

Density Functional Theory (DFT) simulations of polyethylene: principal Hugoniot, specific heats, compression and release isentropes

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Abstract. An accurate equation of state (EOS) for polyethylene is required in order to model high energy density experiments for CH₂ densities above 1 g/cc, temperatures above 1 eV, and pressures above 1 Mbar. Density Functional Theory (DFT) based molecular dynamics has been established as a method capable of yielding high fidelity results for many materials at a wide range of pressures and temperatures and has recently been applied to complex polymers such as polyethylene [1]. Using high density polyethylene as the reference state, we compute the principal Hugoniot to 350 GPa, compression isentrope, and several release isentropes from states on the principal Hugoniot. We also calculate the specific heat and the dissociation along the Hugoniot. Our simulation results are validated by comparing to experimental data [2,3] and then used to construct a wide range EOS.

INTRODUCTION

An accurate equation of state (EOS) is essential for accurate computer simulations. Many equations of state use Hugoniot data to tune models, but once the EOS building tool deviates from this, for example along a compression or release isentrope, the models often have large uncertainties as there is no data to show what corrections are needed. By performing ab initio calculations with Vienna Ab Initio Simulation Package (VASP) [1] [2], that information is created as pseudo-data.

$$2(E - E_0) = (P + P_0)(V_0 - V) \quad (1)$$

When simulating hydrodynamic responses in an MHD code, the simulations deviated from expected results. On examining the SESAME 7171 polyethylene EOS, the principal Hugoniot, calculated using the Rankine-Hugoniot [3] relation (Eq. 1) based on values found in that table, deviated from experimental data [4] [5]. At the time, we could not easily find any other experimental data to compare to. We also checked Mie-Gruneisen as another commonly

used EOS and found that it also stopped following the Hugoniot data, but at a much lower density. This prompted us to create pseudo-data using VASP and apply the additional information to build an EOS.

SIMULATIONS

VASP solves the Kohn-Sham equations [6] in a plane-wave basis set. Projector augmented wave potentials [7] [8] are used with AM05 [9] as the exchange and correlation functional. Our simulations used four strands of polyethylene with 16 carbon atoms in each strand. The ends of each strand were capped with an additional hydrogen to prevent cross bonding giving us C₁₆H₃₄. These strands started parallel to each other but were allowed to move as the forces dictated.

To calculate the Hugoniot, we start by equilibrating a simulation at some reference density and temperature, allowing the ions to move classically until the pressure and energy reach some average obtained through block averaging [10] to reduce correlation.

Once we have the reference points, we increase the density and adjust the temperature until Eq. 1 is true. There are two ways of doing this. The first is by adjusting the temperature slightly too high and, in another simulation, slightly too low and interpolate. Or, using the Nosier-Hoover thermostat, we slowly ramp the temperature until Eq. 1 is true. We then compare our simulated Hugoniot to data [11] as shown in Figure 1. As demonstrated and discussed in Section 4, the inflection at 2g/cc or 130 GPa is due to dissociation [12].

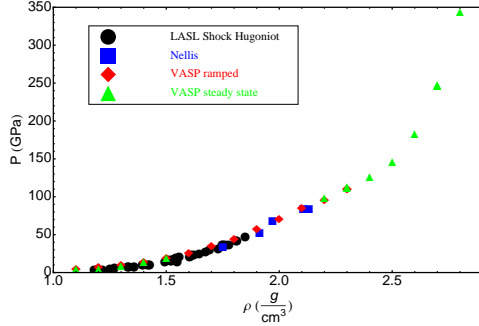


FIGURE 1. LASL Shock Handbook data and Nellis data overlaid with VASP simulations. The dissociation inflection is at approximately 2.0 g/cc to 2.4 g/cc

Using points the principal Hugoniot, we can calculate release isentropes and from our reference simulation, we can find the principal isentrope. Based on the assumption that for very small changes in density, the Hugoniot and isentrope are second order tangent, we actually calculate quasi-isentropes. We still use Eq. 1, but the reference points E_0 , P_0 , and V_0 of the current density are set to the E , P , and V of the previous density. This gives us more points across a broader range of EOS space to fit our equations Figure 2.

