Temperature programmed molecular dynamics (TPMD) method

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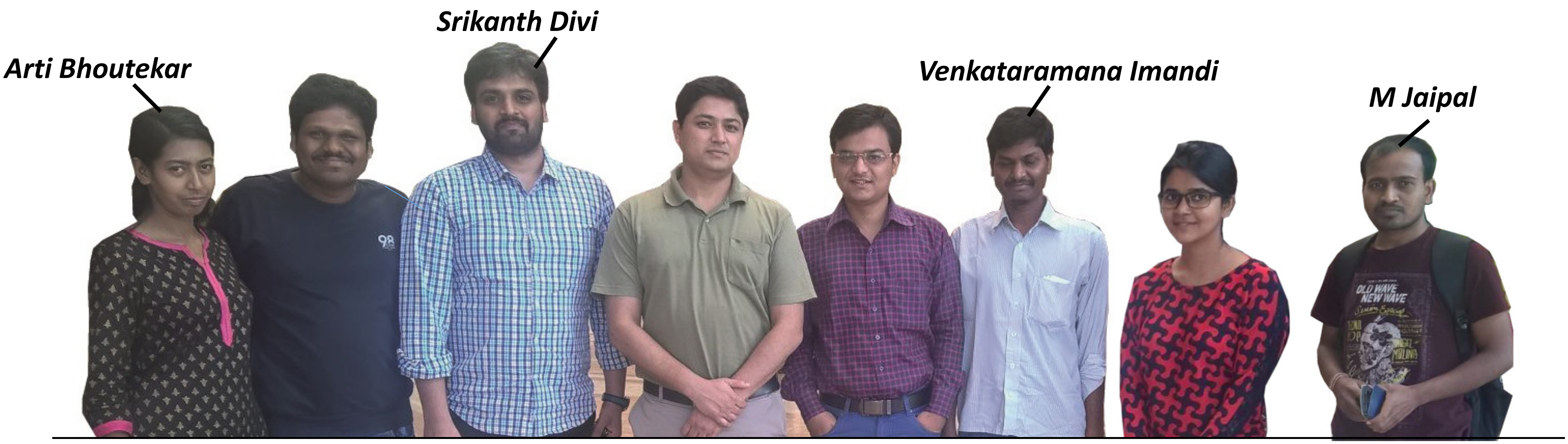
[1] Divi and Chatterjee, JCP, 140, 184115 (2014)
[2] Chatterjee and Bhattacharya, JCP, 2015
[3] Venkaramana and Chatterjee, JCP 2016

Funding: Department of Science and Technology (DST), Indian National Science Academy (INSA)

Students

- Missing in group photo below: Paramita Haldar, Mohit Prateek



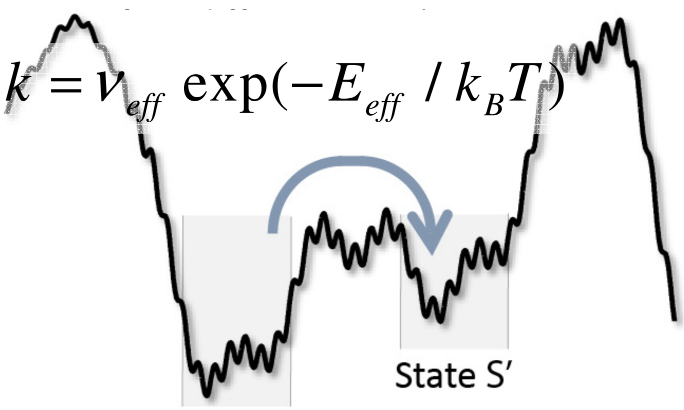
Collaborators

- Prof. Swati Bhattacharya, IIT Guwahati
- Prof. Arindam Sarkar, IIT Bombay

Building KMC models with TPMD…
… some key features of TPMD

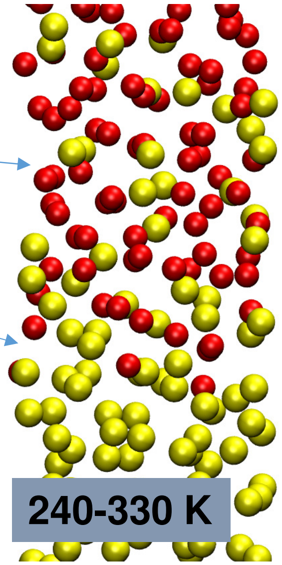
POTENTIAL ENERGY LANDSCAPE

$$k = \nu_{eff} \exp(-E_{eff} / k_B T)$$

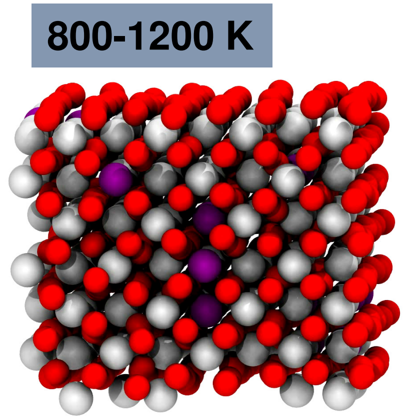


Li-Si phase

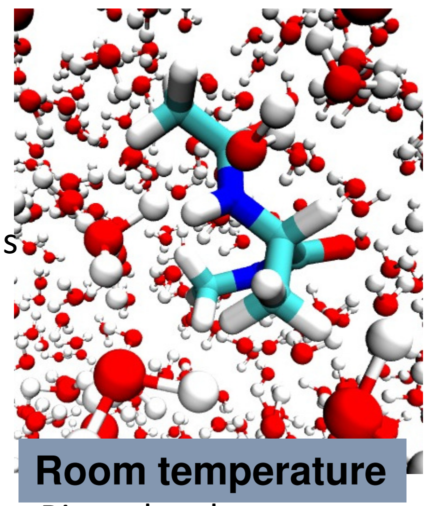
a-Si phase



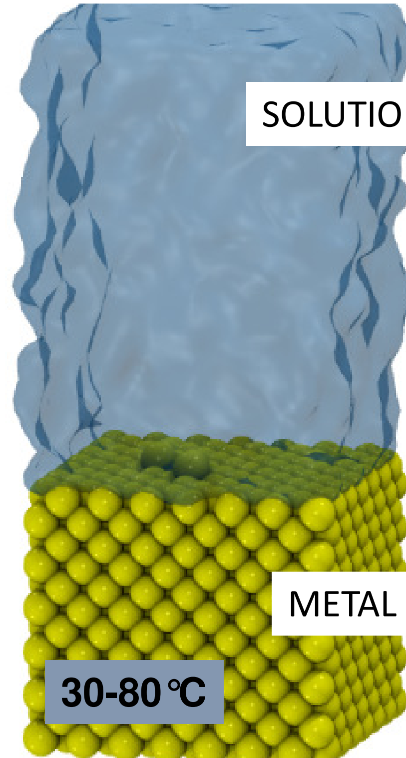
Phase transformations during lithiation and delithiation in Si (lithium ion battery anode material)

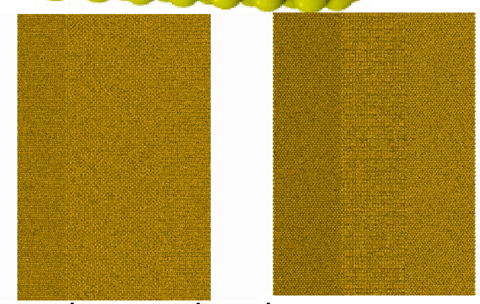


Ion conducting oxides (yttria stabilized zirconia)



Biomolecular systems (with Prof. S. Bhattacharya)

