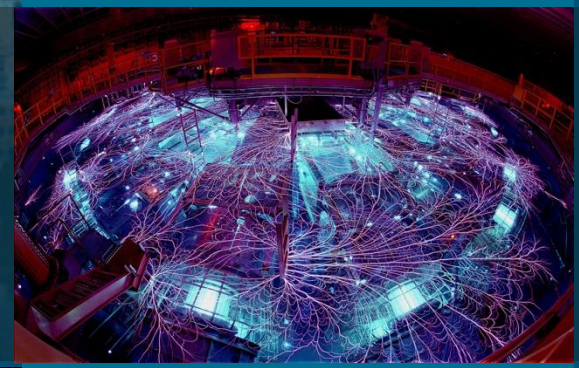
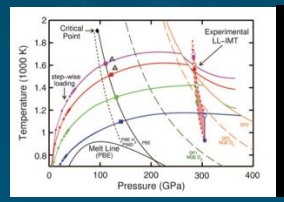
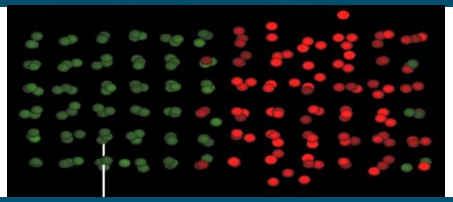
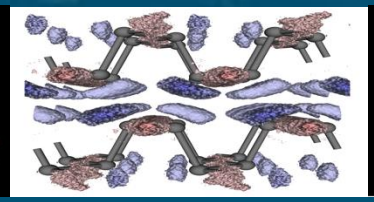
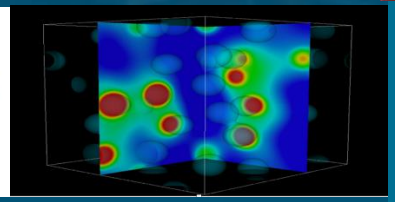
# Exploring the Interplay Between Theory and Experiment in the Study of Materials Under Extreme Conditions









*PRESENTED BY*

Luke Shulenburger

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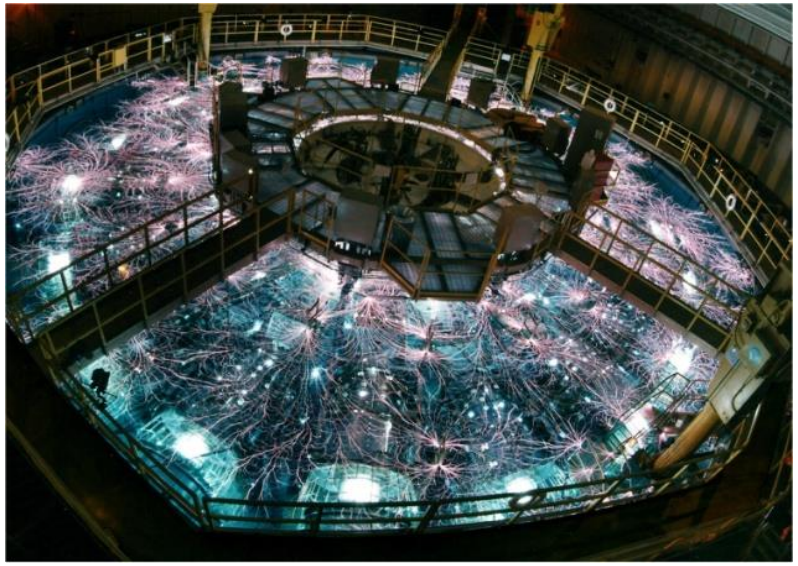
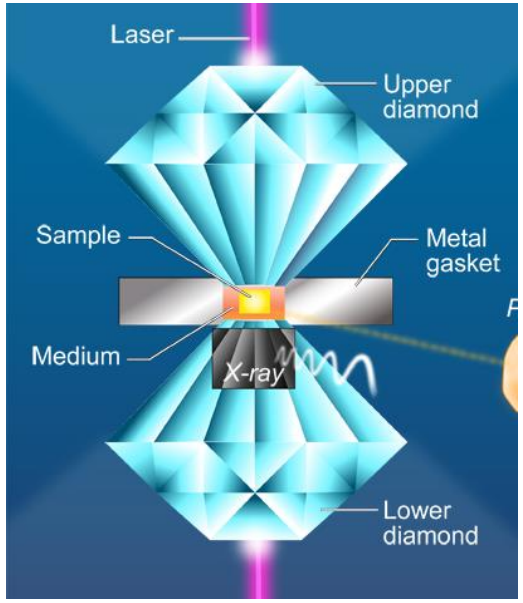
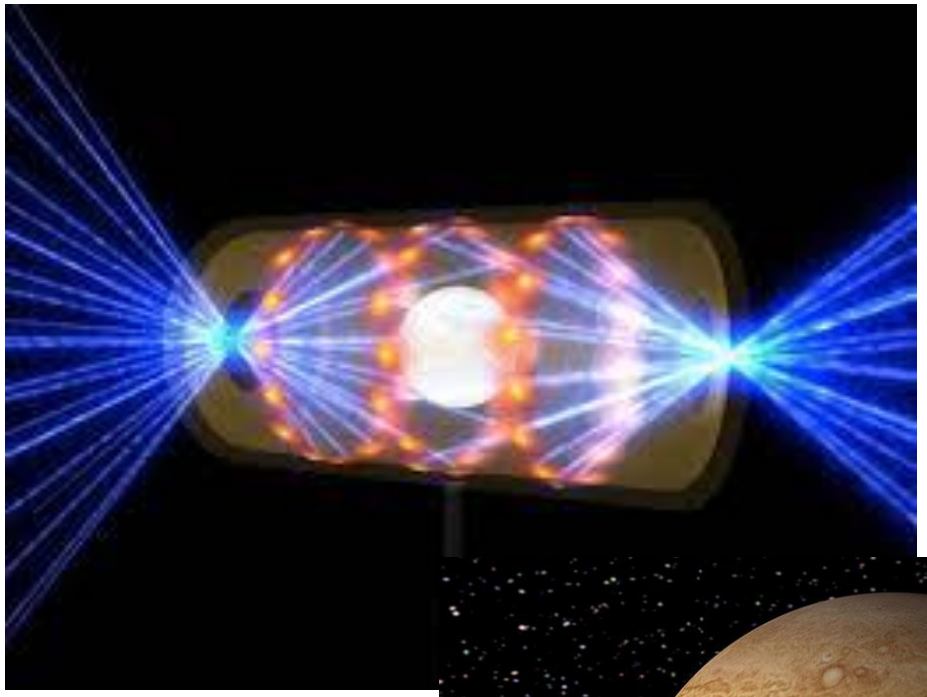
# How do the labs learn about materials under extreme conditions?

