SAND2012-0478 C

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Chemistry in Dynamic Extremes Workshop,
LANL/Buffalo Thunder, NM, Feb 2012

Modeling experiments on Z where chemistry matters: polymers, CO2, and explosives

Thomas R. Mattsson,
S. Root, R.J. Magyar, L. Shulenburger, D.L. Hanson,
K. R. Cochrane, A.E. Mattsson, R. Wixom,
and D. G. Flicker

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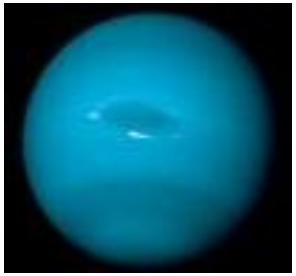
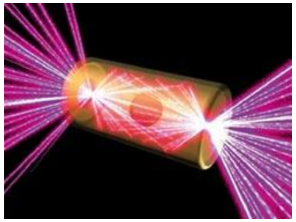
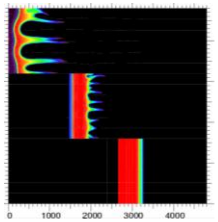
Properties of light elements in the Mbar regime are important for several reasons

- **Planetary science – Uranus & Neptune and exo ice-giants**
  - High-pressure mixtures of H, He, C, O, N
- **Planetary science – earths and super-earths**
  - Equation of state of Fe and subducted CO_2
  - Mbar, 1000 – 4000 K
- **Inertial confinement fusion (ICF) materials**
  - Fundamental behavior of carbon and carbon compounds
  - Mbar, +10 000 K
- **Chemistry at high pressure and temperature**
  - Reactions driven by pressure and temperature
  - Composition under shock compression
  - Complex Hugoniot – flat sections



Ice giants: C-H-N-O mixtures at Mbar





ICF concepts: irradiated hohlraum (left) and Sandia's MagLIF (right)

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Overview of systems with chemistry: first-principles simulations and Z experiments

- **CO_2**
  - Liquid initial state – to 5 Mbar with high precision
- **Hydrocarbons**
  - Polymethyl pentene (PMP/TPX)
  - Polyethylene, Polystyrene
  - Liquid ethane
  - *See poster yesterday by Kyle Cochrane*
- **High explosives**
  - Initial results on PETN
  - *See poster yesterday by Ryan Wixom*
- **Chemistry at high pressure and temperature**
  - Reactions driven by pressure and temperature
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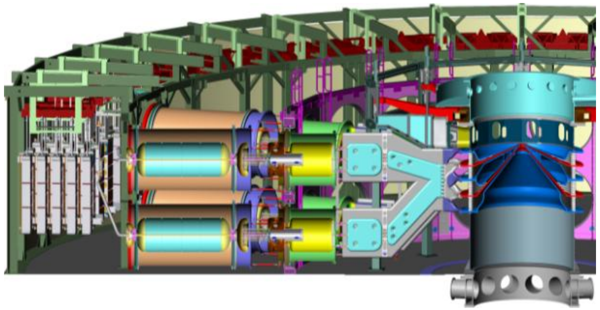
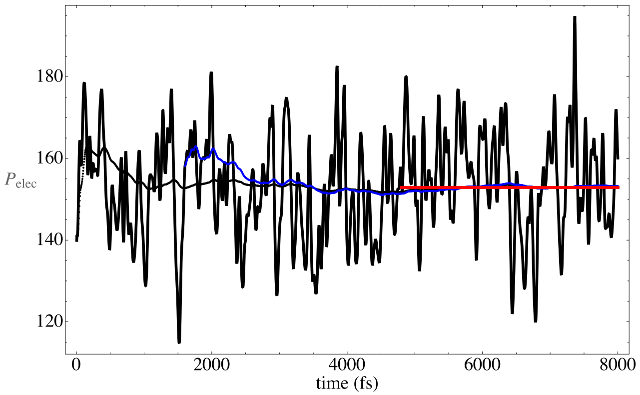


Shock experiments on Sandia's Z machine

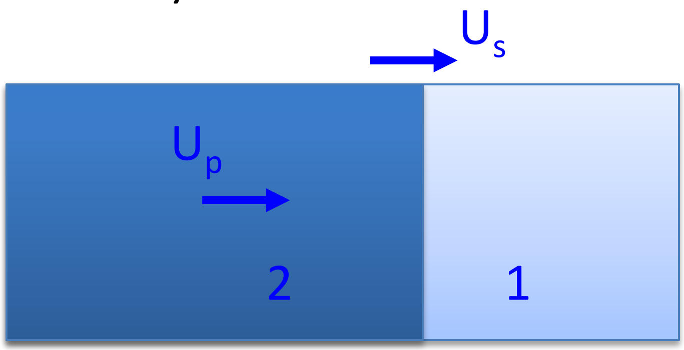


Density Functional Theory simulations

We reach Mbar pressures in liquids and solids by executing flyer-plate impact experiments

- **Advantages of liquid and transparent solids**
  - Uniform sample
  - Initial state EOS well-defined
  - Reproducible state
  - Reflective shock fronts allow very high precision measurements
  - 30 km/s impact velocities
- **Straightforward to analyze**
  - Conservation of mass, momentum, and energy
  - Rankine-Hugoniot relation

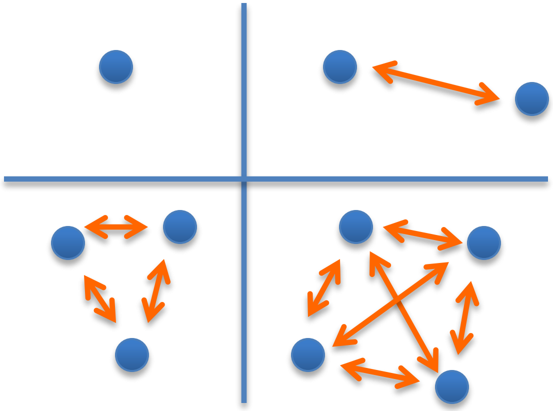
Steady shock wave in matter



$$2(E_2 - E_1) = (P_2 + P_1)(u_1 - u_2)$$

With high accuracy measure and/ or calculate thermo-physical properties

Density functional theory (DFT) based MD is an established approach - HEDP sets additional demands



Treating quantum many-body interactions between electrons correctly is very demanding

Large-scale simulations on super-computers like cielo and Red Sky

DFT calculations can be predictive

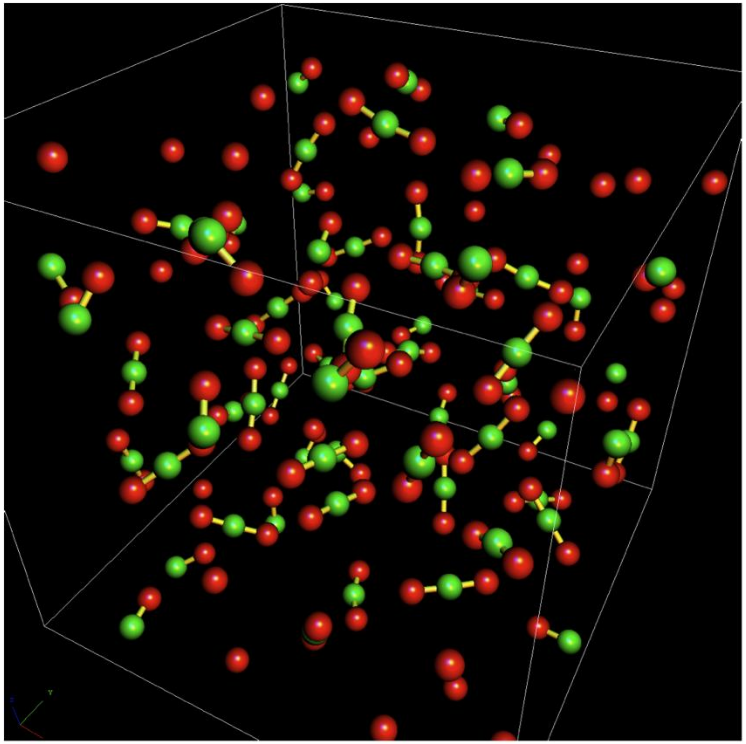
- *Accuracy* set by the exchange-correlation (xc) functional:
- *Convergence* of simulation parameters to desired precision
- W. Kohn won the 1998 Noble prize in chemistry

VASP code (Georg Kresse, Vienna, Austria)

- Finite-temperature DFT (Mermin)
- Plane-wave basis-set for controlled convergence and free electrons/ionization
- Projector augmented wave core functions (PAW)

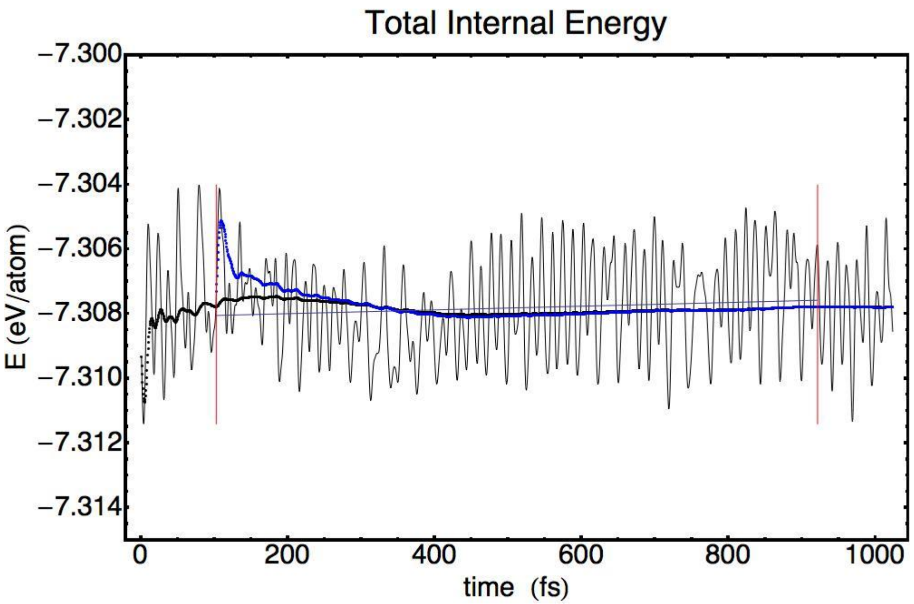
- *First-principles thermodynamics – long simulations yield $P(\rho,T)$, $E(\rho,T)$, structure, diffusivity, etc.*

