

Atomistic aspects: the role of DFT calculations

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How to obtain information about the energetics at the atomic level

From statistical physics to material science:

- In epitaxy, details at the atomistic level may have dramatic effects on the macroscopic morphology → we need knowledge about these details
- For our simulations to be predictive and materials-specific, we need quantitative data for barriers, rates, ...

Methods for atomistic calculations:

- force-field models (embedded-atom potentials, effective medium theory, Tersoff potentials, ...)
- simple quantum-mechanical models with semi-empirical parameters: tight-binding (or extended Hückel)
- density-functional calculations
- quantum-chemical calculations (post Hartree-Fock methods: MCSCF, CI, CCSD, ..)

Calculation of Atomistic Structure and Forces

| | method | | # of atoms | applications | accuracy |
|---------------|-------------------------------------|-----------------------------------|------------|------------------|----------|
| semiempirical | metals | EMT / EAM | 100,000 | elastic prop. | |
| | semiconductors | Stillinger-Weber pot. | | elastic prop. | |
| | | Tersoff pot. | | amorphous solids | |
| | | tight-binding | | surfaces | |
| | | | | | |
| DFT | with localized orbitals | FIREBALL SIESTA | 3000 | all | ~0.2 eV? |
| | with plane waves / pseudopotentials | FHI98MD VASP ... | 300 | all | ~0.1 eV |

From many-particle physics to DFT

Schrödinger (1926)

$$\left[-\sum_{\mathbf{k}} \nabla_{\mathbf{k}}^2 / 2m + \frac{1}{2} \sum_{\mathbf{k}, \mathbf{l}} W(\mathbf{r}_{\mathbf{k}}, \mathbf{r}_{\mathbf{l}}) \right] \phi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N) = E \phi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N)$$

Kohn & Hohenberg (1965), Kohn & Sham (1966)

$$\left[-\nabla^2 / 2m + V_{\text{eff}}[\mathbf{n}](\mathbf{r}) \right] \varphi_j(\mathbf{r}) = \varepsilon_j \varphi_j(\mathbf{r}) \quad \text{density functional theory}$$

$$\mathbf{n}(\mathbf{r}) = \sum_j |\varphi_j(\mathbf{r})|^2$$

in practice:

$$V_{\text{eff}}[\mathbf{n}](\mathbf{r}) \rightarrow V_{\text{eff}}(\mathbf{n}(\mathbf{r})) \quad (\text{LDA})$$

$$V_{\text{eff}}[\mathbf{n}](\mathbf{r}) \rightarrow V_{\text{eff}}(\mathbf{n}(\mathbf{r}), \nabla \mathbf{n}(\mathbf{r})) \quad (\text{GGA})$$

typical implementations of DFT

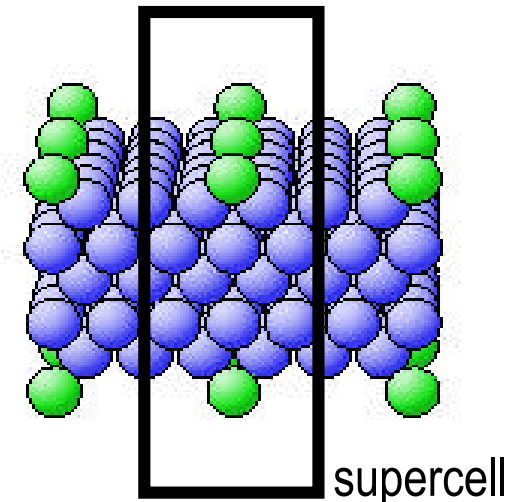
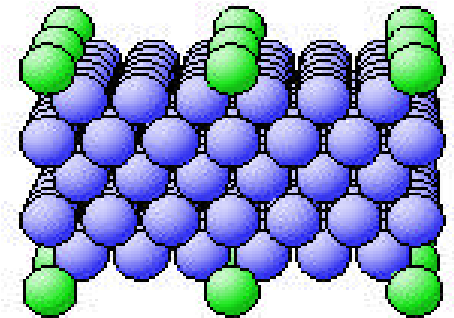
- supercell geometry
 - expansion of ϕ into plane waves
 - total-energy calculation
- $$E_{\text{tot}} = \sum_{\mathbf{k}} \sum_j \varepsilon_j(\mathbf{k}) + \Delta E_{\text{Hartree}} + \Delta E_{\text{XC}} + E_{\text{ionic}}$$
- summation over Brillouin zone is done using special k-point sets

- forces are calculated routinely to relax the surface atoms again for each adatom position

- implementations differ with respect to their main focus on accuracy (e.g. all-electron methods) or on system size (pseudopotential method)

- present status: applicable to wide variety of materials, reasonable accuracy (say 0.1-0.2 eV), limited by the functional

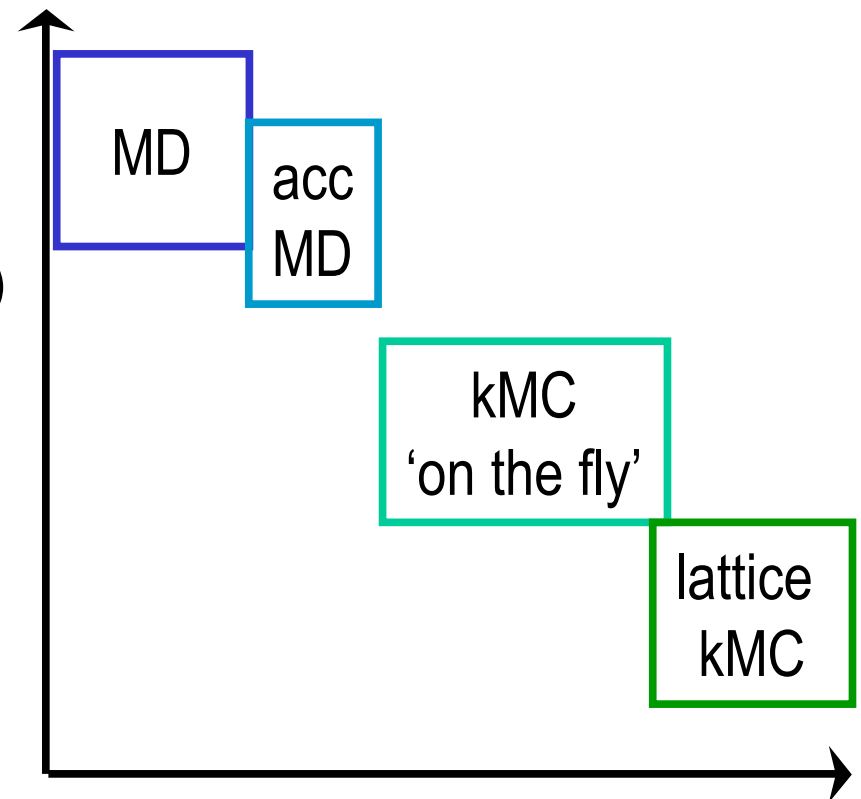
adatom(+superficial periodic images)



Bridging the time-scale gap

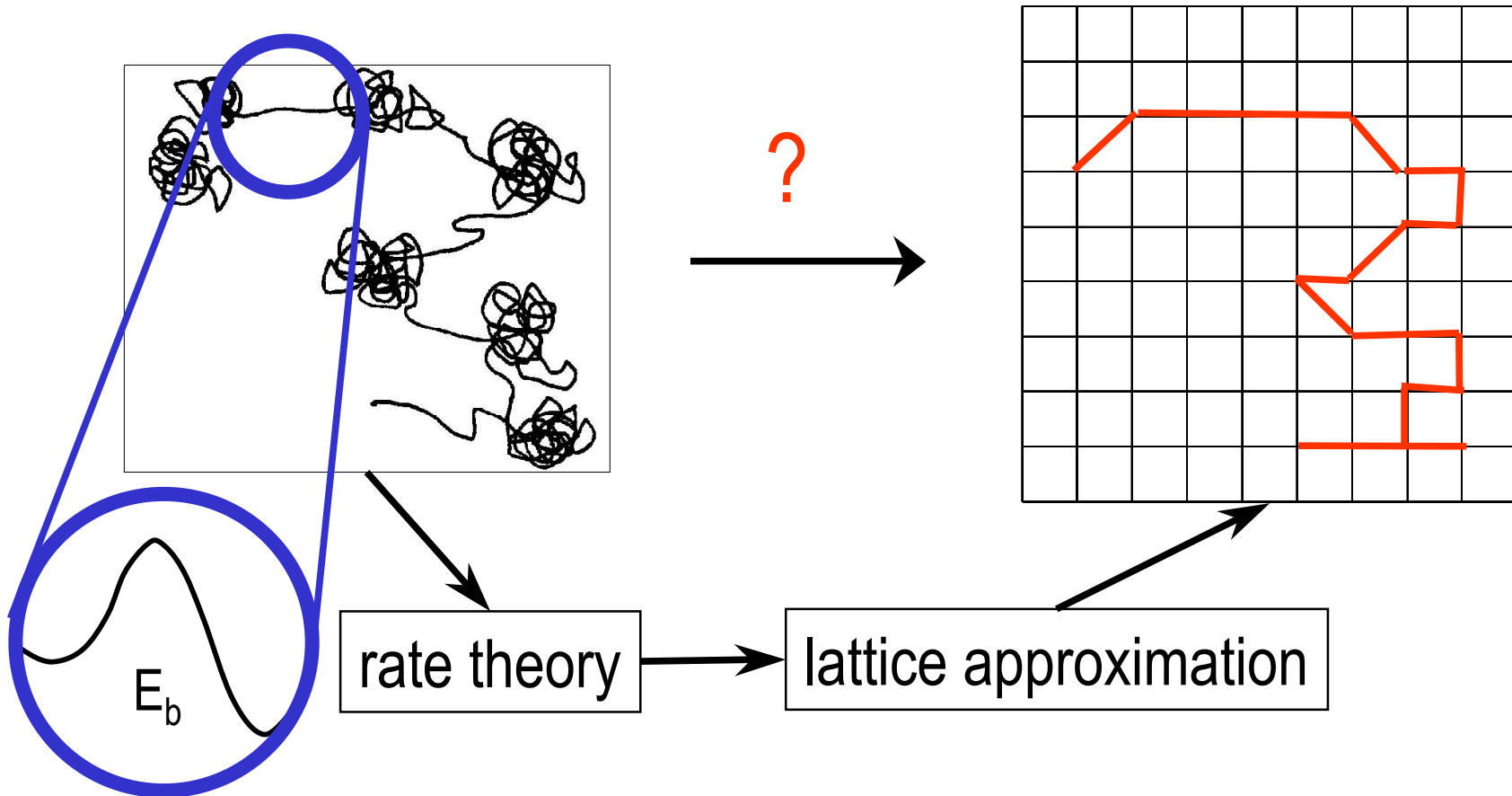
- molecular dynamics
(Car-Parrinello method)
- accelerated molecular dynamics
 - using a boost potential (Voter, Fichthorn,...)
 - temperature-accelerated MD
(Montalenti et al. PRL **87**, 126101 (2001))
- kinetic Monte Carlo with transition state search on the fly (without lattice approximation, without pre-defined rate table)
- lattice kinetic Monte Carlo, N -fold way
(Voter PRB **34**, 6819 (1986))

