Kinetic Monte Carlo

Triangular lattice

Diffusion

$$D = \Theta \cdot D_J$$

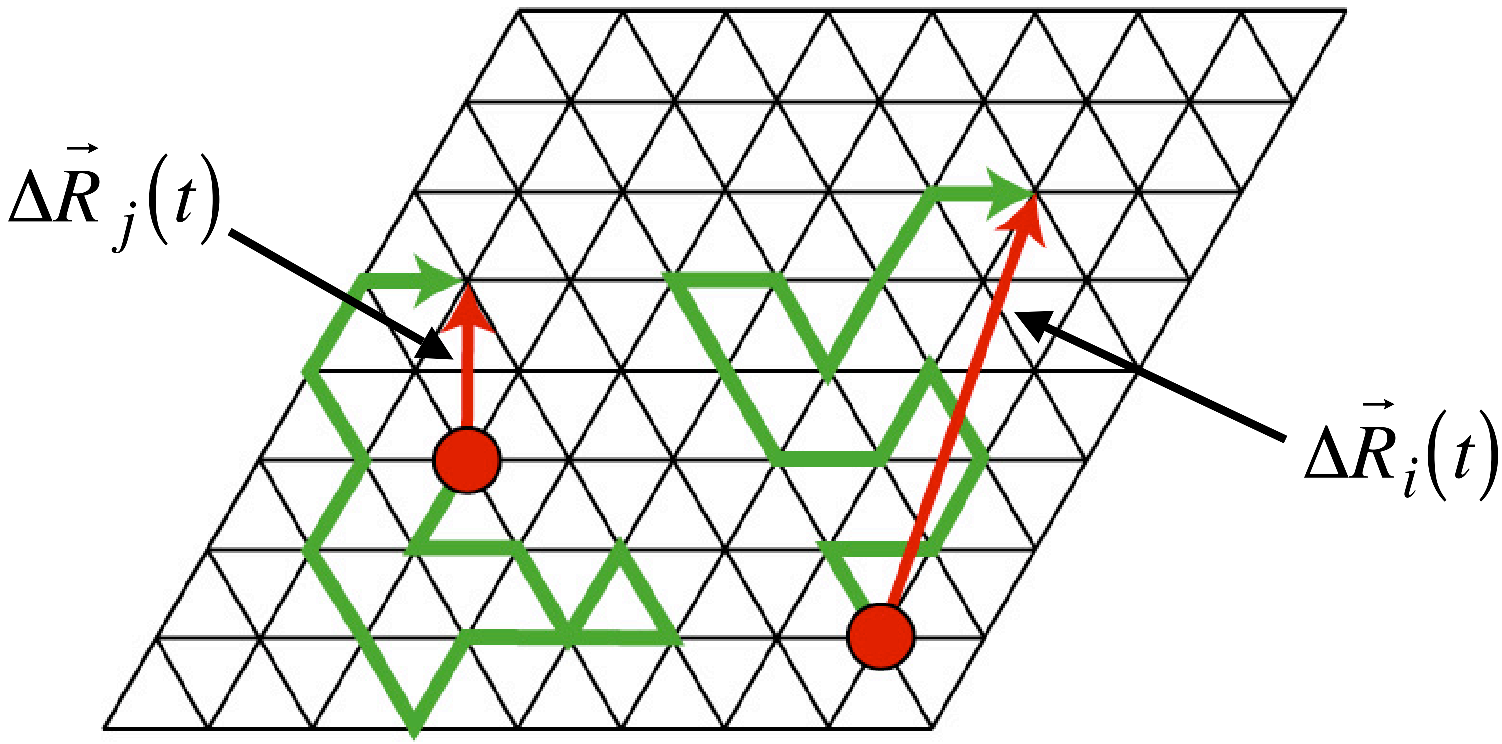
Thermodynamic factor

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

Self Diffusion Coefficient

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

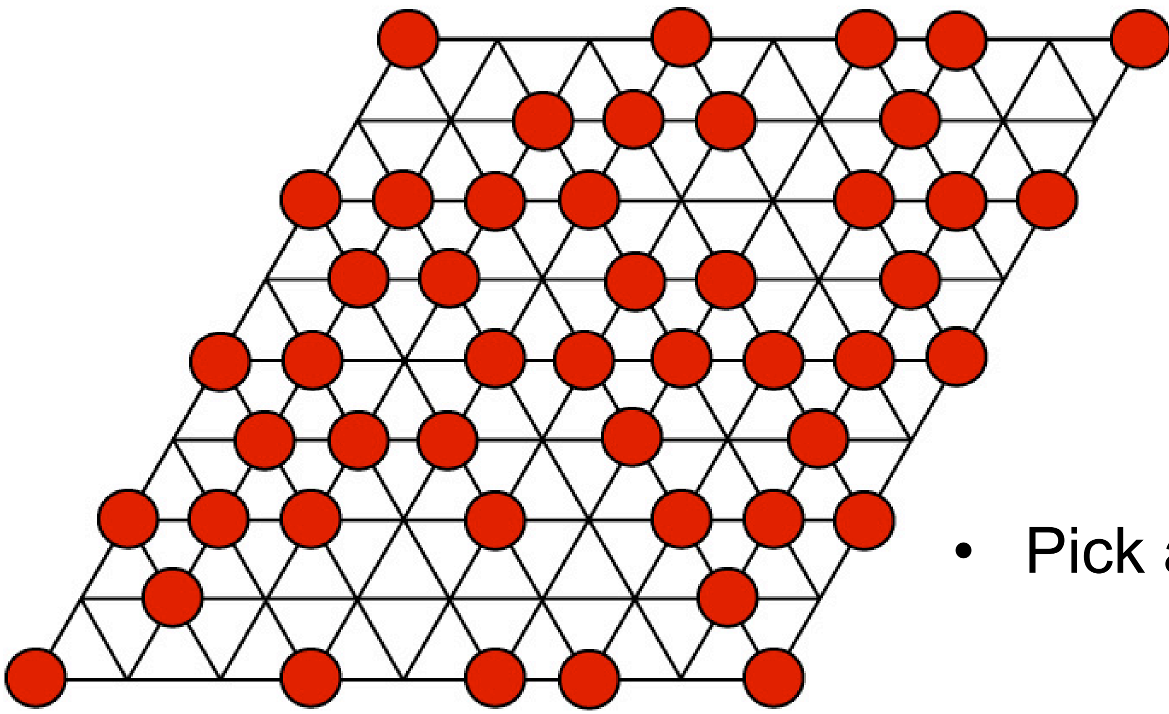
Diffusion



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

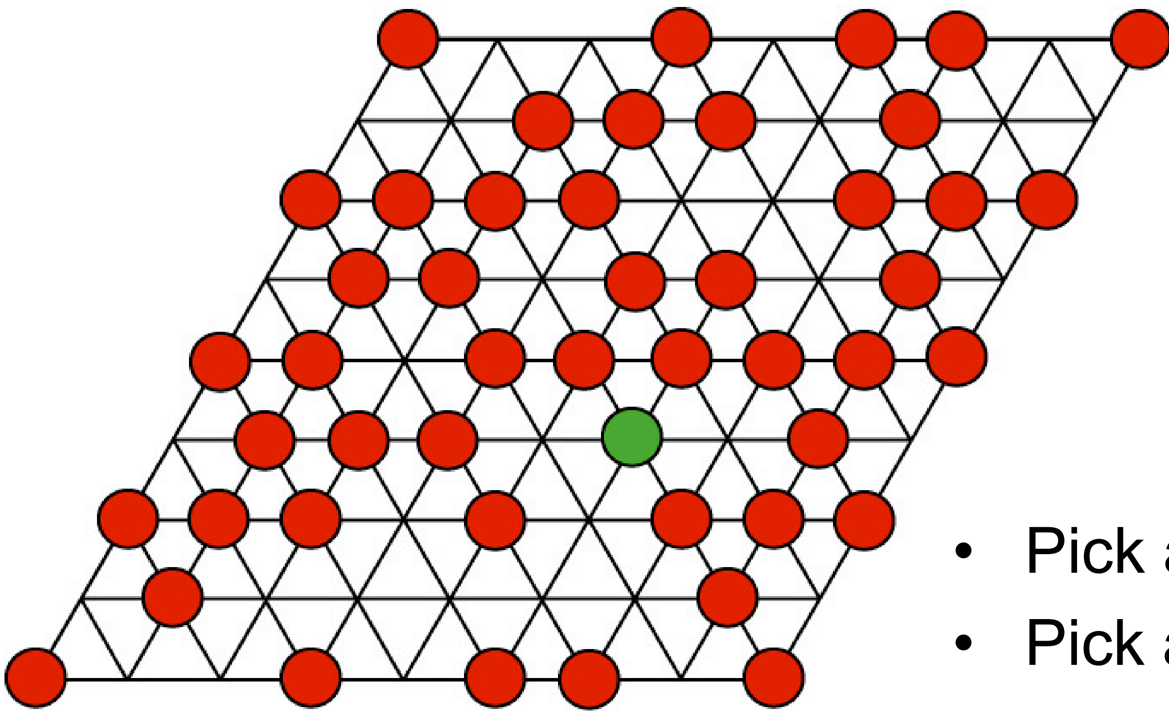
$$D^* = \frac{1}{(2d)t}\left\langle \frac{1}{N}\sum_{i=1}^{N} \Delta \vec{R}_i(t)^2 \right\rangle$$

