APS SCCM/AIRAPT Invited Talk
SAND2013-5495C
Seattle, WA 2013
Session J4 (First Principles Methods IV)
11 AM Tues 7/9 11 Vashon Room

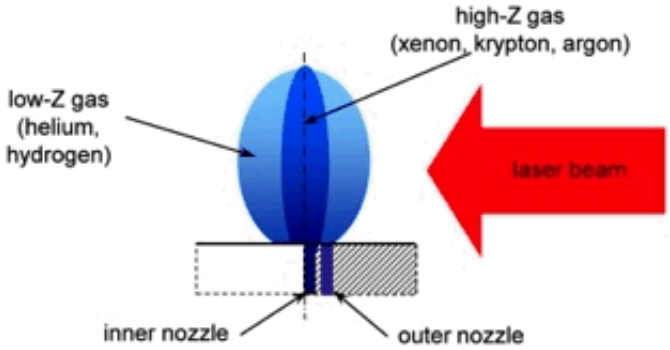
Equations of State for Mixtures: Results from DFT Simulations of Xenon/Ethane Mixtures Compared to High Accuracy Validation Experiments on Z

R.J. Magyar

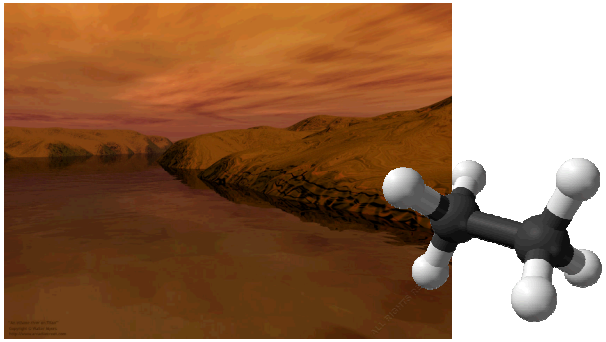
Sandia National Laboratories is a multi program laboratory managed and operated by Sandia Corporation, a wholly owned subsidiary of Lockheed Martin Corporation, for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000.

Properties of Materials in the Mbar regime are Important for Several Reasons

- Inertial confinement fusion (ICF) materials
  - Proposed Xe plasma shell imploding on fuel target
  - Gas puff experiments
  - Fundamental behavior high Z dopant / low Z fuel
  - Mbar pressure, +10 000 K temperature



- Planetary science
  - High-pressure mixtures of Xe, H, and C
- Chemistry at high pressure and temperature
  - Different phases
  - Does Xe continue to be alkane-like when mixing at Mbar pressures



This Region of Phase Space is Important

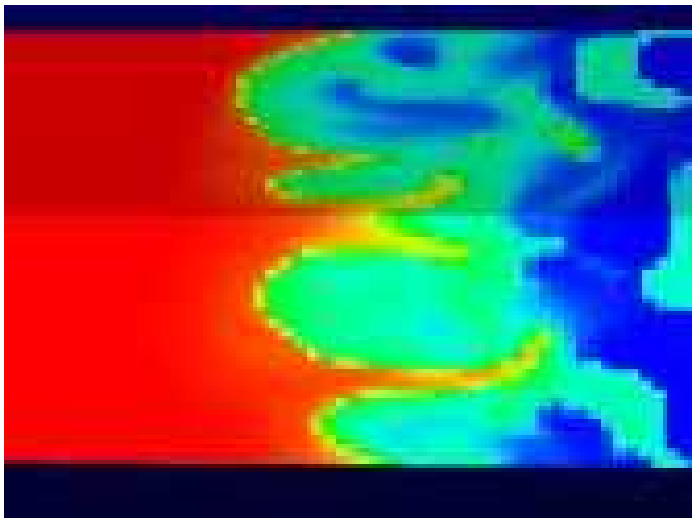
- Low temperature experiments diamond anvil cell < a few kK
- High temperature plasma physics where degeneracies are negligible

- Rick Kraus, “Thermodynamic Paths in Planetary Collisions: Shock Vaporization of SiO2, MgO, and Fe,” Monday, July 8 at 8:00 AM

- Marcus Knudson, “Probing planetary interiors: Shock compression of water to 700

Hydrocodes, Materials, and Mixtures

- High-fidelity hydrodynamics simulations to solve solid dynamics problems
- Require high fidelity equation of state (EOS) models to describe the response of materials to external stimuli e.g. P[ρ,T]
- Materials can mix.
- Dynamic mixing can occur for example through Rayleigh Taylor instabilities.
- For practical reasons, a rule must be used to combine EOS models of pure materials to EOS of mixtures.

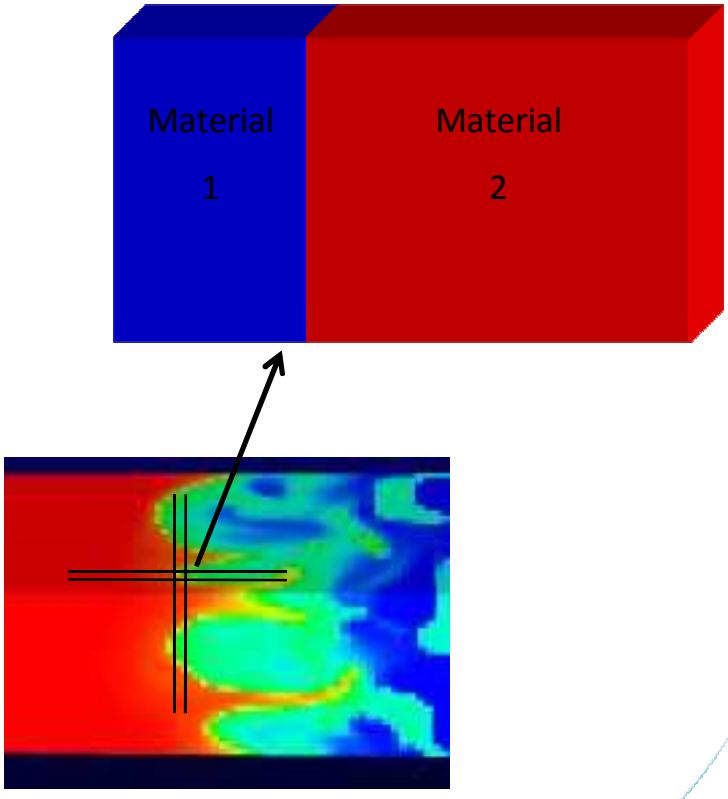


Tom Haill
Al Liner impacting on foam

Curious Physics of Mixtures

- Homogenous mixtures of materials often behave quite differently from what one might expect from studying the pure constituents.
- Examples: impurities in materials, enthalpy of mixing, reactive materials, and so forth
- Bond breaking and forming will vary with mixture composition, temperature, and pressure
- ***Most mixing rules use information about pure materials to interpolate mixture properties.***

A cell in a hydro simulations with two materials “mixed cell”



Problem of Mixing EOS Models

- How do we combine EOS models that are designed for pure materials to describe mix cells?
- Complex physics/chemistry of mixing

1. Classical mixing – pure material largely separate but occupy ever smaller contiguous volumes elements
2. Atomic mix – homogenous at length scales larger than the molecular scale
3. Surface effects
4. Chemistry - covalent, van der Waals, Hydrogen, and dipole bonding
5. Entropic effects – heat of mixing

