University of Nottingham
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Ab initio molecular dynamics and machine learned potentials based molecular dynamics

Lei Lei: Lei.Lei2@nottingham.ac.uk

Sanliang Ling: Sanliang.Ling@nottingham.ac.uk

University of Nottingham

Outline

- Introduction to molecular dynamics
- *Ab inito* molecular dynamics (AIMD) using CP2K
- Hands on AIMD simulation and data analysis on Archer2
- Neural network potentials (NNP) as force evaluation method
- Hands on MD simulation using NNP

Goals of Molecular Dynamics simulations and data analysis

- MD simulations: obtain trajectory data by solving equations of motion

$$F_i = m_i \ddot{r}_i$$

Newton

$$\mathcal{H}(r,p) = \frac{|p|^2}{2m} + \mathcal{U}(r)$$

Hamiltonian

- MD data analysis: calculate ensemble average of properties from trajectory data

$$\langle A \rangle = \int P(p,t)A(p,r)dpdr = \int A\big(p(t),r(t)\big)dt$$

A: target property, P: probability, p: momenta, r: position

Ensembles in MD

Ensemble: all microstates (r, p) accessible to simulation, each microstate occurring with a particular probability

Various possibilities for quantities that may be conserved or fixed in the simulation include:

N: particle number

V: volume

P: pressure

E: energy

T: temperature

μ: chemical potential (not implemented in CP2K)

- NVE: microcanonical
- NVT: canonical
- NPT: isothermal-isobaric

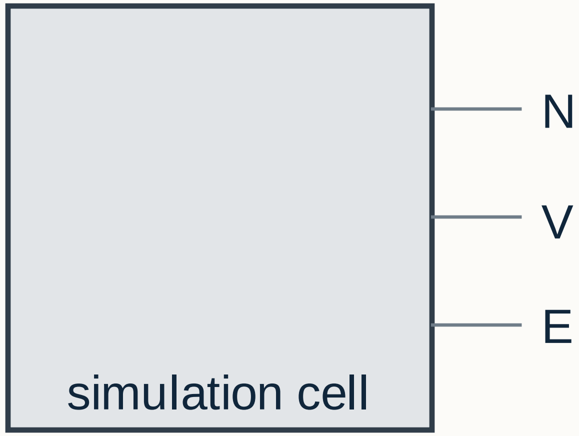
Ensembles in MD: NVE

Isolated system with constant number of particles N, volume V and energy E

Total energy is conserved as the system is isolated

Solving equations of motion without temperature or pressure control

$$F_i = m_i \ddot{r}_i$$



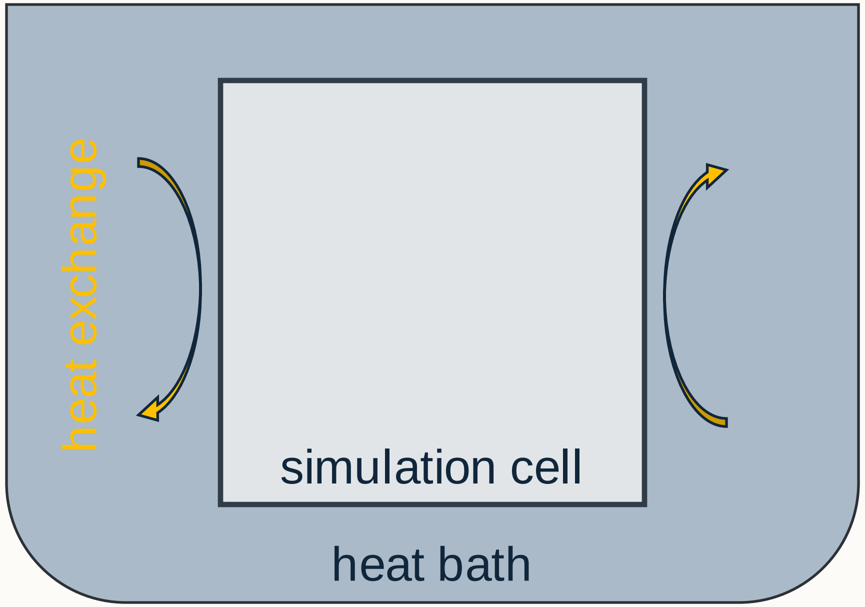
- Drift in E due to rounding and truncation errors
- Dynamical variables well defined
- Required initial conditions: positions and velocities

Ensembles in MD: NVT

System with constant number of particles N, volume V and temperature T (controlled by a thermostat)

Total energy is no longer conserved

- Energy exchange between system and heat bath exists
- Constant of motion: energy of the system + heat bath

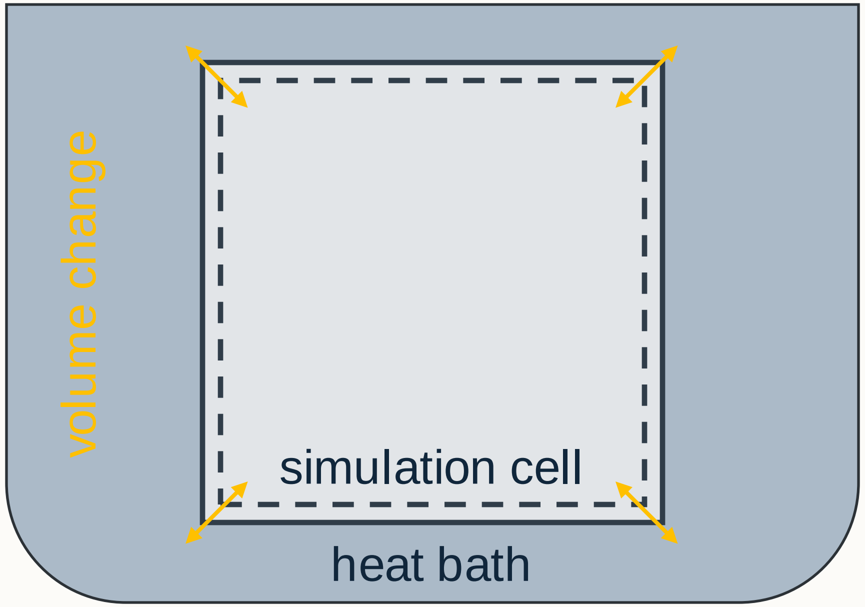


Ensembles in MD: NPT

System with constant number of particles N, pressure P (controlled by a barostat) and temperature T (controlled by a thermostat)

Box size/shape is allowed to change in response to internal stress and external pressure

Energy exchange with the environment: $dW = PdV$



Constant of motion =
energy of the system +
energy of the thermostat +
energy of the barostat

Ensembles in CP2K

```
&MOTION
&MD
ENSEMBLE NVE
STEPS 1000
TIMESTEP 0.5
TEMPERATURE 300.0
&END MD
&END MOTION
```

Choices:

- NVE: microcanonical
- NVT: canonical
- NPT_F: isobaric-isothermic
- NPT_I: isobaric-isothermic in isotropic cell
- NPE_F: constant pressure
- NPE_I: constant pressure in isotropic cell
- LANGEVIN: canonical using Langevin dynamics
- ISOKIN: constant kinetic energy
- HYDROSTATICSHOCK, MSST, MSST_DAMPED, NVT_ADIABATIC …

Thermostats: velocity rescaling

Obtain desired temperature T_0 by a factor:

$$\lambda = \sqrt{\frac{T_0}{T(t)}}$$

$$\Delta T = \frac{1}{2}\sum_{i=1}^{N}\frac{2}{3}\frac{m_i(\lambda v_i)^2}{Nk_B} - \frac{1}{2}\sum_{i=1}^{N}\frac{2}{3}\frac{m_i v_i^2}{Nk_B} = (\lambda^2 - 1)T(t)$$

Straight forward

Does not correspond to any ensemble

Thermostats in CP2K: LANGEVIN

Add a dissipative frictional force and a stochastic force:

$$m\ddot{r}_i = -\frac{\partial U}{\partial r_i} - m\Gamma\dot{r}_i + W_i(t)$$

Γ: friction coefficient
W: random force

Relation between magnitude of force and friction:

$$\langle W_i(t), W_j(t')\rangle = \partial_{ij}\partial(t-t')6m\Gamma k_B T$$

Magnitude of the perturbation depends on the instantaneous temperature

Surprisingly useful in practice!