First-principles thermodynamics: gaining insights into the behavior of matter starting from quantum mechanics



Simulation of CO_2:

64 molecules
one complex k-point
high plane-wave cutoff energy

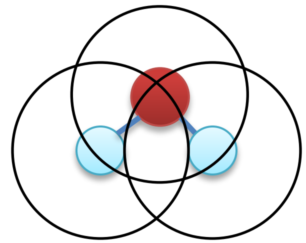


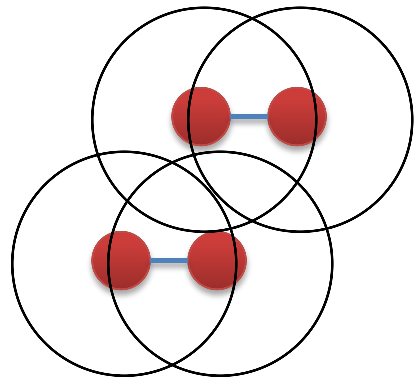
Time averaging over long equilibrated run – the figure shows the last ps of a longer simulation

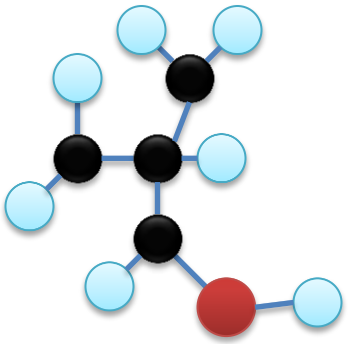
Note the fine energy scale

We also analyze the chemical composition in the cell

- **Bond-distances between atoms**
  - C-C, C-O, O-O
  - Distances from analyzing pair correlation functions
- **Bond Time**
  - Remain bonded over several vibration times – verify using different times
- **Molecule accounting**
  - Identify molecules
  - O_2 is easy
  - Branching
  - Rings
  - Use a recursive algorithm
  - Tracking in time







Identifying molecules, including branching and rings, using a recursive algorithm

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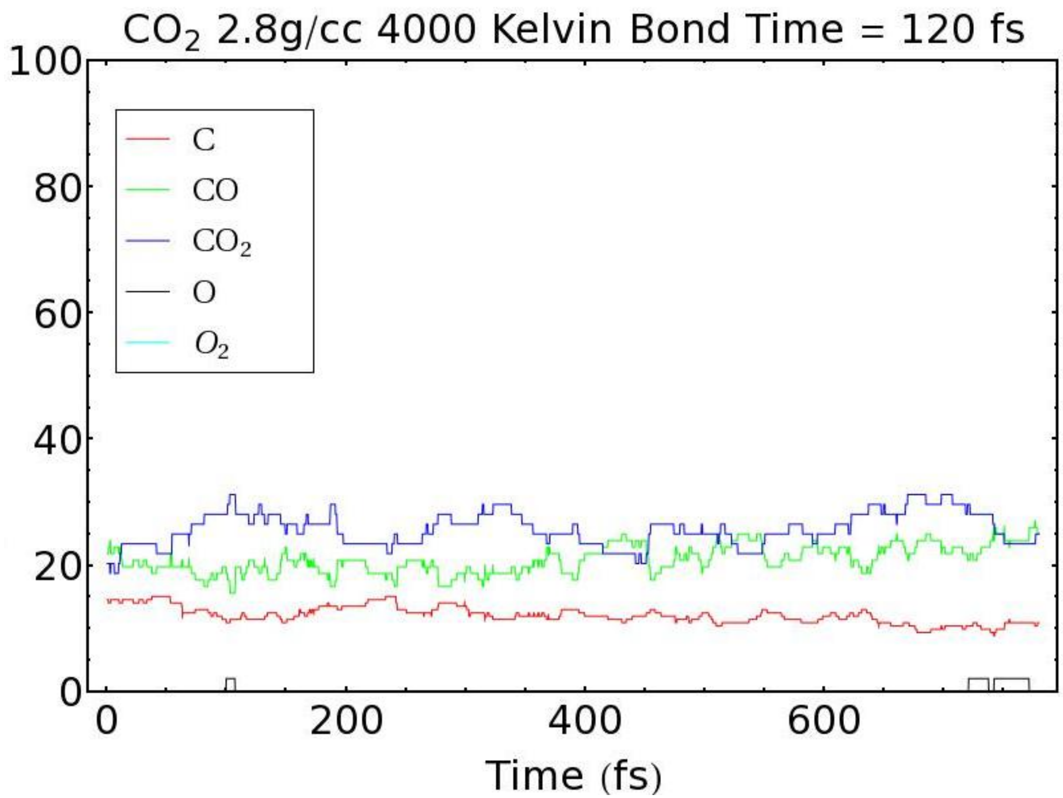
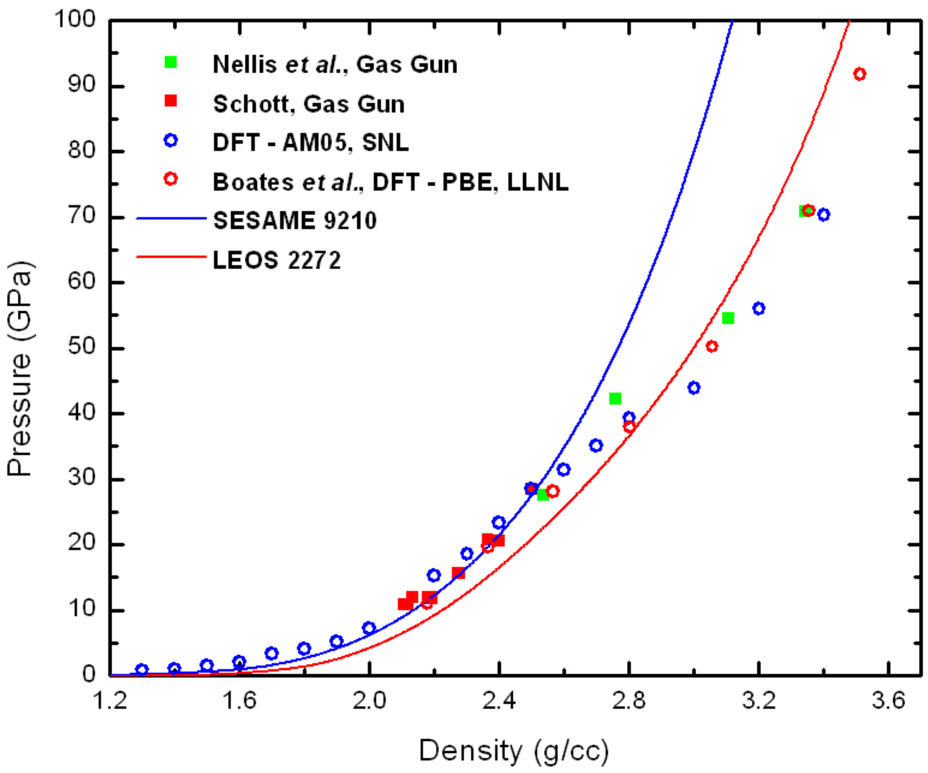


Chemical composition during the last 800 fs of a simulation

DFT calculations on CO_2 are in agreement with available experimental data and predictions up to 100 GPa

- **DFT simulations**
  - Quantitative and qualitative agreement with Schott (High Press. Res. 6, 187 (1991)) and Nellis et al (J. Chem. Phys. 95, 5268 (1991)).
  - Minor difference between PBE and AM05 exchange-correlation functionals
  - Existing EOSs do not capture the full behavior
- **Behavior above 100 GPa**
  - Relatively steep raise in pressure beyond 3-fold compression
  - We confirm very recent DFT results by Boates et al. (J. Chem. Phys. 134, 064504 (2011))



Excellent agreement between results from DFT/QMD and low-pressure gas-gun data

DFT calculations made predictions above 100 GPa – very steep Hugoniot towards 4 g/cm^3

