Diffusive Molecular Dynamics for Mass Transport Applications

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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


Max-Ent Non-Equilibrium SM

- Grand-canonical ensemble, $N$ atoms, $M$ species:
  - State: $(\{q\}, \{p\}, \{n\}) \in \mathbb{R}^{3N} \times \mathbb{R}^{3N} \times O_{NM}$
  - 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: $\langle A \rangle = \sum_{\{n\} \in O_{NM}} \int A(\{q\}, \{p\}, \{n\}) \rho(\{q\}, \{p\}, \{n\}) \, dq \, dp$

J. von Pezold, A. Dick, M. Friak and J. Negebauer,
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: $\langle q_i \rangle = \bar{q}_i$, $\langle p_i \rangle = \bar{p}_i$,

  $\langle h_i \rangle = e_i$, $\langle n_{ik} \rangle = x_{ik}$

- 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: $\rho = \frac{1}{\Omega} e^{-\{\beta\}^T \{h\} - \{\gamma\}^T \{n\}}$,

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

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Max-Ent Non-Equilibrium SM

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

- Local equilibrium relations:
  \[ e_i = -\frac{1}{k_B} \frac{\partial \Phi}{\partial \beta_i}, \quad x_{ik} = \frac{1}{k_B} \frac{\partial \Phi}{\partial \gamma_{ik}} \]

- Mesoscopic dynamics (quasistatic):
  \[ \beta_i \frac{d\bar{q}_i}{dt} = \frac{1}{k_B} \frac{\partial \Phi}{\partial \bar{p}_i}, \quad \beta_i \frac{d\bar{p}_i}{dt} + \frac{1}{k_B} \frac{\partial \Phi}{\partial \bar{q}_i} = 0 \]

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

- \( \Phi \to \Phi_{MF} \) meanfield approximation!

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MPIE 2018
Non-equilibrium SM – Meanfield theory

- Space of trial local Hamiltonians: $\mathcal{H}_0$
- Free-entropy inequality: For all $\{h_0\} \in \mathcal{H}_0$,
  
  i) $\Phi \geq \Phi_0 - k_B \{\beta\}^T \{\langle h - h_0 \rangle_0\} \equiv S[\{h_0\}]$

  ii) $\Phi = S[\{h_0\}] \Leftrightarrow \{h_0\} = \{h\}$

- Best approximation: $\Phi_{MF} = \max_{\{h_0\} \in \mathcal{H}_0} S[\{h_0\}]$

- Meanfield local equilibrium relations:

  $$e_i = -\frac{1}{k_B} \frac{\partial \Phi_{MF}}{\partial \beta_i}, \quad x_{ik} = \frac{1}{k_B} \frac{\partial \Phi_{MF}}{\partial \gamma_{ik}}$$

- Meanfield mesoscopic dynamics:

  $$\beta_i \frac{d\bm{q}_i}{dt} = \frac{1}{k_B} \frac{\partial \Phi_{MF}}{\partial \bm{p}_i}, \quad \beta_i \frac{d\bm{p}_i}{dt} = -\frac{1}{k_B} \frac{\partial \Phi_{MF}}{\partial \bm{q}_i}$$
Non-equilibrium SM – Meanfield theory

- Example: \( \mathcal{H}_0 \equiv \) local harmonic oscillators,

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

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

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

- Meanfield mesoscopic dynamics:

\[
\dot{q}_i = \frac{\bar{p}_i}{m_i}, \quad \dot{p}_i = -\frac{\partial}{\partial \bar{q}_i} \sum_{j=1}^{N} \langle V_j \rangle_0,
\]

- 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 – Kinetics

- Need equations of evolution for \( \{\beta\} \) and \( \{\gamma\} \)

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

  - 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!
  \[
  R_{ij} = f(\beta_i - \beta_j), \quad J_{ij} = g(\gamma_i - \gamma_j)
  \]

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:

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

\[ \text{attempt frequency} \quad \text{energy barrier} \]
Random walk model: \( x(r, t) = \frac{\Omega}{(4\pi D_H t)^{3/2}} \exp\left(-\frac{r^2}{4\pi D_H}\right) \)
Application: Lithium-ion batteries

- Si-based anodes offer the highest specific capacity (ten time the specific capacity of graphite)
- But: 300% expansion during charging (lithiation)
- Si undergoes amorphization upon lithiation
- Mechanical failure (pulverization) after a few cycles...

http://batteryuniversity.com/learn/article/lithium_based_batteries

<table>
<thead>
<tr>
<th>Element</th>
<th>Gravimetric capacity (mAh g⁻¹)</th>
<th>Volumetric capacity (mAh cm⁻³)</th>
<th>Cost</th>
<th>Toxicity</th>
<th>Safety</th>
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</thead>
<tbody>
<tr>
<td>Si</td>
<td>4.200</td>
<td>2.400</td>
<td>Low</td>
<td>No</td>
<td>High</td>
</tr>
<tr>
<td>C</td>
<td>372</td>
<td>890</td>
<td>Low</td>
<td>No</td>
<td>Low</td>
</tr>
<tr>
<td>Ge</td>
<td>1.568</td>
<td>2.300</td>
<td>High</td>
<td>High</td>
<td>High</td>
</tr>
<tr>
<td>Sn</td>
<td>990</td>
<td>2.020</td>
<td>Low</td>
<td>No</td>
<td>High</td>
</tr>
<tr>
<td>P</td>
<td>2.600</td>
<td>2.250</td>
<td>Low</td>
<td>High</td>
<td>Low</td>
</tr>
<tr>
<td>Sb</td>
<td>660</td>
<td>1.890</td>
<td>Low</td>
<td>High</td>
<td>Low</td>
</tr>
<tr>
<td>Pb</td>
<td>549</td>
<td>1.790</td>
<td>Low</td>
<td>High</td>
<td>Low</td>
</tr>
</tbody>
</table>
Nano-engineered Si anodes

Si-nanowire anodes, lithiation-delithiation\(^1\)

Si-nanowire anodes, capacity vs. \#cycles\(^2\)

Lithiation of Si nanowire\(^3\)

Lithiation of Si nanowire\(^4\)

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Hexagonal interstitial: 2 interst./Si atom

Tetrahedral interstitial: 1 interst./Si atom

Bond-centered interstitial: 2 interst./Si atom

Anti-bond interstitial: 4 interst./Si atom

Interstitial sites of diamond Si

Si nanowire lithiation simulations

- Si nanowire @ Li saturation on outer boundary
  - 2NN MEAM for Si-Li\(^1\)
  - \(T = 300K\)
  - Master transport equation\(^2\)
  - Diffusion parameters:
    - \(n = 1013 \text{ } 1/s\)
    - \(\Delta E = 0.55 \text{ } \text{eV}\)
  - 5 interstitials/atom

Hexagonal interstitial: 2 interst./Si atom
Bond-centered interstitial: 2 interst./Si atom
Tetrahedral interstitial: 1 interst./Si atom

10,126 Si atoms, 50,565 interstitials

\(^1\)Z. Cui et al., *J. Power Sources*, 207 (2012) 150–159.
Si lithiation model - Validation

Si nanopillar lithiation – Atomic fractions

Average Li atomic molar fraction $\sim 0.79$

0.0 ms 0.8 ms 5 ms 10 ms 260 ms

Fully lithiated

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MPIE 2018

J.P. Mendez, M. Ponga, M. Ortiz,
*JMPS*, **115**(2018) 123-141.
Si nanopillar lithiation – Volume

Volume expansion of 287%

Si nanopillar lithiation – Interface

Si nanopillar lithiation – Amorphization

Si nanopillar lithiation – Amorphization

Si nanopillar lithiation – Amorphization

0.0 ms  0.8 ms  5 ms  10 ms  260 ms

Fully amorphized
Fully lithiated

Amorphous
Cubic diamond
Cubic diamond (1st neighbor)
Cubic diamond (2nd neighbor)

Si nanopillar lithiation – Porosity

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...

