FRITZ-HABER-INSTITUT
MAX-PLANCK-GESELLSCHAFT

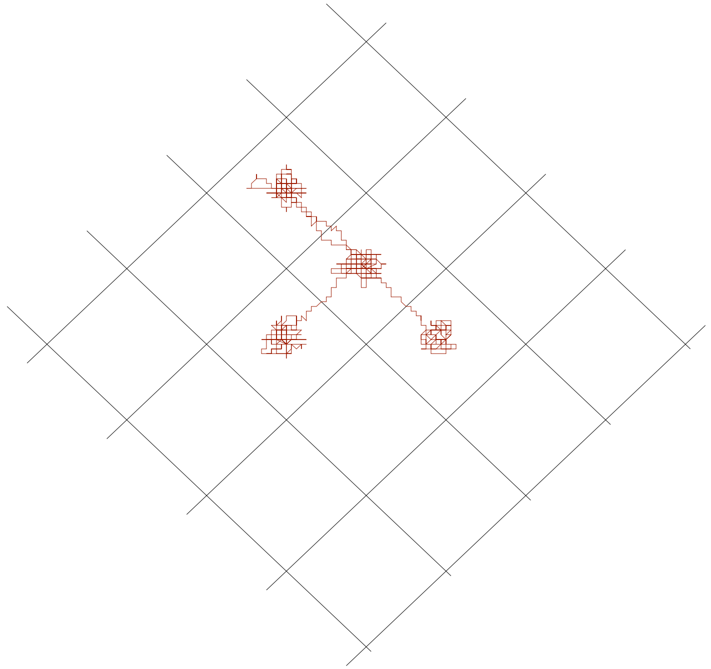
SOME BASIC PRINCIPLES OF KINETICS

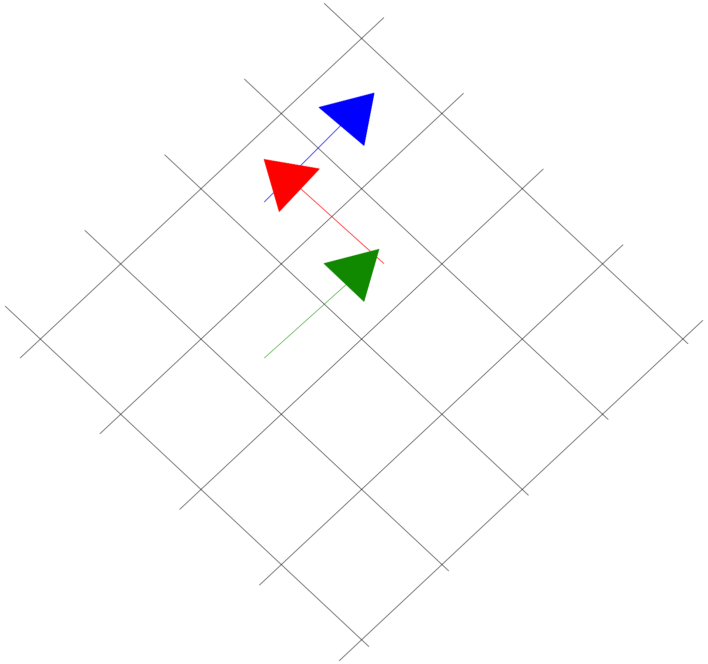
Sebastian Matera

Long time multi-scale simulations of activated events: from theory to practice

June 24 - 28, 2024, SISSA, Trieste

WHAT IS KINETICS?





OUTLINE

Introductory Stochastics

Basic concepts, Stochastic Processes, Markov Jump Processes

Stationary States

Ergodicity, microscopic reversibility, Detailed Balance

Parameter Dependence

Smoothness, Local Sensitivity, Fisher Information, Linear Response

SOME BASIC CONCEPTS FROM PROBABILITY THEORY

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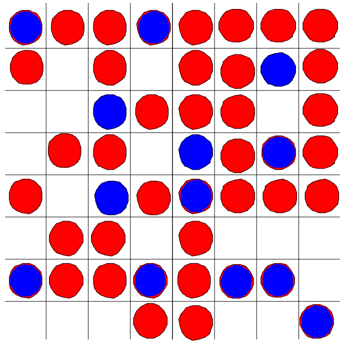
Random variable: I

- outcomes $\quad i \in \Omega \subseteq \mathbb{Z}^D$
- Probability $\quad P(i) \geq 0 \;,\; \sum_{i\in\Omega} P(i) = 1$



$$\begin{pmatrix} 2 & 1 & 1 & 2 & 1 & 1 & 1 & 1 \\ 1 & 0 & 1 & 0 & 1 & 1 & 2 & 1 \\ 0 & 0 & 2 & 1 & 1 & 1 & 0 & 1 \\ 0 & 1 & 1 & 0 & 2 & 1 & 2 & 1 \\ 1 & 0 & 2 & 1 & 2 & 1 & 1 & 1 \\ 0 & 1 & 1 & 0 & 1 & 0 & 0 & 0 \\ 2 & 1 & 1 & 2 & 1 & 2 & 2 & 0 \\ 0 & 0 & 0 & 1 & 1 & 0 & 0 & 2 \end{pmatrix}$$

Expectation

$$\langle f \rangle = \sum_{i\in\Omega} f(i) P(i)$$

Multivariate

$$P(i;j) \quad = \quad P(i|j) \quad P(j)$$

joint
(i AND j)

conditional
(i IF j)

marginal
(ONLY j)

$$P(j) = \sum_{i\in\Omega} P(i;j)$$

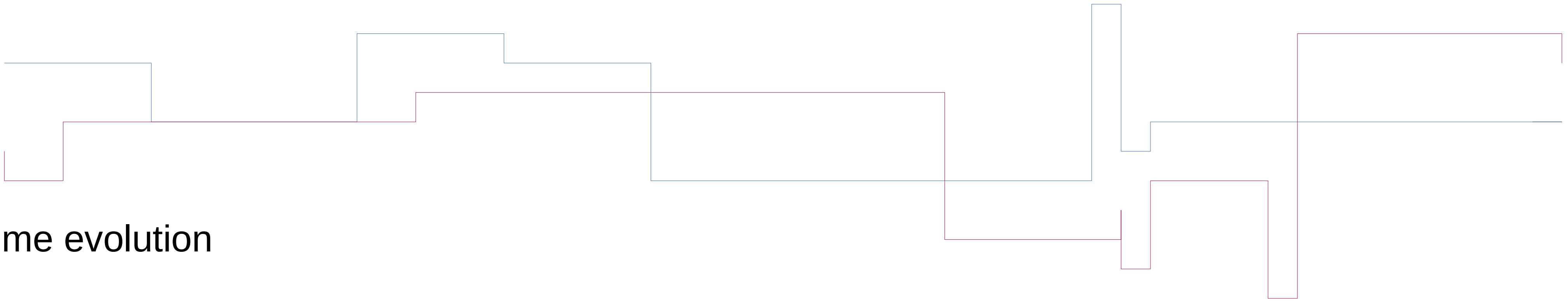
Statistical independence

$$P(i|j) = P(i) \quad \Leftrightarrow \quad P(i;j) = P(i)P(j)$$

STOCHASTIC PROCESSES

Parametric family of random variables $I(t)$

$$i_1, t_1;\ \ i_2, t_2;\ \ i_3, t_3 \ldots \qquad t_1 < t_2 < t_3 \ldots \qquad i_1, i_2, i_3 \ldots \in \Omega$$

