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Liquid-Vapor Critical Region and DC Conductivity of Platinum From Ab Initio Simulation

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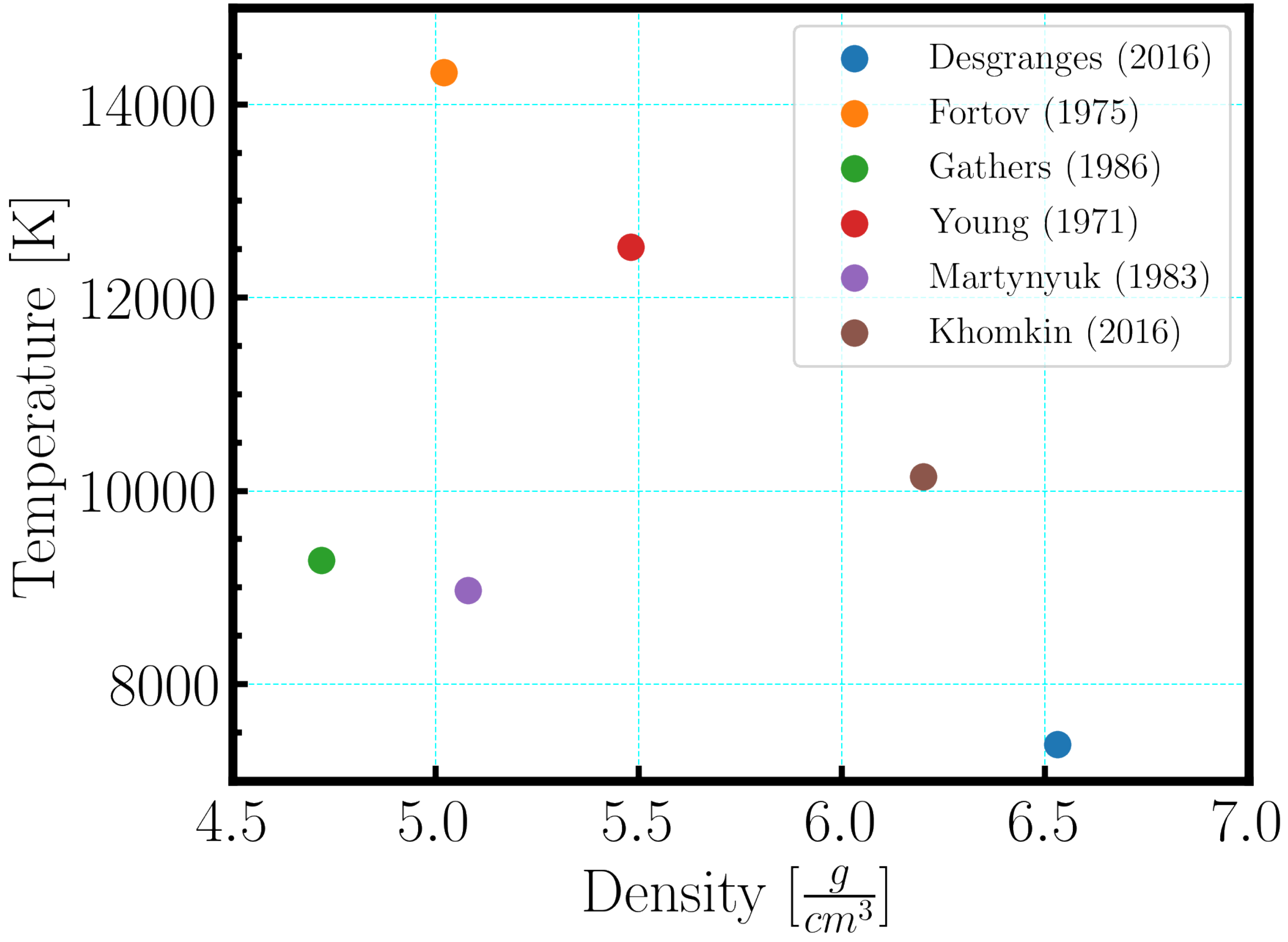
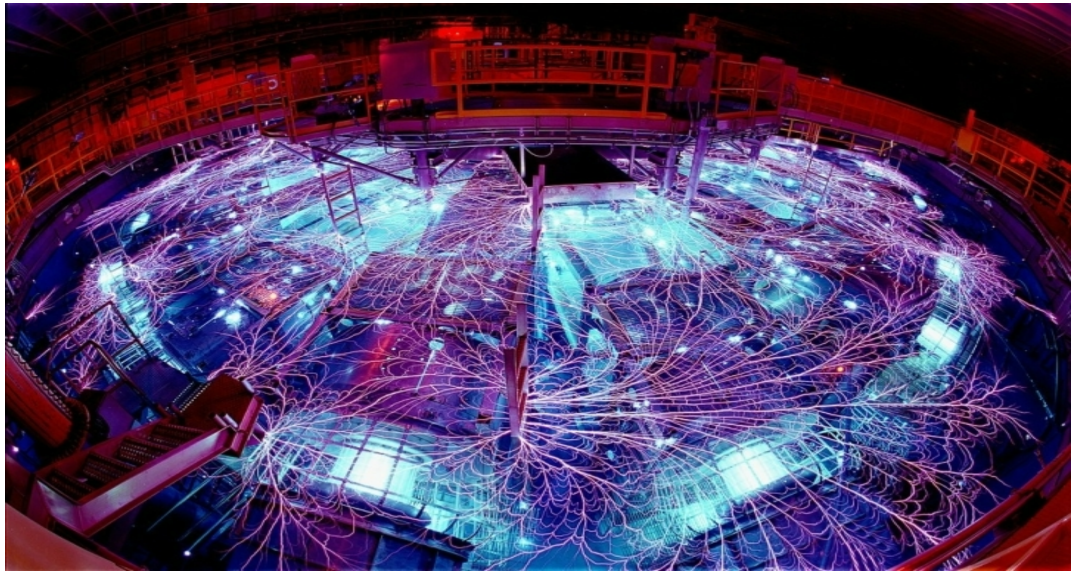
Current Critical Point Data

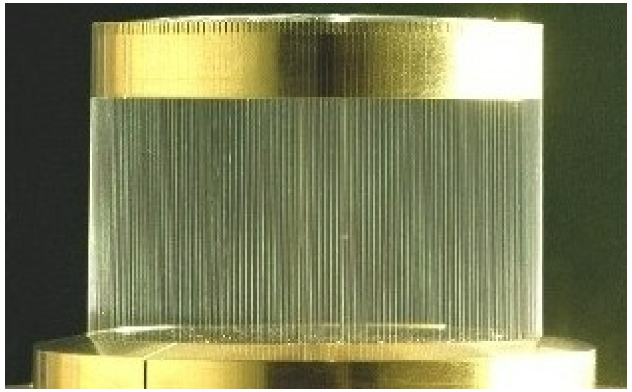
- Platinum is a high pressure standard, poorly understood in critical region
- Experiment: Isobaric pulsed heating
- Theory: Empirical EOS; extrapolation of near critical data; scaling and similarity laws

