Computing the thermodynamic and transport properties of water and hydrogen using machine learning potentials

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The holy grail of computational physics

"The fundamental laws necessary for the mathematical treatment of a large part of physics and the whole of chemistry are thus **completely known**, and the difficulty lies only in the fact that application of these laws leads to equations that are **too complex to be solved**. "

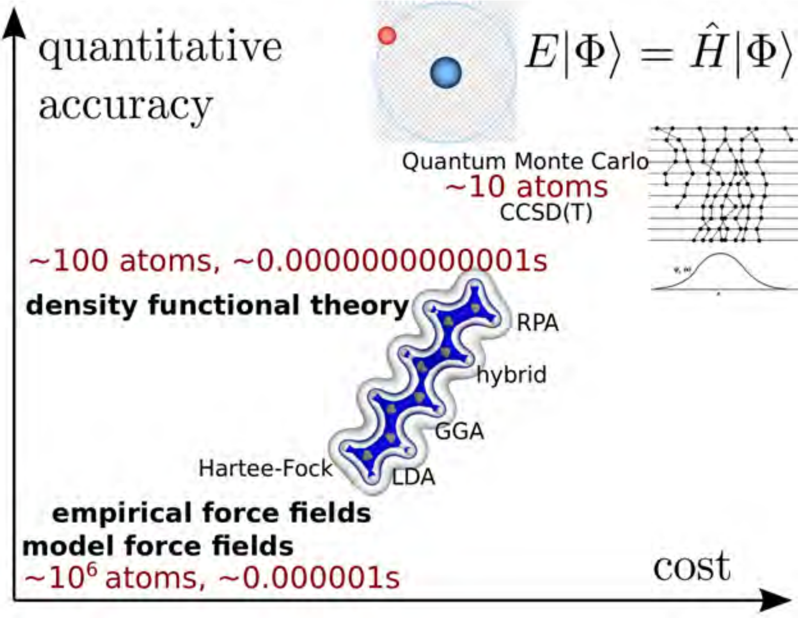
Paul Dirac, 1929

The holy grail of computational physics

"...**approximate practical methods** of applying quantum mechanics should be developed, which can lead to an explanation of the main features of complex atomic systems **without too much computation**."

Paul Dirac, 1929

Trade-off between cost and accuracy



quantitative accuracy

$E|\Phi\rangle = \hat{H}|\Phi\rangle$

Quantum Monte Carlo
~10 atoms
CCSD(T)

~100 atoms, ~0.000000000001s

density functional theory

RPA

hybrid

GGA

Hartee-Fock

LDA

empirical force fields

model force fields

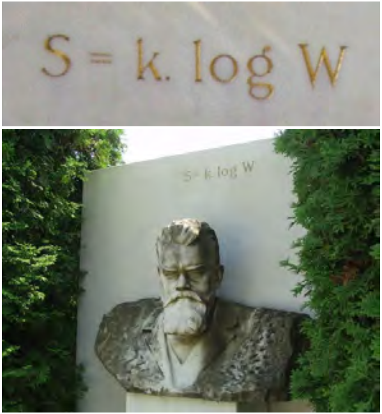
~10^6 atoms, ~0.000001s

cost

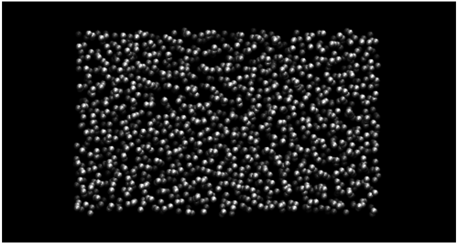
Statistical mechanics

$$P(\Omega) = e^{-\frac{H(\Omega)}{kT}}$$

$$S_I \approx k \sum_{\Omega} P(\Omega) \log(P(\Omega))$$



Ludwig Boltzmann



A microstate is a specific realization of the coordinates and velocities of all atoms in the system.

Outline

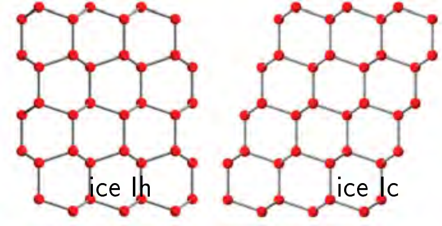
What we will talk about:

- A ML potential for water.
- Hydrogen under high pressure.
- The extend of locality in MLP.
  - Extracting ice-like local environments from liquid water.
  - Water phase diagram.

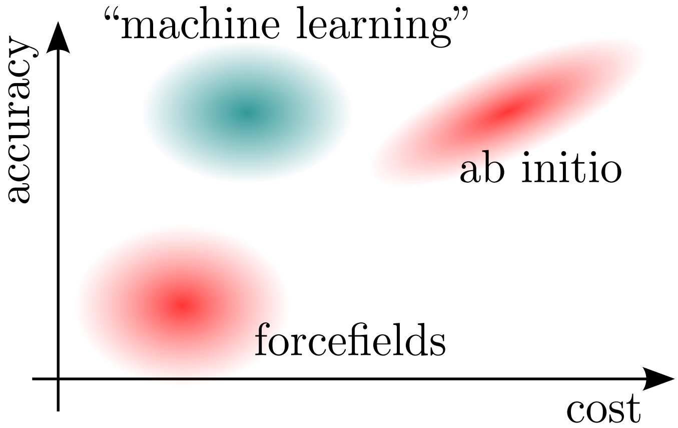
The mystery about water

- Densest at 4 degree Celsius.
- Ice floats on water.
- Unusually high melting point.
- Intricate nuclear quantum effects.

- Why hexagonal ice is more stable?



ML potential, a blackbox view

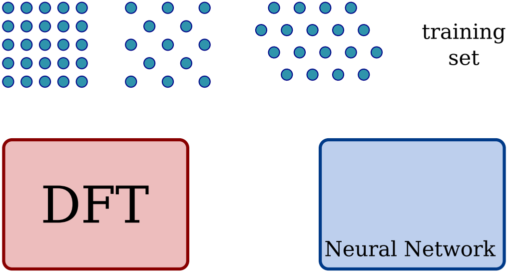


ML potential, a blackbox view

DFT

Neural Network

ML potential, a blackbox view

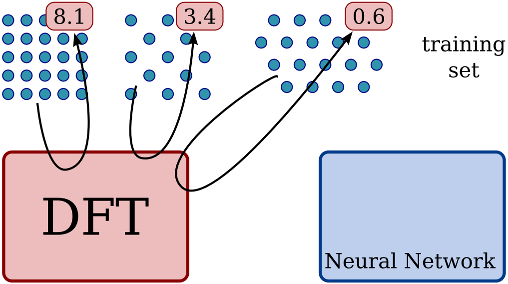


training set

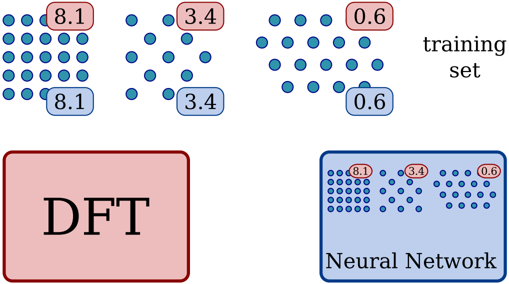
DFT

Neural Network

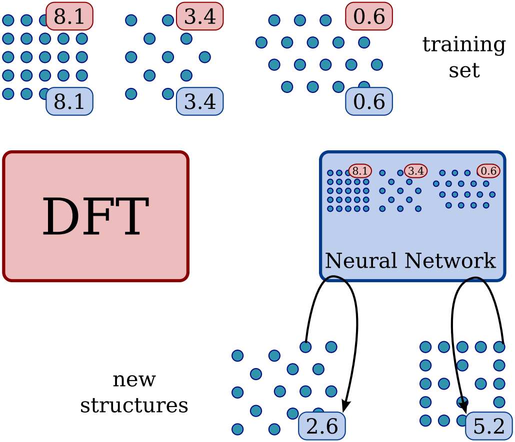
ML potential, a blackbox view



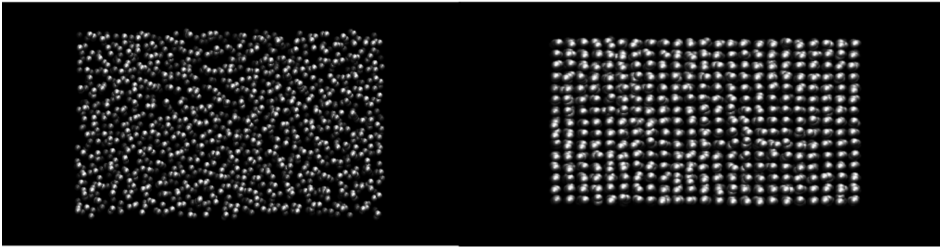
ML potential, a blackbox view



ML potential, a blackbox view



Local atomic environments



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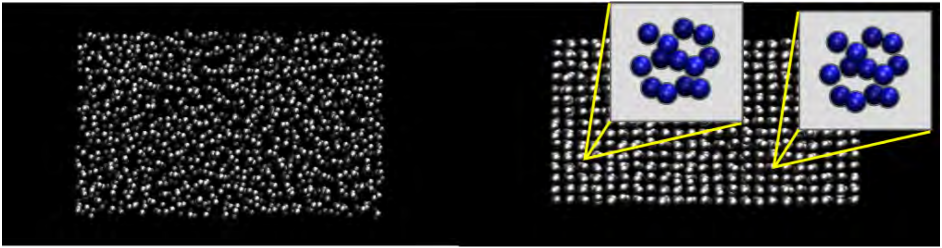
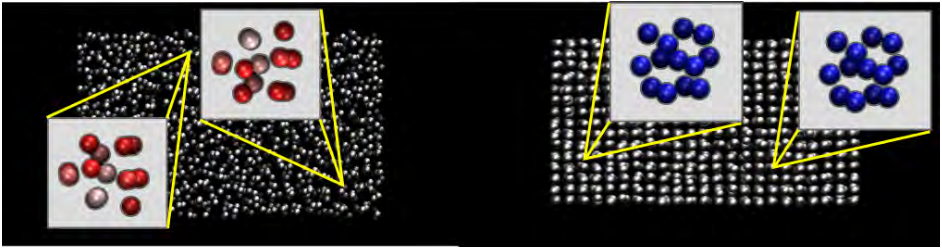


Popular representations for comparing atomic environments

- Smooth overlap of atomic positions (SOAP) [Bartók, Kondor & Csányi PRB 2013]
- Behler-Parrinello symmetry functions [Behler & Parrinello PRL 2008]
- Permutation invariant polynomials [Braam & Bowman 2008]

Local atomic environments



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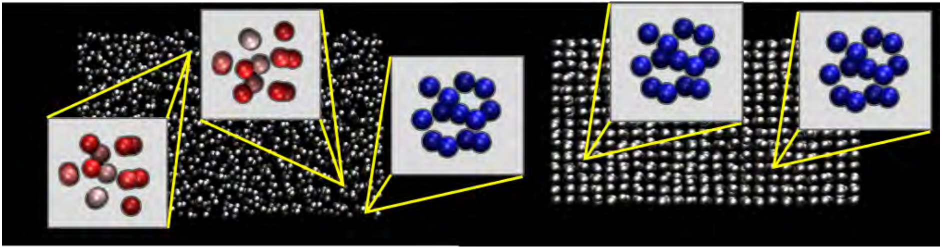

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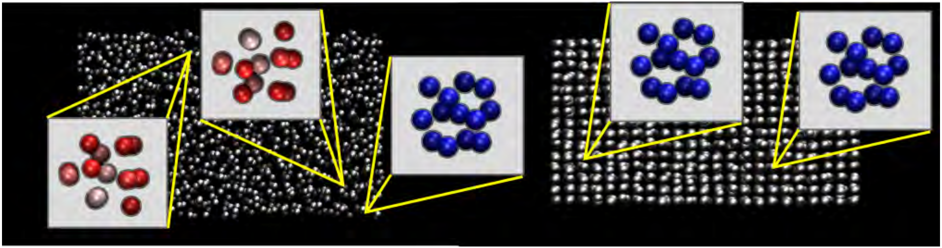
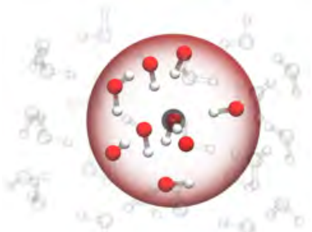


- Similar atomic environments are encountered over and over again.
- If you do MD, you lose!
- Near-sightedness of energy and forces of each environment.

