Molecular Dynamics Simulations of Fusion Materials: Challenges and Opportunities (Recent Developments)

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Limitations of MD

- Time scales
- Length scales (PBC help a lot)
- Accuracy of forces
- Classical nuclei
Computer Simulation – Multi-Scale

- Time scale for radiation damage evolution and the corresponding simulation methods

![Diagram showing time scale and methods]

- PKA creation
- Cascade, thermal spike
- Quench phase
- Annealing and defect migration

Methods:
- BCA – Binary Collision Approximation
- MD – Molecular Dynamics
- KMC – Kinetic Monte Carlo

Defect properties:
- C⁺-Si<100>

![Graph showing defect accumulation]

BCA – Binary Collision Approximation
MD – Molecular Dynamics
KMC – Kinetic Monte Carlo
Computer Simulation – Multi-Scale

- Time and length scales are always challenging for materials science

![Diagram showing multi-scale simulation methods and their time and length scales.](image)
Can’t Just Simulate Everything at Atomic Level: The Human Simulator?

• **Person length scales**
  – Size ≈ 1 m³ ≈ 10⁶ mols ≈ 10³⁰ atoms

• **Person time scales**
  – Lifetime ≈ 100 years ≈ 10⁹ s
  – Time scale for atomic motions is ≈ 10⁻¹² s, so time step is ≈ 10⁻¹³ s
  – Total number of time steps ≈ 10²²

• **Person simulation**
  – At 10 calculations per each atom per each time step we get
    ≈ 10 x 10³⁰ x 10²² = 10⁵³ calculations
  – Present computing capability is teraflop ≈ 10¹² FLOPS
    (floating point operations per second) ⇒ Person simulation takes ≈ 10⁴¹ s ≈ 10³⁴ years.
Limitations of MD – Rare Events, System Size

- **Rare Events**
  - Rare events occur very infrequently, so do not happen on MD time scales.
  - *E.g.*, diffusion ($D \approx 10^{-12} \text{ cm}^2/\text{s}$) has atom hops only every $\approx 10^{-3}$ s. Cannot see them with normal MD simulations (can use temperature accelerated MD, but that is an advanced topic).

- **System size**
  - Time for a simulation scales with number of atoms, i.e, $O(N)$.
  - Programs can be parallelized to work by spatial decomposition of different regions on different processors
  - Can treat up to $10^{10}$ atoms, and increasing, but still limited.
Need for Accelerated Molecular Dynamics Methods

Many important problems lie beyond the timescales accessible to conventional MD, due to the infrequent surface or bulk diffusion mechanisms involved, including:

- Vapor-deposited thin film growth (metals and semiconductors) especially heteroepitaxial layers
- Stress-assisted diffusion of point defects, defect clusters, and dislocations
- Ion implantation or radiation damage annealing
All of these are examples of a more general class of problems, that of infrequent (or activated) event systems:

The system vibrates (and vibrates and vibrates...) in a many-dimensional potential basin the vast majority of the time.

Occasionally – but only very rarely – it escapes through a dividing surface to a new potential basin.

The objective is to accelerate these escapes without corrupting the relative escape probabilities for various exit pathways.
Transition State Theory (TST)

- For infrequent event systems, assuming no correlated crossing events

\[ k_{A \rightarrow B}^{TST} = \text{equilibrium flux through a particular dividing surface} \]

\[ = \langle |v| \delta(x) \rangle_A \]

\[ = v_0 \exp \left( -\frac{E_a}{k_B T} \right) \quad \text{harmonic approximation} \]

- No dynamics required (although minimal dynamics in the dividing surface region can be used to improve the classical TST rate, or in various “quantum transition state theory” methods)

- Can we exploit TST to develop methods which do not require any knowledge of where dividing surfaces are?
Three Recent Methods for Infrequent Events

Hyperdynamics

A method for accelerating the molecular dynamics simulation of infrequent events,

