Atomistic Simulation of hydrogen storage in Pd nanoparticles

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USACM Workshop on Mechanics of Nanoscale Materials
University of Pennsylvania, Philadelphia
August 21-23, 2019
Motivation – Diffusive time scale

- 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$_2$Al$_3$)
- Stress corrosion cracking

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

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Anyone for a little theory?
Max-Ent Non-Equilibrium SM

- 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: $\{q\} = \{q_1, \ldots, q_N\}$
  - Atomic momenta: $\{p\} = \{p_1, \ldots, p_N\}$
  - Occupancy: $n_{ik} = \begin{cases} 1, & \text{site } i \text{ occupied by species } k, \\ 0, & \text{otherwise.} \end{cases}$

- Ensemble average of observable: $\langle A \rangle = \sum_{\{n\} \in \mathcal{O}_{NM}} \int A(\{q\}, \{p\}, \{n\}) \rho(\{q\}, \{p\}, \{n\}) \, dq \, dp$

\[ \uparrow \text{grand-canonical pdf} \]

Max-Ent Non-Equilibrium SM

- Assume $H = \sum_{i=1}^{N} h_i$, (e.g., EAM, TB...)
- Principle of max-ent$^1$: $S[p] = -k_B \langle \log \rho \rangle \rightarrow \text{max!}$
  subject to: $\langle q_i \rangle = \bar{q}_i$, $\langle p_i \rangle = \bar{p}_i$,
  $\langle h_i \rangle = e_i$, $\langle n_{ik} \rangle = x_{ik}$, local constraints!
- Lagrangian: reciprocal temperatures chemical potentials
  $\mathcal{L}[p, \{\beta\}, \{\gamma\}] = S[p] - k_B \{\beta\}^T \{\langle h \rangle \} - k_B \{\gamma\}^T \{\langle n \rangle \}$
- Gran-canonical pdf: $\rho = \frac{1}{\Xi} \cdot e^{-\{\beta\}^T \{h\} - \{\gamma\}^T \{n\}}$
  on affine subspace $\left\{ \langle \{q\} \rangle = \{\bar{q}\}, \langle \{p\} \rangle = \{\bar{p}\} \right\}$

Max-Ent Non-Equilibrium SM

- Gran-canonical free entropy:
  \[ \Phi(\{\bar{q}\}, \{\bar{p}\}, \{\beta\}, \{\gamma\}) = k_B \log \Xi \]

- Local equilibrium relations:
  \[ \frac{1}{k_B} \frac{\partial \Phi}{\partial \beta_i} = e_i \quad \text{Local internal energy vs. temperature relation} \]
  \[ \frac{1}{k_B} \frac{\partial \Phi}{\partial \gamma_{ik}} = x_{ik} \quad \text{Local chemical potential vs. atomic fraction relation} \]
  \[ \frac{1}{k_B} \frac{\partial \Phi}{\partial \bar{q}_i} = 0 \quad \text{Force equilibrium (quasistatic)} \]

- 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,

\[
h_{0i} = \frac{1}{2m(n_i)}|\mathbf{p}_i - \bar{\mathbf{p}}_i|^2 + \frac{m(n_i)\omega_i^2}{2}|\mathbf{q}_i - \bar{\mathbf{q}}_i|^2
\]

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

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

- **Meanfield mesoscopic dynamics:**

\[
- \frac{1}{k_B} \frac{\partial \Phi_{\text{MF}}}{\partial \beta_i} = e_i, \quad \frac{1}{k_B} \frac{\partial \Phi_{\text{MF}}}{\partial \gamma_{ik}} = x_{ik}, \quad \frac{1}{k_B} \frac{\partial \Phi_{\text{MF}}}{\partial \bar{q}_i} = 0
\]

- **Meanfield optimality:**

\[
\frac{\partial}{\partial \omega_i} \sum_{j=1}^{N} \beta_j \langle V_j \rangle_0 + \frac{3}{\omega_i} = 0
\]
Non-equilibrium SM – Onsager kinetics

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

- Local conservation equations:
  \[ \dot{e}_i = \dot{\omega}_i + \mu_i^T \dot{x}_i + \sum_{j \neq i} R_{ij}, \]
  \[ \dot{x}_i = \sum_{j \neq i} J_{ij} \]
  
  energy mass

- Local dissipation inequality:
  \[ \sum_{ij} = k_B (\beta_i - \beta_j) R_{ij} + k_B (\gamma_i - \gamma_j) \cdot J_{ij} \geq 0 \]

- General kinetic relations: calibrate from exp. data!
  \[ R_{ij} = f(\beta_i - \beta_j), \]
  \[ J_{ij} = g(\gamma_i - \gamma_j) \]

