Kinetic modeling in heterogeneous catalysis.

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Modern Methods in Heterogeneous Catalysis Research
Friday, January 27th, 2012

Microkinetic modeling is a valuable tool in catalysis.

- Disentangle complex phenomena
- Provide insight into what’s going on at the atomic level
- Make predictions for new conditions
- Save time and money
- Optimize reactor design

Review: Power Law

$$r = k\left[\mathrm{A}\right]^{n_a}\left[\mathrm{B}\right]^{n_b}$$

Typically a differential reactor is used:

- low loading, low concentration
- isothermal
- high flow rate.

Reaction order n_a, n_b are determined experimentally.

Review: Langmuir-Hinshelwood

$$r = k\frac{K_A K_B[\mathrm{A}][\mathrm{B}]}{\left(1 + K_A[\mathrm{A}] + K_B[\mathrm{B}]\right)^2}$$

A simple, global mechanism is assumed:

- adsorbates are equilibrated with gas phase
- surface reaction is rate determining step

Apparent reaction order varies between -1 and 1:

$$n_a \equiv \frac{\partial \ln r}{\partial \ln[\mathrm{A}]} = 1 - \frac{2K_A[\mathrm{A}]}{1 + K_A[\mathrm{A}] + K_B[\mathrm{B}]}$$

Typically the experimentally observed reaction order is used to interpret a Langmuir-Hinshelwood mechanism.

This approach suffers two flaws:

- Experimental n_a, n_b are only valid over a narrow range of conditions.
  - ➡ *it cannot be used to predict anything*

- The LH mechanism is over simplistic.
  - ➡ *it cannot be used to explain anything*

We need a modeling approach that is *predictive*, not *postdictive*.

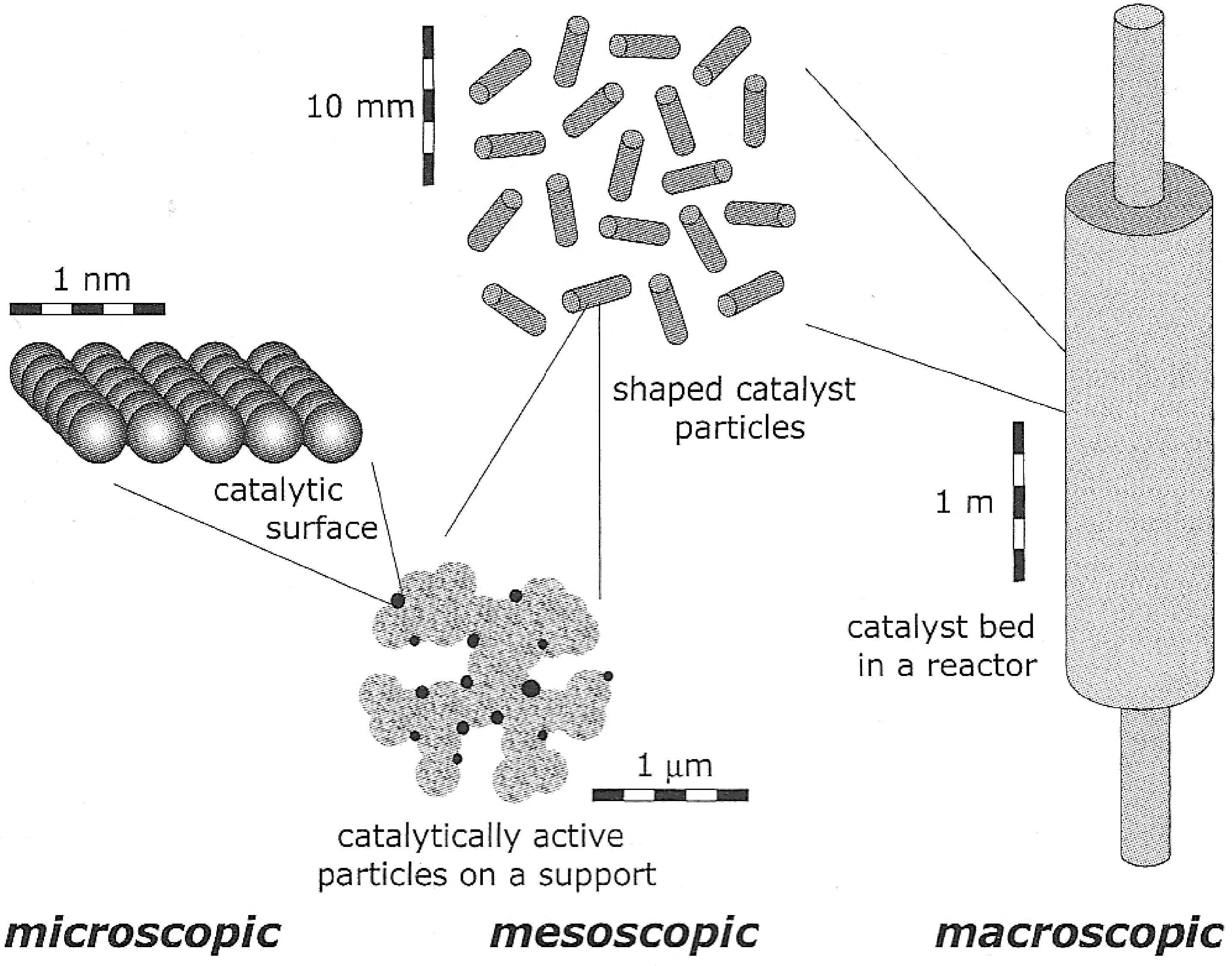
Elementary reaction mechanism:

- attempt to describe real chemistry
- is valid over a broad range of conditions

An elementary reaction occurs in a single step, i.e.

- it can be described by a single reaction coordinate
- or it passes through a single transition state

Catalysis is a multiscale problem.

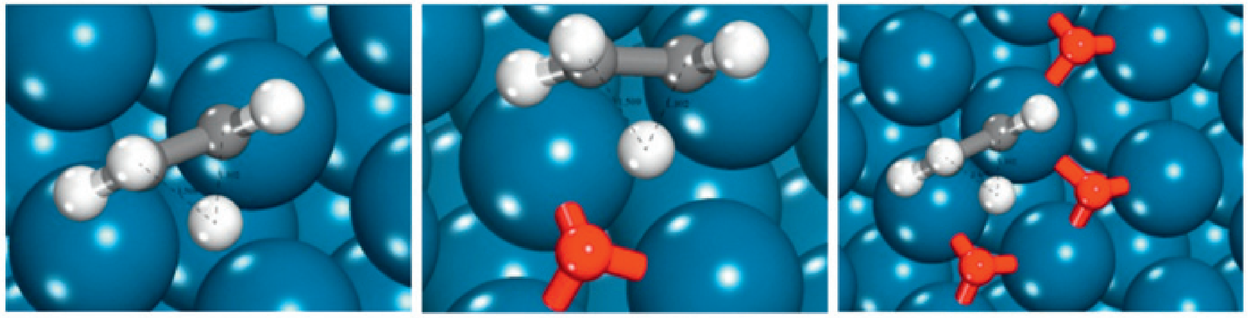


10 orders of magnitude in length.
15 orders of magnitude in time.
14 orders of magnitude in pressure.

Chorkendorff and Niemantsverdriet. *Conc. of Mod. Cat.*

Scale is not the only challenge in catalysis.

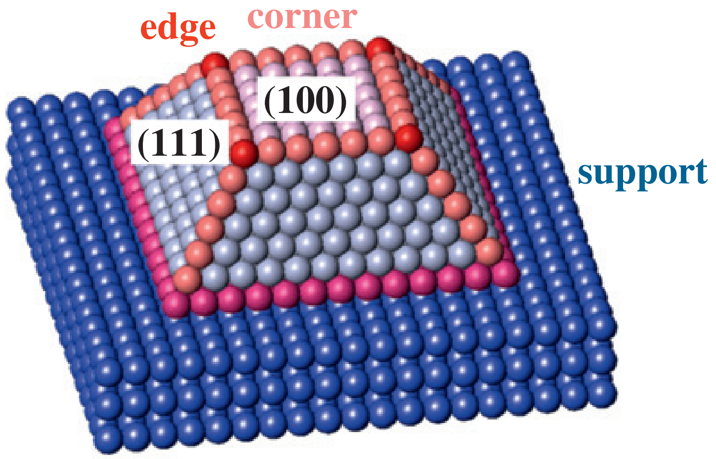
Many-body effects



(a) $\Delta E_i = 54$ kcal/mol (b) $\Delta E_i = 41$ kcal/mol (c) $\Delta E_i = 23$ kcal/mol

Intrinsic heterogeneity in

- adsorbate distribution
- catalyst sites

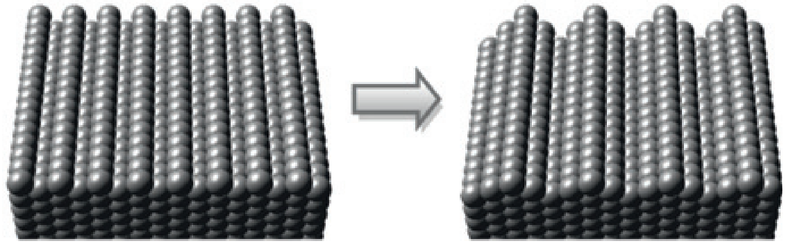


Multiple phases

Catalyst dynamics

- reconstruction
- isomerization

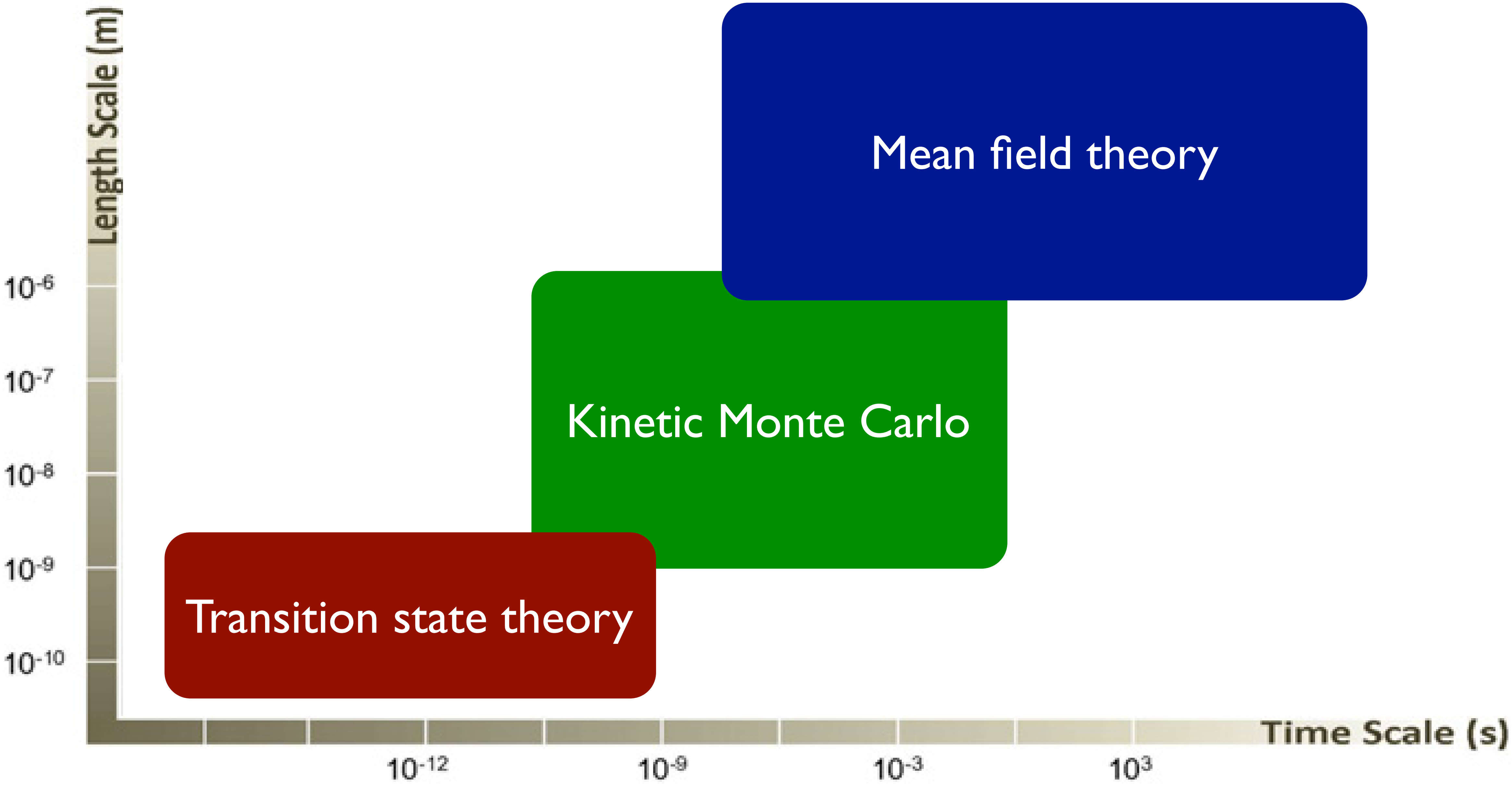
Missing row reconstruction on (110) plane



No single modeling approach can include all effects at all scales.

Salciccioni et al. *Chem. Eng. Sci.* 66 (2011) 4319-4355

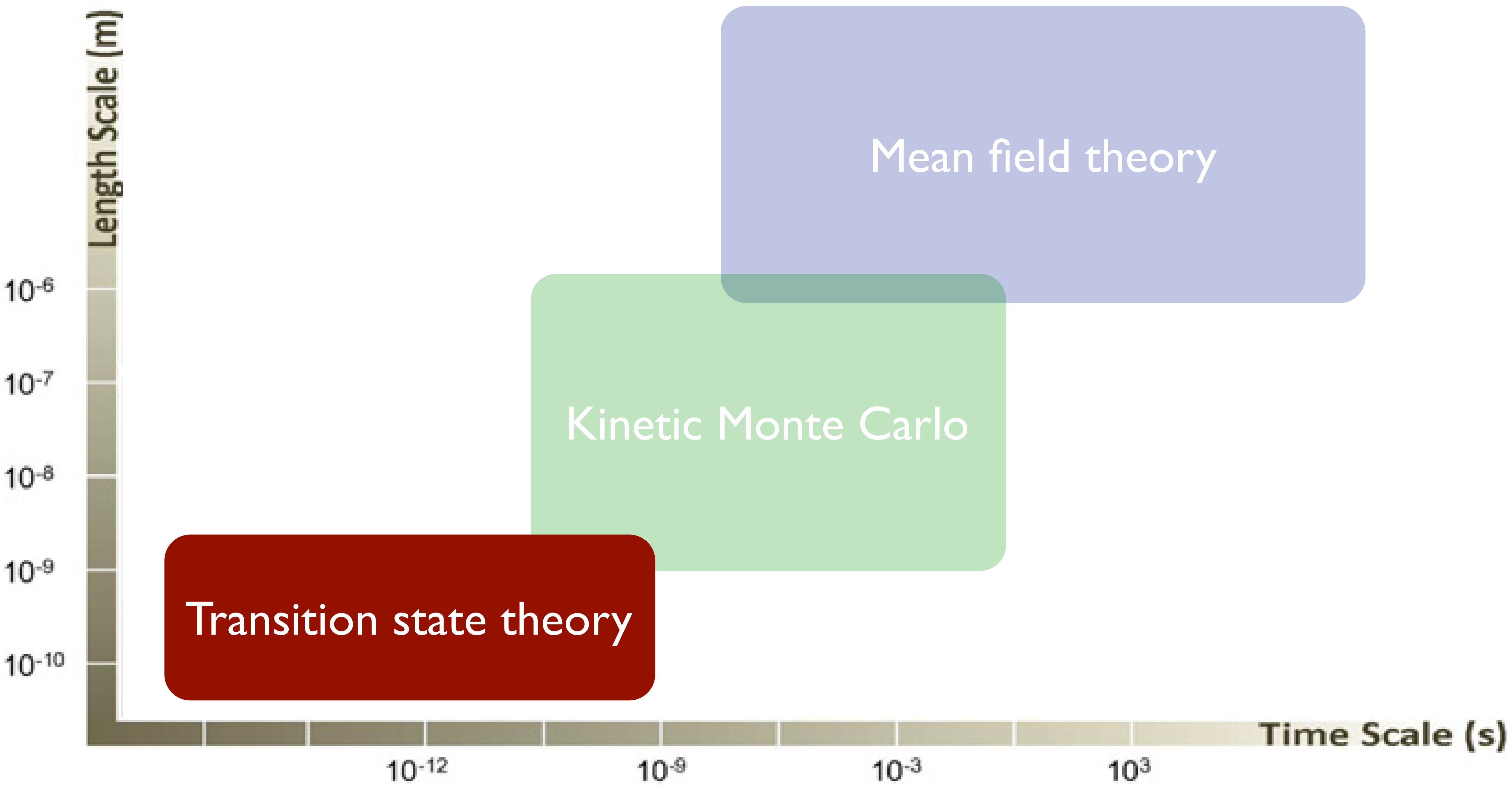
Which modeling method you chose depends upon the length scale you intend to model.