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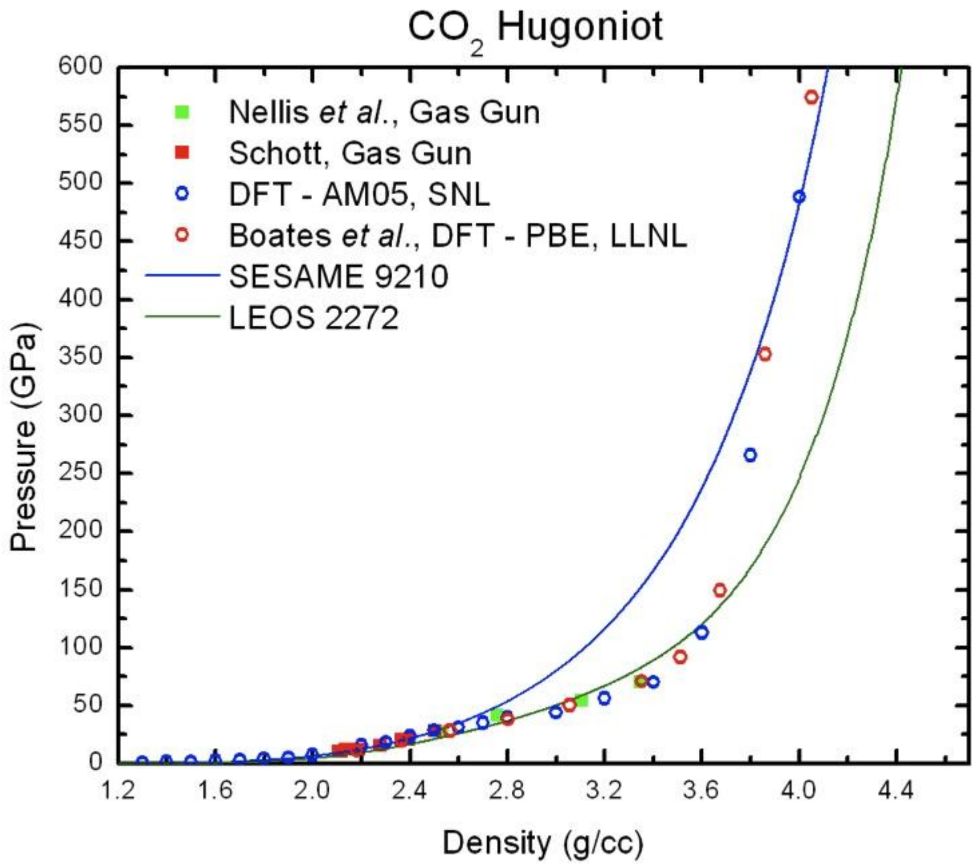
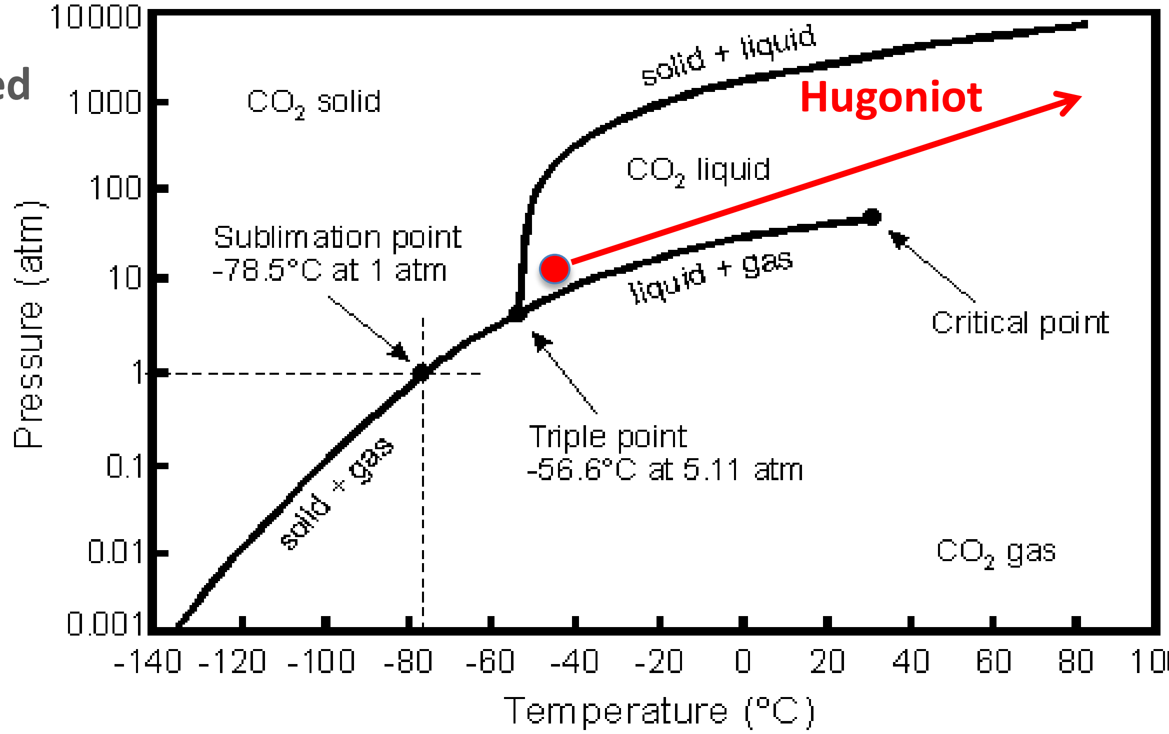


We expect a steep rise in shock pressure towards four-fold compression

We reach Mbars in CO_2 by starting from the liquid phase: it requires an experimental cell under pressure

- **Advantages of liquid**
  - Uniform sample
  - Initial state EOS well-defined
  - Reproducible state
- **Phase-diagram of CO_2**
  - Sublimation at 1 atm
- **Initial state in liquid**
  - 9 bar/ 900 kPa
  - 1.173 g/cm^3
  - 220 K

Phase-diagram of CO_2



The initial state for experiments on Z was a liquid close to the triple points

We reach Mbars in CO_2 by starting from the liquid phase: it requires an experimental cell under pressure

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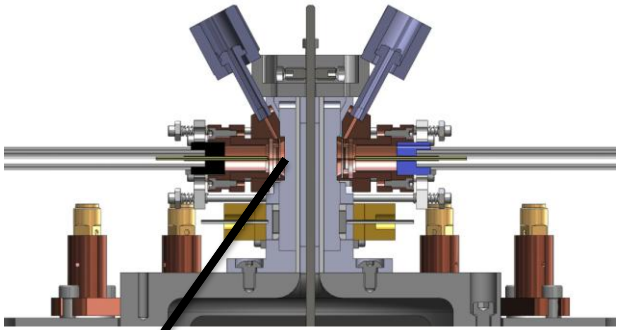
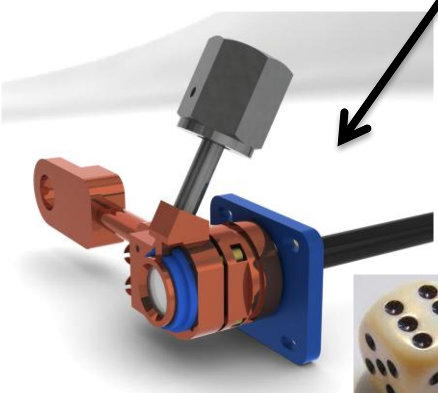
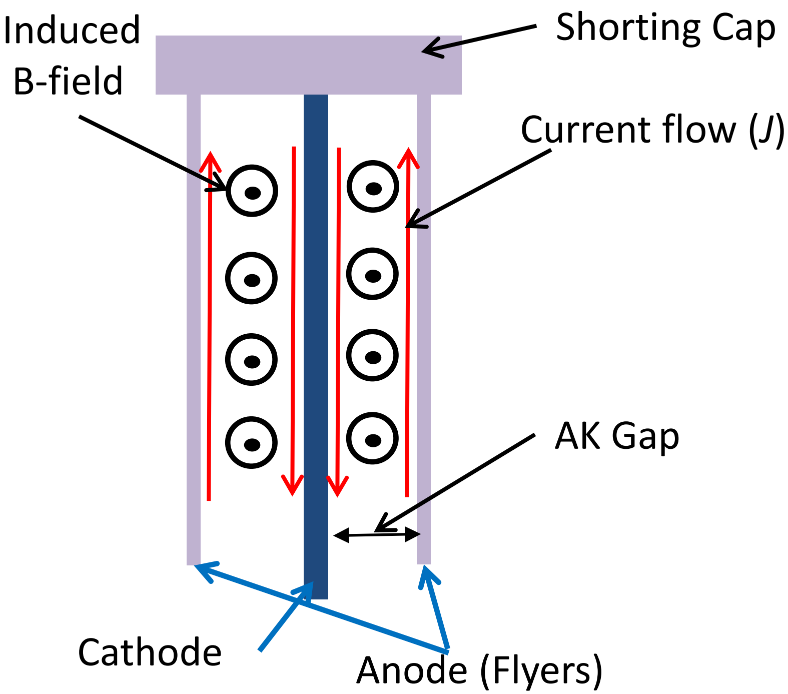


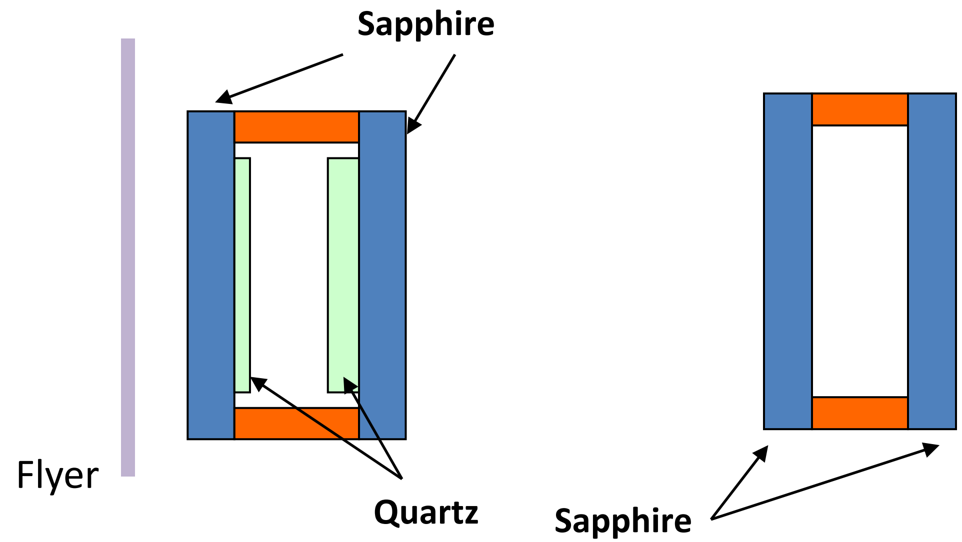
New experimental setup allows for dual cryogenic experiments



The pressure cell is the size of a die

Experimental setup on Z: high-precision temperature control and hypervelocity impact experiments

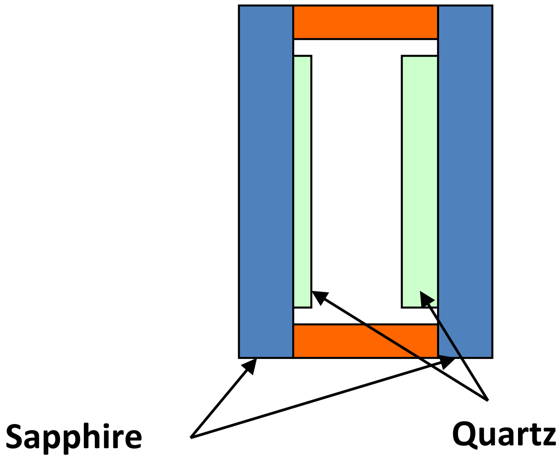




- Current pulse loops through shorting cap inducing a *B* – field.
- Resulting *J x B* force accelerates anodes (flyers) outward (Here 18-30 km/s)
- Asymmetric AK Gaps result in two different flyer velocities (two Hugoniot points per experiment)

