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Density Functional Theory simulations of water: phase-diagram and electrical conductivity

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HEDP Theory and ICF Target Design
Sandia National Laboratories

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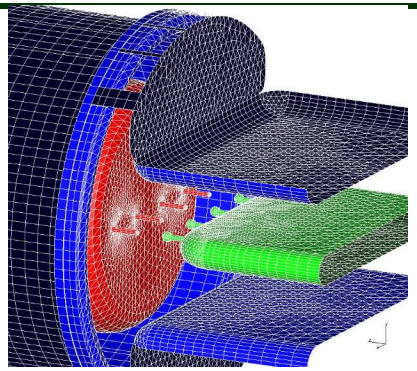
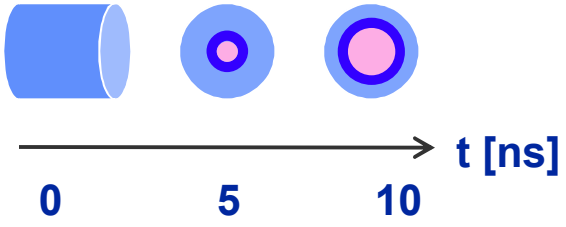
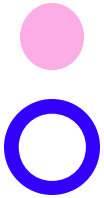
Properties of shocked water is of direct interest to Sandia as well as of general scientific interest.



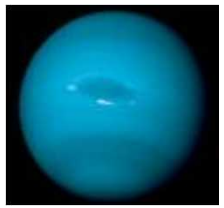


Evolution into two regimes → Hot / thin

Evolution into two regimes → Warm/ dense



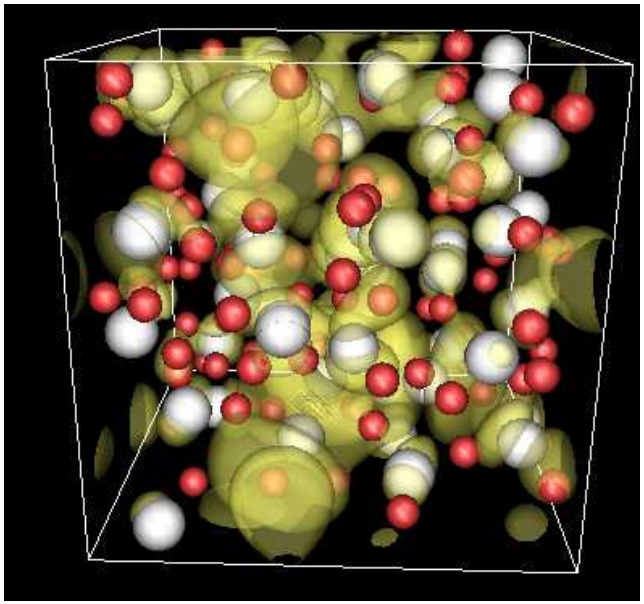
- Water switches are key components in the Z-accelerator.
- Water tampers at exploding wire experiments.
- Shock-waves in water.
- Planetary interiors.



From (300 K / 1 g/cm^3) to between (2000 / 2.5) and (300 000 / 0.05).

H2O a system with ionic and electronic
Must treat both forms of conduction.

Warm-dense matter is a difficult region and predictability requires a first-principles approach



Electron density from a partially occupied band.
H_2O at 4000 K / 1000 kBar.

Demands:

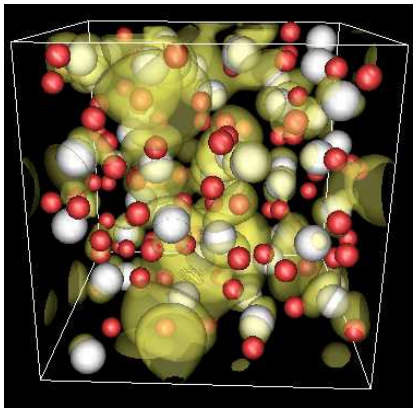
- Free electrons
- Localized electrons
- Solid/ liquid/ vapor/ atom / molecule
- Ionization

Density Functional Theory (DFT) ideally suited for this region:

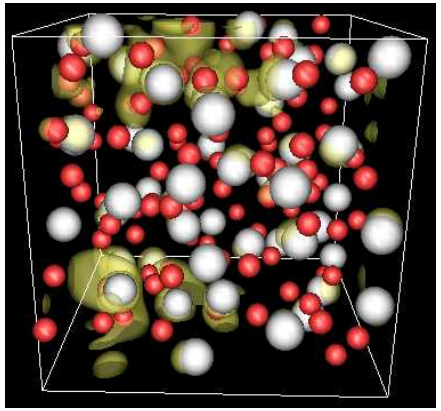
- First-principles quantum theory
- Few approximations (LDA/PBE, etc), no free parameters to set/tune.
- EOS, conductivity, structure, diffusion, and opacity *from one framework*.