Classical Mixing Rules for Binary Mixtures Developed for Nineteenth Century Engineering Problems

$$x = \frac{\rho_L}{\rho_L + \rho_H} = \frac{\rho_L}{\rho}$$

- **Ideal (Ideal gas law astrophysics)**

$$P = x P_L\left[\rho, T\right] + \left(1 - x\right) P_H\left[\rho, T\right]$$

- **Volume (Dalton's law 1801 related to cell approaches)**

$$P = P_L\left[x\rho, T\right] + P_H\left[\left(1 - x\right)\rho, T\right]$$

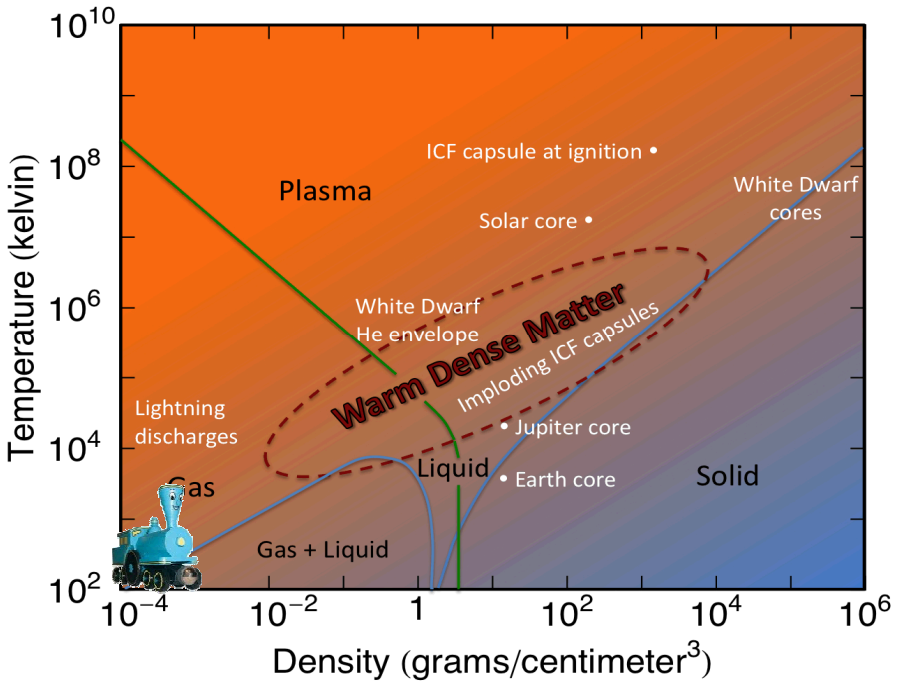
- **Pressure (Amagat's 1880 law of partial volumes some hydro-codes)**

$$P_{MIX} = P_L\left[\tilde{\rho}_L, T\right] = P_H\left[\tilde{\rho}_H, T\right], \quad x/\tilde{\rho}_L + (1-x)/\tilde{\rho}_H = 1/\rho,$$

$$f_L \tilde{\rho}_L = \rho_L, \quad f_H \tilde{\rho}_H = \rho_H$$

- **Relates total pressure of the mixture to equation of state models of the pure states**

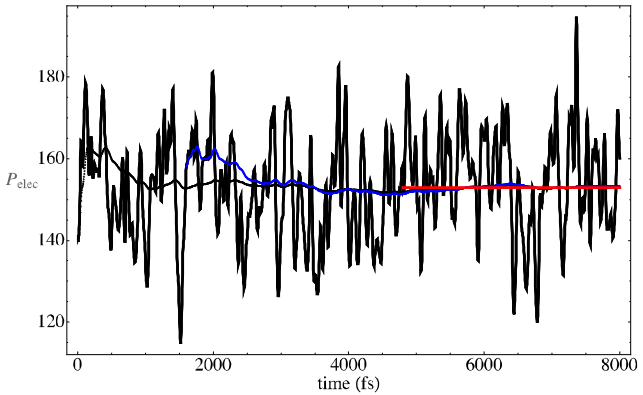
Combining High Fidelity Calculations and Experiments under Warm Dense Matter Conditions



- Warm dense matter regime multi : Mbar, kK.
- Can we efficiently describe the equations of state for a mixture of well-characterized materials?
- What are the limitations of this approach?

First Principles Thermodynamics

- First principles approach to simulations of total energies, pressures, and other physical quantities
- Homogenous (on length scales larger than the molecular scale) materials in the sweet spot for EOS properties of “pure” materials
- Unbiased as to elemental species
- Can be applied to atomic mix situations



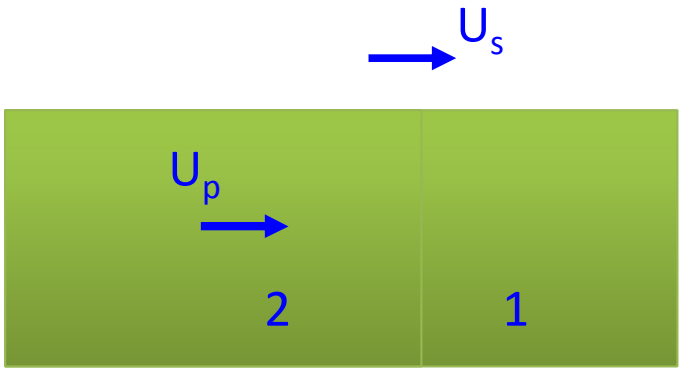
Molecular dynamics (MD) simulations give thermo-physical properties

b-initio VASP ackage ienna imulation

- **First-principles simulations using DFT**
  - **VASP – plane-wave code with PAW core-functions**
  - **Great care in convergence**
    - *A. E. Mattsson et. al. Modelling and Simulation in Material Science and Engineering **13**, R1 (2005)*
  - **Importance of exchange-correlation functional**
    - *A. E. Mattsson et al. JCP **128**, 084714 (2008)*

Validation of the Simulations

- Compare simulation results to Z-data
- Convenient –especially in the warm dense matter regime – connection through the Hugoniot
- Example successes Xe and Ethane
- Note the dissociation of the latter



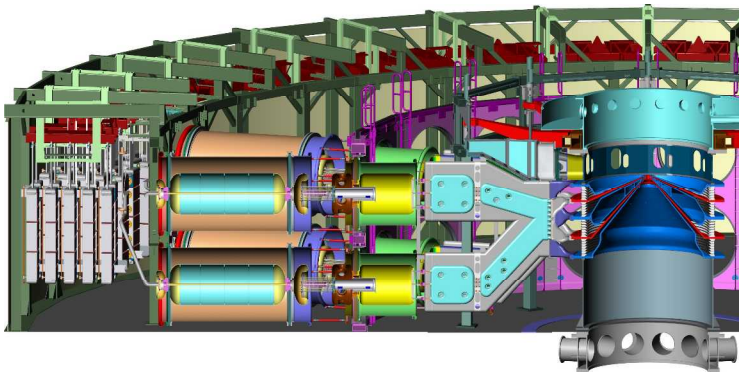
- *Conservation of mass, energy, and momentum* lead to the **Rankine-Hugoniot condition** for the initial (1) and final state (2).
  - E - internal energy
  - P - pressure
  - v – specific volume

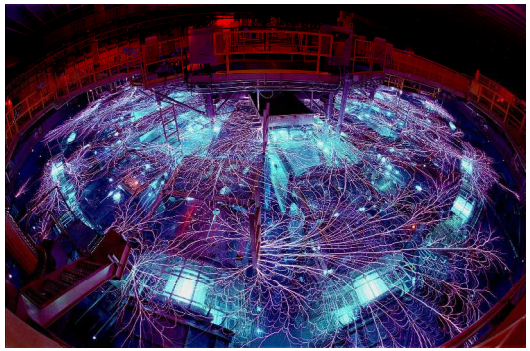
$$2(E_2 - E_1) = (P_2 + P_1)(\upsilon_1 - \upsilon_2)$$

- *High accuracy measurement and/ or calculations of thermo-physical properties* can be compared to validate understanding.