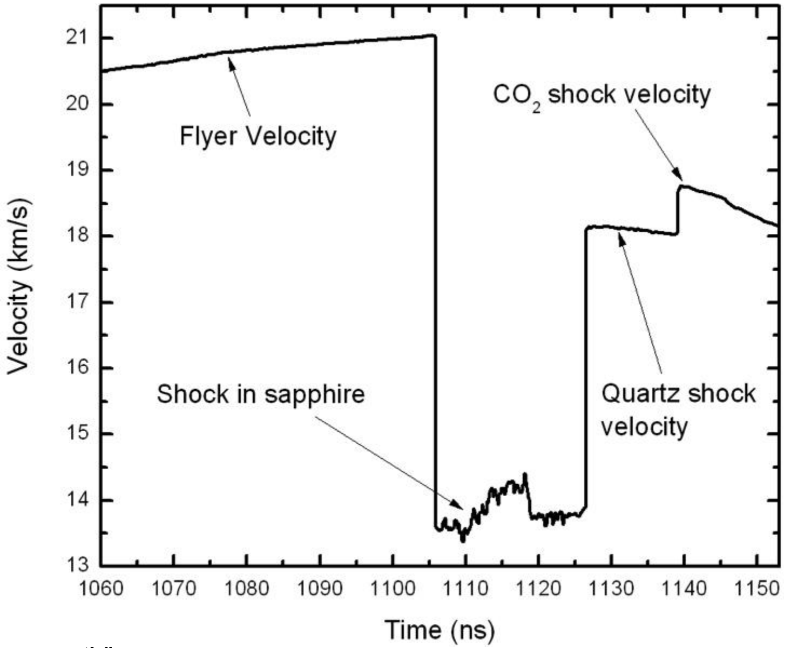
- Target filled to 16.7 PSI CO_2 at 220 K
- Designed the window thickness with margin for break
- Sapphire Reflective above 600 GPa
- Will use quartz plates to measure shock speeds at pressures lower than 600 GPa.
- **Expected CO2 pressure range: 150 GPa – 600 GPa**

We measure shock velocities in CO_2 and other transparent samples with sub-percent accuracy



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 CO_2 experiment with 21 km/s impact velocity

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The Monte Carlo Impedance match method provides accurate EOS and uncertainty information from the data

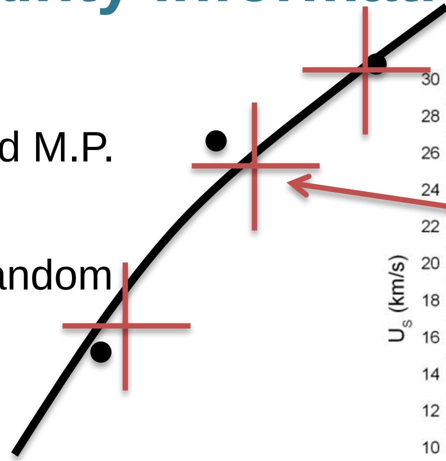
Quartz

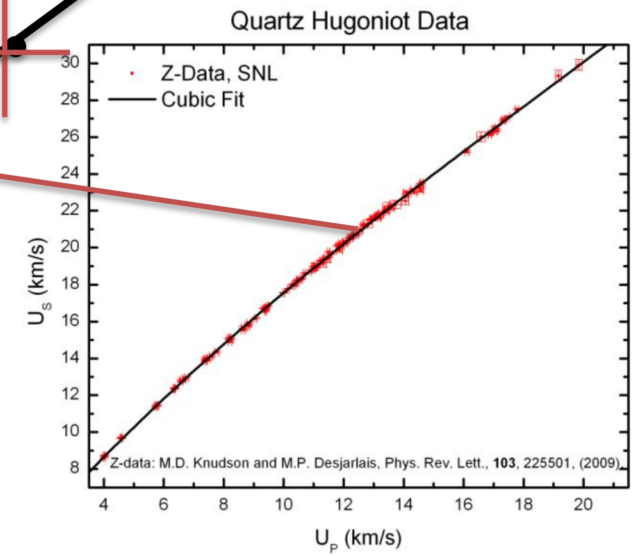
•180+ Hugoniot data points (M. Knudson and M.P. Desjarlais, PRL 2009)

• Varying each U_S - U_P by an *uncertorrelated* random number with σ = experimental uncertainty

• Solve for the cubic fit parameters

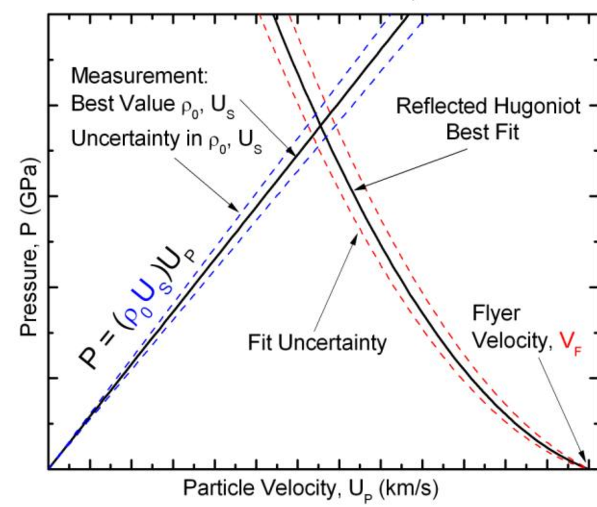
• Determine mean, σ, and correlation of fit parameters





For CO_2

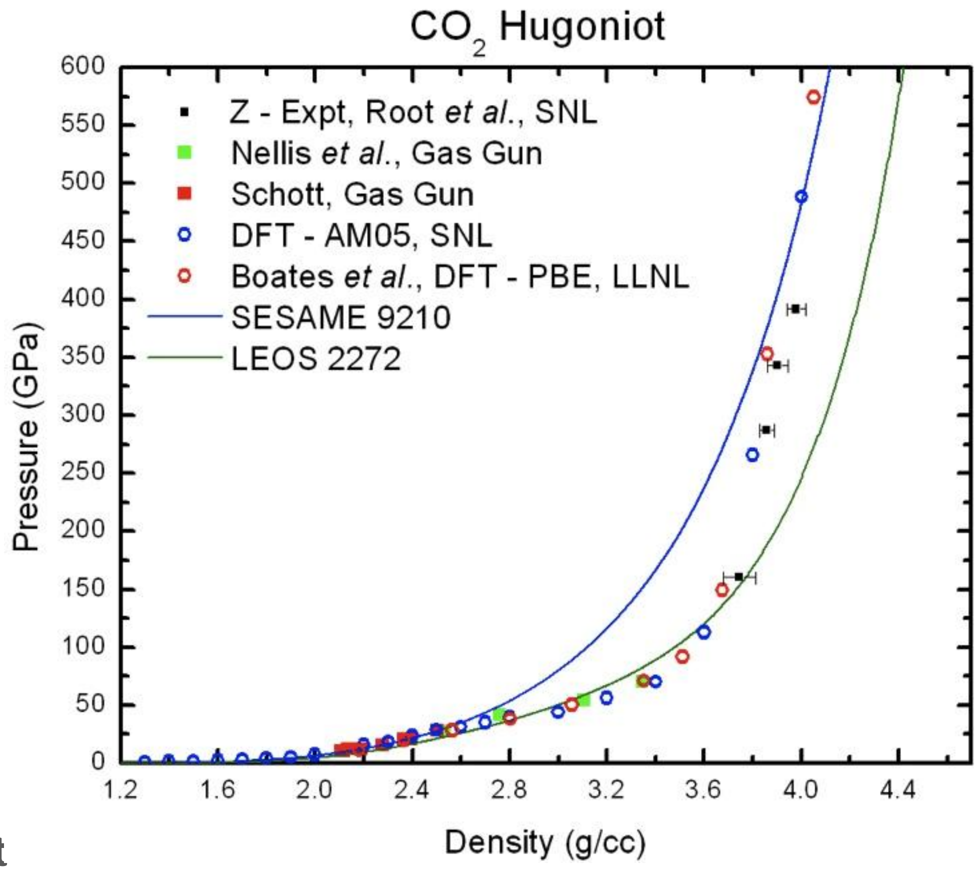
- Vary *measured* parameters V_F, U_S, ρ_0 by an *uncorrelated* random number with σ of experimental uncertainty
- Vary *quartz Hugoniot fit parameters* using *correlated* random numbers
- Calculate U_P, ρ, and P – determine the mean and σ



The reported uncertainties in the CO_2 data include the uncertainty in the quartz standard

Experiments on Z validate DFT simulations to 400 GPa – including the sharp rise post dissociation

- **DFT simulations**
  - Quantitative and qualitative agreement with Schott (High Press. Res. 6, 187 (1991)) and Nellis et al (J. Chem. Phys. 95, 5268 (1991)).
  - Minor difference between PBE and AM05 exchange-correlation functionals
  - Existing EOSs did not capture the full behavior
  - New EOS developed by Wu and Sterne at LLNL.
- **Z-experiments**
  - Reflected Hugoniot: expect -1% shift in density due to quartz release
  - 4 shots 100% data return
  - Reproducible initial state with tight temperature and pressure control



