Title: Simulating Thermal and Quantum Fluctuations in Materials and Molecules

Speakers: Michele Ceriotti

Collection: Machine Learning for Quantum Design

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Abstract: Both electrons and nuclei follow the laws of quantum mechanics, and even though classical approximations and/or empirical models can be quite successful in many cases, a full quantum description is needed to achieve predictive simulations of matter. Traditionally, simulations that treat both electrons and nuclei as quantum particles have been prohibitively demanding. I will present several recent algorithmic advances that have increased dramatically the range of systems that are amenable to quantum modeling: on one hand, by using accelerated path integral schemes to treat the nuclear degrees of freedom, and on the other by using machine-learning potentials to reproduce inexpensively high-end electronic-structure calculations. I will give examples of both approaches, and discuss how the two can be used in synergy to make fully quantum modeling affordable.

Simulating Thermal and Quantum Fluctuations in Materials and Molecules

Michele Ceriotti
https://cosmo.epfl.ch

July 2019, Perimeter Institute, Toronto

EPFL

http://cosmo.epfl.ch

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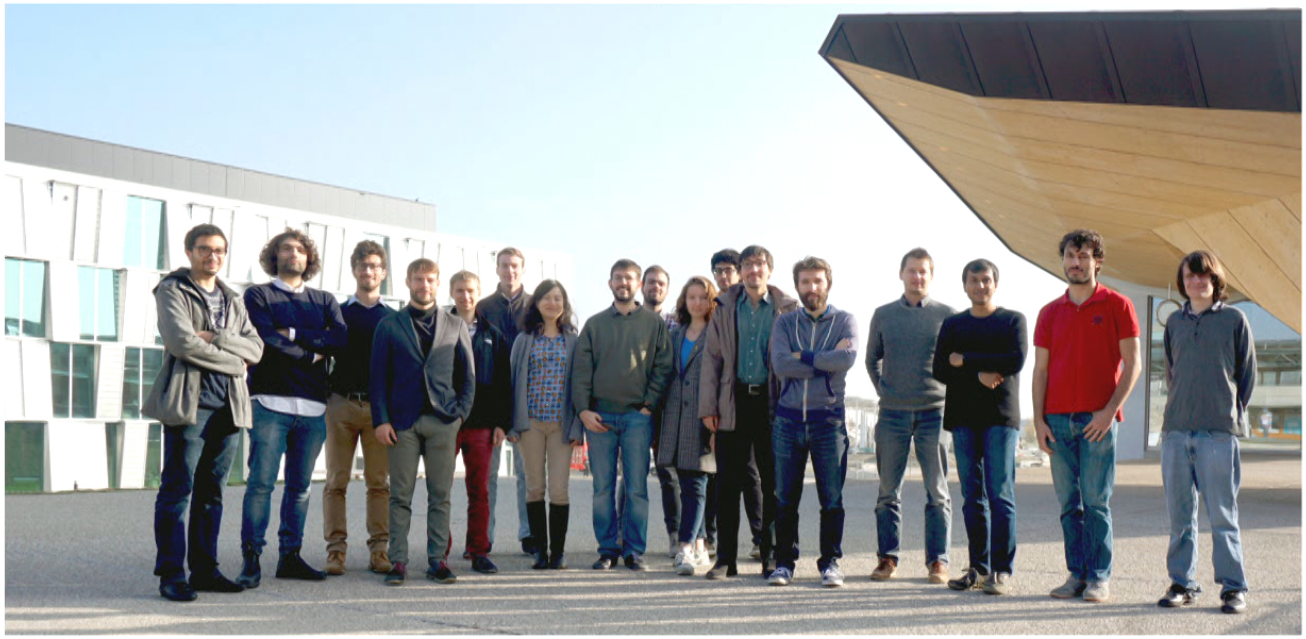


MARVEL

NATIONAL CENTRE OF COMPETENCE IN RESEARCH

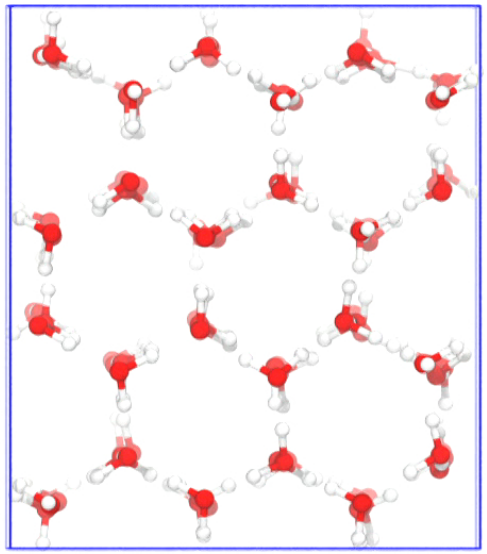
CCMX Competence Centre for Materials Science and Technology

V. Kapil, B. Cheng, S.De, F.Musil, M.Willatt, A.Grisafi, D.Wilkins, A. Anelli, E. Engel, G. Imbalzano

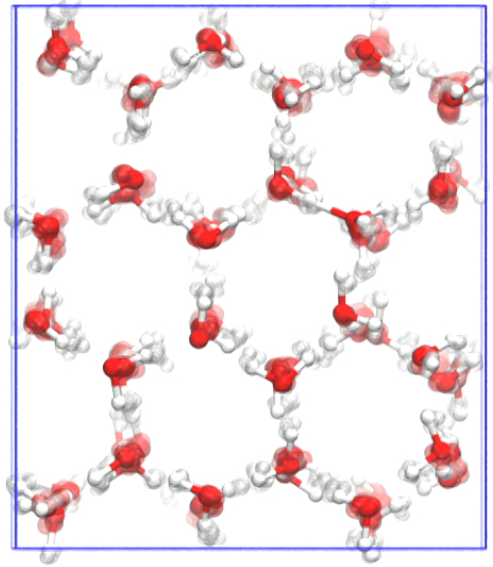
M.Rossi, T.Markland, D.Manolopoulos, M. Parrinello, G.Csányi, J. Behler, L.Emsley, C.Corminboeuf, R.DiStasio

Fluctuations worth caring about

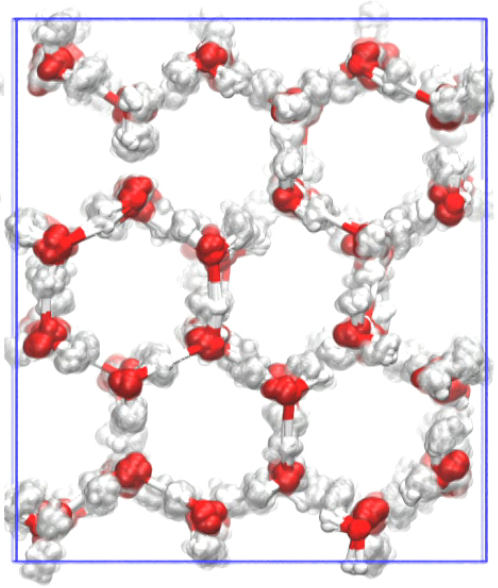
- Potential energy is central to achieve predictive atomic-scale modeling
- The minima of the potential energy surface provide a limited view of the (thermo)dynamics of complex systems



Minimum potential,
$\partial V / \partial \mathbf{x} = 0$



Thermal fluctuations
@ 100K

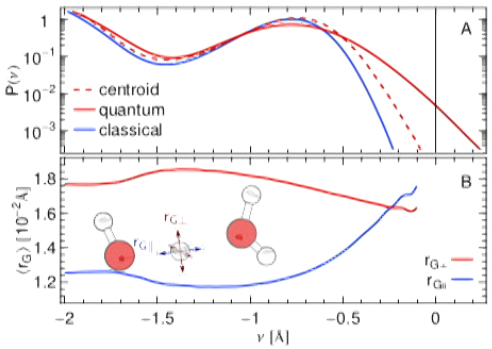


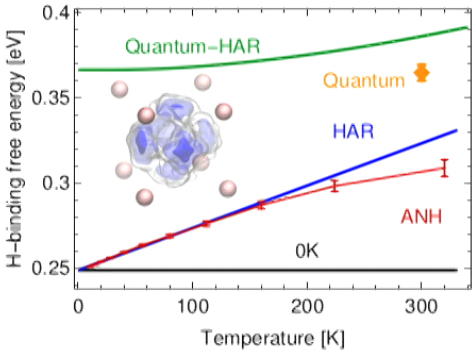
Quantum fluctuations
@ 100K

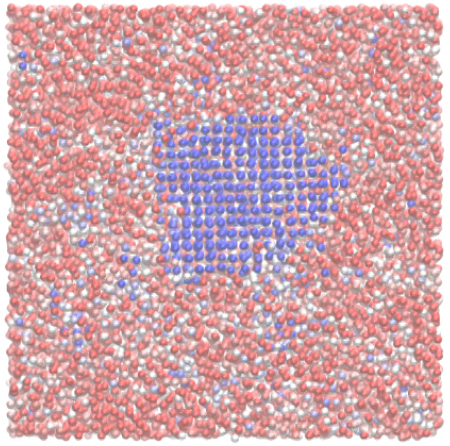

IMETER
INSTITU

Challenges of modeling fluctuations

- Accurate modelling of materials at finite temperature requires accounting for thermal and quantum statistical fluctuations
  - Nuclear quantum effects
  - Anharmonic free energies
  - Activated events and phase transitions
- All of these simulations require evaluating atomic-scale properties an enormous ($\mathcal{O}\left(10^6\right)$) number of times







