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Form 836 (7/06)

Accelerated Molecular Dynamics Methods

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A significant problem in the atomistic simulation of materials, as well as in other areas of chemistry and physics where atomistic simulations are used, is that molecular dynamics simulations are limited to nanoseconds, while important reactions and diffusive events often occur on time scales of microseconds and longer. Although rate constants for these infrequent events can be computed directly using transition state theory (with dynamical corrections, if desired, to give exact rates), this requires first knowing the transition state. Often, however, we cannot even guess what events will occur. For example, in vapor-deposited metallic surface growth, surprisingly complicated exchange events are pervasive. In this talk, I will discuss the accelerated molecular dynamics approach, which we have been developing over the last decade, for treating these complex infrequent-event systems. The idea is to directly accelerate the dynamics to achieve longer times without prior knowledge of the available reaction paths. In some cases, we can achieve time scales with these methods that are many orders of magnitude
beyond what is accessible to molecular dynamics. I will give an introduction to the three main methods in this class, hyperdynamics, parallel-replica dynamics and temperature accelerated dynamics, and discuss their relative merits. I will present some illustrative and recent applications to materials

Accelerated Molecular Dynamics Methods

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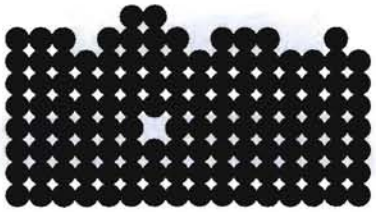
The challenge



We have some material system (e.g., adatoms on a surface).

We know that if we wait long enough, something will happen. And then something else, and then something else,...

Using molecular dynamics, we can run about 1 microsecond -- might not even see first event.

How do we accurately predict the long-time evolution?

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How to get to long times: Kinetic Monte Carlo approach

If we know the relevant reaction pathways, we can use transition state theory to compute rates.

$$k_{A\to B}^{HTST} = \upsilon_0 e^{-\Delta E/k_B T}$$

These rates can be fed into a kinetic Monte Carlo (KMC) simulation.

KMC is now a widely used and powerful tool.

However, if we are seeking high accuracy, KMC has the problem that there may be important reaction pathways that we don't know about.

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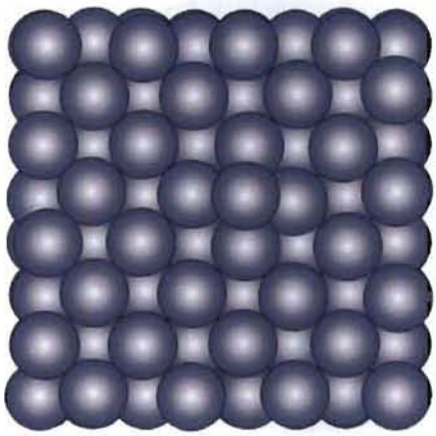
Cu/Cu(100) hop event, T=300K



4 ps shown during transition event.
Rate at T=300K = once per 25 microseconds.

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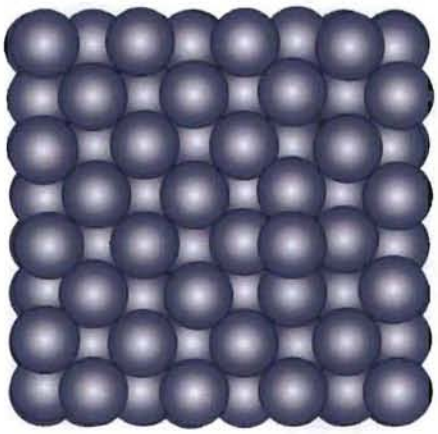
Cu/Cu(100) exchange event, T=300K



First seen by Feibelman, 1990.

4 ps shown during transition event.
Rate at T=300K = once per 14 seconds.
For Pt/Pt(100), exchange barrier is ~0.5 eV *lower* than hop barrier.

