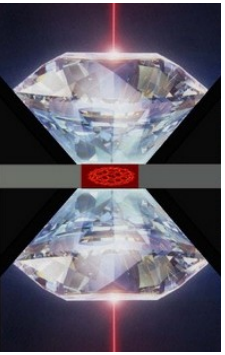
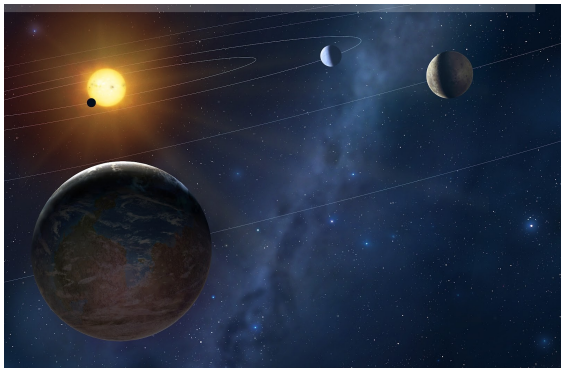
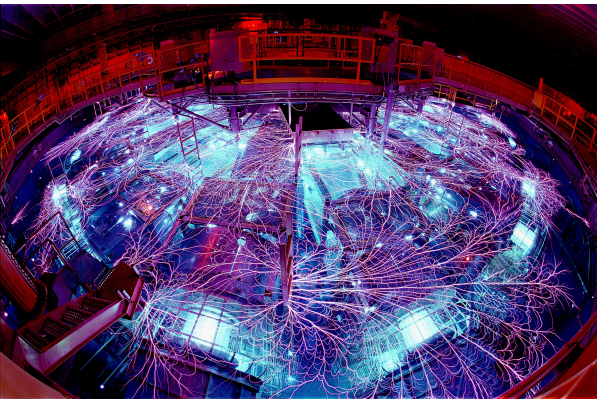
First-Principles Equations of State and Shock Hugoniots of First- and Second-Row Plasmas



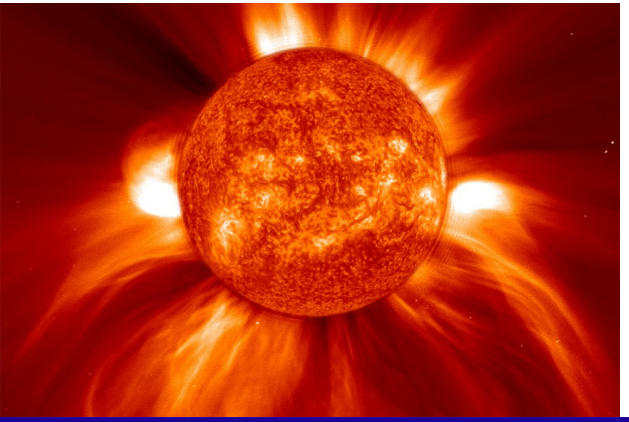
Kevin Driver, Francois Soubiran, Shuai Zhang, Burkhard Militzer
University of California, Berkeley

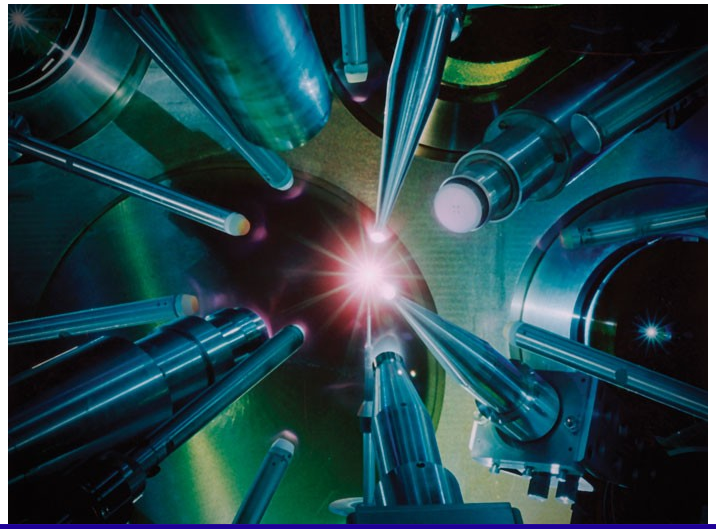
Funding: DOE (DE-SC0010517),
Computational resources: NCAR, NASA, NERSC

