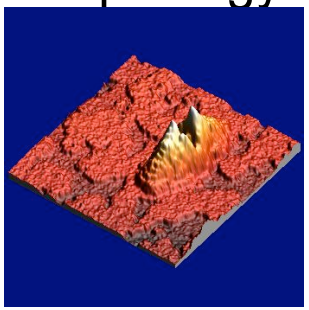
Kinetic Monte Carlo modelling of semiconductor growth

Peter Kratzer

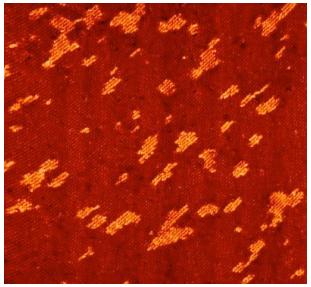
Faculty of Physics, University Duisburg-Essen, Germany

Time and length scales

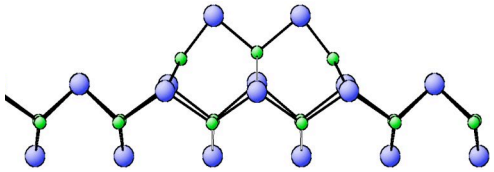
morphology

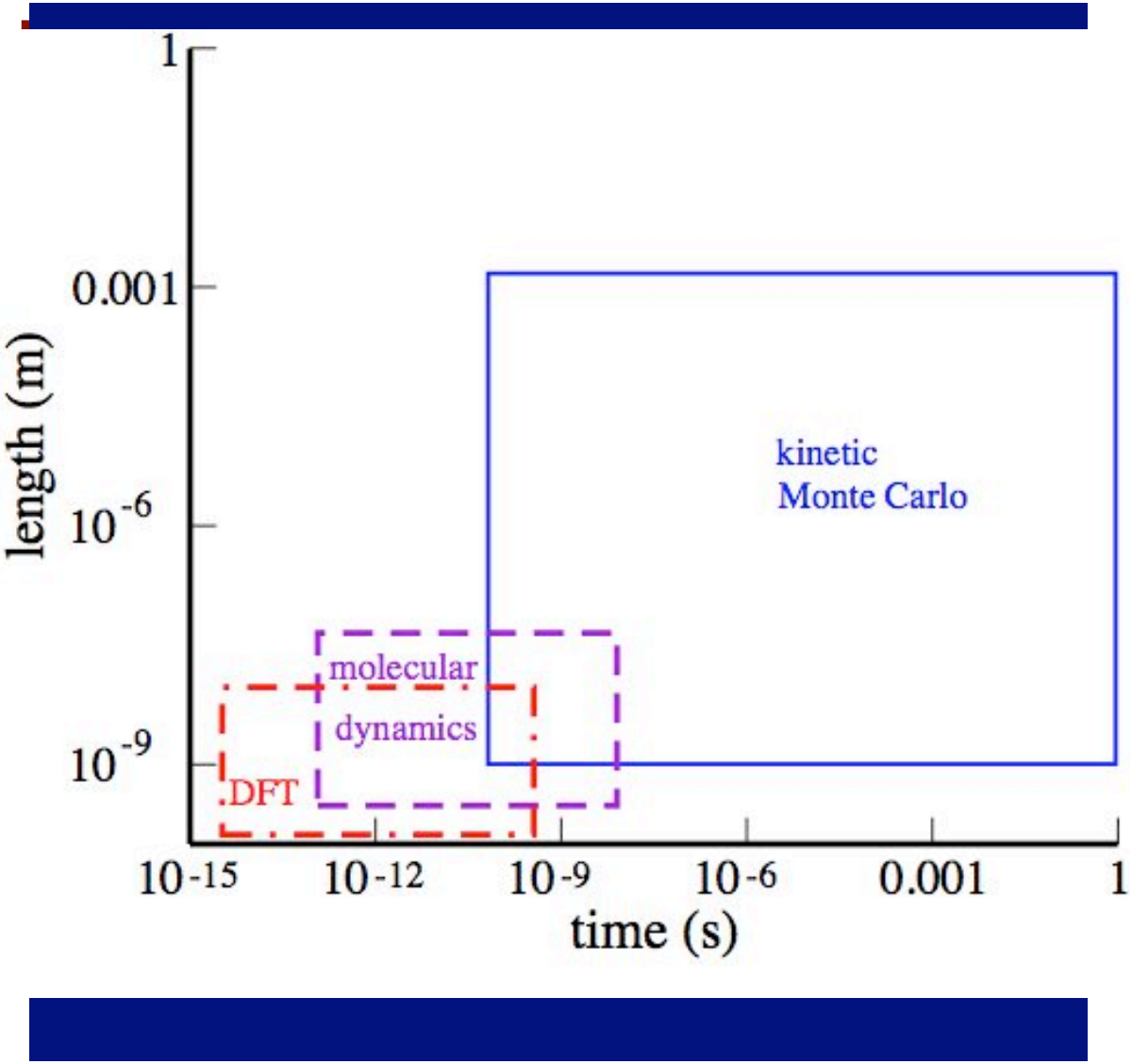


2D islands



surface reconstruction



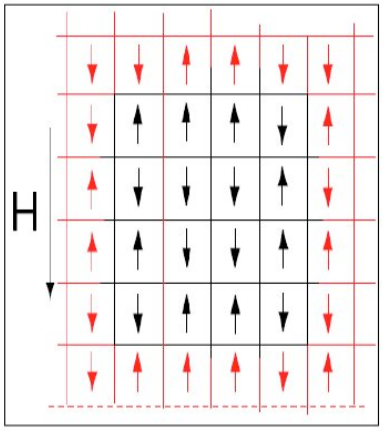


Methods of Statistical Physics

Discrete models in Statistical Physics

- Ising model (magnetism)

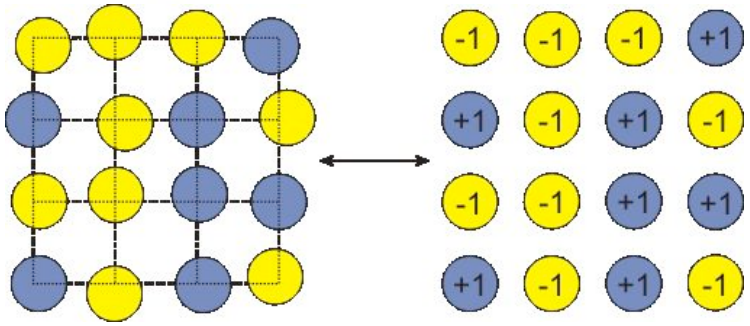
$$H(s) = -J_q \sum_i \sum_{j \in n(i)} s_i s_j - \mu_B B \sum_i s_i$$



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

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

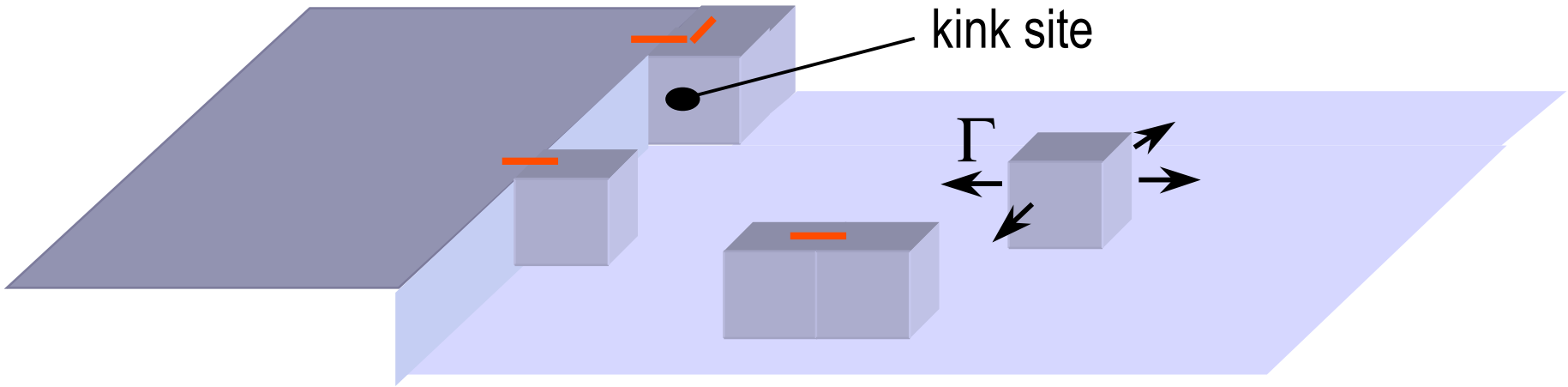
- **Goal:**
  Calculation of thermal averages



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

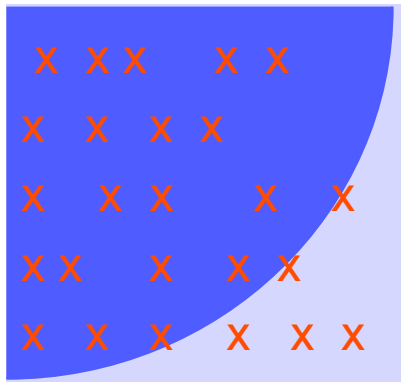
$$E = E_D + n\, E_B$$



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.

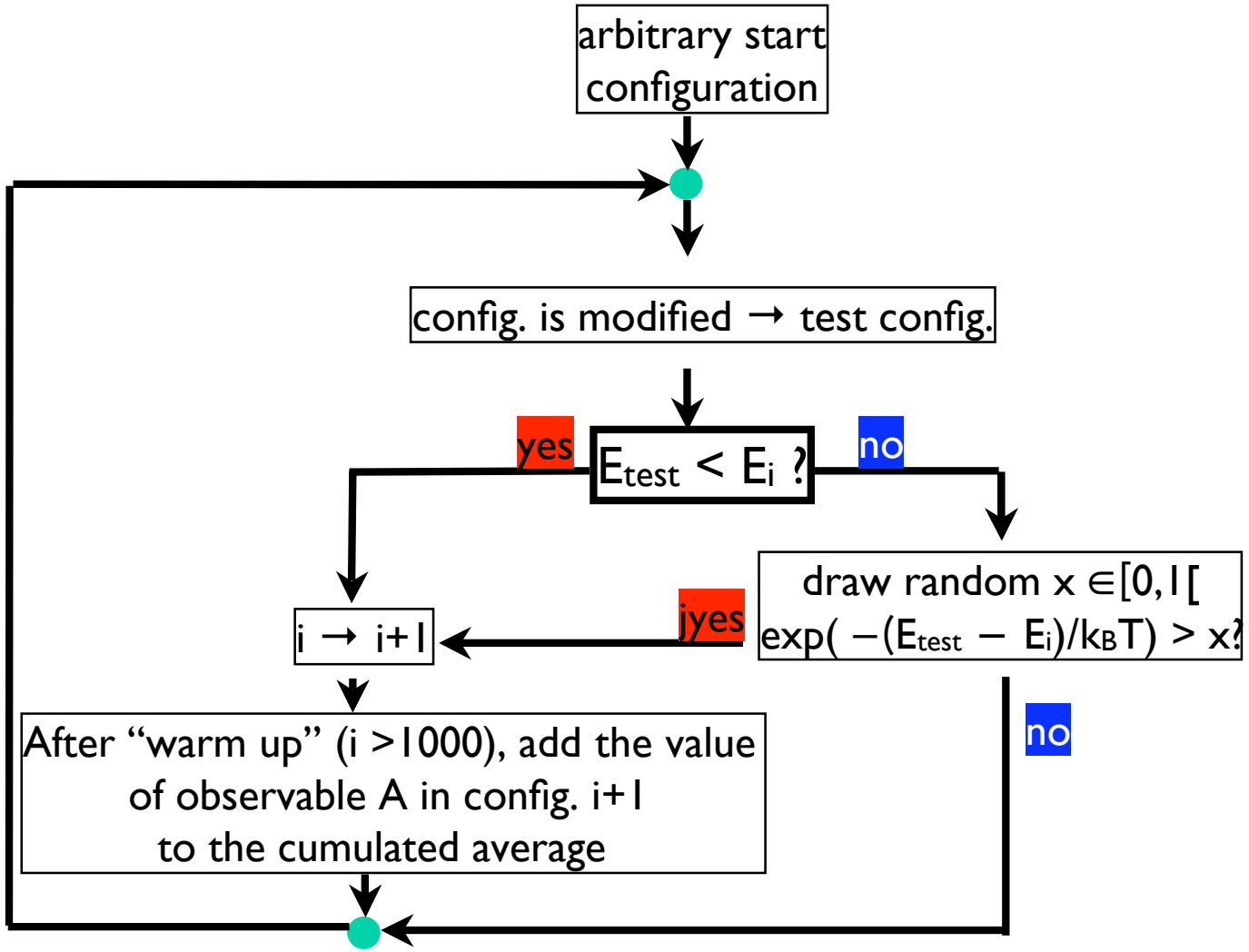
$\pi/4 = 0.78 .. \approx 20/25 = 0.8$



Metropolis Sampling

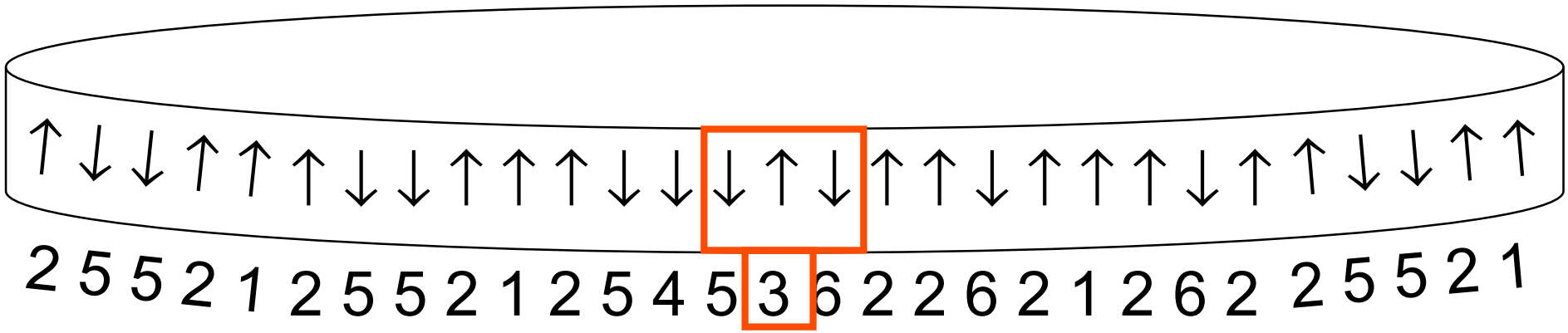
- **Solution:** *Importance Sampling* with $w(\mathbf{q}) = \frac{\exp\left(-V(\mathbf{q})/(k_B T)\right)}{Z'}$
- Generate random support points, distributed according to $w(\mathbf{q})$, i.e., out of total K points, $k_i = K w(\mathbf{q})$ in the unit volume around $\mathbf{q}_i$
- The expectation value 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 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 $\exp\left(-\frac{V(\mathbf{q}_{i+1}) - V(\mathbf{q}_i)}{k_B T}\right) > \mathrm{rnd}$
  - 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

