Molecular Dynamics and Accelerated Molecular Dynamics

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Tutorial Lecture Series
Institute for Pure and Applied Mathematics (IPAM)
UCLA
September 13-16, 2005

Acknowledgment: DOE/BES

A.F. Voter, September, 2005  LAUR-05-8125
Overall Outline

Day 1: Molecular dynamics methods

Day 2: Molecular dynamics methods

Day 3: Infrequent events, transition state theory, saddle finding, etc.

Day 4: Accelerated molecular dynamics methods
Overall Outline

Day 1: Molecular dynamics methods

Day 2: Molecular dynamics methods

Day 3: Infrequent events, transition state theory, saddle finding, etc.

Day 4: Accelerated molecular dynamics methods
- Quick review of key concepts
- Parallel-replica dynamics
- Hyperdynamics
- Temperature accelerated dynamics (TAD)
Review of some key points

For an infrequent-event system, the probability of escaping to any particular final state is proportional to the rate constant for that escape path.

The bottleneck for escape may be energetic (a barrier) or entropic (a free-energy barrier), or some of both.

In transition state theory (TST), we approximate this rate constant as the flux through the dividing surface that separates the two states.

The TST rate is an equilibrium property of the system. We could run a very long MD trajectory and count the crossings per time, or (for the canonical ensemble) we can simply determine the Boltzmann probability of being in the dividing surface subspace and multiply it by the average velocity normal to that dividing surface \([2k_B T/\pi m^{1/2}]\).

Successive crossings may be correlated; so \(k^{\text{exact}}\) is less than or equal to \(k^{\text{TST}}\).
Review of some key points (cont.)

We can correct for these recrossings, to compute $k_{\text{exact}}$, by initiating “half trajectories” at the dividing surface (the same one we used to compute the TST rate), and tallying up where they come to rest. This assumes there is a separation of time scales -- that the correlation time ($\tau_{\text{corr}}$) is much shorter than the average reaction time ($\tau_{\text{rxn}} = 1/k$).

We can actually pick almost any dividing surface we want, and the TST + dynamical corrections formalism will still give the same rate constant.

If there is not a separation of time scales, even the rate itself is ill defined, since there is no longer a first-order (exponential) population decay.

For a true infrequent-event system, after a correlation time has passed since entering the state, the probability distribution function for the time to the next escape event is exponentially distributed (i.e., a poisson process).
Exponential escape-time distribution

Infrequent events give an exponential distribution of first-escape times (after correlation time has passed since entering state).

\[ p(t) = ke^{-kt} \]

\[ \tau_{\text{rxn}} = 1/k \]

We will exploit this in some of the accelerated MD methods.
Accelerated molecular dynamics concept

The trajectory finds an appropriate way out (i.e., proportional to the rate constant) without knowing about any of the escape paths except the first one it sees. In accelerated dynamics we try to maintain this key characteristic, while making the first escape happen sooner.
Parallel Replica Dynamics
Parallel Replica Dynamics

Parallelizes time evolution

Assumptions:

- infrequent events
- transitions can be detected
- exponential distribution of first-escape times
- correlation time known

\[ p(t) = ke^{-kt} \]

Parallel Replica Dynamics - derivation

Consider an infrequent-event system with a set of possible escape events

Total escape rate:

$$k_{\text{tot}} = \sum_i k_i$$

Probability distribution function for time to first event:

$$p(t) = k_{\text{tot}} \exp(-k_{\text{tot}}t)$$
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Now consider a set of $M$ equivalent systems, each in the same state, evolving independently on $M$ identical processors.
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At some point, a transition will occur on one of the processors. What can we say about it?
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This behaves like a physical supersystem that is $M$ times larger, with the simulation time on processor 1 representing the time ($t$) for the whole system.

$$k_{\text{super}} = Mk_{\text{tot}}$$
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This behaves like a physical supersystem that is M times larger, with the simulation time on processor 1 representing the time (t) for the whole system.

\[ k_{\text{super}} = M k_{\text{tot}} \]

\[ p(t) = k_{\text{super}} \exp(-k_{\text{super}} t) \]
Define $t_{\text{sum}}$ as the sum of times on all processors

$$t_{\text{sum}} = Mt$$
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$$t_{\text{sum}} = Mt$$

