

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

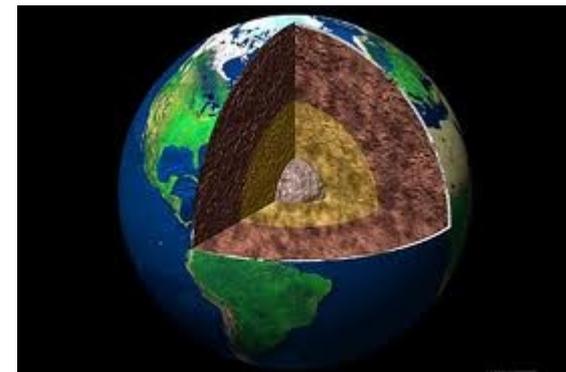
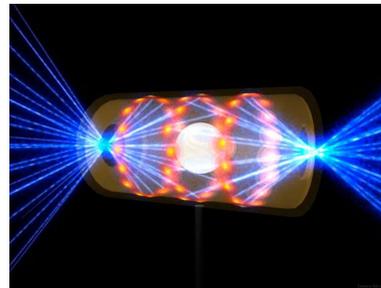
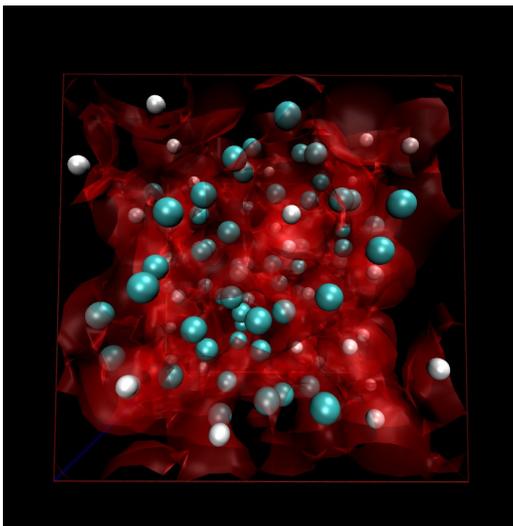


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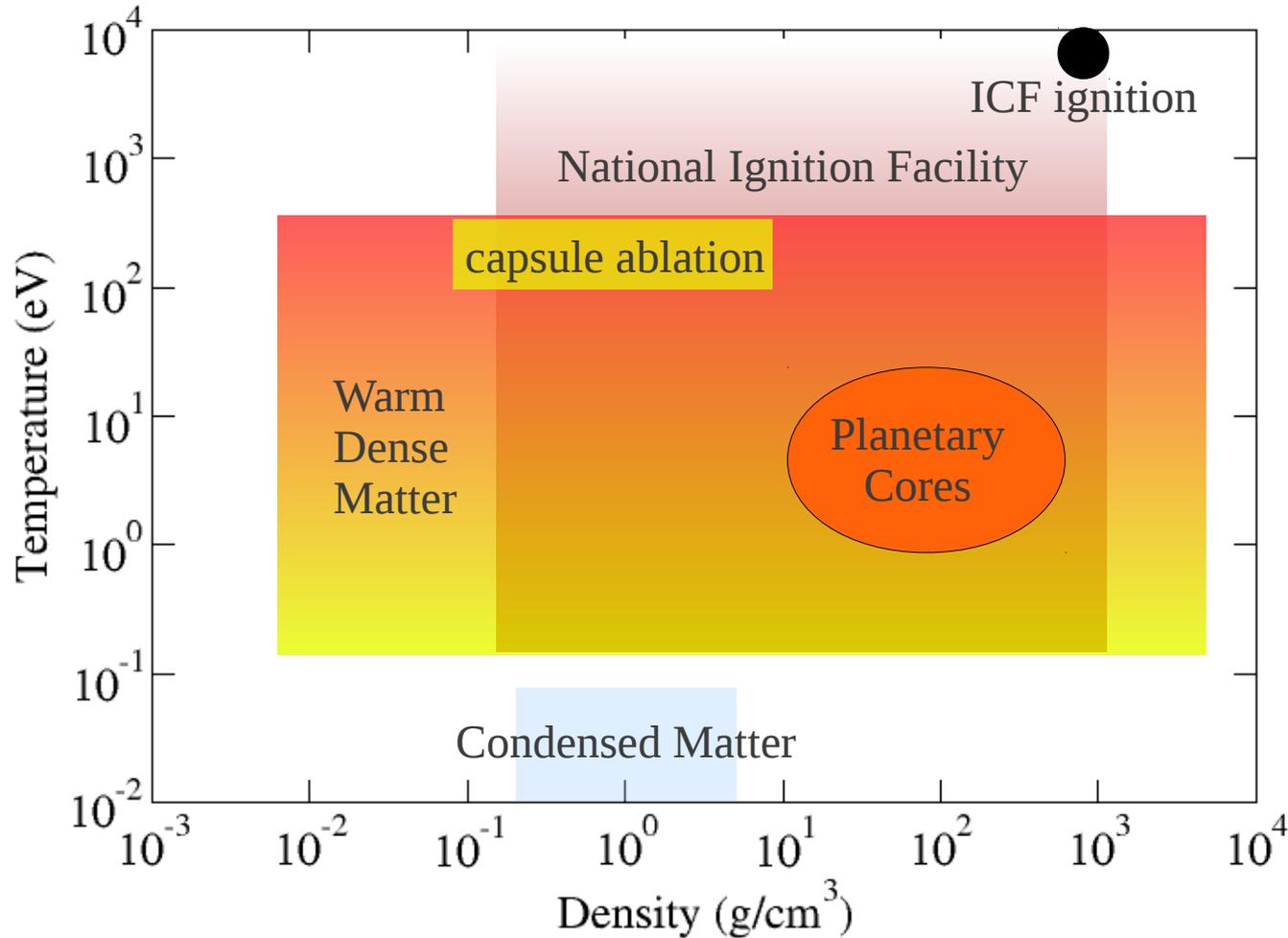


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- Computational support by NCAR, TAC, and TeraGrid



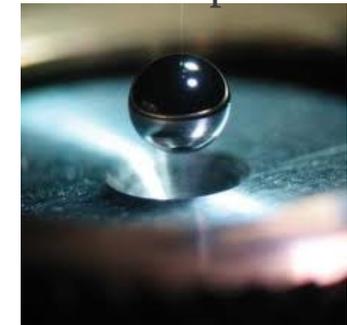
# Motivation: need for new methods in the WDM regime



