SAND2020-7945C

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

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High Energy Density Physics Theory

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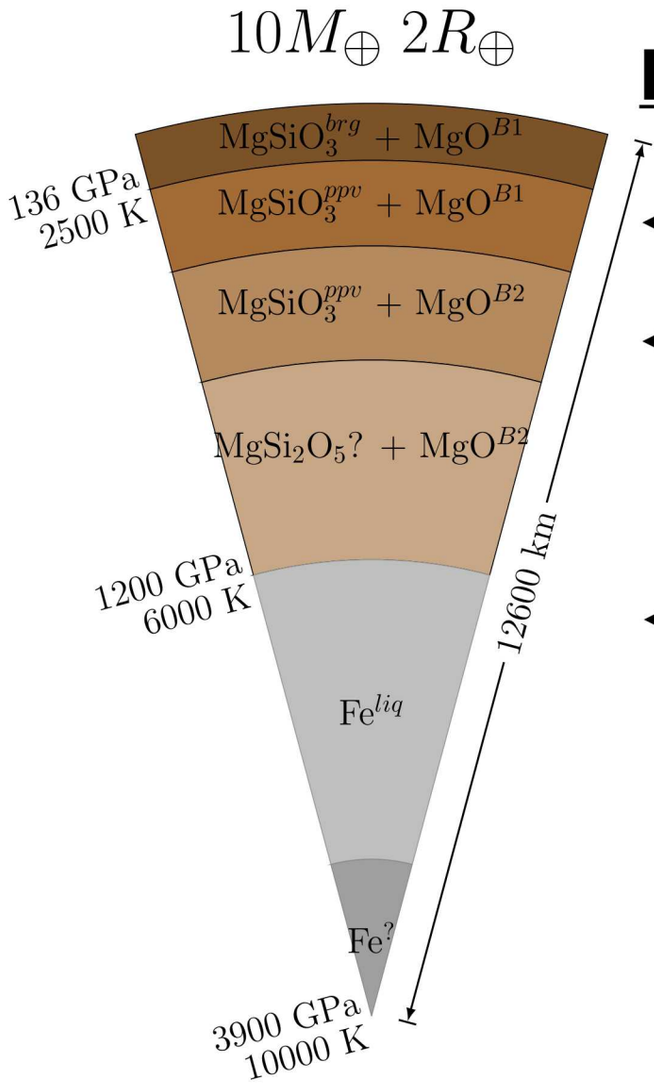
Planetary Interiors are Extreme Environments



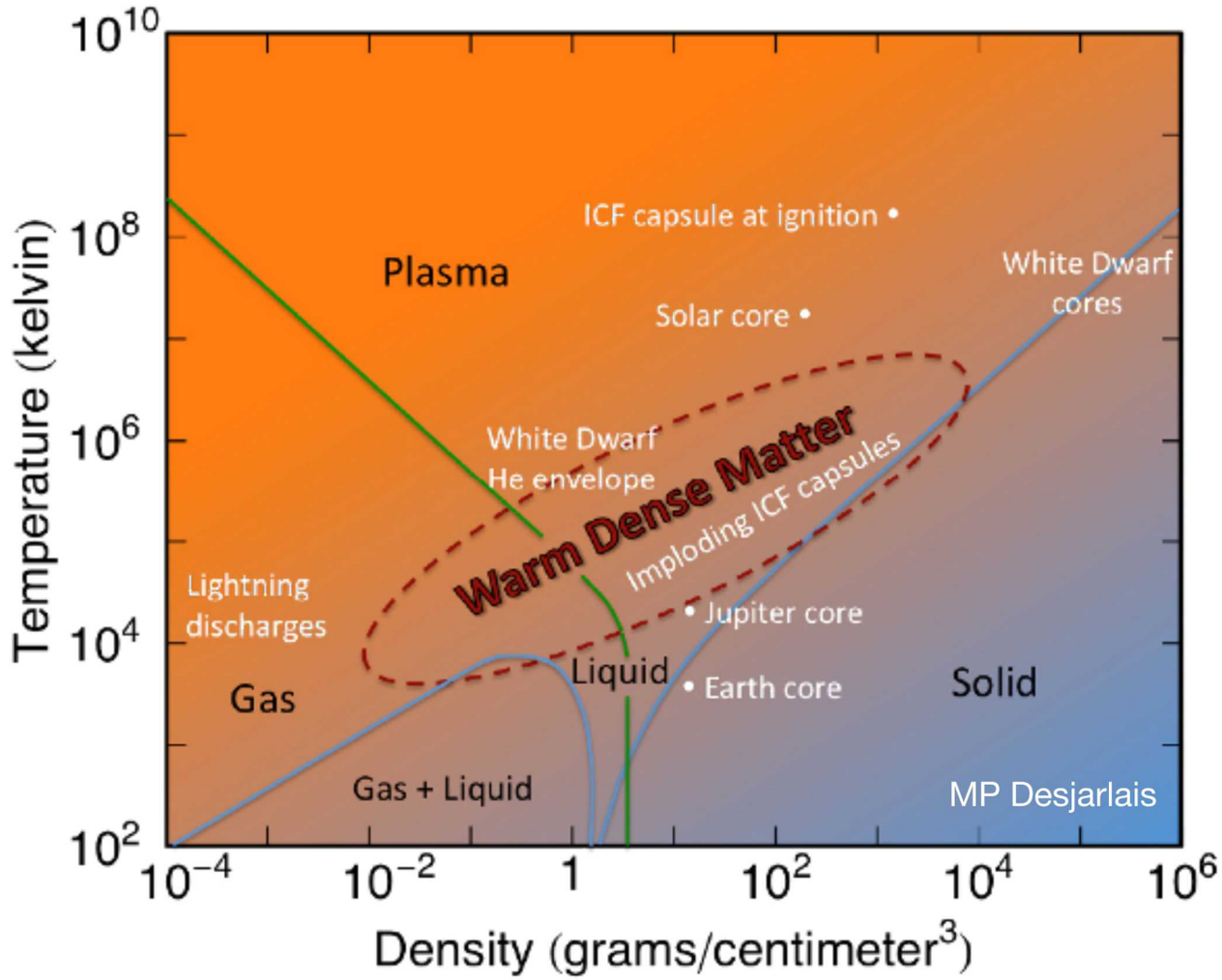
Exp't platform:

DAC

Gas gun

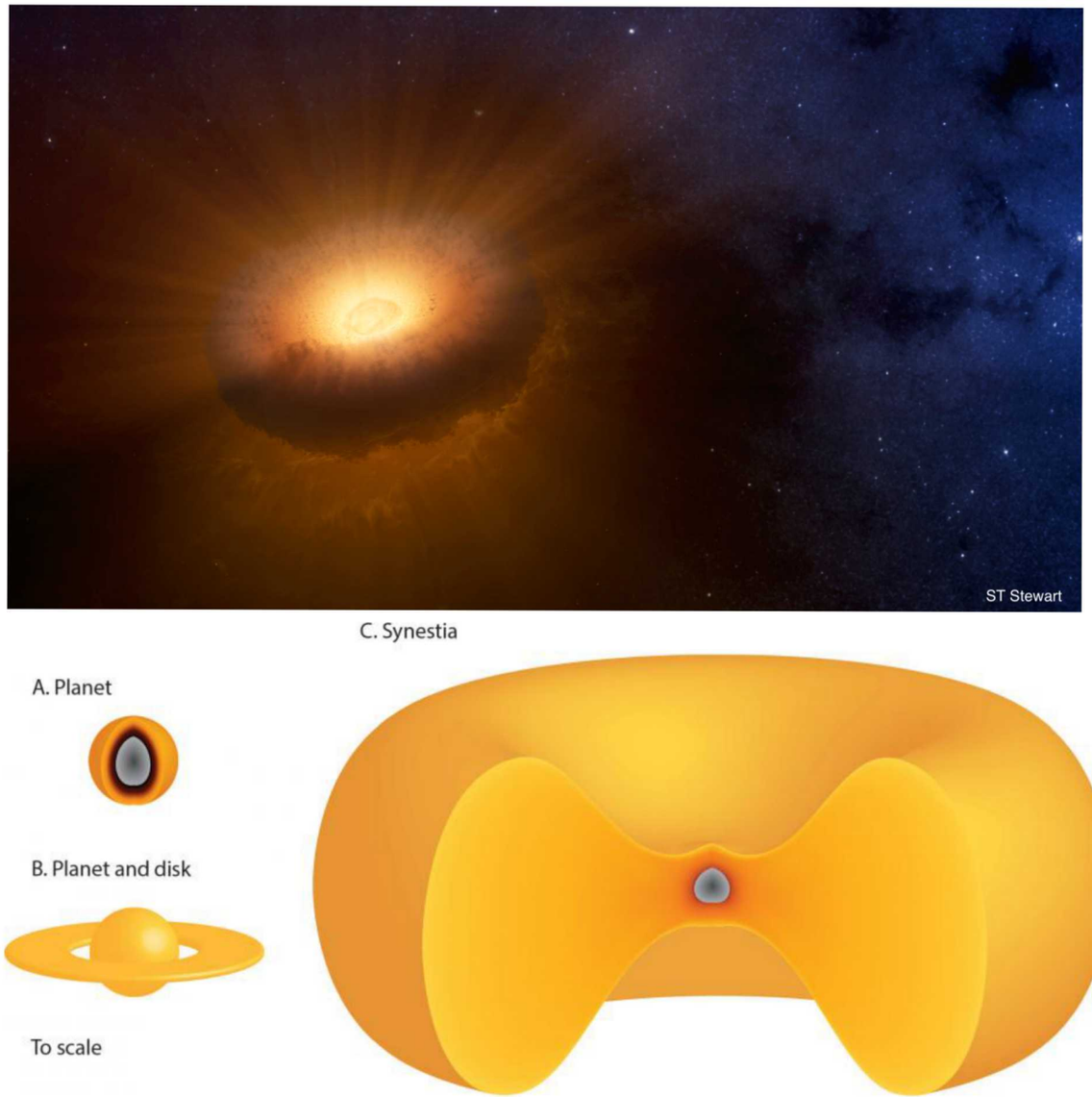
Z Machine

NIF

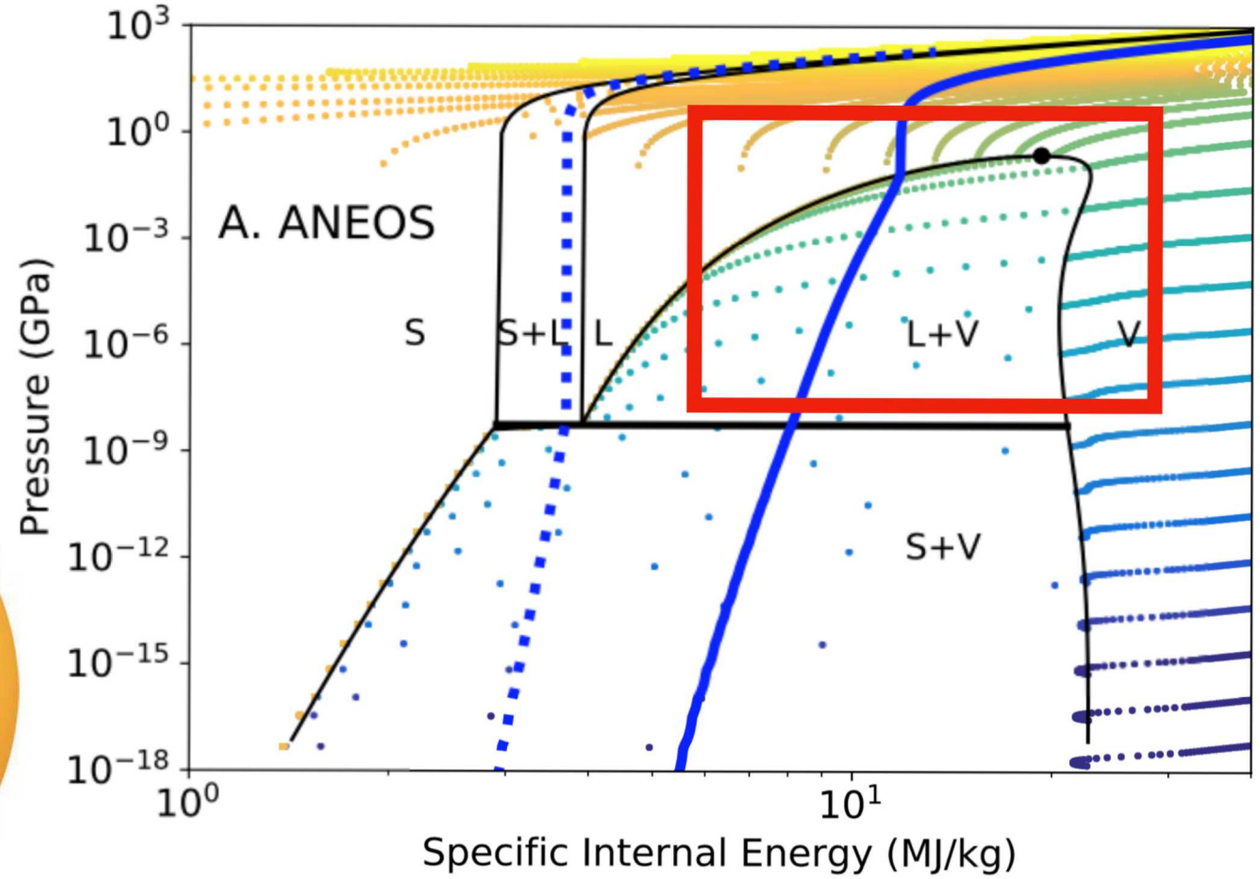


Models for large planets rely on EOS extrapolations
***In-situ* observations remain a challenge**

Outlook



A tour of the Mg_2SiO_4 phase diagram:



Stewart et al., 2019

New & accurate EOS models will advance planetary science and help answer big questions

Density Functional Theory

$$E = \mathcal{F}[\rho], \quad \rho(\mathbf{r}) \equiv \sum_i |\phi_i(\mathbf{r})|^2$$

$$E = \underbrace{-\frac{1}{2}\sum_i \int d\mathbf{r}\ \phi(\mathbf{r})\nabla^2\phi(\mathbf{r})}_{\text{Kinetic}} + \underbrace{\int d\mathbf{r}\ \rho(\mathbf{r}) \sum_I \frac{Z_I}{|\mathbf{r}-\mathbf{R}_I|}}_{\text{Electron-Ion Potential}} + \underbrace{\frac{1}{2}\int d\mathbf{r}d\mathbf{r}'\ \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}}_{\text{Electron-Electron Potential}} + E_{xc}[\rho]$$

