Coupling First Principles Molecular Dynamics with Advanced Sampling

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MICCoM Workshop

Argonne National Lab

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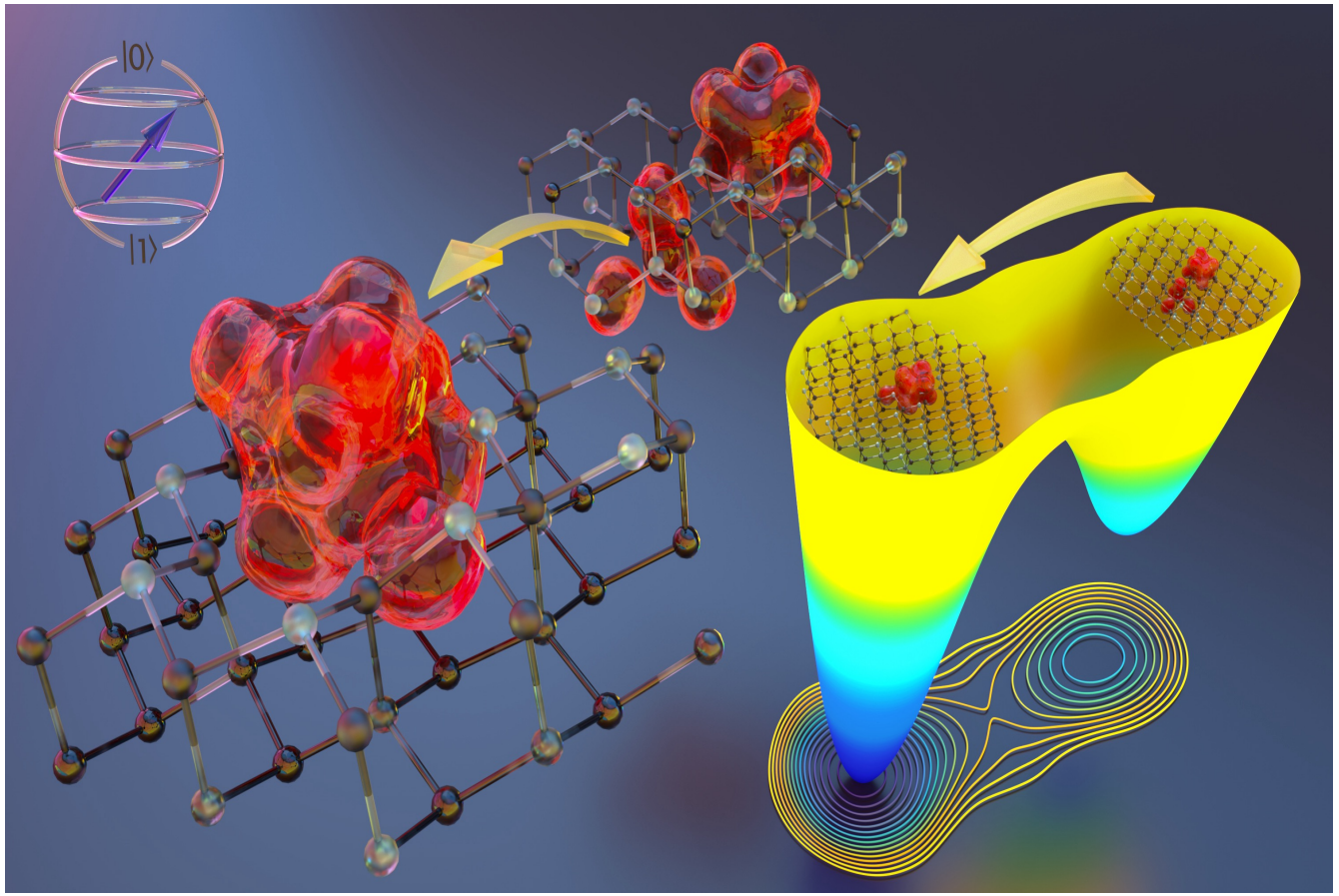
UCI University of California, Irvine

MICCoM

THE UNIVERSITY OF CHICAGO PRITZKER SCHOOL OF MOLECULAR ENGINEERING

Outline

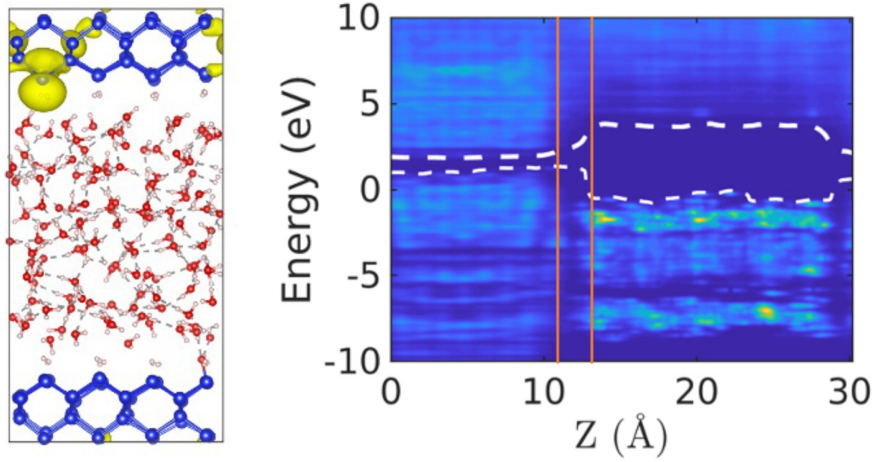
1. Motivation for coupling FPMD + enhanced sampling
2. Introduction to enhanced sampling and SSAGES-Qbox
3. Examples of the coupling
4. Hands-on demonstration (LCRC)



E. M.Y. Lee, A. Yu, J. J. de Pablo, and G. Galli. *Nature Communications* 12, 6325 (2021)

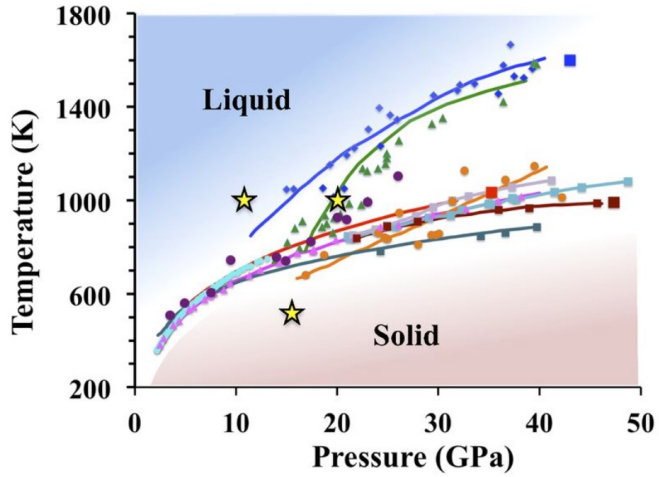
The need for FPMD: materials with dynamical and electronic properties

Solid-liquid Interfaces



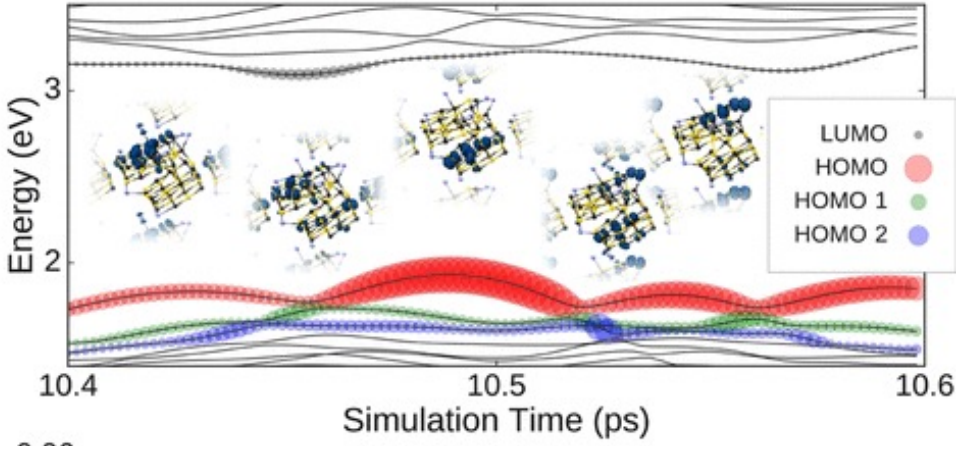
Z. Ye, A. Prominski, B. Tian, G. Galli. PNAS. 118, e2114929118 (2021)

Materials in extreme environments



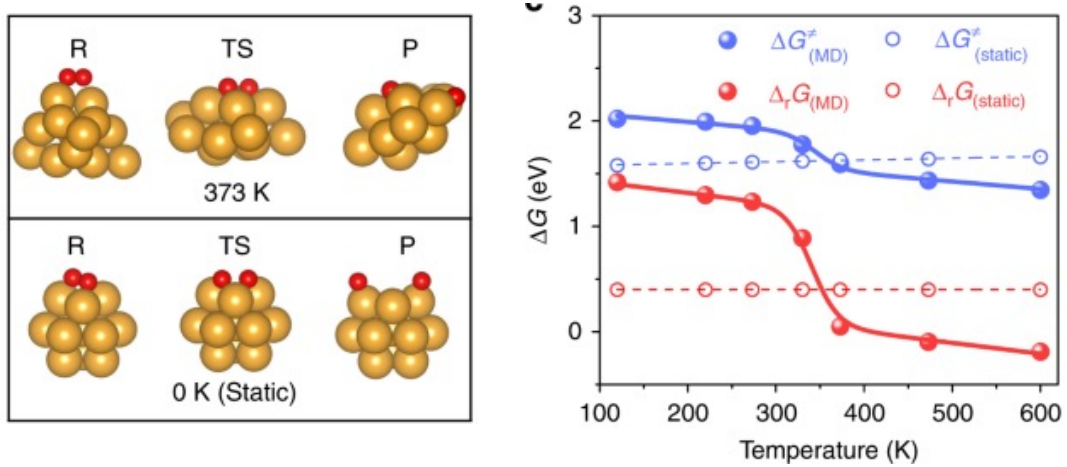
V. Rozsa, G. Galli, et al. PNAS 115 (27), 6952-6957 (2018)