Hyperdynamics: Accelerated Molecular Dynamics of Infrequent Events,

- Assumptions: infrequent events, TST

Parallel Replica Dynamics

Parallel replica method for dynamics of infrequent events,

- Assumption: infrequent events

Temperature Accelerated Dynamics

Temperature-accelerated dynamics for simulation of infrequent events,

- Assumptions: infrequent events, harmonic TST, lower bound on preexponential factor
Hyperdynamics: Basic Approach

- Therefore we are free to modify the basins however we like, as long as the saddle properties are unaffected. Add a positive bias potential $\Delta V_b(r)$ to the potential surface $V(r)$ in the wells:

- The TST rates increase by $e^{\Delta V_b(r_A)/k_BT}$ (neglecting the prefactor)
- Since the escape rates are uniformly raised, a valid state-to-state sequence is obtained, but at an accelerated pace.
- In fact, harmonic TST is not required, only to assume TST is exact (implying no correlated crossing events), as we now show...
Parallel Replica Dynamics: Basic Concept

- Harness parallel or distributed processors to extend *simulation time* for infrequent event systems by independently exploring phase space.

- When any processor detects a transition, sum the trajectory times from all processors, and restart all processors in the new state.
Temperature Accelerated Dynamics

Again, the basic concept is rather simple:

- Run a trajectory at an elevated temperature $T_{high}$, but reject all attempted transitions (more on how this is done in a bit…).
- Extrapolate the high-temperature escape times $\{t_{i, high}\}$ to times $\{t_{i, low}\}$ at the lower temperature $T_{low}$, using the Arrhenius relationship and measured activation energies $\{E_a^i\}$.
- Accept the transition with the shortest $t_{i, low}$.

The key question is how long one needs to run the $T_{high}$ simulation…
Key issue:

As TAD relies upon harmonic TST for validity, any anharmonicity error at $T_{\text{high}}$ will lead to a corruption of the dynamics.
Example of parallel replica hyperdynamics

Ag$_{10}$/Ag(111) diffusion  Cu/Cu(100) epitaxial growth

Example of parallel replica hyperdynamics

Competing Kinetics and He Bubble Morphology in W

Fast and slow growth regimes are defined relative to typical diffusion hopping times of W interstitials around the He bubble

TAD Example: 1/4 ML Cu/Cu(111) at 150 K

Comparison of Different Acceleration Methods

Hyperdynamics
- assumes infrequent events, TST
- requires construction of a valid bias potential
- low barriers are a problem

Parallel Replica Dynamics
- only assumes infrequent events
- can be combined with hyperMD (done) or TAD (harder)
- full parallel efficiency if $\tau_{\text{rxn}} / n_{\text{proc}} \gg \tau_{\text{dephase}}, \tau_{\text{corr}}$

Temperature Accelerated Dynamics
- assumes infrequent events, harmonic TST, minimum prefactor
- synthetic (kMC) mode reduces low-barrier problem
- probably the most powerful of the three, given its assumptions
Accelerated Molecular Dynamics

- **Accelerated Dynamics**
  - Hyperdynamics – boost potential $\Delta V(r)$
  - Parallel replica method for dynamics
  - Temperature accelerated dynamics
  - Long-time dynamics based on the dimer method
  - ABC – slowly add penalty functions + static relaxation

- **Issues**
  - Solve the rough potential surface problem for dynamics simulation
  - Coupling motion of fast and slow dynamics

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Energy Landscape - Rough

Initial

Final
Steady-State Accelerated MD

- **SSAMD method** (*rough potential surface and slow dynamics*)
  - Add boost potentials slowly

- How to determine boost potential during MD simulation
- In normal MD, increase $T$ - the total vibration magnitude of atoms, driving the system to change state smoothly from A to B, and overcoming the energy barrier to state B
Basic Ideas

- Vibration magnitude of atoms at a given temperature

\[ A_i = \left| \vec{R}_i^t - \vec{R}_i^0 \right| \]

\[ \lambda = \sum_{i=1}^{n} A_i \]