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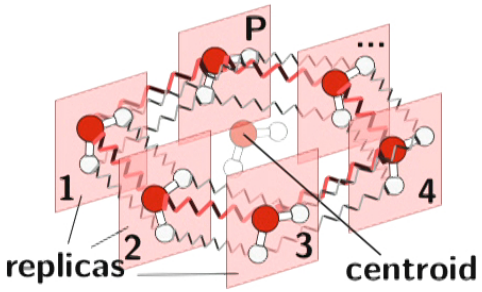
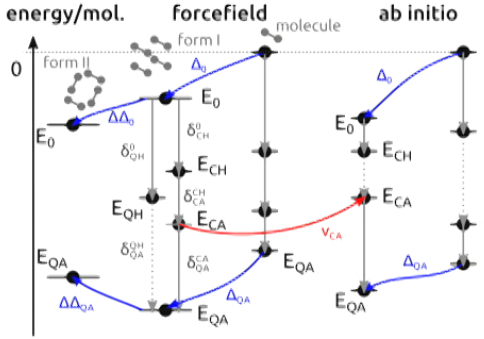
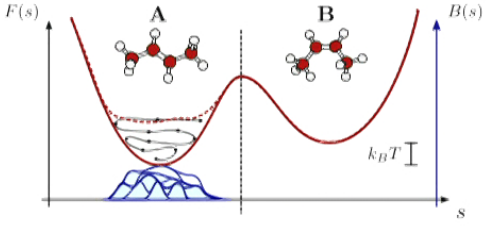
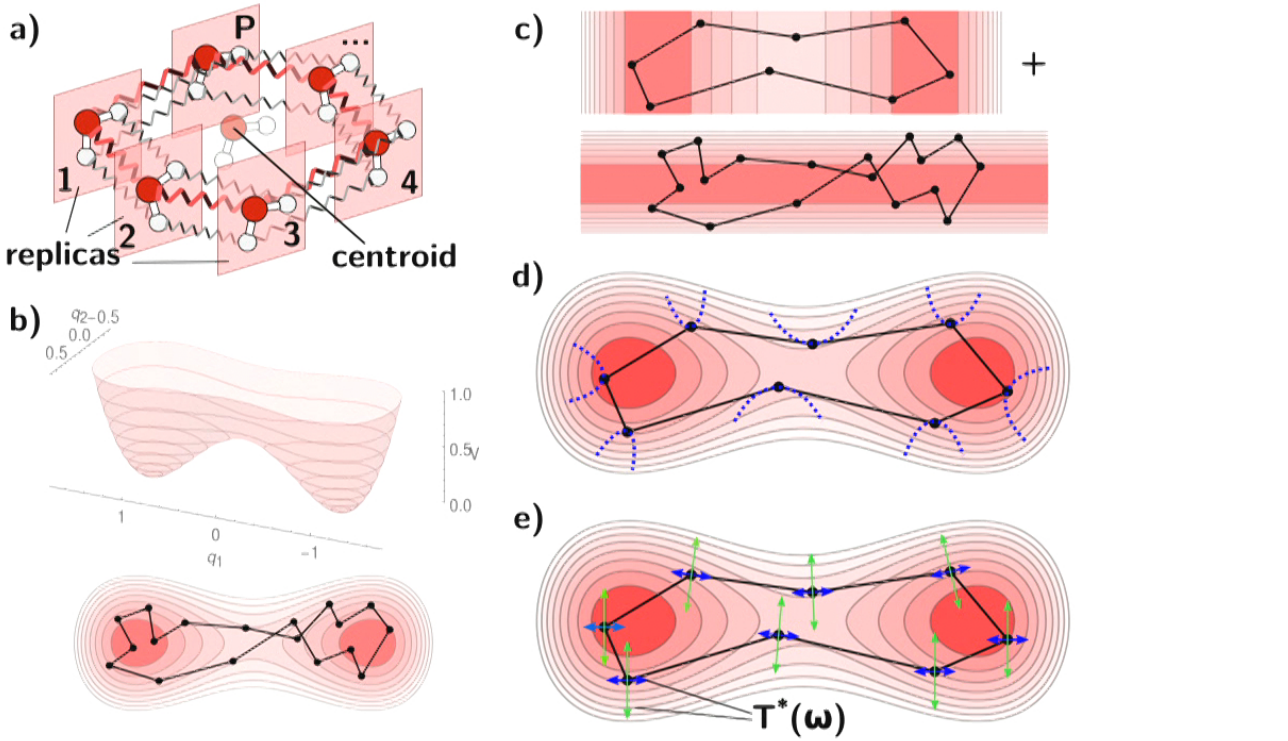






Quantum effects becoming mainstream

- Over the past decade, large community effort to make quantum simulations affordable, exploiting separation of timescales, and the quasi-harmonic behavior of the potential



Markland & Ceriotti, Nature Reviews Chemistry (2018)

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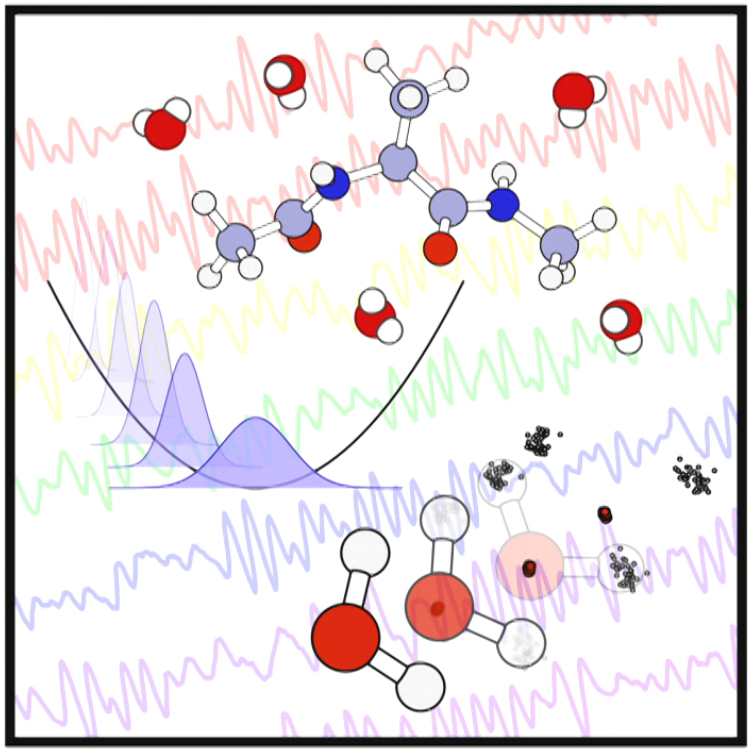

Ceriotti, Bussi, Parrinello PRL 103 (2009)

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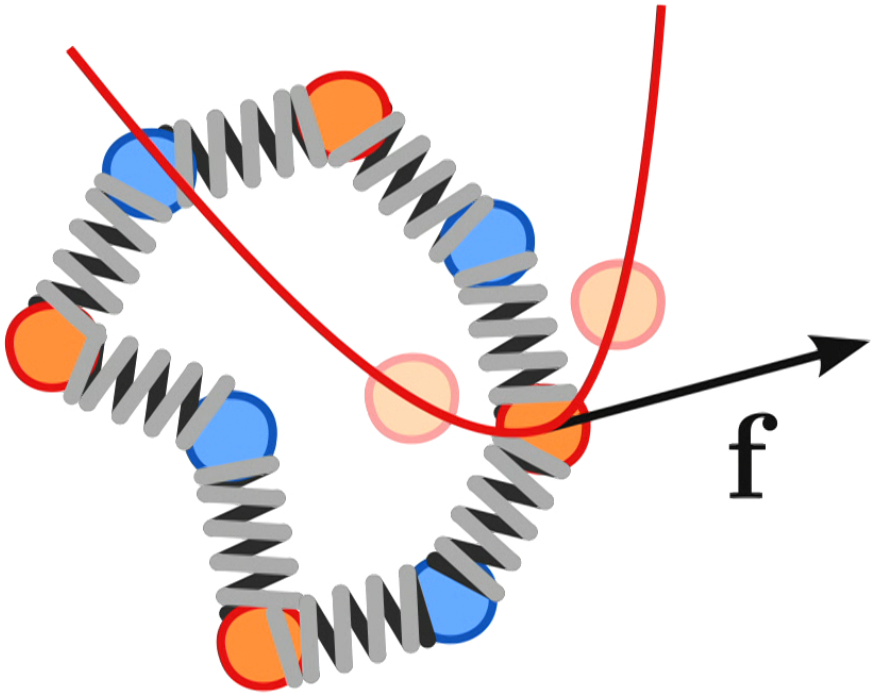
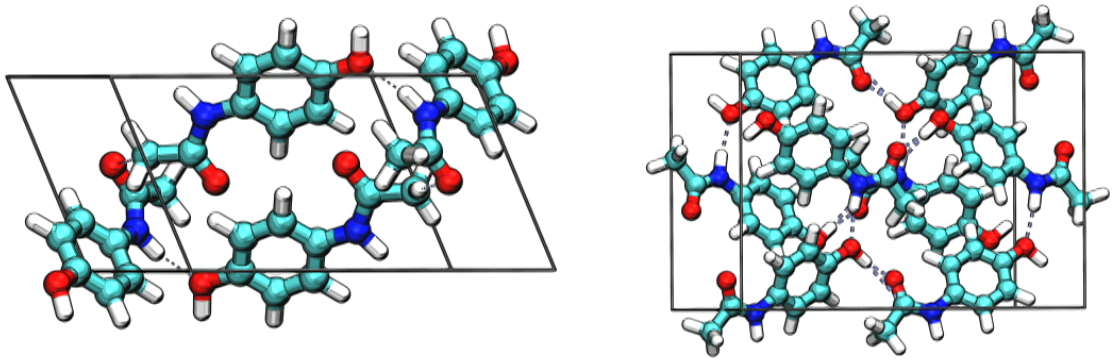


Kapil, Behler, Ceriotti, JCP (2016)

The full quantum deal

Quantum effects in molecular crystals

- Polymorphism of molecular crystals has serious implications for pharma
- Assessing quantum and anharmonic contributions to the stability of paracetamol form I and II
- A complex combination of thermodynamic integration steps:
  - PIMD with multiple time step and GLE acceleration
  - Phonon calculations and thermodynamic integration
- Bottom line: quantum nuclear effects and anharmonic free energy are as important as the details of the electronic structure calculation (PBE+D3)



Rossi, Gasparotto, **MC**, PRL (2016)

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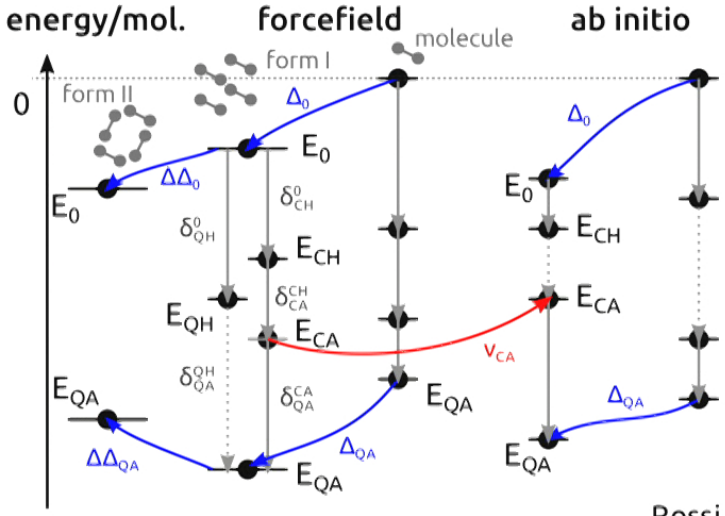

