Kinetic Monte Carlo modelling of semiconductor growth

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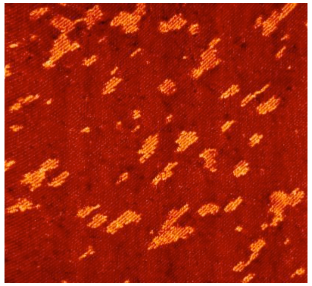
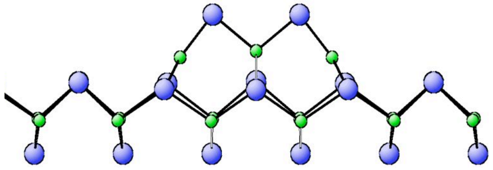
Time and length scales

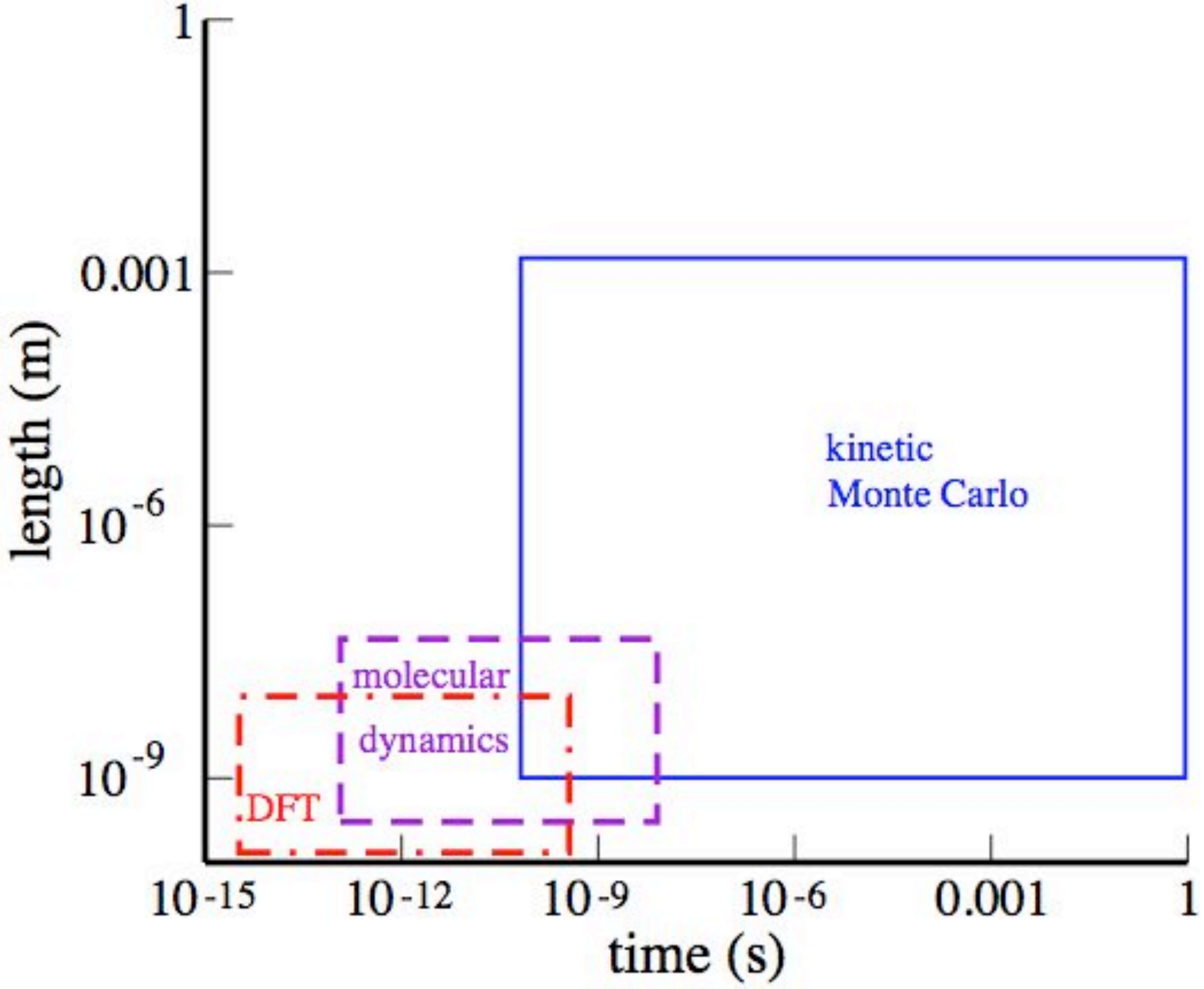
morphology

2D islands



surface reconstruction

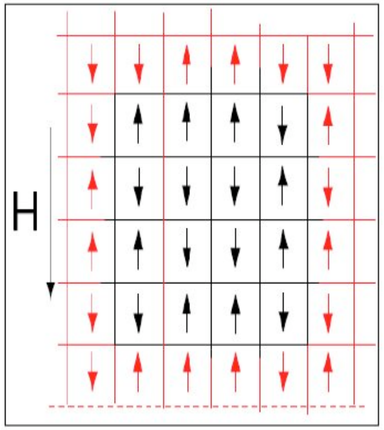




Methods of Statistical Physics

Discrete models in Statistical Physics

- Ising model (magnetism)

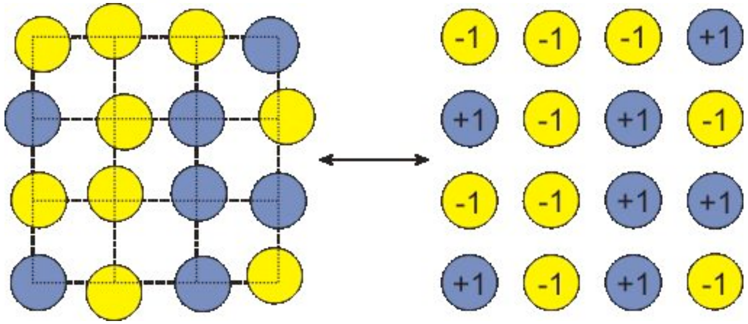


$$H(s) = -J_q \sum_i \sum_{j \in n(i)} s_i s_j - \mu_B B \sum_i s_i$$

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

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

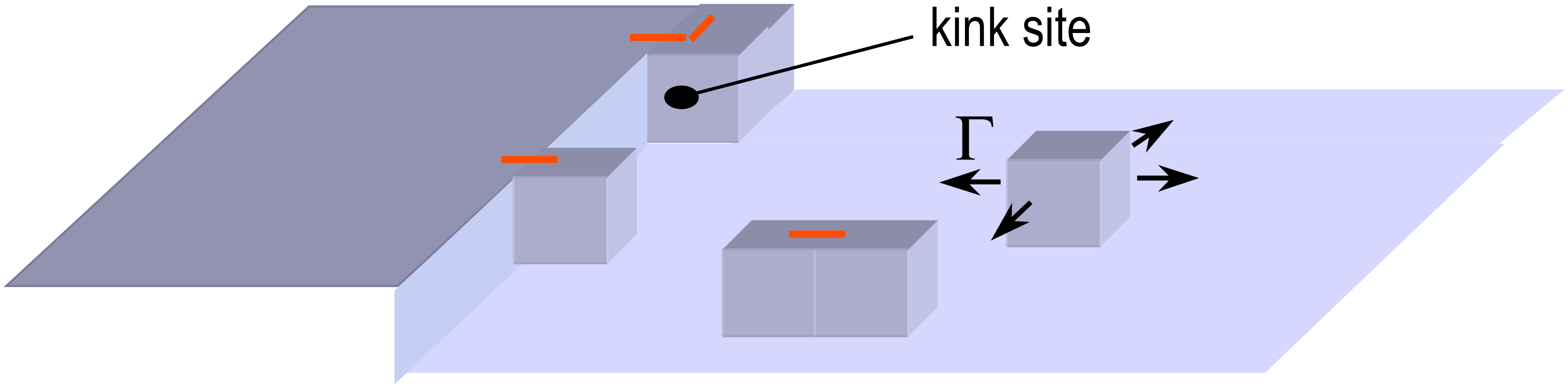
- **Goal:**
  Calculation of thermal averages



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

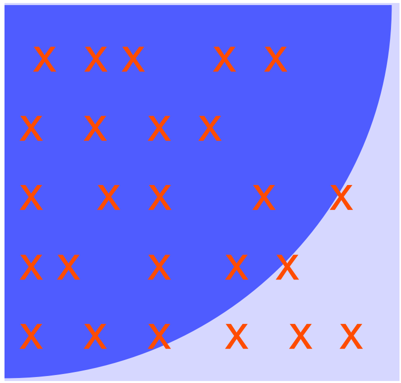
$$E = E_D + n\, E_B$$



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.

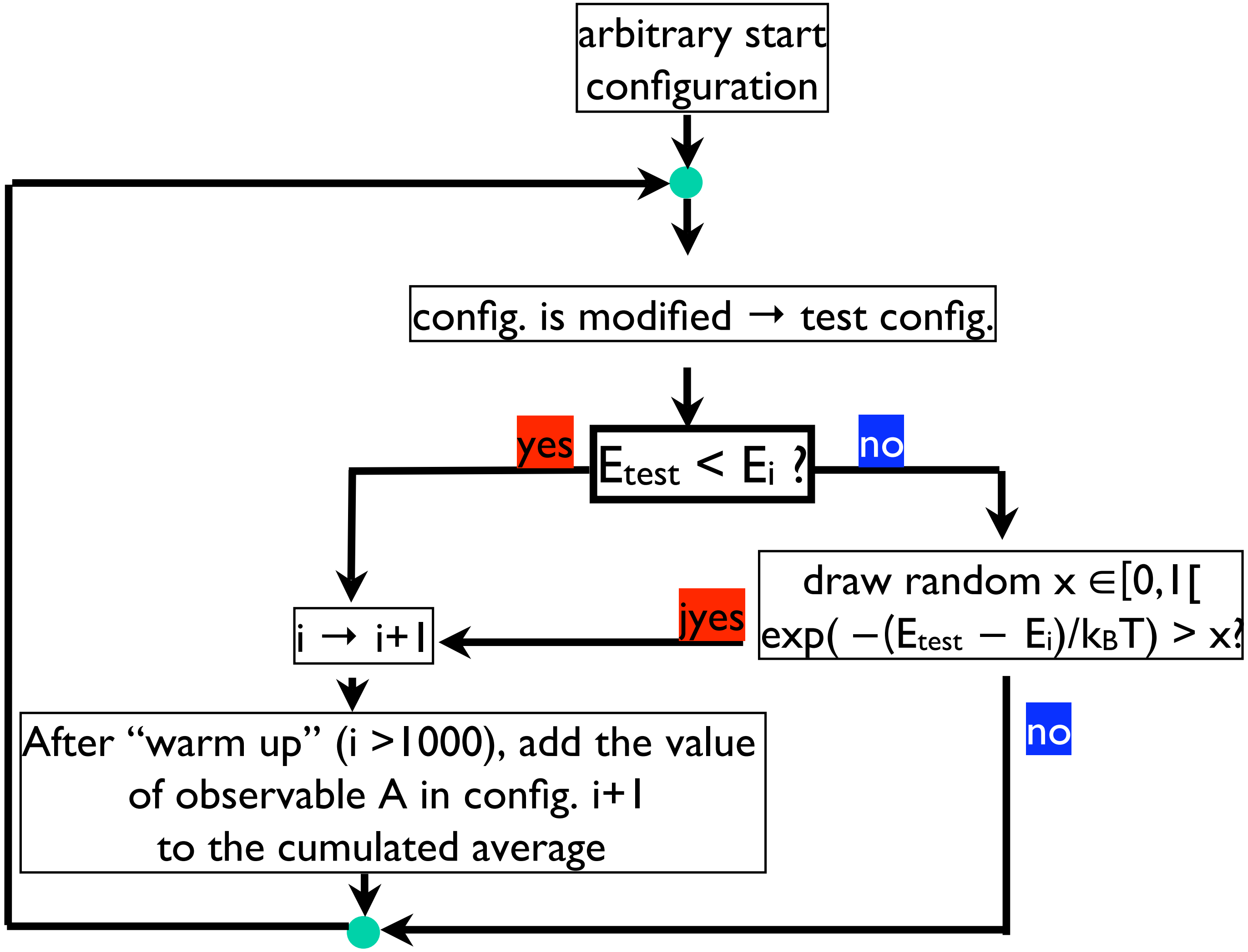
$$\pi/4 = 0.78 .. \approx 20/25 = 0.8$$



Metropolis Sampling

- **Solution:** *Importance Sampling* with $w(\mathbf{q}) = \dfrac{\exp\left(-V(\mathbf{q})/(k_B T)\right)}{Z'}$
- 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 $\langle A \rangle \approx \dfrac{1}{K} \sum_{i=1}^{K} k_i A(\mathbf{q}_i)$
- 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 so 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 $\exp\left(-\dfrac{V(\mathbf{q}_{i+1}) - V(\mathbf{q}_i)}{k_B T}\right) > \mathrm{rnd}$
  - else reject. $\mathrm{rnd} \in [0,1[$
- This assures that $\dfrac{w(\mathbf{q}_{i+1})}{w(\mathbf{q}_i)} = \exp\left(-\dfrac{V(\mathbf{q}_{i+1}) - V(\mathbf{q}_i)}{k_B T}\right)$

Metropolis algorithm



arbitrary start configuration

config. is modified → test config.