computational effort



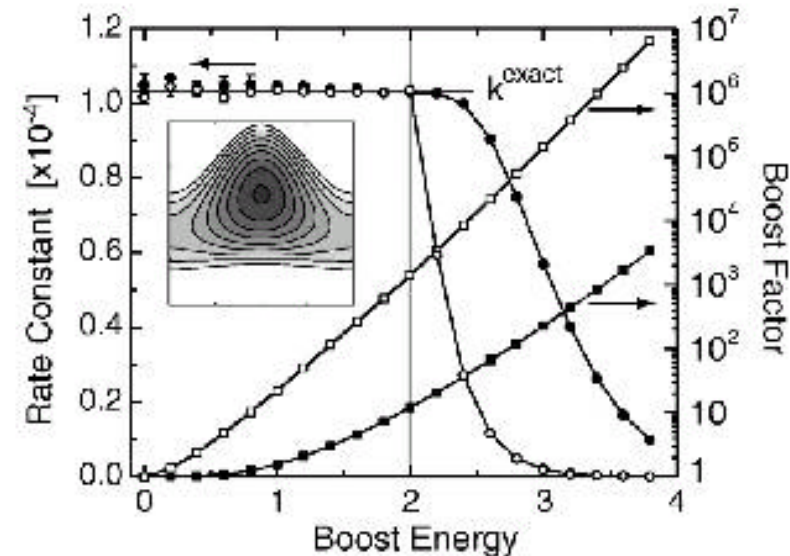
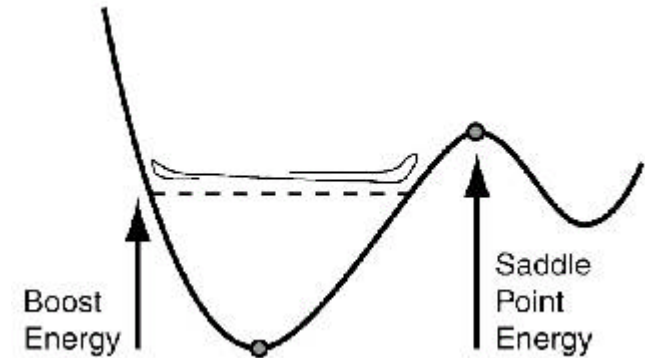
... more and more schematic,
risk of oversimplification

From molecular dynamics to kinetic Monte Carlo



Accelerated MD with 'boost potential'

- In ordinary MD, particles will most of the time perform oscillations in their basins.
- What is really important: **rare events** (transitions from one basin to the next)
- **idea:** add a 'boost potential' to the minima, thus making the particles spend less time there; the boost potential **must not** affect saddle point region
- tricky ways of constructing V_{boost}
- $\max(V_{\text{boost}}) < \text{smallest barrier in the system}$
- in a large N-particle system, the boost potential raises the potential energy of each particle on average only by V_{boost}/N

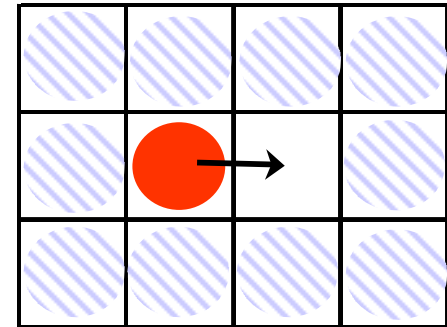


open symbols 1-part.; full symbols: 10-part.

Voter's lattice kMC

Given that ..

- concerted processes are unimportant
- nearest-neighbor interactions are sufficient
- 10 neighboring sites that can be occupied or empty: $\rightarrow N \sim 2^{10}$ process types

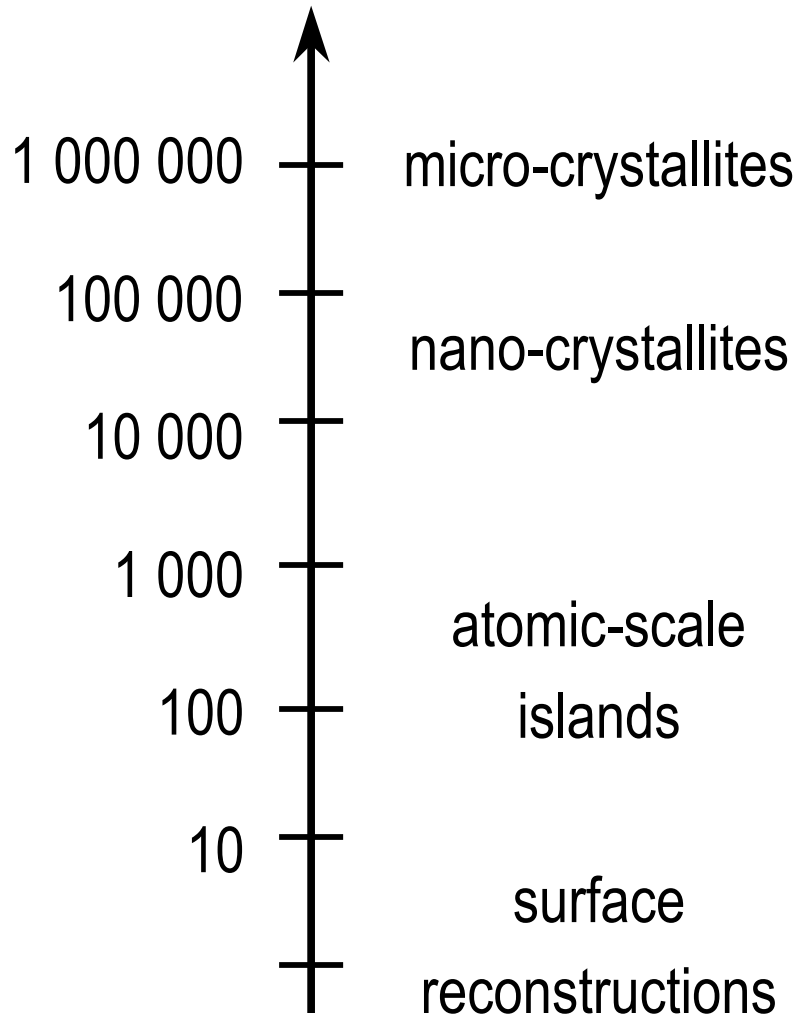


... it follows that

- If we have a systematic way of calculating the rate constants for each process type (e.g. by molecular dynamics), the N-fold way algorithm gives us the full long-time dynamics (essentially as good as MD, but using a “symbolic” rather than the Newtonian dynamics)

number of atoms

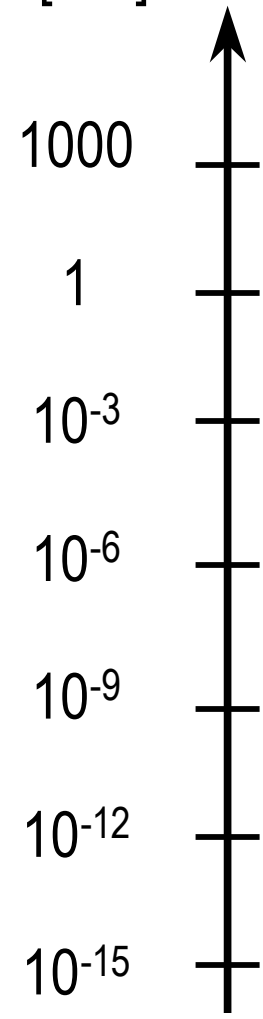
time scale of processes
involved [sec]



**mean-filed
approaches**

kinetic Monte Carlo

***ab initio* molecular
dynamics**



How to calculate rate constants in complex systems

G. Henkelmann, G. Johansson & H. Jonsson, in:

Progr. In Theor. Chemistry, S. D. Schwartz (Ed.), Kluwer Academic Publishers, 2000, p.269ff.

<http://www-theory.chem.washington.edu/~hannes/paperProgrInThChem>

from the PES to rate constants Γ (1-dim)

- Kramer's rate theory (c.f. W. Paul's Monday talk)

$$\Gamma = \frac{I}{w_b} \left(\frac{w_0}{2\pi} \exp\left(-\frac{E_b}{kT}\right) \right) \quad I = \left(\frac{g^2}{4} + w_b^2 \right)^{1/2} - \frac{g}{2}$$

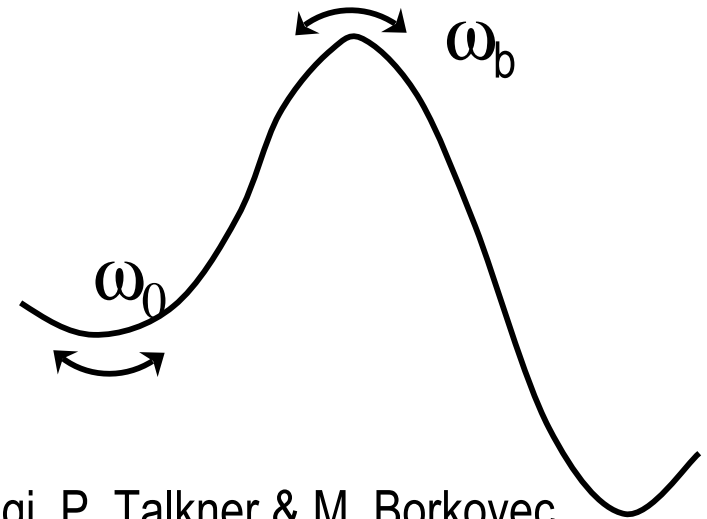
γ : friction due to coupling to the heat bath

- high-friction limit

$$\Gamma = \frac{w_0 w_b}{2\pi g} \exp\left(-\frac{E_b}{kT}\right)$$

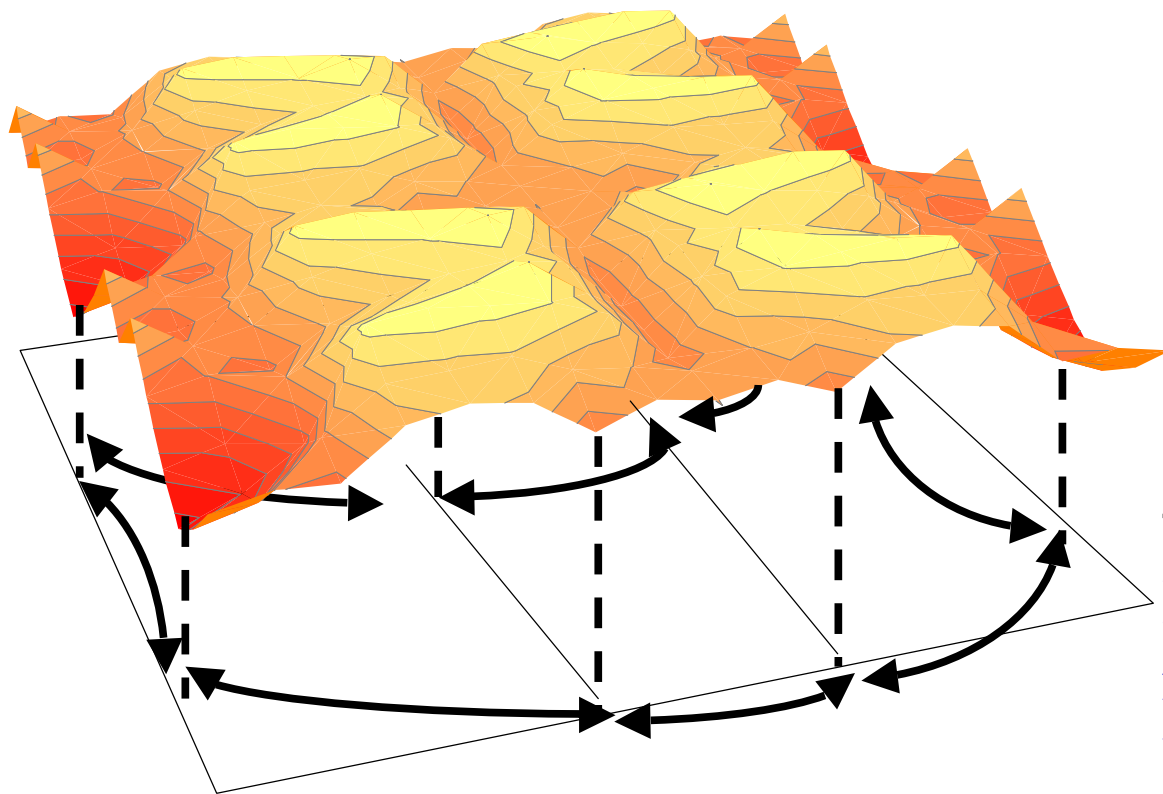
- medium friction \rightarrow transition state theory

$$\Gamma = \frac{w_0}{2\pi} \exp\left(-\frac{E_b}{kT}\right)$$



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

from the PES to rate constants G (N-dim)



idea:

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

hopping rates derived from the PES

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

$$\Gamma = kT/h \frac{Z_{\text{TS}}}{Z_i} = \text{(harmonic \& classical approximation)} = \frac{\prod_N v_{k,i}}{\prod_{N-1} v_{k,\text{TS}}} \exp(-\Delta E/kT)$$

Prefactor: Molecular Dynamics versus 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)

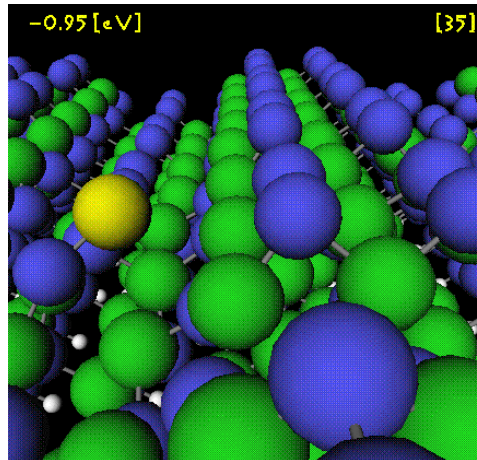
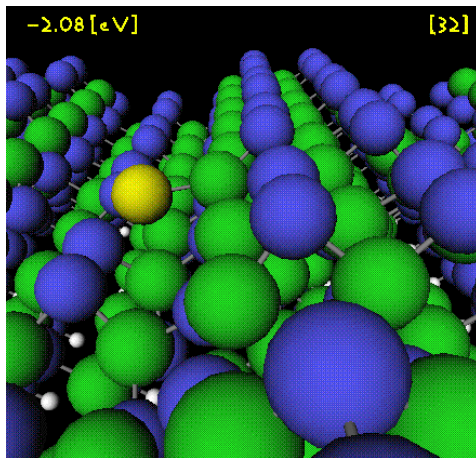
| | $\ln\Gamma_0$ [THz] | | ΔE [eV] | | static |
|----------|---------------------|---------|-----------------|-----------|--------|
| | TI | MD | TI | MD | |
| hop | 2.9±0.2 | 3.0±0.2 | 0.51±0.02 | 0.49±0.01 | 0.50 |
| exchange | 6.5±0.6 | 6.1±0.7 | 0.74±0.02 | 0.70±0.04 | 0.73 |

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

transition states for reactive processes

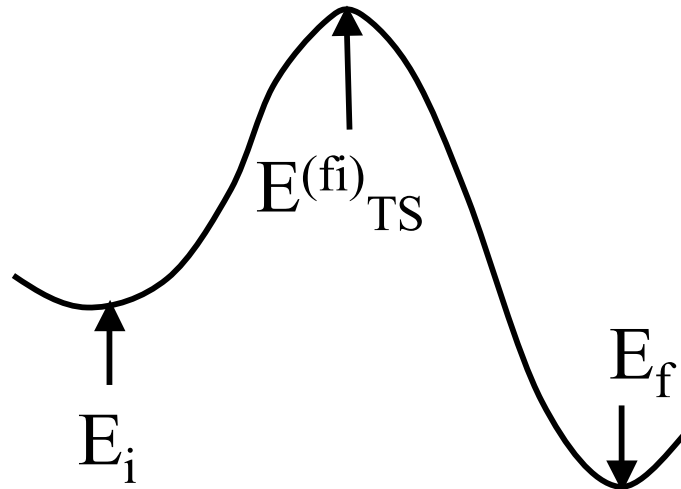
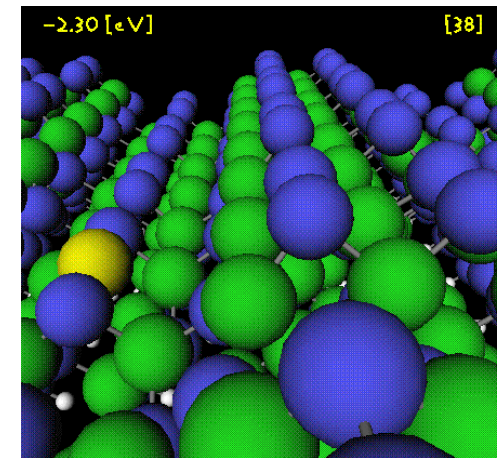
$$\Gamma^{(k)} = W(f,i) = \Gamma^{(fi)}_0 \exp(- (E^{(fi)}_{TS} - E_i) / kT)$$

initial state



transition state

final state



Transition state search methods

Requirements:

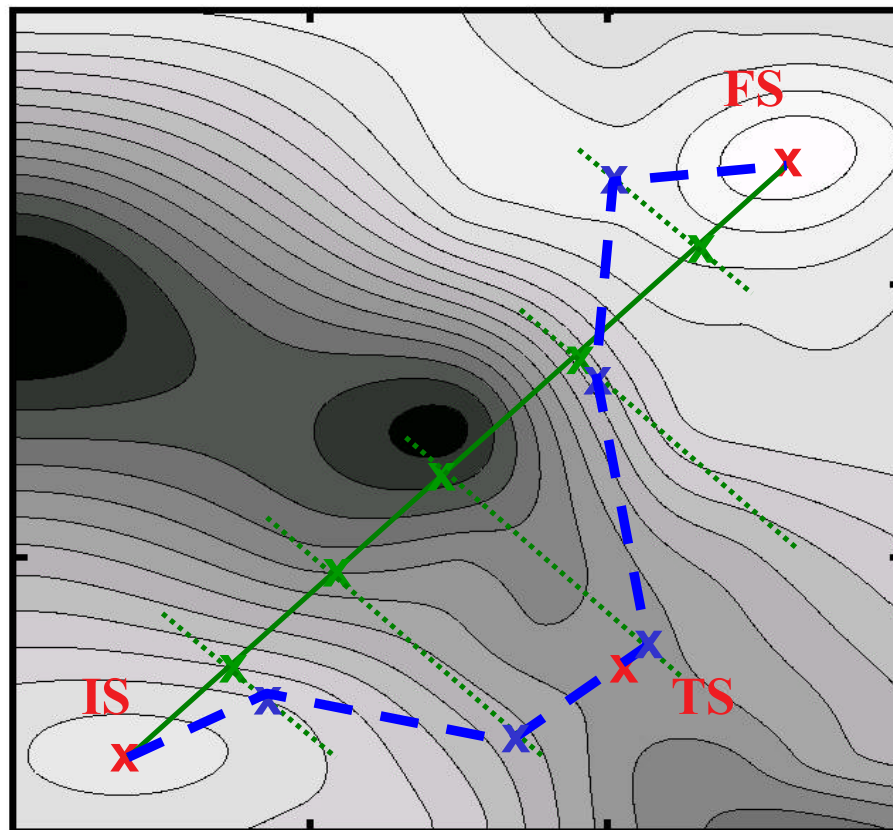
- use first derivatives only (DFT provides forces, but higher derivatives only with substantial effort)
- initial information: either both initial and final state or initial state only (many possible finals)

Methods:

- simple method: dragging
- the ridge method
- the nudged-elastic-band method (NEB)
- the dimer method
- many other, similar methods

Transition state search algorithms I: drag method

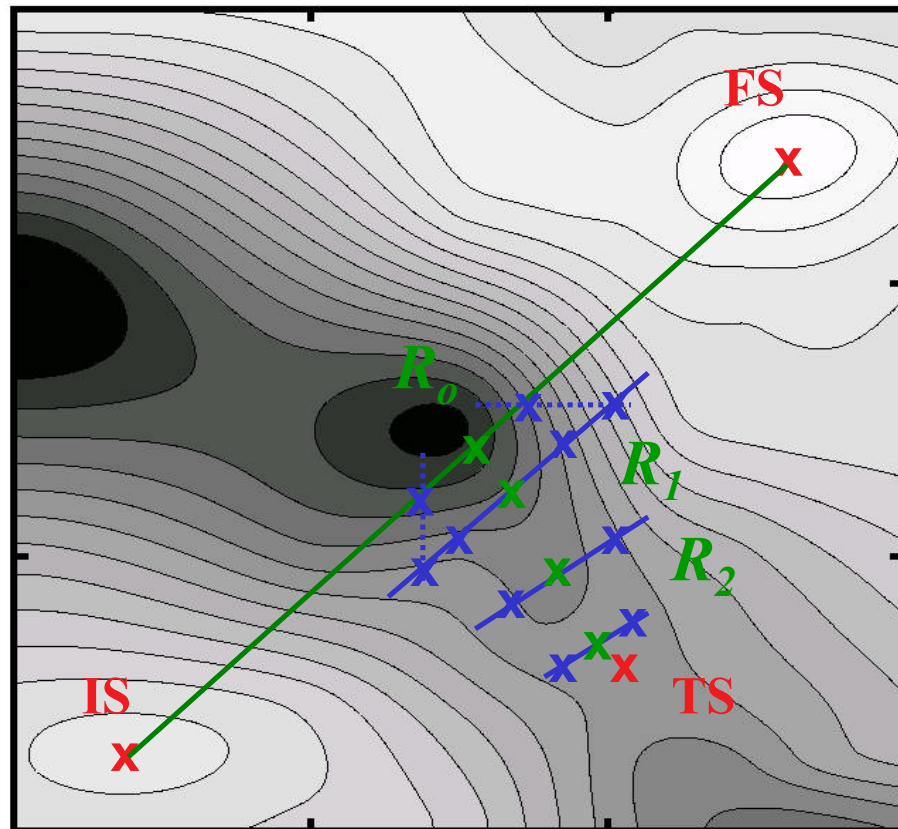
- Choose appropriate reaction coordinate q
- Constrain q and relax all other degrees of freedom
- repeat procedure at several values of q between initial and final state
 - Ⓜ highly dependent on good guess for reaction coordinate
 - Ⓜ if the true reaction coordinate has a sizeable component perpendicular to the guess, the drag method will yield a discontinuous (i.e. unphysical) reaction path!



