SAND2013-10295C

Thermec 2013
Materials Under Extreme Conditions, Las Vegas, NV
6 December 2013

Shock compression of porous soft and hard materials using atomistic simulation

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SAND 2013-

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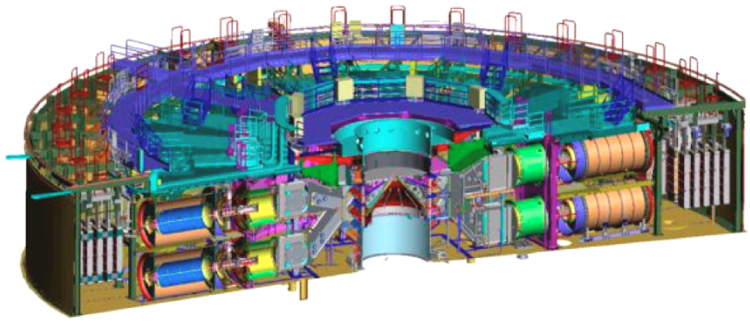
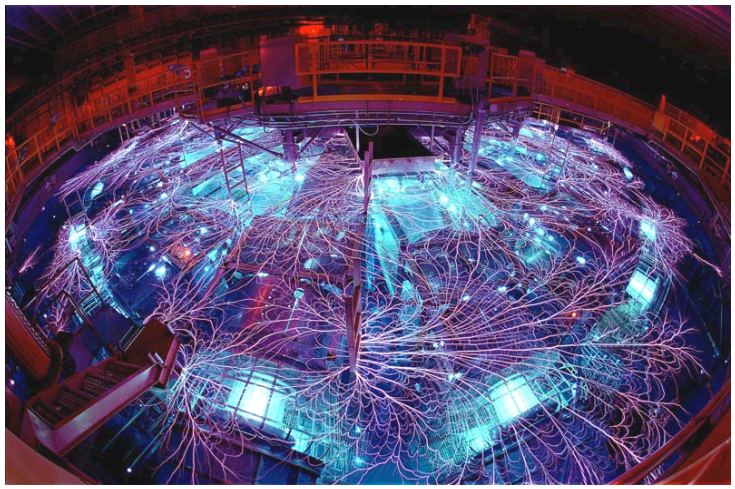
Motivation for polymer shock simulation

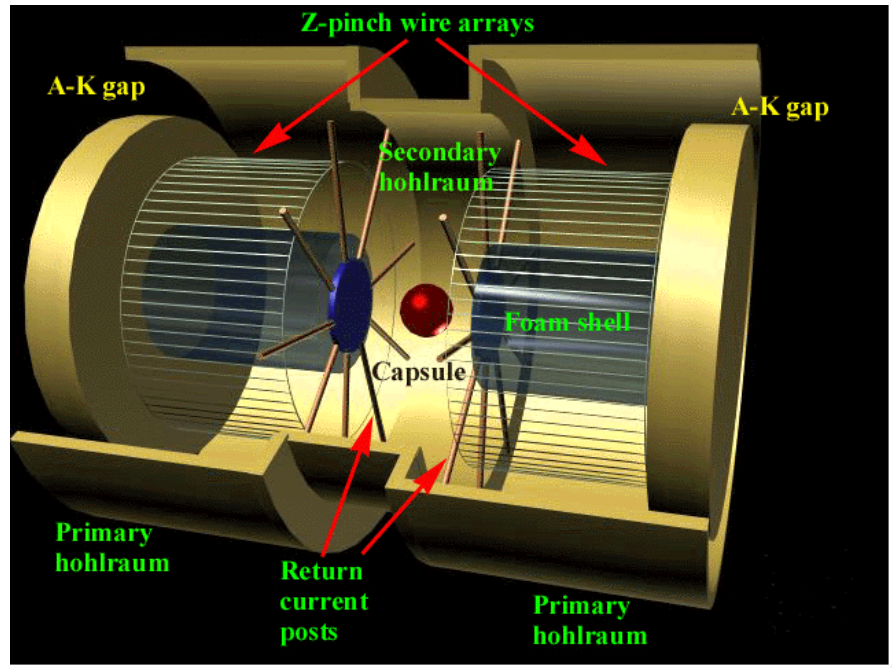
Z-machine at Sandia National Labs





Z-machine experiments allow:

- Extremely high-pressure shock studies
- Inertial confinement fusion (ICF) research
- Better understand EOS for polymers and mixtures

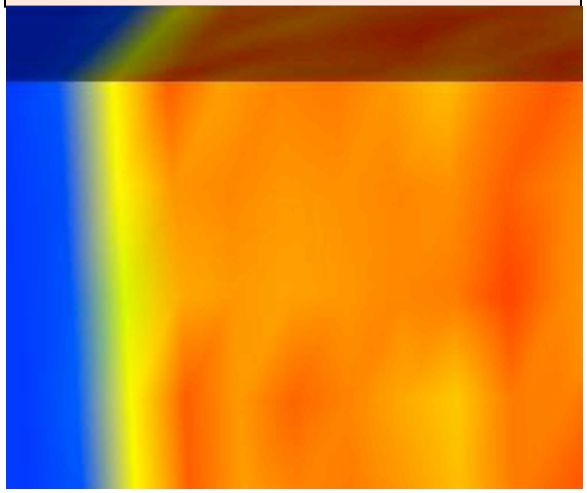


Double-ended Z pinch with foam-shell capsule

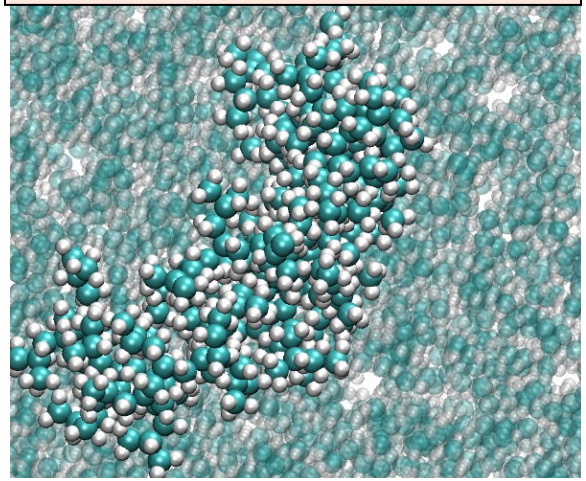
Hierarchy of modeling approaches

Shock response in hydrocarbon foams depend on processes and structure at several length scales:

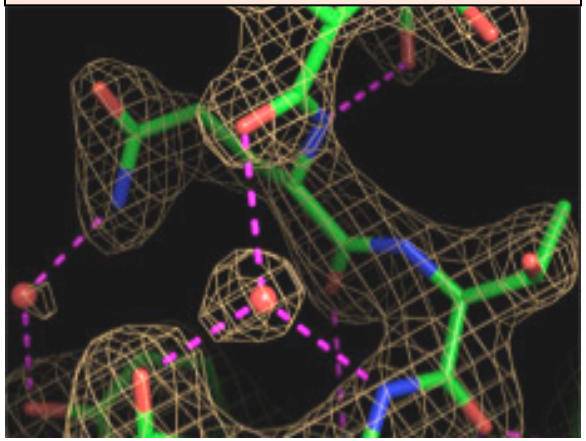
Continuum scale
μs times & nm-mm lengths



Molecular scale
ns times & 10s nm lengths

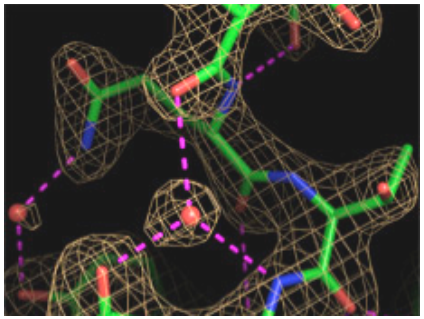


Quantum scale
fs times & Å lengths

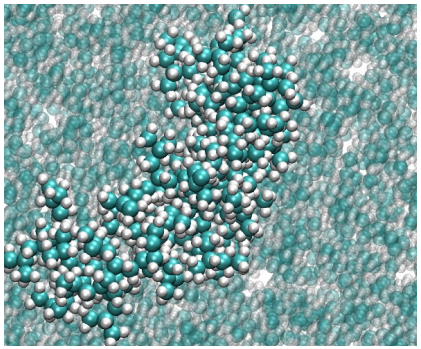


Increasing time and length scales

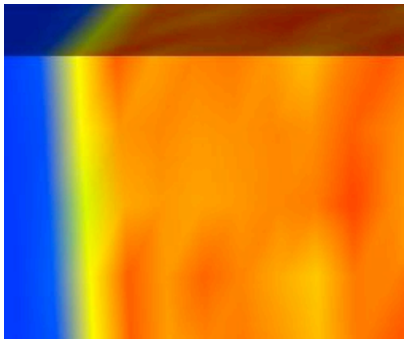
Hierarchy of modeling approaches



- VASP 5.1 code (Georg Kresse, Vienna, Austria)
- Plane-wave basis allows controlled convergence & free electrons/ionization
- Finite-temperature DFT with Projector augmented wave core functions (PAW)
- Sandia developed AM05 functional (Armiento & Mattsson, Phys Rev B 2005)
- Cochrane, et al., *Shock Compression in Condensed Matter Proceedings.* (2011)

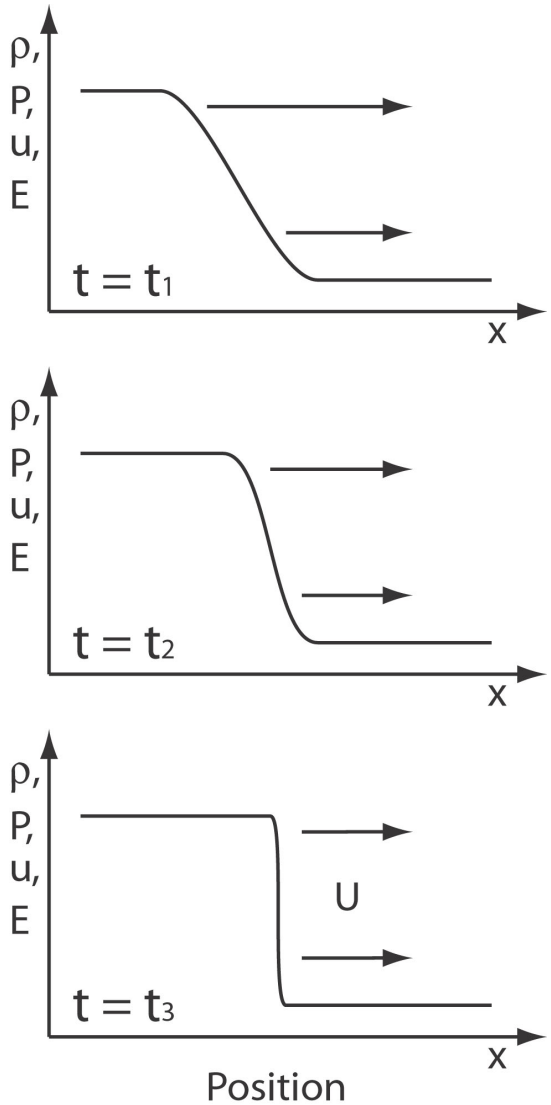


- LAMMPS code (Steve Plimpton, et al., Sandia National Labs)
- MD engine for atoms, molecules, or particles at any length/time scale
- Multiple common interatomic potentials allows for comparison
- Integrated MPI for massively parallel simulations
- http://lammps.sandia.gov
- Lane, et al., *Shock Compression in Condensed Matter Proceedings.* (2011)



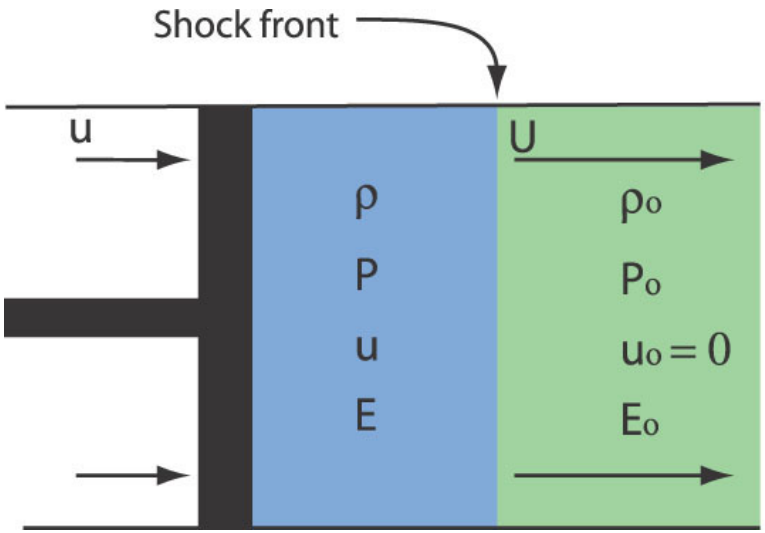
- ALEGRA code (Sandia National Labs)
- MHD engine for 3D modeling of continuum systems
- Mesoscale response with multiple physics models
- http://www.cs.sandia.gov/ALEGRA
- Haill, et al., *Shock Compression in Condensed Matter Proceedings.* (2011)

Shock physics background in 3 slides



1. For most materials, where wave speed increases with pressure, strong pressure pulses (finite amplitude disturbances) sharpen.

Shock physics background in 3 slides



1. For most materials, where wave speed increases with pressure, strong pressure pulses (finite amplitude disturbances) sharpen.

2. If a shock discontinuity exists then 3 quantities are conserved across the front which constrain the final state. But these contraints called "jump conditions" only hold when the front is steady.

Mass:

$$\begin{aligned} \rho_0(U\Delta t)A &= \rho((U-u)\Delta t)A \\ \rho_0 U &= \rho(U-u) \end{aligned}$$

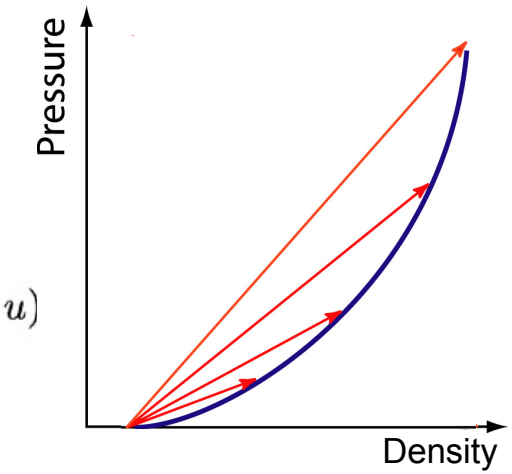
Momentum:

$$\begin{aligned} (P-P_0)A\Delta t &= (\rho_0(U\Delta t)A)(u-0) \\ P-P_0 &= \rho_0 U u \end{aligned}$$

Energy:

$$Pu\Delta t = 1/2(\rho_0 U u^2)\Delta t + \rho_0 U(E-E_0)\Delta t$$

Shock physics background in 3 slides



$$\rho_0 U = \rho(U - u)$$

$$P - P_0 = \rho_0 U u$$

$$(E - E_0) = P\left(\frac{1}{\rho_o} - \frac{1}{\rho}\right) - \frac{u^2}{2}$$

$$E = E\left(P, \frac{1}{\rho}\right)$$

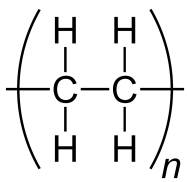
3 jump conditions
<u>+ 1 equation of state</u>
= 4 eqns for 5 unknowns

1. For most materials, where wave speed increases with pressure, strong pressure pulses (finite amplitude disturbances) sharpen.

2. If a shock discontinuity exists then 3 quantities are conserved across the front which constrain the final state. But these contraints called "jump conditions" only hold when the front is steady.

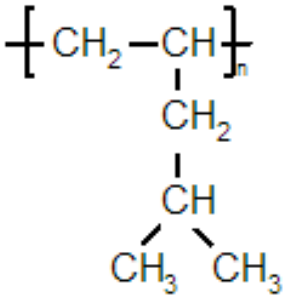
3. The jump conditions with the material specific Equation of State combine to define a Hugoniot curve which is the collection of possible shock final states. Each complete shock experiment produces a single point on the Hugoniot relating any two final state variables.

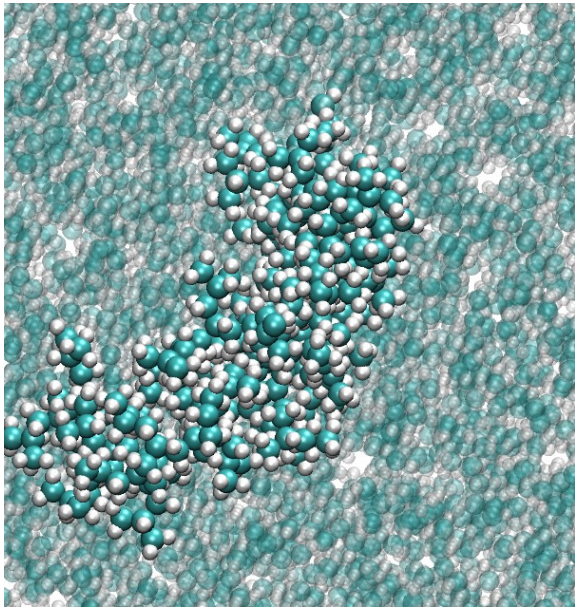
Dense polymer simulation



Polyethylene - simplest possible linear carbon backbone structure forms semi-crystalline solids

PMP (TPX) - branched hydrocarbon with bulky side chains which is good for producing amorphous foams





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

Molecular Dynamics

OPLS, Jorgensen et al., JACS, 118, 11225 (1996)

Borodin-Smith exp-6, JPCB, 110, 6279 (2006)

AIREBO, Stuart et al., JCP, 112, 6472 (2000)

ReaxFF, vanDuin et al., JPCA, 112, 1040 (2008)

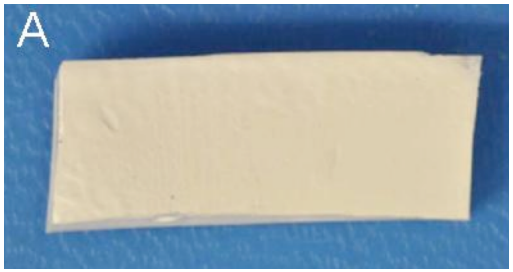
- 22,000+ atom PE sample and 45,000+ atom PMP
- Uniaxial Hugoniotstat method used to compress

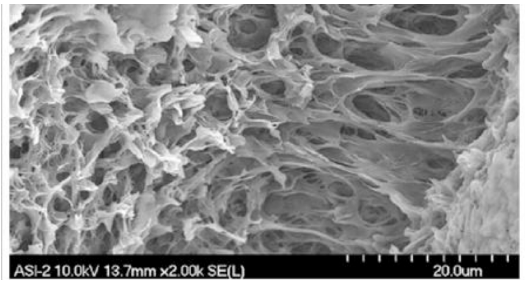
Density Functional Theory

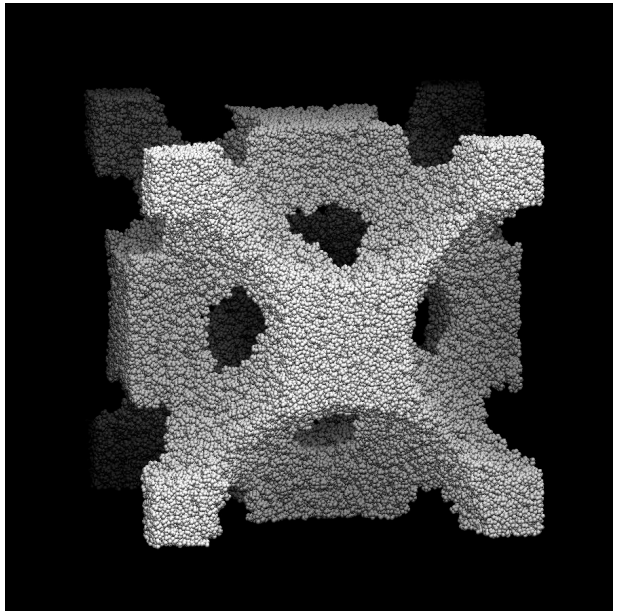
AM05 Functional

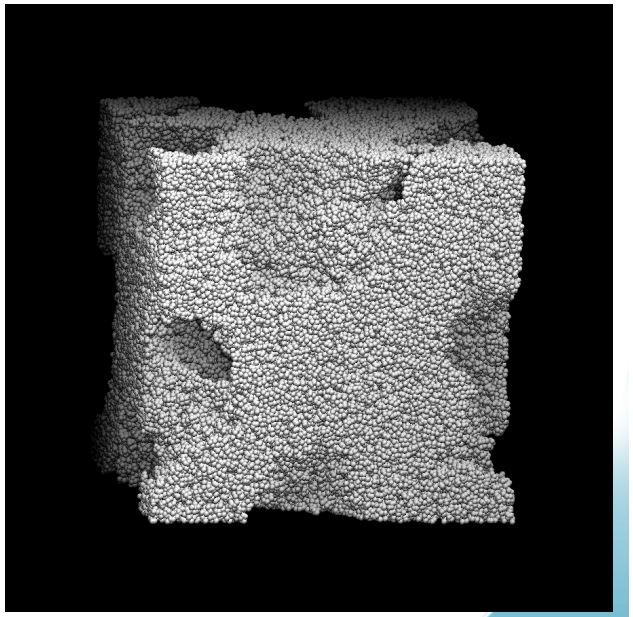
- Several hundred atom samples of PE and PMP