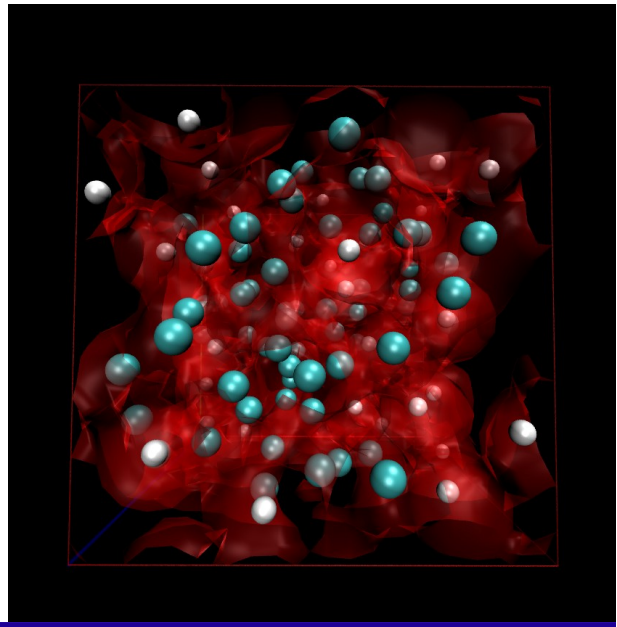




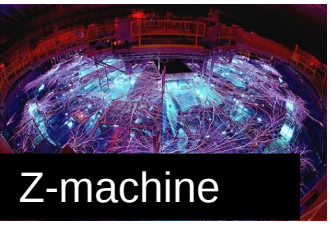
APS 2016
March 13-18
Baltimore, MD

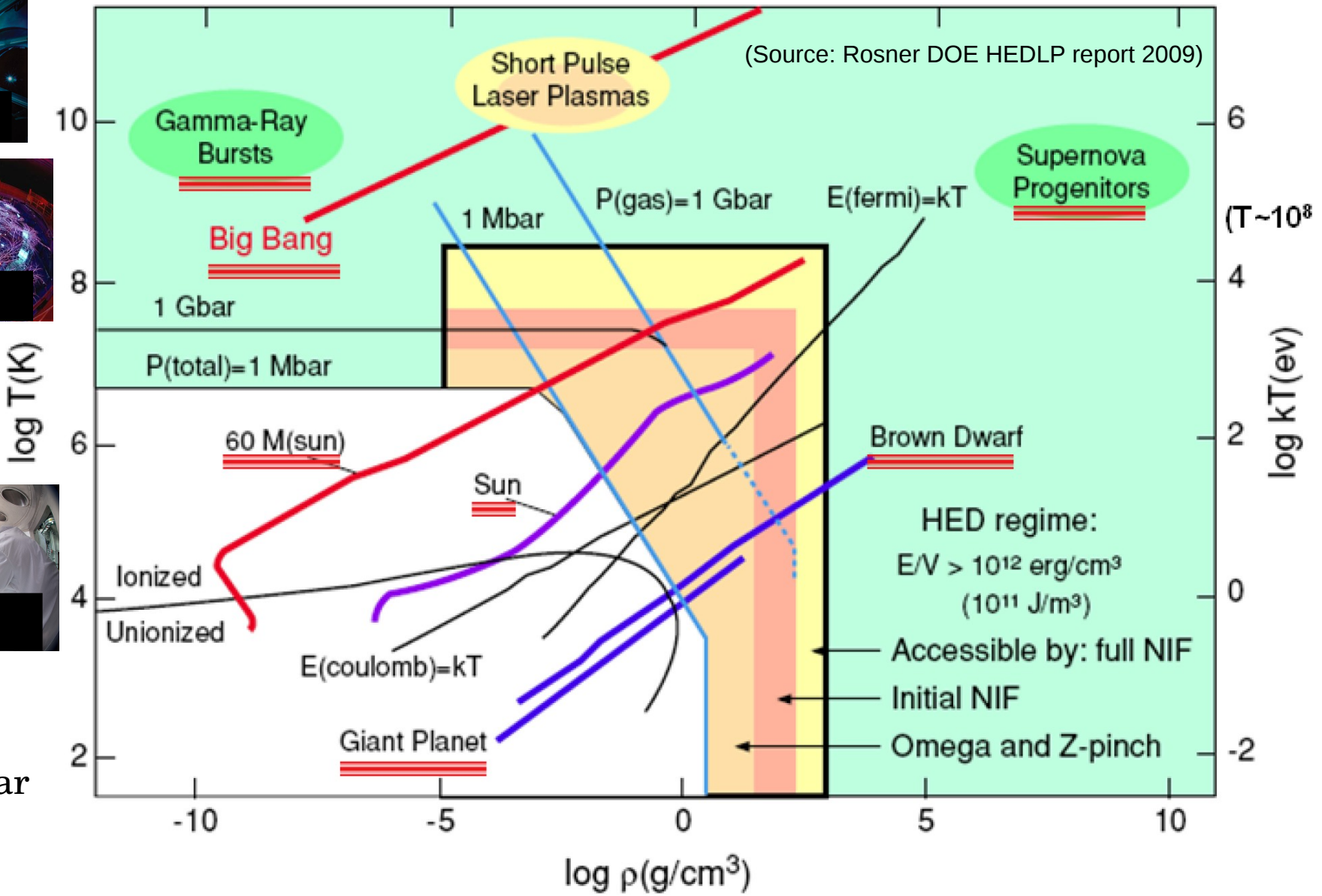






An Exciting Time to Study HEDP

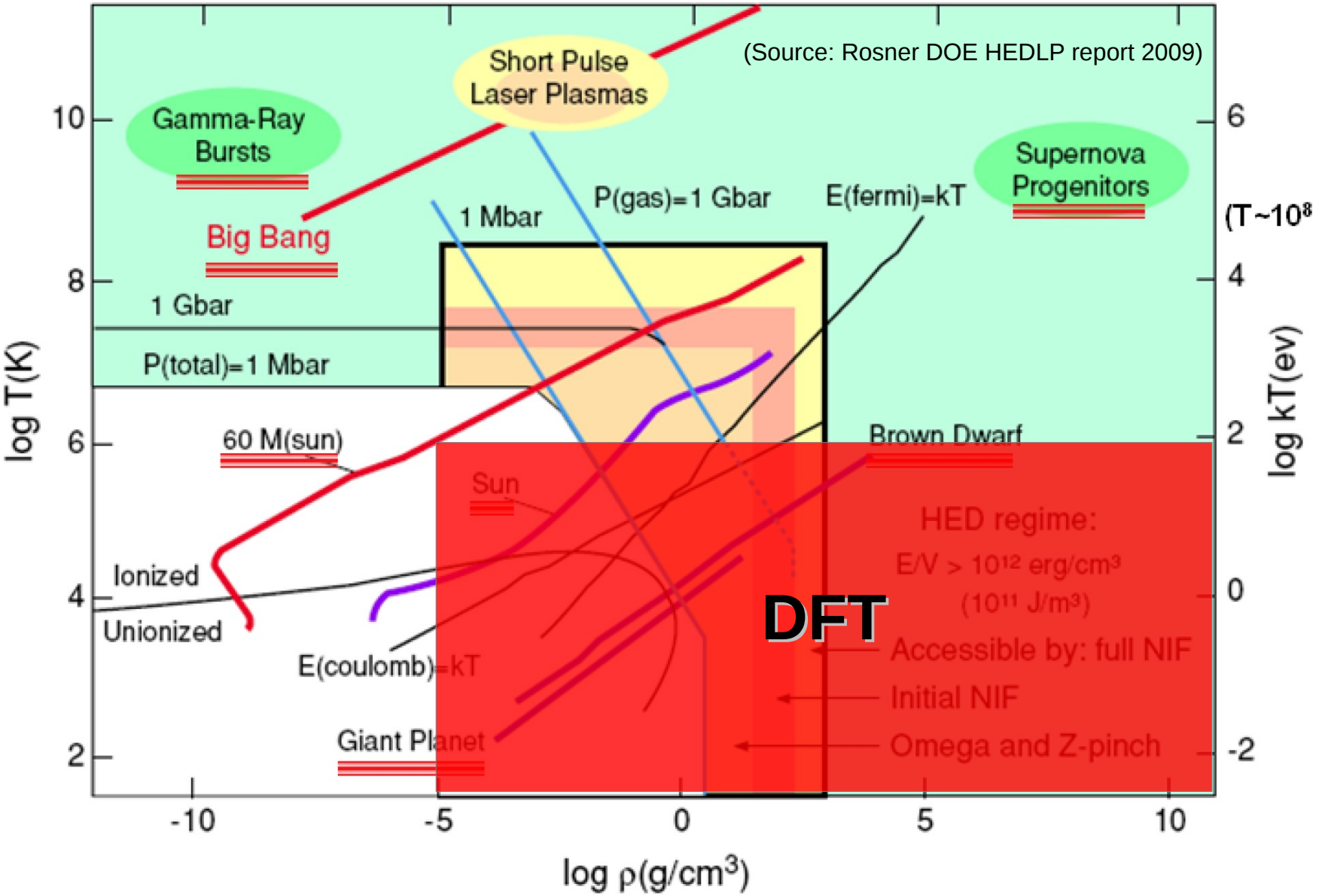




1Gbar
=1000 Mbar
=100 TPa
=10^5 GPa

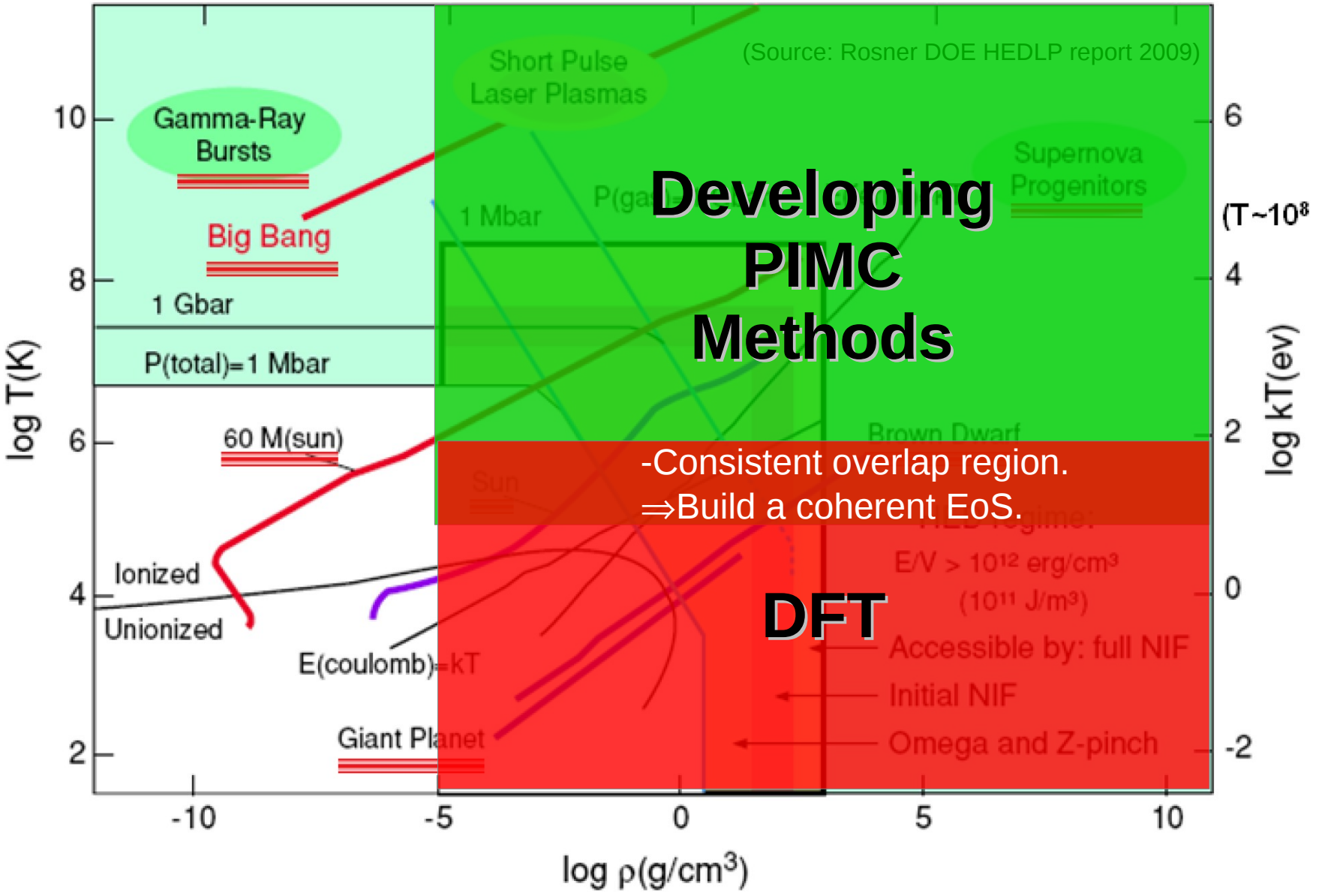
Plasmas, Planetary Science, Astrophysics, and ICF: exoplanets; stars; pathways to ICF.
HED experiments: readily probing giant planet and solar regimes and new frontiers of plasmas.
Theoretical methods: capability, accuracy, and computational power are advancing quickly.

The Range of First-Principles Methods Needs Work



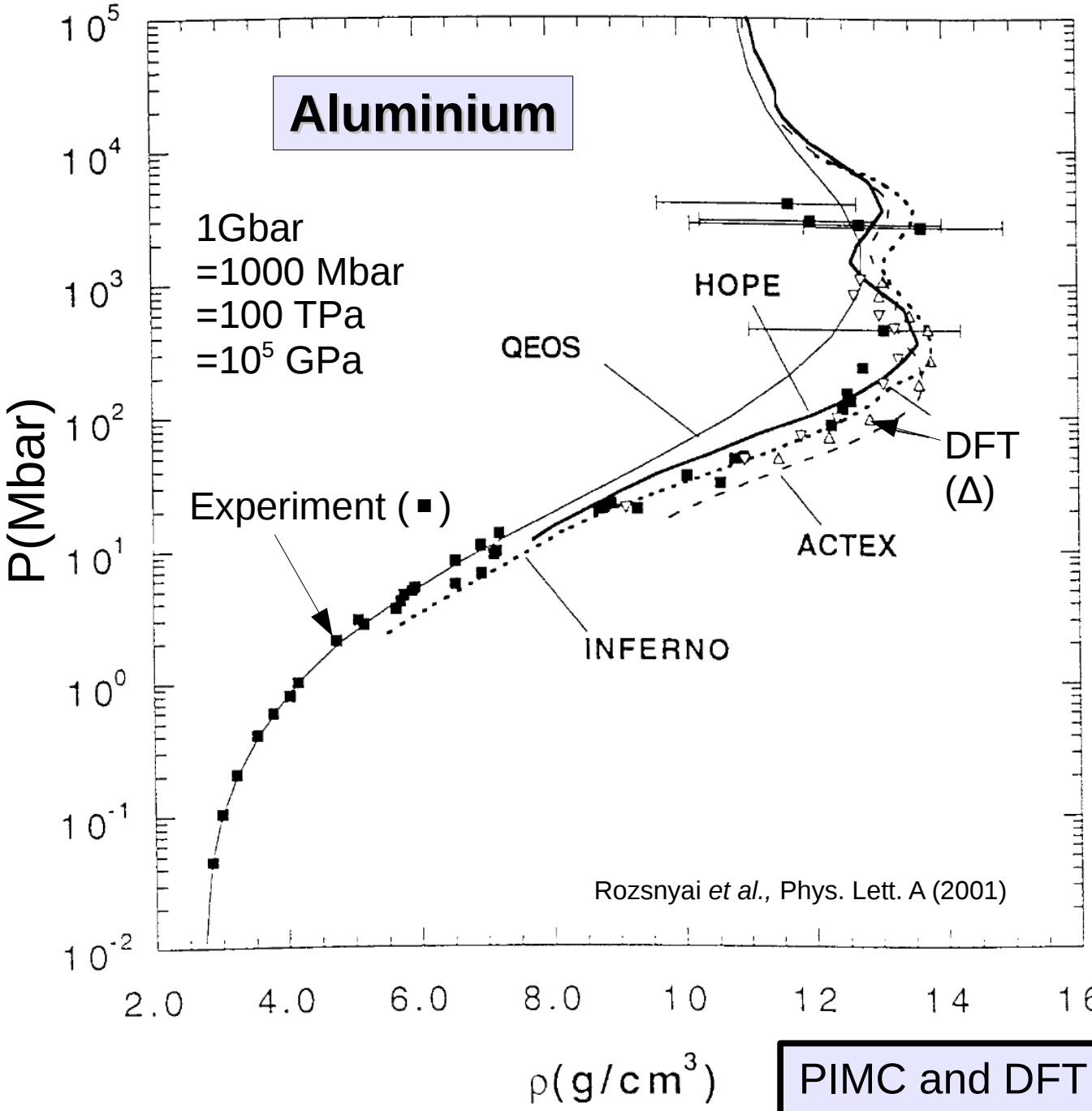
Standard Density Functional Theory (DFT) is efficient for $T < 10^6$ K

Path Integral Monte Carlo (PIMC) for High T



Our Goal: Develop PIMC methodology at high T and Z to provide first-principles data beyond DFT limits.

EoS libraries and semi-analytic models are not sufficient



- Common for semi-analytic or avg-atom plasma models to be off by 5-10% (Rozsnyai 2001)
- DFT generally agrees well with Hugnoiot 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 probe extremes of WDM.

