"Insight Into Chemical Reactions at Interfaces Using Enhanced Sampling and Global Optimization Methods"

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Catalysis and reactions at surfaces

- sustainability challenge:
  fuels, chemicals, energy,
  (in general: modern economy and
  quality of life)
  depend on supply of fossil resources

- alternative:
  convert readily available starting
  molecules such as water, CO_2, N_2 into
  valuable products

- these reactions rely on catalysts
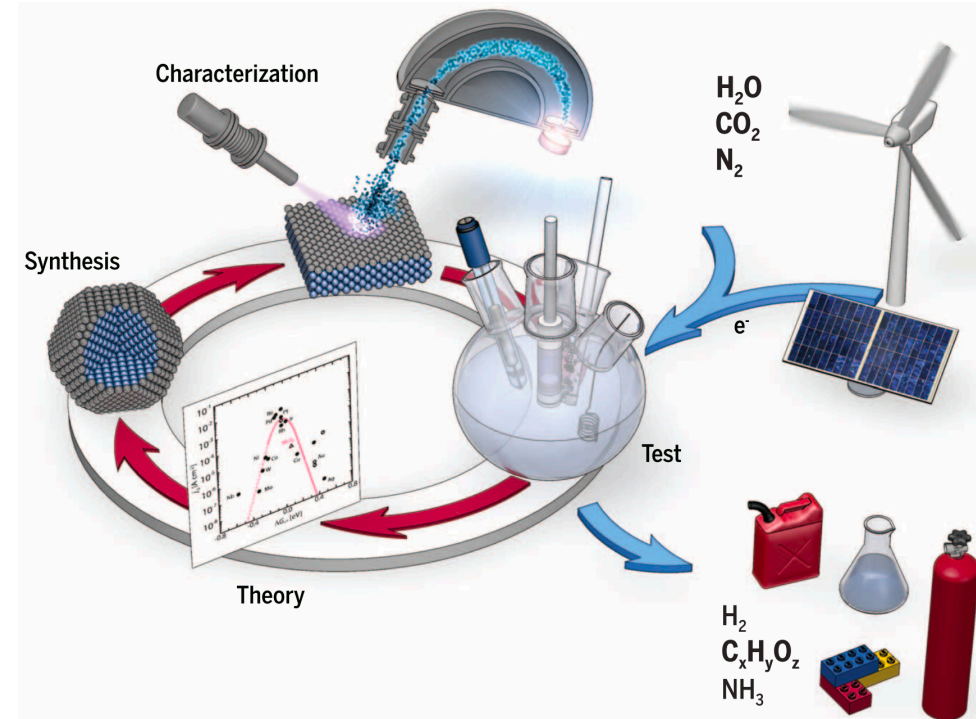 (often heterogeneous catalysts)

Image: Seh, Kibsgaard, Dickens, Chorkendorff, Nørskov.
Science 2017 355 (6321)

The value of theory/computation in catalysis

- Trial-and-error methods are costly:

It is due to this situation that the author and his associates had to carry out about 20,000 small scale tests and to investigate some 3000 different preparations as potential catalysts for the ammonia synthesis.
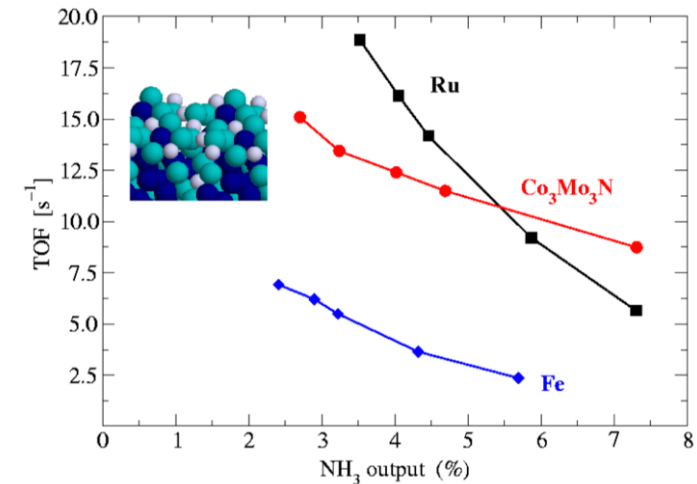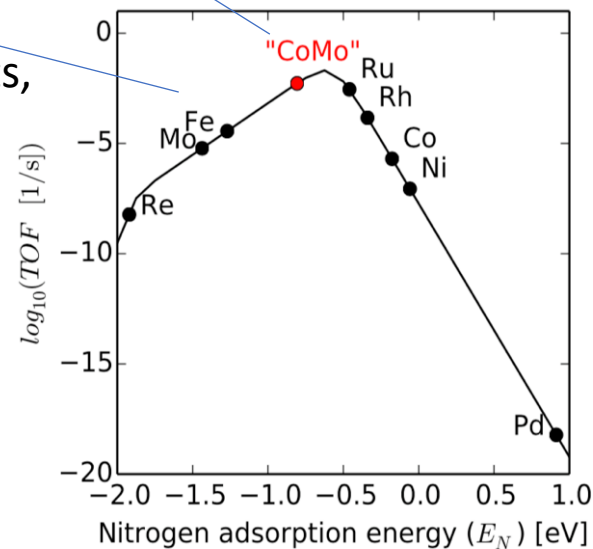
From: Mittasch, Frankenburg, Advances in Catalysis, Volume 2, 1950, Pages 81-104

