Kinetic Monte Carlo Simulation Algorithm $\boxed{4}$

— Master equation: to be simulated

$$\frac{dP_\alpha}{dt} = -\sum_\beta w_{\beta\alpha} P_\alpha(t) + \sum_\beta w_{\alpha\beta} P_\beta(t) \tag{1}$$

(Example — 4 states)

$$\begin{bmatrix} dP_1/dt \\ dP_2/dt \\ dP_3/dt \\ dP_4/dt \end{bmatrix} = \begin{bmatrix} -w_{21}-w_{31}-w_{41} & w_{12} & w_{13} & w_{14} \\ w_{21} & -w_{12}-w_{32}-w_{42} & w_{23} & w_{24} \\ w_{31} & w_{32} & -w_{13}-w_{23}-w_{43} & w_{34} \\ w_{41} & w_{42} & w_{43} & -w_{14}-w_{24}-w_{34} \end{bmatrix} \begin{bmatrix} P_1 \\ P_2 \\ P_3 \\ P_4 \end{bmatrix}$$

— Matrix notation [A.P. Jansen, arXiv:cond-mat/0303028 v1]

Let us define vector $\mathbb{P}$ such that $\mathbb{P}_\alpha = P_\alpha$, and matrices

$$\mathbb{W}_{\alpha\beta} = w_{\alpha\beta} \tag{2}$$

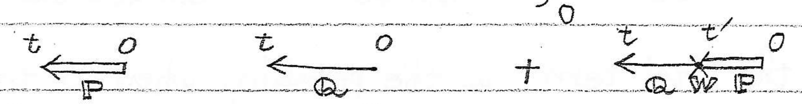
$$\mathbb{R}_{\alpha\beta} = \begin{cases} \sum_\gamma w_{\gamma\alpha} \equiv R_\alpha^{tot} & (\alpha=\beta) \\ 0 & (\alpha\neq\beta) \end{cases} \tag{3}$$

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

$$\frac{d\mathbb{P}}{dt} = -(\overbrace{\mathbb{R}}^{\text{diagonal}} - \underbrace{\mathbb{W}}_{\text{off-diagonal}})\,\mathbb{P}(t) \quad \checkmark \tag{4}$$

The formal solution of Eq. (4) is

$$\mathbb{P}(t) = \mathbb{Q}(t)\mathbb{P}(0) + \int_0^t dt'\,\mathbb{Q}(t-t')\,\mathbb{W}\,\mathbb{P}(t') \quad \checkmark \tag{5}$$



Time-dep perturbation: time-ordered exponential
show ① Abrikosov
② Fetter-Walecka

$G = G_0 + G_0 \Sigma G$

where $\mathbb{Q}(t)$ is the non-transitional solution

$$\mathbb{Q}(t) \equiv \exp(-\mathbb{R}t) \tag{6}$$

$\frac{d}{dt} \times$ Eq. (5)

$$\frac{d\mathbb{P}}{dt} = \underbrace{\frac{d}{dt}\mathbb{Q}(t)}_{-\mathbb{R}\mathbb{Q}(t)}\mathbb{P}(0) + \int_0^t dt' \underbrace{\frac{d}{dt}\mathbb{Q}(t-t')}_{-\mathbb{R}\mathbb{Q}(t-t')} \mathbb{W}\mathbb{P}(t') + \underbrace{\mathbb{Q}(t-t)}_{1}\mathbb{W}\mathbb{P}(t)$$

$$= -\mathbb{R}\underbrace{\left[\mathbb{Q}(t)\mathbb{P}(0) + \int_0^t dt' \mathbb{Q}(t-t')\mathbb{W}\mathbb{P}(t')\right]}_{\mathbb{P}(t)} + \mathbb{W}\mathbb{P}(t)$$

$$= (-\mathbb{R} + \mathbb{W})\,\mathbb{P}(t) \quad \sim \text{satisfies differential equation (4)}$$

Also $\mathbb{P}(t \to 0) = \underbrace{\mathbb{Q}(0)}_{1}\mathbb{P}(0) + \underbrace{\int_0^0 dt' \mathbb{Q}(t-t')\mathbb{W}\mathbb{P}(t')}_{0} = \mathbb{P}(0)$

