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DC Electrical Conductivity of Platinum At Liquid-Vapor Coexistence

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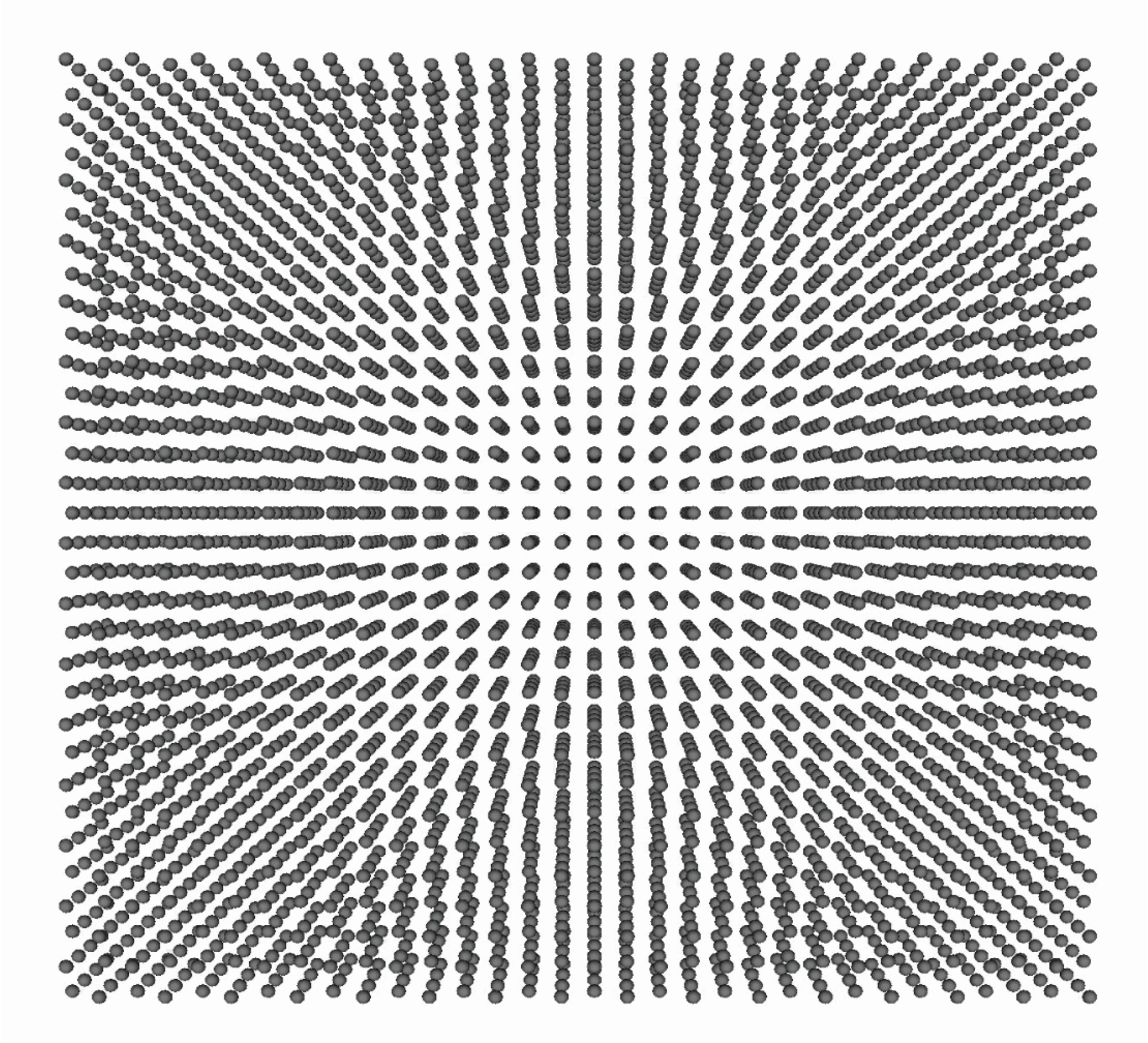
Molecular Dynamics

- VASP
  - DFT – PBE
  - 10 electron Projected Augment Wave (PAW) potential
  - [Xe] $4f^{14}$ $5d^{9}$ $6s^{1}$
  - NVT ensemble

- 32, 108, 256 atom supercells



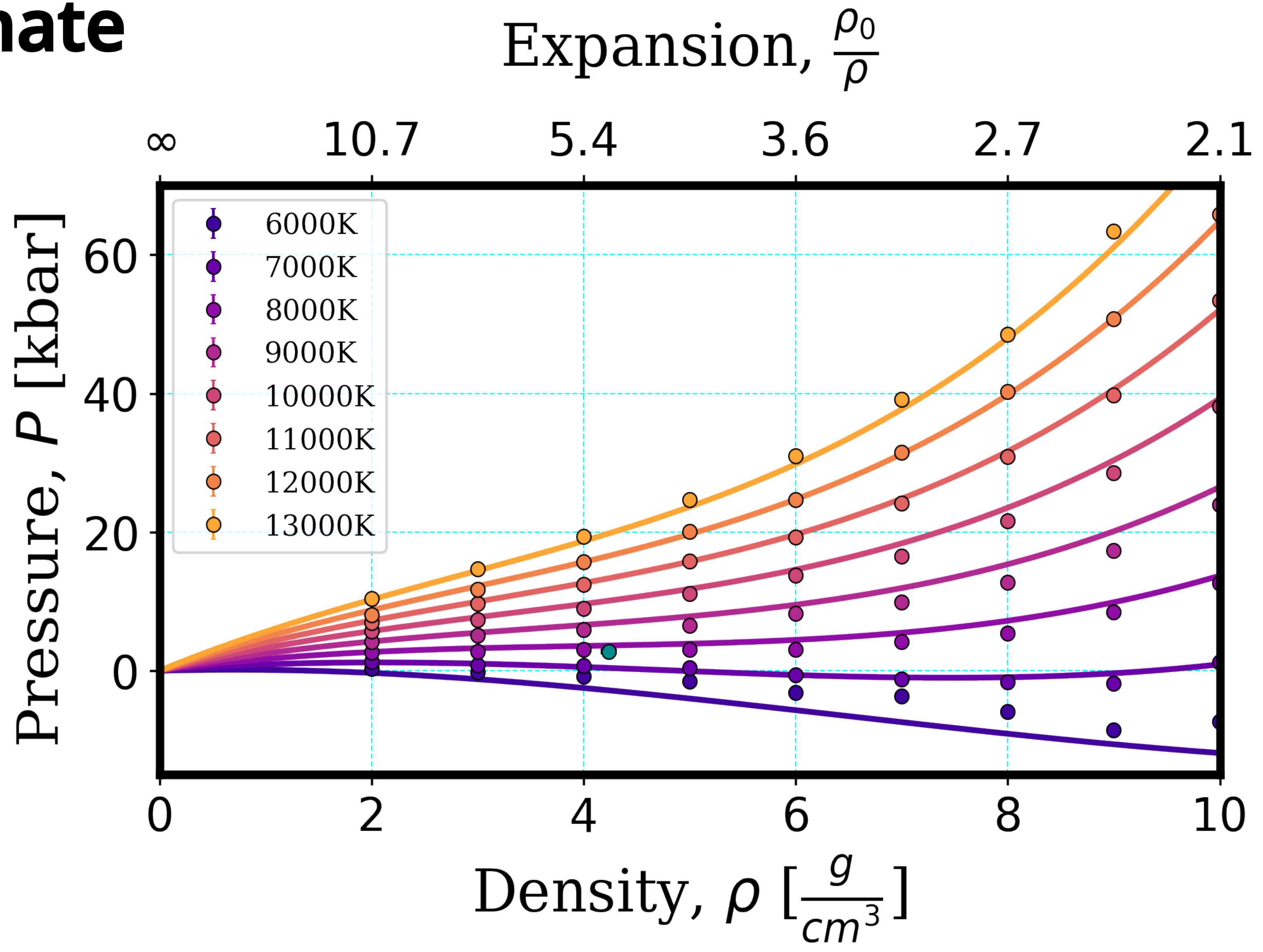
Critical Point Estimate

EOS fit to DFTMD results:

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

Critical Point Condition:

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



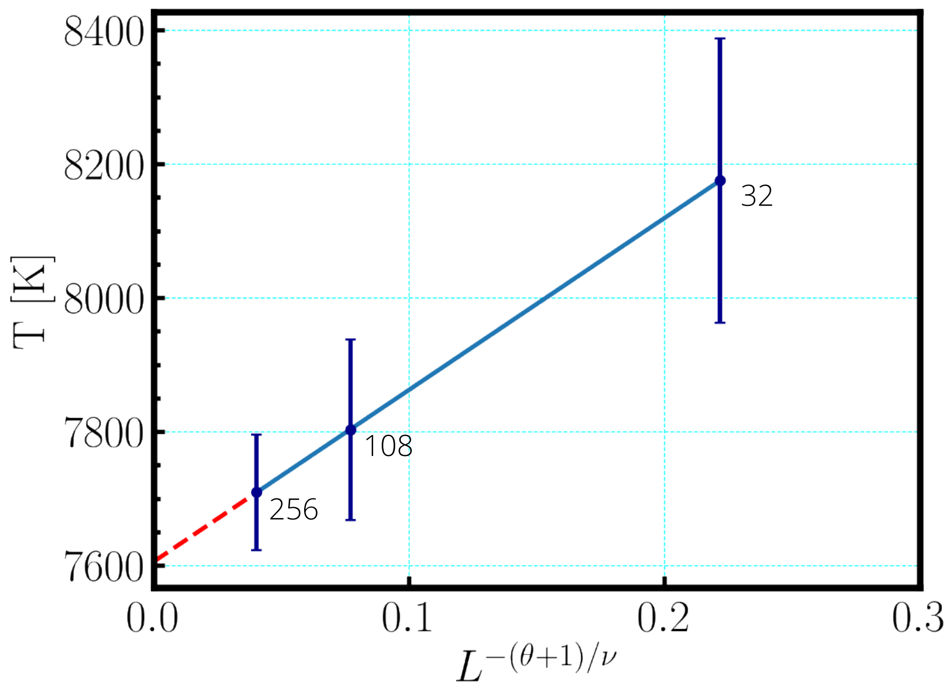
Townsend, J. P., Shohet, G., & Cochrane, K. R. (2020). Liquid-vapour coexistence and critical point of Mg 2 SiO 4 from ab initio simulations. *Geophysical Research Letters*, 47(17), e2020GL089599.

