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Calculating Hugoniot for molecular crystals from First Principles

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Abstract. Density Functional Theory (DFT) has over the last few years emerged as an indispensable tool for understanding the behavior of matter under extreme conditions. DFT based molecular dynamics simulations (MD) have for example confirmed experimental findings for shocked deuterium,¹ enabled the first experimental evidence for a triple point in carbon above 850 GPa,² and amended experimental data for constructing a global equation of state (EOS) for water, carrying implications for planetary physics.³ The ability to perform high-fidelity calculations is even more important for cases where experiments are impossible to perform, dangerous, and/or prohibitively expensive. For solid explosives, and other molecular crystals, similar success has been severely hampered by an inability of describing the materials at equilibrium. The binding mechanism of molecular crystals (van der Waals' forces) is not well described within traditional DFT.⁴ Among widely used exchange-correlation functionals, neither LDA nor PBE balances the strong intra-molecular chemical bonding and the weak inter-molecular attraction, resulting in incorrect equilibrium density, negatively affecting the construction of EOS for undetonated high explosives. We are exploring a way of bypassing this problem by using the new Armiento-Mattsson 2005 (AM05) exchange-correlation functional.^{5,6} The AM05 functional is highly accurate for a wide range of solids,^{4,7} in particular in compression.⁸ In addition, AM05 does not include any van der Waals' attraction,⁴ which can be advantageous compared to other functionals: Correcting for a fictitious van der Waals' like attraction with unknown origin can be harder than correcting for a complete absence of all types of van der Waals' attraction. We will show examples from other materials systems where van der Waals' attraction plays a key role, where this scheme has worked well,⁹ and discuss preliminary results for molecular crystals and explosives.

Introduction

First-principles molecular dynamics (MD) simulations employing density functional theory^{10,11} (DFT) have over the last few years emerged as a powerful and versatile method for studying shock

compression. Quantitative results over a wide range of compression are now routinely obtained for many important classes of materials and a well-founded understanding into how matter behaves under extreme conditions is emerging. Shock compression of liquid hydrogen (deuterium) was one of the

first examples where DFT-MD was demonstrated to yield results of high fidelity¹ compared to accurate Mbar shock experiments.¹² Since then, highly accurate DFT-MD simulations have been reported for shock compression also of for example helium,¹³ carbon,² water,^{3,14,15} quartz,⁸ xenon,¹⁶ and hydrocarbon polymers.⁹ Due to this rapid progress, we expect first-principles simulations to play an increasingly important role in the future of shock- and high energy-density physics. In particular, it can be used to increase our understanding of systems and conditions that are difficult, expensive, or perhaps impossible to study with experimental methods.

The above examples establish with confidence that shock compression can be modeled successfully for pure light elements (H/D, He, and C) as well as compounds like H₂O, SiO₂, and (CH)_N. Energetic materials like PETN are made of the same light elements, plus nitrogen. Then why is it that progress in applying DFT has been slower for molecular crystals in general and energetic materials in particular?¹⁷ The answer lies in the particular interactions present in molecular crystals, the so-called dispersion forces, or van der Waals' attraction.

However, similarly to molecular crystals of energetic materials like PETN, hydrocarbon polymers like polyethylene (PE) and poly(4-methyl-1-pentene) (PMP or TPX) also exhibit significant van der Waals' contributions to the binding energy. The excellent results for shocked polymers⁹ motivated us to study PETN following the same approach.

PETN crystal structure

The pertinent details of the structure of crystalline PETN are described in Figs. 1 and 2. While several DFT exchange-correlation functionals exist for accurately describing the intra-molecular structure of the PETN molecule, none of these also describe the weak intermolecular van der Waals' bonds with the same accuracy.

A PETN molecule contains 29 atoms, see Fig. 1, and the tetragonal unit cell contains two molecules. The molecules are held together in the crystalline structure by weak van der Waals' forces between oxygen and hydrogen atoms on different molecules. These weak bonds involve two different types of oxygen atoms, marked O(1) and O(2) in Fig. 1(b),

and two distinct hydrogen atoms, H(1) and H(2). The experimental distances between these oxygen-hydrogen pairs from Ref. 18 are shown in Fig. 1(b). While the experimental hydrogen positions are uncertain, DFT calculations with several different exchange-correlation functionals¹⁹ confirm the relative intermolecular distances.

