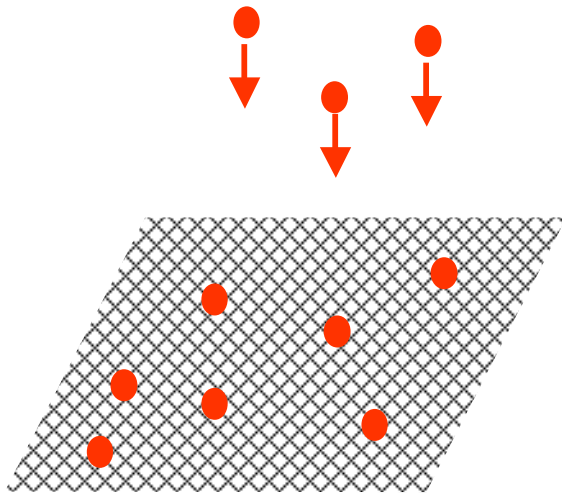# Applications of kinetics to surface science and simulations of epitaxial growth

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Statistical physics approach: discrete models

Why kinetic Monte Carlo ?
two reasons:
- technical
- physical (external time scale
      comes into play)

Ising

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

(simple) lattice gas

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

mapping $n_i \leftrightarrow S_i + \tfrac{1}{2}$

(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 ΔE's rate constants can be pre-computed an 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
    $\rightarrow$ binding energy depends on coverage Θ
- substrate is heated with a constant rate (typically between 0.1 K/sec and 10 K/sec), thereby desorbing particles from the surface
 $\rightarrow$ kinetics enters
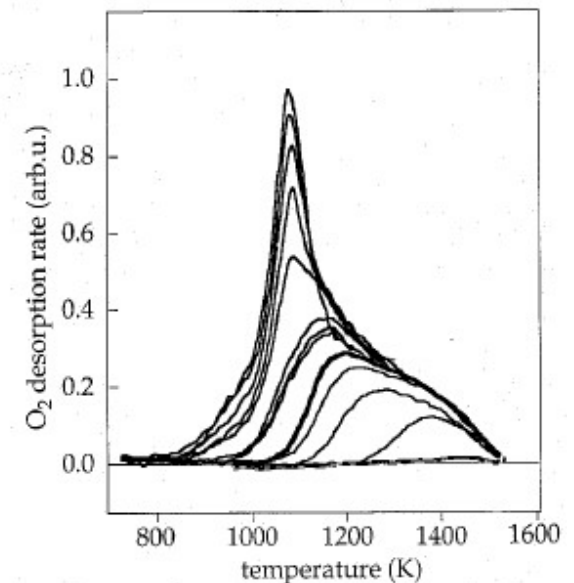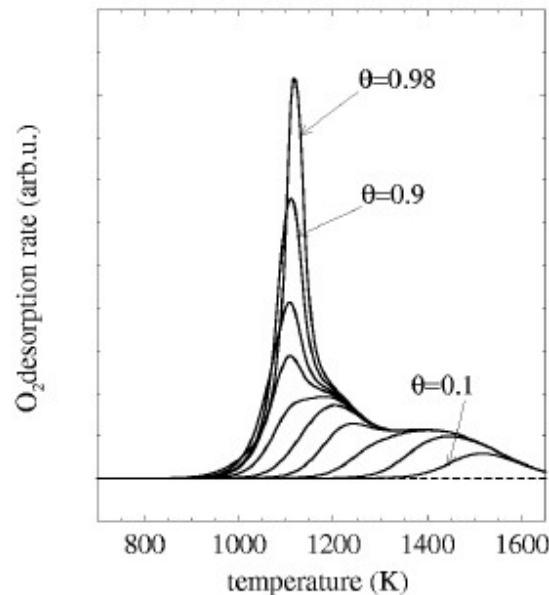
Lattice-gas Hamiltonian
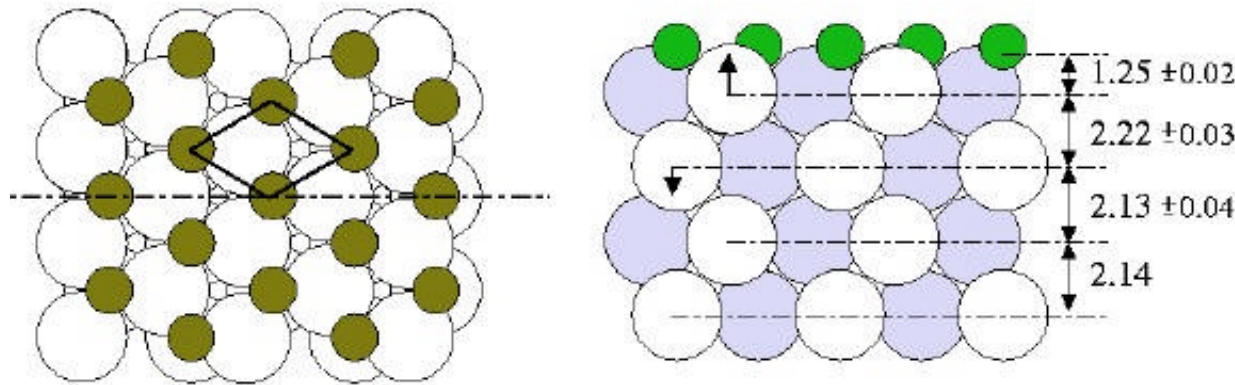
$$H = E_g^{hcp} \sum_i n_i + E_g^{fcc} \sum_i n_i + V_{1n}^{hcp} \sum_{i,a} n_i n_{i+a} + V_{1n}^{fcc} \sum_{i,a} n_i n_{i+a}$$

$$+ V_{1n}^{hcp-fcc} \sum_{i,a'} n_i n_{i+a'} + V_{2n}^{hcp} \sum_{i,b} n_i n_{i+b} + V_{2n}^{fcc} \sum_{i,b} n_i n_{i+b}$$

$$+ V_{2n}^{hcp-fcc} \sum_{i,b'} n_i n_{i+b'} + V_{3n}^{hcp} \sum_{i,c} n_i n_{i+c} + V_{3n}^{fcc} \sum_{i,c} n_i n_{i+c}$$

$$+ V_{3n}^{hcp-fcc} \sum_{i,c'} n_i n_{i+c'} + V_{trio} \sum_{i,a,a'} n_i n_{i+a} n_{i+a''} + \ldots$$
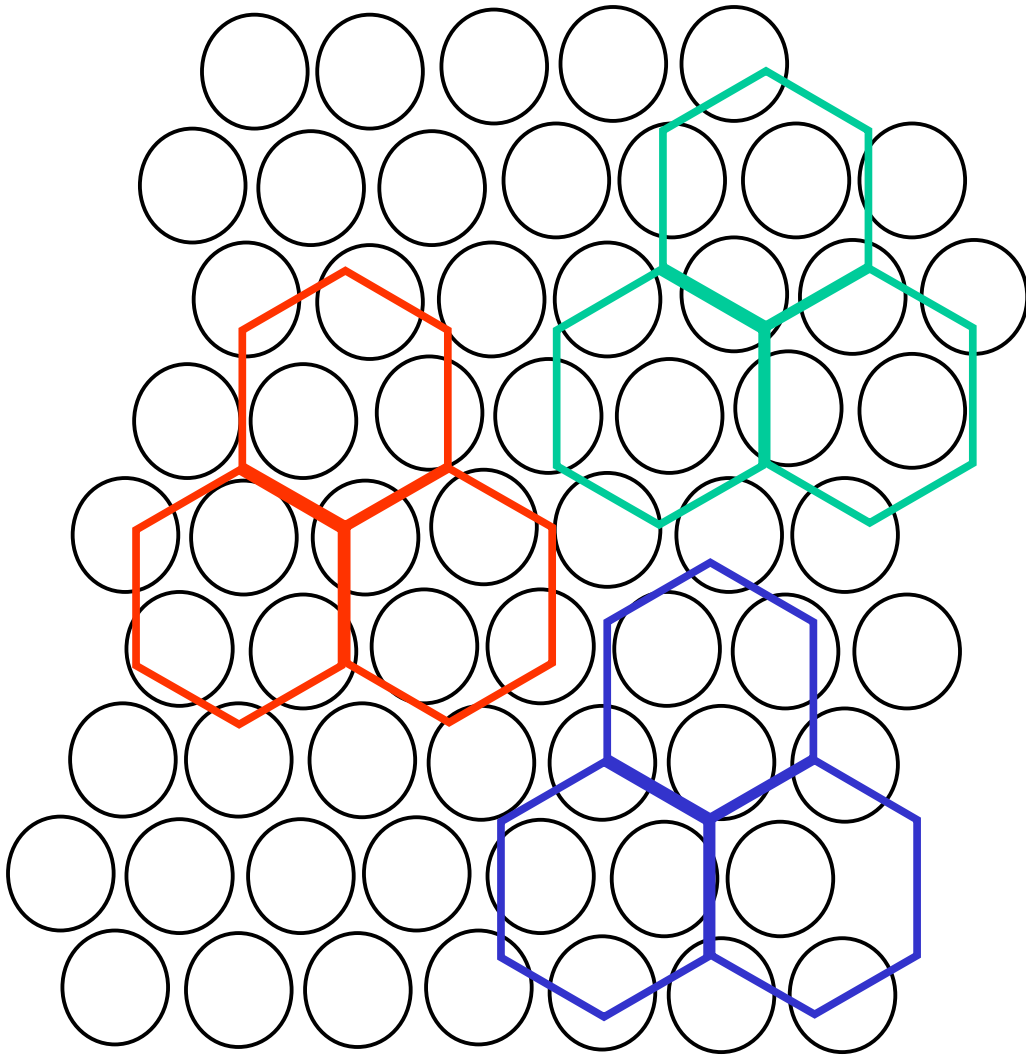
Determining the parameters of the Hamiltonian

