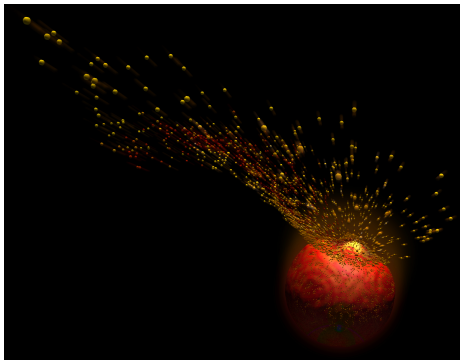
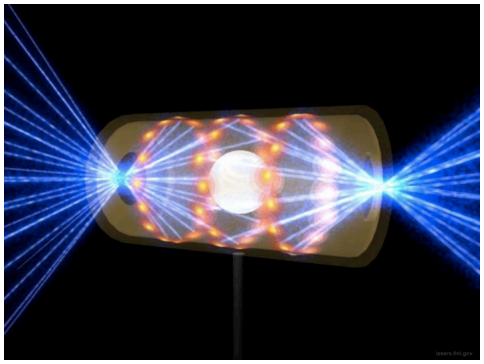
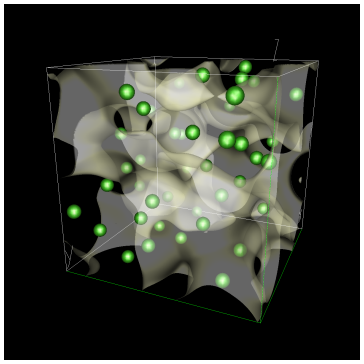
SAND2013-4972C

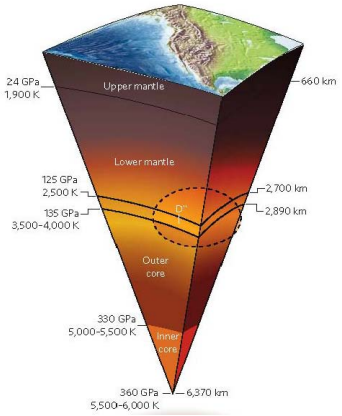
*Exceptional service in the national interest*

Sandia National Laboratories

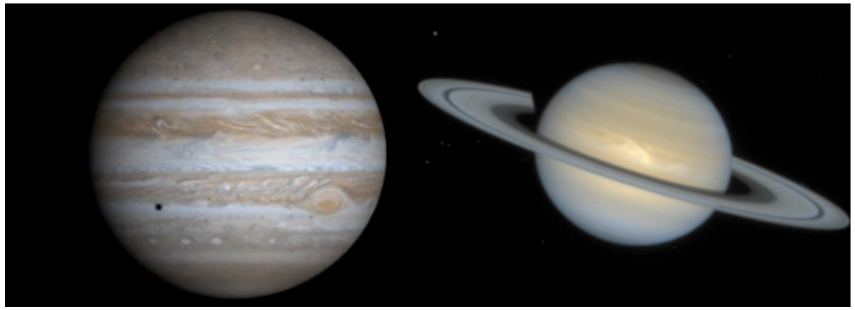









# First-principles simulations of Warm Dense Matter



Mike Desjarlais

Sandia National Laboratories

Albuquerque, New Mexico

U.S. DEPARTMENT OF ENERGY

National Nuclear Security Administration

Sandia National Laboratories is a multi-program laboratory managed and operated by Sandia Corporation, a wholly owned subsidiary of Lockheed Martin Corporation, for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000.

# What is Warm Dense Matter?

Sandia National Laboratories

- Warm Dense Matter is generally associated with strongly coupled ions ($\Gamma_{ii} > 1$) and moderately degenerate electrons ($\theta \sim 1$)

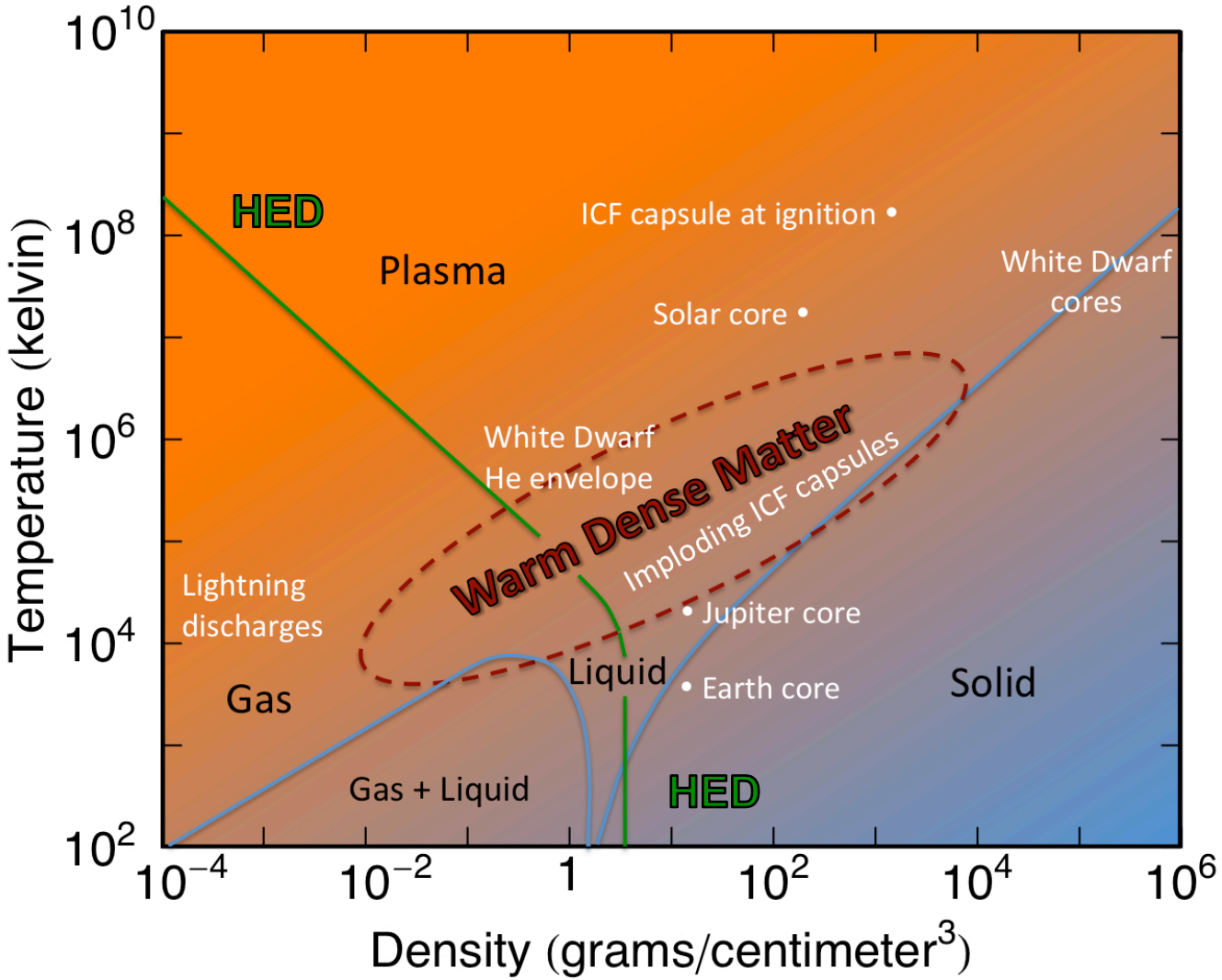
$$\Gamma_{ii} \equiv \frac{\langle PE \rangle_{ion}}{\langle KE \rangle_{ion}} = \frac{e^2 Z_*^2}{k_B T_i R_a} \qquad \theta \equiv \frac{k_B T}{E_{Fermi}}$$

- It is typically found at the junction of solid, liquid, gas, and plasma. The complicated interplay of the physical processes that WDM shares with its neighbors creates considerable difficulties for theory.

- $\Gamma_{ii} << 1$ is equivalent to $g \equiv \frac{1}{n_e \lambda_{Debye}^3} << 1$ where $g$ is the "plasma parameter" (weakly coupled)

- $\theta >> 1$ is equivalent to $\frac{1}{n_e \Lambda^3} >> 1$ where $\Lambda$ is the thermal de Broglie wavelength (Maxwell-Boltzmann statistics)

# Where is Warm Dense Matter found?

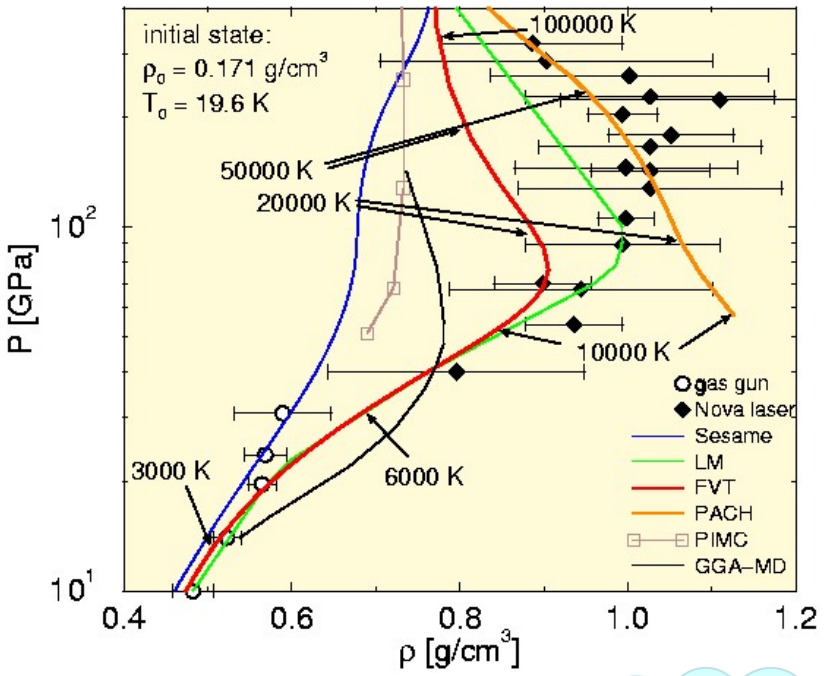


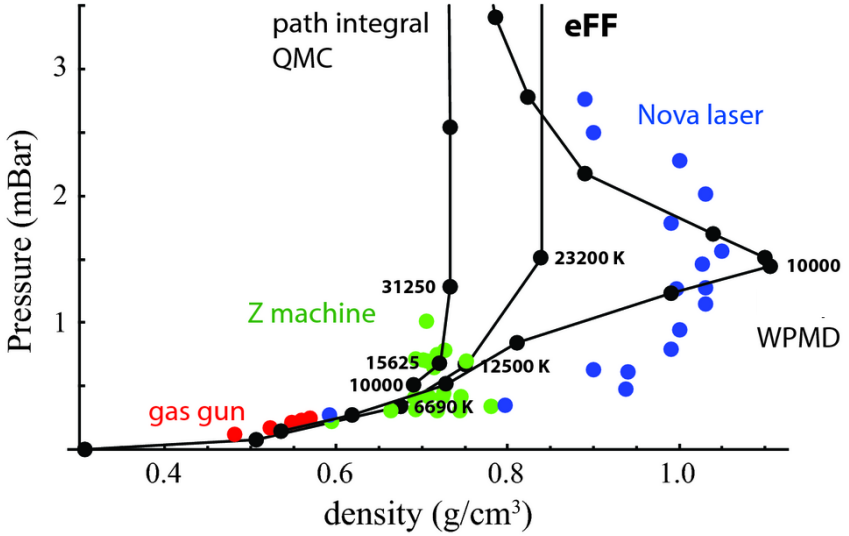

**Warm Dense Matter** is closely connected with **High Energy Density Matter** (**P > 1 Mbar**)

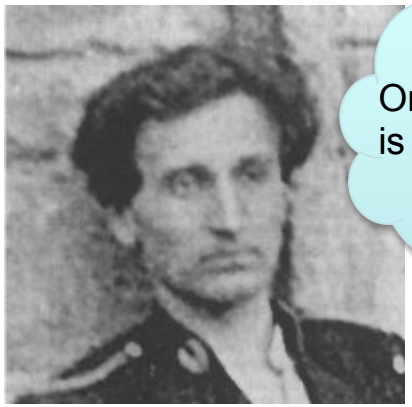
# What makes it difficult?

- There is no small parameter
  - Plasma expansions in $g$, the plasma parameter, fail for WDM
- Many different aspects of the physics contribute at a comparable level and must be included
  - strong correlations
  - ionization
  - bond formation and breaking
  - complex pressure and temperature dependent chemistry
- Computations/simulations are often quite demanding
  - Massively parallel computations are the norm
  - Shortcuts are very tempting
- Experimental conditions are short lived and hard to diagnose
  - Which experimental results should you believe?

