Coarse-graining space and time: kinetic Monte Carlo simulations

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arXiv:0904.2556

Outline

How to harness the power of DFT to solve real-world problems, e.g in materials science, chemical engineering,.. ?

Reliability ⇔ Relevance

numerical accuracy (e.g. of energy barriers) — length and time scales, quality of statistics

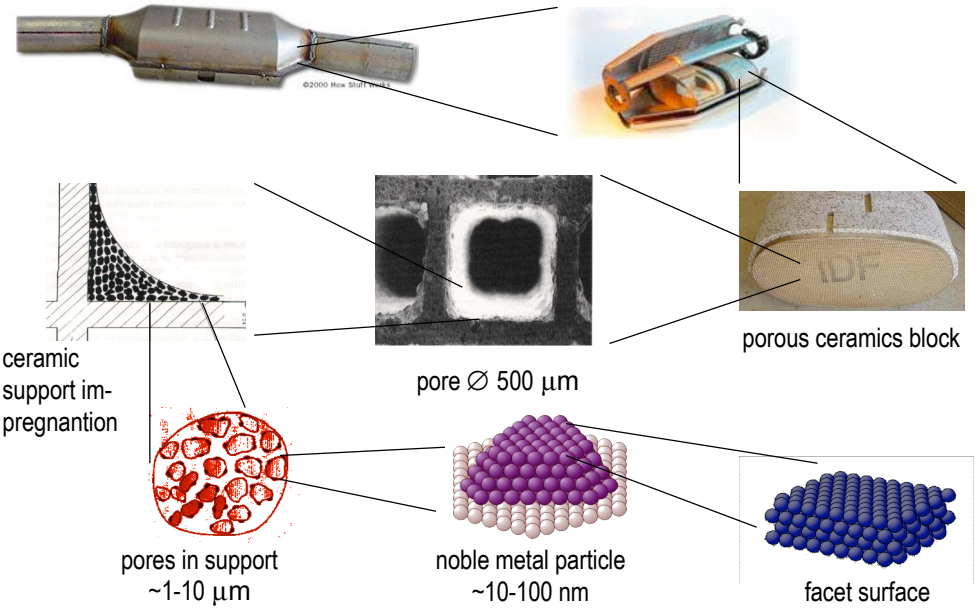
- **coarse-graining in space:** symbolic dynamics ('sites' instead of 'coordinates')
- **coarse-graining in time:** event-driven, variable-time step simulations

Non-equilibrium physics and chemistry of materials

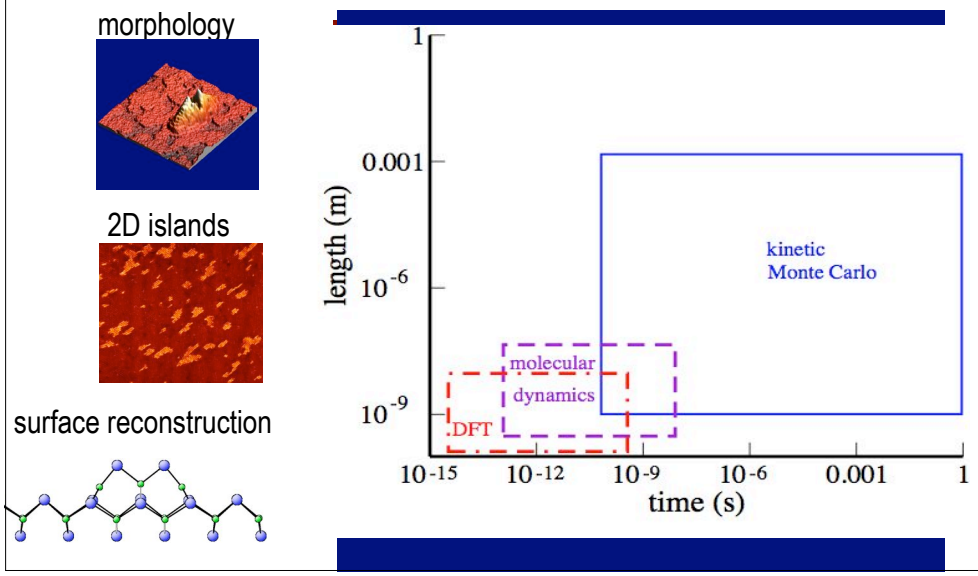
Examples:

- heterogeneous catalysis (fluctuations in a reactive environment)
- epitaxial growth of semiconductors (metastable nanostructured materials)

Example: car exhaust catalyst



Example: Time and length scales in epitaxy

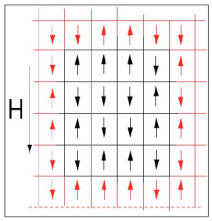


Methods of Statistical Physics (equilibrium)

Discrete models in Statistical Physics

- Ising model (magnetism)

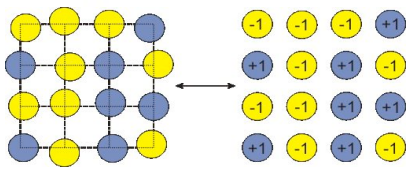
$$H(s) = -J_q \sum_i \sum_{j \in n(i)} s_i s_j - \mu_B B \sum_i s_i$$