The system reaches an equilibrium state – \( \lambda \) becomes a constant

\[ \lambda \text{ of 2000 atoms at 400 K in Fe} \]
Basic Ideas

- Vibration magnitude of atoms at a given temperature

\[ A_i = |\vec{R}_i^t - \vec{R}_i^0| \]

\[ \lambda = \sum_{i=1}^{n} A_i \]

- The system occupies the different steady states at different temperatures.
- The states approach a continuum function as the increase in temperature is infinitesimal (temperature-induced states).
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![Graph showing the relationship between temperature and vibration magnitude](image)
Basic Ideas

- Form boost potential

\[ \Delta V = F(\lambda_s) \quad \lambda_s = \sum A_{i,s} \]

1) \( A_{i,s} \) - the vibration magnitude of \( i \)th atom in \( S \) state

2) Activated volume (only boost atoms in the activated volume)
Boost Potential

- Two conditions:
  1. both the original and biased systems obey transition state theory

\[
k^\text{TST}_{A \rightarrow T} = \frac{\left\langle |V_A| \delta_A(r) e^{\beta \Delta V_b(r)} \right\rangle_{A_b}}{\left\langle e^{\beta \Delta V_b(r)} \right\rangle_{A_b}}
\]

The bias potential vanishes at any dividing surface

\[\Delta V(r)_{A_b} = 0 \quad \text{where } \delta_{A_b}(r) \neq 0\]

- Concave boost potential

\[V_{bias}(\{r_1, \ldots, r_{N_{AV}}\}; t) = E_b(t) \left(1 - \left(\frac{\lambda\{r_1, \ldots, r_{N_{AV}}\}}{q(t)}\right)^2\right) H(q(t) - \lambda\{r_1, \ldots, r_{N_{AV}}\})\]

\(E_b\) is constant parameter related to state s and we slowly increase \(E_b\) (t) and \(q(t)\)
The boost potential allows the system to jump from $S_0 \leftrightarrow S_1 \leftrightarrow S_2$.

When the system reaches state $S_1$, the vibration $\lambda$ reaches to $q_1$.

The system can move along the corresponding constant energy contour.

$$q_k = q_{k-1} + dq$$
$$E_{b,k} = E_{b,k-1} + dE$$
The time processing involving the boost potential at step $k$

$$t^k = t_{MD} \exp\left(\frac{\Delta V^k}{k_B T}\right)$$

$t_{MD}$: normal MD time step

Determine initial $q$

$$V_{bias}(\{r_1, ..., r_{N_{Av}}\}; t) = E_b(t)\left(1 - \left(\frac{\lambda\{r_1, ..., r_{N_{Av}}\}}{q(t)}\right)^2\right)H(q(t) - \lambda\{r_1, ..., r_{N_{Av}}\})$$

At each state, there exists an average value of total vibration magnitude of $n$ atoms:

$q_{s0} \rightarrow$ initial $\lambda$ at a given temperature

$q_{S1} \rightarrow$ state $S^1 q_k = q_{k-1} + dq$
Validate SSAMD

- Migration of a mono vacancy in Fe and Surface Diffusion of Clusters in Cu

- Ackland’s potential for Fe and Cu, and Fe-He potential by PNNL
- Time step – 1 fs, Temperature – 200 ~ 500 K.
- MD simulation in the canonical ensemble of NVT is performed to get the initial equilibrium state and determine the initial \( q \) (initial \( \lambda \) at a given temperature).
- Set appropriate \( dq \) and \( dE \), and add boost potential to system. At each state, the system is relaxed with boost potential and then evolved to next state (\( dq \sim 0.1-0.2 \text{ A} \) and \( dE \sim 0.3 \text{ eV} \)).
- When a transition occurs, the simulation returns to normal MD which will bring the system to another equilibrium state.
- Repeat the above steps, and explore the potential surface
Vacancy Migration

