

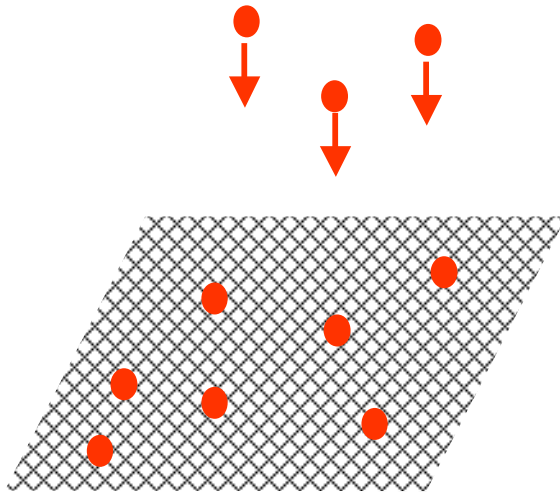
# Applications of kinetics to surface science and simulations of epitaxial growth

Peter Kratzer

Fritz-Haber-Institut der MPG, Berlin, Germany

# Statistical physics approach: discrete models

---



Why **kinetic** Monte Carlo ?

two reasons:

- technical
- physical (external time scale comes into play)

Ising

$$E = - \sum_{j < k} J_{ik} S_i S_k - H \sum_j S_i$$
$$S_i = \pm 1/2$$

(simple) lattice gas

$$E = \sum_{j < k} V_{ik} n_i n_k + E_s \sum_j n_i$$
$$n_i = 0, 1$$

mapping  $n_i \leftrightarrow S_i + 1/2$

(N-states) Potts model

$$E = - \sum_{j < k} J_{ik} \delta_{S_i S_k}$$

# Why **kinetic** Monte Carlo ? (I)

---

- Transition probabilities  $W(i,j)/W(j,i) = \exp(-\Delta E/kT)$
  - There is only a finite number of  $\Delta E$ 's rate constants can be pre-computed and stored in a 'class table' (saves frequent evaluations of  $\exp$  function)
  - At low  $T$ , in the Metropolis algorithm, most of the transitions will be rejected  $\rightarrow$  simulation becomes inefficient
  - solution: N-fold way
    - build a complete class table
    - use a random number to select a class, proportional to the transition probability of that class (the acceptance of this step is 100% !)
    - execute one process (spin flip) from the selected class
- A. B. Bortz, M. H. Kalos and J. L. Lebowitz, J. Comp. Phys. **17**, 10 (1975)

# Why kinetic Monte Carlo ? (II)

---

## Topics to be studied

- Systems in a meta-stable non-equilibrium state: **relative time scales** of different relaxation processes must be represented correctly.
- **absolute time scale** set by external process (e.g. deposition and/or desorption)

## Required features of the algorithm

- The ratio of the “forward” and “backward” probabilities must equal the ratio of “forward” and “backward” rate constants (detailed balance condition; it must be fulfilled by all Monte Carlo methods).
- Strict proportionality between the probability of selecting any process and its rate constant.
- one-to-one mapping between “simulation time” and “physical time”.

# Topics of kinetical simulations

---

## Surface science

- lattice-gas Hamiltonian
- temperature-programmed desorption spectra
- order-disorder phase transitions in adsorbate layers
- surface diffusion
- surface reactions / heterogeneous catalysis

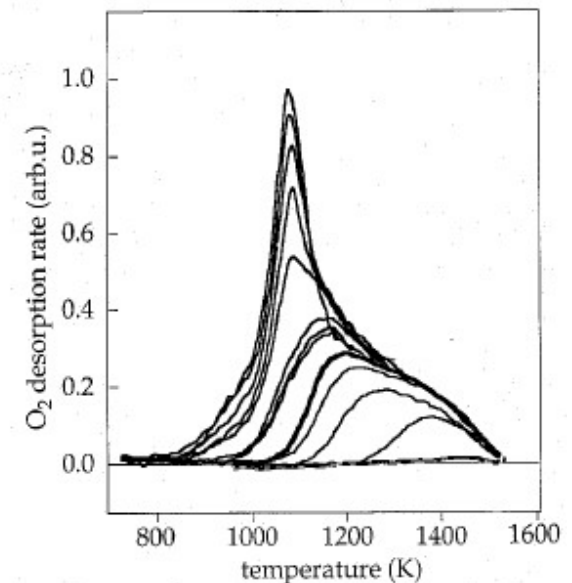
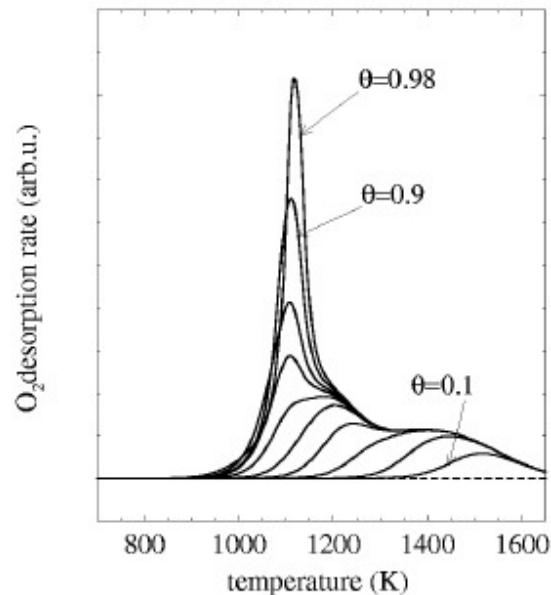
## Epitaxial growth simulations

- SOS model of the crystal
- the roughening transition
- dynamical roughening
- sub-monolayer growth:
  - growth mode transition from step flow to island growth
  - scaling relations in island growth
- ripening phenomena

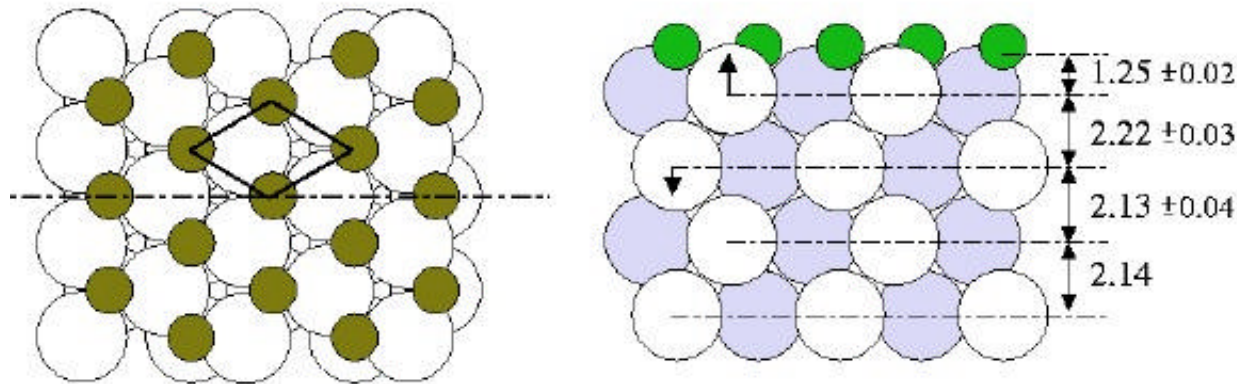
# **Some applications in Surface Science**

# Temperature-programmed desorption

- atoms adsorbed on a surface
- interaction between atoms adsorbed in neighboring sites  
→ binding energy depends on coverage  $\Theta$
- substrate is heated with a constant rate (typically between 0.1 K/sec and 10 K/sec), thereby desorbing particles from the surface  
→ kinetics enters



# Lattice-gas Hamiltonian

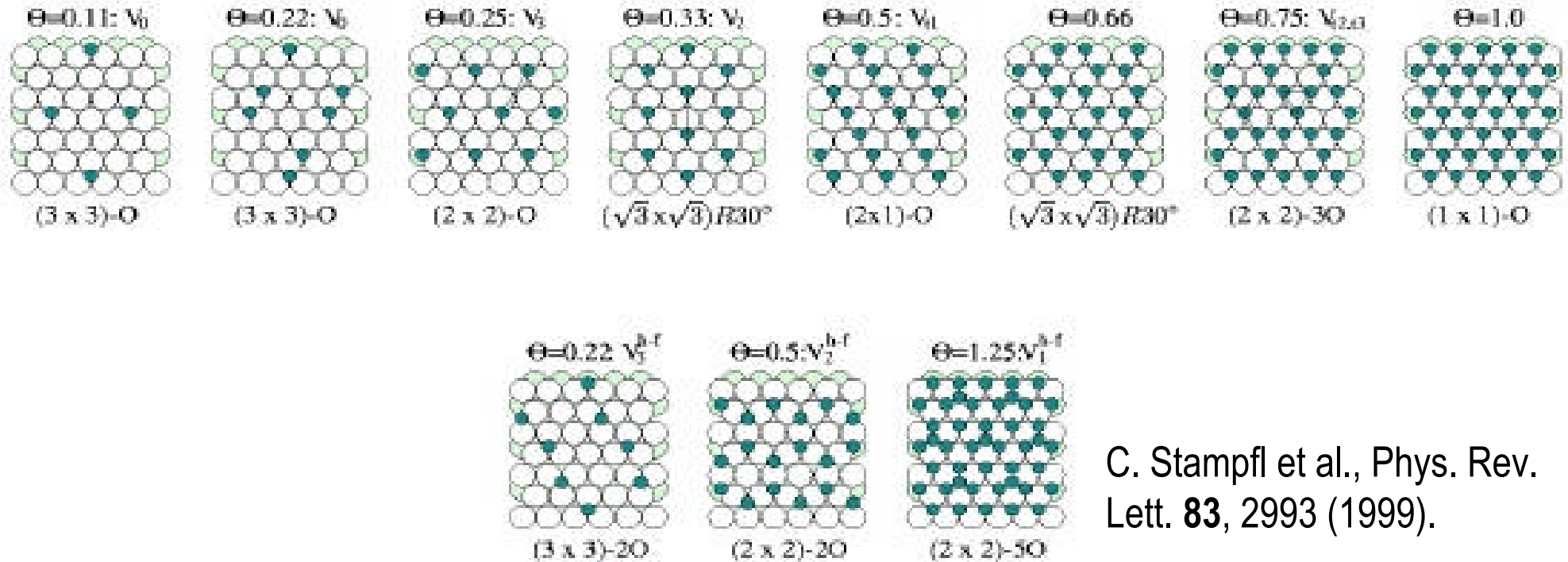


$$\begin{aligned}
 H = & E_s^{\text{hcp}} \sum_i n_i + E_s^{\text{fcc}} \sum_i n_i + V_{1n}^{\text{hcp}} \sum_{i,a} n_i n_{i+a} + V_{1n}^{\text{fcc}} \sum_{i,a} n_i n_{i+a} \\
 & + V_{1n}^{\text{hcp-fcc}} \sum_{i,a'} n_i n_{i+a'} + V_{2n}^{\text{hcp}} \sum_{i,b} n_i n_{i+b} + V_{2n}^{\text{fcc}} \sum_{i,b} n_i n_{i+b} \\
 & + V_{2n}^{\text{hcp-fcc}} \sum_{i,b'} n_i n_{i+b'} + V_{3n}^{\text{hcp}} \sum_{i,c} n_i n_{i+c} + V_{3n}^{\text{fcc}} \sum_{i,c} n_i n_{i+c} \\
 & + V_{3n}^{\text{hcp-fcc}} \sum_{i,c'} n_i n_{i+c'} + V_{\text{trio}} \sum_{i,a,a'} n_i n_{i+a} n_{i+a'} + \dots
 \end{aligned}$$



