Atomistic Long-Term Simulation of Heat and Mass Transport

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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:*
    • *Mechanical properties at moderate strain rates*
    • *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...
Example: Material properties

- Many mechanical properties are rate-controlled by lattice defects
- MD can access strain rates $\sim 10^8$-$10^{12} \text{ s}^{-1}$, nano-samples
- Engineering applications involve lower strain rates, larger sizes
- Materials testing:
  - Servo-hydraulic: $1 \text{ s}^{-1}$
  - Hopkinson bar: $10^4 \text{ s}^{-1}$
  - Plate impact: $10^7 \text{ s}^{-1}$
- MD outside realm of typical engineering application and materials testing...

Example: Heat transport in Si nanowires

- The thermal conductivity of NW exhibits size dependence not predicted by continuum models
- Low thermal conductivity yields high thermoelectric $ZT$ values
- Typical devices are on the mm scale with thermal transients in the second time scale
- Outside range of straight MD...
- Also MD is often thermostated, which introduces artifacts

Example: Hydrogen storage

- Metal hydrides (e.g. MgH$_2$) used for hydrogen storage, e.g., for use in fuel cells
- Absorption/desorption rates controlled at atomic level
- Commercial storage tanks have Kg capacities (McPhy Energy)
- Typical absorption/desorption times are temperature/pressure dependent and in hour range
- Outside range of straight MD...

Example: Energetic materials

- Energetic materials undergo complex chemistry coupled to temperature and deformation
- Reactions take place at atomic scale, involve bond breaking and creation of new bonds
- Reaction paths are extremely complex, defy reduce modeling
- Full chemistry, reaction-front speeds on the order of seconds
- Outside scope of straight MD...

Spacetime atomistic-to-continuum

- **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
  - Approximate grand-canonical free entropy using variational meanfield theory
  - Append Onsager-like empirical atomic-level kinetic laws (heat and mass transport)
  - Treat (smooth) mesodynamics by implicit integration (large time steps >> MD!)
  - **Quasicontinuum** spatial coarse-graining


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: $\langle A \rangle = \sum_{\{n\} \in \mathcal{O}_{NM}} \int A(\{q\}, \{p\}, \{n\}) \rho(\{q\}, \{p\}, \{n\}) \ dq \ dp$
  \[\uparrow\]
  grand-canonical pdf

Max-Ent Non-Equilibrium SM

- Assume $H = \sum_{i=1}^{N} h_i$, (e. g., EAM, TB...)

- Principle of max-ent$^1$: $S[p] = -k_B \langle \log \rho \rangle \to \text{max!}$

  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:

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

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

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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:
  \[ \beta_i \frac{d\bar{q}_i}{dt} = \frac{1}{k_B} \frac{\partial \Phi}{\partial \bar{p}_i}, \quad \beta_i \frac{d\bar{p}_i}{dt} = -\frac{1}{k_B} \frac{\partial \Phi}{\partial \bar{q}_i} \]

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

- Essential difficulty: \( \Phi \) unknown, uncomputable
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:

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

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

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

- Trial Hamiltonians parameterized by $\{\omega\}$

- Meanfield mesoscopic dynamics and optimality:

$$m_i \ddot{q}_i + \sum_{j=1}^{N} \frac{\partial}{\partial q_i} \langle V_j \rangle_0 = 0, \quad \frac{\partial}{\partial \omega_i} \sum_{j=1}^{N} \beta_j \langle V_j \rangle_0 + \frac{3}{\omega_i} = 0$$

- Effective potentials: $\langle V_i \rangle_0(\{\bar{q}\}, \{\bar{p}\}, \{\beta\}, \{\gamma\}) =\sum_{\{n\} \in \mathcal{O}_{NM}} \frac{1}{\Xi_0} \int V_i(\{q\}, \{n\}) e^{-\{\beta\}^T\{h_0\} - \{\gamma\}^T\{n\}} \ dq \ dp$

Gaussian weights: Hermite quadrature!
Non-equilibrium SM – Meanfield validation


\[ \text{Cu-Ni} \]

$\begin{align*}
\text{C}11 - \text{exp} & \quad \text{B - exp} \quad \text{G - exp} \\
\text{C}11 - \text{num} & \quad \text{B - num} \quad \text{G - num}
\end{align*}$