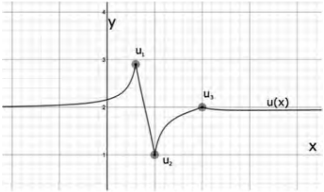
Construct ML potentials

Step 1: Collect environments.

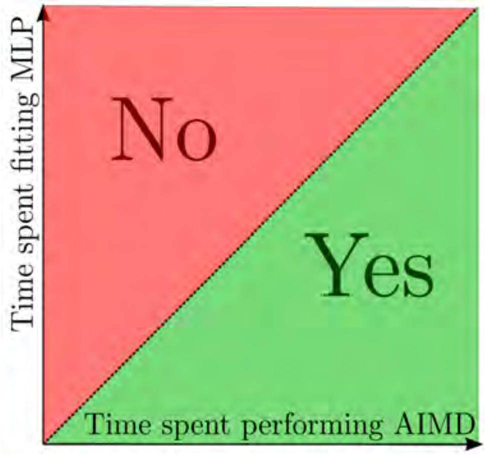


$$E = \sum E_i$$

Step 2: Interpolate.



Decide whether to make ML potentials



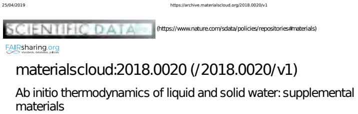
Training set for bulk water

revPBE0-D3 reference:

- AIMD and PIMD simulations [Marsalek & Markland JPCL 2017]
- Benchmarks with CCSD(T) and DMC [Brandenburg 2019]

Trained using BP neural network.
[Behler Parrinello PRL 2008;
Morawietz, et al. PNAS 2016]

Training set:



25/04/2019 https://archive.materialscloud.org/2018.0020/v1

SCIENTIFIC DATA (https://www.nature.com/sdata/policies/repositories#materials)

FAIRsharing.org
standards, databases, policies

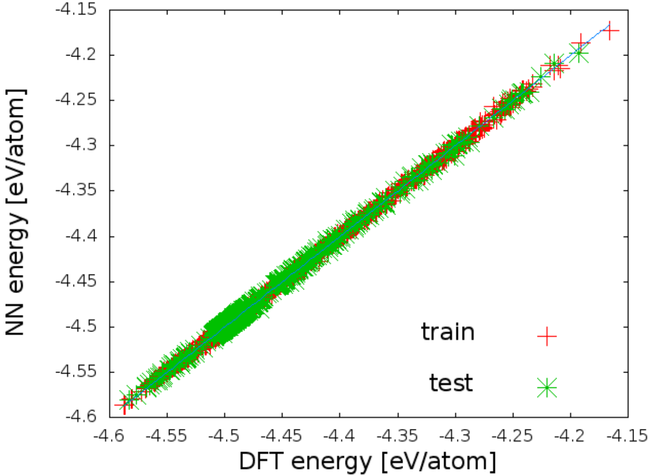
materialscloud:2018.0020 (/2018.0020/v1)

Ab initio thermodynamics of liquid and solid water: supplemental materials

- 1593 bulk liquid 64 water molecules (energy + forces)
- 1000 structures from quenches at a wide range of densities.
- 593 structures from PIMD.

Neural network potential for water

[Cheng, Engel, Behler, Dellago & Ceriotti PNAS 2019]



revPBE0+D3 DFT functional

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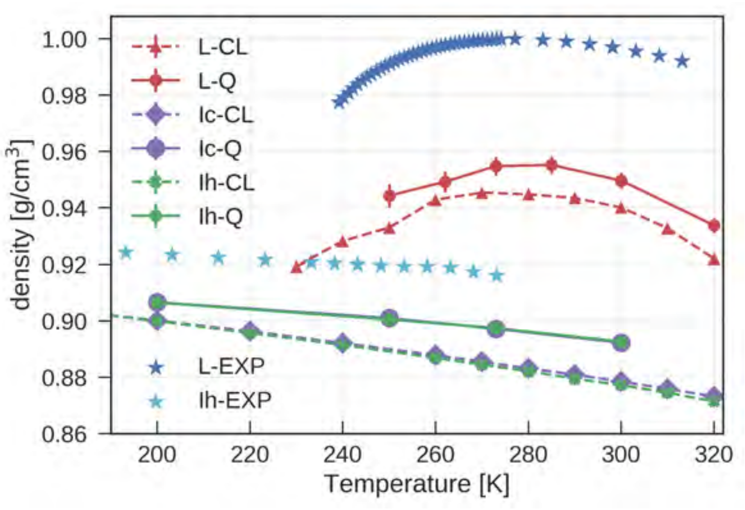

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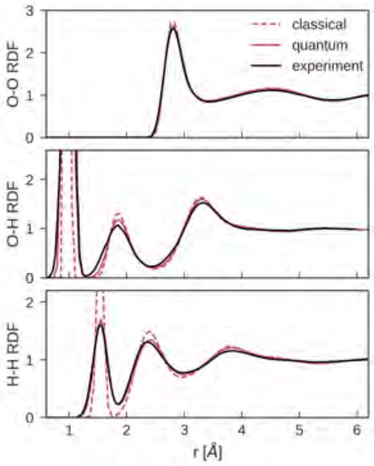
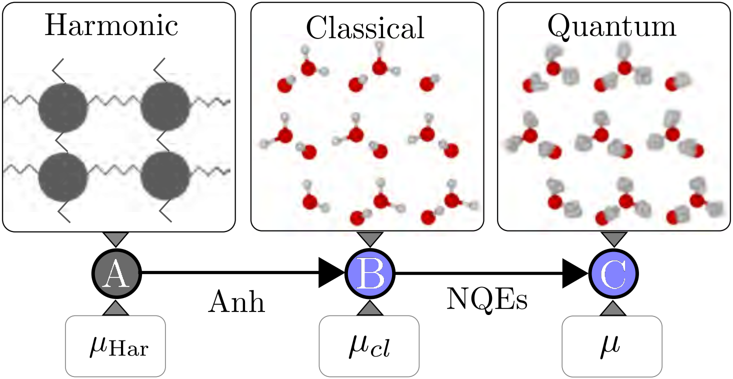


revPBE0+D3 DFT functional

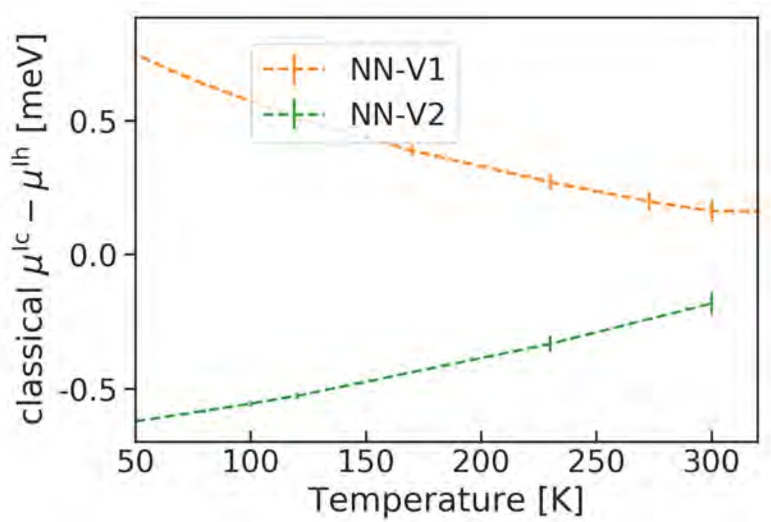
Thermodynamic integration



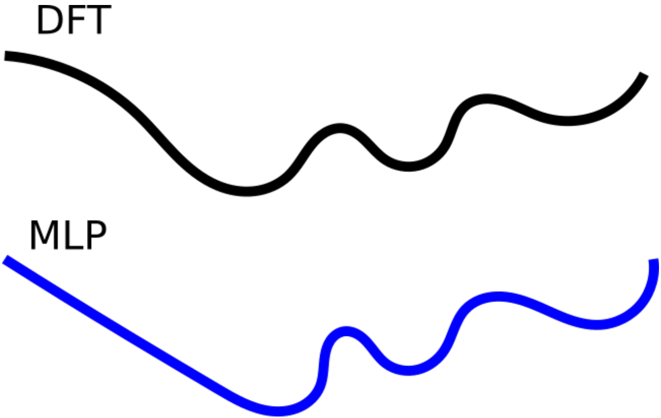
Transform continuously between systems A and B via a parameter λ,

$$F_A - F_B = \int_{\lambda_A}^{\lambda_B} \frac{dF(\lambda)}{d\lambda} d\lambda$$

Comparison between two NN potentials



Promote NNP to DFT



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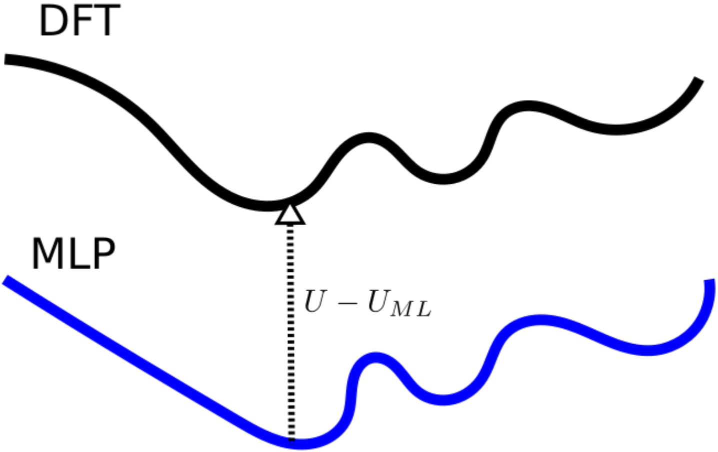

