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13 - 24 August 2012

Introduction to atomistic long time scale methods

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Introduction to atomistic long time scale methods

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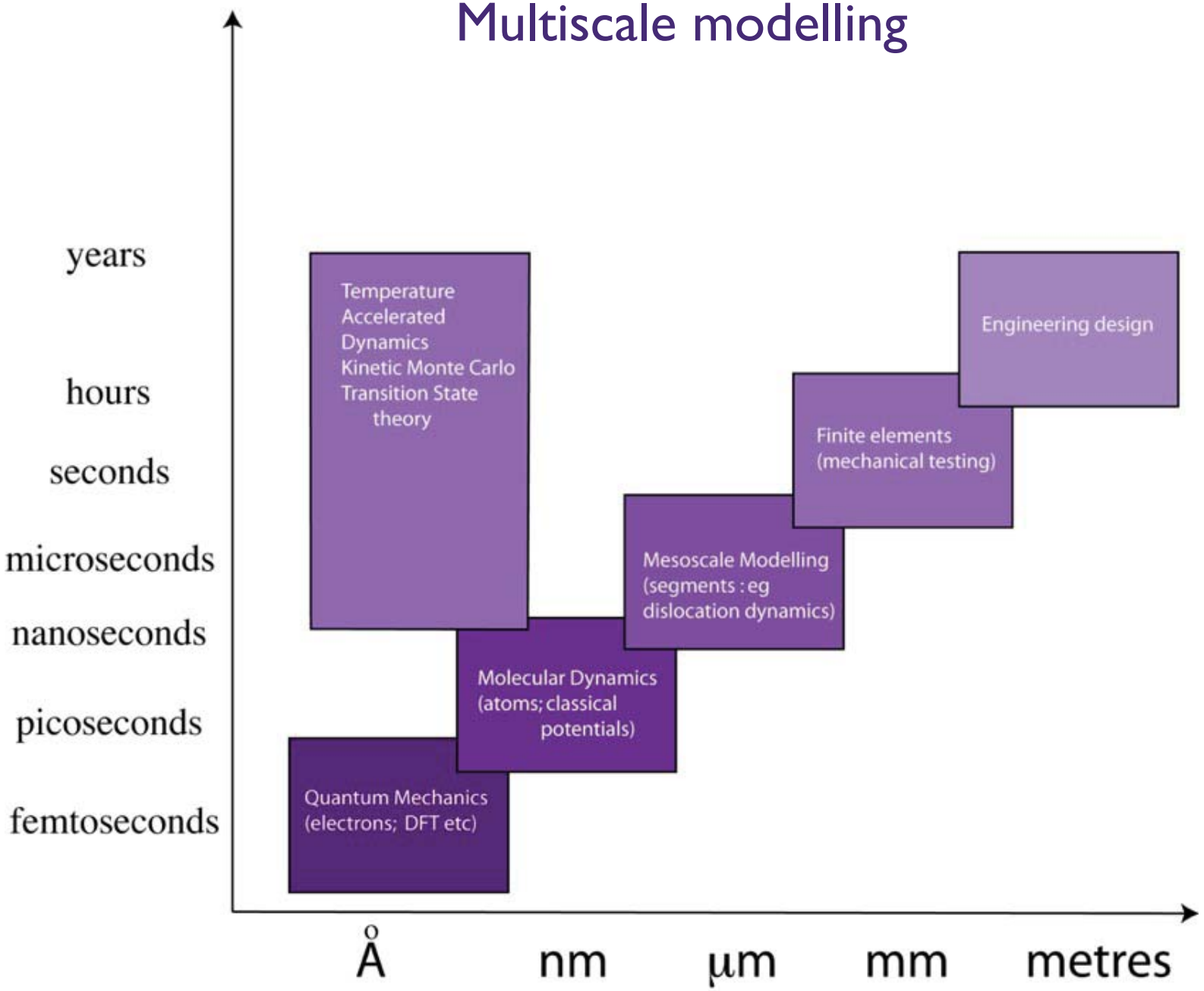
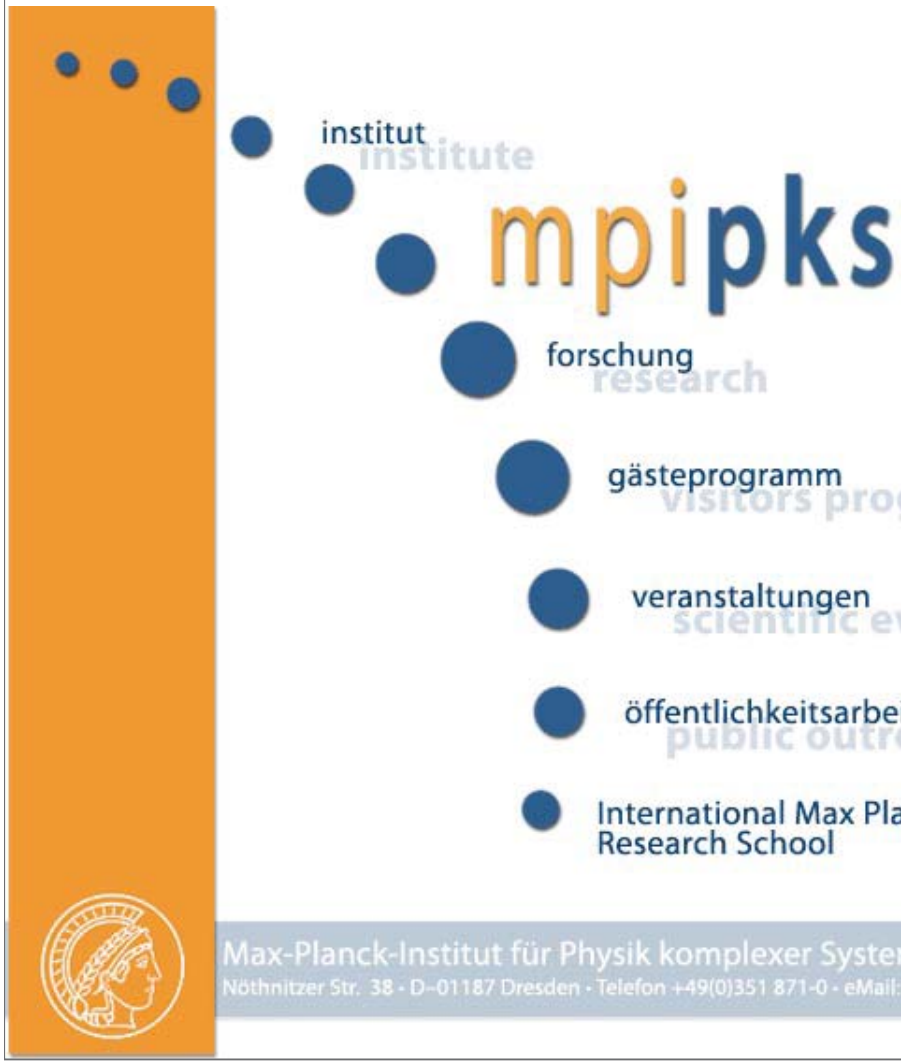
Multiscale modelling



See the website for BEMOD12 for an overview of the latest methods

http://www.mpipks-dresden.mpg.de/~bemod12/



Beyond Molecular Dynamics: Long Time Atomic-Scale Simulations

International Workshop- March 26 - 29, 2012

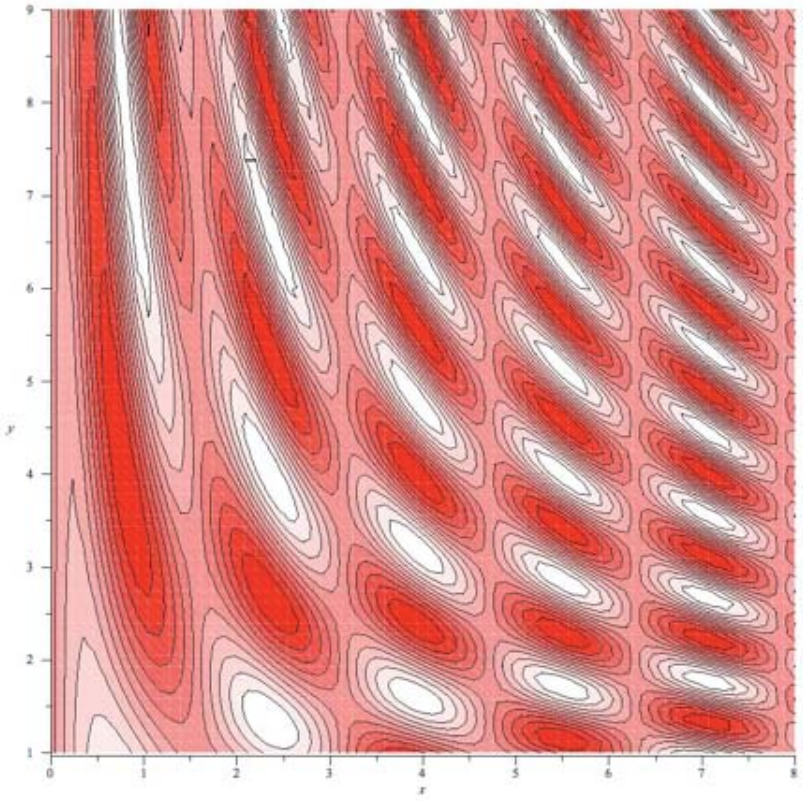
Scientific Coordinators:
Charlotte Becquart (UMET Université Lille 1, France)
Matthias Posselt (Helmholtz-Zentrum Dresden-Rossendorf, Germany)
Roger Smith (Loughborough University, UK)

The time scale bridging problem

- The kinetic effects in a collision cascade or a thin film deposition process using magnetron sputtering are over in a few picoseconds
- The evolution of the system is then governed by unpredictable rare events where concerted motions take place

deep red -- maxima
light red -- minima

The system gets trapped in the basin around a minimum and transits to the next basin over a saddle point

