Atomistic Simulation Methods

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Outline

Molecular Dynamics (MD)

- Introduction
- Current state of art
- Pros and Cons

Accelerated Molecular Dynamics

- Parallel-replica dynamics
- Temperature-accelerated dynamics (TAD)
  - low-energy radiation damage in MgO

Dimer method (On the-fly kinetic Monte Carlo)

Summary

Molecular Dynamics (MD) Simulation

1) Choose an interatomic potential appropriate for the system
   For example:
   - FCC metal - embedded atom method (EAM)
   - Silicon - 3-body + density dependence
   - Ionic system - Coulombic + short-range repulsion
   …

2) Choose appropriate boundary conditions

3) Integrate classical equations of motion to evolve the atoms
   $F=ma$ (force F on each atom from interatomic potential)
   Integration time step = $\sim 10^{-15}$ s

4) Observe behavior and/or evaluate equilibrium or dynamical properties of interest

MD - achievable time scales

With fast empirical potential (e.g., embedded atom method)

nanoseconds

1000 atoms for a few weeks = 1 microsecond

Work generally scales linearly with system size

With first-principles forces (e.g., density functional theory)

few ps

MD - achievable length scales

10^3 - 10^4 atoms easy on single processor

Much larger systems possible via parallelization

Each processor responsible for atoms in a physical cell
Communication required between adjacent cells
>~10^4 atoms per processor to maintain good efficiency

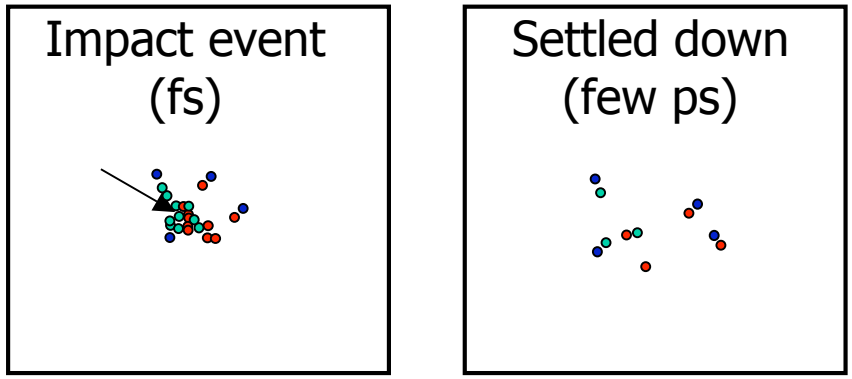
Million atoms -- now fairly routine

Billion atoms -- possible

MD Cascade Simulations

Knock-on event cascade simulations are ideally suited to MD

- good match to MD time scale
  - primary stage of damage reached after a few ps
- MD gives full atomistic detail
- extremely accurate description* if potential is accurate



MD simulation of 25 keV impact in Cu

D.J. Bacon et al

Strengths of MD

- Relatively easy to implement
- Exact dynamics for the chosen interatomic potential (no assumptions of on-lattice behavior, known mechanisms, or thermal behavior)
- Very accurate compared to experiment, if potential is accurate, after the thermal spike stage (> ~1 ps)
- Can probe behavior that is unavailable from experiment
- Some properties are relatively insensitive to the material, and hence are insensitive to errors in potential. For these properties, MD can provide meaningful, general results even with a cheap potential.

Limitations of MD

- Time scale - currently limited to nanoseconds
- Only as good as interatomic potential
- Thermal transport not properly treated for metallic systems
    - Phonon transport included
    - Electron-phonon coupling omitted
- Electronic stopping not directly treated

Some future directions for MD

- With a committed parallel resources, could take a cascade in a full 1M-atom system out to ~1 □s (couple months, 1000 processors)
  - "exact" dynamics (after thermal spike)
  - evolution will probably show unexpected behavior
  - could compare with KMC model prediction for same time

- Very-large-scale MD (10^9 atoms?) could probe interactions of multiple subcascades

- Better theory needed for treating electronic heat transport during thermal spike stage

