Interatomic potential parameters for molecular dynamics simulations of RDX using a reactive force field: A validation study

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Abstract. The parameter sets of the ReaxFF potential distributed with the open source, Large-scale Atomic/Molecular Massively Parallel Simulator (LAMMPS) code, is validated for simulating crystal RDX. These parameters are used to model crystal RDX and obtain its unit cell size and bulk modulus. It is seen that the parameters supplied with LAMMPS (5-April, 2011 release) do not reproduce the unit cell size and bulk modulus of crystal RDX as reported by experiments and by other simulations using the ReaxFF potential. The simulation method and relevant parts of the LAMMPS code implementing the method has been earlier validated for Cu. We conclude that either the parameter sets provided with the LAMMPS distribution or its implementation of the ReaxFF potential are not suitable for modeling crystal RDX.

1. Introduction
LAMMPS [1] is a classical molecular dynamics code distributed as an open-source code and is widely used. It has a wide set of interaction potentials and shows a very good parallel scaling due to which several tens of millions of atoms can be simulated on a modest 128 node compute cluster. Materials like RDX, TATB, HMX, PETN are widely used in defense and in industry [2, 3]. These materials are composed of the elements Carbon, Hydrogen, Nitrogen and Oxygen. Using first principle methods are desirable for simulating reactions due to changes in electron sharing amongst the constituent atoms. This is however not practical due to severe computational time limitations. Van Duin, et al. have developed a reactive force field, ReaxFF [4], which is fitted to first principles generated data which has the capability to model large molecules and reactions between its constituent atomic species. LAMMPS has three sets of parameters for the ReaxFF force field to simulate C, H, N and O interactions [5–7] and therefore can be used to simulate RDX. We hereafter to these parameter sets as the general purpose hydrocarbon parameterization (GPHP) [5], reactive force field for Nitramines (RFFN) [6] and reactive force field for PETN (RFFPETN) [7]. These parameter sets are validated by carrying out MD simulations of crystal RDX to extract the unit cell sizes and the Bulk Modulus of crystal RDX.

We show that none of the above parameter sets reproduce either the reported values for unit cell sizes, or, the bulk modulus of crystal RDX. It should be emphasized that ReaxFF has been earlier used to obtain the unit cell sizes and the bulk modulus of RDX with other MD simulations [8] which show a good match with experiments. We have earlier validated our method
and the parts of the LAMMPS code involved in our calculation by using it to obtain the correct
bulk modulus and unit cell size for Copper using the embedded atom method potential [9].

In the next section, the simulation method to obtain unit cell size and bulk modulus of
a crystal is discussed. The simulations of crystal RDX using the various parameter sets are
described in the third section and the results are presented. Finally we present our conclusions.

2. Method to obtain bulk modulus of crystal RDX

In order to determine the bulk modulus and equilibrium unit cell dimensions of crystal RDX
the parameter sets provided with LAMMPS (RFFN, RFFPETN) are used to carry out 20 NVT
simulations at +10% to −10% of the experimentally reported equilibrium volume in steps of 1%
of equilibrium volume. A single unit cell with periodic boundary conditions is used. An MD
time step of 5 femto-sec is used. Average values of the pressure and total energy of the system
are sampled once the system attains equilibrium.

The variation of energy with volume from the MD simulations were fitted with the Murnaghan
equation of state [10].

\[ E_V = E_o + \frac{B_o V}{B'_o} \left[ \left( \frac{V_o}{V} \right)^{B'_o} - 1 \right] + \frac{B_o V_o}{B'_o - 1} \]  

where, \( E_o \) and \( V_o \) are the energy and volume at zero pressure respectively, \( E_V \) is the energy
corresponding to a volume \( V \), \( B_o \) is the equilibrium bulk modulus at constant temperature and
\( B'_o \) is the pressure derivative of \( B_o \). We obtain the bulk modulus and the equilibrium unit cell
volume of RDX by the Murnaghan EOS fit.

3. Molecular Dynamics Simulations of crystal RDX

20 NVT simulations at 300 K as described in Section.2, for the RFFN and RFFPETN param-
eter sets are carried out. A single unit cell with periodic boundary conditions (PBC) is used.
The MD time step is 0.5 femto-sec. A steepest descent (SD) minimization procedure is used to
initially relax the RDX crystal prior to the MD simulations. The SD method was carried out
for 100 iterations till the energy tolerance was \( 4.47 \times 10^{-5} \).