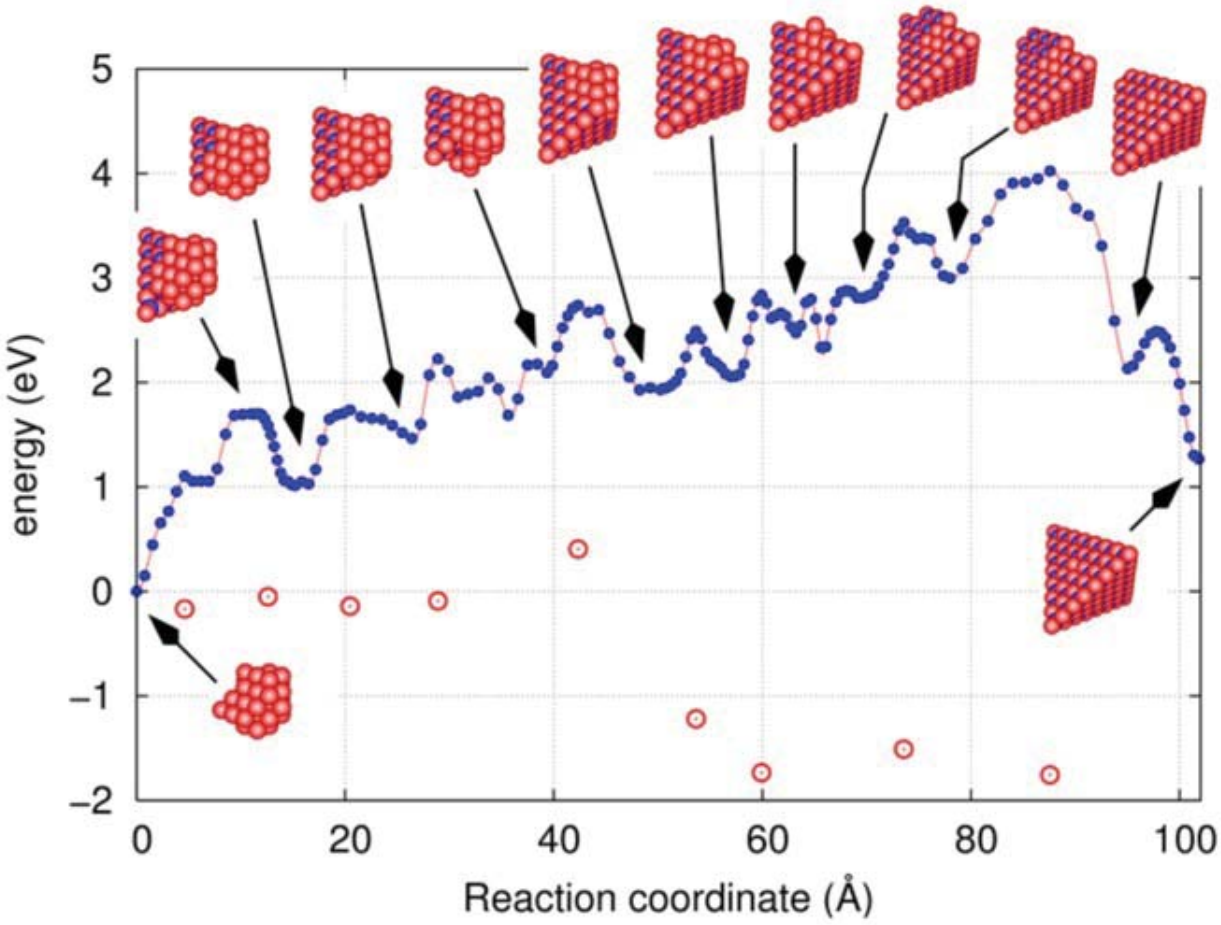


$V(x,y) = \sin(2x)\cos(xy)$

$x_0 = 3\pi/4$

$y_0 = 4.0$

Example of an unpredictable rare event



Void to stacking fault tetrahedra transformation in Cu which takes 0.24 microseconds at 475 K.. a time not accessible by MD (2×10^9 integration steps) (Courtesy Blas Uberuaga LANL)

Barrier Calculating Methods

Rare events occur (assuming harmonicity) with a frequency given by

$$\nu = \nu_0 \exp(\frac{-E}{k_B T})$$

where ν_0 is a prefactor
k_B is Boltzmann's constant
T is the temperature
E is the energy barrier to be overcome

The prefactor can be determined by a number of methods including temperature accelerated dynamics (TAD) and the Vineyard method.

To determine the transition associated with the energy barrier *E, saddle point finding* methods are used

The Vineyard method for the prefactor

- Assumes harmonicity (generally OK for low temperatures)

$$\nu = \nu_0 \exp(\frac{-E}{k_B T})$$

where ν_0 is a prefactor
k_B is Boltzmann's constant
T is the temperature
E is the energy barrier to be overcome

$$\nu_0 = \frac{\prod_i^{3N} \nu_i^{min}}{\prod_i^{3N-1} \nu_i^{sad}}$$

where ν_i are the eigenvalues of the Hessian matrix of the potential energy function, at the saddle point (ν_i^{sad}) or at the minimum (ν_i^{min}).

Method is fairly expensive to calculate and often a constant value is assumed

G Vineyard Frequency factors and isotope effects in solid state rate processes. Journal of Physics and Chemistry of Solids, 3(1–2):121--127, 1957.

Barrier Calculating Methods

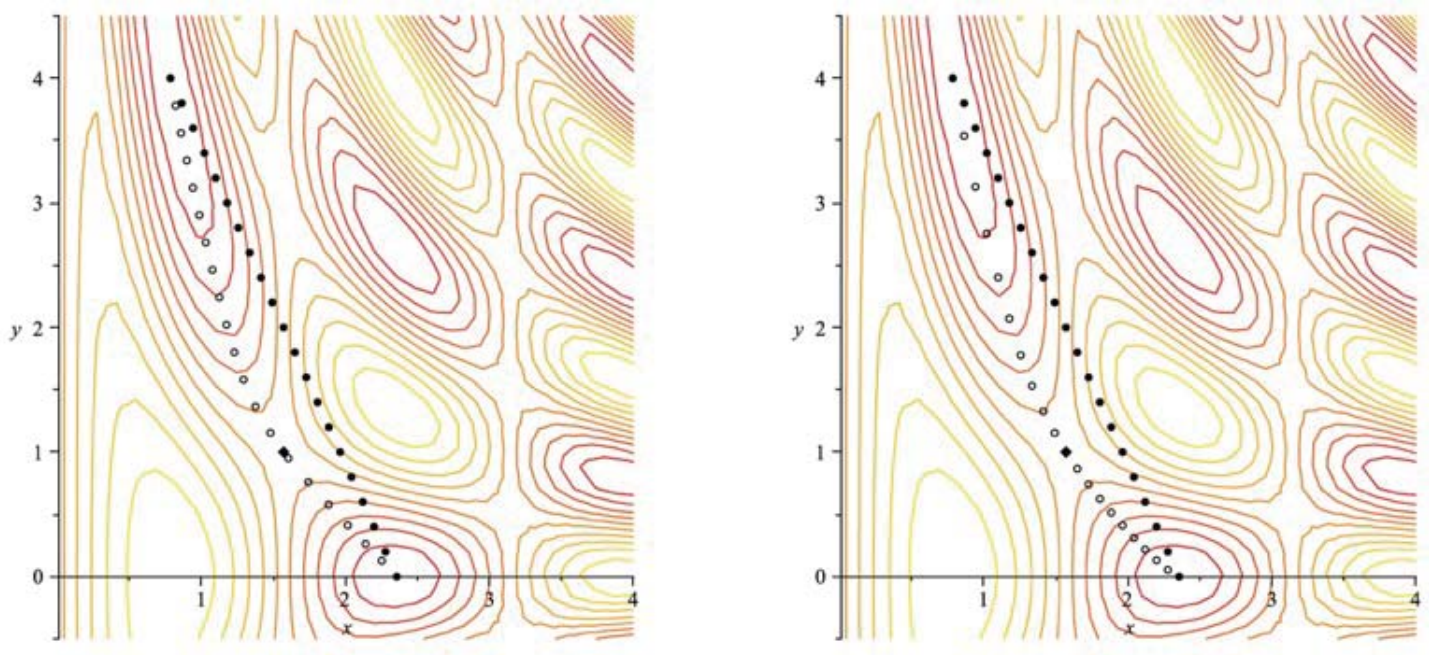
- ***Two types***

- Methods that search for the saddle point with no pre-knowledge of where it is located...*saddle point finding methods* used to determine where the saddle point is located (eg ART, TAD, dimer)

- Methods that accurately calculate the height of the saddle, the energy barrier *E* to be overcome, once the transition has been located (eg. NEB, string method)

Beware of problems dominated by low energy barriers

Barrier finding methods knowing the end points or basins of attractions



a

String

b

NEB

V = 2cos(2x) cos(xy) -y.sin(2x)sin(xy)

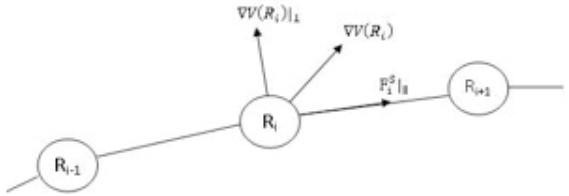
Drag, String and NEB algorithms

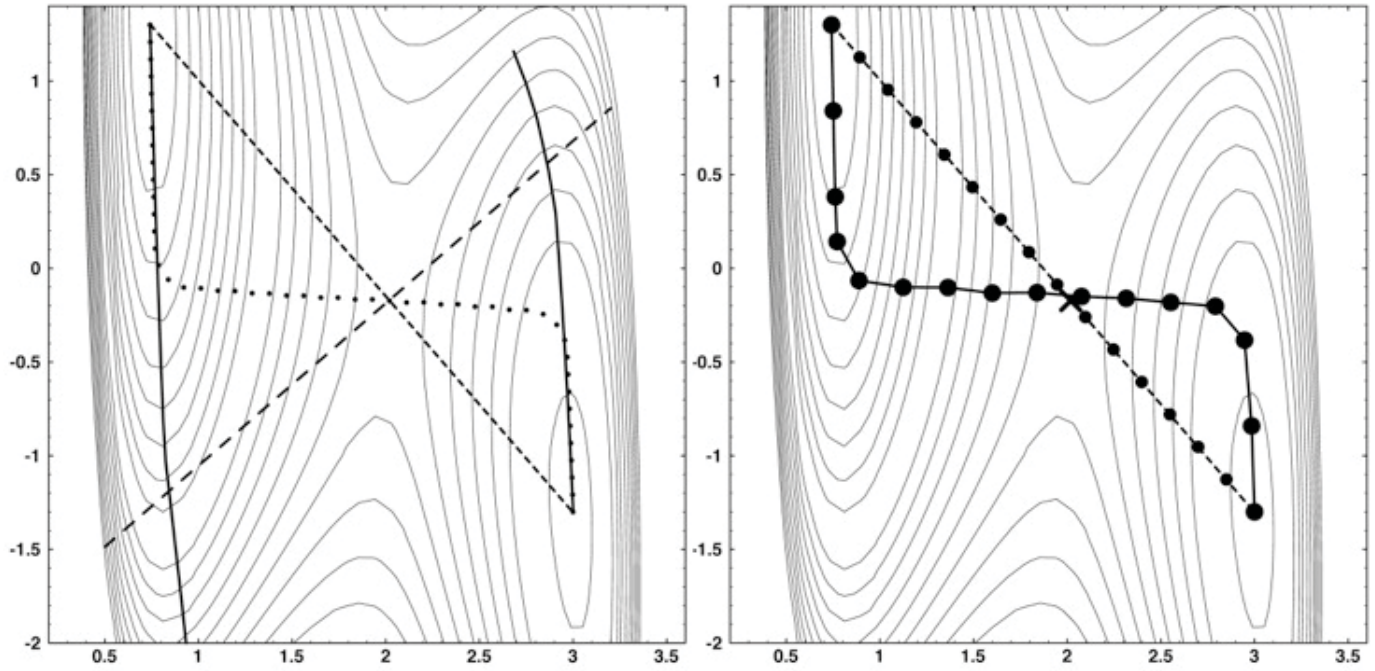
Drag :
(1) Set up a set of n equally spaced points with the ends in the basins of attraction of two minima
(2) Relax the points by minimiksing the energy perpendicular to the path

String :
(1) Set up a string of n equally spaced points with the ends in the basins of attraction of two minima
(2) Choose a small step (small enough to avoid kinks in the string) and follow the gradient of the potential for each point along that small step.
(3) Reinterpolate the new points in the string so they are equally spaced and repeat the process.