Transition state search algorithms II: ridge method

- Initialize with straight line interpolation and choose max-energy point R_0
- Create two replicas slightly displaced from R_0 on either side of the ridge (side-step)
- Displace replicas along gradient (downhill-step)
- Find max-energy point R_i along connecting line between two replicas
- Sequentially decrease displacements in downhill- and side-steps when approaching TS

- Ⓜ instability when long distances must be overcome by side-stepping
- Ⓜ poor performance close to the saddle point



I.V. Ionova and E.A. Carter,
J. Chem. Phys. 98, 6377 (1993)

Transition state search algorithms III: nudged elastic band (NEB) method

- Initialize with several images $\{R_i\}$ along a straight-line interpolation

- Minimize

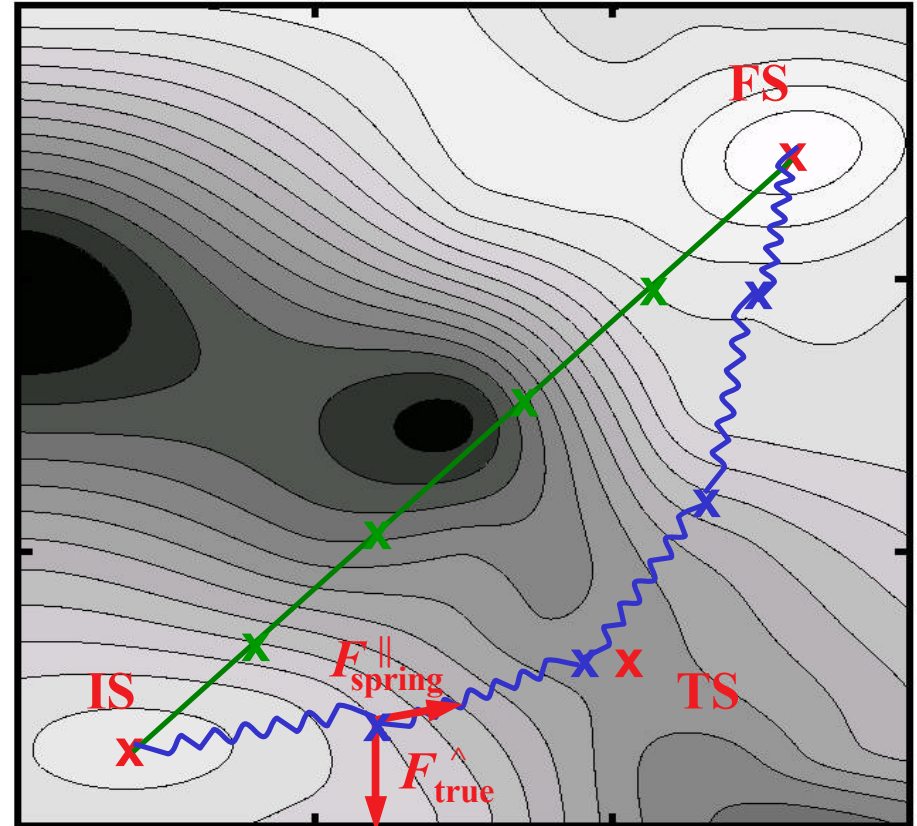
$$S(R_1, \dots, R_N) = \sum_i E(R_i) + \sum_i k/2 (R_{i+1} - R_i)^2$$

- **Problem:**

- elastic band cuts corners
- images tend to slide down towards low-energy IS/FS regions, leaving few images for relevant TS region

- **Solution:**

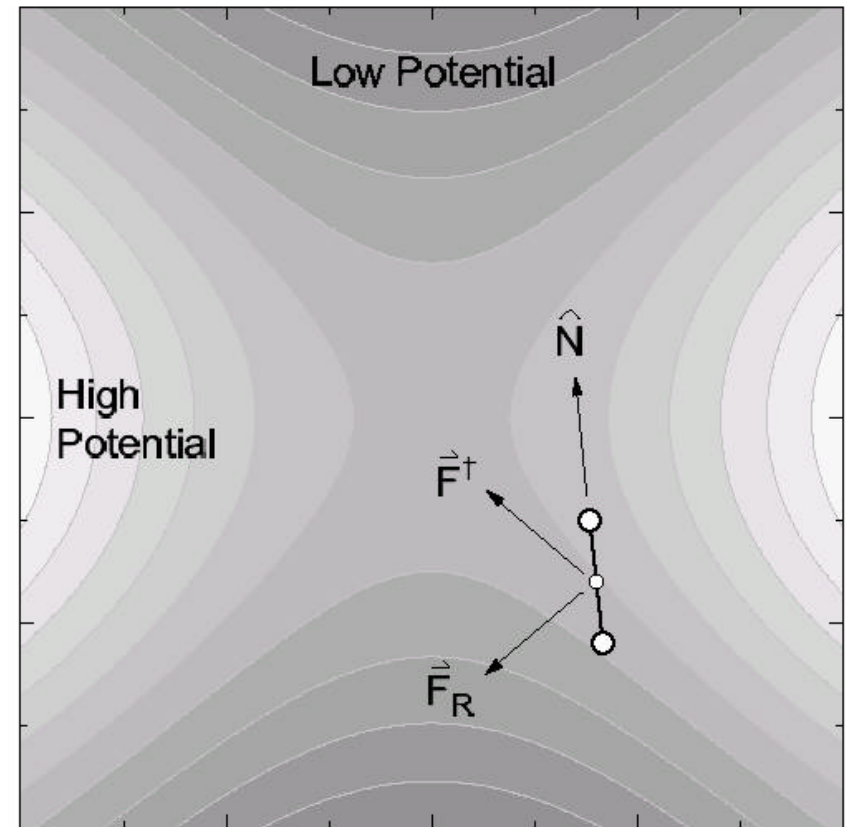
- only spring force component parallel to path (no corner cutting)
- only true force component perpendicular to path (no down-sliding)



G. Mills and H. Jónsson,
Phys. Rev. Lett. **72**, 1124 (1994)

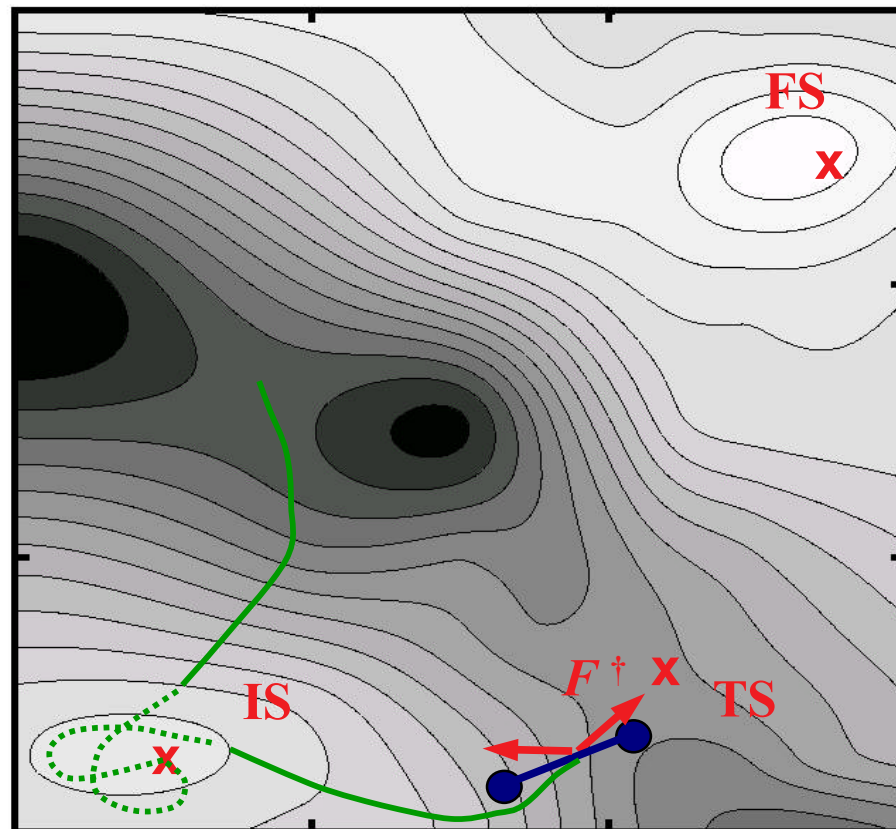
Transition state search algorithms IV: dimer method

- Typically only the initial minimum is known, but we require information about **all** final states which can be reached from there
- ‘uphill-climbing’ methods
 - **alternative 1:**
if the Hessian is known, follow one eigenvector (usually the one with the lowest energy)
 - **alternative 2:**
a small dumbbell free to orient itself in a potential landscape will choose the orientation of lowest curvature



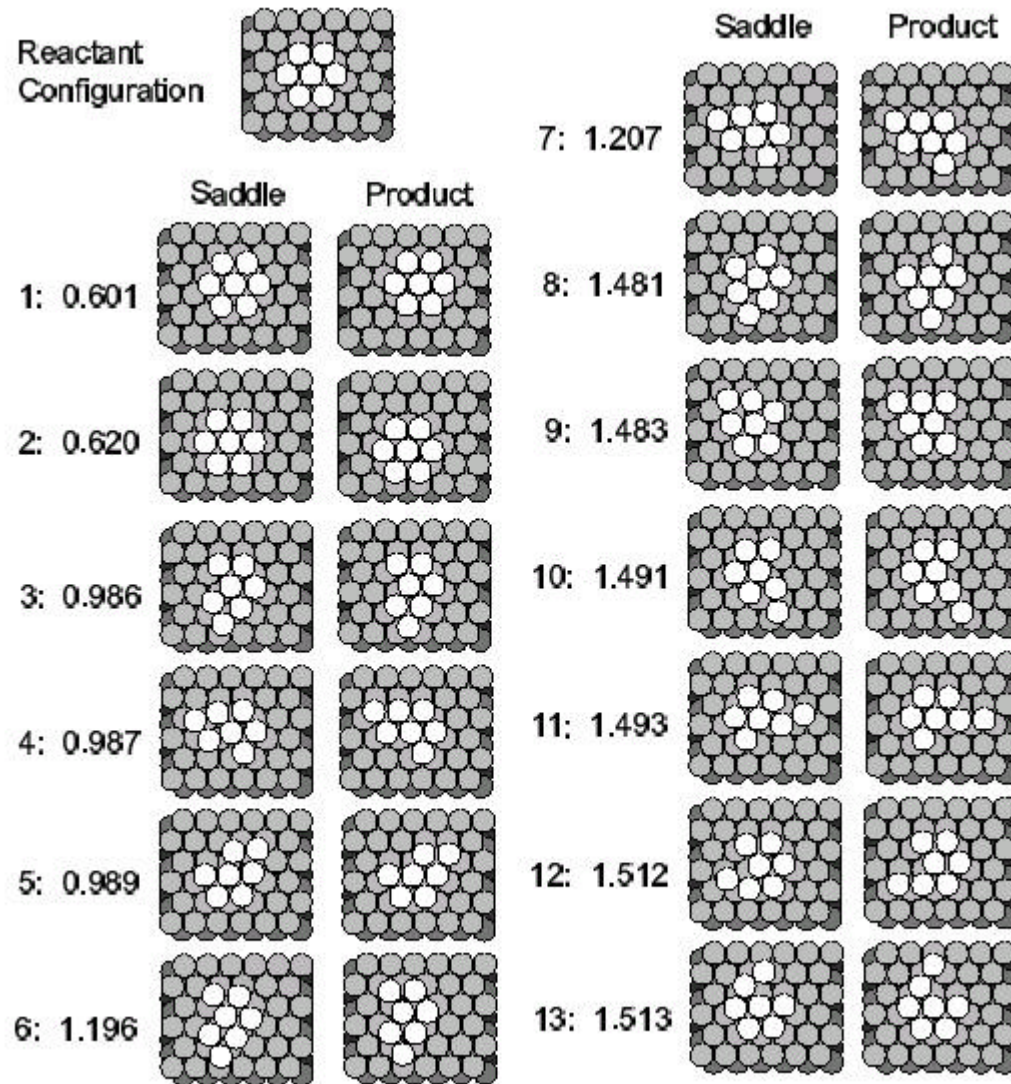
Transition state search algorithms IV: dimer method

