Path Integral Monte Carlo (PIMC) study of Warm Dense Matter: Second-row elements

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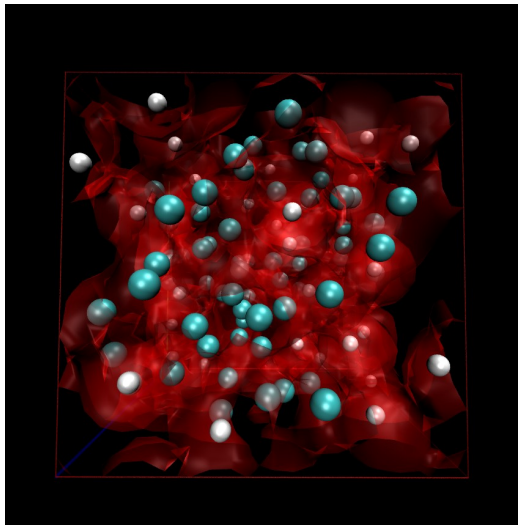
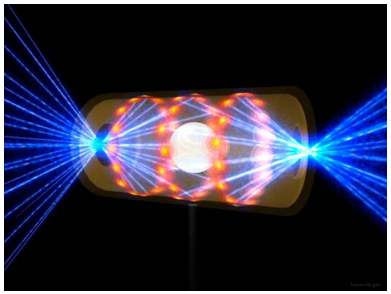
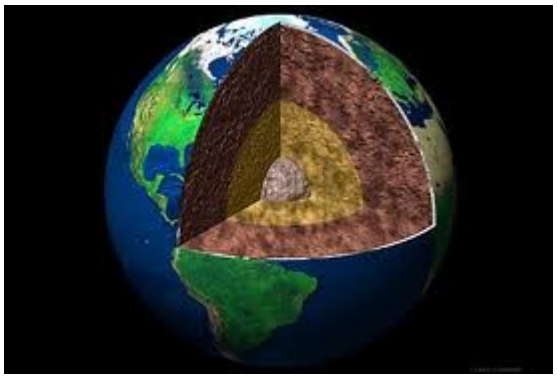
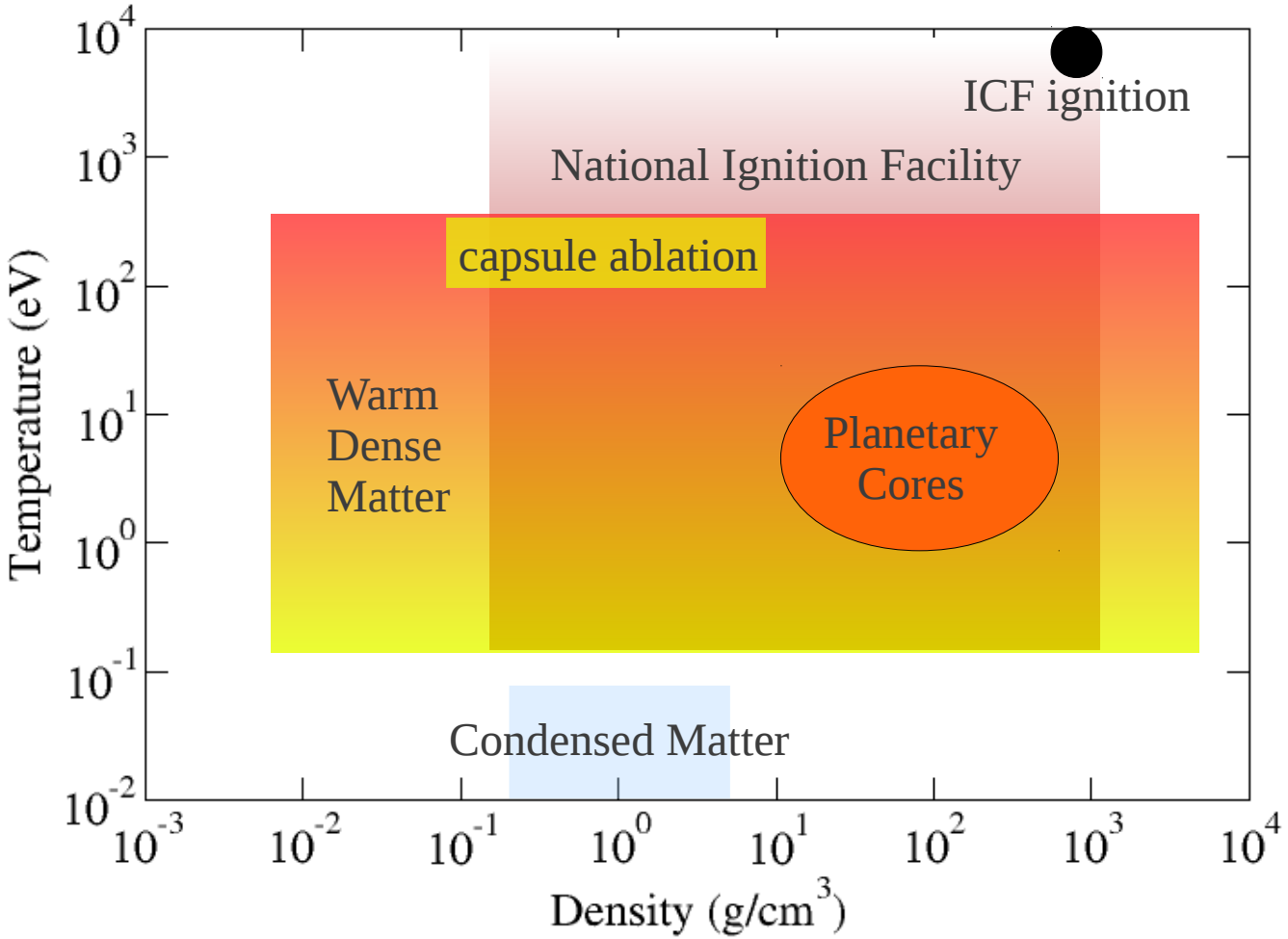