Schneider and Stoll, PRB (1978)

Thermostats in CP2K: LANGEVIN

Produces canonical ensemble (NVT)

Local thermostat

Ergodic

Allows the use of large time steps

But:

- does not conserve momentum (due to drag force)
- only useful for sampling, cannot be used to calculate transport properties, *e.g.*, diffusion coefficient

Schneider and Stoll, PRB (1978)

Thermostats in CP2K: Nosé-Hoover (chains)

Add two additional degrees of freedom:

- s – position of imaginary heat reservoir
- p_s – conjugate momentum of imaginary heat reservoir

Additional parameter

- Q – effective mass

$$p_s = \frac{\partial \mathcal{L}}{\partial \dot{s}} = Q\dot{s}$$

Momenta conjugate to $\boldsymbol{r}_i$:

$$\boldsymbol{p}_i = \frac{\partial \mathcal{L}}{\partial \dot{\boldsymbol{r}}_i} = m_i s^2 \dot{\boldsymbol{r}}_i$$

Hamiltonian:

$$H_N = \sum_i \frac{\boldsymbol{p}_i^2}{2m_i s^2} + \mathcal{U}(\boldsymbol{r}^N) + \frac{p_s^2}{2Q} + g k_B T \ln s$$

Nosé, JCP (1984)

Thermostats in CP2K: Nosé-Hoover (chains)

```
&MOTION
&MD
&THERMOSTAT
TYPE NOSE
&NOSE
TIMECON 1000
&END NOSE
&END THERMOSTAT
&END MD
&END MOTION
```

- Produces canonical ensemble (NVT)
- Local thermostat
- Ergodic (Nosé-Hoover chain only)
- Second order – temperature may oscillate around target

Thermostats in CP2K: CSVR

Kinetic energy:

$$dK = \sum_i \frac{f_i \cdot p_i}{m_i} dt + (\bar{K} - K)\frac{dt}{\tau} + 2\sqrt{\frac{K\bar{K}}{N_f}}\frac{dW}{\sqrt{\tau}} \left(\tau = \frac{1}{2\gamma}\right)$$

Thermostat part:

$$dK = \boxed{(\bar{K} - K)\frac{dt}{\tau}} + \boxed{2\sqrt{\frac{K\bar{K}}{N_f}}\frac{dW}{\sqrt{\tau}}}$$

Berendsen thermostat

Noise gives correct fluctuations

Bussi, Donadio and Parrinello JCP (2007)

Thermostats in CP2K: CSVR

```
&MOTION
&MD
&THERMOSTAT
TYPE CSVR
REGION GLOBAL
&CSVR
TIMECON 50
&END CSVR
&END THERMOSTAT
&END MD
&END MOTION
```

- Stochastic velocity rescaling for $\tau = 0$
- Correct fluctuations
- Reserves dynamic properties
- Recovers Langevin for single degree of freedom

Thermostats in CP2K: tips

- Use a small `TIMECON` for rapid equilibration
- Default `TIMECON` is usually OK for production MD
- Check `PROJECT-1.ener` file, ensure that the constant of motion is conserved
- Check large fluctuations in temperature
- Almost all of the same options apply for barostats
  - `MOTION%MD%BAROSTAT`

Result files from a CP2K MD simulation

`PROJECT-1.cell` →	Cell parameters
`PROJECT-1.ener` →	Restart input script
`PROJECT-1.restart` →	Restart input script
`PROJECT-1.stress` →	Stress tensor
`PROJECT-frc-1.xyz` →	Forces on each atom
`PROJECT-pos-1.xyz` →	Atomic positions
`PROJECT-vel-1.xyz` →	Velocities of each atom

Output settings in CP2K: PRINT

```
&PRINT
&TRAJECTORY SILENT
FORMAT  XMOL
&EACH
MD  10
&END EACH
&END TRAJECTORY
…
&END PRINT
```

set write frequency

```
&PRINT
…
&CELL  SILENT
&EACH
MD  10
&END EACH
&END CELL
…
&END PRINT
```

IR, NMR spectra calculation input settings: refer to [spectroscopy tutorial]

Write cell parameters when using NPT ensemble

Force evaluation in CP2K: DFT

```
&FORCE_EVAL
METHOD  QS
STRESS_TENSOR  ANALYTICAL
&DFT
…
&END DFT
&END FORCE_EVAL
```

Use Quickstep to calculate force

Include this if using NPT

DFT settings here according to purpose

Check manual for options and explanations: [CP2K manual]

Check energy conservation

Plot `PROJECT.ener` file

- use Jupyter Notebook
- use gnuplot

If the constant of motion is not well conserved, try to:

- make `EPS_SCF` tighter (to reduce drift)
- make `TIMESTEP` shorter (to reduce fluctuations)
- play with `EXTRAPOLATION_ORDER` (to reduce drift and or instabilities)

Restart MD simulation in CP2K

Backup original input script:

```
mv PROJECT.inp PROJECT.inp.bak
```

Make a new directory:

```
mkdir restart
```

Copy the input script and make changes on ensemble, steps etc and add:

```
&EXT_RESTART
RESTART_FILE_NAME PROJECT-1.restart
&END EXT_RESTART
```

Re-submit job

```
sbatch job.slurm
```

Alternatively, copy `PROJECT-1.restart and modify` as a new input script.

Data analysis of MD simulation

Trajectory visualisation: VMD, nglview

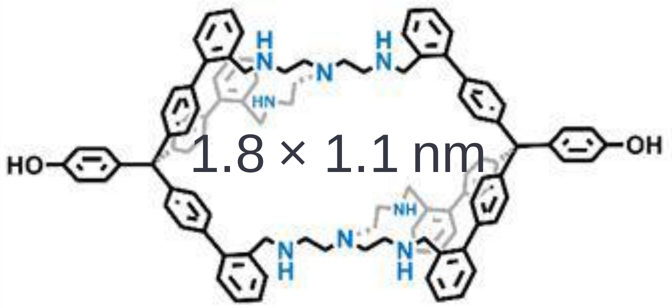
Transport property, eg. diffusion coefficient : MDtraj, ASE

Ensemble average of properties g(r) etc: MDtraj, TRAVIS

Vibration spectra: TRAVIS

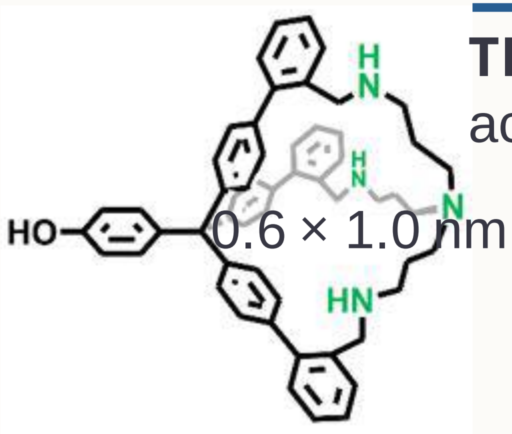
Example: water diffusion in supramolecular cages

