Alexander von Humboldt
Stiftung/Foundation

FRITZ-HABER-INSTITUT
MAX-PLANCK-GESELLSCHAFT

POORMAN'S REVIEW ABOUT: CI - NUDGED ELASTIC BAND

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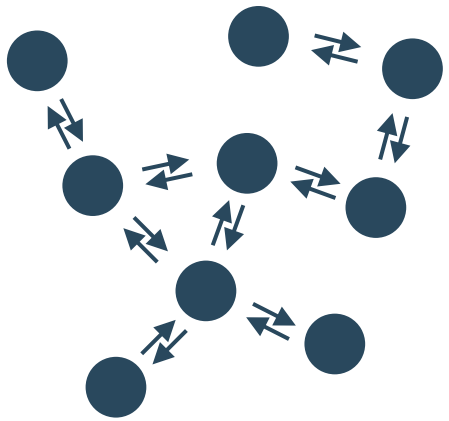
Microkinetics Modeling

Typical approach studying long term behavior

Constructing a Reaction Network → **Microkinetic Model** → **Long Term Behavior**



e.g.
Kinetic Monte Carlo (kMC)
Numerical Master Equation

e.g.
Turnover Frequency
Life-time of Nanostructure
Morphological Change

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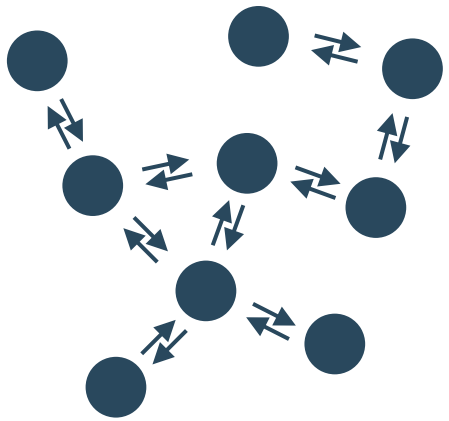
Typical approach studying long term behavior

Constructing a Reaction Network



Microkinetic Model

e.g.

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Long Term Behavior

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Nudged Elastic Band Overview

What you have before NEB:

1) A pair of optimized metastable states

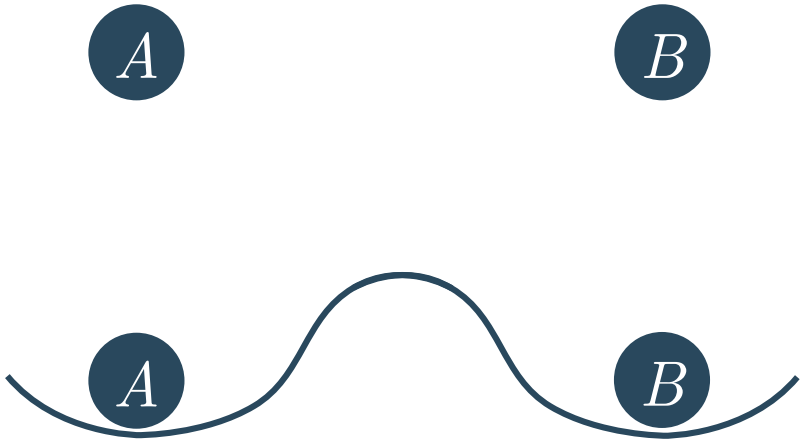
Obtained from some sampling

Handwritten

2) A potential energy surface (PES)

Classical force field (EAM)

Machine learned potential energy (MACE, GAP …)



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What you get from NEB:

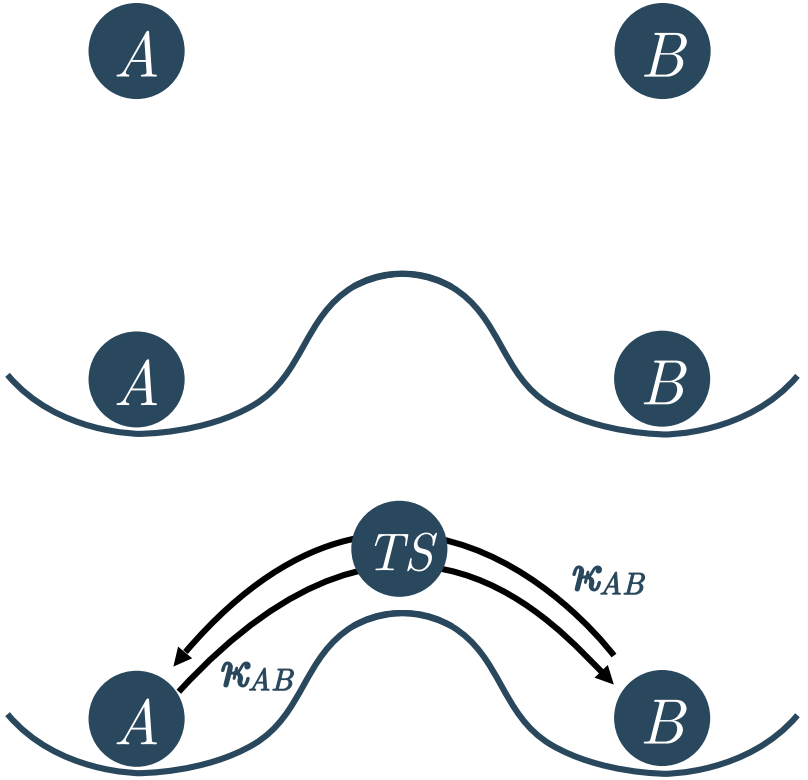
Transition State (TS) on the reaction path linking i,j

