Atomistic Modeling of Amorphous Energetic Materials

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Abstract
A majority of research within the field of energetic materials have been centered around the stable crystalline phase, whilst there has been less about the amorphous phase and the implications of these types of material. In this study, Molecular Dynamics simulations with the General Amber Force Field (GAFF) is used to predict fundamental properties of the nitramine explosives HMX and CL-20 in the amorphous phase. Amorphous structures are obtained by compressing a molecular gas to 4 GPa followed by relaxation and equilibration. The simulations indicate that the amorphous phases of HMX and CL-20 have lower densities than the corresponding crystal phases, 12.7% and 7.3% respectively. Both HMX and CL-20 was found to compress more easily when subject to external pressure, the difference was most significant for HMX. As a second part of this study an amorphous composition of CL-20/HMX/Polyvinylacetate(PVAc) (50/45/5 -wt%) was studied. This was obtained by compressing a molecular gas to varying pressures followed by relaxation and equilibration. Results indicate that the simulated density around 1.64 $[g/cm^3]$ fall close to experimental observations of 1.7 $[g/cm^3]$. The density was observed to not vary significantly for pressures higher than 0.4 $[GPa]$ in accordance to experimental data.
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1 Introduction

A majority of research within the field of energetic materials have been centered around the stable crystalline phase, whilst there has been less about the amorphous phase and the implications of these types of material. Previous studies have shown material compositions consisting of CL-20/HMX/PVAc behaving differently in the amorphous phase than in the crystalline phase such as experiencing a reduced sensitivity to shock and becoming optically transparent[1]. The goal of this study is to investigate if a computational method could produce results within sufficient accuracy to experimental data. The computational method may then be useful in guiding the design of new energetic materials.

There is a lack of data on the Molecular Dynamics (MD) method applied to amorphous energetics and there is also a need for further verification of the MD method applied to energetic materials in general. The aim of this study is to provide new data that can be used in determining the usefulness of the MD method, specifically with the General Amber Force Field when applied on amorphous energetics.

This study utilizes MD to test it as a tool for predicting properties in the widely used nitramine-like explosives CL-20 and HMX in the amorphous phase. A composition that has previously been studied experimentally [1] consisting of CL-20/HMX/Polyvinylacetate(PVAc) (50/45/5 -wt%) is simulated and the results are compared to existing experimental data. The results will give an indication as to whether this method is suited for amorphous energetic materials.

The properties of a material depend on whether it is in a crystalline- or amorphous phase. Analyzing the materials in their amorphous form may reveal differences in properties from their crystalline counterpart and may present opportunities to improve them as energetics. Either by direct improvement in any material properties such as shock insensitivity or compressibility, or through other means resulting from the homogeneous behavior displayed by amorphous materials. For example, it has previously been shown that a composition including PVAc, HMX and CL-20 showed amorphous behaviors and resulted in an optically transparent material as well as significant softening around $50^\circ$C [1], which might be of use in some applications.

There is a natural thermodynamic drive to keep a system in its lowest energy configuration which is in the crystalline phase. Due to kinetic factors during the preparation of a solid, a metastable amorphous phase can be achieved. It has been shown that polymeric additives tend to assist in keeping a metastable amorphous phase and preventing crystallization [1]. One approach to obtain amorphous materials involves heating the system to high temperature, where after the material is quickly cooled before the molecules have time to settle in a crystalline structure. The materials analyzed in this study showed to have a lower density in the amorphous phase than in the crystalline phase which relates to a decreased energetic performance of the explosive. Exposing the metastable amorphous material to high temperatures will cause it to crystallize over time, justifying the addition of a polymeric additive, albeit reducing the performance of the composition. For a specific composition that has been studied previously consisting of (50/45/5 -wt%) CL-20, HMX and PVAc other properties such as sensitivity to shock was altered [1]. This indicates that a

\[ \text{(a) CL-20} \]

\[ \text{(b) HMX} \]

Figure 1: A visual comparison between HMX in the crystalline phase (a) and the amorphous phase (b)

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reduction in performance could be outweighed by advantages found in other properties.

The General Amber Force field [2] has previously shown potential for estimating important physical properties of the nitramine-like explosives CL-20 and HMX in crystalline form [3] and will be used in the simulations.

