Chemical Reactions in Classical Molecular Dynamics

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ABSTRACT An algorithm capable of incorporating multi-step reaction mechanisms into atomistic molecular dynamics (MD) simulations using traditional fixed valence force fields is proposed and implemented within the framework of LAMMPS (Large-scale Atomic Molecular Massively Parallel Simulator). This extension, referred to as *fix bond/react*, enables bonding topology modifications during a running MD simulation using pre- and post-reaction bonding templates to carry out a pre-specified reaction. Candidate reactants are first identified by interatomic separation, followed by the application of a generalized topology matching algorithm to confirm they match the pre-reaction template. This is followed by a topology conversion to match the post-reaction template and a dynamic relaxation to minimize high energy configurations. Two case studies, the condensation polymerization of nylon 6,6 and the formation of a highly-crosslinked epoxy, are simulated to demonstrate the robustness, stability, and speed of the algorithm. Improvements which could increase its utility are discussed.

INTRODUCTION: Carefully parameterized fixed valence force fields are capable of accurately and efficiently modeling the structure and properties of materials with a wide range of chemical compositions. While these force fields are extremely powerful for their intended use, they are not capable of modeling the types of reactive processes being addressed in the present work. The options for on-the-fly topology adjustments in the LAMMPS (Large-scale Atomic Molecular Massively Parallel Simulator) molecular dynamics (MD) software[1], for example, are currently limited to adding a single bond between two given atom types. Other popular molecular dynamics packages face similar limitations, if the ability to create bonds is included at all. In the absence of more advanced capabilities, it is impossible to model most chemical processes because all but the simplest reaction mechanisms involve concerted changes in two or more bonds. Researchers have worked around this problem in an *ad hoc* manner by creating scripts that periodically stop the simulation, apply a desired bond connectivity change, and then restart the simulation, often with an intervening energy minimization run to reduce highly stretched bonds.[2–6] This approach is often applied as an expedient method of creating large polymerized simulation cells while using computationally efficient force fields.[7,8] It has also been used to simulate highly crosslinked epoxies,[9] the formation of hydrogel networks,[10] and to analyze diffusive catalytic systems.[11]

Reactive force fields, such as the widely used ReaxFF, are an alternative approach that enable simulations of systems with dynamically changing bond topologies.[12] Because reactive force fields require potential energy expressions that are much more complex than fixed valence force fields, they are very difficult to parameterize accurately. They are also more computationally expensive, which dramatically limits the practical size and duration of the simulations that can be performed, relative to those done with fixed valence force fields.

This work presents a new approach, referred to as *fix bond/react* in the LAMMPS implementation, that incorporates the reaction process directly into a running molecular dynamics simulation. Each time the *fix bond/react* method is attempted, which occurs at a user defined interval, a generalized topology adjustment algorithm is used to identify groups of atoms matching a pre-reaction template and convert them to a post-reaction topology. Both templates are specified by the user. If successful, this step is followed by a short dynamic relaxation of each reaction to limit the large energy spikes that result from bonding changes. The implementation of this idea is designed to be generally applicable to the wide variety of MD force fields in use and adaptable to their differing treatment of certain potential energy components like improper dihedrals. It is hoped that incorporating this capability will enable novel applications of classical MD, including analysis of complex morphology changes as well as dynamic modeling of multi-step reaction mechanisms.

OVERVIEW OF THE ALGORITHM: *Fix bond/react* effects topology changes during a running simulation by matching sites in the simulation with user-supplied pre- and post-reaction topology templates, and a mapping between these two topologies. In LAMMPS, these pre- and post-reacted topologies are specified in ‘molecule template’ files. The molecule template files can contain a variety of changeable topology features (between the pre- and post-reaction states) including bonds, angles, dihedrals, impropers, and partial charges. In addition, the types of bond, angle, dihedral, impropers,and atom types can be updated. *Fix bond/react* also uses an atom-by-atom mapping between the pre- and post-reacted templates, which is supplied by the user in a ‘reaction map’ file. The topology matching algorithm, referred to as the *superimpose algorithm*, identifies local simulation topologies which are equivalent to the pre-reacted template, and designed to be adaptable to a variety of fixed valence force field styles. A schematic diagram of this process is shown in Figure 1, and a more detailed set of flow charts is provided in the Supporting Information.

