Kinetic or Dynamic Monte Carlo (KMC)

The "dynamics" in ordinary MC is just an artificial sequence of moves. In many cases, however, the actual physical dynamics can be coarse-grained to a Markov process, in particular, a sequence of transitions between states, at least approximately.

e.g.,

1. Diffusion represented via hopping events (defects in metals, lattice gas models)
2. Collisions between gas molecules (kinetic theory)
In KMC models, one needs to identify coarse-grained states and rules (probabilities or rates) for transitioning between them. The Markov assumption is justified (sometimes formally) by the large separation of timescales between the typical waiting time between transitions (e.g., spin flips, atom jumps) and the duration of the actual transition (metastability).

$\Rightarrow$ Formally, limit of zero temperature $k_B T \rightarrow 0$
In material science two types of MCMC models are common:

1. Continuous time discrete space (CTDS)
   - Markov chains, e.g., lattice models such as the Ising model

2. Continuous time continuous space (CTCS)
   - MCs, e.g., continuum diffusion or collision dynamics

There is also mixed continuous-discrete space models (e.g., reaction-diffusion MC)

The only difference is sums versus integrals
The KMC or MCMC model is specified by the transition rates, which are assumed to be stationary:

\[ p(x', t' | x, t) = p(x' | x ; \Delta t = t' - t) \]

\[ p(x' | x ; dt) = dt \cdot w(x' | x) \]

\[ \delta(x - x') \left[ 1 - \int \delta(x - \tilde{x}) w(\tilde{x} | x) \right] \]

Here, \( w(x' | x) \) is the transition rate, which is typically obtained using a transition state theory approximation.
The probability distribution for the chain to be in state \( x \) at time \( t \) obeys the **Master Equation**:

\[
\frac{\partial}{\partial t} P(x', t' \mid x, t) = \int d\tilde{x} \left[ w(x' \mid \tilde{x}; t) P(\tilde{x}, t' \mid x, t) - w(\tilde{x} \mid x'; t) P(x', t' \mid x, t) \right]
\]

Usually \( \text{time-independent} \) \( \Rightarrow \text{in coming flux} \)

\( \text{out going flux} \)

**Differential version of the Chapman-Kolmogorov equation**
Equivalently, we can write a master equation for the probability density of observing the chain at $x$ at time $t$:

$$\frac{\partial P(x, t)}{\partial t} = \int dx \left[ w(x | \tilde{\omega}) P(\tilde{\omega}, t) - w(\tilde{\omega} | x) P(x, t) \right]$$

The probability to remain in the same state during time $\Delta t$ satisfies

$$\frac{\partial Q(y, \Delta t)}{\partial t} = -\left[ \int dx \cdot w(x | y) \right] Q(y, \Delta t)$$

$$\Rightarrow Q(y, \Delta t) = \exp \left[ -\lambda \Delta t \right] \text{ Poisson process}$$
Where \( \lambda(y) = \int dx \cdot w(x \mid y) \) is the total jump rate out of state \( y \).

For discrete space: \( \lambda_i = \sum_j P_{ij} \)

Each of the transitions out of the present state is a Poisson process, and the rates add up.

So simulating such a Markov chain is in principle very simple:

\[ \text{MC} \]

1. Sample an exponentially distributed waiting time at using rate \( \lambda \)

2. Choose a new state with prob. \( \frac{w(x \mid y)}{\lambda} \)
Side-note (for now)

If, in addition to the jump process, there is also a deterministic dynamics with drift rate \( A(x,t) \):

\[
\dot{x} = A \left( x(t), t \right)
\]

this adds a divergence of a flux contribution to the Master Equation:

\[
\partial_t p(x',t'|x,t) = - \nabla_x \cdot \left[ A(x,t') p(x',t'|x,t) \right]
\]

or

\[
\partial_t P(x,t) = - \nabla_x \cdot \left[ A(x,t) P(x,t) \right]
\]

Lioville's equation
For concreteness, let's focus on discrete spaces, e.g., a lattice model where particles occupy sites of a 1D lattice.

\[
\begin{array}{cccccc}
2 & x & x & 5 & 4 & x \times 1 \times 3 \times x
\end{array}
\]  

state with 5 particles and 10 sites.

Since the number of states is so large, solving the full master equation requires, in principle, computing the exponential of the transition matrix of size $N^2$ states (infeasible!).
\[ \frac{\partial}{\partial t} P_i(t) = \sum_j w_{ji} P_j(t) - \left[ \sum_j w_{ij} \right] P_i(t) \]

\[ \frac{\partial}{\partial t} \vec{P}(t) = W \cdot \vec{P}(t) \]

\[ \Rightarrow \vec{P}(t) = e^{Wt} \cdot \vec{P}(0) \]

Instead of trying to compute the full \( \vec{P}(t) \), however, we can just generate a lot of sample trajectories by simulating the Markov chain, and then compute expectation values as averages.
KMC algorithm (synchronous KMC):

1. Build a list of all processes given process configuration.
2. Delete obsolete processes (rebuild).
3. Find new state $\mathbf{i'}$ using $\mathbf{wij} \sim \mathcal{R}_{ij} \sim \frac{1}{\mathbf{wij}}$.

Total rate $R = \sum_{i, j} \mathbf{wij}$.
The key to efficient synchronous KMC is the effective use of data structures:

→ How to quickly select which transition to execute?

→ How to quickly update the list of possible transitions and rates (if "on the fly" KMC then a less coarse grained method is used to do this carefully).

In simple models of lattice gases the best one can usually do is $O(\log n)$ per step.
An alternative KMC algorithm is a time-ordered list KMC or asynchronous algorithm.

1. For each event, assign randomly an exponential waiting time and thus a tentative event time \( t_k \).

2. Sort these times in an event queue (heap).

3. Execute the earliest (first) event in the queue.

4. Update the event queue and go back to 2.
Go through several examples on board:

1. Simple non-interacting diffusion (dropping)
   - with multiple species
     - Distinguishable particles
     - Indistinguishable particles (rejection or sorting)

2. Excluded random walk
   - Rejection based [also boundaries]
     - Rejection-free
     - Relation to Ising-type models

3. Repulsion-driven random walk
   - Particle identity matters (OSMC)
     - Reactive collisions

4. Chemical reaction networks
Briefly: Where do the transition rates come from?

Answer: Transition State Theory, which is based on Large Deviation Theory.

Formally a weak noise limit, maybe also overdamped $k_B T \to 0$
TST-like rate equation:

$$W_{ij} \approx \frac{k_B T}{h} \exp \left[ - \frac{\Delta F_{ij}}{k_B T} \right]$$

$\Delta F_{ij}$ is an activation free energy

$$F = U - T \cdot S$$

$\uparrow$ internal energy

$\rightarrow$ entropy

$\downarrow$ partition function

$$\Delta F_{ij} \approx k_B \log \left[ \frac{Z_i}{Z_{ij}} \right]$$

Constrained "free-energy", hard to calculate
Often the entropic contribution or vibrational free energy is approximated by:

\[ w_{ij} \approx w_0 \exp \left[ -\frac{\Delta E_{ij}}{k_b T} \right] \]

activation energy

attempt frequency prefactor

where \( \Delta E_{ij} \) is also approximated, for example, using "bond counting".

\[ \frac{w_{ij}}{w_{ji}} = \frac{\exp \left[ -\beta E_{TS} + \beta E_i \right]}{\exp \left[ -\beta E_{TS} + \beta E_j \right]} = \frac{\exp(-\beta E_j)}{\exp(-\beta E_i)} \]

satisfies detailed balance