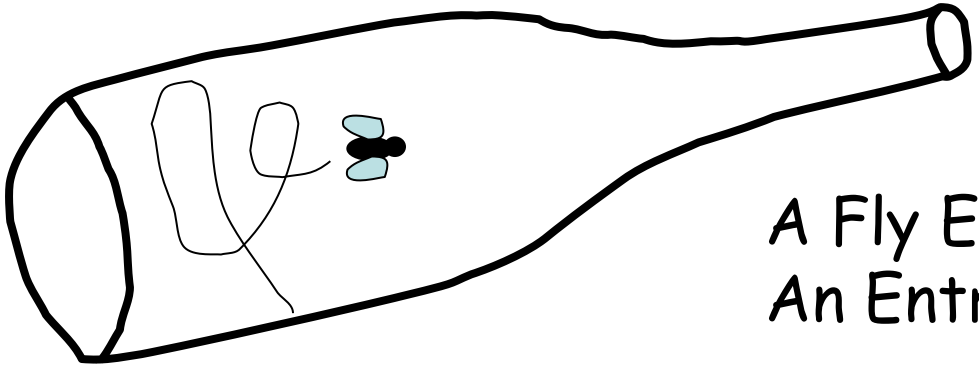
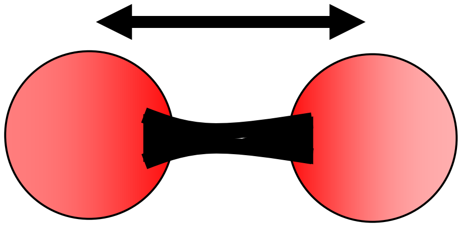
Rare Events: Passage of a Dynamical System from One Free Energy Minimum to Another

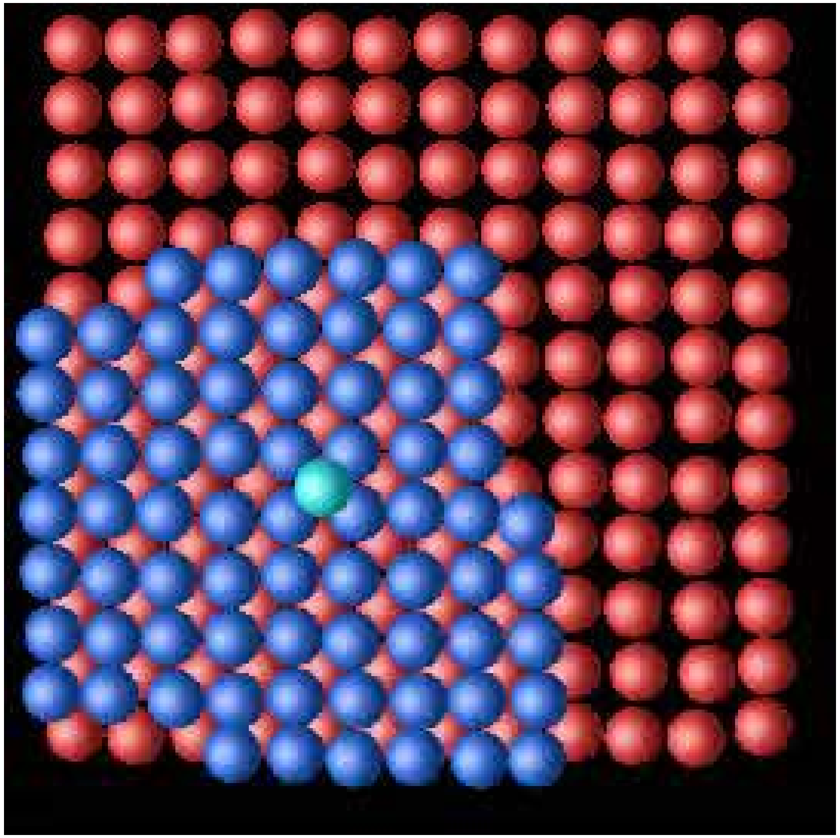


A Fly Escaping from a Bottle:
An Entropic Transition

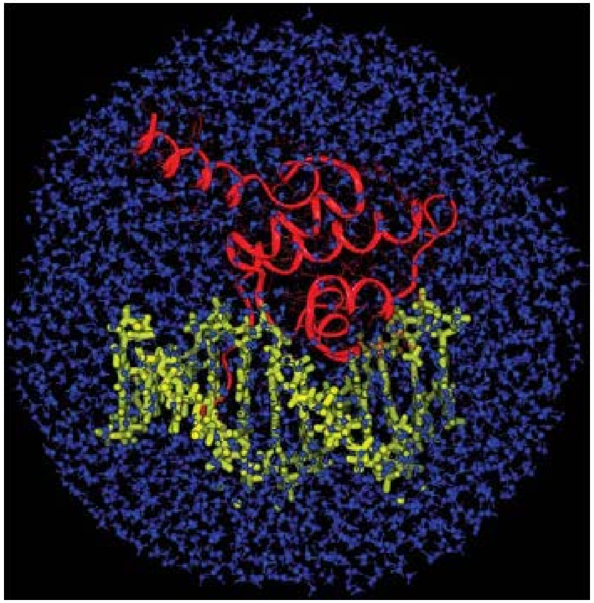


Chemical Bond Breaking:
An Energetic Transition

Rare Events: Passage of a Dynamical System from One Minimum to Another



Diffusion of Atoms on Solid Surfaces – e.g., the growth of Co on Cu

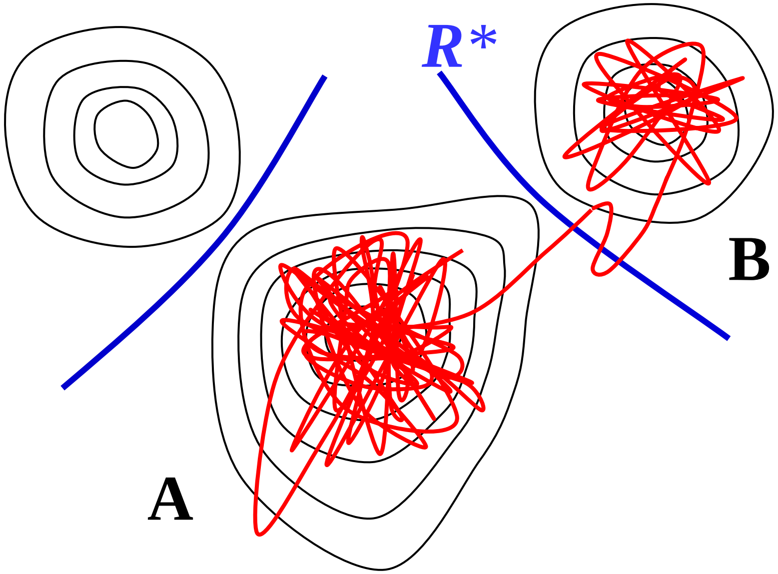


Protein Folding, Catalysis at Solid Surfaces, etc…..

Transition-State Theory (TST)
How Fast Does It Happen?

$$k_{TST,A\to B} = \nu \frac{\int_A \delta(\mathbf{R}-\mathbf{R}^*)\exp(-U(\mathbf{R})/k_BT)}{\int_A \exp(-U(\mathbf{R})/k_BT)}$$

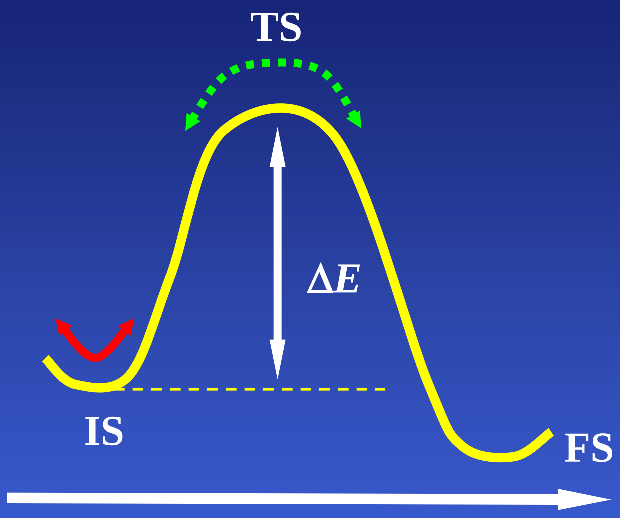
$$= \nu_0 \frac{q^*}{q_A}\exp(-E_0/k_BT)$$



$$\nu_0 = \frac{kT}{h}$$ Quantum Mechanically

$$= \frac{1}{2}\left(\frac{2kT}{\pi m}\right)^{1/2}$$ Classically

Rare event dynamics



Brute force approach to rate constants:

- i) Have accurate potential energy surface (forces)
- ii) Run MD trajectory so long, that it establishes equilibrium, crossing the barrier many, many times back and forth:

$$\Rightarrow \quad k = \frac{\text{no. of crossings IS} \rightarrow \text{FS per unit time}}{\text{fraction of time system has spent in IS}}$$

Yet:

- Relevant time step in MD run is fs (vibrations)
- Typical barrier ΔE for surface reactions ~ 1 eV $\Rightarrow$ 10^{-2} - 10^{2} reactions per second.
- Requires to run trajectory over about $10^{15} - 10^{20}$ time steps → unfeasible…

…and essentially 99.9999% of the time, the system will just vibrate around IS basin (short time dynamics)

⇒ require approximate theories to obtain process rates!

Transition state (activated complex) theory I

Assumptions:

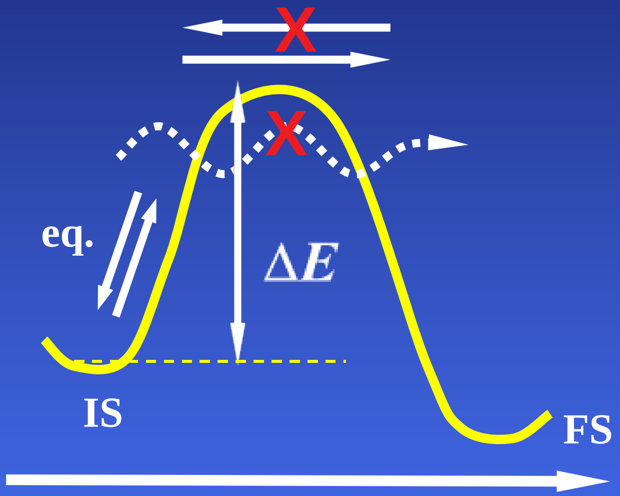
(Eyring, Evans, Polanyi, ~1935)

i) Reaction system passes the barrier only once (no re-crossings)

ii) Energy distribution of reactant DOF is Boltzmann-like (many collisions compared to reaction events yield equilibrium between activated complex and IS, except with respect to the reaction coordinate)

iii) Passage over barrier is the motion of only one DOF, the reaction coordinate, which is independent of all other motions of the activated complex (no concerted motions)

iv) Passage over barrier is a classical event (no tunneling)



Derivation: see e.g.
K.J. Laidler, *Chemical kinetics*,
Harper & Row, New York (1987)

$$\Rightarrow \quad k^{\mathrm{TST}}_{\mathrm{IS}\rightarrow\mathrm{FS}} = \left[\left(\frac{kT}{h}\right) e^{\Delta S/k} \right] e^{-\Delta E/kT}$$

Transition state (activated complex) theory II

- If assumptions i)-iv) are fulfilled, k^{TST} is exact. In general, k^{TST} is an upper limit to the real rate

$$k \;=\; f_{\mathrm{dyn}}\; k^{\mathrm{TST}}$$

In principle, one can compute so-called dynamical corrections. In contrast to liquid & gas phase,

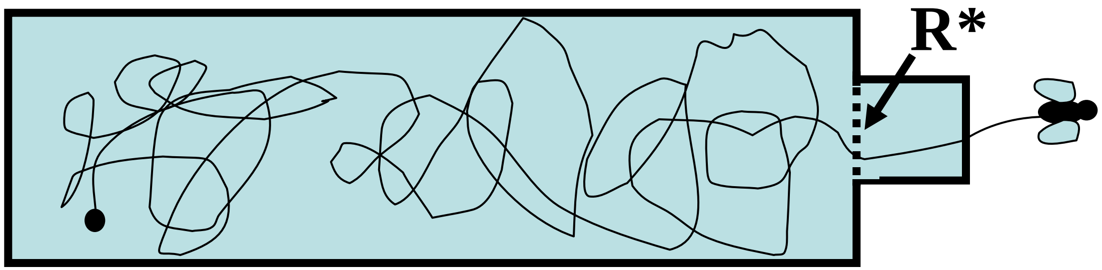
$f_{\mathrm{dyn}} \sim 1$ for solid-state processes (→ TST is a rather good approximation)

- Attempt frequency/preexponential factor $k_o^{\mathrm{TST}} = \underset{\overset{\nearrow}{\sim 10^{13}\,\mathrm{sec}^{-1}}}{\frac{kT}{h}}\;\underset{\overset{\nwarrow}{\sim 1}}{\mathrm{e}^{\,\Delta S/k}}$

- In harmonic TST, k_o^{TST} is given by the harmonic normal modes at the IS and TS

$\Rightarrow$ **problem reduces to locating transition states, i.e. saddle points in high dimensional PES**

TST: Fly in the Bottle Example



"Hard" Walls: $U(\mathbf{R}) = \begin{cases} \infty, & \text{if } \mathbf{R} \text{ is at the wall} \\ 0, & \text{otherwise} \end{cases}$

$$k_{TST} = \nu \frac{\int_V \delta(\mathbf{R}-\mathbf{R}^*)\exp(-U(\mathbf{R})/k_B T)}{\int_V \exp(-U(\mathbf{R})/k_B T)}$$

$$k_{TST} = \nu \frac{A_{neck}}{V_{bottle}} [=] \frac{1}{time}$$

Average Escape Time

$$\tau = 1/k_{TST}$$

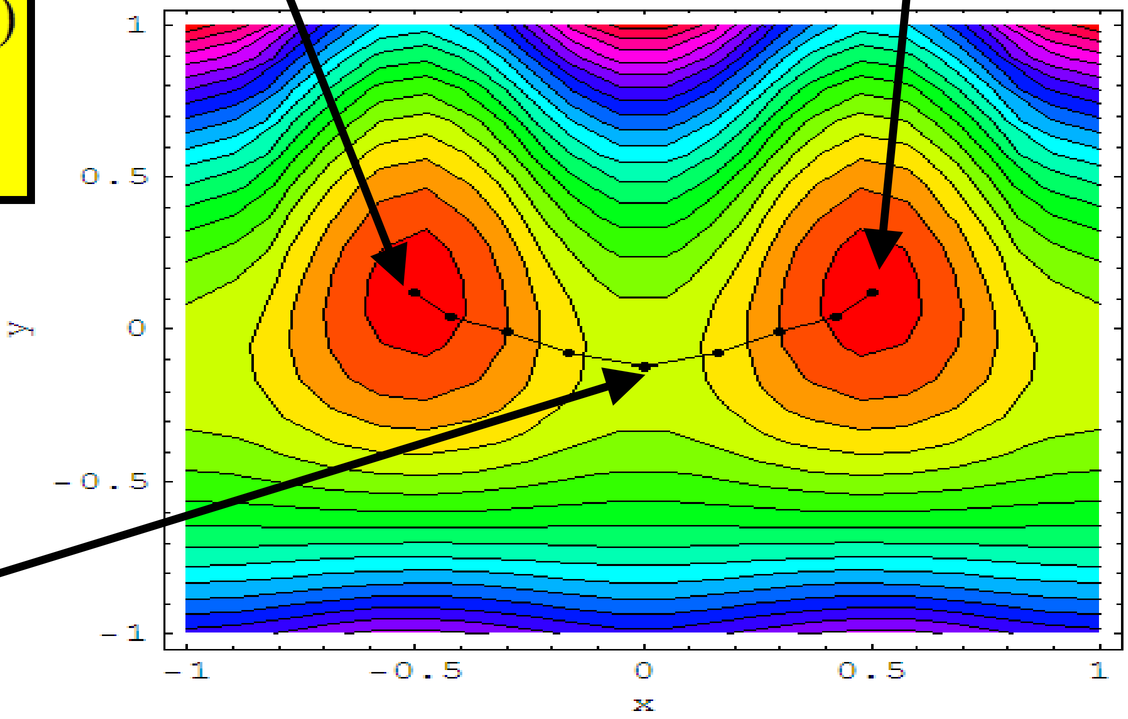
Harmonic Transition-State Theory

G. Henkelman, G. Jóhannesson, and H. Jónsson,
in *Progress on Theoretical Chemistry and Physics*,
(Kluwer Academic Publishers, 2000).

$$k_{TST} = \underbrace{\frac{\prod_{j=1}^{3N} \nu_j}{\prod_{j=1}^{3N-1} \nu_j^{*}}} \exp(-E_0 / k_B T)$$

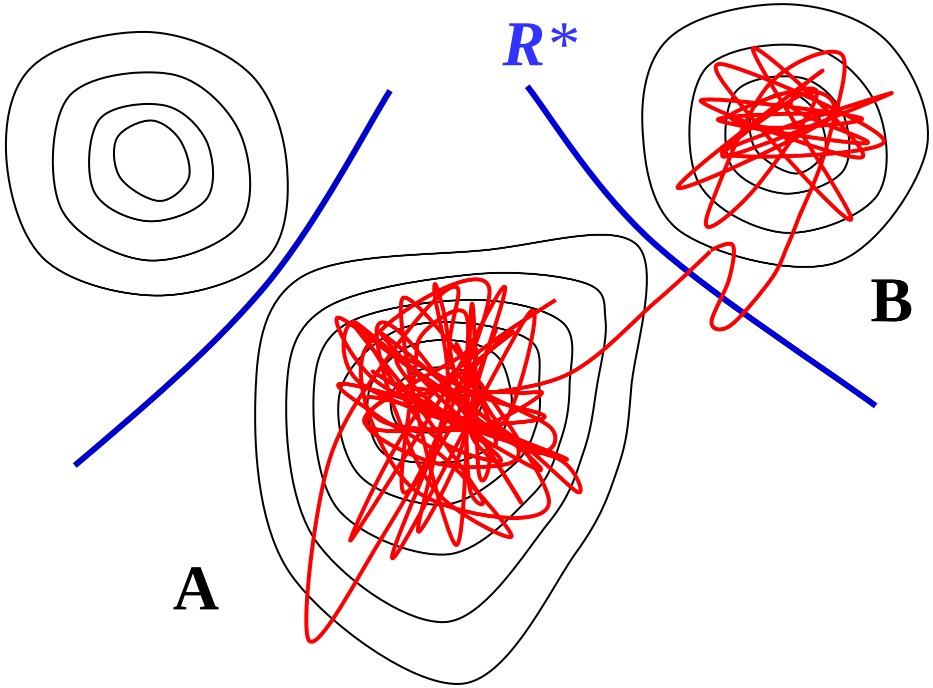
10^{12} - 10^{13} s^{-1}
is a good estimate!