~ satisfies initial condition //

– Physical (multiple-scattering) interpretation

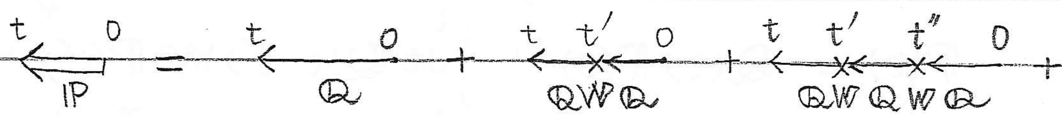
Rewrite Eq. (5) as

$$\mathbb{P}(t) = \mathbb{Q}(t)\mathbb{P}(0) + \int_0^t dt' \mathbb{Q}(t-t')\mathbb{W}\mathbb{Q}(t')\mathbb{P}(0)$$

$$+ \int_0^t dt' \mathbb{Q}(t-t')\mathbb{W} \int_0^{t'} dt'' \mathbb{Q}(t'-t'')\mathbb{W}\,\underbrace{\mathbb{P}(t'')}_{\mathbb{Q}(t'')\mathbb{P}(0) + \int_0^{t''} dt''' \mathbb{Q}(t''-t''')\mathbb{W}\mathbb{P}(t''')} \tag{7}$$

$$= \mathbb{Q}(t)\mathbb{P}(0) + \int_0^t dt' \mathbb{Q}(t-t')\mathbb{W}\mathbb{Q}(t')\mathbb{P}(0)$$

$$+ \int_0^t dt' \int_0^{t'} dt'' \mathbb{Q}(t-t')\mathbb{W}\mathbb{Q}(t'-t'')\mathbb{W}\mathbb{Q}(t'')\mathbb{P}(0) + \cdots \tag{8}$$

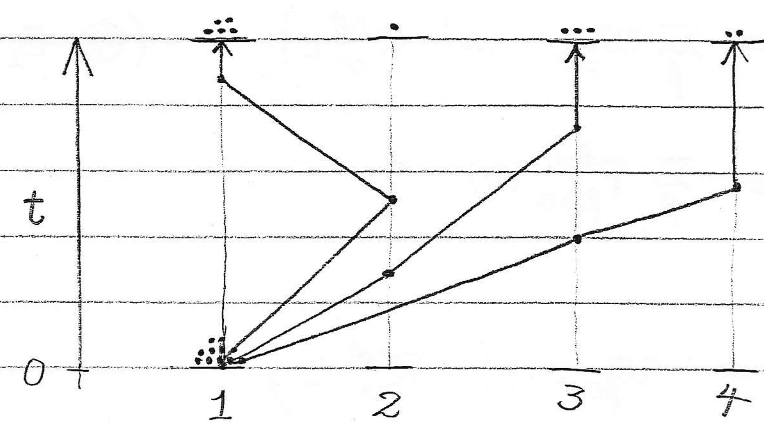


In Eq. (8), the first term is the probability where no transition has occured in [0, t]; the second is that with one transition; third with 2 transitions, etc.

— Ensemble average ✓

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

(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 α (with probability 1) and consider the probability of no transition occuring until time t. From Eq. (5),

$$P_\alpha^{res}(t) = \overset{\text{note diagonal}}{\mathbb{Q}_{\alpha\alpha}(t)}\ \underbrace{\mathbb{P}_\alpha(0)}_{1}$$

$$= \exp\left(-R_\alpha^{tot} t\right) \tag{9}$$

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

$$P_\alpha^{res}(t) = 1 - \int_0^t dt' \, P_{*\leftarrow\alpha}^{fevt}(t') \tag{10}$$

Differentiating Eq.(10) w.r.t. time,

$$\frac{dP_\alpha^{res}}{dt} = -p^{fevt}_{*\leftarrow\alpha}(t) \tag{11}$$

Substituting Eq.(9) in (11),

$$p^{fevt}_{*\leftarrow\alpha}(t) = R_\alpha^{tot}\exp\left(-R_\alpha^{tot}t\right) \tag{12a}$$

$$= \sum_\beta w_{\beta\alpha}\exp\left(-R_\alpha^{tot}t\right) \qquad (\because \text{Eq.}(3)) \tag{12b}$$

$$\equiv \sum_\beta p^{fevt}_{\beta\to\alpha}(t) \tag{12c}$$

where

$$p^{fevt}_{\beta\leftarrow\alpha}(t) = w_{\beta\alpha}\exp\left(-R_\alpha^{tot}t\right) \tag{13}$$

In summary, the probability for the system to stay in α without any transition for time t is

$$P_\alpha^{res}(t) = \exp\left(-R_\alpha^{tot}t\right)$$

and, in addition, for the first event to occur in $[t, t+dt]$ is (for destination state β)

$$p^{fevt}_{\beta\leftarrow\alpha}(t)\,dt = w_{\beta\alpha}dt\,P_\alpha^{res}(t) \;\checkmark \tag{14}$$

