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SAND2019-15183C

Liquid-vapor coexistence and critical point of Mg_2SiO_4 from *ab-initio* simulations

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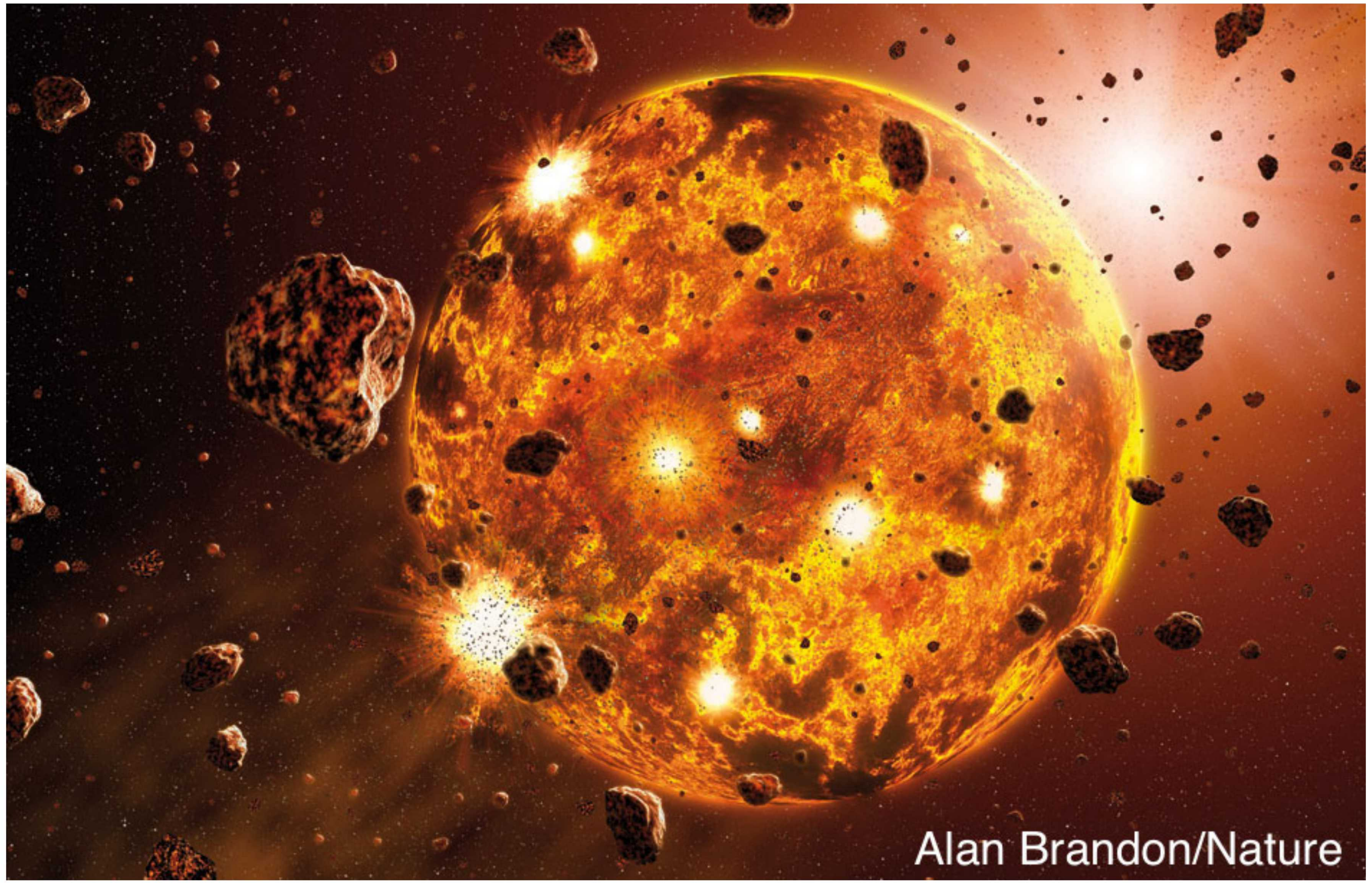
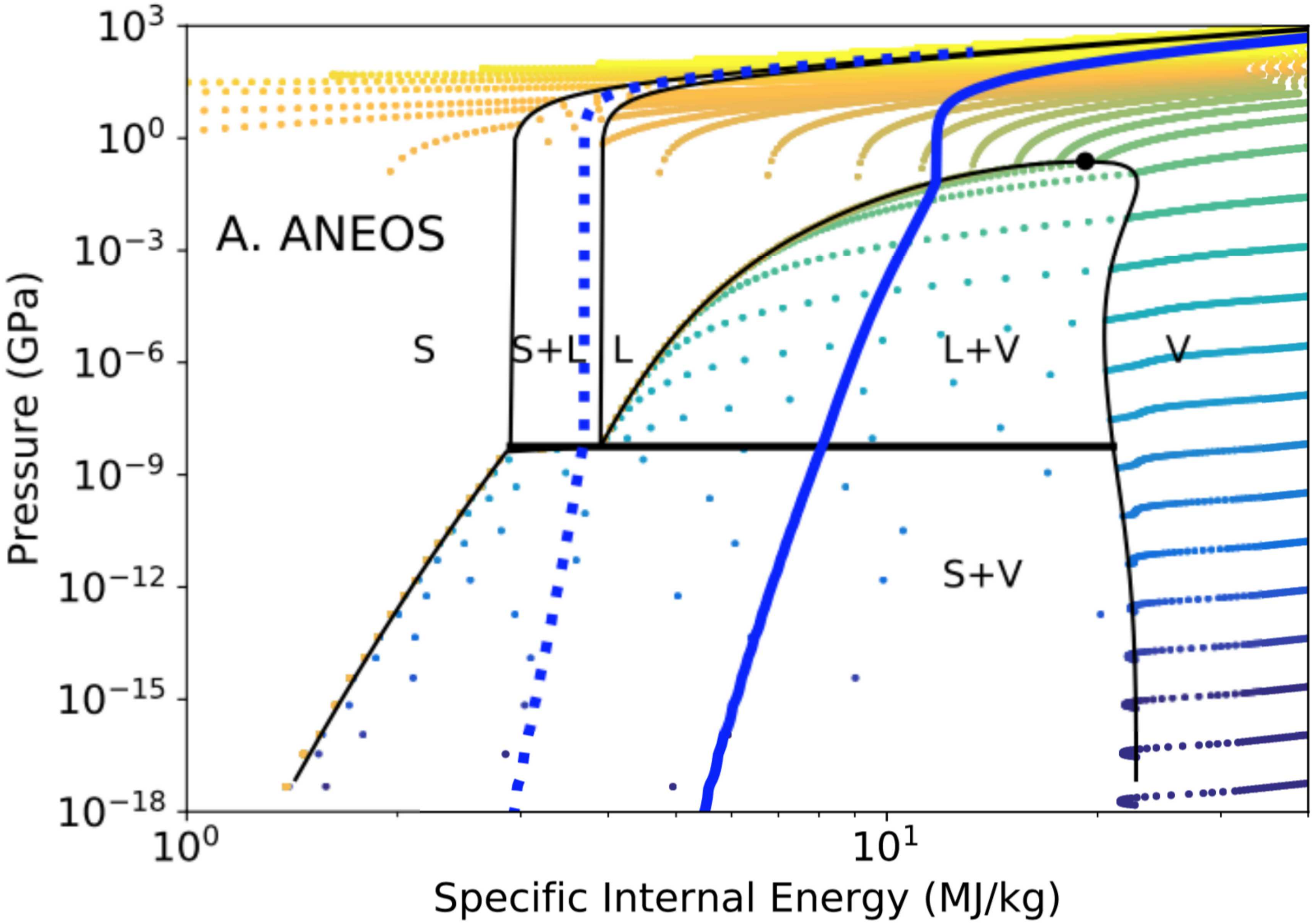
Advance planetary accretion models





Stewart et al., 2019

Extant EOS models rely on simplified models.
But, critical behavior mostly unconstrained.