$\begin{align*}
\text{Cu-Ni} \\
\text{Cu - exp A} \quad \text{Cu - exp B} \quad \text{Ni - exp B} \\
\text{Cu - num} \quad \text{Ni - num}
\end{align*}$

$e_i < 10\% \text{ btw } [0.8T_D, 0.8T_m]$

$e_f < 10\% \text{ btw } [0.7T_D, 0.7T_m]$

$T_c(\text{Cu})$

$T_c(\text{Ni})$

$T_m(\text{Cu}) = 1358 \text{ K}$

$T_m(\text{Ni}) = 1728 \text{ K}$

$1^\text{Simmons, G., The MIT Press (1971).}$


$^B\text{R. Toloukian, The TPRC Data Series, vol. 12, 1975.}$
Non-equilibrium SM – Meanfield validation


Non-equilibrium SM – Meanfield validation


Michael Ortiz
MRS 12/14
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
Verification – Stability of time integration

- Nanovoid cavitation
- Lennard-Jones potential
- Linear heat transport
- Implicit Newmark

27.8% volumetric deformation

Temperature [K]

Time step = MD x 100!

Graph showing virial stress and void fraction versus volume strain.
Kinetic validation – Si nanowires

- Si (111) nanowires\(^1\)
- Radius = 11, 18.5, 28, 57.5 nm
- Data: Thermal conductivity
- Predictive challenge: Size effect!

Experimental rig\(^1\)

![Experimental rig image]

![Graph showing thermal conductivity vs. temperature for different radii of Si nanowires]

Amorphous layer in SiNW!

Kinetic validation – Si nanowires

- Rigid model, linear kinetics
- $\kappa_{\text{xal}} = 0.09 \text{ nW/K}$, $\kappa_{\text{amo}} = 16 \text{ nW/K}$
- Prescribed temperature gradient
- Output: Average axial heat flux
Kinetic validation – H absorption in Pd

- H absorption into (111) Pd foil\(^1\)
- Foil thickness = 460, 1350 Å
- Temperature = 300 K
- Measurement: Surface concentration gradient vs. time

**Experimental configuration\(^1\)**

- Electrolyte solution
- Pd film
- Substrate: Au-coated Ni
- \(h = 1350 \text{ Å}\)
- \(T = 300 \text{ K}\)
- \(h = 460 \text{ Å}\)
- \(T = 300 \text{ K}\)

Kinetic validation – H absorption in Pd

- Linear kinetics, $D = 2.1 \times 10^5 \, \text{Å}^2/\text{s}$
- Ising-type meanfield model
- Johnson EAM potential
- Prescribed surface concentration
- Output: Surface $dc/dx$ vs. time

Kinetic validation – H absorption in Pd

• Linear kinetics, $D = 2.1 \times 10^5 \text{Å}^2/\text{s}$
• Ising-type meanfield model
• Johnson EAM potential$^1$
• Prescribed surface concentration
• Output: Surface $dc/dx$ vs. time

$\alpha + \beta$

$\gamma$ – nondimensional chemical potential

$\alpha$ – classical model: $\gamma = \log(x)$

$\beta$ – proposed model

$\text{displacement}$

$\text{velocity}$

$T = 0.001 \text{s}$

$T = 0.01 \text{s}$

$T = 0.1 \text{s}$

$T = 1.0 \text{s}$

$D$

$i$

$j$

---


Application: Nanovoid cavitation in Cu$^1$

- Parameters:
  - $T_0$ (initial) = 300K
  - Full Size = $72a_0$
  - Atomistic Zone = $14a_0$
  - Diameter = $12a_0$
  - Strain Rate = $10^5$-$10^{12}$ s$^{-1}$

- Loading: Triaxial, uniaxial

- Potential: EAM-Mishin$^2$

Initial quasicontinuum mesh with full atomistic resolution near void

$^1$M. Ponga, M. Ortiz and P. Ariza, Mechanics of Materials (submitted)