Outline:

1. Transition State Theory
2. Kinetic Monte Carlo
3. Mean Field Theory
4. Making sense of complexity

Part I: Transition-State Theory



Part I: Transition-State Theory

Transition-state theory (TST):

- an approximation to dynamic theory (classical or quantum).
- evaluates the reactive flux through a dividing plane on a potential energy surface.

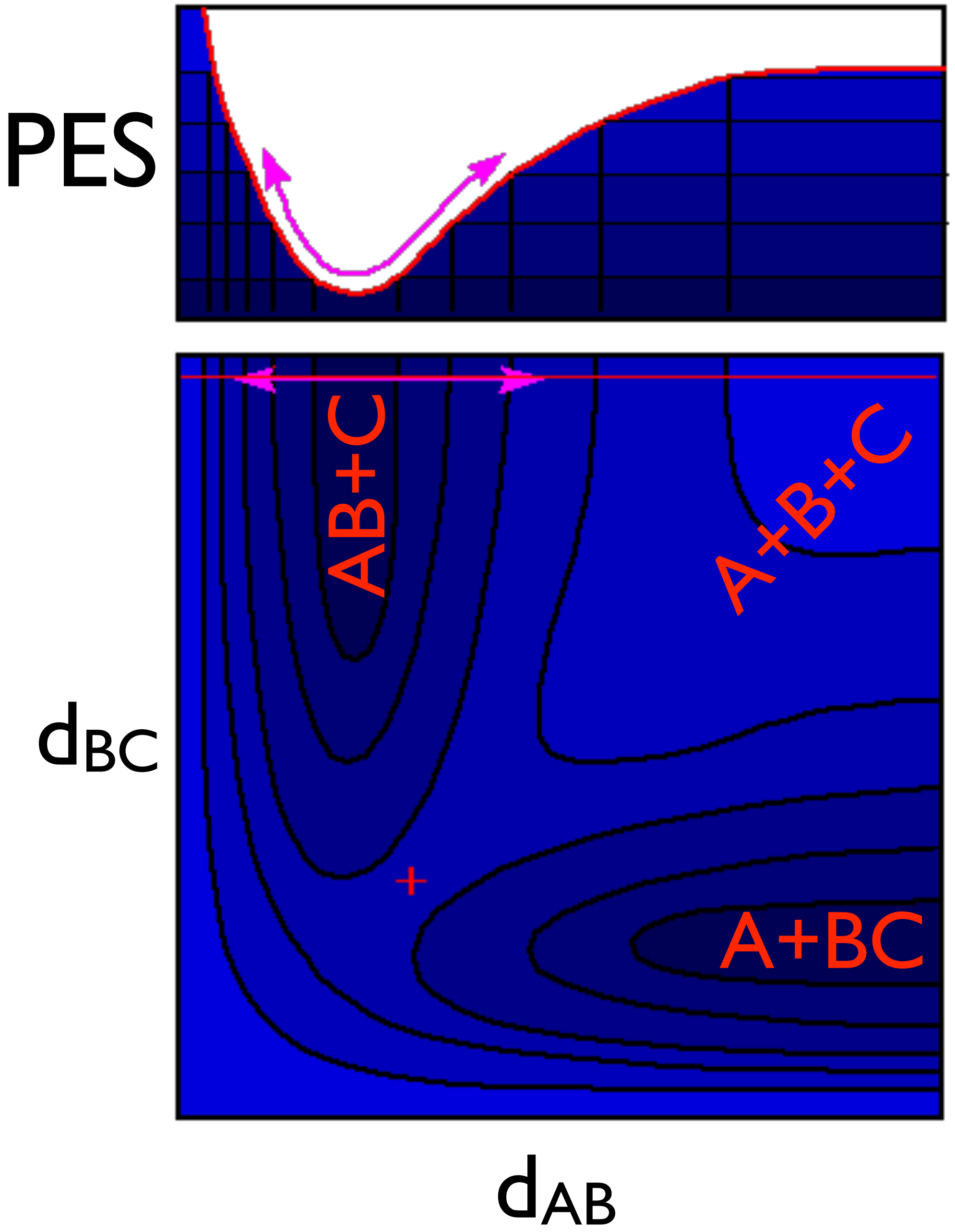
There are many flavors of TST.

For simplicity we will focus on canonical TST.

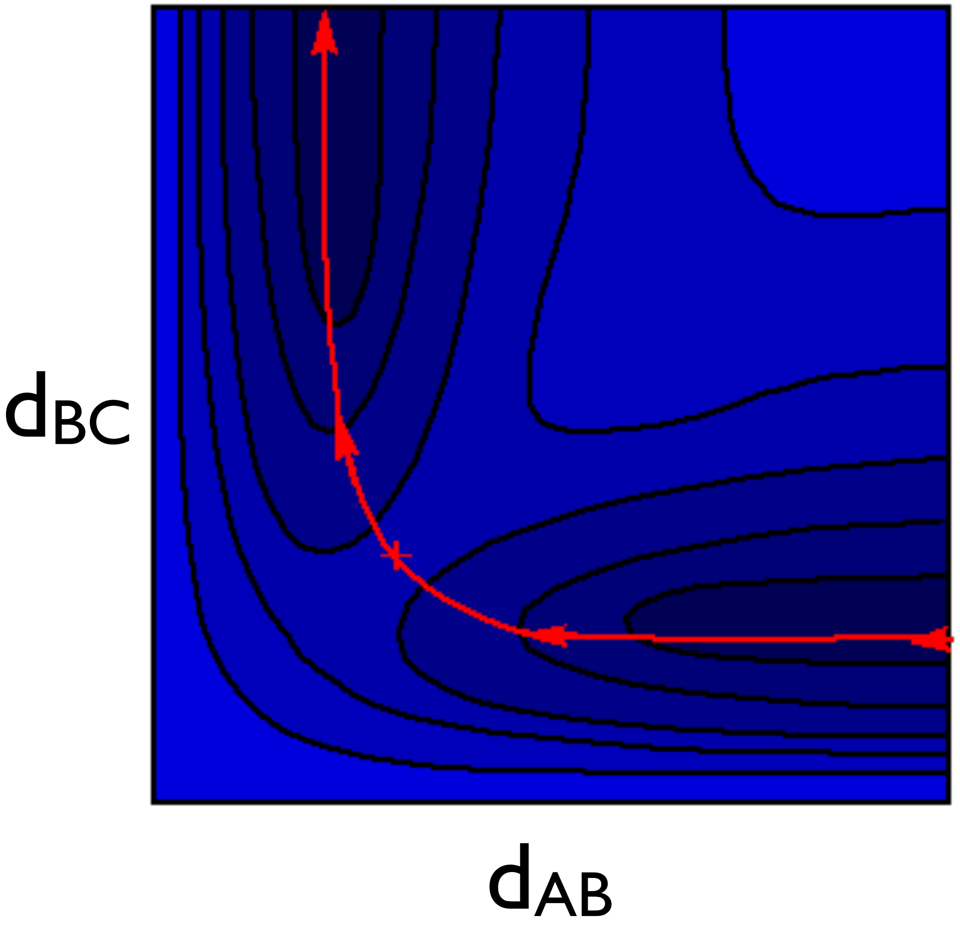
TST Assumptions

1. The Born-Oppenheimer approximation is valid.
2. A dynamic bottleneck between reactants and products can be identified.
3. Reactant molecules are distributed in a Maxwell-Boltzmann distribution.

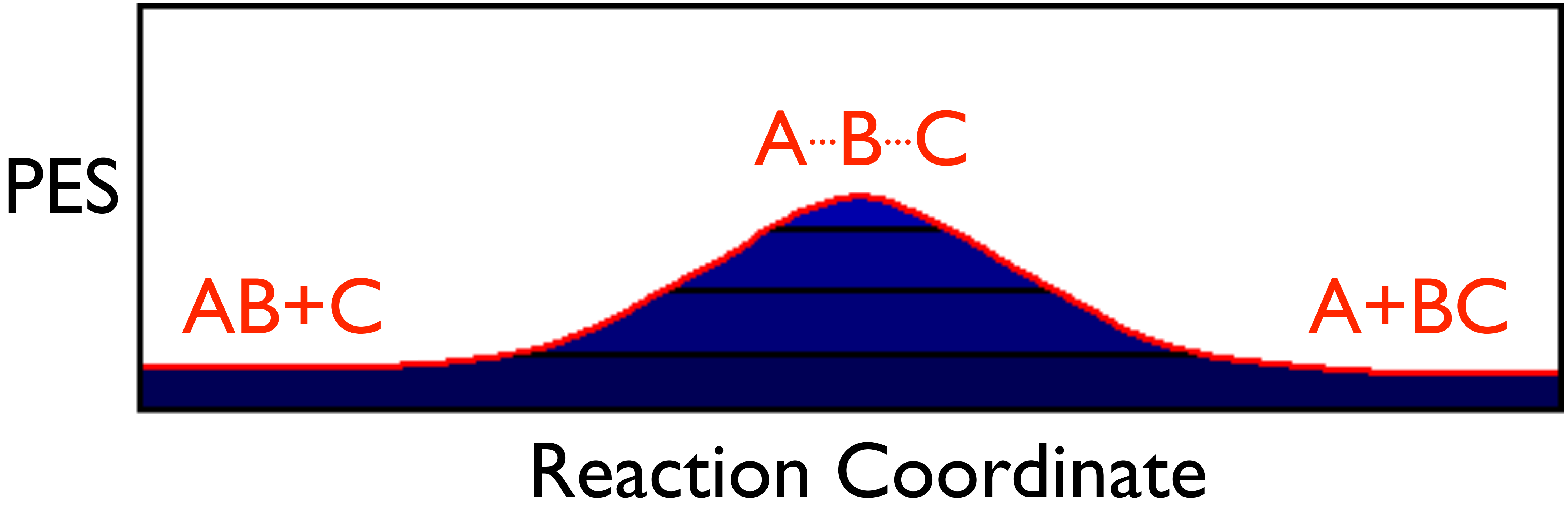
For *n* internal coordinates, the potential energy surface (PES) is an (*n*+*1*)-dimensional hypersurface.



The reaction coordinate is the lowest energy path between reactants and products.



The transition state is the maximum along the reaction coordinate.



TST assumes that the reactant(s) and transition state are equilibrated.

$$\mathrm{R} \overset{K^\dagger}{\rightleftharpoons} \mathrm{TS} \xrightarrow{k^\dagger} \mathrm{P}$$

$$\frac{d[\mathrm{P}]}{dt} = k^\dagger[\mathrm{TS}] = \underbrace{k^\dagger K^\dagger}_{k_{TST}}[\mathrm{R}]$$

The rate constant is proportional to the frequency of passes over the barrier times the transition state equilibrium constant.

$$k_{TST}\left(T\right) = \underbrace{\frac{k_B T}{h}}_{k^\dagger} \underbrace{\frac{Q_{\mathrm{TS}}^\dagger}{Q_{\mathrm{R}}} e^{-E_0/RT}}_{K^\dagger}$$

Note the functional similarity to the Arrhenius equation:

$$k_{Arr}\left(T\right) = Ae^{-E_a/RT}$$

The activation energy and barrier height are correlated but not equivalent:

$$E_a \equiv -R\frac{\partial \ln r}{\partial 1/T}$$

$$= RT^2\frac{\partial}{\partial T}\left(\ln\frac{k_B T}{h}\frac{Q^{\dagger}_{\mathrm{TS}}(T)}{Q_{\mathrm{R}}(T)}\right) + E_0$$

Equivalence can be obtained if we assume:

1. classical oscillators
2. change in all other modes is negligible

$$A \approx \frac{k_B T}{h}\frac{Q^{\dagger}_{\mathrm{TS}}}{Q_{\mathrm{R}}} \approx \nu_n \quad \mathrm{O}\left(10^{13}\ \mathrm{s}^{-1}\right)$$

Transition states are categorized as loose or tight.

Loose transition states:

1. higher in entropy than reactants
2. more energy levels to be occupied
3. $10^{13} < A < 10^{17}$ s^{-1}

Tight transition states:

1. lower in entropy than reactants
2. fewer energy levels to be occupied
3. $10^{9} < A < 10^{13}$ s^{-1}

Calculating k_{TST} from first principles requires electronic structure calculations (e.g. DFT) and statistical mechanics.

E_0 is the difference in the zero-point corrected electronic energy.

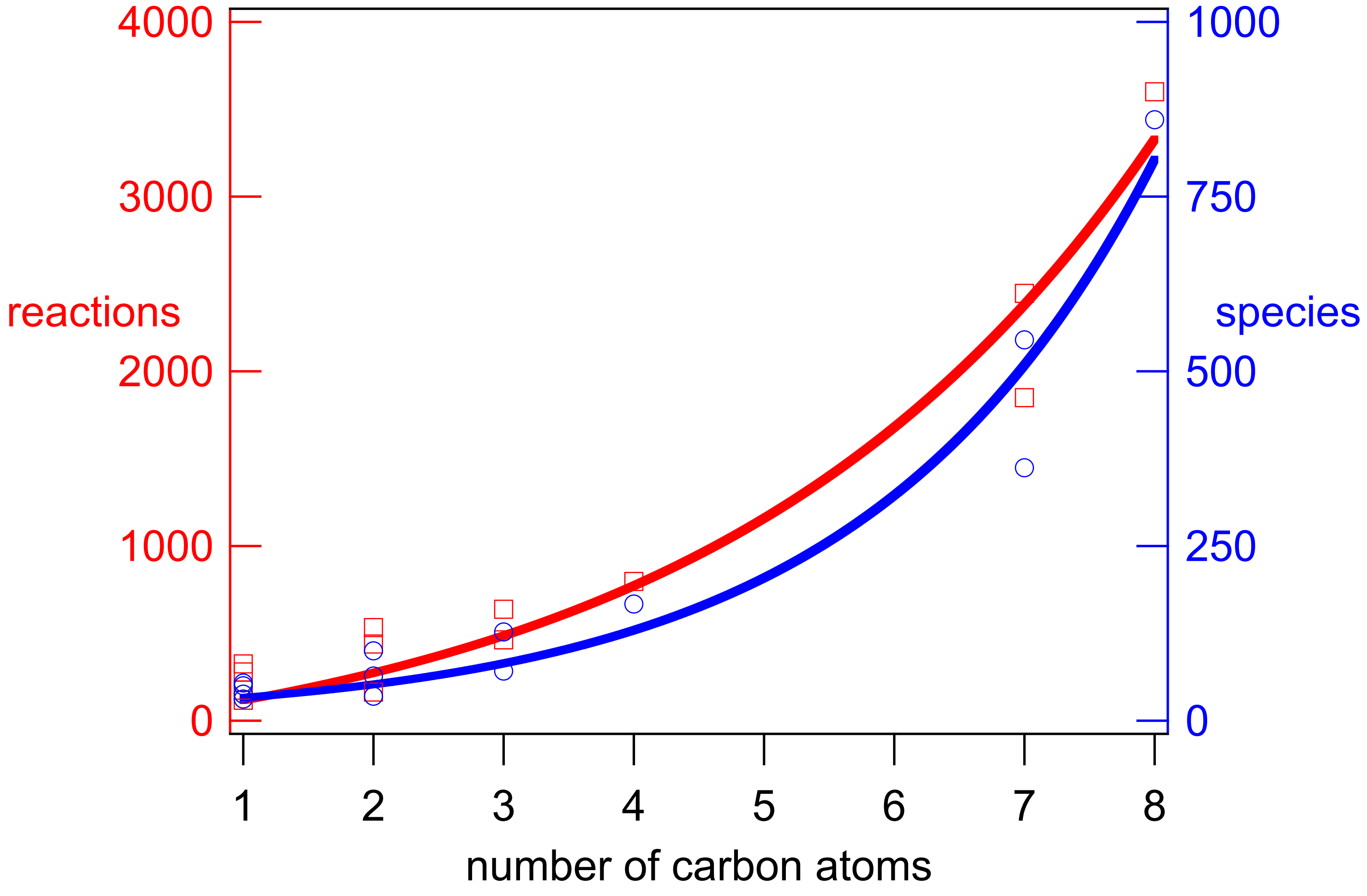
- Typical DFT error is 20 - 30 kJ/mol.
- Need error less than 5 kJ/mol for chemical accuracy.