We employ an ab-initio theory to calculate thermo-physical properties in the HEDP regime.

- **Density Functional Theory** [1, 2]
  - DFT is a formally exact reformulation of the Schrödinger equation
  - PBE for exchange/correlation
  - VASP-code[3]
    - Plane-wave, periodic code
    - PAW potentials yields complete wave-functions for conductivity calculations
  - Quantum molecular dynamics (QMD) simulations
    - **Electronic temperature**
    - Large number of bands
    - High cut-off energy for accurate pressure calculations



Fermi distribution of states.



Zero K distribution of states.

Original papers are readable:

[1]*Hohenberg, Kohn, Phys. Rev.* ***136****, B864 (1964).*

Kohn, Sham, Phys. Rev. ***140****, A1133 (1965).*

Review on making meaningful calculations:

[2]*Mattsson, Schultz, Desjarlais, Mattsson, and Leung, Modeling and Simulation in Materials Science and Engineering* ***13****, R1 (2005).*

VASP code main reference:

[3]*Kresse and Hafner, PRB* ***47****, 6671 (1992).*

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Conductivity in water -- electronic conduction from the Kubo-Greenwood formula.

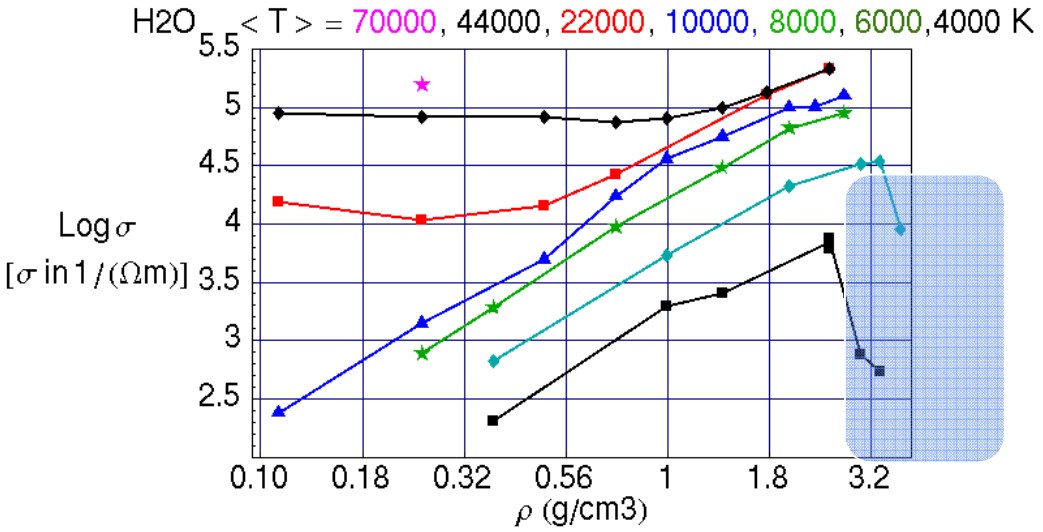
$$\sigma_{\mathbf{k}}(\omega) = \frac{2\pi e^2\hbar^2}{3m^2\omega\Omega}\sum_{\alpha=1}^{3}\sum_{j=1}^{N}\sum_{i=1}^{N}(F(\varepsilon_{i,\mathbf{k}}) - F(\varepsilon_{j,\mathbf{k}}))\left|\left\langle\Psi_{j,\mathbf{k}}\left|\nabla_\alpha\right|\Psi_{i,\mathbf{k}}\right\rangle\right|^2\delta(\varepsilon_{j,\mathbf{k}} - \varepsilon_{i,\mathbf{k}} - \hbar\omega),$$

Fermi weights **Energy conservation**

Sum over bands **Matrix element**

- Wave-function based[4]
  - Kubo-Greenwood (KG) formula yields the conductivity directly from wave-functions
  - Neither cross-sections Σ nor relaxation times τ are required
- Geometries taken from equilibrium 2 – 12 ps of EOS MD simulations
  - Typically 20 -30 geometries
  - σ averaged in x-y-z directions
- Range in this work:
  - 0.1 - 3.3 g/cm^3
  - 4000 - 70 000 K.

