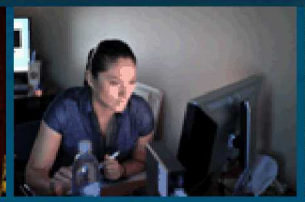
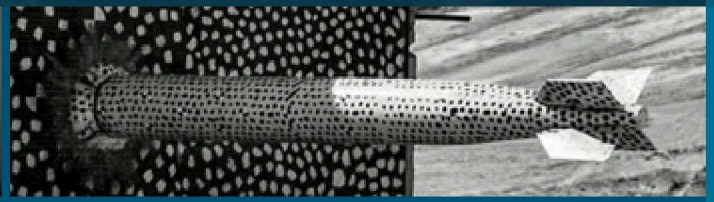
This paper describes objective technical results and analysis. Any subjective views or opinions that might be expressed in the paper do not necessarily represent the views of the U.S. Department of Energy or the United States Government.

SAND2019-13081C

Shock compression of hydrocarbons to Mbar pressures: successes, challenges, and lessons learned





Kyle Cochrane, Patricia Kalita, Tom Ao, Seth Root, John Kaushagen, Keith Jones, Rudy Magyar, Thomas Mattsson, and Michael P. Desjarlais

Sandia National Laboratories,

Albuquerque, NM

Unclassified Unlimited Release

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Which EOS should I use: Either or Neither

Mie Gruneisen

Sesame 7171

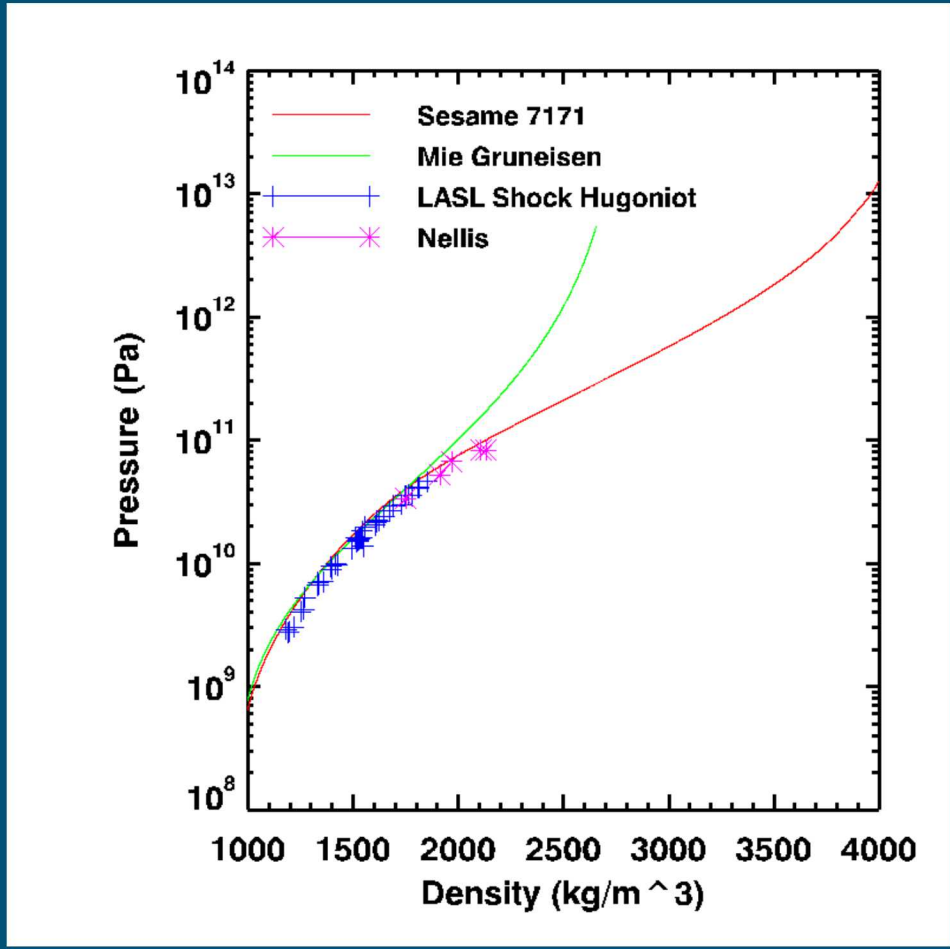
Tuned to gas gun data

Extrapolate to higher pressure correctly?

DFT to confirm EOS if no experimental data

DFT to guide building new EOS

Polyethylene Hugoniots



Create polyethylene strands and use density functional theory (DFT) calculations to simulate

First-principles simulations DFT

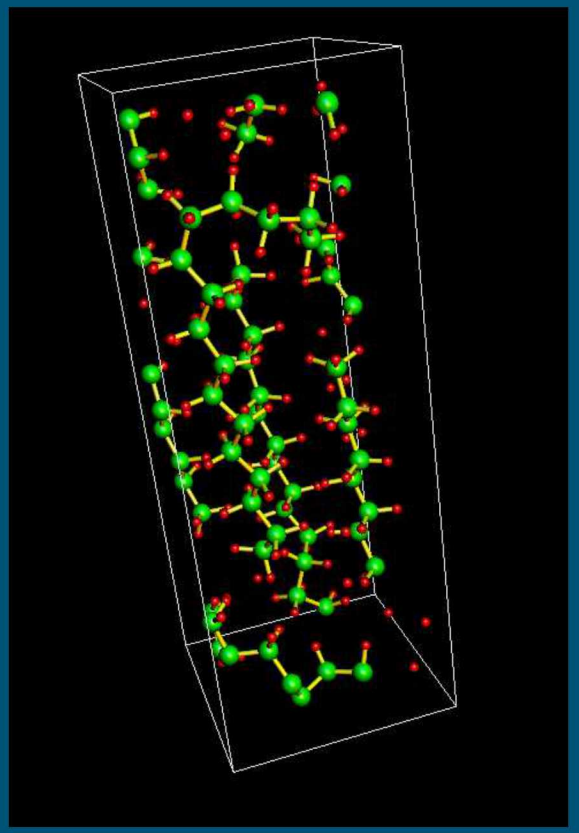
- VASP – plane-wave code w PAW core-functions
- Use of DFT codes simulating warm dense matter
  - M. P. Desjarlais Phys. Rev. B **68**, 064204(2003)
- Great care in convergence
  - A. E. Mattsson et. al. Modelling and Simulation in Material Science and Engineering **13**, R1 (2005)

Assemble reference system

- 4 strands of polyethylene (200 atoms) of $C_{16}H_{34}$
- Ends capped to prevent cross bonding
- Equilibrate at constant temperature and volume.
- Equilibrated for 3000+fs at 0.1 to 0.2 fs
- AM05 potential
- Block averaged Standard deviation of energy and pressure <1%

Lessons Learned:

- Ends capped with H to prevent cross bonding
- Very difficult to continue chains across periodic BC
- 16 atom strands adequate to represent much longer chains



Quantum molecular dynamics (QMD) simulations give thermo-physical properties

DFT simulations are validated with high-precision experimental data

Erpenbeck Hugoniot

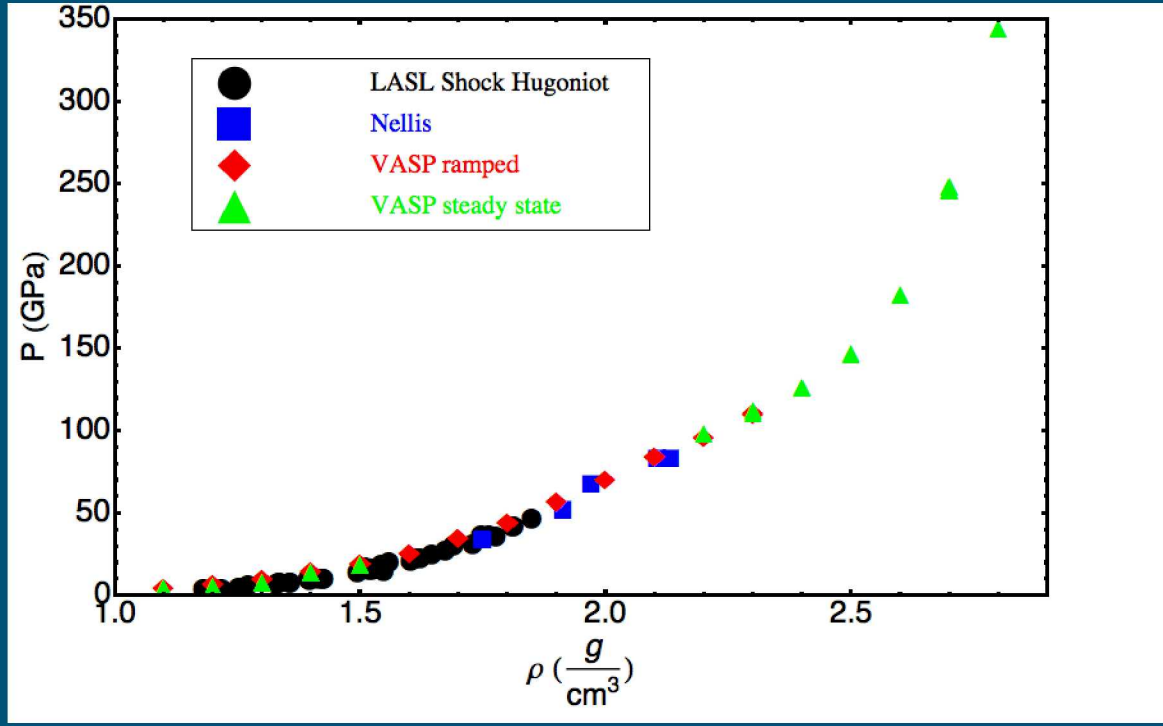
- Lesson Learned: cannot extrapolate/interpolate far in temperature before approximation becomes invalid
- The above stipulation reduces as material approaches ideal gas

Ramped Simulation

- Lesson learned: Ramp temperature slowly enough to approximate constant T

Experimental data into the dissociation regime

Polyethylene Hugoniot



Physical Review B, Vol. 81, No. 5. (Feb 2010)

High fidelity release isentropes for simulations where behavior under release is important.

