Accelerated Dynamics Methods for Infrequent Events

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U.S. Department of Energy
Theory Focus Session on Hydrogen Storage Materials
Crystal City, VA
May 18, 2006

Acknowledgments

Blas P. Uberuaga (LANL, MST-8)
Francesco Montalenti (U. Milano-Bicocca)
Graeme Henkelman (U. Texas at Austin)
Timothy C. Germann (LANL, X-7)
James A. Sprague (NRL)
Mads Sørensen (Novo Nordisk A/S, Copenhagen)
Sriram Swaminarayan (LANL, MST-8)
Steve Stuart (Clemson)
David Sholl (Carnegie Mellon)
John Hamilton (Sandia)
Wolfgang Windl (Ohio State)
Roger Smith (U. Loughborough)
Robin Grimes (Imperial College)
Kurt Sickafus (LANL, MST-8)
Jacques Amar (U. Toledo)

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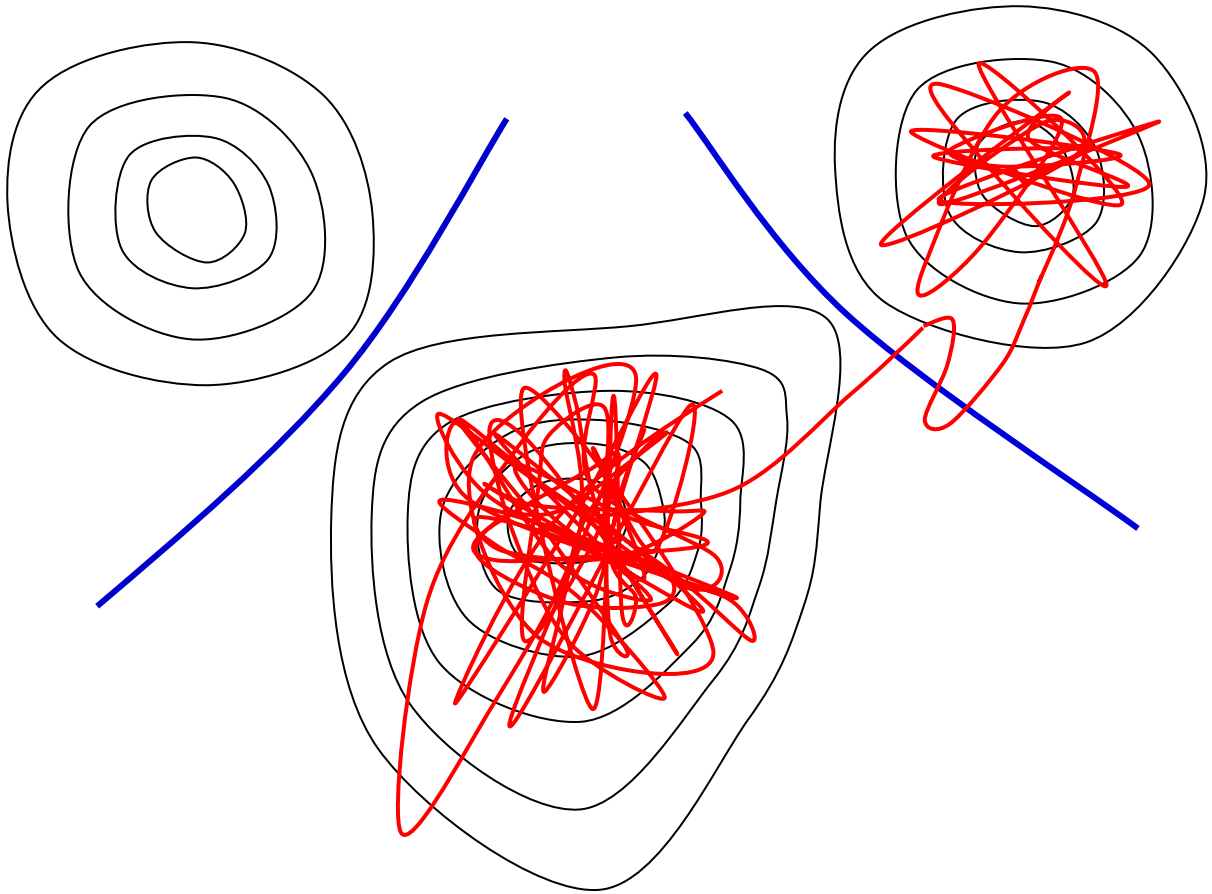
Outline

- The time scale problem
- Infrequent-event systems and the accelerated dynamics concept
- Transition state theory (TST)
- Hyperdynamics
- Parallel-replica dynamics
- Temperature accelerated dynamics (TAD)
- Including quantum effects
- Summary

Infrequent Event System



The 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. 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 statistical mechanical concepts (primarily transition state theory).

With these accelerated dynamics methods, we can follow a system from state to state, reaching time scales that we can't achieve with molecular dynamics.

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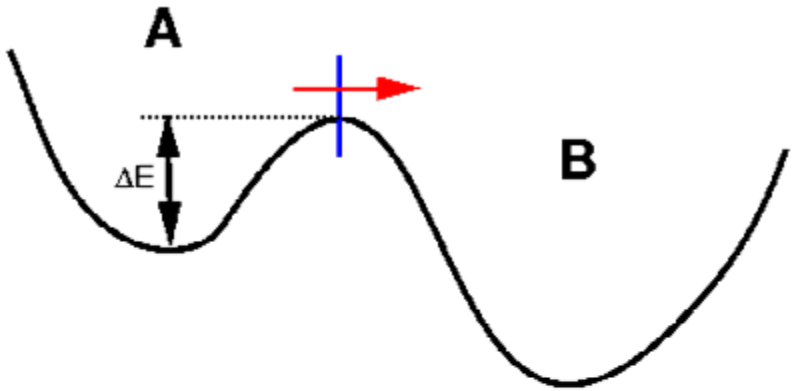
Often, even just one of these long trajectories can reveal key system behavior. If desired, we can go back through the trajectory to determine rates and properties in more detail, using conventional methods, and/or we can run more long trajectories to gather statistics.

Transition State Theory (TST)



Marcelin (1915)
Eyring, Wigner,…

TST escape rate = equilibrium flux through dividing surface at x=q

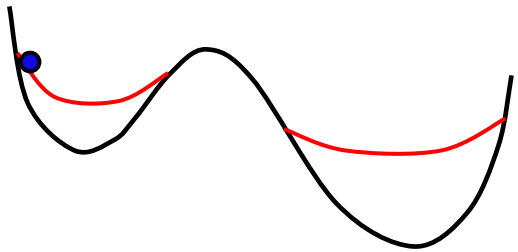
$$k_{A\to B}^{TST} = \langle \delta(x-q) \,|\, \dot{x} \rangle \quad \text{(exact flux)}$$

$$k_{A\to B}^{HTST} = \upsilon_0 e^{-\Delta E/k_B T} \quad \text{(harmonic approx.)}$$

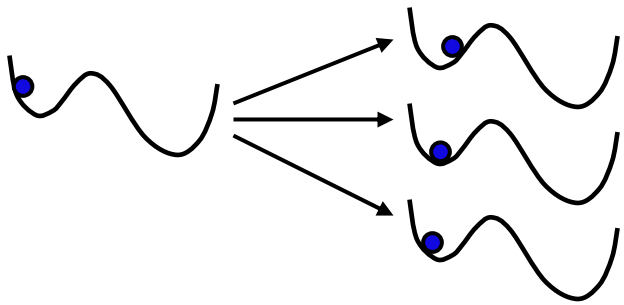
- classically exact rate if no recrossings or correlated events
- no dynamics required
- excellent approximation for materials diffusion
- traditional use of TST requires knowing dividing surface
- can also exploit TST formalism to develop methods that do not require knowing in advance where the dividing surface is

Accelerated Molecular Dynamics Methods

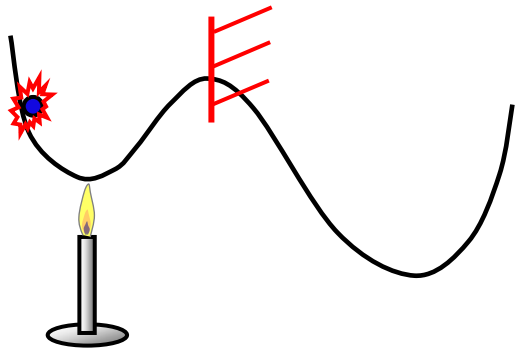
Hyperdynamics (1997)



Parallel Replica Dynamics (1998)



Temperature Accelerated Dynamics (2000)



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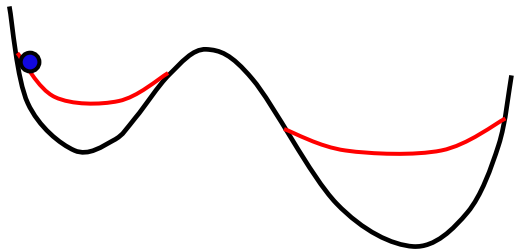