Standard Monte Carlo to study diffusion



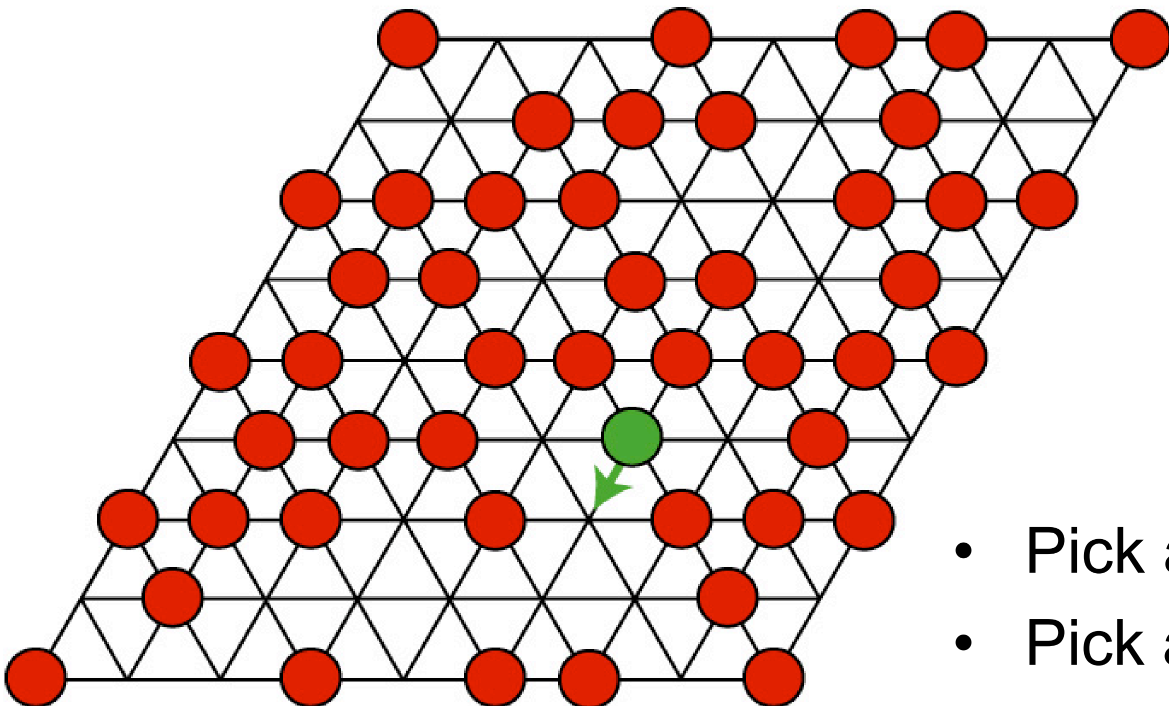
- Pick an atom at random

Standard Monte Carlo to study diffusion



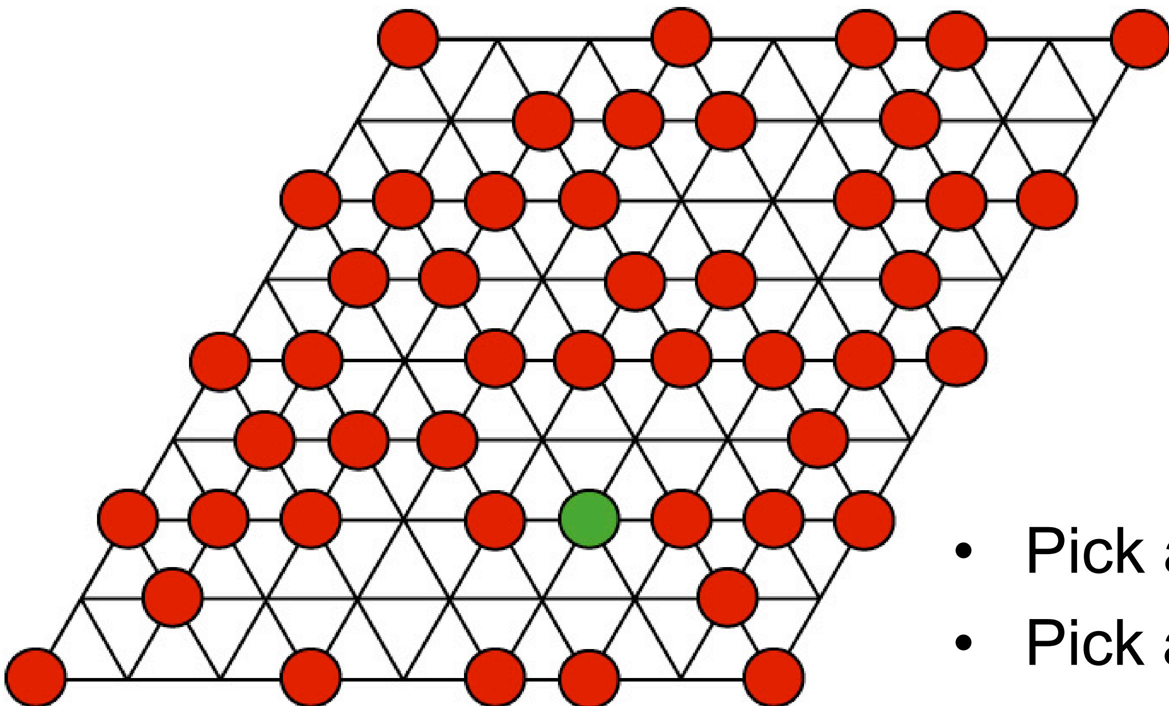
- Pick an atom at random
- Pick a hop direction

Standard Monte Carlo to study diffusion



- Pick an atom at random
- Pick a hop direction
- Calculate $\exp\left(-\Delta E_b / k_B T\right)$

