Kinetic Monte Carlo modelling of semiconductor growth

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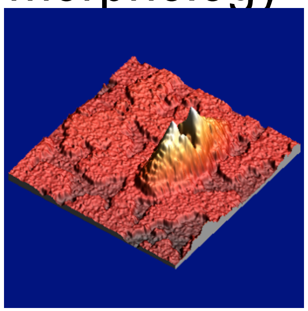
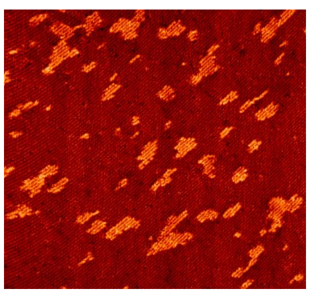
Time and length scales

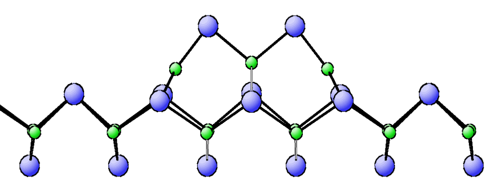
morphology

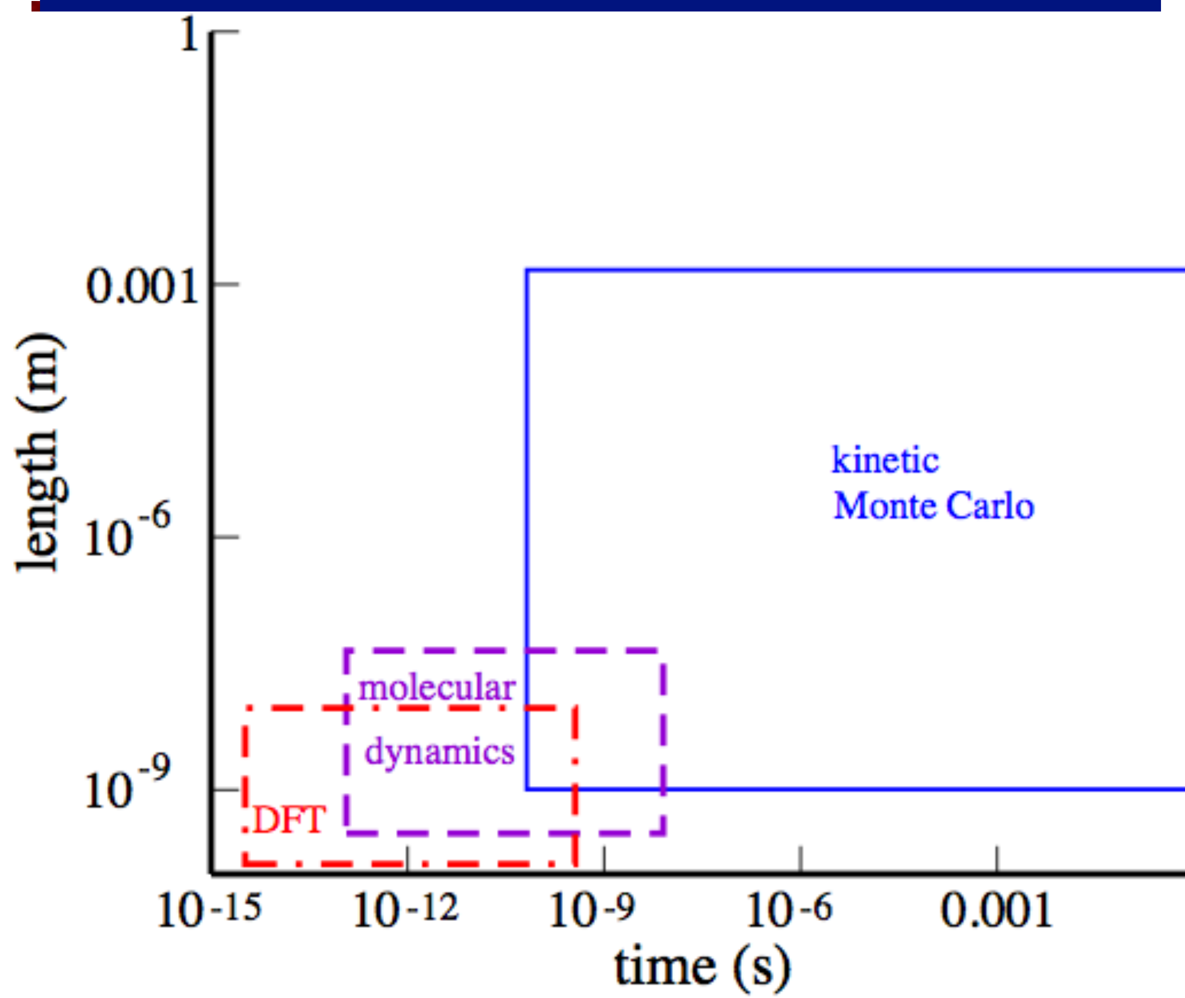


2D islands



surface reconstruction





Outline of this talk

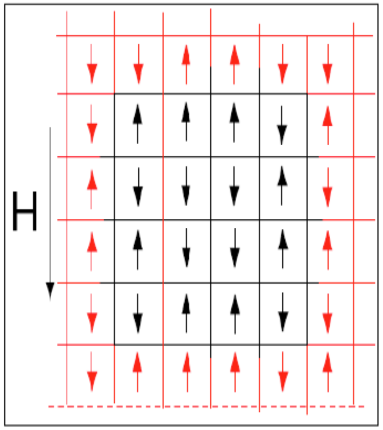
- Models in Statistical Physics, Monte Carlo (MC) methods, thermodynamic equilibrium
- How kinetic Monte Carlo exceeds over MC
- From molecular dynamics to kMC, how to make contact to DFT calculations
- Applications
- Summary

Methods of Statistical Physics

Discrete models in Statistical Physics

- Ising model (magnetism)

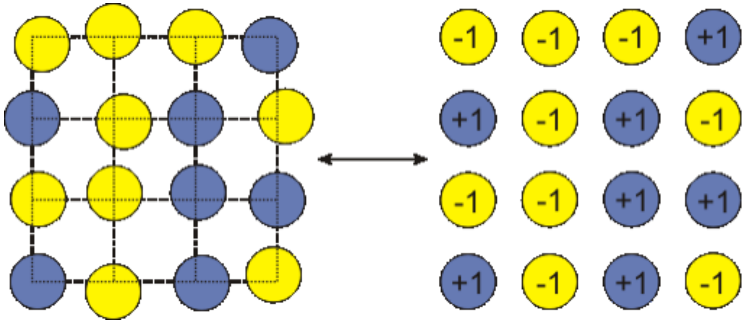
$$H(s) = -J_q \sum_i \sum_{j \in n(i)} s_i s_j - \mu_B B \sum_i s_i$$



- Lattice-gas interpretation $c_1 = 0, 1 \qquad s_i = 2c_i - 1$

$$H = -4J_q \sum_i \sum_{j \in n(i)} c_i c_j + 2(qJ_q - \mu_B B) \sum_i c_i - N(qJ_q - \mu_B B)$$

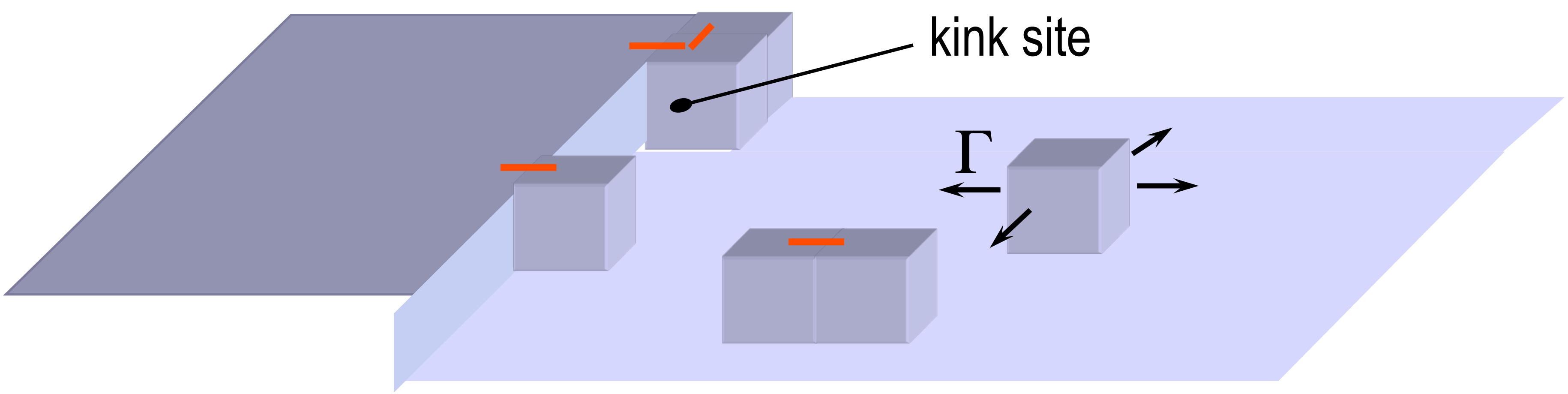
- **Goal:**
  Calculation of thermal averages



A discrete model for epitaxy: solid-on-solid (SOS) model

- Atoms are symbolized by little cubes placed on a lattice.
- The growth surface has no voids, no “overhangs”.
- Atoms move by discrete hops with rate $\Gamma = \exp(-E/kT)$.
- The binding energy is determined by the # of neighbors n

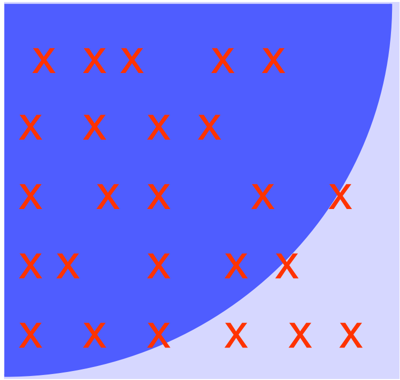
$$E = E_D + n\, E_B$$



Stochastic sampling

- Calculating thermal averages in many-particles systems requires evaluation of high-dimensional integrals.
- Choosing the sampling points in an (almost) random way is a good strategy, in particular in high dimensions !
- Even better: importance sampling -- density of sampling points proportional to local value of the integrand
- Idea: create a stochastic process that achieves importance sampling.