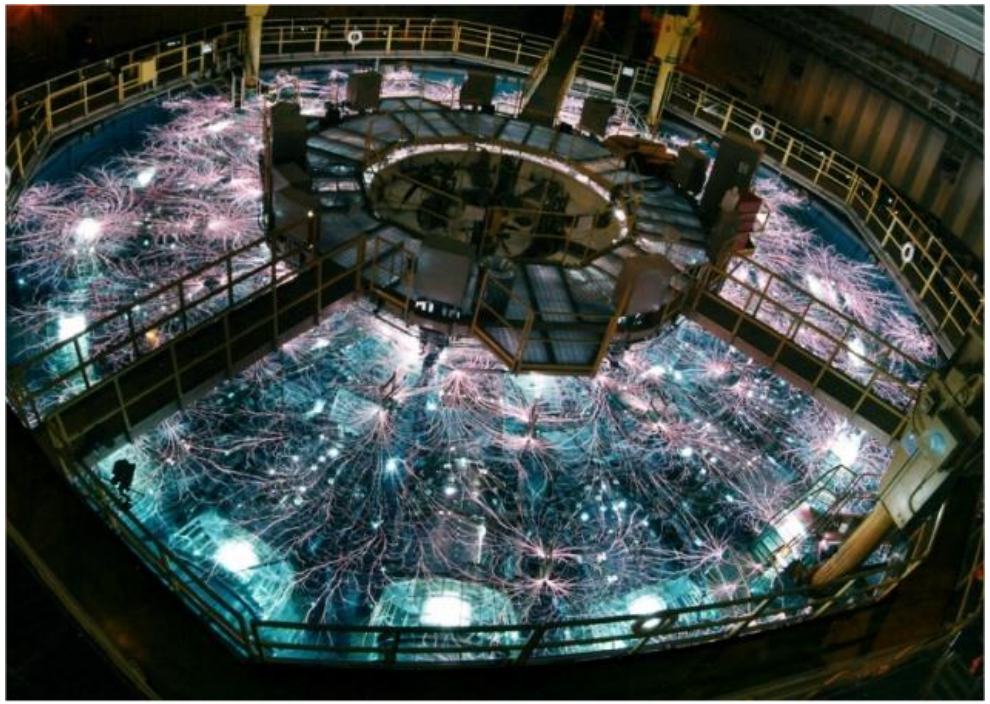


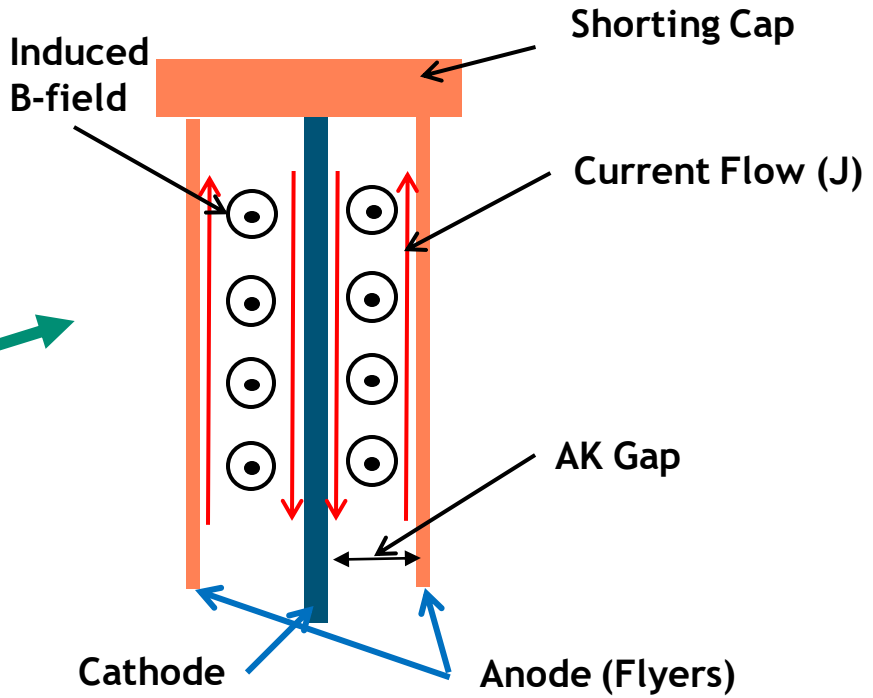



# Hydrogen plays a fundamental role in the universe

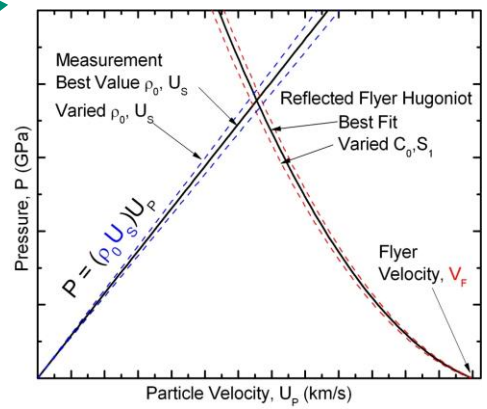


# The Z machine's dynamic materials platform



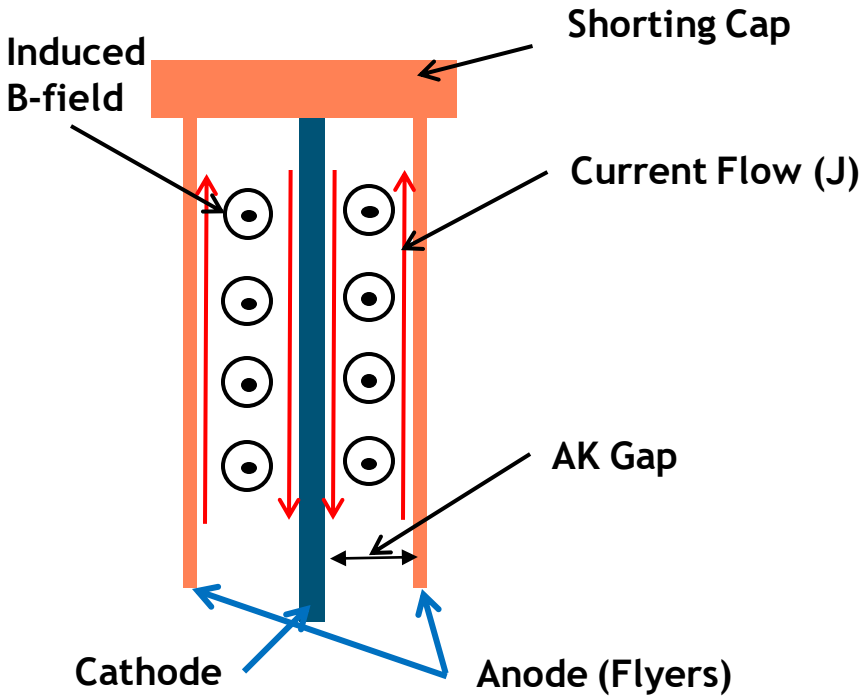



$$2\left(E-E_{ref}\right)-\left(P+P_{ref}\right)\left(v_{ref}-v\right)=0$$



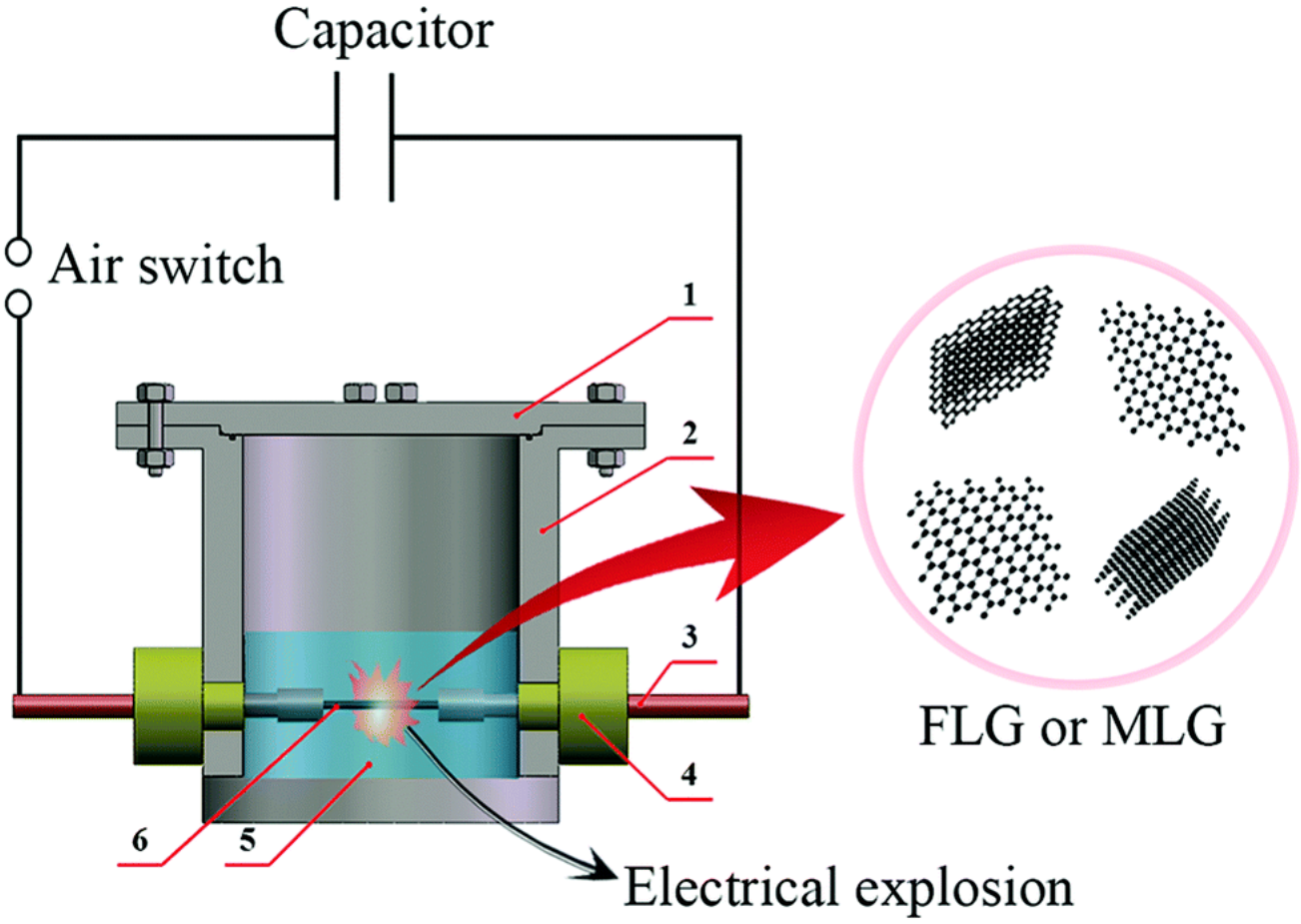
# In order to precisely control the Z experiments a conductivity model is needed

- The extreme electrical current resistively heats the inner surface of the anode
- This quickly melts, changing the density and conductivity
- If the entire anode melts, experiments become difficult to analyze
- **Z is capable of shaping the current pulse, could this be used to keep the front surface of the anode solid?**



# Experiments to determine conductivity have limitations

- Thin wires are exploded by passing a large current through them
- The explosion is imaged
- Magnetohydrodynamic simulations try to reproduce current and density profiles, varying the conductivity model
- Equation of state of wire and tamper are assumed to be known
- Only certain regimes can be accessed



# Quantum calculations offer a flexible alternative

- The equations governing the properties of any material under any conditions are known

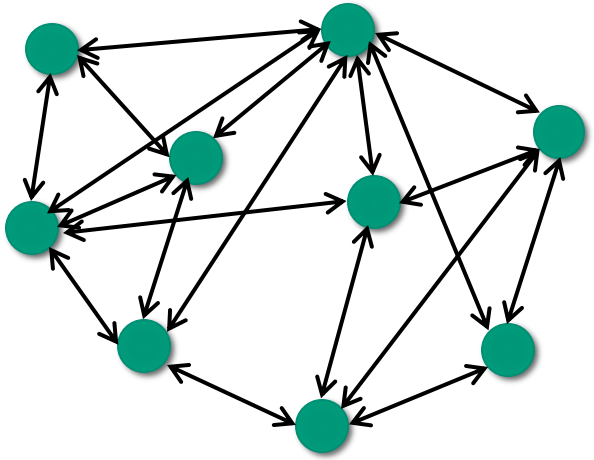
$$\hat{H}\Psi(r_1 \cdots r_N) = E\Psi(r_1 \cdots r_N)$$

$$\hat{H} = -\sum_i \frac{\nabla_i^2}{2m} + \frac{1}{2}\sum_{i \neq j} \frac{e^2}{|\vec{r}_i - \vec{r}_j|} + \sum_{i,I} \frac{Z_I e^2}{|\vec{R}_I - \vec{r}_i|}$$

