SAND2007-2182P

Extreme States of Matter and First-Principles Simulations

Sandia Journal Club Seminar

April 11, 2007

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HEDP Theory (1641)

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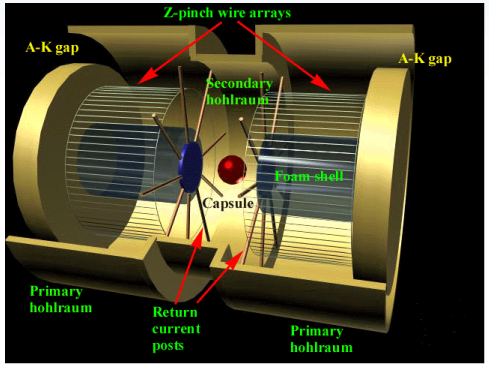
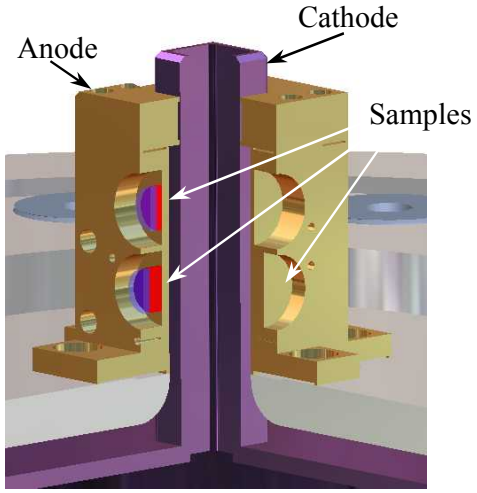
High energy-density physics (HEDP) experiments at the Z accelerator



ICF target in double-ended Z pinch

- DFT simulations are used to develop wide-range materials models:
  - Radiation-hydrodynamics finite-element simulations are routinely performed to model experiments:
    - Common to all simulations of HEDP systems is the need for material models
    - DFT based materials models are in daily use
    - Defects in material models can never be removed at higher levels (rad-hydro algorithms, massive parallelization, finite-element meshing, etc.)
- Direct DFT simulations are made to study the material response under shock conditions:
  - deuterium, aluminum, beryllium, carbon (diamonds)
- Experiments are costly and involved -- first-principles simulations have had a direct impact on our program.



Magnetically launched flyer plates

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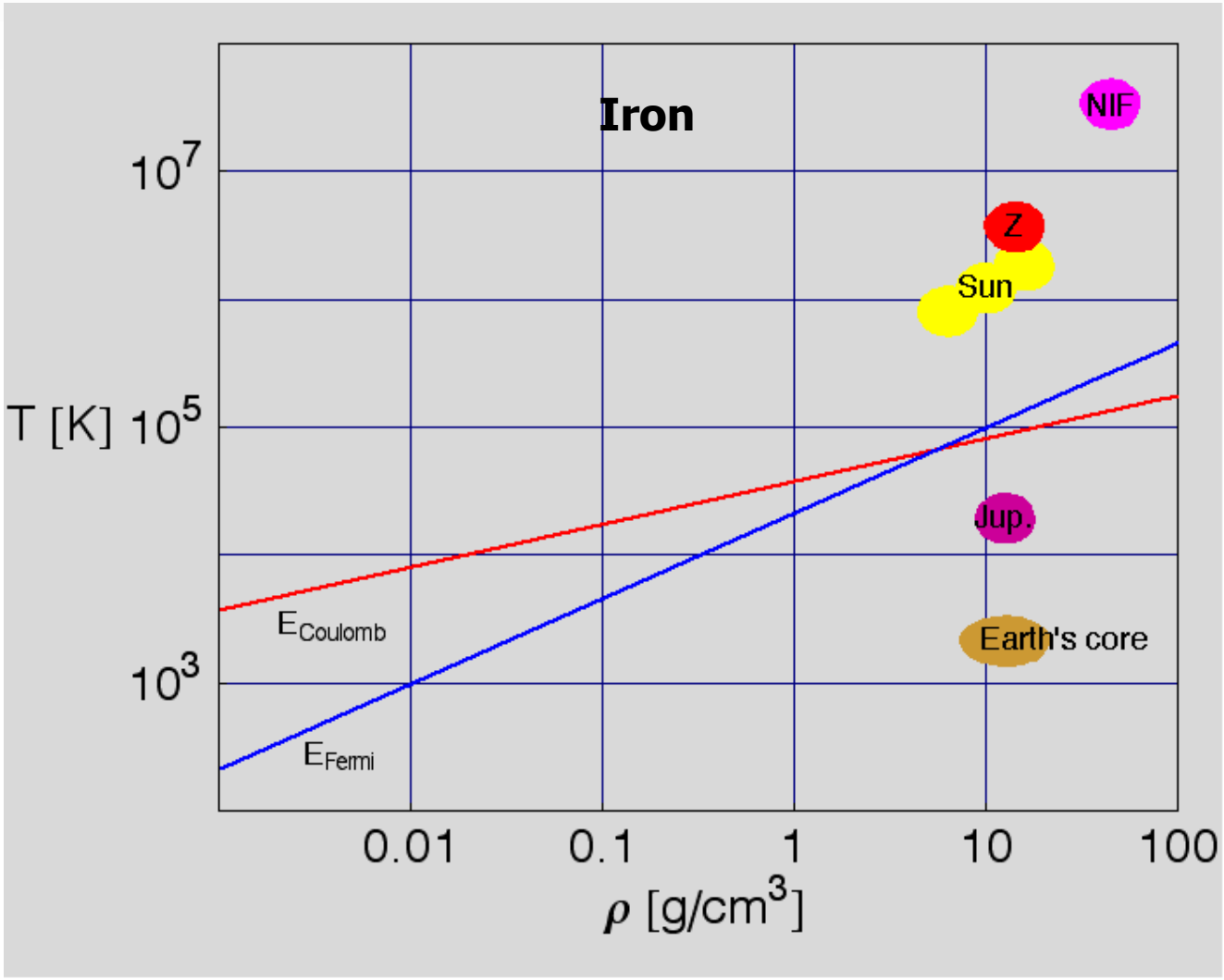
Extreme states of matter