The shortest distance is between the O(1) and H(1) atoms on two molecules in the same unit cell (yellow). The next shortest distance is between the O(2) and H(2) atoms on the same kind of molecule in adjacent unit cells (cyan). The third shortest intermolecular bond (green) is between the O(2) and the H(2) on molecules in the same unit cell, and together with the shortest bond it decides the orientation of the two molecules in one unit cell, as seen in Fig. 2.

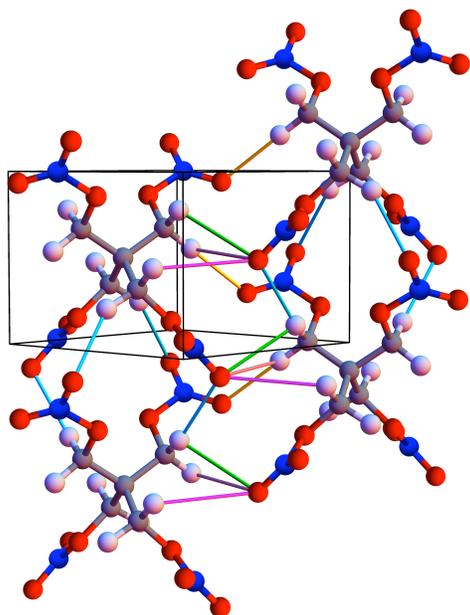
Method

Although DFT is a formally exact representation of the Schrödinger equation, in practice, the choice of exchange-correlation functional determines the accuracy. We employ the multi-purpose Armiento-Mattsson (AM05) functional,⁵ which has no empirically determined parameters and improves upon the local density approximation (LDA) by reproducing two model systems with known solutions: the uniform electron gas and the surface jellium.^{5,7} The lack of van der Waals' attraction in AM05⁴ makes it decidedly different from most other exchange-correlation functionals, which include spurious van der Waals' like interactions.

Byrd and Rice have previously demonstrated the difficulty in applying DFT modeling to energetic molecular solids at low pressures.¹⁷ However, they found an increasing accuracy as the external pressure increases. This is fortuitous for studying molecular crystals under strong shocks where the behavior is dominated by the high pressure response. Moreover, since the AM05 functional displays a monotonic behavior upon expansion and compression,⁴ it is arguably the most suitable functional for studying compression in van der Waals' systems.

AM05 has demonstrated high fidelity for a wide variety of solids;^{4,7} in Ref. 7, the performance of seven functionals was compared for twenty representative semiconductors, simple metals, transi-

(a)



(b)

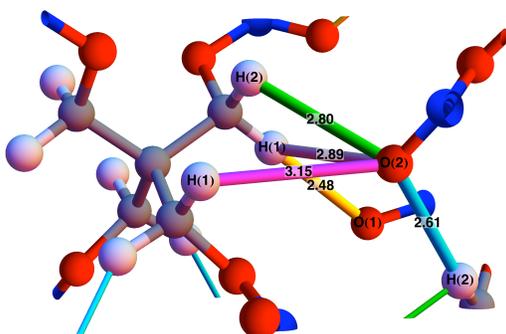


Fig. 1. Two unitcells (four molecules) side view of crystalline PETN. Each molecule contains 29 atoms: 5 carbon (gray), 4 nitrogen (blue), 8 hydrogen (white), and 12 oxygen (red). The molecules are held together by weak van der Waals' forces between oxygen and hydrogen atoms on different molecules. The marked section in (a) is shown in (b) with the experimental distances (in Å) between these oxygen-hydrogen pairs from Ref. 18 given (see text).