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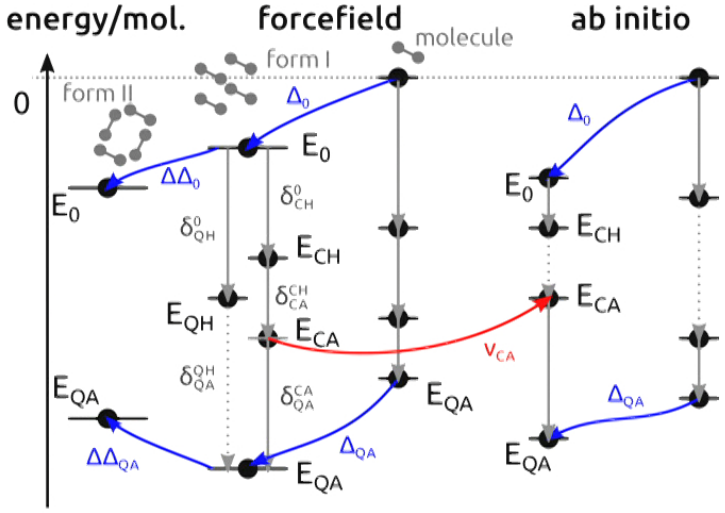
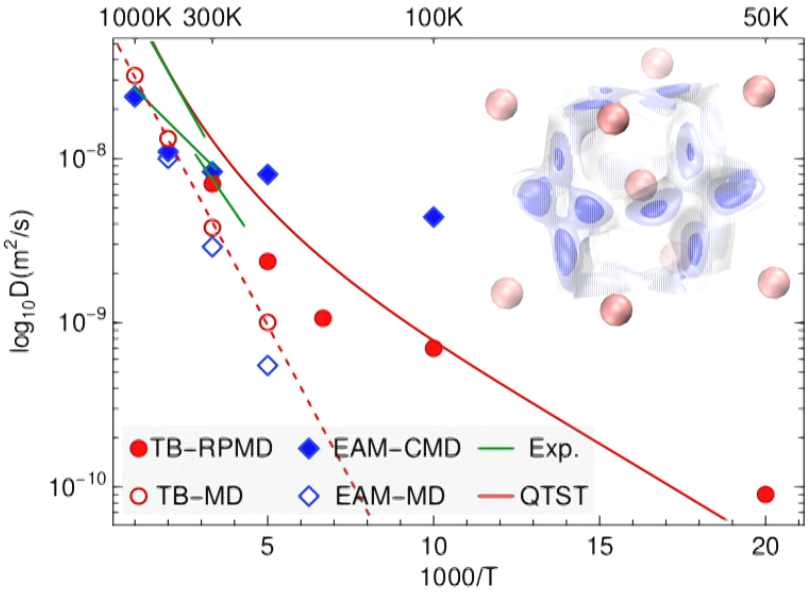


meV/mol	Δ(form I-form II)
Δ_0	-3
Δ_{CH}	-13
Δ_{CA}	-38
Δ_{QH}	-18
Δ_{QA}	-45

Rossi, Gasparotto, **MC**, PRL (2016)

Quantum fluctuations in metallurgy?

- Embrittlement of steel in presence of hydrogen: a decades-old problem
- Hydrogen diffuses rapidly across the tetrahedral sites in the lattice
- Quantum effects, modelled by TRPMD, accelerate diffusion at and below room temperature
- Vacancies act as traps, 30% stabilization for quantum hydrogen



Cheng, Paxton, **MC**, Phys. Rev. Lett. (2018)

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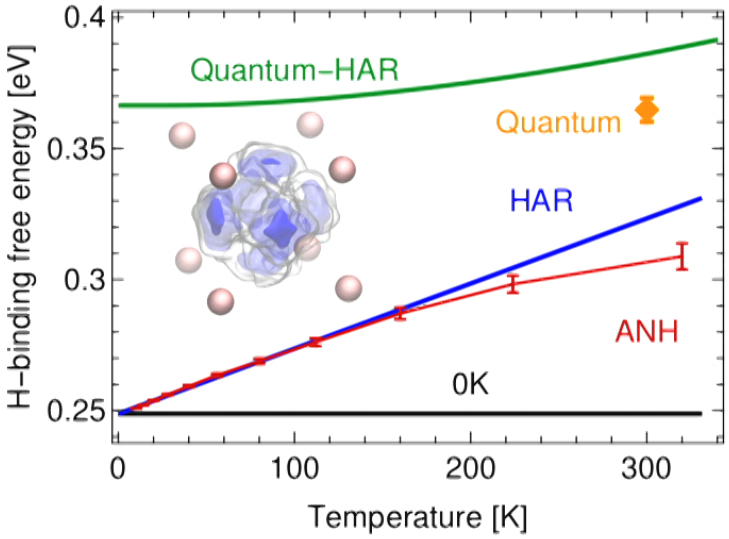
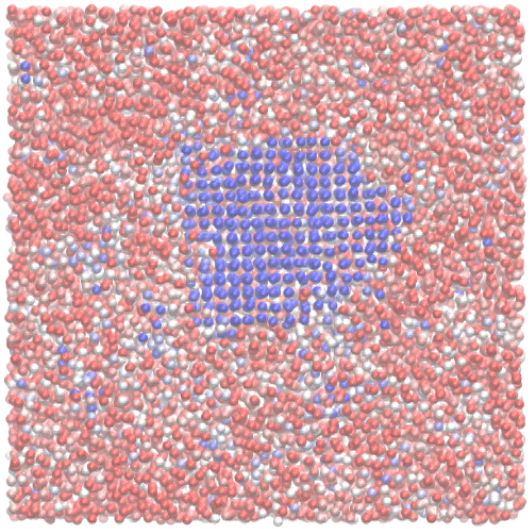


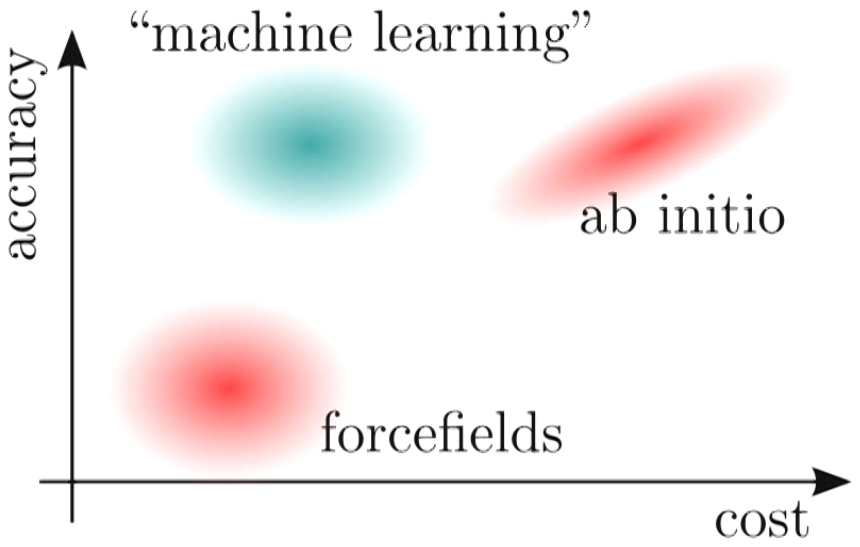
Cheng, Paxton, **MC**, Phys. Rev. Lett. (2018)

Machine learning: why do I care

Machine learning for statistical sampling

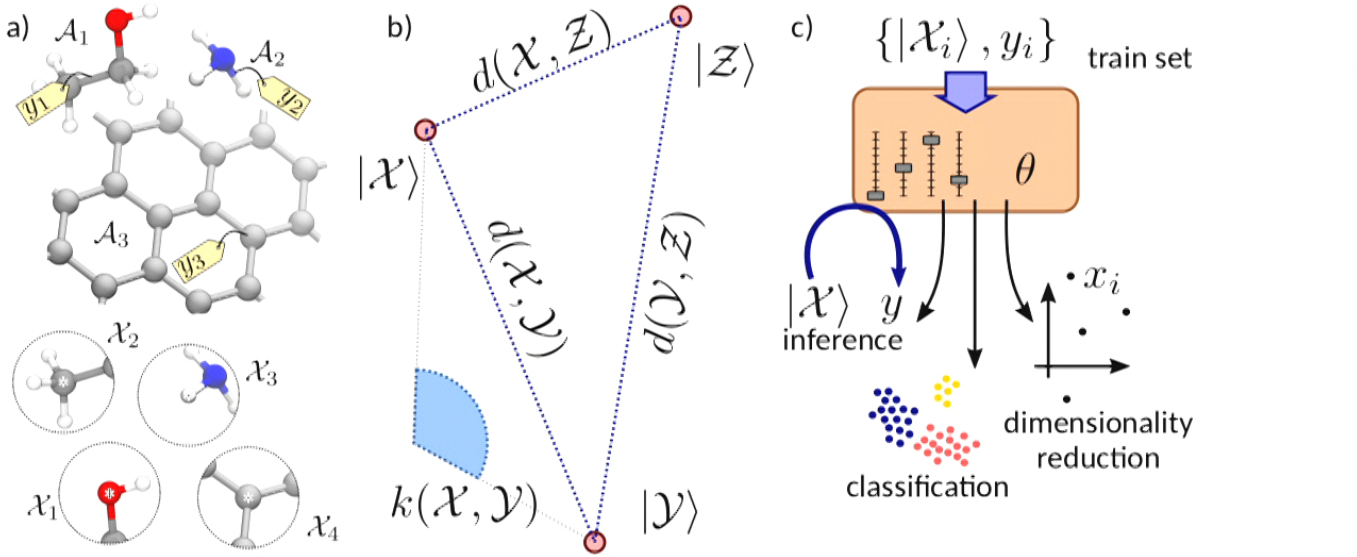
- As much as one can improve sampling methods, convergence still requires millions of energy/force/properties evaluations. Inevitable tradeoff between cost, accuracy and transferability.
- Sampling is a very favorable scenario for ML because it often involves relatively minor variations around meta-stable states





Machine-learning in a nutshell

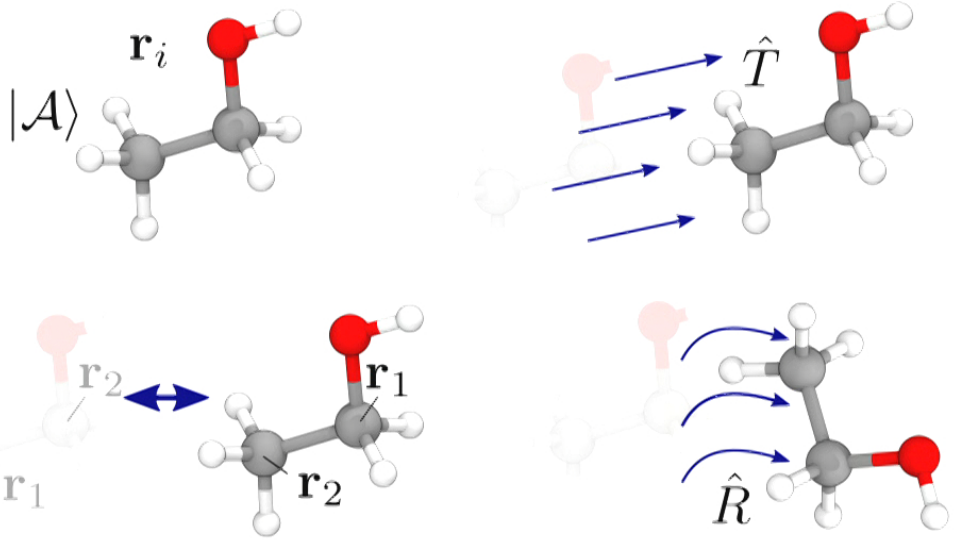
- Chemical structures/environments need to be cast in a complete but concise mathematical representation
- The input/label pairs are fed to a learning scheme, tuned by hyperparameters θ, that can then be used to perform different tasks on new data



JCP Perspective, **MC**, JCP (2019)

A representation for atomic environments

- Incorporating physics and physical symmetries is key to efficient ML of atomic-scale properties
- Most effective ML representations sets can be seen as projections of many-body correlation functions on various bases
- Compressed alchemical representations to learn (across the) periodic table



