Atomistic Modeling and Simulation of Long-Term Transport Phenomena in Nanomaterials

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Motivation - Diffusion

hydrogen storage

Slow deformation-diffusion coupled processes

G.E. Froudakis, Materials Today, 2011

Motivation - Diffusion

Slow deformation-diffusion coupled processes

hydrogen embrittlement in fuel cells

Barnoush, Hydrogen Embrittlement. 2011

MgH$_2$ system

Li et al, JACS (2007)

Mg nanowires collapse after 10 cycles of charging/discharging; temperature: 300K ~ 600K; **time scale: seconds to hours!**
Motivation


Molecular Dynamics, APPLIED OPTICS (2012)

NEED for time coarsening

NEED for spatial coarsening

Wanted: Cavitation pressure as a function void size, strain rate and temperature!
Overview

Long-term atomistic simulation of heat and mass transport

- the essential difficulty: multiple disparate time scales
  - atomic level rate-limiting processes: thermal vibrations, individual hops of atoms
  - macroscopic processes of interest: hydrogen storage, hydrogen embrittlement, ductile fracture, fatigue, etc.
  - time-scale gap: from molecular dynamics (femtoseconds) to macroscopic (seconds, minutes, …)!

- modeling approach
  - fine scale: non-equilibrium statistical thermodynamics
  - coarse scale: discrete kinetic laws

Non-Equilibrium Thermodynamics

Statistical thermodynamics for multi-species crystals

- N particles, M species
  
  • occupancy function
  for $i = 1, \ldots, N, k = 1, \ldots, M$, $n_{ik} = \begin{cases} 
  1, & \text{particle } i \text{ is from species } k \\
  0, & \text{otherwise} 
\end{cases}$

- assumption: separation of time scales
  
  • fine scale: thermal vibration ($\sim$fs) $\Rightarrow$ "modeled"
  • coarse scale: global relaxation ($\gg$fs) $\Rightarrow$ "solved for"

  probability: $\{\{q\}, \{p\}, \{n\}\} \sim p(\{q\}, \{p\}, \{n\}),$

- maximum entropy principle:
  
  $\max_p S[p] = -k_B \langle \log p \rangle$ (information entropy)
  
  with $\langle f \rangle = \sum_{\{n\} \in \Omega_{NM}} \frac{1}{h^{3N}} \int_{\Gamma} f(\{q\}, \{p\}, \{n\}) p(\{q\}, \{p\}, \{n\}) dq dp$

  subject to: $\langle h_i \rangle = e_i \quad i = 1, \ldots, N$ (atomic internal energy)
  $\langle n_{ik} \rangle = x_{ik} \quad i = 1, \ldots, N$ (atomic molar fraction)
Non-Equilibrium Thermodynamics

Thermodynamic potentials

- solve the constrained optimization problem using Lagrange multipliers:

\[ L[p; \{\beta\}, \{\gamma\}] = S[p] - k_B \{\beta\}^T \{h\} + k_B \{\gamma\}^T \{n\} \]

\[ p(\{q\}, \{p\}, \{n\}; \{\beta\}, \{\gamma\}) = \frac{1}{\Xi} \exp[-\{\beta\}^T \{h\} + \{\gamma\}^T \{n\}] \]

with \[\Xi(\{\beta\}, \{\gamma\}) = \sum_{\{n\} \in \mathcal{O}_{NM}} e^{-\{\beta\}^T \{h\} - \{\gamma\}^T \{n\}} \, dp \, dq\]

\[ S = -k_B \langle \log \rho \rangle = k_B \left( \log \Xi + \{\beta\}^T \{e\} + \{\gamma\}^T \{x\} \right) \]

\[ \Phi(\{\beta\}, \{\gamma\}) = \sup_{\rho} L[\rho; \{\beta\}, \{\gamma\}] = k_B \log \Xi(\{\beta\}, \{\gamma\}) \]

\[ \beta_i = \frac{1}{k_B} \frac{\partial S}{\partial e_i} \quad \Rightarrow \quad \text{particle temperature:} \quad T_i = \frac{1}{k_B \beta_i} \]

\[ \gamma_{ik} = -\frac{1}{k_B} \frac{\partial S}{\partial x_{ik}} \quad \Rightarrow \quad \text{particle chemical potential:} \quad \mu_{ik} = \frac{\gamma_{ik}}{\beta_i} = k_B T_i \gamma_{ik} \]

- however, \( p, \Xi, S, \) and \( \Phi \) all depend on Hamiltonian \( h_i = h_i(\{p\}, \{q\}, \{n\}) \).

in general, the closed-form formulation \( p, \Xi, S, \) and \( \Phi \) are intractable
Non-Equilibrium Thermodynamics

Meanfield approximation (Yeomans 1992)