Calculating Hugoniot and quasi-isentropes

$$2(E_2 - E_1) = (P_2 + P_1)(V_1 - V_2)$$

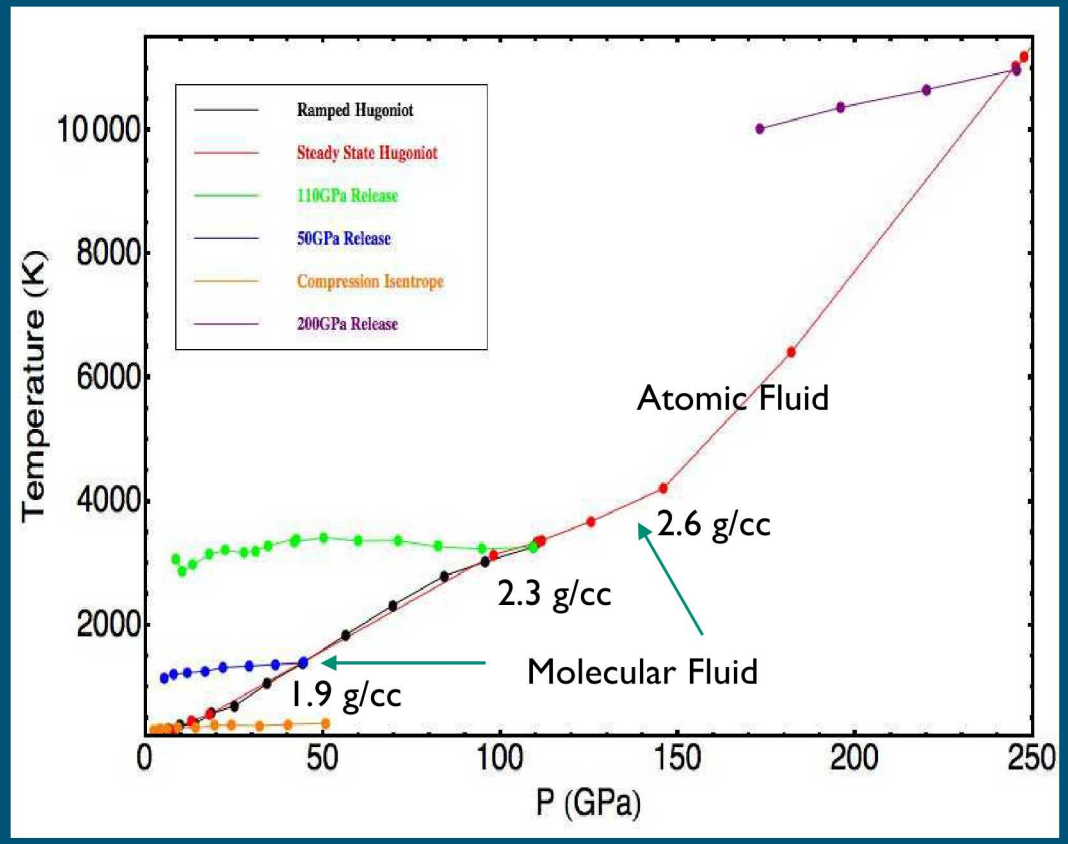
Dissociation Shoulder (more visible in P/T space)

Exothermic from molecular liquid?

Isentropic from atomic fluid

Molecular fluid from ~1.9 g/cc to ~2.5 g/cc

Simulated Hugoniot and quasi-Isentropes

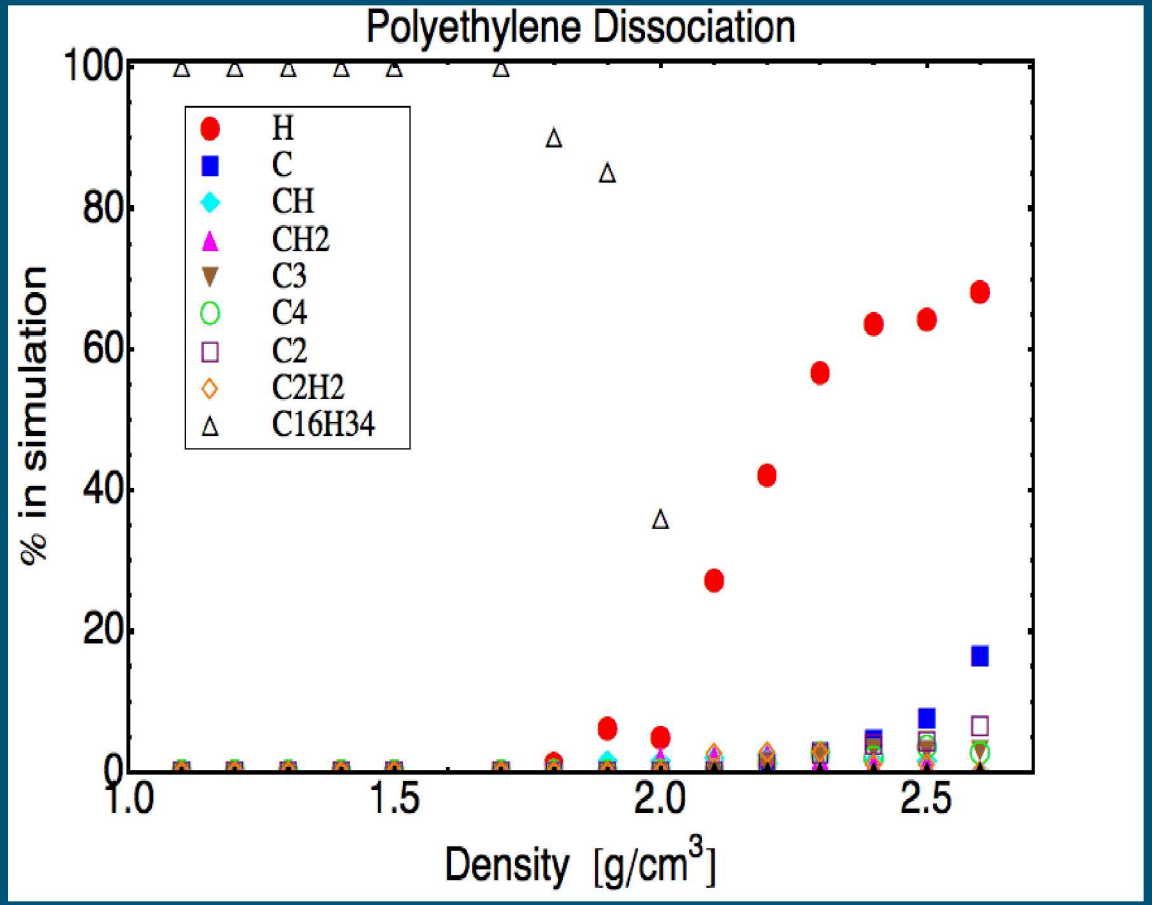


Confirm shoulder in Hugoniot is from dissociation or melt by tracking "bonds"

Set bond lengths
- Found in reference simulation
- If using experimental data, add 5% to 10% for atom vibration
- First minimum of g(r)

Atoms stay within bond distance for Δt (5 carbon vibrations ~90fs)

Lesson Learned:
- Simulation still needs to run long enough for atoms to move apart if not bonded
- Dissociating fluid species are transient



Challenges and Advances in Computational Chemistry and Physics Vol 28, Ed. Goldman, Chapter 1: Simulations of Hydrocarbon Polymers Related to Compression Experiments on Sandia's Z Machine

The thermal component of the EOS is a parameterization of DFT calculated internal energies as a function of temperature

Hydrostatic compression of 300 K isotherm to approximate cold curve

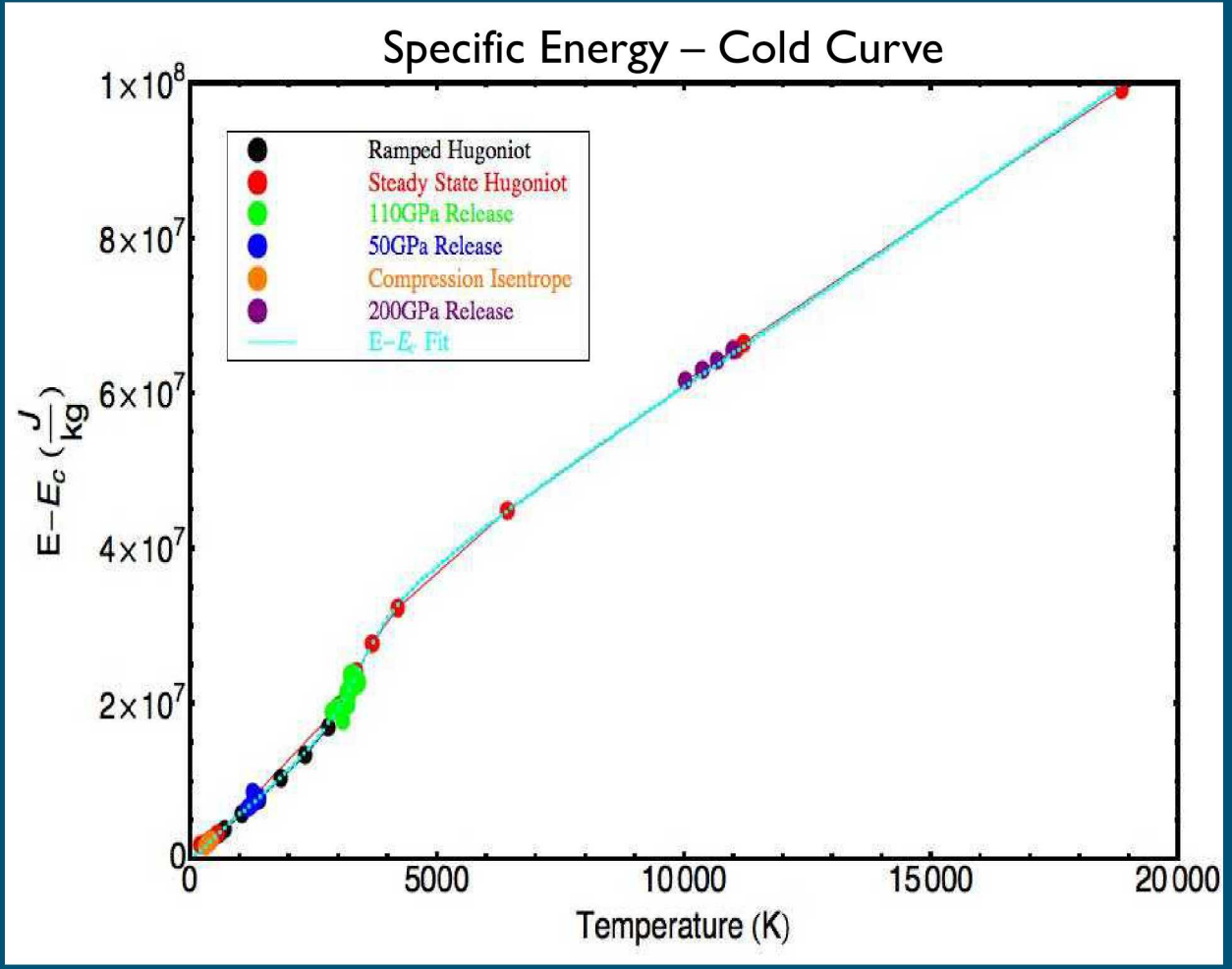
- Lesson Learned: must increase density by a small margin (0.1 g/cc? bigger?)
- Equilibrate for a few hundred fs to not over compress bonds and explode material