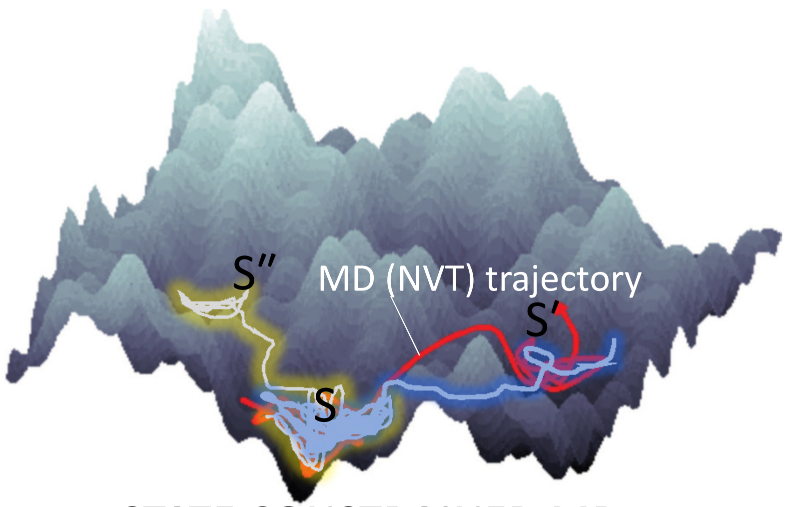




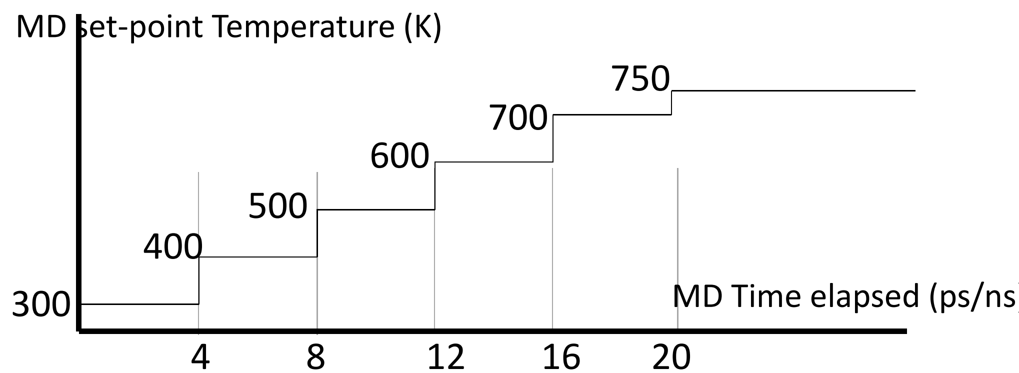
Selective dissolution in metal alloys: Long-time evolution **30-80 ℃**

Steps involved in building KMC model using TPMD

- *Efficiently find states, pathways/rates over a range of temperatures*
- *Probe whether Arrhenius assumption is reasonable and find effective Arrhenius parameters*



STATE CONSTRAINED MD

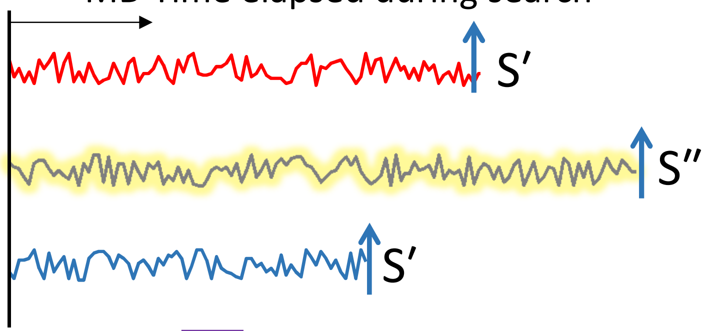


Temperature program

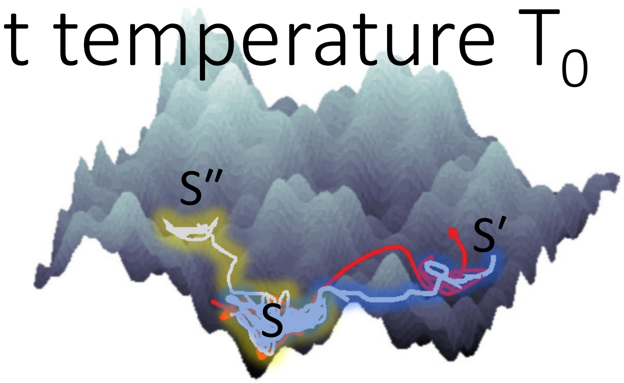
State (collection of potential energy basins)

Rate estimation in MD @ constant temperature T_0

MD Time elapsed during search



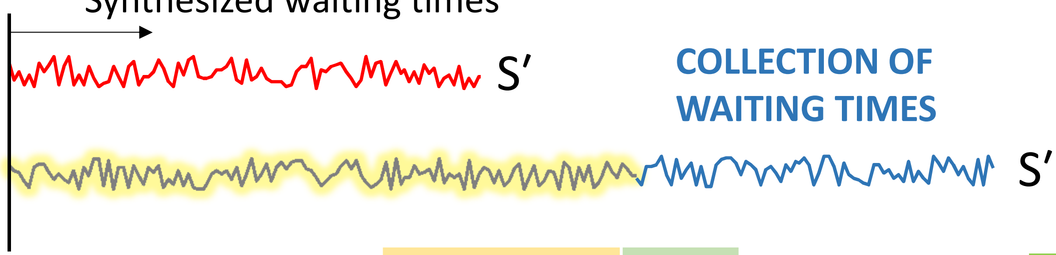
TRAJECTORIES FROM STATE CONSTRAINED MD



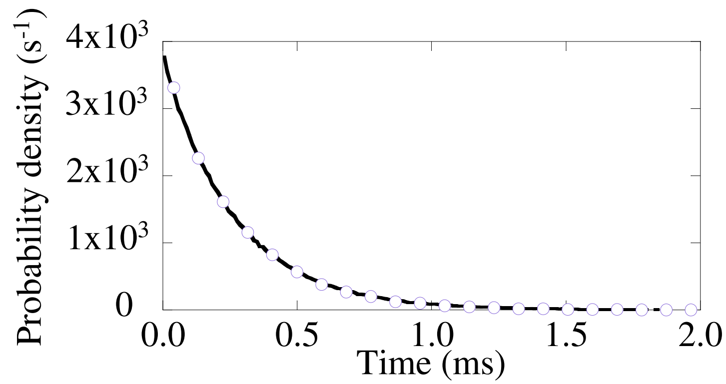
STATE CONSTRAINED MD

Stitching algorithm

Synthesized waiting times



COLLECTION OF WAITING TIMES



$$P(t)dt = \exp(-k_\alpha^0 t)k_\alpha^0 dt$$

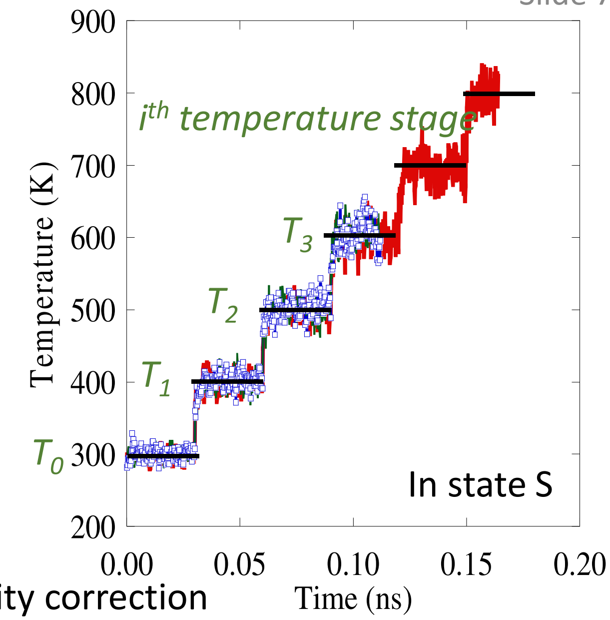
Probability of no escape in time [0, t] x Probability of escape in time [t, t+dt]

Maximum likelihood estimate for rate constant $k_\alpha^0 = \frac{n}{\tau_\alpha}$