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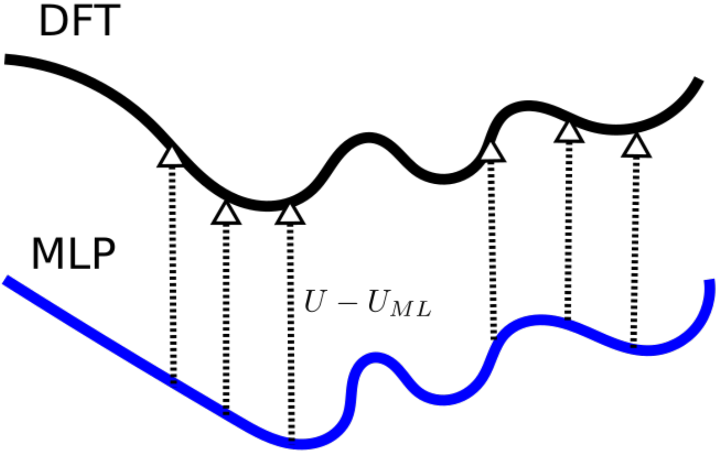

From Neural network potential to DFT

The Gibbs free energy of the system described by the DFT:

$$G = -k_B T \ln \int d\mathbf{q} \exp\left[-\frac{U(\mathbf{q}) + PV}{k_B T}\right]$$

The Gibbs free energy of the system described by the ML potential:

$$G_{ML} = -k_B T \ln \int d\mathbf{q} \exp\left[-\frac{U_{ML}(\mathbf{q}) + PV}{k_B T}\right]$$

$$G - G_{ML} = -k_B T \ln \frac{\int d\mathbf{q} \exp\left[-\frac{U_{ML}(\mathbf{q}) + PV}{k_B T} \frac{U(\mathbf{q}) - U_{ML}(\mathbf{q})}{k_B T}\right]}{\int d\mathbf{q} \exp\left[-\frac{U_{ML}(\mathbf{q}) + PV}{k_B T}\right]}$$

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Free energy perturbation method

From Neural network potential to DFT

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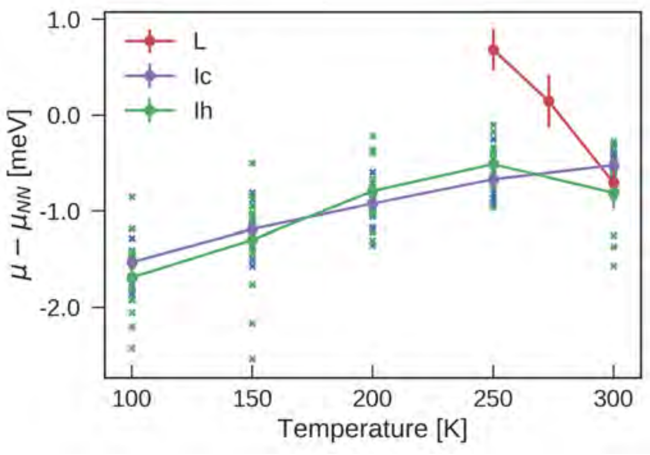
Free energy perturbation method

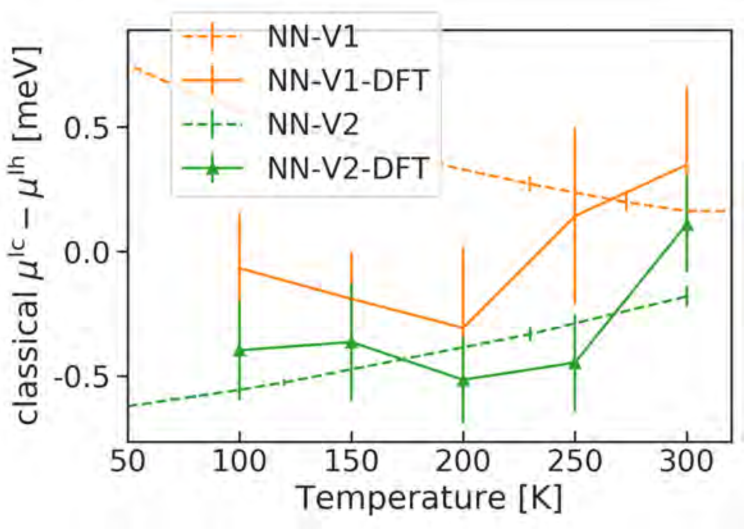
From Neural network potential to DFT

$$G - G_{ML} = -k_B T \ln \left\langle \exp\left[\frac{U(\mathbf{q}) - U_{ML}(\mathbf{q})}{k_B T}\right]\right\rangle_{ML}$$

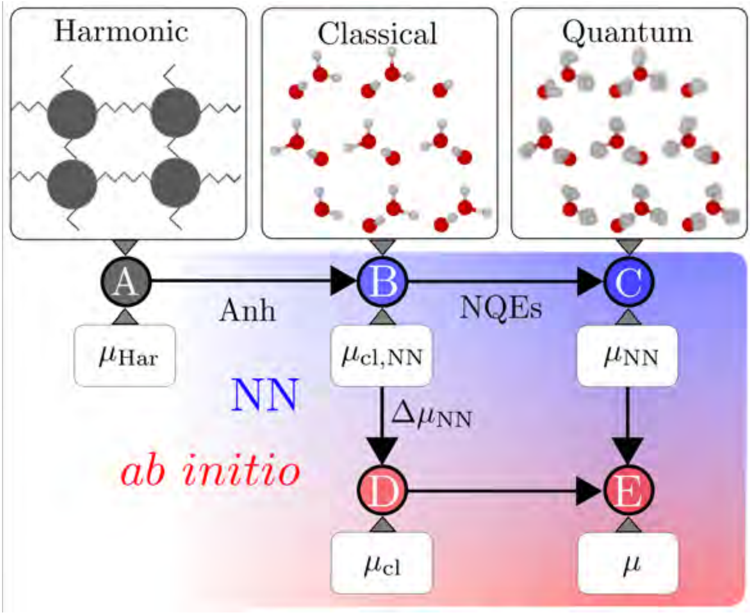
$$\Delta\mu = (G - G_{ML})/N$$



Comparison between two NN potentials

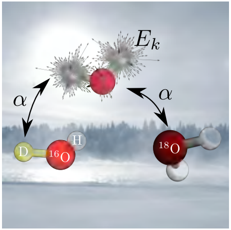


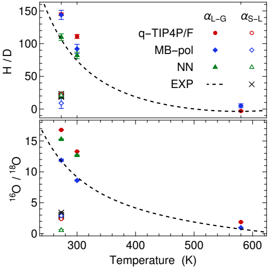
The workflow of ab initio thermodynamics

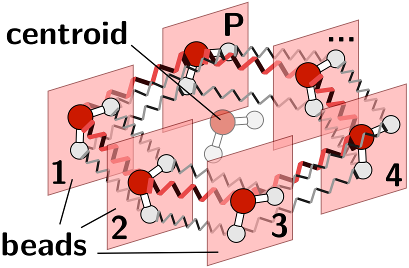


Nuclear Quantum effects

$$H_2O^g + HDO^l \rightleftharpoons HDO^g + H_2O^l$$

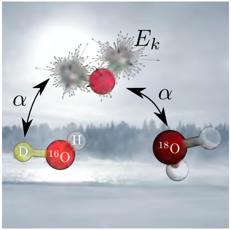






- Particle momentum distribution
- Isotope fractionation
- Heat capacity
- Hydrogen bond strength
- Diffusivity...

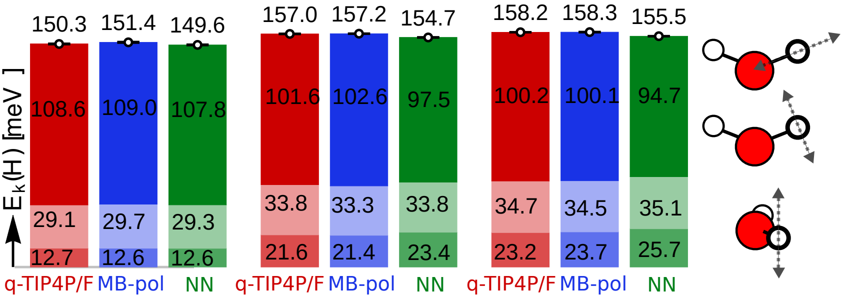
Quantum kinetic energy



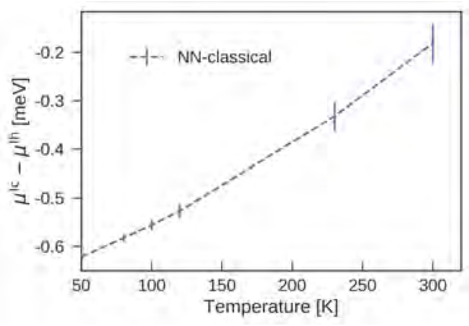
[Cheng & Ceriotti JCP 2014;
Cheng, Behler & Ceriotti JPCL 2016]

$$\frac{dG}{du} = -\frac{\langle E_k(u)\rangle}{u}$$

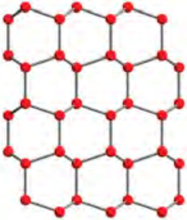
$$G_{qm} - G_{cl} = \int_m^{\infty} du \frac{\langle E_k(u)\rangle}{u}$$



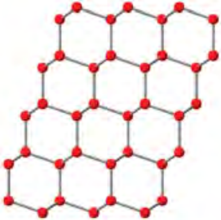
Hexagonal and cubic ice



ice Ih

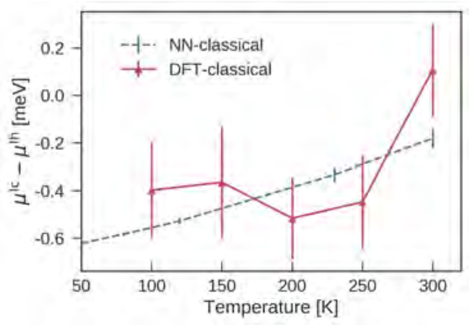


ice Ic

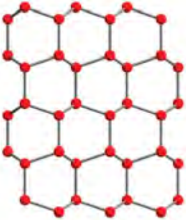


[http://www.phase-trans.msm.cam.ac.uk/dendrites.html]

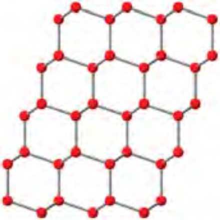
Hexagonal and cubic ice



ice Ih



ice Ic



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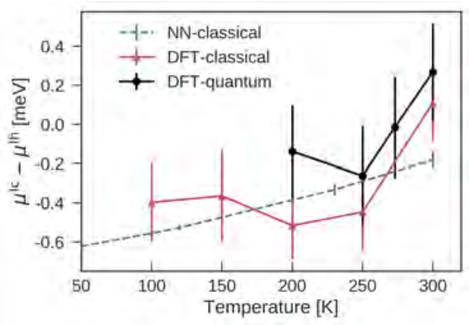
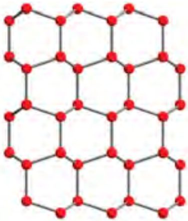
Hexagonal and cubic ice