ICF Hohlräum

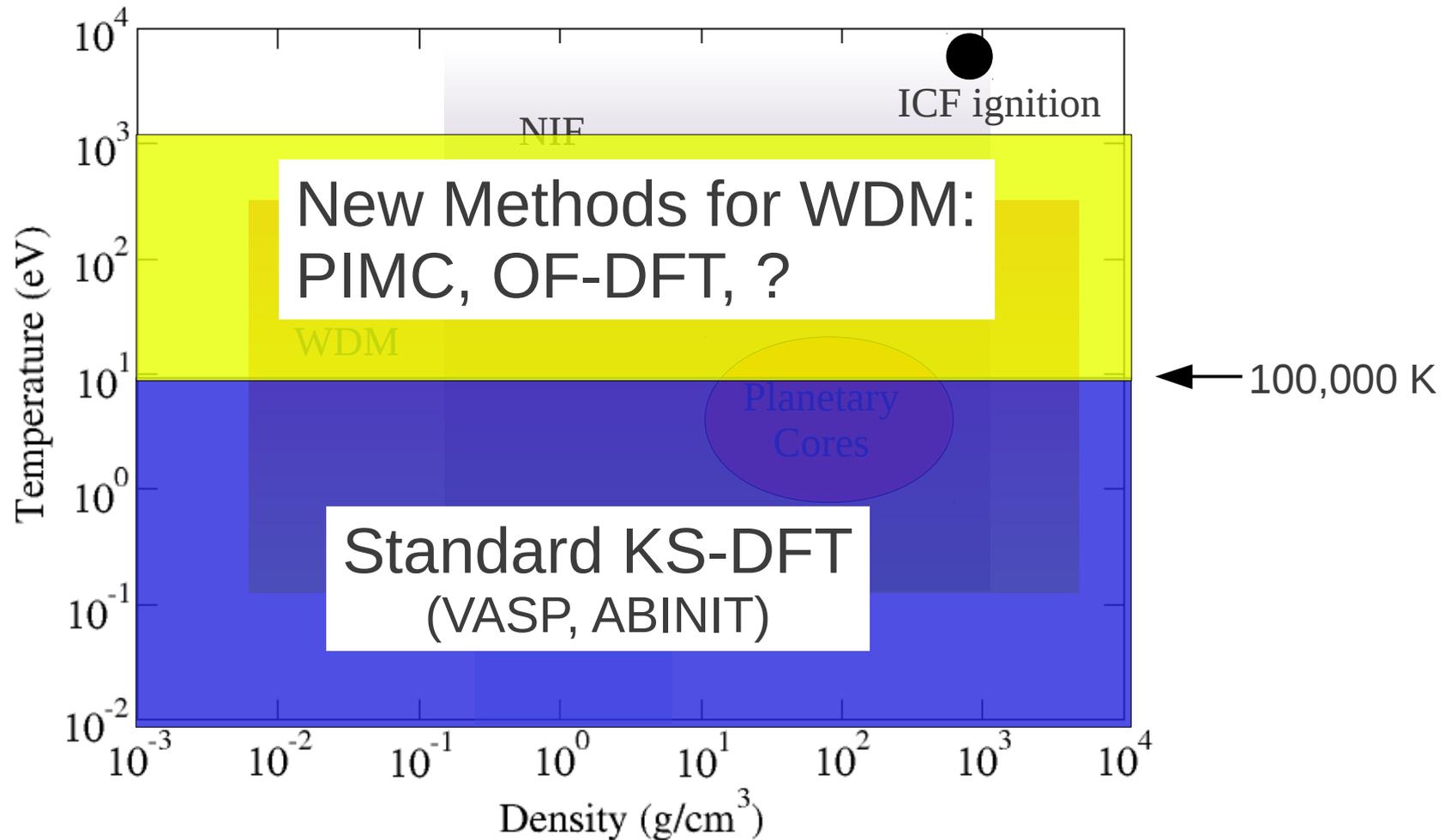


ICF Capsule



- 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 1st and 2nd row

hydrogen 1 <b>H</b> 1.0079															helium 2 <b>He</b> 4.0026		
lithium 3 <b>Li</b> 6.941	beryllium 4 <b>Be</b> 9.0122											boron 5 <b>B</b> 10.811	carbon 6 <b>C</b> 12.011	nitrogen 7 <b>N</b> 14.007	oxygen 8 <b>O</b> 15.999	fluorine 9 <b>F</b> 18.998	neon 10 <b>Ne</b> 20.180

11 <b>Na</b> 22.990	12 <b>Mg</b> 24.305											13 <b>Al</b> 26.982	14 <b>Si</b> 28.086	15 <b>P</b> 30.974	16 <b>S</b> 32.065	17 <b>Cl</b> 35.453	18 <b>Ar</b> 39.948
19 <b>K</b> 39.098	20 <b>Ca</b> 40.078	21 <b>Sc</b> 44.956	22 <b>Ti</b> 47.867	23 <b>V</b> 50.942	24 <b>Cr</b> 51.996	25 <b>Mn</b> 54.938	26 <b>Fe</b> 55.845	27 <b>Co</b> 58.933	28 <b>Ni</b> 58.693	29 <b>Cu</b> 63.546	30 <b>Zn</b> 65.39	31 <b>Ga</b> 69.723	32 <b>Ge</b> 72.61	33 <b>As</b> 74.922	34 <b>Se</b> 78.96	35 <b>Br</b> 79.904	36 <b>Kr</b> 83.80
37 <b>Rb</b> 85.468	38 <b>Sr</b>	39 <b>Y</b>	40 <b>Zr</b>	41 <b>Nb</b>	42 <b>Mo</b>	43 <b>Tc</b>	44 <b>Ru</b>	45 <b>Rh</b>	46 <b>Pd</b>	47 <b>Ag</b>	48 <b>Cd</b>	49 <b>In</b>	50 <b>Sn</b>	51 <b>Sb</b>	52 <b>Te</b>	53 <b>I</b>	54 <b>Xe</b> 131.29
55 <b>Cs</b> 132.91	<p><b>PIMC (with free particle nodes) accurately simulates at least all first and second row elements in the WDM regime.</b></p>															86 <b>Rn</b> [222]	
87 <b>Fr</b> [223]	88 <b>Ra</b> [226]	89-102 * *	103 <b>Lr</b> [262]	104 <b>Rf</b> [261]	105 <b>Db</b> [262]	106 <b>Sg</b> [266]	107 <b>Bh</b> [264]	108 <b>Hs</b> [269]	109 <b>Mt</b> [268]	110 <b>Uun</b> [271]	111 <b>Uuu</b> [272]	112 <b>Uub</b> [277]			114 <b>Uuq</b> [289]		

\* Lanthanide series

lanthanum 57 <b>La</b> 138.91	cerium 58 <b>Ce</b> 140.12	praseodymium 59 <b>Pr</b> 140.91	neodymium 60 <b>Nd</b> 144.24	promethium 61 <b>Pm</b> [145]	samarium 62 <b>Sm</b> 150.36	europium 63 <b>Eu</b> 151.96	gadolinium 64 <b>Gd</b> 157.25	terbium 65 <b>Tb</b> 158.93	dysprosium 66 <b>Dy</b> 162.50	holmium 67 <b>Ho</b> 164.93	erbium 68 <b>Er</b> 167.26	thulium 69 <b>Tm</b> 168.93	ytterbium 70 <b>Yb</b> 173.04
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\*\* Actinide series

actinium 89 <b>Ac</b> [227]	thorium 90 <b>Th</b> 232.04	protactinium 91 <b>Pa</b> 231.04	uranium 92 <b>U</b> 238.03	neptunium 93 <b>Np</b> [237]	plutonium 94 <b>Pu</b> [244]	americium 95 <b>Am</b> [243]	curium 96 <b>Cm</b> [247]	berkelium 97 <b>Bk</b> [247]	californium 98 <b>Cf</b> [251]	einsteinium 99 <b>Es</b> [252]	fermium 100 <b>Fm</b> [257]	mendelevium 101 <b>Md</b> [258]	nobelium 102 <b>No</b> [259]
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# 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.