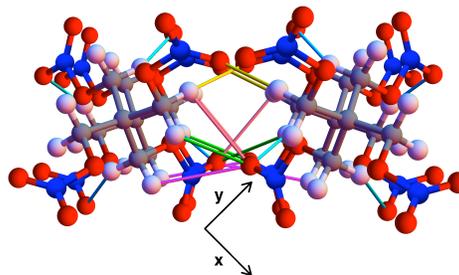


Fig. 2. Top view of crystalline PETN. See Fig. 1 for details.

tion metals, alkali-halides, and oxides. On average, AM05 is better than choosing between LDA and PBE for each solid separately (Table I of Ref. 7) and does as well as decidedly more computationally demanding hybrid functionals.^{20,21} Furthermore, AM05 also works well for hydrogen bonding in the water dimer²² and model chemical reaction energies for a large number of molecular reactions²³ on par with other gradient corrected functionals.

Finally, AM05 was recently the best suited functional to model quartz⁸ up to 1.6 TPa in the development of a high-pressure shock impedance standard. Taken together, we find compelling reasons to employ AM05, and to expect results of high-fidelity for shock compression.

The DFT-MD simulations were performed for a two molecules (58 atoms) unit cell using VASP 5.2²⁴⁻²⁶ using strictly converged settings.^{1,27} The plane wave cutoff was set to 800 eV and k-point sampling with mean-value point $(\frac{1}{4}, \frac{1}{4}, \frac{1}{4})$ was used. The reference state run was repeated with $4 \times 4 \times 4$ Monkhorst Pack sampling to verify convergence of the total energy, which was better than 0.001 eV. The ionic time-step was set to 0.4 fs. For steady-state simulations, a Nosé-Hoover thermostat was used while scaled velocities were used when ramping the temperature.

The principle Hugoniot was mapped by satisfying the Rankine-Hugoniot equation,

$$(U - U_o) = \frac{1}{2}(P + P_o)(V_o - V) \quad (1)$$

where U and U_o are the final and initial internal energies, P and P_o are the final and initial pressures, and V and V_o are the final and initial volumes. Each point on the Hugoniot was found using an iterative compression procedure beginning from a thermally equilibrated initial reference state, chosen as the theoretical values for U_o and P_o calculated at the experimental equilibrium volume, V_o . The system was instantaneously compressed isotropically and equilibrated. The ionic- and electronic temperatures were then ramped, at a rate of 0.1 K per time step, until the sampled thermodynamic variables satisfied Eq. 1. It is worth pointing out that the direct result from the simulation is the Hugoniot P - ρ - T relationship – the jump conditions are subsequently applied to calculate the corresponding shock- and particle velocities.

Regarding other thermodynamic variables, the simulations can be tailored to investigate specific heat, diffusion coefficients, the chemical composition of detonation products, and the timescale for chemical reactions. Such calculations are outside the scope of the present work but can lead to a notably improved understanding of detonation phenomena. For example, single-crystal PETN exhibits anisotropic shock sensitivity towards detonation along the crystallographic directions, with $\langle 110 \rangle$ and $\langle 001 \rangle$ being more sensitive than $\langle 100 \rangle$ and $\langle 101 \rangle$.²⁸ As seen in Figs. 1 and 2, most of the shortest van-der Waals' bonds are engaged during compression along the $\langle 110 \rangle$ and $\langle 001 \rangle$ directions, while none are directly engaged during $\langle 100 \rangle$ and $\langle 011 \rangle$ compression.

Results

Experimental $U_s - u_p$ shock data for single-crystal PETN are plotted alongside our DFT Hugoniot data in Fig. 3. The experimental data are taken from the LASL Shock Hugoniot Data²⁹ and are comprised of three different sets of experiments. Each set has been plotted with uniquely colored markers and labeled *wdg*, *qzi*, or *im1*, corresponding respectively to wedge, quartz impact, and impedance matching experiments. The black and brown data are the computed results for P and V from this work, translated into U_s and u_p using the experimental and theoretical reference pressure re-

spectively. The solid lines are fits to

$$U_s = C + S u_p. \quad (2)$$

The disparate nature of the fits illustrates that there is a bias in each of the various types of measurements and that fitting the $U_s - u_p$ relationship as a straight line is perhaps an oversimplification. It may be more appropriate to fit the data to a higher order equation. But it seems clear that higher fidelity data is needed in order to build a trustworthy EOS.