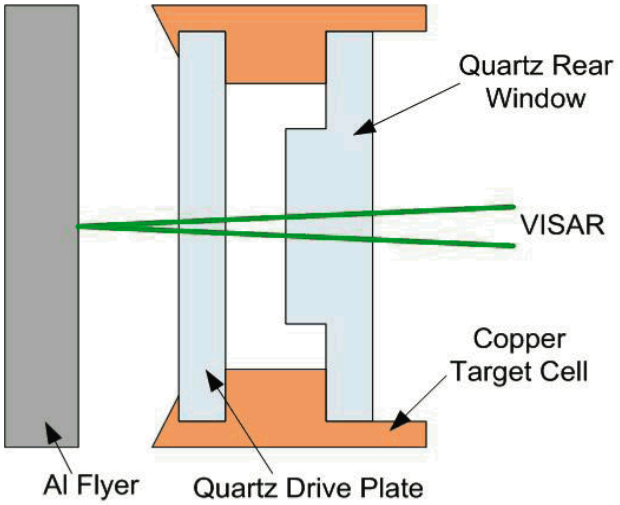
The Z-Machine

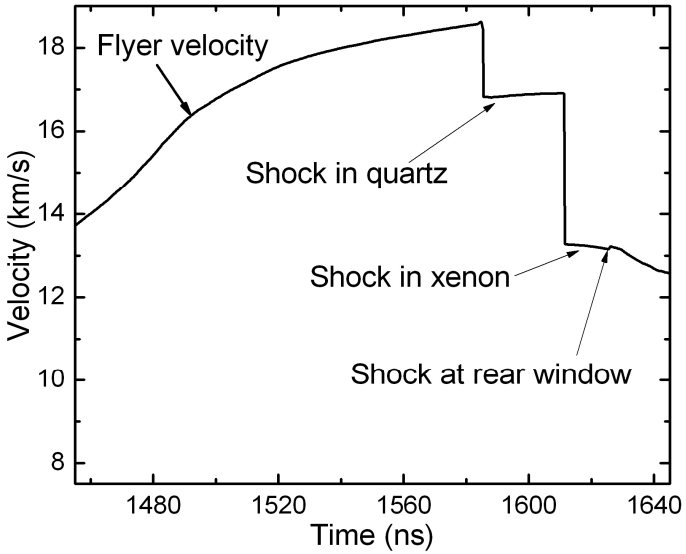
- The world's most powerful pulsed power machine
- Accelerates aluminum flyer plates to 40 km/sec.
- Delivers 27 MegaAmps in 95 nanoseconds.
- Achieves Pressures greater than 10 Mbar (1 TPa).
- Recent work on Xenon reached a state 840 GPa and 149kK
- Compare to diamond Anvil cell – up to 300 GPa and several kK





We Measure Shock Velocities in Materials with Sub-Percent Accuracy





Precision Accuracy and Reproducibility

VISAR main diagnostics

- Flyer velocity, time of impact
- Arrival at interfaces and breakout
- Shock velocity in samples

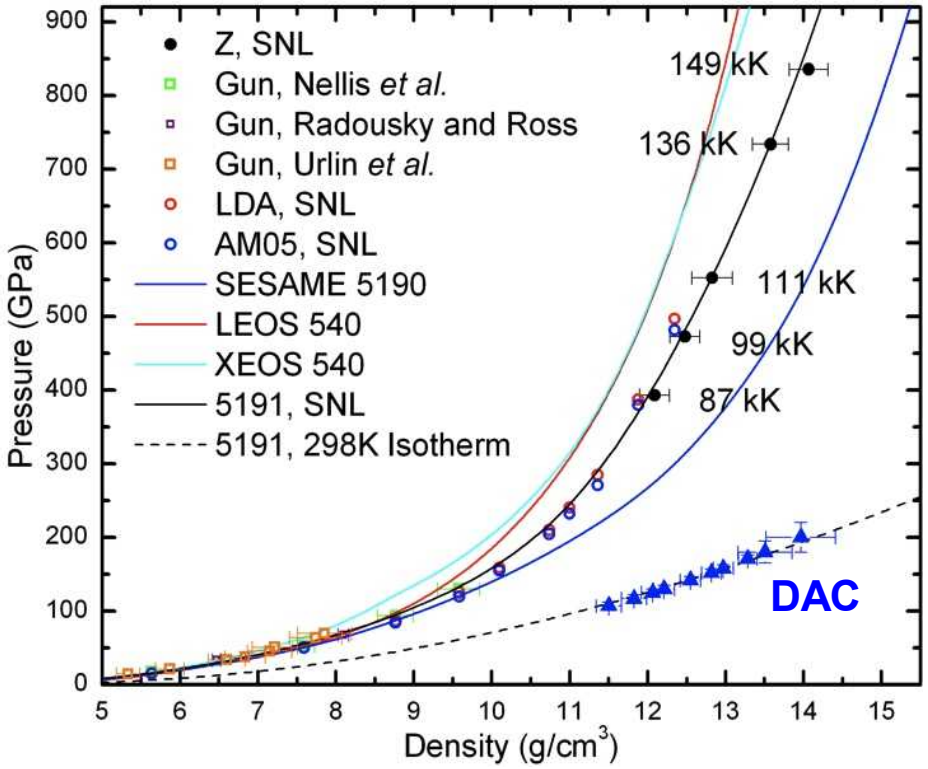
Monte-Carlo error analysis

- Accuracy of shock standards
- Correlation among parameters
- Error propagation

VISAR trace from a xenon experiment with 18.5 km/s impact velocity

Sandia National Laboratories

Experiments on Sandia's Z Machine Obtained High-Precision Data for Xenon to 840 GPa/ 14 g/cm^3



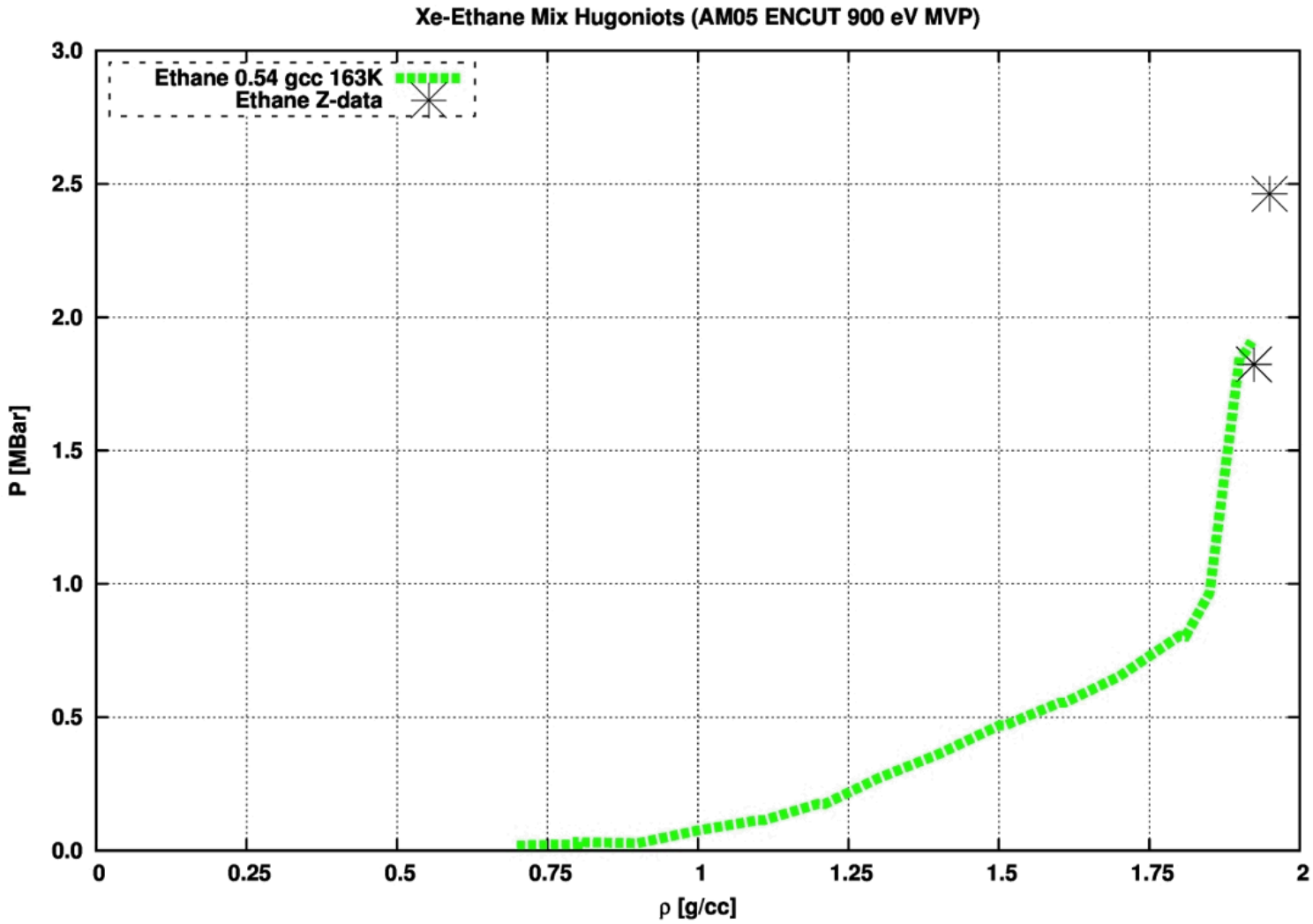
Neither LEOS 540 nor SESAME 5190 captures the behavior of xenon above 100 GPa

