Thermodynamics of Liquid $MgSiO_3$ at High Pressure and Temperature

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1. Summary

- $MgSiO_3$ is one of the most abundant minerals on Earth's crust.
- Equation of state (EOS) fundametal to study planetary formation and evolution.
- Extreme conditions: ionization of electronic shells modify thermodynamic properties.
- Combining DFT-MD + PIMC we produce a consistent equation of state across a wide range of pressures and temperatures.

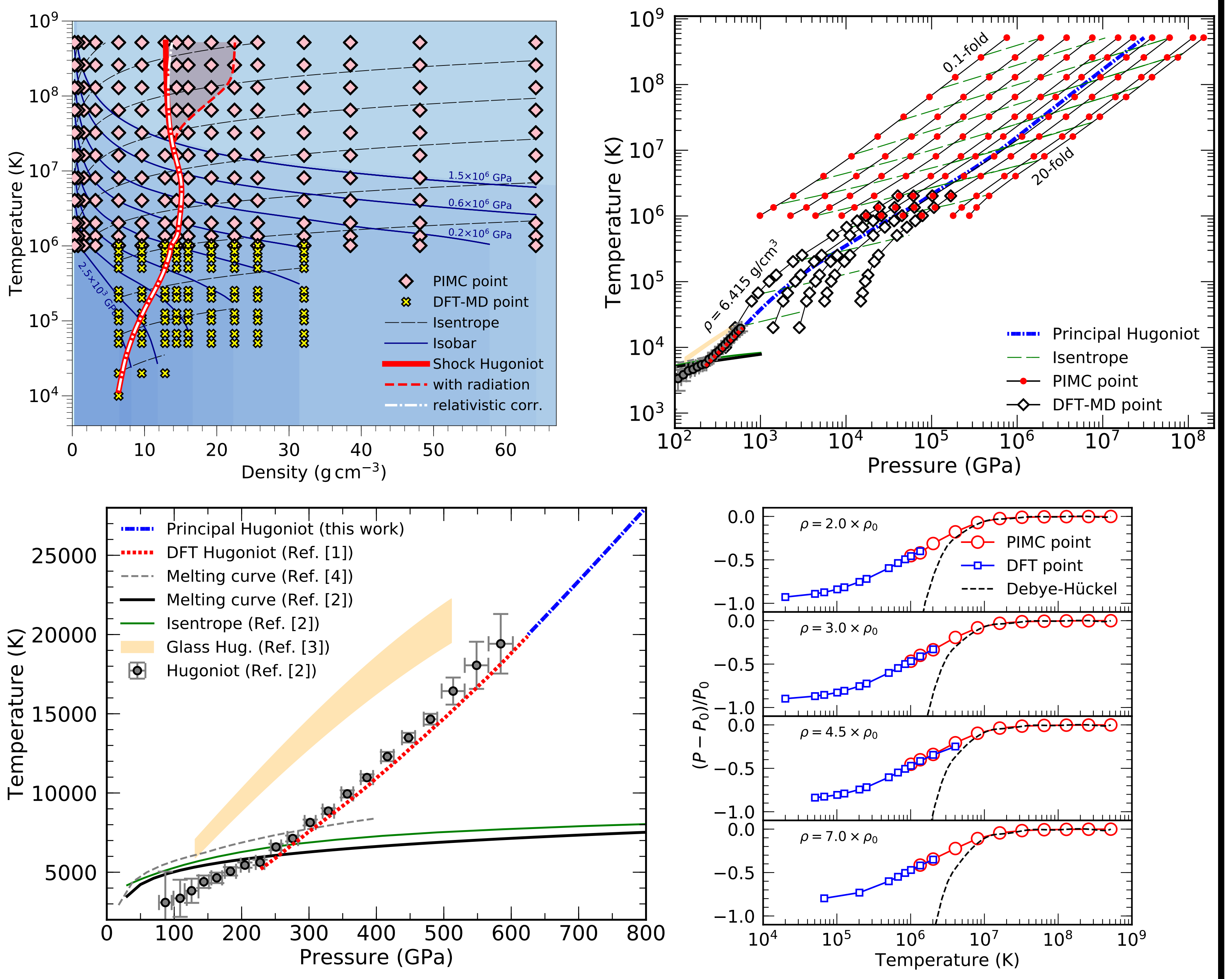

Figure 1: Temperature-density and temperature-pressure conditions of our DFT-MD and PIMC simulations along with computed isobars, isentropes and three principal shock Hugoniot curve that were derived for an initial density of $\rho_0 = 3.207911$ g cm^{-3} ($V_0 = 51.965073$ Å/f.u.). The red dashed line corresponds to the Hugoniot curve from Ref. [1], calculated from DFT-MD simulations. Experimental measurement of the principal Hugoniot curve from Ref. [2], an isentrope derived from this experiment (solid green line), and the Hugoniot curve for $MgSiO_3$ glass [3] (orange region) are shown for reference. The melting line of $MgSiO_3$ derived from two-phase simulations [4] is shown in dashed grey line, while the melting curve derived from shock experiments [2] is represented by the thick black line. Pressure normalized to the ideal Fermi gas pressure, P_0.

⇒ PIMC + DFT-MD: consistent EOS

⇒ Good agreement with the experimental shock Hugoniot curve.

⇒ Prediction of a maximum compression ratio of 4.7.

2. Ionization of K shell

Nuclear-electron pair correlation function:

$$N(r) = \left\langle \frac{1}{N_I}\sum_{e,I}\Theta(r - \|\vec{r}_e - \vec{r}_I\|)\right\rangle, \qquad (1)$$