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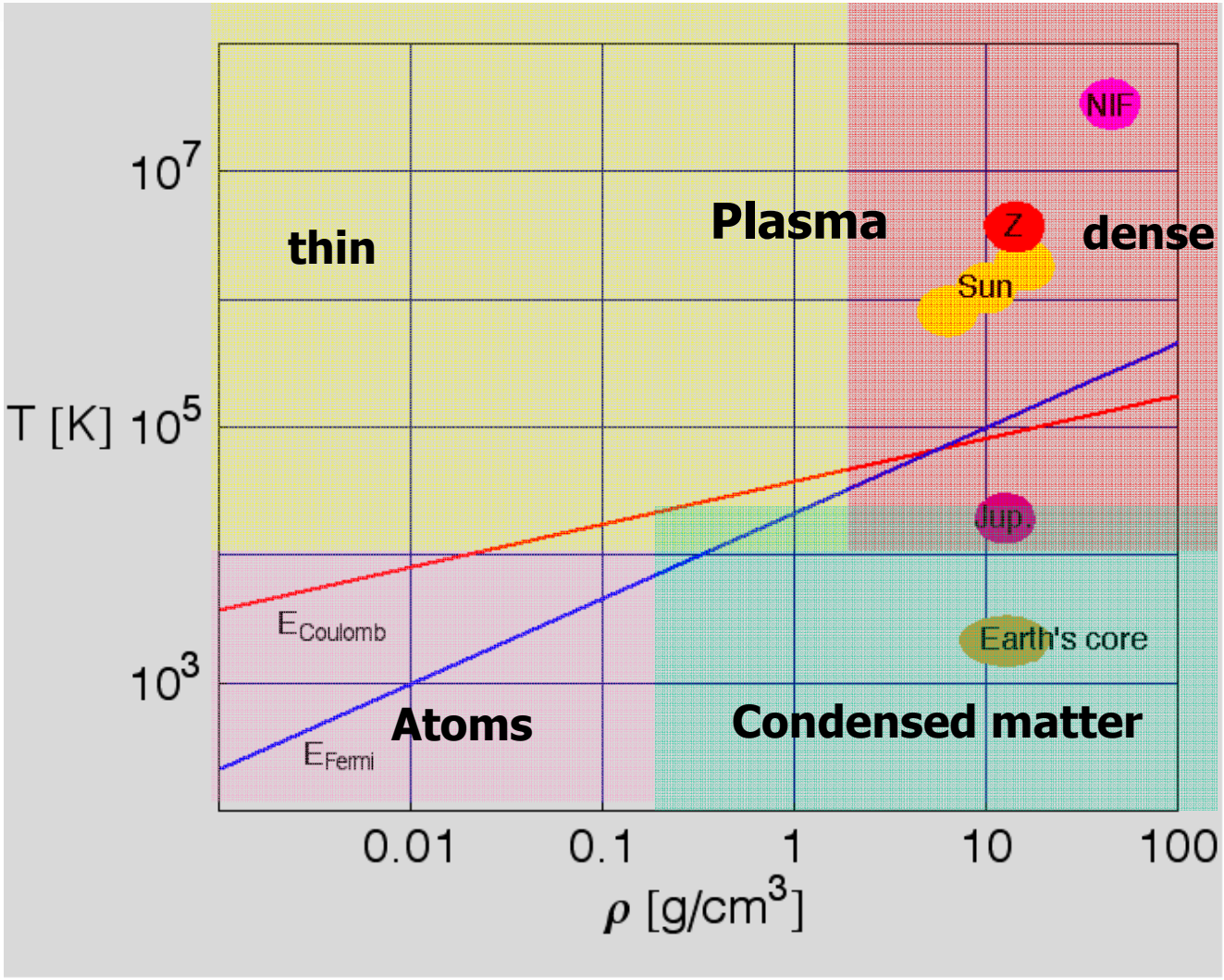
Main regions of the phase-diagram