Willatt, Musil, **MC**, JCP (2019)

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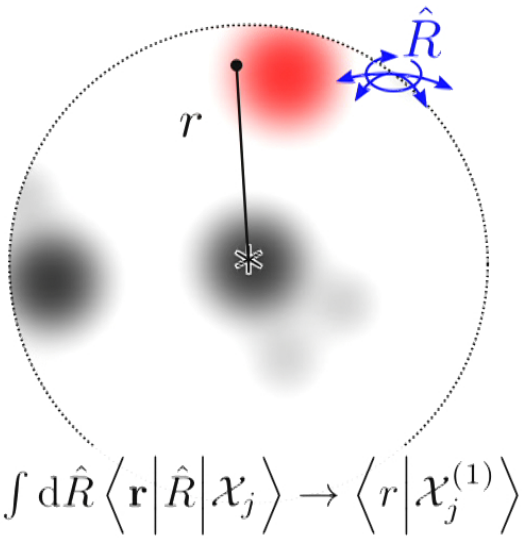
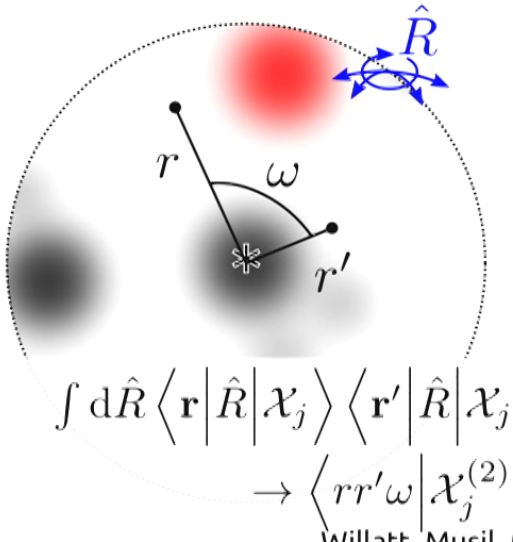


$$\int \mathrm{d}\hat{R} \left\langle \mathbf{r} \middle| \hat{R} \middle| \mathcal{X}_j \right\rangle \rightarrow \left\langle r \middle| \mathcal{X}_j^{(1)} \right\rangle$$



$$\int \mathrm{d}\hat{R} \left\langle \mathbf{r} \middle| \hat{R} \middle| \mathcal{X}_j \right\rangle \left\langle \mathbf{r}' \middle| \hat{R} \middle| \mathcal{X}_j \right\rangle \rightarrow \left\langle r r' \omega \middle| \mathcal{X}_j^{(2)} \right\rangle$$

Willatt, Musil, **MC**, JCP (2019)

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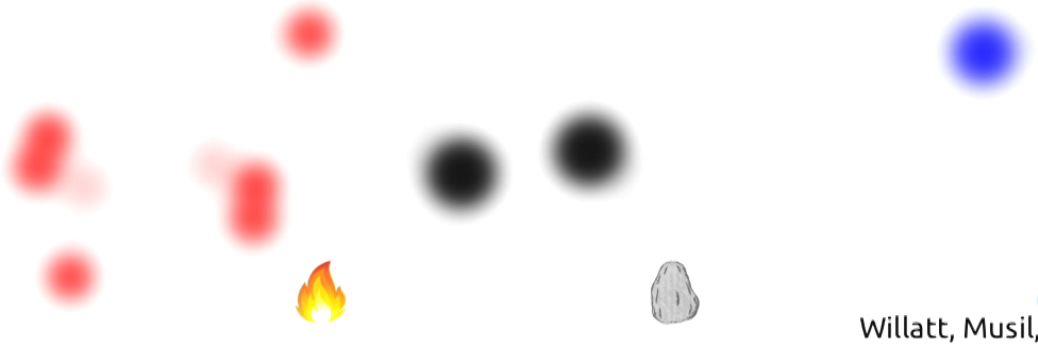
$$|\mathrm{H}\rangle = 0.5\,|🔥\rangle + 0.1\,|🪨\rangle + 0.2\,|💧\rangle$$
$$|\mathrm{C}\rangle = 0.2\,|🔥\rangle + 0.8\,|🪨\rangle + 0.3\,|💧\rangle$$
$$|\mathrm{O}\rangle = 0.1\,|🔥\rangle + 0.1\,|🪨\rangle + 0.6\,|💧\rangle$$



Willatt, Musil, **MC**, PCCP (2018)

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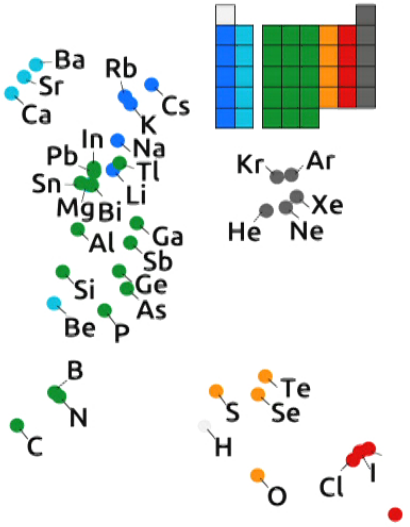
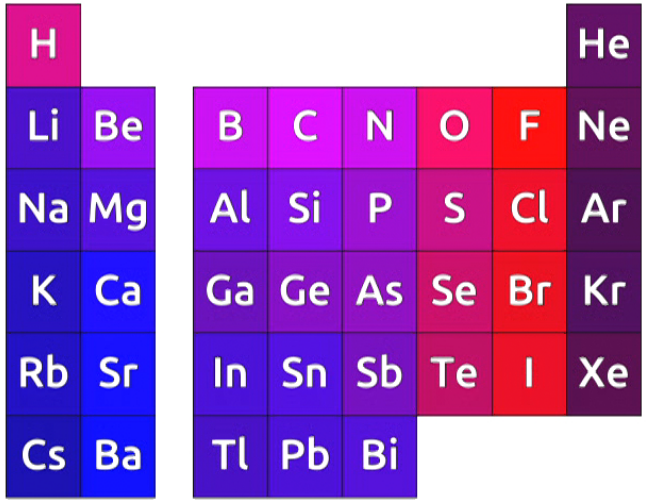
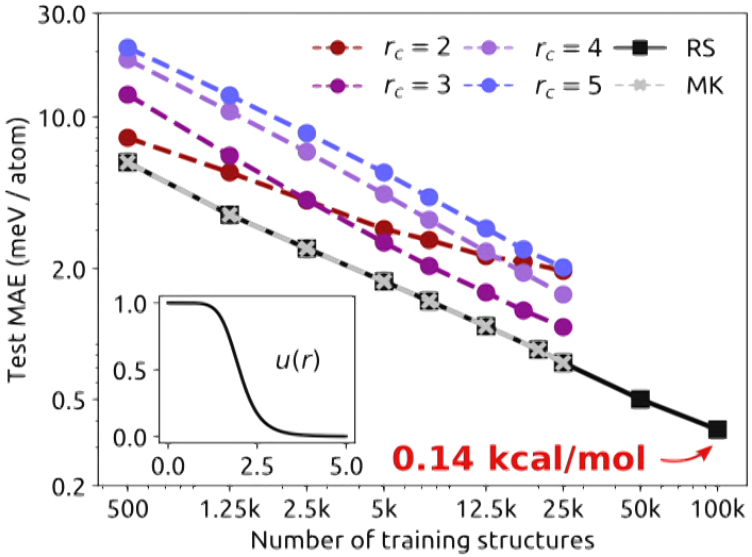


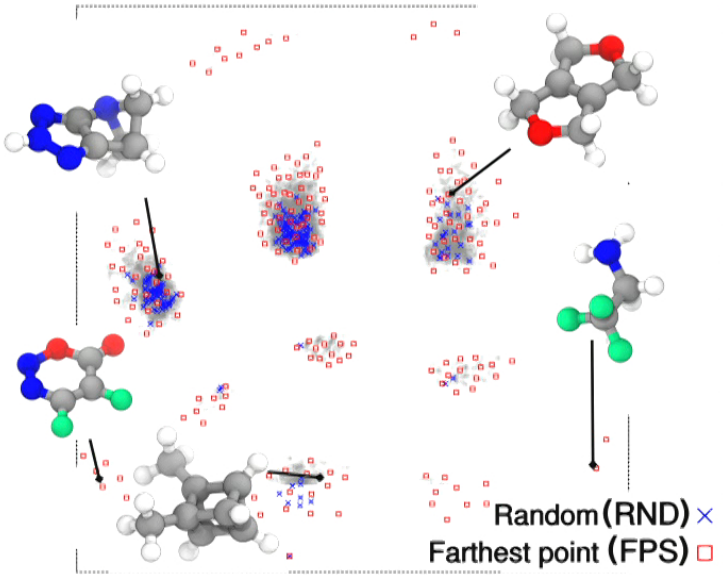


Willatt, Musil, **MC**, PCCP (2018)

A brief overview of ML applications

- ML can be pretty versatile, when applied to atomistic problems. Molecular and crystals energetics, NMR crystallography, fully anisotropic molecular polarizabilities with coupled-clusters accuracy, charge density.





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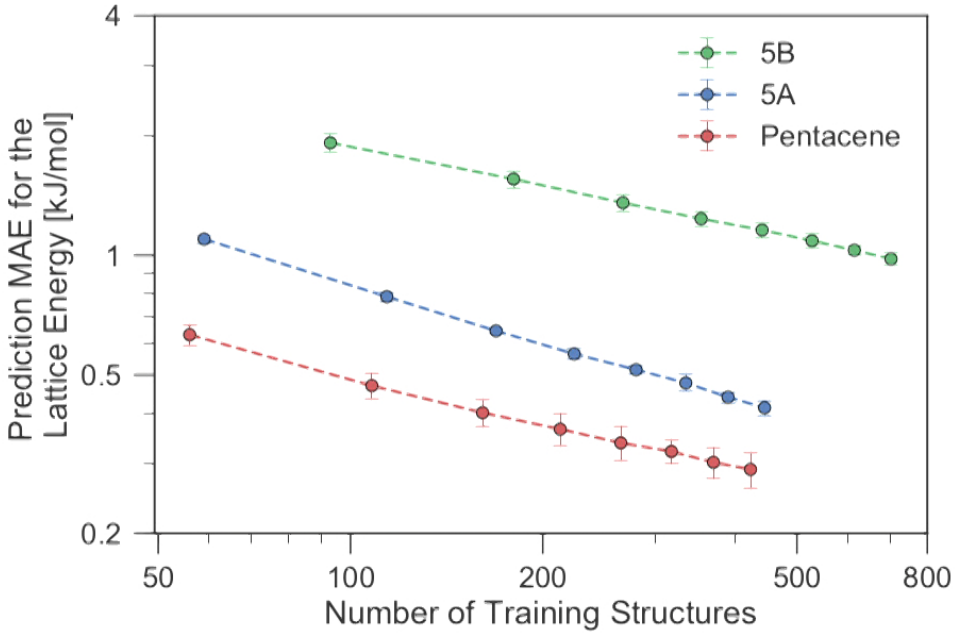