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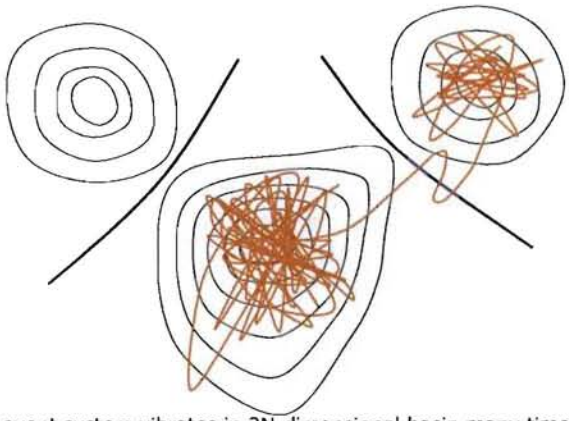
Accelerated Molecular Dynamics



An infrequent-event system vibrates in 3N-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. *In the AMD methods, we exploit this property, letting the trajectory find an appropriate escape path, but we carefully trick it into doing this more quickly.*

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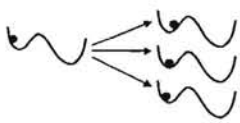
Accelerated Molecular Dynamics Methods

Hyperdynamics

- Design bias potential that fills basins.
- MD on biased surface evolves correctly from state to state.
- Accelerated time is statistical quantity.

(AFV, J. Chem. Phys., 1997)

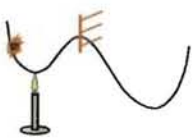
Parallel Replica Dynamics



- Parallelizes time.
- Very general -- any exponential process.
- Gives exact dynamics if careful.
- Boost requires multiple processors

(AFV, Phys. Rev. B, 1998)

Temperature Accelerated Dynamics



- Raise temperature of MD in this basin.
- Intercept and block every attempted escape.
- Accept event that would have occurred first at the low temperature.
- More approximate; good boost.

(M.R. Sorensen and AFV, J. Chem. Phys., 2000)

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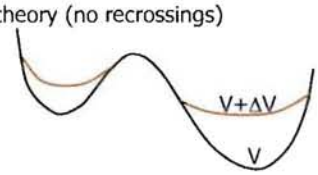
Hyperdynamics

Builds on umbrella-sampling (Valleau 1970's); takes it into time domain.

Assumptions:

- infrequent events
- transition state theory (no recrossings)



Procedure:

- design bias potential ΔV (zero at dividing surfaces; causes no recrossings)
- run thermostatted trajectory on the biased surface ($V+\Delta V$)
- accumulate hypertime as

$$t_{hyper} = \Sigma \Delta t_{MD} \exp[\Delta V(R(t))/k_B T]$$

Result:

- state-to-state sequence correct (because *relative* rates are preserved)
- time converges on correct value in long-time limit (vanishing relative error)

AFV, J. Chem. Phys. 106, 4665 (1997)

Hyperdynamics - characteristics

Designing valid and effective bias potential is the key challenge.

Bias potential can be a function of

- the shape of the energy surface (AFV, 1997)
- the energy (Steiner, Genilloud and Wilkins, 1998)
- the geometry (e.g., bond lengths, Miron and Fichthorn, 2003, 2005)

Must be careful that bias is zero on all dividing surfaces or dynamics will be wrong.

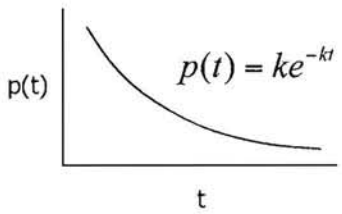
When barriers are high relative to T, boost can be orders of magnitude.

See Michael Falk's talk, next.

Parallel Replica Dynamics

Parallelizes time evolution

Assumptions:
- infrequent events
- exponential distribution of first-escape times



Must know:
- how to detect transitions
- correlation time

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

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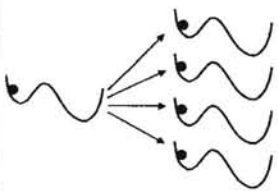
Parallel Replica Dynamics Procedure

Replicate entire system on each of M processors.



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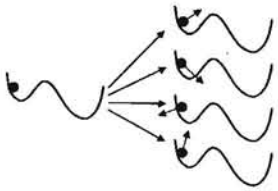
Parallel Replica Dynamics Procedure

Randomize momenta independently on each processor.



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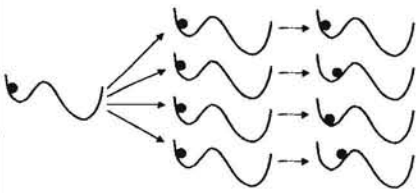
Parallel Replica Dynamics Procedure

Run MD for short time ($\tau_{dephase}$) to dephase the replicas.