Potential-Energy Minima



Saddle Point

The Accelerated MD Concept



If We Could Run MD Simulations Indefinitely, We Would Model the Exact Dynamical Behavior…

Can We Make MD Simulations to Run Faster??

Accelerated MD

Courtesy:

Dr. Art Voter, *LANL*

Prof. Kristen Fichthorn, *Penn State*

Accelerated MD Methods

Hyper dynamics

- A. Voter, *J. Chem. Phys.* **106**, 11 (1997).
- A. Voter, *Phys. Rev. Lett.* **78**, 3908 (1997).
- M. Steiner, P.-A. Genilloud, & J. Wilkins, *Phys. Rev. B* **57**, 10236 (1998).
- R. Miron & K. Fichthorn *J. Chem. Phys.* **119**, 6210 (2003).

Parallel Replica Dynamics

- A. Voter, *Phys. Rev. B* **57**, R13985 (1998).

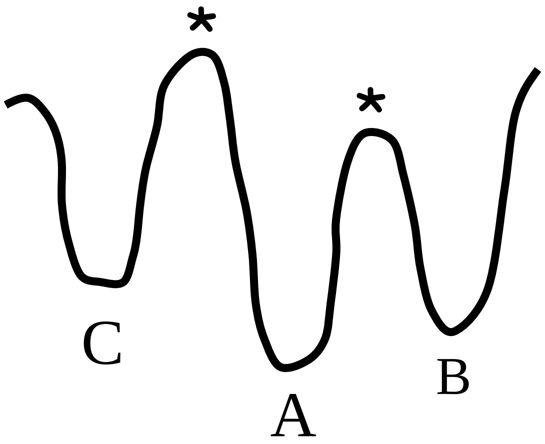
Temperature Accelerated Dynamics

- M. Sorensen & A. Voter, *J. Chem. Phys.* **112**, 9599 (2000).

Hyper dynamics

A. Voter, *J. Chem. Phys.* **106**, 11 (1997).

$$k_{TST,A\rightarrow B}=\nu\frac{\int_A \delta(\mathbf{R}-\mathbf{R}^*)\exp(-V(\mathbf{R})/k_BT)}{\int_A \exp(-V(\mathbf{R})/k_BT)}$$

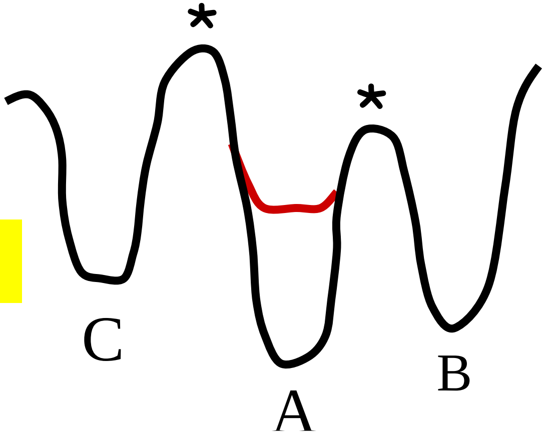


$$k_{TST}=\nu\frac{\int \delta(\mathbf{R}-\mathbf{R}^*)W(\mathbf{R})\exp(-V(\mathbf{R})/k_BT)/W(\mathbf{R})}{\int W(\mathbf{R})\exp(-V(\mathbf{R})/k_BT)/W(\mathbf{R})}$$

$$W(\mathbf{R})=\exp\left(\frac{V(\mathbf{R})-V(\mathbf{R})}{k_BT}\right)$$

$$k_{TST}=\quad k_{TST}/\langle 1/W(\mathbf{R})\rangle$$

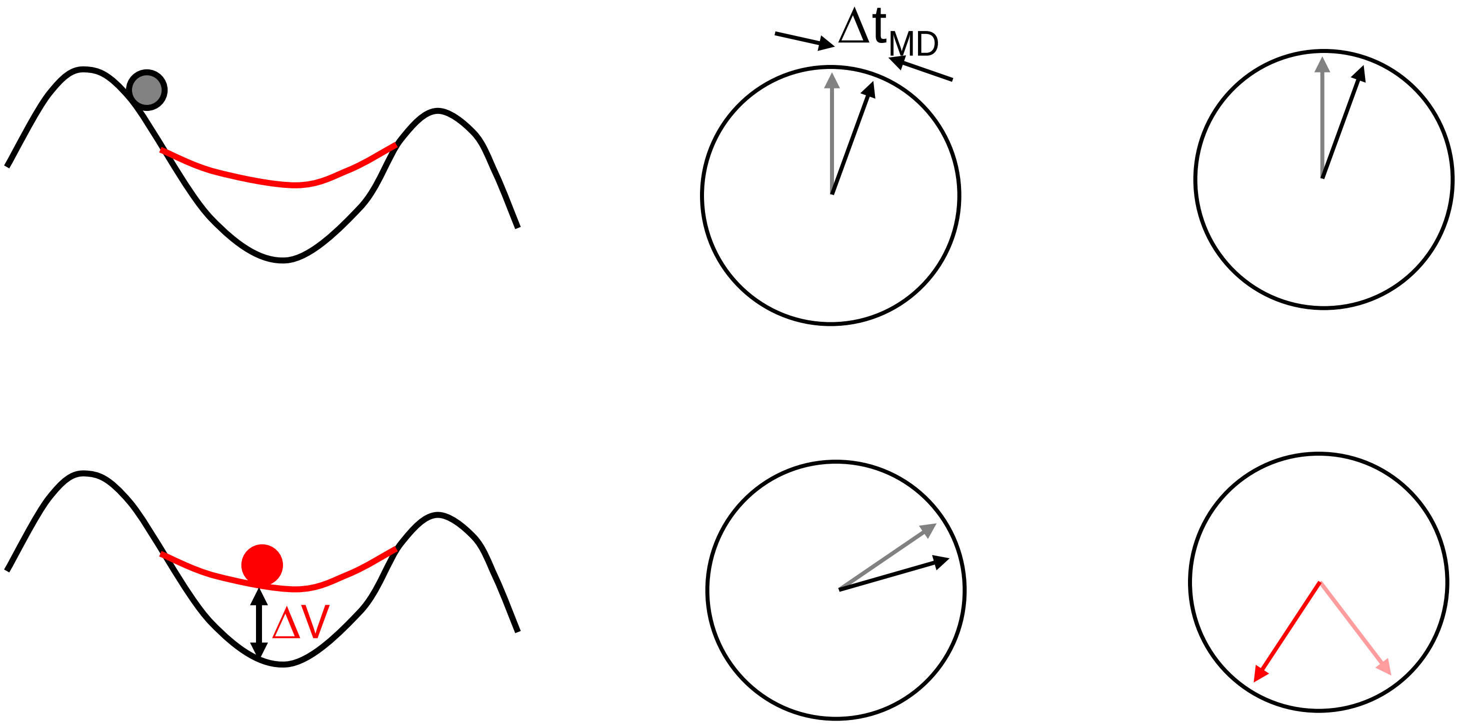
Detailed Balance!



G. Torrie & J. Valleau, *Chem. Phys. Lett.* **28**, 578 (1974).
E. Grimmelmann, J. Tully & E. Helfand, *J. Chem. Phys.* **74**, 5300 (1981).

The Hyper time Clock

System Coordinate | MD Clock | Hyper time Clock



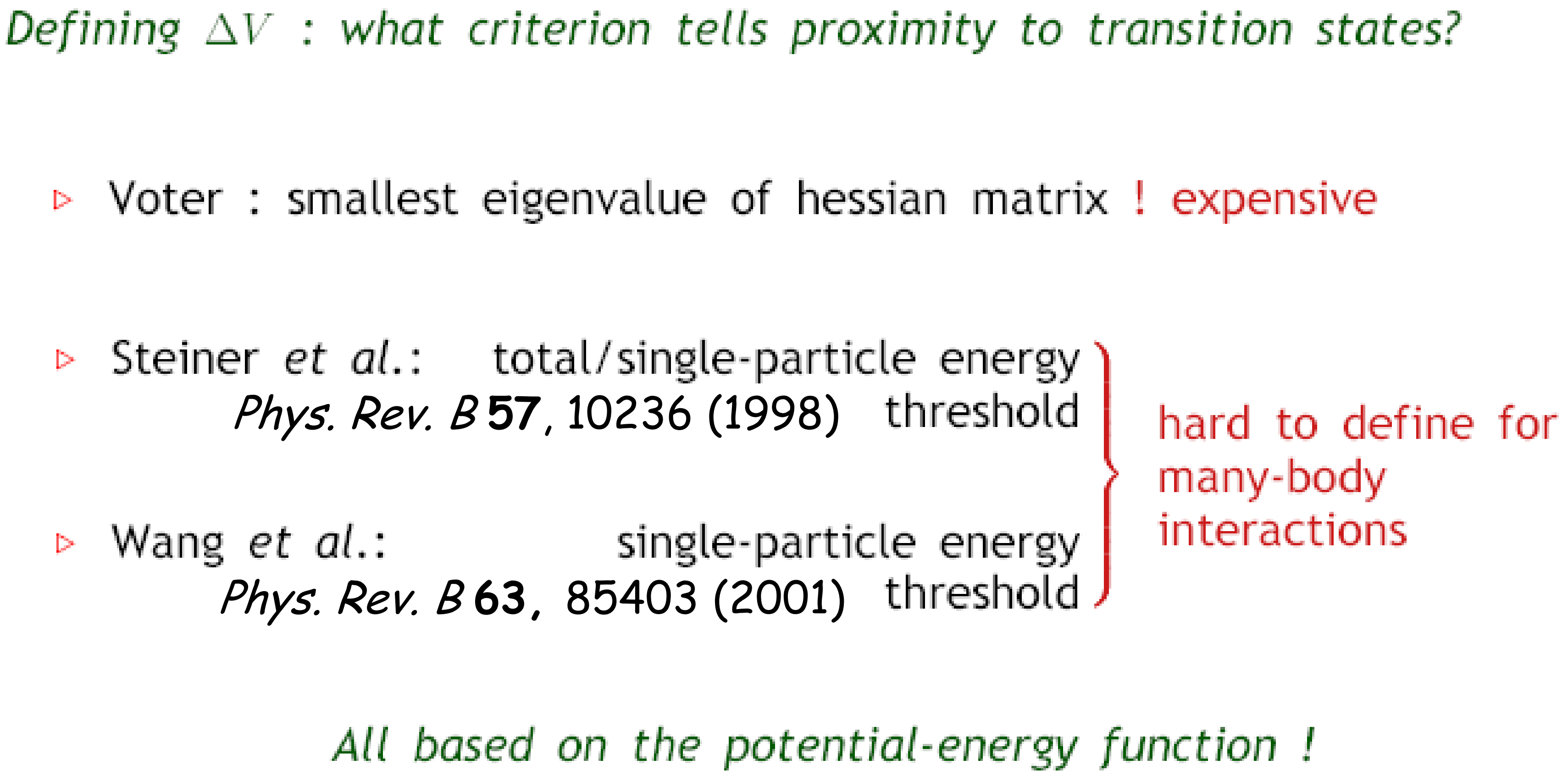
Boost = Hyper time/(MD clock time)

$\Delta t_{hyper} = \Delta t_{MD}\, e^{\Delta V/kT}$

Hyper dynamics Challenges…..

Accelerated dynamics: implementations

How to select ΔV so that in Proximity to Transition States



Defining ΔV : what criterion tells proximity to transition states?

- Voter : smallest eigenvalue of hessian matrix ! expensive
- Steiner *et al.*: total/single-particle energy threshold
  Phys. Rev. B **57**, 10236 (1998)
- Wang *et al.*: single-particle energy threshold
  Phys. Rev. B **63**, 85403 (2001)

hard to define for many-body interactions

All based on the potential-energy function !

Not Generally Transferrable to Entropic Transitions – but Possible

Accelerated Molecular Dynamics The Bond Boost Method

Accelerated dynamics: the Bond-Boost method

(Miron, Fichthorn *J.Chem.Phys.* **119**, 2003)

- Local minima defined by

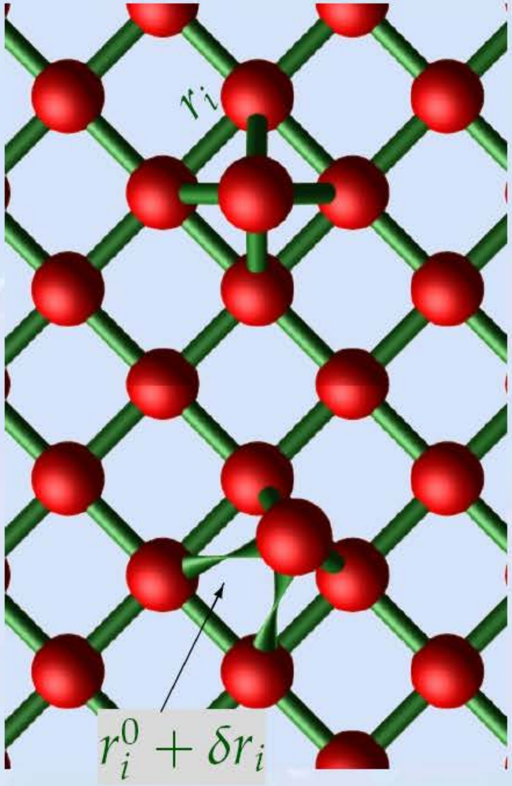
  bond lengths: $\{r_i^0\}_{i=1 \ldots N}$

