Kinetic Monte Carlo method

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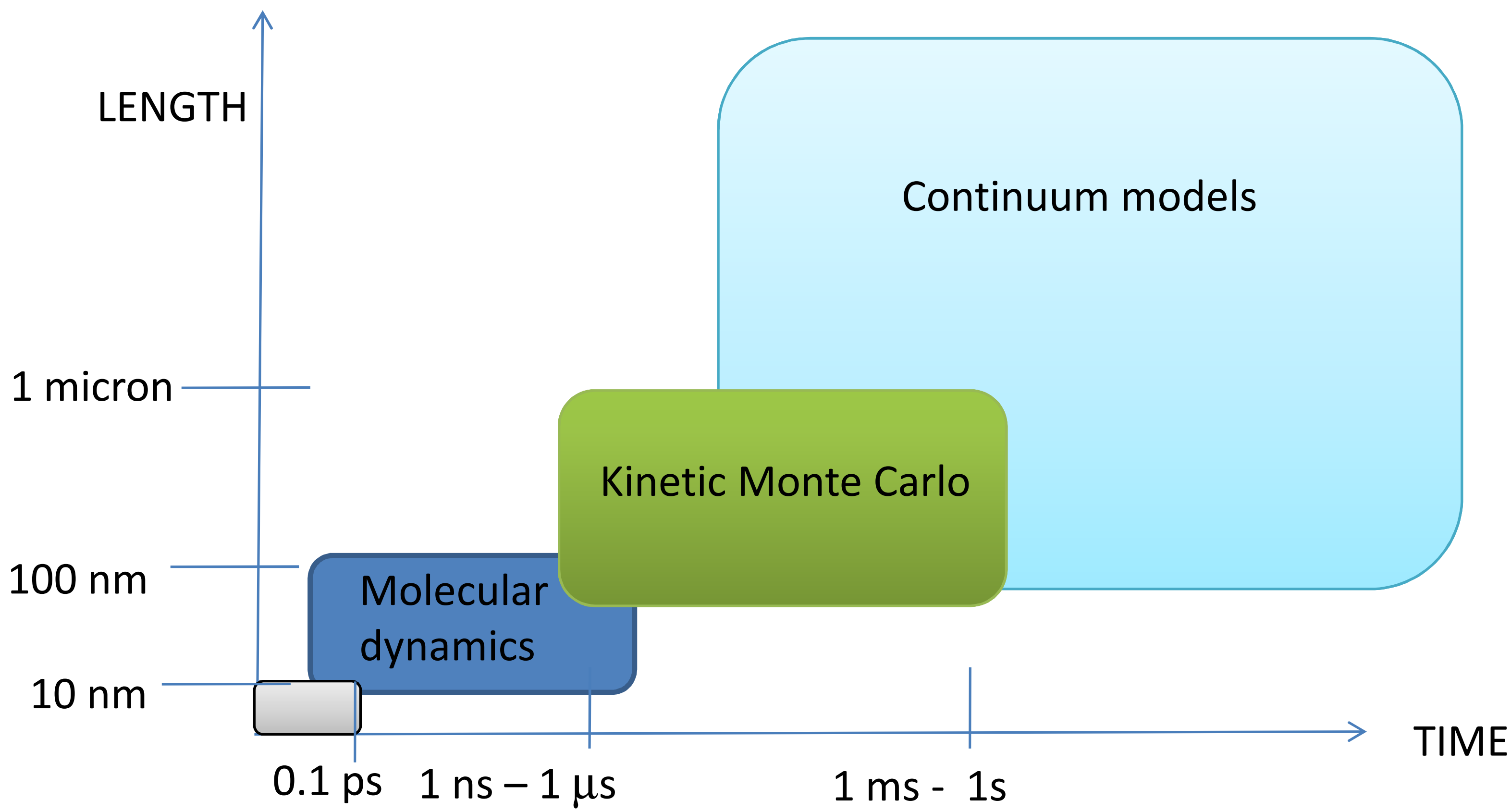
Molecular dynamics is expensive

- Example of adatom diffusion

Multiscale modeling



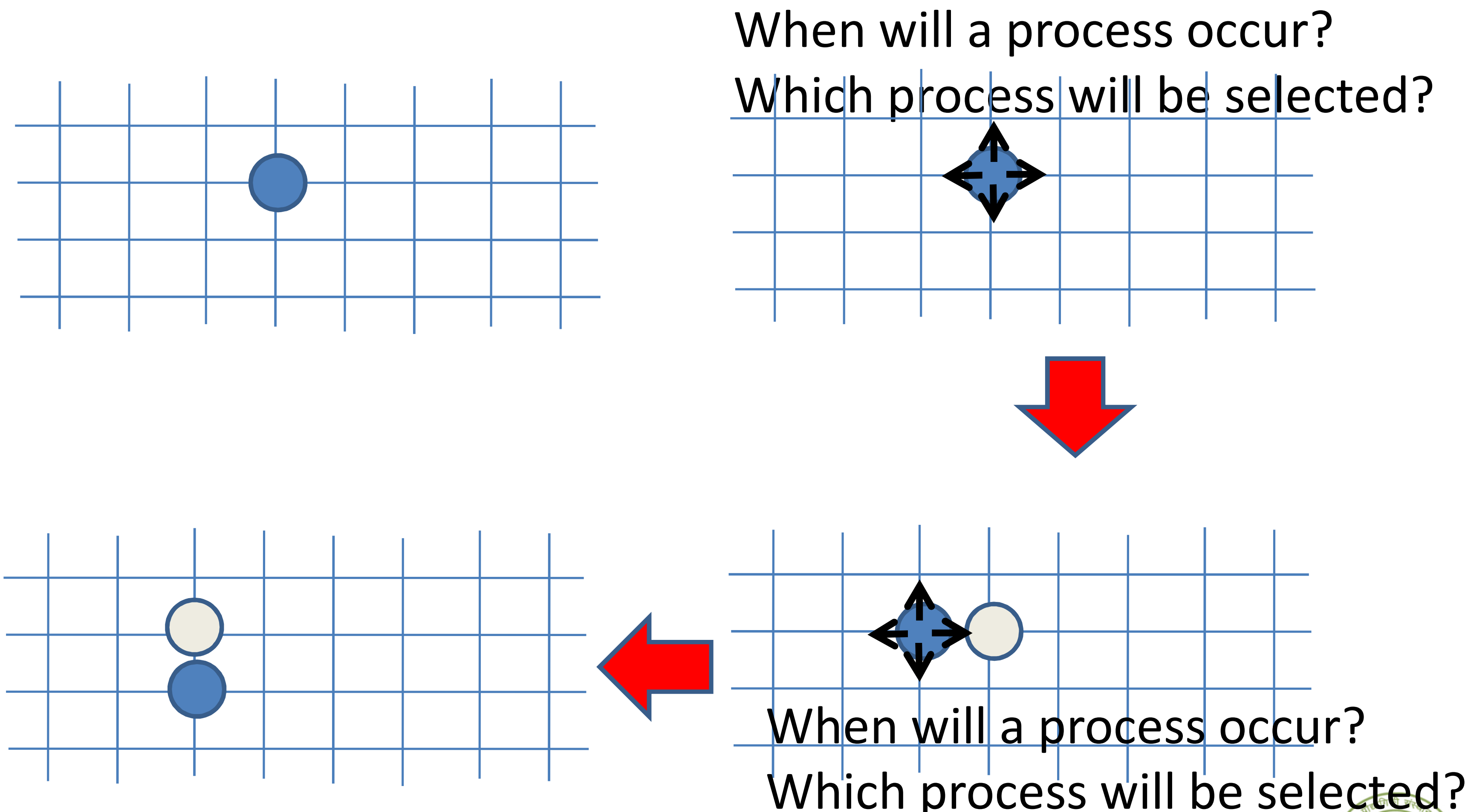
Applications of kinetic Monte Carlo

- Radiation damage in materials
- Surface science
- Thin film and crystal growth
- Metals and semiconductor alloys
- Adsorption/desorption phenomena
- Catalysis
- Biological systems
- …

How does KMC compare to MD?