First-Principles Methodology

DFT-MD: Kohn and Pople nobel prize (1998)

$$E_{TOT} = T[n] + E_{ion}[n] + E_H[n] + E_{XC}[n] \quad V_{eff} = V_{ion} + V_H + V_{XC}$$

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

- Maps many-body problem to single-particle framework (Hohenberg-Kohn)
- Computational efficiency **decreases** with temperature due to occ. ortibals.
- Exchange-Correlation functionals: LDAs, GGAs (Designed for T=0 K).
- Solve Newton equations of motion for Molecular Dynamics

PIMC: Based on Feynman's path integral formalism of quantum statistics (1940)

$$\rho_F(\boldsymbol{R}, \boldsymbol{R}'; \beta) = \frac{1}{N!}\sum_{\wp}(-1)^{\wp} \int_{\boldsymbol{R}\to\wp\boldsymbol{R},\rho_T} e^{-S[\boldsymbol{R}_t]} d\boldsymbol{R}_t$$

Density matrix:

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

Partition Function:

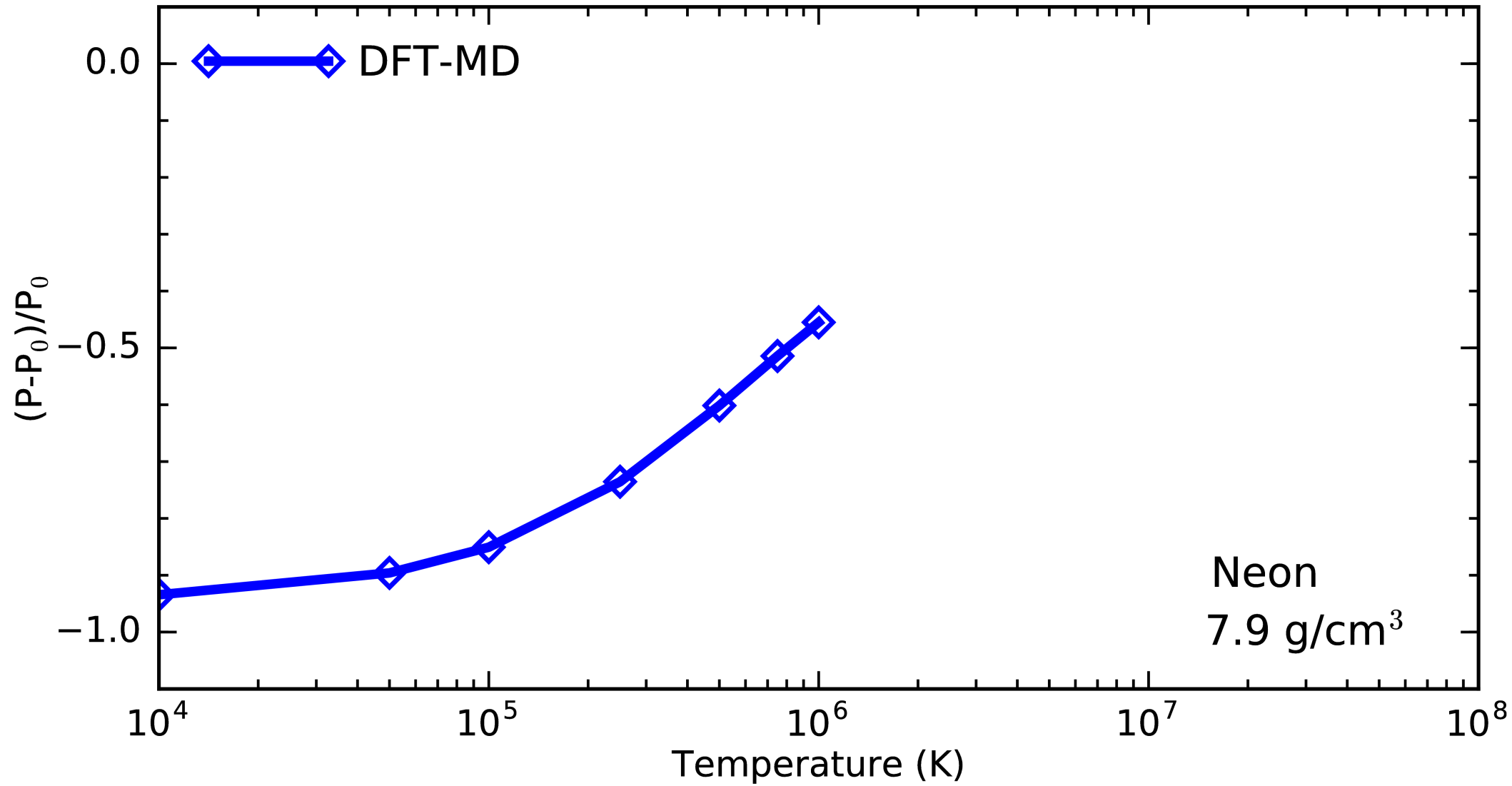
$$Z = Tr[\hat{\rho_F}]$$

- **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.

$$\rho_T(\boldsymbol{R}, \boldsymbol{R}'; \beta) > 0$$ (Choose either free particle[5] and localized nodal surface[6])

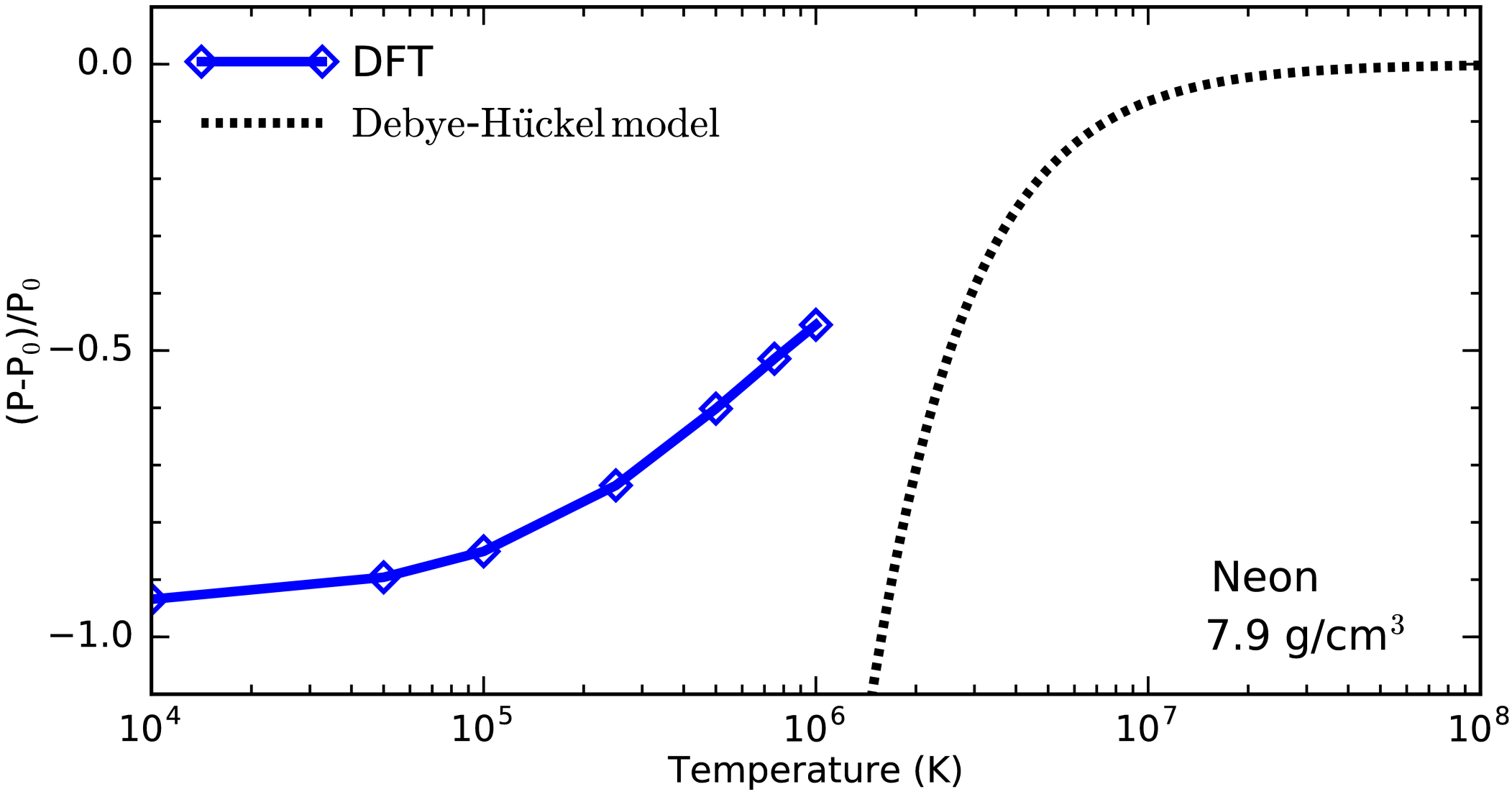
- Temperature explicitly included in the formulation.
- Computational efficiency **increases** with temperature (shorter paths).
- Historically, PIMC focused on H and He; we now extend it to 2nd row.

Neon P vs. T: DFT-MD



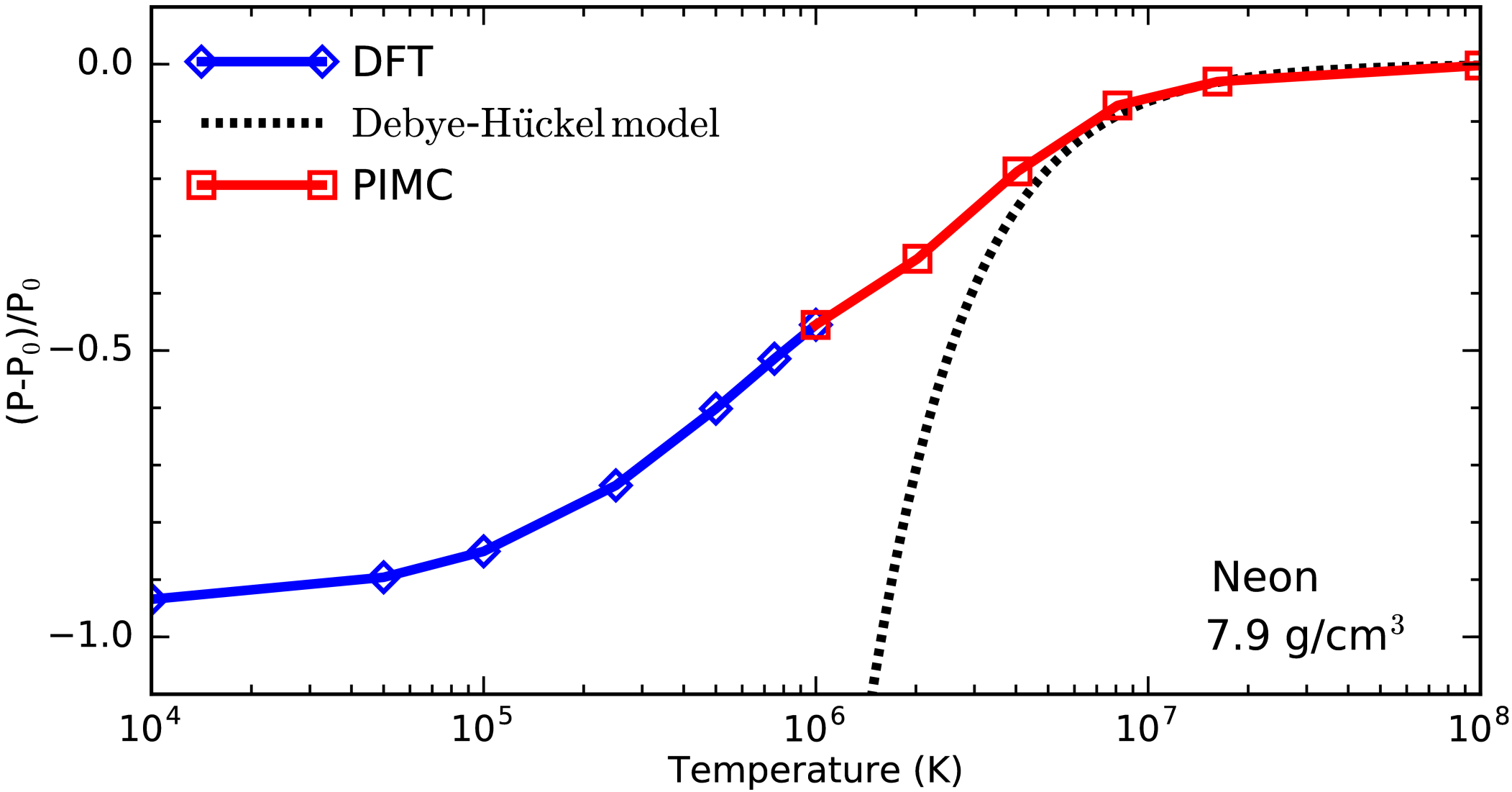
- DFT-MD (VASP, PAW pseudopotentials, PBE XC functional).
- Gamma point calculations; at least 1000 eV plane wave energy cutoff.
- Use up to 8000 bands to converge partial occupancy to 10^{-4}.