- Transitions occur via

  bond breaking: $\max\limits_i \left| \frac{\delta r_i}{r_i^0} \right| > q$

  empirical threshold

- Define bias potential



$$\Delta V\{x\} \sim A\{r_i\} \sum_{i=1}^{N} \delta V(r_i)$$

envelope boost-per-bond

Accelerated Molecular Dynamics

Details of the Bond Boost Method

Accelerated dynamics: the Bond-Boost method

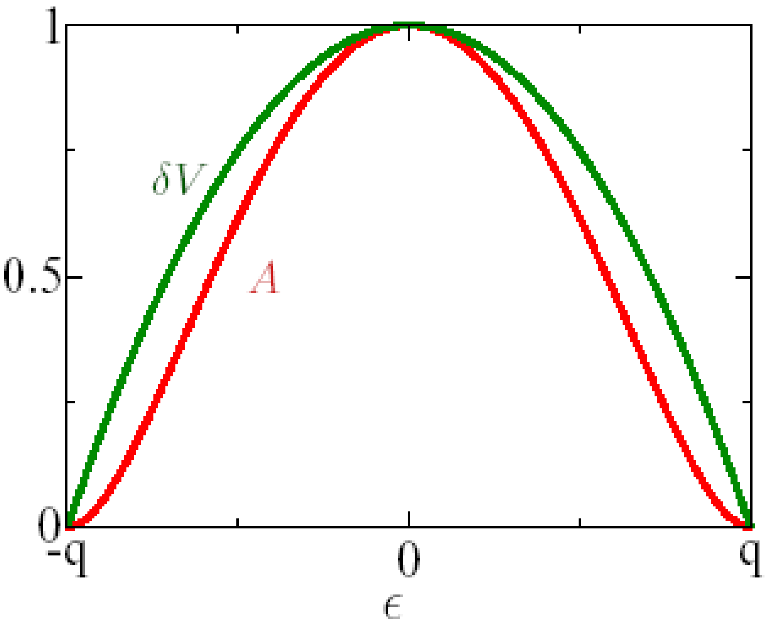
Bias potential has empirical form

$$\Delta V\{r_i\} = \frac{\Delta V^{max}}{N} A(\epsilon_{max}) \sum_{i=1}^{N} \delta V(\epsilon_i) \qquad , \qquad \epsilon_i = \frac{\delta r_i}{r_i^0}$$

Sample choice of functions:

$$\delta V(\epsilon) = 1 - \left(\frac{\epsilon}{q}\right)^2$$

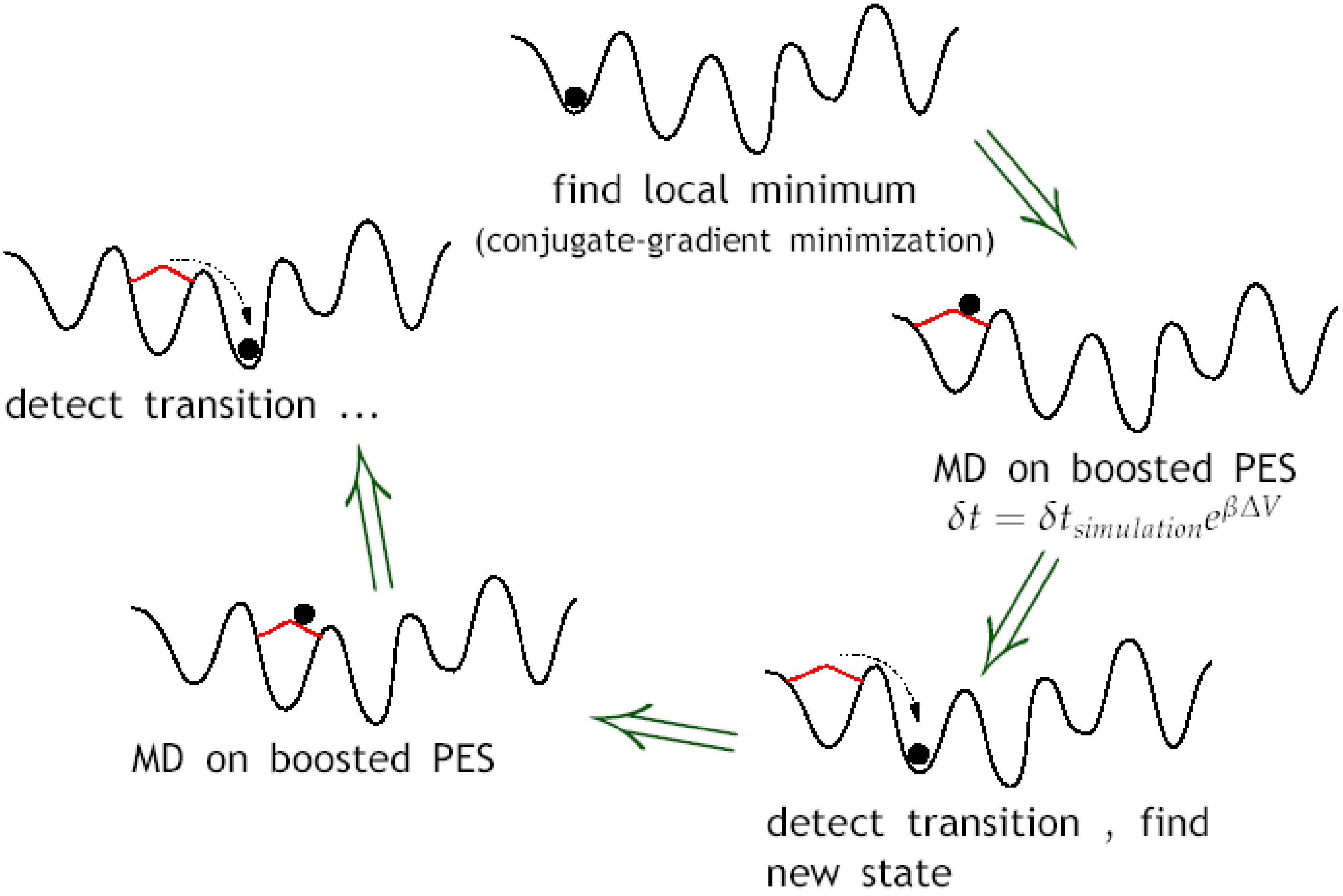
$$A(\epsilon_{max}) = \left[1 - \left(\frac{\epsilon_{max}}{q}\right)^2\right] \times \text{smoothing factor}$$



Overview of the Bond Boost Method

Accelerated dynamics: the Bond-Boost method

(Miron, Fichthorn *J.Chem.Phys.* **119**, 2003)



find local minimum

(conjugate-gradient minimization)

MD on boosted PES

$\delta t = \delta t_{simulation} e^{\beta \Delta V}$

detect transition , find new state

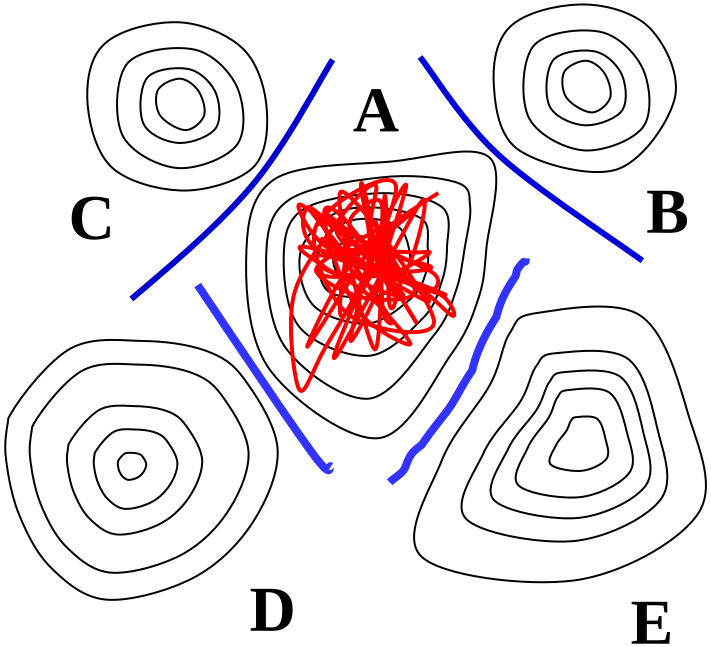
MD on boosted PES

detect transition ...

Parallel Replica Dynamics

A. Voter, *Phys. Rev. B* **57**, R13985 (1998).
Cited as of 02/01/12: 174

General Rare-Event System with Various Possible First-Order Rate Processes



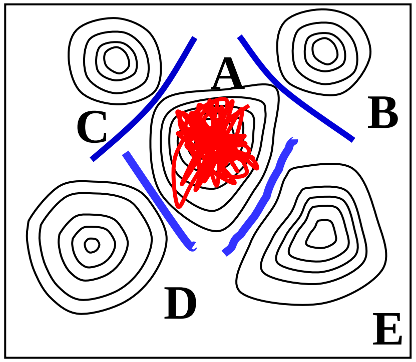
$$k_{tot} = \sum_i k_{A \to i}$$

$$p(t) = k_{tot} e^{-k_{tot} t}$$

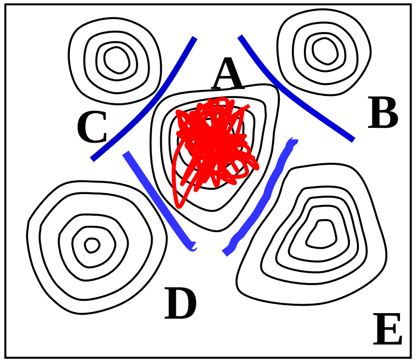
A Poisson Process

Parallel Replica Dynamics

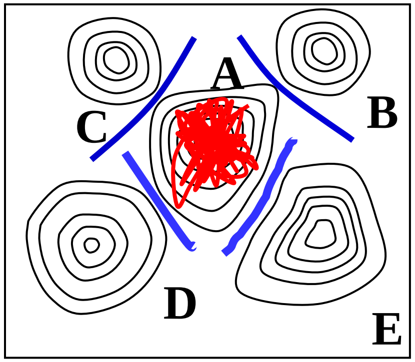
Make **N Replicas** of the System, Place Each Replica on a Different Processor



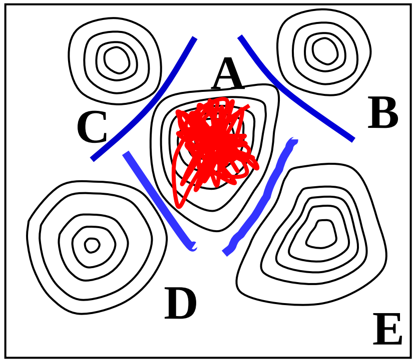
k_{tot}



k_{tot}



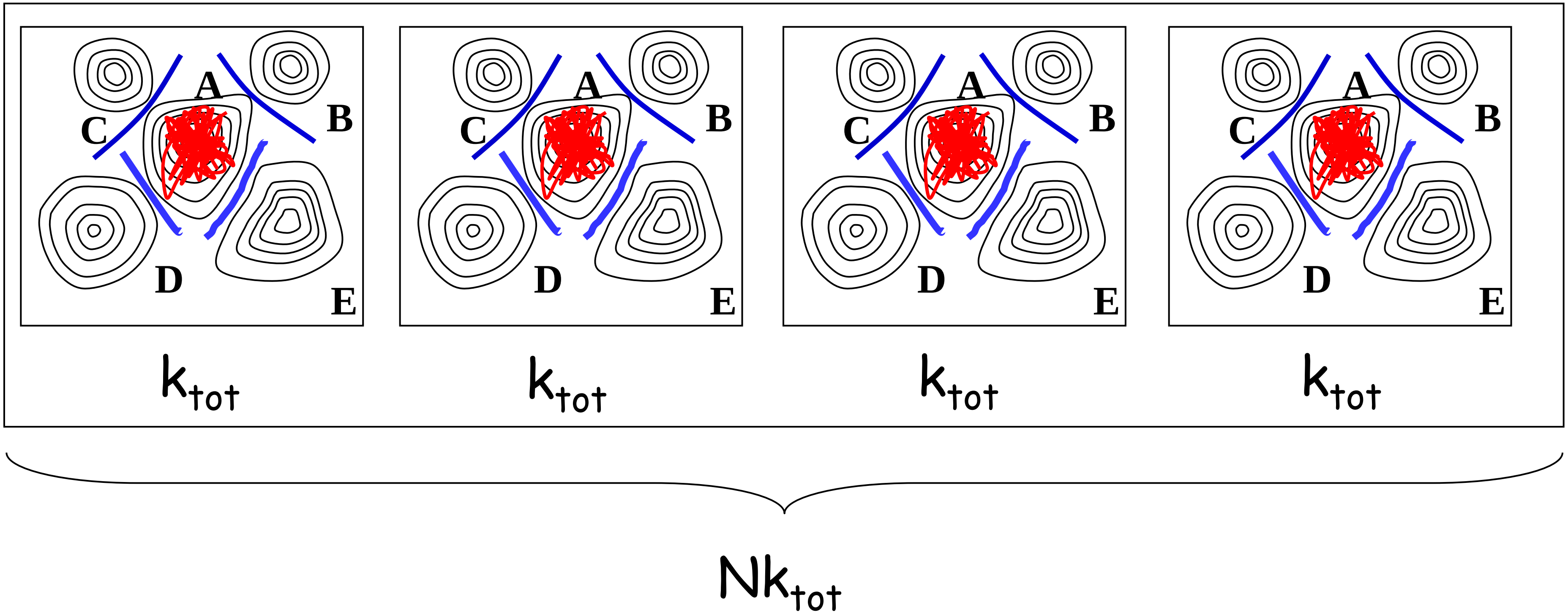
k_{tot}



k_{tot}

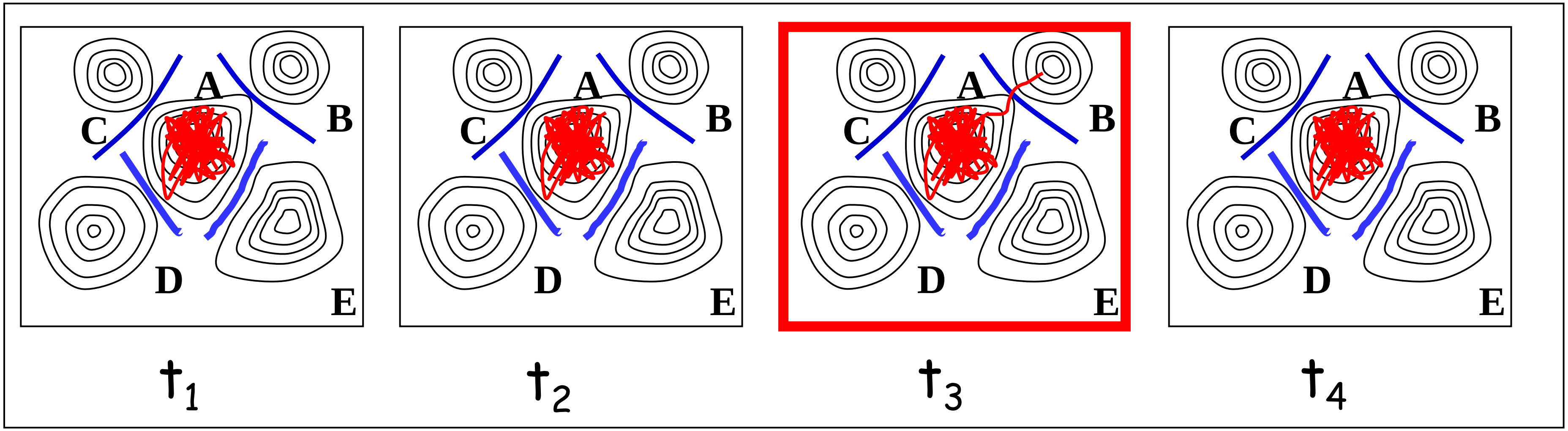
Parallel Replica Dynamics

The N Replicas Now Make One Big System and the Total Escape Rate is Nk_{tot} ($-r_A=k_{tot}N$), with $p(t)=Nk_{tot}e^{-Nk_{tot}t}$



Parallel Replica Dynamics

Wait Until a Transition Occurs at Time t_i on Processor i…

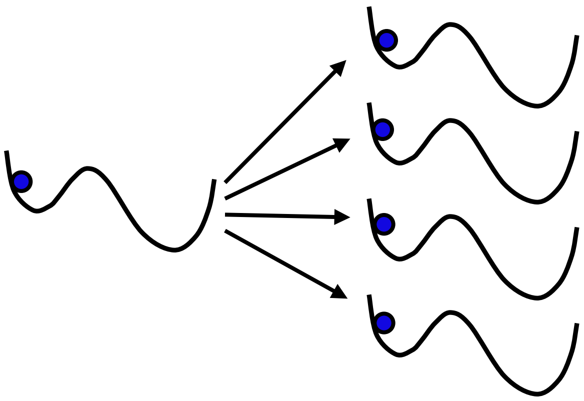


The Time is Incremented by $\Sigma t_i \approx N t_3$

With N Processors, the First Transition Time is t_1/N Faster…

Parallel Replica Dynamics Procedure

Replicate entire system on each of M processors.

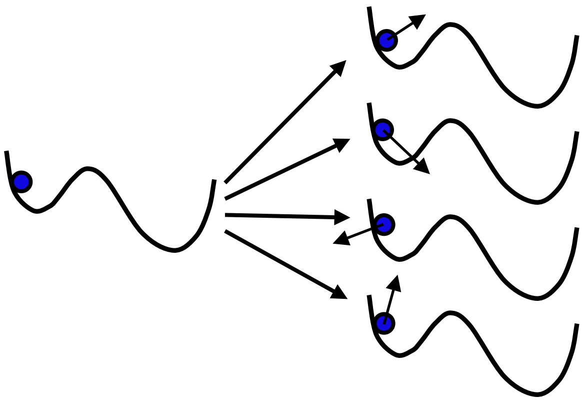


Slide Courtesy of Art Voter

Los Alamos

Parallel Replica Dynamics Procedure

Randomize momenta independently on each processor.