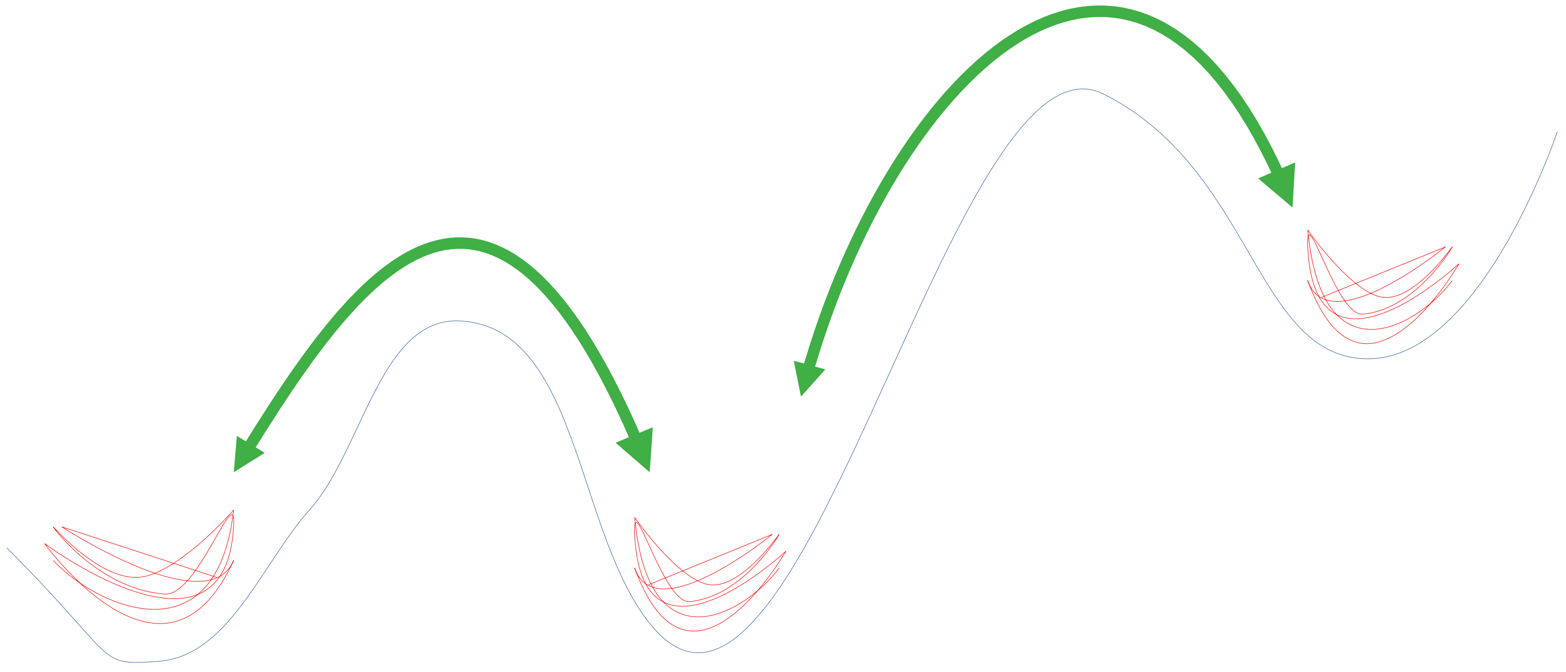


Time evolution

$$P(i_3, t_3) = \sum_{i_2} P(i_3, t_3; i_2, t_2) = \sum_{i_2} P(i_3, t_3 | i_2, t_2) P(i_2, t_2)$$

$$P(i_3, t_3 | i_1, t_1) = \sum_{i_2} P(i_3, t_3; i_2, t_2 | i_1, t_1) = \sum_{i_2} P(i_3, t_3 | i_2, t_2; i_1, t_1) P(i_2, t_2 | i_1, t_1)$$

MARKOV JUMP PROCESSES



MARKOV PROCESSES

$$P(i_3,t_3|i_1,t_1)=\sum_{i_2} P(i_3,t_3;i_2,t_2|i_1,t_1)=\sum_{i_2} P(i_3,t_3|i_2,t_2;i_1,t_1)P(i_2,t_2|i_1,t_1)$$

Markov property

$$P(i_3,t_3|i_2,t_2;i_1,t_1\ldots)=P(i_3,t_3|i_2,t_2) \qquad t_3>t_2>t_1$$

Chapman-Kolgomorov equation

$$\Rightarrow \quad P(i_3,t_3|i_1,t_1)=\sum_{i_2} P(i_3,t_3|i_2,t_2)P(i_2,t_2|i_1,t_1)$$

$$\Rightarrow \quad P(i_N,t_N;i_{N-1},t_{N-1};\ldots;i_2,t_2|i_1,t_1)=P(i_N,t_N|i_{N-1},t_{N-1})P(i_{N-1},t_{N-1}|i_{N-2},t_{N-2})\ldots P(i_2,t_2|i_1,t_1)$$

Markov chain

$$P(i,N\Delta t|j,0)=(F_N\cdot F_{N-1}\cdot\ldots\cdot F_1) \quad \text{with} \quad F_{n,ij}=P(i,n\Delta t|j,(n-1)\Delta t)$$

CKE AS ODE: THE MASTER EQUATION

- Based on transitions (events) i → j : $$\frac{d}{dt}P(i,t)=\sum_j w_{ij}(t)P(j,t)-\sum_j w_{ji}(t)P(i,t)$$

  with the transition rate $$w_{ij}(t):=\lim_{\Delta t\to 0}\frac{P(i,t+\Delta t\,|\,j,t)}{\Delta t}$$