Demonstrated the need for validating EOS tables to enable high-fidelity simulations

We developed a new multi-phase wide-range EOS table: 5191 in the LANL database

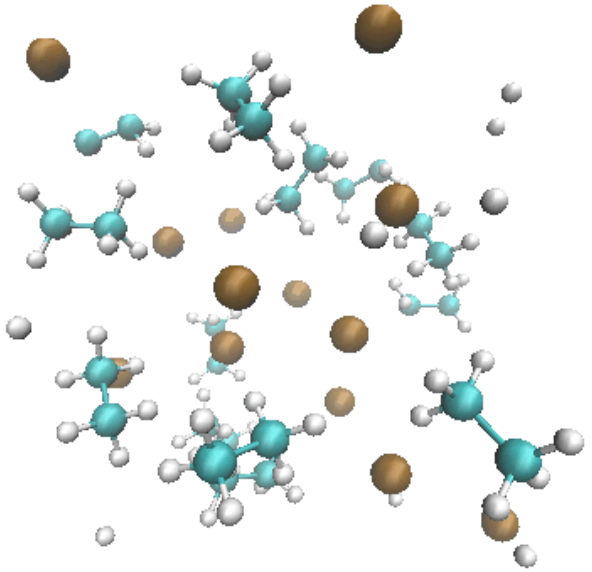
Seth Root et al Phys. Rev. Lett. **105**, 085501 (2010)

Ethane Hugoniot Provides Insight into Shock Dissociation



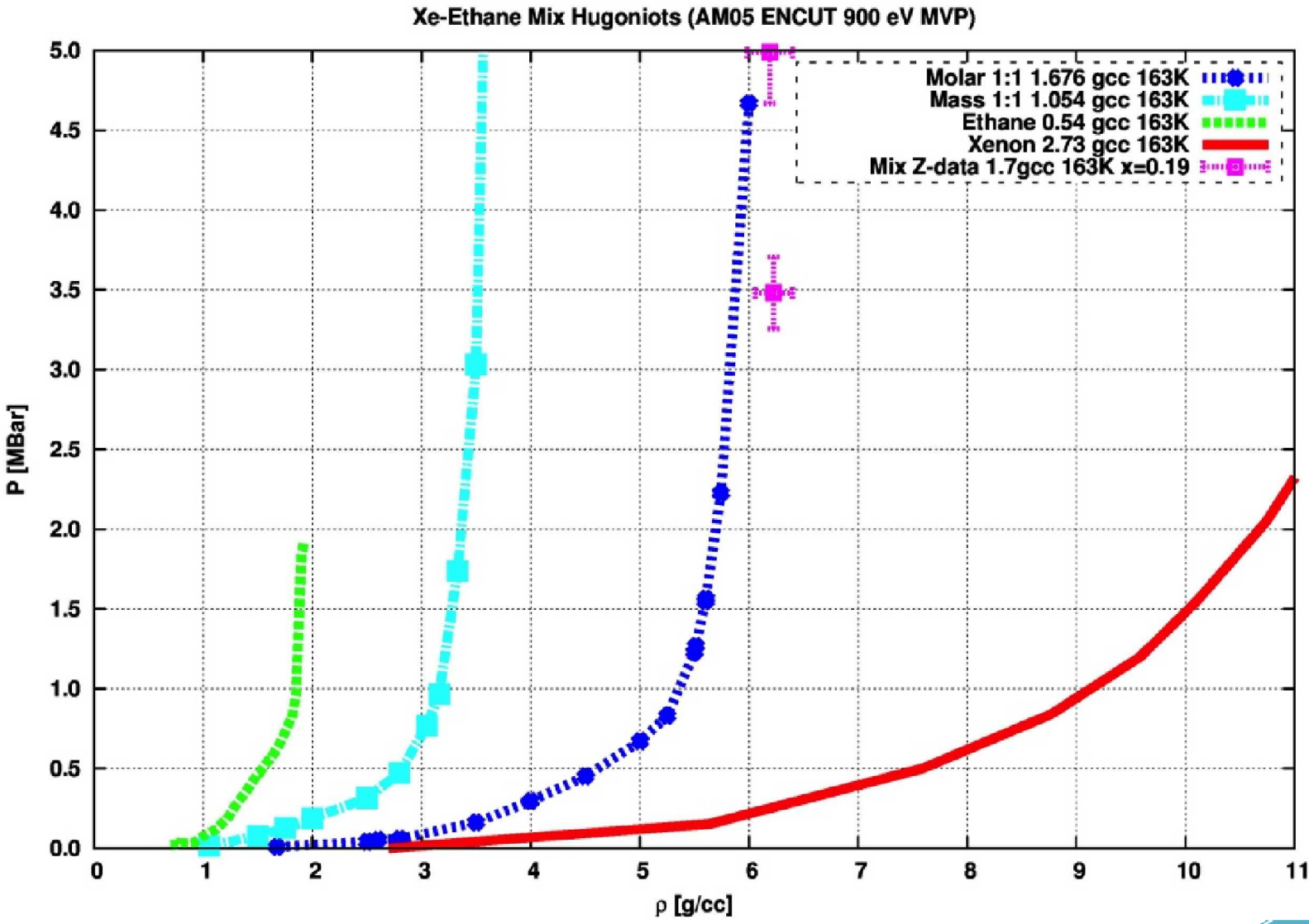
Xe-Ethane (C_2H_6) Mix Hugoniot Reference State

- T=163.5 K
- Rho=1.5 and 1.7 gcc
- P=16.8 psi
- Molar mix ratios 42% and 50%
- Mass mix 5 Xe:18 Ethane (159 atoms per simulation) x=0.5
- Molar mix 13 Xe:13 Ethane (117 atoms per simulation) x=0.19
- Plane-wave energy cut off 900 eV
- Time steps 0.8-0.04 fs
- 8000 time steps
- Mean value point
- AM05 exchange-correlation results shown