Then

$$p(t) = k_{\text{super}} \exp(-k_{\text{super}}t)$$

$$p(t_{\text{sum}}/M) = Mk_{\text{tot}} \exp(-Mk_{\text{tot}}t)$$

$$(1/M)p(t_{\text{sum}}/M) = k_{\text{tot}} \exp(-k_{\text{tot}}Mt)$$

$$p(t_{\text{sum}}) = k_{\text{tot}} \exp(-k_{\text{tot}}t_{\text{sum}})$$

Recall

$$k_{\text{super}} = Mk_{\text{tot}}$$

And note

$$(1/a)p(t'/a)dt' = p(t)dt$$
Notice

\[ p(t_{\text{sum}}) = k_{\text{tot}} \exp(-k_{\text{tot}} t_{\text{sum}}) \quad \iff \quad p(t) = k_{\text{tot}} \exp(-k_{\text{tot}} t) \]

Expressed in this summed time, the probability distribution function for the first escape time from this state is exactly that for the original system.

We have done nothing to corrupt the relative escape rates for the different pathways.

The time \( t_{\text{sum}} \) for the supersystem accumulates \( M \) times faster.

We have parallelized the time leading up to the first escape event.
Comment

Processors need not run at the same speed, nor at constant speed.
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 ($\tau_{\text{dephase}}$) 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 $t_{\text{sum}}$
Parallel Replica Dynamics Procedure

On the processor where a transition occurred, continue trajectory for a time $\tau_{\text{corr}}$ to allow correlated dynamical events.
Parallel Replica Dynamics Procedure

Advance simulation clock by $\tau_{\text{corr}}$. 
Parallel Replica Dynamics Procedure

Replicate the new state and begin procedure again.
Parallel Replica Dynamics

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

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

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

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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Parallel-replica dynamics example

Ag(111) island-on-island decay

Embedded atom (EAM) potential

Temperature = 400K

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

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

For this case, parallel replica is even faster than temperature-accelerated dynamics, since barriers are low relative to T.

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Must $p(t)$ be exponential?

What if $p(t)$ looks like this? $p(t)$
Must $p(t)$ be exponential?

What if $p(t)$ looks like this?

This is a problem.

Imagine the limiting case:

If $p(t)=\delta(t-t_0)$, parallel replica simulation will detect an event on all $M$ processors at the same time ($t_0$), giving no boost. Worse, the summed time will predict a transition time too large by exactly a factor of $M$. 

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General comments about non-exponential $p(t)$

A non-exponential $p(t)$ is almost certainly caused by “hidden” transitions, or, similarly, a diffusive character to some coordinate(s).

Thus, applying parallel-replica dynamics when $p(t)$ is non-exponential will give incorrect times, and incorrect dynamics.

If every transition is detected, each $p(t)$ will be exponential for a (non-diffusive) infrequent-event system, and parallel-replica dynamics will be valid.
Parallel Replica Dynamics
Can we overlook fast transitions?

The maximum boost is limited by the fastest processes in the system.

If the rapid transitions seem to be unimportant, can we ignore them?

Yes - but be careful...
Safe case

Trajectory will go back and forth many times before escaping

\[ p(t) \]

\[ t \]
Dangerous case

Transitions we ignore

Transition we detect

Trajectory may fall off right-hand end on first pass - acts like an exponential preceded by a lag time while system diffuses from left to right

\[ p(t) \]
Parallel replica on floppy systems
(ignoring fast conformational transitions)

Small “fast folding” proteins (Pande et al, 2000, 2001,...)
- folding transitions detected based on energy fluctuations
- screen-saver based (SETI-at-home-like) parallelization
- microsecond time scales, folding seen

Hydrocarbon pyrolysis (Kum, Stuart et al, Clemson, 2002)
- bond-breaking transitions detected
- microseconds at T=2000K (usually T=3000K with MD)
- unexpected ring-formation observed
Pyrolysis of n-hexadecane (C$_{16}$H$_{34}$)

3-carbon-ring formation (not in standard models)

Subsequent ring opening leads to branched structure

Cyclic intermediate (11 carbons left)

Branched radical after ring reopens.
REBO potential

Reactive Bond-Order potential

- fit to lots of C and C-H data
- improved property predictions relative to “Tersoff Brenner” form
- dihedral angle term for C=C bonds
- good description of graphite
Summary - Parallel replica dynamics