Standard Monte Carlo to study diffusion

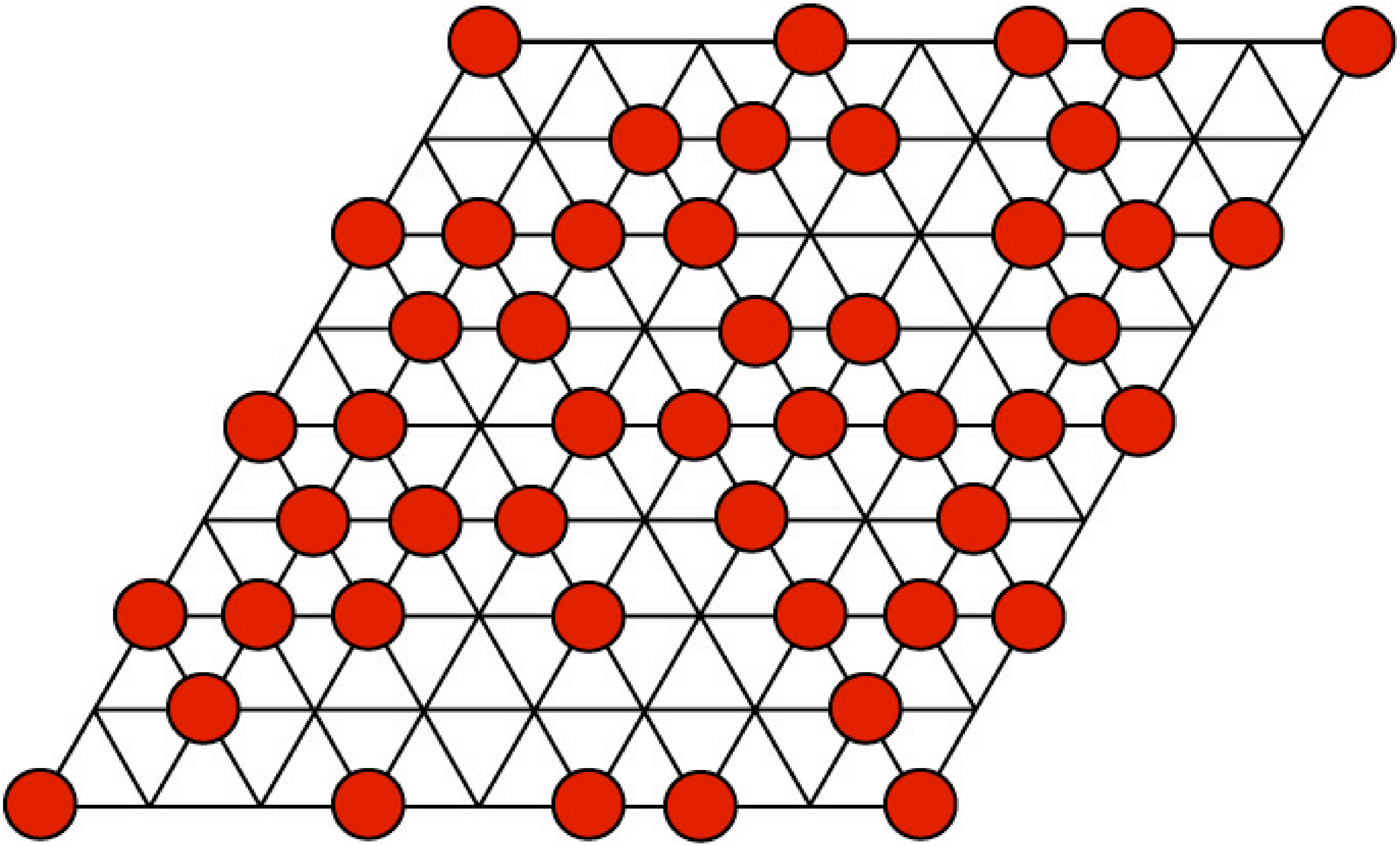


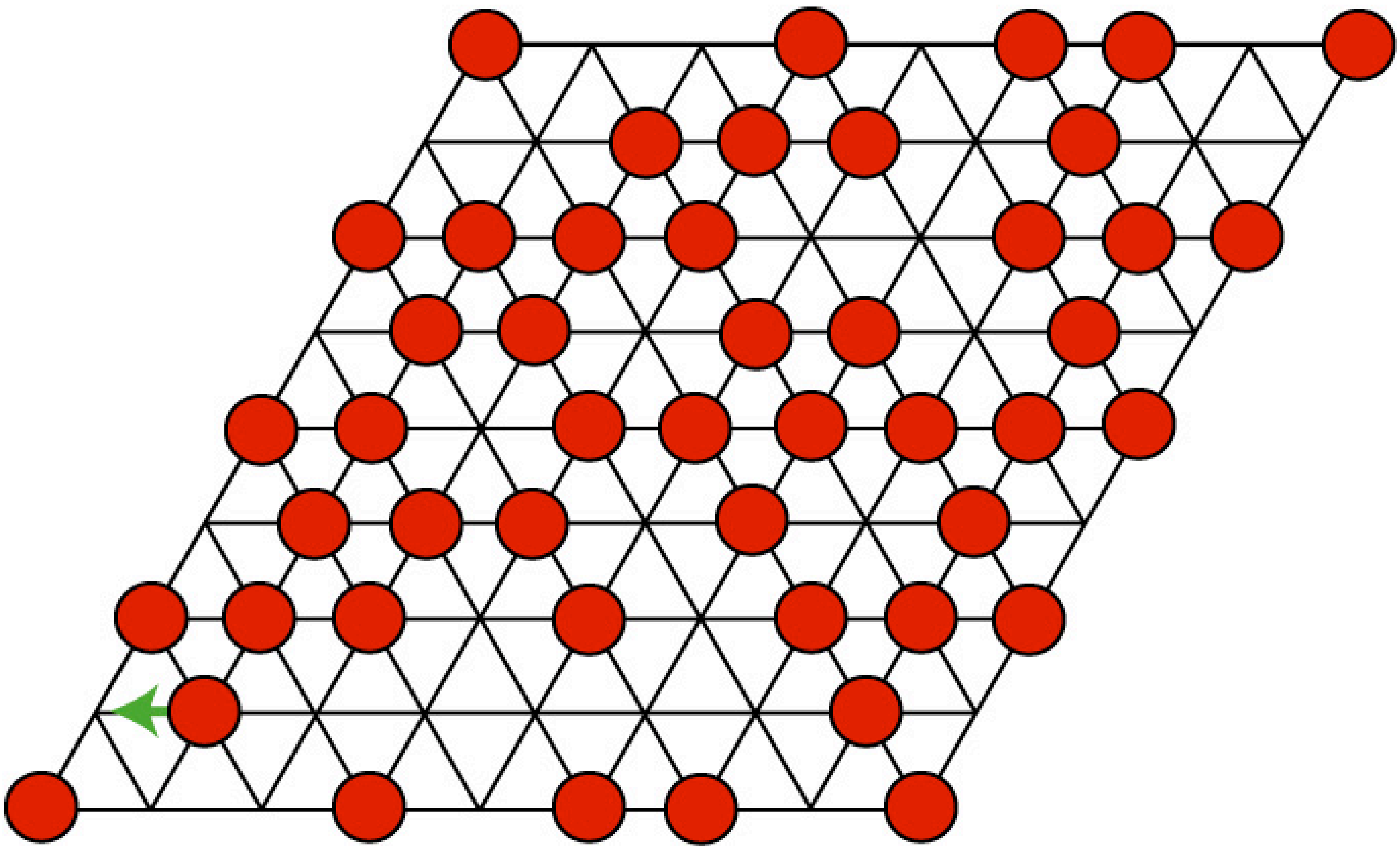
- Pick an atom at random
- Pick a hop direction
- Calculate $\exp(-\Delta E_b / k_B T)$
- If ($\exp(-\Delta E_b / k_B T)$ > random number) do the hop