Foam introduction









Densities

- Experimental foam – 0.309 +/- 0.025 g/cc
- Simulated foam – 0.300 g/cc

Experimental fabrication:

- 0.833 g/cc PMP dissolved in cyclohexane & evaporated

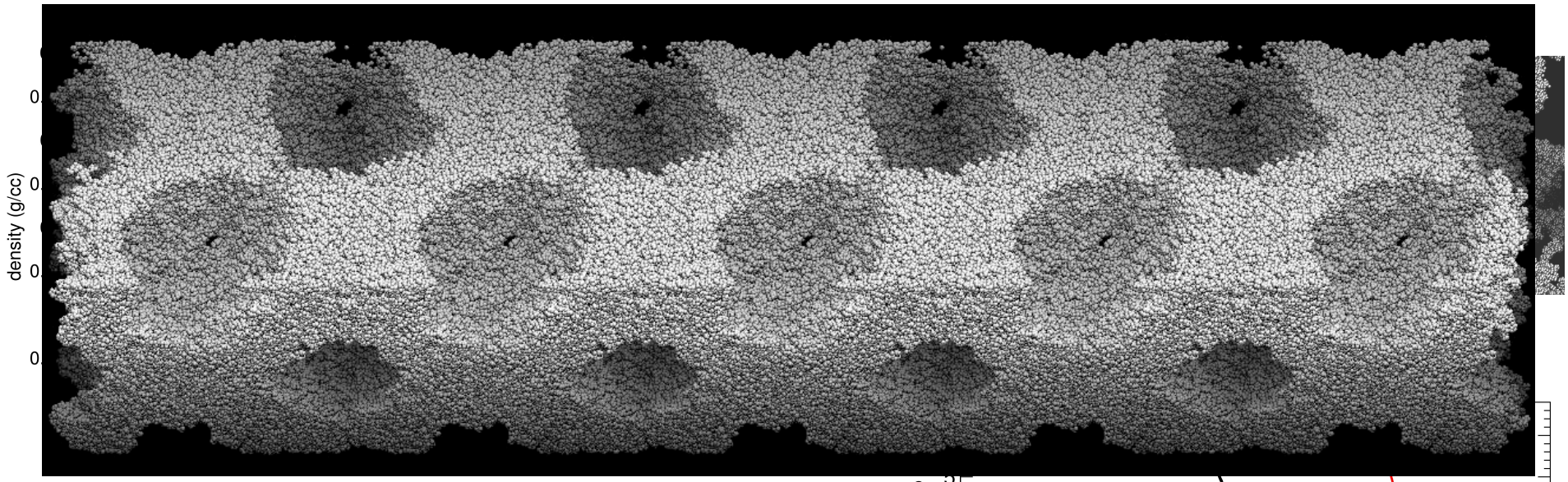
Simulation fabrication:

- 0.833 g/cc PMP perforated with growing spherical indenters placed on an fcc lattice, creating a unit cell of foam with unit cell of 20x20x20 nm.

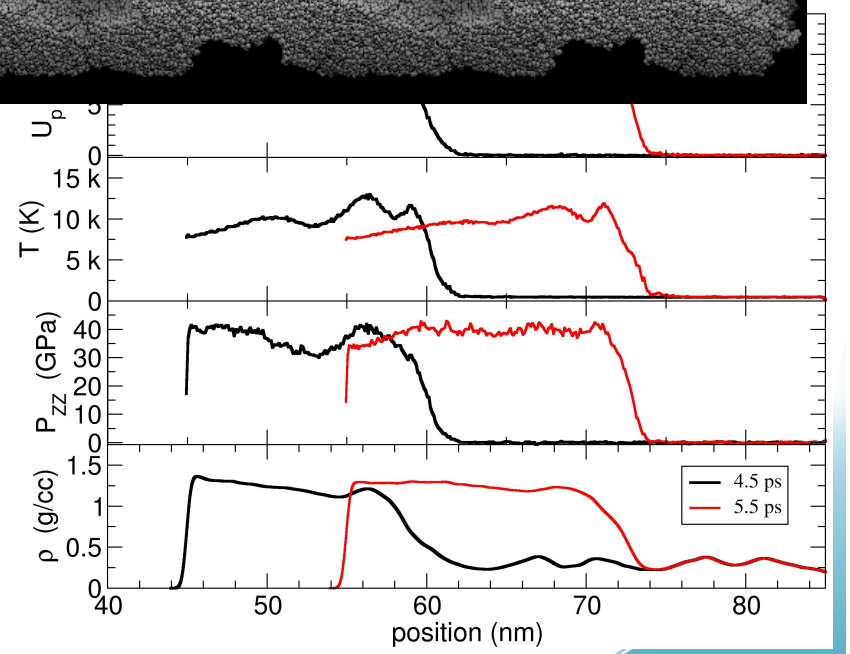
ReaxFF potential was used exclusively.

Lane, et al., APS SCCM Proc. (2011)
Root, et al., (submitted JAP)

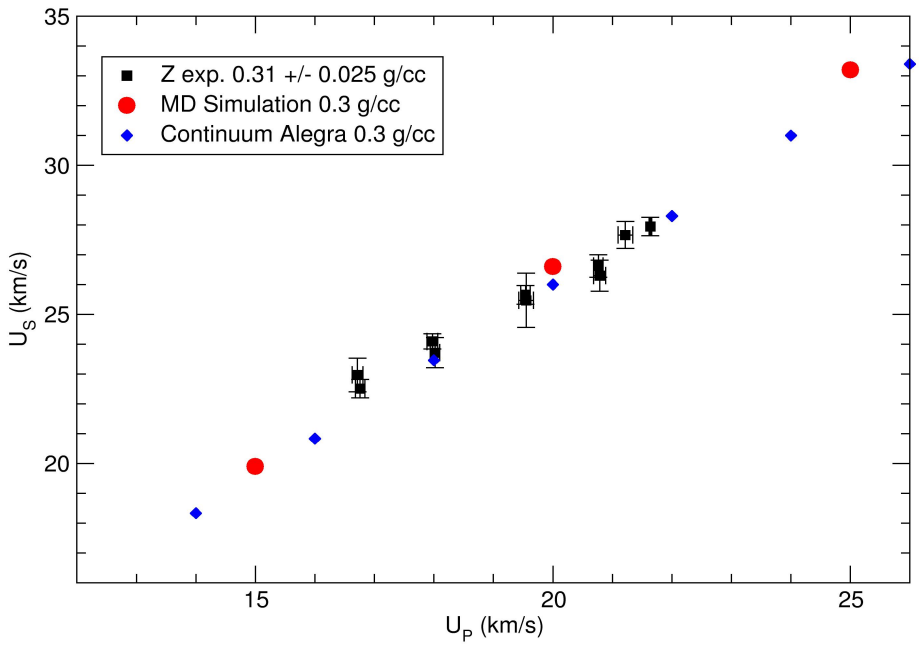
Foam shock methodology

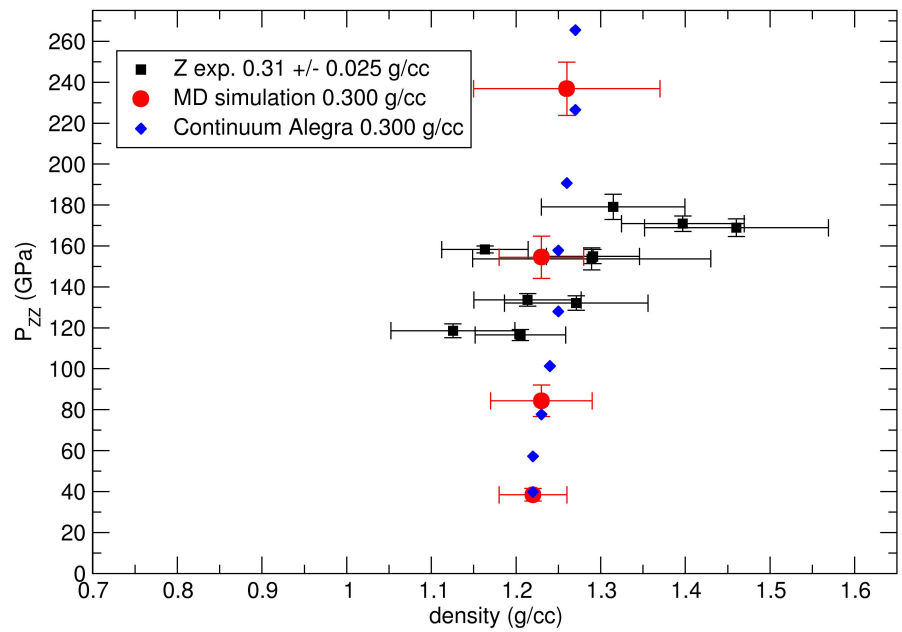


- Shock Hugoniotstat method could not be used, so long simples were constructed from foam unit cells.
- Shock is driven by warm momentum mirror using standard NEMD techniques.
  - Piston velocities ranged from 10 to 30 km/s.
  - Very short simulation timesteps (0.01 to 0.05 fs) were required
- Profiles were calculated from per-atom variables



Foam results – Hugoniot data

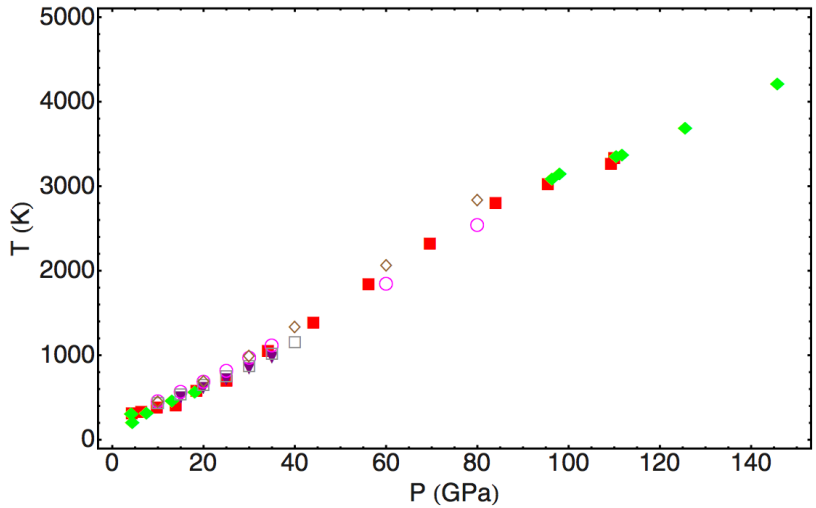


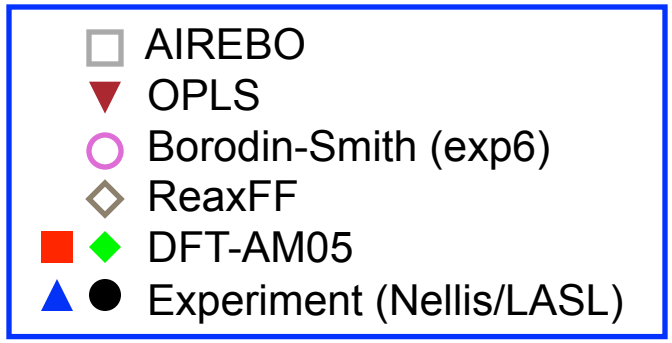


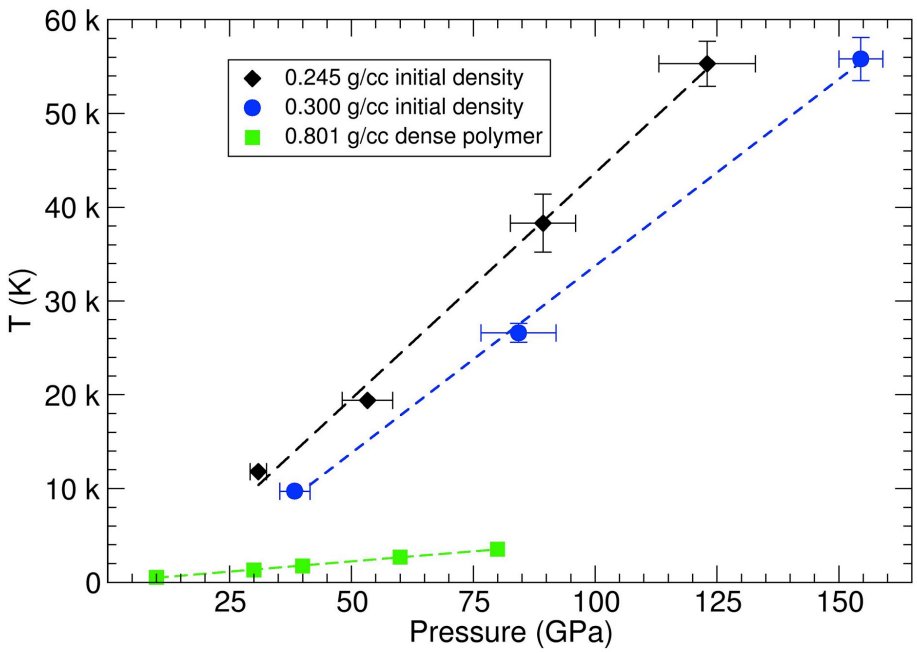
- Good quantitative agreement between Z experimental data, and both MD and continuum simulations for ~ 0.310 g/cc foam shock loading

- Spread in experimental data comes from variation is sample density and inhomogeneity.

Temperature dense polymer vs foam





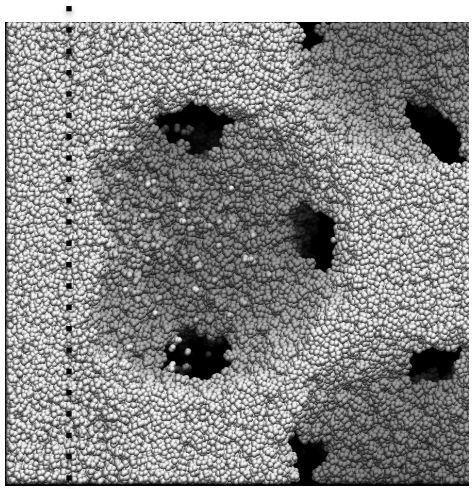


Temperatures in dense polymer were < 5000 K through 150 GPA

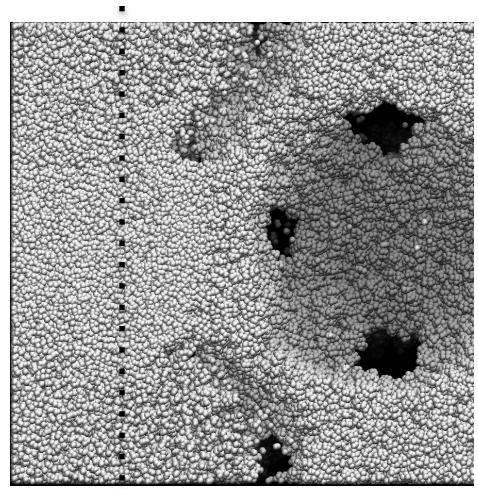
Temperatures in foams spike comparatively higher, driving dissociation at much lower densities and pressures

Spatially-resolved temperature hotspots

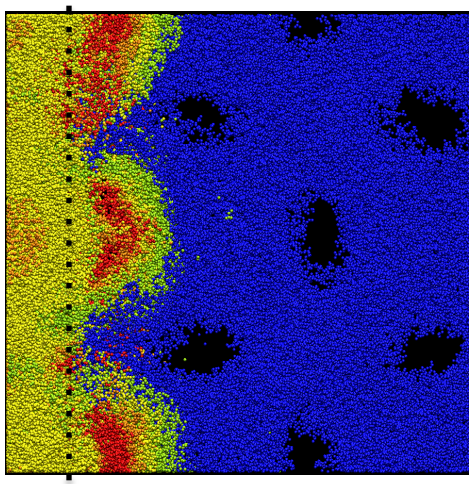
10 km/s piston velocity, final state ~40 GPa, 1.23 g/cc, ~10,000 K



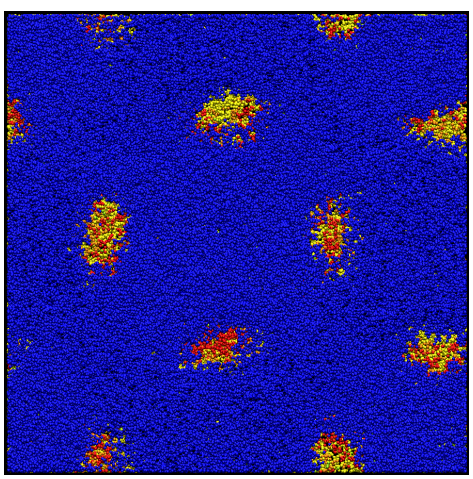
timesteps
< 1ps



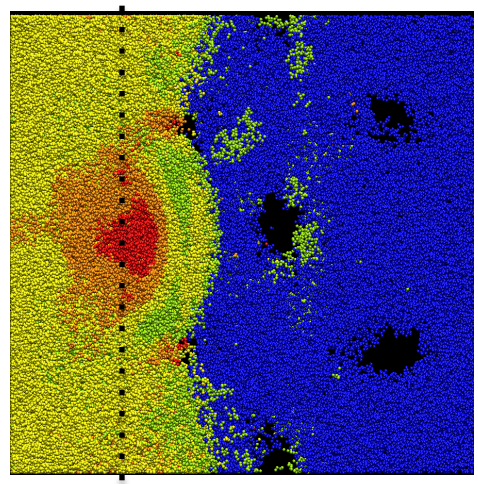
T=50k timesteps
~ 1ps



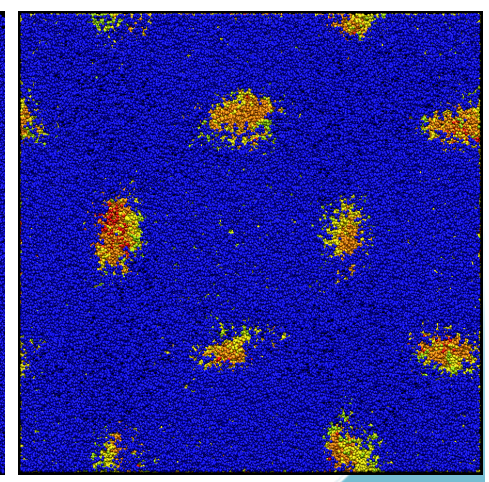
Temperature
Side view



Temperature
On-axis view



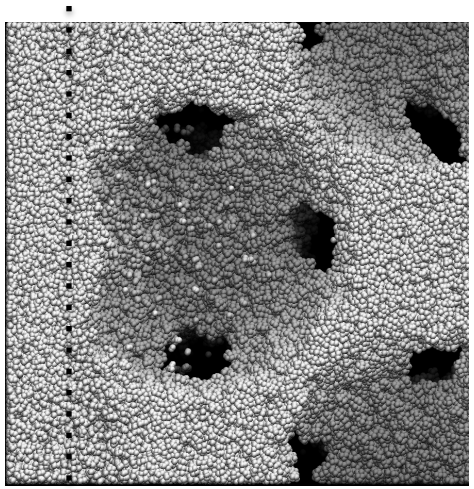
Temperature
Side view



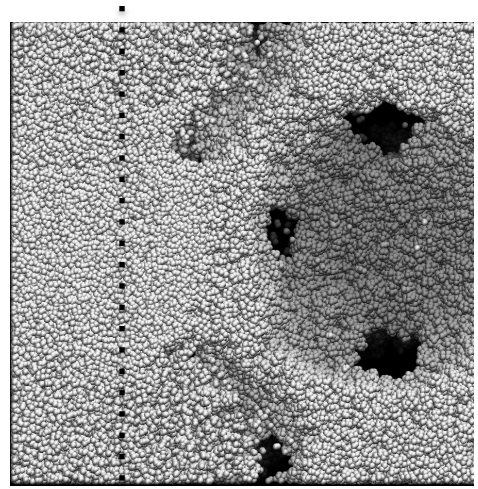
Temperature
On-axis view

Spatially-resolved temperature hotspots

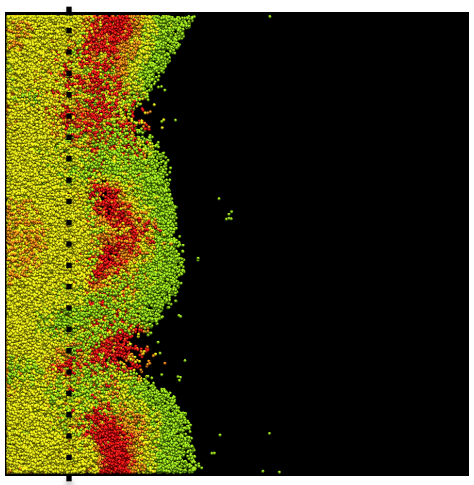
10 km/s piston velocity, final state ~40 GPa, 1.23 g/cc, ~10,000 K



