

TRIBOLOGICAL AND MECHANICAL BEHAVIOR OF METALS AND POLYMERS SIMULATED BY MOLECULAR DYNAMICS

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ABSTRACT

Molecular dynamics computer simulations provide experimentally inaccessible insights into behavior of materials. The insights facilitate development of materials with improved properties, but at the same time are quite useful in instruction. We describe recent applications of the molecular dynamics technique in simulations of mechanical behavior of metals and polymeric materials and also of tribological behavior of polymers. Simulation results in the form of computer animations can be used as a powerful teaching tool to complement traditional instruction methods.

1. INTRODUCTION

The key advantage of computer simulations of materials is the fact that they provide us with information that cannot be obtained experimentally. Fossey has discussed this situation eloquently in a detailed review¹. At the same time, simulations have a significant instructional value. The instructor and the student can observe phenomena and processes as they happen – particularly so when the results are treated graphically in the form of computer animations. Therefore, in the present article we discuss various kinds of information available from computer simulations of materials and some ways to make use of this information in instruction.

There are two main types of computer simulation that can be applied to materials: Monte Carlo (MC) and molecular dynamics (MD). The MC method has an interesting history. It was originally thought of as a mathematical way of winning at the casino game of roulette by a group of mathematicians associated with the University and the Politechnika in what is now Lviv, Ukraine. In the late 1930's this group, which included Stanislaw Ulam², met frequently at the Scottish Cafe and attempted several methods to solve the casino problem - as well as other problems. Dan Mauldin has published a Scottish Cafe book which contains their problems – solved as well as those which still await solution³. While the Casino in Monte Carlo is still safe from

bankruptcy brought about by mathematicians, the Cafe discussions gave Ulam the idea for the computer simulation method. Working at Los Alamos during World War II, Ulam realized that his method might have a potential military value to Hitler and his helpers, and the Los Alamos National Laboratory did not encourage publications by its employees anyway. As a consequence, the Monte Carlo method was only published by Metropolis and Ulam as a problem-solving procedure in science in 1949⁴. To get a better perspective we also need to note that ENIAC, the first computer in the world, was constructed at the University of Pennsylvania in Philadelphia in 1943; it had thousands of vacuum tubes and was very slow. We realize now that Ulam had foreseen the future of computers and how much we shall be able to get out of them.

MC relies on making one step at a time, and taking stock of the situation after a certain number of these steps. To apply MC to materials, we create a system consisting of N particles, such as polymer segments (or atoms, or monoatomic molecules, or ions). One can construct a $6N$ -dimensional phase space, since each particle has three coordinates of position (for instance the Cartesian ones) plus three coordinates of momentum. One calculates the equilibrium properties of a system by averaging over a large number of states of the system, each state created by the MC procedure. For instance, one can determine experimentally the average radius of gyration $\langle R_g \rangle$ of a polymer. MC gives us two ways of obtaining $\langle R_g \rangle$. We can either obtain a large number of chains and perform averaging over them, or we can create just one chain, perform several thousand MC steps, and average over all these states of a single chain. We know from statistical mechanics that the resulting $\langle R_g \rangle$ should be the same. The equivalence between averages over ensembles and averages over time is an intrinsic property of all ergodic systems. Because of its nature, MC is well suited for the evaluation of equilibrium properties.

Janszen *et al.*⁵ have reported on an interesting use of MC simulations to investigate the size

and shape of polymers. Their work provides a very detailed description of the elongated bimodal shape of a Gaussian chain.

MD was developed by Berni J. Alder and collaborators at the Lawrence Livermore Laboratory; the first paper authored by Alder and Wainwright was published in 1957⁶. In this method we also consider a system of N particles; at a given time each particle is at a specified location with a specified velocity (or momentum). In contrast to MC in which one particle moves at a time, here all particles are moved at once at each time step. After all particles have been moved, the forces acting on the particles are re-calculated for the next step. The force, determined from potentials which describe the interactions between particles in the system, is the main variable influencing the new positions where the particles will be moved to in the next time step. Since in MD time is an explicit variable, the method can be used to simulate not only equilibrium properties but also time dependent ones. This is particularly important for the viscoelastic materials with which we are dealing; MD gives us the capability to investigate processes such as diffusion, flow and fracture. This is a powerful feature since the motions of polymer chains constitute the key to understanding their properties.

Another method for computer simulation of polymers is the kinetic model of fracture, used by Termonia and Smith to simulate the mechanical behavior of polymers⁷. In this method, various structural elements are connected in a two- or three-dimensional lattice. The elements, which can be crystallites, elastic rubbery chains, or crystal/amorphous interphases, interact with each other according to the properties of each element. Primary and secondary bonds in the system follow different behaviors. Primary bonds break when they have been excited beyond their activation energy. Local stress may decrease the activation energy. Secondary bonds fail by slippage, which is defined by their shear modulus. The method consists of applying a certain value of strain at the boundaries of the system and then allowing

the system to relax until the forces on a specified element are at equilibrium. After relaxation occurs throughout the material, the method simulates broken bonds by randomly picking a bond and breaking it following a law of probabilities based on the rate of bond breakage. After this stage, a new simulation step starts with the material again being subjected to a small strain applied at the boundaries. The process is repeated until fracture of the material occurs. Termonia⁸ applied this method to the simulation of spider silk fibers, tackling an interesting problem: why the *spider dragline silk* structure exhibits a combination of such high mechanical strength, stiffness and elongation at break. He was able to study effects such as the crystallite size influence on the properties.