- Builds on umbrella-sampling techniques
- Design bias potential ΔV (zero at DS's)
- Run thermostatted trajectory on the biased surface ($V+\Delta V$)
- Accumulate hypertime as

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

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

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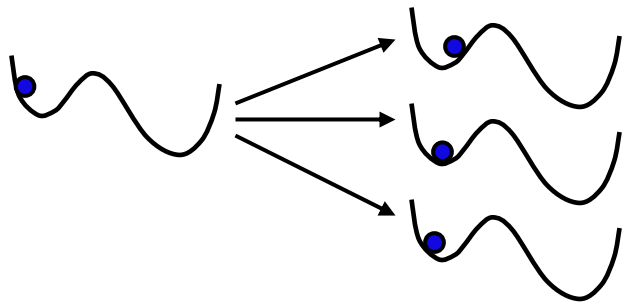

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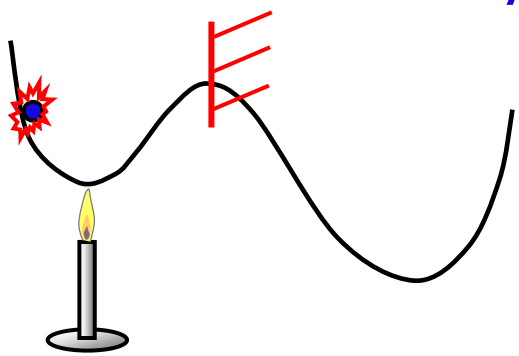


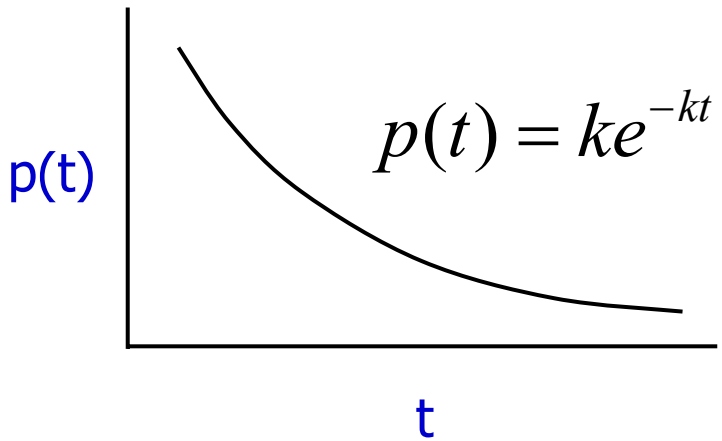
Parallel Replica Dynamics

Parallelizes time evolution

Assumptions:

- infrequent events

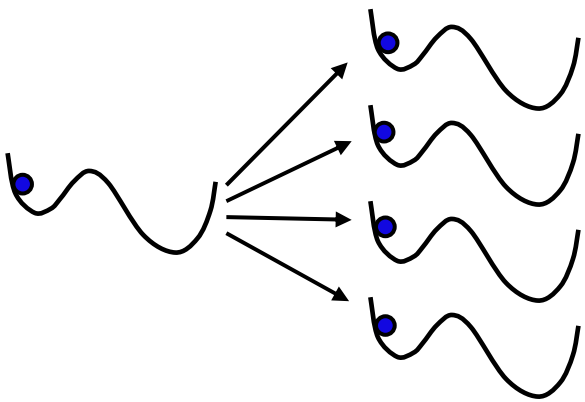
- exponential distribution of first-escape times



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

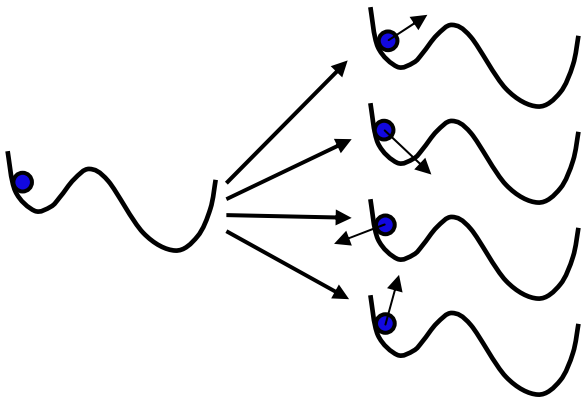
Parallel Replica Dynamics Procedure

Replicate entire system on each of M processors.



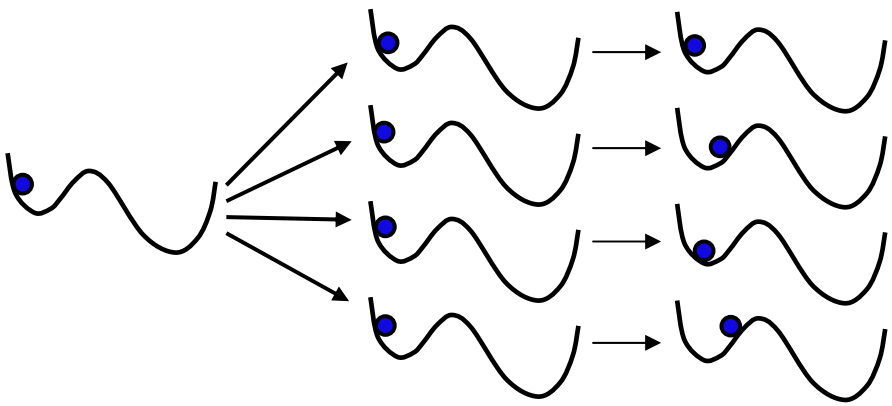
Parallel Replica Dynamics Procedure

Randomize momenta independently on each processor.