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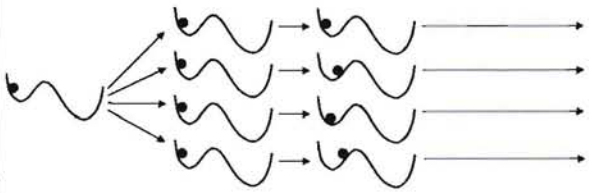
Parallel Replica Dynamics Procedure

Start clock and run thermostatted MD on each processor.
Watch for transition...



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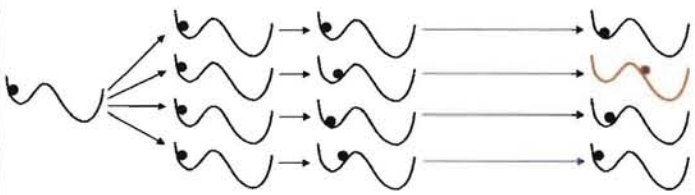
Parallel Replica Dynamics Procedure

Stop all trajectories when first transition occurs on *any* processor.



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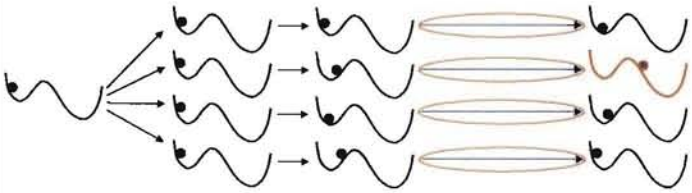
Parallel Replica Dynamics Procedure

Sum the trajectory times over all M processors. Advance simulation clock by this t_{sum}



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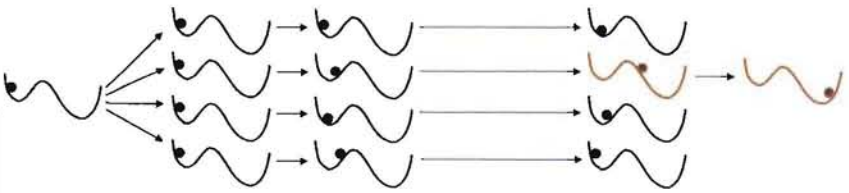
Parallel Replica Dynamics Procedure

On the processor where a transition occurred, continue trajectory for a time τ_{corr} to allow correlated dynamical events.



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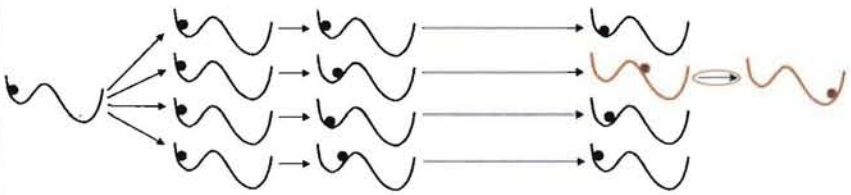
Parallel Replica Dynamics Procedure

Advance simulation clock by τ_{corr}.



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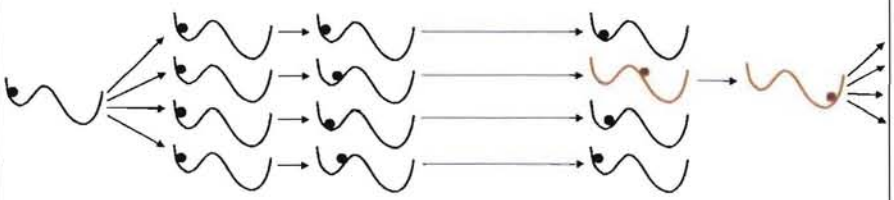
Parallel Replica Dynamics Procedure

Replicate the new state and begin procedure again.



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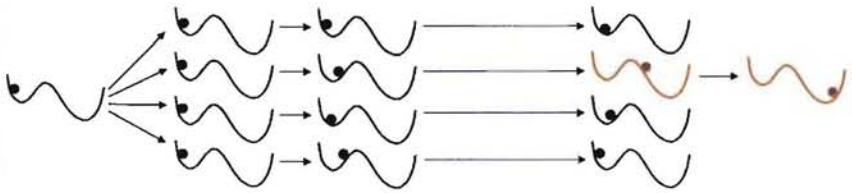
Parallel Replica Dynamics



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 $\tau_{rxn} / M >> \tau_{dephase}+\tau_{corr}$.