# Determining the parameters of the Hamiltonian

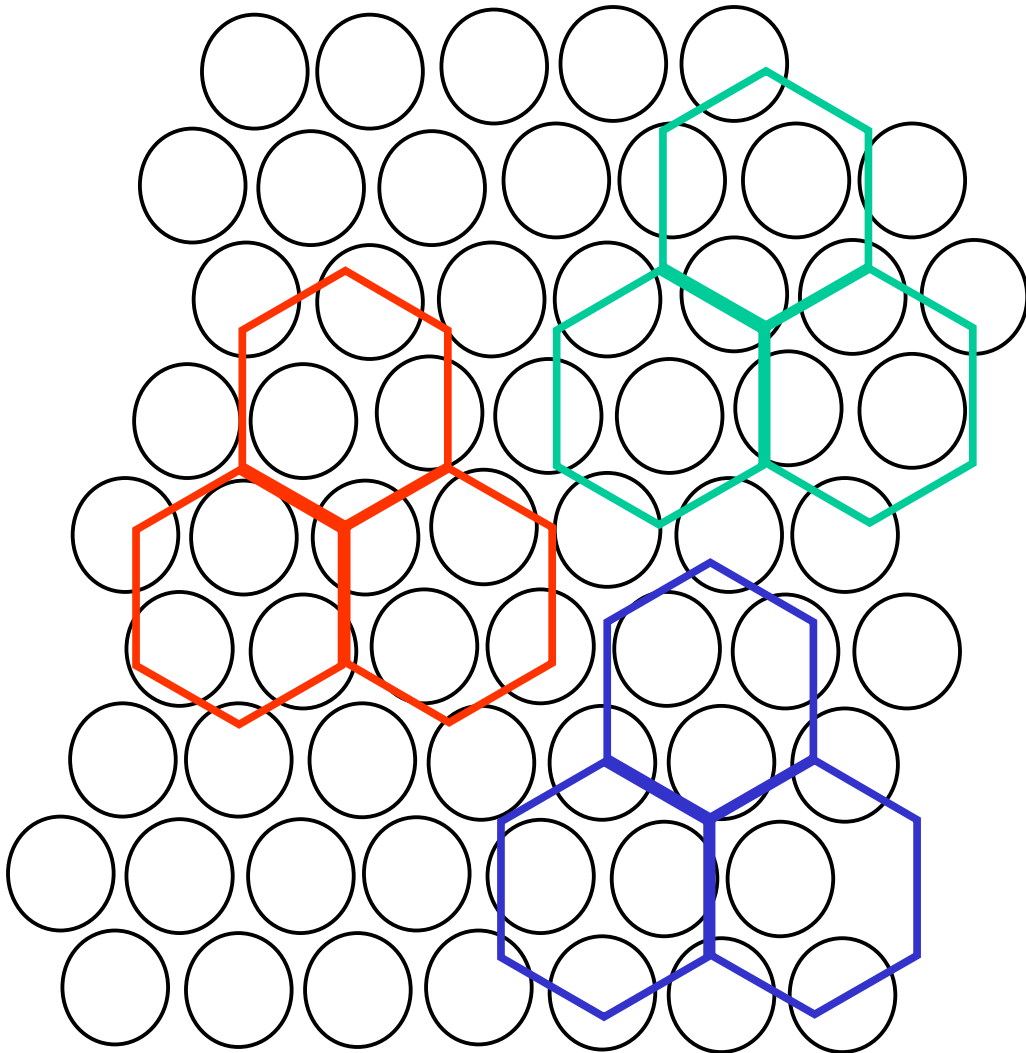
The energy of numerous ordered structures must be determined (e.g. by DFT calculations). Then a system of linear equations for the parameters is set up and solved.



C. Stampfl et al., Phys. Rev. Lett. **83**, 2993 (1999).

# Order-disorder phase transitions

---



- adsorbate layer may form an ordered sublattice
- registry of the sublattice w.r.t. the substrate defines a multi-valued order parameter (N-states Potts model)
- quenching below the transition temperature leads to domain wall formation
- domain growth as a function of time shows power law scaling

# Surface diffusion

---

- diffusion constant  $D = K_{th} \Gamma$
- tracer diffusion: only  $\Gamma$  is relevant
- thermodynamic factor is an equilibrium property

$$K_{th} = \left( \frac{dm}{dn} \right)_T = \left( \frac{dn}{dm} \right)_T^{-1} = C_T^{-1}$$

- hopping rate  $\Gamma$  obtainable from kinetic Monte Carlo simulations, using the relation  $\Delta x = 4 a^2 \Gamma t$  (for a square lattice)
- dynamical correlations important (e.g. in vacancy-assisted diffusion)
- chemical diffusion in kMC: analyse decay of density profile, starting with a given distribution (e.g. Gaussian) of particles.

# Kinetic simulations in epitaxy

A.-L. Barabasi and H.E. Stanley, Fractal Concepts in Surface Growth, Cambridge University Press, 1995

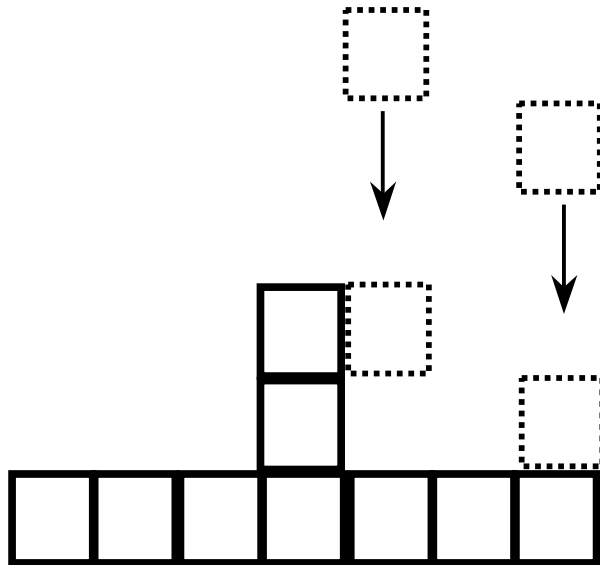
J. Venables et al., Rep. Prog. Phys. **47**, 399 (1984);  
R. M. Tromp and J. B. Hannon, Surf. Rev. Lett. **9** 1565 (2002).

# Simple discrete models of interface dynamics

---

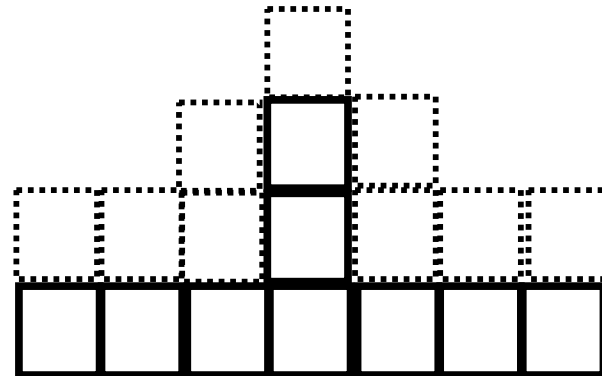
ballistic deposition model:

particles stick as soon as they find a neighbor (or, likewise an NNN)



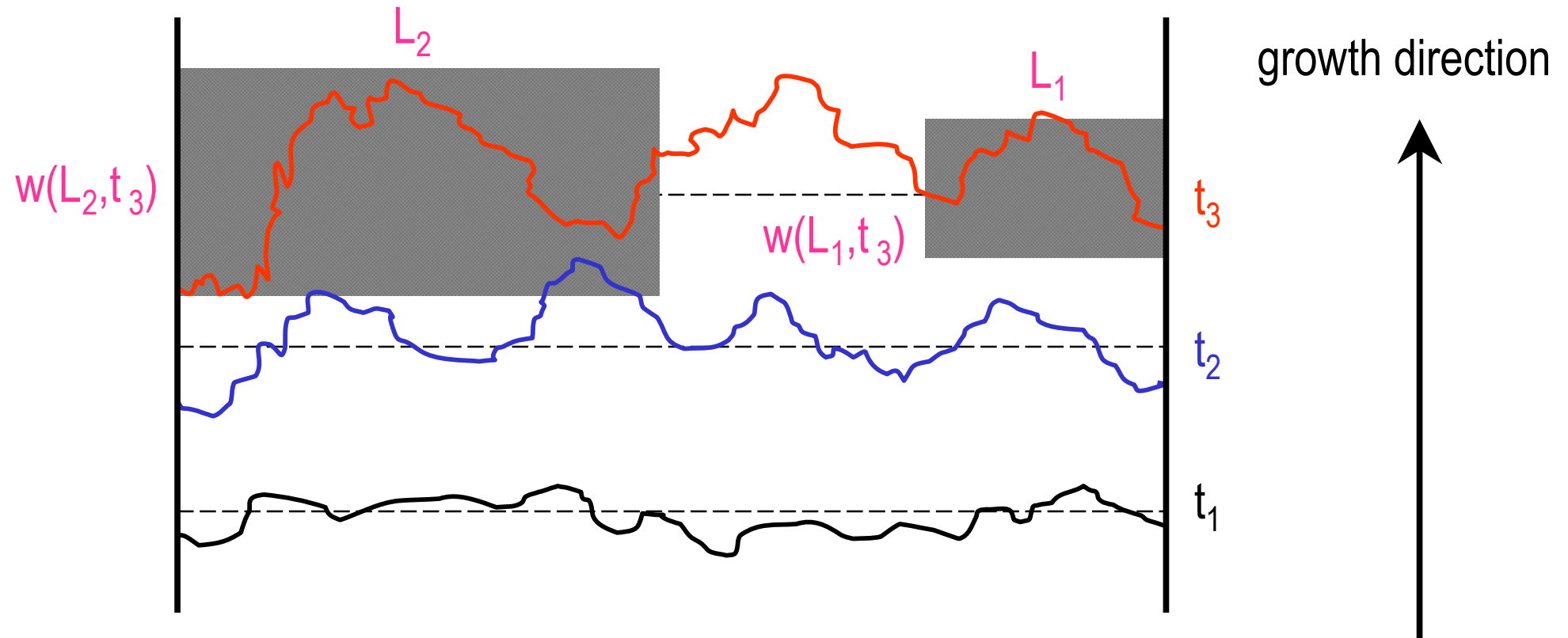
Eden model:

sites where the new particles will have a neighbor get occupied randomly (with equal probability, or some modification thereof)



continuum model: Kardar-Parisi-Zhang equation

# Scaling of surface roughness



$$w(L, t) = L^\alpha$$

small times:  $w(L, t) = t$   
larger times:  $w(L, t) = t^\beta$

$$\text{crossover time} = L^z$$

# Solid-on-Solid (SOS) models

General feature of SOS models:

- no voids
- no overhangs

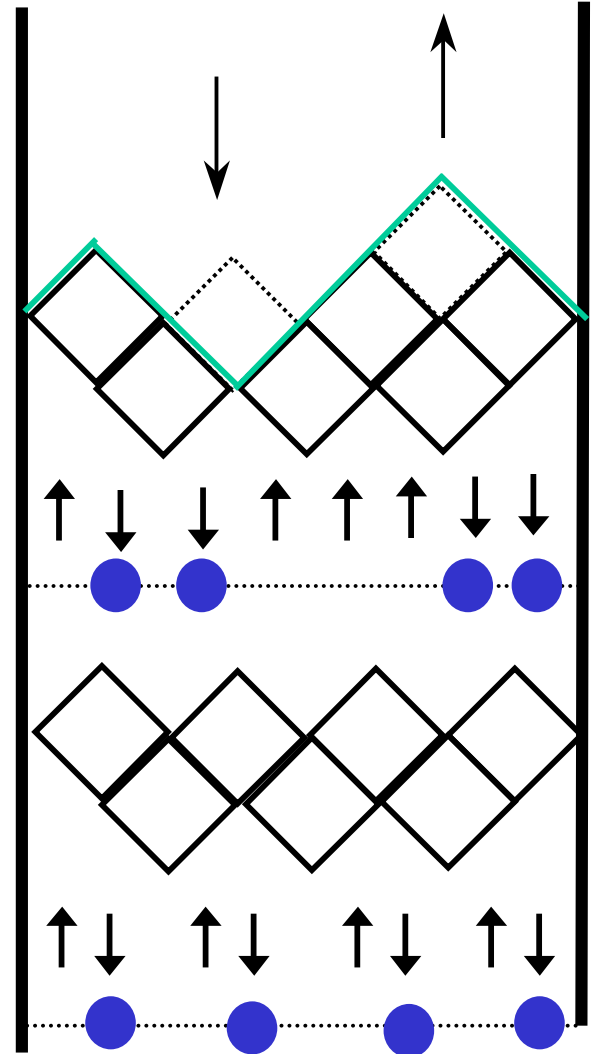
“single-step” model:

adsorption and desorption at local minima / maxima

equivalence to Ising model or lattice gas model

exponents in 1+1 dimensions:

$$\alpha = \frac{1}{2} \quad \beta = \frac{1}{3}$$



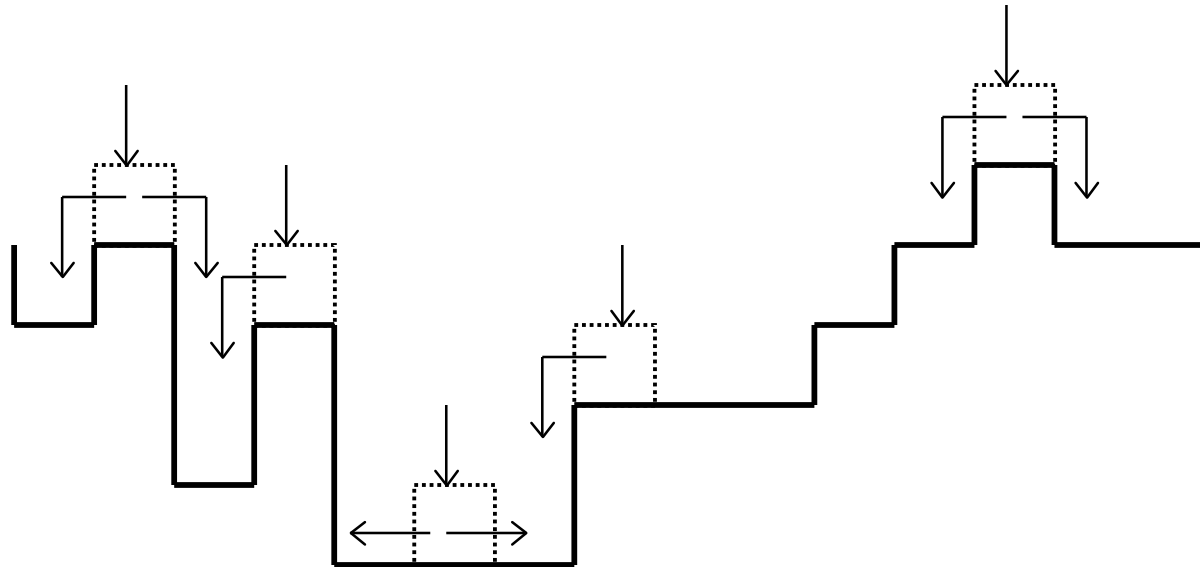
# MBE: models with transient diffusion

---

Wolf-Villain model:

randomly deposited particles have transient mobility:

they move to the neighboring sites(s) with highest coordination



similar model by Das Sarma-Tamborenea



# MBE: models with activated diffusion

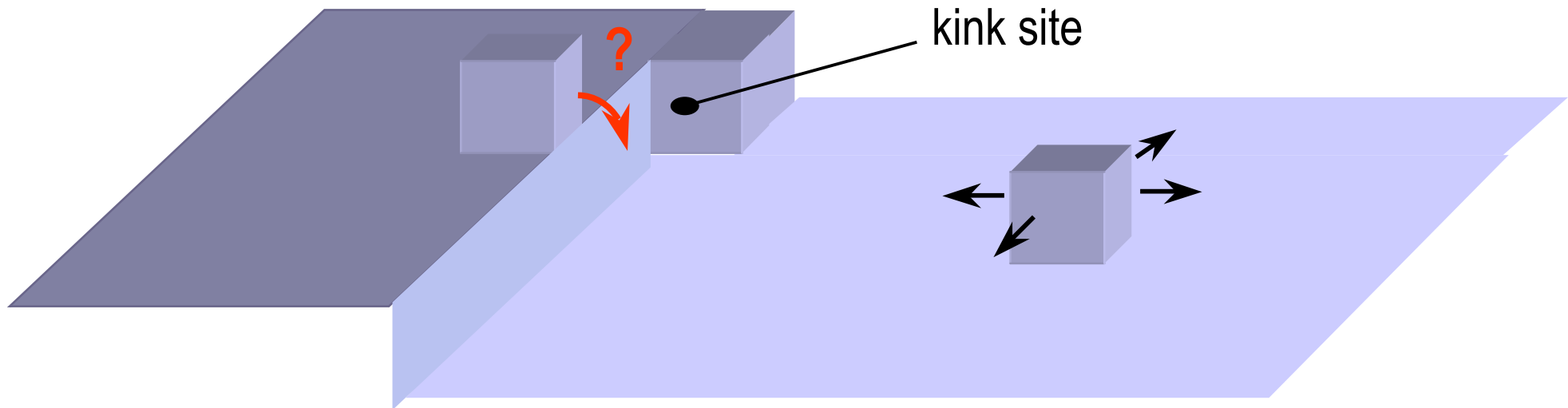
---

Schwoebel-Ehrlich effect

$$\Gamma = \Gamma_0 \exp( -(E_A + E_s) / kT )$$

hopping diffusion

$$\Gamma = \Gamma_0 \exp( -E_A / kT )$$



**simplest model:** atoms with at least one in-plane neighbor are immobile (irreversible attachment)

# nucleation theory

assumption: only single atoms are mobile, larger clusters with  $i > 1$  atoms immobile

## idea:

We can ascribe a chemical potential  $\mu_i$  to each particle in a cluster of  $i$  atoms.