This study is composed of two parts. In the first part, the explosives CL-20 and HMX are simulated in their amorphous form by compressing a box of 2400 molecules with varying pressures. The MD is performed with the GROMACS [4] software using constructed parameters defining interactions between atoms contained in the General Amber Force Field (GAFF) model. By compressing a box of a molecular gas isothermally, the solid is prepared in the amorphous phase ready to be analyzed. The radial distribution function, which is a measure of recurring distances between atoms in a system, is computed. The radial distribution function provides information on the molecular structure of the material. The main property of interest is the density, for pure CL-20/HMX the density will be compared to previous simulations in the crystalline phase [3].

The second part of this study aims to use MD again using GROMACS and GAFF to simulate a composition comprised of CL-20 and HMX together with the polymeric additive PVAc, which has been used in experiment to ensure stability of the amorphous composition. A topology that contains information on the chemical bonds between atoms in the system was constructed for the Polyvinylacetate and the composition CL-20/HMX/PVAc (50/45/5 -wt%) was be simulated and the measured properties compared to experimental data [1].
2 Background

2.1 Molecular Dynamics

Ideally, a system could be described entirely using the time-dependent relativistic Schrödinger equation. Due to the complexity of the calculations a computer can only handle a systems of limited size using this approach. Thus a number of approximations are needed in order to use a computational method to describe a larger system. To use a model based on classical physics, the underlying physical processes needs to be parametrized as contributions to a potential functions which allow the computation of forces and thus the dynamics of the system. All of the computations done in MD is classical using Newton's laws of motion. Parameterizing the system and solving classical equations of motion allows handling large systems in reasonable time frames. The performance of a simulation is determined by the amount of time-steps that are computed in a set time unit for a set number of atoms.

Molecular Dynamics (MD) simulations requires a set of atoms, respective coordinates and definitions of chemical bonds between atoms to compute the classical force on each atom according to

\[ \vec{F}_i = \frac{dV}{d\vec{r}_i}, \]

where \( V \) is the potential function determined by the force field. The force is computed for each atom from which the acceleration can be derived from the force according to Newton's equation of motion

\[ \vec{F}_i = m \frac{d^2\vec{r}_i}{dt^2}, \]

and thus we obtain the following differential equation for the position of the atoms.

\[ \frac{d^2\vec{r}_i}{dt^2} = -\frac{1}{m} \frac{dV}{d\vec{r}_i}, \]

at this point it is necessary to rely on some form of numerical integration to perform the integrals appearing in the equations of motion. The preferred method of integration in this study is the leap-frog integrator \[5\] which takes the following relations

\[ \vec{v}(t + \frac{1}{2}\Delta t) = \vec{v}(t - \frac{1}{2}\Delta t) + \Delta t \frac{\vec{F}(t)}{m}, \]

\[ \vec{r}(t + \Delta t) = \vec{r}(t) + \Delta t \vec{v}(t + \frac{1}{2}\Delta t), \]

from which the the new positions a time step \( \Delta t \) later can be computed. The parameters used to compute the forces are defined by the force field that is used and thus different force fields will yield different results. Which force field to use depends on the system and the physical processes under study. The new positions of each atom at a time step later is computed simultaneously. If required, macroscopic properties such as energy and temperature can be written out to an output file at each time step as well. This is then repeated with the new atomic coordinates that were computed in the previous step.

The accuracy of the simulation mainly depends on the parametrization of the force field and how well it reproduces reality. The statistical accuracy of the results will mainly depend on two factors, both resulting from increasing the data sets: the time step and the length of the simulation. The time steps are usually in the range of \( 10^{-15} \) seconds and the simulation time is typically within the range of \( 10^{-9} \) seconds.

2.2 GROMACS

GROMACS \[4\] is a freely available tool that is used to perform molecular dynamics simulations. GROMACS has been successfully applied in areas such as protein modeling and drug design. As mentioned a number of approximations need to be made in order to perform a calculation in a reasonable time frame. Apart from parameterizing the underlying model, GROMACS incorporates a number of other approximations that needs to be acknowledged which will be mentioned briefly below.

