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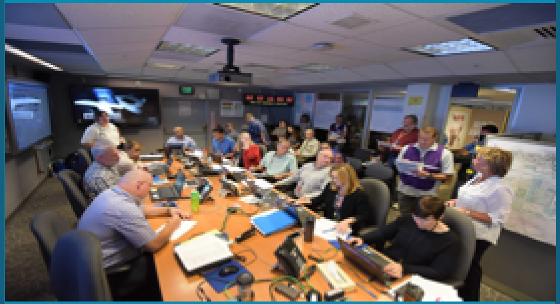
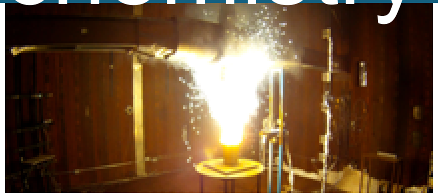
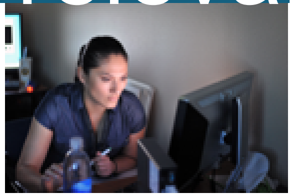
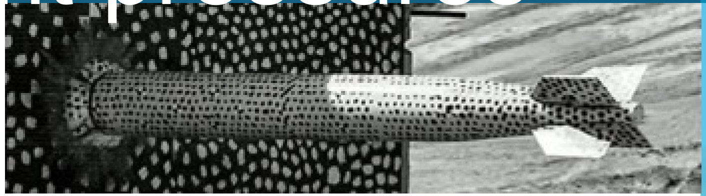
Molecular dynamics simulations of a phenolic polymer shocked to chemistry-relevant pressures









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Background – Phenolic polymers under shock

Phenolic polymers

- Commonly used in extreme environments – subjected to heating and shock.
- Have a ”cusp” in Hugoniot (20 - 30 GPa)
  - Observed to be due to chemical reactions in other polymers.

Shock induced chemistry and Hugoniot cusp - common in polymers.

- Reaction previously characterized in polytetrafluoroethylene $(-(CF_2)-(CF_2)-)_n$ as a dissociation reaction into amorphous carbon and gaseous fluorocarbons.

<u>Questions</u>

1. Can we capture shock-induced chemistry and the Hugoniot cusp in phenolic polymers with reactive molecular dynamics?
2. Can chemical mechanisms explain the cusp?

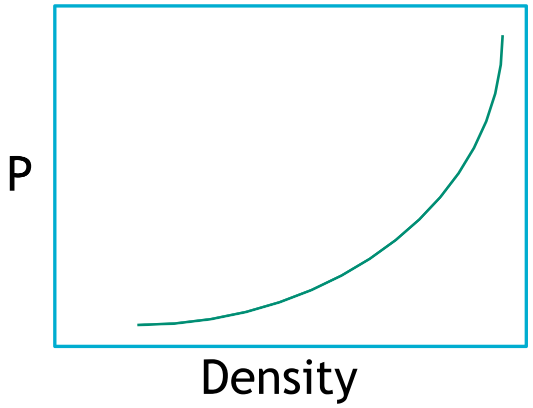
W. J. Carter and S. P. Marsh, *Hugoniot Equation of state of polymers* (University of California Press, Berkeley, 1995).
C. E. Morris et al. *J. Chem. Phys.* **80**(10), 5203-5218 (1984).
J. M. Lang et al. *AIP Conf. Proc.* **1979**, 090008 (2018).

Hugoniot: the locus of points representing a series of final, shock states originating from a single reference state. The state variables of the shock (1) and reference (0) states obey mathematical relationships (Rankine-Hugoniot (jump) conditions) to conserve energy, mass and momentum.