$$x = \frac{Ethane\ mass}{Xenon\ and\ Ethane\ mass}$$

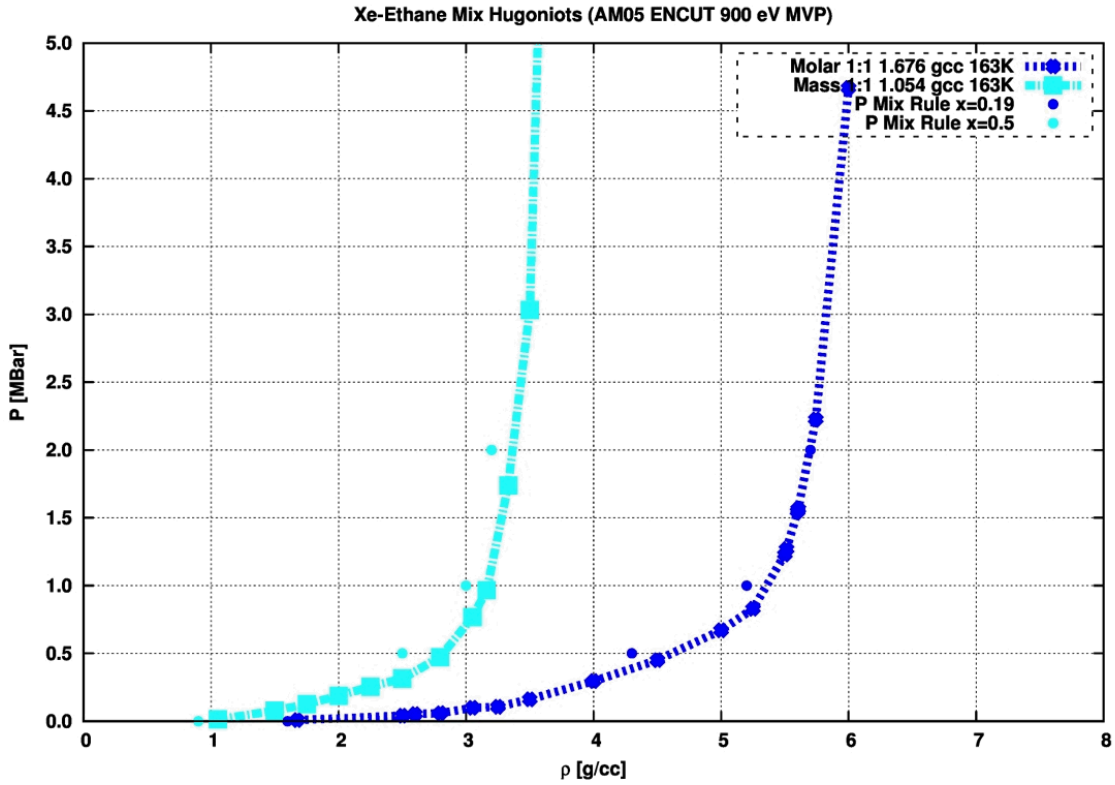
Xe-Ethane Mix Hugoniot



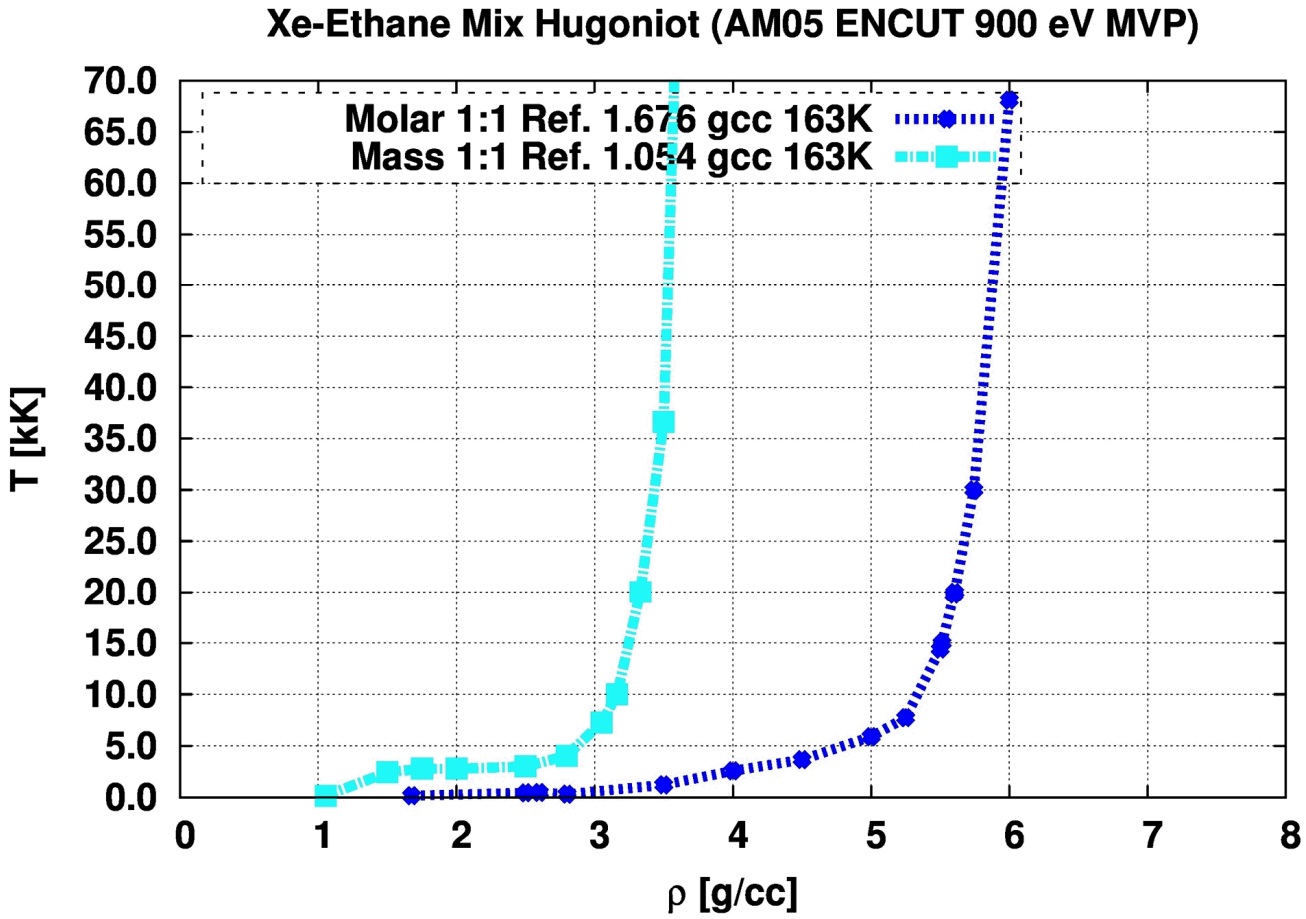
Xe-Ethane Mix Hugoniot

Approximate P rule Hugoniot

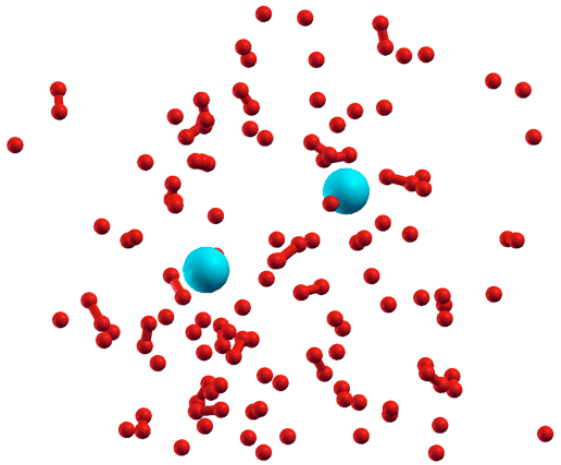
- Choose P and use pure material EOSs to determine species densities
- Find ρ_{tot} using density portion of Amagat's rule
- Note the approximation that no special treatment of the reference state is assumed