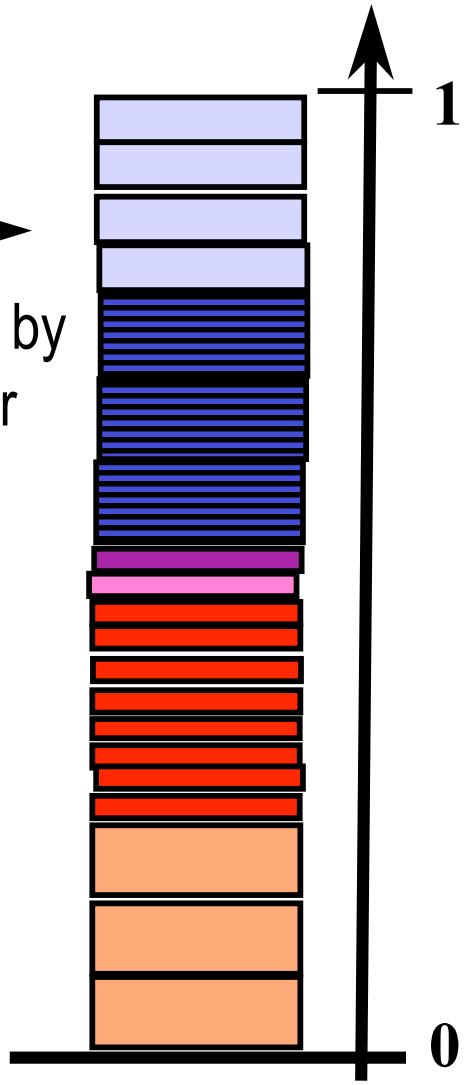


class	central spin	neighbors	class members n_i
1	↑	↑, ↑	4
2	↑	↑, ↓	12
3	↑	↓, ↓	1
4	↓	↓, ↓	1
5	↓	↑, ↓	8
6	↓	↑, ↑	3

The *N*-fold way algorithm in MC

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

pointer steered by random number



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

Simulations of non-equilibrium processes: kinetic MC

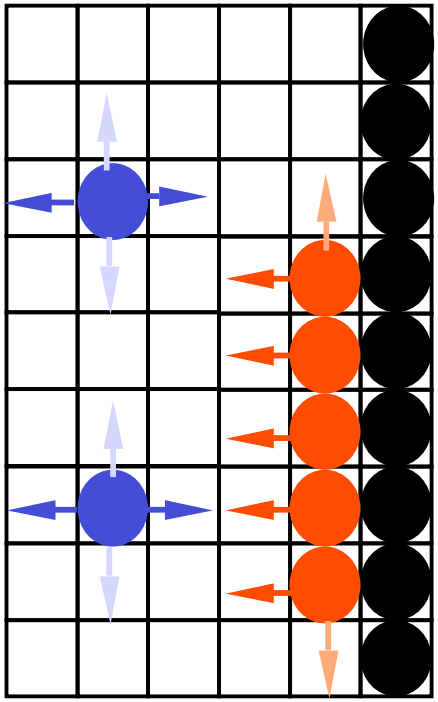
- While being aware of all processes possible at an instant of time, we need a way of (randomly) selecting one process with the appropriate relative probability.
- An internal clock keeps track of the advancement of physical time.
  - If the processes are clearly separated in time, i.e. processes are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

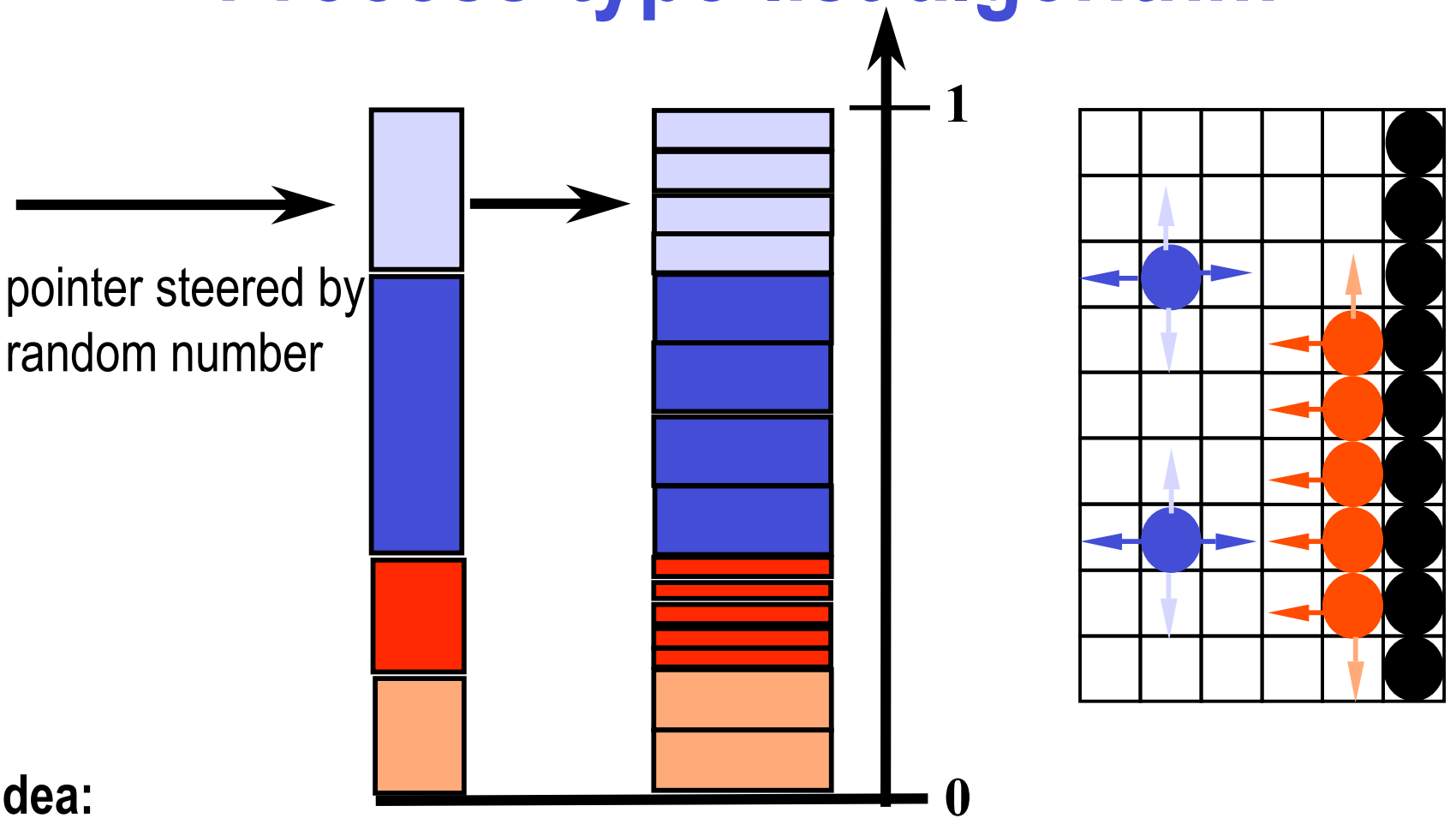
- process-type list algorithm
- binary-tree algorithm
- time-ordered-list algorithm

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.



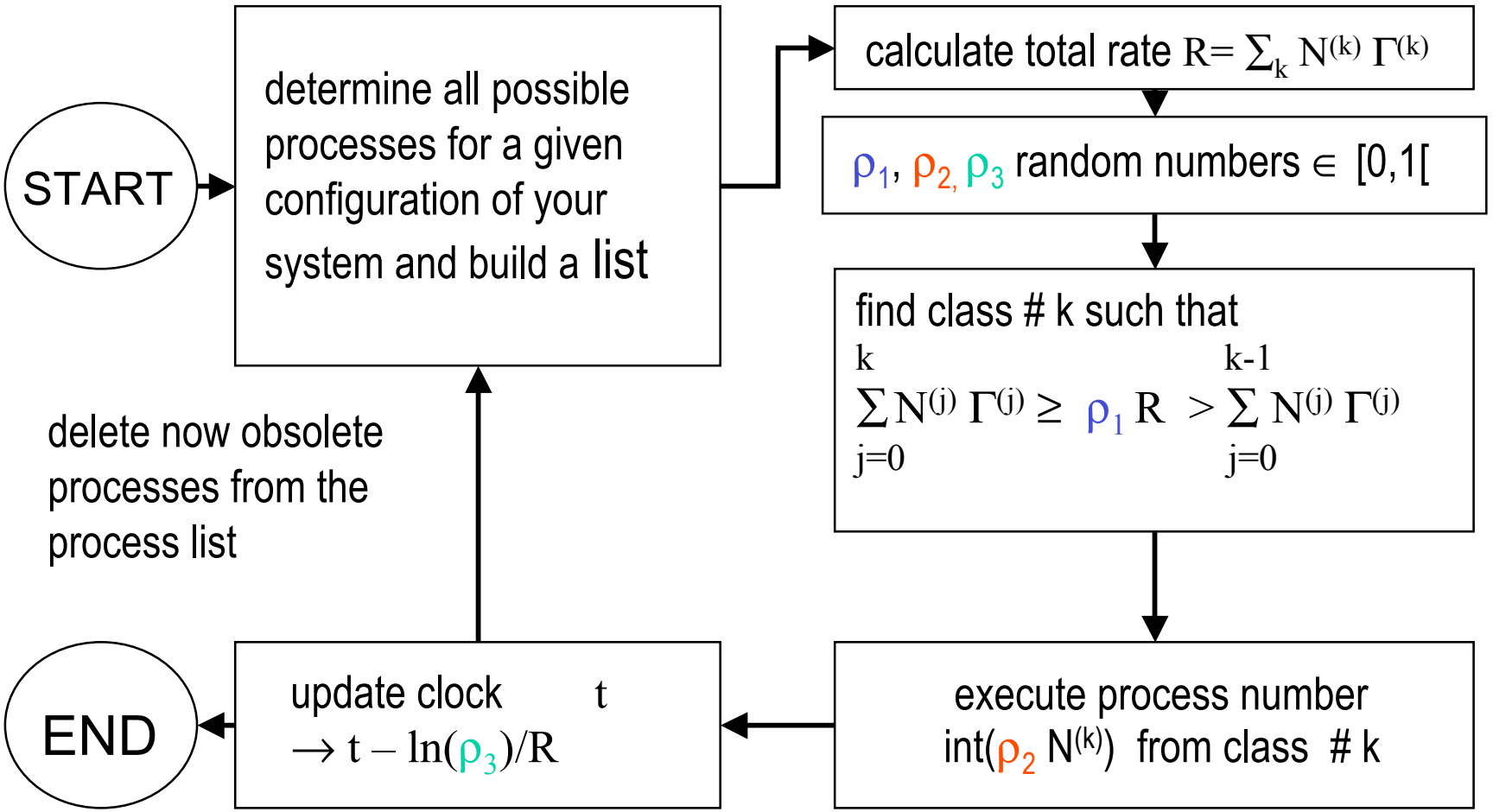
Process-type-list algorithm



idea:

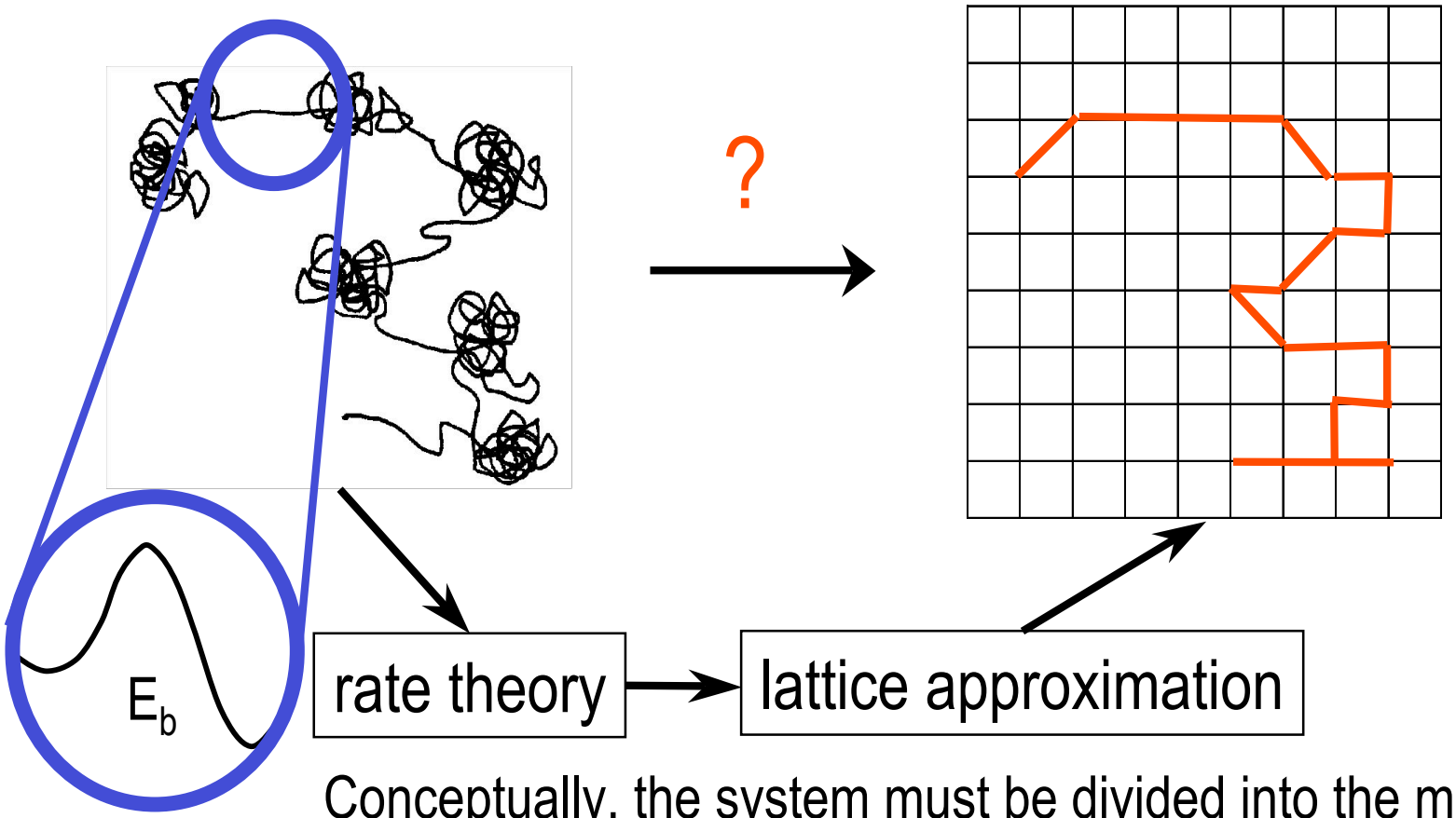
for p process types, we need to compare only to the p numbers $N^{(k)}\,\Gamma^{(k)}$, $k=1,p$, rather then to **all** r_k/R (which are much more numerous)

flow chart for a kMC algorithm



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”.