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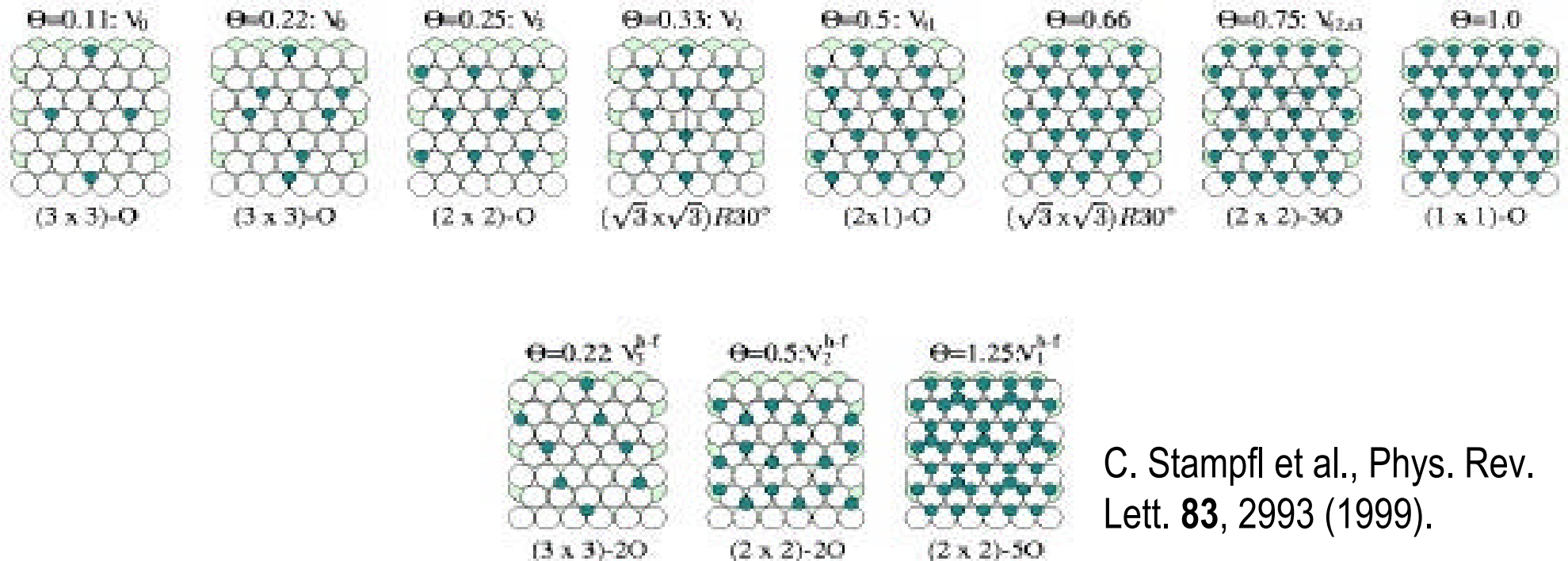
C. Stampfl et al., Phys. Rev. Lett. **83**, 2993 (1999).

Order-disorder phase transitions

- adsorbate layer may form an ordered sublattice

- registry of the sublattice w.r.t. the substrate defines a multi-values 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 Γ is relevant

- thermodynamic factor is an equilibrium property

$$K_{th} = \left(\frac{d\text{m}}{dn}\right)_T = \left(\frac{dn}{d\text{m}}\right)_T^{-1} = c_T^{-1}$$

- hopping rate Γ 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
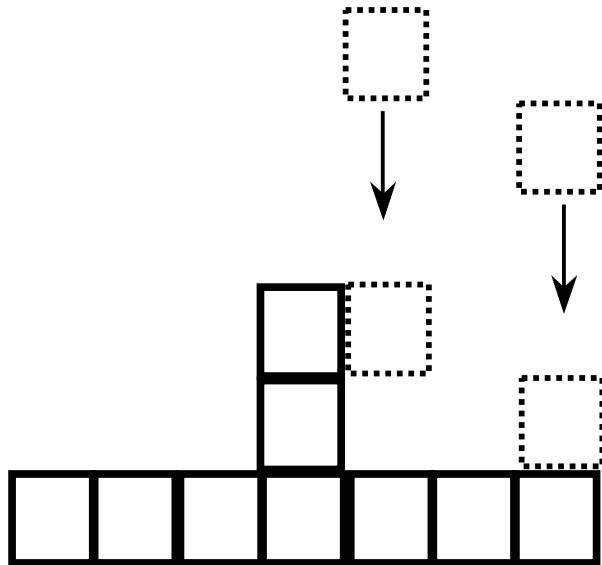
J. Venables et al., Rep. Prog. Phys. **47**, 399 (1984); R. M. Tromp and J. B. Hannon, Surf. Rev. Lett. **9** 1565 (2002).
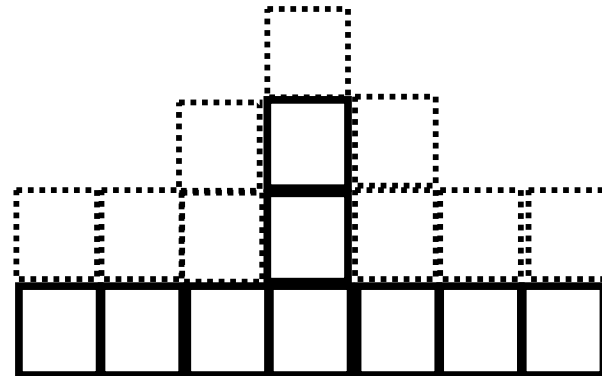
Simple discrete models of interface dynamics

particles stick as soon as they find a
neighbor (or, likewise an NNN)
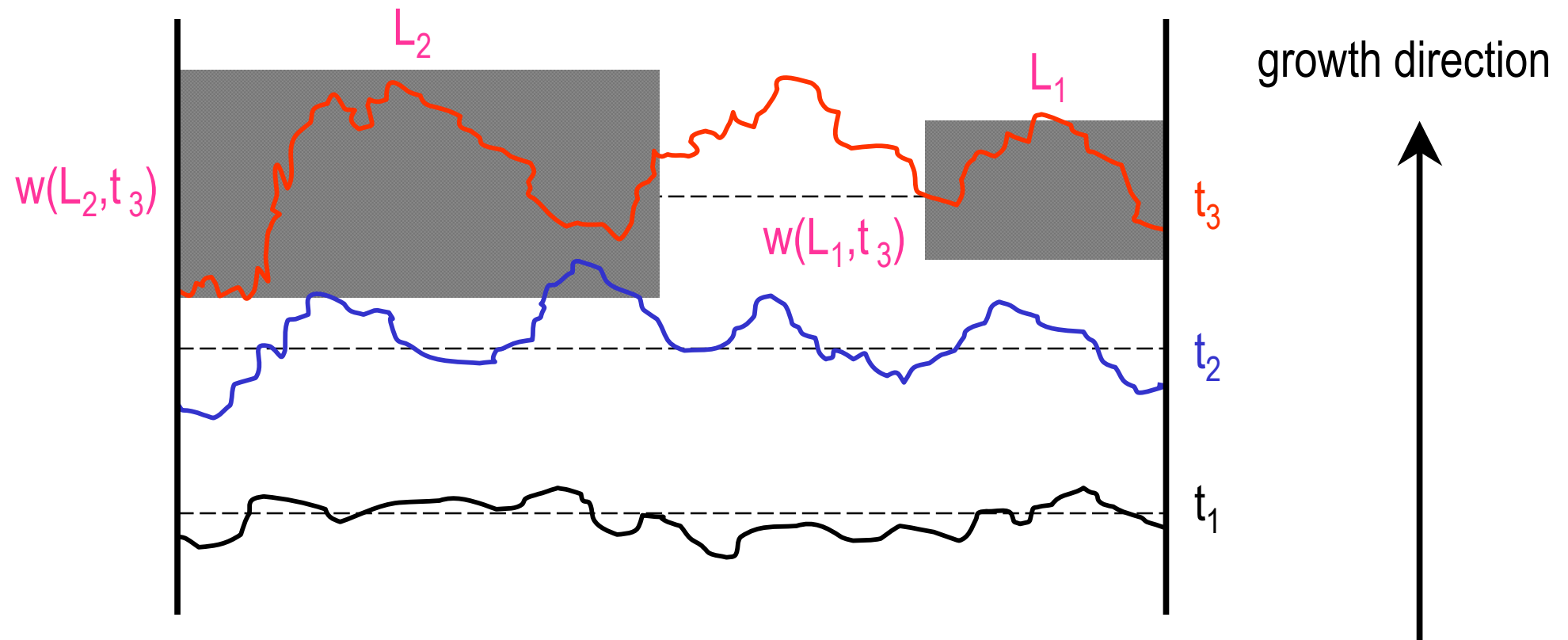
sites where the new particles will
have a neighbor get occupied
randomly (with equal probability,
or some modification thereof)