Reaching longer time scales

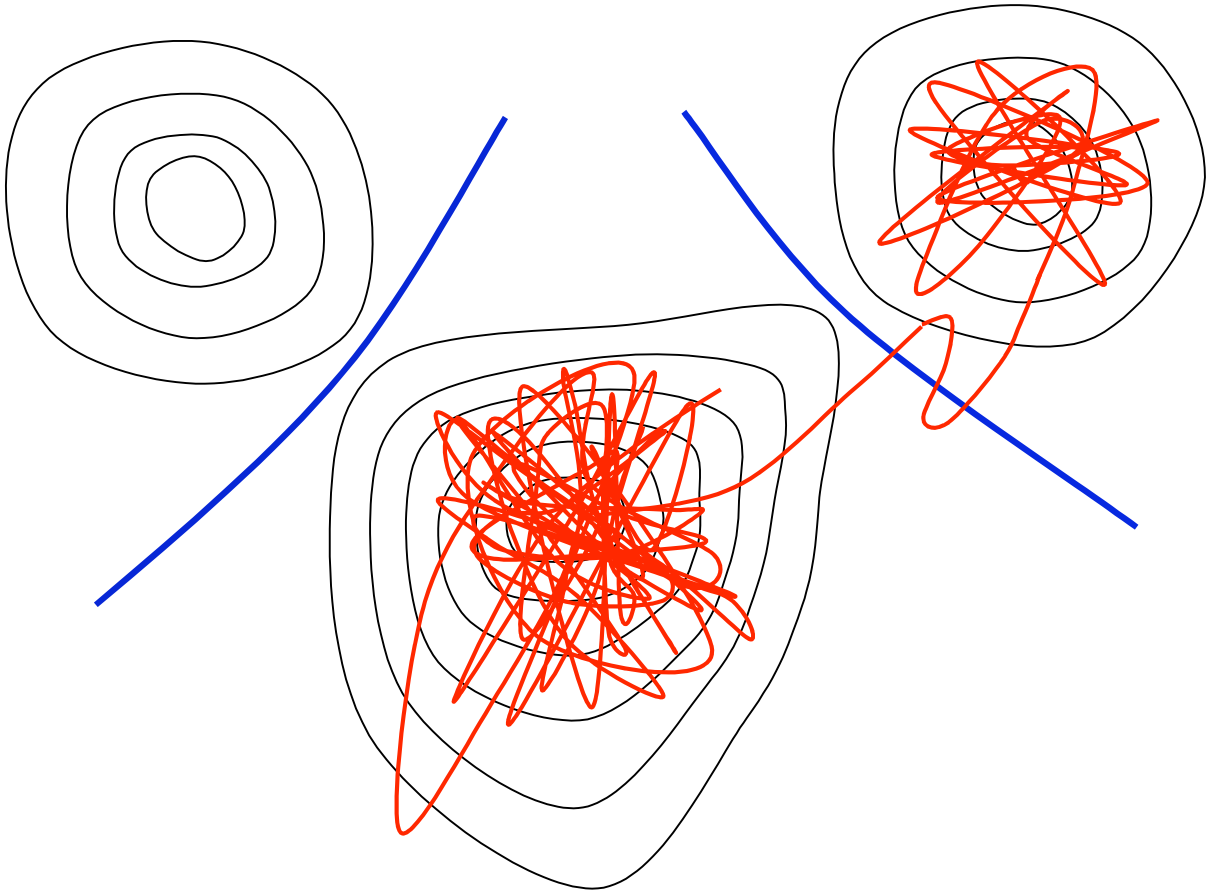
MD is limited to nanoseconds (may *never* reach 1 millisecond)

Many events of interest take place on much longer time scales:

- Diffusion/annihilation/coalescence of interstitials and vacancies formed in cascade
- Formation of dislocation loops, voids, bubbles, etc.
- Diffusive communication between nearby subcascades
- Stress-driven microstructural evolution
- …

These are all activated processes.

Infrequent Event System



The system vibrates in 3-N dimensional basin many times before finding an escape path. The trajectory finds an appropriate way out (i.e., proportional to the rate constant) without knowing about any of the escape paths except the one it first sees. Can we exploit this?

Accelerated dynamics concept

Let the trajectory, which is smarter than we are, find an appropriate way out of each state, The key is to coax it into doing so more quickly, using sound statistical mechanical concepts.

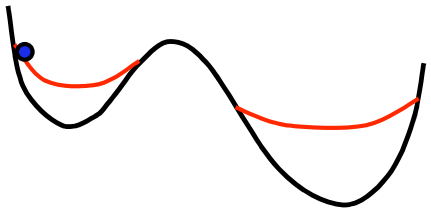
With these accelerated dynamics methods, we can follow a system from state to state, reaching time scales that we may never be able to reach with molecular dynamics.

Often, even just one of these long trajectories can reveal key system behavior. If desired, we can go back through the trajectory to determine rates and properties in more detail, using conventional methods, and/or we can run more long trajectories to gather statistics.

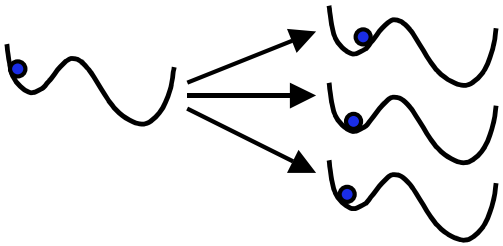
Using these methods, almost every system we have studied has behaved in a way that surprised us.

