SAND2007-3857C

Density Functional Theory in High Energy Density Physics: phase-diagram and electrical conductivity of water

SCCM-2007

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HEDP Theory
Sandia National Laboratories

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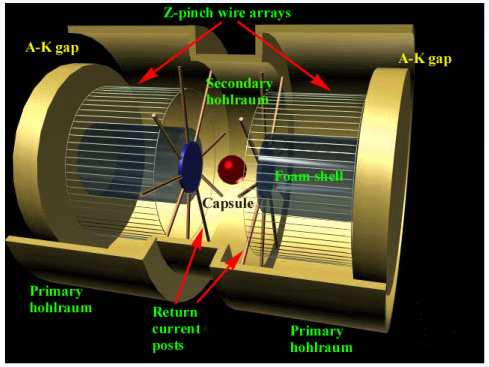
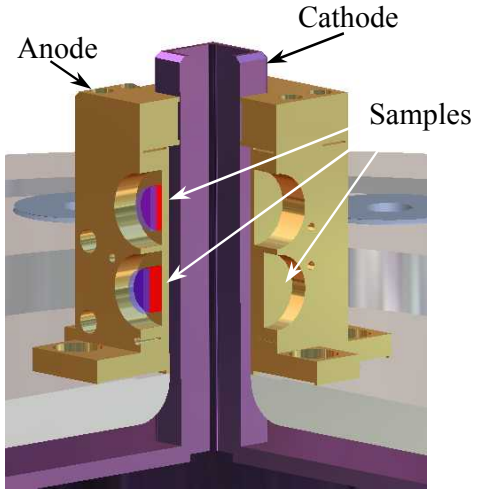
High energy-density physics (HEDP) experiments at the Z accelerator



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, more.
- Experiments are costly and involved -- first-principles simulations have had a direct impact on the progress.



Magnetically launched flyer plates

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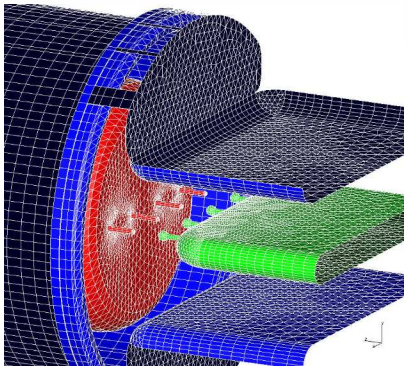
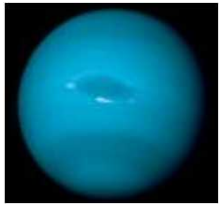
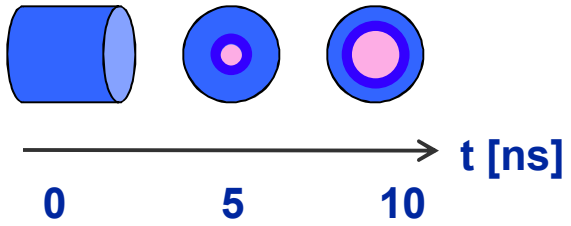
Properties of shocked water is of direct interest to Sandia as well as of general scientific interest.



- Water switches as pulse-shaping components.
- 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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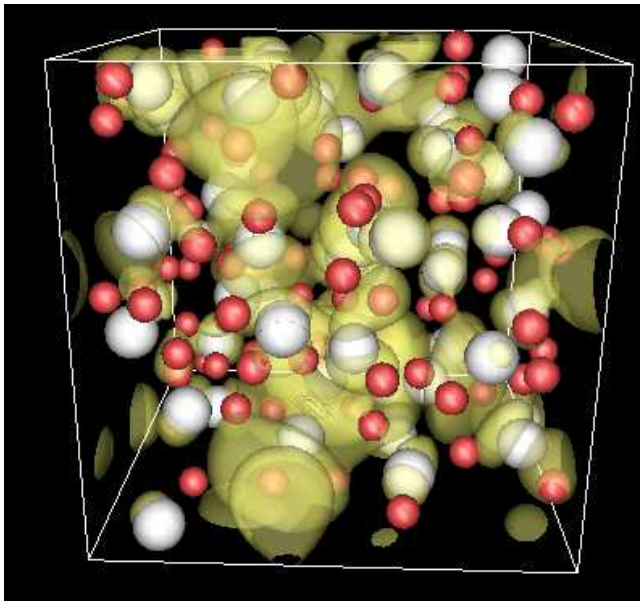
Warm-dense matter is a difficult region and predictability requires a first-principles approach



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
- Main approximation the exchange/correlation functional choice, no free parameters.
- EOS, conductivity, structure, diffusion, and opacity *from one framework*.

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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*.
  - Finite-temperature formulation, allows for thermal ground state of the system.
- 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).*
Walter Kohn received the 1998 Nobel Prize in chemistry.

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

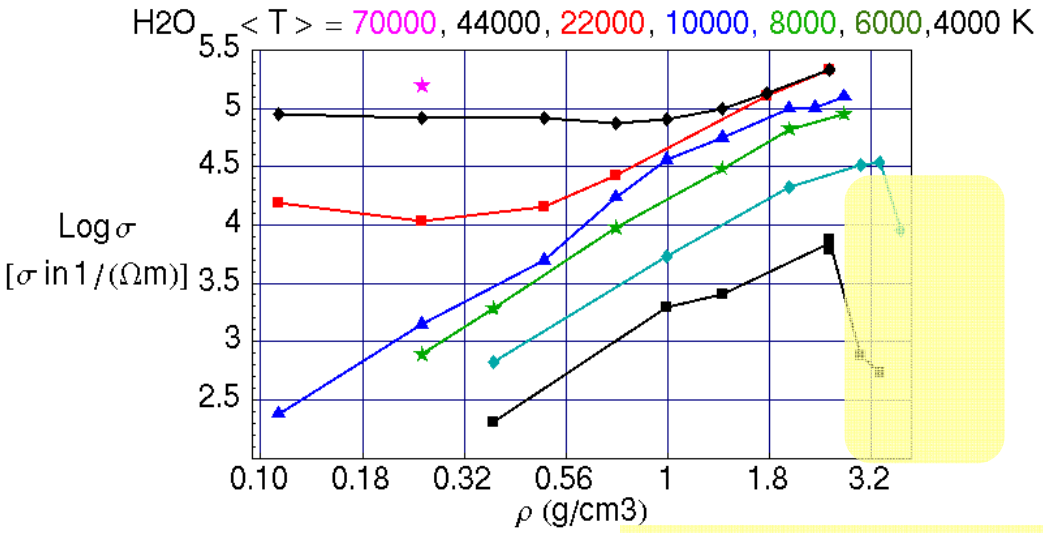
$$\sigma_{\mathbf{k}}(\omega) = \frac{2\pi e^2\hbar^2}{3m^2\omega\Omega}\sum_{\alpha=1}^{3}\sum_{j=1}^{N}\sum_{i=1}^{N}(F(\varepsilon_{i,\mathbf{k}}) - F(\varepsilon_{j,\mathbf{k}}))\left|\left\langle\Psi_{j,\mathbf{k}}\left|\nabla_\alpha\right|\Psi_{i,\mathbf{k}}\right\rangle\right|^2\delta(\varepsilon_{j,\mathbf{k}}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

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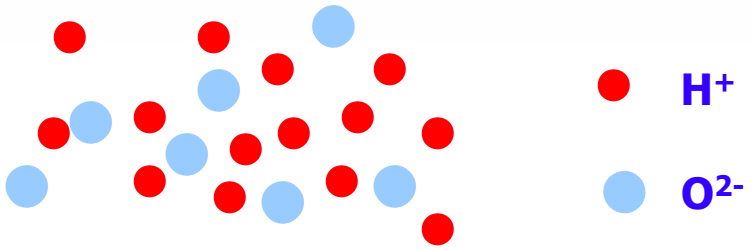
Conductivity in water -- proton conduction from QMD simulations of proton diffusion.

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.

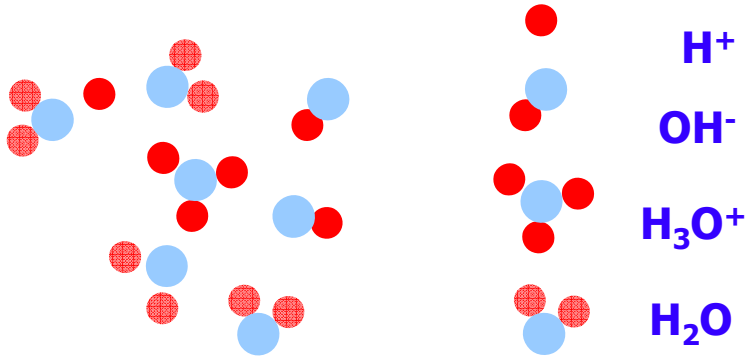


Full dissociation, all protons contribute.