CONS: RARE EVENTS ARE POORLY SAMPLED

Temperature programmed MD

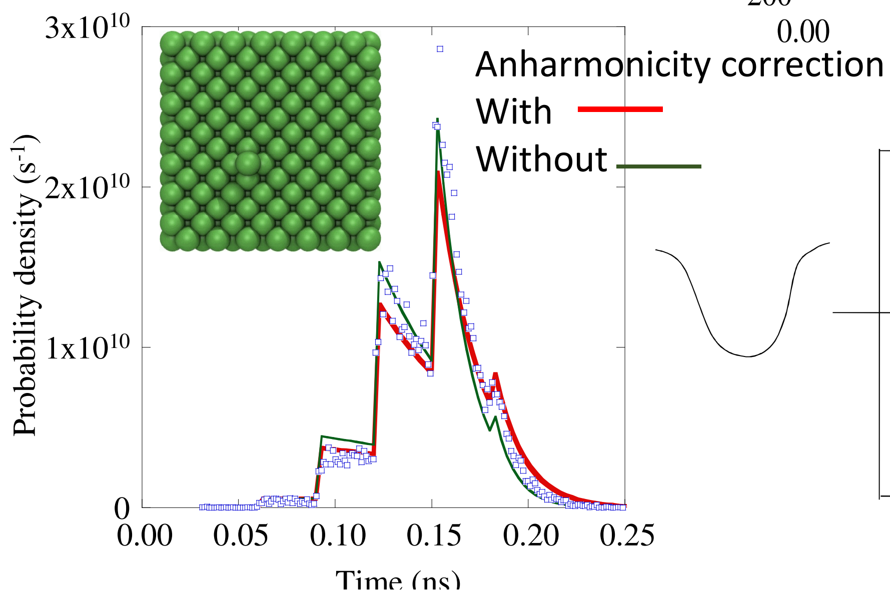
- Increase temperature in steps
- Langevin thermostat is employed
- Kinetic pathways can be sought in parallel

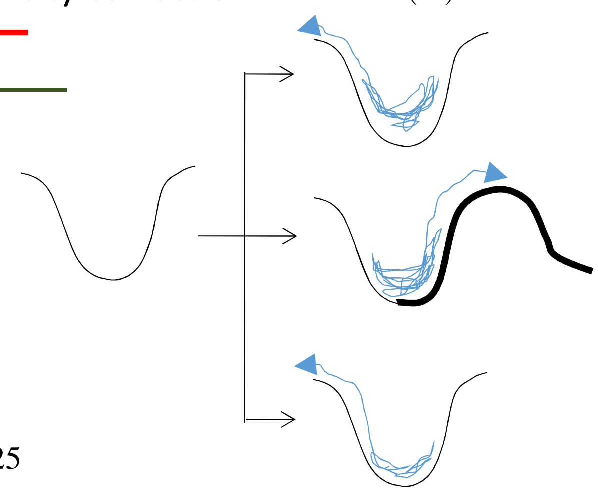


TPMD distribution

$$P(t) = \left[\prod_{i=0}^{n} \exp\left(-k_{\alpha}^{i} \tau_{i}\right) \right] k_{\alpha}^{n} dt,$$

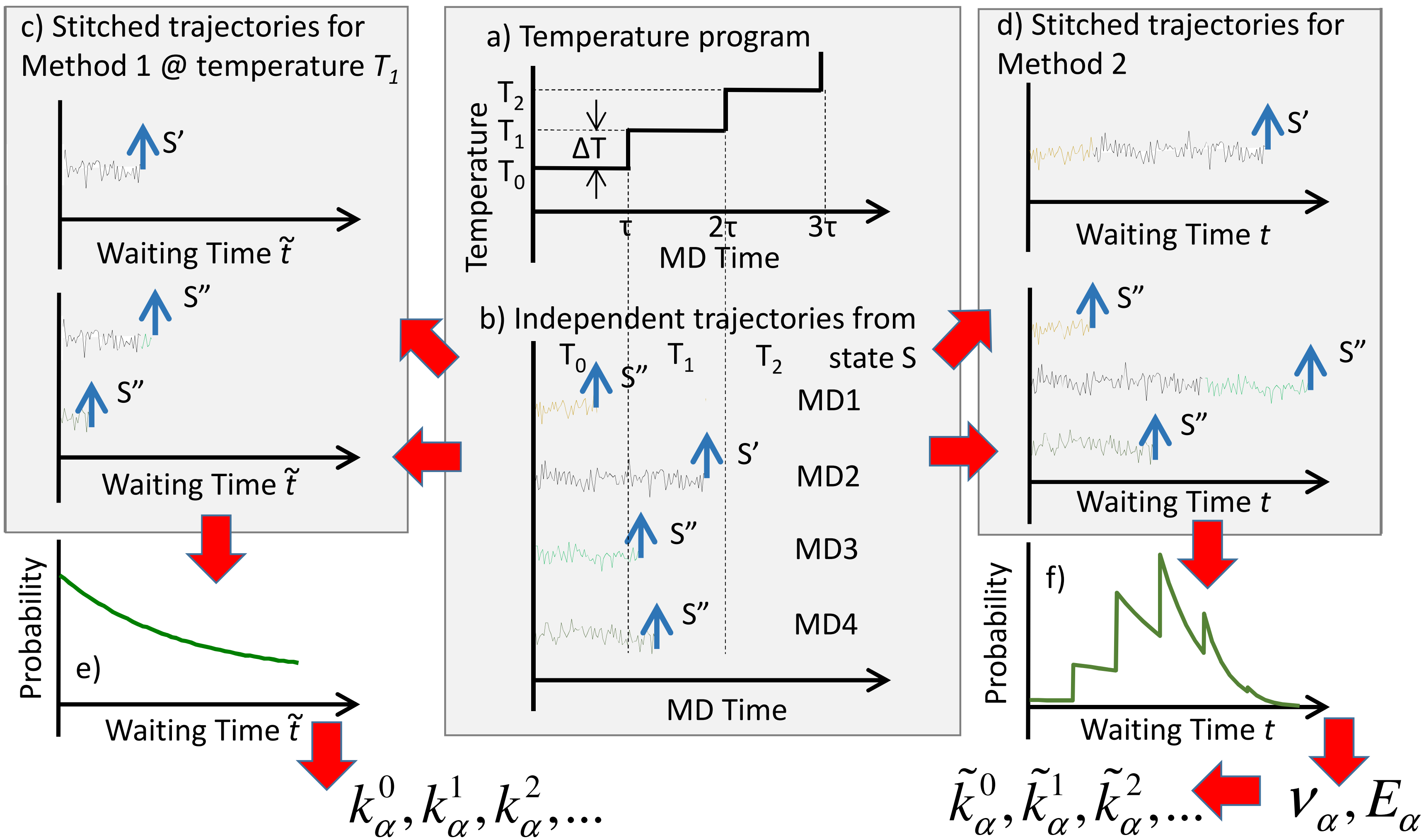
$$n\tau < t \leq (n+1)\tau$$





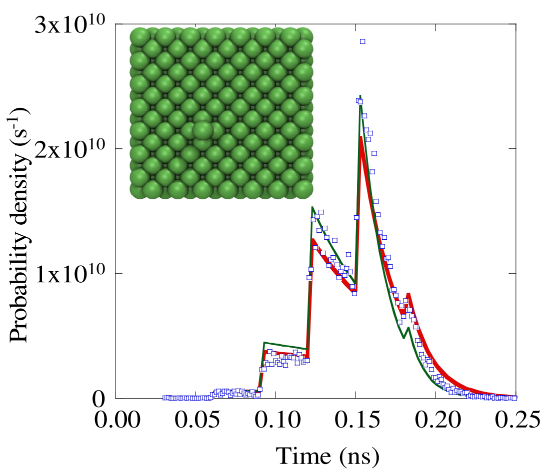
Dynamically relevant pathways selected with higher probability at low temperatures

Estimating rates at different temperatures



Estimating effective Arrhenius parameters for a pathway

- Assume Arrhenius behavior for the pathway $k_{\alpha}^{0} = v_{\alpha} \exp\left(\frac{-E_{\alpha}}{k_B T_0}\right)$