Transition State Theory (1-dim)

- Kramer's rate theory

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

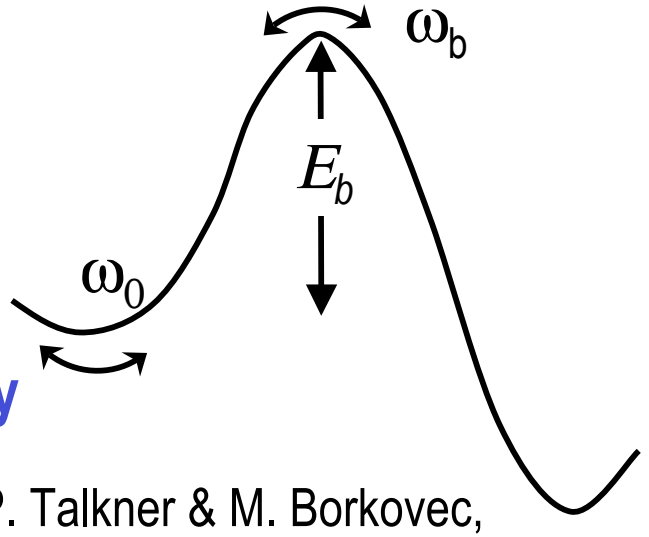
γ: friction due to coupling to the heat bath

- high-friction limit

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

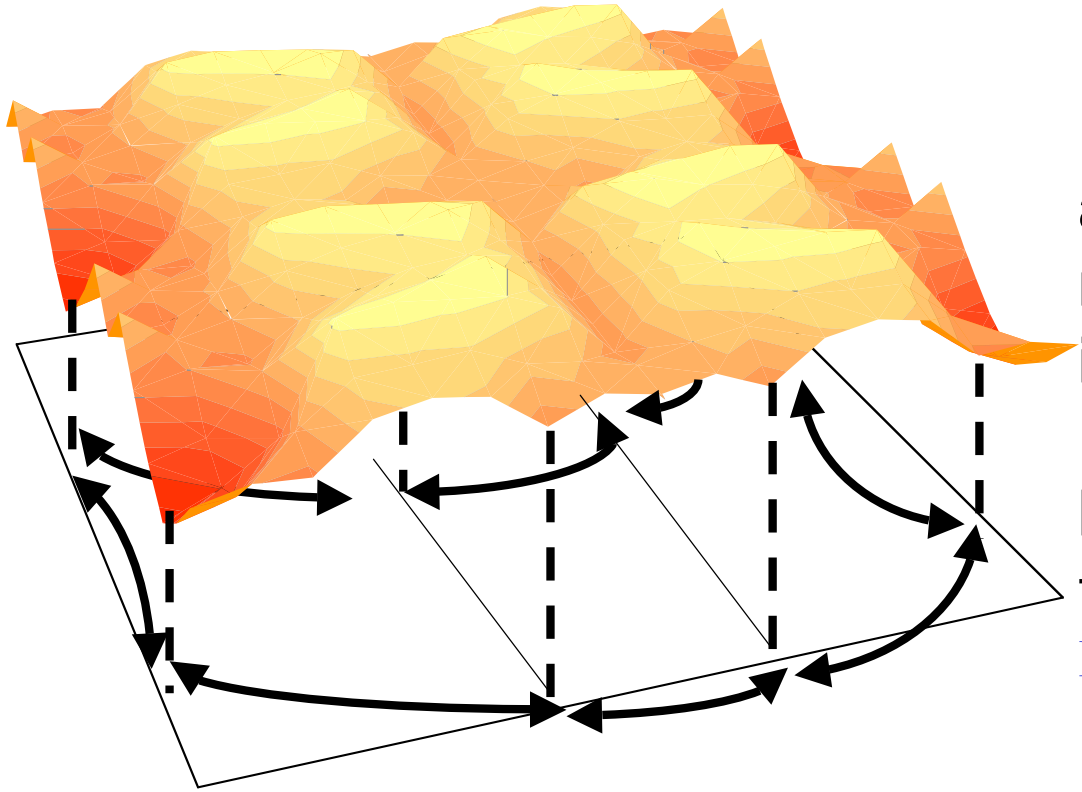
- 'medium' friction $\rightarrow$ **transition state theory**

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



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

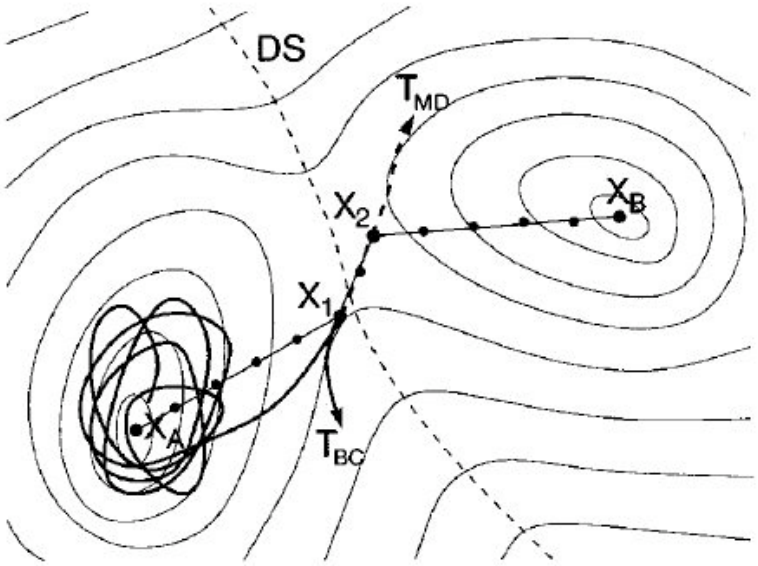
hopping rates derived from the PES

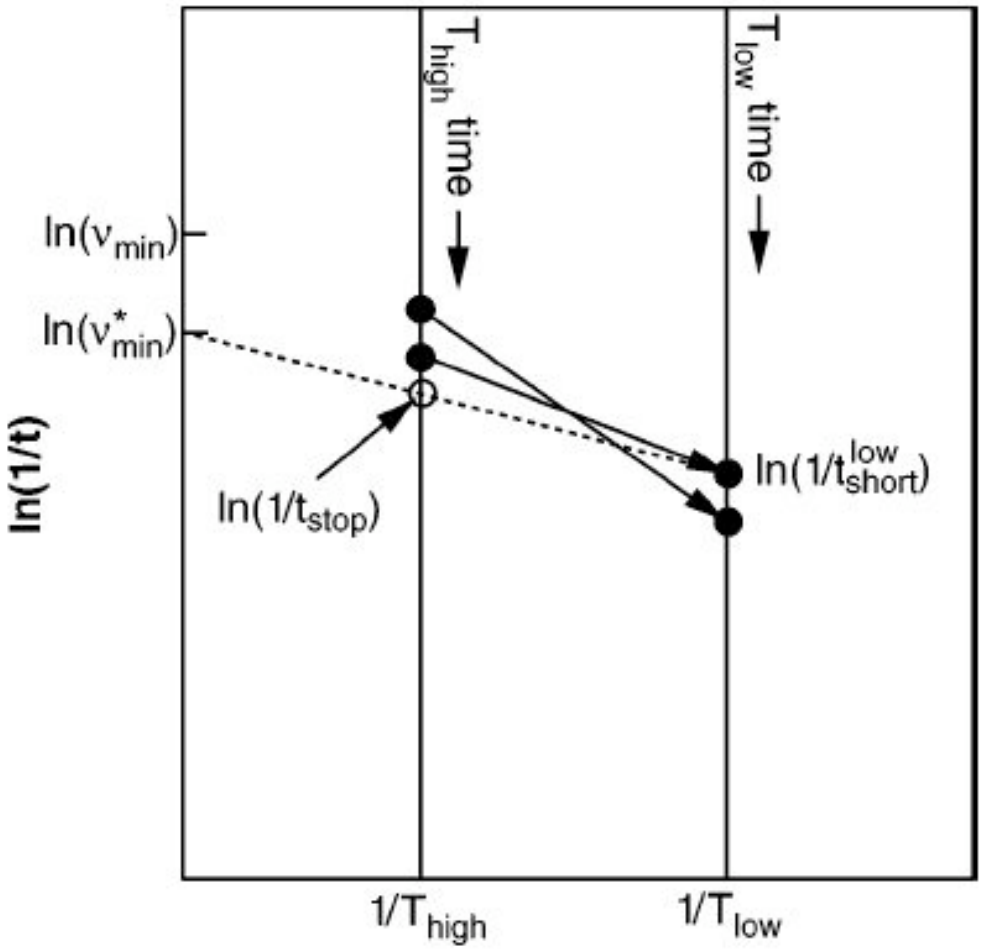
$$E(x_i,y_i) = \min_{z_i,\, c_\alpha} E_{tot}(x_i, y_i, z_i, c_\alpha)$$

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

Temperature-accelerated dynamics (TAD)

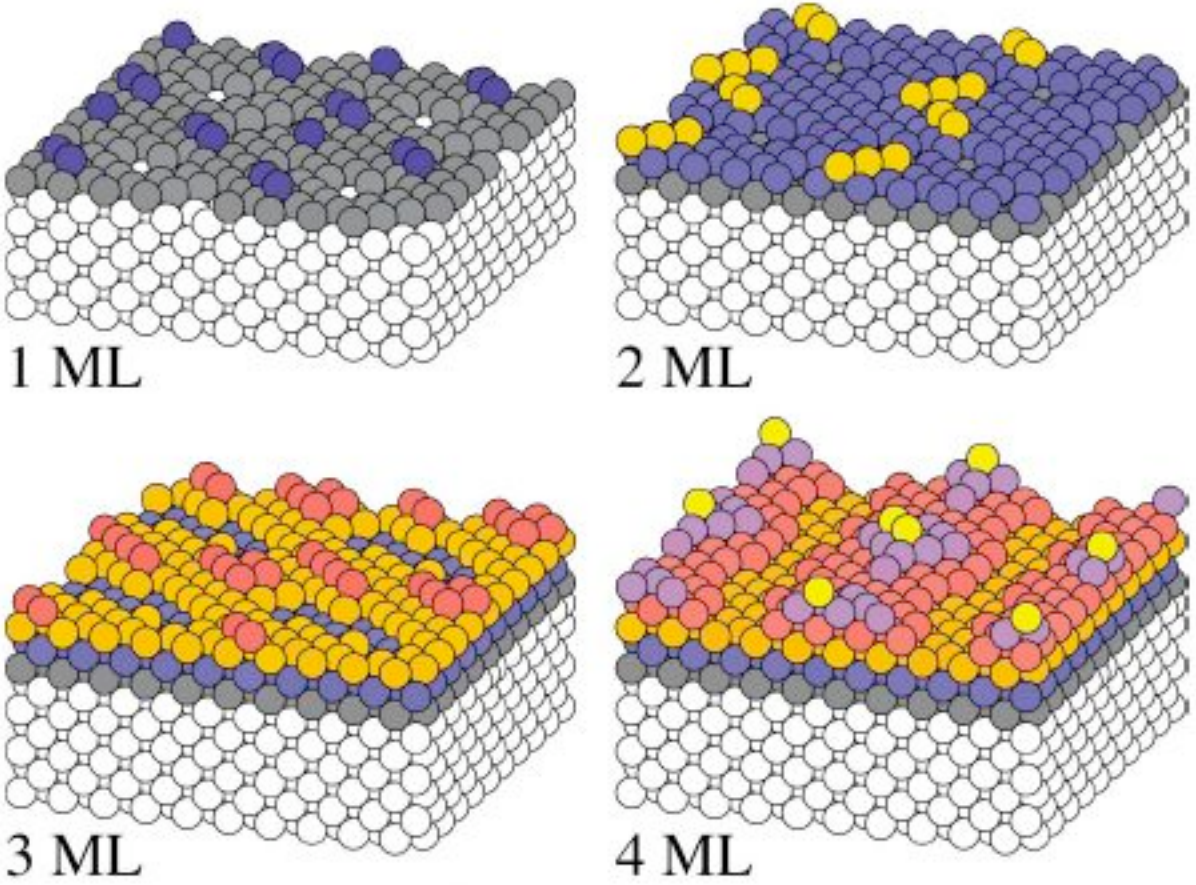
Event is observed at T_{high}, but its rate is extrapolated to T_{low} (using the TST rate law).