$E_{test} < E_i$?

yes

no

draw random $x \in [0,1[$

$\exp(-(E_{test} - E_i)/k_B T) > x$?

jyes

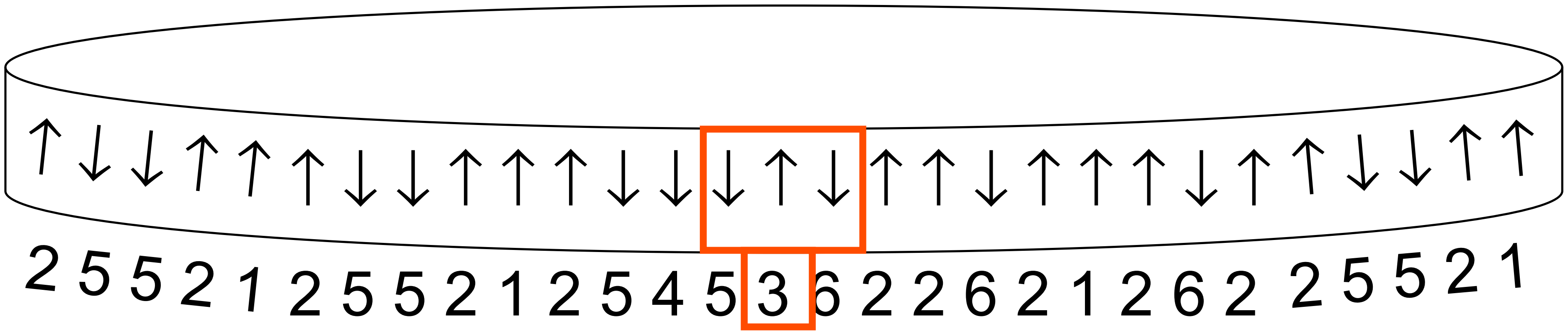
no

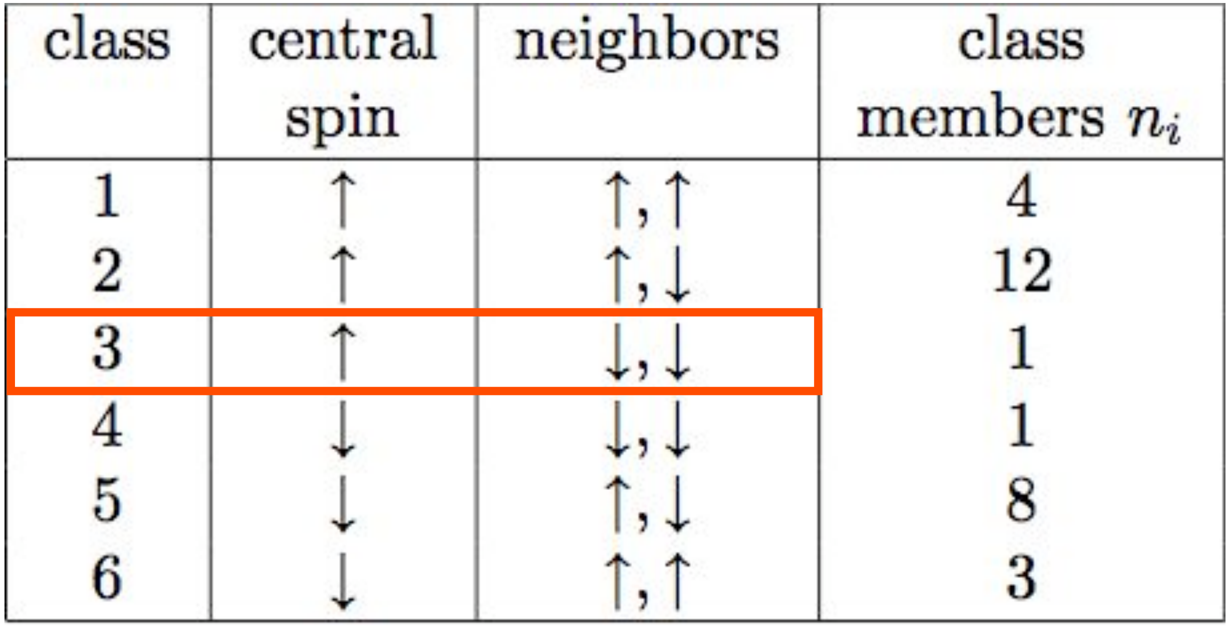
$i \rightarrow i+1$

After “warm up” (i >1000), add the value of observable A in config. i+1 to the cumulated average

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

Classification of spins according to their neighborhood

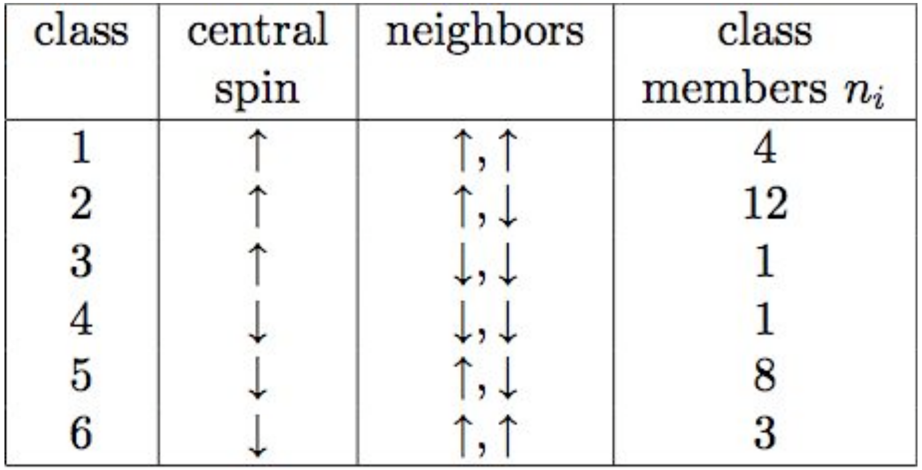




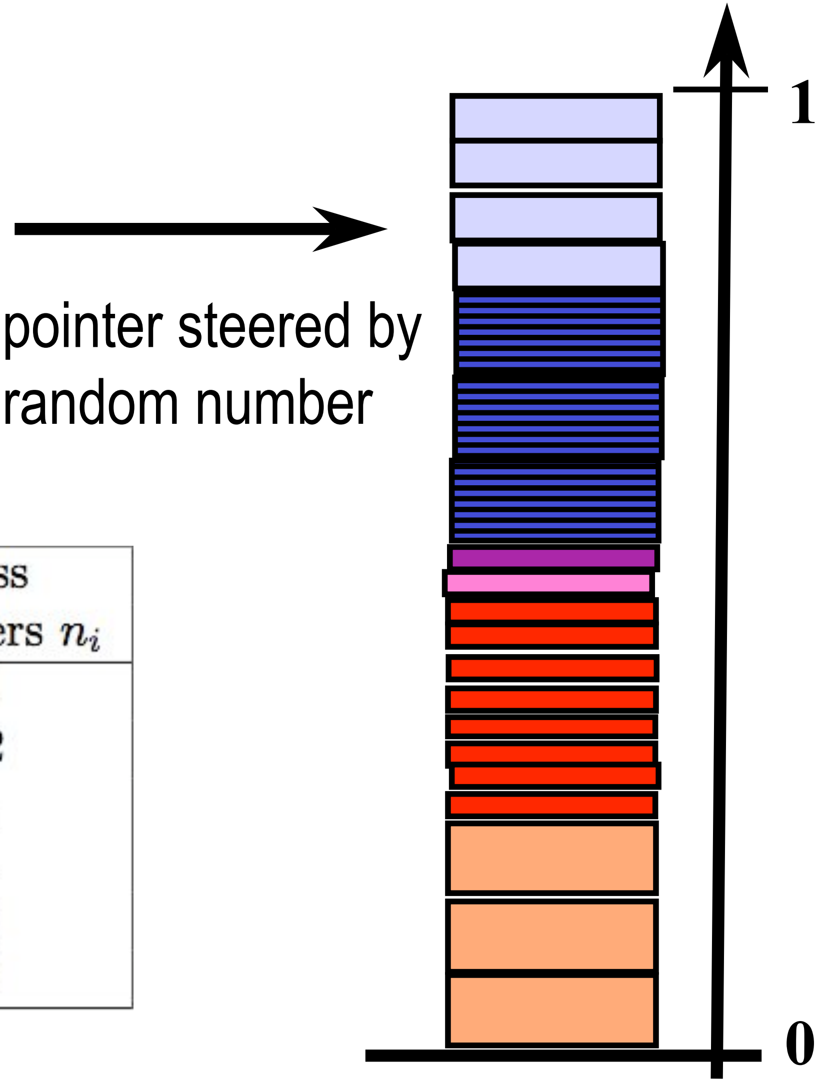
class	central spin	neighbors	class members n_i
1	↑	↑, ↑	4
2	↑	↑, ↓	12
3	↑	↓, ↓	1
4	↓	↓, ↓	1
5	↓	↑, ↓	8
6	↓	↑, ↑	3

The *N*-fold way algorithm in MC

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



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



pointer steered by random number

Simulations of non-equilibrium processes: kinetic MC

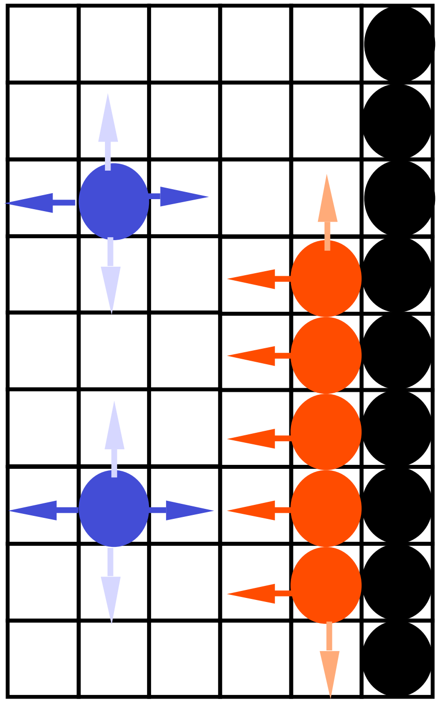
- While being aware of all processes possible at an instant of time, we need a way of (randomly) selecting one process with the appropriate relative probability.
- An internal clock keeps track of the advancement of physical time.
  - If the processes are clearly separated in time, i.e. processes are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

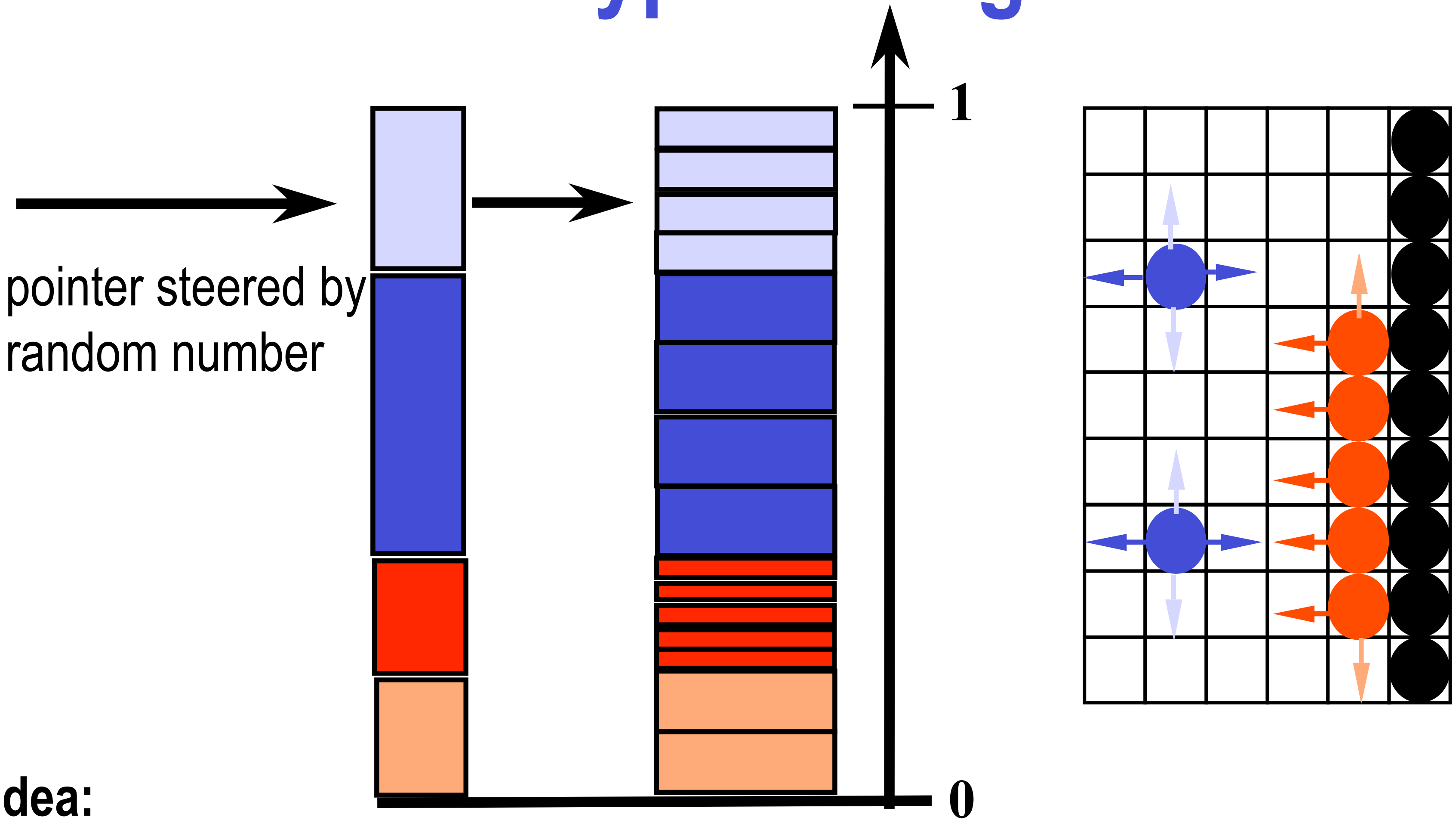
- process-type list algorithm
- binary-tree algorithm
- time-ordered-list algorithm