The partition function requires physical properties:

- vibrational frequencies
- reduced moments of inertia for weakly bound rotors

$$Q = Q_{elec} Q_{trans} Q_{rot} Q_{vib}$$

Most systems are too large for first-principles calculations.



We need tools to generate large-scale mechanisms rapidly but accurately.

We can combine methods to estimate the kinetic parameters.

DFT → Compute atomic binding energies

Scaling relations
UBI-QEP → Estimate adsorbate binding energies

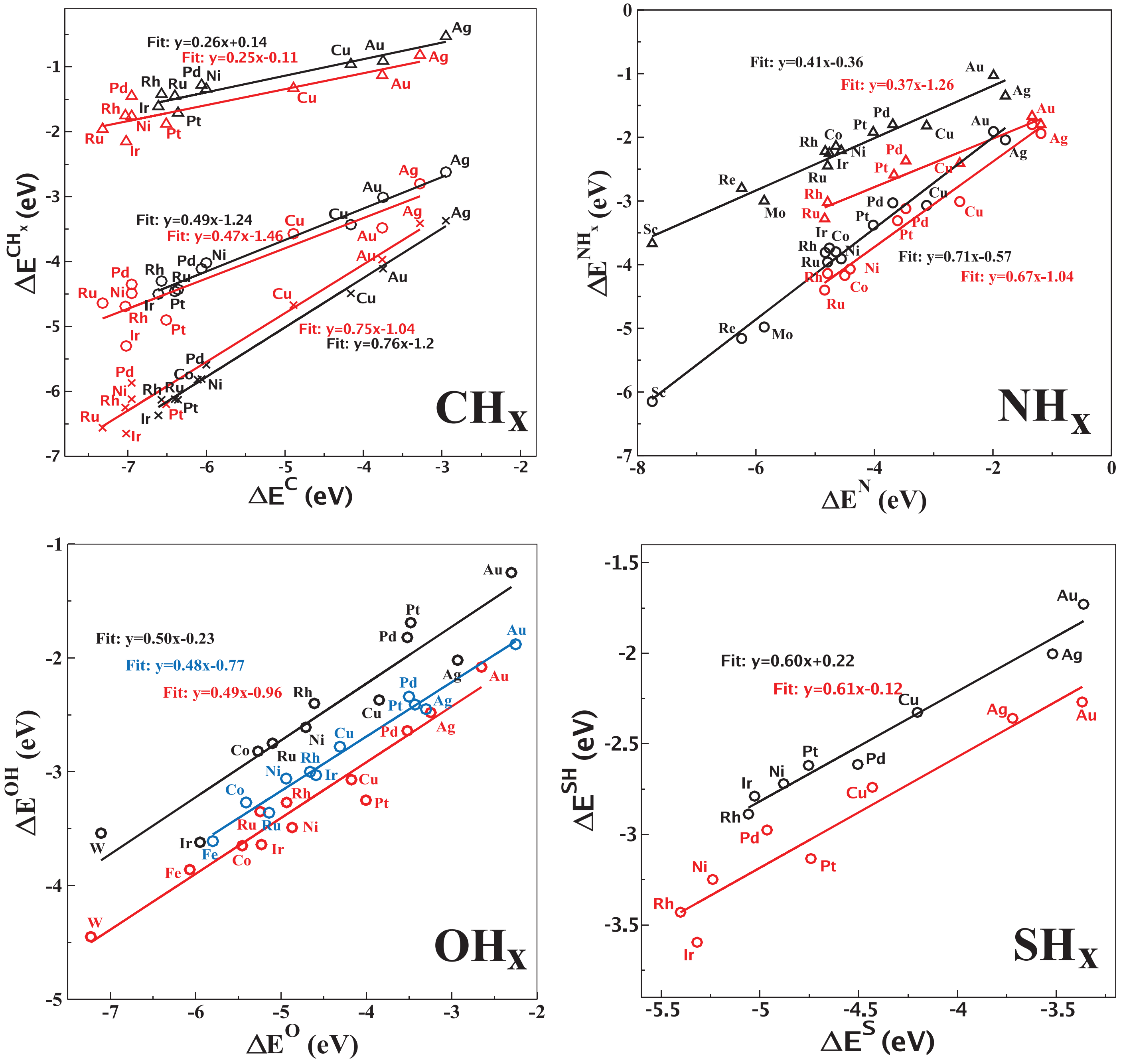
BEP
UBI-QEP → Estimate activation energies

Reaction type → Estimate pre-exponential factors

Two methods are commonly used to estimate energies.

1. Linear scaling relations (Nørskov)
2. Unity Bond Index - Quadratic Exponential Potential (UBI-QEP)

The binding energy of a molecule is linearly proportional to the binding energy of the central atom.



$$\Delta E^{AH_x} = \gamma \Delta E^{A} + \xi$$

$$\gamma = \frac{x_{\max} - x}{x_{\max}}$$

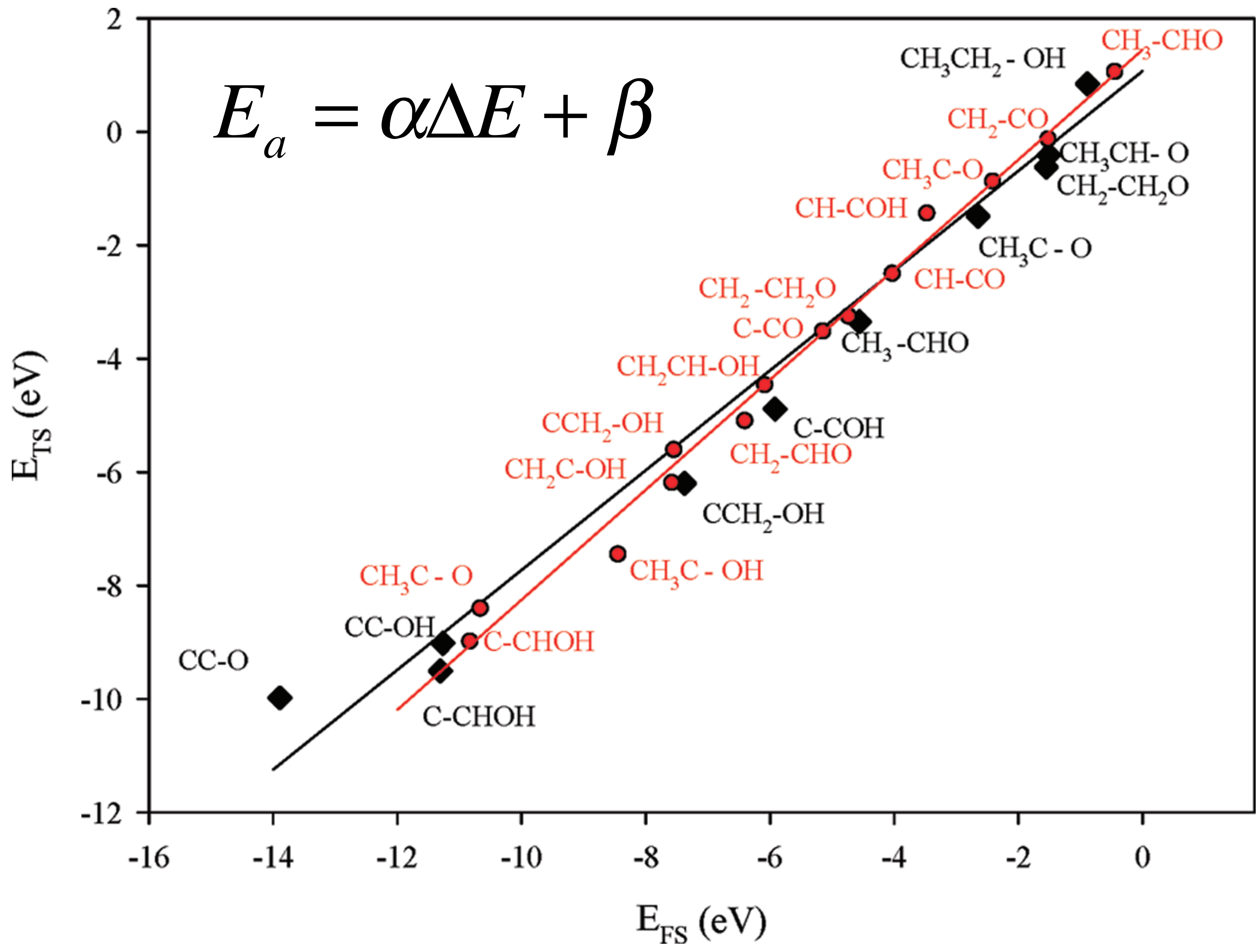
$$x_{\max} = 4 \text{ for } A = C$$

$$= 3 \text{ for } A = N$$

$$= 2 \text{ for } A = O, S$$

Abild-Pederson et al. *Phys. Rev. Let.* 99 (2007)

Brønsted-Evans-Polanyi (BEP) can be used to estimate the activation energy.

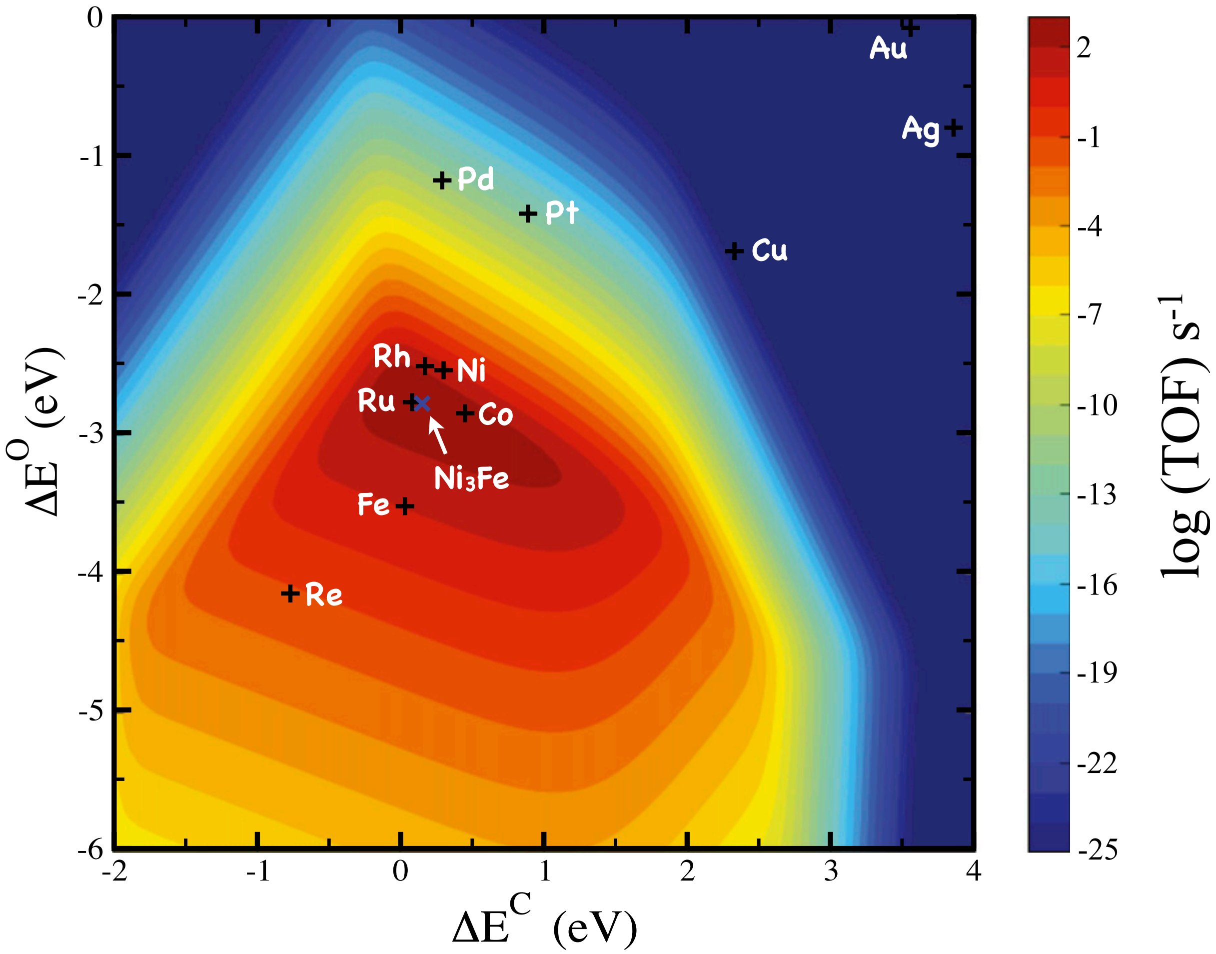


α, β can be refined based upon type of bond broken, surface, etc.

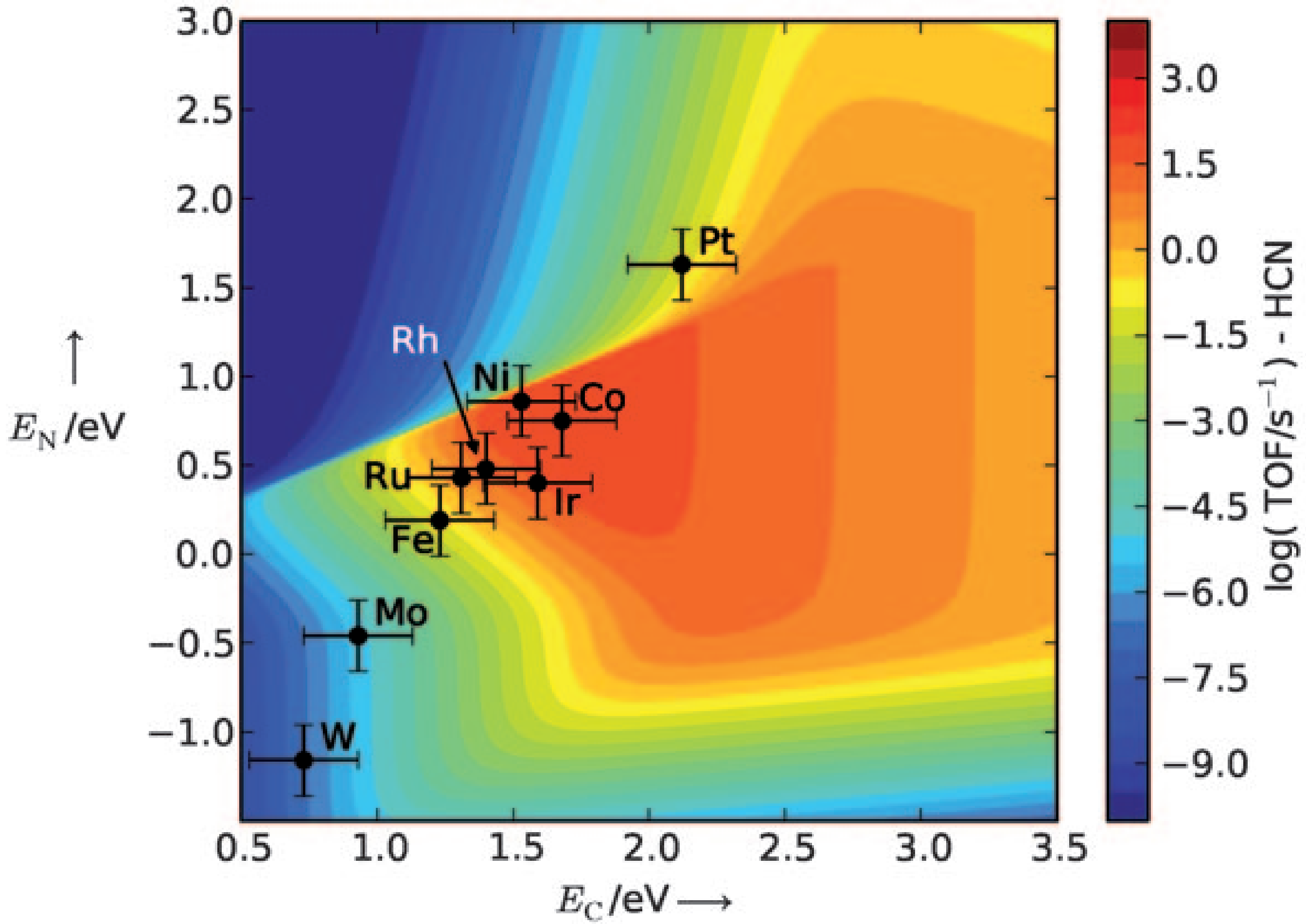
Ferrin et al. *JACS*. 131, (2009)

Linear scaling relations reduce a complex mechanism down to a minimum set of descriptors.