- Based on processes ξ (d_ξ =j-i): $$\frac{d}{dt}P(i,t)=\sum_\xi a_\xi(i-d_\xi,t)P(i-d_\xi,t)-\sum_\xi a_\xi(i,t)P(i)$$

  with the propensity/rate/intensity function $$a_\xi(i,t)=w_{i+d_\xi,i}(t)$$

- Short hand notation

$$\frac{d}{dt}P(t)=\Gamma(t)P(t)$$

$\Gamma^T(t)$: Generator of the stochastic motion

FORMULATION IN TERMS OF POISSON PROCESSES

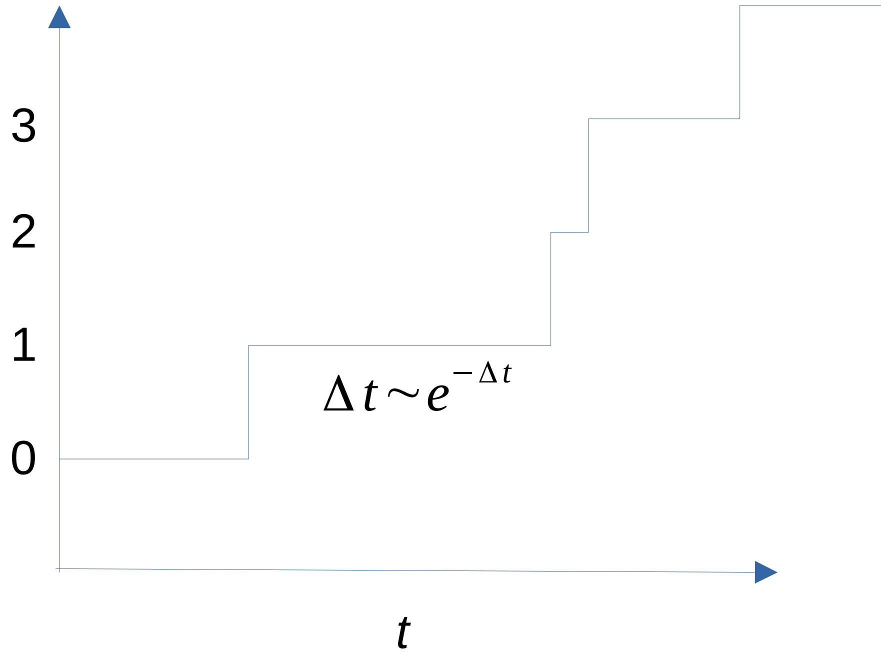
Temporal evolution of probabilities

$$\frac{d}{dt}P(i,t)=\sum_{\xi} a_{\xi}(i-d_{\xi},t)P(i-d_{\xi},t)-\sum_{\xi} a_{\xi}(i,t)P(i)$$

Temporal evolution of states

$$\Leftrightarrow \quad I(t)=I_0+\sum_{\xi} d_{\xi}N_{\xi}\left(\int_{t_0}^{t} a_{\xi}(I(t'),t')dt'\right)$$

- Independent unit rate Poisson processes N_{ξ}
- Basis of the First Reaction kMC



ENOUGH OF MATHEMATICS

Reduction of surface oxide on Pd(100) by CO (M.J. Hoffmann, K. Reuter, M. Scheffler)

FOR A MINUTE

STATIONARY PROCESSES

Same statistics for

$$I(t) \text{ and } I(t+\delta t) \quad , \quad \forall t, \delta t$$

Multitime probabilities

$$P(i_n, t_n; i_{n-1}, t_{n-1}; i_{n-2}, t_{n-2}; \dots) = P(i_n, t_n + \delta t; i_{n-1}, t_{n-1} + \delta t; i_{n-2}, t_{n-2} + \delta t; \dots)$$

Markov processes

$$P(i,t) = P_s(i)$$

$$P(i, t+\Delta t \mid j, t) = P(i, \Delta t \mid j, 0)$$

ERGODICITY

Does a stochastic process relax towards a stationary distribution?
Is it unique?
Can we employ time averaging?

Homogeneous Process:

$$\Gamma(t) = G = const \qquad \Rightarrow \frac{d}{dt} P(t) = G\, P(t)$$

$$\Rightarrow P(i, t+\Delta t \,|\, j, t) = P(i, \Delta t \,|\, j, 0) = \left(e^{G \Delta t}\right)_{ij} \qquad \Rightarrow P(t) = e^{G t} P(0)$$

Observables

$$\langle f \rangle(t) = \sum_i f_i P_i(t) =: (f, P(t)) = (f, e^{G \Delta t} P(0)) = (e^{G^T \Delta t} f, P(0)) = (f(t), P(0))$$

$$\frac{d}{dt} f(t) = G^T f(t)$$

ERGODICITY

Frobenius Theorem:
Let $|\Omega| < \infty$ and let the generator G be irreducible. Then, there is a unique stationary distribution P_s, , i.e.

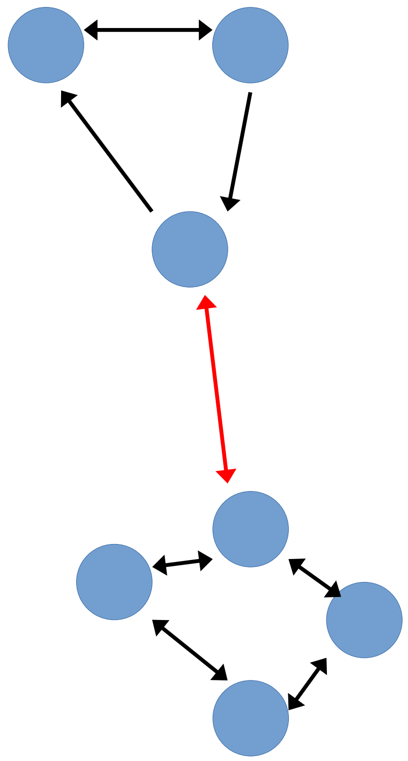
$$G P_s(t)=0,\quad P_{s,i}>0,\quad \sum_i P_{s,i}=1$$

is invertable.
Further, the solution of the ME P(t) relaxes against P_s.

$$\lim_{t\to\infty} P(i,t\,|\,j,0)=P_s(i)$$

Or, in physical language:
For a finite state Markov model, there exist no multiple stationary distributions if we can reach from every state i every other state.