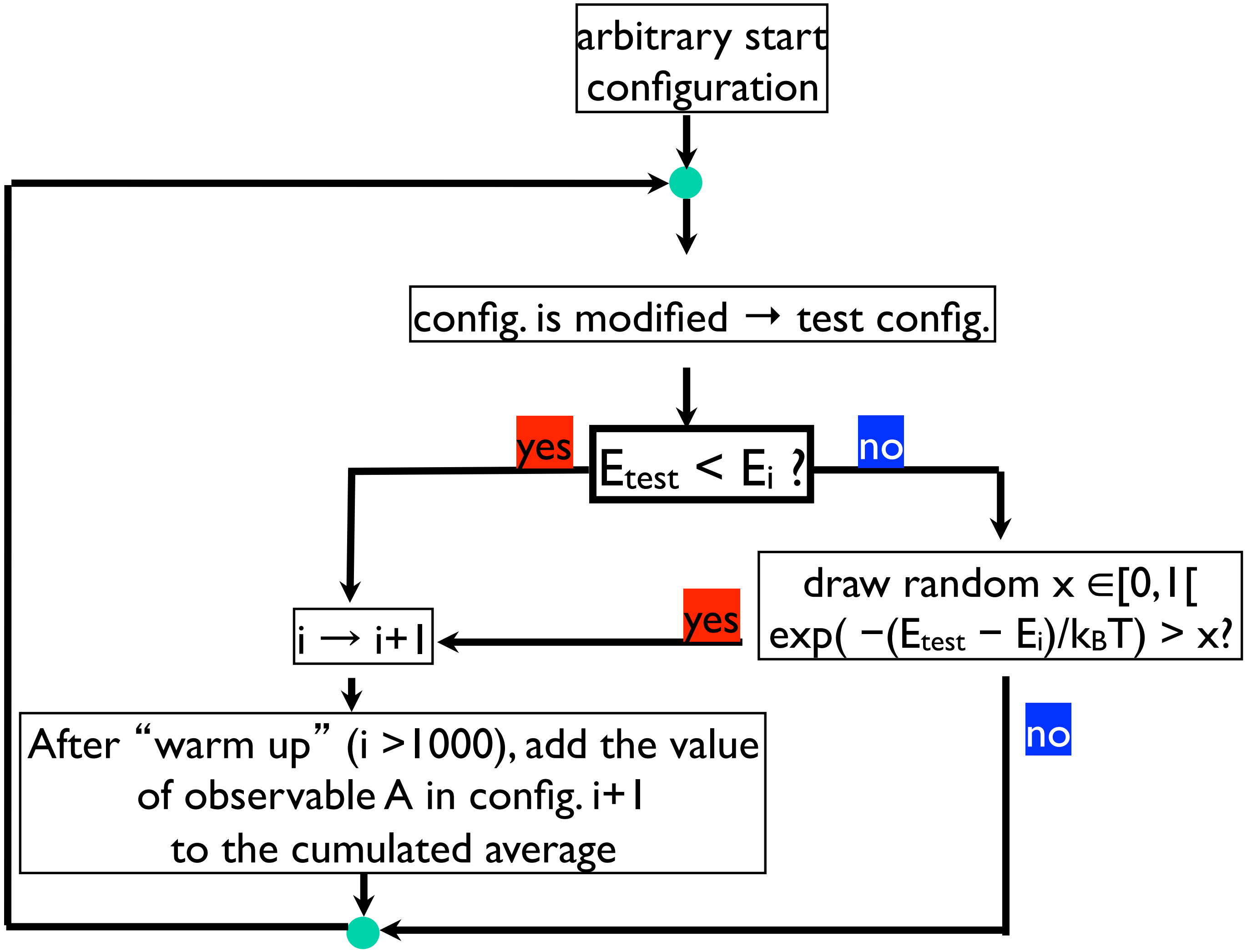
$\pi/4 = 0.78 .. \approx 20/25 = 0.8$



Metropolis Sampling

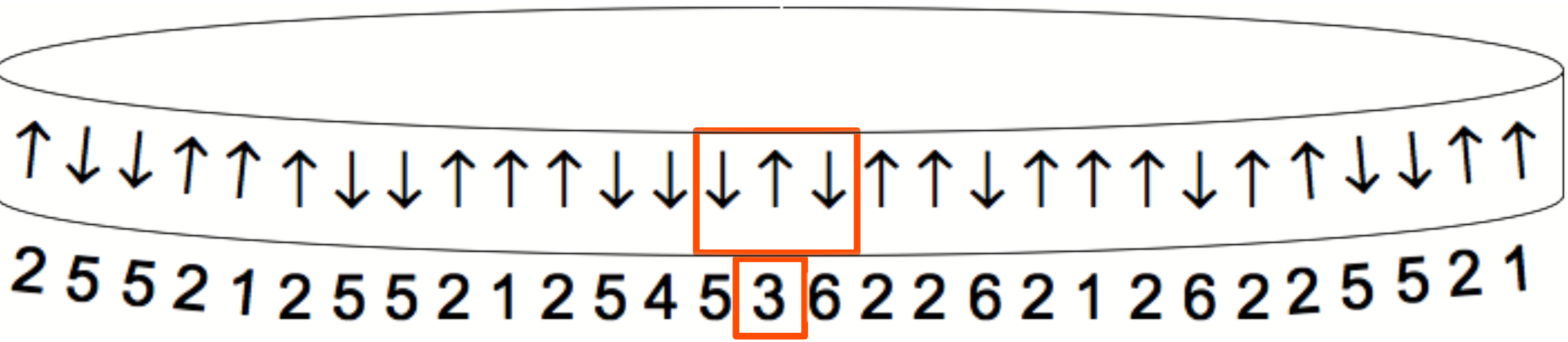
- **Solution:** *Importance Sampling* with $$w(\mathbf{q}) = \frac{\exp\left(-V(\mathbf{q})/(k_B T)\right)}{Z'}$$
- Generate random support points, distributed according to $w(\mathbf{q})$, i.e., out of total K points, $k_i = Kw(\mathbf{q})$ in the unit volume around $\mathbf{q}_i$
- The expectation value of an observable is calculated as $$\langle A \rangle \approx \frac{1}{K} \sum_{i=1}^{K} k_i A(\mathbf{q}_i)$$
- The Metropolis algorithm generates, starting from $\mathbf{q}_0$, successively a sequence of K configurations $\mathbf{q}_i$, distributed according to $w(\mathbf{q})$.
- Even though we don't know Z', this is possible, because it is just the correct **relative** probabilities that matter:
  - accept new config. $\mathbf{q}_{i+1}$, if $$\exp\left(-\frac{V(\mathbf{q}_{i+1}) - V(\mathbf{q}_i)}{k_B T}\right) > \mathrm{rnd}$$
  - else reject. $\mathrm{rnd} \in [0,1[$
- This assures that $$\frac{w(\mathbf{q}_{i+1})}{w(\mathbf{q}_i)} = \exp\left(-\frac{V(\mathbf{q}_{i+1}) - V(\mathbf{q}_i)}{k_B T}\right)$$

Metropolis algorithm



From MC to kMC:
the *N*-fold way

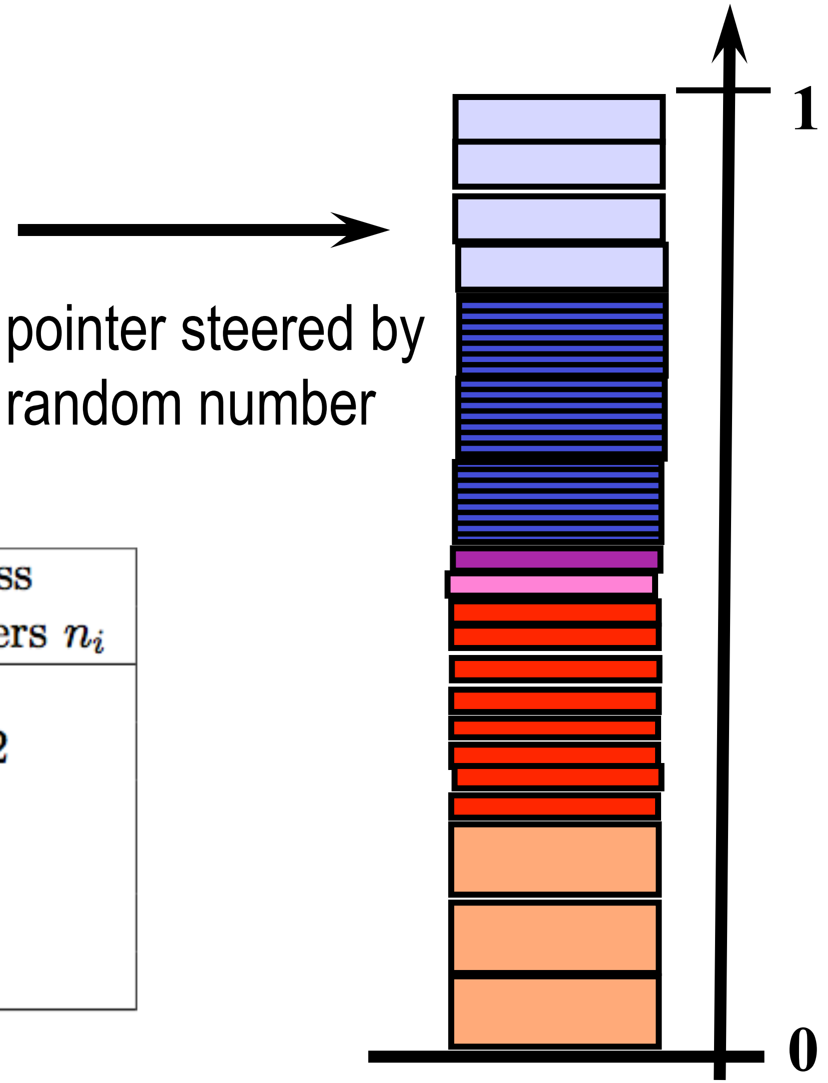
Classification of spins according to their neighborhood



class	central spin	neighbors	class members n_i
1	$\uparrow$	$\uparrow, \uparrow$	4
2	$\uparrow$	$\uparrow, \downarrow$	12
3	$\uparrow$	$\downarrow, \downarrow$	1
4	$\downarrow$	$\downarrow, \downarrow$	1
5	$\downarrow$	$\uparrow, \downarrow$	8
6	$\downarrow$	$\uparrow, \uparrow$	3

The *N*-fold way algorithm in MC

- processes are chosen with a probability proportional to their rates
- no discarded attempts (in contrast to Metropolis)



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6	$\downarrow$	$\uparrow,\uparrow$	3

Simulations of non-equilibrium processes: kinetic MC

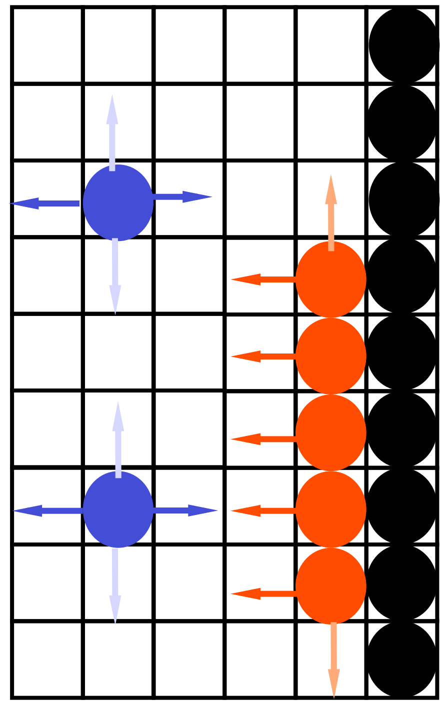
- While being aware of all processes possible at an instant of time, we need a way of (randomly) selecting one process with the appropriate relative probability.
- An internal clock keeps track of the advancement of physical time.
  - If the processes are clearly separated in time, i.e. processes are 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 all possible processes according to the new situation after the move.

Specific algorithms:

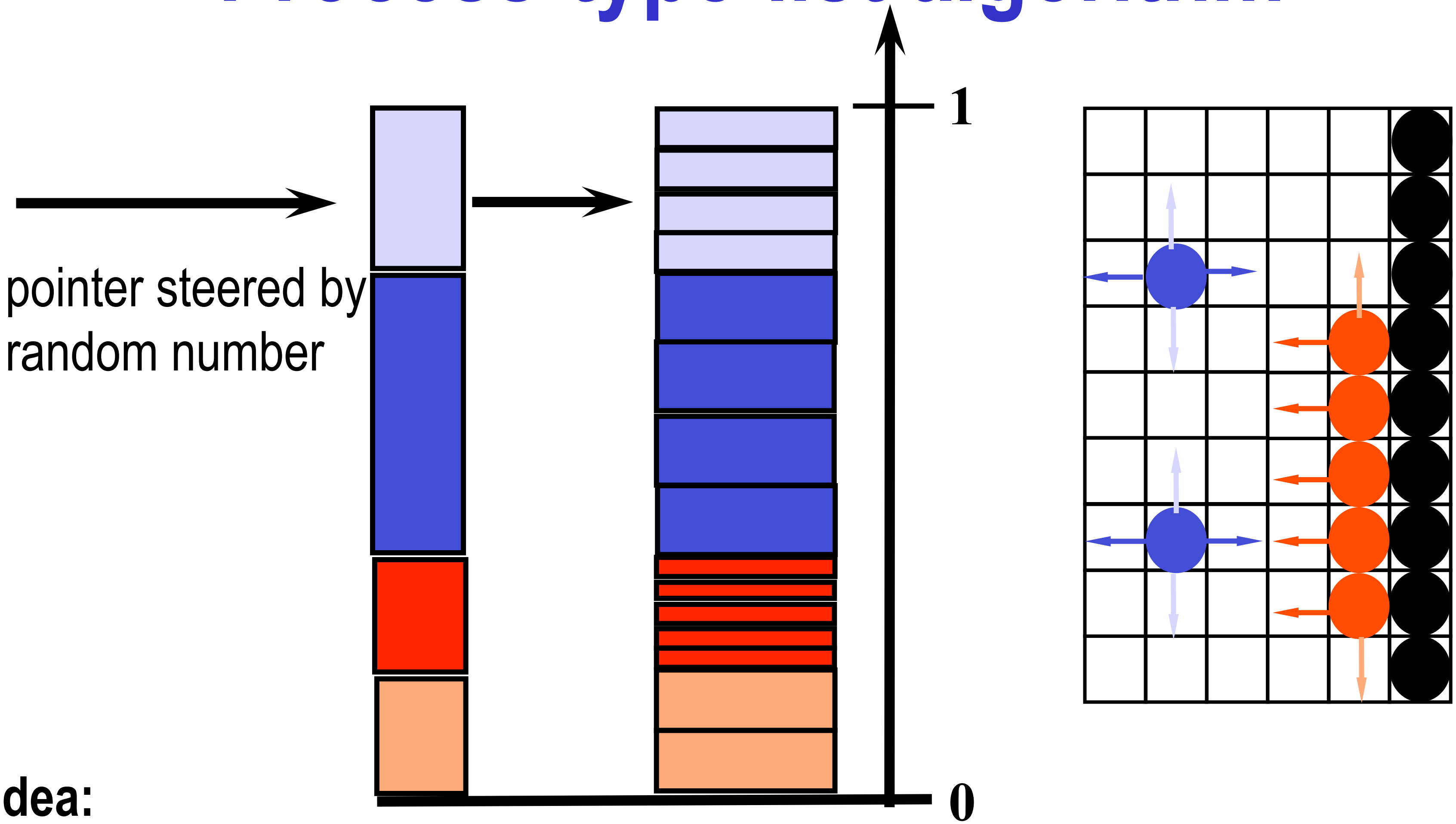
- process-type list algorithm
- binary-tree algorithm
- time-ordered-list algorithm

Application to a lattice-gas model

- 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.