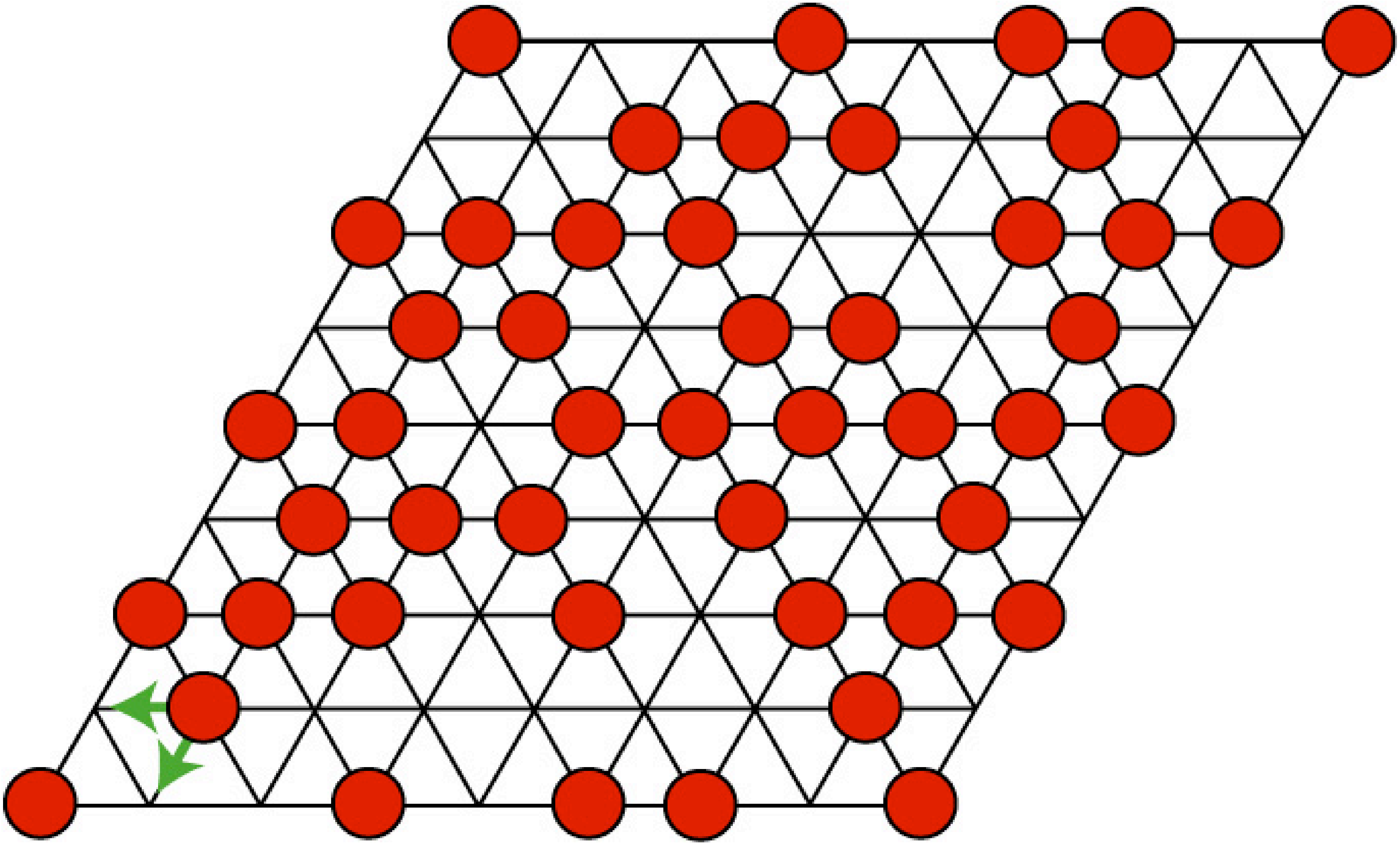
Kinetic Monte Carlo

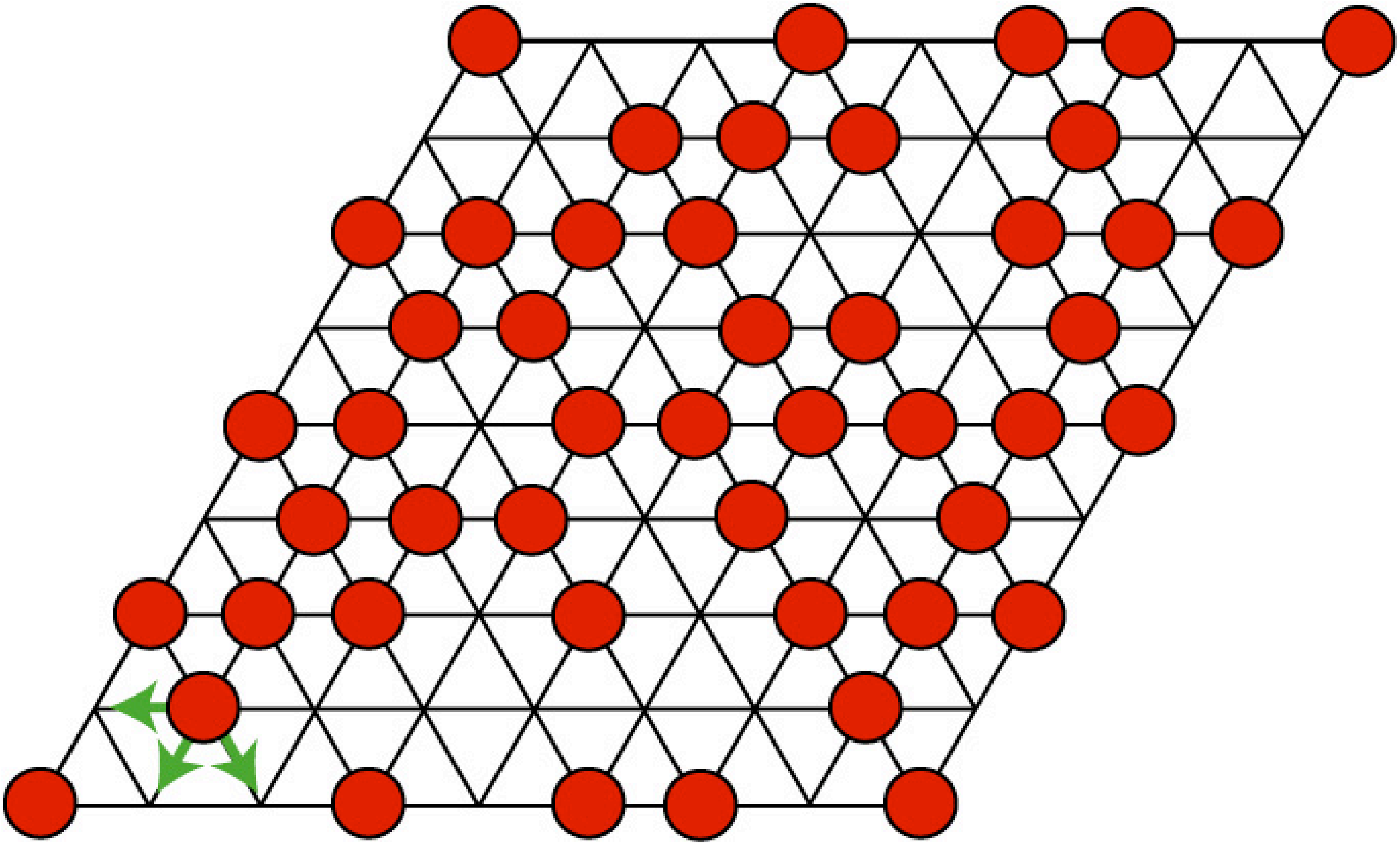
Consider all hops simultaneously

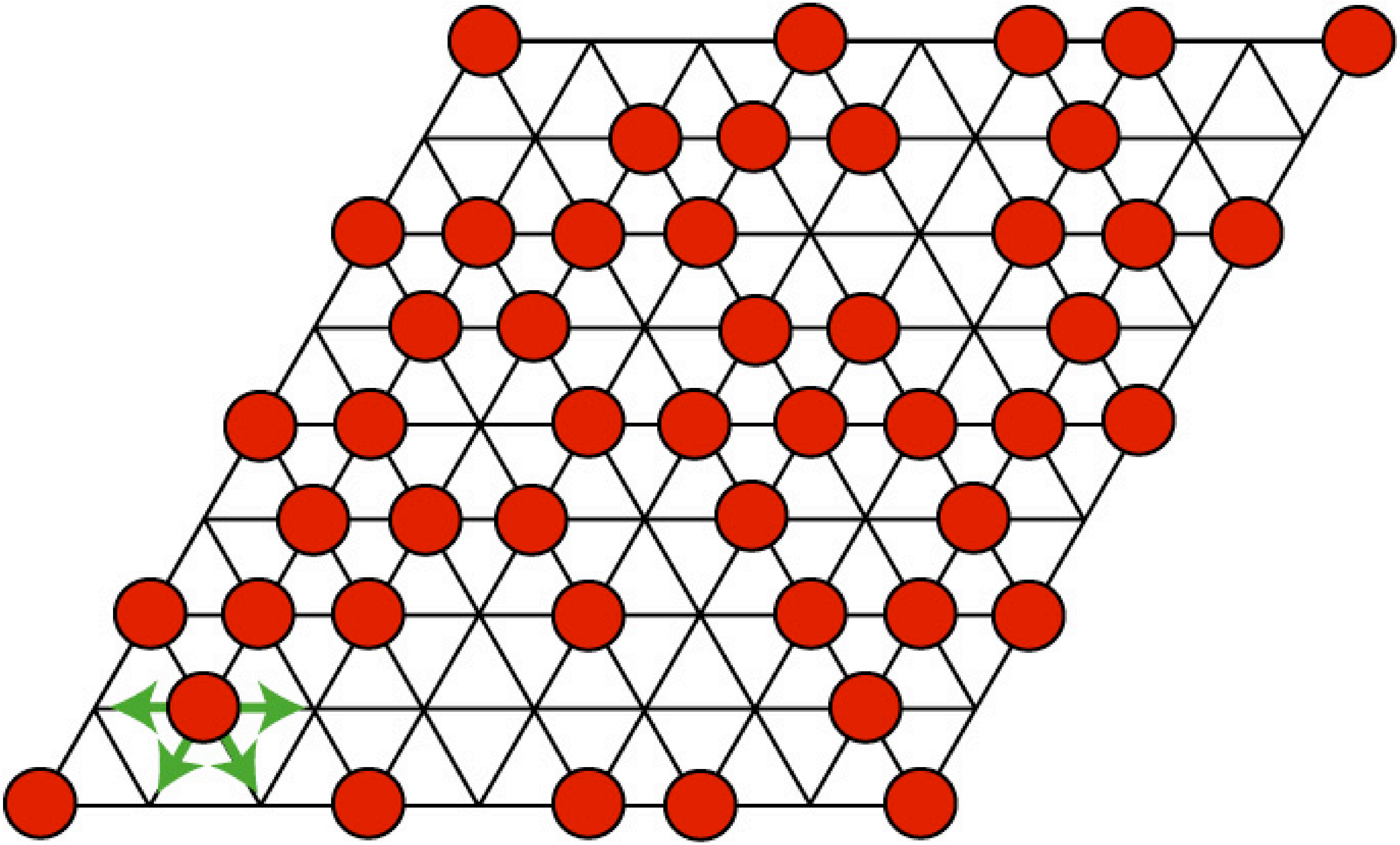
A. B. Bortz, M. H. Kalos, J. L. Lebowitz, J. Comput Phys, **17**, 10 (1975).
F. M. Bulnes, V. D. Pereyra, J. L. Riccardo, Phys. Rev. E, **58**, 86 (1998).