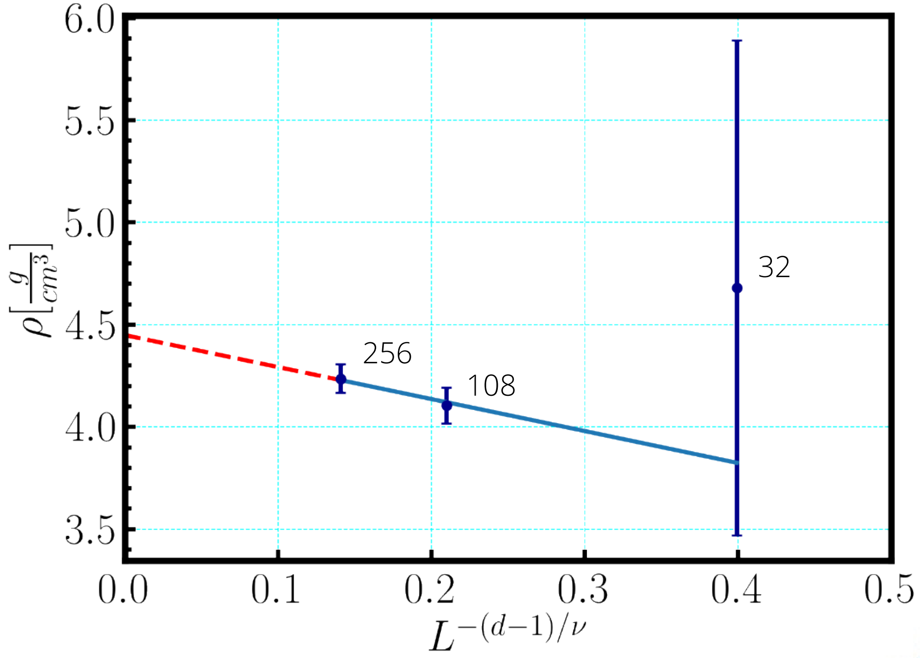
Critical Point – Extrapolation to Infinite System Size

$$\rho_c = 4.5 \pm 0.1 \frac{g}{cm^3}$$

$$T_c = 7600 \pm 100\ K$$

$$P_c = 2.7 \pm 0.4\ kbar$$



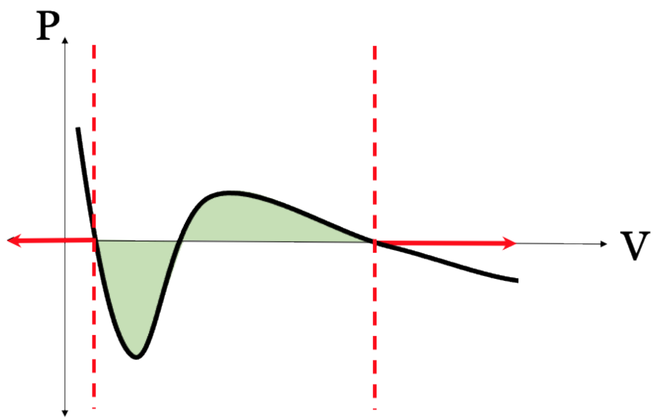


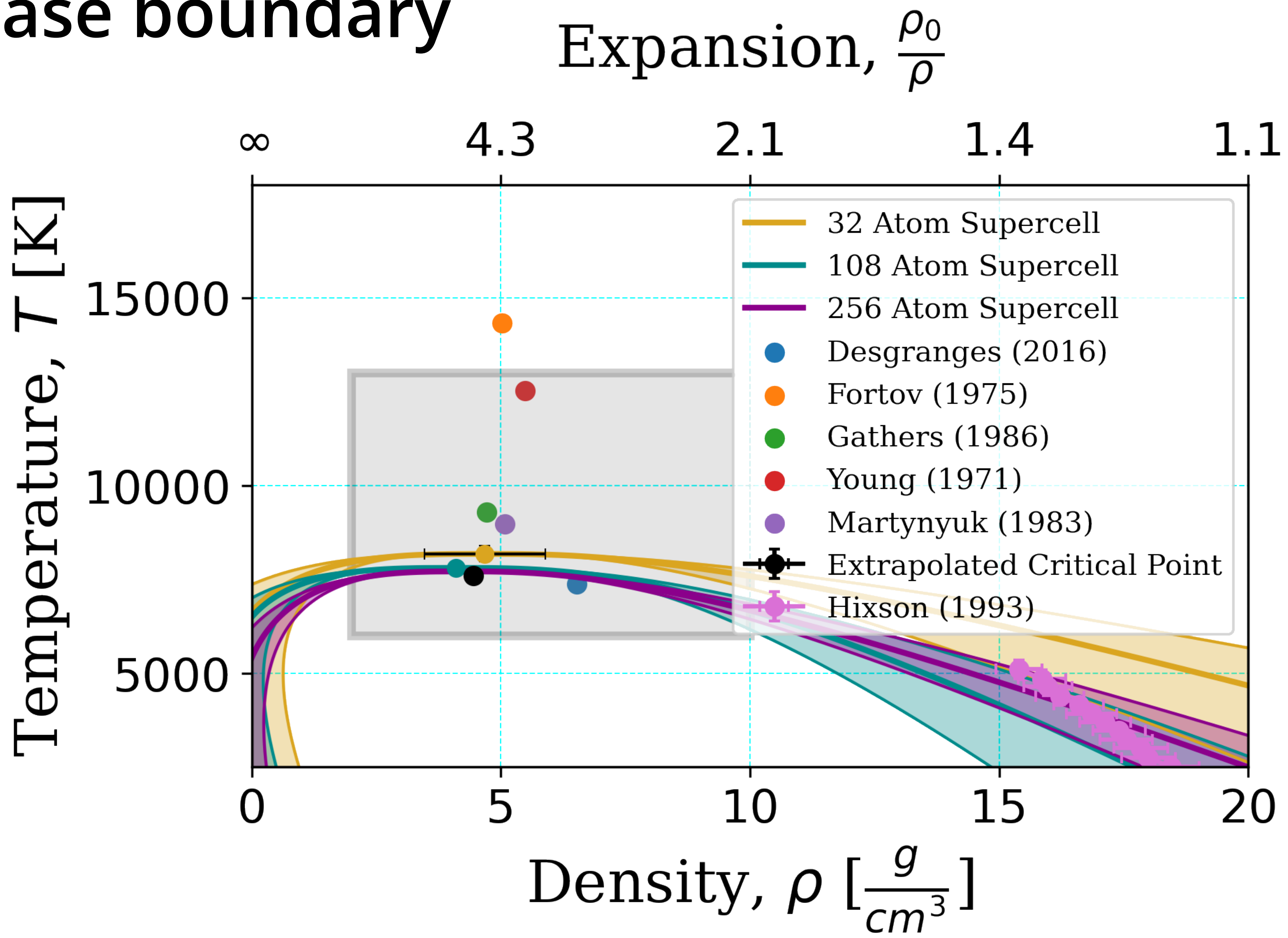
Nigel B. Wilding. Critical-point and coexistence-curve properties of the lennard-jones fluid: A finite-size scaling study. Phys. Rev. E, 52:602–611, Jul 1995.

D. M. Saul, Michael Wortis, and David Jasnow. Confluent singularities and the correction-to-scaling exponent for the d = 3 fcc ising model. Phys. Rev. B, 11:2571–2578, Apr 1975.