Models obeying the Frobenius theorem are ergodic



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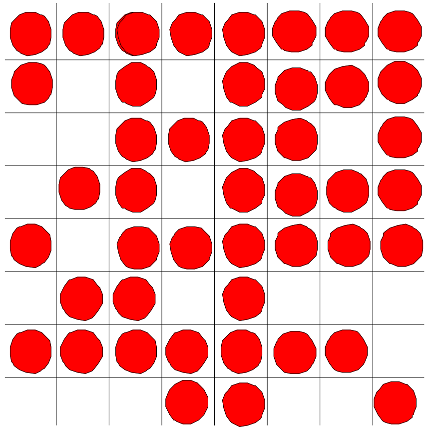
ERGODICITY: EXAMPLES

Ergodic: Ising model

$$CO(gas) + * \leftrightarrow CO^*$$

- Nearest neighbor interactions



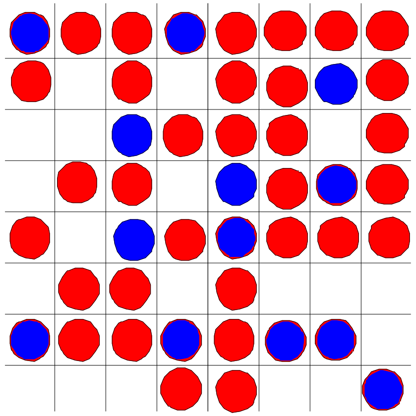
Non-ergodic: dissociative ad/desoprtion

$$O_2(gas) + 2* \leftrightarrow 2O^*$$

- Two stationary states: Even vs. Odd #O
- No Langmuir isotherm

Non-ergodic: ZGB model

$$O_2(gas) + 2* \rightarrow 2O^*$$
$$CO(gas) + * \rightarrow CO^*$$
$$O^* + CO^* \rightarrow CO_2(gas) + 2*$$



ERGODICITY: CONSEQUENCES

- Expected values

$$\langle f\rangle_s=\sum_{i\in\Omega} f(i)P_s(i)=\lim_{t\to\infty}\lim_{N\to\infty}\frac{1}{N}\sum_{n=1^N} f(I_n(t))$$

Estimator

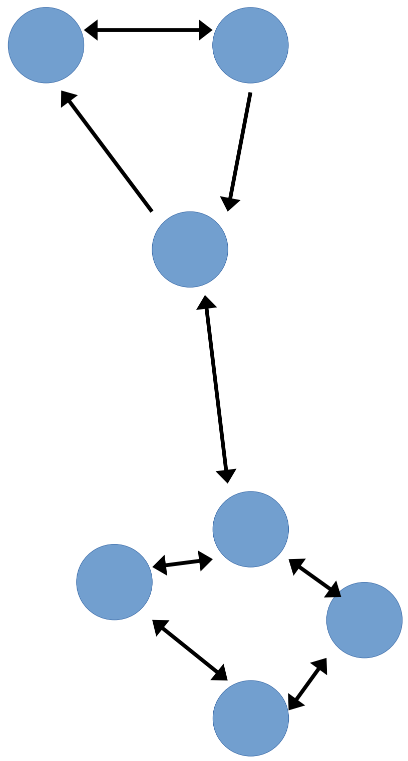
$$\langle f\rangle_s\approx\bar f(t):=\frac{1}{N}\sum_{n=1^N} f(I_n(t)),\quad t\gg t_{relax},\quad t_{relax}=|\lambda_2(G)|^{-1}$$

- Time averaging

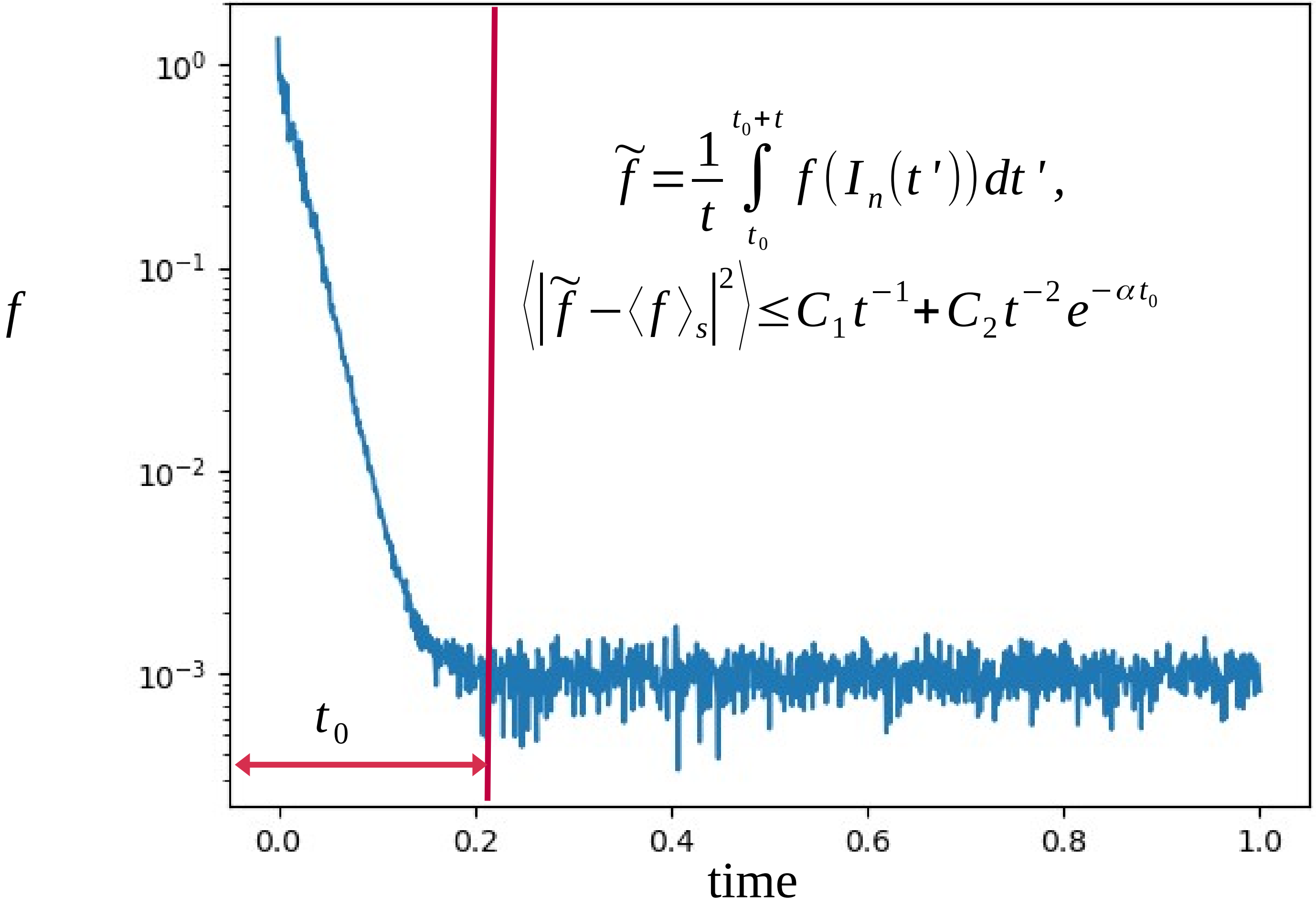
$$\langle f\rangle_s=\sum_{i\in\Omega} f(i)P_s(i)=\lim_{t\to\infty}\frac{1}{t}\int_{0^t} f(I_n(t'))\,dt'$$

estimator

$$\tilde f=\frac{1}{t}\int_{t_0}^{t_0+t} f(I_n(t'))\,dt',\quad \left\langle\left|\tilde f-\langle f\rangle_s\right|^2\right\rangle\le C_1t^{-1}+C_2t^{-2}e^{-\alpha t_0}$$