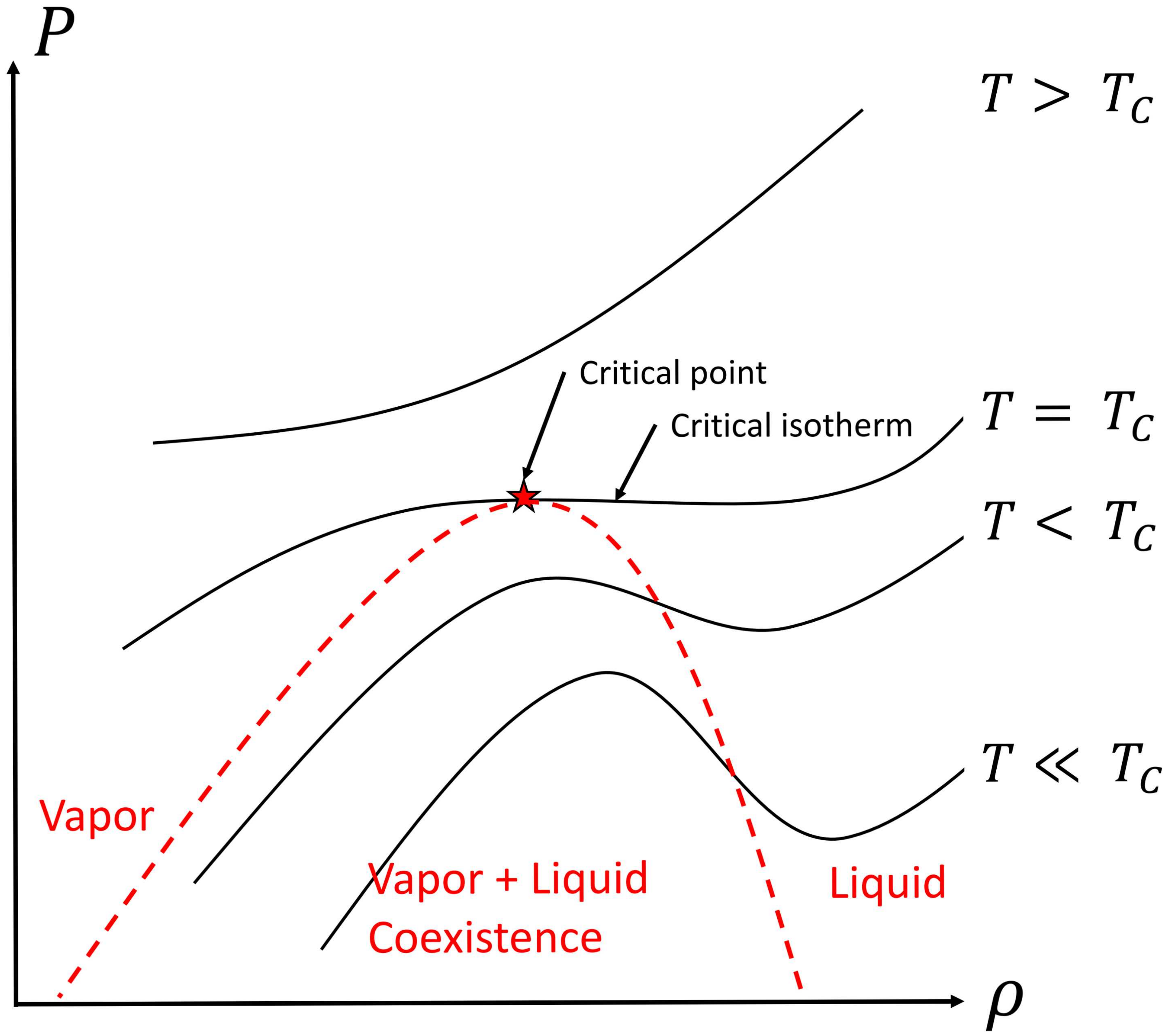
Computational Approach

Simplest EOS with a critical point:

$$P(\rho, T) = a(T) + b(T)\rho + c(T)\rho^2 + d(T)\rho^3$$

At the critical point:

$$\left(\frac{\partial P}{\partial \rho}\right)_T = \left(\frac{\partial^2 P}{\partial \rho^2}\right)_T = 0$$

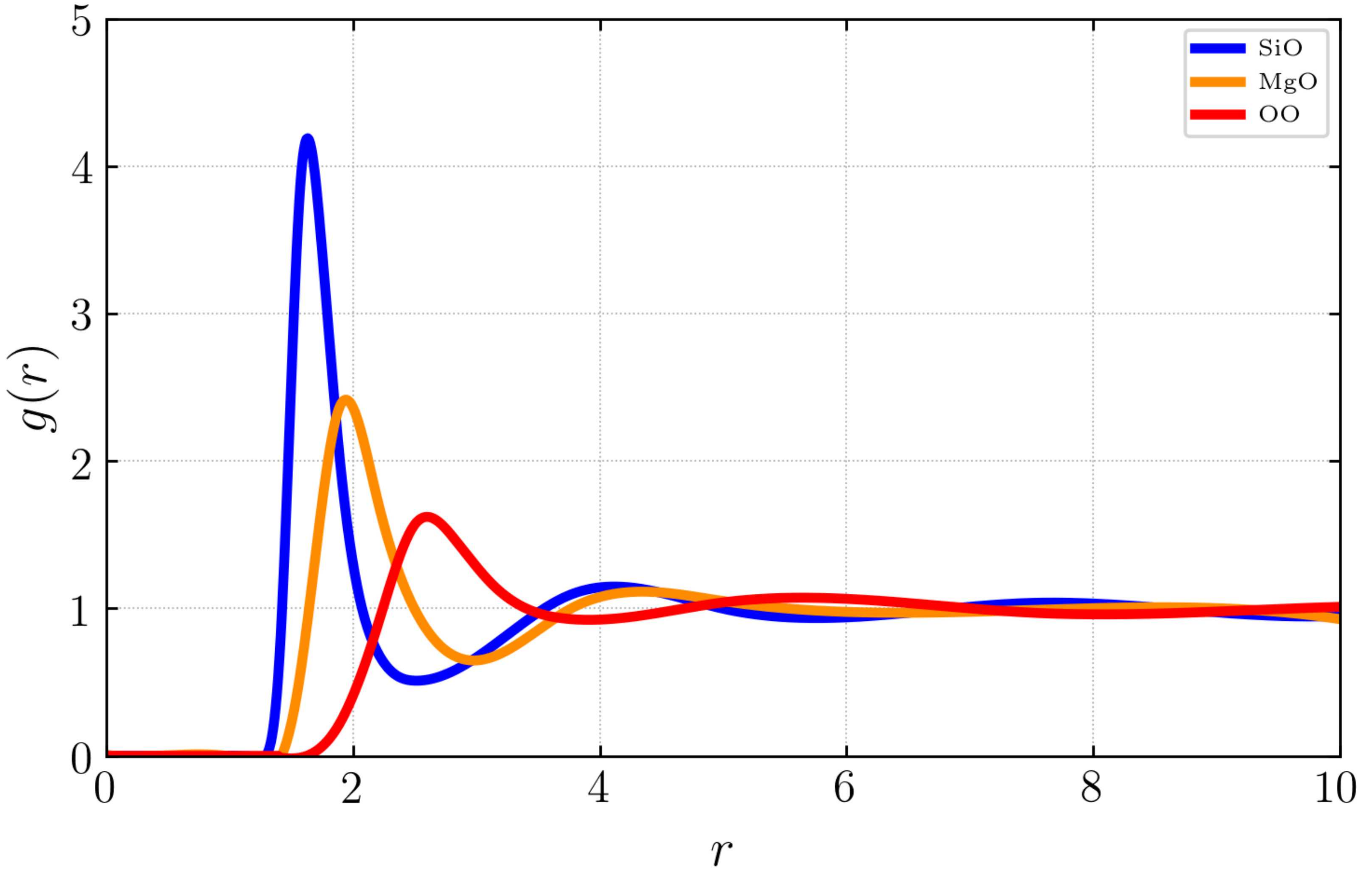


DFT-MD Approach:

- **VASP + PAW's**
- **Mermin functional**
- **NVT with N=28/56/112**
- **PBE xc functional**