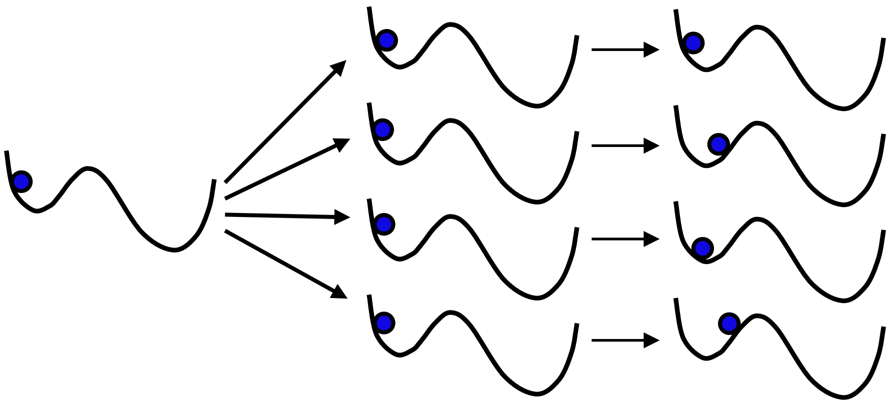


Slide Courtesy of Art Voter

Los Alamos

Parallel Replica Dynamics Procedure

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

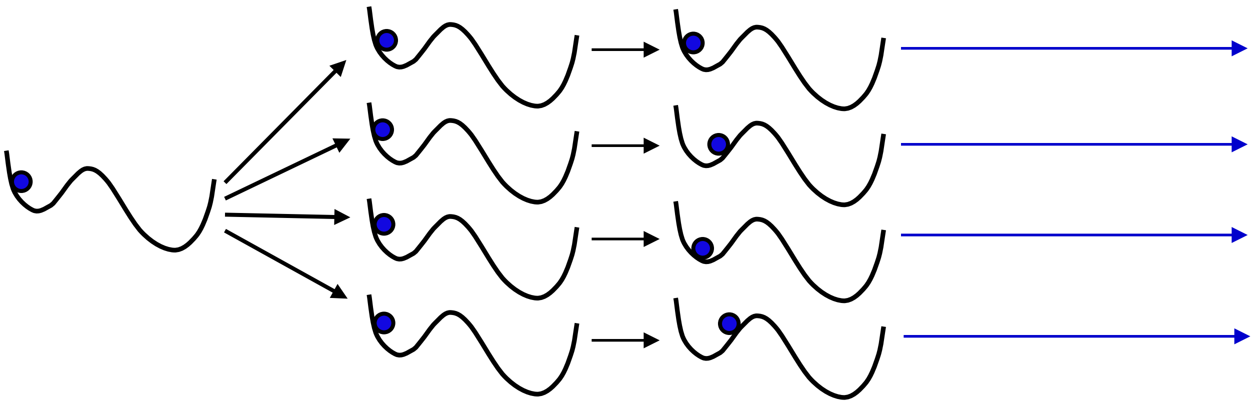


Slide Courtesy of Art Voter

Los Alamos

Parallel Replica Dynamics Procedure

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

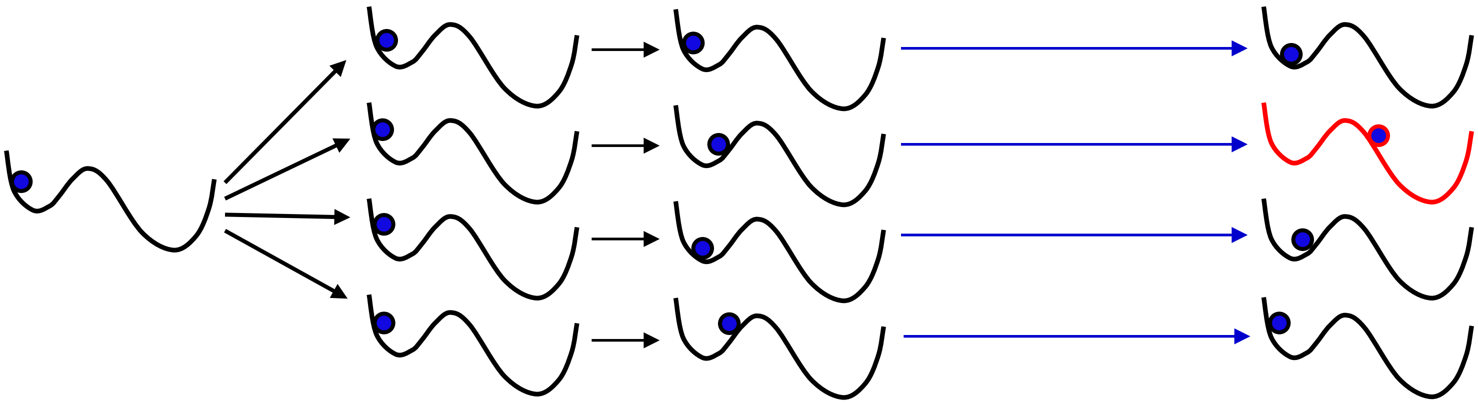


Slide Courtesy of Art Voter

Los Alamos

Parallel Replica Dynamics Procedure

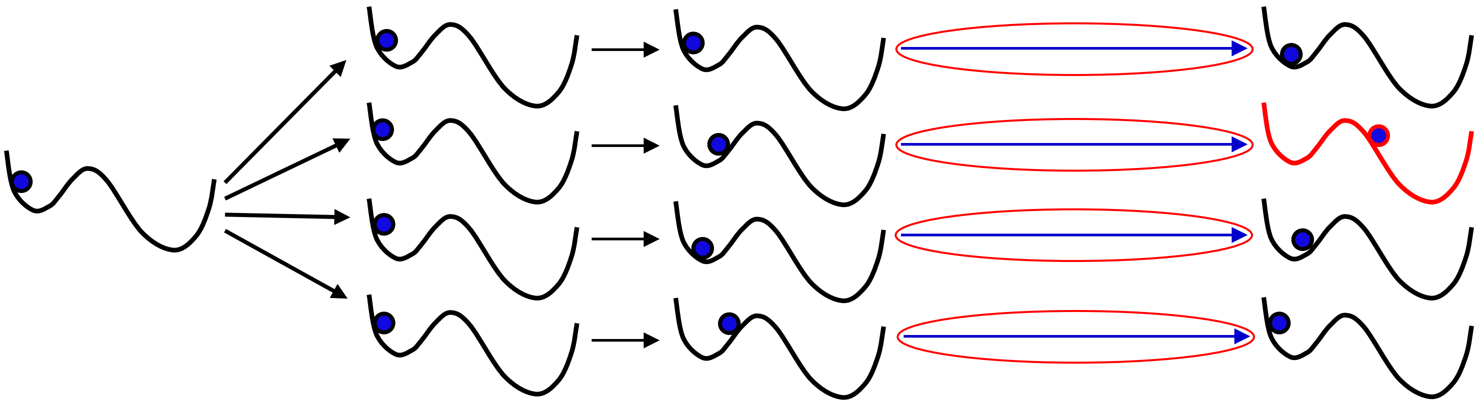
Stop all trajectories when first transition occurs on *any* processor.



Slide Courtesy of Art Voter

Parallel Replica Dynamics Procedure

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

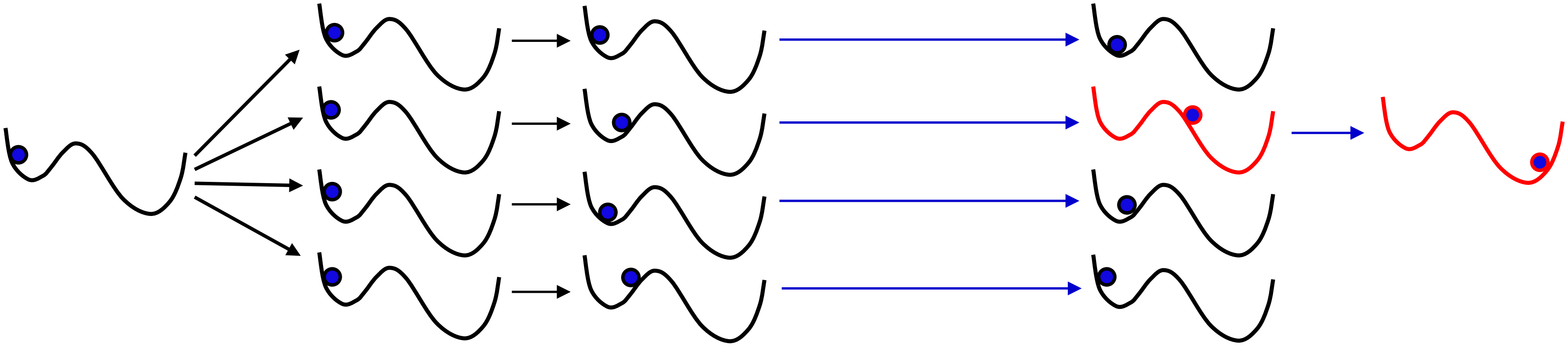


Slide Courtesy of Art Voter

Los Alamos

Parallel Replica Dynamics Procedure

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



Slide Courtesy of Art Voter

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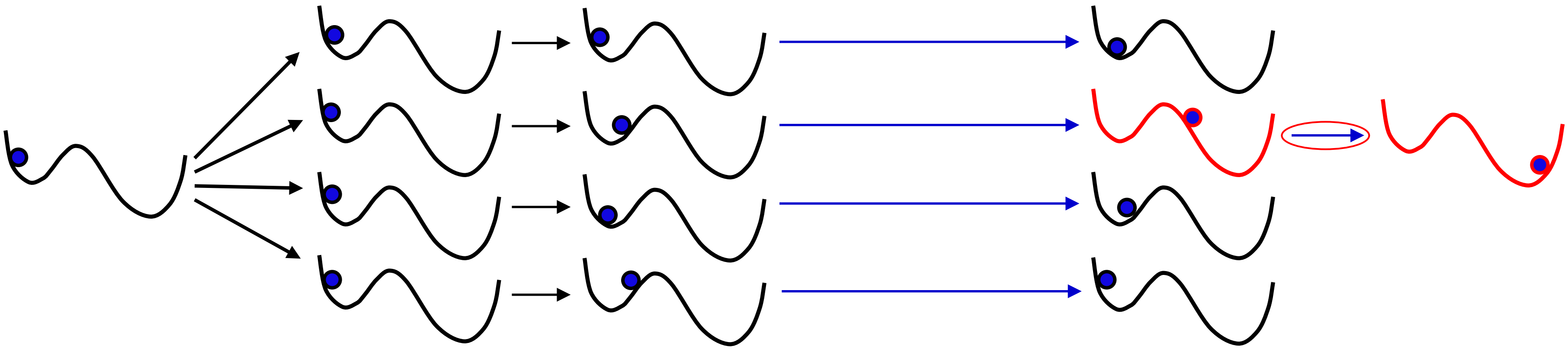
Parallel Replica Dynamics Procedure

Advance simulation clock by τ_{corr}.

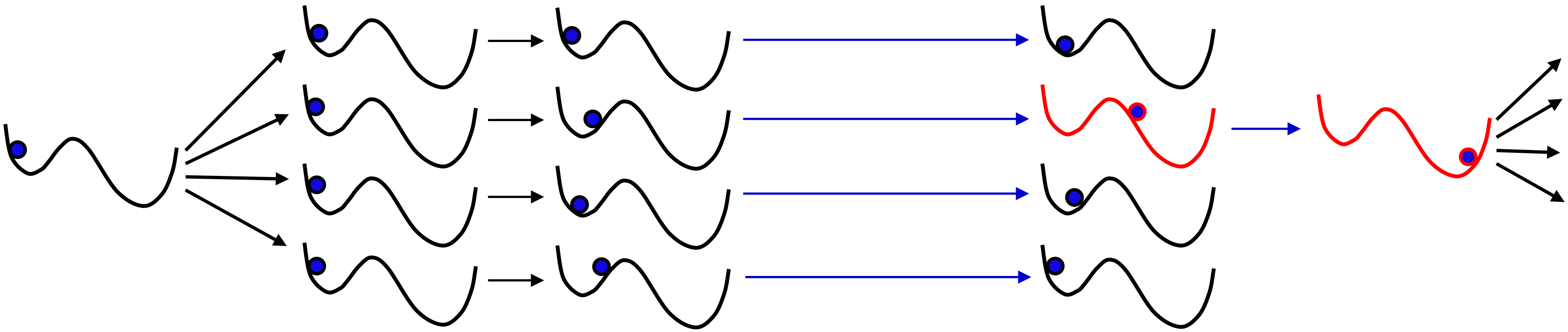


Slide Courtesy of Art Voter

Los Alamos

Parallel Replica Dynamics Procedure

Replicate the new state and begin procedure again.



Slide Courtesy of Art Voter

Los Alamos

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.

Assumptions:

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

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

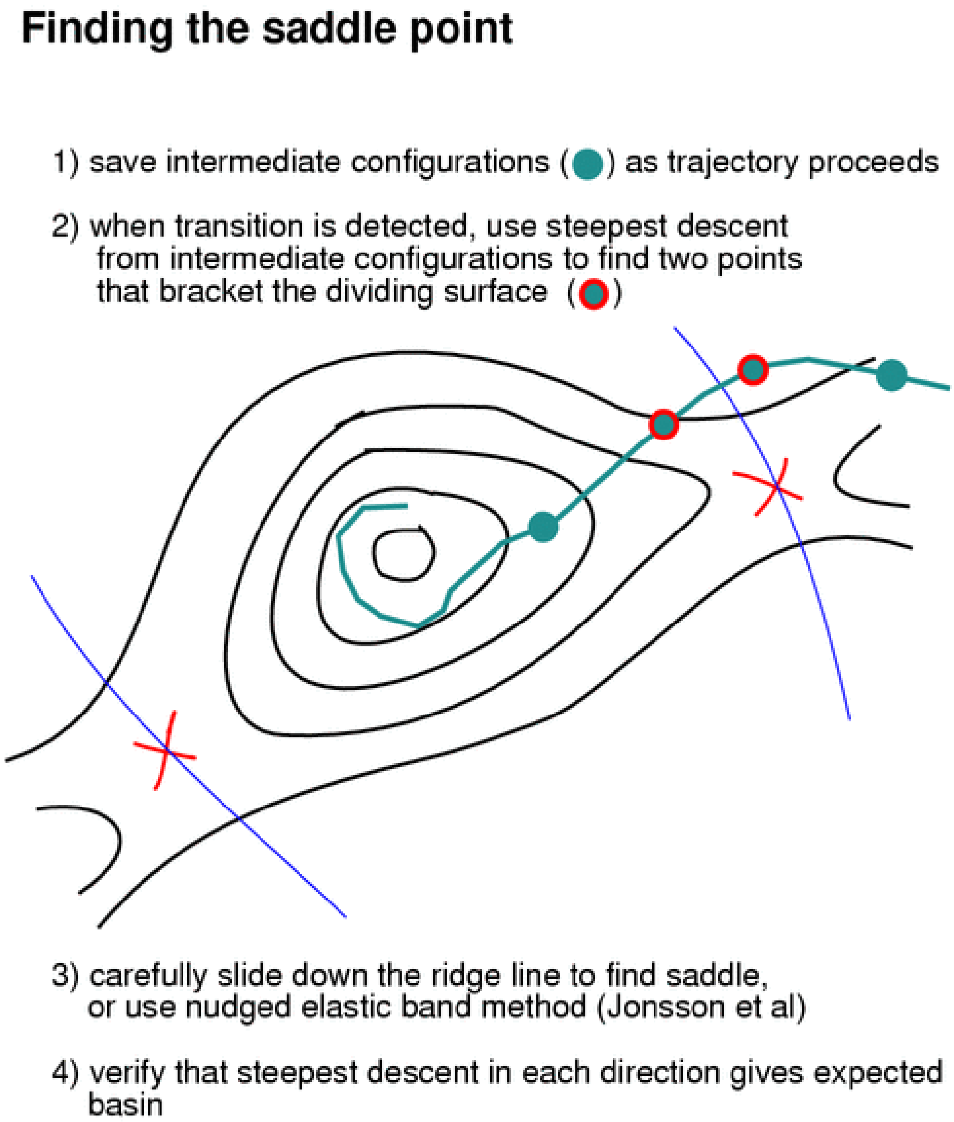
- all preexponentials (ν_0) are greater than ν_{min}

[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.