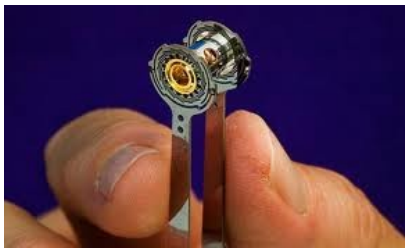




Motivation: need for new methods in the WDM regime



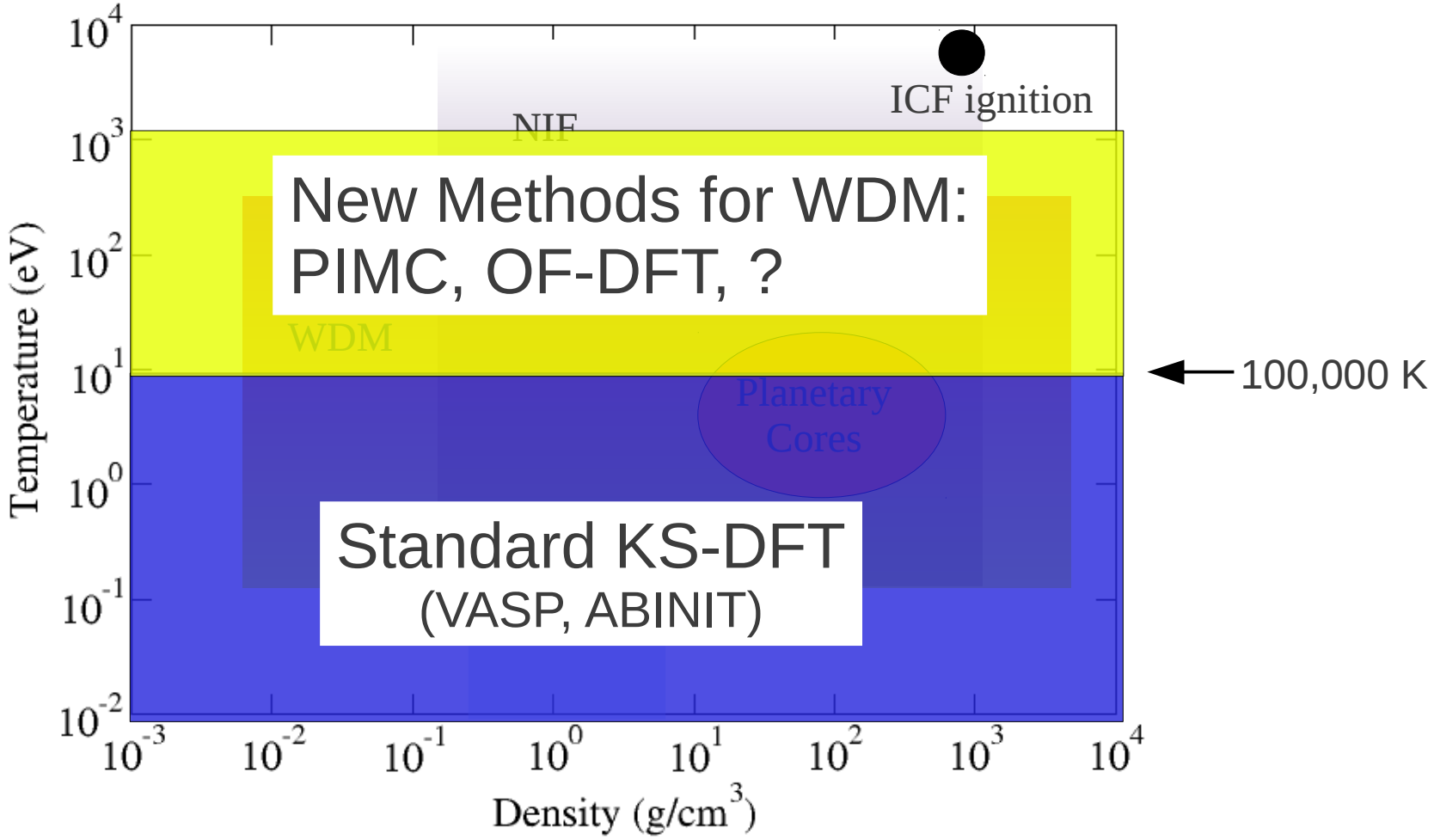
ICF Hohlraum



ICF Capsule

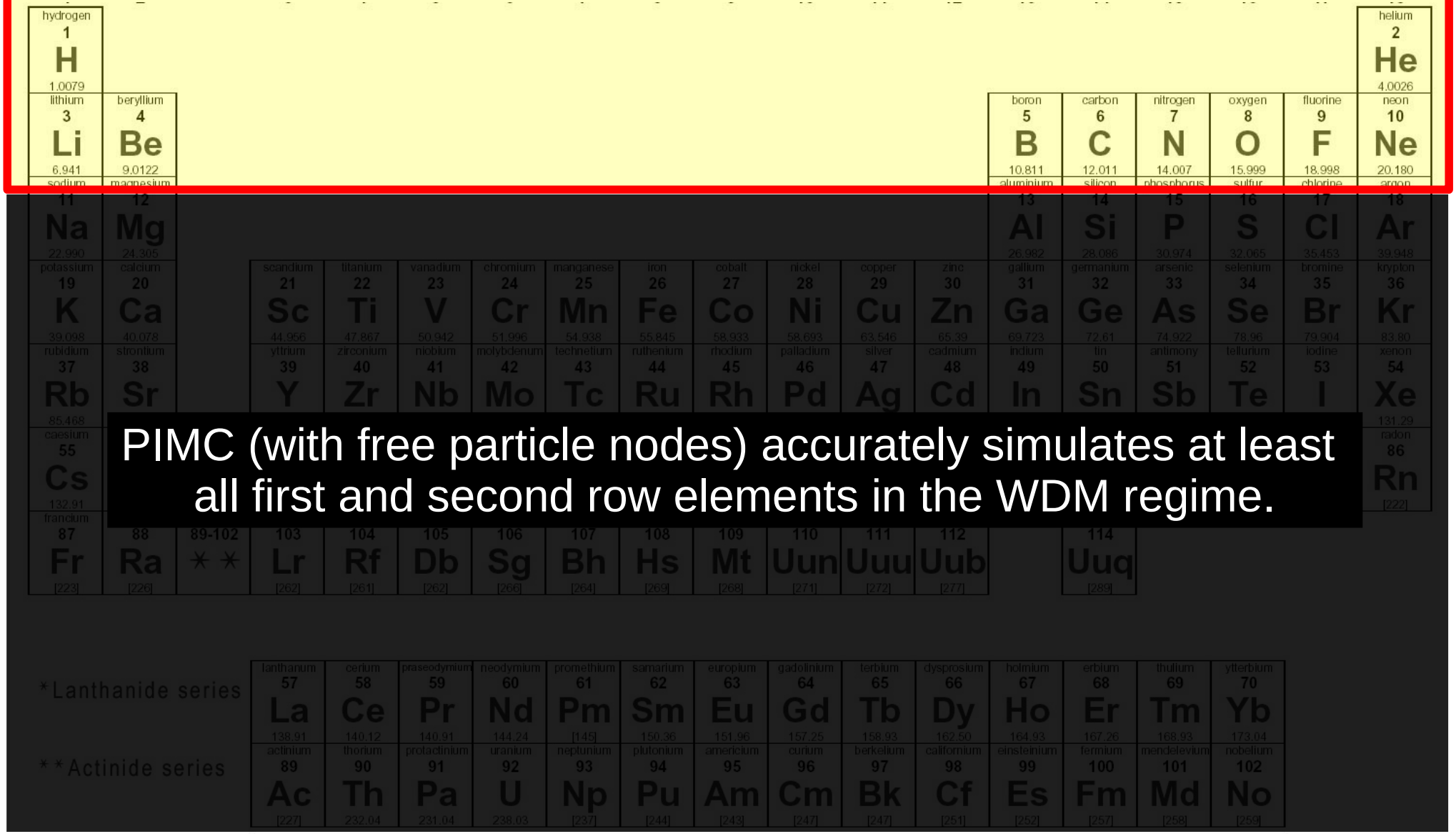
- Warm dense matter physics occurs between condensed matter and plasma regimes.
- Effects of bonding, ionization, XC, and quantum degeneracy are all important.
- WDM methods are important for inertial confinement fusion (ICF) and planetary cores.

Motivation: Standard KS-DFT not sufficient for WDM



- Standard KS-DFT intractable by T=10 eV due to large number of occupied orbitals.
- No reason to assume ground-state XC-functionals are valid for T > 0 eV.
- PIMC offers a highly accurate route to simulate WDM.

Take home message: PIMC works for 1rst and 2nd row



Overview of Path Integral Monte Carlo

Method:

- PIMC is the quantum generalization of classical Lagrangian action principle.
- Thermal density matrix determines all thermodynamic properties of a many-body system.

$$\hat{\rho} = e^{-\beta \hat{H}} = \left[e^{-\frac{\beta}{M}\hat{H}} \right]^M = \left[e^{-\tau \hat{H}} \right]^M$$ (*product property* - time slicing)

- Imaginary time path integral at temperature T with time step tau.
- Sample paths from R to R' using action to accept/reject moves.

$$\hat{\rho}(\boldsymbol{R}, \boldsymbol{R}'; \beta) = \int \dots \int d\boldsymbol{R}_1 \dots d\boldsymbol{R}_{M-1} \rho(\boldsymbol{R}, \boldsymbol{R}'; \tau) \dots \rho(\boldsymbol{R}_{M-1}, \boldsymbol{R}'; \tau)$$

$$Z = Tr[\hat{\rho}], \quad \langle \hat{O} \rangle = Z^{-1} Tr[\hat{\rho}\hat{O}]$$

Approximations:

- Many-body density approximated as pair density; valid for converged time step or T large.