Collection of waiting times $\{\tilde{t}_1, \tilde{t}_2, .., \tilde{t}_m\}$

$$\frac{\sum_{i=0}^{N_{\max}} \theta_i T_i^{-1} \exp(-E_{\alpha} / k_B T_i)}{\sum_{i=0}^{N_{\max}} \theta_i \exp(-E_{\alpha} / k_B T_i)} = T_X^{-1}$$

$$\nu = \frac{m}{\sum_{i=0}^{N_{\max}} \theta_i \exp(-E_a / k_B T_i)}$$

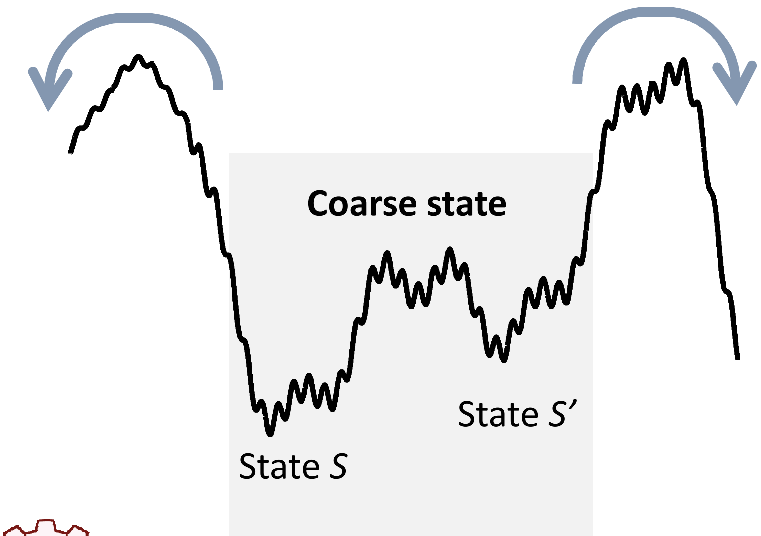
$$T_X = m / \sum_{\alpha=1}^{m} T_{n\alpha}^{-1}$$

Waiting time distribution for coarse-states

- Double benefit from TPMD
  - Overcoming large activation barriers
  - Access low probability states

$$p(t) = \pi_{s,n} k_n \prod_{i=1}^{N_{\max}} \exp(-\pi_{s,i} k_i \tau_i)$$

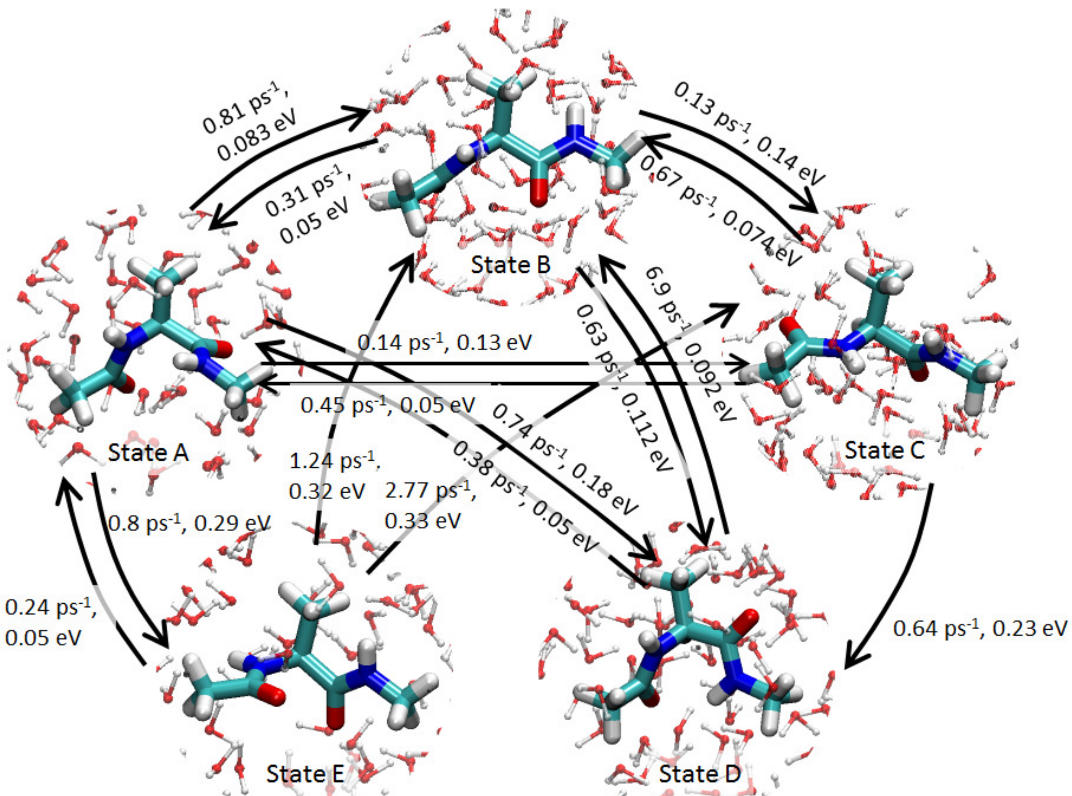
$$\frac{d\pi}{dt} = T\pi$$



$$\frac{\sum_{i=0}^{N_{\max}} \pi_{s,i} \theta_i T_i^{-1} \exp(-E_\alpha / k_B T_i)}{\sum_{i=0}^{N_{\max}} \pi_{s,i} \theta_i \exp(-E_\alpha / k_B T_i)} = T_X^{-1}$$

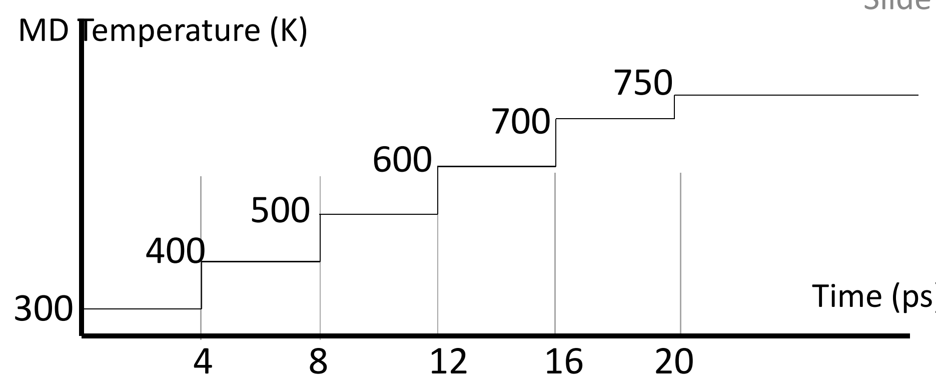
$$\nu = \frac{m}{\sum_{i=0}^{N_{\max}} \pi_{s,i} \theta_i \exp(-E_a / k_B T_i)}$$