Solid-state and Nanomaterials



A. Greenwood, G. Galli. Nano Lett. 18, 255 (2018)

Clusters and molecule-surface phenomena

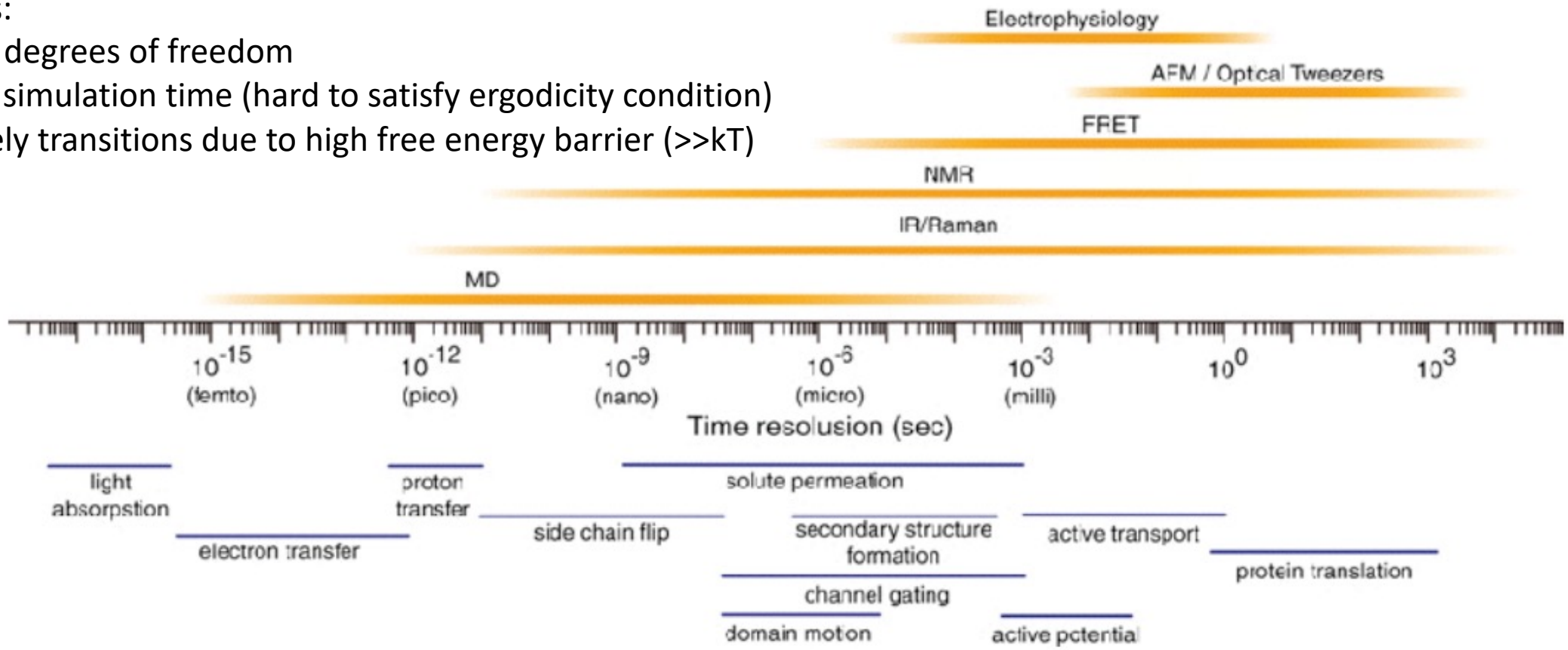


J-J Sun and J. Cheng. Nat. Commun. 10, 5400 (2019)

Computational challenges

Complications:

- Many degrees of freedom
- Finite simulation time (hard to satisfy ergodicity condition)
- Unlikely transitions due to high free energy barrier (>>kT)



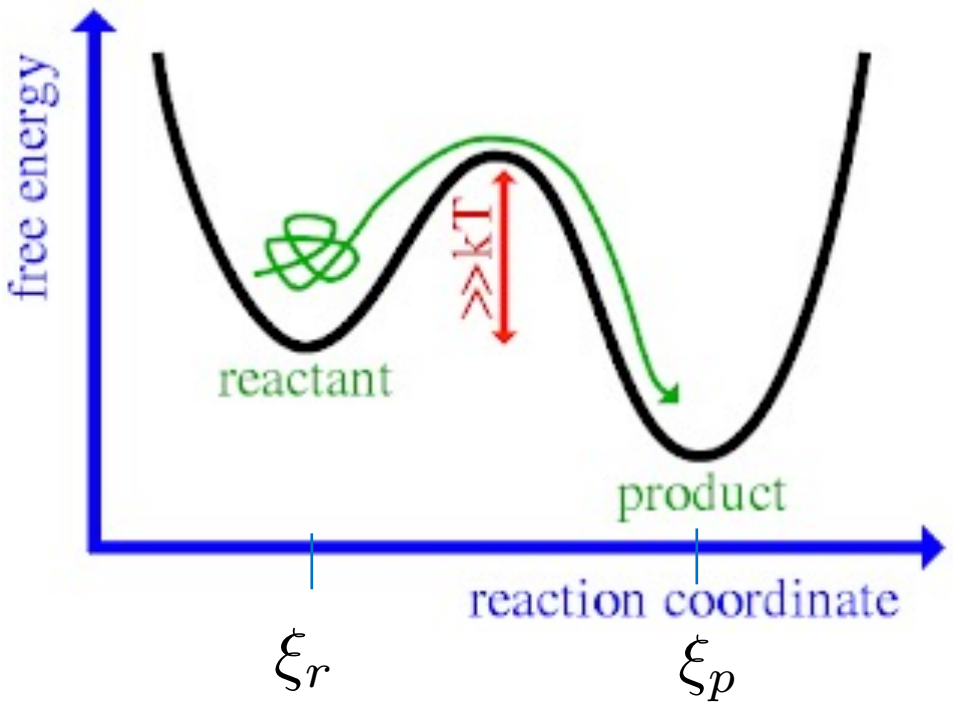
Rare events: Phase transition, chemical reaction, ion transport, …

What can we do? Parallel computing, hardware, **software/simulation techniques**

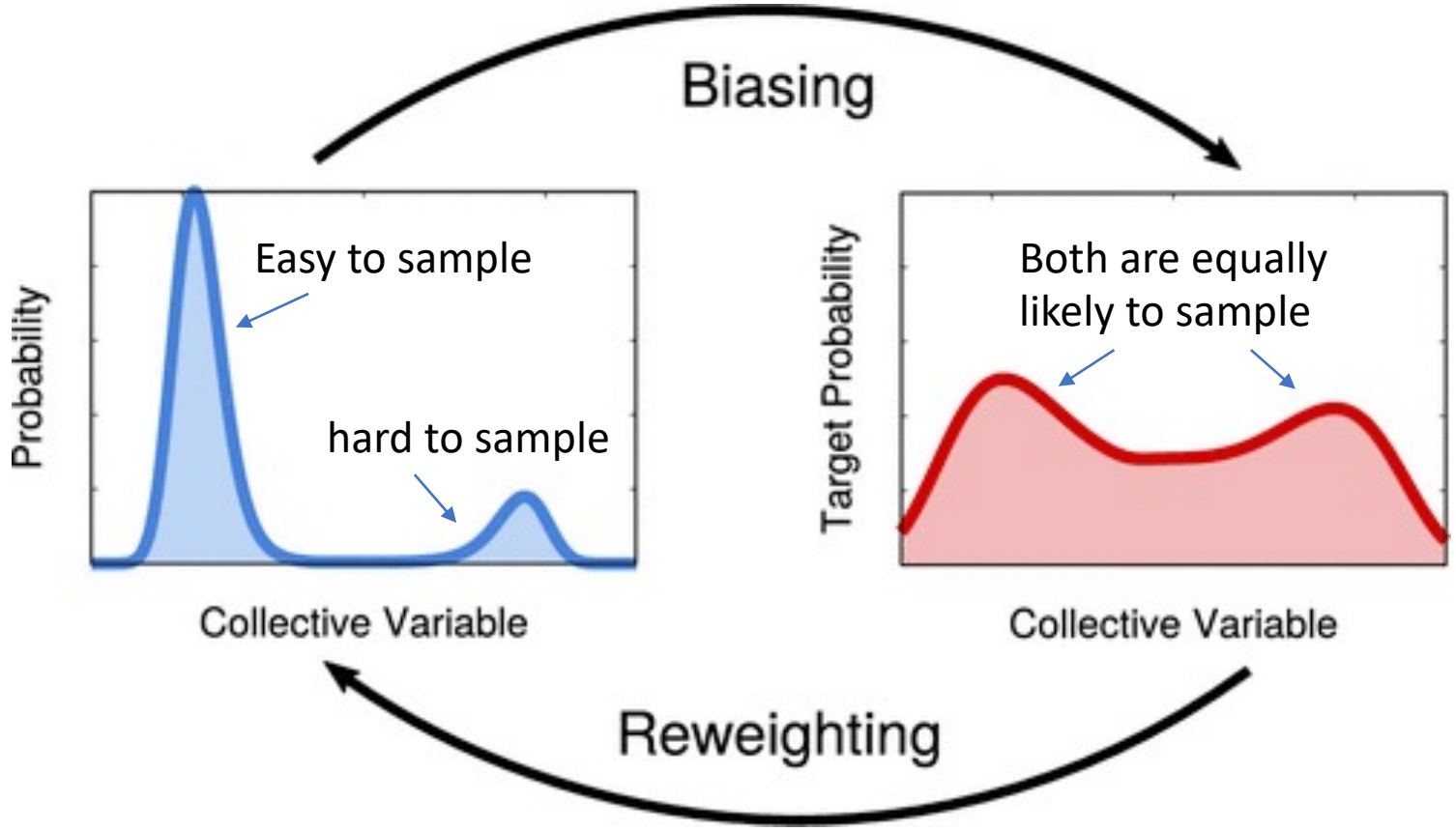
Coupling FPMD with enhanced sampling

FPMD with enhanced sampling

Transitions with high barrier



Enhanced sampling strategy



CV based methods, e.g, umbrella sampling, metadynamics, adaptive biasing force
Non-CV based methods, e.g., parallel tempering (replica-exchange)

Examples of FPMD and enhanced sampling

With Metadynamics

Structural changes in SiO_2

R. Martonak. D. Donadio, A. R. Orrganov. And M. Parrinello. Nature Mater. 5, 623 (2006)

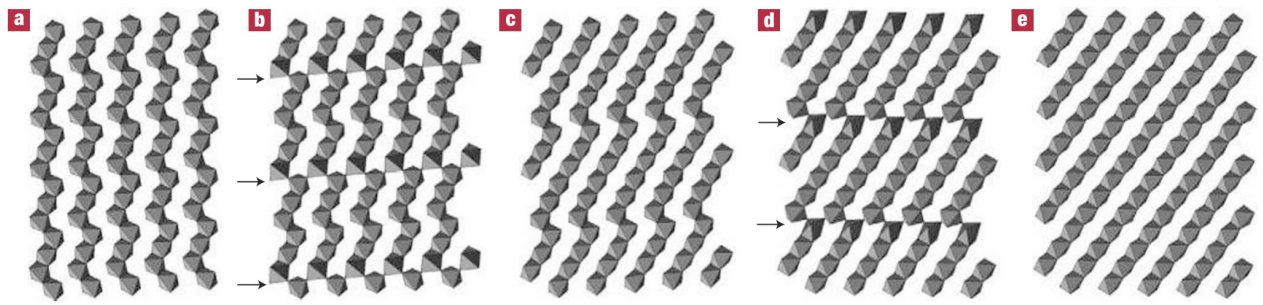


Figure 2 Transition from the 3 × 2 structure to stishovite. a–e, Two steps of the transition from the 3 × 2 structure (**a**) to stishovite (**e**). Elimination of the kinking of octahedral chains proceeds via an intermediate 6 × 2 structure (**c**). The arrows denote the presence of corner-sharing octahedra in the transition states (**b**) and (**d**).