Reduction due to H_2O diffusion

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

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



Diffusion as H_2O is non-conducting.

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

Wide-range modeling of conductivity in water:
*Mattsson and Desjarlais, PRL **97**, 017801 (2006).*

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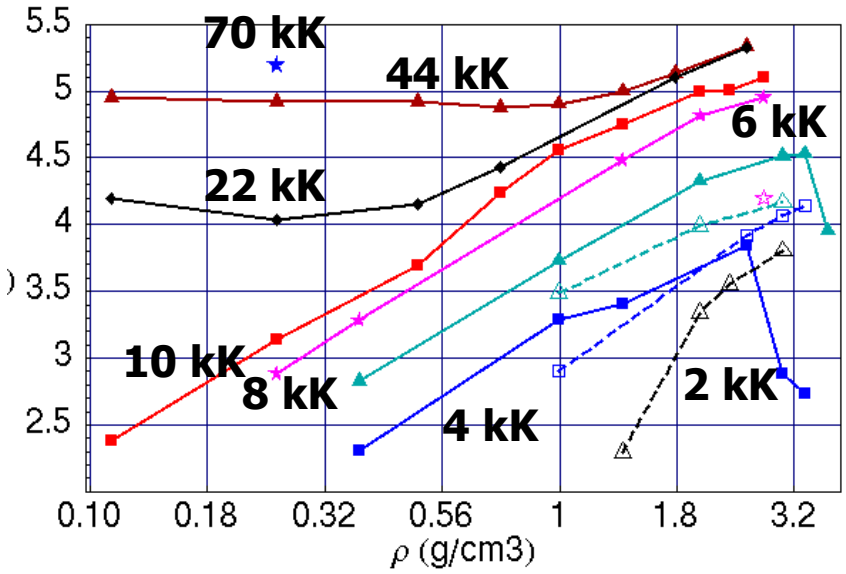
Wide-range picture of conduction in water from DFT simulations

Ionic and electronic conductivity



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

Wide-range modeling of conductivity in water:
*Mattsson and Desjarlais, PRL **97**, 017801 (2006).*

- **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.

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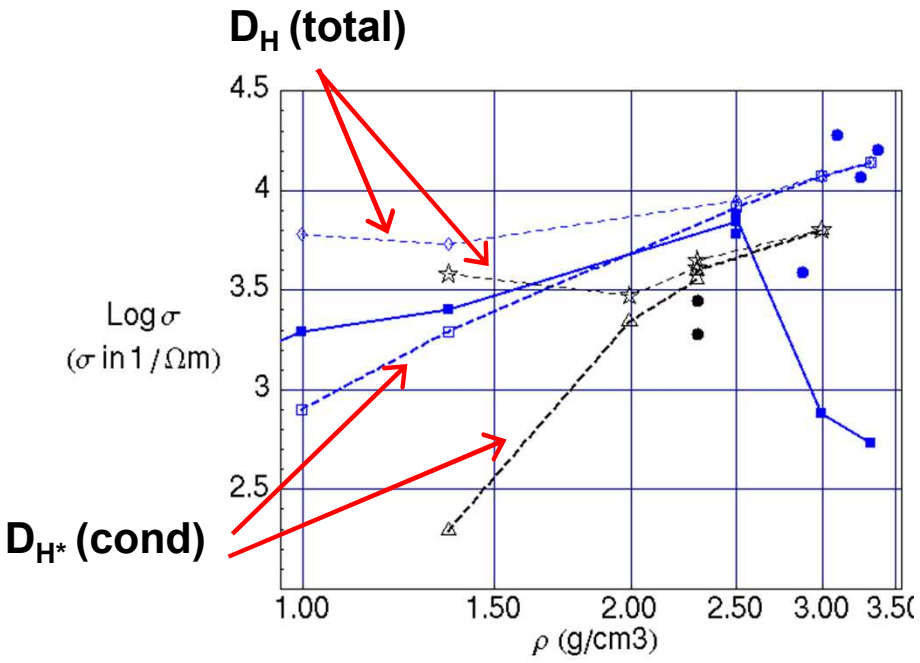
Conductivity in water -- simulations compare well to available experimental data.

- 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 H2O diffusion.
- We predict that conductivity measurements at 200K and 1.5 g/cm^3 would yield low conductivity.



● **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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Hugoniot from DFT/QMD compared to experimental data shows remarkable agreement for weak shocks

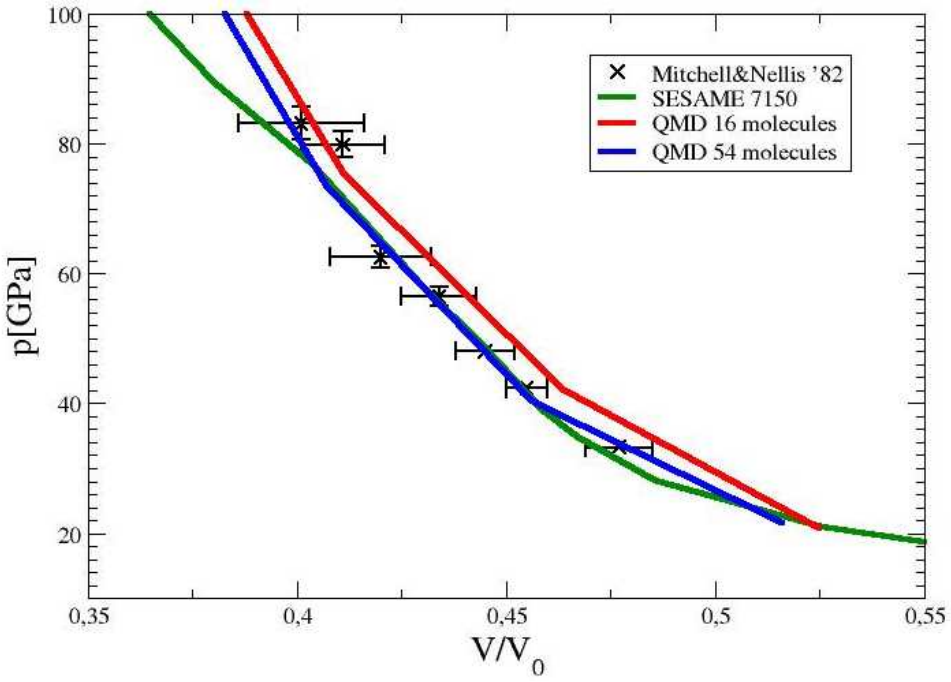

Figure by Martin French,
University of Rostock, Rostock, Germany,

- Mitchell and Nellis 1982:
  - J. Chem. Phys. **76**, 6273 (1982).
  - Gas gun
- DFT/QMD simulations:
  - Convergence wrt system size
  - High plane-wave cutoff to converge pressure (900 eV) to 2%.
- QMD simulations are in excellent agreement with high-precision experimental data for weak shocks.

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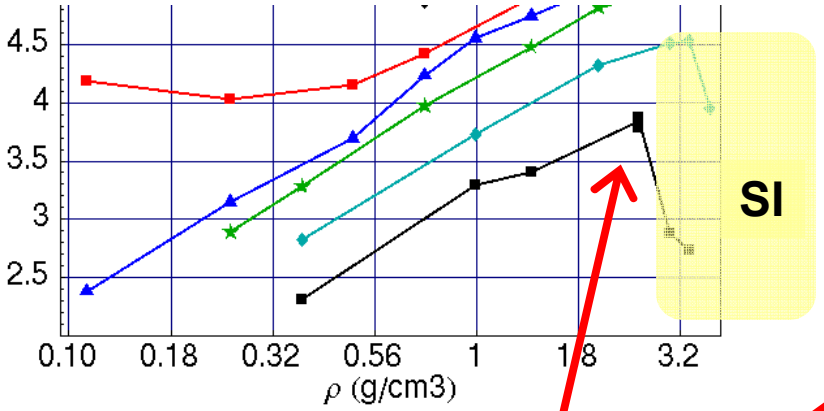
Revision of the phase-diagram of HEDP water

DC electronic conductivity of water



Significant electronic conductivity

Superionic phase

- Cavazzoni et. al. (Science **283**, 44 (1999))
  - O atoms frozen into a BCC lattice **OK**
  - Highly mobile H atoms **OK**
  - Gap in electronic structure **OK**
  - Bordering to an ionic liquid, with gap **NO**

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

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The effect of including thermal occupation of electronic degrees of freedom

Fermi occupation modeling the thermal ground state:

f_i -- occupation of band i.

ε_i -- energy of band i.