We measure a steep rise in shock pressure towards four-fold compression

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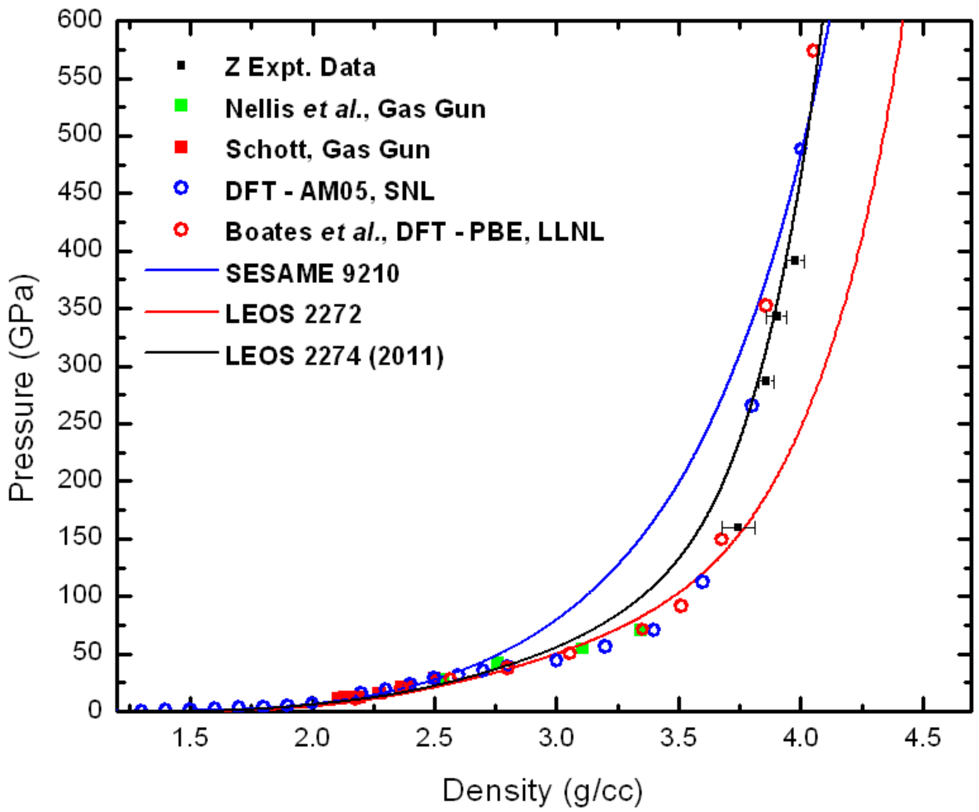
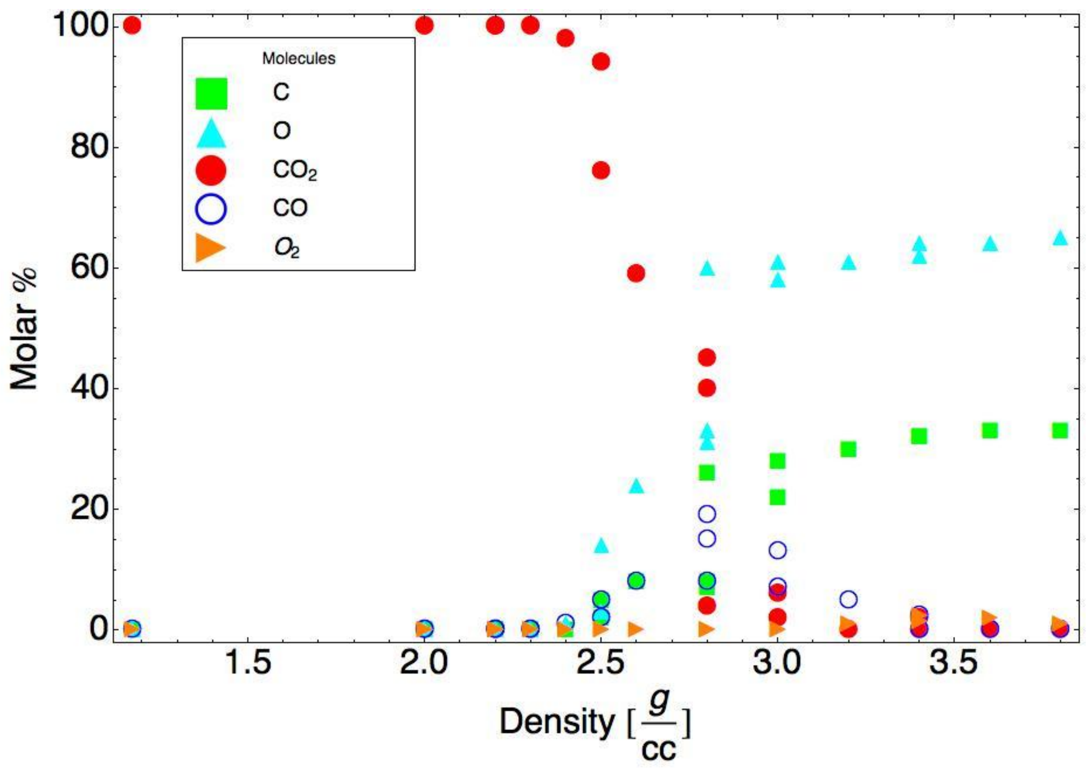


LEOS 2274, preliminary (C. Wu and P. Sterne, 2011).

DFT simulations contribute to understanding the physical behavior of the system

- **Shoulder in shock pressure**
  - Nellis et al attributed it to dissociation
- **We analyze the simulations along the Hugoniot**
  - Dissociation begins at 2.5 g/cm3 and is completed above 3.0 g/cm^3
  - Confirm dissociation as the cause for a shoulder in the Hugoniot pressure
- **After dissociation is complete, we predicted and measured a strong increase in shock pressure**



Mole % of CO, CO_2, O, C, and O_2 as a function of density along the Hugoniot

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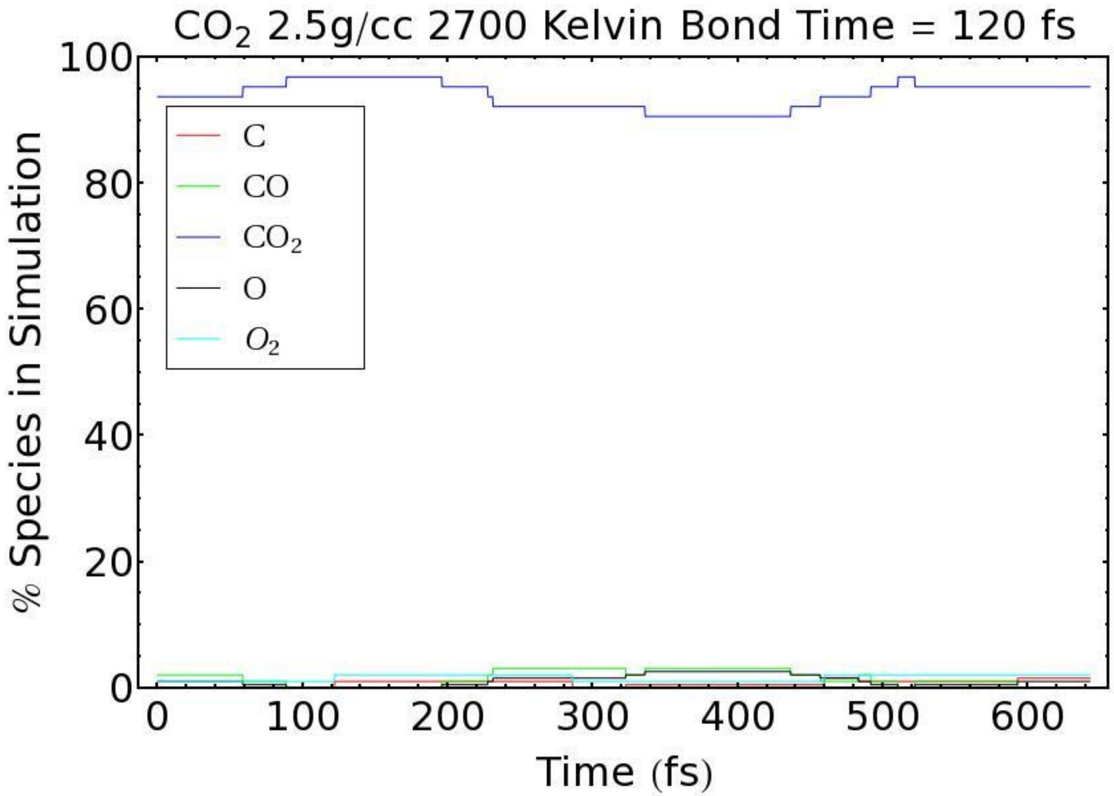

Chemical composition during the last 800 fs of a simulation

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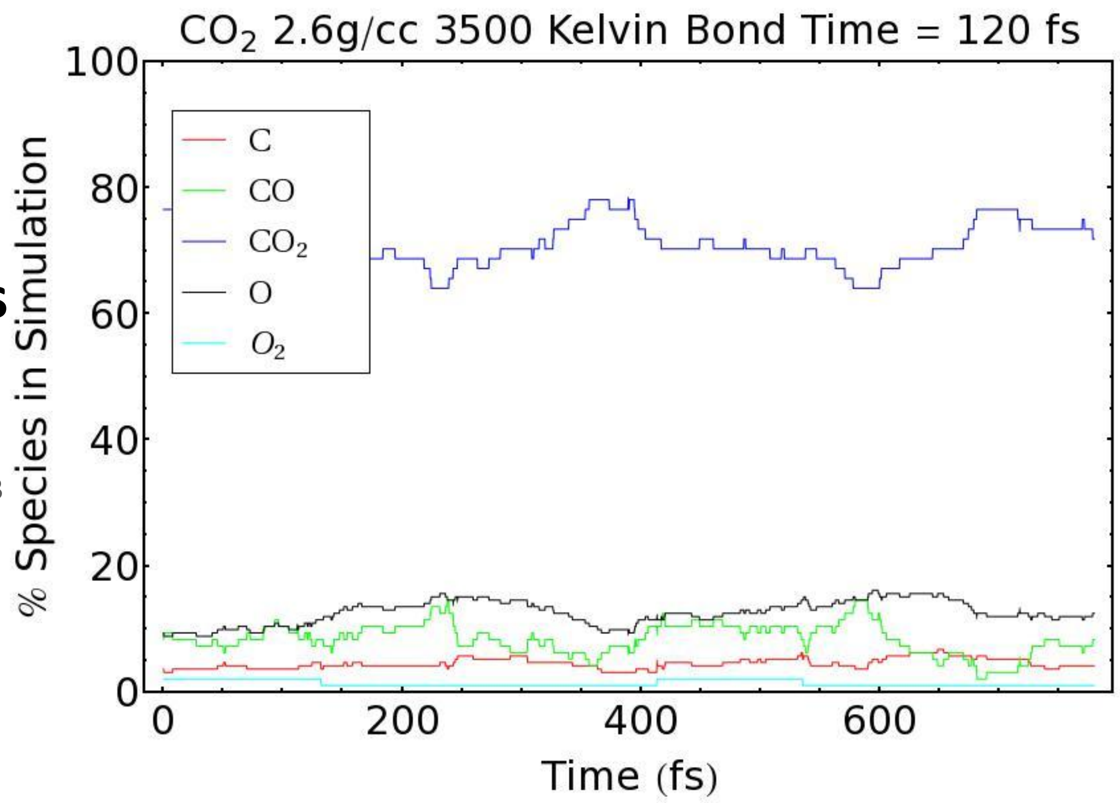