ERGODICITY: CONSEQUENCES



$$\tilde{f} = \frac{1}{t} \int_{t_0}^{t_0+t} f(I_n(t'))\,dt',$$

$$\left\langle \left| \tilde{f} - \langle f \rangle_s \right|^2 \right\rangle \leq C_1 t^{-1} + C_2 t^{-2} e^{-\alpha t_0}$$

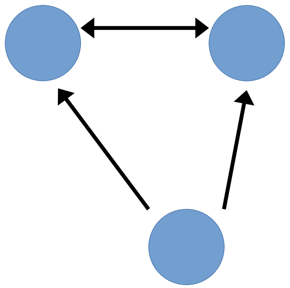
CONDITIONALLY ERGODIC/STATIONARY

- Original state space Ω

- Initial state I_0

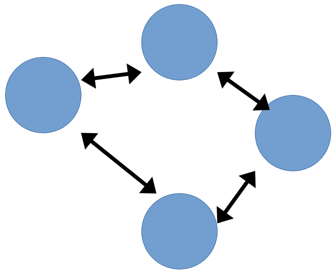
- Define restricted state space

$$\Omega(I_0) = \{ i \in \Omega \mid i \text{ can be reached from } I_0 \}$$



- The inverse process should exist for physically meaningfull models

$$w_{ij} \neq 0 \;\; \Rightarrow \;\; w_{ji} = 0$$



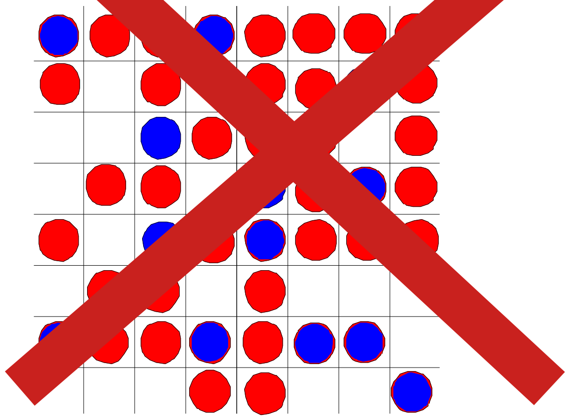
→ Every state in Ω (I_0) is connected to every other

→ Ergodic in Ω (I_0)

CONDITIONAL ERGODICITY/STATIONARITY

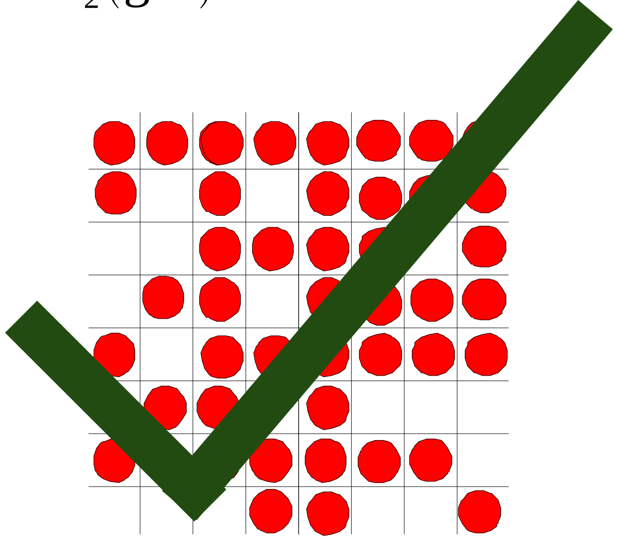
ZGB model

$$O_2(\text{gas}) + 2* \rightarrow 2O^*$$
$$CO(\text{gas}) + * \rightarrow CO^*$$
$$O^* + CO^* \rightarrow CO_2(\text{gas}) + 2*$$



O_2 ad/desoprtion

$$O_2(\text{gas}) + 2* \leftrightarrow 2O^*$$



DETAILED BALANCE: EQUILIBRIUM

Stationarity:

$$\sum_j w_{ij} P_s(j) - w_{ji} P_s(i) = 0$$

Equilibrium: Detailed Balance

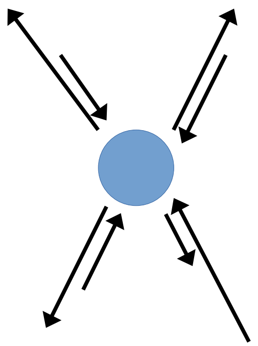
$$w_{ij} P_s(j) - w_{ji} P_s(i) = 0$$

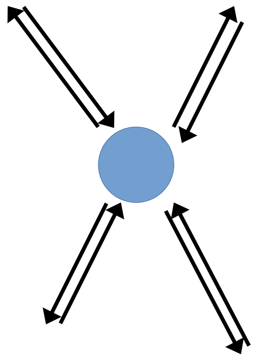
$$\frac{w_{ij}}{w_{ji}} = \frac{P_s(i)}{P_s(j)} = \frac{P_c(i)}{P_c(j)} = \exp\left(-\frac{E_f(i) - E_f(j)}{kT}\right)$$

