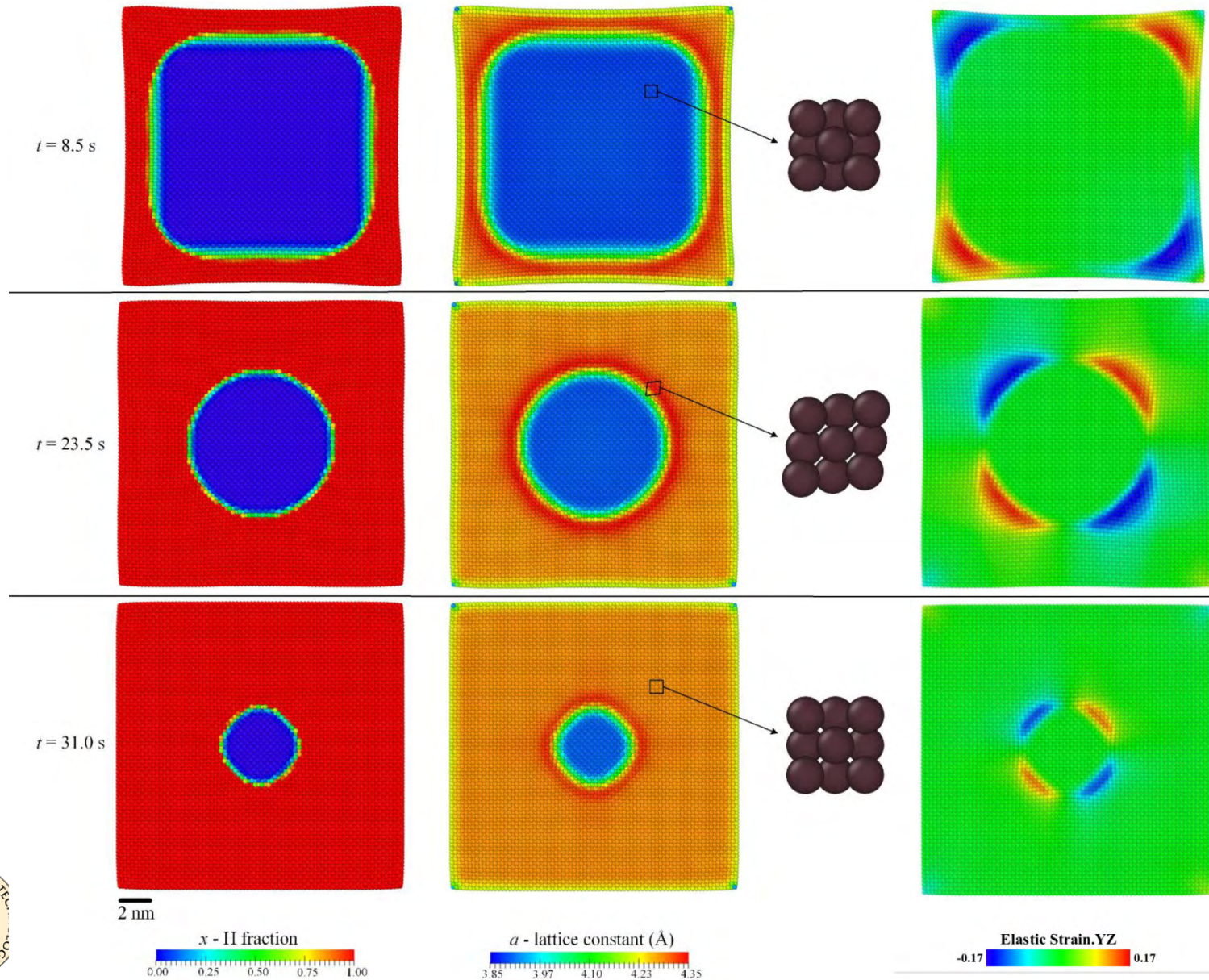
α - β interphase



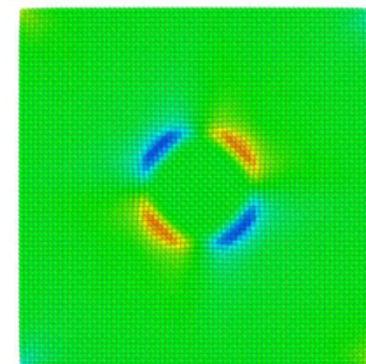
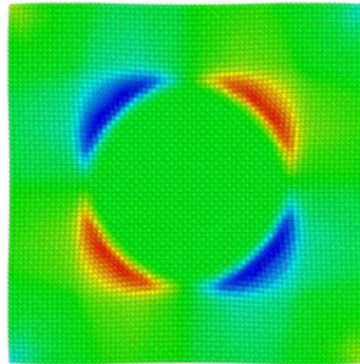