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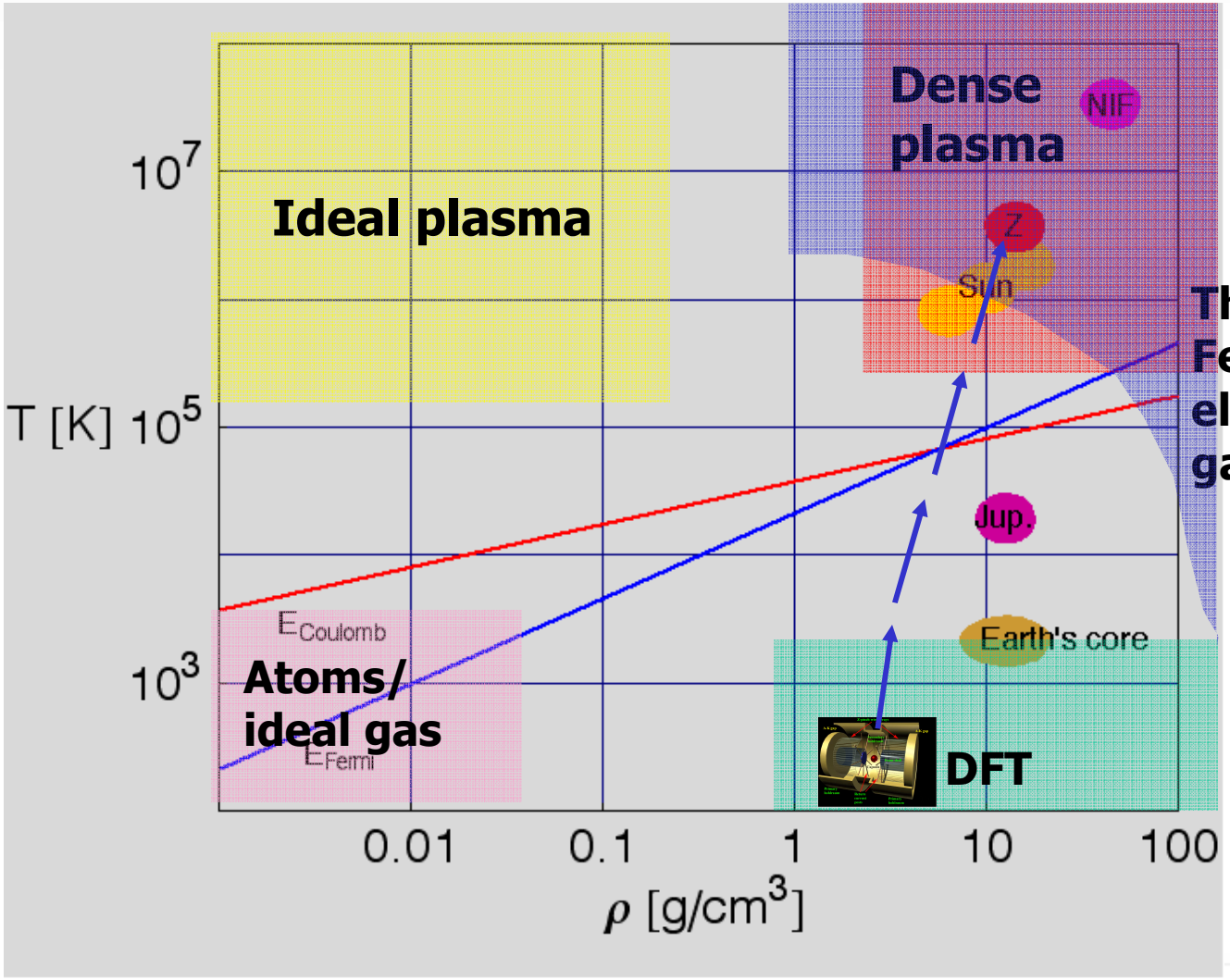
Mature fields with well-developed models describing the physics in each respective area



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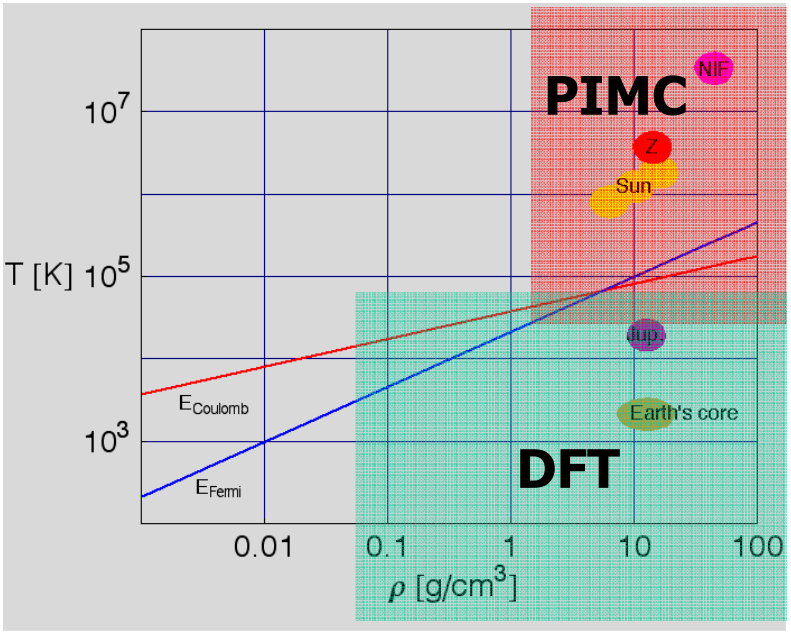
A need for first-principles modeling, obtaining properties where little exp. data is available



Path-Integral Monte Carlo (PIMC)

H: Militzer, Ceperley, PRL **85**, 1890 (2000).

He: Militzer, PRL **97**, 175501 (October 2006).

Density Functional Theory (DFT)

H: Desjarlais, PRB **68**, 64204 (2003);
Bonev, Militzer, Galli, PRB **68**, 14101 (2004);
Bonev, et al. Nature **431**, 669 (2004).

H2O: Cavazzoni, et al., Science **283**, 44 (1999);
Mattsson, Desjarlais, PRL **97**, 17801 (July 2006).

He: Kietzmann et al. (MPD,TRM), PRL (submitted).

Al: Desjarlais, et al, PRE **66**, 25401 (2002).

Cu: Clerouin et al. (MPD), PRB **71**, 64203 (2005).

Au: Mazevet el al., PRL **95**, 85002 (2005).

Steel: Desjarlais, Mattsson, PRE (submitted).

MPD = Mike Desjarlais
TRM = Thomas Mattsson

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Density Functional Theory (DFT) is a formally exact reformulation of the Schrodinger equation.

