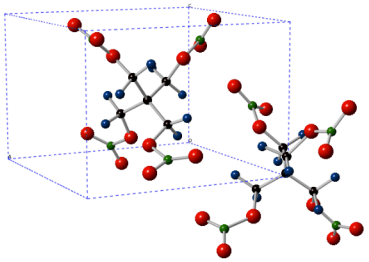
SAND2011-3152C



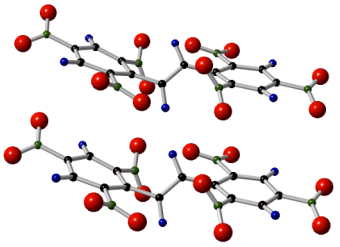
# Calculating Hugoniots for molecular crystals from first principles

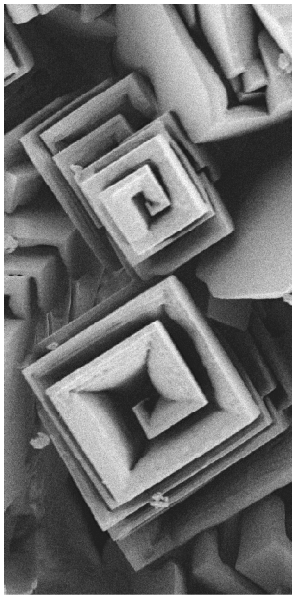


**Dr. Ryan R. Wixom**

**Dr. Ann E. Mattsson and Dr. Thomas R. Mattsson**

**Sandia National Laboratories, NM USA**





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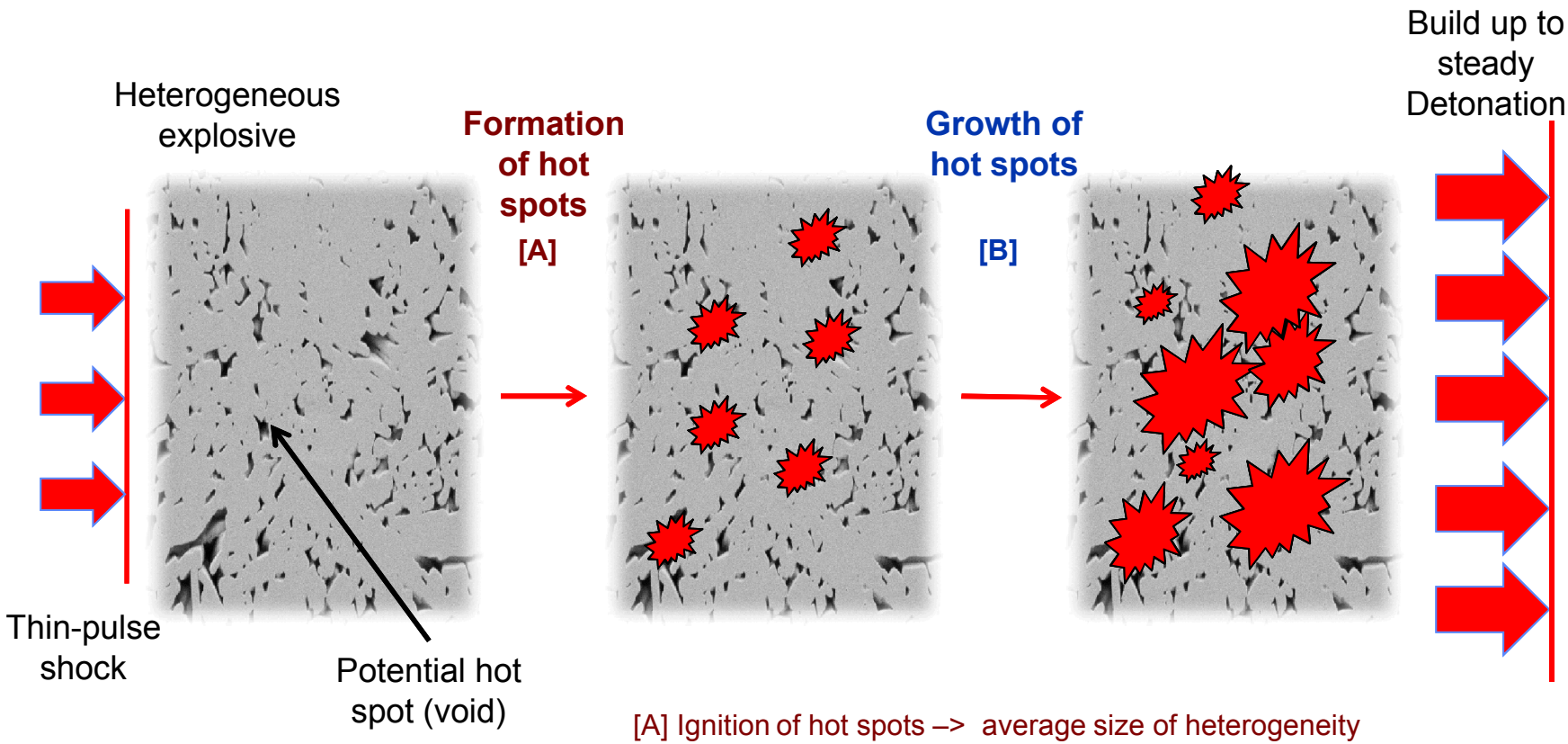
# 2: Motivation: Modeling shock initiation in consolidated molecular crystal explosives (HNS, TATB, CL-20)






[A] Ignition of hot spots –> average size of heterogeneity
[B] Growth to sustained detonation –> interface area

Sensitivity reversal goes away for high pressure shocks. Some of the above results contradict the grain burn concept.
**Sensitivity (?) : Critical Pressure and Critical Diameter have opposite dependence on microstructure**

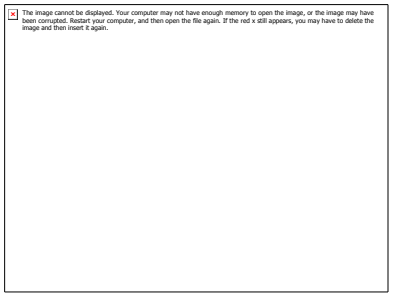


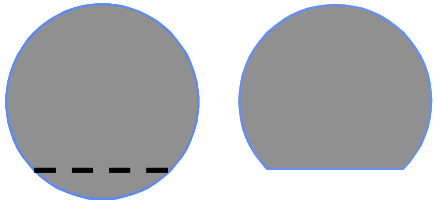
Adapted from Khasainov et al. Shock Waves (1997) 7:89-105

