# Molecular Dynamics Simulation of Cohesion within Solid Propellants

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## ABSTRACT

Composite rocket propellants and plastic bound explosives are both based on elastomeric binder matrices that contain either oxidizer particles or high explosives. The components in a formulation differ widely in terms of crystallinity, thermal expansion behaviour and thus mechanical properties. Therefore, composites can exhibit a combination of brittle and ductile behaviour, stemming from filler and binder polymer, respectively. The binder-filler interaction is the weakest in the system, and their interface is prone to detach irreversibly, when stretched beyond a critical separation distance. In experiments, the effect of adhesion can be monitored by dynamic mechanical analysis (shape of loss factors), surface tension measurements and solution calorimetry. On a microscopic level, the cohesive zone model serves as a separation law for mechanical failure. It mimics the irreversibility of crack formation: While small loading and unloading is reversible, higher strain beyond a threshold value changes the given distanceforce function for further loading cycles (local damage). Quantitative parameters for this model are hardly measured, although they are of interest for finite element simulations, to explore the material on a larger space and time scale. Here, we present the complete model of a pull-off experiment in the framework of a molecular dynamics simulation. In a MD-simulation, single atoms are modelled by point masses that interact via force-fields. It can reproduce thermodynamic and mechanical properties of multi-component systems. In an earlier contribution, the thermodynamic work of adhesion (equal to a surface tension) has been presented. Now, work and force of separation including local deformation of the surfaces is presented. It includes irreversibility during pull-off: As external stimulus, the interface is stressed until mechanical failure. This procedure yields higher order mechanical parameters beyond the linear elasticity model, which are input parameters for finite elements simulations: energy/force of detachment, and interaction length of entangled polymer at the interface.

## Introduction

This contribution is an overview of our recently developed algorithms within the framework of molecular dynamics simulation for the implementation of crystalline surfaces (chapter 2), the generation of cross-linked polymer networks (3), their primitive path analysis (4), and explicit pull-off dynamics of networks from crystal surfaces (5), alongside preliminary results. The motivation is to address effects (non-linearity in forces, viscoelasticity) on larger time scales than those presently accessible by molecular dynamics.

The motivation is to create a computational method to probe the viscoelastic regime of polymer motion and deformation near surfaces. Especially for small particles, strengths of adhesion or the functional form of detachment potentials cannot be probed directly by measurements. There exist several mechanisms of mechanical resilience that overlap in time and length scale: The stiffness and dissociation barrier of chemical bonds itself, entropic penalty of stretching a chain conformation (that also has the functional form of spring force), and the physical entanglement of polymers. Commonly, these are condensed in one simple law, the cohesive zone model [1, 2]. It is a simple bilinear relation of traction versus displacement of cohesive plates. At small separations, the traction rises linearly, until a maximum value, and then drops linearly to zero. The first slope mimics elastic stiffness, the second one gradual failure until detachment. Their parameters are vital for finite element simulations.

Recently, efforts have been made to extract these parameters from atomistic molecular dynamics simulations of nanostructures in metallic matrices [3], or crack propagation in solids [4]. Our efforts aim at modelling the cohesion of polymers and especially polymer networks on crystalline surfaces. Unlike metals or ceramics, polymers feature viscoelastic behaviour, which is still a prevailing topic of polymer simulation. While elasticity is probed straightforwardly in simulations by small and reversible deformations, the viscous contribution of larger time scales and elongations has to be calculated by a series of dynamics calculations. Thus, we developed a calculation scheme to extract the response to large deformations. In the following, the principle molecular dynamics is explained shortly.

The method is based on the approximation of atoms as point masses and point charges in space. They interact via distance dependent force functions, as the Coulomb law and dispersive terms, e.g. a Lennard-Jones function for van-der-Waals forces. Chemical bonds in turn are modelled by higher order spring forces. Each functional group is parameterized to model the potential energy landscape provided by quantum mechanical calculations and experiments. The parameter set (also called force field) employed here is from COMPASS<sup>TM</sup> II, [5], provided in the program package used, Materials Studio<sup>TM</sup> by BIOVIA.

