Kinetic Monte Carlo (KMC)

- **Molecular Dynamics (MD):** high-frequency motion dictate the time-step (e.g., vibrations).
  - Time step is short: pico-seconds.

- **Direct Monte Carlo (MC):** stochastic (non-deterministic) dynamics.
  - Relation between t_{sim} and t_{real} must be established, perhaps by MD simulations.

- **Kinetic MC (KMC):** we take the dynamics of MC seriously.
  - We consider the state space to be discrete (for example assign an atom to a lattice site).
  - "Multi-scale" or "course graining"
  - Using MD, we calculate rates from one state to another.

READING: Lesar Chapter 9

Kinetic Monte Carlo (KMC)

- With KMC we take the dynamics of MC seriously.
- Some applications:
  - Magnetism (the original application)
  - Particles diffusing on a surface.
  - MBE, CVD, vacancy diffusion on surface, dislocation motion, compositional pattering of irradiated alloys,…

ASSUMPTIONS

- States are discretized: s_i, spending only a small amount of time in between states.
- Hopping is rare so atoms come into local thermodynamic equilibrium in between steps (hence we have Markov process).
- We know hopping rates from state to state.   (Detailed balance gives relations between forward and reverse probabilities.)

Return to the Ising Model

- Suppose we have a lattice, with L^2 lattice sites and connections between them. (e.g. a square lattice).
- On each lattice site, is a single spin variable: $s_i = \pm 1$.
- The energy is:
  where h is the magnetic field

$$H = \sum_{(i,j)} J_{ij} s_i s_j - \sum_{i=1}^{N} h_i s_i$$

- J is the coupling between nearest neighbors (i,j)
  - J<0 ferromagnetic
  - J>0 antiferromagnetic.

$$and \quad Z = \sum e^{-\beta H}$$

- Alloy model
- Spin model
- Liquid/gas
- How do we make into KMC?
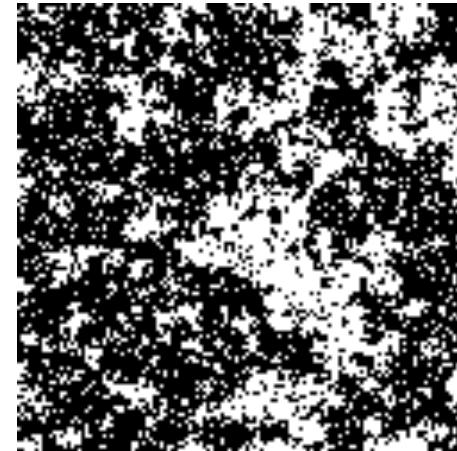
- Suppose the spin variable is (0,1)
  - S=0   the site is unoccupied
  - S=1   the site is occupied
- 4J is energy to break a bond.
- At most one particle/lattice site.
- Realistic dynamics must:
  - Satisfy detailed balance
  - Conserve particle number
  - Be local
- Assume W is nonzero only for hopping to neighboring sites.
- Since there are a finite number of possibilities we can assign a transition rate to all moves (from MD) .
- Detailed balance gives relationship between pairs of moves that are inverses of each other.
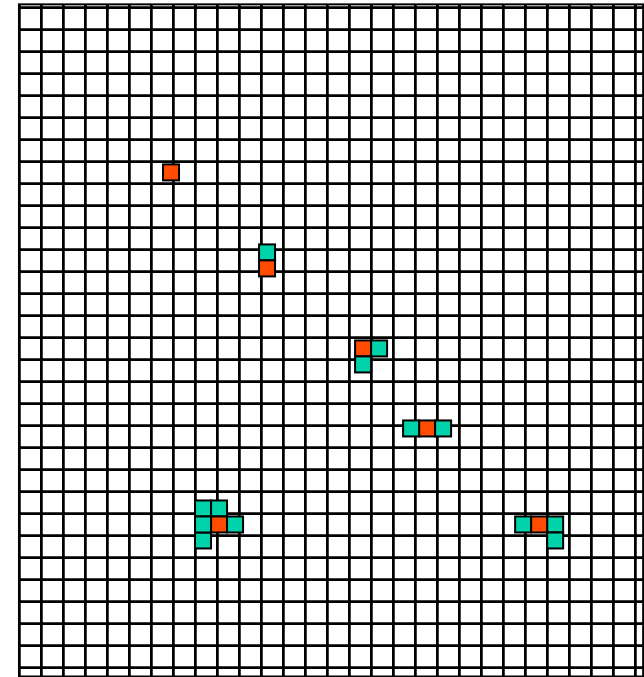
1-D example