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

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

$$\hat{\rho}(\mathbf{R}, \mathbf{R}'; \beta) = \int \dots \int d\mathbf{R}_1 \dots d\mathbf{R}_{M-1} \rho(\mathbf{R}, \mathbf{R}'; \tau) \dots \rho(\mathbf{R}_{M-1}, \mathbf{R}'; \tau)$$
$$Z = \text{Tr}[\hat{\rho}], \quad \langle \hat{O} \rangle = Z^{-1} \text{Tr}[\hat{\rho} \hat{O}]$$

## Approximations:

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

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

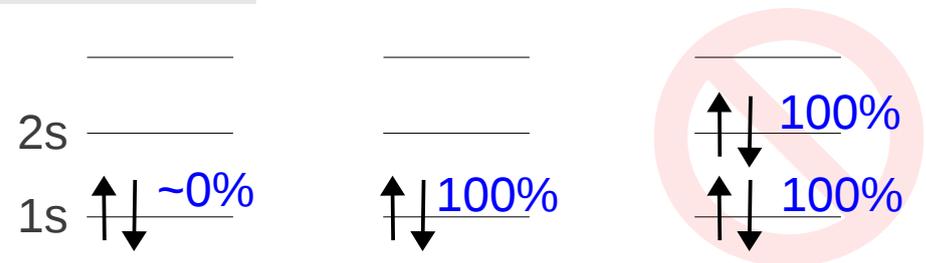
- Fermion sign problem: positive and negative contributions to observable cancel.

$$\rho_{\text{Trial}}^{\hat{}}(\mathbf{R}, \mathbf{R}'; \beta) > 0 \quad \text{Use trial nodes of free particle density matrix.}$$

# Free particle nodes (FPN) first row elements and beyond

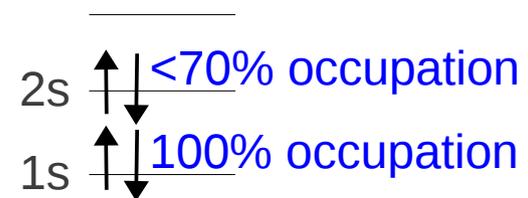
- Previous works shows FPN work for carbon and water.
- At what point will FPN break down?

• High temperature ionization of a system:



- Case 1: A fully ionized system (no bound states) => FPN valid.
- 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?

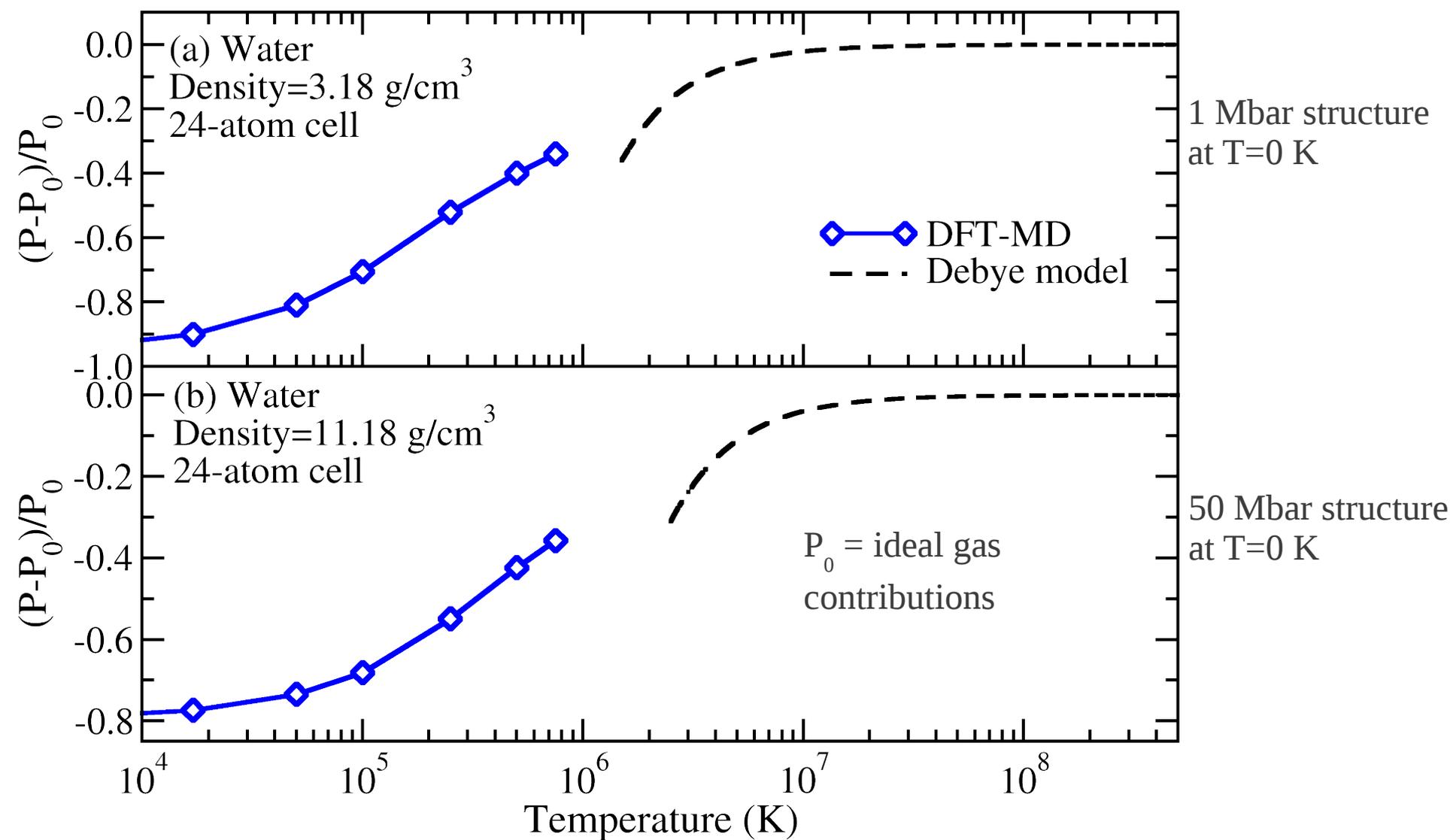


- DFT occupation levels indicate 2s is ~70% occupied at  $T=250,090$  K for 2nd row elements.
- Cross-validation between our PIMC and DFT results in the coming slides will show that FPN become valid near this condition for water and carbon.

• FPN accurate for  $T > 250,000$  K for 1st and 2nd row plasmas.