Consider equilibrium  $N_i + N_1 \leftrightarrow N_{i+1}$

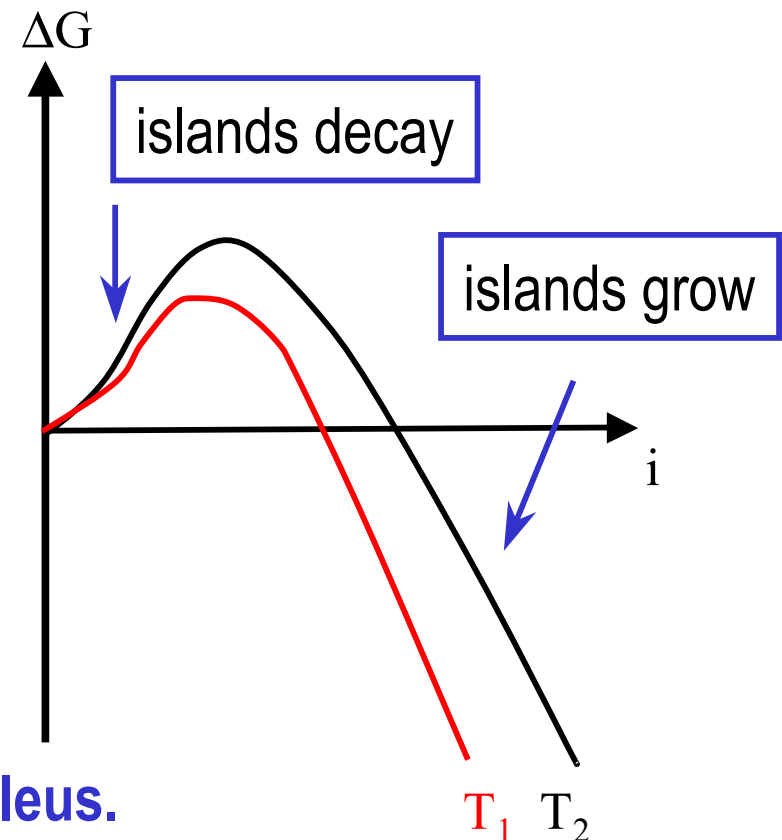
Then, for all  $i \Rightarrow \mu_i = i \mu_1$

non-equilibrium:

$\mu_1(p, T)$  is fixed externally (supersaturation due to incoming flux),

$$\Delta G = \mu_i - i \mu_1$$

**Maximum of  $\Delta G$  defines the critical nucleus.**



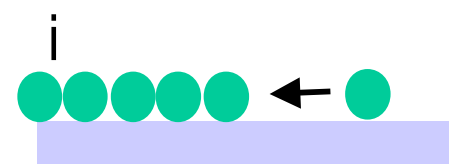
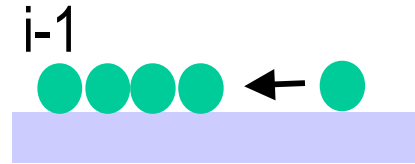
# island density: scaling laws

coupled hierarchy of rate equations

$$\frac{dN_1}{dt} = R - \frac{N_1}{t} - \underbrace{2DS_1N_1^2}_{\text{nucleation}} - \underbrace{\sum_{i=2}^{\infty} DS_iN_1N_i}_{\text{attachment}}$$

deposition
evap.
nucleation
attachment

$$\frac{dN_i}{dt} = DS_{i-1}N_{i-1}N_1 - DS_iN_iN_1$$



important special result

(for diffusion-limited growth in 2D):

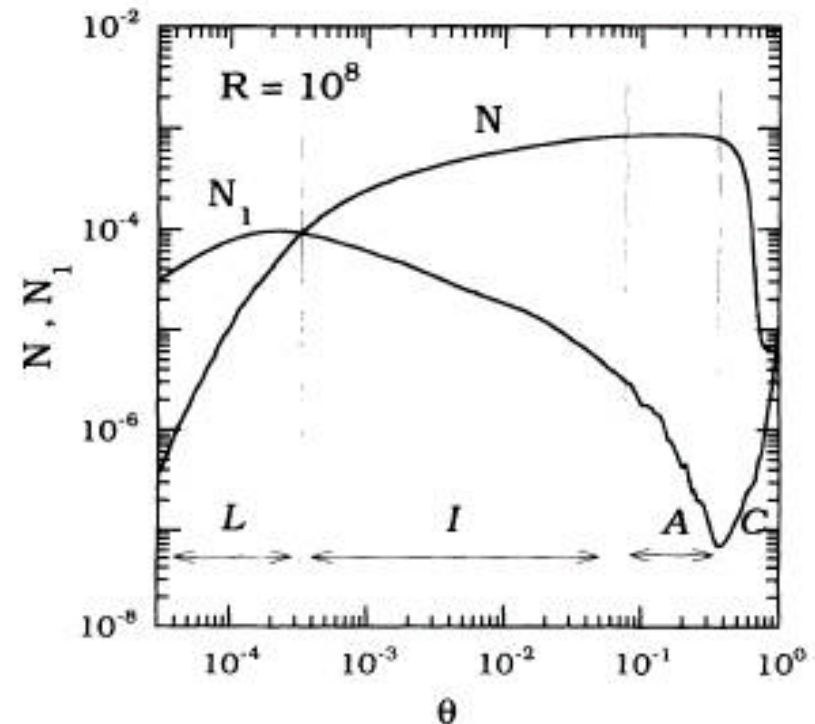
$$N_x \sim \left( \frac{R}{D} \right)^{\frac{i_c}{i_c+2}}$$

# discussion for critical island size $i_c=1$

- evaporation neglected: 
$$\frac{dN_1}{dt} = R - 2DS_1N_1^2 - DS_iN_1N$$

$$N = \sum_{j=2}^{\infty} N_j \quad \frac{dN}{dt} = DS_1N_1^2$$

- very short times:**  $R$  dominates !  
 $N_1 = Rt$ ;  $N = S_1 R^2 D t^3$
- medium times:** no new nucleation, flux is consumed by attaching to existing islands  
 $N_1 \sim R/(DS_i N)$ ;  $N \sim (3t)^{1/3}$ ;  
 $N_1 \sim R^{2/3} D^{-1/3} t^{-1/3}$



# simple treatment of $i_c > 1$

---

- islands with  $i > i_c$  are stable and are treated with a single variable

$$N_x = \sum_{j=i_c+1}^{\infty} N_j$$

- only two eq.s remain:  $\frac{dN_1}{dt} = R - \frac{N_1}{t} - \frac{d(w_x N_x)}{dt}$

$$\frac{dN_x}{dt} = DS_{i_c} N_{i_c} N_1 - \underline{U_c} \text{ loss term due to coalescence}$$

- saturation of island density for  $i_c=1$ :

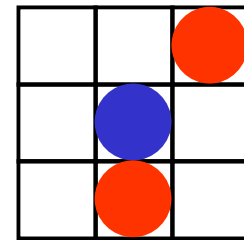
- equate  $DS_I N_I^2$  and  $U_c$ :  $N_x = N_I^2$
- insert into eq. (1):  $DS_I N_I^3 = R$
- use medium-time-scale relation  $N_x = 1/N_I$
- result:  $N_x \sim (D/R)^{1/3}$

$$U_c = 2N_x \frac{dZ}{dt}$$

# kMC simulations of the SOS model

---

- simulation on a grid, associate potential minima with grid points
- classification of initial and final state by 'atomic neighborhoods'  
e.g., the **number and relative position of neighbors** could define the class



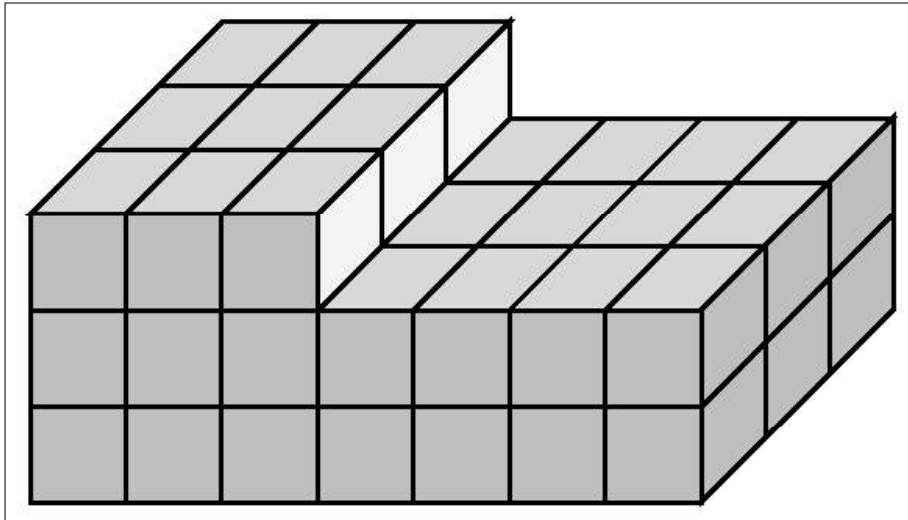
- classify possible transitions  $W(f,i)$  from  $i$  to  $f$ ,  
each class  $k$  is characterized by a rate (input to the simulation).  
concerted events (simultaneous motion of several atoms) can  
be accounted for
- detailed balance (ensures that thermal equilibrium is reached)  
 $W(i,j)/W(j,i) = \exp( - (G_i - G_j)/kT )$

# bond-counting models

- Let's assume that the energy at the transition state is equal for all transitions
- Let the binding energy  $E_i$  be a function of the number of neighbors ( Kossel crystal ).
- Let all prefactors be equal.

$$\Gamma^{(i)} = \Gamma_0 \exp( -f(n)/kT )$$

specific models for  $f(n)$ :



- **metal:**  
 $f(n) = A \sqrt{n} + B n$
- **semiconductor:**  
 $f(n) = E_S + n E_B$

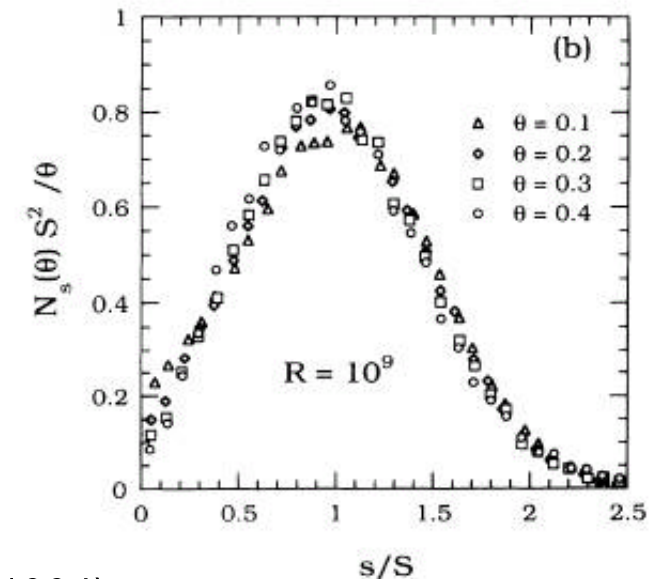
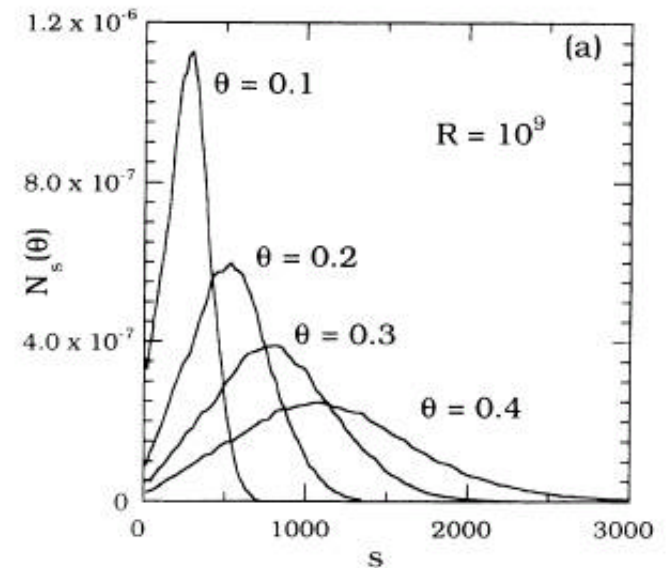
# Island distributions: scaling

$$Z = \sum_{j \geq 2}^{\infty} j N_j$$

$$N = \frac{Z}{N_x} = \frac{\Theta - N_1}{N_x}$$

Provided that there is only a **single length scale** in the problem (the diffusion length, or the average island size  $N$ ), the island size distribution displays scaling:

$$N_j = G(\Theta, N) f\left(\frac{j}{N}\right) \propto \frac{\Theta}{N^2} f\left(\frac{j}{N}\right)$$