- MD can reach 100 ns MD time in 1 day on a standard desktop computer
- In contrast, KMC can reach several milliseconds with the same CPU effort
- KMC dynamics is as accurate as the MD dynamics as long as certain assumptions made in KMC are valid

Discrete states and atomic processes



Assumptions in KMC

- Atomic process is Markov process
- Atomic processes are independent of each other
- Discrete number of states accessible from the current state i
- The list of processes from each state of the system is known
- Probability of selecting more than one process at the same time is zero

Master equation

- Discrete time version

$$\pi_j(n+1)-\pi_j(n)=\sum_{\substack{i\\ i\neq j}} p_{ij}\pi_i(n)-\sum_{\substack{i\\ i\neq j}} p_{ji}\pi_j(n)$$

- Continuous time version

$$\frac{d\pi_j}{dt}=\sum_{\substack{i\\ i\neq j}} p_{ij}\pi_i(n)-\sum_{\substack{i\\ i\neq j}} p_{ji}\pi_j(n)$$

$$p_{ij}\equiv P(t,i\rightarrow j)=P(t)P(i\rightarrow j)$$

Probability of escape

- The rate of a process from state i to j is given by

$$k_{ij} = \nu_{ij} \exp\left(-\frac{E_{ij}}{k_B T}\right)$$

- First escape from state i to j obeys

$$P(t, i \to j)dt = k_{ij} \exp(-k_{i,total} t)dt$$

- First escape from state i

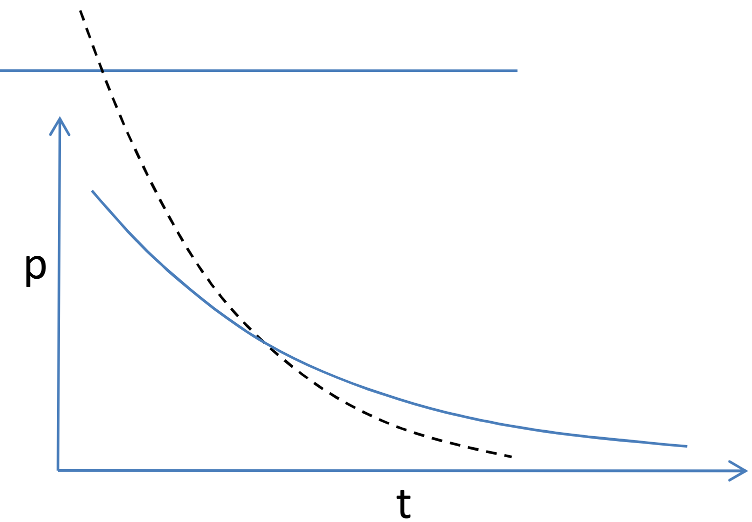
$$P(t, i \to)dt = k_{i,total} \exp(-k_{i,total} t)dt$$

(see Gillespie, 76 for derivation)

Features of the probability density function

- Will an escape occur?

$$\int_0^{\infty} k_{i,total} \exp(-k_{i,total} t) dt = 1$$



- What is the average time for one escape?

$$\int_0^{\infty} t P(t, i \rightarrow) dt = \int_0^{\infty} k_{i,total} t \exp(-k_{i,total} t) dt = \frac{1}{k_{i,total}}$$

When does a process get selected?

$$P(t, i \rightarrow)dt = k_{i,total} \exp(-k_{i,total} t)dt$$

- It can be shown that the first escape time can be sampled as

$$t = \frac{\ln(1/\xi_2)}{k_{i,total}}$$

Which process is selected?

- The probability of selecting process from i to j is

$$P(i \rightarrow j) = \frac{k_{ij}}{k_{i,total}}$$

All KMC algorithms solve the same dynamics

- Rejection-based
  - Dynamic Monte Carlo method (Fichthorn, 91)
  - Null-event Monte Carlo method (Vlachos, 98)
- Rejection free
  - Direct method (Gillespie, 76)
  - N-fold or BKL method (Bortz, Kalos, Lebowitz, 75)
  - First reaction method (Gillespie, 76)
  - Next reaction method (Gibson, 00)
  - Stochastic simulation algorithm (Gillespie, 76)

Direct method

- Rather easy to implement
- Select one process at a time (i.e., algorithm is rejection free) and advance the time

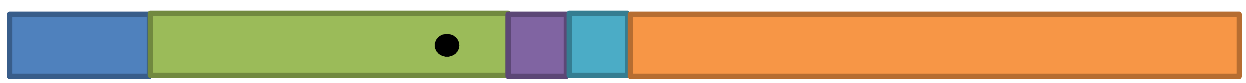
1. Obtain the initial conditions
2. Find the processes and their rates from the current state i
3. Find which process will be selected and when the process will occur
4. Move the final state of the selected process
5. Advance the time
6. New process is denoted i
7. Go to step 2

Which process gets selected?

- Length of the bars below is proportional to the value of the rate constant

$$P(i \rightarrow j) = \frac{k_{ij}}{k_{i,total}}$$

- Find the process



$k_{i,total}\xi_1$

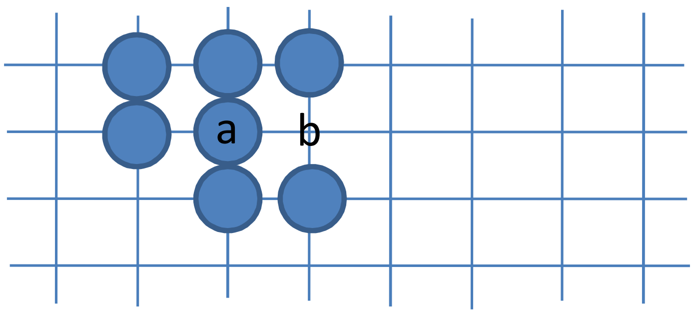
- Selection criterion $\sum_{j=1}^{J-1} k_{ij} < k_{i,total}\xi_1 \leq \sum_{j=1}^{J} k_{ij}$

Time increment

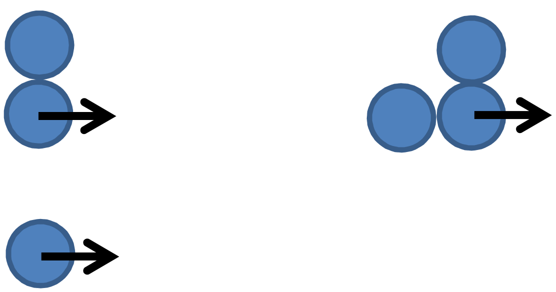
- Each time a process is selected increment time as

$$t \leftarrow t + \frac{\ln(1/\xi_2)}{k_{i,total}}$$

Bond-counting method



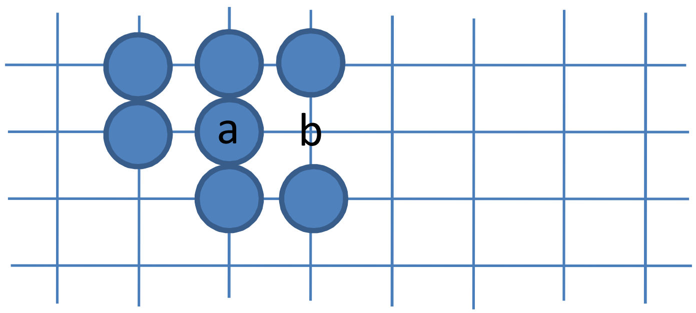
$$k_{ab} = \nu_{ab} \exp\left(-\frac{E_{ab}}{k_B T}\right)$$