Microscopic reversibility

$$\frac{w_{ij}}{w_{ji}} = \exp\left(-\frac{E_f(i) - E_f(j)}{kT}\right)$$

$$w_{ij} P_s(j) - w_{ji} P_s(i) \neq 0$$



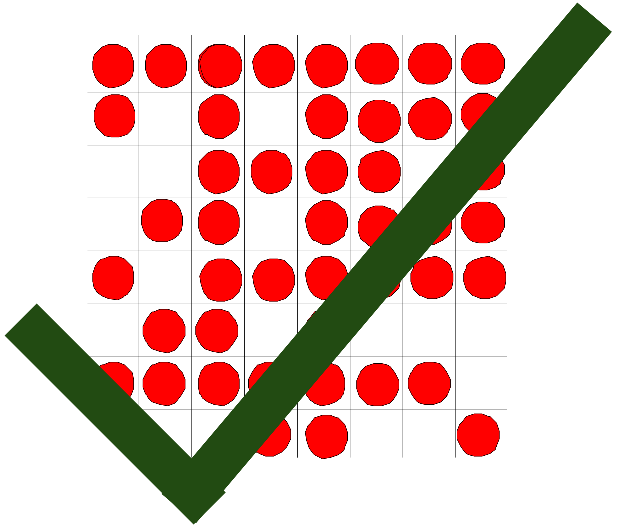


DETAILED BALANCED

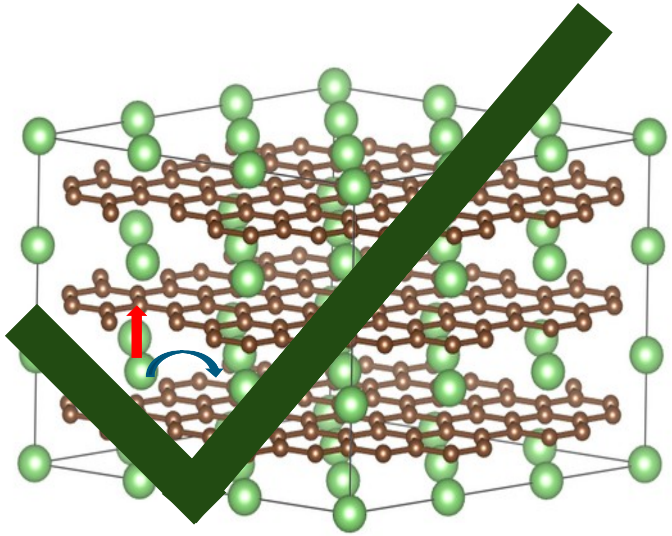
Ad/desoprtion

$$CO(gas) + * \leftrightarrow CO^*$$

$$O_2(gas) + 2* \leftrightarrow 2O^*$$



Diffusion

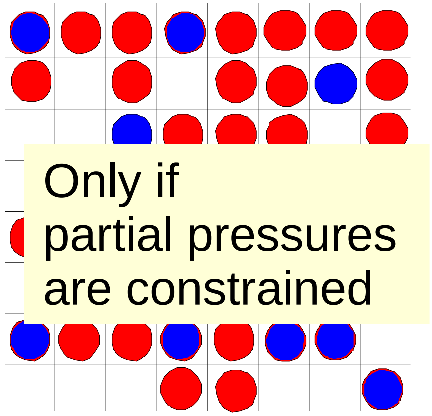


Catalysis

$$O_2(gas) + 2* \leftrightarrow 2O^*$$

$$CO(gas) + * \leftrightarrow CO^*$$

$$O^* + CO^* \leftrightarrow CO_2(gas) + 2*$$



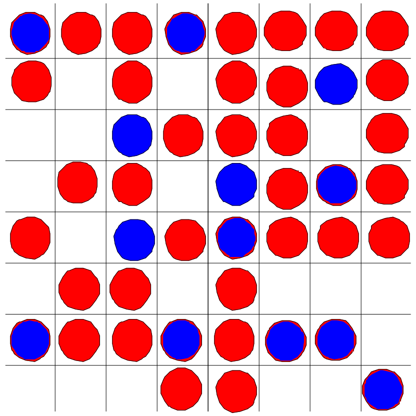
ANOTHER LITTLE PAUSE

PARAMETER DEPENDENCE

Typically models depend some parameter k ∈ R^M

$$\frac{d}{dt}P(t)=G(k)P(t) \quad \Rightarrow \quad \langle f\rangle(t,k)=\sum_i f(i|k)P(i,t|k)$$

$$O_2(gas)+2* \leftrightarrow 2O^*$$
$$CO(gas)+* \leftrightarrow CO^*$$
$$O^*+CO^* \leftrightarrow CO_2(gas)+2*$$



Restrict to

$$G(k)=\sum_{m=1}^{M} k_m G_m$$

e.g. for CO oxidation

$$G(k)=k_{CO\,ad.}G_{CO\,ad.}+k_{CO\,des.}G_{CO\,des.}+k_{O_2\,ad.}G_{O_2\,ad.}+k_{O_2\,des.}G_{O_2\,des.}+k_{CO_2\,ad.}G_{CO_2\,ad.}+k_{CO_2\,des.}G_{CO_2\,des.}$$

Rate constants

PARAMETER DEPENDENCE

Derivatives of expected values

$$\frac{\partial^L}{\partial k_{m_1} \ldots \partial k_{m_L}} \langle f \rangle (t,k) = \sum_i \sum_S \frac{\partial^{|S|} f(i|k)}{\prod_{m' \in S} \partial k_{m'}} \frac{\partial^{|S|} P(i,t|k)}{\prod_{m' \in S} \partial k_{m'}}$$

Suppose *t*, |Ω| <∞, *f*(*i*|*k*) from C^∞, then

$$\left| \frac{\partial^L}{\partial k_{m_1} \ldots \partial k_{m_L}} \langle f \rangle (t,k) \right| < \infty$$

Idea of proof

$$\left| \frac{\partial}{\partial k_m} P(t|k) \right| = \left| \frac{\partial}{\partial k_m} e^{tG} \right| = \left| \int_0^t e^{(t-u)G} G_m e^{uG} du \right| < \infty$$

Why
- Sensitivity Analysis
- Optimize
- Couple with other simulations
- Surrogates

Remark:

For $t \rightarrow \infty$ (stationary case), it is more complicated. Seems to hold if the process is ergodic.

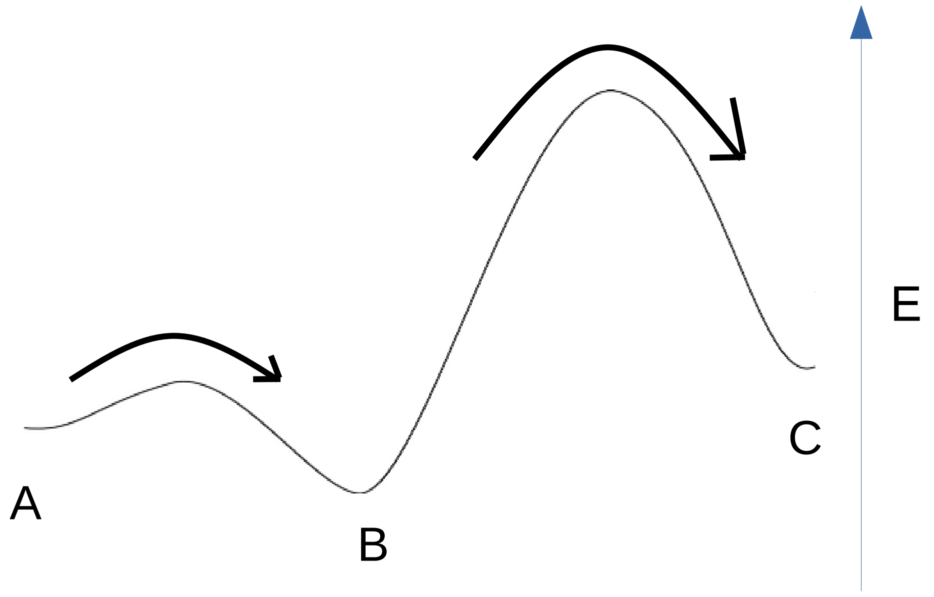
LOCAL SENSITIVITY ANALYSIS

Sensitivity analysis:
Parameters are typically uncertain!
Which uncertainties influence the outcome of our model?