Molecules can be sketched as in a graphic chemical structure editor, and assigned their force field type. Also a certain volume, a simulation "box" can be created, which is a representative volume of space (in the order of nanometres), to simulated bulk media, such as crystals or liquids, densely filled with molecules.

Iterative solution of classical equations of motion with interatomic forces yields correct time evolution of structure and energy within a simulated volume element: Thus, molecules diffuse, rotate, align to surfaces, oscillate within crystals, etc. A typical simulation box used here contains about 10 000 atoms. Commonly, periodic boundaries rules apply: Each molecule that leaves the box in one direction reenters the box on the opposite side. This mimics an infinitely extended bulk of matter.

Temperature and pressure are adjusted by additional algorithms that change the kinetic energy ("heat bath" provided by Andersen thermostat) of particles and alter the cell volume ("pistons" pressing on the system, e.g. Berendsen barostat). The systems then propagate in the NPT-ensemble (corresponds to normal real experimental situations where particle number N, pressure p and temperature T are under control of the experimentalist) and the obtained simulated values can be compared to experimental results straightforwardly. Of importance, the barostat used here (Rahman-Parrinello barostat) allows for independent change of edge lengths and angles of the simulation box. Thus, anisotropic structures can relax to equilibrium. Properly employed, it allows for the determination of interaction energies, heat capacity, mechanical properties, etc. from statistical thermodynamic relations, as long as quantum mechanical effects do not contribute to a macroscopic property.

In a former contribution [6], crystal surfaces have been loaded with HTPB (hydroxyl-terminated polybutadiene), azido-terminated glycidyl polymer, or diehtylhexyl apdipate to calculate the surface tension of the phase boundary. Now, the simulations are extended to direct dynamic separation of phases.

#### **Building surfaces**

First, crystal structures are generated from X-ray diffraction data. Clearly, structure data at the correct temperature and pressure – i.e. the same values that are used for the simulation – have to be chosen, means the crystal modification has to be correct. By an initial molecular dynamics run of a representative super cell, the applicability of the force field is tested. Using an appropriate force field, the cell parameters remain within given boundaries, in addition to the properties that are specific for the system: For ammonium perchlorate (AP), ammonium groups have to rotate freely within a framework of perchlorate ions [7]. By iterative fitting of partial charges, following Ref. [8], both requirements are fulfilled.

In a next step, sets of representative crystal surfaces are identified that comprise the majority of particle surfaces. The algorithm employed calculates the attachment energy of a new crystal layer deposited from vacuum to the bulk. Possible surface configurations are screened, starting from the initial assumption that surfaces with low Miller indices are most likely to grow, according to the Donnay-Harker

rule [9]. The growth rate of each crystal face is assumed to be proportional to its attachment energy; that is, faces with the lowest attachment energies are the slowest growing and, therefore, have the most morphological importance and so dominate the habit facet. Note that this method does not include effects of solvent type, temperature/pressure, saturation or stirring, and rearrangement during growth. However, comparison to experimental data of crystallites grown form good solvent or vacuum deposition shows good agreement. This hold true for ammonium perchlorate, aluminium and nitramines tested so far. In Figure 1, the crystal habit of ammonium perchlorate is shown, with three of its five different surface types as molecular structures.



Figure 1: Calculated crystal habit of ammonium perchlorate relative to the unit cell, alongside selected surfaces with their molecular structure. Number triplets in brackets are Miller indices. They denote the orientation vector of the respective surface.

If possible, the surface vectors are recalculated to be perpendicular in order to get a rectangular surface unit cell. Adding AP bulk groups and a vacuum layer yields an orthorhombic simulation box. Then, the cell can be loaded with adsorbate molecules in a constraint volume above the crystal, see Figure 2. The adsorbate molecules themselves are picked from a pool of randomly created configurations and enantiomers.

In a former contribution [6], these free volumes have been loaded with HTPB (hydroxyl-terminated polybutadiene, azido-terminated glycidyl polymer, or diehtylhexyl apdipate. Further on, energies of detachment in the framework of surface tensions have been calculated.



Figure 2: Steps of generating a simulation box for interphases. From a surface unit cell to a supercell, a crystal bulk, transferred to a box, with free volume.