Burke, 2012

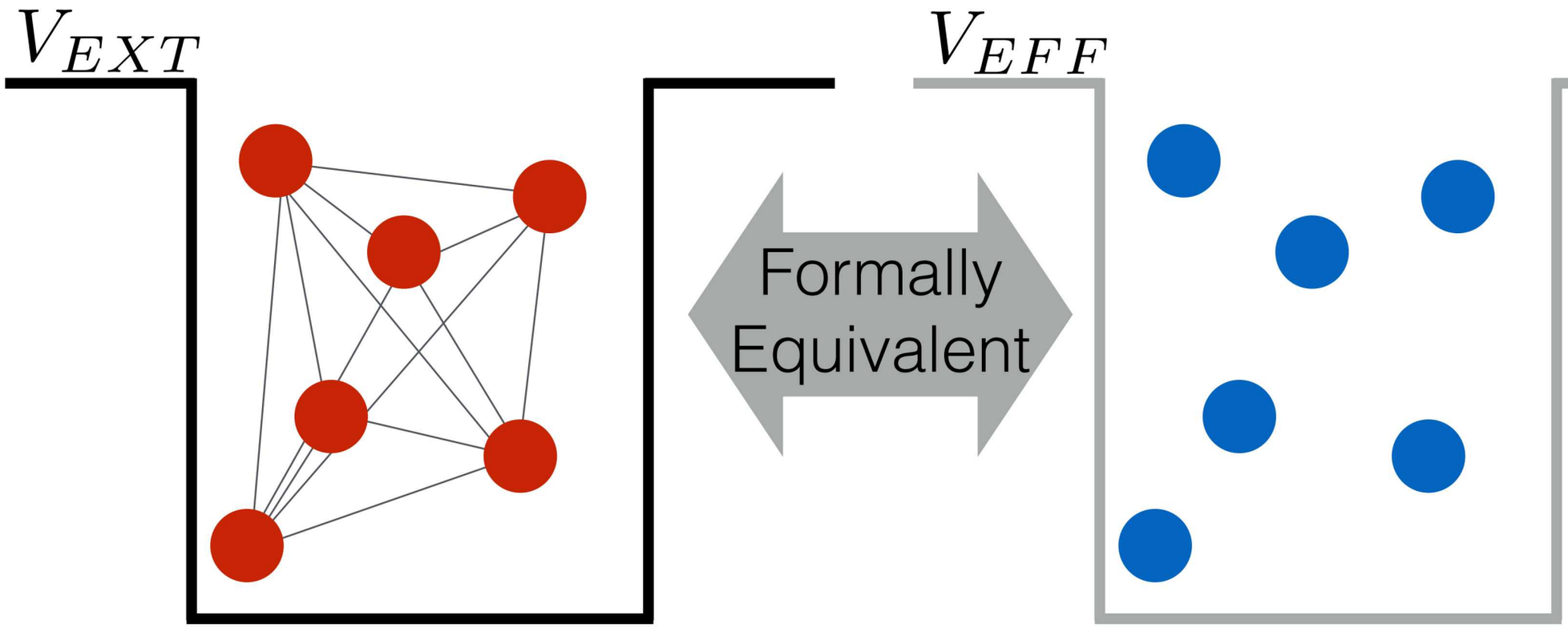
Exchange-correlation functional *not exact!*

Work presented today uses "PBE"

Density Functional Theory

"Nature"
Fully interacting system
Hard

DFT
Non-interacting system
Easy

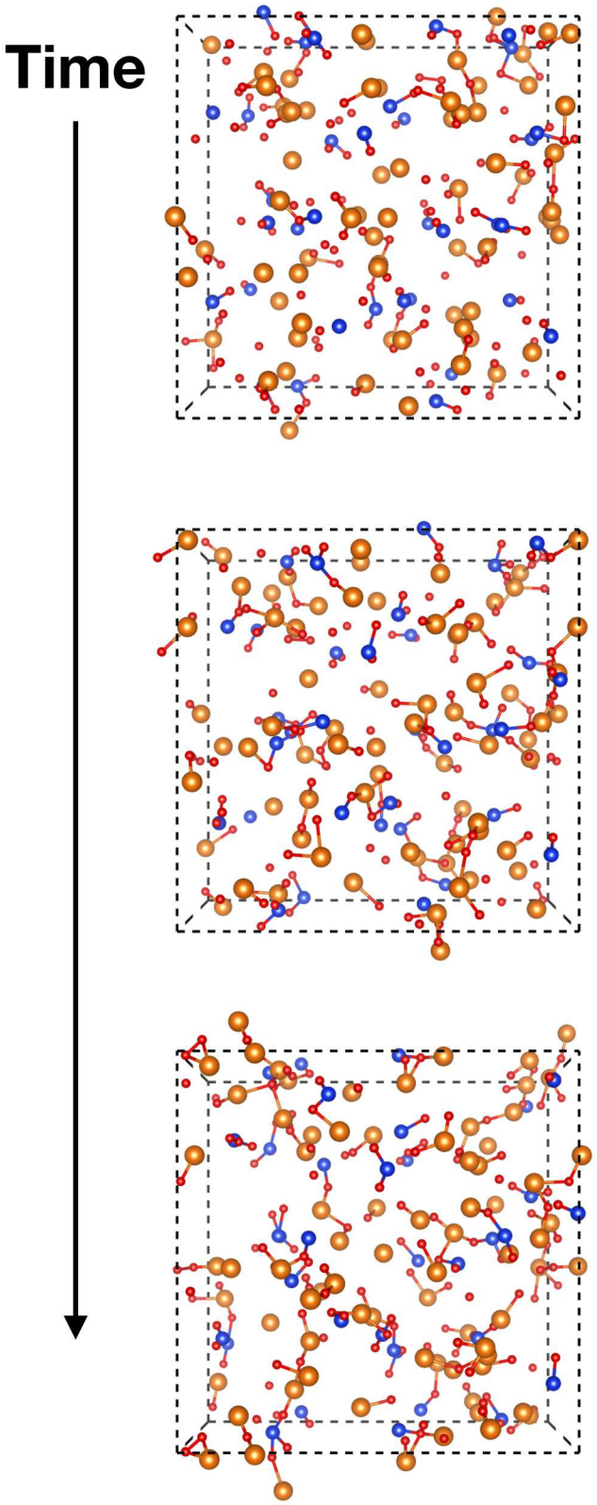


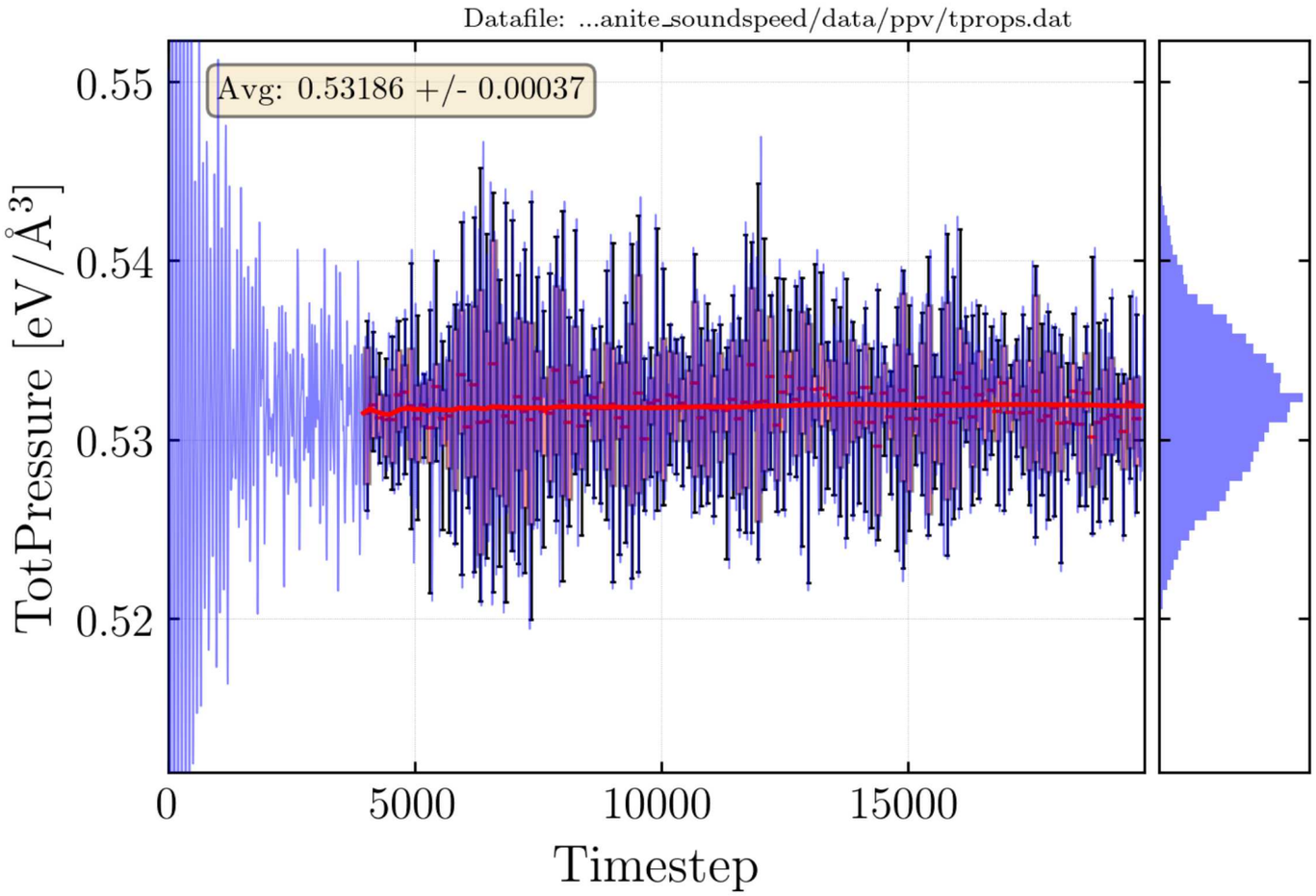
$$E = \int \Psi^* \hat{H} \Psi \; d\mathbf{r}_1 \ldots d\mathbf{r}_N \qquad E = \sum_i^N \int \Phi_i^* \hat{H}_i \Phi_i \; d\mathbf{r}$$

