Towards realistic atomistic models of nitrocellulose degradation

Catriona Gibbon[1], Poppy Di Pietro[2], Duncan Broughton[2], Mark Storr[2], Chris-Kriton Skylaris[1]

[1]School of Chemistry, University of Southampton, UK
[2]AWE, Aldermaston, UK

Computational Chemistry

Molecular dynamics is a computational chemistry technique used to simulate systems of 1000s of atoms. Classical mechanics are used, considering atoms and bonds as balls and springs respectively.
For this project structures are formed using Moltemplate [1], and simulated using LAMMPS [2] with the OPLSAA forcefield [3] and NPT conditions - fixed number of atoms, pressure and temperature.

Cellulose and Nitrocellulose

Cellulose is a well studied polymer found in cotton and rayon, formed from chains of dimer glucose units shown in Figure 1. Cellulose is found naturally in many different states with varying levels of crystallinity. This project aims to obtain paracrystal structures, where the strong intermolecular forces in the crystal structure are overcome.

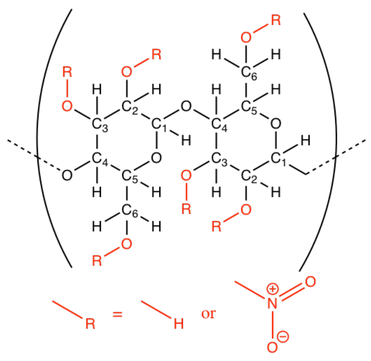

Fig. 1: Structure of a cellulose dimer unit. There are six locations that can be nitrated to form nitrocellulose, which are highlighted in red.

Nitrocellulose is a highly reactive chemical formed by nitrating cellulose. Due to its instability, there is very little literature available on nitrocellulose. However cellulose is a reasonable analogue for nitrocellulose when considering large scale structures. This means that techniques can be tested on cellulose and compared to literature data, and then used on nitrocellulose to give more confidence in the results.

Nitration levels

The higher the Degree of Substitution (DS), the more unstable the nitrocellulose is [4].

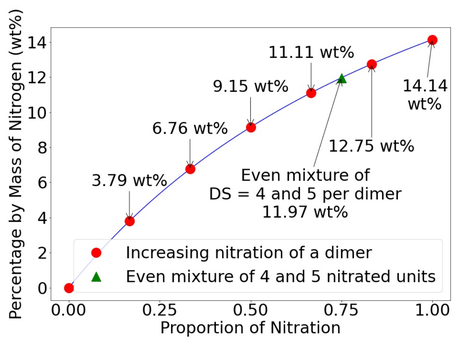

Fig. 2: Degree of Substitution.

Although the highest nitrogen content theoretically is 14.14 wt%, as shown in Figure 2, experimentally the highest obtained nitrogen content is 13.9 wt% [4].
For this project nitrocellulose of approximately 12.0 wt% is being considered, and can be obtained by using an even mixture of units with dimer DS = 4 and 5.

Crystalline Cellulose

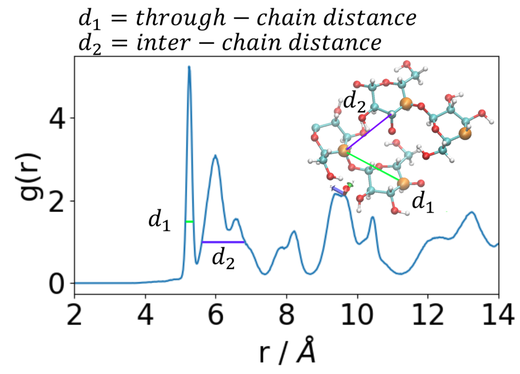

Fig. 3: Radial Distribution Function (RDF) between all C_4 atoms. Oxygen atoms are shown as red, hydrogen atoms white and carbon atoms blue. C_4 atoms are highlighted in orange.

RDF calculations between C_4 environments were performed as it is one of the carbons linked by the glucosidic bond between the units, so it is not affected by the twisting of units. Figure 3 shows the RDF of data for a cellulose structure that was created from a grid of 10 x 10 chains 5 dimers long (21,000 atoms), using triclinic periodic boundary conditions. The structure was first energy minimised, and then was equilibrated at a constant pressure and temperature, 1 atm and 300 K, for 10 ns.

Creating Paracrystalline Structures

To break the organised nature of the crystal built using Moltemplate, a simulated system of cellulose containing 21,000 atoms was heated at a rate of 50 K per ns. The paracrystallinity can be seen visually in Figure 4 where the chains are no longer strictly arranged, having twisted and moved. The RDF data can also be used as a diagnostic tool - as the regular positions of the atoms becomes more random in the paracrystalline structure the peaks of the RDF will become lower and broader, as seen in the 900 K case in Figure 5.