Birch Muraghan fit to isotherm and called cold curve

Fit to energy

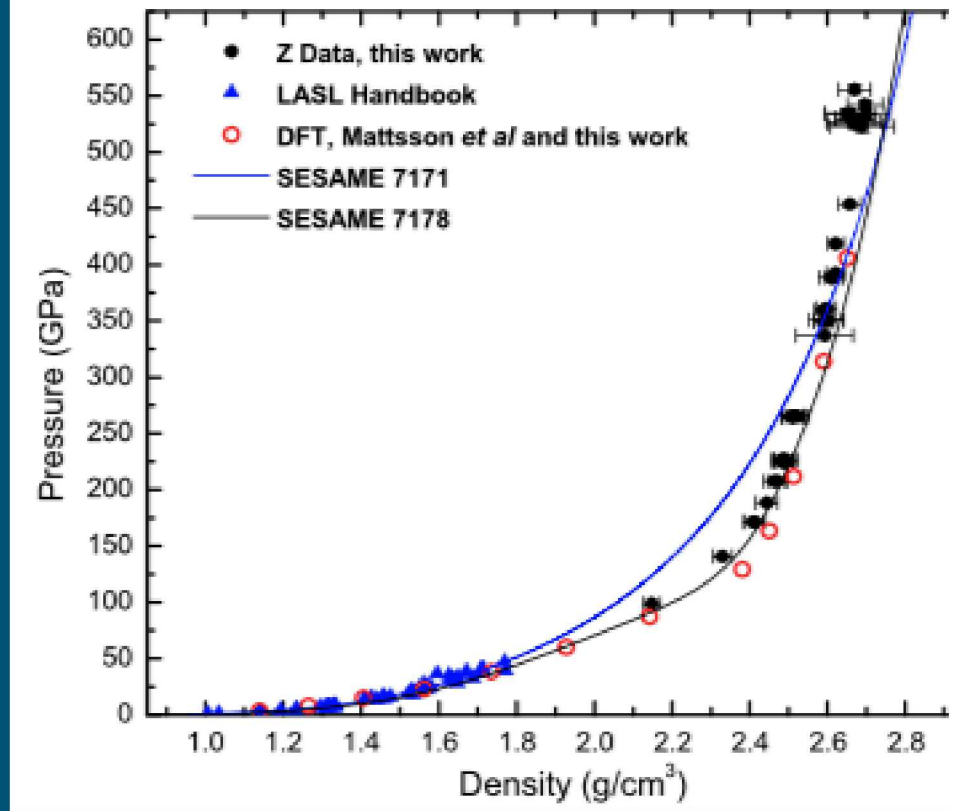
- Energy – E_c is only a function of T
- Temperature based curve fit to energy E[T] gives thermal part of EOS

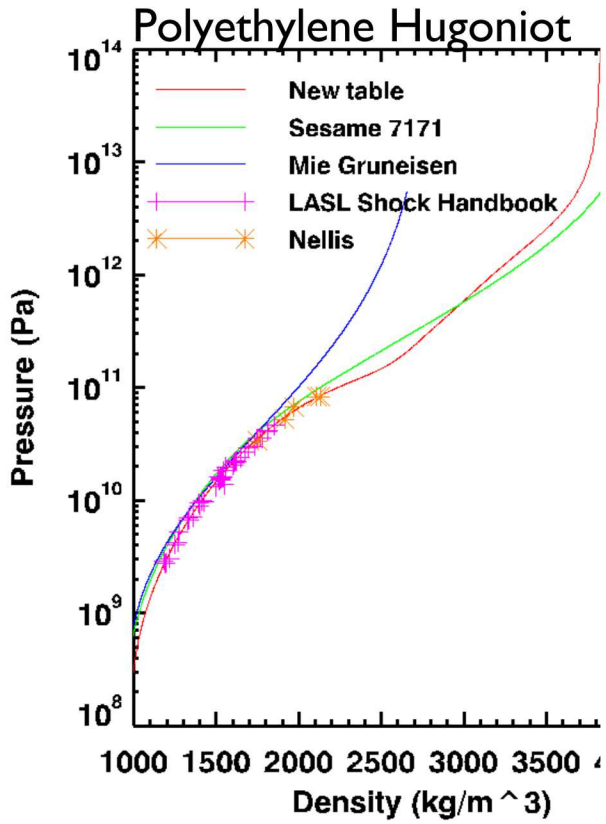
- $E[\rho,T] = E[T]+Ec[\rho]$ spans most of energy space

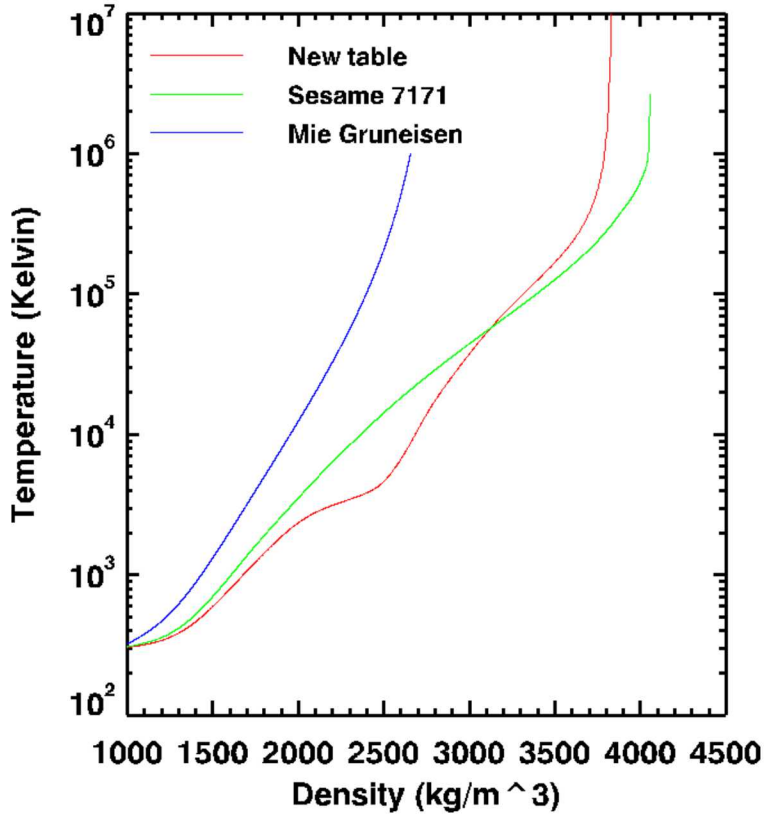


There are key differences in behavior between the new EOS and existing models

Poly (4-methyl-1 pentene) Hugoniot





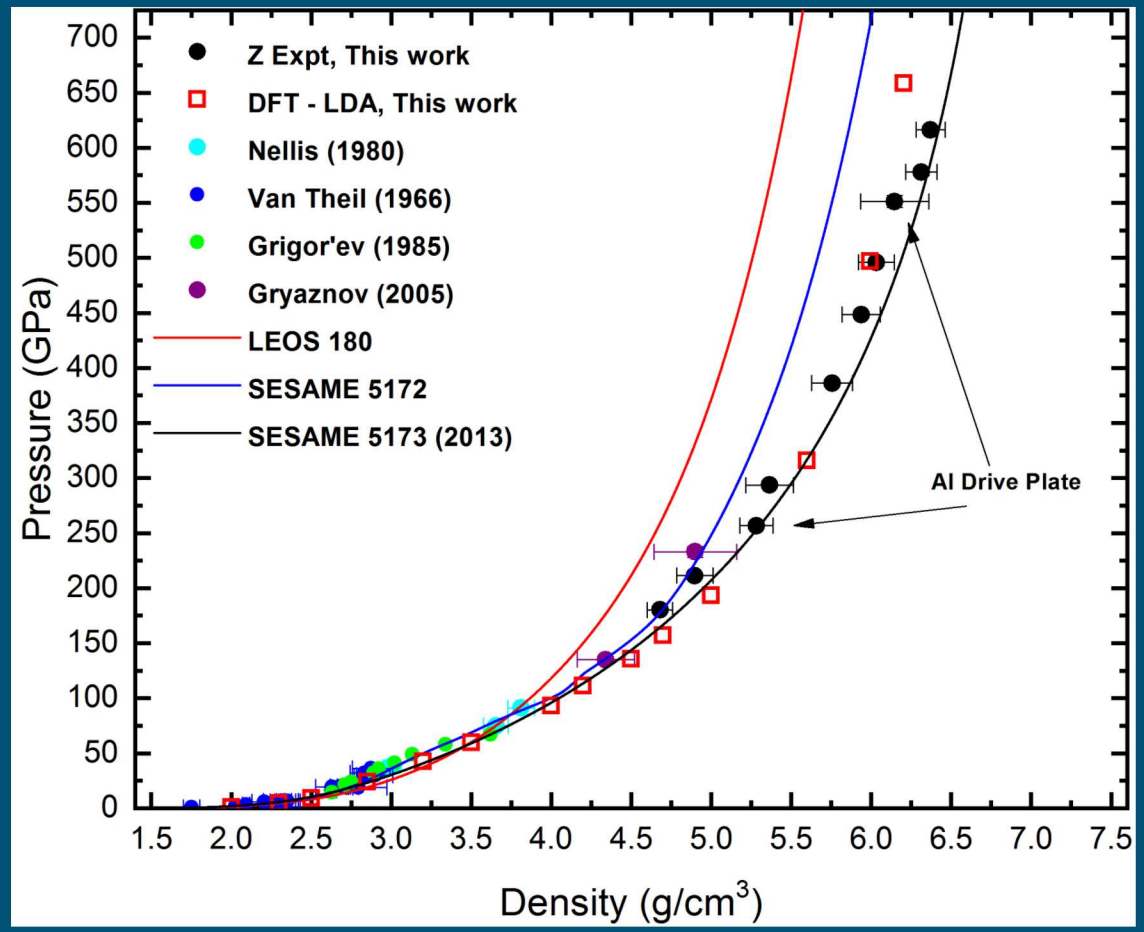


Lesson Learned:

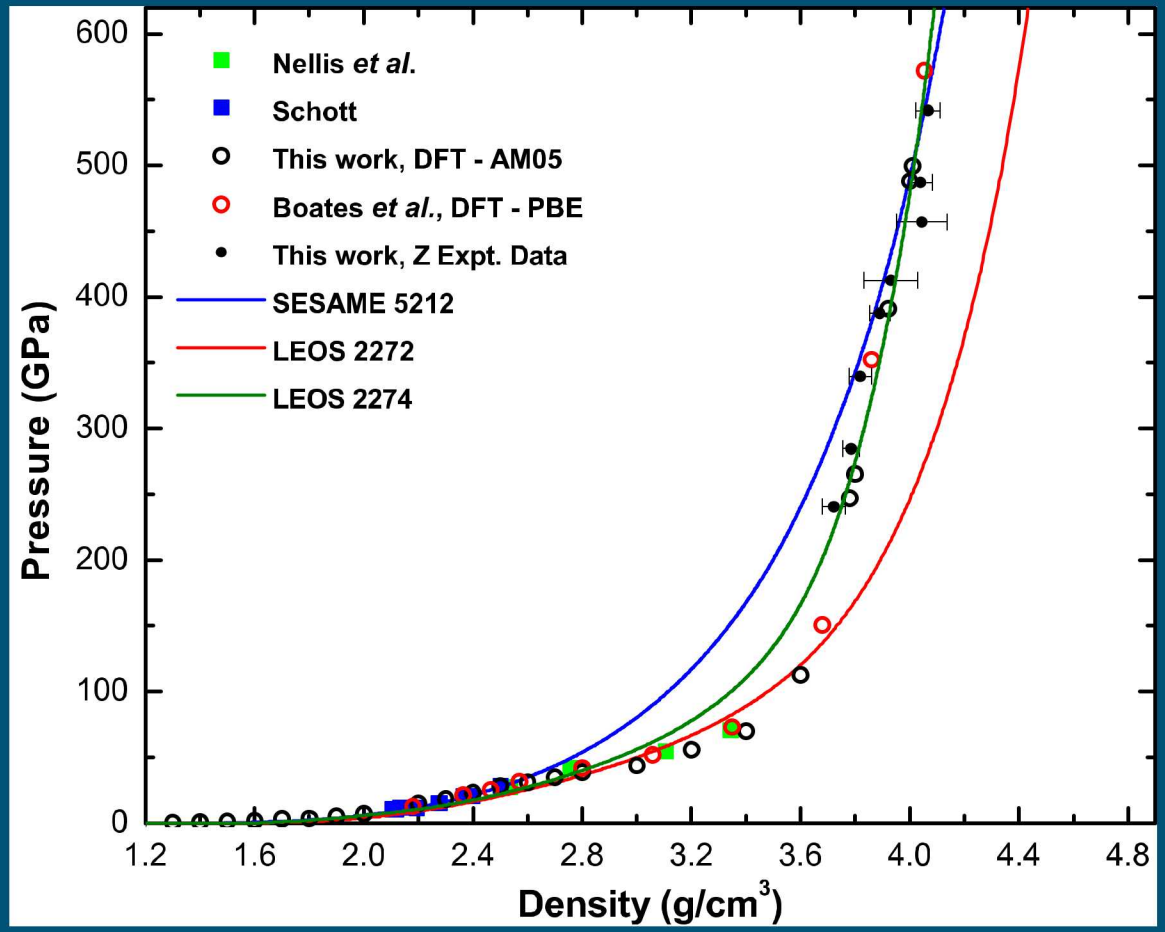
- Most EOS models are currently based on data taken at a different regime than that of interest. Check! (and yes, the EOS model worked for both PMP and HDPE)

More EOS examples

Argon Hugoniot



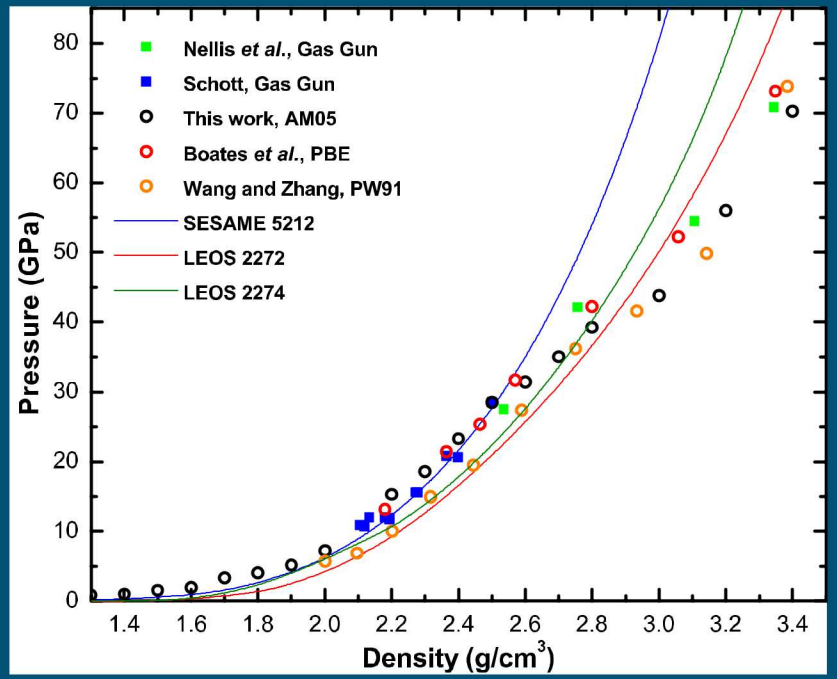
CO_2 Hugoniot

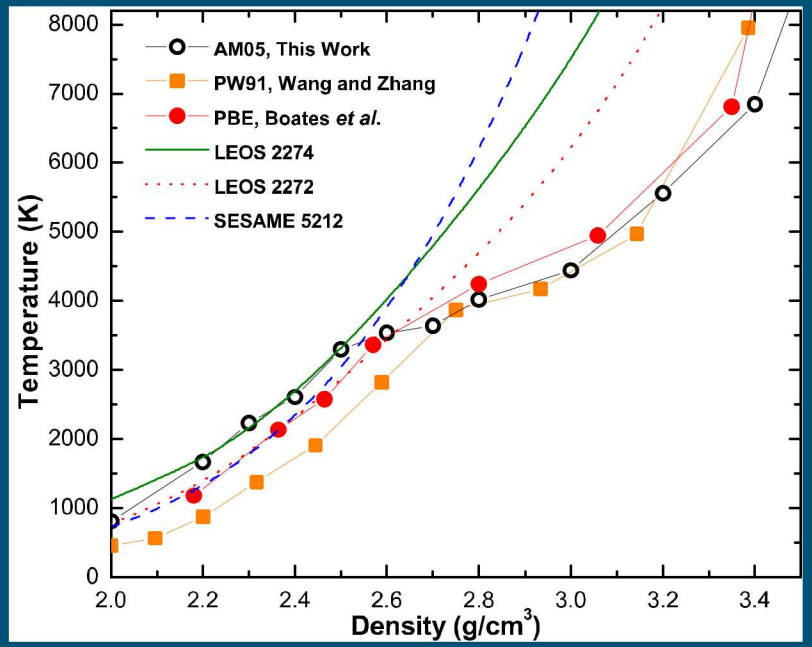


EOS models have difficulty fitting both the molecular liquid and the atomic liquid while capturing the behavior of the dissociation regime

CO2 Hugonoit: Low Pressures

- **Three different exchange-correlation functionals used: AM05, PBE, PW91**
- **The PBE functional matches the data the best**
- **All DFT simulations show the Hugoniot inflection – better observed in ρ – T**
- **Below inflection, SESAME 5212 describes the Hugoniot the best**
- **LEOS 2272 and 2274 include dissociation, but need improvement in this region**



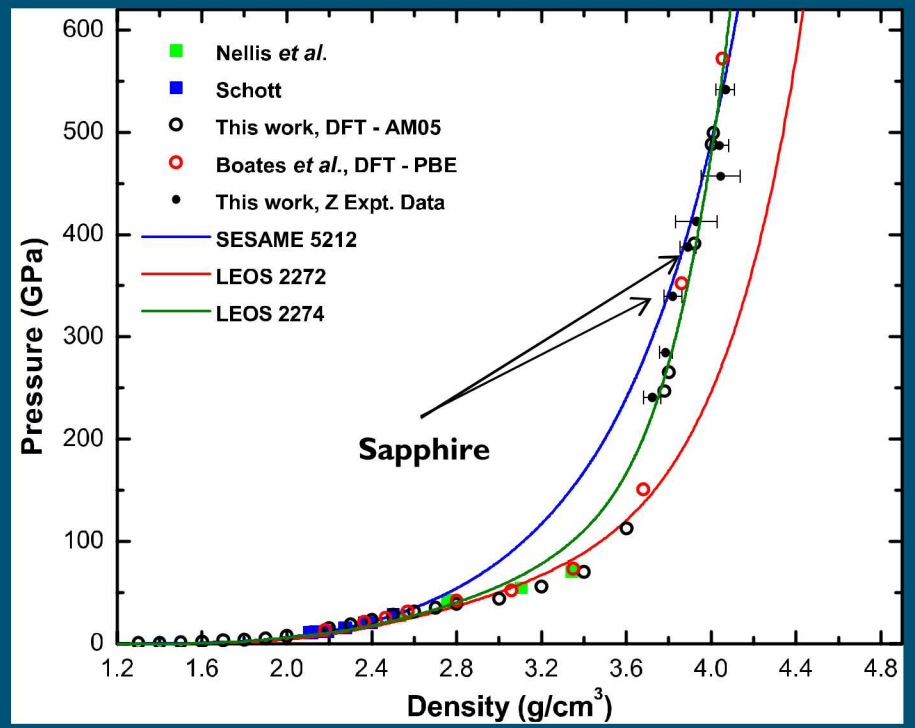


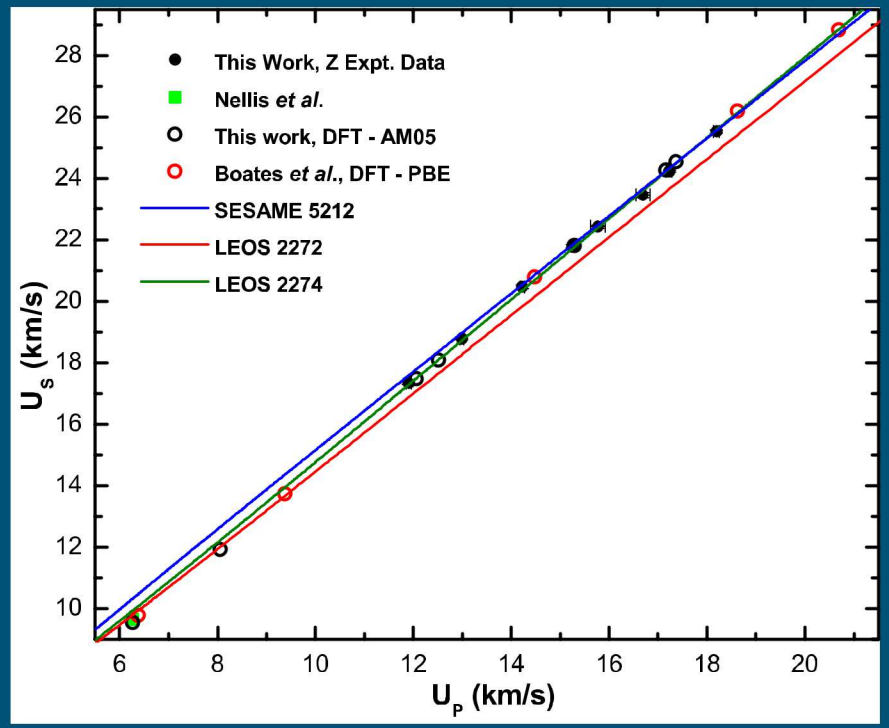
C. Wang and P. Zhang, J. Chem. Phys. **133**, 134503 (2010)
B. Boates *et al.*, J. Chem. Phys. **134**, 064504 (2011)