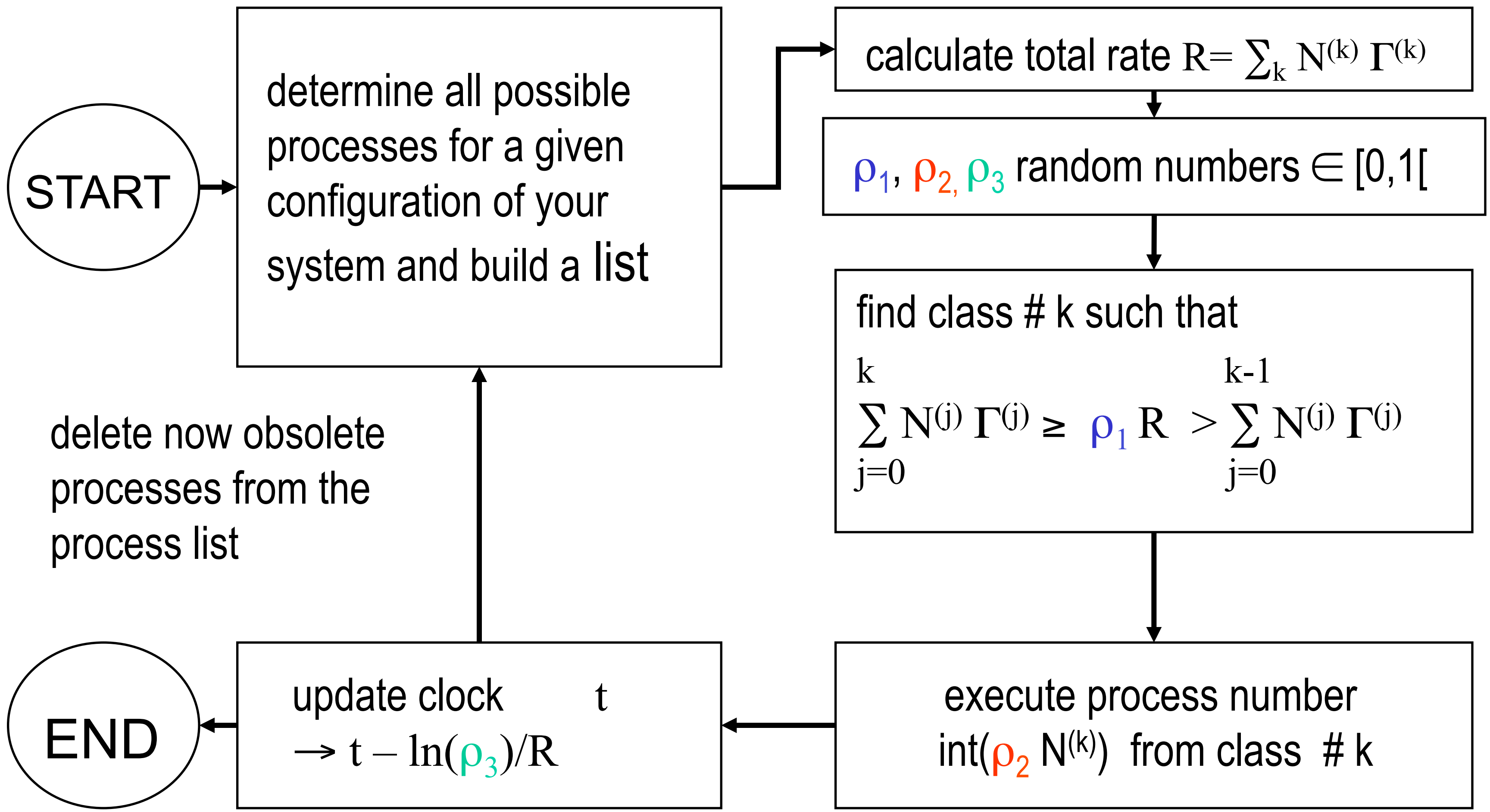
Process-type-list algorithm



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 a kMC algorithm



Time-ordered list algorithm

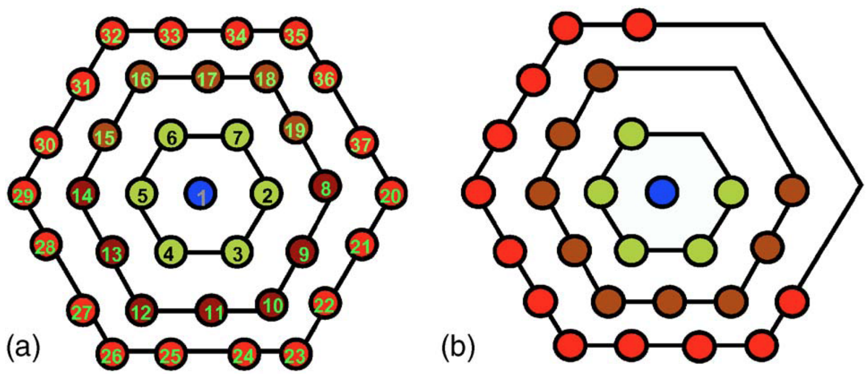
1. assign a random waiting time t_i to each individual process
2. sort all processes according to ascending waiting time (requires only log(N) comparisons, if done in a way similar to the binary tree)
3. always select the first process and execute it
4. advance the clock by $t \to t + t_i$
5. Update the list and return to 1.

- This algorithm requires many exponentially distributed random numbers; thus it‘s advisable to use specially a designed random number generator.

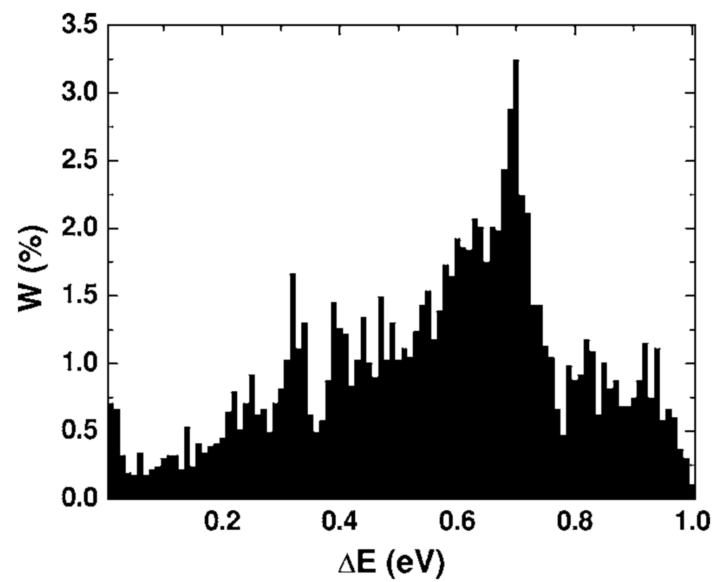
B. Lehner, M. Hohage & P. Zeppenfeld, Chem. Phys. Lett. **336**, 123 (2001)

Self-learning kMC

- **Idea:** build up a database of rates on the fly
- If a certain environment/certain process is missing in the database, spawn a calculation of the barrier for this process.
- All environments **on a lattice** can be classified by the occupancy of neighbor shells.



Shell	Base 2	Base 10
1	111110	31
2	111111111000	511
3	00111111111111110000	16380



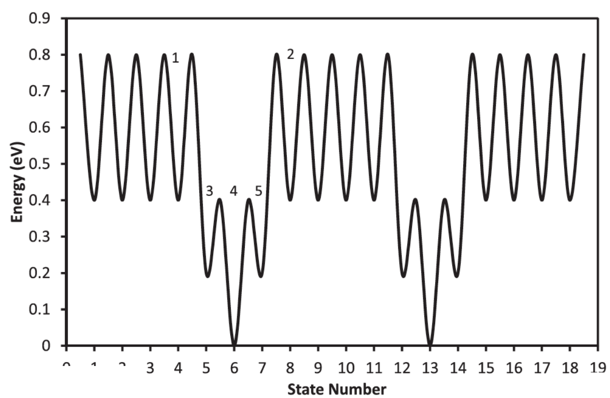
O. Trushin, A. Karim, A, Kara, T. S. Rahman, Phys. Rev. B **72**, 115401 (2005)

superbasin algorithm

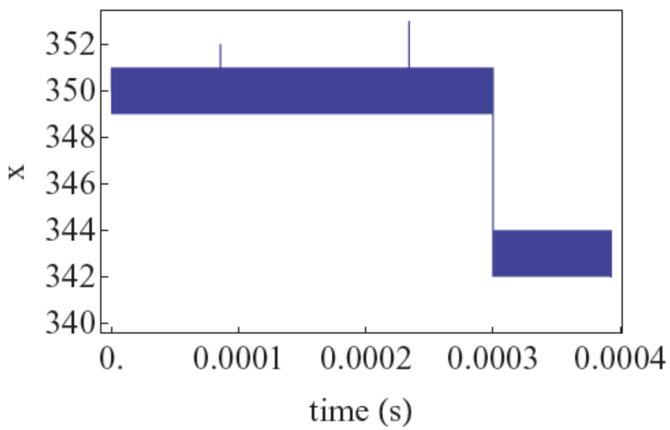
- If "fast" hops occur, consolidate them into a superbasin
- several exits with analytically calculated partial probabilities
- various models for exit time distributions available
- superbasins can be created or dismantled "on the fly"

example:

1D potential

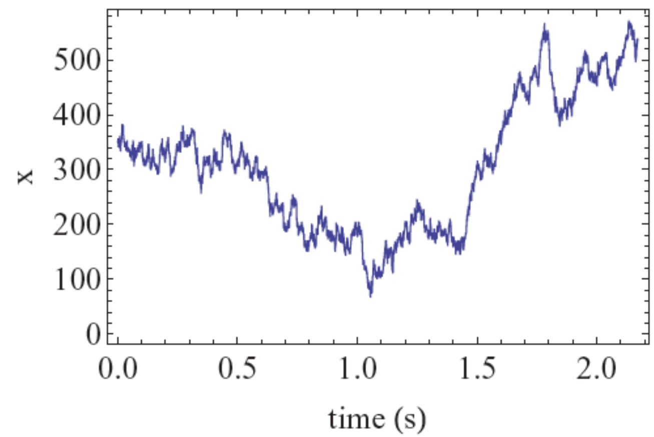


conventional kMC



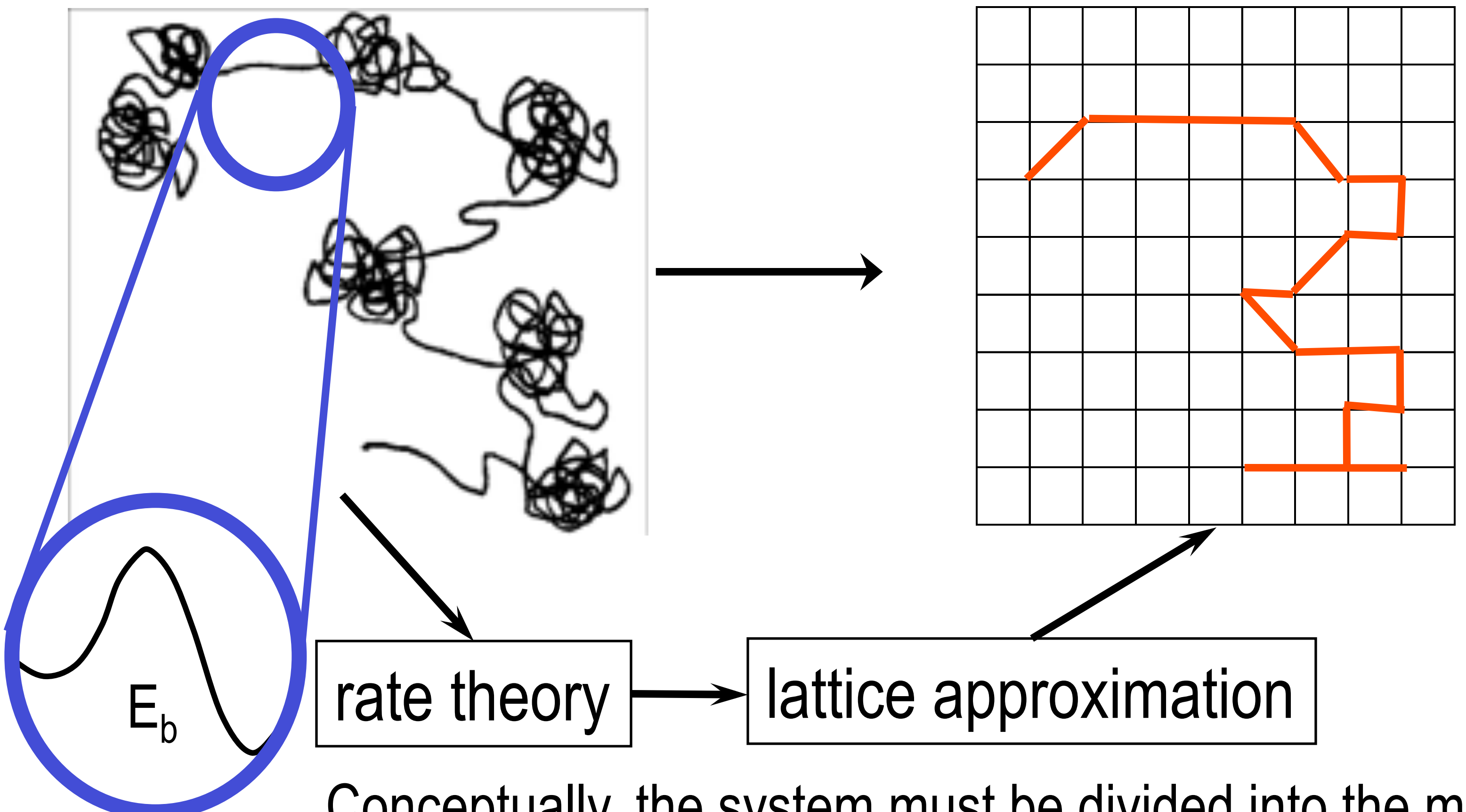
K. Fichthorn & Y. Lin, J. Chem. Phys. **138**, 164104 (2013)