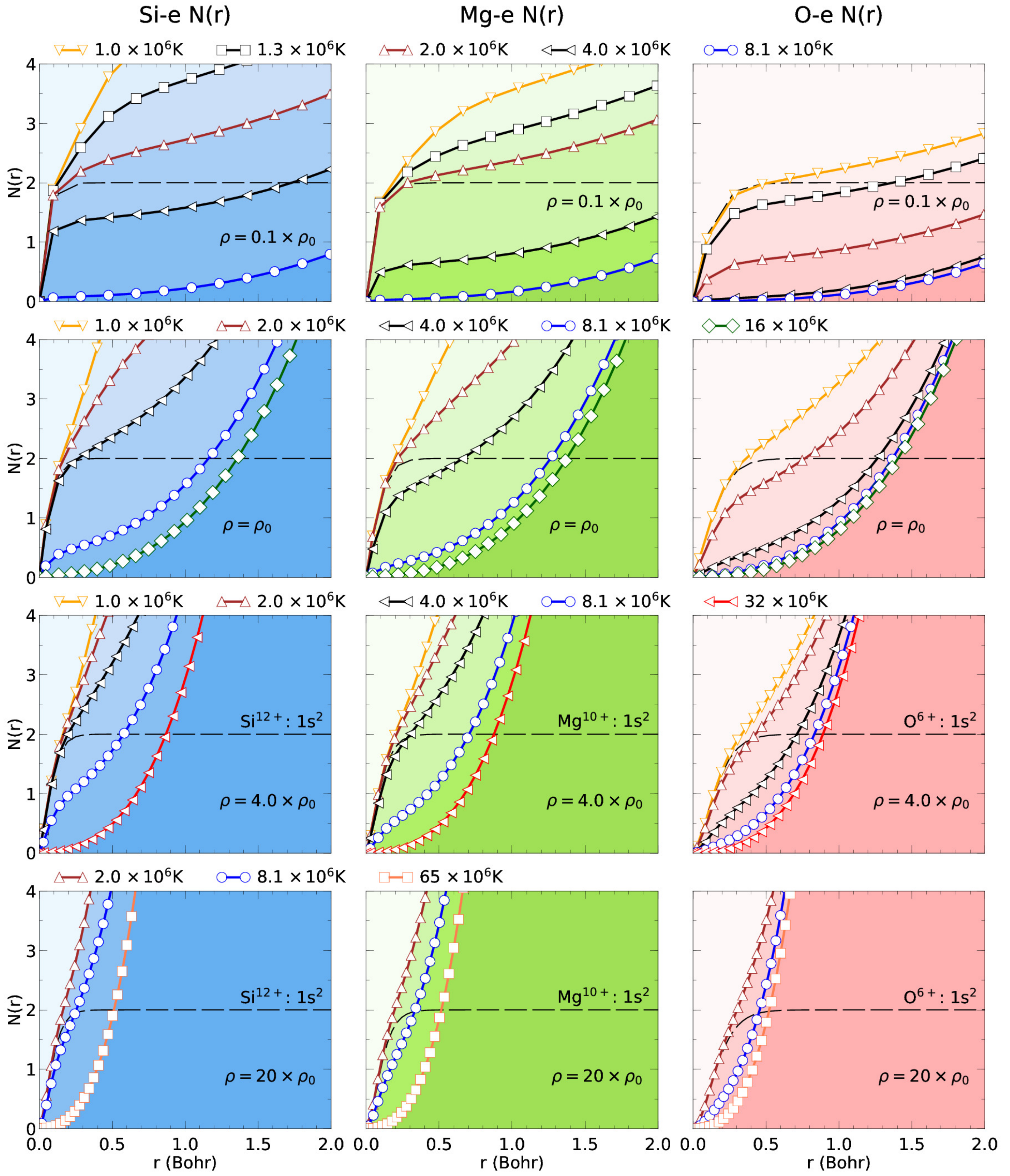

Figure 2: $N(r)$ functions for Mg, Si, and O atoms in the $MgSiO_3$ system.

Effects of ionization in the heat capacity, $C_v = (\partial E/\partial T)_V$, and Grüneisen parameter, $\gamma = V\,(\partial P/\partial E)_V = \frac{V}{C_V}\,(\partial P/\partial T)_V$,