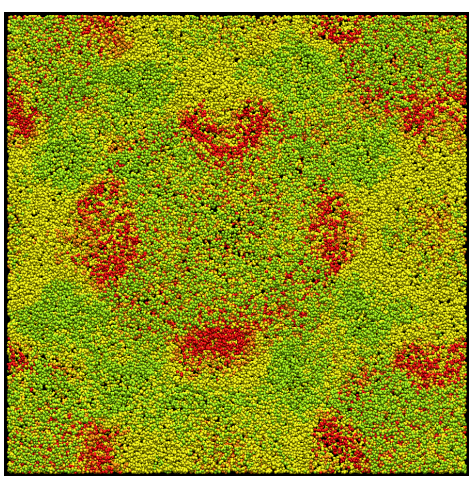
t=25k timesteps
< 1ps



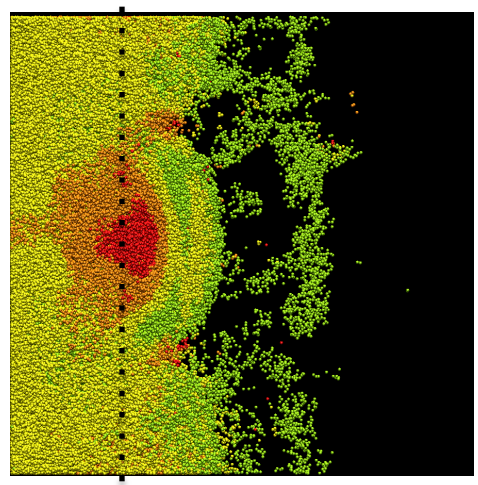
T=50k timesteps
~ 1ps



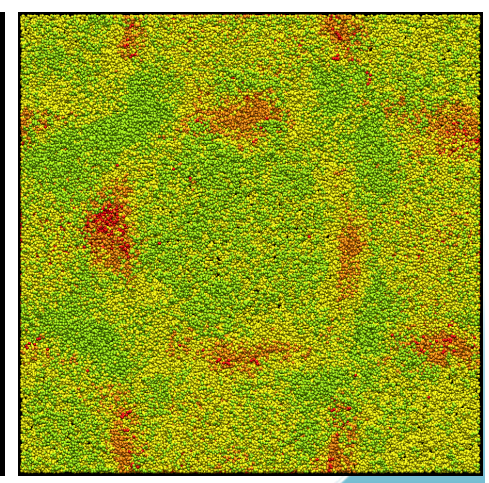
Temperature
Side view



Temperature
On-axis view



Temperature
Side view



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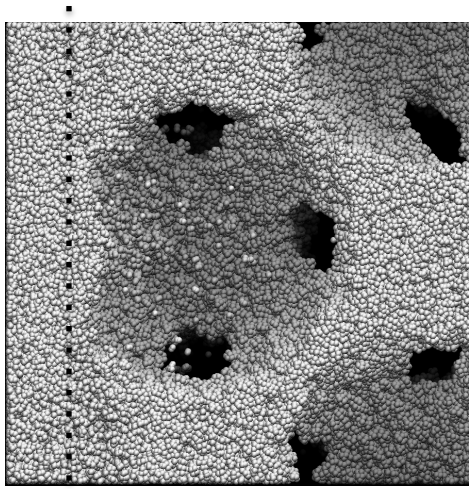
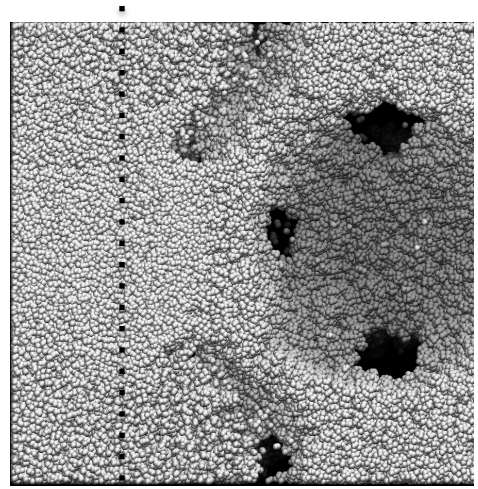
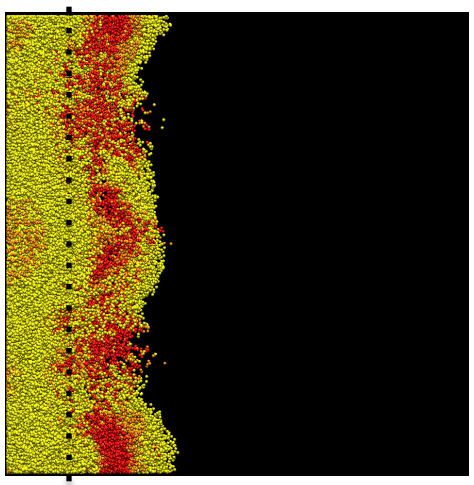


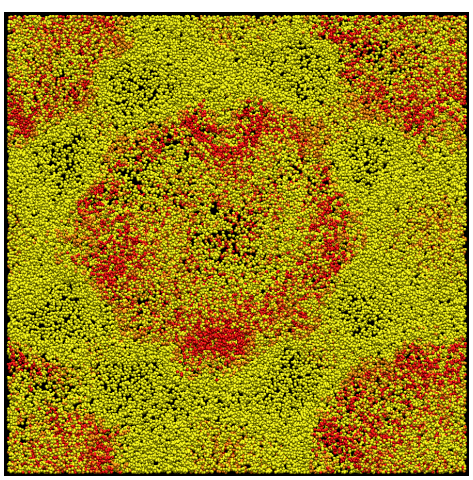
t=25k timesteps
< 1ps



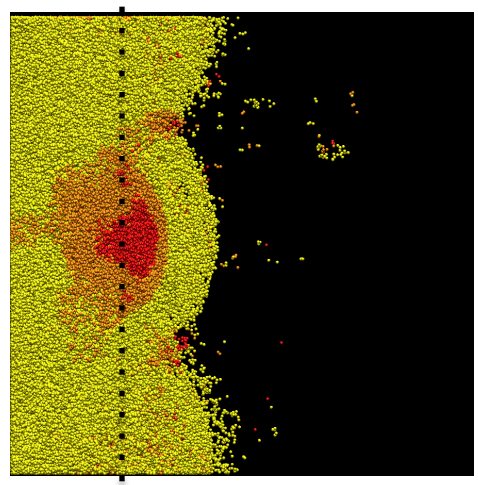
T=50k timesteps
~ 1ps



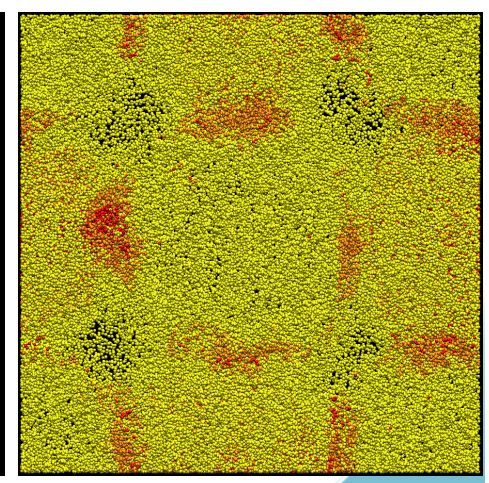
Temperature
Side view



Temperature
On-axis view



Temperature
Side view



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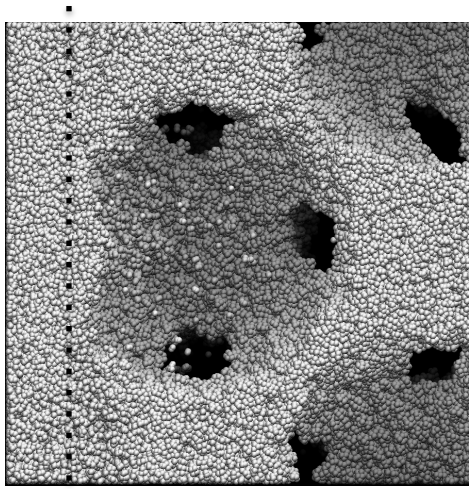

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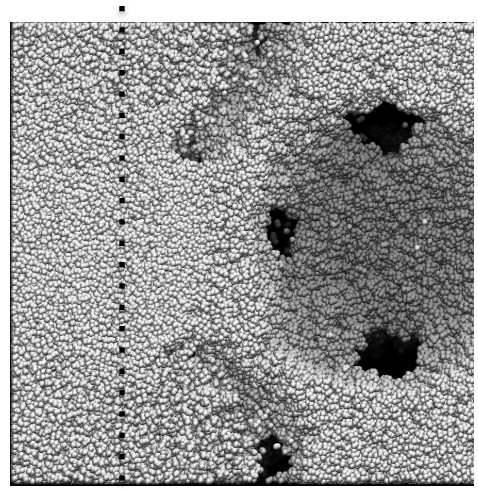

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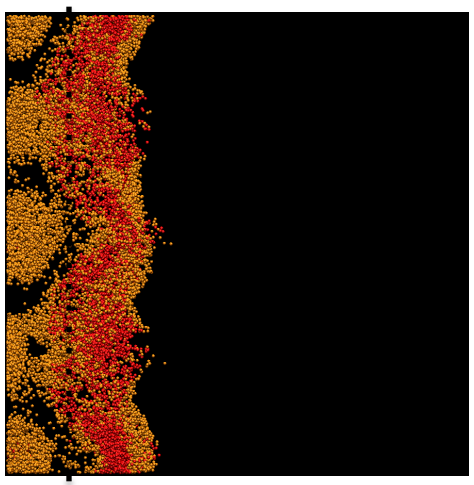

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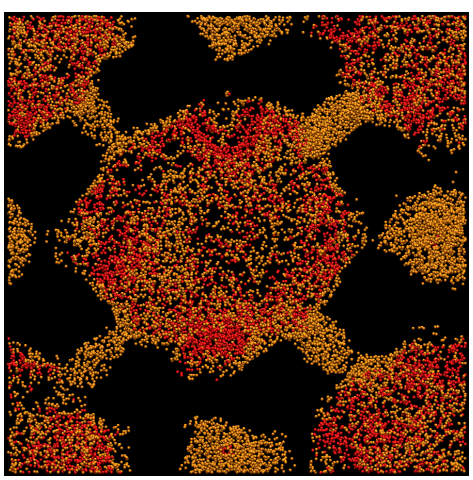
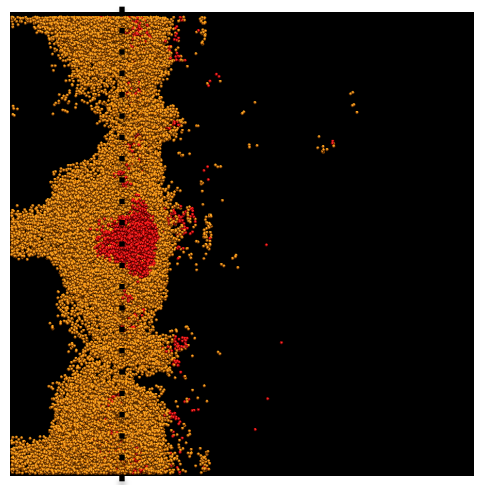
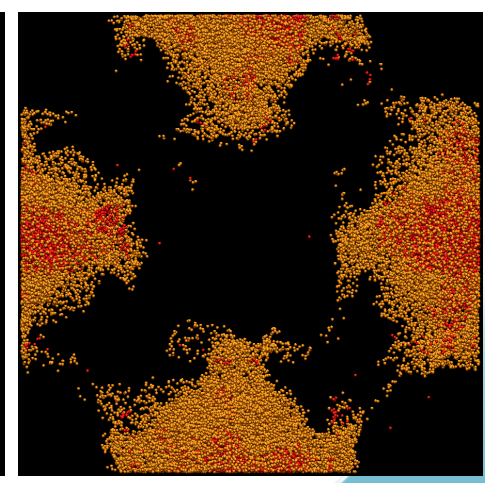


Temperature
On-axis view



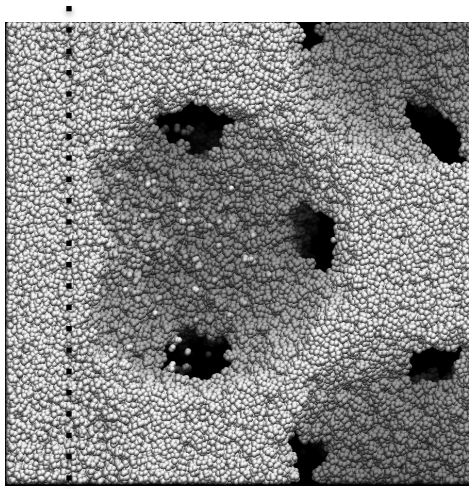
Temperature
Side view



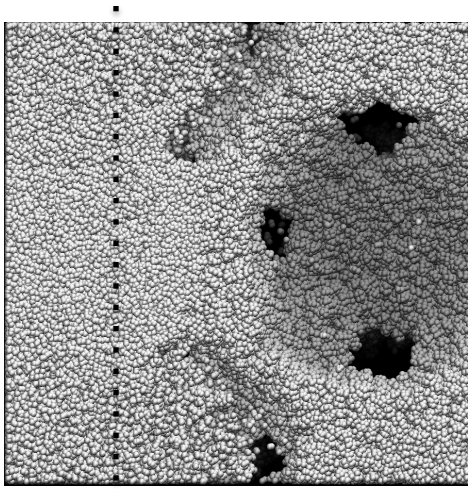
Temperature
On-axis view

Spatially-resolved dissociation & hot spots

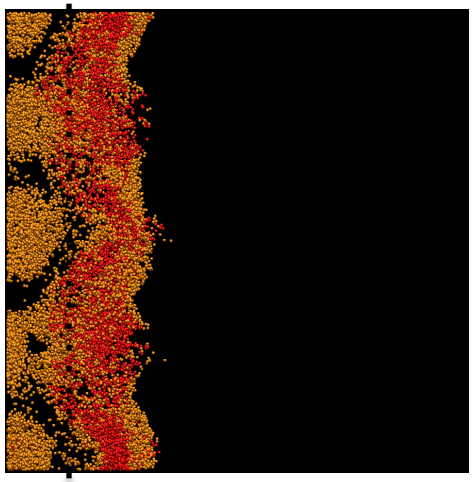
10 km/s piston velocity, final state ~40 GPa, 1.23 g/cc, ~10,000 K