# Consider something as “simple” as the deuterium Hugoniot

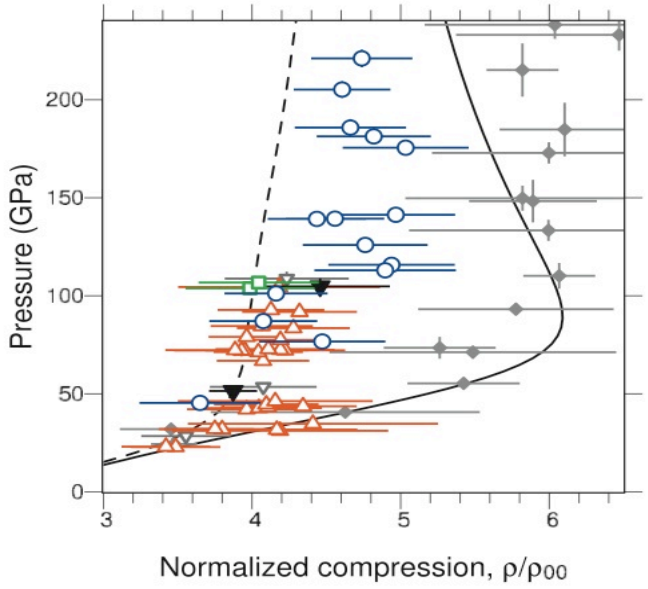


One of these things is not like the others

Pierre Henri Hugoniot






See McMahon *et al.*, Rev. Mod. Phys. **84**, 1607 (2012) for a recent review on H and He

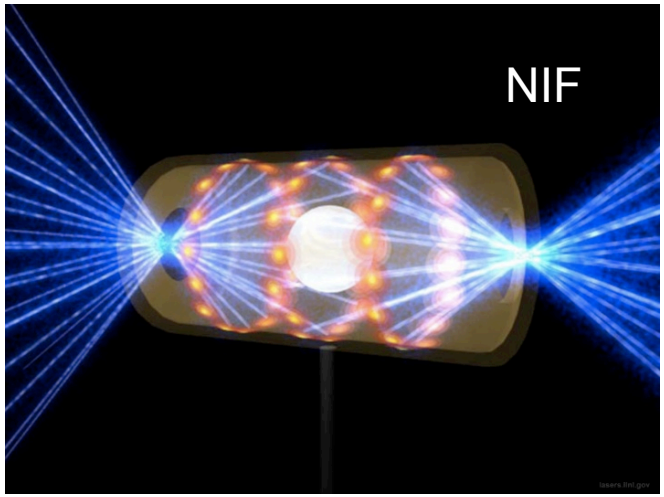
# Areas of Active Research

Sandia National Laboratories

- Creating Warm Dense Matter in the laboratory
  - High Intensity Lasers
  - Pulsed power (magnetically driven compression)
  - Explosively driven compressions
  - Gas gun shock experiments
  - Free electron lasers
  - Ion beams
  - Electron beams

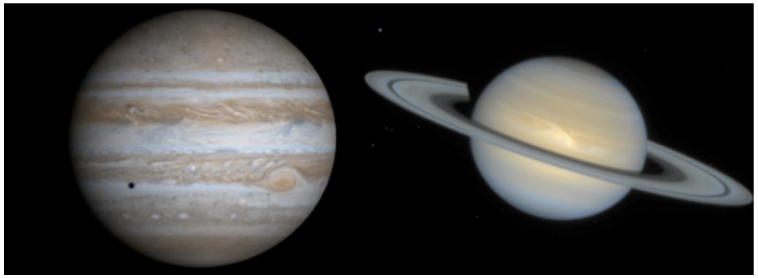
# Areas of Active Research

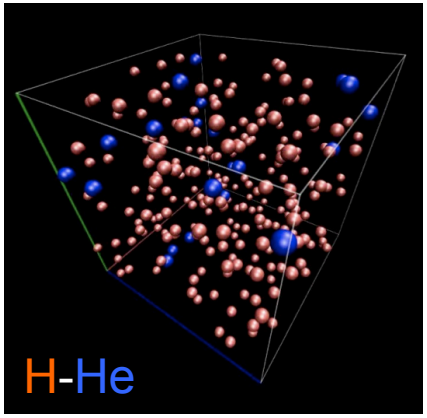
- Inertial Confinement Fusion – starts from cold condensed matter and ends up as a very hot dense plasma, spending much of the implosion path as warm dense matter. All sorts of bad things can happen there. Capsule design simulations need
  - Equations of state for warm dense hydrogen, the ablator material, and hydrogen/ablator mixtures
  - Thermal conductivities
  - Ion-electron equilibration rates
  - Viscosities
  - Optical properties



# Areas of Active Research

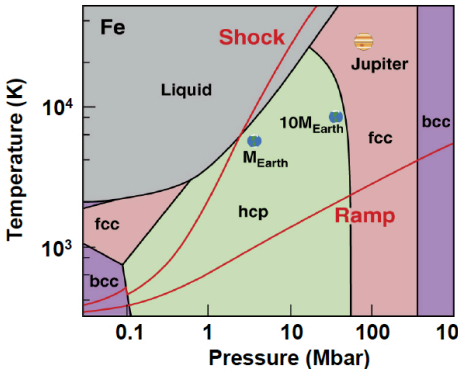
- Planetary Science – WDM research is broadly relevant here
  - Hydrogen-Helium de-mixing (the Saturn problem)
  - Equations of state for gas giants and exo-planets
    - Hydrogen
    - Water
    - Helium
    - $CO_2$
    - Methane

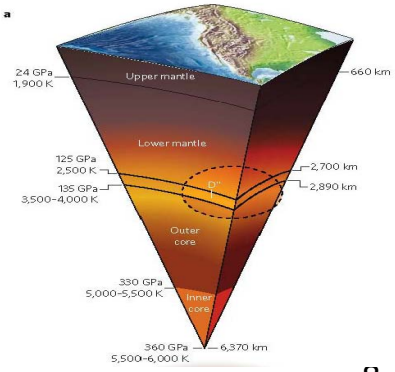





Winfried Lorenzen

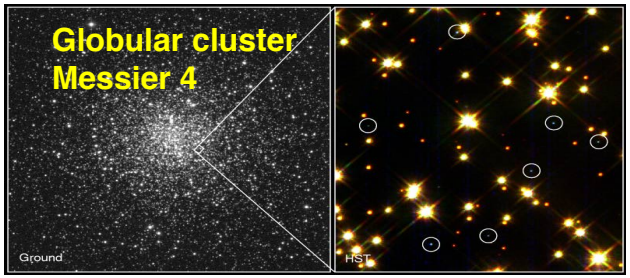
  - Conductivities for dynamo models
  - The properties of iron and iron + impurities for earth core conditions
    - Phase boundaries, particularly melt
    - Thermal and electrical properties
  - Properties of silicates
    - The earth-moon problem
    - Mars, Mercury



# Areas of Active Research

- White Dwarfs
  - Cosmochronology – age of white dwarfs through cooling rate
    - Equations of state for C, O, and He at extreme conditions
    - Thermal conductivities, viscosities, diffusion coefficients
  - Asteroseismology – model pulsating white dwarf, to infer
    - Total mass and mass composition
    - Interior rotation profile
    - Surface temperature
    - Structural details




NASA/HST

Due to the intense gravity, white dwarfs are highly stratified:

C/O core, remnant from nuclear burning
He envelope
H outer layer
Mixing at the boundaries

Conditions at the C/He boundary (model dependent)
T from 30 to 300eV, P from 100 to $10^5$ Mbar

# Areas of Active Research

Sandia National Laboratories

- Diagnosing Warm Dense Matter
  - Traditional shock experiments and diagnostics
    - VISAR (velocity interferometry, back out density and pressure)
    - Pyrometry (temperature, needs good WDM emissivity models)
  - X-ray Thomson scattering
    - Non-collective (high **k**, Compton limit), pretty well understood
    - Collective limit (low **k**, plasmons), not so well
  - X-ray diffraction (for warm dense solids)
    - Debye-Waller effects
    - Material strength of warm dense solids
  - X-ray absorption fine structure (XAFS)
    - XANES
    - EXAFS

# Areas of Active Research

Sandia National Laboratories

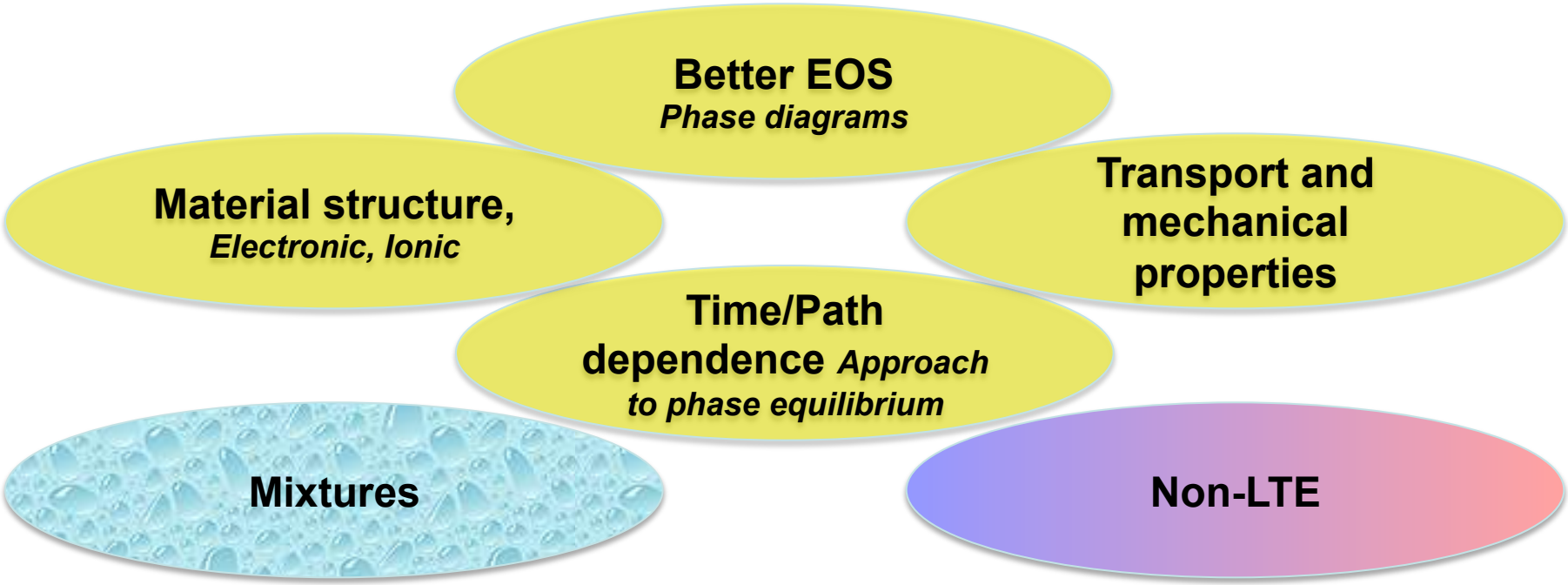
- Theoretical and Computational Methods
  - More atoms, and faster (meso and macro scales)
    - Faster molecular dynamics algorithms
    - Orbital free density functional theory
    - Wave packet molecular dynamics
    - Warm Dense Matter with classical and semi-classical potentials
  - More electrons, and faster (extreme conditions, core excitations)
    - All electron calculations and dynamics
    - Orbital free DFT
  - Improved average atom methods, and beyond (multi-center techniques)

# Areas of Active Research

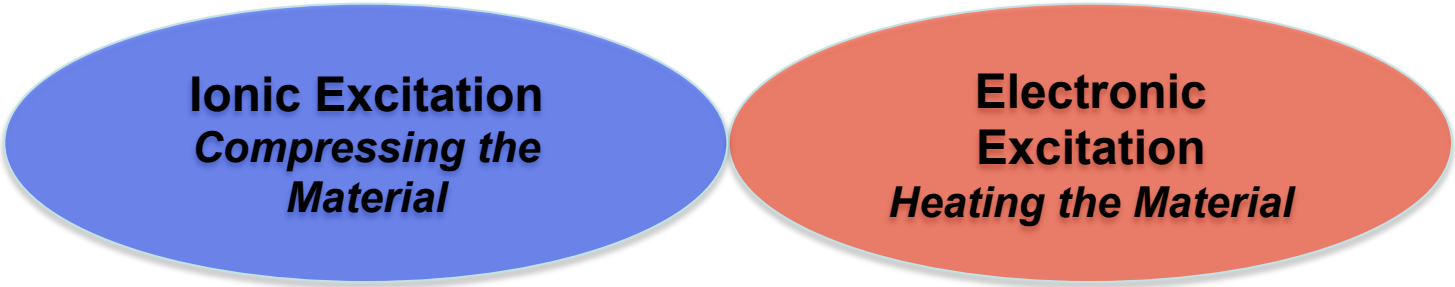
Sandia National Laboratories

- Theoretical and Computational Methods
  - More accurate electronic structure methods
    - Better functionals for density functional theory
      - Finite temperature
      - Exact exchange
      - Hybrids
      - Kinetic Energy in Orbital Free DFT
    - Better potentials for density functional theory
      - Good high energy scattering properties
      - Handle a broad range of conditions
    - Time dependent density functional theory
      - Beyond ground state electronic densities
      - Electron ion coupling
    - Quantum Monte Carlo
      - PIMC, CEIMC, DMC

