Water: Fundamental Properties at Ambient and Extreme Conditions, and at Interfaces

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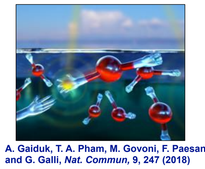
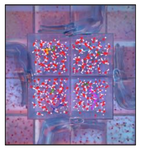
Introduction

We use a*b initio* molecular dynamics to study the molecular behavior of water at ambient conditions, under thermodynamic extremes and at interfaces:

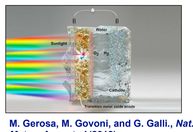
- The fundamental behavior of liquid water at ambient conditions is still a significant challenge to understand and simulate [i].
- High pressure/temperature conditions exist in the Earth's mantle, where the amount of water stored in hydrous minerals and reservoirs/fluxes may be much greater than the amount in the oceans [ii][iii]. Water mediates critical chemical reactions of the deep carbon cycle, with consequence for global carbon transport.
- Understanding water at interfaces is essential to energy conversion processes such as photoelectrochemical cell and water purification technologies. [iv].



A. Gaiduk, T. A. Pham, M. Govoni, F. Paesani, and G. Galli, *Nat. Commun*, 9, 247 (2018)



V. Rozsa, D. Pan, F. Giberti, G. Galli, *PNAS, 201800123* (2018)

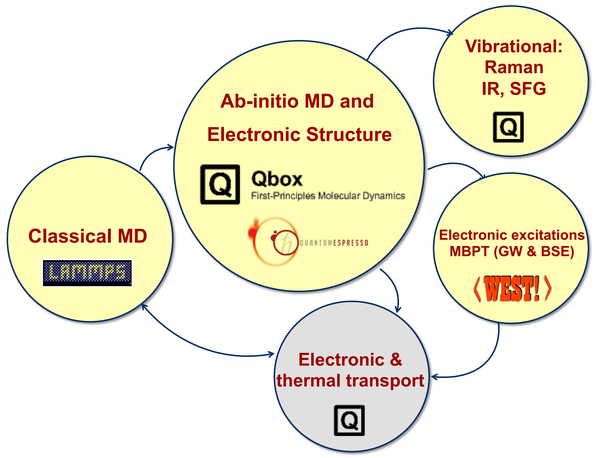


M. Gerosa, M. Govoni, and G. Galli., *Nat. Mater., Accepted* (2018)

[i] Hassanali et al., *Phil. Trans. Royal Soc. A*, 372, 2011 (2014)
[ii] M. Nishi, *Nat. Geosci.*, 8, 9 (2015).
[iii] Fei et al., *Sci. Adv.*, 3, e1603024 (2017).
[iv] T. A. Pham et al., *JACS*, 136, 1701, (2014).

Computational Framework

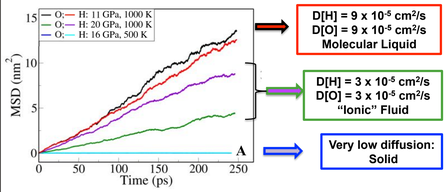
- In collaboration with experimentalists, we **develop code validation protocols for aqueous systems.**
- **We disseminate ab initio molecular dynamics (AIMD) trajectories** for aqueous systems at: http://quantum-simulation.org/reference/index.htm
- **Data and workflows** of all papers available at: http://qresp.org/



Papers curated at:

http://Qresp.org "Curation and Exploration of Reproducible Scientific Papers"

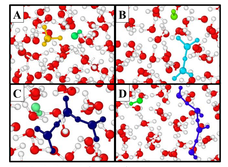
High P/T Water: Structure and Diffusion



D[H] = 9 x 10⁻⁵ cm²/s
D[O] = 9 x 10⁻⁵ cm²/s
Molecular Liquid

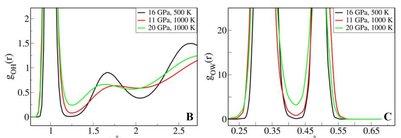
D[H] = 3 x 10⁻⁵ cm²/s
D[O] = 3 x 10⁻⁵ cm²/s
"Ionic" Fluid

Very low diffusion: Solid



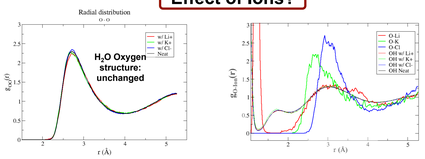
V. Rozsa, D. Pan, F. Giberti, G. Galli, *PNAS, 201800123* (2018)

- Snapshots of short-lived, dissociative ionic species at 20 GPa, 1000 K. Color coding is based on the O-H RDF cutoff distance.
- Considerable differences in diffusion at controversial P/T conditions



- Strong evidence of pressure-induced dissociation in O-H and O-MLWF radial distribution functions

Effect of Ions?