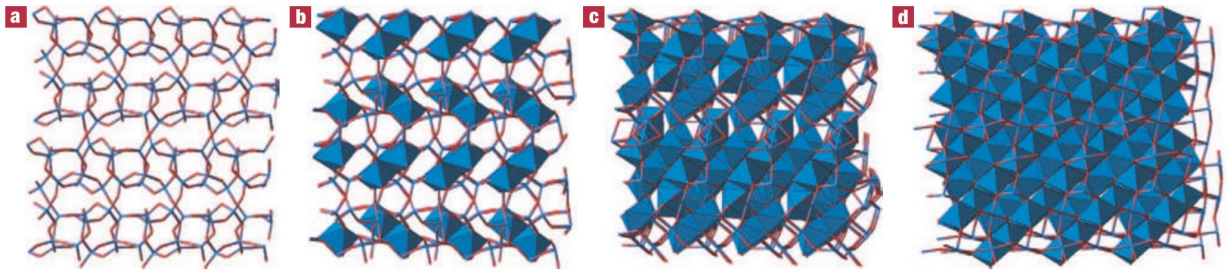
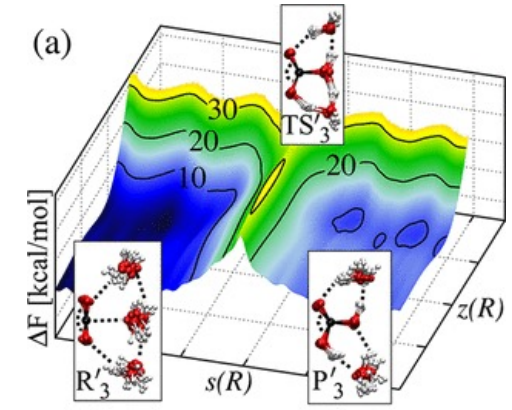
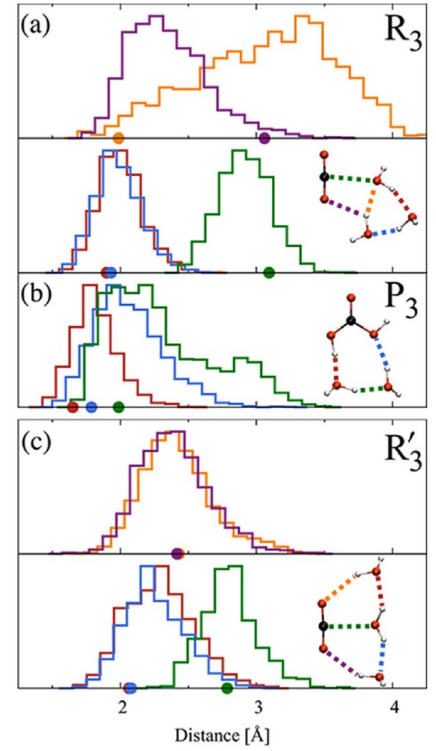


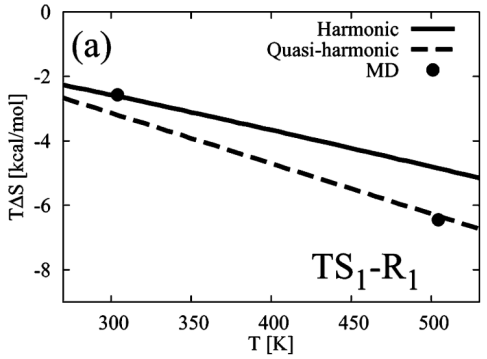
Figure 4 Transition from coesite to the α-PbO_2 phase. a–d, Structural evolution during the transition from coesite (**a**) to the α-PbO_2 phase (**d**). Intermediate states (**b**) and (**c**) show the initial growth and competition of chains of octahedra in different planes.

Chemical reaction of CO_2 and water

G. A. Gallet, G. Pietruccci, W. Andreoni. JCTC, 8, 4029 (2012)





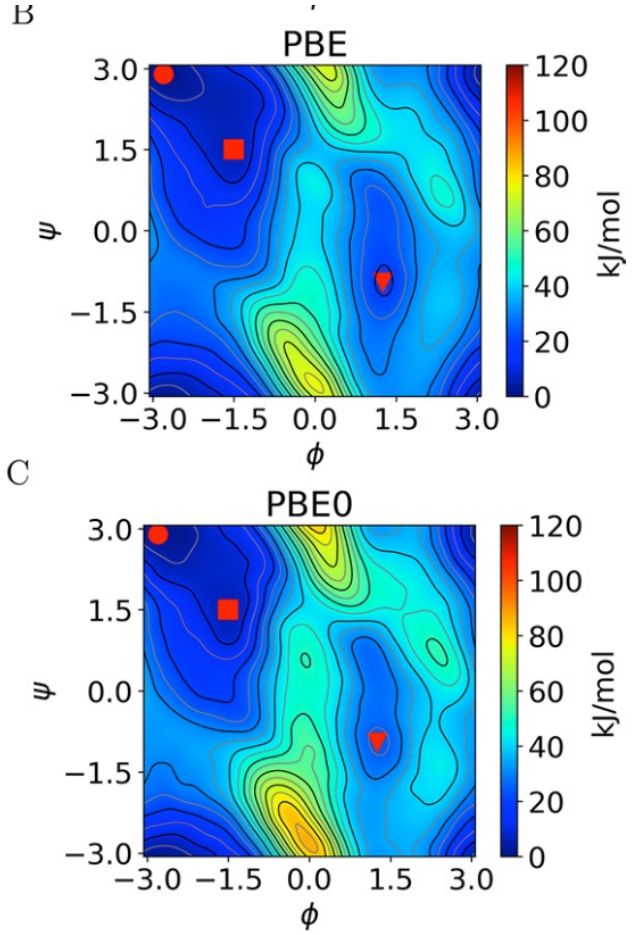


$CO_2 + n\ H_2O \rightarrow H_2CO_3 + (n\text{-}1)\ H_2O$

FPMD and enhanced sampling

Alanine dipeptide beyond DFT-GGA

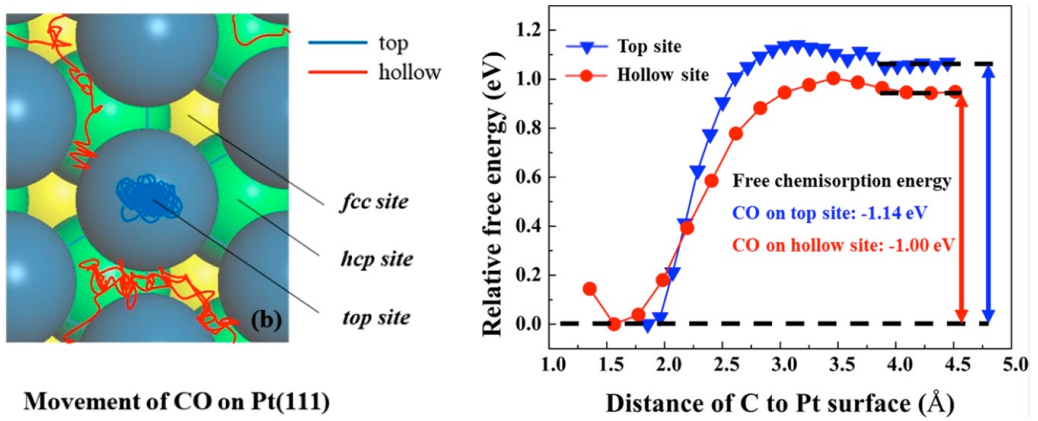
E. Sevgen. F. Gygi, J. de Pablo et al, JCTC, 14, 2882 (2018)



Adaptive biasing force

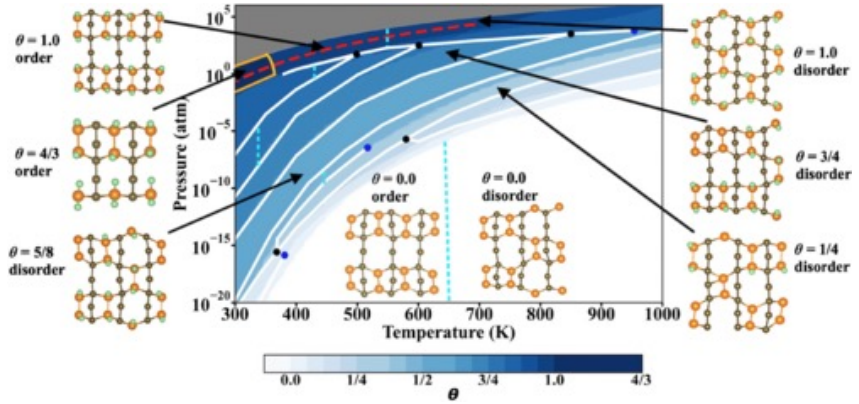
Molecular adsorption and reaction on surfaces