- Thus theoretical insight can be useful

Density Functional Theory (DFT), reaction rate theories, microkinetic modeling, scaling

2001: discovery aided by theory/computation

trial and error:
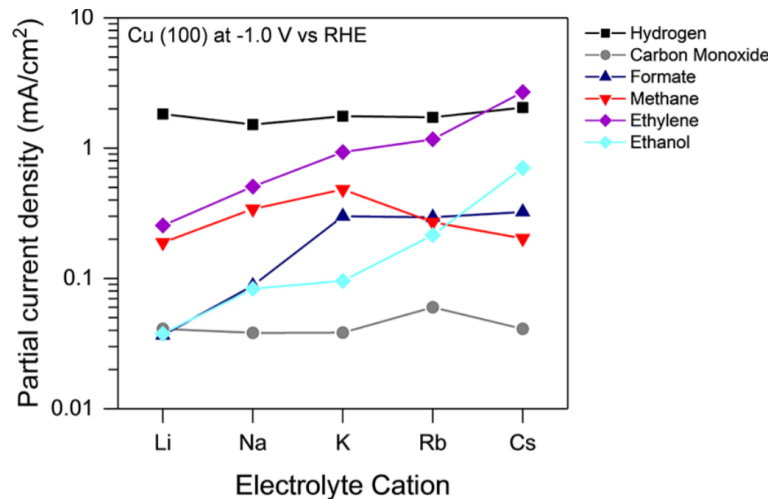~thousands of experiments,
~thousands of catalysts

Jacobsen, Dahl, Clausen, Bahn, Logadottir, Nørskov, *JACS* **123,** 8404 (2001)

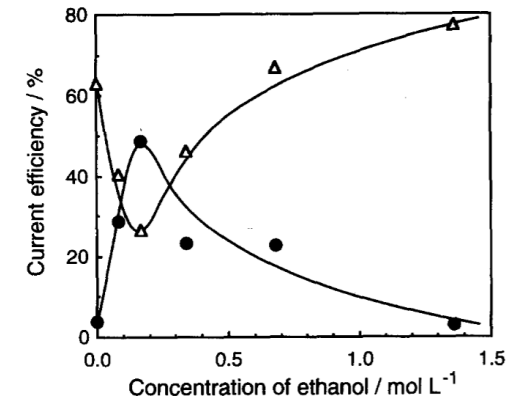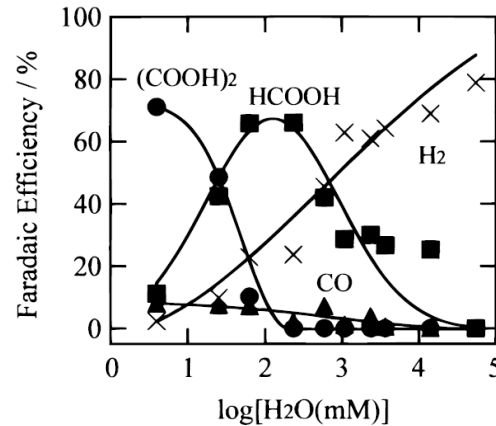# Current challenges in modeling reactions at surfaces

- models of chemical reactions are becoming increasingly complex
  - Electrolyte interfaces (structural complexity) – how to optimize electrolyte

A few (not exhaustive!) examples:

ion effects

solvent effects

Resasco, Chen, Clark, Tsai, Hahn, Jaramillo, Chan, Bell.
J. Am. Chem. Soc., 2017, 139 (32), pp 11277–11287

Tomita, Teruya, Koga, Hori.
J. Electrochem. Soc. 2000 147, 11, 4164-4167

Akira Tsuneto, Akihiko Kudo, Tadayoshi Sakata,
J Electroanalytical Chem,
367,1–2,1994,183-188,