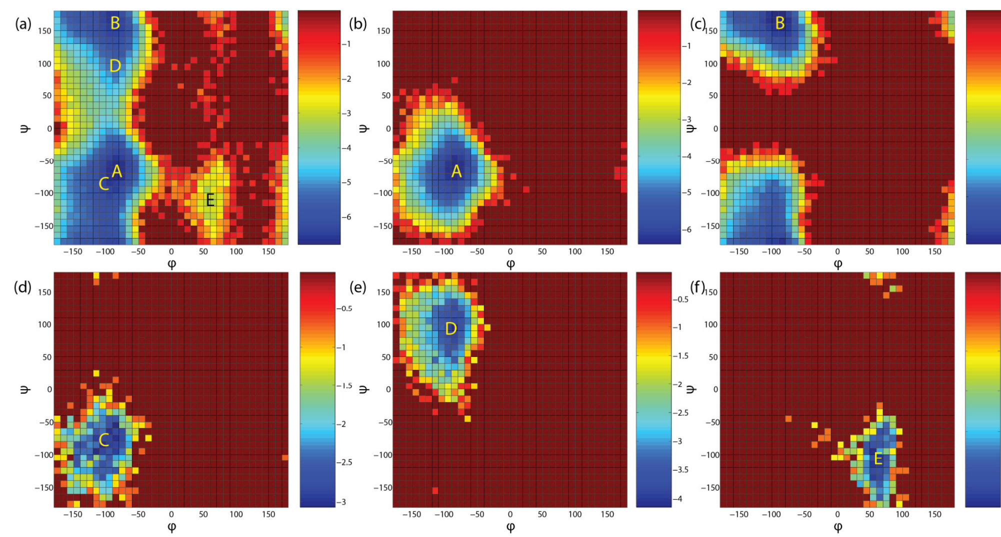
Example: Alanine dipeptide



MARKOV STATE MODEL FOR ALANINE DIPEPTIDE

with Prof. S. Bhattacharya, IIT Guwahati

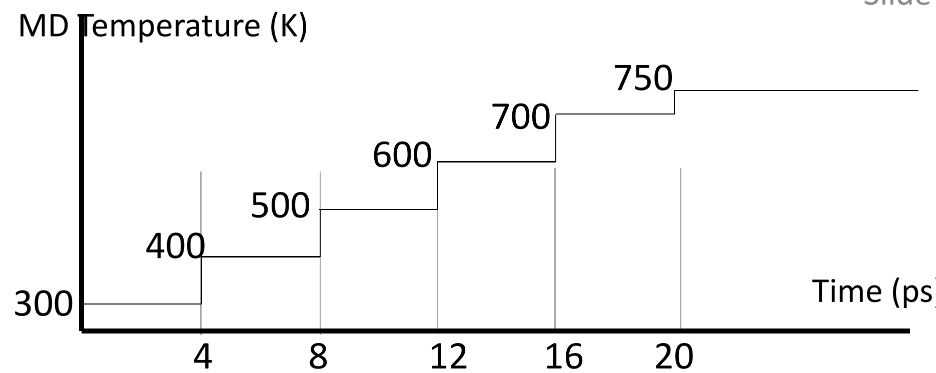


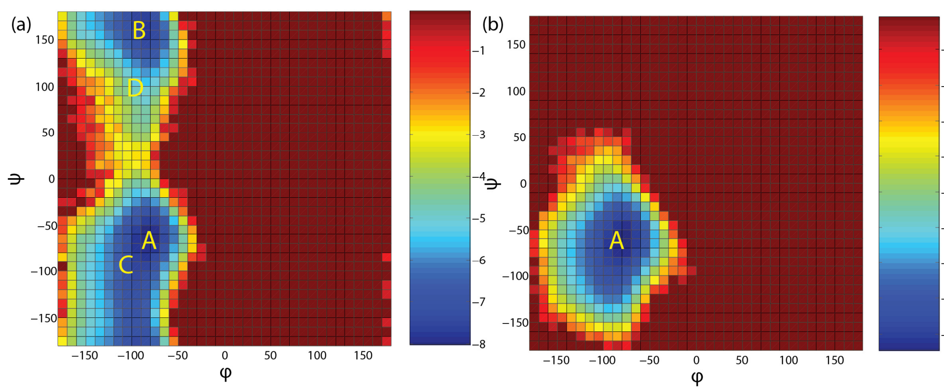


Free energy map @ 600 K

NOTE: WE DON'T EMPLOY FREE ENERGY MAPS IN TPMD

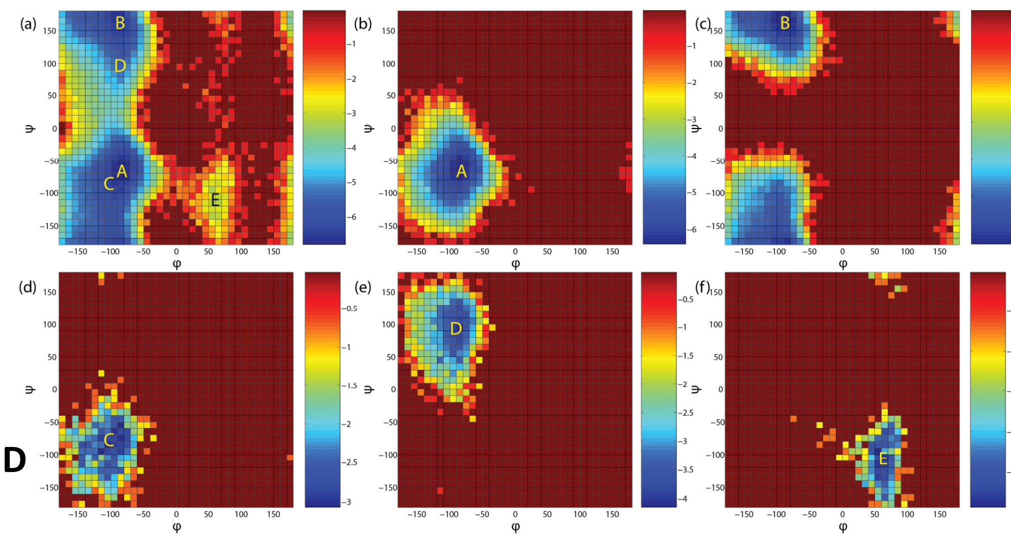
Example: Alanine dipeptide





Free energy map @ 300 K

NOTE: WE DON'T EMPLOY FREE ENERGY MAPS IN TPMD