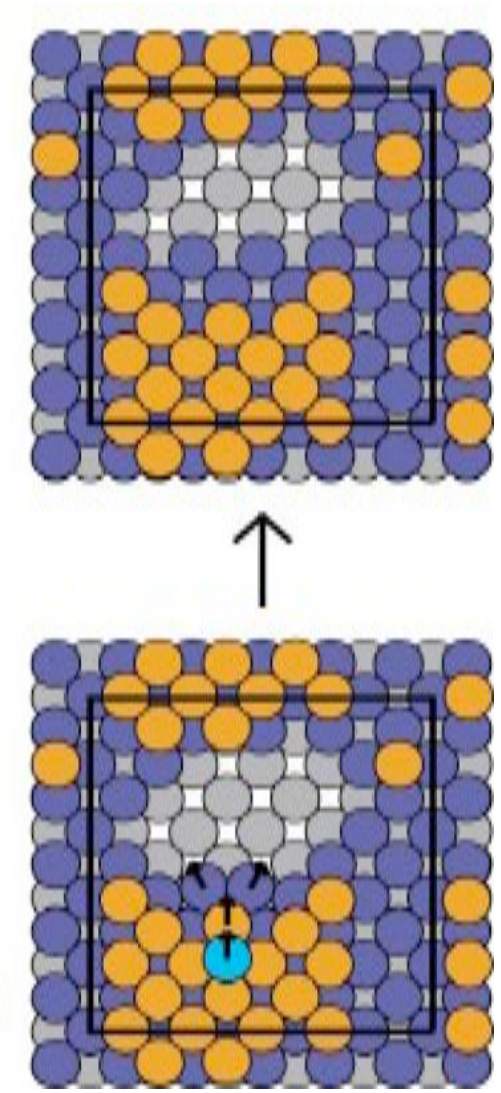




M.R. Sørensen and A.F. Voter, J. Chem. Phys. **112**, 9599 (2000)

TAD: Collective processes



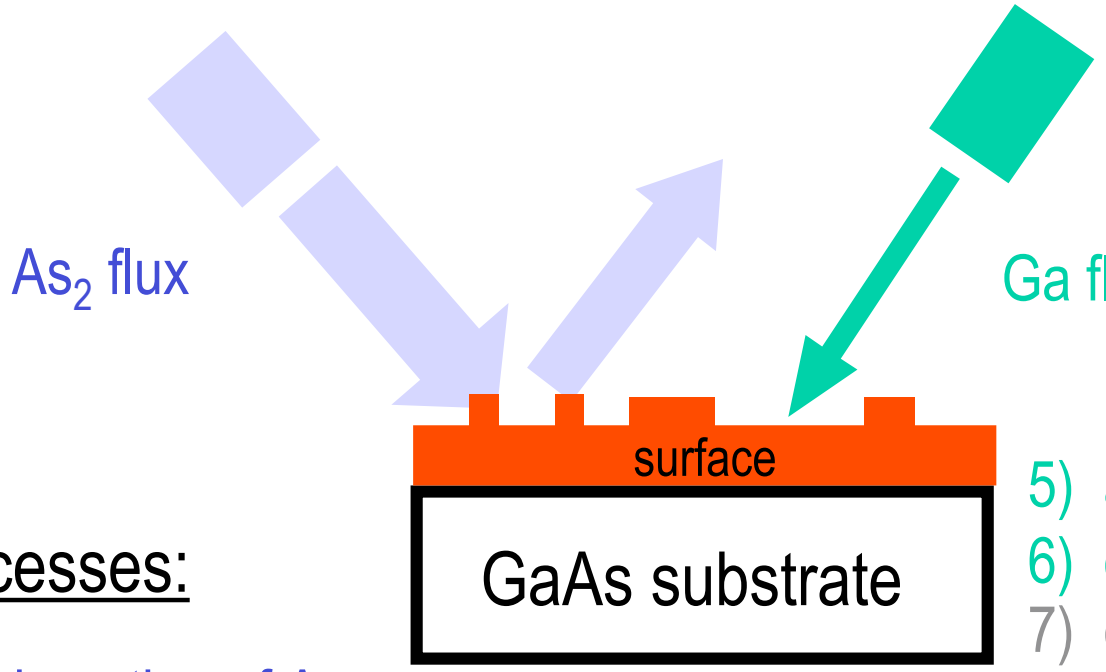


F. Montalenti, M.R. Sørensen and A.F. Voter,
Phys. Rev. Lett. **87**, 126101 (2001)

Application I:

GaAs nanowire growth

Molecular beam epitaxy of III-V semiconductors



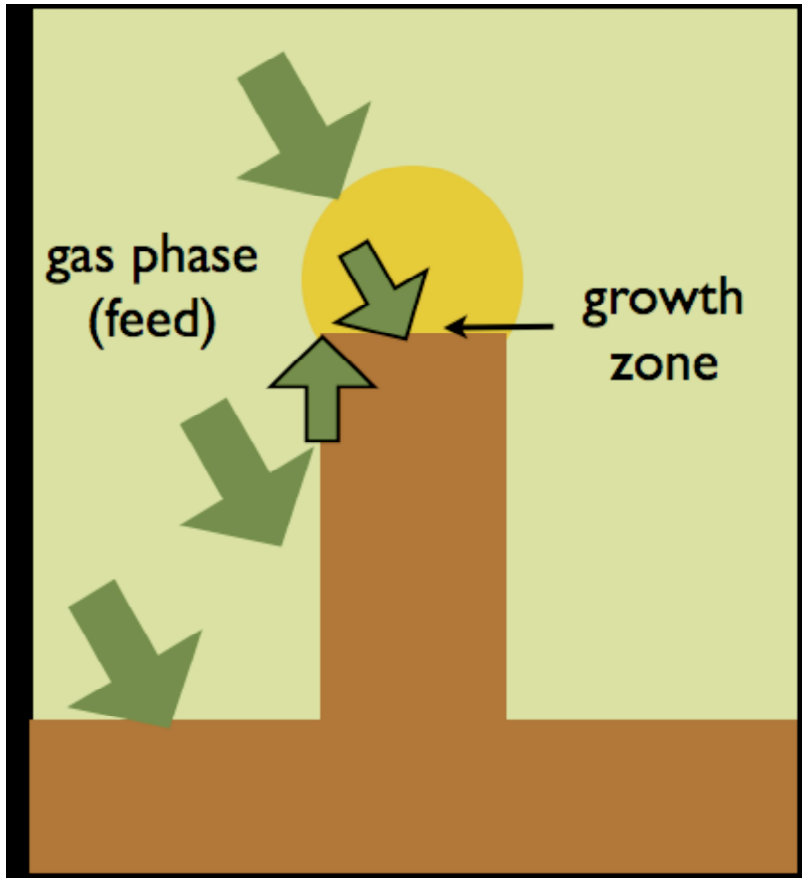
Processes:

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

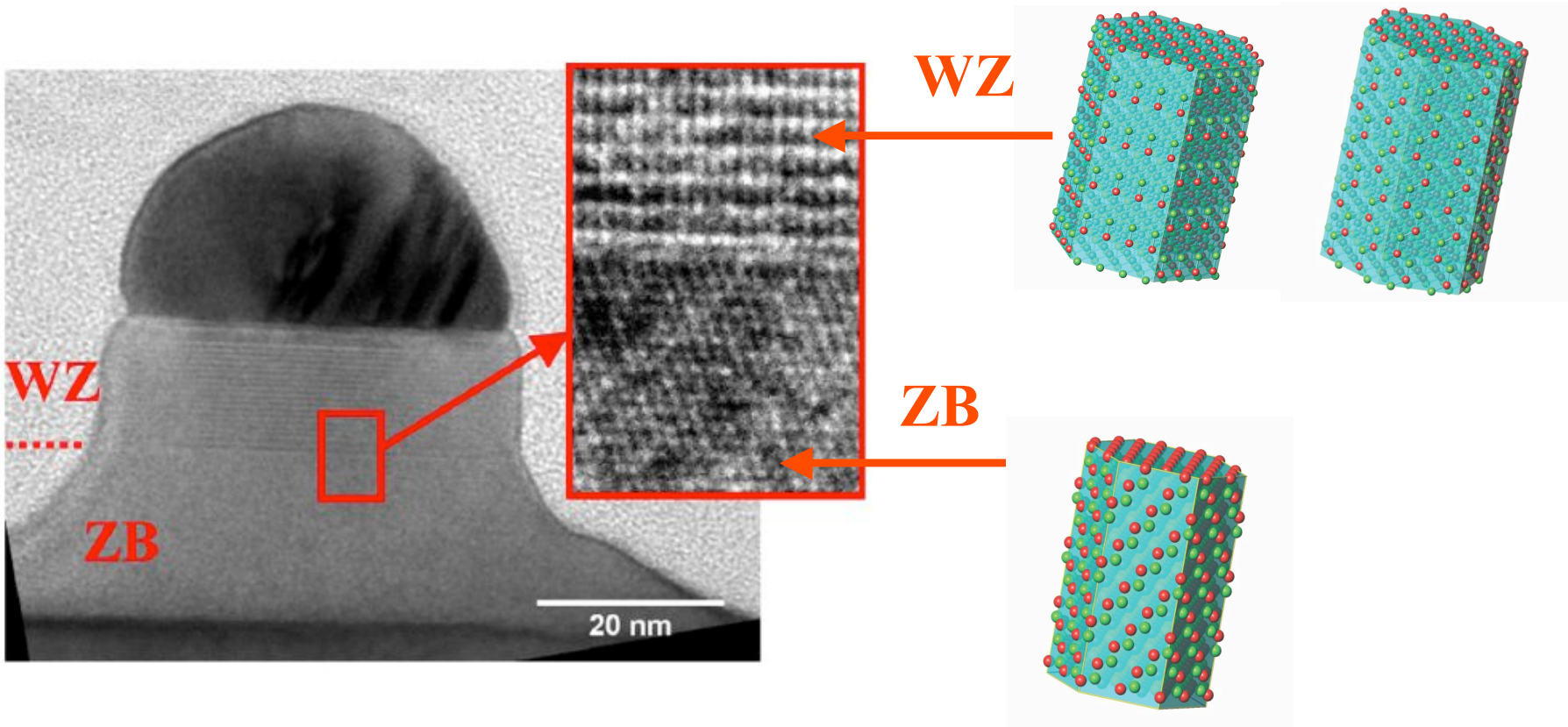
- much higher growth speed in a particular crystallographic direction [GaAs(111)B] compared to extended substrate
- liquid Au droplet used to store Ga (as Au-Ga alloy), but inefficient for As species
- role of material transport along the wire side walls ?



Polytypism in GaAs nanowires

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

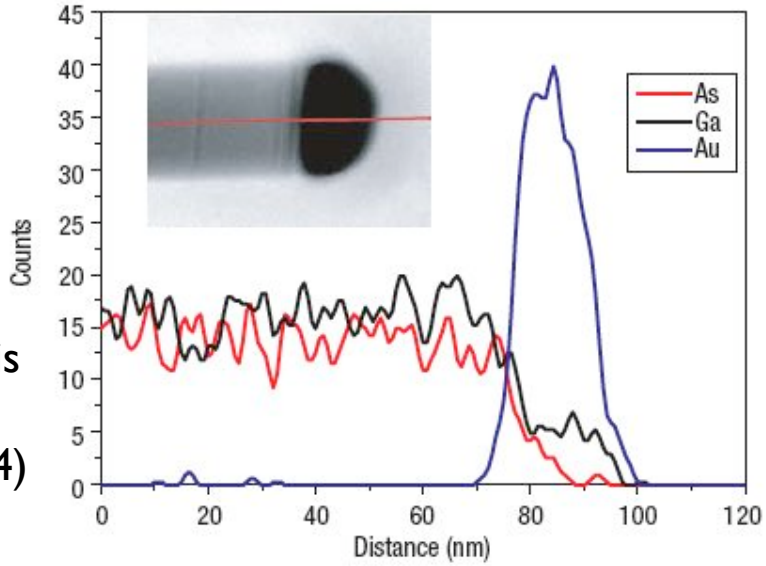
2 types of structurally different facets !



Arsenic supply to the interface

- arsenic vacancy emission into the solid

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

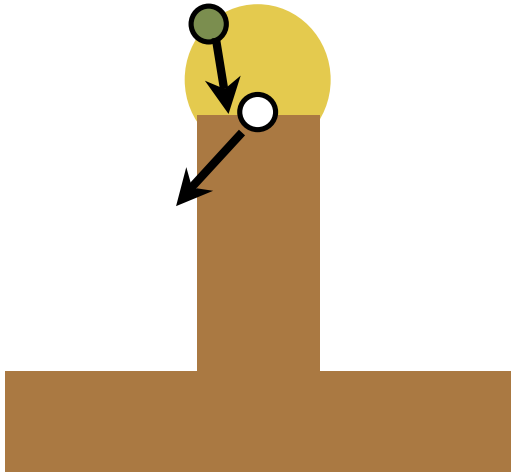


element-specific XEDS analysis
A.I. Persson et al.,
Nature Materials **3**, 667 (2004)

or

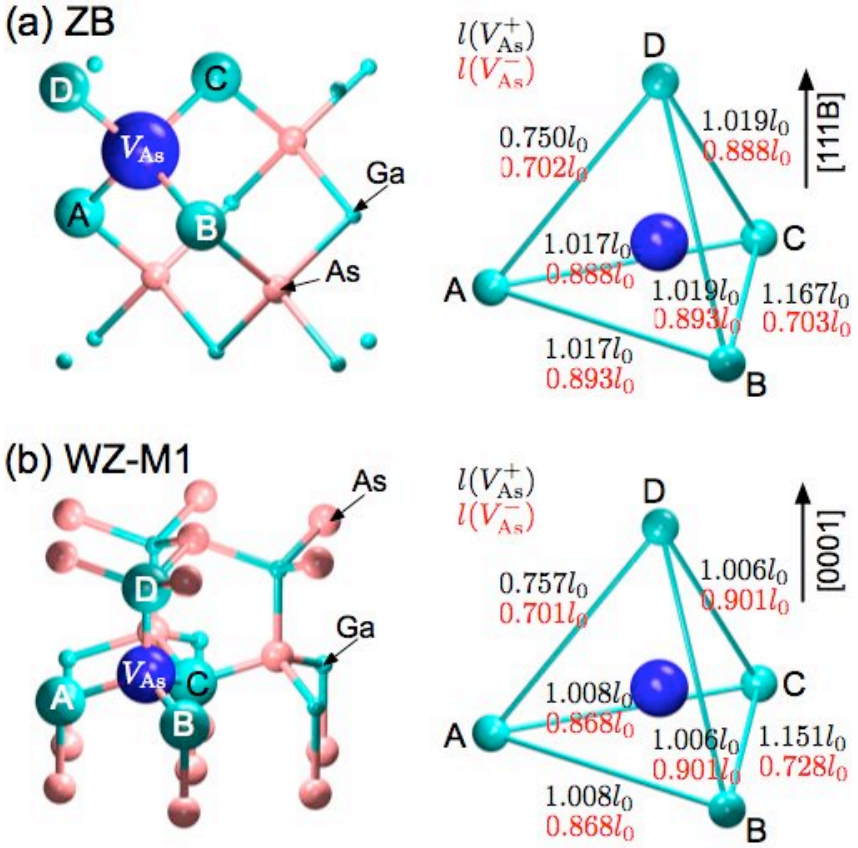
- diffusion of As dissolved in the liquid
  Stokes-Einstein relation