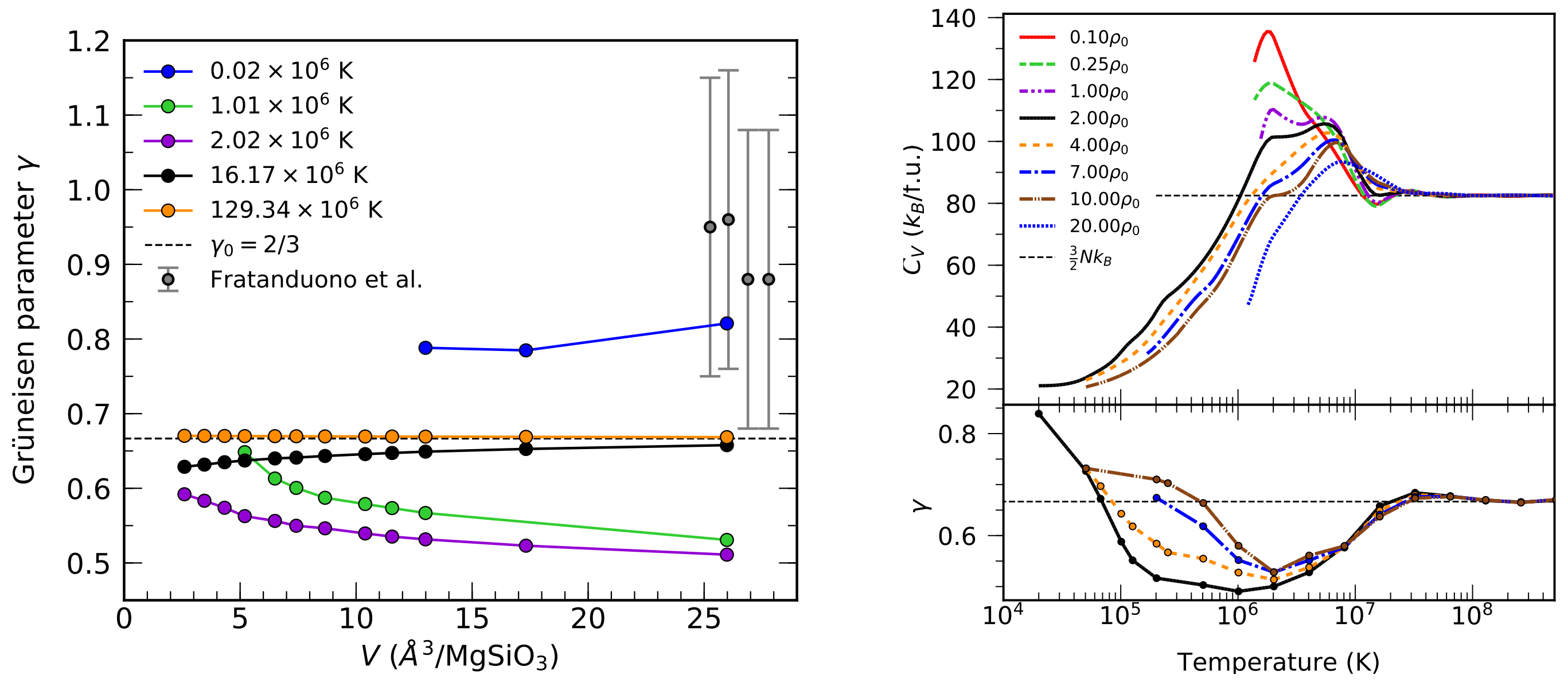

Figure 3: Grüneisen parameter, γ, and heat capacity, C_v as a function of temperature.

3. Hugoniot curves

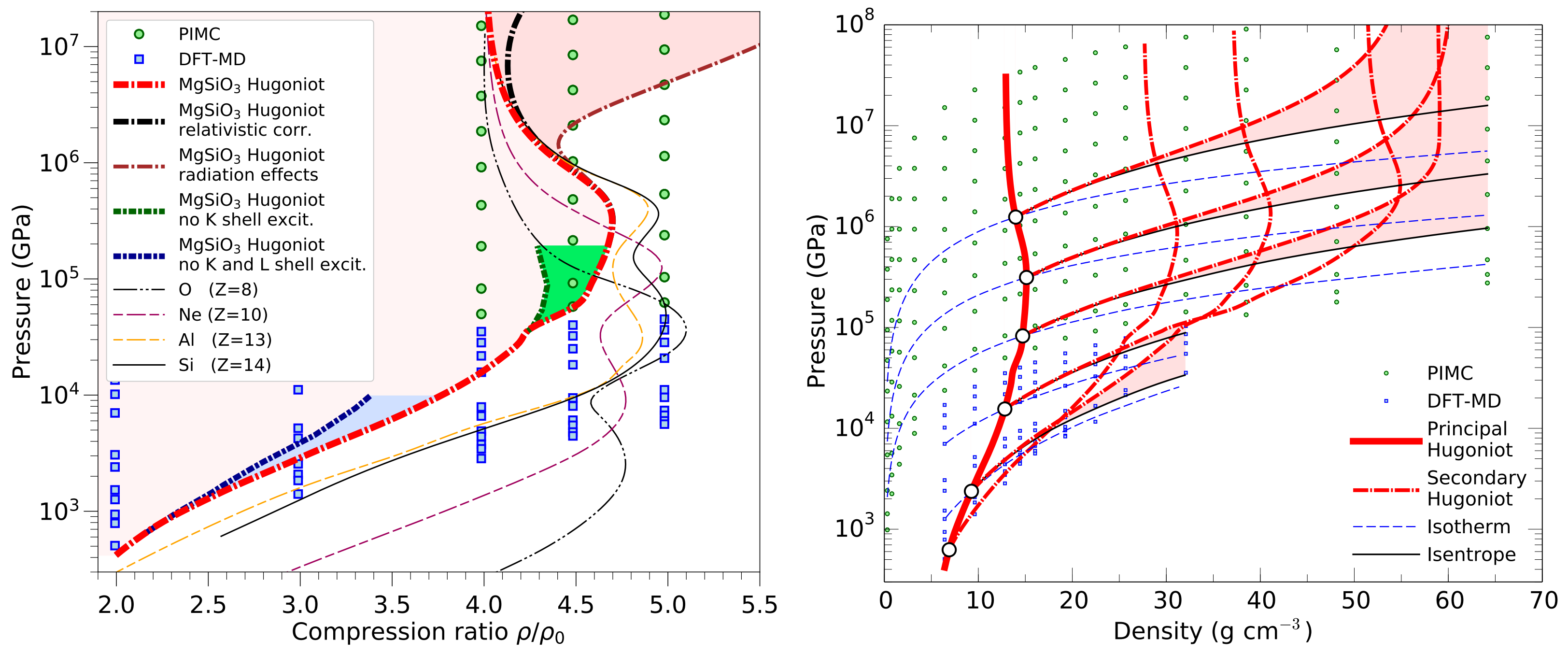

Figure 4: Principal Hugoniot curve, with and without electronic excitations, compared to other materials. Secondary shocks are compared to isentropes, providing a guide for ramp compression experiments.