Since AM05 does not bind PETN at equilibrium (no van der Waals' forces), it should not be expected that our computed Hugoniot will agree with experiment at very low compression. However, at some finite compression van der Waals' forces will become much less important and the DFT-MD predictions will be accurate. This concept is further developed in the Discussion section.

Fig. 4 shows the computed and experimental Hugoniot data from Fig. 3 along with isothermal compression data³⁰ plotted as P vs. V/V_o . In the range $1.0 > V/V_o > 0.75$ the isothermal compression data matches pretty well with LASL shock data. Within this range, the temperature disparity is not that great, as the predicted Hugoniot temperature at $V/V_o = 0.75$ is only 445 K. However, at higher compression, the 'cold-curve' should not be expected to approximate the Hugoniot data since the predicted temperatures at $V/V_o = 0.67, 0.61,$ and 0.56 are 766, 1202, and 2030 K.

Conclusion and discussion

We know that AM05 cannot correctly describe the very weak van der Waals' bond but we also know from previous work that AM05 works adequately for the water dimer.²² The O-H distance of the water dimer is around 1.9 Å ($2.85 - 0.97 = 1.88$). We can thus expect AM05 to work well for O-H distances of around 2 Å.

We can expect that compression will first shorten the weak intermolecular bonds until the long van der Waals' bonds (that AM05 cannot handle) become shorter hydrogen bonds (that AM05 can handle). The question is then, at what volume compression can we expect AM05 to give a correct description of the system?

We can define a characteristic length scale from

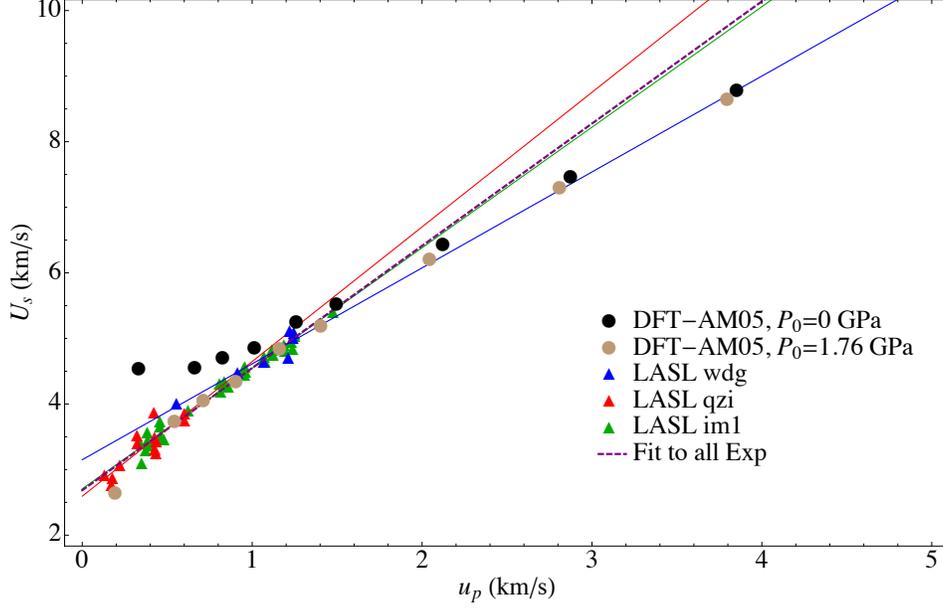


Fig. 3. Computed and experimental $U_s - u_p$ Hugoniot data for single-crystal PETN. The black and brown circles represent molecular dynamics results based on density functional theory and the AM05 functional. The blue, red, and green symbols are data from LASL Shock Hugoniot Data.²⁹ Solid lines are linear fits to the corresponding data.

the volume that one PETN molecule occupies in the crystal at equilibrium:

$$L = \left(\frac{(9.38 \text{ \AA})^3 \times 0.715}{2} \right)^{1/3} = 6.66 \text{ \AA}. \quad (3)$$