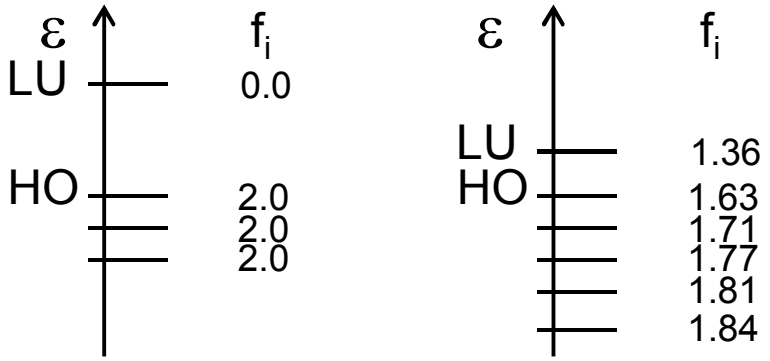
HO -- highest occupied (0 K)

LU -- lowest unoccupied (0 K)

$\Delta E = \varepsilon_{LU} - \varepsilon_{HO}$ (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



0 K: insulating **Finite T: conducting**

Using Finite Temperature is necessary in the HEDP area[#].

Effects of including electronic temperature (H2O, He):

*[#] Mattsson and Desjarlais, PRL **97**, 017801 (2006) [**H2O**]; Militzer, PRL **97**, 175501 (2006) [**He**]; Kietzmann, Holst, Redmer, Desjarlais, and Mattsson, PRL **98**, 190602 (2007) [**He**];*

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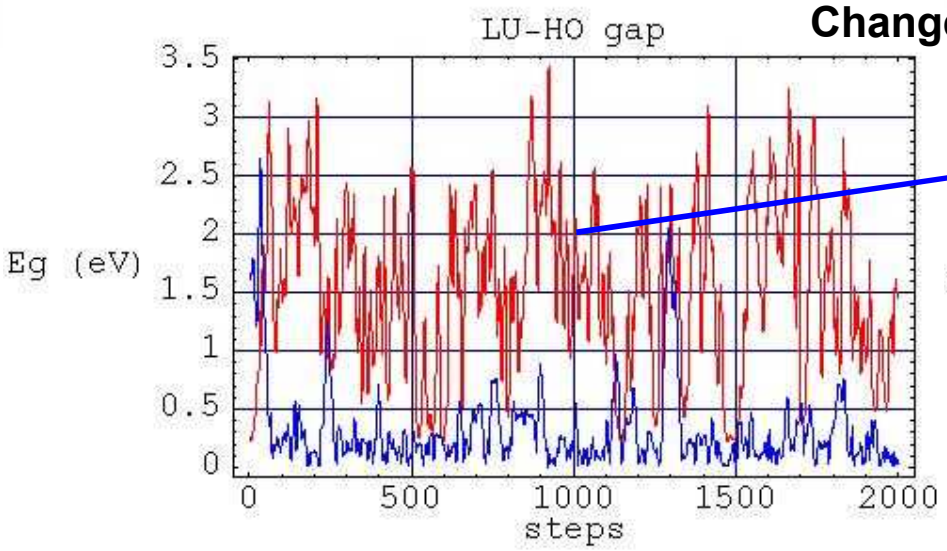
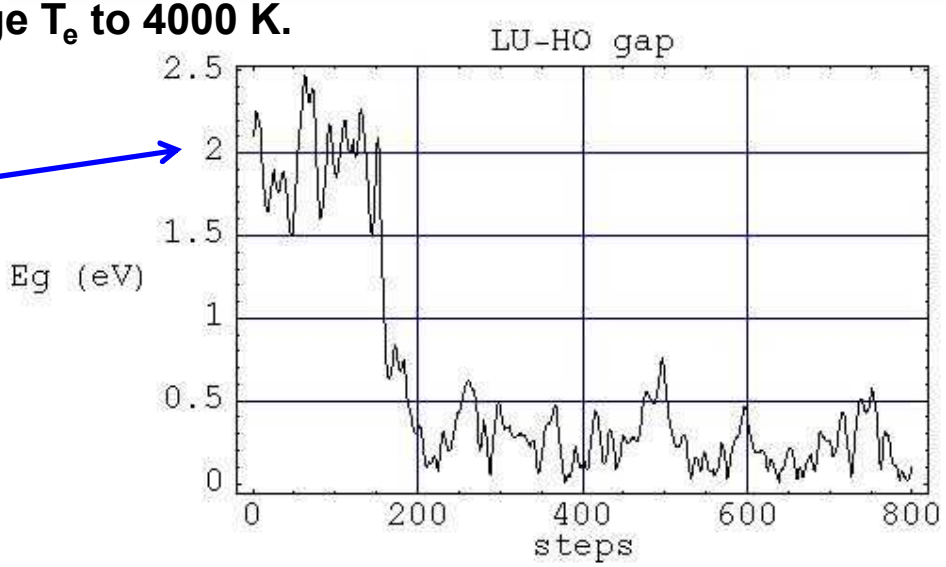
The effect of including thermal occupation is not instantaneous with change in T_e.



Change T_e 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/ post-processing snapshots from an MD simulation using 0 K electrons will not necessarily yield the same electronic structure as when doing a full MD simulation with temperature.

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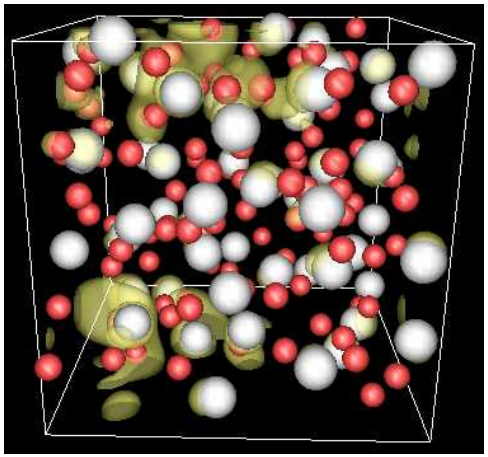
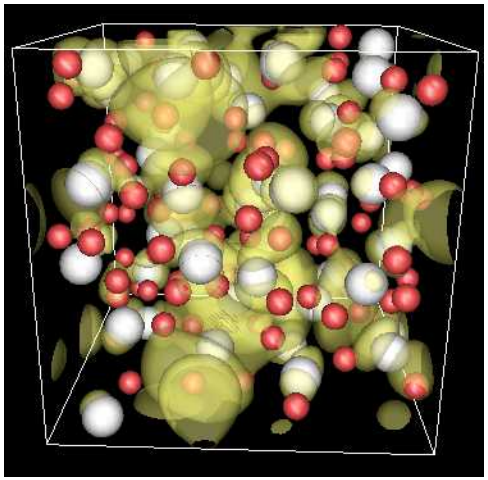
A thermal distribution of states leads to a conducting liquid state.

Electron density iso-surface from the HO state: T=4000 K, ρ =2.5 g/cm^3



T_e=1000: localized character:
not spanning the system -- insulating.



T_e=4000: delocalized character of states:
spanning the system -- conducting,

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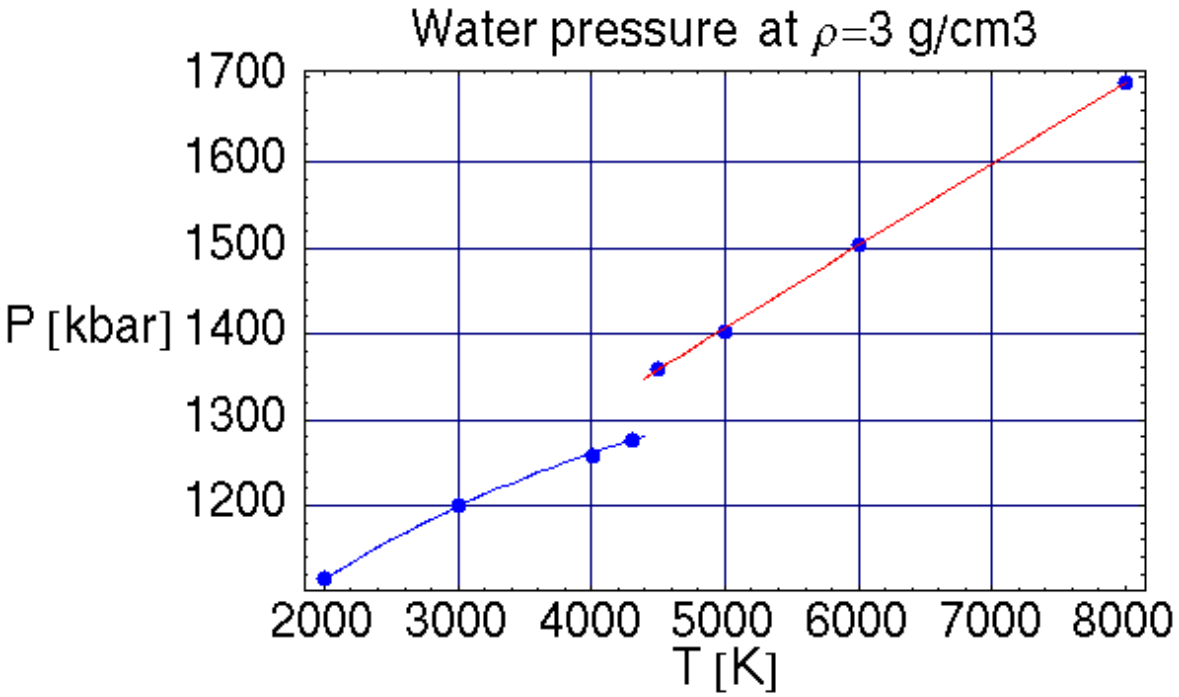
A closer look at the phase-transition from superionic to conducting liquid: pressure



A discontinuous jump in pressure as the superionic phase melts into a conducting liquid.