Liquid-Vapor phase boundary

Maxwell Construction for isotherms 7000-7600K





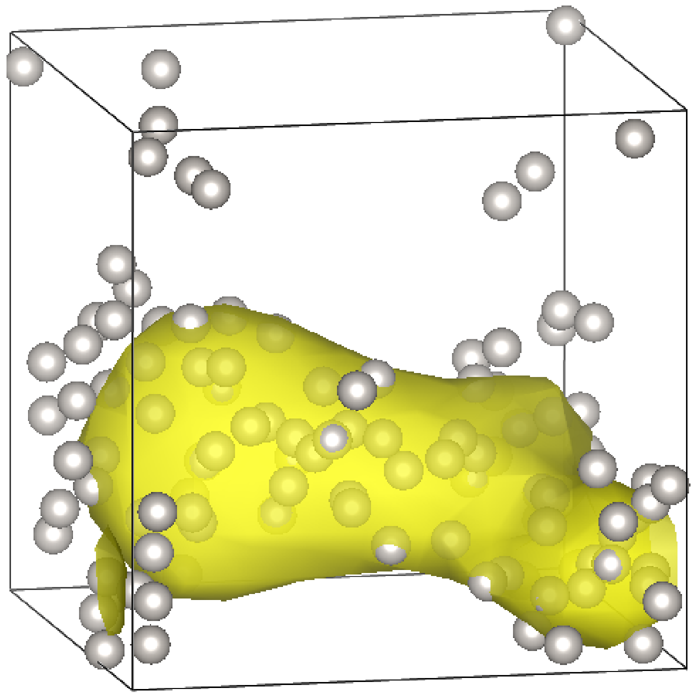
Xiao, B., and L. Stixrude (2018), Critical vaporization of MgSiO3, Proceedings of the National Academy ofSciences,115,5371-5376,doi:10.1073/pnas.1719134115.

Summary / Future Work

- The critical point calculated for the 256 atom supercell is within the error of the extrapolated point.

- Liquid-vapor phase boundary agrees very well with Hixson data far outside the simulation region

- Currently performing a dividing surface calculation to check validity of Maxwell construction



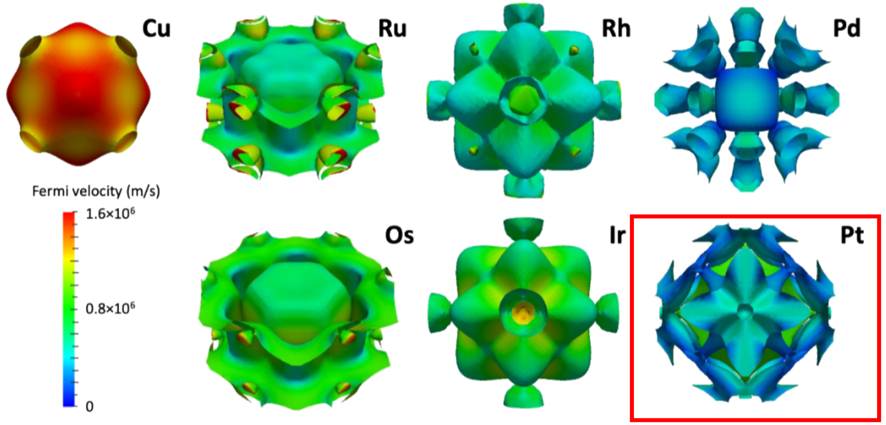
Calculate the liquid and vapor densities at the phase boundary using atomic positions

Electrical Conductivity – Kubo-Greenwood (K-G)

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

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

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



Pt has a complex Fermi surface

Dutta, Shibesh et al. "Thickness dependence of the resistivity of platinum-group metal thin films." *Journal of Applied Physics* 122 (2017): 025107.

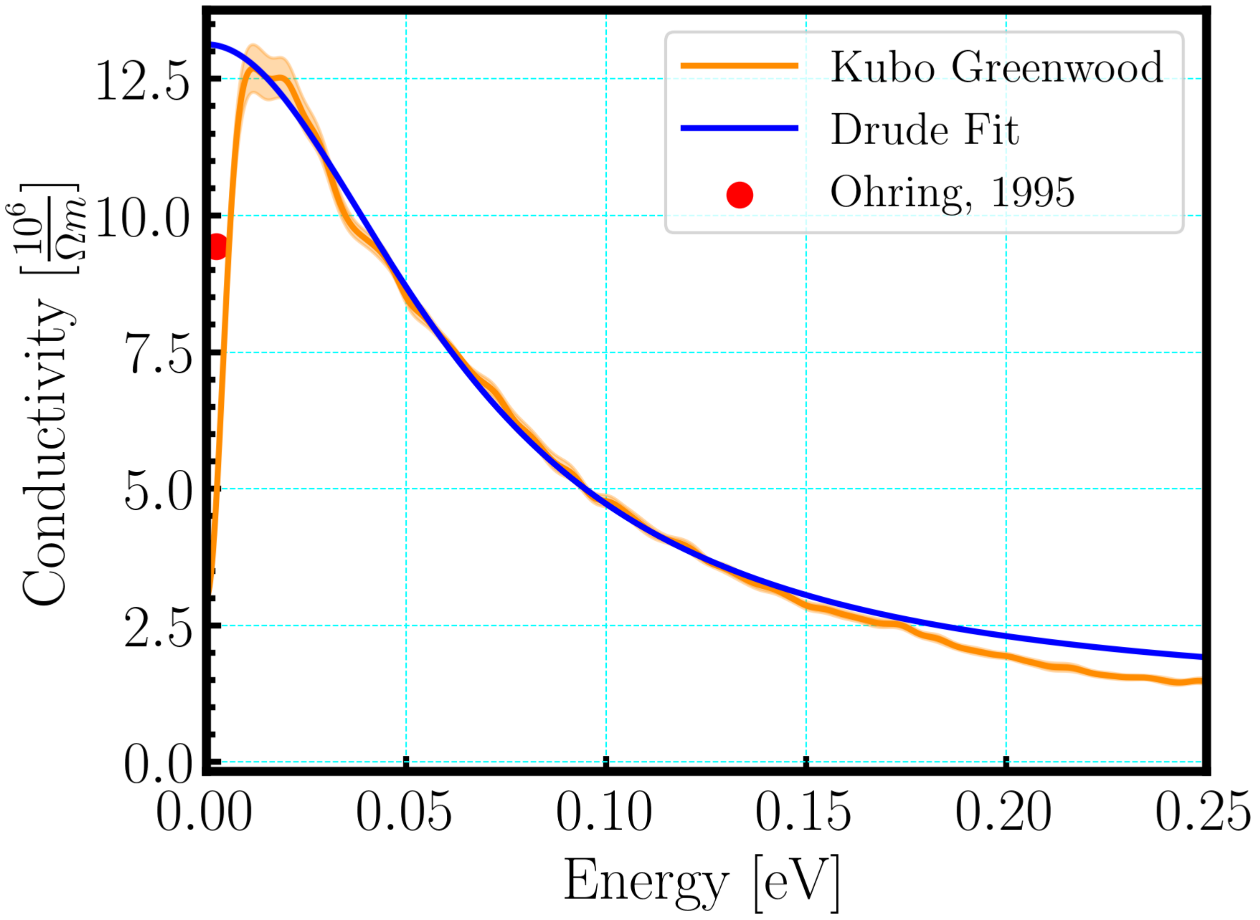
M. P. Desjarlais, J. D. Kress, and L. A. Collins Phys. Rev. E **66**, 025401(R) 26 August 2002.

Ambient DC Electrical Conductivity

- 108 atoms, ambient conditions
  - $\rho = 21.45 \frac{g}{cm^3}$
- 10x10x10 Monkhorst-Pack grid
- VASP KG results fit to Drude Model

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

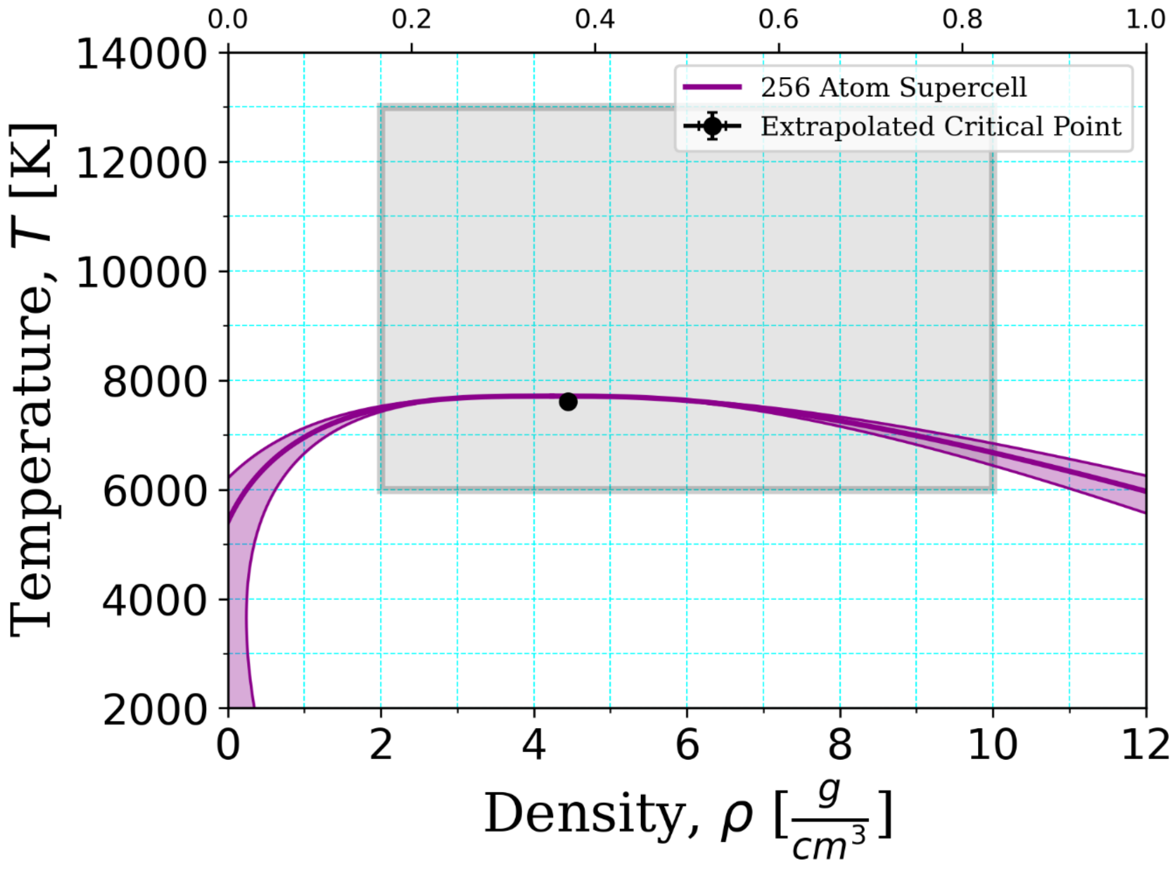
- $\sigma_{DC} = 13.1 \pm 0.7 \frac{10^6}{\Omega m}$
- Within 28% of $\sigma_{DC,exp} = 9.434 \frac{10^6}{\Omega m}$