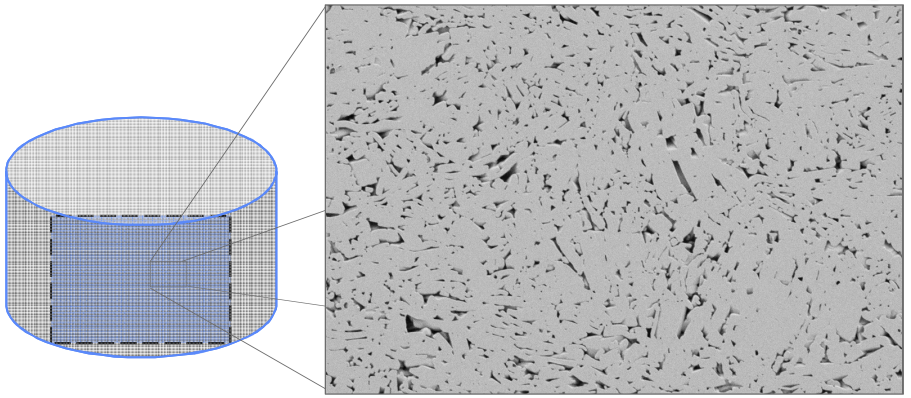
# 3: Motivation: Hydrocode simulations with explicit microstructure



HNS-FP, 90% TMD







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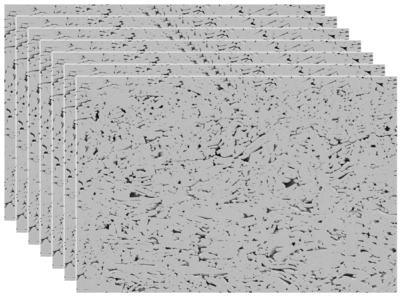
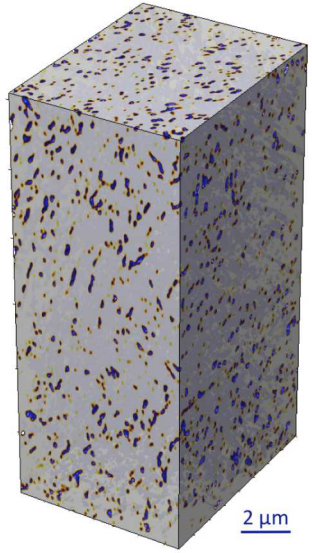
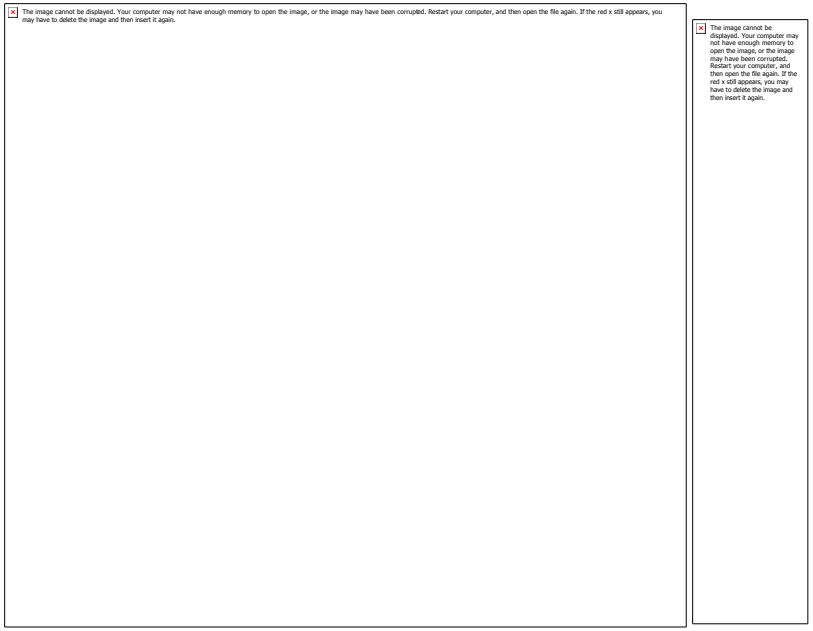