C. Guo, H-F. Wang, P. Hu, et al. JPCC, 122, 21478 (2018)



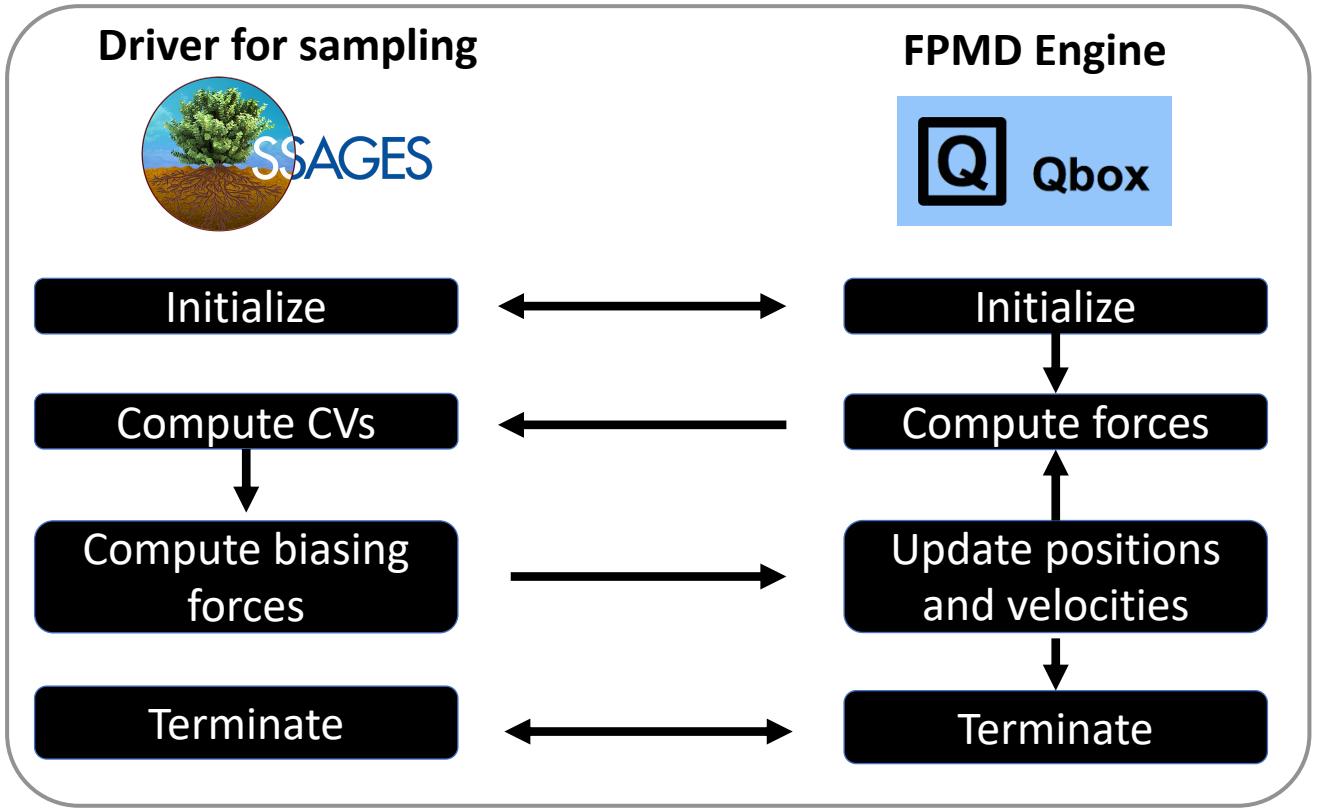
Umbrella sampling and accelerated MD

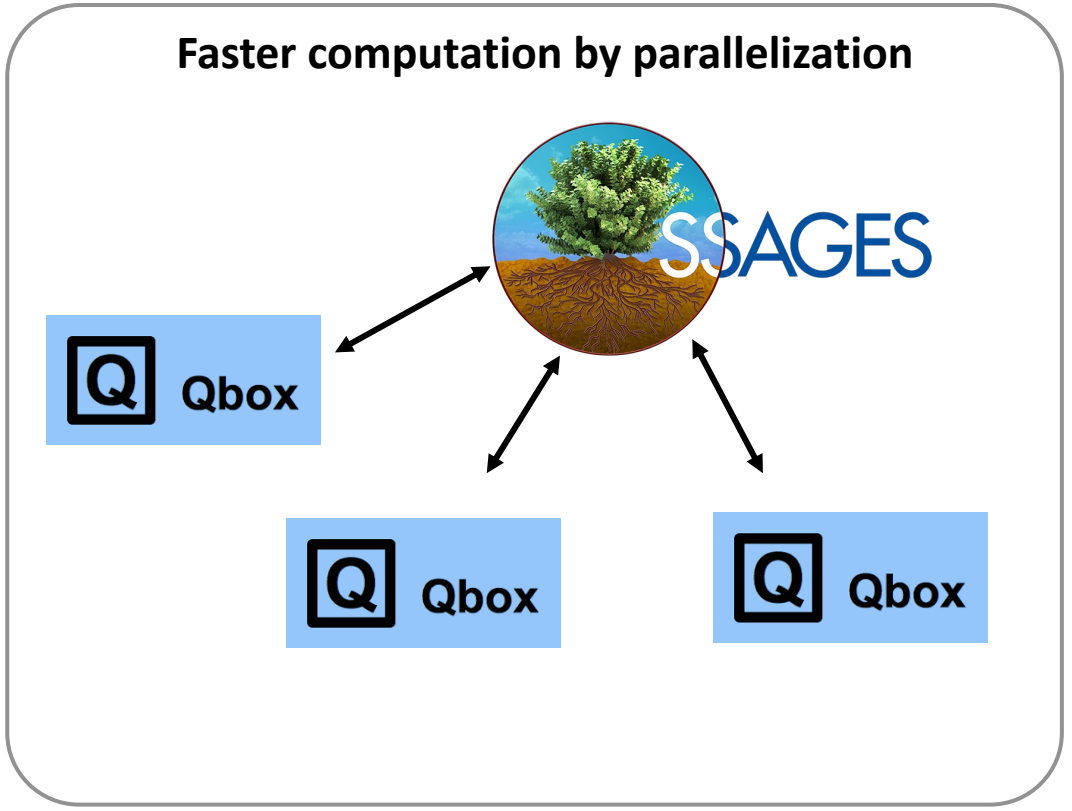
Y. Zhou, L. Ghiringhelli, et al, PRL, 128, 246101 (2022)



Replica exchange

Computational framework for FPMD-enhanced sampling simulations





E. Sevgen, F. Giberti, H. Sidky, J. Whitmer, G. Galli, F. Gygi, J. de Pablo, JCTC, 14, 2882 (2018)

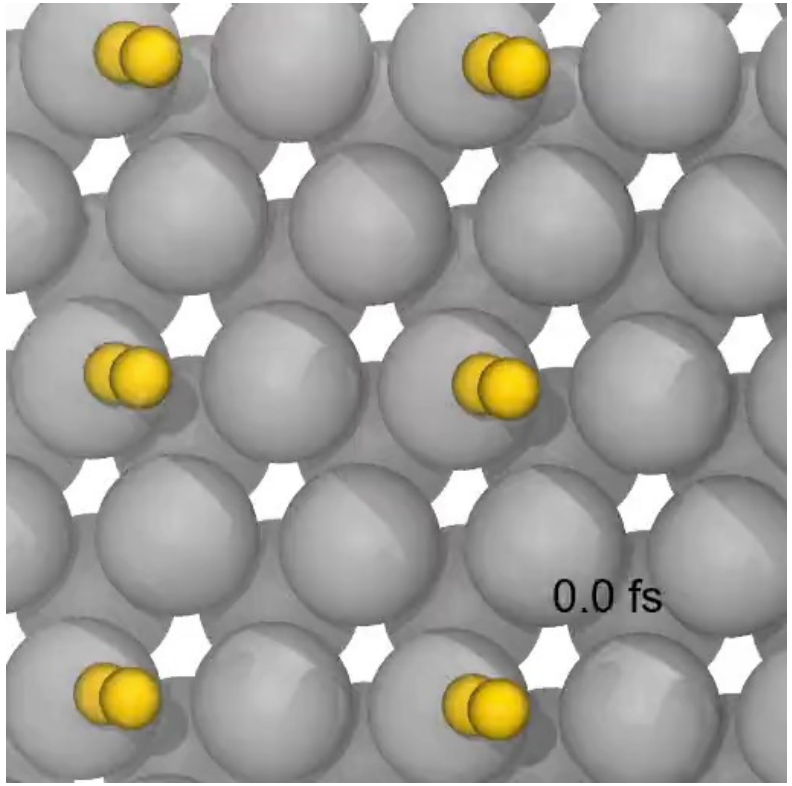
Greater user flexibility and expanded engines via PySAGES

https://github.com/SSAGESLabs/PySAGES

MICCoM

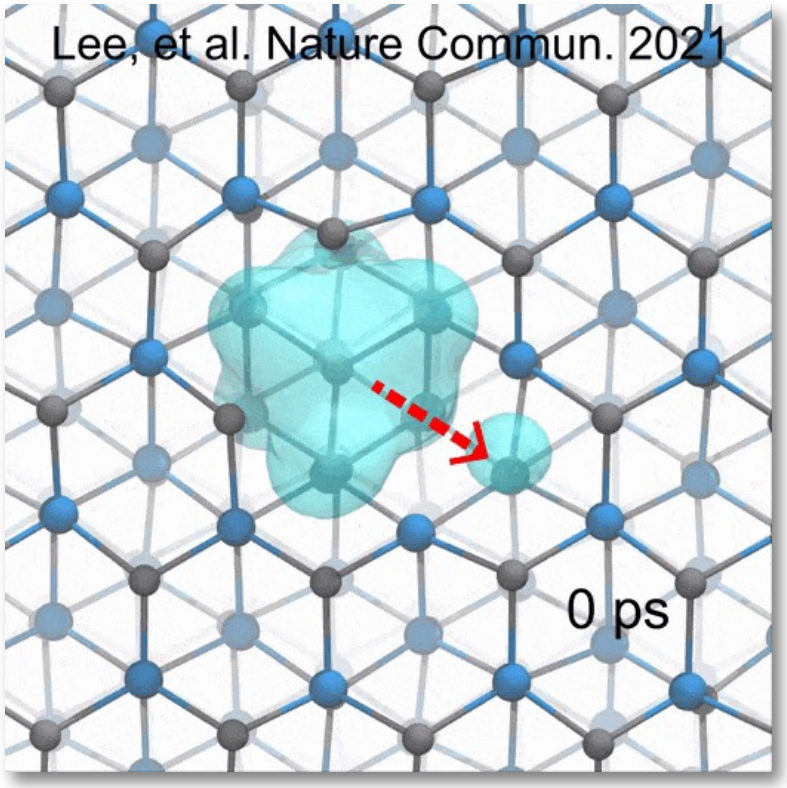
Applications to solid-state and surface reactions using SSAGES-Qbox

Nitrogen gas dissociation on metal surface



EMY Lee, T. Ludwig, B. Yu, A. Singh, F. Gygi, J. K. Norskov, J. J. de Pablo.
J. Phys. Chem. Letters 12, 2954-2962 (2021)