with superbasins



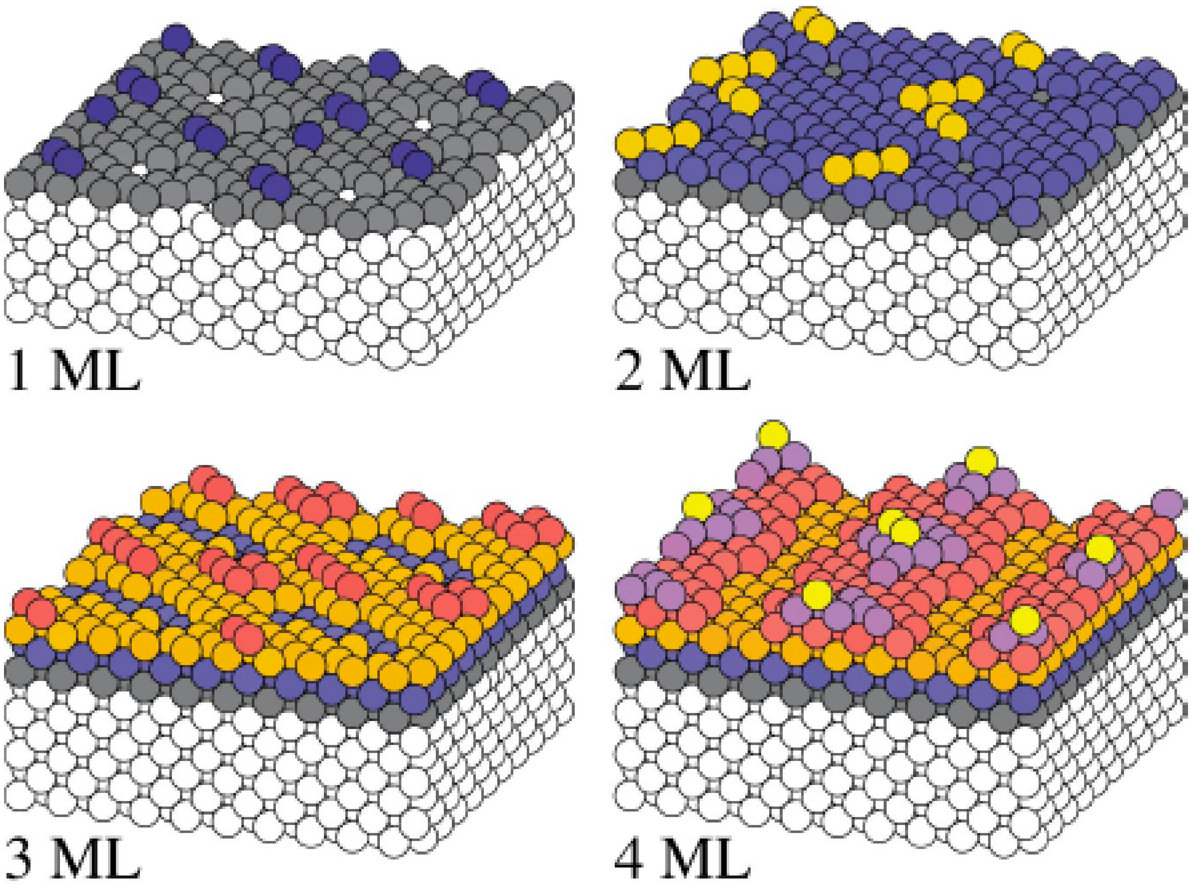
From molecular dynamics to kinetic Monte Carlo

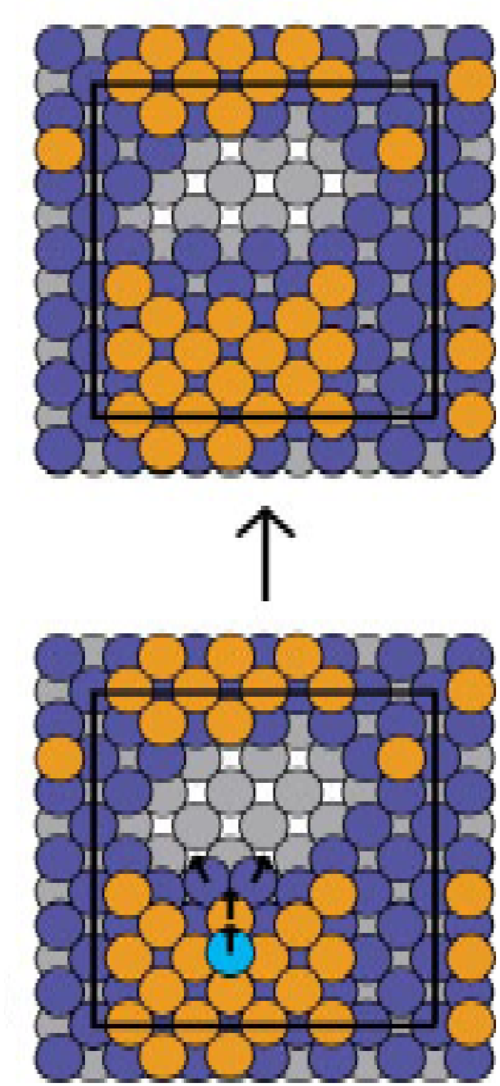
From molecular dynamics to kinetic Monte Carlo



Conceptually, the system must be divided into the motion along the reaction coordinate and a "heat bath".

Collective processes

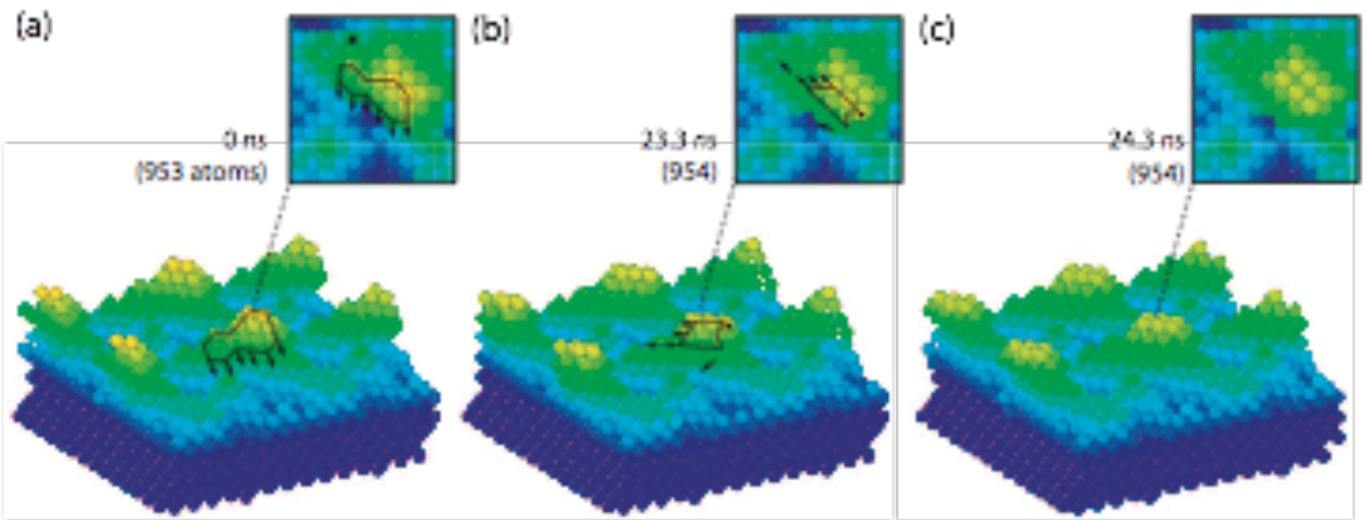


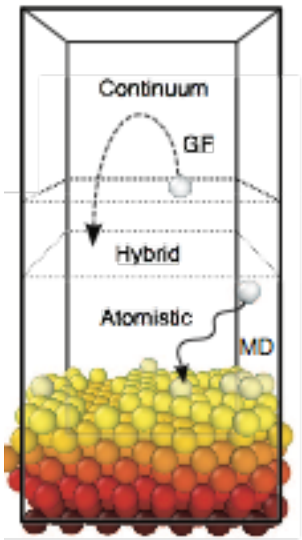


F. Montalenti, M.R. Sørensen and A.F. Voter,
Phys. Rev. Lett. **87**, 126101 (2001)

Counter-example: liquid-solid epitaxy

- Molecular dynamics (MD) may be unavoidable in cases when the atoms **not** are sitting on lattice sites
- possibly use some **accelerated** MD
- here: only the solid phase is treated atomistically





Chun-Yaung Lu, A.F. Voter, D. Perez, J. Chem. Phys. **140**, 044116 (2014)

Transition State Theory (1-dim)

- Kramer's rate theory

$$\Gamma = \frac{\lambda}{\omega_b}\left(\frac{\omega_0}{2\pi}\exp\left(-E_b/kT\right)\right) \qquad \lambda = \left(\gamma^2/4 + \omega_b^2\right)^{1/2} - \frac{\gamma}{2}$$

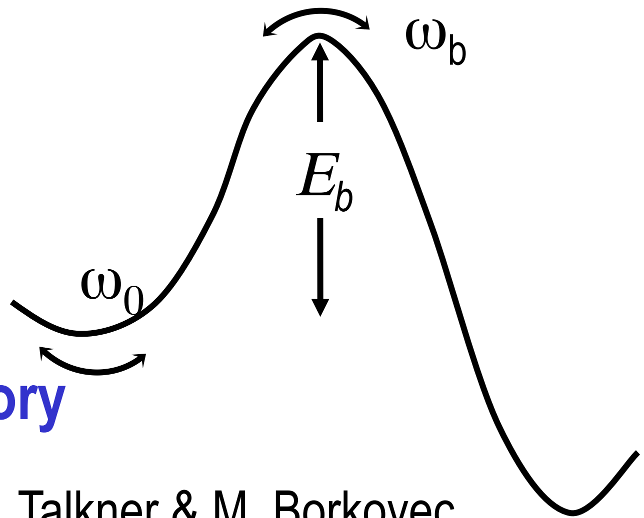
γ: friction due to coupling to the heat bath

- high-friction limit

$$\Gamma = \frac{\omega_0\omega_b}{2\pi\gamma}\exp\left(-E_b/kT\right)$$

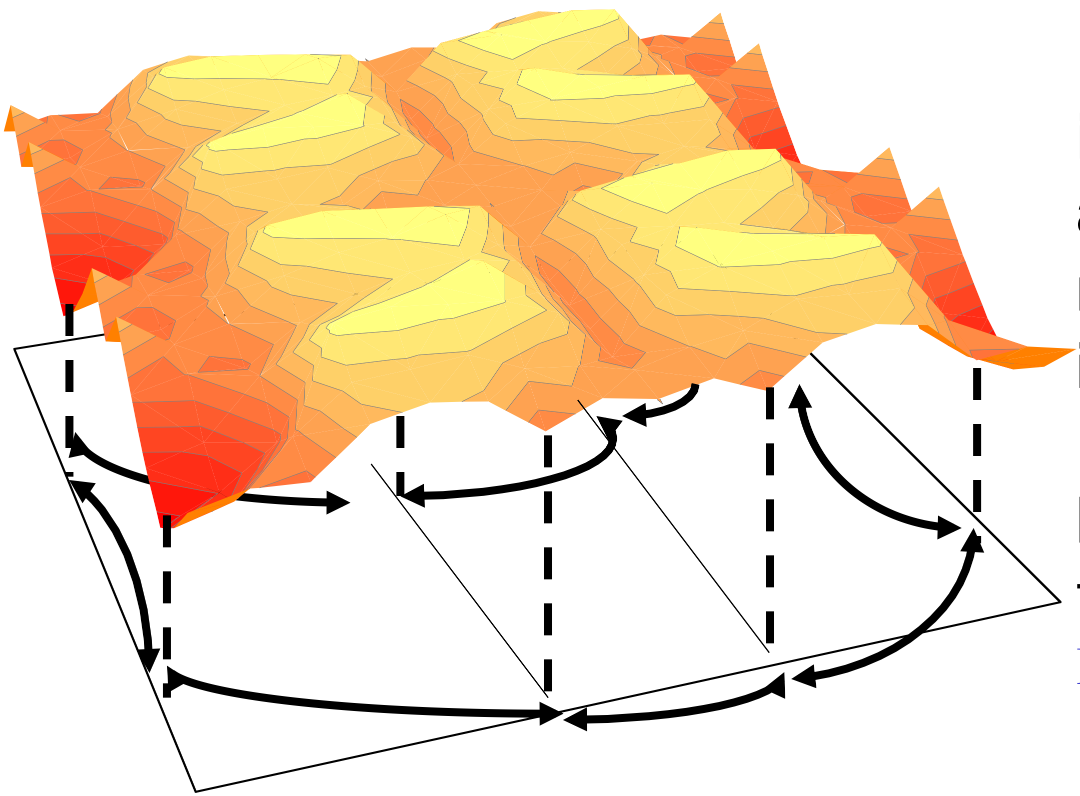
- 'medium' friction → **transition state theory**

$$\Gamma = \frac{\omega_0}{2\pi}\exp\left(-E_b/kT\right)$$



P. Hänggi, P. Talkner & M. Borkovec, Rev. Mod. Phys. **62**, 251 (1990)

From the PES to rate constants Γ (multi-dimensional)



idea:
associate minima with the nodes, hops with the interconnects in a network

hopping rates derived from the PES

$$E(x_i, y_i) = \min_{z_i,\, c_\alpha} E_{tot}(x_i, y_i, z_i, c_\alpha)$$

$$\Gamma = kT/h \;\; Z_{TS}/Z_i = \text{(harmonic \& classical approximation)} = \Pi_N \, \nu_{k,i} \, / \Pi_{N-1} \, \nu_{k,TS} \;\; \exp(-\Delta E/kT)$$

How accurate is Transition State Theory ?