$$\hat{\rho}(\boldsymbol{R}, \boldsymbol{R}'; \beta) \rightarrow \hat{\rho}(\boldsymbol{r}_{ij}, \boldsymbol{r}'_{ij}; \beta)$$

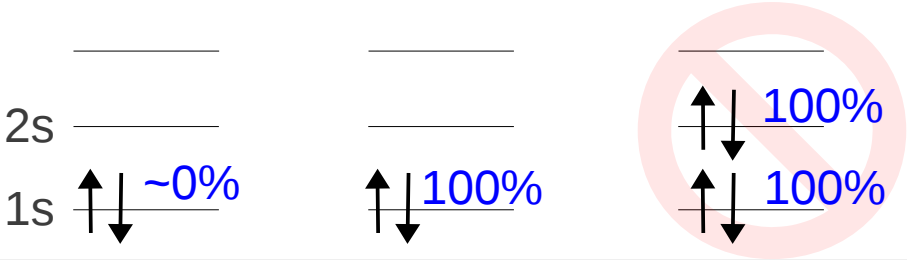
- Fermion sign problem: positive and negative contributions to observable cancel.

$$\hat{\rho}_{Trial}(\boldsymbol{R}, \boldsymbol{R}'; \beta) > 0$$ Use trial **nodes of free particle** density matrix.

Free particle nodes (FPN) first row elements and beyond

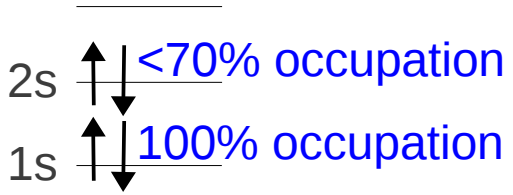
- Previous works shows FPN work for carbon and water.
- At what point will FPN break down?

- High temperature ionization of a system:



- Case 1: A fully ionized system (no bound states) => FPN vaild.
- Case 2: 1s is the only occupied state. No node required => FPN valid.
- Case 3: 1s and 2s fully occupied. Node between 1s-2s needed for correct shell structure. => FPN not valid.

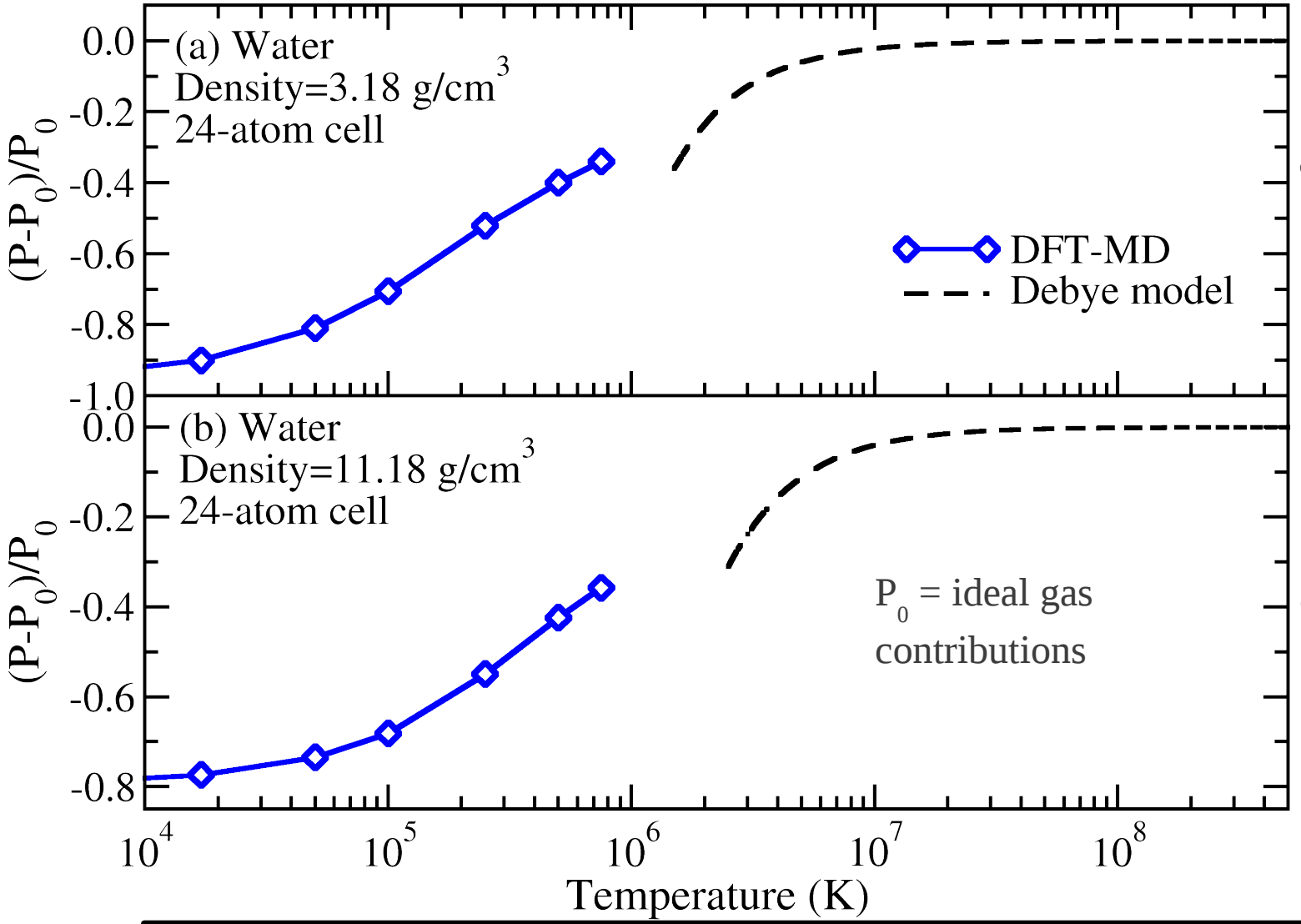
- What if 2s and other states are just partially occupied?



- DFT occupation levels indicate 2s is ~70% occupied at T=250,090 K for 2nd row elements.
- Cross-validation between our PIMC and DFT results in the coming slides will show that FPN become valid near this condition for water and carbon.

- FPN accurate for T > 250,000 K for 1rst and 2nd row plasmas.