- Just need to solve the 3N dimensional partial differential equations
- Approximations are necessary for real materials

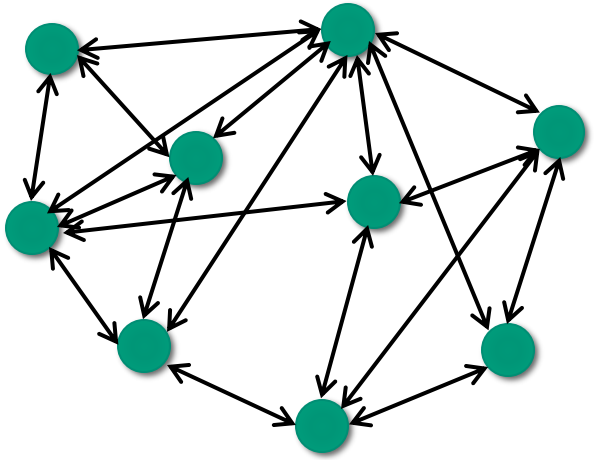
# Parallel problem: Measuring capital flow

- Goal: model capital flow in the economy
- Strategy: Track all transactions



# Parallel problem: Measuring capital flow

- Goal: model capital flow in the economy
- Strategy: Track all transactions
  - Strength – Exact Solution!
  - Weakness – Cost grows prohibitively with size of network analyzed
- Analogous to quantum chemistry wavefunction based methods

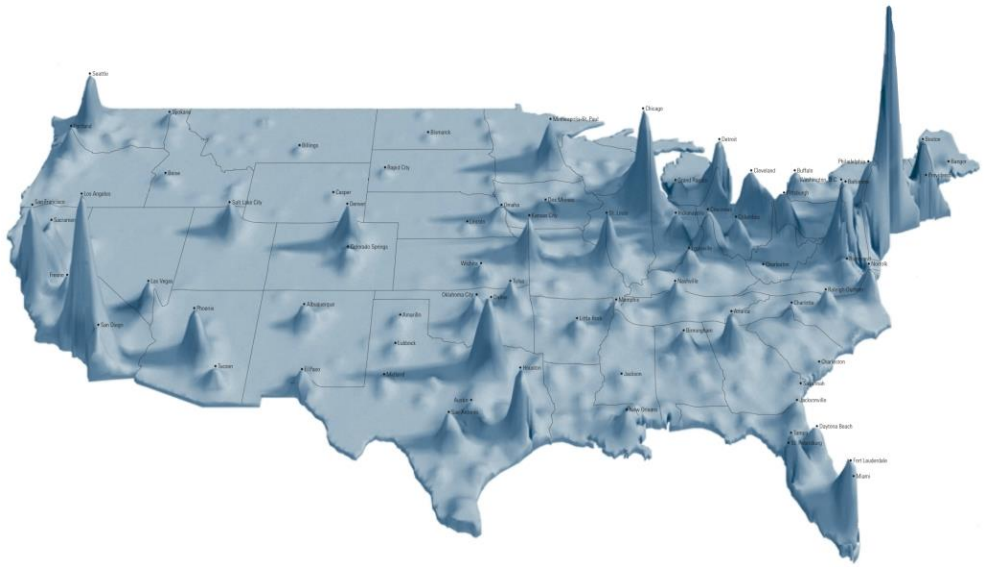


Economic problem $O(N^2)$
Electronic structure $O(N^7)$ - $O(N!)$

# Parallel Problem: Measuring capital flow

Strategy:

- Study transactions in representative population densities
- Map population density across the economy



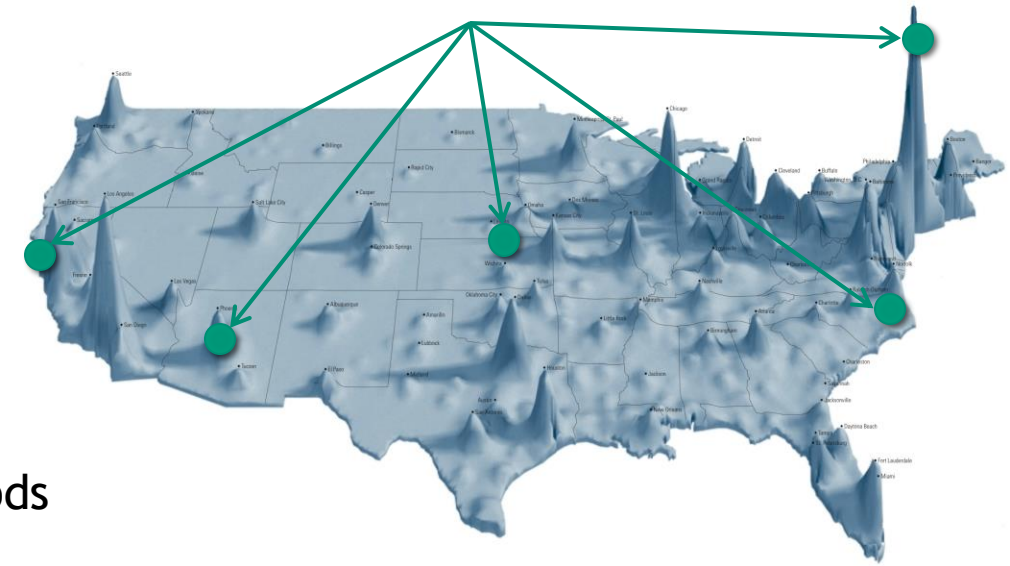
# Parallel Problem: Measuring capital flow

Strategy:

- Study transactions in representative population densities
- Map population density across the economy

Strength – Scales well to larger economies, accurate where model performs well

Weakness – Difficulties with rare but important factors, difficult to improve model



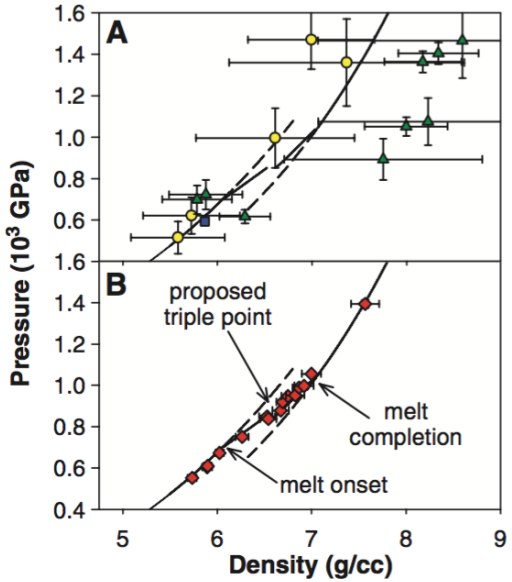
Analogous to density functional theory (DFT) methods

# DFT is a very successful technique

Careful DFT / QMD calculations can complement experiment by providing additional information

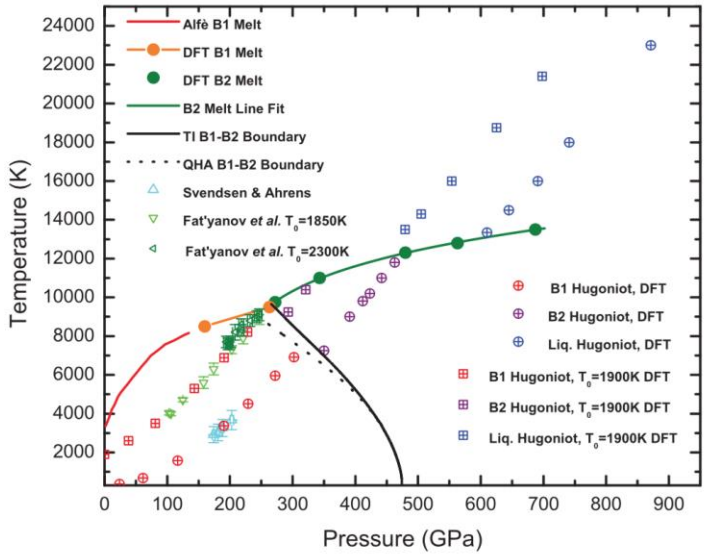
This is especially powerful when experiments can validate approximations

## Shock melting of diamond




Knudson, Desjarlais and Dolan, Science **322**, 1823 (2008)

## Phase diagram of MgO

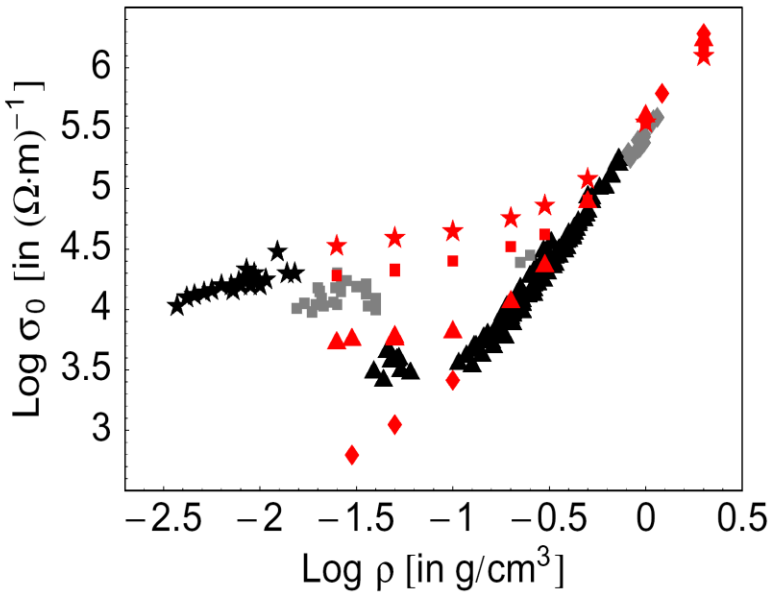



Root, LNS, Lemke, Dolan, Mattsson and Desjarlais, PRL **115**, 198501 (2015)