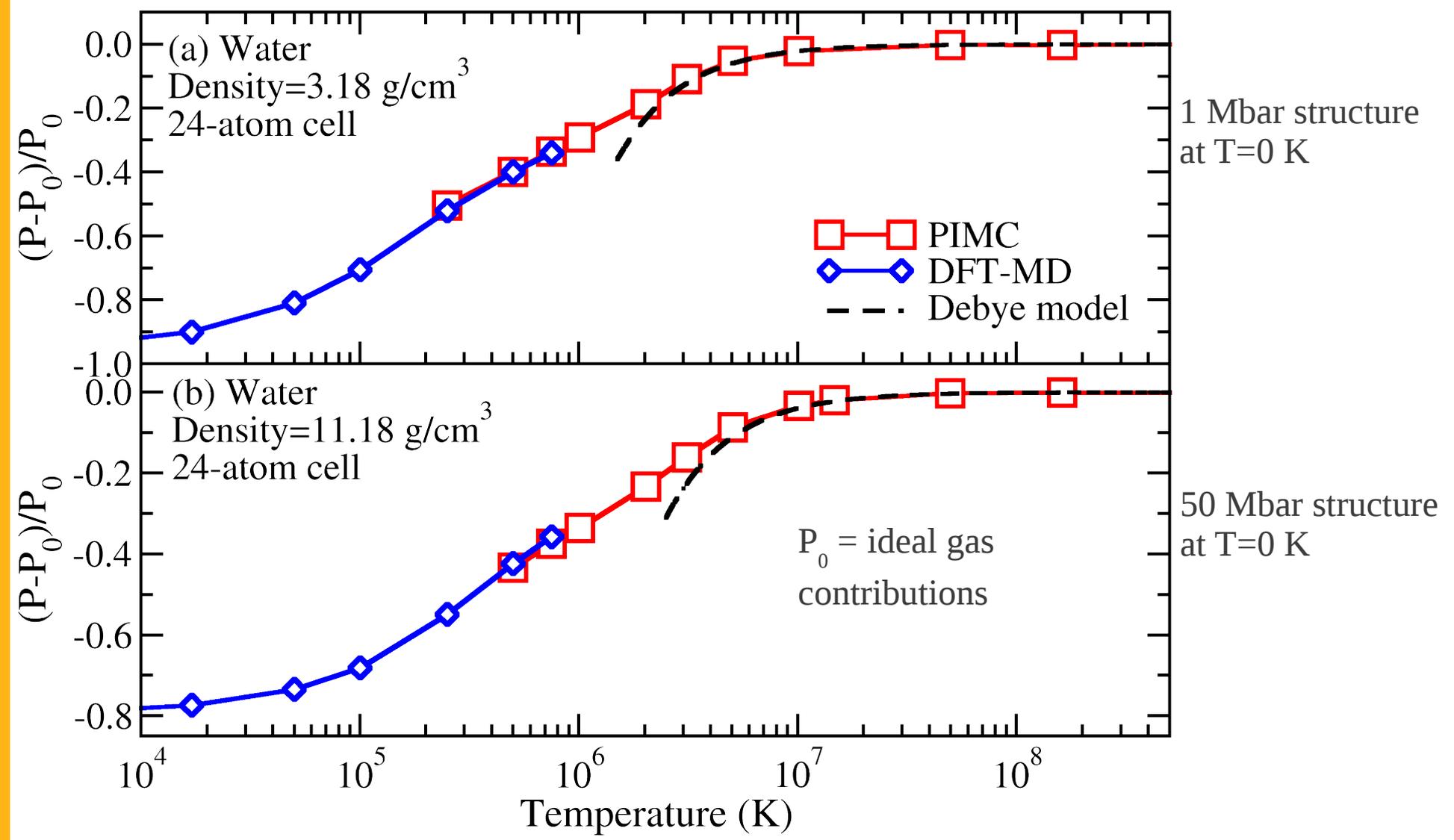
# Water: Pressure vs Temperature



- 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  $10^{-4}$ .



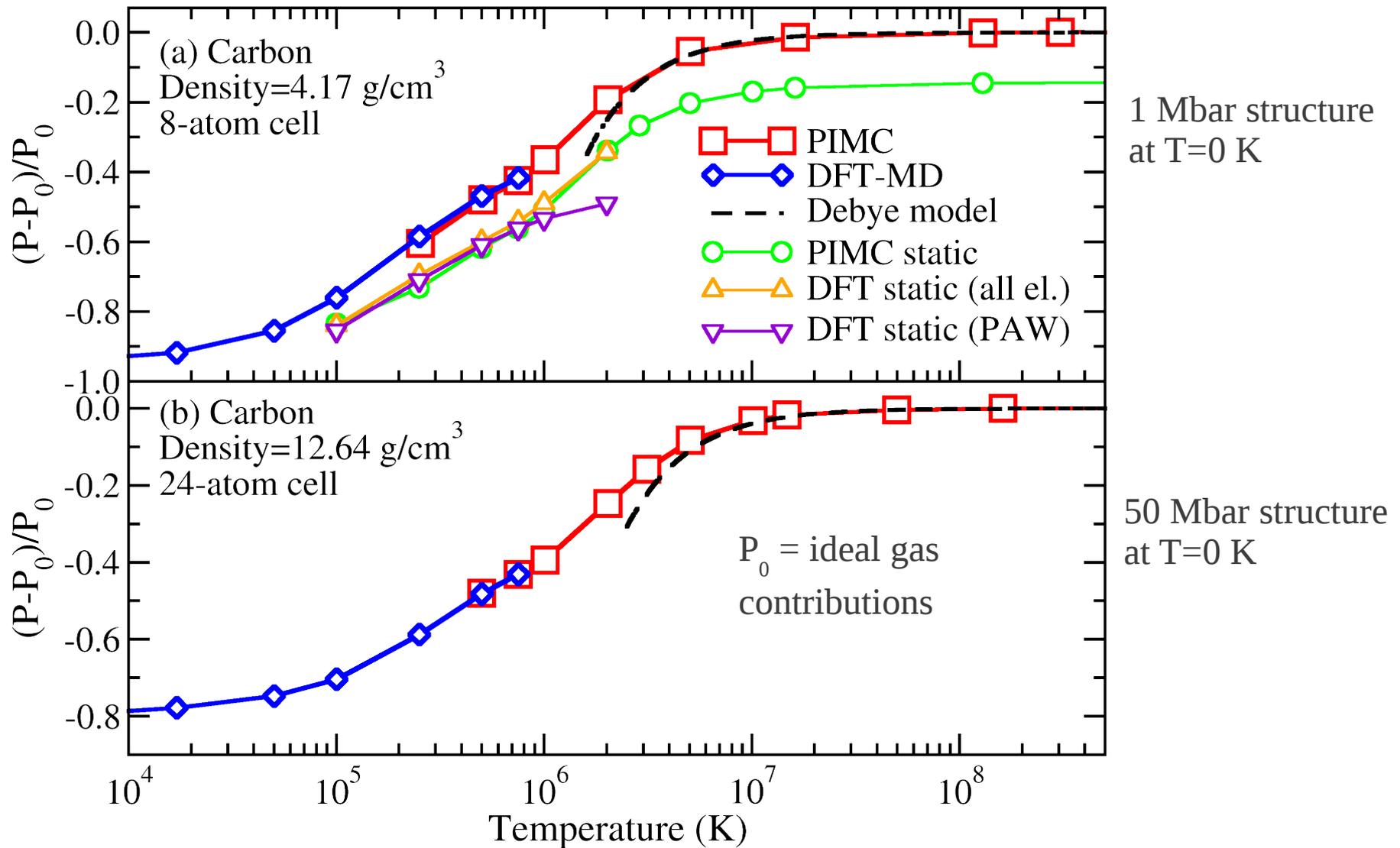
# Water: Pressure vs Temperature



- 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.