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

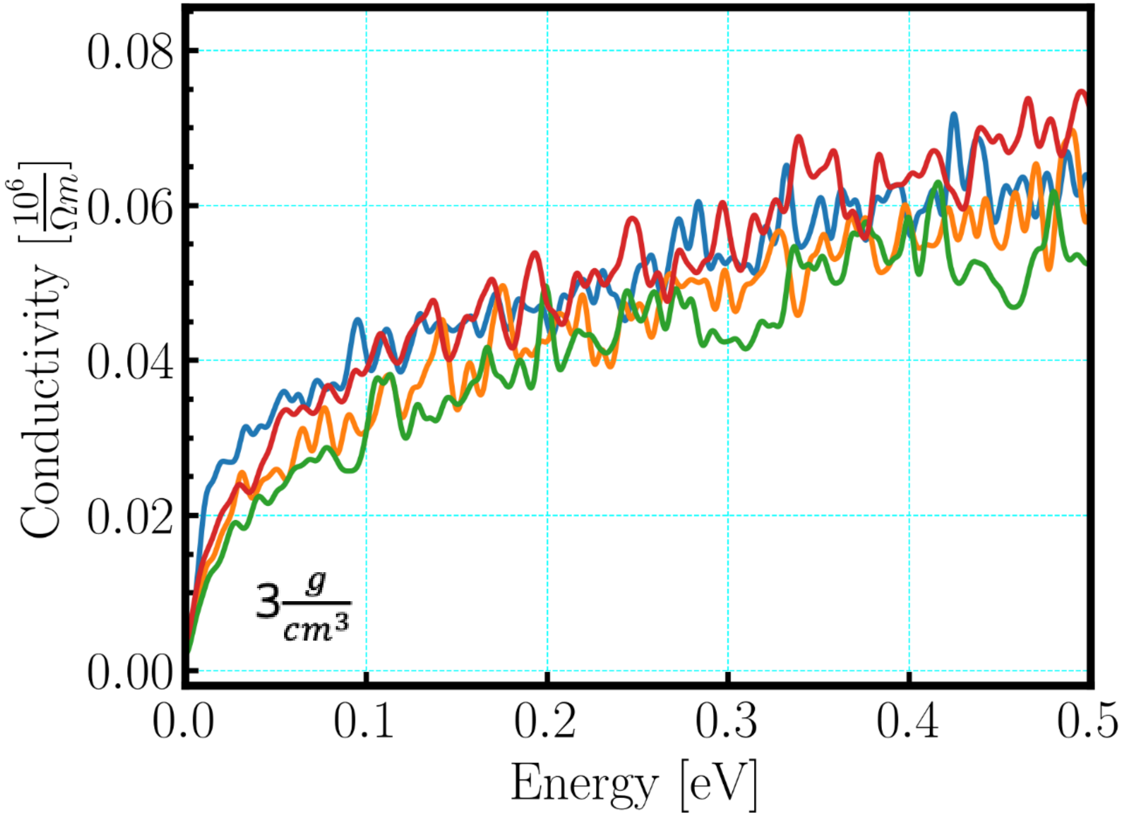
Electrical Conductivity in the Coexistence Region

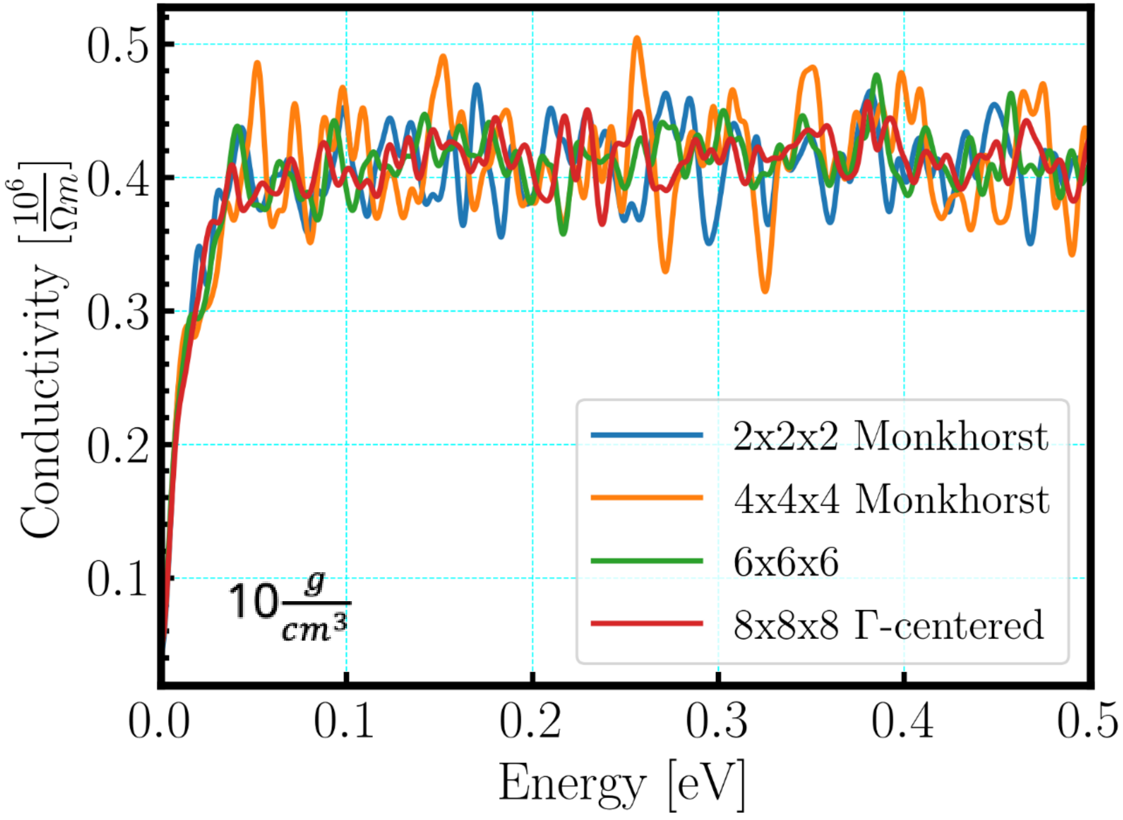
- 72 total ρ-T points
- Need K-G parameters for entire region
- Check convergence at density and temperature extremes