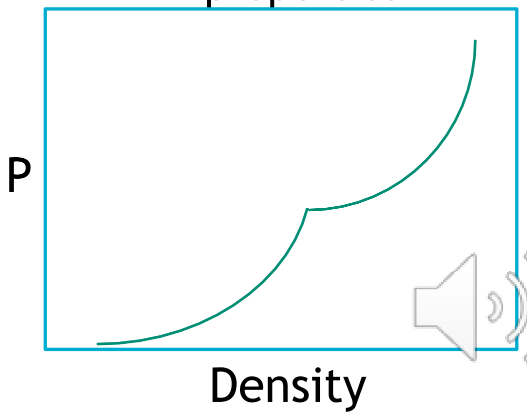
Rankine-Hugoniot energy equation

$$(E_1 - E_0) = \frac{1}{2}(P_1 + P_0)(V_0 - V_1)$$

Hugoniot



Hugoniot with shock induced change of material properties



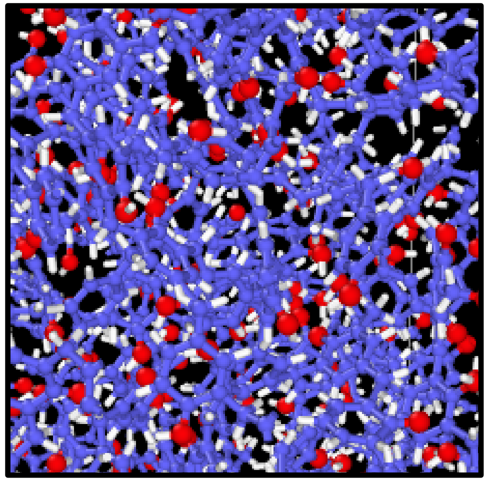
Hugoniot simulations

Non-propagating, constant stress Hugoniostat method by Ravelo uniaxially compresses system until the final pressure is reached. Thermostatted to satisfy jump conditions. More affordable than traditional non-equilibrium molecular dynamics. Previous success with polyethylene.

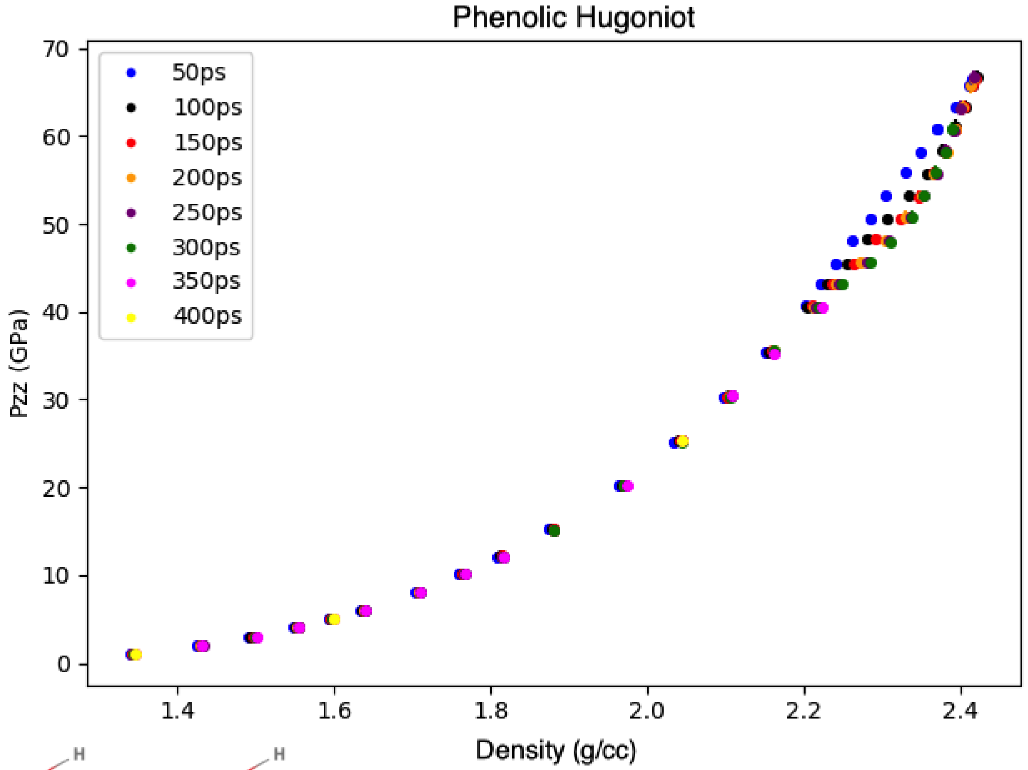
$$(E_1 - E_0) = \frac{1}{2}(P_1 + P_0)(V_0 - V_1)$$