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

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

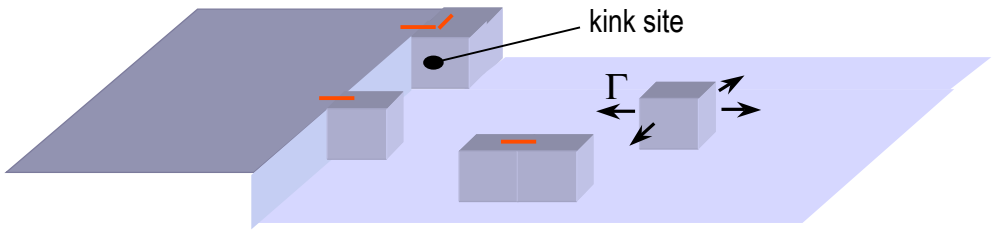
- **Goal:**
  Calculation of thermal averages



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

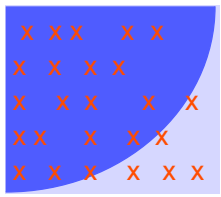
- Atoms are symbolized by little cubes placed on a lattice.
- The growth surface has no voids, no “overhangs”.
- Atoms move by discrete hops with rate $\Gamma = \exp(-E/kT)$.
- The binding energy is determined by the # of neighbors n

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



Stochastic sampling

- Calculating the partition function $Z = \int \frac{d^{3N}q\, d^{3N}p}{N!(2\pi\hbar)^{3N}} \exp\left(-\frac{H(\mathbf{q},\mathbf{p})}{k_B T}\right)$ 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.
- Application: Metropolis algorithm (this afternoon)

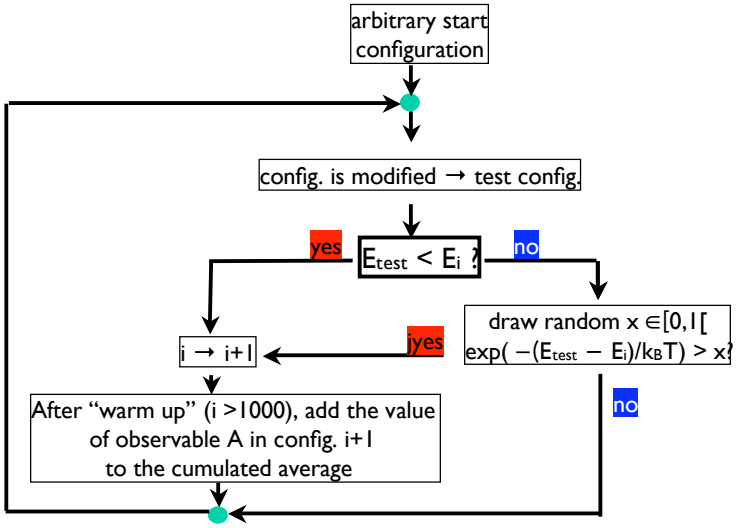


$\pi / 4 = 0.78 .. \approx 20/25 = 0.8$

Metropolis Sampling

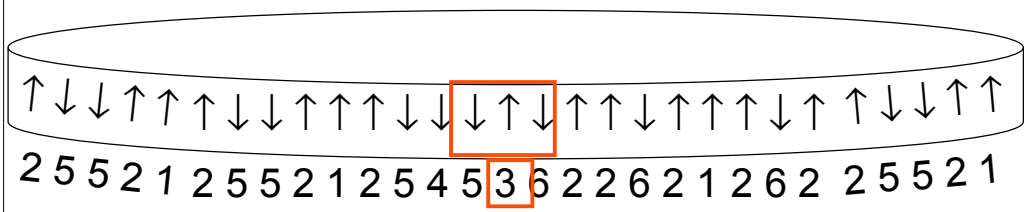
- **Solution:** *Importance Sampling* with $w(\mathbf{q}) = \frac{\exp\left(-V(\mathbf{q})/(k_B T)\right)}{Z'}$
- Generate random support points, distributed according to $w(\mathbf{q})$, i.e., out of total K points, $k_i = K w(\mathbf{q})$ in the unit volume around $\mathbf{q}_i$
- The expectation value 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 $\exp\left(-\frac{V(\mathbf{q}_{i+1}) - V(\mathbf{q}_i)}{k_B T}\right) > \text{rnd}$
  - else reject. $\text{rnd} \in [0,1[$
- 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 (non-equilibrium)

Classification of spins according to their neighborhood

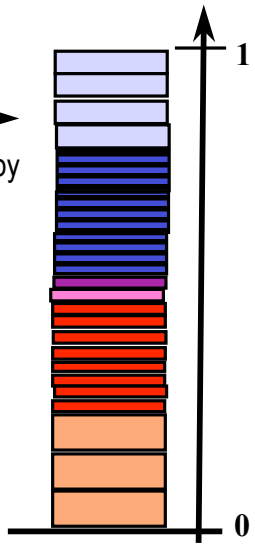


class	central spin	neighbors	class members n_i
1	↑	↑, ↑	4
2	↑	↑, ↓	12
3	↑	↓, ↓	1
4	↓	↓, ↓	1
5	↓	↑, ↓	8
6	↓	↑, ↑	3

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



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Simulations of non-equilibrium processes: kinetic MC

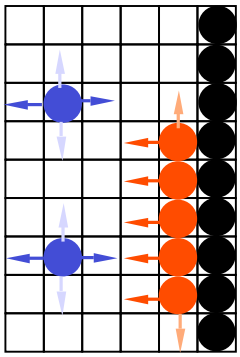
- While being aware of all processes possible at an instant of time, we need a way of (randomly) selecting one process with the appropriate relative probability.
- An internal clock keeps track of the advancement of physical time.
  - If the processes are clearly separated in time, i.e. processes are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