Electron spin defect formation in silicon carbide



E. M.Y. Lee, A. Yu, J. J. de Pablo, and G. Galli.
Nature Communications 12, 6325 (2021)

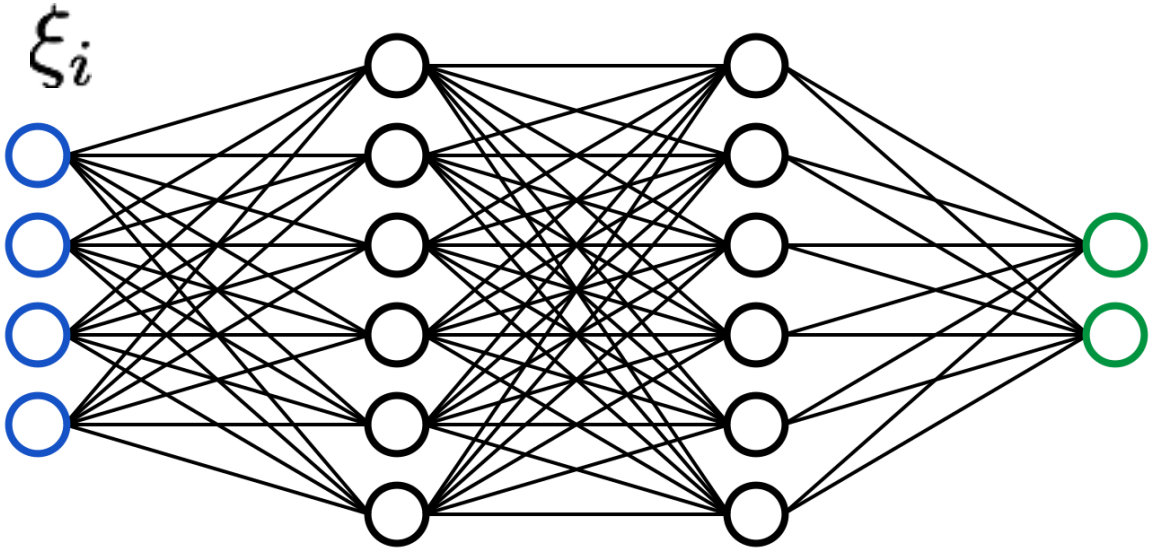
Adaptive biasing with machine learning methods

$$F_{\text{bias}} = -Q(\xi^*)\nabla\xi$$

Input

Biased probability distribution, P_i

Mean forces, F_i



Output

Free energy, Q

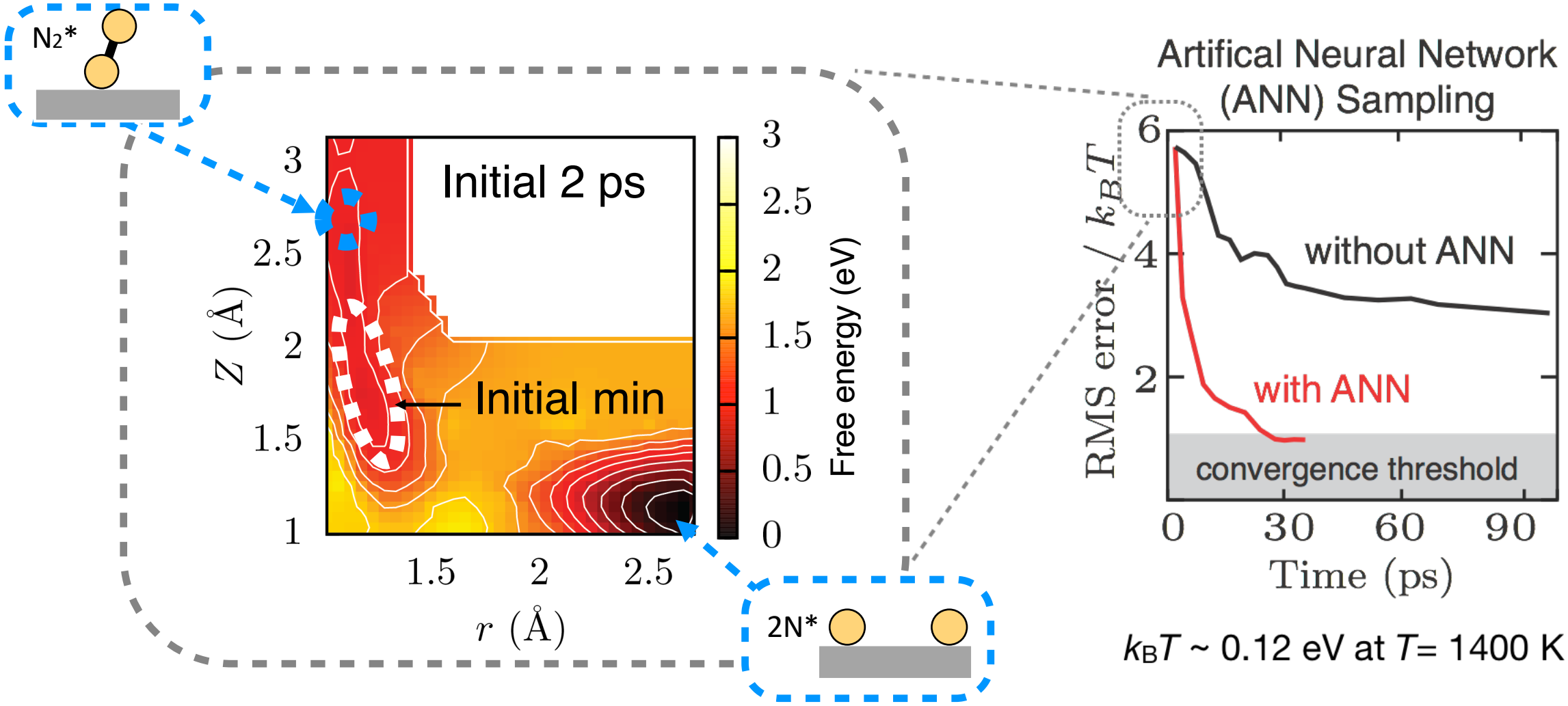
In SSAGES/PySAGES

- **ANN Sampling:** H. Sidky & J. Whitmer, JCP, 148, 104111 (2018)
- **FUNN:** A. Z. Guo, J. de Pablo, et al. JCP, 148, 134108 (2018)
- **CFF:** E. Sevgen, J. de Pablo, et al. JCTC, 16, 1448 (2020)
- **SIREN:** P. F. Zubieta Rico & J de Pablo. arXiv:2202.01876 (2022)

J. Zhang. Y. I. Yang, F. Noe, JPCL, 10, 5791 (2019)

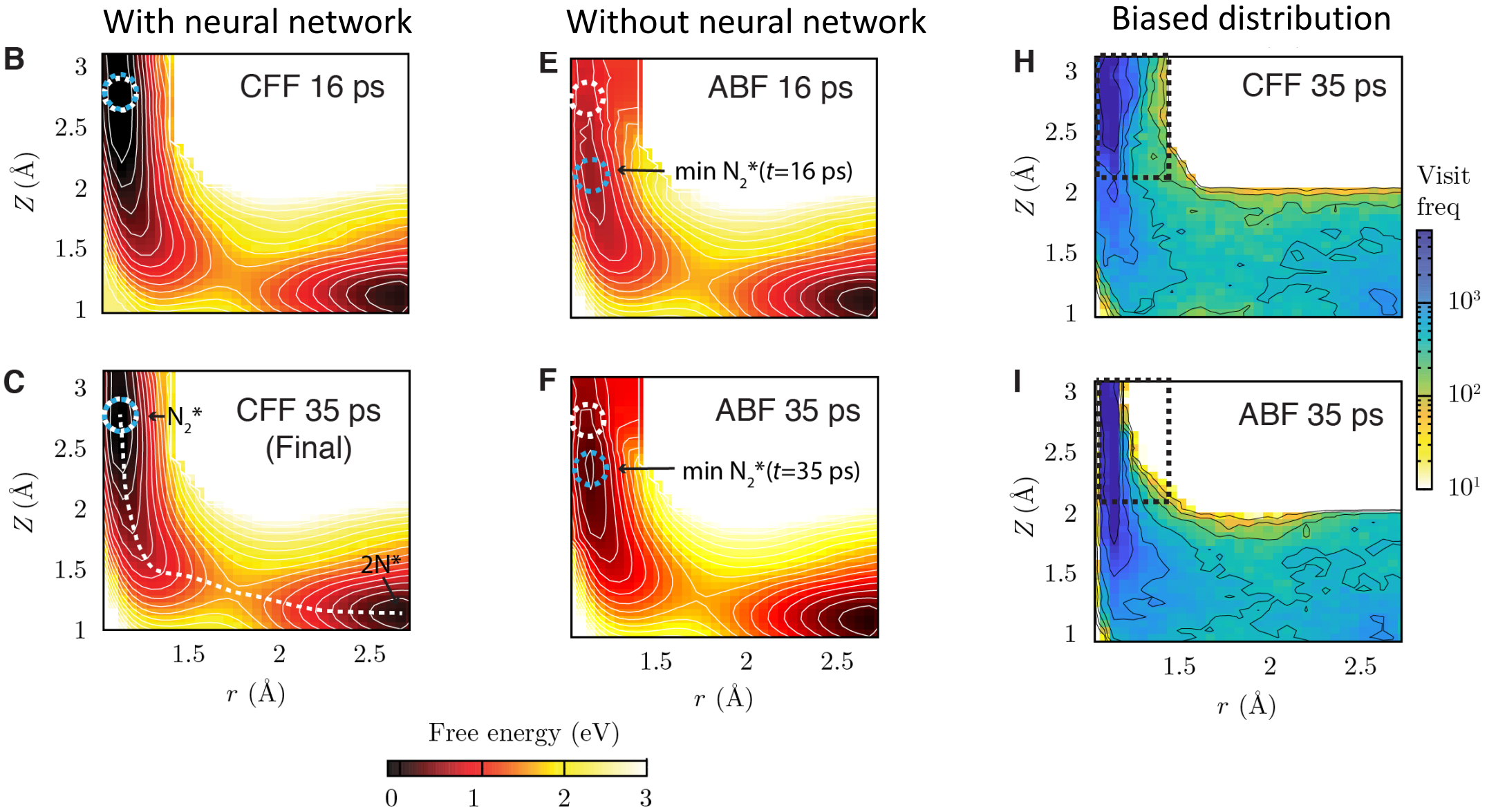
L. Bonati, Y-Y Zhang, M. Parinello. PNAS, 116, 17641 (2019)