Accelerated Molecular Dynamics Methods

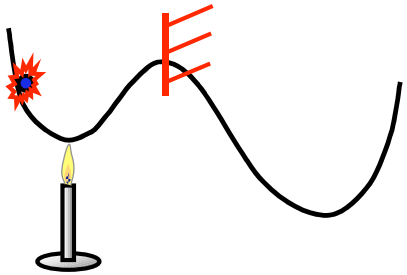
Hyperdynamics (1997)



Parallel Replica Dynamics (1998)



Temperature Accelerated Dynamics (2000)



Review: Voter, Montalenti, and Germann, Ann. Rev. Mater. Res. 32, 321 (2002)

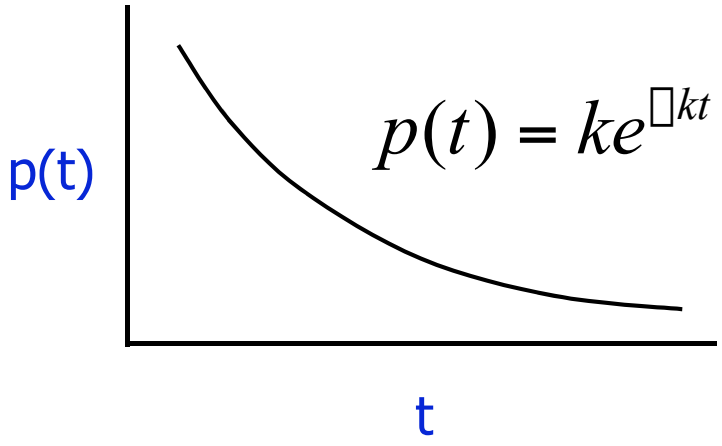
Parallel Replica Dynamics

Parallelizes time evolution

Assumptions:

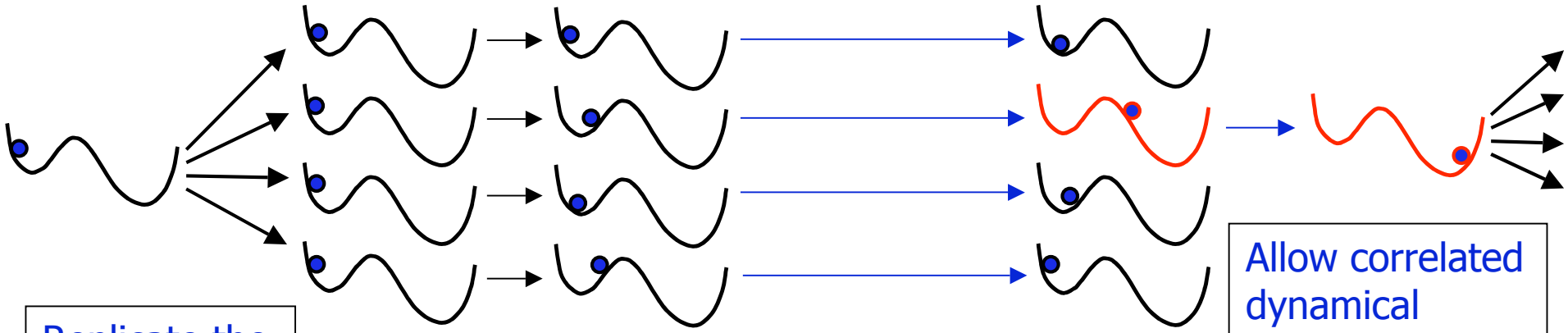
- infrequent events

- exponential distribution of first-escape times



AFV, Phys. Rev. B, 57, R13985 (1998)

Parallel Replica Dynamics Procedure



Replicate the system on M processors

Independently thermalize each of the systems.

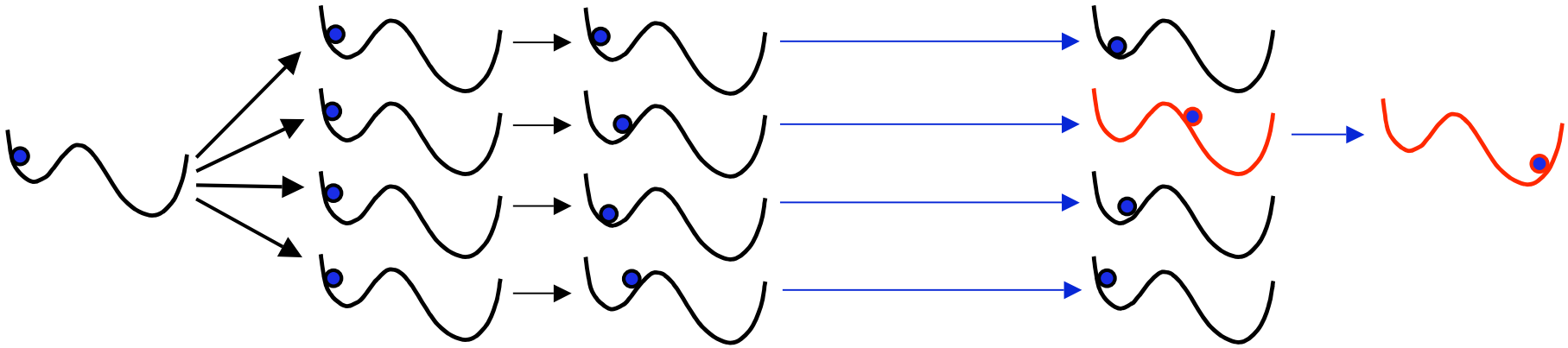
Run MD on all systems until transition occurs one some processor.