- Uphill climbing is achieved by mirroring the force along the dimer axis different saddle points can be reached by
 - initializing with a short MD run, or
 - initializing with a set of random point around the minimum, and
 - following the second lowest mode, rather than the lowest
- re-orientation of the dimer after each move



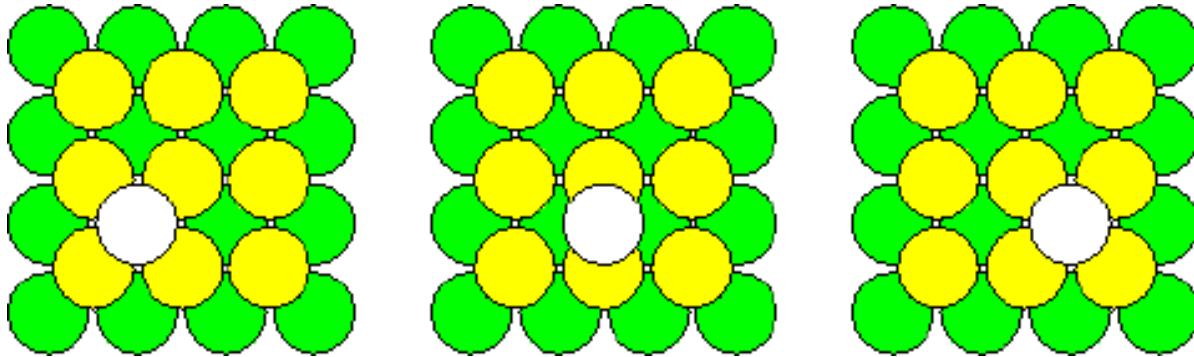
G. Henkelman and H. Jónsson,
J. Chem. Phys. **111**, 7010 (1999)

Example: collective motion of an island



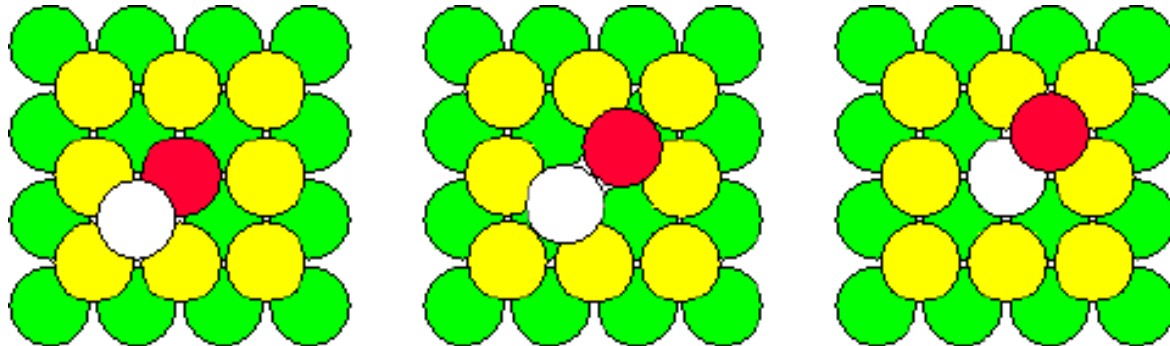
diffusion on metal surfaces

- typical case: diffusion by hopping between surface sites



Ag(100) $E_d=0.45$ eV
Au(100) $E_d=0.83$ eV

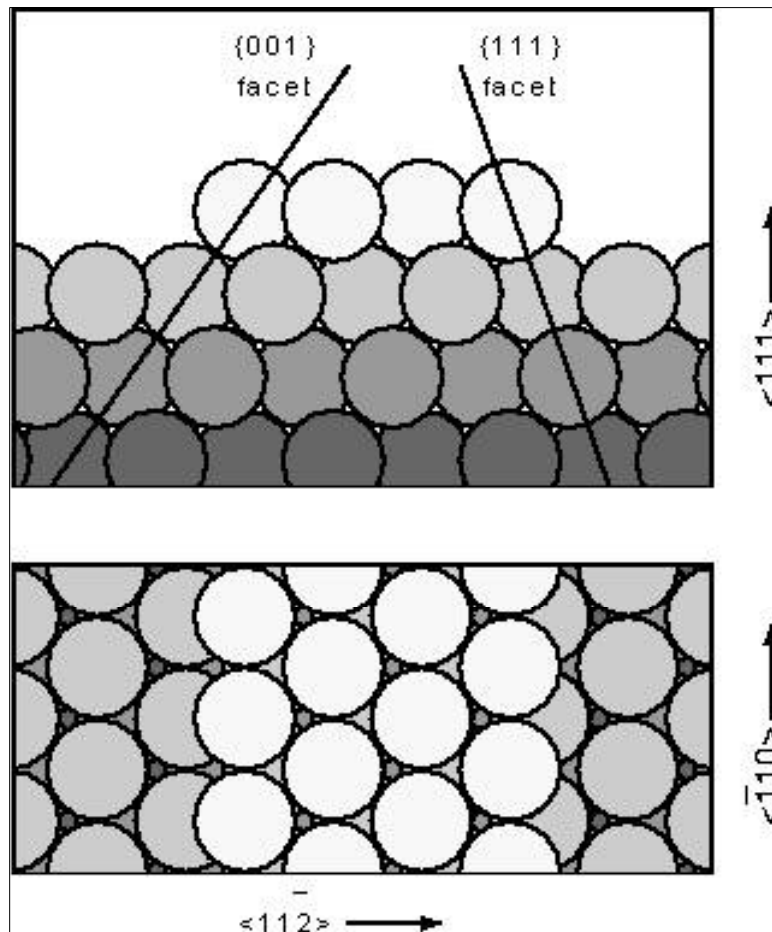
- sometimes exchange is favored (in particular for high intrinsic stress)



Ag(100) $E_d=0.73$ eV
Au(100) $E_d=0.65$ eV

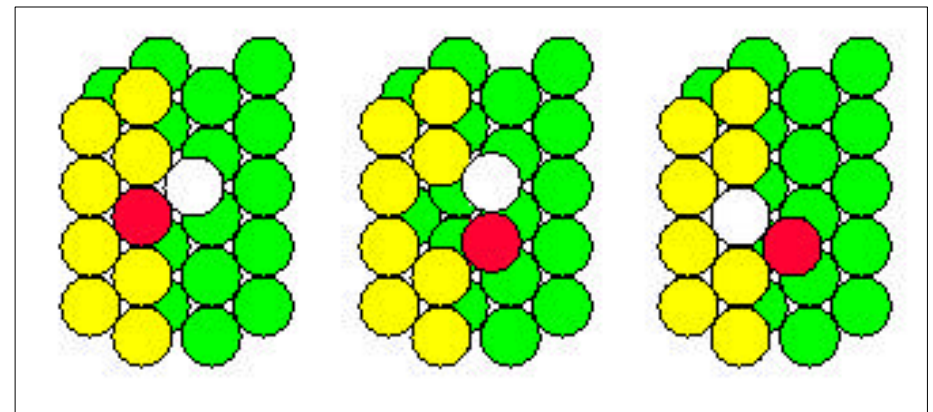
B.D. Yu & M. Scheffler,
PRB **56**, R15569 (1997).

diffusion at step edges



DFT calculations for Al(111) show that exchange is the preferred mechanism for diffusion along close-packed steps.

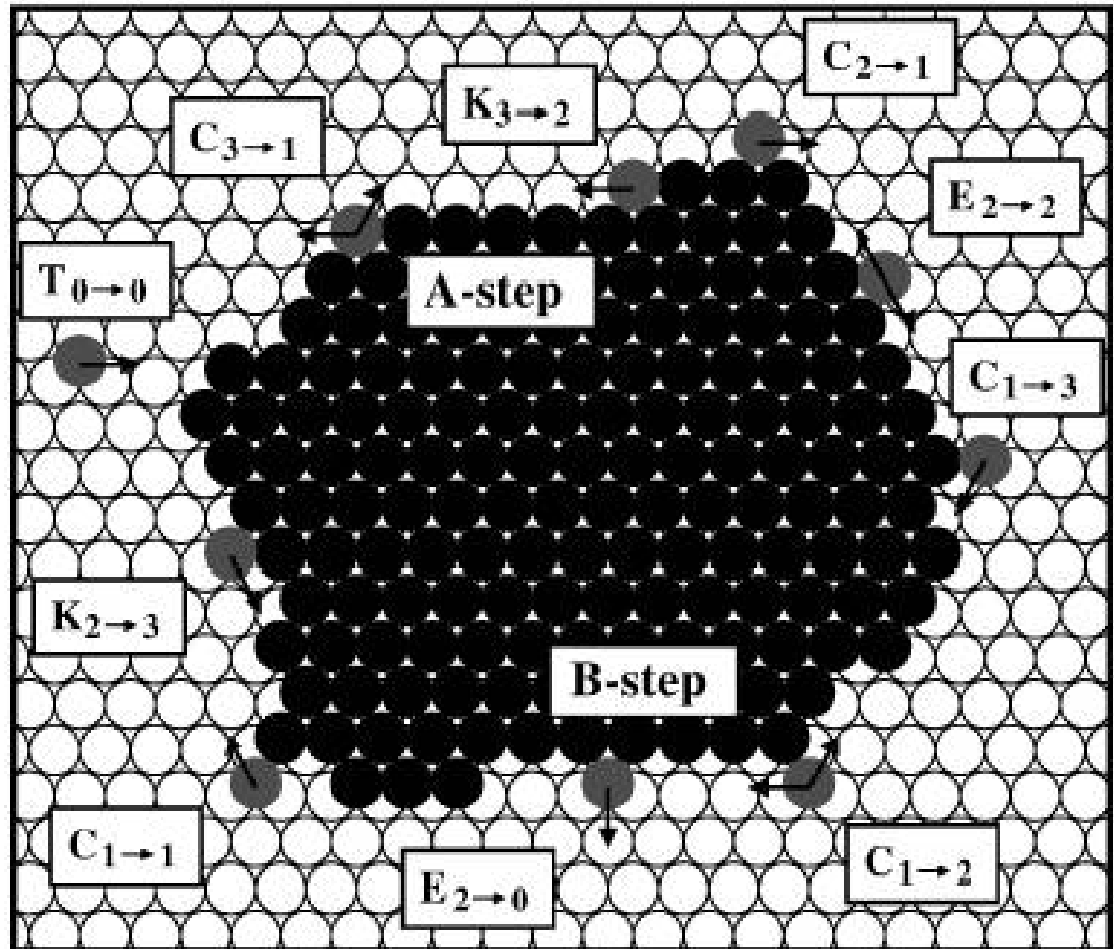
R. Stumpf & M. Scheffler, PRL **72**, 254 (1994)



low-symmetry diffusion paths at islands

T: terrace diffusion
E: step diffusion
K: kink diffusion
C: corner diffusion

A. Bogicevic, J. Strömquist &
B. Lundqvist,
PRL **81**, 637 (1998)
S. Ovensson, A. Bogicevic &
B. Lundqvist,
PRL **83**, 2608 (1999)