\(^2\)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:
  - $\alpha$ phase: $0 < x \leq 0.03$
  - $\beta$ 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

H storage in Pd NW – α–β interface

- Phase boundary
- β phase
- α phase

Time: 0.00000 s

Hydrogen atomic fraction

Lattice constant (angstrom)

[110] [111] [112]
H storage in Pd NW – α–β interface

- Phase transition predicted (3.27% vs. 3.35%)
- Phase boundary motion, velocity, predicted (~100 nm/s)
- In progress: MgH₂ (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.

\[ t = 23.5 \text{ s} \]

Two local extrema

H storage in Pd NP – Interfacial strain

\( t = 8.5 \text{ s} \)

\( t = 23.5 \text{ s} \)

\( t = 31.0 \text{ s} \)

2 nm

<table>
<thead>
<tr>
<th>x - H fraction</th>
<th>a - lattice constant (Å)</th>
<th>Elastic Strain YZ</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.00</td>
<td>3.85</td>
<td>-0.17</td>
</tr>
<tr>
<td>0.25</td>
<td>3.95</td>
<td></td>
</tr>
<tr>
<td>0.50</td>
<td>4.00</td>
<td></td>
</tr>
<tr>
<td>0.75</td>
<td>4.25</td>
<td></td>
</tr>
<tr>
<td>1.00</td>
<td>4.35</td>
<td>0.17</td>
</tr>
</tbody>
</table>
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 \(1/6[112]\{111\}\)
- Leading Dislocations on \(\{111\}\) plane

$t = 5.0$ s

$t = 10.0$ s

$t = 20.0$ s

$t = 22.0$ s

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PdH: Interfacial misfit dislocations

PdH: Interfacial misfit dislocations

(100) plane (111) direction

(100) plane (111) direction


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Work in progress: Mg–Al alloys

- Al-Mg 5xxxx series alloys
- Sensitization due to GBs
- Formation of β phase (Mg$_2$Al$_3$)
- Stress corrosion cracking

Time scale: ~ days!
Not accessible to MD

R. Zhang et al., Scientific Reports, 7 (2017) 2961
DMD validation – Surface segregation

Al-4%Mg alloy at 600K

(100) surface

(110) surface

D(T=600K) = 5.4914^{-16} m^2/s

(111) surface

Free BC

Periodic BCs

Free BC

After 71 ms

After 82 ms

After 142 ms

DMD validation – GB segregation

Al-4%Mg alloy at 600K

Symmetric grain boundary energies

53.13°  67.38°  11.42°
DMD validation – GB segregation

Al-4%Mg alloy at 300K

After 377 days

After 97 days

After 245 days

DMD validation – GB segregation

Al-4%Mg alloy at 300K

DMD validation – GB segregation

- Mg segregation to Al GBs takes place on time scale of days or months.
- Mg segregation to Al GBs depends on misorientation angle.
- Mg segregation to Al GBs depends on temperature.
- An increase in temperature reduces segregation.

Summary of DMD results

After 43 days
After 70 days
After 60 days
DMD validation – GB segregation

Al-4%Mg alloy at 300K
Dissolution of Mg precipitate

Al-4%Mg Polyxals – Mechanical testing

After 84 hours

D(T=300K) = 3.3364^-26 m^2/s
Hopping frequency (1/s) = 1.0e13
Barrier energy (eV) = 1.1542

ε = 0.15

Dislocation analysis
Concluding remarks

- **Diffusive Molecular Dynamics** (DMD) provides a useful paradigm for describing slow/long term diffusion/transport phenomena with atomistic realism.
- Non-equilibrium thermodynamics without all the thermal vibrations; mass transport without all the hops; atomistics without all the atoms...
- Work in progress: Microstructure evolution in alloys (work in collaboration with SINTEF/Norway, NTNU, HZG...)