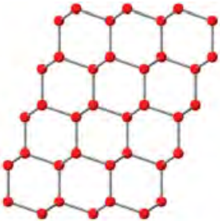


- NQEs significantly stablize hexagonal ice.
- Hexagonal ice is more stable.

ice Ih



ice Ic



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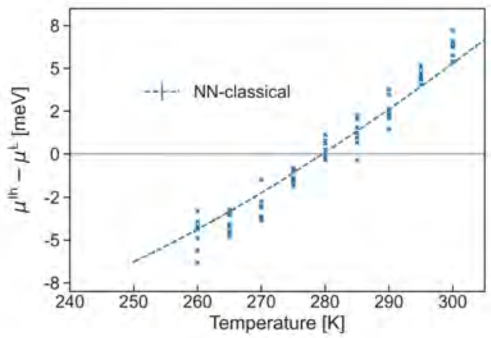
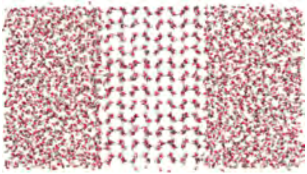
Ice and liquid water



PLUMED

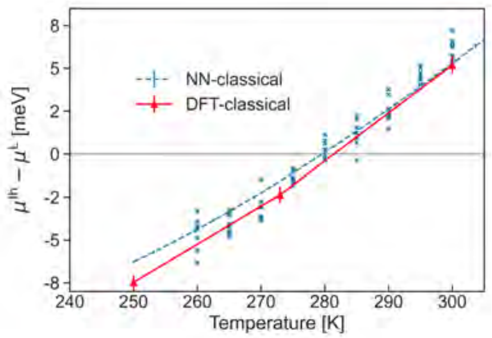
Umbrella simulation using NN potential:

$$\mathcal{H}_{biased}(\mathbf{q}) = \mathcal{H}_{ML}(\mathbf{q}) + \frac{\kappa}{2}\left(\Phi - \bar{\Phi}\right)^2$$



- The difference between the melting points of H2O and D2O agrees with experiment (3.82 K).
- Error in melting point of H2O is about 1%.

Ice and liquid water



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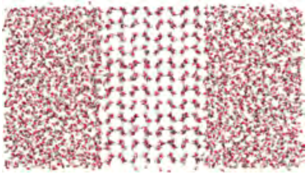
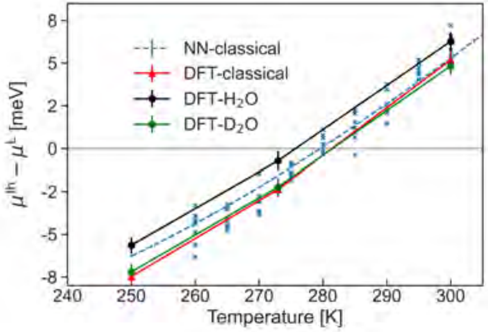
$$\mathcal{H}_{biased}(\mathbf{q}) = \mathcal{H}_{ML}(\mathbf{q}) + \frac{\kappa}{2}\left(\Phi - \bar{\Phi}\right)^{2}$$



- The difference between the melting points of H2O and D2O agrees with experiment (3.82 K).
- Error in melting point of H2O is about 1%.

Ice and liquid water



Umbrella simulation using NN potential:

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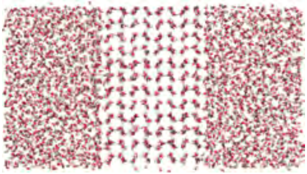

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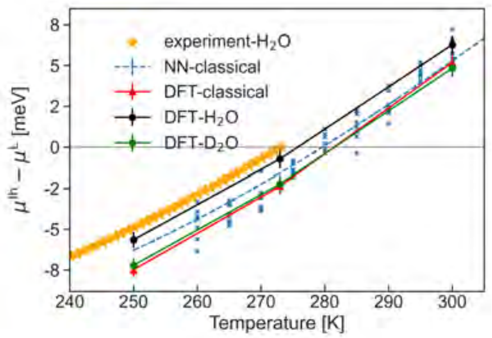

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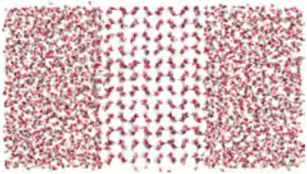

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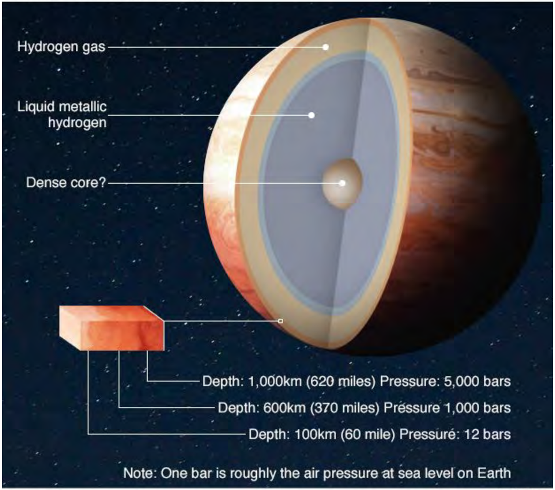
High pressure hydrogen

- Center of giant planets.
- Exotic properties, e.g. room-temperature superconductor.



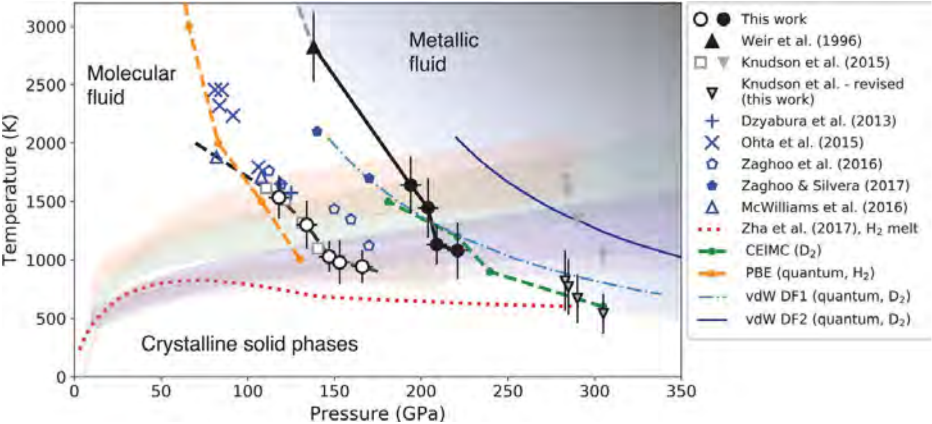
Juno probe reaches Jupiter

Note: One bar is roughly the air pressure at sea level on Earth

Source: Nasa

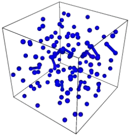
BBC

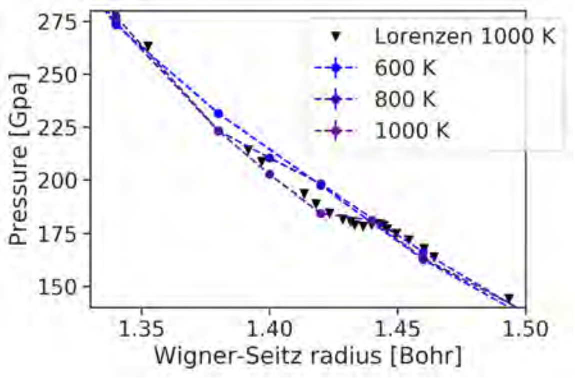
Experimental measurement of liquid-liquid Transition



[Celliers et al., Science 361, 677–682 (2018)]

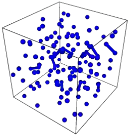
Probe LLT using DFT calculations





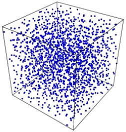
ML potentials

Density functional theory



Size: ~100 atoms
Time: picoseconds (10^{-12} S)
Scaling: cubic ($\mathcal{O}N^3$)
Cost: up to millions of CPU hours

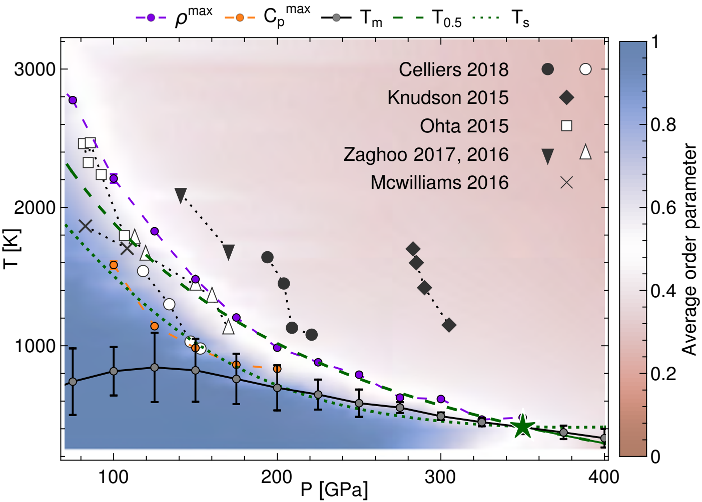
ML atomic interactions
[Behler & Parrinello PRL 2008;
Bartók et al PRL 2010]



Size: >1,000 atoms
Time: nanoseconds (10^{-9} S)
Scaling: linear ($\mathcal{O}N$)
Cost: laptop friendly

Phase diagram of high pressure hydrogen

[Cheng, Mazzola, Pickard & Ceriotti Nature 2020]



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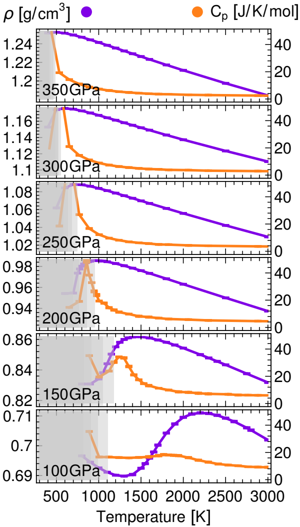