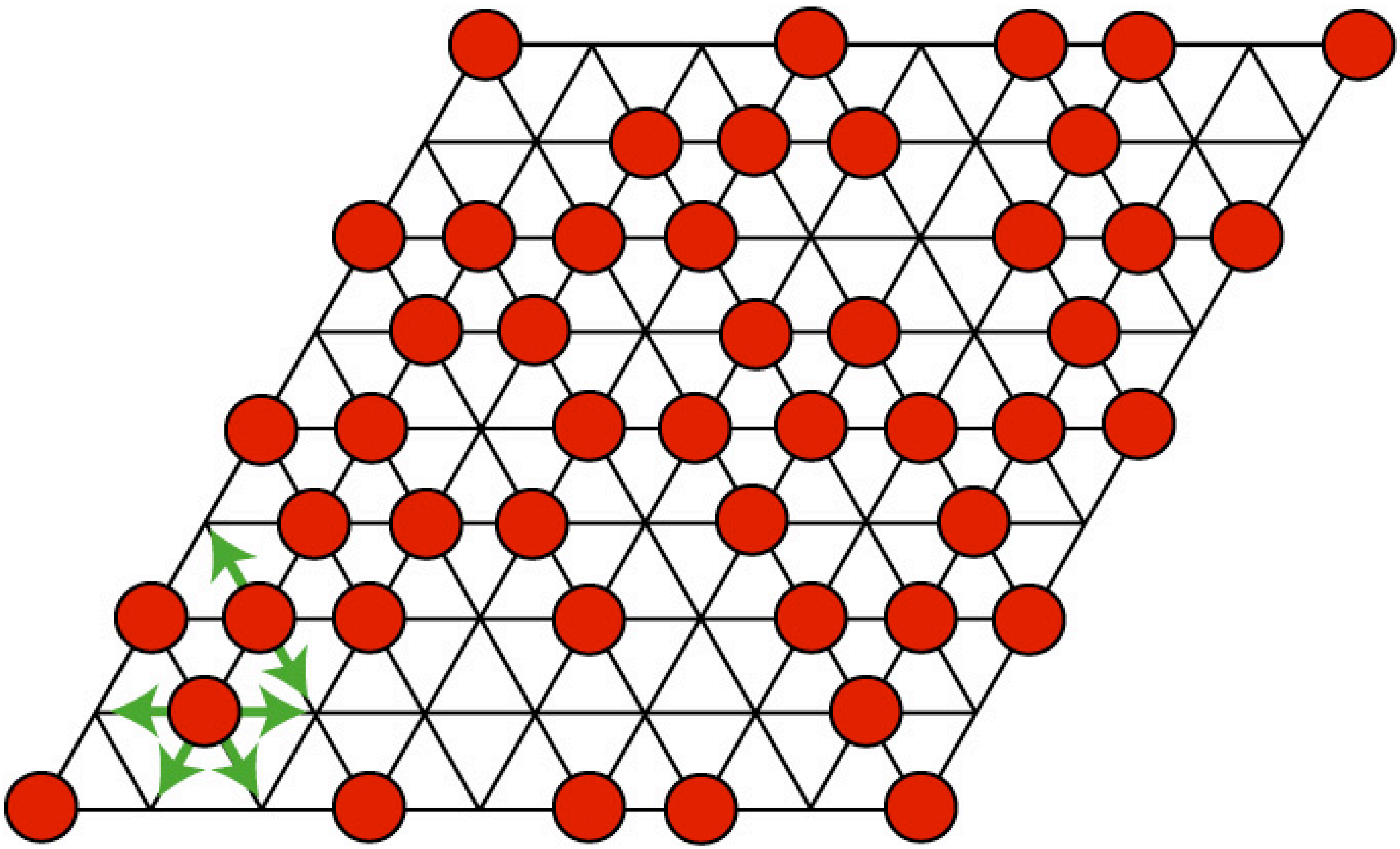


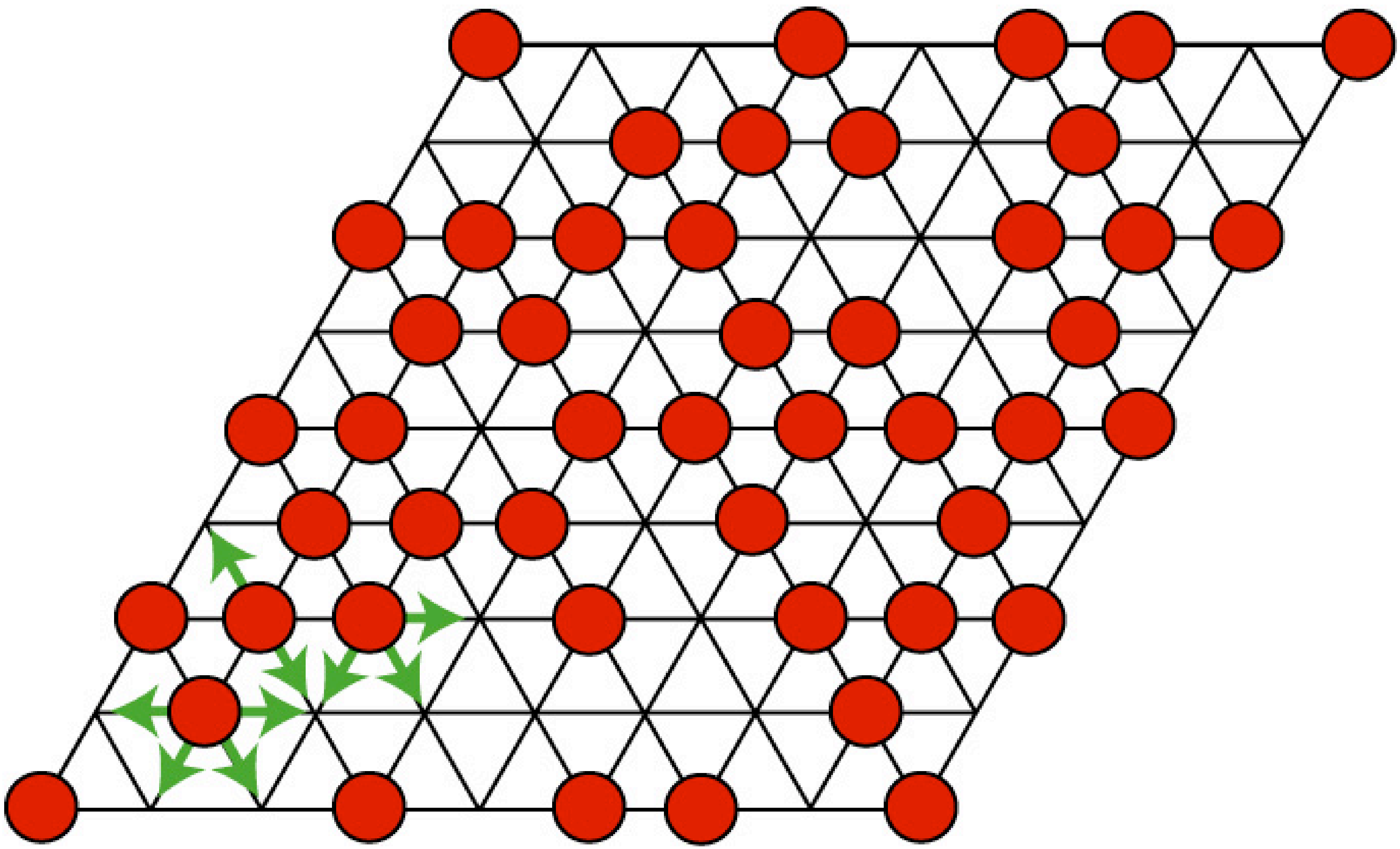


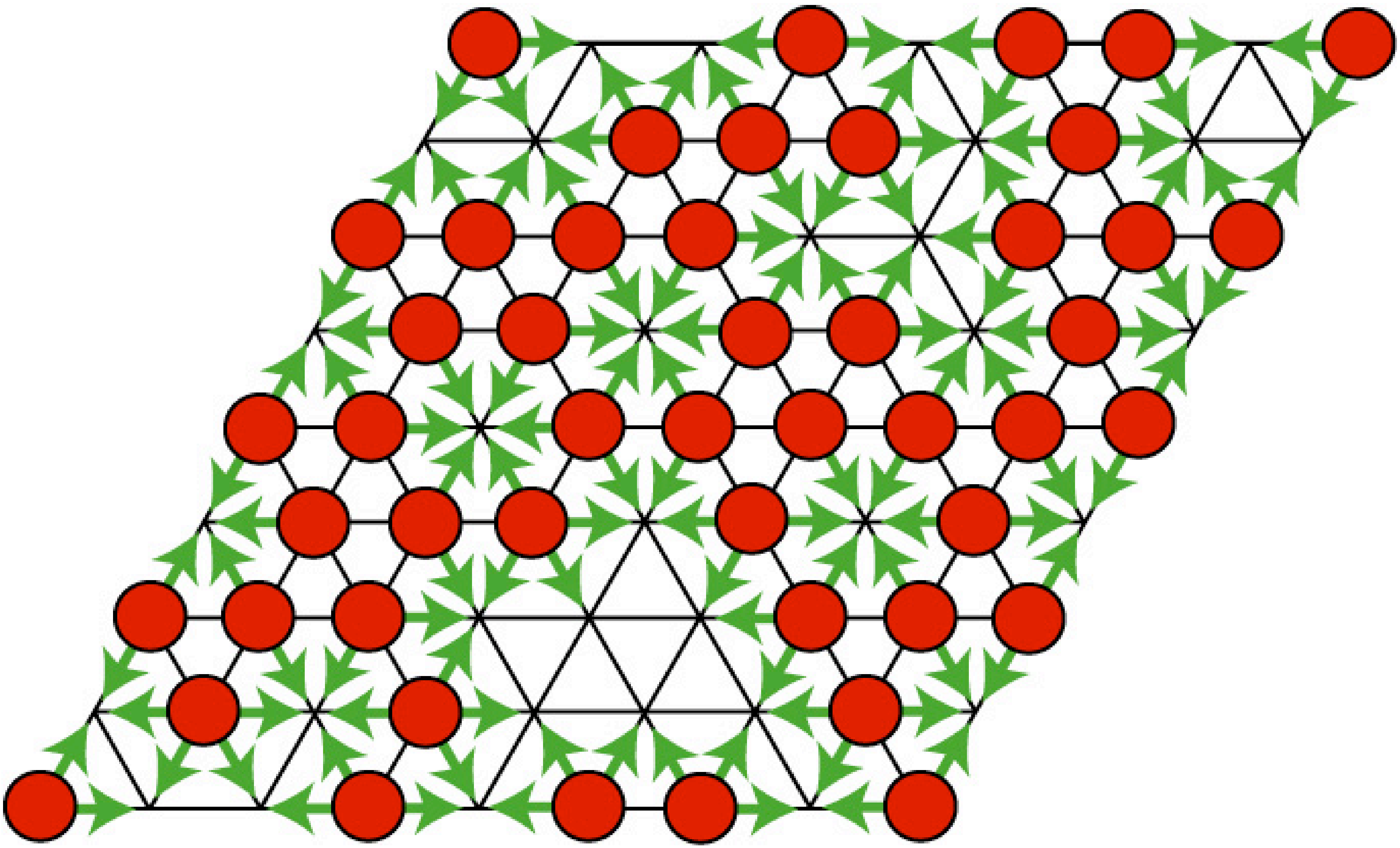


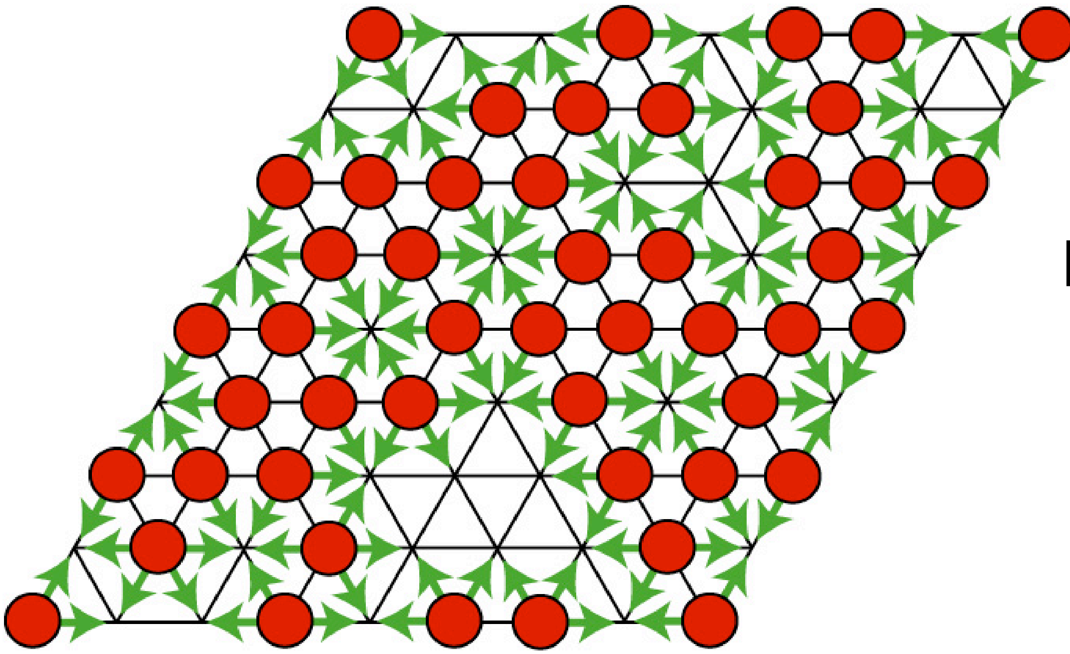






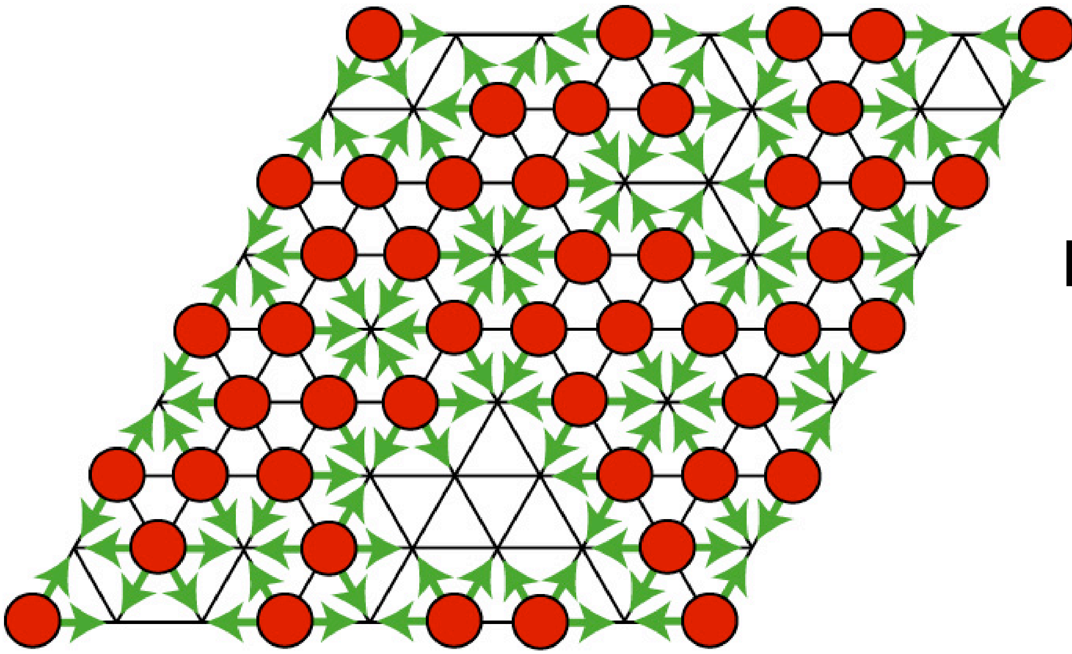






For each potential hop *i*, calculate the hop rate

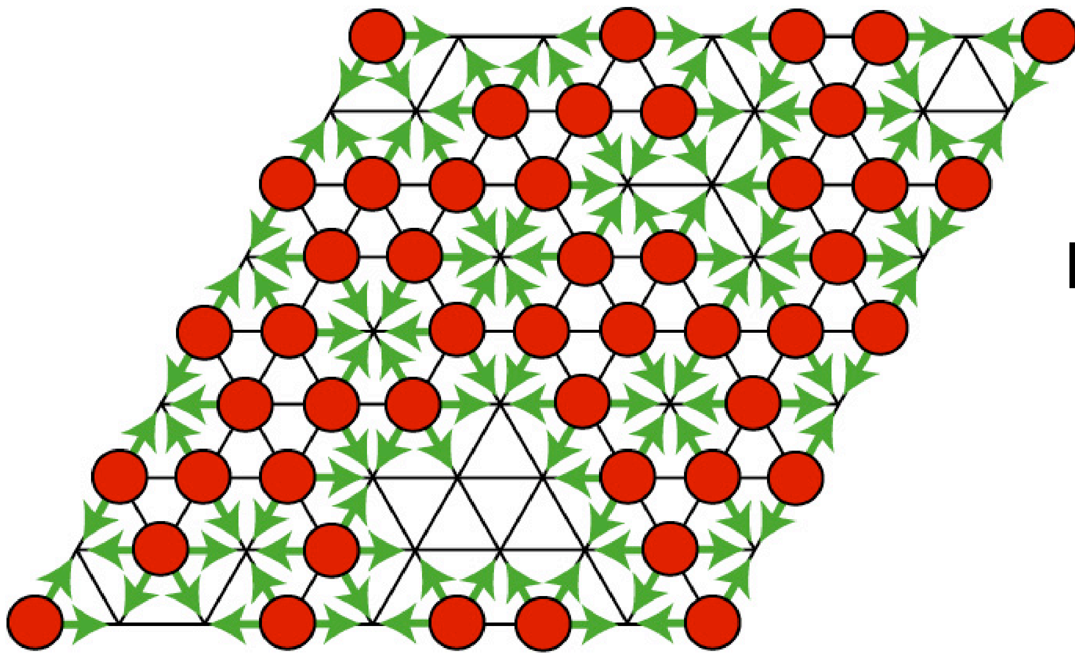