Simplest approach: Linearize!

$$X_m = \frac{\partial \langle f \rangle}{\partial k_m}$$

Local Sensitivity Analysis
- Errors must be small!
- Everything but simple for kMC
- Therefore seldom conducted



RATE-DETERMINING STEPS

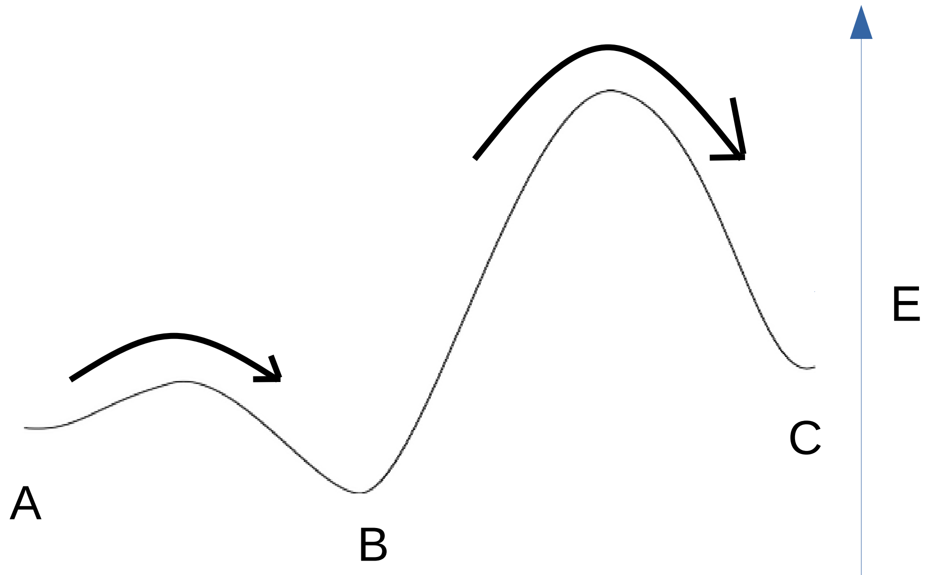
Expected reaction rate (turnover frequency)

$$\mathrm{TOF} := \sum_{\xi \in R} \langle a_{\xi} \rangle_s = \langle R \rangle_s$$

Degree of Rate Sensitivity

$$X_m = \frac{k_m}{\mathrm{TOF}} \frac{\partial \mathrm{TOF}}{\partial k_m} = \frac{k_m}{\mathrm{TOF}} \sum_{\xi \in R} \left\langle \frac{\partial a_{\xi}}{\partial k_m} \right\rangle + \frac{1}{\mathrm{TOF}} X_{0,m}$$

$$X_{0,m} = \sum_{\xi \in R} \sum_i a_{\xi}(i) \frac{\partial P_s(i)}{\partial \log k_m}$$



BOUNDS FOR THE SENSITIVITY

Pathwise relative entropy: Upper bound for sensitivity index

$$|X_{0,m}| \leq \sqrt{C\, I_{mm}}$$

Fischer-Information

Integrated time correlation function

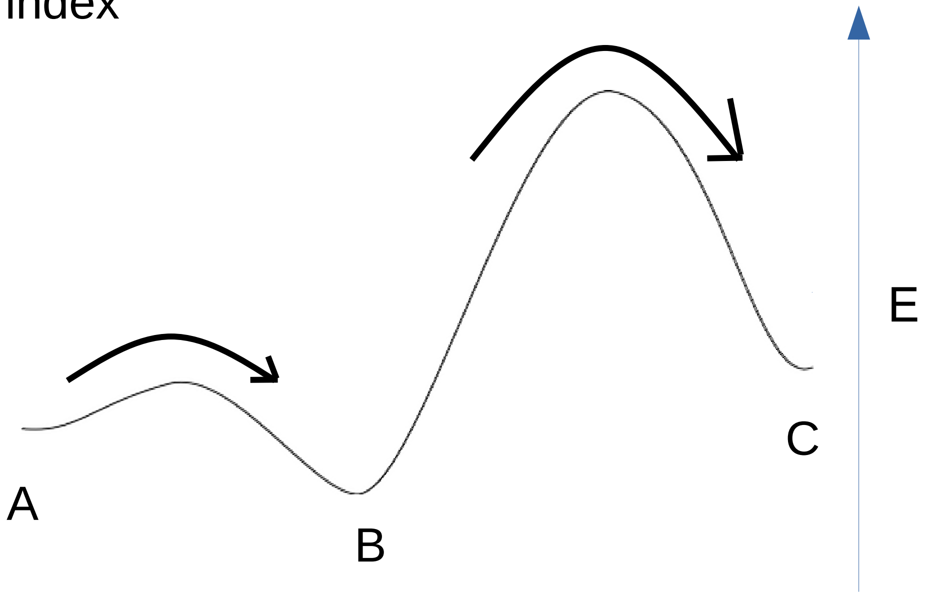
$$C = \int_0^\infty \langle \delta TOF (e^{tG}\, \delta TOF) \rangle_s \, dt$$

For the problem at hand

$$I_{mm} = \langle R_m \rangle$$

which is a consequence of

$$G(k) = \sum_{m=1}^{M} k_m G_m$$



Take home

Results are insensitive to rare reactions!

LINEAR RESPONSE THEORY

Idea:

$$\frac{d}{dt}P(t)=(G+\epsilon G_m)P(t)$$

Standard 1st order perturbation theory

$$X_{0,m}=\int_0^\infty \left(\delta R, e^{Gt} G_m P_s\right) dt=\left(\delta R, G^{\#} G_m P_s\right)$$

$$=\left(\delta R \Delta t, \sum_{l=0}^{\infty} P_{\mathrm{kMC}}^{l} G_m P_s\right)$$