Adapted from Mattsson et al. 2004

Molecular Dynamics

Time





Thermodynamic quantities like *E*, *P*, *T* directly accessible *without* assuming material response

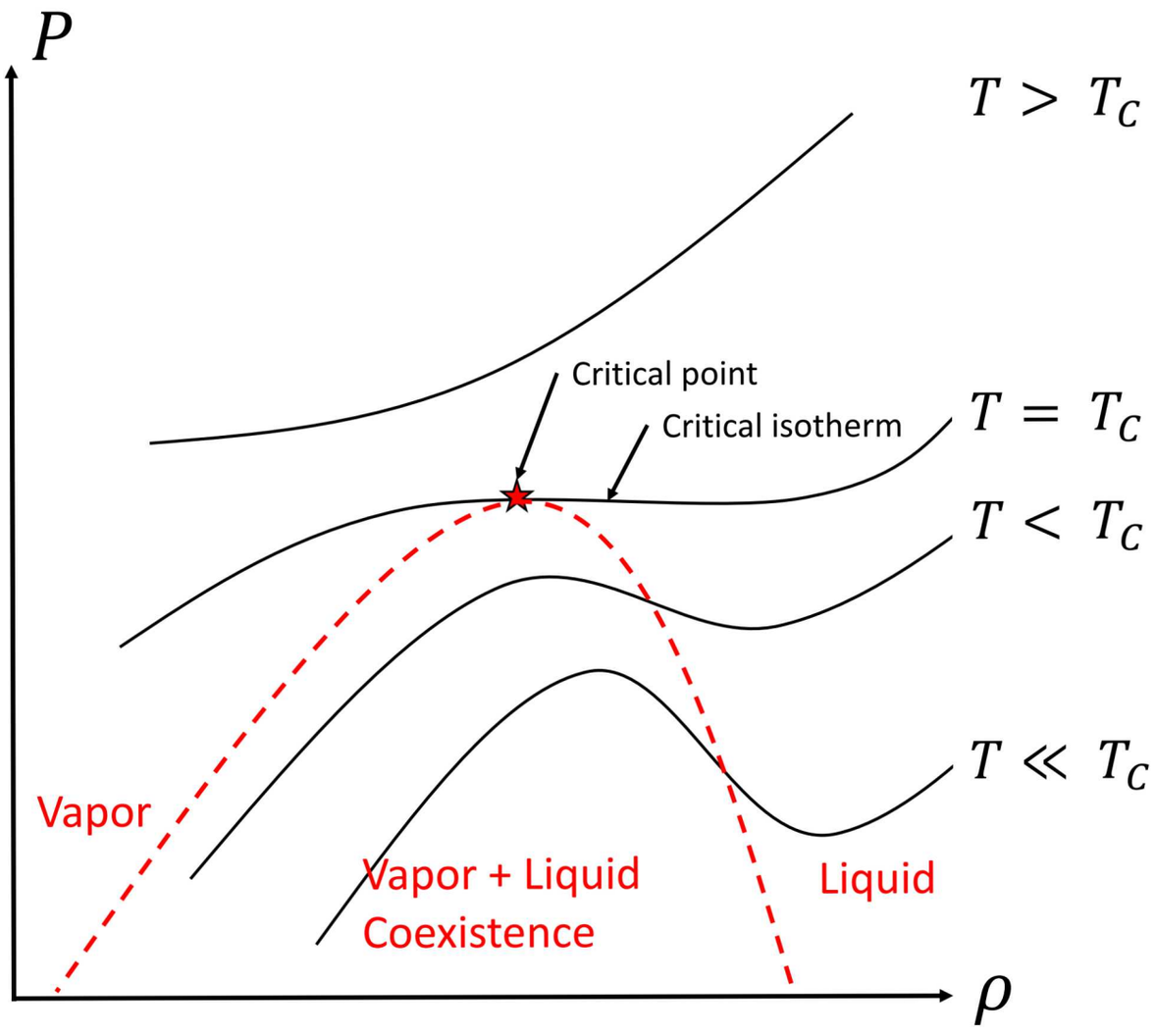
Computational Approach

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:

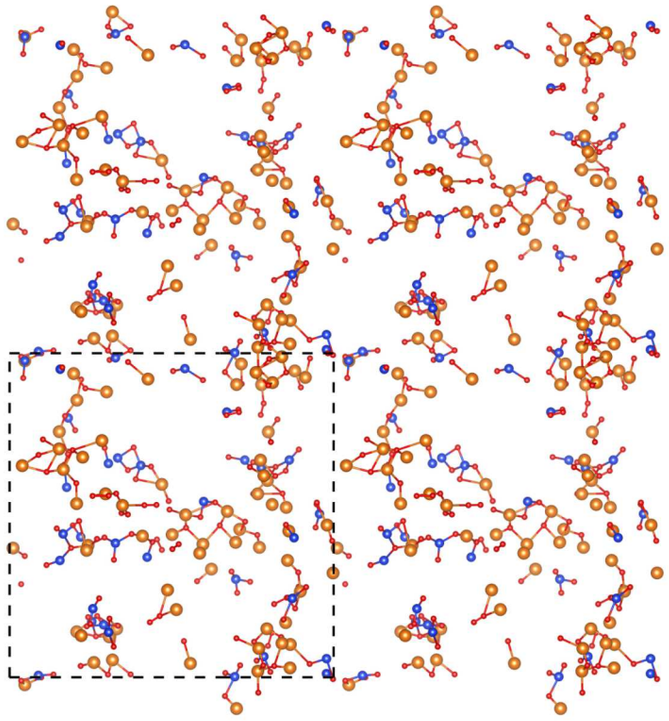
$$\left(\frac{\partial P}{\partial \rho}\right)_T = \left(\frac{\partial^2 P}{\partial \rho^2}\right)_T = 0$$

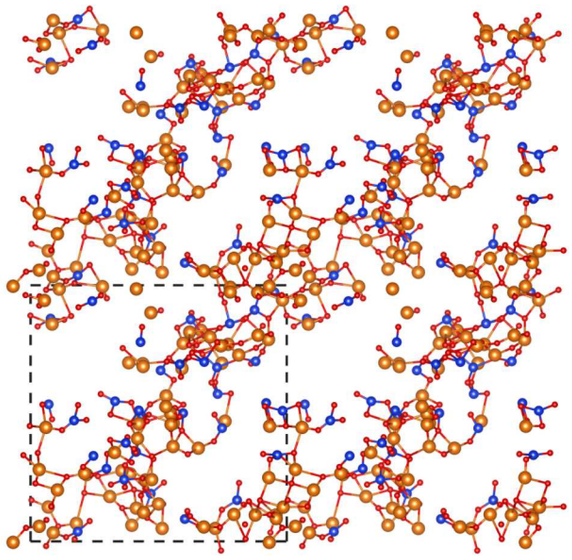


MD calculations:

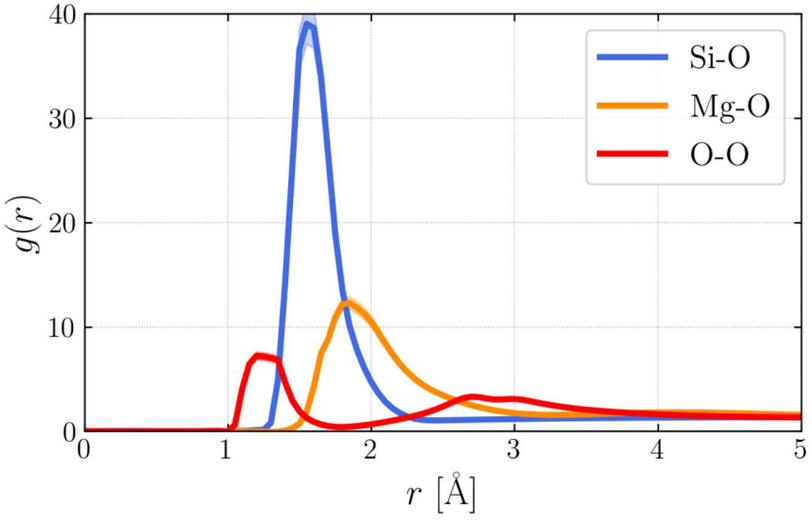
- **VASP + PAW's**
- **Mermin functional**
- **NVT with N=56/112**
- **PBE xc functional**

Structural Changes

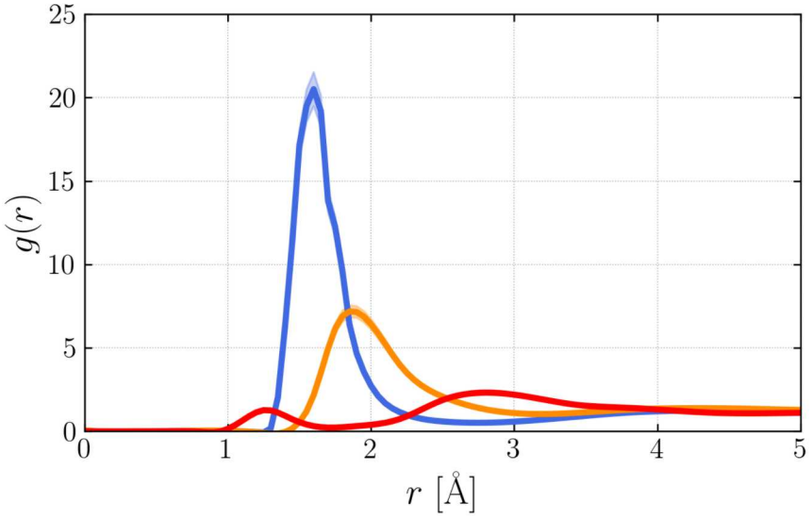




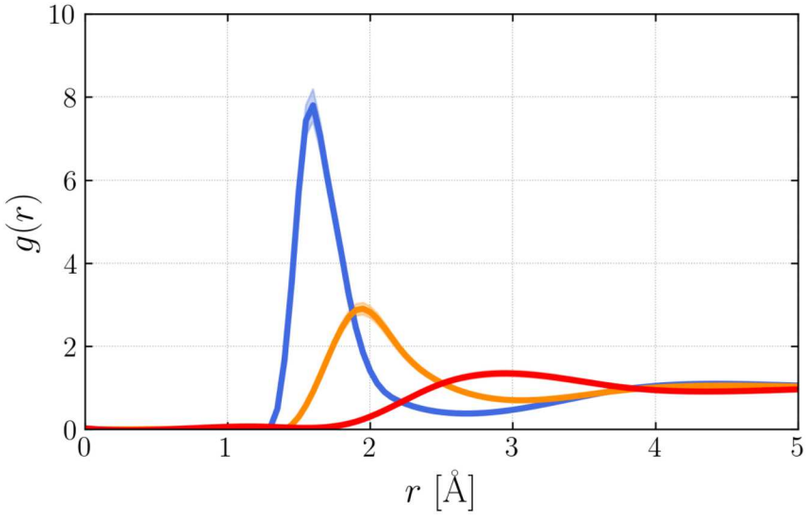
$\rho = 0.22$ g/cc, $T = 6000$ K



$\rho = 0.50$ g/cc, $T = 6000$ K

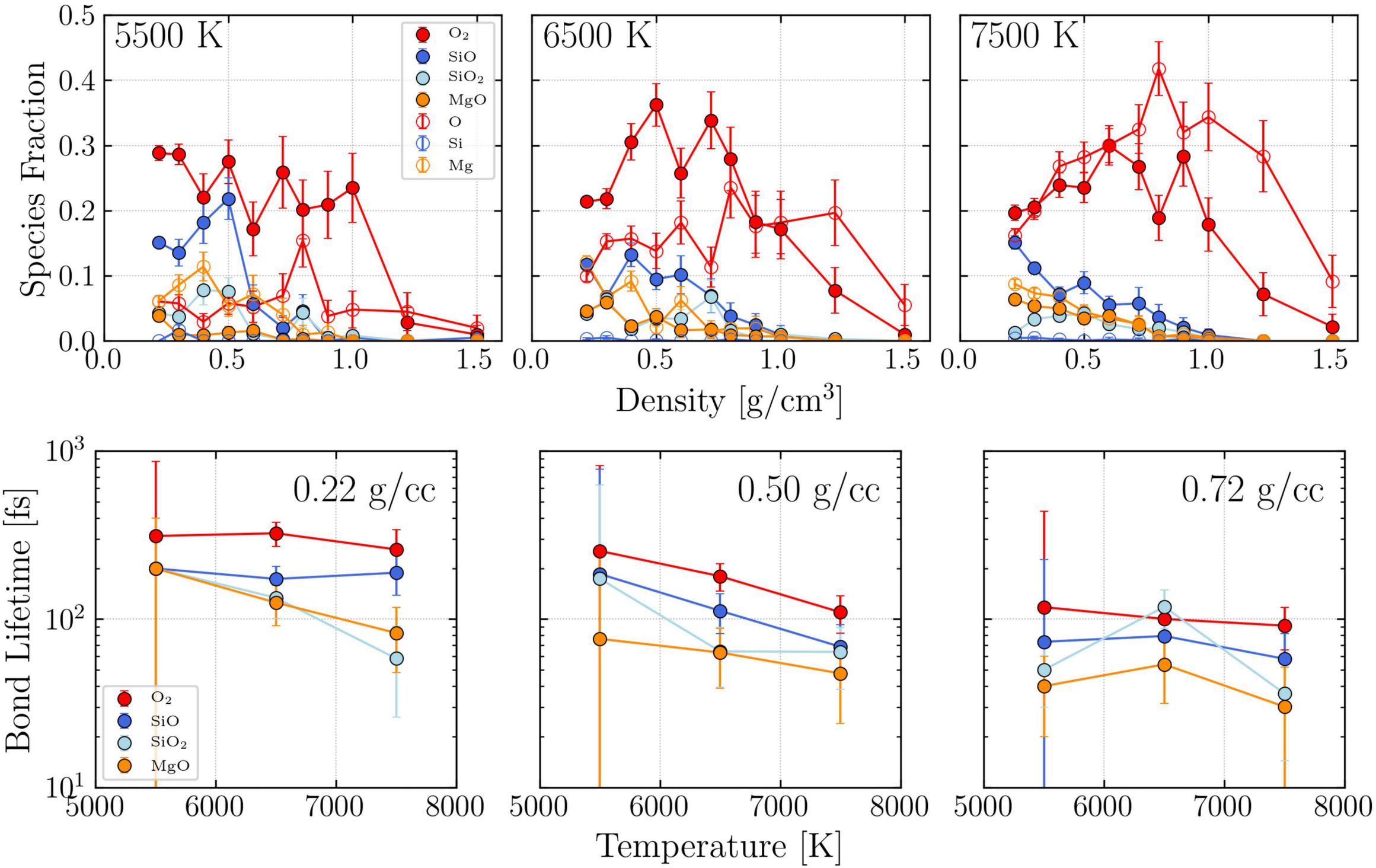


$\rho = 1.00$ g/cc, $T = 6000$ K



Movie

Speciation


5500 K
6500 K
7500 K
Species Fraction
O_2
SiO
SiO_2
MgO
O
Si
Mg
0.0
0.1
0.2
0.3
0.4
0.5
0.5
1.0
1.5
Density [g/cm^3]
0.22 g/cc
0.50 g/cc
0.72 g/cc
Bond Lifetime [fs]
10^1
10^2
10^3
5000
6000
7000
8000
Temperature [K]

Critical point estimation

C.P. condition:

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

Just a quadratic eqn:

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

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

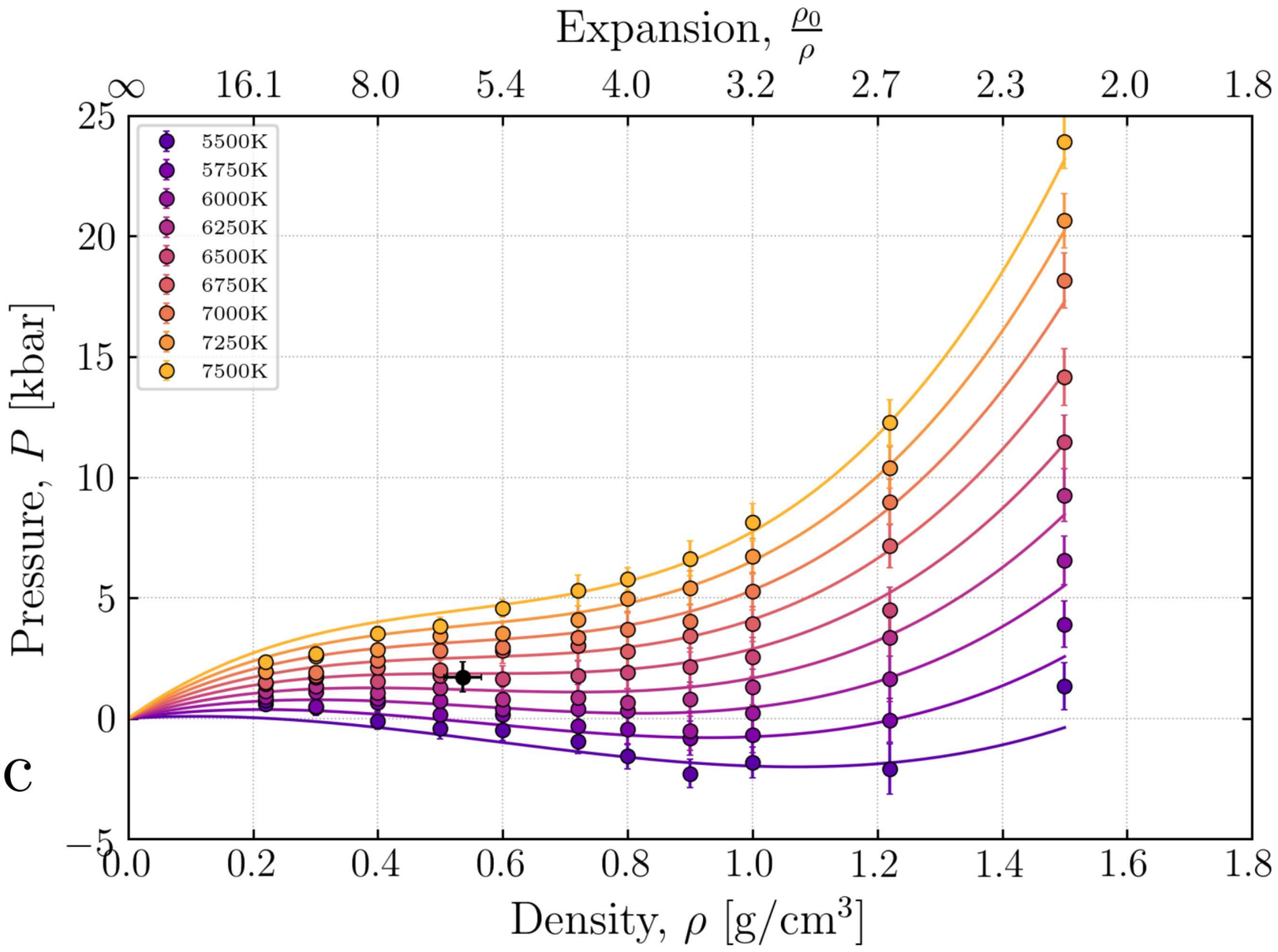
$$P_c = P(\rho_c, T_c)$$

$$\rho_c = 0.54 \pm 0.04 \text{ g/cc}$$

$$T_c = 6500 \pm 200 \text{ K}$$

$$P_c = 1.7 \pm 0.3 \text{ kbar}$$

56 atoms



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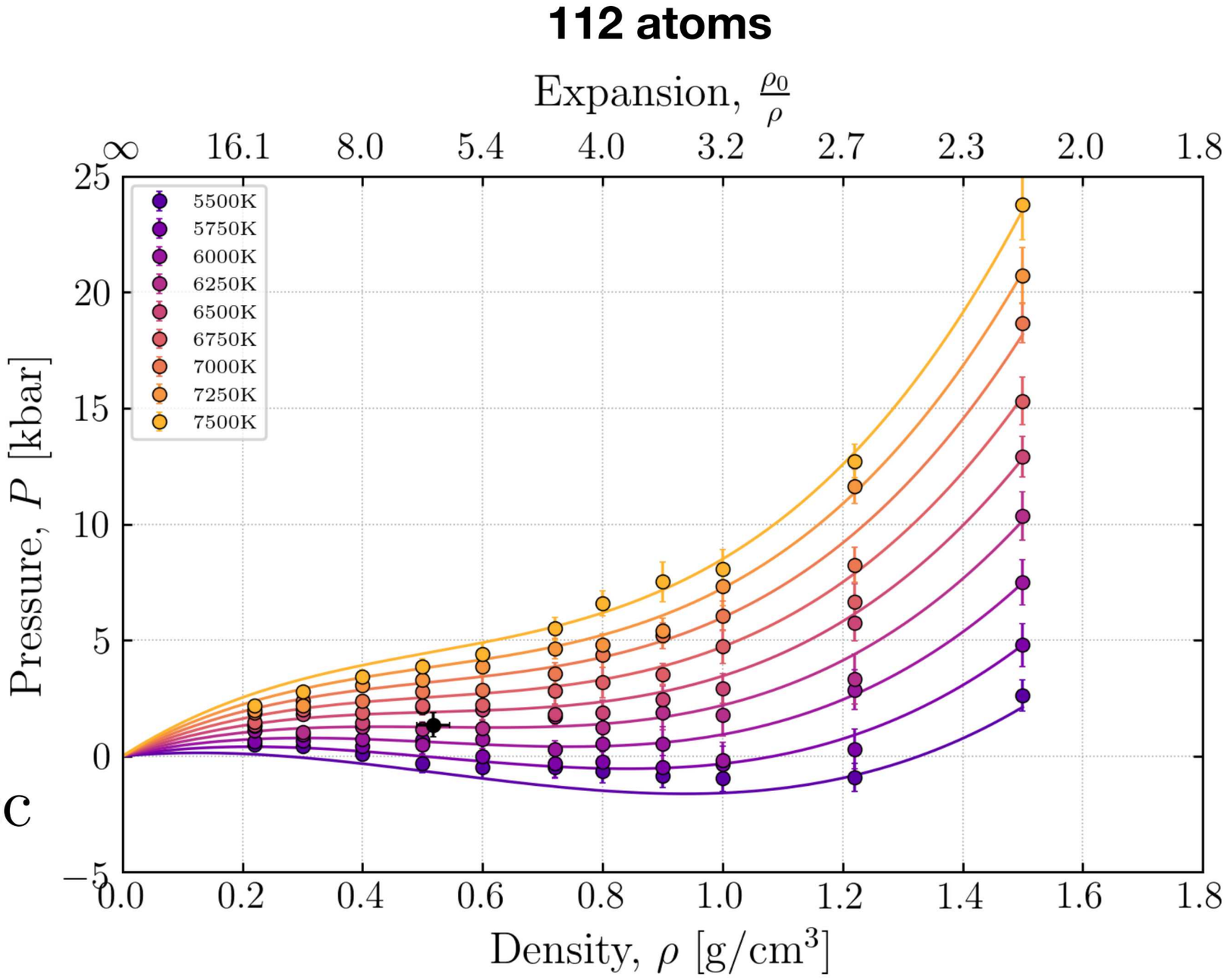
$$\rho_c = -\frac{c(T_c)}{3d(T_c)}$$