Nanotomography: 25 nm slices



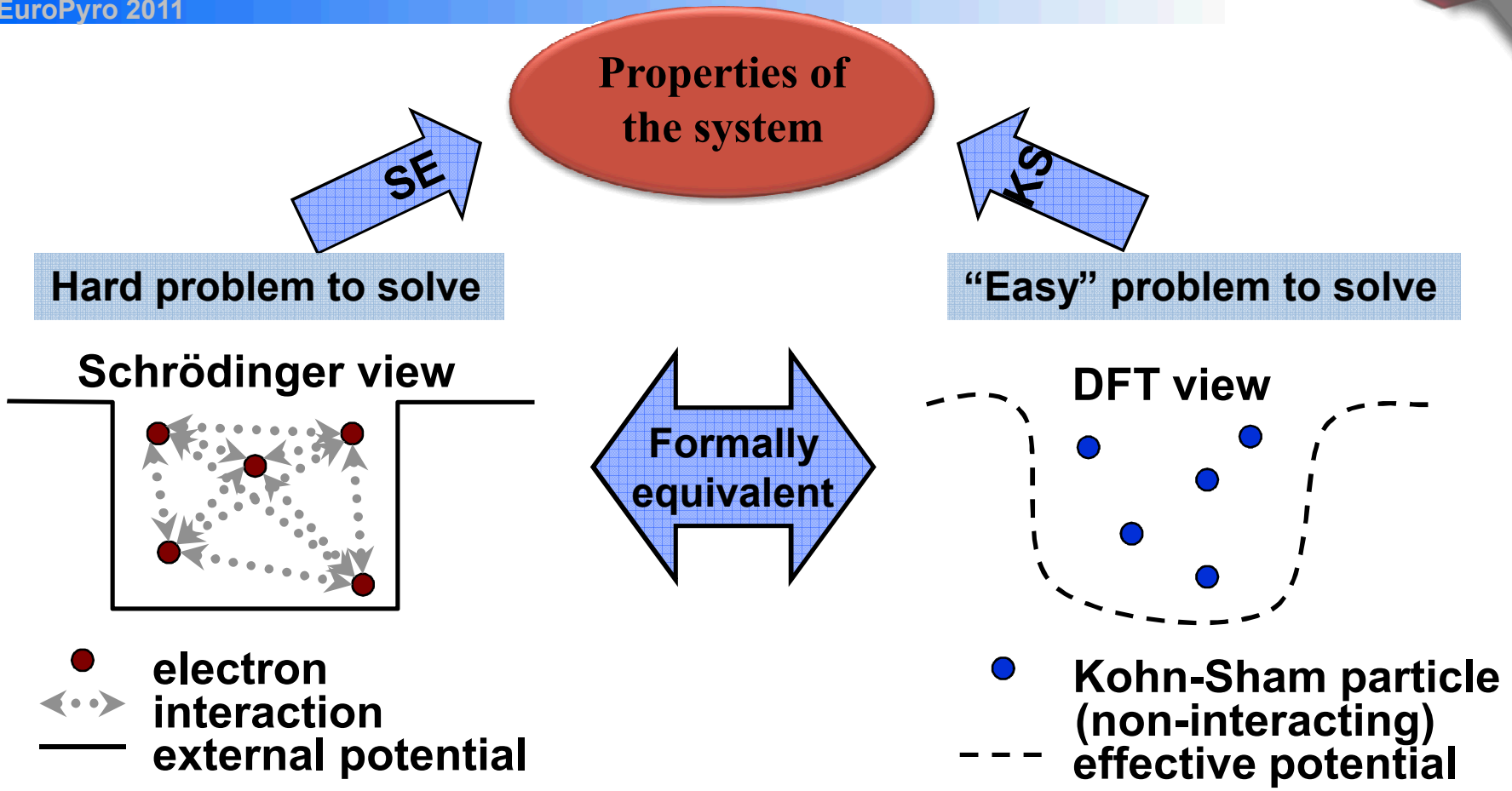

80,000 pores



R.R. Wixom et al. J. Mater. Res. 25 (2010) 1362

# 4: Density Functional Theory and XC functionals






$$v_{eff}(\boldsymbol{r}) = v(\boldsymbol{r}) + \int \frac{n(\boldsymbol{r}')}{|\boldsymbol{r}-\boldsymbol{r}'|}\, d\boldsymbol{r}' + \frac{\delta E_{xc}[n(\boldsymbol{r})]}{\delta n(\boldsymbol{r})}$$

AM05, LDA, GGA, Meta-GGA, Hybrids

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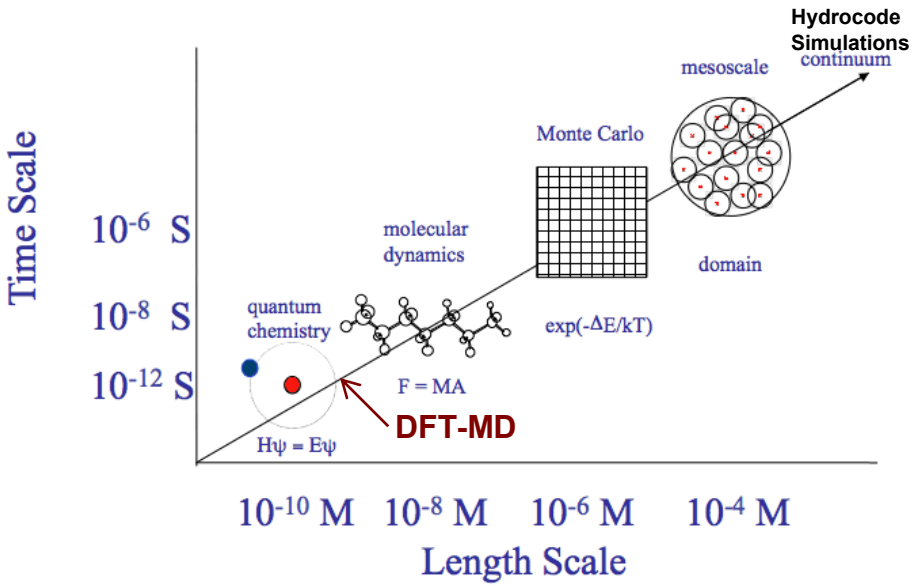
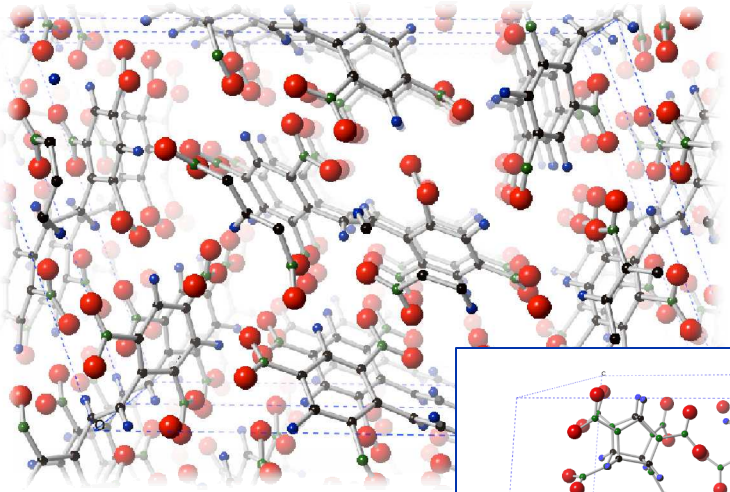
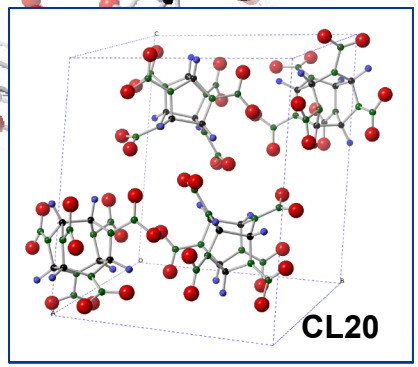
# 5: DFT based Molecular Dynamics (DFT-MD)