Neon P vs. T: DFT-MD + Debye



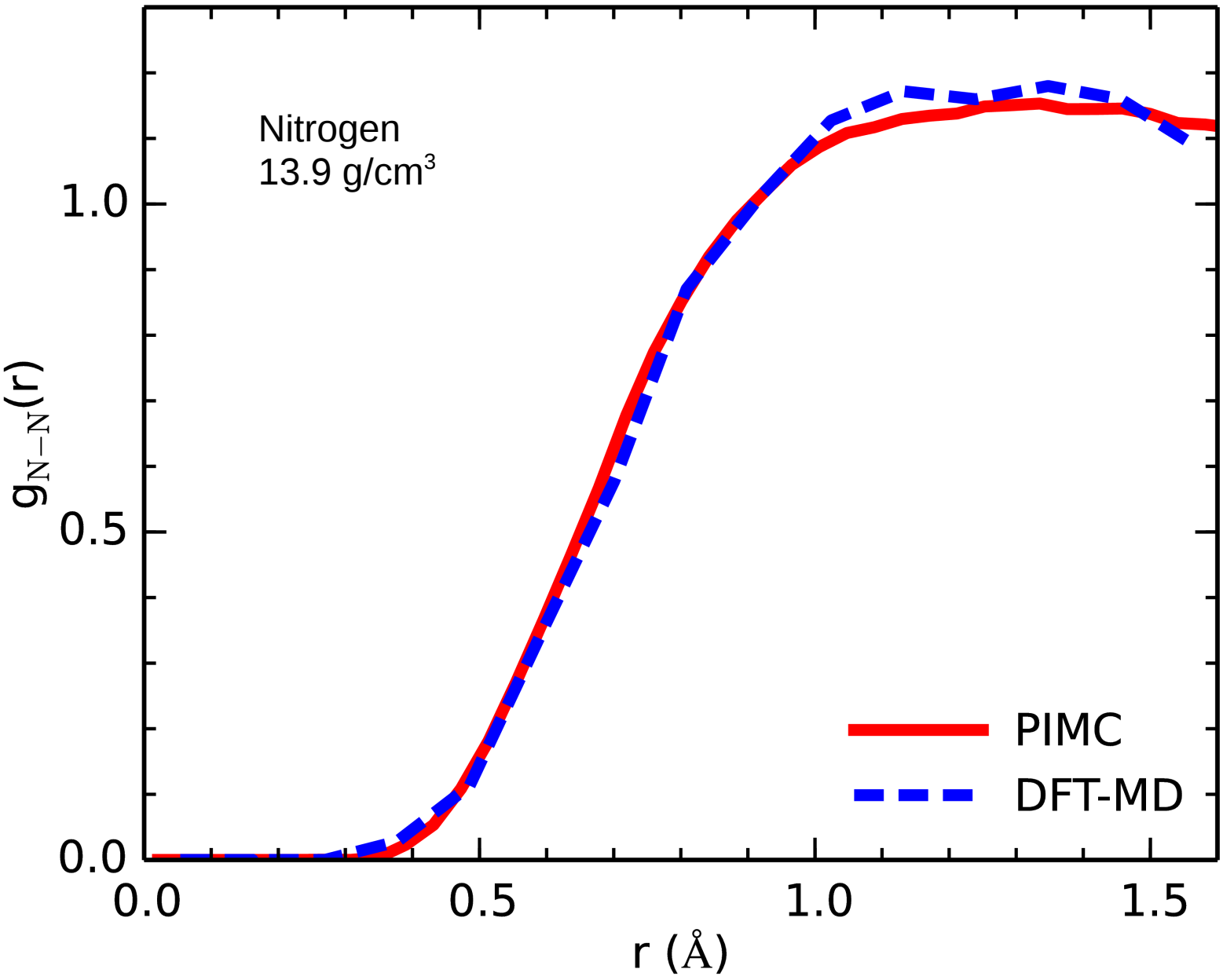
•DFT-MD and classical Debye-Hückel plasma model.

Neon P vs. T: DFT-MD + Debye + PIMC



- DFT-MD and PIMC results are consistent; PIMC converges to Debye-Huckle
- Consistent results imply FPN sufficient and XC-functionals valid at high-T.
- Free-particle nodes work as long as 2nd shell is sufficiently ionized.

Nitrogen nuclear-nuclear pair-correlation



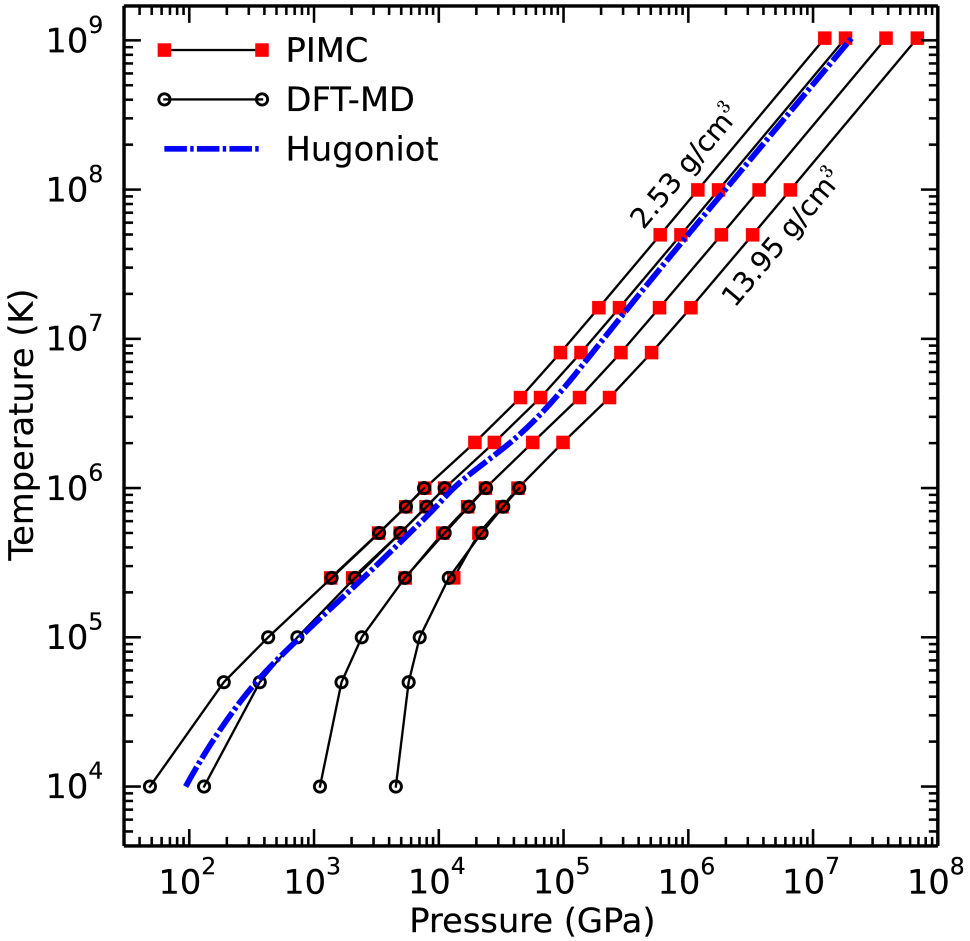
•DFT and PIMC predict the same ionic plasma structure.

Free-Particle PIMC EoSs up to Neon

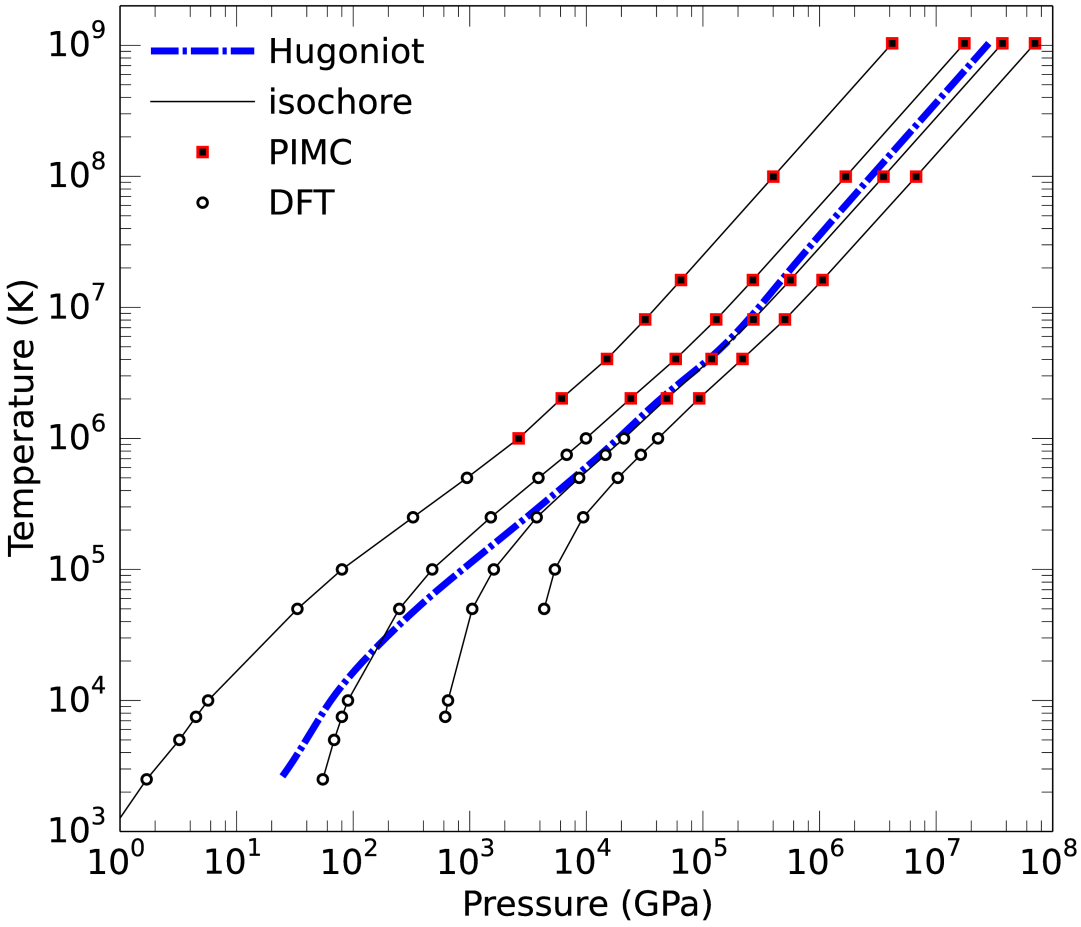
Using *free-particle nodes* we have computed EoSs for **water, carbon, nitrogen, oxygen, neon.**