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

$$\rho_c = 0.52 \pm 0.02 \text{ g/cc}$$

$$T_c = 6300 \pm 200 \text{ K}$$

$$P_c = 1.3 \pm 0.3 \text{ kbar}$$



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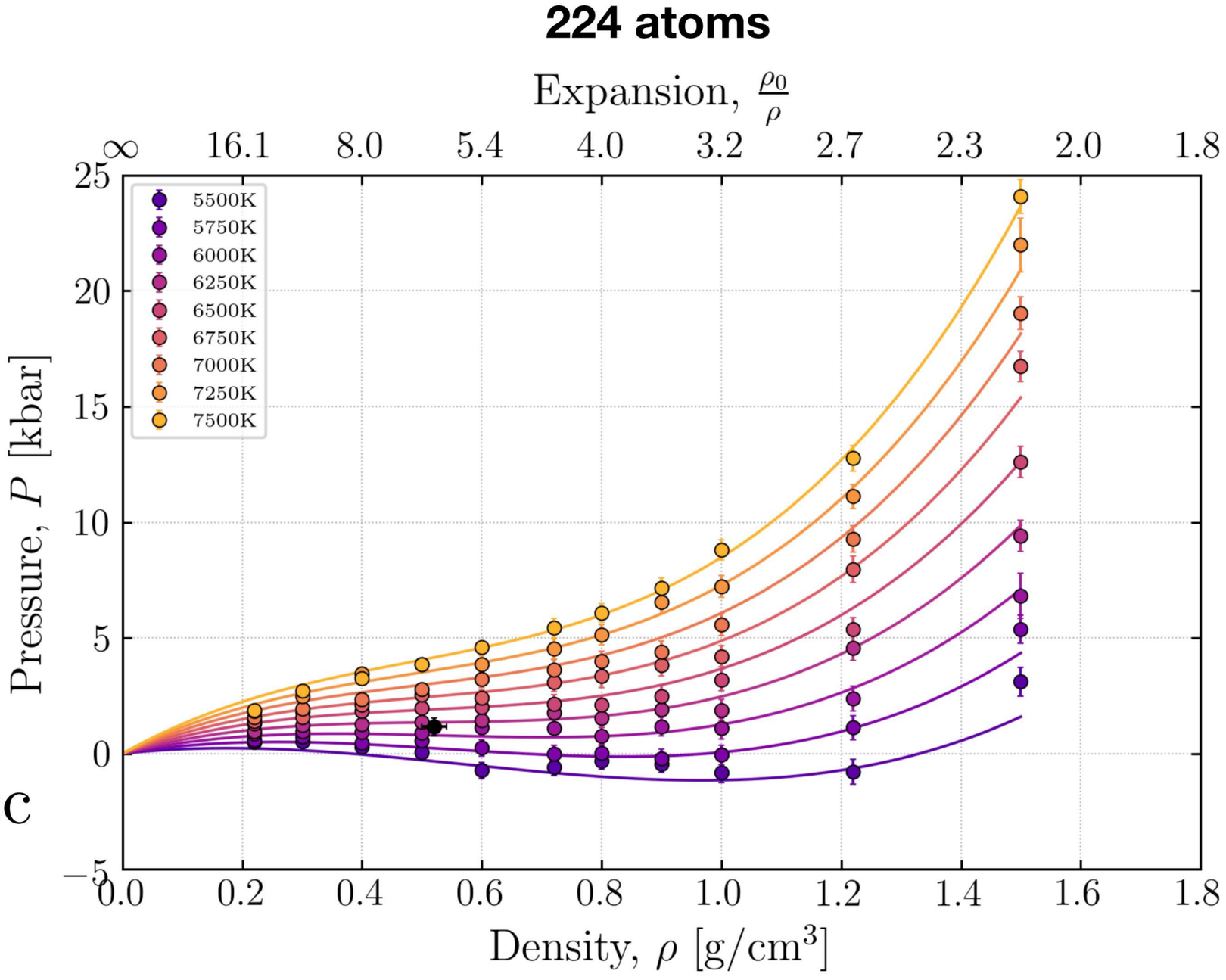
$$\rho_c = -\frac{c(T_c)}{3d(T_c)}$$