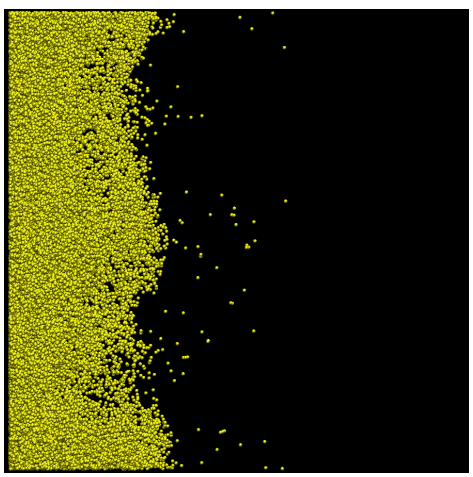
t=25k timesteps
< 1ps



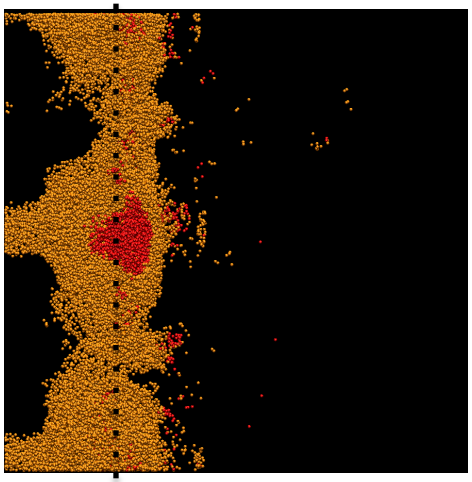
T=50k timesteps
~ 1ps



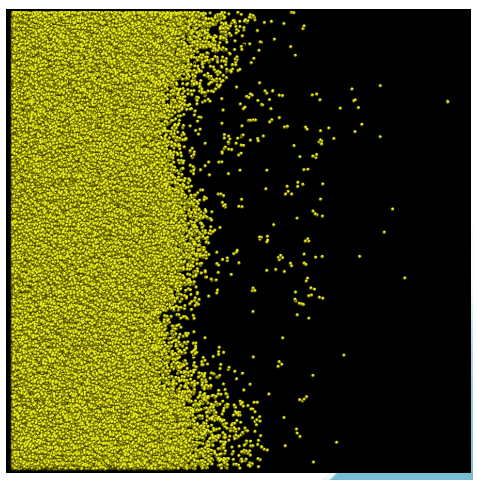
Side view
hot spots



Side view of only
dissociated carbon



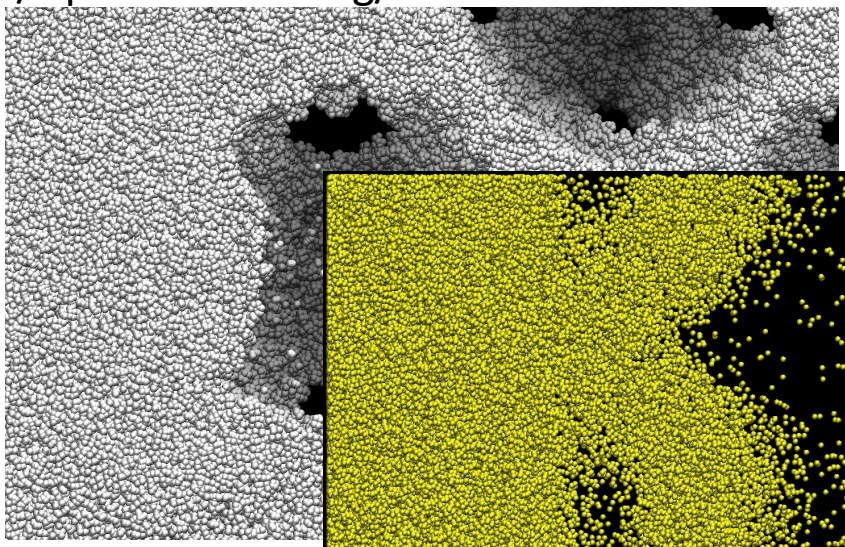
Side view
hot spots

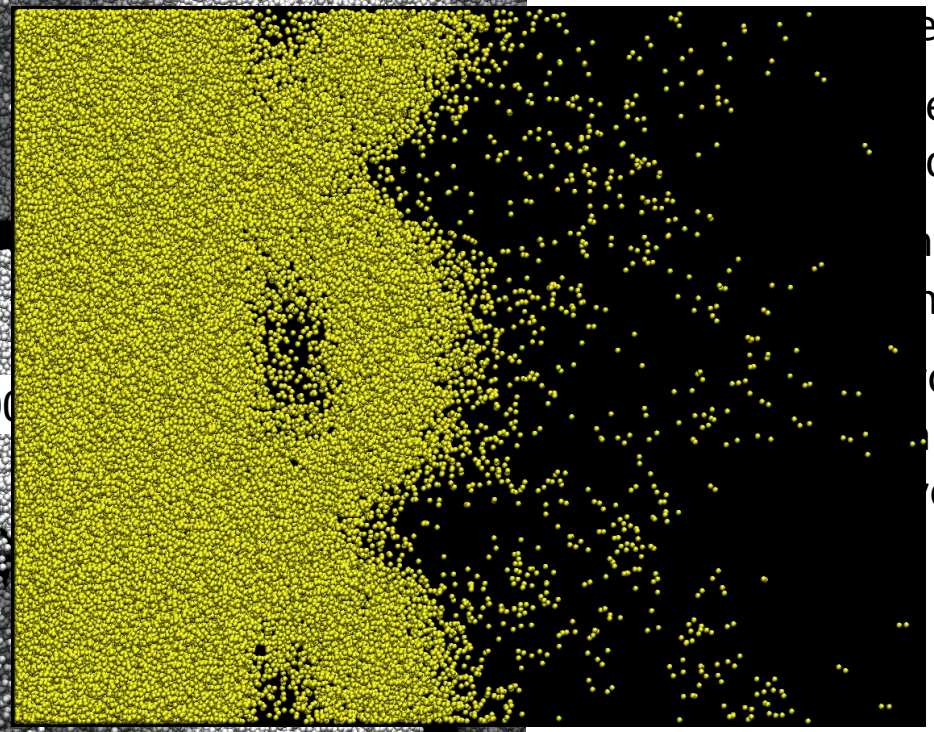


Side view of only
dissociated carbon

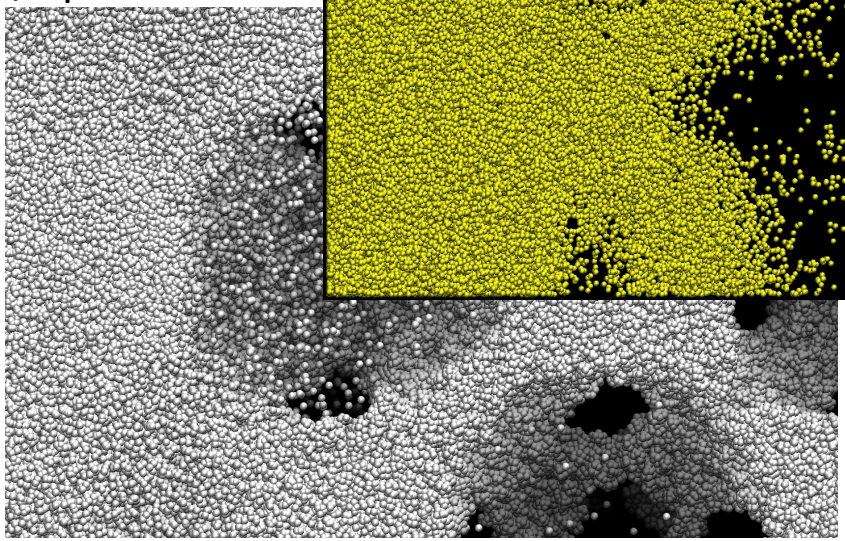
Spatially-resolved polymer dissociation

10 km/s piston – 0.300 g/cc PMP foam





25 km/s piston – 0.300



- Dissociation and vaporization at
  er velocities.
- e surface expansion
  d hot spots
- d surface blow out
  hock profile
- oids vapor material
  litatively differently
  oids.

Summary and conclusions

- For dense polymers, **shock response depends more on accurate potentials than on structure**. Thus, DFT is excellent in dense polymers
- **MD potentials exist, such as ReaxFF, which capture the quantitative shock response** of both dense polymers and foams up to 50 GPa in dense polymers and higher in foams
- Good agreement found with experiment and continuum simulation for shock compressed polymer foam. Much is left to explore in determining the **role of inhomogeneity, detailed structure and length scales on shock response**

Acknowledgments

Gary Grest, Aidan Thompson, Thomas Haill, Seth Root, Kyle Cochrane, Mike Desjarlais, Thomas Mattsson

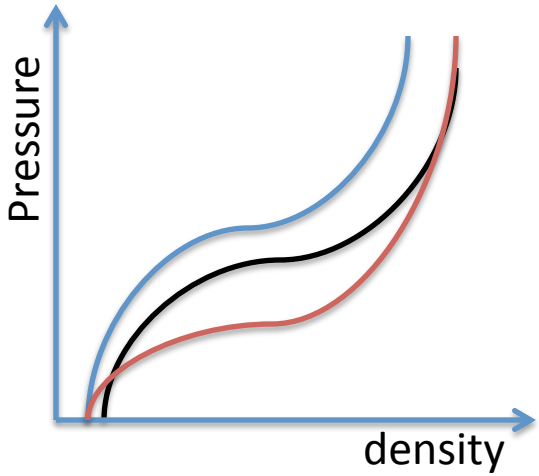
Enhanced densification in some porous materials

Some porous materials (notably SiO_2 and certain ceramics) exhibit an unusual enhanced densification compared to the principle Hugoniot.

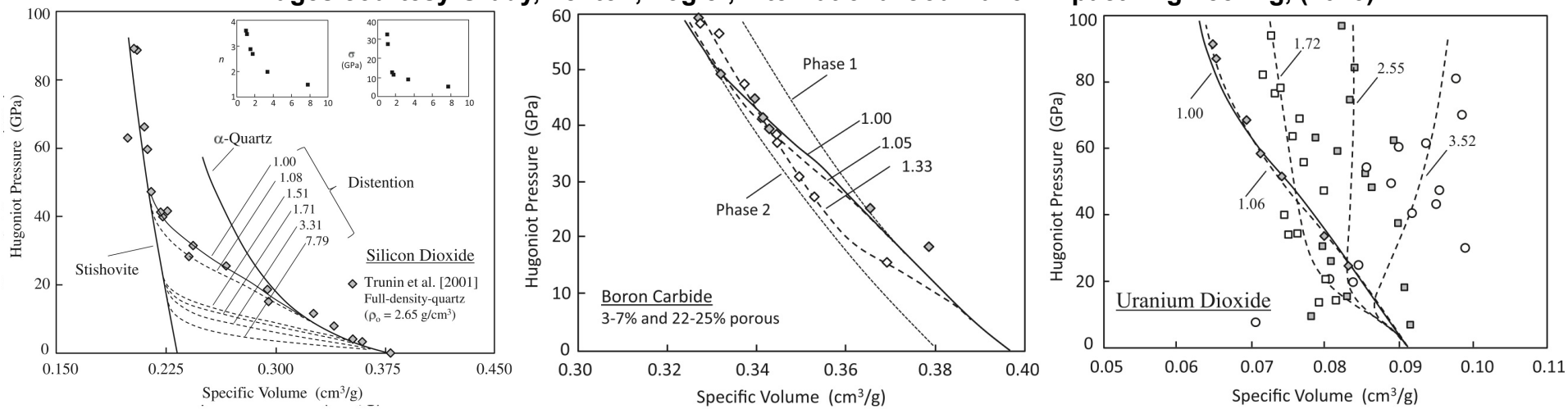
Grady, Fenton & Vogler published a collection of experimental data and proposed an improved EOS to capture this effect in porous media.

There are several proposed mechanisms, from chemical dissociation to evidence for an accelerated solid-solid phase transition.

Most agree that enhanced shear deformation resulting from void collapse likely plays a role in countering normal thermal expansion.



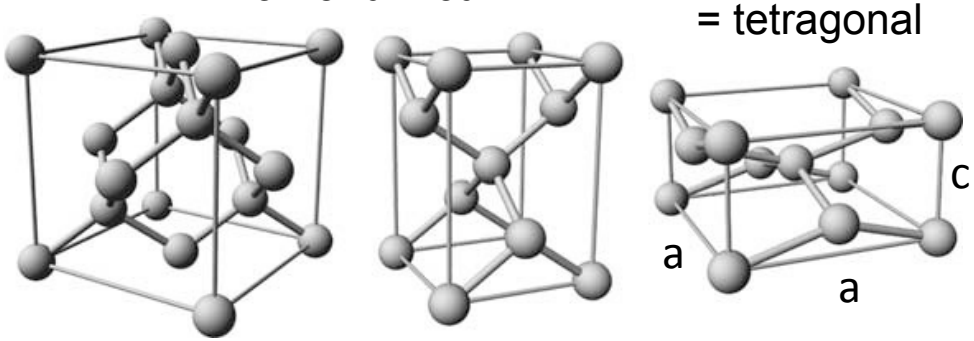
Images courtesy Grady, Fenton, Vogler, International Journal of Impact Engineering, (2013)

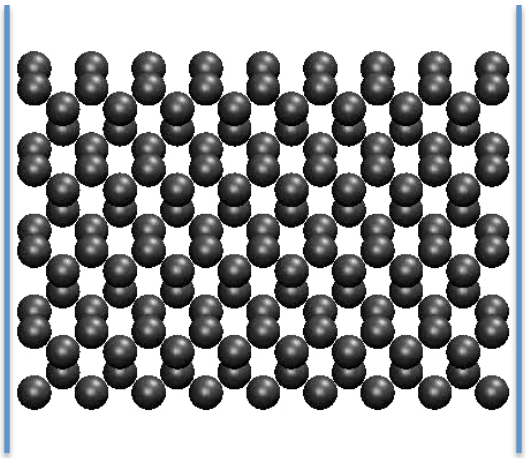


Silicon as a model system

Diamond = cd

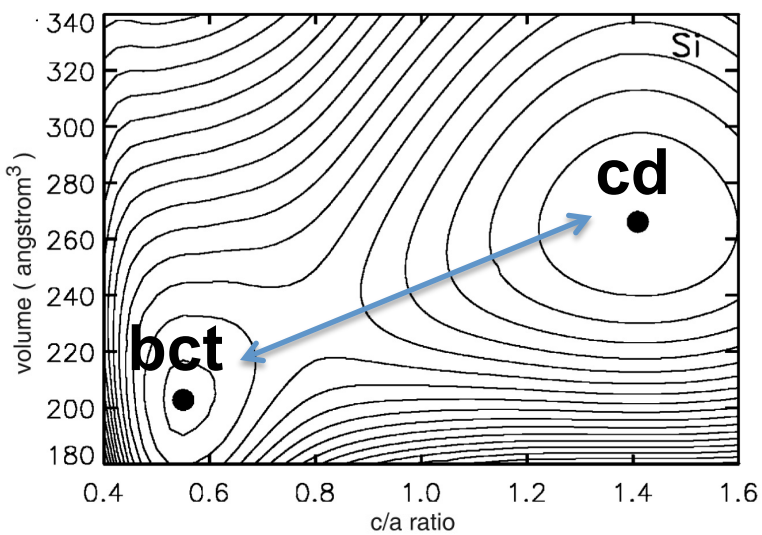
β-tin = bct
= tetragonal

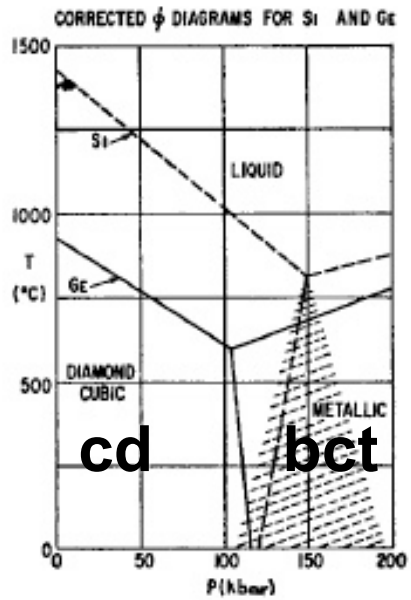




DFT

Gaal-Nagy, et al., Comp. Mat. Sci., 30, 1 (2004)





Bundy, J. Chem Phys., 41, 3809 (1964)

Silicon and germanium, like many ceramics, are brittle covalently-bonded materials

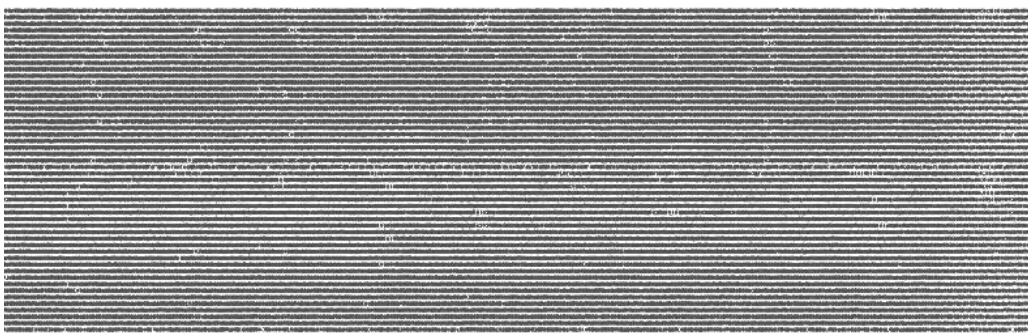
Ambient diamond phase is a special case of the tetragonal crystal structure with c/a = $\sqrt{2}$

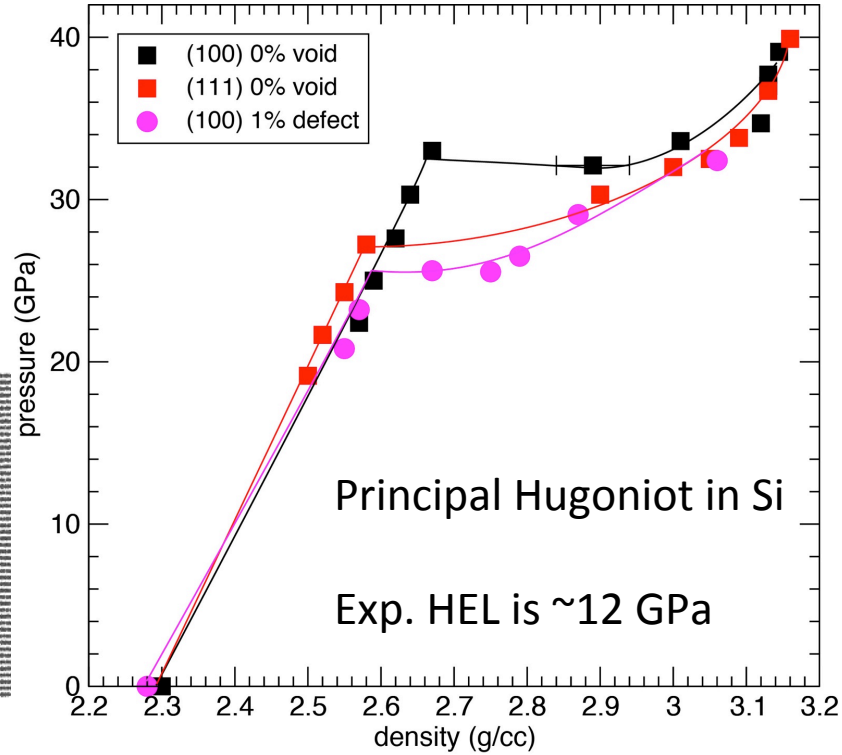
Phase diagram shows low temperature solid-solid phase line and melt line above 1300-1700 K

Full-density silicon partial phase transition

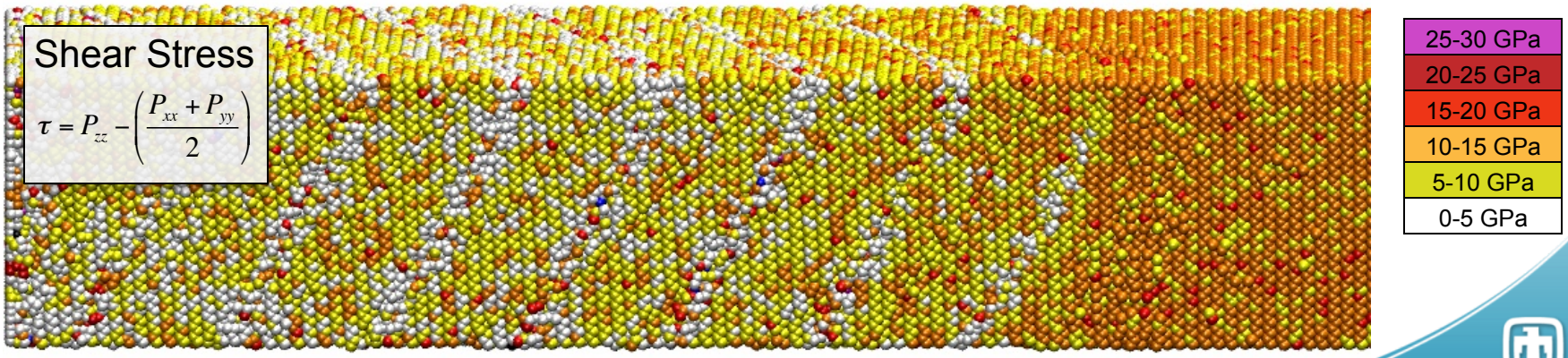
Our 2009 paper on Ge and more recent work in Si shows MD captures a shear-induced transition with tilt conveniently accommodating transverse dilation.

Transition is driven by shear stress and arrests when shear stress in relieved, coexisting bct with diamond





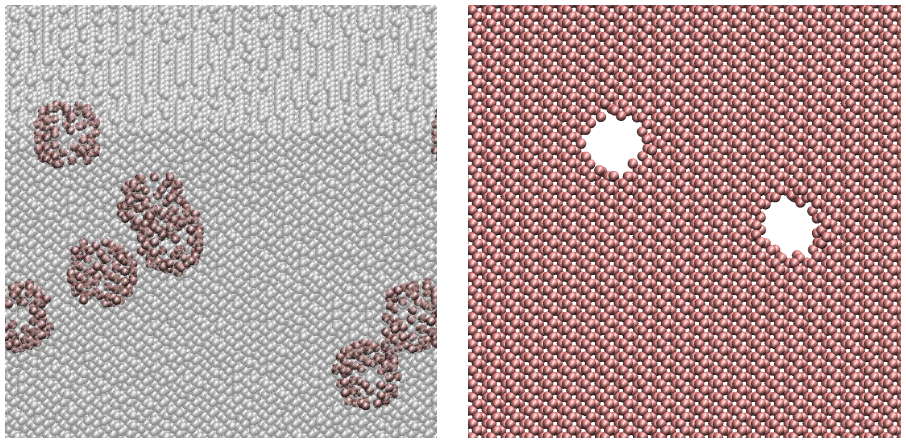
J.M.D. Lane and A.P. Thompson, AIP SCCM (2009)



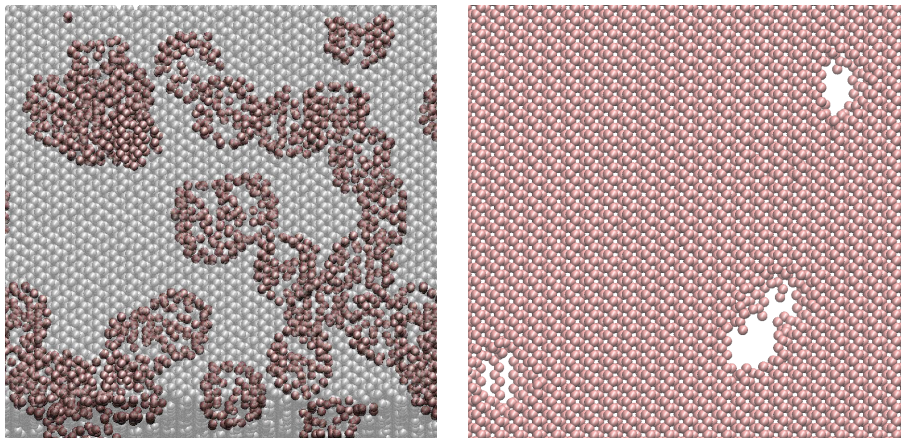
Low porosity silicon Hugoniots

Low porosity systems created by cutting randomly spaced 2 nm diameter spherical voids from single-crystal silicon.