LEOS 2274 – recently developed, Sterne and Wu, LLNL

Experimental CO2 Hugoniot Results

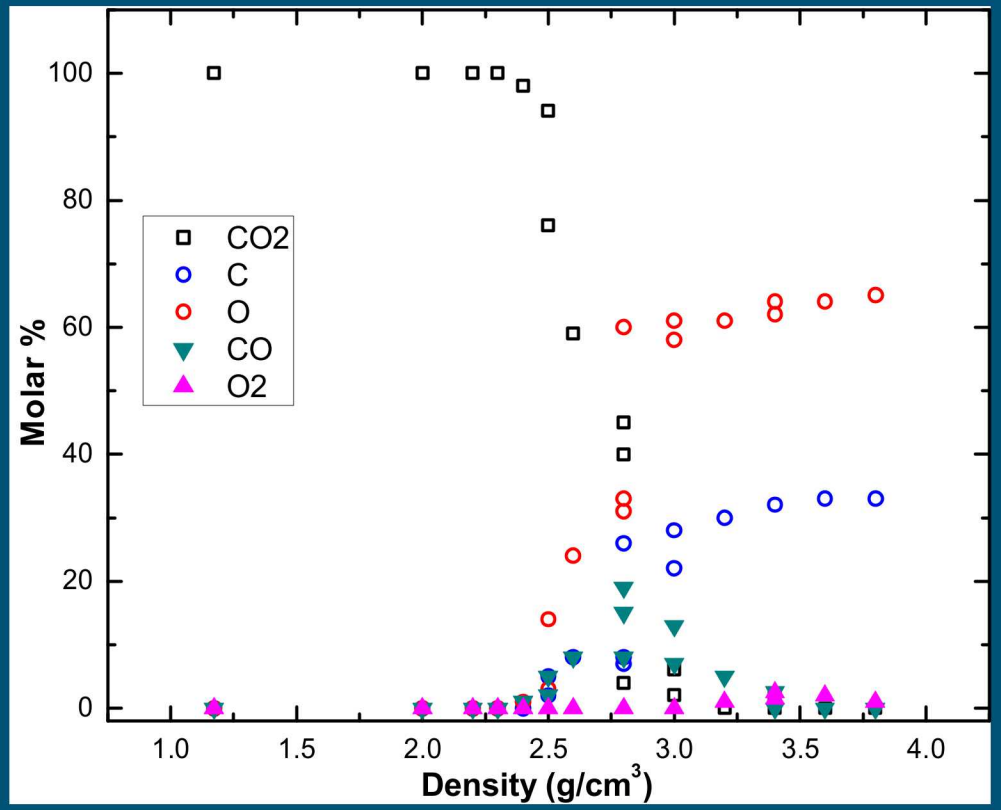
- **Hugoniot measured to 5.5 Mbar – validate the DFT results**
- **Data determined using quartz and sapphire impedance matching – consistent results regardless of impedance standard**
- **Experiments show a less compressible Hugoniot after dissociation**
- **LEOS 2272 is too compressible and SESAME 5212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





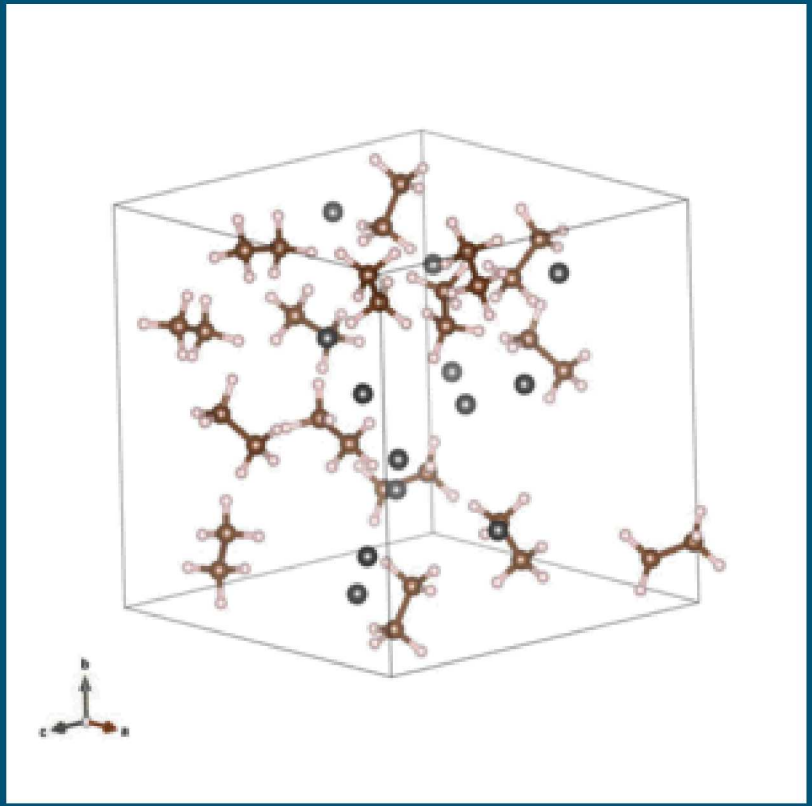
CO2 Dissociation on the Hugoniot

- **Utilize a bond tracking scheme to examine dissociation in the DFT simulations**
- **Dissociation begins approximately 30 GPa**
- **Complete dissociation by 55 GPa**
- **CO2 dissociates into atomic C and O**
- **Small amounts of CO exist between 40 GPa and 55 GPa**



Above 80 Gpa, liquid CO2 is now only atomic C and O, which influences the equation of state

Liquid Ethane and Ethane/Xenon mixture

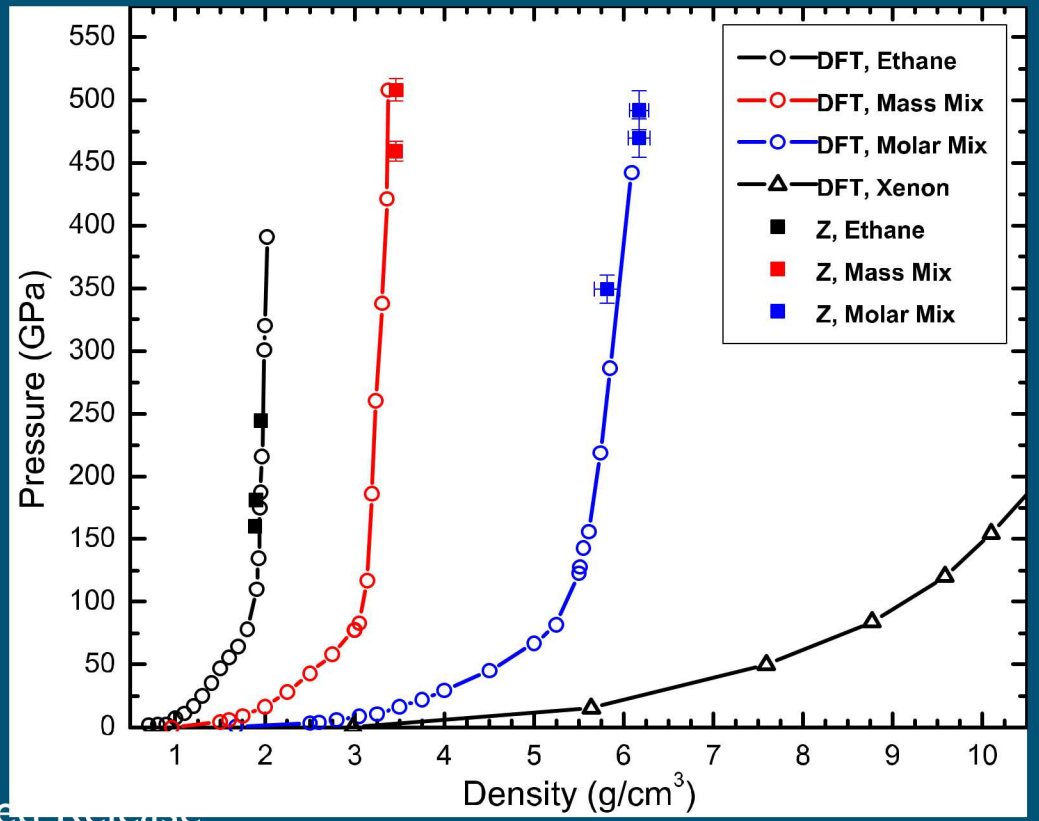


Ethane and ethane/xenon mixtures (xenon immiscible in ethane)

Higher Z element dopants give the impression of softening the Hugoniot

Molar compression ratio at 375 GPa = 3.6. Mass compression ratio = 3.45

AND…when you are ordering gas, make sure the supplier understands the difference between molar and mass mix!!!



Liquid Ethane and Ethane/Xenon mixture

Ethane $\rho_0 = 0.571$ g/cc $T_0 = 163$ K

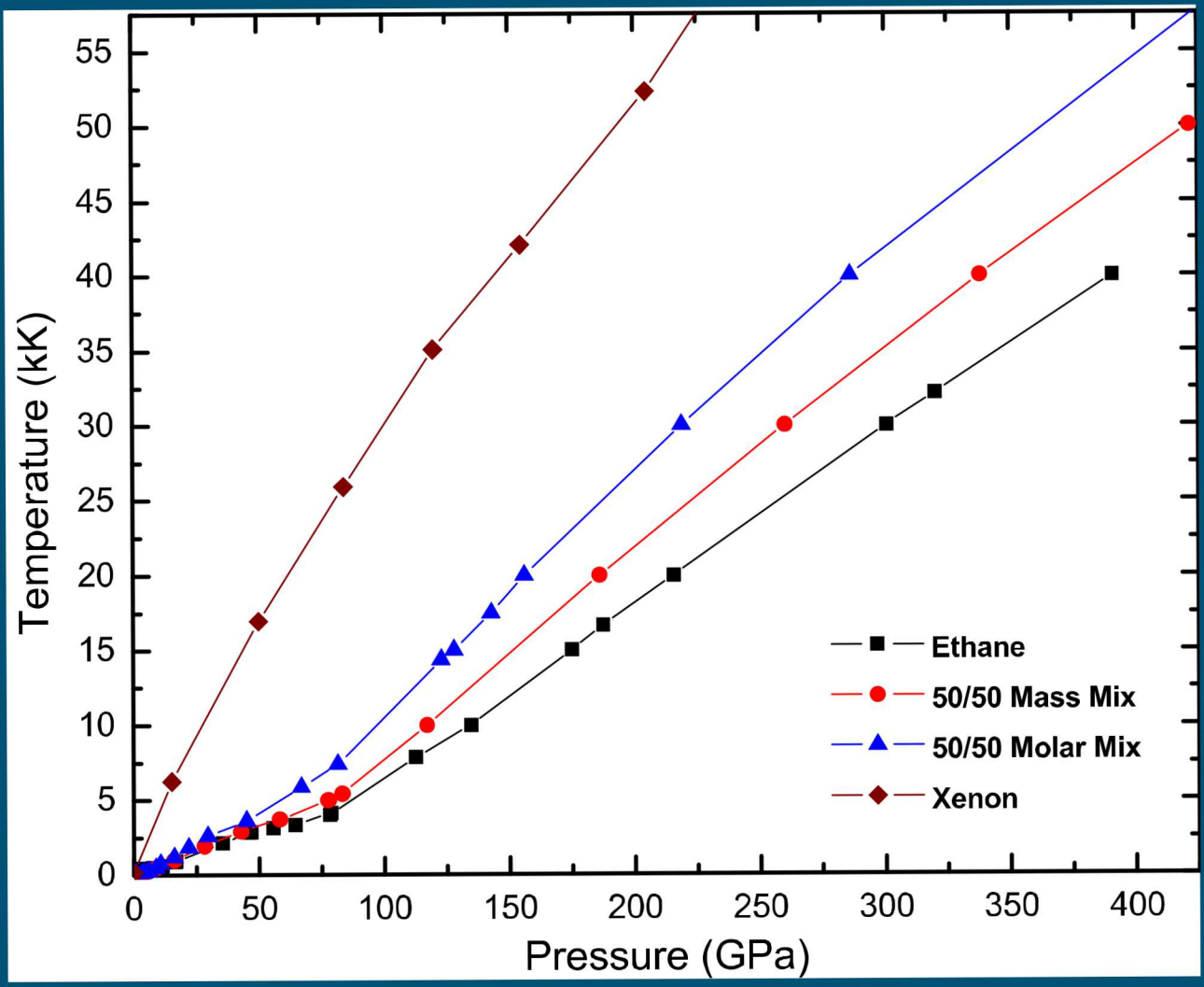
50/50 Mass $\rho_0 = 0.96$ g/cc

50/50 Molar $\rho_0 = 1.676$ g/cc

Xenon $\rho_0 = 2.97$ g/cc

Pure xenon has a higher temperature for a given pressure than any of the ethane mixtures