Bond-counting method

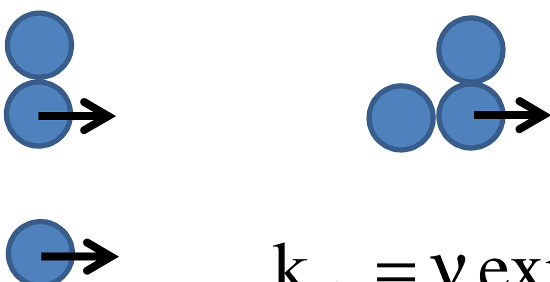
$$k_{ab} = \nu \exp\left(-\frac{E_{ab}}{k_B T}\right)$$

$$\nu = 10^{11} - 10^{13}\,s^{-1}$$



$$E_{ab} = f(n_a, n_b)$$

$$E_{ab} = J n_a$$



$$k_{ab} = \nu \exp\left(-\frac{E_{ab}}{k_B T}\right)\sigma_a$$

$$\sigma_a = \begin{cases} 0, & \text{unoccupied} \\ 1, & \text{occupied} \end{cases}$$

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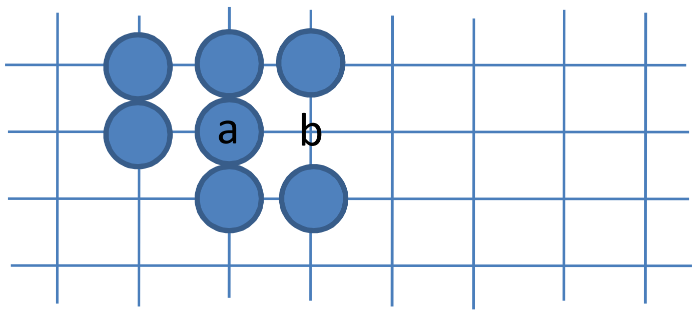
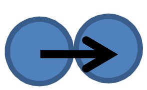
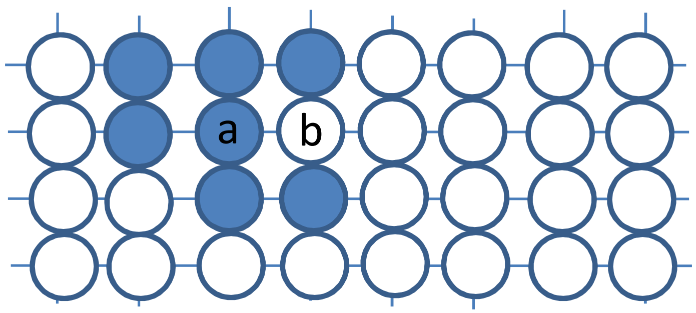
Lattice gas model

$$k_{ab} = \nu \exp\left(-\frac{E_{ab}}{k_B T}\right)$$



 $$k_{ab} = \nu \exp\left(-\frac{E_{ab}}{k_B T}\right)\sigma_a(1-\sigma_b)$$

Lattice gas model



$$k_{ab} = \nu \exp\left(-\frac{E_{ab}}{k_B T}\right)$$

$$k_{ab} = \nu \exp\left(-\frac{E_{ab}}{k_B T}\right)\sigma_a(1-\sigma_b)$$

Implementation

K(σ) = Rate vector =

DiffusionNorth(Site 1)
DiffusionSouth(Site 1)
DiffusionEast(Site 1)
DiffusionWest(Site 1)
DiffusionNorth(Site 2)
DiffusionSouth(Site 2)
DiffusionEast(Site 2)
DiffusionWest(Site 2)
…

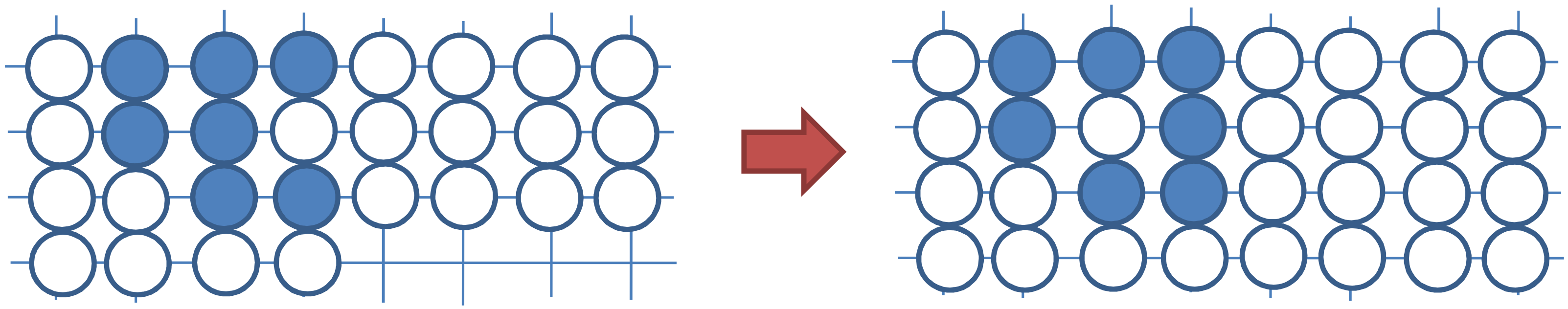
4nx1

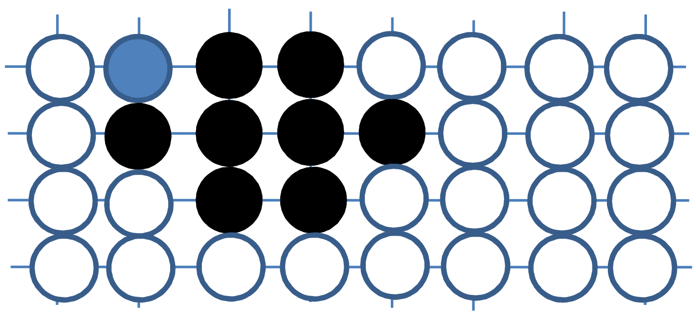
K_sum

$$t = \frac{\ln(1/\xi_2)}{k_{total}}$$

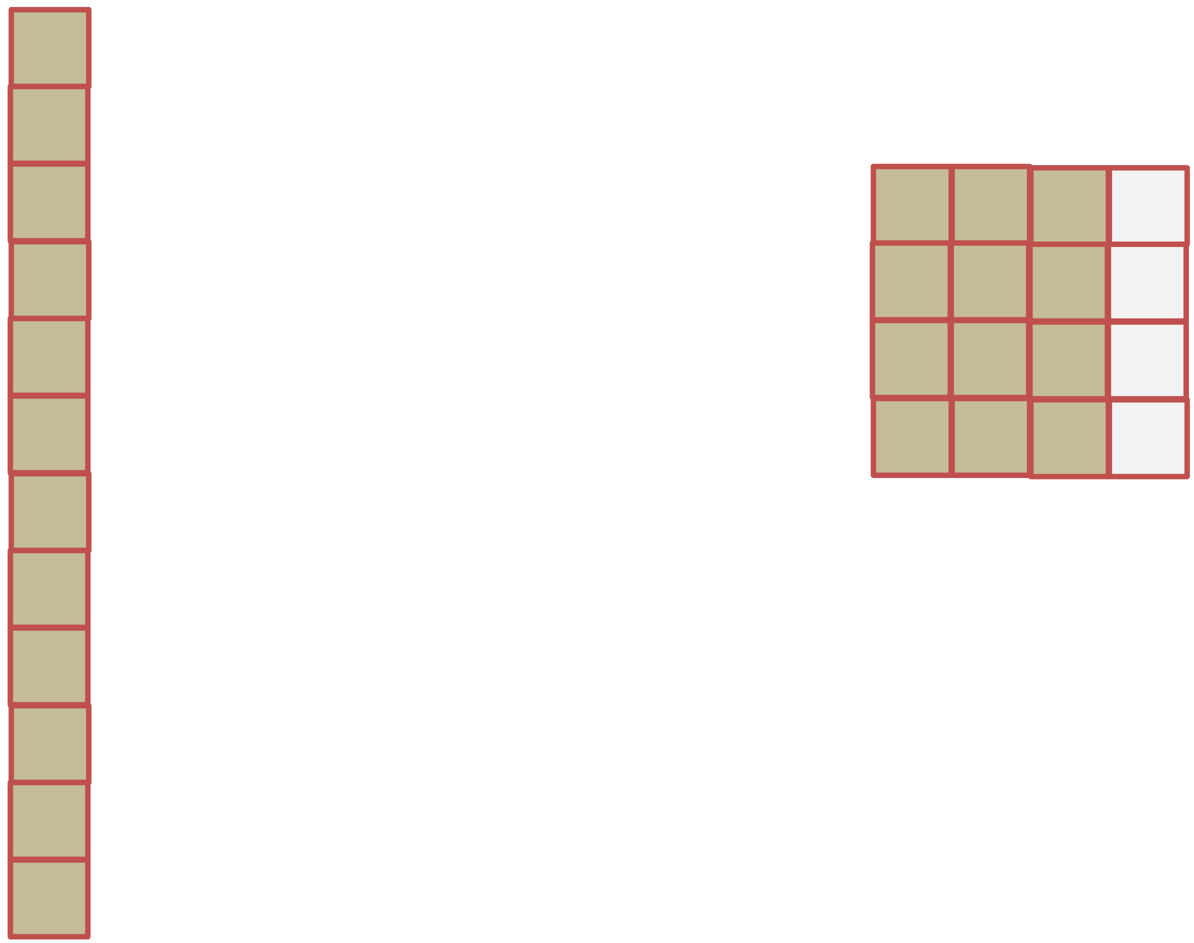
$$\sum_{a=1}^{A}\sum_{b=1}^{B-1} k_{a,b} < k_{total}\xi_1 \le \sum_{a=1}^{A}\sum_{b=1}^{B} k_{a,b}$$