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

$$\rho_c = 0.52 \pm 0.02 \text{ g/cc}$$

$$T_c = 6200 \pm 200 \text{ K}$$

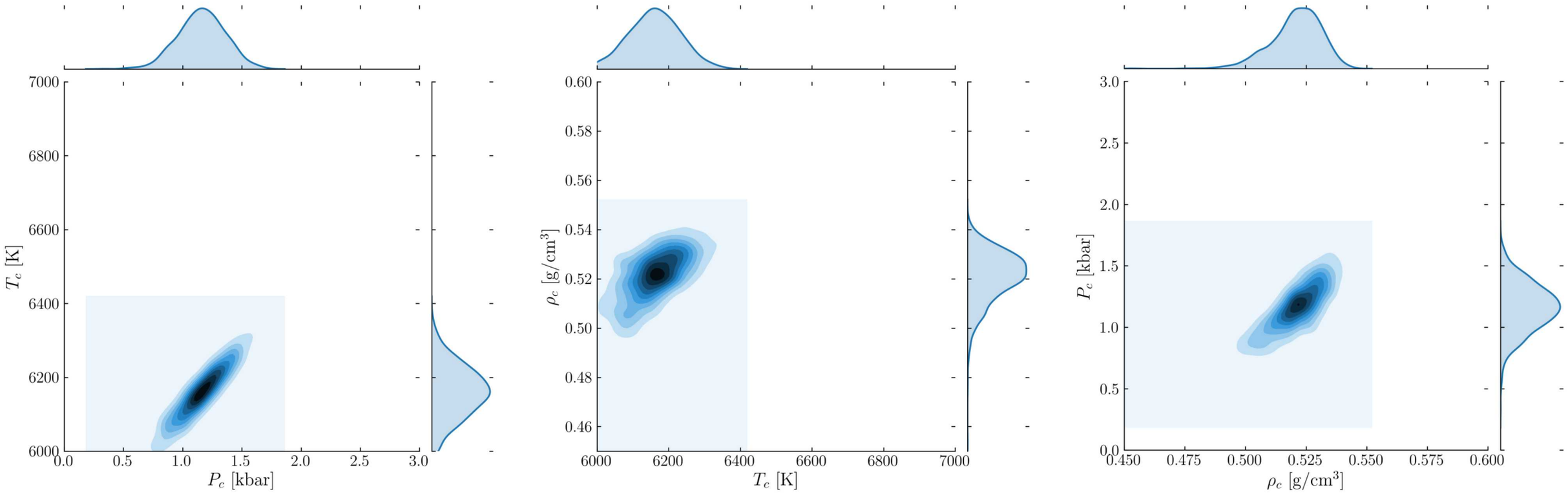
$$P_c = 1.2 \pm 0.2 \text{ kbar}$$



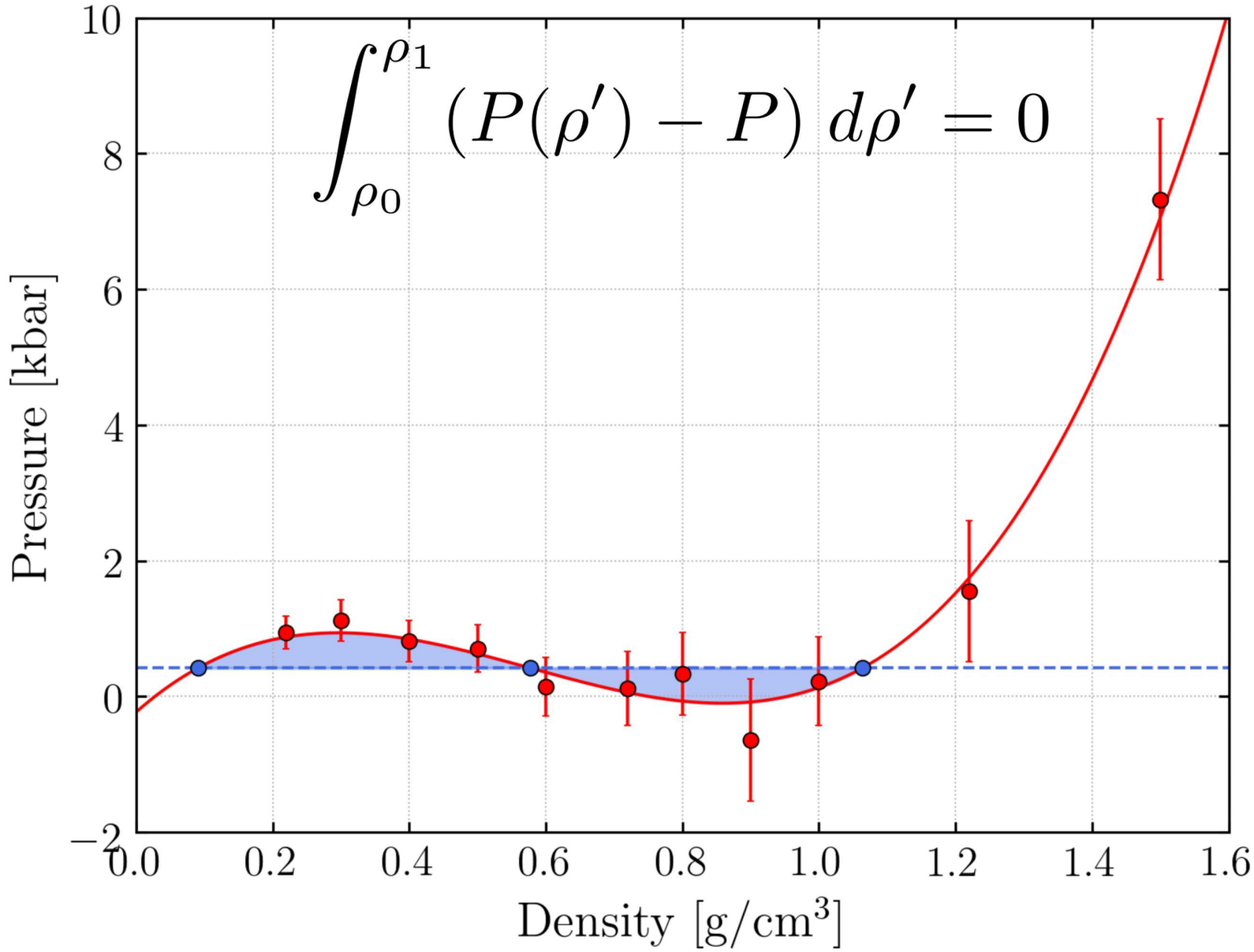
Critical point estimation

$$\rho_c = 0.52 \pm 0.02 \text{ g/cc}$$
$$T_c = 6200 \pm 200 \text{ K}$$
$$P_c = 1.2 \pm 0.2 \text{ kbar}$$

$$C = \begin{bmatrix} 1.00 & 0.64 & 0.81 \\ 0.64 & 1.00 & 0.96 \\ 0.81 & 0.96 & 1.00 \end{bmatrix}$$



Maxwell construction



Coexistence curve

Renormalization Group result:

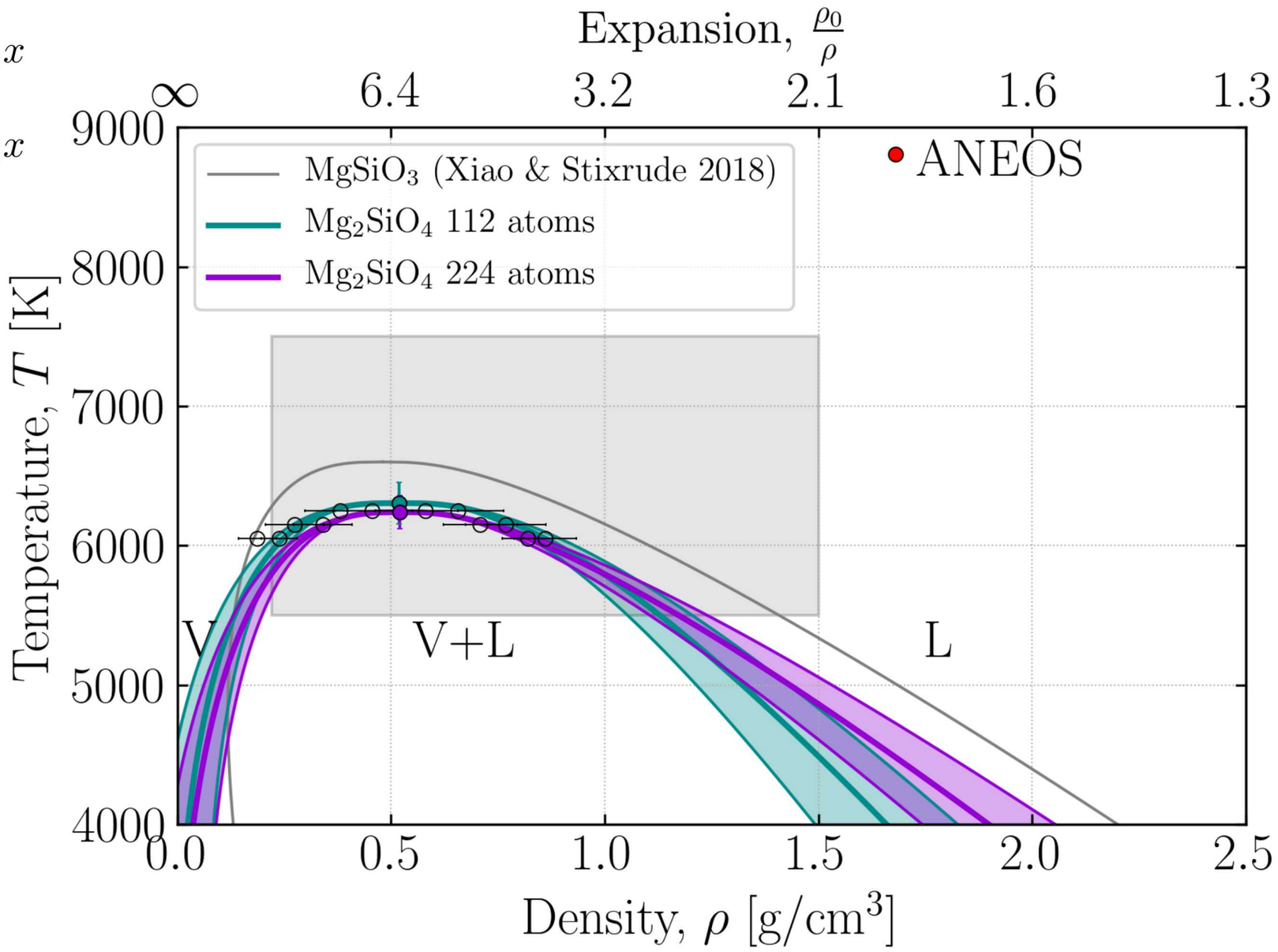
$$\rho_v = \rho_c - \frac{1}{2}\left(C_1 x^{\beta} + C_2 x^{\beta+\Delta}\right) + C_2 x$$

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

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

$$\beta \equiv 0.325$$

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



Summary

- **DFT-MD spans <16x expanded & 5000-8000 K**
- **Direct observation of incongruent vaporization**
- **Critical point estimated from EOS**
  - ***Small* finite size effect**
- **RG-coexistence phase boundaries**
  - ***Large* finite size effect**

The Many Body Problem

Electronic many-body Hamiltonian (fixed nuclei):

$$\hat{H}^{el} = -\frac{1}{2}\sum_{i}^{N_{elec}} \nabla_i^2 + \sum_{i<j} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} - \sum_i \sum_I \frac{Z_I}{|\mathbf{r}_i - \mathbf{R}_I|}$$

Assume simplest many-body wave function:

$$\Psi(\{\mathbf{r}\}) = \det \begin{vmatrix} \phi_1(\mathbf{r}_1) & \phi_1(\mathbf{r}_2) & \cdots & \phi_1(\mathbf{r}_N) \\ \phi_2(\mathbf{r}_1) & \phi_2(\mathbf{r}_2) & \cdots & \phi_2(\mathbf{r}_N) \\ \vdots & \vdots & \ddots & \vdots \\ \phi_N(\mathbf{r}_1) & \phi_N(\mathbf{r}_2) & \cdots & \phi_N(\mathbf{r}_N) \end{vmatrix}$$