Finding the saddle point



Finding the saddle point

1) save intermediate configurations (●) as trajectory proceeds

2) when transition is detected, use steepest descent from intermediate configurations to find two points that bracket the dividing surface (◉)

3) carefully slide down the ridge line to find saddle, or use nudged elastic band method (Jonsson et al)

4) verify that steepest descent in each direction gives expected basin

TAD temperature-extrapolated time

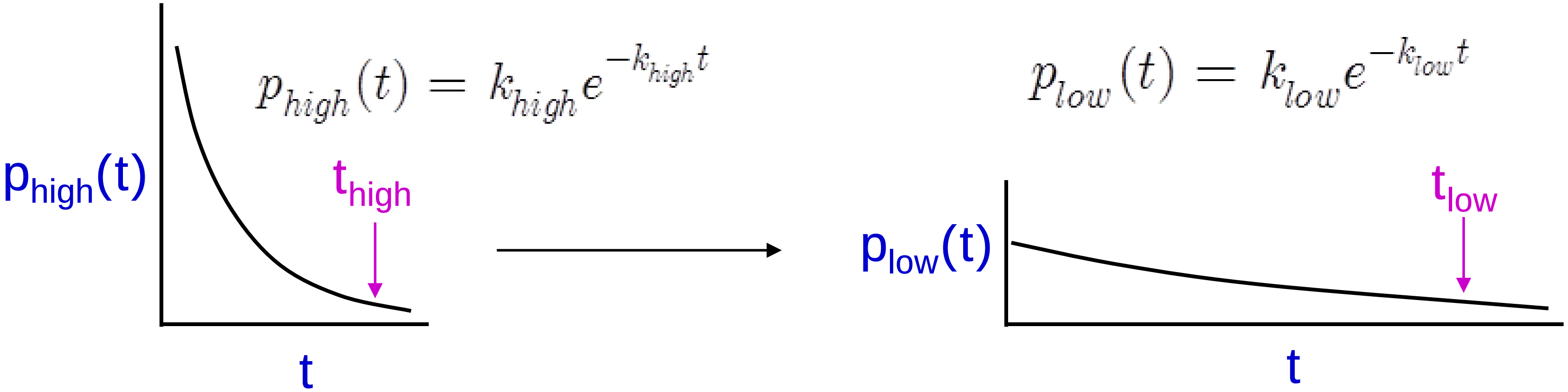
Because each rate is assumed to be Arrhenius,

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

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

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

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

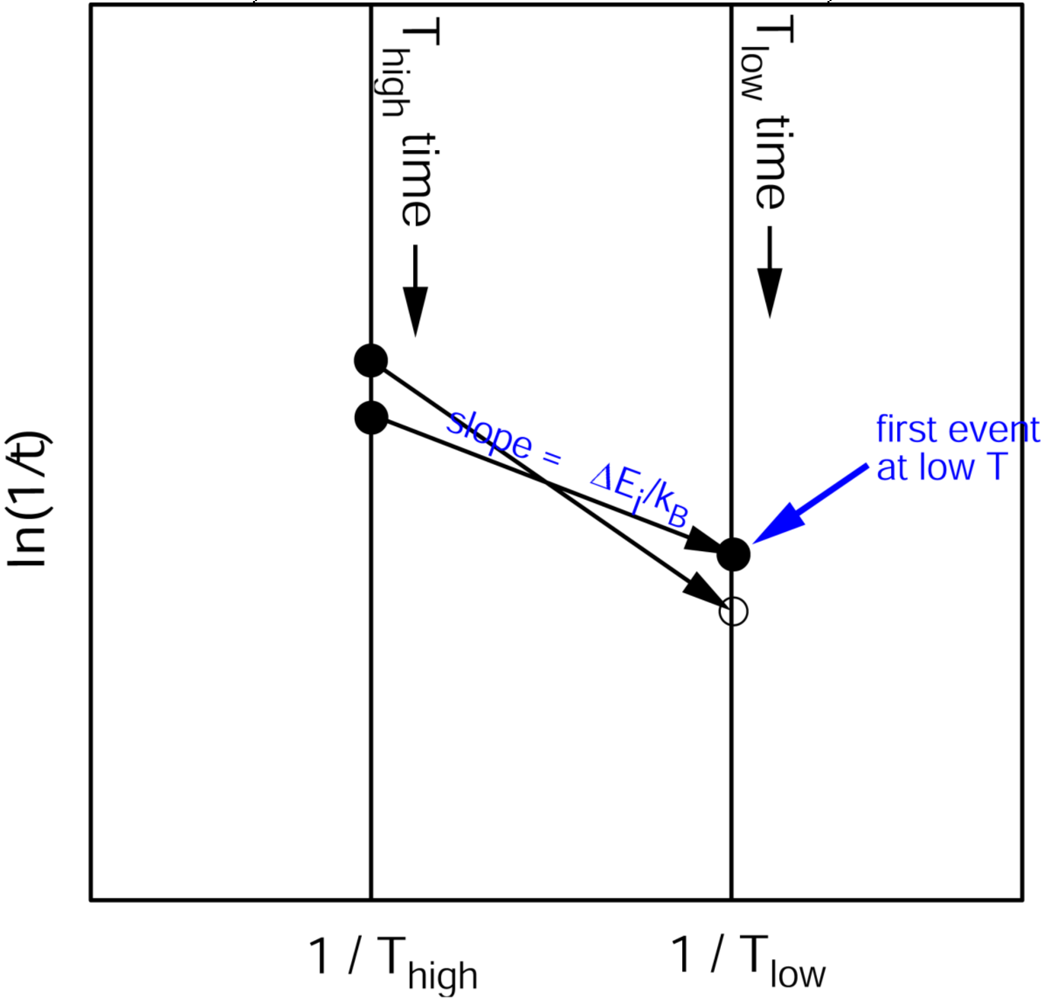


$$p_{high}(t) = k_{high} e^{-k_{high} t}$$

$$p_{low}(t) = k_{low} e^{-k_{low} t}$$

The Arrhenius view

$$\ln(1/t) = \ln(k) = \ln \nu_0 - \Delta E / k_B T$$



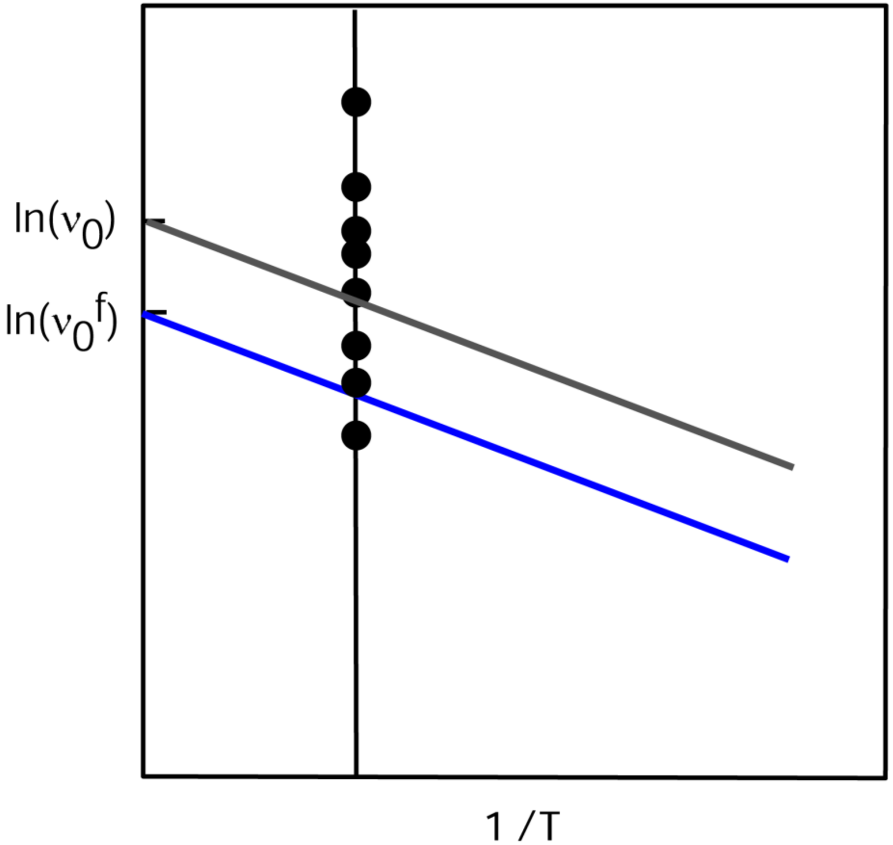
When can we stop the simulation? The confidence line

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

$$\tau_i^f = (1/k_i)\ \ln[1/(1-f)]$$

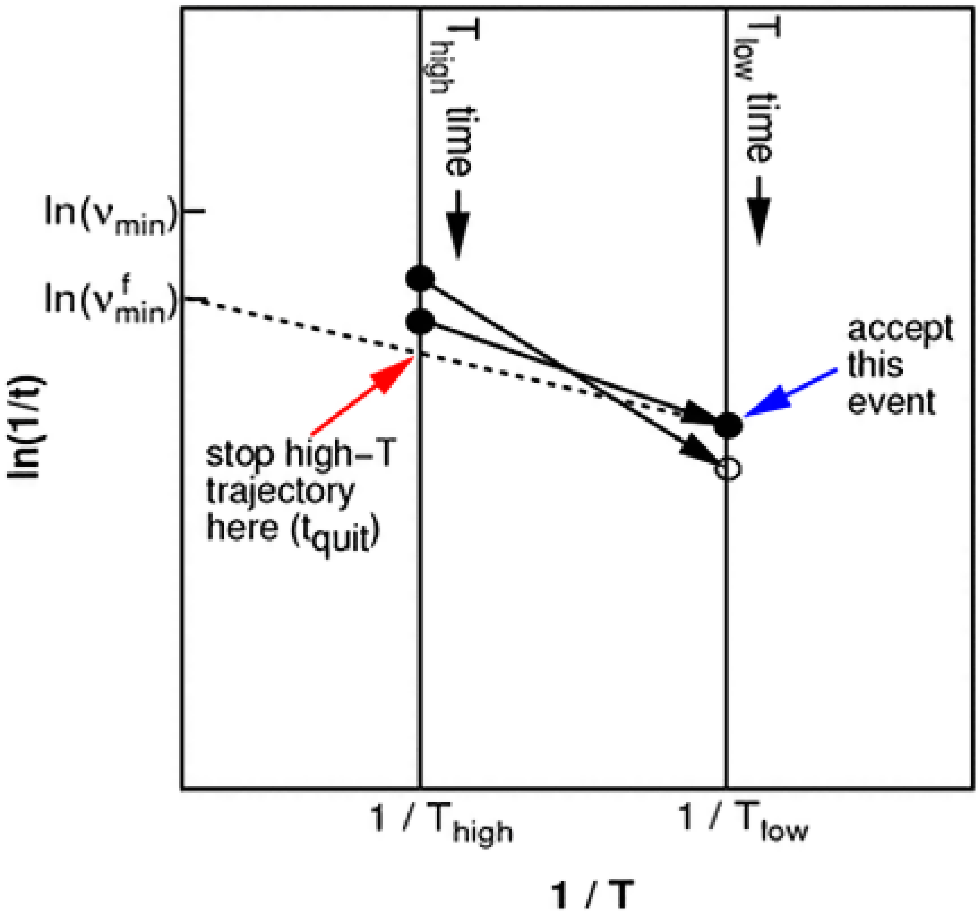
(or $\delta = 1-f$)

If rate is Arrhenius ($k = \nu_0 \exp[-\Delta E/k_B T]$), then fraction f of first attempts will occur *above* the line with slope $-\Delta E/k_B$ and intercept $\nu_0^f = \nu_0/\ln[1/(1-f)]$



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

TAD – the big picture



- after time t_{quit}, with confidence f, no new event can replace the first low–T event ($\nu^{f}_{min} = \nu_{min}/\ln[1/(1-f)]$).
- move along first–event pathway to new basin, start again.
- exact dynamics, assuming harmonic TST, ν_{min}, confidence f

Kinectic Monte Carlo (Coarse-Grained MD)

Kinetic Monte Carlo

Know locally stable states of a system

Know kinetic mechanism to move between different states (e.g. hopping of atoms along a particular trajectory)

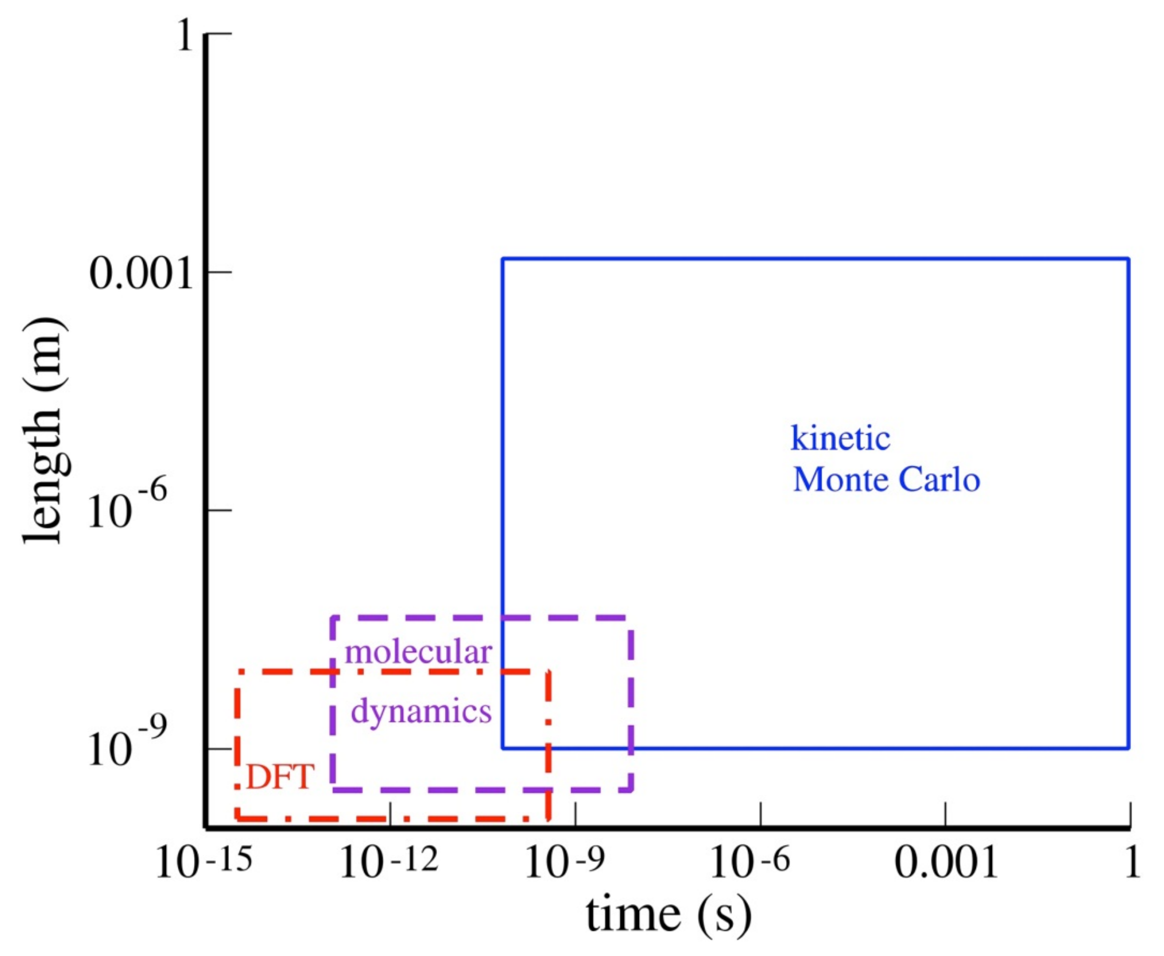
Perform Monte Carlo simulation over possible states with transition rates similar to the “real” transition rates

Methods to find transition states:

- Accelerated MD methods
- Elastic band
- others

Why KMC?

KMC is designed to simulate the evolution of **non-equilibrium systems** in macroscopic length scales and time scales.