# Transport Properties: Kubo-Greenwood

- Can calculate electronic and thermal conductivity using DFT
- Calculate imaginary part of dielectric function using the Kubo-Greenwood relation
  - Linear response
  - Matrix elements of single particle wavefunctions
- Works well in WDM regime
- Issues if band gap is not closed

Aluminum electrical conductivity



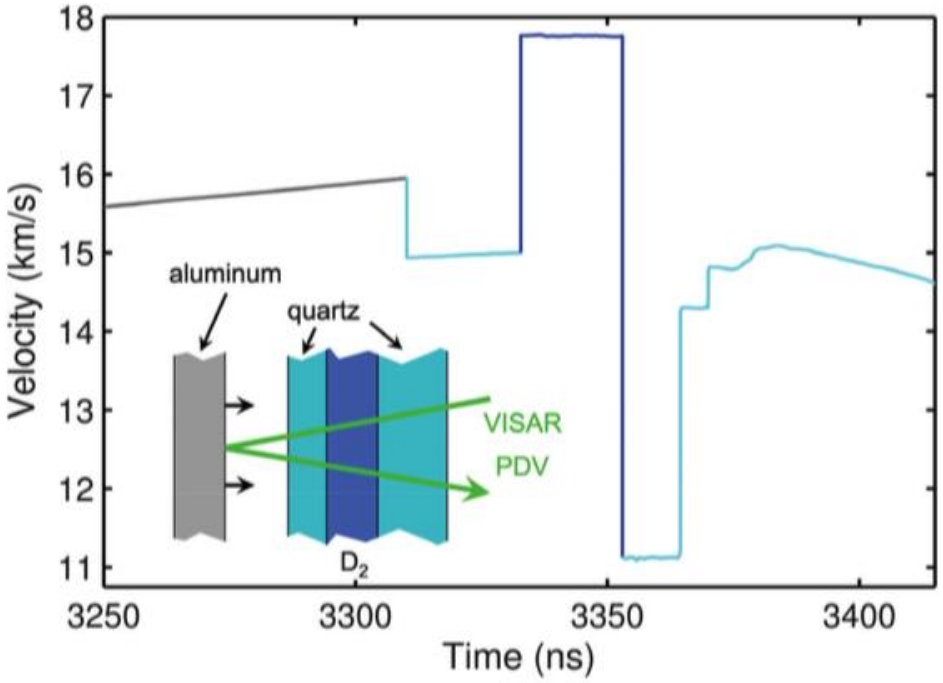

DeSilva and Katsouros data in black or grey, MD-KG results in red

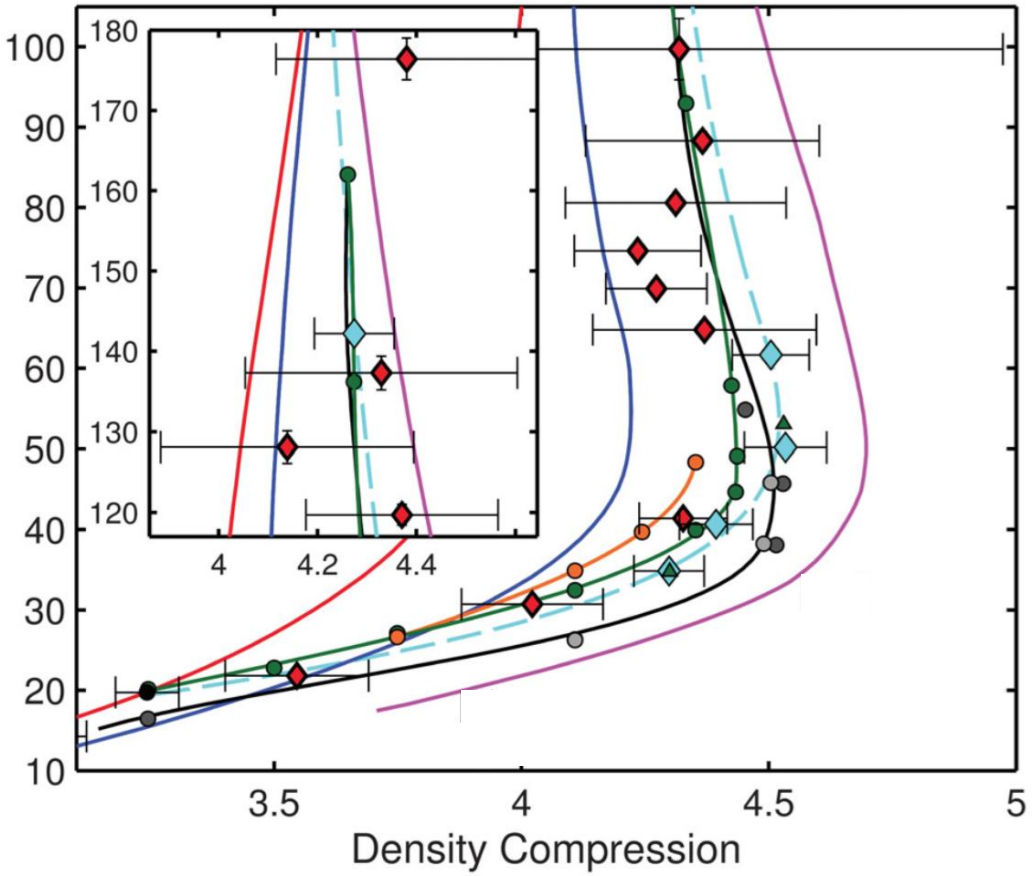
★ 30000 K, ■ 20000 K, ▲ 10000 K, ◆ 6000 K

Desjarlais, Kress, and Collins, Phys. Rev. E **66**, 025401 (2002)

# This success laid a foundation to measure the Hugoniot of $D_2$

- High precision plate impact experiments
- Utilize high precision knowledge of Al and Quartz equations of state
- DFT predictions (solid lines) show various levels of agreement

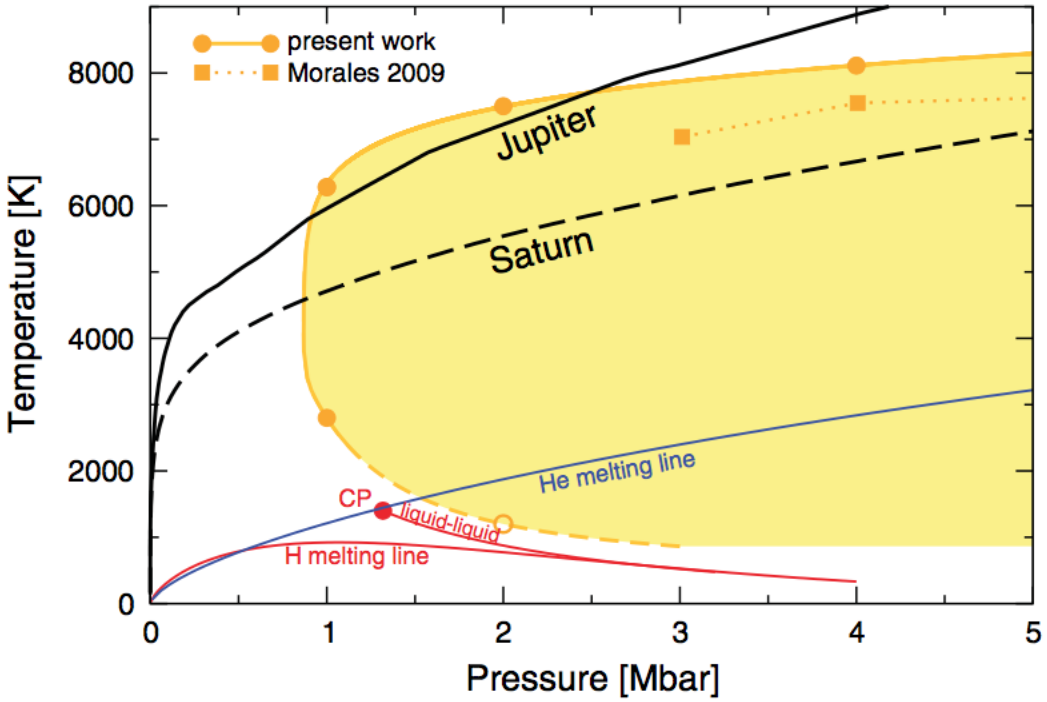



Knudson and Desjarlais, PRL **118**, 035501 (2017)

# Metalization off Hugoniot?

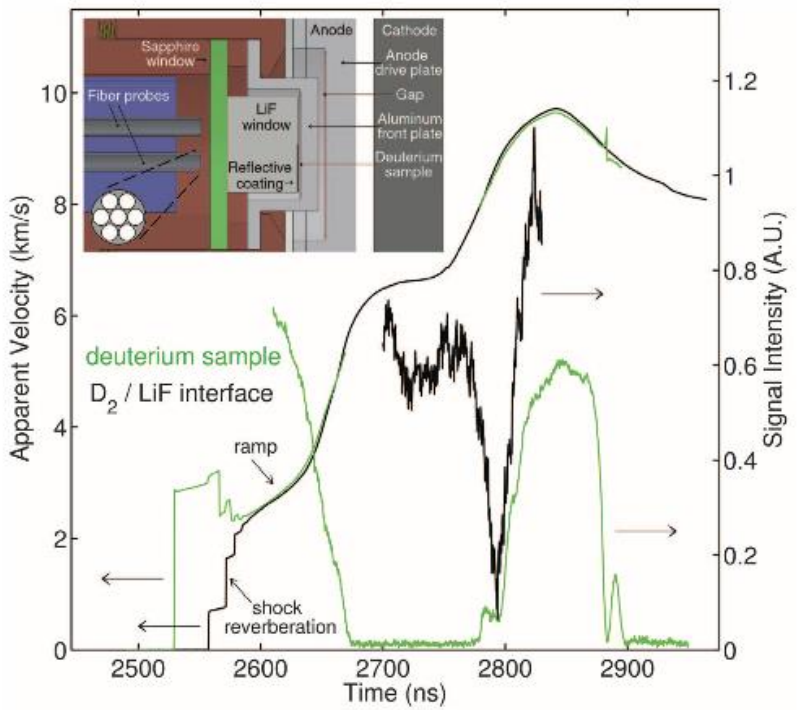
- Fluid hydrogen is also thought to undergo a first order phase transition from insulating to metallic
- This also affects its miscibility with Helium
- This potentially affects knowledge of the interiors of giant planets
- Can this be measured experimentally?