H storage in Pd NP – Interface evolution



H storage in Pd NP – Interfacial strain

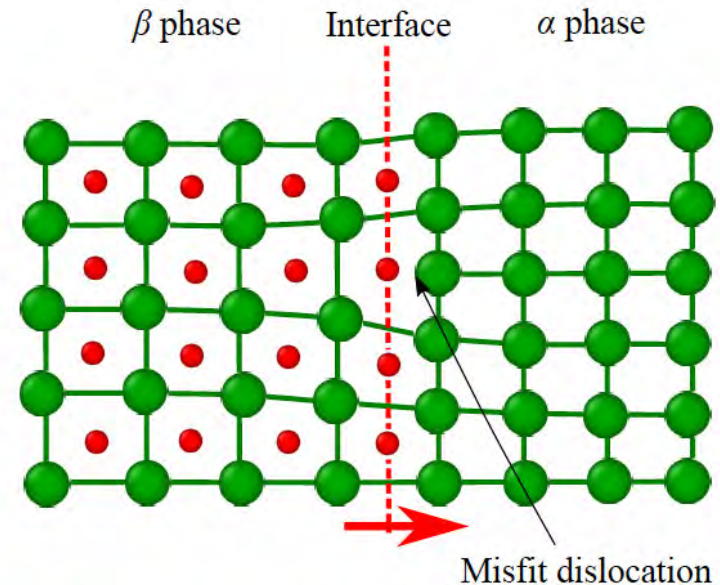
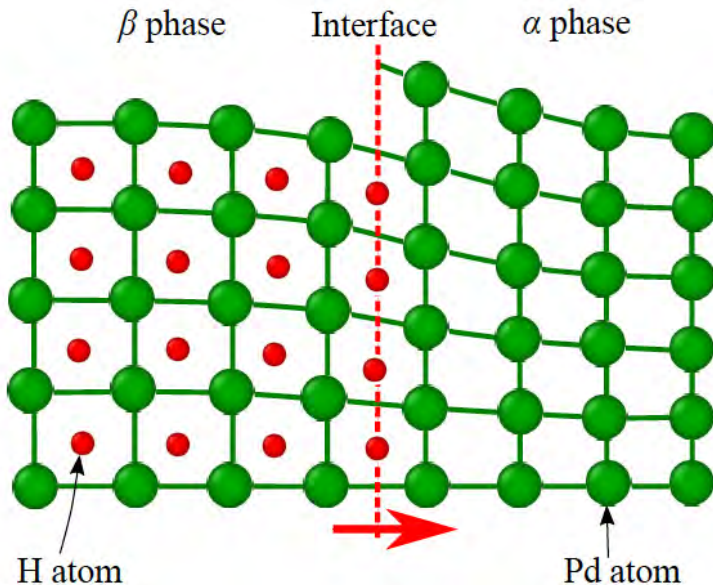