(Oxygen was presented by S. Zhang in session V21)

Nitrogen (1-14 g/cm^3) (PRB 2016)

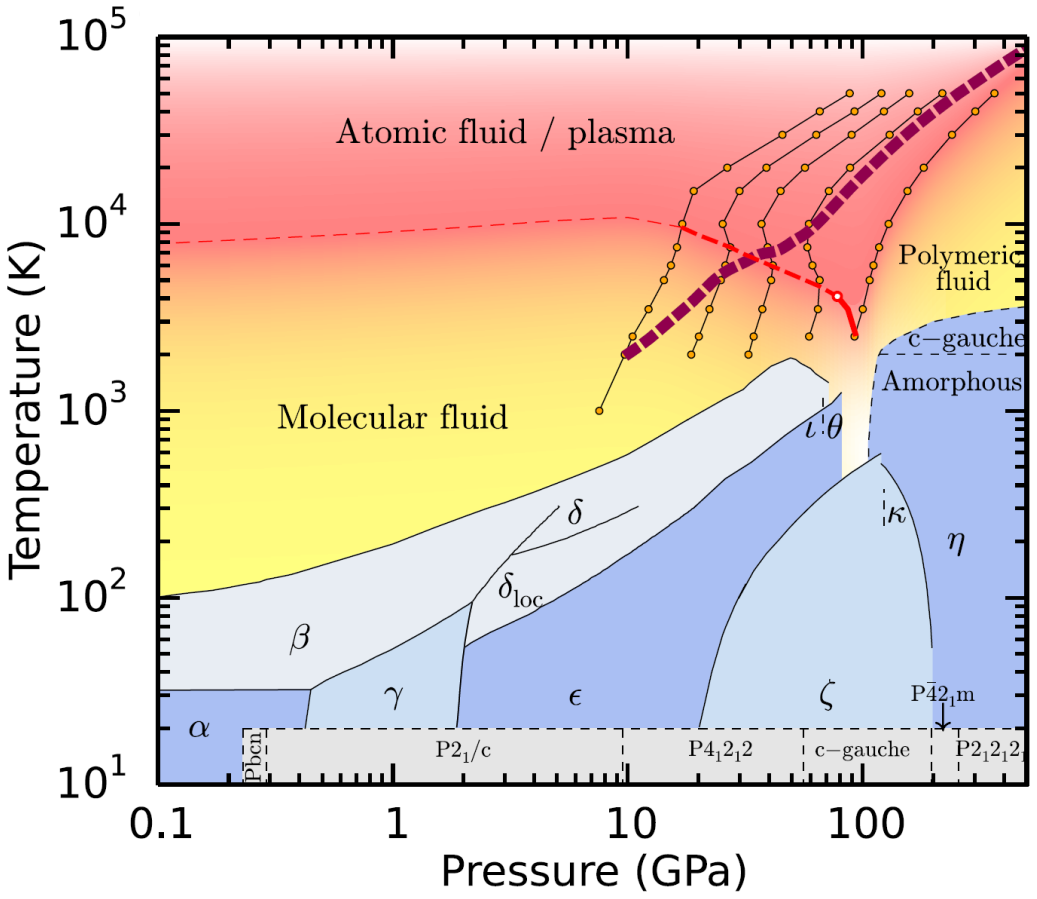


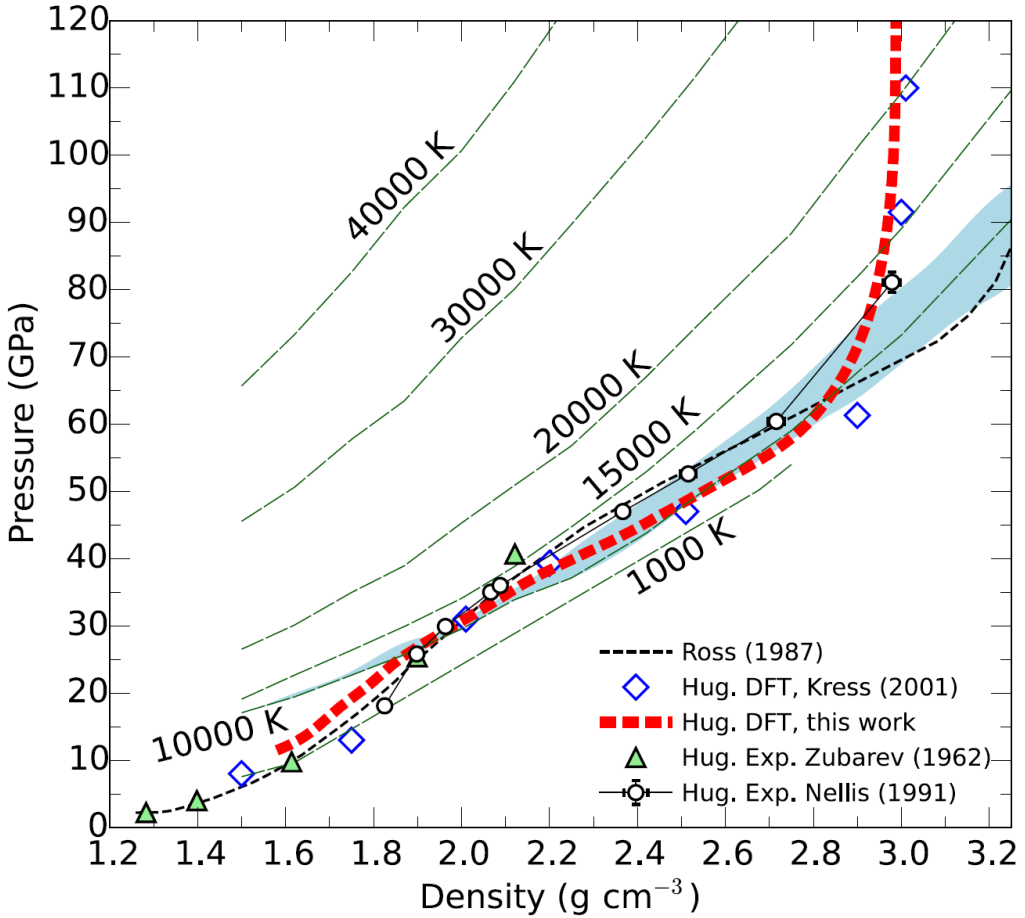
Neon (1-15g/cm^3) (PRB 2015)



- DFT-MD and PIMC provides accurate EoS for all first-row plasmas.
- Free-particle nodes work as long as 2nd shell is sufficiently ionized.

