Kinetic Monte Carlo Simulation Algorithm

- Master equation: to be simulated

\[
\frac{dP_\alpha}{dt} = -\sum_\beta \frac{w_{\beta \alpha}}{\beta} P_\alpha(t) + \sum_\beta \frac{w_{\alpha \beta}}{\beta} P_\beta(t)
\]  \hspace{1cm} (1)

(Example - 4 states)

<table>
<thead>
<tr>
<th>(dP_1/dt)</th>
<th>(dP_2/dt)</th>
<th>(dP_3/dt)</th>
<th>(dP_4/dt)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(-w_{11} -w_{12} -w_{14})</td>
<td>(w_{11})</td>
<td>(w_{13})</td>
<td>(w_{14})</td>
</tr>
<tr>
<td>(w_{12})</td>
<td>(-w_{12} -w_{12} -w_{13})</td>
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</table>

\(P_1\) \hspace{1cm} \(P_2\) \hspace{1cm} \(P_3\) \hspace{1cm} \(P_4\)


Let us define vector \(\mathbf{P}\) such that \(P_\alpha = P_\alpha\), and matrices

\[
W_{\alpha \beta} = w_{\alpha \beta}
\]  \hspace{1cm} (2)

\[
R_{\alpha \beta} = \begin{cases} 
\frac{\sum_\gamma w_{\gamma \alpha}}{\gamma} &= P^{tot}_{\alpha} \quad (\alpha = \beta) \\
0 &= (\alpha \neq \beta)
\end{cases}
\]  \hspace{1cm} (3)

Then the master equation, Eq. (1), is cast into a matrix form

\[
\frac{d\mathbf{P}}{dt} = -(R - W) \mathbf{P}(t)
\]  \hspace{1cm} (4)

The formal solution of Eq. (4) is

\[
\mathbf{P}(t) = \mathbf{Q}(t) \mathbf{P}(0) + \int_0^t \mathbf{Q}(t - t') W \mathbf{P}(t') dt'
\]  \hspace{1cm} (5)

The time-dependent perturbation: time-ordered exponential

\[
\mathbf{Q}(t) \equiv \exp(-Rt)
\]  \hspace{1cm} (6)

where \(\mathbf{Q}(t)\) is the non-transitional solution
\[ \frac{dP}{dt} = \frac{d}{dt} \left[ Q(t) P(0) + \int_0^t dt' Q(t-t') WP(t') + \frac{1}{R} \int_0^t dt' Q(t-t') WP(t') \right] \]

\[ = -R \left[ Q(t) P(0) + \int_0^t dt' Q(t-t') WP(t') \right] + WP(t) \]

\[ = \left( -R + WP \right) P(t) \sim \text{satisfies differential equation (4)} \]

Also \( P(t \to 0) = Q(0) P(0) + \int_0^t dt' Q(t-t') WP(t') = IP(0) \sim \text{satisfies initial condition} \]

- Physical (multiple-scattering) interpretation

Rewrite Eq. (5) as

\[ P(t) = Q(t) P(0) + \int_0^t dt' Q(t-t') WP(t') + \int_0^t dt' \int_0^{t'} dt'' Q(t-t') W Q(t-t'') WP(t'') \]

\[ = Q(t) P(0) + \int_0^t dt' Q(t-t') W Q(t) P(0) \]

\[ + \int_0^t dt' \int_0^{t'} dt'' Q(t-t') W Q(t-t'') W Q(t-t''') P(0) + \cdots \] (7)

In Eq. (8), the first term is the probability when no transition has occurred in \([0,t]\); the second is that with one transition; third with 2 transitions, etc.
Ensemble average

Kinetic Monte Carlo (KMC) simulation represents $P(t)$ as an ensemble of random realizations of state-transition sequences, starting from an initial state drawn from $P(0)$.

(Example - 4 states with $P_\alpha(0) = \delta_{\alpha 1}$)

Rejection-free "residence time" procedure

Assume at time $t=0$, the system is in state $\alpha$ (with probability $1$) and consider the probability of no transition occurring until time $t$. From Eq. (5),

$$P_{\alpha}^{\text{res}}(t) = \mathcal{Q}_{\alpha}(t) \frac{P_\alpha(0)}{1 - \exp(-R_\alpha^{\text{tot}} t)}$$

Let, $P_{\ast \rightarrow \alpha}^{\text{fev}}(t) dt$ is the probability that the first transition from state $\alpha$ to one of the other states occurs in $[t, t+dt]$, then

$$P_{\alpha}^{\text{res}}(t) = 1 - \int_0^t dt' P_{\ast \rightarrow \alpha}^{\text{fev}}(t')$$
Differentiating Eq. (10) w.r.t. time,
\[
\frac{dP_{\alpha}}{dt} = -p_{\text{fext}}^{\alpha}(t) \quad (11)
\]

Substituting Eq. (9) in (11),
\[
p_{\text{fext}}^{\alpha}(t) = R_{\alpha}^{\text{tot}} \exp(-R_{\alpha}^{\text{tot}} t) \quad (12a)
\]
\[
= \sum_{\beta} w_{\beta \alpha} \exp(-R_{\alpha}^{\text{tot}} t) \quad (\therefore \text{Eq. (3)}) \quad (12b)
\]
\[
= \sum_{\beta} p_{\beta \alpha}^{\text{fext}}(t) \quad (12c)
\]

where
\[
p_{\beta \alpha}^{\text{fext}}(t) = w_{\beta \alpha} \exp(-R_{\alpha}^{\text{tot}} t) \quad (13)
\]