The electrons are not explicit in the simulations, instead they are modeled as charges of the cores. Long range interactions such as the Coulomb interaction and the Lennard-Jones interaction
are cut off at a certain cut-off radius from the source. As such, no contributions outside the cut-off radius of the sources are considered. Periodic boundary conditions are used, hence some error will arise in liquid systems[4] due to the lack of periodicity in those systems.

GROMACS has a few different tools available to perform energy minimization on the system. In this study the steepest descent method is used. In the steepest descent method the atoms are moved towards the negative gradient in set time-steps and continues until it reaches a local minimum. The steepest descent method is useful for finding the local minima quickly, making it a time efficient method.

### 2.3 The General Amber Force Field (GAFF)

The General Amber Force Field [3] is, as indicated by the name, a general force field that is applicable to a large range of systems due to the inclusion of all available parameters. The generality of GAFF is largely the reason why it was chosen for this study, as any indications of GAFF’s compatibility with the systems studied in this paper could carry over to similar systems. GAFF uses the simple harmonic functional form to compute the potential energy between a pair of atoms:

\[
E_{\text{pair}} = \sum_{\text{bonds}} K_r (r - r_{eq})^2 + \sum_{\text{angles}} K_\theta (\theta - \theta_{eq})^2 + \sum_{\text{dihedrals}} V_n/2[1 + \cos(n\phi - \gamma)] + \sum_{i<j} \left[ A_{ij} \frac{R_{ij}^6}{R_{ij}^6} - B_{ij} \frac{R_{ij}^{12}}{R_{ij}^{12}} + q_i q_j \frac{\epsilon_{ij}}{R_{ij}} \right]
\]

Where \( r_{eq} \) and \( q_{eq} \) are structural parameters, \( K_r, K_\theta, V_n \) are force parameters, \( n \) is multiplicity and \( \gamma \) is phase angle for torsional angle parameters. The derivation of these parameters can be found in Wang et. al. [2]. The terms involving summation over bonds corresponds to the bond vibration contribution, the angles to rotation, the dihedrals to van der Waals interaction and the indexes \( i,j \) to the Coulomb interaction.

### 2.4 Amorphous structure

![HMX in the crystalline phase](a) 
![HMX in the amorphous phase](b)

Figure 2: A visual comparison between HMX in the crystalline phase (a) and the amorphous phase (b)

Lack of long range periodicity is a characteristic of amorphous materials. Computing the radial distribution function allows for analysis of recurring distances within the system, any long range periodicity will thus occur as a pattern of higher intensities appearing at large distances from the reference point. An amorphous system on the other hand would appear as an even distribution at large distances. Should a homogeneous structure that lacks long range periodicity (the distribution should appear random at large distances) be found, the composition can be confirmed to be in the amorphous phase.

### 2.5 Energetic performance

The performance of an explosive is usually measured in terms of its metal pushing capability which is determined by the detonation velocity and detonation pressure and is dependent on its density. Detonation velocity is determined by the velocity of the burn wave traveling through the explosive during detonation.

A comparison between the amorphous and crystalline simulations will indicate any resulting difference in performance. In the figure 2 the detonation velocity (left) and detonation pressure
(right) are presented as a function of the density of the CL-20 (blue) and HMX (red) respectively. The data has been supplied by FOI and was obtained through thermo chemical computations. As can be seen both the detonation velocity and detonation pressure are decreasing with decreasing density, meaning that a CL-20 and HMX has a lower performance with lower densities.

Figure 3: Performance of the energetic materials CL-20 and HMX in terms of detonation velocity (left) and detonation pressure (right). Calculations were performed by Magnus Bergh at FOI.
3 Method

3.1 Molecular dynamics in GROMACS

Molecular dynamics in GROMACS is performed by supplying the program with input files. Usually, there are three different types of input files required to perform a simulation within GROMACS. A structure file (.gro) contains all the information about the atoms in the system, it contains the atomic coordinates and the atom type. A topology (.top) file contains the information about the atomic interactions defined by the force field. A .mdp file contains the specifications of the simulation.

The structure file is not useful on its own, besides for visualizing the system. In order to make sense of all of the atoms and coordinates when not in equilibrium the atoms need to know how to interact with each other. All of the interactions between atoms are specified in a topology file, which contains information of the constant attributes of the atoms. Inside the topology file interaction between atom pairs and restraints are specified. Combining this with the structure file gives a full description of the system in the equilibrium state.