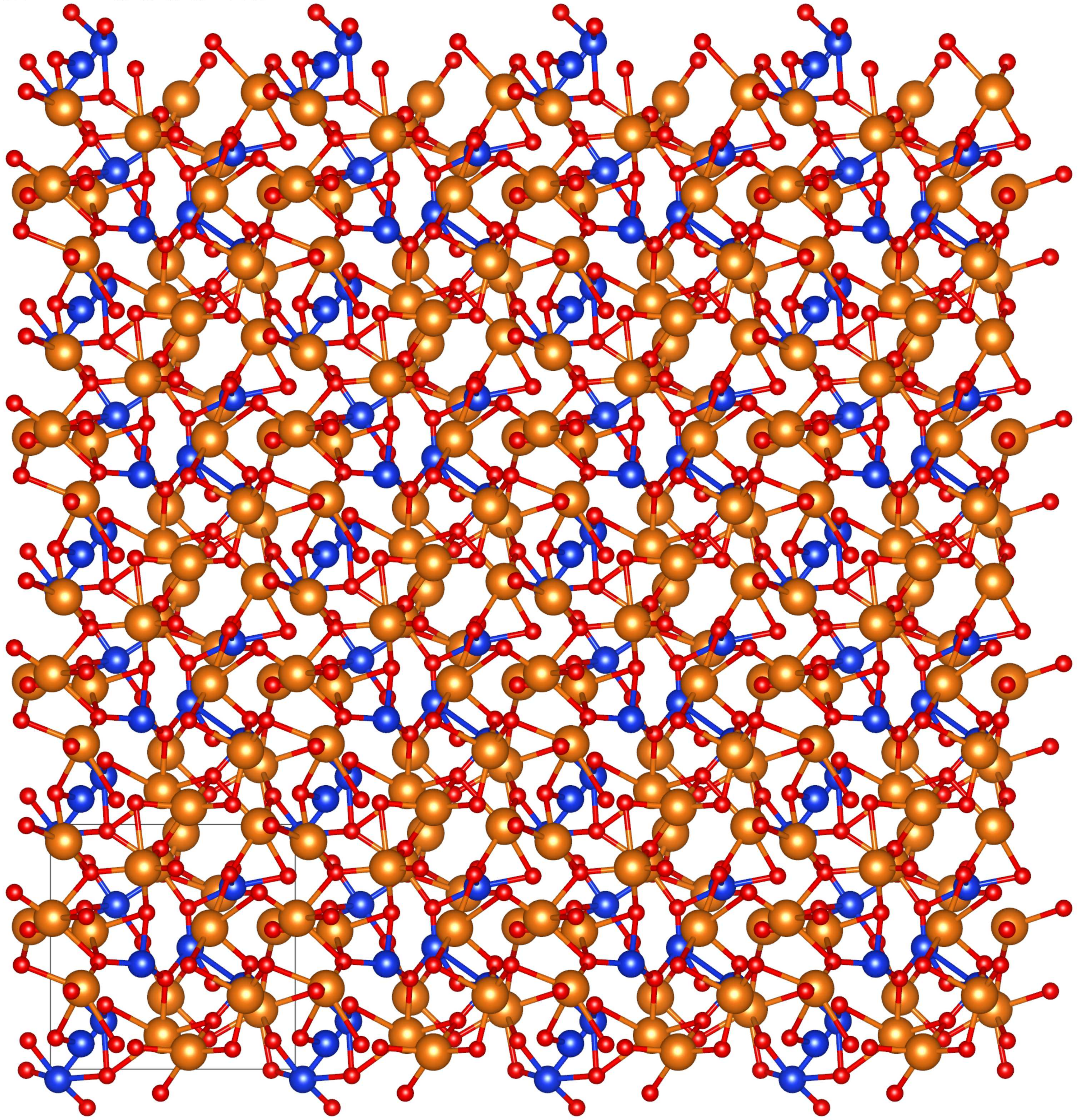
Continuous structural evolution

Single fluid phase



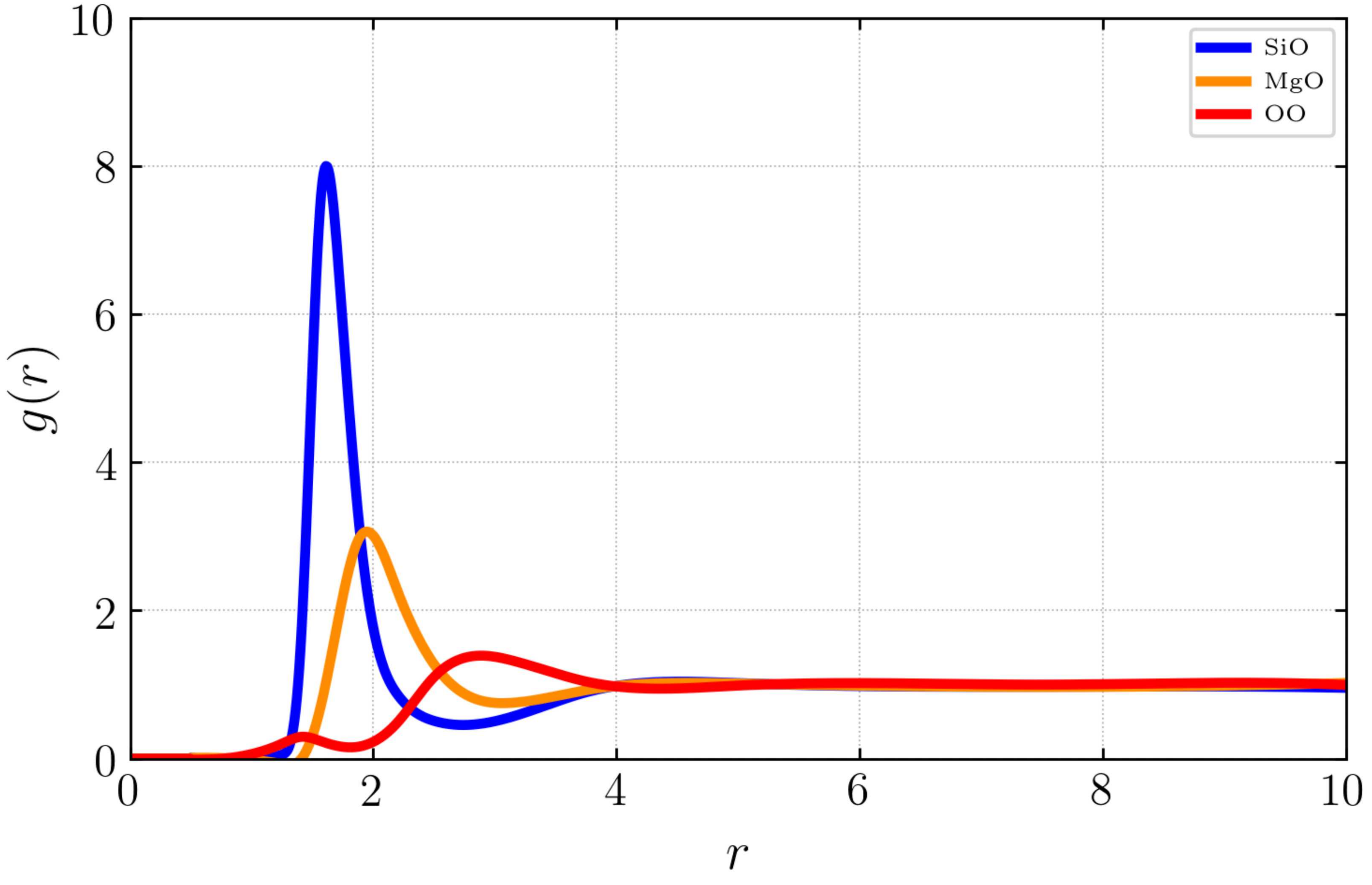
$\rho = 3.22$ g/cc

$T = 6000$ K



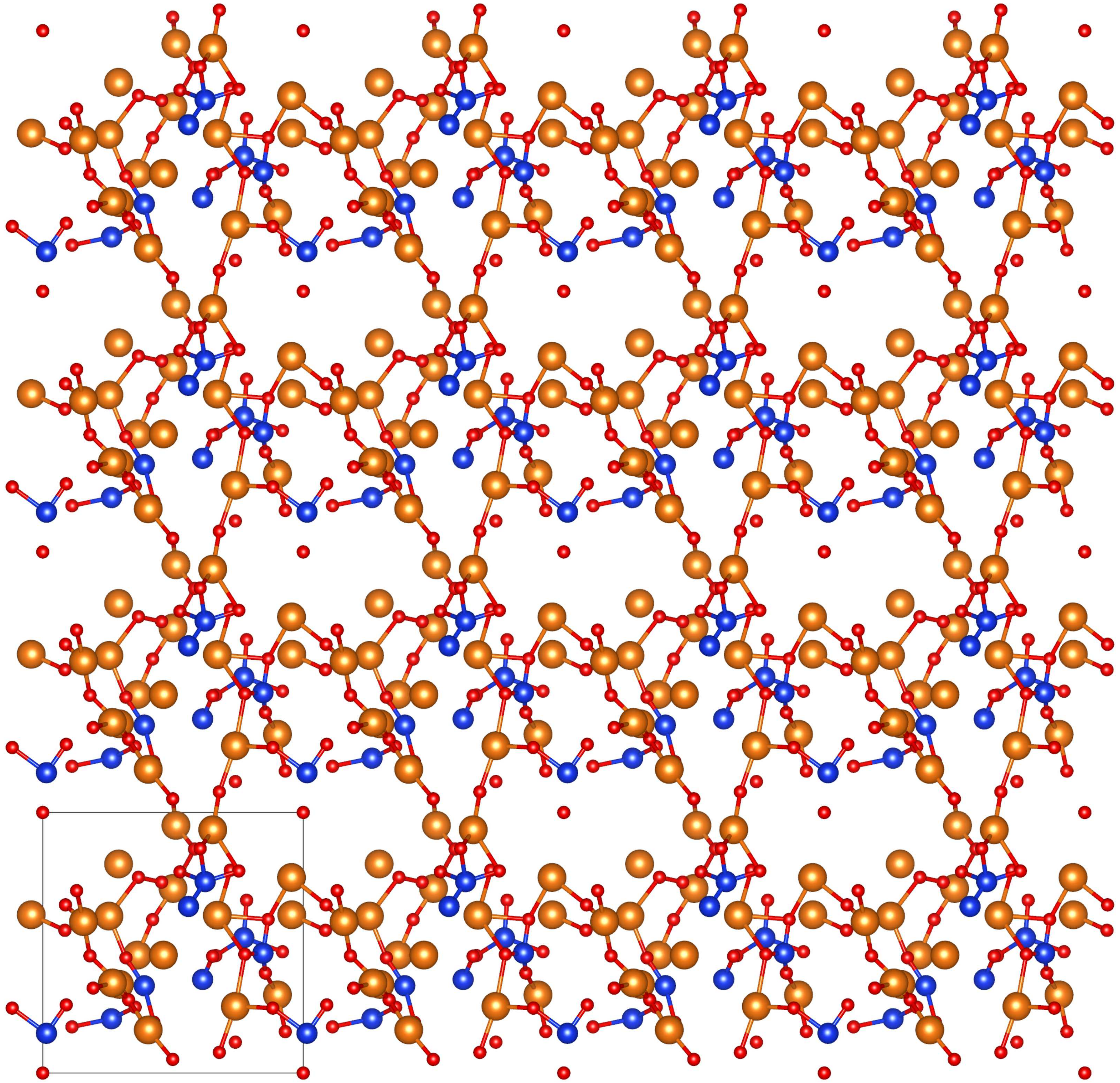
