

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.
 - Or Transition State Theory (TST) to relate energy barriers to rates

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 patterning of irradiated alloys,...

ASSUMPTIONS

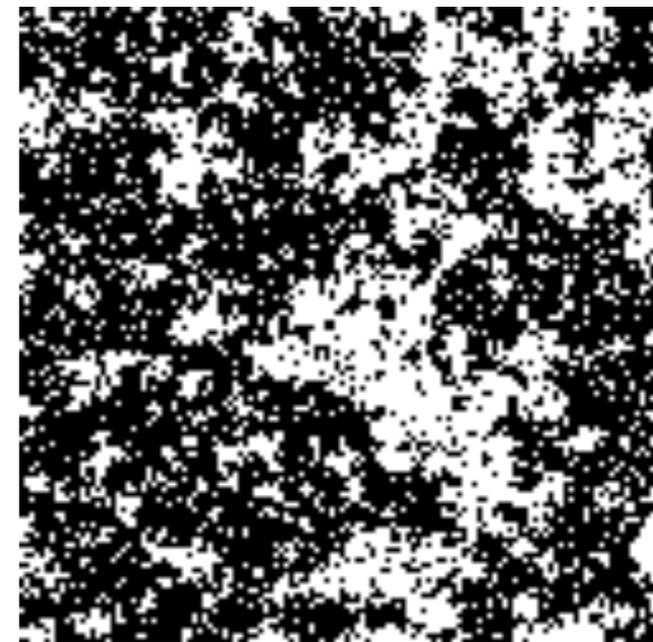
- States are discretized: s_i , spending only a small amount of time in between states.
- Hopping is rare so atoms come into local thermodynamic equilibrium in between steps (hence we have Markov process).
- We know hopping rates from state to state. (Detailed balance gives relations between forward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

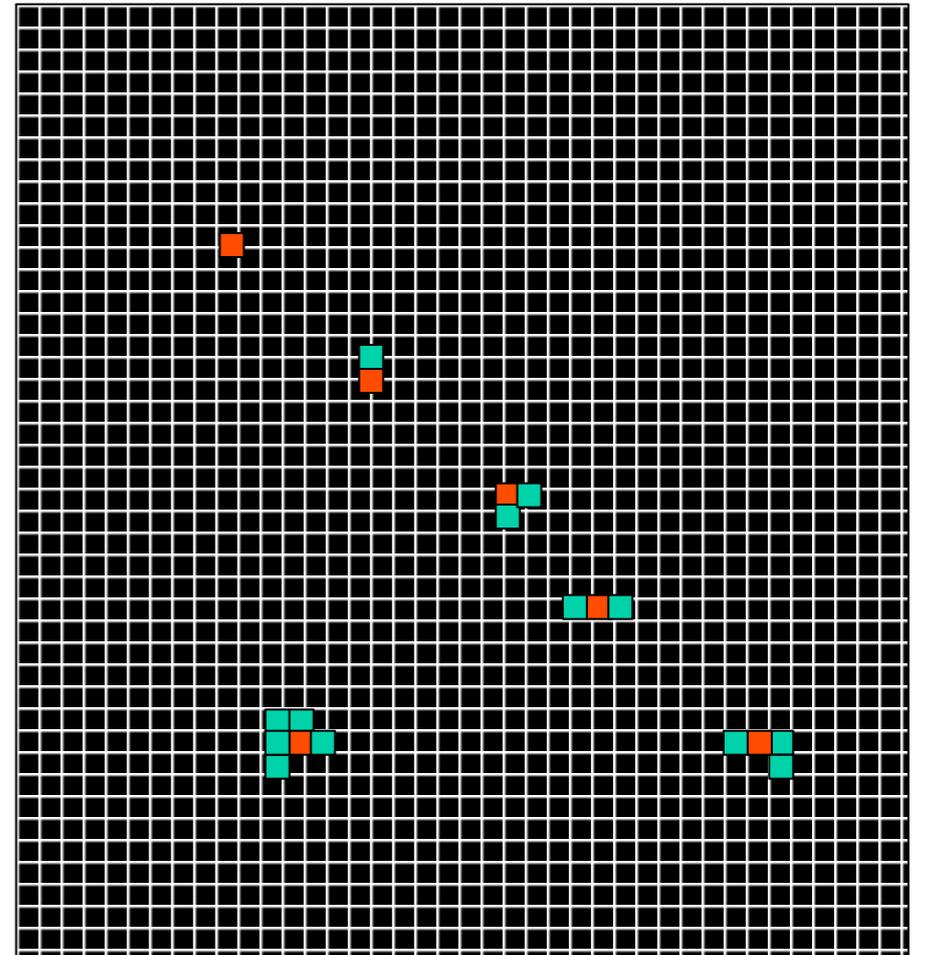
$$H = -J \sum_{\langle ij \rangle} s_i s_j - h \sum_i s_i$$

$$Z = \sum_{s_i = \pm 1} e^{-\beta H}$$



Return to the Ising Model

- 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 rate 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, or TST) .
- 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	$\Delta E=2J$
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	$\Delta E=-2J$