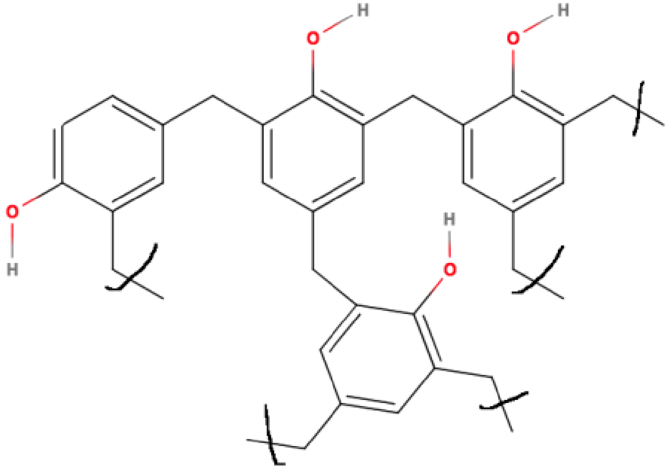
-LAMMPS molecular dynamics 3d atomistic simulation code

-Periodic boundary conditions



Shoulder or cusp appears in Phenolic Hugoniot above 40 Gpa over finite timescale.





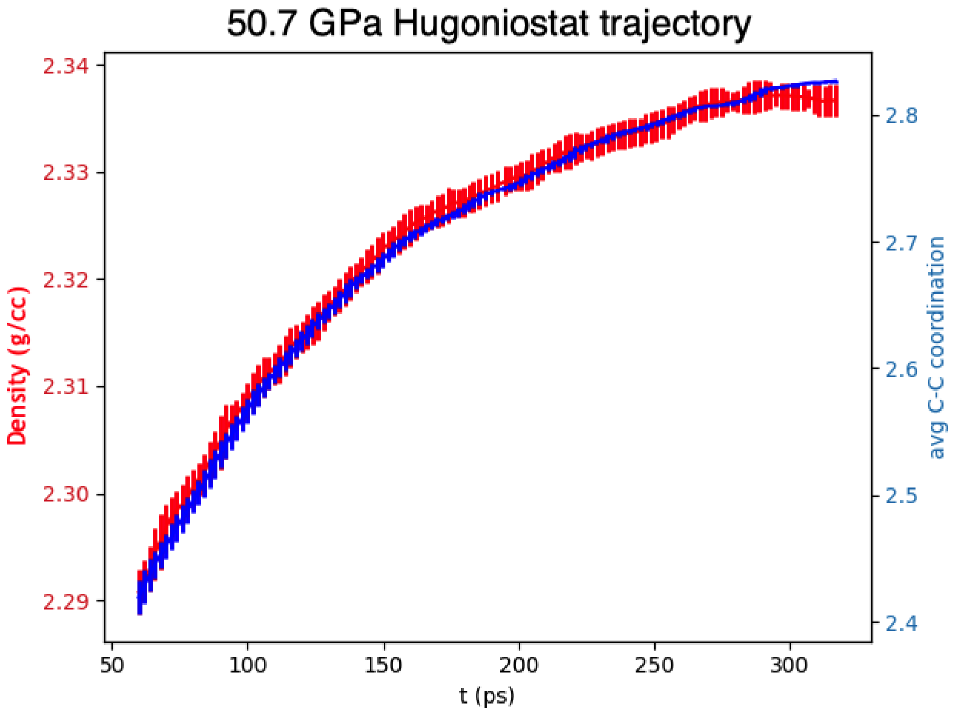
R. Ravelo et al., *Phys. Rev. B* **70**, 014103 ([illegible]4).
T. R. Mattsson et al., *Phys. Rev. B* **81**, 054103 (2010).
S. Plimpton, *J. Comput. Phys.* **117**, 1 (1995).