# Scientific needs in Warm Dense Matter Research



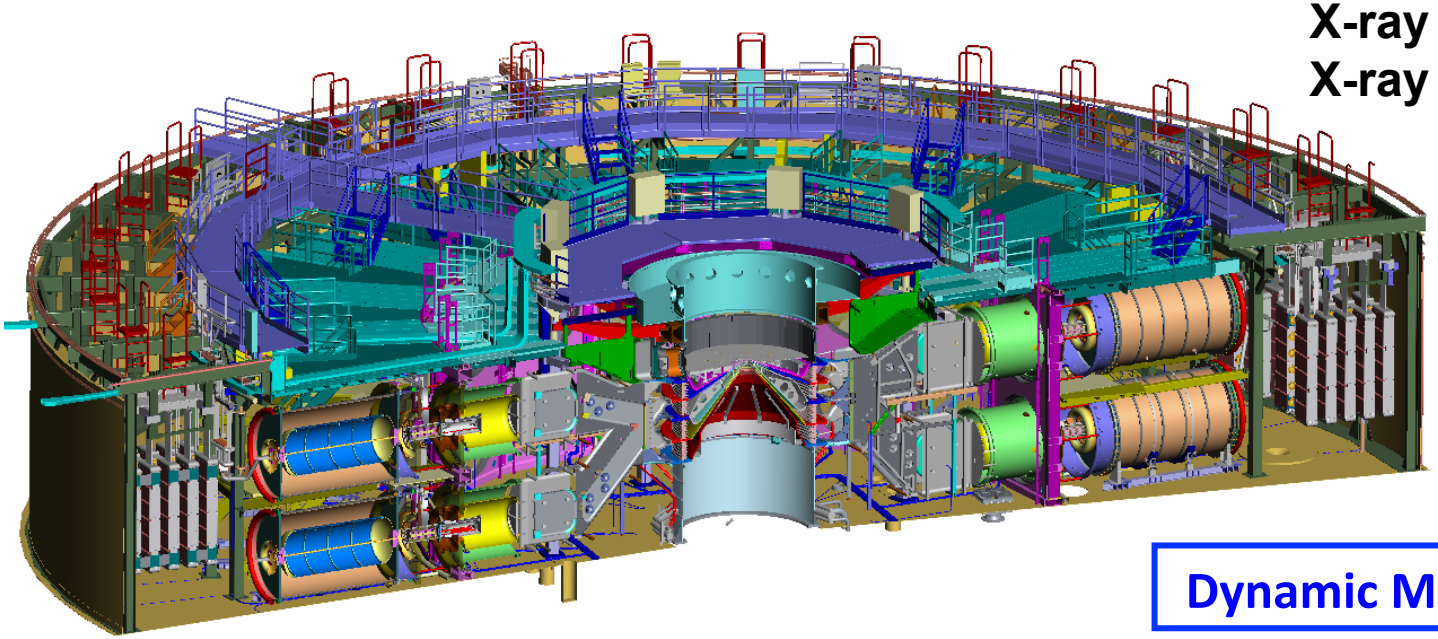

## Experimental approaches



# Sandia's Z Machine is a unique platform for multi-mission research on high energy density (HED) environments

Sandia National Laboratories

**I ~ 26 MA, τ ~100 ns**
**X-ray power > 250 TW**
**X-ray energy > 2 MJ**

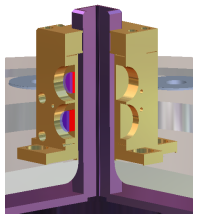


**Dynamic Materials**

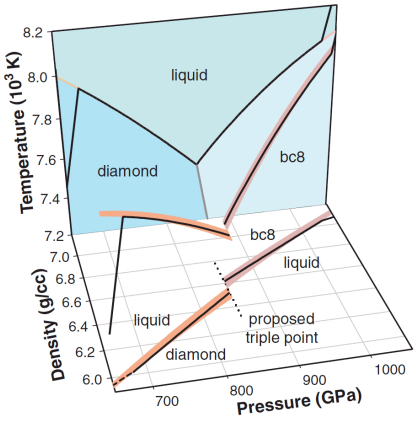
**Pulsed Power Technology**

**Magnetically Driven Implosions**

**Inertial Confinement Fusion**

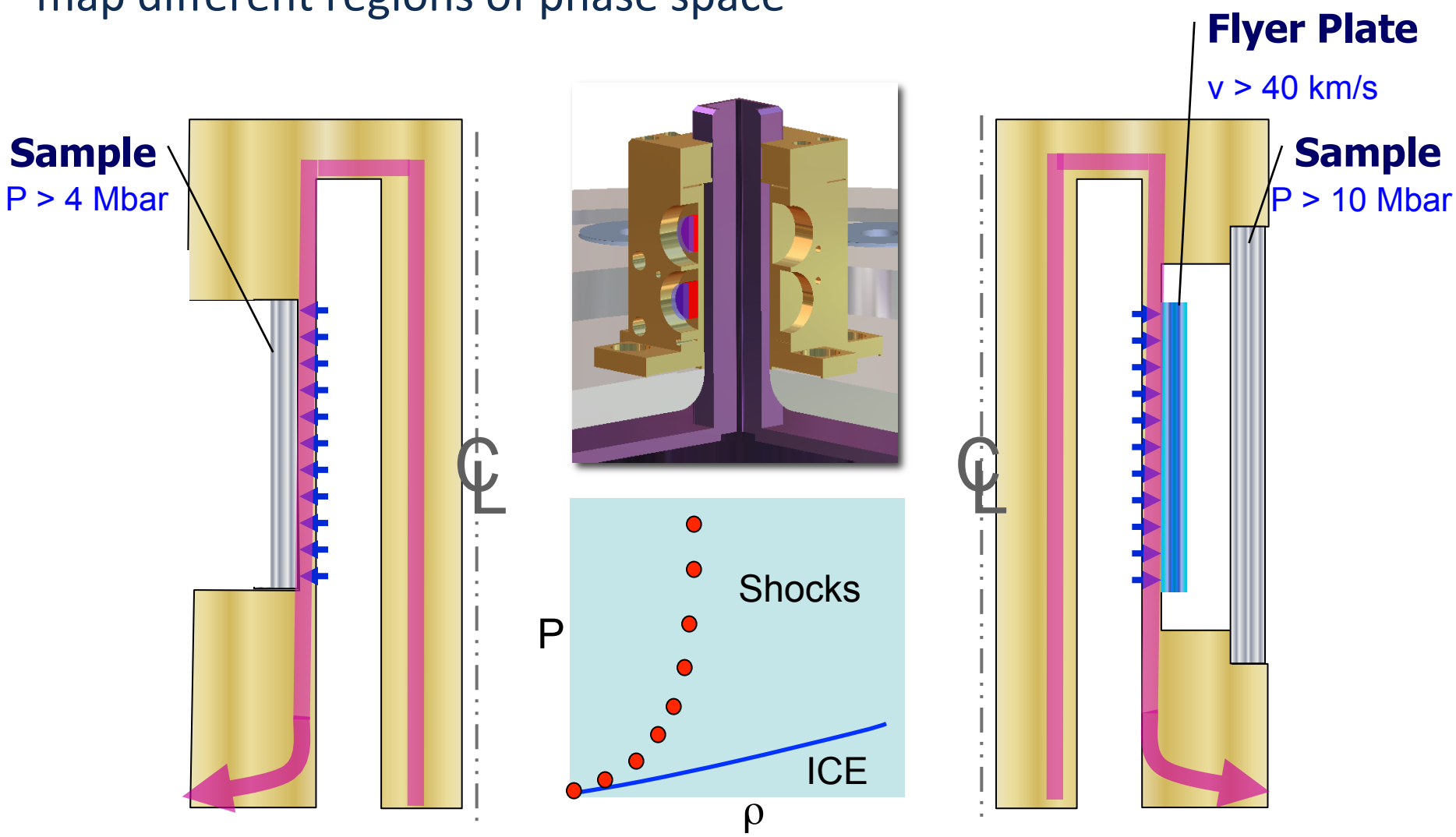


**Equation of State**



# Isentropic compression and shock wave experiments map different regions of phase space

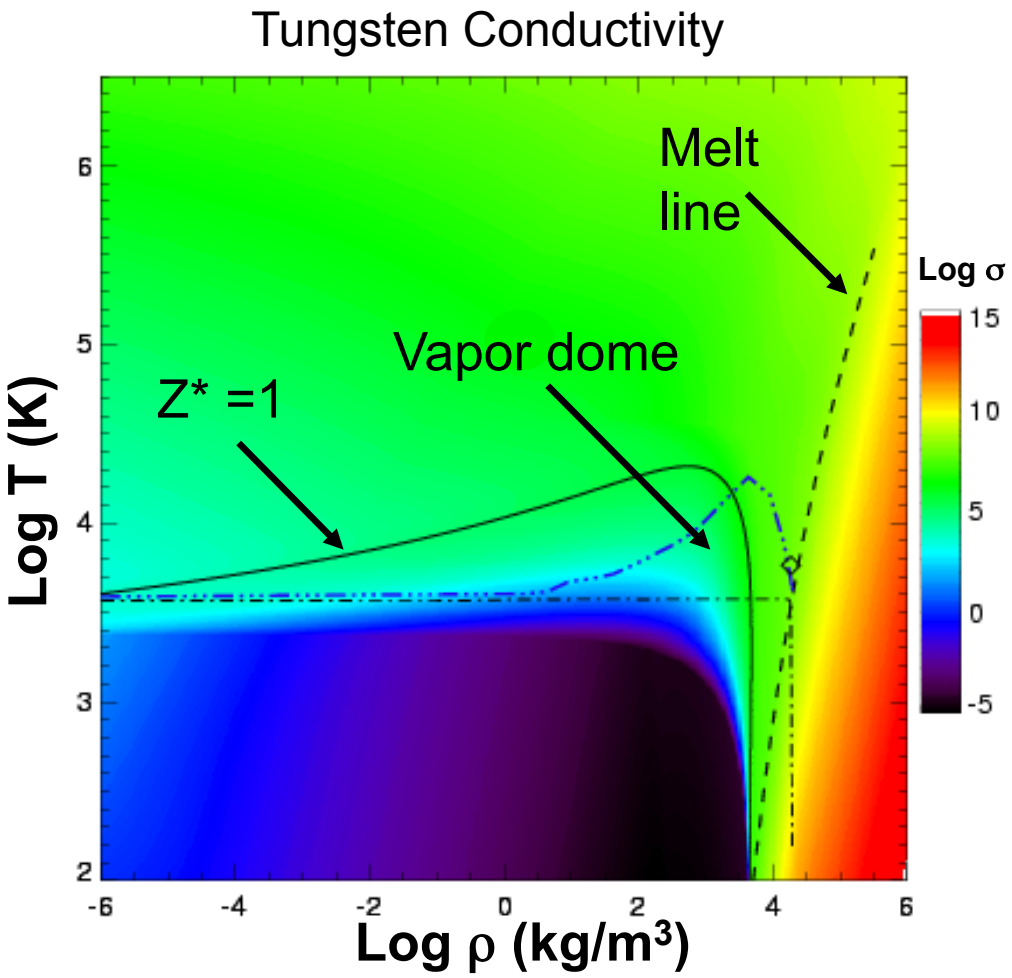
Sandia National Laboratories




**Isentropic Compression Experiments:** gradual pressure rise in sample

**Shock Hugoniot Experiments:** shock wave in sample on impact

# HEDP computer simulations rely on "physics packages": Conductivities, Equations of State, and Opacities




Degeneracy and magnetization effects

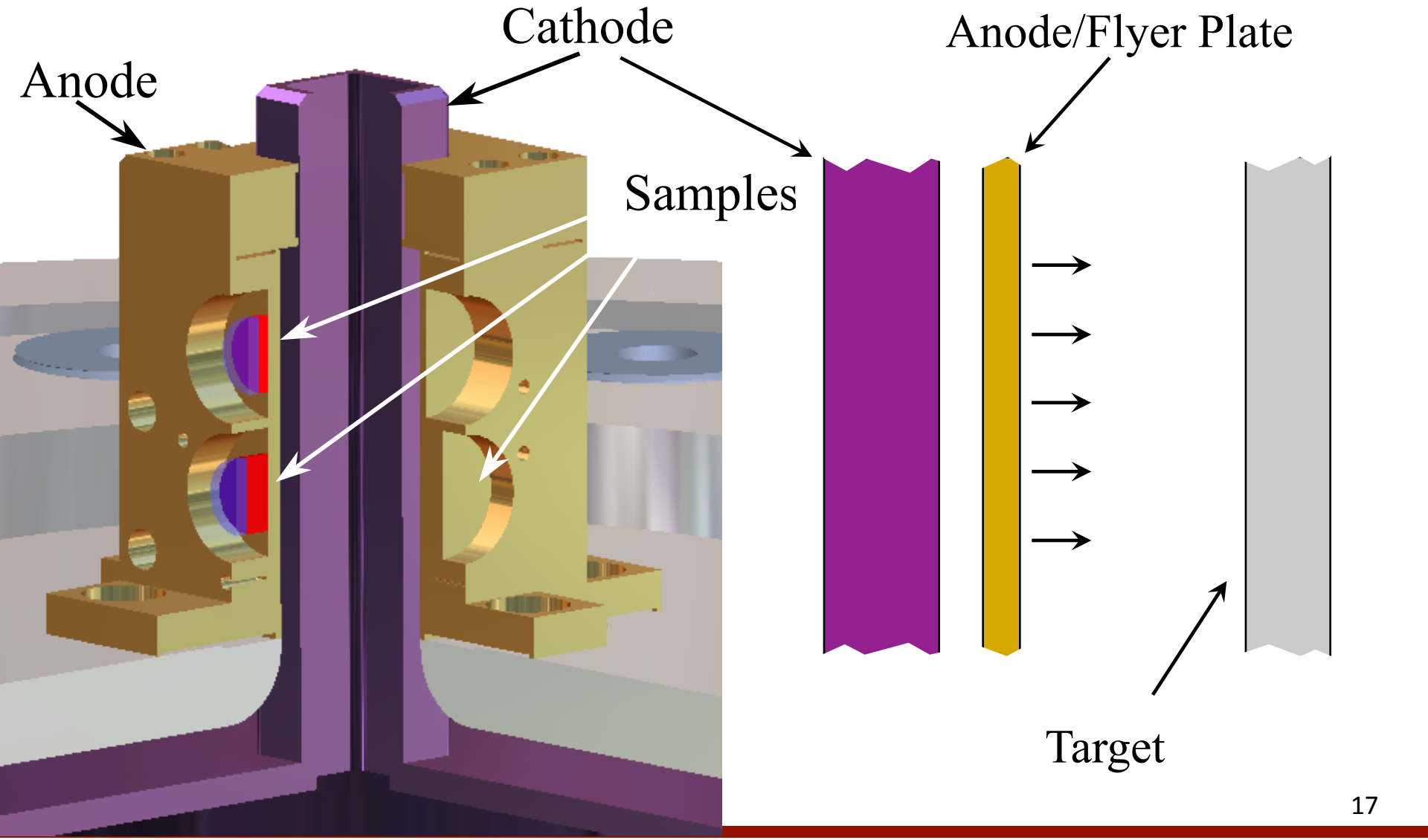
$$\sigma = n_e \, A\left(\frac{\mu}{kT}, \Omega\tau\right) \frac{e^2}{m}\tau$$

Pressure ionization, metal-insulator transition, Thomas-Fermi at high T, ρ

Coulomb and electron-neutral collisions, Bloch-Gruneisen solid, Lindemann melting law

This highly structured portion of phase space is Warm Dense Matter

# A demanding application: Ultra-high velocity magnetically launched flyer plates (> 40 km/sec)

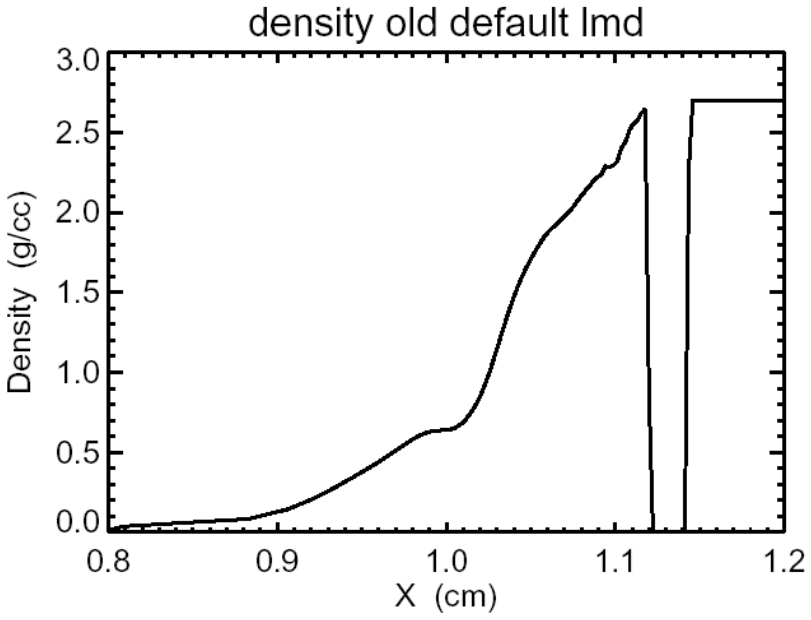


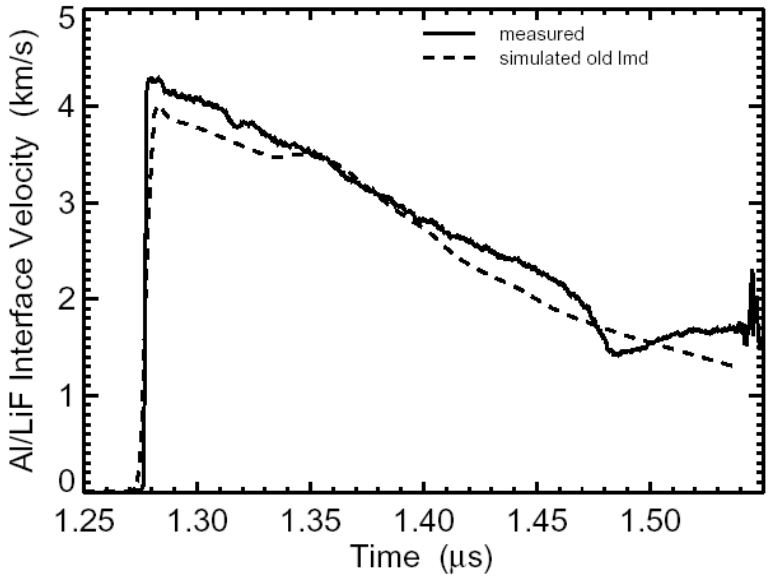
# We simulated these magnetically launched flyer plates using the modified Lee-More (LMD) conductivities

Sandia National Laboratories

Detailed comparison between simulations and experiments for magnetically launched flyer plates suggested that our *improved* conductivities were still not sufficiently accurate for the warm dense liquid aluminum.