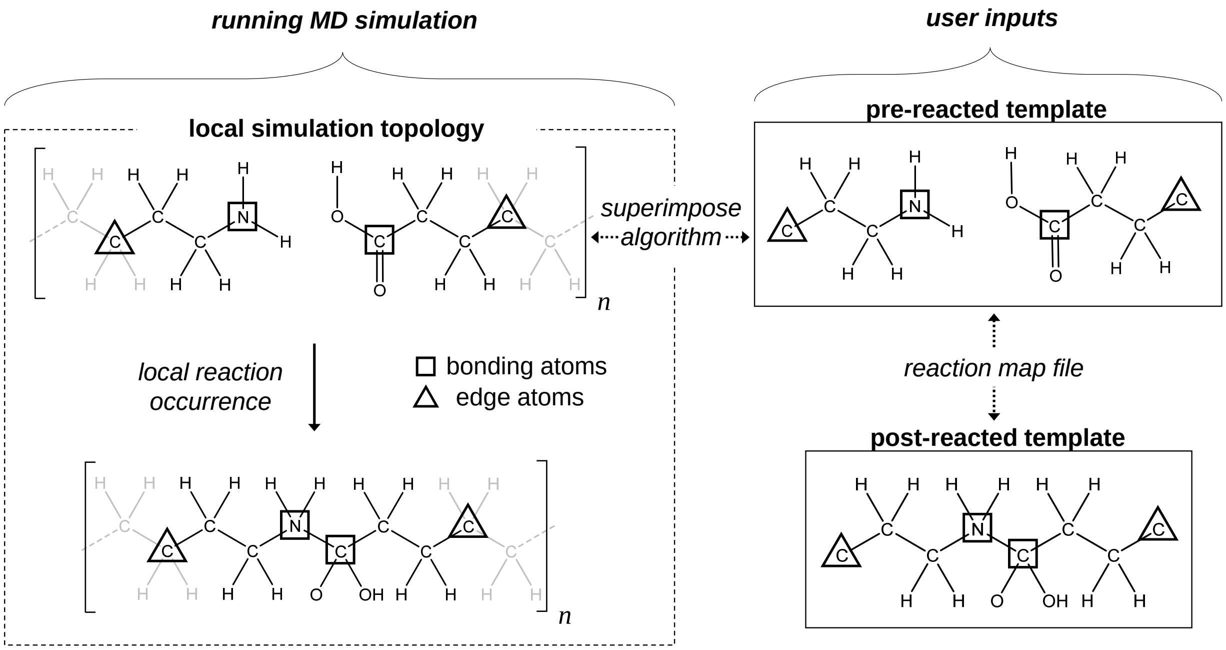

Figure 1: The *fix bond/react* procedure for incorporating a simple reaction step into classical molecular dynamics. The user-specified post-reacted topology is related, atom-by-atom, to the pre-reacted topology, which is mapped onto a local simulation topology by the superimpose algorithm. This local reaction site is then updated to reflect the post-reacted molecule template.

Once a reaction site is positively identified, all bond topology definitions and all atom, bond, angle, dihedral, and improper types in the pre-reaction template are changed to reflect the post-reacted template. Because topology changes often result in high energy configurations, a dynamic relaxation is performed on the reacted atoms during the MD run, as described below.

TEMPLATE MATCHING AND TOPOLOGY REASSIGNMENT: The process of effecting a reaction begins with the superimpose algorithm, which first searches the local simulation topology for groups of atoms corresponding to reaction sites, as defined in the pre-reacted template. Building from the existing *fix bond/create* command in LAMMPS, a reaction is triggered if two atoms of ‘bonding atom’ types are found within a user defined distance and a probability of reaction occurrence is met. The two bonding atoms are equated to two atoms in the pre-reacted template using information in the reaction map file. The superimpose algorithm then walks along the simulation bond topology, starting from these two bonding atoms, and compares connectivity and atom type with the pre-reacted template. A reaction site is positively identified when the superimpose algorithm has equated simulation atoms to each atom in the pre-reacted template. To maximize computational speed and parallel computing efficiency, pre-reacted templates should contain as few atoms as possible while ensuring that all atoms involved in the reaction remain fully defined. For example, if the force field being used includes dihedral angle terms, atoms more than three bonds from reacting atoms should be excluded.

Some reactions, such as the condensation polymerization of Nylon 6,6 reported below, result in a loss of atoms that makes it impossible to use the pre-reacted templates in ensuing sweeps of the superimpose algorithm. In the present implementation, the new terminal atoms are referred to as *edge atoms,* and the topology checks normally performed by the superimpose algorithm are skipped for the atoms no longer present. This approach works well for the reactions considered in this study, but modeling more complex chemistries may require an extension of the method to enable the use of intermediate template files.

