Comparison of molecular dynamics simulation methods of methane shockwave compression

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Abstract. Shockwave compression of methane was simulated using the molecular dynamics method with Hugoniostat and MSST approach. The calculation was carried out employing ReaxFF\(^{lg}\) potential. We show comparison of simulated Hugoniots for pressure range 0.1 – 44 GPa and times required for simulation run of two different methods. We also compare two ReaxFF potentials: ReaxFF(2008) and ReaxFF-\(^{lg}\)

1. Introduction

The study of material properties after shockwave compression has been actively developed for almost a century. This studies require precise measurement devices with highest timescale resolutions possible. The most recent studies report 10 ps timescale resolution achieved by using of method based on time delayed and chirped probe pulses [1]. But this is not the only method available for shockwaves study. Molecular dynamics method is widely used for simulation of physical processes and thermodynamic properties of different substances. This method is based on a numerical integration of classical equations of motion for every particle in the system. The key component of the MD simulation is a force field that describes interactions among particles and method that describes the process or final state of desired physical phenomenon. This work is devoted to study of shockwave compression of liquid methane.

There has been numerous studies to investigate this problem by means of molecular dynamics. Different authors use different approaches to get realistic results, increase size of simulated system and lower computational expenses. We will review some of the works related to this problem. Despite its importance there are not too many experimental works dedicated to shockwave compression of liquid methane [2], [3]. Li [4] employed Vienna ab initio simulation package. In his study electrons receive a fully quantum mechanical treatment through solving the Kohn-Sham (KS) equations for a set of orbitals and energies within a plane-wave FT-DFT formulation where the electronic states are populated according to the Fermi-Dirac distribution. The all-electron projector augmented wave method is adopted, and the exchange-correlation energy is described employing the Perdew-Wang 91 parametrization of the generalized gradient approximation (GGA). Atoms move classically according to the forces, which originate from the interactions of ions and electrons. According to Goldman [5] DFT-MD simulations lowers Hugoniot temperatures for covalently bonded materials by considerable value which is crucial for studying chemistry in shock waves. Thus he proposes an original methodology to correct this flaw. This was made possible by implementing expressions relating the thermal energies for the classical and quantum systems. Goldman was not the only person trying to...
resolve this problem of lower Hugoniot temperature. Qi [6] solved this problem using another approach. In his work he use colored thermostat for quantum nuclear effects. It's difference from traditional Langevin thermostat is in more complicated forces distribution. In general all this studies were dedicated to shockwave compression of liquid methane with time scale about 10 ps.

Previously discussed studies have almost exclusively focused on final state of matter. But Lummen [7] in his article pays close attention for chemical reactions of chemical decomposition of methane. The main idea of his work was to study the ways carbon particles form from methane without oxidants involved. The initial process of thermal decomposition of methane is the first step in producing carbon nanoparticles from this kind of precursor material in a non-oxidative process. He investigated various conditions of system with different densities and temperatures of thermal decomposition.

In our present work we expand his research by studying different physical process to reach the same goal. Though shockwave compression involves decomposition of methane due to high temperature behind the shockwave, processes in shockwave front could result in additional chemical reactions which need to be considered. To conduct this simulation there are different available techniques discussed below.

First one is called uniaxial Hugoniostat or Hugoniostat. It is based on reproducing the final state of substance compressed by a shockwave. The system is uniaxially and homogeneously compressed to a final stress value [8]. The second is called multi-scale shock technique (MSST) [9]. The MSST is based on the Navier-Stokes equations for compressible flow. Instead of simulating a shock wave passing through a whole system this technique follows a Lagrangian point through the shock wave. This approach requires fewer amount of simulated particles and as a result lower computational cost. To start calculation in LAMMPS you need to set initial parameters (cell mass-like parameter, initial pressure, initial cell volume, initial total energy) of the system (energy, pressure and volume could be calculated automatically) and intensity of shockwave which is determined by shock velocity. Hugoniostat requires initial temperature and final pressure so it could be more descriptive.

2. Calculation details
In this work, for the molecular dynamics simulation, the LAMMPS software package was used [10]. As the interaction potential we used the ReaxFF-lg potential [11]. The system contains 1000 molecules of methane. It was equilibrated for 10 ps at 110 K and 1000 atm resulting in initial density equal to 0.475 g/cm³ (NPT ensemble). Following simulation of shockwave were run using timestep of 0.1 fs until system parameters stopped drifting.

3. Results
Hugoniot curves for two shockwave compression methods and experimental results [2] are shown on Figure 1.
Figure 1. Hugoniot curve for liquid methane ($T_0 = 110$ K). The crosses correspond to experimental results [2], the open triangles to the MD calculation via Hugoniostat method, the open circles to the MD calculation via MSST method.

We can see that starting from ~23 GPa Hugoniostat gives us slightly better agreement with the experiment than MSST method. Considering this small discrepancy we decided to test another aspect of two methods – calculation times. In order to compare them we set up a test calculation with condition similar to previous simulations of shockwave. Calculation was run on HPC cluster “Basov” located in NRNU MEPhI using 4 CPU cores. The details of the simulation are presented in Table 1.

| $P$ (GPa) | $D$ (km/s) | $dt$ (ps) | $N_{\text{particles}}$ |
|-----------|------------|-----------|------------------------|
| 44        | 12.55      | 0.1       | 1000                   |

Simulation times for Hugoniostat and MSST were 7912 and 2385 seconds respectively. That means MSST is approximately 3.3 times faster than Hugoniostat method.

ReaxFF have various parametrization sets. In this work we also compared two of them: ReaxFF(2008) [12] and ReaxFF-lg [11]. Results of this comparison are shown on Figure 2.
Below 20 GPa ReaxFF-lg shows better agreement with experimental data and for pressure higher than 20 GPa ReaxFF(2008) shows better agreement.

4. Discussion
In this work we compared two methods uniaxial Hugoniotstat and MSST. Both of them show good agreement with experimental data [2]. MSST has the advantage of faster computation time, but Hugoniotstat has more descriptive initial parameters (shock pressure instead of shock velocity). We also compared two ReaxFF parameter sets with result of ReaxFF-lg having good agreement with experimental data.

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