Continuous structural evolution

Onset of vaporization



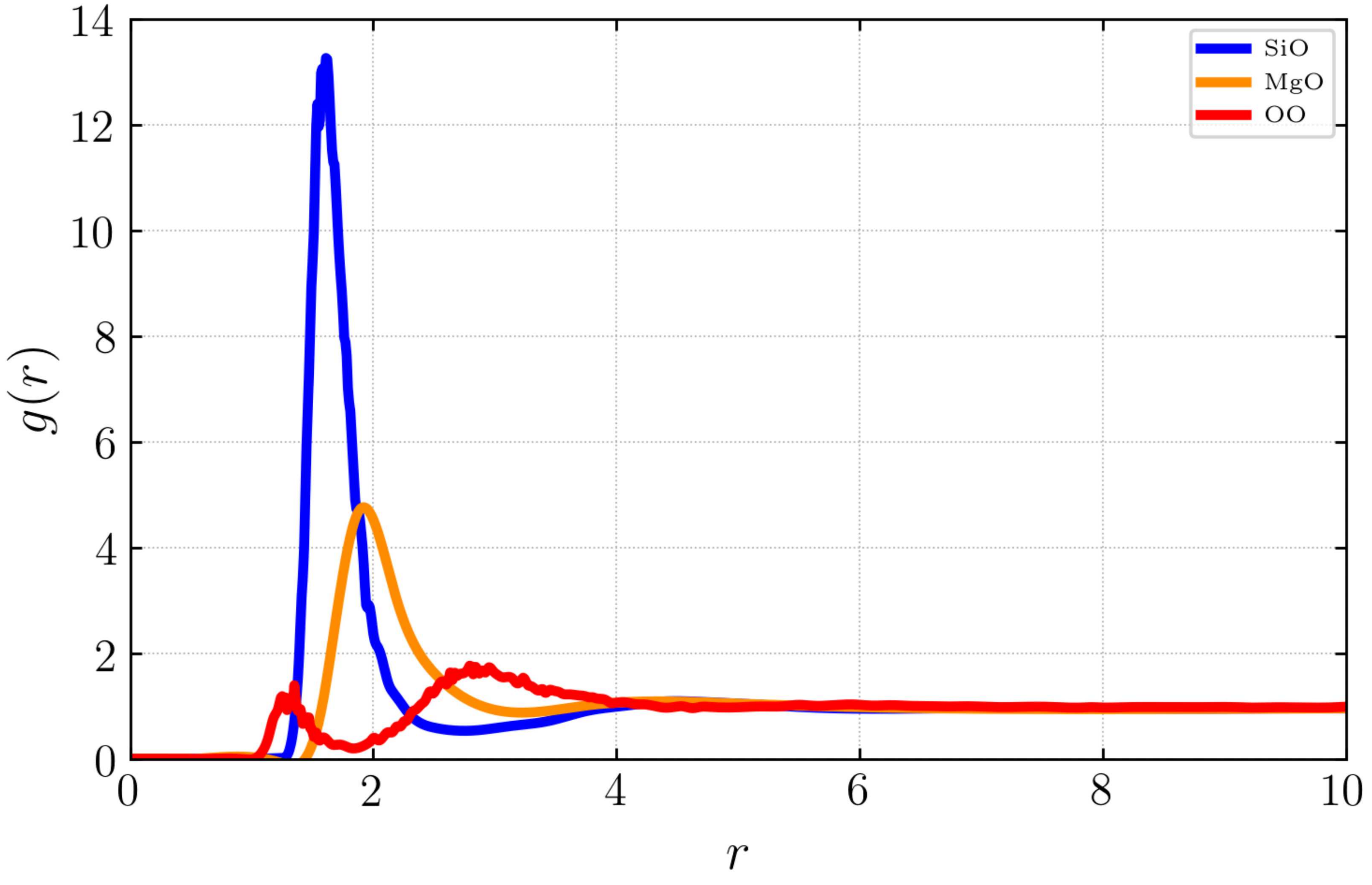
$\rho = 1.22$ g/cc

$T = 6000$ K



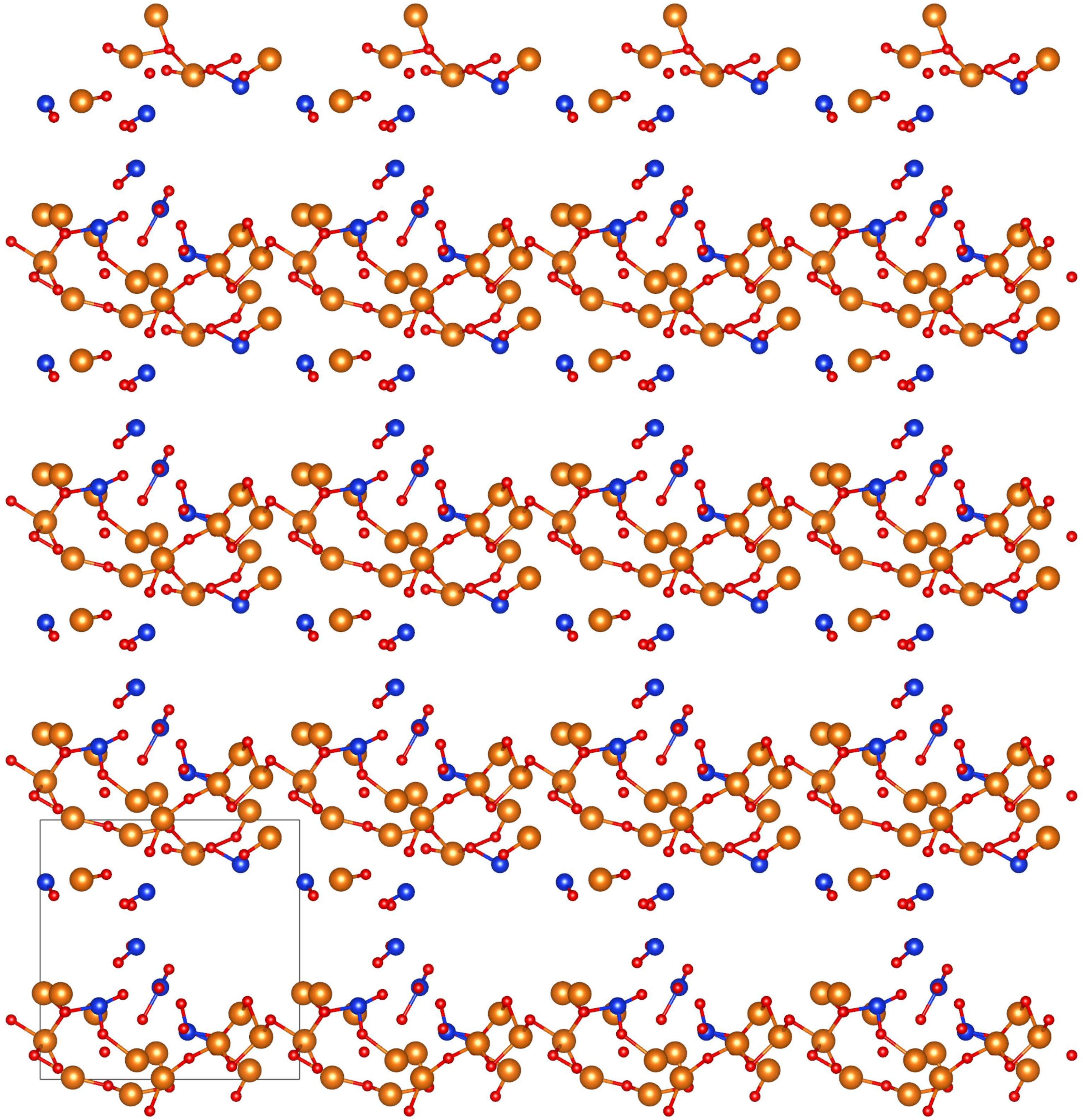
Continuous structural evolution

Coexistence of L + V (incongruent)