DC electronic conductivity of water



Superionic phase

First application of K-G DFT to HEDP area:
*[4]Desjarlais, Kress, and Collins PRE **66**, R025401 (2002).*

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Conductivity in water -- proton conduction from QMD simulations of proton diffusion.

Classical Kubo expression for proton conductivity:

$$\sigma = \frac{ne^2}{m}\int_0^\infty \frac{\langle v(\tau)v(0)\rangle}{\langle v(0)v(0)\rangle}d\tau$$

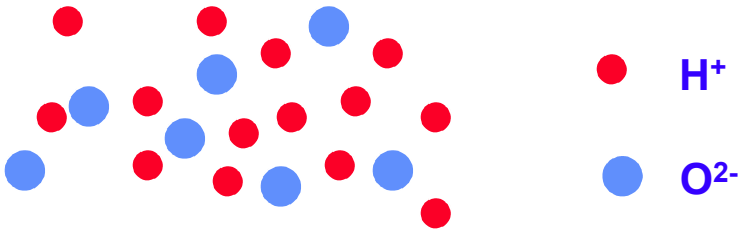
- Valid when all protons are free/equivalent.

Reduction due to H_2O diffusion

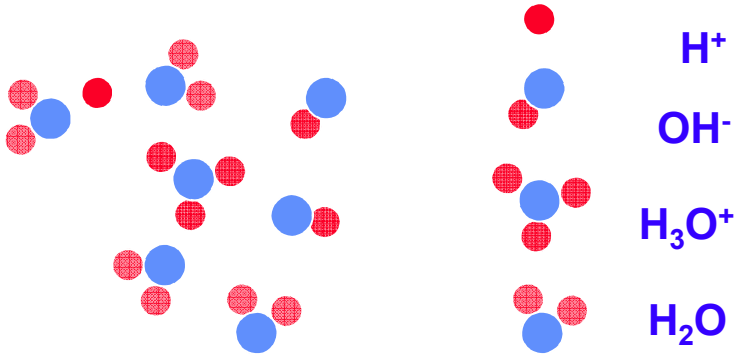
$$D_H = (1-\gamma)D_{H^*} + \gamma D_O$$

$$D_{H^*} = \frac{1}{1-\gamma}\left(1-\gamma\frac{D_O}{D_H}\right)D_H$$

γ -- fraction H atoms bound as H_2O.
D_H -- diffusion ALL H atoms.
D_{H^*} -- diffusion all H species but H_2O.



Full dissociation, all protons contribute.



Diffusion as H_2O is non-conducting.

T.R Mattsson and M.P Desjarlais, Phys. Rev. Lett. **97**, 017801 (2006).

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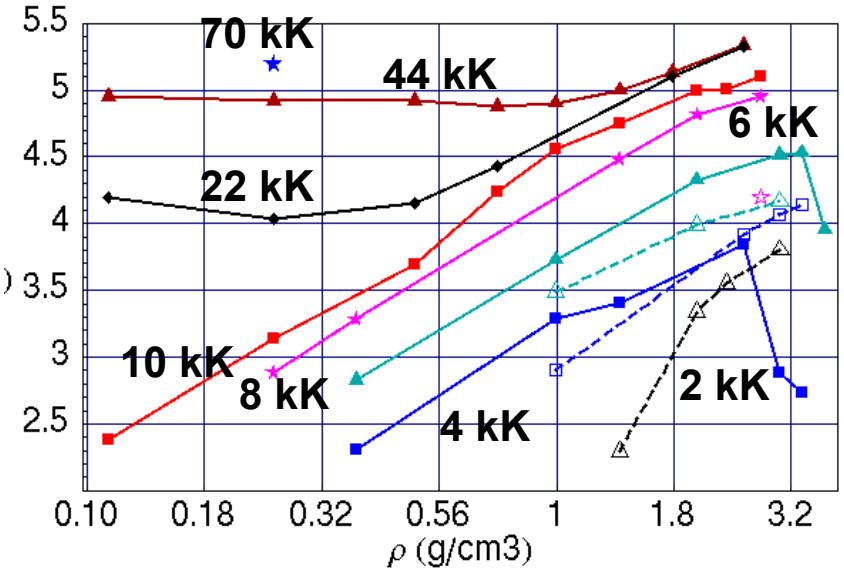
Wide-range picture of conduction in water

Ionic and electronic conductivity



Full lines -- electronic conduction.
Dashed lines -- ionic conduction.