continuum model: Kardar-Parisi-Zhang equation

Scaling of surface roughness

L_2

L_1

growth direction

$w(L_2, t_3)$

$w(L_1, t_3)$

t_3

t_2

t_1

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

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

crossover time $= L^z$

Solid-on-Solid (SOS) models

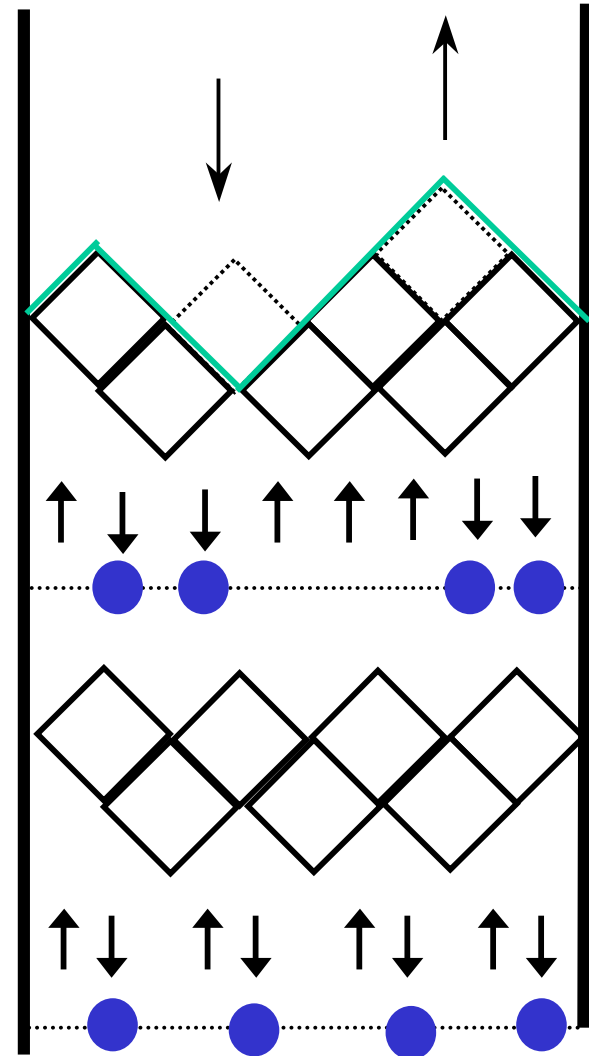General feature of SOS models:

- no voids
- no overhangs

"single-step" model:
adsorption and desorption at local
minima / maxima

equivalence to Ising model or lattice gas
model
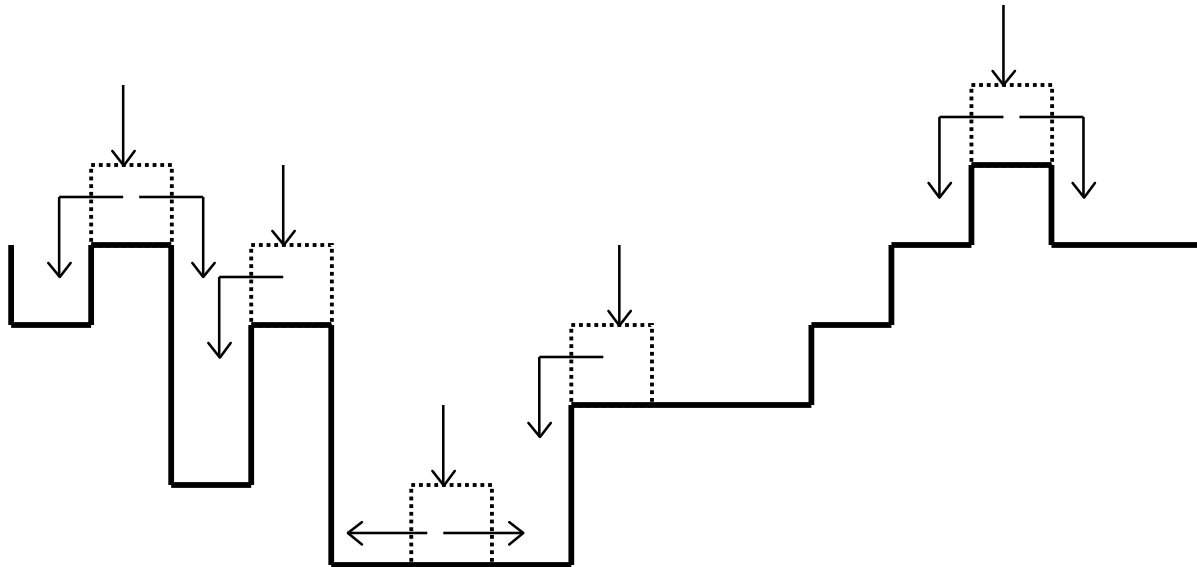exponents in 1+1 dimensions:
$\alpha=\frac{1}{2}$ $\beta=\frac{1}{3}$

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
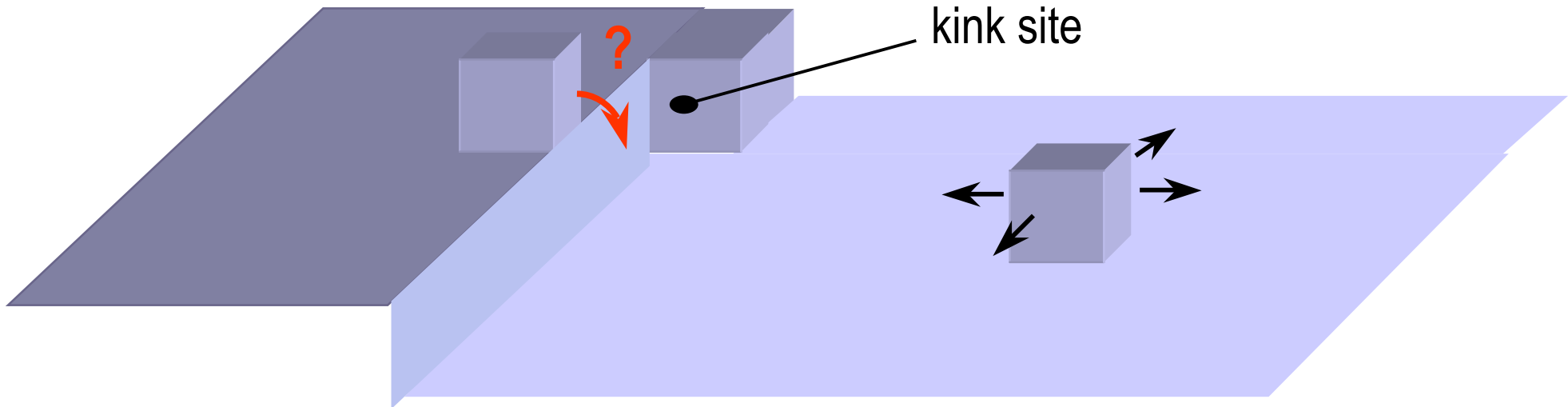
MBE: models with activated diffusion

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

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

kink site

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 μ_i to
each particle in a cluster of i atoms.
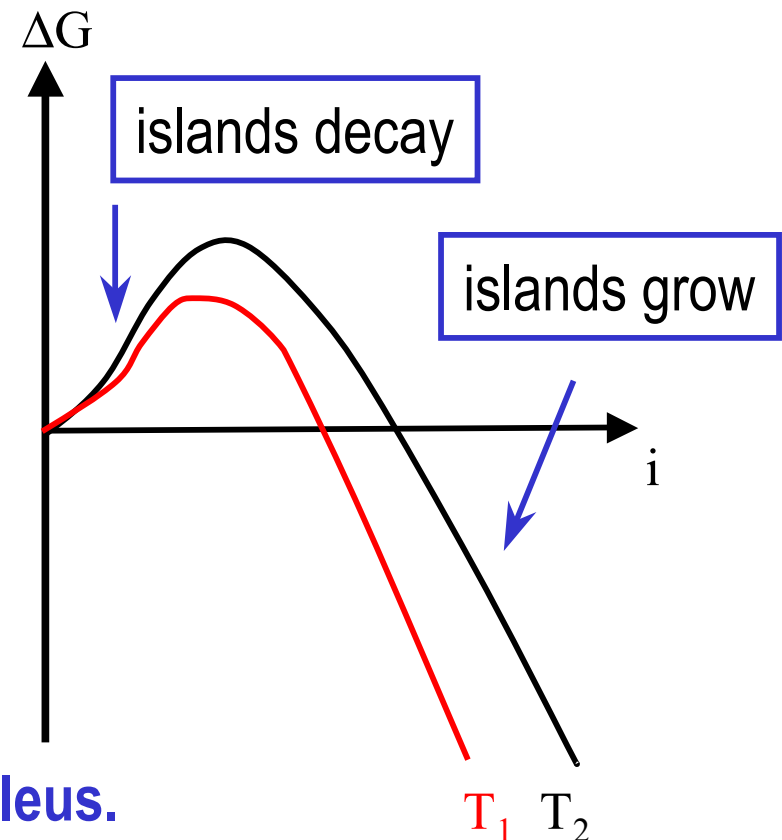Consider equilibrium $N_i + N_1 \leftrightarrow N_{i+1}$
Then, for all i $\Rightarrow$ $\mu_i = i\,\mu_1$

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

$$\Delta G = \mu_i - i\,\mu_1$$
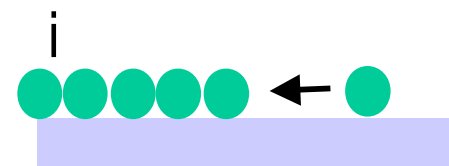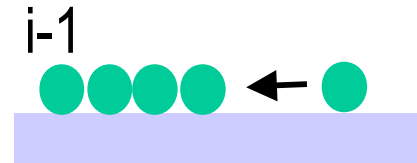
Maximum of DG defines the critical nucleus.