Current challenges in modeling reactions at surfaces

Standard practices in computational modeling (usually with DFT)
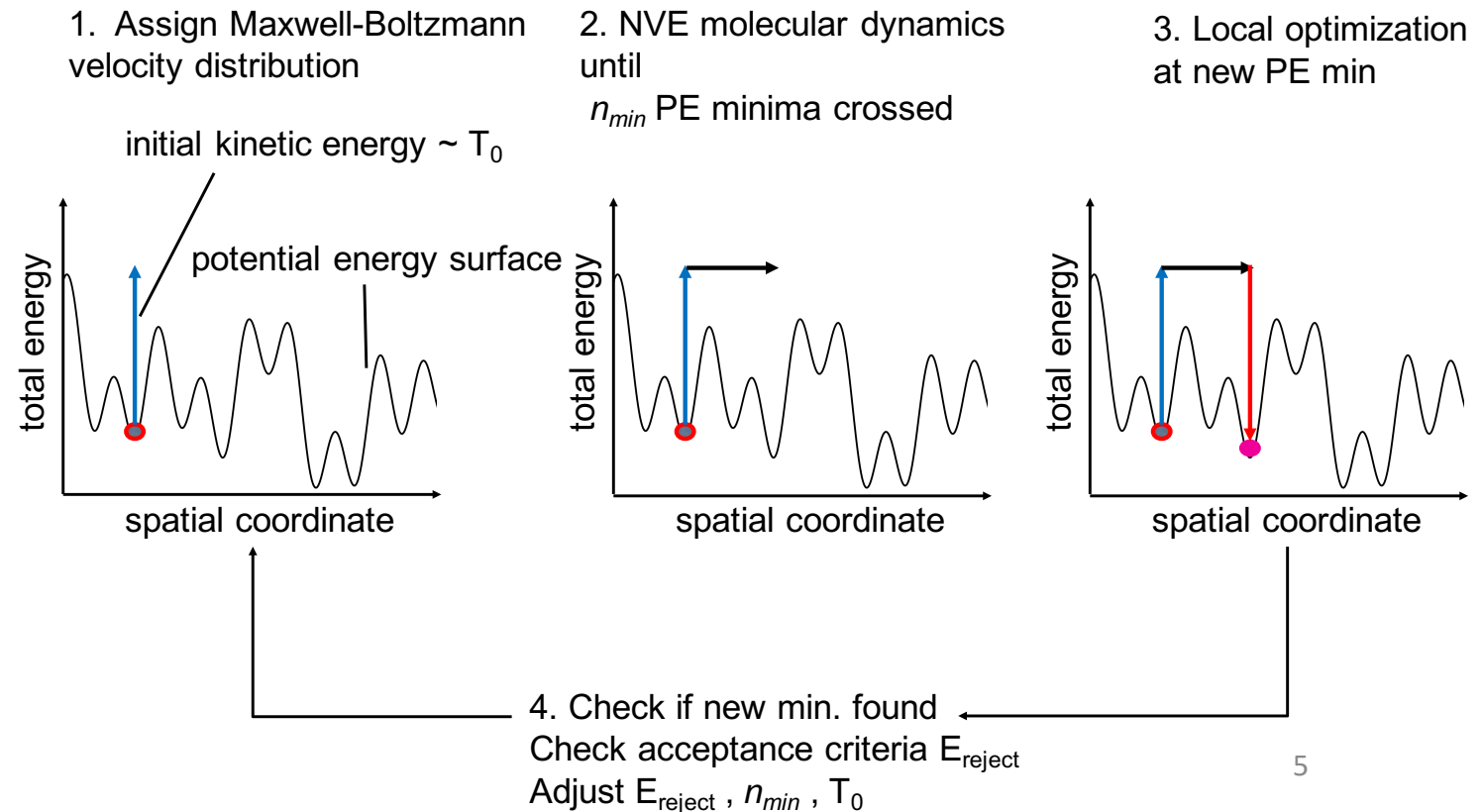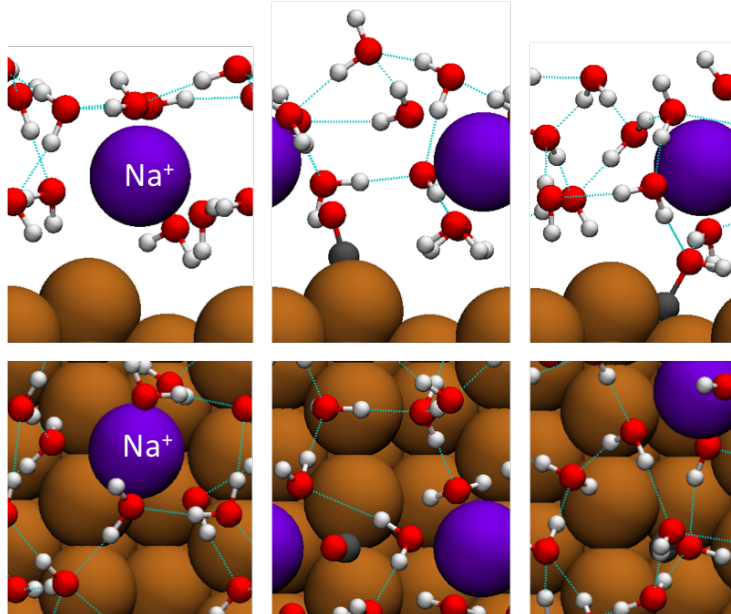
- Standard free energy approximations (harmonic oscillator, etc) may not work well for complex degrees of freedom (solvents, etc) – need more generalizable methods