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

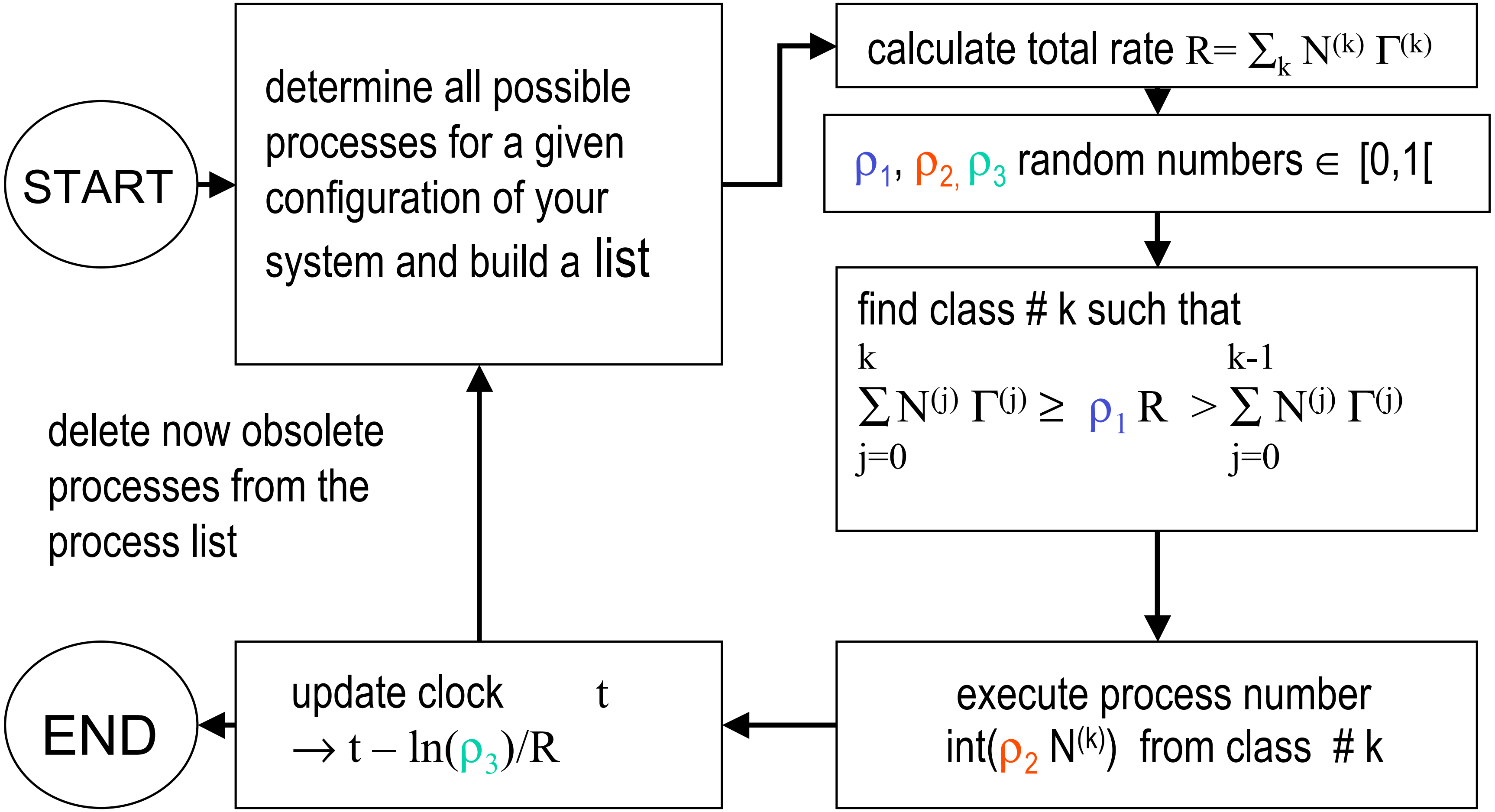


pointer steered by random number

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 a kMC algorithm



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

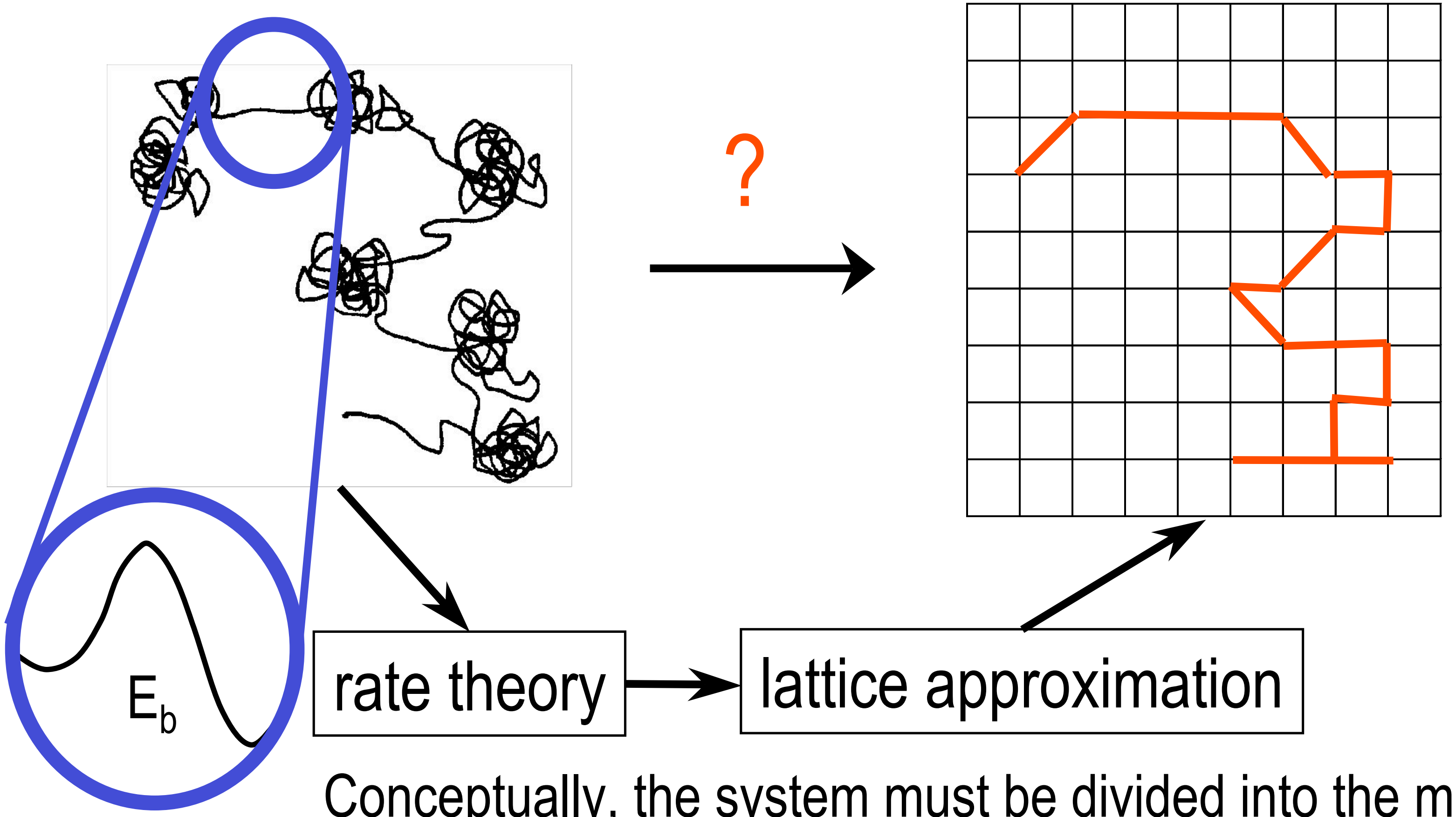
update clock t $\rightarrow t - \ln(\rho_3)/R$

delete now obsolete processes from the process list

END

From molecular dynamics to kinetic Monte Carlo

From molecular dynamics to kinetic Monte Carlo



rate theory

lattice approximation

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

Transition State Theory (1-dim)

- Kramer's rate theory

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

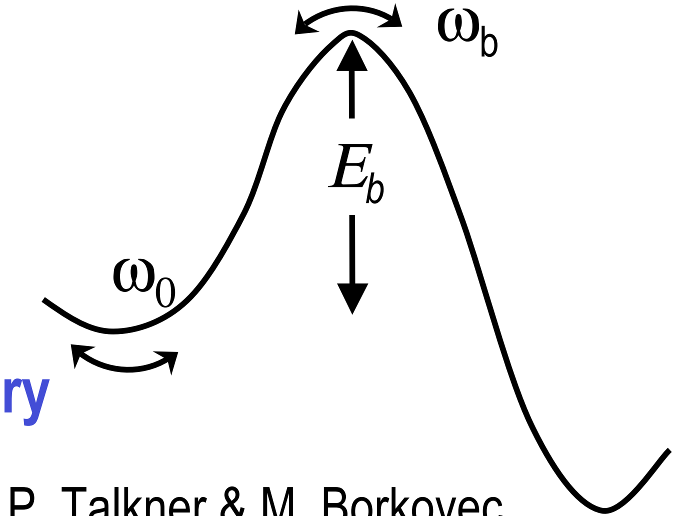
γ: friction due to coupling to the heat bath

- high-friction limit

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

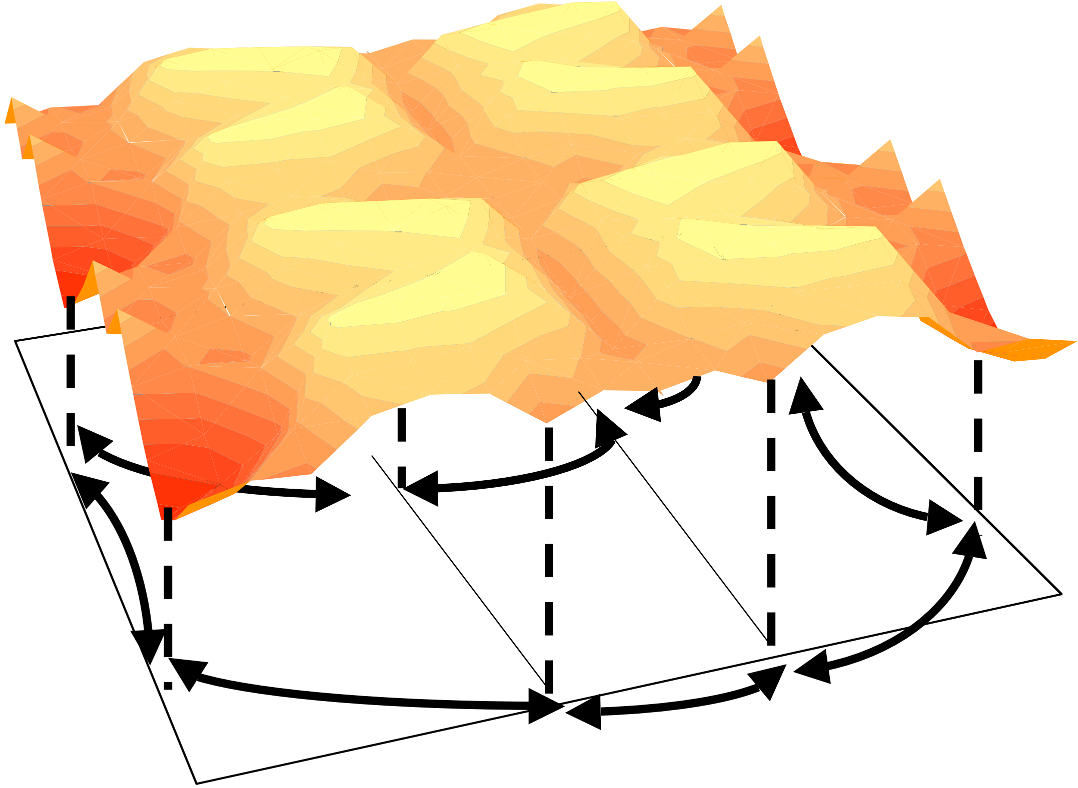
- ‘medium’ friction → **transition state theory**

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



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

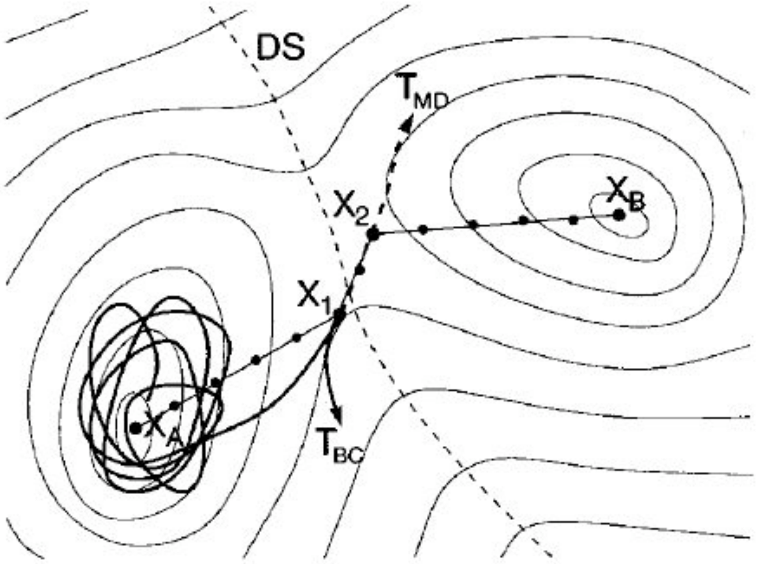
$$E(x_i,y_i) = \min_{z_i,\, c_\alpha} E_{tot}(x_i,\, y_i,\, z_i,\, c_\alpha)$$

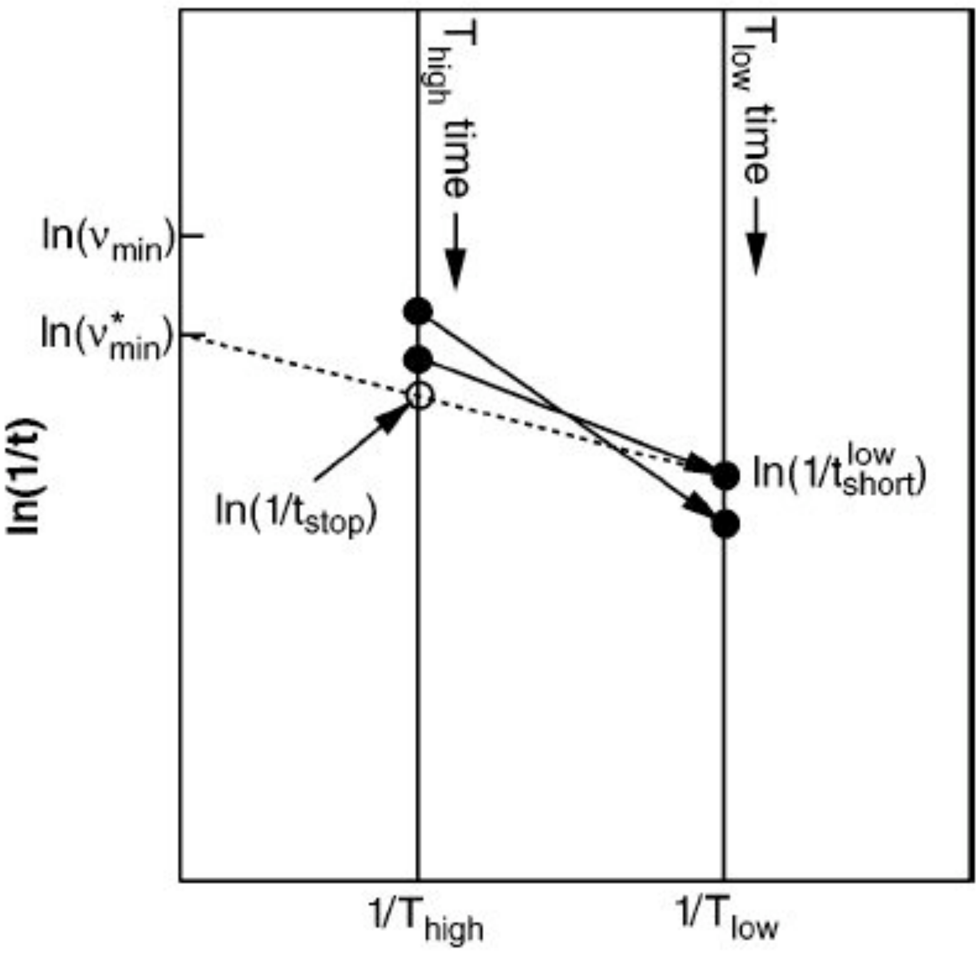
$$\Gamma = kT/h \;\; Z_{TS}/Z_i = \underset{\text{(harmonic \& classical approximation)}}{} = \Pi_N \, \nu_{k,i} \,/\Pi_{N-1} \, \nu_{k,TS} \;\; \exp(-\Delta E/kT)$$

(harmonic &
classical
approximation)

Temperature-accelerated dynamics (TAD)

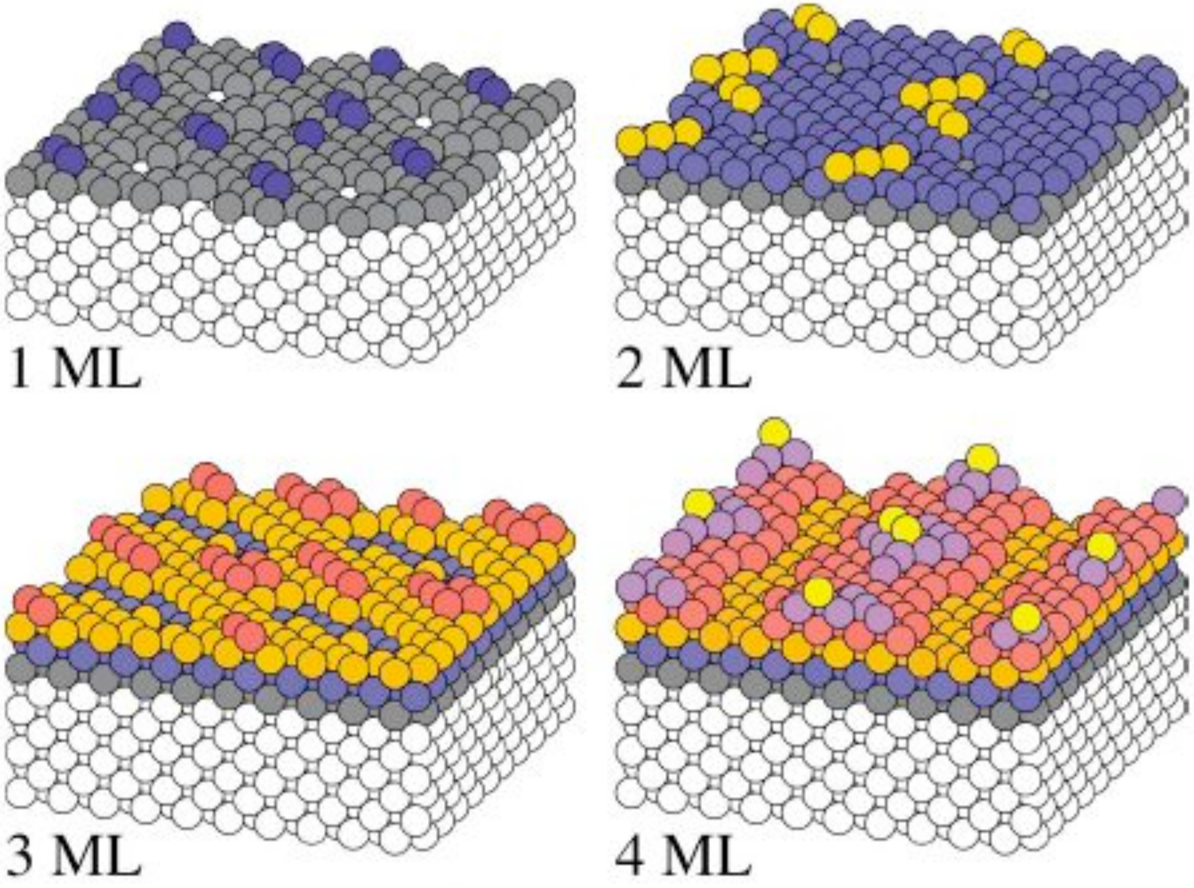
Event is observed at T_{high}, but its rate is extrapolated to T_{low} (using the TST rate law).