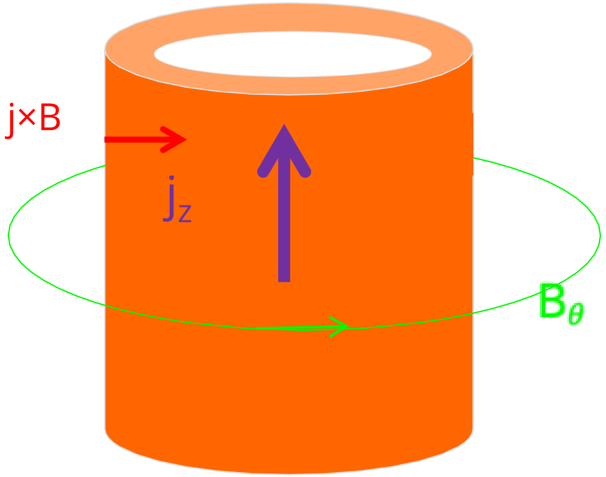


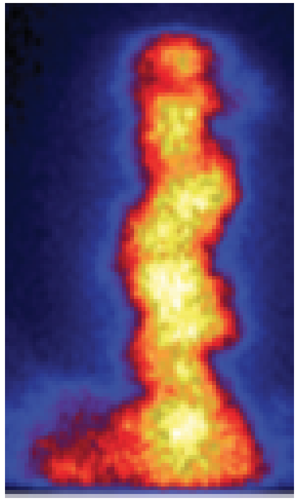
Z Pinch Experiments



- Current driven through fine wires
  - Explode producing HED plasma
- Material enters vapor dome, follows coexistence boundary, or bypasses



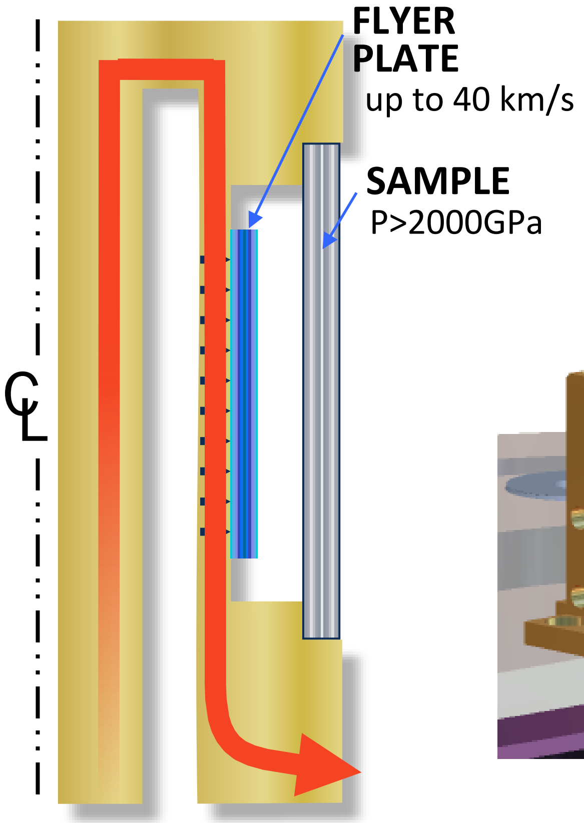


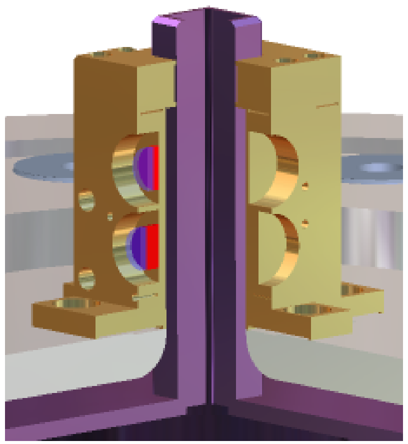


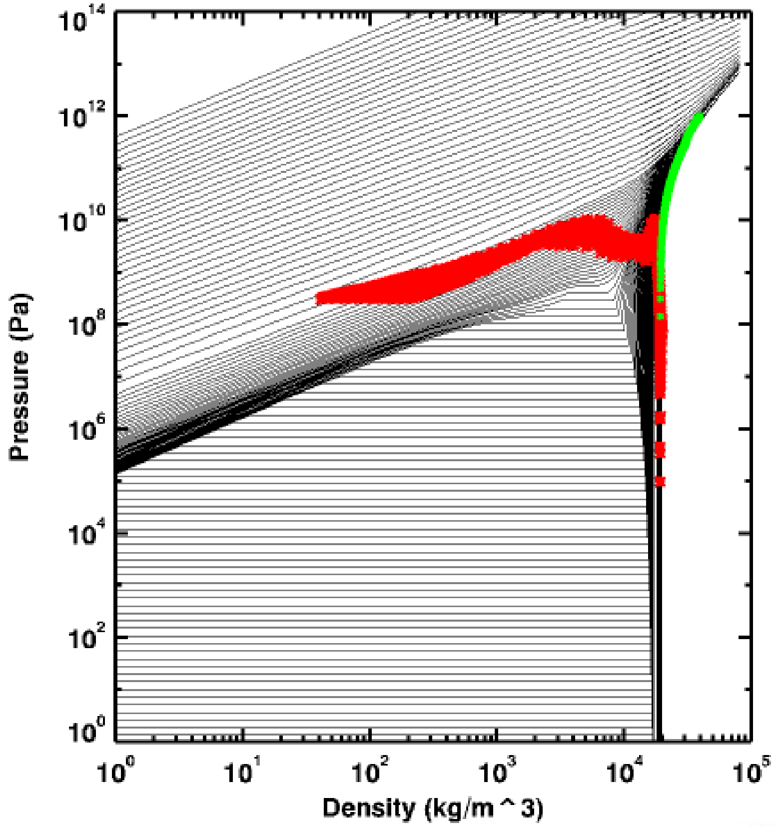
D.B. Sinars et al., PRL 100, 145002 (2008)

High Impedance Measurements on Z

- Reverse ballistic impact experiments
  - Measure high pressure shock Hugoniot of sample
- Pressures up to 20 Mbar
- Temperatures up to 60,000 K