Yet there has been no mention on how GROMACS will handle the system and the subsequent moving of atoms inside of the system. This is done by supplying GROMACS with a .mdp file containing information on how GROMACS should process the supplied information in the structure and topology file. Inside of the run file there is opportunity to specify options for GROMACS to process. Such options include the length of the simulation, the time step, reference pressure and reference temperature etc.

In some cases, the simulation might need to take into consideration what happened to the system before it was put in the current state. Whenever a simulation is started, the atoms starts moving, to take into account how the system moved before it was put into a final state, the velocities of each of the atoms are being recorded in the final step and processed into a checkpoint (.cpt) file. This can be used to continue on a previous simulation but with altered parameters etc. and will provide a more continuous behavior in these cases.

With all of the input files in place, GROMACS will process them into a final run file (.tpr) that is used to run the simulation.

Running the simulation with the preprocessed run file will start computing the interactions according to the topology file for each of the atoms specified in the structure file with the options specified in the .mdp file.

The simulation is now computing interactions on all of the atoms and will update to the computed position and velocity a time step later simultaneously. This is repeated until the system has taken enough steps to reach the specified simulation length.

There is an option to record the atomic coordinates and macroscopic properties of the system at each time step, this is usually only used in the final step of the simulation and will not be used in the steps leading up to it. If specified, at each time step the positions of each of the atoms will be recorded on an output file called the trajectory file (.xtc) and the macroscopic properties of the system will be recorded on another output file called the energy file (.edr). The trajectory and energy files is the result of the simulation and will contain the motion of the system over time as well as any macroscopic properties that might be of interest.

To perform meaningful analysis on the system macroscopic quantities needs to be computed. This is conveniently handled automatically within GROMACS. A number of macroscopic quantities that might be of interest in analysis are recorded at a set interval of time step and recorded onto the energy file (.edr). Ideally, the properties should be recorded at every frame but may be altered to reduce the output file size and compute time. The energy file contains macroscopic quantities such as total energy, density and temperature of the system at each of the time steps.

In this study the main properties of interest will be the density and energy of the system. The density because of the relation to energetic performance and total energy to check for the convergence of the system. The final result is computed by taking the statistical mean of the quantity over time and the statistical standard deviation is computed to give an indication of the statistical accuracy of the quantities.

The Simulation will be carried out on the GROMACS software [4] running on a 32 virtual core CPU.

For numerical integrations the leap-frog integrator [5] was used. A short-range neighbor list cutoff of 1 nm was used. For the short range Coulomb electrostatic interaction, a cutoff of 1 nm was also used. Similarly for the Van der Waals interaction a cutoff radius of 1 nm was used.
GROMACS was used to simulate the composition in a specified environment controlling the pressure and temperature using the modified Berendsen thermostat and the Berendsen barostat [5]. A time constant of 0.1 ns was used for the thermostat and 2.0 ps for the barostat. The temperature coupling was applied for the whole system. Particle Mesh Ewald (PME) [6] with cubic interpolation was used for long-range electrostatics and a grid spacing of 0.16.

The energy minimization was performed using the steepest descent method with a step size of 0.01. The tolerance for the energy minimization to stop was when the maximum force was below \[ \frac{500}{\text{kJ/m} \cdot \text{mol}} \]. The maximum number of steps for the energy minimization was set to 500 000.

In the subsequent text the following abbreviations are used to define different systems with different constant attributes: An NVT system is defined by keeping the number of atoms, volume and temperature constant. An NPT system is defined by keeping the number of atoms, pressure and temperature constant. Where N is used for constant number of atoms, V for volume, P for pressure, and T for temperature.

### 3.2 HMX and CL-20 simulations

The structure files containing atomic coordinates of the energetic molecules HMX and CL-20 was retrieved from the Cambridge Crystallographic Data Center (https://www.ccdc.cam.ac.uk/). Topologies of the HMX and CL-20 molecules was obtained through the use of the Antechamber software [7] for the GAFF topology and was provided by Bergh and Caleman [3].

First a box of size 7x7x7 nm was specified and then filled with a total of 300 molecules of CL-20 and HMX respectively. The molecules was ensured to be oriented randomly when filling the box by letting the molecules act as a solute. For more accurate simulations a bigger box was required and thus the previous box of 300 molecules was copied and placed side to side with itself. In three dimensions the box was copied and placed side to side with itself 2x2x2 times resulting in a larger box of 2400 molecules which should be sufficient for this simulation.