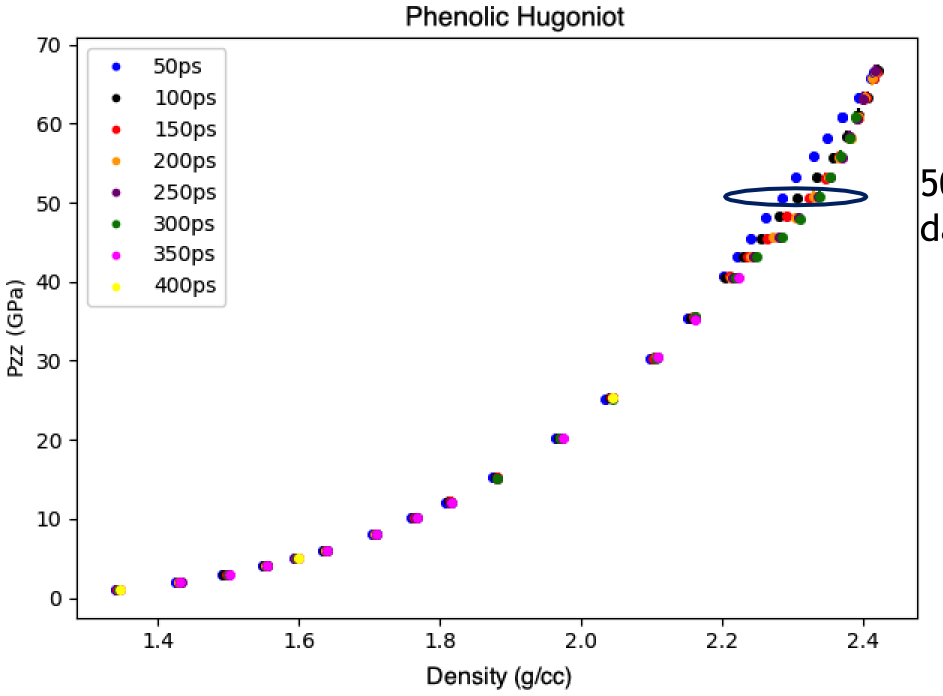
Results

What occurs during this transition?