Good match to increasing emphasis on multicore and massively parallel architectures.

Applicable to any system with exponential first-event statistics.

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Temperature Accelerated Dynamics (TAD)

Assumptions:

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

$$k^{HTST} = \nu_0 \exp[-\Delta E/k_B T]$$

- all preexponentials (ν_0) are greater than ν_{min} (e.g., 10^{11} s^{-1})

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

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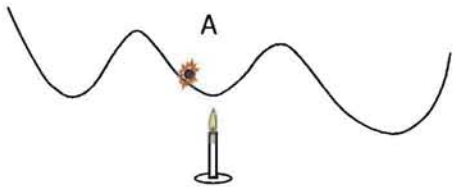
TAD Procedure

- Run MD at elevated temperature (T_{high}) in state A.
- Intercept each attempted escape from basin A
  - find saddle point (and hence barrier height)
    (e.g., using nudged elastic band method of Jonsson et al).
  - extrapolate to predict event time at T_{low}.
- Reflect system back into basin A and continue.
- When safe, accept transition with shortest time at T_{low}.
- Go to new state and repeat.



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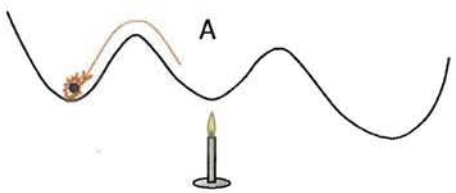

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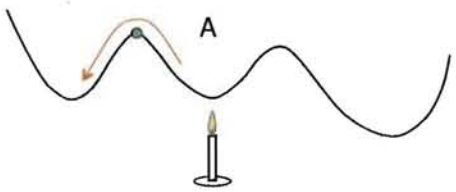

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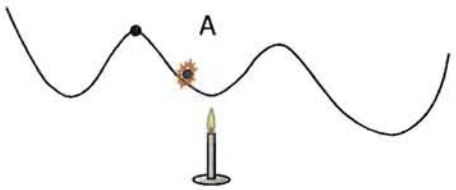

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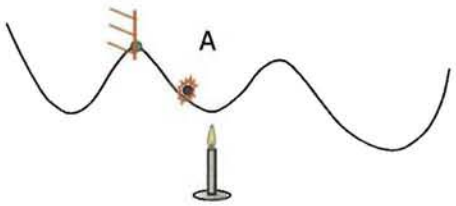

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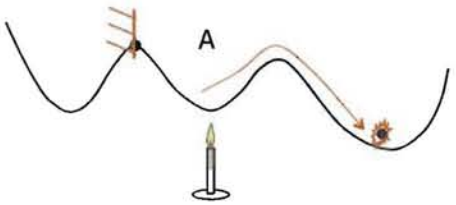

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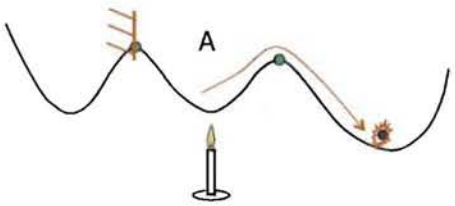

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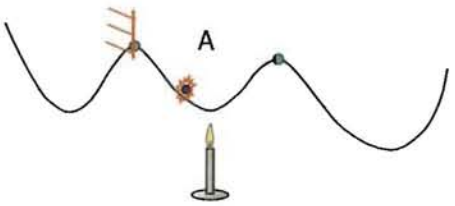

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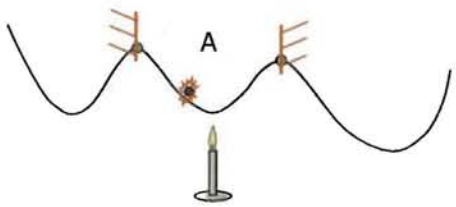

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TAD - Characteristics

Most approximate of the three methods, but requires only one processor and no bias potential.

As for hyperdynamics, TAD gives large boost for large barriers.

Required saddle search can sometimes cause problems.