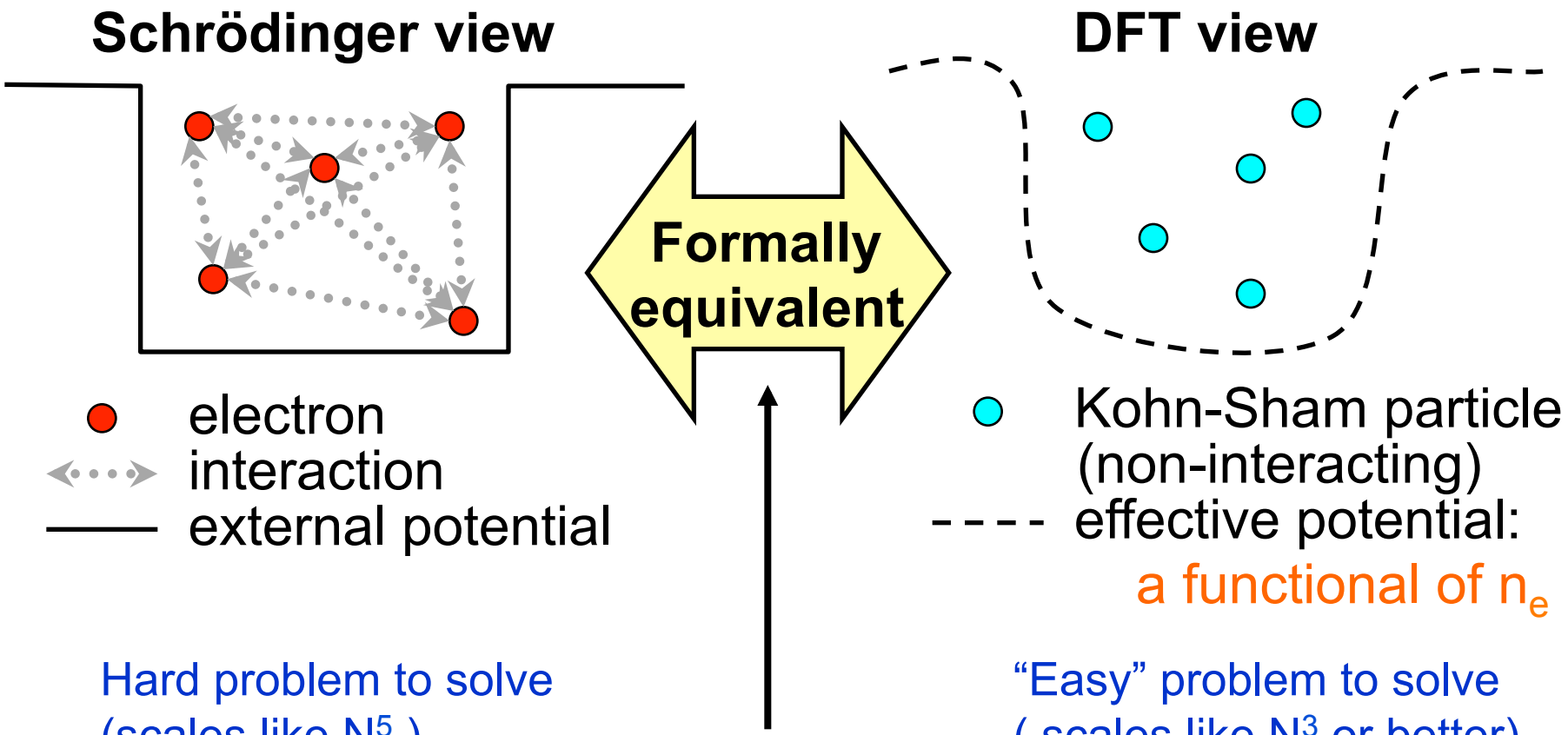
Simulations by Ray Lemke with Sandia's 3D Rad-MHD ALEGRA code




**For many of our applications we require conductivities accurate to well within a factor of two**

# Density Functional Theory (DFT) is a formally exact representation of the N electron Schrödinger Equation




Hohenberg and Kohn proved this (1964)

Nobel prize in Chemistry for Walter Kohn in 1998

# We are using Density Functional Theory (DFT) to perform Quantum Molecular Dynamics (QMD) simulations of Warm Dense Matter

Sandia National Laboratories

Density Functional Theory is formally exact, but is, in practice, a good approximate solution to the N electron Schrödinger equations. DFT is a work-horse tool in condensed matter physics, but a relative newcomer to Warm Dense Matter and High Energy Density Physics.

**QMD**: The **Kohn-Sham* DFT** equations are solved for a given atomic configuration (fixed in the Born-Oppenheimer approximation) and the **quantum mechanical forces** on all the atoms are calculated from the wavefunctions following the Feynman-Hellmann theorem, **the atomic positions are advanced <u>classically</u>,** and a new solution to the DFT equations is calculated.

*Kohn and Sham,1965

QMD is also known as
*ab initio* molecular dynamics (AIMD)

See Car and Parrinello (PRL, 1985), for the original DFT/QMD paper.

# What do the Kohn-Sham equations look like?

Kinetic Energy term

$$\left(-\frac{1}{2}\nabla^2 + V_{eff}(\vec{r}_1)\right)\Psi_i = \varepsilon_i \Psi_i$$

Electron and Ion Coulomb terms

Exchange and Correlation
We don't know this piece exactly, but simple approximations work surprisingly well

$$V_{eff}(\vec{r}_1) = \int \frac{\rho(\vec{r}_2)}{r_{12}} d\vec{r}_2 - \sum_A \frac{Z_A}{r_{1A}} + V_{xc}(\vec{r}_1)$$

$$V_{xc}(\vec{r}_1) \equiv \frac{\delta E_{xc}[\rho(\vec{r}_1)]}{\delta \rho(\vec{r}_1)}$$ where $E_{xc}$ is the Exchange and Correlation Functional,

e.g., Dirac exchange ( $C_x \int \rho(\vec{r}_1)^{4/3} d\vec{r}_1$ ) , LDA , GGA , Exact Exchange, ....

$$\rho(\vec{r}_1) = \sum_i f_i \left|\Psi_i(\vec{r}_1)\right|^2$$ (The $f_i$ are Fermi occupation numbers)

# Details of the QMD simulations

Sandia National Laboratories

- The simulations are performed with VASP, a plane wave density functional code.
- Exchange and Correlation functionals are typically Local Density Approximation (LDA) or Generalized Gradient Approximation (GGA).
- We typically use up to 250 atoms, but it varies depending on density and the number of electrons we need to carry (the valence) ; We use Projector Augmented Wave (PAW) all-electron, frozen core potentials for the atoms.
- We generally perform our simulations in the Canonical Ensemble (N,V,T) using thermostats to regulate the temperature; Fermi statistics for the electrons; Spin included as needed, e.g., iron.
- Typical runs cover one to tens of picoseconds.

# Frequency-dependent electrical conductivities are calculated with the Kubo-Greenwood formula

Sandia National Laboratories

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

Difference of Fermi occupations

Energy Conservation

Dipole matrix elements

where *e* and *m* are the electron charge and mass. The *i* and *j* summations are over the *N* discrete bands of the triply periodic calculation for the cubic supercell with volume Ω. The coordinate index is $\alpha$ and in general we average over $\alpha$ to improve the statistics. $F(\varepsilon_{i,\mathbf{k}})$ is the Fermi weight corresponding to the energy for the *i*-th band at ***k*** with orbital $\Psi_{i,\mathbf{k}}$.

We integrate over the Brillouin zone using the method of special **k**-points

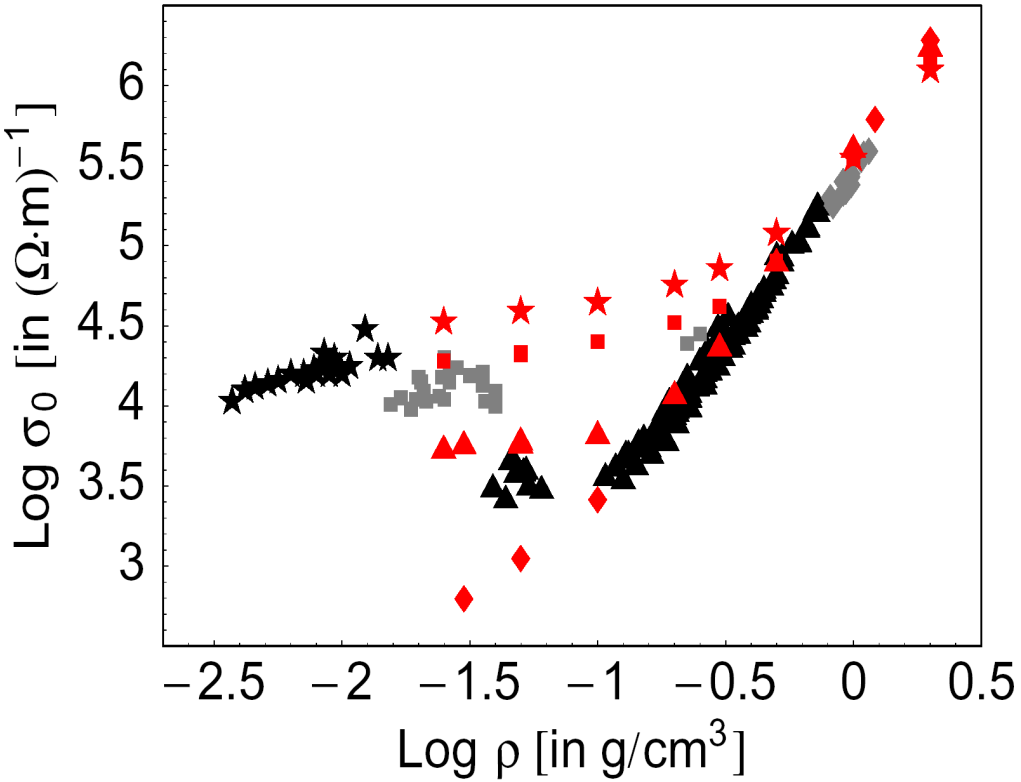
$$\sigma(\omega) = \sum_{\mathbf{k}}\sigma_{\mathbf{k}}(\omega)W(\mathbf{k}) \quad ,$$

and average over 10 to 20 configurations selected from the MD run.

This representation of the conductivity is really nothing more than the quantum analog of the classical current-current correlation function.