What you usually do with that TS:

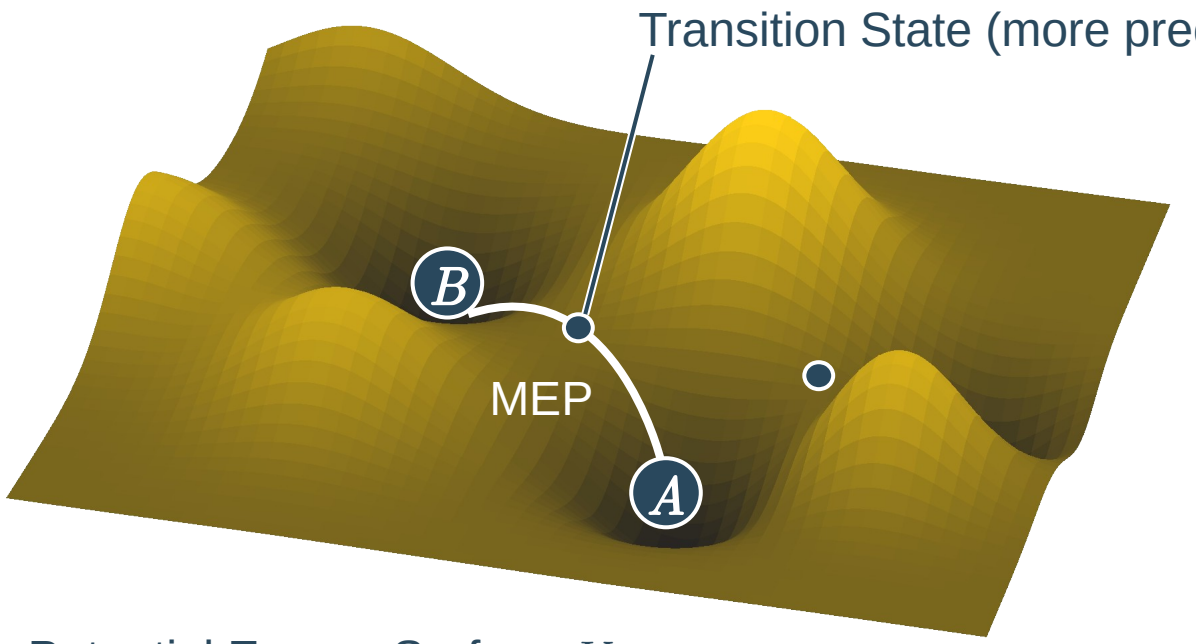
Model the kinetic rate κ_{AB} , κ_{AB} (back-and-forth)

Usually simple Arrhenius form

$$\kappa = \nu \exp\left(-\Delta E_{\mathrm{act}}/k_B T\right)$$



~~Nudged~~ Elastic Band Overview



Transition State (more precise, 1st order saddle point)

Only one eigenvalue
of the Hessian is negative

Potential Energy Surface V:

Practically $3N$-Dimension $R_{0<m\leq 3N}$

N: Number of atoms free to move

Minimum Energy Path (MEP):