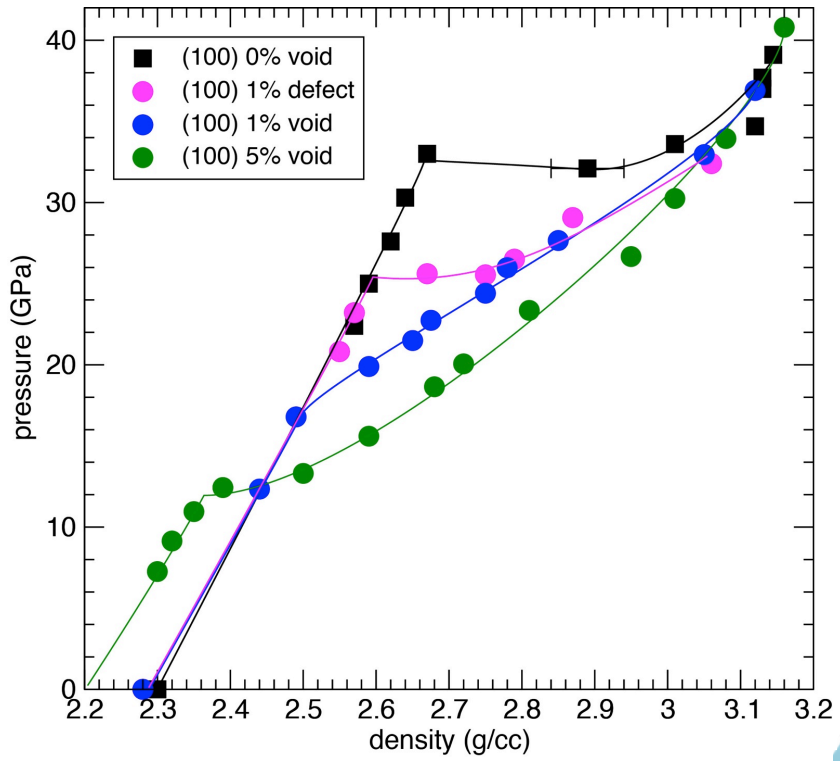
1% porosity: cut voids



5% porosity: cut voids



Hugoniot density rises at lower pressure as seen in experiments, then joins the principal Hugoniot at higher pressures.

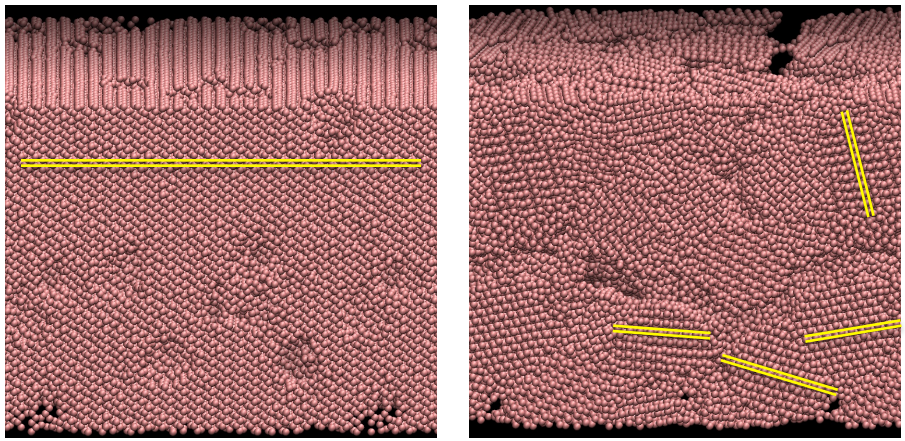


Experimentally porous silicon has been created and rigorously studied through high-energy helium implantation and annealing

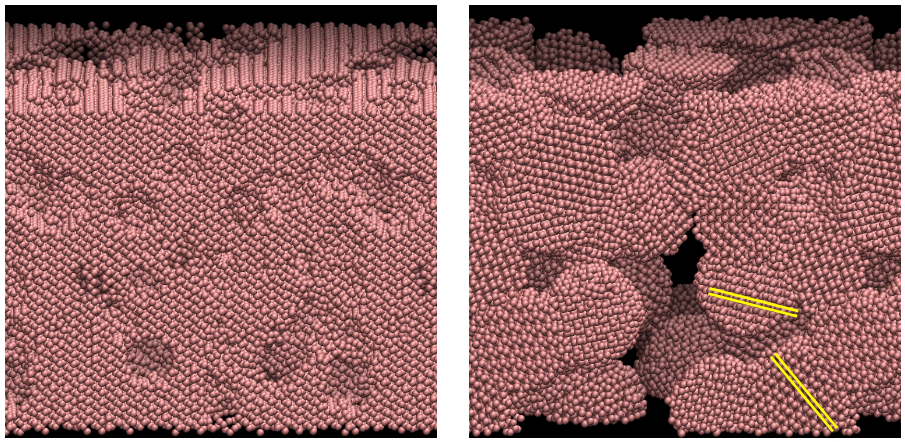
High porosity silicon Hugoniots

High porosities are made by cutting 2 nm spherical voids from single crystal, or as a polycrystal of 4 nm spherical grains, w/ overlap removal, and annealing.

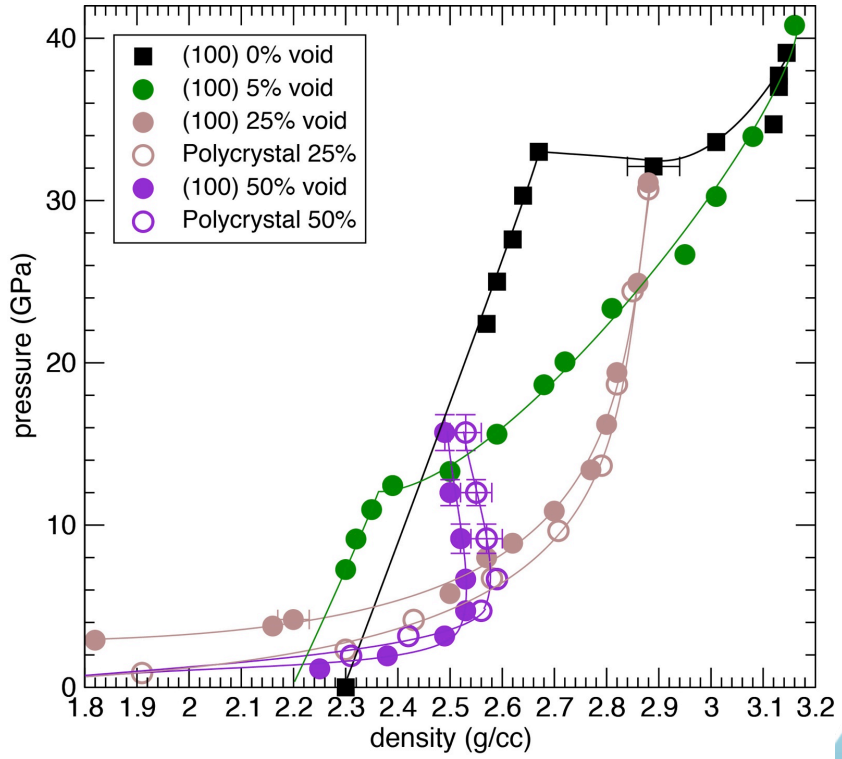
25% porosity: (l) cut voids, (r) polycrystal spheres



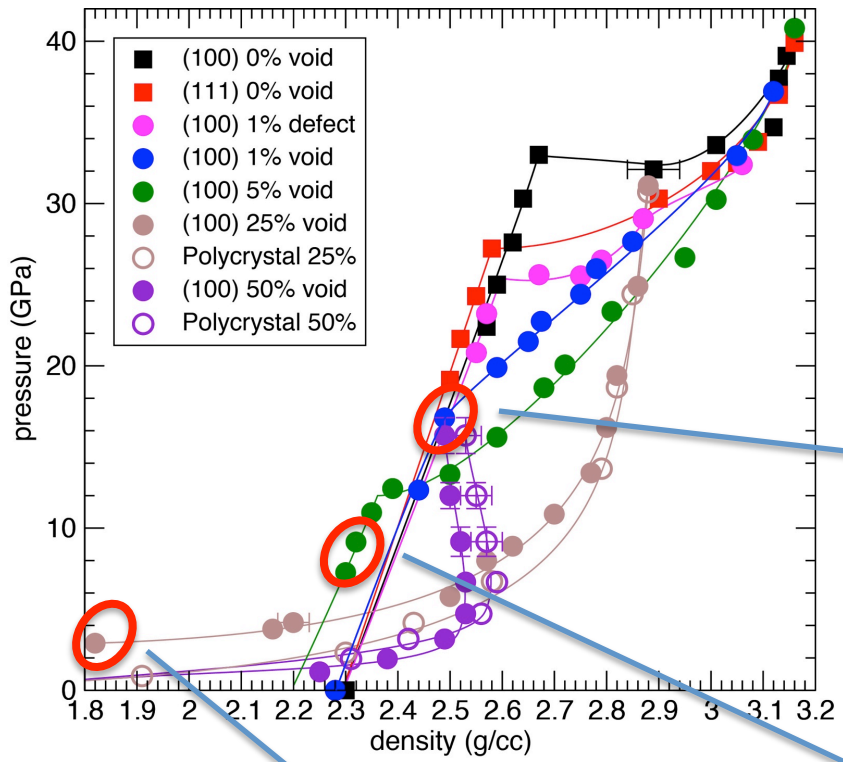
50% porosity: (l) cut voids, (r) polycrystal spheres



The Hugoniot density quickly collapses in the polycrystal, and slightly more slowly in the void-cut single crystal before rising steeply due to heating from rapid void collapse.

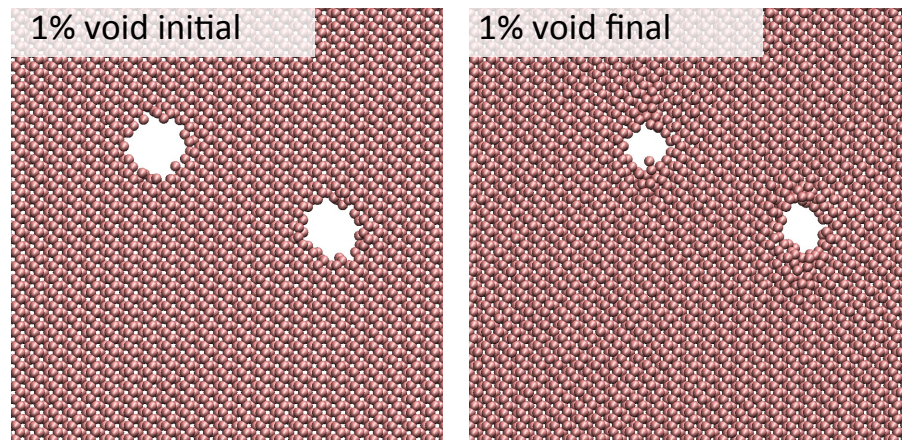


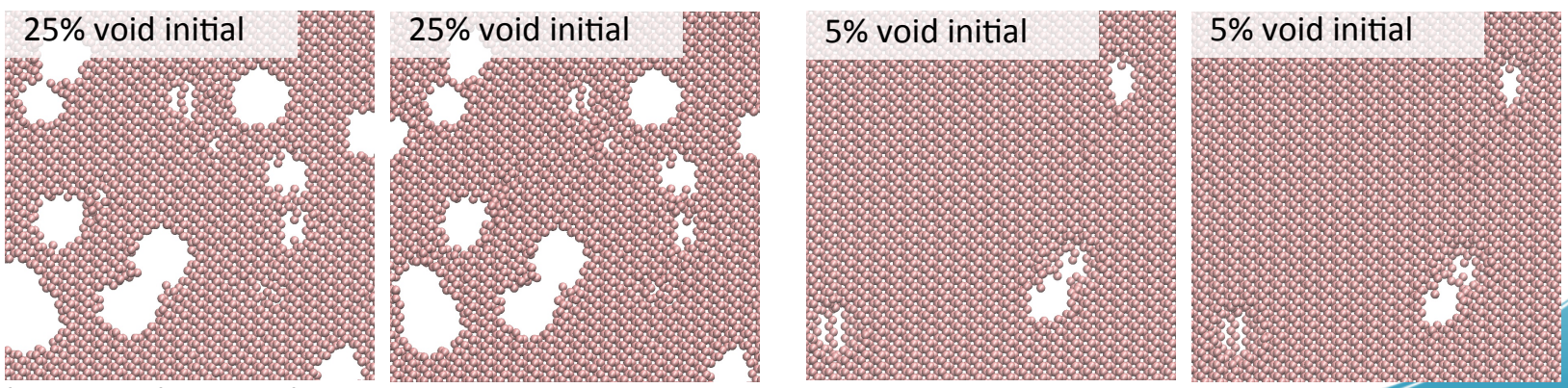
Elastic response in weak shocks and precursors



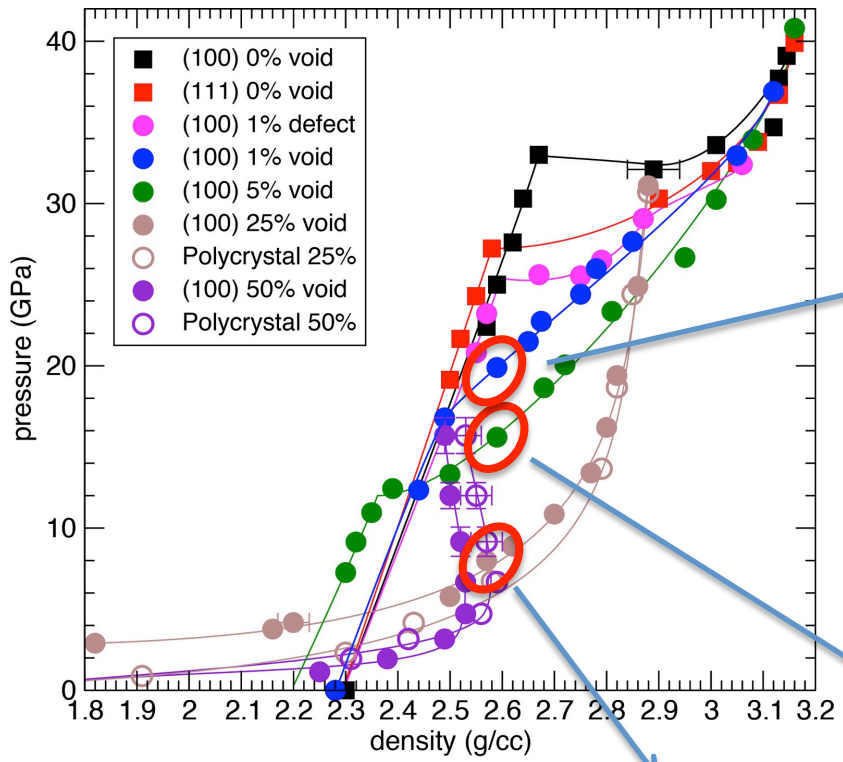
Under weak shock loading all systems compressed elastically with voids deforming nearly hydrostatically, causing shear deformation in the void vicinity.

Increased porosity dramatically lowered the Hugoniot Elastic Limit and altered the precuror behavior

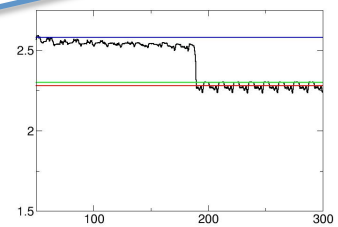


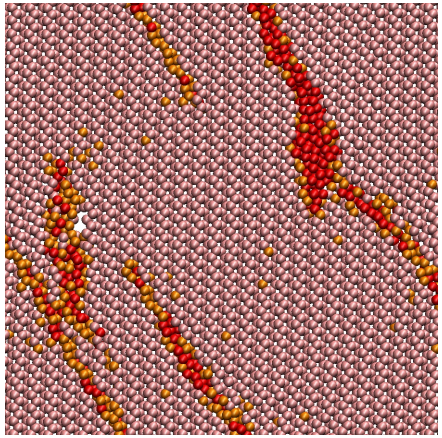


Enhanced densification to 2.6 g/cc

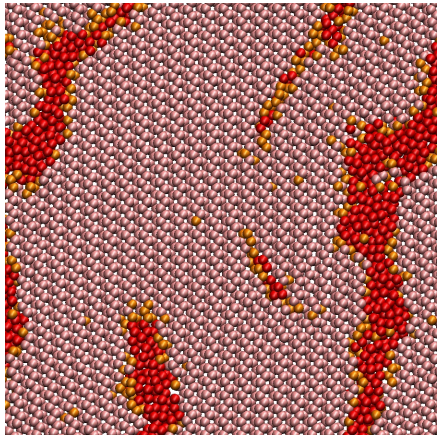


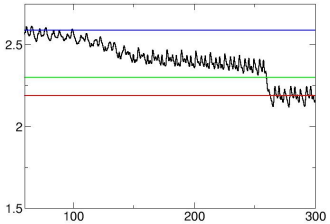
1% void initial
T_f = ~500 K
V_p = 1.0 km/s



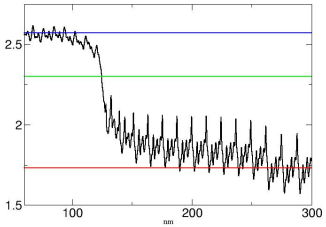


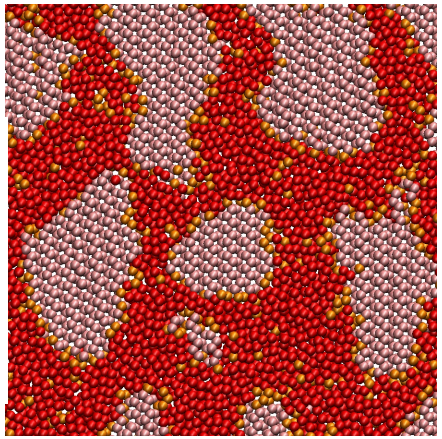
5% void initial
T_f = ~750 K
V_p = 1.0 km/s





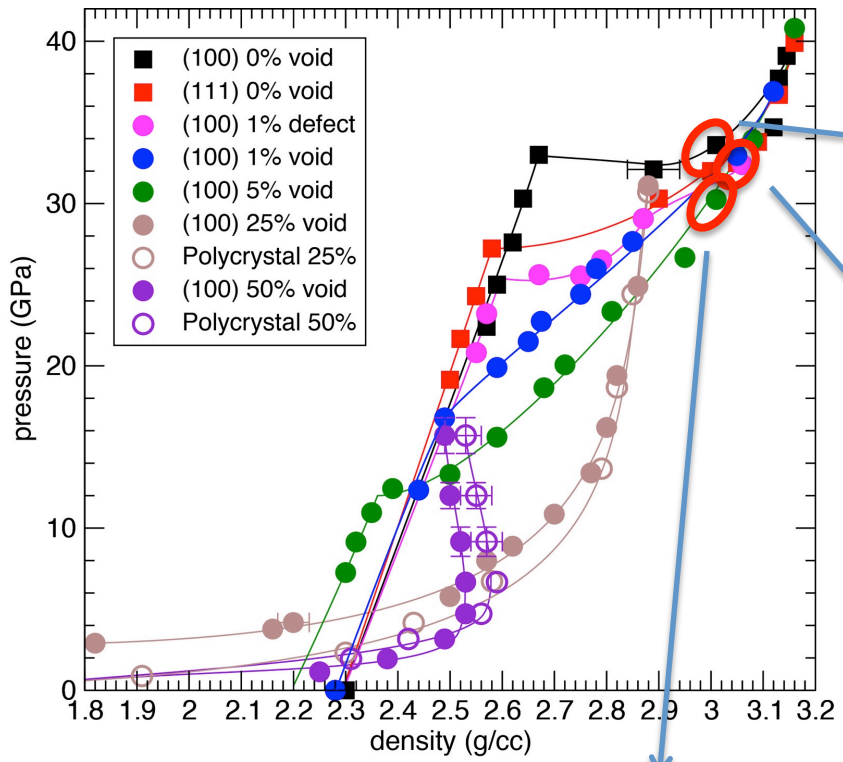
25% void initial
T_f = ~1200 K
V_p = 1.2 km/s



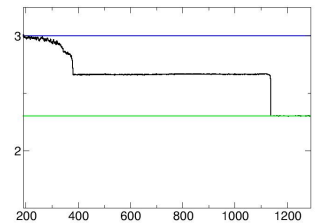


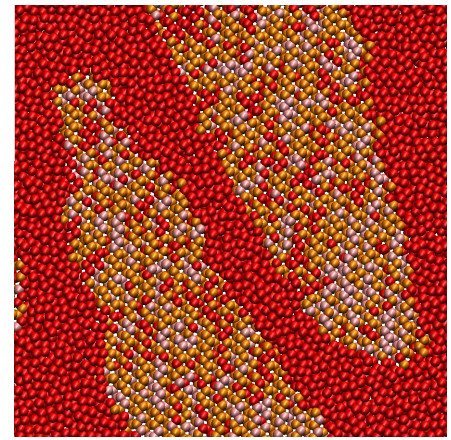
Atoms colored by coordination number such that cd atoms are pink and bct atoms are red