- **2000 K**
  - Ionic conduction H, H_3O, OH.
  - Gap in electronic structure, no electronic component to conductivity.
- **4000 K**
  - Electronic component of conductivity similar to ionic.
  - Transition into superionic phase (with gap) at higher density.
- **6000 K**
  - Electronic component begins to dominate conductivity.
- **22 000 K** and above.
  - Fully dissociated into H, O ions with significant ionization / free electrons.

T.R Mattsson and M.P Desjarlais, Phys. Rev. Lett. **97**, 017801 (2006).

High-fidelity modeling of HEDP systems requires high-quality materials models.

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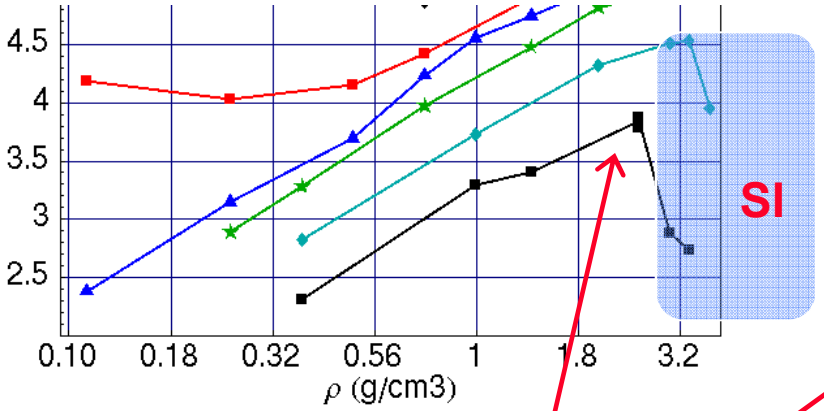
Revision of the phase-diagram of HEDP water

DC electronic conductivity of water

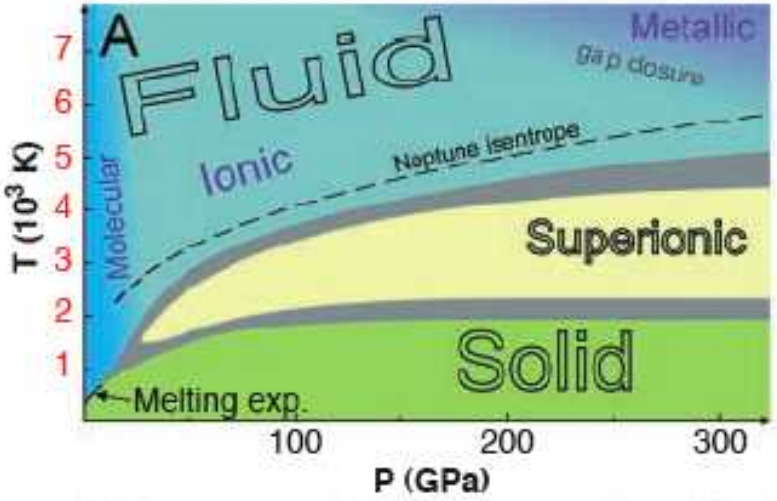


Significant electronic conductivity

Superionic phase

- Cavazzoni et. al. (Science **283**, 44 (1999))
  - O atoms in lattice **OK**
  - Highly mobile H atoms **OK**
  - Gap in electronic structure **OK**
  - Bordering to an ionic liquid, with gap **NO**
  - Gap closure 7000 K, 300 GPa **NO**

Cavazzoni, et. al. (Science **283**, 44 (1999)).



The two DFT simulations differ in one major way, the use of temperature for band occupation.

The effect of including thermal occupation of electronic degrees of freedom

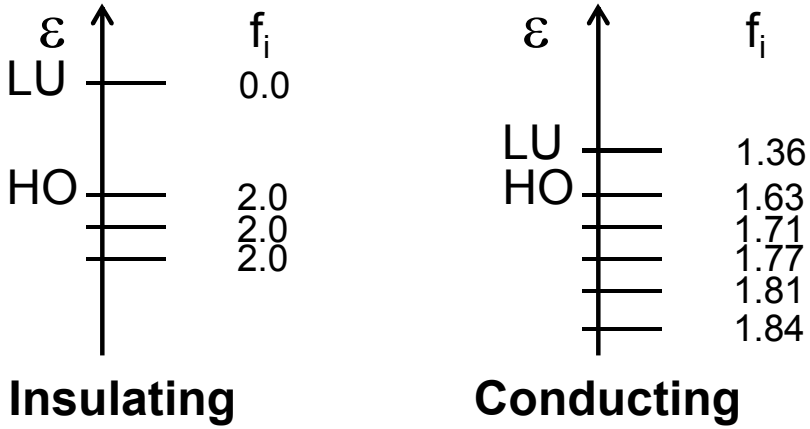
Fermi occupation of bands

f_i -- occupation of band i.
ε_i -- energy of band i.