Molecular to atomic gas (bond breaking/dissociation) absorb a lot of energy



Glow Discharge Polymer (GDP)

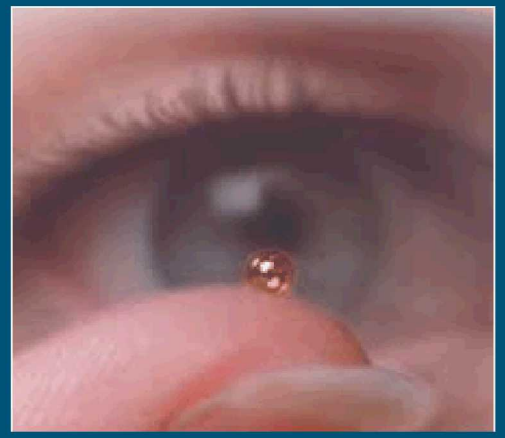
Used as fusion capsule plastic

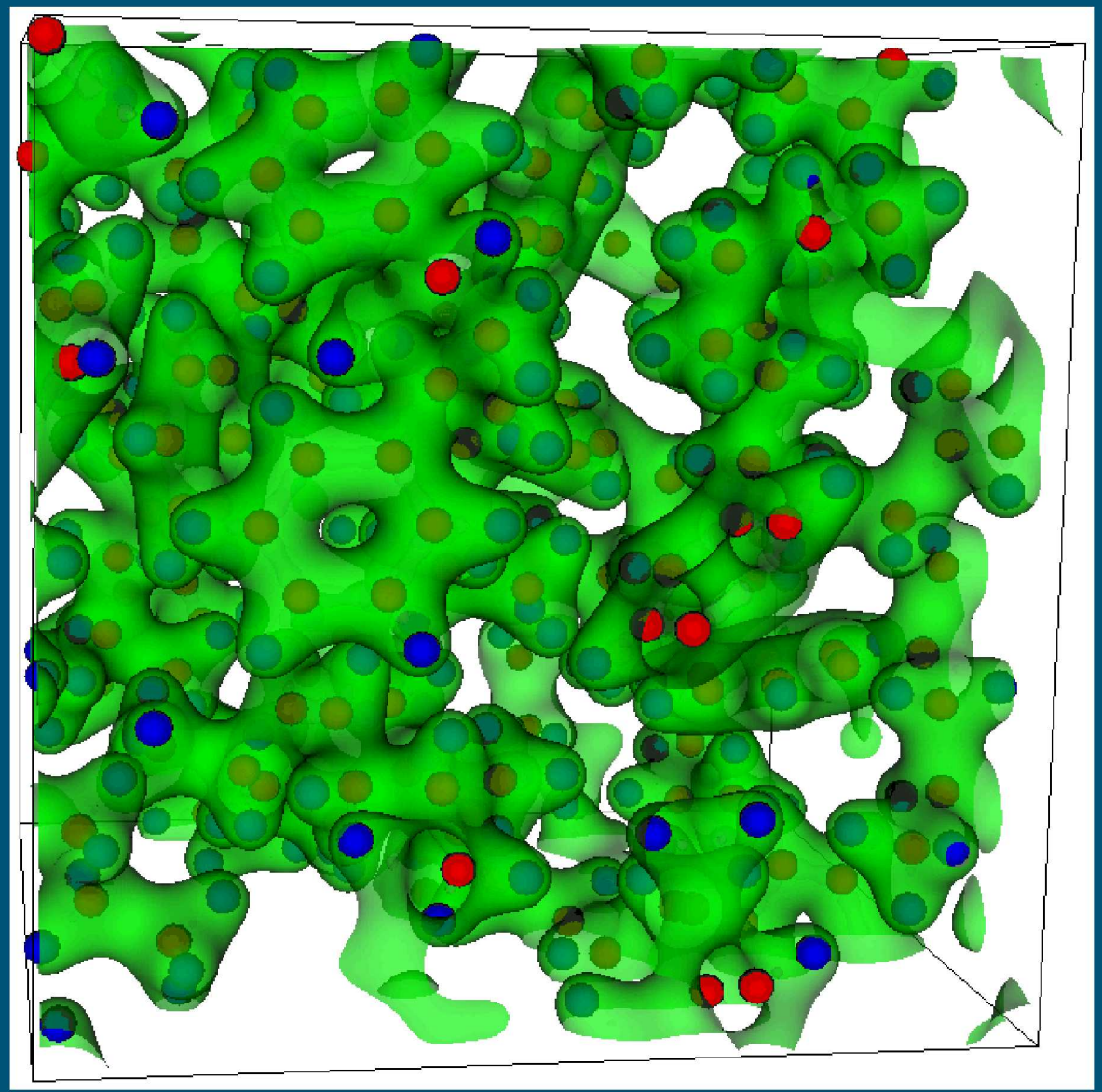
Can have germanium or silicon dopants

Simulation heated system and then cooled to find initial state

Lesson: this type of quenching often (always?) produces benzene rings which may not be correct structure. Manufacturers work hard to get the correct plastic structure in general.

Wrong color to have benzene rings





VASP QMD simulations compared to experimental data

VASP has good agreement with LLNL data at relevant pressure

The large error bars on the VISAR data are from samples too thick to see through (250 micron)

Thinner samples (180 micron) both VISAR and PDV can see through

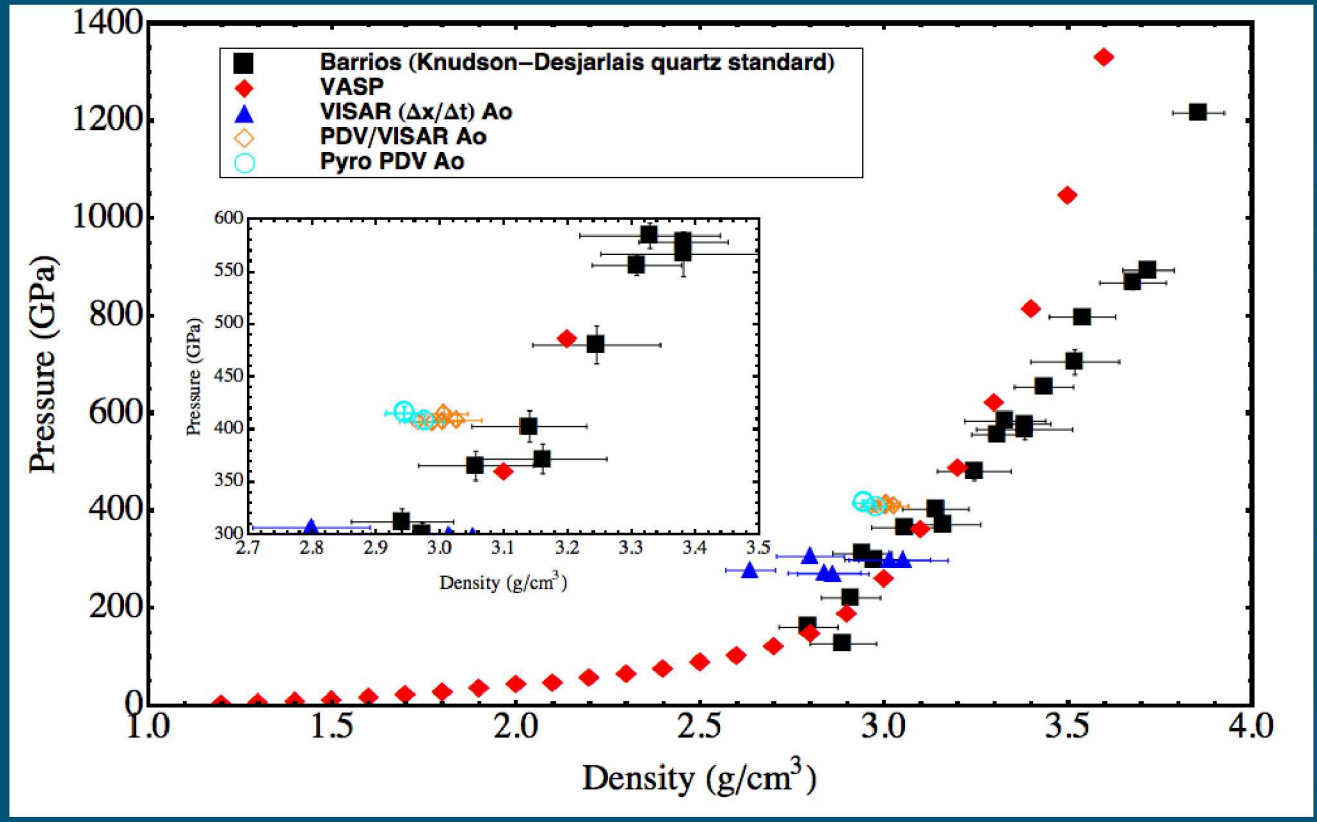
LLNL (Omega)/VASP differ from Z data by 6% in density and 25% in pressure

Z data has 2% error bars in density (primarily from reference density of 1.03 +/- 0.02)

Incorrect reference structure?

Adsorption of other elements (water)?

Both cause initial density and energy to be different than simulated.