Most exact of the accelerated dynamics methods
- no harmonic approximation
- goes beyond TST to include correlated dynamical events
- no assumption that barrier is energetic - can be entropic

Easy to implement; Requirements:
- transition detection
- good estimate of correlation time

Very general applicability
- any system with exponentially distributed events

Good match to increasing availability of parallel processing power, distributed computing, etc.
Limitations - Parallel replica dynamics

Only get parallel boost

Boost drops off when events are frequent (or become frequent because so many processors)

Boost especially limited if correlation time is long

For complex systems (e.g., proteins) even transition detection can be tricky.
Hyperdynamics

Builds on umbrella-sampling techniques (e.g., Valleau 1970’s)

Assumptions:
- infrequent events
- transition state theory (no recrossings)

Procedure:
- design bias potential $\Delta V$ (zero at dividing surfaces; causes no recrossings)
- run thermostatted trajectory on the biased surface ($V + \Delta V$)
- accumulate hypertime as
  
  $t_{\text{hyper}} = \sum t_{\text{MD}} \exp[\Delta V(R(t))/k_B T]$

- time converges on correct value in long-time limit (vanishing relative error)

The hypertime clock

System coordinate

MD clock

hypertime clock

Boost = hypertime/(MD clock time)
The hypertime clock

System coordinate

Boost = hypertime/(MD clock time)

Δ\text{t}_{\text{hyper}} = \Delta t_{\text{MD}} e^{\Delta V/kT}

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Hyperdynamics - derivation

Viewgraphs here
Hyperdynamics

Key challenge is designing a bias potential that meets the requirements of the derivation and is computationally efficient.

A few forms have been proposed and tested. Still a subject of ongoing research...
Flat bias potential

An extremely simple form: flat bias potential

\[ V + \Delta V \]


- no more expensive than normal MD (negative overhead(!))
- very effective for low-dimensional systems
- diminishing boost factor for more than a few atoms.
Hessian-based bias potential

Detect ridgetop using local approximation of Sevick, Bell and Theodorou (1993),

\[ \varepsilon_1 < 0 \quad \text{and} \quad C_1 g = 0 \]

(\( \varepsilon_1, C_1 = \text{lowest eigenvalue, eigenvector of Hessian; } g = \text{gradient} \))

Design bias potential that turns off smoothly in proximity of ridgetop

Iterative method for finding \( \varepsilon_1 \) using only first derivatives of potential

Iterative method for finding \( C_1 g \) and its derivative using only first derivatives of potential

Good boost, but very tight convergence required for accurate forces

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Bond-boost bias potential

R.A. Miron and K.A. Fichthorn  

Assumes any transition will signal itself by significant changes in bond lengths

\[ \Delta V = \text{sum of contributions from every bond} \]

Total \( \Delta V \) --> 0 when any bond is stretched beyond some threshold value

Looks promising:
- fairly general
- very low overhead
- for metal surface diffusion, boost factors up to \( 10^6 \)
Summary - Hyperdynamics

Powerful if an effective bias potential can be constructed

Need not detect transitions

Exponential boost factors possible

Especially effective if barriers high relative to $T$

Possibilities for powerful system-specific bias potentials

Lots of possibilities for future development of advanced bias potential forms
Limitations - Hyperdynamics

Must design bias potential

Assumes TST holds (though Langevin jiggle recrossings may be OK)

Boost drops off when events are frequent

Harder to implement properly if bottlenecks are entropic (but possible)
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.

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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 (\( \nu_0 \)) are greater than \( \nu_{\text{min}} \)

TAD Procedure

- Run MD at elevated temperature ($T_{\text{high}}$) 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 $T_{\text{low}}$.
- Reflect system back into basin A and continue.
- When safe, accept transition with shortest time at $T_{\text{low}}$.
- Go to new state and repeat.
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TAD temperature-extrapolated time

Because each rate is assumed to be Arrhenius,

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

the time for each particular event at high T can be extrapolated to low T:

\[ t_{\text{low}} = t_{\text{high}} \exp[\Delta E(1/k_B T_{\text{low}} - 1/k_B T_{\text{high}})]. \]

This time is sampled correctly from the exponential distribution at low T, mapped from the high T sample:
The Arrhenius view

when can we stop?