Water: Pressure vs Temperature

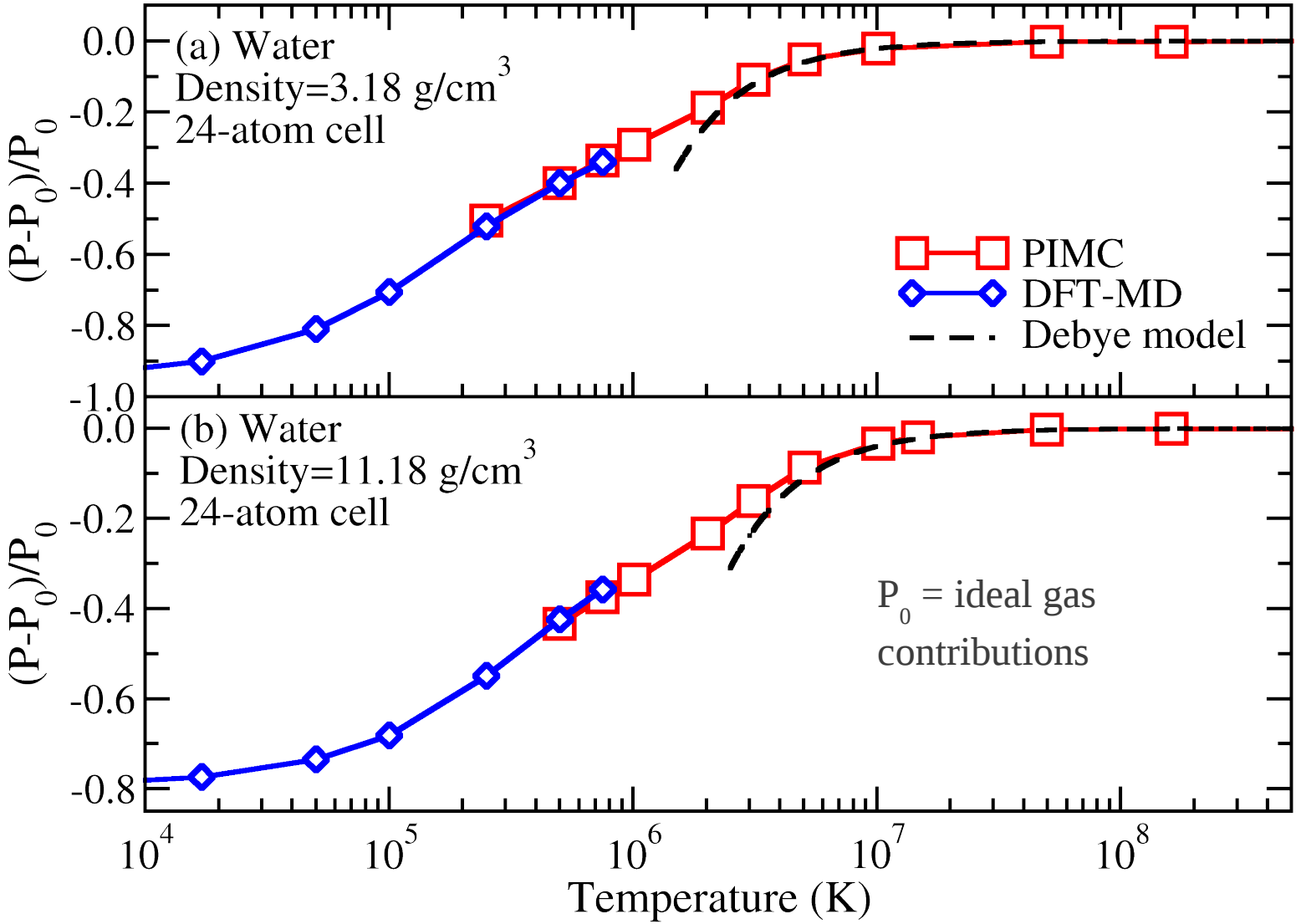


1 Mbar structure at T=0 K

50 Mbar structure at T=0 K

- DFT-MD (VASP, PAW, PBE XC) and Debye-Hückel plasma model.
- Gamma point calculations; at least 1500 eV plane wave energy cutoff.
- Use up to 1500 bands to converge partial occupancy to 10^{-4}.

Water: Pressure vs Temperature

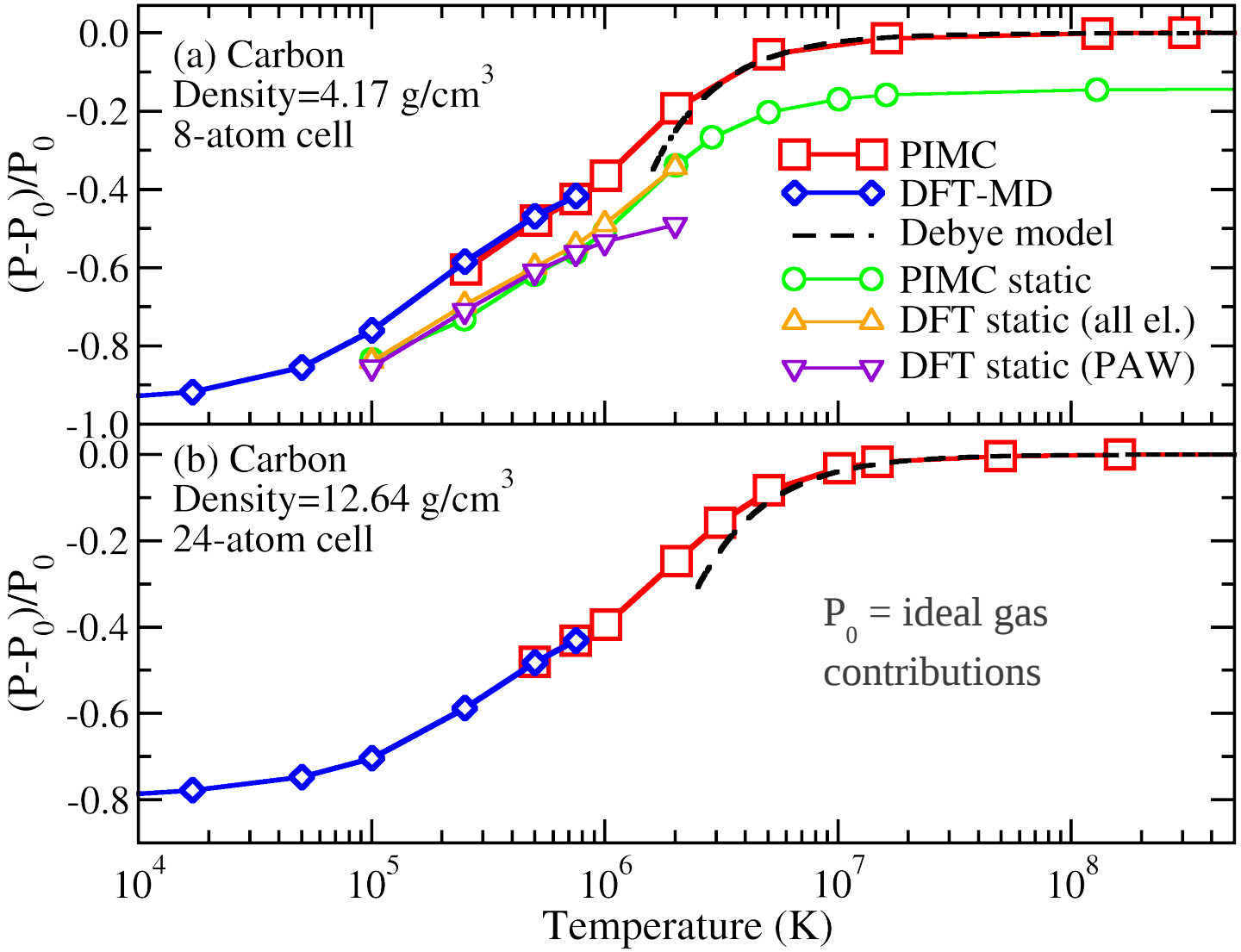


1 Mbar structure at T=0 K

50 Mbar structure at T=0 K

- DFT-MD and PIMC results overlap from 250,000 – 750,000 K.
- Cross-validation implies FPN sufficient and XC-functionals valid at high-T.
- PIMC results converge to the classical plasma (Debye-Hückel) model.