- Consider the 1D Ising model with local moves.
- We consider a move of site 2 to site 3

    X **1 0** Y   to   X **0 1** Y

- There are 4 possibilities for the neighbors (X , Y)

    A: 1 1 0 0   to 1 0 1 0   state –D $\Delta E = 4J$

    B: 1 1 0 1   to 1 0 1 1   state –B $\Delta E = 0$

    C: 0 1 0 0   to 0 0 1 0   state –C $\Delta E = 0$

    D: 0 1 0 1   to 0 0 1 1   state -A $\Delta E = -4J$

Using Detailed balance, we have 3 independent rates

    $W(A \rightarrow D) = \exp(- DE/(k_B T))\ W(D \rightarrow A)$

    $W(B \rightarrow B)$

    $W(C \rightarrow C)$

- How do we get these rates? From MD or experimental data.

The Master Equation: stochastic dynamics

- W(s→s') is the <u>probability per unit time</u> that the system hops from s to s'
- Let P(s;t) be probability that system is in state s at time t. *Assume Markov process*, then the master equation for *P(s;t)* is:

$$\frac{dP(s,t)}{dt} = \sum_{s'} \left[P(s',t)W(s' \to s) - P(s)W(s \to s') \right]$$

- Given ergodicity, there is a unique equilibrium state, perhaps determined by detailed balance.

$$P(s', t=\infty)W(s' \to s) = P(s,t=\infty) \ W(s \to s')$$

Steady state is often Boltzmann distribution.

$$P(s', t=\infty)=exp(-V/kT)$$

(Detailed balance is sufficient not necessary)

- With KMC, we are interested in the dynamics not equilibrium distribution. How do we simulate the master equation?

How to simulate? Simple approach

Trotter's formula: at short enough time scale we can discretize time and consider events independent.

- Examine each particle: sample the time that particle k will hop. (OK as long as hops are non-interfering.)

- Solution to problem with a single event

$$\frac{dP(s,t)}{dt} = -W(s \rightarrow s')P(s)$$

$$P(s,t) = e^{-Wt} \qquad t(s \rightarrow s') = \frac{-\ln(u)}{W(s \rightarrow s')}$$

Alternative procedure sample the time for all the events and take the one that happens first (N-fold way).

N-fold way

Bortz, Kalos, Lebowitz, 1975

- Arrange different type of particles in lists
  - N_1 moves with transition W_1
  - N_2 moves with transition W_2
  - N_3 moves with transition W_3
  - N_4 moves with transition W_4

- Select a time for each class: $t_k = -ln(u_k)/W_k N_k$
  (Prove to be correct by considering the cumulant)
- Find j such that t_j =minimum $\{t_k\}$.
- Select a member of that class $i=N_j u$
- Make the move: time=$time+t_j$
- Update the lists. *(This is the key to an efficient algorithm)*

- To calculate averages, weight previous state by time, t_k;

- **Efficiency is independent of actual probabilities.**
- **No time step errors.**

Example: simple adsorption-desorption of atom on surface.