**Includes electron-ion, electron-neutral, and electron-electron contributions!**

# The QMD-KG results are in good agreement with DeSilva's data over a two decade range of density

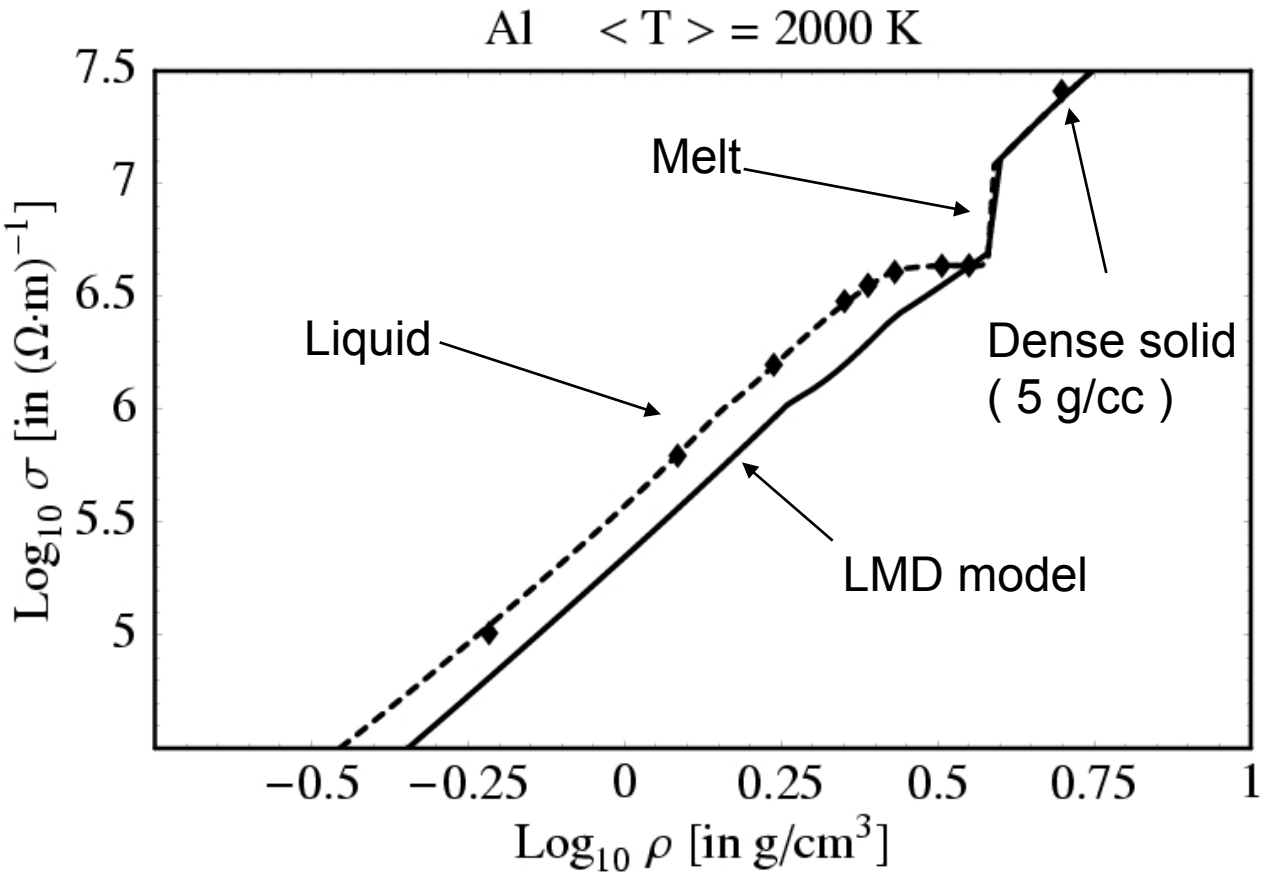



DeSilva and Katsouros data in black or grey, MD-KG results in red

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

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

# The calculated liquid aluminum conductivities are higher than the *modified* Lee-More (LMD) model predictions

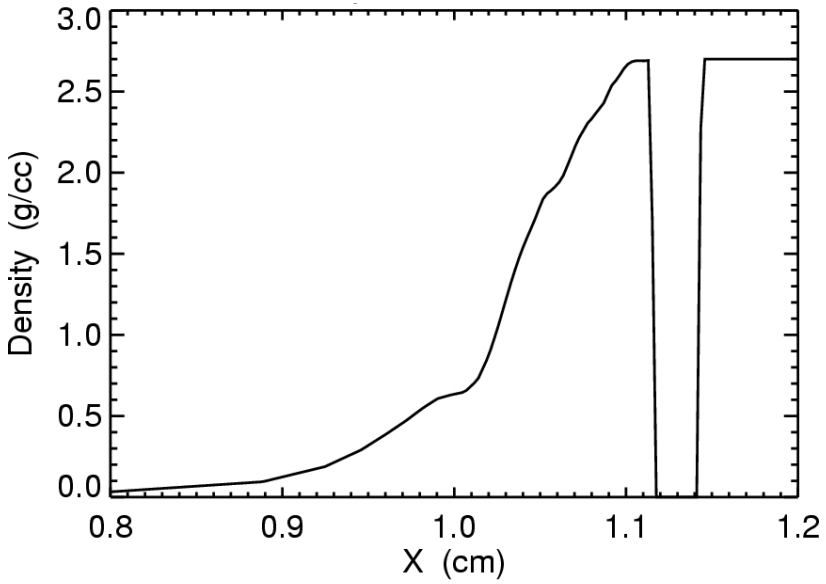


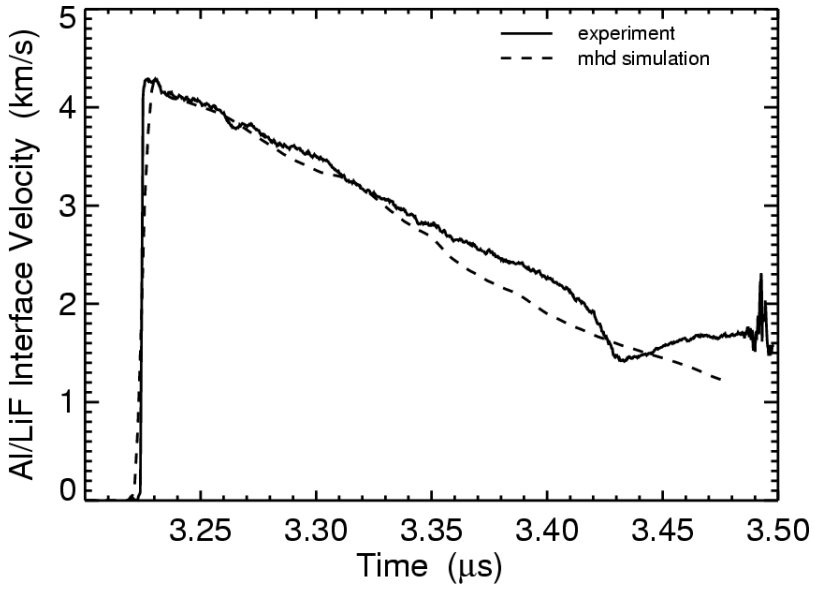

The dashed line shows the 2000 K isotherm from our QMD-tuned wide-range aluminum model

# Flyer plate simulations with the QMD based conductivities give very good agreement with experiment

Sandia National Laboratories

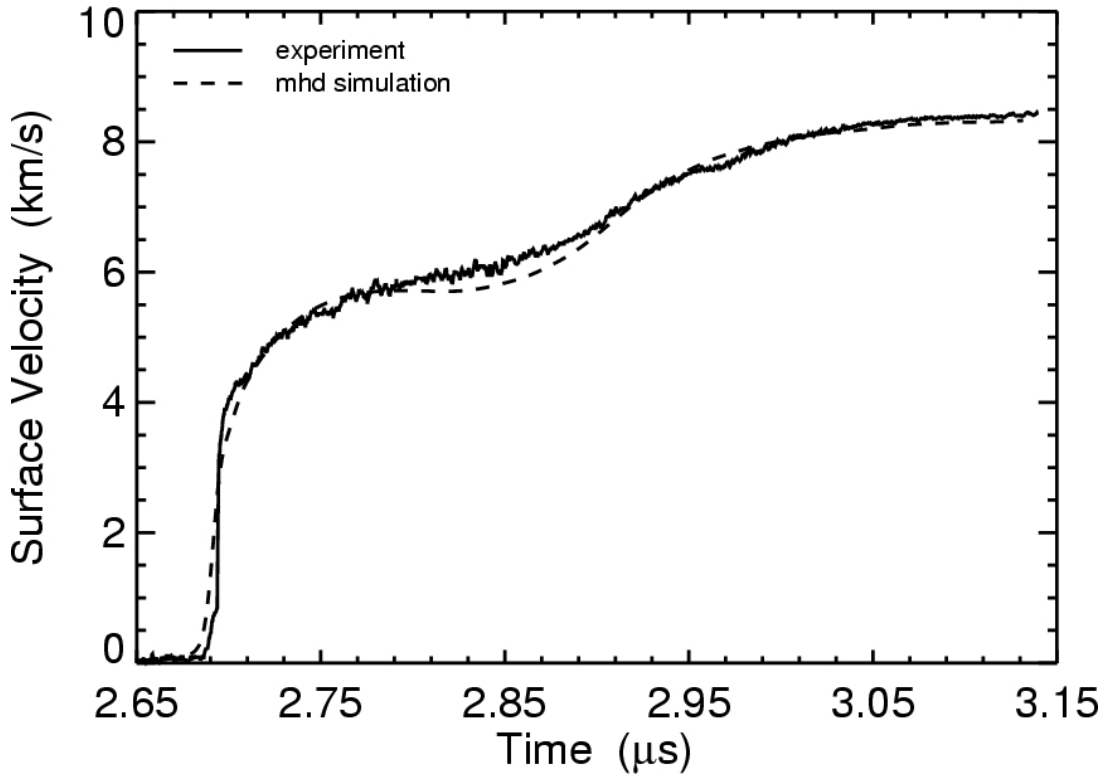
## Simulations by Ray Lemke with Sandia's 3D Rad-MHD ALEGRA code




Conductivities based on the QMD calculations have given us a new predictive capability

# Simulations of the flyer velocities with ALEGRA are now in very good agreement with experiments



# Shock Hugoniot experiments are routinely used on HED facilities to probe the equation of state

Sandia National Laboratories

The Hugoniot is the locus of single shock end states satisfying the Rankine-Hugoniot relation for various $U_s$

Mass conservation

$$\rho_1/\rho_0 = U_s/(U_s - u_p)$$

Momentum conservation

$$U_s u_p = (P_1 - P_0)/\rho_0$$

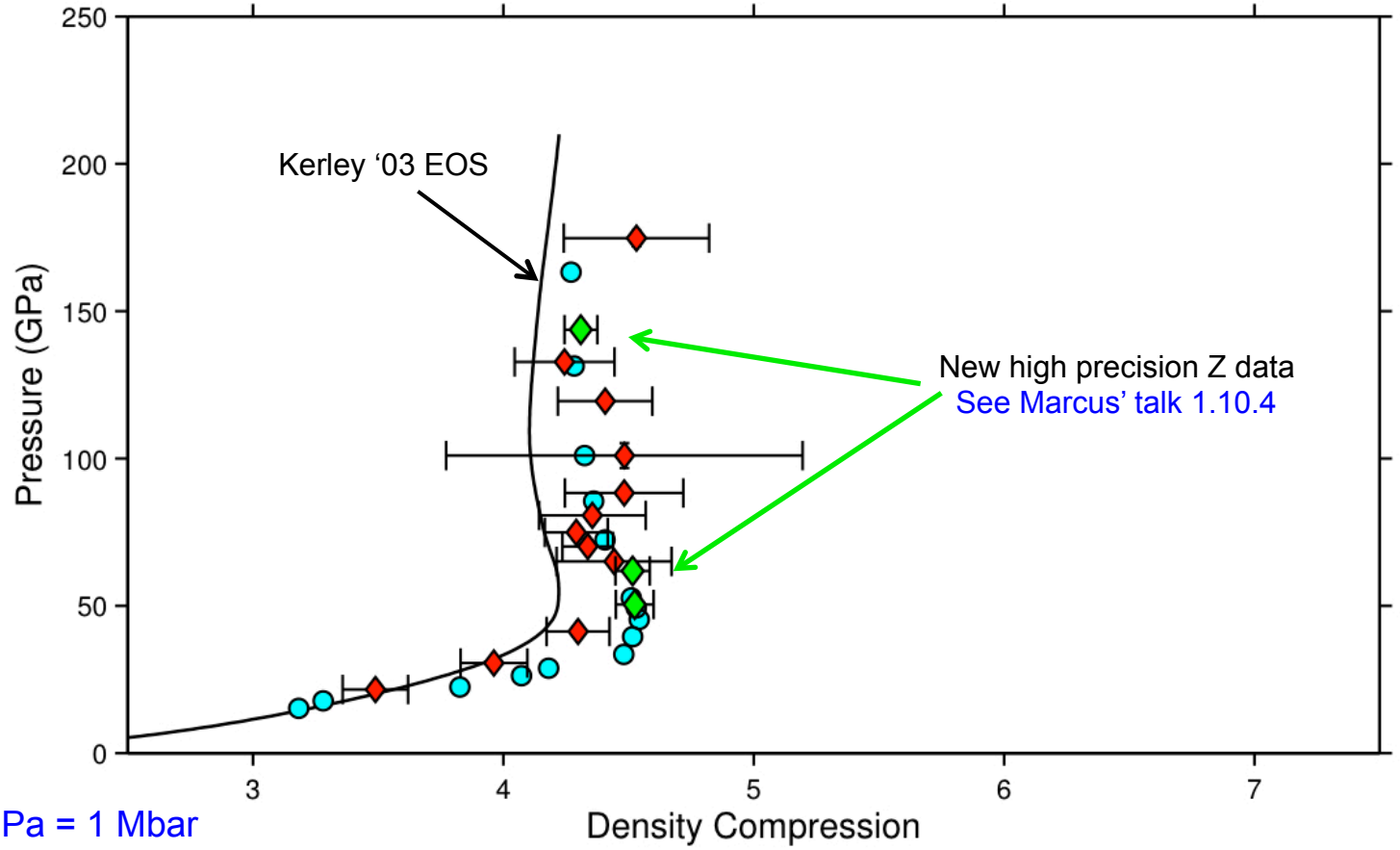
Energy conservation

$$E_1 - E_0 = \frac{P_1 + P_0}{2}(V_0 - V_1)$$

Rankine-Hugoniot relation

Hugoniot calculations are relatively straightforward

# Deuterium equation of state experiments and theory have been very active areas of research

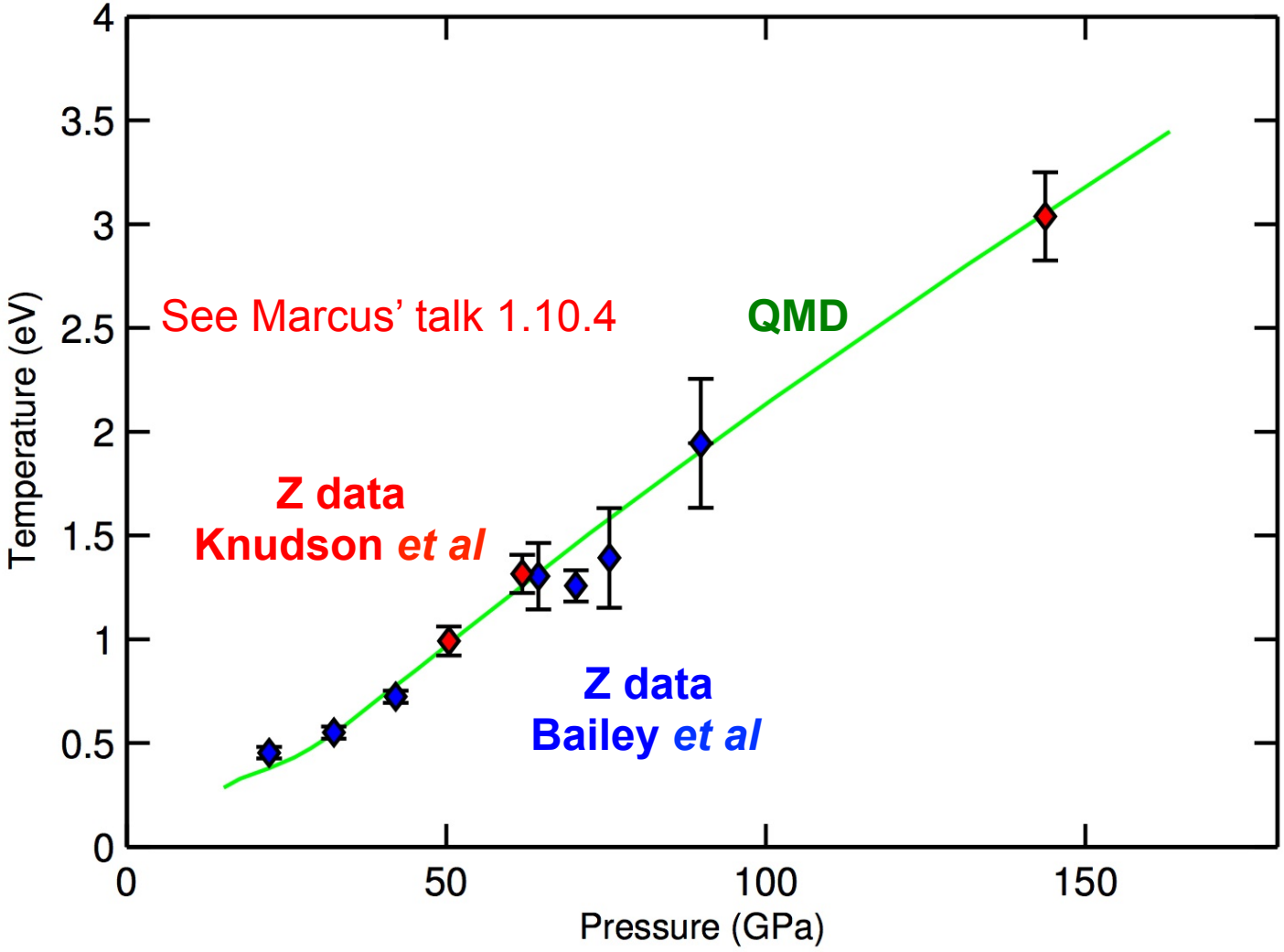



100 GPa = 1 Mbar

M. D. Knudson *et al.*, Phys. Rev. Lett. **87**, 225501 (2001)
M. P. Desjarlais, Phys. Rev. B **68**, 064204 (2003)

See McMahon *et al.*, Rev. Mod. Phys. **84**, 1607 (2012) for a recent review on H and He