Our simulation code was developed to study molecular-level phenomena in materials. We have investigated metals⁹ and, in more detail, polymers. Simulation results give pertinent information about the behavior of these materials and provide some insight on how to improve their mechanical properties. From simulations of tensile deformation we found the most probable *loci* for crack initiation in polymer liquid crystals (PLCs) and the mechanisms of crack propagation¹⁰. We have also developed scratching simulations that tell us which structures are most resistant to scratch¹¹.

In order to analyze the simulation results we have developed three-dimensional (3D) computer graphical tools. This type of graphical representation of polymeric systems is still practically nonexistent; however, its uses and advantages are obvious. A particularly interesting possibility of OpenGL graphic programming is its use as an instructional tool. It simplifies teaching a variety of topics, such as the structure of two-phase polymers, the step-wise polymerization process and the arrangement in three-dimensions (3D) of coiled polymeric chains, as shown in Figure 1. 3D graphics can be particularly useful for cases involving dynamic phenomena. The same method we used can be employed to represent

the structure of metals, ceramics or any other materials.

We have created computer animations illustrating several of the topics mentioned above and included them on our web page <http://www.unt.edu/LAPOM> under "Resources for Education". They can be downloaded freely and used as a teaching aid. However, since the original focus of this project was research, we have only created a small number of animations to show the capabilities of this method. Any lecturers interested in developing their own code to create this type of OpenGL 3D representation should consult References 12-14. Coding one's own three-dimensional graphical software requires a significant time investment; however, as in our case, one is usually unable to find adequate commercial 3D graphics software focusing on teaching in a particular field or allowing sufficient flexibility to be modified for particular needs. Obviously, many topics and phenomena have already been included in different commercially available 3D graphics software. Some investigation on what is already available should be conducted before deciding to code new software for teaching a particular topic.

2. SIMULATION METHOD

For performing the simulations we use the MD method, already defined in Section 1. The reasons for choosing this method have been stated before^{10, 15}. In the simulation of stress relaxation in metals, the system is initially equilibrated without an external stress applied. This step is fundamental to ensure that the configuration of the system, initially created on the triangular lattice, is adequate for the *off-lattice* MD simulation. In the simulation of metals, the pairwise interactions are described by a single Mie 6-12 potential⁹. A strain such as 10 % is applied along one direction of the sample and an external stress is found such that the strain remains at a constant value. The internal stress in the direction of strain application is then reported as the stress on the material.