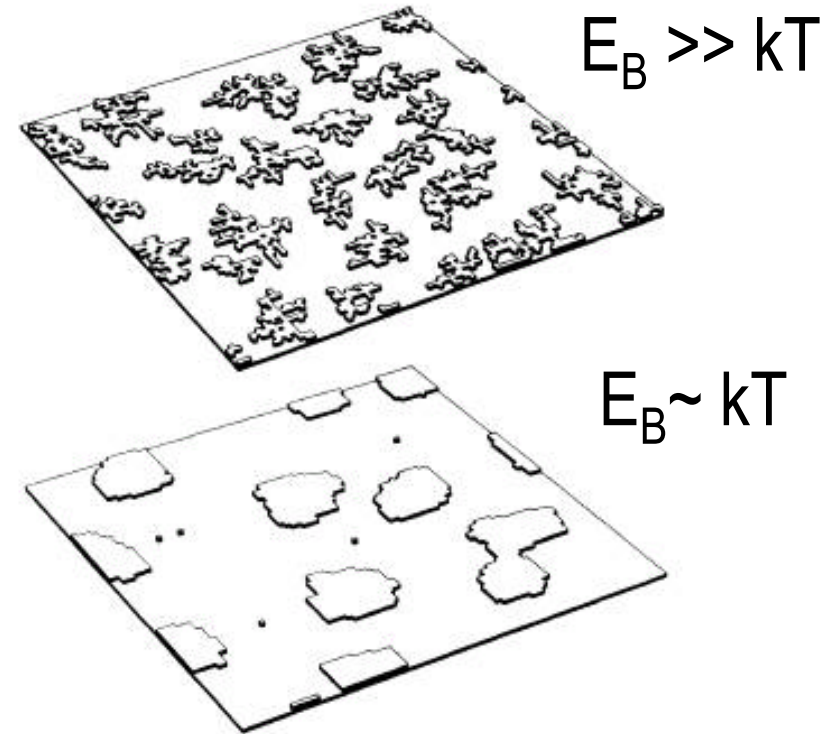




# island distributions: scaling

---

- bond-counting model, reversible attachment
- islands are not fractal, but compact
- scaling property of the island density still valid, but scaling function is different for reversible and irreversible case

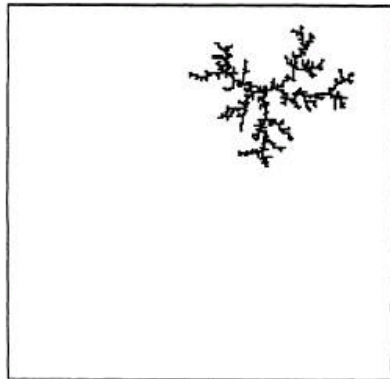


C. Ratsch, A. Zangwill, P. Smilauer and D.D. Vvedensky,  
Phys. Rev. Lett. **72**, 3194 (1994)

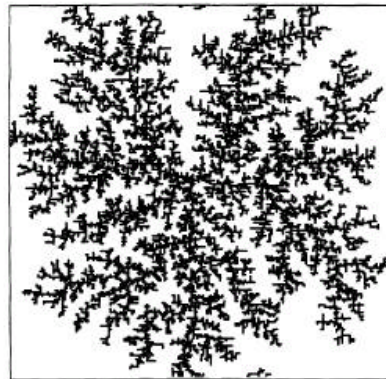
# Island growth (including diffusion of islands)

---

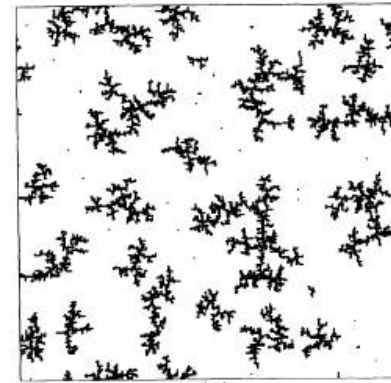
diffusion low: single fractal island



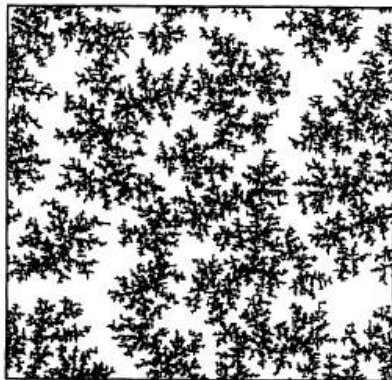
(a)



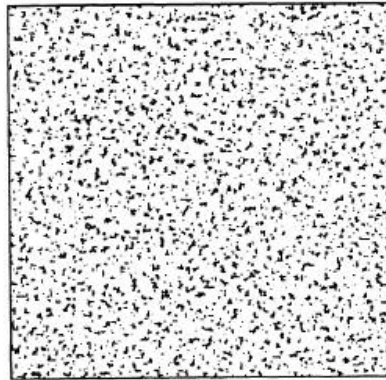
(b)



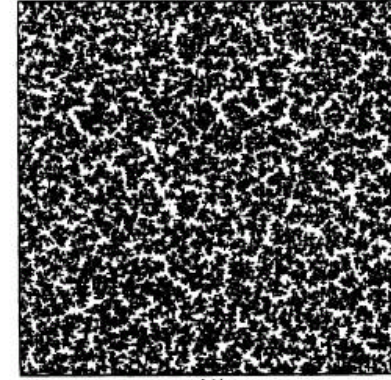
(c)



(d)



(e)



(f)