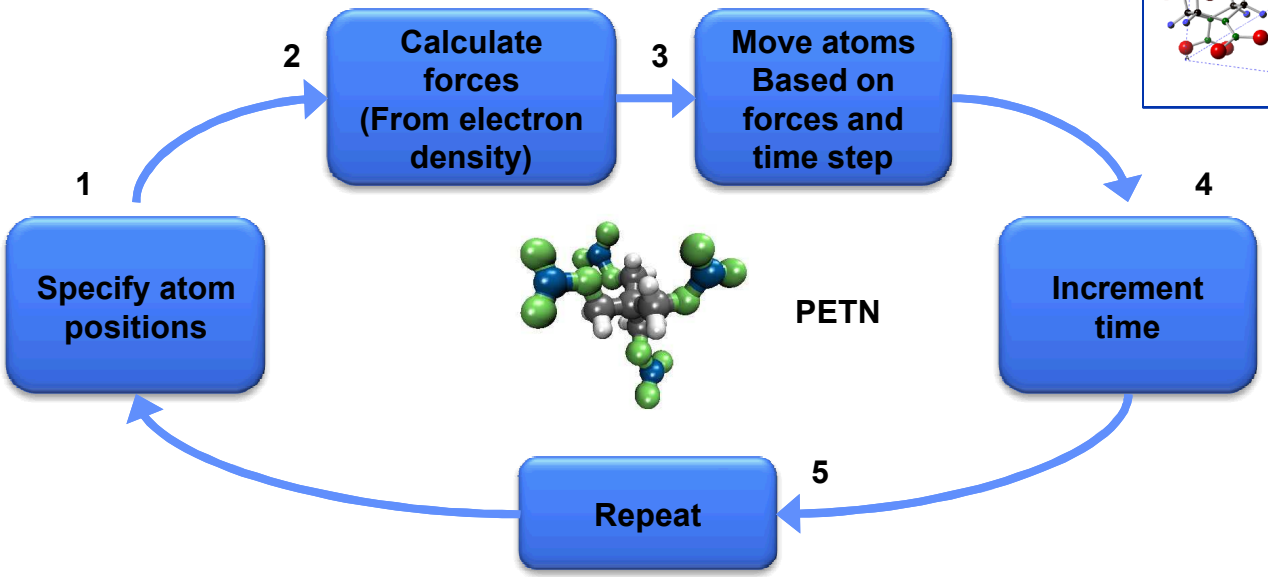


HNS

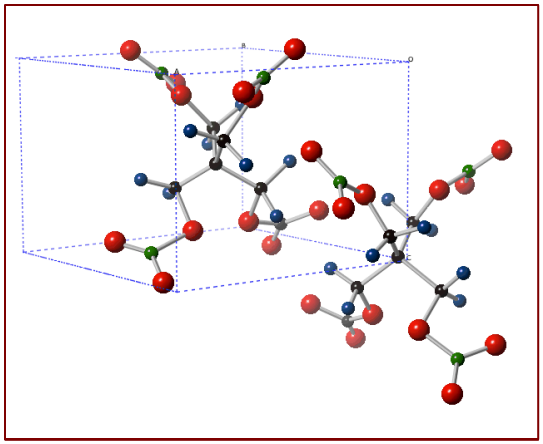


CL20



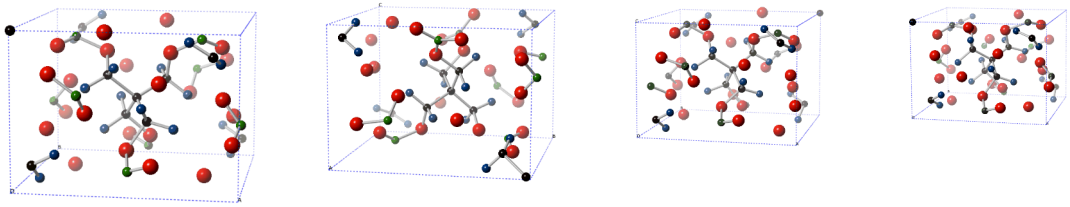
# 6: Finding the Hugoniot State (P,T,E) for any V.



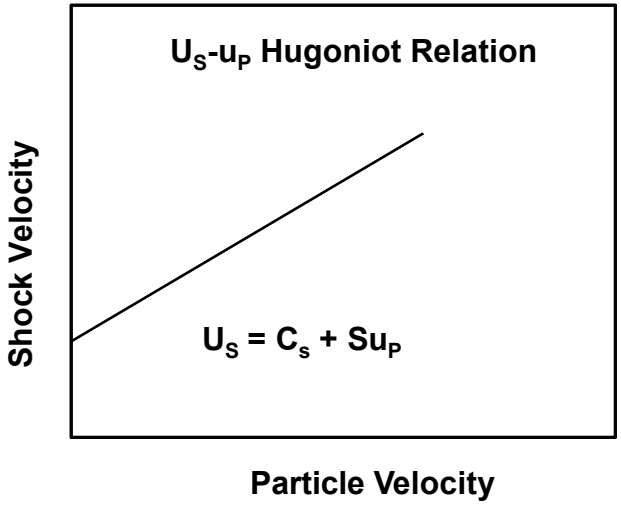


PETN, $V_o$ at 300K

1 unit cell → Iterative compression



| 1.0 a | 0.95 a | 0.90 a | 0.85 a |
|---|---|---|---|
| 1.0 V | 0.85 V | 0.72 V | 0.61 V |




**Mass** $\rho_o D = \rho_1 (D - u_1)$

**Momentum** $P_1 = \rho_o D u_1$

**Energy** $E - Eo = \frac{1}{2}(P + Po)(Vo - V)$ **R.H. equation**

**Key Point: jump conditions are only valid on the Hugoniot**

**Approach 1:** Set V, ramp T, and solve for where above is true.
**Approach 2:** Set V, run several Ts, fit to P(T) and E(T) and solve.