Consistent with expansion upon melting, and $(dT/dP)_{melt} > 0$.

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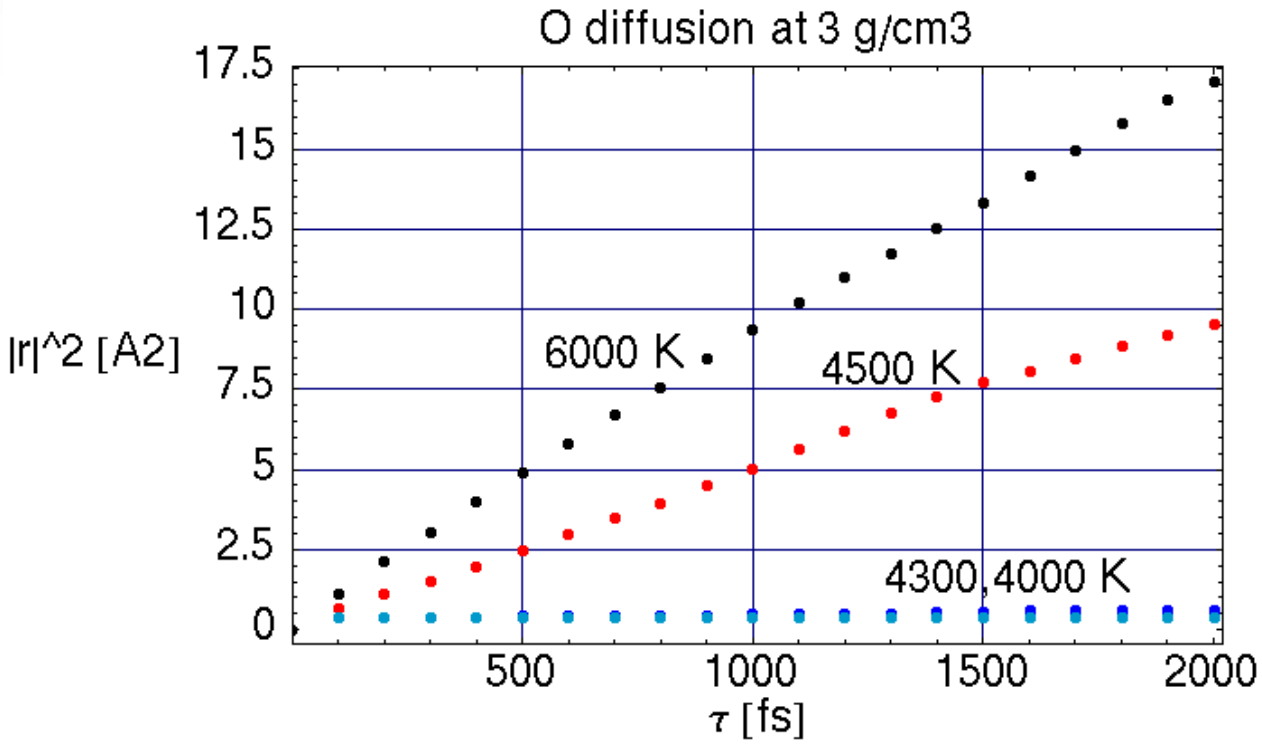
A closer look at the phase-transition from superionic to conducting liquid: O diffusion



Below 4300 K, there is no long-time displacement of O atoms.

The O atoms form a BCC lattice (pair-correlation and neighbor analysis).

Above 4500 K, O atoms diffuse.

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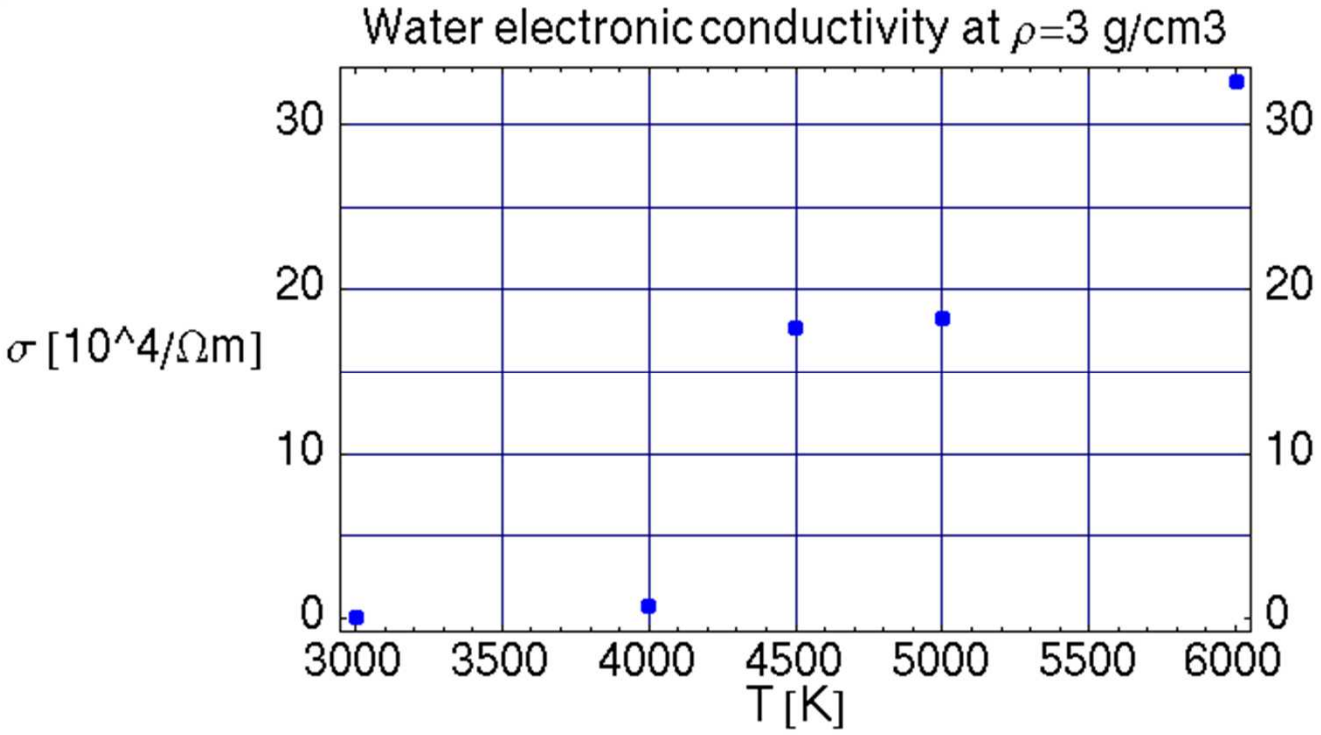
A closer look at the phase-transition from superionic to conducting liquid: conductivity



Conductivity increases dramatically (20x) from 4000 K to 4500 K.