- given a class of trial Hamiltonian:
  \[ h_{0i}(\{p\}, \{q\}, \{n\}) \]
  the trial probability density function can be defined as
  \[ p_0 = \frac{1}{\Xi_0} e^{-\{\beta\}^T h_0 + \{\gamma\}^T n} \]

- for fixed Lagrange multipliers \(\{\beta\}, \{\gamma\}\), the optimal probability of the trial space \(\{p_0^*\}\) is obtained by maximizing the constrained entropy, i.e.

  \[ \mathcal{L} [p_0^*, \{\beta\}, \{\gamma\}] = \sup_{p_0 \in \mathcal{P}_0} \mathcal{L} [p_0, \{\beta\}, \{\gamma\}] \]

- theorem (bounding principle for the free entropy):

  \[ \Phi(\{\beta\}, \{\gamma\}) \geq - \inf_{\{h_0\} \in \mathcal{H}_0} \mathcal{F}[\{h_0\}, \{\beta\}, \{\gamma\}] \]

  ➞ the maximum free entropy of the trial space provides a lower bound of the actual free entropy

  ➞ \(p_0^*\) converges to \(p^*\) as \(h_0 \to h\)
Non-Equilibrium Thermodynamics

Meanfield model: an example

- in practice there is always a trade-off between accuracy and computability

- we define the trial Hamiltonian as

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

\[
\{\pi}\quad \text{“uncoupled harmonic oscillators”}
\]

\[
p_0({\{q}, {p}, {n}) = \frac{1}{\Xi_0} \exp \left[ - \sum_{i=1}^{N} \beta_i \left( \frac{1}{2\overline{m}_i} |{p_i - \bar{p}_i}|^2 + \frac{\overline{m}_i \omega^2_i}{2} |{q_i - \bar{q}_i}|^2 \right) \right]
\]

Gaussian distribution

\[
p^*_0 = \arg\max_{\{\bar{p}_i, \{\overline{q}_i}, \{\omega_i},\{\overline{m}_i\}} L[p_0, \{\beta\}, \{\gamma \}]
\]

- meanfield parameters: \(\overline{q}_i\) (mean atomic position), \(\bar{p}_i\) (mean atomic momentum), \(\omega_i\) (frequency of oscillation), \(\overline{m}_i\) (mean atomic mass)

\[
h_i = -\frac{|p - p_0|^2}{2m} + V_i({\{q})
\]

\[\rightarrow \text{explicit formulations of } S, \Phi, F, \ldots\]
Discrete kinetic laws

Detailed balance of energy
- balance of energy at a particle
\[ \dot{u}_i = \dot{w}_i + \mu_i^T \dot{x}_i + \dot{q}_i \quad (\dot{w}_i = \sum_{\alpha=1}^{v} \frac{\partial h_i}{\partial A_\alpha} \dot{A}_\alpha \text{ is the external power}) \]
• requires kinetic models for \( \dot{x}_i \) and \( \dot{q}_i \)
- assume \( \dot{x}_i \) and \( \dot{q}_i \) can be divided into particle-to-particle fluxes of the form
\[ \dot{q}_i = \sum_{j \neq i} Q_{ij} \quad \dot{x}_i = \sum_{j \neq i} J_{ij} \quad \text{with} \quad Q_{ij} = -Q_{ji} \quad J_{ij} = -J_{ji} \]
- assume linear kinetics
\[ Q_{ij} = \kappa_{ij}(\beta_i - \beta_j) \]
\[ J_{ij} = D_{ij}(\gamma_i - \gamma_j) \]
\( \kappa_{ij} \): pairwise conductivity coefficient
\( D_{ij} \): pairwise diffusivity coefficient
- question: how to determine \( \kappa_{ij} \) and \( D_{ij} \)?
Discrete kinetic laws

A simple example

- consider only pairwise flux for only the nearest neighbors (based on a perfect crystal lattice)

\[ J_{ij} = \begin{cases} D_{ij} (\gamma_i - \gamma_j), & \text{if } i \text{ and } j \text{ are nearest neighbors} \\ 0, & \text{otherwise} \end{cases} \]

- require consistency with Fick’s law in continuum mechanics (in a finite-difference sense)

Fick’s second law: \[ \dot{x} = D_0 \nabla \cdot (x \nabla \gamma) \]

discrete diffusion model: \[ \dot{x}_i = \sum_{j \in \text{Nei}(i)} D_{ij} (\gamma_i - \gamma_j) \]

assume \( x, \gamma \in C^2(\mathbb{R}^3) \),

\[ \dot{x}_i = D_0 \nabla \cdot (x_i \nabla \gamma_i) + O(a^2) \]

iff \[ D_{ij} = \frac{D_0}{2a^2} (x_i + x_j) \]

(for fcc and bcc lattices)

- can be extended to more than one layers of neighbors
- the same procedure can be applied to heat conduction
Summary