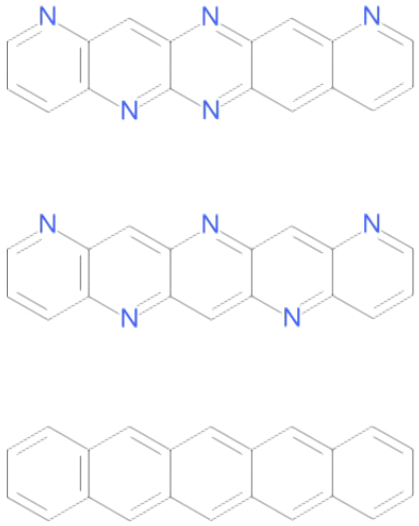

Musil, De, Yang, Campbell, Day, **MC**, Chemical Science (2018) *[data: G.Day, J.Yang]*

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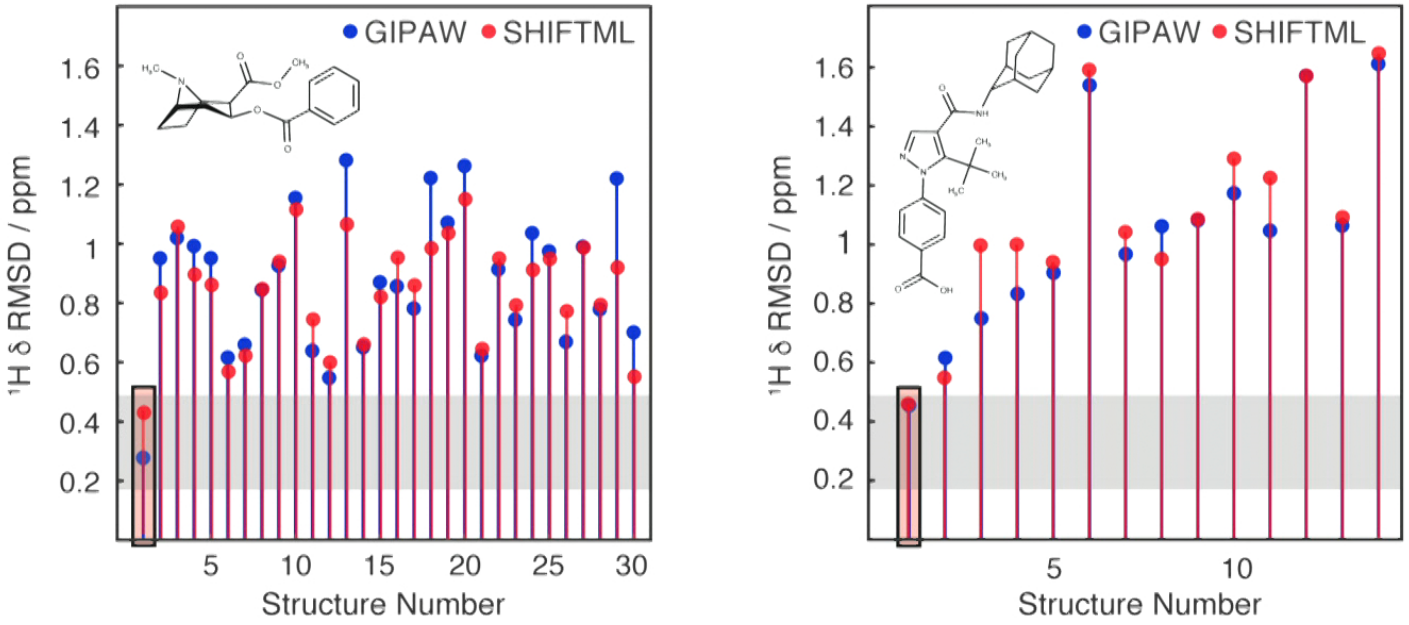

Paruzzo, Hofstetter, Musil, De, **MC**, Emsley, Nature Comm. (2018); http://shiftml.org *[data: CSD-500]*

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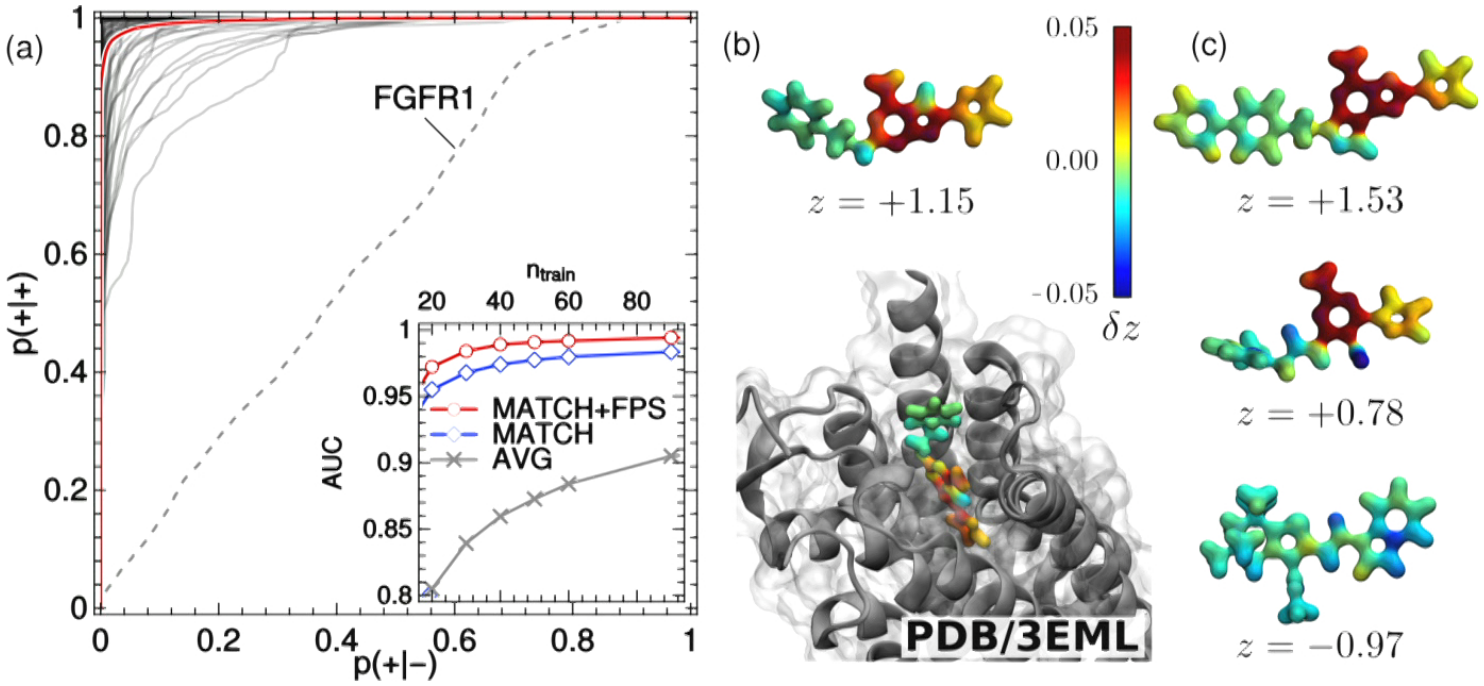

Bartok, De, Kermode, Bernstein, Csanyi, **MC**, Science Advances (2017) *[data: DUD-E, Shoichet]*

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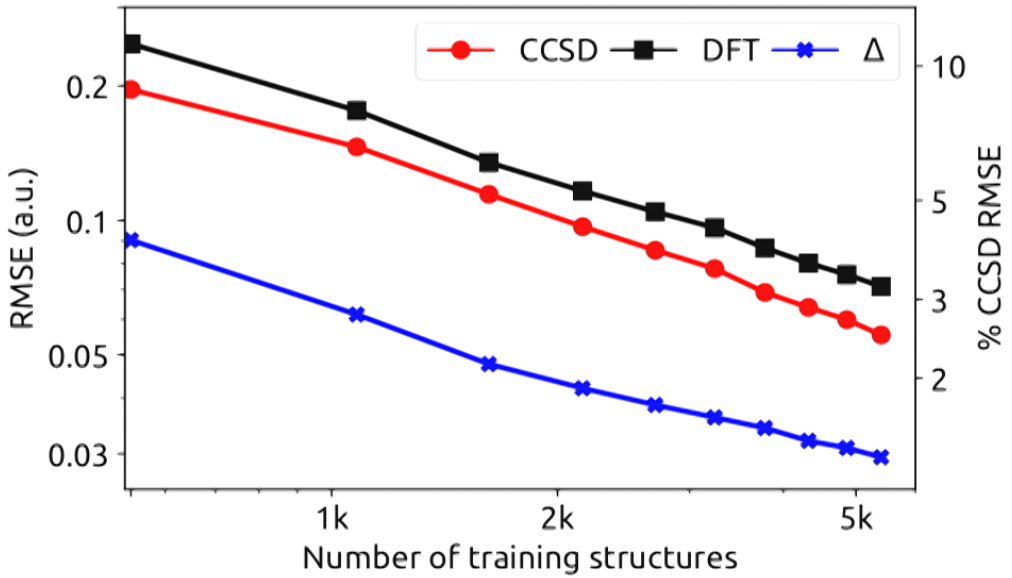

Wilkins, Grisafi, Yang, Lao, DiStasio, **MC**, PNAS (2019); `http://alphaml.org`

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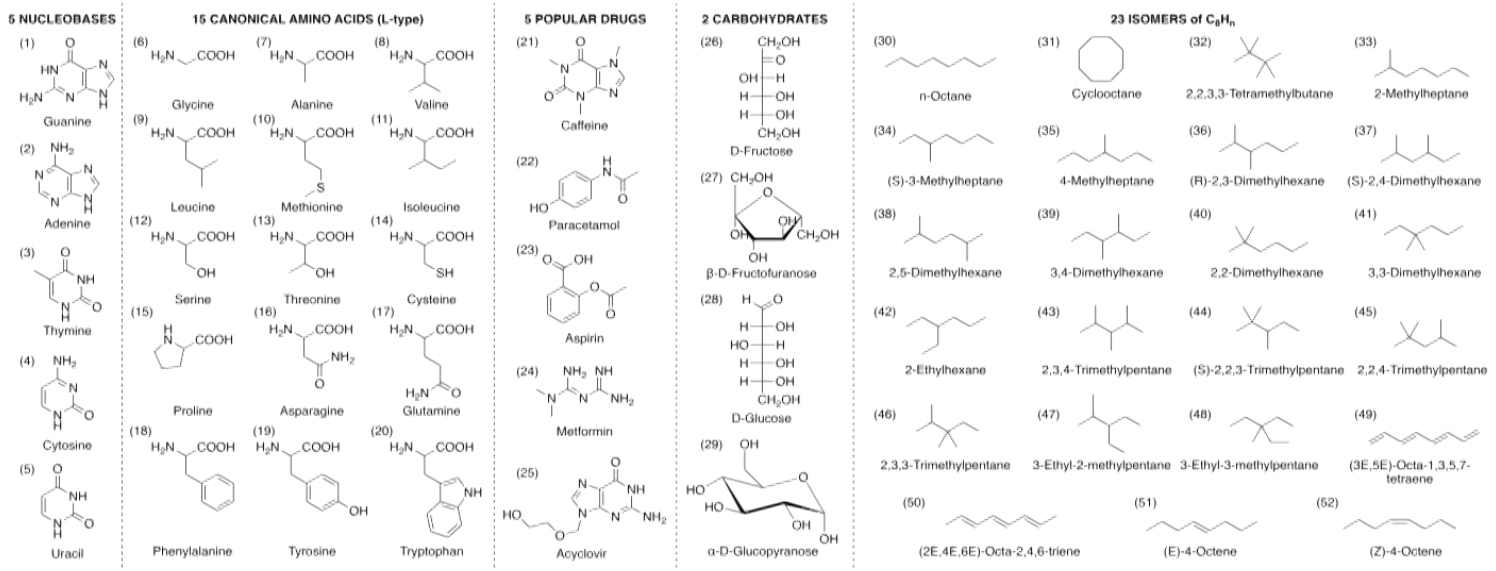