HO -- highest occupied (0 K)
LU -- lowest unoccupied (0 K)
$\Delta E = \varepsilon_{LU} - \varepsilon_{HO}$ (eigenvalue gap).

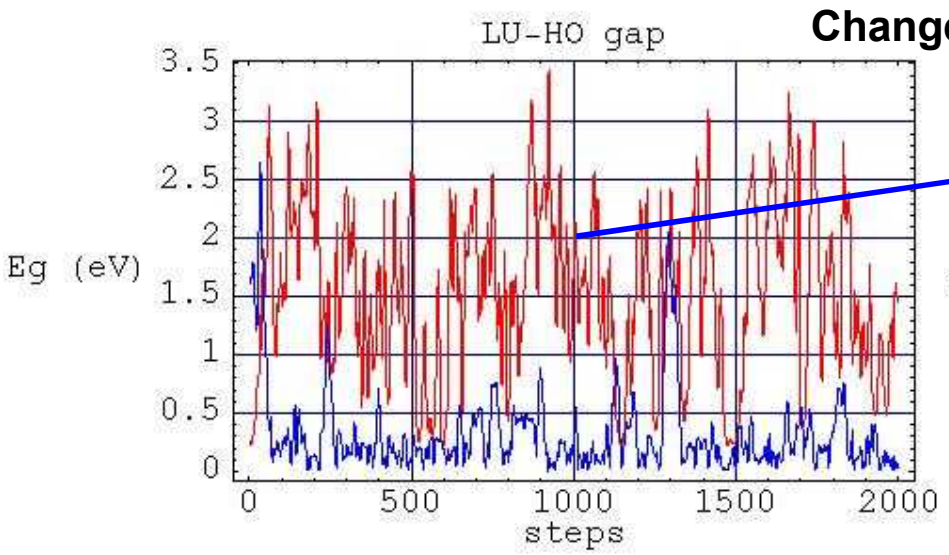
for both 54 and 128 molecules cells. Units are molecules/cell, g/cm^3, Kelvin, 1/(Ω m), occupation, and eV.

n	ρ	T_{ion}	T_e	$\log_{10}(\sigma)$	f_{HO}	f_{LU}	ΔE
54	2.5	4000	1000	0.7	1.98	0.03	1.53
54	2.5	4000	2000	1.2	1.97	0.04	1.74
54	2.5	4000	4000	3.84	1.63	1.25	0.38
128	2.5	4000	4000	3.78	1.63	1.36	0.26
128	2.5	4000	1000	1.0	1.96	0.05	1.01
54	3.0	6000	6000	4.5	1.43	1.25	0.22
54	2.7	8000	8000	5.0	1.28	1.18	0.14

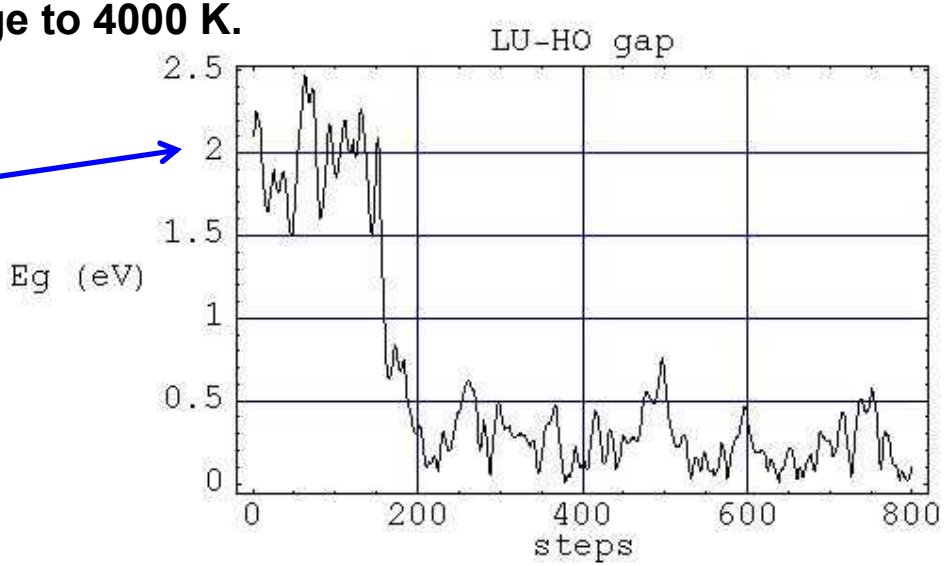


It is necessary to include the electronic temperature to capture the behavior of HEDP systems.