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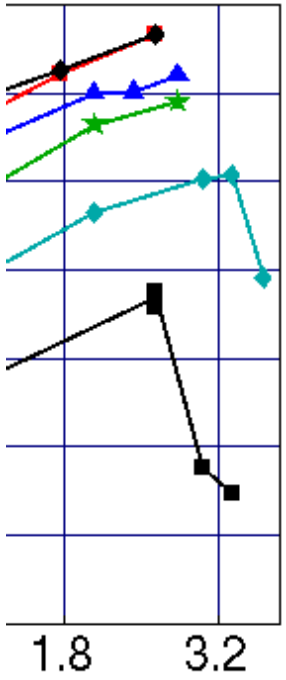
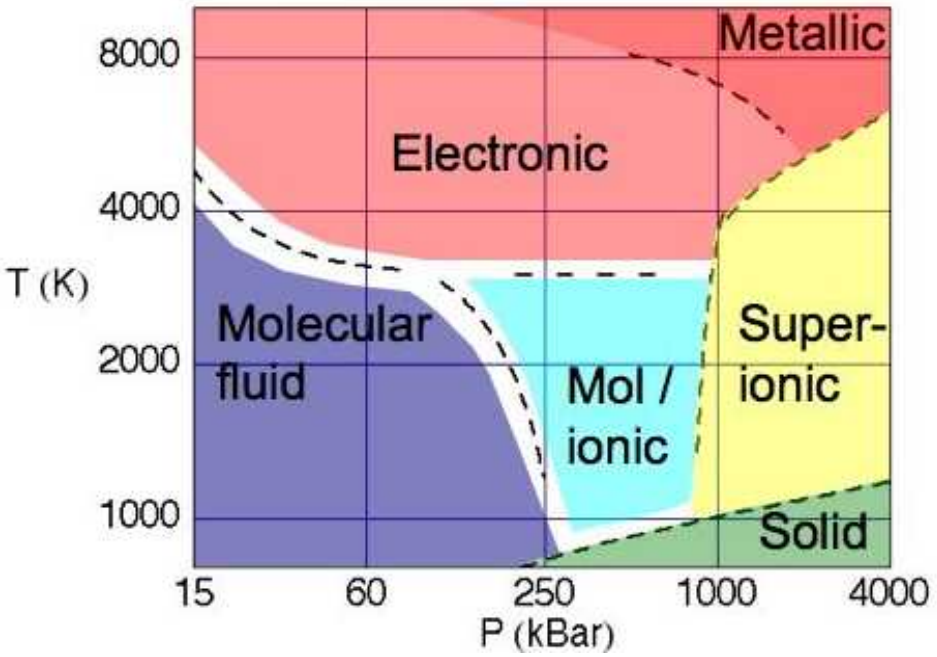
A closer look at the phase-transition from superionic to conducting liquid: conclusion



- O atoms from BCC lattice to fluid: immobile to moving freely.
- Pressure discontinuity, consistent with $(dT/dP)_{melt} > 0$.
- Step-like onset of conductivity.

Water exhibits a simultaneous phase-transition in structural- and electronic properties when going from the superionic phase to a fluid.

Phase-diagram of HEDP water from DFT/QMD



- Molecular fluid:
  - No dissociation of H_2O
  - Neither ionic nor electronic conductivity
- Mol/ionic:
  - Partial dissociation: H, OH, H_2O, H_3O
  - Ionic conduction
  - No electronic conductivity
- Super-ionic:
  - BCC lattice of O, H diffusion
  - Ionic conduction
  - No electronic conductivity
- Electronic:
  - O and H diffusion
  - Ionic conduction
  - Electronic conductivity
- Metallic:
  - Rapid O and H diffusion
  - High electronic conductivity

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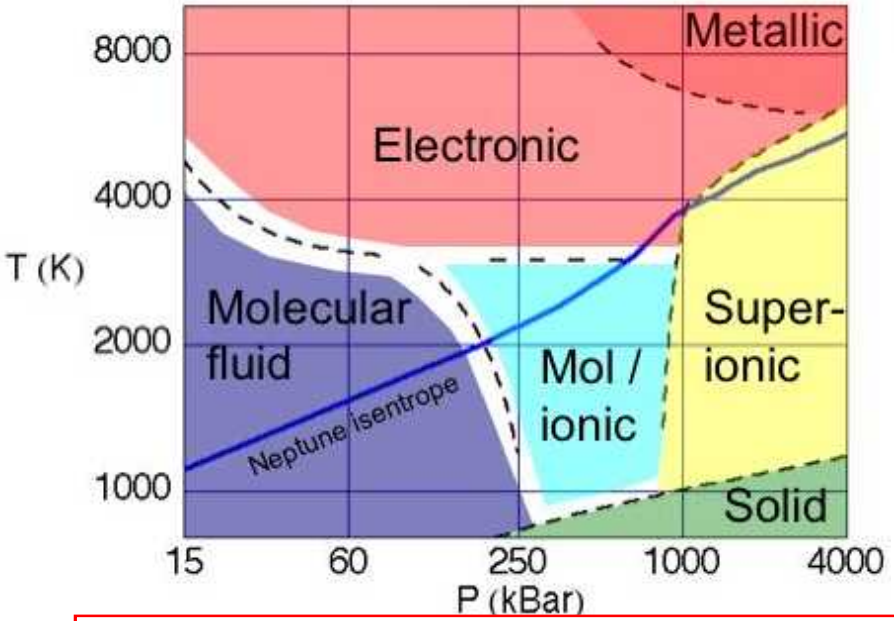
Phase-diagram of HEDP water: revisions from previous theory



Neptune isentrope:
Nadine Nettelman and Roland Redmer
University of Rostock, Rostock, Germany.

- Direct transition from superionic to conducting fluid at 100 GPa, 4000 K.
- Electronic conduction over a large region previously described as insulating (Cavazzoni et al. Science **283**, 44 (1999).
- Metallic conductivity earlier than previously concluded.
- Superionic phase boundary at higher pressure (100 GPa at 2000 K).
- Neptune isentrope traverses a segment of conducting water, consistent with a conducting layer at a shallow depth.

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

Full consequences yet to be determined.

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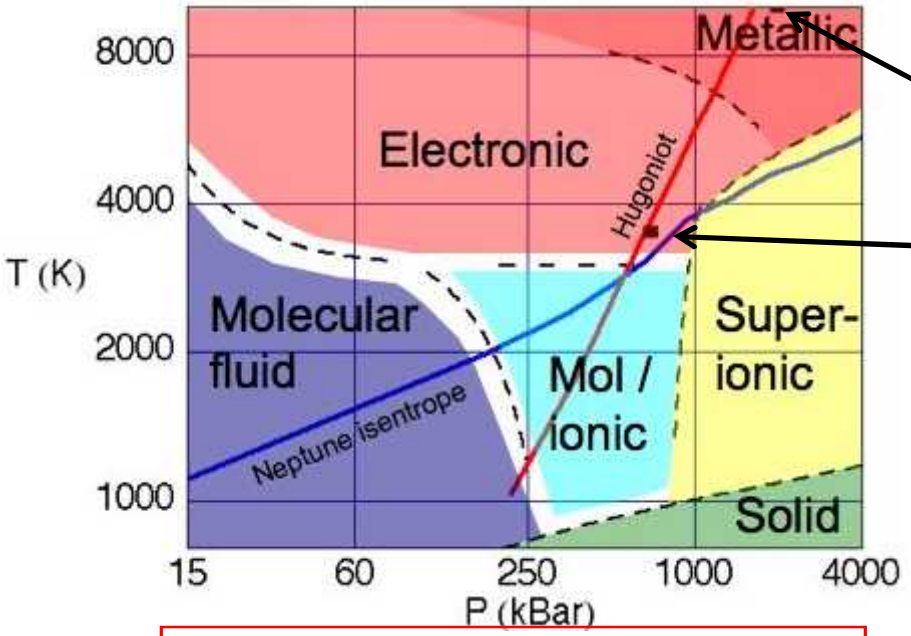
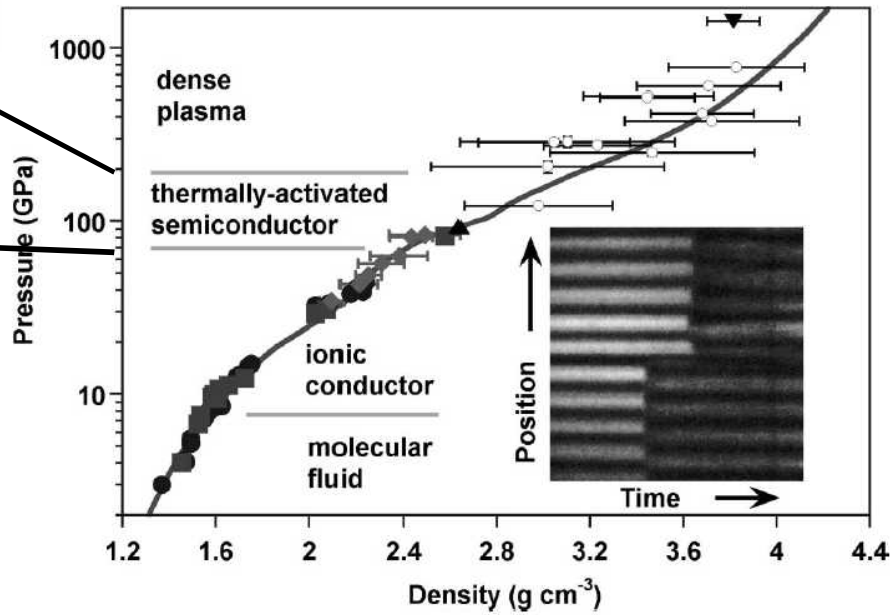
Phase-diagram of HEDP water: comparison with single shock experiments



DFT/ QMD study of HEDP water:
*Mattsson and Desjarlais, PRL **97**, 017801 (July 2006).*



Experimental study of shocked water:
*Celliers et al. , Phys. Of Plasmas **11**, L41 (2004).*

Significant difference between Hugoniot and planetary conditions.