Brillouin Zone Sampling

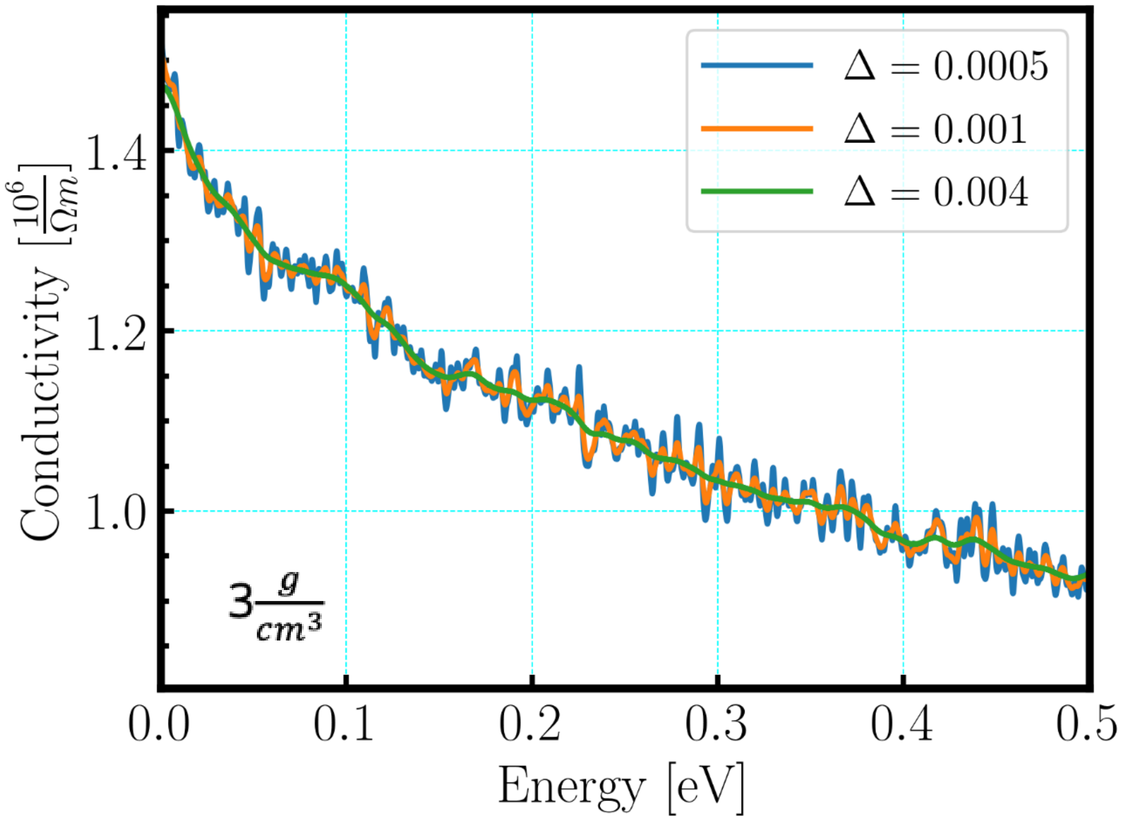
108 Atom Supercell at 6000K, single snapshot