Example 1: shape of metal islands

onset temperature for a process with barrier E_b

$$T_b = E_b / [k_b \ln(\Gamma_0 / \Gamma)]$$

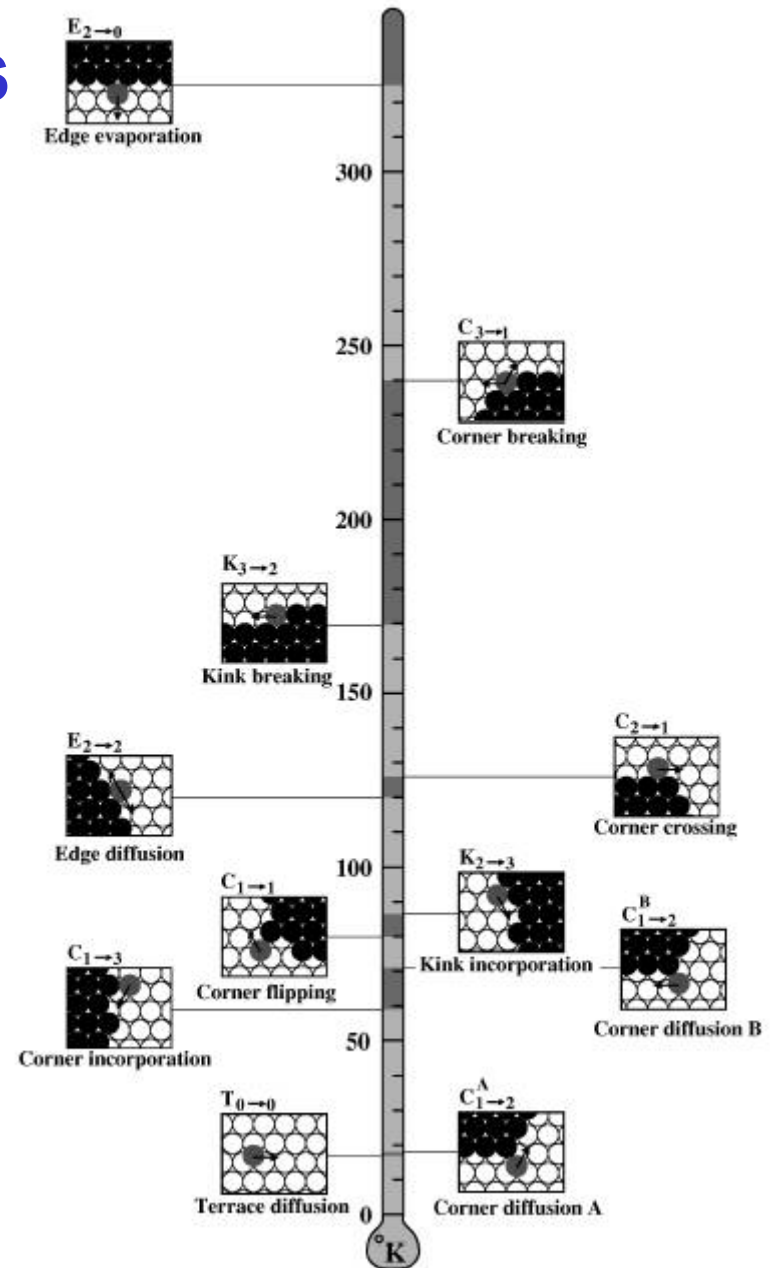
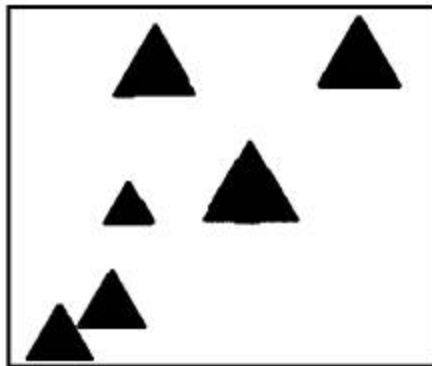
with $\Gamma \cong 1 \text{ sec}^{-1}$ and $\Gamma_0 \cong 10^{13} \text{ sec}^{-1}$.

Edge diffusion anisotropy is the main reason for triangular island shape.

$T = 80 \text{ K}$

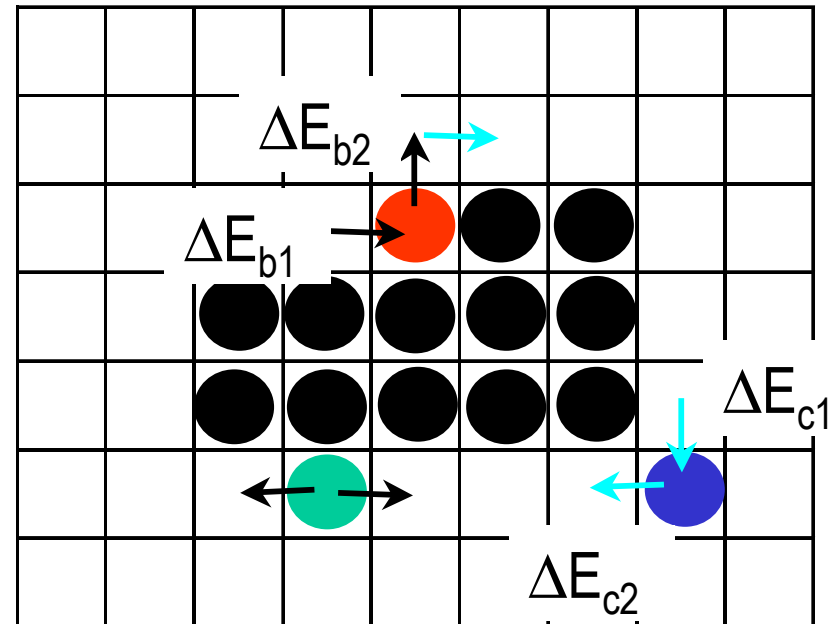


$T = 200 \text{ K}$



Problems and pitfalls

DFT calculations are usually done separately for each process type. Some caution must be exercised to ensure that the total set of rate constants is in accordance with the detailed-balance condition.



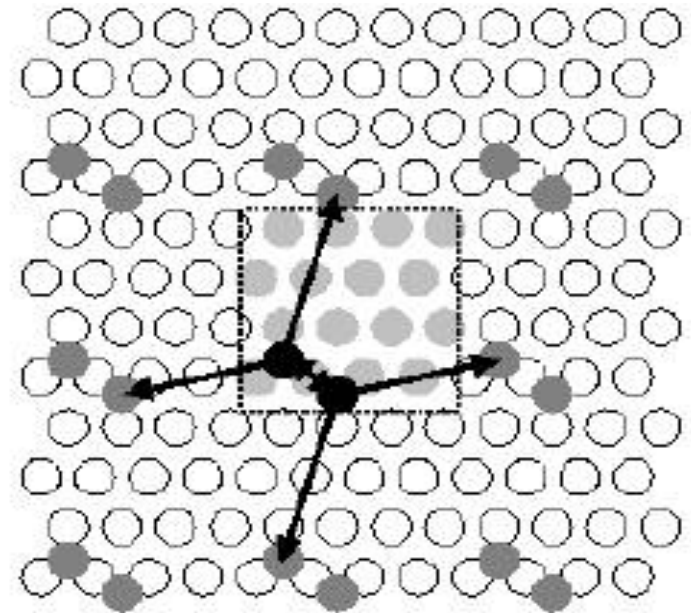
$$4(\Delta E_{c1} + \Delta E_{c2}) + \Delta E_{b1} + \Delta E_{b2} + \Delta E_{c2} = 0$$

The problem is avoided if rate constants derived from a (unique) lattice-gas Hamiltonian are used.

From DFT to a lattice-gas Hamiltonian

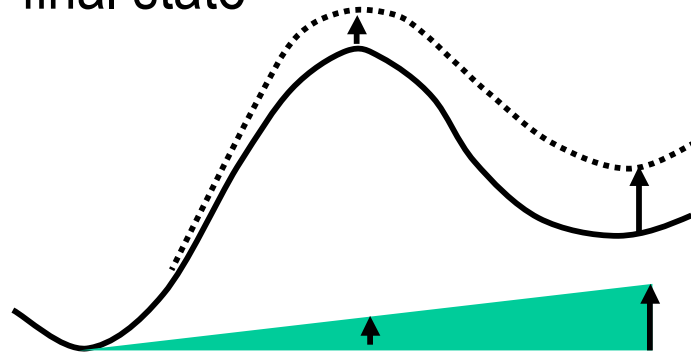
Fit the parameters of a lattice-gas Hamiltonian to interaction energies from DFT:

- perform a series of (periodic) DFT calculations with 2 adatoms at various distances within the unit cell
- set up linear systems of equations for the Hamiltonian parameter
- N.B.: interactions with periodic images must be included !
- solve for the Hamiltonian parameters