Laser-driven shocks in pre-compressed water (Lee et al. JCP 2006).

LAPLAS collaboration at future FAIR facility, Darmstadt, Germany.

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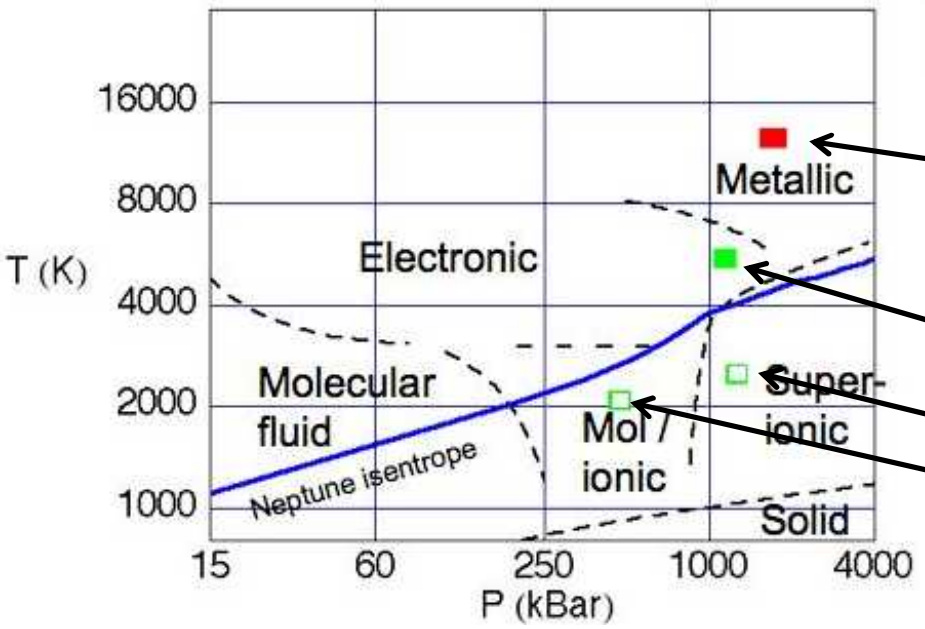
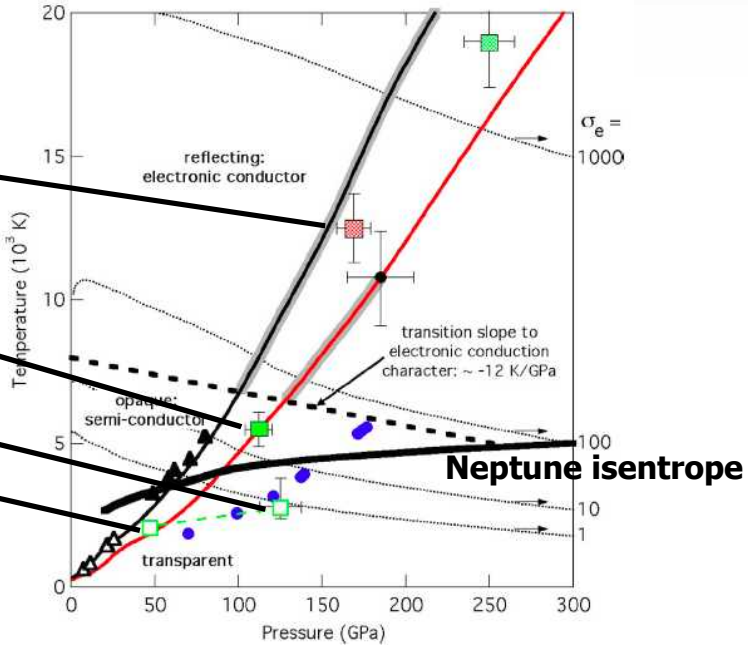
Phase-diagram of HEDP water: comparison with experiments aimed at planetary cond.





DFT/ QMD study of HEDP water:
*Mattsson and Desjarlais, PRL **97**, 017801 (July 2006).*

Experimental study of pre-compressed shocked water:
*Lee et al. , JCP **125**, 014701 (July 2006).*

Our understanding of water under extreme conditions has recently advanced significantly by theoretical as well as experimental work.

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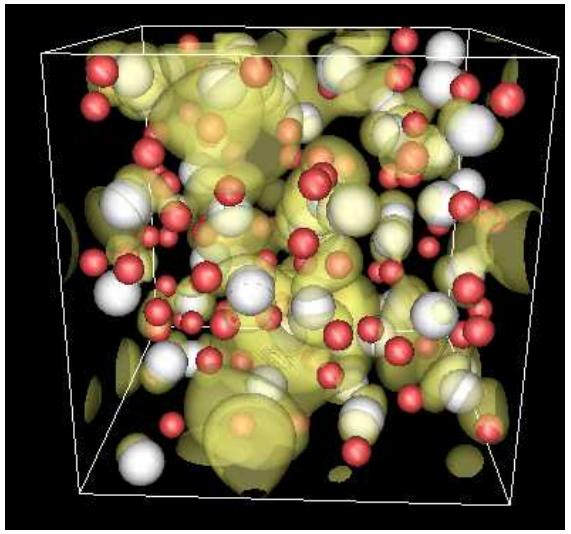
DFT/QMD simulations of HEDP water have advanced our understanding

- **Water in the HEDP region**
  - Confirm existence of HEDP superionic phase
  - Phase-transition from superionic directly to a conducting fluid phase, not insulating liquid
  - Neptune isentrope largely traverses the superionic phase, with a segment of conducting fluid (*potentially very important*)
  - Independent theoretical prediction of phase-diagram confirmed by experimental results on pre-compressed water
- **First-principles HEDP simulations**
  - Decidedly important to employ a finite temperature method when using DFT
  - Snapshots are not necessarily enough to determine the correct structure



Conducting water at 4000 K, 2.5 g/cm^3.

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

- **Summary**
  - DFT provides insights and data that are very difficult to obtain otherwise.
- **Enabling impact on HEDP modeling**
  - 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.

First-principles simulations are indispensable elements of many types of projects on Z.

Acknowledgment

Mike Desjarlais, pioneered DFT in the HEDP area.

Tom Mehlhorn, for strong support of our work.

Larry Warne, for discussions on electrical break-down in water.

Ronald Redmer, and students Martin French, Bastian Holst, Andre Kietzmann, and Nadine Nettelman for fruitful collaborations.

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Hugoniot from DFT/QMD agree with experiments

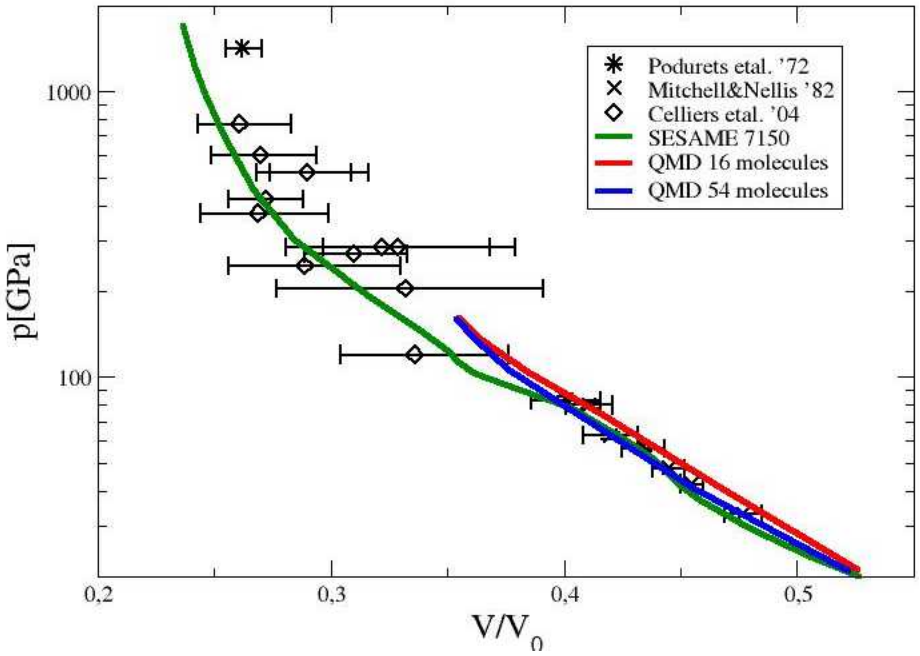

Figure by Martin French, University of Rostock, Rostock, Germany,

- Podurets et al 1972:
  - JETP **35**, 375 (1972).
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- Celliers et al 2004:
  - Physics of Plasmas, **11**, 41 (2004).
  - Laser
- QMD simulations are in quantitative agreement with experimental data.