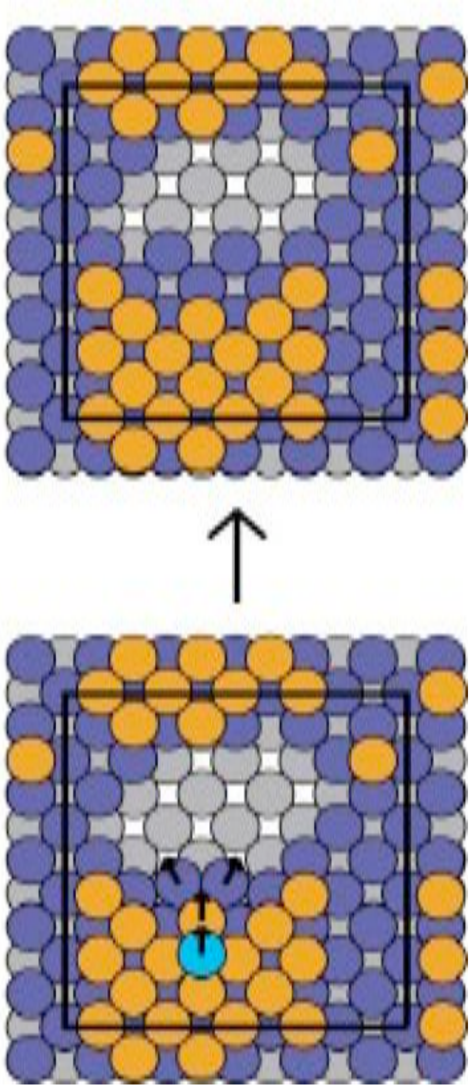




M.R. Sørensen and A.F. Voter, J. Chem. Phys. **112**, 9599 (2000)

TAD: Collective processes



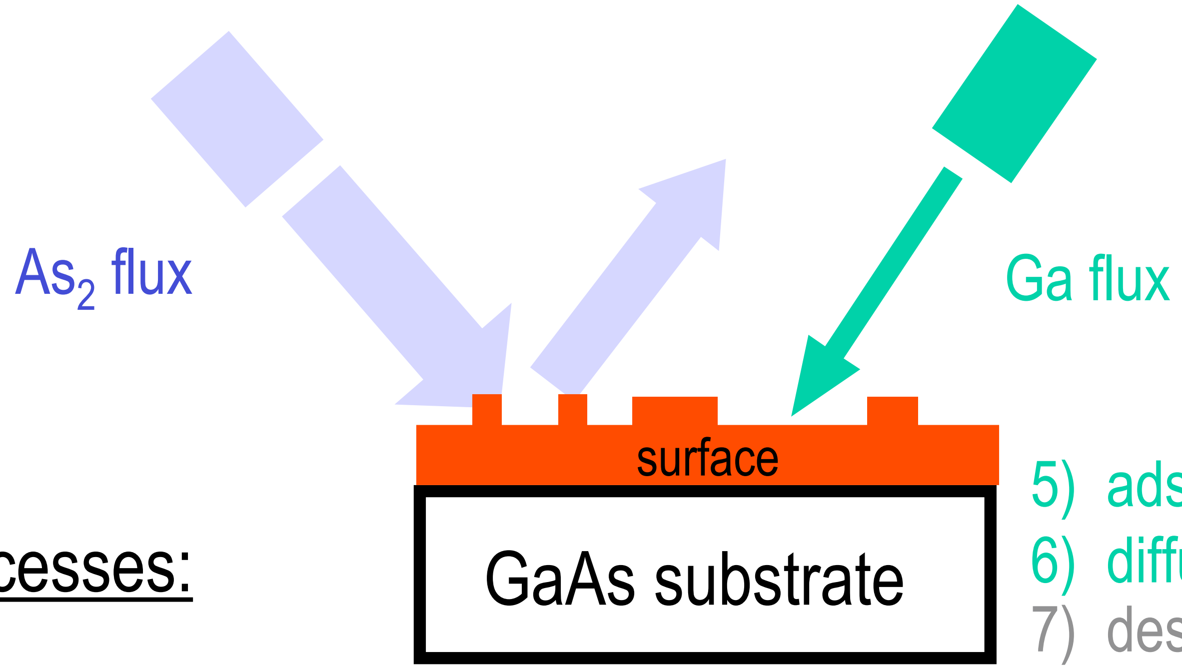


F. Montalenti, M.R. Sørensen and A.F. Voter,
Phys. Rev. Lett. **87**, 126101 (2001)

Application I:

GaAs nanowire growth

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

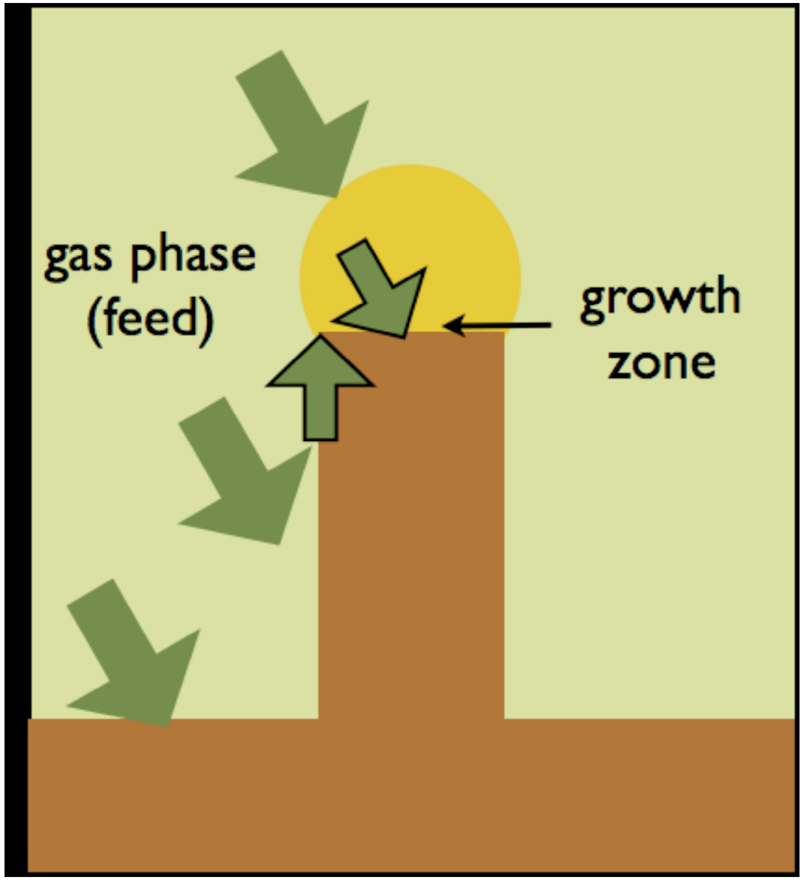
5) adsorption of Ga
6) diffusion of Ga
7) desorption of Ga

8) island nucleation
9) growth

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

Gold-catalysed nanowire growth

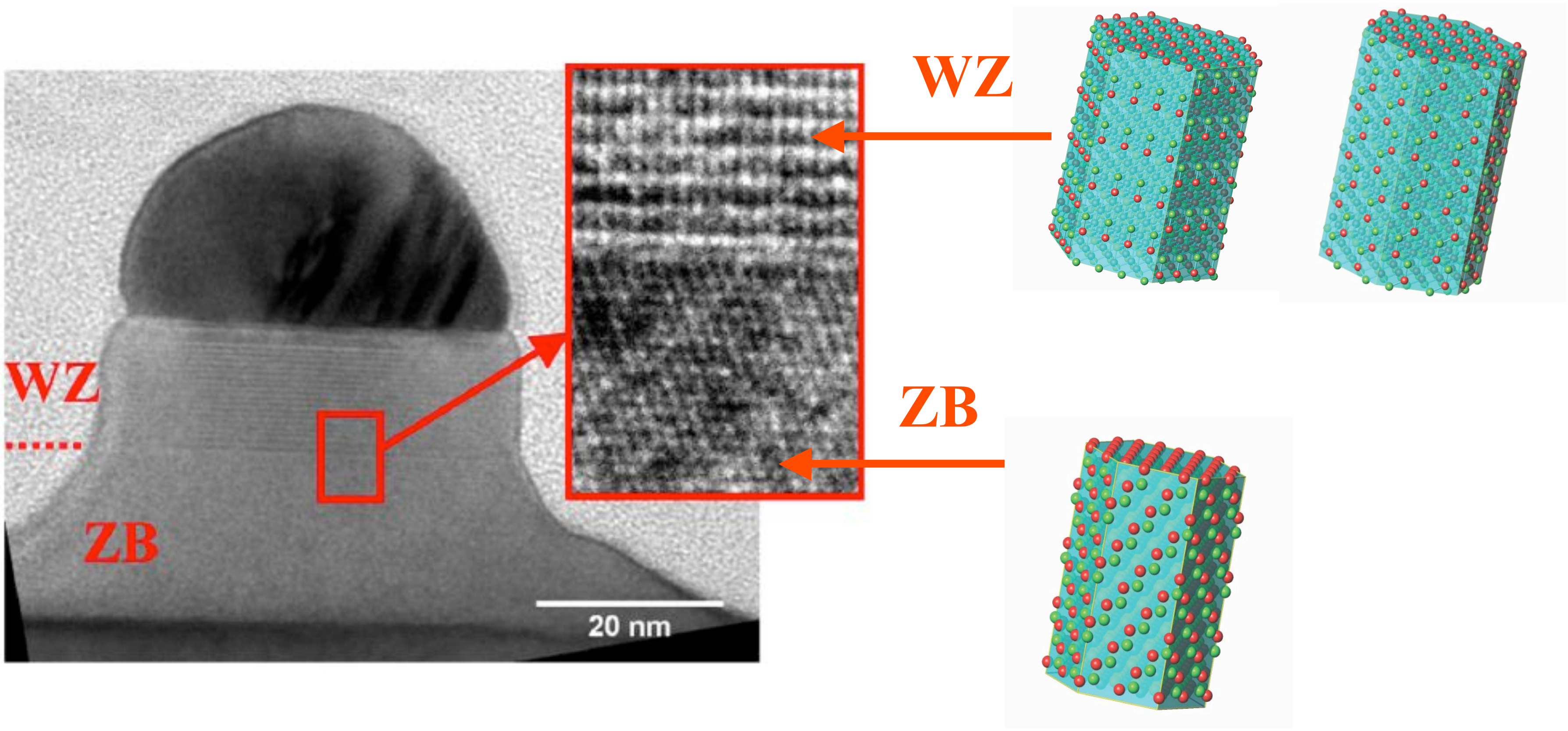
- much higher growth speed in a particular crystallographic direction [GaAs(111)B] compared to extended substrate
- liquid Au droplet used to store Ga (as Au-Ga alloy), but inefficient for As species
- role of material transport along the wire side walls ?



Polytypism in GaAs nanowires

- segments of zincblende (ZB, which is the ground state in bulk) and wurtzite (WZ) crystal structure, depending on growth conditions

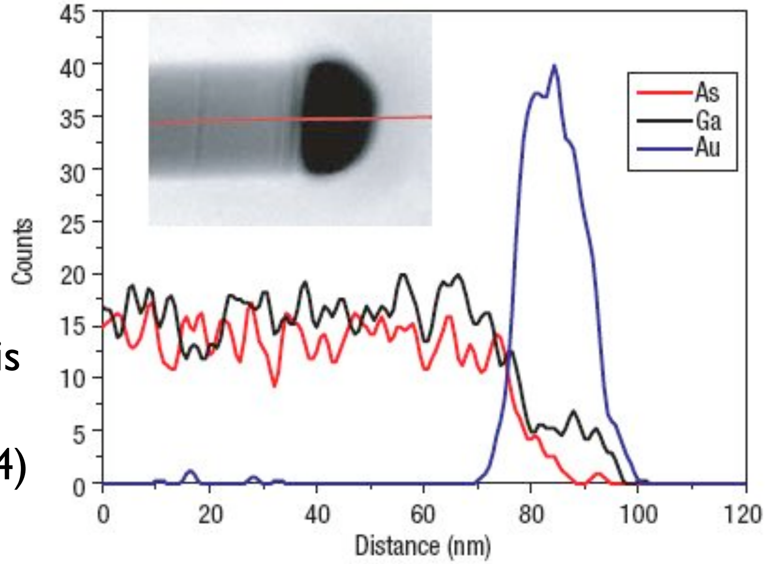
2 types of structurally different facets !