- Wave-function formulation
  - N electrons
  - $\Psi(\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_3\ldots,\mathbf{r}_N)$
  - $H\,\Psi = E\,\Psi$
  - 3 N dimensional space
- Density Functional Theory[1, 2]
  - Equations formulated in terms of the electron density n(**r**).
  - **r** is position in 3 dim space **r** =(x,y,z).
  - One term in the equations is unknown/approximated, the exchange-correlation energy. *Sets the accuracy*.
    - LDA, PBE, AM05, EXX, etc.
  - After this choice remaining parameters are technical. *Sets the precision*.
- VASP-code[3]
    - Plane-wave, periodic code
    - PAW potentials yields complete wave-functions

[1]*Hohenberg and Kohn, Physical Review* ***136****, B864 (1964); Kohn and Sham, Physical Review* ***140****, A1133 (1965).*

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

[3]*Kresse and Hafner, Physical Review B* ***47****, 6671 (1992).*

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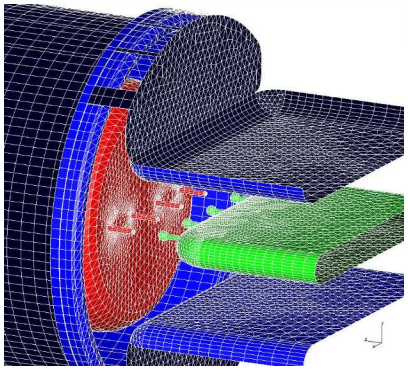
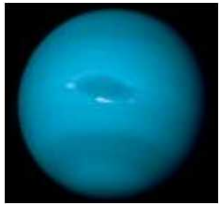
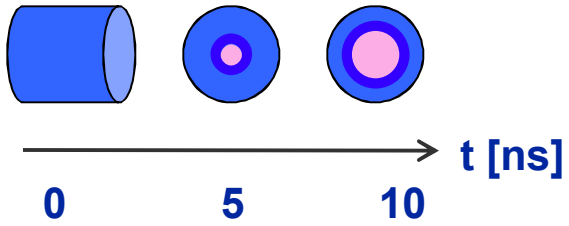
Properties of shocked water is of direct interest to Sandia as well as of general scientific interest.



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





Water at 300 K and 1 g/cm^3; 10 ns later:

× 50 density (0.05 to 2.5 g/cm^3).

×100 temperature (2500 to 300 000 K).

Demanding range of conditions.

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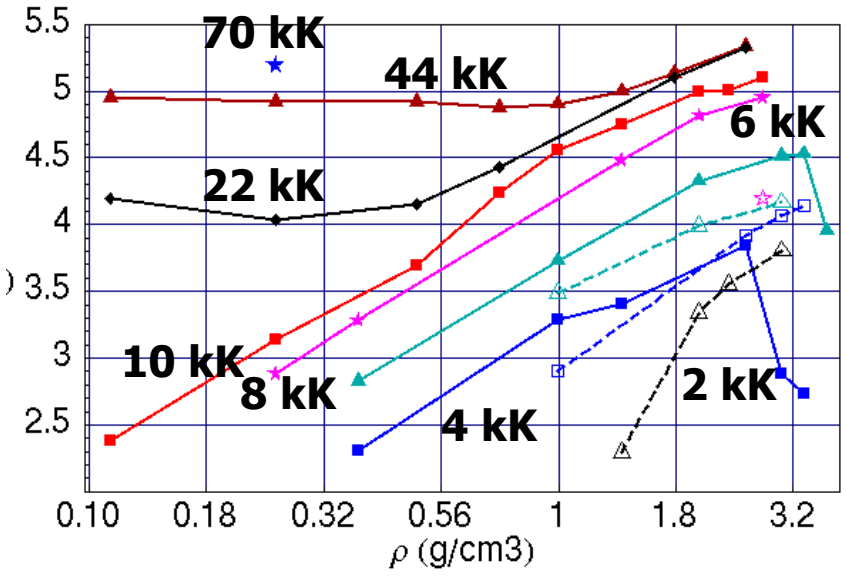
Wide-range picture of conduction in water from DFT simulations

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, Physical Review Letters **97**, 017801 (2006).

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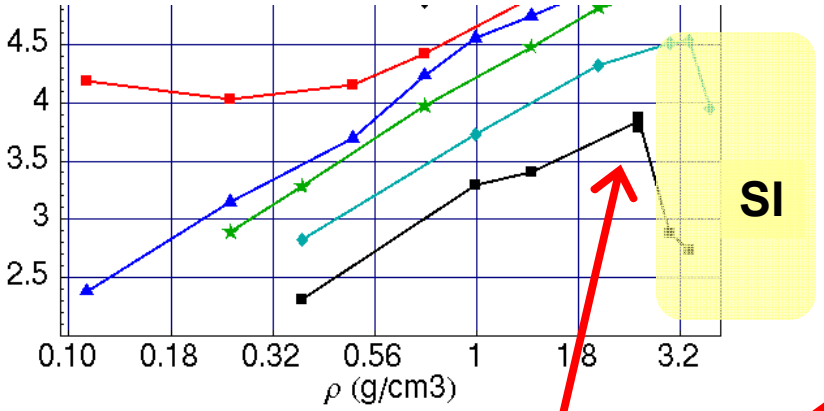
Revision of the phase-diagram of HEDP water

DC electronic conductivity of water



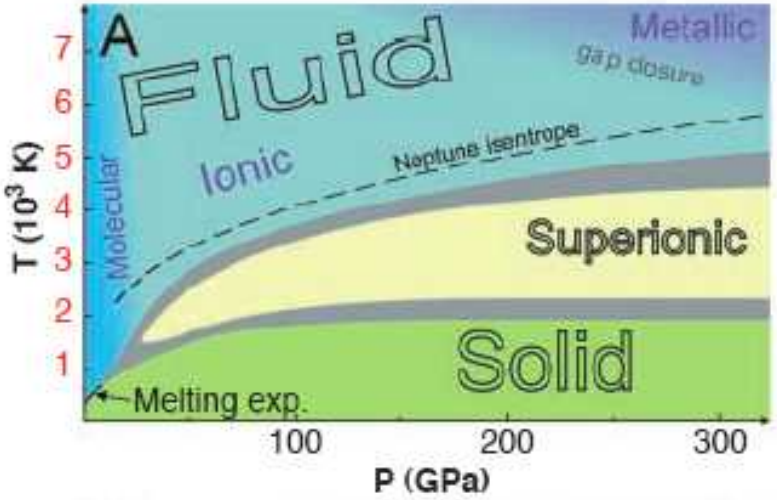
Significant electronic conductivity

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

Superionic phase

- Cavazzoni et. al. (Science **283**, 44 (1999))
  - O atoms frozen into a 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)).