Three levels of approximation:

1 direct molecular dynamics

2 TST with thermodynamic integration of partition functions from restricted molecular dynamics at the 'ridge' ('blue-moon-ensemble')

3 TST within harmonic approximation

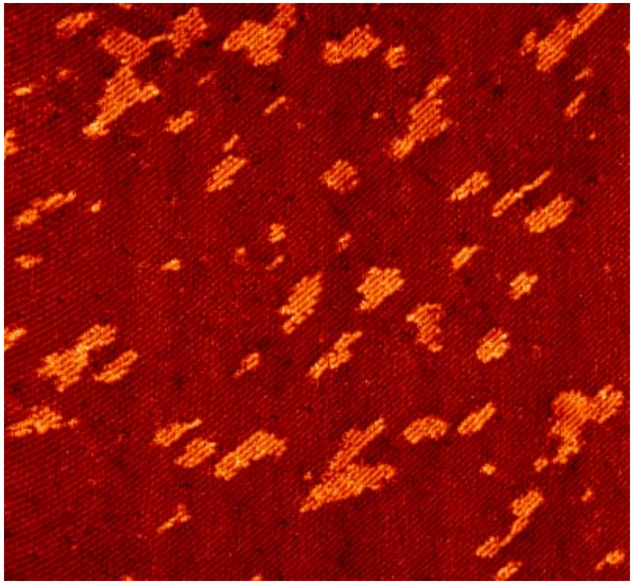
Cu/Cu(100): good agreement between method 1) and 2)

	$\ln\Gamma_0$ [THz]		ΔE [eV]		
	TI	MD	TI	MD	static
hop	2.9±0.2	3.0±0.2	0.51±0.02	0.49±0.01	0.50
exchange	6.5±0.6	6.1±0.7	0.74±0.02	0.70±0.04	0.73

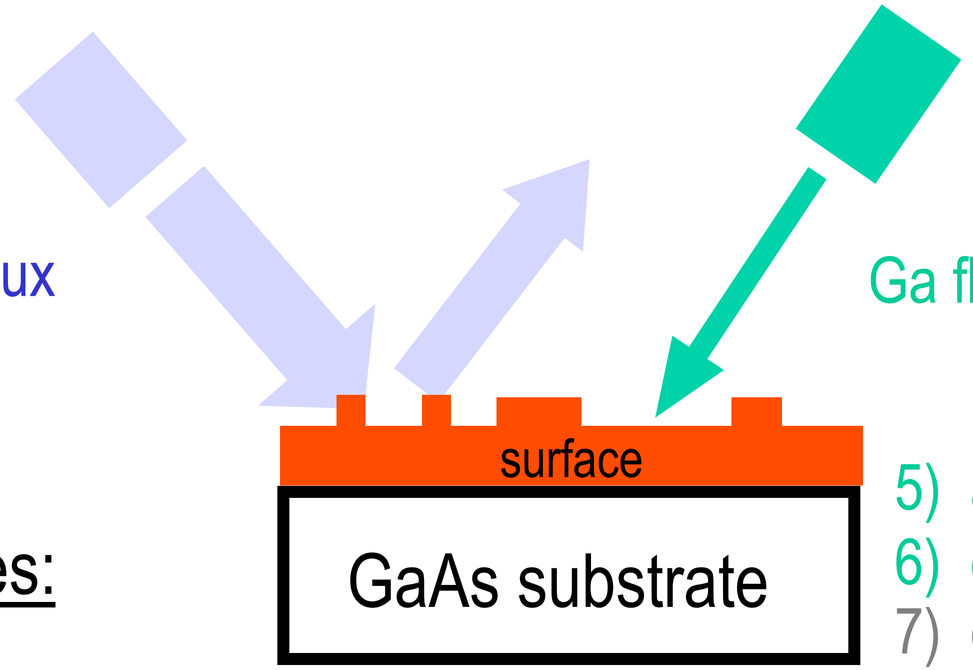
G. Boisvert, N. Mousseau & L.J. Lewis, PRB **58**, 12667 (1998)

Application I:

Molecular beam epitaxy on GaAs(001) β2(2x4)



Molecular beam epitaxy of III-V semiconductors



Processes:

1) adsorption of As_2
2) dissociation of As_2
3) diffusion of As
4) desorption of As_2

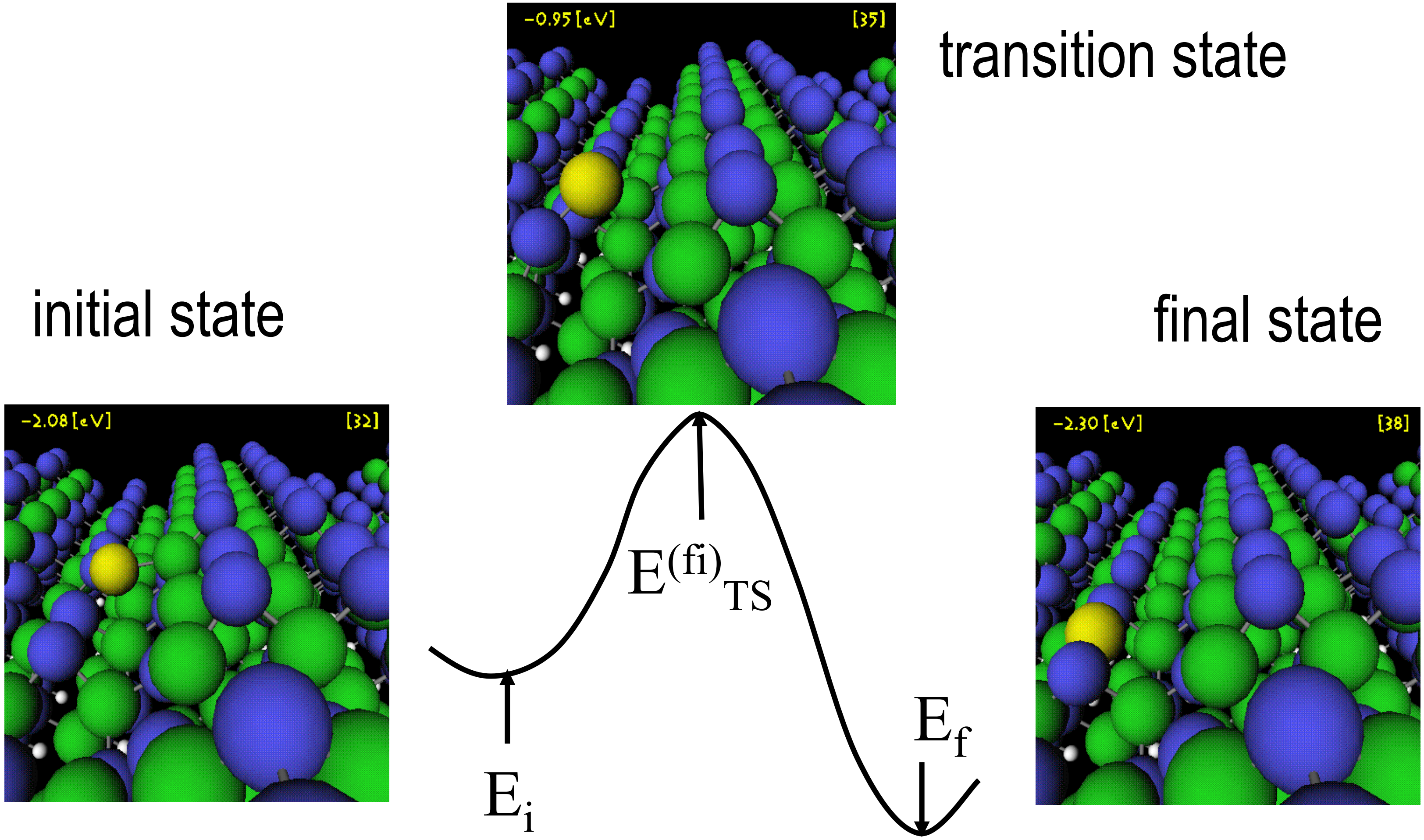
5) adsorption of Ga
6) diffusion of Ga
7) desorption of Ga

8) island nucleation
9) growth

What is the interplay of these processes for a given temperature and flux ?

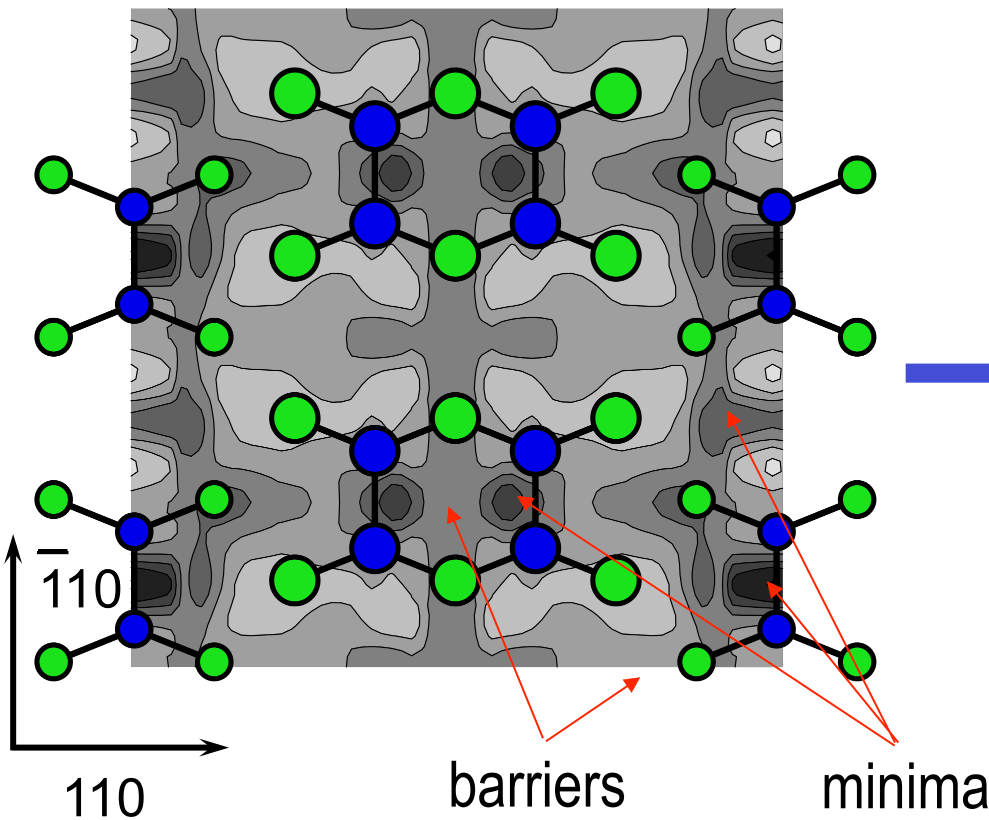
Rates from first-principles calculations

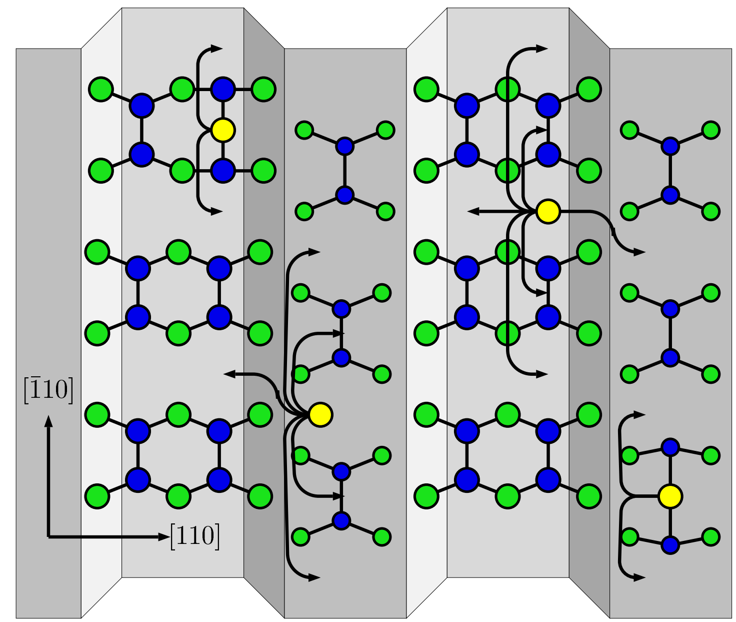
$$\Gamma^{(k)} = W(f,i) = \Gamma^{(fi)}_0 \exp(-(E^{(fi)}_{TS} - E_i)/kT)$$



Surface diffusion on GaAs(001): mapping of PES to network graph

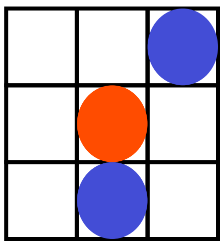
PES from DFT calculations → network of hops





kMC with explicit list of process types

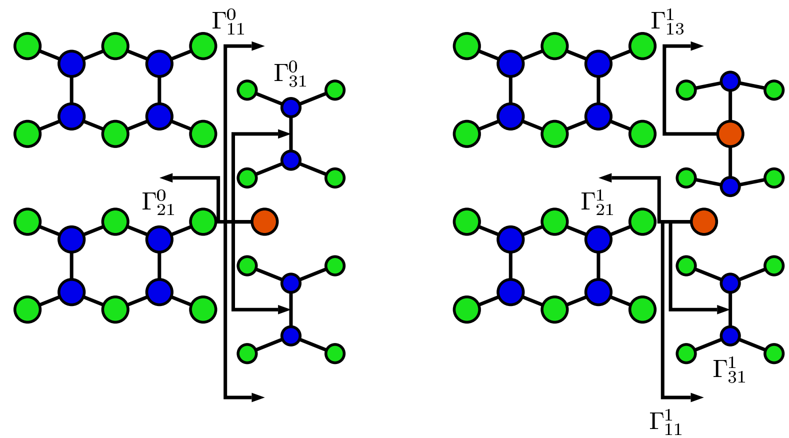
Voter's lattice kMC:



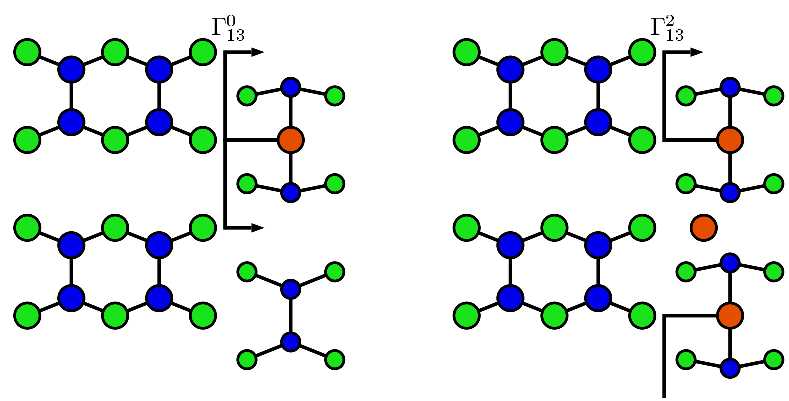
A.F. Voter PRB **34**, 6819 (1986)