Nudged elastic band :
(1) Identify the local minima in the two basins of attraction and join them by a line (usually equally spaced) containing n points
(2) Assume this line is a spring with a spring constant k so that any point on the line has a parallel force exerted on it due to the relative extensions of the adjoining line segments
(3) Assume a force acts on each point being equal to the gradient of the potential field plus the spring force
(4) Evolve the system in time, either using MD or a gradient descent method.

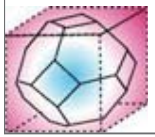
NEB method





Molecular Statics NEB method

G. Henkelman, B.P. Uberuaga, and H. Jonsson, *J. Chem. Phys.*, **113**, 9901 (2000)



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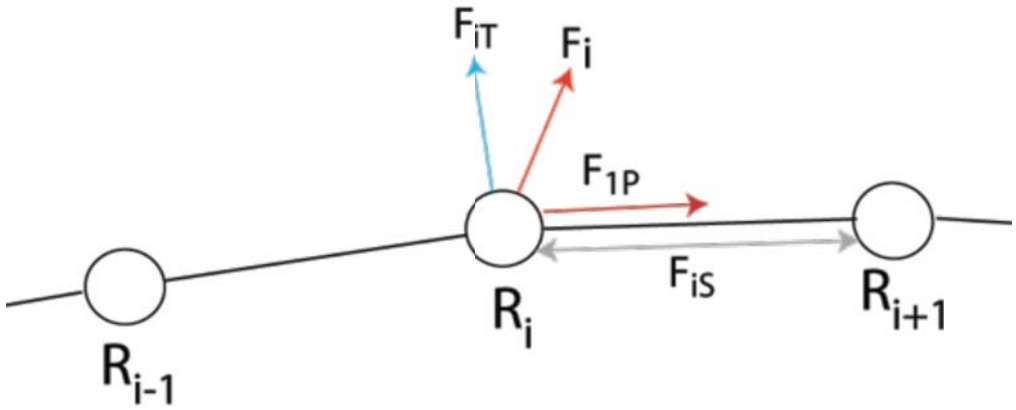
Nudged Elastic Band

- An artificial spring force is introduced parallel to the spring:

$$F_{iS} = k(|R_{i+1} - R_i| - |R_i - R_{i-1}|)\tau$$

- and a modified force is formed from the perpendicular component of the real force along with the spring force:

$$G = F_{iS} + F_T$$



- The entire system is then considered to be a point in 3N space and relaxed using the conjugate gradient scheme.
  - The spring force acts to keep images evenly spaced along the NEB.
  - The best choice of k is variable.

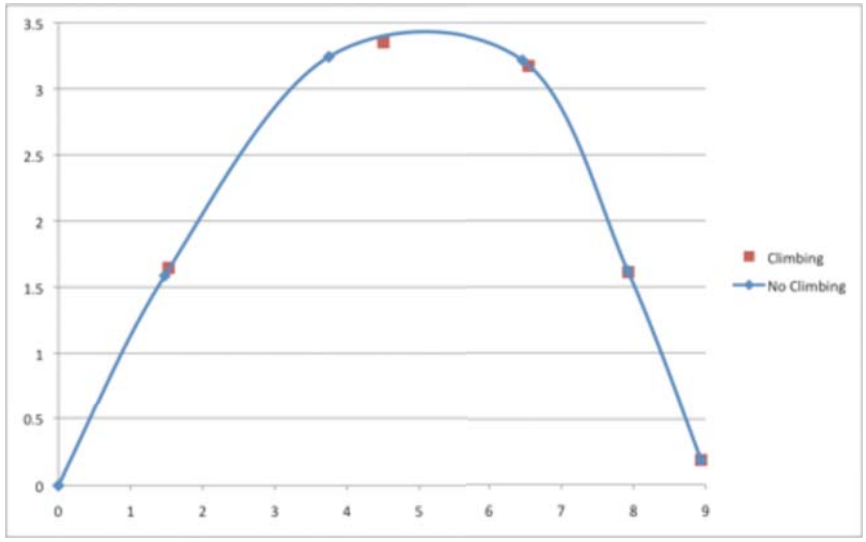
Climbing NEB

After relaxation the NEB will lie along the Minimum Energy Path but unless *n* is very large no image will lie directly on the saddle point.

- After converging the CNEB changes the modified force on the highest energy image to:

$$F_{i_{max}} = F_i - 2F_{iP}$$

- i.e. the image is relaxed perpendicularly to the string, whilst being forced uphill parallel to the string.



3% error in standard NEB cf CNEB

Barrier finding methods from a local minimum **not** knowing the end points or surrounding basins of attractions

Dimer Method : Henkelmann and Jonnson also Dimer-Lancoz

ART Method and variants : Barkema and Mousseau

Gentlest ascent methods : Samanta and E

Art Voter methods : TAD, hyperdynamics, parallel replica

Energy Landscape methods : David Wales

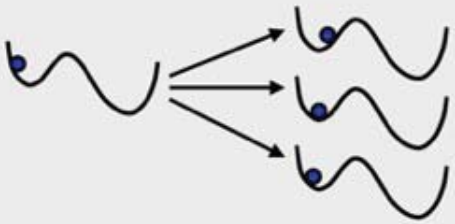
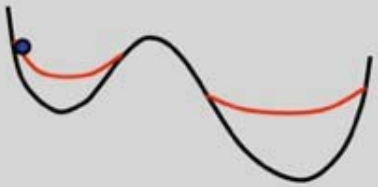
Forward flux sampling : R.J. Allen et al

Transition path sampling : P. Bolhuis et al

Metadynamics : Laio, Quigley

Milestoning : Elber

Accelerated Molecular Dynamics Methods

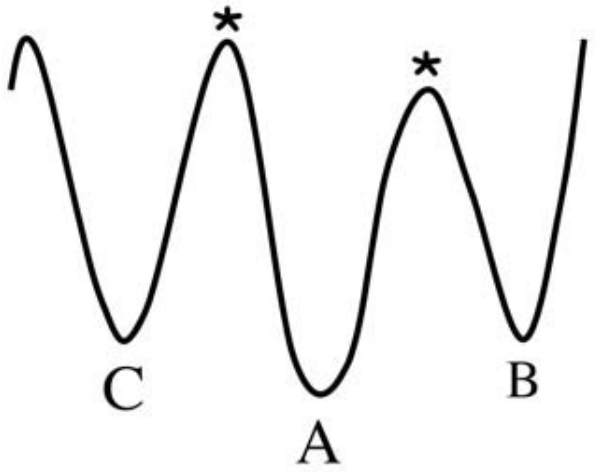
Parallel Replica Dynamics (1998) 	Explore basin with many processors *M*
Hyperdynamics (1997) 	Increase rate by reducing effective barriers
Temperature Accelerated Dynamics (2000) 	Increase rate by raising temperature

Methods pioneered by Art Voter at LANL. They coax the system to move more quickly.

Accelerated Molecular Dynamics
(Hyperdynamics)

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

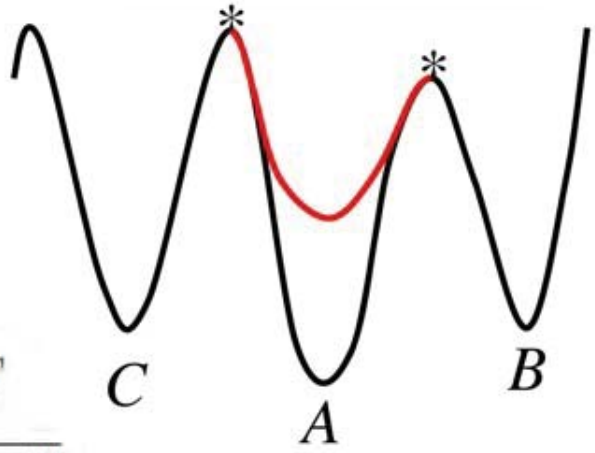
$$k^{TST}_{A\to B} = \frac{1}{2}\frac{\int_A \delta^*_{AB}|v_{\perp,AB}|e^{-V(\mathbf{R})/k_BT}}{\int_A e^{-V(\mathbf{R})/k_BT}}$$



$$k^{TST}_{A\to B} = \nu\frac{\int \delta^*_{AB} W(\mathbf{R})e^{-V(\mathbf{R})/k_BT}/W(\mathbf{R})}{\int W(\mathbf{R})e^{-V(\mathbf{R})/k_BT}/W(\mathbf{R})}$$

Relative Rates

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



$$k^{TST}_{A\to B} = \nu\frac{\int \delta^*_{AB} e^{-V(\mathbf{R})/k_BT}/\int e^{-V(\mathbf{R})/k_BT}}{\int e^{-V(\mathbf{R})/k_BT}/W(\mathbf{R})/\int e^{-V(\mathbf{R})/k_BT}}$$

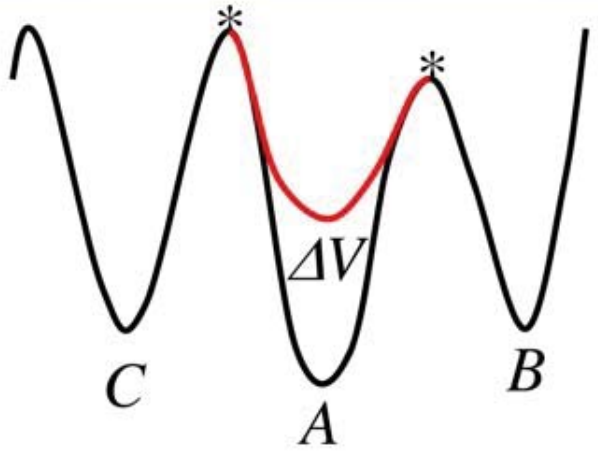
Accelerated Molecular Dynamics
(Hyperdynamics)

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

$$k^{TST}_{A\to B} = \frac{k^{TST}_{A\to B}}{\langle W(\mathbf{R})\rangle_A}$$

$$k^{TST}_{A\to C} = \frac{k^{TST}_{A\to C}}{\langle W(\mathbf{R})\rangle_A}$$

$$\frac{k^{TST}_{A\to B}}{k^{TST}_{A\to C}} = \frac{k^{TST}_{A\to B}}{k^{TST}_{A\to C}}$$



MD Time:

$$t_{MD} = N\Delta t$$

Real Time:

$$t = \sum_{i=1}^{N} \frac{\Delta t}{W(R_i)} = \Delta t \sum_{i=1}^{N} \exp\left(\Delta V_i / kT\right)$$

$$\text{Boost} = \left\langle \exp\left(\frac{\Delta V}{kT}\right)\right\rangle$$

The Trick is How to Construct $\Delta V(R)$...