Arsenic supply to the interface

- arsenic vacancy emission into the solid

$$D_{\mathrm{V_{As}}}(T) = \Gamma_0 \exp\left(-\frac{\Delta E}{k_B T}\right)$$



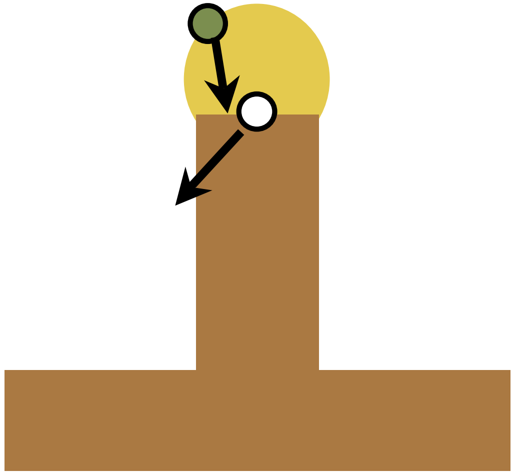
element-specific XEDS analysis
A.I. Persson et al.,
Nature Materials **3**, 667 (2004)

or

- diffusion of As dissolved in the liquid

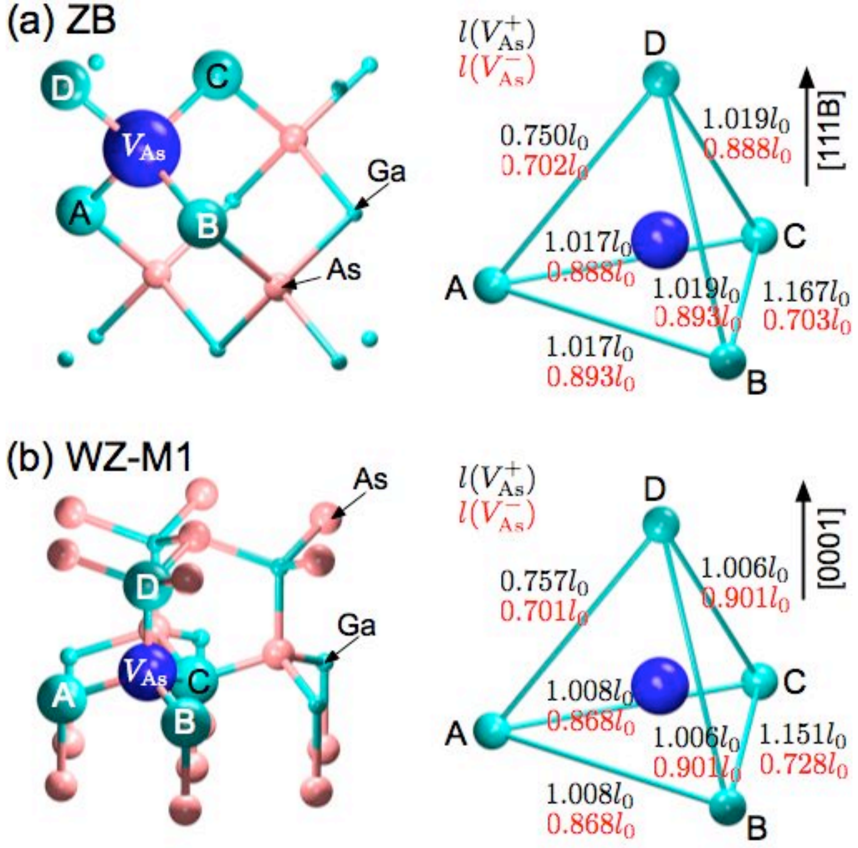
Stokes-Einstein relation

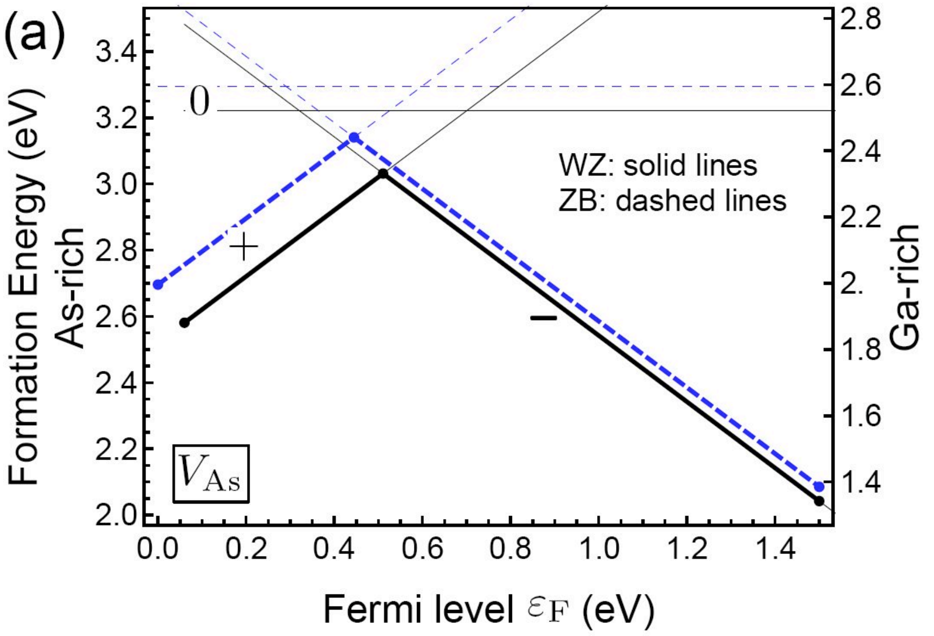
$$D_{\mathrm{As@Au}}(T) = \frac{k_B T}{6\pi r_{\mathrm{As}} \eta_{\mathrm{Au}}(T)}$$



Arsenic vacancies

- unstable as neutral vacancy (a so-called “negative-U” system)
- strong contraction of the vacancy tetrahedron for negatively charged vacancy, as bonding linear combination of Ga dangling bonds becomes occupied

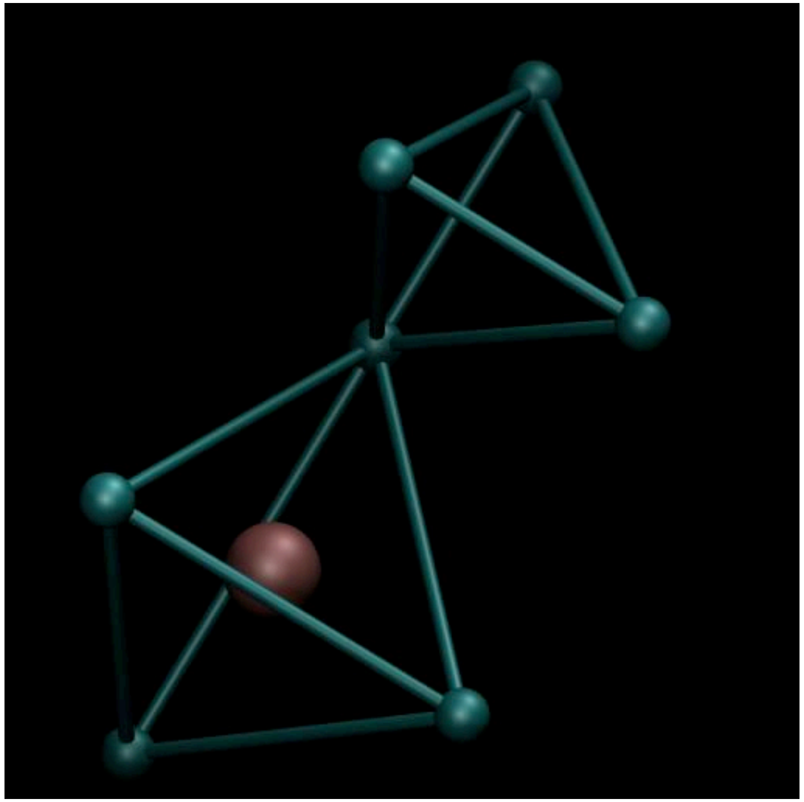


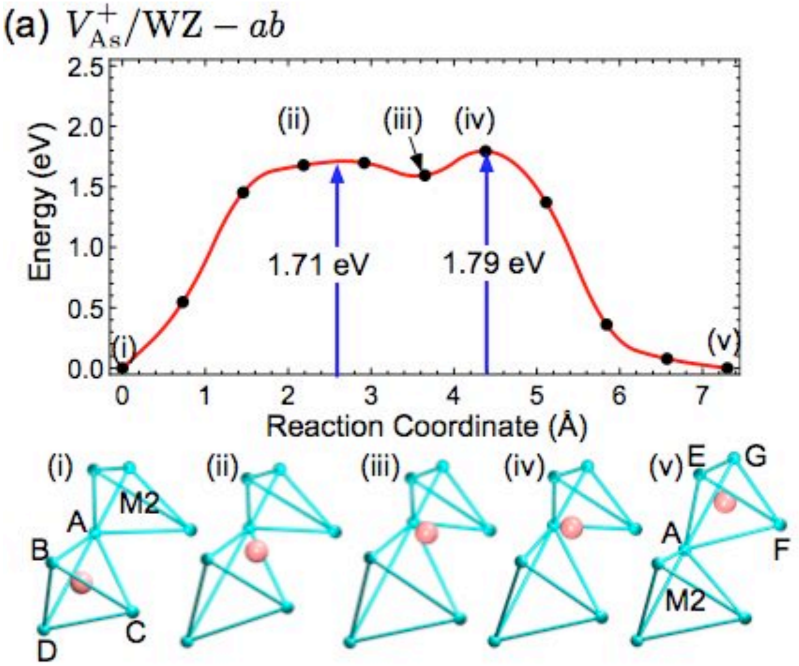


Y.A. Du, S. Sakong and P. Kratzer, PRB **87**, 075308 (2013)

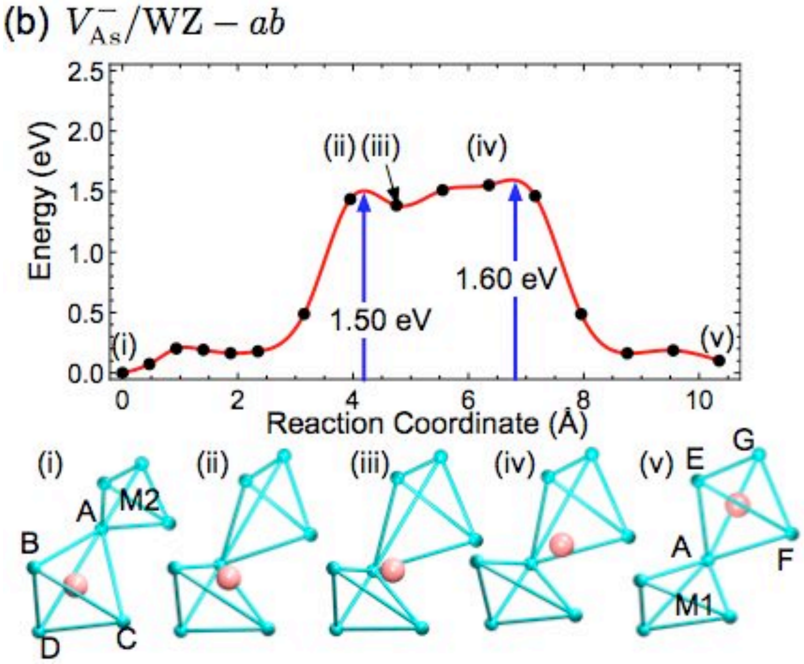
V_{As} diffusion in wurtzite

- in wurtzite *ab*-plane, barriers are lower as compared to zincblende case





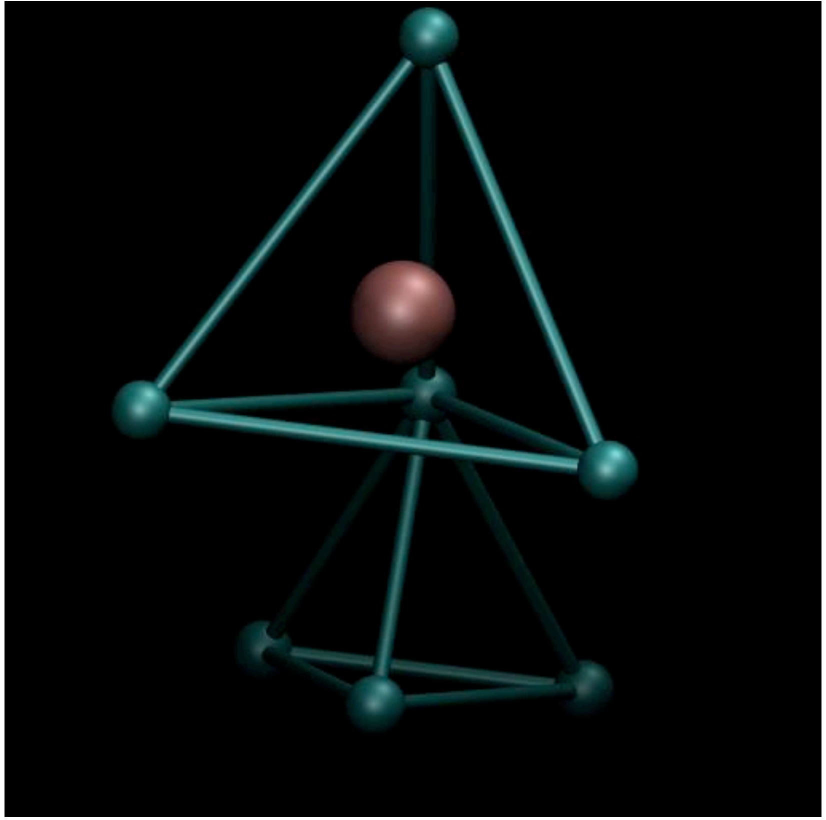
(a) $V_{As}^{+}/\mathrm{WZ}-ab$

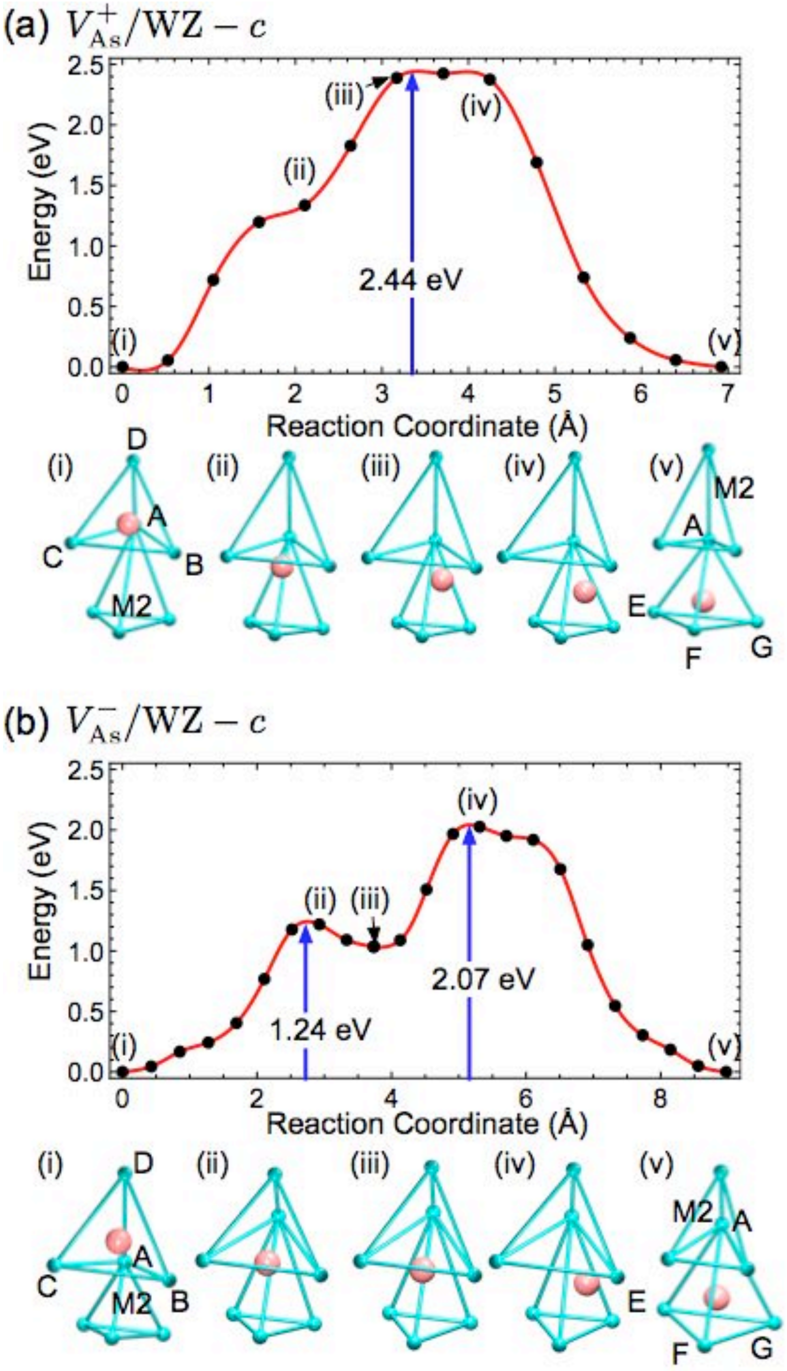


(b) $V_{As}^{-}/\mathrm{WZ}-ab$

V_{As} diffusion in wurtzite

- along the c-axis, V_{As} needs to go a detour to avoid crossing the Ga-Ga coordination line → higher barrier than in zincblende

