Molecular-dynamic simulation of isotherm of cyclotetramethylenetetranitramine with the nanopore type defect

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Abstract. Molecular dynamic simulation of isothermal compression parameters are performed for a cyclotetramethylenetetranitramine single crystal (C₄H₈N₈O₈, HMX) using a modified ReaxFF-lg reactive force field. The unit cell consisted of eight C₄H₈N₈O₈ molecules (144 atoms). The calculated supercell consisted of an optimized unit cell and was created with a periodicity of 6×6×6 (48384 atoms). Our calculations were performed for the pressure range of 1–40 GPa, and the state of the single crystal C₄H₈N₈O₈ under the conditions of P = 0.05 GPa and T = 300 K was chosen as the initial state. The calculated isotherm of the material is consistent with experimental data. Static compression calculations of molecular crystal C₄H₈N₈O₈ with the nanopore type defect were carried out to study the effect of defects on the compressibility of crystals. Nanopores two sizes were considered. By results of calculations it was performed that the material with nanopore type defect is deformed more strongly, and the greater the defect, the stronger the deformation. At the same pressure value, the nanopore crystal has a higher compression ratio than an ideal single crystal.

1. Introduction

Molecular dynamics (MD) is based on direct calculation of the coordinates and velocities of a fairly large ensemble of particles (atoms or molecules) as they evolve over time. MD is widely used to simulate different physical processes in molecular systems, enabling us to obtain reliable information on the properties of investigated substances. The simulations in this work were performed using the LAMMPS MD software package that allows us to study processes of chemical interaction and predict the behavior of different materials under the action of extreme pressures and temperatures. These transformations depend strongly on the loading of a material and include deformation, rising temperature, and the emergence of defects in a crystal. The ReaxFF-lg [1] modified reactive force field allowed us to describe the thermophysical properties of the isothermal compression of organic single crystals over a wide range of pressures and temperatures, including molecular crystals with nanopore type defects. The software implementation of this interatomic force field is available in LAMMPS.
The goal is study the effect of the nanopore type defects on the compressibility of C$_4$H$_8$N$_8$O$_8$ crystal via MD simulations.

The results of the response of three nanofluid systems to an impact loading are presented in [2]. The authors conducted a series of experiments where they studied the dynamics of filling of nanoporous granular media Libersorb 23 (L23) and Polysorb-1 with water and silochrome (SCh-1.5) with Wood's alloy. The pore volumes were from 60 to 120 cm$^3$ with the filling start pressures from 0.6 to 15 MPa. In work [2] the compressibility of the liquids was determined from experiments with the chamber filled only with the liquid without any porous medium. The compressibility of the liquids coincides within the measurement accuracy with the tabulated values. As a result, the authors obtained the experimental time dependences of the pressure the internal volume in the chamber for different values of the impact energy ($E = 5$–70 J). Thus, the filling pressure is constant during the entire time of the filling absorption at filling, it means the force acting on the protected object is constant in the presence of a nanoporous medium and is weaker by a factor of 1.3–8.5 than the force created by external loading in the absence of the nanoporous medium. In [2] was also found that the possibility of choosing a (nanoporous medium–nonwetting liquid) system and the conditions of their application that ensure the highly efficient operation of devices at various energies and momentum of external loading.

The paper [3] presents the results of molecular-dynamic modeling of the formation of a hot spot and the initiation of a chemical reaction in a PETN crystal under shock loading. Conditions under which a shock wave with a velocity of 2 km/s passes through a PETN crystal containing a spherical void of 20 nm in diameter were simulated. The results of MD modeling showed that a hot spot forms on the boundary of the void in the crystal, after the formation, chemical reactions are initiated, during which final decomposition products such as N$_2$ and H$_2$O are formed. In other words, the chemical reactivity of the PETN crystal significantly increases in the presence of there are voids in it.

2. Reactive force field ReaxFF-lg

In this paper, the reaction force field ReaxFF (Reactive Force Field) was used for the MD of modeling the properties of a HMX. The ReaxFF force field was developed by Andri van Duin [4], as a realization of reactive molecular dynamics, to describe the chemical interaction, dissociation and formation of chemical bonds, and to describe the properties of defects and imperfect crystal surfaces. This approach allows modeling modern systems with a number of atoms of the order of $10^6$–$10^9$ on modern high-performance parallel computing clusters. The essence of the reaction force field ReaxFF is reduced to the parameterization of interatomic interactions in the molecules present in the ensemble under consideration. For each of the components of the atomic ensemble, a certain set of parameters is set, including parameters determined experimentally, parameters calculated using ab-initio methods or calculated by processing experimental data on the properties of the materials in question. The MD simulations in this work were performed using a modified version of the ReaxFF reactive force field [4] that considered the Van der Waals interactions between molecules, allowing us to reproduce molecular crystals thermophysical properties more accurately. ReaxFF-lg, corrects London dispersion interaction (van der Waals attraction) by adding an extra term using low-gradient model, $E_{lg}$, as follows:

\[ E_{ReaxFF-lg} = E_{ReaxFF} + E_{lg}; \]  \hfill (1)

\[ E_{ReaxFF} = E_{bond} + E_{ip} + E_{over} + E_{under} + E_{val} + E_{pen} + E_{coa} + E_{c2} + E_{tors} + \]
\[ + E_{con} + E_{H-bond} + E_{vdWaals} + E_{Coulomb}; \]  \hfill (2)

\[ E_{lg} = \sum_{i<j=1}^{N} \frac{c_{lg,ij}}{r_{ij}^6 + d r_{ij}^6} \]  \hfill (3)