Images Courtesy Thomas Mattsson

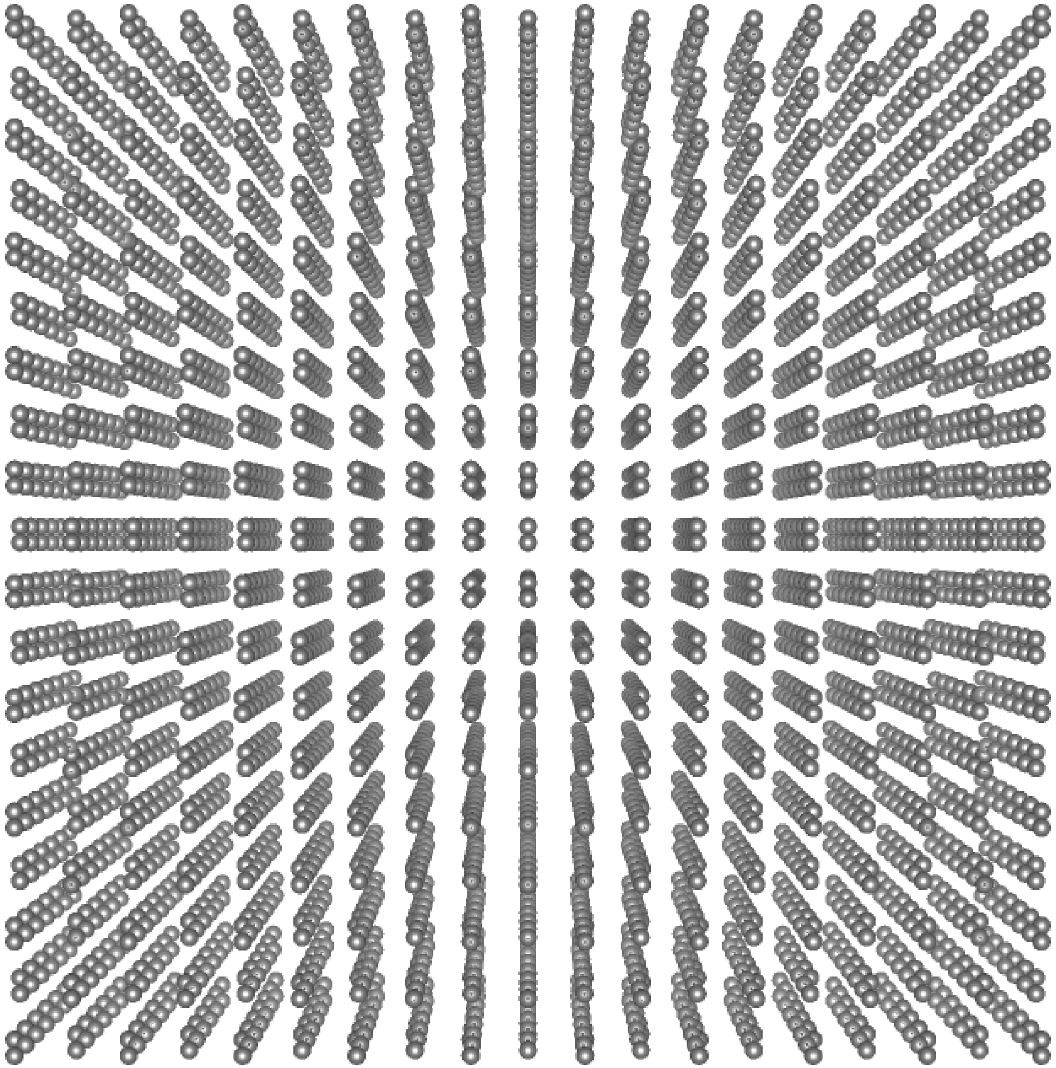
Methods – Molecular Dynamics

VASP

- DFT – PBE
- PAWs
- 10 e^- Pseudopotential

  [Xe] $4f^{14}\ 5d^{9}\ 6s^{1}$
- NVT ensemble

108 atom supercell



Critical Point Estimate

EOS fit to DFTMD results:

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

Critical Point Condition:

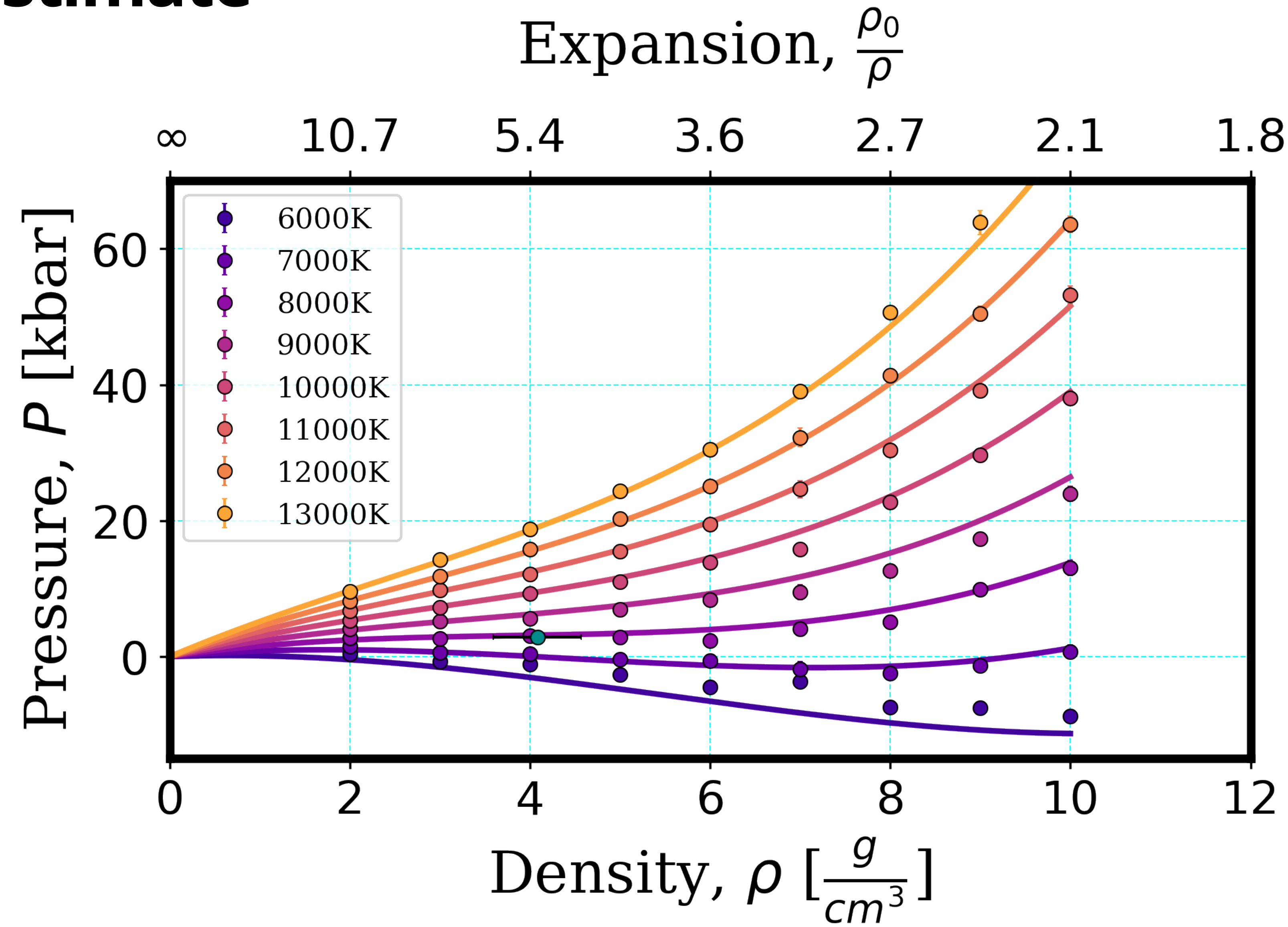
$$\left(\frac{\partial P}{\partial \rho}\right)_T = \left(\frac{\partial^2 P}{\partial \rho^2}\right)_T = 0$$

Estimated Critical Point:

$$\rho_c = 4.1 \pm 0.7 \frac{g}{cm^3}$$

$$T_c = 7800 \pm 190\ K$$

$$P_c = 2.8 \pm 0.5\ kbar$$

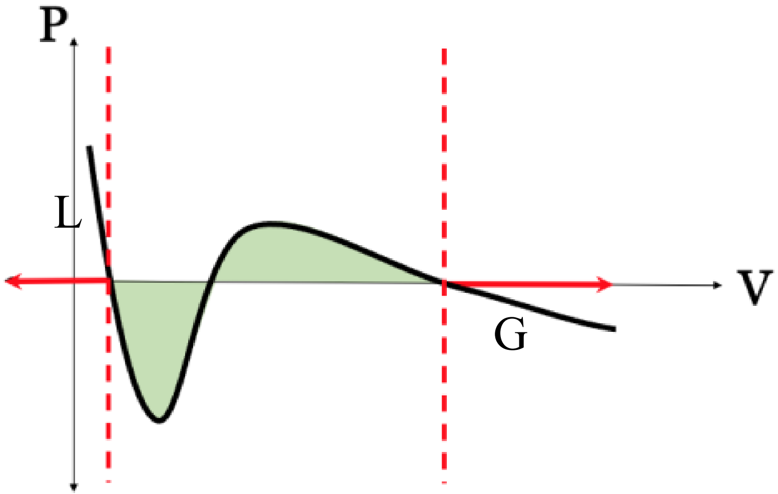


Townsend, J. P., Shohet, G., & Cochrane, K. R. (2020). Liquid-vapour coexistence and critical point of Mg 2 SiO 4 from ab initio simulations. *Geophysical Research Letters*, **47**(17), e2020GL089599.