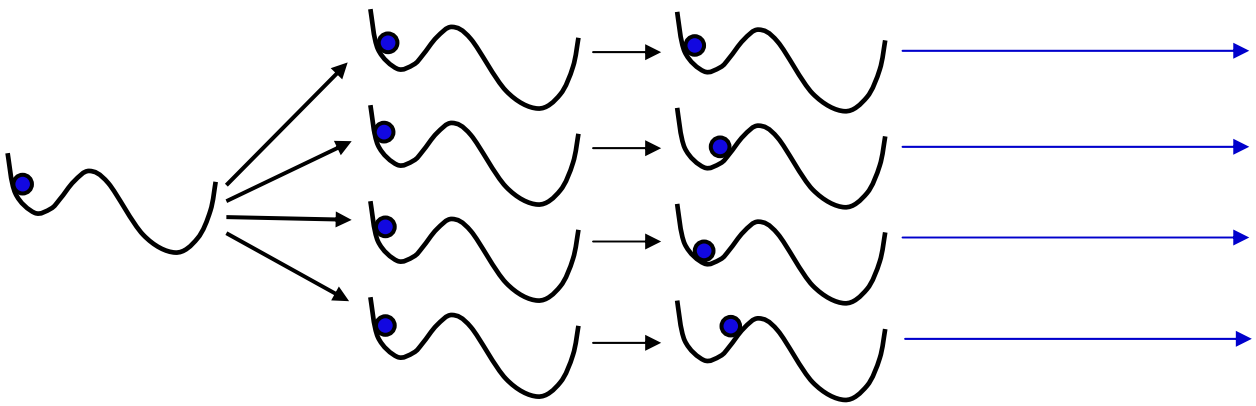
Parallel Replica Dynamics Procedure

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



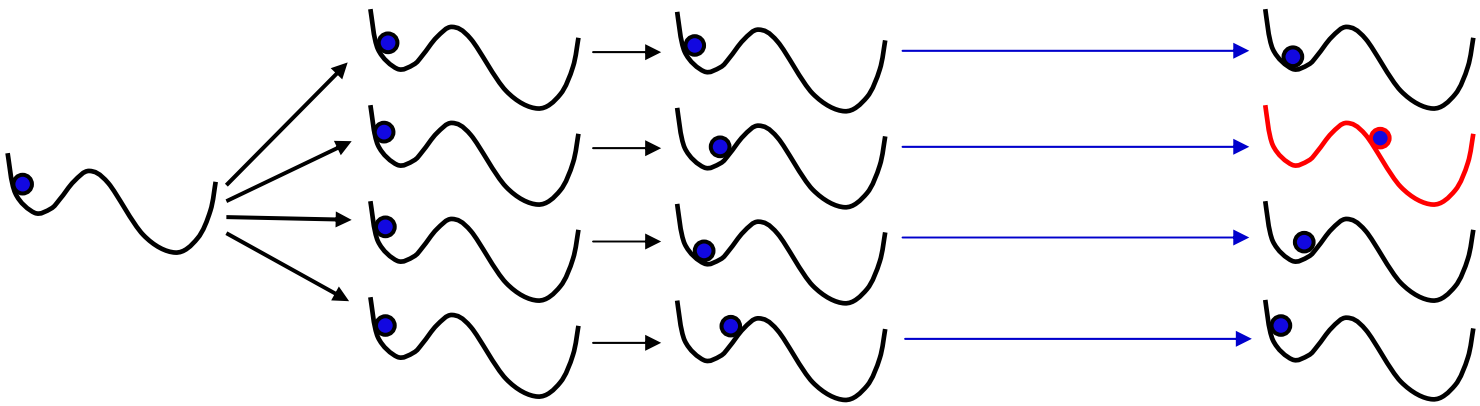
Parallel Replica Dynamics Procedure

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



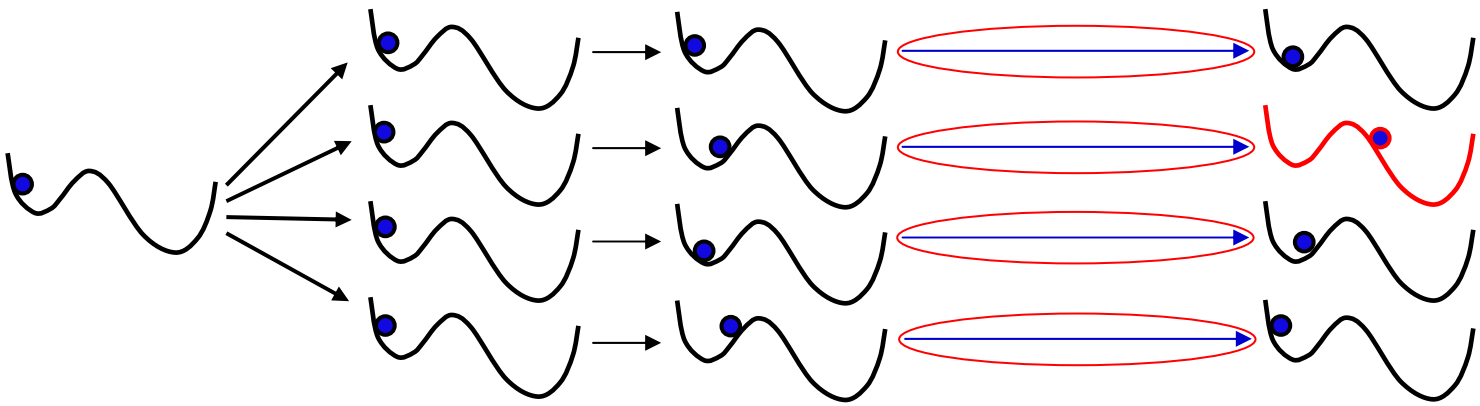
Parallel Replica Dynamics Procedure

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



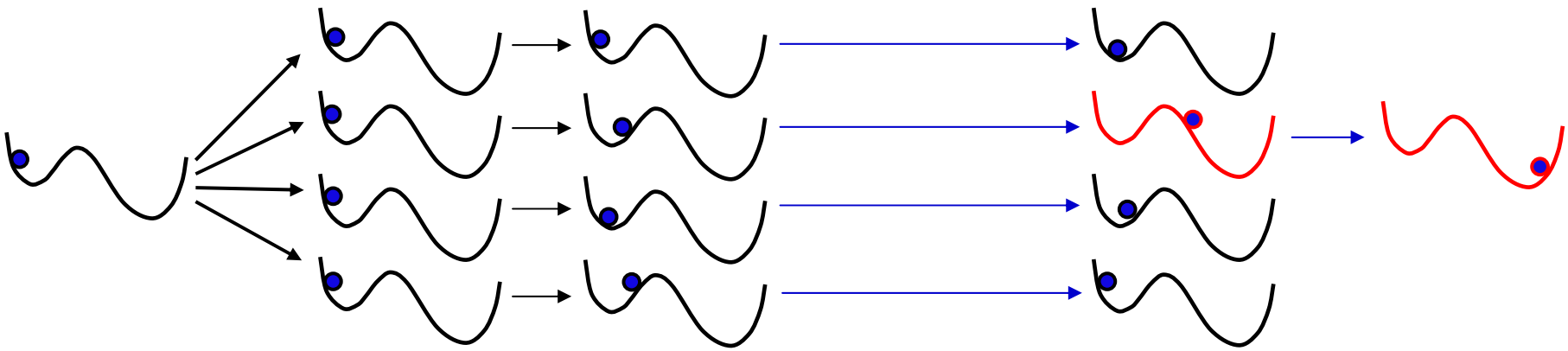
Parallel Replica Dynamics Procedure

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



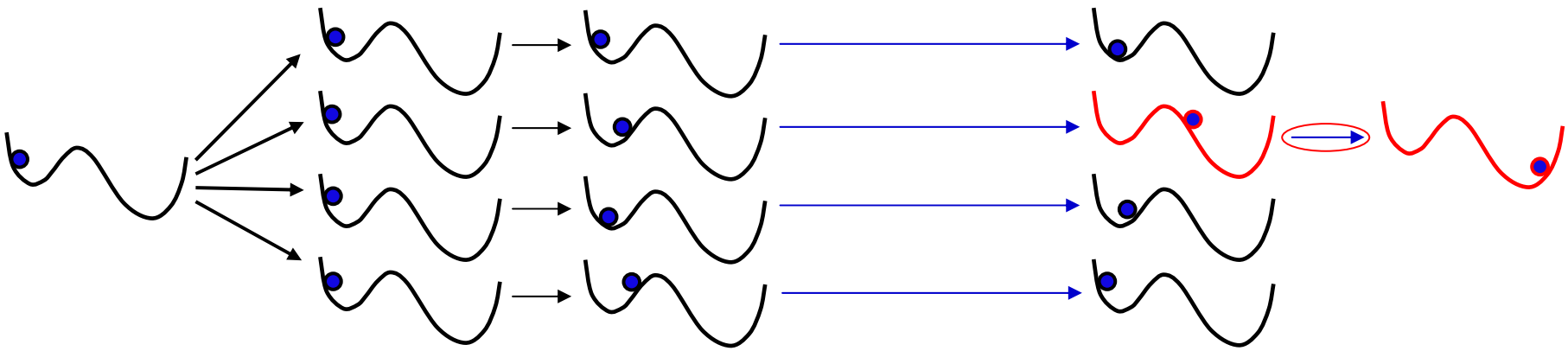
Parallel Replica Dynamics Procedure

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



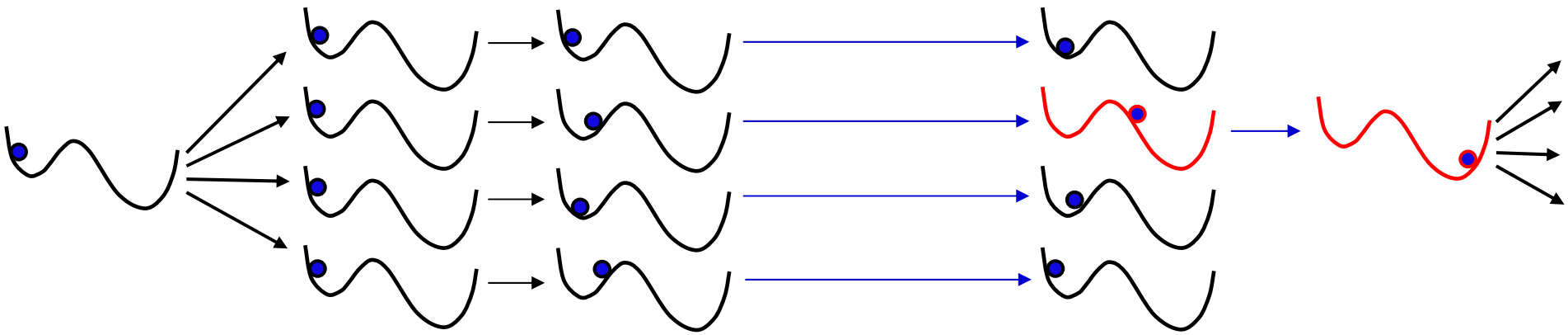
Parallel Replica Dynamics Procedure

Advance simulation clock by τ_{corr}.

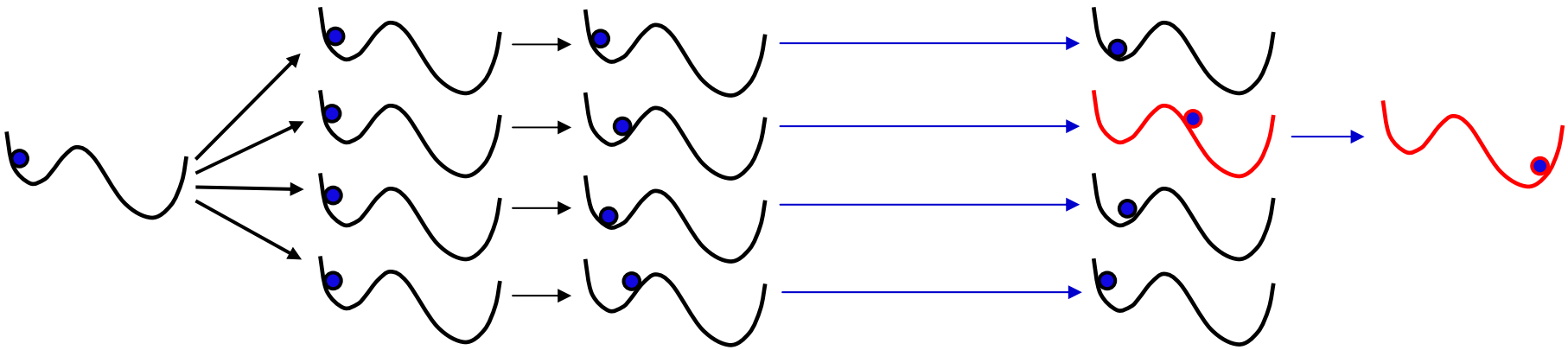


Parallel Replica Dynamics Procedure

Replicate the new state and begin procedure again.