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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.

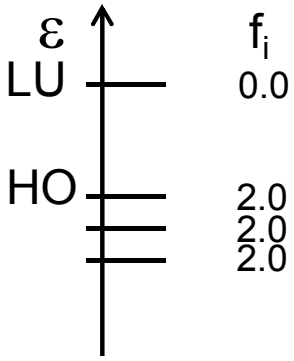
HO -- highest occupied (0 K)

LU -- lowest unoccupied (0 K)

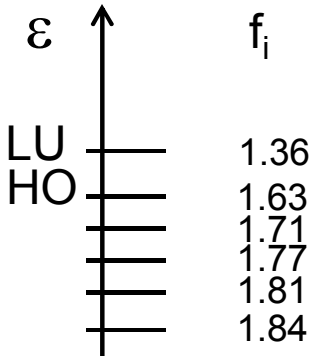
$\Delta E = \varepsilon_{LU} - \varepsilon_{HO}$ (eigenvalue gap).

for both 54 and 128 molecules cells. Units are molecules/cell, g/cm^3, Kelvin, $1/(\Omega\ m)$, 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



0 K: insulating



Finite T: conducting

Using Finite Temperature is necessary for the HEDP area.

Not used as a numerical technique.

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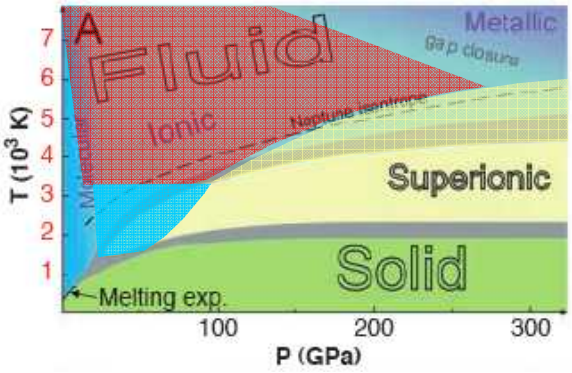
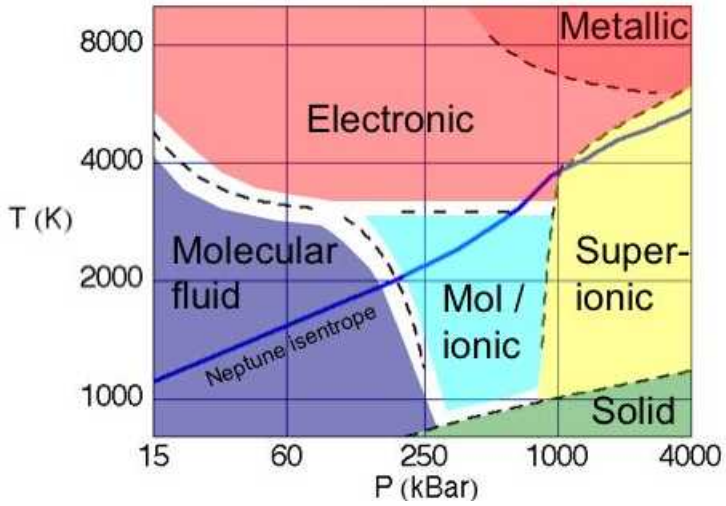
Phase-diagram of HEDP water -- revised



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

- Direct transition from superionic to conducting fluid at 100 GPa, 4000 K.
- Electronic conduction over a large region previously described as insulating.
- Metallic conductivity at lower T/P.
- Superionic phase boundary at higher pressure (100 GPa at 2000 K).



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

Revision of a large region of the phase-diagram, including a significant range of the Neptune isentrope.

Full consequences will have to be determined by planetary researchers.

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How can we rely on FT-DFT at conditions relevant for HEDP?

PIMC

Path-Integral Monte Carlo (PIMC)

H: Militzer, Ceperley, PRL **85**, 1890 (2000).
He: Militzer, PRL **97**, 175501 (October 2006).

- Solving the Schrodinger equation directly
  - First-principles method
  - Still involves approximations
    - "sign problem" of fermions
- Computationally highly demanding
  - H, He, (few electrons)
- Independent from DFT
- Provides an important second opinion.

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PIMC is a first-principles method in density matrix-formulation of quantum mechanics

$$\Psi_{GS}(\mathbf{R}) = \begin{vmatrix} \Phi_1(\mathbf{r}_1) & \dots & \Phi_N(\mathbf{r}_1) \\ \dots & \dots & \dots \\ \Phi_1(\mathbf{r}_N) & \dots & \Phi_N(\mathbf{r}_N) \end{vmatrix}.$$

Wave-function repr.

Thermal density-matrix representation

$$\rho(\mathbf{R},\mathbf{R}';\beta) = \langle \mathbf{R} | e^{-\beta\mathcal{H}} | \mathbf{R}' \rangle = \sum_s e^{-\beta E_s} \Psi_s(\mathbf{R}) \Psi_s(\mathbf{R}')$$

at finite temperature ($\beta = 1/k_B T$)

Expectation values in density-matrix repr.

$$\langle \mathbf{O} \rangle = \frac{\mathrm{Tr}[\mathbf{O}\rho]}{\mathrm{Tr}[\rho]}.$$

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PIMC reduces the calculation to small steps in temperature, or "imaginary time" τ

Quantum operators can be multiplied

$$e^{-\beta\mathcal{H}} = \left(e^{-\tau\mathcal{H}}\right)^{M} \qquad \tau = \beta/M \rightarrow 1/(\, k_B T\, M)$$

Free particle limit τ=0 : $\tau = \beta/M \rightarrow 0$

$$\rho(\mathbf{R},\mathbf{R}';\beta) \rightarrow \exp[-(\mathbf{R}-\mathbf{R}')^2/4\lambda\beta]/(4\pi\lambda\beta)^{3N/2}$$

Large M is equivalent to the high-temperature limit ($\beta \rightarrow 0$)

PIMC becomes more efficient at high temperature.