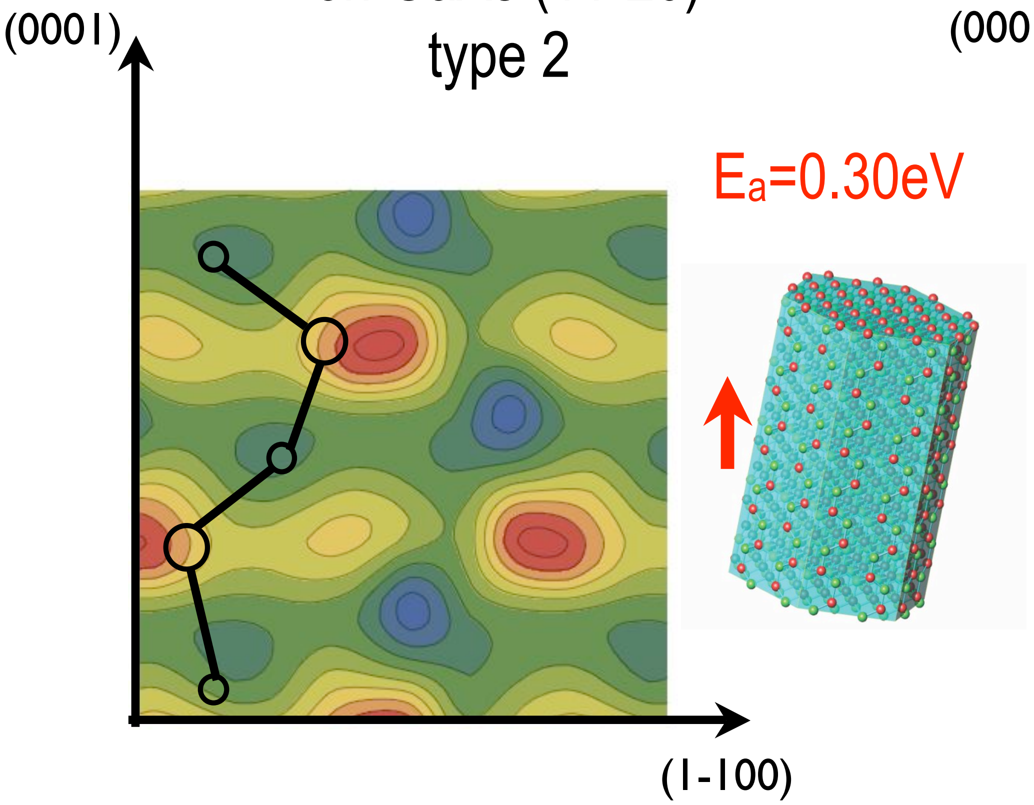




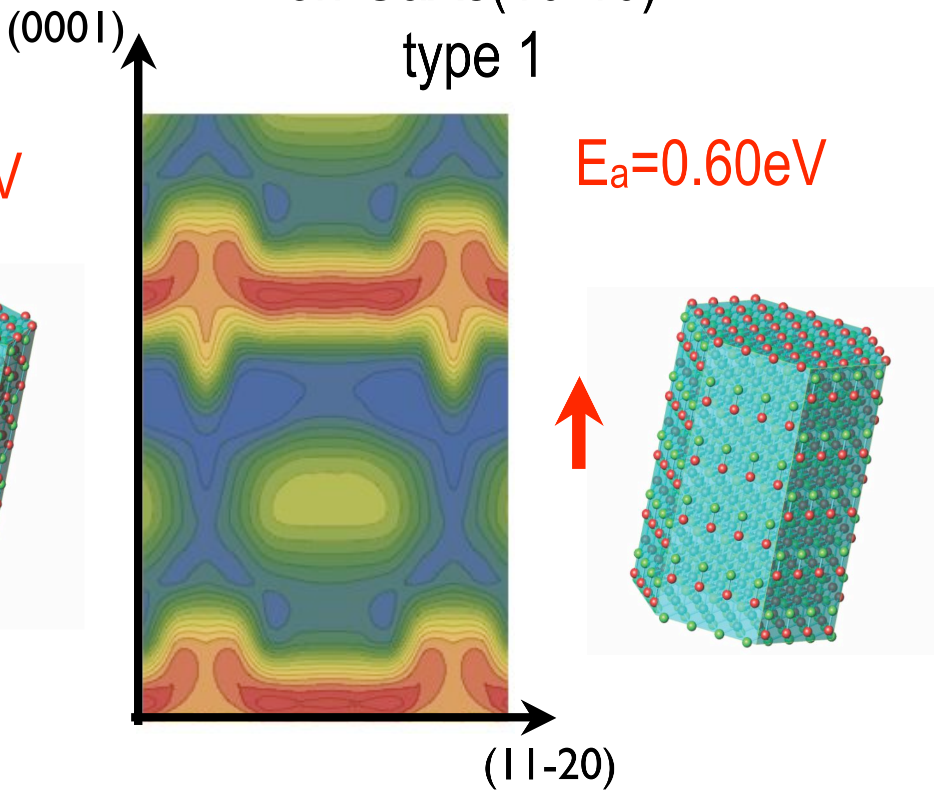
Facet-dependent Ga diffusion

potential energy surface for Ga adatom

on GaAs (11-20)
type 2



on GaAs(10-10)
type 1

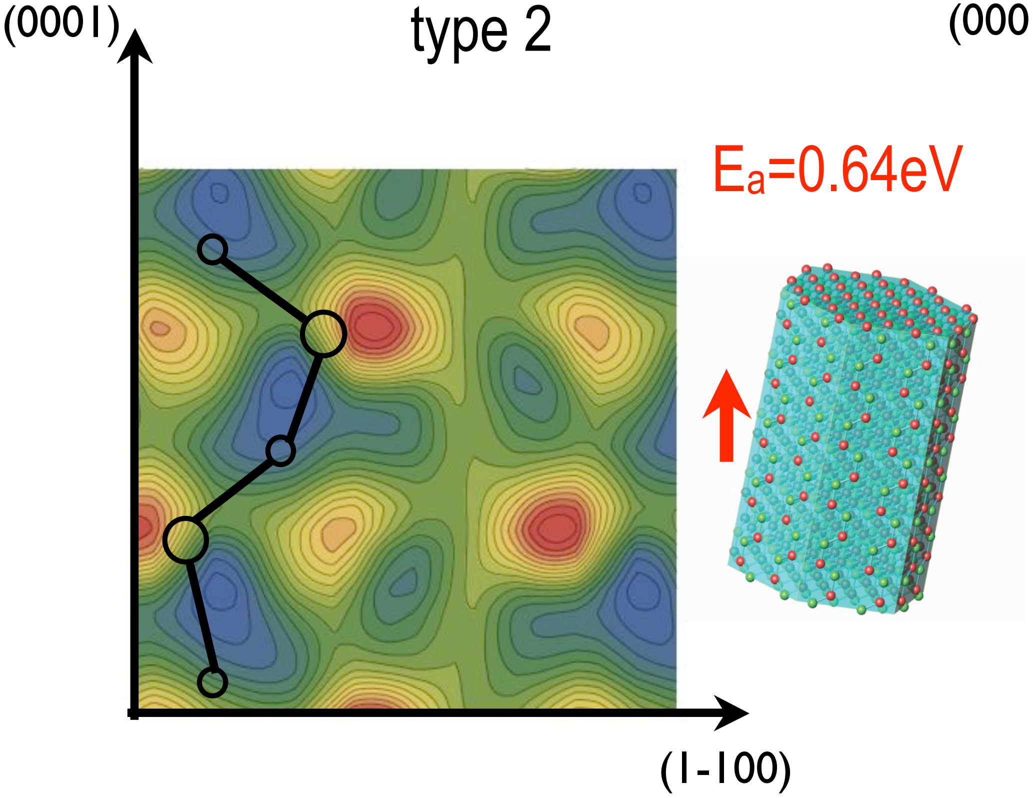


→ type 2 wurtzite wires support **faster** diffusion on the side wall.

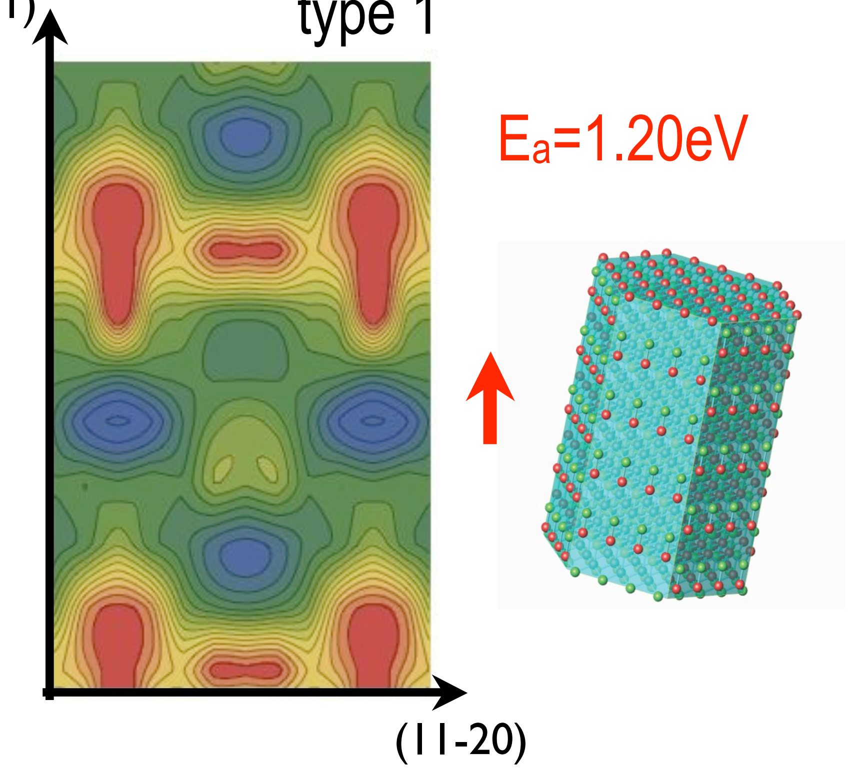
As diffusion is much slower !

potential energy surface for As adatom

on GaAs (11-20)
type 2



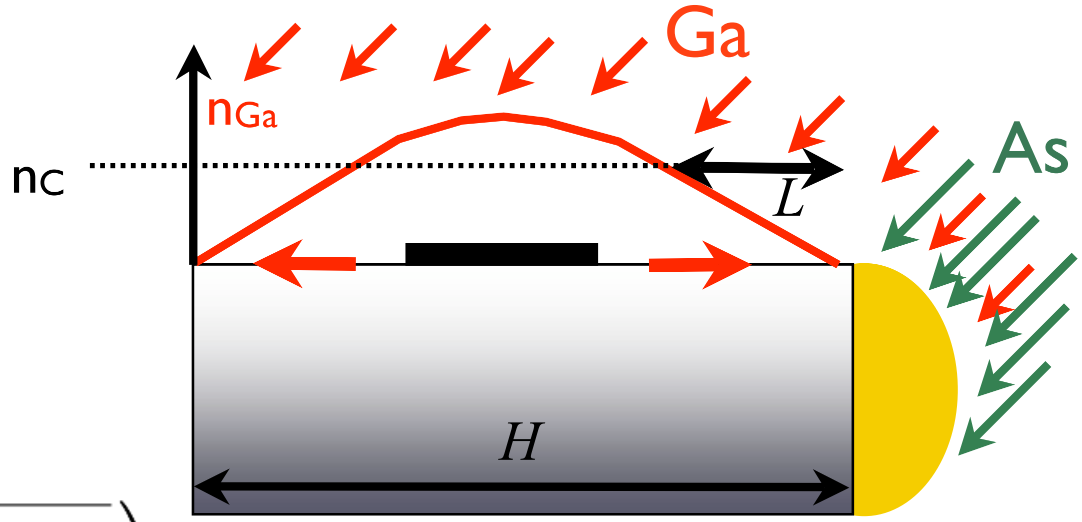
on GaAs(10-10)
type 1



→ It is easier to supply arsenic to the growth zone via **direct impingement** on the Au particle, rather than via diffusion on the side facets.

Side wall nucleation and radial growth

- type-II wires: immobile surface GaAs species leads to nucleation
- type-I wires: critical nucleus of more than one Ga atom (+ some As), critical adatom density n_C



$$L = \frac{H}{2}\left(1 - \sqrt{1 - \frac{16 n_c^{1/2} D(T)}{H^2 a_0^2 F_{\mathrm{Ga}} \sin\theta}}\right)$$

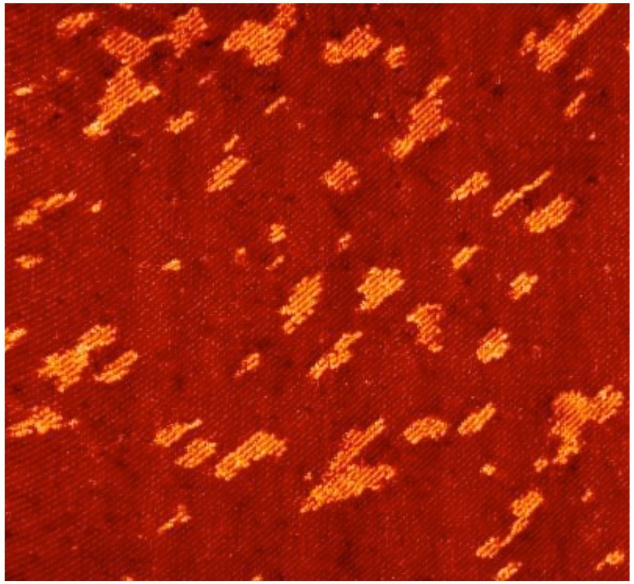
$D = 2\times10^{-6}$ cm^2/s; $H = 80$ µm
$\Rightarrow L = 22$ µm

- Tapering of the wires after sidewall nucleation if L exceeds the collection length

V. Pankoke, S. Sakong and P. Kratzer, PRB **86**, 085425 (2012)

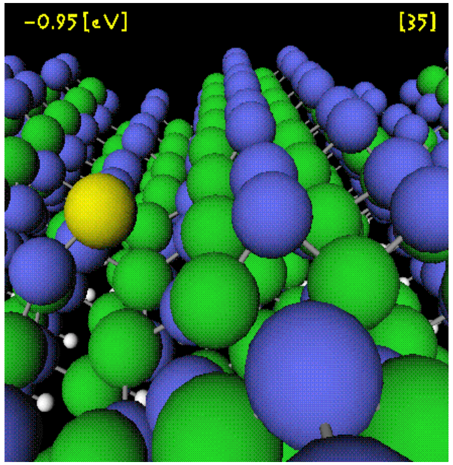
Application II:

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



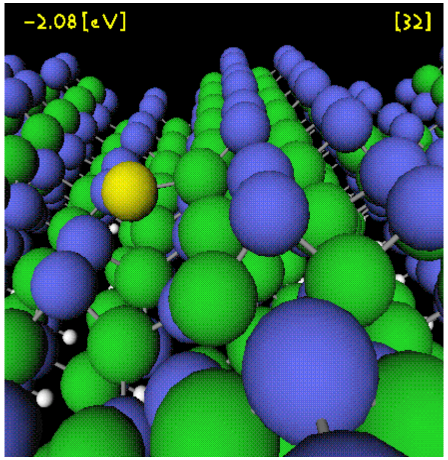
Rates from first-principles calculations

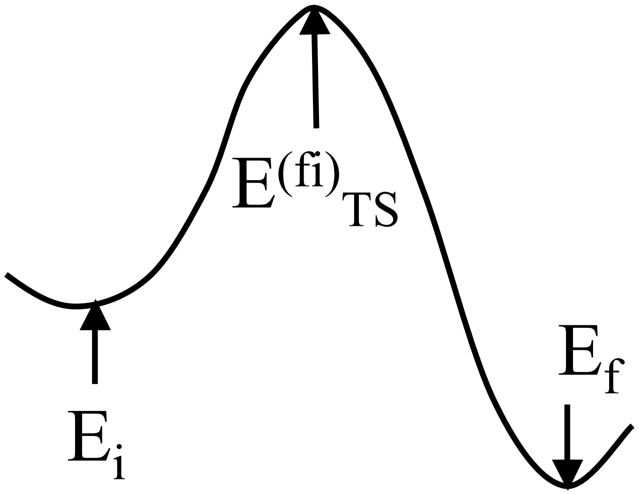
$$\Gamma^{(k)} = W(f,i) = \Gamma^{(fi)}_0 \exp(-(E^{(fi)}_{TS} - E_i)/kT)$$



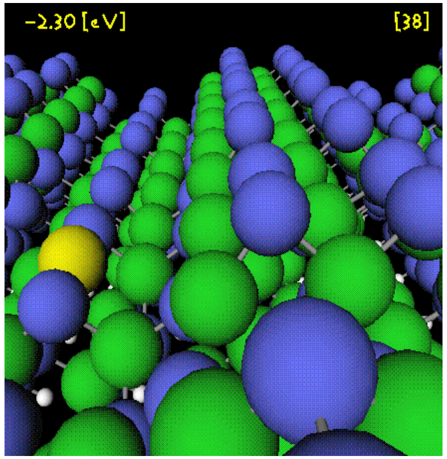
transition state

initial state



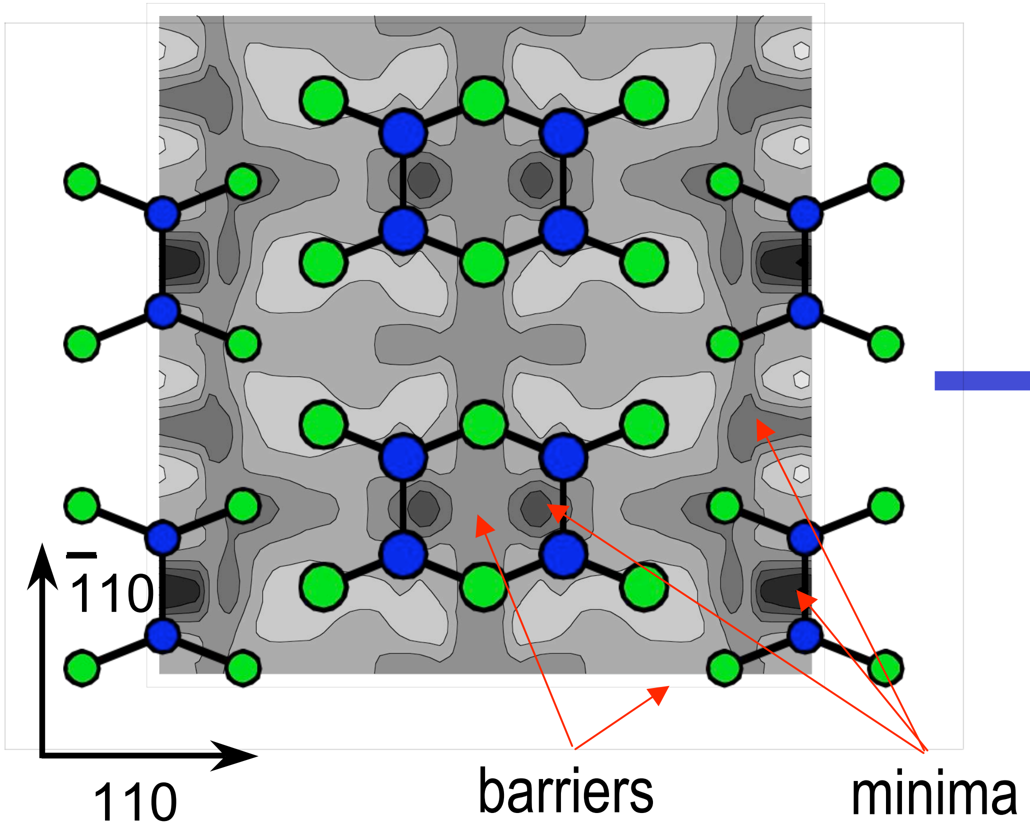


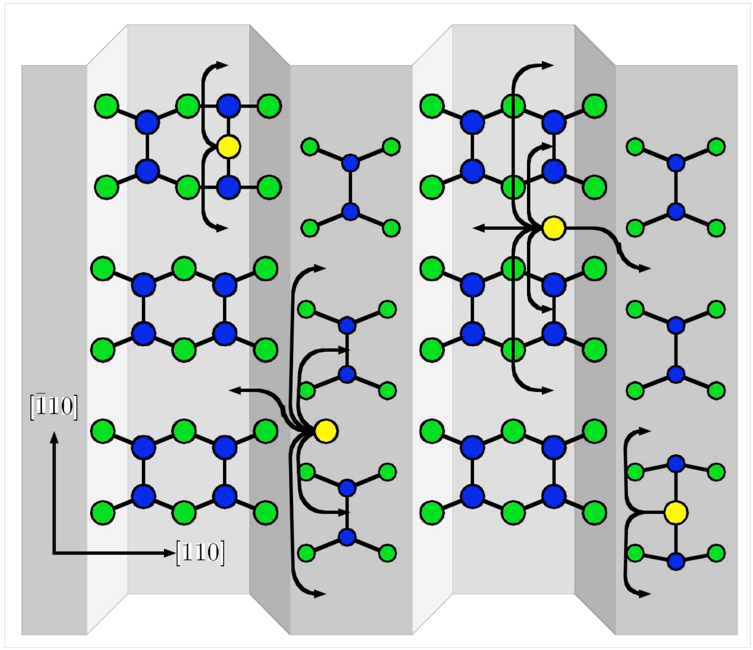
final state



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

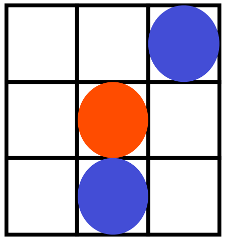
PES from DFT calculations → network of hops





kMC with explicit list of process types

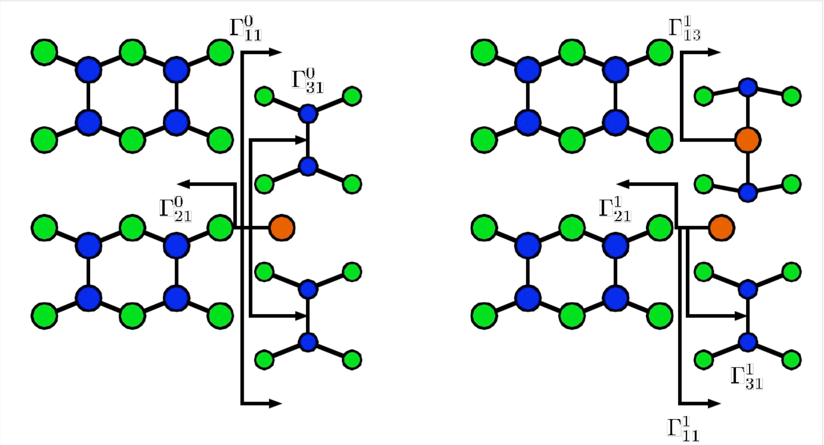
Voter's lattice kMC:



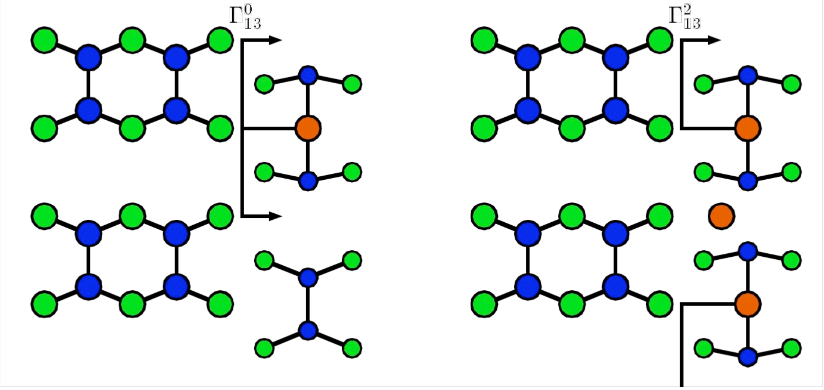
A.F. Voter PRB **34**, 6819 (1986)

- 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:

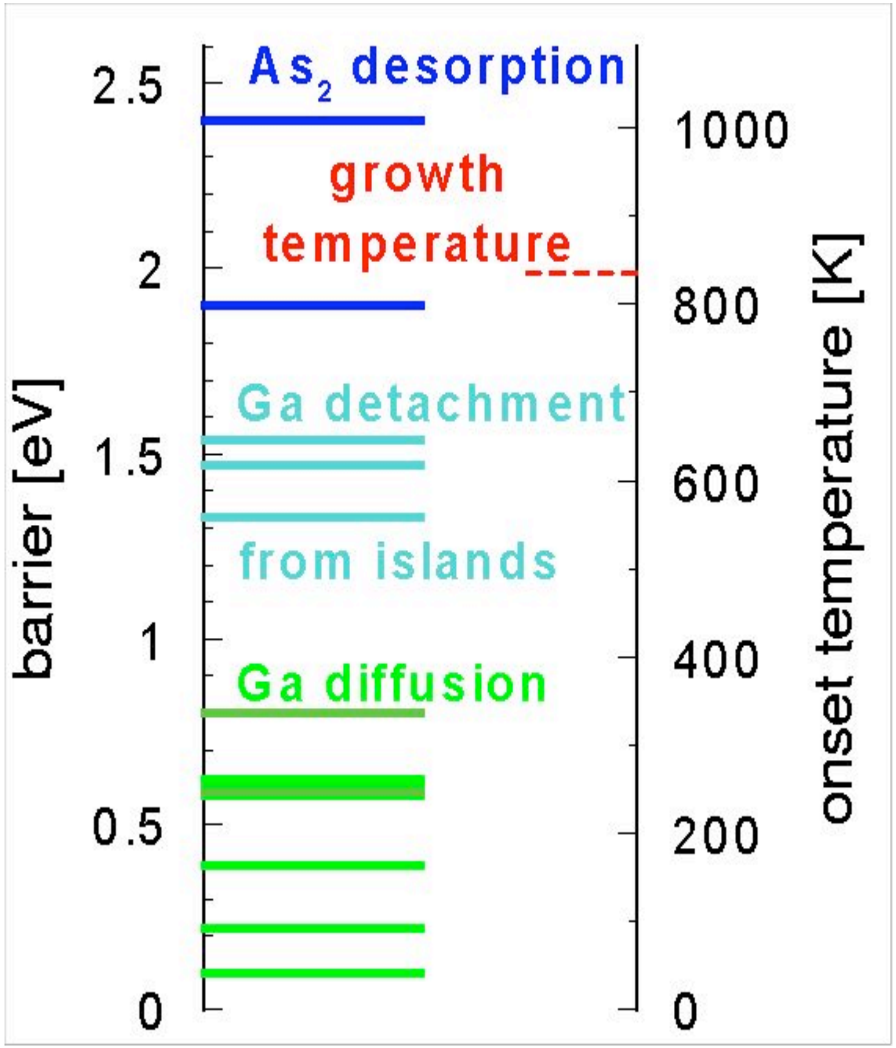


possible hops in the trench... .. modified rates due to neighbors.

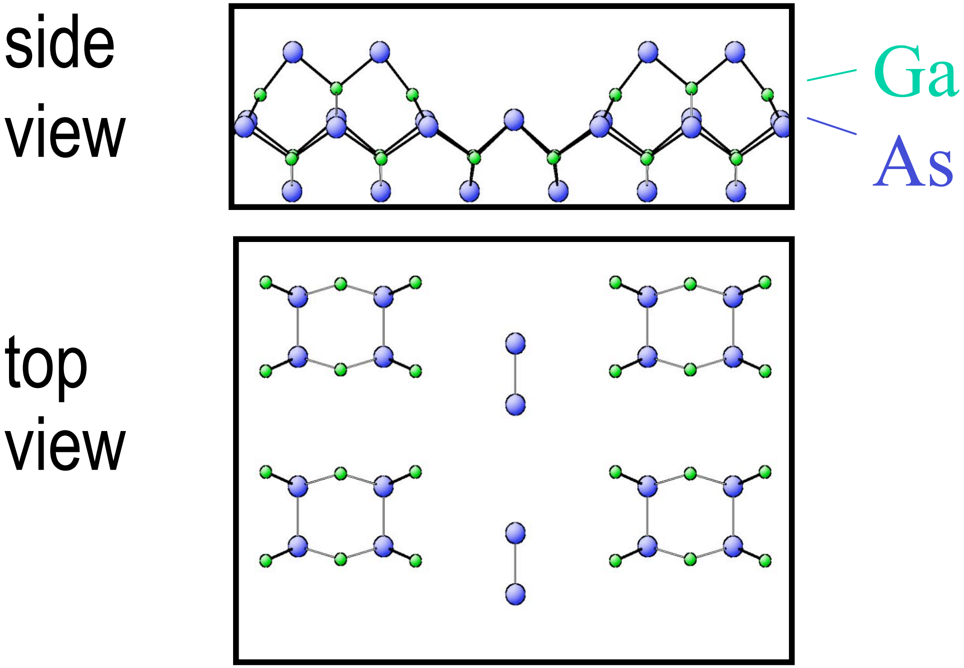


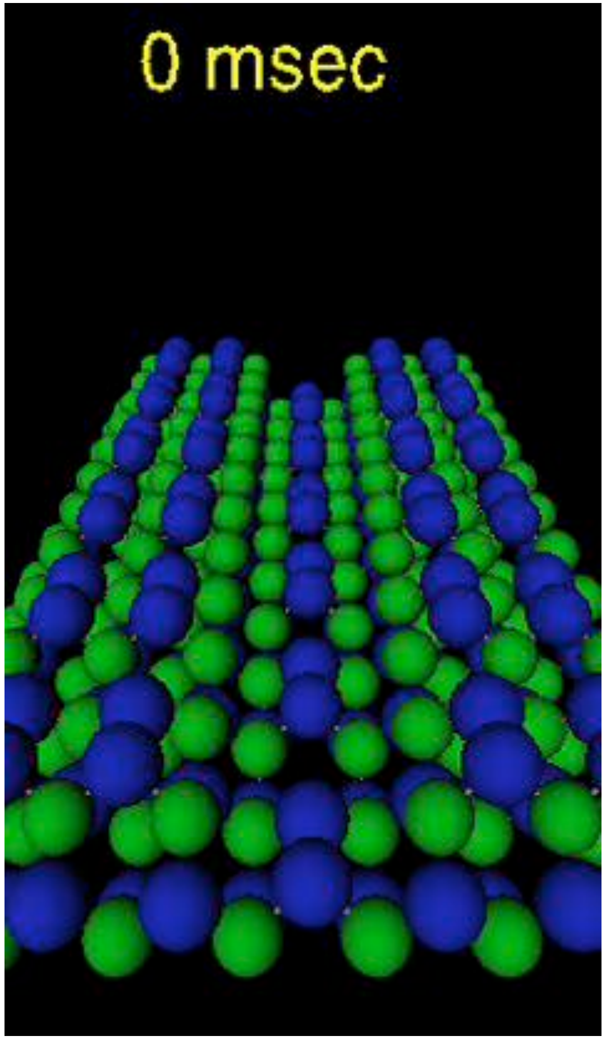
kinetic Monte Carlo simulations for GaAs epitaxy