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The confidence line

For a given rate $k_i$, the time required to be $f$-confident to see the first event (e.g., $f=0.99$ for 99% confidence) is

$$\tau_f = \frac{1}{k_i} \ln\left(\frac{1}{1-f}\right)$$

(or $\delta = 1-f$)

If rate is Arrhenius ($k = v_0 \exp\left(-\Delta E/k_B T\right)$), then fraction $f$ of first attempts will occur above the line with slope $-\Delta E/k_B$ and intercept $v_0^f = v_0 \ln\left(\frac{1}{1-f}\right)$.
TAD - when can we stop the MD and accept an event?

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

Move system to this state and start again.

Exact dynamics, assuming harmonic TST, $\nu_{\text{min}}$, uncertainty $\delta$. 

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MD+TAD metal deposition simulation

- MD for each deposition event (2 ps)
- TAD for intervening time (~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 $= 0.04 \text{ ML/s}$, matching deposition conditions of Egelhoff and Jacob (1989).


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MD+TAD deposition of Cu/Cu(100)

Concerted events observed at T=77K and T=100K:
Slice of a nanotube evolved with TAD

High Temperature: 3000K
Low Temperature: 1500K
States Visited: 100 shown
Boost: 129
Slice of a nanotube evolved with TAD

High Temperature: 3000K
Low Temperature: 1500K
States Visited: 100 shown
Boost: 129

after 14 µs  Blas Uberuaga
Steve Stuart

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TAD: More 60-atom Nanotube Fragments

T=1500K (High T = 3000K), after first 1000 transitions

<table>
<thead>
<tr>
<th>Geometry</th>
<th>Boost</th>
<th>Total Simulation Time (µs)</th>
<th>(133 states)</th>
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<td>59</td>
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Blas Uberuaga  Los Alamos
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Blas Uberuaga  Los Alamos
Slice of a 7x7 nanotube evolved with TAD

High Temperature: 3000K
Low Temperature: 1500K

first few transitions
Slice of a 7x7 nanotube evolved with TAD

$t=0$

$8.5 \mu s$

$(\sim 25 \text{ eV above buckyball})$

Blas Uberuaga
A.F. Voter, September, 2005 LAUR-05-8125

Los Alamos
Using minimum barrier to stop TAD sooner

Assume we know the minimum barrier ($\Delta E_{\text{min}}$) for escape from this state

\[ \text{slope} = - \Delta E_{\text{min}} \]

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 ($\Delta E_{\text{min}}$) is among them
- Supply this $\Delta E_{\text{min}}$ to ETAD for this state

----> accuracy of TAD (unless lowest barrier missed), with roughly the speed of the dimer method
MgO Radiation Damage Annealing
T=300K

Impact event (fs)

Settled down (ps)

Longer times (ns - µs - ...)

MD → Dimer-TAD

Coulombic Buckingham potential

Interesting picture emerges for annealing after 400 eV cascade.


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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-\(\mu\)s time scale

Di-interstitial - diffuses on s time scale

Tetra-interstitial - immobile (years)
Growth of interstitial clusters in MgO, T=300K

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Is the tetramer a sink for all larger clusters?
Growth of interstitial clusters in MgO, T=300K

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Tetra-interstitial - immobile (years)

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

(perfect bulk atoms not shown, red=O--, blue=Mg++)
• Diffusion barrier follows no clear pattern versus cluster size

• Metastable clusters can be surprisingly mobile

• Metastable clusters can be very stable:
  - metastable I₆ lifetime is years at room temperature

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Interstitial Cluster Mobility

- Diffusion barrier follows no clear pattern versus cluster size
- Metastable clusters can be surprisingly mobile
- Metastable clusters can be very stable:
  - metastable $I_6$ lifetime is years at room temperature
Issues for future

• Boost limited by lowest barrier - general problem for many realistic systems (e.g., interstitials in metals)

• Roughness in potentials lowers effectiveness/efficiency of saddle searches (e.g., needed in TAD) and transition detection
  - shallow local minima
  - cusps at cutoffs and bond-switching points

• Currently limited to small systems
  – Trying to achieve N scaling
  – Spatial parallelization (with Jacques Amar at U. Toledo)

• Feeding information about atomistic behavior to higher-level models
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
• Ongoing challenges
  – low barriers and pesky local minima
  – cuspy potentials
  – scaling with system size