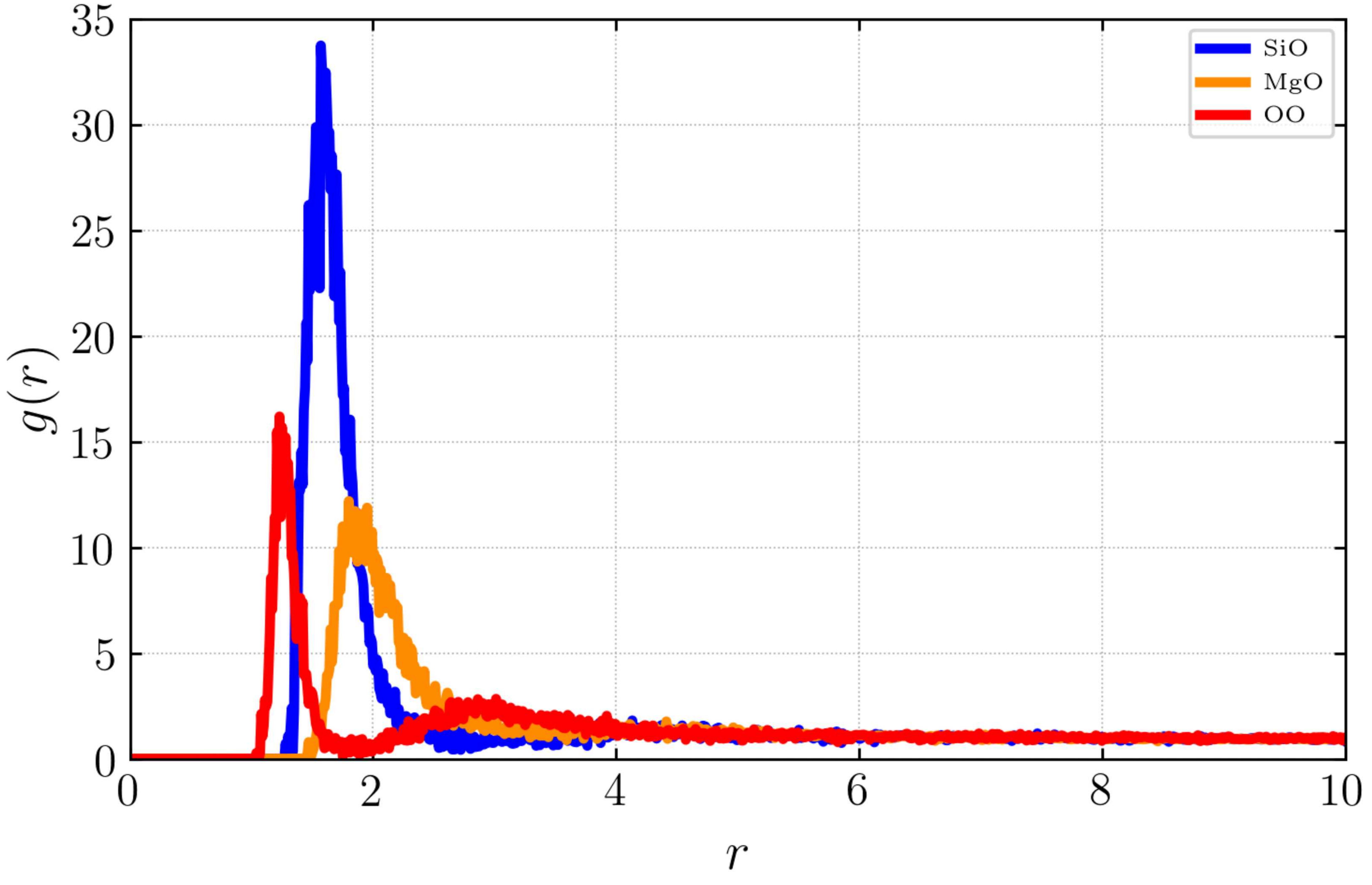
$\rho = 0.72\ \mathrm{g/cc}$

$T = 6000\ \mathrm{K}$

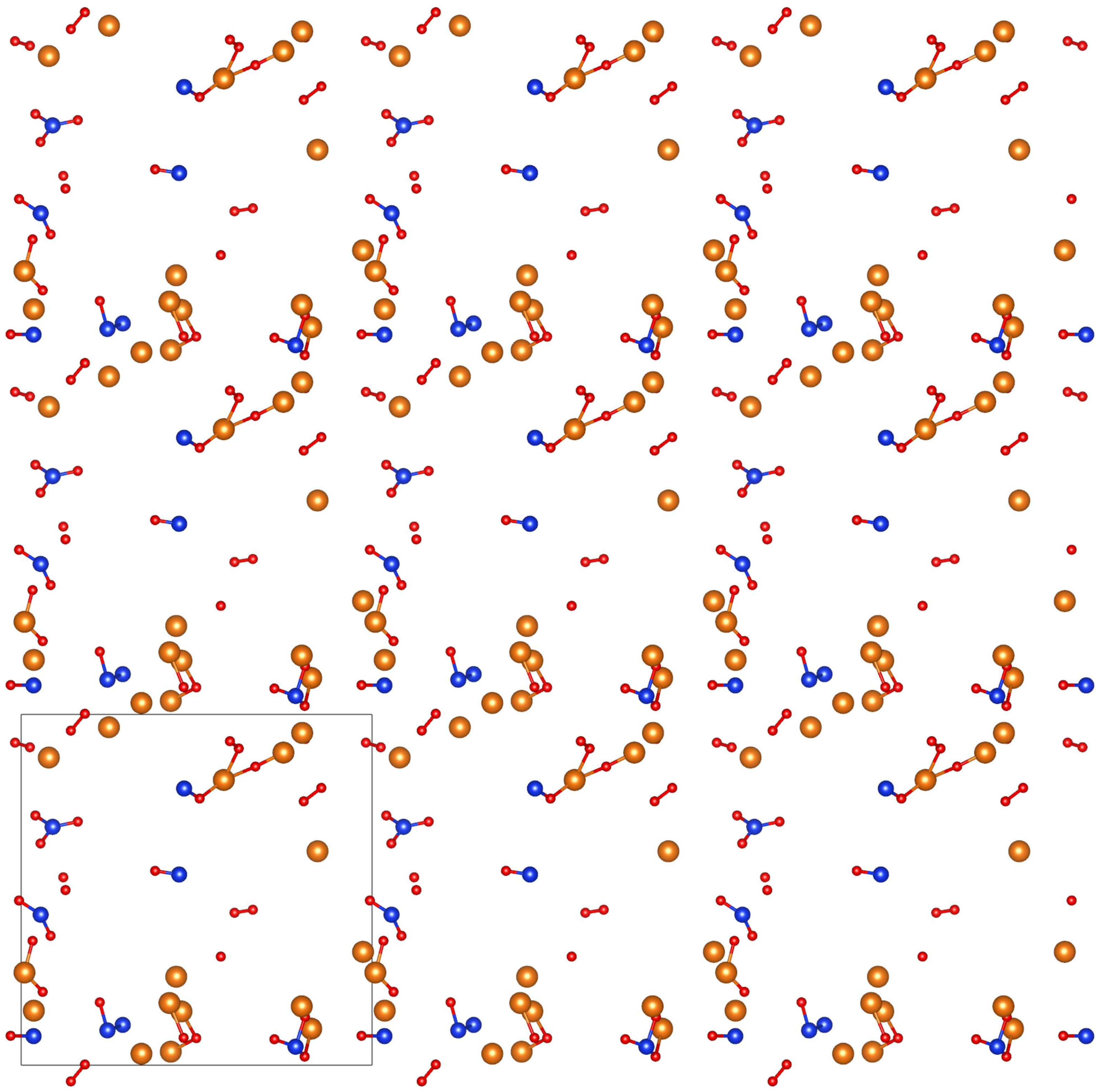


Continuous structural evolution

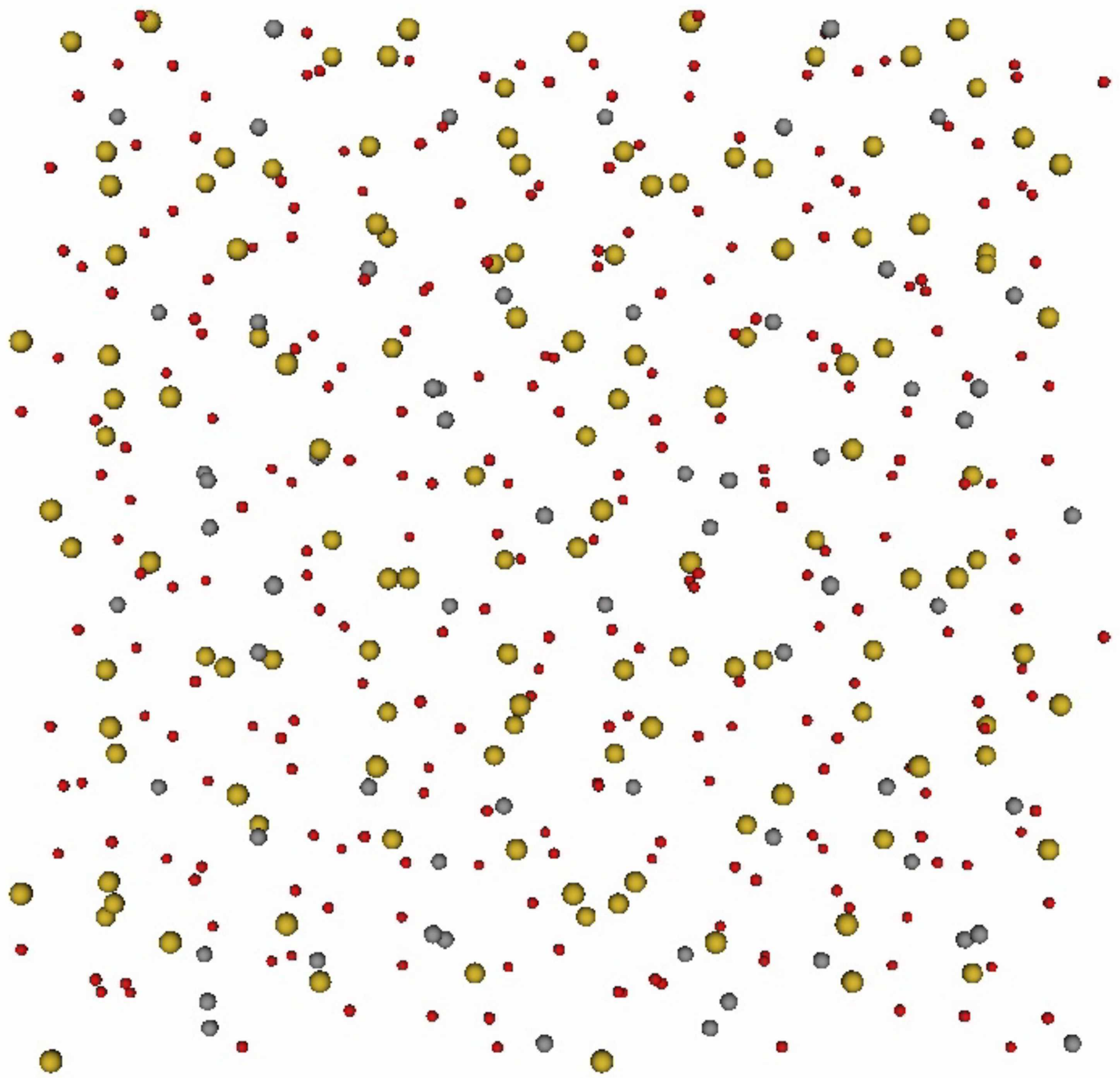
Nearly pure vapor



$\rho = 0.22$ g/cc
$T = 6000$ K

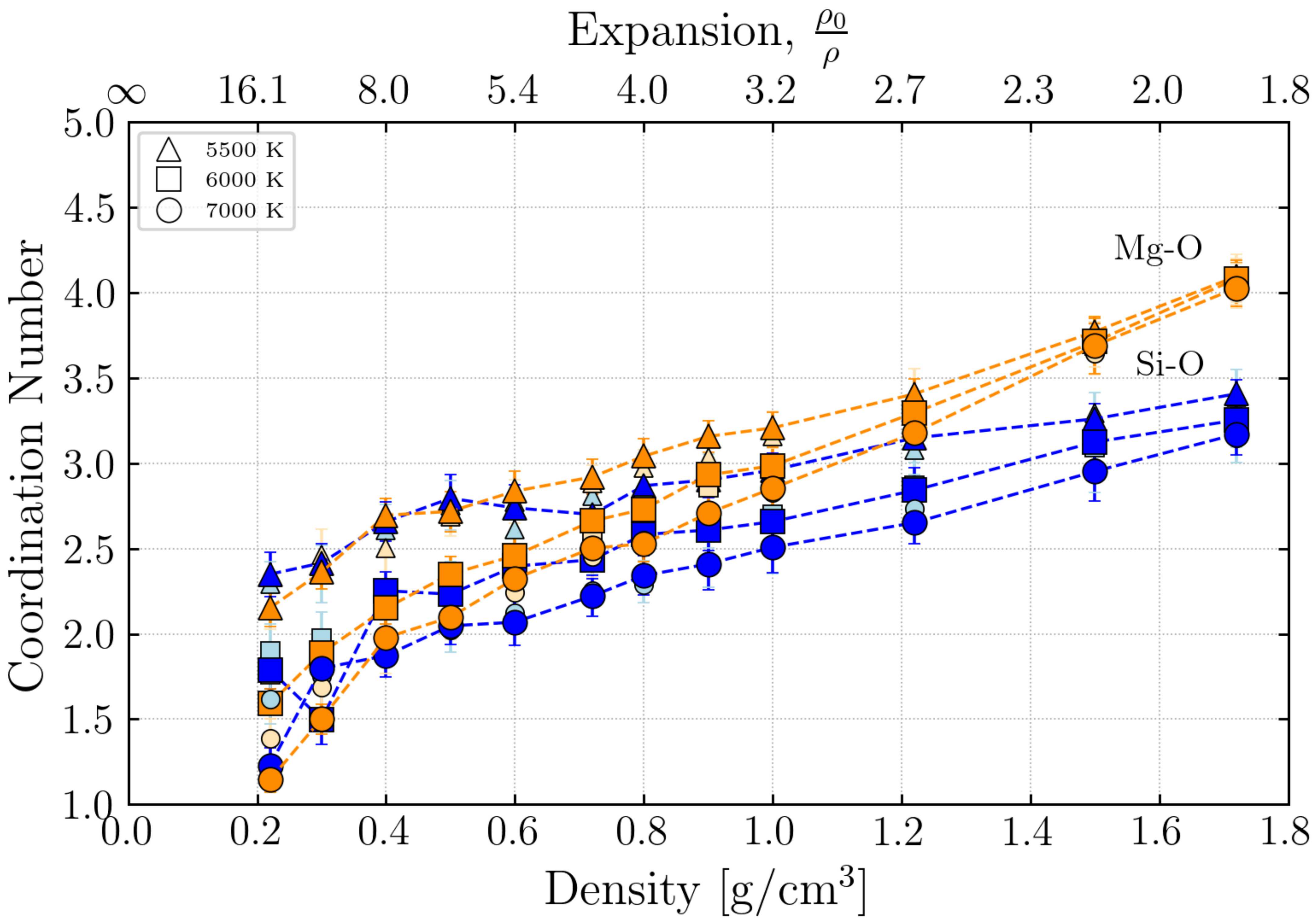


Dynamics in 2-phase region



Mg2SiO4 N112 5500 K 0.50 g/cm^3 2x2x1 tiling

Continuous structural evolution



Decrease in Mg-O & Si-O due to formation of O_2

Critical point estimation

Impose C.P. condition:

$$\left(\frac{\partial P}{\partial \rho}\right)_T = \left(\frac{\partial^2 P}{\partial \rho^2}\right)_T = 0$$