Molecular Cage 1



React with

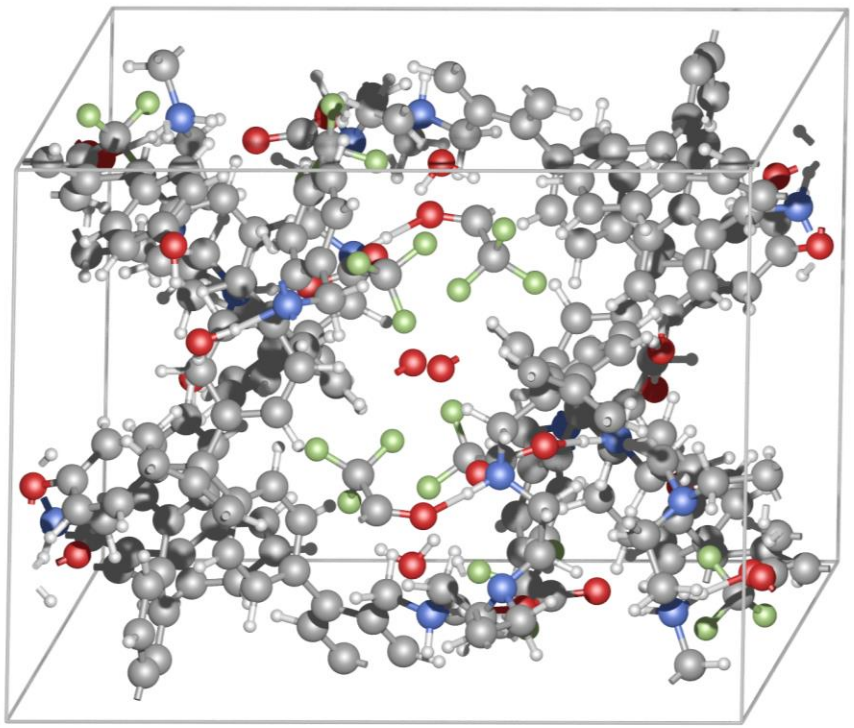
TFA: trifluoroacetic acid



Molecular Cage 2

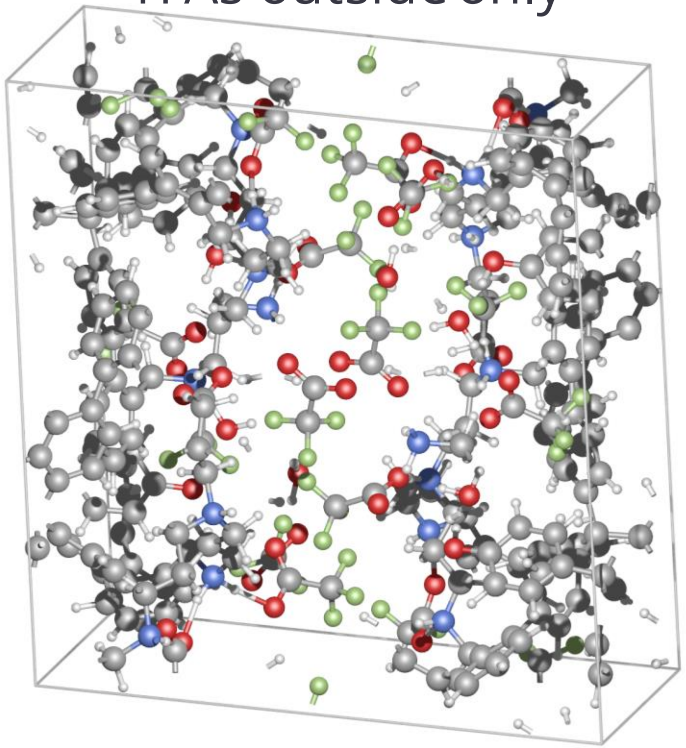
Cage 1

“Plum pudding”
TFAs inside and outside



Cage 2

“Sandwich”
TFAs outside only



My input settings

- Orbital transformation (OT) method
- Full single inverse considering the system size
- VDW

```
&MD
ENSEMBLE NVT
TIMESTEP 0.5
…
&THERMOSTAT
TYPE CSVR
&CSVR
TIMECON 50
&END CSVR
&END THERMOSTAT
&END MD
```

```
METHOD  QS
…
&SCF
&OT  T
MINIMIZER  DIIS
PRECONDITIONER
FULL_SINGLE_INVERSE
&END OT
…
&XC
…
&XC_FUNCTIONAL  NO_SHORTCUT
&PBE  T
&END PBE
&END XC_FUNCTIONAL
```

```
&VDW_POTENTIAL
POTENTIAL_TYPE
PAIR_POTENTIAL
&PAIR_POTENTIAL
TYPE  DFTD3
PARAMETER_FILE_NAME
dftd3.dat
REFERENCE_FUNCTIONAL PBE
CALCULATE_C9_TERM  T
&END PAIR_POTENTIAL
&END VDW_POTENTIAL
&END XC
```

My data analysis

Python code FishMol + ASE

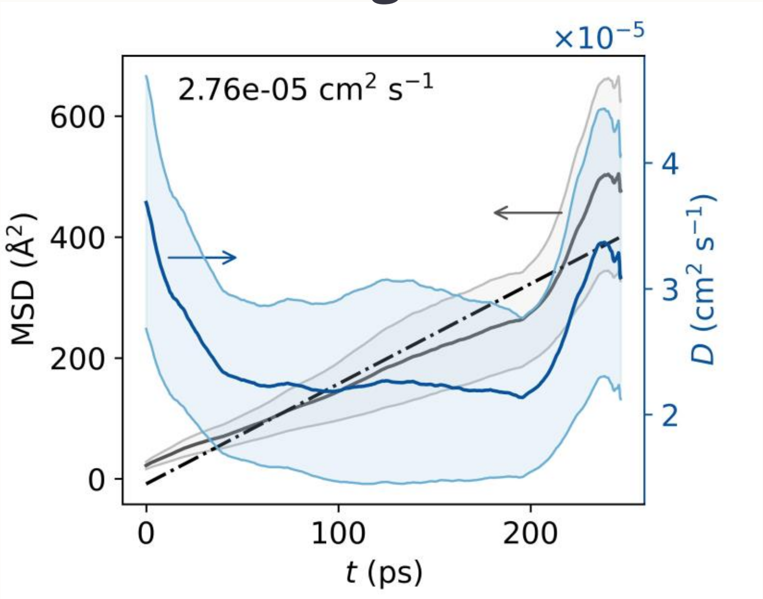
Properties:

- Diffusion coefficient using original trajectory
- H bond analysis using wrapped trajectory
  - H bond recognition
  - Radial distribution function, angular distribution function, combined distribution function
  - H bond lifetime analysis based on time auto correlation function

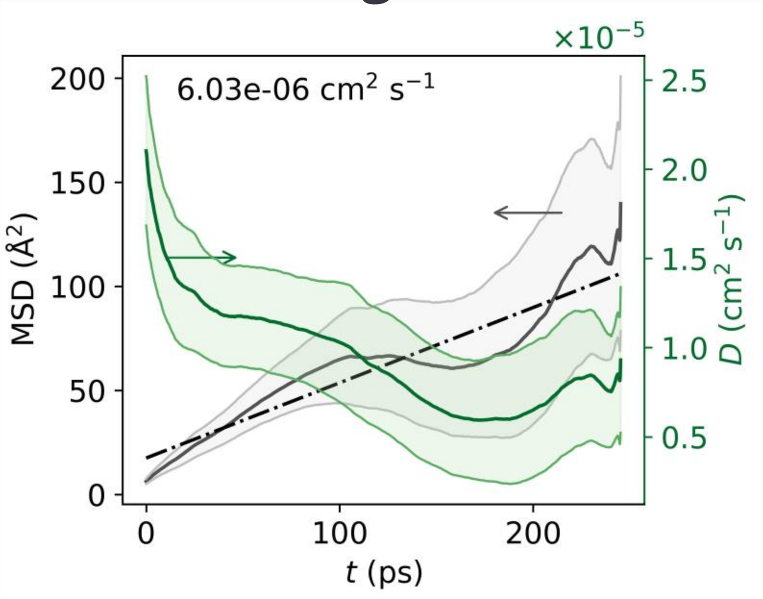
Example: water diffusion in supramolecular cages