1. Increase in average carbon-carbon coordination number, correlated in time with the increase in density.

2. Breakdown of C-H and C-O bonds to facilitate additional C-C bonding. This is a densifying mechanism for the carbon.





50.7 Gpa Hugoniot data points

Results

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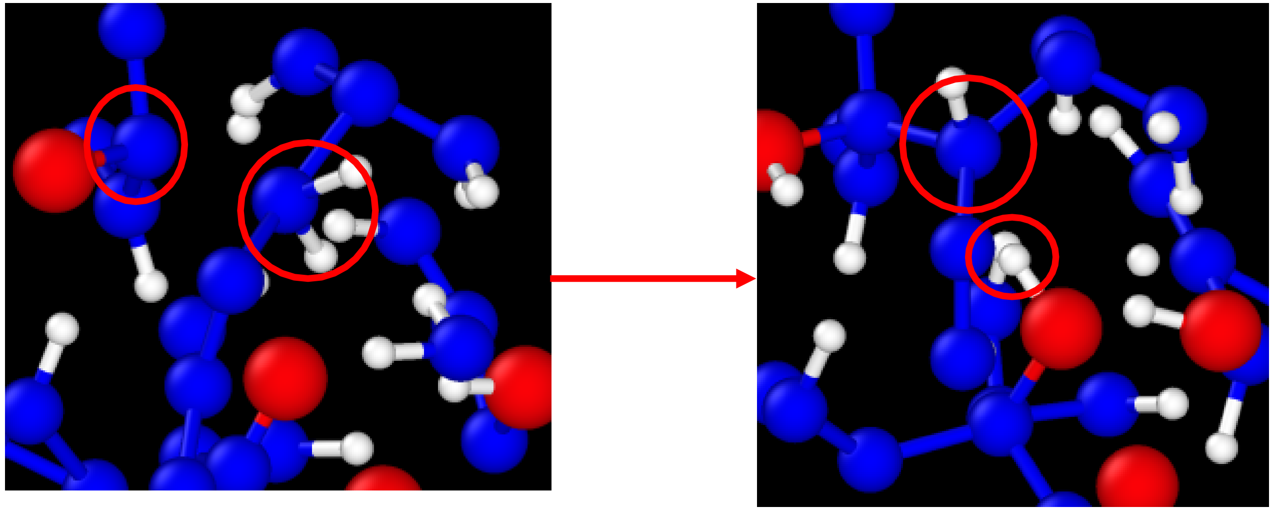
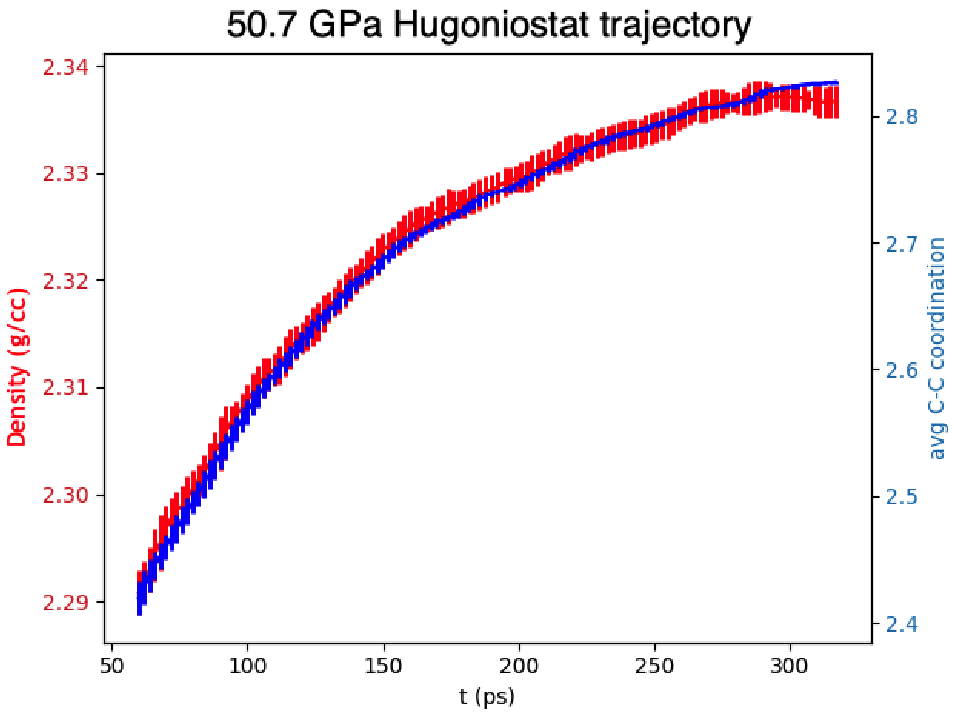


Dehydrogenation and formation of C-C bond



Conclusions

- The cusp or shoulder in the phenolic Hugoniot is captured with ReaxFF/Hugoniostat combination.
- This cusp appears as a result of the increase in C-C bonds under shock loading, forming a dense, highly crosslinked, carbonaceous solid.