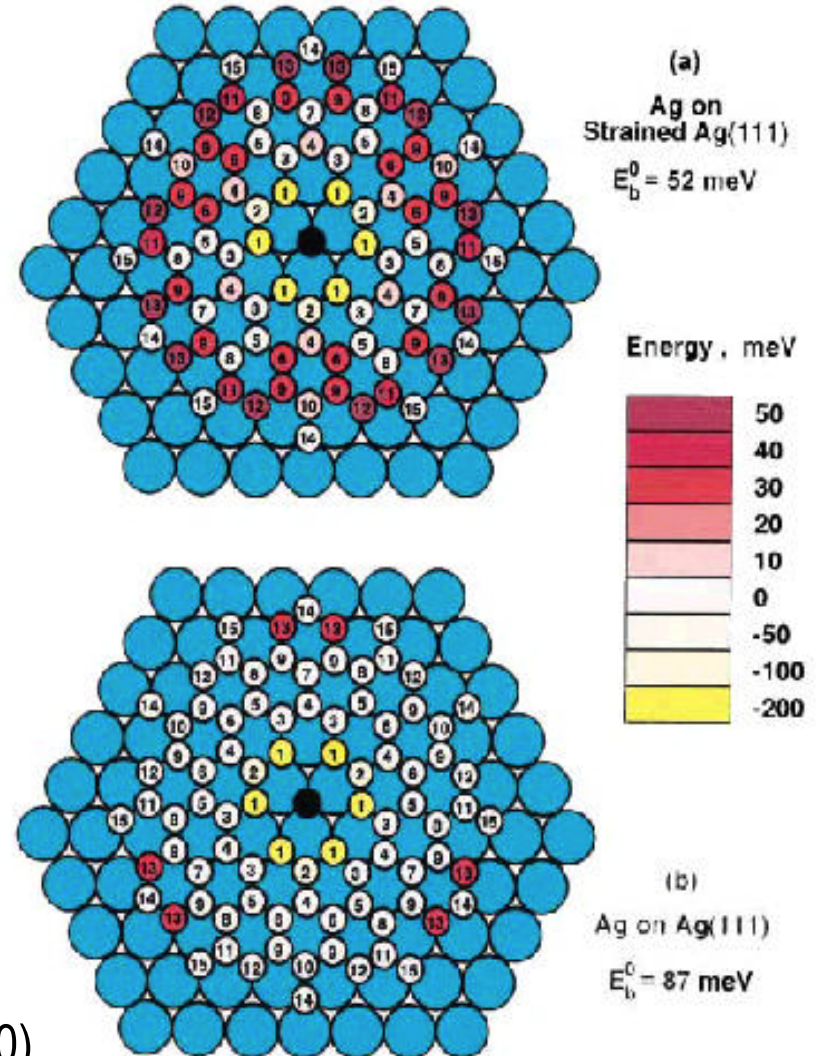


Rate constants from a lattice-gas Hamiltonian

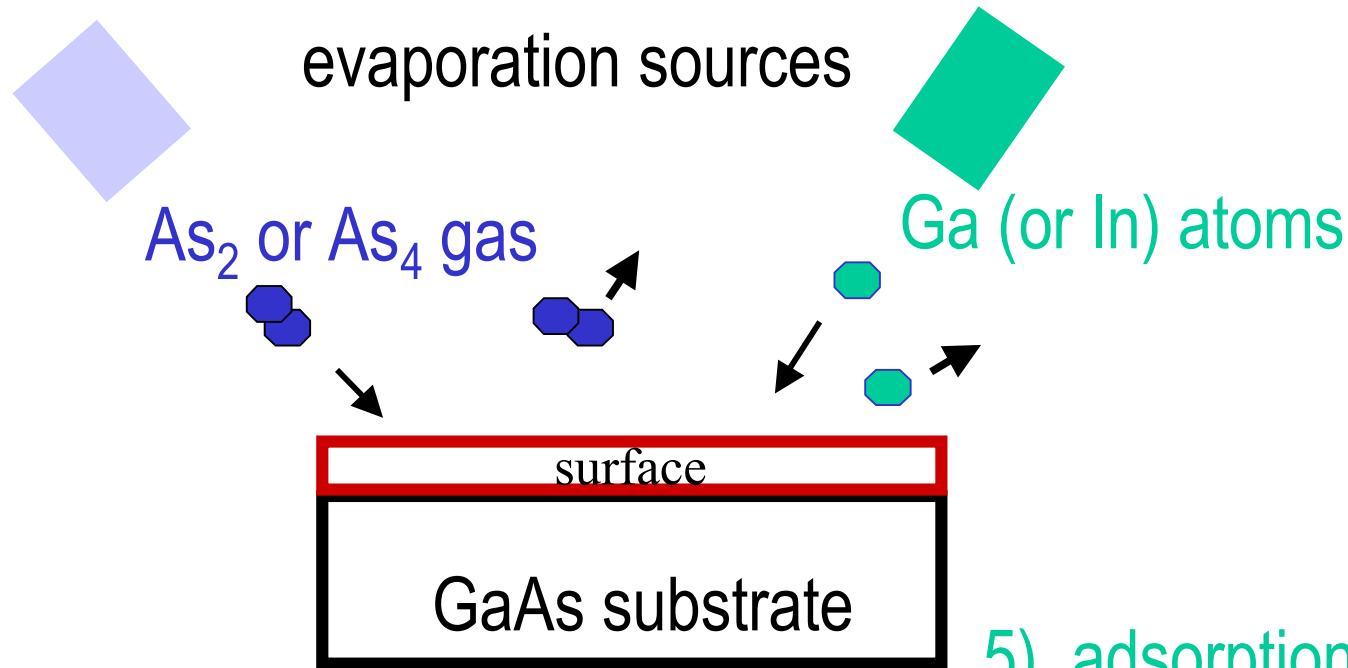
- Interaction energies of adsorbed particles small compared typical barriers
→ barriers become “modified” by the interaction in initial and final state



$$E_b = E_b^0 + a(E_f^{\text{int}} - E_i^{\text{int}})$$



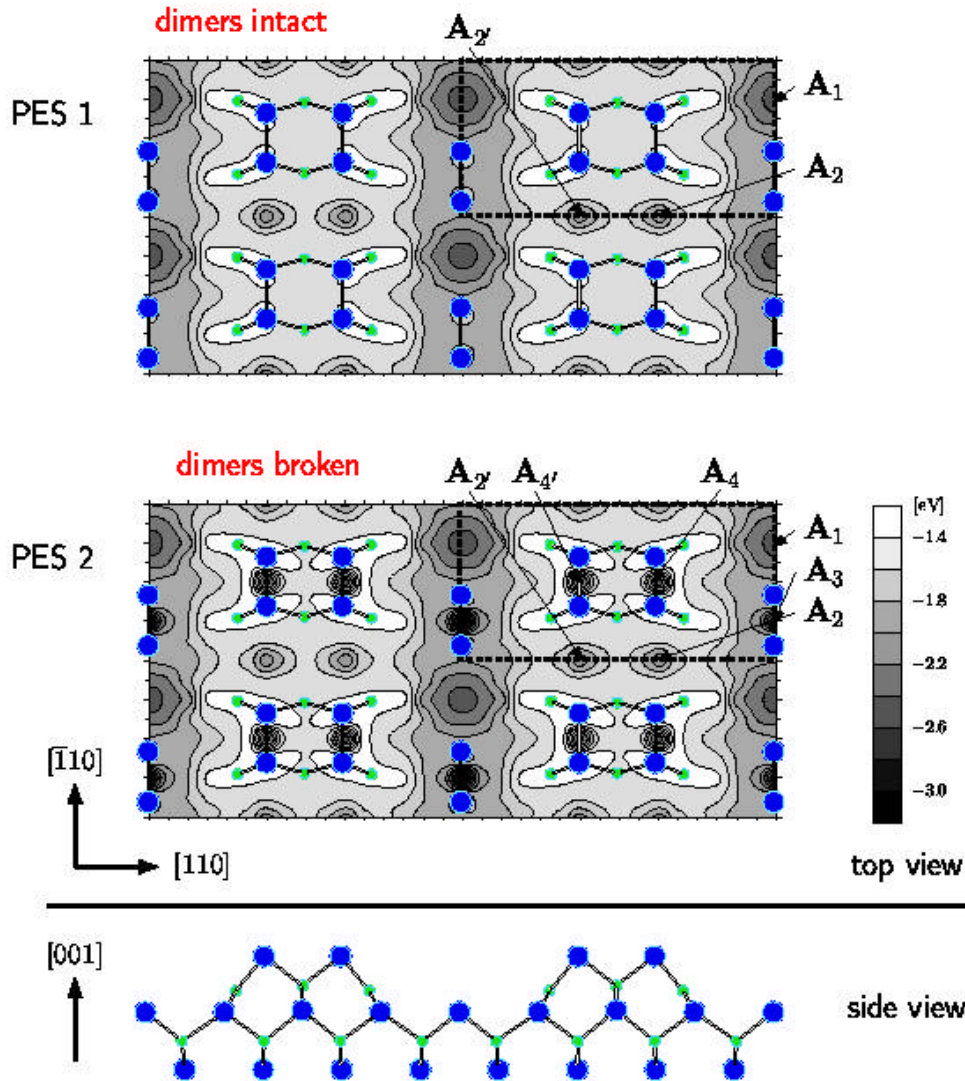
Example 2: Molecular beam epitaxy of III-V semiconductors



- 1) adsorption of As₂
- 2) dissociation of As₂
- 3) diffusion of As
- 4) desorption of As₂

- 5) adsorption of Ga
- 6) diffusion of Ga
- 7) desorption of Ga
- 8) island nucleation
- 9) growth

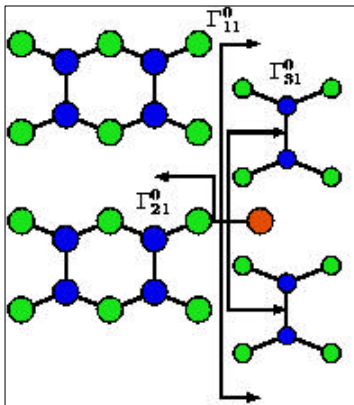
PES for Ga diffusion



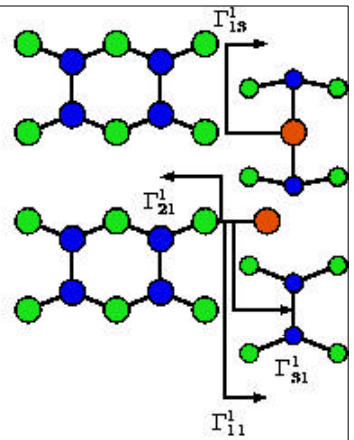
- GaAs(001) substrate typically in the β_2 reconstruction
- Ga diffusion along trenches faster than between trenches
- strongly bound two-fold coordinated Ga in split As dimers

Kley, Ruggerone & Scheffler,
Phys. Rev. Lett. **79**, 5278 (1997)

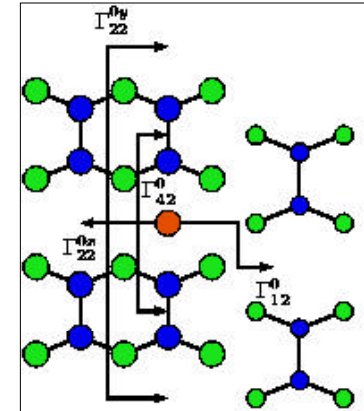
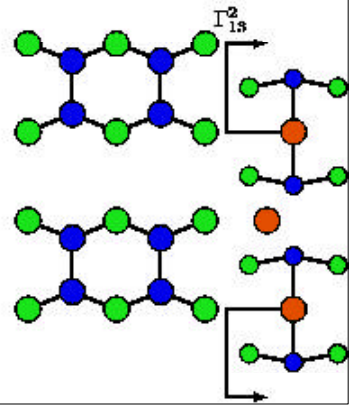
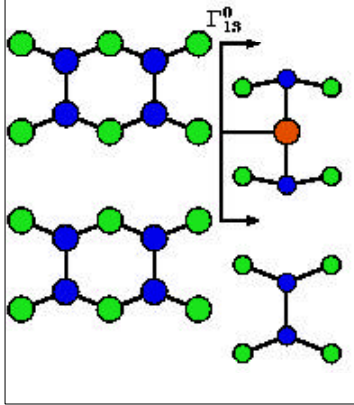
Rates are determined by local environments



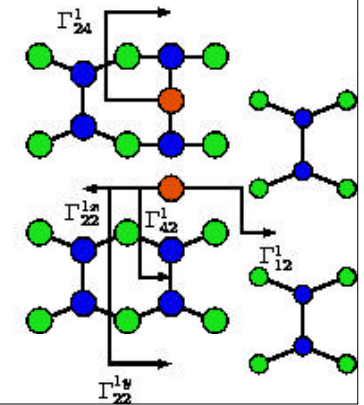
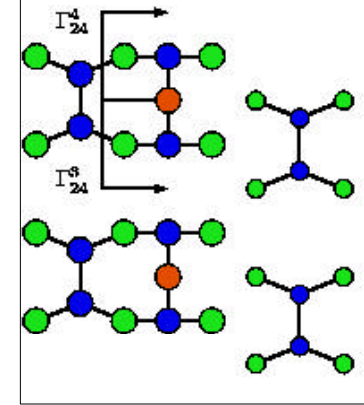
possible hops
in the trench...



..modified by
neighbors.