(Another derivation of Eq.(14))

easier

Let $N = t/dt$. The probability that no transition occurs in $[0,t]$ and then the first transition of type $\beta\leftarrow\alpha$ occurs in $[t, t+dt]$ is

$$\left(1-R_\alpha^{tot}dt\right)^N\cdot w_{\beta\alpha}dt = \underbrace{\left(1-\frac{R_\alpha^{tot}t}{N}\right)^N}_{\xrightarrow[N\to\infty]{}\exp\left(-R_\alpha^{tot}t\right)}\cdot w_{\beta\alpha}dt \quad //$$

(Normalization)

$$\int_0^\infty dt\, P^{fevt}_{*\leftarrow\alpha}(t) = \int_0^\infty dt\, R^{tot}_\alpha e^{-R^{tot}_\alpha t} = \left[-e^{-R^{tot}_\alpha t}\right]_0^\infty = 1 \qquad (15)$$

$$\int_0^\infty dt\, P^{fevt}_{\beta\leftarrow\alpha}(t) = \int_0^\infty dt\, w_{\beta\alpha} e^{-R^{tot}_\alpha t} = \left[-\frac{w_{\beta\alpha}}{R^{tot}_\alpha} e^{-R^{tot}_\alpha t}\right]_0^\infty$$

$$= \frac{w_{\beta\alpha}}{R^{tot}_\alpha} = \frac{w_{\beta\alpha}}{\sum_\beta w_{\beta\alpha}} \qquad (16)$$

– Kinetic Monte Carlo algorithm

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

$$r = \exp\left(-R^{tot}_{\alpha} t\right) \tag{17}$$

Then,

$$P'(t)\, dt = \overbrace{P(r)}^{1} \underbrace{dr}_{\left|\frac{dr}{dt}\right| dt = R^{tot}_{\alpha} e^{-R^{tot}_{\alpha} t}\, dt}$$

$$\therefore P'(t) = R^{tot}_{\alpha} e^{-R^{tot} t} = P^{fevt}_{*\leftarrow\alpha}(t) \tag{18}$$

Next, note that event $(*\leftarrow\alpha)$ is a union of events $(\beta\leftarrow\alpha)$ $\left(P^{fevt}_{*\leftarrow\alpha}(t) = \sum_{\beta} P^{fevt}_{\beta\leftarrow\alpha}(t)\right)$ and the thus the event that has occured at t is type β with probability $w_{\beta\alpha}/R^{tot}_{\alpha}$.

(Algorithm: Single KMC step)

0. Let the current state α
1. Generate a uniform random number $r \in [0,1]$ and let

$$t \leftarrow -\frac{1}{R^{tot}_{\alpha}} \ln r\ ; \tag{19}$$

increment the time by t

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

$$P_{\beta\leftarrow\alpha} = \frac{w_{\beta\alpha}}{R^{tot}_{\alpha}} = \frac{w_{\beta\alpha}}{\sum_{\gamma} w_{\gamma\alpha}} \tag{20}$$

Self-Adjoincy

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

$$\langle A(t) \rangle = \int d\mathbf{x}\, A(\mathbf{x})\, f(\mathbf{x}, t) \tag{19}$$

Note

$$\frac{d}{dt}\langle A(t) \rangle = \int d\mathbf{x}\, A(\mathbf{x}) \frac{\partial f}{\partial t}$$

(∵ Eq. (17))

$$= -\int d\mathbf{x}\, A(\mathbf{x}) \frac{\partial}{\partial \mathbf{x}} \cdot (\dot{\mathbf{x}} f)$$

$$= -\int d\mathbf{x} \frac{\partial}{\partial \mathbf{x}} \cdot (\dot{\mathbf{x}} A(\mathbf{x}) f(\mathbf{x})) + \int d\mathbf{x}\, f\, \dot{\mathbf{x}} \cdot \frac{\partial A}{\partial \mathbf{x}} \tag{20}$$

From Gauß' theorem,

$$\int_{\text{volume}} d\mathbf{x} \frac{\partial}{\partial \mathbf{x}} \cdot (\dot{\mathbf{x}} A(\mathbf{x}) f(\mathbf{x})) = \int_{\text{surface}} d\mathbf{S} \cdot (\dot{\mathbf{x}} A(\mathbf{x}) f(\mathbf{x})) \tag{21}$$

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

$$\frac{d}{dt}\langle A(t) \rangle = \int d\mathbf{x} \left[\dot{\mathbf{x}} \cdot \frac{\partial}{\partial \mathbf{x}} A(\mathbf{x}) \right] f(\mathbf{x}, t)$$

$$= \int d\mathbf{x} \left[L\, A(\mathbf{x}) \right] f(\mathbf{x}, t) \tag{22}$$