David M. Ceperley, Rev. Mod. Phys. **67**, 279 (1995).

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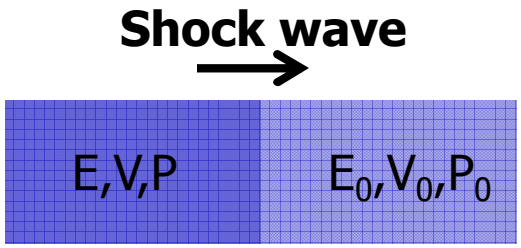
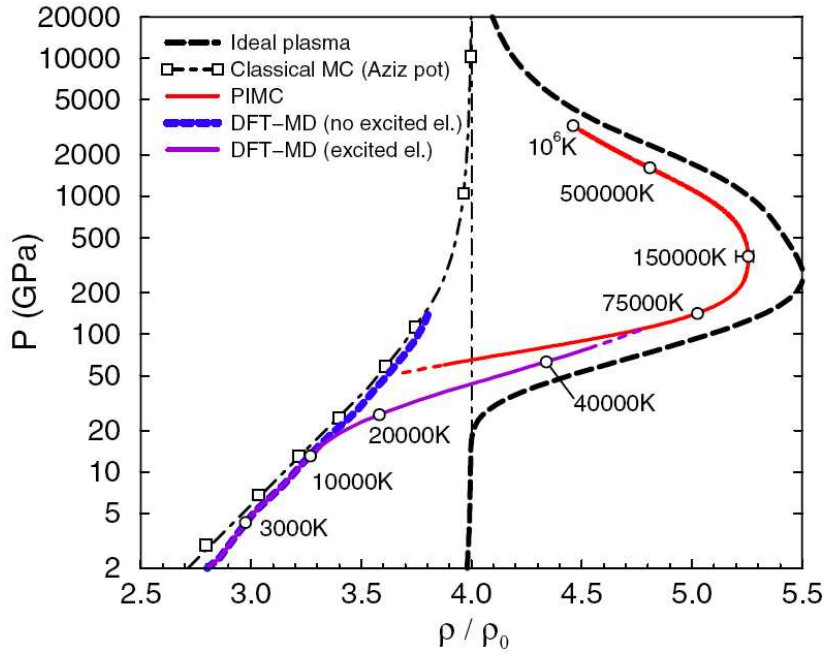
PIMC results for He compares very well to finite-temperature DFT calculations



Rankine-Hugoniot condition for a single shock relates change in pressure, volume and energy.

$$H = E - E_0 + \tfrac{1}{2}(V - V_0)(p + p_0) = 0.$$



- PIMC approaches ideal plasma at 10^6 K
- FT-DFT approaches PIMC results.
- Deviations from ground state DFT (Car-Parrinello) as temperature increases.
- Classical MC results deviate too, no electronic degrees of freedom.

B. Militzer Phys. Rev. Lett **97,** 175501 (October 2006).

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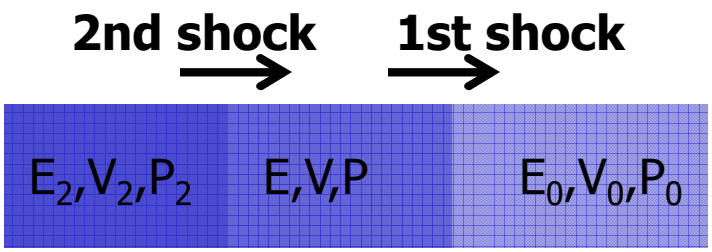
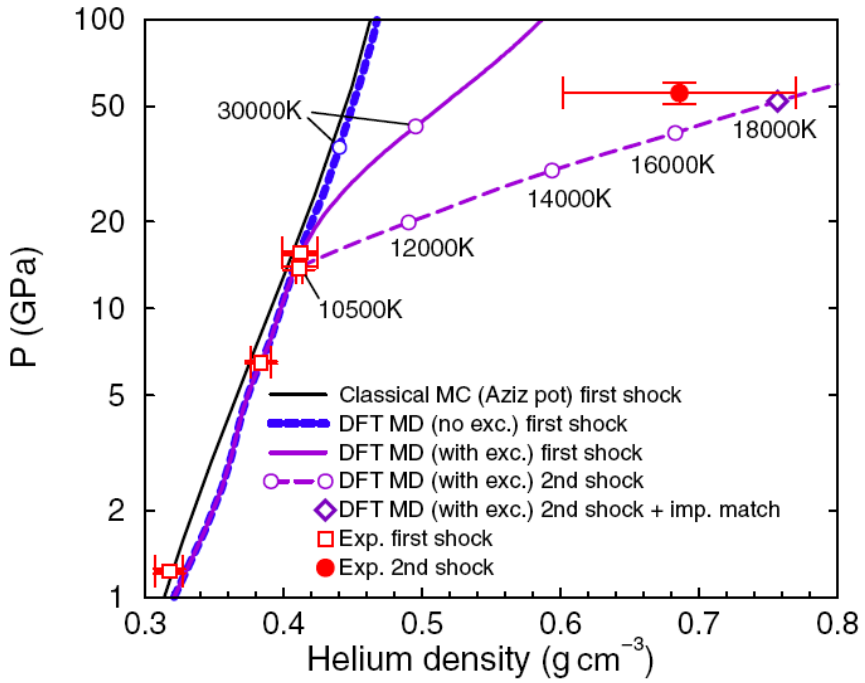
Available (few) experimental results agree with finite-temperature DFT





- Shock experiments probe only certain regions of the phase-diagram.
- FT-DFT captures both first- and second shock data.
- Simulations can go outside the area where experimental data is available -- perhaps even impossible to obtain.
- Note that PIMC is not even on this plot.