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\[ + E_{con} + E_{H-bond} + E_{vdWaals} + E_{Coulomb}; \]  \hfill (2)

\[ E_{lg} = \sum_{i<j=1}^{N} \frac{c_{lg,ij}}{r_{ij}^6 + d r_{ij}^6} \]  \hfill (3)
where $E_{vdWals}$ and $E_{Coulomb}$ are the energy of non-bonded interactions, namely the van der Waals and Coulomb interactions. In addition to $E_{H-bond}$, the energy of hydrogen bond, the rest of the energy terms are the bond order dependent and account for the bonded interactions that consists of $E_{bond}$, the energy of bond, $E_{lp}$ for energy of lone-pairs, $E_{over}$ of over-coordination, $E_{under}$ of under-coordination, $E_{val}$ of valence angle, $E_{pen}$ of energy penalty for handling atoms with two double bonds, $E_{coal}$ of coalition (three-body conjugation), $E_{conj}$ of conjugated bonds (four-body conjugation), $E_{tors}$ of torsion angles. $E_{lg}$ to account for long range London Dispersion and $r_{ij}$ is the distance between atom $i$ and atom $j$, $R_{eq}$ is the equilibrium vdW distance, and $C_{lg,ij}$ is dispersion energy coefficients, $d$ is a scaling factor.

3. Calculation parameters

Firstly, we calculate isothermal parameters for a HMX single crystal via MD simulations. The unit cell consisted of 8 HMX molecules, i.e. 224 atoms. Further from the optimized unit cell, a calculated super-cell with a period of 6x6x6: 1728 molecules (48384 atoms) was made. Figure 1 shows the type of the calculated super-cell. The simulation was carried out in the pressure range from 0.05 to 40 GPa at a constant temperature of $T = 300$ K.

![Figure 1. The calculated super-cell of HMX.](image)

Static compression calculations of molecular crystal C$_4$H$_8$N$_8$O$_8$ with the nanopore type defect were carried out to study the effect of defects on the compressibility of crystals. Two sizes nanopores were considered. In the first case, to create a nanopore with the volume 0.209 nm$^3$, 163 atoms were removed from the calculation supercell (6048 atoms) and the porosity of the crystal was estimated at 2.7% of the total volume of the calculated supercell. The same way, it was created by removing 66 atoms of identical estimated supercell to obtain crystal C$_4$H$_8$N$_8$O$_8$ with a porosity of about 1%, in this case, the pore volume was 0.085 nm$^3$. Figure 2 shows the calculated super-cell of HMX crystal with two sizes nanopores.
Figure 2. The calculated super-cell of HMX with nanopore: a porosity of 2.7% and 1%, respectively.

4. Results and discussion

Obtained in this work HMX isotherm is shown in figure 3, it is also in comparison with the known experimental and calculated results. At a pressure of 40 GPa, the compression ratio of the HMX reached a value of $V/V_0 = 0.7$.

Figure 3. Pressure versus compression ratio in the HMX single crystal: 1, 2 – experimental isotherms for a single crystal HMX [6], [7]; 3 – MD calculations of experimental isotherms for a single crystal HMX [8]; 4, 5 – approximation of the experimental data 1 and simulations data 3 according to the third-order Murnaghan equation in [6], [8], respectively.
Figure 3 shows that the calculated pressure values in the isotherm of HMX single crystal obtained in this paper agree well with experimental data over a wide pressure range (0.05 - 40 GPa). Also we can note an excellent agreement with the results of [8], where MD simulation of the isothermal compression of HMX single crystal was carried out using the quantum-chemical approach. The approximation of the results of the MD simulation of work [6] to 30 GPa also agrees well with the results of the MD simulation of this work.

MD simulations results of isotherms of crystal C₄H₆N₆O₈ with nanopore type defects (with different porosity values) are shown in figure 4.

![Figure 4](image)

**Figure 4.** Isotherms of HMX crystals with nanopore type defects in comparison with the isotherm for a single crystal HMX.

5. Conclusions
By results of calculations it was performed that the material with nanopore type defect is deformed more strongly, and the greater the defect, the stronger the deformation. At the same pressure value, the nanopore crystal has a higher compression ratio than an ideal single crystal. The ReaxFF-lg modified reactive force field allowed us to describe the thermophysical properties of the isothermal compression of organic single crystals over a wide range of pressures and temperatures, including molecular crystals with nanopore type defects.

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