Local updates

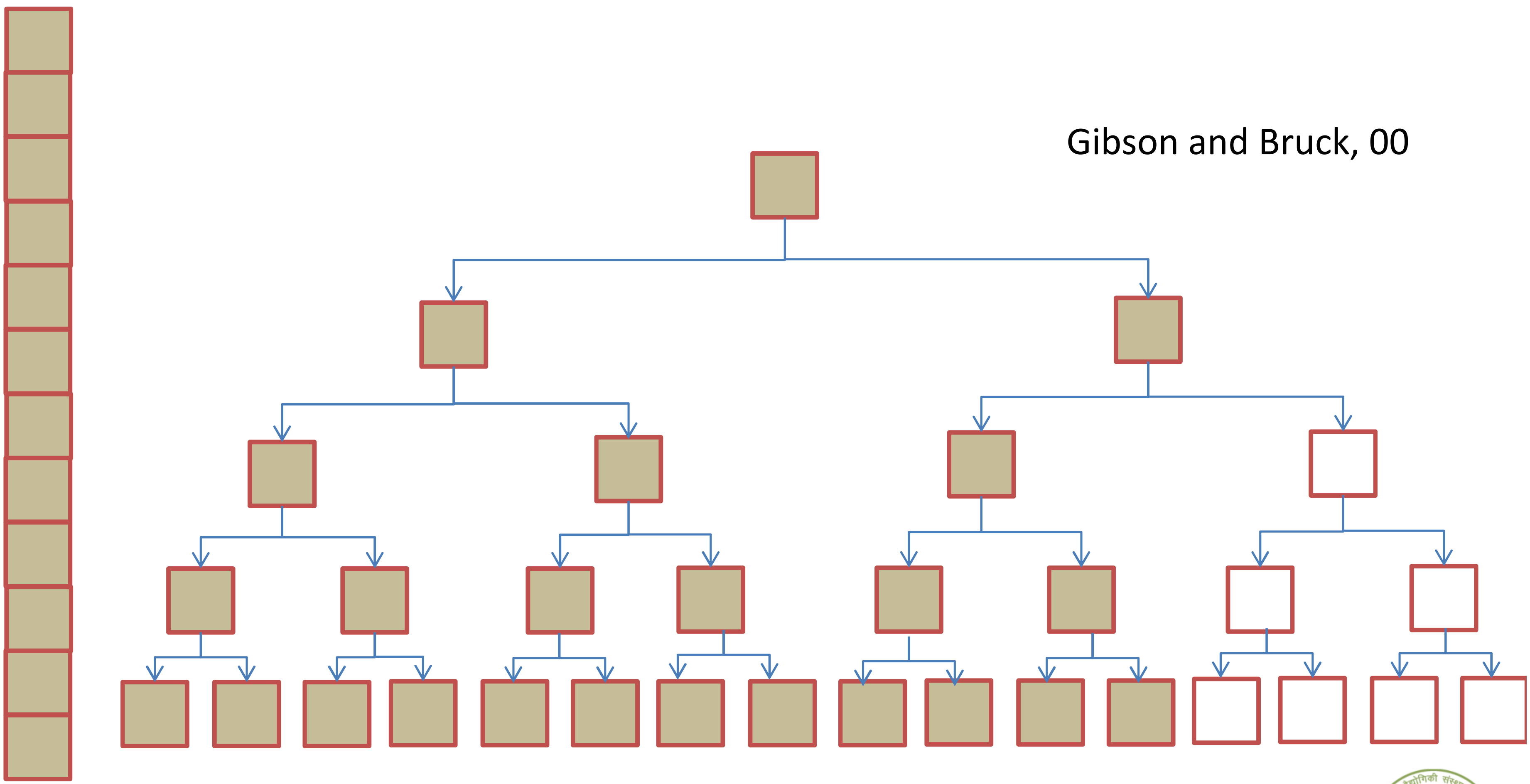




A more efficient implementation



Binary tree search



Gibson and Bruck, 00

N-fold or BKL method

Class number	Number of neighbors	Process Rate	# sites	Total rate	Cumulative sum	List
1	0	R1	N1	R1N1	R1N1	…
2	1	R2	N2	R2N2	R1N1+R2N2	
3	2	R3	N3	R3N3	R1N1+R2N2+R3N3	
4	3	R4	N4	R4N4	…	