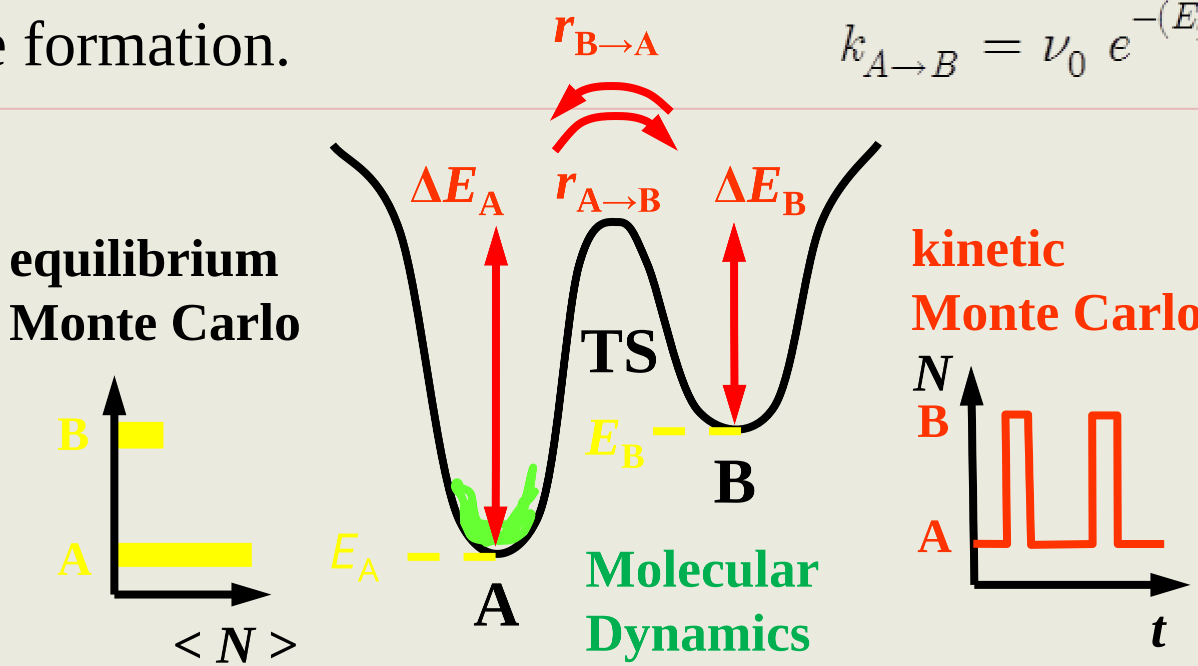
MC and kMC

- Metropolis Monte Carlo

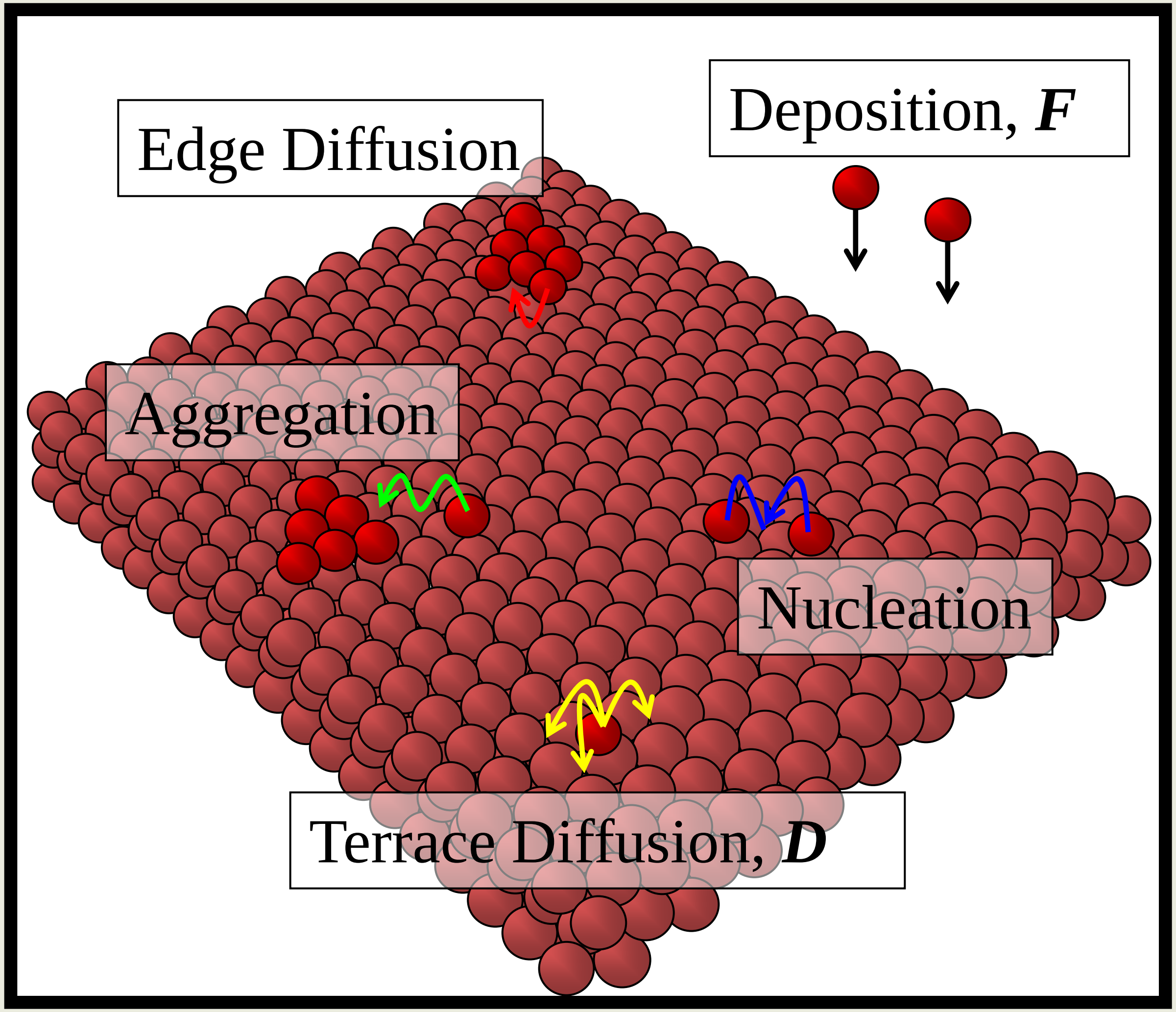
Rate determined by energy difference between initial and final states. Efficient for free energy minimization (thermodynamic equilibrium) $k_{A\to B} = \nu_0 \, e^{-(E_B - E_A)/k_B T}$

- Kinetic Monte Carlo

Rate determined by activation energy barrier. Use for meta-stable structure formation. $k_{A\to B} = \nu_0 \, e^{-(E_{TS} - E_A)/k_B T}$

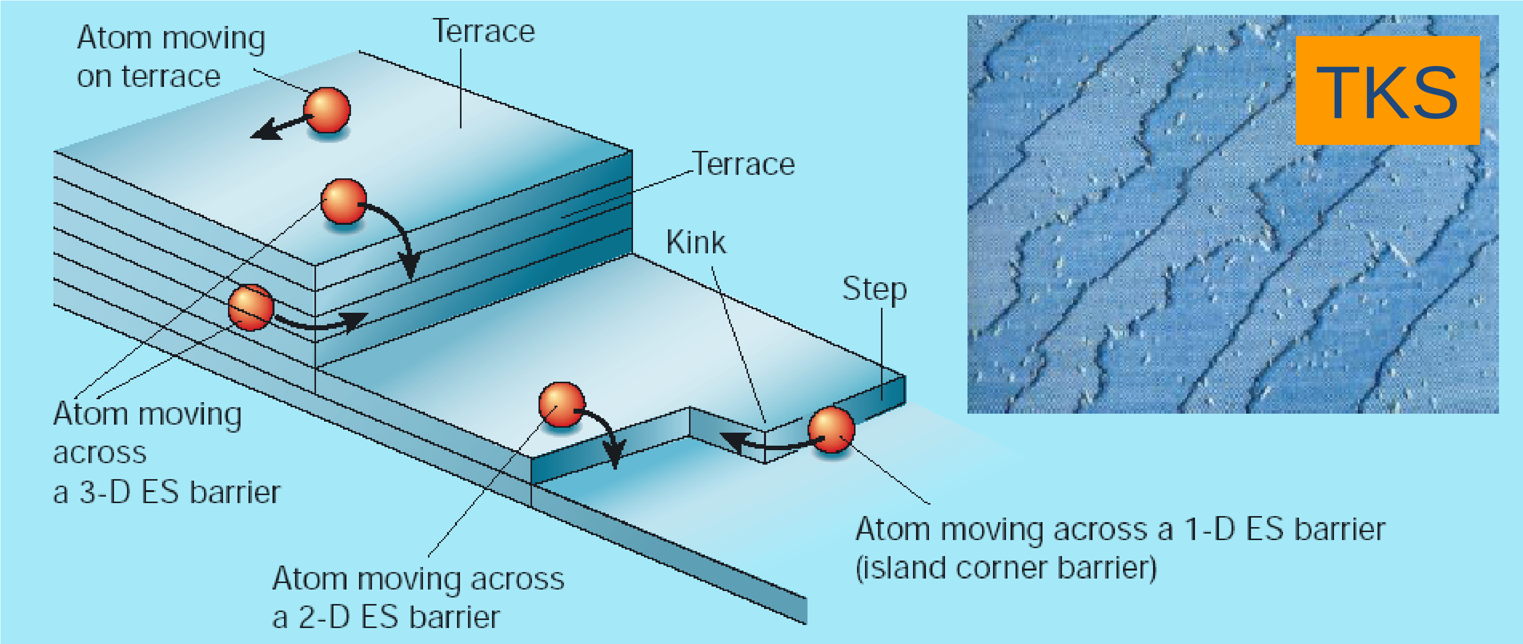


Important Atomic Rate Processes in Thin Film Growth



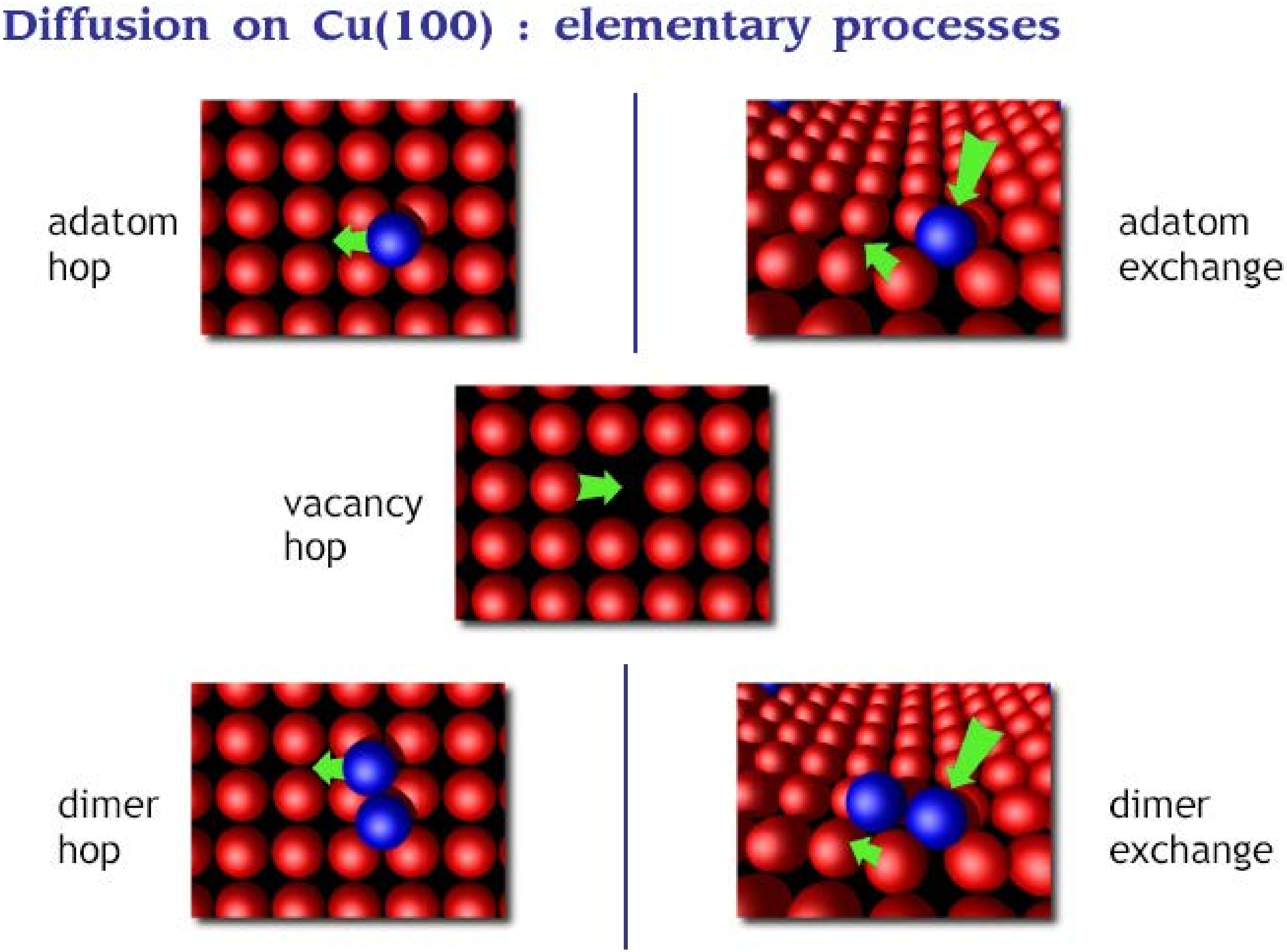
K. Fichthorn *et al.*, *Appl. Phys. A* **75**, 17 (2002).

Important Atomic Rate Processes in Thin Film Growth



Terrace-Step-Kink Model of Surface: *Burton, Cabrera, Frank (1951)*
STM confirmation: *Swartzentruber, et al., Phys Rev Lett (1989)*
Important Atomic Rate Processes: *Lagally & Zhang, Nature (2002)*

Important Elementary Processes of Adatom Diffusion on Crystal Surface

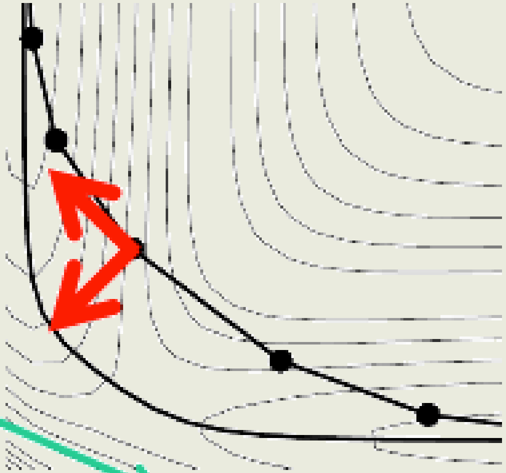

Diffusion on Cu(100) : elementary processes

Nudged Elastic Band (NEB) method

The force can be divided to two contributions:

Parallel force

Perpendicular force



$$S(\mathbf{R}_1, \mathbf{R}_2, \cdots, \mathbf{R}_{P-1}) = \sum_{i=0}^{P} E(\mathbf{R}_i) + \sum_{i=1}^{P} \frac{Pk}{2}(\mathbf{R}_i - \mathbf{R}_{i-1})^2$$

causing non-equidistance distribution of images along the energy pathway.

$$\left(\frac{\partial E(\mathbf{R}_k)}{\partial \mathbf{R}_k}\right)_{\parallel} \quad \boxed{\left(\frac{\partial E(\mathbf{R}_k)}{\partial \mathbf{R}_k}\right)_{\perp}} \quad \boxed{\left(\frac{\partial E_{\text{spring}}}{\partial \mathbf{R}_k}\right)_{\parallel}} \quad \left(\frac{\partial E_{\text{spring}}}{\partial \mathbf{R}_k}\right)_{\perp}$$

causing the drift of energy pathway upward along the perpendicular direction.

To calculate the force, only two terms are taken into account among four contributions.