# Hugoniot temperature measurements for deuterium on Z using pyrometry also agree well with the first-principles results

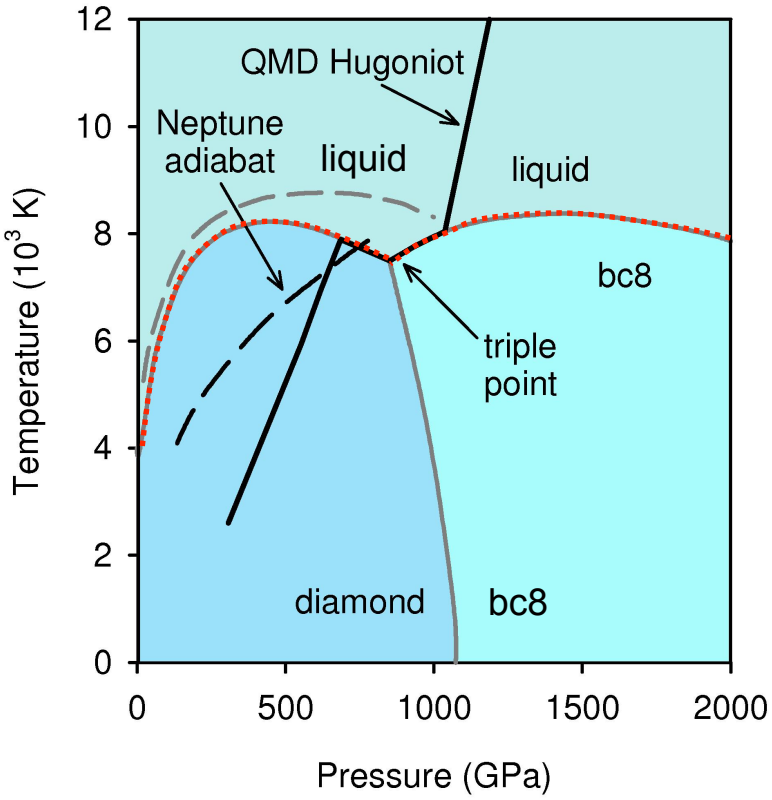


# Experiments on Z explored the shock melting of diamond in support of the National Ignition Campaign

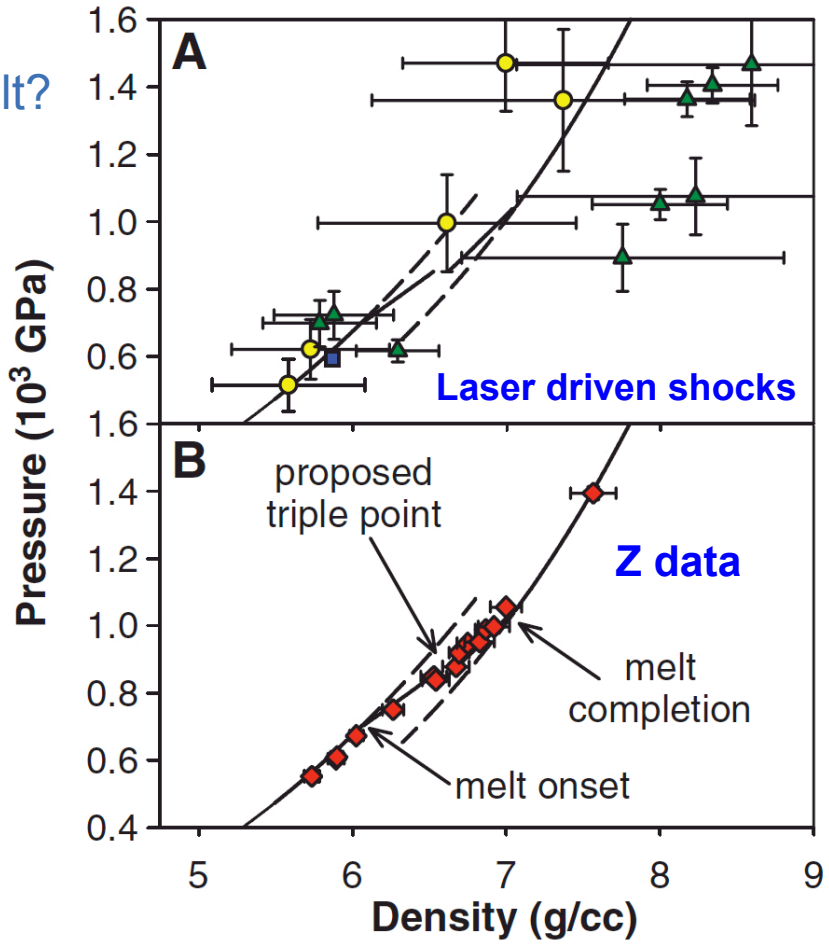
Sandia National Laboratories

## Motivated by ICF capsule designs

At what shock pressure does diamond melt?

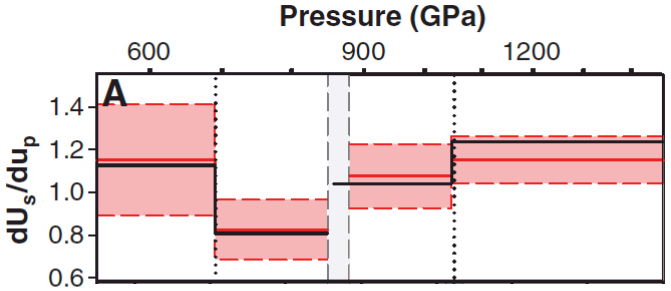



1000 GPa = 10 Mbar

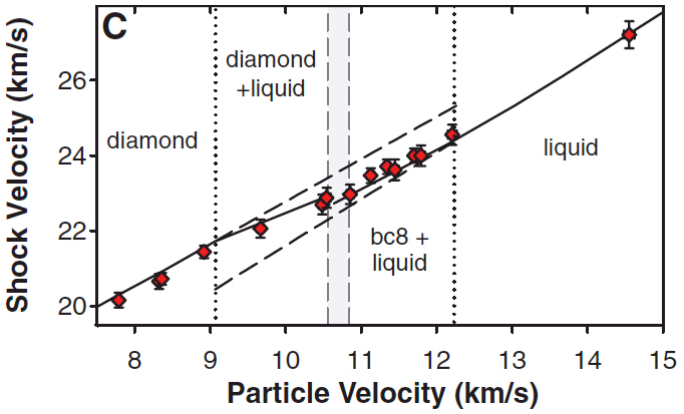



Our Z experiments achieved unprecedented accuracy for shocked diamond

# QMD calculations predicted measurable changes in the shock velocity at the phase boundaries




**QMD predictions in black**
**Z data in red**





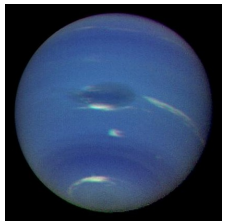
**Shock-Wave Exploration of the High-Pressure Phases of Carbon**

M. D. Knudson,* M. P. Desjarlais, D. H. Dolan

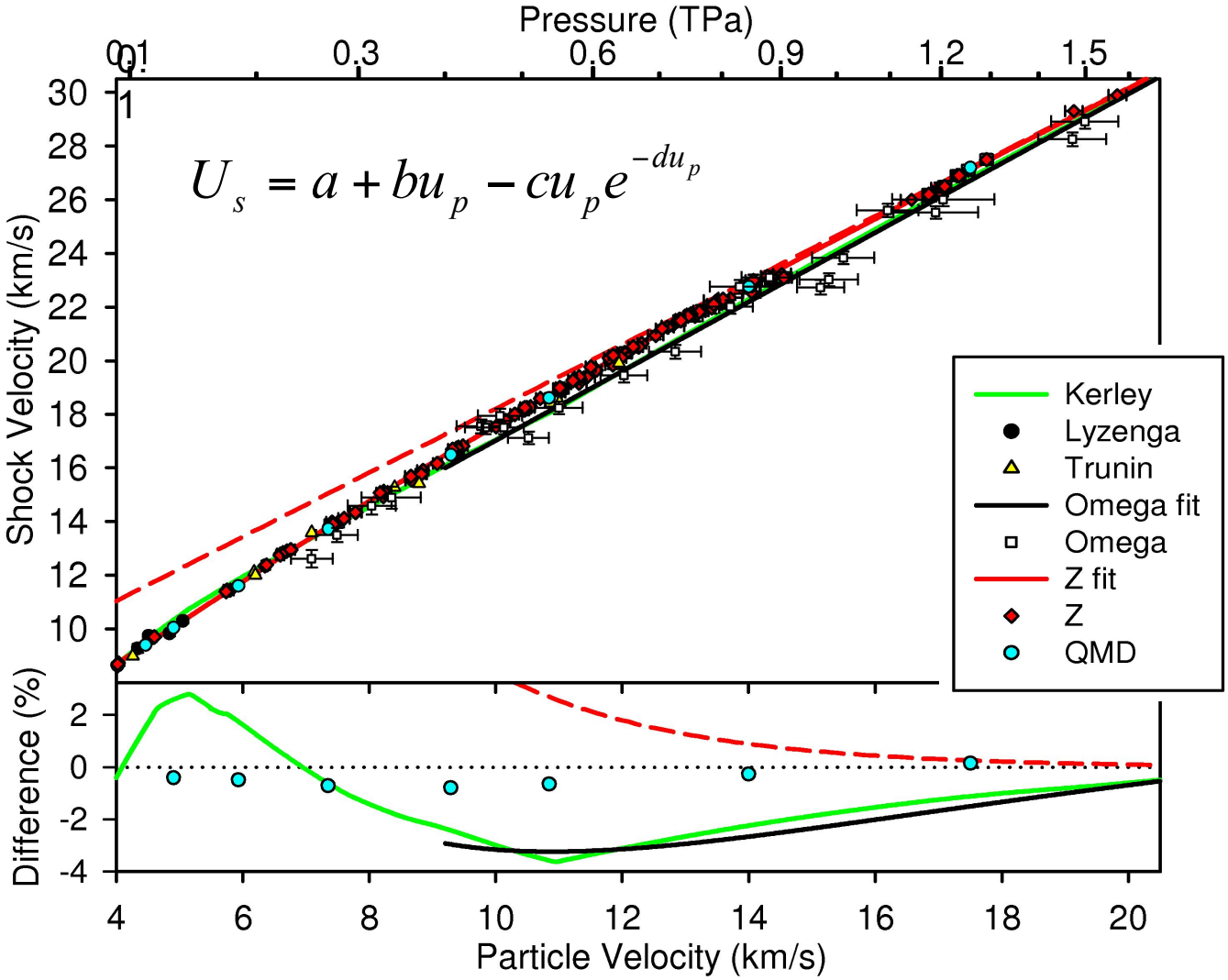
19 DECEMBER 2008 VOL 322 SCIENCE

Melt onset: 6.9 Mbar
Melt completion: 10.4 Mbar
First experimental evidence for BC8 phase in carbon

Neptune



# The α-quartz Hugoniot is now the most extensively explored Hugoniot in the warm dense matter regime

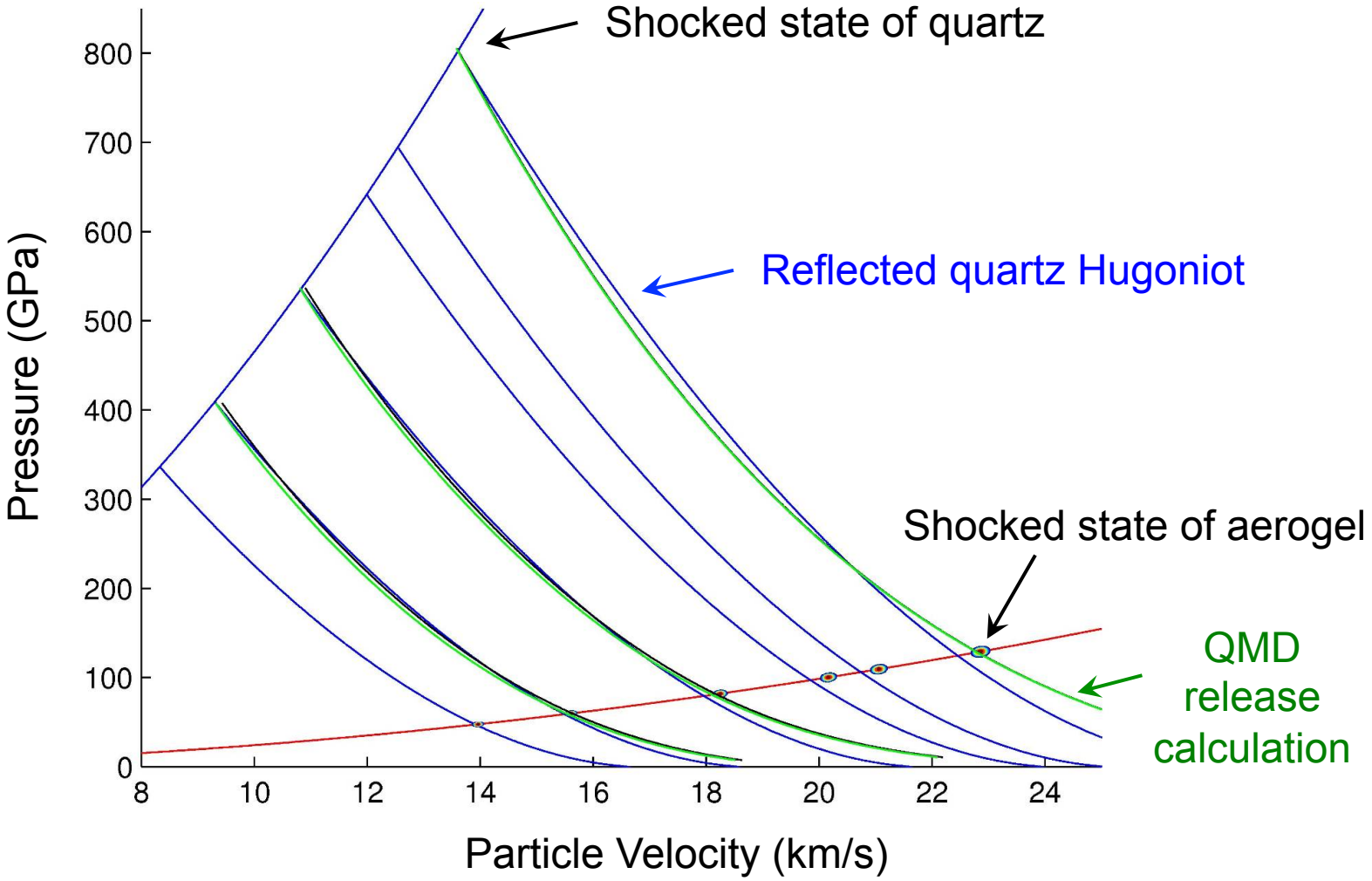



Knudson and Desjarlais, PRL **103**, 225501 (2009)