- One of the 1\textsuperscript{st} nearest neighbor jumps to vacancy site

At 300 K, a jump $\sim 2.8 \times 10^{-5}$ s

100 jumps $\sim 2.8 \times 10^{-3}$ s

$E_m \sim 0.6$ eV

$E_m (\text{NEB}) \sim 0.63$ eV

(Ackland JPCM)
Surface Diffusion of Cu Atom

- Surface diffusion – atoms go underground

[Images of hopping, vacancy, and exchange processes]
Surface Diffusion of Cu Atom

- Surface diffusion – hop-exchange of a dimer

T = 300 K
Simulation time
~ 5.6 x10^{-3} s (5.6 ms)
Material Issues in Fission and Fusion Reactors

- Radiation damage – defects
- He accumulation – alters microstructures and properties

- Annual defect production in fission and fusion reactor environments

<table>
<thead>
<tr>
<th>Defects</th>
<th>Fission (LWR)</th>
<th>Fusion (3.5 MW/m²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Displacement per atom/year</td>
<td>5</td>
<td>40</td>
</tr>
<tr>
<td>Helium (appm/year)</td>
<td>25</td>
<td>504</td>
</tr>
<tr>
<td>Hydrogen (appm/year)</td>
<td>250</td>
<td>1865</td>
</tr>
</tbody>
</table>

- Helium has significant effects in fusion structure materials, affecting the global evolution of microstructures and degrading the mechanical properties of materials.
- One of the most important issues is helium bubble formation and growth
HeV$_2$ Cluster at 400 K

- **Two paths**
  - Path I
  - Path II

- Both paths are consistent with *ab initio* calculations (CC Fu, PRB)
- Vacancy driven migration of the H$_n$V$_m$ clusters (m>n)
Migration of $\text{He}_n\text{V}_m$ Cluster ($n>m$)

- $\text{He}_6\text{V}_3$ ($\text{He}_9\text{V}_6$)

(a) Creation of SIA

(b) Orientation change of the dumbbell interstitial to crowdion

(c) The crowdion diffuses along the cluster surface

(d) Combination with original vacancy: $\text{V} + \text{SIA} \rightarrow 0$

- SIA driven migration of $\text{He}_n\text{V}_m$ ($n>m$) clusters (a two-step mechanism — creation of an SIA and recombination of the SIA with a vacancy)
SSAMD – Migration of He-V clusters

Total diffusion time is around 0.22s.

He$_6$V$_4$

$T = 500$ K

- He atom
- Vacancy
- Interstitial

- Mass center of He atoms
- Original mass center of He atoms

➢ An self-interstitial atom driven migration
Migration of He$_n$V$_m$ Cluster (n>m)

- Migration energies of He$_n$V$_m$ clusters (200, 300, 400 and 500 K)

\[
D = D_0 \exp\left(-\frac{E_a}{k_B T}\right)
\]

- $D_0$ and $E_a$ for the He$_6$V$_4$ are $1.0756 \times 10^{14}$ and 0.88 eV, respectively.
- $D_0$ and $E_a$ for the He$_9$V$_6$ are $2.1445 \times 10^{13}$ and 0.87 eV

- The migration energy is close.
- The mechanisms are same for these two He-V clusters.
Growth of A $\text{He}_n V_m$ cluster from Small Clusters

- $\text{He}_6 V_4$ and $\text{He}_9 V_6$ → $\text{He}_{13} V_{10}$ (600K)

The temporal vacancy and interstitial are formed: $\text{He}_6 V_4$ → $\text{He}_6 V_5$ + SIA
Mass transfer occurs between them.
SSAMD – Growth of He-V clusters

Total time is around 6.79µs.