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)].

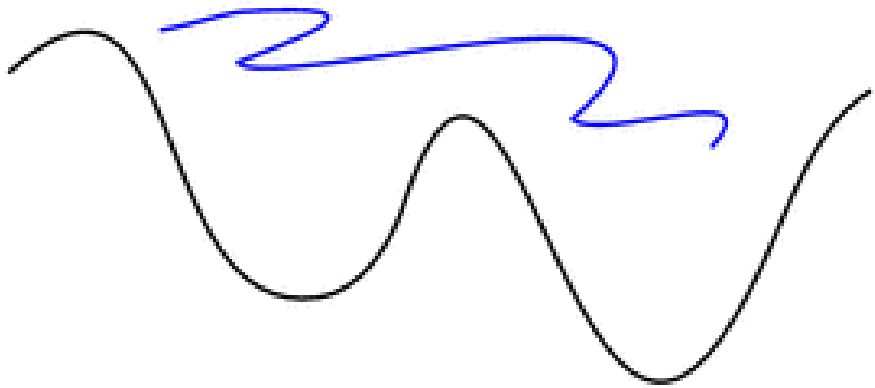
Good parallel efficiency if $\tau_{rxn} / M >> \tau_{dephase} + \tau_{corr}$

Applicable to any system with exponential first-event statistics

Detecting a transition

- best method depends on the system

- simple method for EAM metal systems:
  periodically perform steepest-descent quench;
  see if geometry at basin minimum has changed



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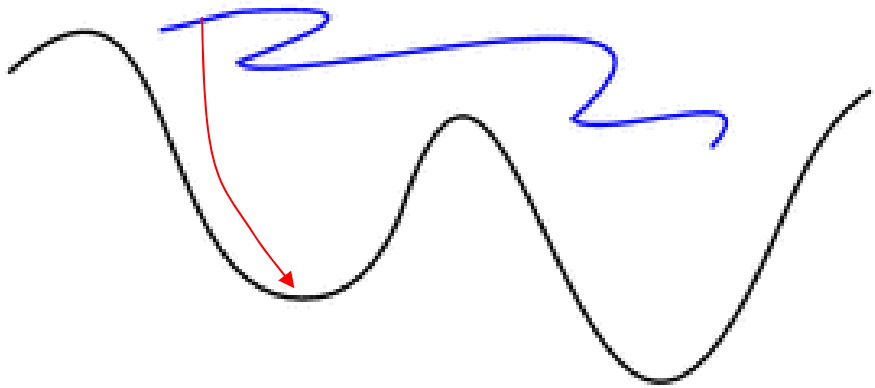

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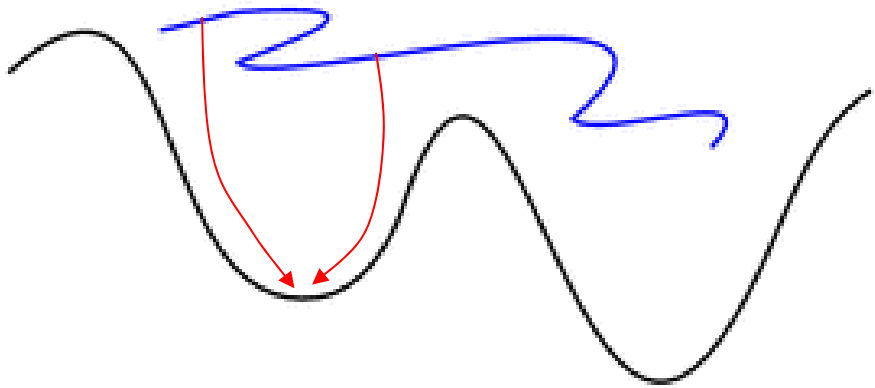

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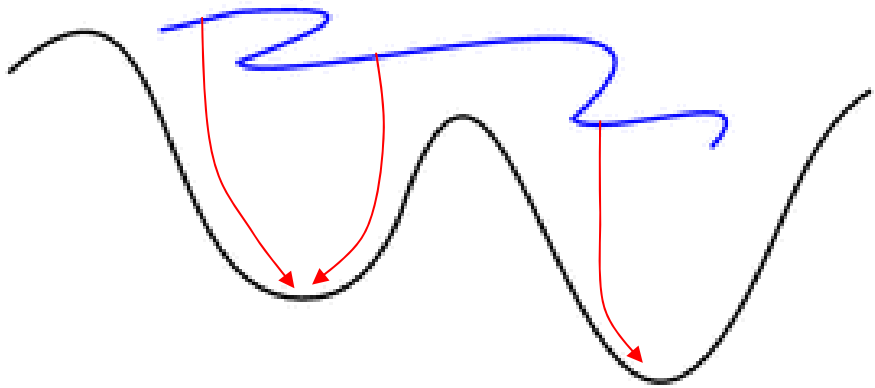


Parallel-replica dynamics example

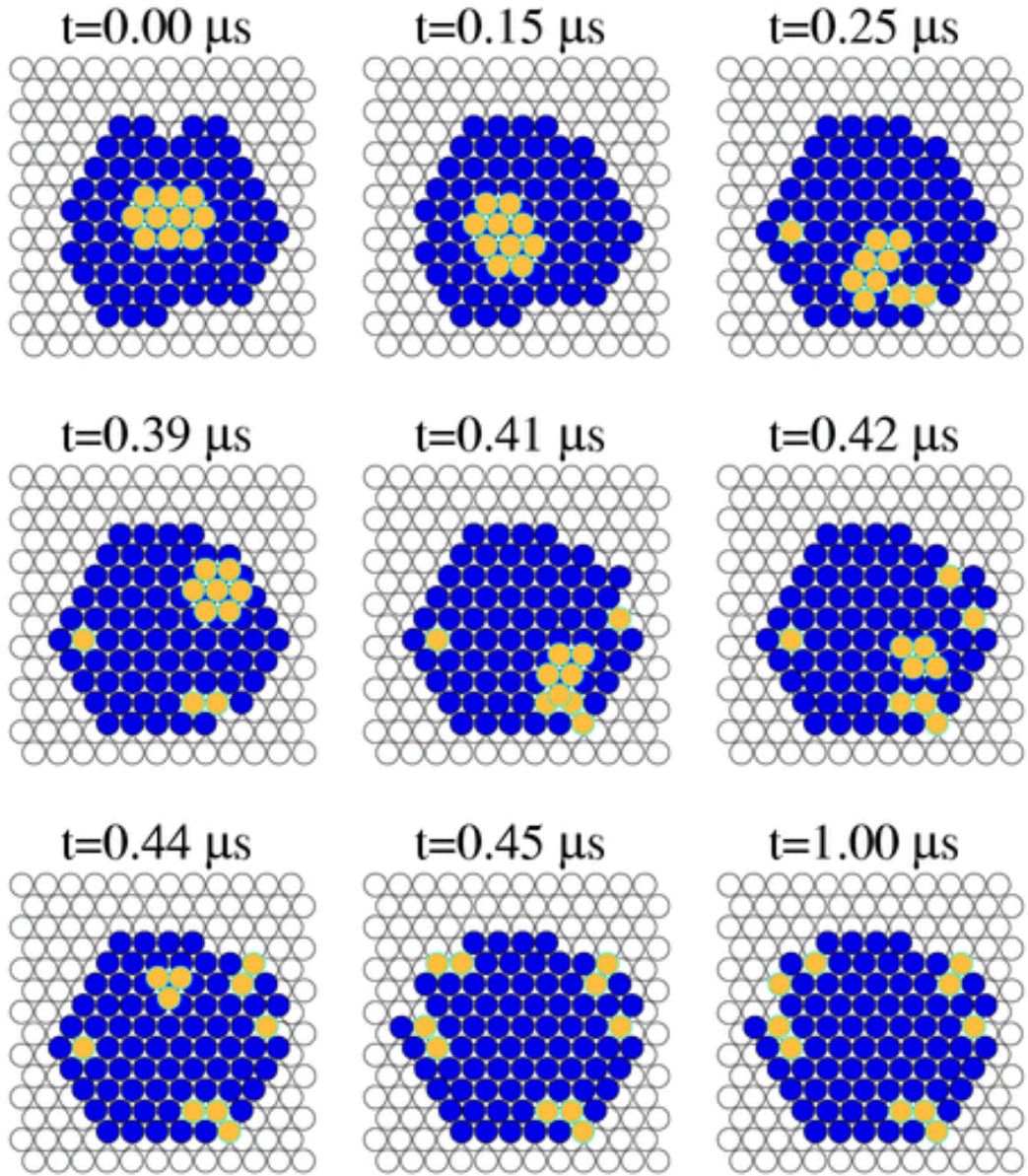
Ag(111) island-on-island decay

Embedded atom (EAM) potential

Temperature = 400K

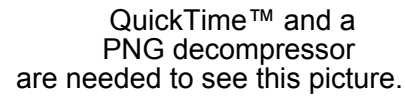
5 days on 32 processors
(1 GHz Pentium-IIIs)

Upper island decays into lower island via step-edge exchange events.