Let us assume
- Adsorbed molecules do not interact (otherwise, we have to consider rates for dimer formation and dimer splitting, etc.)
- Molecule arrives at surface at random, uncorrelated times characterized by average rate r_A, similarly for desorption.
- Then, the surface coverage (or probability of adsorption) is:

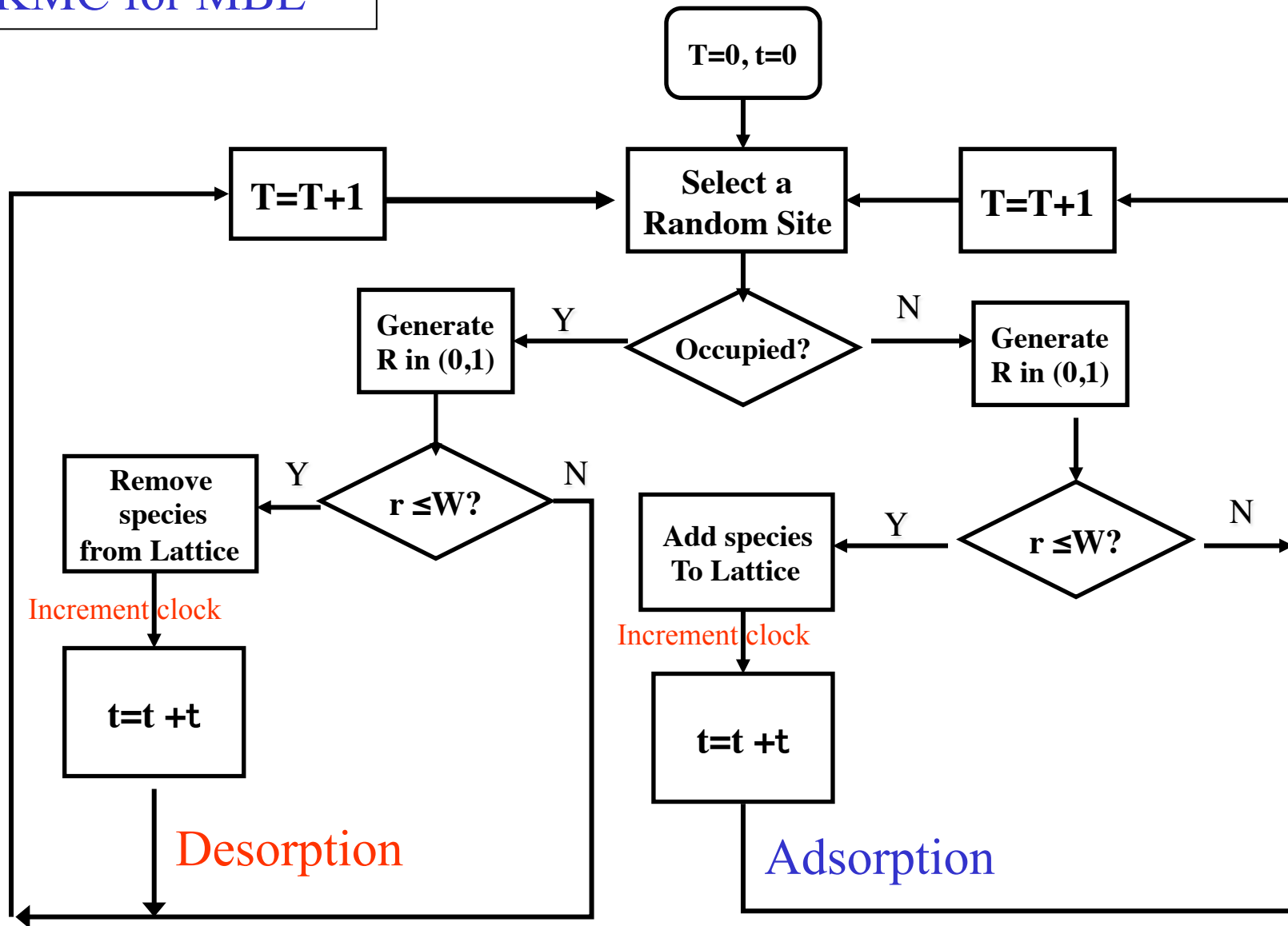$$\frac{d\theta(t)}{dt} = r_A[1 - \theta(t)] - r_D\theta(t)$$

Analytic Solution
$$\theta(t) = \frac{r_A}{r_A + r_D}[1 - e^{-(r_A + r_D)t}] \xrightarrow[t \to \infty]{} \frac{r_A}{r_A + r_D}$$

• Transition Probabilities W_A and W_D should obey detailed balance since they are chosen at random and independently such that successful adsorption is $W_A[1-\theta(t)]$ and desorption is $W_D\theta(t)$.