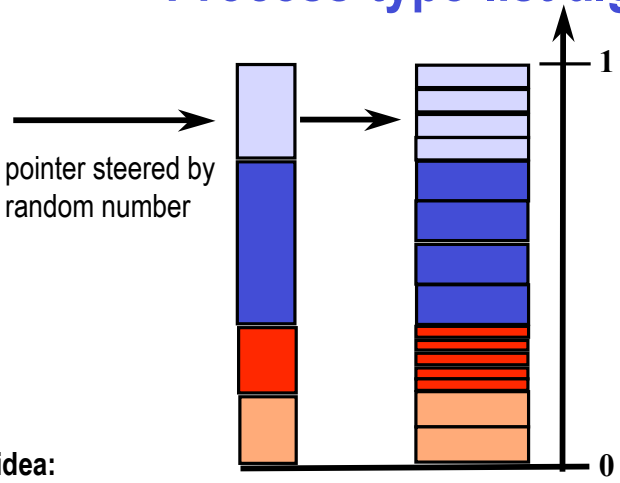
- process-type list algorithm
- binary-tree algorithm
- time-ordered-list algorithm

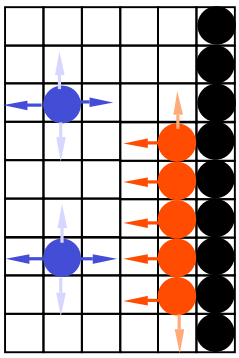
Application to a lattice-gas model

- 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.



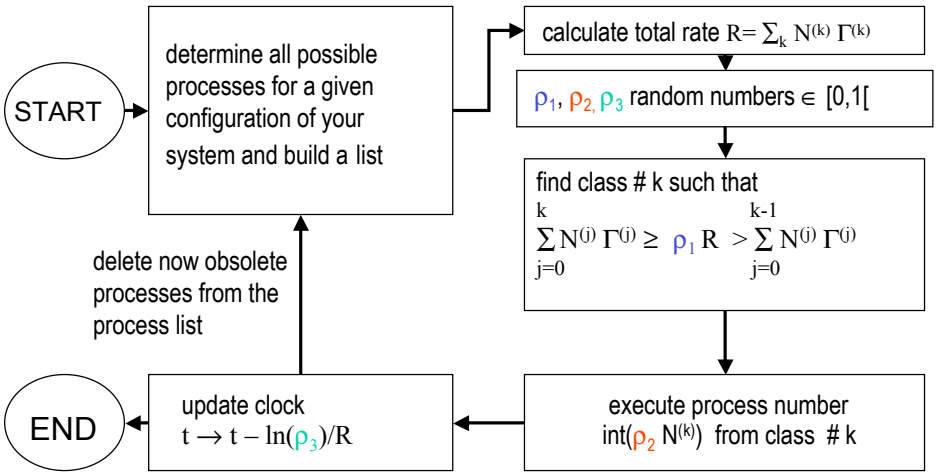
Process-type-list algorithm





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

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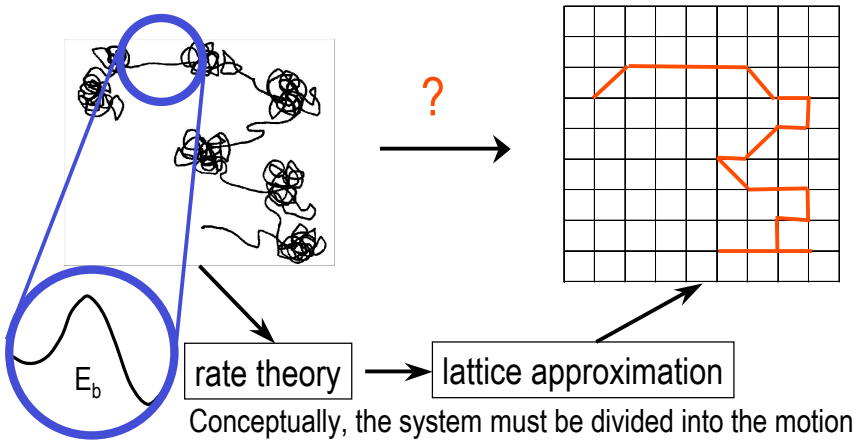


Conceptually, the system must be divided into the motion along the reaction coordinate and a "heat bath".

Transition State Theory (1-dim)

- Kramer's rate theory

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

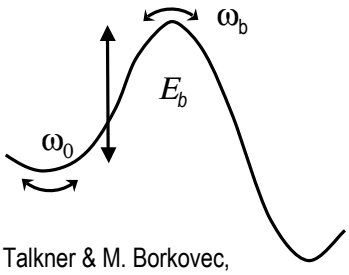
  γ: friction due to coupling to the heat bath