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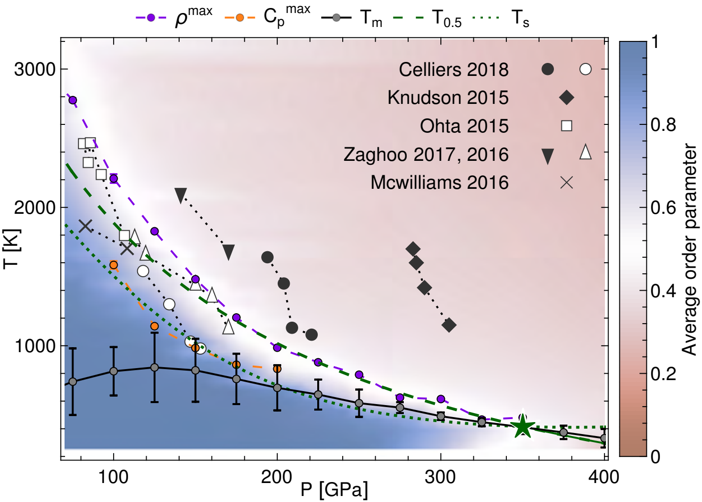
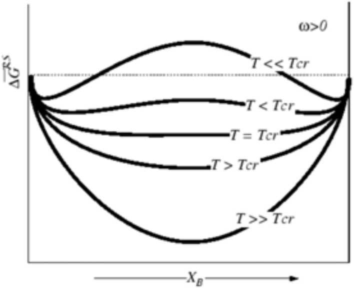


Phase diagram of high pressure hydrogen

[Cheng, Mazzola, Pickard & Ceriotti Nature 2020]

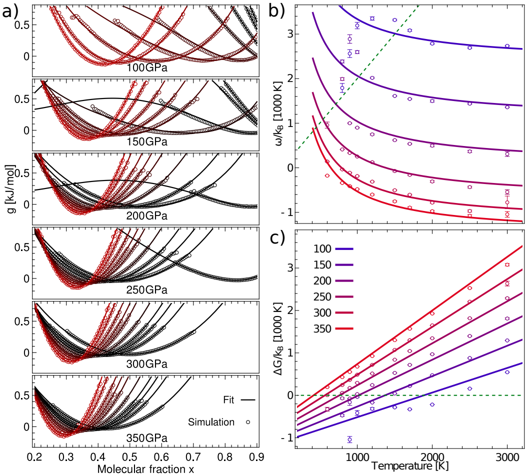
Regular solution model:

$$g(x) = x\Delta g + k_B Tx\ln(x) + k_B T(1-x)\ln(1-x) + \omega x(1-x)$$



Phase diagram of high pressure hydrogen

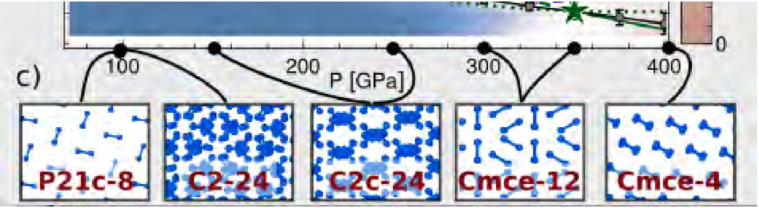
[Cheng, Mazzola, Pickard & Ceriotti Nature 2020]



(metadynamics simulations for computing free energy profiles)

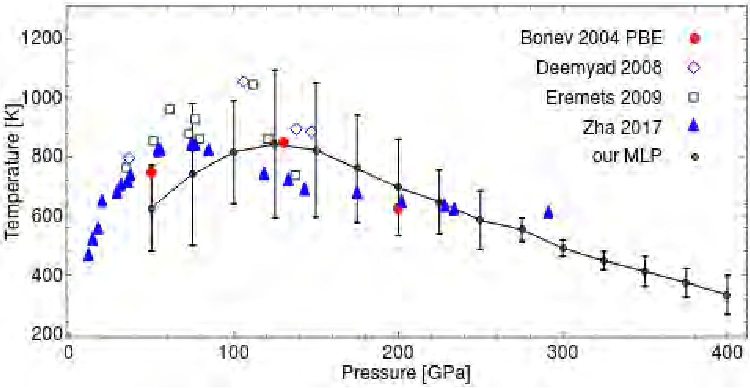
Phase diagram of high pressure hydrogen

[Cheng, Mazzola, Pickard & Ceriotti Nature 2020]



Phase diagram of high pressure hydrogen

[Cheng, Mazzola, Pickard & Ceriotti Nature 2020]



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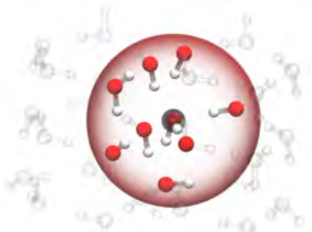
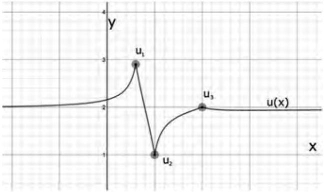
Construct ML potentials

Step 1: Collect environments.

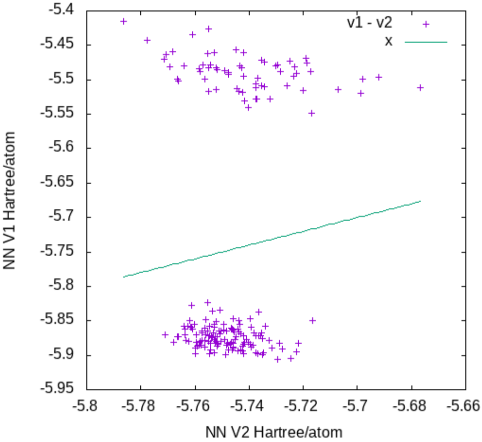


$$E = \sum E_i$$

Step 2: Interpolate.

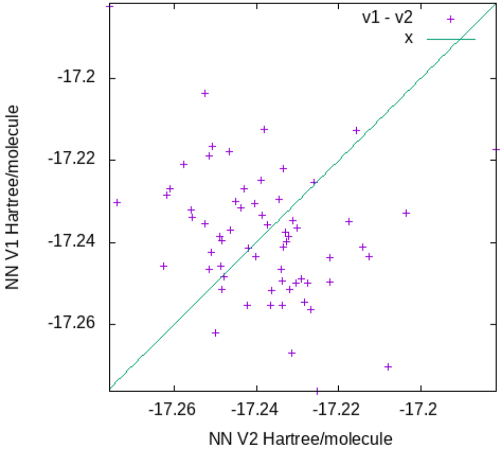


Use the atomic energies of MLPs



Compare the atomic energies (O, H) from two NNPs

Use the atomic energies of MLPs



Compare molecular energies from two NNPs

Green-Kubo for heat conductivity

The Green-Kubo (GK) relationship states that

$$\lambda = \frac{1}{Vk_B T^2} \int_0^\infty dt \langle \mathbf{J}(0)\mathbf{J}(t) \rangle$$

where the heat flux is

$$\mathbf{J}(t) = \sum_i^N e_i \mathbf{v}_i + \sum_{i<j} (\mathbf{F}_{ij} \cdot \mathbf{v}_i)\mathbf{r}_{ij}$$

The problem:
the atomic energy e_i and forces $\mathbf{F}_{ij}$ between two atoms are poorly defined.

Heat conductivity from density fluctuations

Take a Fourier expansion of the density field in space

$$\widetilde{\rho}(\mathbf{k},t) = \frac{1}{V}\int_V d\mathbf{r}\rho(\mathbf{r},t)\exp(-i\mathbf{k}\cdot\mathbf{r}) = \frac{1}{V}\sum_{i=1}^{N}\exp(-i\mathbf{k}\cdot\mathbf{r}_i(t))$$

The approximate solution of the hydrodynamic equations of $\widetilde{\rho}$ to the second order of $\mathbf{k}$:

$$C_{\widetilde{\rho}}(\mathbf{k},t) = \int_0^t dt\langle\widetilde{\rho}(\mathbf{k},0)\widetilde{\rho}(\mathbf{k},t)\rangle$$

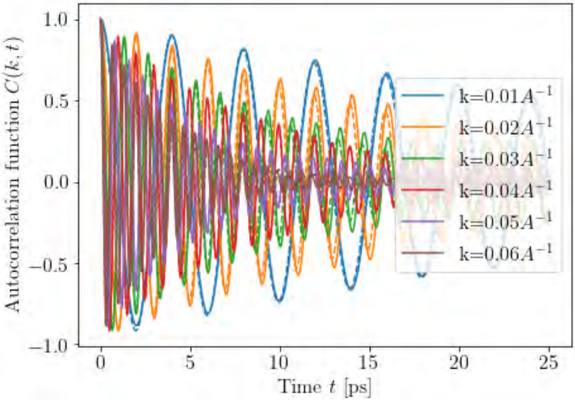
$$= \rho_k^2\left[\frac{\gamma-1}{\gamma}\exp(-\frac{\lambda}{c_P}k^2t) + \frac{1}{\gamma}\exp(-\Gamma k^2 t)\cos(c_s kt)\right]$$

Two poles modes: $-i\frac{\lambda}{c_P}\mathbf{k}^2$ and $c_s k - i\Gamma\mathbf{k}^2$.

λ: heat conductivity c_s: speed of sound Γ: sound attenuation constant

High-pressure hydrogen fluid

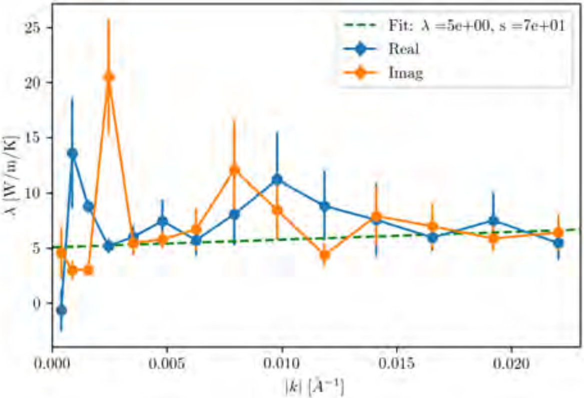
[Cheng & Frenkel PRL 2020]



MLP of high-P hydrogen.
2000 K, 33 GPa

High-pressure hydrogen fluid

[Cheng & Frenkel PRL 2020]



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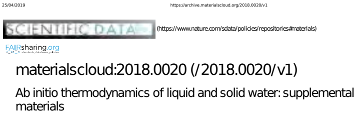
Training set for bulk water

revPBE0-D3 reference:

- AIMD and PIMD simulations [Marsalek & Markland JPCL 2017]
- Benchmarks with CCSD(T) and DMC [Brandenburg 2019]

Trained using BP neural network.
[Behler Parrinello PRL 2008;
Morawietz, et al. PNAS 2016]

Training set:



25/04/2019 https://archive.materialscloud.org/2018.0020/v1

SCIENTIFIC DATA (https://www.nature.com/sdata/policies/repositories#materials)