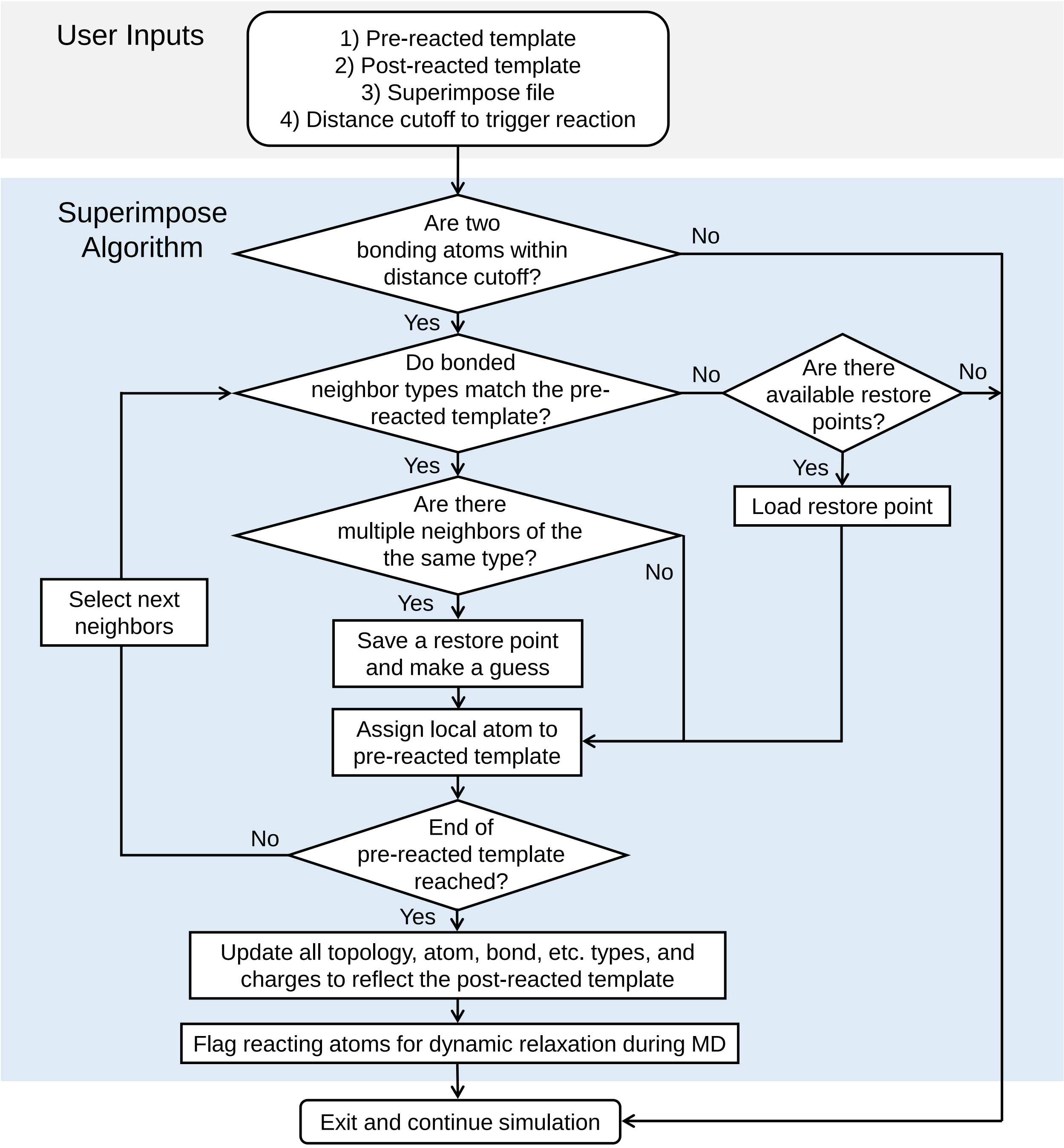

Figure 2: A flow chart illustrates the logic of *fix bond/react* at a conceptual level.

Figure 2 illustrates the iterative process used by the superimpose algorithm to match a local simulation reaction site topology with the pre-reacted template. The bonding atoms are the first atoms successfully assigned to the pre-reacted template. If the atom types and connectivity of all of their covalently-bonded first neighbors match the pre-reacted template, those neighbors are assigned to their counterpart in the pre-reacted template, and become the starting point for the next iteration. However, if an already assigned atom does not have the same connectivity as its counterpart in the pre-reacted template, the algorithm exits and no reaction occurs.

The superimpose algorithm becomes more complicated when an atom is bonded to two or more atoms of the same type. In this case, it stores the current state of the algorithm and simply makes a guess. If the topology of a subsequent atom does not match the template after making this guess, it returns to this restore point and takes the next branch. If none of the branches match the template, the algorithm returns to the simulation without modifying the topology. Otherwise, after all atoms in the pre-reacted template have been successfully matched with a simulation atom, the reaction proceeds.

Due to the large number of possible simulation topologies, careful construction was required to ensure the algorithm's robustness and broad applicability. Since there is no looping over nearby non-bonded atoms or numerical calculations involved, the superimpose algorithm remains quite fast, even for highly symmetric or cyclic molecules. This allows very complex local topologies to be matched on an atom-by-atom basis to a pre-reacted template. Ultimately, *fix bond/react* makes it possible for multistep reaction mechanisms to be treated in a running MD simulation, as demonstrated in the epoxy crosslinking case study below.

DYNAMIC RELAXATION OF REACTIONS: Performing bonding topology changes in simulations using traditional fixed valence force fields results in an instantaneous energy jump due to differences in the total potential energy and equilibrium configuration of the pre- and post-reacted structures. In addition, bonding topology changes can result in morphological changes in the system that are incompatible with physical constraints. For example, if a group of monomers in solution forms a bond across a periodic boundary to form a periodic chain, the newly formed bonds may be stretched or compressed due to incommensurability with the box length. These stability issues can be resolved by adjusting the duration of the post-reaction relaxation period, the probability of reaction occurrence, or the cutoff distance used to search for bonding partners.