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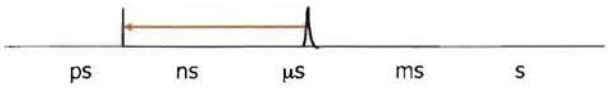
AMD characteristics/challenges

All three methods can give very large boost factors when events are very infrequent.

Basically, the MD time to next event (+overhead) is collapsed to ~ps time scale.



Similarly, low barriers mean low boost.

Systems with persistent low barriers are our biggest ongoing challenge (e.g., soft-matter systems!).

In principle, electronic structure forces can be used, but they are still pretty expensive (e.g., if we cannot reach ~10 ps, we cannot see any events).

Larger systems are also harder, although we are making progress [ParTAD (Shim, et. al. 2007), TAD-KMC (Chatterjee and Voter, 2010), local hyperdynamics (Kim, Perez, AFV, 2010).

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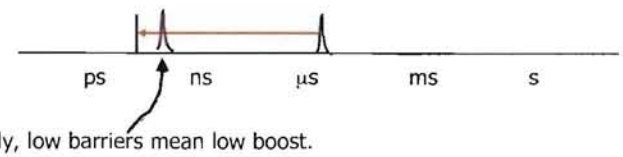

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Uses for AMD

- Learn about behavior of system to build higher-level model(s)

- Run benchmark for testing higher-level model(s)

- Directly study long-time behavior

Often, when we run a system out to long time, it behaves in a way that surprises us.

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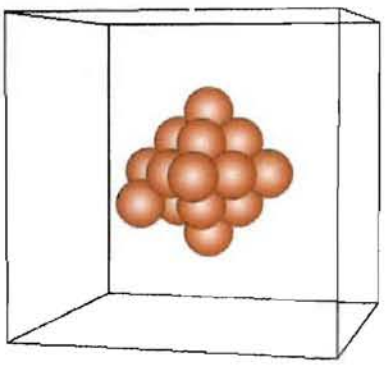
Long time annealing of 20 vacancy void in Cu

- EAM Copper
- Parallel-replica simulation of 20-vacancy void annealing at T=400 K
  - 20 vacancies is one too many for "perfect" void
- 79% efficiency on 39 processors
- At 1.69 μs, void transforms to SFT



Red atoms=vacancies
Blue atoms=interstitials
Bulk atoms not shown

Completely new transformation pathway for the formation of stacking fault tetrahdera (SFT)

Uberuaga, Hoagland, Voter, Valone, PRL **99**, 135501 (2007)

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ParRep of stretching Ag nanowire

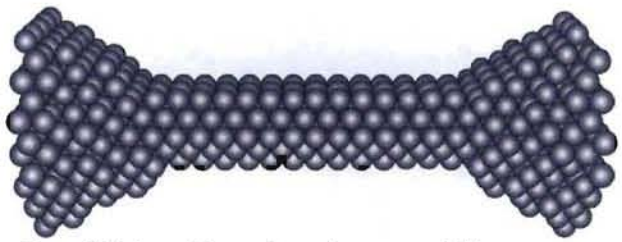
Run on LANL Roadrunner (1 PFLOPS if using all 12,240 cell processors)

Boost good at first; drops as events become more frequent.

Outer edge atoms clamped, advanced 0.01A at regular intervals

Preliminary results...

Ag[110] nanowire, 1.d5 A/s, 1 us per frame



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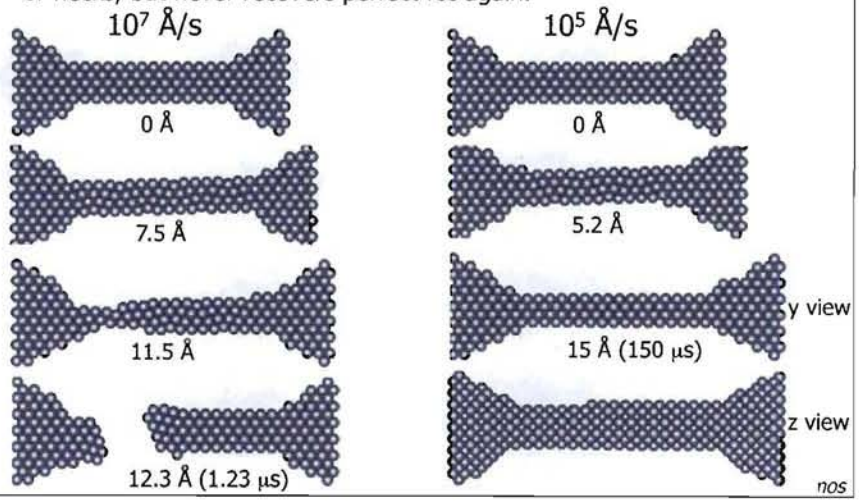
Pulling slower changes behavior