Liquid-Vapor phase boundary

Maxwell Construction

- Sample temperatures near critical point
- Removes metastable states



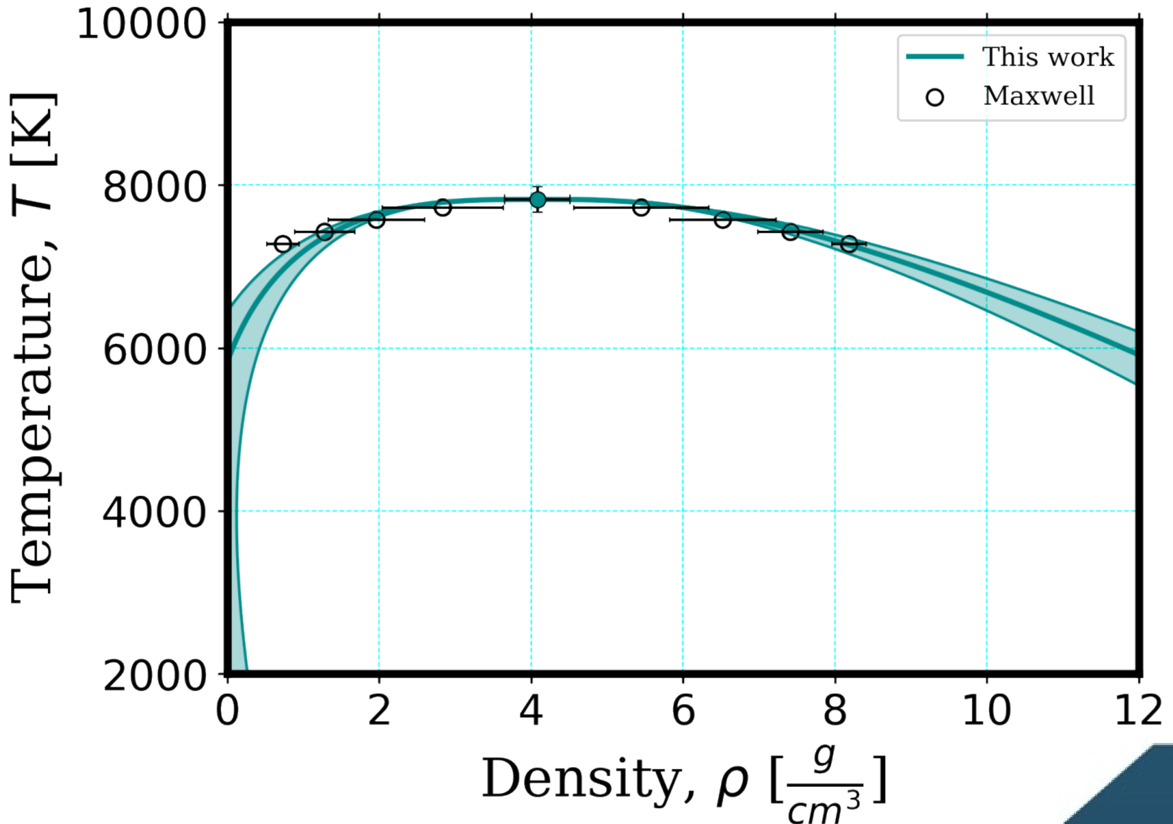
Renormalization group fit

- Mean Field Approximation
- $\beta = 0.325$
- $\delta = 0.500$

Near critical point, correlation length diverges

$$\xi \propto \left|\frac{T_c}{T - T_c}\right|^{\beta}$$

Map system with large correlation length to system with smaller length

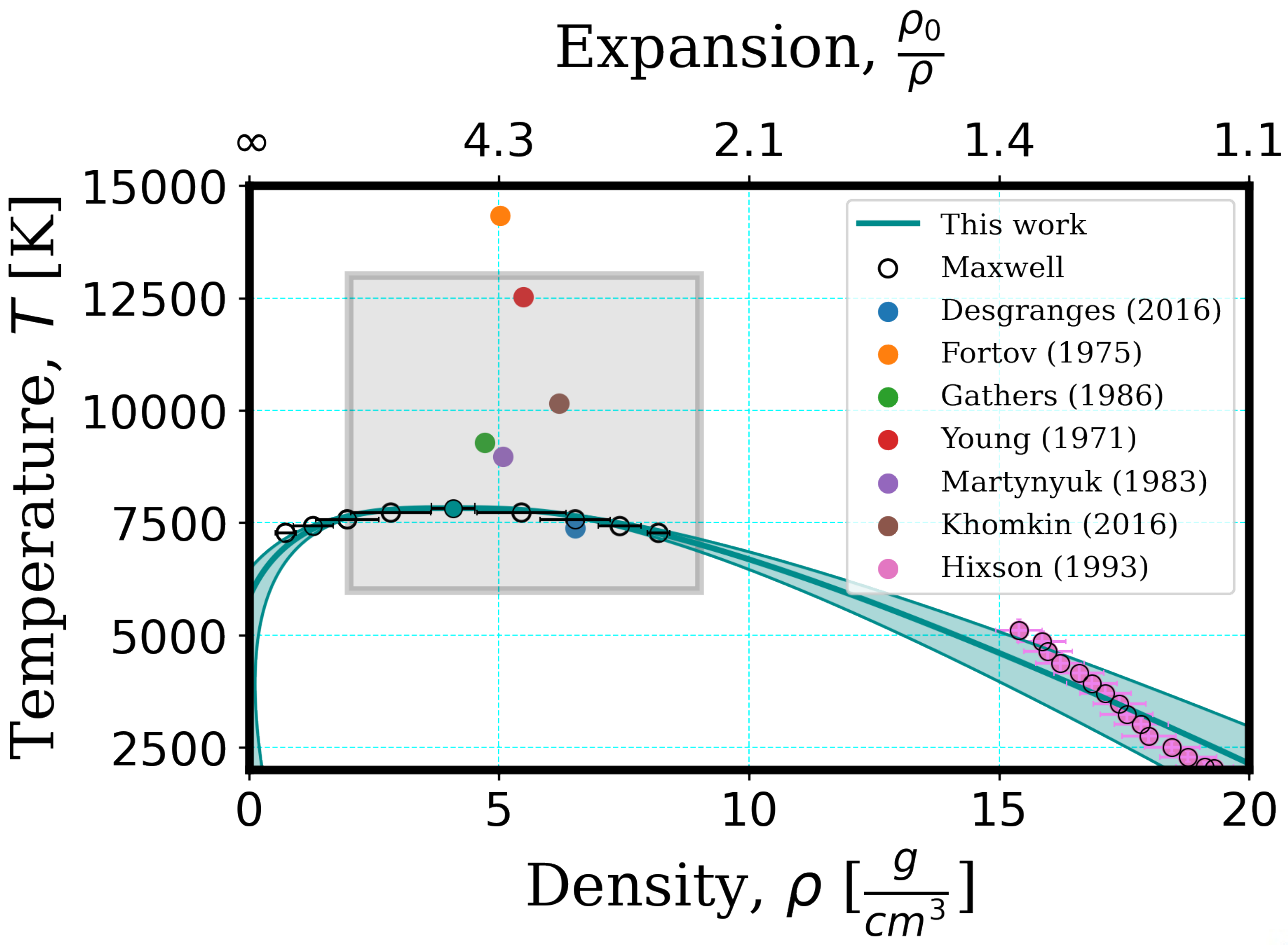


Liquid-Vapor phase boundary

Hixson: Resistive pulse heating at constant pressure, ~10^{-4} s

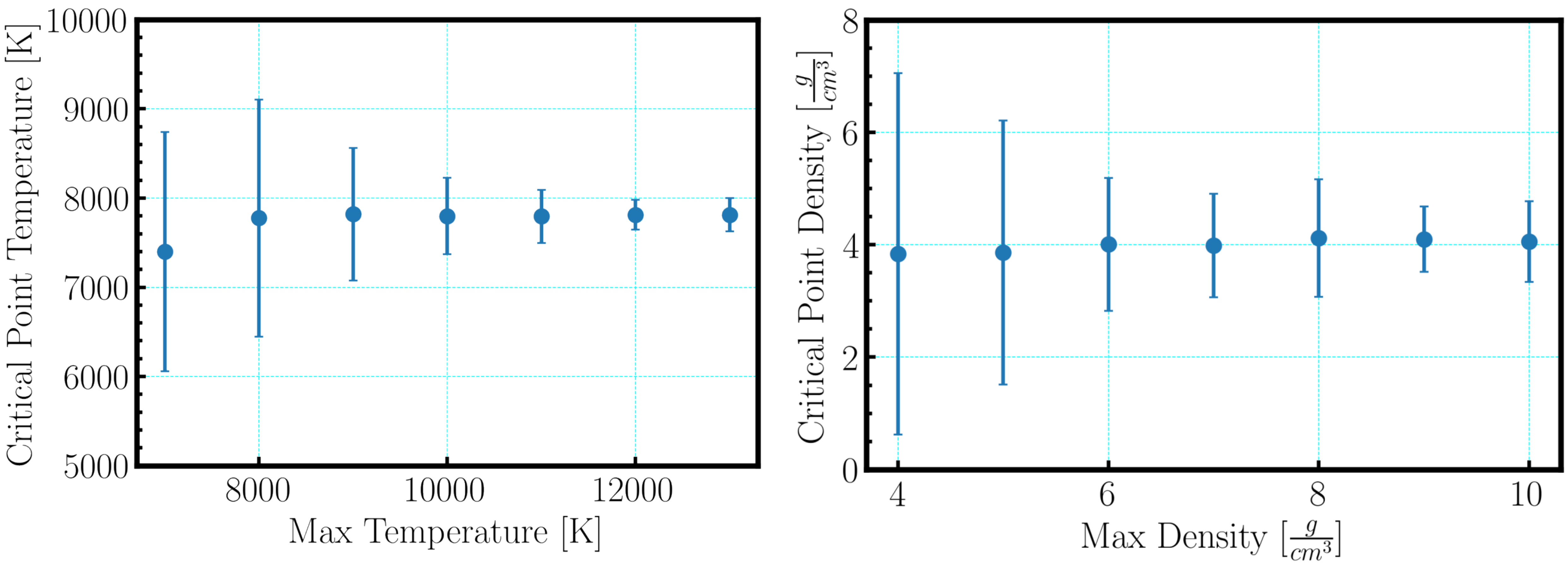
From melt to ~5100K

Pressure = 2 kbar



Hixson, R.S., Winkler, M.A. Thermophysical properties of liquid platinum. *Int J Thermophys* **14,** 409–416 (1993).