The most energetically favorable path linking A, B

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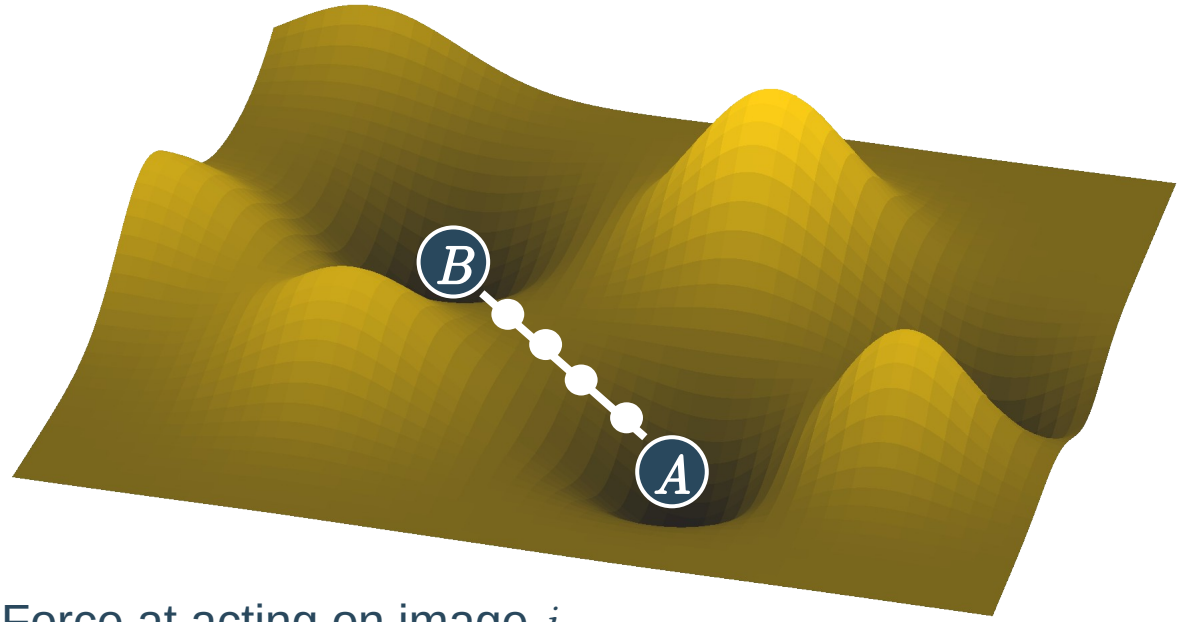

Force at acting on image i

$$\mathrm{F}_i = -\nabla V(\mathbf{R}) + \mathbf{F}_i^{\mathrm{band}}$$

$$\mathrm{F}_i^{\mathrm{band}} = k\left(\mathbf{R}_{i+1} - \mathbf{R}_i\right) + k\left(\mathbf{R}_{i-1} - \mathbf{R}_i\right)$$

To get MEP:

1) Guess a path, typically straight line

2) Put some state-images in between

3) Put springs between the ‘beads’
(Each spring has a spring constant k)

4) Optimize image-states on the band

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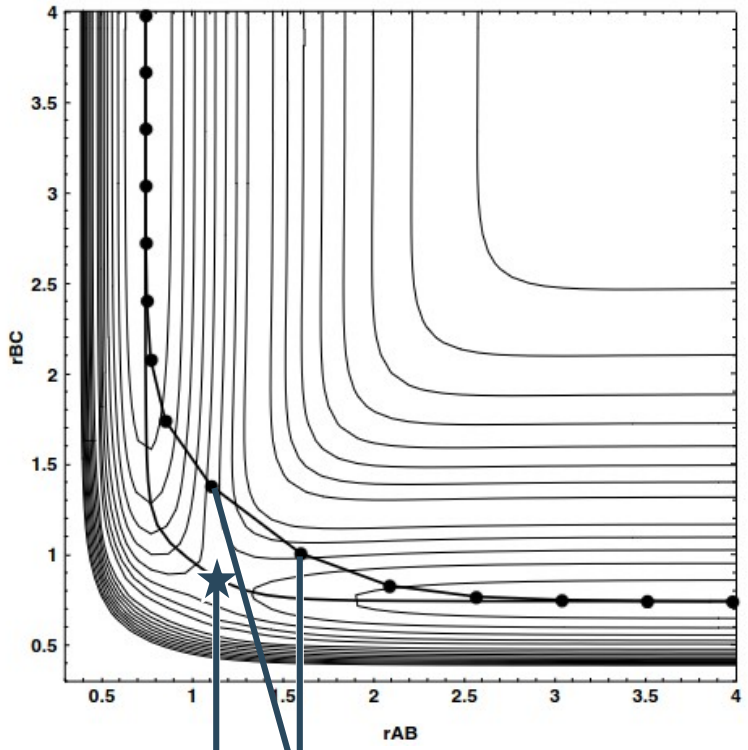

i) The cuts the corner
ii) It doesn't give the maximum along the band

To get MEP:

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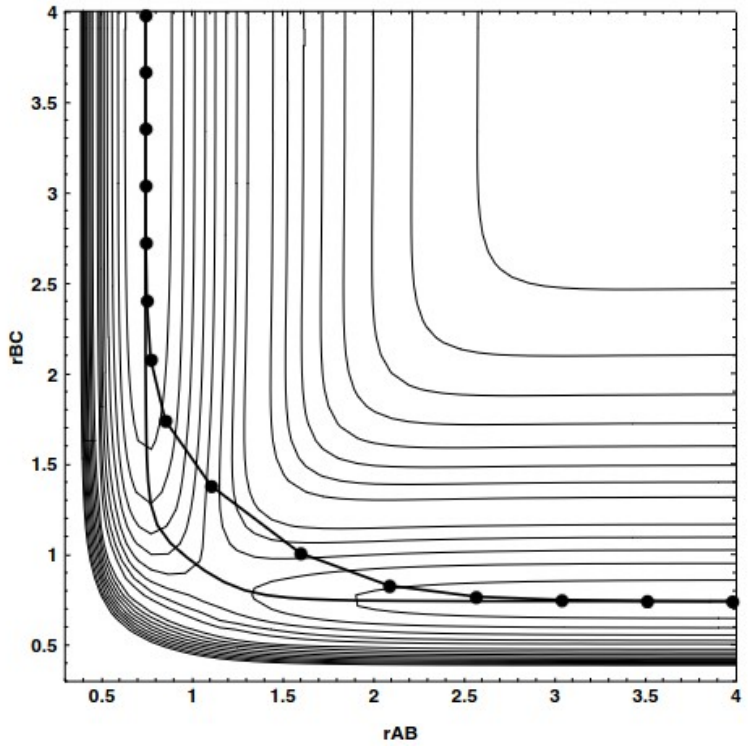

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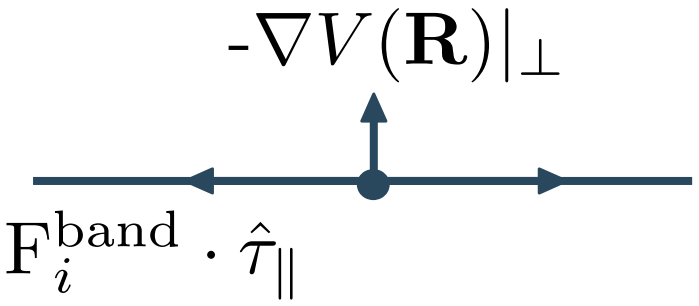
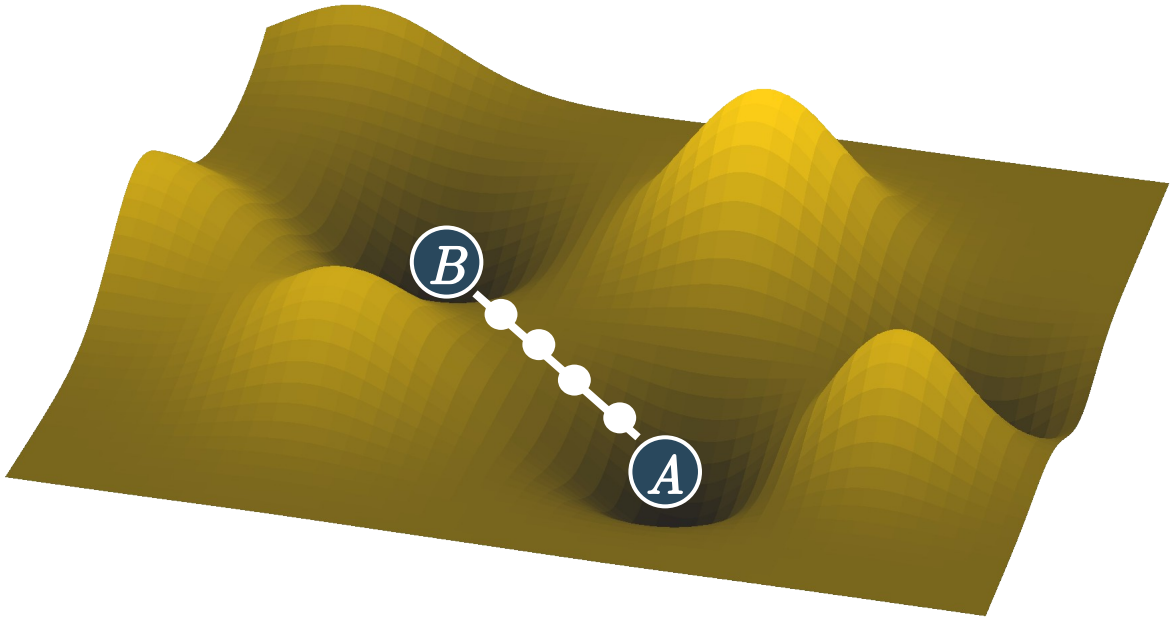