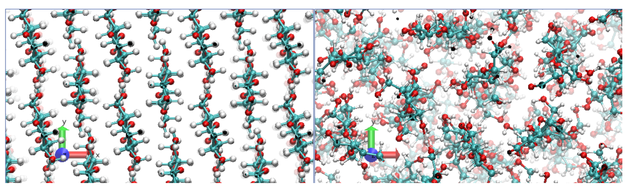

Fig. 4: Cellulose structures, an atomistic initial structure (left) and after having been heated to 900 K (right).

The structure was heated to 700 K, 800 K and 900 K, left at that temperature for 1 ns, then cooled to an intermediate temperature (500 K for 700K, 550 K for 800 K, and 600 K for 900 K) for 100 ps, then further to 300 K where it was equilibrated 1 ns.

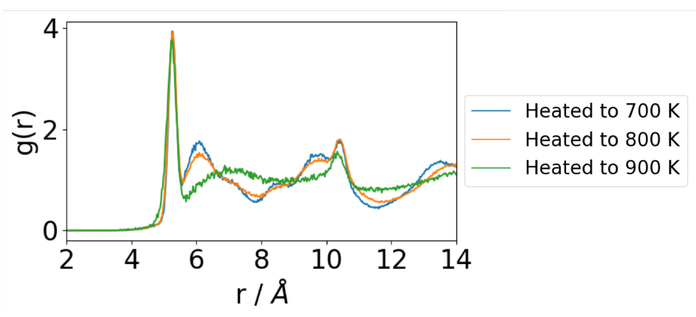

Fig. 5: RDF graphs for C_4 interactions in cellulose heated to different maximum temperatures.

Nitrocellulose Structures

A structure of crystal nitrocellulose has also been built by Moltemplate using a mixture of 4 and 5 nitrated dimer units.

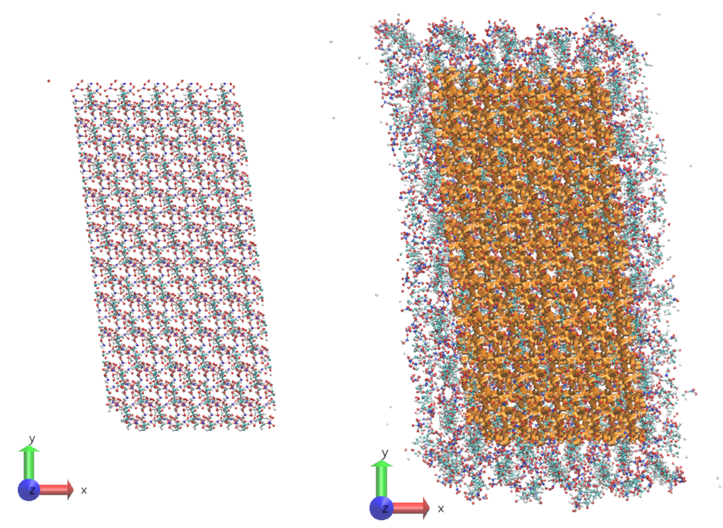

Fig. 6: Initial structure of nitrocellulose, containing 24,186 atoms. Left is the initial structure. Right shows the structure after it has been allowed to expand with the original structure highlighted in orange.

The nitrocellulose is built by adding nitrate groups onto the cellulose structure which increases the density of the structure greatly.
Literature values for the density of experimental nitrocellulose of 1.65-1.67 g cm^{-3} [5]. Figure 7 shows that the initial density is 2.51 g cm^{-3}, but after just 0.5 ns of equilibration at 1 atm and 300 K, where the volume is allowed to change, the density averages to 1.58 g cm^{-3}, which is much closer to the experimental values.

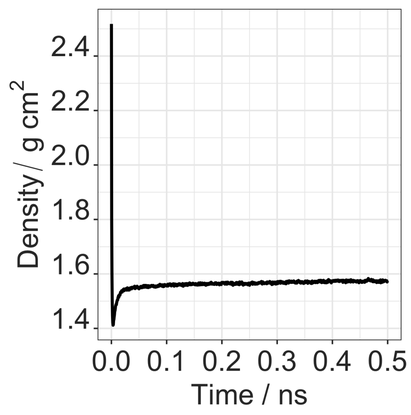

Fig. 7: The decompression of a nitrocellulose structure when equilibrated with constant temperature and pressure, allowing the volume to change.

Conclusions and Further Plans

Using the OPLSAA [3] forcefield in LAMMPS [2] on structures built using Moltemplate [1], paracrystalline structures of cellulose have been created that have properties that match with paracrystalline structures described in literature. A crystalline structure of nitrocellulose can also be created using Moltemplate [1], and this will be used to create paracrystalline nitrocellulose structures using the same methods.
Next, another computational chemistry technique, Density Functional Theory (DFT), will be used to study the mechanisms of the degradation reactions in the context of a larger system of paracrystalline nitrocellulose. DFT uses quantum mechanics, and focuses on the electrons, which means that it can be used to study reactions in a way that molecular mechanics cannot.

References

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