Simulation Region Influence on Critical Point



Electrical Conductivity – Kubo Greenwood (KG)

$$\sigma_k(\omega) = \frac{2\pi e^2\hbar^2}{3m^2\omega\Omega}\sum_{j=1}^{N}\sum_{i=1}^{N}\sum_{\alpha=1}^{3}\left[F(\epsilon_{i,k}) - F(\epsilon_{j,k})\right]\left|\langle\Psi_{j,k}|\nabla_\alpha|\Psi_{i,k}\rangle\right|^2\delta(\epsilon_{j,k} - \epsilon_{i,k} - \hbar\omega)$$

N discrete bands, Ω cubic supercell volume element, F Fermi weight, Ψ electronic wave function.

Calculated directly from electronic wave function

Dirac-delta approximate form

M. P. Desjarlais, J. D. Kress, and L. A. Collins Phys. Rev. E **66**, 025401(R) 26 August 2002.

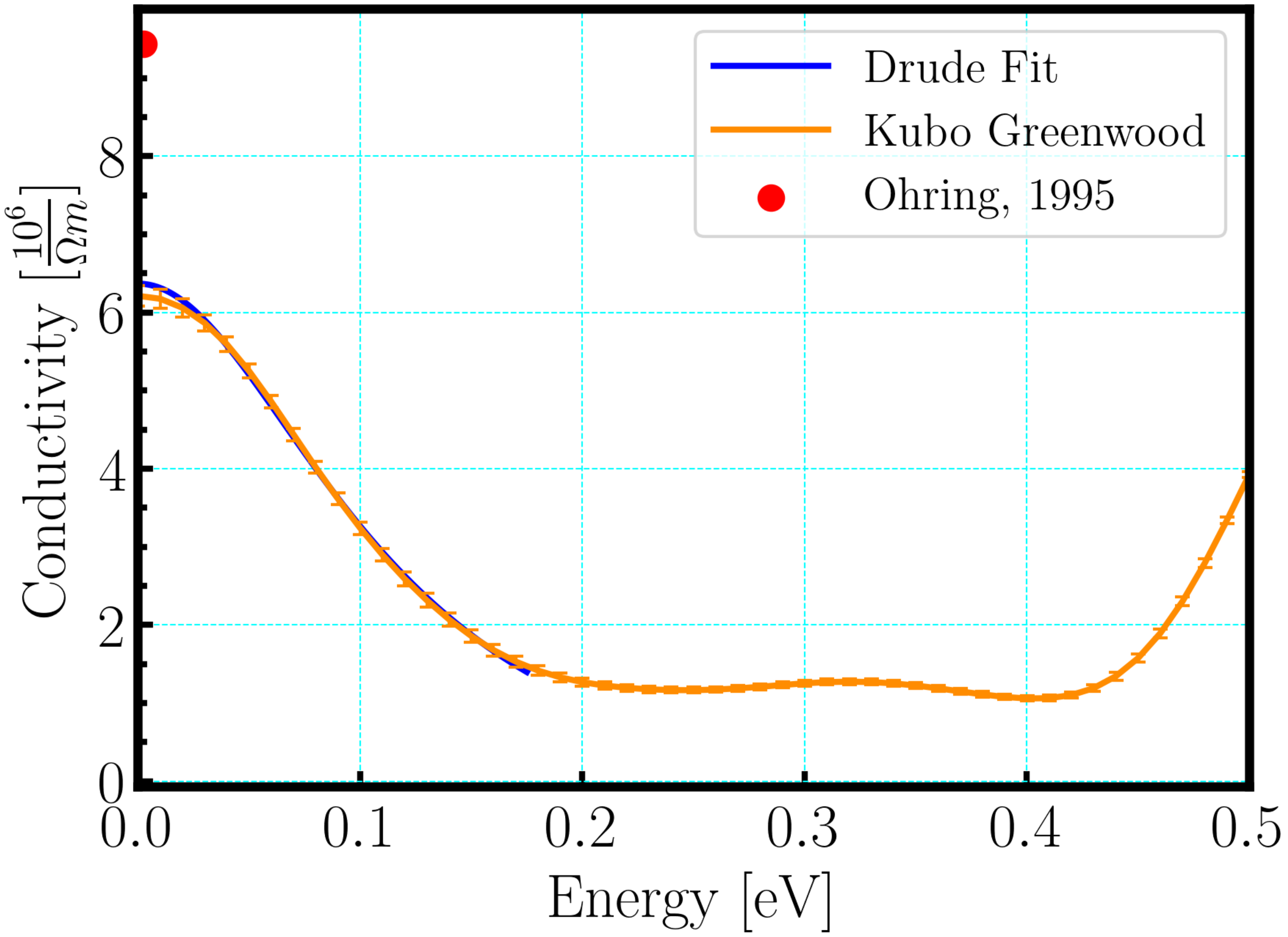
DC Conductivity

- VASP KG simulations – average over many snap shots
- Ambient conditions
- VASP KG results fit to Drude Model