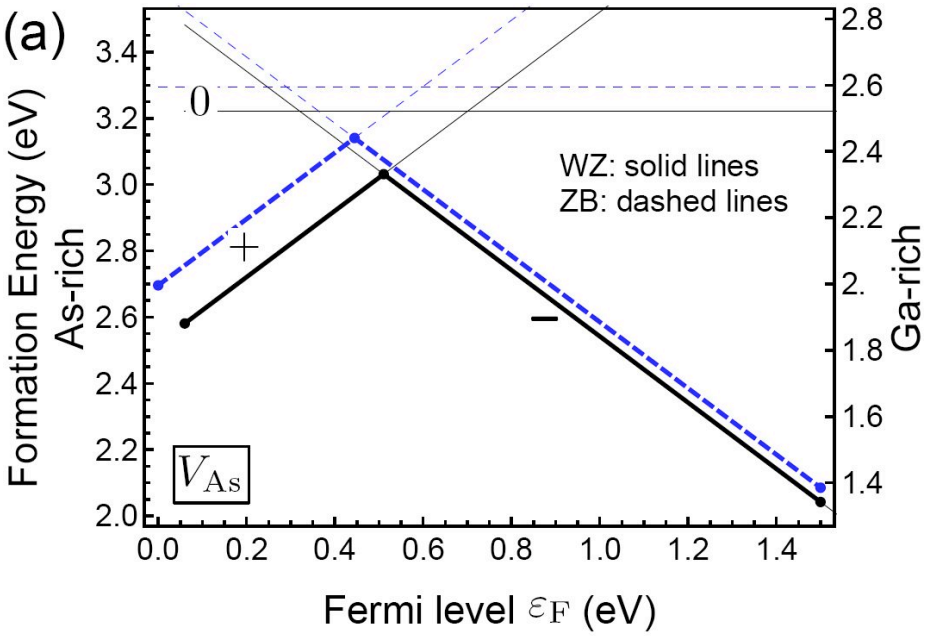
$$D_{\mathrm{As@Au}}(T) = \frac{k_B T}{6\pi r_{\mathrm{As}} \eta_{\mathrm{Au}}(T)}$$



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

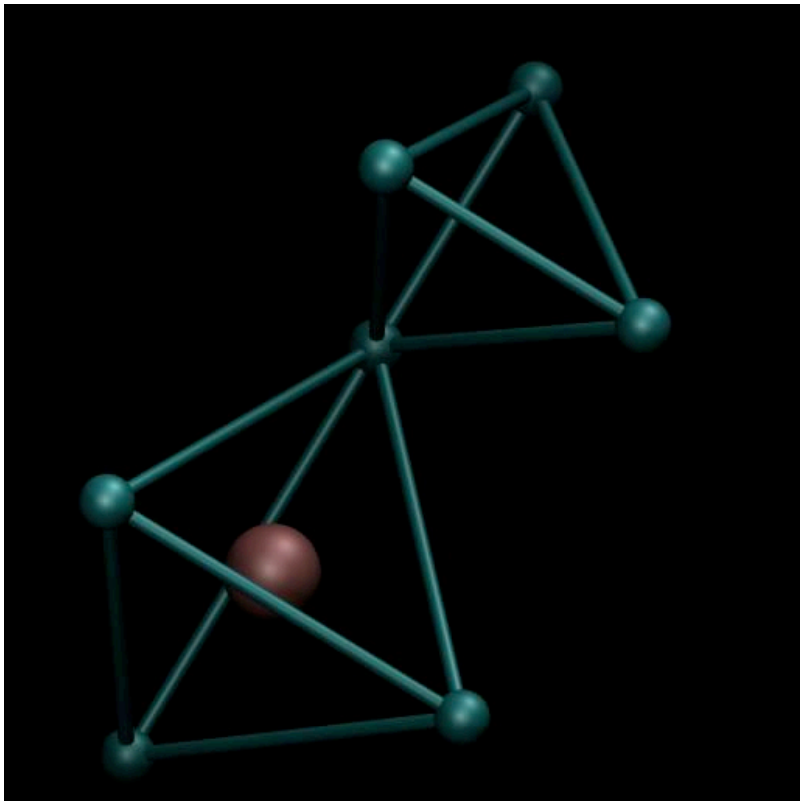


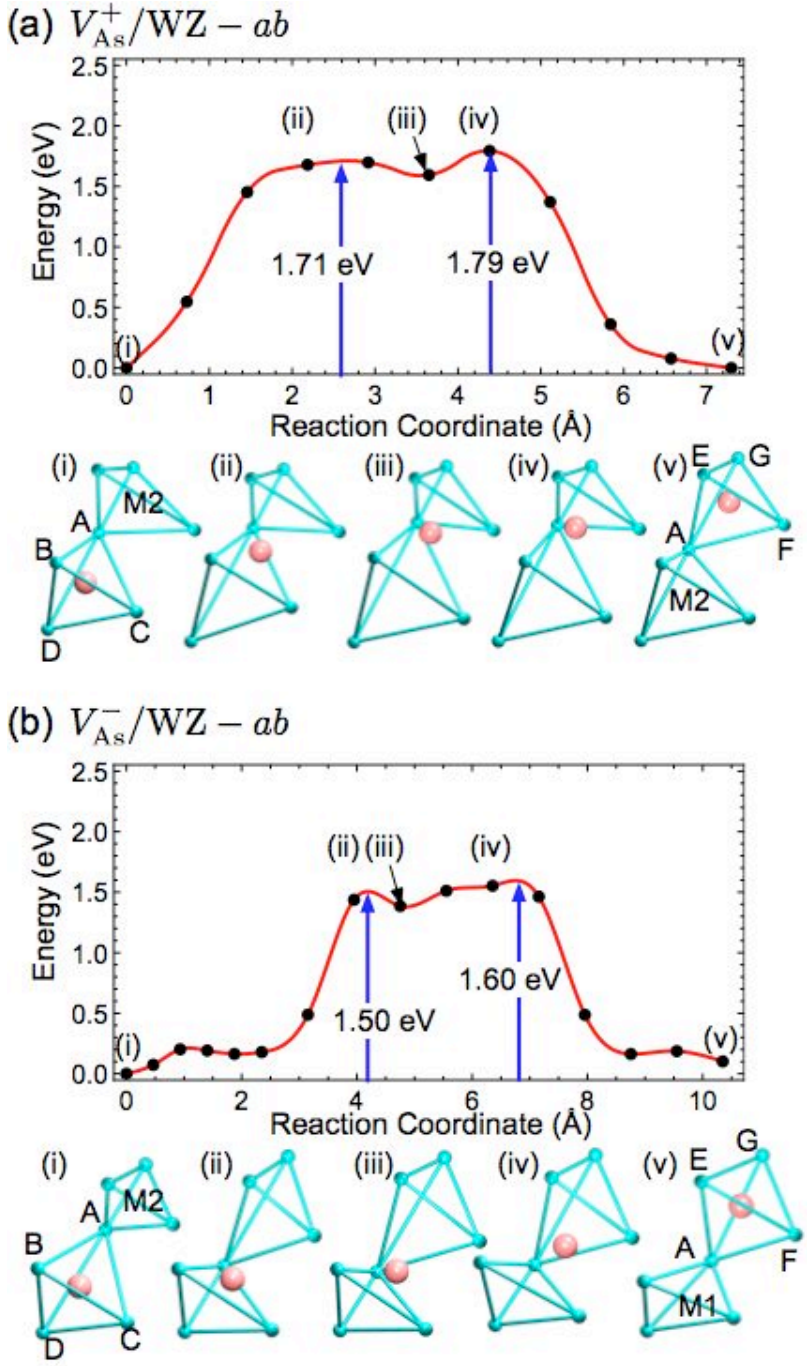


Y.A. Du, S. Sakong and P. Kratzer, PRB **87**, 075308 (2013)

V_{As} diffusion in wurtzite

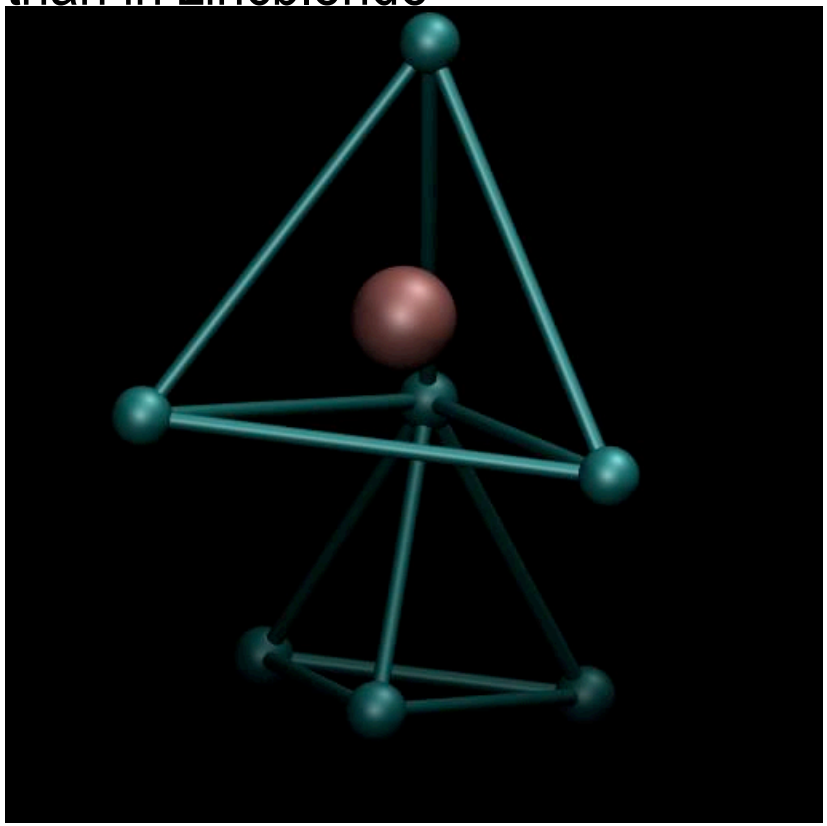
- in wurtzite *ab*-plane, barriers are lower as compared to zincblende case