BKL, 1975

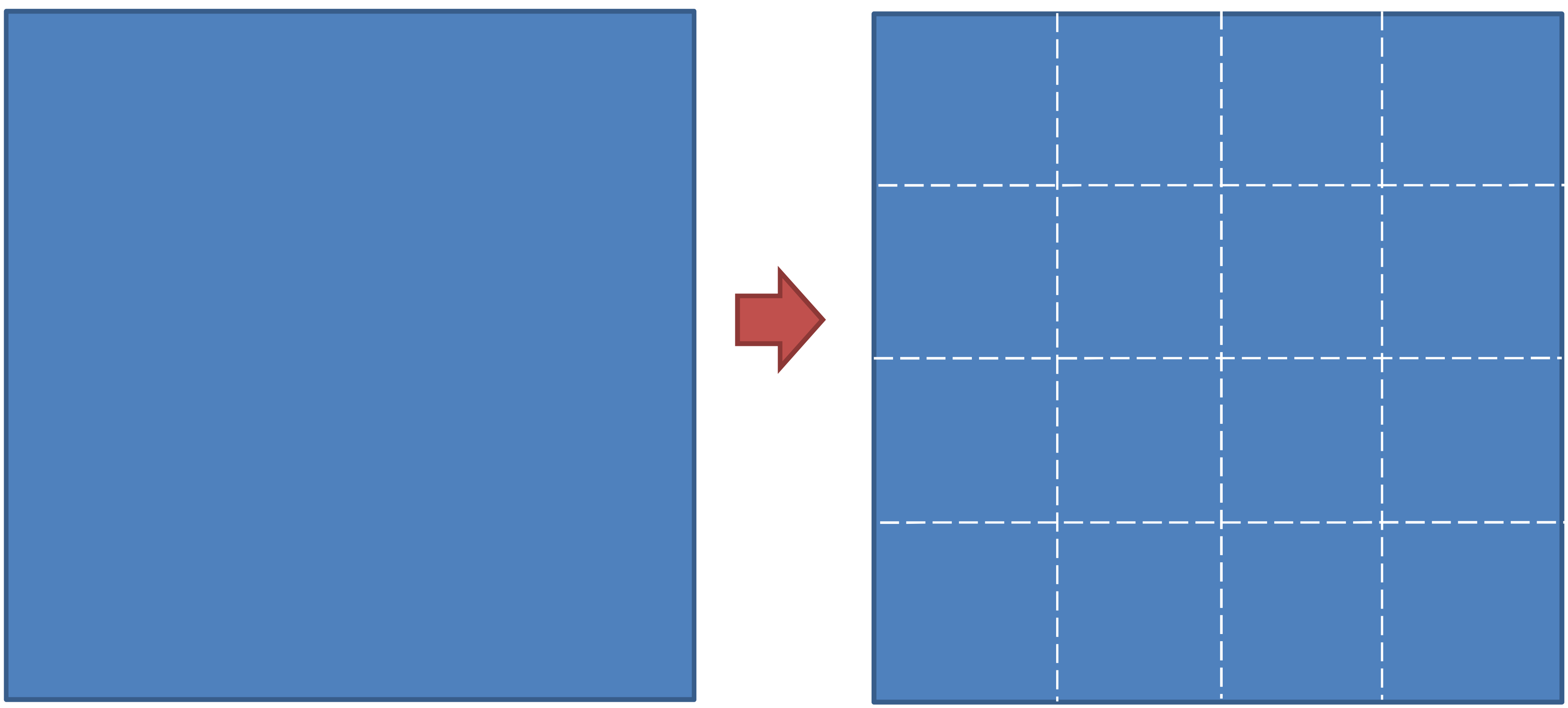
Challenges with KMC

- Cost of KMC can be high
- One process at a time
- Time scales accessible to KMC can be small in many situations
- Memory cost
- Other challenges

Recent advances in KMC

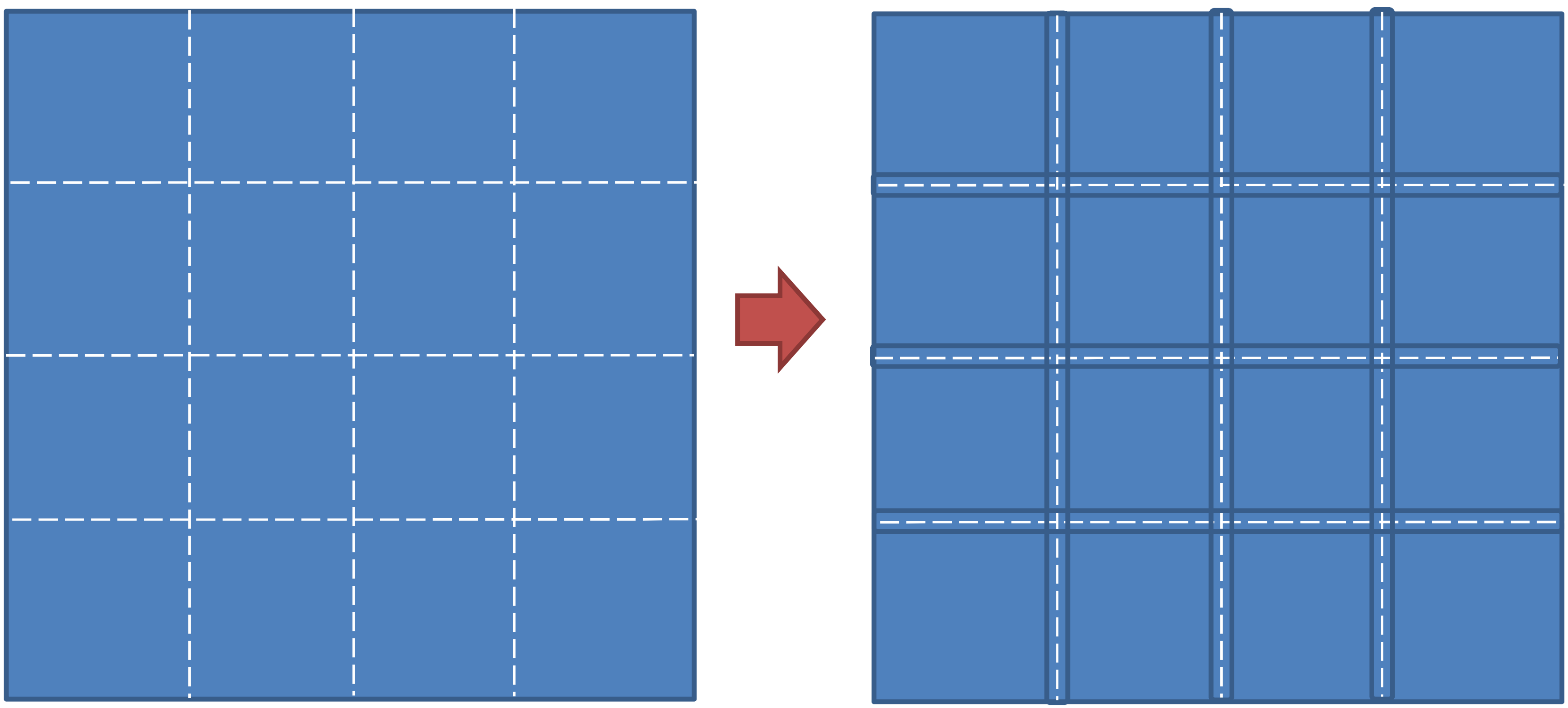
- Parallelization
- Spatial coarse-graining techniques
- Temporal coarse-graining techniques
- Spatio-temporal coarse-graining
- Time scale separation problems
- Other advances