Convergent sum (truncate) → direct sampling of sensitivities

Some properties

$$\sum_m X_{0,m}=0$$

$$\sum_m X_m=1$$

$$\mathrm{TOF}=\sum_m \frac{\partial\, TOF}{\partial k_m} k_m$$

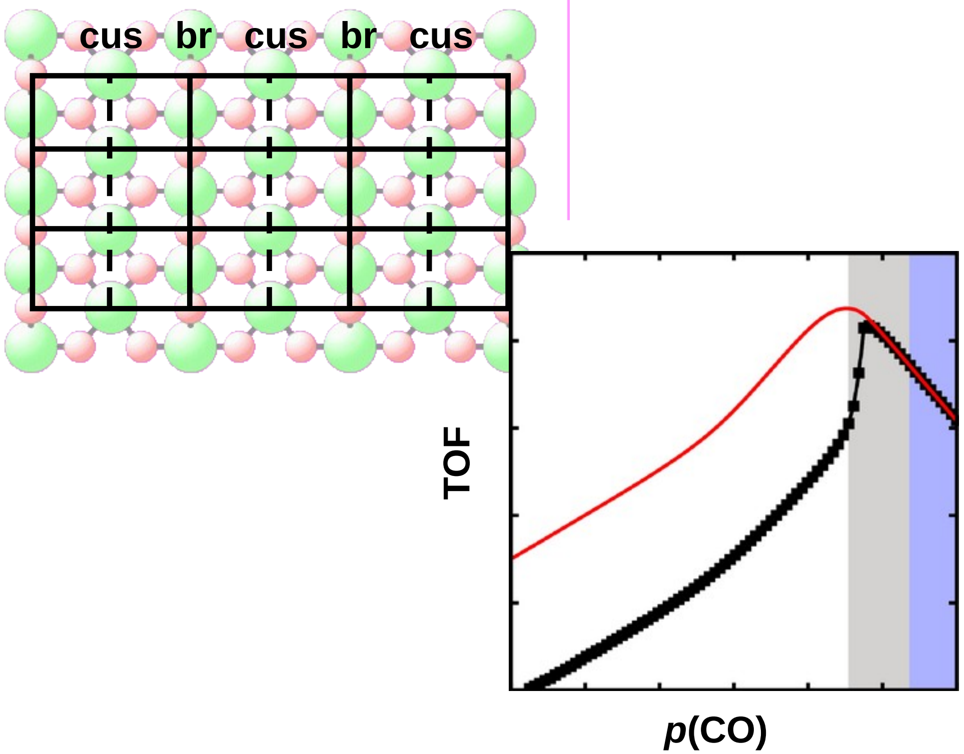
$$E_{app.}:=\frac{\partial\, TOF}{\partial \beta}=\sum_m X_m E_{act.,m}$$

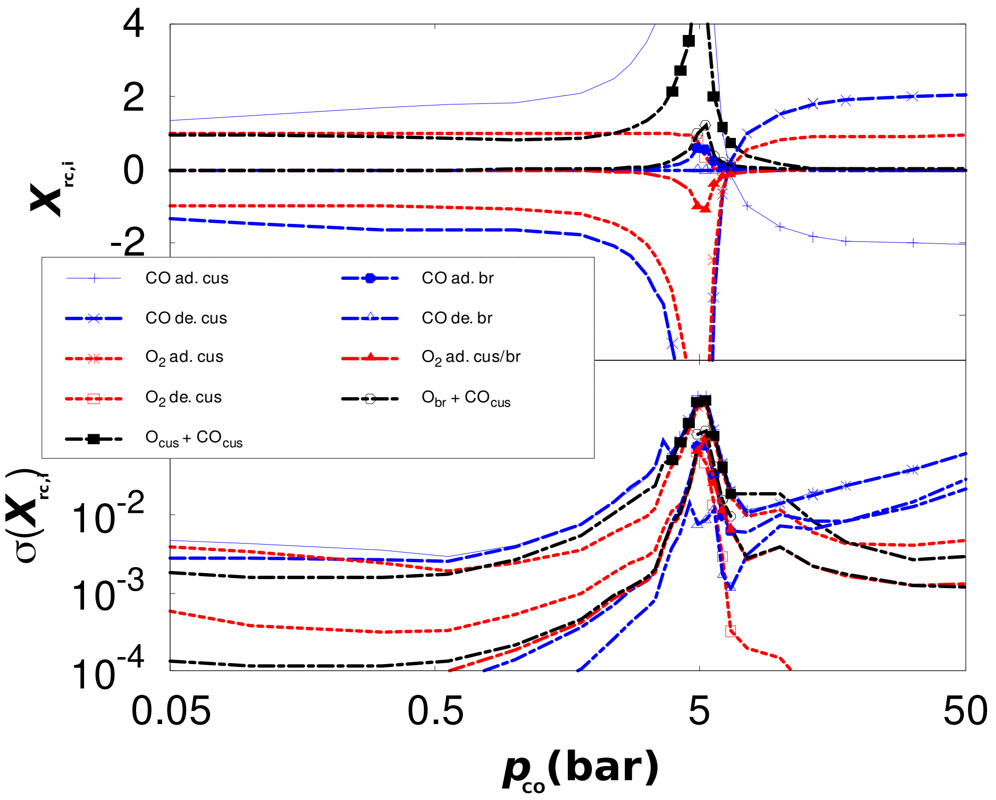
Campell's Degree of Rate Control

$$X_{rc,\alpha}=X_{f(\alpha)}+X_{r(\alpha)}$$

LOCAL SENSITIVITY ANALYSIS

CO oxidation on RuO_2 (110)
- 26 elementary steps
- There is no single RDS





FINAL SLIDE

- Intro Markov jump procresses
- Relaxation, stationary behavior
  - Ergodicity
- Parameter dependicity
  - Smoothness
  - Local sensitivity
  - Rate-determining steps
- What I did not talk about
  - Relaxation times, Eigenmodes, Oscillations
  - Global Sensitivity
  - The „curse“
  - How to get approximations aside traditional kMC (Meanfield, hierarchies, tensor networks, accelleration)

ECMath
MATH+
SFB 1114
unisyscat
BIG NSE
Funded by
DFG Deutsche Forschungsgemeinschaft
German Research Foundation

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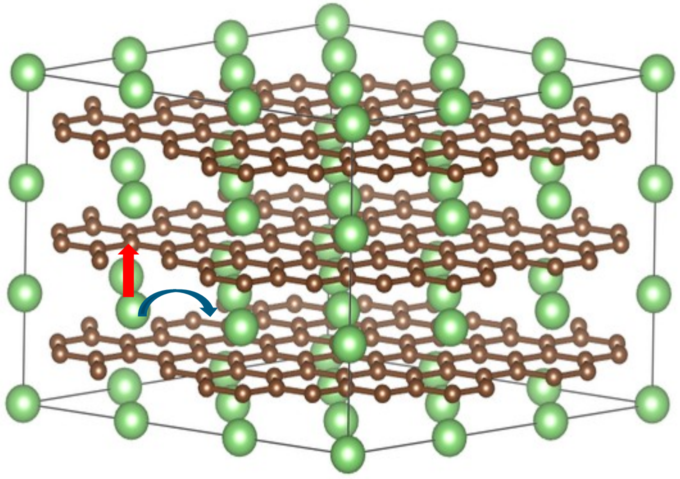
ERGODIC EXAMPLES

Ising model

- Spins on a lattice
- Flip „spin“ up or down
- Nearest neighbor interactions

Li diffusion in graphite



- Cross-layer diffusion >5eV vs. ~1eV intralayer.
- Cross-layer diffusion happens on timescales of 10^x years at room temperatur