AFV, F. Montalenti and T.C. Germann, Ann. Rev. Mater. Res. 32, 321 (2002).

Ag island/Ag(111)



Ag/Ag(111) 2-atom exchange at step

QuickTime™ and a
PNG decompressor
are needed to see this picture.

Interstitial H_2 in FCC fullerene lattice

Parallel-replica simulation revealed unexpected double occupancy of stable site (two H_2 molecules in one octahedral site).

Uberuaga, Voter, Sieber and Sholl, Phys. Rev. Lett. 91, 105901 (2003)

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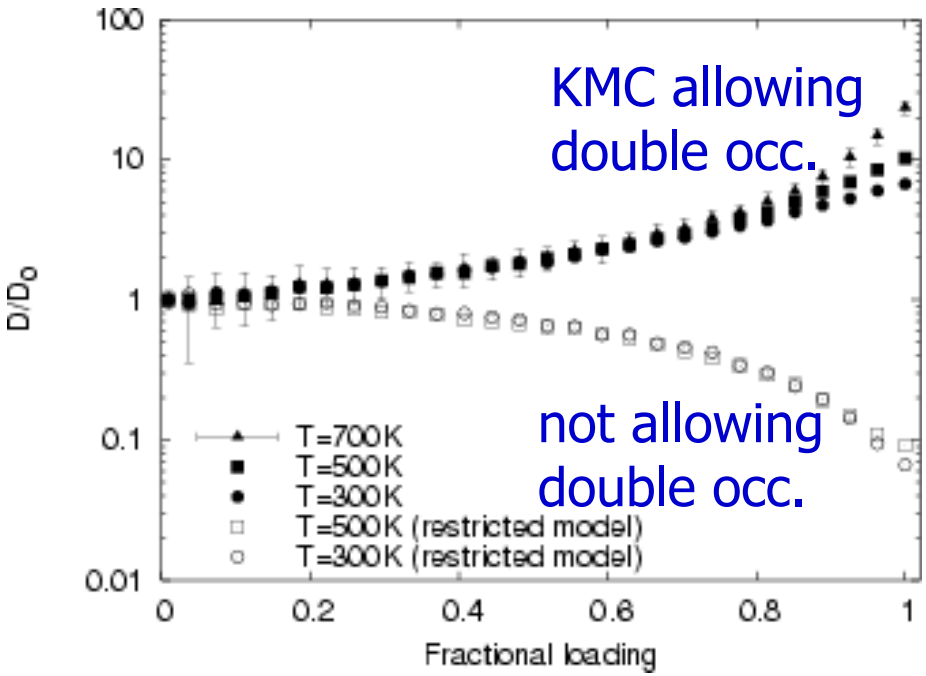
Significant effect on self diffusivity:



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TAD

Temperature Accelerated Dynamics (TAD)

Concept:

Raise temperature of system to make events occur more frequently. Filter out the events that should not have occurred at the lower temperature.

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

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Raise temperature of system to make events occur more frequently. Filter out the events that should not have occurred at the lower temperature.

Assumptions:

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

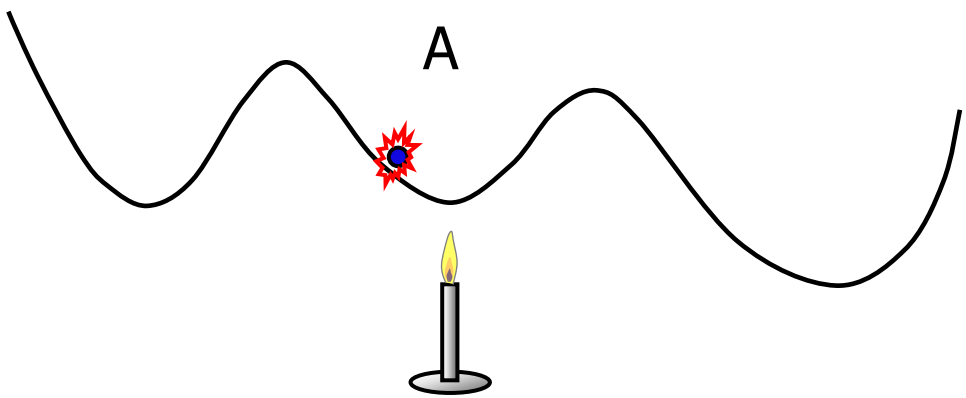
$$k = \nu_0 \exp[-\Delta E/k_B T]$$

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

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

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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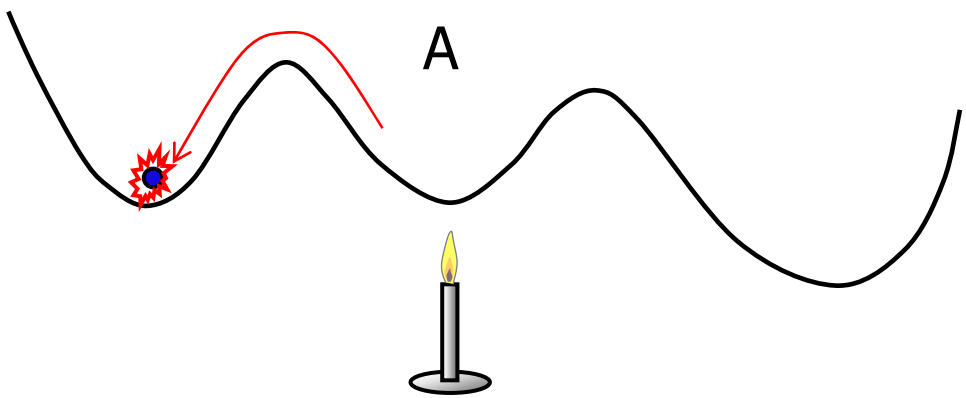

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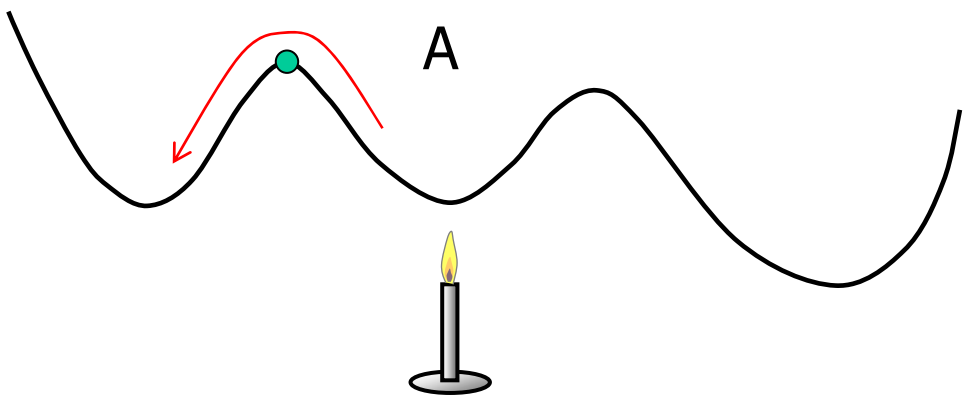

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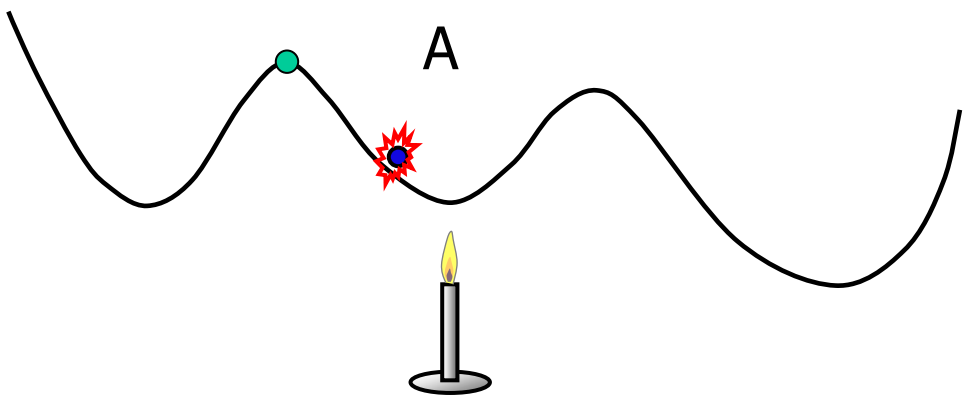