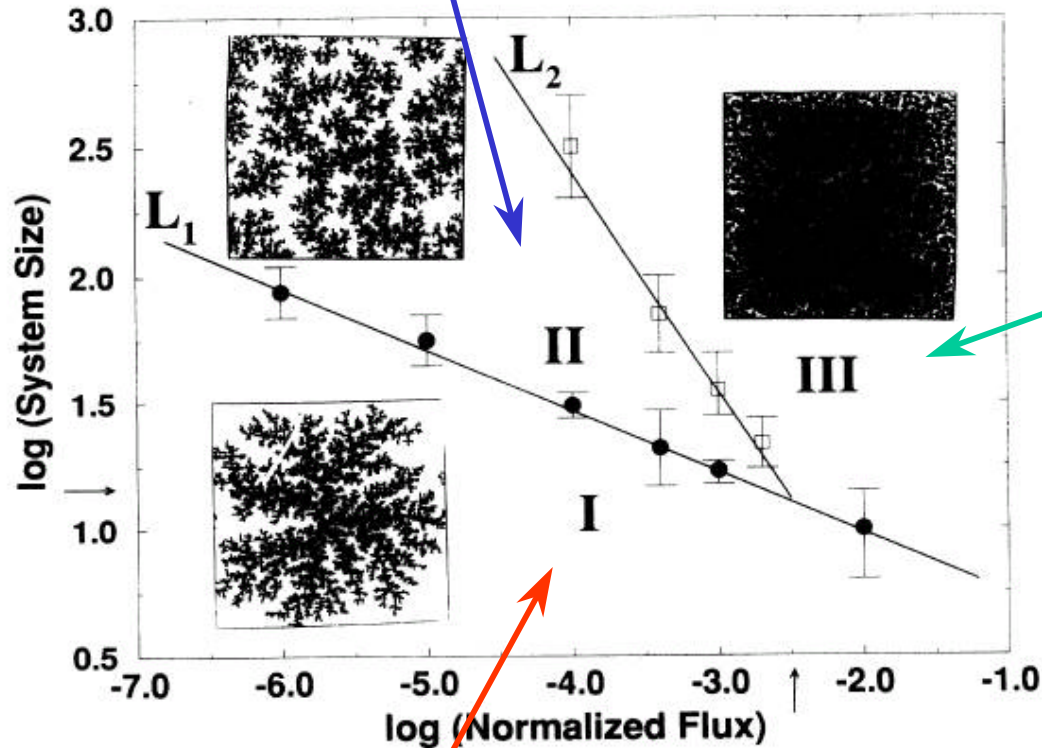
percolating network of fractal islands

diffusion along island edges: compact islands,  
ordinary percolation transition

# Scaling regimes

$$L_1 < \text{system size} < L_2$$

$$\text{cluster diffusion length } L_2 = (D_{cl} a^2 / F)^\Psi$$

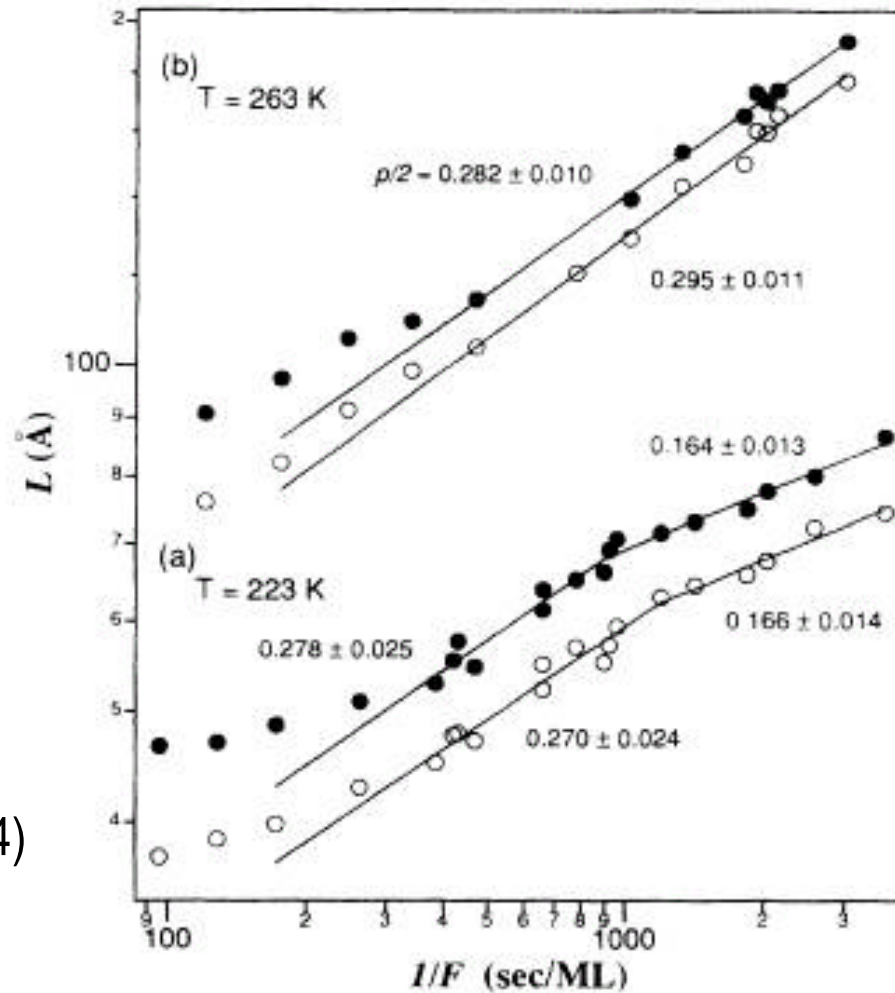


$$L_2 > \text{system size}$$

$$L_1 > \text{system size}$$

$$\text{particle diffusion length } L_1 = (D/F)^{1/4}$$

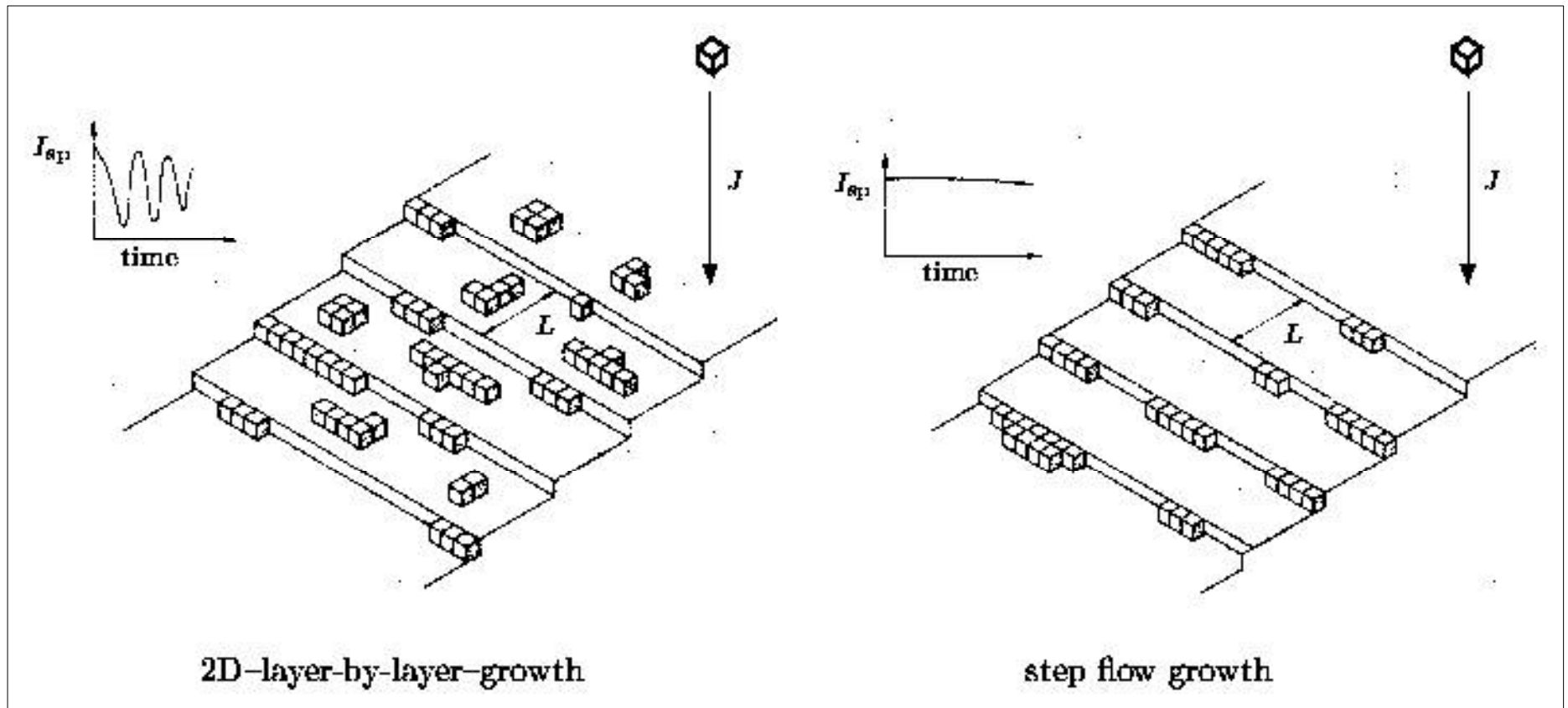
# Experimental test: Cu on Cu(001)



J.-K. Zuo et al., Phys.  
Rev. Lett. **72**, 3064 (1994)

# Diffusion and the onset of step-flow growth

$D = \lambda^2/4\tau$ ;  $\tau^{-1} = Ra^2$  mean time between two depositions;  $\lambda$ : diffusion length



growth mode transition at  $\lambda = L$  ?

J. H. Neave *et al.*, Appl. Phys. Lett. **47** (1985), 100

# Ripening Phenomena

---

Set of rate equation with quasi-continuous indices (island radii) of the variables (island size distribution)  $N_j(t) \rightarrow f(r, t)$

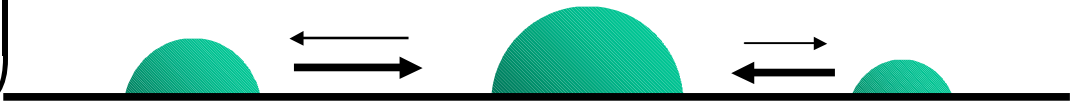
partial differential equation  $\frac{\partial f(r, t)}{\partial t} + \frac{\partial}{\partial r} [r(r, t) f(r, t)] = 0$

scaling solution (for material transport by surface diffusion)

$$r^*(t) = r^*(0) \left( 1 + \frac{t}{t_0} \right)^{1/4}$$

$$f(r, t) = g \left( \frac{r}{r^*(t)} \right) / \left( 1 + \frac{t}{t_0} \right)$$

Without external flux, islands  
'cannibalize each other !



I.M. Lifshitz & V.V. Shlezhov, J. Phys. Chem. Solids **19**, 35 (1961).

B. K. Chakraverty, J. Phys. Chem. Solids **28**, 2401 (1967).

# Algorithms for kinetic Monte Carlo

---

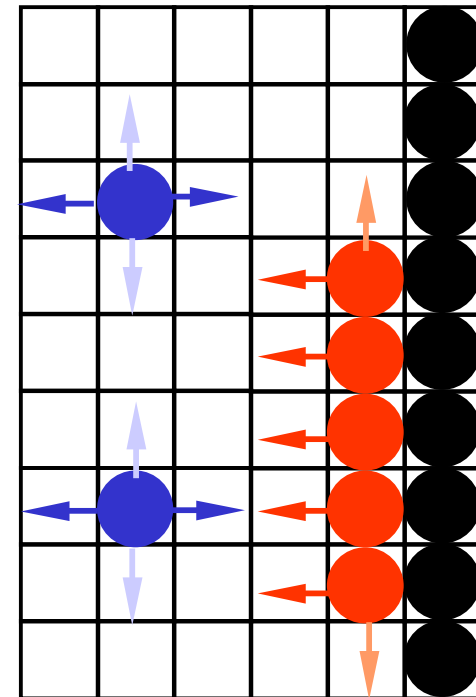
- While being aware of all possible processes at an instant of time, we need a way of stochastically selecting one process.
- An internal clock keeps track of the advancement of **physical** time.
  - If the processes are clearly separated in time, i.e. processes are uncorrelated on the time scale *during which* the processes takes place), the waiting time for each individual process has Poissonian distribution  
(K. A. Fichthorn and W.H. Weinberg, J. Chem. Phys. 95, 1090 (1991) )
- We need to update the list of possible processes according to the new situation after the move.