- Li+ causes LiOH formation, close solvation shells.
- K+ and Cl- maintain large solvation shells under pressure

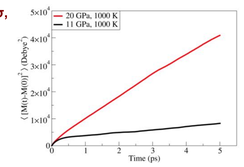
High P/T Water: Ionic Conductivity and Dielectric Constant

We computed ionic conductivity, σ, using the Green Kubo relation:

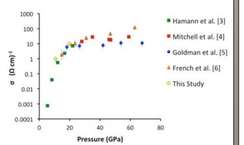
$$\sigma = \frac{1}{3k_bTV}\int_0^\infty \langle \dot{\vec{M}}(0)\dot{\vec{M}}(t)\rangle dt$$

-or-

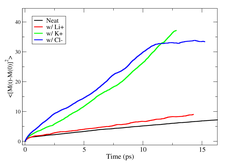
$$\sigma = \lim_{t\to\infty}\frac{1}{6tk_bTV}\langle[\vec{M}(t)-\vec{M}(0)]^2\rangle$$



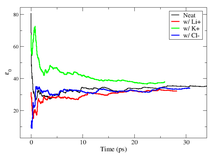
- Order of magnitude increase in σ from 11 to 20 GPa
- Results in good agreement with experimental data



Effect of Ions?



- K+ and Cl- ions cause order of magnitude increase in ionic conductivity of water at 11 GPa, 1000 K



The dielectric constant is computed as:

$$\varepsilon_0 = 1 + \frac{4\pi}{3k_BTV}\left(\langle \mathbf{M}^2\rangle - \langle \mathbf{M}\rangle^2\right)$$

Where M is the total dipole moment

- Small enhancement of ε_0 in presence of K+ cation

High P/T Water: Ab Initio Raman/IR Spectroscopy

Fourier transform of dipole moment time correlation function is proportional to the IR spectrum:

$$A(\omega) \propto \frac{2\pi\omega^2\beta}{3cV}\int dt e^{-i\omega t}\langle \vec{M}(0)\vec{M}(t)\rangle$$

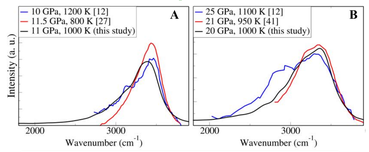
Fourier transform of polarizability time correlation function is proportional to the Raman spectrum:

$$R_{iso}(\omega) \propto \frac{\hbar\omega}{kT}\int dt e^{-i\omega t}\left\langle \bar{\alpha}(0)\bar{\alpha}(t)\right\rangle$$

$$R_{aniso}(\omega) \propto \frac{\hbar\omega}{kT}\int dt e^{-i\omega t}\left\langle \frac{2}{15}\mathrm{Tr}\beta(0)\beta(t)\right\rangle$$

M are calculated from maximally localized Wannier functions

Raman Spectra

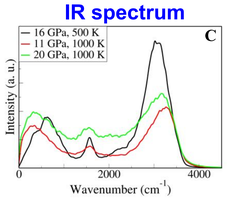


Computed spectra reproduce major exp. trends

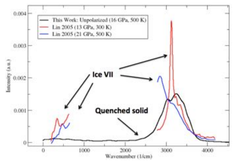
Spectroscopic signatures of dissociating water:

- Present in IR but not in Raman spectra

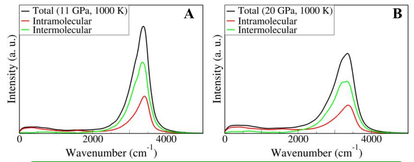
IR spectrum



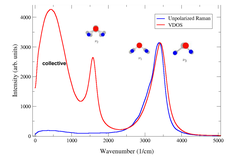
Broad mid-IR continuum increases w/ pressure