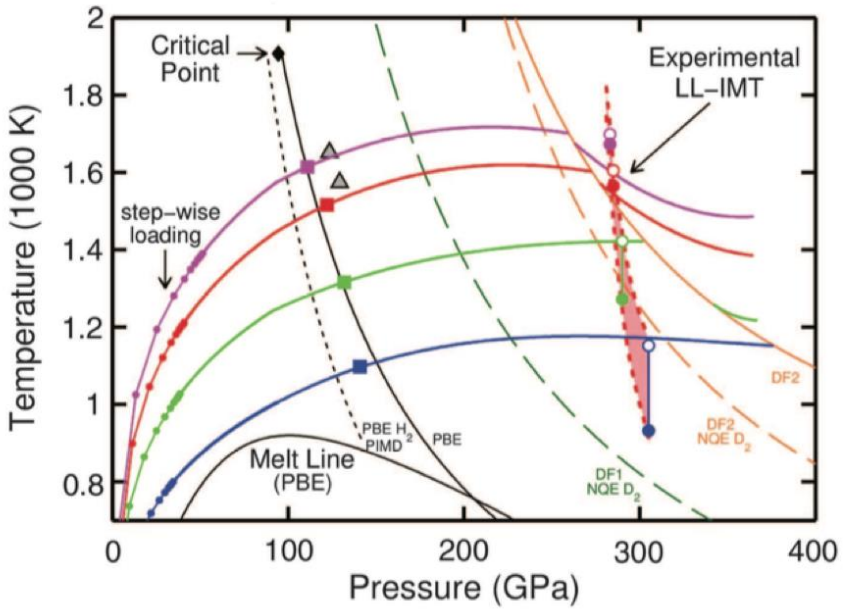



Lorenzen, Holst and Redmer, Physical Review B, **84**, 235109 (2011)

# Experiments on Z demanded a more complex loading path

- Reverberating shock led to lower temperature loading
- Broad-Band reflectivity and velocimetry allowed continuous monitoring of conditions
- Abrupt phase transition (first order?)

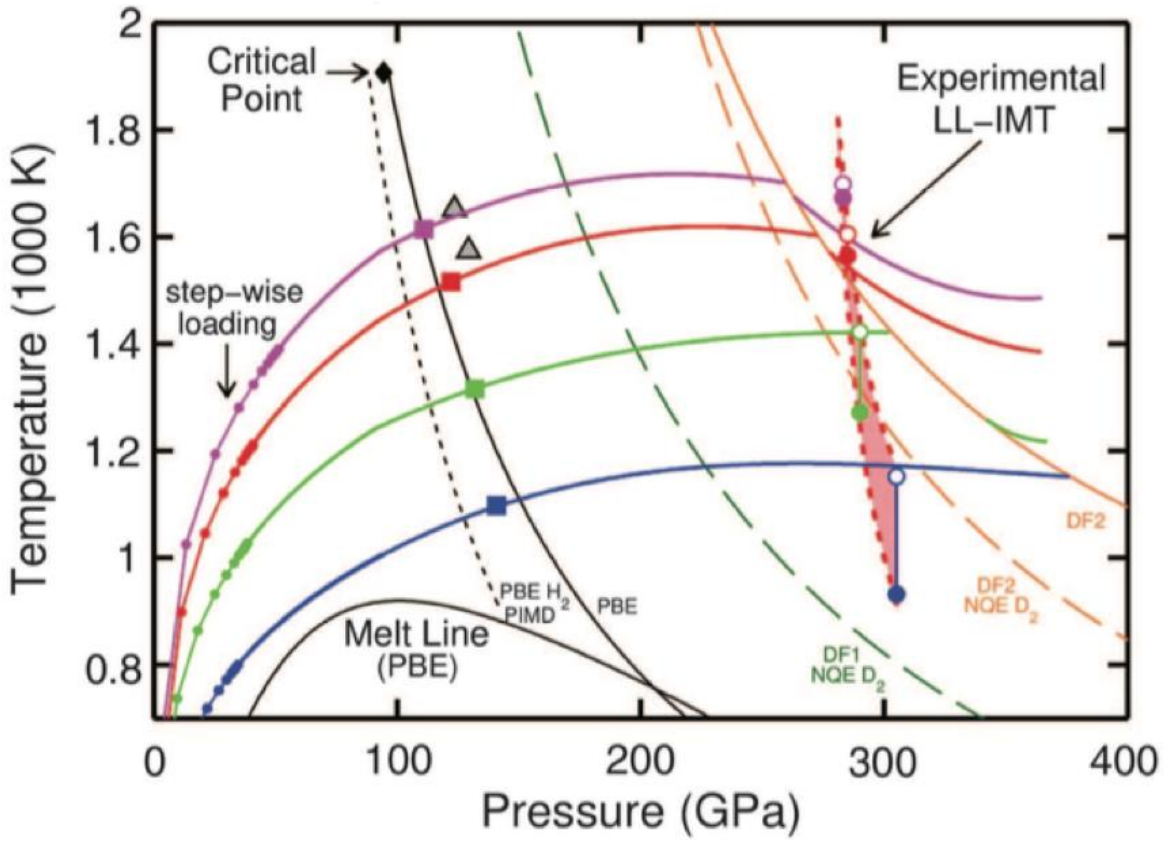



Knudson, Desjarlais, Becker, Lemke, Cochrane, Savage, Bliss, Mattsson and Redmer, Science **348**, 1455 (2015)

# Density functional theory predictions vary widely in behavior

- DFT predictions of pressure vary widely between approximations
  - Impossible to determine a priori which one is correct
- Particularly troubling given complexity of experimental analysis
- Can we do better?



# Quantum Monte Carlo Calculations offer another possibility

- Recast Schrodinger equation as an integral problem in 3N dimensions

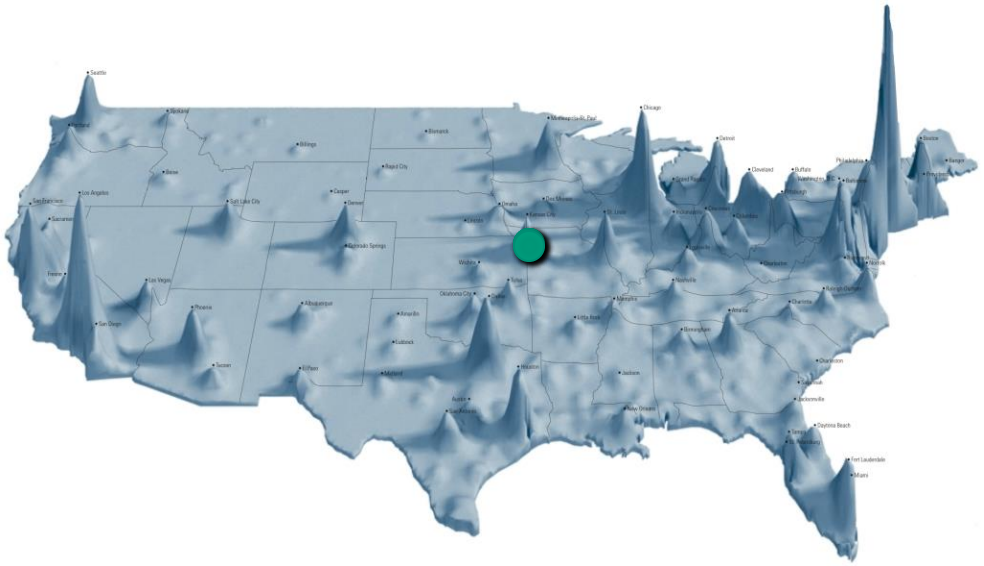
$$< \hat{H} >= \frac{\int \Psi^*(\mathbf{R}) \hat{H}(\mathbf{R}) \Psi(\mathbf{R}) d\mathbf{R}}{\int \Psi^*(\mathbf{R}) \Psi(\mathbf{R}) d\mathbf{R}}$$

- Massive parallelism available, each point can be calculated independently
- Variational principle lets you know when your approximation is improving
- Poor scaling if nontrivial trial wavefunction
  - 3 dimensions per electron
  - 20 points in each direction
  - $20^9 \approx 512$ billion points for 3 electrons
    - 3.8 TB just to store!
- Stochastic Methods scale much better for multidimensional integrals
- Effort for constant error scales as $1/\sqrt{N}$ regardless of dimensionality

# Parallel Problem: Measuring capital flow

Strategy:

- Mark random bills and follow them as they are used
- Sample full system based on transaction frequency and amount