$$W_i = \nu * \exp\left(\frac{-\Delta E_i}{k_B T}\right)$$



For each potential hop i, calculate the hop rate

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

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

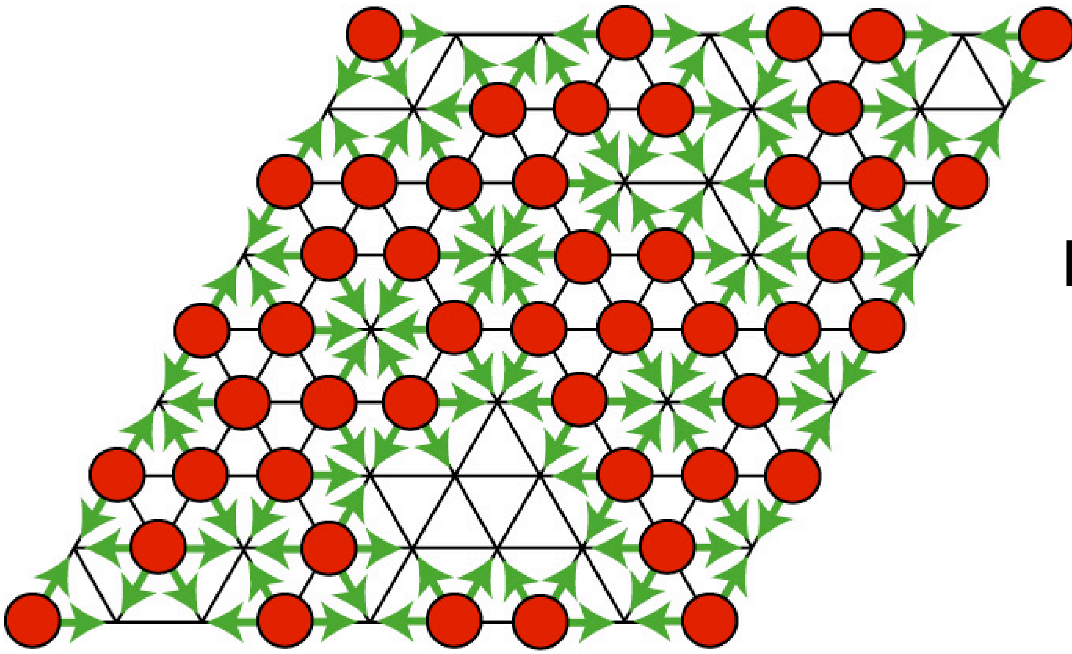


For each potential hop i, calculate the hop rate