Currently, *fix bond/react* makes use of the dynamic group feature in LAMMPS to relax high-energy interactions in the post-reaction configuration. After applying the topology changes, the modified atoms are temporarily added to a dynamic group that is time-integrated using the *fix nve/limit* command, which limits the distance an atom can move in a single time step. The atoms in the dynamic group interact with the rest of the atoms in the simulation in a normal fashion. After a specified number of time steps, the reacting atoms are placed back under the control of the system-wide thermostat and barostat specified by the user. In the case studies described below, adjusting the duration of this relaxation time was sufficient to produce stable simulations. This parameter is dependent on the system and reaction, and should be adjusted by the user to the minimum duration needed to provide numerical stability for a given system and reaction. No additional reactions that include the atoms in the dynamic group are initiated while the relaxation process is occurring.

LIMITATIONS: A few limitations of *fix bond/react* should be highlighted to prevent misapplication. First, it is only useful for reactions with known mechanisms or for examining the structure and properties of materials produced using one or more proposed mechanisms. Second, because the method is only intended to reproduce the end-result of a reaction, and not the detailed mechanism, some transient unphysical behavior is to be expected of the atoms being altered by the topology change. Other methods, such as quantum mechanical modeling, path-integral molecular dynamics, or reactive empirical potentials, are more appropriate for cases in which predicting reactivity or reaction mechanisms is the objective. Finally, the initiation of a given reaction is currently based on the proximity between two atom types, defined in the reaction templates, and a user-defined probability. A probability of one was used in both case studies presented in this work, meaning that all reactions meeting the initiation criteria occurred. As discussed later, more exacting criteria may be necessary for some systems.

CASE STUDIES: To illustrate the versatility of *fix bond/react*, it has been used to simulate the formation of both a linear thermoplastic, nylon 6,6, and a highly-crosslinked thermoset, an epoxy formed from diglycidyl ether of bisphenol A (DGEBA) and diethylenetriamine (DETA). In both cases, the Polymer Consistent Force Field (PCFF), a Class II force field which includes partial charges and improper dihedral angles, is used to demonstrate the ability of the algorithm to handle relatively complex potential energy functions.[13]

NYLON 6,6 SETUP: The polymerization of nylon 6,6 proceeds by a sequential linear condensation reaction of hexamethylenediamine and adipic acid. The accepted mechanism of this reaction[14] is shown in Figure 3, rendered using the Visual Molecular Dynamics graphics program.[15] The polycondensation reaction was modeled using two *fix bond/react* commands. The first *fix bond/react* creates a bond between a carbonyl carbon and a nitrogen when a pair is found within a cutoff distance of 3 Å, and is followed by a 30 ps dynamic relaxation of the newly formed intermediate state. A second *fix bond/react* creates a free water molecule (condensate) from the acid's hydroxyl group and a proton from the nearest secondary amine. Reaction processes resulting in the liberation of a small molecule, water in the present case, typically require longer relaxation runs. For this reaction, a 60 ps dynamic relaxation time was found to be sufficient.

The simulation begins with a periodic box filled with 100 monomers of each reactant at a density of 1.0 g/cm^3. This mixture is relaxed for 10 ps at 298K and 1 atmosphere of pressure prior to the initiation of the polymerization process. Five independent initial monomer melt simulation cells were created and each was run for 200 ps at constant volume and temperature using the Nosé-Hoover thermostat and a time step of 1 fs. During the simulation, the algorithm searched for potential reaction sites on every time step.

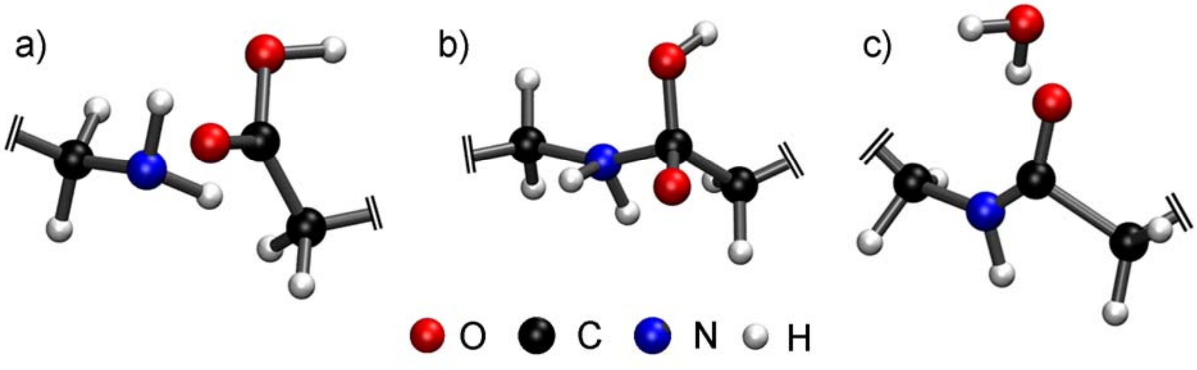

Figure 3: Polycondensation of nylon 6,6 during a running MD simulation. The transition structure (b), was dynamically relaxed after the reaction for 30 ps. Steps which involve small molecule creation (c) often require longer dynamic relaxations. In this case, 60 ps was used.