• Average adsorption in T trials is $<N_{A,T}> = W_A[1-\theta(t)]T$; thus steady-state is $<N_{A,T}>=<N_{D,T}>$ or $W_A[1-\theta]=W_D\theta$.   Detailed Balance!

KMC for MBE

T=0, t=0

Select a Random Site

T=T+1

T=T+1

Occupied?

Generate R in (0,1)   Y

Generate R in (0,1)   N

r ≤W?   Y   N

r ≤W?   Y   N

Remove species from Lattice

Add species To Lattice

Increment clock

Increment clock

t=t +t

t=t +t

Desorption

Adsorption

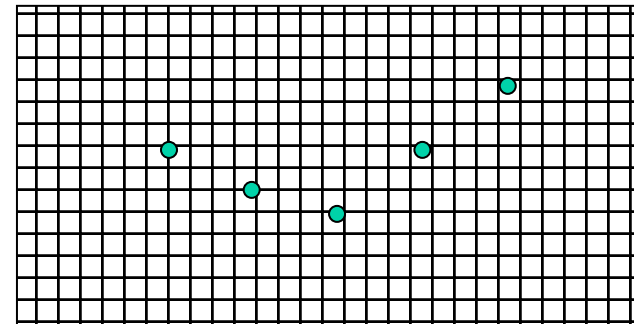# Kinetic Monte Carlo (KMC)

In other words

- Dynamical hierarchy is established for the transition probabilities.
- Independence of each event can be achieved.
- Time increments are calculated properly for successful (independent) events given by *Poisson Process*.
  - e.g. probability of particular rate process: $P(t) = e^{-Rt}$

Example: simple adsorption-desorption of atom on surface.

Time-dep. coverage of atoms matters.
Dictates whether site is occupied or not.
r_A = **adsorption rate**
r_D = **desorption rate**

Kinetic Monte Carlo (KMC)

Example: simple adsorption-desorption of atom on surface.

- W_{Ai} = adsorption transition rate at site i.
- W_{Di} = desorption rate at site i.
- r_A = overall rate for event A.
- r_D = overall rate for event D.   Total rate $R = r_A + r_D$.
- Event probability: $P_A = r_A/R$ and $P_D = r_D/R$.

- Hierarchy:
  - Defined by $W_i = r_i/r_{max}$.
  - e.g., If $r_A > r_D$, then $W_A = 1$ and $W_D = r_D/r_A$.
  - Then, $W_A > W_D$ and a hierarchy exists.
 - This generalizes to many process, etc.

- Time will be reflected in these rates - the more probable an event, the less time passes between them.

Example of KMC - Vacancy Mediated Diffusion (thanks to E. Ertekin)

Diffusion in solids is a complex, thermally activated process which can occur through a variety of mechanisms.

We will use KMC to consider vacancy mediated diffusion, in which a vacancy undergoes a "random walk" through a discrete atomic lattice.