Temperature Along the Xe-Ethane Hugoniot



Mixing Ratio for Binary Mixtures



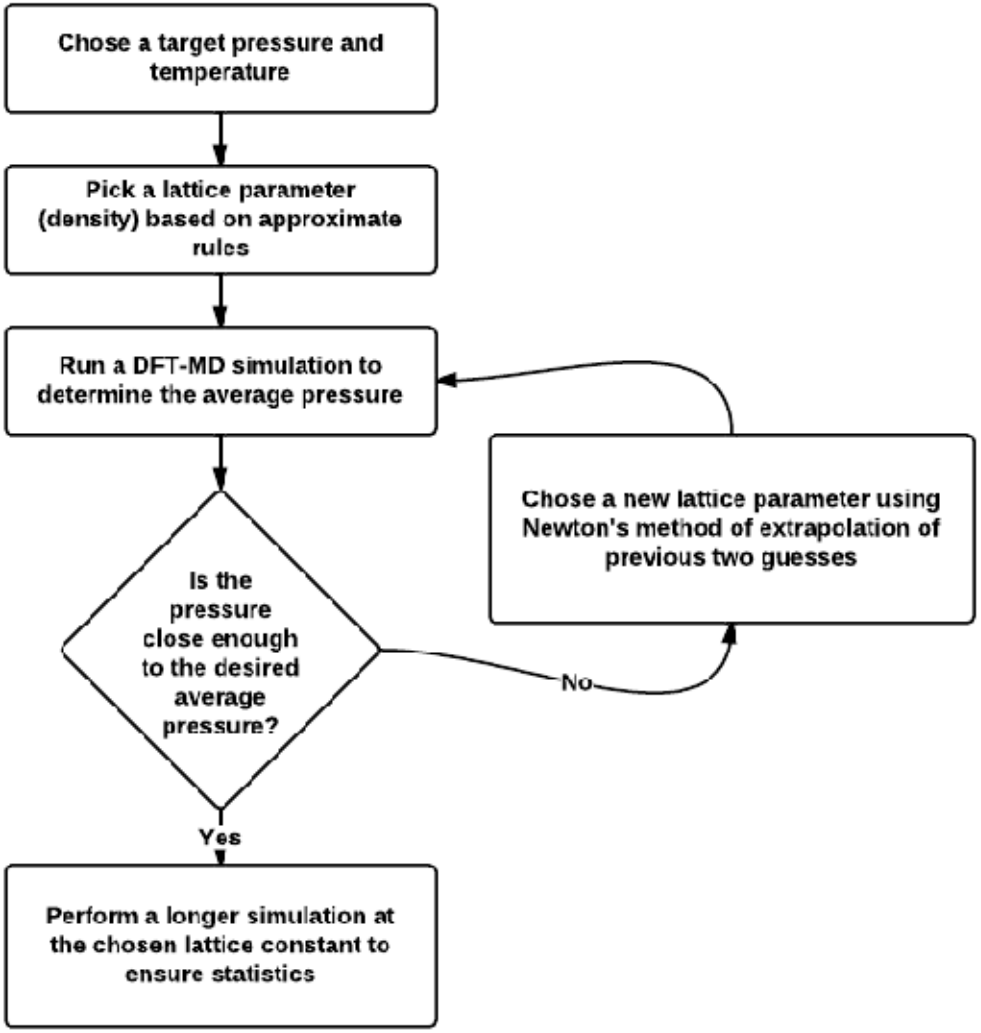
High Z- low Z mixture used in gas puff experiments
Difficult to mix experimentally

$$x = \frac{Deuterium\ mass}{Xenon\ and\ Deuterium\ mass}$$

Mix Ratio	# of Xe Atoms / Cell	# of D Atoms / Cell
0.0	32	0
0.3	3	84
0.5	2	132
0.67	1	132
1.0	0	200

Note: Deuterium mass / Xenon mass ≈ 0.015
According to the ideal gas law: P is proportional to n the number density
To achieve similar pressures the mass densities are related $\rho_{Xe} \approx 100\ \rho_D$

Constant Pressure Calculations Implementation at First Principles Simulations



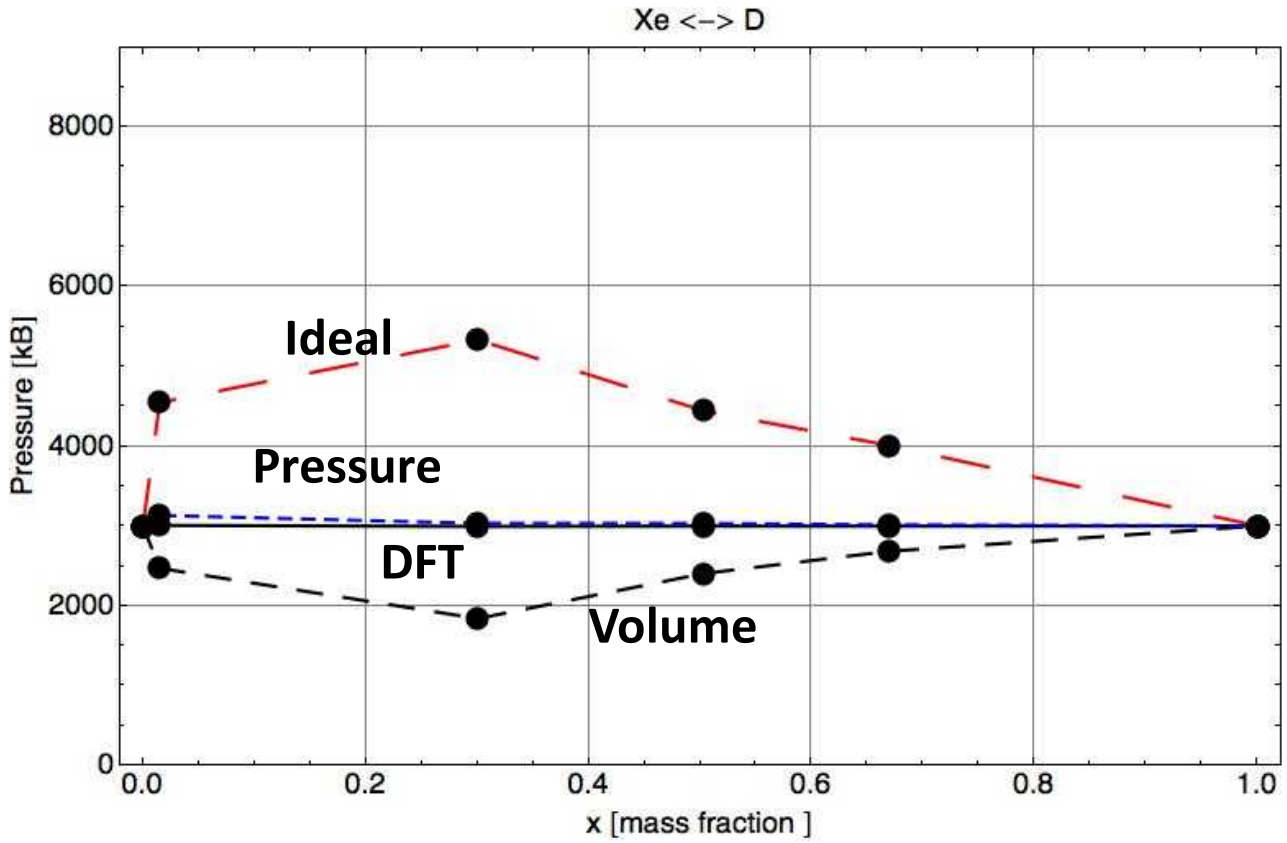
Scaling of the EOS Models

- Fix the pressure and energy of the pure material EOS models to match the DFT-MD results
- Facilitate comparison of mixing rule models
- Small differences but must be removed to focus on mixing

$$P_{Scaled}[\rho, T] = \frac{P_{DFTMD}[\rho_{DFTMD}, T]}{P[\rho_{DFTMD}, T]} P[\rho, T]$$

$$E_{Scaled}[\rho, T] = \frac{P_{DFTMD}[\rho_{DFTMD}, T]}{P[\rho_{DFTMD}, T]} E[\rho, T] - \frac{P_{DFTMD}[\rho_{DFTMD}, T]}{P[\rho_{DFTMD}, T]} E[\rho_{DFTMD}, T] + E[\rho_{DFTMD}, T]$$