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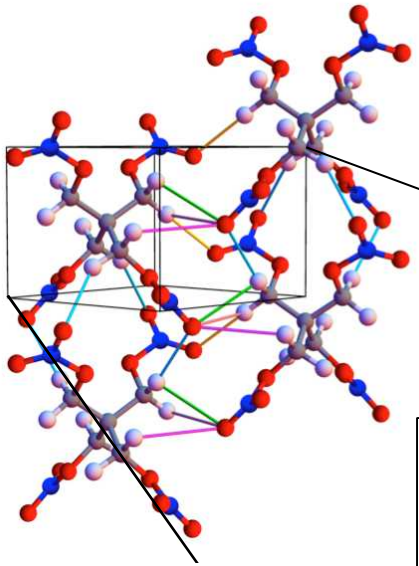
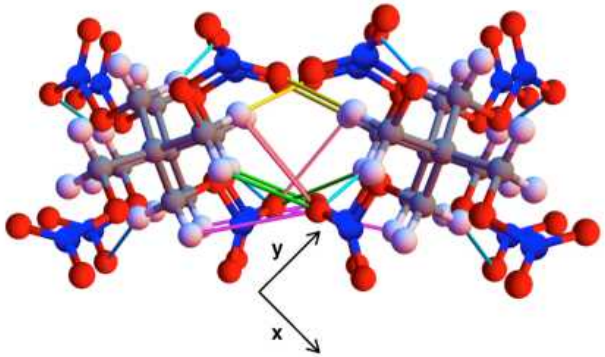
# 7: DFT-MD Reference State

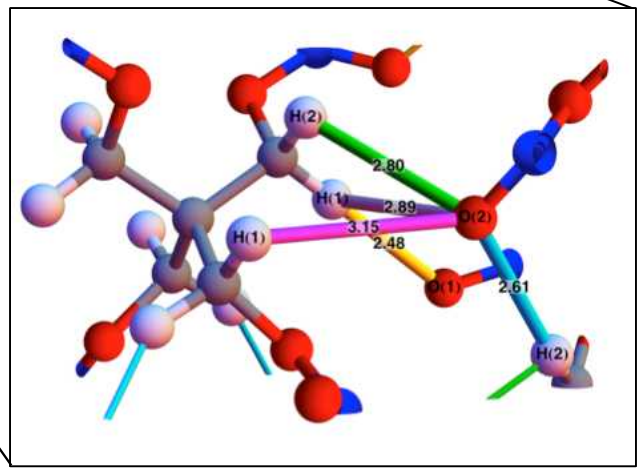


**PETN: Equilibrium volume and 300K ($P_0$, $T_0$, $V_0$).**






29 atoms in a molecule, 2 molecules in a unit cell.




van der Waals' bonds between O-H pairs. Experimental distances (Å).

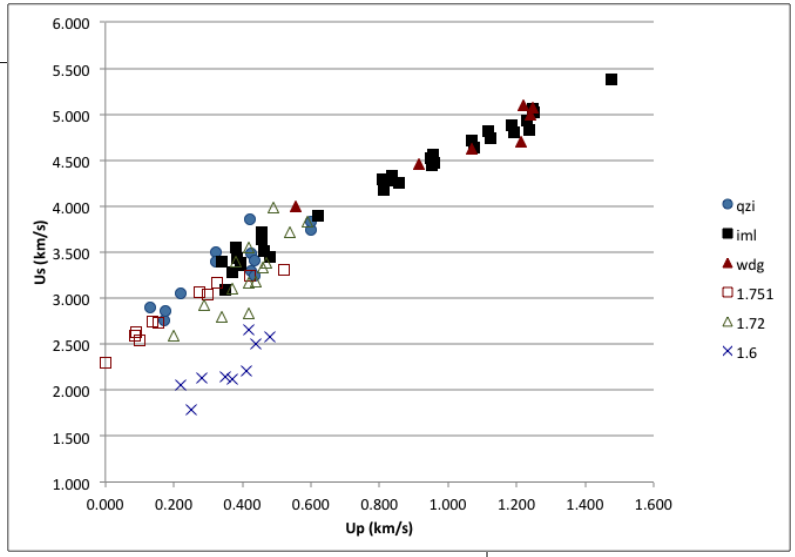
1. Intermolecular bonding is not described by AM05. Incorrectly described by other functionals.
2. Under strong compression, these errors should vanish.
3. A.E. Mattsson and G. Cragg currently working on a cure.

# 8: PETN experimental shock data



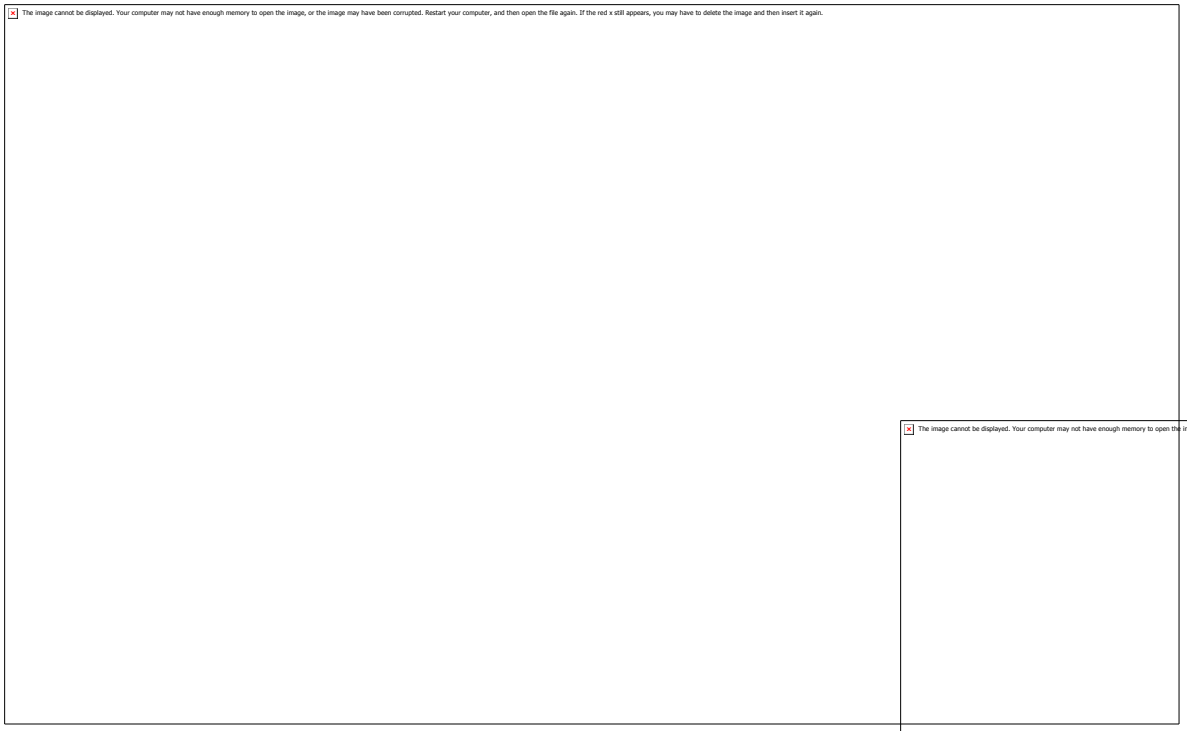
## Single Crystal Shock data from the LASL shock handbook (Marsh)

The image cannot be displayed. Your computer may not have enough memory to open the image, or the image may have been corrupted. Restart your computer, and then open the file again. If the red x still appears, you may have to delete the image and then insert it again.