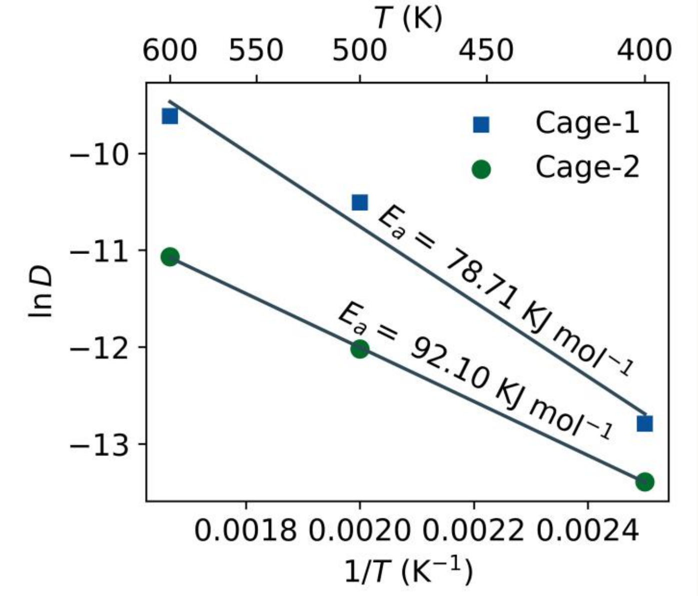
MSD: mean square displacement
D: water diffusion coefficient

Cage 1



Cage 2





Simulation: *D* of Cage 1 is **4.5** times larger
Experimental data: Cage 1 is **100** times more proton conductive

E_a: apparent activation energy

Example: water diffusion in supramolecular cages

Diffusion anisotropy

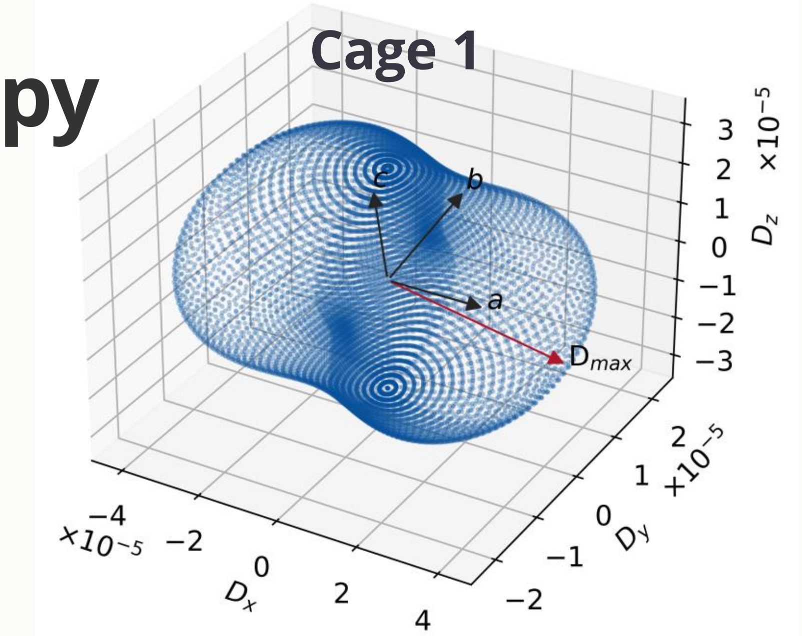
1D diffusion coefficients

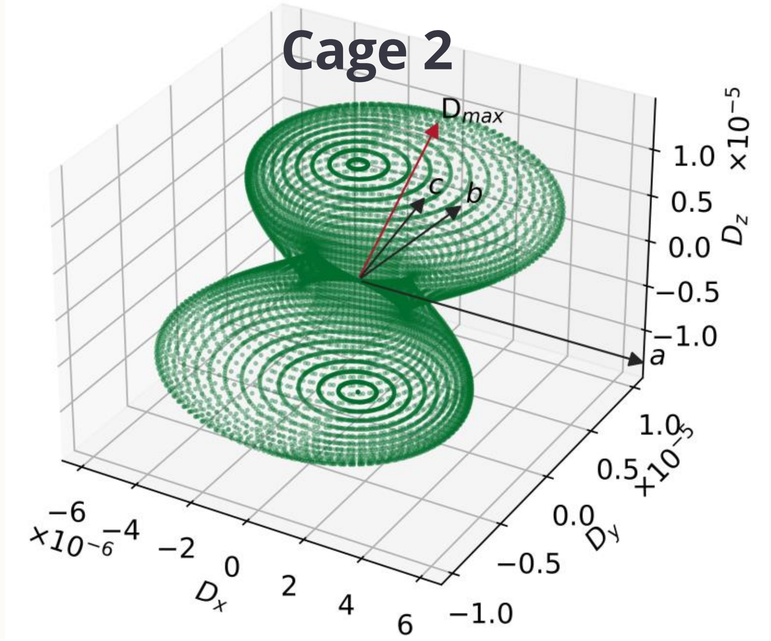
Cage 2 has a much smaller “neck”

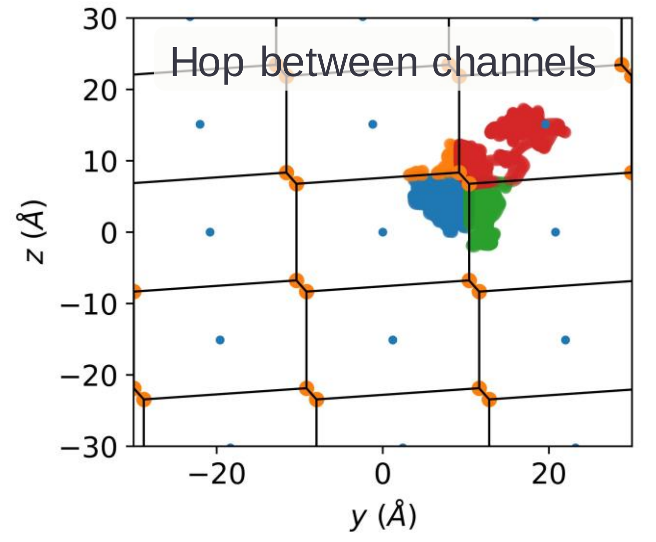
Voronoi diagrams of diffusion channels

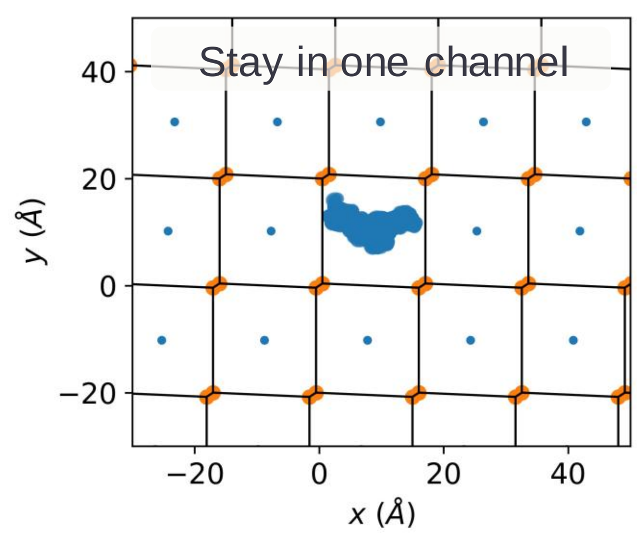
Cage 1: 7/8 switches channels
Cage 2: all stay inside channel