Sum up the MD times.

Allow correlated dynamical events.

Then start all over again from the new state.

Parallel Replica Dynamics



The summed time (t_{sum}) obeys the correct exponential distribution, and the system escapes to an appropriate state.

State-to-state dynamics are thus correct; τ_{corr} stage even releases the TST assumption [AFV, Phys. Rev. B, 57, R13985 (1998)].

Good parallel efficiency if $\tau_{rxn} / M >> \tau_{dephase} + \tau_{corr}$

Applicable to any system with exponential first-event statistics

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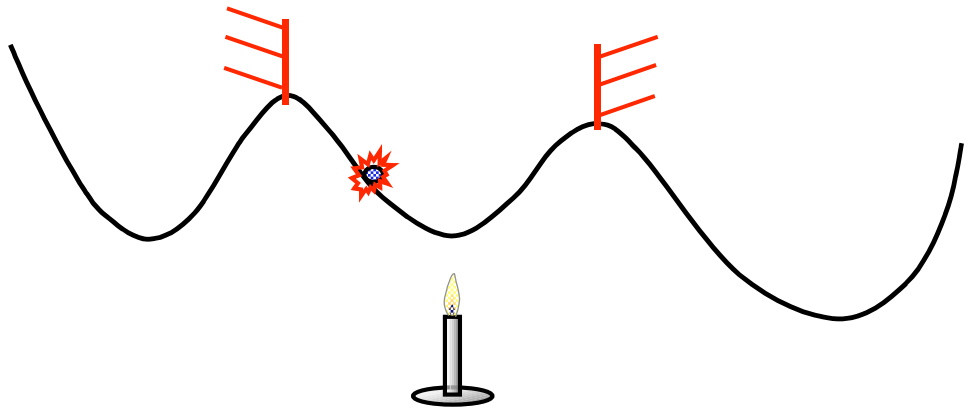
Temperature Accelerated Dynamics (TAD)



Concept:

Raise temperature of system to make events occur more frequently.
Intercept each attempted escape and extrapolate time to low T.

After a few attempted events, we know with desired confidence which one would have occurred first at low temperature -- accept that event.

Correct dynamics within following assumptions:

- infrequent-event system
- transition state theory (no correlated events)
- harmonic transition state theory (gives Arrhenius behavior)

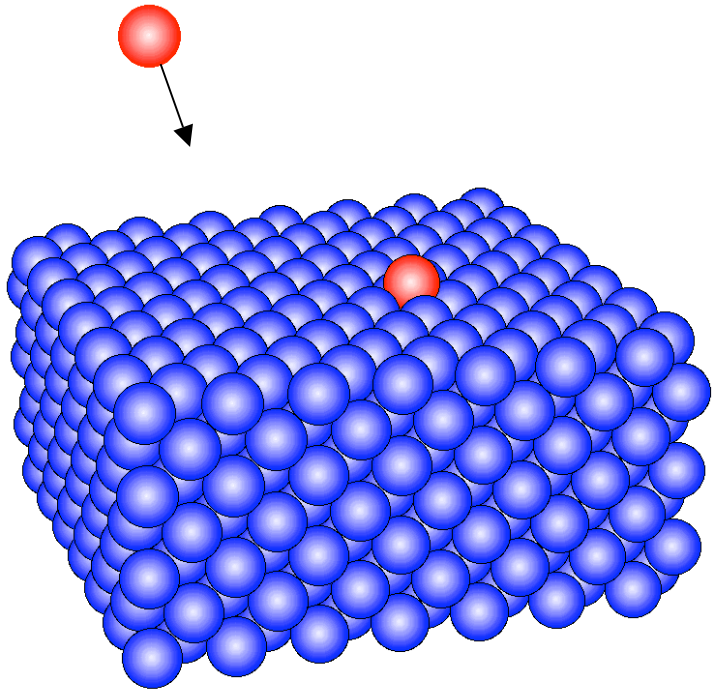
$$k = \nu_0 \exp[-\Delta E/k_B T]$$

- all preexponentials (ν_0) are greater than ν_{min}

[Sørensen and Voter, J. Chem. Phys. 112, 9599 (2000)]