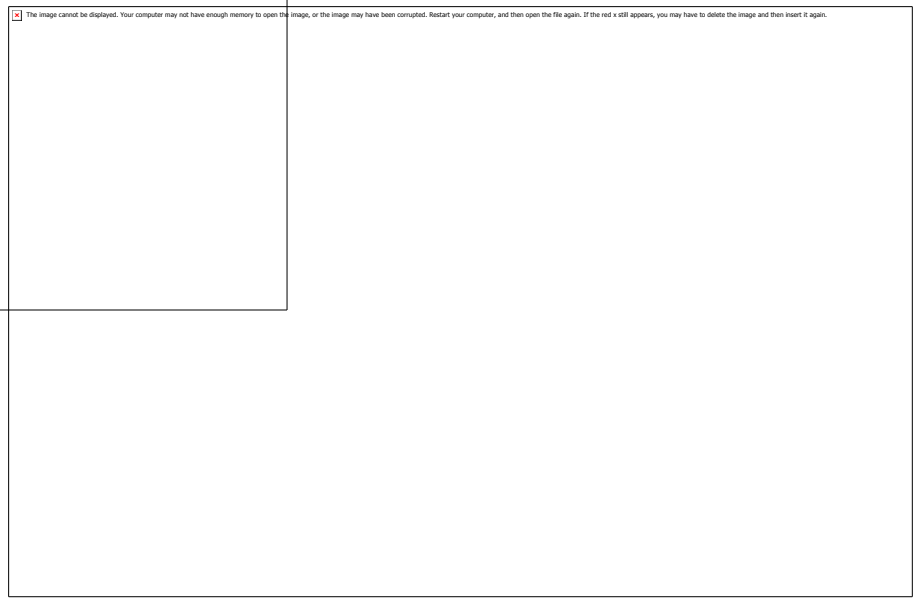


# 9: DFT-MD Hugoniot Relations for PETN



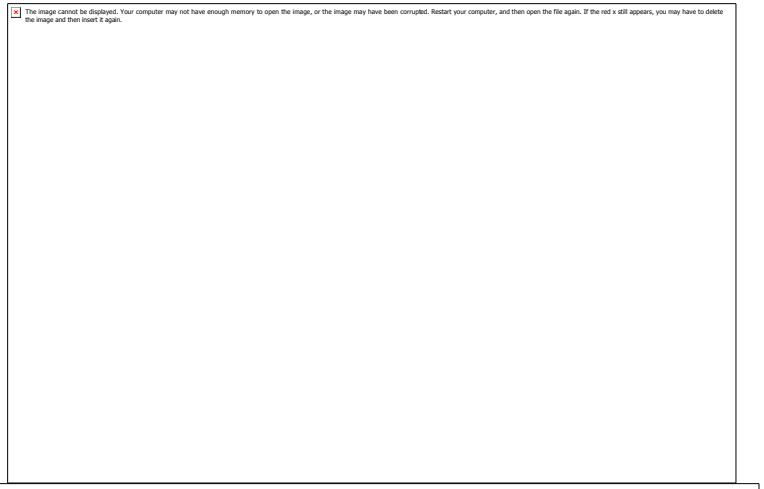


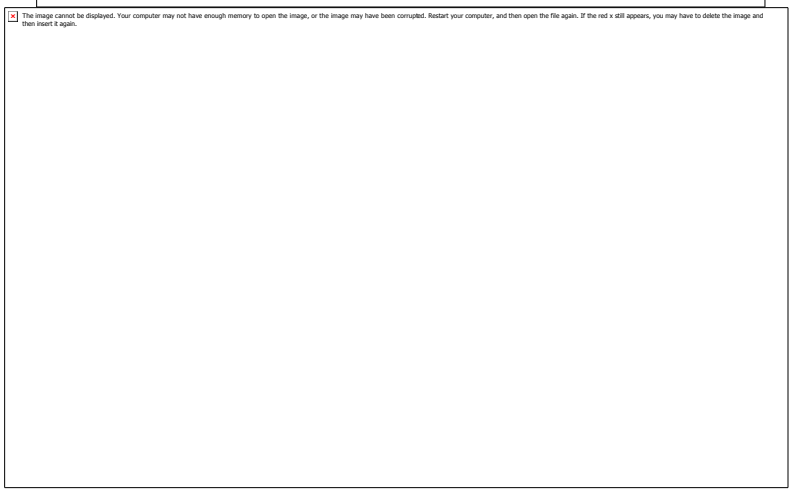

**Remarkable agreement!**



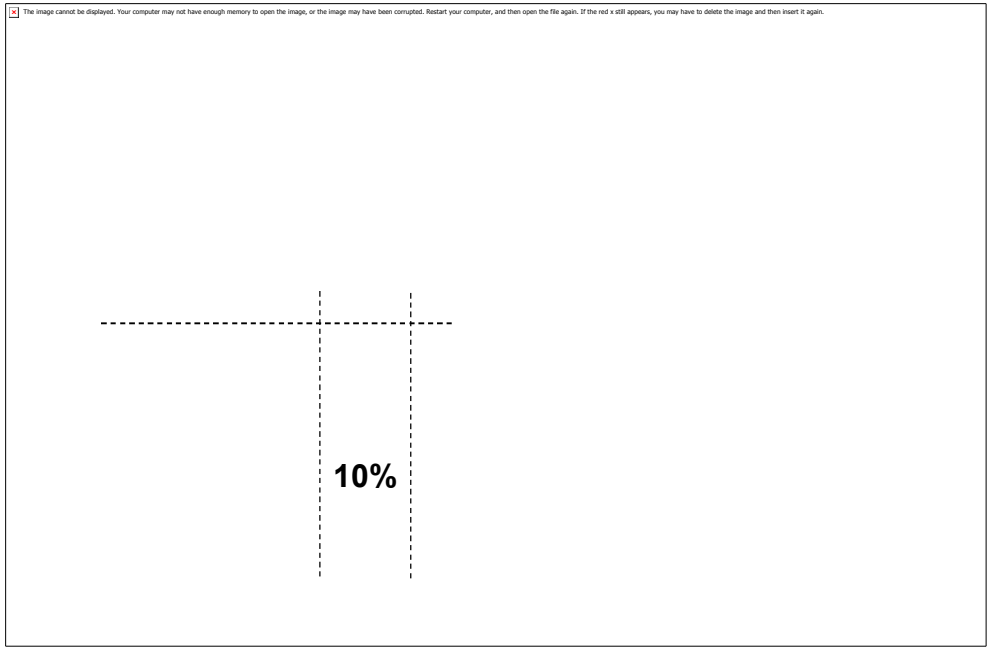
# 10: PETN experimental shock data





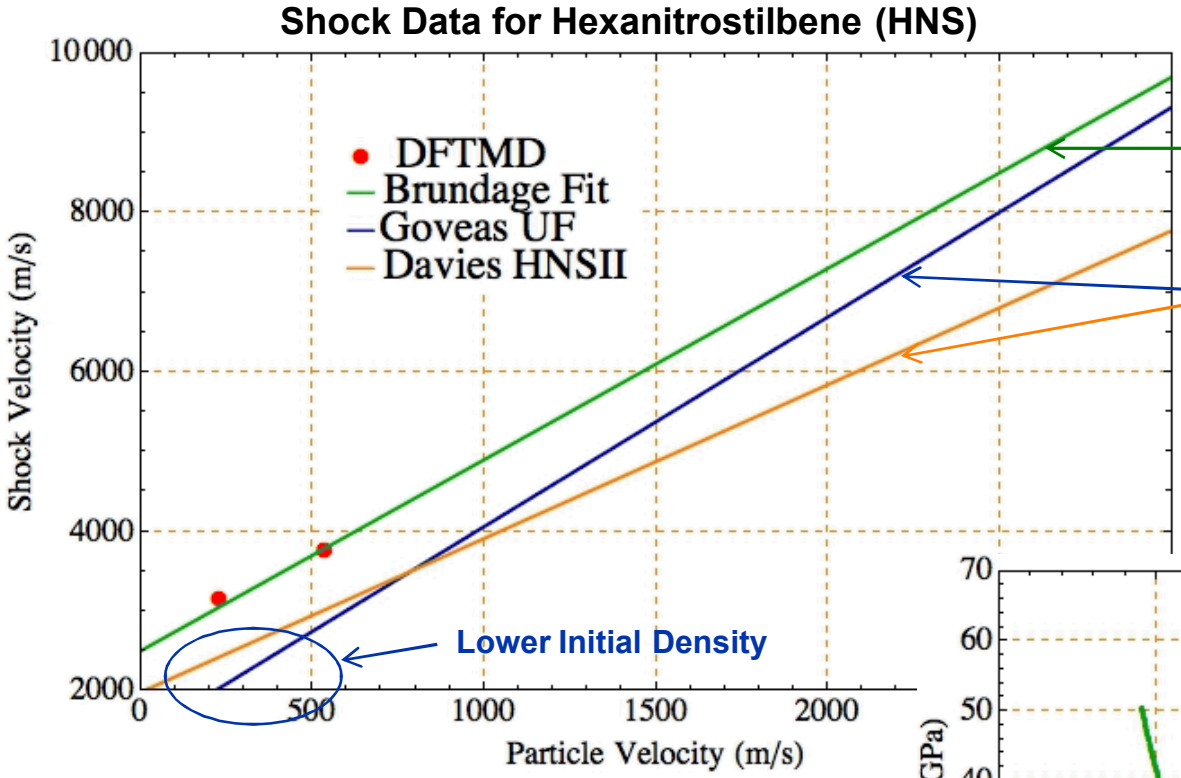




1. **Predicted Hugoniot for PETN is not a straight line.**