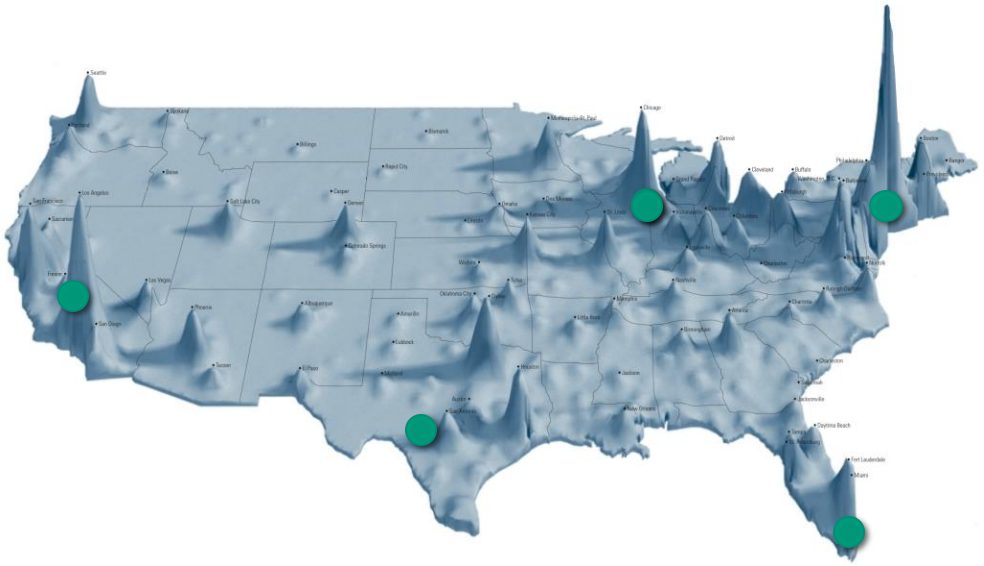


Simulation method following Metropolis procedure

# Parallel Problem: Measuring capital flow

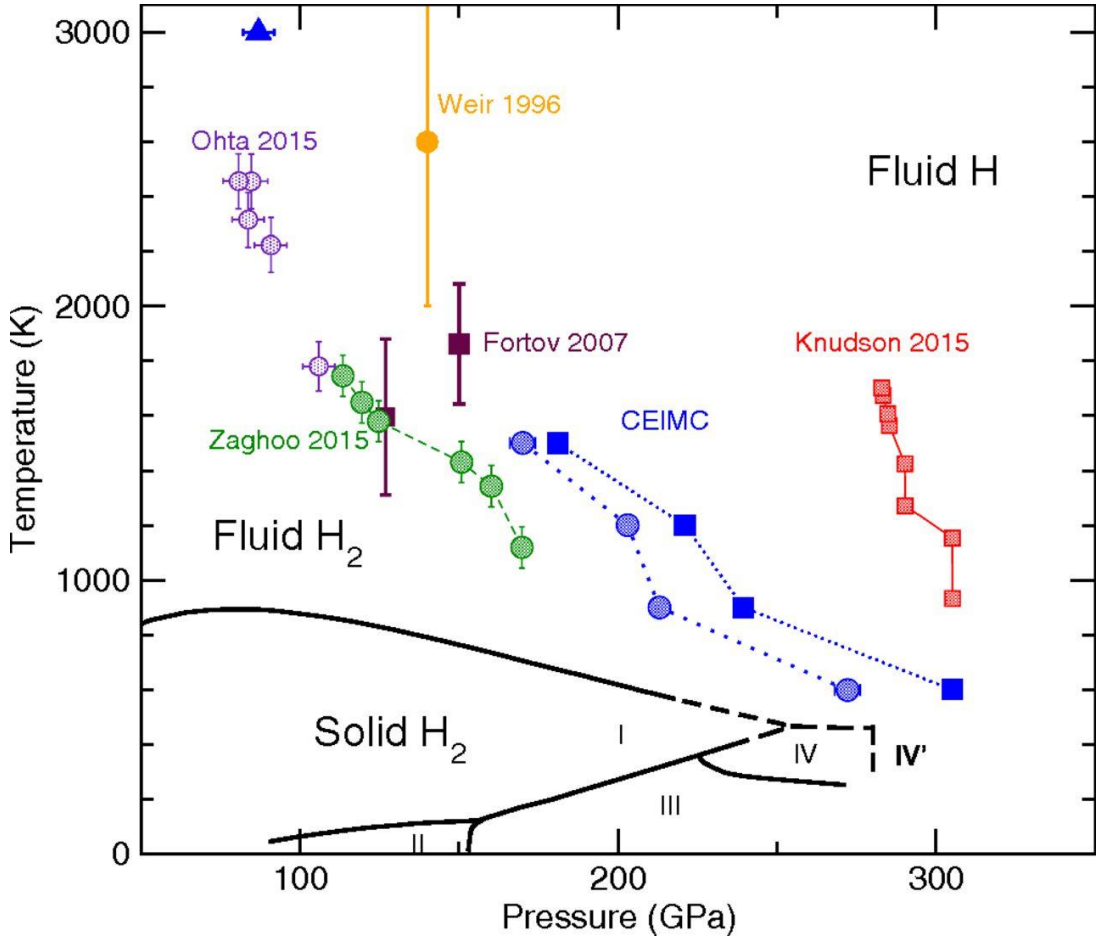
Strategy:

- Mark random bills and follow them as they are used
- Strength – No problems with singular effects, no model dependency, parallelizes well
- Weakness – May require many samples (marked bills) to accurately represent economy



Simulation method following Metropolis procedure

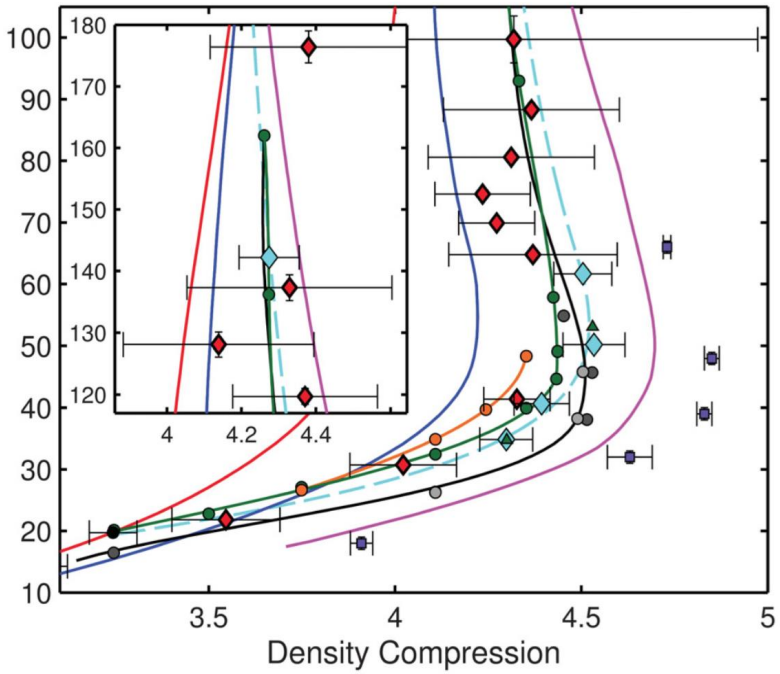
# Results of applying QMC to liquid-liquid transition are unclear



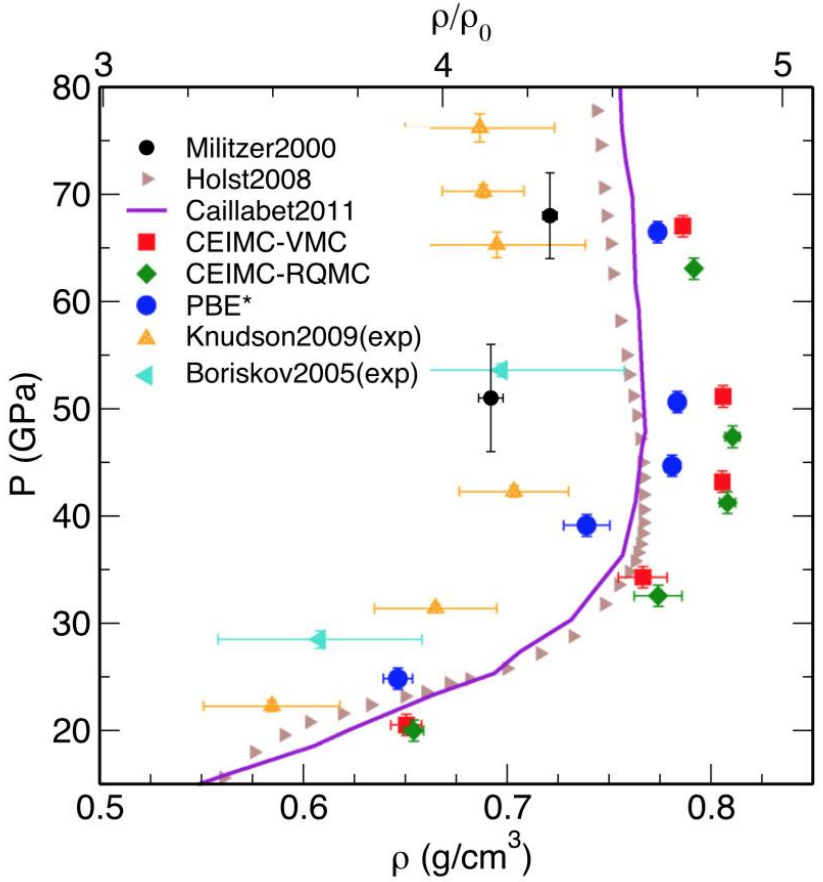

Pierleoni, Morales, Rillo, Holzmann, and Ceperley. PNAS **113**, 4953 (2016)

# What about conceptually simpler Hugoniot measurement?

- Coupled electron-ion calculation of Hugoniot
- Significantly more compressible than experiment
- This includes non-controversial gas gun experiments
- Was QMC worth the effort?