The effect of including thermal occupation is not instantaneous with change in Te.



Change to 4000 K.

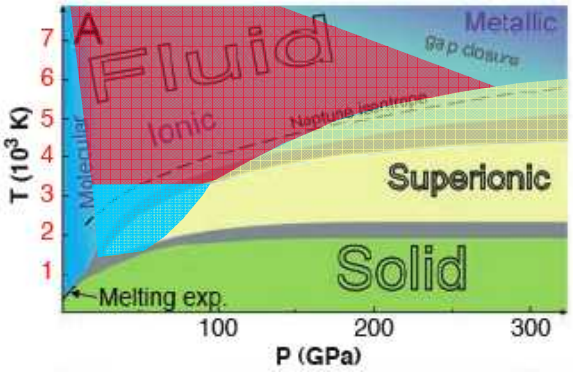


Red 1000 K electrons.
Blue 4000 K electrons.

Structure changes after 100 fs with the higher electronic T.

Doing finite T calculations on snapshots from an MD simulation using 0 K electrons will not yield the same electronic structure as a finite-temperature MD simulation.

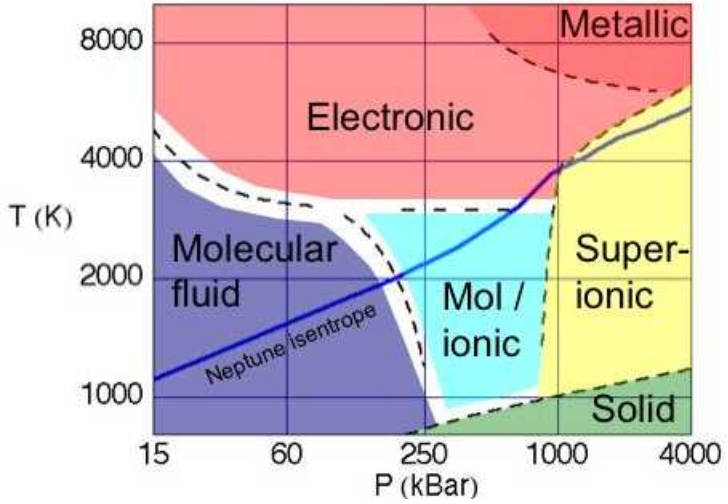
Phase-diagram of HEDP water -- revised



Cavazzoni, et. al. (Science **283**, 44 (1999)).

- Earlier calculations by Cavazzoni et. al. (Science **283**, 44 (1999)).
  - Car-Parrinello Method for ab-initio MD:
    - Electrons moving on zero K Born-Oppenheimer surface.
    - Method has been very popular also in the HEDP community, even for metals, despite the obvious uncertainty of the electronic zero K treatment.
- **Neptune isentrope traverses the revised region.**

For HEDP systems, it is necessary to include the electronic temperature



Mattsson and Desjarlais, PRL **97**, 017801 (2006).

- The present calculation include thermal occupation of the electronic degrees of freedom.
  - Direct transition from superionic to conducting fluid already at 100 GPa, 4000 K.
  - Superionic phase boundary at higher pressure (100 GPa at 2000 K).

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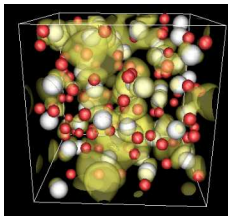
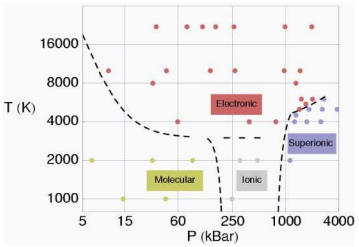
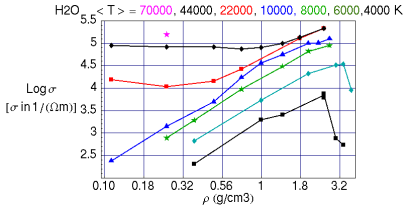
QMD simulations are key to accurate materials models in the warm-dense matter regime.

