**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 $t_{\text{sim}}$ and $t_{\text{real}}$ 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.

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**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:
  \[ H = \sum_{(i,j)} J_{ij} s_i s_j - \sum_{i=1}^{N} h_i s_i \]
  where \( h \) is the magnetic field

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

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
  \[
  X \begin{array}{c} 1 \end{array} 0 \begin{array}{c} Y \end{array} \quad \text{to} \quad X \begin{array}{c} 0 \end{array} 1 Y
  \]
- There are 4 possibilities for the neighbors \((X, Y)\)
  
  A: \begin{array}{c} 1 \end{array} 1 0 0 \quad \text{to} \quad \begin{array}{c} 1 \end{array} 0 1 0 \quad \text{state} -D \quad \Delta E=4J
  
  B: \begin{array}{c} 1 \end{array} 1 0 1 \quad \text{to} \quad \begin{array}{c} 1 \end{array} 0 1 1 \quad \text{state} -B \quad \Delta E=0
  
  C: \begin{array}{c} 0 \end{array} 1 0 0 \quad \text{to} \quad \begin{array}{c} 0 \end{array} 0 1 0 \quad \text{state} -C \quad \Delta E=0
  
  D: \begin{array}{c} 0 \end{array} 1 0 1 \quad \text{to} \quad \begin{array}{c} 0 \end{array} 0 1 1 \quad \text{state} -A \quad \Delta E=-4J
  
  Using Detailed balance, we have 3 independent rates
  
  \[
  W(A\rightarrow D)=\exp\left(-\frac{\Delta E}{k_BT}\right) \quad W(D\rightarrow A)
  
  W(B\rightarrow B)
  
  W(C\rightarrow C)
  \]

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

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

- 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).

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: \( t_k = \frac{-\ln(u_k)}{W_kN_k} \)  
  (Prove to be correct by considering the cumulant)

- Find \( j \) such that \( t_j = \text{minimum} \{t_k\} \).

- Select a member of that class \( i = N_ju \)

- 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, \( t_i \);
  - 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

$$\theta(t) = \frac{r_A}{r_A + r_D} \left[ 1 - e^{-(r_A + r_D)t} \right] \rightharpoonup \frac{r_A}{r_A + r_D}$$

- 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!*

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KMC for MBE

- $T=T+1$
- Select a Random Site
- Generate $R$ in $[0,1]$
  - Occupied? Y N
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