Parallelization of KMC



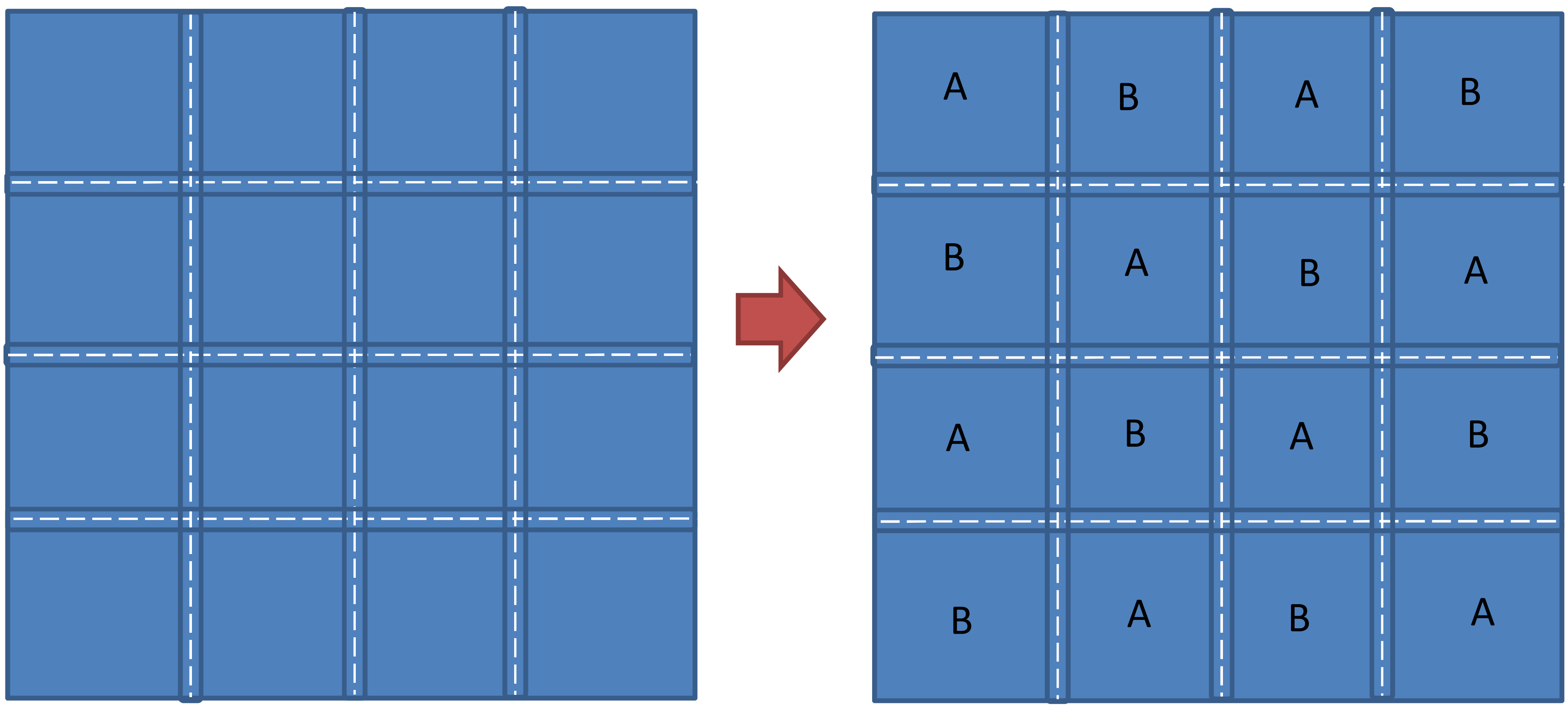
Amar, 05; Fichthorn, 07

Parallelization of KMC



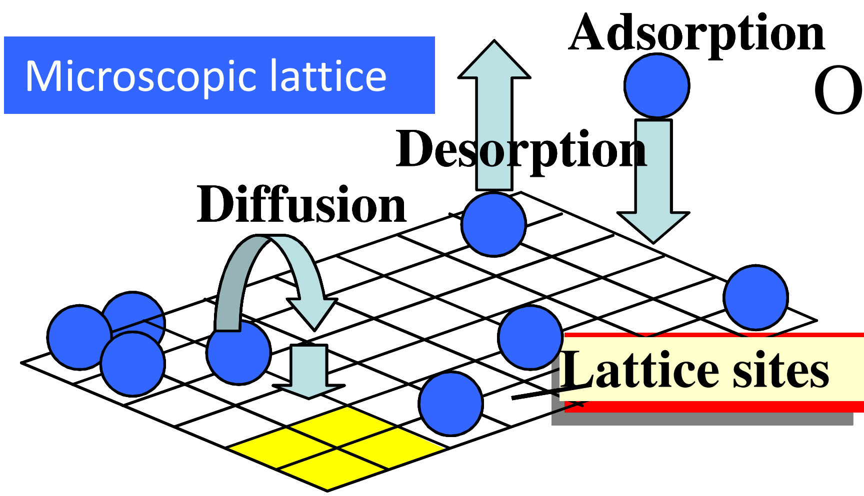
Amar, 05; Fichthorn, 07

Parallelization of KMC

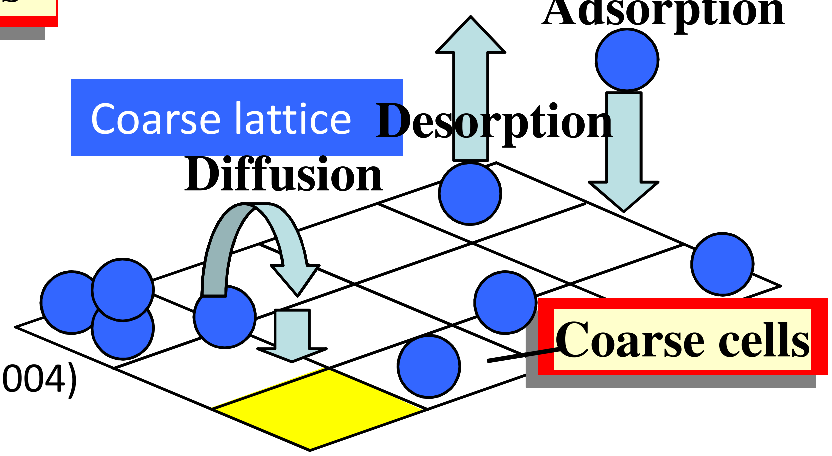


Amar, 05; Fichthorn, 07

Spatial coarse-graining



Occupancy vector σ

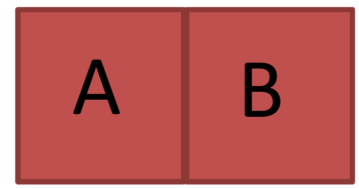


[1]M.A. Katsoulakis and D.G. Vlachos, JCP (2003)
[2]M.A. Katsoulakis, A.J. Majda, and D.G. Vlachos, PNAS (2003), JCompP (2003)
[3]A. Chatterjee, M.A. Katsoulakis and D.G. Vlachos, JCP (2004)
[4]A. Chatterjee and D.G. Vlachos, JCompP (2006)

Coarse – grained occupancy vector η

Features of spatial coarse-graining

- Adsorption, desorption, reaction, diffusion can be modelled



$$\eta_A \leftarrow \eta_A - 1 \qquad \eta_B \leftarrow \eta_B + 1$$

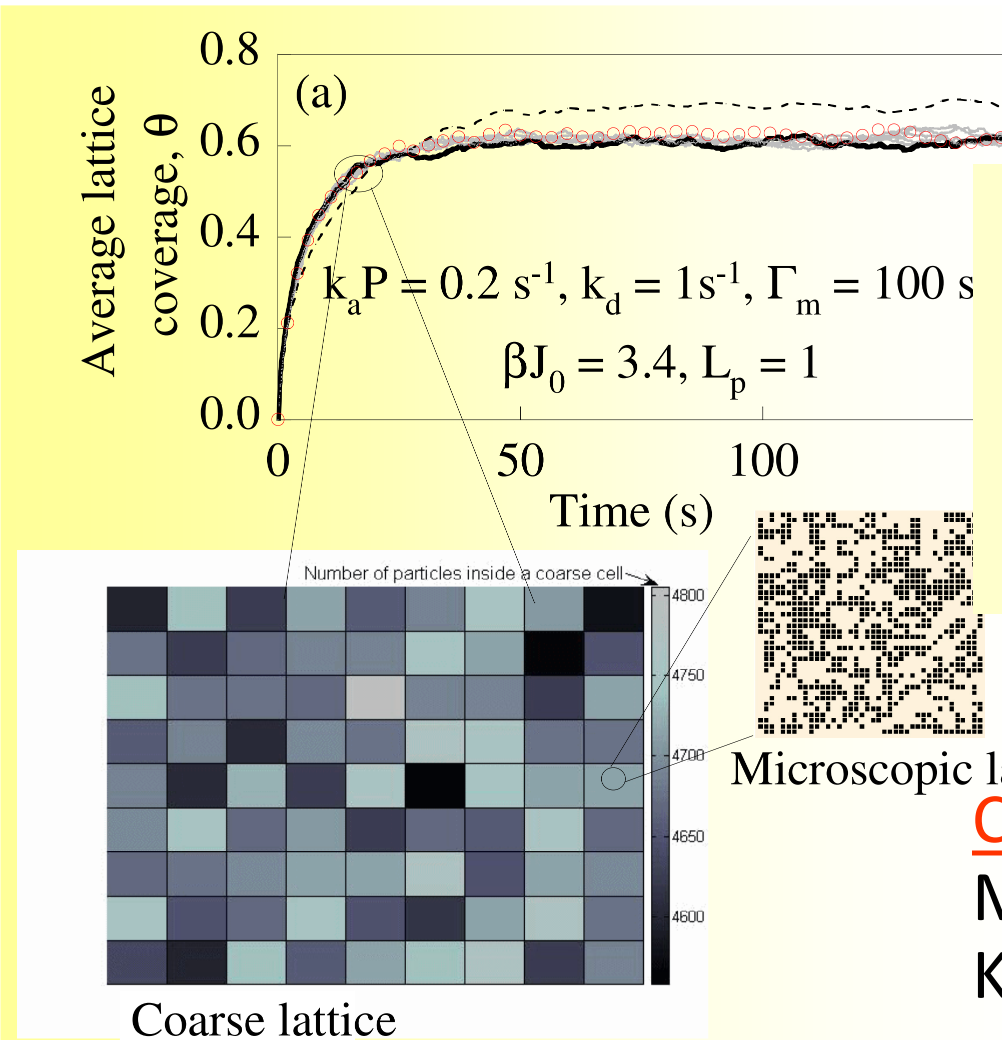
- Spatial resolution is lost
- Obtain in terms of coarse-grained variables
  - Rates
  - Transition probabilities
  - Energetics