High pressure response

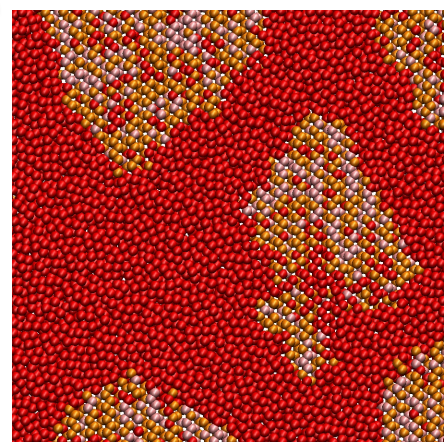


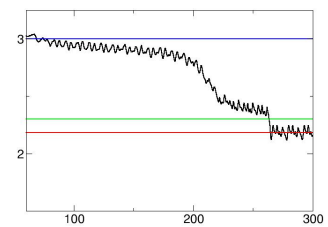
Perfect initial
T_f = ~1300 K
V_p = 1.6 km/s



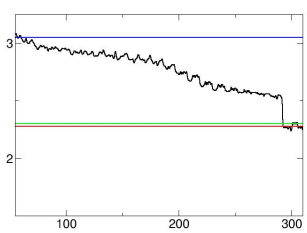


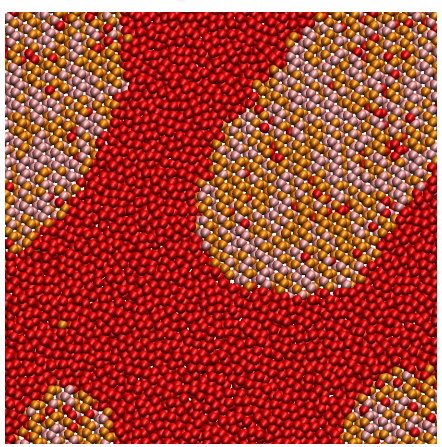
1% void initial
T_f = ~1400 K
V_p = 1.8 km/s



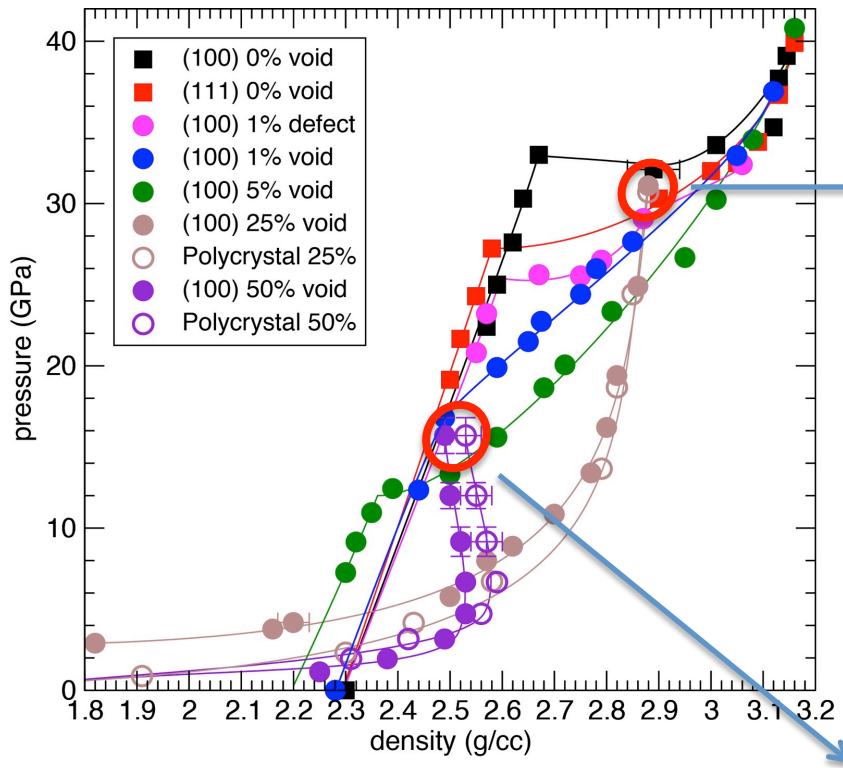


5% void initial
T_f = ~1300 K
V_p = 1.9 km/s

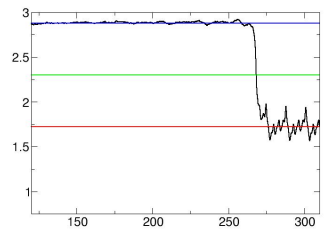


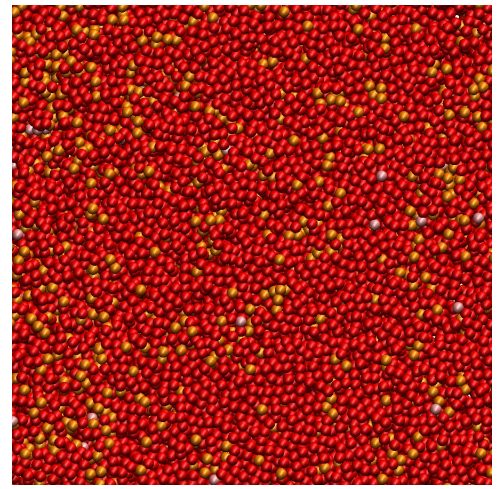


Local heating and hot spot formation

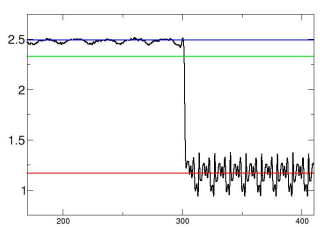


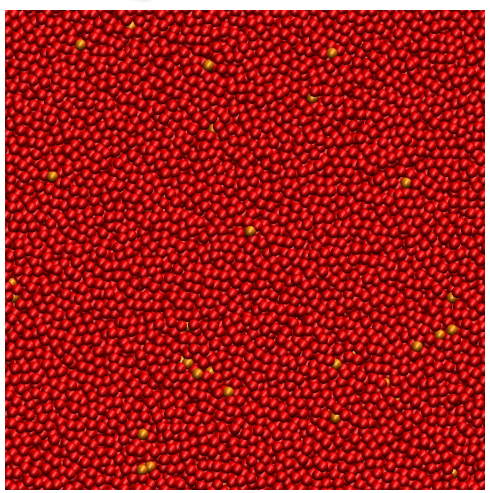
25% void initial
T_f = ~3500 K
V_p = 2.7 km/s





50% void initial
T_f = ~4000 K
V_p = 2.7 km/s





Matthew Lane - jlane@sandia.gov

Sandia National Laboratories

Summary and conclusions

- Silicon is a good model system for exploring the mechanisms of enhanced densification seen in brittle ceramic porous materials

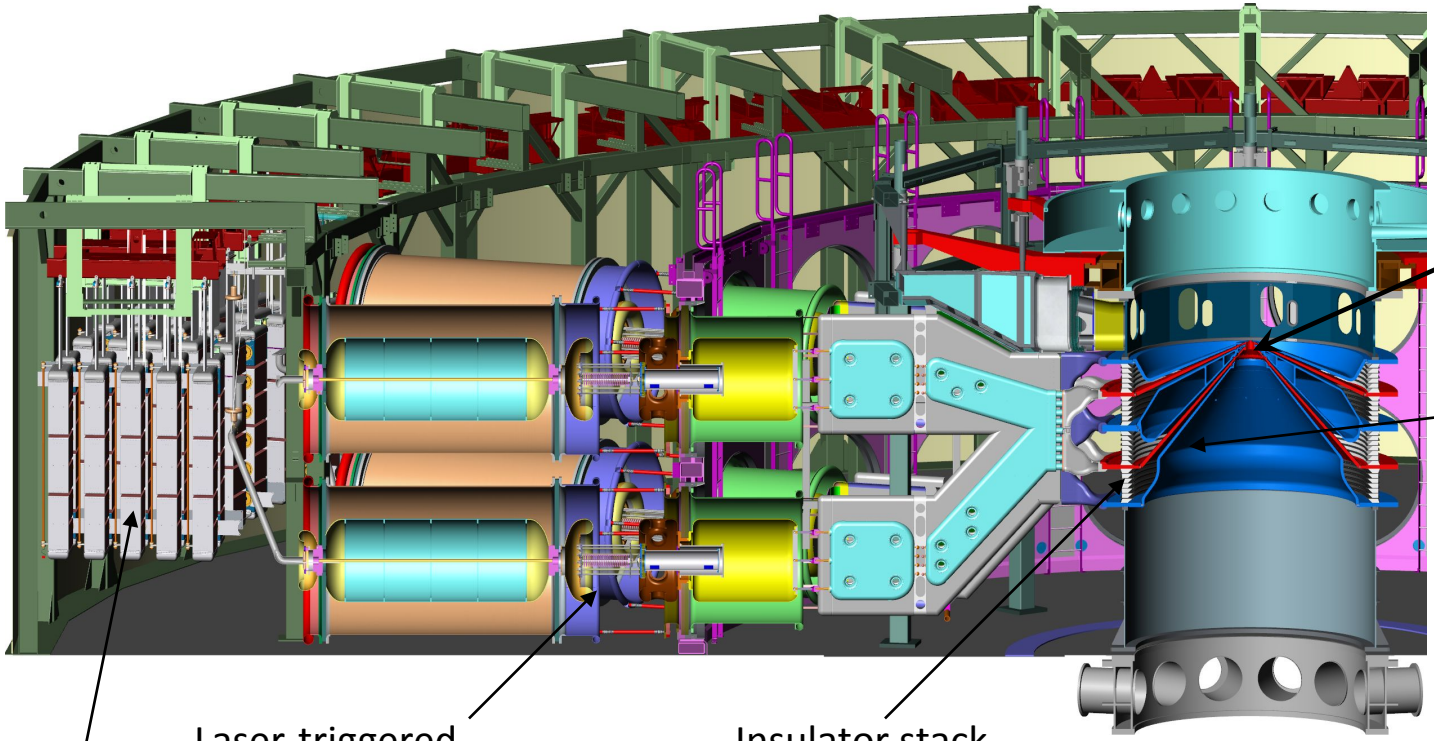
- In low porosity materials voids collapse spawning local high density phases of bct crystal, local plasticity, and local melt, but ultimately respond along the principal Hugoniot at high pressure.

- At high porosity, voids collapse quickly, with the rate somewhat determined by initial structure. Hot spots form which produce enough heat to fully melt the material and produces steep pressure increases with density, diverging significantly from the principal Hugoniot at high pressures.

SUPPLEMENTARY SLIDES

Motivated by an amazing machine

The Sandia Z Machine is 33 m in diameter, 3 stories high, and combines power-plant current with sub microsecond time scale



22 MJ stored energy

25 MA peak current

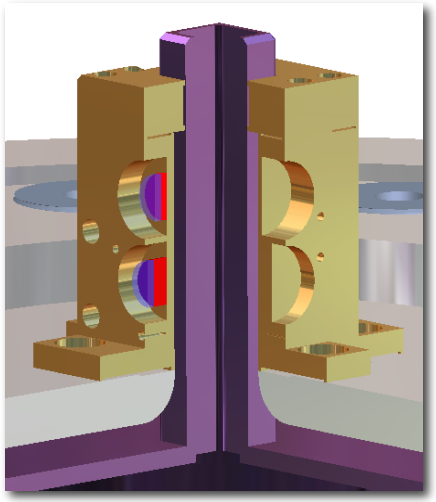
100-600 ns rise time

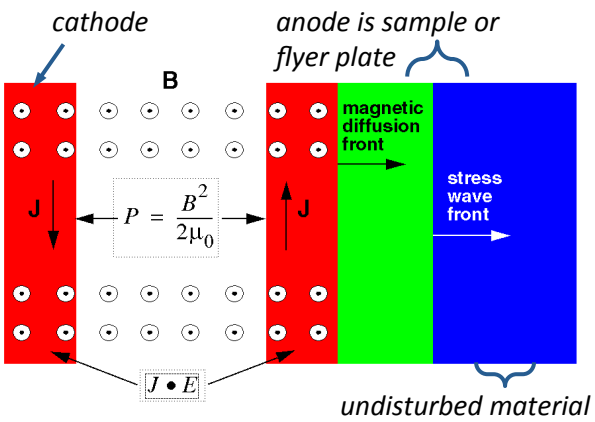
25 MA is the max current load of 160,000 homes

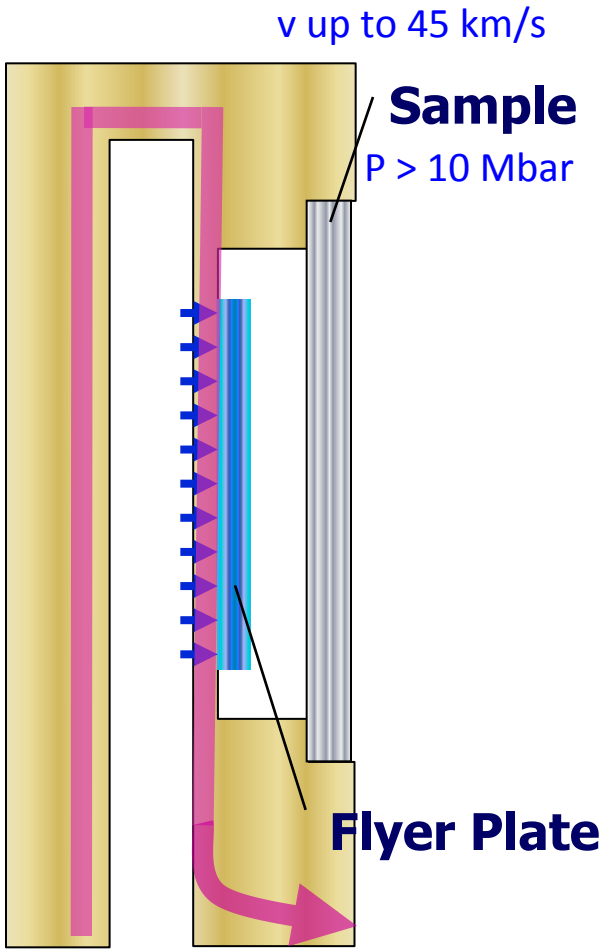
Light travels 30 m in 100 ns

Motivation for polymer shock simulation

Z can perform both shock-less compression of materials and plate-impact shock wave experiments







Shock Hugoniot Experiments:
shock wave in sample on impact

Other amazing machines…

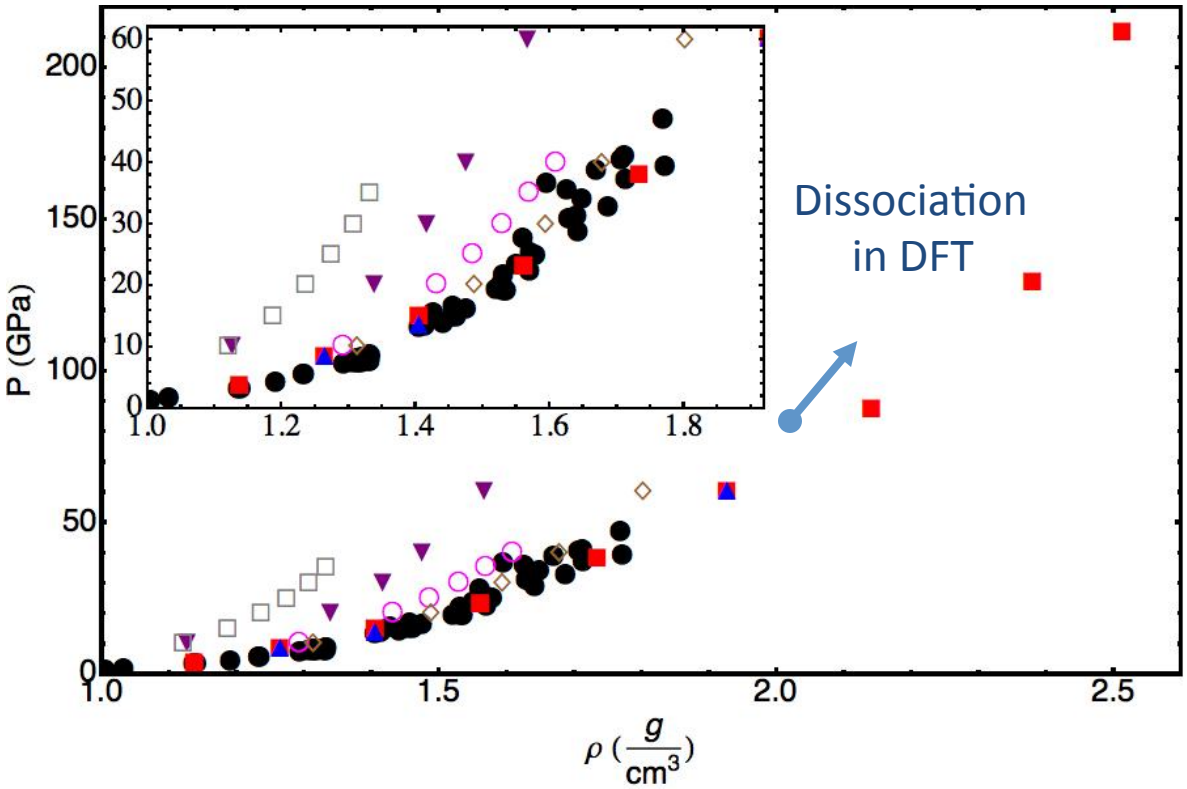
Chama – 2012
19,712 2.6 GHz procs
392 TFlops

Cielo – 2011
143,040 2.4 GHz procs
1.37 PFlops

Redsky – 2010
22,528 2.9 GHz procs
264 TFlops

- Molecular dynamics scales spatially for large systems
  - hardware – clusters of thousands of processors
  - software – efficient parallel MD code – LAMMPS
- High rate shock studies become large quickly
- Accurate results depend on complex/expensive interaction potentials

Poly(4-methyl 1-pentene) shock Hugoniot



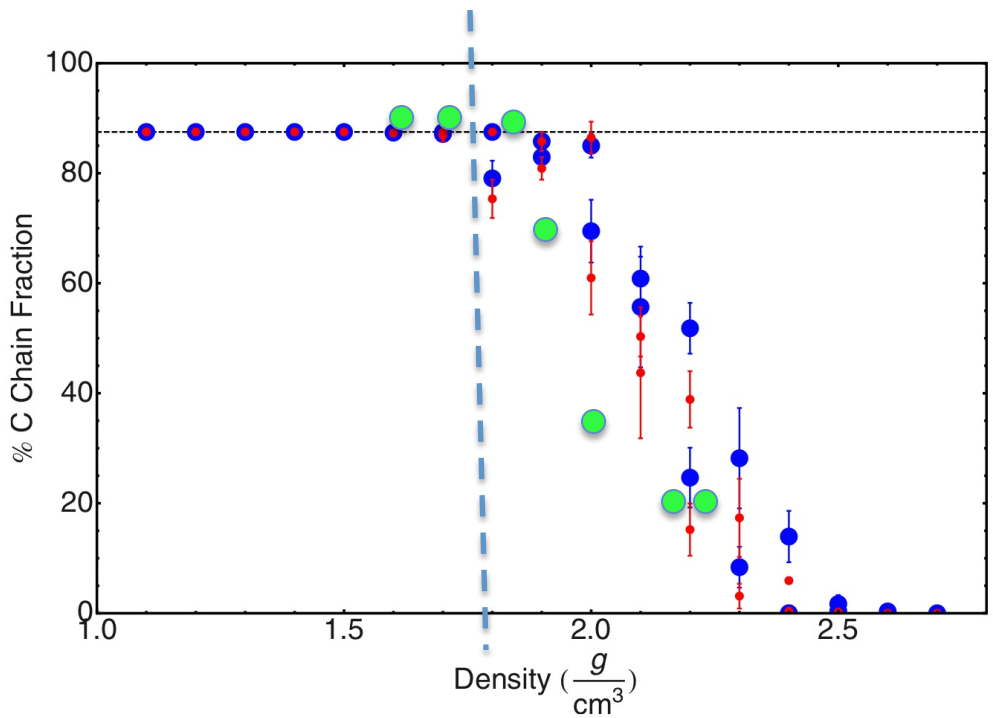
- 50 chains with 50 units in amorphous arrangement
- 45,100 atoms
- 7.5 nm x 7.5 nm x 7.5 nm