Application: Nanovoid cavitation in Cu

Uniaxial loading

Initial Void

Void at 6.5%

Void at 6.7%

Void at 8.5%

Void at 10.0%

Void at 12.0%

cavitation

Octahedron {111} planes
Application: Nanovoid cavitation in Cu

Leading Shockley partial dislocations on {111} planes

Uniaxial loading, \( \varepsilon = 6.6\% \)

Trailing Shockley partial dislocations on {111} planes
Application: Nanovoid cavitation in Cu

Shear to Prismatic loop reactions:

On \(<110>\) directions

\[
\frac{1}{6}[\bar{2}11] + \frac{1}{6}[\bar{2}1\bar{1}] + \frac{1}{6}[\bar{1}21] + \frac{1}{6}[12\bar{1}] \rightarrow [\bar{1}10]
\]
\[
\frac{1}{6}[211] + \frac{1}{6}[21\bar{1}] + \frac{1}{6}[121] + \frac{1}{6}[\bar{1}21] \rightarrow [\bar{1}10]
\]
\[
\frac{1}{6}[1\bar{2}1] + \frac{1}{6}[\bar{1}2\bar{1}] + \frac{1}{6}[2\bar{1}1] + \frac{1}{6}[21\bar{1}] \rightarrow [1\bar{1}0]
\]
\[
\frac{1}{6}[211] + \frac{1}{6}[12\bar{1}] + \frac{1}{6}[21\bar{1}] + \frac{1}{6}[121] \rightarrow [110]
\]

On \(<110>\) directions

\[
\frac{1}{6}[211] + \frac{1}{6}[1\bar{1}2] + \frac{1}{6}[21\bar{1}] + \frac{1}{6}[112] \rightarrow [101]
\]
\[
\frac{1}{6}[1\bar{1}2] + \frac{1}{6}[211] + \frac{1}{6}[21\bar{1}] + \frac{1}{6}[112] \rightarrow [10\bar{1}]
\]
\[
\frac{1}{6}[2\bar{1}1] + \frac{1}{6}[211] + \frac{1}{6}[1\bar{1}2] + \frac{1}{6}[112] \rightarrow [101]
\]
\[
\frac{1}{6}[1\bar{1}2] + \frac{1}{6}[211] + \frac{1}{6}[2\bar{1}1] + \frac{1}{6}[112] \rightarrow [101]
\]

On \(<110>\) directions

\[
\frac{1}{6}[\bar{1}21] + \frac{1}{6}[\bar{1}12] + \frac{1}{6}[\bar{1}21] + \frac{1}{6}[112] \rightarrow [011]
\]
\[
\frac{1}{6}[\bar{1}21] + \frac{1}{6}[\bar{1}12] + \frac{1}{6}[\bar{1}21] + \frac{1}{6}[112] \rightarrow [01\bar{1}]
\]
\[
\frac{1}{6}[\bar{1}21] + \frac{1}{6}[\bar{1}12] + \frac{1}{6}[\bar{1}21] + \frac{1}{6}[1\bar{1}2] \rightarrow [0\bar{1}1]
\]
\[
\frac{1}{6}[\bar{1}21] + \frac{1}{6}[\bar{1}12] + \frac{1}{6}[\bar{1}21] + \frac{1}{6}[12\bar{1}] \rightarrow [01\bar{1}]
\]

Triaxial loading
Application: Nanovoid cavitation in Cu

Prismatic loop structure, triaxial loading

Prismatic loop evolution ($\varepsilon = 5, 6, 7\%$)

(Images obtained with DXA and Paraview)
Application: Nanovoid cavitation in Cu

Prismatic loop structure, triaxial loading

Prismatic loop evolution ($\varepsilon = 5, 6, 7\%$)

(Images obtained with DXA and Paraview)
Application: Nanovoid cavitation in Cu

Temperature increase on \{111\} planes due to dislocation activity

Temperature field @ $\varepsilon=2.7\%$

Temperature evolution
- Void Surface
- Near to Void
- Far from Void

- First dislocation
- Prismatic Loop
Application: Nanovoid cavitation in Cu

- Transition between quasistatic-isothermal to dynamic-adiabatic behavior at $10^7$-$10^8$ s$^{-1}$
- Quasistatic regime: Time scale set by heat conduction
- Dynamic regime: Time scale set by microinertia
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Summary and concluding remarks

Thank you!