Polycrystalline samples:
high density of grain boundaries







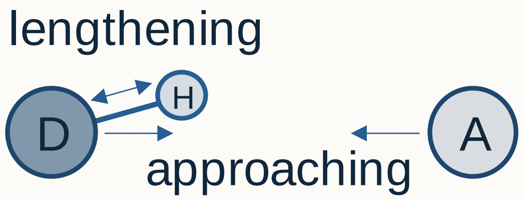


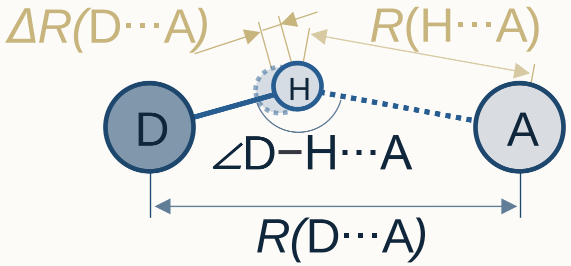
Example: water diffusion in supramolecular cages

Hydrogen bonding from geometry criteria

Formation of H bond

D: donor atom
A: acceptor atom





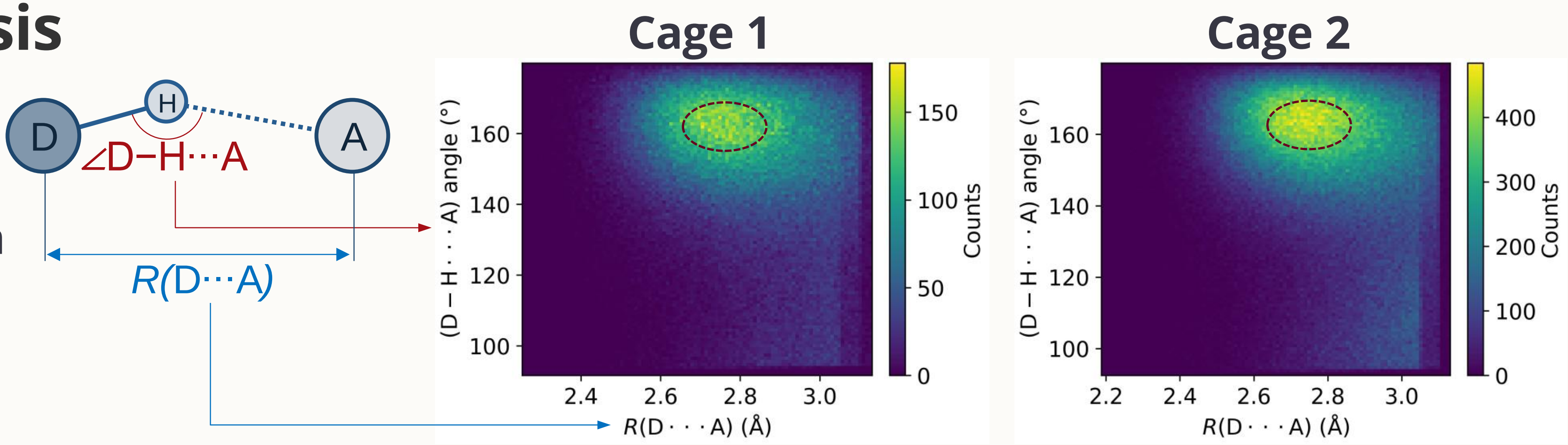
Geometry criteria	Strong	Moderate	Weak
D⋯A separation: *R*(D⋯A) (Å)	2.2 - 2.5	2.5 - 3.2	> 3.2
D−H⋯A angle: ∠D−H⋯A (°)	170 - 180	> 130	> 90
Lengthening of D−H: Δ*R*(D−H) (Å)	0.08 - 0.25	0.02 - 0.08	< 0.02
Proton acceptor distance: *R*(H⋯A) (Å)	1.2 - 1.5	1.5 - 2.2	> 2.2
D−H vs H⋯A	D−H ≈ H⋯A	D−H < H⋯A	D−H << H⋯A

Example: water diffusion in supramolecular cages

H bond analysis

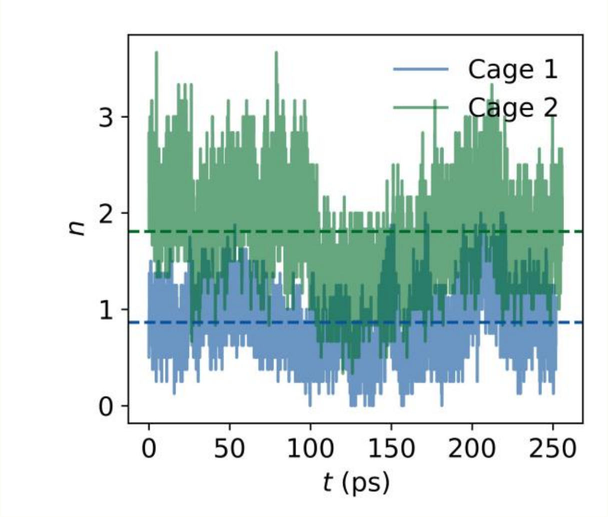
Strength:

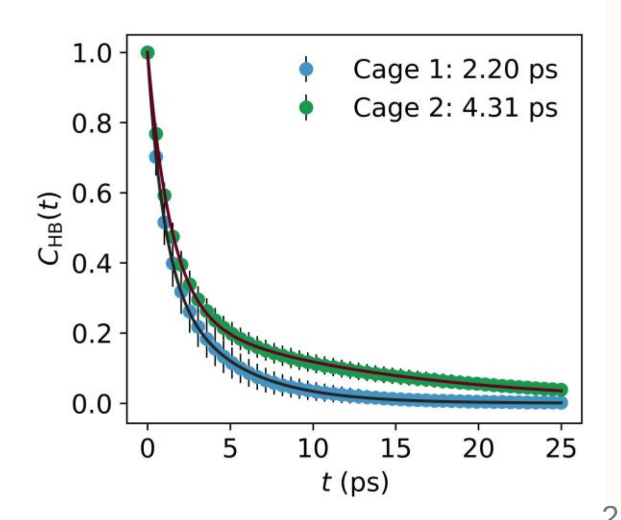
- about the same
- moderate strength (16.74 - 62.76 kJ mol^{-1})