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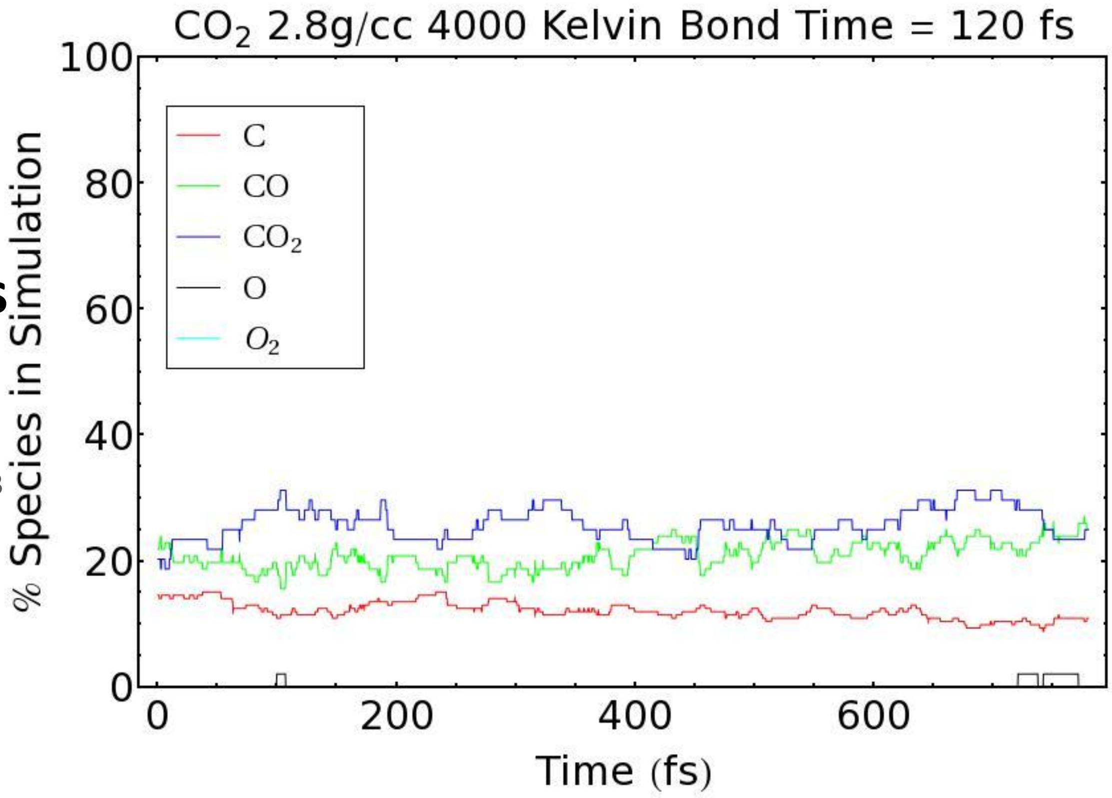
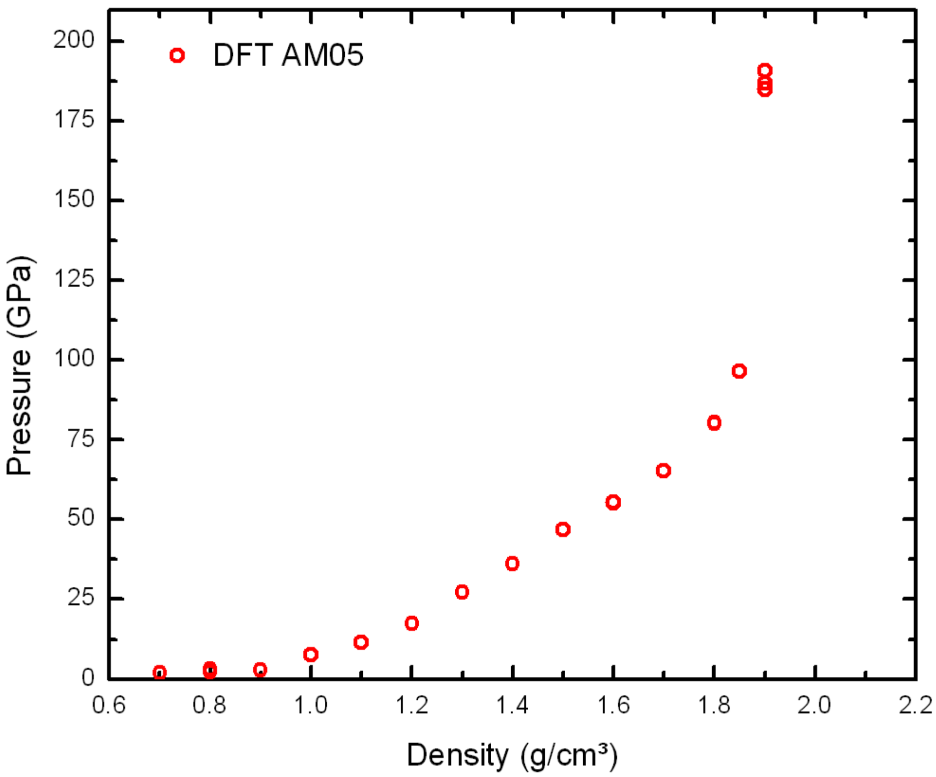


Chemical composition during the last 800 fs of a simulation

DFT/QMD simulations predicted the Hugoniot for ethane – shoulder at 50 GPa followed by a sharp rise

- **DFT simulations**
  - 64 molecules 512 atoms
  - Complex k-point (0.25,0.25,0.25)
  - 800/1600 eV plane-wave energy
  - Well described shoulder/dissociation
  - 0.56 g/cm³; 163 K initial state

Principal Hugoniot for liquid ethane

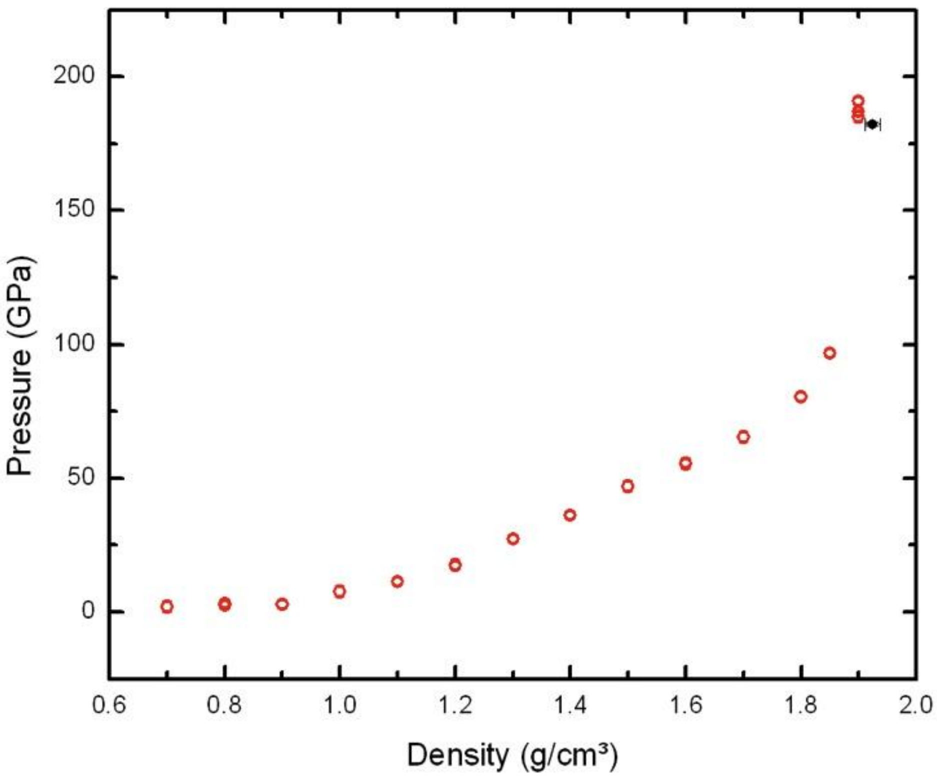


See Kyle's poster for more results on hydrocarbons

Initial data from Z validates the DFT/QMD results – obtaining a shock pressure of 180 GPa

- **DFT simulations**
  - 64 molecules 512 atoms
  - Complex k-point (0.25,0.25,0.25)
  - 800/1600 eV plane-wave energy
  - Well described shoulder/dissociation
  - 0.56 g/cm^3; 163 K initial state
- **Z-experiments**
  - Initial results at 180 GPa
  - Will continue the experimental series
  - Temperature measurements using optical pyrometry – analysis in progress will add new data to EOS comparisons

Principal Hugoniot for liquid ethane



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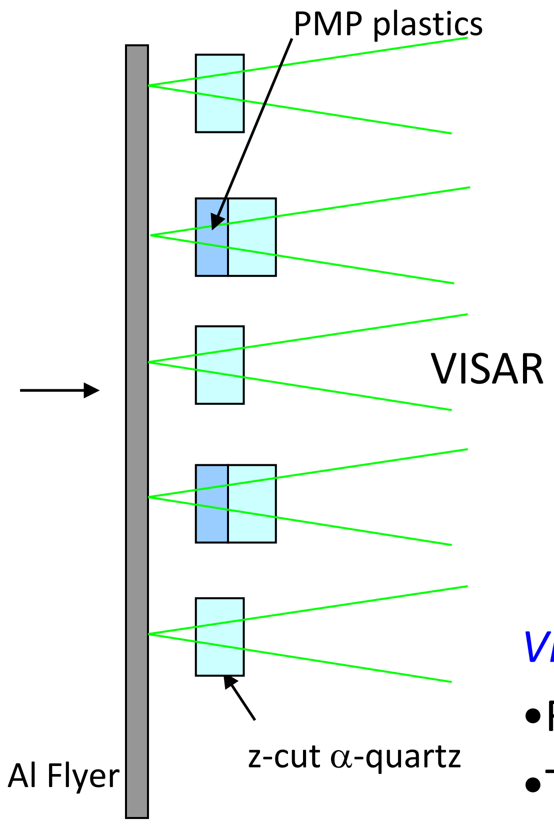
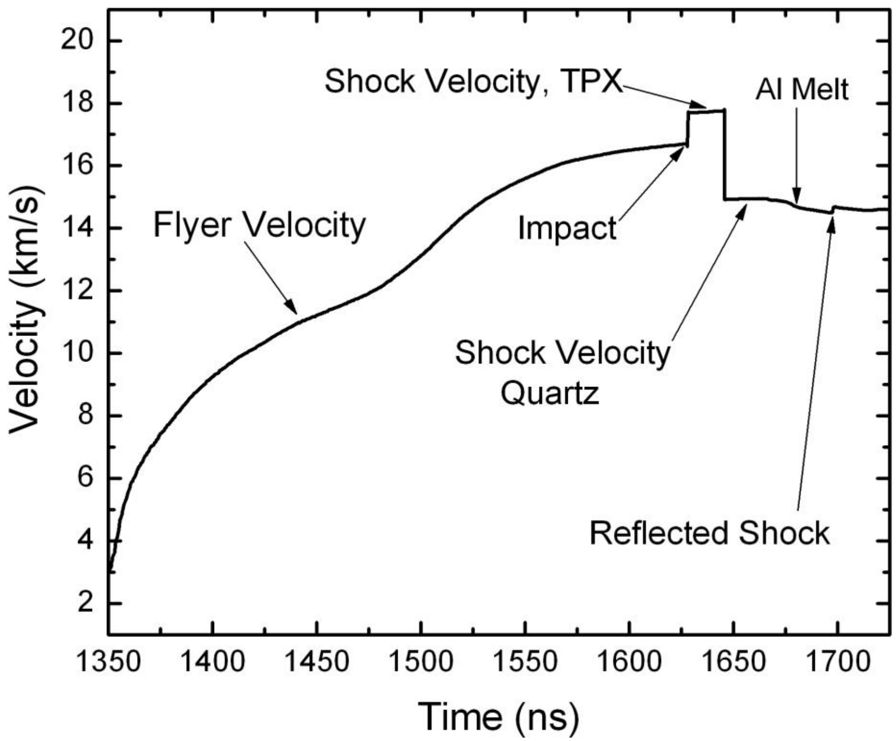
We measure shock velocities in plastic and other transparent materials with sub-percent accuracy