The vacancy moves by swapping locations with neighboring atoms.
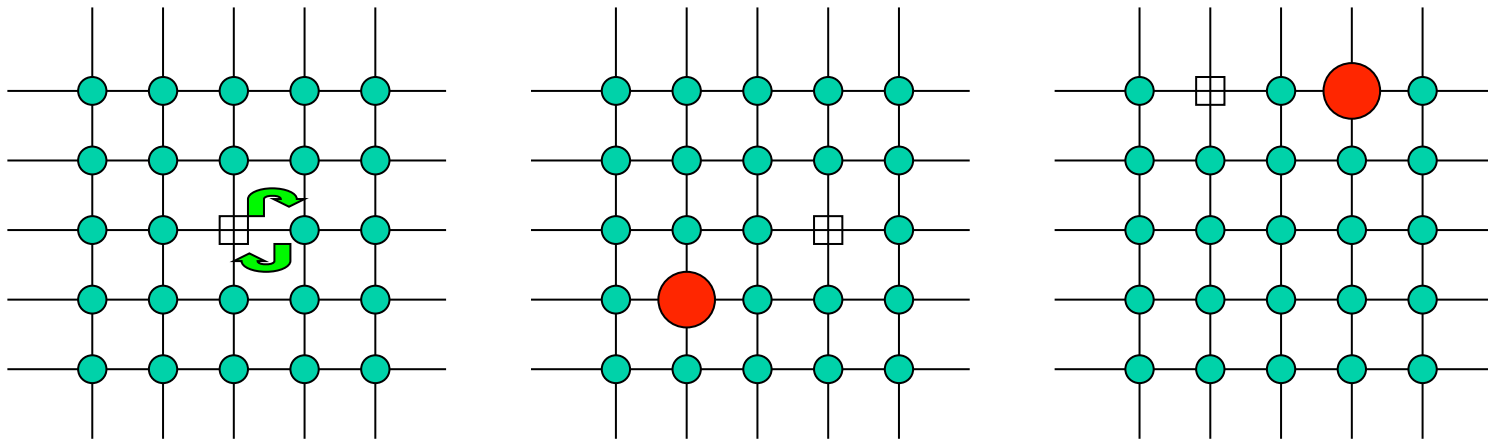

If we choose an atom at random to "trace", and keep track of its position over the course of the KMC simulation, we can estimate things like diffusion coefficients.

From some remarkably general considerations (that I will not describe here), we can relate mean-field quantities such as diffusion coefficients to discrete systems

$$J = -D \bullet \nabla C \ , \ \frac{\partial C}{\partial t} = D\nabla^2 C, \text{ probability distributions governing random walks} \quad \Rightarrow \quad 2dDt = \left\langle R^2 \right\rangle$$

Atomic Scale Simulation

Example of KMC - Vacancy Mediated Diffusion

1. Identify all the relevant processes for your system.
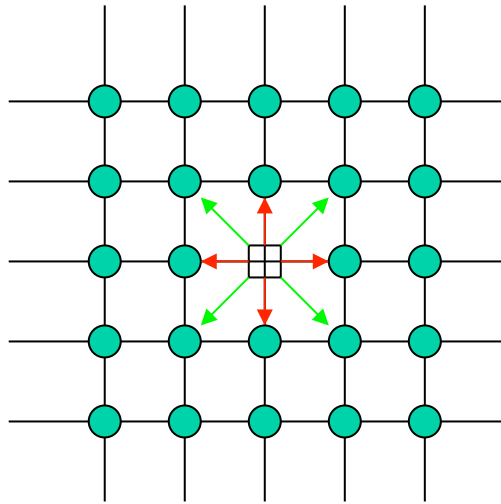

8 "obvious" processes:

- p_1, p_2, p_3, p_4 have barrier E_N
- p_1, p_2, p_3, p_4 have barrier E_D

What are other possible processes?

- two vacancies come into contact with some binding energy

- atoms swap locations with each other

- atom adsorption from gas, desorption to a gas (vacancy destruction or creation)