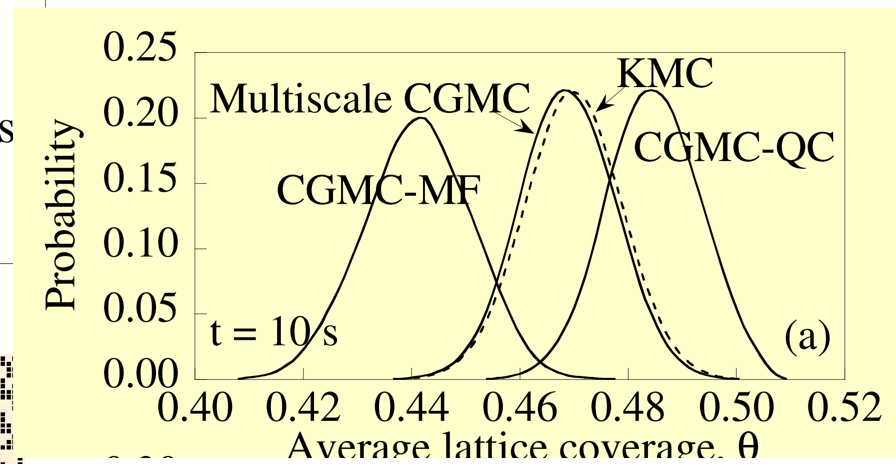
Correlations

- Mean-field approximation
- Quasi-chemical approximation
- Cluster expansion
- Numerical methods

Spatial coarse-graining

Katsoulakis et al 03,
Chatterjee et al, 06
Chatterjee et al, 08





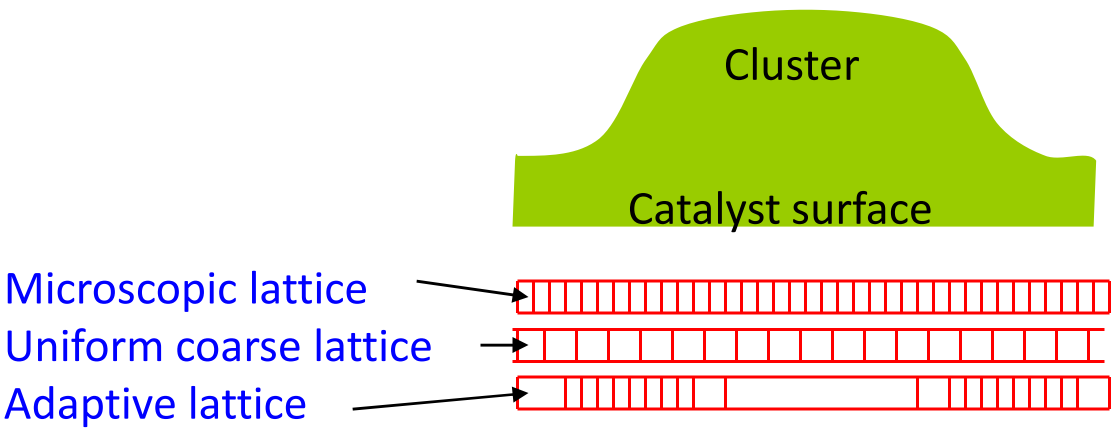
<u>CPU comparison</u>

MS-CGMC ~5-8 h

KMC simulation ~ 34,000 h (est.)

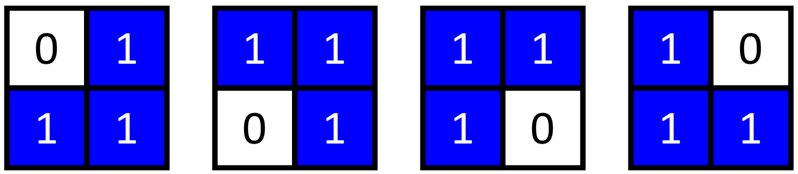
Adaptive spatial coarse-graining

Chatterjee et al, 04



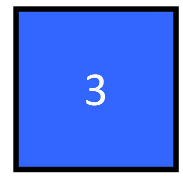
A posteriori error estimate

$$\mu_{micro} = Z_{micro}^{-1} e^{-H_{micro}/kT} P_{micro}(\underline{\sigma})$$

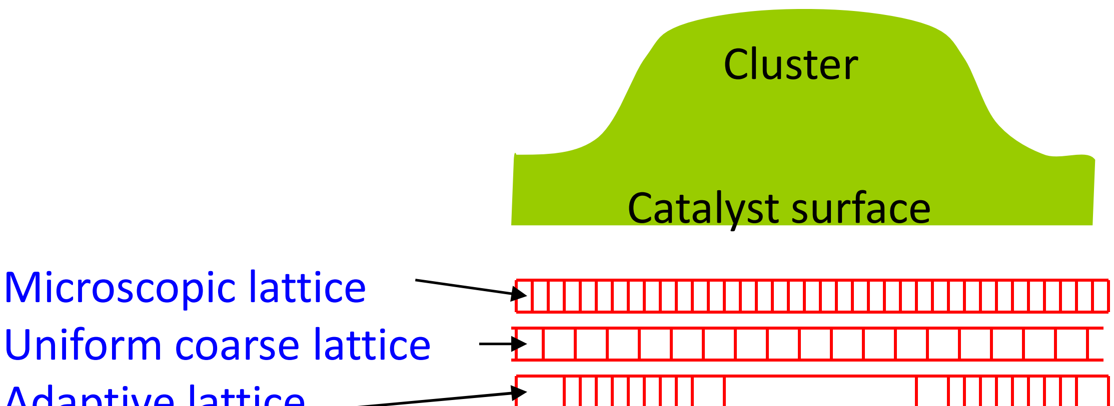


MICROSCOPIC (4 states)

$$\mu_{CG} = Z_{CG}^{-1} e^{-H_{CG}/kT} P_{CG}(\underline{\eta})$$



COARSE-GRAINED (1 state)



$$R = \left\langle \log \frac{\mu_{CG}}{\mu_{micro}} \right\rangle$$

Chatterjee et al, 05
Katsoulakis et al, 07

$$R = \langle \Delta H \rangle + \left\langle \log \frac{P_{CG}(\underline{\eta})}{\sum_{cell} e^{-\Delta H/kT} P_{micro}(\underline{\sigma})} \right\rangle$$

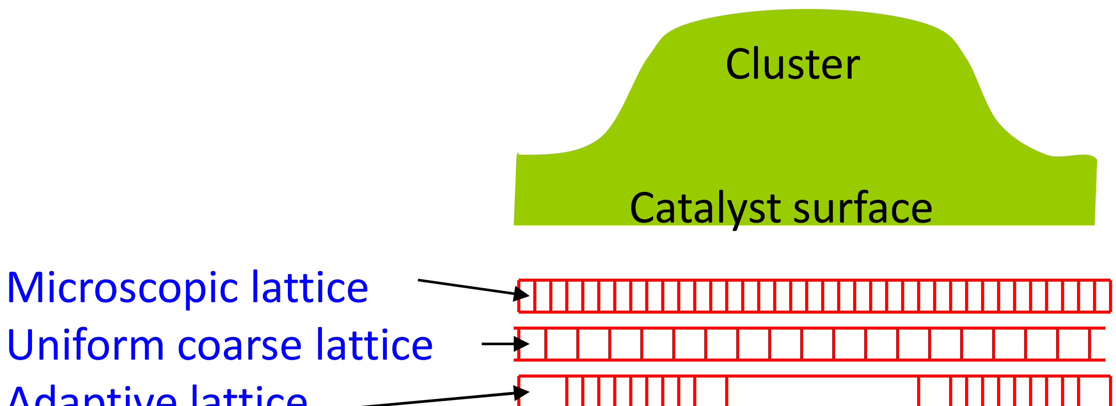
$$\Delta H = H_{micro} - H_{CG}$$

A posteriori error estimate

$$R = \langle \Delta H \rangle + \left\langle \log \frac{P_{CG}(\underline{\eta})}{\sum_{cell} e^{-\Delta H / kT} P_{micro}(\underline{\sigma})} \right\rangle \quad \rightarrow \quad R \leq c \langle \Lambda(\underline{\eta}) \rangle$$