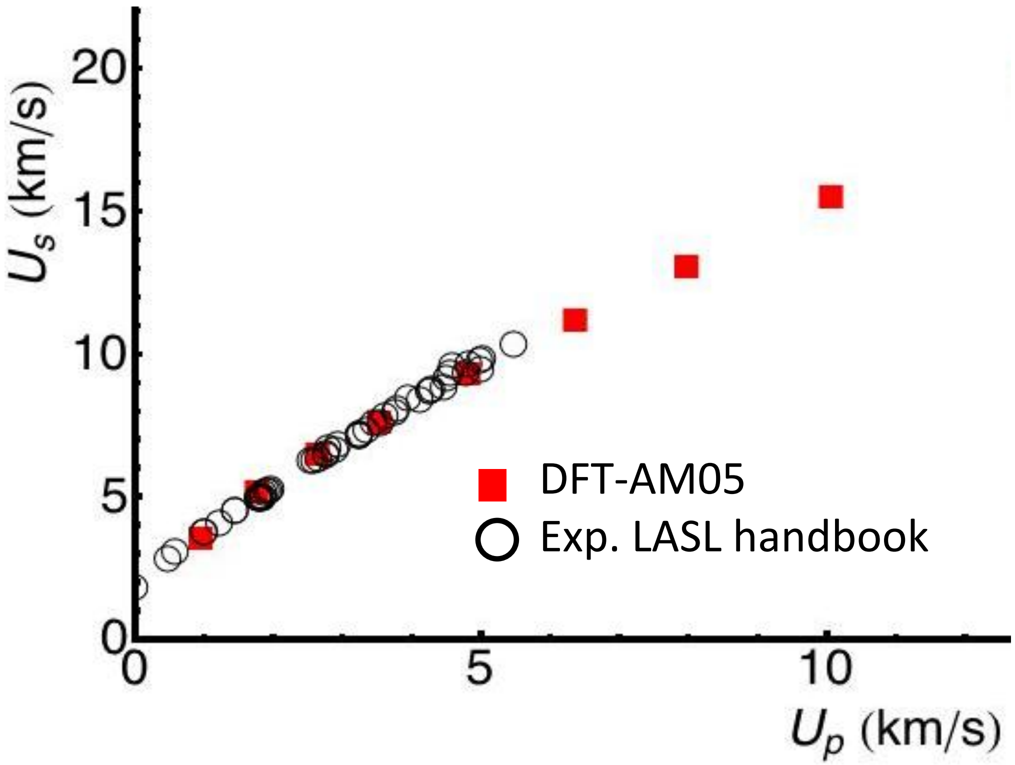


VISAR measurements as main tool:

- Flyer velocity
- Time of impact
- Shock arrival at plastics/quartz interface
- Shock velocity in sample and breakout time
- *Steady shocks, large samples, and long times yield high precision measurements*

DFT-AM05 is of high fidelity for shock compression of poly(4-methyl 1-pentene) (PMP) to 50 GPa

Principal Hugoniot for poly(4-methyl 1-pentene)

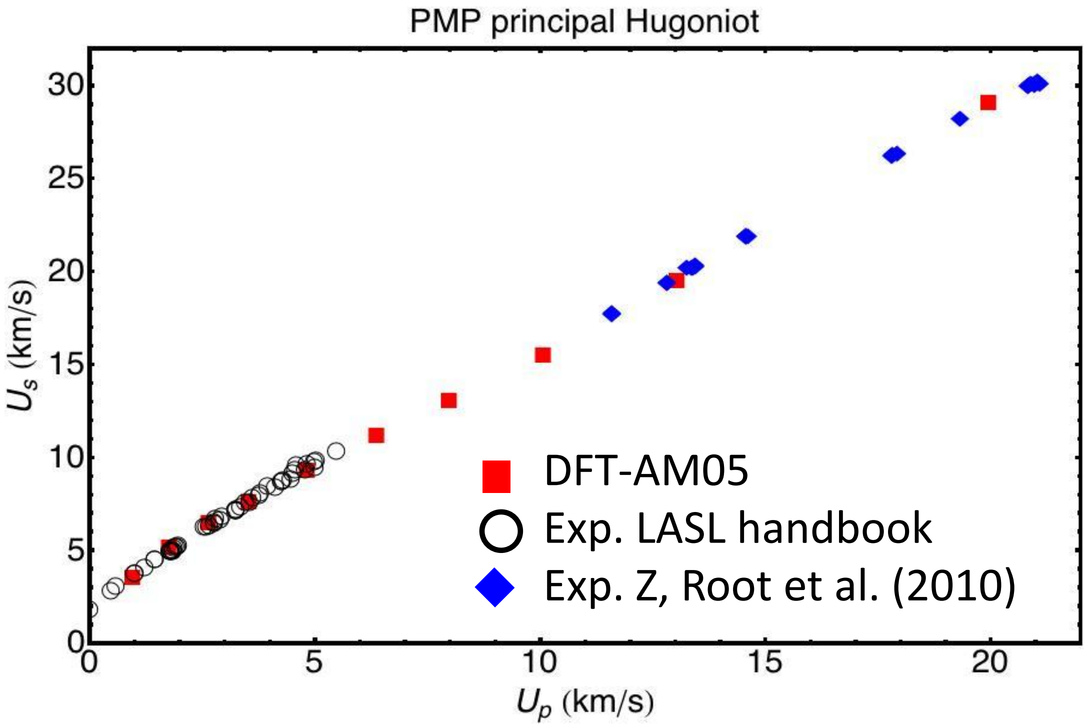


T.R. Mattsson et al. Phys. Rev. B **81**, 054103 (2010).

- 440 atom simulations
- DFT-AM05 is of high fidelity also for PMP
- Curvature for low shock speeds

Results from recent shock experiments on Z for poly(4-methyl 1-pentene)

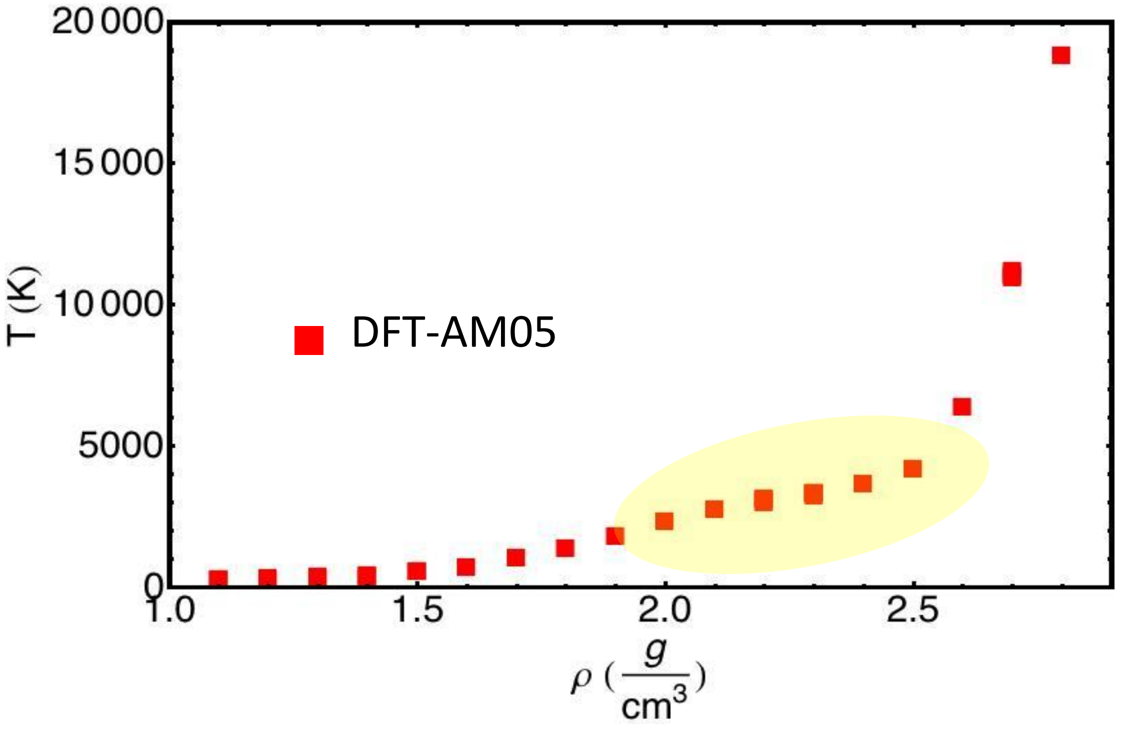
Principal Hugoniot for poly(4-methyl 1-pentene)



- Shock experiments up to 30 km/s shock velocity
- 200 – 530 GPa pressure
- *Also polymers can be modeled with high fidelity using DFT-AM05*
- Promising for extending beyond plastics to foams

Simulations allow a detailed analysis of the physics and chemistry of shock compression of hydrocarbon polymers

Temperature along the Hugoniot for polyethylene

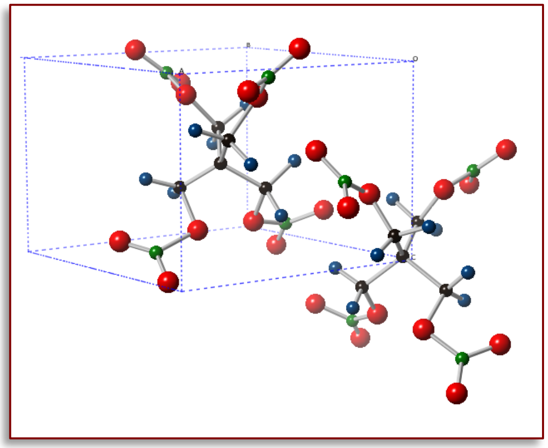


T.R. Mattsson et al. Phys. Rev. B 81, 054103 (2010).