- etc, etc but we will ignore these

Atomic Scale Simulation

Example of KMC - Vacancy Mediated Diffusion

2. Determine (guess, estimate, calculate …) the activation barrier for each process. Use transition state theory to assign a rate to each process. We'll denote by r_i the rate of the i_{th} process.
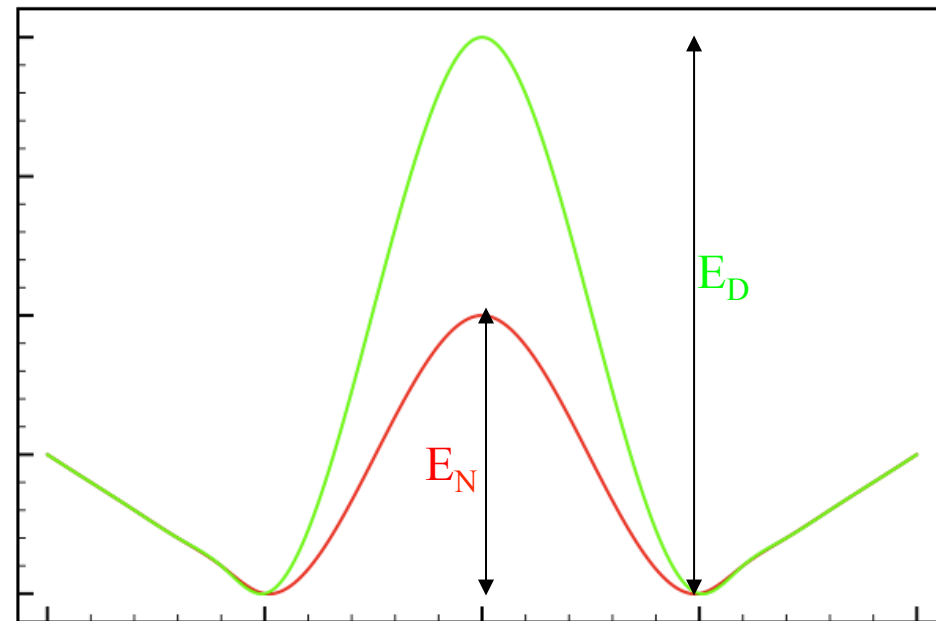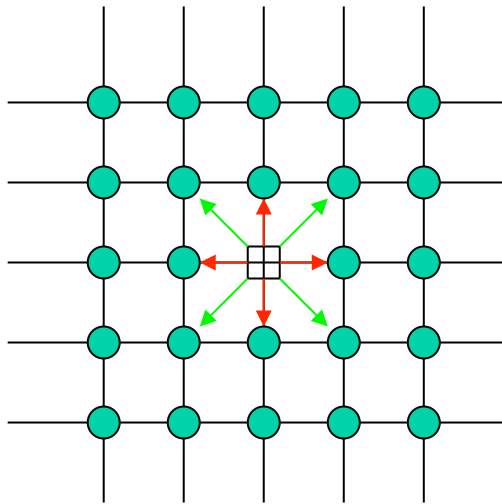
What are some ways to determine the transition barriers?

Atomic Scale Simulation
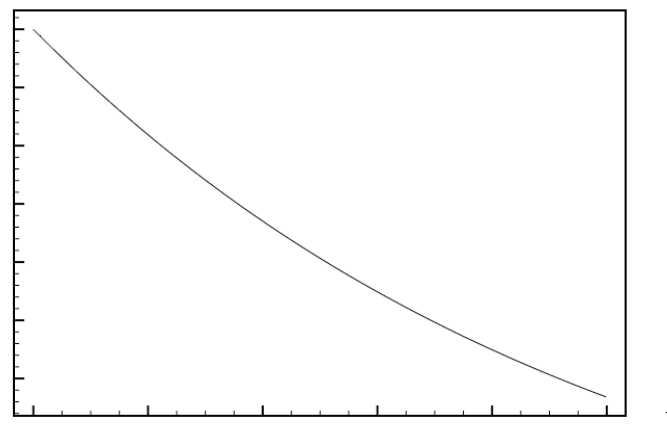
Example of KMC - Vacancy Mediated Diffusion

3. The total rate at which "anything" happens is then given by

$$R = \sum_i r_i = 4\nu\left(\exp\left[-\beta E_N\right] + \exp\left[-\beta E_D\right]\right)$$

4. Use R to choose from a poisson distribution the time at which the next event happens (first random number picked here).

$$p(t) = R\,\exp(-Rt)$$

probability distribution for the next event to occur

p(t)

t

How does one choose a number according to a poisson distribution?
We want to identify a function f(x) so that computing $f(x_i)=t_i$ generates
t_i according to p(t) (where x_i is a random number uniformly distributed
between 0 and 1.