$$\sigma(\omega) = \frac{\sigma_0}{1 + \omega^2\tau^2} + constant$$

$$constant = -0.064$$

- Compare to $\sigma_{0,exp} = 9.434 \ \frac{10^6}{\Omega m}$

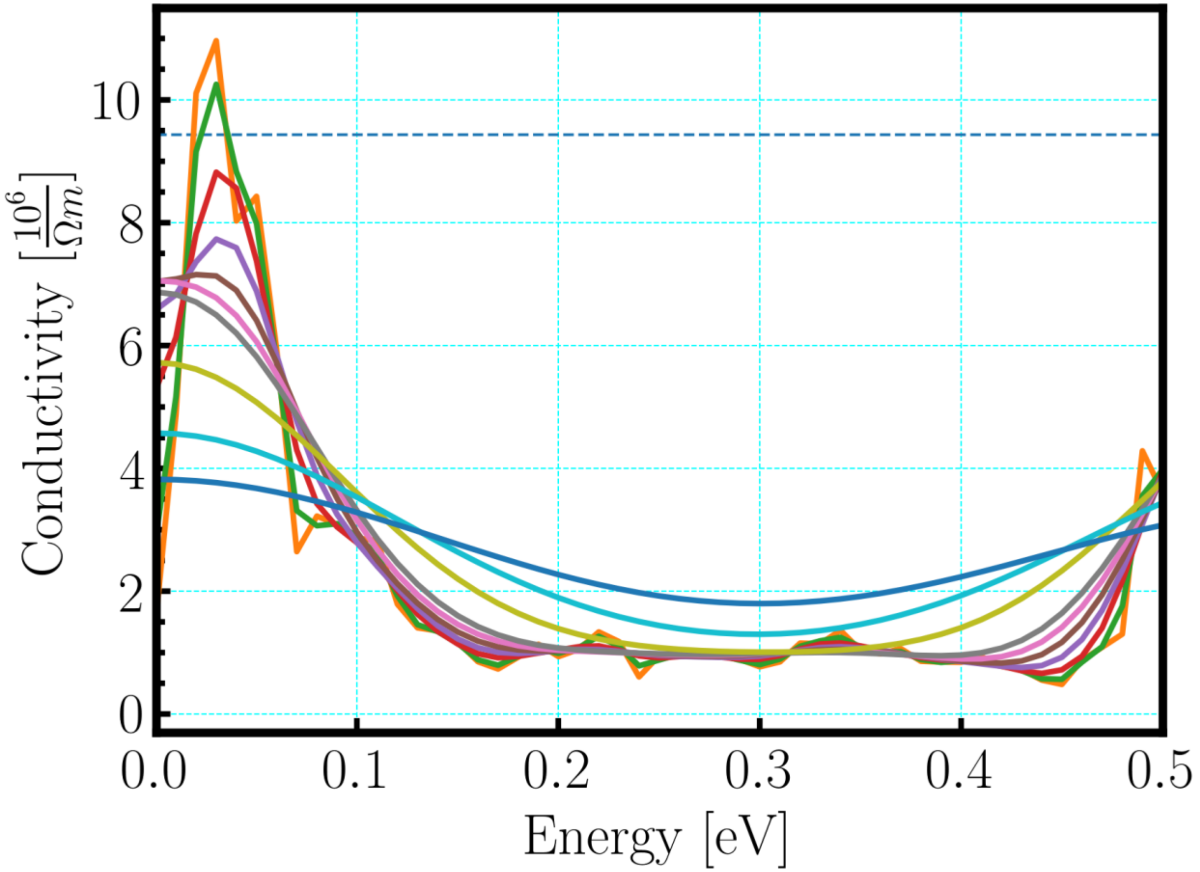


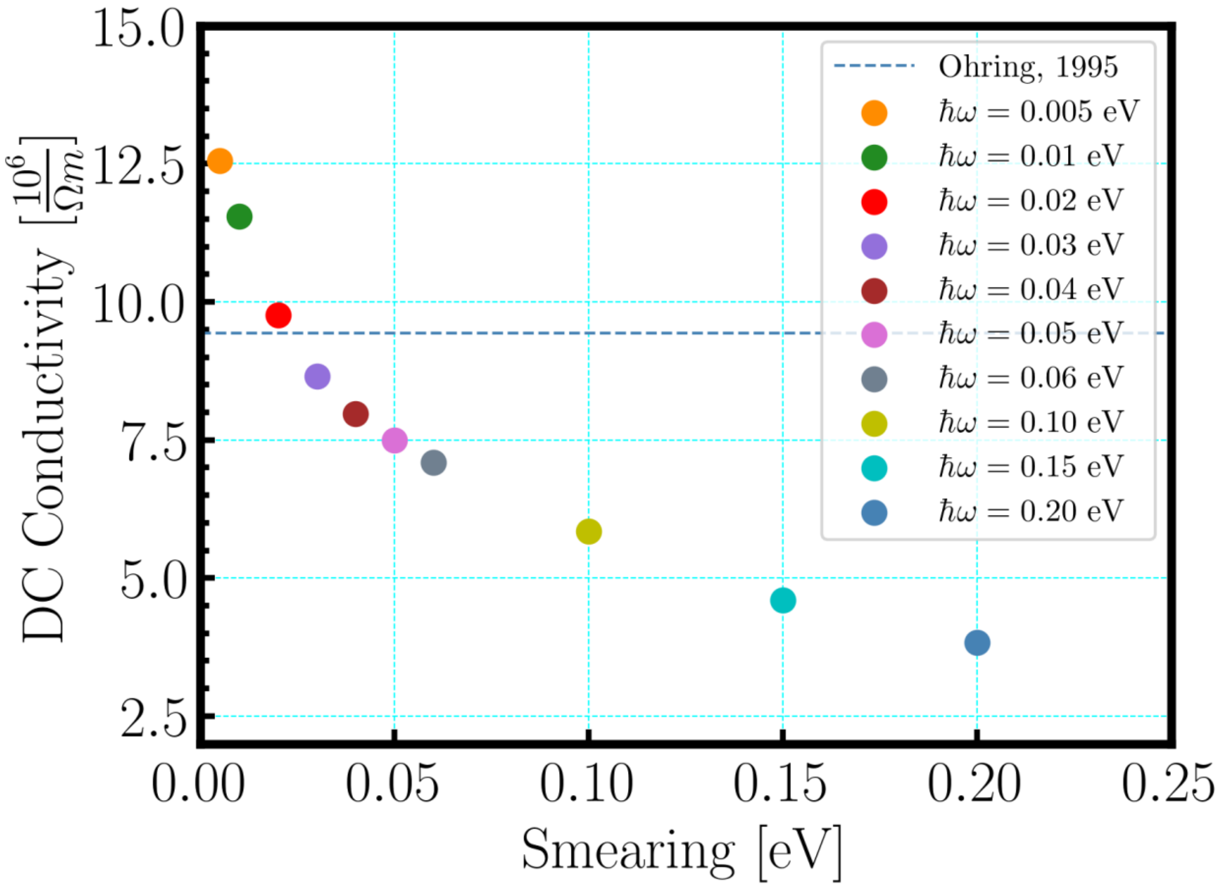
Ohring, Milton. "Engineering Materials Science." New York: Academic Press, 1995.