Knudson and Desjarlais, PRL **118**, 035501 (2017)



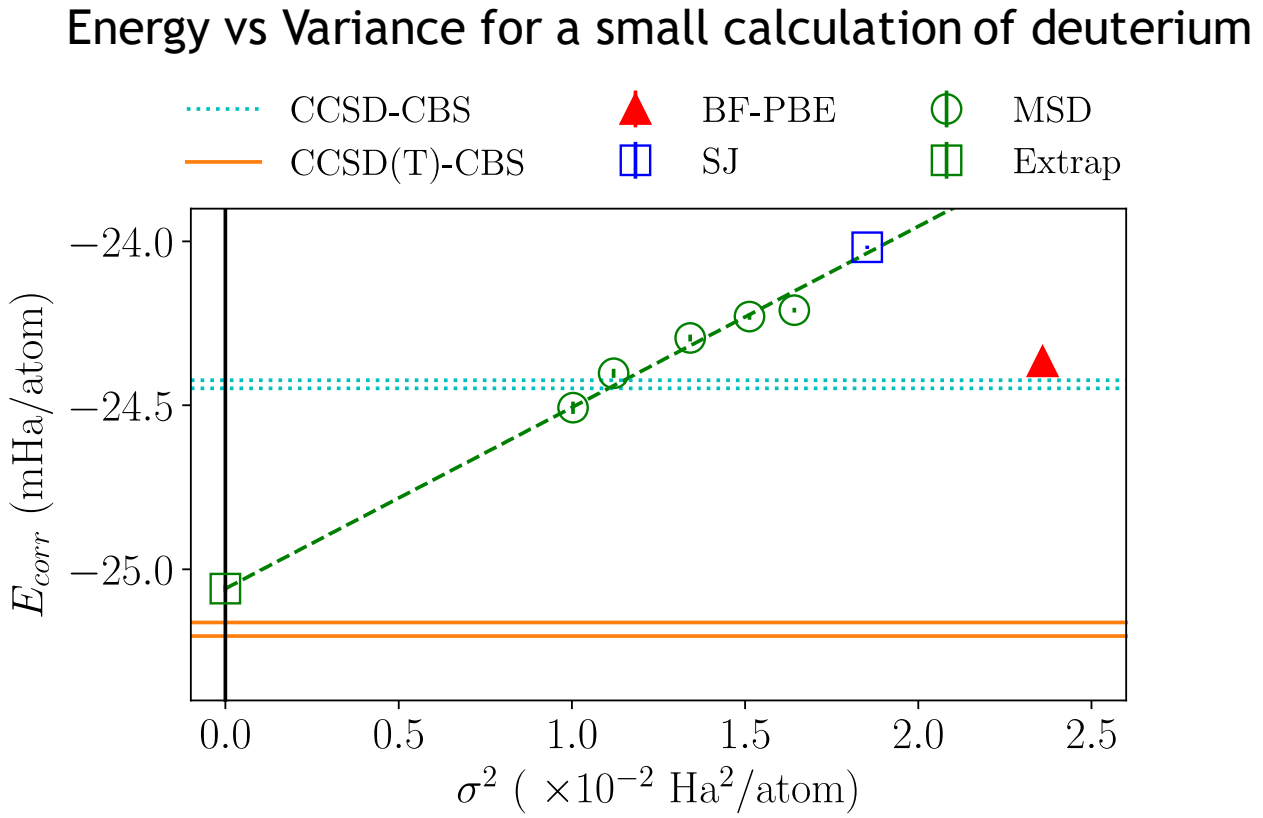

Tubman, Liberatore, Pierleoni, Holzmann and Ceperley, PRL **115**, 045301 (2015)

# Why are QMC calculations not exact?

- Monte Carlo Samples a probability distribution
  - Electrons are Fermions! (wavefunction is not >0 everywhere)
- Use guiding (trial) wavefunction, $\Psi$, for importance sampling and for fixed node approximation
- $\Psi$ is not the exact many-body wavefunction
  - Built using single particle orbitals calculated externally
  - Energy only depends on $\Psi=0$ manifold

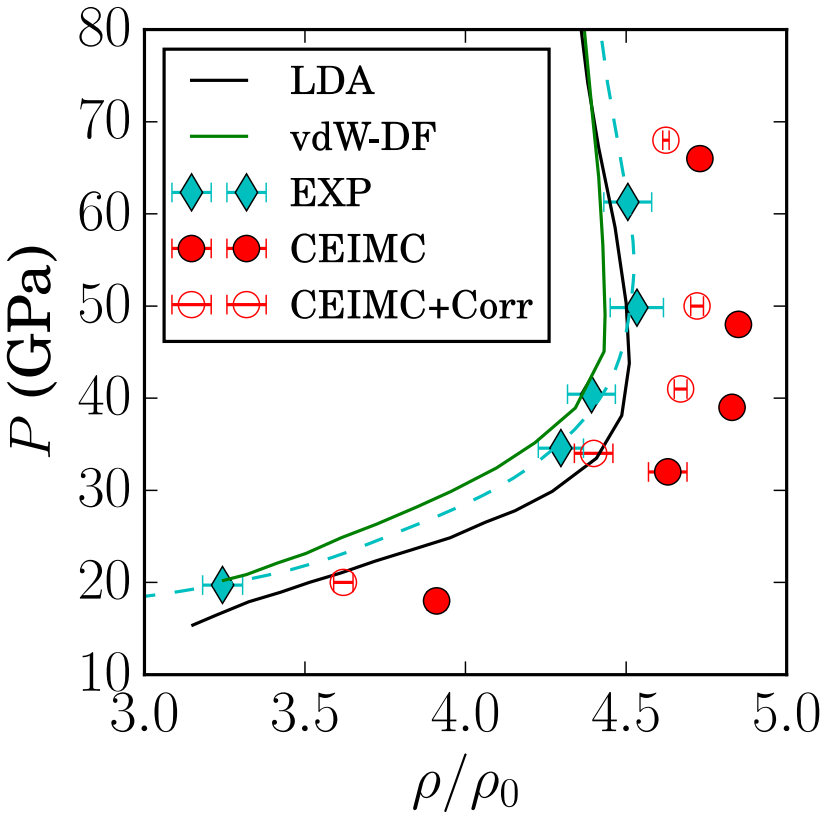
# The case for QMC: Systematically Improvable Electronic Structure

- QMC gives a hint about how accurate the calculation is: Follow the noise!
  - As sampling variance goes down, answer improves
- Carefully constructed classes of trial wavefunctions allow for extrapolation
- Currently only possible for small systems



# Leverage this to understand effects of errors on the calculated Hugoniot

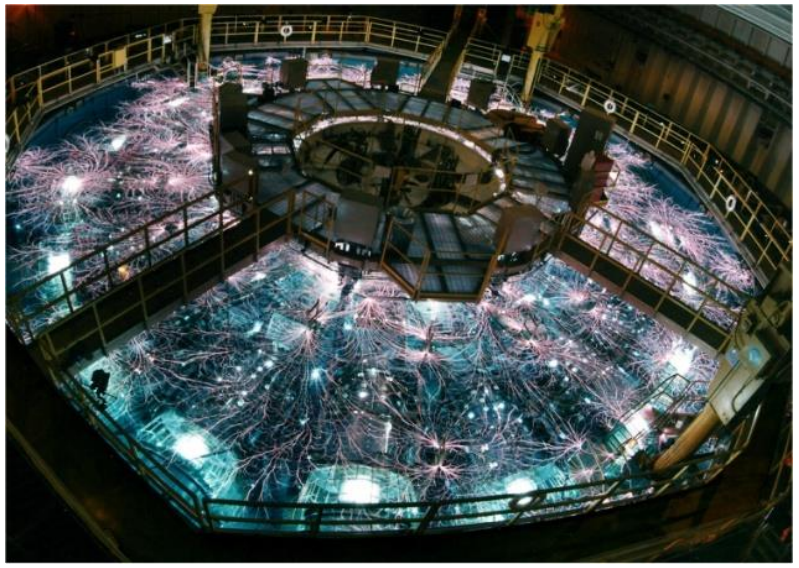
- Principle problem was QMC errors were small but unbalanced
  - Initial dilute gas was almost exact
  - Shocked state had errors
- DFT errors were much larger, but largely cancelled
- Systematic improvement was much more important (and feasible) than eliminating errors entirely




