First-Principles Equation of State and Electronic Structure of Oxygen, Neon, and Silicon Plasmas

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Introduction
- HEDP experiments are probing new extremes to explore plasma technologies
- Theoretical models are important aids to the design and execution of these experiments
- WDM regime is a particular difficult challenge for theory;

First-principles methods for computing WDM properties
- Density Functional Theory (DFT)-based methods
- Path Integral Monte Carlo (PIMC)

Recent progress in the PIMC method
- Construct coherent, consistent EoS by combining DFT and PIMC
- PIMC with free-particle nodes for first row elements
- PIMC with localized nodes – extension to Silicon

Conclusion
- First-principles methods need development for WDM regime
- Update semi-analytic EoS databases
- Provide better aid to experiments and design

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HEDP Experiments Probe New Extremes

HEDP experiments are being designed to probe increasingly extreme environments. Accurate theoretical prediction of plasma equations of state, transport, and optical properties is one key component to the success of these experiments.

<table>
<thead>
<tr>
<th>Facility</th>
<th>Type</th>
<th>Max T (K)</th>
<th>Max P (Gbar)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LCLS</td>
<td>X-ray laser</td>
<td>$10^7$</td>
<td>0.001</td>
</tr>
<tr>
<td>Z-machine</td>
<td>Pulsed-pwr</td>
<td>$10^9$</td>
<td>0.01</td>
</tr>
<tr>
<td>NIF (2 MJ)</td>
<td>UV lasers</td>
<td>$10^8$</td>
<td>1</td>
</tr>
<tr>
<td>LMJ (2 MJ)</td>
<td>UV lasers</td>
<td>$10^8$</td>
<td>1</td>
</tr>
</tbody>
</table>

(Driver, PRL, 2012)  
(Lorin, PRB, 2014)  
(Hu, Phys. Plas. 2015)
An Exciting Time to Study HEDP

Plasma Science, Astrophysics and ICF: 2000+ exoplanets; stars; pathways to ICF emerging.

**HED experiments:** readily probing giant planet and solar regimes and new frontiers of plasmas.

**Theoretical methods:** capability, accuracy, and computational power are advancing quickly.

1Gbar = 1000 Mbar = 100 TPa = $10^5$ GPa
The Range of First-Principles Methods Needs Work

Standard Density Functional Theory (DFT) is great for $T < 10^6$ K
Our Goal: Develop PIMC method for heavy elements at high T to provide first-principles data beyond DFT limits.
EoS libraries and semi-analytic models are not sufficient

Aluminium

1Gbar
=1000 Mbar
=100 TPa
=10^5 GPa

Common for semi-analytic plasma models to be off by 5-10% (Rozsnyai 2001)

DFT generally agrees well with Hugoniot data (Mattsson PRB 2014)

DFT is unable to predict results for temperatures (pressures) beyond the first ionization.

PIMC is needed to predict Higher-temperature features of the Hugoniot, such as subsequent ionization peaks.

PIMC and DFT needed for accurate EoSs as new experiments to probe extremes of WDM
**Density Functional Theory Method**

- Kohn and Pople awarded Nobel Prize in Chemistry, 1998
- Often sufficient for condensed matter; **efficient at low T**

\[ H\Psi = E\Psi \]  (many-body Schrödinger equation)

One-to-one mapping to a single particle framework

Hohenberg-Kohn Theorems

Minimize total energy functional wrt density

\[ E_{TOT}[n] = T[n] + E_{e-ion}[n] + E_{ee}[n] + E_{XC}[n] \]

One-particle Kohn-Sham equations:

\[ H\psi_i = \left[ \frac{1}{2}\nabla^2 + V_{\text{eff}}(r) \right]\psi_i = \epsilon_i(r) \]

\[ V_{\text{eff}} = V_{e-ion} + V_{ee} + V_{XC} \]

- Use DFT potential to simulate Newtonian molecular dynamics.

**Critical approximation:** exchange correlation

- LDAs, GGAs, metaGGAs, Hybrids
- XC-functionals are not always accurate (derived for T=0)
- **Ground-State Method; inefficient at high temperature**

**KS-DFT inefficient at high T**

due to smearing of electrons over orbitals. (Marx 2009)


**Avg. Atom DFT** improves efficiency further by describing electronic properties by that of a single atom in the plasma (Rozsnyai 2014, Starrett 2015).
Path Integral Monte Carlo Method

- 1940's: Feynman develops path integral formalism of quantum statistics.
- Maps the thermal density matrix to a classical polymer model.

\[ \rho_F(R, R'; \beta) = \frac{1}{N!} \sum_\varphi (-1)^\varphi \int_{R \to \varphi R, \rho_T} e^{-S[R_t]} dR_t \]

\[ Z = \text{Tr} [\hat{\rho}_F] \]

\[ \hat{\rho} = e^{-\beta \hat{H}} = [e^{-\tau \hat{H}}]^M \]

- **Fermion Sign problem**: permutation summation instability of positive and negative terms.
- **Solution**: restrict the simulation to a uniform nodal cell of a trial density matrix.

\[ \rho_T(R, R'; \beta) > 0 \]

(Ceperley, Rev. Mod. Phys., 1995)
(Ceperley, “PIMC for Fermions”, 1996)

How do we choose boundaries of density matrix nodal structure?