#### **Generation of networks**

The direct generation of highly cross-linked polymer structures is an important step for the simulation of representative structures. Although a number of algorithms exist [10], they influence the polymeric material properties to some extent, according to the building scheme [11]. A typical way is to generate a volume of a polymer melt first, and cross-link them in a next step. The generation of melts has been researched and scrutinized over the past 40 years. Now, properties of melts can be simulated successfully, in accordance with experimental results. These now common procedures yield linear or branched topologies (star, comb, dendritic), but fail to create representative cross-linked structures that interconnect to itself, beyond the periodic boundaries of a simulation cell. So, recently, generated melts are subjected to different reactive crosslinking algorithms that should resemble the progress of a curing reaction [12].

Direct reactive dynamics is computationally too expensive. Reactions occur on time scales that exceed those accessible to molecular dynamics simulations by far. Real curing can take hours or days, while molecular dynamics is bound the simulation of pico- or nanoseconds at best. Even calculating the self-diffusion of polymer melts is beyond the capabilities of common computational setups. Therefore, devised procedures make use of either Monte-Carlo simulations (probe the statistical ensemble by random changes of chain configuration, and accept or reject the change according to the Boltzmann energy distribution), or pseudo-dynamics: Here the random change is induced by dynamic simulation of movement with a physically wrong force field that allows chains to move unphysically fast and interpenetrate.

For this work we programmed an algorithm that links HTPB pre-polymers with di-isocyanide crosslinkers, to form urethane functionalities with the terminal hydroxyl groups of the polymer, by pseudodynamics. Its single steps are in the following:

- Build up a set of molecules to react, they include uncured pre-polymers of various topologies, i.e., linear, star-shaped, comb connectivity, or dendritic structures. Note that for the generation of a chemically cross-linked network, single chains are required to have at least three connection points for crosslinking. Otherwise, only linear structures and ring topologies will be the result. The latter kind of systems only show physical entanglement and possibly concatenated rings. Polymers used for a first test are a 1:1 mixture of linear chains and 3-armed regular star topologies. The reactive ends, the -OH groups are located at the ends as terminal functional groups. Used molecular structures are presented in Figure 3.

- From the set of pre-polymers alongside the cross-linker molecules, a simulation box with a preexisting crystal surface is loaded by a hybrid Monte-Carlo algorithm, and relaxed in a geometry optimization a dynamics run. The reactive groups of the pre-polymer are labelled as "reactive", to be addressed by the algorithm.

- Distances between reactive groups of HTPB are evaluated and groups, which are within a certain reaction distance (10 Angströms) are marked, and unique pairs to be cross-linked are identified.

- On the respective pairs, an additional spring force, much weaker than those of a chemical bond, is added to effectively draw the groups together in a next short geometry optimization run, by minimization of the spring forces. This serves as a preparation step to position already neighbouring groups in a fashion that allows for easy interconnection without tampering with the statistical distribution of conformation too much.



**Figure 3:** HTPB pre-polymers used, with linear and star-branched topology; reactive groups are located at the chain ends (left); Urethane repeat unit to by inserted between end groups (spheres marked with "X" are place holders for the urethane bond. (right,bottom); Isocyanide cross-linker (right, top).

- If the optimization managed to successfully draw the groups together, they are cross-linked chemically by deleting terminal hydrogens of the hydroxyl groups and introducing the urethane group. This step of pulling together groups may fail because a chain is in a highly stretched conformation already. In such a case, the procedure is terminated for the pair. Also, a random free cross-linker molecule in the system is deleted. The completely correct way from a statistical thermodynamic way would have been to define reactive centres not only on polymers, but also on the cross-linker, and then, during a dynamics run to , wait" for polymer ends to meet a cross-linker, and eventually another polymer end group. The reason behind this specific approach is that the diffusion coefficient of low-molecular compounds in polymer is much higher than those of specific groups within the polymer chains. Thus, the mutual approach of end groups happens on a much slower time scale than the diffusion of a cross-linker to an end group. Following from reptation theory of chain segments, the disentanglement time  $\tau$  scales as  $\tau \sim \zeta_R N_R^3$ , with the friction coefficient of reptation  $\zeta_R$  and chain length N<sub>R</sub>. Given a similar friction coefficient and same volume of a cross-linker molecule as a repeat unit of the polymer, the hypothetical ratio of  $\tau_{\text{eross-linker}}/\tau_{\text{polymer}}$  would be 1:125000 for HTPB of 50 repeat units. [13] Thus, the reaction speed is controlled by the diffusion of end groups only. This means, once an end-end close contact between chains is established for a time span, it is almost certain that the "fast" cross-linker molecule will diffuse in their vicinity Therefore, it is not necessary to simulate this diffusion process of the cross-linker explicitly. Also, this method also does not violate the thermodynamics of a reaction of ends with cross-linker in two consecutive steps.  $(R_1 + L \rightarrow R_1 - L, \text{ then } R_1 - L + R_2 \rightarrow R_1 - L - R_2)$ 