- simulation on a lattice
- group possible transitions Γ(f,i) from i to f into classes, each class is characterized by a rate
- classification of initial and final state by 'atomic neighborhoods' e.g., the number and relative position of neighbors define a process type

DFT-based kMC:

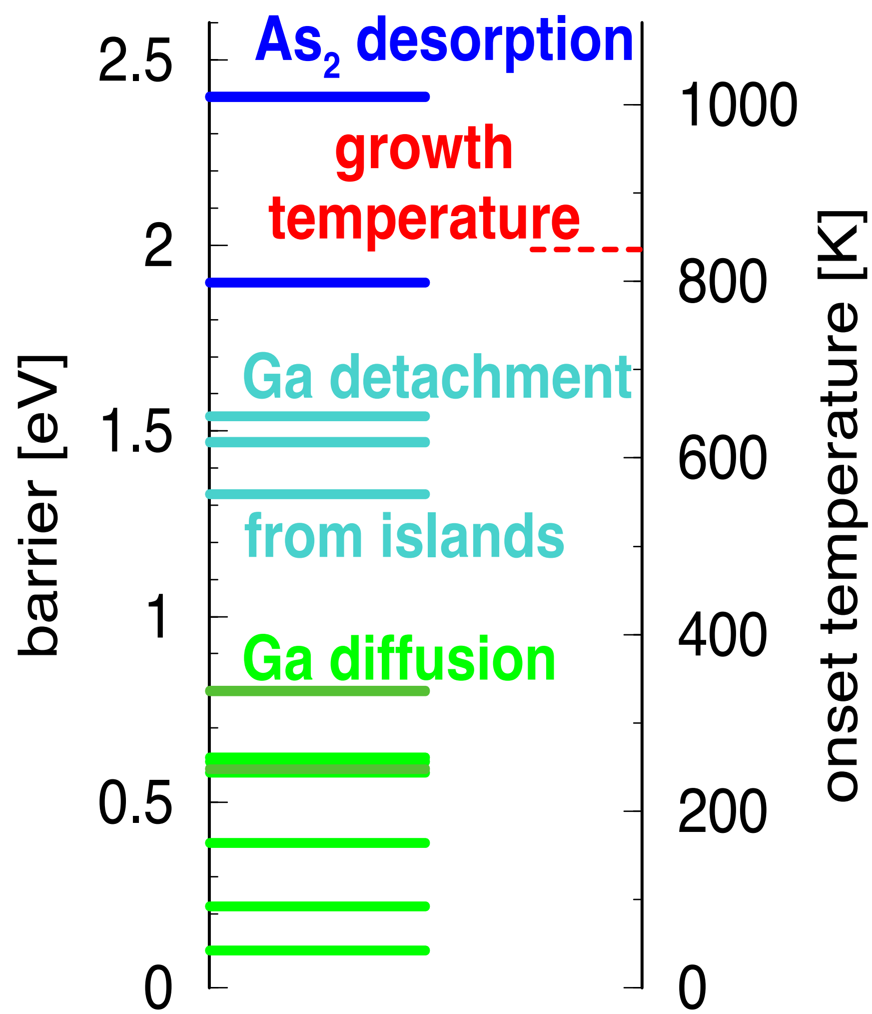


possible hops in the trench... .. modified rates due to neighbors.



kinetic Monte Carlo simulations for GaAs epitaxy

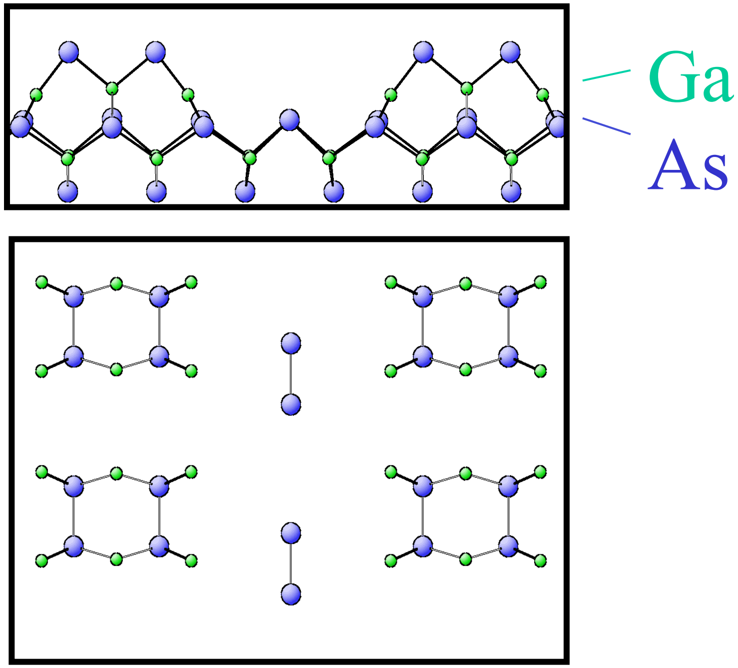
- 32 microscopically different Ga diffusion processes, and As_2 adsorption/desorption are included explicitly
- computational challenge: widely different time scales (10^{-12} sec to 10 sec)
- simulation cell 160 x 320 sites (64 nm x 128 nm)

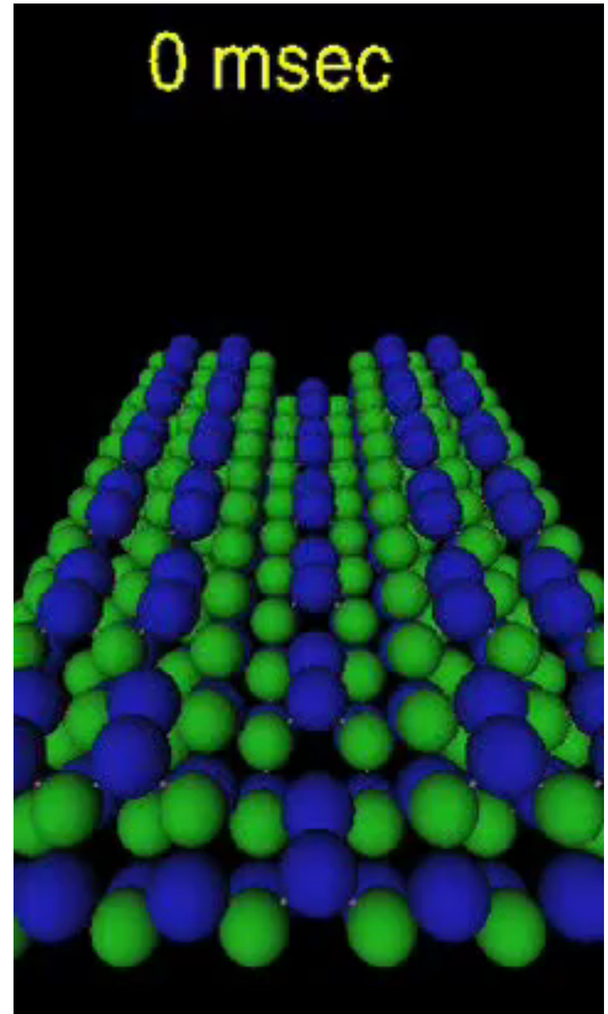


kinetics of island nucleation and growth

side view

top view





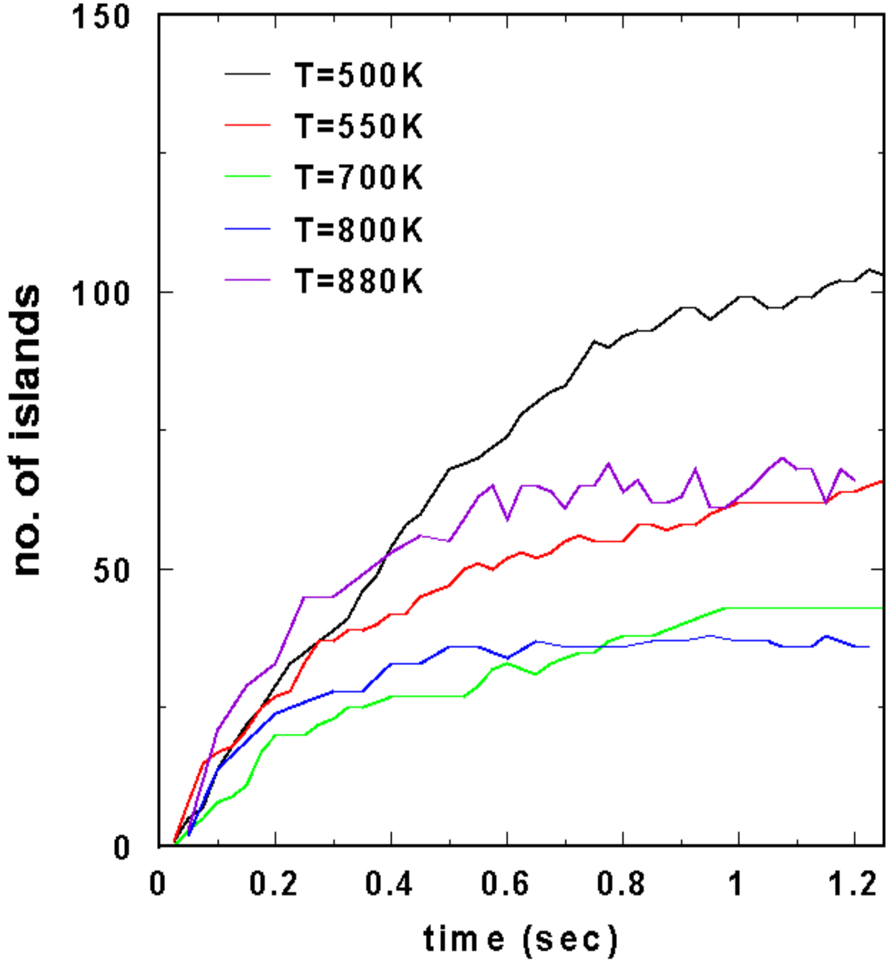
1/60 of the full simulation cell

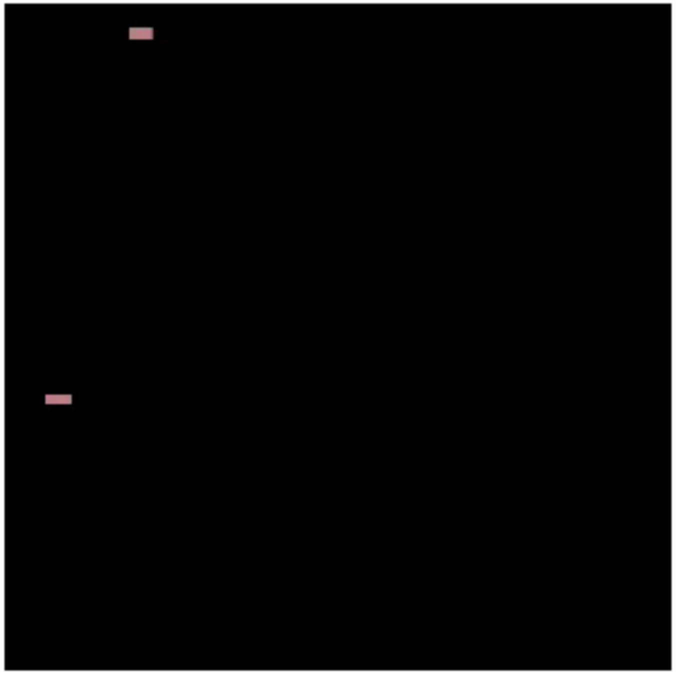
As_2 pressure = 0.85 x 10^{-8} bar

Ga deposition rate = 0.1 ML/s

T = 700 K

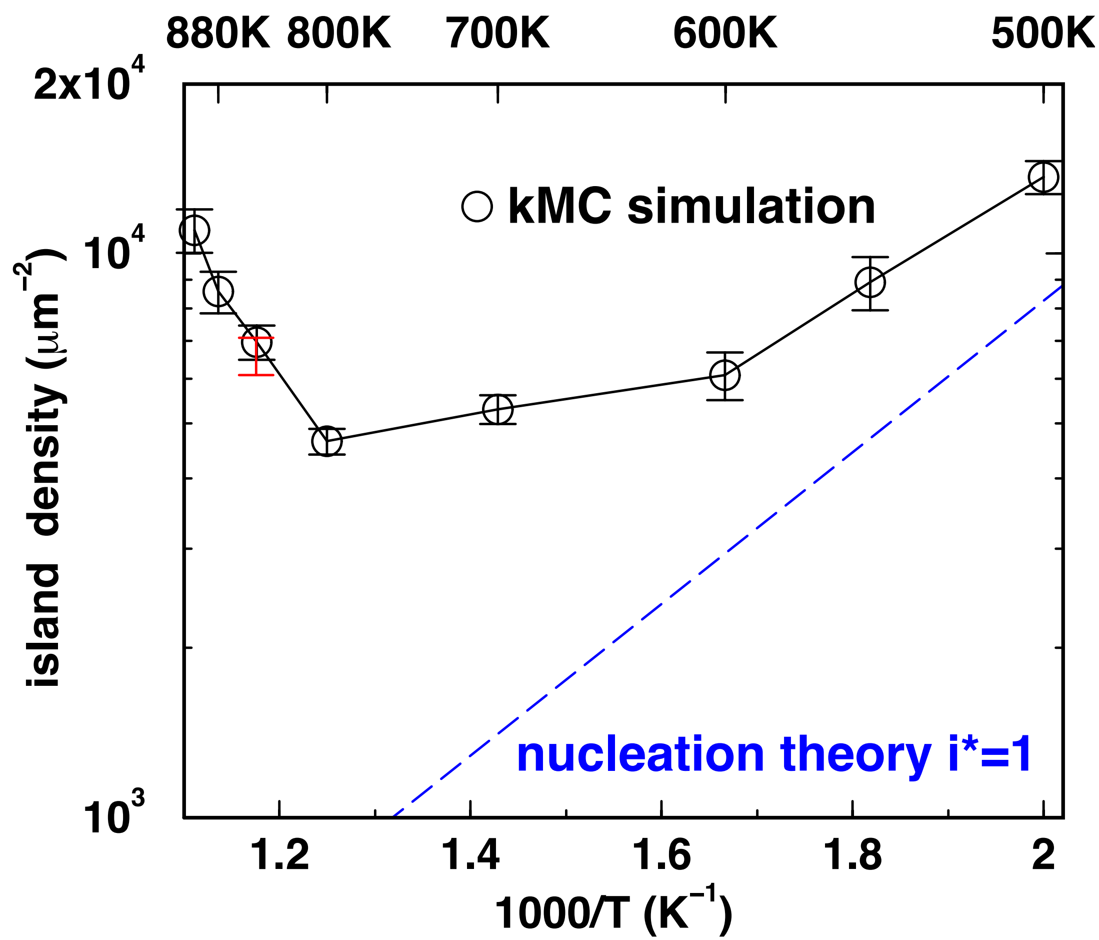
island density





deposition rate
0.1 ML Ga per second, III/V
ratio 1:1000, T=700K

scaling with temperature ?