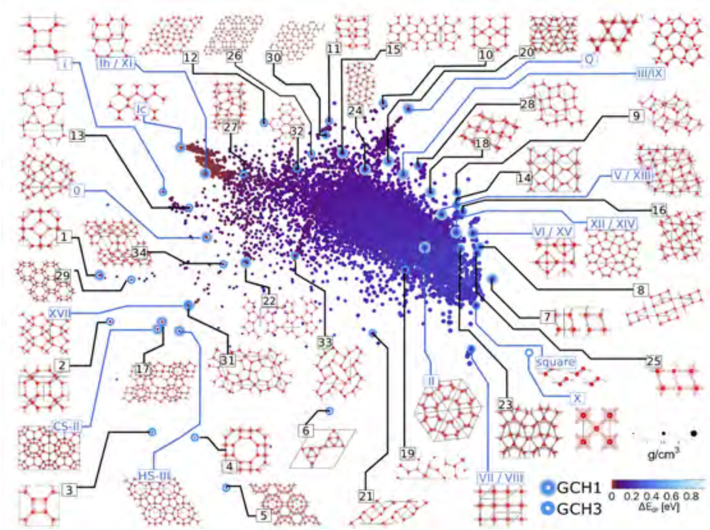
FAIRsharing.org standards, databases, policies

materialscloud:2018.0020 (/2018.0020/v1)

Ab initio thermodynamics of liquid and solid water: supplemental materials

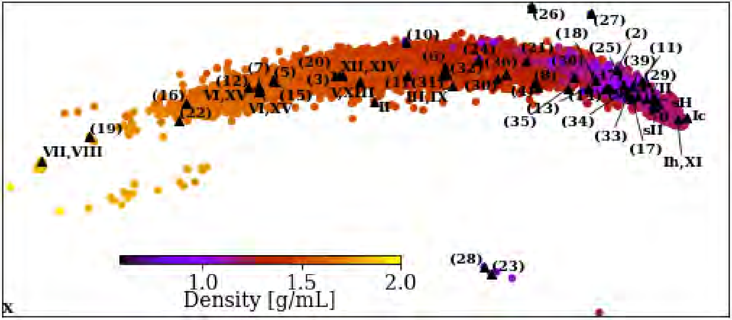
- 1593 bulk liquid 64 water molecules
  (energy + forces)
- 1000 structures from quenches at a wide range of densities.
- 593 structures from PIMD.

Candiate ice phases



[Engel, et al. Nature Comm. 2018]

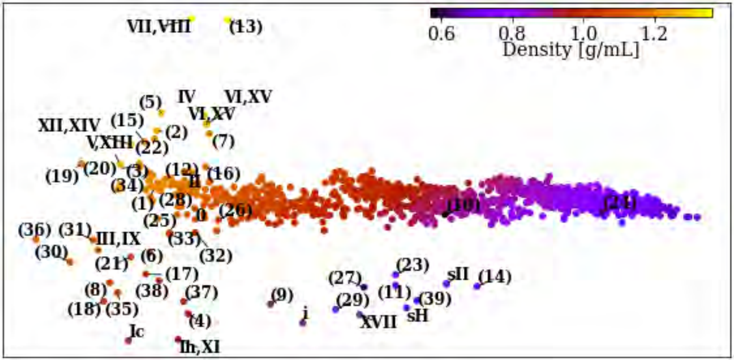
Candiate ice phases



PCA map for the ice phases

PCA map of Ice and water

[Monserrat, Brandenburg, Engel & Cheng arXiv 2020]



1,000 liquid water + 54 ice phases

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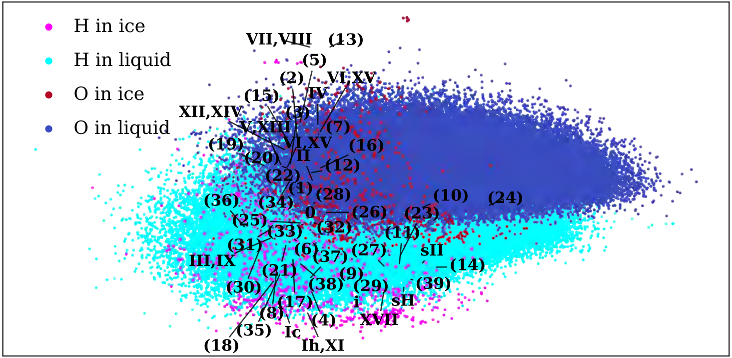
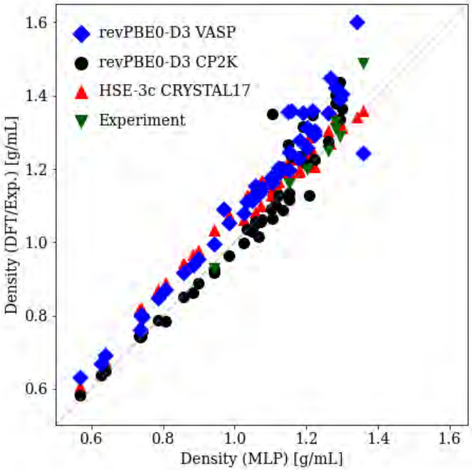
[Monserrat, Brandenburg, Engel & Cheng arXiv 2020]



Cutoff radius for atomic environment: 6 Angstrom

DFT Vs. NNP

[Monserrat, Brandenburg, Engel & Cheng arXiv 2020]



revPBE0-D3 (CP2K), revPBE0-D3 (VASP), HSE-3c (CRYSTAL07)

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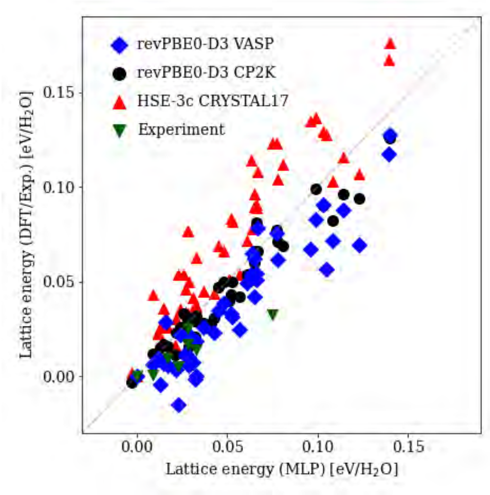
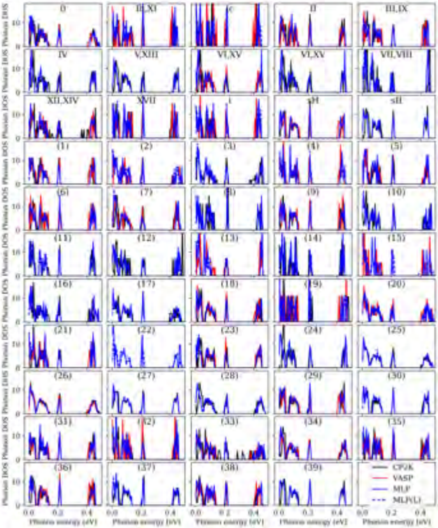


revPBE0-D3 (CP2K), revPBE0-D3 (VASP), HSE-3c (CRYSTAL07)

Phonon density of states

[Monserrat, Brandenburg, Engel & Cheng arXiv 2020]



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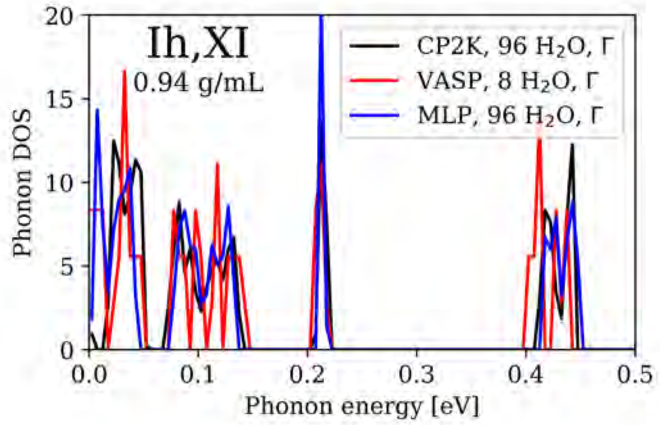

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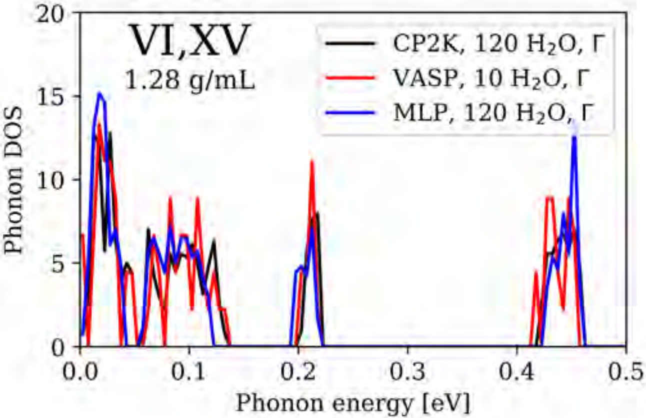

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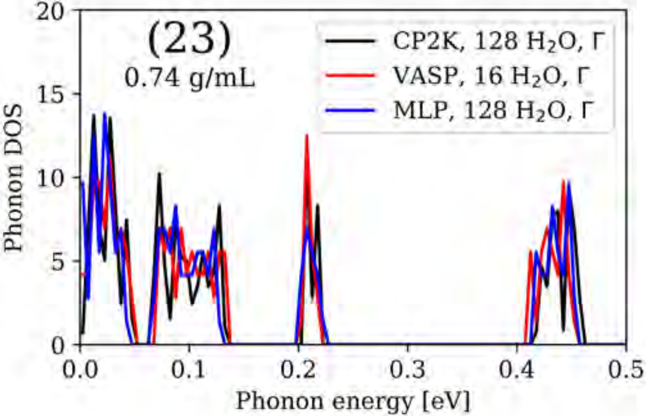

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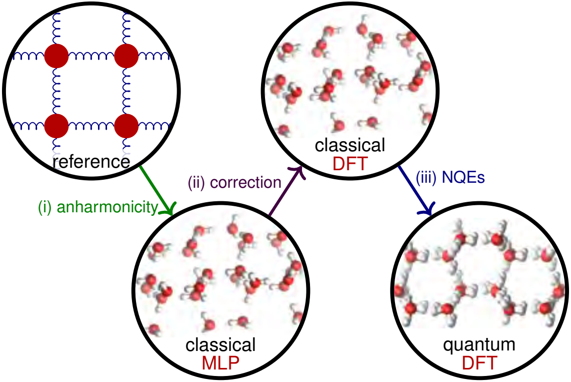
Hybrid DFT phase diagram of water

[Reinhardt & Cheng arXiv 2020]



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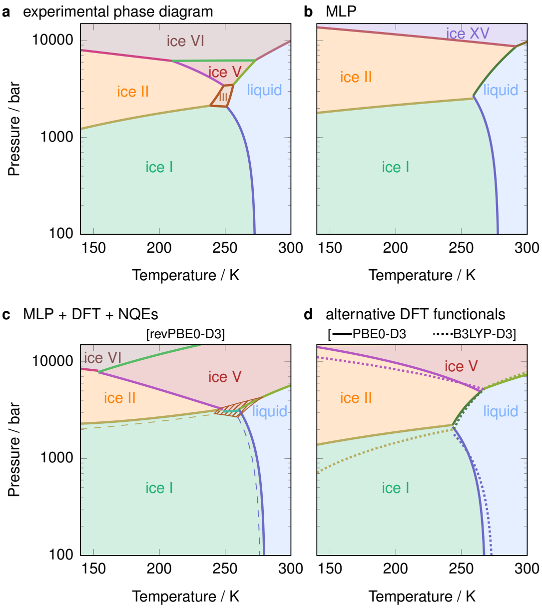