$$t_i = -\frac{1}{R}\ln x_i$$

Example of KMC - Vacancy Mediated Diffusion

5. Choose which event actually happens (second random number) from the rate catalog

$$p_{N_1} = \frac{r_{N_1}}{R} = \frac{\exp[-\beta E_N]}{4(\exp[-\beta E_N] + \exp[-\beta E_D])}$$

$$p_{N_2} = \frac{r_{N_2}}{R} = \frac{\exp[-\beta E_N]}{4(\exp[-\beta E_N] + \exp[-\beta E_D])}$$

$$p_{N_3} = \frac{r_{N_3}}{R} = \frac{\exp[-\beta E_N]}{4(\exp[-\beta E_N] + \exp[-\beta E_D])}$$
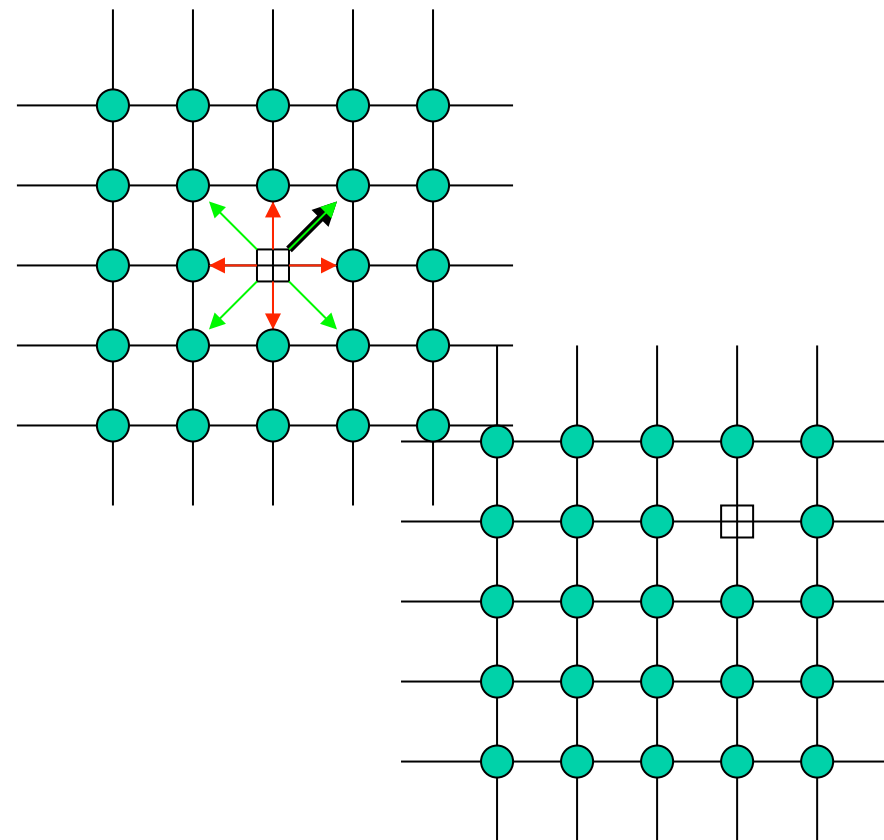
$$p_{N_4} = \frac{r_{N_4}}{R} = \frac{\exp[-\beta E_N]}{4(\exp[-\beta E_N] + \exp[-\beta E_D])}$$

$$p_{D_1} = \frac{r_{D_1}}{R} = \frac{\exp[-\beta E_D]}{4(\exp[-\beta E_N] + \exp[-\beta E_D])}$$

$$p_{D_2} = \frac{r_{D_2}}{R} = \frac{\exp[-\beta E_D]}{4(\exp[-\beta E_N] + \exp[-\beta E_D])}$$

$$p_{D_3} = \frac{r_{D_3}}{R} = \frac{\exp[-\beta E_D]}{4(\exp[-\beta E_N] + \exp[-\beta E_D])}$$

$$p_{D_4} = \frac{r_{D_4}}{R} = \frac{\exp[-\beta E_D]}{4(\exp[-\beta E_N] + \exp[-\beta E_D])}$$

Advance the clock, update the configuration, and record whatever properties you are interested in for the new configuration.

Atomic Scale Simulation

Example of KMC - Vacancy Mediated Diffusion

Repeat this process as long as reasonable. At the end of the day, you
will have something that looks like:

Step	Time	Configuration
1	Δt_1	C_1
2	$\Delta t_1 + \Delta t_2$	C_2
…	…	…
n	$\sum_{i=1}^{n} \Delta t_i$	C_n

From this, we can compute
properties of interest such as
diffusion coefficients.