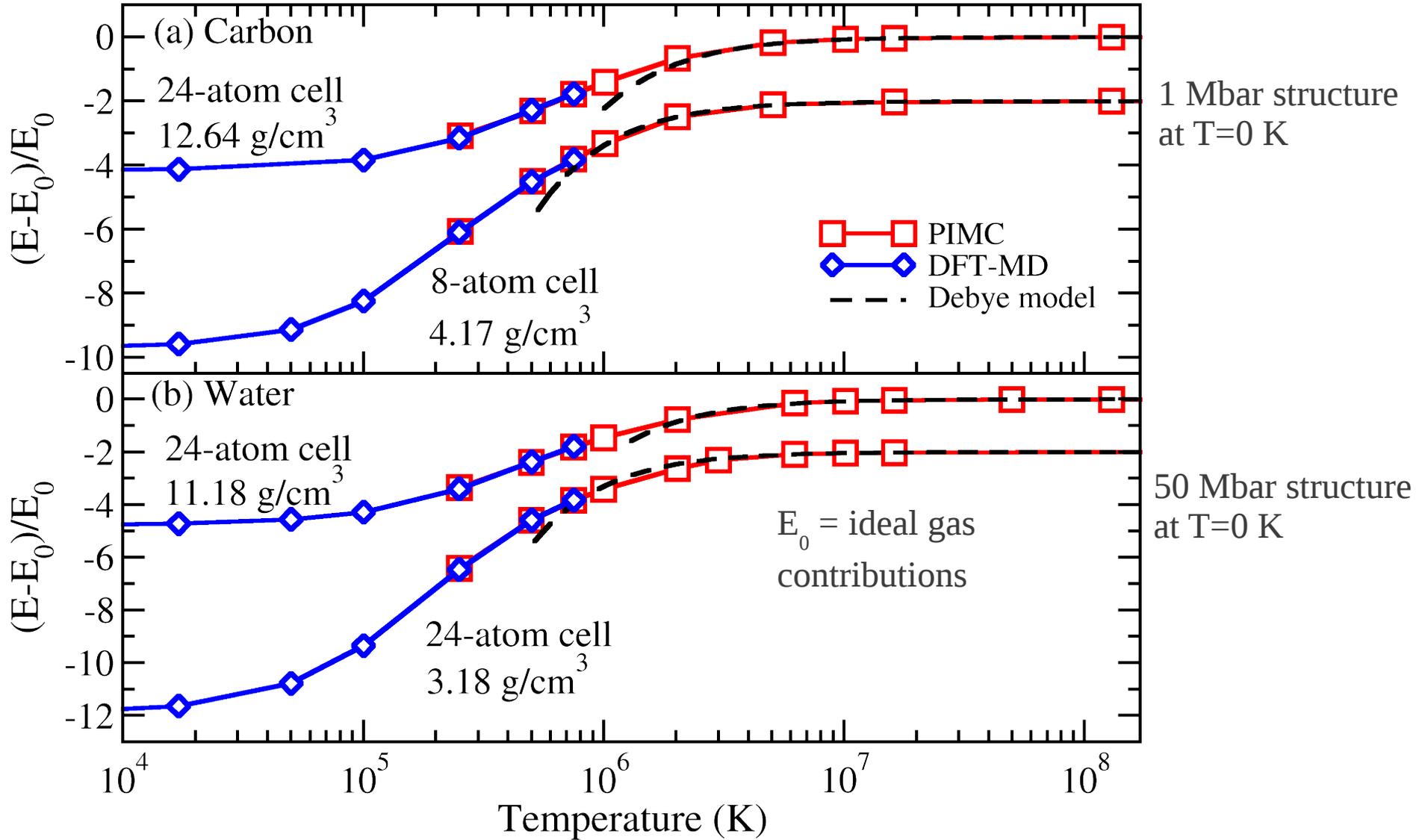
# Carbon: Pressure vs Temperature



- 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  $2 \times 10^6$  K due to missing core excitation contributions.



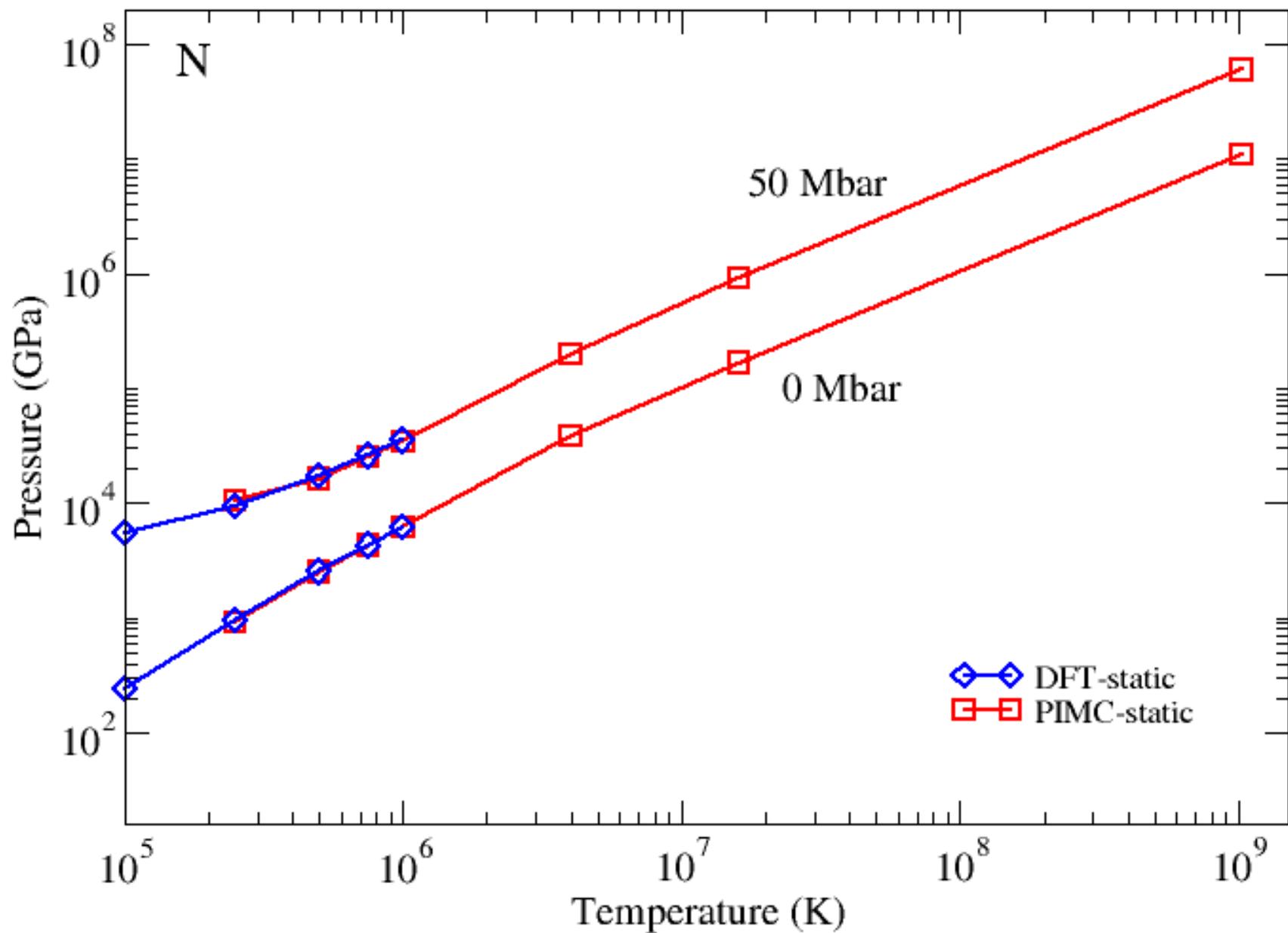
# Water and Carbon: Energy vs Temperature