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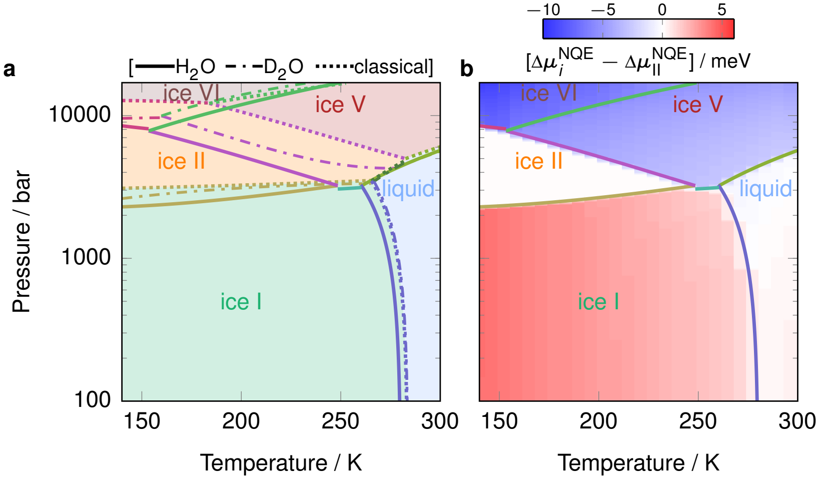
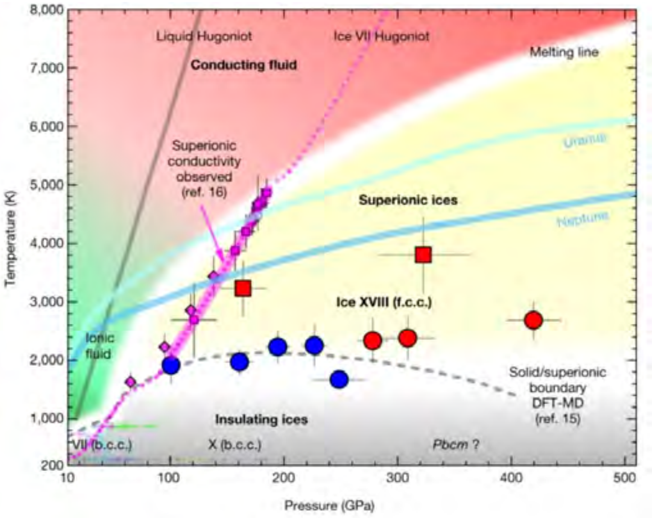


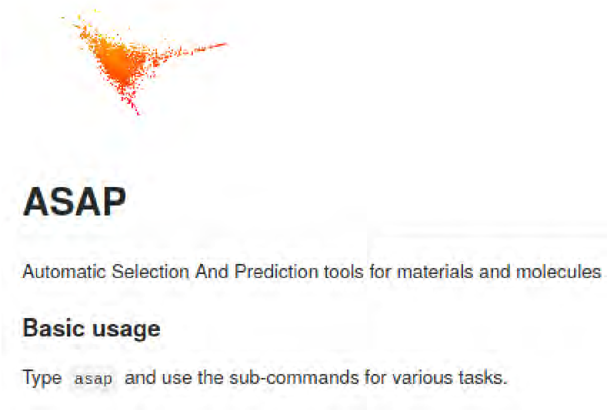
Future work: high-pressure water



[Millot et al. Nature 569,251-255 (2019)]

https://github.com/BingqingCheng/ASAP

Contributors: Ryan-Rhys Griffiths, Tamas Stenczel, Bonan Zhu, Felix Faber, Noam Bernstein



ASAP

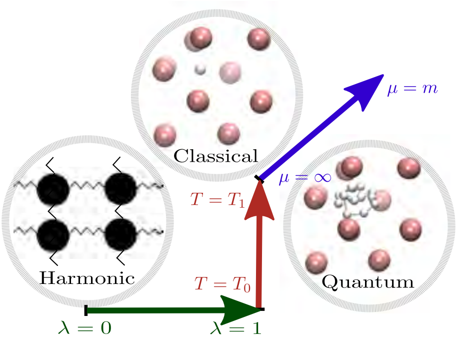
Automatic Selection And Prediction tools for materials and molecules

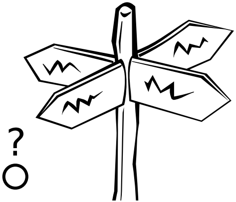
Basic usage

Type `asap` and use the sub-commands for various tasks.

- Low-dimensional embedding, regression
- Sparsification
- Clustering, kernel density estimation

Thermodynamic integration





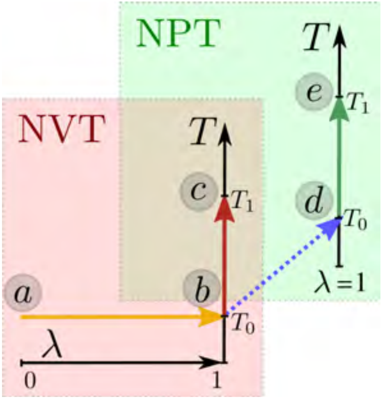
Consider two systems, A and B, which can be transformed continuously between each other via a parameter λ,

$$F_A - F_B = \int_{\lambda_A}^{\lambda_B} \frac{dF(\lambda)}{d\lambda} d\lambda$$

This parameter can be

- Thermodynamic variables (temperature, volume, concentration, etc.)
- Switching parameter between different Hamiltonians
- Order parameters (reaction coordinates)

Thermodynamic integration routes



[Cheng & Ceriotti PRB 2018]

$\longrightarrow$ Between harmonic and real crystal.
$\Delta A = \int_0^1 d\lambda \, \langle U - U_\mathrm{h} \rangle_{V,T_0,\lambda}$

$\longrightarrow$ Integrate with respect to temperature.
$$\Delta A = -\int_{T_0}^{T_1} \frac{\langle K + U \rangle_{V,T}}{T^2} dT$$

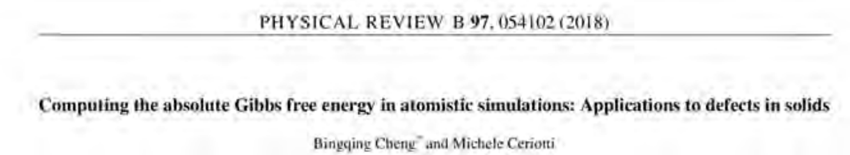
$\longrightarrow$ From NVT to NPT ensemble; from A to G.

$\longrightarrow$ Integrate with respect to temperature.
$$\Delta G = -\int_{T_0}^{T_1} \frac{\langle H \rangle_{P,T}}{T^2} dT$$

- To get the Helmholtz free energy A : $\longrightarrow \longrightarrow$
- To get the Gibbs free energy G: $\longrightarrow \longrightarrow \longrightarrow$

Getting started

A detailed yet simple description of the methodology

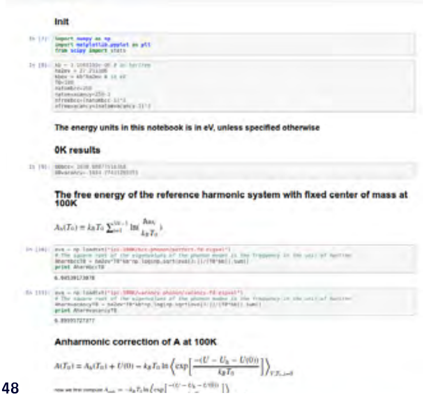


PHYSICAL REVIEW B 97, 054102 (2018)

Computing the absolute Gibbs free energy in atomistic simulations: Applications to defects in solids

Bingqing Cheng* and Michele Ceriotti

Python notebooks and scripts



Init

```
import numpy as np
import matplotlib.pyplot as plt
from scipy import stats
```

The energy units in this notebook is in eV, unless specified otherwise

0K results

The free energy of the reference harmonic system with fixed center of mass at 100K

$A_h(T_0) = k_B T_0 \sum_{i=1}^{3N-3} \ln(\frac{\hbar\omega_i}{k_B T_0})$

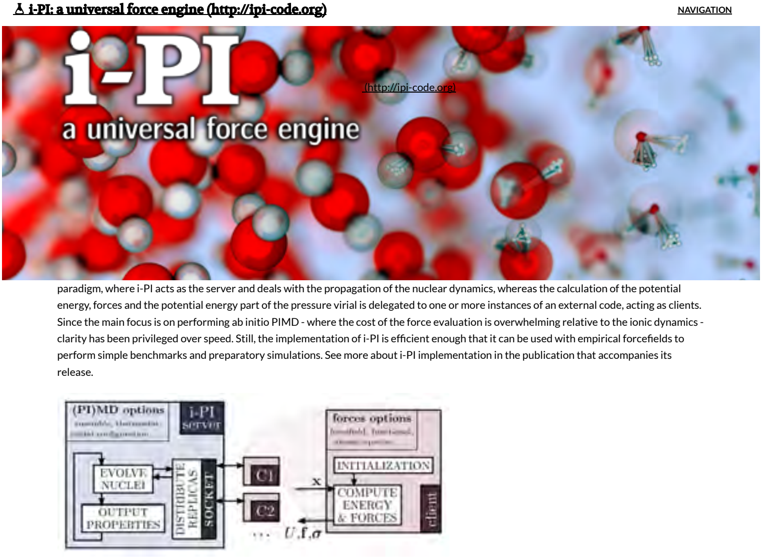
Anharmonic correction of A at 100K

$A(T_0) = A_h(T_0) + U(0) - k_B T_0 \ln\left\langle \exp\left[\frac{-(U - U_h - U(0))}{k_B T_0}\right]\right\rangle_{V,T_0,\lambda=0}$

Sample input files

The i-PI 2.0 code

[V. Kapil, et al. Computer Physics Communications (2018).]



i-PI: a universal force engine (http://ipi-code.org)

NAVIGATION

paradigm, where i-PI acts as the server and deals with the propagation of the nuclear dynamics, whereas the calculation of the potential energy, forces and the potential energy part of the pressure virial is delegated to one or more instances of an external code, acting as clients. Since the main focus is on performing ab initio PIMD - where the cost of the force evaluation is overwhelming relative to the ionic dynamics - clarity has been privileged over speed. Still, the implementation of i-PI is efficient enough that it can be used with empirical forcefields to perform simple benchmarks and preparatory simulations. See more about i-PI implementation in the publication that accompanies its release.