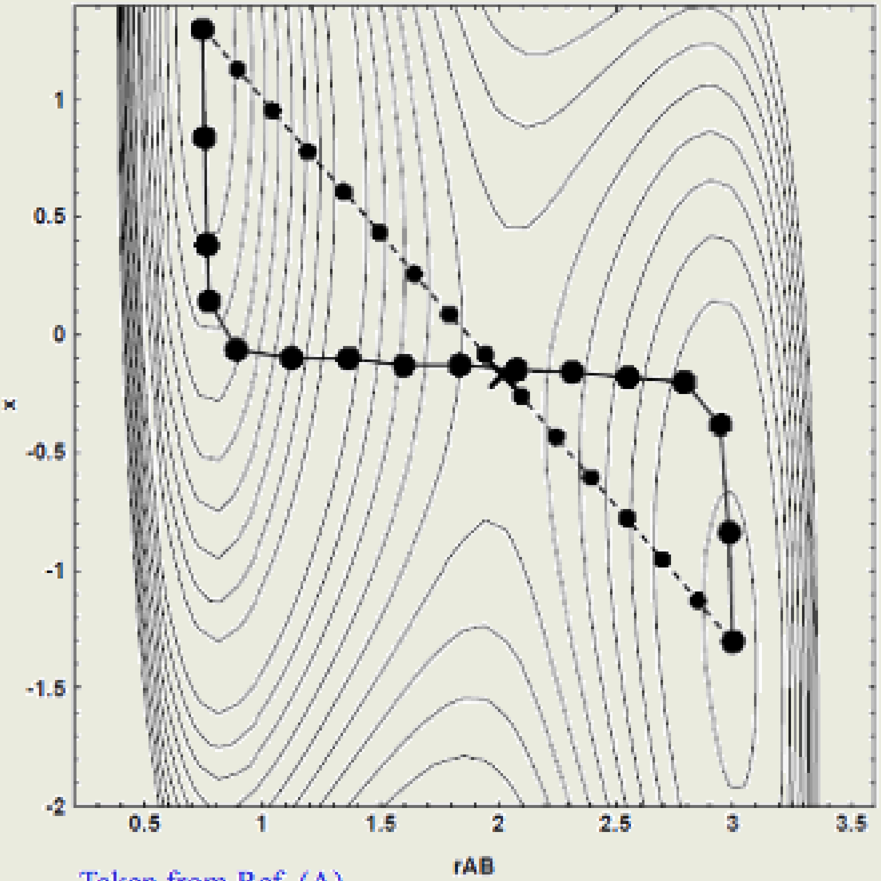
$$\mathbf{F}_k = -\left(\frac{\partial E(\mathbf{R}_k)}{\partial \mathbf{R}_k}\right)_{\perp} - \left(\frac{\partial E_{\text{spring}}}{\partial \mathbf{R}_k}\right)_{\parallel}$$

The treatment allows us to avoid the drift of energy pathway, while the physical meaning of the object function is not clear anymore.

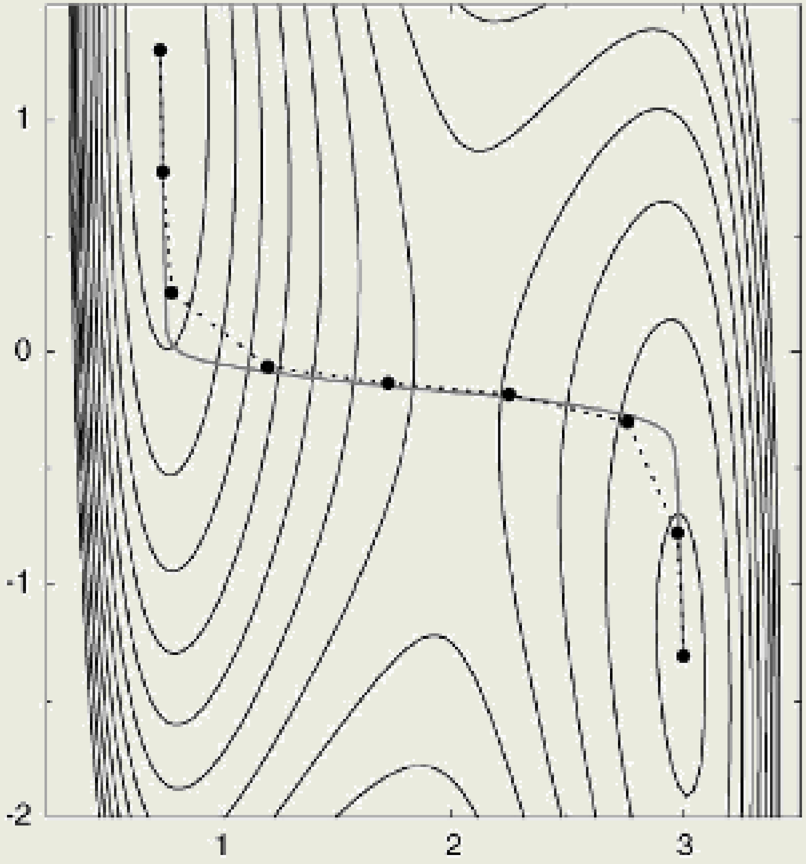
Nudged Elastic Band (NEB) method

The NEB method provides a way to find a minimum energy pathway (MEP) connecting two local minima.

A: NEB; B: improved NEB

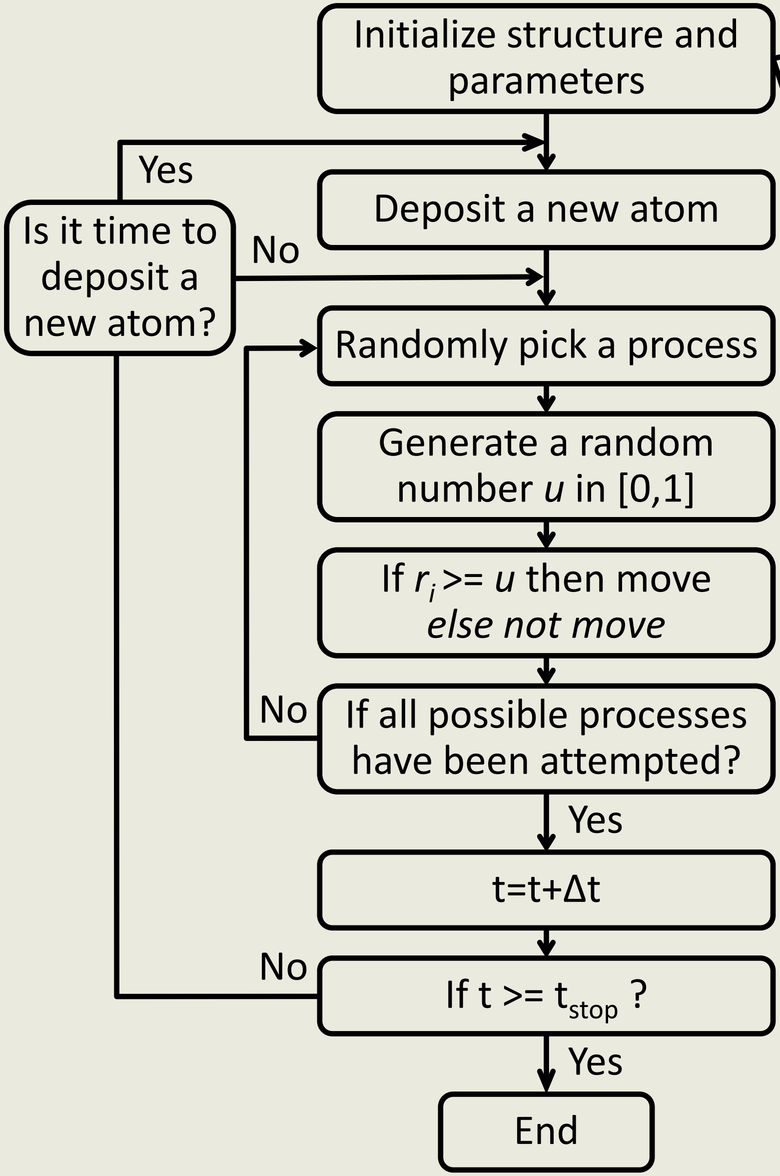


Taken from Ref. (A).



Taken from Ref. (B).

KMC Algorithm I



Initialize structure and parameters

Deposit a new atom

Is it time to deposit a new atom?

Yes

No

Randomly pick a process

Generate a random number *u* in [0,1]

If r_i >= *u* then move *else not move*

If all possible processes have been attempted?

No

Yes

t=t+Δt

If t >= t_{stop} ?

No

Yes

End

<u>Input</u>:

temperature T

deposition rate D

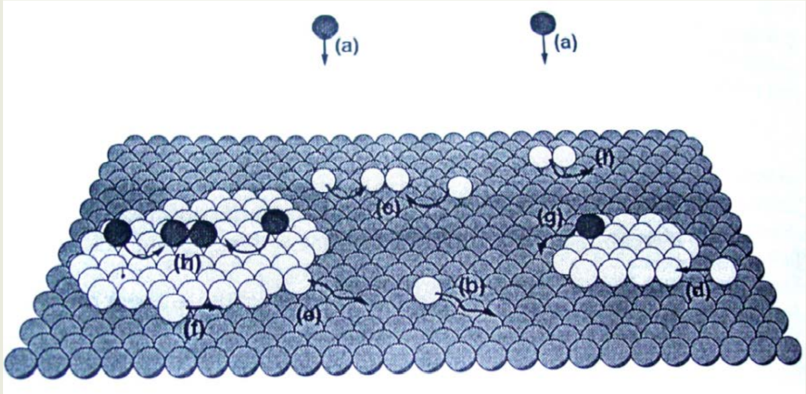
activation barriers E_i

total simulation time t_{stop}

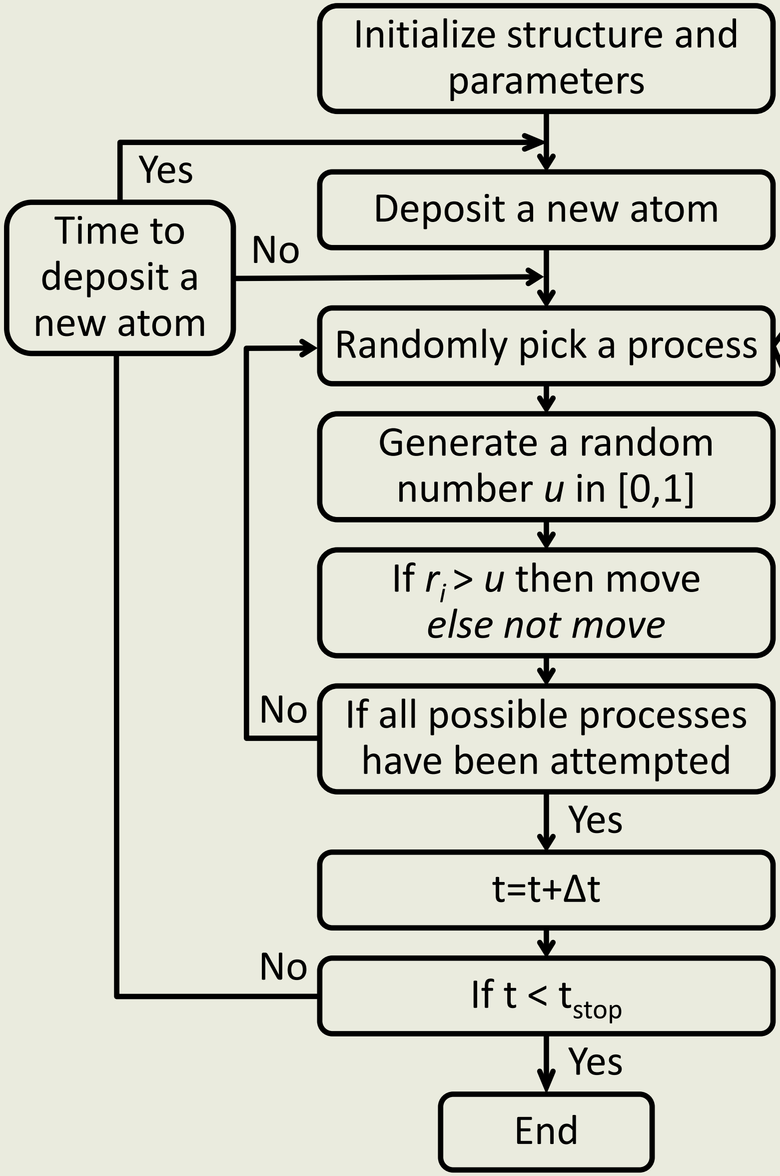
<u>Compute</u>:

time step $\Delta t = 1/v_0$

event rate: $r_i = v_0 \exp(-E_i/k_BT)$



kMC Algorithm I



Initialize structure and parameters

Deposit a new atom

Time to deposit a new atom

Yes

No

Randomly pick a process

Generate a random number *u* in [0,1]

If $r_i > u$ then move *else not move*

If all possible processes have been attempted

No

Yes

$t=t+\Delta t$

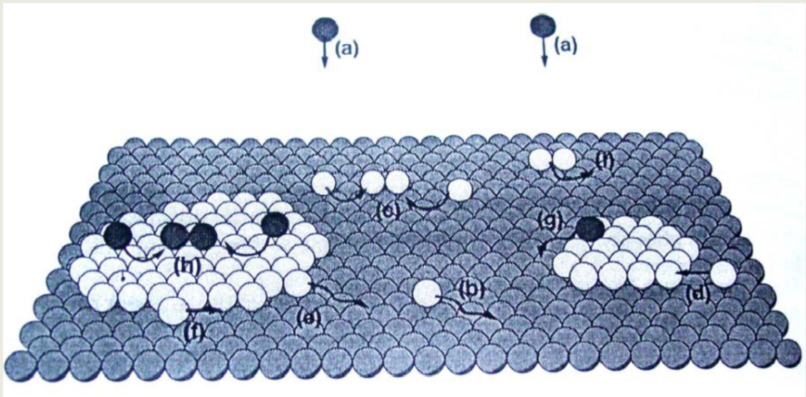
If $t < t_{stop}$

No

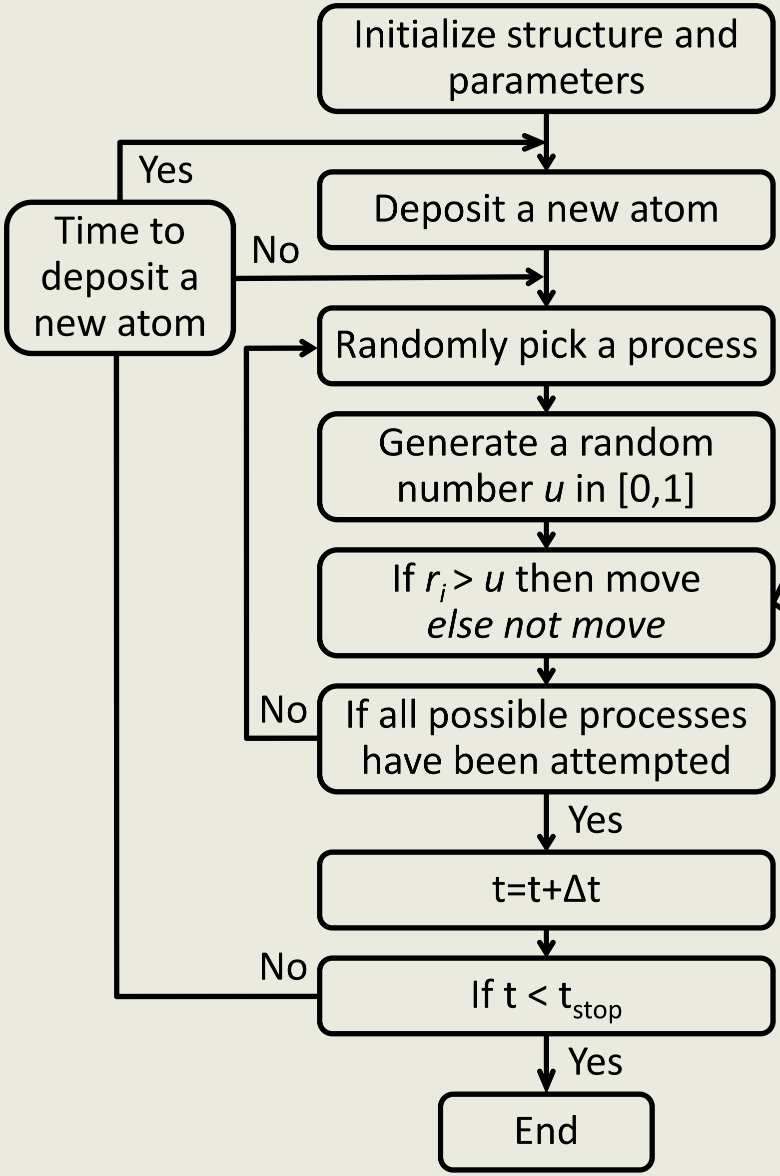
Yes

End

1. randomly pick a live atom
2. randomly pick a direction
3. determine the corresponding r_i according to the local coordination to the neighbors (tricky in programming; logic is very important!)