- high-friction limit

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

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

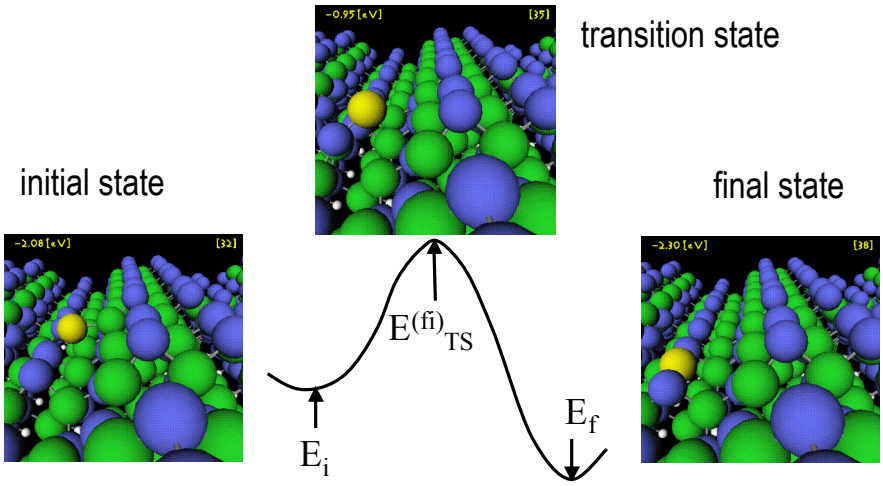
$$\Gamma = \frac{\omega_0}{2\pi}\exp\left(-E_b/kT\right)$$



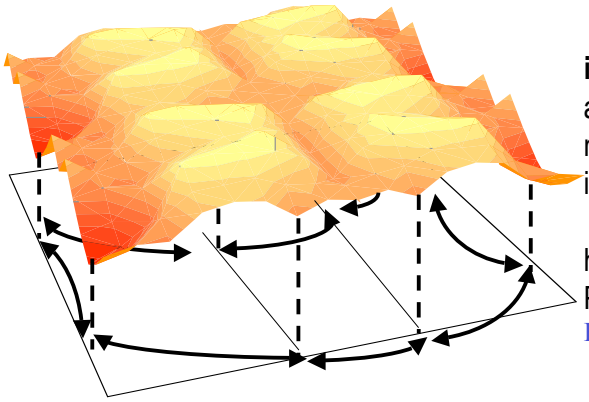
P. Hänggi, P. Talkner & M. Borkovec, Rev. Mod. Phys. **62**, 251 (1990)

Rates from first-principles calculations

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



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



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

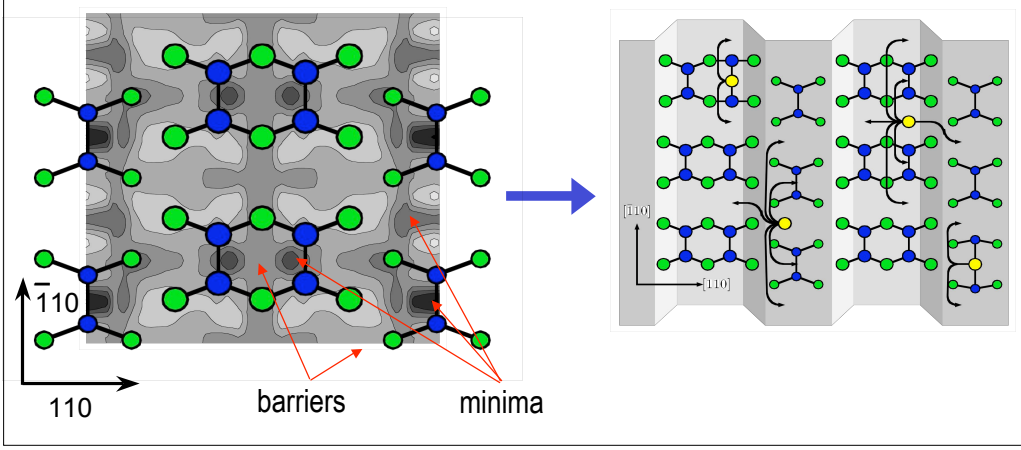
hopping rates derived from the PES

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

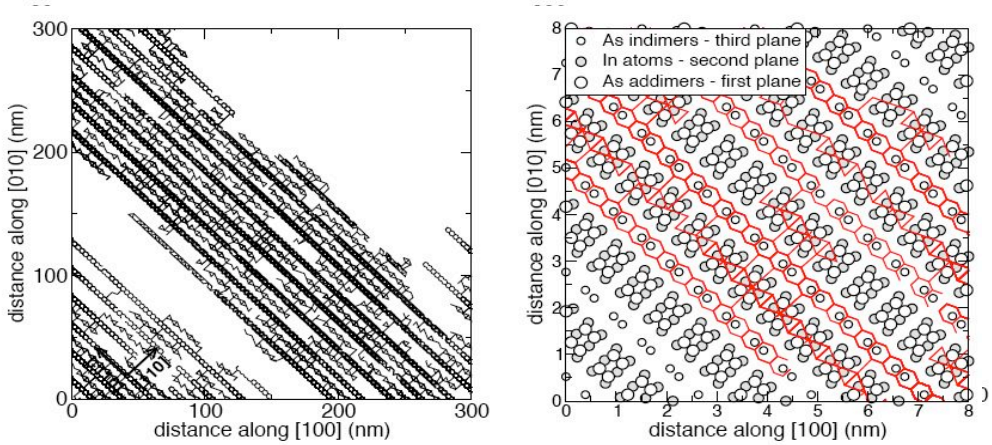
$$\Gamma = kT/h \; Z_{TS}/Z_i = \text{(harmonic \& classical approximation)} = \Pi_N \nu_{k,i} / \Pi_{N-1} \nu_{k,TS} \; \exp(-\Delta E/kT)$$