Barrios data taken from Knudson and Desjarlais, PRB 88, 184107 (2013)

Characterization of GDP

Water absorption between 5% and 1% linearly to 50 microns (Stadermann et al)

Barrios sample 30 micron so 5% to 3% water

Baked sample (Pyro)…slightly stiffer

Water is not the difference in this case as the un-baked Z data (orange) should match Omega data…unsure why they are different

Z data does not match simulation either

Wrong color so no benzine rings

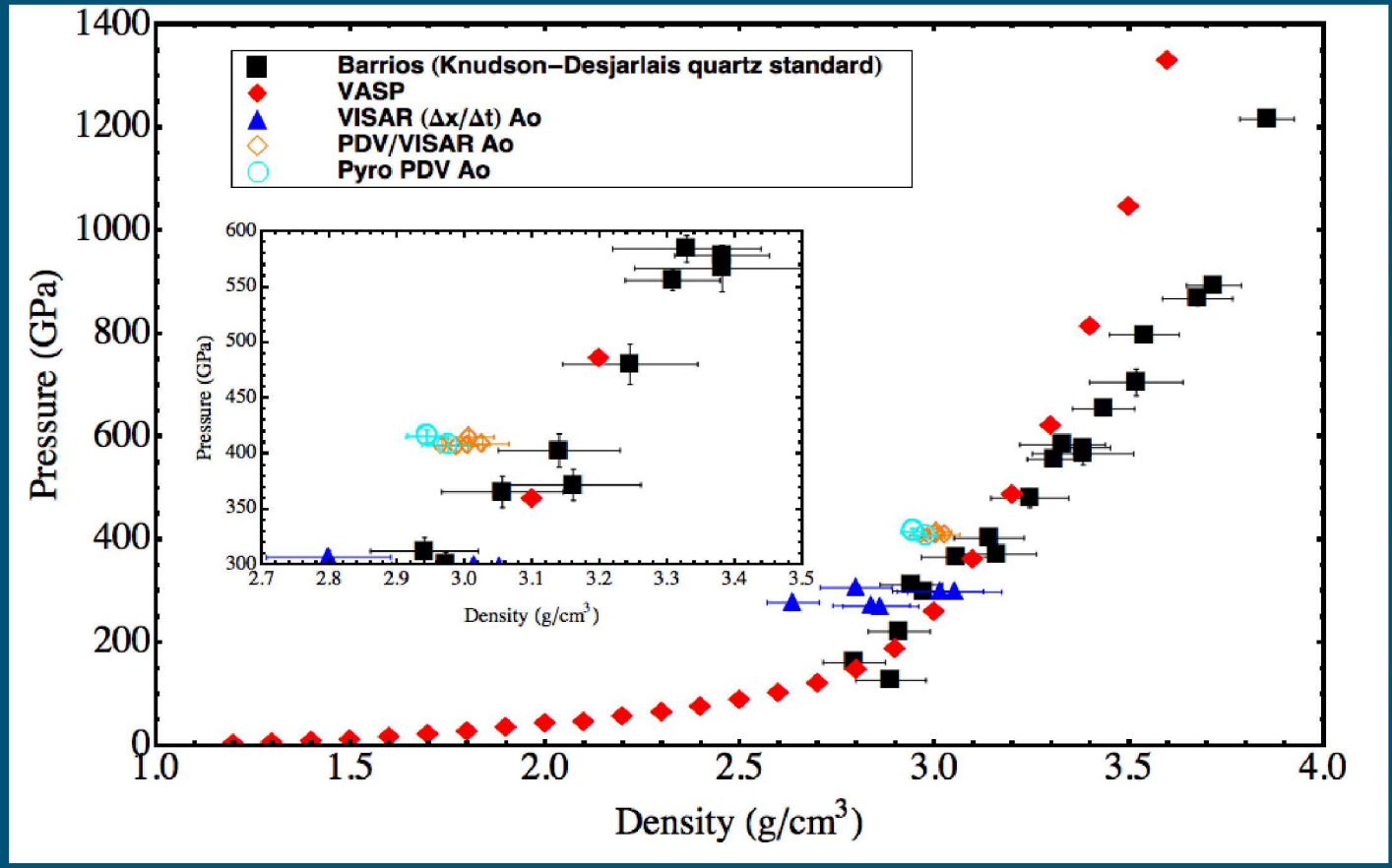
- yellow color=conjugation or alternating single and double bonds
- Conjugation lowers transition energy into the visible
- Electrons can delocalize in a conjugated system

Wrong initial structure?

- Monomer for polymerization is trans-2-butene not benzine

Van der Waals potential?

Try to reverse engineer initial structure.



Barrios data taken from Knudson and Desjarlais, PRB 88, 184107 (2013)

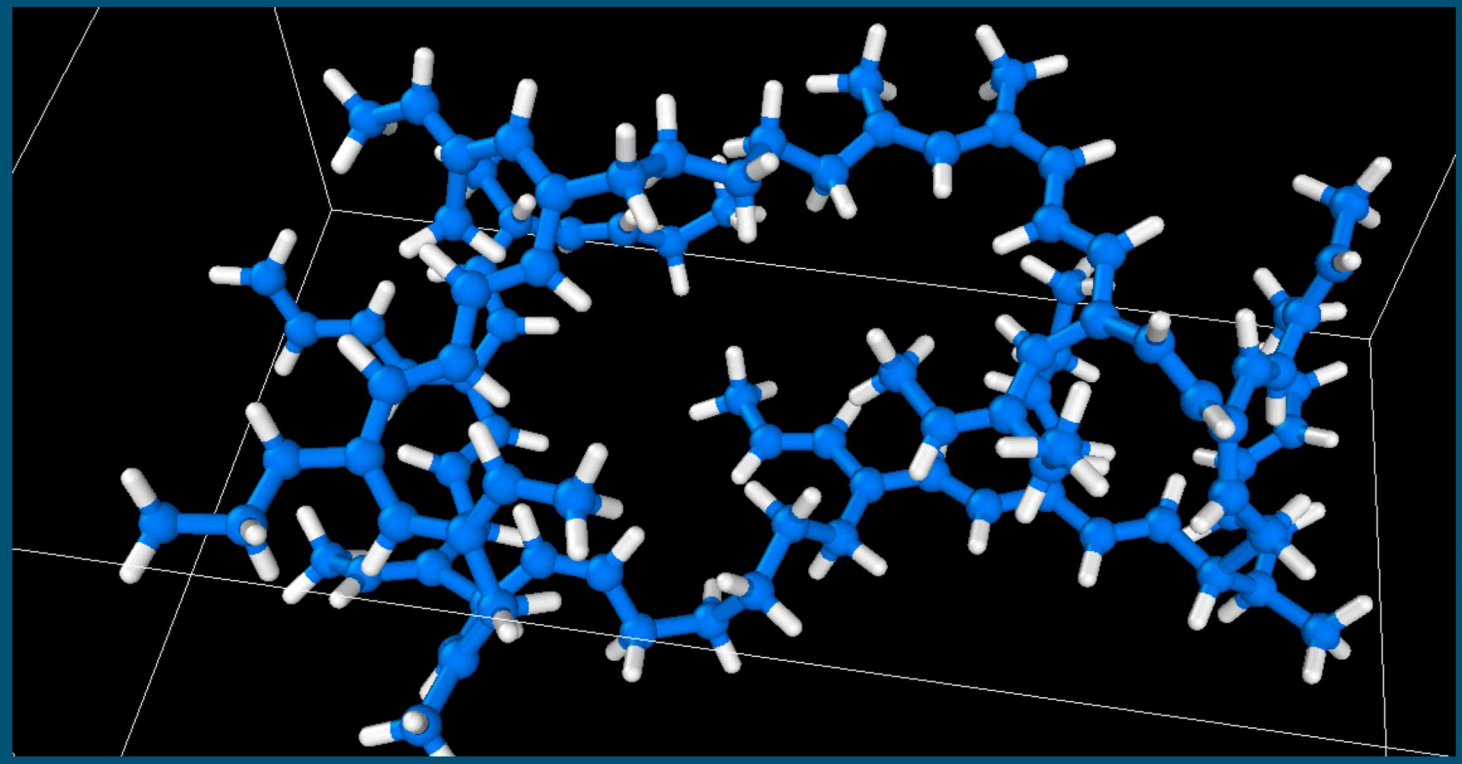
Creating new GDP

New structure based on what happens during:

- Plasma polymerization process
- Photo-oxidation of polymers
- Photo-degradation of polymers
- UV glue curing accelerate photo breakdown
- The apparent IR spectrum (not shown here)

Constraints:

- Must be branching
- Must be conjugation
- H/C ratio must remain approximately the same
- Ketones?
- hydroxyl groups?
- Example to right but many other examples can exist