NYLON 6,6 RESULTS: One of the key metrics of success for this method is its ability to maximize the conversion of monomers into polymer. Four out of the five nylon simulations achieved 98% conversion during a 200 ps simulation run, and over 99% conversion was obtained in the fifth case. Inspection of the structure produced in the latter simulation revealed that the higher conversion was due to the formation of a single chain, consisting of 95% of the monomers, as well as three small loops of 2-4 monomers each.

An example of a final polymerized system is shown in Figure 4. This figure highlights two notable structures that are not typically produced by traditional polymer building software: a small ring and a polymer chain that is continuous across the periodic boundary cell, making it effectively infinitely long. While the system sizes used to demonstrate the method in the present study are too small to assess statistical properties, the diversity of polymer sizes found in the final structures indicates that the method has the potential to reproduce chain length polydispersity, particularly if chain initiators and terminators were included. This is currently being investigated.

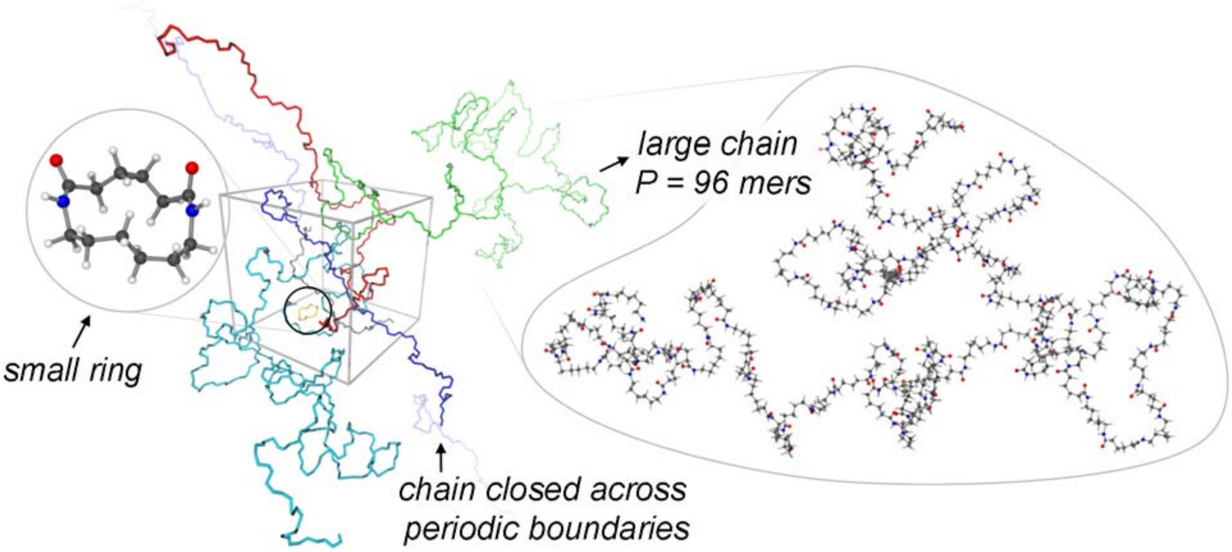

Figure 4: An example final polymerized system, after unwrapping the long chains from the periodic cell (only polymer backbone atoms are shown, colored by chain). A two-monomer ring and an infinite loop are labeled. Four large non-periodic chains were produced, one of which contained almost half the total monomers.

Although reproducing the microscopic kinetics of the polymerization reactions was not an objective of the current work, it is of interest to determine if the overall rate of monomer conversion follows experimentally expected trends. Based on his seminal work on the kinetics of step-growth polymerization, Flory found a linear relationship between 1/(1-*p*), where *p* is the extent of reaction, and reaction time.[16] Figure 5 shows that the simulations done using *fix bond/react* produce a qualitatively comparable linear relationship. This positive result indicates that the use of a short post-reaction equilibration period does not lead to a substantial deviation from the expected conversion rate. If this result is found to hold for other related reactions with similar mechanisms, it might be possible to use *fix bond/react* to address phenomena currently reserved for theory, such as the competition between cyclization and propagation in kinetically controlled step growth polymerizations.[17–19]