2. **Predicted Hugoniot fits the available data very well.**
3. **Large errors in P&V in extrapolated region when relying on experimental data.**



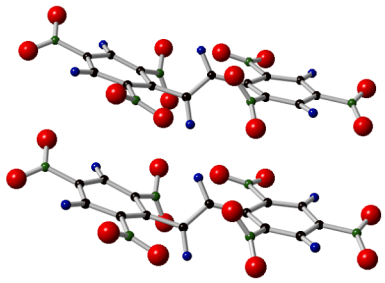
# 11: DFT-MD Hugoniot HNS (Preliminary!)

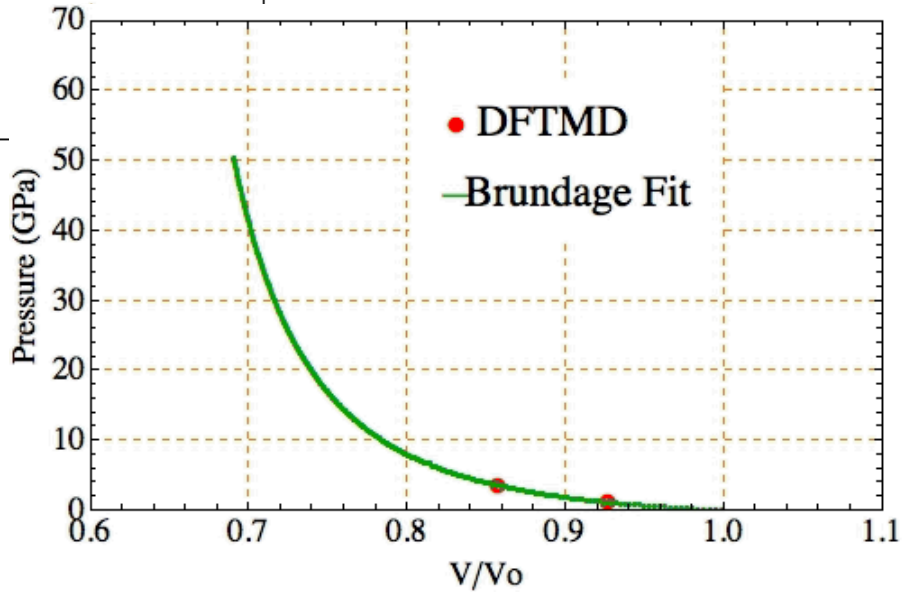





Fit to Sheffield / Goveas data combined with inter-granular stress measurements (2010 IDS)