- setting up atomic structures "by hand" for each system and "hoping" they are the right structures (intuition) – not generalizable/systematic, not able to be scaled up very easily also there is the ideal of "reproducibility"
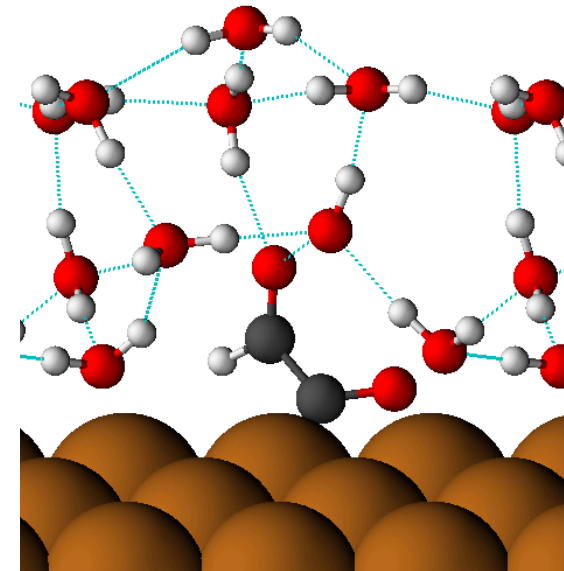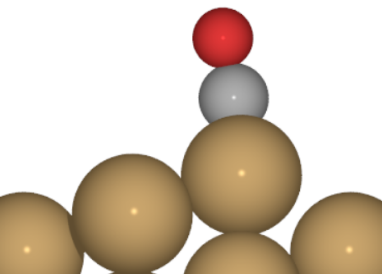
Global optimization: minima hopping algorithm

- problem: how to generalize finding relevant structures (for DFT calculations)
- The most physically relevant structures have low energies

→ Global optimization

1. Assign Maxwell-Boltzmann velocity distribution

initial kinetic energy ~ T_0

potential energy surface

total energy / spatial coordinate

2. NVE molecular dynamics until n_{min} PE minima crossed

total energy / spatial coordinate

3. Local optimization at new PE min

total energy / spatial coordinate

4. Check if new min. found
Check acceptance criteria E_{reject}
Adjust E_{reject}, n_{min}, T_0

Insights from global optimization results

- Solvation effects, error estimates
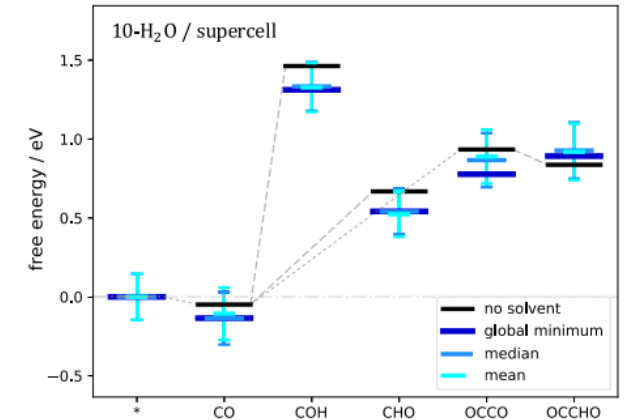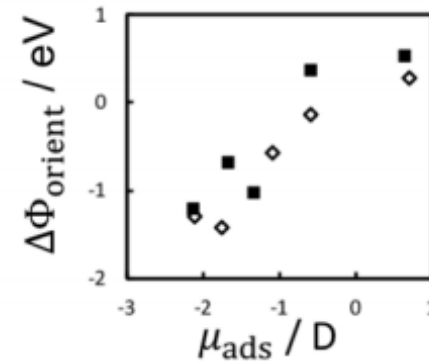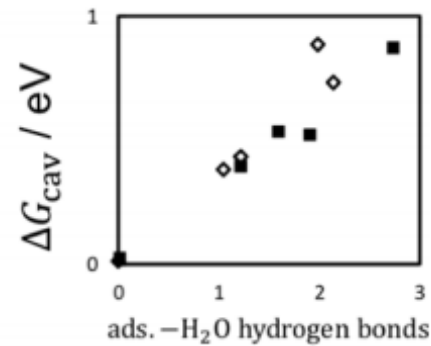
- Ion effects:
  - Electrostatic model
  - Coverage dependence

Ludwig et al, J. Phys. Chem. C 2019, 123, 5999−6009 6

Free energy: what is it?