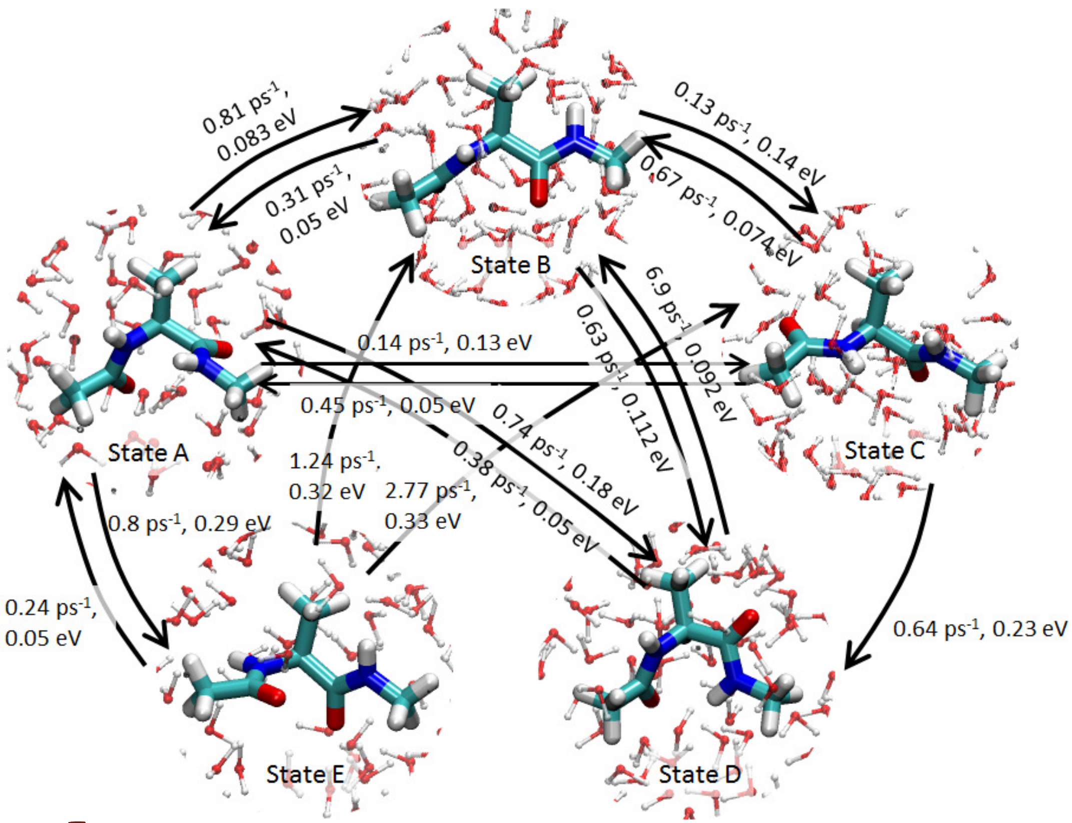


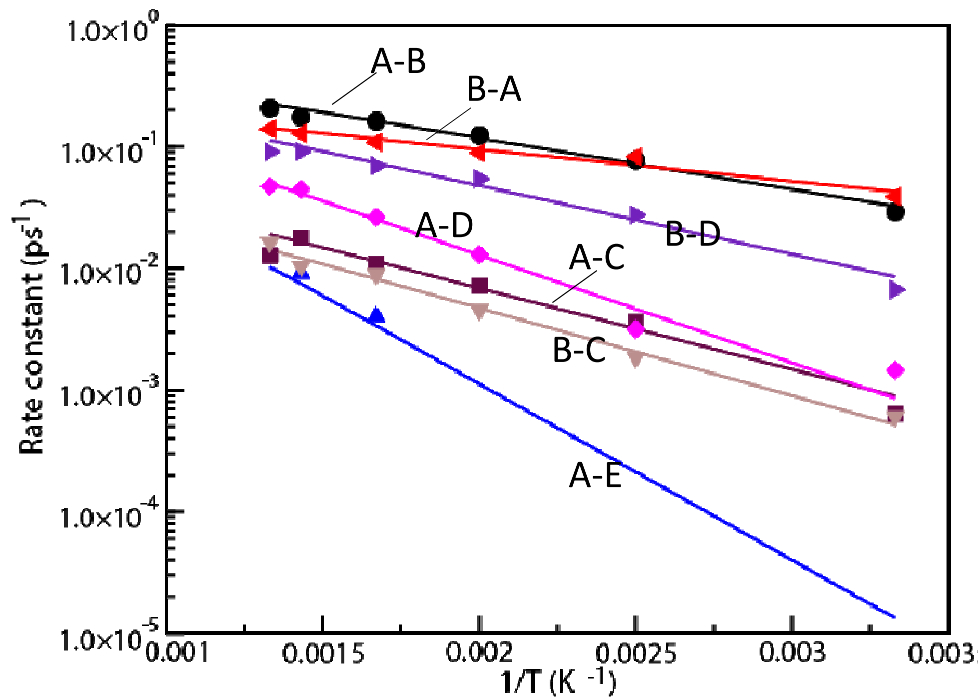
with Prof. S. Bhattacharya, IIT Guwahati

Free energy map @ 600 K

NOTE: WE DON'T EMPLOY FREE ENERGY MAPS IN TPMD

Example: Alanine dipeptide





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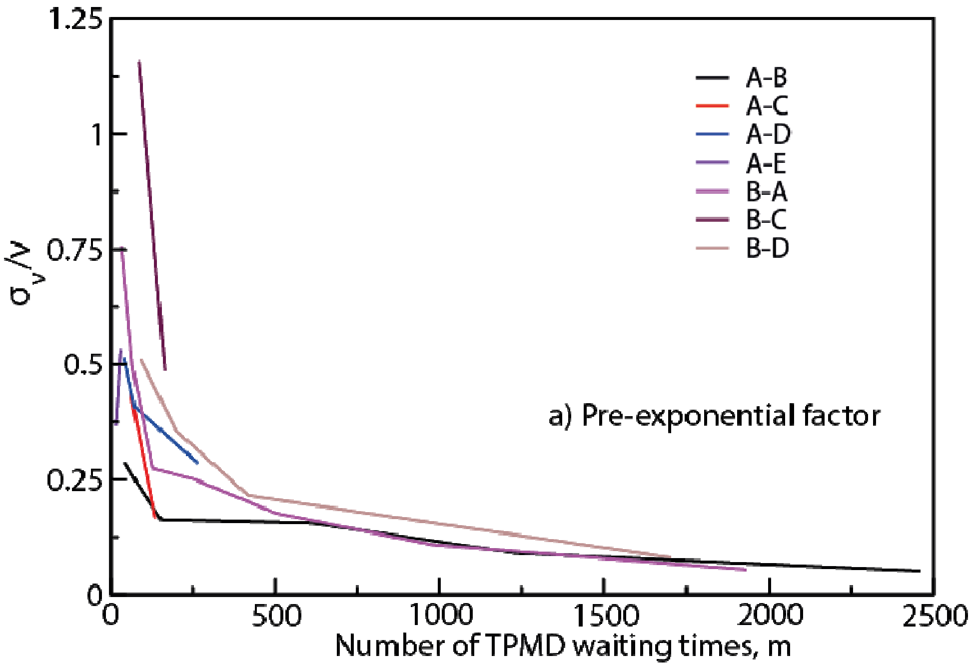
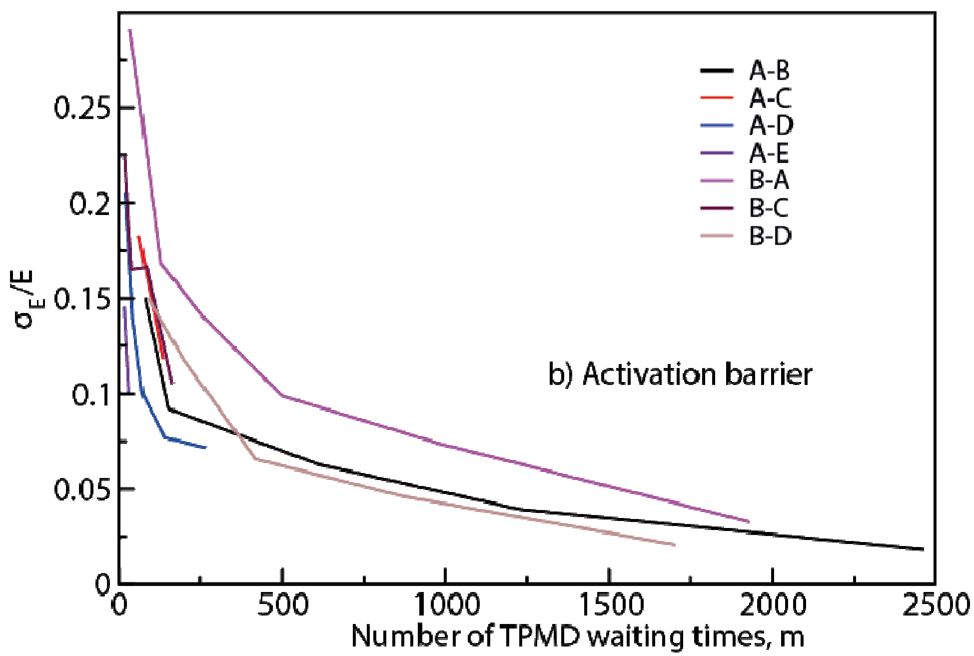
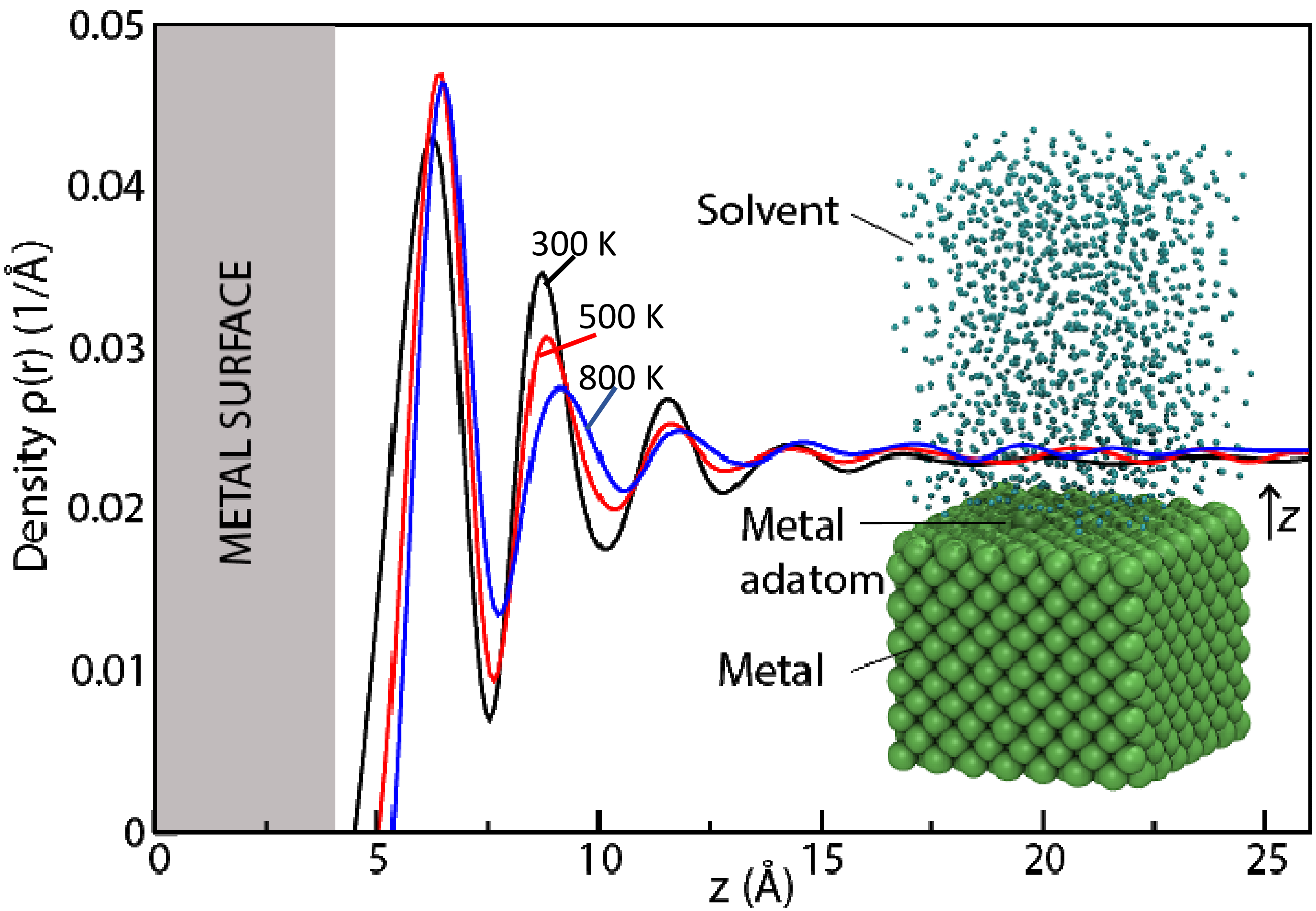
Example: Alanine dipeptide