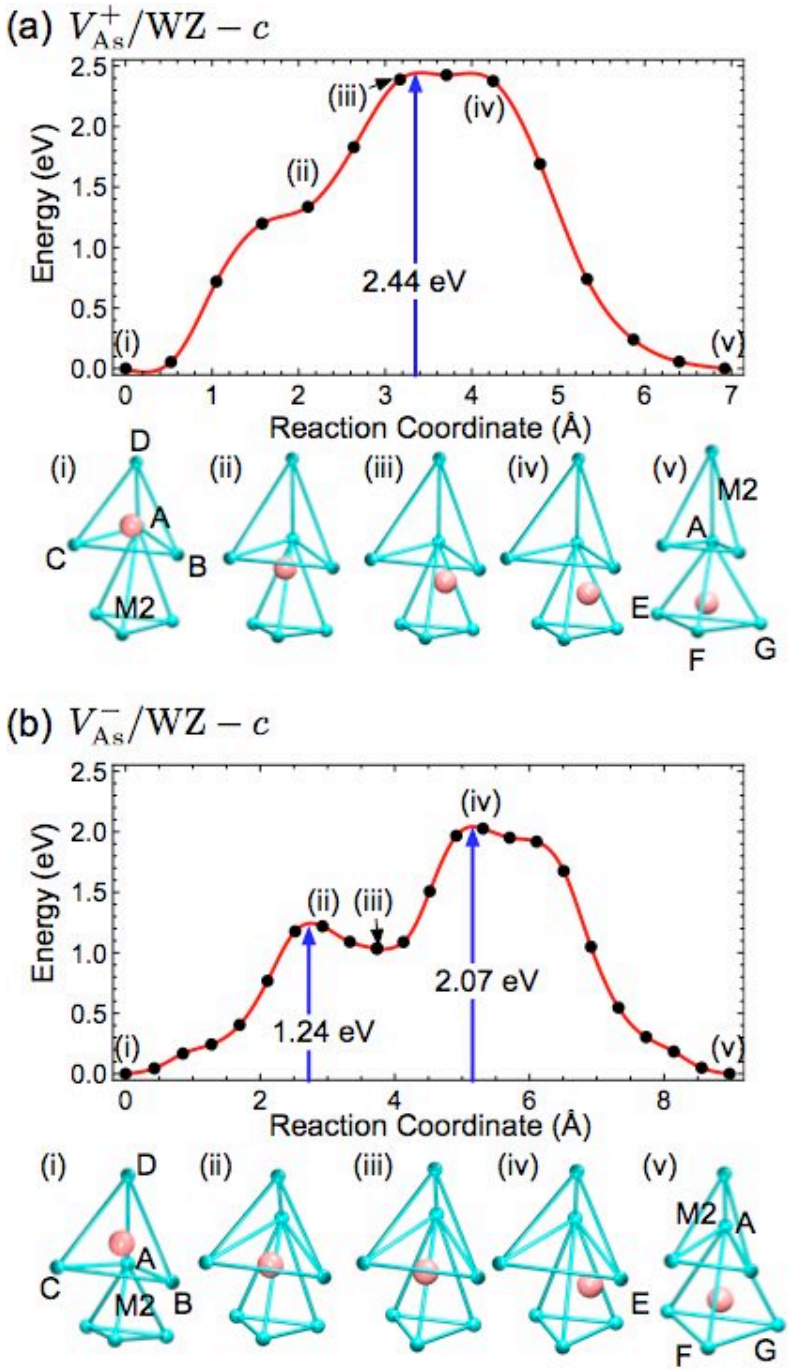




V_{As} diffusion in wurtzite

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

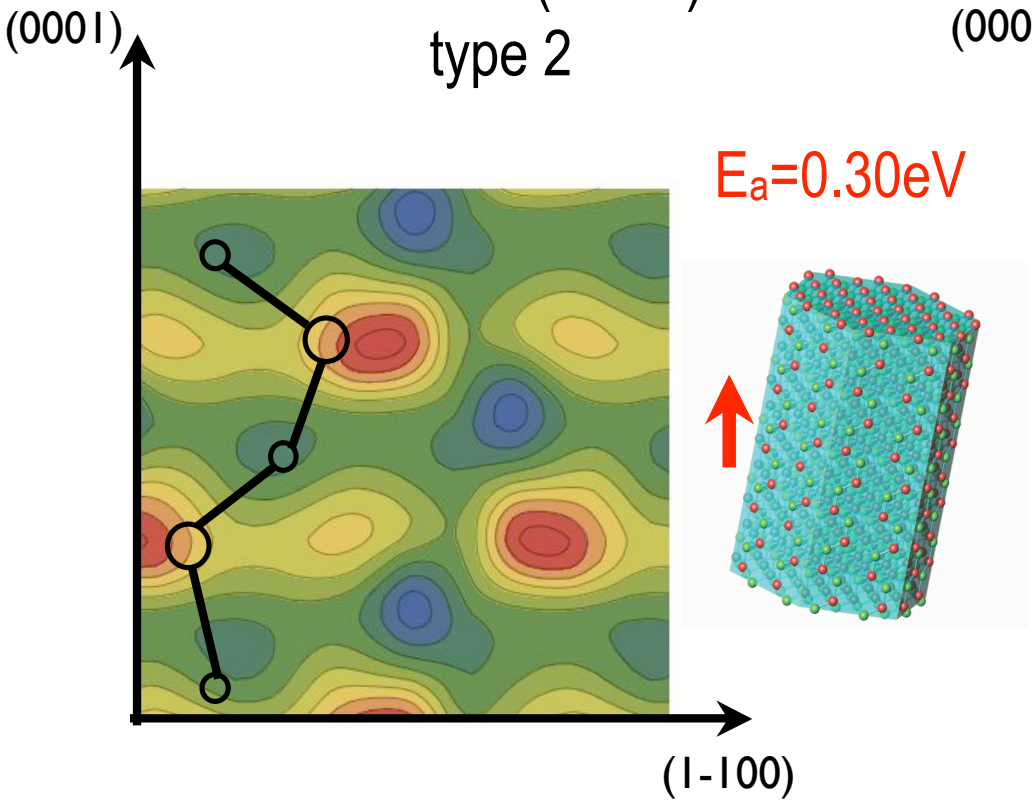




Facet-dependent Ga diffusion

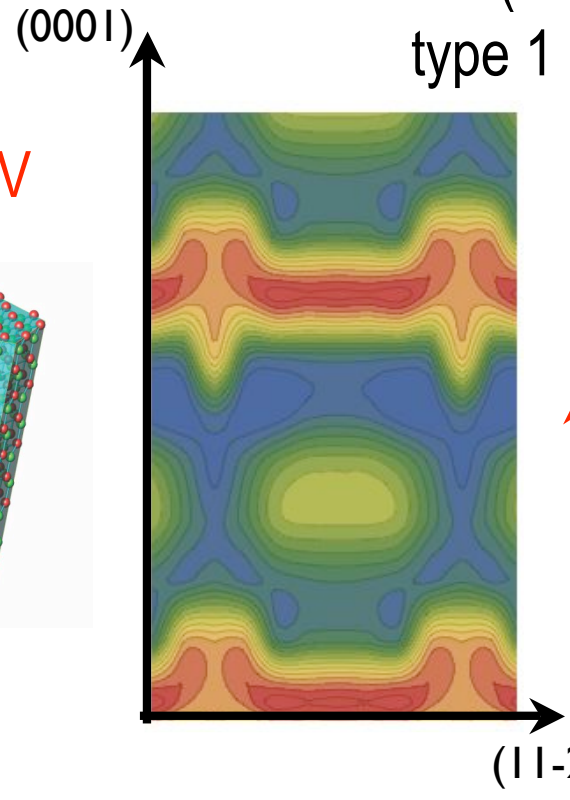
potential energy surface for Ga adatom

on GaAs (11-20)
type 2

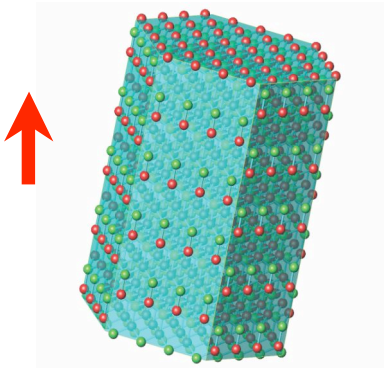


E_a=0.30eV

on GaAs(10-10)
type 1



E_a=0.60eV

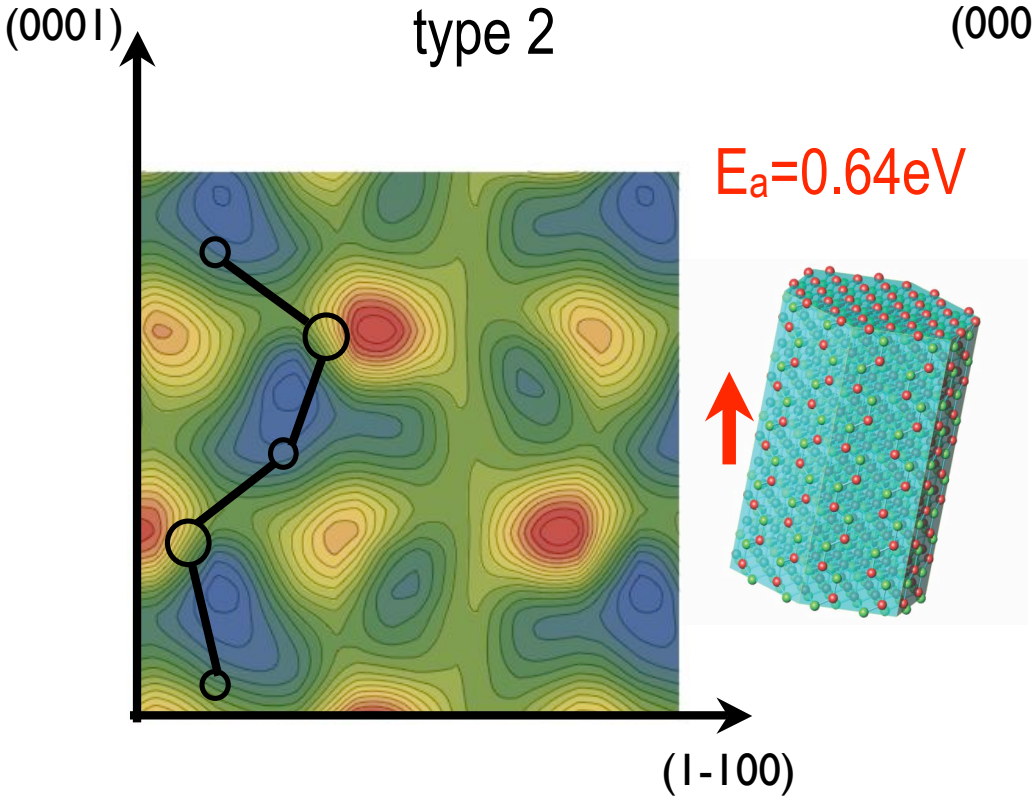


→ type 2 wurtzite wires support **faster** diffusion on the side wall.

As diffusion is much slower !

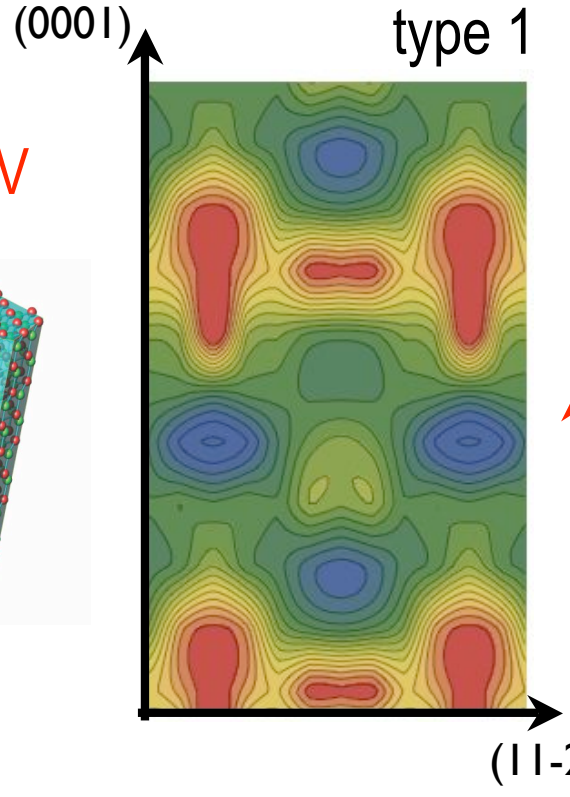
potential energy surface for As adatom

on GaAs (11-20)
type 2

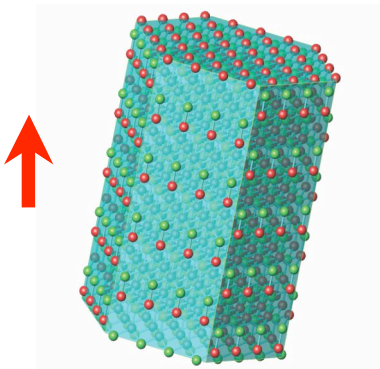


E_a=0.64eV

on GaAs(10-10)
type 1



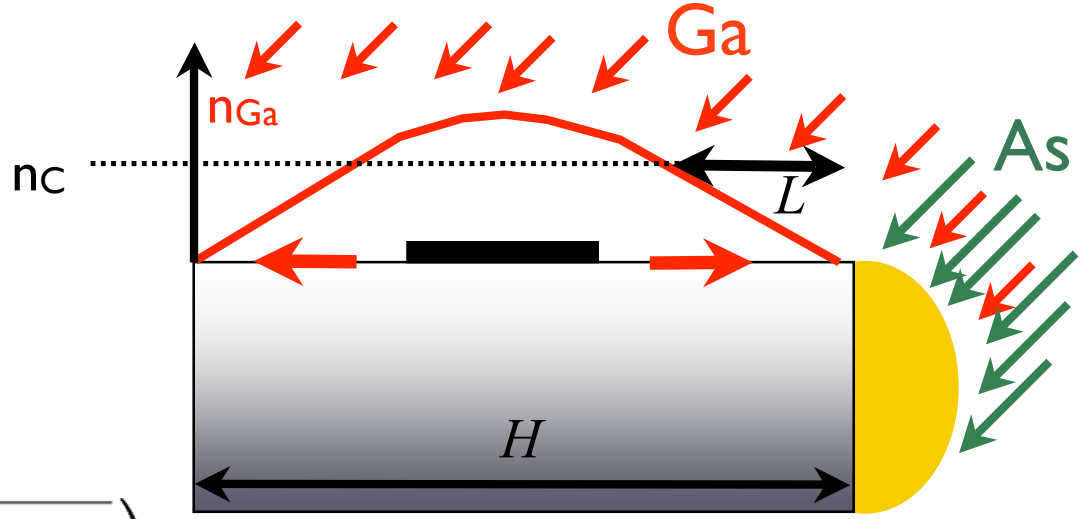
E_a=1.20eV



→ 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



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

$D = 2\times10^{-6}$ cm^2/s; H= 80 μm

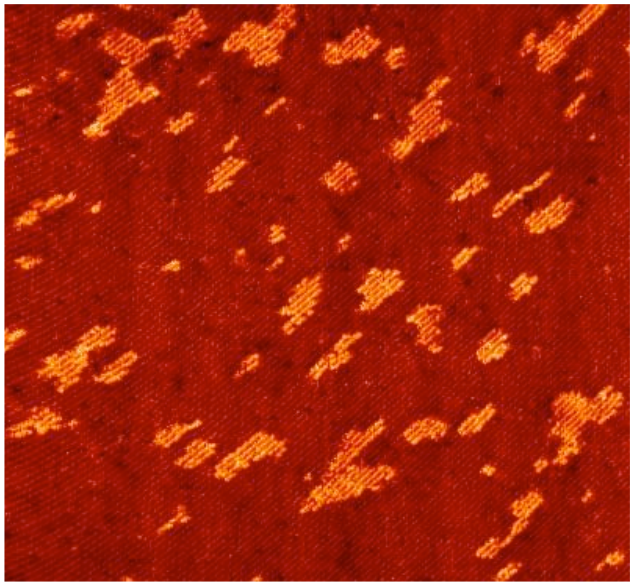
$\Rightarrow L$= 22 μm

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

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

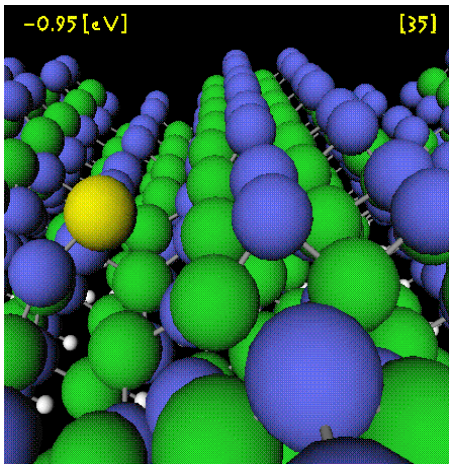
Application II:

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



Rates from first-principles calculations

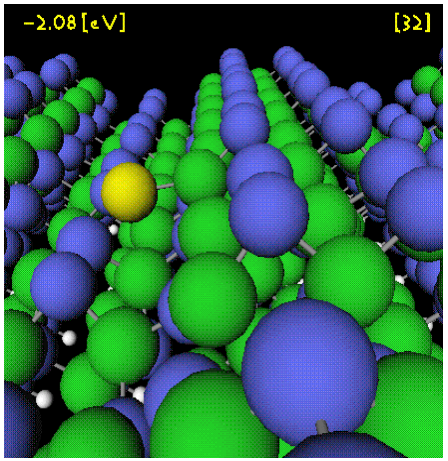
$$\Gamma^{(k)} = W(f,i) = \Gamma^{(fi)}_0 \exp(- (E^{(fi)}_{TS} - E_i)/kT)$$