After the box had been generated it was run through an energy minimization simulation. The energy minimization serves to remove any discrepancies that follows from generating the box. It happens that the molecules will be placed too close to each other or that they are overlapping. Should any such discrepancies be ignored, the forces would become much too large and the system will yield unrealistic results.

When the box had been energy minimized it followed a 100 ps NVT equilibration. During the NVT equilibration the number of atoms, volume and temperature are held constant, whereas the pressure is allowed to vary. Such equilibrations can be useful to picture as a mixing between two liquids in a glass. Initially there might be a structure, say if you first pour the first liquid and then the second. The first liquid will be located at the bottom of the glass while the second liquid will be at the top. This pouring of the liquids can be likened to the generation of the simulation box. As time goes on the liquids will mix and eventually will become indistinguishable, this is what happens when the system undergoes the NVT simulation.

Up to this point the system has taken the form of a molecular gas. The next step is to compress it into an amorphous solid. This is done by running the system through an NPT equilibration. As is implied by the name, this simulation is run under a constant number of atoms, pressure and temperature, allowing the volume to vary. Varying pressures are applied and the box edges are allowed to expand and compress anisotropically. By applying this large pressure the molecular gas will be compressed into a solid phase. The amorphous structure is ensured by the random orientation of the molecules during the generation of the box. Furthermore, the simulations are running for a very short time compared to the time it would take for the system to crystallize. Also, the system is equilibrated to ambient temperature (298 K) and for the system to crystallize within a considerable timeframe, a higher temperature would need to be applied.

In the last simulation step the data is saved every 2 ps in what is called a trajectory file which will be used to carry out the analysis.

To ensure that the analysis is conducted on the system after it has been fully converged the dataset was cut to only include data after the first 100 ps when the system had converged.

The NVT equilibration ran for 100 ps using a time step of 2 fs. During the NVT equilibration the simulation were carried out under a temperature of 298 K which was specified by setting the reference temperature for the Berendsen thermostat to be 298 K. No pressure coupling was specified during the NVT equilibration thus allowing the pressures inside of the box to vary.

The first NPT equilibration ran for another 100 ps again using a timestep of 2 fs. The NPT
simulations used temperature coupling with a reference temperature of 298 K for the thermostat and pressure coupling with varying reference pressures for the barostat. By specifying the use of the pressure coupling, the box will compress according to the specified reference pressure.

The final NPT simulation which was used to record the trajectory of the system once it had been equilibrated to specified temperature and pressure conditions ran for 2.0 ns with a time step of 2 fs. Similarly to the first simulation a reference temperature of 298 K was used and the reference pressure was varied for each of the simulations to be the same as in the first NPT simulation, as to not compress or relax the box further. The difference between the first and final NPT simulation is that the final simulation is used for producing accurate results and recording atomic coordinates and macroscopic properties at each time step for the equilibrated system.

The system was simulated for pressures from 0 to 4 GPa in steps of 0.5 GPa, in order to be easily compared to previous results obtained from simulating a similar system in the amorphous phase [3].

3.3 CL-20/HMX/PVAc simulations

A chain of 9 monomers of Polyvinylacetate was used where the topology was obtained through the use of the Antechamber software [8] for the GAFF topology.

In a similar fashion a box of 8x8x8 nm was specified and filled with 300 total molecules oriented randomly by specifying it as a solvent, this time using 150 molecules of CL-20, 135 HMX and 15 PVAc in order to keep concentrations of (50/45/5 -wt%). The box was copied and placed side by side to itself 2x2x2 times resulting in a box of 2400 total molecules.

The simulation box was energy minimized, followed by 100 ps NVT equilibration subject to 298K followed by a 100 ps NPT equilibration where the pressure was varied between simulations from 0.4 [GPa] to 10 [GPa] and the temperature was held constant at 298 K.

The system is now subject to a large pressure. The last step before conducting analysis is then to relax the system to ambient conditions. Another NPT simulation was carried out on the system but this time with a pressure of 1 bar. The box edges were then allowed to expand anisotropically again subject to 298 K. The relaxation was run for 1 ns and The data was saved every 0.2 ps.