H bonds on water:
One less in Cage 1

H bond lifetime:
Cage 1 ≈ ½ Cage 2

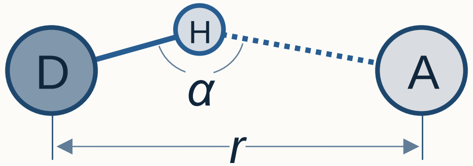




Example: water diffusion in supramolecular cages

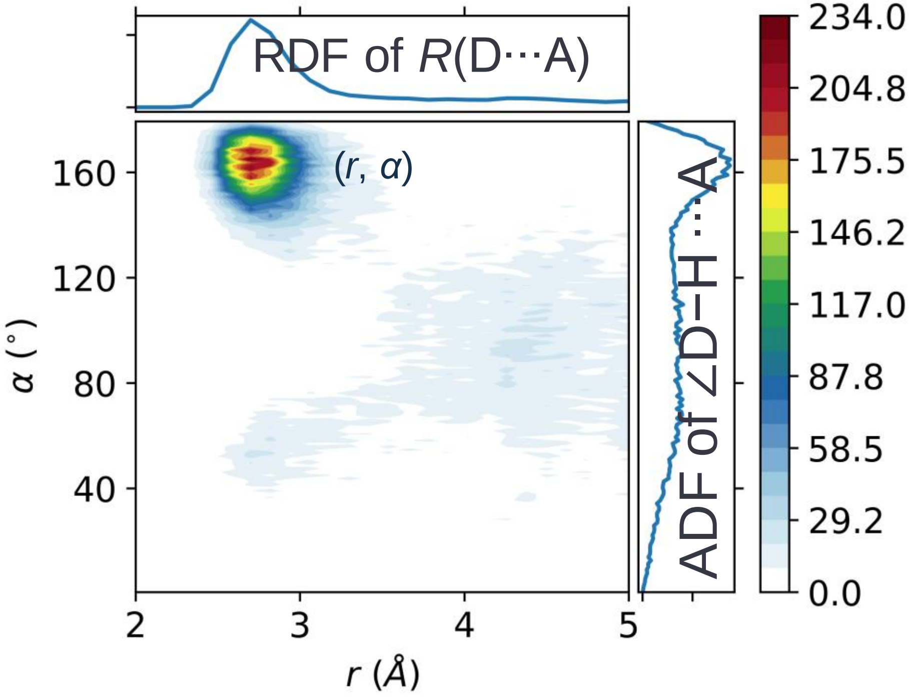
H bond behaviours

Strong H bonds: distinct centres

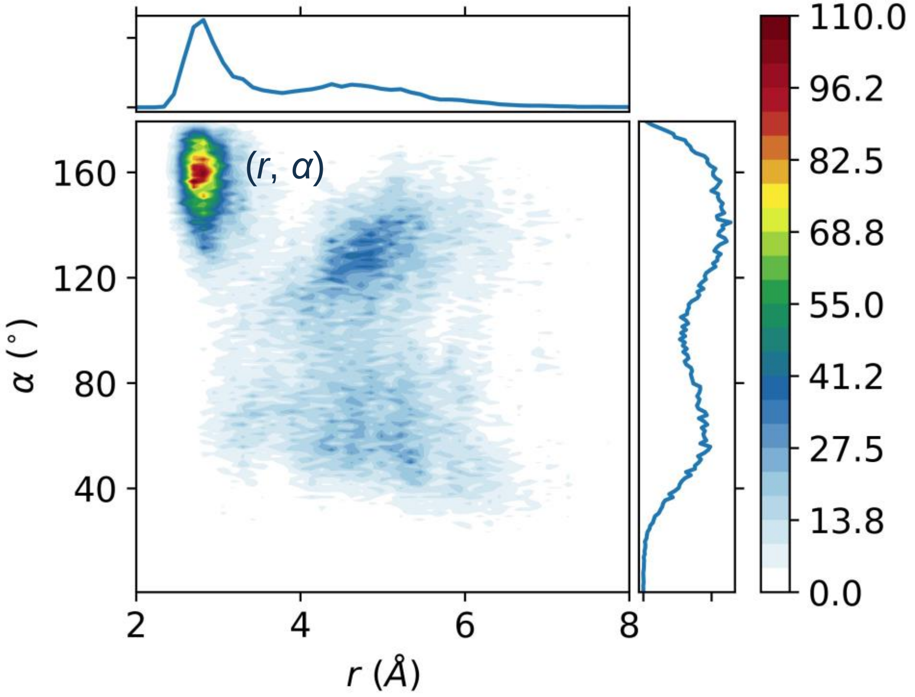


RDF: radial distribution function
ADF: angular distribution function
CDF: combined distribution function

Donor: water -OH
Acceptor: amine N

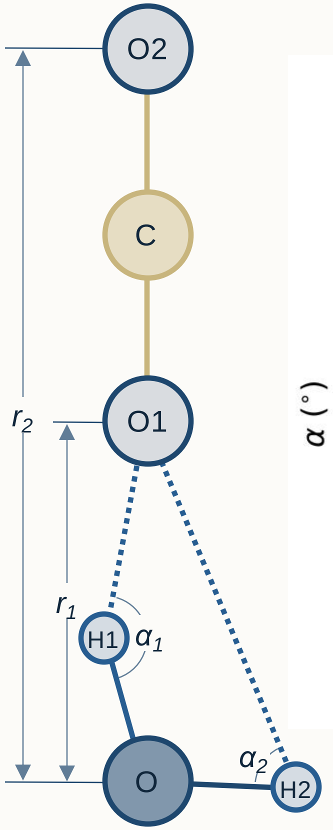


Donor: -ph-OH
Acceptor **:** water O



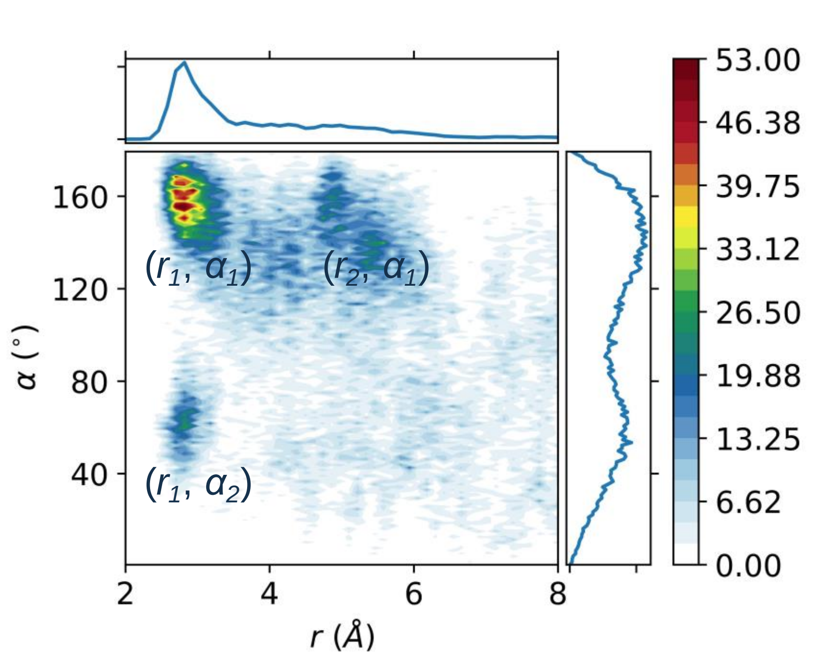
Example: water diffusion in supramolecular cages

Acceptor: TFA Os

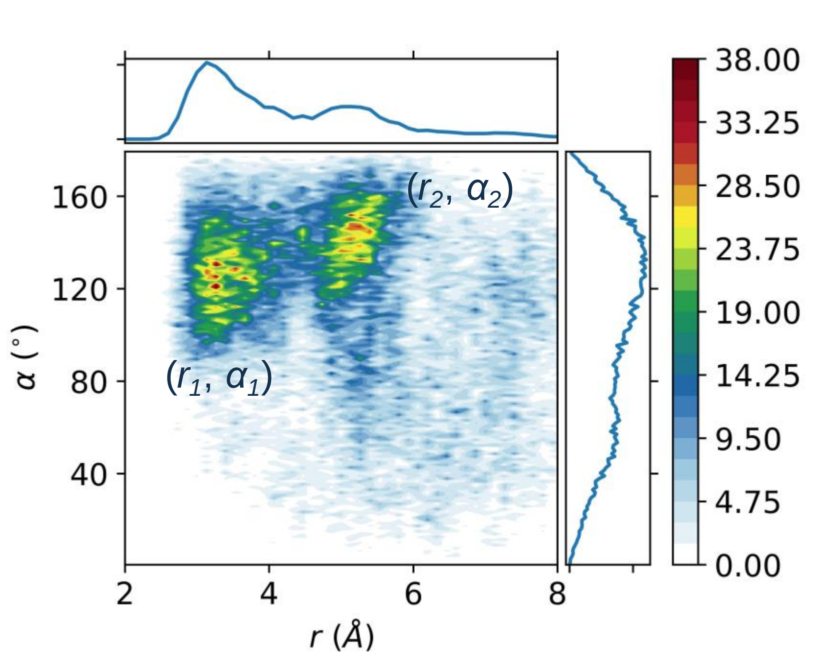


Donor: water OH

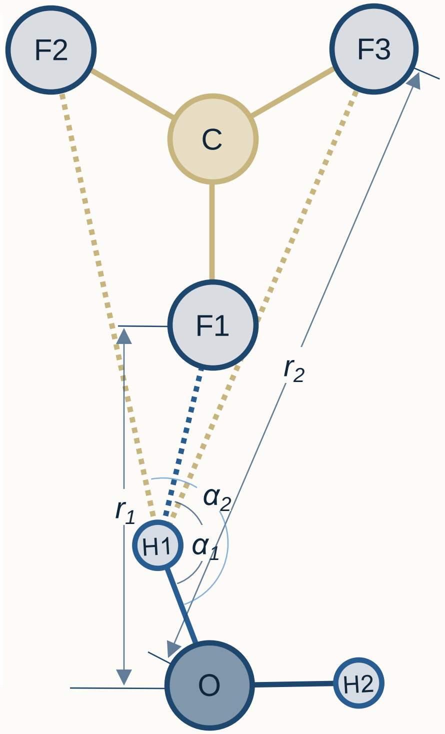
Sub-centres due to equivalent H/O and rotational dynamics