EOS CONSTRUCTION

Once we have finished the simulations, we start fitting equations to data and building an EOS. We use the Birch-Murnaghan Eq. 2 equation for the cold curve. Calculating the minimum energy for an amorphous system is computationally very difficult, so we fit the Birch-Murnaghan functions to the compression isentrope. Next we subtract the cold curve energy from the total energy and find that, in this

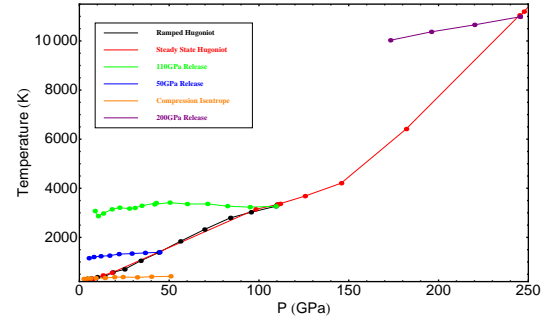


FIGURE 2. VASP simulations of the principal Hugoniot, compression isentrope, and several release isentropes.

case, the remaining energy is independent of density which allows us to use a function of temperature to fit all of energy space. The same technique is used for pressure, but, even without the cold curve, it still has a temperature dependence so an additional temperature parameter is included in the fit to take this into account. The result shown in Figure 3 is the wide range pressure of the new EOS. The difference in the principal Hugoniot of our new EOS and the others is shown in Figure 4

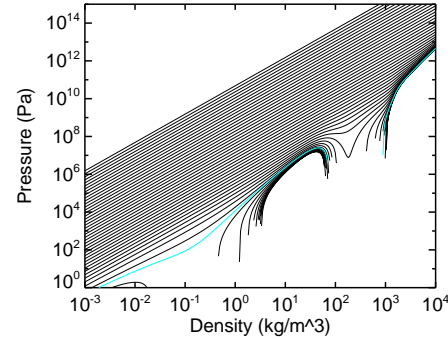


FIGURE 3. Wide range polyethylene EOS isotherms. From 10^{-2} to 10 g/cc below 500 Kelvin (cyan line) "foam" or porous region, the table is not realistic. This second minimum is an artifact of the equations used to design it.

Because the Birch-Murnaghan pressure is thermodynamically consistent with its energy and we are creating fits to thermodynamically consistent VASP data, we assume the pressure and energy functions will be consistent. Most of the hydrodynamic codes we have are designed to read tables and so the func-

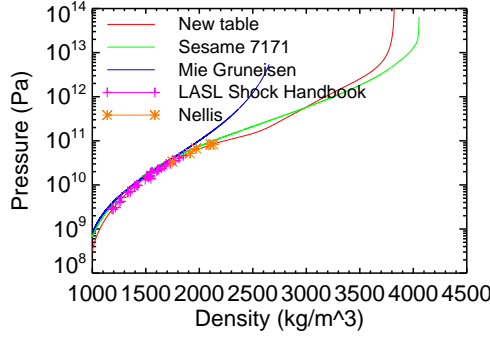


FIGURE 4. The Hugoniot from SESAME 7171, Mie-Grüneisen, and our new polyethylene EOS. The inflection in the new Hugoniot is from dissociation.

tions were written to a pressure table and an energy table at an arbitrary but fine density and temperature spacing. We use Eq. 3 to check. $\frac{\delta \varepsilon}{\delta V}|_T$ is calculated using Gaussian integration and $\frac{\delta P}{\delta T}|_V$ is center differenced from these tables. The maximum error was under 3% and the average error was less than 1% throughout the table.

$$E(V) = E_0 + \frac{9V_0B_0}{16} \left\{ \left[\left(\frac{V_0}{V} \right)^{\frac{2}{3}} - 1 \right]^3 B'_0 + \left[\left(\frac{V_0}{V} \right)^{\frac{2}{3}} - 1 \right]^2 \left[6 - 4 \left(\frac{V_0}{V} \right)^{\frac{2}{3}} \right] \right\} \quad (2)$$

$$\frac{\delta \varepsilon}{\delta V}|_T = T \frac{\delta P}{\delta T}|_V - P \quad (3)$$

As can be seen in Figure 3, the EOS has a second minimum well below the reference density of 0.995 g/cc. This second minimum from approximately 10 kg/m³ to 10⁻² kg/m³ is an artifact of the functions used to build the EOS. Unfortunately, this renders the table incorrect when attempting to simulate foams and other porous media at cold temperatures. The cyan line is the 500 Kelvin isotherm and is there to help show the bounds of this regime.