The analysis was conducted on the trajectory file cut from 100 ps when the system had converged.

The trajectory files contain the coordinates of each atom in the system at every time during the simulation from which it was produced. The analysis of the system will be carried out by extracting macroscopic properties from the trajectory file at different times. To perform a good analysis the system must first have converged. During the last simulation where the trajectory file is recorded, the system will not have converged during the first time steps since the system have not yet adapted to the new lower pressure. It is crucial that any further analysis is not conducted on the part of the trajectory where the system has not converged. Convergence is determined by analyzing the energy of the system as a function of time. If the energy curve is contained within an interval that does not increase or decrease with time, the system is said to be converged. The trajectory files were cut respectively at 100 ps only carrying over data that was simulated after that point in time.

GROMACS has built in functionality to extract macroscopic data from the trajectory files with specified time intervals between each data point. This was utilized in order to extract macroscopic data, the final value was computed by taking the mean over time.

The NVT equilibration ran for 100 ps and used a time step of 2 fs. A reference temperature of 298 K was used in the Berendsen thermostat for the temperature coupling throughout the simulations. In the NVT equilibration no pressure coupling is specified again allowing the pressure to vary.

The first NPT equilibration for 100 ps and again a time step of 2 fs. For the pressure coupling, the Berendsen barostat was specified to have varying reference pressures. Again the reference temperature was set to 298 K. During the pressure equilibration the box edges were allowed to expand anisotropically.

The final NPT simulation ran for 1.0 ns and used the same reference temperature. In this step the system was relaxed to ambient conditions by specifying the reference pressure to be 1 bar. Again, during the final NPT simulation on the equilibrated system the atomic coordinates and macroscopic properties are recorded onto a .xtc and .edr file respectively, allowing for analysis.

The system was simulated for pressures from 0.1 to 1 GPa in steps of 0.1 GPa for a detailed
look on how compression effects the density of the material. The range was selected based on previous experimental results, which pointed towards the density increasing with compression up to around 1 GPa, where after the density seemed to not be effected by further compression. Three more pressures of 1.5 GPa, 4 GPa and 10 GPa was applied to the system to study whether further compression had any effect on the density of the material.

4 Results

This section presents the results from the simulations. Firstly the densities and structural information obtained from simulation of pure CL-20 and HMX in the amorphous phase will be presented. Secondly the density and structural information obtained from the simulation of the composition of CL-20/HMX/PVAc will be considered.

4.1 CL-20 (100-wt%) & HMX (100-wt%)

<table>
<thead>
<tr>
<th>IUPAC name</th>
<th>Abbrev.</th>
<th>$\rho_{\text{sim}}$ ($\text{kg/m}^3$)</th>
<th>St. dev.</th>
</tr>
</thead>
<tbody>
<tr>
<td>octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine</td>
<td>HMX</td>
<td>1577</td>
<td>± 1.5</td>
</tr>
<tr>
<td>2,4,6,8,10,12-hexanitro-2,4,6,8,10,12-hexaazaisowurtzitane</td>
<td>CL-20</td>
<td>1784</td>
<td>± 2.3</td>
</tr>
</tbody>
</table>

Table 1: The resulting densities and standard deviations obtained from the simulation of pure CL-20/HMX at ambient conditions (T=300 K, P= 1 bar).

The first investigation considered the densities of pure HMX and CL20 subject to ambient conditions in the amorphous phase respectively, the results are displayed in table 1. Results indicate that the simulated amorphous HMX had a density 12.7% below simulated crystalline HMX. The simulated amorphous CL-20 had a density 7.3% below simulated crystalline CL-20 as can be seen in Table 2.

<table>
<thead>
<tr>
<th>Abbrev.</th>
<th>$\rho_{\text{sim}}$ Amorphous Phase ($\text{g/cm}^3$)</th>
<th>$\rho_{\text{sim}}$ Crystalline Phase [3] ($\text{g/cm}^3$)</th>
<th>Difference [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>HMX</td>
<td>1.58</td>
<td>1.81</td>
<td>12.7</td>
</tr>
<tr>
<td>CL-20</td>
<td>1.78</td>
<td>1.92</td>
<td>7.3</td>
</tr>
</tbody>
</table>

Table 2: The difference in density when in the amorphous phase versus the crystalline phase, all data was obtained under ambient conditions

The relative volume as a function of compression pressure was computed and compared to previous data from simulations in the crystalline phase [3]. The results for pure CL-20 and pure HMX are presented in figure 3 and 4 respectively.