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

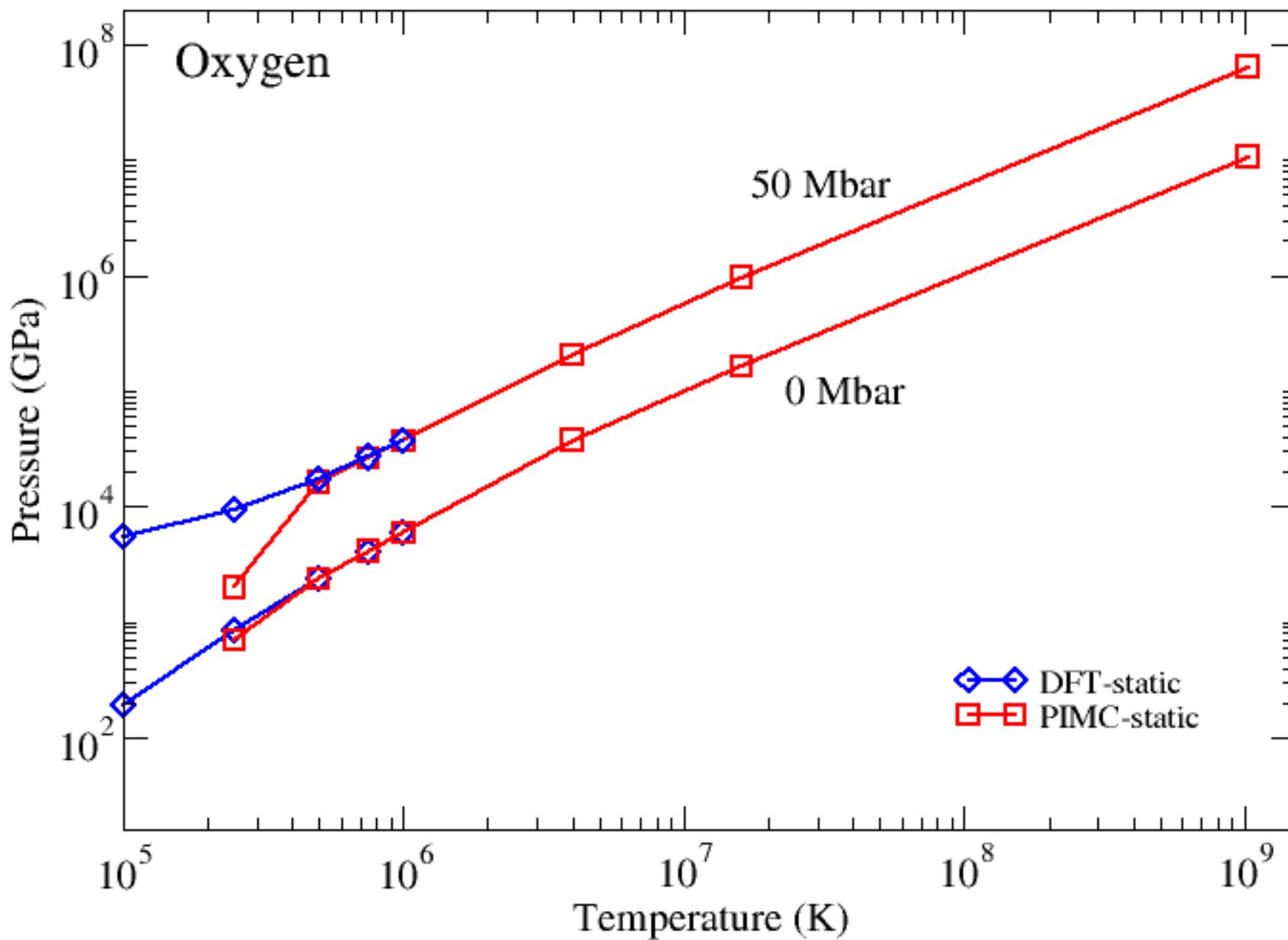


# Nitrogen



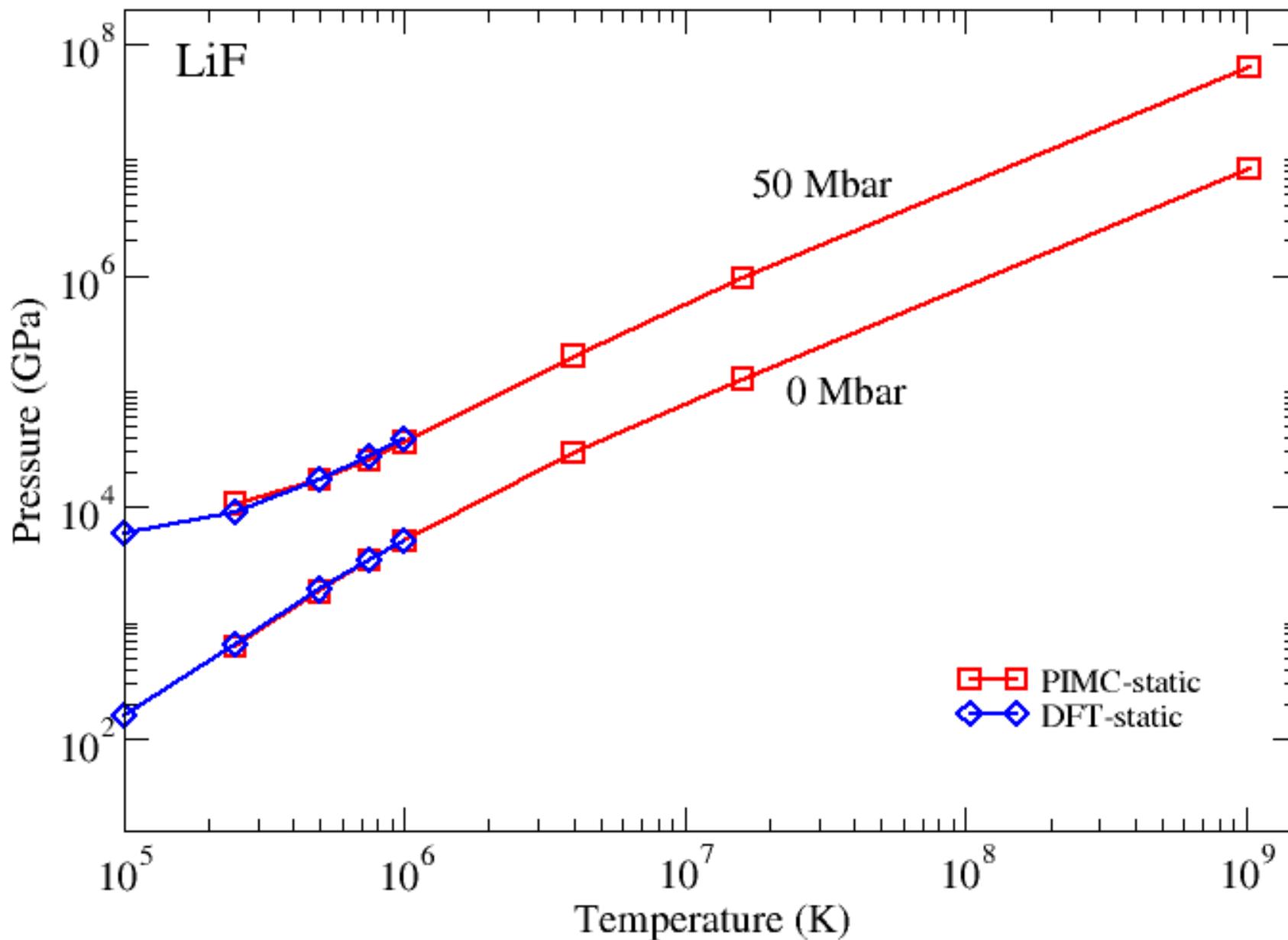