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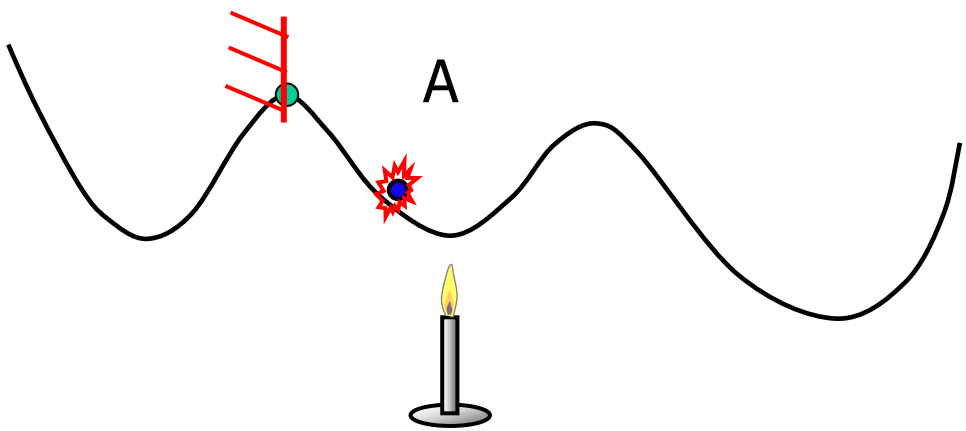

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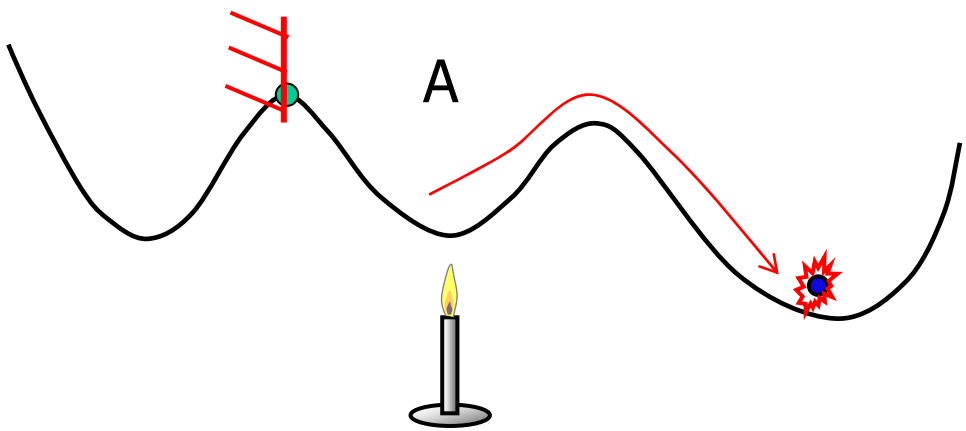

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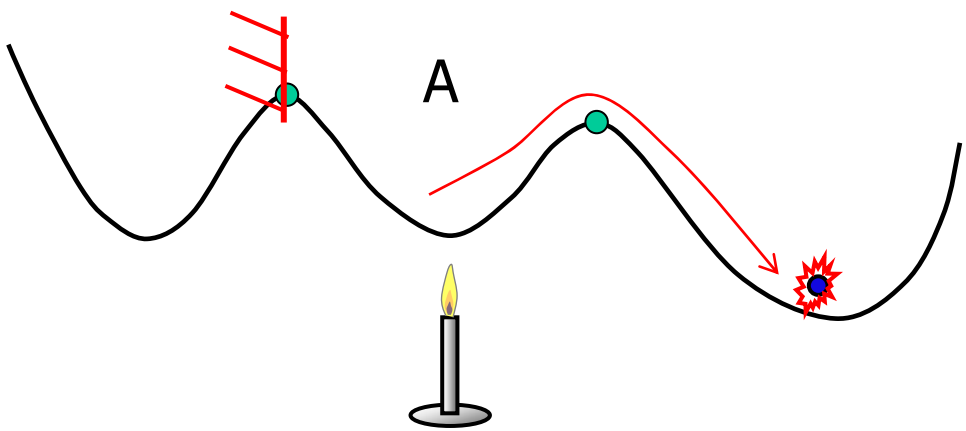

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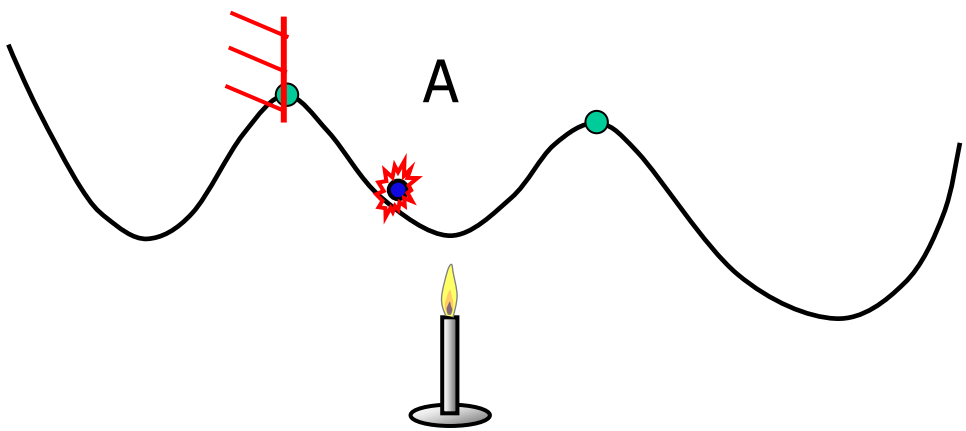