- Describes the equilibrium / probability distributions

consider a system of interacting atoms. At any instant t_i , it is described by a "microstate" x_i (e.g. the positions & velocities)
the set of all possible microstates is the "phase space" Ω

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Example: chemical reaction $N_2 \rightarrow 2N$

$$N_2 \stackrel{\text{def}}{=} \{x_i \in \Omega|\ d_{NN} < r_1\}$$

$$2N \stackrel{\text{def}}{=} \{x_i \in \Omega|\ d_{NN} > r_2\}$$

"states" like N_2 or $2N$ are basically subsets of Ω the probabilities of those subsets are given by:

$$P(N_2) = e^{-F_{N_2}/k_B T}$$

$$P(2N) = e^{-F_{2N}/k_B T}$$

→ Free energy describes the probabilities of physically meaningful states

Free energy: what is it?

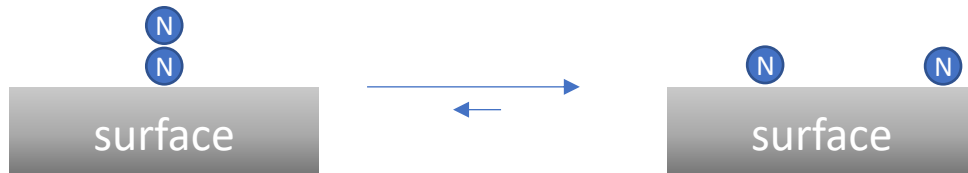- Describes the equilibrium / probability distributions

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reaction equilibrium: $\dfrac{P(2N)}{P(N_2)} = \dfrac{e^{-F_{2N}/k_BT}}{e^{-F_{N_2}/k_BT}} = e^{-\Delta F_{rxn}/k_BT}$

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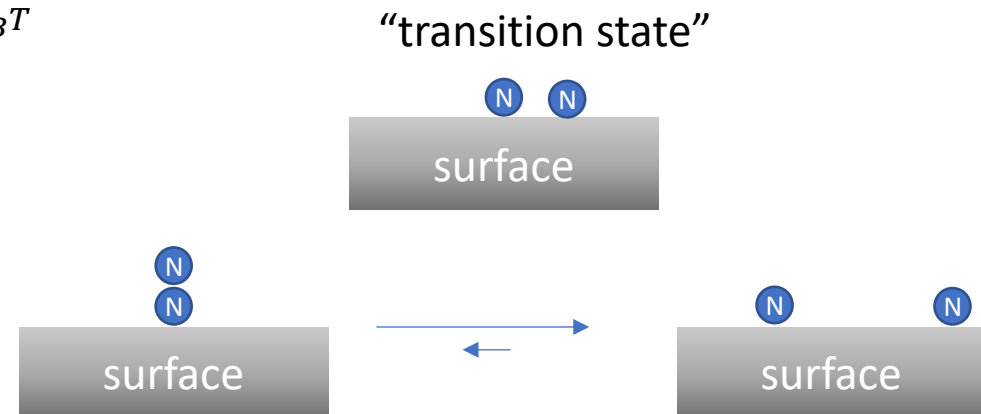
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"transition state"

rate theory: $TS \stackrel{\text{def}}{=} \{x_i \in \Omega| \; d_{NN} \approx d_{TS}\}$
under certain assumptions,

$$R_{N_2 \rightarrow 2N} \sim e^{-\Delta F_a/k_B T}$$

Free energy

Absolute free energies

$$A = -\beta^{-1} \ln Q(N, V, T).$$ (free energy)

$$Q(N, V, T) = \int \exp(-\beta\mathscr{E}) \, \Omega_{\text{tot}}(N, V, \mathscr{E}) \, d\mathscr{E}$$

~ total probability

probability of a single microstate/ configuration.
~one evaluation DFT (potential energy)

number/density of microstates

this integral is, in general, not really practically computable

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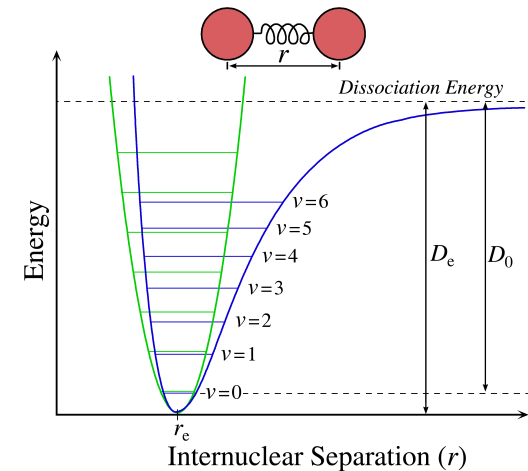
Harmonic approximation:
   if the forces are always linear in the displacements for all relevant degrees of freedom

$$\vec{F} = -k\vec{x}$$

then the motion can be decomposed into "normal modes"