Carbon: Pressure vs Temperature

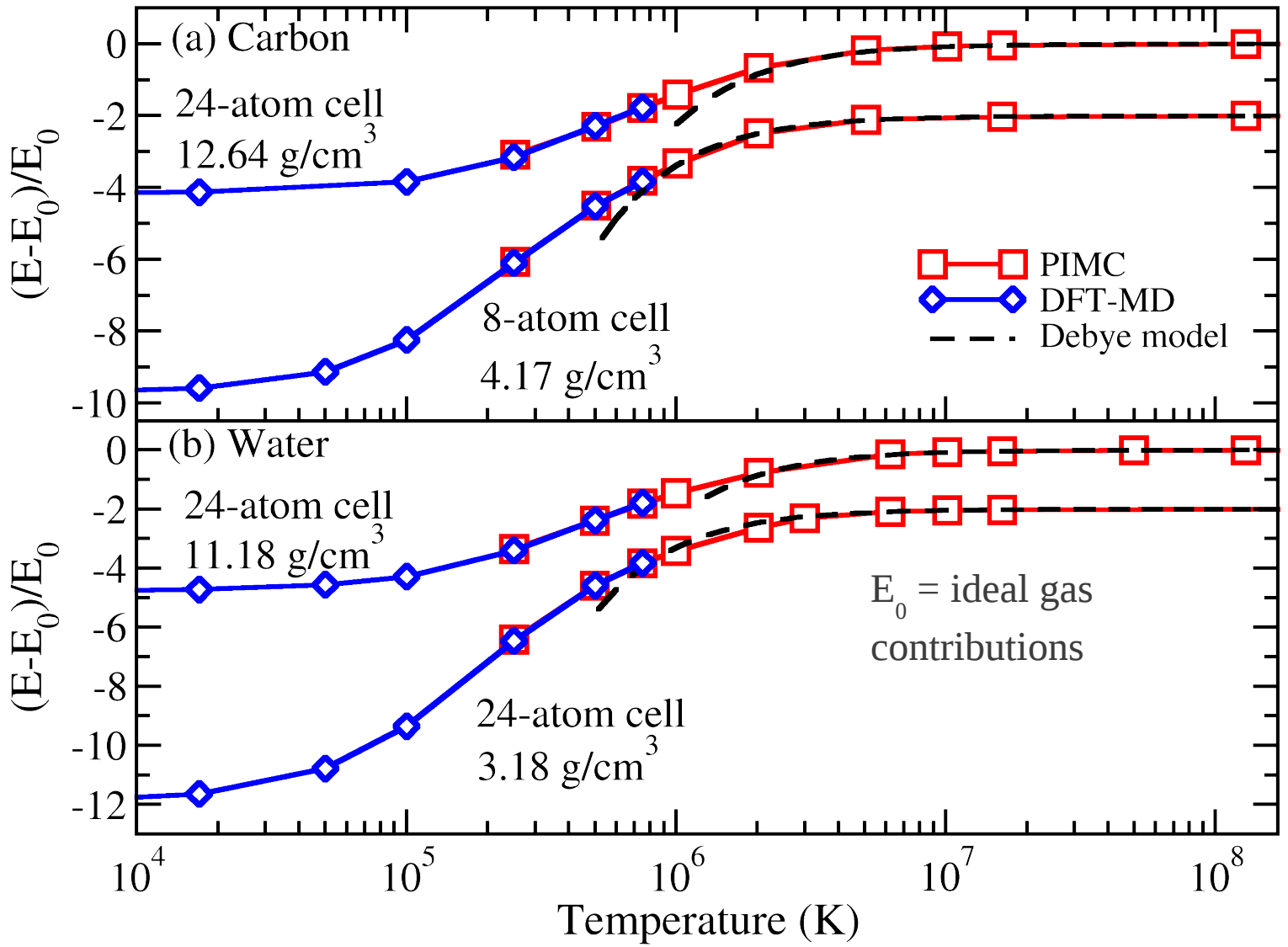


1 Mbar structure at T=0 K

50 Mbar structure at T=0 K

- DFT and PIMC results overlap from 250,000 – 750,000 K.
- Instantaneous AE-PP vs PAW-PP pressure comparison shows VASP-PAW PP fails at 2×10^6 K due to missing core excitation contributions.