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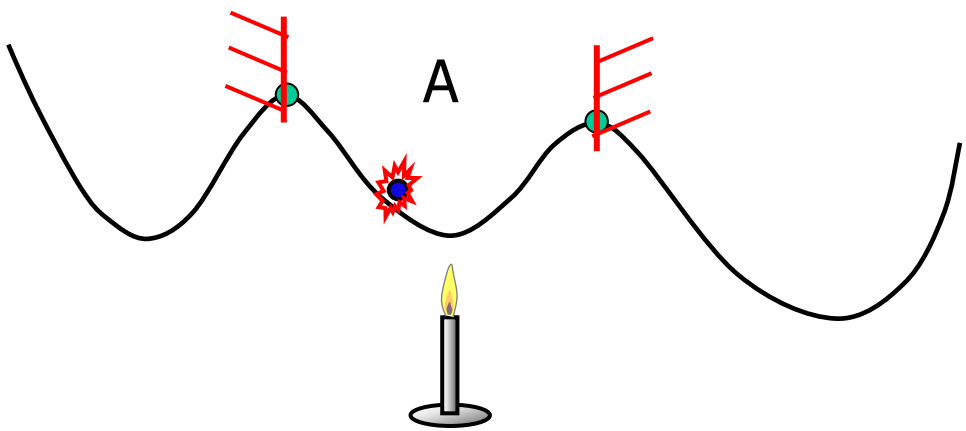
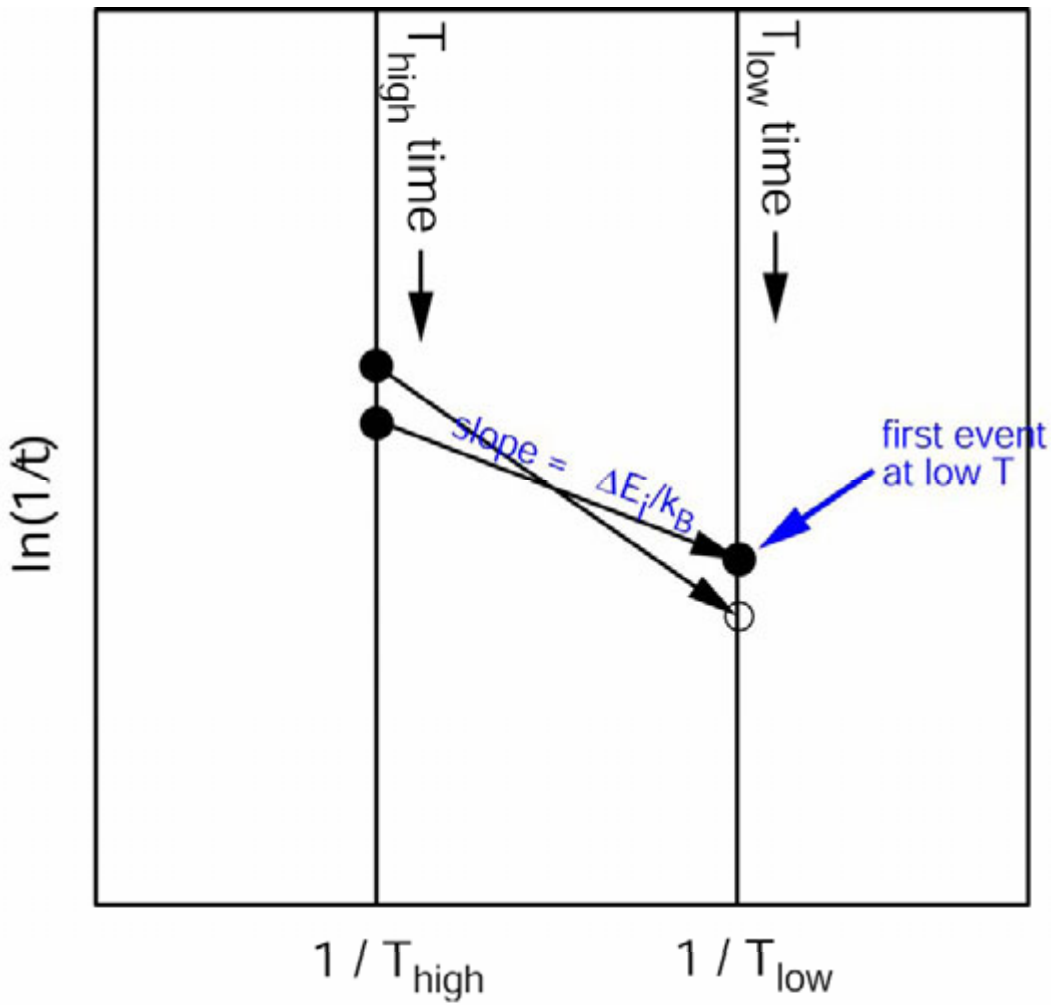
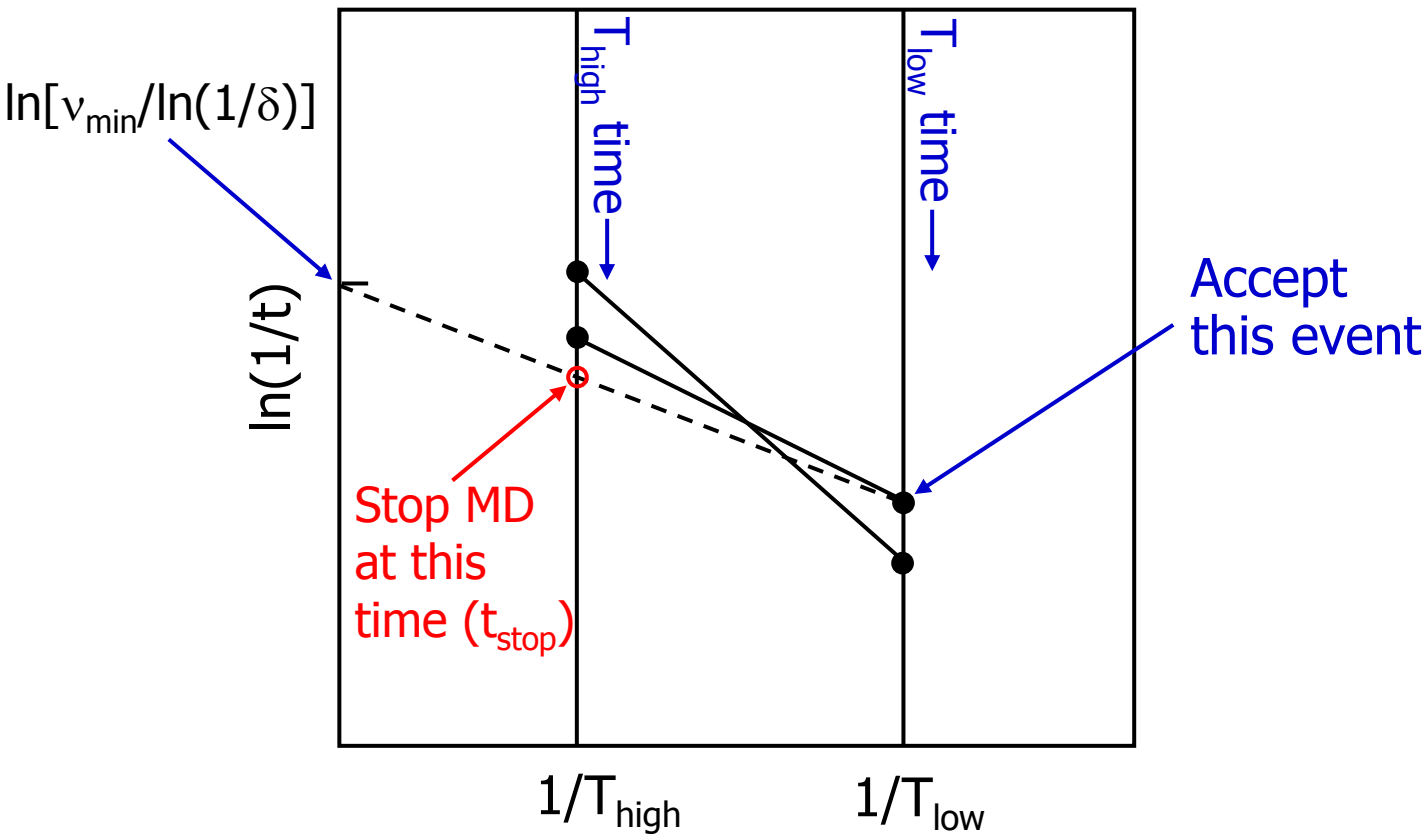


The Arrhenius view



when can we stop?

TAD - when can we stop the MD and accept an event?



After time t_{stop}, with confidence 1-δ, no event can replace shortest-time event seen at low T.

Move system to this state and start again.

Exact dynamics, assuming harmonic TST, ν_{min}, uncertainty δ.

Combining dimer method with TAD

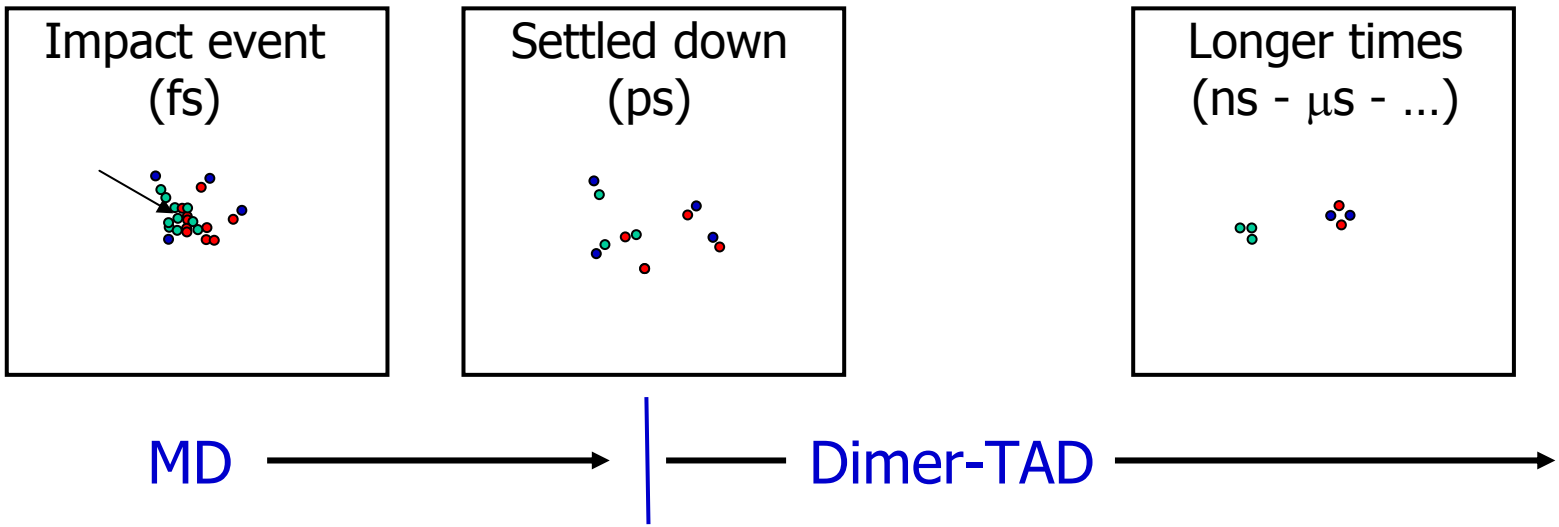
Dimer-TAD

- Use dimer method (Henkelman and Jonsson, 1999) to find a number of saddles and assume the lowest barrier (ΔE_{min}) is among them

- Supply this ΔE_{min} to TAD for this state -- gives earlier acceptance

----> accuracy of TAD (unless lowest barrier missed), with roughly the speed of the dimer method

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).