We cannot expect AM05 to give correct results until at least the shortest intermolecular bond is compressed to a distance that AM05 can handle. The experimental value for the shortest intermolecular bond is 2.48 Å (see Fig. 1(b)) and it needs to be compressed to 1.88 Å for AM05 to give correct binding properties, a compression of 0.60 Å. If we assume only the intermolecular bonds are compressed while the intra-molecular distances are fixed this means that the volume compression needs to be $(6.66 - 0.60)^3 / 6.66^3 = 0.75$. This exercise can be repeated for all intermolecular distances. However, a reasonable general estimate of the compression required for AM05 to treat all the essential bonds accurately, is when the 2.80 Å bond is compressed to 2.00 Å, which implies a volume compression of $(6.66 - 0.80)^3 / 6.66^3 = 0.68$.

The Hugoniot response suggests that AM05 gives a useful description of unreacted PETN above 15 GPa, and we extend the unreacted shock response to 60 GPa. Although PETN reacts well before that pressure under shock loading, the unreacted Hugoniot is useful for modeling.

The high reference pressure (P_o) for PETN in the AM05 calculations at normal density (1.76 GPa at 1.779 g/cm³) underscores that van der Waals' interactions are substantial in PETN, and quite possibly other energetic materials.

Although the high-fidelity modeling of PETN under strong shocks is an important finding in itself; the regime of weak shocks is arguably even more important for this and other explosives. Predictive modeling of weak shocks is required in order to support modern detonator designs based on insensitive high explosive materials. In order to realize our predictive modeling goals for these important applications, exchange-correlation functionals that treat van der Waals' and chemical bonding (hydrogen- and covalent bonding) with the same high accuracy

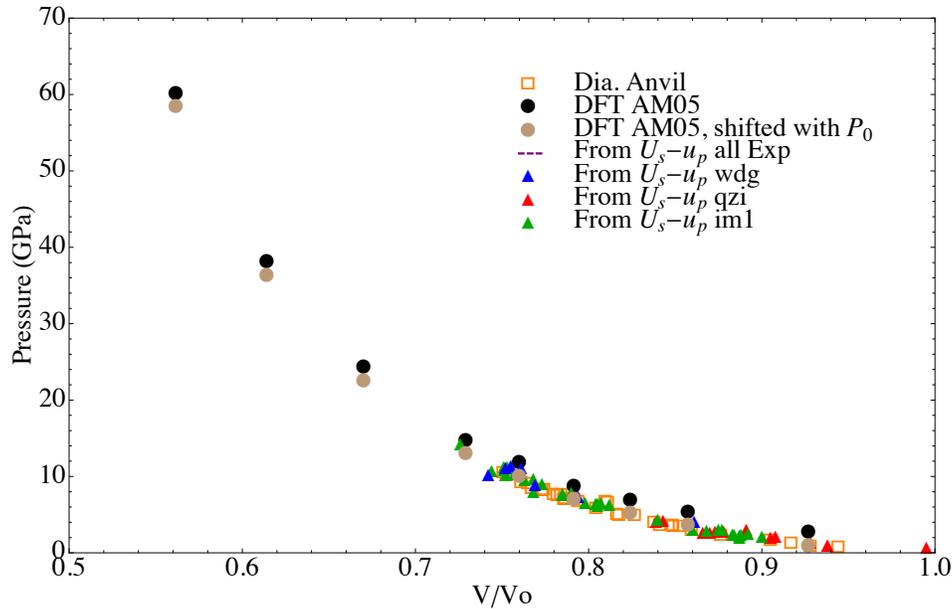


Fig. 4. PETN single-crystal $P - V/V_0$ Hugoniot curve. Black and brown circles; this work. Orange squares; Olinger³⁰ et al. isothermal compression experiments. Colored triangles with corresponding fits; LASL Shock Hugoniot Data.²⁹ The solid lines are the linear fits from Fig. 3, mapped into $P - V$ space.

simultaneously and self-consistently are required.

Acknowledgments

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