Accelerated Molecular Dynamics

The Bond-Boost Method

R. Miron & K. Fichthorn, *J. Chem. Phys.* **119**, 6210 (2003)

Define Local Minima by Bond Lengths

$$\{r_i^o\}_{i=1,N}$$

Transitions Occur via Bond Breaking

$$\max_i \left| \frac{\delta r_i}{r_i^o} \right| > q$$

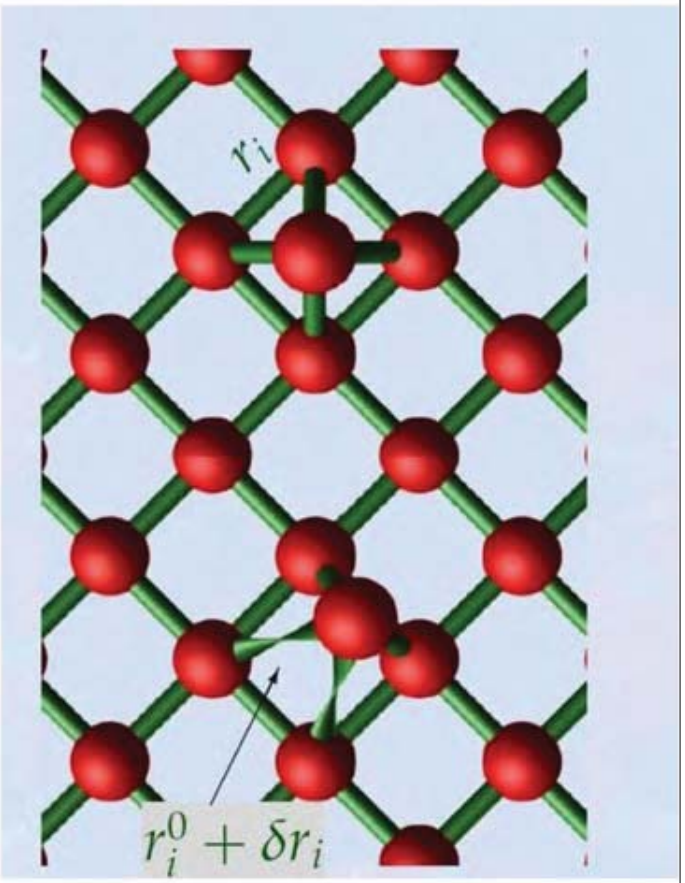
Empirical Threshold

Boost the Bonds: Purely Geometric

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

Envelope Function

Boost per Bond



Details of the Bond Boost Method

Boost Potential

$$\Delta V(\mathbf{r}) = \frac{\Delta V_{\max}}{N} A(\varepsilon_{\max}) \sum_{i=1}^{N} \delta V(\varepsilon_i)$$

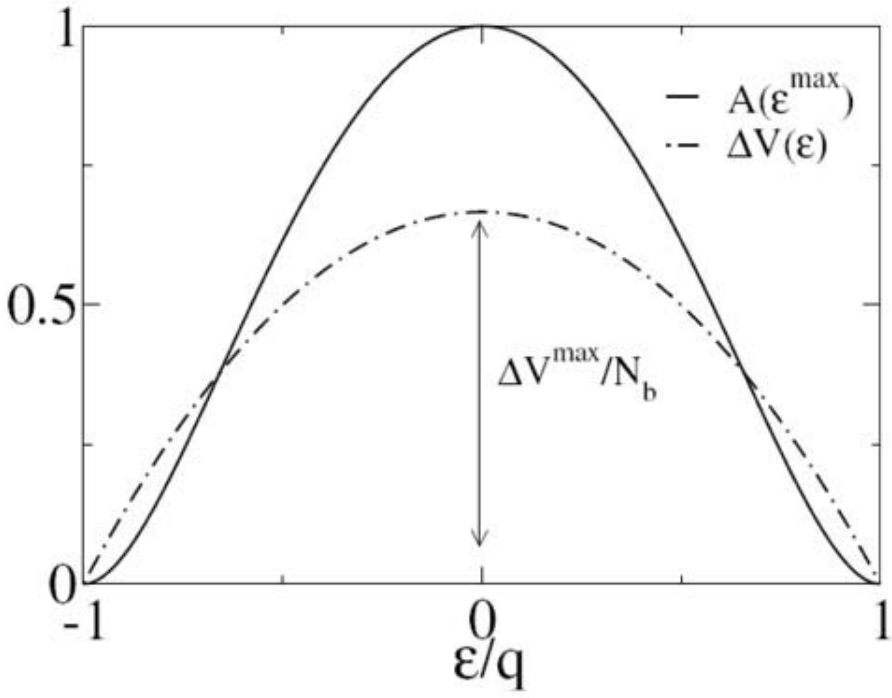
$$\varepsilon_i = \frac{\delta r_i}{r_i^0}$$

Nominal Boost per Bond

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

Envelope: Channels Boost into the Bond Most Ready to Break

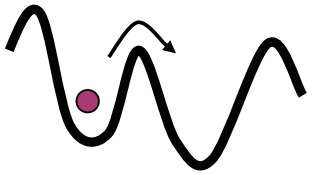
$$A(\varepsilon_{\max}) = f \times \left[1 - \left(\frac{\varepsilon_{\max}}{q}\right)^2\right]$$



Temperature Accelerated Dynamics

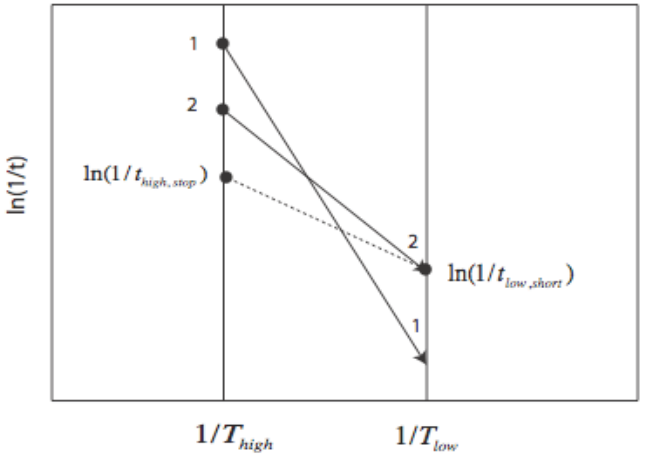
- Concept:
  - System characterised by deep energy wells
  - Run basin constrained MD at high temperature
  - Extrapolate behaviour to low temperature

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



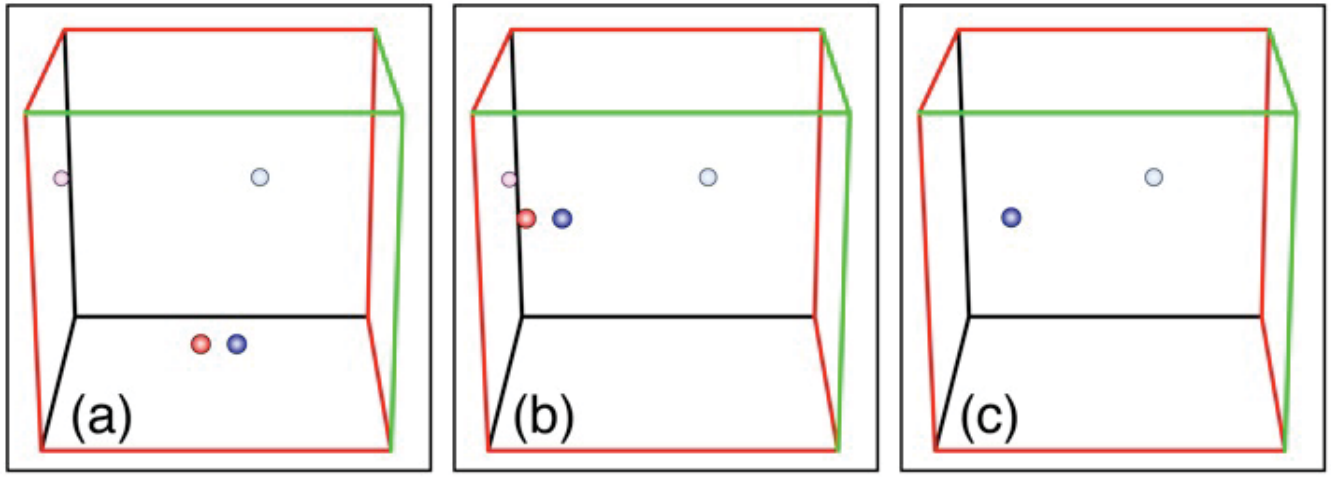
Sørensen and Voter,
JCP **112**, 9599 (2000)

- Approximations:
  - Harmonic Transition State Theory
  - (Prefactor is temperature independent)
  - Assumed minimum prefactor in system ν_{min}
  - Uncertainty level δ of missing the correct event
  - *Very powerful when barriers are high relative to temperature*



The method finds the transitions and includes the time for the transitions but the energy barriers are usually determined by NEB

Example of TAD: Di-interstitial recombination in MgO



(a) t=0 (b) t=0.081s (c) t=0.081s

The dimer moves as a unit until the O atom recombines. The Mg recombination then quickly follows.

The Dimer Method

- In common with all 3 methods a point **R** in 3N dimensional space is created through randomly stepping away from a local minimum.