Discrete Band Structure Smearing

Smooth out local oscillations without losing structure

$$\sigma_k(\omega) = \frac{2\pi e^2\hbar^2}{3m^2\omega\Omega}\sum_{j=1}^{N}\sum_{i=1}^{N}\sum_{\alpha=1}^{3}[F(\epsilon_{i,k}) - F(\epsilon_{j,k})]\,|\langle\Psi_{j,k}|\nabla_\alpha|\Psi_{i,k}\rangle|^2\,\delta(\epsilon_{j,k} - \epsilon_{i,k} - \hbar\omega)$$

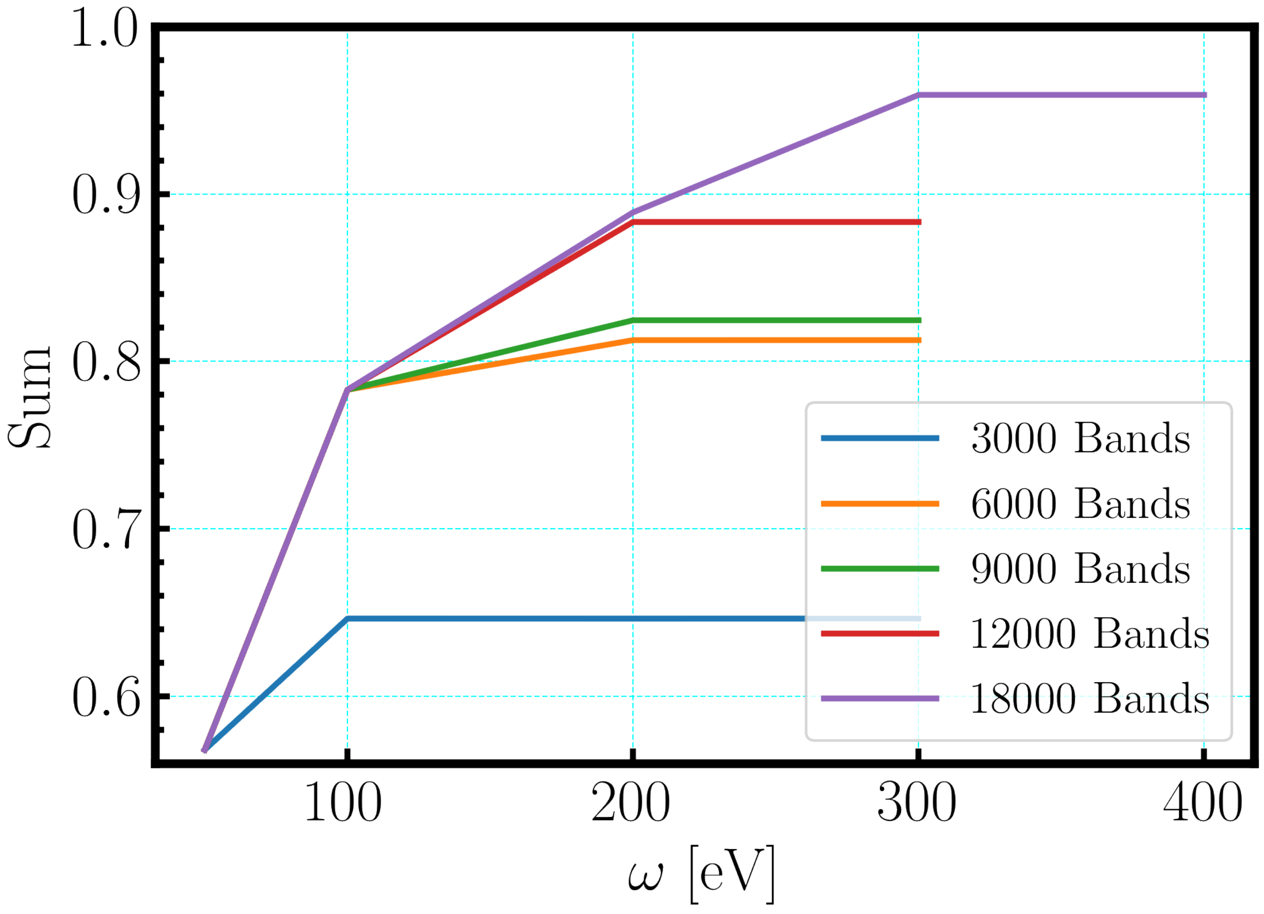


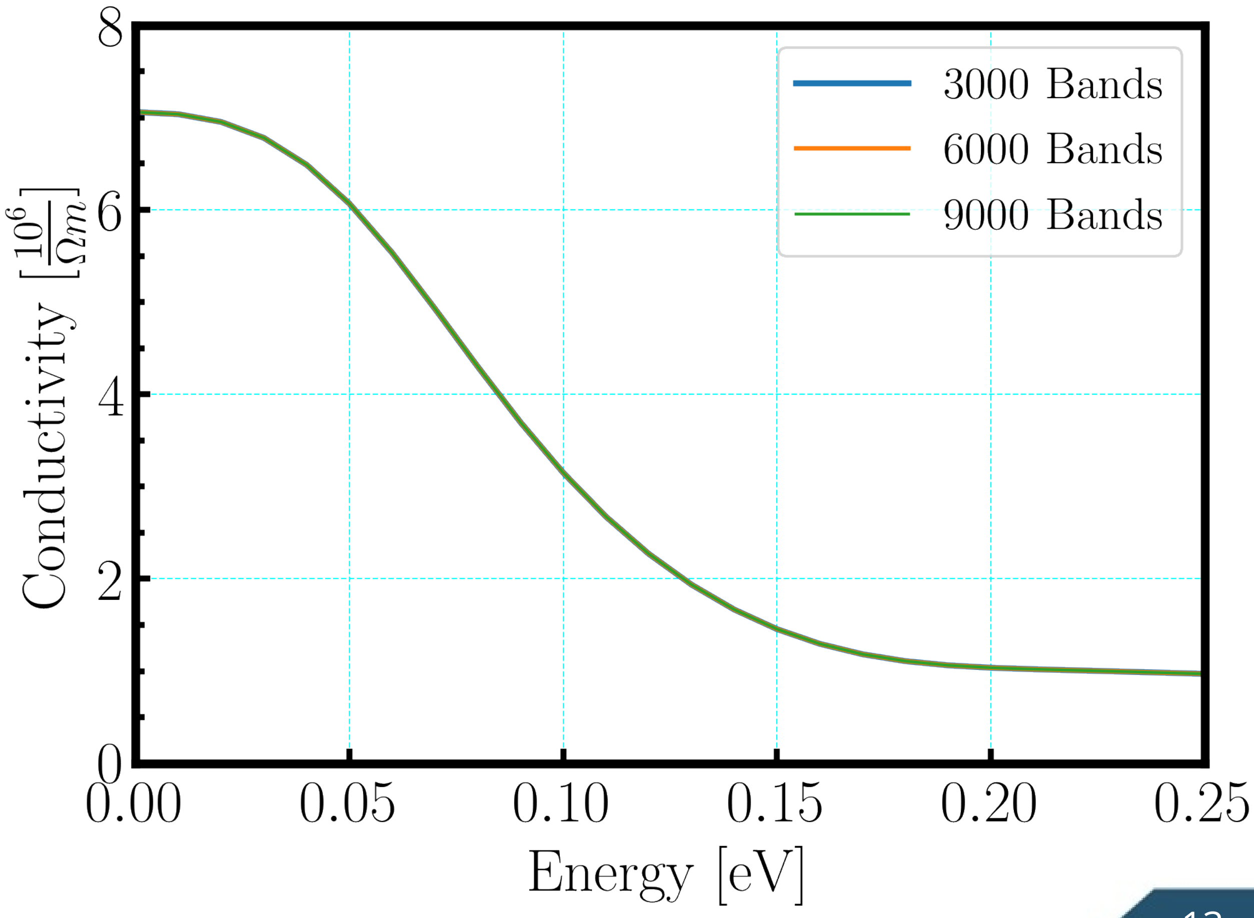


Sum Rule

DC conductivity converges much quicker than sum rule with increasing band number

$$S = \frac{2m\Omega}{\pi e^2 N_e}\int_0^\infty \sigma(\omega)d\omega = 1$$





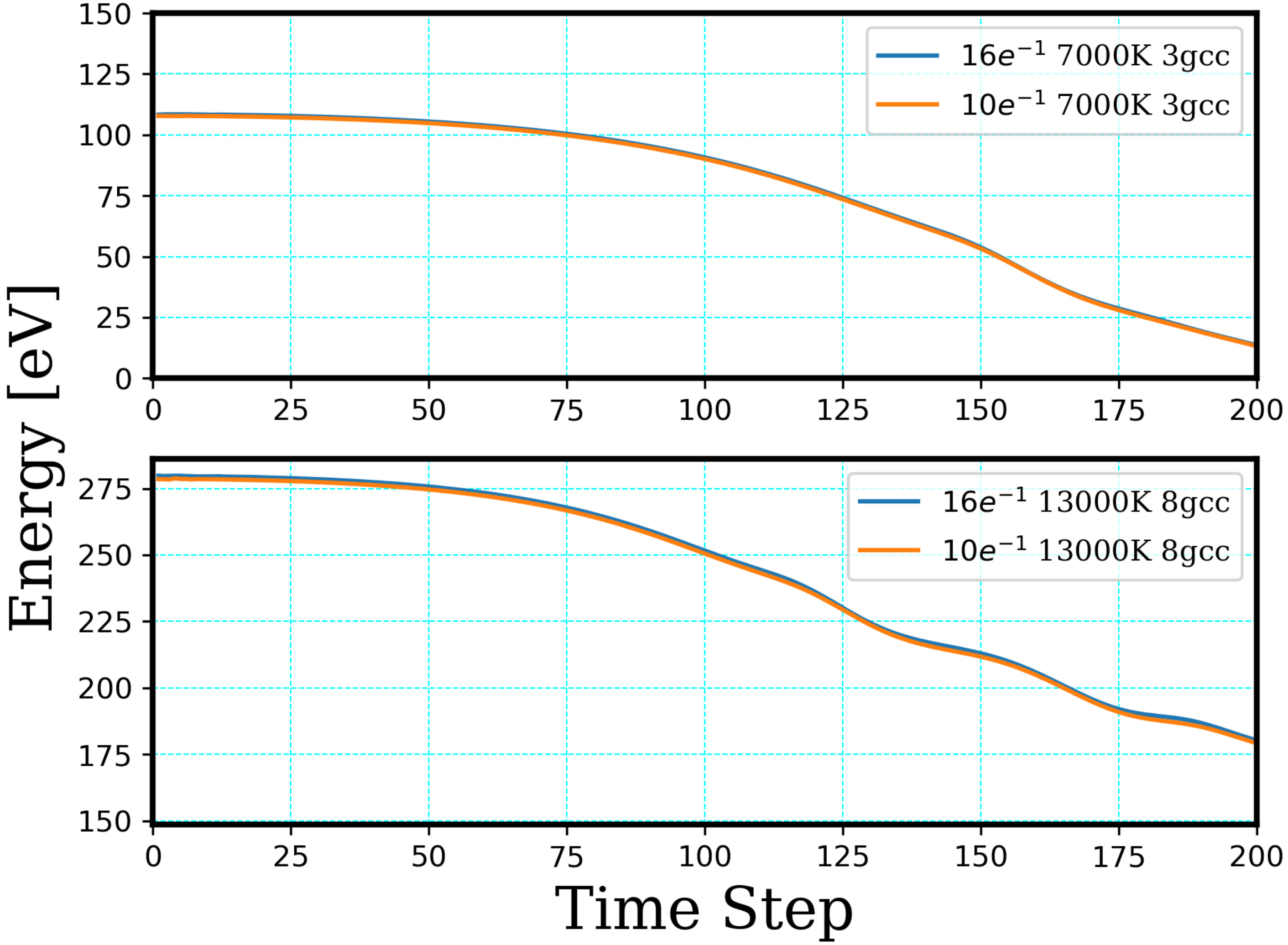
Conclusions