$CO + 3H_2 \rightarrow CH_4 + H_2O$



$CH_4 + NH_3 \rightarrow HCN + 3H_2$



Nørskov et al. *PNAS.* 108, 3, (2011)

Grabow et al. *Angew. Chem.* 50, (2011)

UBI-QEP is a semi-empirical method for coverage-dependent activation energies.

Requires atomic binding energies and gas-phase molecular dissociation energies.

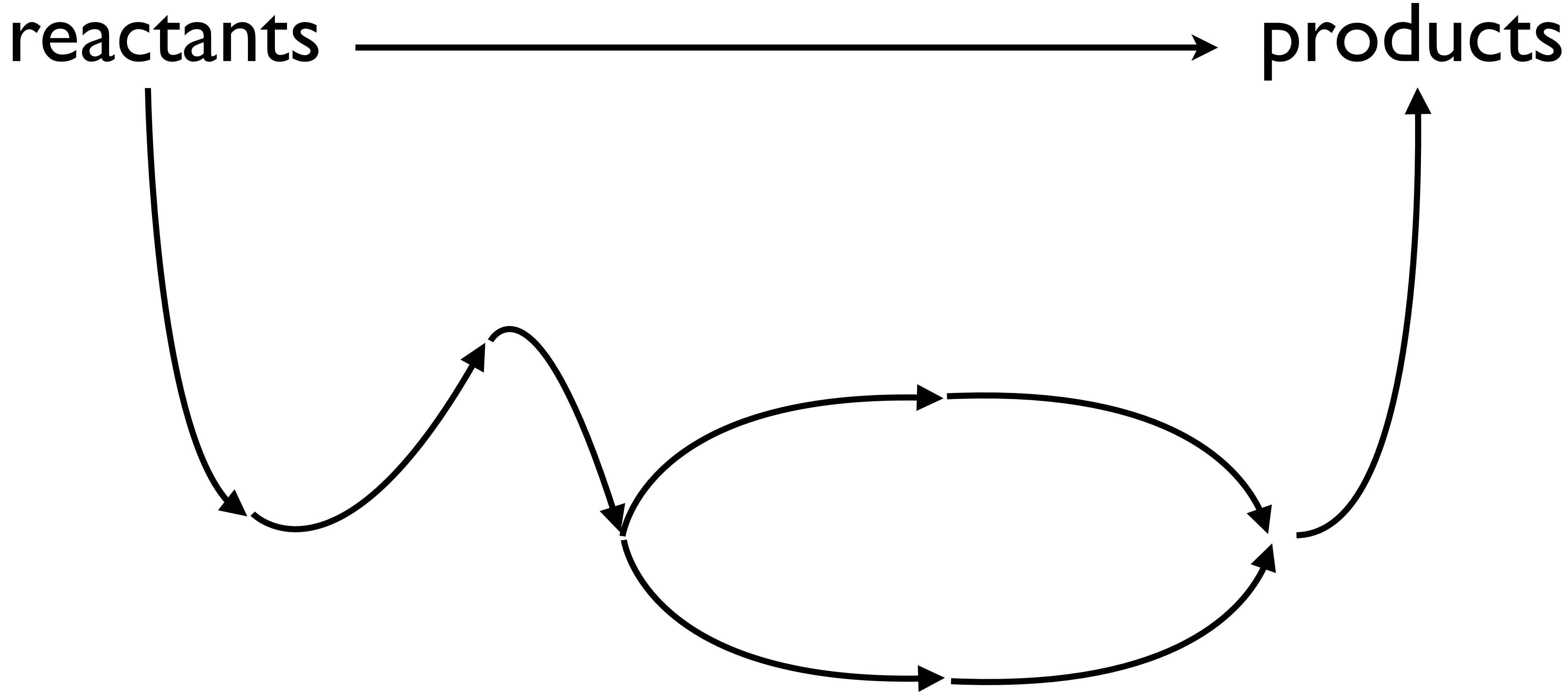
1. Two-body interactions are described by a quadratic potential, exponential in distance (Morse).
2. Total energy of many-body system is the sum of two-body interactions.

Fast, easy, popular -- but can lead to big errors for larger molecules.

Shustorovich and Sellers. *Surf. Sci. Rep.* 31 (1998)

Maestri and Reuter. *Angew. Chem.* 50 (2011)

A kinetic mechanism must conserve enthalpy and entropy.



ΔH_{rxn} and ΔS_{rxn} must be the same for either path.

Thermodynamic consistency constrains the Arrhenius parameters:

$$\Delta H_{\mathrm{rxn}} = E_{a,f} - E_{a,r}$$

$$\Delta S_{\mathrm{rxn}} = R \ln \frac{A_f}{A_r}$$

Most mechanisms are not consistent!

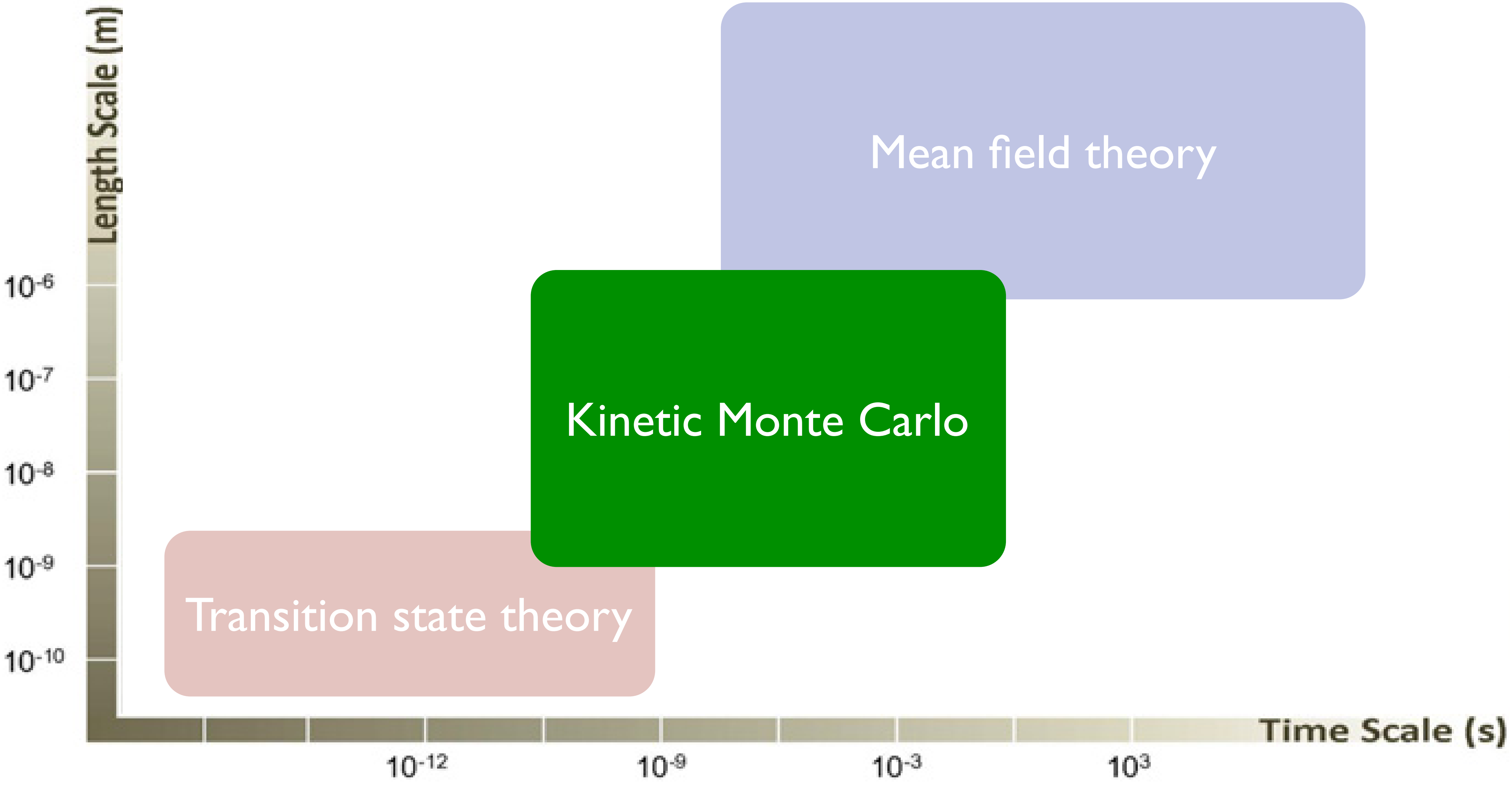
Typically entropy is not conserved;
equilibrium constants are off by orders of magnitude.

There are two approaches to enforcing thermodynamic consistency:

1. Constrain all $E_{a,rev}$ and A_{rev} according to a basis set*.
    - Requires accurate $k_{adsorption}$, $k_{desorption}$ for all intermediates
2. Compute k_r directly from the equilibrium constant.
    - Requires accurate *H(T)*, *S(T)* for all intermediates

*Mhadeshwar, Wang, & Vlachos. *J. Phys. Chem. B., 107,* 2003

Part II: Kinetic Monte Carlo



Mean field theory

Kinetic Monte Carlo

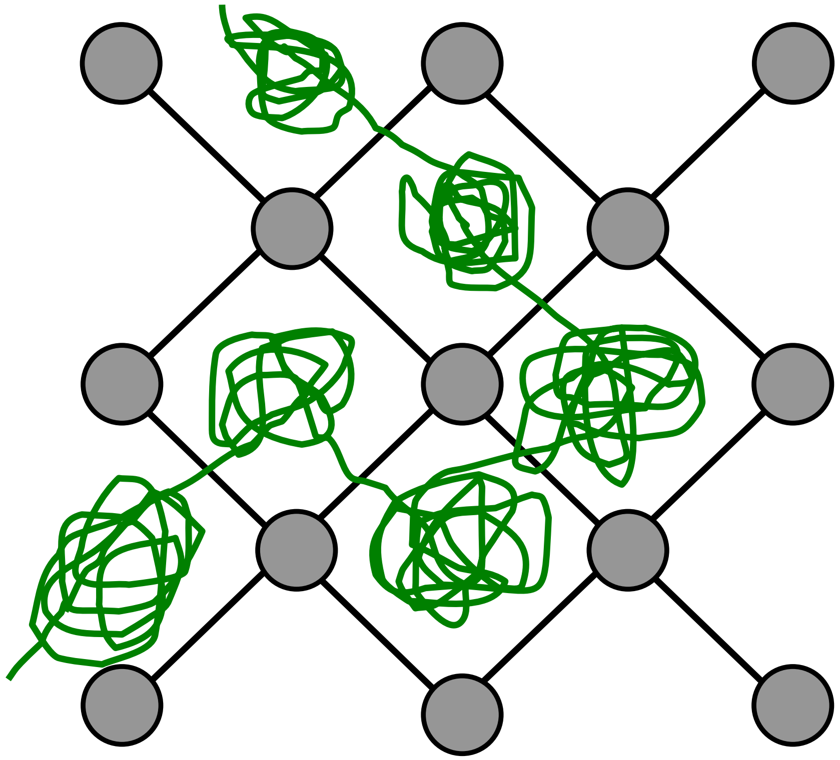
Transition state theory

Part II: Kinetic Monte Carlo

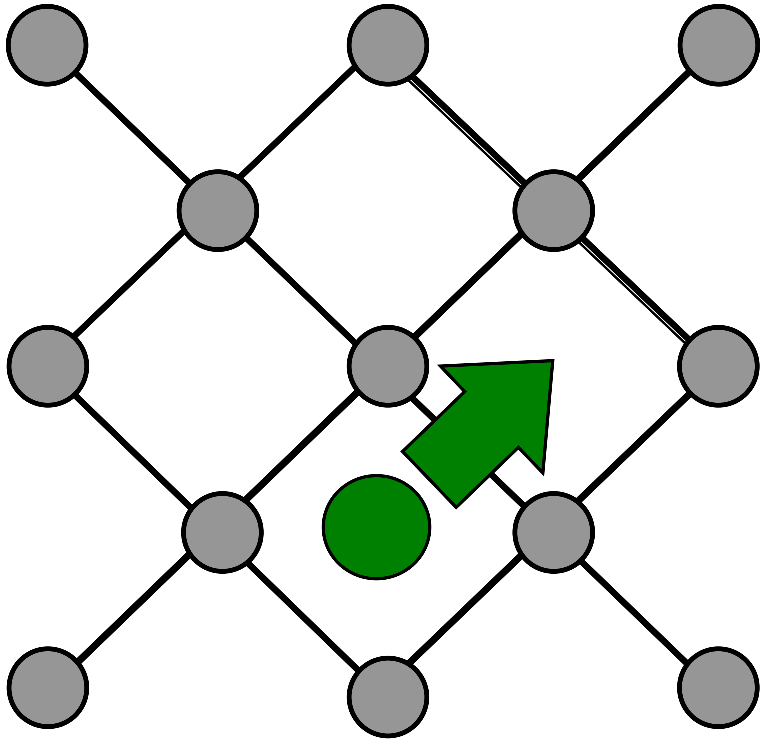
KMC is a method for simulating state-to-state dynamics of a rare event system.

- Can span a large range of time scales by neglecting unimportant ultrafast phenomena.
- Explicitly accounts for spatial heterogeneity in competing processes:
  - adsorption/desorption
  - surface diffusion
  - surface reactions

Coarse-grain time scales allows us to model chemical reactions.



