Kinetic Monte Carlo

Triangular lattice
Diffusion

\[ D = \Theta \cdot D_J \]

**Thermodynamic factor**

\[
\Theta = \frac{\partial \left( \frac{\mu}{k_B T} \right)}{\partial \ln x} = \frac{\langle N \rangle}{\langle N^2 \rangle - \langle N \rangle^2}
\]

**Self Diffusion Coefficient**

\[
D_J = \frac{1}{(2d)t} \left\langle \frac{1}{N} \left( \sum_{i=1}^{N} \Delta \vec{R}_i(t) \right)^2 \right\rangle
\]
Diffusion

\[ D_J = \frac{1}{(2d)t} \left\langle \frac{1}{N} \left( \sum_{i=1}^{N} \Delta \vec{R}_i(t) \right)^2 \right\rangle \]

\[ D^* = \frac{1}{(2d)t} \left\langle \frac{1}{N} \sum_{i=1}^{N} \Delta \vec{R}_i(t)^2 \right\rangle \]
Standard Monte Carlo to study diffusion

- Pick an atom at random
Standard Monte Carlo to study diffusion

- Pick an atom at random
- Pick a hop direction
Standard Monte Carlo to study diffusion

• Pick an atom at random
• Pick a hop direction
• Calculate $\exp(-\Delta E_b / k_B T)$
Standard Monte Carlo to study diffusion

- Pick an atom at random
- Pick a hop direction
- Calculate $\exp(-\Delta E_b/k_B T)$
- If $\exp(-\Delta E_b/k_B T) >$ random number) do the hop
Kinetic Monte Carlo

Consider all hops simultaneously

For each potential hop $i$, calculate the hop rate

$$W_i = \nu \exp\left(\frac{-\Delta E_i}{k_B T}\right)$$
For each potential hop $i$, calculate the hop rate

$$W_i = \nu \ast \exp\left(\frac{-\Delta E_i}{k_B T}\right)$$

Then randomly choose a hop $k$, with probability $W_k$
For each potential hop $i$, calculate the hop rate

$$W_i = \nu \exp\left(\frac{-\Delta E_i}{k_B T}\right)$$

Then randomly choose a hop $k$, with probability $W_k$

$$\xi_1 = \text{random number}$$
For each potential hop i, calculate the hop rate

\[ W_i = \nu \exp\left(\frac{-\Delta E_i}{k_B T}\right) \]

Then randomly choose a hop k, with probability \( W_k \)

\[ \xi_1 = \text{random number} \]

\[ \sum_{i=1}^{k-1} W_i < \xi_1 \cdot W \leq \sum_{i=0}^{k} W_i \]

\[ W = \sum_{i=0}^{N_{\text{hops}}} W_i \]
Then randomly choose a hop \( k \), with probability \( W_k \)

\[ \xi_1 = \text{random number} \]

\[ \sum_{i=1}^{k-1} W_i < \xi_1 \cdot W \leq \sum_{i=0}^{k} W_i \]

\[ W = \sum_{i=0}^{N_{hops}} W_i \]
Time

After hop $k$ we need to update the time

$$\xi_2 = \text{random number}$$

$$\Delta t = -\frac{1}{W} \log \xi_2$$
Two independent stochastic variables:
the hop $k$ and the waiting time $\Delta t$

$$\sum_{i=1}^{k-1} W_i < \xi_1 \cdot W \leq \sum_{i=0}^{k} W_i$$

$$W_i = \nu * \exp\left(\frac{-\Delta E_i}{k_B T}\right)$$

$$W = \sum_{i=0}^{N_{hops}} W_i$$

$$\Delta t = -\frac{1}{W} \log \xi_2$$
Kinetic Monte Carlo

• Hop every time
• Consider all possible hops simultaneously
• Pick hop according its relative probability
• Update the time such that $\Delta t$ on average equals the time that we would have waited in standard Monte Carlo

Triangular 2-d lattice, 2NN pair interactions

\[
E(\vec{\sigma}) = \sum_{l=1}^{N_{\text{lattice-sites}}} \left( V_0 + V_{\text{pot}} \sigma_l + \frac{1}{2} V_{\text{NNpair}} \sigma_l \sum_{i=\text{NNpairs}} \sigma_i + \frac{1}{2} V_{\text{NNNNpair}} \sigma_l \sum_{j=\text{NNNNpairs}} \sigma_j \right)
\]
\[ \Delta E_{kra} = E_{\text{activated-state}} - \frac{1}{2}(E_1 + E_2) \]

\[ \Delta E_{\text{barrier}} = \Delta E_{kra} + \frac{1}{2}(E_{\text{final}} - E_{\text{initial}}) \]
Thermodynamics

\[ D = \Theta \cdot D_J \]

\[ \Theta = \frac{\partial \left( \frac{\mu}{k_B T} \right)}{\partial \ln x} = \frac{\langle N \rangle}{\langle N^2 \rangle - \langle N \rangle^2} \]
Kinetics

\[ D = \Theta \cdot D_J \]

\[ D_J = \frac{1}{(2d)t} \left( \frac{1}{N} \left( \sum_{i=1}^{N} \Delta \vec{R}_i(t) \right)^2 \right) \]