$$\Delta H = H_{micro} - H_{CG}$$

$$\Lambda(\underline{\eta}) = \text{Upper bound}(\Delta H)$$



Chatterjee et al, 05

Katsoulakis et al, 07

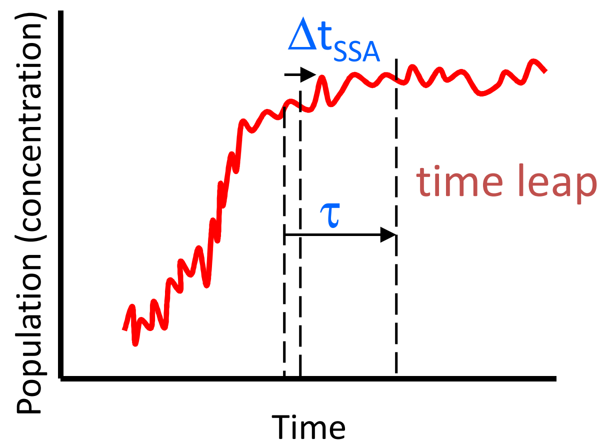
$$\langle \Lambda(\underline{\eta}) \rangle = 4 \sum_{cells,k} \left\{ \begin{array}{l} \dfrac{j_{kk}}{q_k(q_k-1)} \langle \eta_k(q_k - \eta_k)[\eta_k(\eta_k - 1) + (q_k - \eta_k)(q_k - \eta_k + 1)] \rangle + \\ \displaystyle\sum_{interacting\ cells,l} \dfrac{j_{kl}}{q_k q_l} \langle q_k{}^2 \eta_l (q_l - \eta_l) - 2\eta_k \eta_l (q_k - \eta_k)(q_l - \eta_l) \rangle \end{array} \right\}$$

Temporal coarse-graining

- Poisson tau leap

$$P_{PD}(k_j; a_j\tau) = \frac{e^{-a_j\tau}}{k_j\,!}(a_j\tau)^{k_j}$$

Gillespie, 01

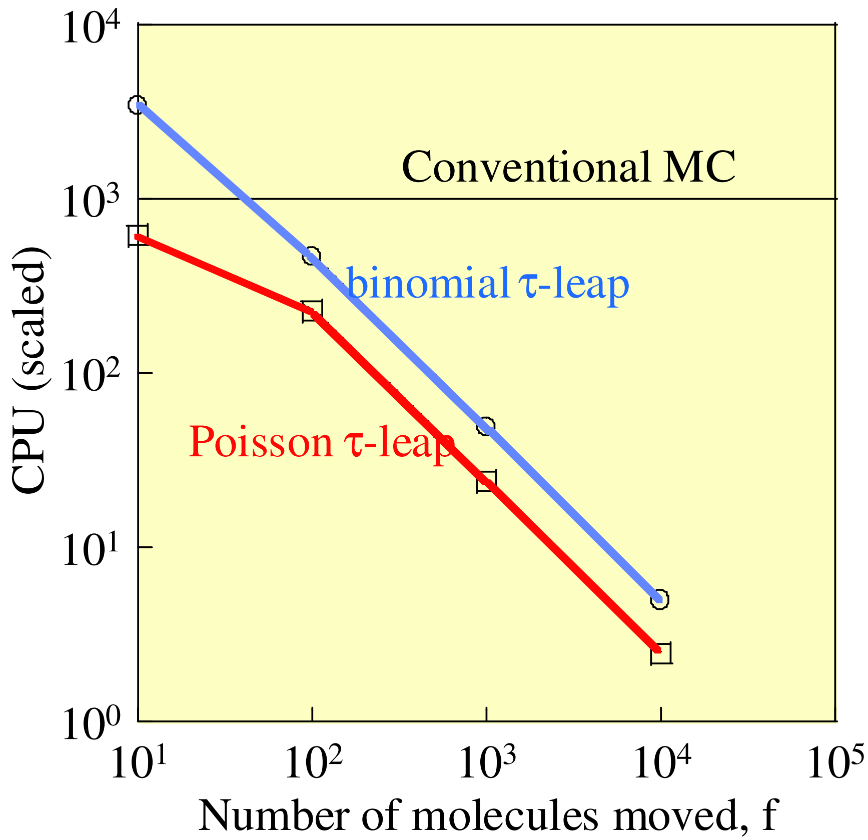


- Binomial tau leap

$$P_{BD}\left(n_j; \frac{a_j\tau}{k_{max}^{(j)}}, n_{max}^{(j)}\right) = \frac{n_{max}^{(j)}\,!}{n_j\,!\left(n_{max}^{(j)} - n_j\right)!}\left(\frac{a_j\tau}{k_{max}^{(j)}}\right)^{n_j}\left(1 - \frac{a_j\tau}{k_{max}^{(j)}}\right)^{n_{max}^{(j)} - n_j}$$

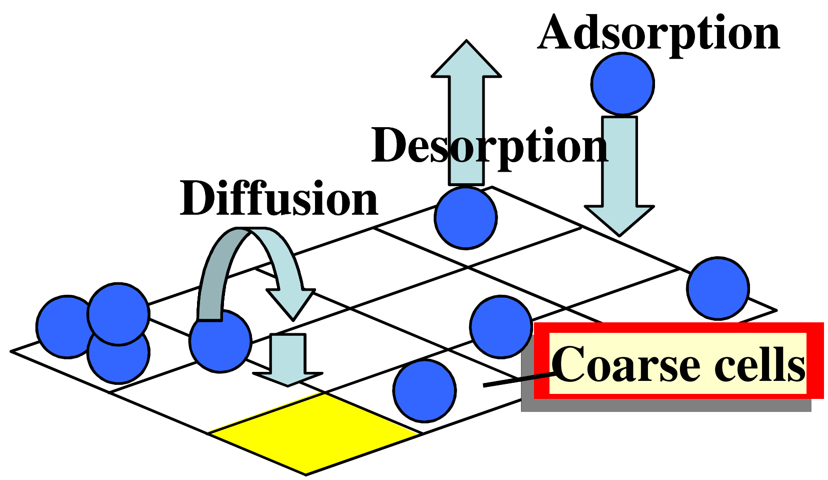
Chatterjee et al, 05

Temporal coarse-graining



Spatio-temporal coarse-graining

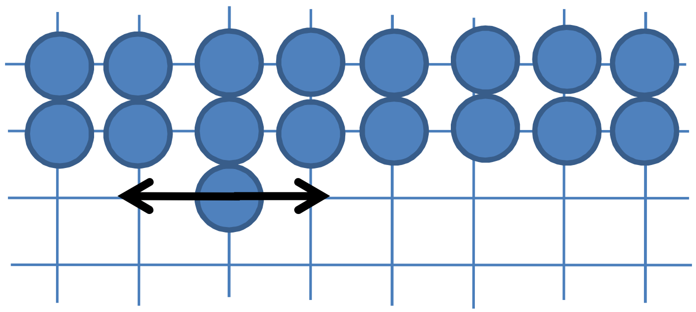
- Apply tau leap method to spatially coarse-grained cells



Chatterjee et al, 06

Time scale separation problem

- Adatom detachment from a step is a slow process



- Probability of selecting a process is proportional to the rate

Methods for addressing time scale separation

- Net-event KMC (Vlachos 96, Chatterjee et al, 05)
- Probability-weighted method (Resat 01)
- Novotny method (Novotny, 95, Puchala et al, 10)
- Singular perturbation methods (Chatterjee, 06)
- Fuzzy superbasin KMC method (Chatterjee et al , 10)

For more information

- Chatterjee, Vlachos, An overview of spatial microscopic and accelerated kinetic Monte Carlo methods, Journal of Computer-Aided Materials Design, 2007