- **Summary**
  - First-principles calculation of ionic- and electronic conductivity in water valid across 3 phase transitions.
  - Revision of the HEDP phase-diagram of H_2O
  - Importance of finite temperature method
- **SNL QMD based materials models:**
  - Several QMD-based materials models are in use for macroscopic simulations.
  - Wide-range water EOS and conductivity conductivity models are in preparation
- **Crucial dimension of HEDP modeling**
  - Simulations are never better than the underlying physics models.
  - High-fidelity materials models accelerate development of macroscopic (rad-hydro) simulation methods.







A key component of high-fidelity HEDP modeling.

Acknowledgment: Larry Warne, Tom Mehlhorn, LDRD office at SNL, and the computer staff at SNL.

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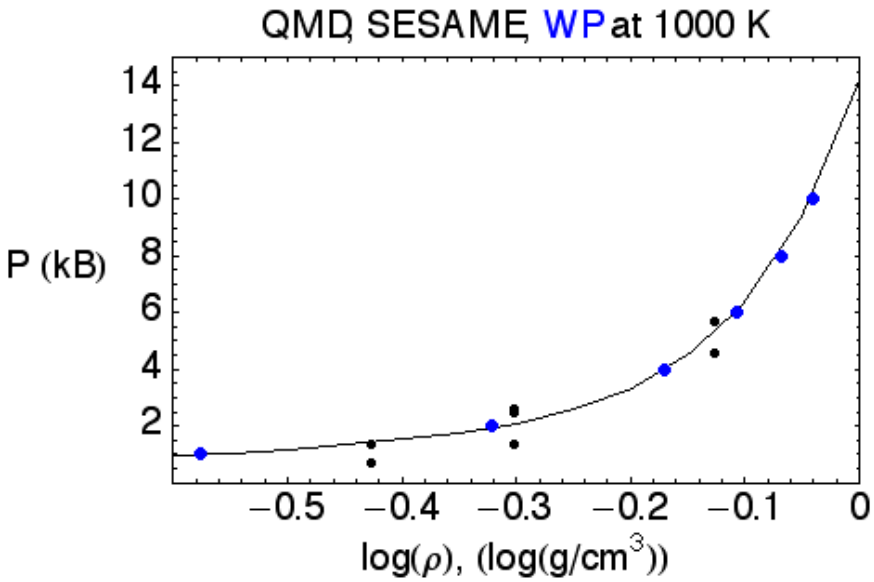
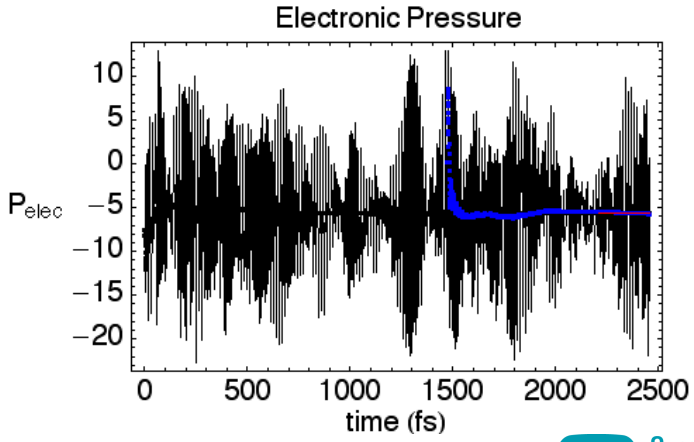
Supplementary slides HEDP water

Benchmarking the QMD-EOS simulations to data in the steam/vapor region.

- Water EOS is *very* well known up to 1000 C (steam).
- Wagner-Pruss[4] (WP) is the state-of-the-art EOS (compiled exp data fitted to a highly complex free-energy function).
- QMD benchmark at 1000 K.
- Conclusion:
  - Within statistical- and finite size effects the QMD approach is *quantitative* with the PBE functional.
  - The high pressure makes convergence faster than at zero pressure (normal conditions).





[4]W. Wagner and A. Pruss,
J. Phys. Chem. Ref. Data **31**, 387 (2002).