## Specific algorithms:

- process-type list algorithm
- binary-tree algorithm
- time-ordered-list algorithm

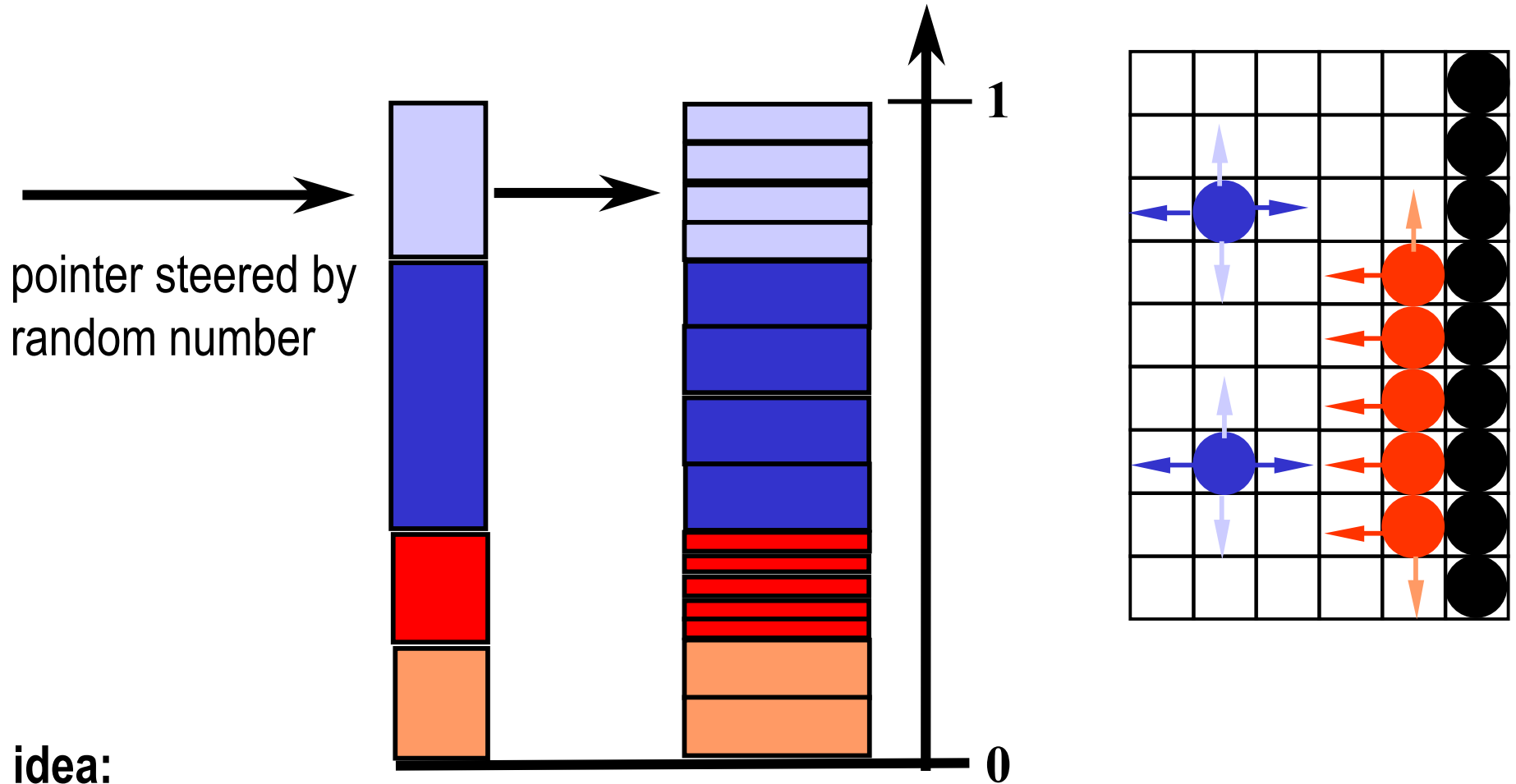
# First thoughts

- example: lattice  $L_x \times L_y$
- ~~foo's algorithm: first select one particle, then select one move of that particle~~
- **the correct solution:** cumulated partial rates  
$$r_k = \sum_{i=1}^k \Gamma_i$$
, normalized to the total rate  $R = r_N$
- **selection process:** draw a random number  $\rho$  and compare it to all the  $r_k/R$  sequentially; as soon as  $\rho$  exceeds  $r_k/R$ , execute process  $k$
- **problem:** we need to compare  $\rho$  to many (in the worst case all) of the  $r_k/R$
- **note:** Selecting a process with the right probability requires that we **can enumerate** all  $N$  processes.



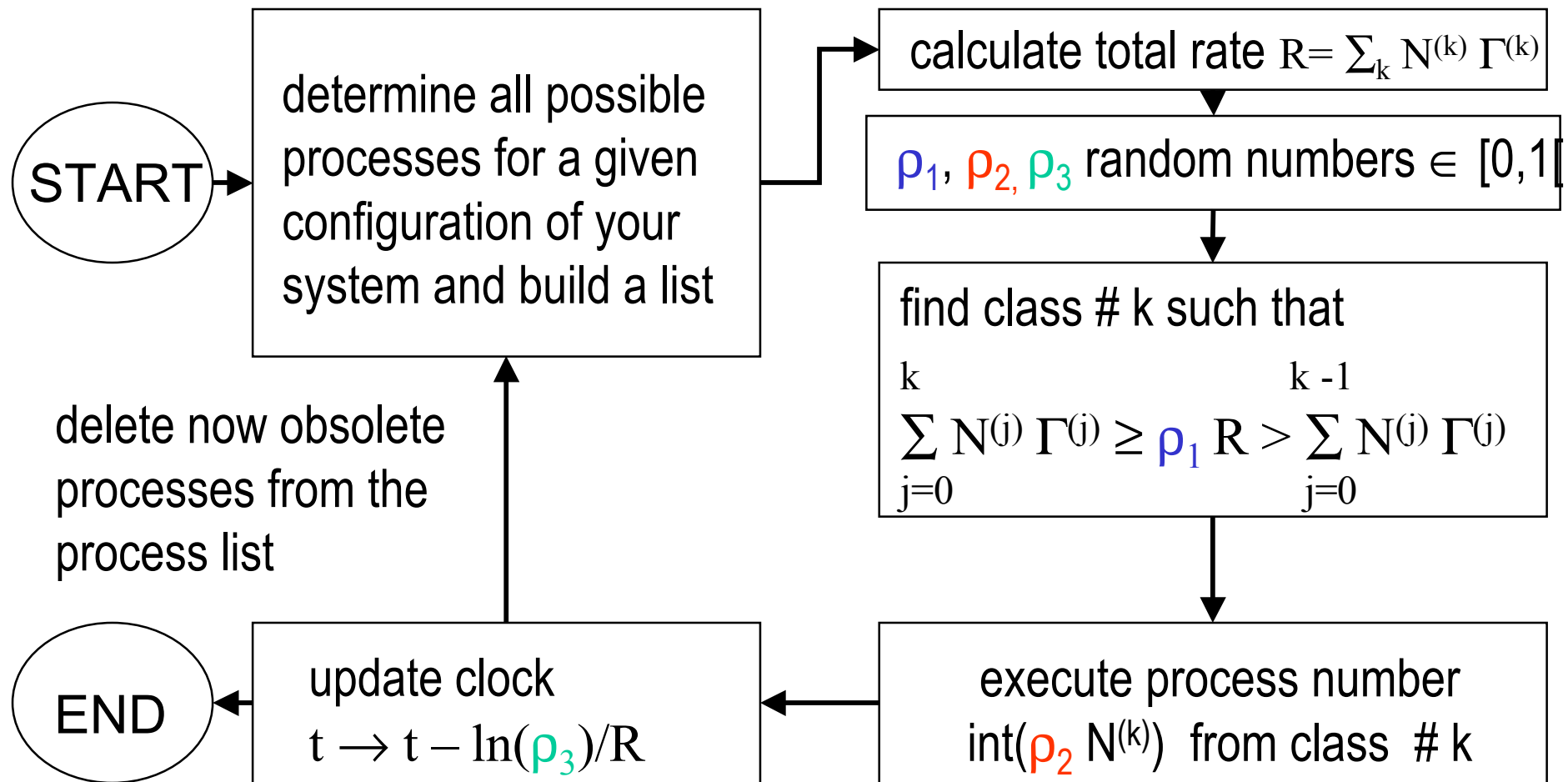


# Process-type-list algorithm



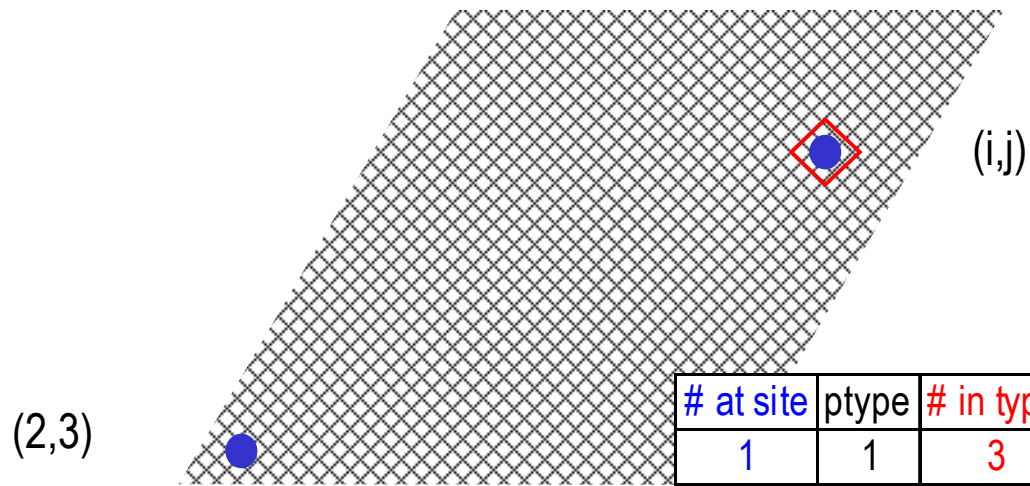
for  $p$  process types, we need to compare only to the  $p$  numbers  $N^{(k)} \Gamma^{(k)}$ ,  $k=1, p$ , rather than to **all**  $r_k/R$  (which are much more numerous)

# flow chart for process-type-list kMC



# Local updating in the process-type list

process type	1				2			
# in type	1	2	3	4	1	2	3	4
from	(2,3)	(2,3)	(i,j)	(i,j)	(2,3)	(2,3)	(i,j)	(i,j)
to	(1,3)	(3,3)	(i-1,j)	(i+1,j)	(2,4)	(2,2)	(i,j-1)	(i,j+1)
# at its site	1	3	1	3	2	4	2	4



double-entry accounting:  
 Tables attached to the lattice sites tell us which processes to delete from the process list !