Interfacial dislocations



misfit
strain
evolution

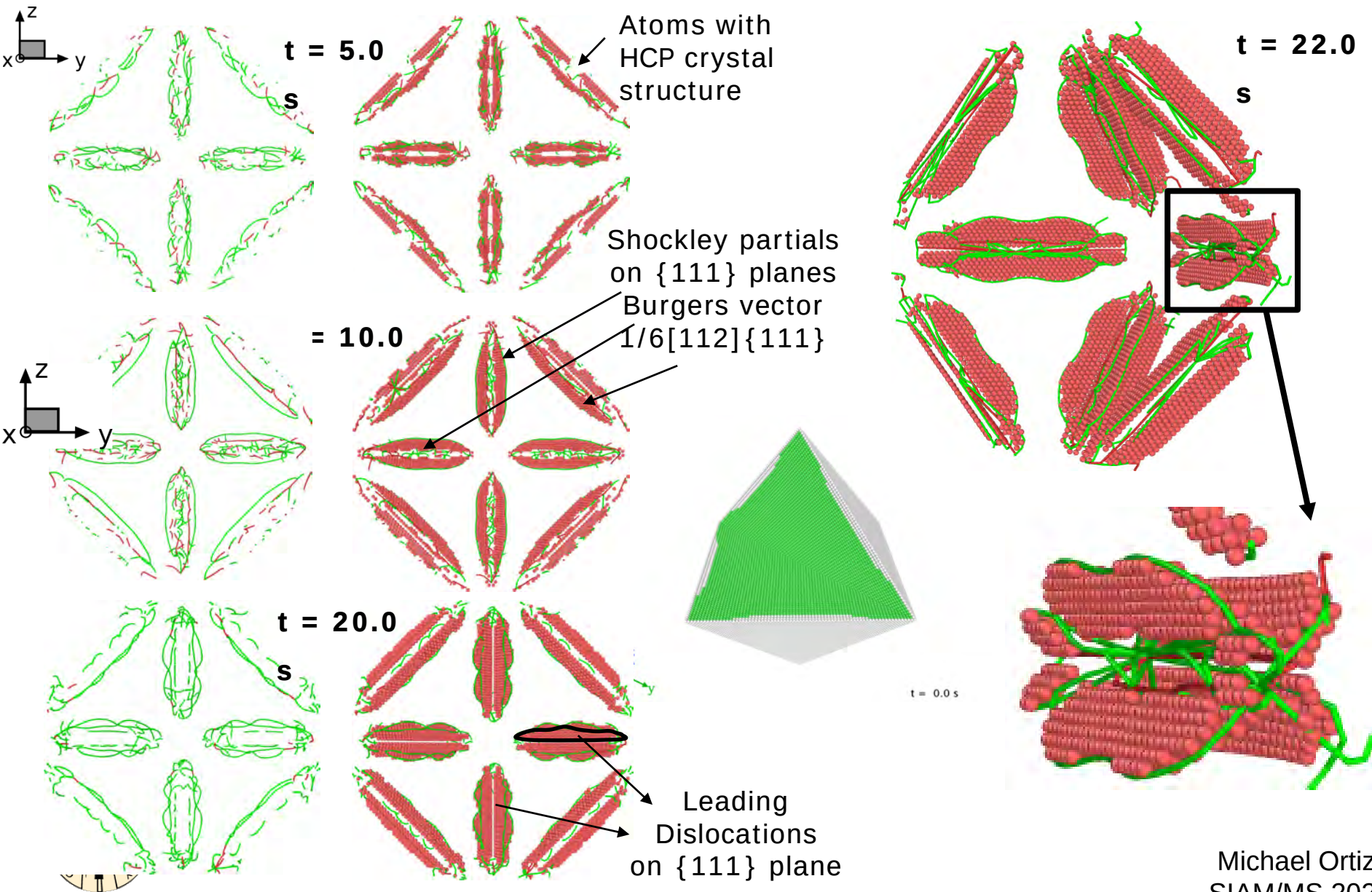
Elastic Strain.YZ
-0.17 0.17