‘conventional’ nucleation theory

$N_{is} = \eta \, (R/D)^{i^*/(i^*+2)}$

N_{is}	island density
D	diffusion constant
R	deposition flux
η	numerical const.
i^*	critical nucleus

simulation: P. Kratzer and M. Scheffler , Phys. Rev. Lett. **88**, 036102 (2002)

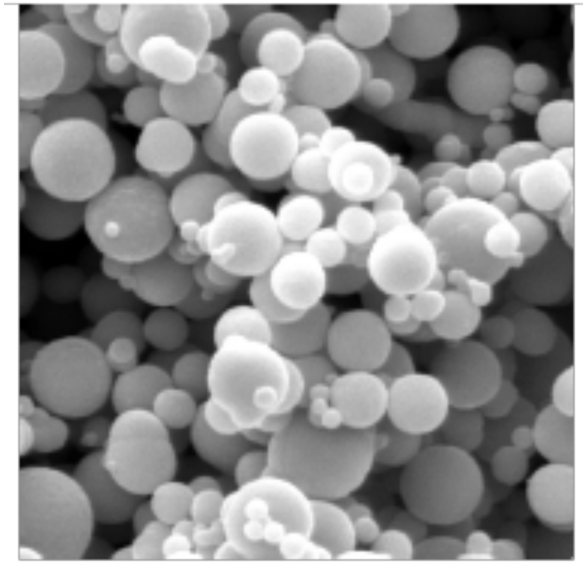
experiment: G.R. Bell et al., Surf. Sci. **423**, L280 (1999)

Application II:

kinetics of sintering

Sintering in materials synthesis

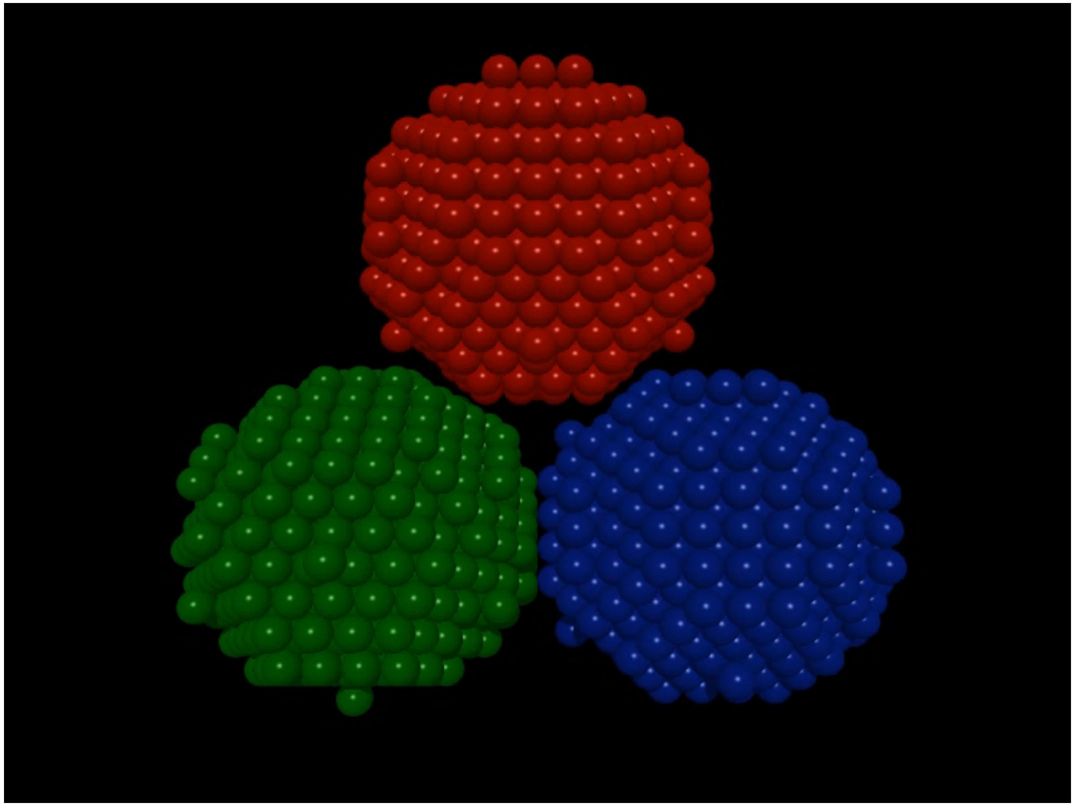
- For thermodynamics reasons, some materials (e.g. alloys) cannot be grown from solution
- polycrystalline samples may be obtained by synthesising small particles and compaction, followed by a temperature and/or heat treatment
- large crystals grow on the expense of smaller ones and may enforce re-orientation of neighbouring crystallites



Carbonyl iron powder (electron microscopy image)

Hybrid simulation

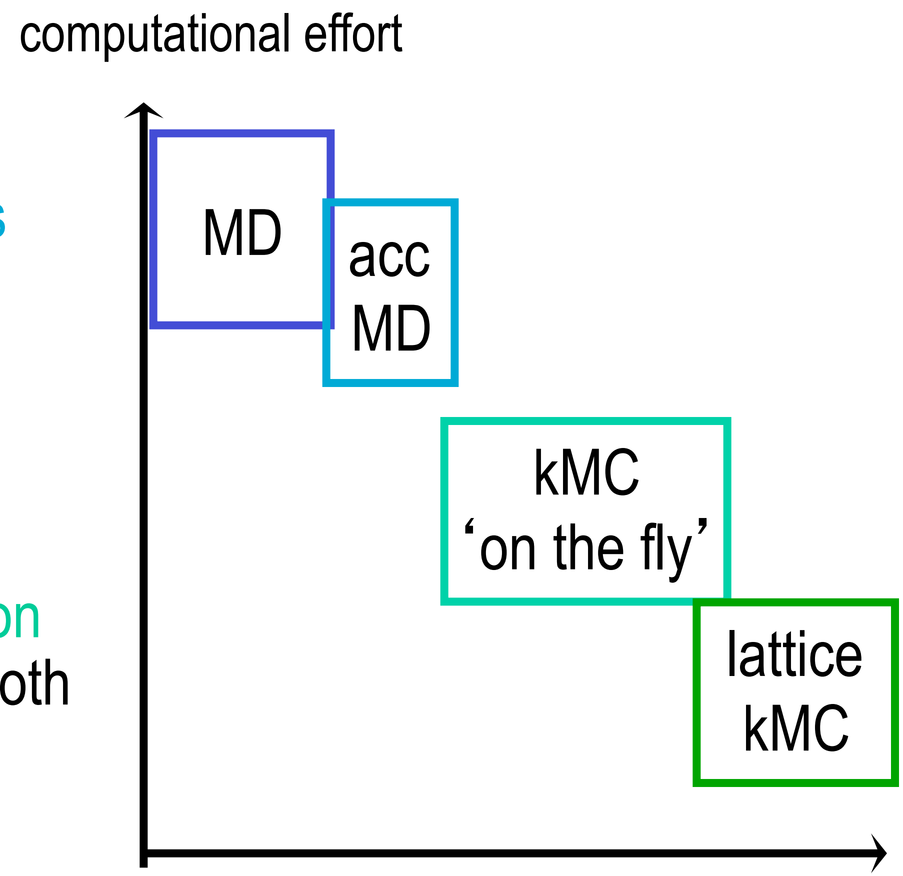
- particles treated as rigid bodies, using molecular dynamics with few collective variable
- contact dynamics for touching particles
- surface diffusion and growth treated by self-learning kMC



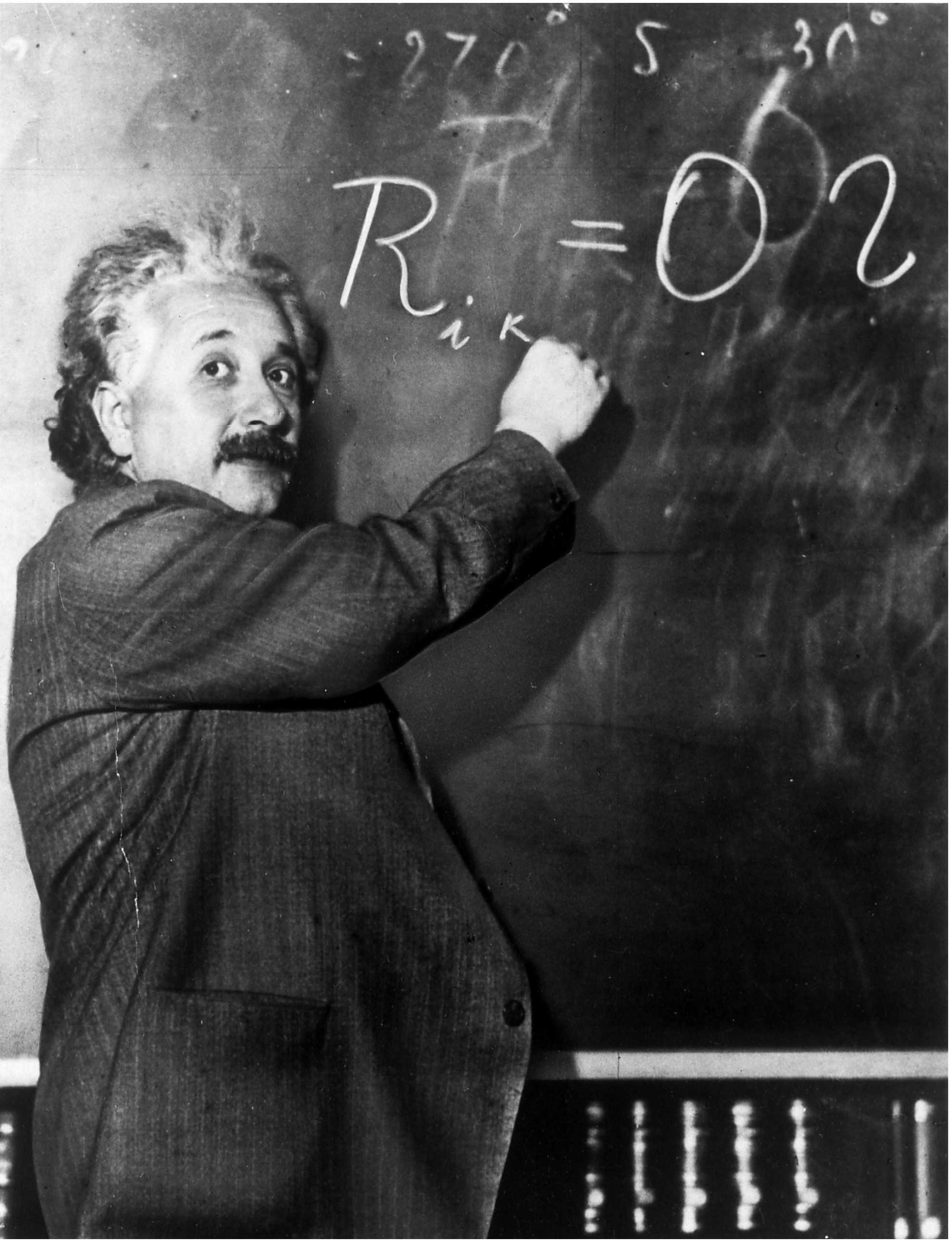
L. Brendel & D.E. Wolf,
University Duisburg-Essen

Summary: Bridging the time-scale gap

- molecular dynamics (Car-Parrinello method)
- accelerated molecular dynamics
  - using a boost potential (Voter, Fichthorn,…)
  - temperature-accelerated MD (Montalenti et al. PRL **87**, 126101 (2001))
- kinetic Monte Carlo with transition state search on the fly (avoids both lattice approximation and pre-defined rate table)
- lattice kinetic Monte Carlo, N -fold way (Voter PRB **34**, 6819 (1986))



… more and more schematic, risk of oversimplification



"Keep things as simple as possible, but not simpler .."