AIREBO
OPLS
Borodin-Smith (exp6)
ReaxFF
DFT-AM05 (struct A/B)
Experiment (LASL)

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

- AIREBO and OPLS both give significantly too stiff shock response at all pressures
- Borodin-Smith and ReaxFF better choices for weak shocks in polyethylene
- Only the DFT-AM05 simulation of high fidelity also for strong shocks
- Significant deviations already well before the regime where dissociation occurs
- Reactive properties of force-fields are not important for weak shocks

Dissociation in dense polymer, DFT

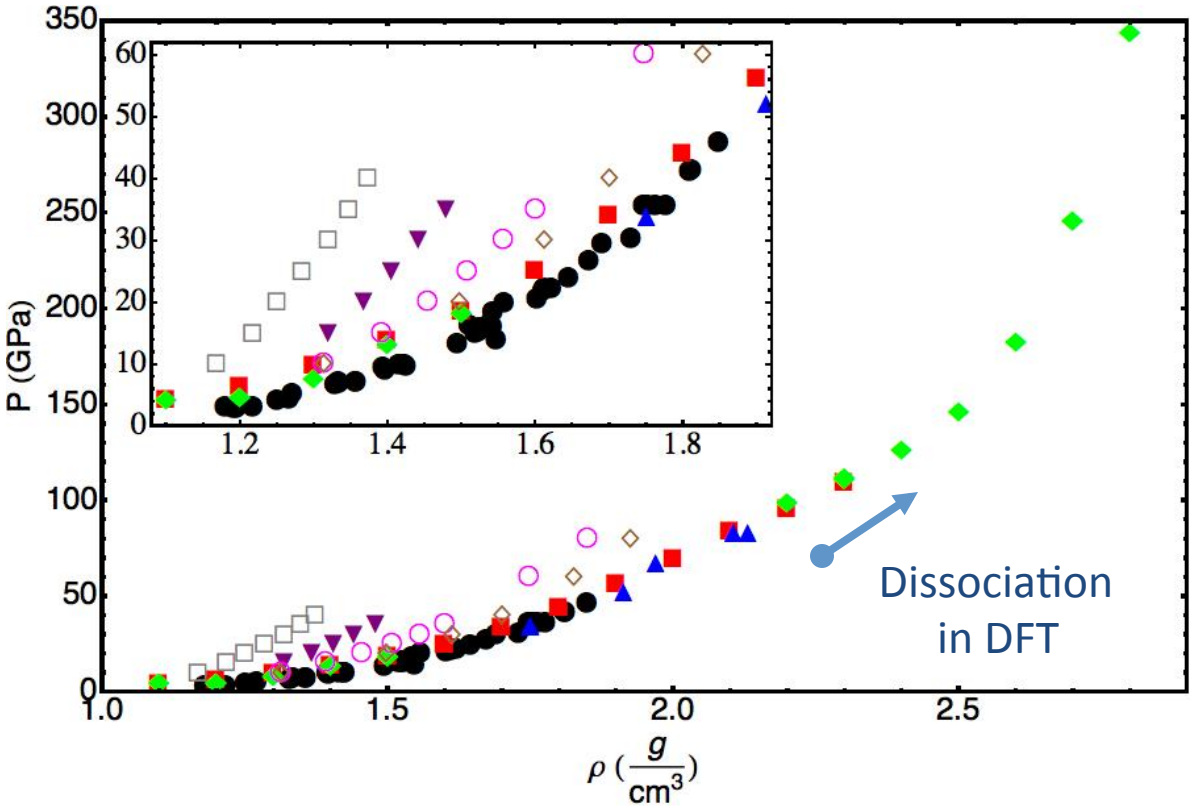


DFT MD results
Classical MD (ReaxFF)

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

- DFT results showed not dissociation to approximately 2.0 g/cc, or ~60 GPa
- Dissociation above the pressure range at Classical MD was demonstrated to be reliable.
- Recent checks verify that ReaxFF predicts dissociation in this same density range.

Polyethylene shock Hugoniot



- 168 $C_{44}H_{88}$ chains in crystalline arrangement
- 22,176 atoms
- 5.2nm x 6.0 nm x 6.0 nm

AIREBO
OPLS
Borodin-Smith (exp6)
ReaxFF
DFT-AM05
Experiment (Nellis/LASL)

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

- AIREBO and OPLS both give significantly too stiff shock response at all pressures
- Borodin-Smith and ReaxFF better choices for weak shocks in polyethylene
- Only the DFT-AM05 simulation of high fidelity also for strong shocks
- Significant deviations already well before the regime where dissociation occurs
- Reactive properties of force-fields are not important for weak shocks

Molecular dynamics (NEMD) methodology

Solve Newton's equations

$$m_i \frac{d^2 \mathbf{r}_i}{dt^2} = \mathbf{F}_i$$

$$\mathbf{F}_i = -\nabla V_i$$

Mathematical Formulation

Classical Mechanics

Atoms are Point Masses: $\boldsymbol{r}_1, \boldsymbol{r}_2, \ldots\ldots \boldsymbol{r}_N$

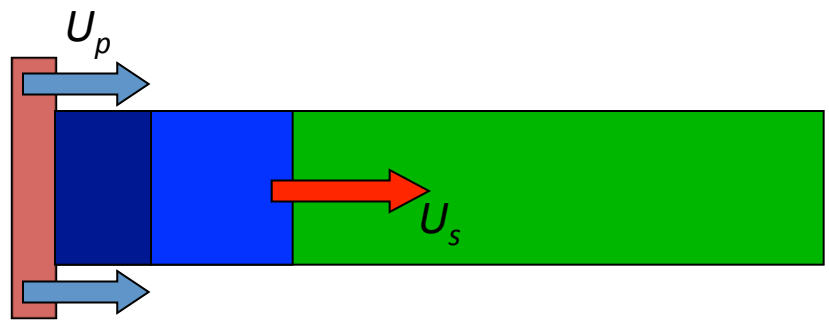
Positions, Velocities, Forces: $\boldsymbol{r}_i, \boldsymbol{v}_i, \boldsymbol{F}_i$

Sandia's LAMMPS code is spatially parallel

Large-scale **A**tomic/**M**olecular **M**assively **P**arallel **S**imulator

Porosity Creation

Voids are introduced either by carving out atoms from a single crystal, or by building up polycrystals from nano-grains



Shock Driver

Warm piston driving into 300 K single-crystal Silicon along <111> and <100>

Systems 13.1 x 13.1 x 320 nm^3 and periodic

Timescales 60 to 150 ps

Interatomic Potential

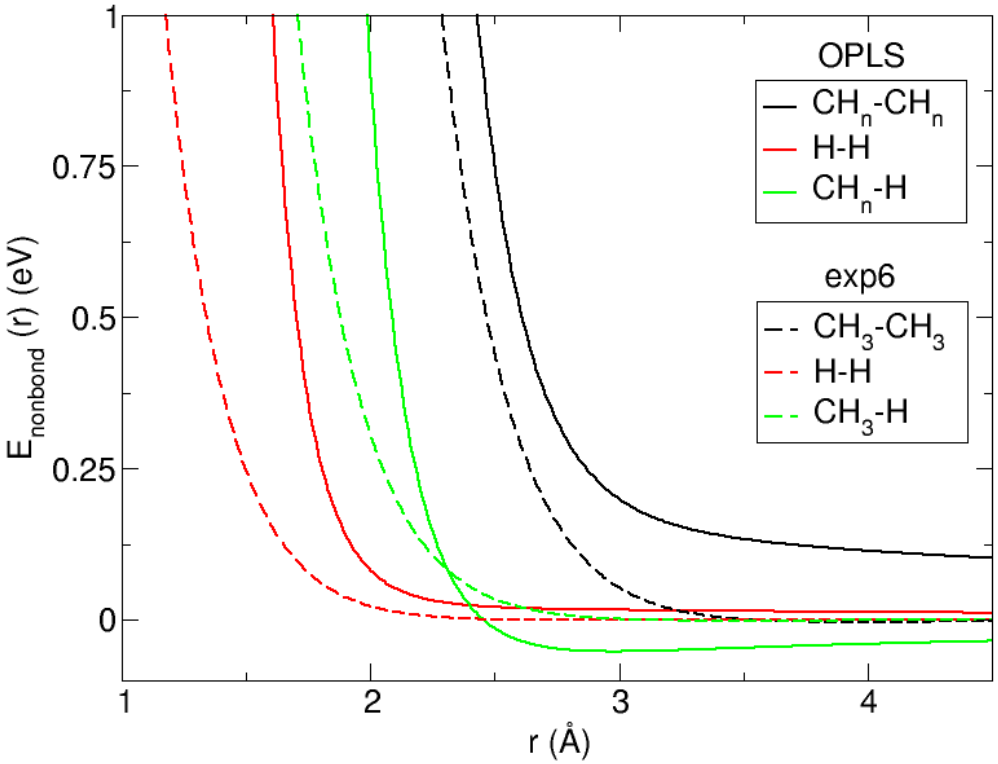
Modified Embedded Atom Method (MEAM)

– LAMMPS parameter file "Si97"

– Two-body and environment dependent terms

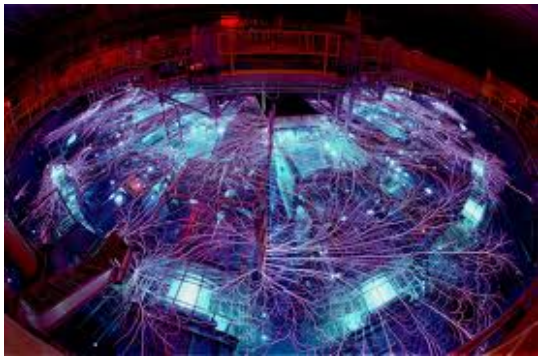
– Validated at high pressure by Badis et al. (2003)

Core repulsion model is critical



- AIREBO and OPLS share L-J 12-6 functional form for core interaction
- Borodin-Smith exp-6 has a weaker exponential form, more physical shock behavior
- Potentials parameterized near ambient conditions where core interactions are small, unlike in high-density shock conditions
- Behavior under shocks are difficult to predict from equilibrium properties

Summary and conclusions

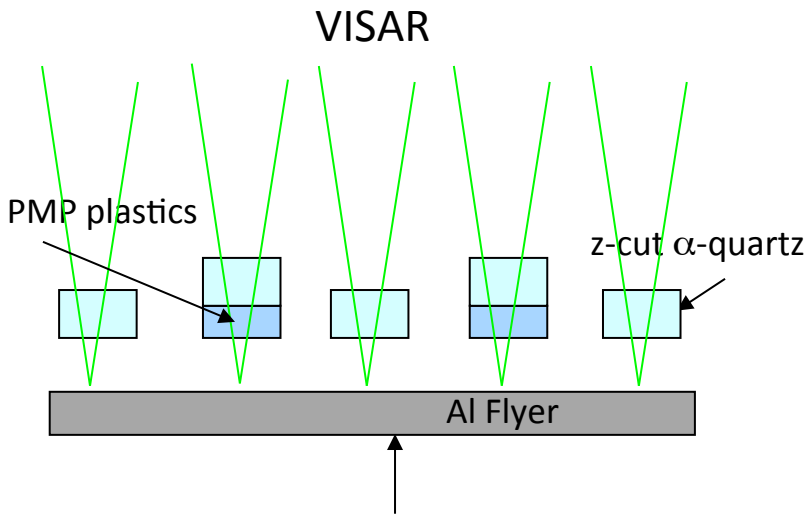


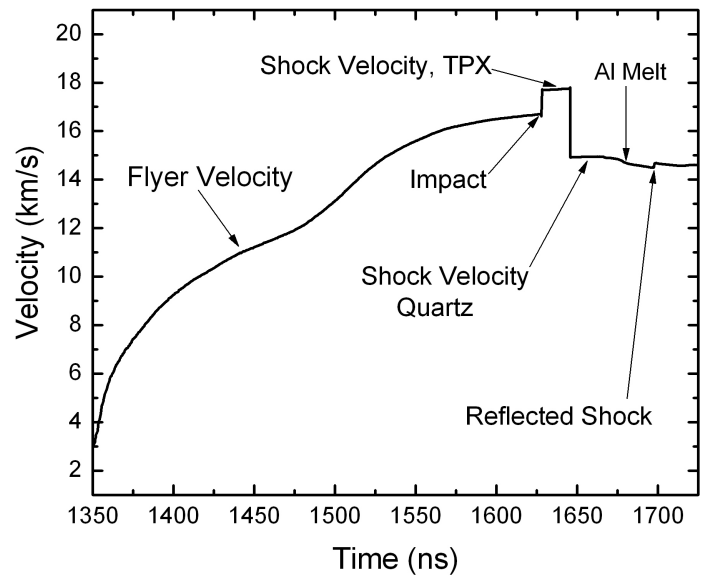
- **Sandia's Z machine is a versatile platform for high-precision experiments in the Mbar regime**
  - **Shock-compression and Shock-less compression of solids**
- **We extensively use DFT/QMD simulations to develop quantitative material models, predict experiments, and understand the dynamics**
  - **Changes in chemical composition, dissociation**
  - **Structure, diffusion, and conductivity**
- For dense polymers, **shock response depends more on accurate potentials than on structure**. Thus, DFT is excellent in dense polymers
- **MD potentials exist, such as ReaxFF, which capture the quantitative shock response** of dense polymers up to densities of 1.8 g/cc and pressures of 50 GPa
- Where the classical potentials fail, **core repulsion rather than bonding/ reactivity appear to be to blame for the discrepancy.**

Classical MD with ReaxFF appears to be an appropriate tool to study polymer foams where larger system sizes are required to capture the material's macroscopic structure. DFT MD can't currently go to these system sizes.

Sandia National Laboratories

Motivation for polymer shock simulation





- Magnetically driven flyer plates in shock Hugoniot experiments at velocities up to 45 km/s
- Exceeds gas gun velocities by > 5X and pressures by > 7-8X with comparable accuracy
- Accelerations of up to 22.5 billion time the gravitational constant

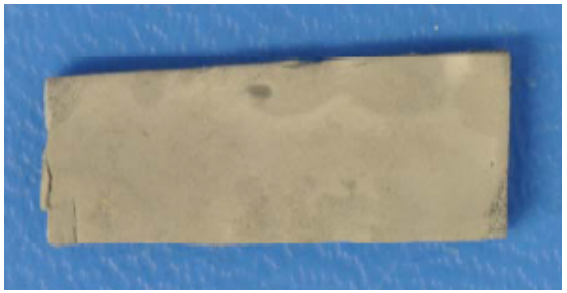
Shock velocities are measured in plastics and other transparent materials with sub-percent accuracy…

Why do we need modeling?

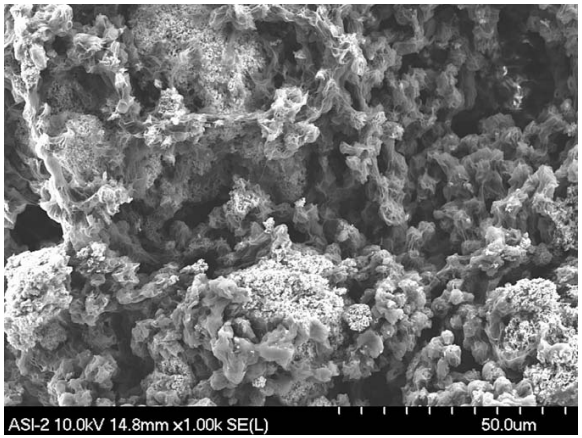
temperature, transitions, opaque materials, mechanisms

Nanocomposite (doped foam) introduction

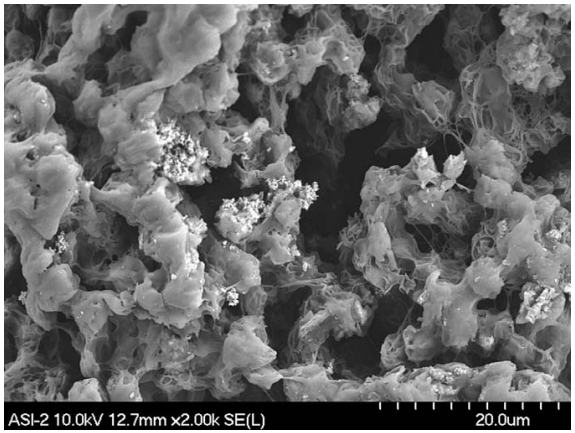
Doped 300 mg/cm^3 foam



50 μm resolution



20 μm resolution



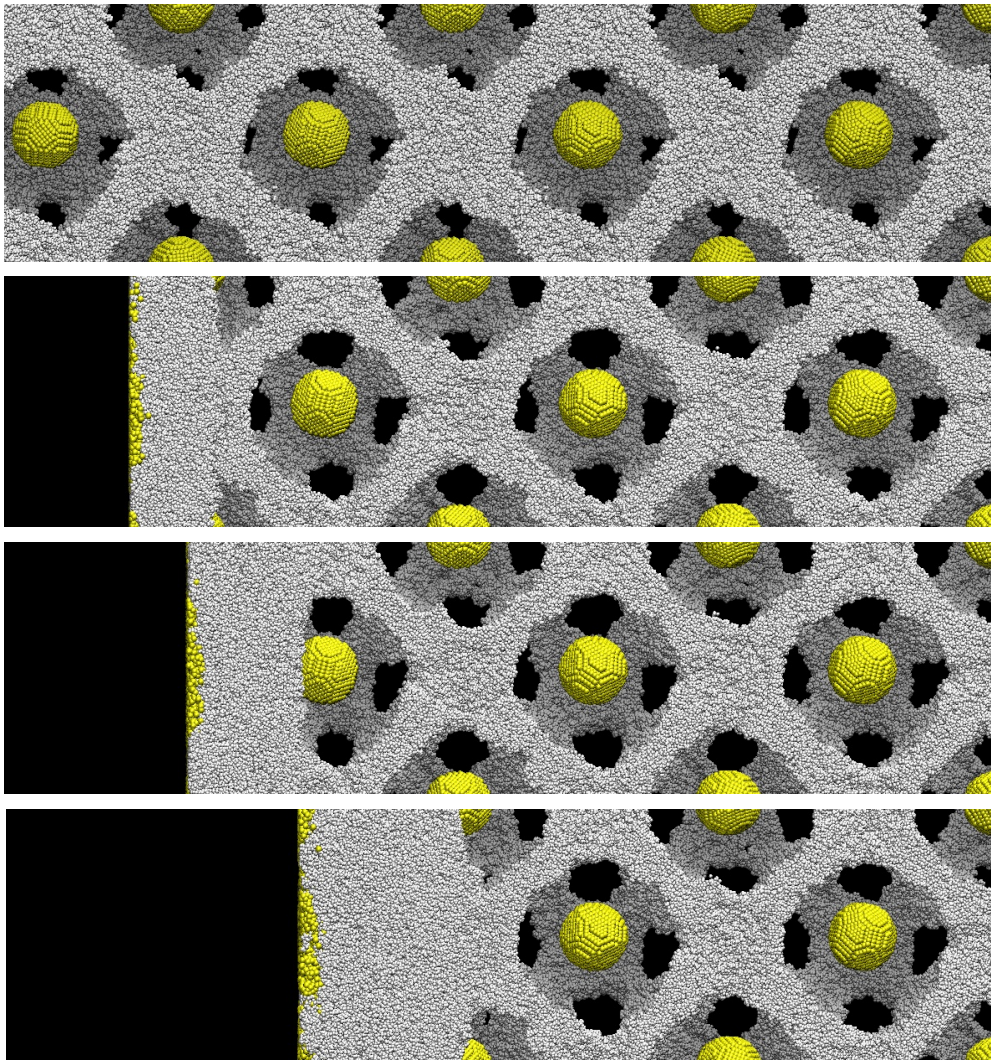
Experimental properties

- Platinum doped foam with overall density of approximately 0.30 g/cc
- 50/50 mass fraction of platinum to foam produces extremely low 1.54% volume fraction
- Some clustering and aggregation of particles noted – not well characterized
- Micron scale voids and submicron metal particles

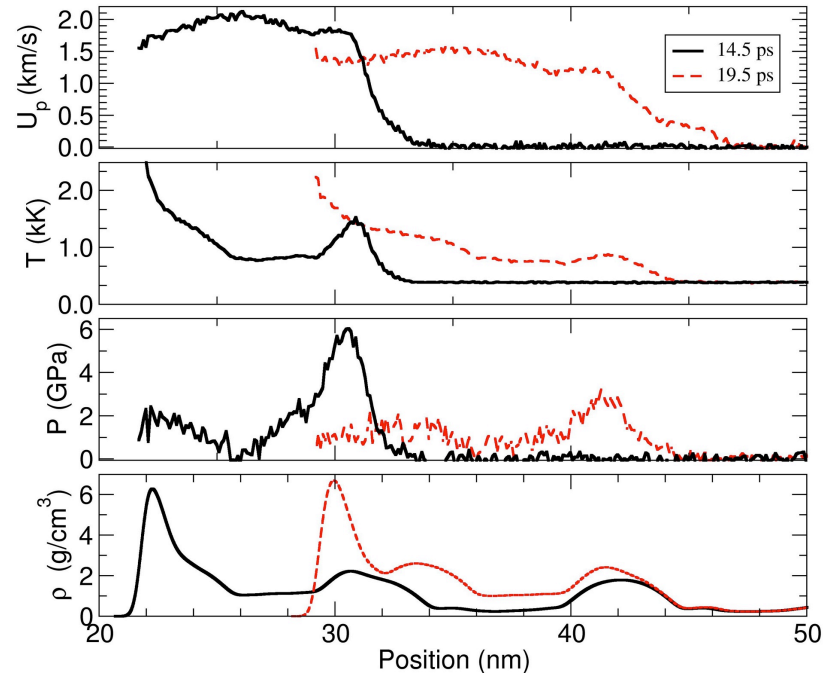
Simulated properties

- Gold doped foam with overall density of approximately 0.80 g/cc
- 60/40 mass fraction of gold to foam
- Regular pattern of 5 nm particles centered on 16 nm diameter voids
- 20x20x80 nm system with 16 nanoparticles. ReaxFF potential was used.