Less distinct centres due to weaker H bonds and rotational dynamics



Acceptor: TFA Fs



Donor: water OH

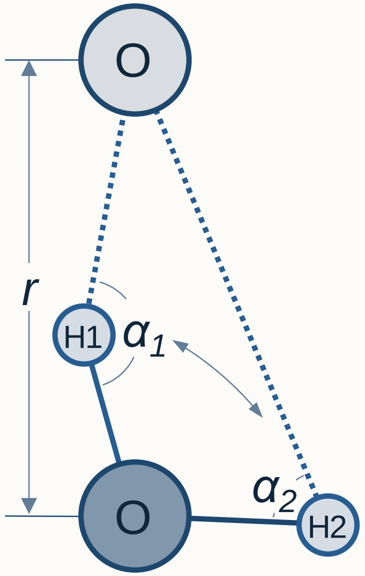
Example: water diffusion in supramolecular cages

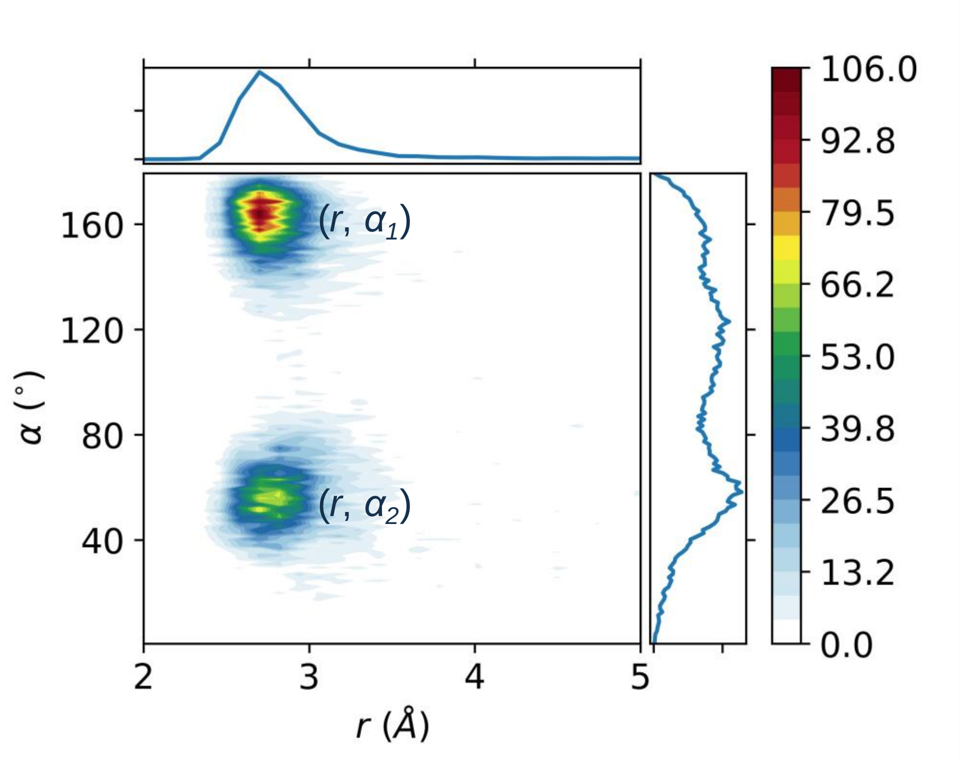
Water clustering

Donor: water OH
Accepter: water O

Two distinct centres due to equivalent positions

Potential to be as proton conductive as Nafion





Preparation for practical session

- Copy files from shared folder:

```
cp /work/ta154/shared/cp2k_md_training.tar.gz .
```

- Unzip the files:

```
tar -xvf cp2k_md_training.tar.gz
```

- Open a new tunneling session (check your port_num from the port.txt file):

```
grep name port.txt
ssh -L ****:localhost:**** username@login.archer2.ac.uk
```

- Load python module for data analysis:

```
cd /work/ta154/ta154/username
module load PrgEnv-gnu
module load cray-python
python -m venv --system-site-packages /work/ta154/ta154/username/mdana
source /work/ta154/ta154/username/mdana/bin/activate
pip install nglview ase
cd cp2k_md_training && jupyter notebook --no-browser --port=****
```

Practical session I

AIMD-equilibration

- Input file and script preparation
- Submit equilibration job

- Files:
  - mg.xyz
  - sys.inp
  - job.slurm

- Submit

```
sbatch job.slurm
```

Practical session I

AIMD-production job

- Check energy and temperature
- Prepare files, change settings
- Submit job
- Data analysis using provided trajectory data

Restart from equilibration

- Create new folder:
  - mkdir ensemble-temp
- Files:
  - cp sys-1.restart ensemble-temp
  - modify the settings: `ENSEMBLE, THERMOSTAT, TIMECON and add EXT_RESTART` session
  - cp job.slurm ensemble-temp
- Submit

  sbatch job.slurm

Force evaluation in CP2K: machine learning based methods

Supported machine learning based molecular dynamics:

- Nequip and Allegro
- Neural Network Potentials
- PAO-ML
- DeePMD-kit

Force evaluation in CP2K: NNP

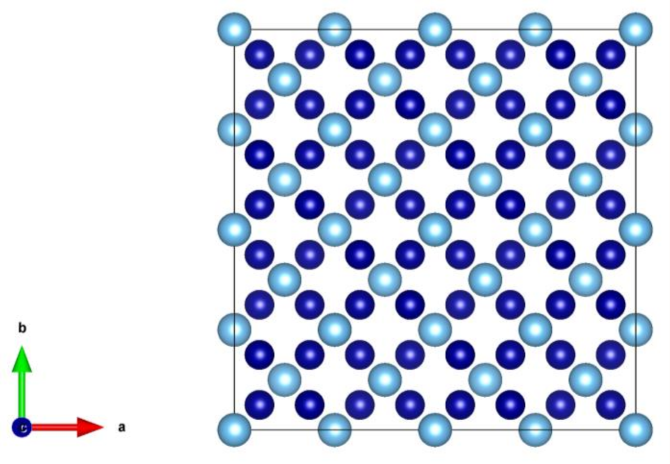
NNP: Parinello-Behler Neural Network Potential (PBNNP)