Dissociation Energy

Energy

$v=6$
$v=5$
$v=4$
$v=3$
$v=2$
$v=1$
$v=0$

D_e D_0

r_e

Internuclear Separation (r)

there are analytical solutions for the free energies of local potential energy minima

$$S_{vib} = k_B \sum_i \left[\frac{\epsilon_i}{k_B T \left(e^{\frac{\epsilon_i}{k_B T}} \right) - 1} - \ln\left(1 - e^{-\frac{\epsilon_i}{k_B T}} \right) \right]$$

– this is the standard approximation for DFT surface calculations
– anharmonic corrections can be applied, but rely on intuition

$$\int_0^T C_{V,vib} \, dT = \sum_i^{DOF} \frac{\epsilon_i}{e^{\frac{\epsilon_i}{k_B T}} - 1}$$

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Free energy

Absolute free energies

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probability of a single microstate/ configuration.

number/density of microstates

this is, usually, not really practically computable

General methods (no harmonic approximation):
relative free energies from atomic simulations

$$\Delta A = -\beta^{-1} \ln \frac{P_1}{P_0}$$ "probability distribution"

$$\frac{\mathrm{d}A}{\mathrm{d}\lambda} = \frac{\int \frac{\partial \mathscr{H}}{\partial \lambda} \exp\left(-\beta\mathscr{H}\right) \, \mathrm{d}\mathbf{x} \, \mathrm{d}\mathbf{p}_x}{\int \exp\left(-\beta\mathscr{H}\right) \, \mathrm{d}\mathbf{x} \, \mathrm{d}\mathbf{p}_x} = \left\langle \frac{\partial \mathscr{H}}{\partial \lambda} \right\rangle_\lambda$$

"thermodynamic integration"

other methods also exist
but this talk is based on the above

Enhanced sampling

- often simulations are "stuck" in free energy basins
    - High energy barriers relative to kT or bottlenecks: "rare event"
    - results of a simulation depend on the initial conditions, or converge extremely slowly

probability distribution
along any collective variable(ξ) :

$$P(\xi) \sim e^{-F_\xi/kT}$$

physical distribution

$$P_{biased}(\xi) \sim e^{-(F_\xi + F_{bias})/kT}$$

biased distribution

Enhanced sampling

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$$P_{biased}(\xi) \sim e^{-(F_\xi + F_{bias})/kT}$$
   biased distribution $\longleftarrow$ $F_{bias} = f(F_\xi)$ seems optimal,
but of course we don't know F_ξ - that is what we are trying to calculate

Adaptive enhanced sampling

- Adaptive biasing methods: update bias as they proceed, such that the bias converges toward an optimal bias / does not need to be known beforehand

$$P(\xi) \sim e^{-F_\xi/kT} \longrightarrow P_{biased}(\xi) \sim e^{-(F_\xi+F_{bias})/kT}$$
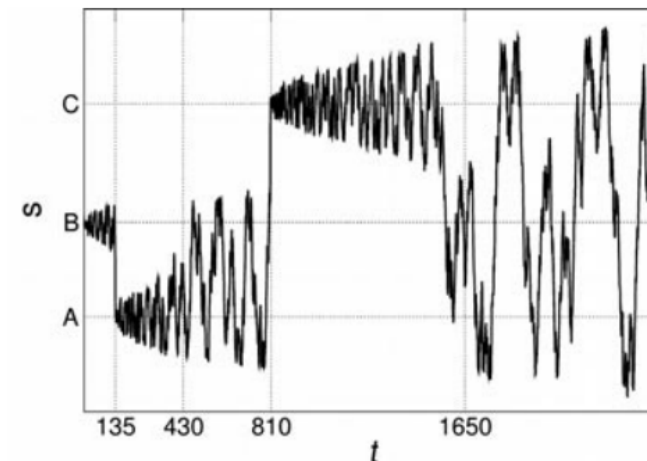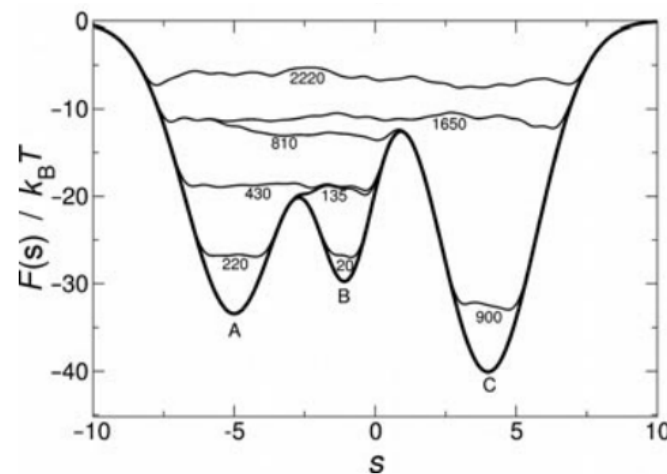
physical distribution   biased distribution