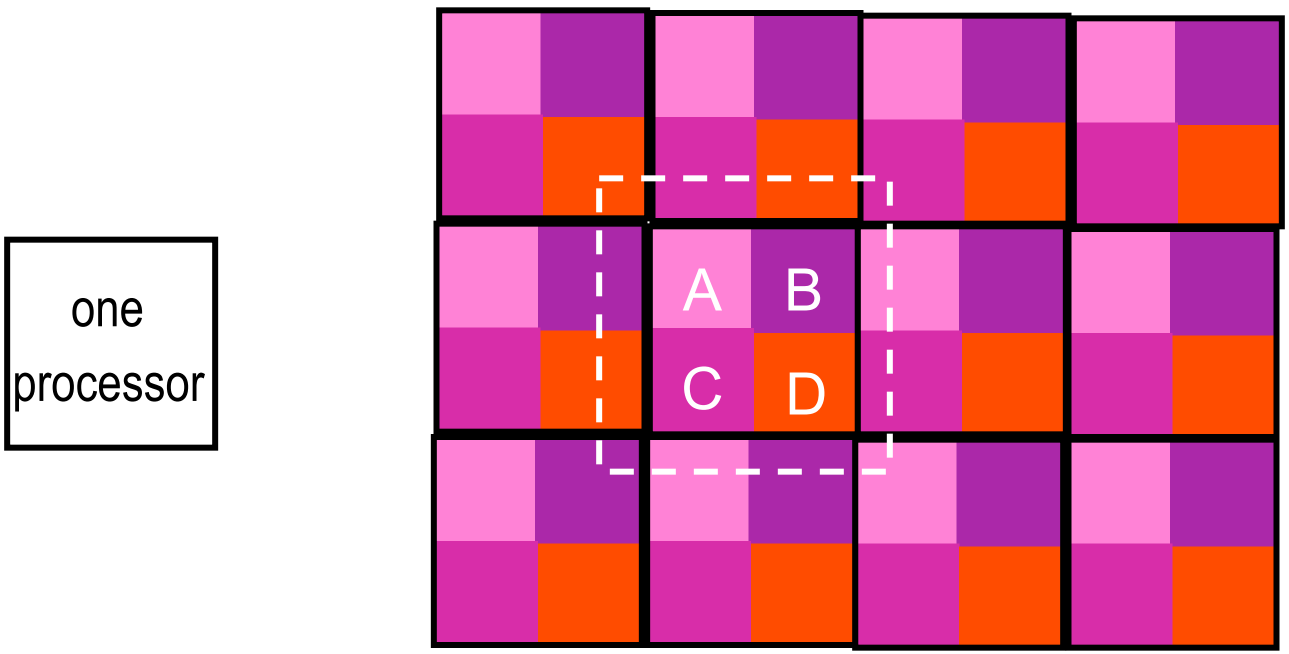
Thank you for your attention !

Summary: arXiv:0904.2556

Parallelization of kMC

semi-rigorous synchronous sublattice algorithm

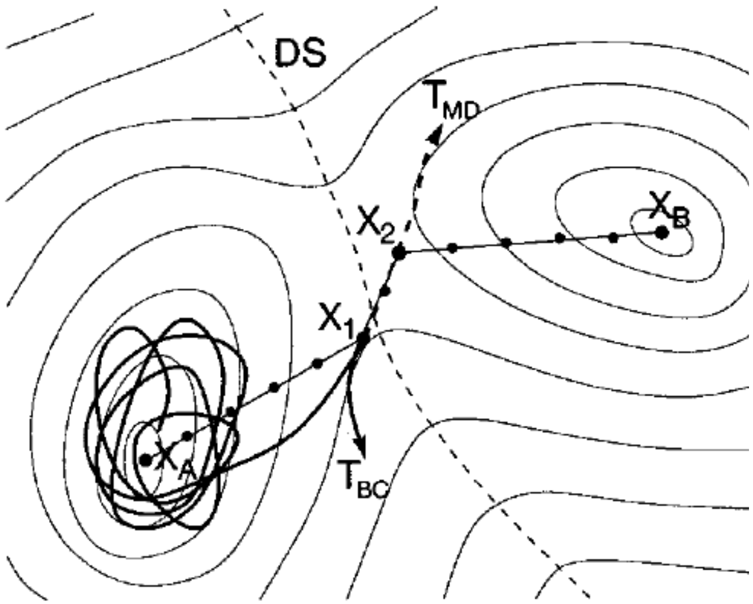
[Y. Shim and J.G. Amar, PRB **71**, 115436 (2005)]

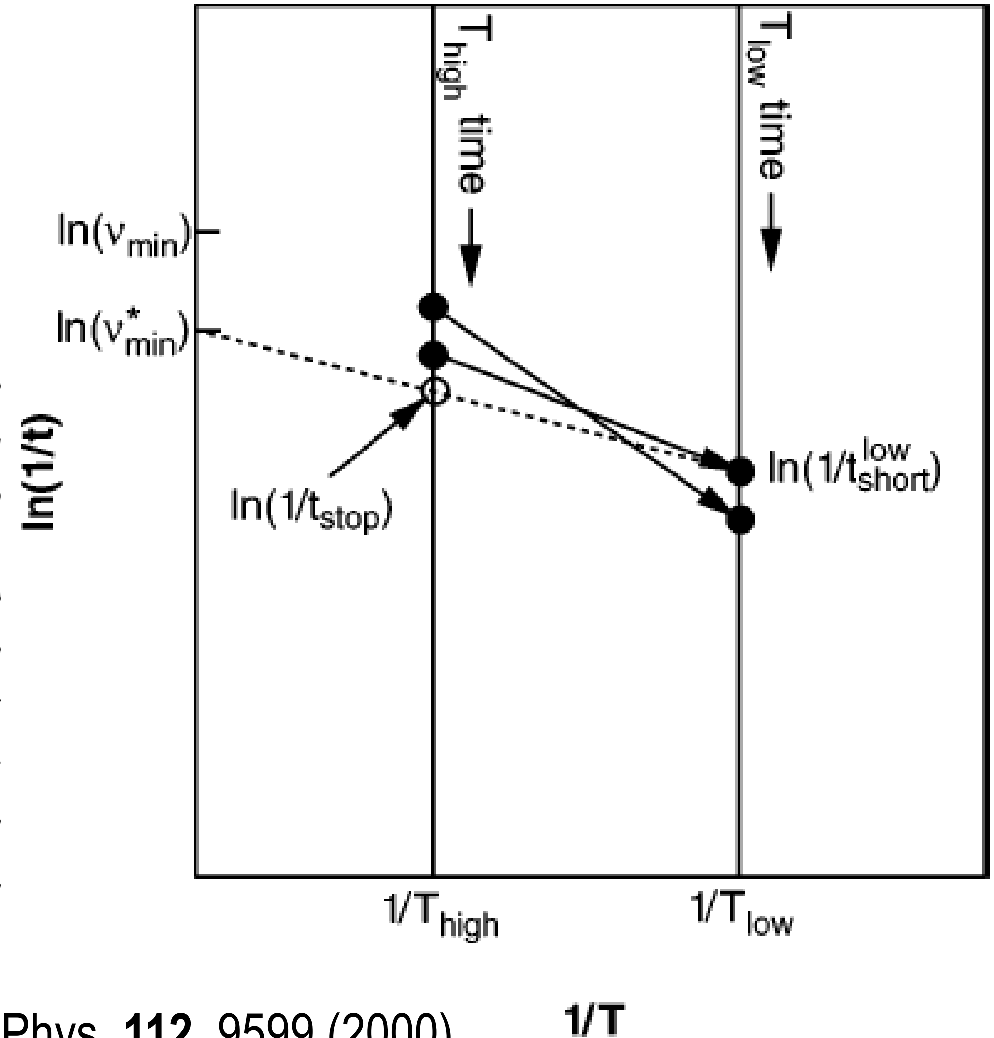


A-B-C-D-A-B-C-D- …

Temperature-accelerated dynamics (TAD)

Event is observed at T_{high}, but its rate is extrapolated to T_{low} (using the TST rate law).





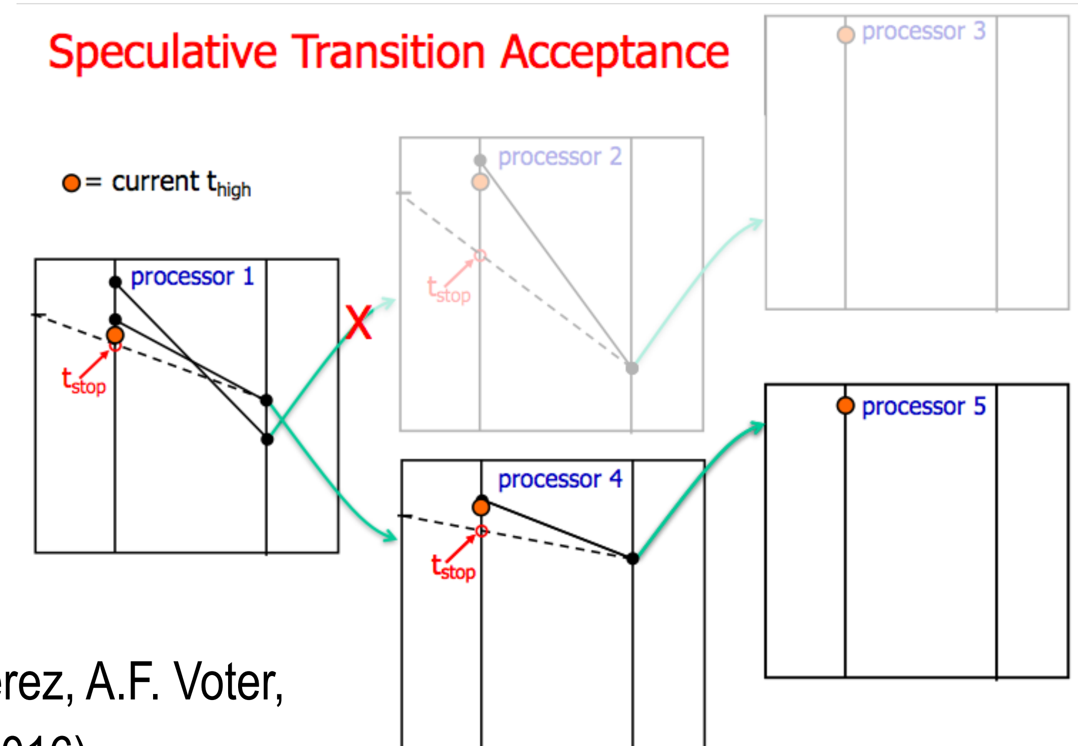
M.R. Sørensen and A.F. Voter, J. Chem. Phys. **112**, 9599 (2000)

“Speculative" TAD

A way to use computational **parallelism** in kinetic simulations ..

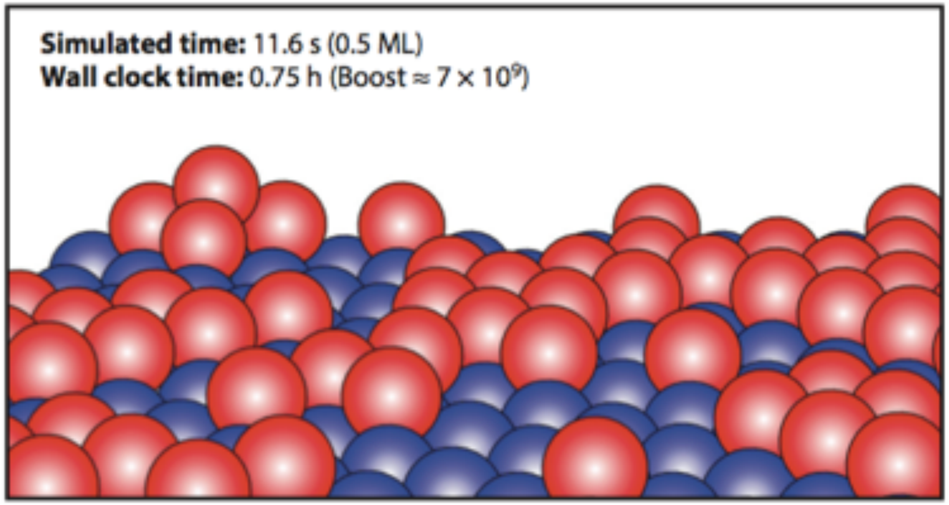
If you have many processor cores available,

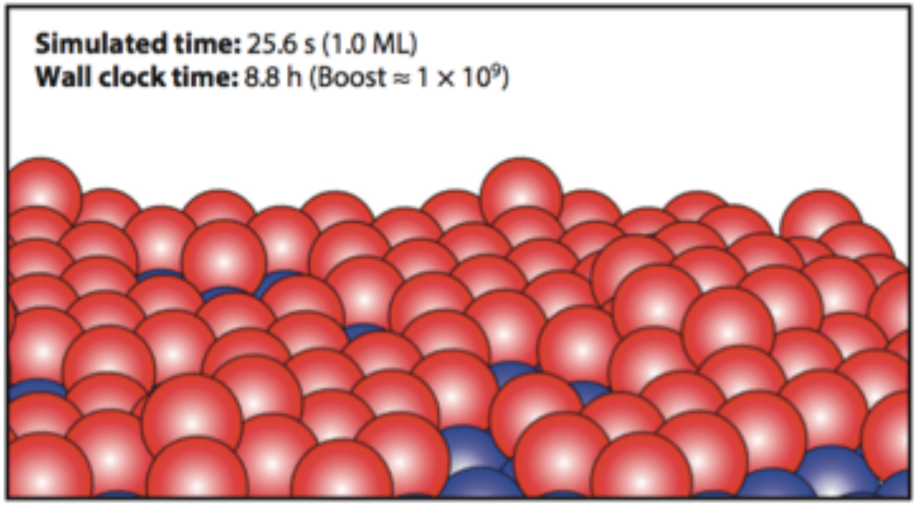
- spawn a new TAD sub-simulation as soon as a transition is seen
- use the retro-diction from T_{high} to T_{low} to assign a time when to expect this event
- branching continues until/unless it has become clear that this transition is **not** the one to be accepted (at T_{low}).



R.J. Zamora, B.P. Uberuaga, D. Perez, A.F. Voter, Ann. Rev. Chem. Biomol. Eng. **7** (2016)

Example: Vapor-phase epitaxy of Cu on Ag(100)





It took ~1 year to grow 1.5 ML with serial TAD.

(Sprague et al, Phys. Rev. B 66, 205415 (2002))