- Critical point estimated from EOS compares well with experimental data
  - $\rho = 4.1 \pm 0.7 \ \frac{g}{cm^3}$
  - $T = 7800 \pm 190 \ K$
  - $P = 2.8 \pm 0.5 \ kbar$
- At ambient, Kubo Greenwood approach agrees well with conductivity data

Future Work

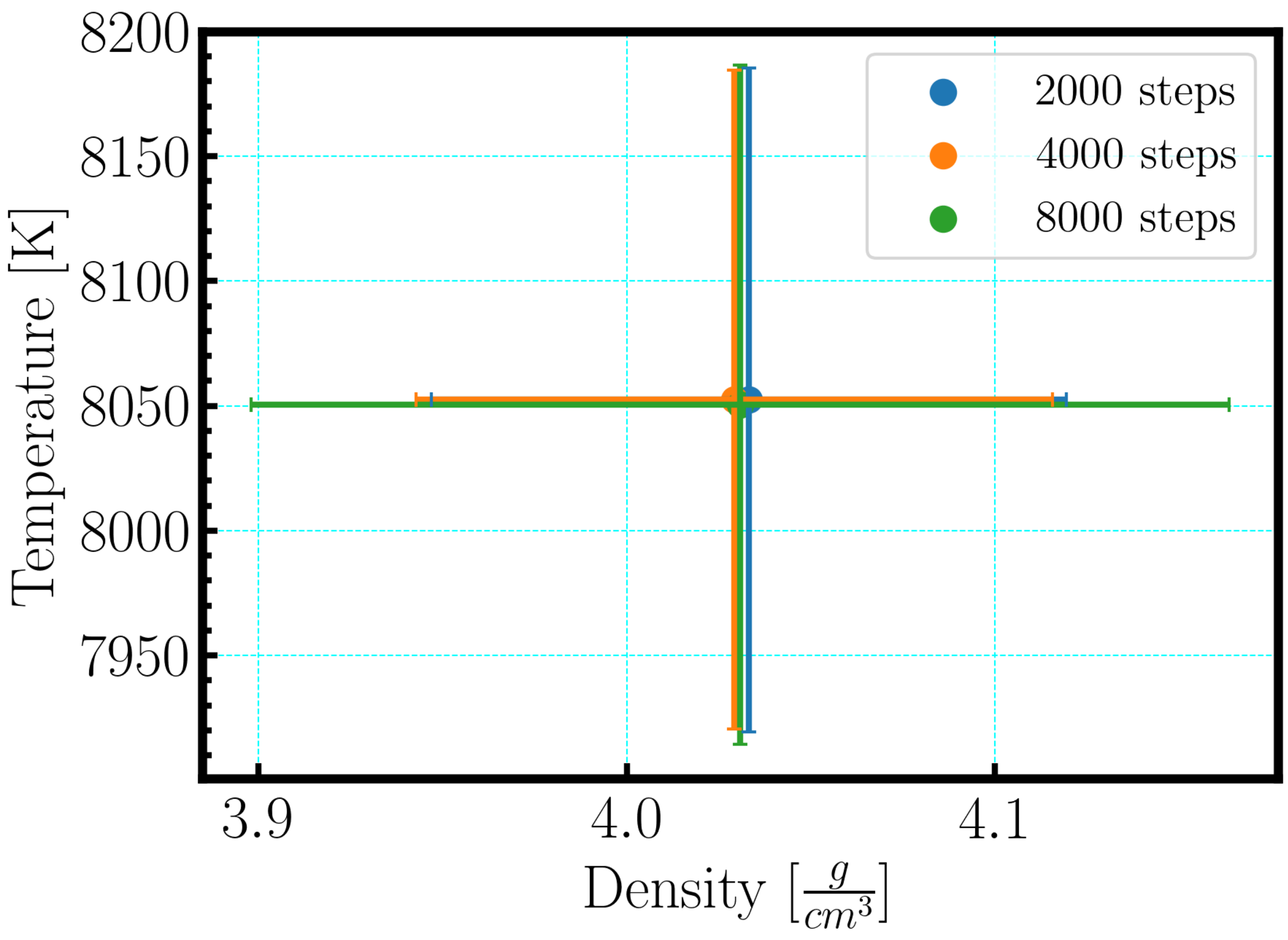
- DFTMD: Bond lifetime and speciation in coexistence
- Finite size effects will be quantified
- DC conductivity extrapolated at vapor dome

Supplemental Material – DFTMD



Supplemental Material – Critical Point Bootstrap

- 2000, 4000, 8000 steps
- Variance:
  - $\sigma_T^2 = 1.374$ K
  - $\sigma_\rho^2 = 1.982\times10^{-5}\ \frac{g}{cm^2}$



Supplemental Material – Conductivity