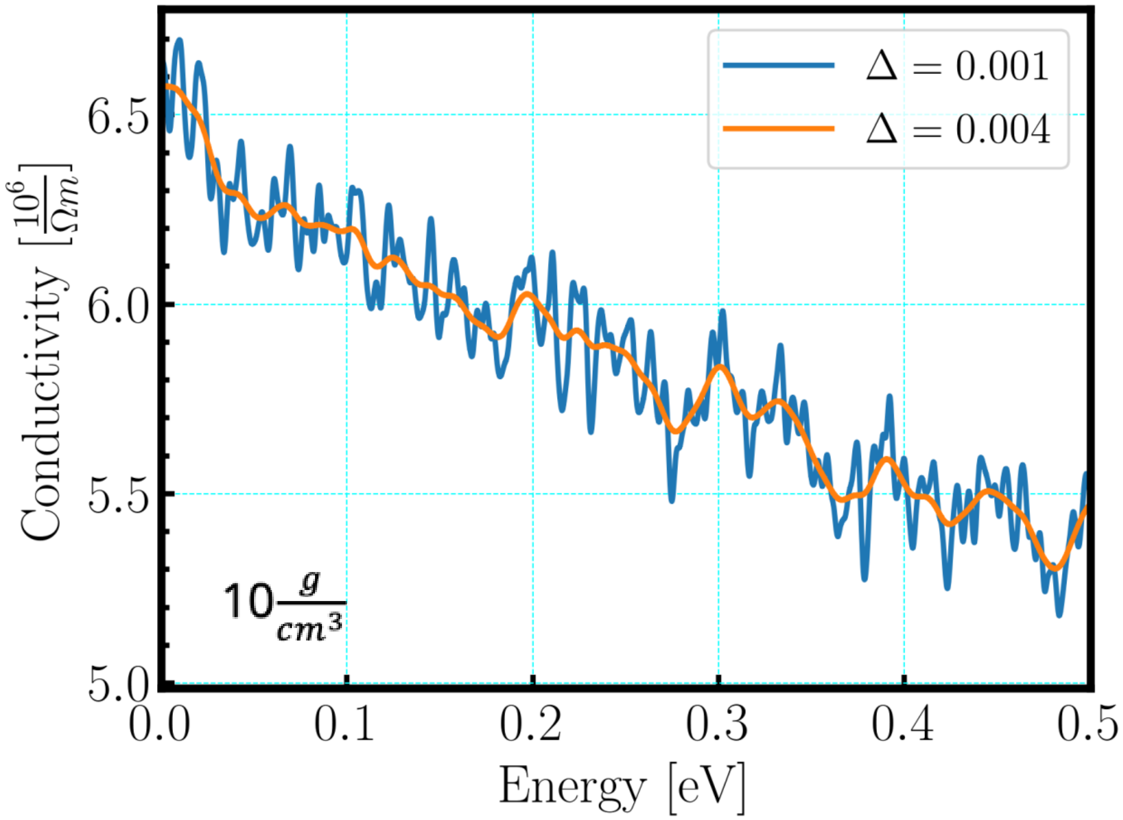




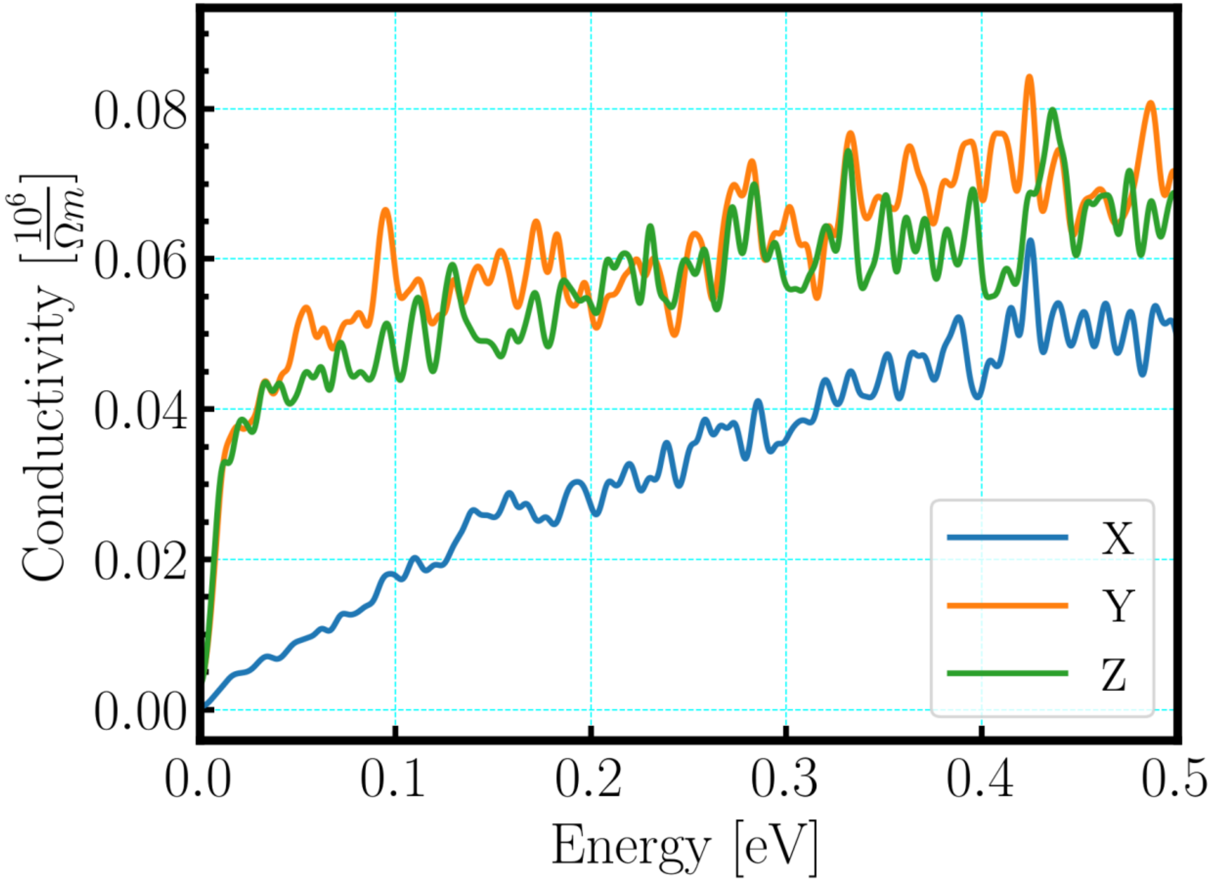
Discrete Band Structure Smearing

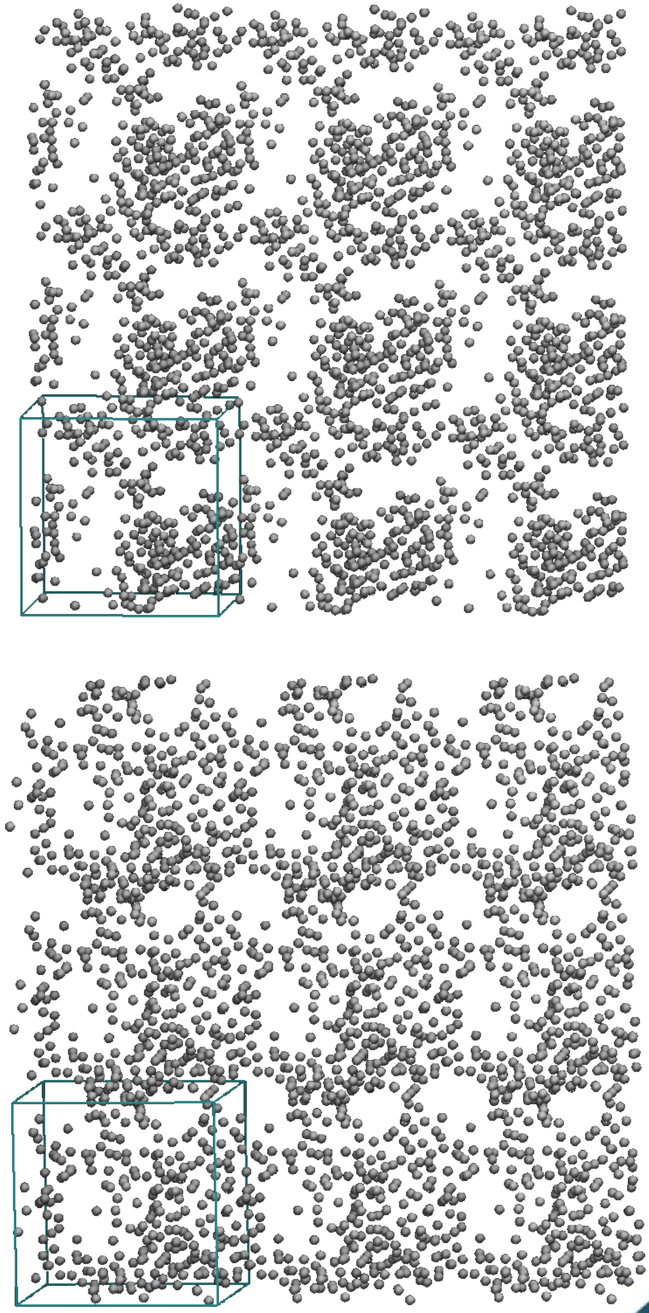
108 Atom Supercell at 13000K, single snapshot





Electrical Conductivity in Coexistence





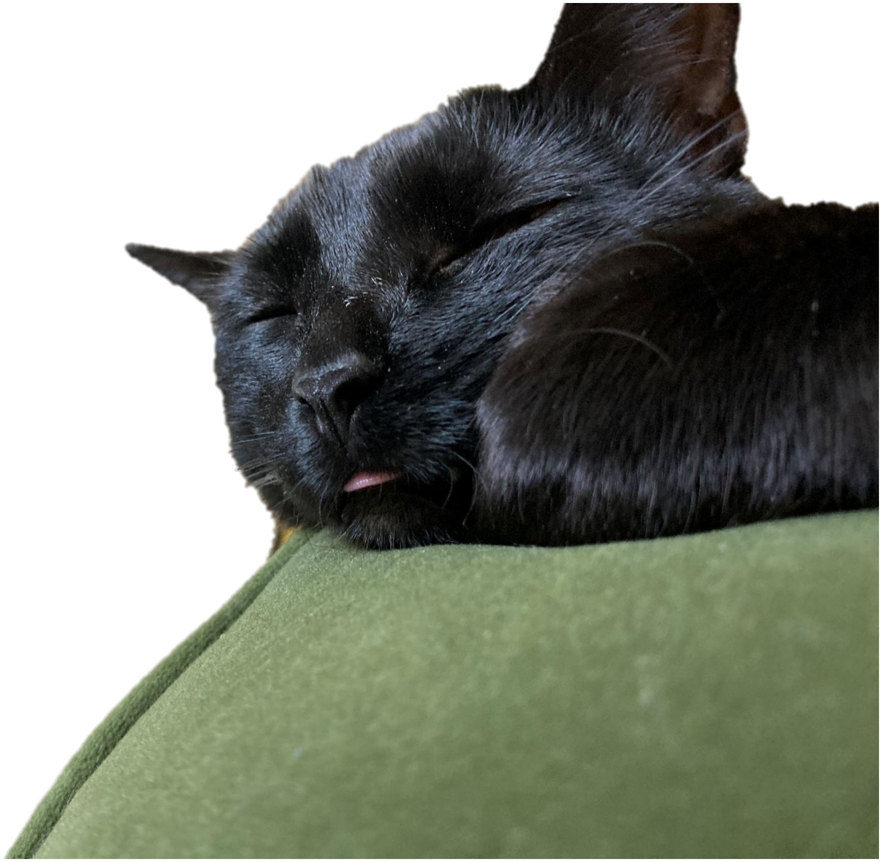
Structures emerging inside the vapor dome can lead to large heterogeneities in the conductivity

Summary / Future Work

- For robust conductivity calculations in the region of interest, K-G parameters must be calibrated to boundary extremes

- Calculations inside of the coexistence region experience large variations in structure between snapshots

- Large spatial and temporal heterogeneities in the electrical conductivity must be accounted for in assigning a macroscopic conductivity value