# Oxygen



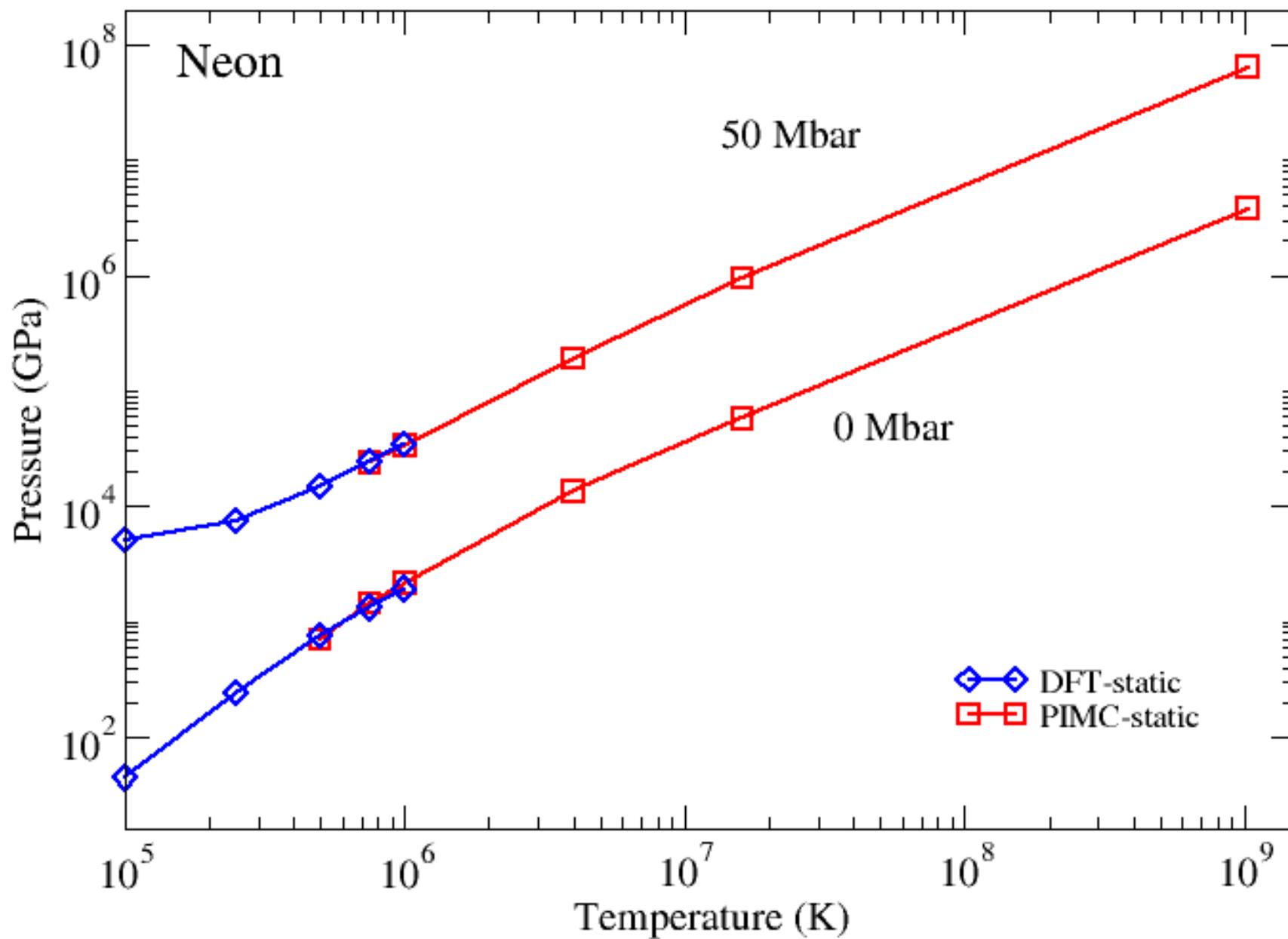


# Lithium Fluoride





# Neon





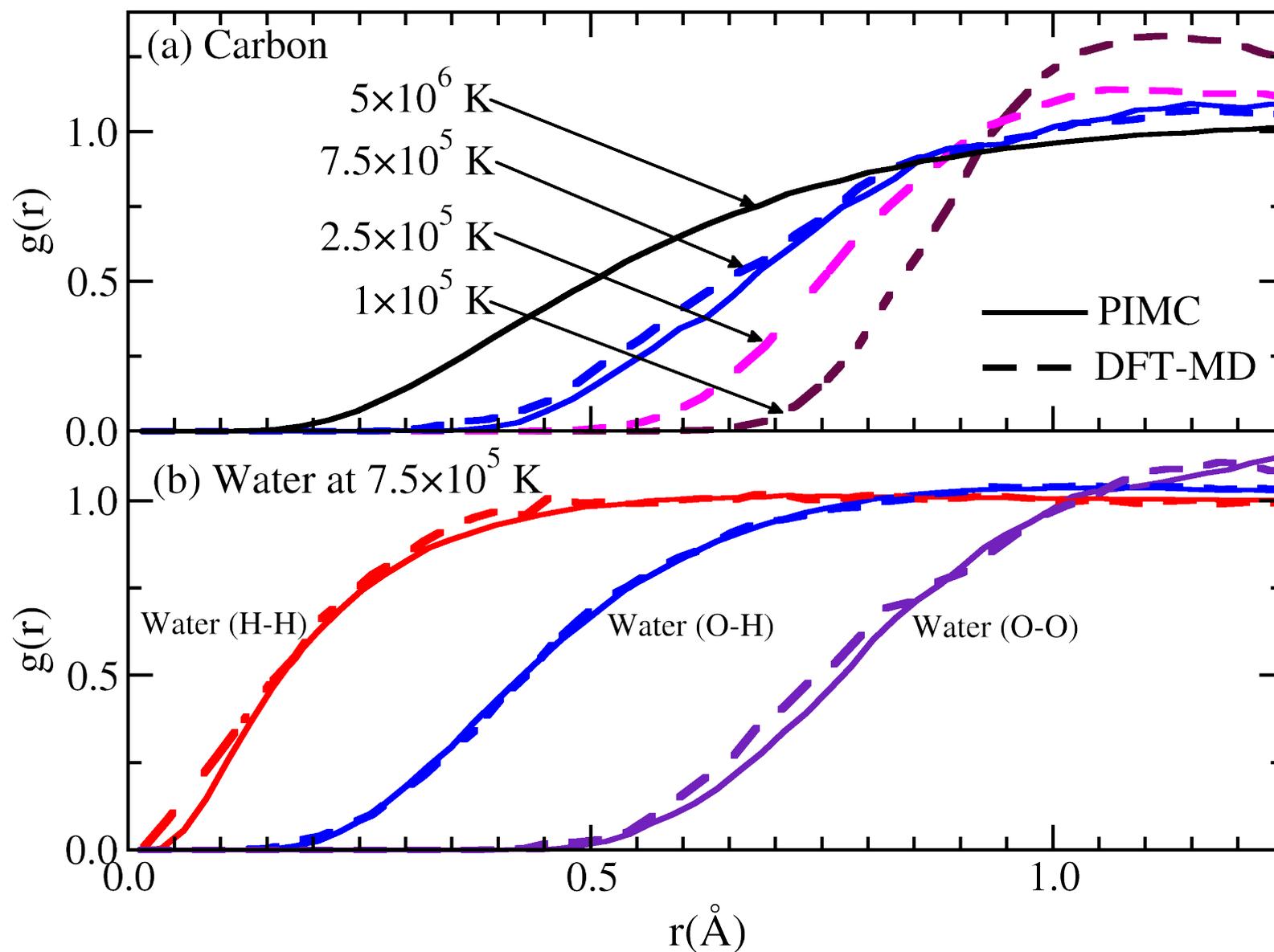
# Conclusions

- 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.

