Thermodynamics of Liquid $MgSiO_3$ at High Pressure and Temperature

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Abstract

Studying the properties of the liquid phase of minerals at high pressure is important to understand the structure and evolution of deep magma oceans, as well as guiding high pressure experiments that reach the conditions in the interiors of rocky planets. We use density functional theory molecular dynamics (DFT-MD) and path integral Monte Carlo (PIMC) simulations to generate a consistent equation of state (EOS) for liquid MgSiO3 that spans across a wide range of temperatures and pressures. We study its thermodynamic properties, such as the heat capacity, and characterize the atomic structure of the liquid. From our simulations, we are able to determine the onset of ionization of the inner electronic shells and relate the thermodynamic properties to the electronic structure. Finally, in order to guide future ramp and shock compression experiments, we derive isentropic temperature-pressure profiles and calculate the shock Hugoniot curve, which is in good agreement with existing experimental data.

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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.

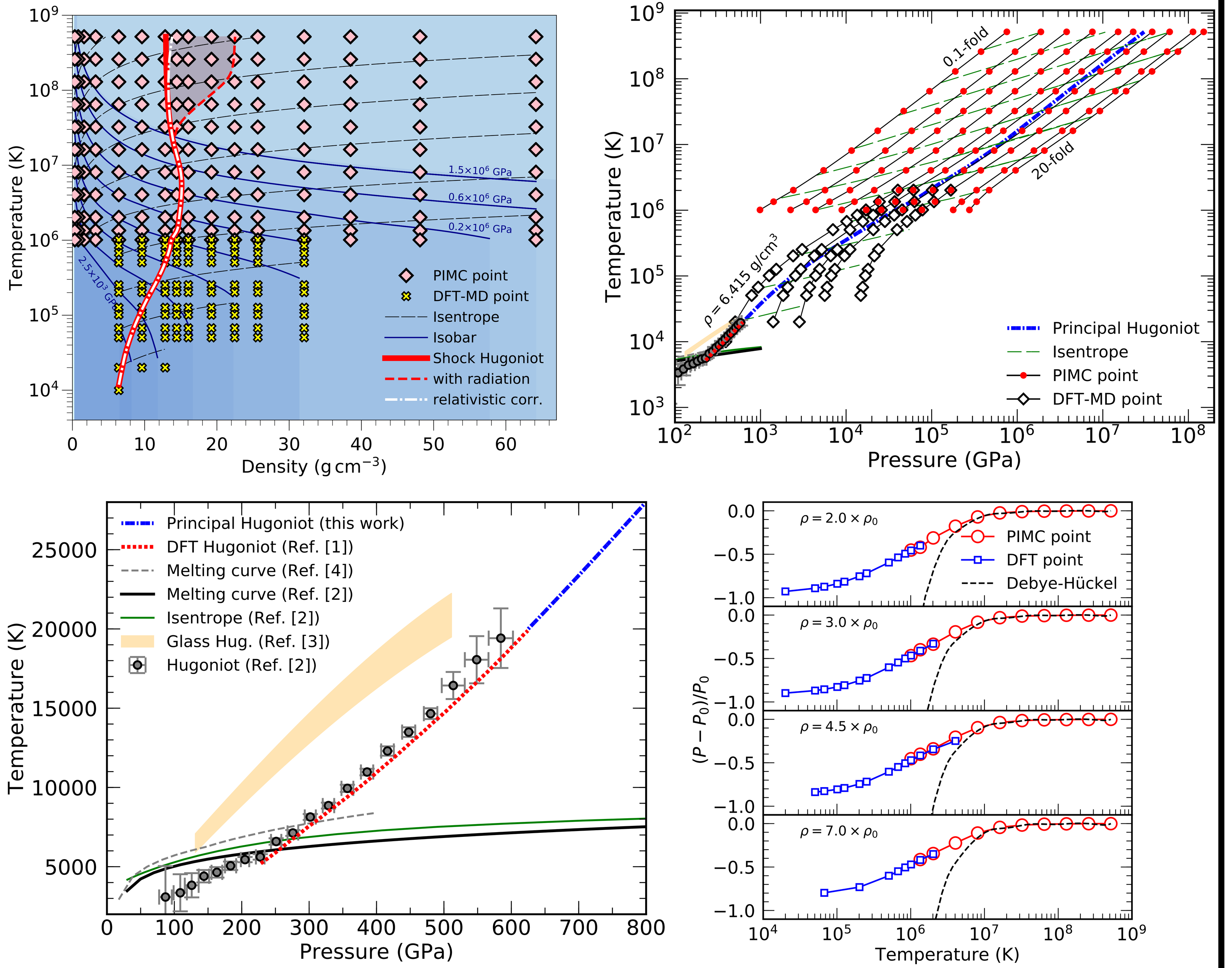

Figure 1: Temperature-density and temperature-pressure conditions of our DFT-MD and PIMC simulations along with computed isobars, isentropes and three principal shock Hugoniot curve that were derived for an initial density of $\rho_0 = 3.207911$ g cm^{-3} ($V_0 = 51.965073$ Å/f.u.). The red dashed line 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:

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

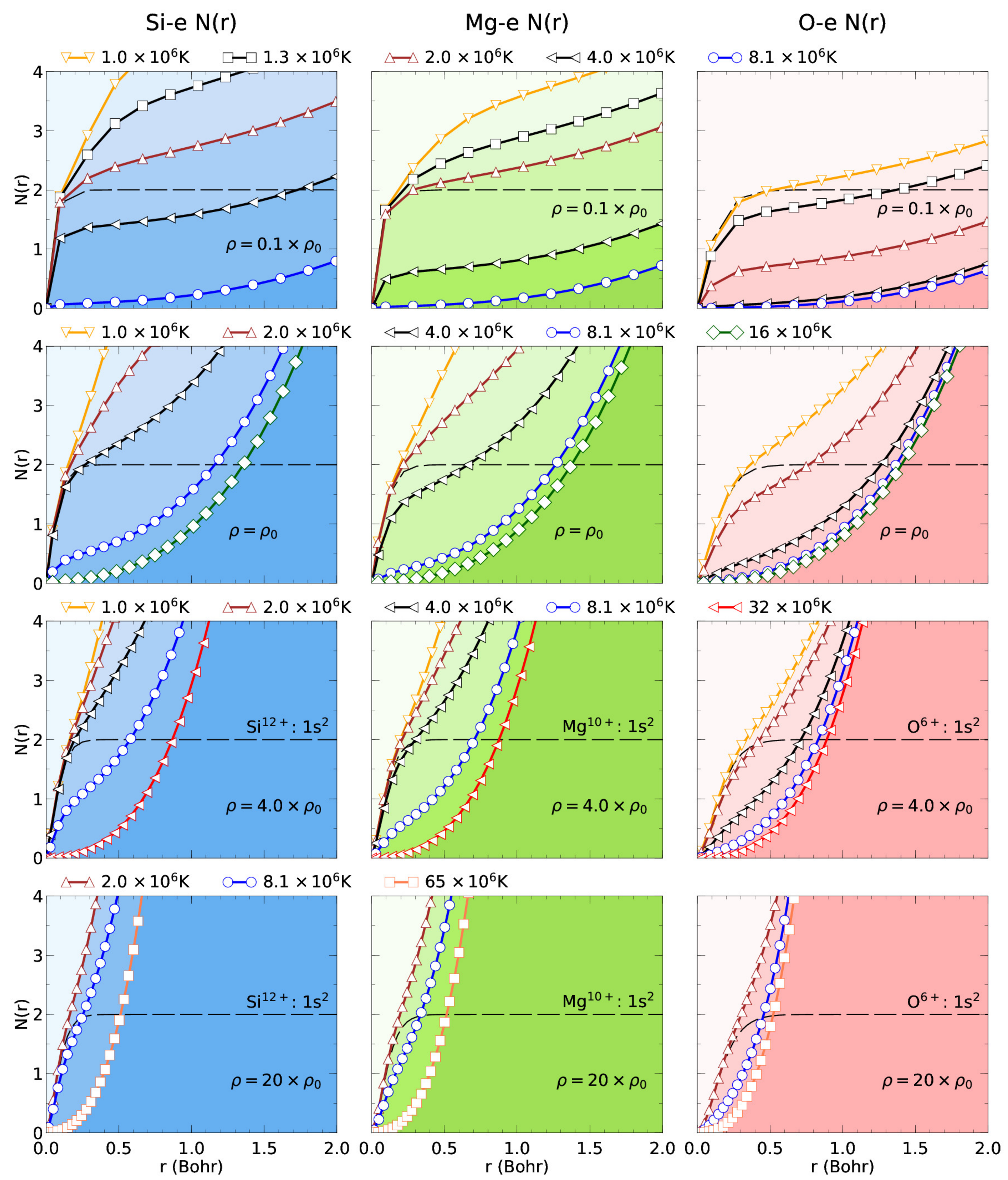

Figure 2: $N(r)$ functions for Mg, Si, and O atoms in the $MgSiO_3$ system.