Here is an example:

starting in well A, a simulation
would ordinarily be stuck

metadynamics is used
to adaptively bias the simulation
so that all wells are sampled

(frequency-based method)

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State-of-the-art adaptive enhanced sampling

- Adaptive Biasing Force: ABF

$$\langle F_\xi | \xi^* \rangle = -\frac{dA(\xi^*)}{d\xi}$$ $\longrightarrow$ apply external biasing force $-\langle F_\xi | \xi^* \rangle \nabla \xi$ $\longrightarrow$ uniform sampling along ξ

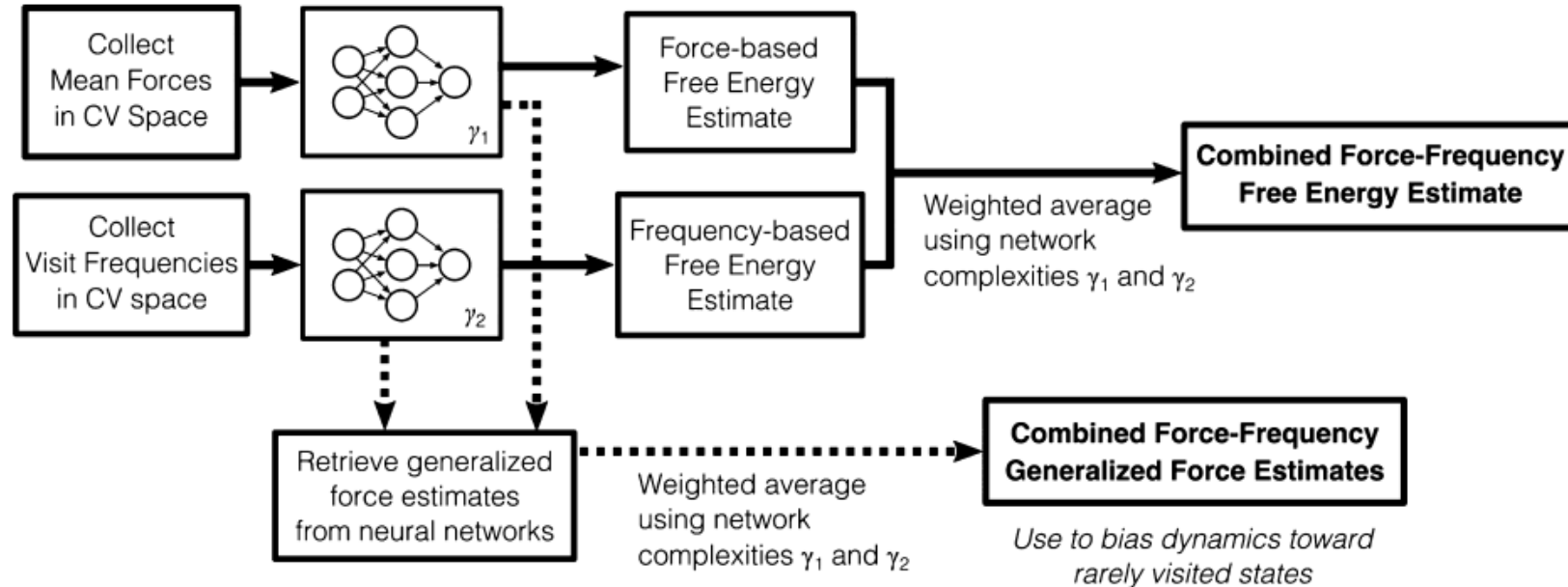# State-of-the-art adaptive enhanced sampling

- ## Adaptive Biasing Force: ABF

$$\langle F_\xi | \xi^* \rangle = -\frac{dA(\xi^*)}{d\xi}$$ apply external biasing force $-\langle F_\xi | \xi^* \rangle \nabla \xi$ uniform sampling along ξ