Path-integral formulism

The density of states: $\rho(q) = \langle q | e^{-\frac{\hat{K}+\hat{U}}{k_B T}} | q \rangle$

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Trotter expansion:

$$e^{-\frac{\hat{K}+\hat{U}}{k_B T}} = \lim_{p\rightarrow\infty} \left[e^{-\frac{\hat{U}}{2Pk_B T}} e^{-\frac{\hat{K}}{Pk_B T}} e^{-\frac{\hat{U}}{2Pk_B T}} \right]^P = \lim_{p\rightarrow\infty} \hat{\Omega}^P$$

Insert identity: $1 = \int dq \langle q | q \rangle$

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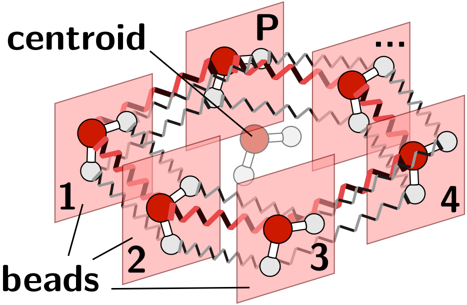
Ring polymer molecular dynamics



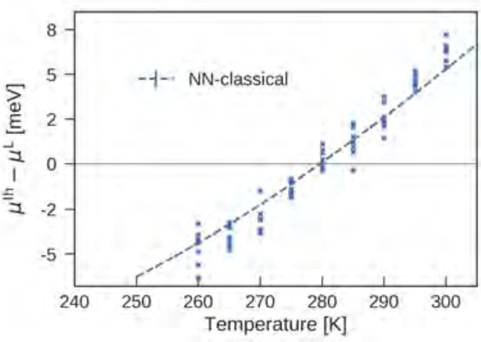
Isomorphism between a quantum mechanical particle and a ring polymer connected by harmonic springs. The Hamiltonian can be expressed as

$$H(\mathbf{p},\mathbf{q}) = \sum_{j=1}^{P} \frac{[\mathbf{p}^{(j)}]^2}{2m} + V(\mathbf{q}^{(j)}) + \frac{1}{2}m(\frac{Pk_B T}{\hbar})^2[\mathbf{q}^{(\mathbf{j})} - \mathbf{q}^{(\mathbf{j-1})}]^2$$

$$\mathbf{q}^{(\mathbf{0})} = \mathbf{q}^{(\mathbf{P})}$$

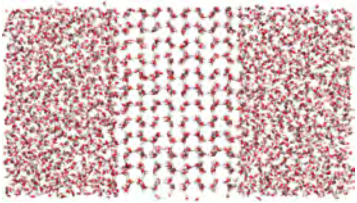
[Tuckerman, Statistical Mechanics]

Ice and liquid water



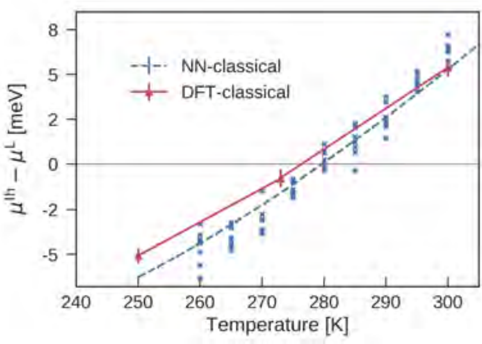
Umbrella simulation using NN potential:

$$\mathcal{H}_{biased}(\mathbf{q}) = \mathcal{H}_{ML}(\mathbf{q}) + \frac{\kappa}{2}\left(\Phi - \bar{\Phi}\right)^2$$



- The difference in the melting points of H2O and D2O is compariable with experiment (3.82 degrees).
- D2O and classical water have almost the same chemical potential, why?
- Error in melting point of H2O is about 2%.

Ice and liquid water



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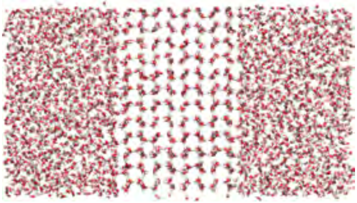

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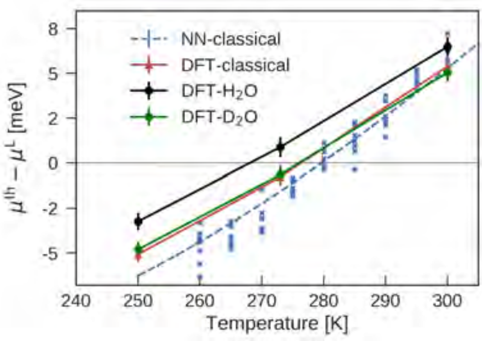

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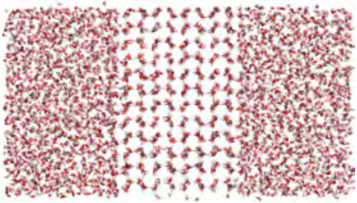

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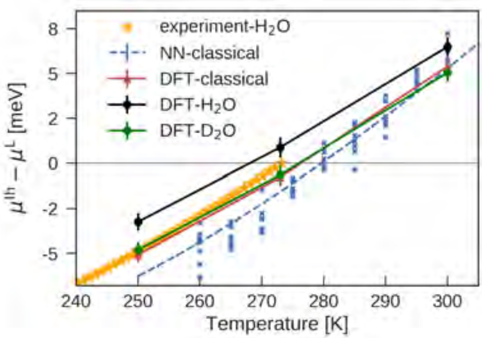

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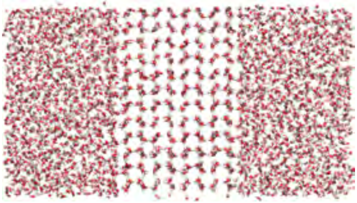

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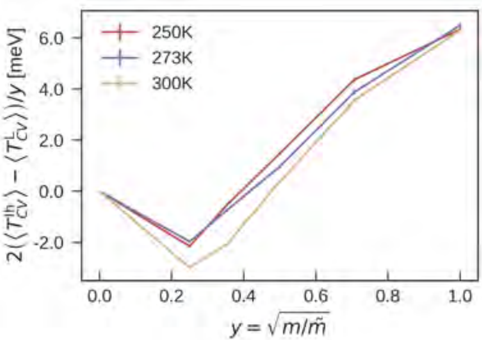

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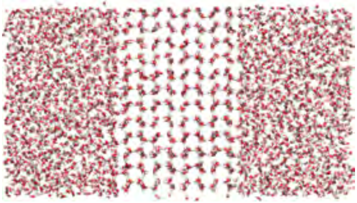

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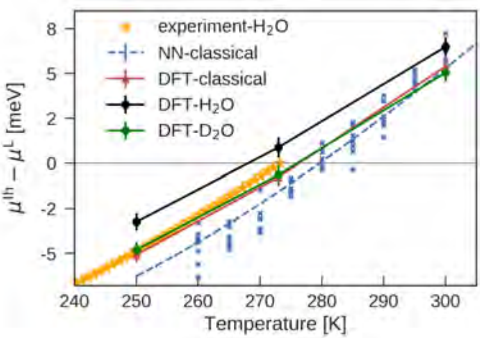

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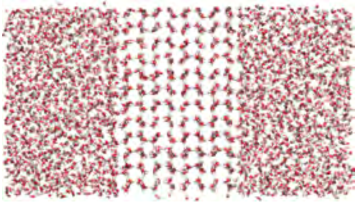

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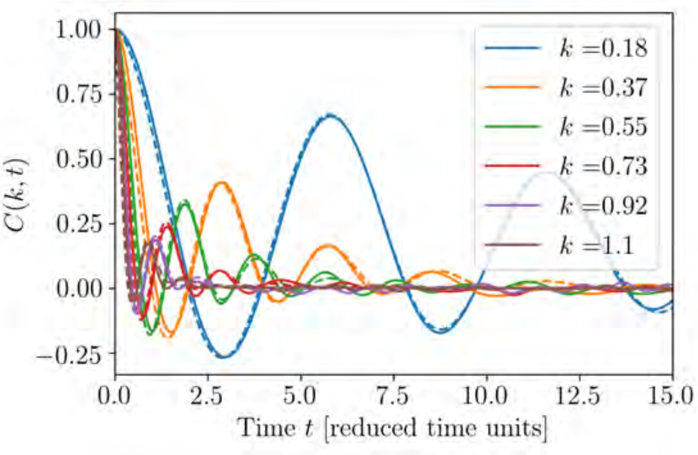
Benchmark on Lennard-Jones

[Cheng & Frenkel arXiv 2020]



Dashed lines: simulations

Solild lines: fits using the hydrodynamic equation.

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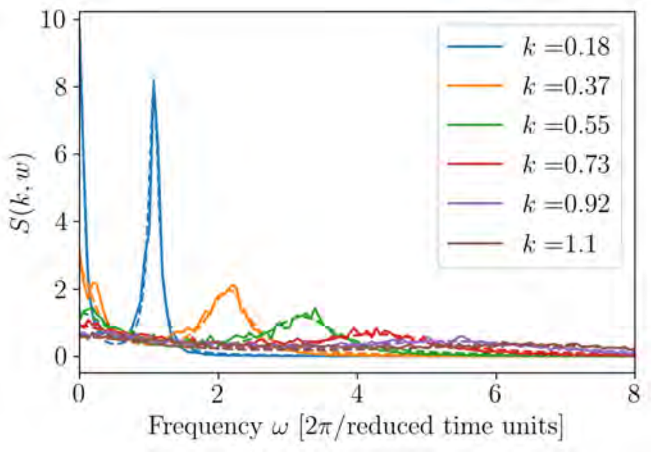

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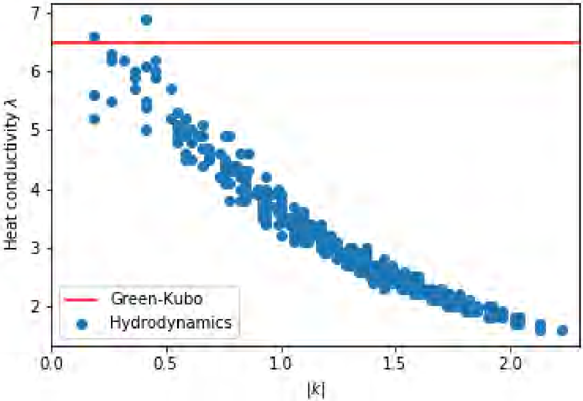
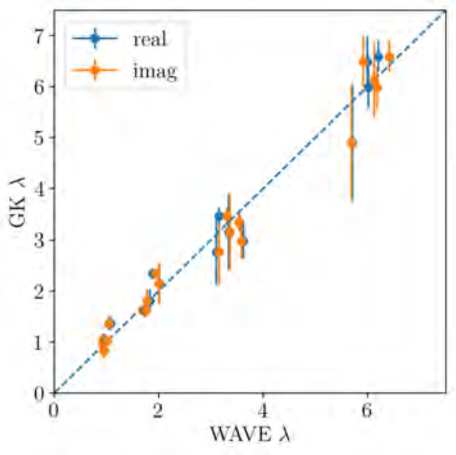


Blue dots: heat conductivity computed with WAVE at different k.
Solid line: Green-Kubo

Benchmark on Lennard-Jones

[Cheng & Frenkel arXiv 2020]



WAVE Vs. Green-Kubo
at different thermodynamic conditions