In summary, the probability for the system to stay in \( \alpha \) without any transition for time \( t \) is
\[
P_{\alpha}^{\text{res}}(t) = \exp(-R_{\alpha}^{\text{tot}} t)
\]

and, in addition, for the first event to occur in \([t,t+dt]\) is (for destination state \( \beta \))
\[
p_{\beta \alpha}^{\text{fext}}(t) dt = w_{\beta \alpha} dt \frac{P_{\alpha}^{\text{res}}(t)}{N} \quad (14)
\]

(Another derivation of Eq. (14))

Let \( N = t/dt \). The probability that no transition occurs in \([0,t]\) and then the first transition of type \( \beta \rightarrow \alpha \) occurs in \([t,t+dt]\) is
\[
(1 - R_{\alpha}^{\text{tot}} dt)^N w_{\beta \alpha} dt = \left(1 - \frac{R_{\alpha}^{\text{tot}} t}{N}\right)^N w_{\beta \alpha} dt \quad \therefore \text{as } N \rightarrow \infty
\]
\[
= \exp(-R_{\alpha}^{\text{tot}} t)
\]
\[(\text{Normalization})\]

\[
\int_{0}^{\infty} dt p^{\text{ext}}_{\alpha}(t) = \int_{0}^{\infty} dt R_{\alpha}^{\text{tot}} e^{-R_{\alpha}^{\text{tot}} t} = \left[ e^{-R_{\alpha}^{\text{tot}} t} \right]_{0}^{\infty} = 1 \quad (15)
\]

\[
\int_{0}^{\infty} dt p^{\text{ext}}_{\beta\alpha}(t) = \int_{0}^{\infty} dt w_{\beta\alpha} e^{-R_{\alpha}^{\text{tot}} t} = \left[ \frac{w_{\beta\alpha}}{R_{\alpha}^{\text{tot}}} e^{-R_{\alpha}^{\text{tot}} t} \right]_{0}^{\infty} = \frac{w_{\beta\alpha}}{R_{\alpha}^{\text{tot}}} = \frac{w_{\beta\alpha}}{\sum_{\beta} w_{\beta\alpha}} \quad (16)
\]
Kinetic Monte Carlo algorithm

First, randomly draw a time $t$ when the first transition occurs according to probability density $P^{\text{ext}}_{\star \leftarrow \alpha}(t)$ in Eq. (12). Let $r \in [0,1]$ be a uniform random number and let $t$ be defined as

$$r = \exp(-R_{\alpha}^{\text{tot}}t)$$

(17)

Then,

$$P'(t) \, dt = \frac{1}{P(r)} \, dr$$

$$\left| \frac{dr}{dt} \right| \, dt = R_{\alpha}^{\text{tot}} e^{-R_{\alpha}^{\text{tot}}t} \, dt$$

$$\therefore P'(t) = R_{\alpha}^{\text{tot}} e^{-R_{\alpha}^{\text{tot}}t} = P^{\text{ext}}_{\star \leftarrow \alpha}(t)$$

(18)

Next, note that event $(\star \leftarrow \alpha)$ is a union of events $(\beta \leftarrow \alpha)$ ($P^{\text{ext}}_{\star \leftarrow \alpha}(t) = \sum_{\beta} P^{\text{ext}}_{\beta \leftarrow \alpha}(t)$) and the thus the event that has occurred at $t$ is type $\beta$ with probability $w_{\beta\alpha} / R_{\alpha}^{\text{tot}}$.

(Algorithm: Single KMC step)

0. Let the current state $\alpha$

1. Generate a uniform random number $r \in [0,1]$ and let

$$t \leftarrow -\frac{1}{R_{\alpha}^{\text{tot}}} \ln r$$

(19)

increment the time by $t$

2. Change the state from $\alpha \rightarrow \beta$ with probability

$$P_{\beta \leftarrow \alpha} = \frac{w_{\beta\alpha}}{R_{\alpha}^{\text{tot}}} = \frac{w_{\beta\alpha}}{\sum_{\gamma} w_{\gamma\alpha}}$$

(20)
Self-Adjointness

Consider the time change of the expectation value of an arbitrary physical quantity, \( A(x) \),

\[
\langle A(t) \rangle = \int dx \ A(x) \ f(x,t)
\]

(19)

Note

\[
\frac{d}{dt} \langle A(t) \rangle = \left\{ \int dx \ A(x) \frac{\partial f}{\partial t} \right\} \tag{17} \\
= \left\{ \int dx \ A(x) \frac{\partial}{\partial x} \cdot (\dot{x} f) \right\} \\
= \left\{ \int dx \ \frac{\partial}{\partial x} \cdot (\dot{x} A(x) f(x)) + \int dx \ \int \dot{x} \ \frac{\partial A}{\partial x} \right\}
\]

(20)

From Gauss' theorem,

\[
\int dV \ \frac{\partial}{\partial x} \cdot (\dot{x} A(x) f(x)) = \int \text{surface} \ \text{(\dot{x} A(x) f(x))}
\]

(21)

For the coordinates outside the finite region and infinite momenta, \( f(x) \to 0 \), and thus the r.h.s. of Eq. (21) vanishes, and thus Eq. (20) becomes

\[
\frac{d}{dt} \langle A(t) \rangle = \int dx \ \int \dot{x} \ A(x) \ f(x,t)
\]

\[
= \int dx \ [\dot{L} A(x)] \ f(x,t)
\]

(22)