Spring contributes only along the band
PES contributes perpendicular to the band

Climbing Image Nudged Elastic Band Overview



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4) After a few NEB steps:

Special treatment for **the bead with highest energy**

$$\mathrm{F}_{i_{\mathrm{max}}}^{\mathrm{ciNEB}} = -\nabla V(\mathbf{R}_{\mathbf{i}_{\mathrm{max}}})|_{\perp} + \nabla V(\mathbf{R}_{\mathbf{i}_{\mathrm{max}}})|_{\parallel}$$

i) No effect from the band
ii) Invert the force from PES along the band

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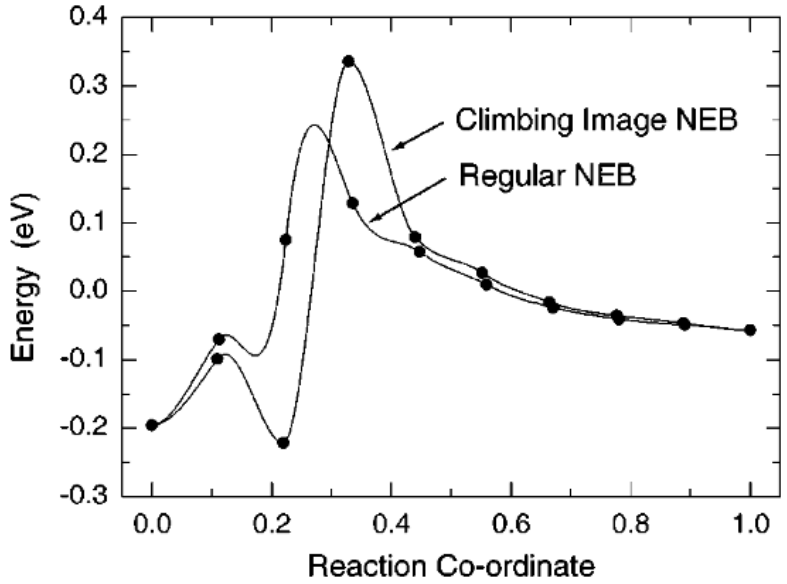

Henkelman, G., Uberuaga, B. P., & Jónsson, H. J. Chem. Phys. 113.22 (2000): 9901-9904.

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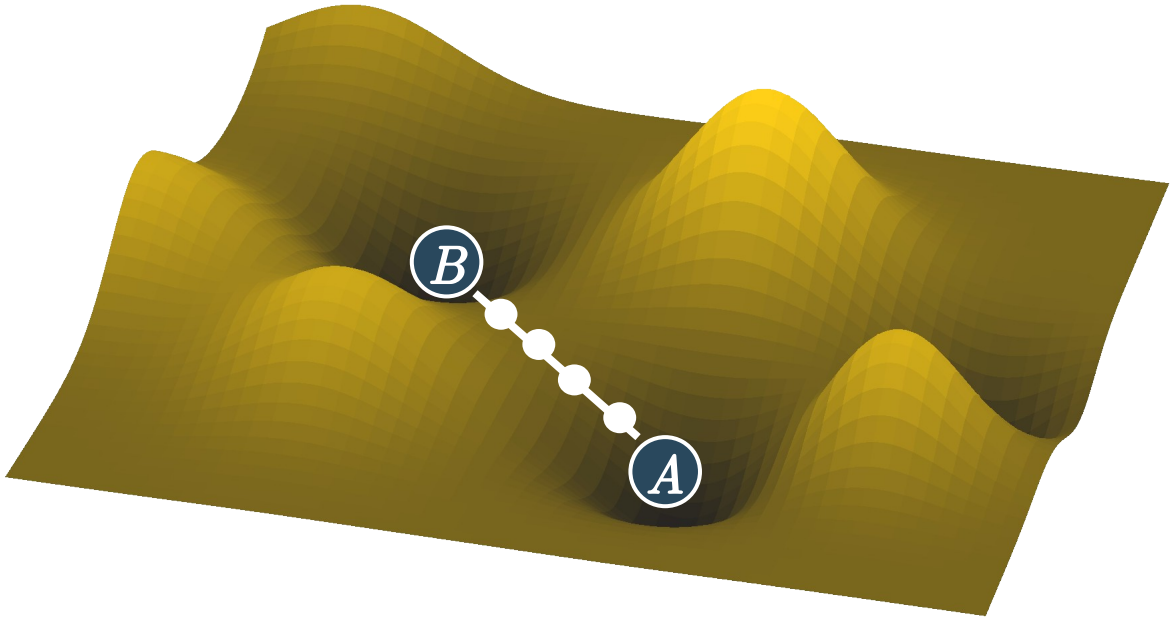

When generating the initial guess of the band: Besides trivial interpolation of AB, here is a better way
Smidstrup, S., Pedersen, A., Stokbro, K., & Jónsson, H. J. Chem. Phys., 140(21) (2014).

