Density Functional Theory (DFT) Simulations of Shocked Liquid Xenon

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Abstract. Xenon is not only a technologically important element used in laser technologies and jet propulsion, but it is also one of the most accessible materials in which to study the metal-insulator transition with increasing pressure. Because of its closed shell electronic configuration, Xenon is often assumed to be chemically inert, interacting almost entirely through the van der Waals interaction, and at liquid density, is typically modeled well using Leonard-Jones potentials. However, such modeling has a limited range of validity as Xenon is known to form compounds under normal conditions and likely exhibits considerably more chemistry at higher densities when hybridization of occupied orbitals becomes significant. We present DFT-MD simulations of shocked liquid Xenon with the goal of developing an improved equation of state. The calculated Hugoniot to 2 MPa compares well with available experimental shock data. Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy’s National Nuclear Security Administration under contract DE-AC04-94AL85000.

Keywords: xenon, hugoniot, DFT, simulations

INTRODUCTION

First-principles simulations in combination with increasingly accurate shock experiments at multi-Mbar pressure have, over the last few years, yielded important insights into how matter behaves under extreme conditions. An interesting material to study under these warm dense conditions is Xenon. While under normal conditions, Xenon, consisting of closed shell atoms, is generally considered inert and well described through Lennard-Jones type potentials; there are many instances when Xenon behaves exotically. For example, Xenon has been shown to chemically bond with Flourine and is known to become metallic under cold compression. On the other hand, it is still unknown how temperature affects this pressure-induced metallization and in detail what the Hugoniot of Xenon would be when shocked.

For many years, the cold compressed properties of Xenon have been the focus of theoretical and experimental studied. The zero temperature isotherm was calculated within X-α theory [2] and compares well with shock data upto 130 kbar. Reliable gas gun data by Nellis and coworkers provides Hugoniot points up to 1.3 MBar [7]. Additional experiments and linear-muffin tin calculations were in agreement and extended the cold curve to 170 GPa [4]. Augmented plane-wave calculations were used to investigate the pressure-induced, low-temperature transition from insulator to metal, putting the critical pressure around 130 GPa and providing equation of state data to 1.3 Mbar. The insulator metal transition was further investigated using an augment plane-wave approach with norm conserving pseudopotentials and was found to occur at about 30% compression [3]. Less extreme data for liquid xenon has been tabulated up to 350 MPa [11]. Recently, there has been diamond anvil experiments up to 80 GPa [9, 8]. The metallic like behavior of pressurized liquid xenon has been studied theoretical and experimentally [10]. A free energy model relying on chemical potentials of xenon ions has recently been used to predict the Hugoniot to ultrahigh pressures [6].

Recent theoretical work has demonstrated that
quantum molecular dynamics simulations of liquid noble Helium can provide accurate equation of state data up to high pressure regimes where path integral monte carlo becomes accurate [5]. Our work generates the Hugoniot of shocked liquid xenon to 2 MPa and compares well with available experimental shock data. The 5\textit{p}-d hybridization becomes important at these high compression ratios.

**COMPUTATIONAL METHOD**

Central to the goal of predictive simulations in density functional theory (DFT) [12, 13] is the need for convergence [14]. The DFT-MD simulations were performed with VASP 5.1.40 [15, 16, 17], a plane-wave projector augmented-wave (PAW) core function code. [18, 19] using stringent convergence settings [14]. Steady-state simulations in the NVT ensemble used a Nosé-Hoover thermostat with velocities scaled to control temperature in the ramped-temperature simulations. Complex k-point sampling with a mean-value point ($\frac{1}{4}, \frac{1}{4}, \frac{1}{4}$) was used and is known to provide high precision for disordered structures at high temperature. Mermin’s finite temperature density functional theory [20], used here, is critical for high energy-density applications [21]. In our investigations, we had use several exchange-correlation functionals but report only the results for the generalized gradient functional, AM05 [22, 23], for simplicity. Results within the local density approximation and within other compatible generalize gradient approximations were comparable.