Low T: Nitrogen in the molecular dissociation regime



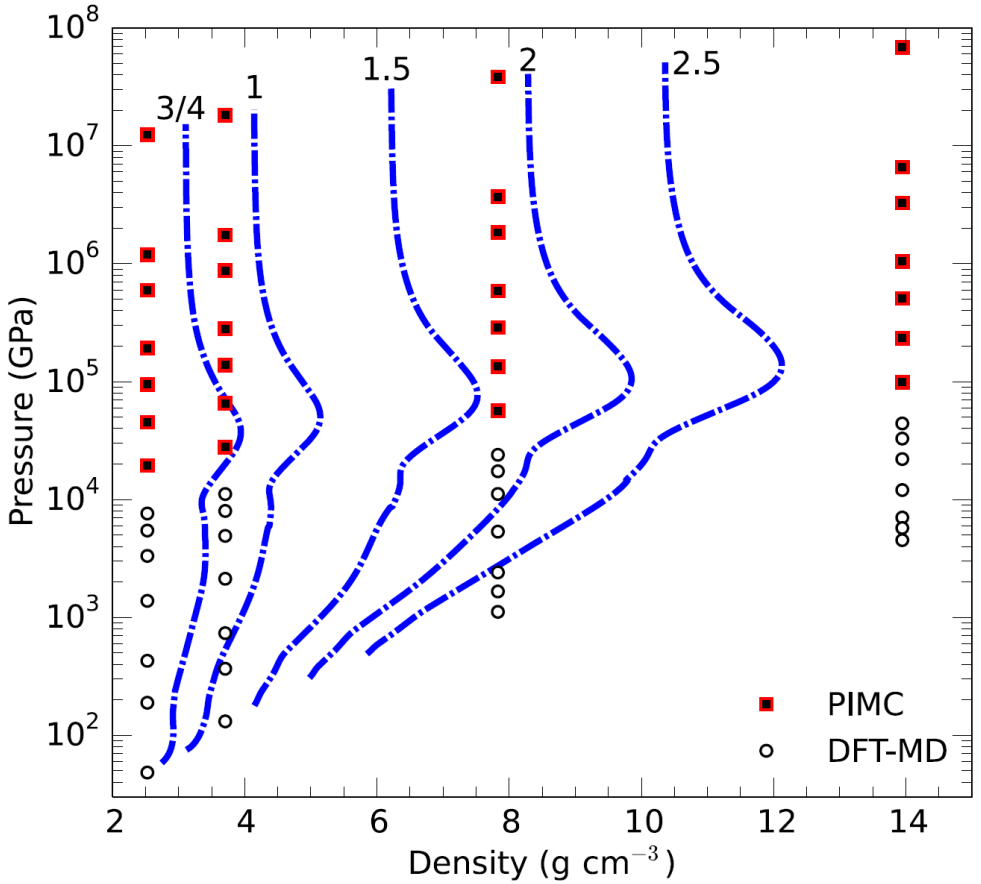


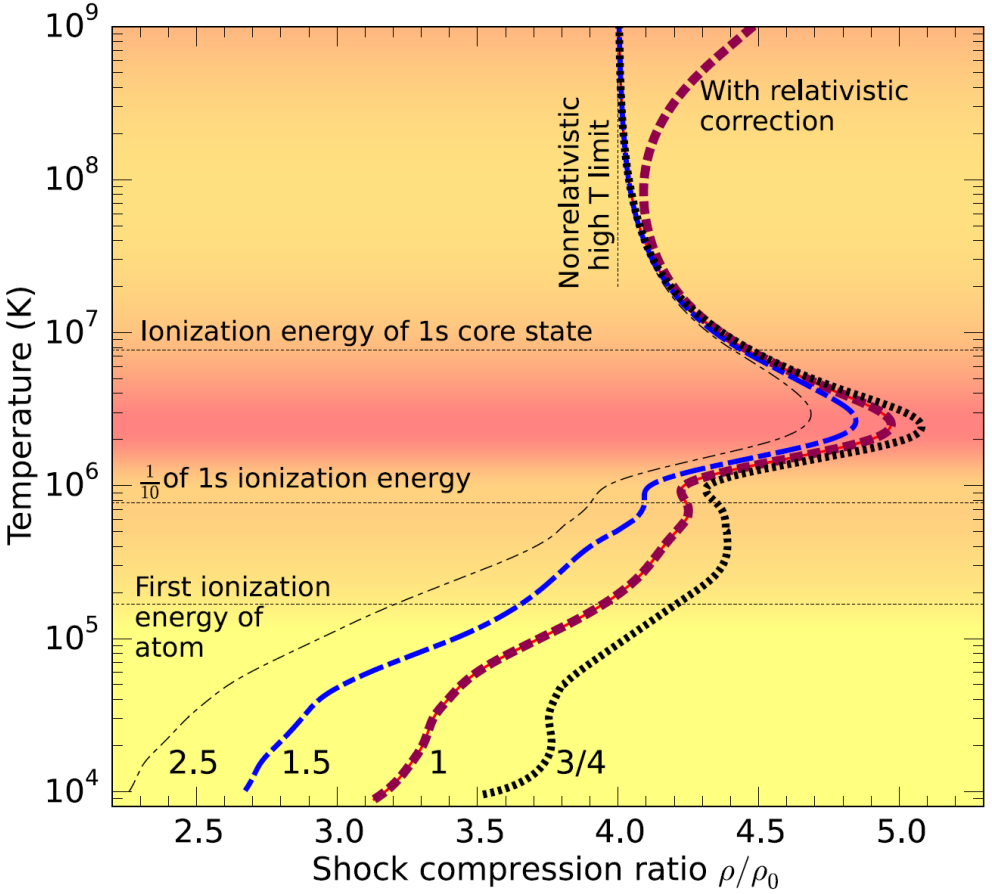
- We computed isochores in the dissociation transition regime with DFT-MD and found a first order transition neat 78-90 GPa.

- Our DFT-MD Hugoniot curve agrees well with experiments and other DFT-MD and semi-analytic (ACTEX) calculations

High T: PIMC Shock Hugoniot curves for Nitrogen

- Shock experiments measure the Hugoniot (locus of final states from different shock velocities).

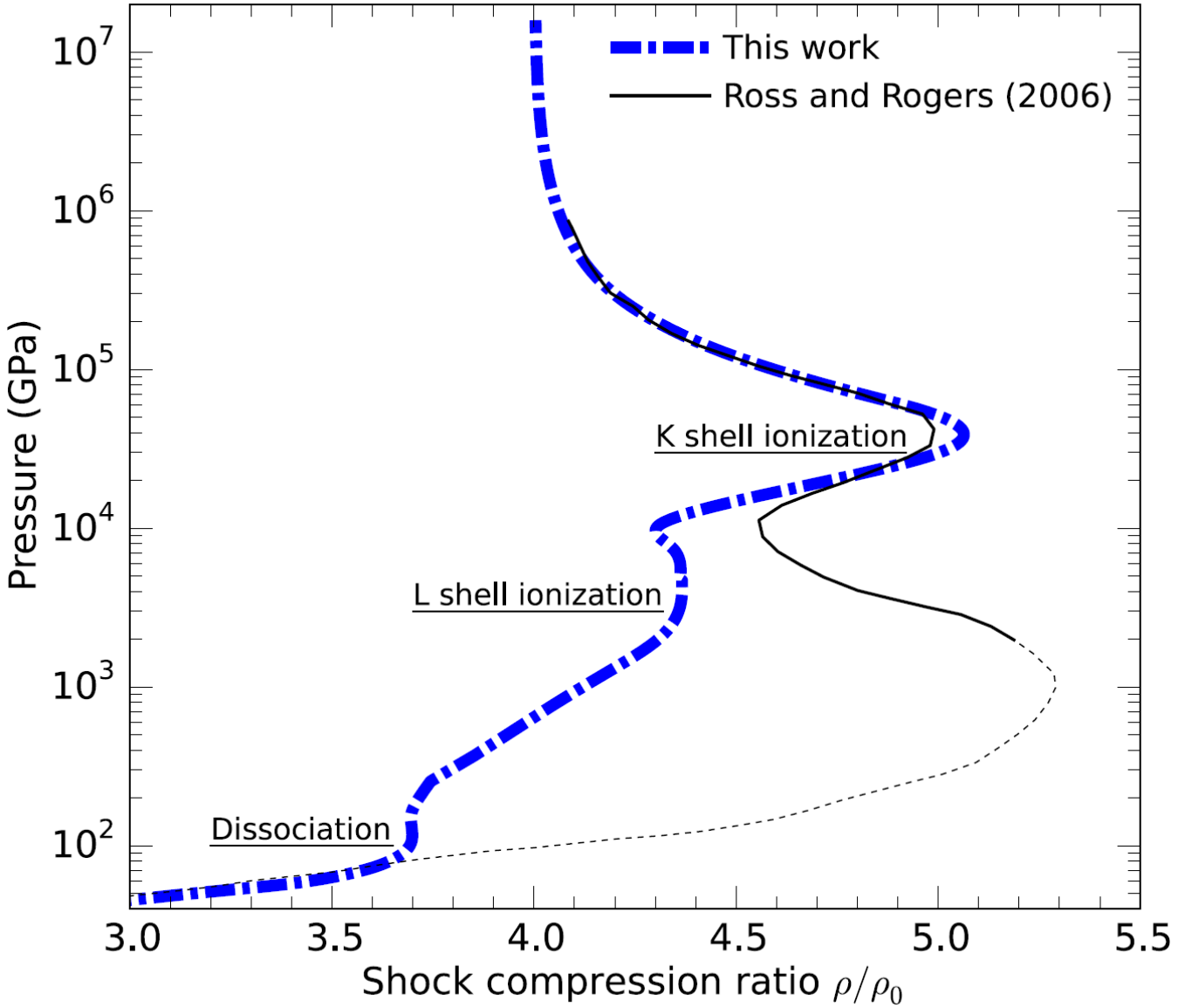




Family of shock Hugoniot curves for different initial densities up to 2.5-fold of ambient. 2.5-fold precompression leads to max shock density Of 12.1 g/cc.

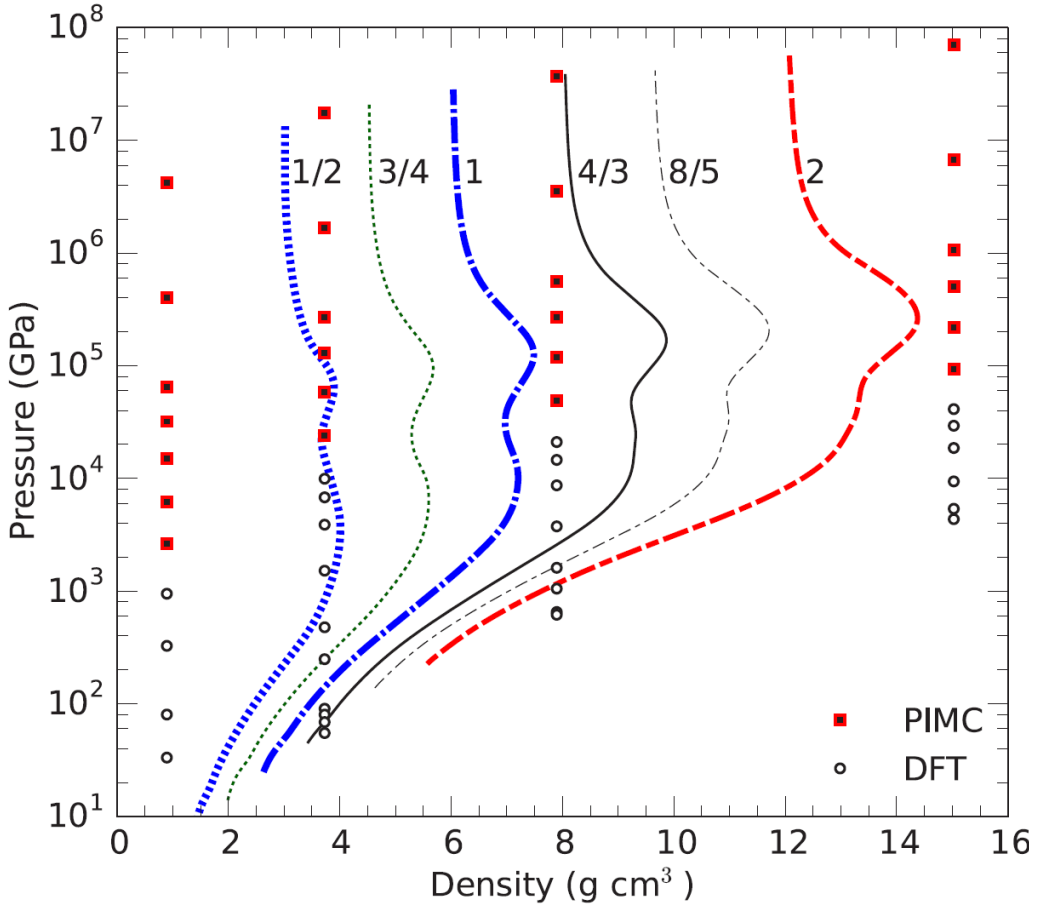
Temperature dependence of Hugoniot curves. Curves show an increase in compression as first and second shells are ionized. The temp of the 1s ionization is too high for KS-DFT – we need PIMC to study all Hugoniot features.