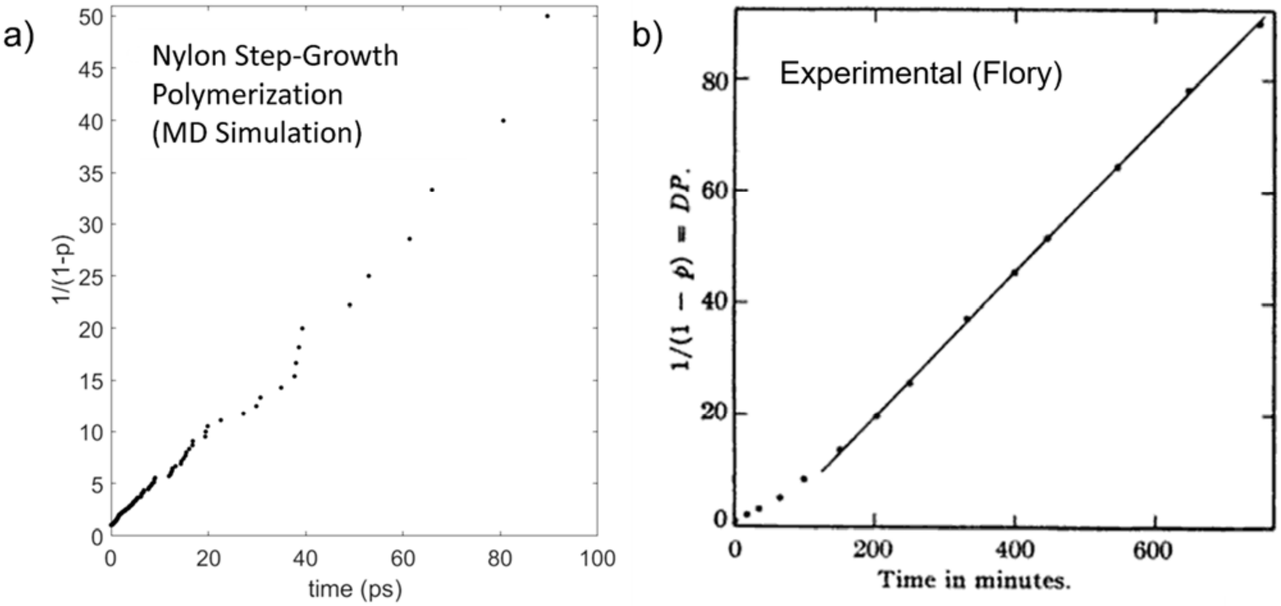

Figure 5: The dependence of extent of reaction, *p*, on reaction time for the step-growth polymerization of nylon 6,6. (a) Simulation results produced using *fix bond/react.* (b) Experimental results for a similar reaction, polyesterification of adipic acid with ethylene glycol

at 439 K. *(Panel (b) adapted with permission from Reference (14). Copyright 1939 American Chemical Society.)*

While the existence of undesired reaction byproducts is typically neglected in MD simulations of polymers, these impurities are a significant concern in polymer manufacturing due to their impact on material structure and properties. The present method makes it easy to incorporate the effect of these species because they naturally emerge from the simulation process. Figure 6, for example, highlights the water molecules produced during the nylon polycondensation reaction. Formed from hydroxyl groups which are initially uniformly distributed, the water molecules are found to aggregate into clusters over the course of the simulation. Although not explored in the present work, the effect of these clusters on the polymerization reaction could be studied by removing the water molecules as they are produced in order to mimic evaporation. This ability to control the concentration of reaction byproducts or solvent molecules during a running MD simulation of a multi-phase system could yield interesting new insights into the polymerization process.