- The system is subjected to another geometry optimisation to relax the highly unfavourable conformation of the newly formed connection and the void of the deleted molecule elsewhere in the box.

- The previous steps are repeated until the system is depleted of close contacts. In this case a pseudodynamics run is performed: An ordinary molecular dynamics run, but the intermolecular interaction forces are gradually scaled to zero in a series of runs, while the intramolecular terms are kept. By this, polymers interpenetrate and move to new positions in a comparably short time span. Then, force terms are gradually restored. The resulting system is now in completely different, but thermodynamically accessible and realistic state of conformation. This procedure is analogous to a step in a Monte-Carlo simulation: A system is changed randomly and the probability of such a change is given by the energy difference of these stepwise random changes. Now with a new conformation at hand, the procedure of finding close contacts, etc. can begin anew until the reaction is complete: either the cross-linker or the end groups of the polymers are depleted.

Note that there exist procedures that pull together directly without any dynamics. This of course yields cross-linked systems quickly, but leads to immense and unrealistic internal stresses that cannot be resolved by relaxation algorithms. Also, the algorithm is designed to accept pre-polymers with correct chemical structure, meaning, that HTPB molecules feature OH terminal groups to be replaced by the respective urethane bonds during crosslinking. Another possibility would have been to use dummy atoms as placeholders to be replaced when linked. But, by using realistic end groups, properties of the system can also be extracted during the crosslinking procedure, even when the reaction is not finished yet.



Figure 4: Example of a filled box (left); change of bulk modulus vs. number of cross-links (right).

The result of this procedure is a cross-linked polymer over the crystalline surface. In 6 steps, the algorithm managed to create 17 out of 18 possible links. From each step the bulk modulus has been calculated and plotted against the number of cross-links in the system, as shown on the right hand side of Figure 4. At least for this box size, the bulk modulus rises linearly, as the system gets stiffer because of the introduced topological constraints. This result is in accordance with experimentally observed hardening from viscous melt to rubber state.

#### **Primitive Path**

To generate input structures for future coarse grained simulations, a called primitive path algorithm has been developed. The dynamics and viscoelastic behaviour of polymer melts, and also cross-linked chains is determined by their microscopic structure. Chains slide past each other, and form entanglements, which serve as topological constraints. [14] This is especially the case for long polymers with a chain length larger the mean length between entanglement points, and always the case for cross linked polymers. These effects can be explained by so called universal properties of the polymer, mainly the chain topology, regardless the chemical details. According to the Doi-Edwards theory [15], viscoelastic behaviour is based on the Kuhn-Length, i.e., the contour length of chain segments between to entanglement points. Between these points, the chain is can move freely in a tube-like confinement. While the tube represents a volume of space that can be explored by a chain without violating the topological constraints, the "primitive path" is the shortest path the chain could take without violating these constraints. One approach, amongst others, would be a purely geometric path analysis, without the use of energy expressions [16].

For this work, a procedure has been implemented in Materials Studio, in which backbone atoms and bonds are replaced by dummy types, while all other atoms are deleted. The ends of chains are held fixed in space, while the backbone contour is gradually shortened, by increasing the spring constant of bonds between dummy atoms. By this dynamic approach, no special care has to be taken for correct treatment of rings, branching centres, etc., as it is the case for geometric algorithms. This procedure corresponds roughly to a total length minimization. Figure 5 shows an example for the gradual straightening of segments. As periodic boundaries apply, each segment outside the box is folded back.