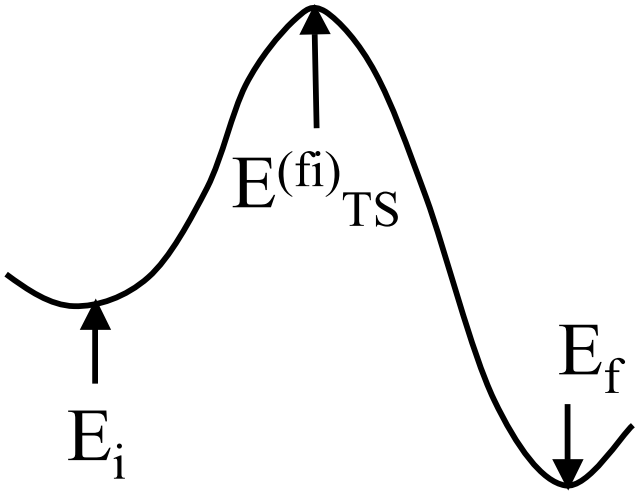


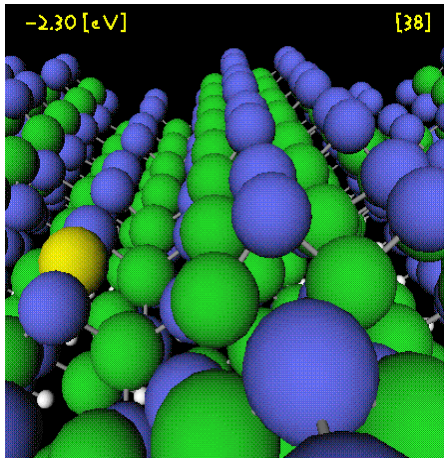
transition state

initial state

final state

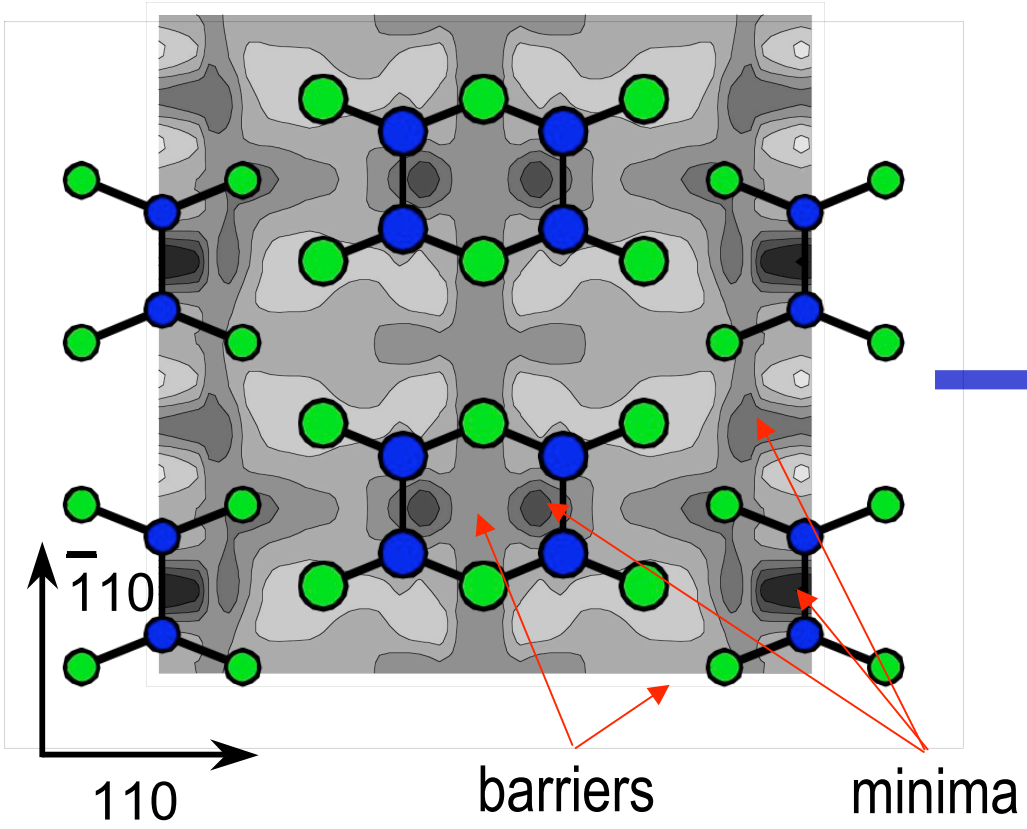


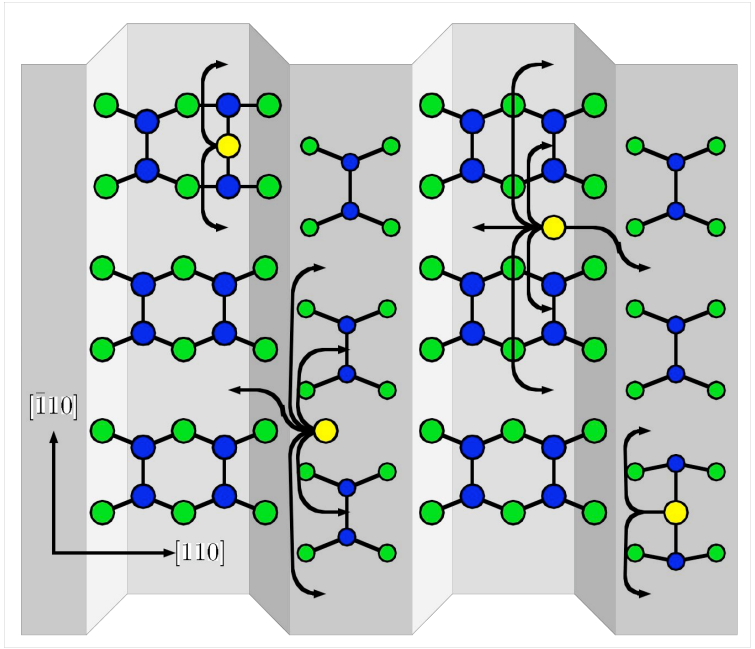




Surface diffusion on GaAs(001): mapping of PES to network graph

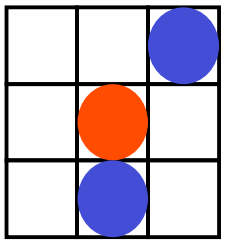
PES from DFT calculations → network of hops





kMC with explicit list of process types

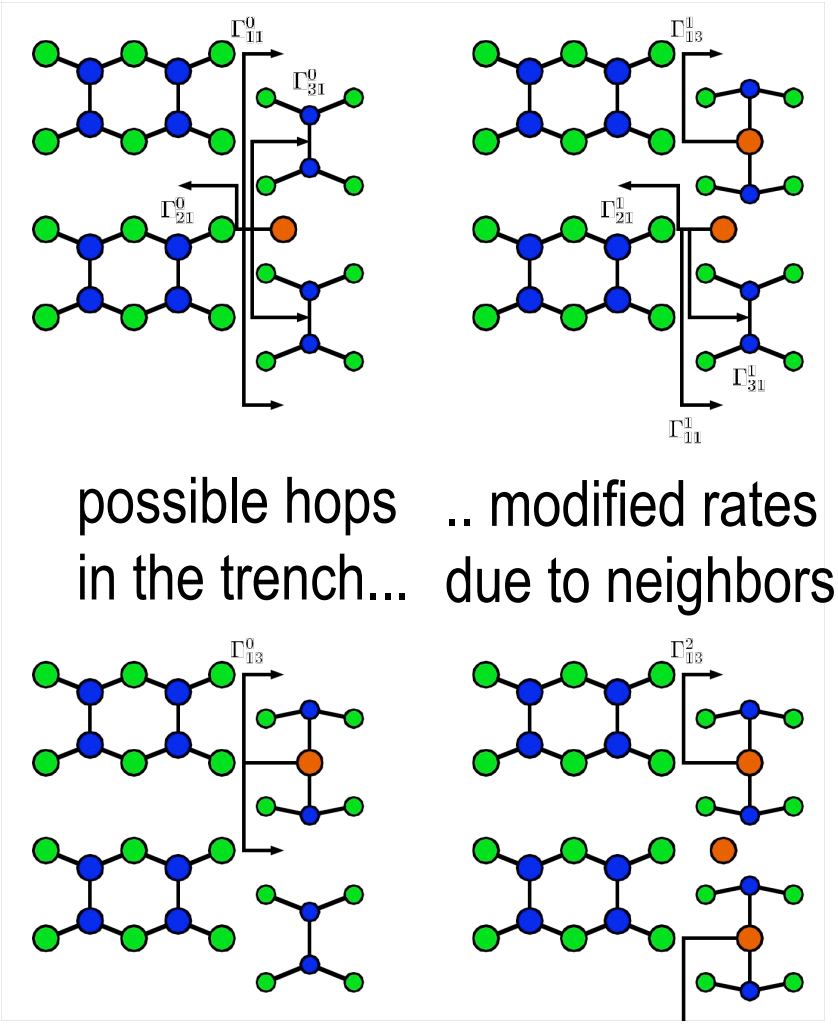
Voter's lattice kMC:



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

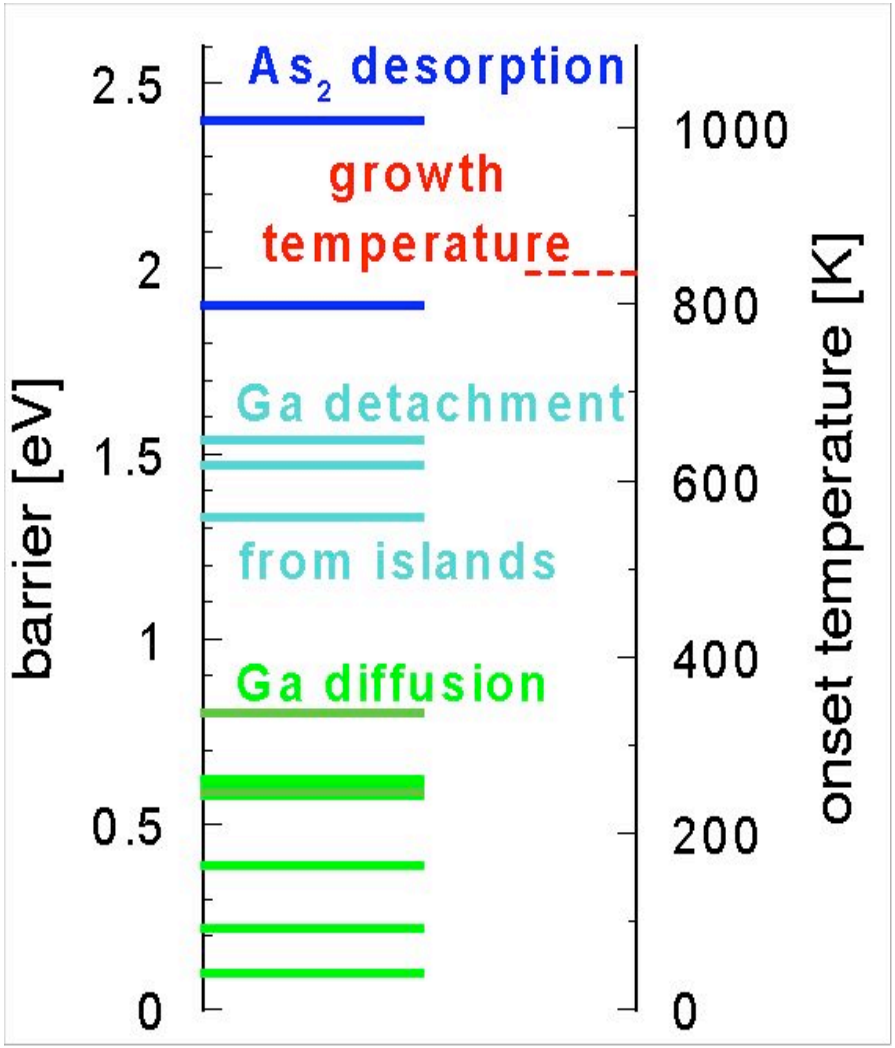
- simulation on a lattice
- group possible transitions Γ(f,i) from i to f into classes, each class is characterized by a rate
- classification of initial and final state by 'atomic neighborhoods' e.g., the number and relative position of neighbors define a process type

DFT-based kMC:



kinetic Monte Carlo simulations for GaAs epitaxy

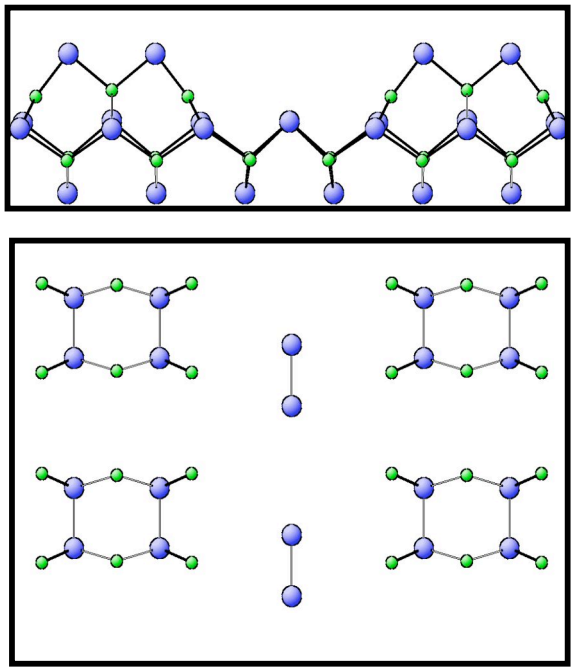
- 32 microscopically different Ga diffusion processes, and As_2 adsorption/desorption are included explicitly
- computational challenge: widely different time scales (10^{-12} sec to 10 sec)
- simulation cell 160 x 320 sites (64 nm x 128 nm)