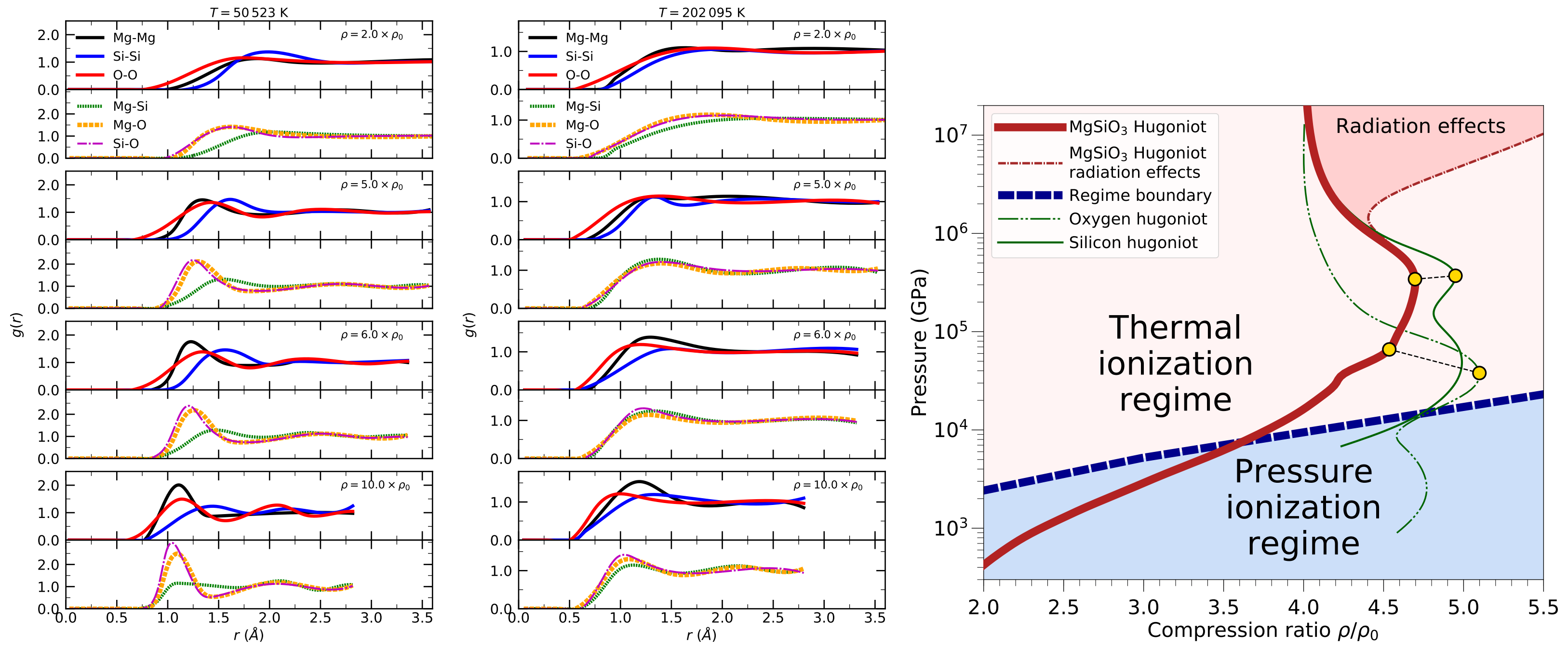

Figure 5: Pair distribution function, $g(r)$, at 5×10^4 K and 2×10^5 K for different densities. Pressure ionization regime determined by $\frac{dE}{dV}\big|_V = 0$ (equiv. to $P/T = (\partial P/\partial T)_V$).

4. Conclusions

1. Hugoniot curve: good agreement with experiments.
2. Consistent EOS (DFT-MD + PIMC).
3. Maximum shock compression ratio: 4.7 (5.13×10^6 K and 3.01×10^5 GPa).
4. No L shell ionization peak.
5. Ramp compression: secondary shocks close to isentropes.
6. Full K shell ionization consistent with ideal gas limit.
7. PBE functional can accurately describe $MgSiO_3$ up to temperatures of $\sim10^6$ K.

References

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