The band is a set of straight lines linking the beads!
How to estimate “tangential”/”perpendicular” direction
G. Henkelman and H. Jonsson,
J. Chem. Phys. 113, 9978 (2000)

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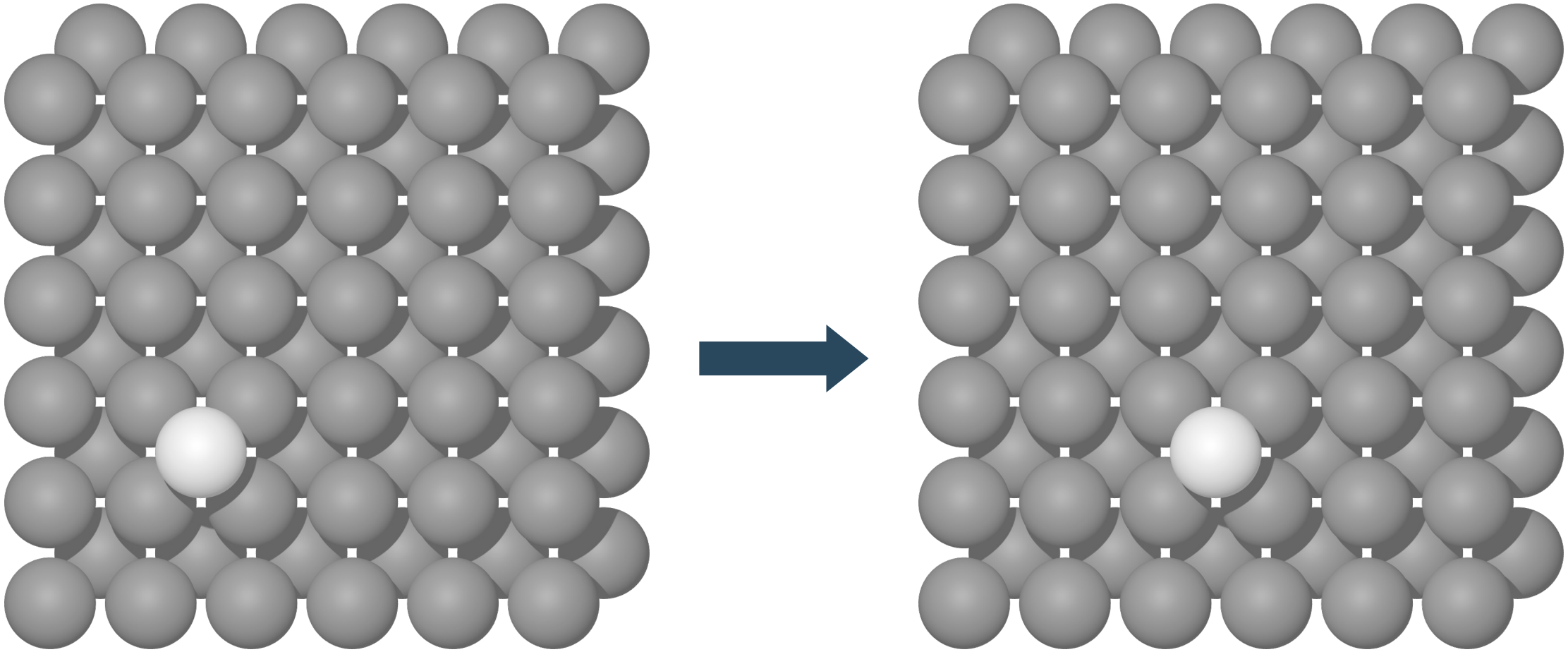
Demo Time Please Look at the Jupyter Notebook