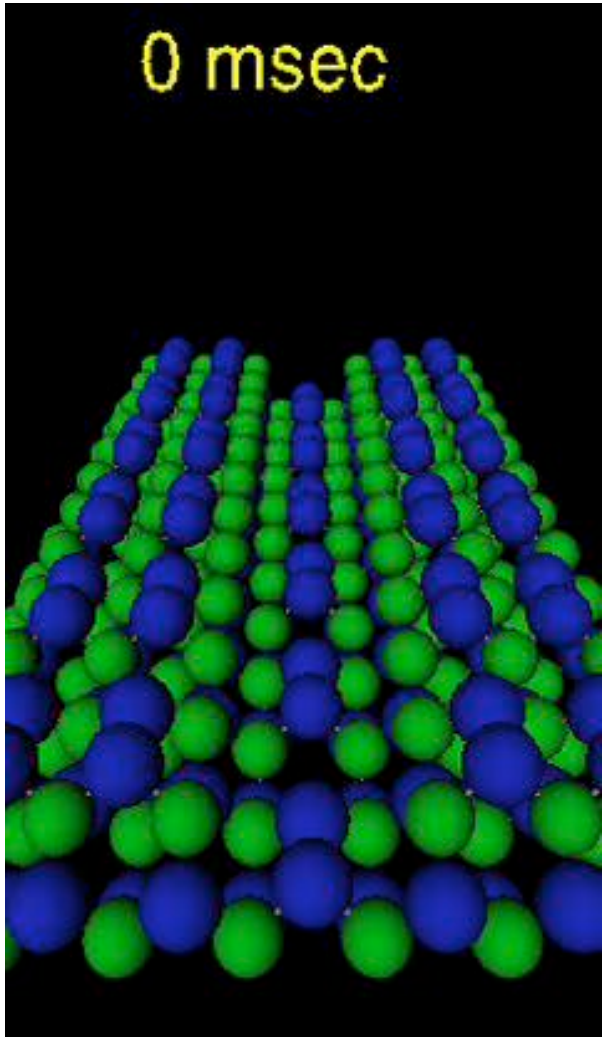


kinetics of island nucleation and growth

side view

top view





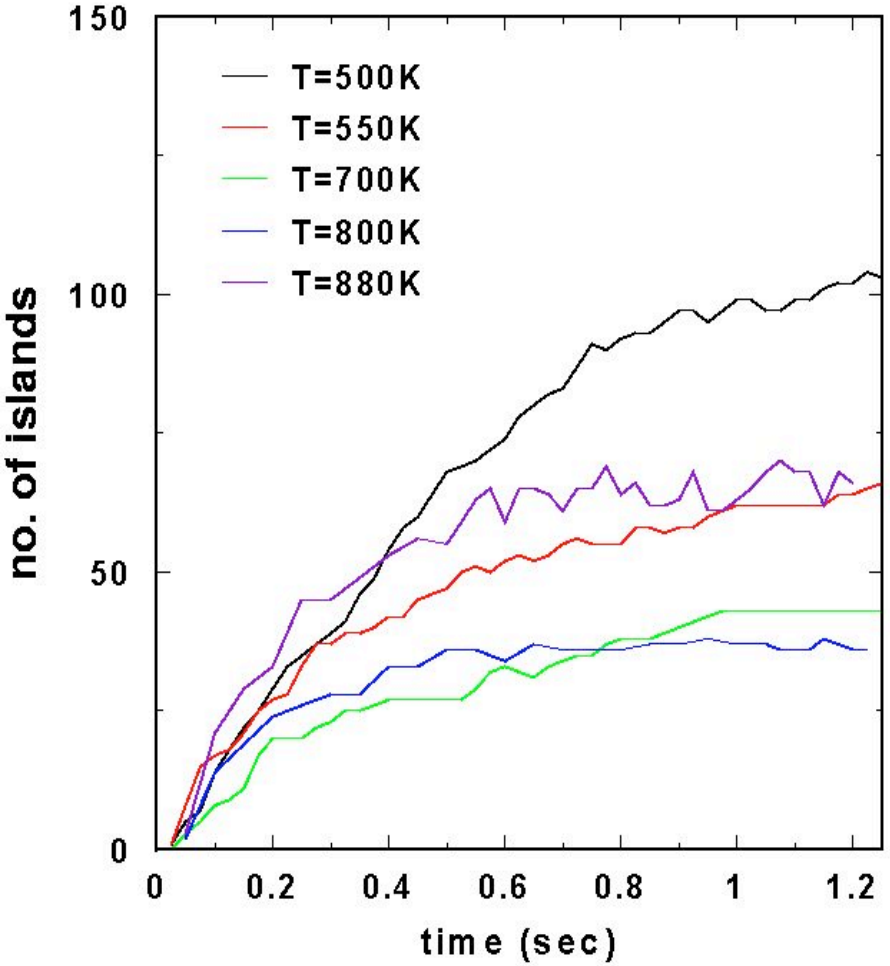
1/60 of the full simulation cell

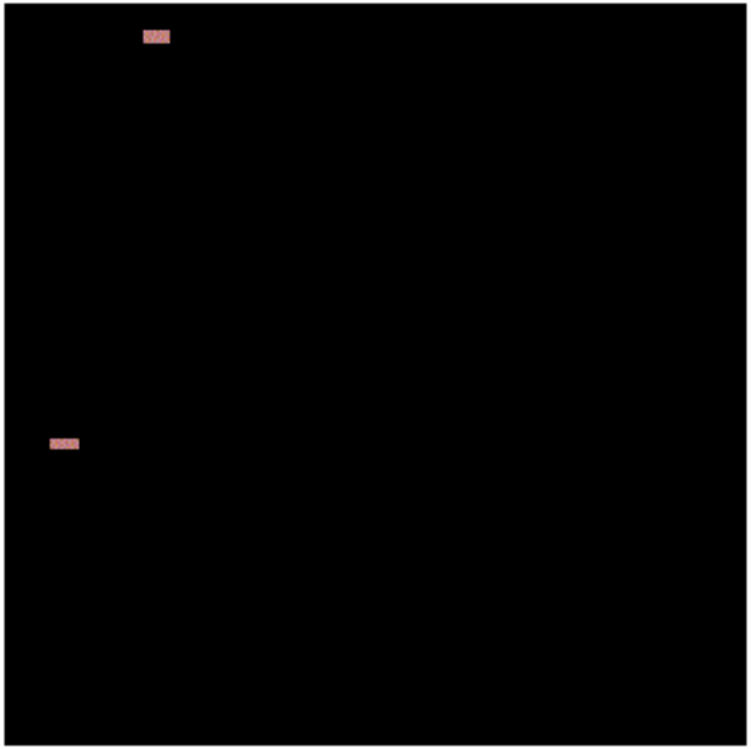
As_2 pressure = 0.85 x 10^{-8} bar

Ga deposition rate = 0.1 ML/s

T = 700 K

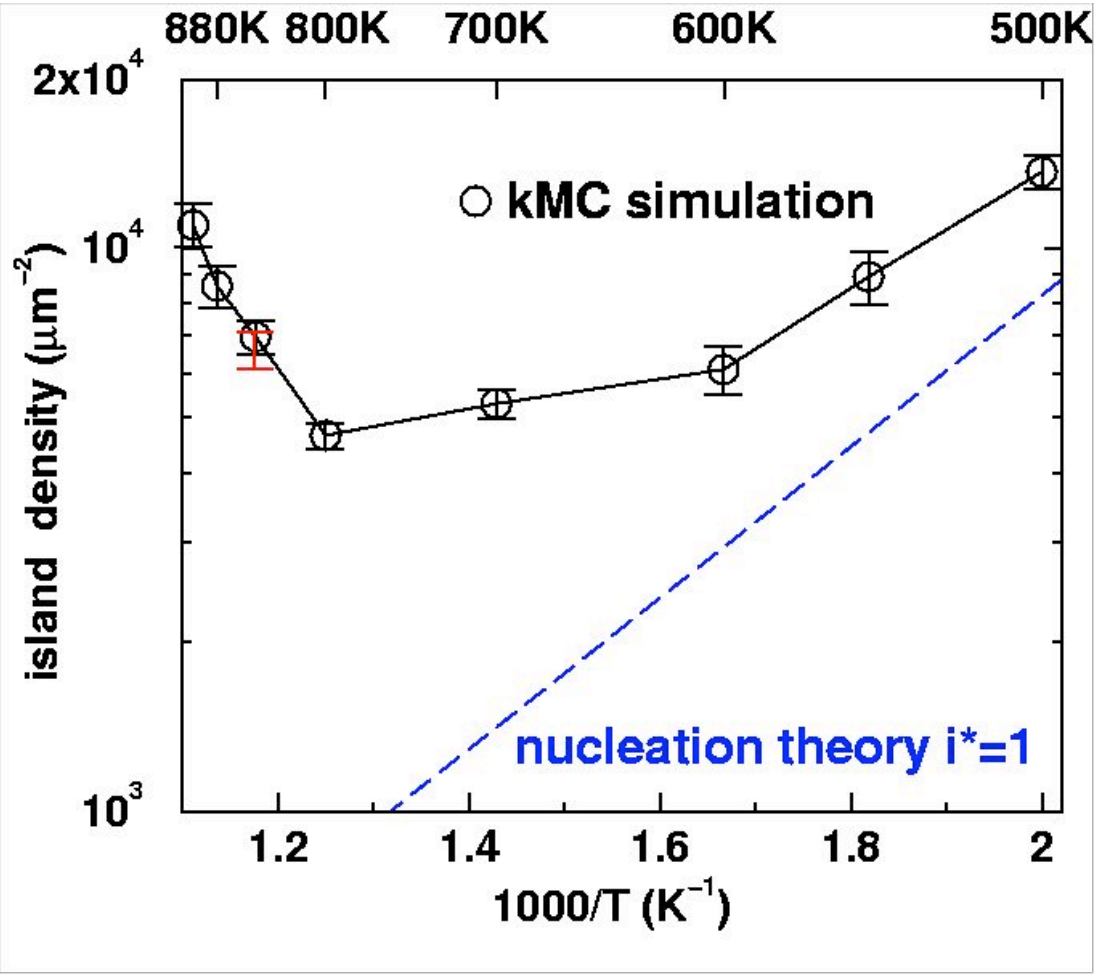
island density





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

scaling with temperature ?



'conventional' nucleation theory

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

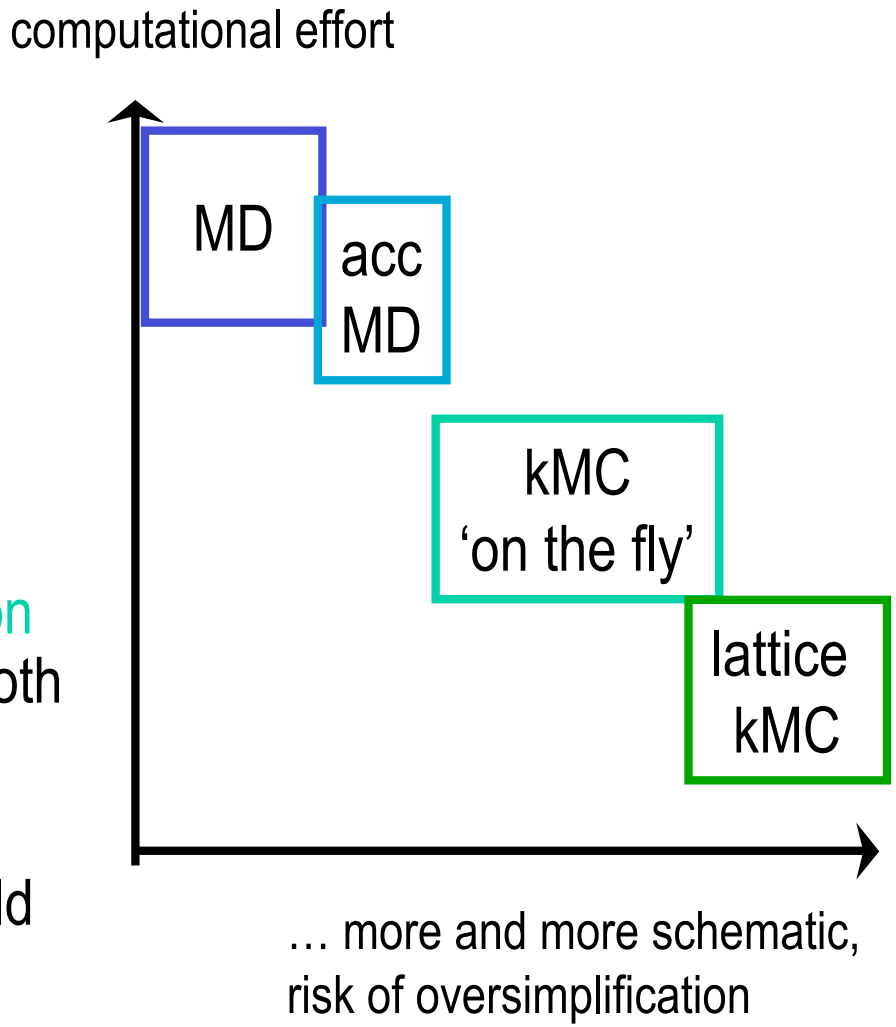
N_{is}	island density
D	diffusion constant
R	deposition flux
η	numerical const.
i^*	critical nucleus

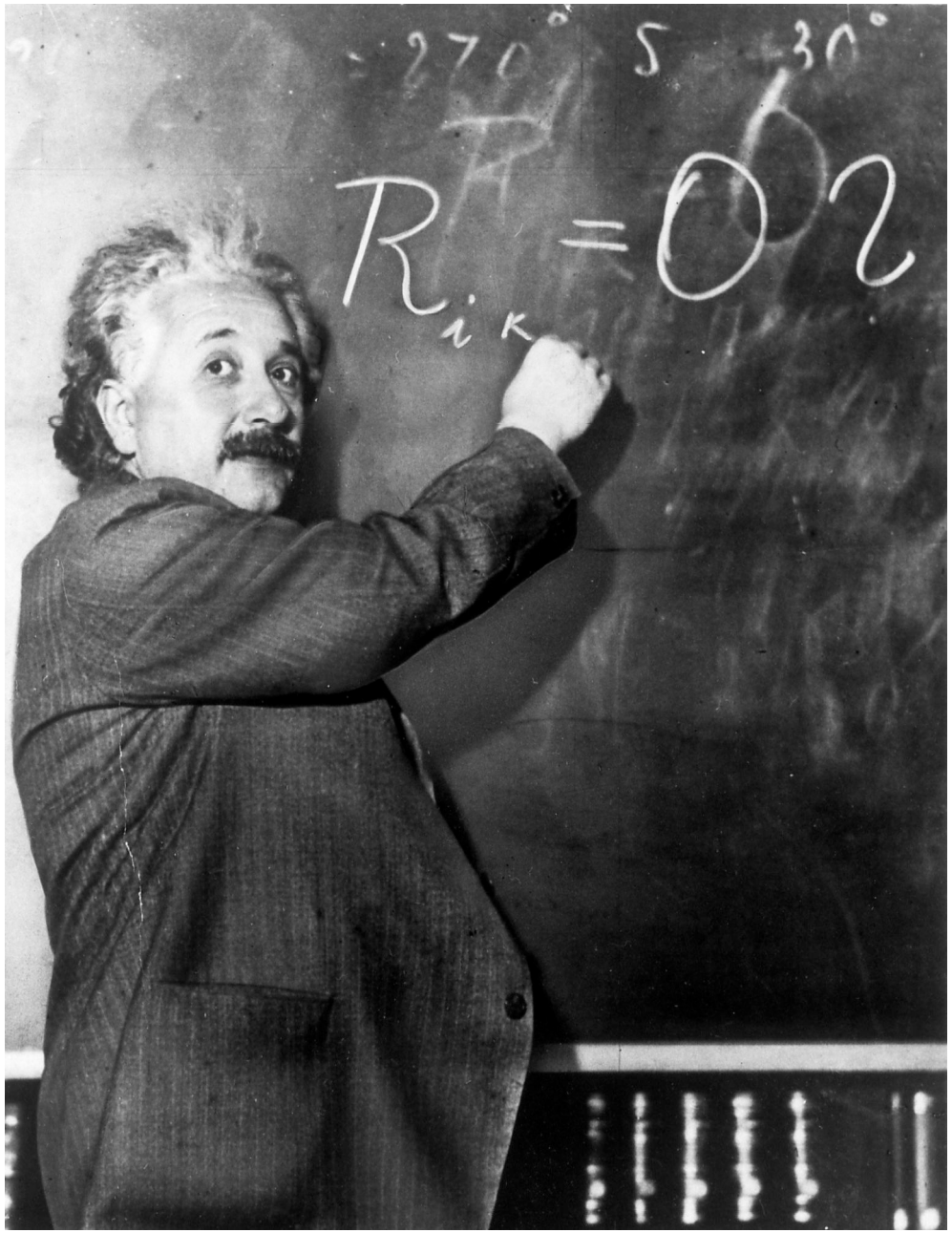
simulation: P. Kratzer and M. Scheffler , Phys. Rev. Lett. **88**, 036102 (2002)

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

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))





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

Thank you for your attention !

Summary: arXiv:0904.2556