ΔG

islands decay

islands grow

i

T_1 T_2

island density: scaling laws

coupled hierarchy of
rate equations

$$\frac{dN_1}{dt} = R - \frac{N_1}{t} - 2D s_1 N_1^2 - \sum_{i=2}^{\infty} D s_i N_1 N_i$$

deposition   evap.   nucleation   attachment

$$\frac{dN_i}{dt} = D s_{i-1} N_{i-1} N_1 - D s_i N_i N_1$$

i-1

i

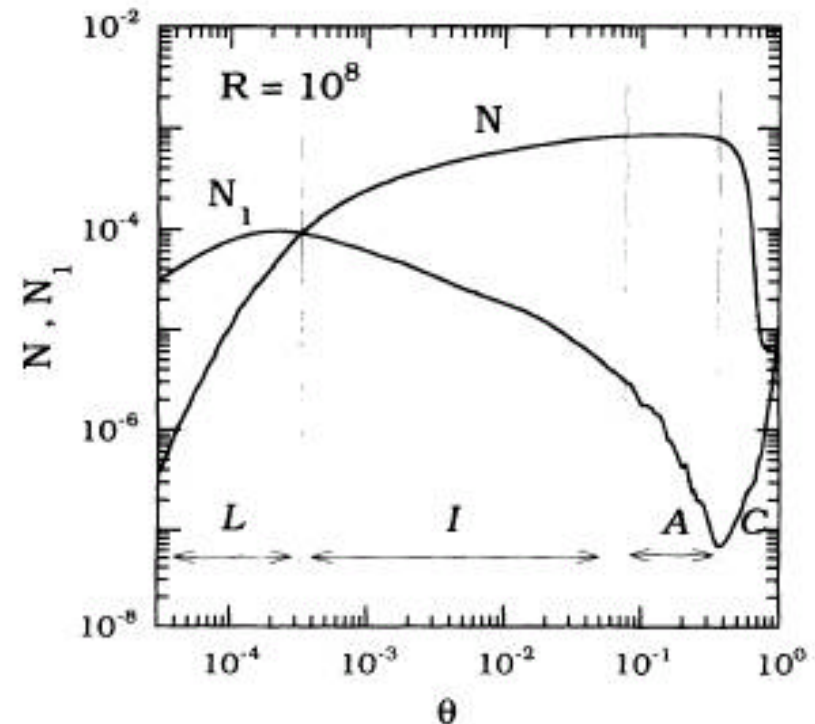important special result
(for diffusion- limited growth in 2D):

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

discussion for critical island size $i_c=1$

- evaporation neglected:
$$\frac{dN_1}{dt} = R - 2D s_1 N_1^2 - D s_i N_1 N$$

$$N = \sum_{j=2}^{\infty} N_j \qquad \frac{dN}{dt} = D s_1 N_1^2$$

- very short times: R dominates !
$$N_1 = Rt; \quad N = s_1 R^2 D\, t^3$$

- medium times: no new nucleation, flux is consumed by attaching to existing islands
$$N_1 \sim R/(D s_i N); \quad N \sim (3t)^{1/3};$$
$$N_1 \sim R^{2/3} D^{-1/3} t^{-1/3}$$

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:
$$\frac{dN_1}{dt} = R - \frac{N_1}{t} - \frac{d(w_x N_x)}{dt}$$

$$\frac{dN_x}{dt} = D s_{i_c} N_{i_c} N_1 - U_c \underline{\quad} \text{loss term due to}$$

coalescence

$$U_c = 2N_x \, dZ/dt$$

- saturation of island density for $i_c = 1$:
  - equate $D s_1 N_1^2$ and U_c: $N_x = N_1^2$
  - insert into eq. (1): $D s_1 N_1^3 = R$
  - use medium-time-scale relation $N_x = 1/N_1$
  - result: $N_x \sim (D/R)^{1/3}$

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
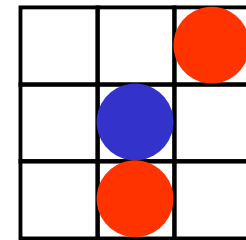
- classify possible transitions $W(f,i)$ from i to f,
  each class k is characterized by a rate (input to the simulation).
  concerted events (simultaneous motion of several atoms) can
  be accounted for

- detailed balance (ensures that thermal equilibrium is reached)
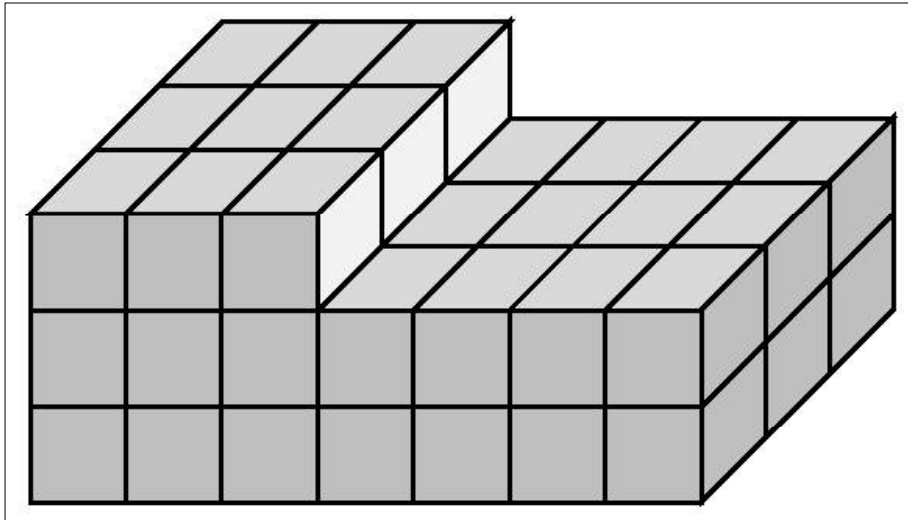 $$W(i,j)/W(j,i) = \exp(-(G_i - G_j)/kT)$$

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.

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

specific models for f(n):

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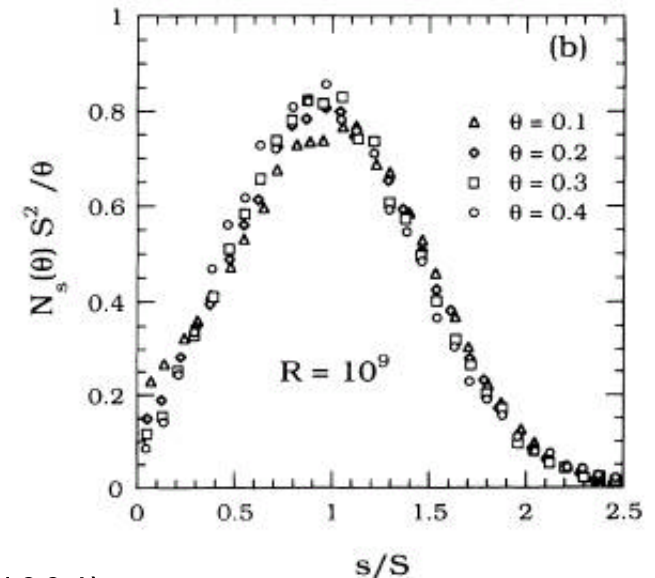
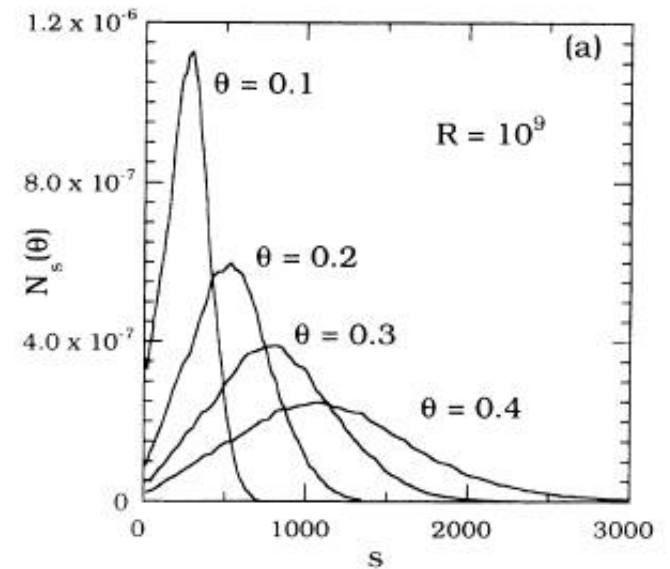- **semiconductor:**
  $f(n) = E_S + n \, E_B$