Xe-D with fixed pressure: DFT/AM05, SESAME 5365 for D

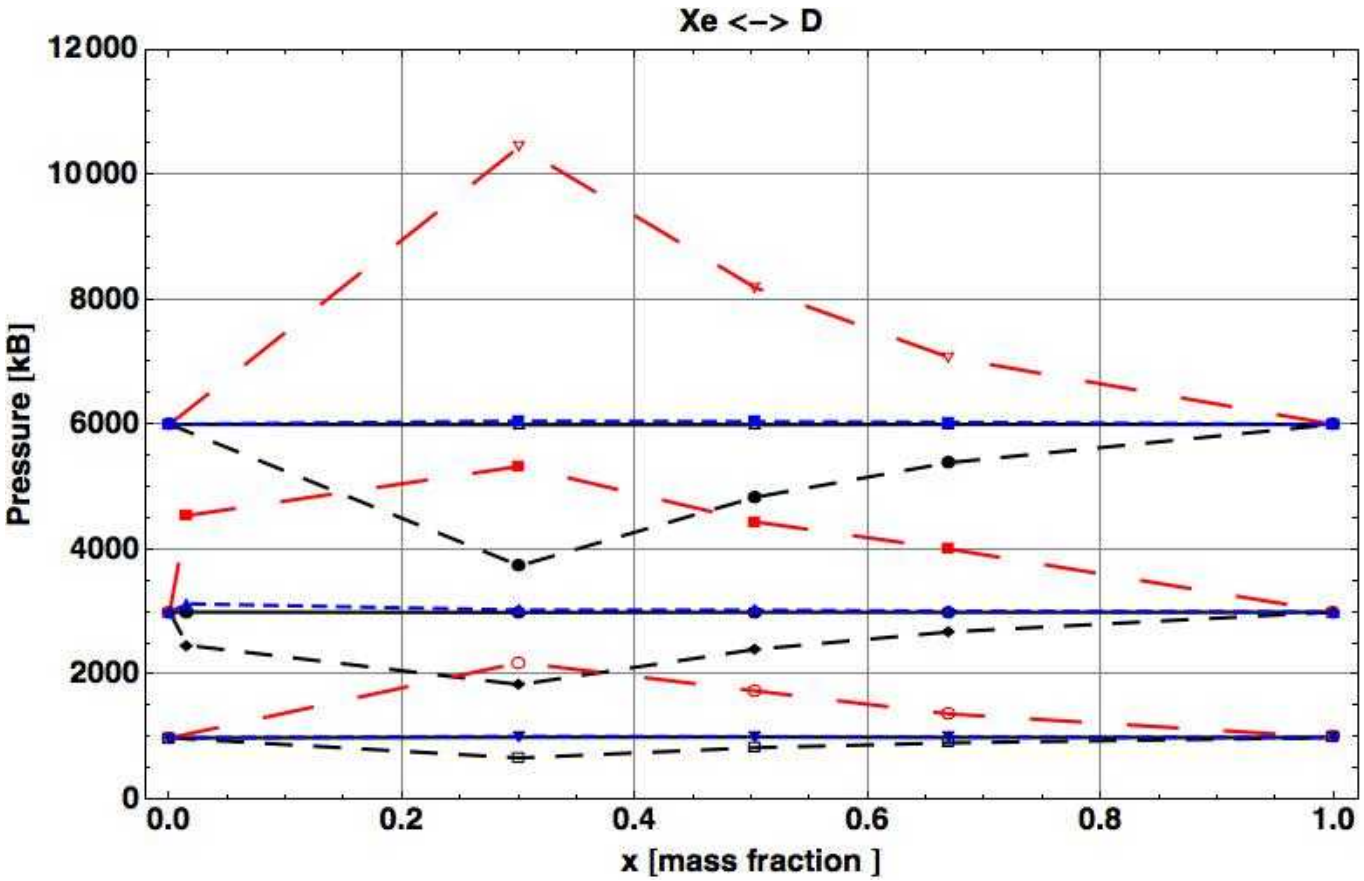


- **T = 10 kK**

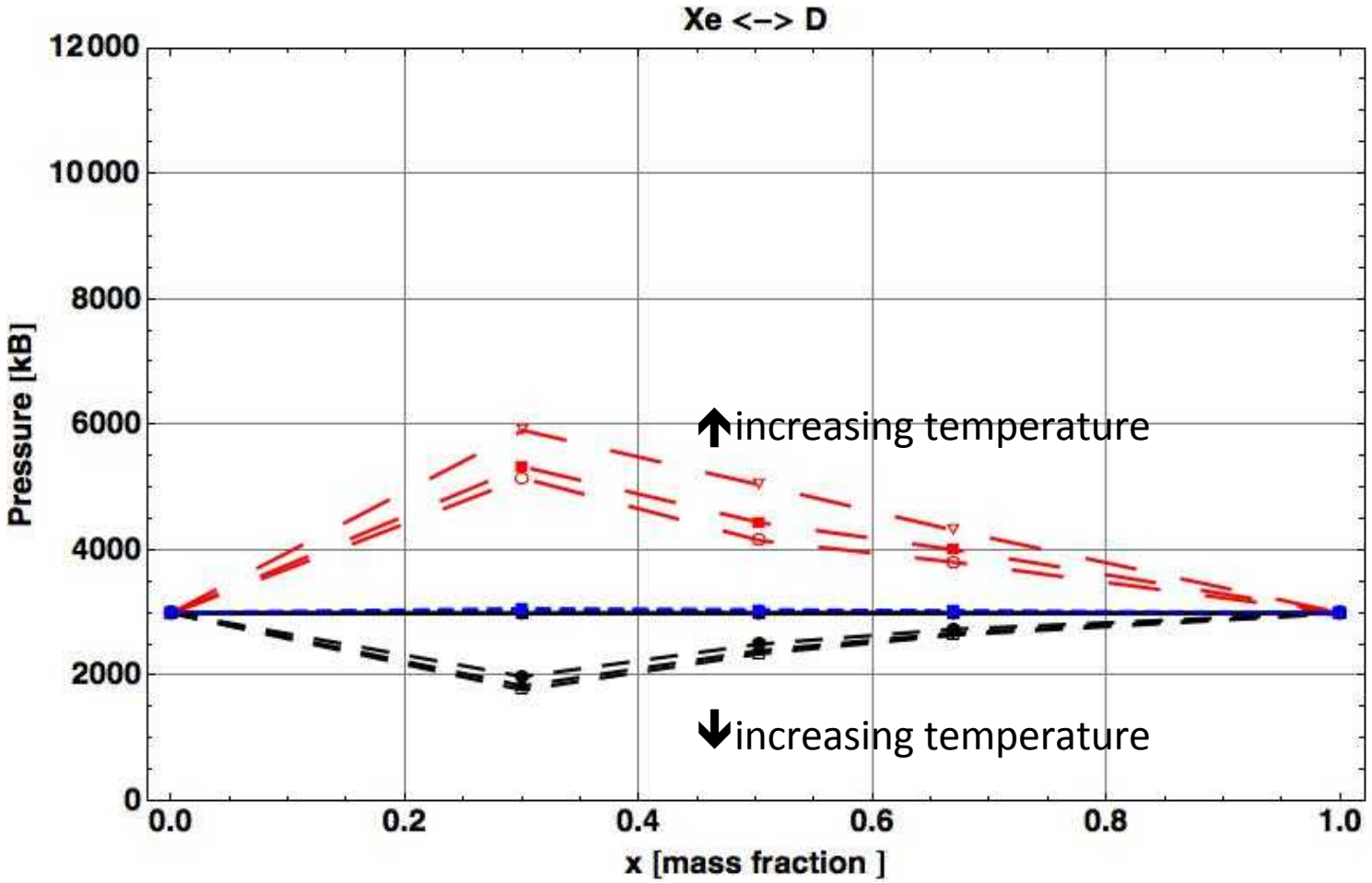
Pressure: blue short-dashed
Ideal: red long-dashed
DFT: solid black
Volume: black medium-dashed
ρ_{Xe}= 15.9 g/cc

Magyar and Mattsson, Phys. Plasmas **20**, 032701 (2013)
Notes: Ideal mixing rule is clearly flawed especially for small x.
Volume mixing predicts lower pressures than DFT-MD.