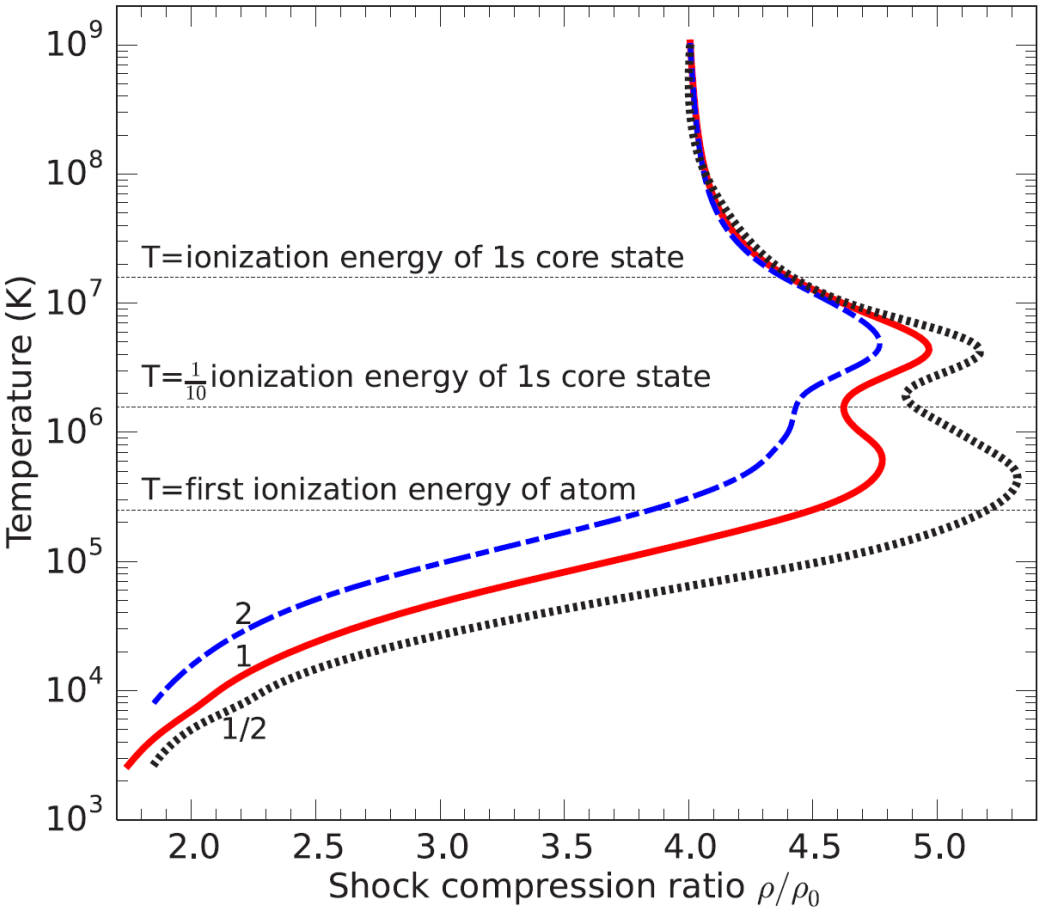
Nitrogen: Hugoniot Comparison with ACTEX model



Semi-analytic ACTEX plasma model incorrectly predicts L-ionization compression peak

PIMC Shock Hugoniot curves for Neon



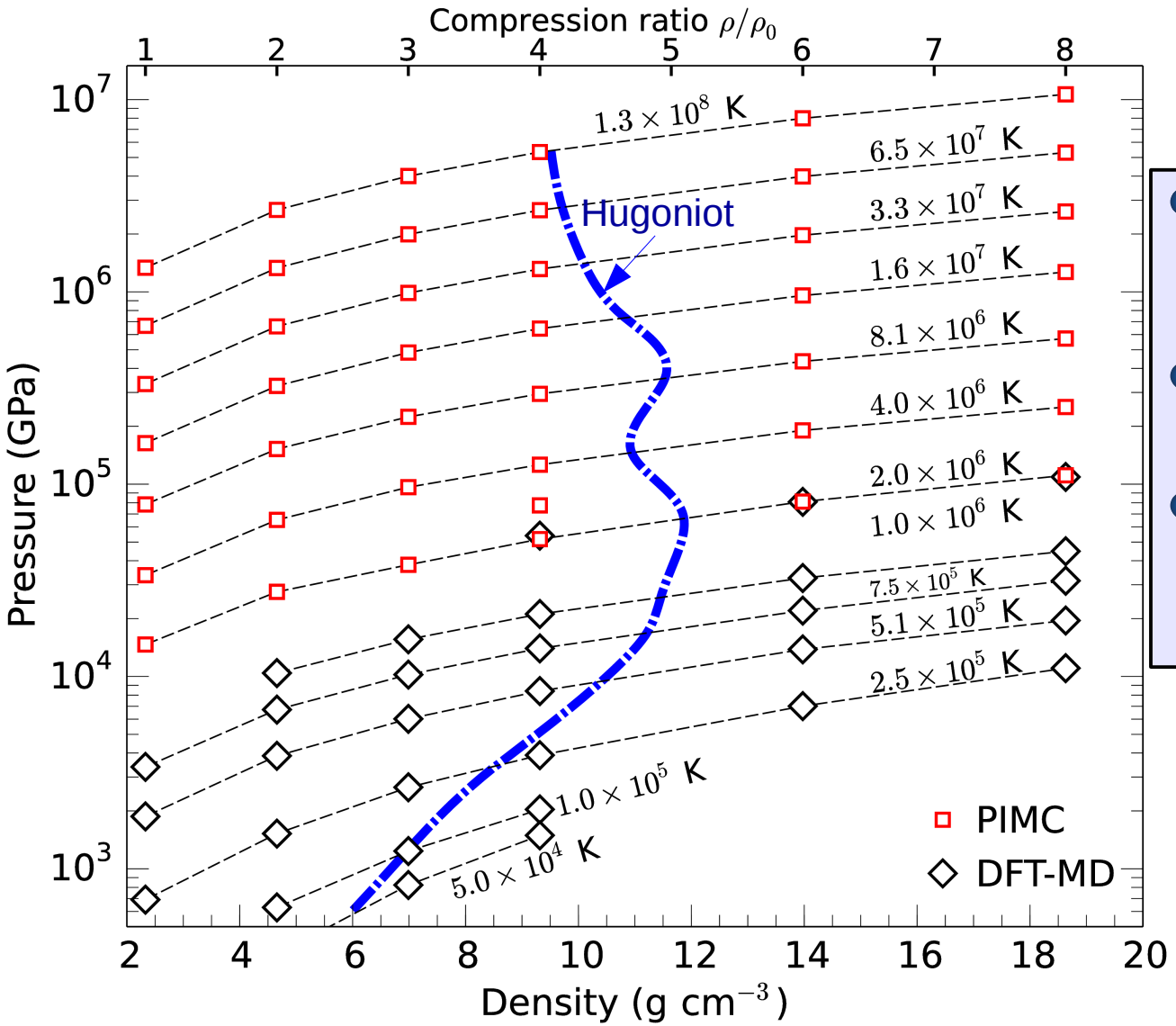


Family of shock Hugoniot curves for different initial densities up to 2-fold of ambient. 2-fold precompression leads to max shock density of 14.4 g/cc.

Temperature dependence of Hugoniot curves. Curves show an increase in compression as first and second shells are ionized. Temperature of the 1s ionization peak is inacccessible by KS-DFT or OF-DFT – we need PIMC to study all Hugoniot features.

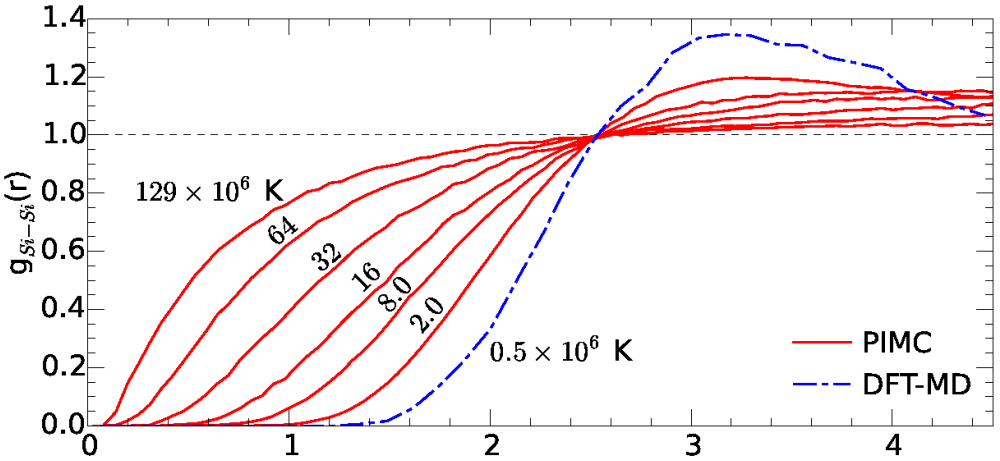
Beyond free-particle nodes: PIMC for Silicon

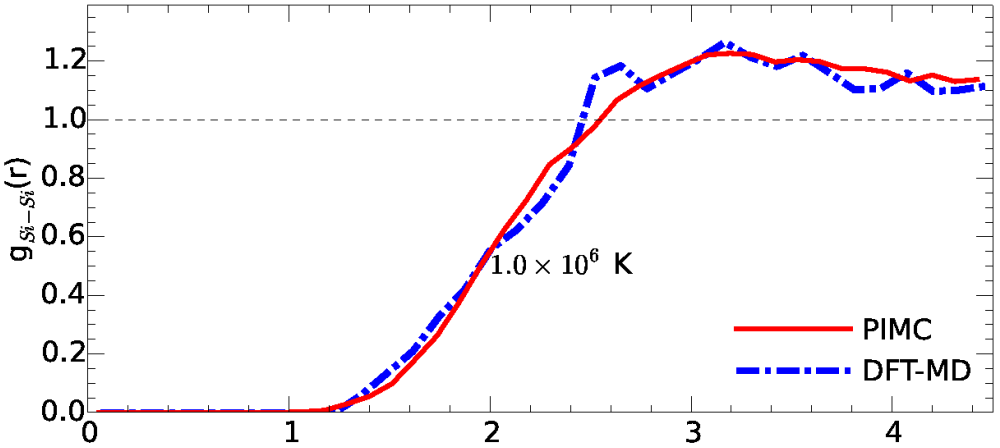
- We have developed a localized nodal approximation to PIMC to allow for the computation of EoSs of partially ionized plasmas with bound states. We find consistent results with DFT at 2x10^6 K (**B. Militzer and K. Driver, PRL, 115, 176403, 2015**).