# at site	pctype	# in type
1	1	1
2	1	2
3	2	1
4	2	2

# at site	pctype	# in type
1	1	3
2	1	4
3	2	3
4	2	4

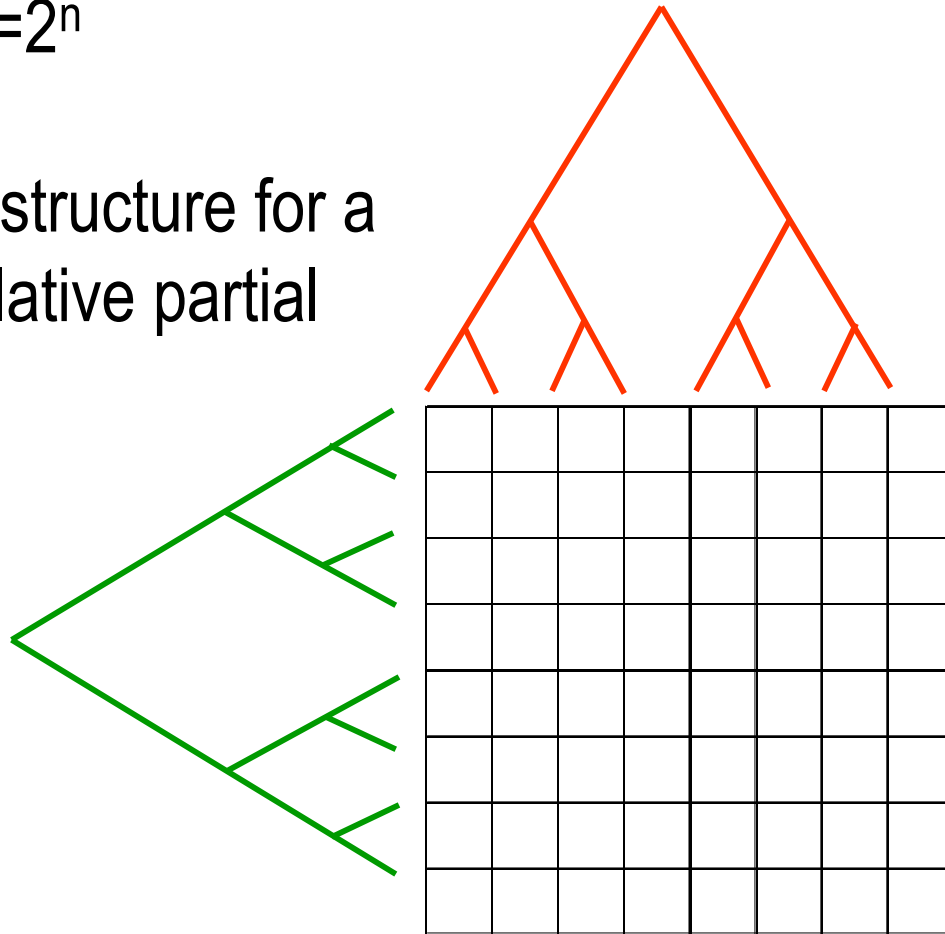
# Binary (or quaternary) tree

---

simulation area  $L \times L$ ,  $L=2^n$

**idea:**

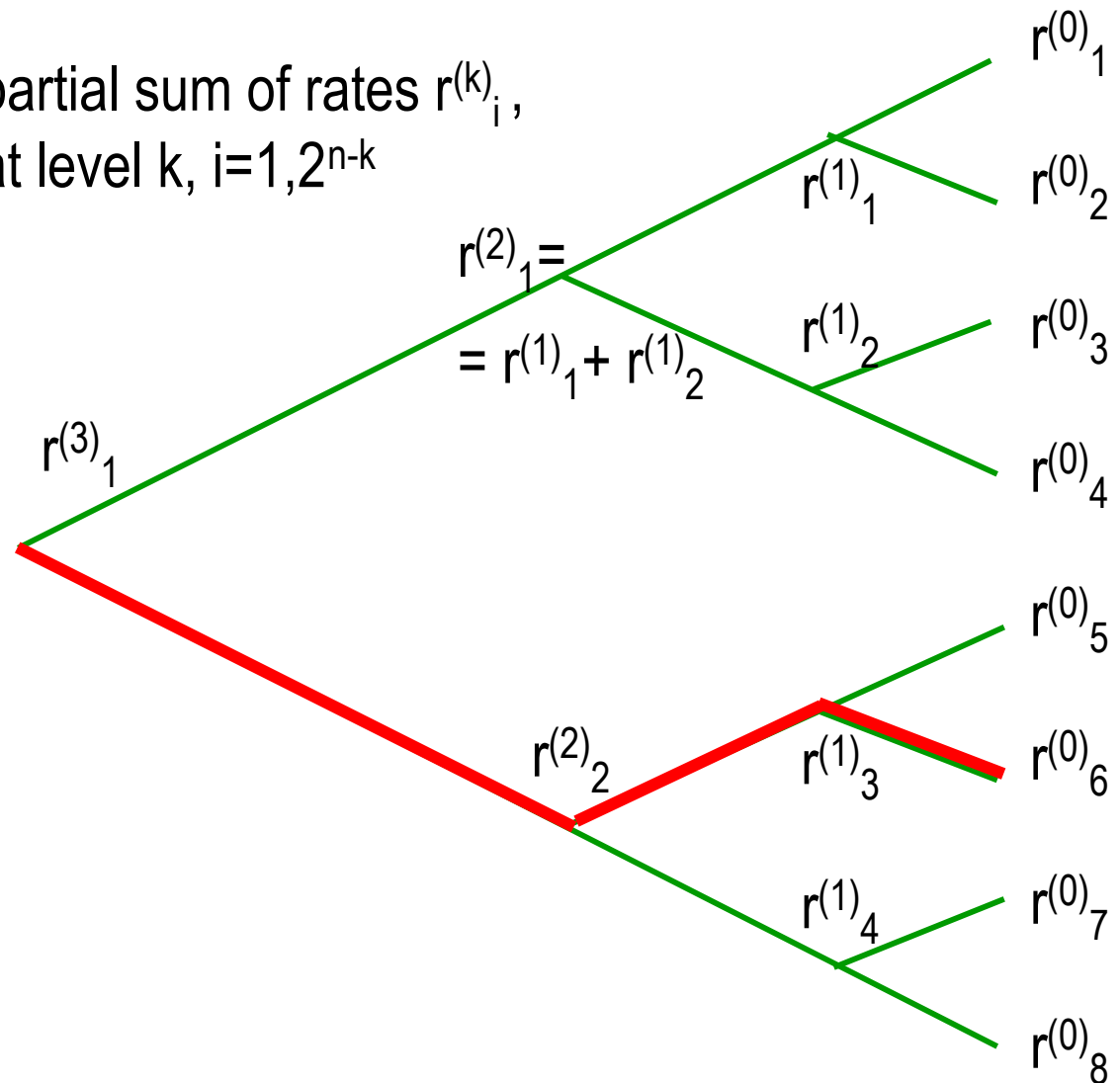
use the real-space tree structure for a partitioning of the cumulative partial rates



# Selecting a process from the tree

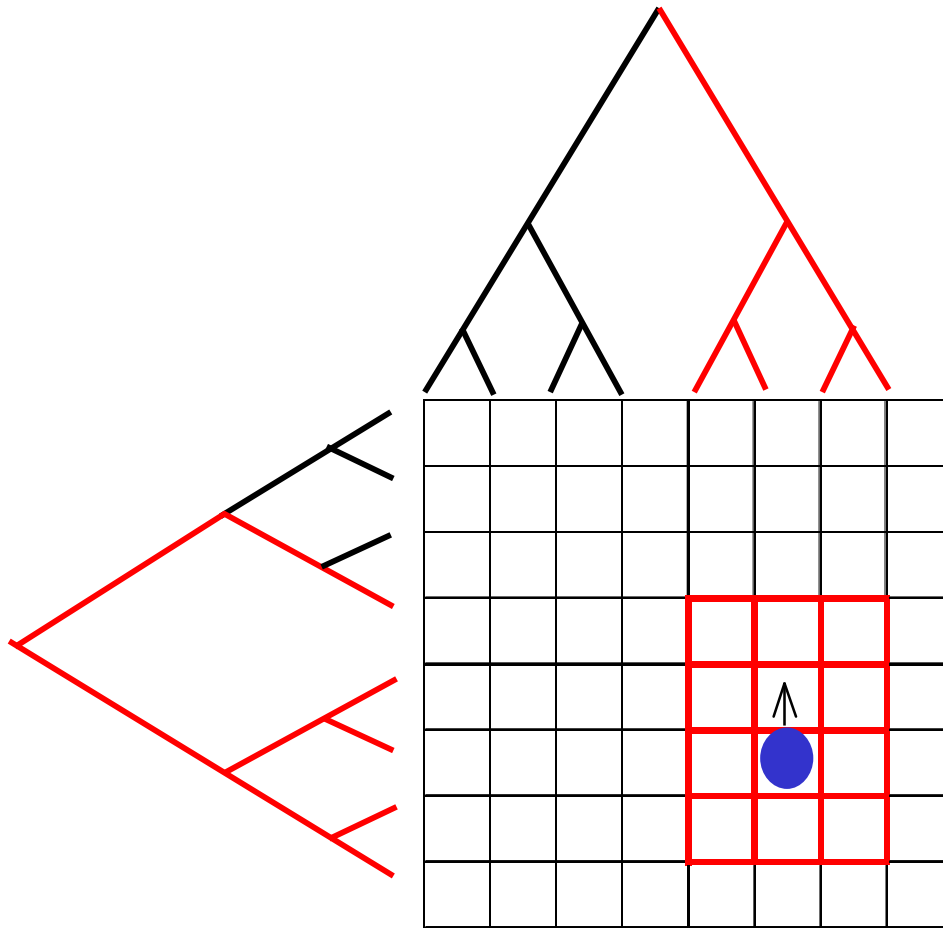
- generate a random number  $\rho'$
- normalize to the total rate  $R=r^{(n)}_1$ ,  $\rho=\rho'/R$
- run through the tree from left to right, if  $\rho < r^{(k)}_i$ , branch upward, else branch downward and replace  $\rho \rightarrow \rho - r^{(k)}_i$ ,

partial sum of rates  $r^{(k)}_i$ ,  
at level  $k$ ,  $i=1,2^{n-k}$



# Local update in the binary tree

---



Since the arrangement of partial sums of rates reflects the lattice topology, the update only affects few 'branches' of the tree (selective update).

# Time-ordered list algorithm

---

- assign a random waiting time  $t_i$  to each individual process
- sort all processes according to ascending waiting time (requires only  $\log(N)$  comparisons, if done in a way similar to the binary tree)
- always select the **first** process and execute it
- advance the clock by  $t \rightarrow t + t_i$
- this algorithm requires many exponentially distributed random numbers; thus it's advisable to use specially a designed random number generator

B. Lehner, M. Hohage & P. Zeppenfeld, Chem. Phys. Lett. **336**, 123 (2001)