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.

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

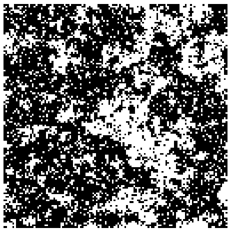
- States are discretized: s_i, spending only a small amount of time in between states.
- Hopping is rare so atoms come into local thermodynamic equilibrium in between steps (hence we have Markov process).
- We know hopping rates from state to state. (Detailed balance gives relations between forward and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

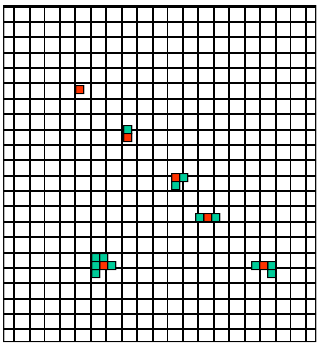
Return to the Ising Model

- 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
- J is the coupling between nearest neighbors (i,j)
  - J<0 ferromagnetic
  - J>0 antiferromagnetic.
- Alloy model
- Spin model
- Liquid/gas
- How do we make into KMC?

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

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





- 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

$W(A\to D)=\exp(-\Delta E/(k_BT))\ W(D\to A)$

$W(B\to B)$

$W(C\to C)$

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

The Master Equation

- $W(s\to s')$ 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:

$$dP(s,t)/dt = \Sigma_{s'}\ [\ \mathbf{P(s')W(s'\to s)}\ -\ \mathbf{P(s)\ W(s\to s')}\ ]$$

- 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 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

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

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

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: $\mathbf{t_k = -\ln(u_k) / W_k N_k}$
  (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 moving 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 **$\langle N_{A,T}\rangle = W_A[1-\theta(t)]T$**; thus steady-state is **$\langle N_{A,T}\rangle = \langle N_{D,T}\rangle$** or **$W_A[1-\theta] = W_D\theta$.** **Detailed Balance!**

KMC for MBE