As can be seen the density is lower in the amorphous phase compared to the crystalline phase. This is because of the close packing that occurs in the crystalline phase. It seems that on a structural level, the most optimal way to fill the space is achieved in the crystalline phase. Thus, when the material is in the disordered amorphous phase there is some space between the molecules that is underutilized because of the non optimal packing. The wasted space then results in a lower density. It should be noted that there are exceptions to this, for example, ice has a lower density than water.
The relative volume as a function of compression pressure is displayed in figure 3 and 4 for CL-20 and HMX respectively. It is observed that the system compresses more easily for lower pressures for both pure CL-20 and pure HMX, however the difference is more significant for HMX. The HMX, which was observed to have a density 12.7% below the density for the crystalline phase at ambient conditions appears to be significantly easier to compress. By compressing the HMX with a pressure of 0.5 GPa the density rises to around 1.72 g/cm$^3$ which is around 6.3 % lower than the density in the crystalline case, which will have a density of around 1.86 g/cm$^3$ for the same pressure.
The obtained Radial Distribution Functions (RDF) that were computed for the simulated amorphous phase are presented in Figure 6, 8 along with comparisons to radial distribution functions computed for the same composition in the crystalline phase. The radial distribution functions computed in figures 6, 8 are averages over all atoms in the systems. The intensity of inter-atomic distances are displayed as a function of the distance in nm. Figures 7, 9 displays the separated radial distributions functions for CL-20 and HMX respectively. It displays the intensity of recurring inter-atomic distances for separate atoms denoted by C-C, O-O and N-N. Where C-C is the distance between atoms of carbon, O-O is oxygen and N-N is nitrogen.

(a) CL-20 in the amorphous phase
(b) CL-20 in the crystalline phase

Figure 6: A comparison between the obtained radial distribution functions for CL-20 for the amorphous phase (a) and crystalline phase (b) taking the average over all atoms in the system

By analyzing Figure 5 (a) and (b) and comparing to Figure 6 it is observed that the intense peak of between carbon (C-C) and nitrogen (N-N) at around 0.15 nm is not present in either the amorphous or crystalline case, which indicates that they likely arise from the homogeneous structure. In figure 6 between 0.2-0.26 nm there are a number of peaks present, one for oxygen (O-O) two for nitrogen (N-N) and two indistinct peaks from carbon (C-C). In figure 5 (a) there is a wide peak around this same interval, meaning that this peak likely arises from the combined intensities of each of the aforementioned. Figure 5 (a) points to the structure being homogenized to a larger degree when compared to figure 5 (b). The structure observed in figure 5 (b) contains
some long range structure which is not observed in figure 5 (a) where the curve appears smooth after surpassing 0.6 nm.

Figure 8: A comparison between the obtained radial distribution functions for HMX for the amorphous phase (a) and crystalline phase (b) taking the average over all atoms in the system

Figure 9: The separated rdf obtained for pure HMX

In figure 7 (a), there is a strong peak that appears around 0.18-0.19 nm radius. In figure 8 there are no peaks present in the interval 0.15-0.2 nm, hence the first peak in figure 7 (a) is not due to any of the couples present in figure 8, indicating that they likely arise due to homogeneous behavior in the amorphous structure. A weaker intensity peak can be observed shortly after 0.2 nm radius in figure 7 (a). Looking at figure 8 there are 3 peaks present at the interval 0.2-0.26 nm. The weaker rise in intensity observed in figure 7 (a) shortly after 0.2 nm is likely the combined intensities of the aforementioned contributions observed in figure 8 between 0.21-0.26 nm. Comparing to figure 7 (b) there appears to be two intense peaks in the same interval, by again analyzing figure 8 it is likely that the first intense peak can be attributed to be O-O and second to a combination of C-C and N-N, seeing as they are overlapping in figure 8. The amorphous structure in figure 7 (a) lacks any long range structure whilst the crystalline structure is accentuated clearly in figure 7 (b).