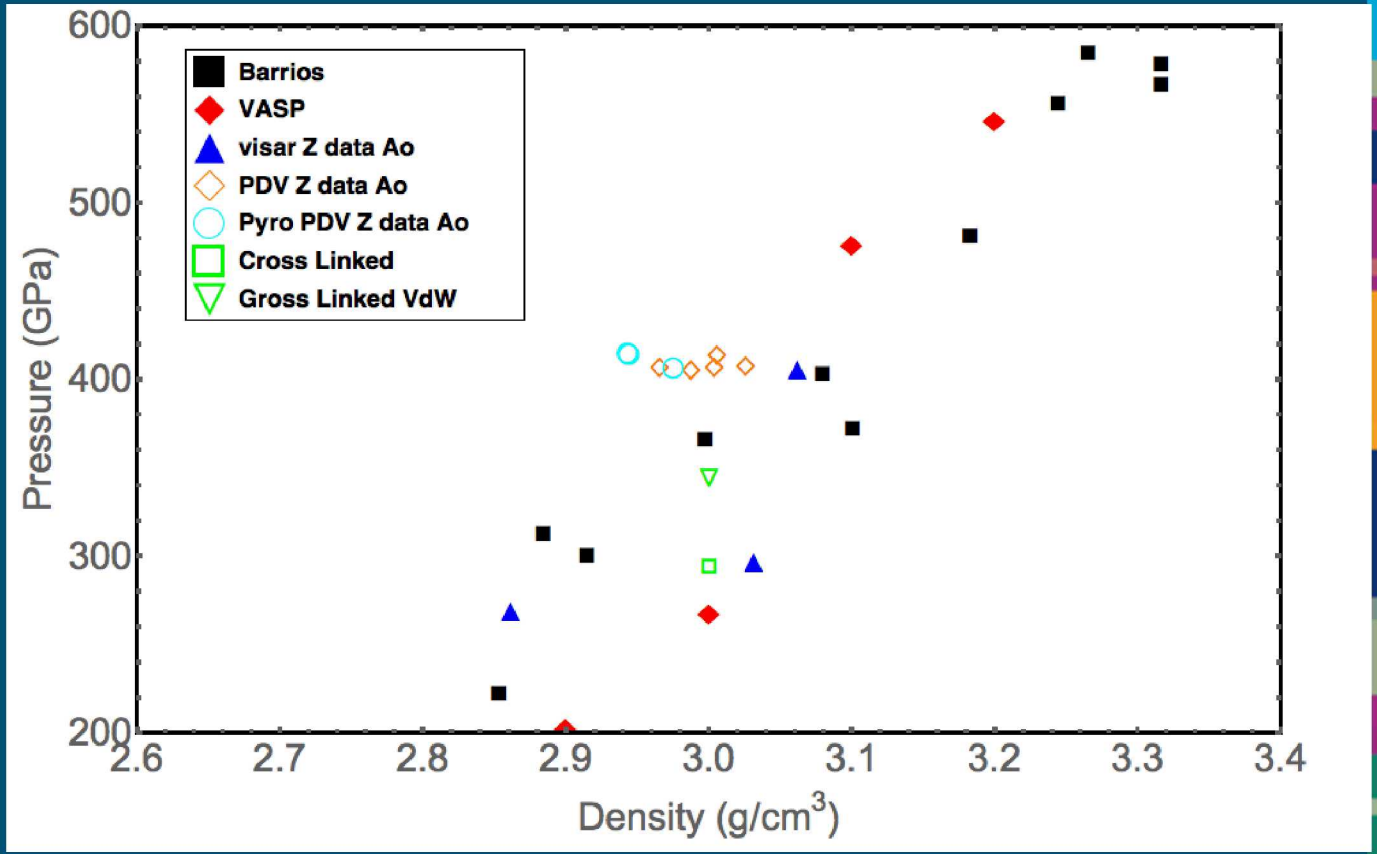
Courtesy of Keith Jones

New GDP results

3.0 g/cc T ~15,000 K

3.1 g/cc T~30,000 K

Streak camera and fit to grey body T~26,000 +/- 3000 K



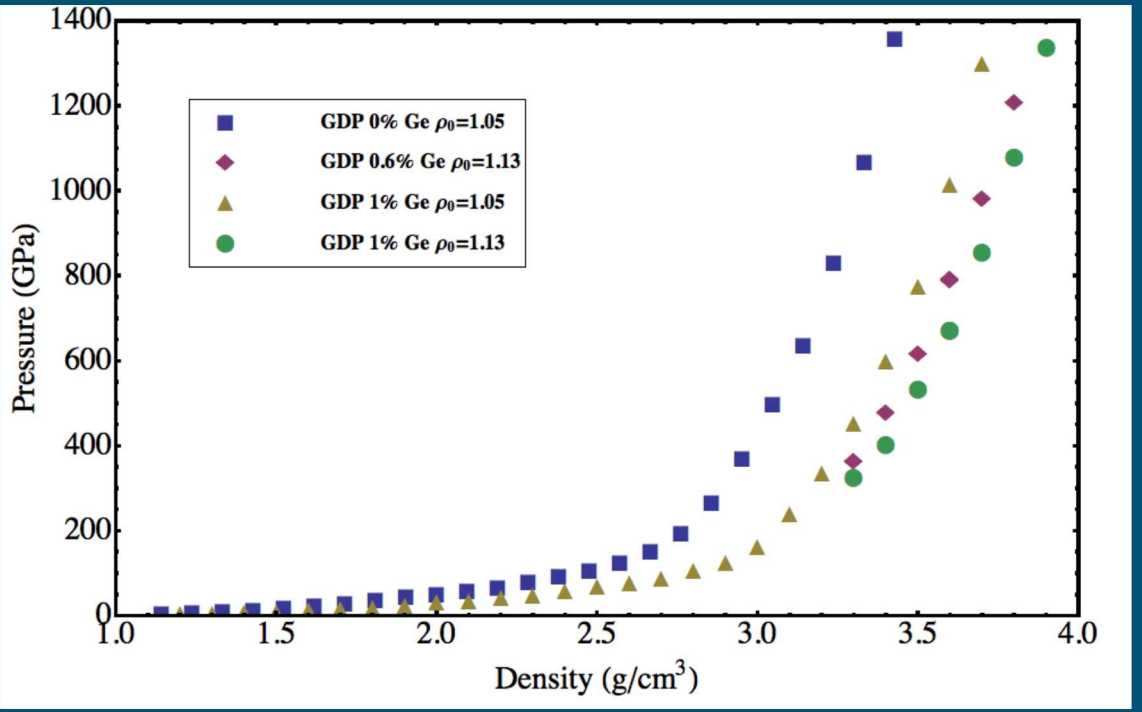
GDP with germanium dopant

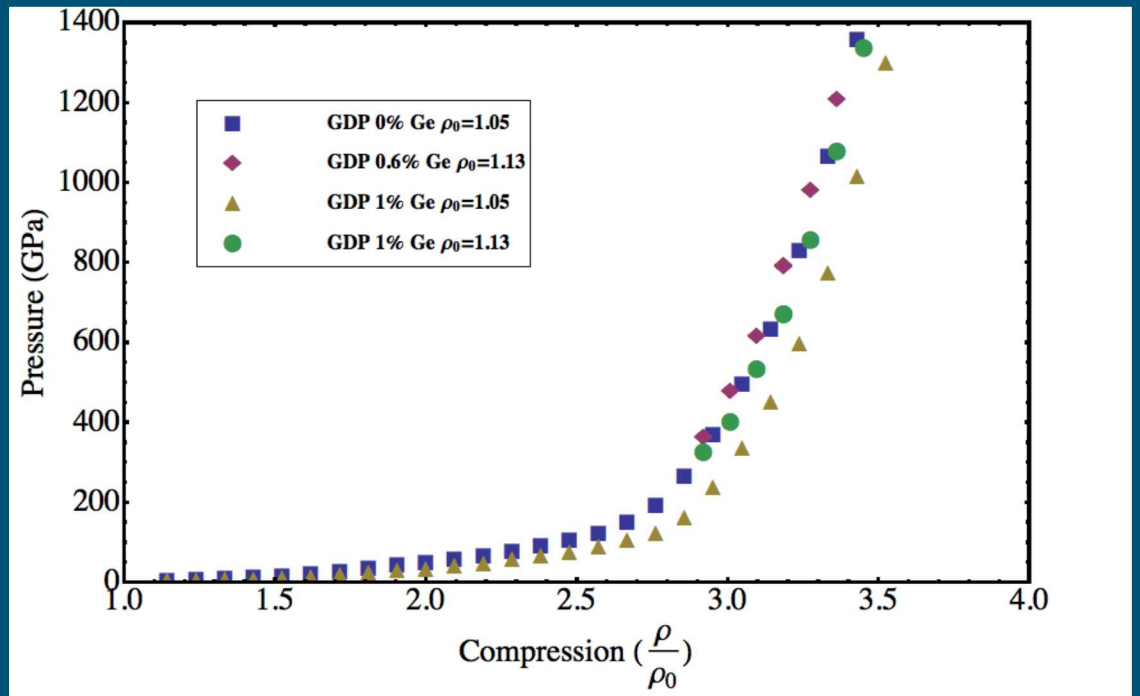
Ge dopant at 0%, 0.6%, and 1%

Density at 1.05 g/cc and 1.13 g/cc

In some cases, substituted Ge for carbon and others just randomly placed Ge in the simulations

Method of Ge placement made minor difference





- At 1.05 g/cc, Ge significantly softens Hugoniot
- Keeping initial volume and adding germanium such that density increased to 1.13 g/cc shows compression ratio is similar but different enough to warrant a new EOS

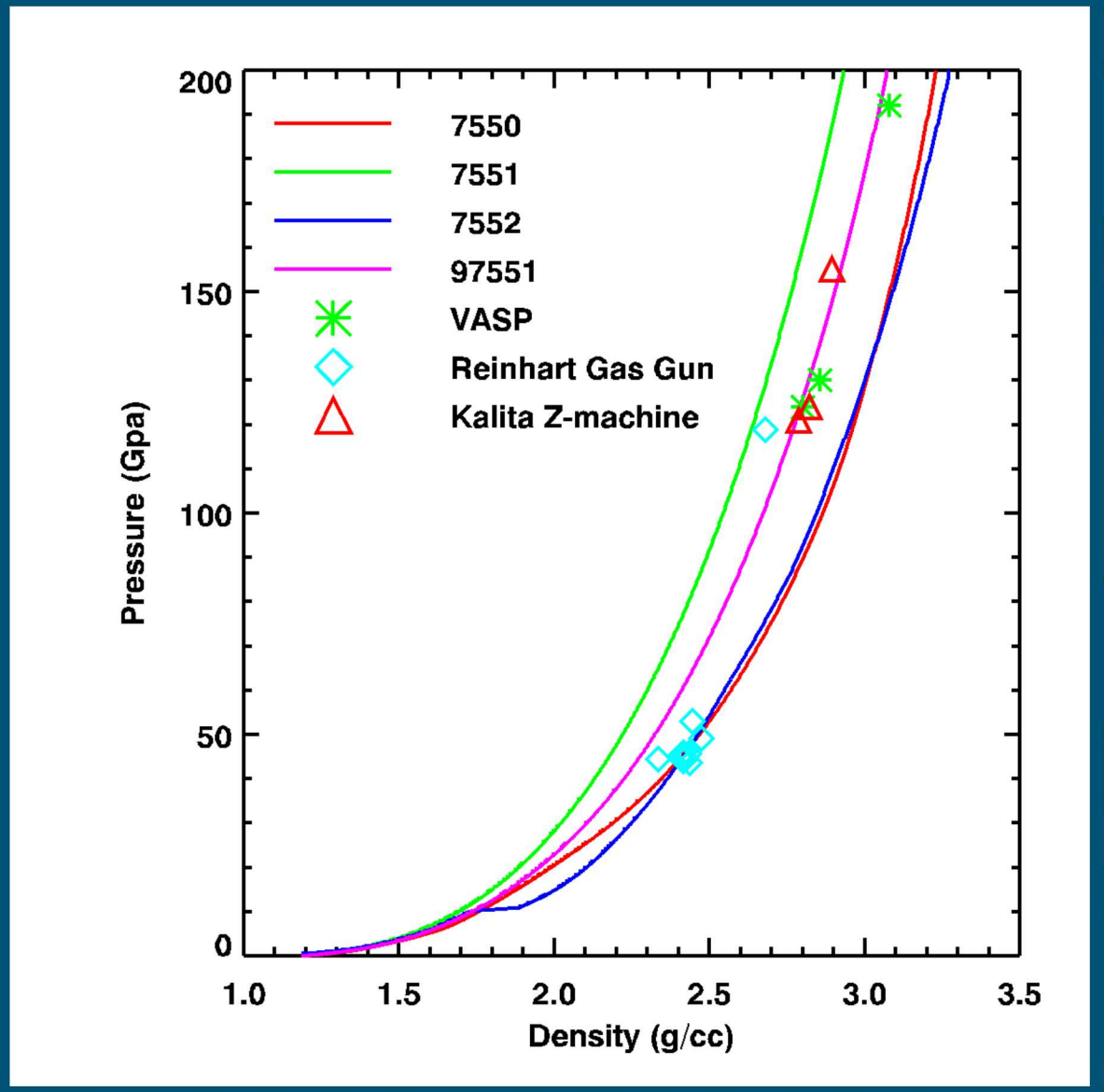
Poly(methyl methacrylate) aka PMMA

PMMA initial structure is well known (unlike GDP)

VdW potential

Experimental and DFT simulations match very well

EOS models have difficulty fitting both the before and after dissociation regimes simultaneously



Summary and Conclusions

All hydrocarbons examined this far dissociate at approximately the same compression along the Hugoniot

Complex, long chain hydrocarbon systems can be approximated with shorter chains and periodic systems

Structure of they hydrocarbon system must be reasonably close to actual structure

VdW usually matters (but not always)

Higher Z dopants soften Hugoniot (in density or compression space)

Dopants can often be substituted for carbon or just added to the system with little difference noticed in the final Hugoniot pressure

Make sure your supplier gives you what you asked for

We have no idea the correct structure of GDP and are still trying to reverse engineer the initial conditions

Z and Omega data don't match and we don't understand why

Get the initial structure correct and DFT matches experiment quite well (HDPE, CO2, PMMA, Xenon/Ethane, others)