Misfit strain is relieved by misfit dislocations

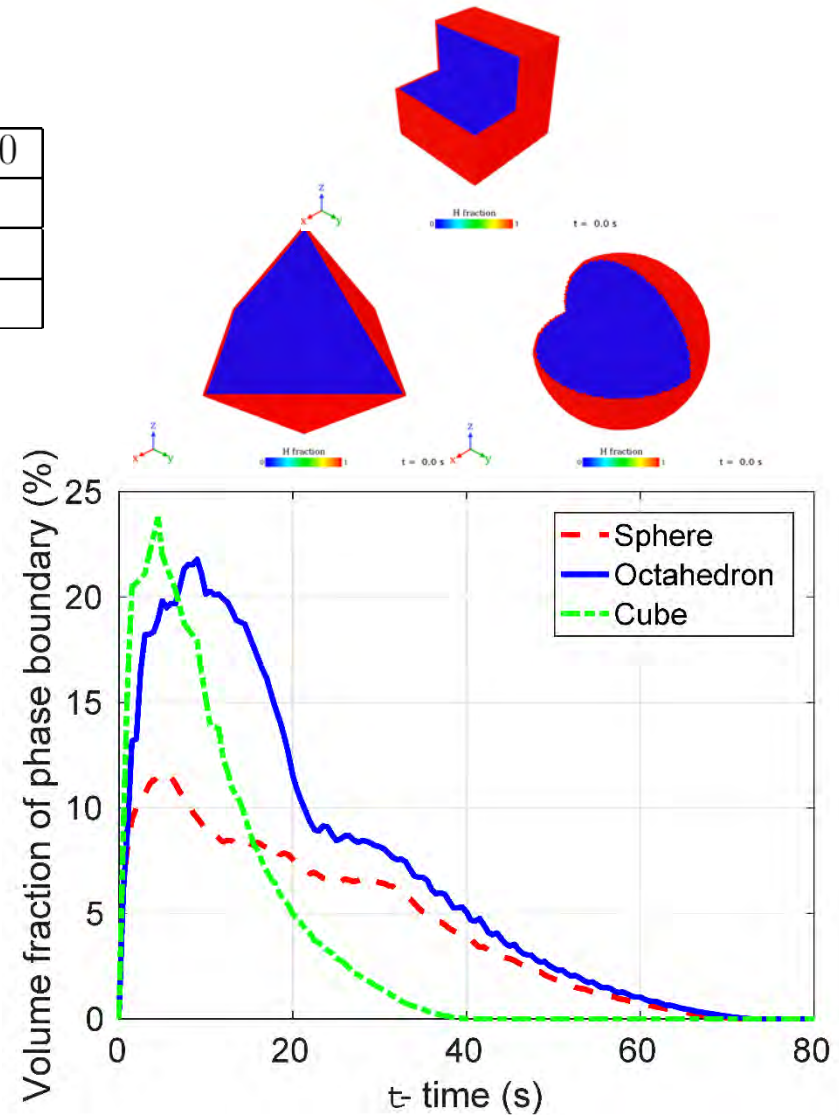
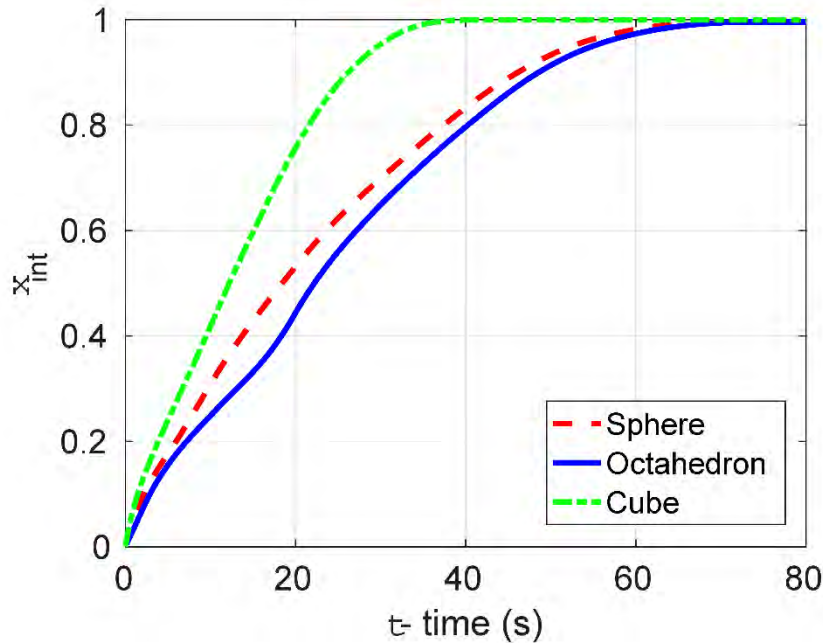