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

PES from DFT calculations → network of hops



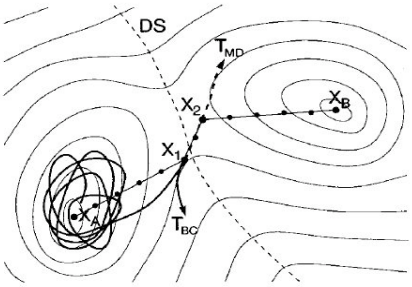
Surface diffusion in lattice-kMC

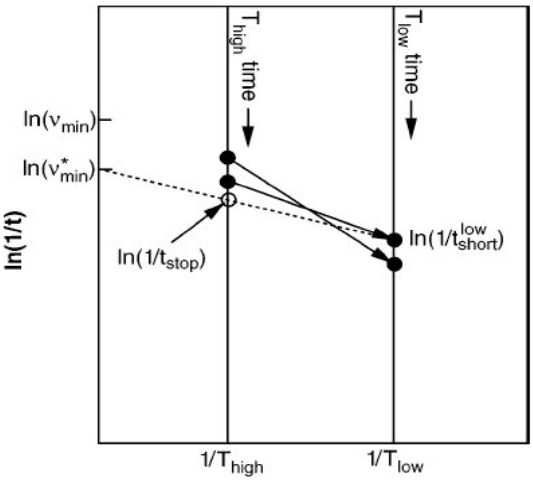


M. Rosini, M.C. Righi, R. Magri, P. Kratzer, Phys. Rev.B **79**, 075302 (2009)

Temperature-accelerated dynamics (TAD)

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

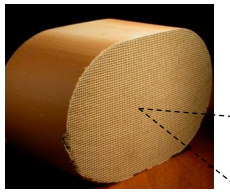




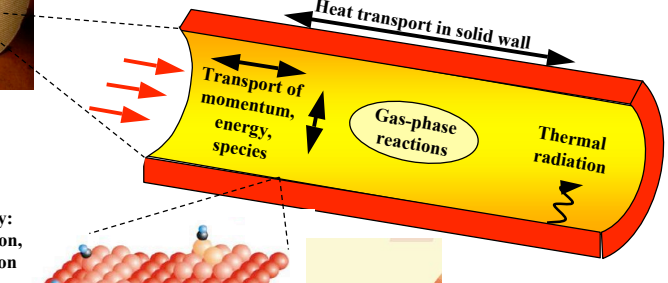
M.R. Sørensen and A.F. Voter, J. Chem. Phys. **112**, 9599 (2000)

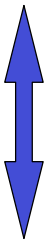
Applications to real-world problems

Catalysis: Challenges for scale-bridging simulations

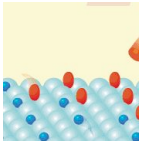


Self-consistent coupling to reactive flow field and appropriate heat balance





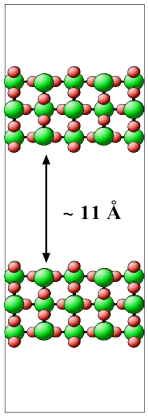
Surface chemistry: adsorption, diffusion, reaction, desorption

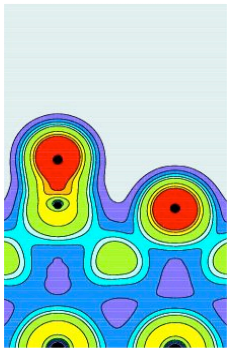


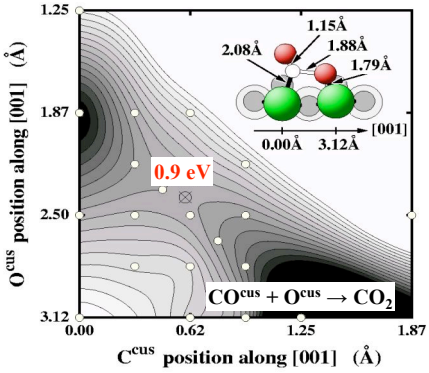
Accurate (first-principles) energetics of individual elementary processes

Quantitative transient and steady-state surface kinetics

Energetics of elementary processes





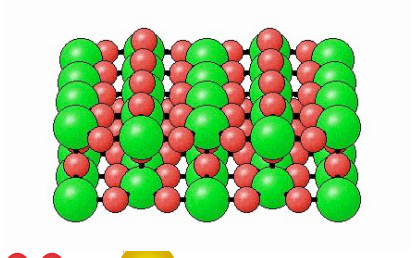


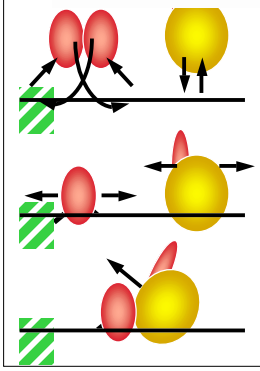
Density-Functional Theory

V_{xc} = GGA (PBE…)

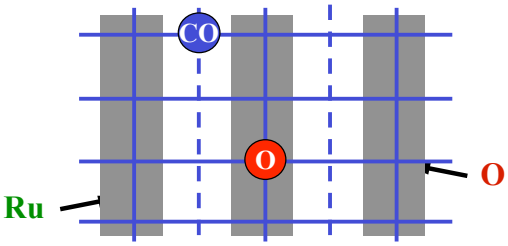
K. Reuter and M. Scheffler, Phys. Rev. B 68, 045407 (2003)

Building a first-principles kinetic Monte Carlo model





CO oxidation @ RuO_2(110)