Yields a simple quadratic eqn:

$$T_c = \frac{-B \pm \sqrt{B^2 - 4AC}}{2A}$$

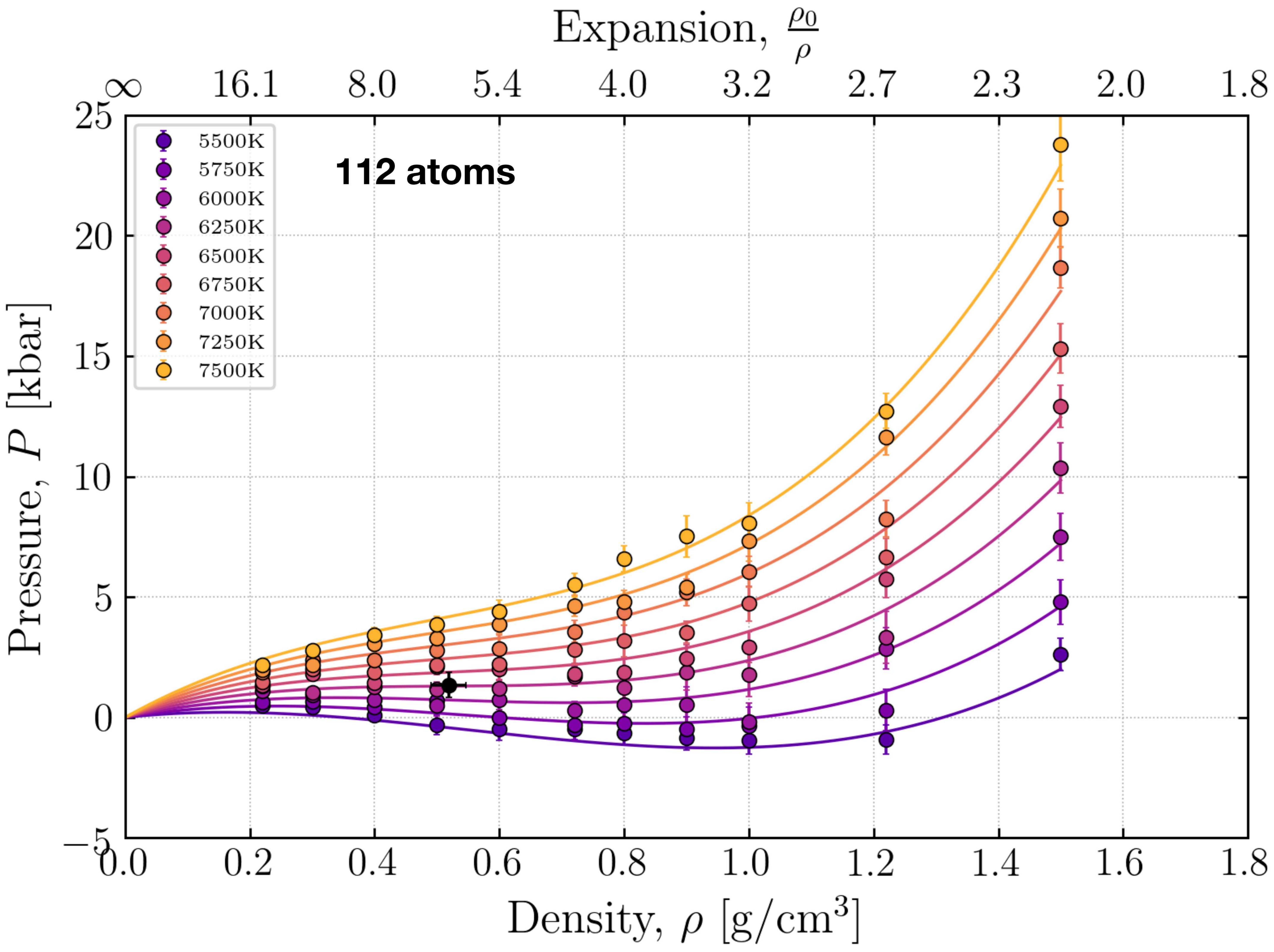
$$\rho_c = -\frac{c(T_c)}{3d(T_c)}$$

$$P_c = P(\rho_c, T_c)$$

$$\rho_c = 0.52 \pm 0.05 \text{ g/cc}$$

$$T_c = 6340 \pm 200 \text{ K}$$

$$P_c = 1.54 \pm 0.1 \text{ kbar}$$



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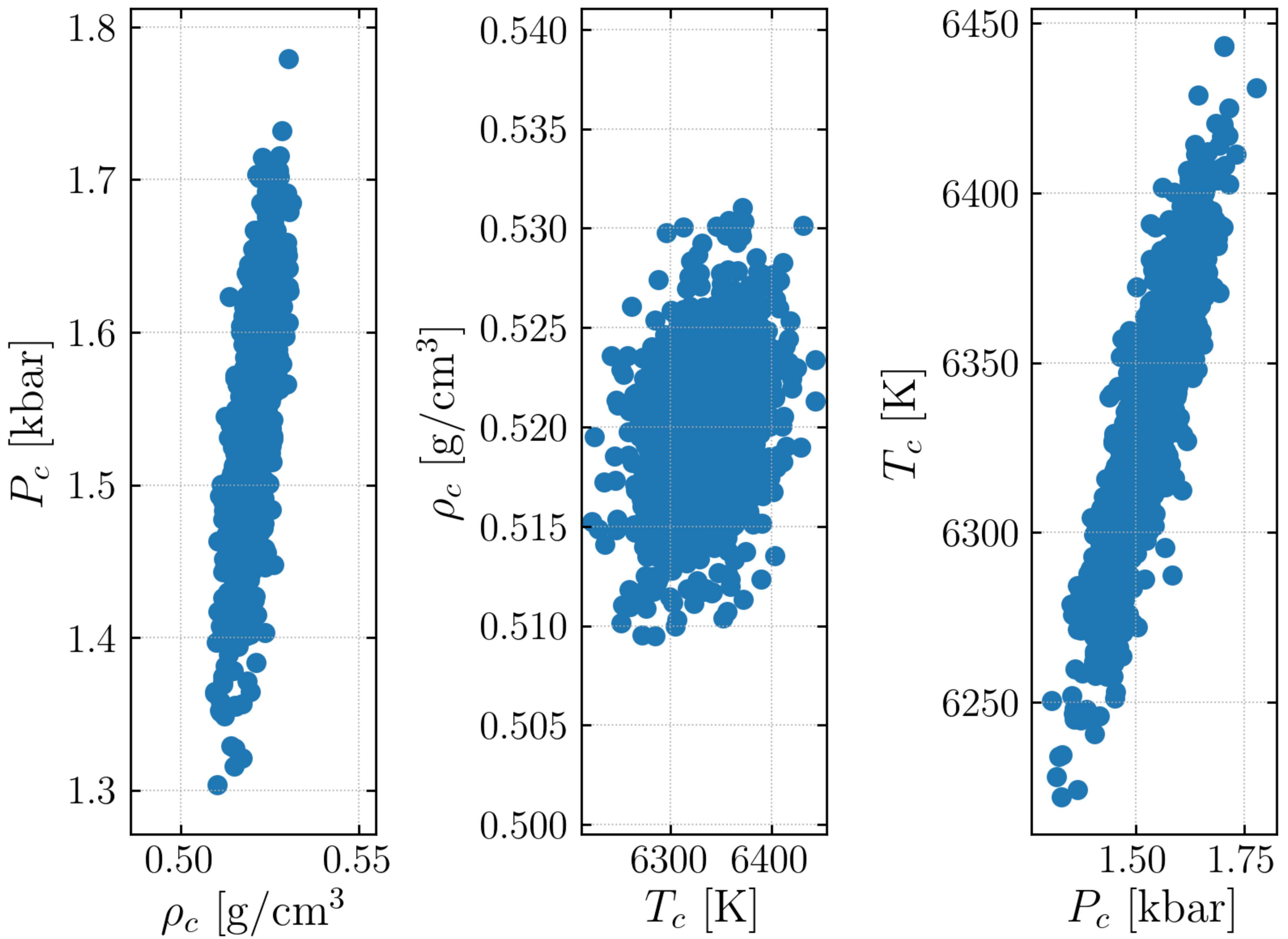
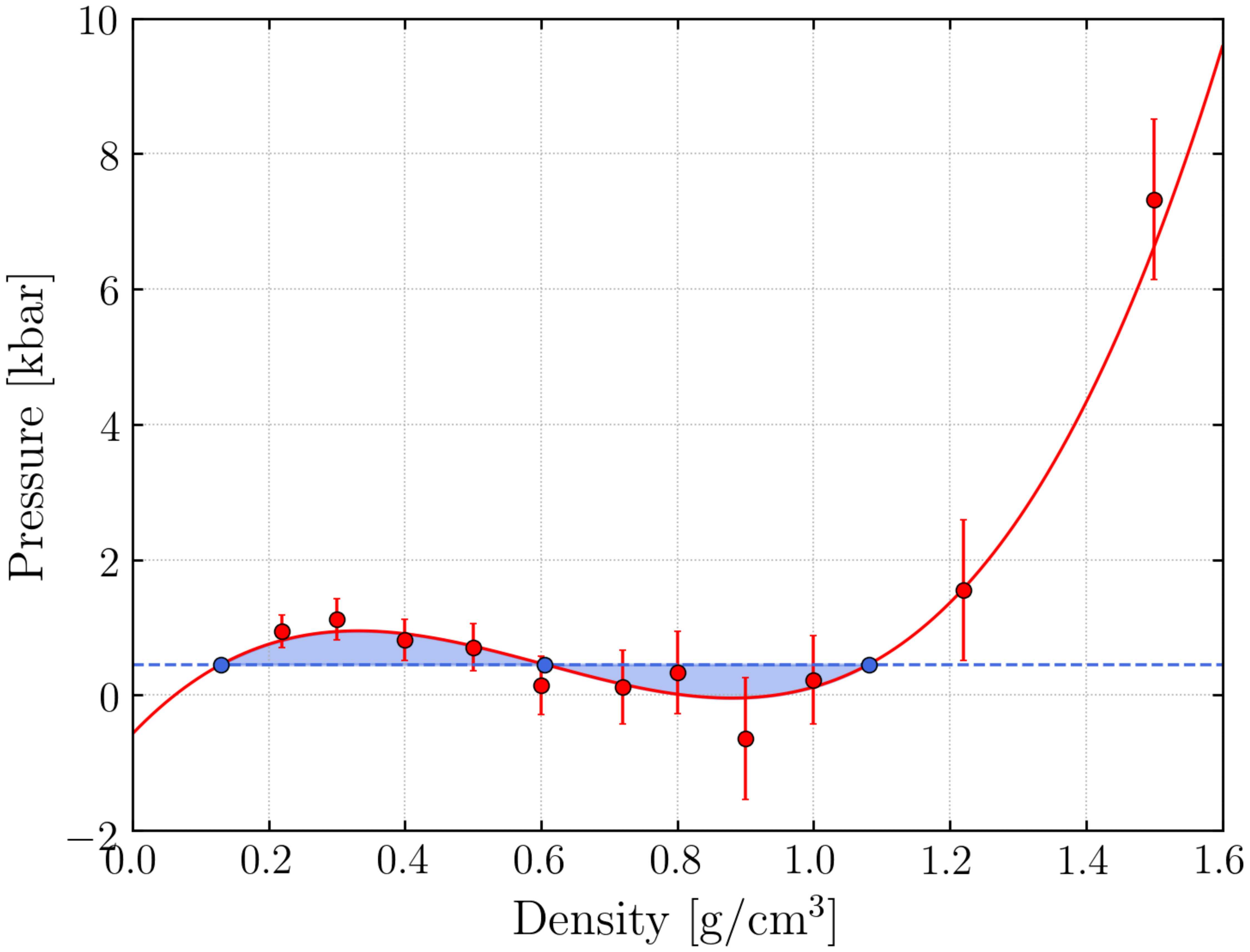