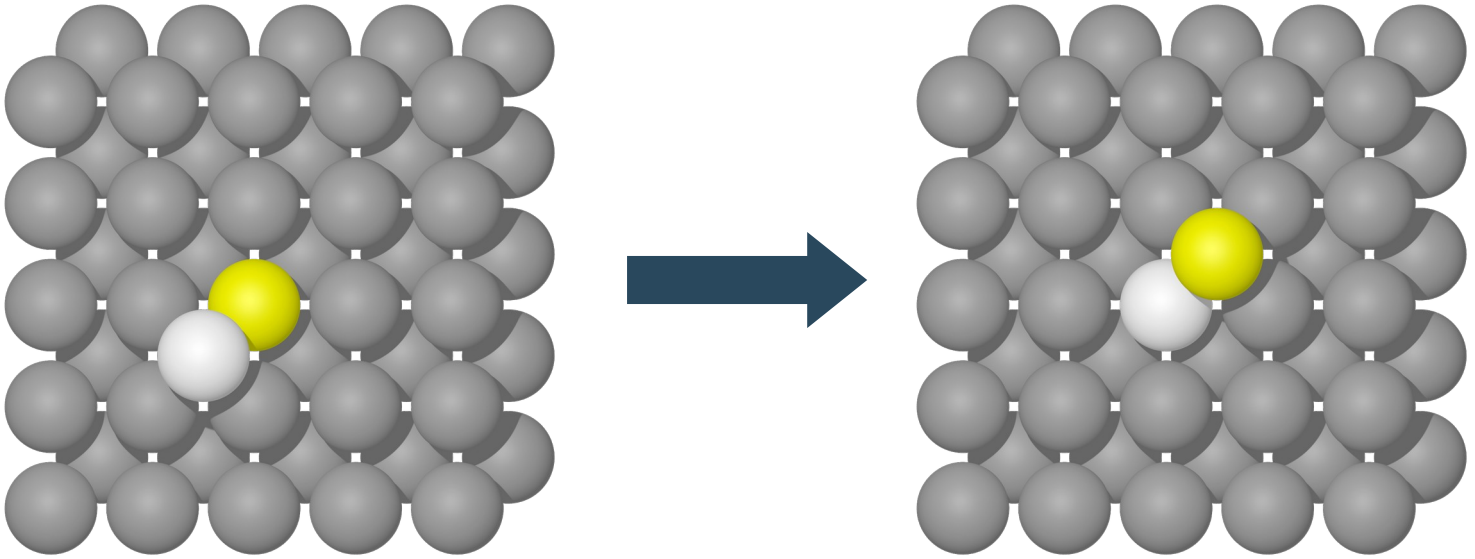


Initial State

Final State

The Simplest Example: Direct Hop of Adatom on FCC(100) Pd
With Classical Force Field (EAM)