Free energy calculations: with and without neural networks



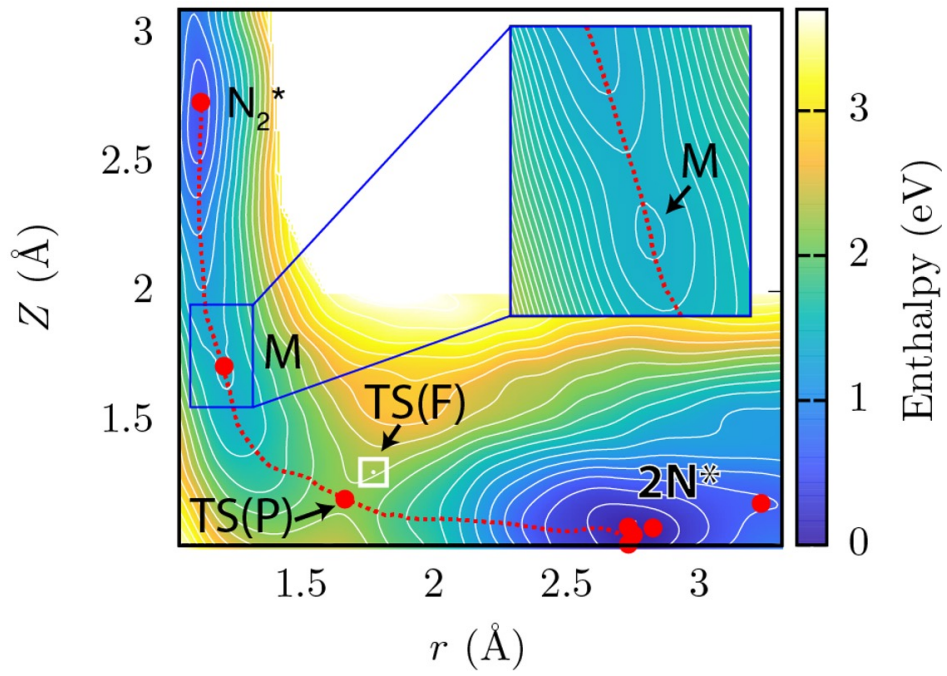
EMY Lee, T. Ludwig, B. Yu, A. Singh, F. Gygi, J. K. Norskov, J. J. de Pablo. *J. Phys. Chem. Letters* 12, 2954-2962 (2021)

Accelerated sampling with neural networks

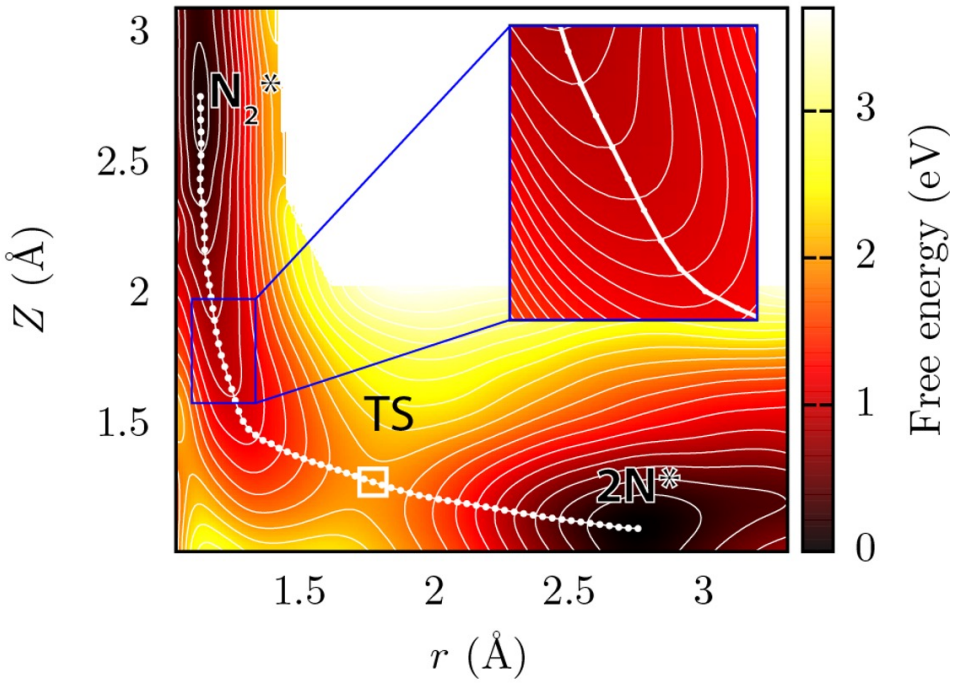


The need to identify critical points on the free energy surface

Enthalpy



Free energy



EMY Lee, T. Ludwig, B. Yu, A. Singh, F. Gygi, J. K. Norskov, J. J. de Pablo. *J. Phys. Chem. Letters* 12, 2954-2962 (2021)

Opportunities for simulating complex chemical reactions

Applications to solid-state and surface reactions

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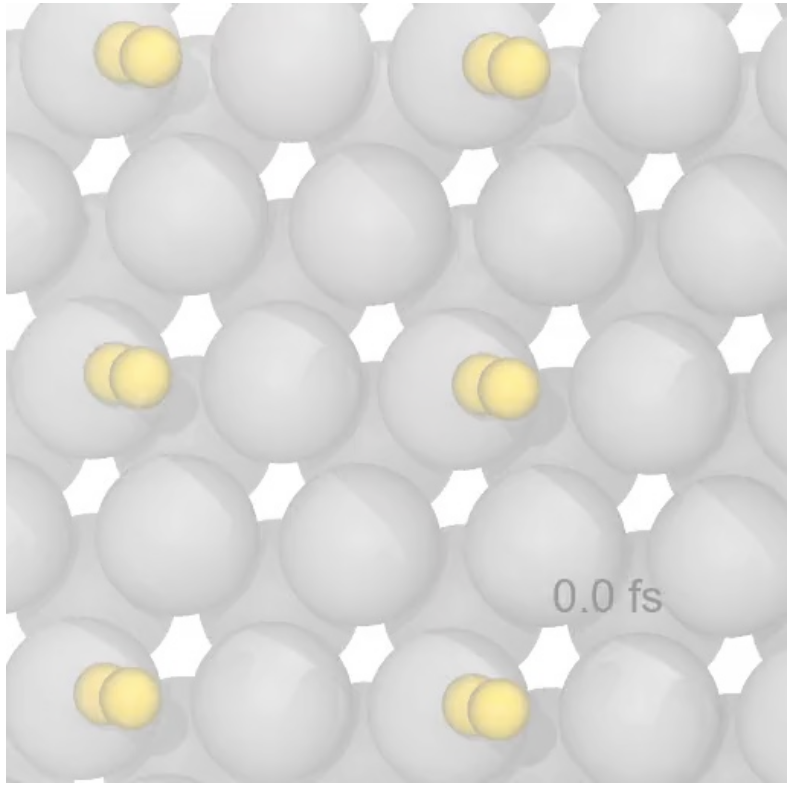

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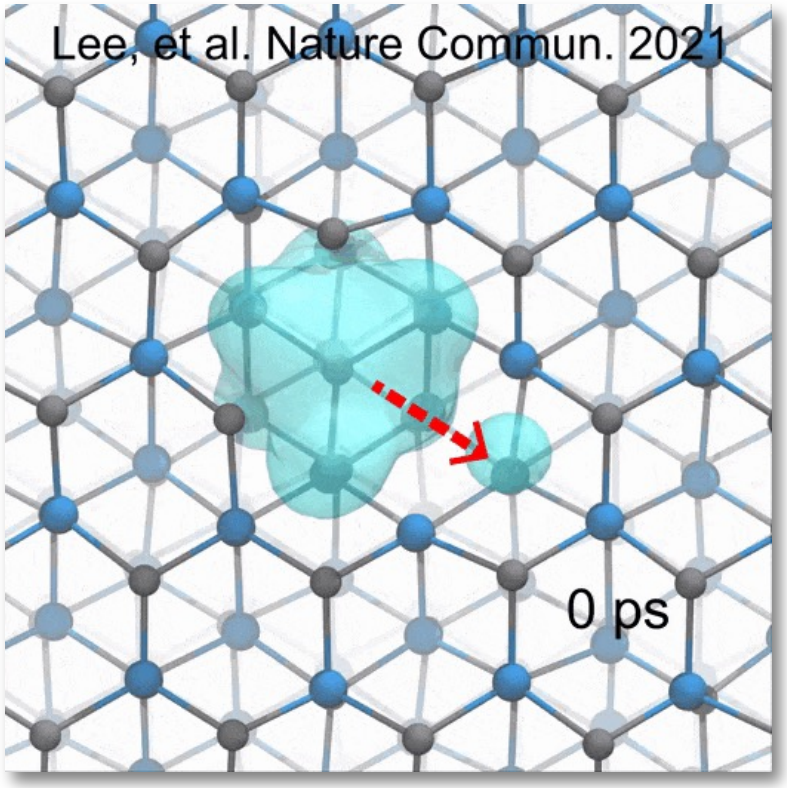
Electron spin defect formation in silicon carbide



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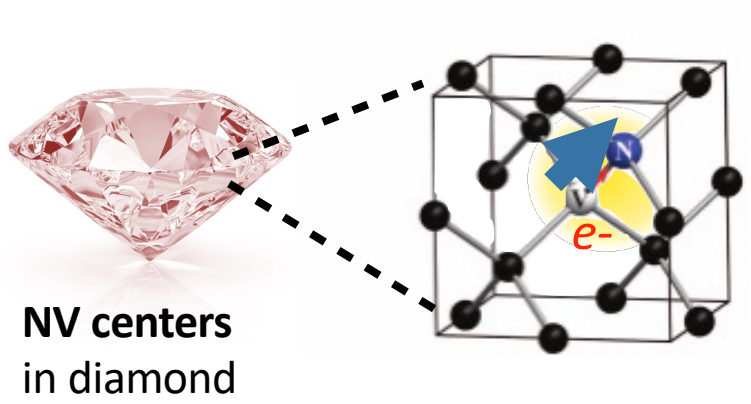
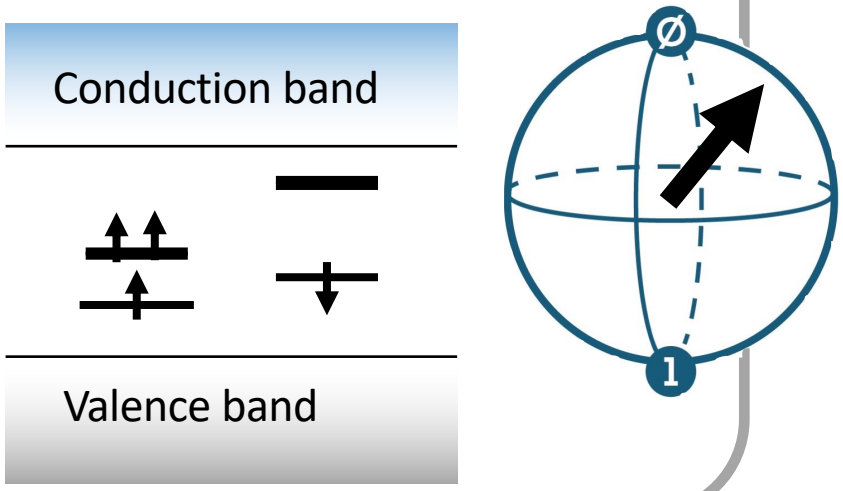
Nature Communications 12, 6325 (2021)