Discrete Fourier law 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:

\[ \mu_i = \frac{k_B T}{2} \log \frac{x_i}{1 - x_i} \]

- Master equation:

\[ \frac{\partial x_i}{\partial t} = \sum_{\langle i,j \rangle} (\psi_{j \rightarrow i} - \psi_{i \rightarrow j}) \]

- Transition probabilities:

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

\[ \uparrow \text{ attempt} \]
\[ \text{frequency} \]
\[ \uparrow \text{energy barrier} \]
MD vs. DMD in pictures

MD: must track thermal vibrations of the atoms

DMD: atoms are quiescent but hot (mean flow)

FCC-Al
T=900K
NVT ensemble
Random walk model: $x(r, t) = \frac{\Omega}{(4\pi D_H t)^{3/2}} \exp\left(-\frac{r^2}{4\pi D_H}\right)$
Liouville equation

- Liouville equation: \( \partial_t \rho + \text{div} (\rho \, X_H) = 0 \)

- Weak form: \( \int \left( \partial_t \rho + \text{div} (\rho \, X_H) \right) \pi \, dz = 0 \)

- Non-equilibrium Boltzmann: \( H = \sum_{i=1}^{N} h_i \),
  \( \rho = \frac{1}{Z} \exp \left( -\alpha \cdot z - \beta \cdot h \right) \), \( \pi = \xi \cdot z + \eta \cdot h \)

- Mesodynamical equations:
  \[ \dot{q}_i = \frac{\vec{p}_i}{m_i}, \quad \dot{\vec{p}}_i = -\left\langle \frac{\partial V}{\partial q_i} \right\rangle, \]
  \[ \dot{h}_i = \sum_{j=1}^{N} \left( \frac{\partial V_i}{\partial q_j} \right) \cdot \frac{\vec{p}_j}{m_j} - \left\langle \frac{\partial V}{\partial q_i} \right\rangle \cdot \frac{\vec{p}_i}{m_i} + \left\langle \partial_t V_i \right\rangle. \]
Statistical mechanics (beating the Avogadro and fs curses)

- Ludwig Boltzmann (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...


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H storage in Pd NW – α–β interface

- PdHₓ exists in two phases at room temperature:
  • α phase: 0 < x ≤ 0.03  • β phase: 0.608 ≤ x ≤ 1
- In both phases: H occupies octahedral sites of FCC Pd lattice
- Phase transition (α → β): 10.4% volume expansion
- Computational setup: EAM potential¹, NN transport kinetics

H storage in Pd NW – $\alpha$–$\beta$ 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)

Application: H storage in Pd nanoparticles

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.

\(t = 23.5\) s

\(\alpha-\beta\) interphase

\(\beta\) phase

\(\alpha\) phase

Two local extrema

H storage in Pd NP – Interface evolution

3800 nm$^3$
516000 atomic sites
(Pd and H)
H storage in Pd NP – Interfacial strain

$t = 8.5 \text{ s}$

$t = 23.5 \text{ s}$

$t = 31.0 \text{ s}$

2 nm
Interfacial dislocations

Misfit strain is relieved by misfit dislocations

PdH: Interfacial misfit dislocations

Atoms with HCP crystal structure

Shockley partials on \{111\} planes
Burgers vector $\frac{1}{6}[112] \{111\}$

Leading Dislocations on \{111\} plane

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PdH: Interfacial misfit dislocations

PdH: Interfacial misfit dislocations

(100) plane (111) direction

(100) plane (111) direction

PdH: Dislocations vs. kinetics

4.5 s

9.0 s

Volume fraction of stacking faults (%)
### PdH: Morphology vs. kinetics

<table>
<thead>
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<th>$x_{\text{int}}$</th>
<th>0.3</th>
<th>0.7</th>
<th>1.0</th>
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<tr>
<td>Cube</td>
<td>7.0 s</td>
<td>18.5 s</td>
<td>36.5 s</td>
</tr>
<tr>
<td>Sphere</td>
<td>9.0 s</td>
<td>26.5 s</td>
<td>59.5 s</td>
</tr>
<tr>
<td>Octahedron</td>
<td>12.0 s</td>
<td>27.0 s</td>
<td>60.0 s</td>
</tr>
</tbody>
</table>

**Graphs:**
- **Left graph:** Shows the evolution of phase fraction $x_{\text{int}}$ over time for different morphologies (Cube, Sphere, Octahedron) at different $x_{\text{int}}$ values.
- **Right graph:** Shows the volume fraction of phase boundary over time for different morphologies (Cube, Octahedron, Sphere).
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...)

²J.P. Mendez, M. Ponga and M. Ortiz, JMPS, 115 (2018) 123.