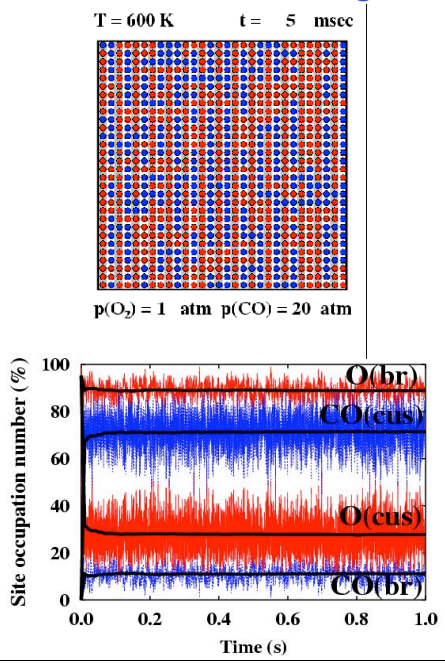


26 elementary processes (site-specific):

- O_2 adsorption/desorption (dissociative/associative)
- CO adsorption/desorption (unimolecular)
- O and CO diffusion
- CO + O reaction

K. Reuter, Oil&Gas Sci. Technol. 61, 471 (2006)
K. Reuter and M. Scheffler, Phys. Rev. B 73, 045433 (2006)

Surface coverage in the reactive environment



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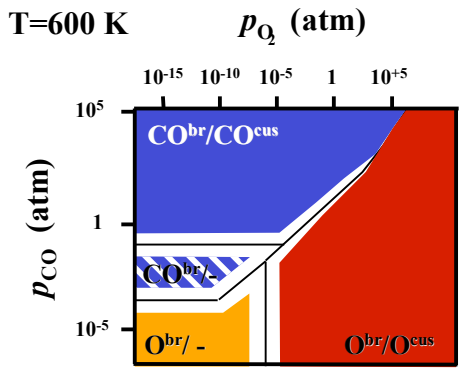
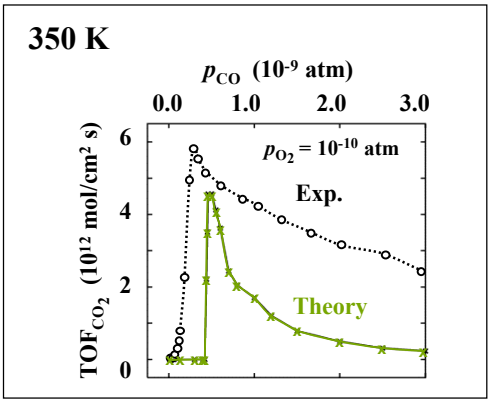
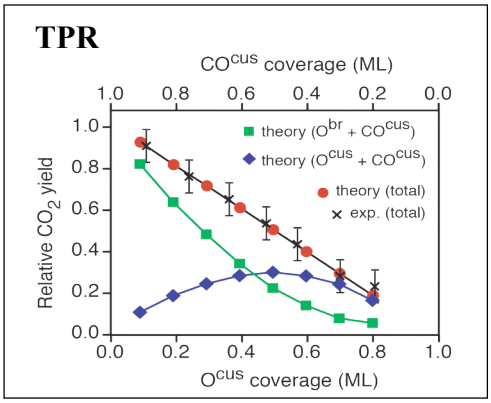


K. Reuter, D. Frenkel and M. Scheffler,
Phys. Rev. Lett. 93, 116105 (2004)

Steady state, and parameter-free transient turnover frequencies



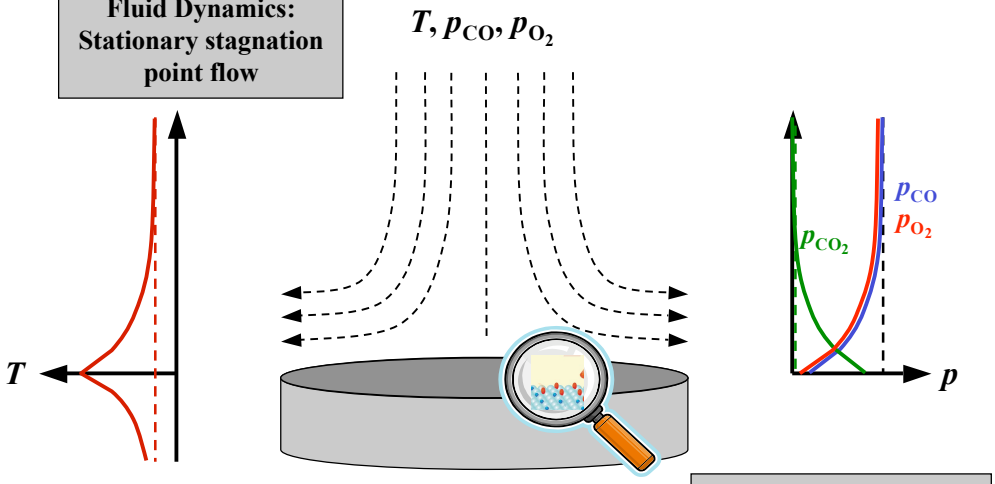


K. Reuter and M. Scheffler,
Phys. Rev. B 73, 045433 (2006)

M. Rieger, J. Rogal, and K. Reuter,
Phys. Rev. Lett. 100, 016105 (2008)

Macro-scale: Heat and mass transfer

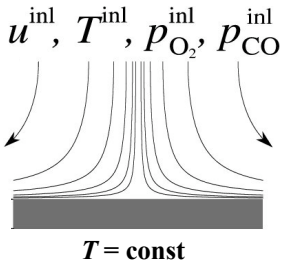
Computational Fluid Dynamics: Stationary stagnation point flow