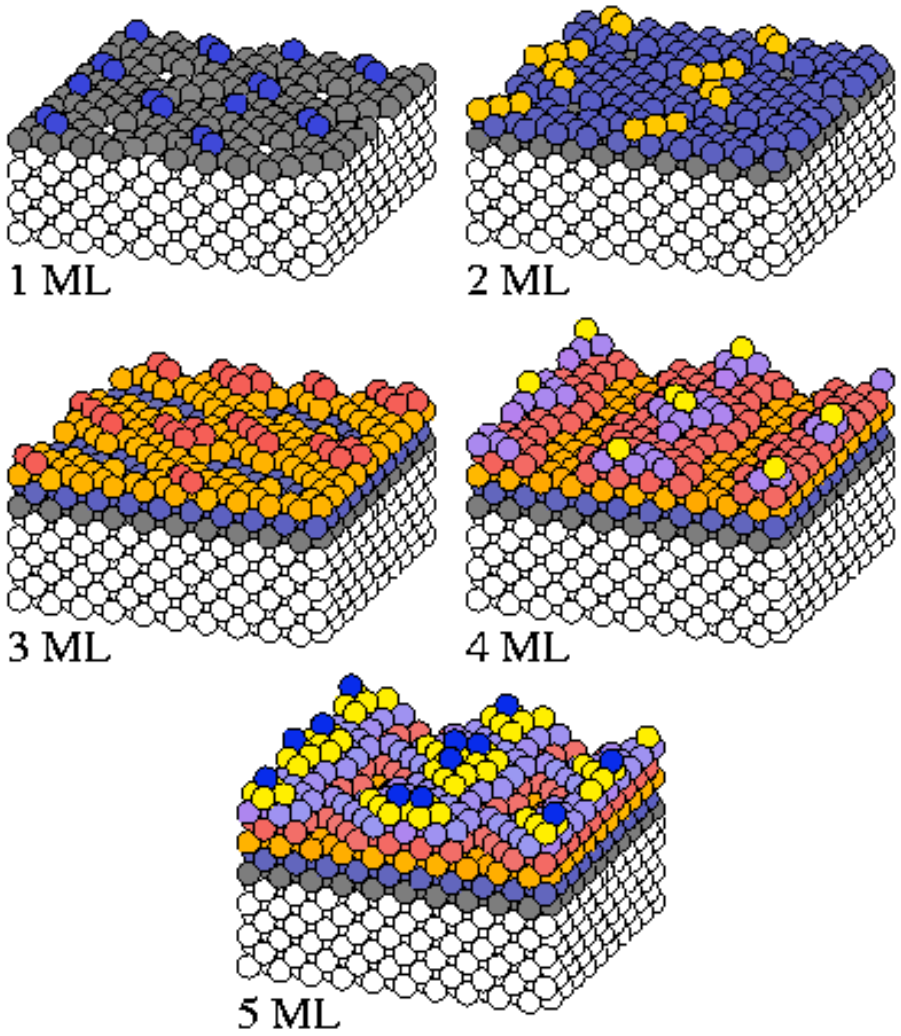
MD+TAD metal deposition simulation

- MD for each deposition event (2 ps)
- TAD for diffusive events in intervening time until next deposition (~1 s)
- Embedded atom method (EAM) for fcc metals (e.g., Cu, Ag, …; LANL fit)



MD+TAD deposition of Cu/Cu(100)

T=77K, flux= 0.04 ML/s, matching deposition conditions of Egelhoff and Jacob (1989).



boost factor ~10^7

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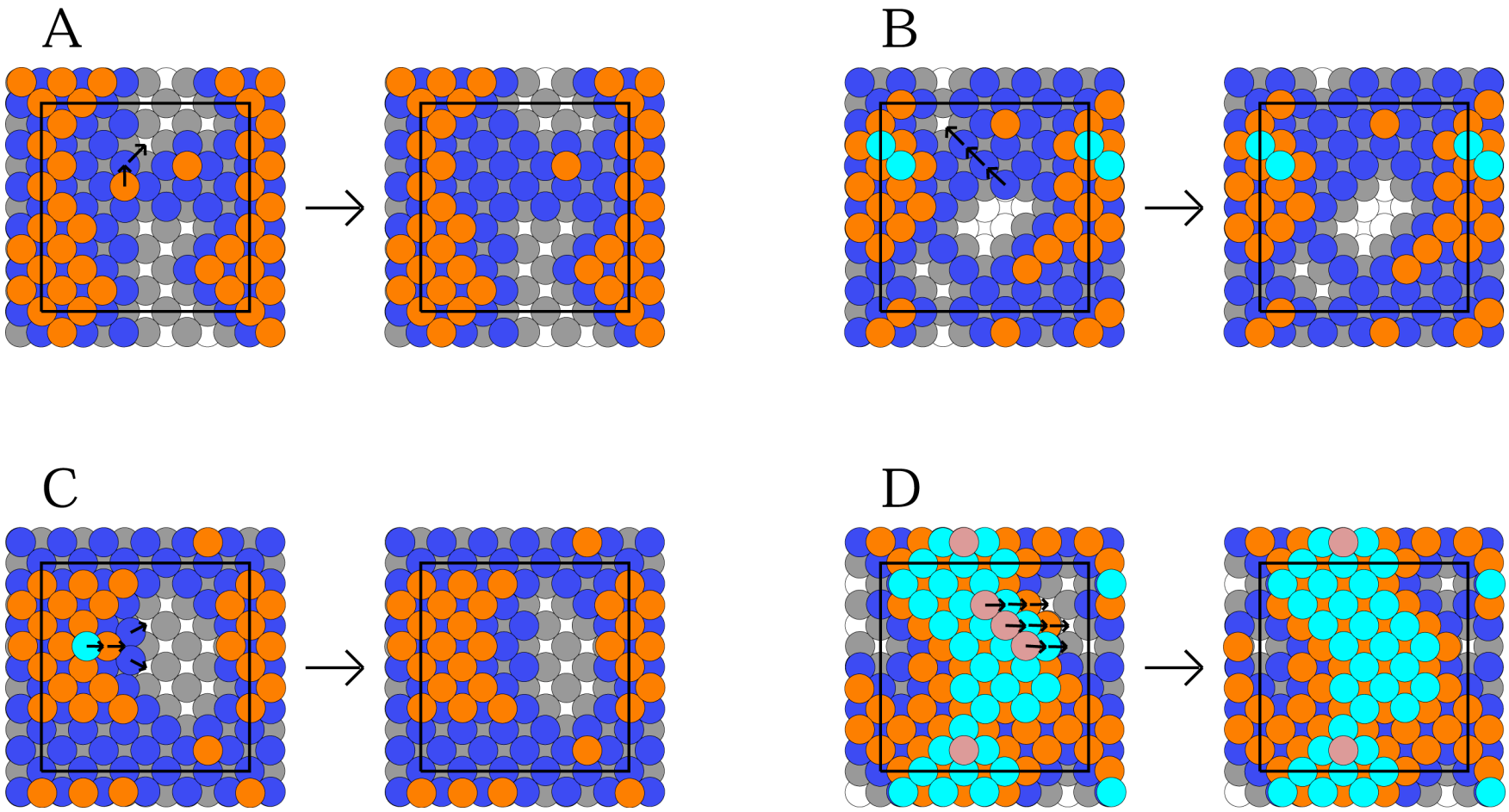
MD+TAD deposition of Cu/Cu(100)