- From R, 2 replica images are created through diametric displacement a fixed distance along a randomised vector N.

$$\mathbf{R}_1 = \mathbf{R} + \Delta R \hat{\mathbf{N}}$$

and

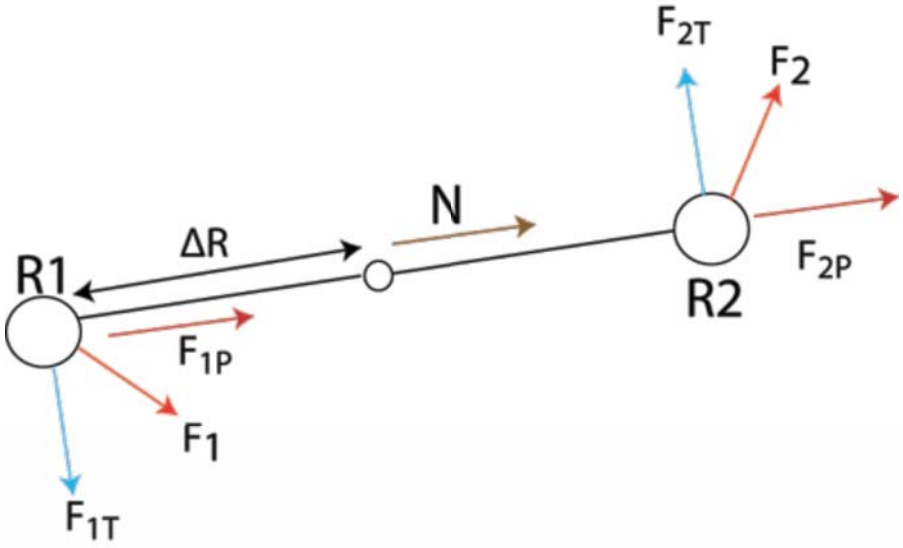
$$\mathbf{R}_2 = \mathbf{R} - \Delta R \hat{\mathbf{N}}.$$

- An initial offset of ~0.1Å along with a replica displacement of ~0.01Å works well.

The Dimer

- 2 lattice force evaluations are required in order to find the force acting on the dimer.

- $\mathbf{F}_1$ and $\mathbf{F}_2$ are decomposed into their perpendicular and parallel components with respect to their normalised displacement vector **N**.



$$F_T = F_{1T} - F_{2T}, \text{ where } F_{iT} = F_i - (F_i \cdot N)N \text{ for } i = 1, 2$$

- The total rotational force acting on the dimer, F_T is given by the difference in the perpendicular component of force on $\mathbf{R}_1$ and $\mathbf{R}_2$; $F_T = F_{1T} - F_{2T}$

Minimising Rotational Force

- The method then seeks to minimise F_T through rotating the dimer.
  - This has 2 components; a conjugate gradient method to choose successive planes of minimisation and a rotational line minimiser.

- Henkleman suggests using a modified Newton method, however we have better success with a simple quadratic $A(x+b)^2$ approximation:

$$\text{Guess} = \frac{F(x_1).V(x_2) - F(x_2).V(x_1)}{F(x_1) - F(x_2)}$$

- x_1 and x_2 are trial rotational angles. $F(x_1)$ is the dot product of F_T and the current minimisation direction, normalised by the sqrt of the number of atoms in the dimer vector.

- Another good rotational line minimiser is to approximate to a sinusoidal form

- Minimisation is performed until F(x) is less than 0.001.

Translation

- Once relaxed the dimer is translated in the direction of modified force.
  - There are 2 schemes depending on the curvature of the local potential surface:

$$F_M = \begin{cases} -F_P & \text{if } C > 0, \\ F - 2F_P & \text{if } C \leq 0. \end{cases}$$

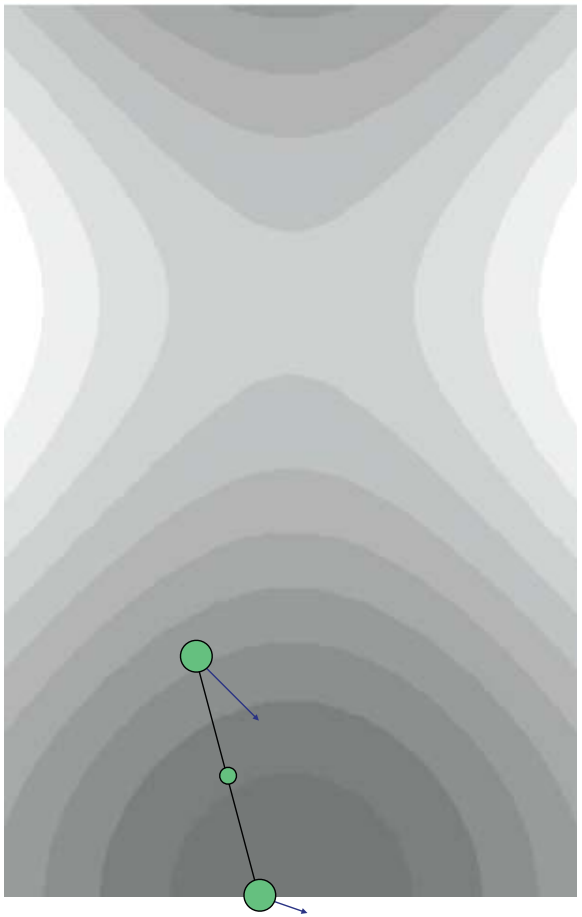
- Where the curvature is given by:

$$C = \frac{(\mathbf{F}_2 - \mathbf{F}_1) \cdot \hat{\mathbf{N}}}{2\Delta R}$$

  - This allows the dimer to rapidly climb out of the minimum energy region before more accurately moving towards the saddle point.

A simple example of the dimer method

- Dimer – two nearby points on the potential surface
- The dimer is rotated to a line of lowest curvature
- It is then translated towards the saddle using the effective force
- The saddle height is the energy barrier



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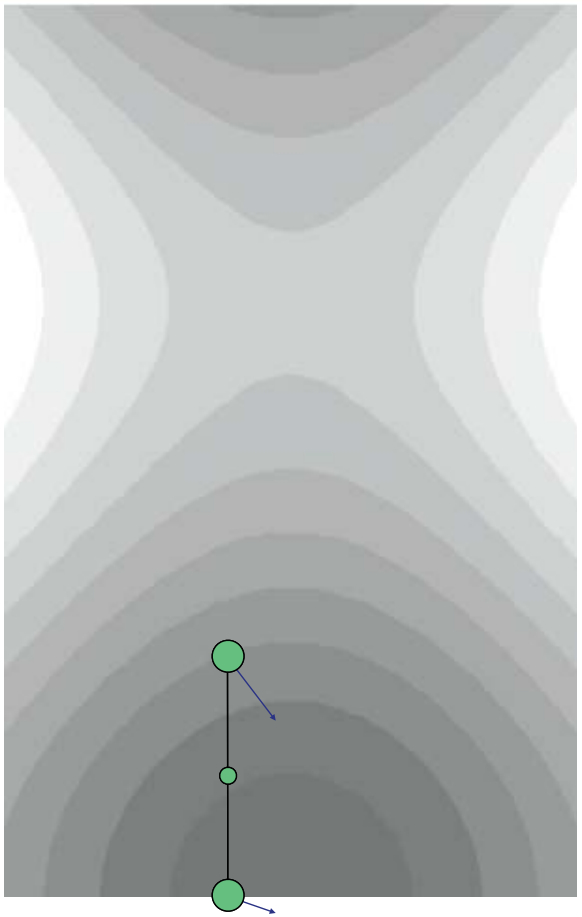

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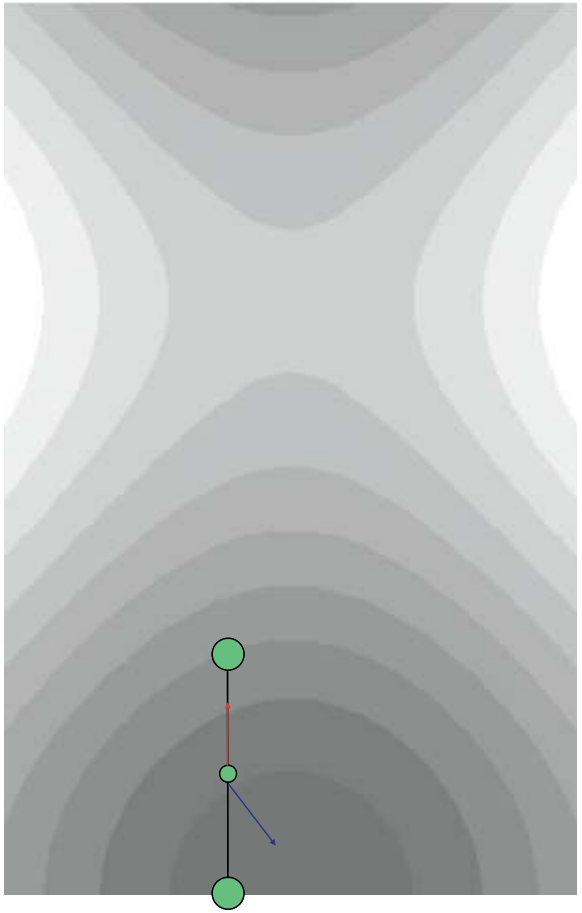

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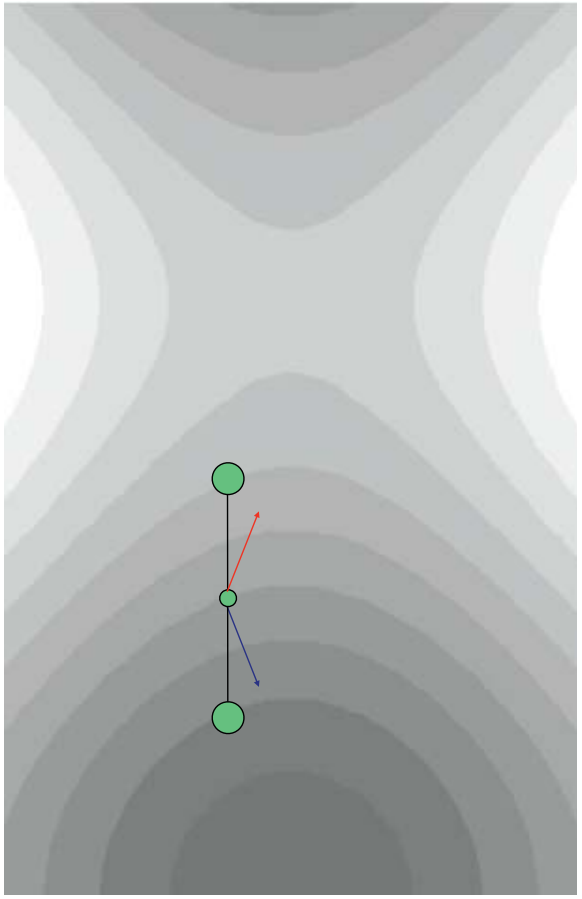