DISSOCIATION

In Figures 1 and 2, we find an inflection in the Hugoniot from approximately 2g/cc to 2.4 g/cc. We attribute this to dissociation. To confirm it, we wrote a program [12] that uses a recursive algorithm that

tracks molecules. Using the first minimum of the pair correlation function for C-C and C-H atom positions from our reference simulation we assumed a "bond" length of 1.68 Å and 1.28 Å respectively. We chose a bond length of 0.8 Å for H-H from a different simulation. These bond lengths are longer than those listed in most literature because of atom vibration. At atom pair is considered bonded if they stay within these respective lengths for a user defined period of time, in our case 90 femtoseconds or about 5 carbon vibrations. By tracking tracer species such as C₂, C₃, and our starting material of four strands of C₁₆H₃₄ (the extra hydrogens are because we capped the strands to prevent cross bonding) across multiple simulations, we can confirm that we find dissociation at the densities in question (Figure 5).

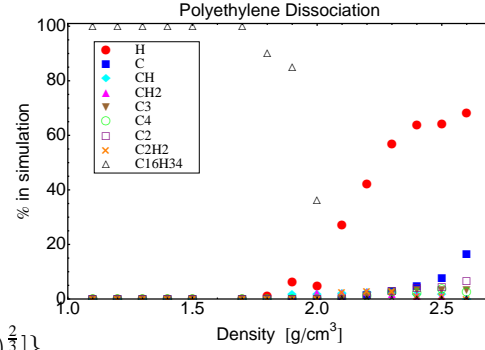


FIGURE 5. The percent of all atoms in the system that are in each molecule type. Not all molecules found are listed, only some of the key ones.

CONCLUSIONS

We have presented a method for developing a new high density polyethylene EOS that is thermodynamically consistent. By creating pseudo-data, we cover a broader range of EOS space in which to fit our functions and so have a better approximation of pressure and energy in those regimes. The internal energy with the cold curve subtracted off is a function of temperature only while the pressure retains some temperature dependence. We do not have a good VASP representation of low density, porous (foam) media for this material and our EOS is not valid in that regime. Finally we found the inflection in the principal Hugoniot is due to dissociation.

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REFERENCES

1. Kresse, G., and Hafner, J., *Phys. Rev. B*, **47**, 558–561 (1993).
2. Kresse, G., and Furthmüller, J., *Phys. Rev. B*, **54**, 11169–11186 (1996).
3. Zel'dovich, Y. B., and Raizer, Y. P., *Physics of Shock Waves and High-Temperature Hydrodynamic Phenomena*, Dover, 2002.
4. Nellis, W. J., Ree, F. H., Trainor, R. J., Mitchell, A. C., and Boslough, M. B., *J. Chem. Phys.*, **80**, 2789 (1984).
5. Marsh, S. P., editor, *LASL Shock Hugoniot Data*, University of California Press, 1980.
6. Kohn, W., and Sham, L. J., *Physical Review*, **140**, 1133–1138 (1965).
7. Blöchl, P. E., *Phys. Rev. B*, **50**, 17953–17979 (1994).
8. Kresse, G., and Joubert, D., *Phys. Rev. B*, **59**, 1758–1775 (1999).
9. Armiento, R., and Mattsson, A. E., *Phys. Rev. B*, **72**, 085108 (2005).
10. Allen, M. P., and Tildesley, D. J., editors, *Computer Simulations of Liquids*, Oxford Science Publications, 2006.
11. Mattsson, T. R., Lane, M., Cochrane, K. R., Desjarlais, M. P., Thompson, A. P., Pierce, F., and Grest, G. S., *Phys. Rev. B*, **81**, 054103 (2010).
12. Cochrane, K., Mattsson, T. R., and Desjarlais, M. P., to be submitted.