Wilkins, Grisafi, Yang, Lao, DiStasio, **MC**, PNAS (2019); `http://alphaml.org`

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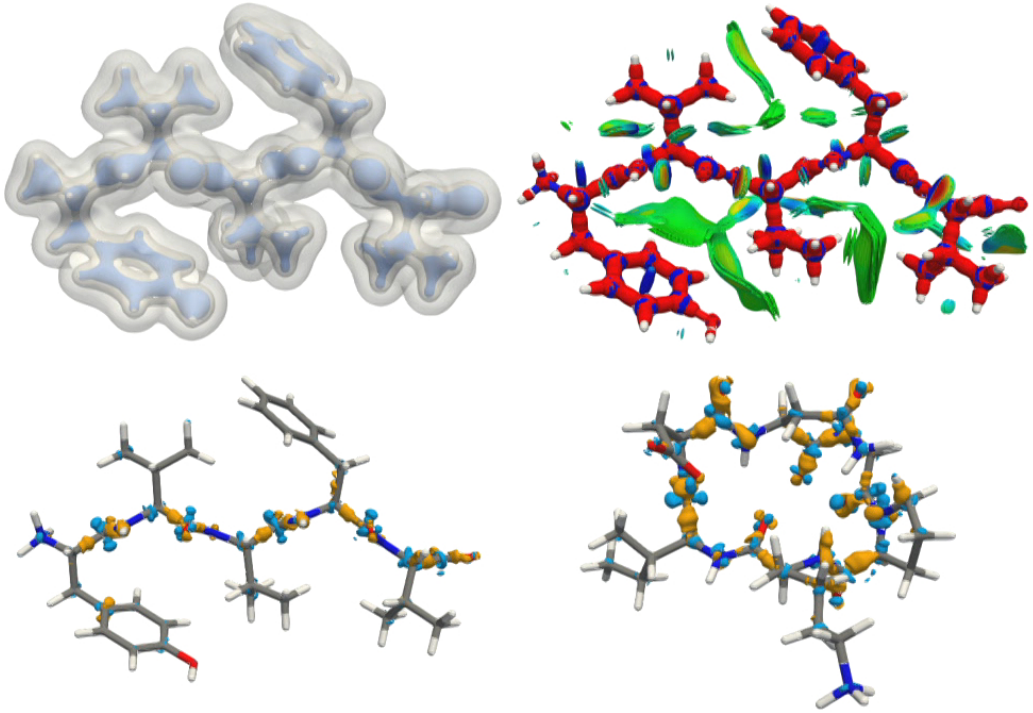
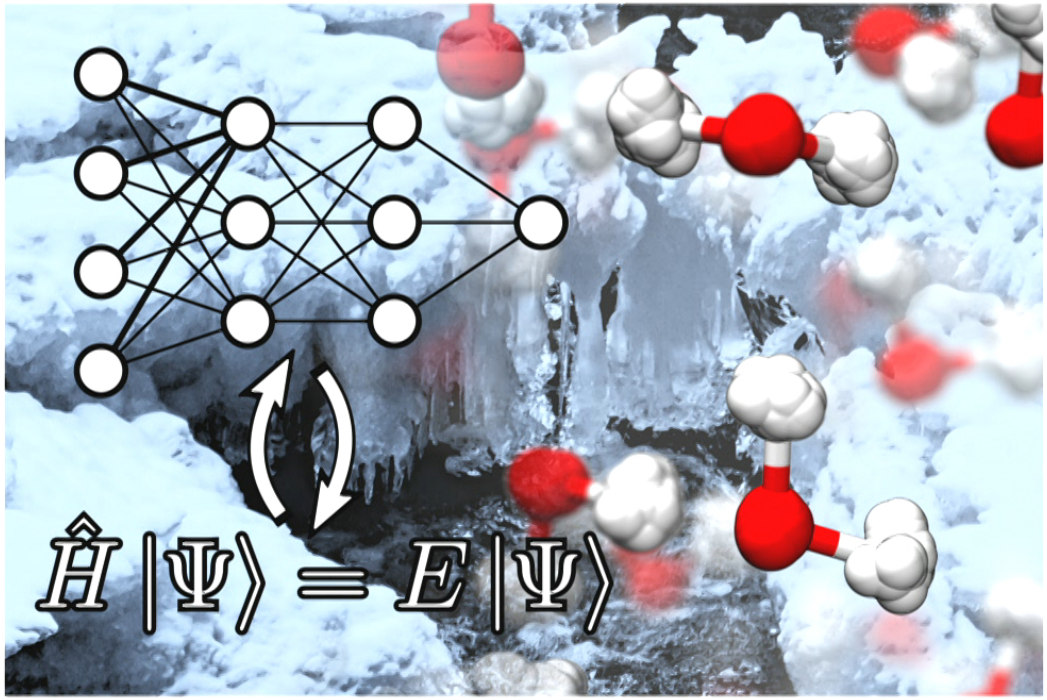


Grisafi, Wilkins, Meyer, Fabrizio, Corminboeuf, **MC**, ACS Central Science (2019)

Ab initio thermodynamics of water

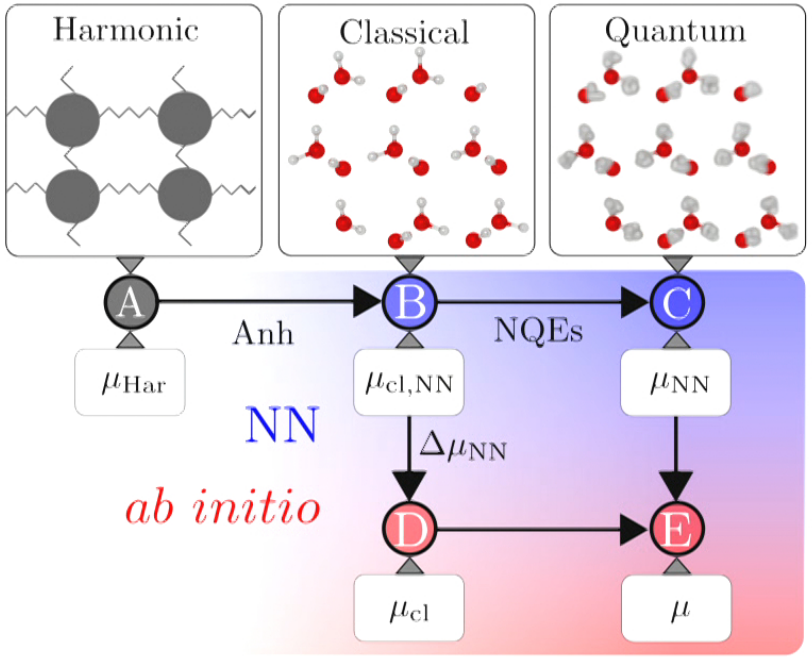
Ab initio thermodynamics of water

- Huge challenge: determining the thermodynamics of Ih/Ic polymorphism (and the liquid, as a bonus) at the hybrid DFT+D3 level



Machine learning is key (but not quite enough)

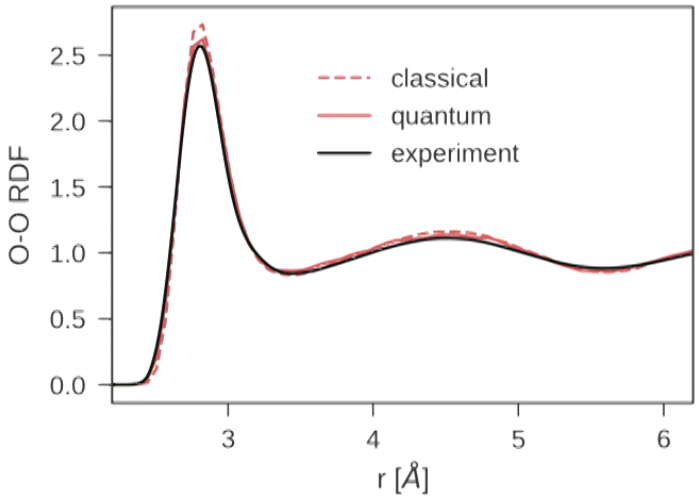
- Use a machine-learned potential (Behler-Parrinello NN) as a stepping stone, for all thermodynamic integration.
- Still missing subtle long-range physics (proton disorder, ...). Sample with NN, and promote to full-DFT level by free-energy perturbation!

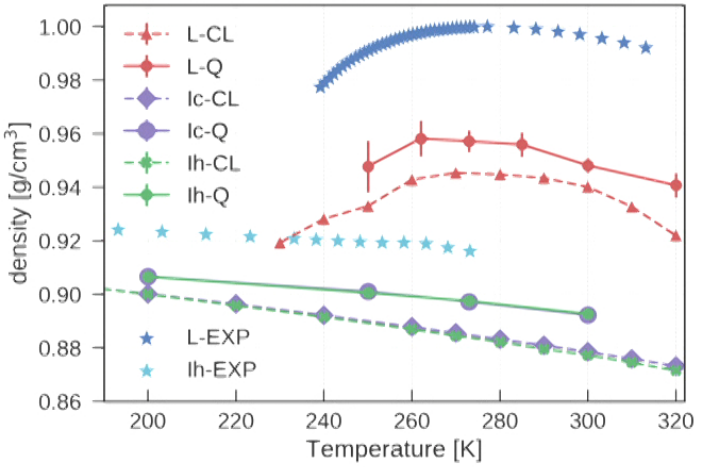


Cheng, Engel, Behler, Dellago, **MC**, PNAS (2019)

meV/molecule accuracy pays off

- Excellent agreement with experiments. REVPBE0-D3 confirmed to be really good for water
- Nuclear quantum effects contribute a small (crucial!) stabilization to the hexagonal phase





Cheng, Engel, Behler, Dellago, **MC**, PNAS (2019)