B. Militzer Phys. Rev. Lett **97,** 175501 (October 2006).

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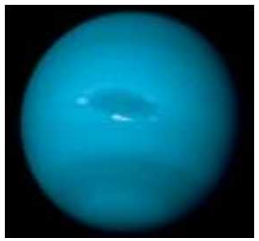
DFT has had an enabling impact on pulsed power programs at Sandia

- Predictive modeling of flyer-plate experiments after DFT simulations of Al electrical conductivity and development of wide-range materials models.
- Direct DFT simulations strongly supporting deuterium shock Hugoniot measurements on Z.
- Developed high-fidelity materials models for Army Research Laboratory (ARL).
- Direct DFT simulations predicting shock melting of Be and C for National Ignition Campaign. Steered experiments and reduced the number of required shots (cost per shot: +$ 100 000).
- Improved wire-explosion simulations with DFT steel conductivity data.

Jupiter: H and He



Neptune: H2O, He, H

- Direct DFT simulations of compressed deuterium.
- Improved our understanding of water at conditions directly applicable to modeling conditions in planets.
- Simulations of He at conditions of importance to giant planets.

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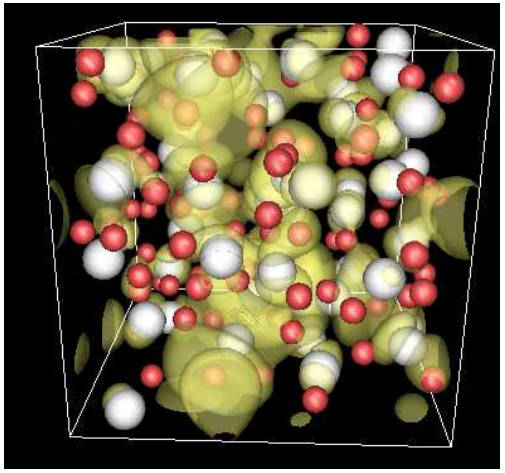
First-principles simulations are key to improving our understanding of HEDP

- **Summary**
  - PIMC and DFT are complementary methods to model physics in the HEDP region.
  - Importance of finite temperature method when using DFT.
- **Enabling impact on Sandia's mission**
  - Several DFT based materials models are in *daily use* at SNL (Al, Cu, steel, W).
  - Direct DFT simulations helps design and analyze experiments (shock melting).
- **Crucial dimension of HEDP modeling**
  - Simulations are never better than the underlying physics models.



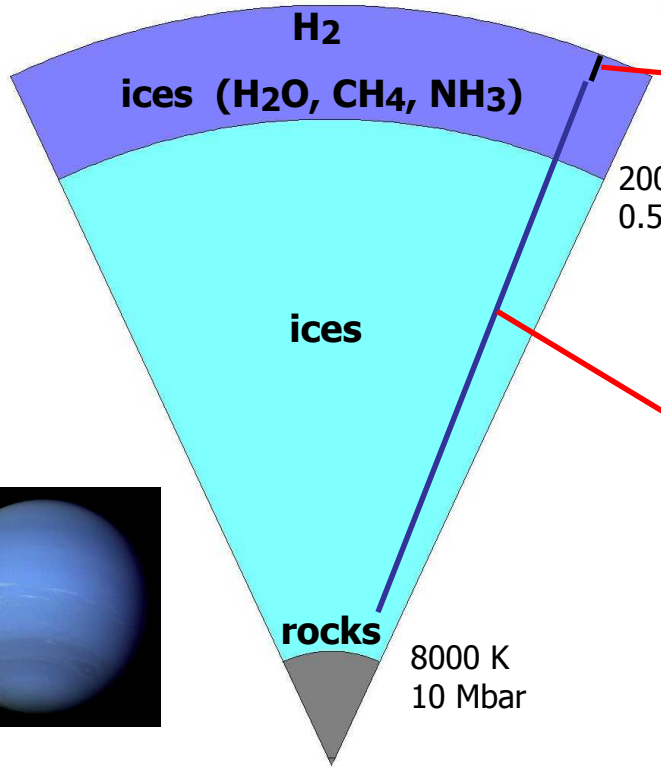
54 water molecules at 4000 K

Acknowledgment

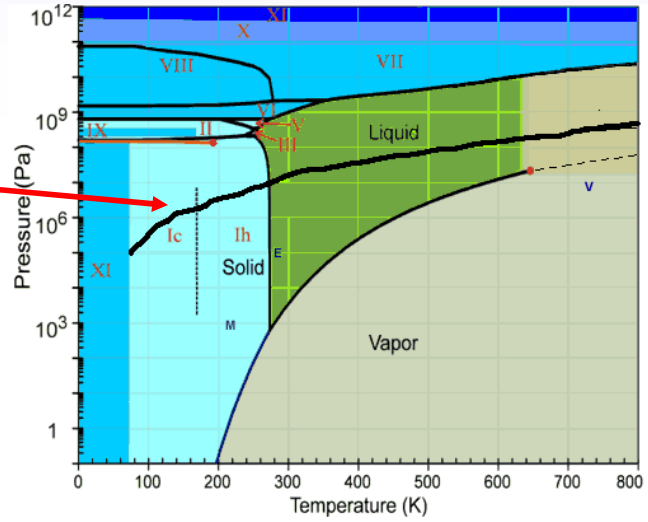
Mike Desjarlais (1640) -- pioneered DFT in the HEDP area