The higher the entanglement, the higher is the bulk modulus of the polymer, as the degree of entanglement rises linearly with cross-linking, with a total number of 8 entanglements in the nearly fully cross-linked case, in a volume of 30x30x40 Angström. The resulting structure of completely straight chain segments also serves as input parameters for coarse grained simulations in the future of this project, to yield the universal properties of the polymer.



Figure 5: From polymer backbones (left), over an intermediate structure (midde), to the primitive path (right).

#### **Pull-off simulation**

By direct simulation of a pull-off experiment of networks on crystalline surfaces, the elastic behaviour beyond the scope the bulk modulus is probed. The latter is yielded from elastic constants only, meaning from small elongations of the system around the equilibrium conformation, as described above, and in the framework of linear elasticity, with quadratic elastic potentials.

By pulling off the network, chains are stretched and in addition to the spring-like retaining force of stretched chemical bonds, the entropic contribution of elongated chain conformations as well as the slip movement of cross links is probed. Also, these pull off tests can probe the irreversible regime. At high elongations, the stretched chains keep their conformation for a time span equal to their diffusion time. In this work, different approaches have been tested:

- Addition of a vacuum slab within the box and definition of a set of atoms to pull apart, implementation of a constant pulling force. Then, in a dynamics run the system evolves accordingly, and the phases are pulled apart. Snapshots of such a simulation are shown in Figure 6 for AP with uncured HTPB: Voids form near the surface that are gradually enlarged, while the polymer chains are stretched A major drawback of this approach is that certain atom positions of the AP crystal have to be held positions fixed, and the pulling force has to act on certain, manually assigned chains explicitly. It may introduce a man-made bias to the system. Also, the additional pulling force greatly increases the total energy of the system at low elongations. This can be seen on the left graph of Figure 8. Here, the total potential energy of the system is plotted against the relative elongation of the polymer. Up to elongations of 0.2, the energy follows a quadratic fit. This means that pulling is energetically favourable, mainly from the contribution of the pulling (quadratic) spring force, and from the expansion of the HTPB in vacuum. After that, the potential energy shows the expected linear behaviour from chain disentanglements. Note that, as the polymer is uncured, some chains remain at the surface. Necking (lateral thinning of the polymer) is observed. Also, strain rates are extremely high compared to common experiments (order of billions /s).



Figure 6: Snapshots from a pull off simulation: AP/uncured HTPB with explicit atom sets to be driven apart by an external force.

- Another type of pulling to gradually increase the size of the simulation box, by simple scaling of the coordinates in small steps, as shown in Figure 7. This method has two advantages over the first one: There are no pull-atoms to be defined, as the system itself is stretched. The components then adapt to this anisotropic pressure acting on the system in total. This effectively pulls it apart, and cracks will form at the weakest spots. Also this allows for a stepwise pull-off: The system is elongated, and then, during a dynamics simulation of arbitrary length, it can relax to equilibrium under the constraint of the pulling pressure. Afterwards, the elongation is increased for a further step. By this, the strain rate determined by the length of the equilibration runs: If the system is equilibrated perfectly, the formal strain rate would be 0.



Figure 7: Snapshots of a pull-off simulation of the system AP/cured HTPB by stepwise increasing the boundary box length.

The potential energy difference vs. strain is given in Figure 8 (right). The quadratic contribution is completely absent, and the increase in energy is nearly linear. Still, the statistical error of this method is greatly increased.



Figure 8: Potential energy versus strain for two different algorithms.

Conclusions

A molecular dynamics simulation procedure for the generation of crystalline surfaces, generation of polymer networks, primitive path analysis, and pull-off dynamics have been presented, alongside preliminary results. The motivation is to address effects (non-linearity in forces, viscoelasticity) on larger time scales than those presently accessible by molecular dynamics.

In summary, it can be stated that generation of networks is possible and yields thermodynamically consistent structures. Mechanical resilience increases with progress of the crosslinking reaction, as expected from experiments and theory. Pull-off itself is also achieved, but highly biased by the type of scheme applied. Still, the functional form of the potential at high elongation features the theoretically accepted linear relation. A next step, after variation of input parameters, is to implement bond breaking criteria to simulate damage within the polymer itself. This will expand the range of accessible elongations beyond the entropic contribution of highly stretched chains.

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