Creating quantum bits using defects in semiconductors

Solids with spin defects



NV centers
in diamond

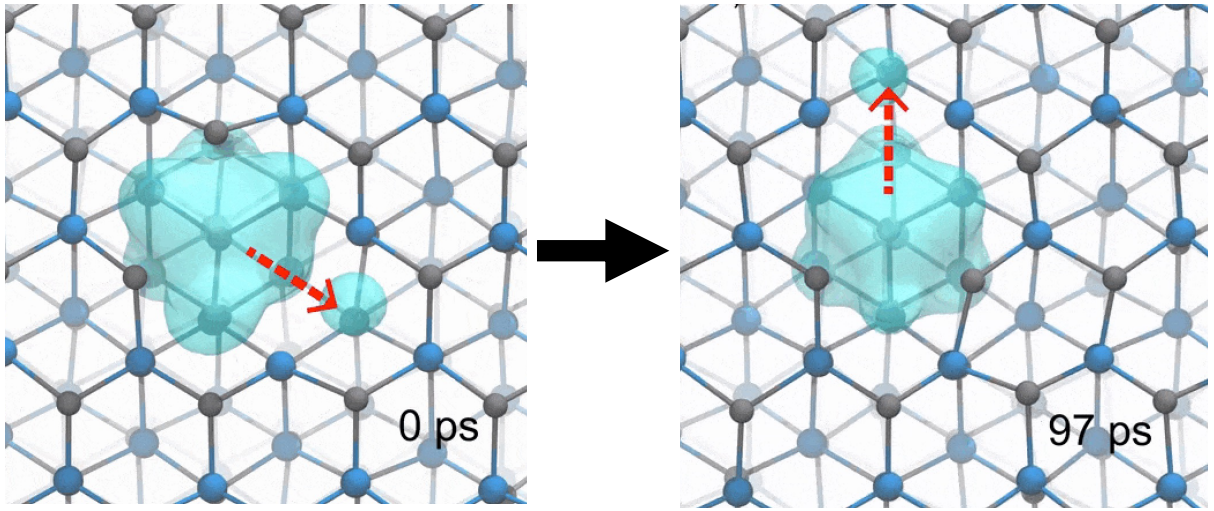


Motivation for FPMD + enhanced sampling:

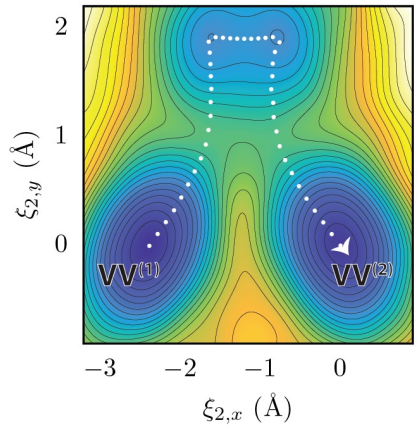
- Defect formation at high temperatures, $T > 1000$ K
- Bond breaking and formation
- Strong electronic properties
- Limited accuracy for defects and for solids using force fields (i.e., classical MD)

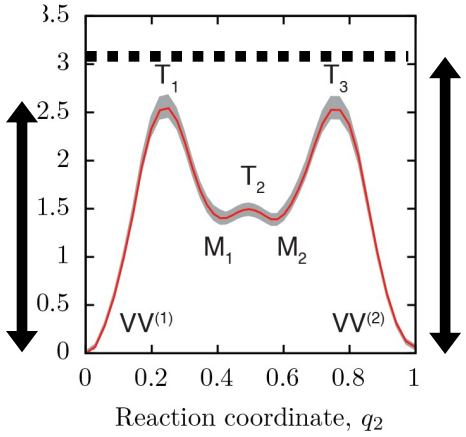
Changes in the crystallographic orientation of VV without dissociation

Crystallographic reorientation



Free energy surface from FPMD





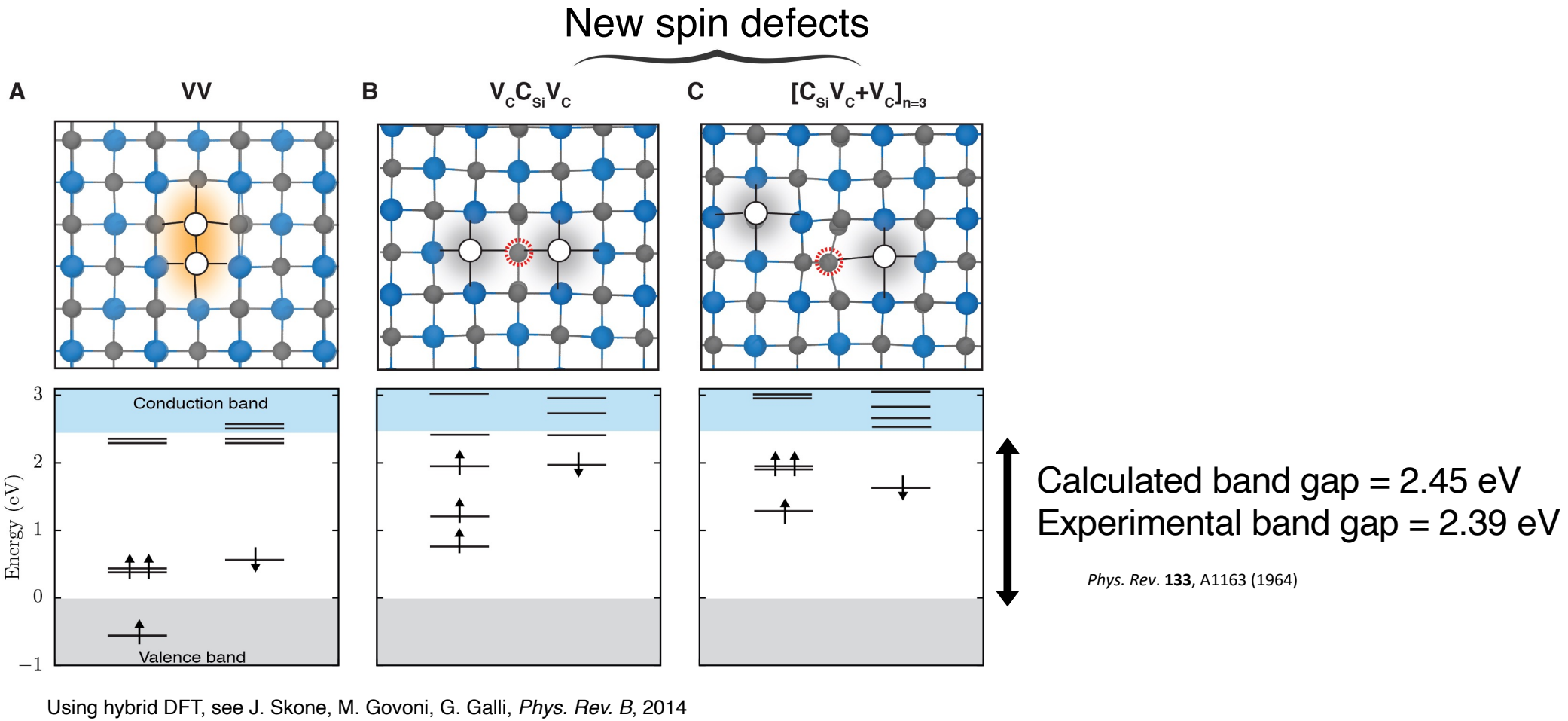
Energy to reorient ~2.5 eV

Energy to dissociate ~3.1 eV

EMY Lee, et al, *Nature Commun.* (2021)

Spin defects can be reoriented controllably without destroying it

New spin defects from high temperature simulations (T > 1000 K)



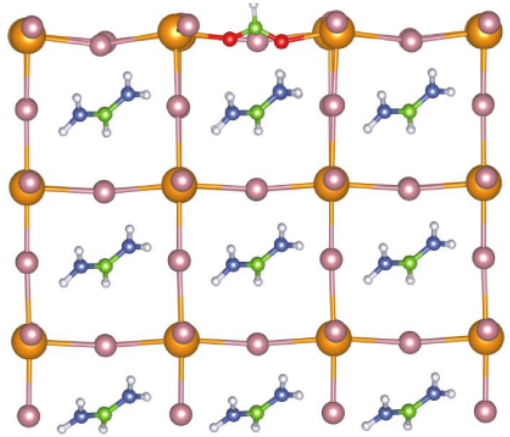
Using hybrid DFT, see J. Skone, M. Govoni, G. Galli, *Phys. Rev. B*, 2014

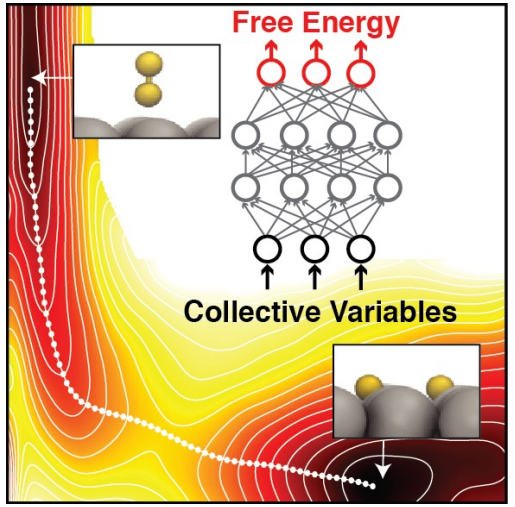
E. M.Y. Lee, A. Yu, J. J. de Pablo, and G. Galli. *Nature Communications* 12, 6325 (2021)

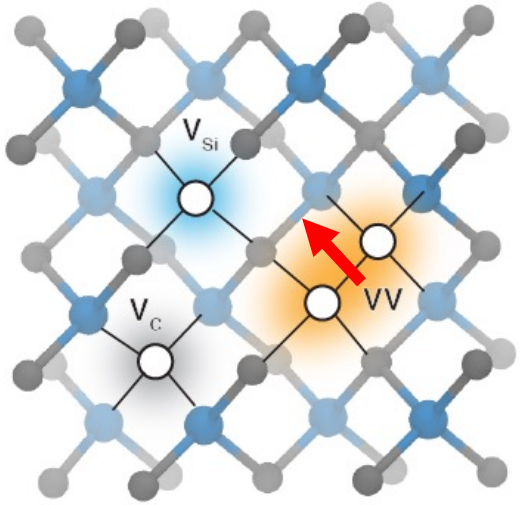
Opportunities for discovering of spin defects using dynamical simulations and *ab initio* methods

Outlook on FPMD with enhanced sampling

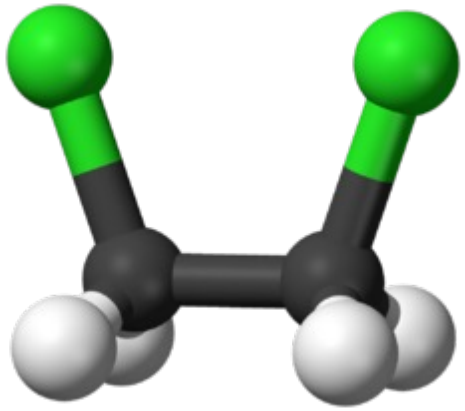
- Need for systems with strong dynamical and electronic descriptions
- Development of enhanced sampling strategies tailored to FPMD applications
- Discovery of new chemical species and materials from *ab initio*