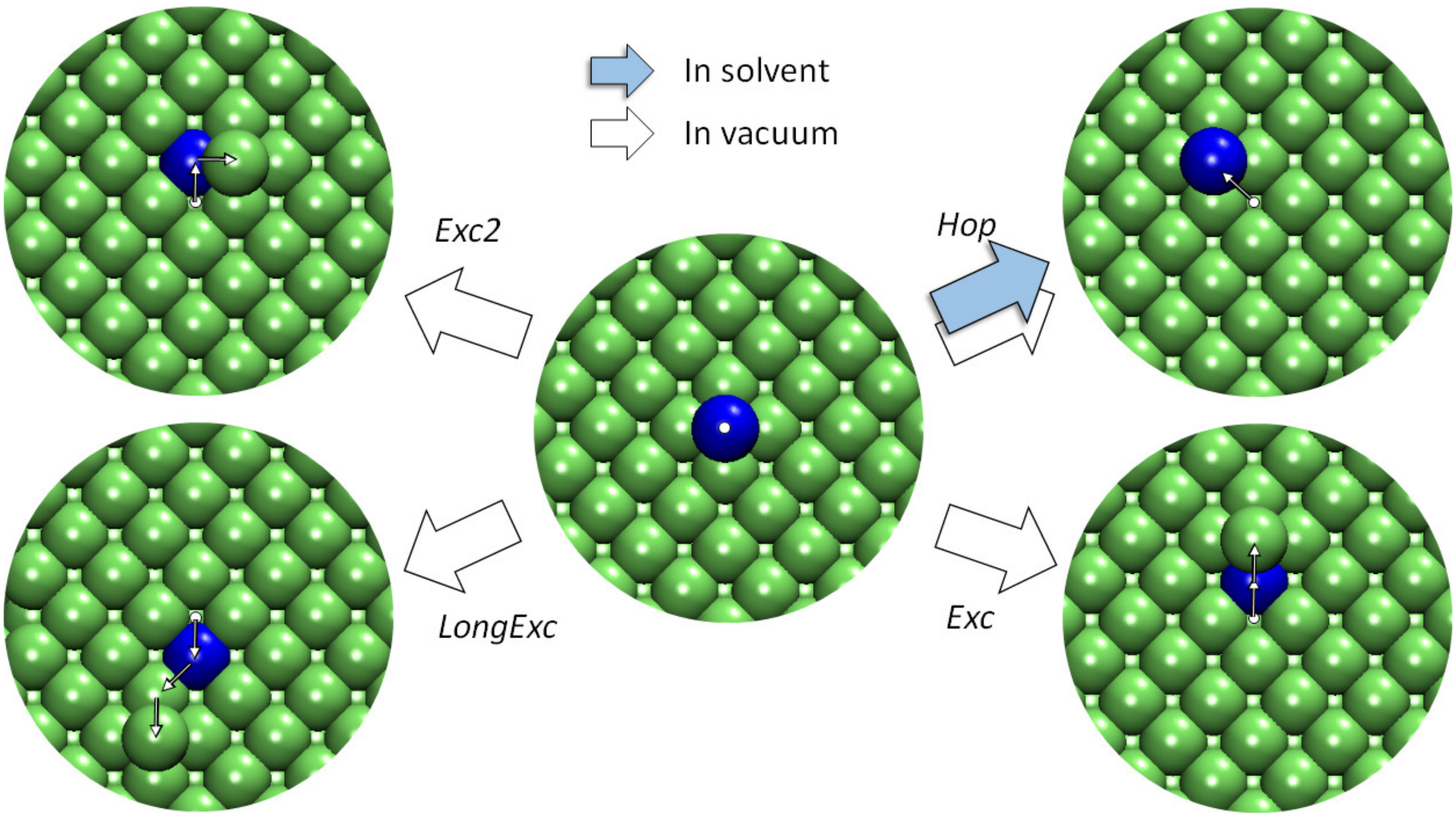


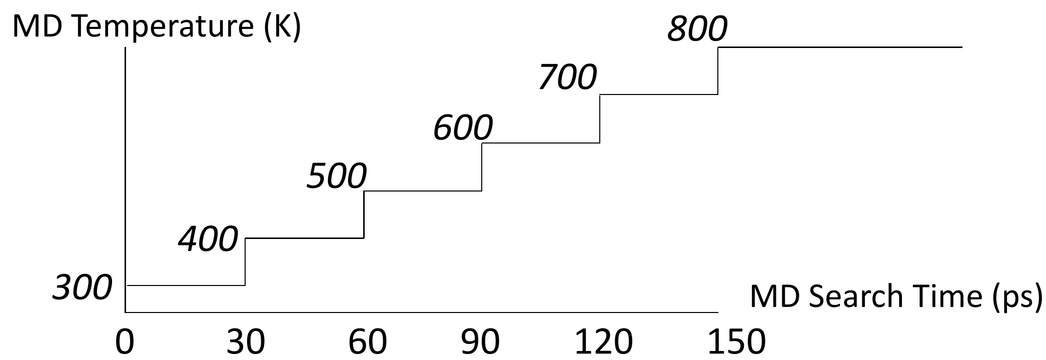


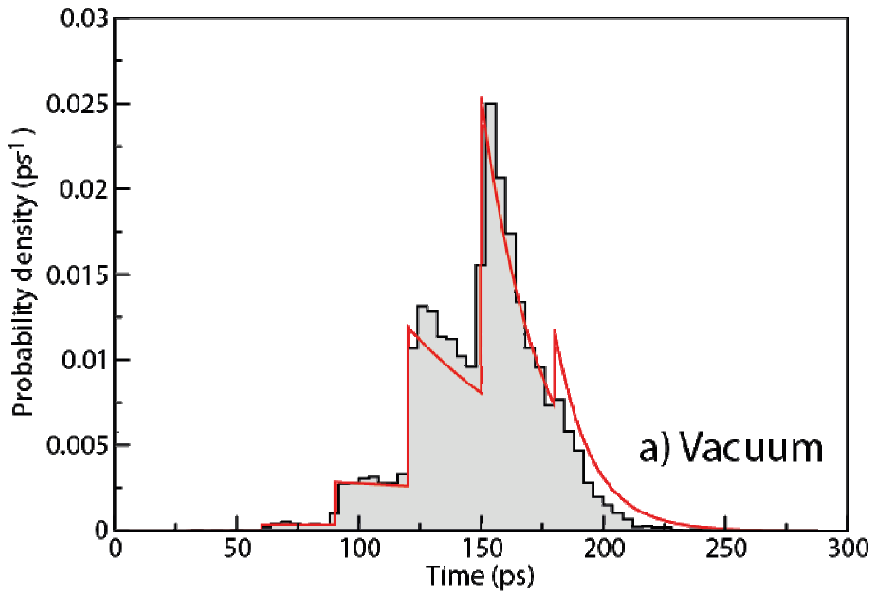
500-2000 waiting times are sufficient

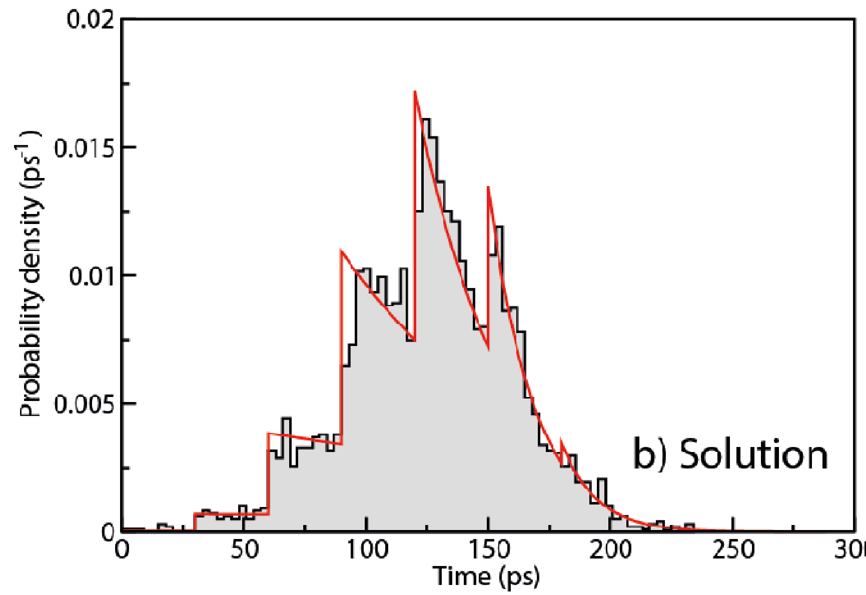
Example: Surface diffusion @ metal-solvent interface




In solvent
In vacuum
Exc2
Hop
LongExc
Exc





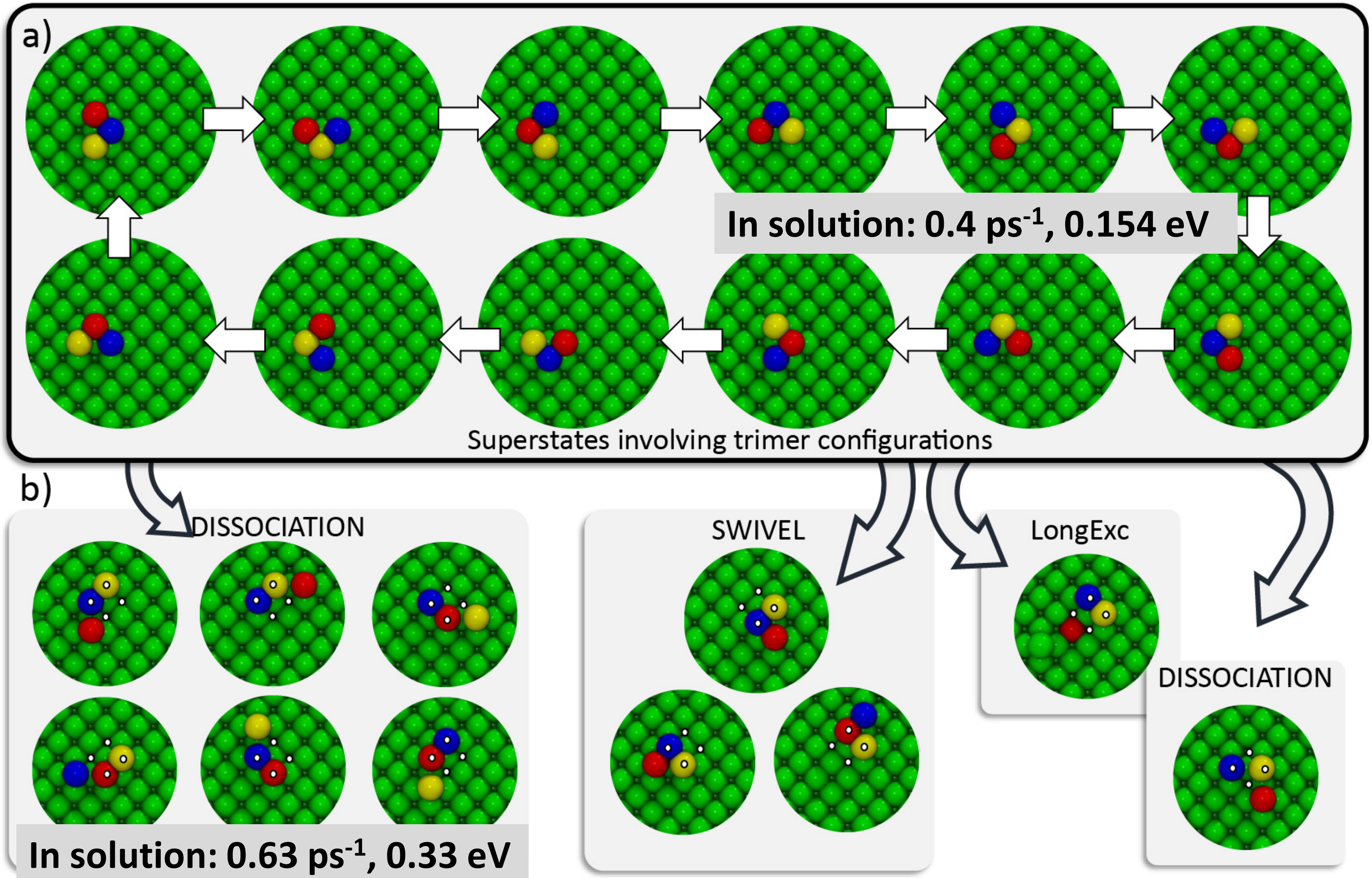


Hop: ν= 10.3 ps^{-1}, E_a=0.525 eV
Exchange: ν= 19.3 ps^{-1}, E_a=0.592 eV } Ag/Ag(100)

Hop: E_a=0.57 eV using NEB } Ni/Ni(100)

Hop: ν= 1.2 ps^{-1}, E_a=0.297 eV Ag/Ag(100)

Hop: ν= 2.3 ps^{-1}, E_a=0.448 eV Ni/Ni(100)


a)
In solution: 0.4 ps^{-1}, 0.154 eV
Superstates involving trimer configurations
b)
DISSOCIATION
In solution: 0.63 ps^{-1}, 0.33 eV
SWIVEL
LongExc
DISSOCIATION

Conclusions

LIST OF FEATURES OF TPMD
Application to wide range of problems – metals, semiconductor materials, ionic materials, biomolecules
State recognition allows for off-lattice description
Rate estimation at multiple temperature for multiple pathways
Can handle rugged energy landscapes
Tackle low energy barrier problem, On-the-fly coarse-graining of states possible
No reaction coordinate/collective variables/minimum energy path
Automatic construction of local environment KMC models
Probe Arrhenius behavior (no requirement for HTST)
Parallelizable to large number of processors
Orders-of-magnitude time acceleration over MD
Error control is possible