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

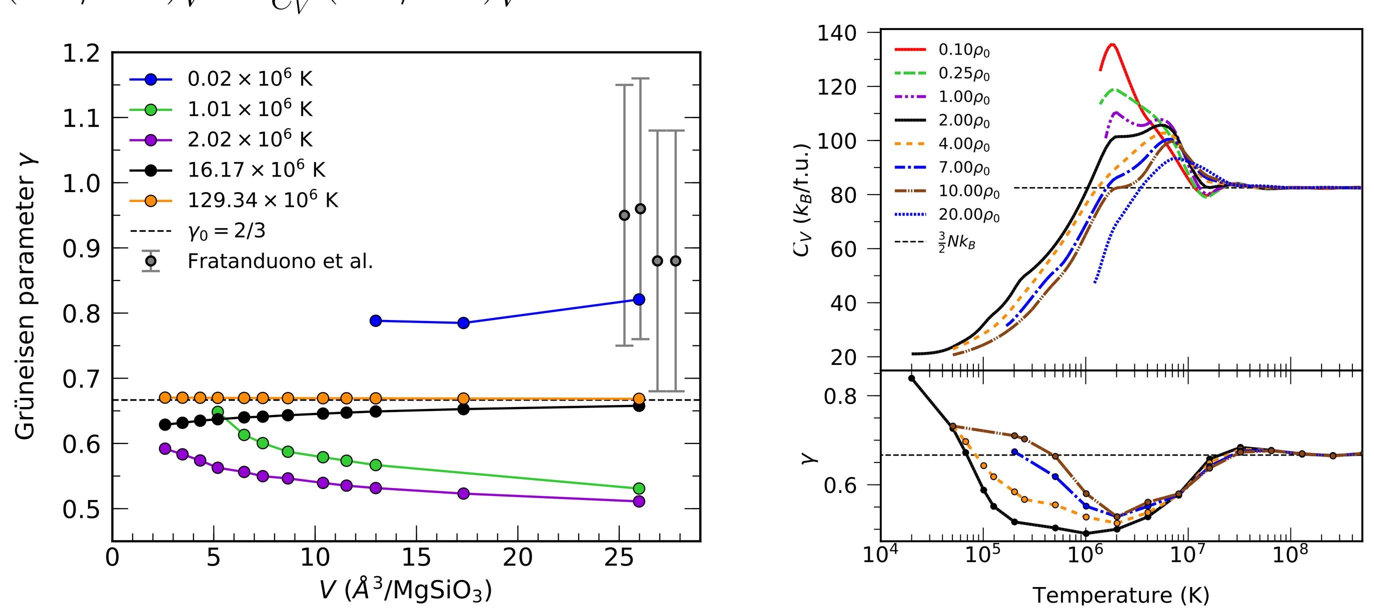

Figure 3: Grüneisen parameter, γ, and heat capacity, C_v as a function of temperature.