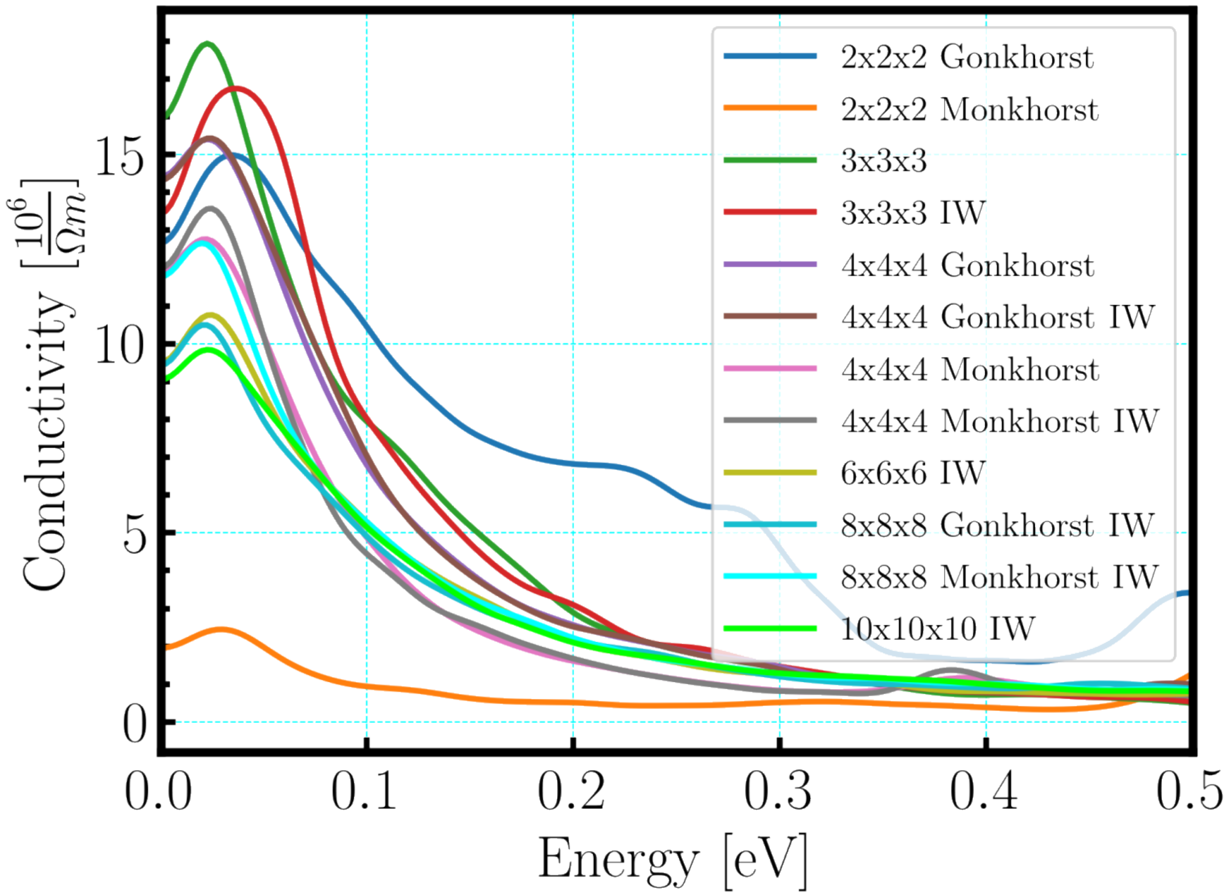


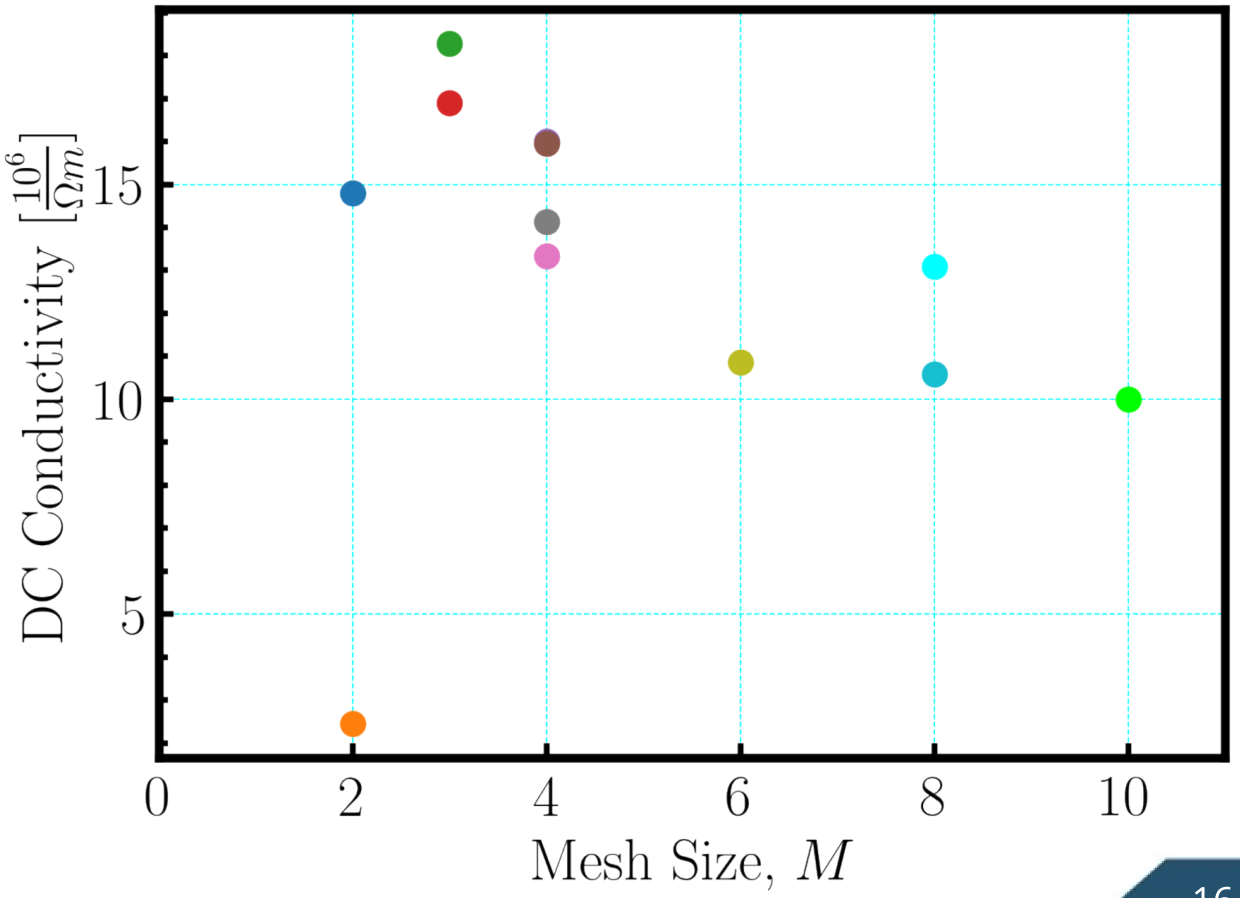
Supplemental

Brillouin Zone Sampling – Ambient

Number of k points increase as M^3 for $M \times M \times M$ mesh

Irreducible wedge reduces computation costs.