~91% TMD Pressings (APS SCCM 2005)



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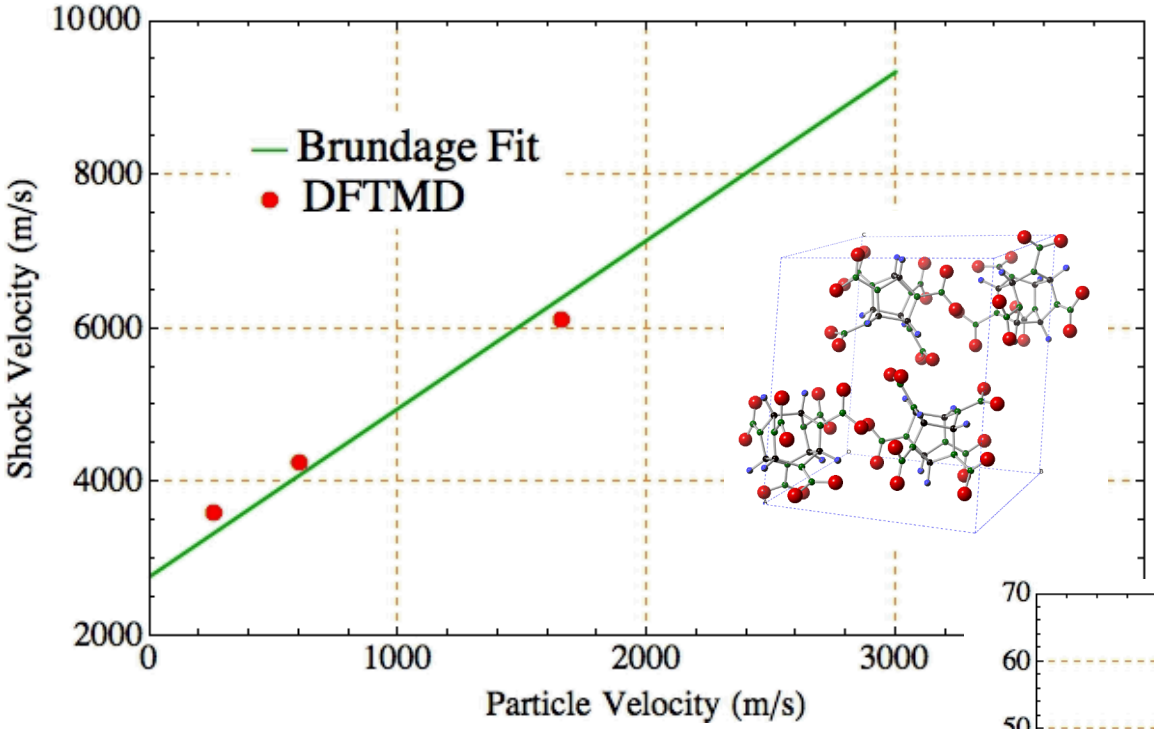
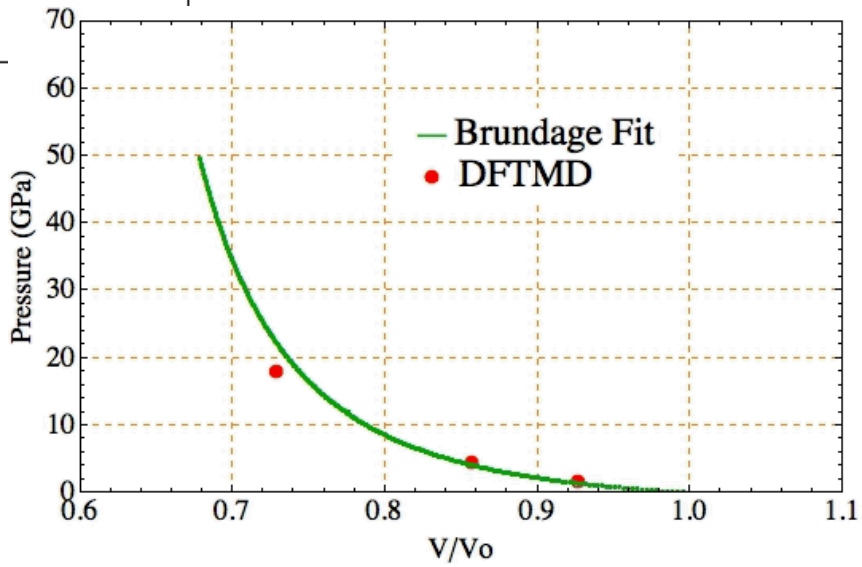
# 12: DFT-MD Hugoniot CL-20 (Preliminary!)



**Shock Data for hexanitrohexaazaisowurtzitane (HNIW / CL-20)**




A.L. Brundage: EOS DEVELOPMENT AND NUMERICAL MODELING OF CL-20 COMPACTION, in 16th APS Topical Group on Shock Compression of Condensed Matter (American Institute of Physics, Melville, NY, 2009).




**Note: DFTMD data analyzed with slightly higher density.**
**Gump and Peiris: 1423 $A^3$**
**Nielsen …. Gilardi et al.: 1424 $A^3$, 2.044 $g/cm^3$**
**Sorescu: 1412 $A^3$ , 2.06 $g/cm^3$**

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# 13: Summary, Conclusions, Future Work



**Summary:**

① Crystalline Hugoniot (full EOS if possible) is needed for accurate hydrocode modeling and for predicting performance of new device designs.

② Shock data from the literature may not provide adequate accuracy or cover desired range (extrapolation above 15GPa). For many explosives, the data doesn't exist.

③ DFT-MD can be used to accurately predict shock response of explosives.

④ DFT-MD also provides access to temperature data (full EOS), specific heat, diffusion coefficients, reaction dynamics, etc…

**Future Work:**

① Additional explosives and material properties. (CL-20,HNS,TATB, DNTF, HNAB)

② Functional Development to correctly describe vdWs' forces near the equilibrium volume.

③ Diamond Anvil Cell experiments on HNS for validation of MD calculations and functional development.