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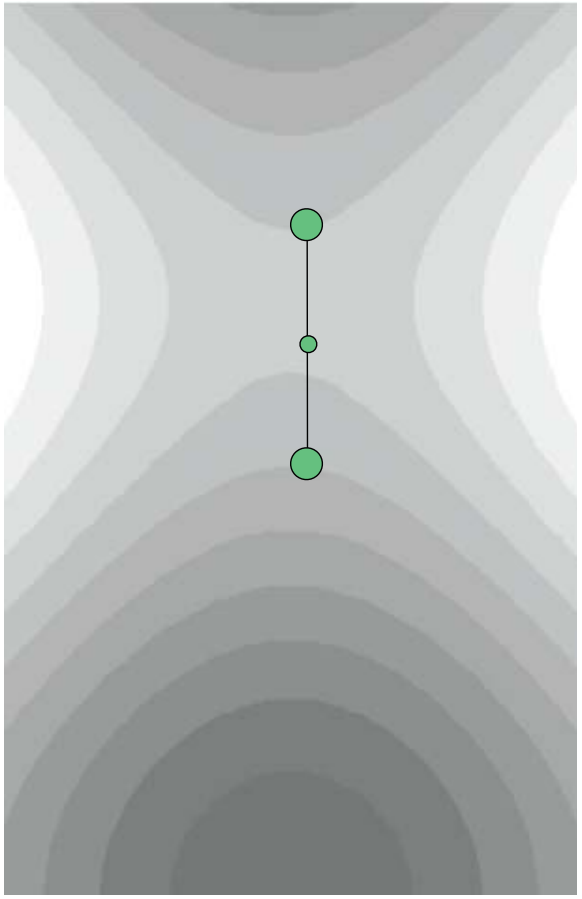

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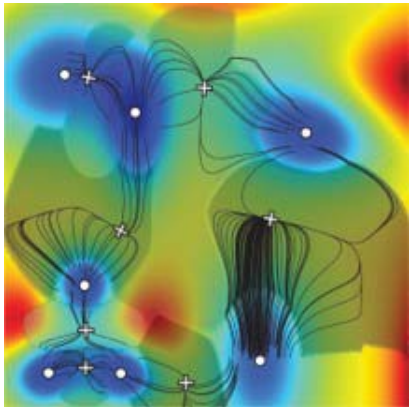
Dimer plus Lanczos algorithm

At a local minimum all eigenvalues of the Hessian matrix **H** are positive.

$$\mathbf{H} = \begin{bmatrix} \frac{\partial^2 E}{\partial x_1 \partial x_1} & \frac{\partial^2 E}{\partial x_1 \partial x_2} & \cdots & \frac{\partial^2 E}{\partial x_1 \partial x_{3N}} \\ \frac{\partial^2 E}{\partial x_2 \partial x_1} & \frac{\partial^2 E}{\partial x_2 \partial x_2} & \cdots & \frac{\partial^2 E}{\partial x_2 \partial x_{3N}} \\ \vdots & \vdots & \ddots & \vdots \\ \frac{\partial^2 E}{\partial x_{3N} \partial x_1} & \frac{\partial^{3N} E}{\partial x_{3N} \partial x_2} & \cdots & \frac{\partial^2 E}{\partial x_{3N} \partial x_{3N}} \end{bmatrix}.$$



Pedersen and Jonnson SIAM 2011

At a rank 1 saddle (most of them) one of the eigenvalues of the Hessian matrix is negative.

Method: Use the dimer method to climb out of the basin of attraction of the minimum until one of the eigenvalues of the Hessian is negative, i.e. C < 0

Reverse the force along the direction of the negative eigenvalue (determined by the Lanczos method) and use the conjugate gradient algorithm, which now thinks the saddle is a minimum.

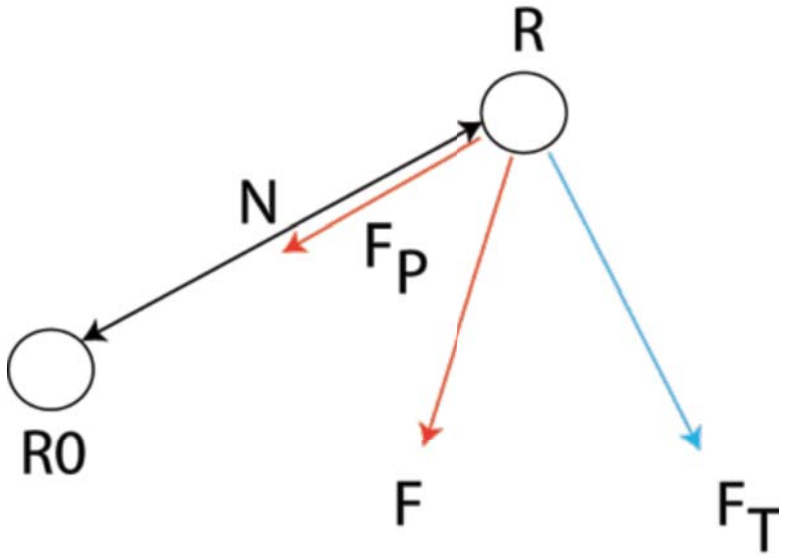
The advantage of the new method is that it is much faster than the Dimer method.

This is currently our preferred method for determining saddles.

ART Method

The first step is to offset from the origin in a random direction.

At each step a displacement vector with unit normal **N**, connecting **R** to the original local minimum $\mathbf{R_0}$ is. calculated



Code is available from Norman Mousseau's web site

ART - Translation

- Once decomposed a modified force, G, is created:

$$\mathbf{G} = \mathbf{F} - (1+\text{alpha})\,(\mathbf{F} \cdot \mathbf{N})\mathbf{N}$$

- alpha is a control parameter that influences the aggressiveness of the search.

A large alpha will climb away from the minimum rapidly but may miss the saddle point by overshooting. Too small a value can miss some of the saddles.

Different saddles are found by different initial random displacements.

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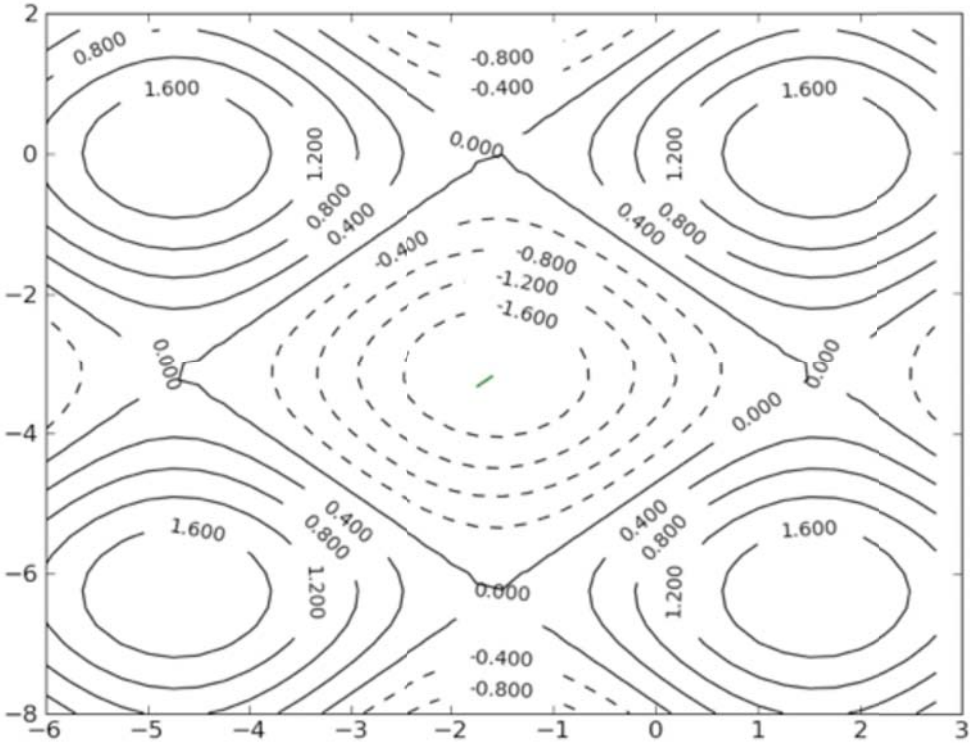
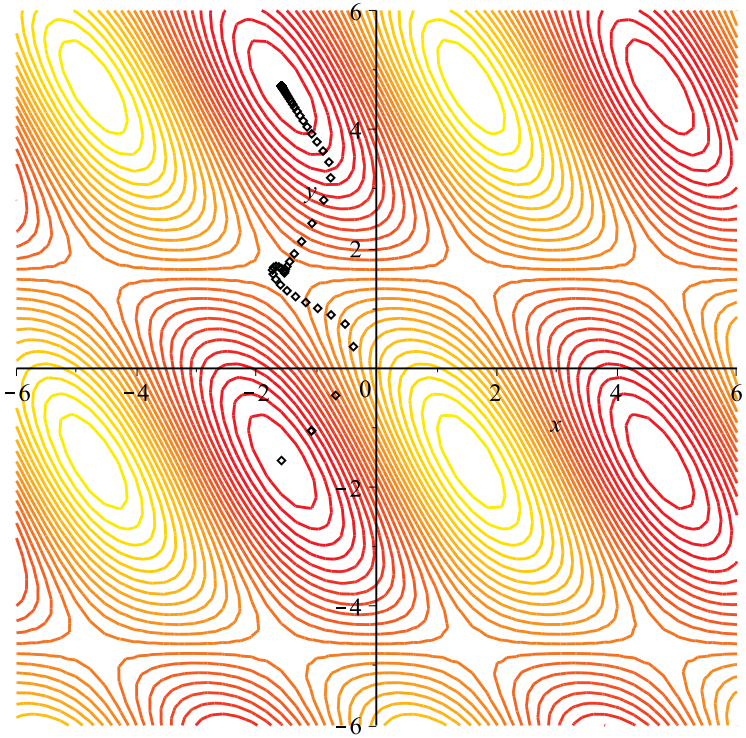
ART Method





Kinetic Monte-Carlo Methods

Approach 1

- "Guess" which the important transitions might be. Calculate the barrier heights, e.g. using NEB.
- Make a list of all the events and then evolve the system by choosing an event from the prepared list.
- *Disadvantage : It is quite possible to miss important transitions.*

Approach 2

- Calculate the transitions and prefactors "on-the-fly"
- *Disadvantage : the speed boost is not so good when the energy barriers are low*

Rate theory methods

The rate theory methods use pre-determined hop or diffusion rates in differential equations to model the defect evolution; e.g. the growth of clusters or accumulation at grain boundaries.