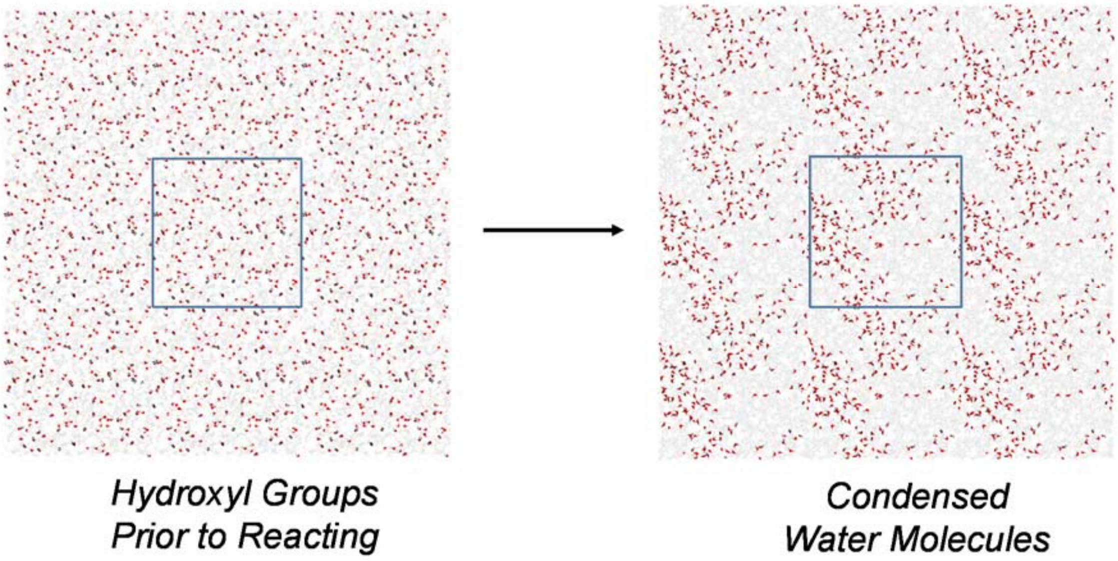

Figure 6: The dynamic creation and aggregation of reaction products, such as condensed water during nylon polycondensation, can provide insight into physical mechanisms and kinetics. Several periodic images are shown; the actual simulation box is denoted by the blue square.

EPOXY SETUP: Having demonstrated the capability of *fix bond/react* for a linear polymerization, we next applied it to a more challenging case, the formation of a highly-crosslinked epoxy from diglycidyl ether of bisphenol A (DGEBA) and diethylenetriamine (DETA). Figure 7 illustrates the two reaction steps involved in the bond formation process using snapshots taken from a running simulation. Following a similar protocol to the nylon example, each linking reaction was divided into two *fix bond/react* steps. The first step of each reaction is a ring-opening process in which a primary amine nitrogen attacks an epoxide group within a predefined cutoff of 3.5 Å. In the second step, the transient quaternary amine is deprotonated by the oxygen group of the ring-opened epoxide, within a cutoff distance of 5 Å, to yield the final tertiary amine and hydroxyl groups. A dynamic relaxation of 30 ps was used after each step.

Five independently generated simulation cells containing a mixture of 100 DGEBA and 50 DETA molecules, matching the 2:1 stoichiometry of this reaction, were created at a system density of 1 g/cm^3. Prior to initiating the *fix bond/react* simulations, each cell was relaxed for 10 ps at constant volume and temperature using the Nosé-Hoover thermostat and 1 fs time steps. To increase the monomer mobility, and therefore the rate of network formation, the epoxy simulations were conducted at 800 K. This emulates the elevated temperature curing process that is frequently used with epoxies, albeit at a much higher temperature. After an initial reactive run of 200 ps, the systems were run for another 200 ps at constant temperature and pressure without reactions, followed by a second 200 ps reactive run using the same conditions as the first. The intervening 200 ps non-reactive equilibration was inserted to allow the periodic cell dimensions to adjust to the partially reacted epoxy system and to allow redistribution of unreacted monomers.

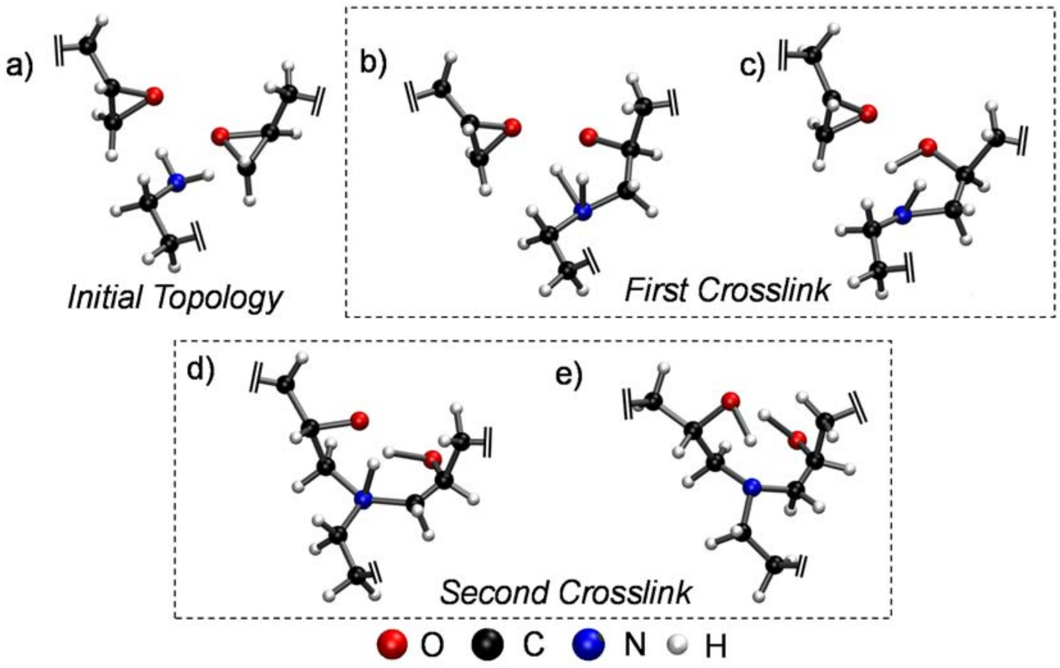

Figure 7: Bond formation mechanism of one difunctional end of a DETA amine to two DGEBA epoxide groups. All three molecules need not initially be close to each other as depicted in (a). The second reaction step (d-e) could occur long after the first reaction step (b-c).