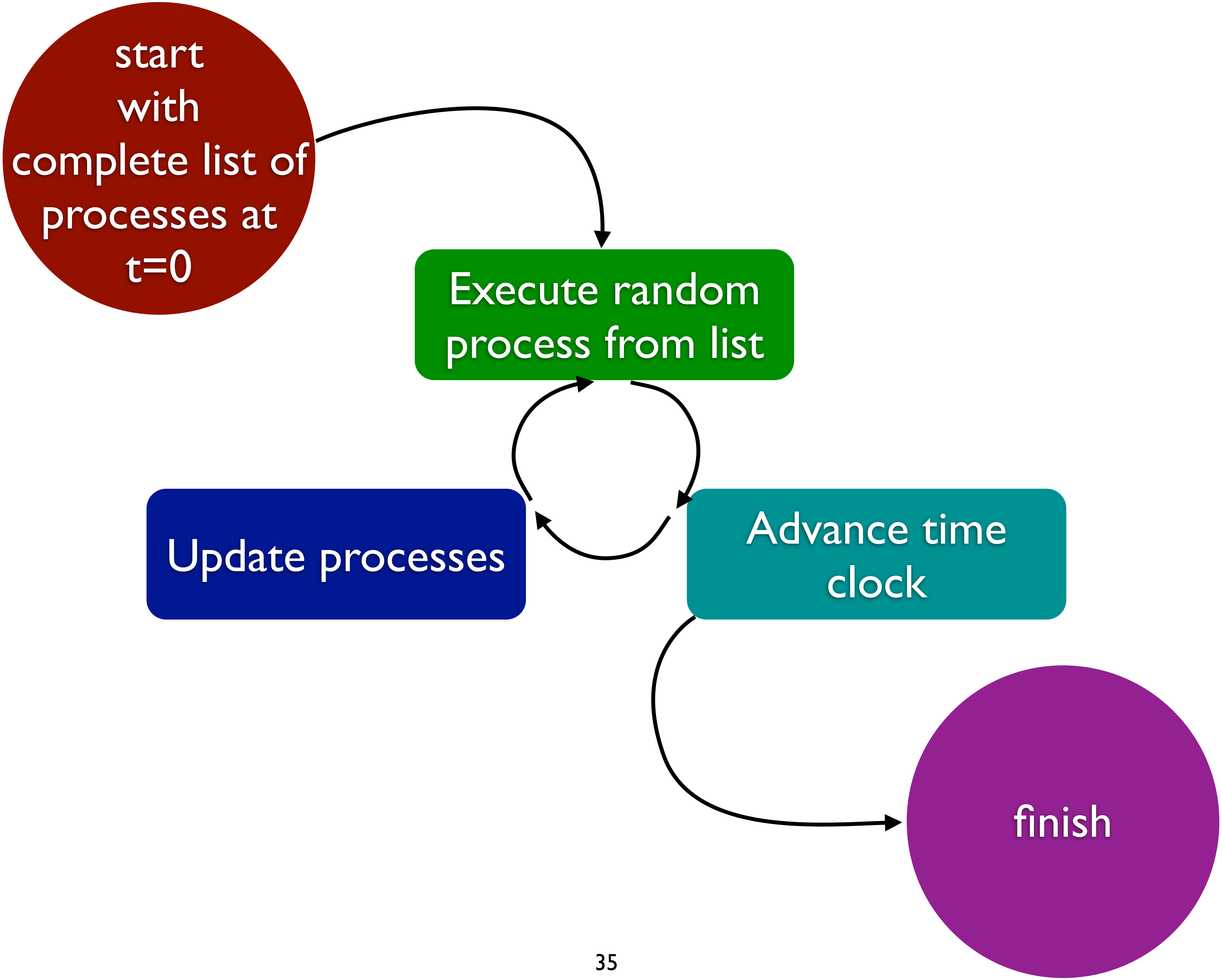
Molecular Dynamics:
the whole trajectory



Kinetic Monte Carlo:
coarse-grained hops

Molecular Dynamics wastes time modeling the 10^9 thermal vibrations between diffusion events.

Reuter, K. *Wiley* (2009)



start with complete list of processes at t=0

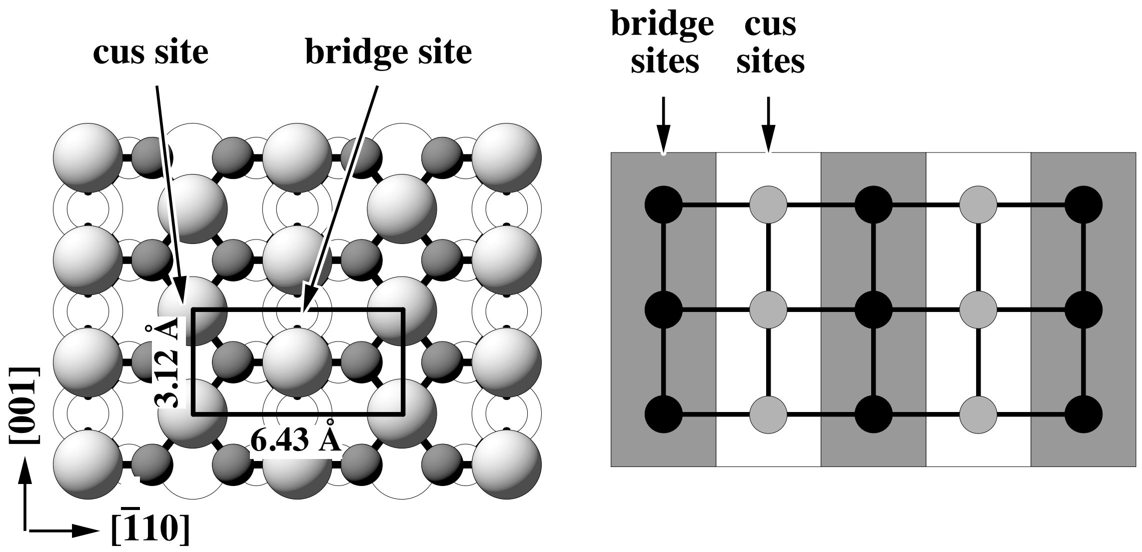
Execute random process from list

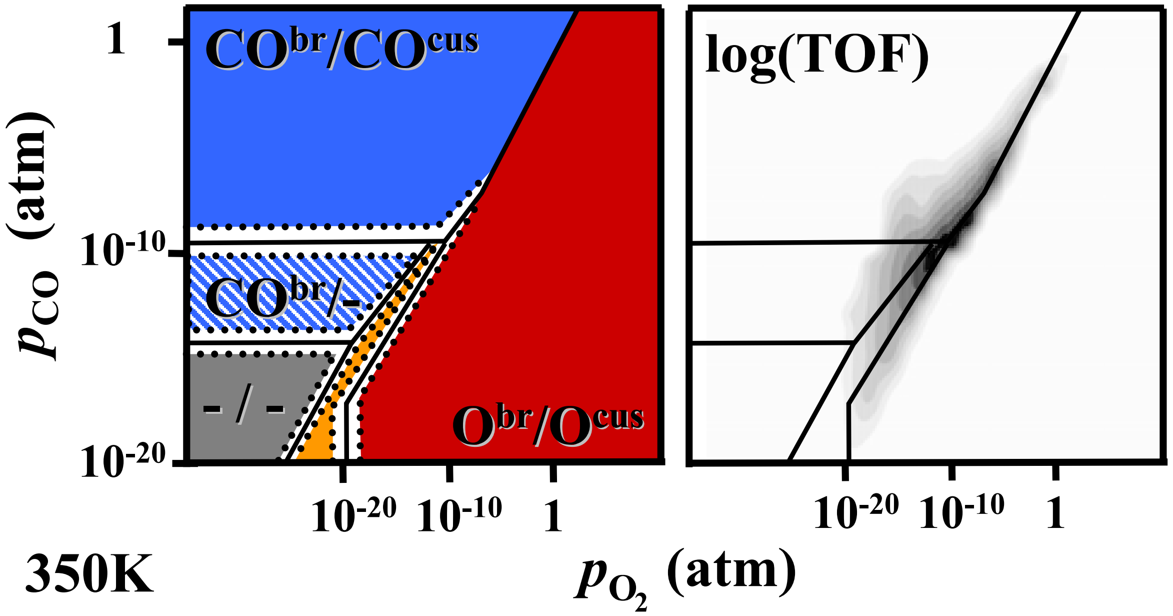
Advance time clock

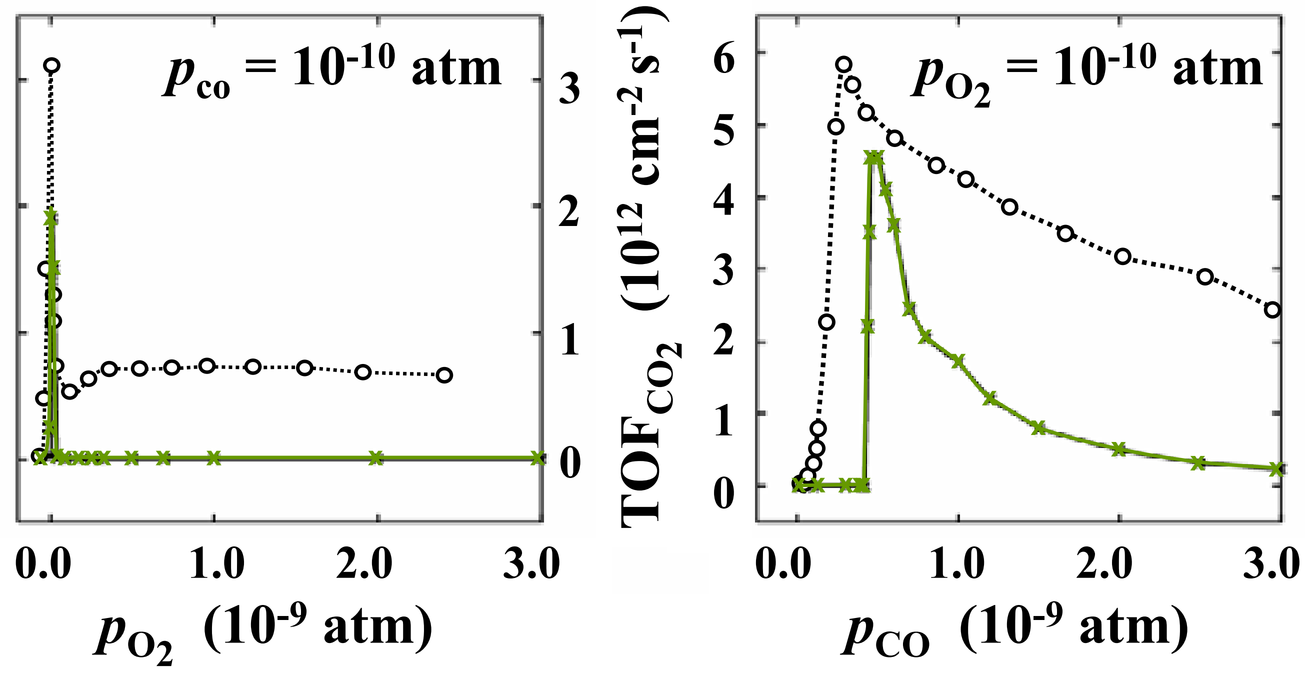
Update processes

finish

kMC can yield accurate results for model systems.

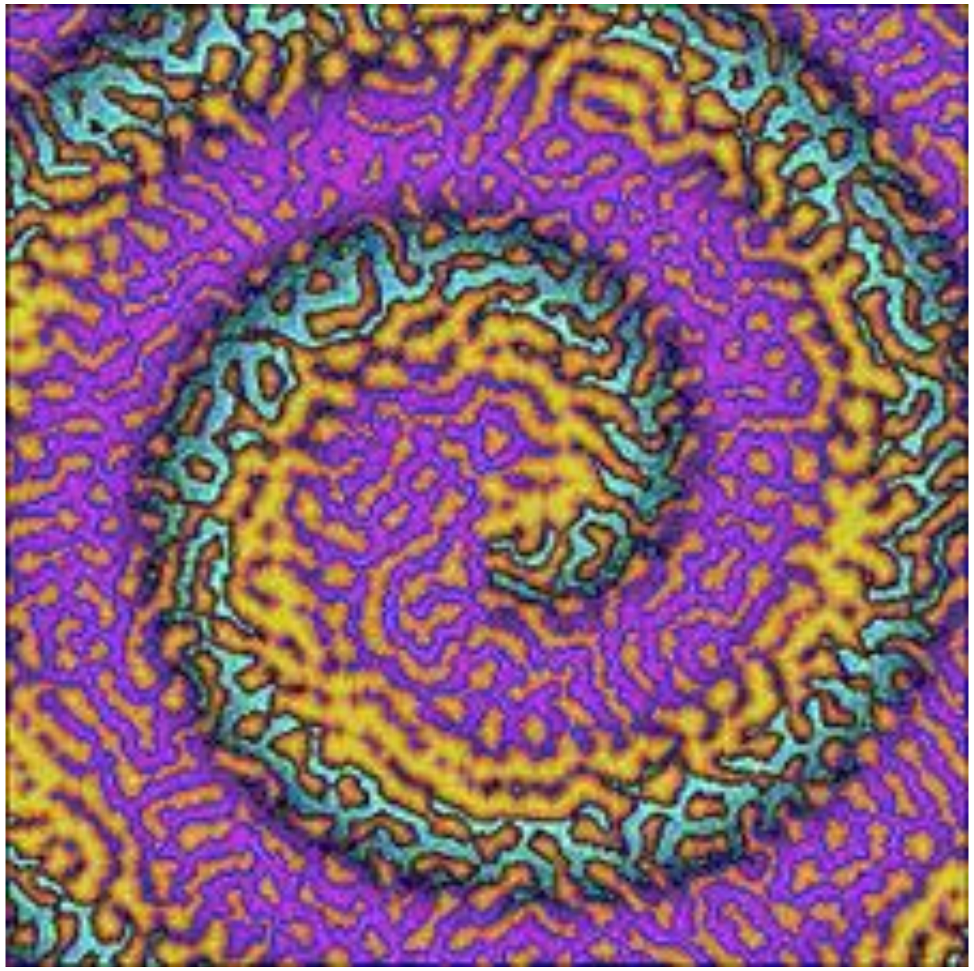






Reuter, K. *Wiley* (2009)

A key advantage of kMC is the spatial resolution and the ability to model adsorbate-adsorbate interactions.



$$\Delta H_i = \Delta H_{i,0} + \sum_{j=1}^{N_{species}} c_j \delta_{j,nn} + \sum_{j=1}^{N_{species}} \sum_{k=1}^{N_{species}} c_{j,k} \delta_{j,nn} \delta_{k,nn} + \ldots$$

$$E_a = E_{a,0} + \sum_{j=1}^{N_{species}} \varepsilon_j \delta_{j,nn} + \sum_{j=1}^{N_{species}} \sum_{k=1}^{N_{species}} \varepsilon_{j,k} \delta_{j,nn} \delta_{k,nn} + \ldots$$

Neighboring molecules can affect the stability of a species or transition state.

Jansen, APJ. *chembond.catalysis.nl/kMC*

Summary: Kinetic Monte Carlo

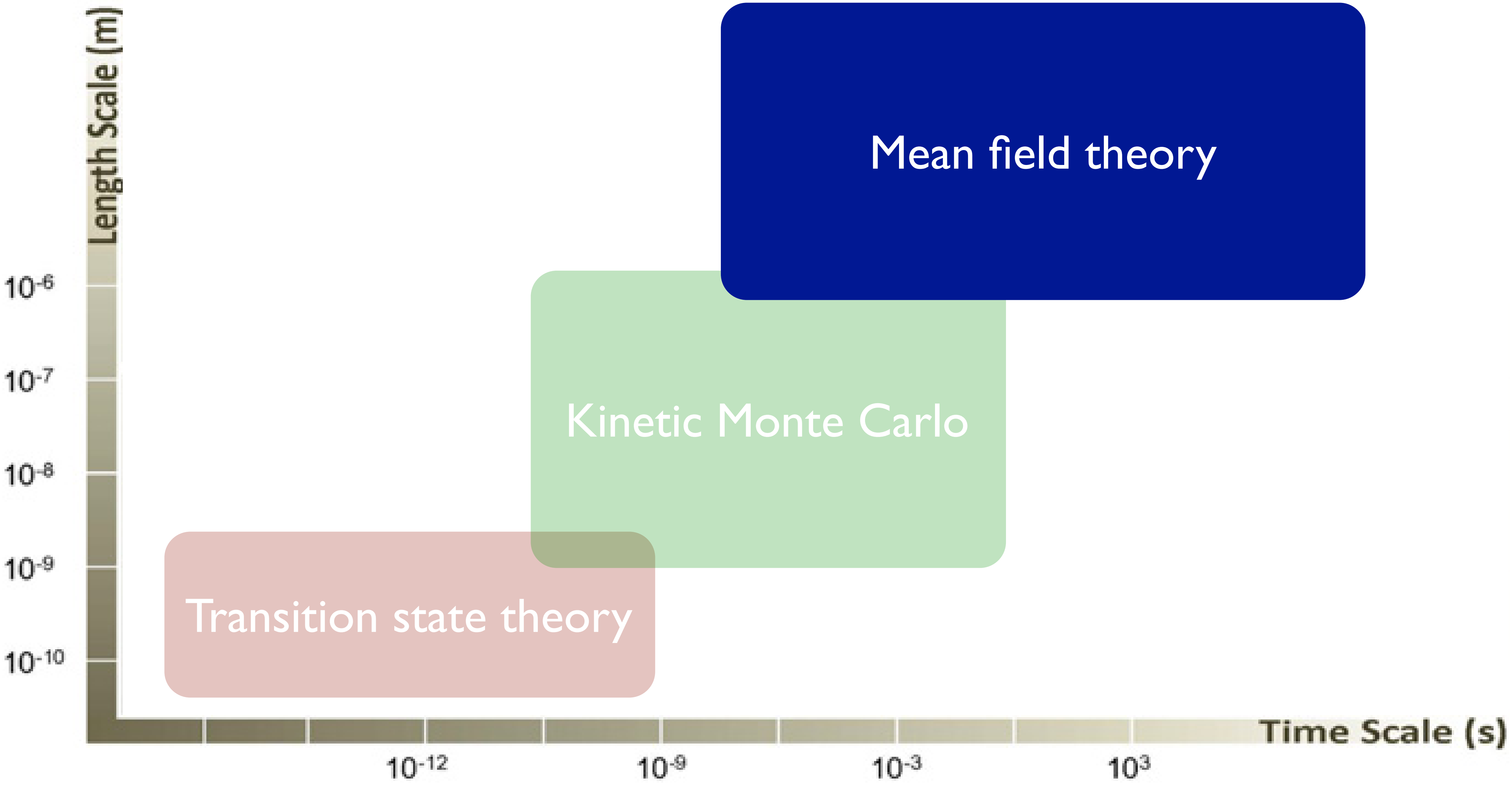
Pros:

- detailed chemistry over large time scale.
- accurate representation surface heterogeneity.