Shock-compressed nanocomposite results

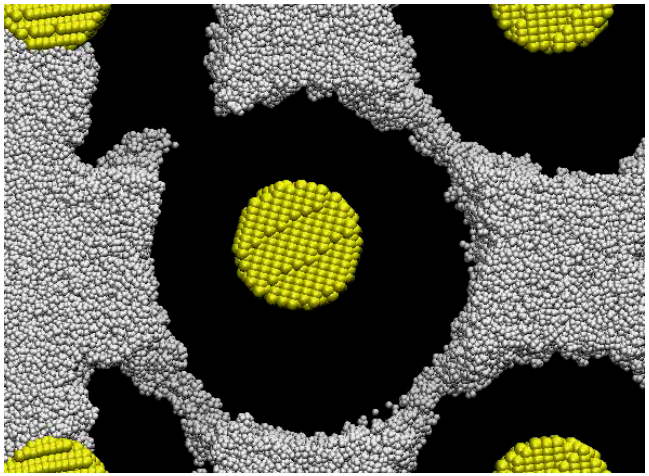


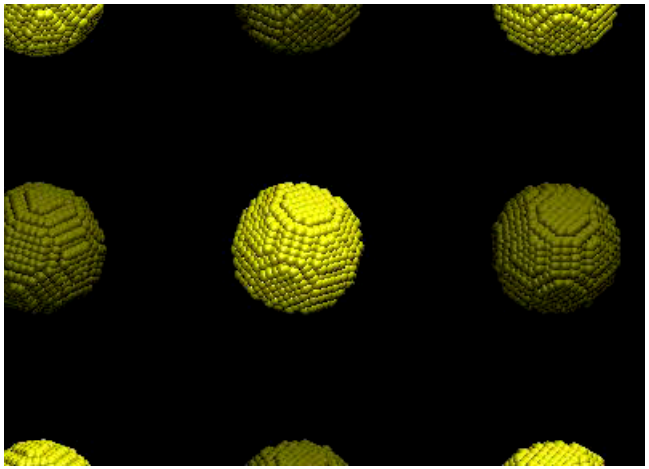
1.5 km/s impact, etc.



- Shock response in transient regime
- Gold and polymer slow mechanical coupling due to large mechanical impedance mismatch

Shock-compressed nanocomposite results

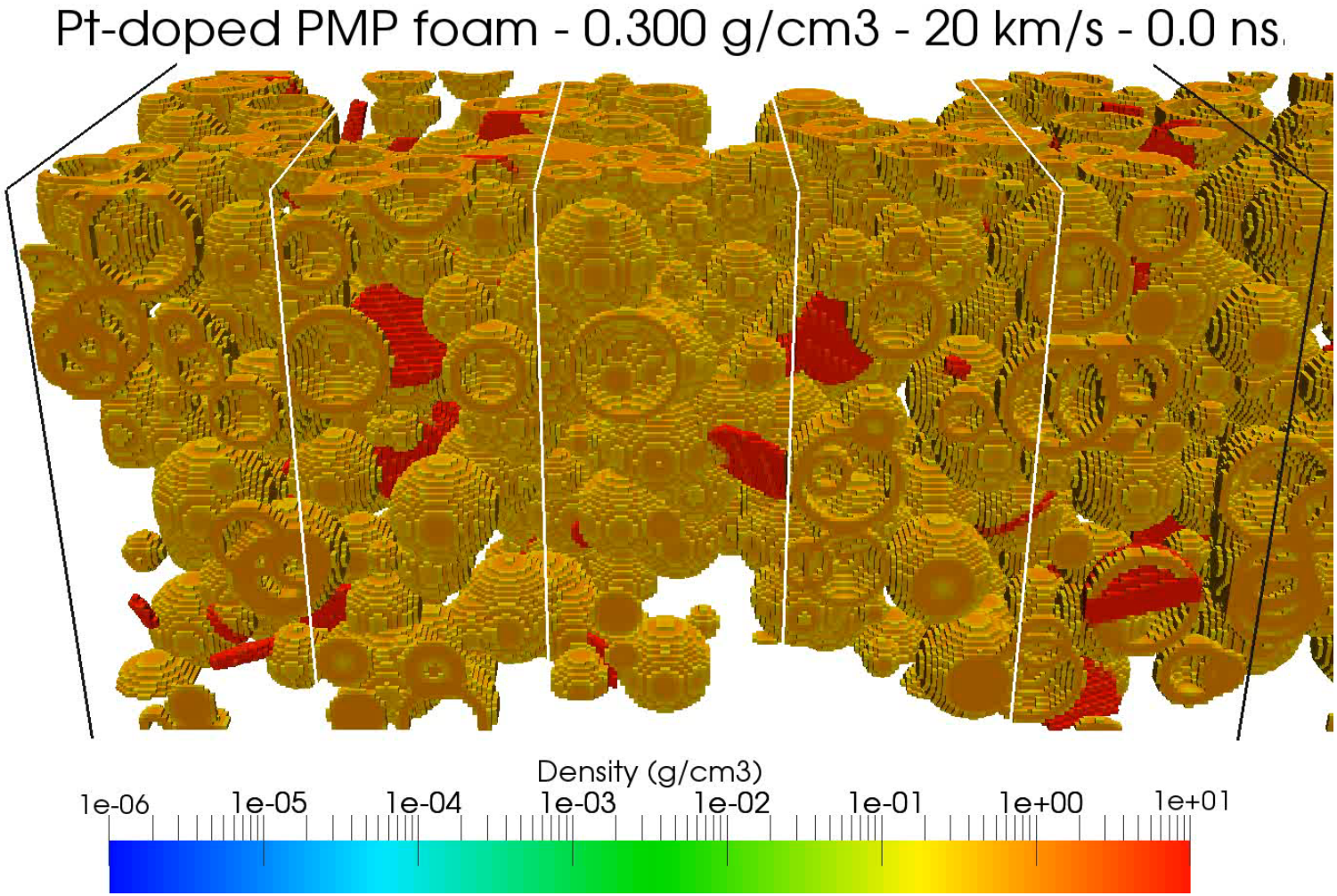




- Shock response in transient regime
- Gold and polymer slow mechanical coupling due to large inertial mismatch
- Polymer flows around gold while gold initially compresses elastically
- Density segregation apparent with vaporized polymer ahead of flowing hydrocarbon and molten metal
- **Wide and diffuse "shock" front**

Larger systems and longer times will be necessary with aggressive attempts to coarse grain or couple to continuum representations – informed by quantitative atomistic models.

Platinum doped foam 3D mesoscale simulation



Courtesy of Thomas Haill, Sandia – Hypervelocity Impact last week

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  - Cochrane, K.R., Desjarlais, M.P. and Mattsson, T.R., 2012. "Density Functional Theory (DFT) Simulations of Polyethylene: Principal Hugoniot, Specific Heats, Compression and Release Isentropes," in Shock Compression of Condensed Matter, American Institute of Physics, 4126, pp. 1271-1274.
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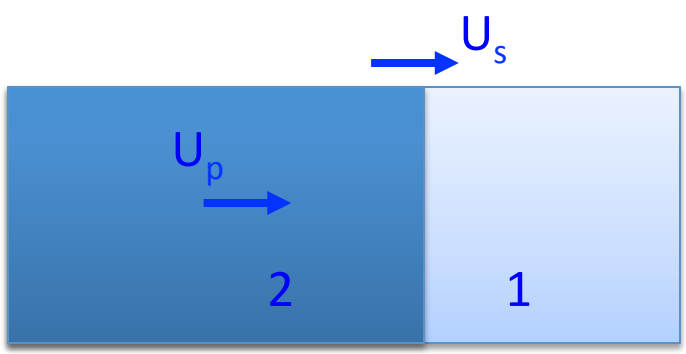
  - Lane, J.M.D., Grest, G.S., Thompson, A.P., *et al.*, 2012. "Shock Compression of Hydrocarbon Polymer Foam Using Molecular Dynamics," in Shock Compression of Condensed Matter, American Institute of Physics, 1426, pp. 1435-1438
- **Mixed EOS**
  - Magyar, R.J., Root, S., Haill, T.A., *et al.*, 2012. "Equations of State of Mixtures: Density Functional Theory (DFT): Simulations and Experiments on Sandia's Z Machine," in Shock Compression of Condensed Matter-2011, American Institute of Physics, 1426, pp. 1195-1198.
  - Magyar, R.J., Root, S., Mattsson, T.R. and Cochrane, K., 2012. "Ethane and xenon mixing: density functional theory (DFT) simulations and experiments on Sandia's Z machine," Technical report SAND2012-1942C, Sandia National Laboratories, Albuquerque, NM, March 2012 (presented at the American Physical Society March Meeting 2012, Boston, MA.).

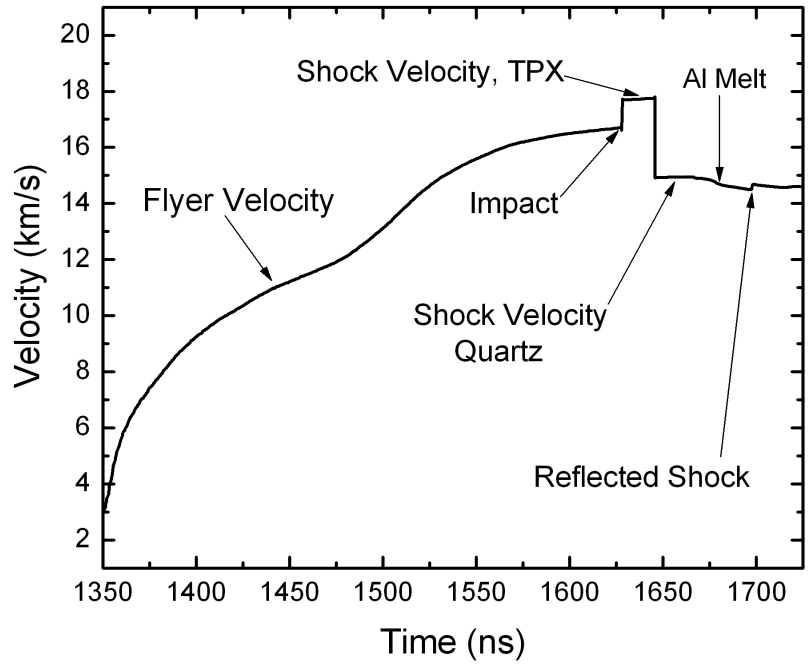
We reach Mbar pressures in materials by executing flyer-plate impact experiments

- **Straightforward to analyze plate-impact data**
  - Long steady shocks
  - Conservation of mass, momentum, and energy
  - Rankine-Hugoniot relation

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



Steady shock wave in plastics



Data from a flyer impact experiment: tracking flyer velocity and shock speeds in quartz and TPX, both having reflective shock fronts.

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

Molecular Dynamics (MD) simulations

- Solve Newton's equation…

$$m_i \frac{d^2 \mathbf{r}_i}{dt^2} = \mathbf{F}_i$$

$$\mathbf{F}_i = -\nabla V_i$$

6*N* coupled ODEs

$$\begin{aligned}
\mathbf{v}_i^{(l+\frac{1}{2})} &= \mathbf{v}_i^l - \frac{\mathbf{F}_i^l}{2m_i}\Delta t \\
\mathbf{r}_i^{(l+1)} &= \mathbf{r}_i^l + \mathbf{v}_i^{(l+\frac{1}{2})}\Delta t \\
\mathbf{v}_i^{(l+1)} &= \mathbf{v}_i^{(l+\frac{1}{2})} - \frac{\mathbf{F}_i^{(l+1)}}{2m_i}\Delta t
\end{aligned}$$

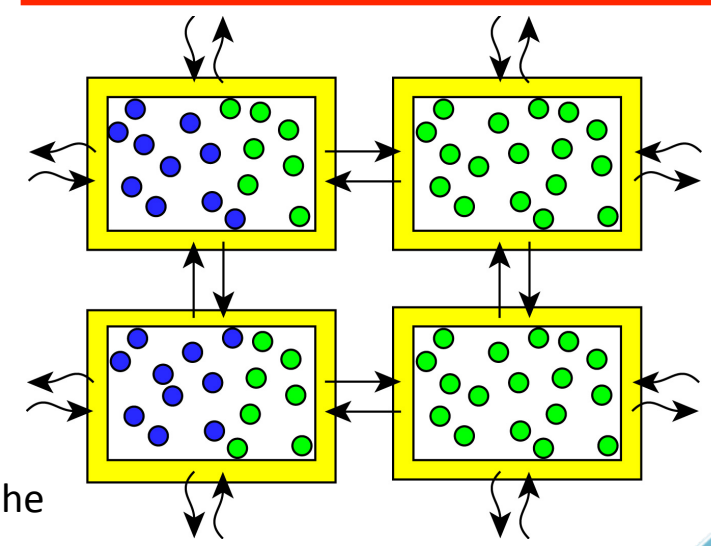
Mathematical Formulation

Classical Mechanics

Atoms are Point Masses: $\boldsymbol{r}_1, \boldsymbol{r}_2, \ldots\ldots \boldsymbol{r}_N$

Positions, Velocities, Forces: $\boldsymbol{r}_i, \boldsymbol{v}_i, \boldsymbol{F}_i$

Potential Energy Function = $V_i(\boldsymbol{r}^N)$



Sandia's LAMMPS code is spatially parallel

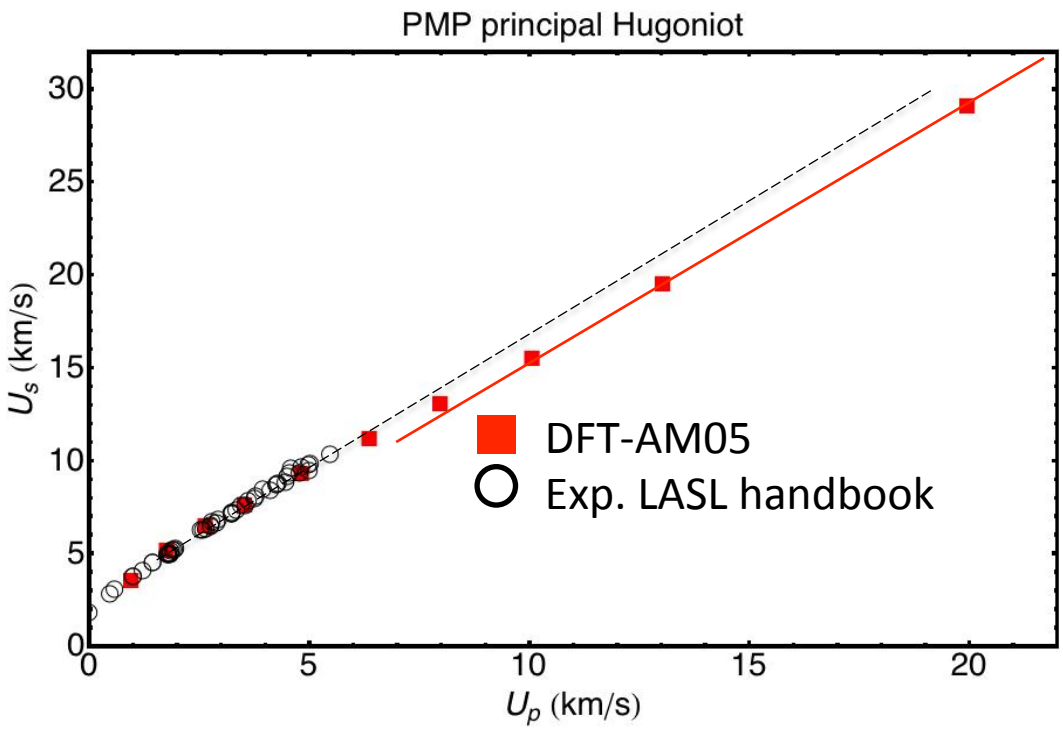
Large-scale **A**tomic/**M**olecular **M**assively **P**arallel **S**imulator

Problem: Δt tied to the fastest atomic motion t is the timescale of physical interest

$nsteps = t / \Delta t = 10^6 \ldots 10^{15}$

DFT/QMD shock compressed plastic to 500 GPa

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

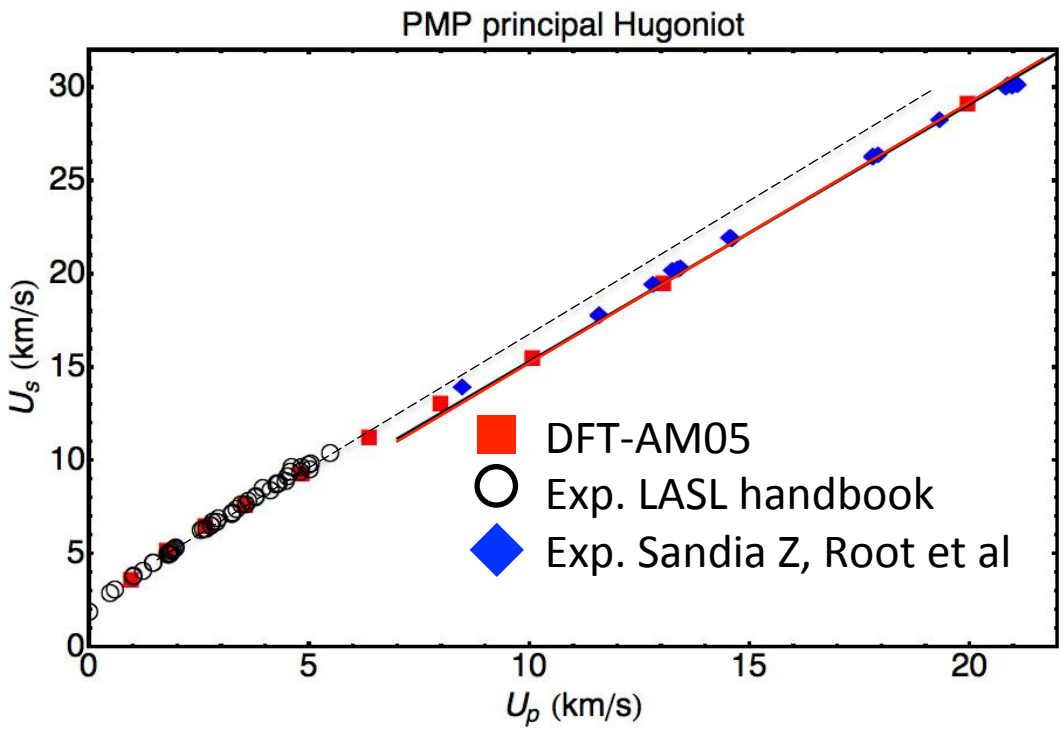


- DFT/QMD validated for polymers under shock compression to 50 GPa
- Curvature for weak shocks
- Prediction to shock velocity of almost 30 km/s (500 GPa)

T.R. Mattsson et al. «First-principles and classical molecular dynamics simulation of shocked polymers », Phys. Rev. B 81, 054103 (2010).

DFT/QMD validated to 500 GPa for dense plastic

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



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