The variation of energy of RDX with volume for the RFFN and RFFPETN cases are shown
in Fig.1 and Fig.2 respectively. Note that the variation is neither smooth nor monotonous and
does not have a well defined minima as seen for copper [9]. There seems to be non-monotonic
shifts in energy. The MD data is fitted with the Murnaghan Equation of State (Eqn.1). From
the fit, the bulk modulus of RDX at 300 K is 5.905 GPa \( (B'_o = 8.96) \) for the RFFN case and 7.22
GPa \( (B'_o = 6.88) \) for the RFFPETN case. These are smaller than the experimentally reported
values of 13.0 GPa [11] and results (13.7 GPa) from other MD simulations [8] using ReaxFF. The
equilibrium volume from the fit is 1774.2 Å\(^3\) for the RFFN case and 1795.9 Å\(^3\) for the RFFPETN
case. The corresponding unit cell sizes for these and for the NPT simulations that follow are
compared in Table.1.

Atomic visualization software show no obvious structural changes in the RDX crystal. The SD
minimization method in LAMMPS, used to relax the RDX crystal does not allow volume change,
thereby not really taking the RDX crystal to a minimum energy state and also disallowing
molecular adjustments that may occur with a varying volume. This, coupled with the above
mismatches with experimental and simulation results motivates us to carry out NPT simulations
of crystal RDX. This would also yield the unit cell size parameters which can be verified with
the above results.
Figure 1. Total energy variation with volume for RDX for the RFFN case

Figure 2. Total energy variation with volume for RDX for the RFFPETN case

Table 1. Comparison of unit cell sizes from our NVT and NPT simulations of crystal RDX using the RFFN and RFFPETN parameter sets, with reported experimental and simulation results

| NVT | NVT | NPT | NPT | Expt. [11] | Sim. [8] |
|-----|-----|-----|-----|------------|---------|
| RFFN | RFFPETN | RFFN | RFFPETN |            |         |
| a 13.55 Å | 13.60 Å | 14.04 Å | 14.60 Å | 13.18 Å | 13.78 Å |
| b 11.89 Å | 11.95 Å | 12.36 Å | 12.84 Å | 11.57 Å | 12.03 Å |
| c 11.01 Å | 11.05 Å | 11.43 Å | 11.88 Å | 10.71 Å | 10.96 Å |

3.0.1. NPT simulations of crystal RDX  NPT simulations of a $2 \times 2 \times 2$ unit cells of RDX are carried out by varying the crystal temperature from 50 K to 300 K over 100 pico-seconds using a Nose-Hoover thermostat and barostat. The system is then allowed to relax at 300 K for 200 pico-seconds. A time step of 0.1 femto-sec is used with PBC along all the three axes. The simulations are carried for all the parameter sets (GPHP, RFFN, RFFPETN). Note that in these simulations the volume of the simulation box will change to accommodate stresses that develop within the molecules, thereby allowing molecular reorientation and structural changes within the molecule.

Table 1 shows the average unit cell sizes along X, Y and Z for the three parameter sets and also from the equilibrium volume values obtained from the NVT simulations. Fig.3 shows the initial configuration of the $2 \times 2 \times 2$ unit cells of RDX. Fig.4 shows the final configuration of the RDX molecules at the end of the NPT simulation. Structural changes in the molecular crystal structure of RDX is seen around 180 K as the crystal temperature is changed from 50 K to 300 K. The RFFPETN and GPHP results for RDX crystal structure also do not preserve the RDX crystal structure, but are not displayed here due to lack of space. From these results it is evident that none of the parameter sets preserves the crystal structure of RDX.

4. Conclusions and discussion
We have explored the possibility of simulating crystal RDX with three parameter sets (GPHP, RFFN and RFFPETN) supplied with LAMMPS. We see that the RFFN and RFFPETN parameter sets yield wrong results for the bulk modulus. We see from Table 1 that the unit
cell sizes of crystal RDX obtained from the NVT simulations with the RFFN and RFFPETN parameter sets are close to the NVT simulation results [8] and Experiments [11]. However the NVT simulations constraints the molecular readjustments by imposing a constant volume. We see that NPT simulations of RDX crystal, which allows more scope for molecular position adjustments due to variable volume, do not preserve the RDX crystal structure. The average value of the unit cell sizes in the NPT case do not match the reported NVT simulation [8] and experimental [11] results (Table.1). Therefore we conclude that the ReaxFF implementation in LAMMPS is not suitable for simulating RDX. In the future we will explore the applicability of the provided parameter sets to simulate single RDX molecule.

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