- 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)



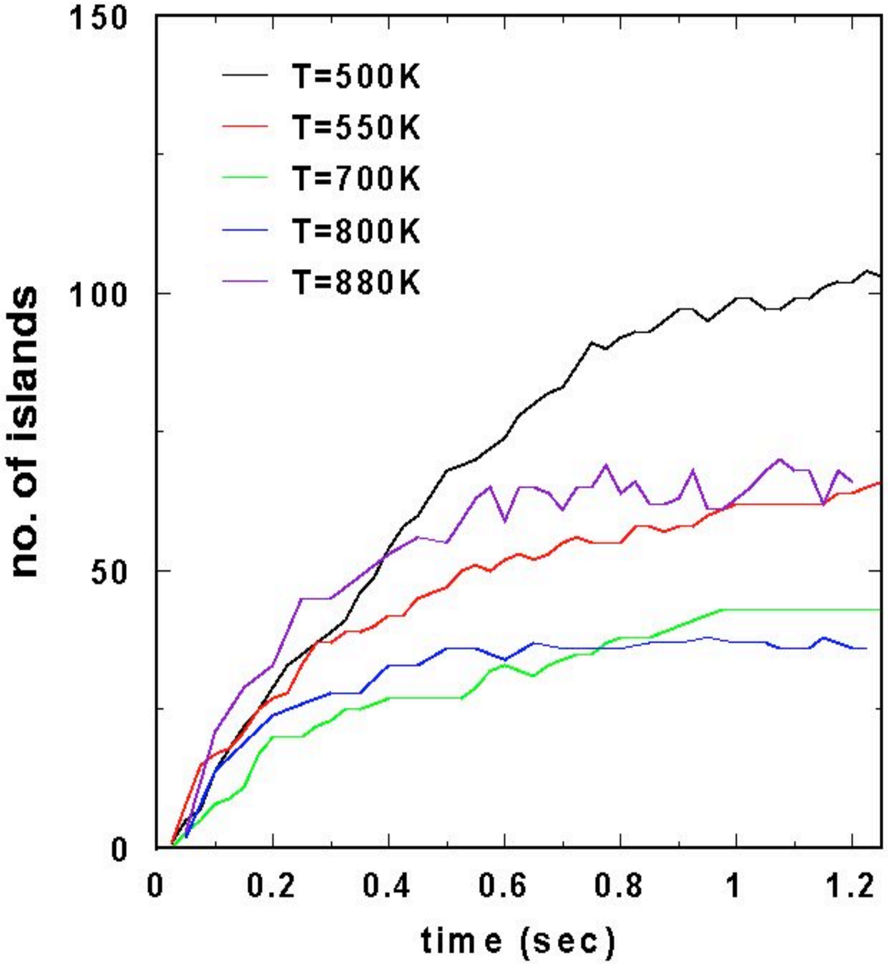
kinetics of island nucleation and growth

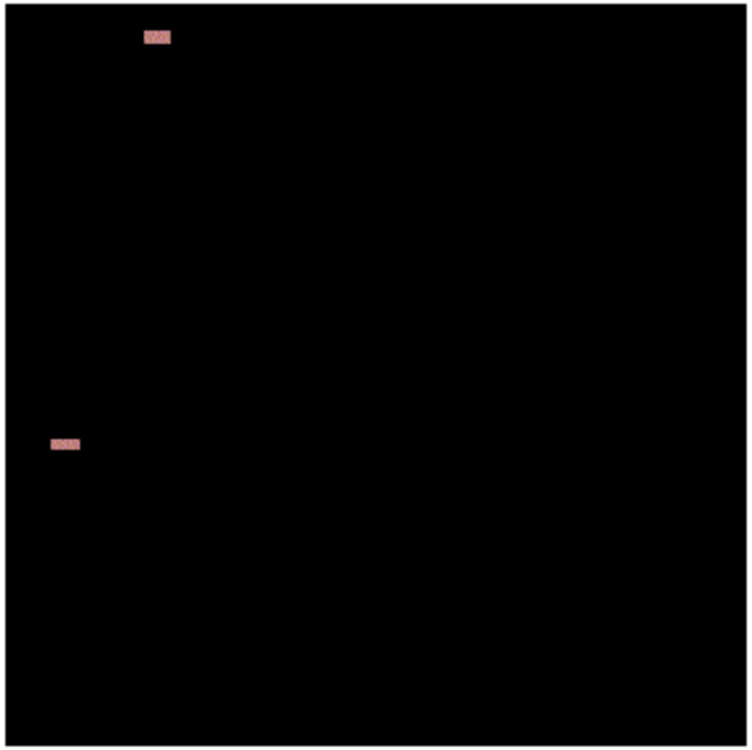




1/60 of the full simulation cell
As_2 pressure = 0.85 x 10^{-8} bar
Ga deposition rate = 0.1 ML/s
T = 700 K

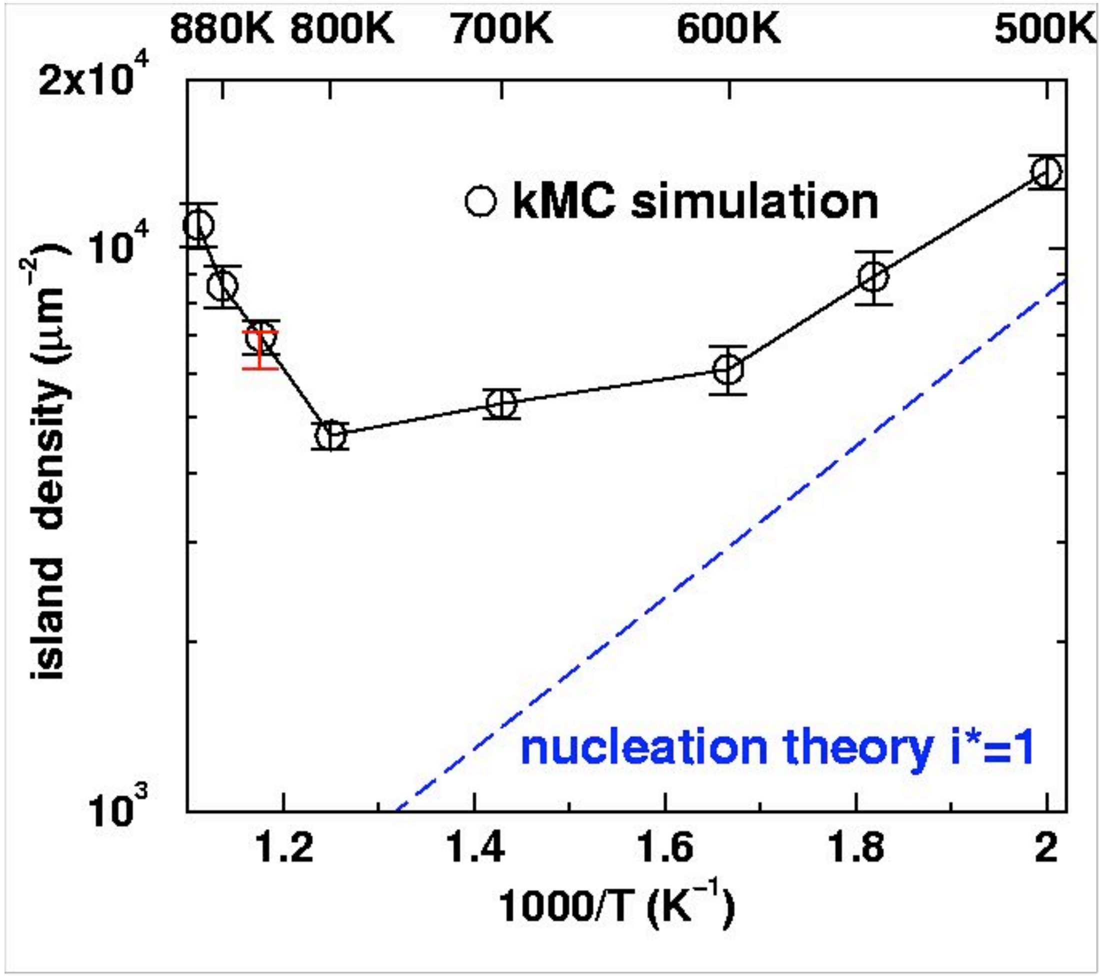
island density





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

scaling with temperature ?



'conventional' nucleation theory

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

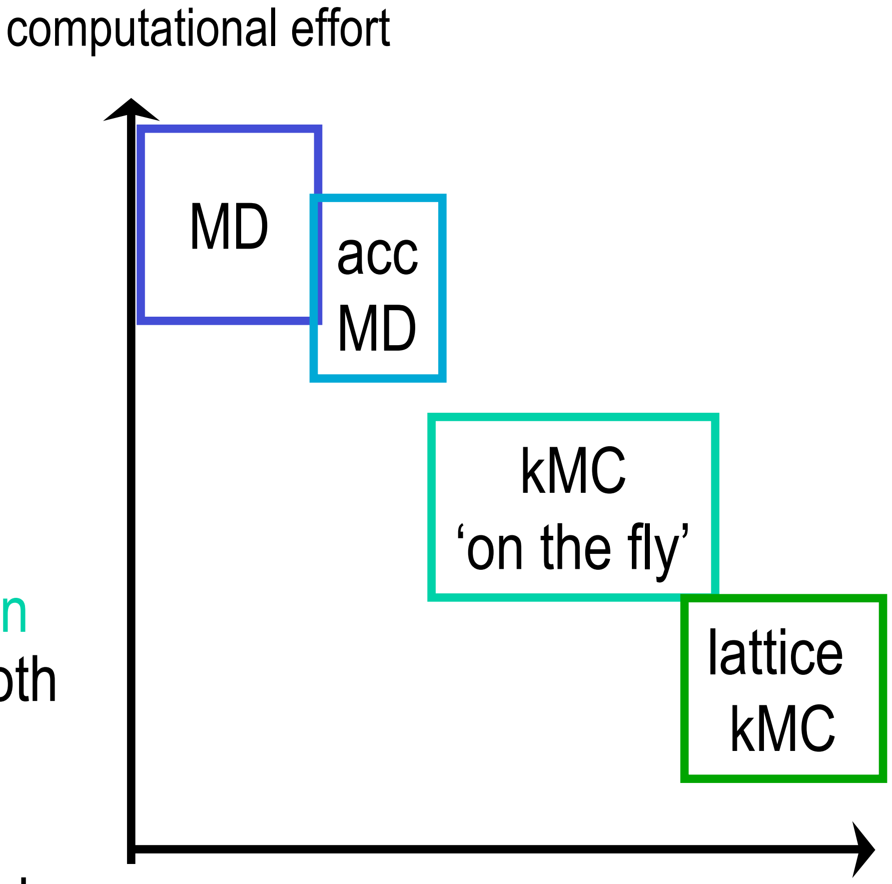
N_{is}	island density
D	diffusion constant
R	deposition flux
η	numerical const.
i^*	critical nucleus

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

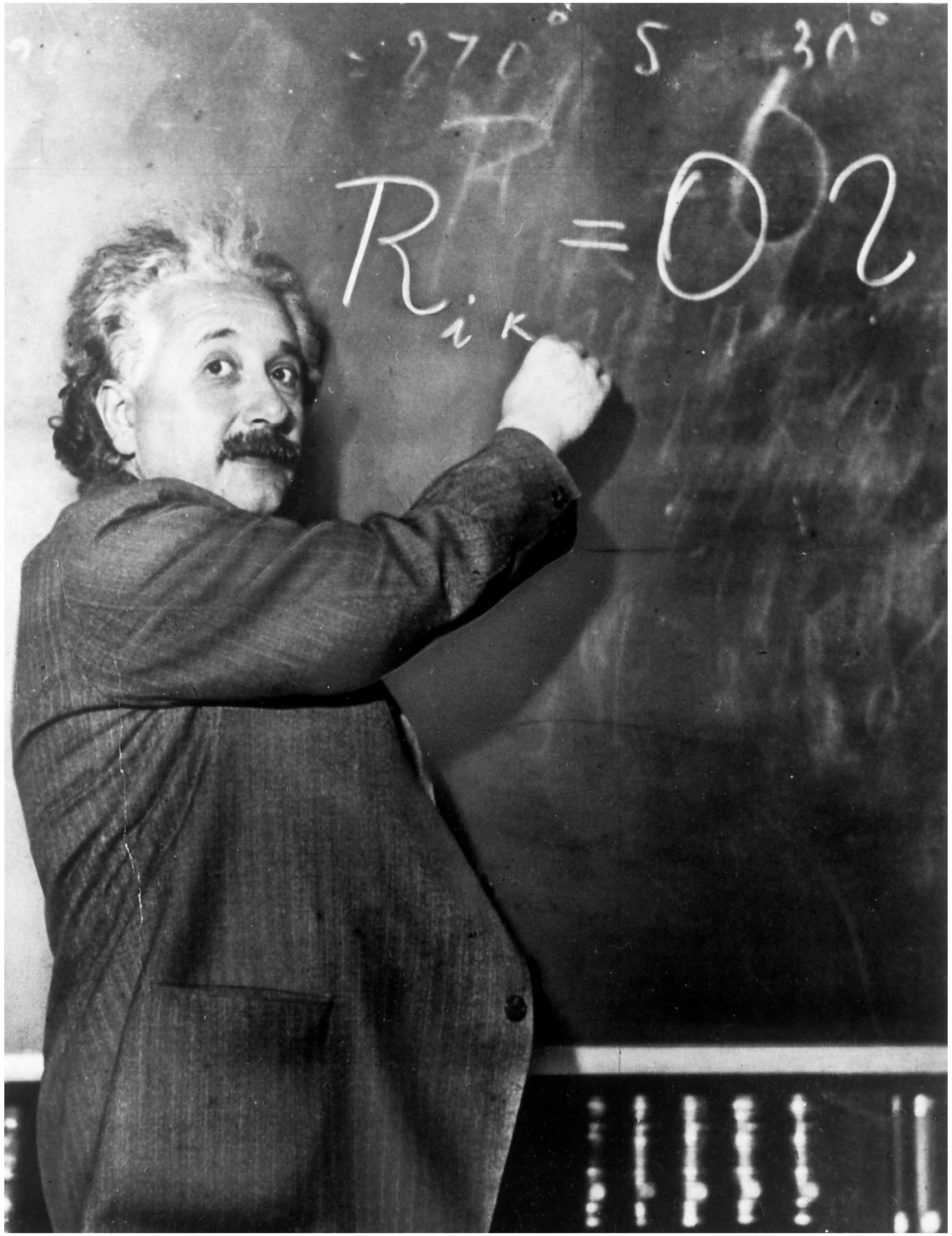
experiment: G.R. Bell et al.,
Surf. Sci. **423**, L280 (1999)

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