Interaction between \(\text{He}_9\text{V}_7\) and \(\text{He}_6\text{V}_3\)

\(T = 600\ \text{K}\)

- The small He-V disappears and transfers to the larger one
- Ostwald Ripening (mass transportation) – an important mechanism

\(\text{He}_{13}\text{V}_{10}\)
Electronic Effects: Two Temperature Model

- Model radiation-excited carrier gas consisting of hot electrons and holes
- Provide a mechanism for energy exchange between radiation-excited carrier gas and atoms
- Conserves energy (electronic and atomic)
- Electron-ion energy transfer based on a Langevin thermostat
- Electronic temperature controlled by a heat diffusion equation
Electronic Effects: Two Temperature Model

Langevin thermostat

\[ ma = F_i(t) - \gamma_i v_i + F'(t) \]

- conservative force
- friction term (energy loss)
- random force (energy loss or gain) (usually a net gain)

Electron stopping effects

\[ \gamma_i = \gamma_p + \gamma_s \]

- Friction due to electron-atom interactions
- Friction due to electron stopping

For \( v_i > v_o \)

\[ \gamma_i = \gamma_p \]

For \( v_i \leq v_o \)

\( \gamma \) values are user-specified constants related to relaxation times (\( \tau \))
Energy transport in the electronic subsystem via the heat diffusion equation

\[
C_e \frac{\partial T_e}{\partial t} = \nabla (\kappa_e \nabla T_e) - g_p (T_e - T_a) + g_s T_a
\]

- Electron temperature ($T_e$) varies locally.
- $T_e$ is taken as an average in a spatial cell.
- Heat eqn is discretized and solved numerically.
- User supplies initial $T_e$ values.
- LAMMPS keeps track of time evolution of $T_e$ values.
- $C_e$ and $\kappa_e$ are user-specified constants.
- The $T$ values and “coupling constants” ($g_p$ and $g_s$) vary spatially and temporally.
Link between the electronic and atomic sub-systems

Energy loss of the atomic sub-system:

\[ \Delta U_i = F_i \cdot v_i \Delta t = \gamma_i v_i^2 \Delta t \]
\[ \Delta U_i = \Delta t \sum_{i \in J} \gamma_i v_i^2 = \Delta t \sum_{i \in J} \gamma_p v_i^2 + \Delta t \sum_{i' \in J} \gamma_s v_i^2 \]

Energy gain of the electronic sub-system:

\[ \Delta U_{eg} = g_p T_a \Delta V \Delta t + g_s T_{a'} \Delta V \Delta t. \]

Equate the two:

\[ \sum_{i \in J} \gamma_p v_i^2 = g_p T_a \Delta V \]
\[ \sum_{i' \in J} \gamma_s v_i'^2 = g_s T_{a'} \Delta V. \]

And solve for the coupling "constants":

\[ g_p = \frac{3Nk_B\gamma_p}{\Delta Vm} \]
\[ g_s = \frac{3N'k_B\gamma_s}{\Delta Vm}. \]

Define the atomic T values:

\[ \frac{3}{2}k_BT_a = 1/N \sum_{i \in J} \frac{1}{2}mv_i^2 \]
\[ \frac{3}{2}k_BT_{a'} = 1/N' \sum_{i' \in J} \frac{1}{2}mv_i'^2 \]
TTM input parameters (fix ttm)

- Electron specific heat*
- Electron density*
- Electron thermal conductivity
- Electron-ion interaction coefficient, $\gamma_p$*
- Electron stopping friction coefficient, $\gamma_s$ (SRIM tables, www.srim.org)
- Electron stopping critical velocity, $v_0$
- Number of electronic grid points
- Initial electron temperature

* DFT calculations can be used to estimate these values
Example: cascade damage simulation

- Gadolinium pyrochlore waste form (Gd$_2$Zr$_2$O$_7$)
- Large initial velocity (10 keV) imparted to the primary knock-on atom (PKA) to simulate a radiation recoil event

Non-TTM results: Gd defects

Blue = PKA (U)
Red = defect Gd
Results of defect analysis

Averages from 20 random PKA directions

- No electronic subsystem
- $\gamma_p = 0.277$
- $\gamma_p = 1.385$
- $\gamma_p = 2.77$
Atomic and electronic temperature

No TTM

$\gamma_p = 0.277$

$\gamma_p = 1.385$

$\gamma_p = 2.77$