Maxwell construction

$$\int_{\rho_0}^{\rho_1} \left(P(\rho') - P\right) d\rho' = 0$$



Coexistence curve

Renormalization Group result:

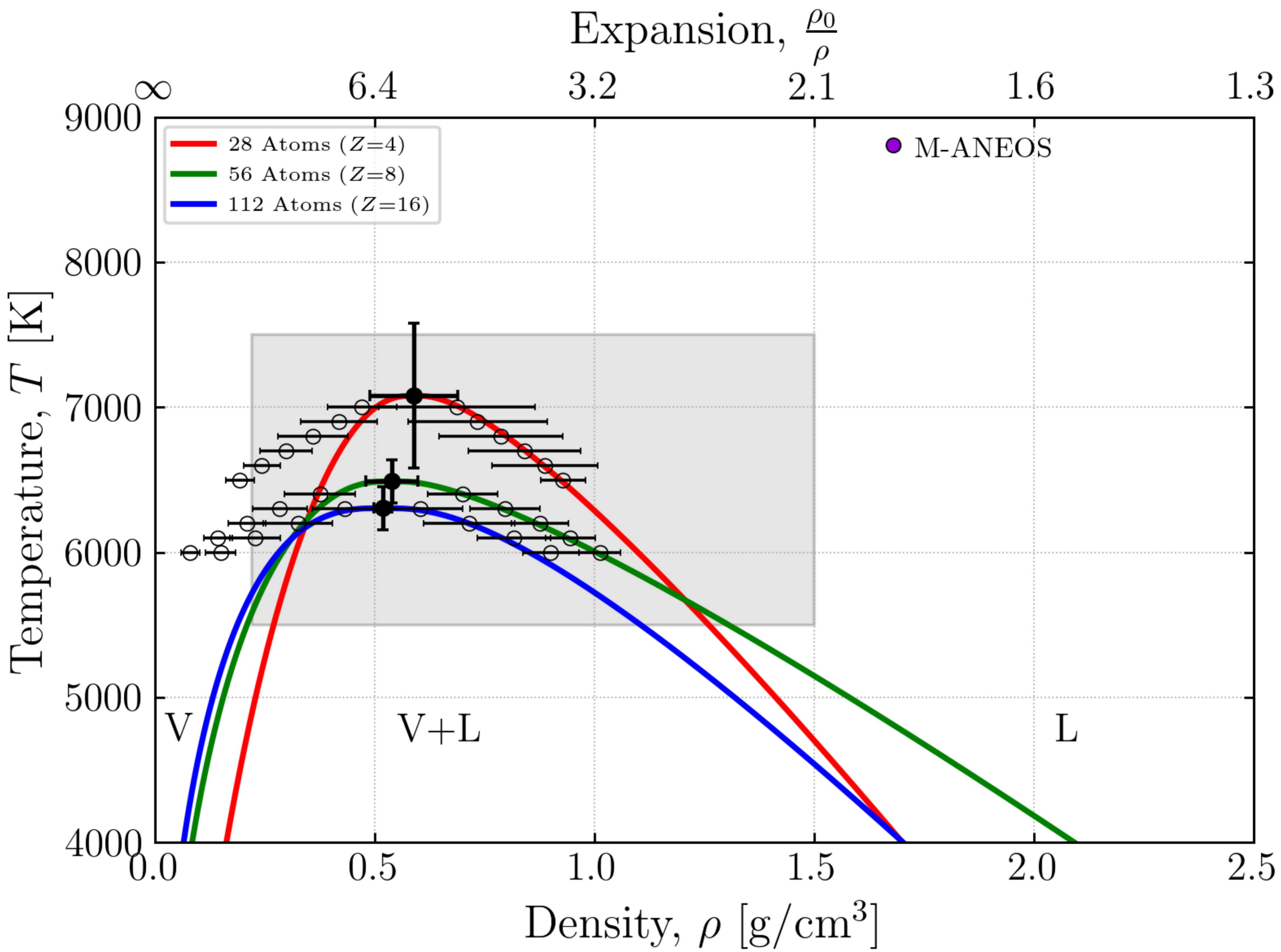
$$\rho_v = \rho_c - \frac{1}{2}\left(C_1 x^\beta + C_2 x^{\beta+\Delta}\right) + C_2 x$$

$$\rho_l = \rho_c + \frac{1}{2}\left(C_1 x^\beta + C_2 x^{\beta+\Delta}\right) + C_2 x$$

$$x \equiv \left(1 - \frac{T}{T_C}\right)$$

$$\beta \equiv 0.325$$

$$\Delta \equiv \frac{1}{2}$$



Summary

- **DFT-MD spanned 1-16x expanded & 5000-8000 K**
- **Incongruent vaporization**
- **Critical point from EOS & phase boundaries from RG**
- **Critical point 3x lower in density, 30% lower in temperature than M-ANEOS.**