33

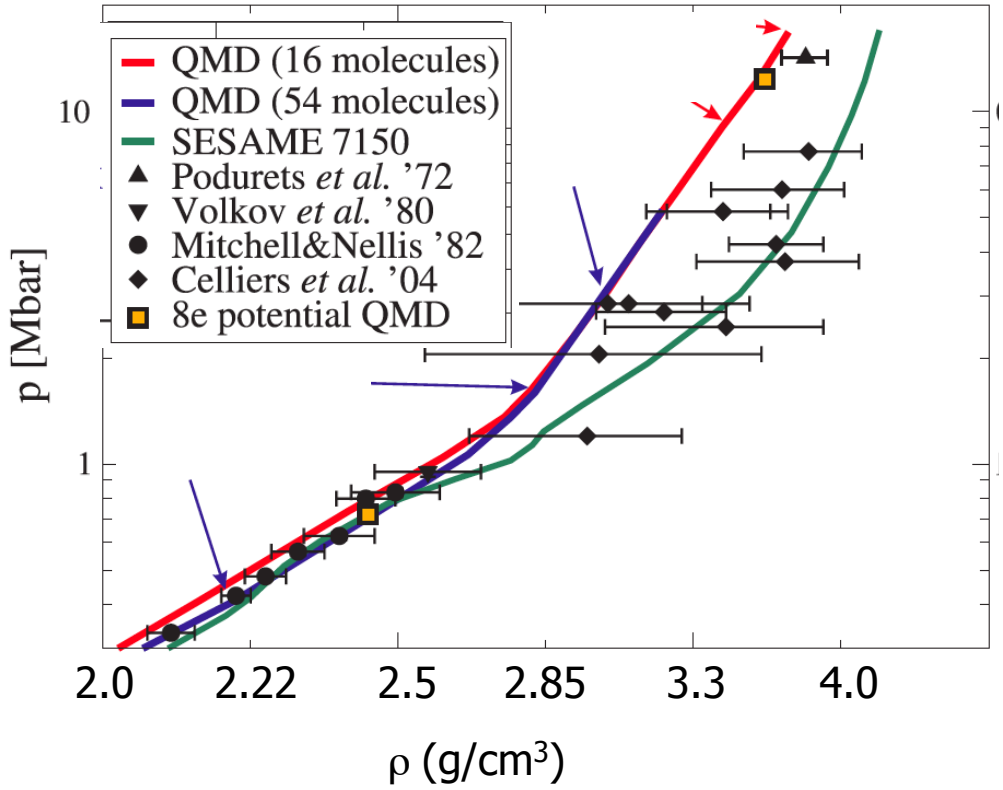
# We have also performed six release experiments from α-quartz Hugoniot states in the 3 to 8 Mbar range






**See poster 2.30, Knudson and Desjarlais for our new quartz release model**

# Simulations predicted that the principal Hugoniot of water was stiffer than SESAME 7150 and earlier data



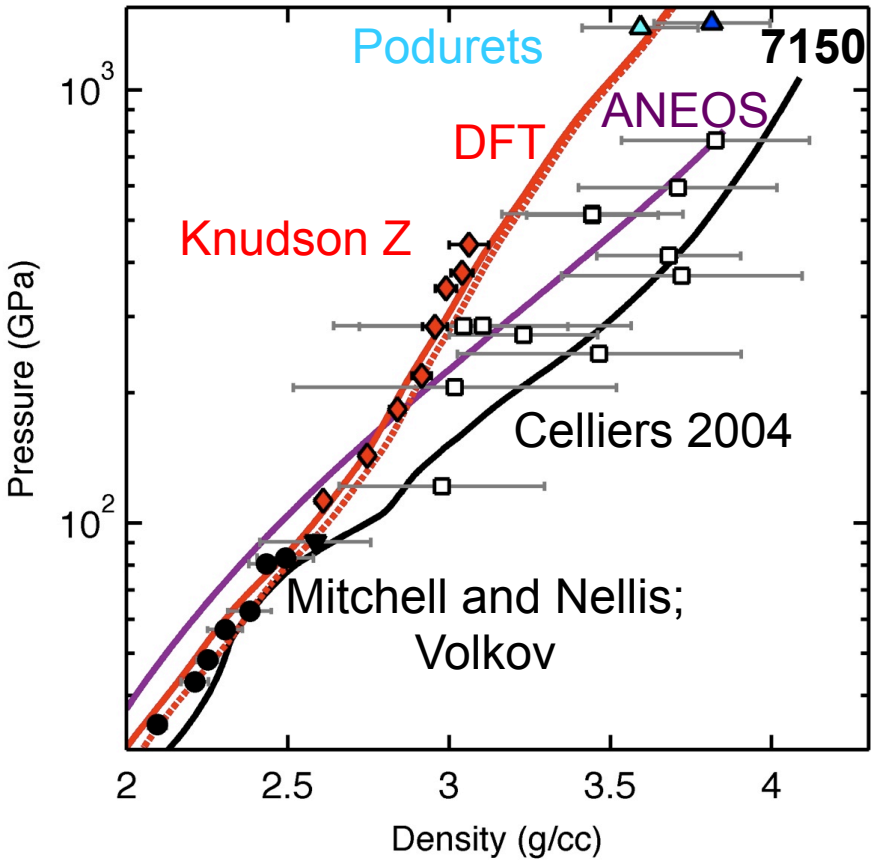

*Equation of state and phase diagram of water at ultrahigh pressures as in planetary interiors*
French, Mattsson, Nettelman, and Redmer
PRB **79**, 054107 (2009).

- QMD results agree with gas-gun data (<1 Mbar)
- QMD results agree with very high P result from Russia

- QMD results disagree with SESAME 7150
- QMD results disagree with prior data

- Technical detail: all-electron calculations (8 $e^-$ O potential)
- Careful calculations but disagreement with data is a point of concern

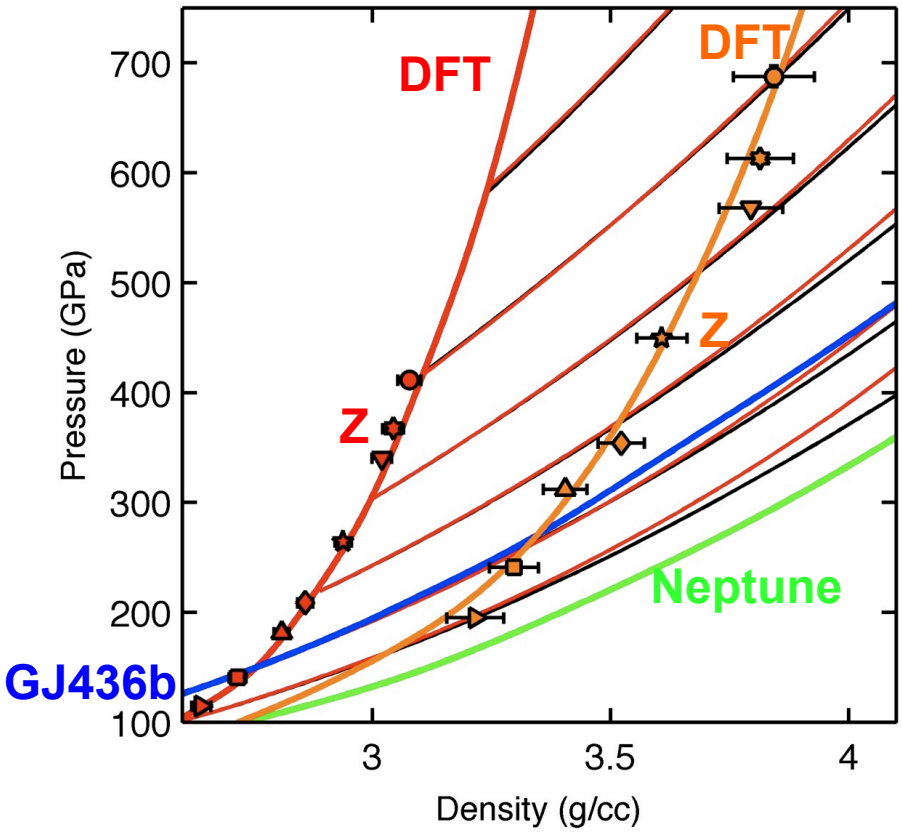
# New experimental data from Z validates the QMD calculations and the equation of state from the Rostock group




- QMD results agree with gas-gun data (<1 Mbar)
- QMD results agree with very high P result from Russia
- QMD results agree with high P result from Sandia's Z machine

*Probing the interiors of the ice giants: Shock compression of water to 700 GPa and 3.8 g/cc,* Knudson, Desjarlais, Lemke, Mattsson, French, Nettelmann, and Redmer, Phys. Rev. Lett. **108**, 091102 (2012).

# Re-shock states approximate isentropic compression and are relevant to planetary interiors



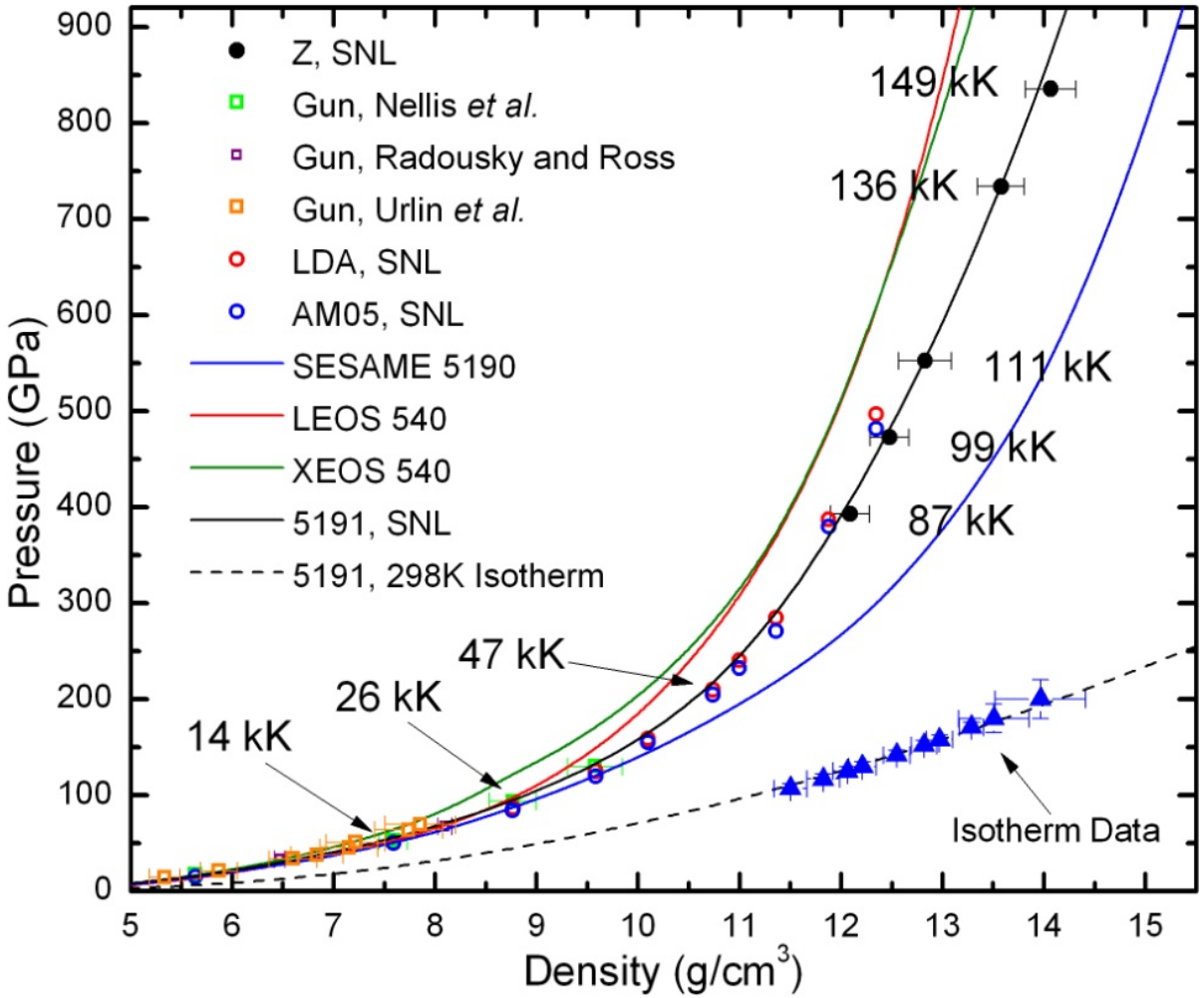

- Re-shock results validate isentropic compression results obtained from DFT
- Data along planetary isentropes for Neptune and hot exoplanets like GJ436b
- *Data with unprecedented accuracy for second shock in water*

*Probing the interiors of the ice giants: Shock compression of water to 700 GPa and 3.8 g/cc,* Knudson, Desjarlais, Lemke, Mattsson, French, Nettelmann, and Redmer, Phys. Rev. Lett. **108**, 091102 (2012).

# We have performed experiments and simulations for xenon at high pressures

Sandia National Laboratories

- Measured the xenon Hugoniot to 840 Gpa
- Problems with the original PAW potential identified
- Developed a new wide-range, multi-phase equation of state for xenon