Atomic positions

Features

Neural Network

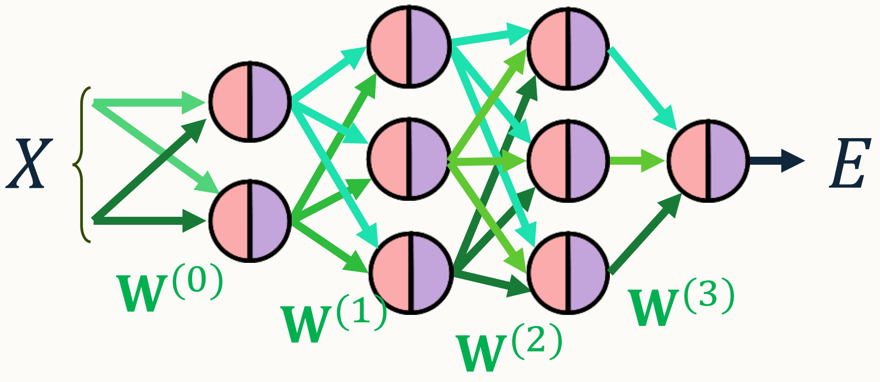
Energy Prediction



Parinello-Behler descriptor

$$G_{RAD} = \sum_{i \neq j} F[r_{ij}]$$

$$G_{ANG} = \sum_{\substack{i,k \neq j \\ j < k}} F[r_{ij}, r_{jk}, r_{ik}]$$

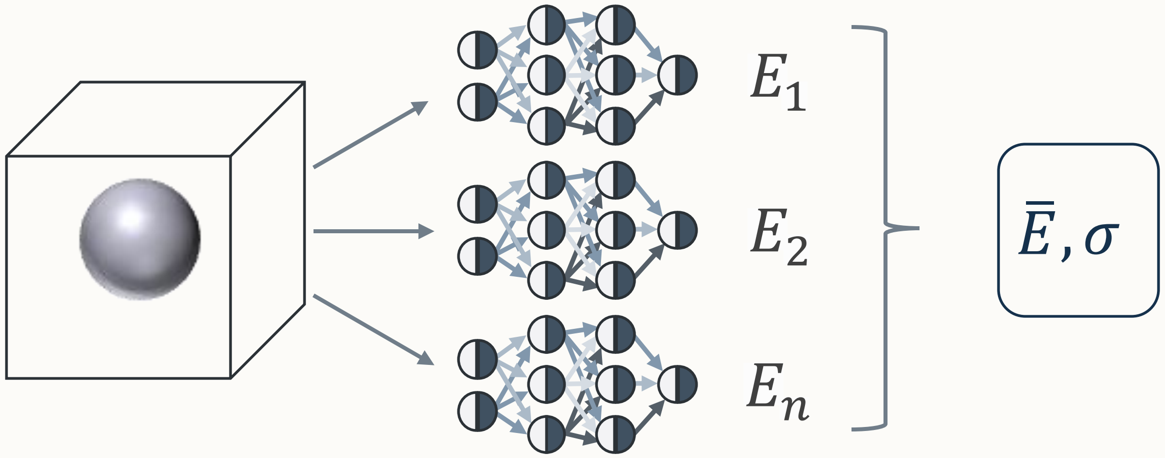


J. Behler and M. Parrinello Phys. Rev. Lett. (2007)

Why NNP?

Committee Neural Network Potentials:

- Reduce data usage
- Improve accuracy

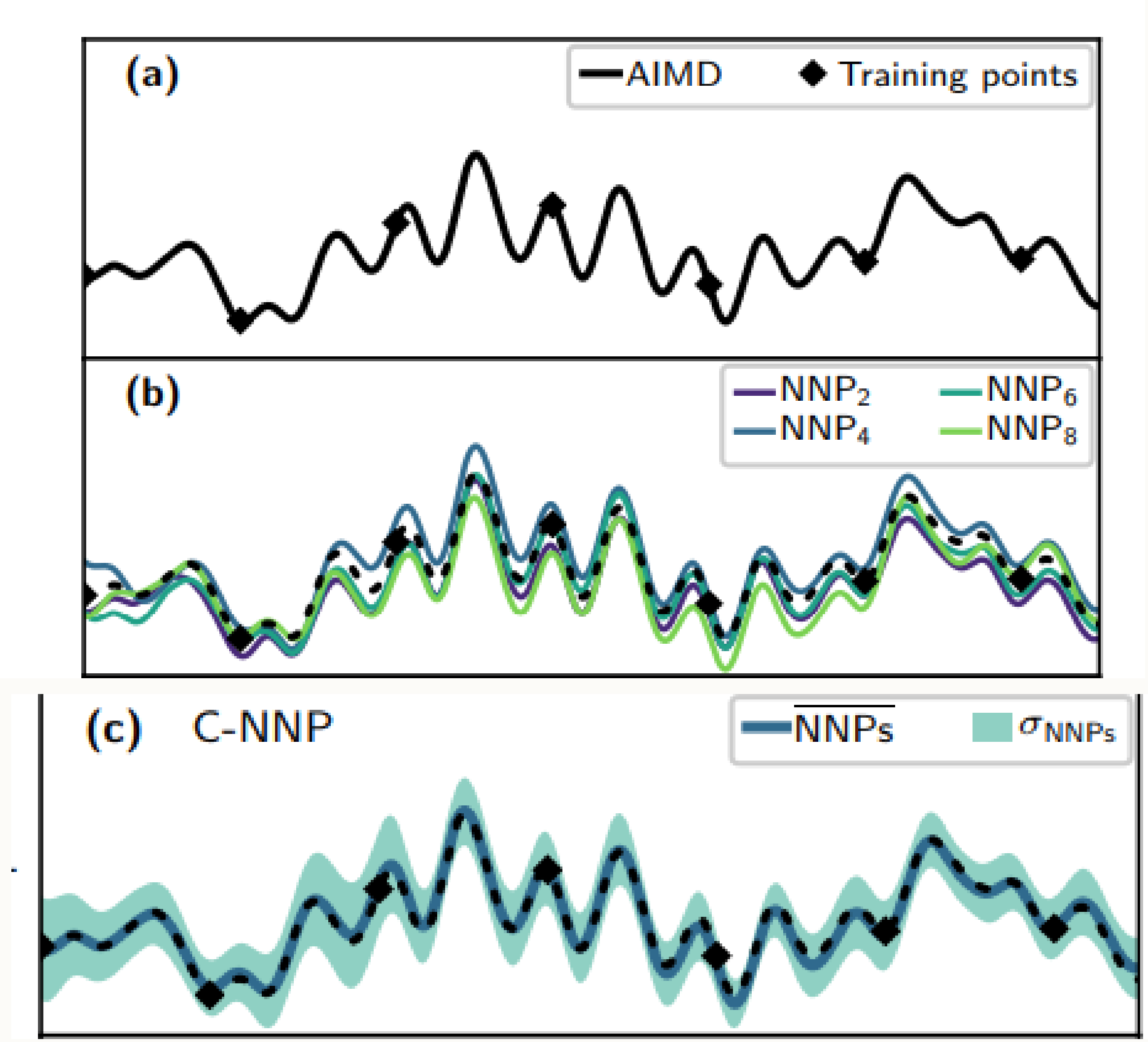


Atomic positions

Member PBNNPs

Member Predictions

Final Prediction



C.Schran, K.Brezina and O.Marsalek, JCP (2020)

Training data from CP2K AIMD data

Use AML to convert AIMD data generated by CP2K to N2P2 format

Note: the original package takes constant cell parameters only, which means NPT data cannot be correctly converted

A copy of modified AML which read and write changing cell data is provided, refer to the `Prepare_N2P2_training_data.ipynb` Notebook on usage

Force evaluation using NNP

NNP: nearual network potentials

```
&FORCE_EVAL
METHOD  NNP
STRESS_TENSOR  ANALYTICAL
&NNP
NNP_INPUT_FILE_NAME ${PATH}/input.nn
SCALE_FILE_NAME  ${PATH}/scaling.data
&MODEL
WEIGHTS ${PATH}/weights
&END MODEL
&END FORCE_EVAL
```

Use NNP to calculate force

Include this if using NPT

NNP file paths here

Practical session II

MLMD

- MLIP MD: equilibration
- MLIP MD production run
- Compare time taken / step
- Compare the $g(r)$ obtained by AIMD and MLMD

- Use pretrained committee NNPs
- Files
  - input script
  - job submission script
  - NNP files
- Submit
- Use the Jupyter Notebook to plot your results.

Further readings

- CP2K
  - CP2K manual
  - CP2K useful tools
- Thermostats:
  - Brief introduction to the thermostats
  - MD Ensembles and Thermostats
- Spectroscopy
  - Infrared spectra
  - Vibrational spectroscopy
- Machine learned interatomic potentials
  - Machine Learning Force Fields
  - Applications and Advances in Machine Learning Force Fields

Also, check out CP2K exercises (where some contents on MD and thermostats are taken from):

exercises [CP2K Open Source Molecular Dynamics]