Disadvantage
They are require parameters which are often not known with certainty

Rate theory example for long time scale effects (radiation damage defect accumulation in MgO)

$$\frac{dC_v}{dt} = (1 - C_v)(1 - Z_1 C_v)P - Z_1 \sum_{n=1}^{n_{max}} \Gamma_{i_n} C_v C_{i_n}, \quad (1)$$

$$\frac{dC_{i_n}}{dt} = (1 - C_v)(1 - Z_1 C_v)P\delta_{n1} + Z_2 \sum_{p=1}^{n-1} \sum_{q \geqslant p}^{n-1} \delta_{n(p+q)} (\Gamma_{i_p} + \Gamma_{i_q}) C_{i_p} C_{i_q} - Z_3 \Gamma_{i_n} \sqrt{C_{iL} C_L} C_{i_n} - Z_1 \Gamma_{i_n} C_v C_{i_n} - Z_2 \sum_{p=1}^{p \leqslant n} (\Gamma_{i_n} + \Gamma_{i_p}) C_{i_n} C_{i_p}, \quad (2)$$

$$\frac{dC_L}{dt} = Z_2 \sum_{p=1}^{n_{max}} \sum_{q \geqslant p}^{n_{max}} \Theta(p + q - n_{max})(\Gamma_{i_p} + \Gamma_{i_q}) C_{i_p} C_{i_q}, \quad (3)$$

$$\frac{dC_{iL}}{dt} = Z_3 \sum_{p=1}^{n_{max}} p \Gamma_{i_p} \sqrt{C_{iL} C_L} C_{i_p} + A \frac{dC_L}{dt}. \quad (4)$$

Dependent variables

C_V- concentration of vacancies
C_{in} - concentration of interstitial clusters of size n
C_L - concentration of interstitial loops
C_{iL} - concentration of interstitials in the above loops

Parameters
P - damage production rate of interstitials and vacancies
Z_1 - capture volume of the vacancies (for interstitials)
Z_2 - capture volume of interstitials with each other
Z_3 - capture volume of interstitial loops with interstitial clusters
n_{max} - largest interstitial cluster size considered. Anything > n_{max} is considered to be a loop
A - average number of interstitials put into new loops when a new loop is formed
Γ_{i_n} - hopping rate of interstitial clusters of size n

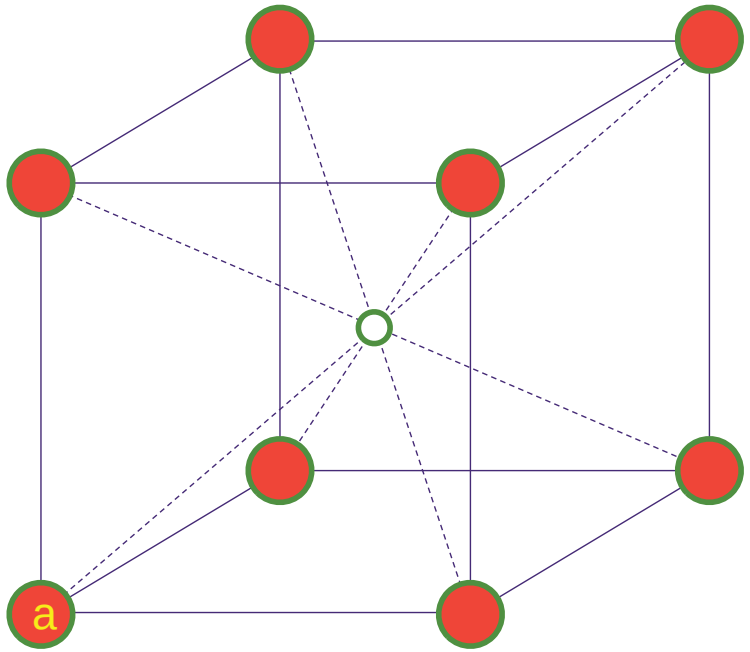
See e.g. Yoshida and Kiritani (1973); Uberuaga, Smith et al NIMB (2005)

Example of an easily guessed transition : Isolated vacancy diffusion mechanism in Fe

- Vacancy in bcc unit cell
- Fe atom moves halfway towards vacancy
- Main energy barrier: 0.64eV (a to b)
- Then it moves to fill the vacancy

Fe atom

Vacancy



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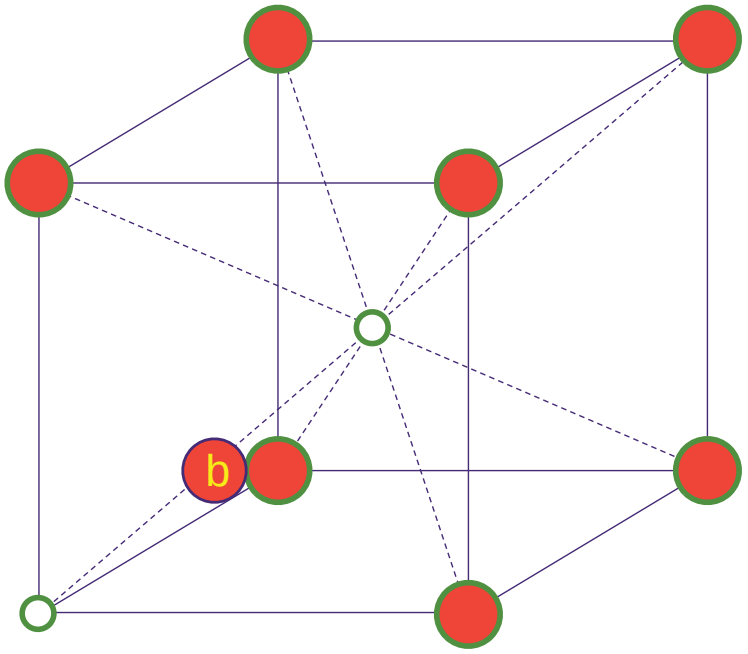

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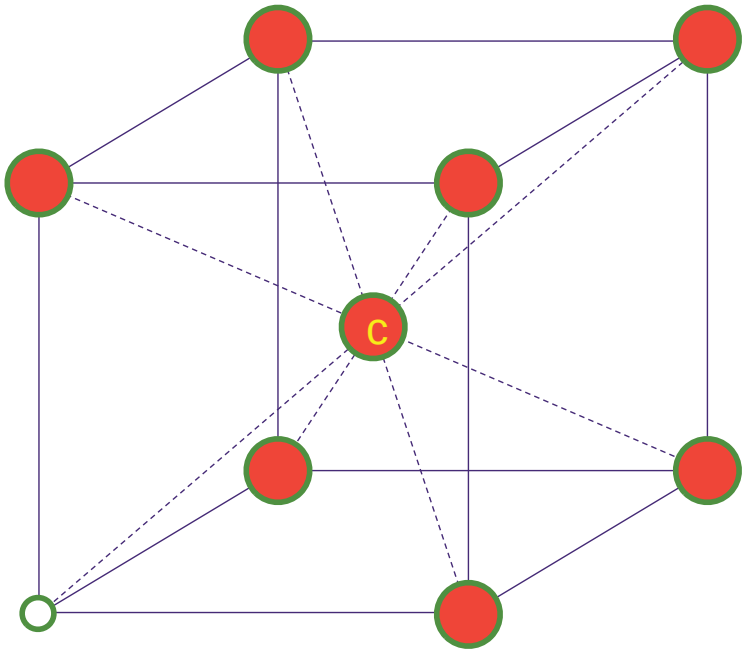

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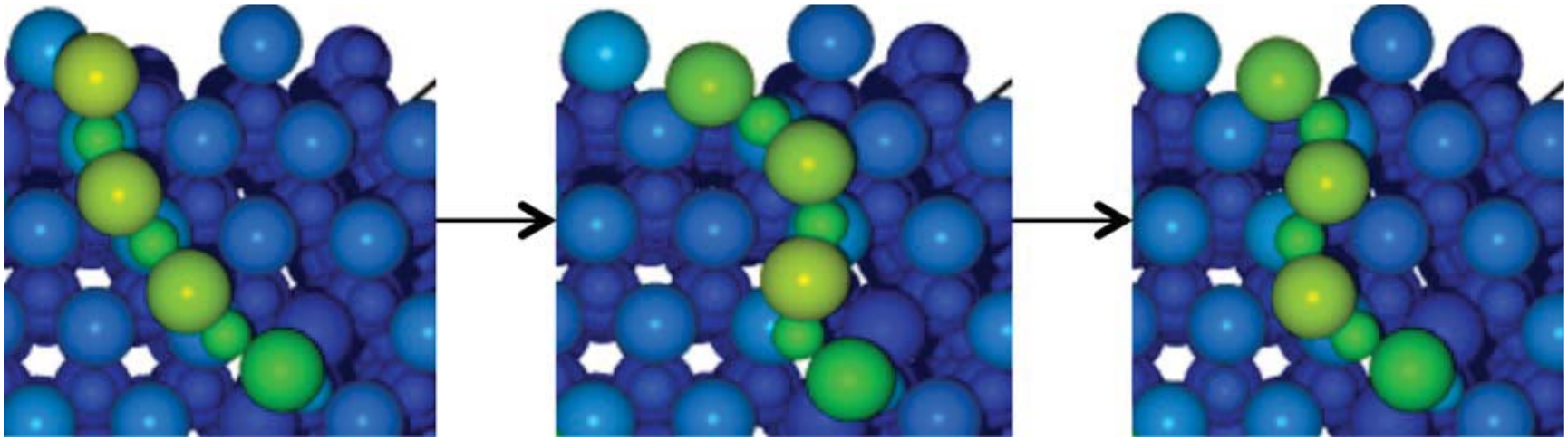
Example of an complex transition which cannot be guessed : String vibration on a ZnO surface



Small spheres represent Zn, large spheres O atoms

ZnO strings form on the surface and move with barriers of around 0.3eV.
When interacting with other such strings they form the hexagonal structures for the next crystalline layers

OTF-Kinetic Monte Carlo

$$r_{ij} = \nu * e^{(-\frac{E_{ij}}{k_B T})}$$

- On-the-fly KMC : system sizes typically 800-2000 atoms in our applications.

- For each minimum found, a list of *n* unique transitions from i to j with rates r_{ij}, *j=1..n* is constructed. Typically the search is terminated when no new unique transition is found after a fixed number of searches, *or* when a fixed number of transitions have been found *or* after a fixed search time.

- Normally we assume a fixed prefactor but could use the Vineyard method instead.