Cons:

- limited in length scale.
- difficult to couple with continuum (i.e. no transport limitations).
- “home cooked” code.

Part III: Mean field theory

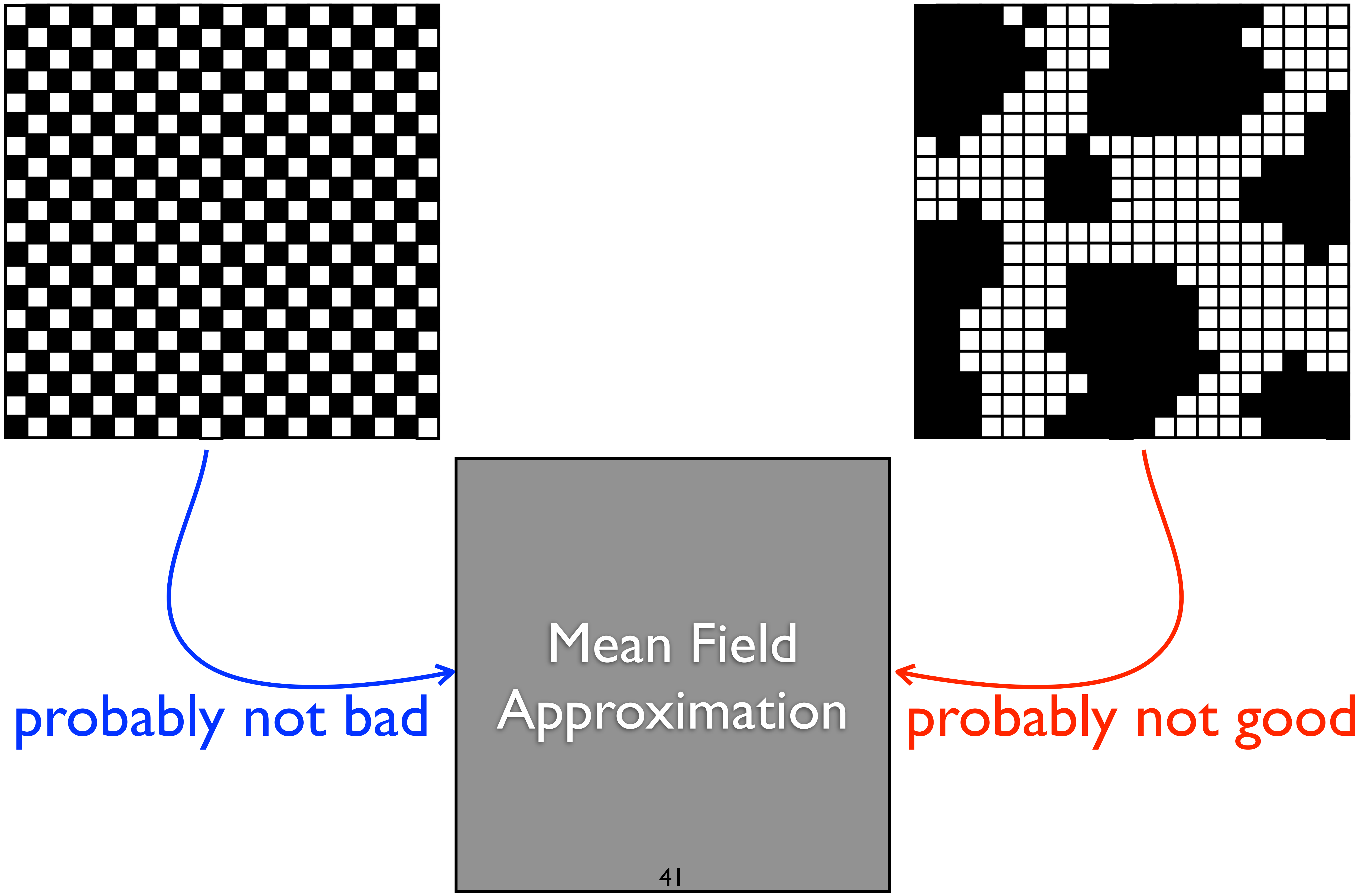


Part III: Mean Field Theory

MFT assumes a uniform distribution of adsorbates and catalyst sites.

- Can span a large range of length and time scales.
- Computationally efficient
- Only real option for process modeling.
- Lots of software available (CHEMKIN, CANTERA)

MFT is a poor approximation for heterogeneous processes.



probably not bad

Mean Field Approximation

probably not good

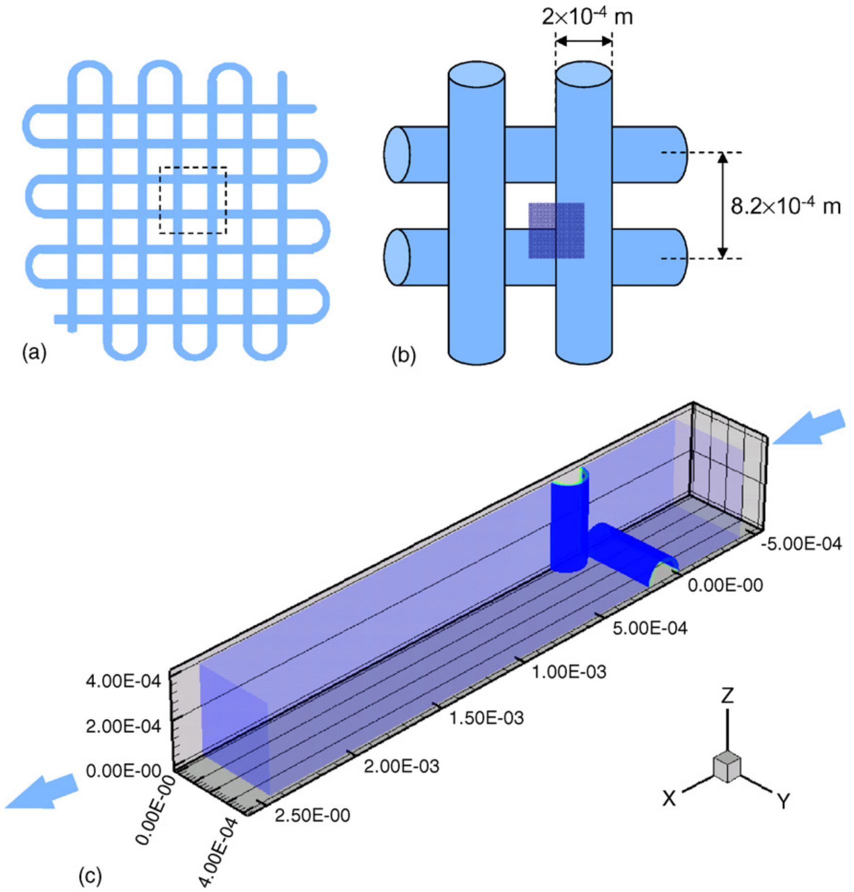
MFT generally is more accurate at higher temperatures.

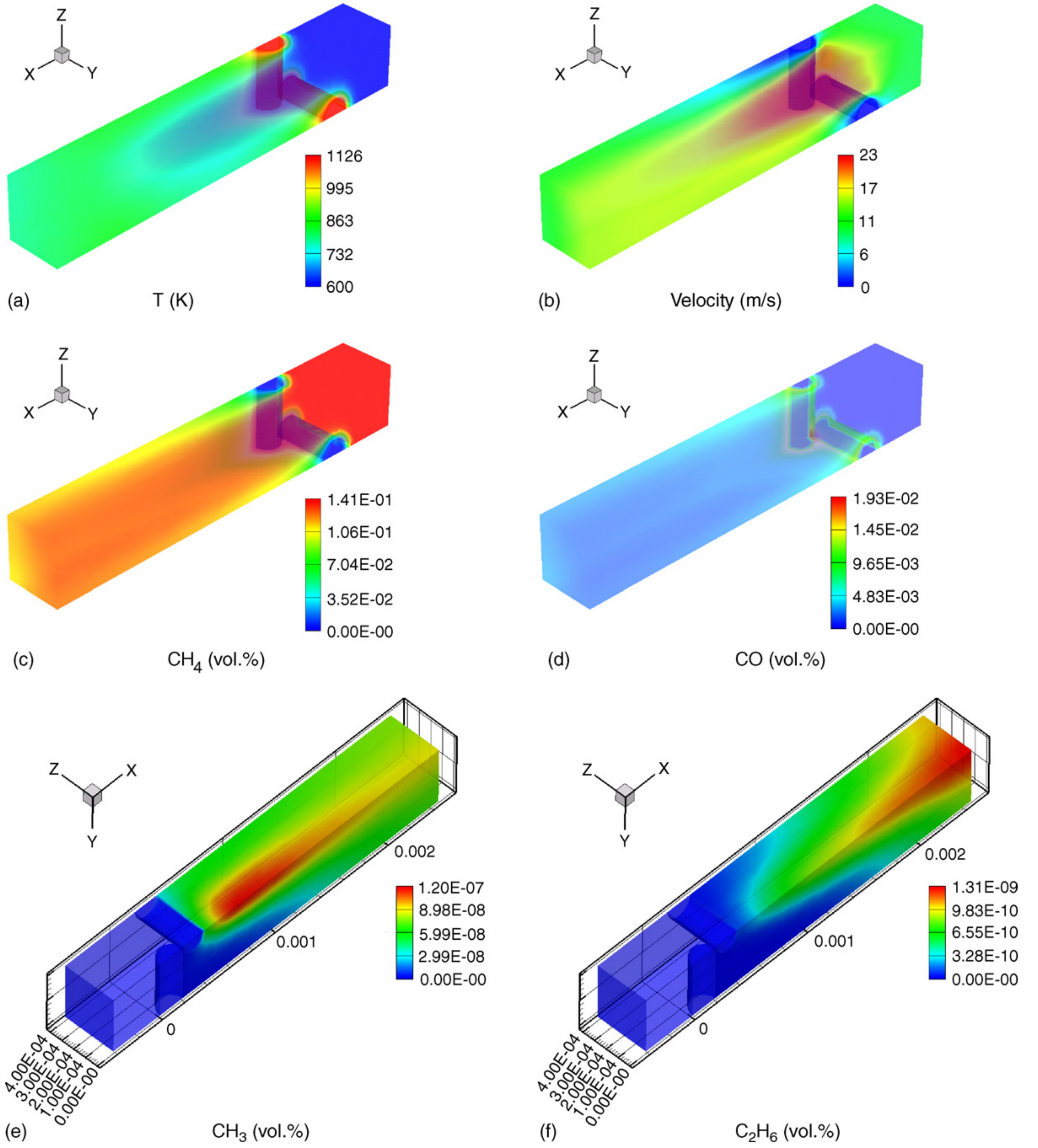
$$\Delta G = \Delta H - T\Delta S$$

Disordered surfaces are higher in entropy.

- desorption increases with temperature, yielding more empty sites.
- repulsive lateral interactions increase homogeneity.

One advantage of MFT is the ability to couple detailed chemistry with fluid mechanics.

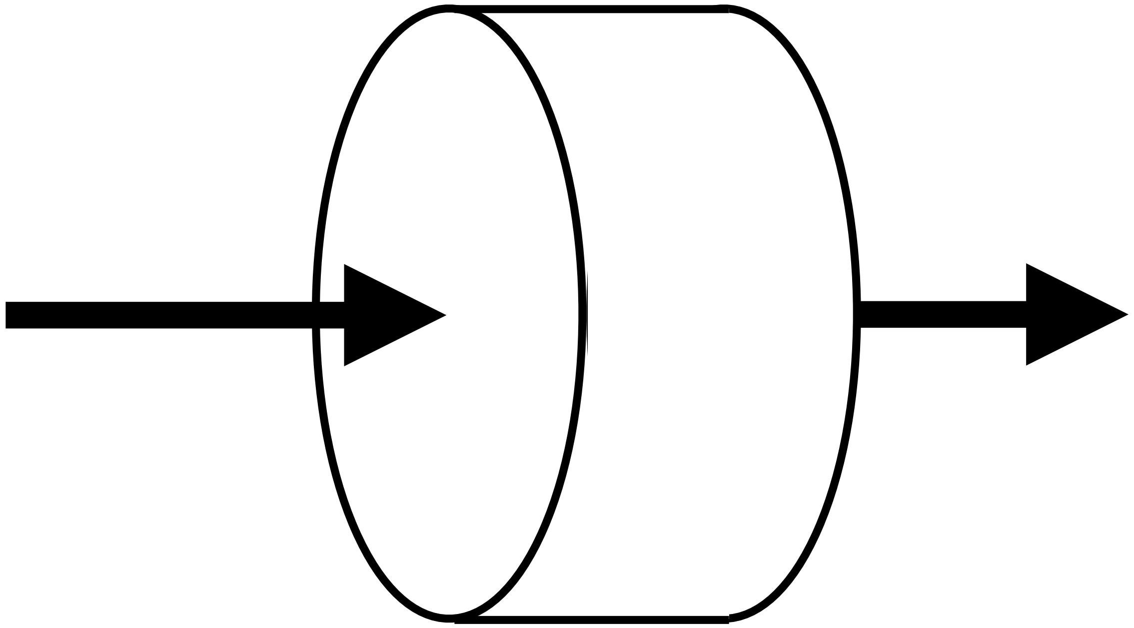




Quinceno et al. *Cat. Today, 119 (2007)*

Conservation of mass, energy, and momentum share a common formalism.

$$\begin{bmatrix}\text{Mass}\\ \text{Energy}\\ \text{Momentum}\end{bmatrix}_{in}$$



$$\begin{bmatrix}\text{Mass}\\ \text{Energy}\\ \text{Momentum}\end{bmatrix}_{out}$$

accumulation = bulk transport

+ molecular transport

+ chemical reaction

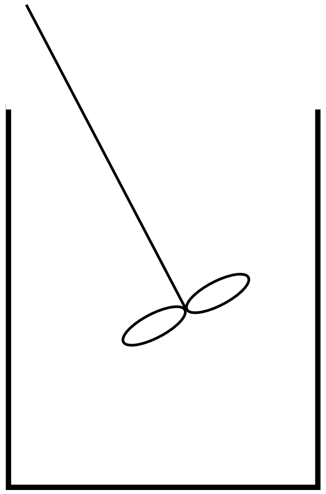
Quinceno et al. *Cat. Today, 119 (2007)*

Simple systems can be modeled with ideal reactors.