PdH: Interfacial misfit dislocations



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



Concluding remarks

- *Mesodynamics* 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
- *Spatial coarse-graining* via quasi-continuum
- Open mathematical questions:
 - *Convergence* of Galerkin-Liouville approximations (e.g., cluster expansions, Hermite polynomials)
 - *Effective long-term behavior* of Liouville transport (weak convergence of trajectories upon long-term time rescaling)



A word cloud featuring the phrase "thank you" in various languages and scripts. The central text "thank you" is in large blue letters. Surrounding it are numerous other expressions of gratitude in different colors and sizes, including:

- danke (German)
- 謝謝 (Chinese)
- ngiyabonga (Ndebele)
- teşekkür ederim (Turkish)
- спасибо (Russian)
- Баярлалаа (Mongolian)
- faafetai lava (Tongan)
- mersi (Arabic)
- kia ora (Māori)
- barka (Hausa)
- welalin (Yoruba)
- tack (Swedish)
- vinaka (Samoan)
- спасиби (Ukrainian)
- blagodaram (Serbian)
- dank je (Dutch)
- misaotra (Malagasy)
- matondo (Zulu)
- paldies (Latvian)
- grazzi (Italian)
- maialo (Tahitian)
- tapadh leat (Irish Gaelic)
- хвала (Serbian/Croatian)
- asante (Swahili)
- manana (Tagalog)
- obrigada (Portuguese)
- tenki (Japanese)
- chokrane (Hindi)
- murakoze (Kisumu)
- mamnun (Arabic)
- мохчаккерам (Chechen)
- tau (Hawaiian)
- дякую (Ukrainian)
- go raibh maith agat (Irish Gaelic)
- arigatō (Japanese)
- takk (Norwegian)
- dakujem (Slovak)
- trugarez (Breton)
- merci (French)
- merci (French)
- xiexie (Chinese)
- 감사합니다 (Korean)
- তোমাকে ধন্যবাদ (Bengali)
- rahmat (Arabic)
- terima kasih (Indonesian)
- tanemirt (Hawaiian)
- rahmet (Turkish)
- diolch (Welsh)
- dhanyavadagalu (Kannada)
- shukriya (Urdu)
- mercé (Catalan)
- merci (French)
- ευχαριστώ (Greek)
- taiku (Lithuanian)
- sulpáy (Quechua)
- gracias (Spanish)
- gracies (Catalan)
- chnorakaloutioun (Armenian)
- sukriya (Hindi)
- najis tuke (Sinhala)
- kam sah hamnida (Burmese)
- didid madioba (Yoruba)
- sagolun (Yoruba)
- mèsi (Yoruba)
- dekuji (Yoruba)
- sobodi (Yoruba)
- dziękuję (Polish)
- hvala (Slovene)
- gracie (Polish)
- dhanyavad (Sinhala)
- kiitos (Finnish)
- nandri (Sinhala)
- nanni (Sinhala)
- bedankt (Dutch)
- enkosi (Zulu)
- mauruuru (Samoan)
- köszönöm (Hungarian)
- hvala (Slovene)