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:

$$N_j = G(\Theta, N) f\left(\frac{j}{N}\right) \propto \frac{\Theta}{N^2} f\left(\frac{j}{N}\right)$$
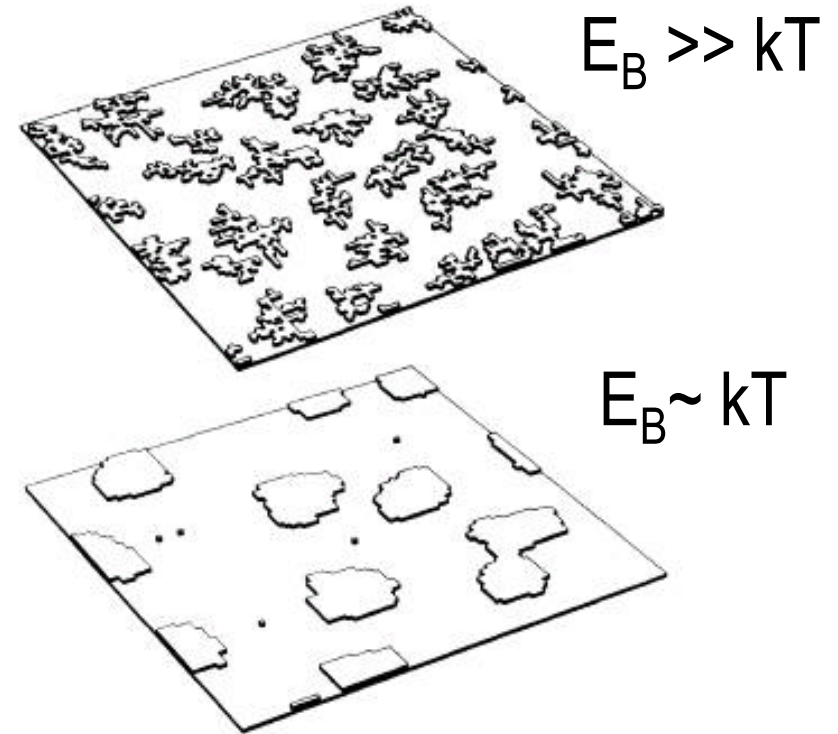
J.G. Amar, F. Family & P.M. Lam, Phys. Rev. B **50**, 8781 (1994)

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
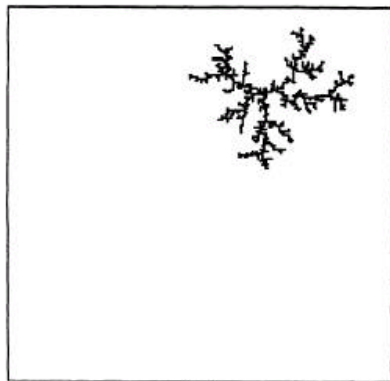
$E_B \gg kT$

$E_B \sim kT$

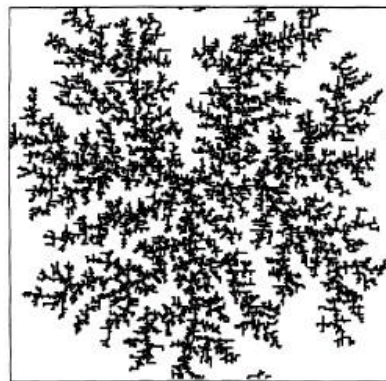C. Ratsch, A. Zangwill, P. Smilauer and D.D. Vvedensky, Phys. Rev. Lett. **72**, 3194 (1994)

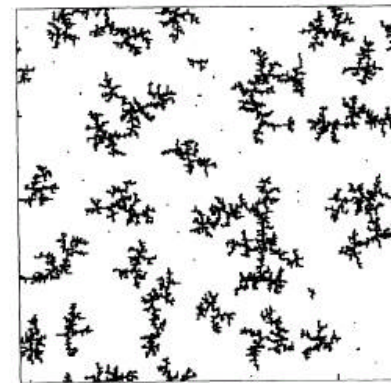# Island growth (including diffusion of islands)

diffusion low: single fractal island   diffusion high: many fractal islands
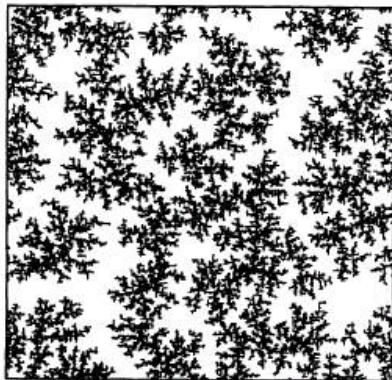
percolating network of fractal islands   diffusion along island edges: compact islands, ordinary percolation transition

Scaling regimes

$L_1 <$ system size $< L_2$

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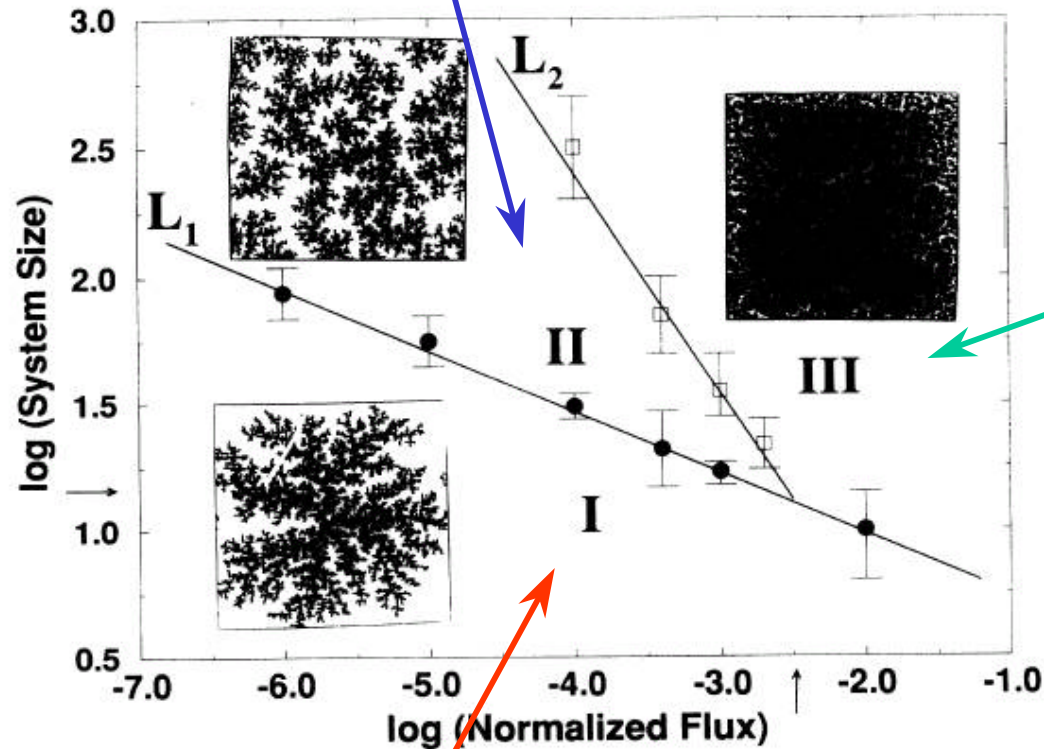
$L_2 >$ system size

$L_1 >$ system size

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

Experimental test: Cu on Cu(001)
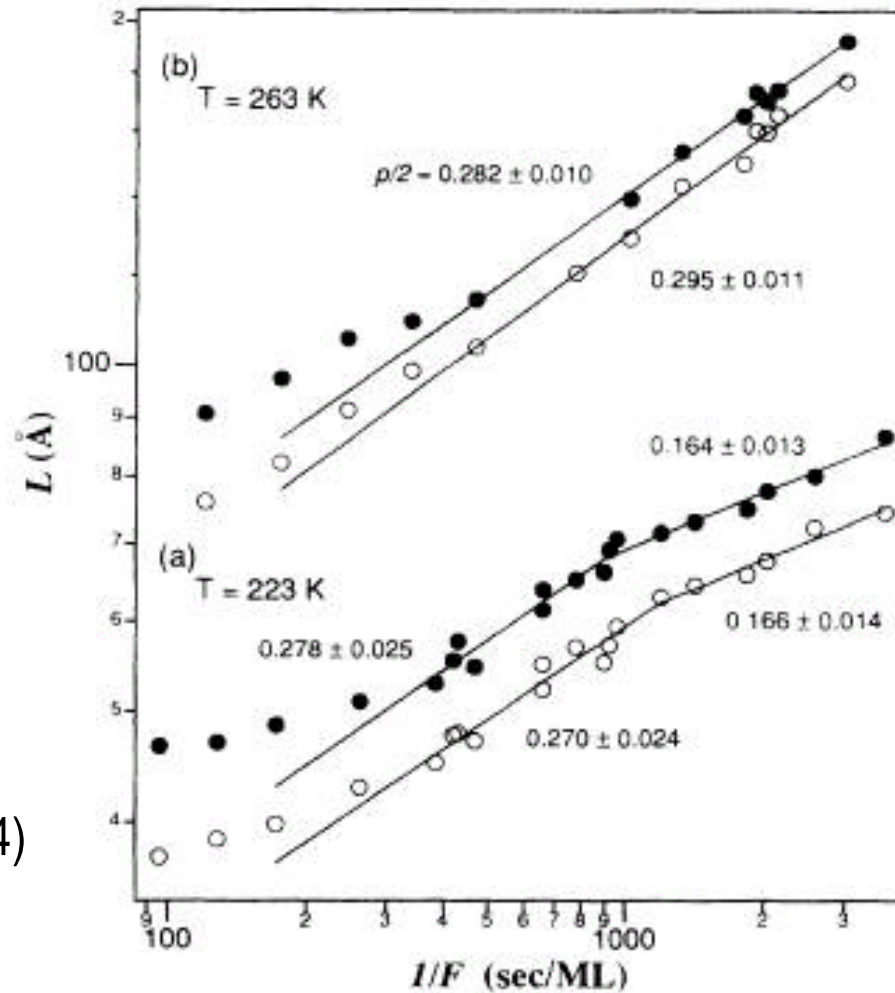
J.-K. Zuo et al., Phys. Rev. Lett. **72**, 3064 (1994)