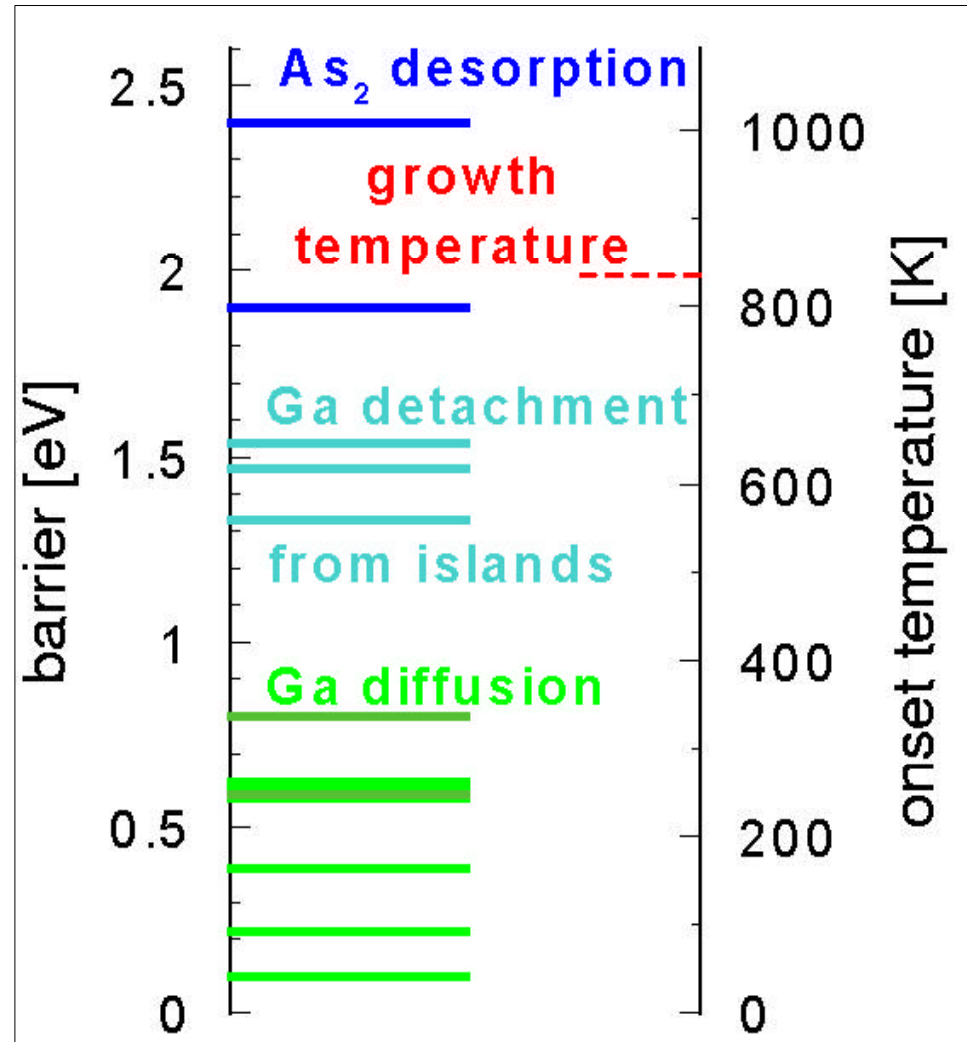


possible hops of an adatom
in the top layer



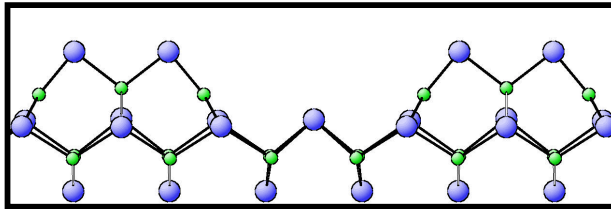
hierarchy of processes

- 32 microscopically different Ga diffusion processes, and As₂ 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)



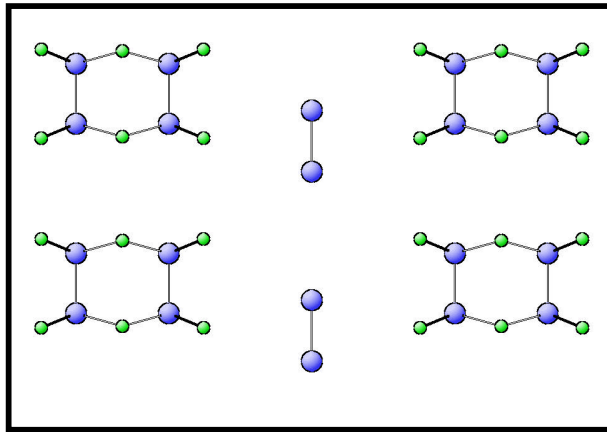
kinetics of island nucleation and growth

side
view

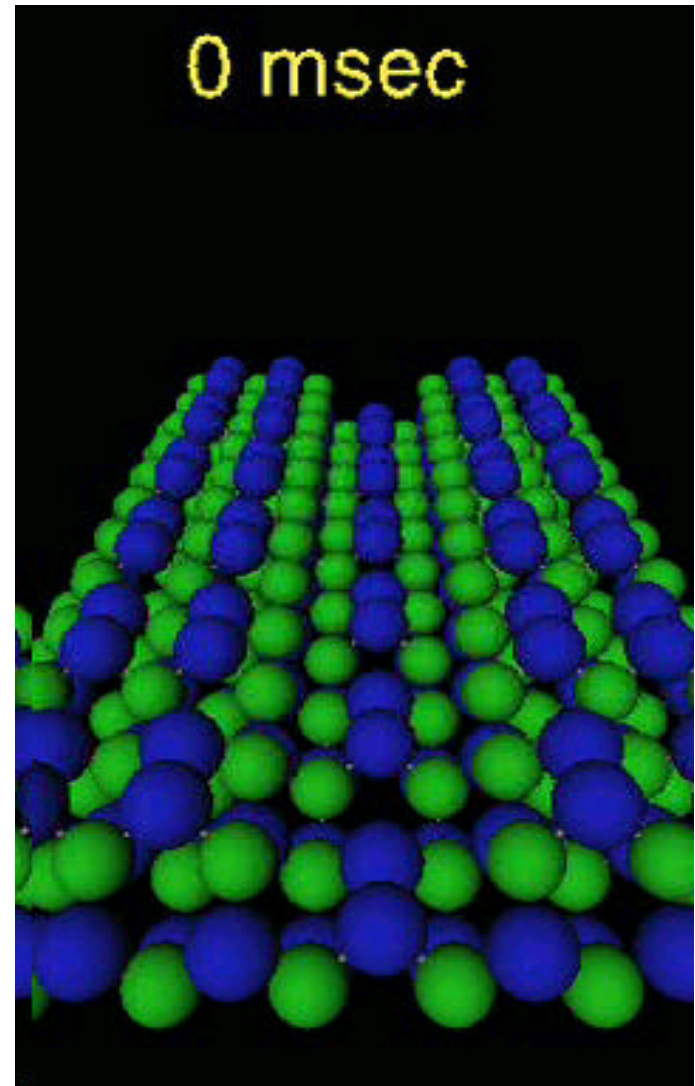


Ga
As

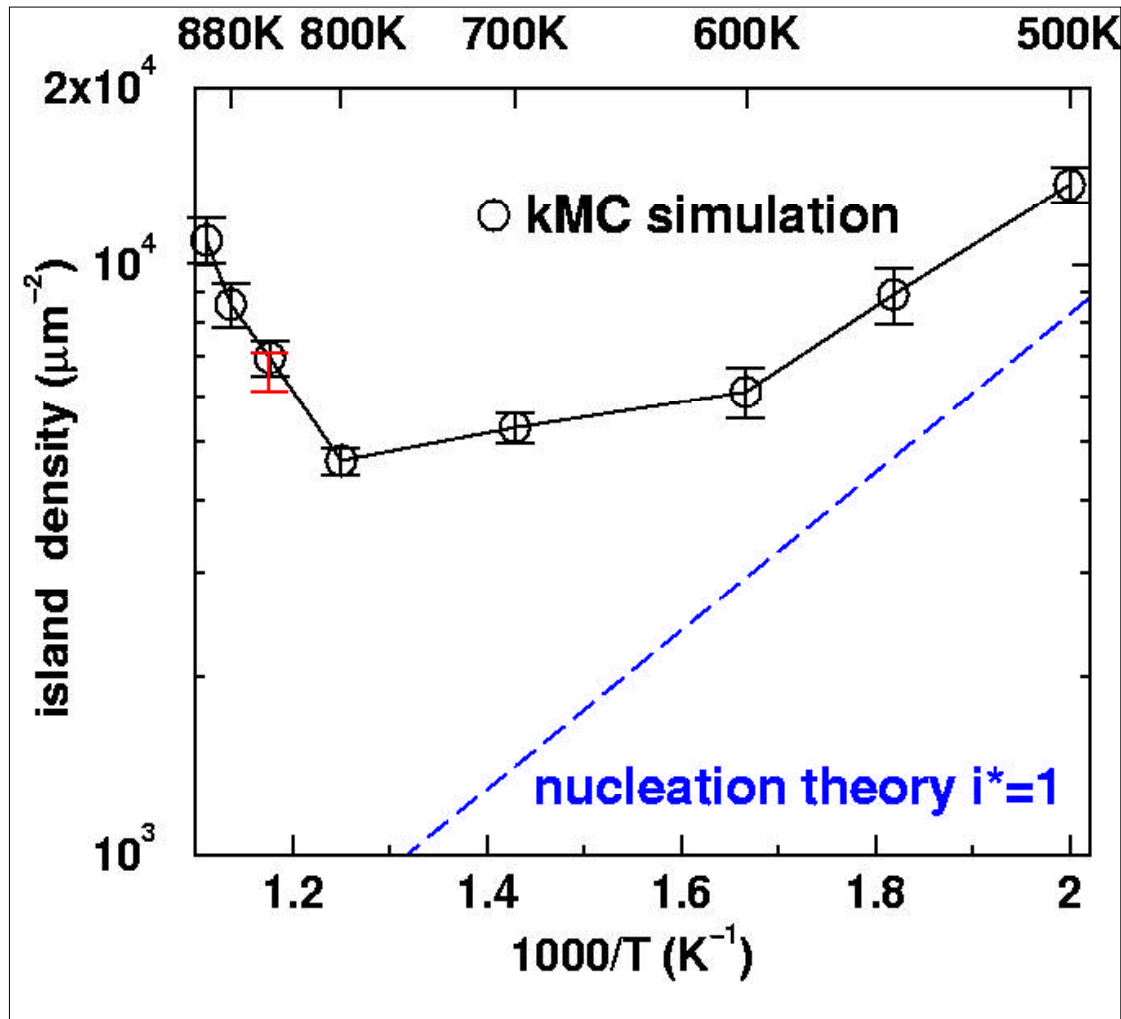
top
view



1/60 of the full simulation cell
As₂ pressure = 0.85×10^{-8} bar
Ga deposition rate = 0.1 ML/s
 $T = 700$ K



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

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

Concluding Remarks

- Kinetic Monte Carlo simulations in conjunction with DFT calculations are a tool that
 - can handle a wide range of length and time scales.
 - is very flexible.
 - can be as accurate and detailed as you require your simulation to be.
- Detailed understanding of the growth process on the atomic level can be gained, e.g. about the interplay of species in growth of a two-component material (GaAs).
- Simulations can help you to elucidate specific atomistic aspects; however, it is important to see that a variety simulation tools is required to cover the full range of time and length scales.