Example: Dichloroethane isomerization



CV: Cl-C-C-Cl angle

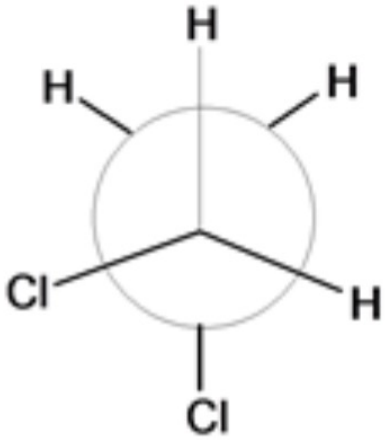
Learning objectives:

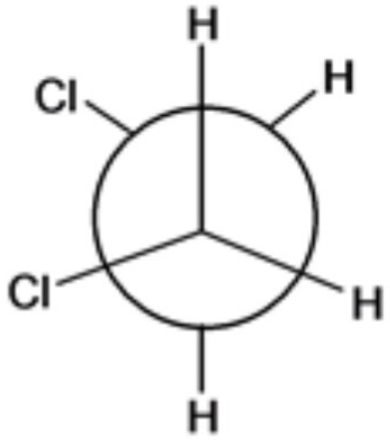
1. Setting up enhanced sampling with FPMD
2. Understanding SSAGES and Qbox inputs/outputs
3. Analyzing raw data for free energy calculations

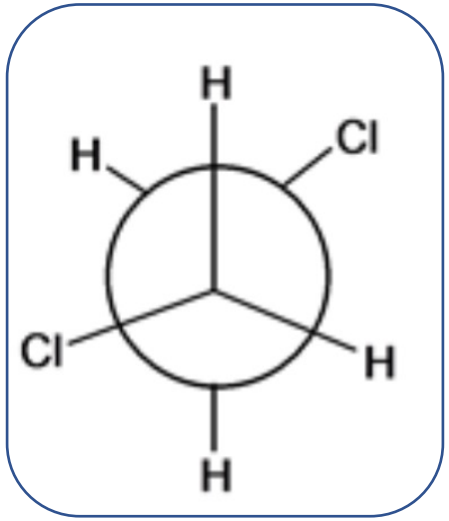
SSAGES

Q Qbox

Dichloroethane

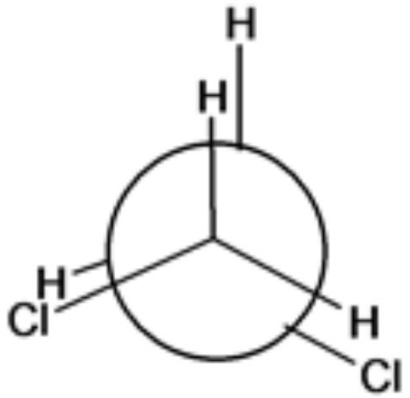


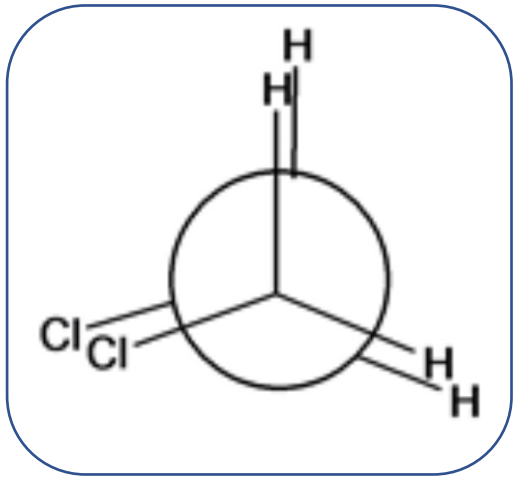




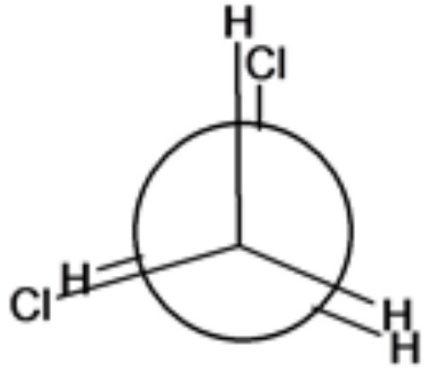
trans-

Staggered conformations (energy min)





cis-



Eclipsed conformations (energy max)

Commands: log into LCRC and prepare the system

1. Logging into LCRC with X-forwarding
ssh -X -Y [username]:bebop.lcrc.anl.gov

2. Copy the tutorial files
cd
cp -r /lcrc/project/MICCoM-train/qbox-ssages_tutorial/dichloroethane/ .

3. Equilibration using Qbox
cd dichloroethane/step1_eqm
Open input files (e.g., use vi/vim): md.i, job-b.sbatch

4. Submit job
sbatch --job-name=qs_eqm job-b.sbatch
Takes about 4-5 minutes

5. [Optional, while waiting] Testing X-forwarding
Try both login node & interactive node
module load gcc/8.2.0-xhxgy33 mesa/21.0.3-uottzmb vmd/1.9.3
Vmd

If fails, download VMD to a local computer
https://www.ks.uiuc.edu/Development/Download/download.cgi?PackageName=VMD

Commands: check equilibration outputs

1. Logging in interactively to analyze eqm results

salloc -N 1 -n 1 -p knlall -t 01:00:00 -A miccom-train
module load gcc/8.2.0-xhxgy33 mesa/21.0.3-uottzmb vmd/1.9.3
module load gnuplot/5.0.6

2. Analyze qbox output

e.g., Changes in the Kohn-sham energy (etotal) and constant of the motion (econst)
../../scripts/econste.plt md.r
../../scripts/temp_ion.plt md.r

e.g., molecular dynamics trajectory
python2 ../../scripts/qbox_xyz.py md.r > md.xyz

vmd md.xyz

Commands: prepare and launch qbox-ssages jobs

1. FPMD with ABF using qbox-ssages
cd ~/dichloroethane/step2_eqm/
cd single_walker/

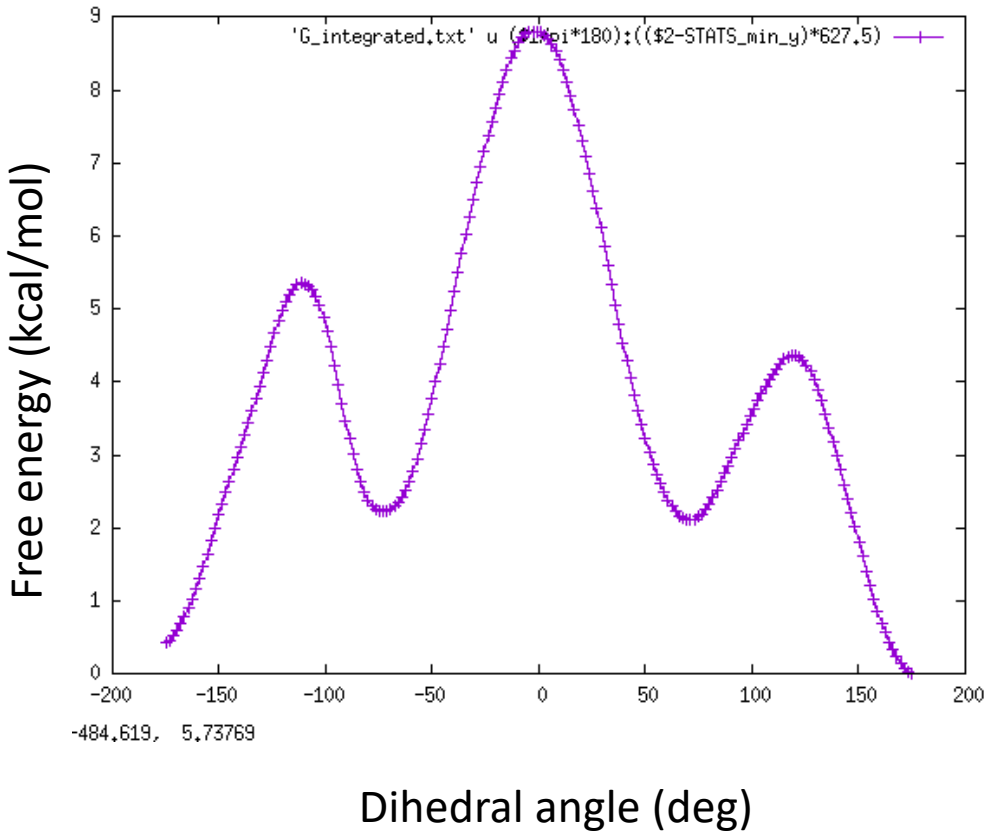
2. Single-walker ABF simulation
cd single_walker/
Open input files (e.g., use vi/vim): md.i, input.json, job-b.sbatch

sbatch --job-name=qs_1w job-b.sbatch

3. Analyze results
cd results
Open output files (e.g., use vi/vim): Nworld, F_out

Calculate free energy by integrating the mean forces
python ../../../scripts/ABF_integrator.py
gnuplot
plot 'G_integrated,txt' u 1:2

Apply unit conversions and define free energy min
stats 'G_integrated,txt' u 1:2
plot 'G_integrated,txt' u ($1/pi*180):(($2-STATS_min_y)*627.5) w lp



Commands: Analyze abf results

1. Post-process abf data

module load anaconda/4.4.0
python ../../../scripts/Qbox-xml-cleaning.py -i ssages_out_0_run_0.xml -o ssages_clean.xml
python2 ../../../scripts/qbox_xyz.py ssages_clean.xml > dce_out.xyz

2. **Interactive login to analyze enhanced sampling result**

salloc -N 1 -n 1 -p knlall -t 01:00:00 -A miccom-train
module load gcc/8.2.0-xhxgy33 mesa/21.0.3-uottzmb vmd/1.9.3
module load gnuplot/5.0.6

vmd dce_out.xyz
[Compare this with that of *step1_eqm*]

gnuplot
plot ‘cvs0.dat’ u 1:2 w p

Commands: [Optional] Multi-walker & restart

1. Multi-walker ABF simulation
cd multi_walker/
Open input files (e.g., use vi/vim): md*.i, input.json, job-b.sbatch

#Note: Using bdwall nodes in Bebop
sbatch --job-name=qs_4w job-b.sbatch

2. Analyze results
cd results

gnuplot
plot for [i=0:3] ‘cvs’.i.’.dat’ u 1:2

#Repeat steps 1&2 in Slide 24

3. restart from a previous ABF simulation
cd ../restart
Check changes in input.json!