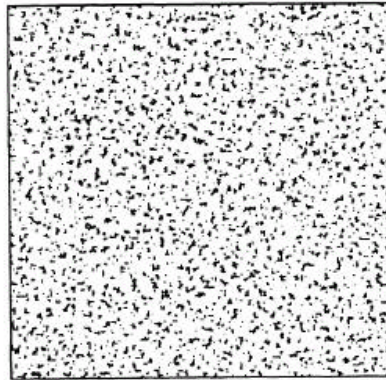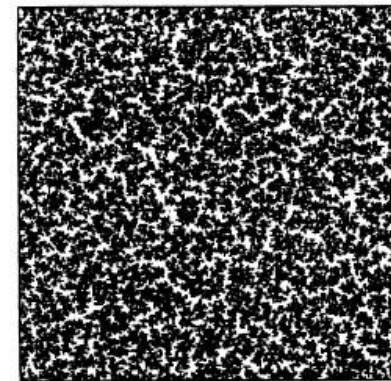# Diffusion and the onset of step-flow growth

$D = \lambda^2/4\tau$; $\tau^{-1} = Ra^2$ mean time between two depositions; λ: 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) $N_j(t) \rightarrow f(r,t)$
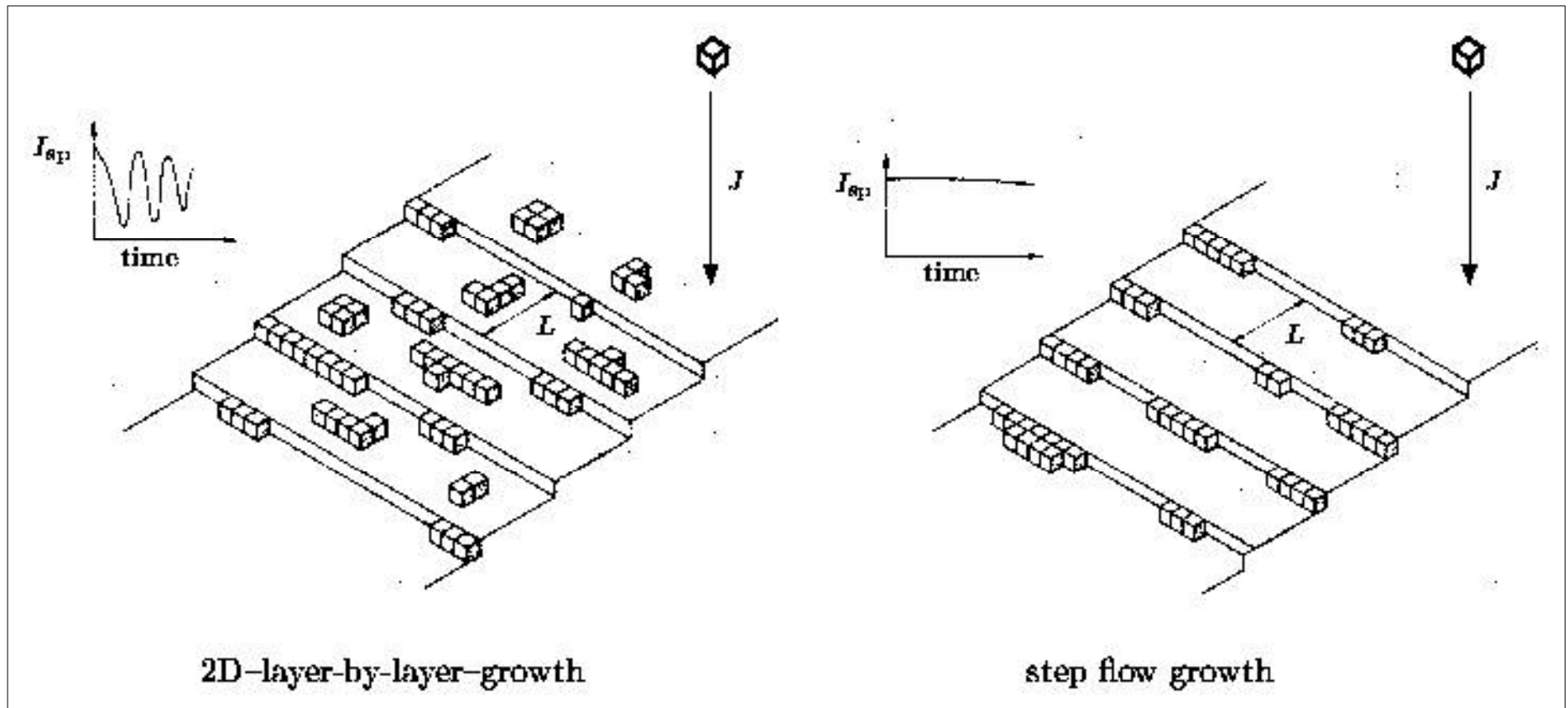
partial differential equation $\dfrac{\partial f(r,t)}{\partial t} + \dfrac{\partial}{\partial r}[\dot{r}(r,t)f(r,t)] = 0$

scaling solution (for material transport by surface diffusion)

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

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

Without external flux, islands 'cannibalize each other !
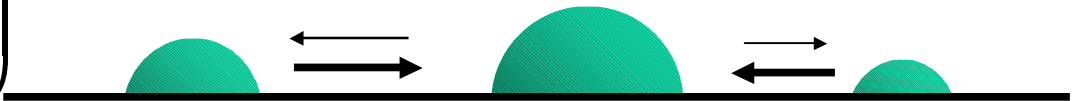
I.M. Lifshitz & V.V. Shlezhov, J. Phys. Chem. Solids **19**, 35 (1961).
B. K. Chakraverty, J. Phys. Chem. Solids **28**, 2401 (1967).

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 x L_y

- ~~fool'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 ρ and compare it to all the r_k/R sequentially; as soon as ρ exceeds r_k/R, execute process k

- problem: we need to compare ρ 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

pointer steered by
random number
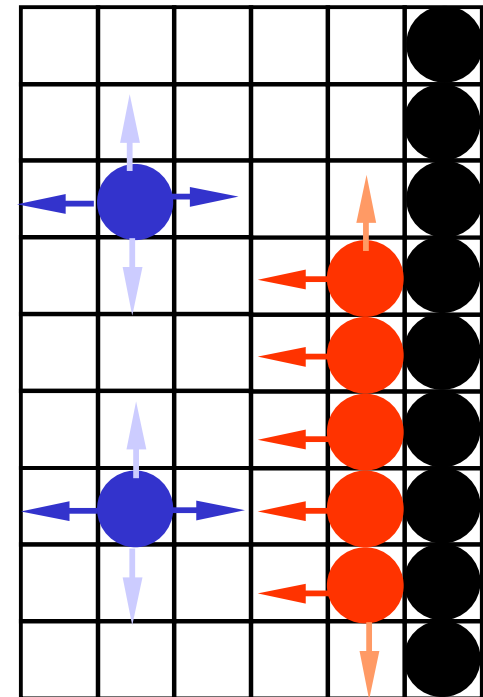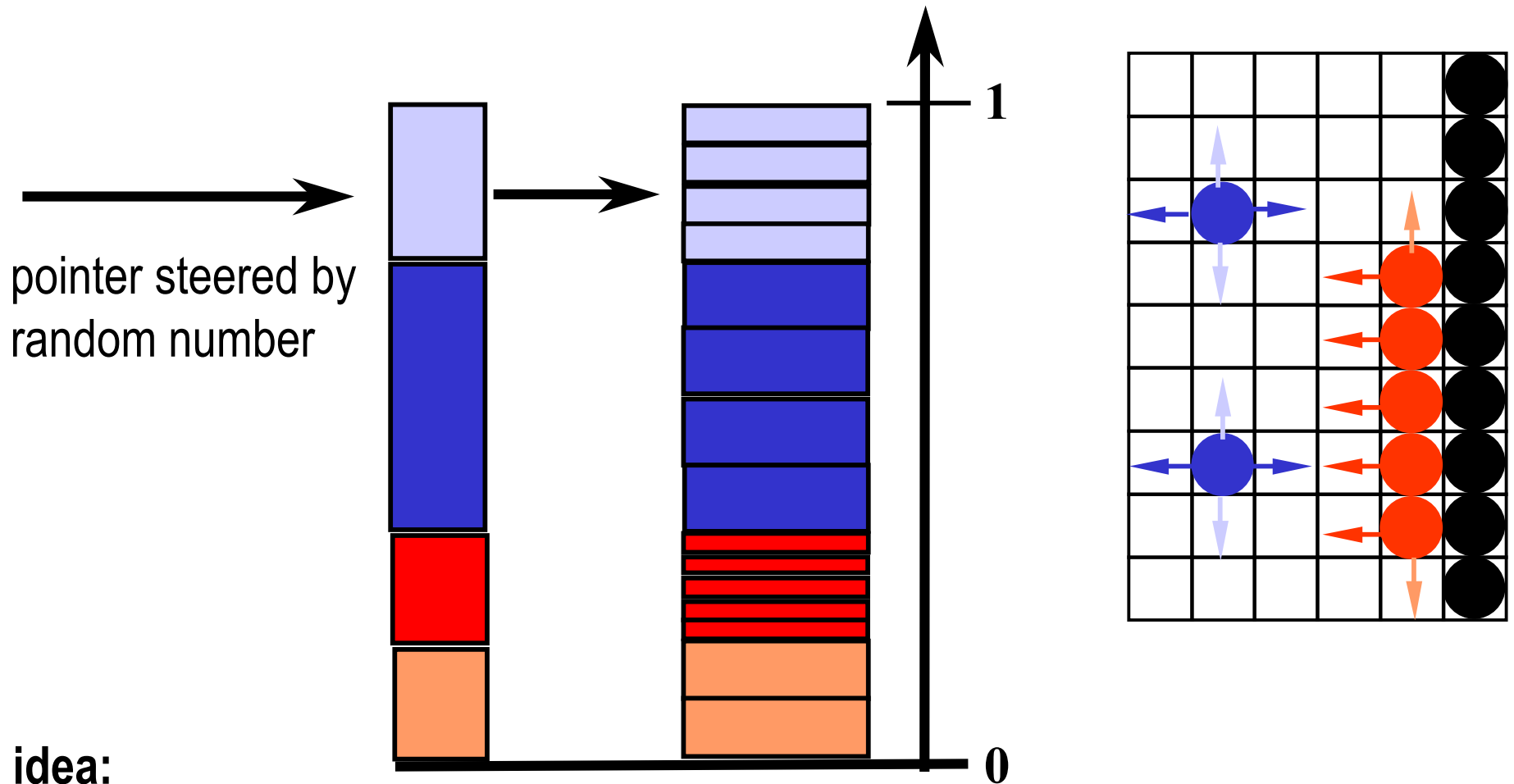
idea:
for p process types, we need to compare only to the p numbers $N^{(k)} \Gamma^{(k)}$, k=1,p,
rather then to **all** r_k/R (which are much more numerous)