Clay et al. in preparation

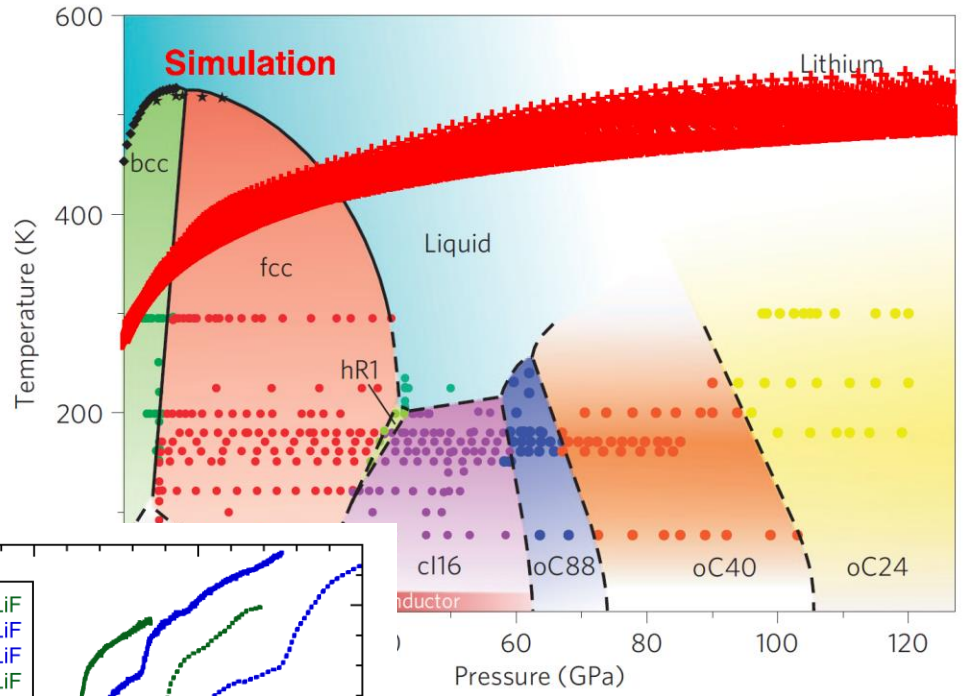
# Theory and Experiment fuel each other

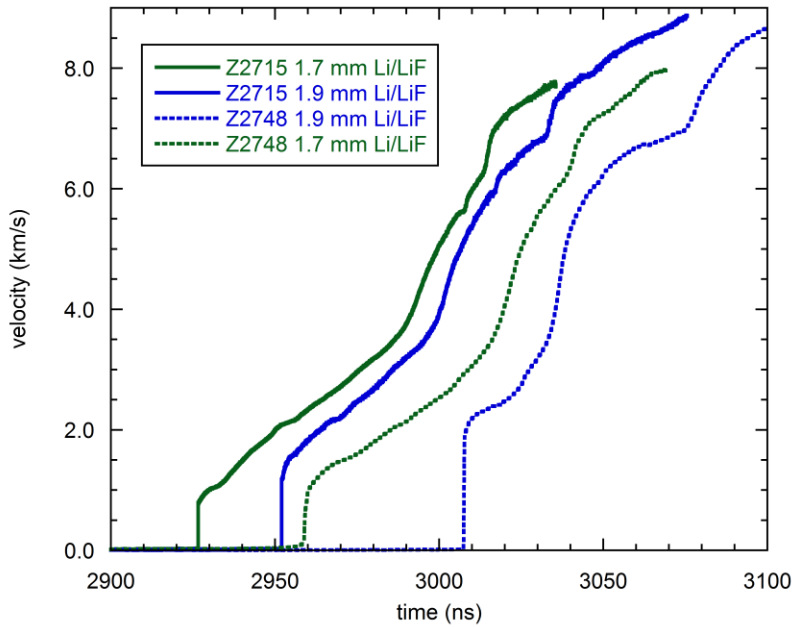
- Ab initio calculations of conductivity enabled high precision experiments on Z
- Highly accurate measurements in extreme environments uncover inaccuracies in ab initio calculations
- The ability to fill in hard to observe quantities with ab initio calculations continually pushes the methods
- For hydrogen, this is leading to a new approach for electronic structure calculations where results can be quantified



# Probing the lithium phase diagram

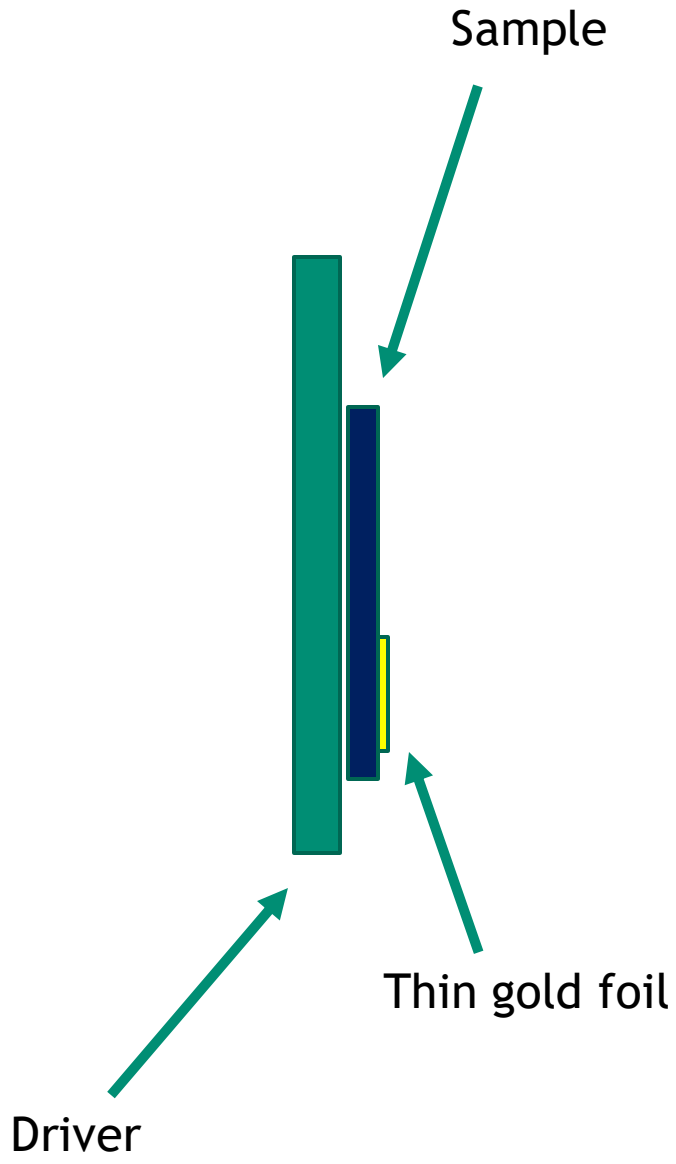
- Ramp compression of lithium may see a variety of features
- Experimental evidence comes largely from velocimetry
- How to efficiently determine location of melt to look for kinetic effects in the experiment?
- QMD calculations do not directly produce free energies
- Leaning on direct calculation of entropy Desjarlais PRE **88**, 062148 (2013)



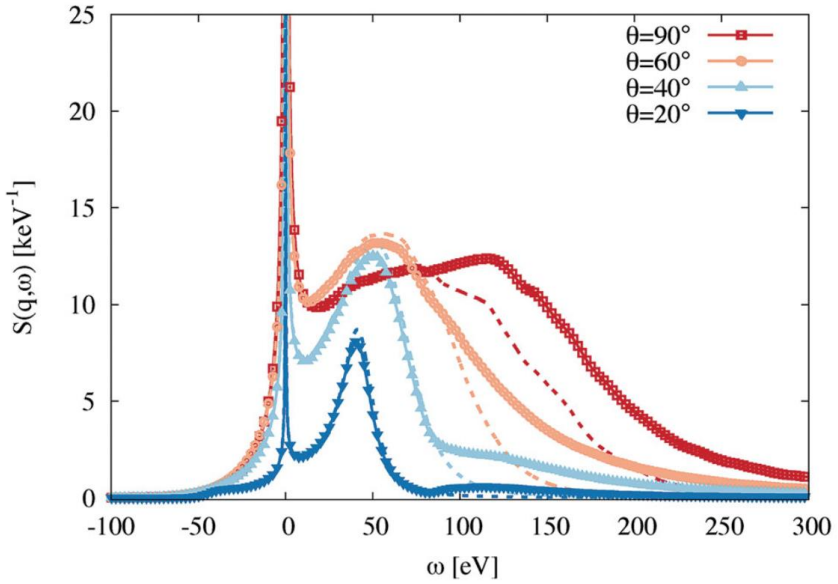
# Reflectivity model for gold could provide a window into temperature

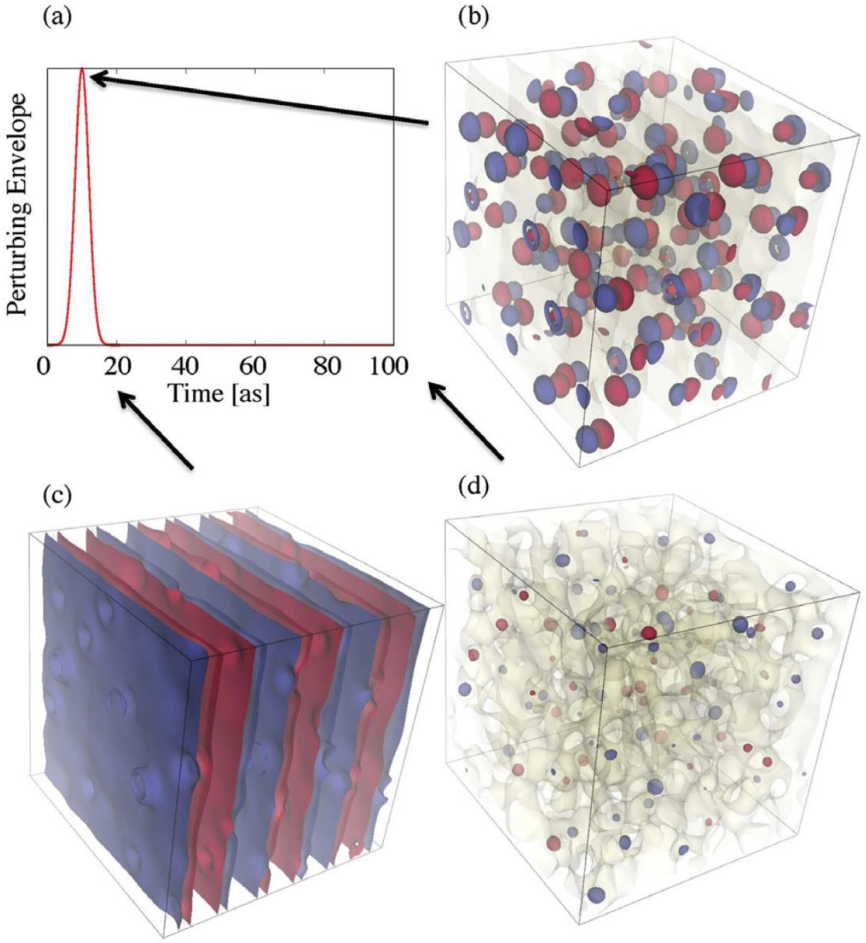
- Ramp compression is primarily isentropic, but not entirely
- Precise temperature measurements could help understand this
- Optical pyrometry is not well suited as the material does not emit much
- Gold's reflectivity is known to change with pressure and temperature
  - A thin foil could be used as a thermometer
- Standard DFT techniques are not predictive
  - Also thermal conductivity would have to be known



# X-Ray Thomson scattering is possible on Z, but noisy, can theory help?

- XRTS can probe bulk material (not just surface)
- Could get information about both structure and temperature
- Z experiments are a noisy environment
- Standard DFT approaches do not have dynamical electrons
- Have worked to make TDDFT a viable alternative




Baczewski, LNS, Desjarlais, Hansen, Magyar, PRL 116, 115004 (2016)

# Dynamic materials experiments provide a fruitful playground to develop electronic structure

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