The main result of shock experiment is a Hugoniot curve, the set of pressure-density points achieved through varying impulses. Each point is determined by requiring that conservation of mass, momentum, and energy hold true across a shock front. Thus, the Hugoniot curve is defined with respect to a given reference state. In our instance, this reference is liquid xenon which has a molar volume 44.21 cc/mol or density of 2.97 g/cc at T=163K and room pressure. With respect to the reference state, the Hugoniot condition is expressed $2(U - U_{ref}) = (P - P_{ref})(v + v_{ref})$ with $U$ the internal energy per atom, $P$ the system pressure, $v$ the volume per atom, and $ref$ designates that a value is from the unshocked reference state. In order to simulate the Hugoniot, several temperature-points for each desired density were simulated. A typical fully thermalized simulation requires up to 4000 times-steps of 4 femtoseconds each.

**RESULTS AND DISCUSSION**

We calculated shock curves to be compared to high quality experimental data (Nellis) and frequently used equation of state models (SESAME 5190 and LEOS 540). The equation of state models diverge in the higher pressure regime of the points we considered. It was found that accurate Hugoniot curves at high temperatures were unachievable without revised 4f scattering properties in PAW potentials. Careful convergence tests and comparison to experimental results are important first steps in predictive modeling. Computationally controllable parameters such as the plane-wave cut-off should be chosen to sufficiently model the system in the sense that increasing its quality further does not affect the simulation within an desired tolerance.

In Fig. 1, we display the average pressure at 10kK for a 32 atom supercell of Xe within the LDA and at 10kK. MV23.28 corresponds to a density of 5.64 g/cc and MV13.70 corresponds to 9.58 g/cc. Better than 1% convergence is achieved at 300 eV cut-off.
FIGURE 2. Pressure convergence with respect to the number of atoms per super cell with a 340 eV plane-wave cut-off for of Xe within the LDA. Convergence to well within 0.1 % is found with a 32 atom super-cell.

FIGURE 3. DFT-MD Hugoniot of shocked liquid Xenon using the AM05 GGA. Pot. 1 refers to the original pseudopotential that lacked proper description of f-shell phase shifts. Pot. 2 is the corrected pseudopotential. The solid lines are SESAME and LEOS equation of state models, and the squares with error bars represent the available gas gun data.
(solid lines) are empirical equation of state models and while both are clearly within the experimental margins, they are not consistent with each other. Since the DFT result lies close to the SESAME curve we might be tempted to conclude that the SESAME model is more accurate, but without tighter error bars on the experiment, this is hard to say with certainty.

Another observation is that it is important to include thermal occupation of the electronic states. The dashed curve is the result found when performing the simulation at fixed electron temperature of 163K and may be interpreted as an approximate Carr-Parinello treatment. Also shown is the Hugoniot curve that would result from theoretical calculations fixing the electrons to a cold temperature. Forcing cold electrons increases the pressure. Thus, the cold Hugoniot curve is much higher than the more accurate ones. In practice, the error may go unnoticed or perhaps compensated by other factors. Referring to our earlier convergence test, we see that not converging the plane-wave energy lowers the pressure. Thus, if we were to run cold electrons and low plane-wave cut-off, one can fortuitously get close to experimental at least over some range.

Figure 4 illustrates the density of the system in liquid insulator and metal phases. The liquid density is mostly non-overlapping and localized to the nuclei while in the metallic phase, the density is often shared between several ions. For the shock Hugoniot from liquid Xenon, we estimate the metal insulator transition pressure to be about 195 MBar (T=6800K) which is the first point calculated on our Hugoniot.

CONCLUSIONS

The importance of highly converged simulations cannot be over-estimated. DFT simulations are never better than numerical precision of the calculation. In this work, we have carefully tested convergence with respect to the energy cut off by requiring that both pressure and energy are converged within 1 %. The simulations were run long enough to ensure statistical uncertainties are smaller than the error introduced by a finite energy cut off. We used 1 mean-value point, an approximation that is known to be reliable. Our calculations were carefully compared to available experimental data allowing us to identify certain short comings of the PAW potentials. The resulting analysis predicts a Hugoniot curve is in excellent agreement with experiment and the SESAME 5190 EOS.

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REFERENCES