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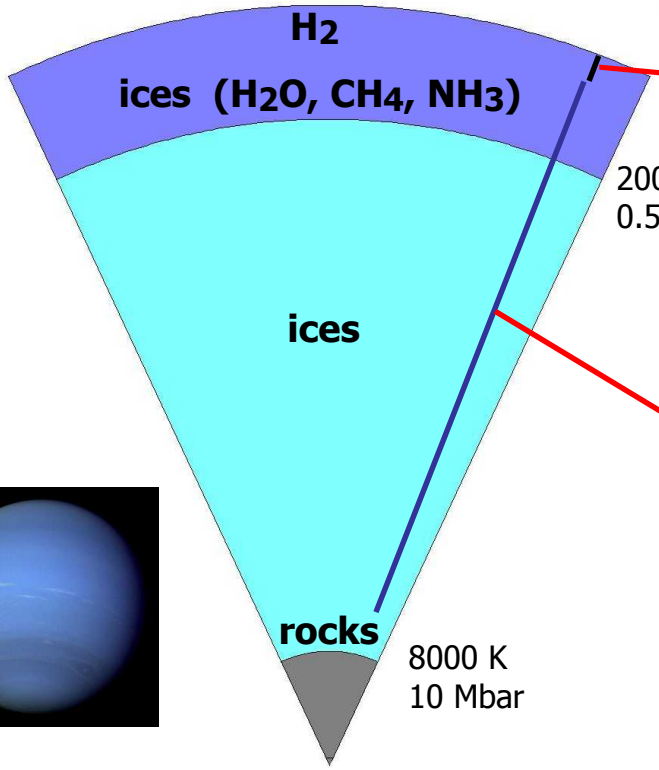
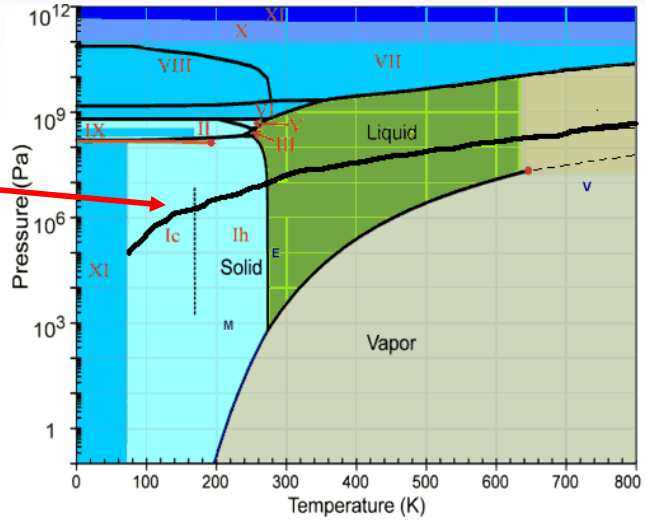
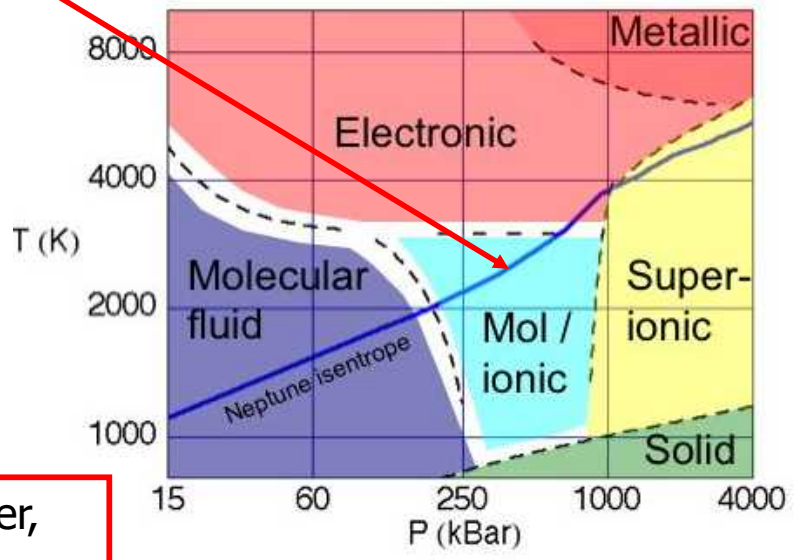
General structure of giant planets : three layer model



Neptune-like giant planet





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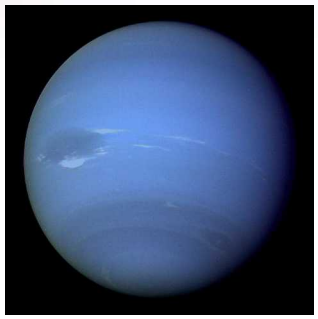
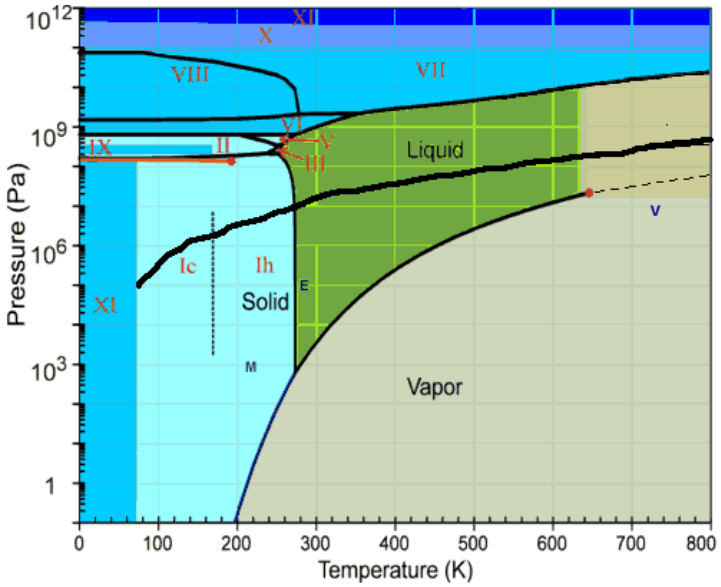
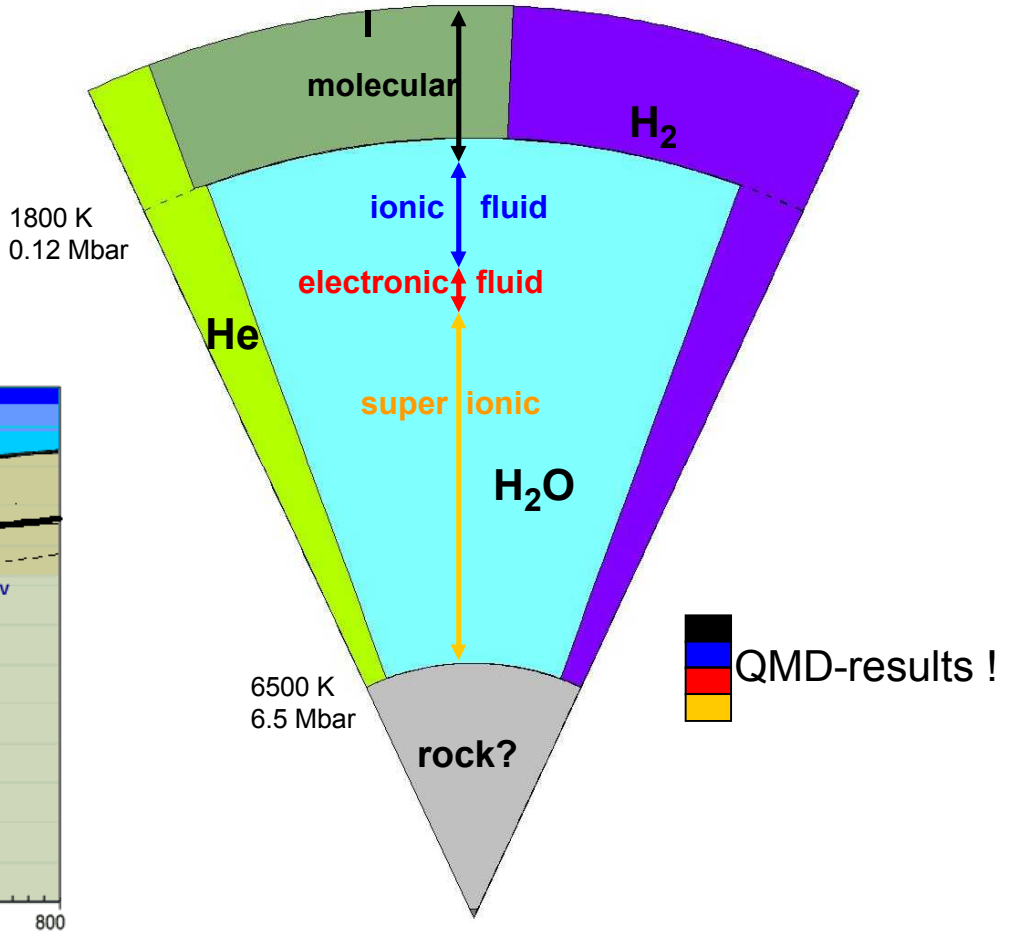
Results : interior composition using Sesame-EOS (H,He,H2O)