Pressure Mixing Rule Remains Robust Over a Wide Range of Pressures



Temperature Variation Has Only Limited Effects



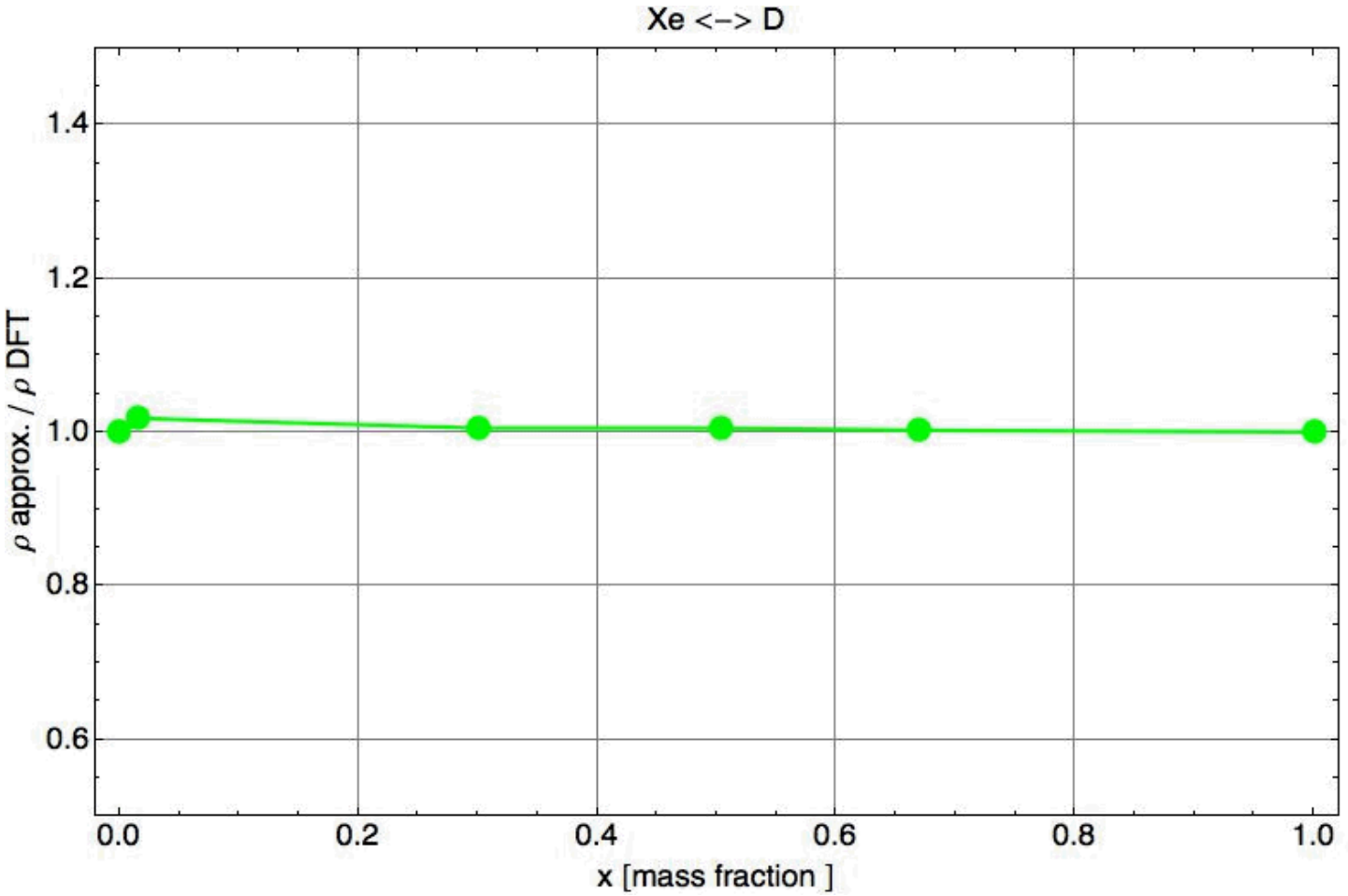
How Good Is the Scaled EOS Approximation?

$$Eq.1. \quad P_L\left[\tilde{\rho}_L, T\right] = P_H\left[\tilde{\rho}_H, T\right]$$

$$Eq.2. \quad x/\tilde{\rho}_L + (1-x)/\tilde{\rho}_H = 1/\rho$$

1. Use Eq. 1 with DFT-MD values for P_L and P_H to find ρ_L and ρ_H.
2. x and ρ are determined by the DFT-MD simulations
3. Does the left hand side of Eq. 2 equal the right hand side?

DFT Mixtures Compared to Amagat's Rule within DFT Only



The energy mixing rules

- **Ideal**

$$E = x\,E_D\left[\rho, T\right] + \left(1-x\right)E_{Xe}\left[\rho, T\right]$$

- **Volume**

$$E = E_D\left[x\rho, T\right] + E_{Xe}\left[\left(1-x\right)\rho, T\right]$$

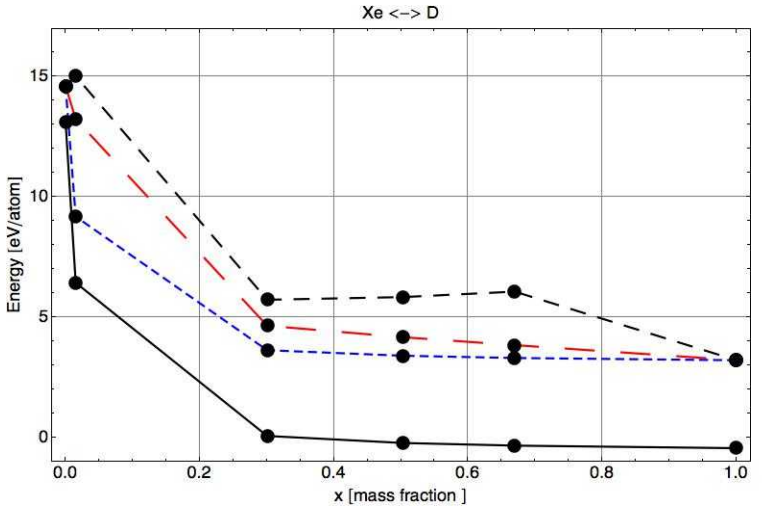
- **Pressure**

$$E_{mix} = y(x)E_D\left[\tilde{\rho}_D, T\right] + \left(1-y(x)\right)E_{Xe}\left[\tilde{\rho}_D, T\right],$$

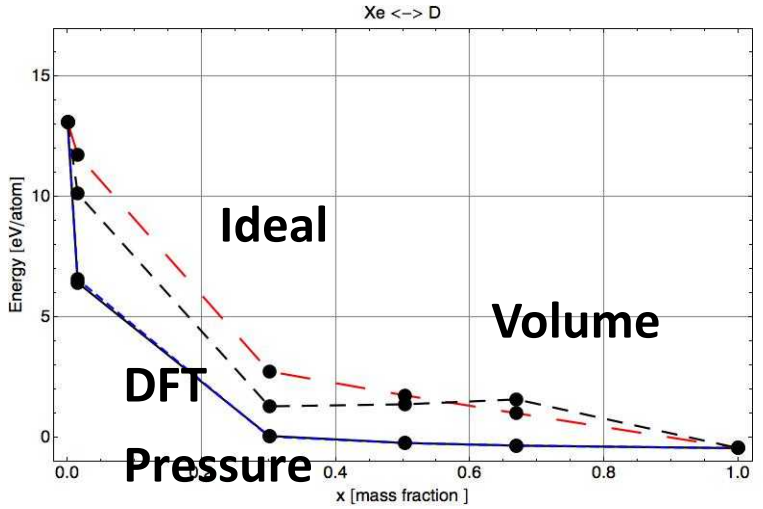
$$P_D\left[\tilde{\rho}_D, T\right] = P_{Xe}\left[\tilde{\rho}_{Xe}, T\right], \quad x/\tilde{\rho}_D + (1-x)/\tilde{\rho}_{Xe} = 1/\rho$$

The Energy Predicted Using Mixing Rule

Energy Mixing Models with Raw EOS Tables



Energy Mixing Models with Scaled EOS Tables



- The total energy is related to heat capacity.
- Limited inter-species chemistry
- Uncertainties in the EOS coupled with model mixing rules can give qualitatively different behaviors.

Summary and Conclusions

- DFT based MD simulations to model shock compression of mixtures under WDM conditions
- Experimental validation through shots on the Z-machine
- Amagat's rule is extremely accurate for High-Z / Low-Z materials when limited interspecies chemistry is likely to occur
- Magyar and Mattsson, Phys. Plasmas 20, 032701 (2013)
- Mixing models based off pressure equilibration for other material's properties are expected to be accurate.

Thank You

- The Z team
- Thomas Mattsson
- Dawn Flicker
- Seth Root
- Programmatic leadership
- The Cryogenic Team – D. L. Hanson
- Sandia High-Performing Computing (HPC) – S. Corwell
- SCCM AIRAPT
- And you for listening

Sandia National Laboratories

National Nuclear Security Administration

APS-SCCM & AIRAPT-24 JOINT CONFERENCE
July 7-12, 2013 in Seattle, Washington