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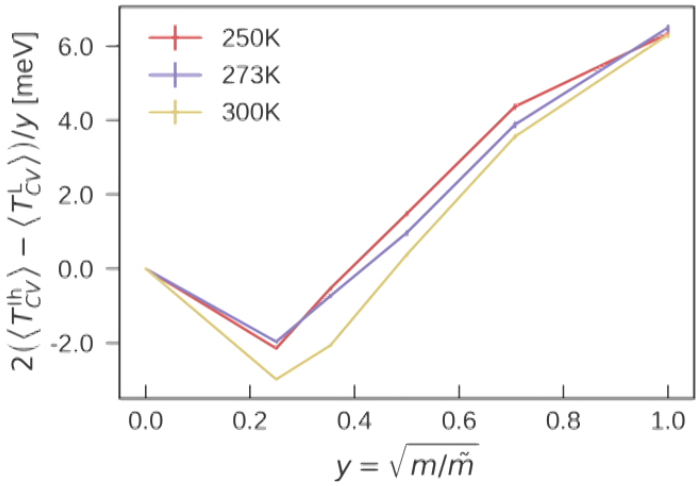

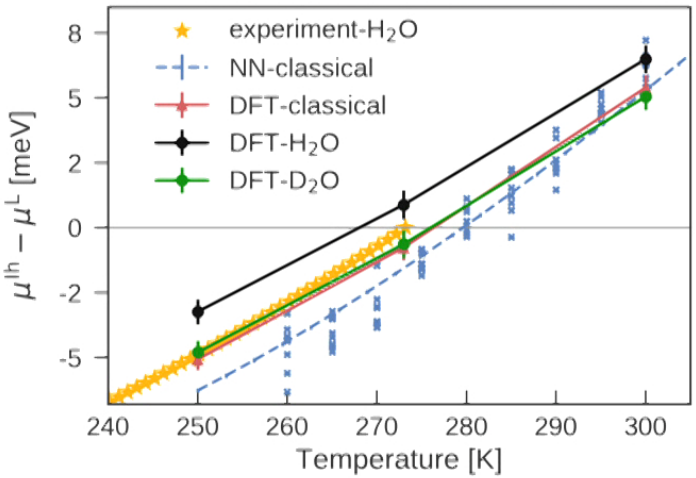

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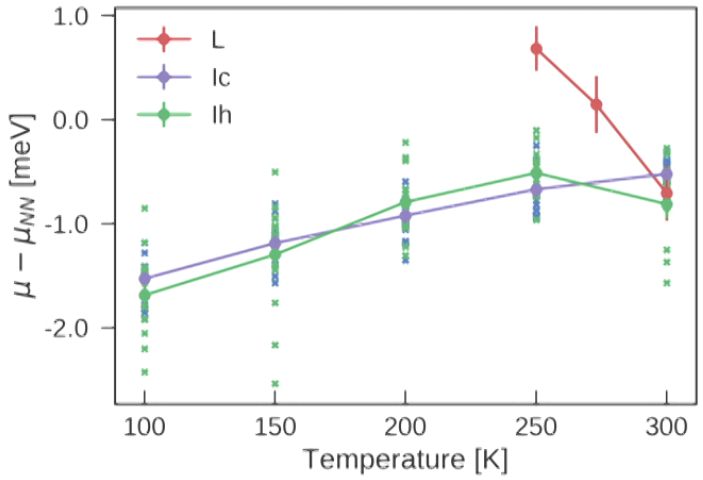
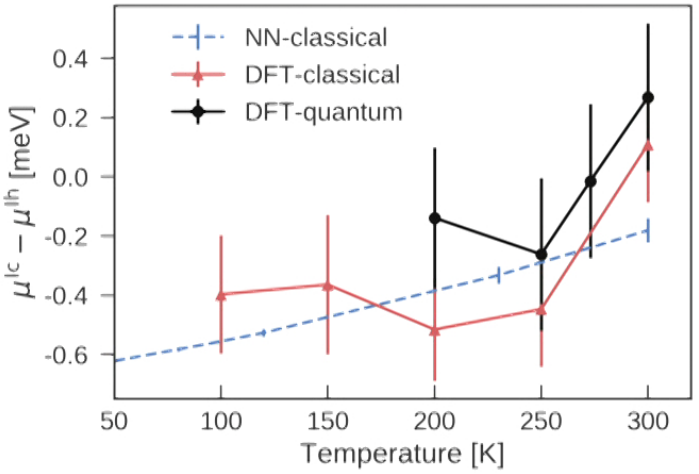


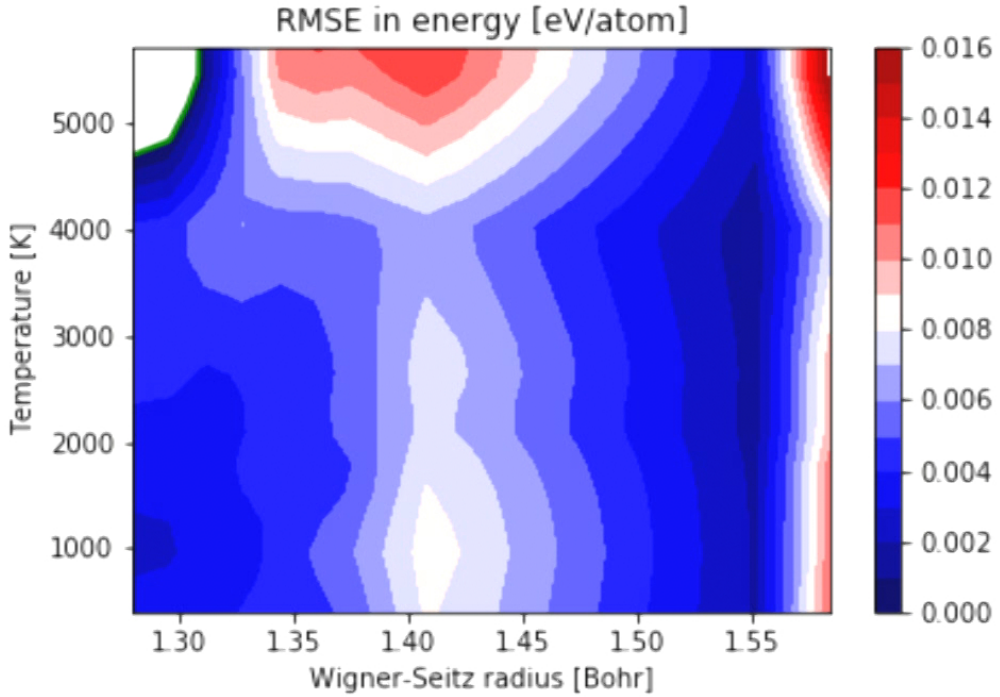


Cheng, Engel, Behler, Dellago, **MC**, PNAS (2019)

The phase diagram of high-pressure hydrogen

A ML potential for high-pressure H_2

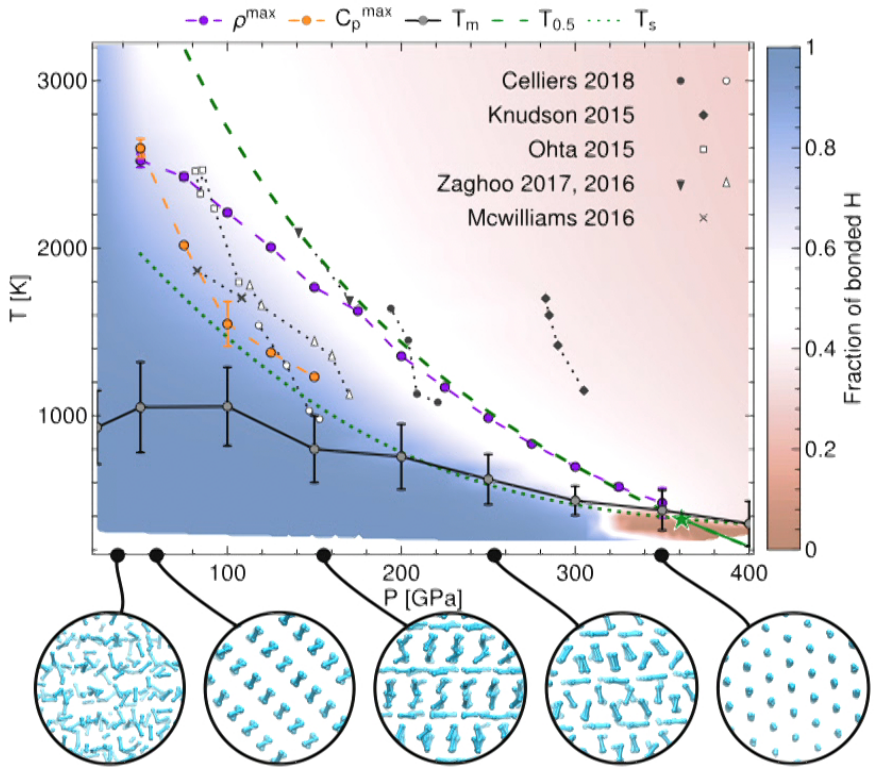
- High-pressure hydrogen has a complex phase diagram that includes polimorphic solid phases, a metallic monoatomic fluid and an insulating diatomic fluid
- One can train a pretty accurate neural-network potential model to electronic-structure calculations



Cheng, Mazzola, **MC**, arxiv:1906.03341

Supercritical behavior of liquid H_2

- ML reproduces solid polymorphism, melting line, eqn. of state.
- No trace of a liquid-liquid phase transition. Regular solution model fits simulation well, predicting a critical point at high-ρ and low-T



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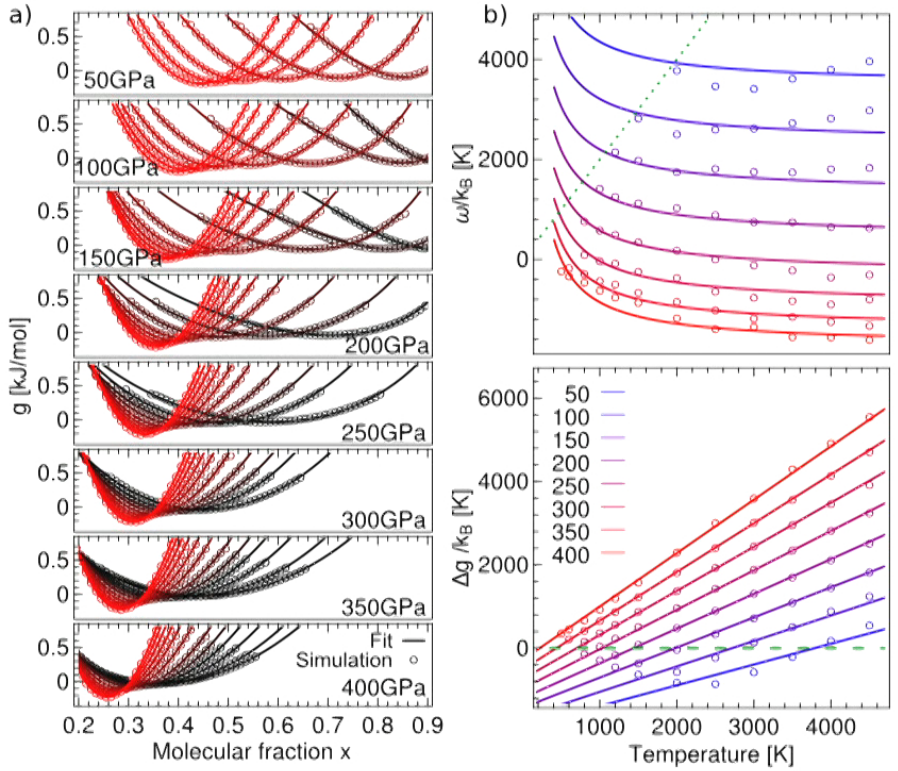