Batch reactor:

perfect mixing

concentration versus time

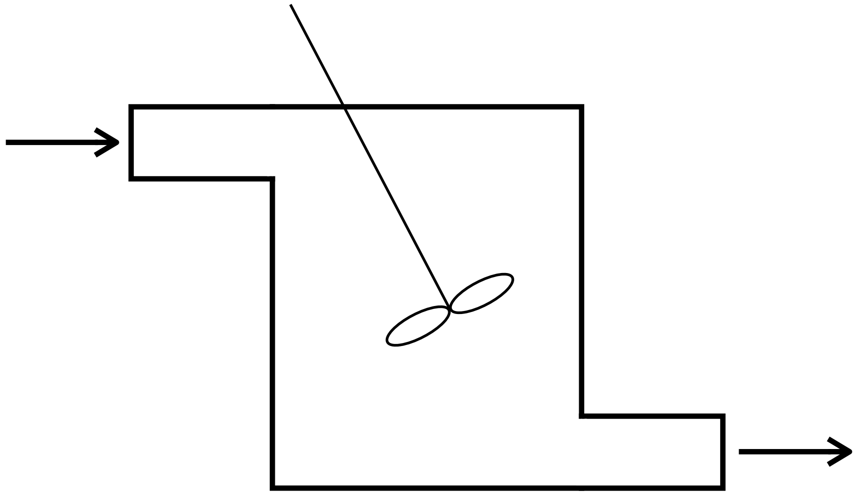


Perfectly stirred reactor:

perfect mixing

lower conversion per unit volume (generally)

concentration versus time

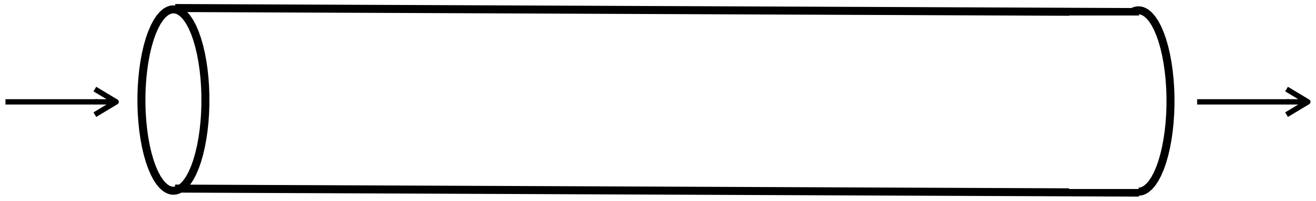


Plug flow reactor:

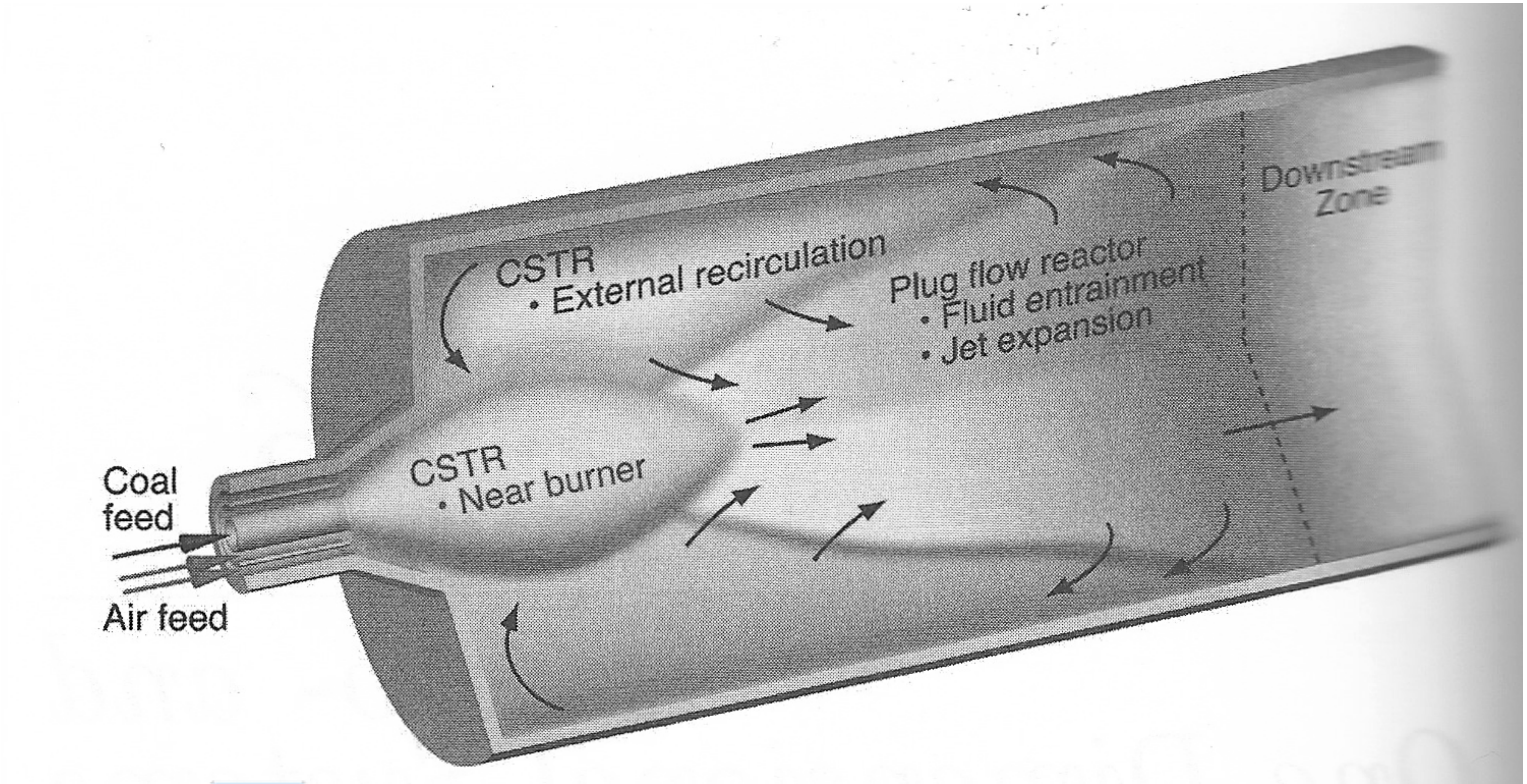
no radial gradients

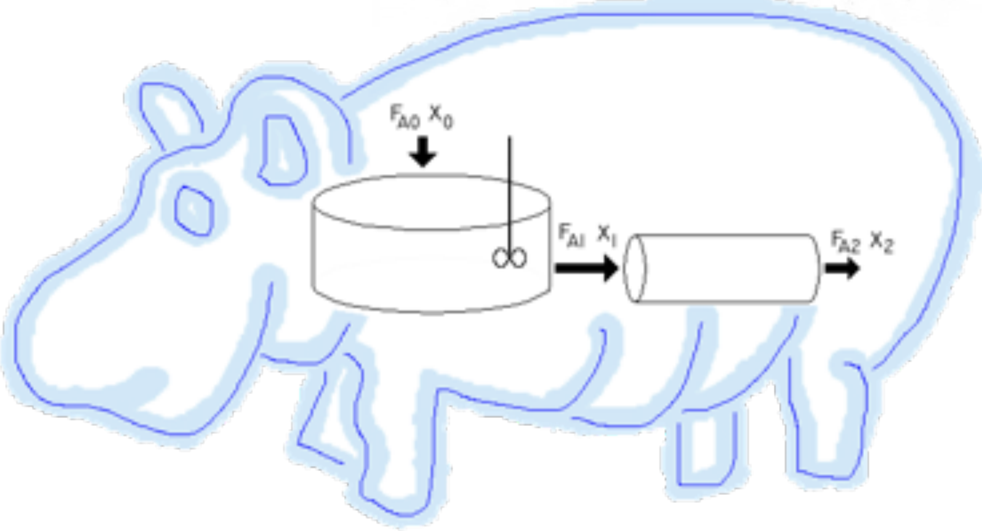
higher conversion per unit volume

concentration versus position

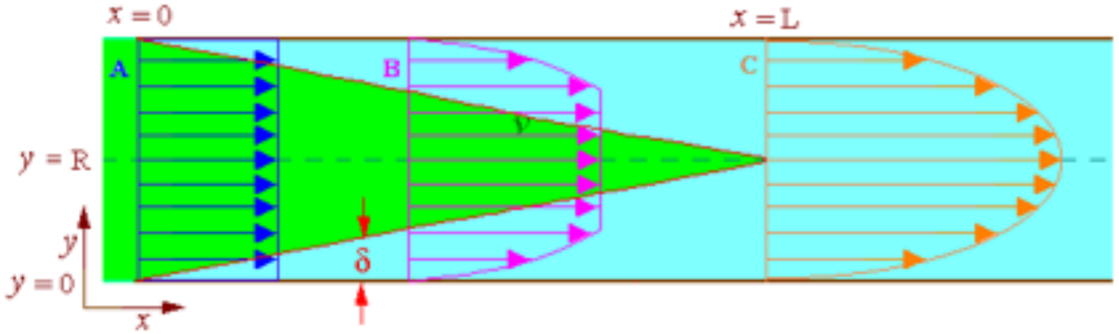


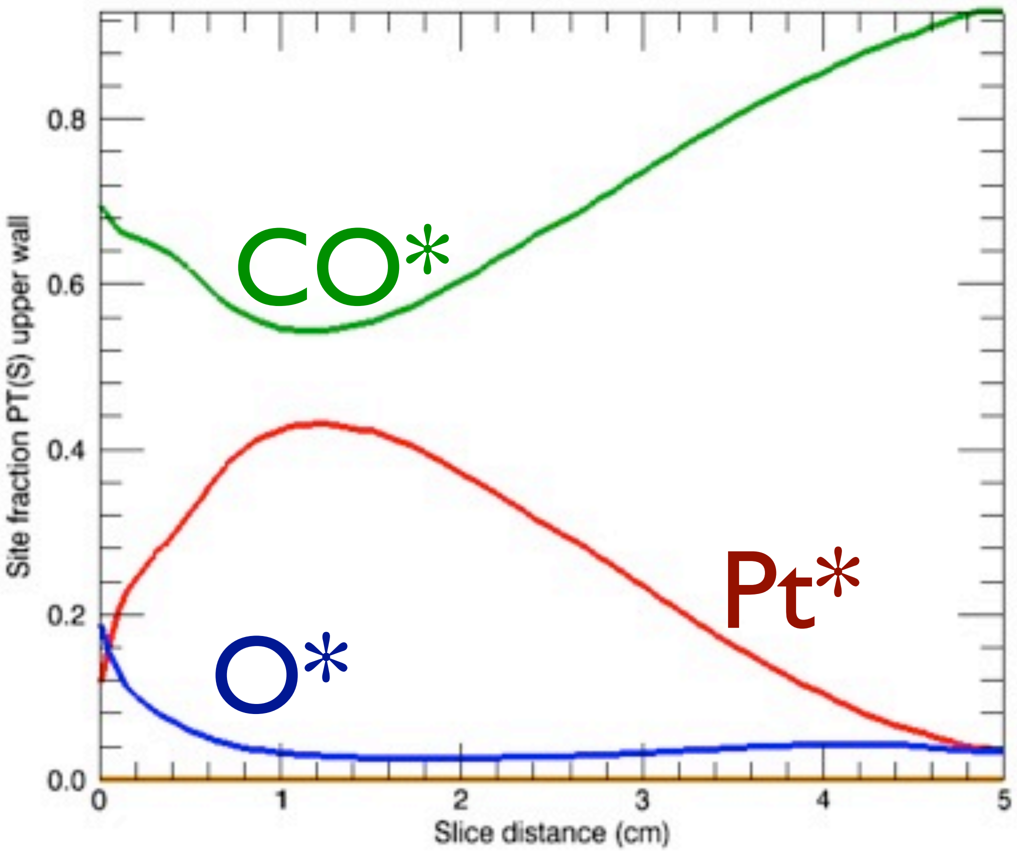
Networks of ideal reactors can model more complex phenomena.

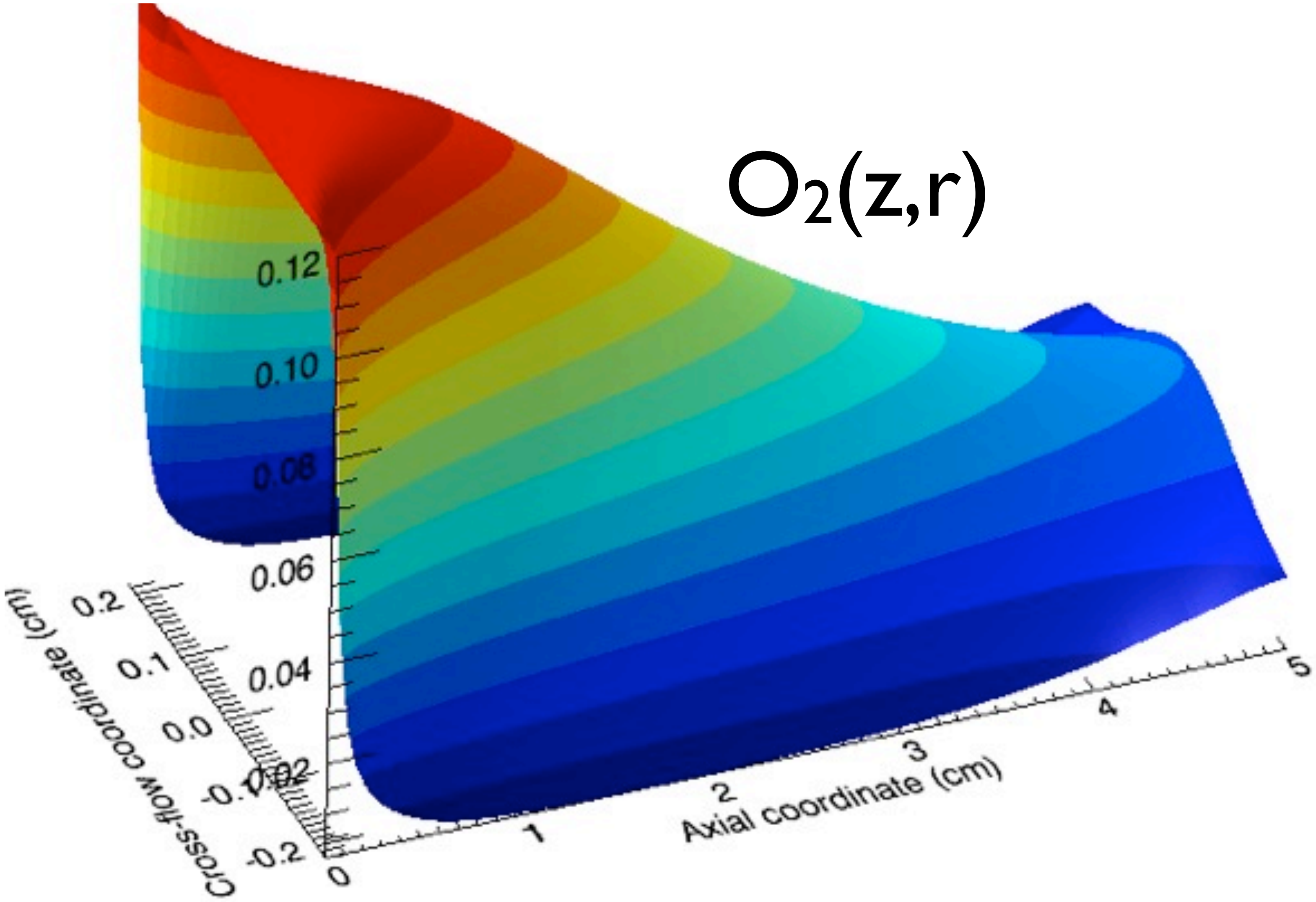




Two-dimensional reactor models include mass transport limitations.







More complex geometries or problems require computational fluid dynamics.

Most CFD codes are developed for fluid mechanics (chemistry is an afterthought).