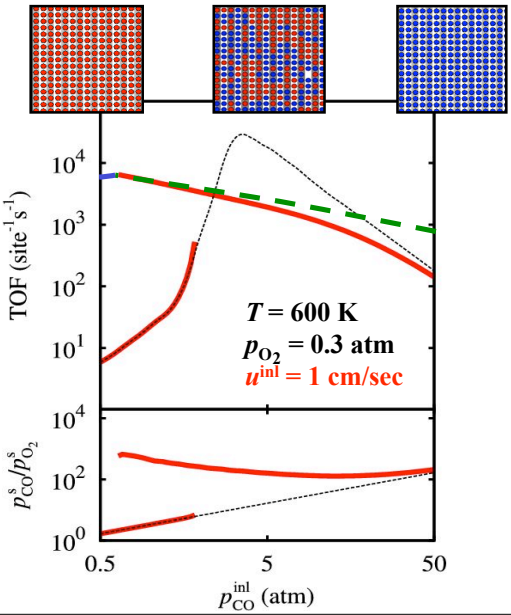


Chemical source terms from 1p-kMC

S. Matera and K. Reuter, Phys. Rev. B 82, 085446 (2010)

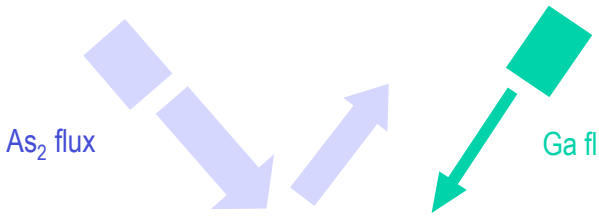
Isothermal limit: Mass transfer limitations





S. Matera and K. Reuter, Catal. Lett. 133, 156 (2009)

Example II: MBE growth of III-V semiconductors



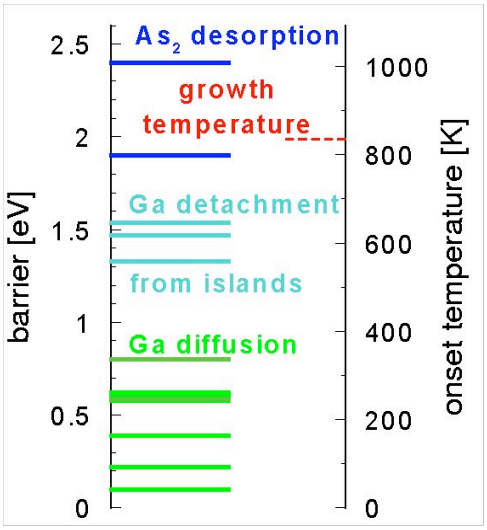
Processes:

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 ?

Kinetic Monte Carlo simulations of GaAs epitaxy

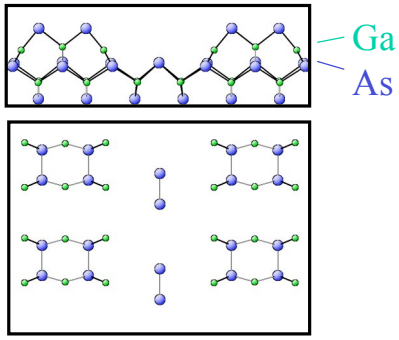
- 32 microscopically different Ga diffusion processes, and As_2 adsorption/desorption are included explicitly
- computational challenge: widely different time scales (10^{-12} sec to 10 sec)
- simulation cell 160 x 320 sites (64 nm x 128 nm)



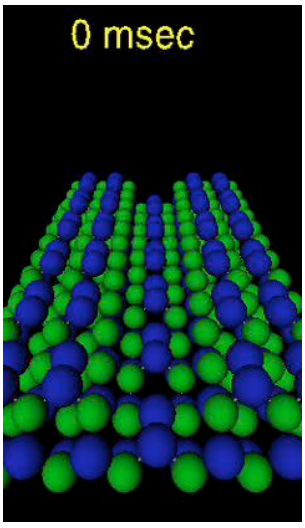
kinetics of island nucleation and growth

side view

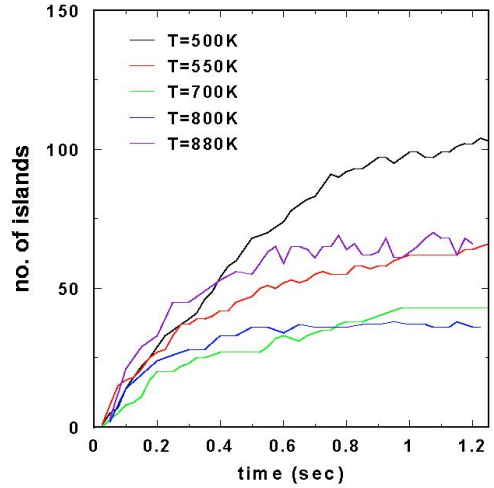
top view

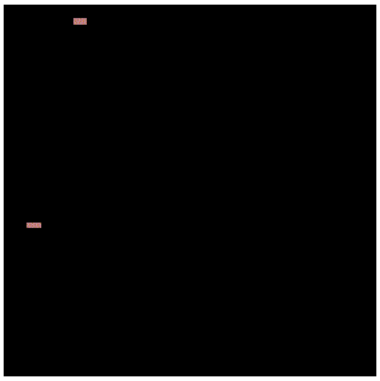


1/60 of the full simulation cell
As_2 pressure = 0.85 x 10^{-8} bar
Ga deposition rate = 0.1 ML/s
T = 700 K