3. Hugoniot curves

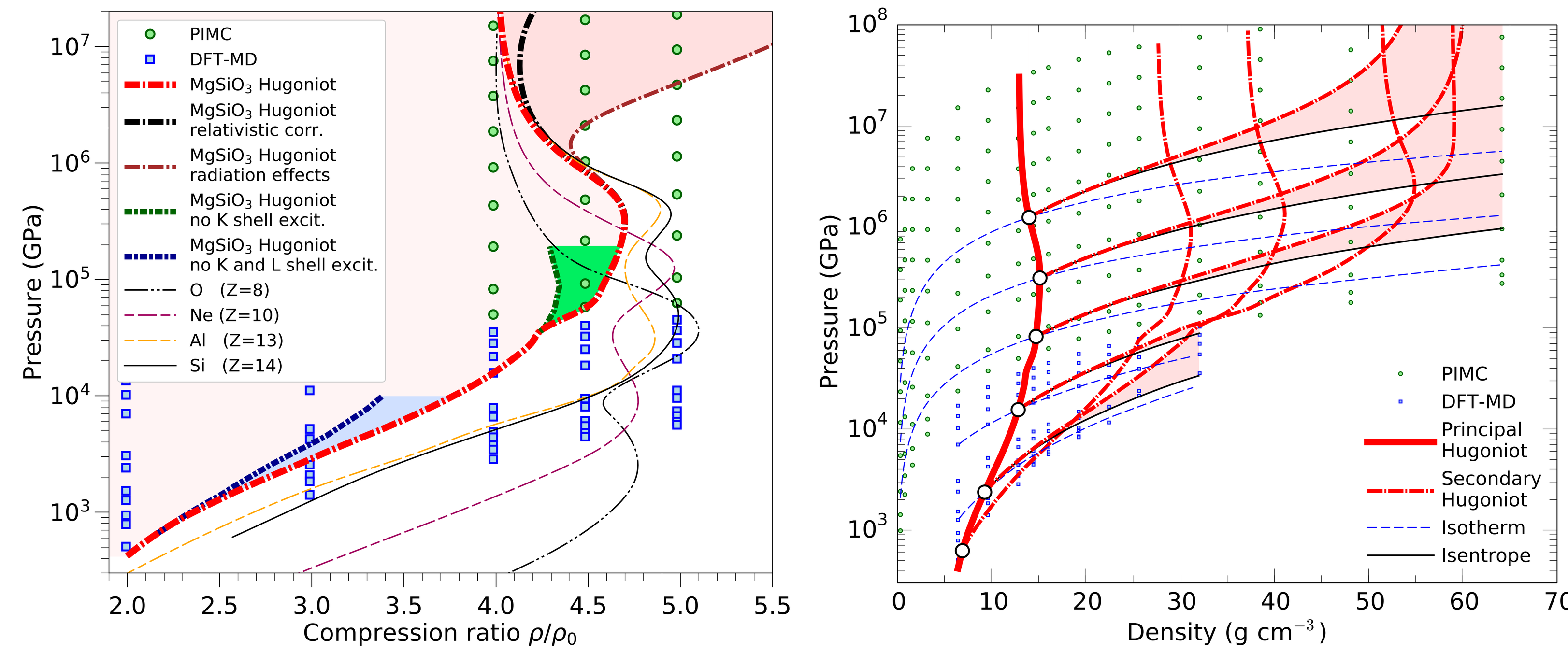

Figure 4: Principal Hugoniot curve, with and without electronic excitations, compared to other materials. Secondary shocks are compared to isentropes, providing a guide for ramp compression experiments.

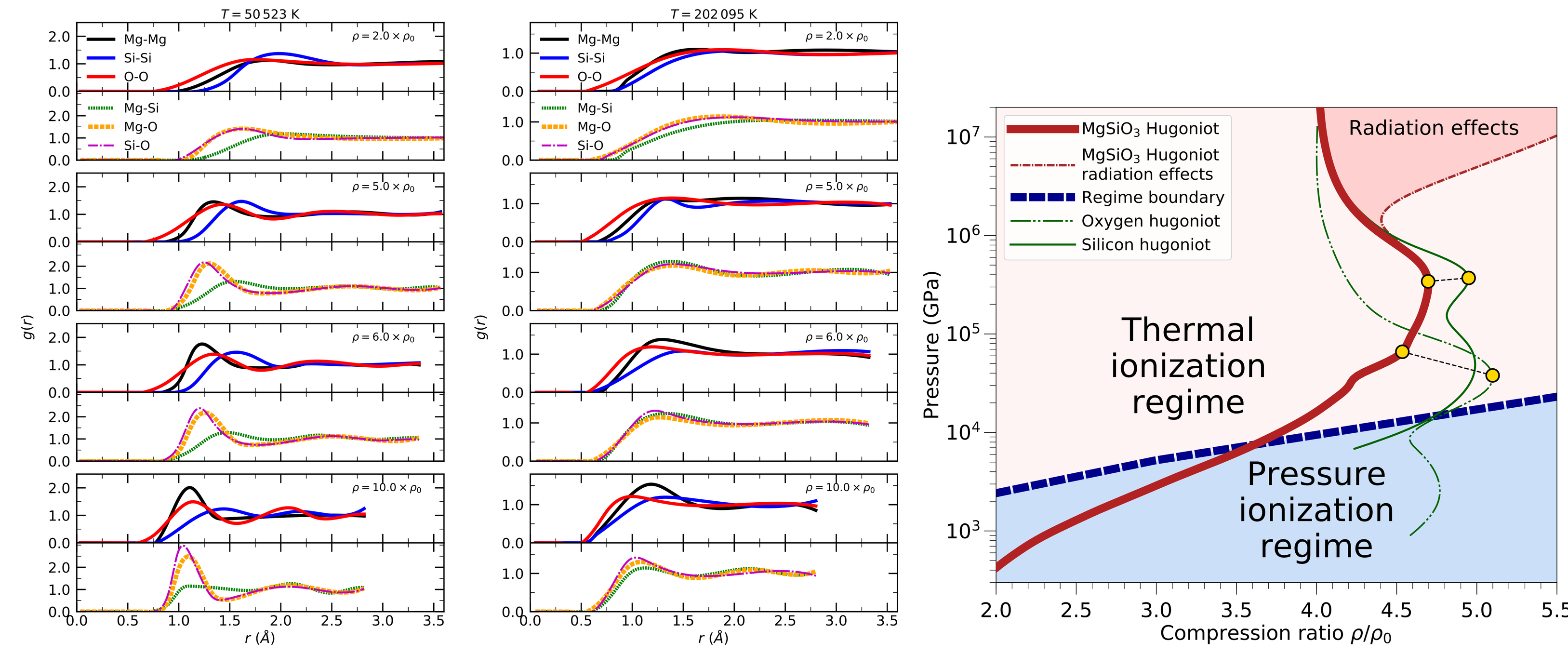

Figure 5: Pair distribution function, $g(r)$, at 5×10^4 K and 2×10^5 K for different densities. Pressure ionization regime determined by $\frac{dE}{dV}|_V = 0$ (equiv. to $P/T = (\partial P/\partial T)_V$).

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 $\sim 10^6$ K.

References

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