KMC Algorithm I



Initialize structure and parameters

Deposit a new atom

Time to deposit a new atom

Yes

No

Randomly pick a process

Generate a random number u in [0,1]

If $r_i > u$ then move *else not move*

If all possible processes have been attempted

No

Yes

$t = t + \Delta t$

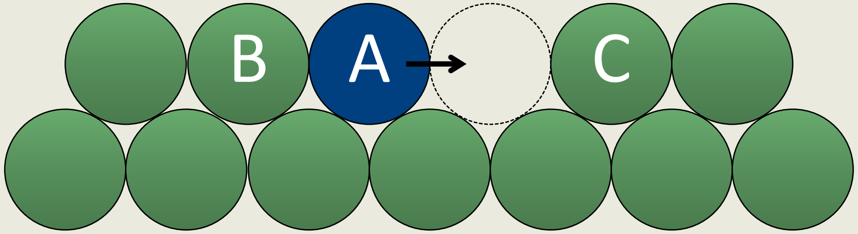
If $t < t_{stop}$

No

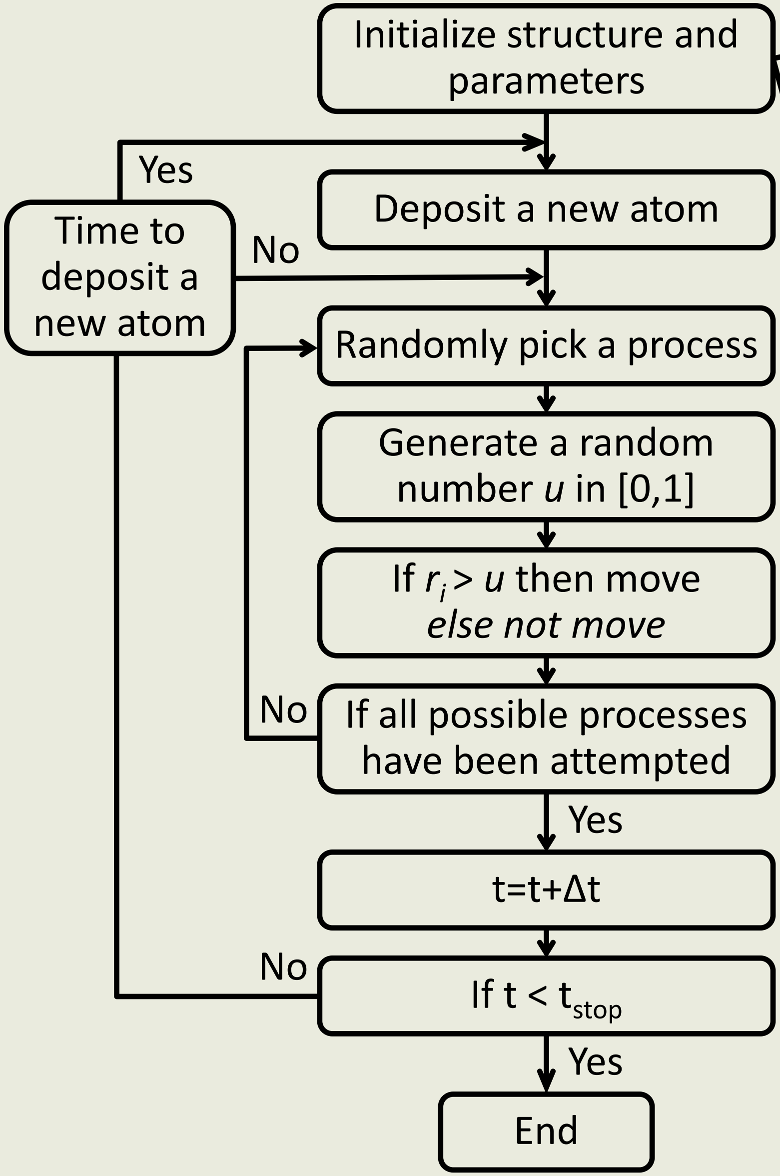
Yes

End

After an atom moved, update the live atom list! Besides the action atom, all the neighbors before and after the process need to be considered.



KMC Algorithm I



Initialize structure and parameters

Deposit a new atom

Time to deposit a new atom

Yes

No

Randomly pick a process

Generate a random number *u* in [0,1]

If $r_i > u$ then move *else not move*

No

If all possible processes have been attempted

Yes

t=t+Δt

No

If t < t_{stop}

Yes

End

time step $\Delta t = 1/v_0$

event rate: $r_i = v_0 \exp(-E_i/k_B T)$

An improvement:

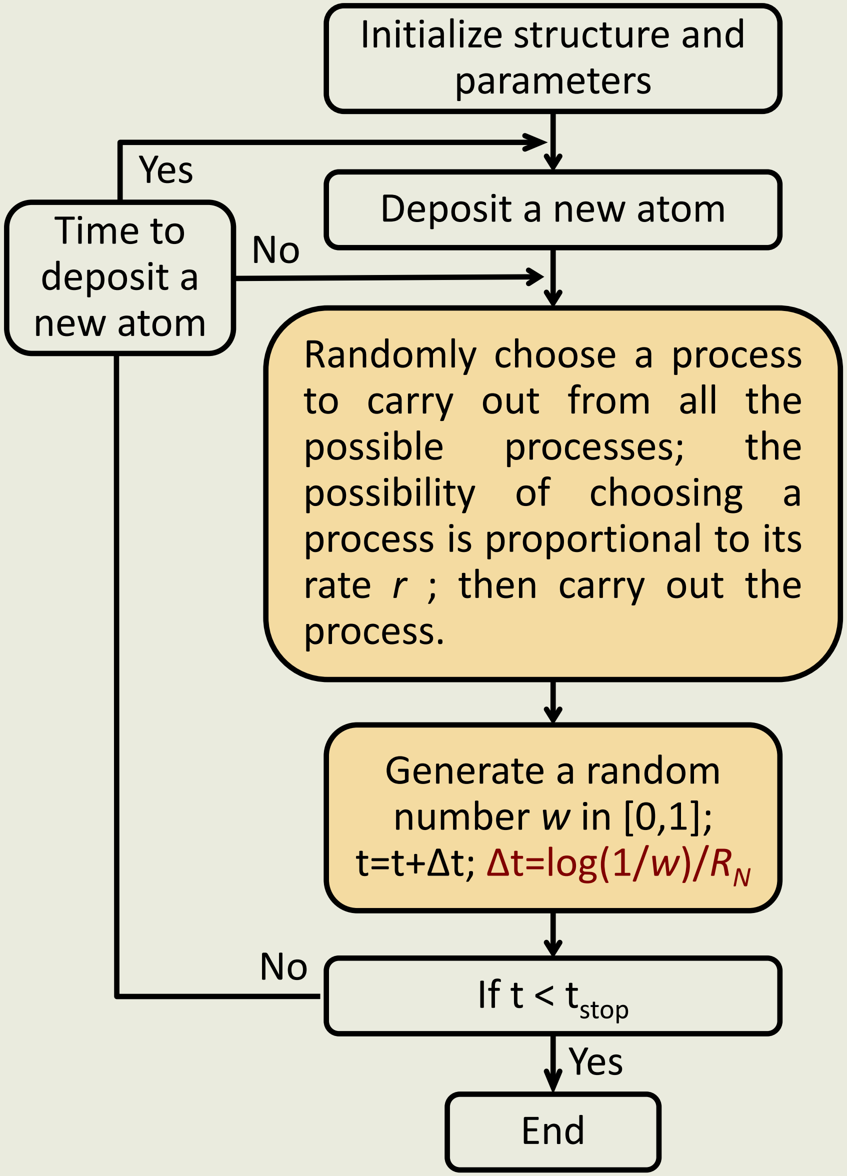
time step $\Delta t = 1/r_{fastest}$

event rate:

$r_i = v_0 \exp(-(E_i - E_{fastest})/k_B T)$

Note: rescale the rates to void a lot of unavailing attempts.

KMC Algorithm II



Initialize structure and parameters

Deposit a new atom

Time to deposit a new atom

Yes

No

Randomly choose a process to carry out from all the possible processes; the possibility of choosing a process is proportional to its rate *r* ; then carry out the process.

Generate a random number *w* in [0,1]; $t=t+\Delta t$; $\Delta t=\log(1/w)/R_N$

If $t < t_{stop}$

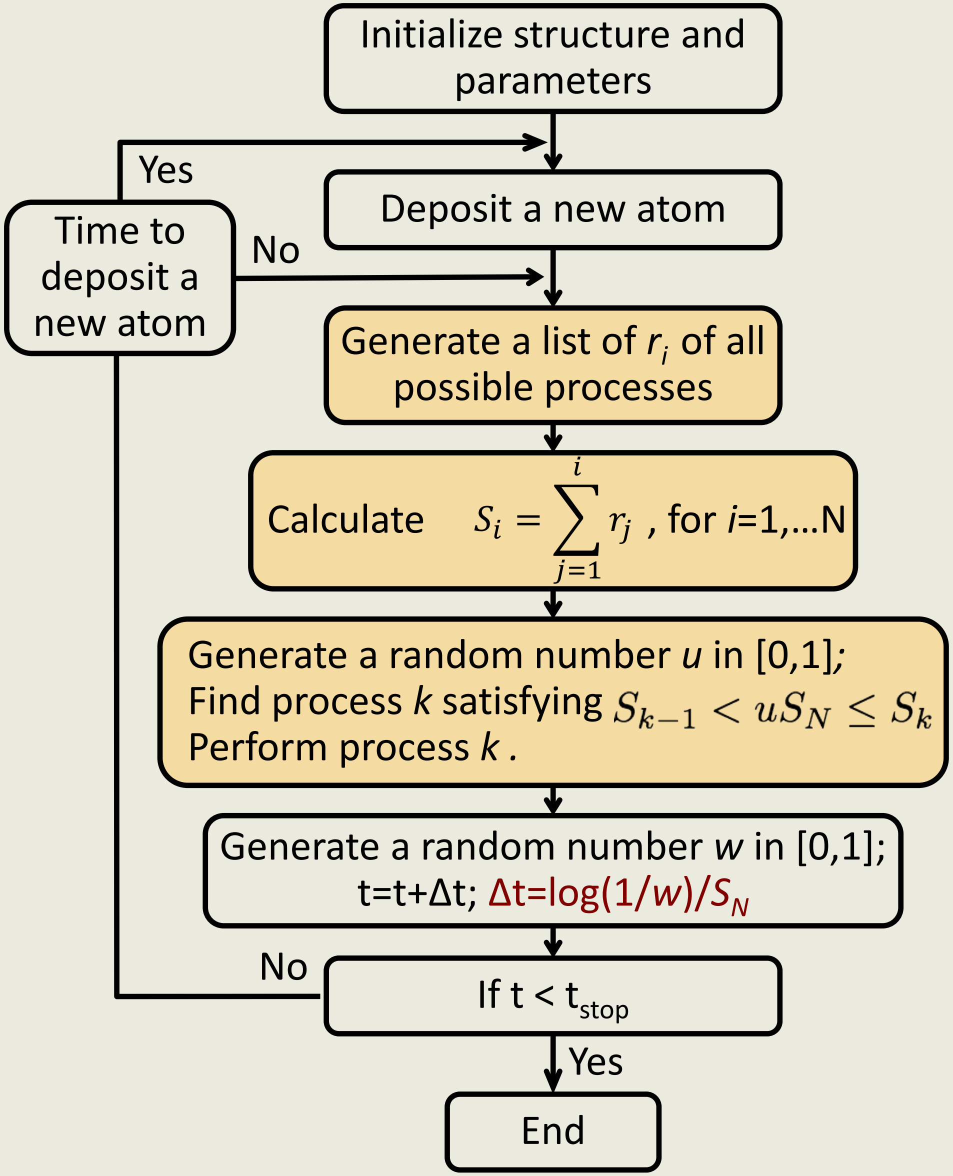
No

Yes

End

$$S_i = \sum_{j=1}^{i} r_j$$

KMC Algorithm II



Initialize structure and parameters

Deposit a new atom

Time to deposit a new atom

Yes

No

Generate a list of r_i of all possible processes

Calculate $S_i = \sum_{j=1}^{i} r_j$, for i=1,…N

Generate a random number u in [0,1];
Find process k satisfying $S_{k-1} < uS_N \leq S_k$
Perform process k .

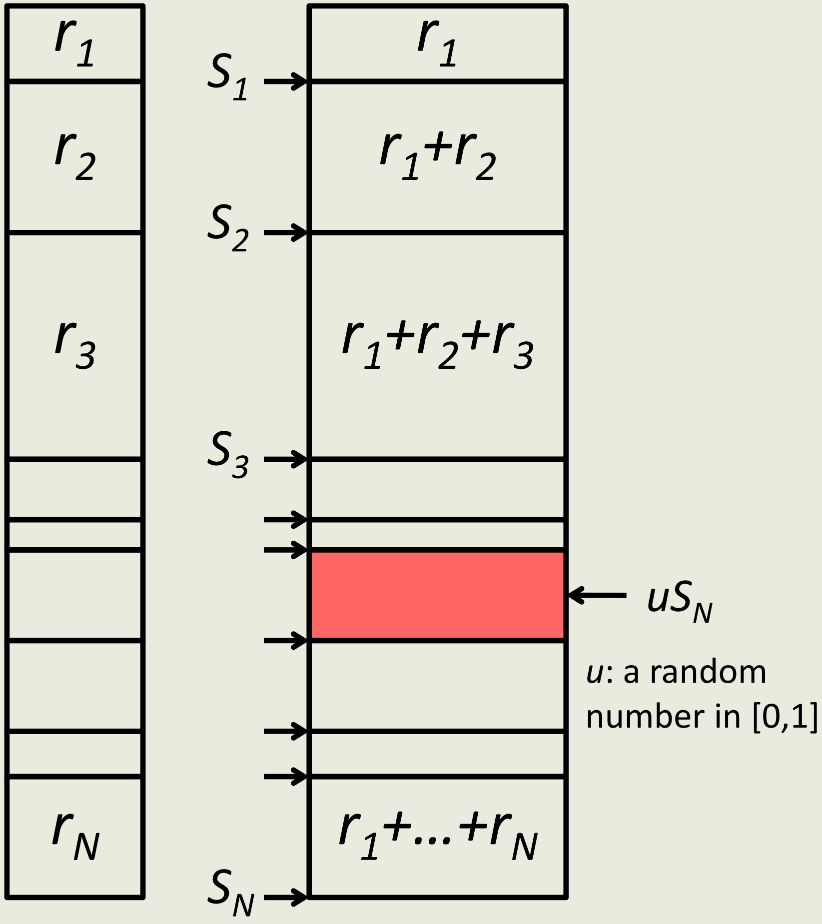
Generate a random number w in [0,1];
t=t+Δt; $\Delta t = \log(1/w)/S_N$

If $t < t_{stop}$

No

Yes

End



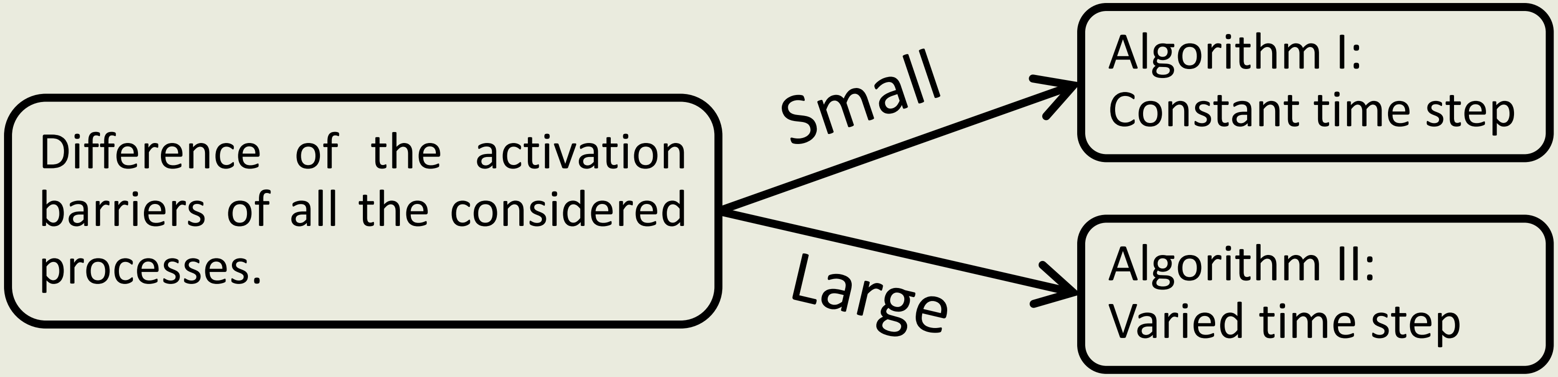
u: a random number in [0,1]

Tricky part: effectively find the process to be carried out and update the S list.

Comparison of the Two Algorithms

	Algorithm I	Algorithm II
Features	Constant time step; Pick atom then pick process; however the process is not guaranteed to be carried out.	Varied time step; Pick process and the process is guaranteed to be carried out.
Advantage	Intuitive; Programming is relatively easy	Programming is relatively difficult
Disadvantage	Not effective in some cases	More effective

Practical strategy to choose a proper algorithm:



Difference of the activation barriers of all the considered processes.

Algorithm I:
Constant time step

Algorithm II:
Varied time step

Case Study of kMC: CO Oxidation on Pt(111)