Kinetic Monte Carlo vs. MD

MD: choose a potential, choose boundary conditions, and propagate the classical equations of motion forward in time. If potential is accurate, if electron-phonon coupling (non Born-Oppenheimer behavior) is negligible, then the dynamical evolution will be a very accurate representation of the real physical system.

Limitation is the time steps required by accurate integration (10^{-15} s to resolve atomic vibrations), generally limiting the total simulation time to microseconds.

KMC: attempts to overcome this by exploiting that the long-time dynamics of a system typically consist of jumps from one configuration to another.

In KMC, we do not follow trajectories, but treat the state transitions directly. Time scales are seconds or longer (in fact, achievable time varies with simulation temperature by orders of magnitude).

A key feature of KMC is that the configuration "sits" in some local minimum of configuration space for some time. It then transitions out of that state and into others with the transition rates related to the barriers. It does not matter how the system got into the current state in the first place - it is memoryless, and the process is Markovian.

Kinetic Monte Carlo vs. MD

What about the computational time in KMC?

  Limited by searching through the rate catalog for the process   that has been selected, so for the most elementary searches,   KMC computational time will scale linearly with the number of processes. More sophisticated search algorithms can give log(M) scaling.

Why is KMC not exact?

  - Inexact barriers. That is, inexactly computed.

  - In fact, the TST rate is not exact (harmonic approximation to the minima & saddle point) but are pretty good (within 10-20%).

  - Incomplete rate catalog. This is arguably the biggest problem in KMC. Our intuition cannot often capture surprising reaction pathways, and we neglect relevant physics.

Example: Adatom surface diffusion on Al(100)

After Voter, A.F. Radiation Effects in Solids, 2005:

- Until 1990, diffusion of an adatom on an fcc(100) surface was thought to occur by a simple hopping from one site to another
- Feibelman (1990) discovered using density functional calculations that the primary diffusion pathway is quite different

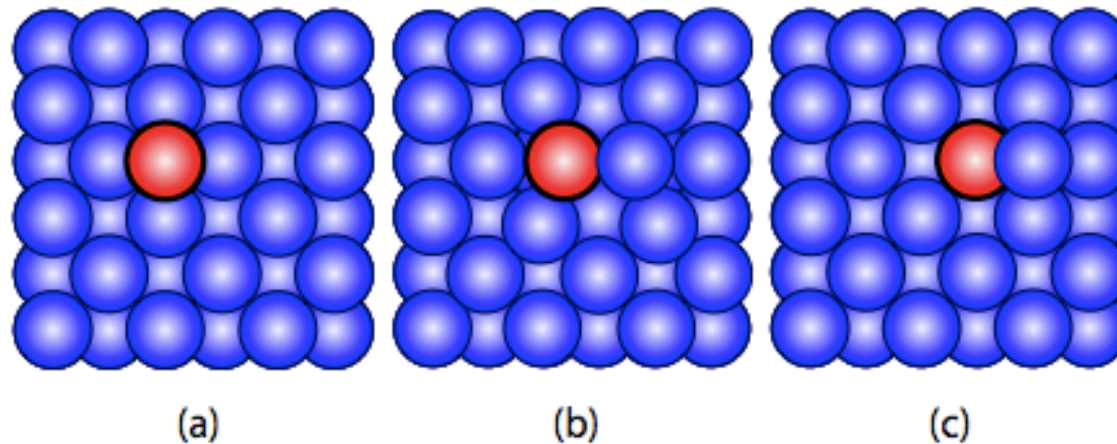

(a)   (b)   (c)

Fig. 6. Exchange mechanism for adatom on fcc(100) surface. (a) initial state; (b) saddle point; (c) final state. This mechanism, unknown until 1990 [52], is the dominant diffusion pathway for some fcc metals, including Al, Pt, and Ir.

- This new mechanism has now been observed for Pt(100) and Ir(100) surfaces via field ion microscopy