flow chart for process-type-list kMC

START

determine all possible processes for a given configuration of your system and build a list

calculate total rate $R = \sum_k N^{(k)} \Gamma^{(k)}$

ρ_1, ρ_2, ρ_3 random numbers $\in [0,1[$

find class # k such that

$$\sum_{j=0}^{k} N^{(j)} \Gamma^{(j)} \geq \rho_1 R > \sum_{j=0}^{k-1} N^{(j)} \Gamma^{(j)}$$

execute process number int($\rho_2 N^{(k)}$) from class # k

update clock $t \rightarrow t - \ln(\rho_3)/R$

delete now obsolete processes from the process list

END
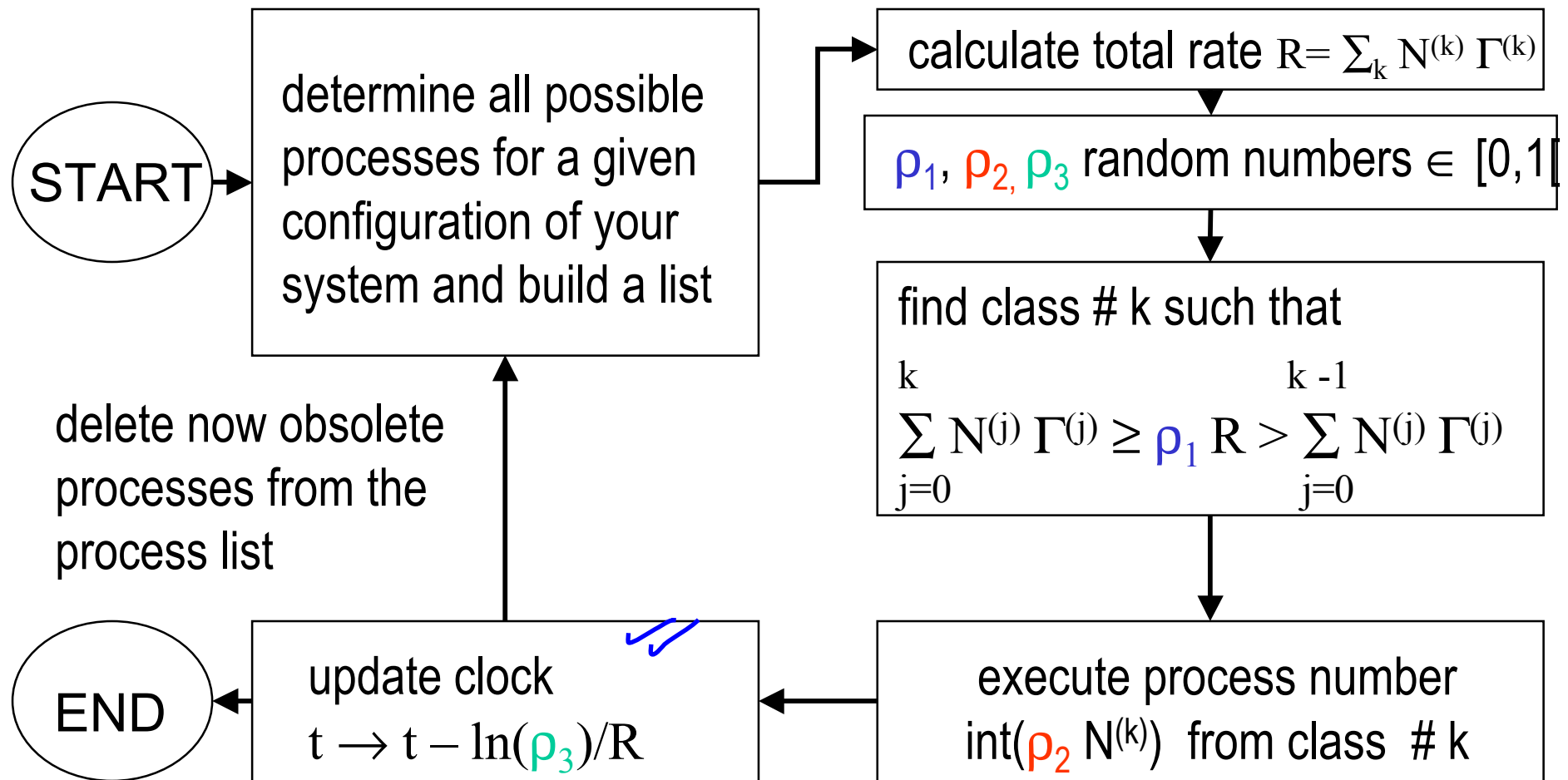
Local updating in the process-type list

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

(i,j)

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

(2,3)

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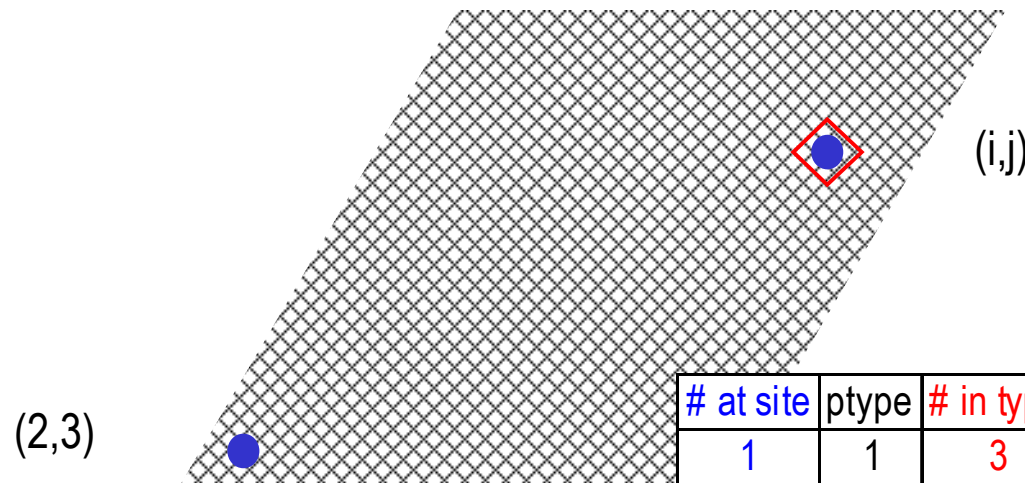
# at site	ptype	# in type
1	1	1
2	1	2
3	2	1
4	2	2