Neptune

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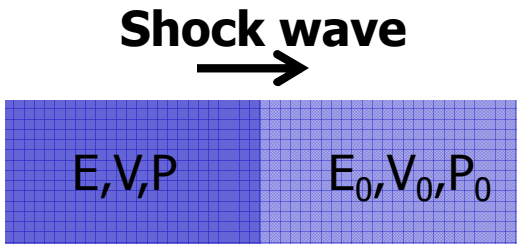
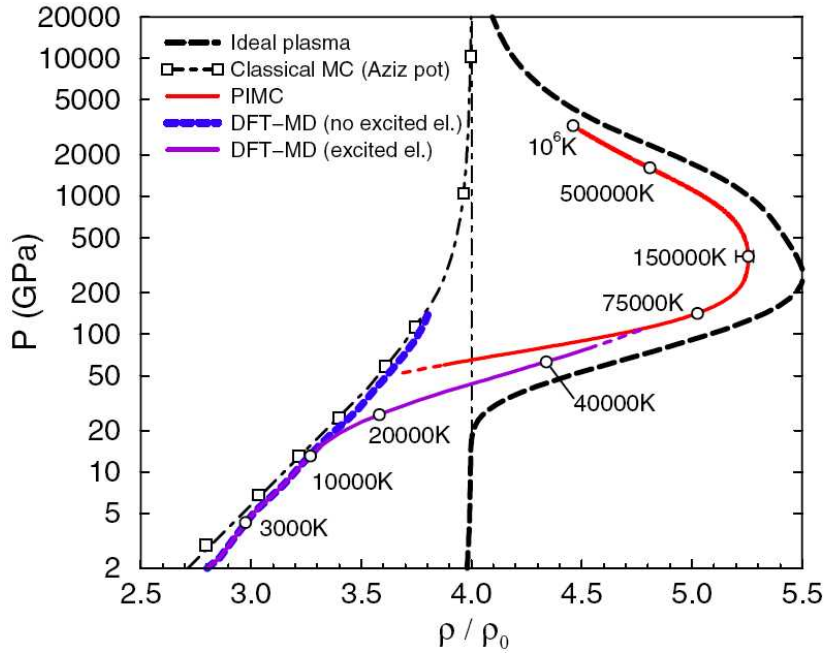
PIMC results for He compares very well to finite-temperature DFT calculations



Rankine-Hugoniot condition for a single shock relates changes 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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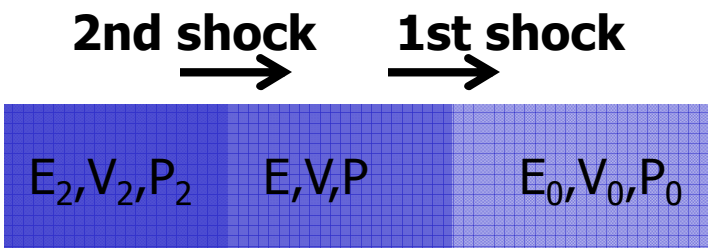
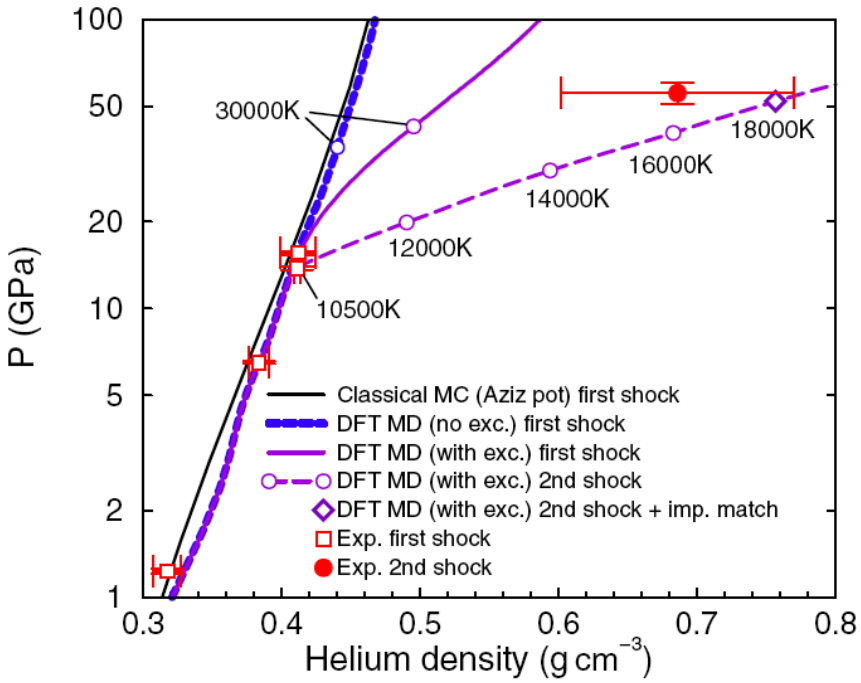
Available (few) experimental results agree with finite-temperature DFT





- 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.

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

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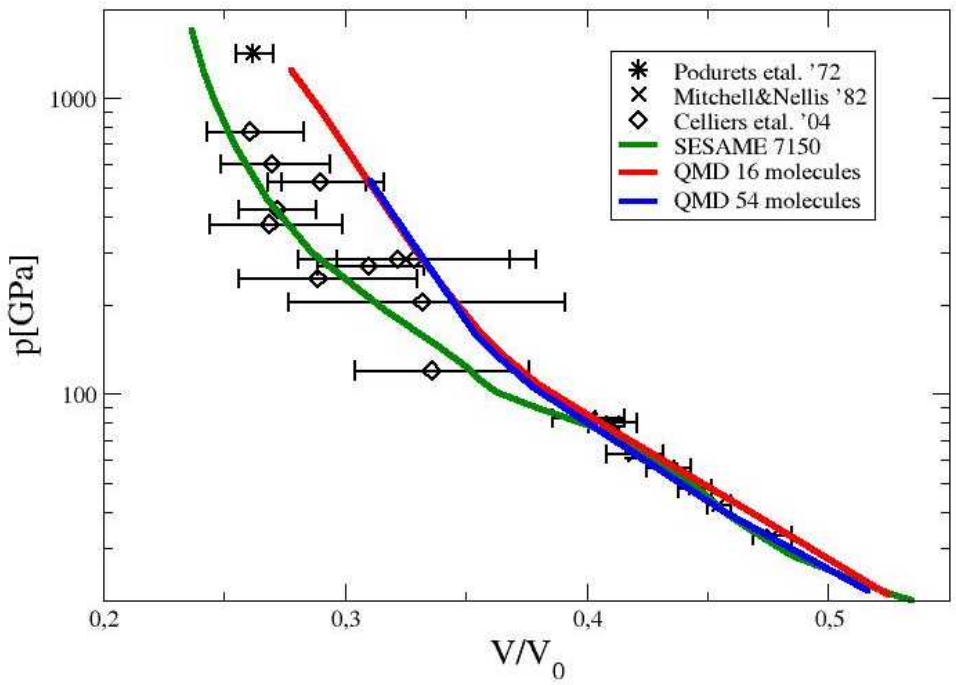
Hugoniot from DFT/QMD slightly stiffer than most recent laser shock measurements of strong shocks



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  - Gas gun
- Celliers et al 2004:
  - Physics of Plasmas, **11**, 41 (2004).
  - Laser
- QMD simulations are in quantitative agreement with most experimental data
- Work in progress exploring the approach to 4-fold compression

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