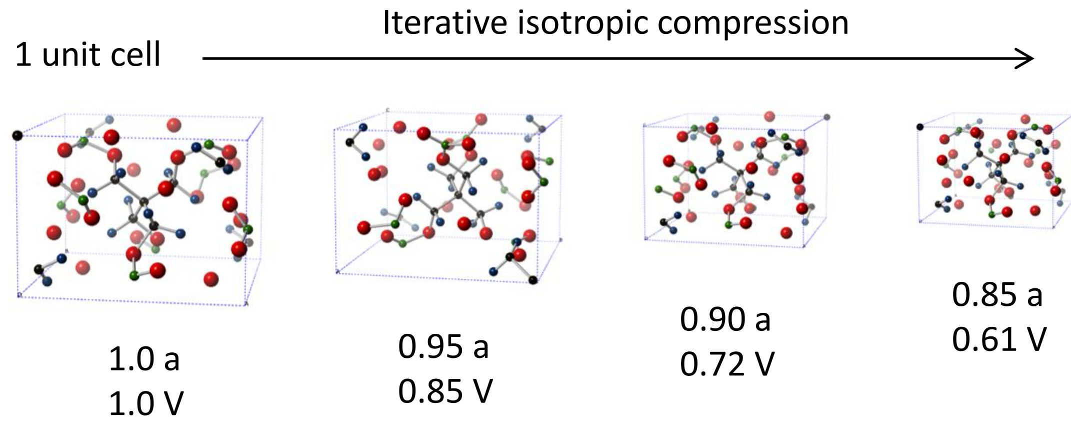
- Temperature is the missing link in P/rho; Us/Up analysis
- *Temperature almost flat during the shoulder in pressure*
- Detailed modeling of chemistry during the shock compression
- *Temperature measurements are being introduced on Z*

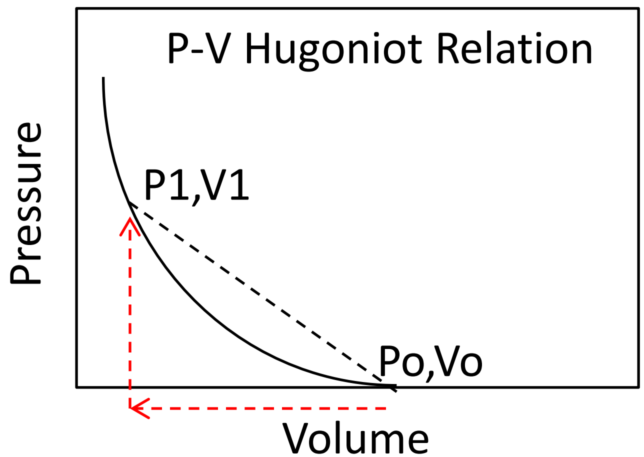
We compress PETN in the simulations and tune the temperature to locate the Hugoniot State (P,T,E)

Density Functional Theory based Molecular Dynamics (DFT-MD)

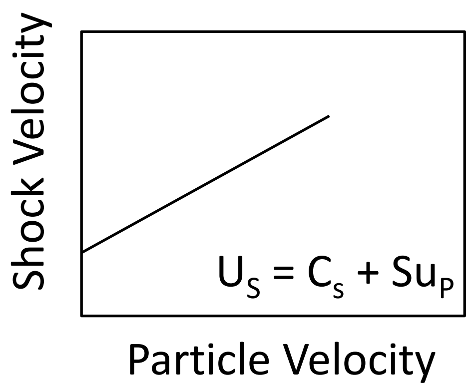


PETN, V_o at 300K





U_S-u_P Hugoniot Relation

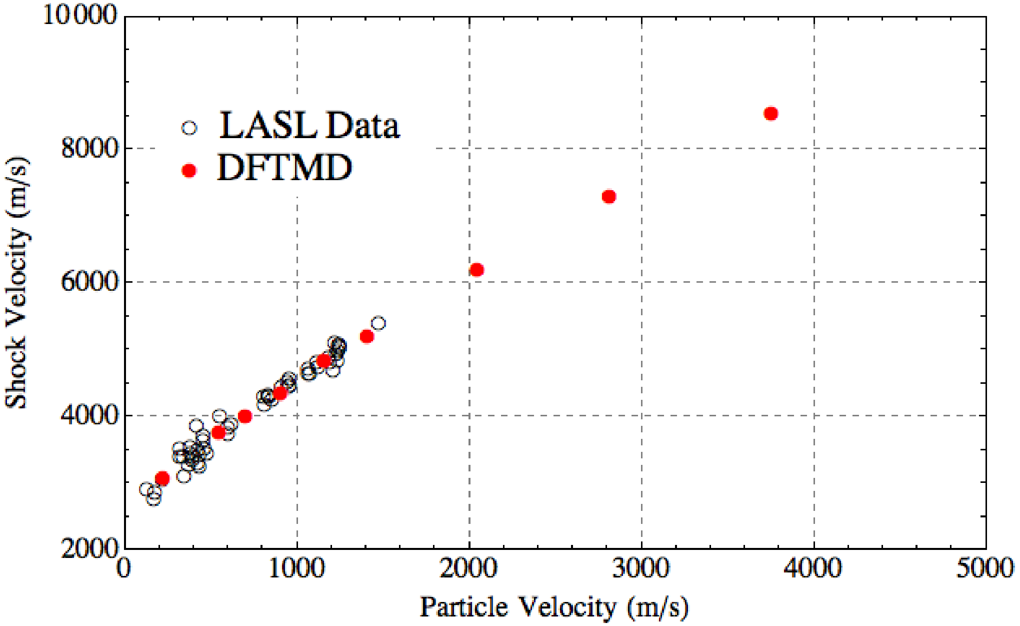


Mass Momentum Energy

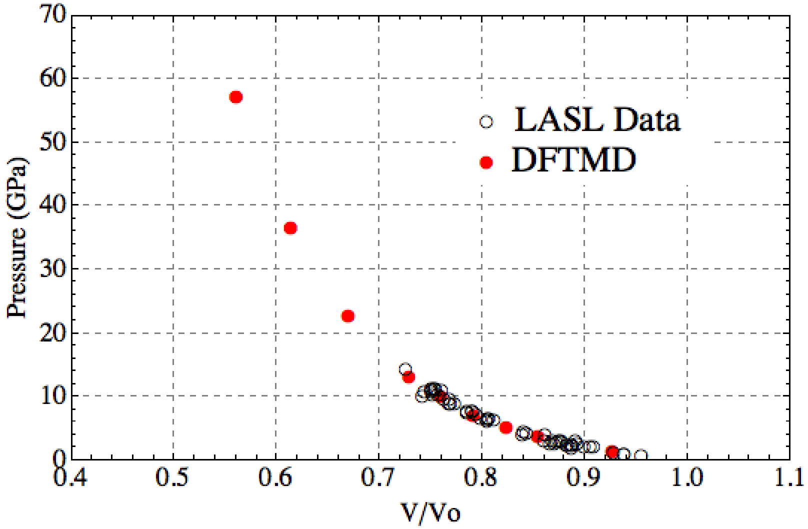
$$\rho_o D = \rho_1 (D - u_1)$$
$$P_1 = \rho_o D u_1$$
$$E - Eo = \tfrac{1}{2}(P + Po)(Vo - V)$$

Employed DFT-MD to calculate the PETN crystalline Hugoniot to 60 GPa; validating the approach to LASL data

Single Crystal Data



P-V Hugoniot



We obtain the un-detonated Hugoniot well above experimentally accessible regimes and reproduce low-pressure data

Ryan Wixom's poster yesterday and Mattsson, Wixom, Mattsson, Proceedings to the 14th international Detonation Symposium (2010).

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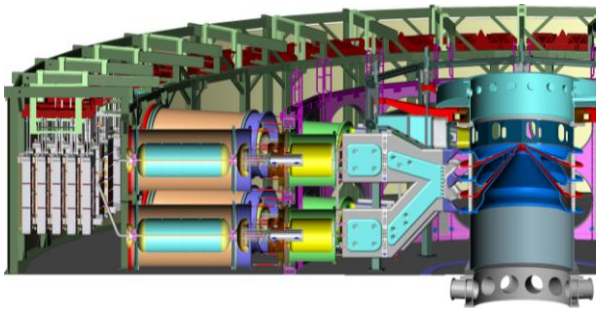
Integration of DFT/QMD and high-precision multi-Mbar experiments on Z serve as a solid foundation for understanding chemistry in dynamic extremes

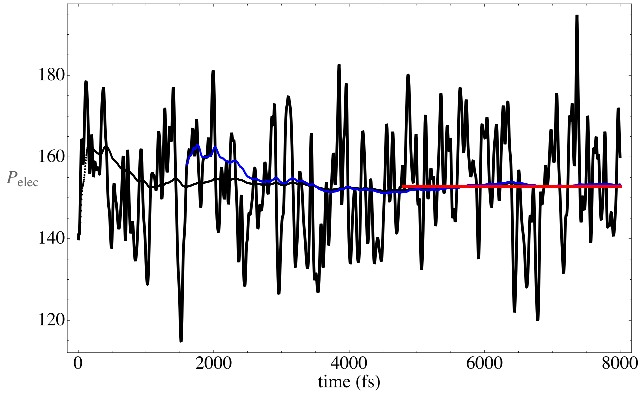
- **Employed DFT based MD simulations to model shock compression of CO_2, C_2H_6, CH_2, and PETN**
  - Agreement with existing data
  - Confirm a CO_2 dissociation plateau at 60 GPa
  - Predictions for shock compression to 500 GPa in CO_2
  - Steep rise in shock pressure following the dissociation region for several materials with chemistry
- **Executed experiments on Z to measure the shock Hugoniot of CO_2, C_2H_6, and CH_2**
  - High-precision measurements can distinguish between different EOS models
  - Broad platform for studying cryogenic liquids up to initial pressures of 1 MPa
  - Temperature measurements coming online - exciting

Acknowledgments

- The large team operating the Z-machine – Mike Lopez
- The cryogenic team – Dave Hanson, Andrew Lopez, Keegan Shelton, and Jose Villalva
- Sandia High-Performing Computing – Sophia Corwell
- Program leadership – Dawn Flicker and Mark Herrmann
- Scientific leadership – Mike Desjarlais



Shock experiments on Sandia's Z machine



Density Functional Theory simulations

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