Your Turn! Exercise 1: Exchange Terrace Diffusion



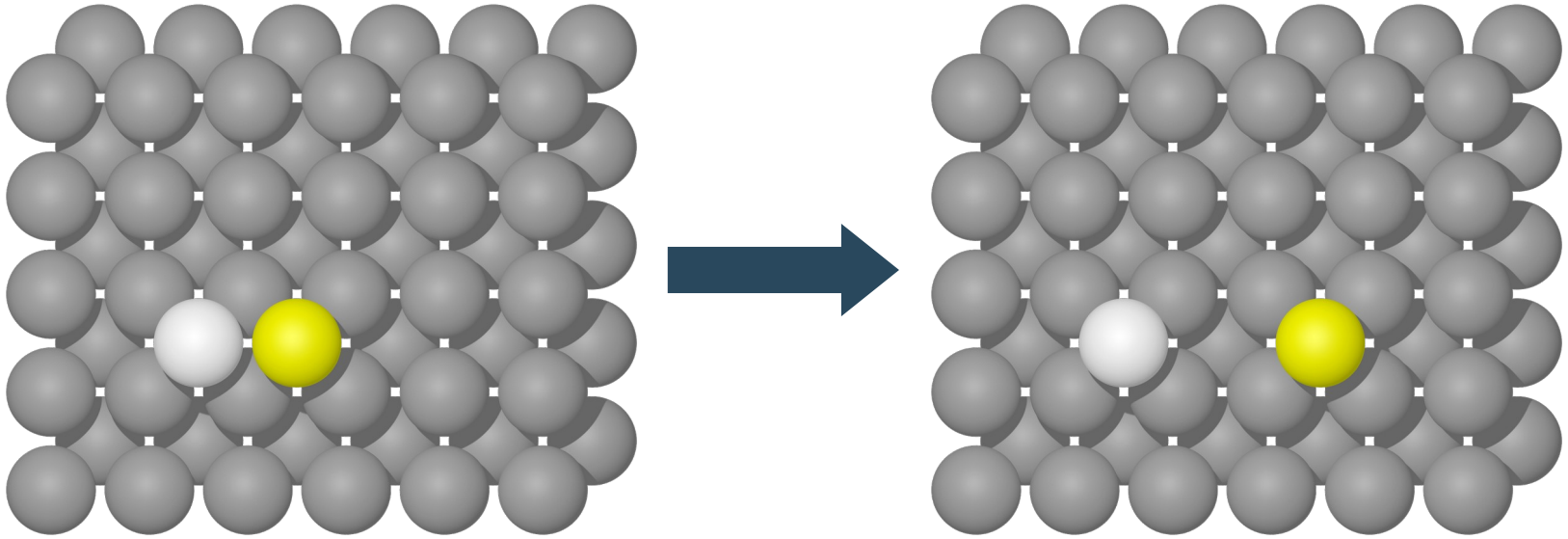
Initial State Final State

Consider the exchange terrace diffusion on Pd(100) surface (all atoms shown are Pd)
1) Perform ciNEB and find the energy barrier and prefactors in both directions
2) Plot the energy on the minimal energy pathway from ciNEB

CAUTION:

It is an exchange process, white atom is squeezing out the yellow atom.
NOT the white atom jumping to the diagonal site!
When you calculate the vibrational modes, which atoms should be included???

Your Turn! Exercise 2: Bond Breaking Direct Hop?



Initial State

Final State

Consider the bond breaking process on Pd(100) surface (all atoms shown are Pd)
1) Perform ciNEB and find the energy barrier and prefactors in both directions
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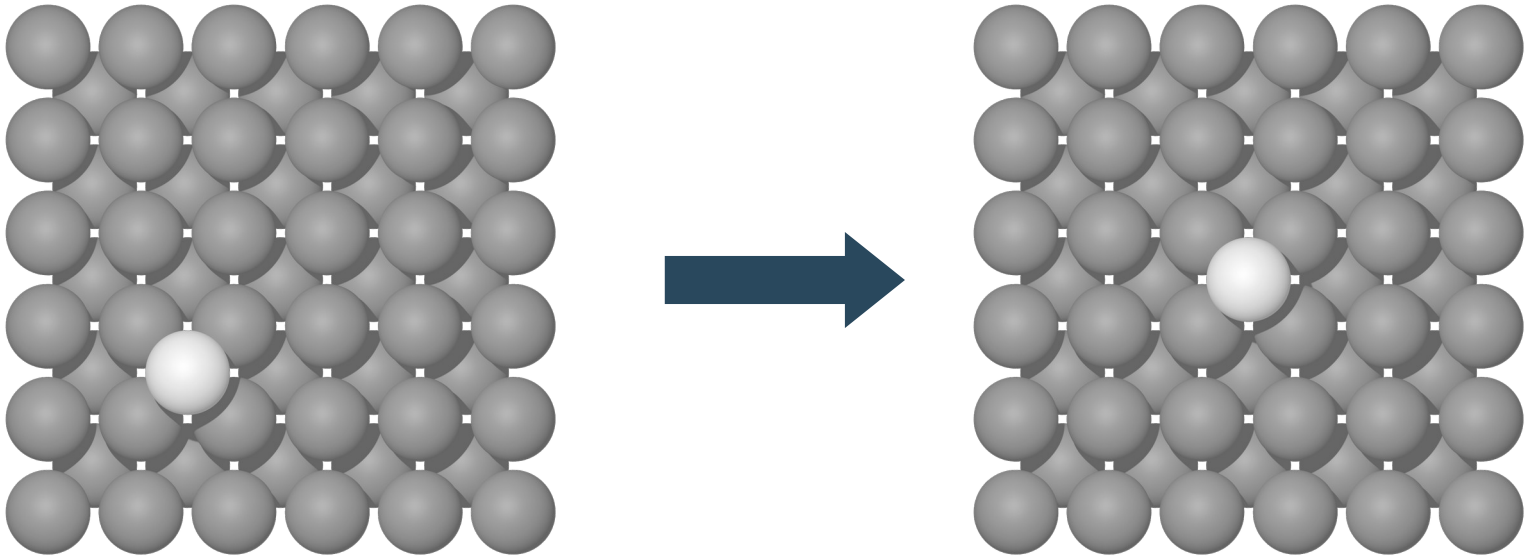
CAUTION:
Take a closer look at the MEP plot.

Your Turn! Exercise 3: Hmmm



Initial State

Final State

What about this process, if you perform ciNEB, take a closer look at the results.
Why is it not physical? How would you model this instead???

Footnote

Think about it again!

In general,
You want to calculate energy (construct PES) with a different force field /potential
    What to do?

You may identify which atoms to include in the vibrational mode calculation
    Do you want to do this identification by-hand every time?

Here the initial and final states are given, no matter they are physical or not
    What structures / systems you are going to consider is up to you.
    How you organize the work flow to generate these?

If you are choosing other tools instead of ASE, the idea of doing it is basically the same.
    How you substitute each step with the tool(s) you choose?