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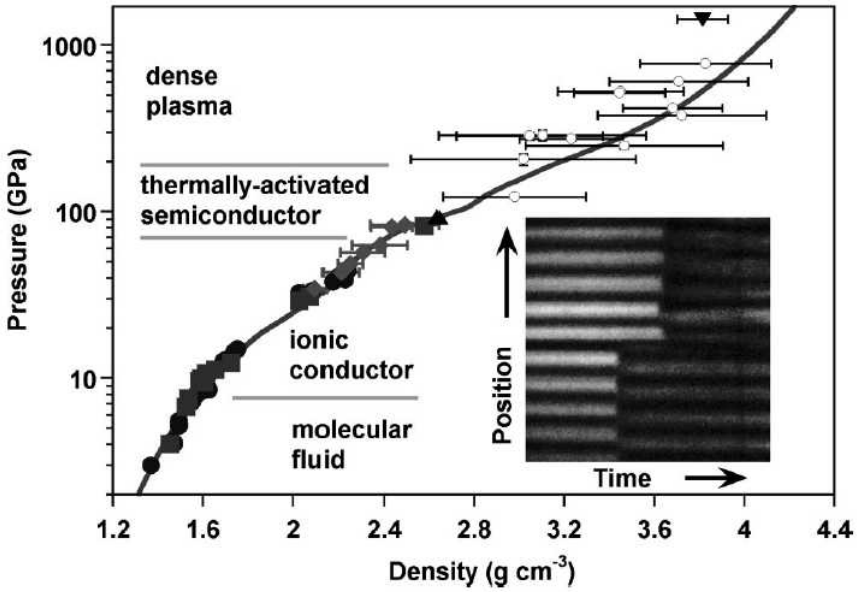
Conductivity in water -- background.

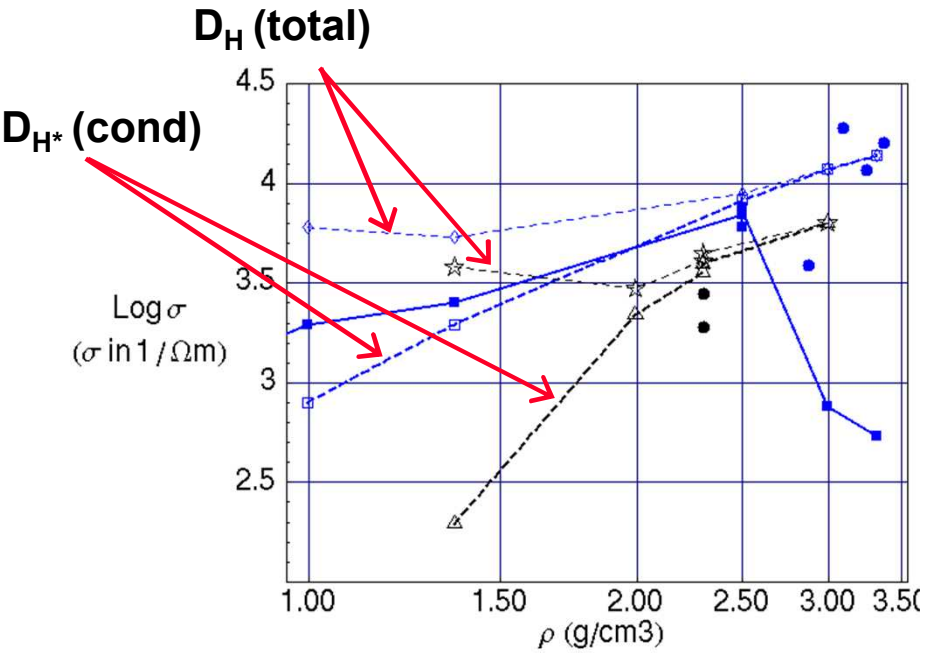
- Continuous changes between regimes -- approach that spans several phases.
- Electronic conduction.
  - Will dominate at higher ρ/T
  - Calculate w Kubo-Greenwood.
- Ionic conduction.
  - Simulations of proton diffusion with Green-Kubo formalism.
- **Where is the transition electronic/ ionic conduction?**
- **Information over a wide range?**
- Few experiments
  - Hugoniot (Mitchell and Nellis 1982)
  - Multiple shock (Chau, et al. 2001)



Water along the Hugoniot
(Celliers, Phys. Of Plasmas **11** L41 (2004).)

Conductivity in water -- simulations compare well to available experimental data.

- Mitchell and Nellis[5]: single shock measurements.
  - Our simulations (2000 K -- open black triangles) are in the same range.
- Chau, Mitchell, Minich, and Nellis[6]: multiple shock measurements.
  - Our simulations (4000 K -- blue squares) are also in the same range.
- QMD simulations are in line with experimental data.
- Significant reduction of conductivity due to subtraction of H_2O diffusion.
- Prediction for low conductivity at 1.5 g/cm^3.



● **Mitchell and Nellis, 1982.**
● **Chau, et al. 2001.**

[5] *A.C. Mitchell and W.J. Nellis, J. Chem. Phys.* ***76****, 6273 (1982).*
[6] *R. Chau, et al. J. Chem. Phys.* ***114****, 1361 (2001).*

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