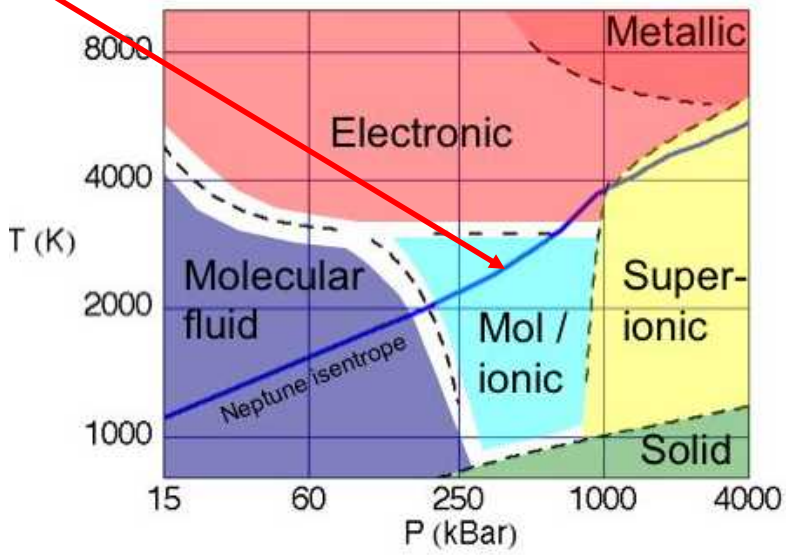
Tom Mehlhorn (1640) -- has strongly supported our work

General structure of giant planets : three layer model



Neptune-like giant planet





Nadine Nettelman, Univ. of Rostock, Rostock, Germany.

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

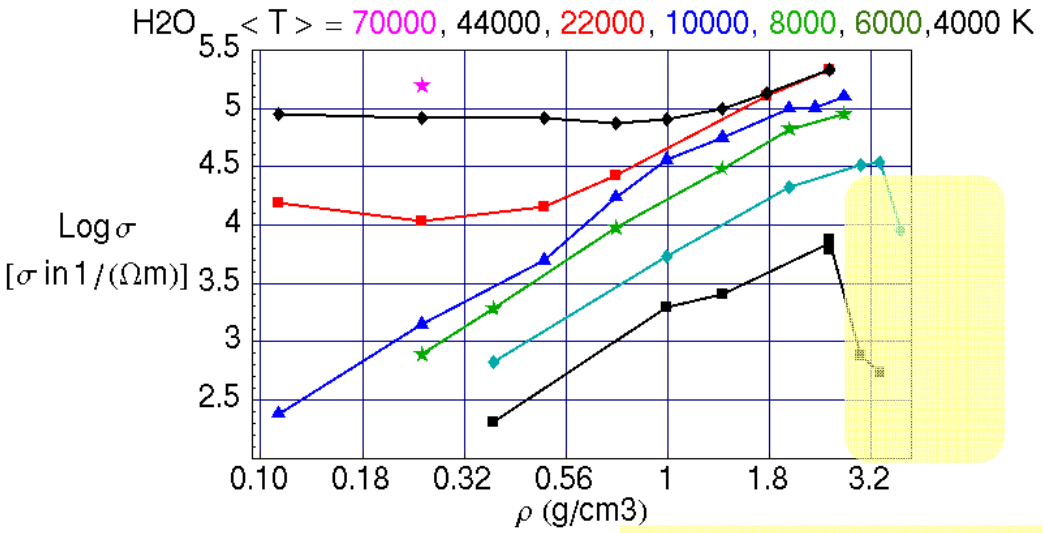
$$\sigma_{\mathbf{k}}(\omega) = \frac{2\pi e^2\hbar^2}{3m^2\omega\Omega}\sum_{\alpha=1}^{3}\sum_{j=1}^{N}\sum_{i=1}^{N}(F(\varepsilon_{i,\mathbf{k}}) - F(\varepsilon_{j,\mathbf{k}}))\left|\left\langle\Psi_{j,\mathbf{k}}\left|\nabla_\alpha\right|\Psi_{i,\mathbf{k}}\right\rangle\right|^2\delta(\varepsilon_{j,\mathbf{k}}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

Fermi weights **Energy conservation**

Sum over bands **Matrix element**

- **Wave-function based[1]**
  - Kubo-Greenwood (KG) formula yields the conductivity directly from wave-functions
  - Neither cross-sections nor relaxation times required
- **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:

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

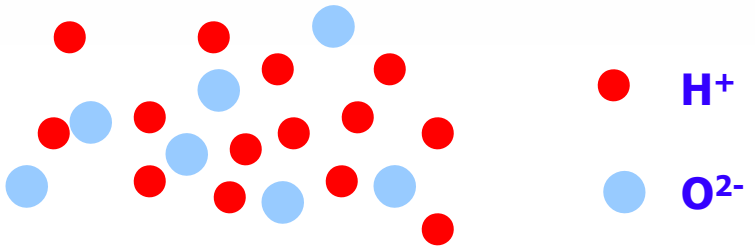
- Valid when all protons are free/equivalent.

Reduction due to H_2O diffusion

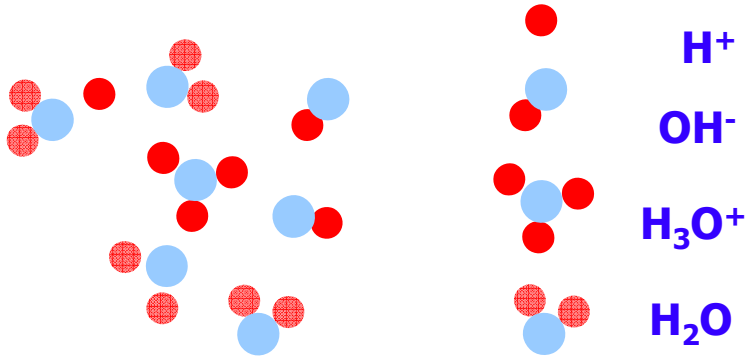
$$D_H = (1-\gamma)D_{H^*} + \gamma D_O$$

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

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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