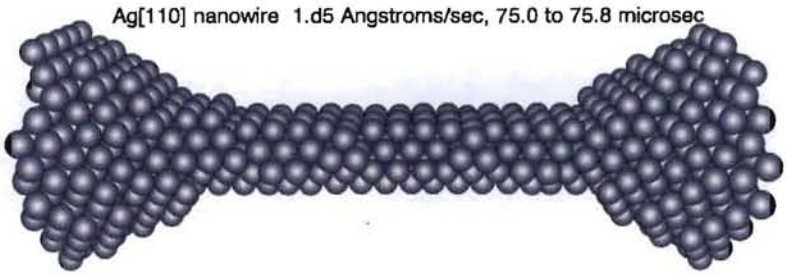
At stretching speeds below ~10^6 Å/s, the system can thin down to four layers, coming back to perfect fcc. At higher speeds, it disorders or necks, but never recovers perfect fcc again.



nos

Active surfaces

Surface diffusion is sometimes highly active – both adatoms and clusters.



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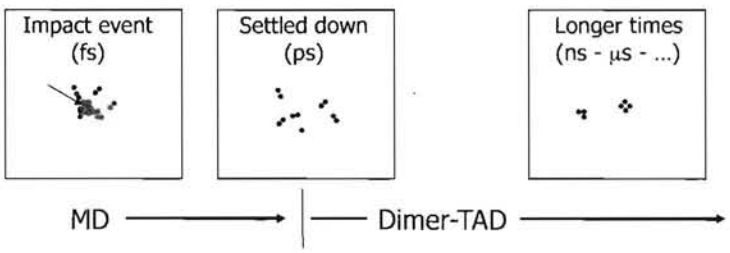
MgO Radiation Damage Annealing T=300K



Coulombic Buckingham potential

Interesting picture emerges for annealing after 400 eV cascade.

Uberuaga, Smith, Cleave, Montalenti, Henkelman, Grimes, Voter, and Sickafus, Phys. Rev. Lett., **92**, 115505 (2004); Phys. Rev. B **71**, 104102 (2005).

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Growth of interstitial clusters in MgO, T=300K

Typical 400 eV collision event forms a few vacancies and interstitials

Diffusing interstitials coalesce into clusters (vacancies are immobile)

Mono-interstitial - diffuses on ns-μs time scale

Di-interstitial - diffuses on s time scale

Tetra-interstitial - immobile (years)

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

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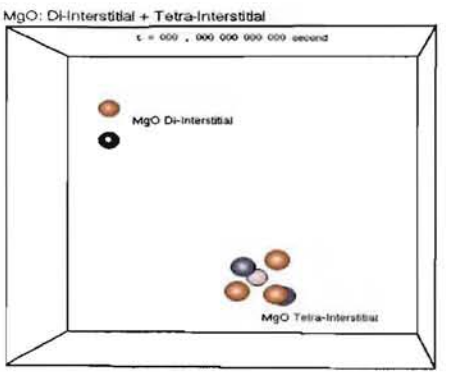
TAD Simulation: dimer + tetramer interstitial clusters

- In this case, 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



(perfect bulk atoms not shown,
red=O--, blue=Mg++)

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Summary

- Accelerated molecular dynamics concept:
  - Let the trajectory find an appropriate way out or state, but coax it into doing so sooner
- Significant speedup over standard MD when barriers are high relative to temperature
- All three methods can give very large boosts when events are very infrequent
- Often encounter unexpected behavior
- Recent advances
  - Self-learning bond boost hyperdynamics
  - Par-Rep on cell architecture
  - Spatial parallelization (TAD, but could do all three)
  - Solid-liquid interface (parallel-replica dynamics, hyperdynamics)
  - P-TAD and TAD-KMC (attaches TAD confidence to KMC)
- Ongoing challenges
  - Low barriers (but see Miron and Fichthorn bond bridging)
  - Detecting and exploiting Markovian state groupings on the fly
  - First-principles forces

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