Water and Carbon: Energy vs Temperature

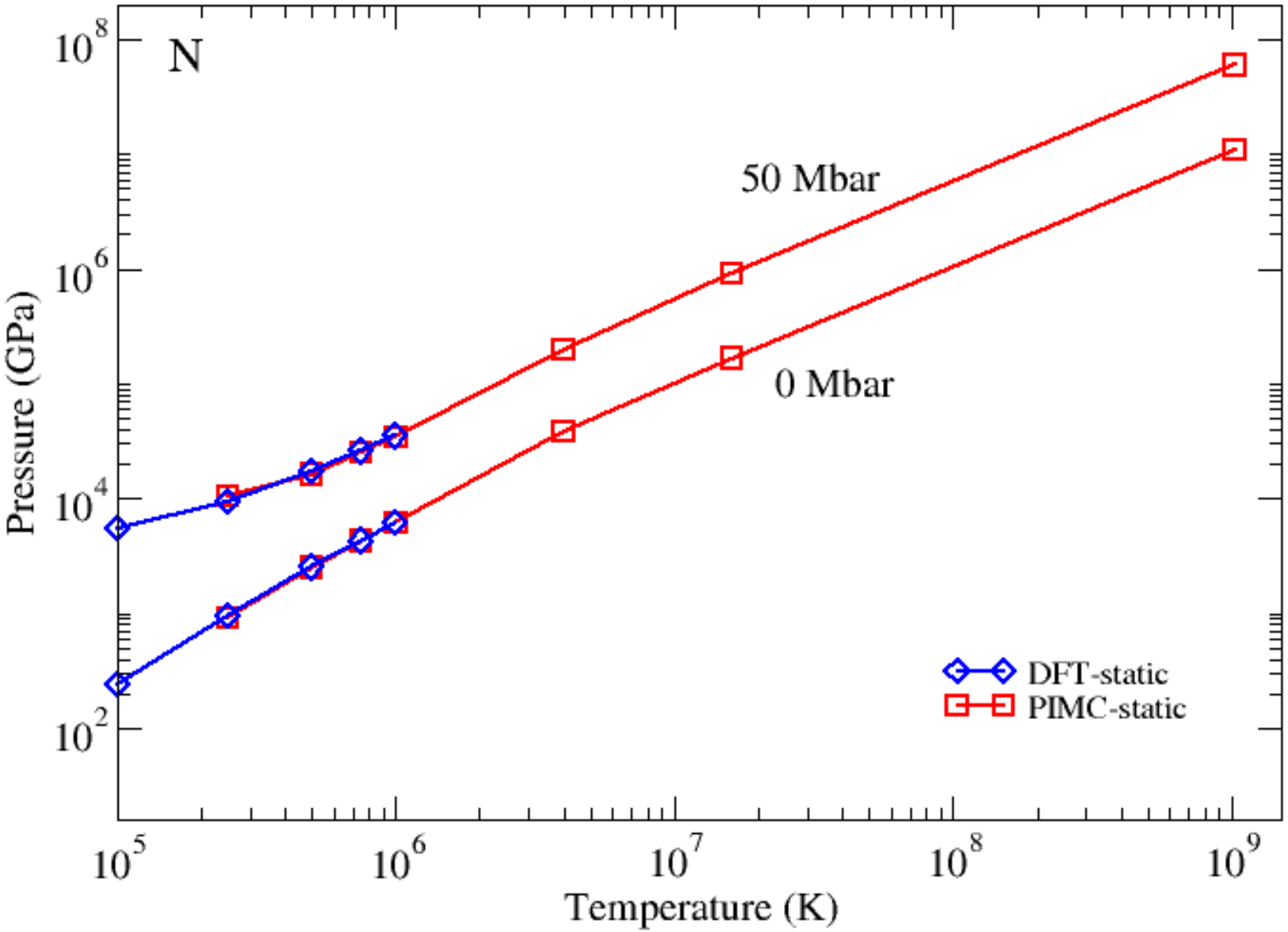


1 Mbar structure at T=0 K

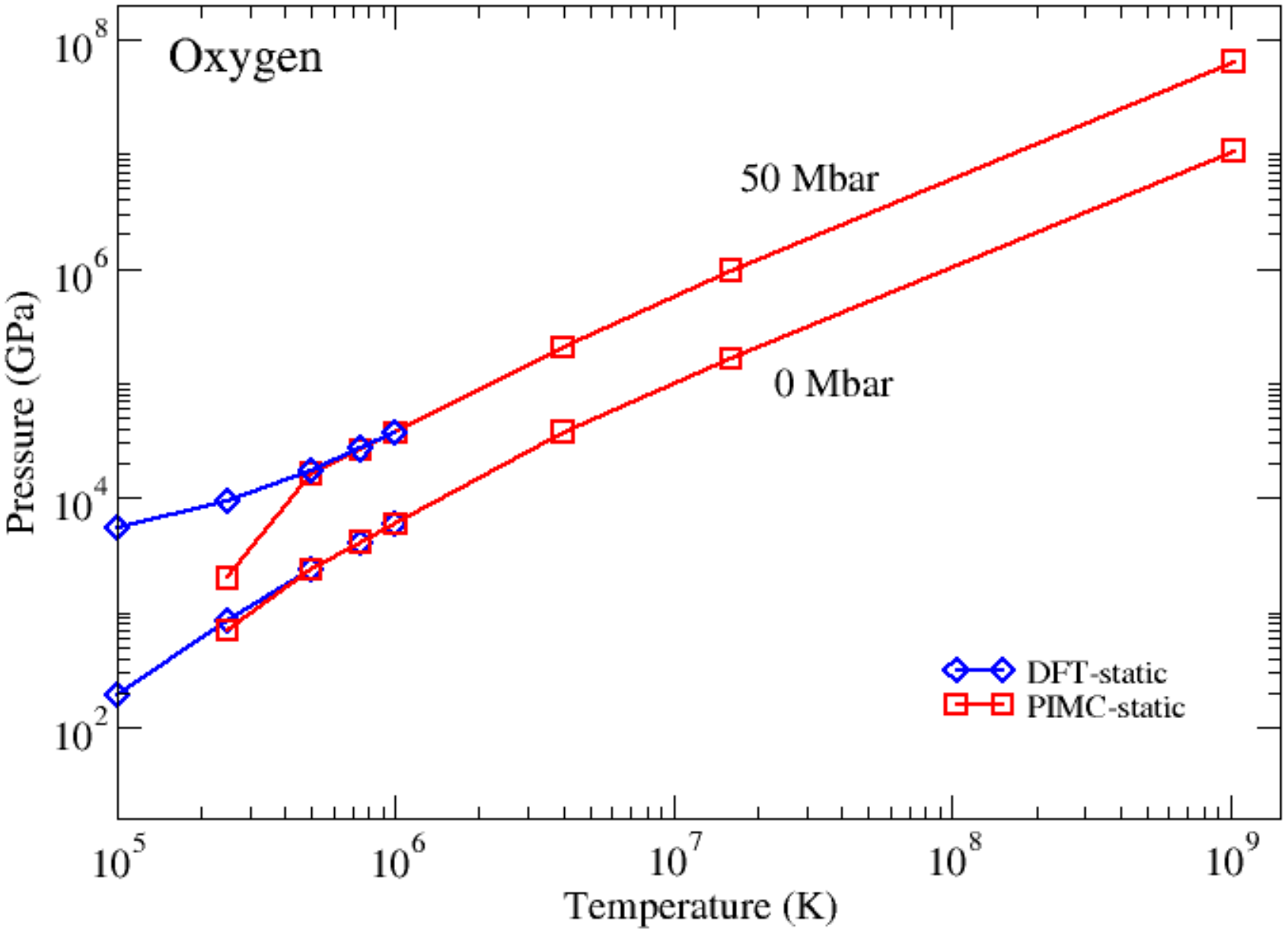
50 Mbar structure at T=0 K

•DFT and PIMC results overlap from 250,000 – 750,000 K.

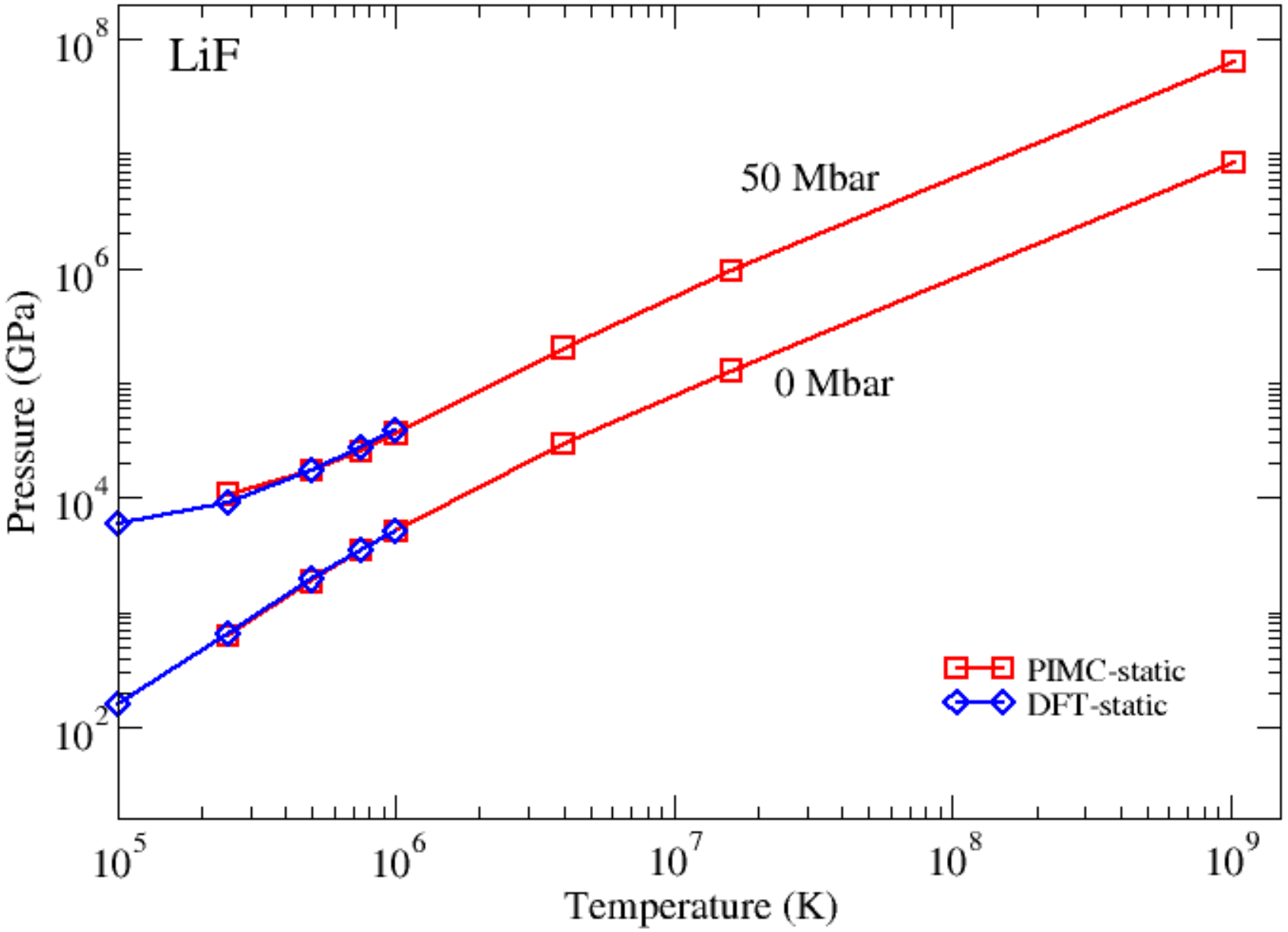
Nitrogen


N
50 Mbar
0 Mbar
DFT-static
PIMC-static
Pressure (GPa)
Temperature (K)
10^8
10^6
10^4
10^2
10^5
10^6
10^7
10^8
10^9