Thermo-chemo-mechanical coupled analysis

given \(\{\bar{m}^{n-1}\}, \{\bar{q}^{n-1}\}, \{\bar{p}^{n-1}\},\)
\(\{\omega^{n-1}\}, \{\beta^n\}, \{x^n\}\)

[1] assume trial Hamiltonian
\(H_0(\{q\}, \{p\}; \{\pi\})\) with \(\pi_i = (\bar{m}_i, \bar{q}_i, \bar{p}_i, \omega_i)\)

[2] obtain optimal \(\pi^n\) by maximizing free entropy:
\[
\max_{\{\bar{m}_i\}, \{\bar{p}_i\}, \{\bar{q}_i\}, \{\omega_i\}} L[\rho_0, \{\beta\}, \{\gamma\}]
\]

[3] extract quantities of interest
e.g. \(S^n, \Phi^n, E^n, \ldots\)

[4] solve kinetic equations and obtain \(\{\beta^{n+1}\}, \{x^{n+1}\}\)

[5]
Model validation

Heat conduction in Si nanowires

- experiment (D. Li et al. 2003)
  • specimen: single-crystal Si (111) nanowires
    \( R = 11, 18.5, 28, 57.5 \) nm
  • measurement: thermal conductivity
  • main discovery: significant size effect

HRTEM image of a 22 nm SiNW

Thermal Conductivity (W/m-K)

Temperature (K)

(a)
Model validation

Computational model and simulations

- consider a slice of the SiNWs
- create amorphous layer by random perturbation
- pair-wise thermal conductivity:

\[
A_{ij} = \begin{cases} 
A_{amo}, & \text{if } i \in \Omega_{amo} \text{ or } j \in \Omega_{amo}, \ r_{ij} < r_c, \\
A_{xal}, & \text{if } i, j \in \Omega \setminus \Omega_{amo}, \ r_{ij} < r_c, \\
0, & \text{if } r_{ij} \geq r_c,
\end{cases}
\]

![Graph showing thermal conductivity vs. nanowire radius](image)

- Thermal conductivity
- Experimental result
- Spline fitting of experimental result
- Numerical result

![Diagram showing atomic temperature and amorphous layer](image)
Model Validation

Hydrogen diffusion in Pd nanofilms

- experiment (Y. Li and Y.-T. Cheng, 1996)
  - specimen: Pd (111) thin films with thickness \( L = 22 \text{ nm}, 46 \text{ nm}, 135 \text{ nm} \)
  - method: electrochemical stripping
    - step 1: introduce H to Pd by cathodic polarization (set \( \Delta V = -0.83V \))
      \[
Pd + H_2O + e^- \rightarrow Pd \cdot H_{ads} + OH^- \]
    - step 2: remove H from Pd-H by anodic stripping (switch \( \Delta V \) to \(-0.5V\))
      \[
Pd \cdot H_{ads} + OH^- \rightarrow Pd + H_2O + e^- \]
  - measurement: time history of discharge current at the surface of Pd film
    \[
    I(t) = -FSJ_H(l,t) = FSD_H \left( \frac{\partial C(l,t)}{\partial l} \bigg|_{l=0} \right) = \frac{FSD_HZ}{NAV_{cell}} \left( \frac{\partial x(l,t)}{\partial l} \bigg|_{l=0} \right)
    \]
Model Validation

Models and simulations

- simplification of thermodynamic model
  - 1D, constant temperature, fixed Pd lattice
  - linearization of Pd-H interatomic potential


  equilibrium condition
  \[
  \gamma_i = \log \frac{x_i}{1 - x_i} + \sum_{j \in I_H, j \neq i} \frac{C_{ij}}{k_B T} x_j + \frac{B_i}{k_B T}
  \]

- discrete Fick’s law
  \[
  \dot{x}_i = \sum_{j \in Nei(i)} D_{ij} (\gamma_j - \gamma_i) x_{ij}
  \]
  - mass transport restricted to nearest neighbors
  - discretized in time by the mid-point rule

- highlights
  - fully atomistic
  - \( t_{\text{max}} = 1.0 \) sec, \( dt \sim 10^{-6} \) sec
Summary and Future work

- Long-term atomistic simulation of heat and mass transport
  - non-equilibrium statistical thermodynamics model
    - maximum entropy principle
    - meanfield approximation
  - discrete kinetic laws
    - discrete Fick’s law
    - discrete Fourier’s law
  - coupling: a partitioned procedure
  - validations and applications

- Future work
  - computational methods for thermo-chemo-mechanical coupling
  - design and validation of discrete kinetic laws
  - validations and applications

- References
  - Venturini, Wang, Romero, Ariza, and Ortiz, JMPS (submitted)
  - Wang, Ortiz and Ariza, Int. J. Hydrogen Energy (submitted)
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