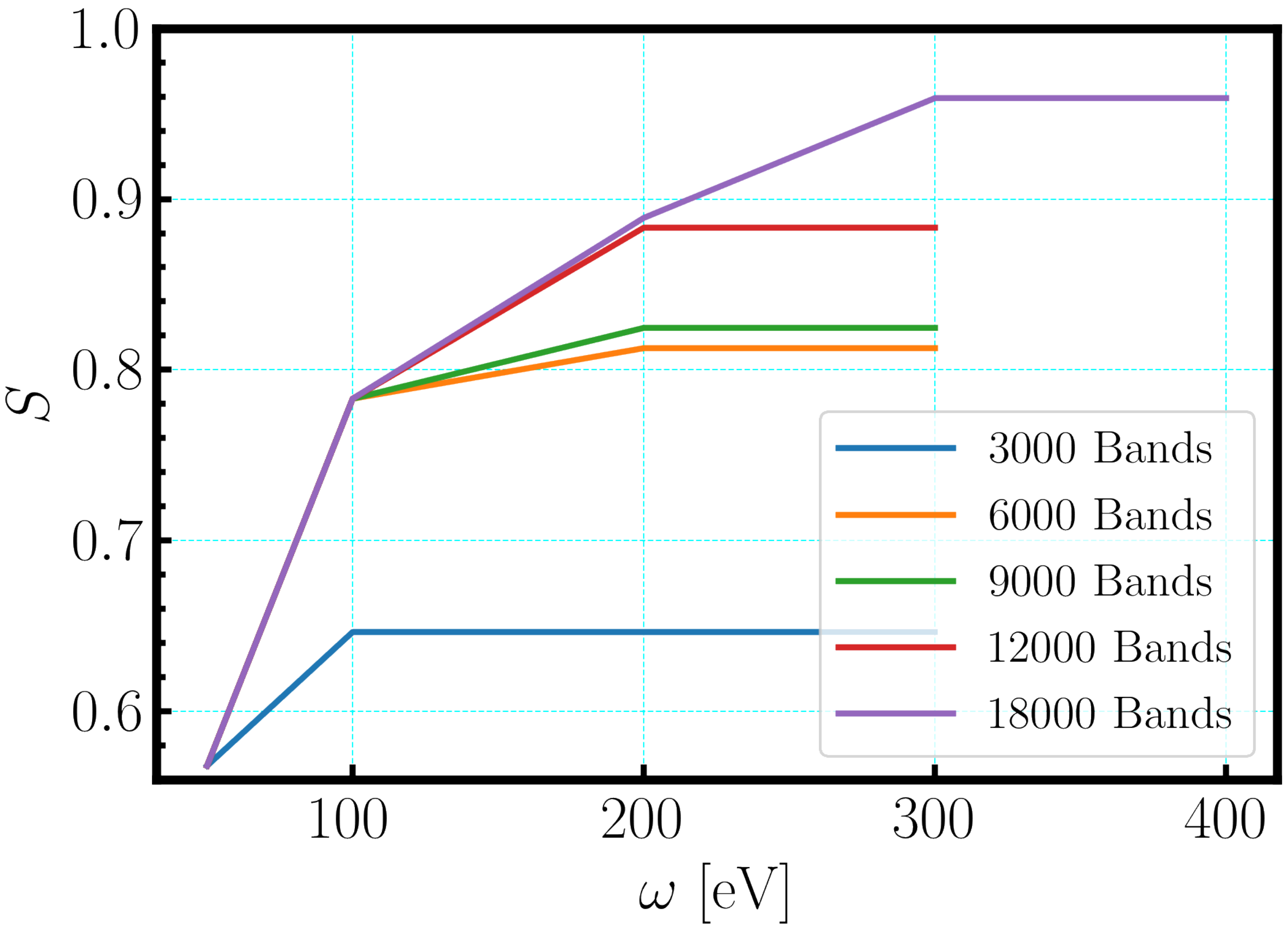




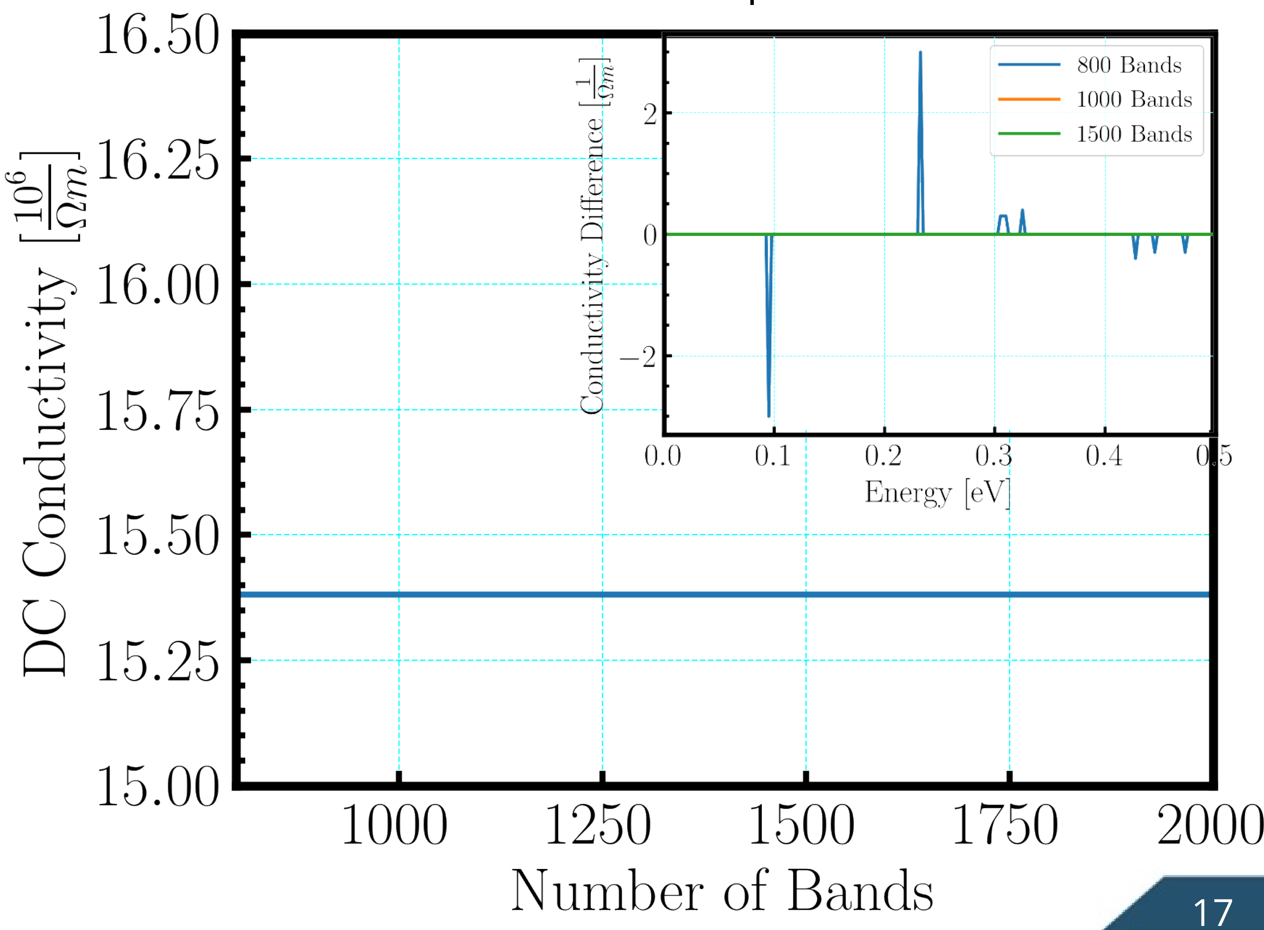
Number of Orbitals – Ambien

NO

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

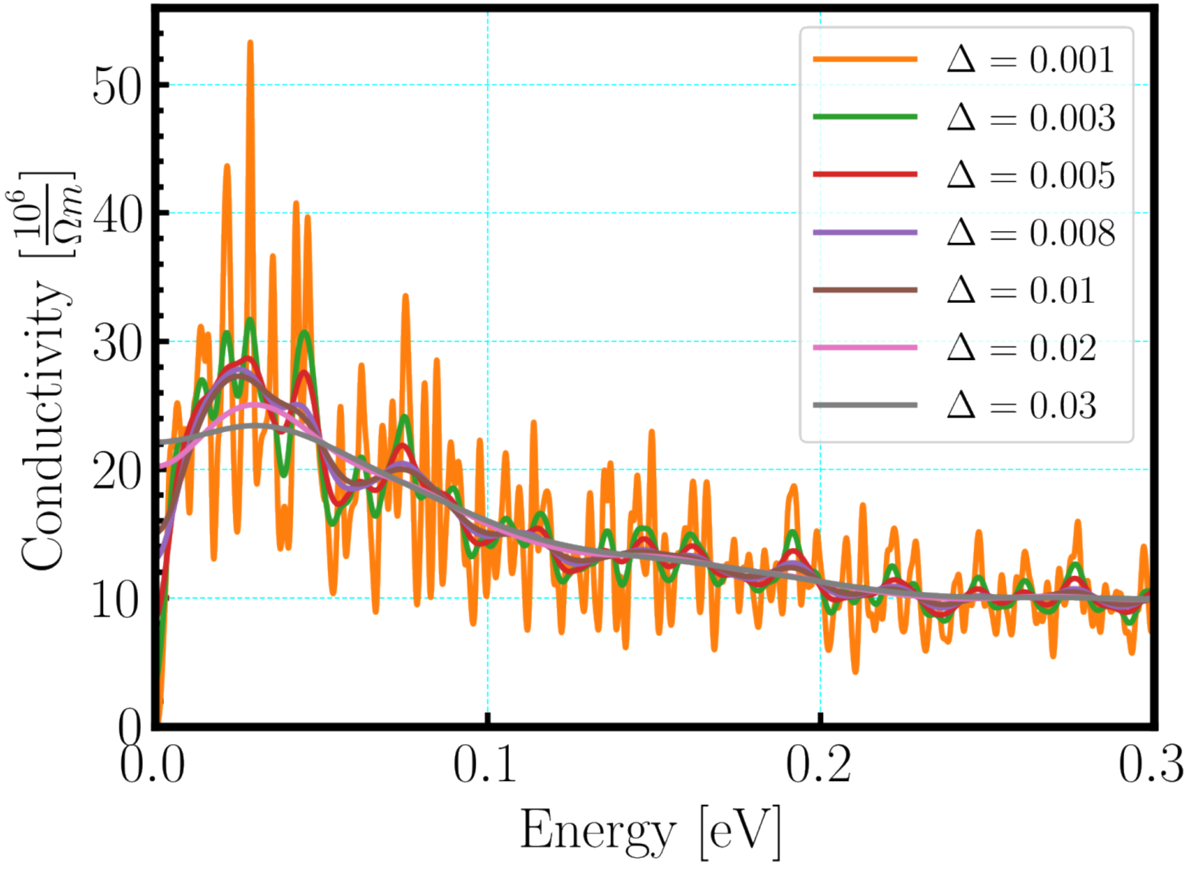


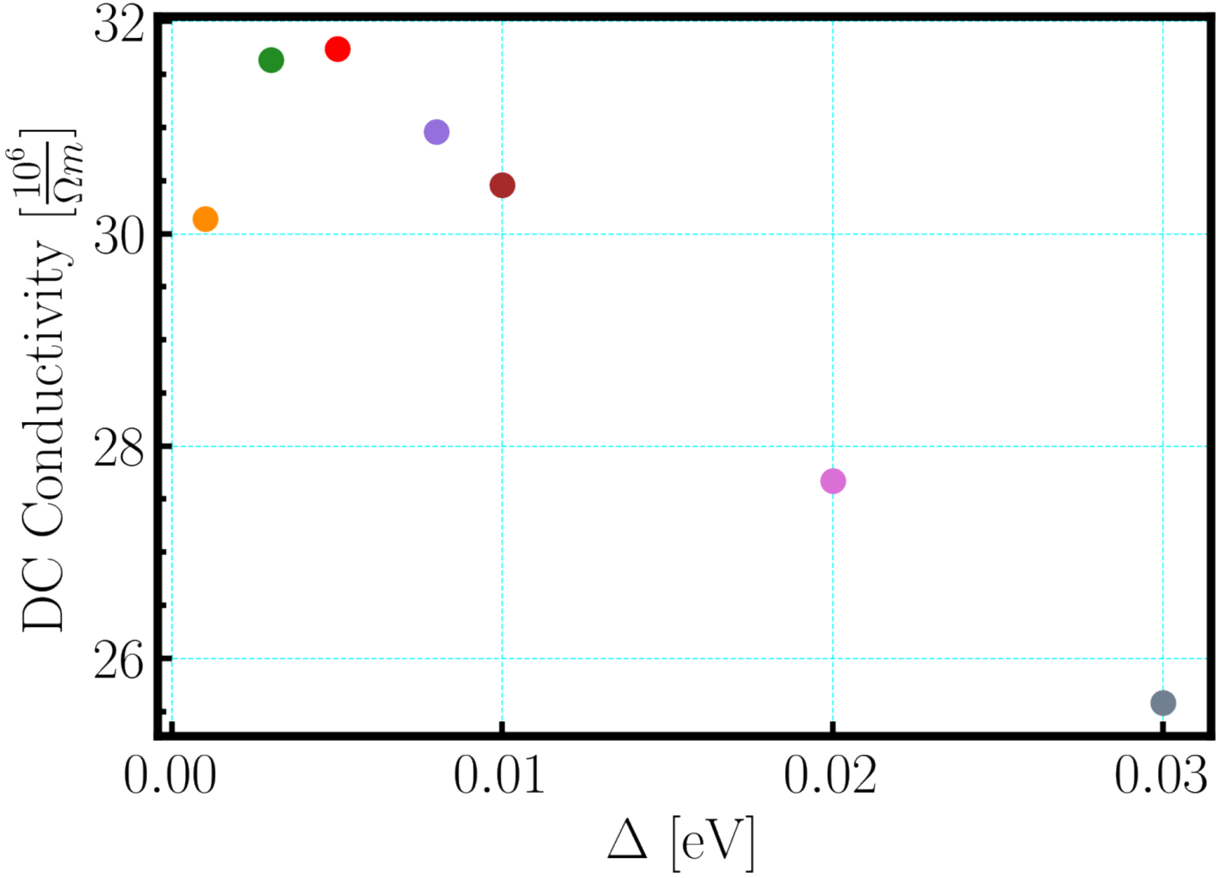
With respect to 2000 bands



Discrete Band Structure Smearing – Ambient

Smooth out local oscillations without losing structure





Sampled on 4x4x4 Monkhorst Irreducible Wedge

Number of Snapshots – Ambient

Taken from end of MD simulation to ensure equilibrium

Snapshots spaced by nearest prime number to twice the correlation time