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)

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

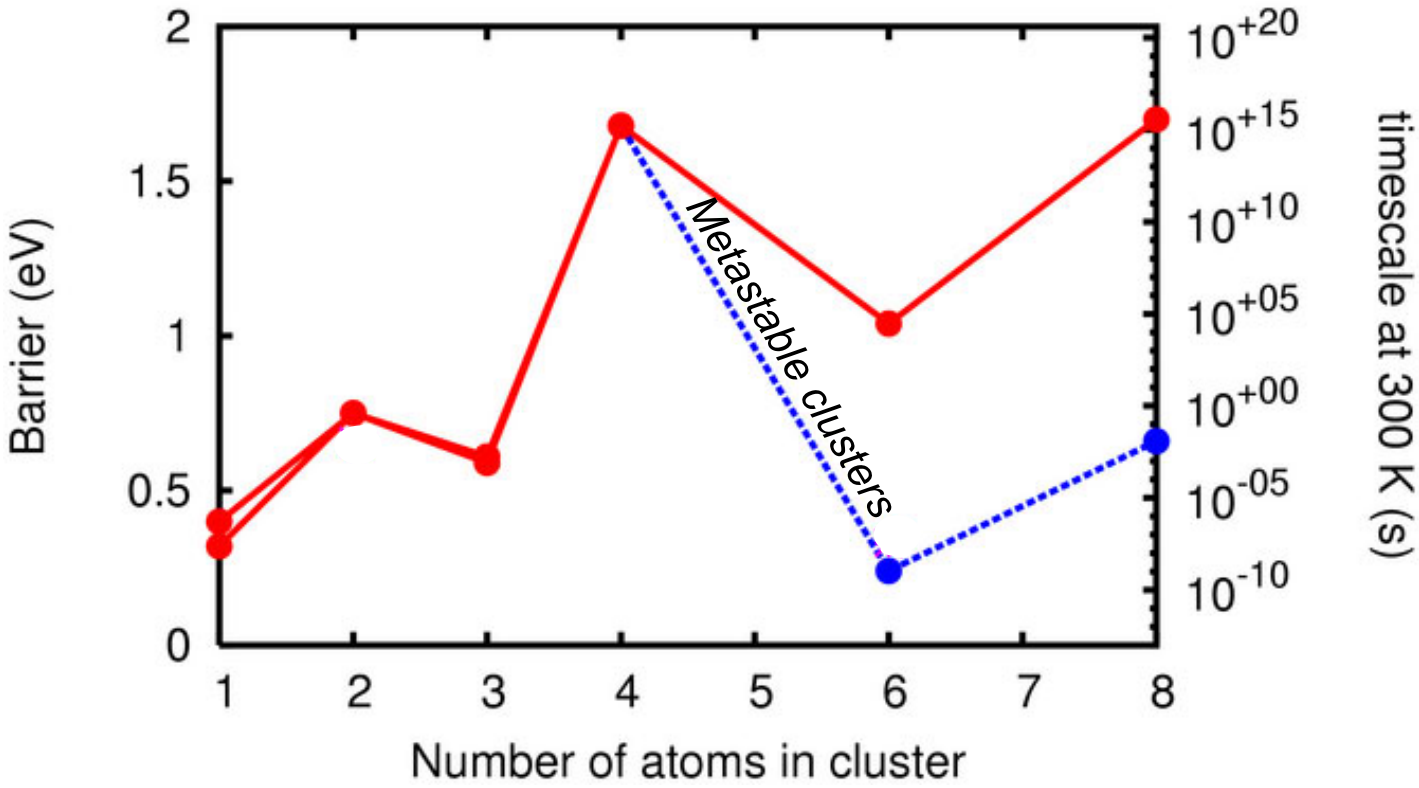
TAD Simulation: dimer + tetramer interstitial clusters

- 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

QuickTime™ and a
GIF decompressor
are needed to see this picture.

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

Interstitial Cluster Mobility



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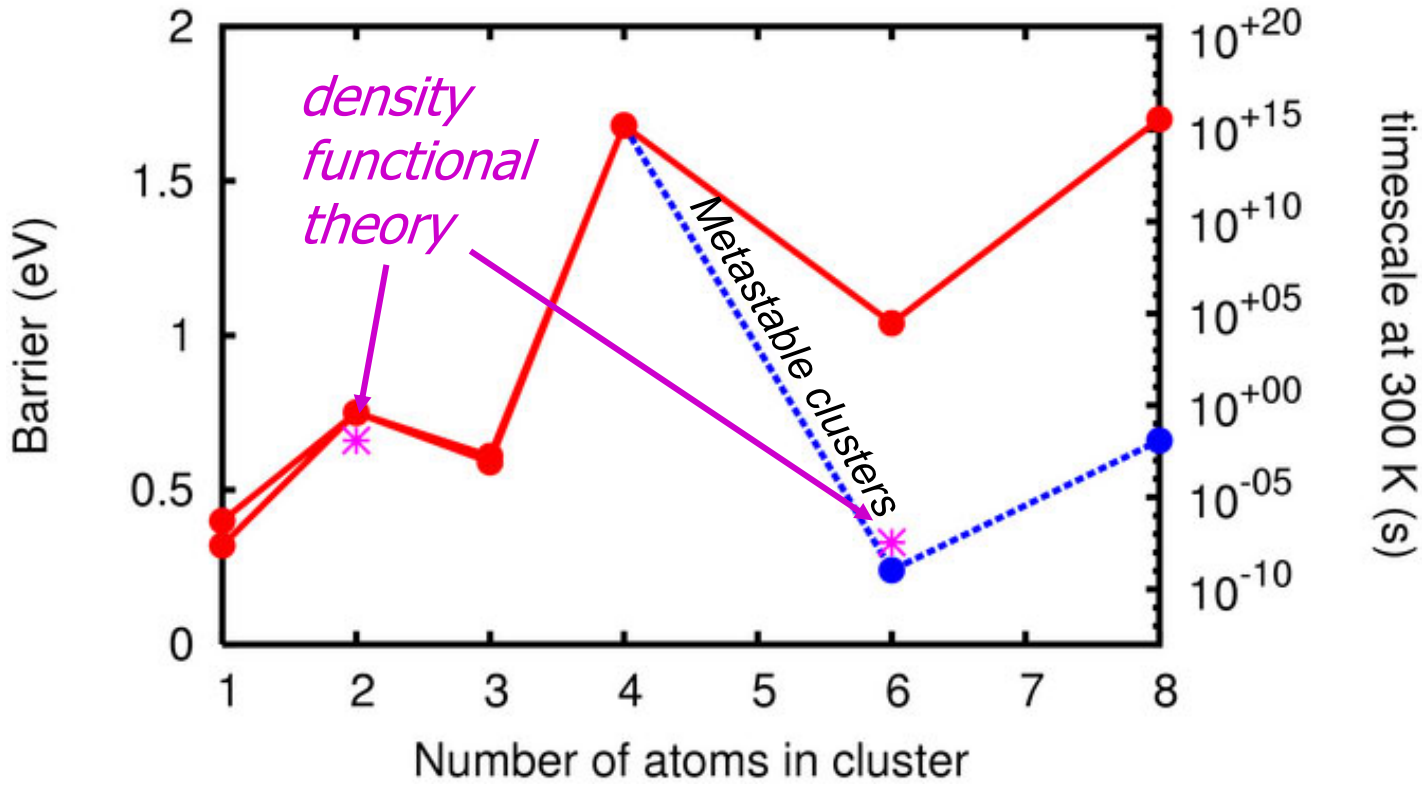

Including Quantum Effects

Because hydrogen has a very low mass, quantum effects will change the transition rates

- Zero point energy effectively raises minimum
- Tunneling effectively lowers barrier

Typical result is increased escape rates

Can we include these quantum effects in the accelerated molecular dynamics?

Harmonic Quantum Correction

Feynman path integral correction to activation energy assuming saddle is harmonic:

$$E_a^{eff} = E_a - \hbar^2(\omega_a^2+|\omega_c|^2)/24k_BT$$

- Easy to evaluate if saddle is known

- TAD can be modified to incorporate this rate correction

- Won't work for hyperdynamics or parallel-replica dynamics

Quantum effective potential surface

Appeal to Feynman path-integral density matrix

Classical: $\rho(x,x) \propto exp[-\beta V(x)]$

Quantum-Boltzmann $\rho(x,x) \propto \int Dx(u) exp[-\frac{1}{\hbar}\int_0^{\beta\hbar} \frac{1}{2} m\dot{x}(u)^2 + V(x(u))du]$

Appropriate "smearing" of potential due to effect of delocalized particle can give an effective potential. Classical dynamics on this transformed potential will give (approximately) quantum dynamics.

E.g., use centroid molecular dynamics (Cao and Voth, 1993-1994) to transform on the fly.

Builds in approximate quantum effects without identifying saddle points, though much more expensive

Could be used in hyperdynamics or parallel-replica dynamics

Good quality expected if quantum effects not too strong

Summary

- Accelerated molecular dynamics concept:
  - Let the trajectory find an appropriate way out or state, but coax it into doing so more quickly
- Significant speedup over standard MD when barriers are high relative to temperature
- Often encounter unexpected behavior
- Quantum effects can be incorporated
- Ongoing challenges
  - low barriers and pesky local minima
  - cuspy potentials
  - scaling with system size

Reviews: Voter, Montalenti, and Germann, Ann. Rev. Mater. Res. 32, 321 (2002); Uberuaga, Montalenti, Germann, and Voter, in *Handbook of Materials Modeling*, *Part A - Methods*, edited by S. Yip (Springer, 2005), p. 629.