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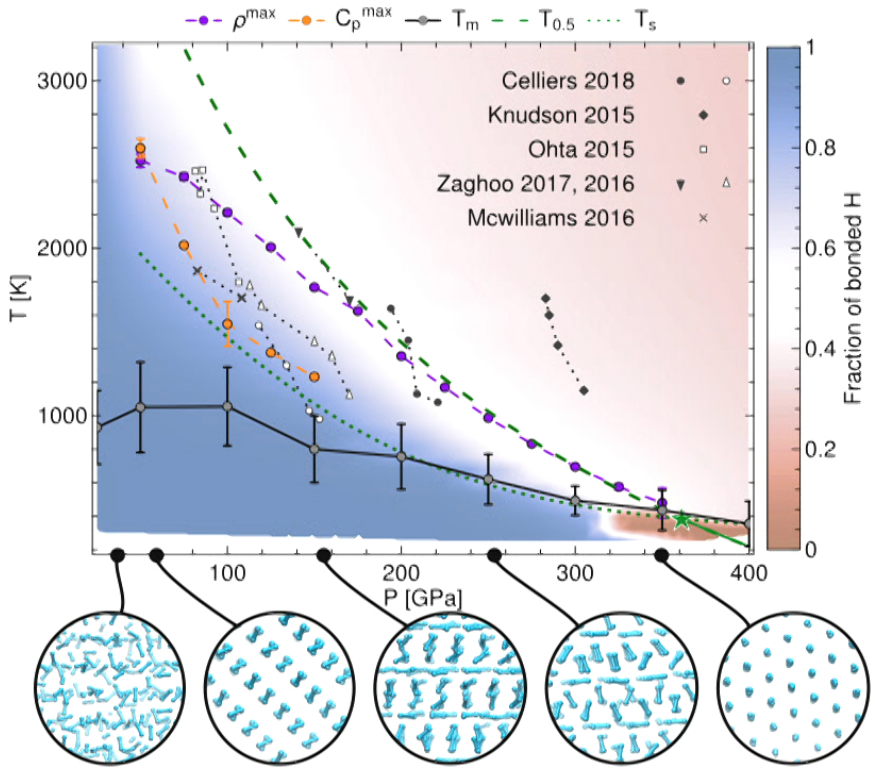
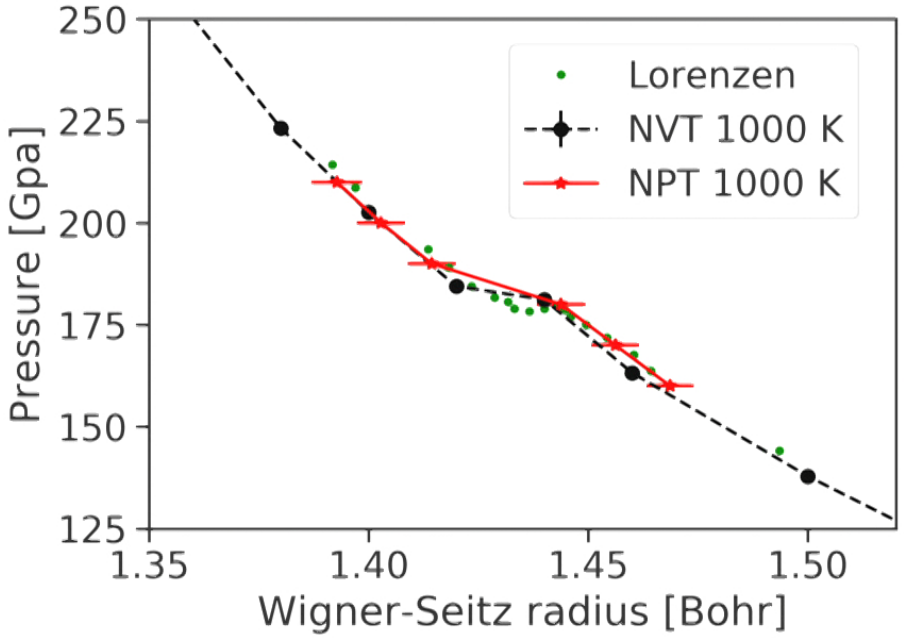


How about AIMD results?

- DFT calculations report quite consistently a sharp transition
- Actually, both DFT and ML show sharp drop in diffusivity when crossing the transition region
- AIMD simulations at constant pressure show clear signs of solidification
- Very strong finite-size effects. Need both high accuracy and thorough sampling



Lotenzen, Holst, Redmer, PRB (2010)

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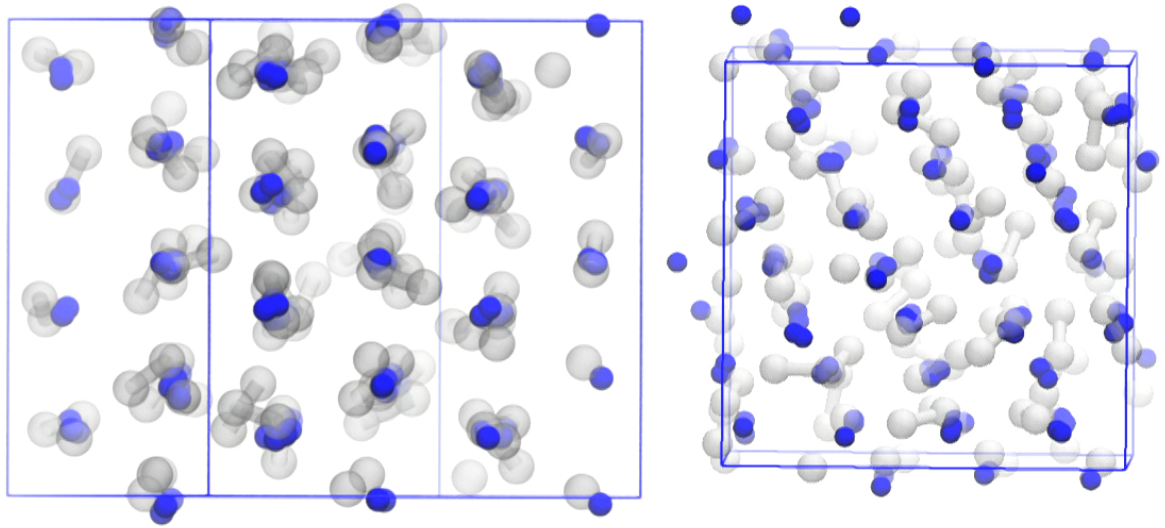

$T = 1000\text{K}, p = 180\text{GPa}$ $T = 1250\text{K}, p = 130\text{GPa}$

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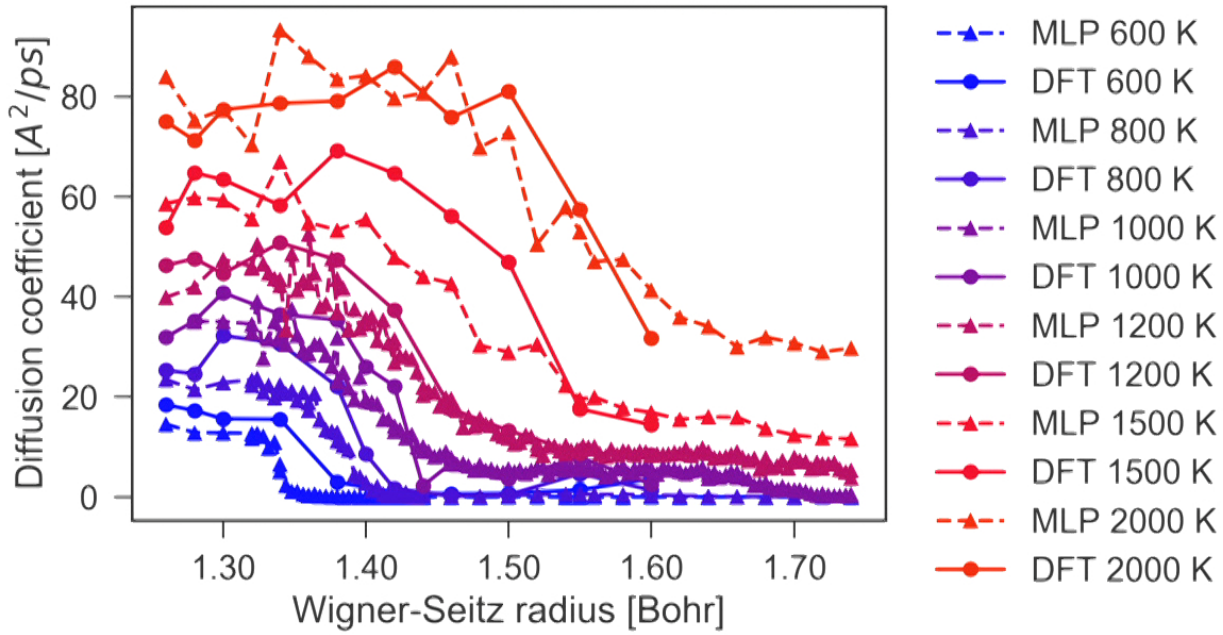
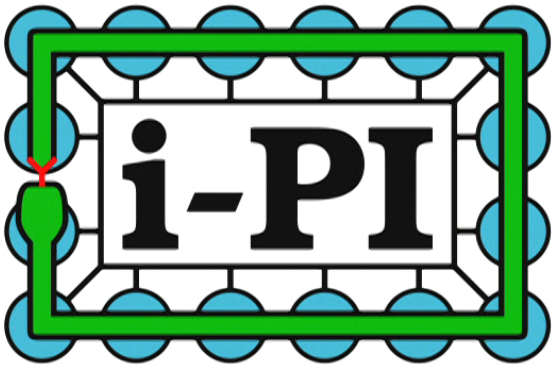
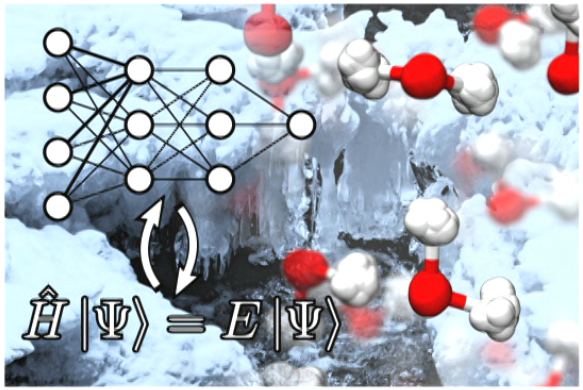


Conclusions

- Finite-temperature and quantum fluctuations are the new frontier of predictive chemical and materials modeling
- Many recent advances have reduced the computational cost associated with path integral simulations
- Machine learning potentials provide the missing ingredient to achieve first-principles accuracy and thorough statistical sampling





Markland & Ceriotti, Nature Reviews Chemistry (2018); http://ipi-code.org