- ## Combined Force-Frequency: CFF

E. Sevgen, A.Z. Guo, H. Sidky, J.K. Whitmer, J. J. de Pablo JCTC 16, 1448 (2020)

Applying enhanced sampling / free energy methods to a surface reaction

- N_2/Ru(0001) – a "prototypical" highly-activated surface reaction
  - Collective variables:
    - r (N-N distance)
    - h (surface-center of mass distance)
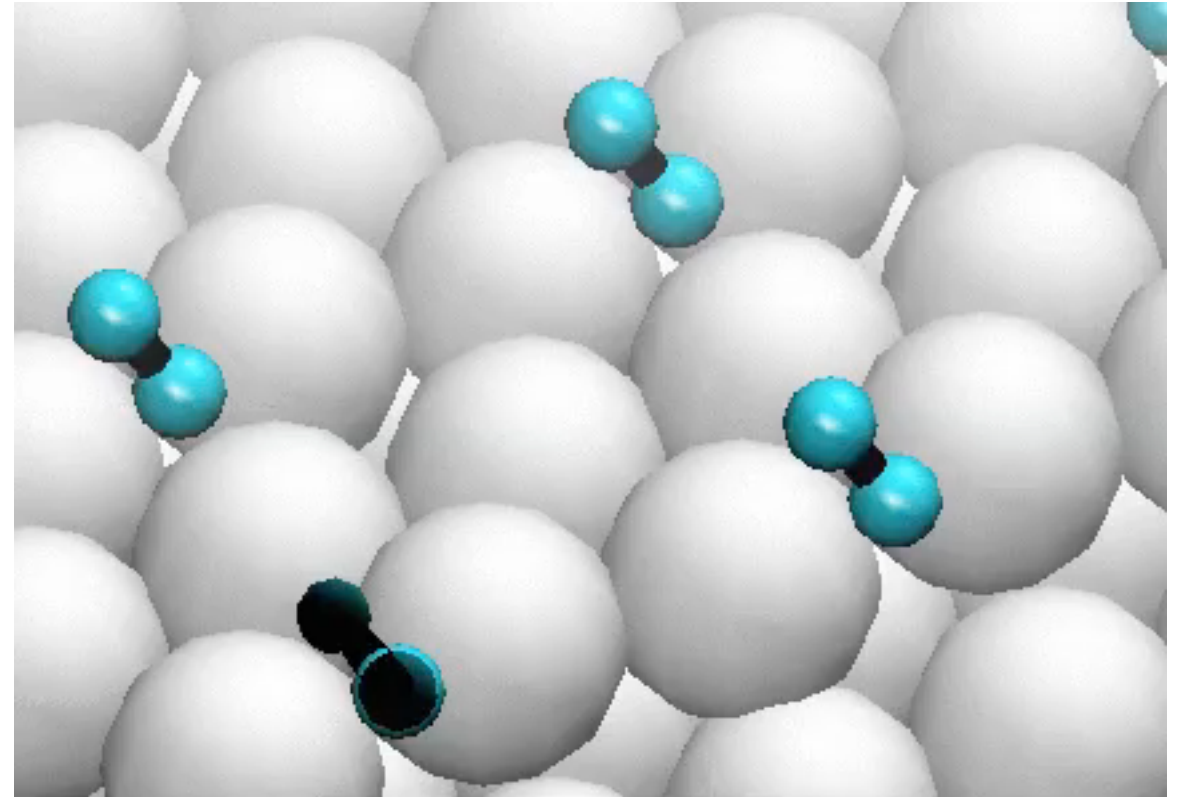
Enhanced sampling: N2/Ru(0001): results

- CFF displayed dramatically faster convergence than even an efficient ABF implementation

(figure removed)

Enhanced sampling: N2/Ru(0001): results

- Combined ABF and CFF results → free energy surface
- →full equilibrium probabilities, and the minimum free-energy path
  - More general than TS search – this self-consistently find the free-energy path, rather than finding a potential-energy minimum path and adding a correction

(figure removed)

Enhanced sampling: N2/Ru(0001): results

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- Comparison to harmonic TST shows
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(figure removed)

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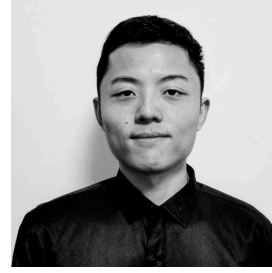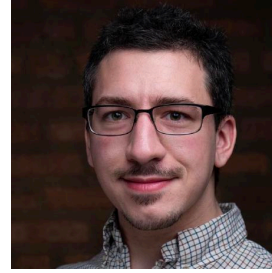
(figure removed)

- This is one of the first demonstrations of a state-of-the-art enhanced sampling method for a chemical reaction on a metal catalyst
  - More general method → more complex models
  - Less reliance on "intuition", less approximation

People

Argonne, UChicago: Elizabeth M. Y. Lee,   Emre Sevgen,   Boyuan Yu,   Juan J de Pablo

- Enhanced sampling:

Stanford ChemE/DTU Fysik:
Aayush R. Singh, Jens K. Nørskov

UC Davis: Francois Gygi

- Global optimization/electrochemical catalysis:

Joseph A Gauthier
Stanford ChemE

Karen Chan
DTU Fysik

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- Many collaborators

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