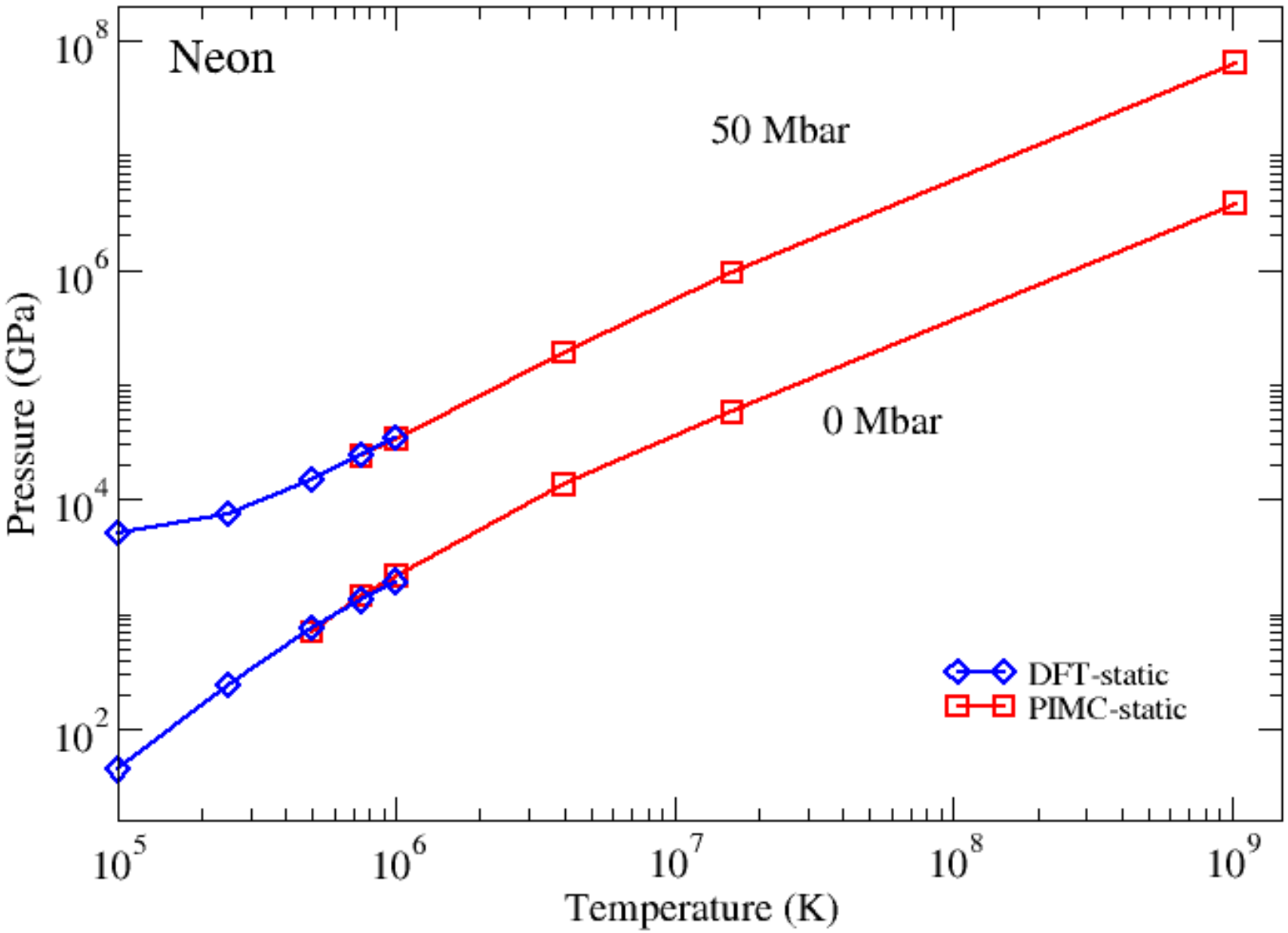
Oxygen


Oxygen
50 Mbar
0 Mbar
DFT-static
PIMC-static
Pressure (GPa)
Temperature (K)
10^2
10^4
10^6
10^8
10^5
10^6
10^7
10^8
10^9

Lithium Fluoride



Neon


Neon
50 Mbar
0 Mbar
DFT-static
PIMC-static
Pressure (GPa)
Temperature (K)
10^2
10^4
10^6
10^8
10^5
10^6
10^7
10^8
10^9

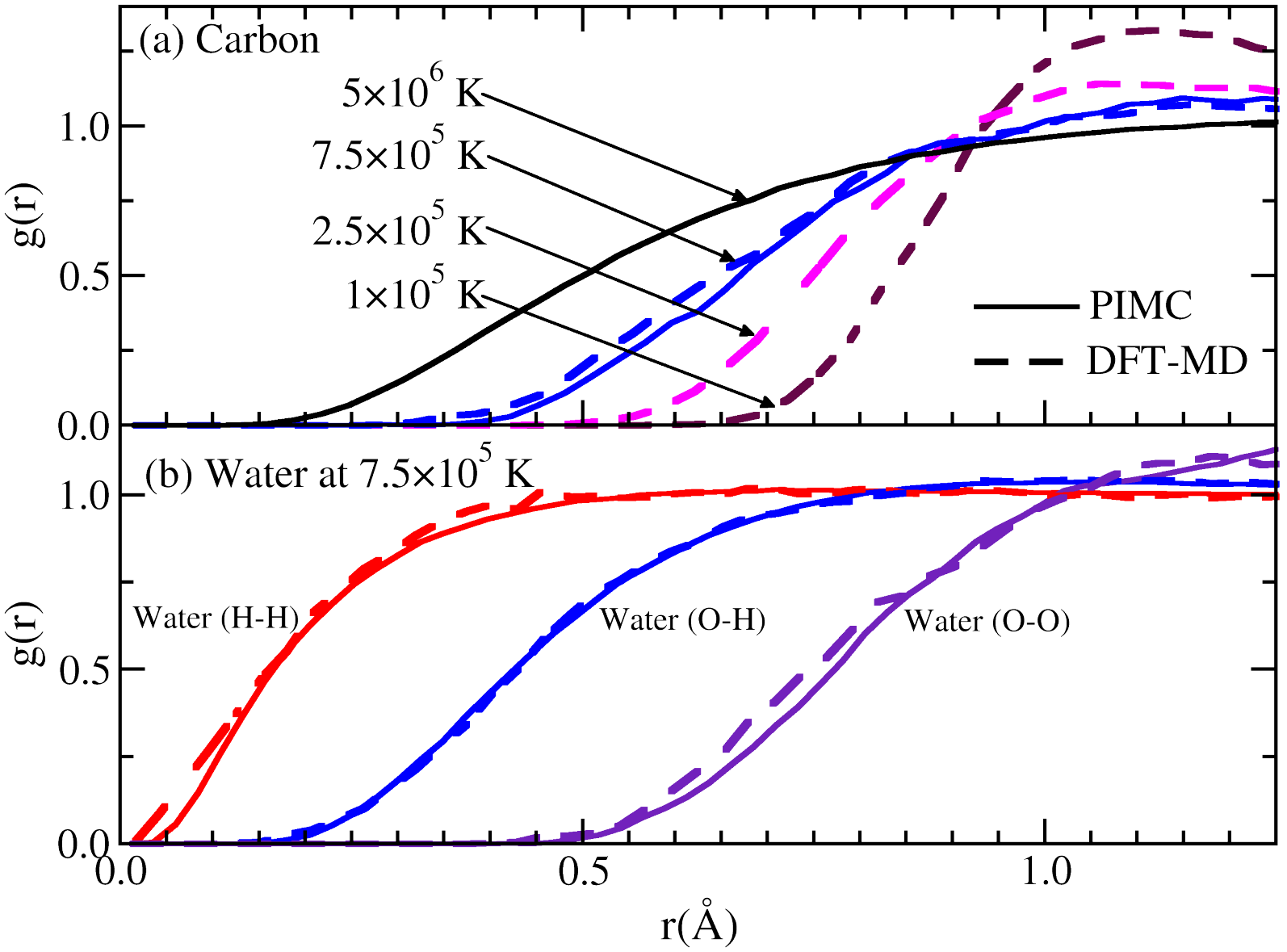
Conclusions

- PIMC works for all first and second row elements in WDM regime.
- PIMC and DFT-MD together form a coherent equation of state from condensed matter to the plasma limit.
- PIMC pressures, internal energies, and pair correlation functions agree with DFT-MD in the range of 250,000 – 750,000 K.
- Phys. Rev. Lett. 108, 115502 (2012).