- Free-particle nodes (H, He, 1\textsuperscript{st}-row)
- Construct a localized nodes (2\textsuperscript{nd}-row: new (2015) development!)

Prior to 2012, only H and He had been studied with PIMC
(Carbon and Water Plasmas: Driver, Militzer PRL 2012)
Oxygen P vs. T: DFT-MD

- DFT-MD (VASP, PAW pseudopotentials, PBE XC functional).
- Gamma point calculations; at least 1000 eV plane wave energy cutoff.
- Use up to 8000 bands to converge partial occupancy to $10^{-4}$. 

![Graph showing the relationship between oxygen pressure (P) and temperature (T)]
Oxygen P vs. T: DFT-MD + Debye

- DFT-MD and classical Debye-Hückel plasma model.
DFT-MD and PIMC results are consistent for $T = 5.0 \times 10^5$ – $10^6$ K.

Consistent results imply FPN sufficient and XC-functionals valid at high-T.

PIMC results converge to the classical plasma (Debye-Hückel) model.
● PIMC and DFT-MD internal energies are consistent for T=5x10^5 – 10^6 K.
● Free-particle nodes work as long as 2^{nd} shell is sufficiently ionized.
DFT and PIMC predict the same ionic plasma structure.

Oxygen nuclear-nuclear pair-correlation

Oxygen
14.9 g/cm³
T=10⁶ K

- DFT and PIMC predict the same ionic plasma structure.
Using free-particle nodes we have computed EoSs for carbon, nitrogen, water, oxygen, neon.

- **Oxygen (1-100 g/cm$^3$) (Submitted 2015)**
- **Neon (1-15 g/cm$^3$) (PRB 2015)**

- DFT-MD and PIMC provides accurate EoS for all first-row plasmas.
- Free-particle nodes work as long as 2$^{nd}$ shell is sufficiently ionized.
Commonly, shock experiments determine the Hugoniot, which is the locus of final states that can be obtained from different shock velocities.

Family of shock Hugoniot curves for different initial densities up to 25-fold of ambient. 25-fold precompression leads to max shock density of 71 g/cc.

Temperature dependence of Hugoniot curves. Curves show an increase in compression as first and second shells are ionized. The temp of the 1s ionization is too high for KS-DFT – we need PIMC to study all Hugoniot features.
Beyond free-particle nodes: PIMC for Silicon

We have developed a localized nodal approximation to PIMC to allow for the computation of EoSs of partially ionized plasmas with bound states. We find consistent results with DFT at $2 \times 10^6$ K (B. Militzer and K. Driver, submitted to PRL, 2015).

- Maximum compression ratio of 5.1 g/cc reached for 4-fold precpompression at $2 \times 10^6$ K
- The compression maxima correspond to ionization of the three shells.
- The temperature of the compression maxima corresponding to the first shell is too high to study with KS-DFT; PIMC is needed.
**PIMC and DFT Silicon Pair-correlation Functions**

PIMC and DFT predict similar plasma structure at $10^6$ K. Additional analysis of pair-correlation functions reveal an evolving plasma structure and an ionization process driven by temperature and pressure.
Conclusions

- Design and execution of plasma experiments is aided by accurate theory.
- Development of first-principles methods is needed to obtain highly accurate predictions of plasma properties, such as the EoS.
- Need to update semi-analytic EoS databases, such as SESAME and QEOS.
- Future work: PIMC for heavier elements; transport and optical properties.

References:
Backup slides
Propagation of radiation in plasma is of central importance for plasma physics.

Precise control of radiation flux on an ICF capsule is key for indirect-drive fusion.

Transport properties: ionic diffusion and viscosity, electrical and thermal conductivity

Optical properties: reflectivity, absorption (radiative opacity).

Quantum Molecular Dynamics (QMD) readily provides transport and optical properties:

**Diffusion** – computed with velocity autocorrelation function

**Viscosity** – computed with stress-tensor autocorrelations of off-diagonal components

**Electrical conductivity** – computed with Kubo-Greenwood formalism

**Optical properties** – computed with Kramers-Kronig relations
Equation of State accuracy is important

- EoS describes how materials behave under various energy, pressure, density, and temperature conditions. Determines many thermodynamic properties.

- Results of experiments and simulations are highly dependent on the quality and accuracy of the EoS.

- Inaccuracies in the EoS can arise from unknown phase transitions, dissociation, ionization, especially for new materials.

- EoS models in different regimes must be combined in thermodynamically consistent ways for physical, thermodynamic results.

**EoS accuracy important for many HEDP issues:**
- experiment design (phase space, dynamics)
- hydrodynamics simulations (constrain parameters)
- SESAME and QEOS databases are out of date and based on semi-analytic models. E.g. density can be off by 10-50% in WDM regime.

(D. Swift, LLNL)

NIF, carbon Hugoniot up to 0.8 GBar (Kritcher, 2015)