EPOXY RESULTS: After the first 200 ps reactive run, the 5 epoxy simulations reached an average extent of reaction of 94%. By the end of the second 200 ps reactive run, the systems reached an averaged extent of reaction of 96% and all systems were within the interval of 95.0-97.5%. The extent of reaction achieved with this method is 2-5 times greater than what is typically reached with *ad hoc* scripts using a comparable cutoff distance of 3.5-5 Å.[20] This dramatic improvement in monomer conversion is a result of the ability to search for potential bonding partners at every time step, due to the limited computational demands of the superimpose algorithm. Previous methods for generating crosslinked polymer simulation cells typically resorted to using much larger bond search cutoff distances to achieve reasonably high levels of bond formation. That approach has the unfortunate side effect of producing unphysically long bonds and, as a result, large internal stresses. In some cases, these long bonds can result in ring-spearing or bond formation through a filler particle in a composite simulation.

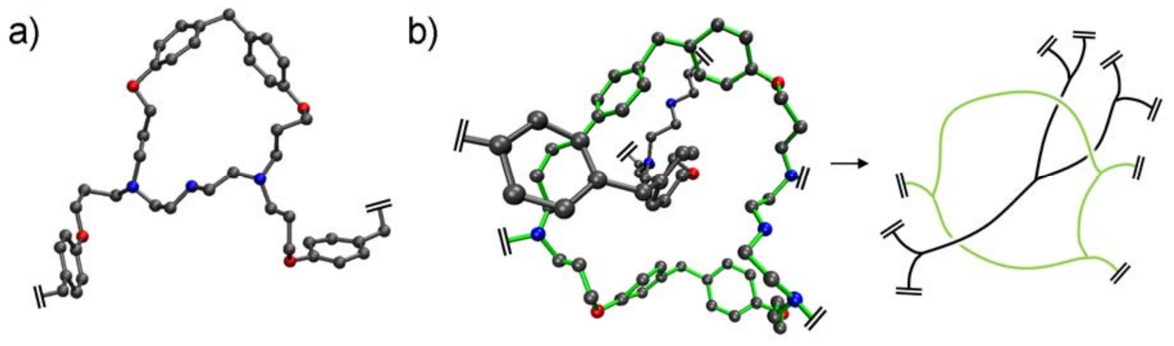

Figure 8: Several interesting topologies were observed to form during the epoxy case studies. (a) The formation of small loops between DGEBA and DETA may be detrimental to mechanical properties. (b) Part of the matrix is seen passing through a large loop highlighted in green. Hash marks indicate connectivity with the rest of the matrix, and only backbone atoms are shown for clarity.

The formation of elastically inactive loops, illustrated in Figure 8(a), during epoxy resin formation is detrimental to stiffness and strength. Although this kind of loop formation is to be expected when using short aliphatic amines, in general it is important to consider interference from cyclization when designing any new epoxy system.[21] *Fix bond/react* can be used to screen systems for the tendency to form kinetically-generated, elastically inactive loops. It may also be useful in clarifying the role of larger epoxy cycles. For example, the next largest loop, composed of four monomers, was observed to be topologically constrained by another part of the matrix passing through its center (Figure 8b). This observation of topological interlocking implies that some cycles of this size may not be as detrimental to mechanical properties as is typically assumed in theoretical and experimental studies.[22]

SUMMARY AND OUTLOOK: *Fix bond/react* enables complex topology modifications to occur in running molecular dynamics simulations that use fixed-valence force fields. The usefulness of the method was demonstrated by creating two different polymer structures: a linear thermoplastic and a highly-crosslinked epoxy. Work is currently underway to expand these simulations to much larger simulation cells, which will demonstrate the scalability of the method and permit a much more detailed statistical characterization of the resulting structures. One can easily imagine many other interesting applications to which it could be applied: diffusive catalytic systems, highly crosslinked networks such as hydrogels, other epoxies, and the carbonization of polyacrylonitrile or pitch fiber, to mention just a few.

There are several features that could be added in the future to increase the predictive power and usefulness of *fix bond/react*. First, expanding the current list of criteria for triggering a reaction should be explored. These new criteria could include the proximity of three or more atoms or the relative velocities of bonding atoms. Global rate laws could also be imposed in accordance with known processes. Secondly, the development of a specialized thermostat for reacting classical force field simulations could yield more physically correct behavior of atoms at all times and better address the energy spikes that result from the instantaneous changes of bond topology and atom type. This thermostat could, for example, adjust the velocities of the reacting atoms to ensure conservation of energy, which is not the case in the present implementation. Finally, it would be useful to be able to simulate bond dissociation reactions by reversing the pre- and post-reacted topologies. This would open the door for consideration of resonance structures and equilibrium reactions, as well as mechanically-induced bond breaking during a simulation.

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