Using Detailed balance, we have 3 independent rates

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

$$W(B \rightarrow B)$$

$$W(C \rightarrow C)$$

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

The Master Equation

- $W(s \rightarrow s')$ is the probability per unit time 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:

$$dP(s,t)/dt = \sum_{s'} [P(s')W(s' \rightarrow s) - P(s) W(s \rightarrow s')]$$

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

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

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

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

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

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

Can also select event from cumulative probability

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 cumulative distribution)
- Find j such that $t_j = \text{minimum } \{t_k\}$.
- Select a member of that class $i = N_j u$
- Make the move: $\text{time} = \text{time} + t_j$
- 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.**

Kinetic Monte Carlo (KMC)

In other words

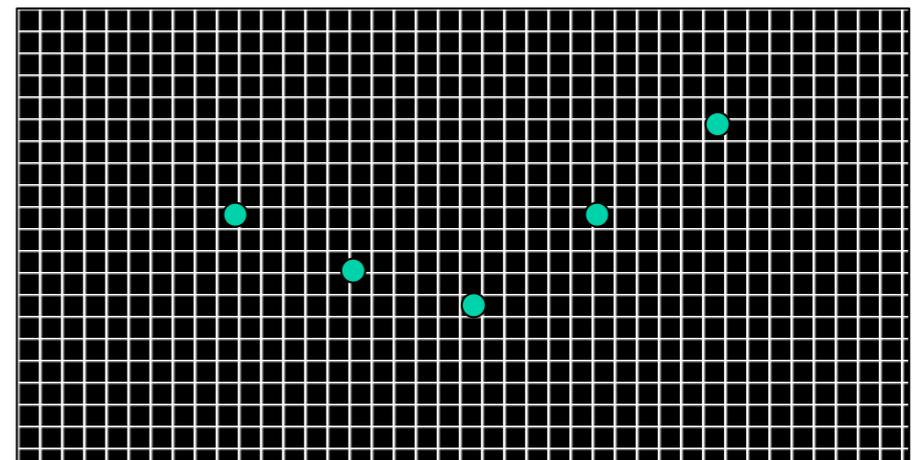
- Dynamical hierarchy is established for the transition probabilities.
- Independence of each event can be achieved.
- Time increments are calculated properly for successful (independent) events given by *Poisson Process*.
 - e.g. probability of particular rate process: $P(t) = e^{-Rt}$

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: 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

$$\theta(t) = \frac{r_A}{r_A + r_D} [1 - e^{-(r_A + r_D)t}] \quad \lim_{t \rightarrow \infty} \theta(t) = \frac{r_A}{r_A + r_D}$$

- 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!**

Evolution of the Master Equation: beware of approximation and their failures

Sometimes the Master Equation is approximated via a Taylor's series method, e.g. for the probability distribution $P(s,t)$.

Example: $P(x,t)$ is sharply peaked, $P(x,t) \propto e^{-Nf(x)}$,
for N atoms and $f(x)$ is intrinsic function.

- Expand $P(x+s, t)$ to first order in small s , which is often called the *Fokker-Planck equation*.
- In such cases, care must be taken to avoid large errors.

Taylor's series

$$P(x + s) = \sum_{n=0}^{\infty} \frac{1}{n!} (s \cdot \nabla)^n P(x)$$

all terms contribute $O(N)$ with no $(1/N)^n$ convergence!

However, see Kubo et al. J. Stat. Phys. 8, 51 (1973), **expand $f(x)$** via Taylor's series as above and the Master Equation becomes:

$$\frac{df(x,t)}{dt} = \sum_s W(x \rightarrow x + s) \left[e^{s \cdot \nabla f(x,t)} - 1 \right]$$

Results agrees with Thermodynamic method up to $O(N^{-1})!$

Kinetic Monte Carlo (KMC)

- **General approach:**
 - Generate list of events from state
 - Generate rates of events and compute *total rate*
 - Select uniform random number u , identify *event* to choose
 - Either *store inverse total rate* or *generate exponentially distributed time step from rate*
 - Update list of events, repeat
 - *Thermodynamic averages: weight states by average escape time*
- **When is KMC appropriate?**
 - Able to *define discrete states* and *efficiently compute transition rates*
 - Especially efficient when events are *local* so that rate update is fast
 - Useful if state-to-state dynamics are needed
 - *Rejection free method*
- **Pitfalls:**
 - Can get stuck in “superbasins”: fast transitions are most probable and dominate
 - GIGO: if you don't have all of the necessary transitions, KMC won't find it.
 - Tricky to parallelize for large systems