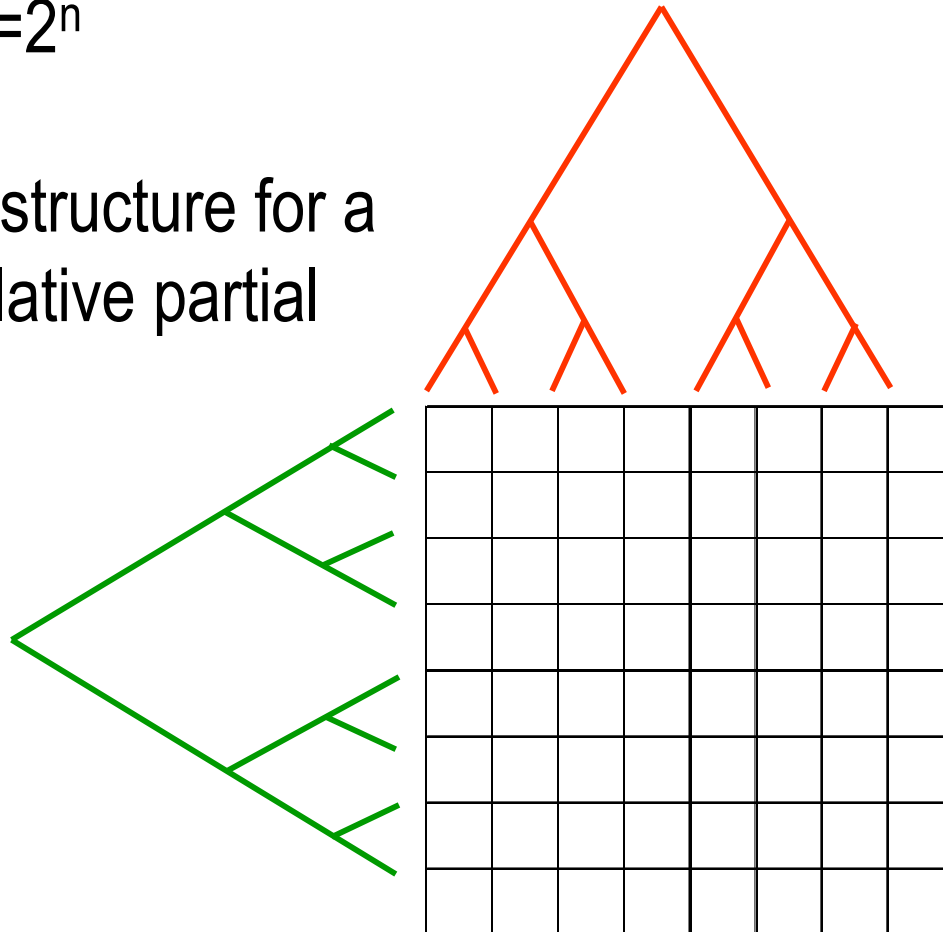# Binary (or quaternary) tree

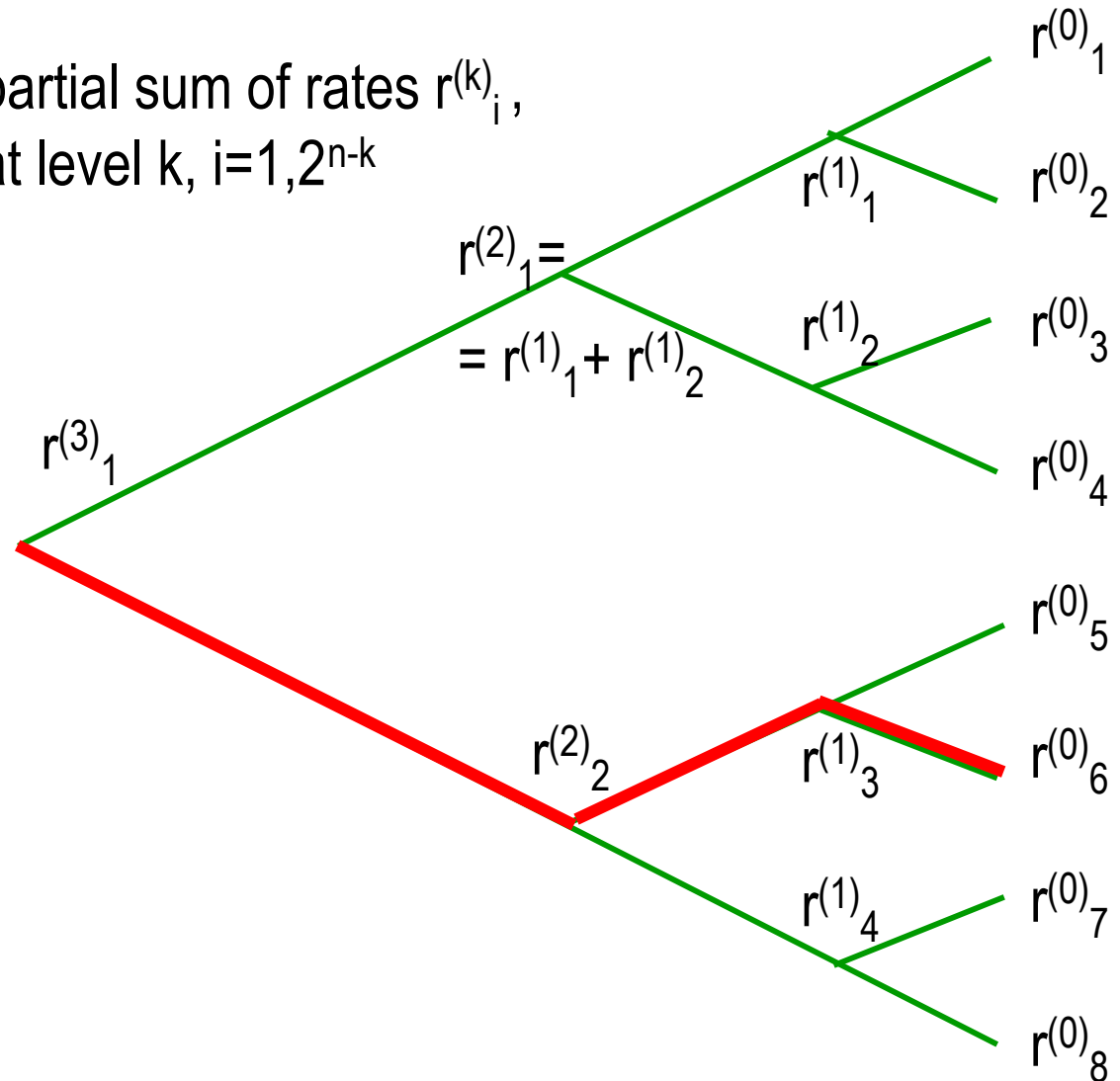simulation area L x L, $L=2^n$

idea:

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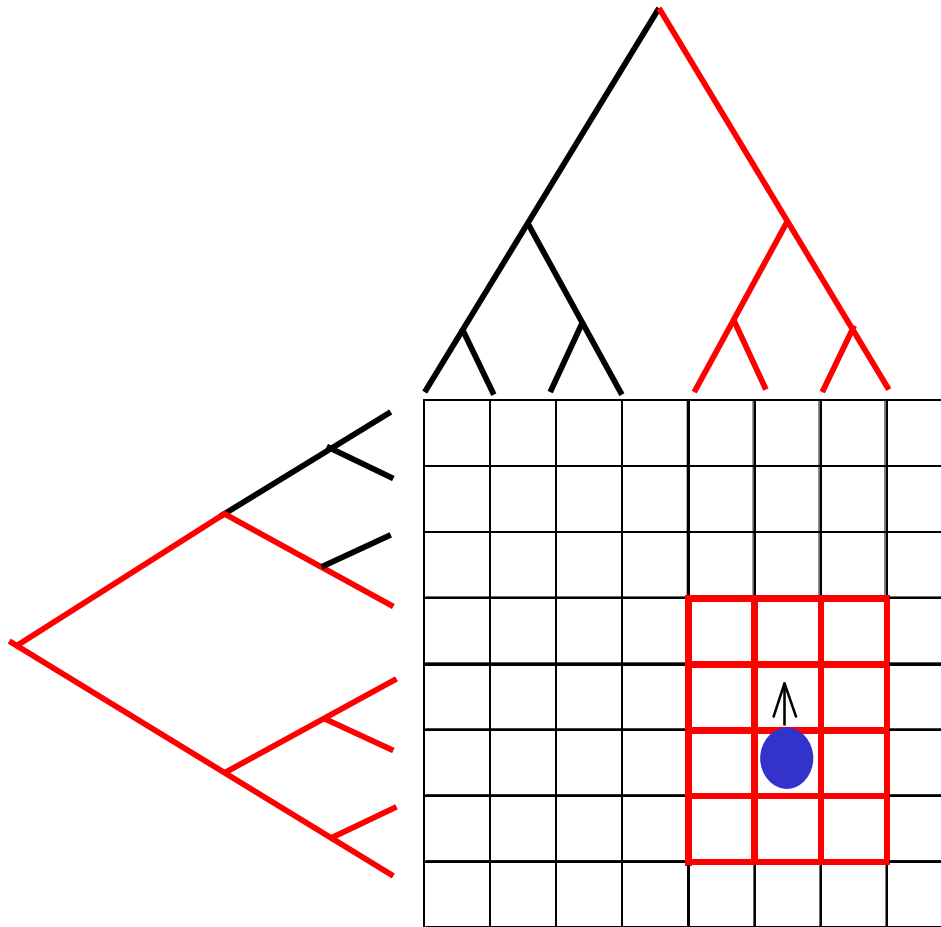
Selecting a process from the tree

- generate a random number ρ'

- 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}

$r^{(2)}_1 =$

$= r^{(1)}_1 + r^{(1)}_2$

$r^{(3)}_1$

$r^{(1)}_1$

$r^{(1)}_2$

$r^{(2)}_2$

$r^{(1)}_3$

$r^{(1)}_4$

$r^{(0)}_1$

$r^{(0)}_2$

$r^{(0)}_3$

$r^{(0)}_4$

$r^{(0)}_5$

$r^{(0)}_6$

$r^{(0)}_7$

$r^{(0)}_8$

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)