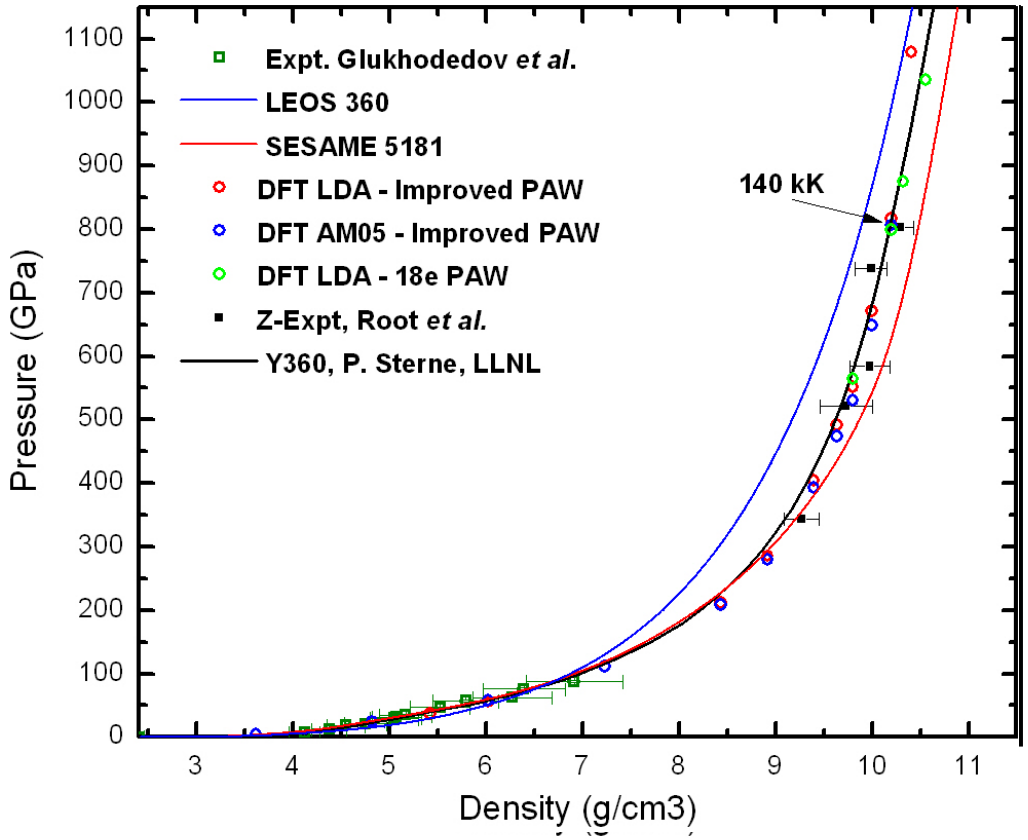


S. Root *et al.*, Phys. Rev. Lett. 105, 085501 (2010).

J. H. Carpenter *et al.*, EPJ Web of Conf. 10, 00018 (2010).

# We have now executed similar experiments for krypton

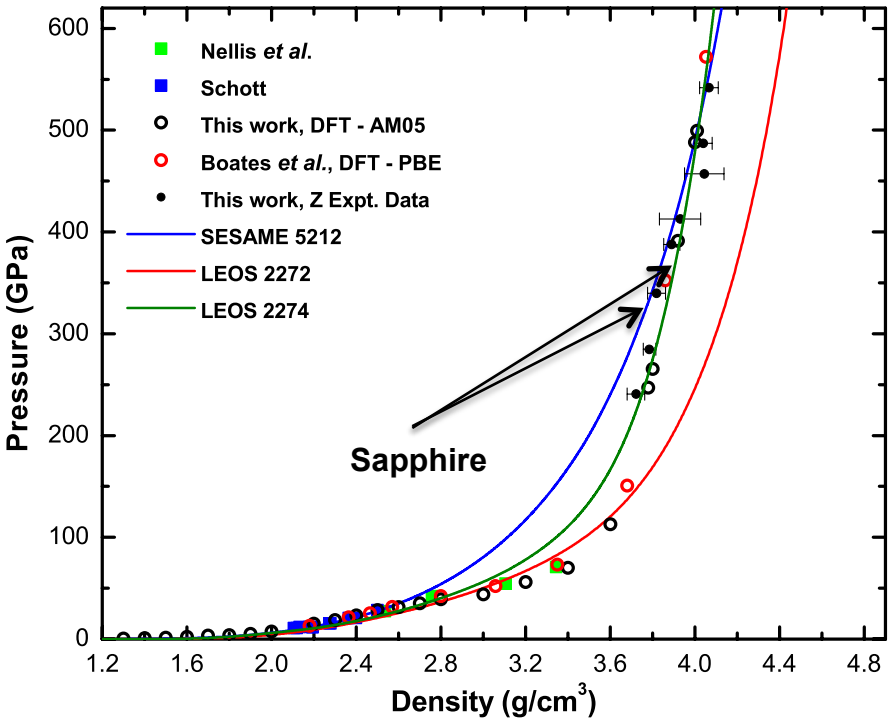
- Hugoniot determined to 8 Mbar
- Used reflected Al Hugoniot to calculate Kr state
- Using SESAME 3700 release shifts density lower ~ 1%
- Improved PAW results agree with experimental data
- VASP Original PAW too stiff
- SESAME 5181 agrees to 4 Mbar

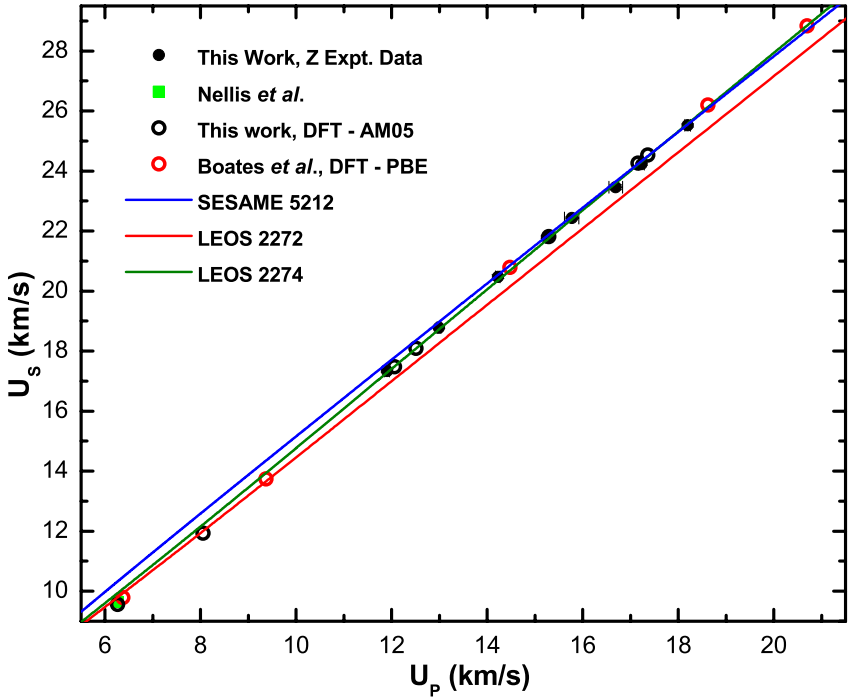



Phil Sterne (LNLL) developed Y360 using DFT and Z Results

# Recent work has explored the Hugoniot of $CO_2$

- Hugoniot measured to 5.5 Mbar – consistent with DFT results
- Data determined using quartz and sapphire impedance matching – consistent results regardless of impedance standard
- Experiments show a less compressible Hugoniot after dissociation
- LEOS 2272 is too compressible and SESAME 5212 has different trajectory
- LEOS 2274 (Wu) utilized the DFT and Z experimental results for high pressure Hugoniot

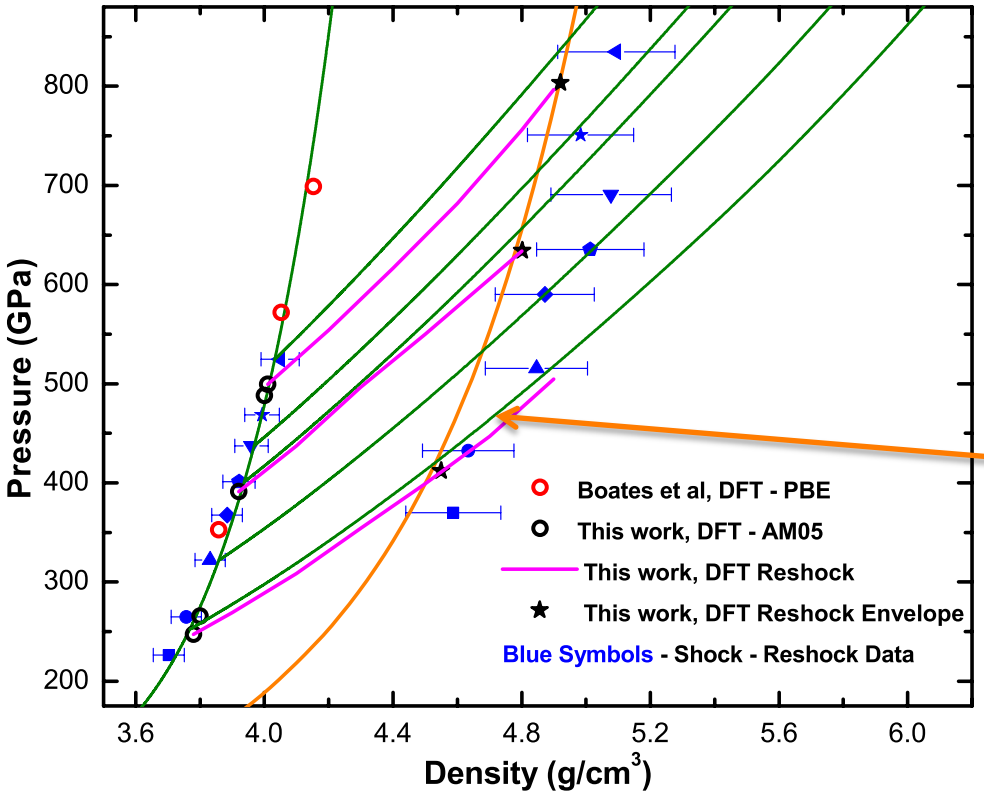


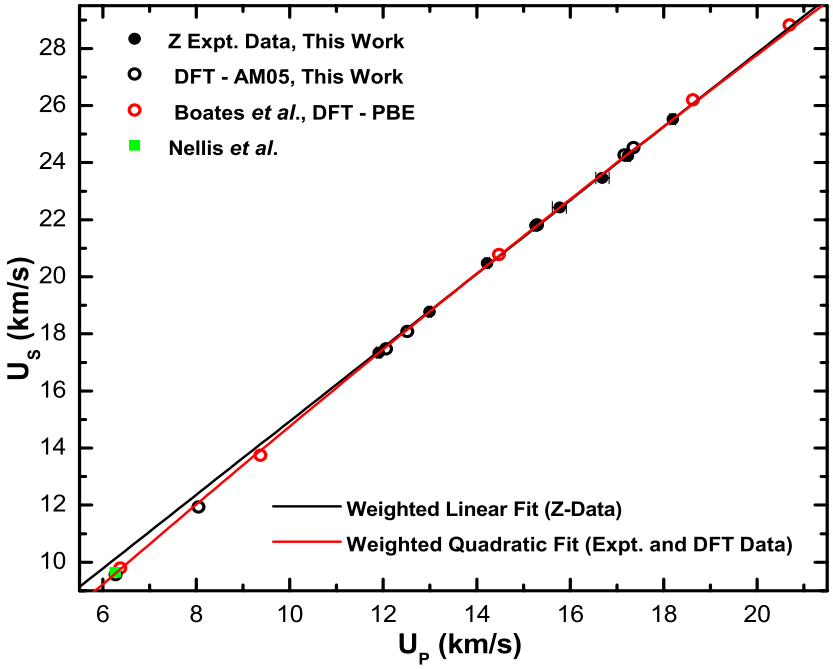




Root, Cochrane, Carpenter, and Mattsson, Phys. Rev. B **87**, 224102 (2013)

# We have also obtained data on reshock states of $CO_2$

- A weighted linear fit and weighted quadratic fit determined for the data
- Because of some attenuation of the shock we use fit and $CO_2$ shock velocity to calculate state prior to reshock at rear quartz window
- Reshock state determined from quartz shock velocity

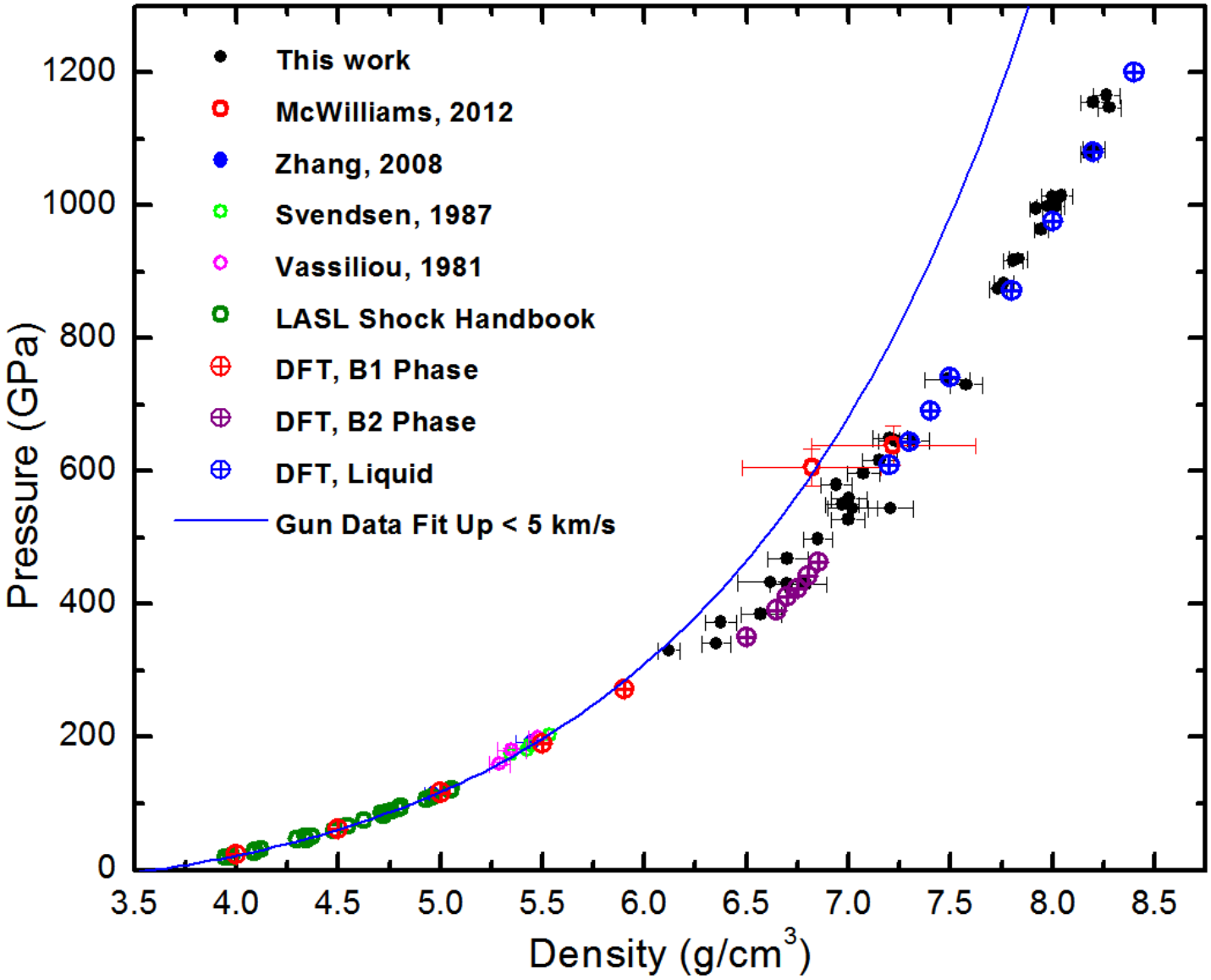



- $CO_2$ reshock state measured to 8.4 Mbar
- Reshock end states determined from LEOS 2274 and quartz Hugoniot
- Experimental data shows more compressibility on reshock than predicted by DFT

Root, Cochrane, Carpenter, and Mattsson, Phys. Rev. B **87**, 224102 (2013)

# We have developed an extensive set of data and simulations for MgO






See talk 1.5.4 (Root, *et al.*) and poster 2.34 (Shulenburger, *et al.*)

# Summary

- First-principles molecular dynamics with density functional theory (a.k.a QMD or AIMD) has emerged over the last decade as a very powerful tool for studying warm dense matter
- New insights have been obtained into the high pressure phase diagram and behavior of materials
- Extensive validation experiments for a wide range of materials have been carried out on Sandia's Z machine
- Greatly improved transport models and equations of state have been developed with input from QMD simulations