The graphs for the respective crystalline phases are significantly less smooth resulting from smaller data sets from these simulations. The crystalline data was obtained from a 100 ps long simulation whereas the amorphous data was obtained from a 1 ns long simulation.
4.2 CL-20/HMX/PVAc (50/45/5 -wt%)

A composition that was previously studied experimentally [1] of CL-20/HMX/PVAc (50/45/5 -wt%) was simulated to have a density of around 1.64 \( \text{g/cm}^3 \). Experimental measurements of the density of the same composition was found to have a density of 1.7 \( \text{g/cm}^3 \). By comparing the obtained simulated density to that of experiment it is found that the simulated density is lower by a factor 3.5%.

![Figure 10: The density as a function of pressure applied during the compression phase, note the scale on the y-axis](image)

As can be seen in figure 9, by inspection of the scale on the y-axis the density did not vary significantly for the different pressures applied during the compression phase, which indicates that the density had converged. Experimental measurements [1] which found that the density appeared to reach it’s maximum density of 1.7 \( [\text{g/cm}^3] \). The densities for pressures higher than 1000 \( [\text{MPa}] \) are presented in table 3.

<table>
<thead>
<tr>
<th>Pressure [GPa]</th>
<th>( \rho_{\text{sim}} ) [\text{g/cm}^3]</th>
<th>St. dev.</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.15</td>
<td>1640</td>
<td>2.5</td>
</tr>
<tr>
<td>0.4</td>
<td>1637</td>
<td>1.5</td>
</tr>
<tr>
<td>4</td>
<td>1640</td>
<td>2</td>
</tr>
<tr>
<td>10</td>
<td>1640</td>
<td>1.1</td>
</tr>
</tbody>
</table>

Table 3: The resulting densities when simulating the composition under three different pressures.

As can be seen the density does not appear to vary significantly on the pressure applied during the compression phase. The experimental data used for comparison for the CL-20/HMX/PVAc composition was obtained by preparing the materials by spray drying acetone-based solutions. The Polyvinylacetate(PVAc) had a molecular weight of 100,000 M.W [1].
In figure 11 there are two peaks present for N-N and C-C at around 0.15 nm that are not observed in figure 10 again suggesting that they arise from the homogeneous behavior displayed by the amorphous structure. Furthermore, the same pattern that was observed in the two previous cases seems to arise here again. Between 0.21-0.26 nm there are one peak from C-C, one from N-N and two indistinct peaks from C-C that appears as a combined peak in figure 10, this is to be expected since our composition is composed of the two previously mentioned molecules, hence the first peak is attributed to the inter-atomic distances that occur for HMX and CL-20.
5 Outlook

Our use of a Polyvinylacetate chain of 9 monomers is short in comparison to those used by Stepanov [1]. The reason being the increased computational cost for simulating long polymer chains. This is a matter of computational cost. Repeating the simulations with chain lengths close to those used by Stepanov would require too many CPU hours. Although theoretically possible, the amount of required CPU hours would be too high to be feasible using current day technology. Instead one should look to investigate the effect of polymer length on the density. By analyzing and comparing the resulting density when simulating a box of polymers all with the same length, one may draw conclusions on the effect of polymer length on the density. This is out of the scope for this project but would be an interesting analysis.

There are interesting properties found in the amorphous composition that could be of use in applications. One such property is the reduced sensitivity to shock found in the amorphous phase of the CL-20/HMX/PVAc composition compared to the crystalline phase. One could use this property to increase the safety of the explosive by storing it in the amorphous phase where the sensitivity to shock is reduced.

6 Conclusion

To conclude, the densities for simulated CL-20 and HMX in the amorphous phase resulted to be lower than simulated results for the same materials in the crystalline phase. The compressibility of CL-20 was observed to be close to that in the crystalline phase. For HMX however the composition compressed significantly more in the amorphous case versus the crystalline case. Structural analysis points towards the HMX being largely homogenized, whilst CL-20 retains some structure even when prepared as a molecular gas.

For the composition of 50/45/5 -wt% of CL-20/HMX/PVAc a density of 1.64[g/cm³] was found. The density did not appear to depend on the pressure applied when compressing the molecular gas, which indicates that the density has converged to a large degree already for low pressures applied during the compression phase. Structural analysis points to the composition being homogenized to a large degree.
7 References