High-pressure amorphous ice may give liquid-like Raman signatures

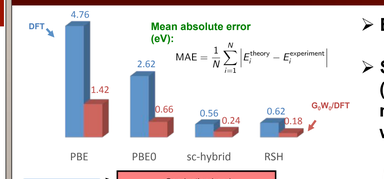


- *Inter Signal:* Lower frequency, higher intensity in OH peak.
- *Intra Signal*: Higher frequency, lower intensity in OH peak
- Decrease in Raman intensity with pressure



Vib. density of states is a poor approximation of Raman spectra

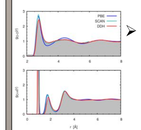
Electron Affinity of Ambient Water



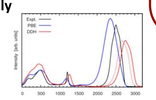
- Electron affinity of liquid water has been unknown
- Strategy: MB-Pol for bulk water and surface of water (with NQE); computed orbital energies along the molecular-dynamics trajectory using G_0W_0 starting with several DFT functionals
- Accurate estimate of the energies of occupied and empty states for water clusters
- EA of water surface (0.8 eV) is in agreement with the expt. of Stähler et al. (2015); value for bulk water is predicted to be 0.1-0.3 eV
- Presence of surface affects the position of CBM but not VBM; nuclear quantum effects are crucial for an accurate description of the electronic structure of water

A. Gaiduk, T. A. Pham, M. Govoni, F. Paesani, and G. Galli, *Nat. Commun*, 9, 247 (2018)

- A previously developed dielectric dependent hybrid (DDH) functional has been applied to liquid water



- DDH accurately describes the structural properties of liquid water.

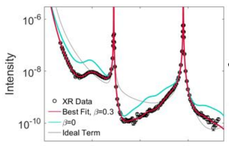


- IR spectrum w/ DDH is blueshifted, however inclusion of NQEs may bring it in better agreement with expt.

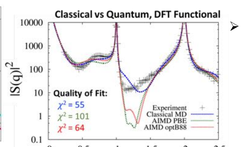
A. Gaiduk, J. Gustafson, F. Gygi, and G. Galli, *J. Phys. Chem. Lett.*, 9 3068 (2018)

Water at Interfaces

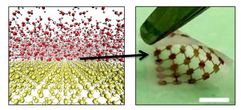
- Interfacial water essential to many emerging energy technologies: Al_2O_3/water interface studied with AIMD and experimental x-ray reflectivity measurements

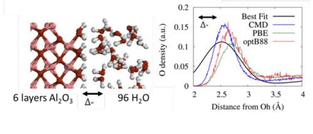


6 Al_2O_3 layers, 96 H_2O

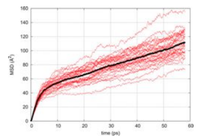


- Developed validation protocol comparing x-ray reflectivity measurement to computed interfacial x-ray structure factors
- Bioengineering application: optB88 functional to study interaction between water and Si 100 surface

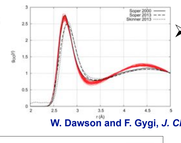




Statistically Robust Analysis of AIMD trajectories of Aqueous Solutions



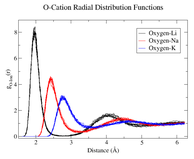
- 32 independent ~58 ps trajectories of PBE water at 400K
- Combining all trajectories leads to average diffusion: 1.96 ± 0.1 x10^{-5} cm²/sec

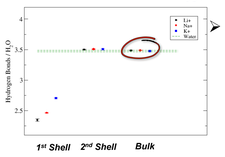


- Focus on variability and uncertainty in common averaged quantities

W. Dawson and F. Gygi, *J. Chem. Phys.*, 148 124501 (2018)

- 10 independent ~50 ps trajectories for each type of ion:
- Li+ → Na+ → K+ brings larger, floppier solvation shells with greater exchange of H_2O





- H-bond density analysis indicates that Li+, Na+, or K+ cannot be identified as either "structure maker" or "breaker" in bulk water (w/ PBE model)

Acknowledgements

Funding for these project was provided by the U.S. Department of Energy (DOE), the Midwest Integrated Center for Computational Materials, Alfred. F. Sloan foundation, the DOE NNSA Stewardship Science Graduate Fellowship, and the Natural Sciences and Engineering Research Council of Canada

We also acknowledge computational time provided by the University of Chicago Research Computing Center, Argonne Leadership Computing Facility, and the INCITE program