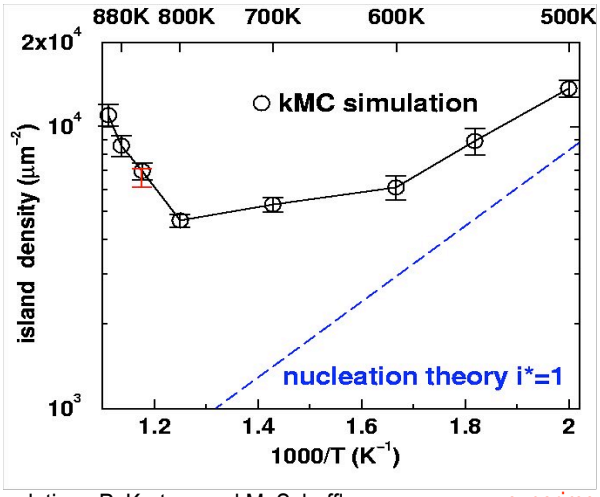
island density





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

scaling with temperature ?



'conventional' nucleation theory

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

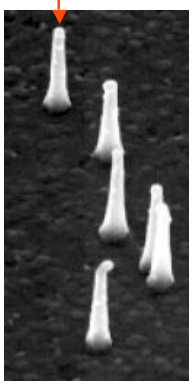
N_{is}	island density
D	diffusion constant
R	deposition flux
η	numerical const.
i^*	critical nucleus

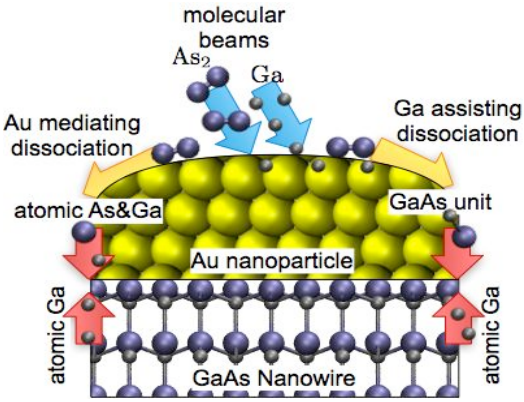
simulation: P. Kratzer and M. Scheffler , Phys. Rev. Lett. **88**, 036102 (2002)

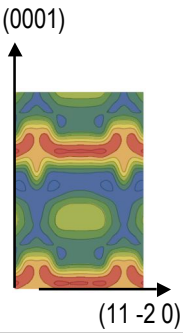
experiment: G.R. Bell et al., Surf. Sci. **423**, L280 (1999)

Current work: GaAs nanowire growth

- unidirectional growth of hexagonal GaAs along (0001) direction
- Au droplet acts as catalyst



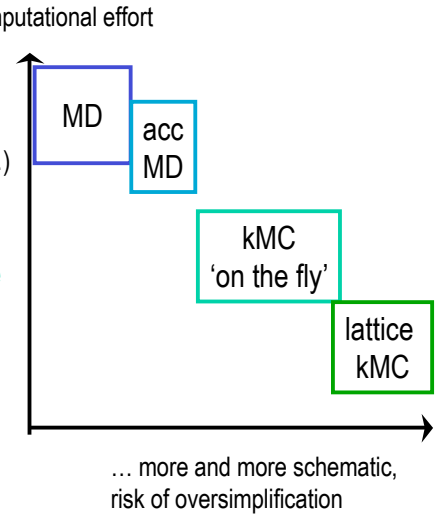


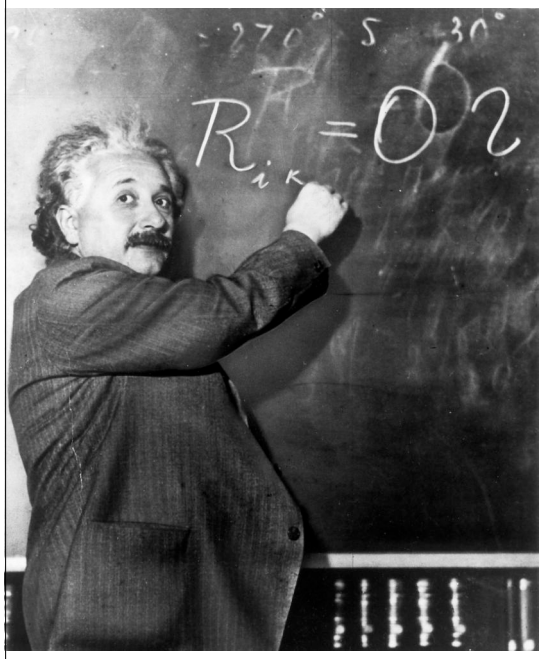


P.K., S. Sakong & V. Pankoke, NanoLett. **12**, 943 (2011)
V. Pankoke, S. Sakong & P.K., Phys. Rev. B **86**, 085425 (2012)

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 more simple .."

Thank you for your attention !

Summary: arXiv:0904.2556