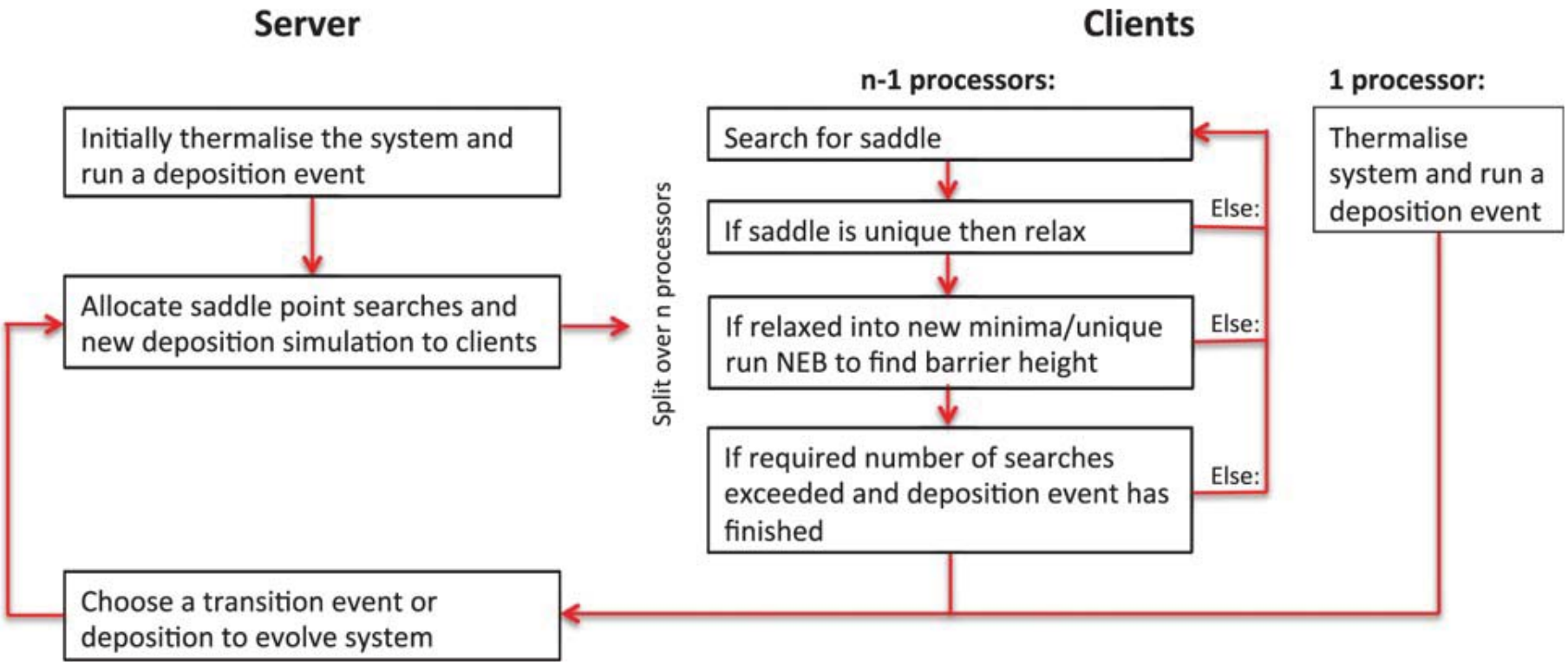
(G.H. Vineyard J. Phys. Chem. Solids **3** 121(1957))

The sum of the transition rates, R is calculated and a random numbers, P_r and u between 0 and 1 are generated and multiplied by R.

- We cumulatively step through the rates R_i until we exceed P_r.R. The selected transition R_i is performed and the time of the system is increased by Δt where:

$$\Delta t = -\frac{\log u}{R}.$$

OTF-KMC method



Code is written in Python and wraps around standard MD packages. In our case LBOMD and LAMMPS. The code was developed by Louis Vernon now at LANL and other PhD students in the group

The technique is time consuming so we need computational tricks to improve efficiency so we :

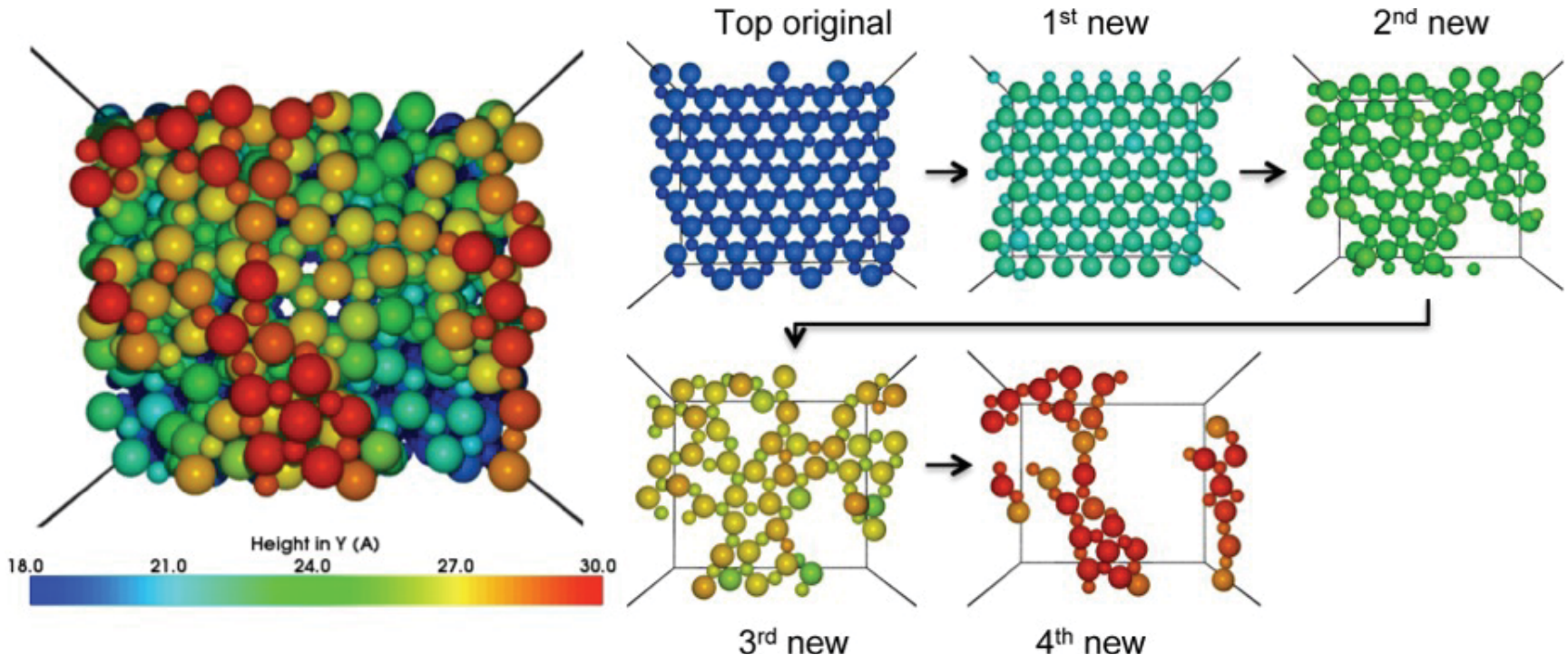
(1) Minimise the number of searches while retaining good statistics; typically we would perform > 200 such searches

(2) Initialise our initial search directions so as to sample the search space in the best way

(3) Minimise the search space volume, i.e. only consider the defective regions

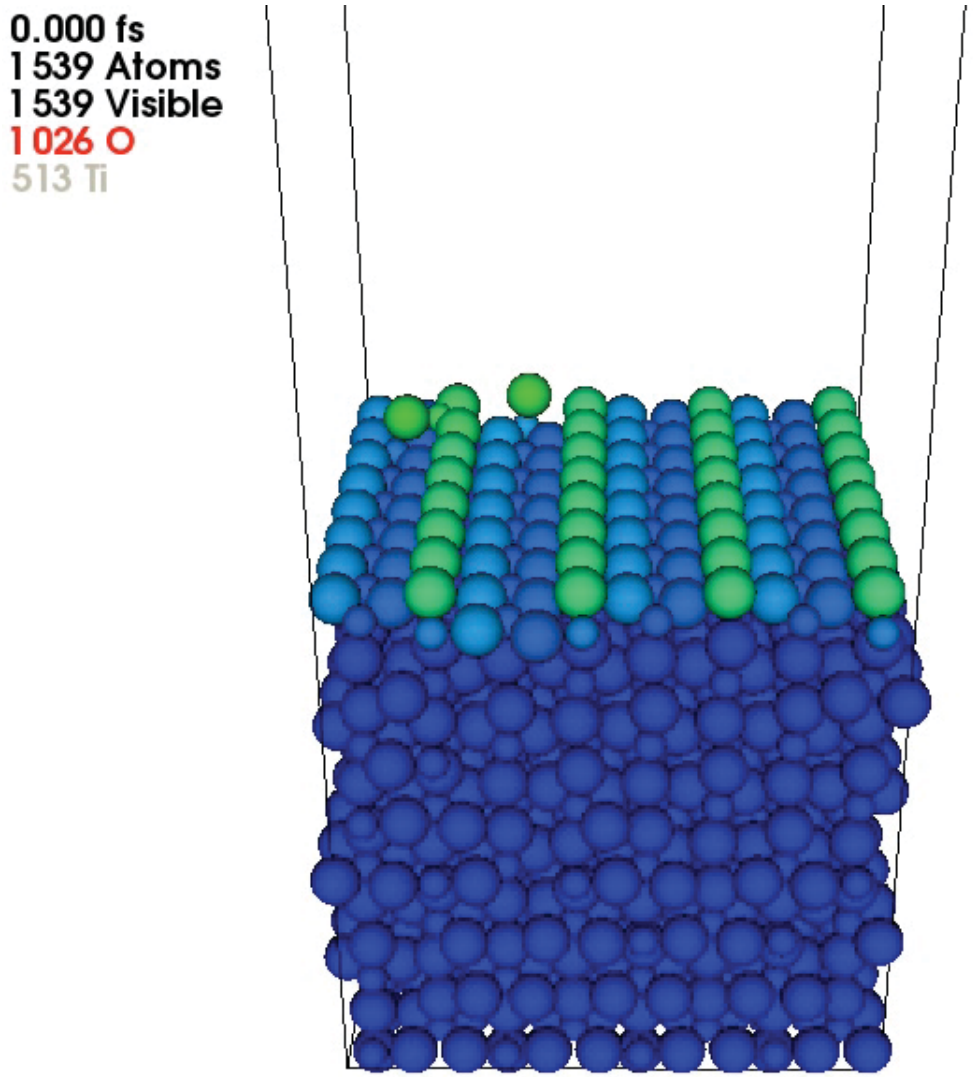
(4) Reuse previously determined transitions by recognising similar geometries (Pederson and Jonnson use path skipping also)

Example : ZnO film deposited at 40 eV and grown at 3 monolayers per second



Large spheres are O; small spheres are Zn; Atoms coloured by height. The equivalent of 3 monolyers were deposited

40 eV TiO_2 deposition movie : on rutile {110}



Conclusions

- Long time scale methods have made significant advances over recent years.
- They can be used to model growth at surfaces
- Initial simulations are being performed to extend MD so that dose rates can be studied

Diffusion constant for simple mechanisms

- In time t, the average distance moved from the origin is proportional to $\sqrt{t}$
- The diffusion constant formula is $D = \frac{\langle r^2 \rangle}{6t}$
- It is necessary to average many samples
- Typically varies according to the Arrhenius relation

$$D = D_0 \, \mathrm{e}^{-\frac{E}{k_B T}}$$

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