Future Work:

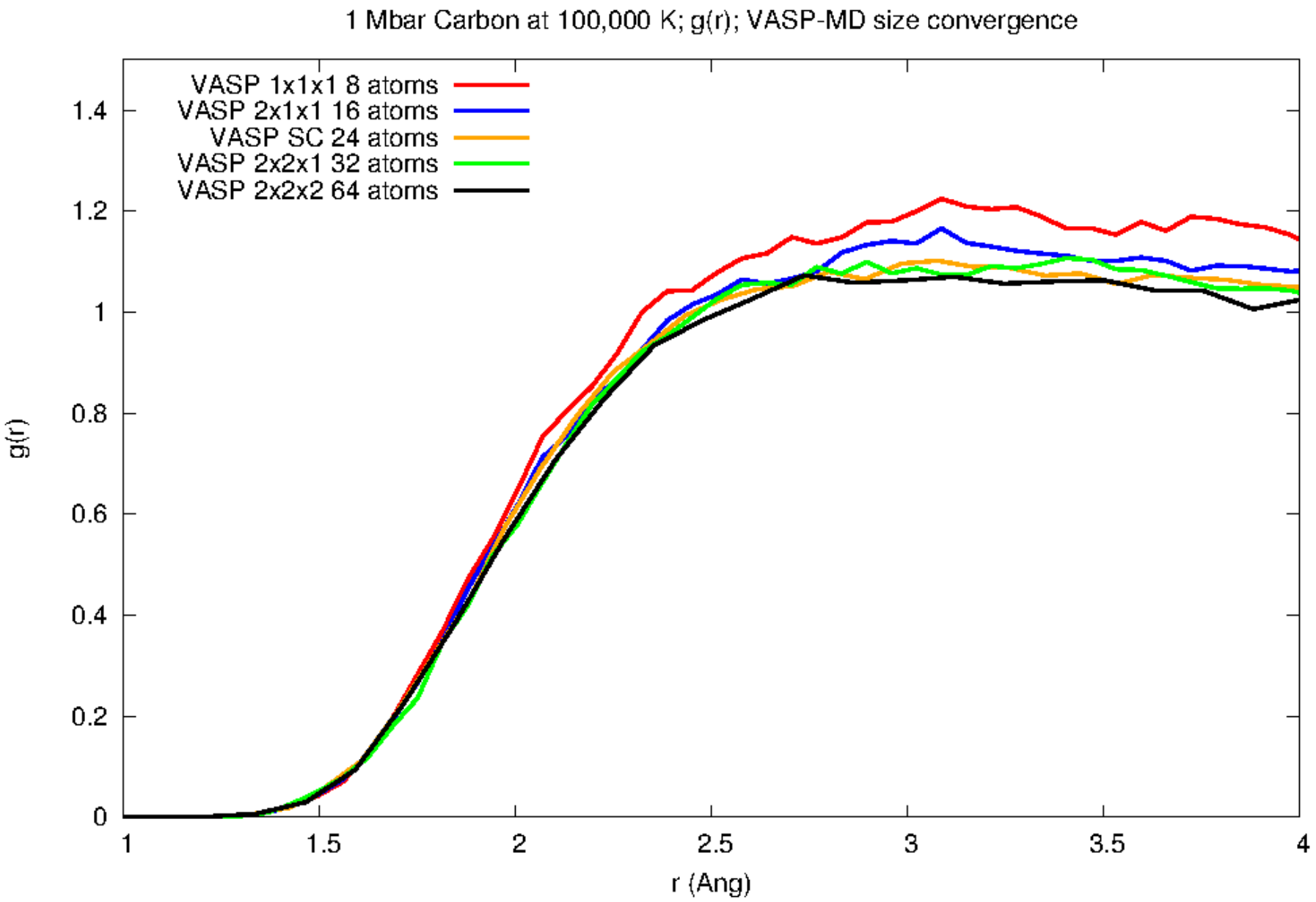
- Continue developing PIMC for heavier elements.

Water and Carbon: Pair Correlation Functions

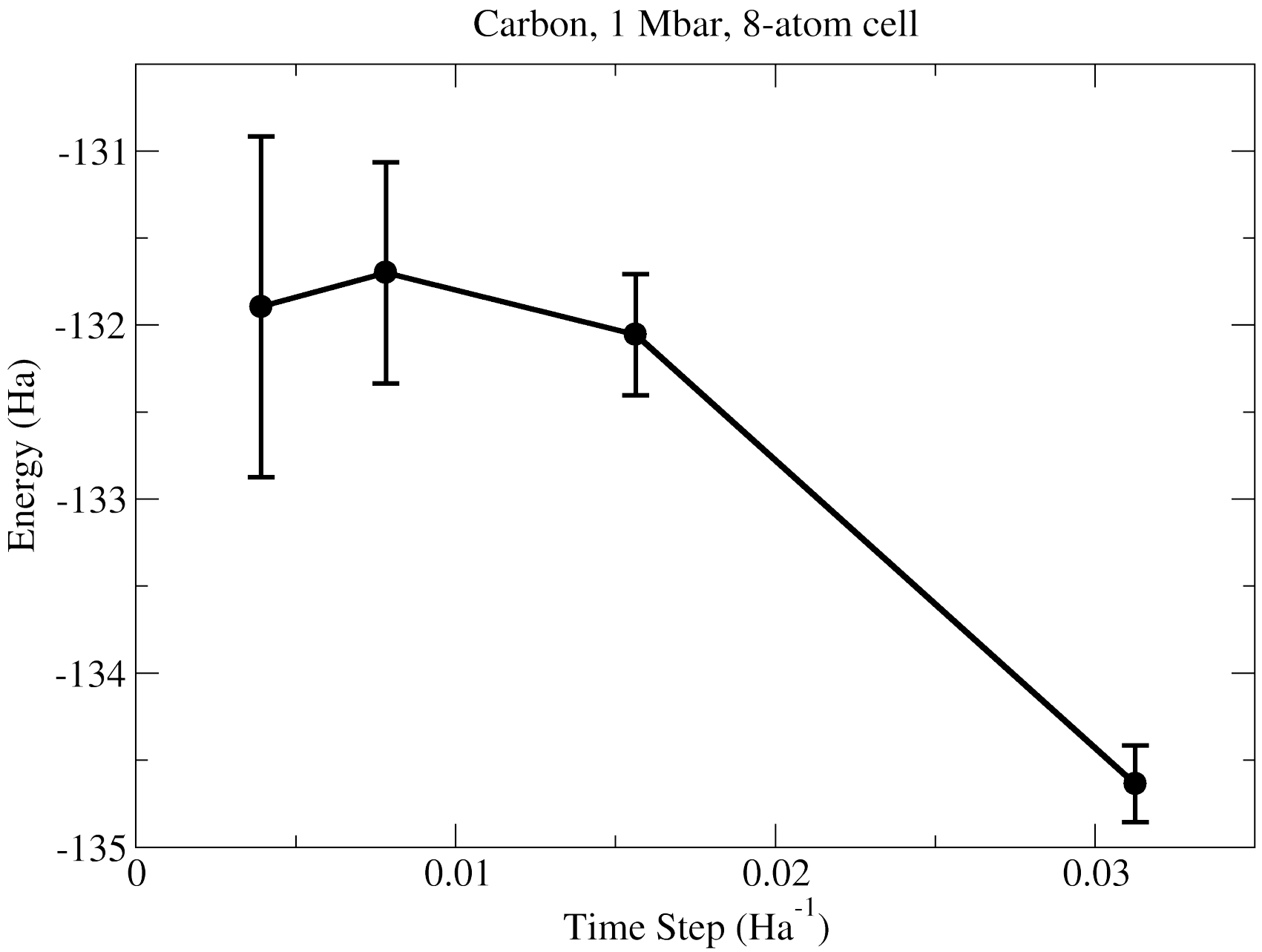


- PIMC and DFT-MD predict consistent structural properties.
- PCFs show sensitive temperature dependence.

DFT-MD cell-size convergence for pair-correlation function



PIMC Energy vs. Time Step



Water: PIMC P vs. T for 24- and 6- atom cells