Concerted events observed at T=77K and T=100K:



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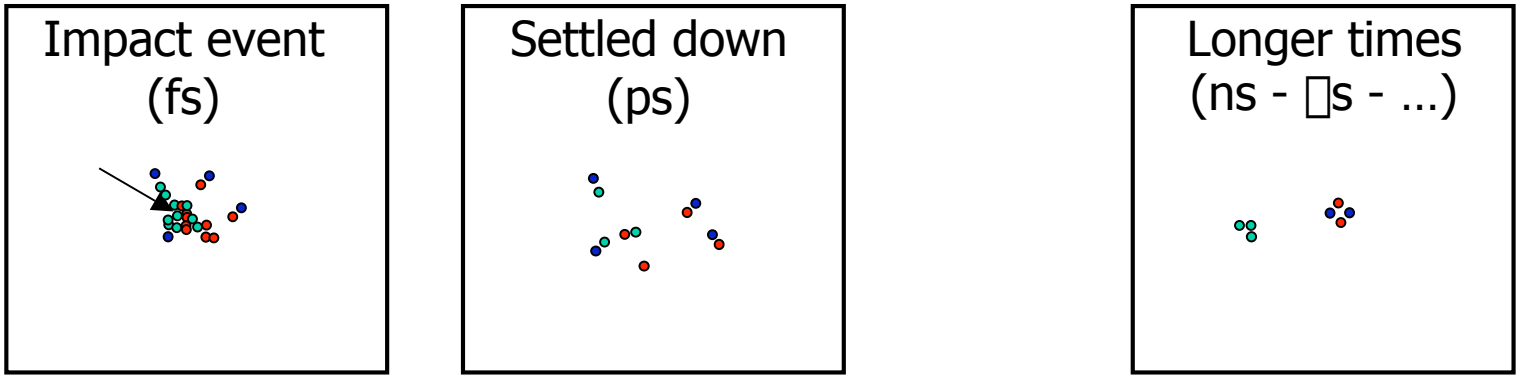
MgO Radiation Damage Annealing



Molecular dynamics (MD) to simulate knock-on event and cascade. System settles down (becomes thermal) in a few ps.