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

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

ξ_1 = 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

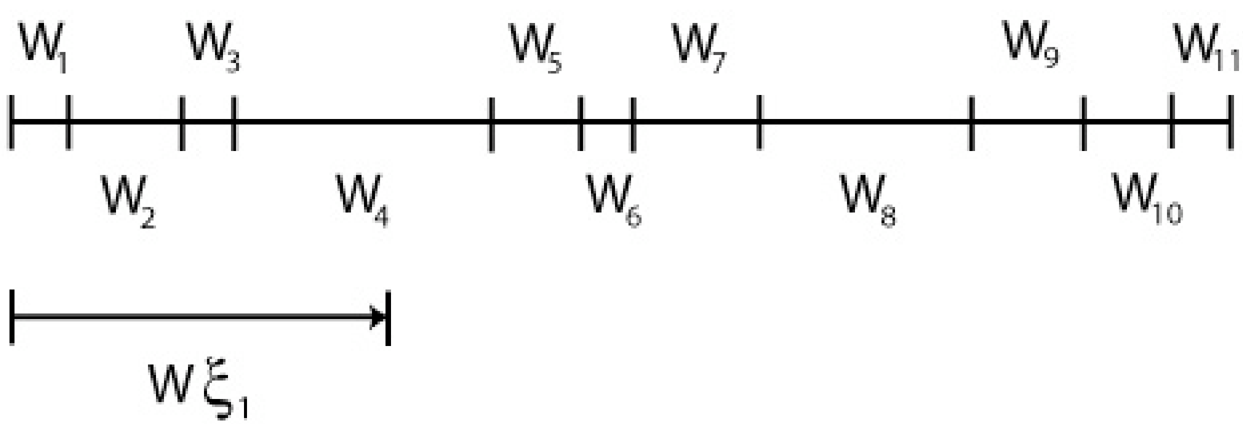
ξ_1 = random number

$$\sum_{i=1}^{k-1} W_i < \xi_1 \cdot W \le \sum_{i=0}^{k} W_i \qquad W = \sum_{i=0}^{N_{hops}} W_i$$