- CFD code spends >95% computer time on chemistry, not transport
- Simplified, lumped models must be used
  - ➡*New computational paradigms are needed*

Summary:
Mean Field Theory

Pros:

- covers a broad range of time and length scales.
- Allows for easy modeling of transport limitations.
- easily coupled with reactor models and CFD.
- standard software available.

Cons:

- mean field is a poor approximation for inherently heterogeneous phenomena.

Part IV: Understanding the results

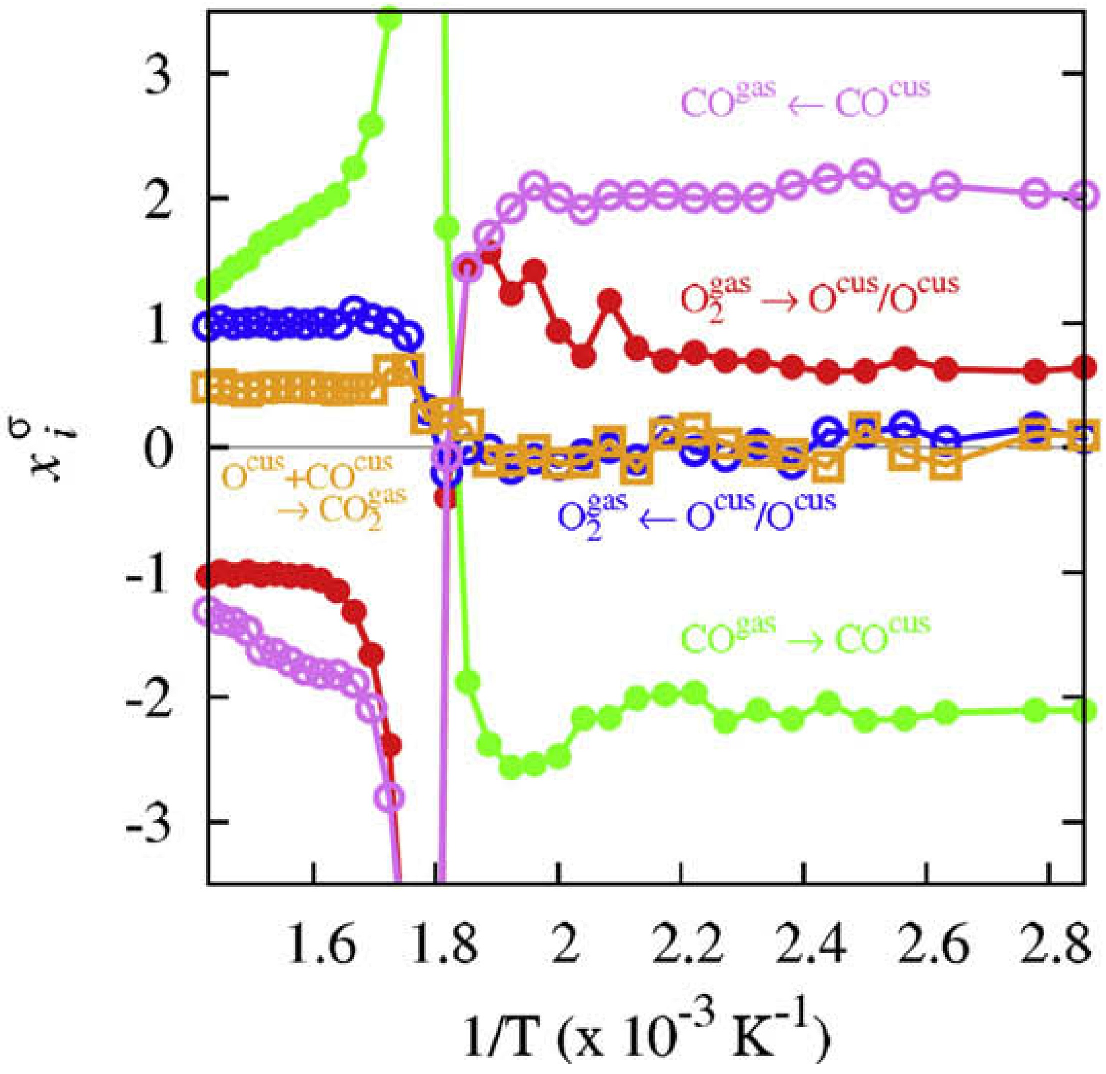
So you've successfully modeled a system with 100's of species and 1000's of reactions.

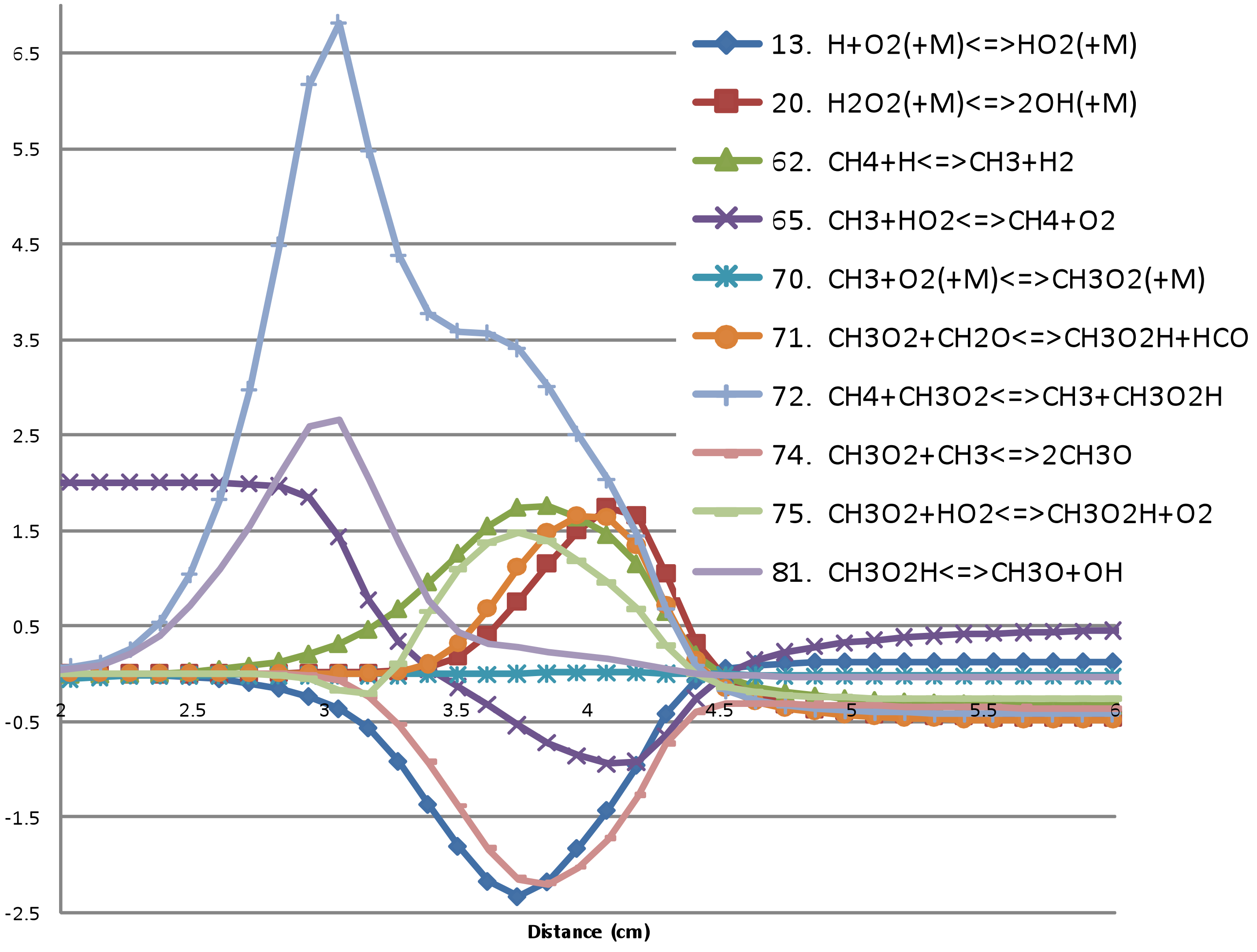
Now what?

Sensitivity analysis:
determine which rates are most important.

$$x_i = \frac{\partial \ln\left(\mathrm{TOF}_{\mathrm{CO}_2}\right)}{\partial \ln\left(k_i\right)}$$

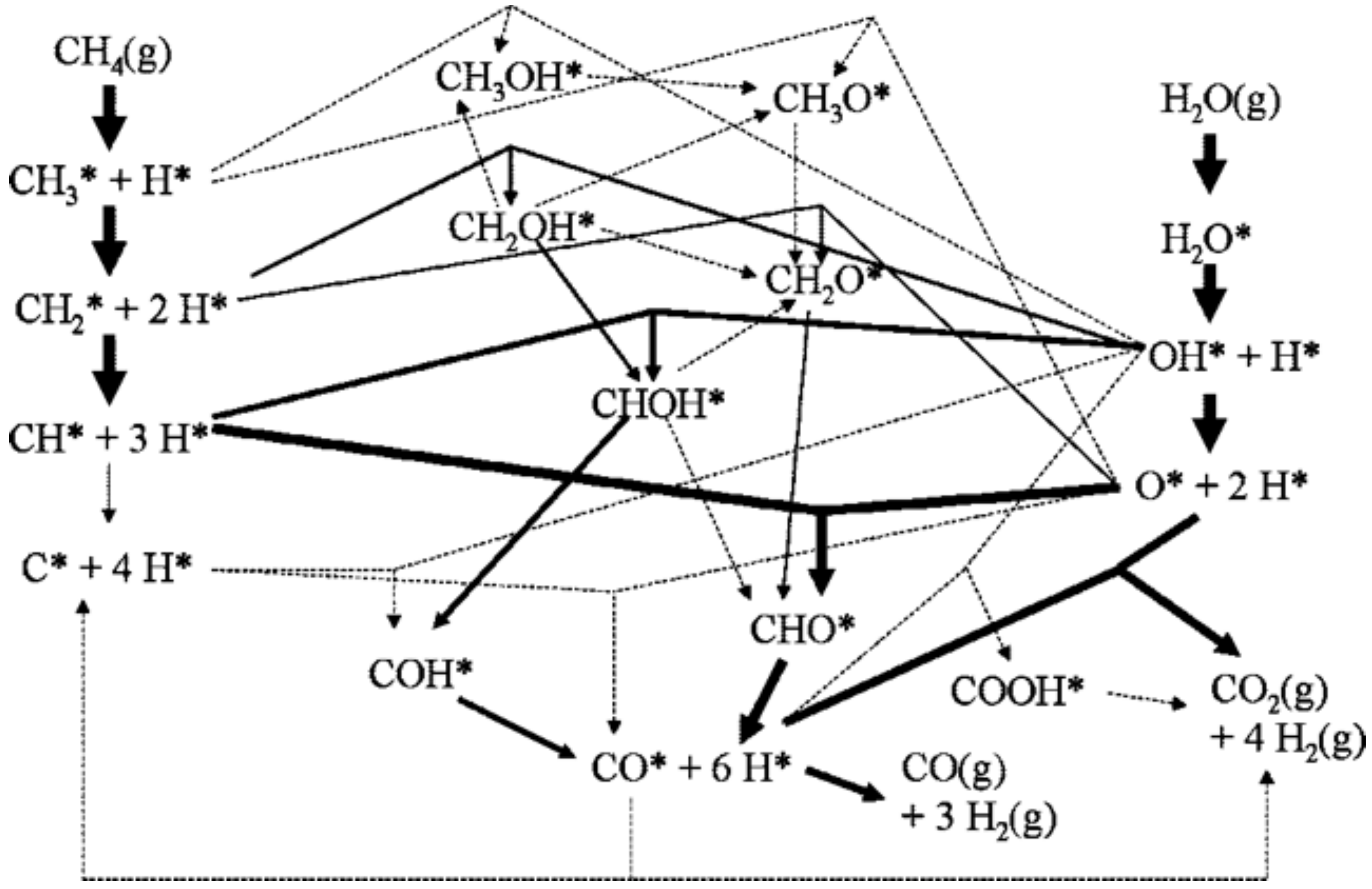
$$s_i = \frac{\partial \ln\left(\left[\mathrm{C_2H_4}\right]\right)}{\partial \ln\left(k_i\right)}$$





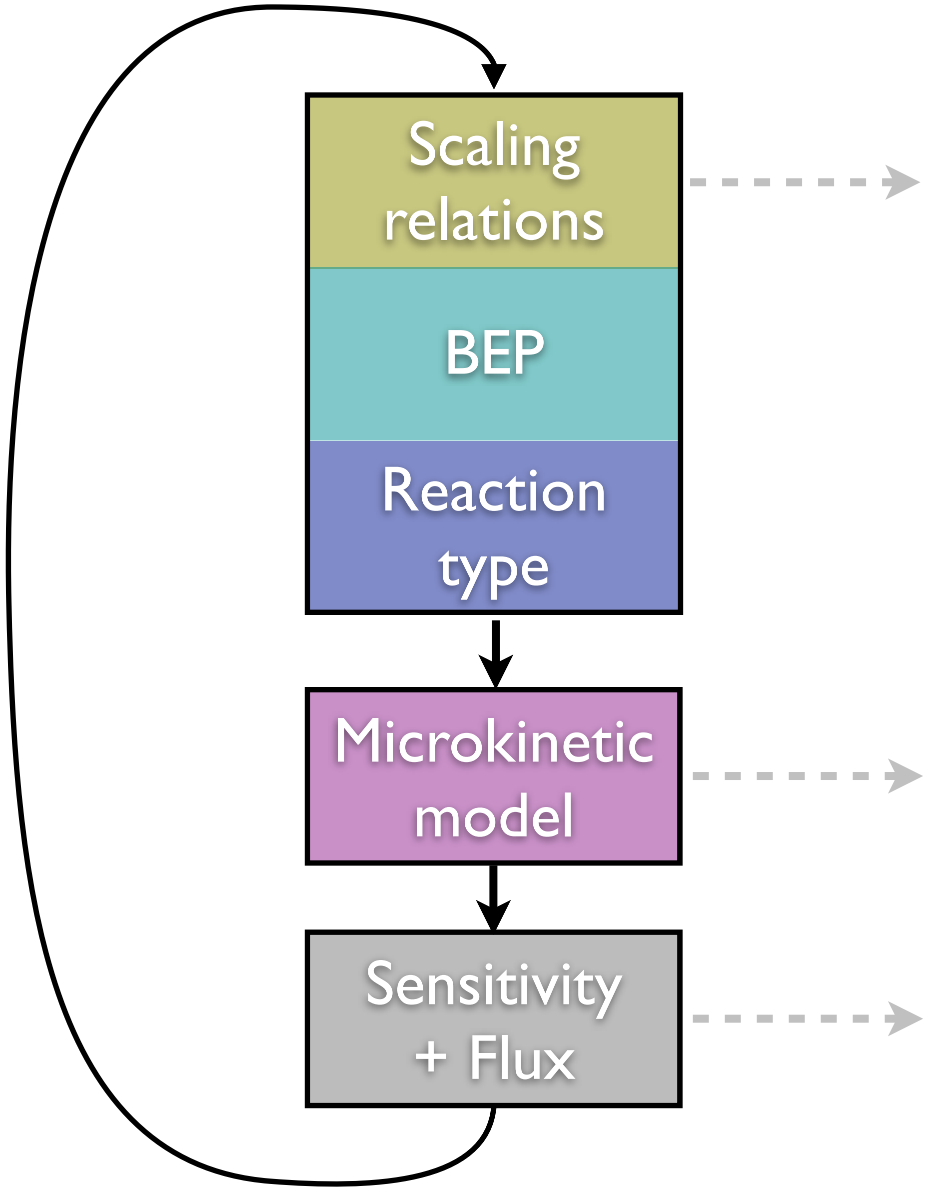
Flux path analysis:

determine which intermediates are most important.



Blaylock et al. *JPCC, 113 (2009)*

We can combine all these techniques to build accurate mechanisms with minimal computational effort.



Scaling relations

BEP

Reaction type

Microkinetic model

Sensitivity + Flux

adsorbate binding energies
activation energies
pre-exponential factors

Reactor simulations
(e.g. TOF, concentration profiles)

Determine the most important parameters and refine them.