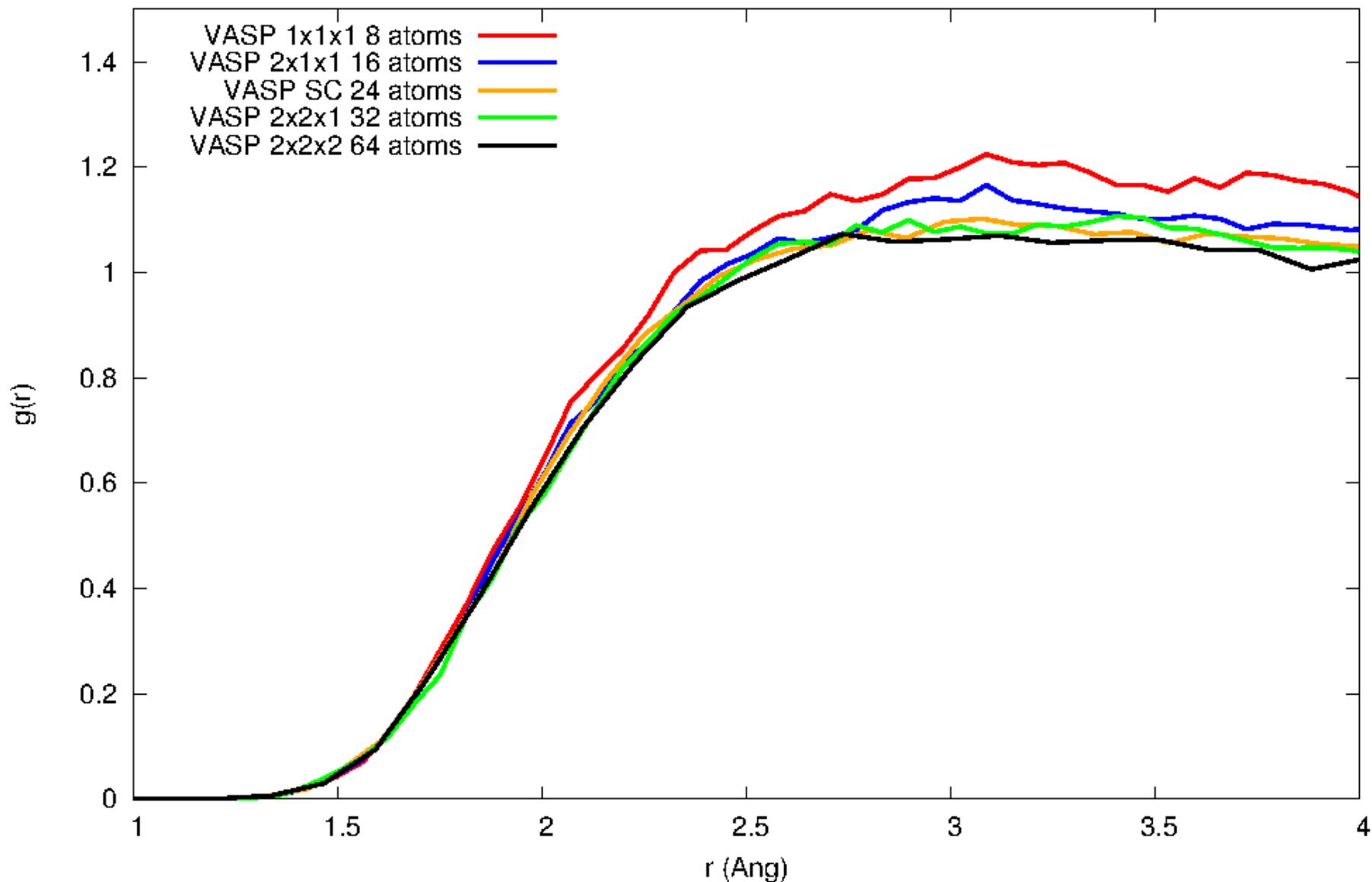
# Water and Carbon: Pair Correlation Functions



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

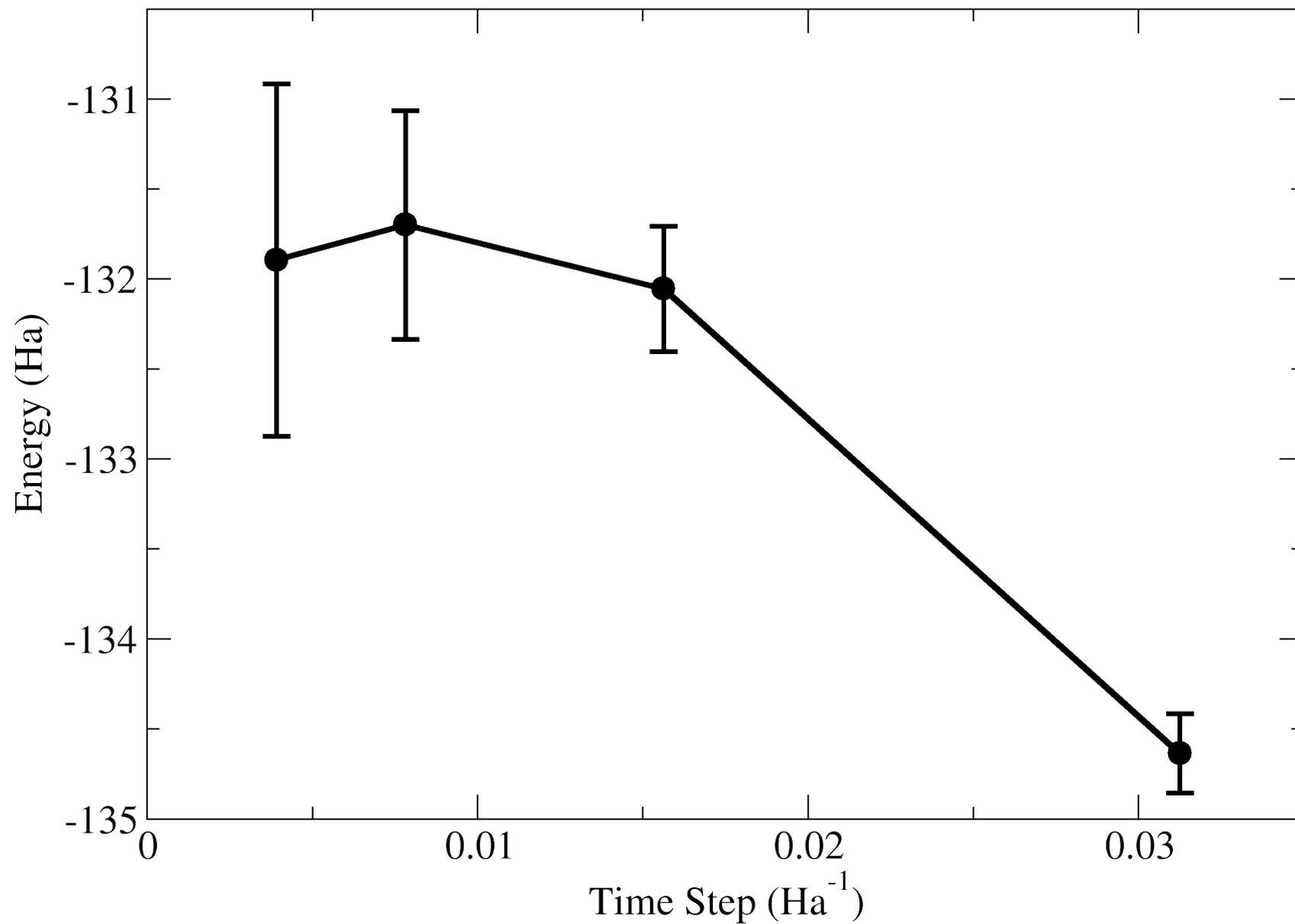
# DFT-MD cell-size convergence for pair-correlation function

1 Mbar Carbon at 100,000 K;  $g(r)$ ; VASP-MD size convergence



# PIMC Energy vs. Time Step

Carbon, 1 Mbar, 8-atom cell



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