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

ξ_1 = random number

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



Time

After hop *k* we need to update the time

ξ_2 = random number

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

Two independent stochastic variables:

the hop k and the waiting time Δt

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

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

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

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

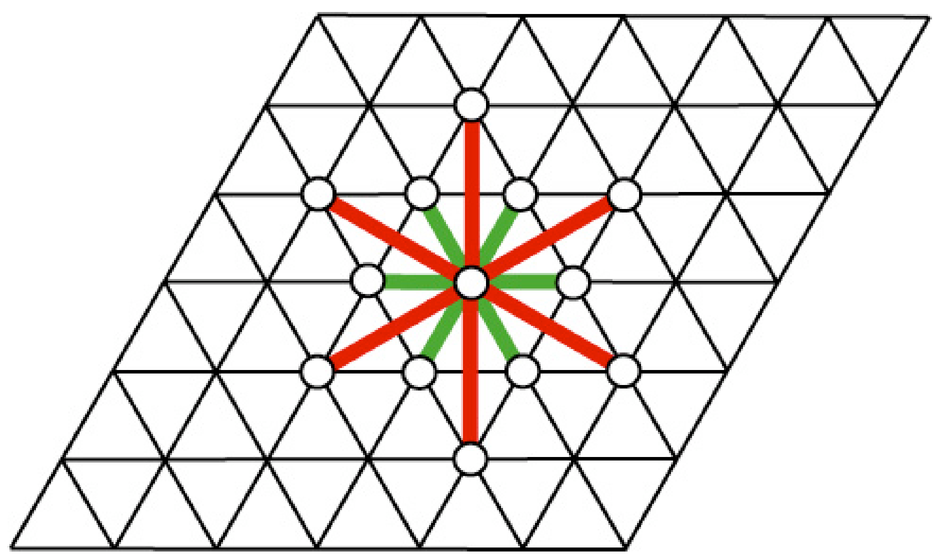
Kinetic Monte Carlo

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

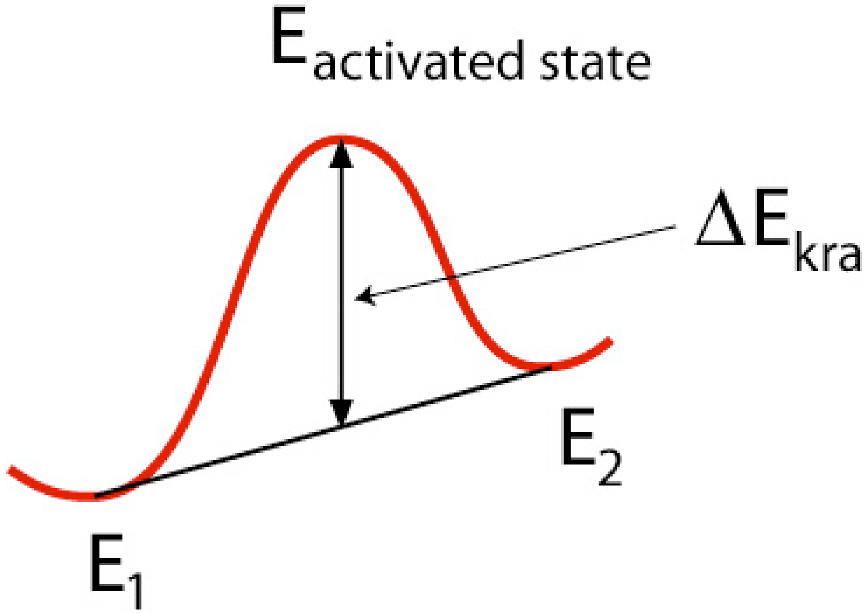
A. B. Bortz, M. H. Kalos, J. L. Lebowitz, J. Comput Phys, **17**, 10 (1975).
F. M. Bulnes, V. D. Pereyra, J. L. Riccardo, Phys. Rev. E, **58**, 86 (1998).

Triangular 2-d lattice, 2NN pair interactions

$$E(\vec{\sigma}) = \sum_{l=1}^{N_{lattice-sites}} \left(V_o + V_{po\,\mathrm{int}}\sigma_l + \frac{1}{2} V_{NNpair}\sigma_l \sum_{i=NNpairs} \sigma_i + \frac{1}{2} V_{NNNpair}\sigma_l \sum_{j=NNNpairs} \sigma_j \right)$$



Activation barrier



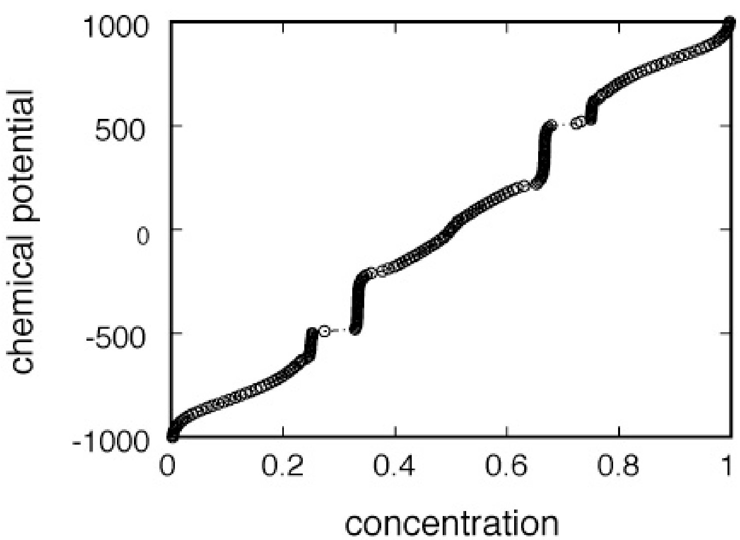
$$\Delta E_{kra} = E_{activated-state} - \frac{1}{2}\left(E_1 + E_2\right)$$

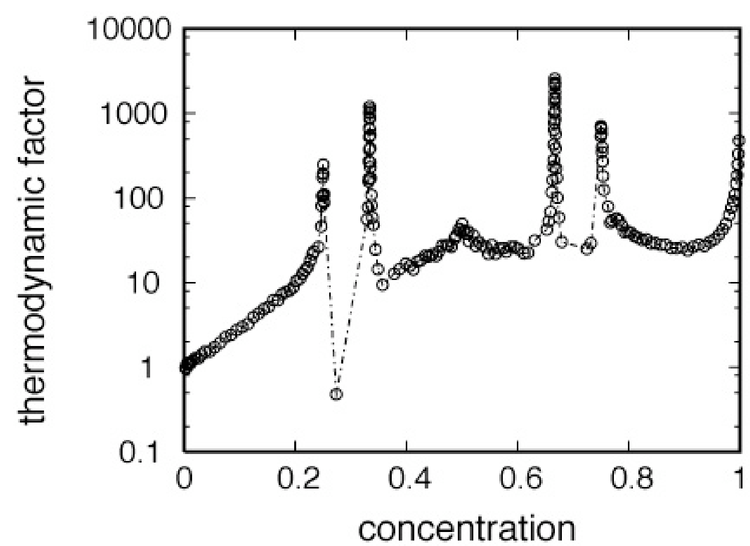
$$\Delta E_{barrier} = \Delta E_{kra} + \frac{1}{2}\left(E_{final} - E_{initial}\right)$$

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

$$D = \Theta \cdot D_J$$

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