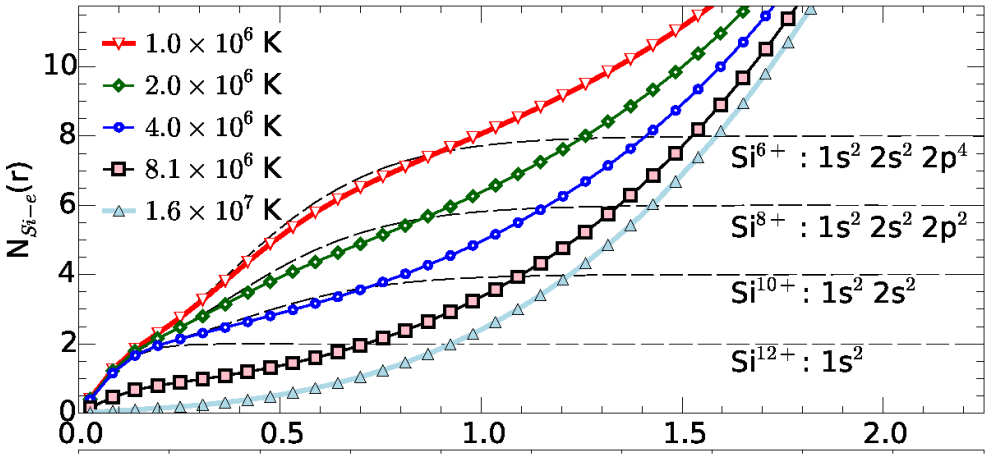


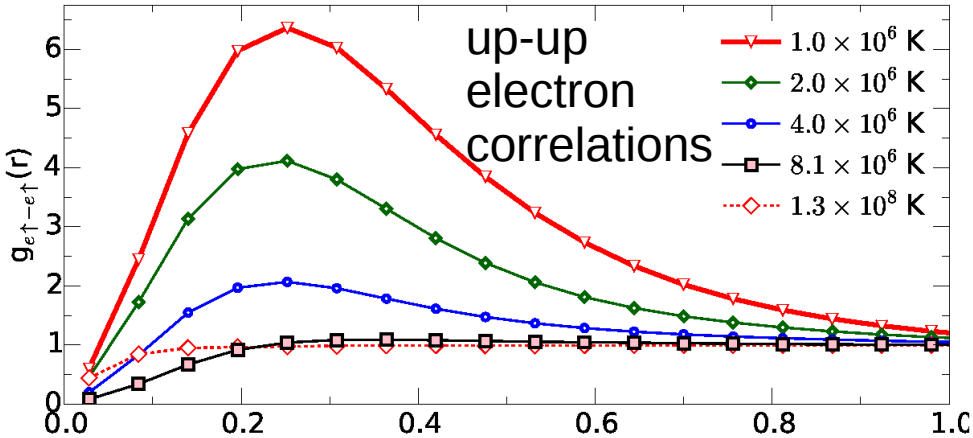
- Maximum compression ratio of 5.1 g/cc reached for 4-fold precpompression at 2x10^6 K
- The compression maxima correspond to ionization of the three shells.
- The temperature of the compression maxima corresponding to the first shell is too high to study with KS-DFT; PIMC is needed.

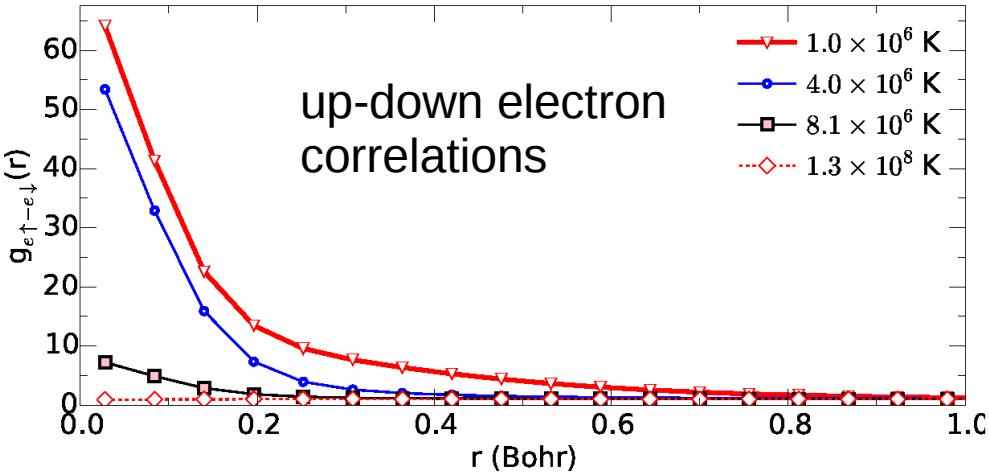
PIMC and DFT Silicon Pair-correlation Functions











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

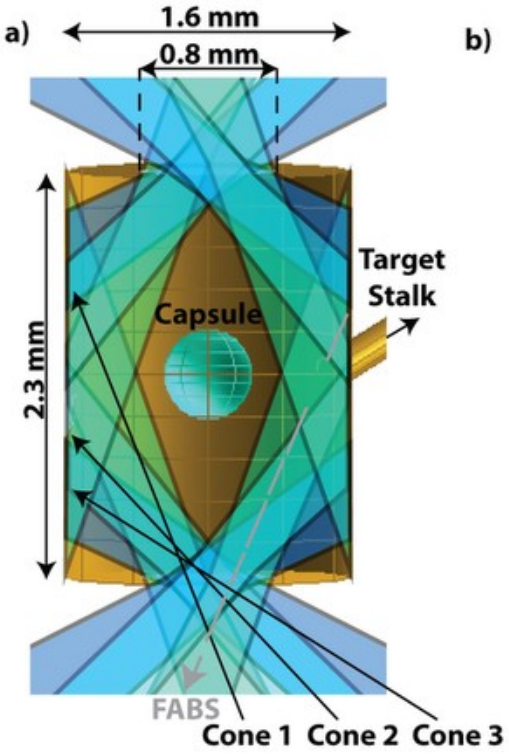
References:

1) **Carbon PIMC EOS:** K. P. Driver and B. Militzer, Phys. Rev. Lett. 108, 115502 (**2012**).
2) **Carbon multi-phase EOS:** Benedict, Driver, Hamel, Militzer, el al., Phys. Rev. B, 89, 224109 (**2014**).
3) **Neon:** K. P. Driver and B. Militzer, Phys. Rev. B 91, 04510 (**2015**).
4) **Oxygen:** J. Chem. Phys. 143, 164507 (**2015**)
5) **Nitrogen:** Phys. Rev. B 91, 064101 (**2016**)
6) **Silicon:** Phys. Rev. Lett. 115, 176403 (**2015**)

Backup slides

Transport and Optical Properties

- 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).



J.S. Ross, 2013

<u>Quantum Molecular Dynamics (QMD) readily provides transport and optical properties:</u>

Diffusion – computed with velocity autocorrelation function

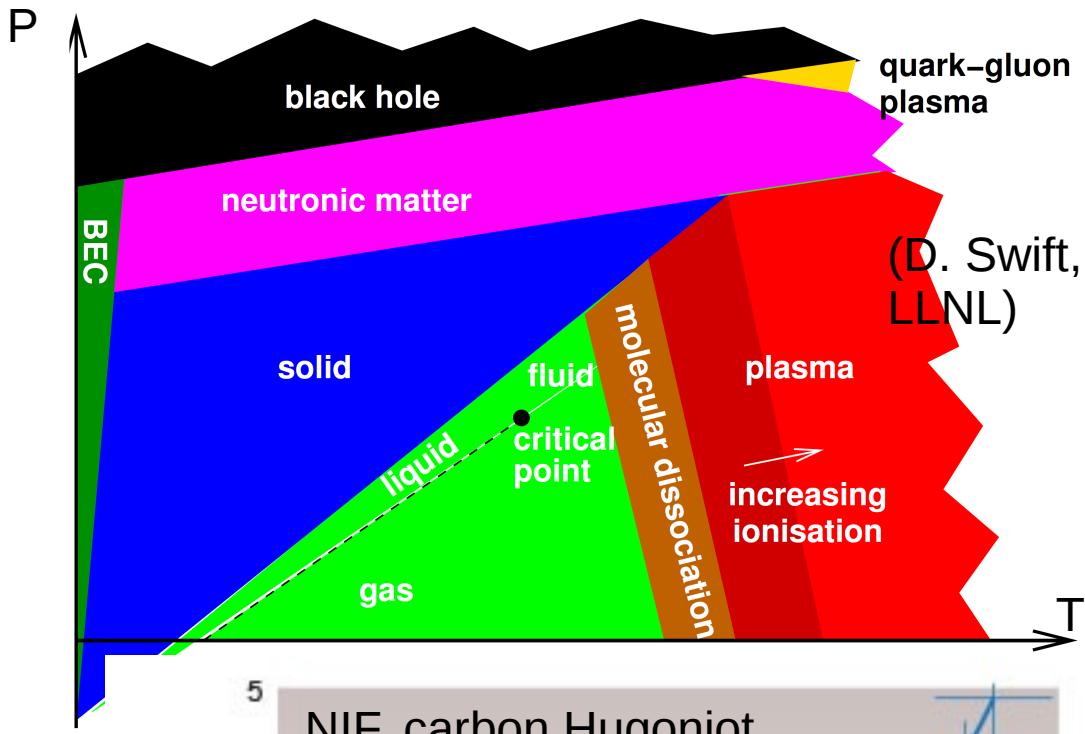
Viscosity – computed with stress-tensor autocorrelations of off-diagonal components

Electrical conductivity – computed with Kubo-Greenwood formalism

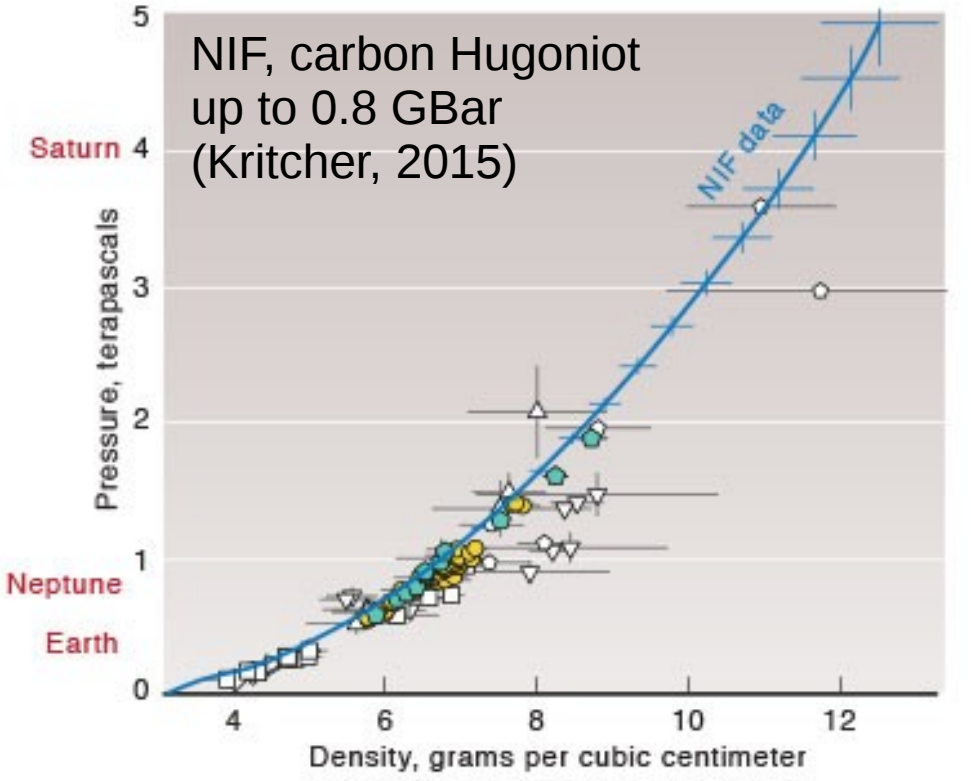
Optical properties – computed with Kramers-Kronig relations

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.



(D. Swift, LLNL)



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.