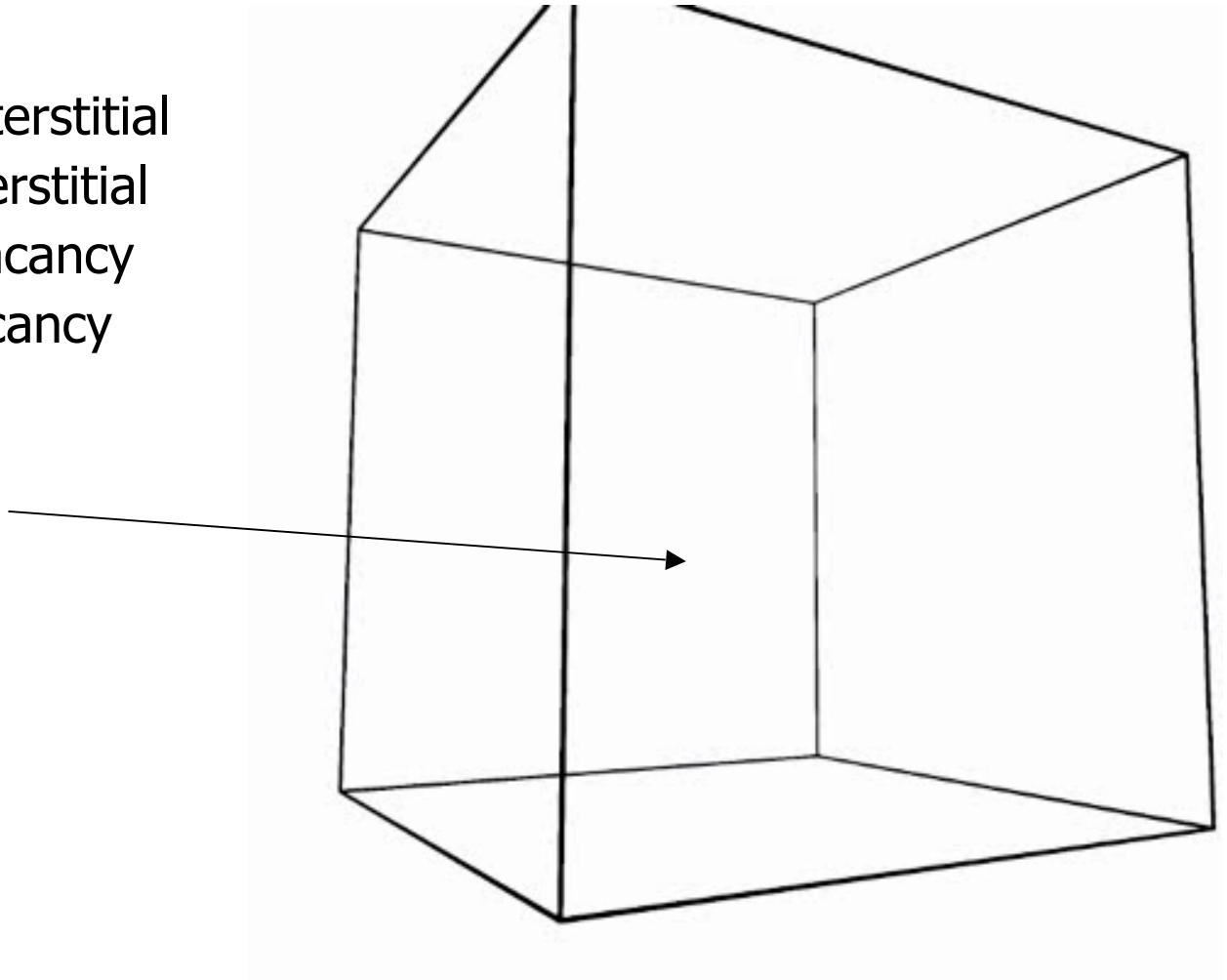
Temperature accelerated dynamics to follow diffusive events from then on: ns, □s, ms,...

- diffusion of interstitials
- formation of interstitial dimers (e.g., Mg-O)
- diffusion of dimers to form larger clusters ...

Uberuaga, Smith, Cleave, Montalenti, Henkelman, Grimes, Voter, and Sickafus, Phys. Rev. Lett., in press (2004)

MD simulation of 400 eV impact in MgO

- Color Scheme
  - Dark blue: Mg interstitial
  - Dark red: O interstitial
  - Light blue: Mg vacancy
  - Light red: O vacancy
- O PKA at 0.4 keV
- Peak damage at 80 fs
- I_2 formation at 6.5 ps



MgO defect dynamics after 400 eV cascade

Defects are charged (with this Buckingham potential)

Vacancies are immobile

Interstitials diffuse on ns-□s time scale

Interstitials can annihilate with vacancy

Oppositely charged interstitials (O^{2-} + Mg^{2+}) join to form dimer

Dimers diffuse on s time scale

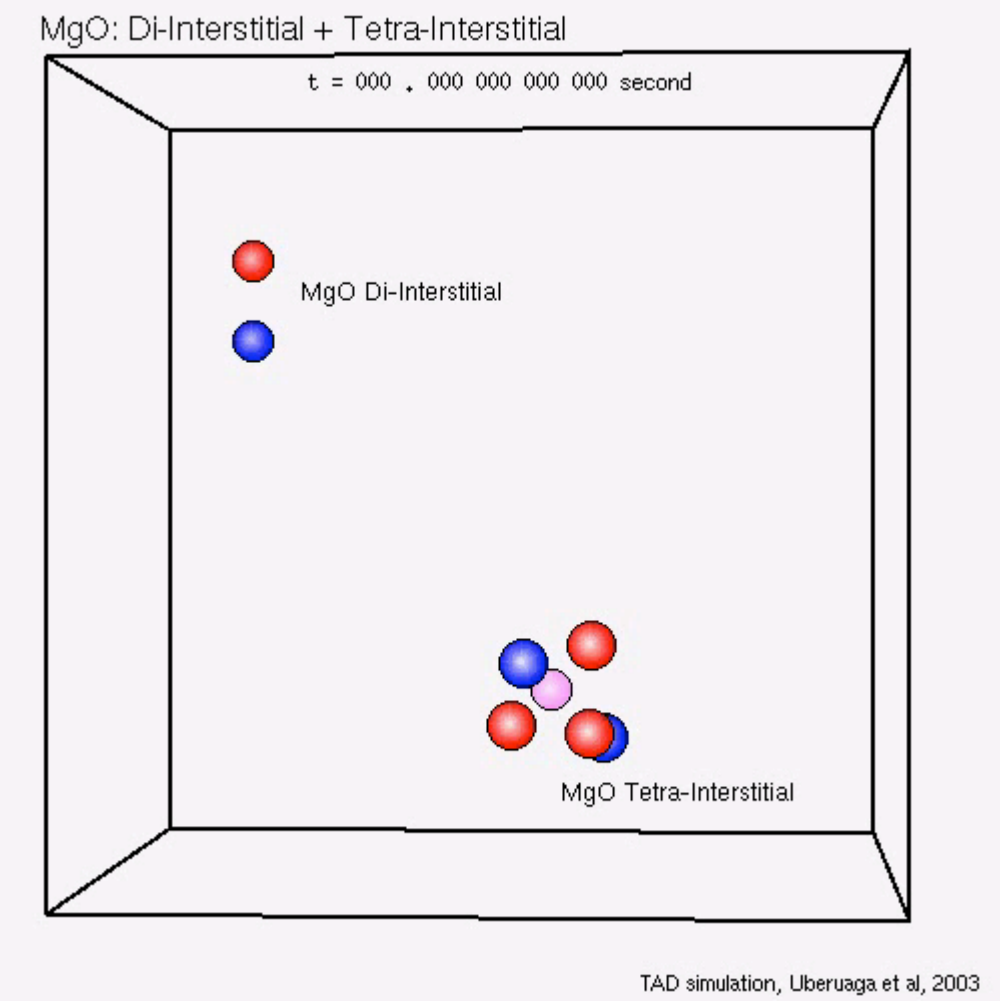
Dimers can encounter other interstitials and dimers to form larger clusters

Interstitial tetramer is stable and immobile.

Is the tetramer a sink for growth of all larger clusters? No!

TAD Simulation: Interstitial dimer joining interstitial tetramer

- dimer + tetramer forms hexamer in metastable state
- Metastable hexamer exhibits fast one-dimensional diffusion!
  - ns timescale
  - diffusion is 1D along <110>
  - decay to ground state takes years



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Dimer method

[Henkelman and Jonsson, J. Chem. Phys. 111, 7010 (1999).]

Optimize rotation angle of a vector between a pair of 3N-dimensional configurations, giving lowest eigenvector of Hessian using only first derivatives (AFV, 1997; H&J 1999).

Follow eigenvector direction uphill while minimizing along all other directions (H&J, 1999, Munro and Wales, 1999) - I.e., mode-following.

Result: Very efficient first-derivative-only saddle search method.

Dimer-based on-the-fly kinetic Monte Carlo

[G. Henkelman and H. Jonsson J. Chem. Phys. 115, 9657 (2001)]

Procedure:

Initiate a number of dimer searches from random positions within current potential basin to find saddles and escape pathways.

Calculate activation energy and prefactor for each pathway.

Assume that most or all relevant low-lying saddles have been found.

Use rates for this set of pathways to take an "on-the-fly" KMC step.

Repeat from new basin.

Off-lattice configurations allowed, concerted mechanisms allowed

More expensive, but much more accurate, than conventional kinetic Monte Carlo

Faster, but less accurate, than TAD, since pathways can be missed

Issues for future

- Boost limited by lowest barrier - general problem for many realistic systems (e.g., interstitials in metals)
- Currently limited to small systems
  - Trying to achieve N scaling
  - Spatial parallelization
- Gaining more experience in effective use of these long-time-scale methods

Summary

- Molecular dynamics (MD)
  - direct, powerful probe giving full atomistic detail
  - limited to ns
- Accelerated dynamics concept:
  - Let the trajectory find an appropriate way out or state, but coax it into doing so more quickly
- Parallel-replica dynamics
  - Very general; exact for infrequent events
  - boost = ~ number of processors
- Temperature accelerated dynamics (TAD)
  - more approximate, larger boost factor (when $\Delta E >> T_{low}$)
  - boost factor can reach millions in favorable cases
  - possibility for fast N-scaling method if minimum barrier supplied externally (e.g., from dimer searches)
- Dimer-based On-the-fly kinetic Monte Carlo
  - Search for saddles bounding a state
  - No lattice assumption, no presumed mechanisms
  - Faster than TAD, but more approximate
  - Much slower than conventional kMC, but much more accurate