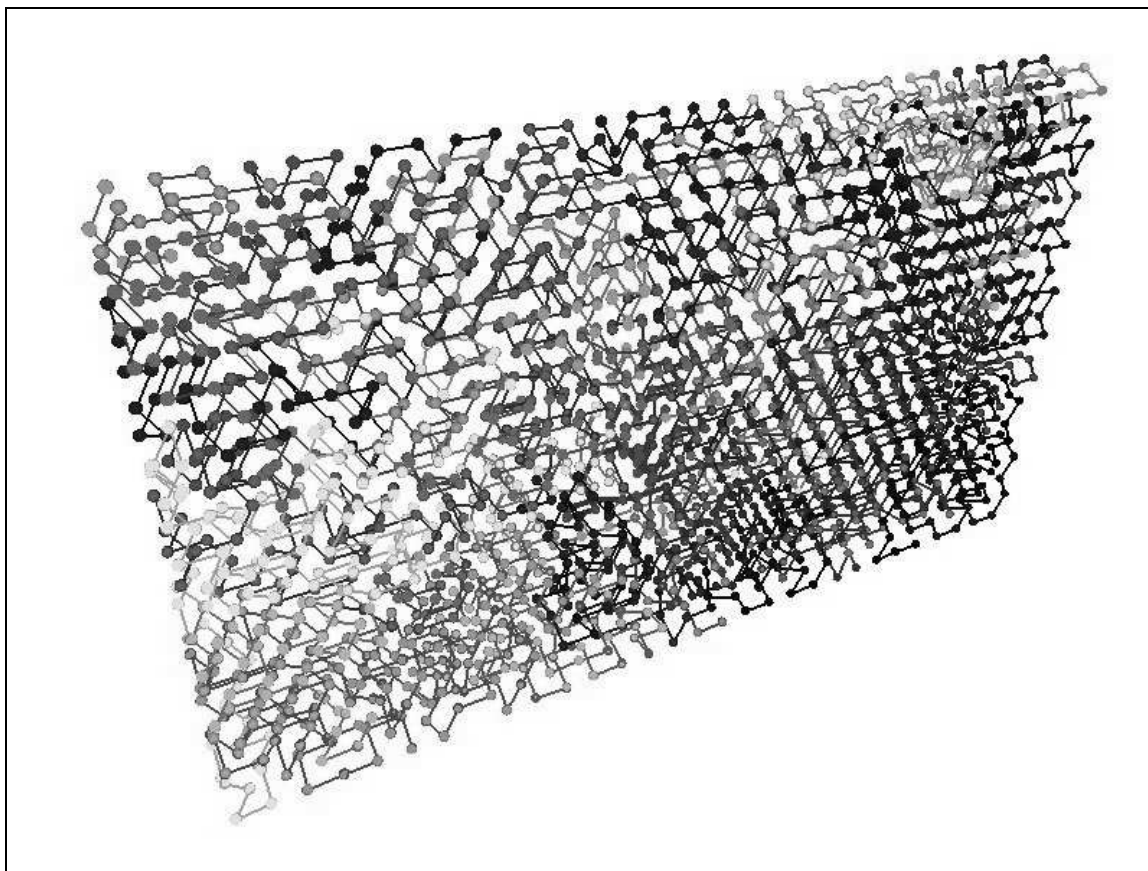


Figure 1. The 3D coiled chain structure of a polymer. Each chain is shown in a different shade of gray for ease of visualization.

In simulations of tensile deformation in polymers we also begin with the equilibration step without external stress applied. However, in polymers we have two types of pairwise interactions: primary interactions (chemical bonds) between segments inside a chain and weak secondary interactions (van der Waals or dispersive forces) between segments in different chains. Tensile force is applied on both sides of the material along a certain direction and the resulting deformation is measured. The force can be kept constant or varied over time. The simulation continues until fracture is observed, although the definition of fracture in computer simulations can be arguable: it may be defined as the point when there are a significant number of bonds breaking throughout the material, when there is physical separation between at least two parts of the material, or by considering other criteria.

The simulation of the scratching phenomena follows a very similar method to tensile deformation simulations. However, in this case, the force is applied perpendicularly to a surface of the material and the resulting local deformation is measured. To prevent the material from simply being displaced in space, the opposite surface is kept at fixed positions, as is a sample standing on a bench or in a specimen holder. As before, the force can be controlled during the simulation.

Together with the program used for performing the simulations, creation of the material on a computer is one of the most important components of the procedure. Creation of metallic structures on a computer is quite simple; one can use a triangular lattice with all sites occupied and then, if desired, introduce defects on the structure. However, creating

polymeric structures is more complex. Polymers have many chains with varying length, orientation, and composition. The results will be partially determined by how accurately the computer-generated material mimics features of the real material. Thus, a significant amount of effort must be spent on trying to create *realistic* materials on the computer¹⁶.

Our polymeric materials consist of self-avoiding chains, each with a different number of segments due to the random nature of the generation method. Besides pairwise interactions between the segments, the materials can also contain physical entanglements between chains. We create both one and two-phase materials. In the latter case, the chains are initially created on the flexible matrix and then the second phase is added in the form of islands – similar to the structure of polymer liquid crystals (PLCs) as found experimentally in Ref. 17. The two-phase materials allow us to study the effects of the second phase concentration and its distribution. Details of the material generation procedure were previously reported^{10,16}.

A different approach to the generation of polymeric chains was developed by Theodorou and Suter^{18, 19} for the structures of glassy polymers. They have proposed a method for the generation of a material on the computer based on the rotational isomeric state (RIS) theory as espoused by Flory²⁰. After an initial guess of the chain conformation, the system is brought to a low energy state at or near the minimal potential energy.

Fossey and Tripathy²¹ have provided an improved way of modeling spider silk elasticity. They have combined the method of Theodorou and Suter to form a polypeptide glass and Termonia's three-phase system model of the spider silk elasticity⁸.

Non-atomistic methods also exist, such as the use of fracture mechanics for the study of crack formation and propagation phenomena as well as calculation of stress intensity factors in

materials. Binienda and coworkers²²⁻²⁴ have been using this method for the analysis of interfacial and interactive cracks.

3. THREE-DIMENSIONAL VISUALIZATION

One important issue related to computer simulations is the large amount of information produced in every simulation. Moreover, the results are usually produced in the form of cryptic text files, which cannot be interpreted in their raw format. Thus, we have developed graphical tools to help us in interpreting results from simulations.

We use OpenGL programming in Microsoft Visual C++ in a Microsoft Windows environment. The choice over other systems was based on the number of users and the accessibility of a computer running Windows for any student. OpenGL is a programming interface which allows full three-dimensional (3D) representation. Using OpenGL we can draw 3D objects in a virtual world, represent them on the screen and control them in real time.

In order to represent our polymeric systems of many chains, each consisting of a certain number of segments, we have decided to use spheres for the segments and lines for the primary bonds between segments. Using this simple representation we can adequately show the chain structure and bonding. For two-phase materials we use different colors for each phase. An example of a two-phase computer-generated material is shown in Figure 2.

Our coding algorithm is quite simple, and can be mimicked for the representation of many other types of materials. Our simulations create result files containing information about the number of chains in the system, number of segments in each chain, the type of each segment (rigid or flexible in the case of PLCs), and the Cartesian coordinates of every segment in the system at every time step. Then, for the 3D representation we read from those files and draw the segments and the intra-chain bonds.

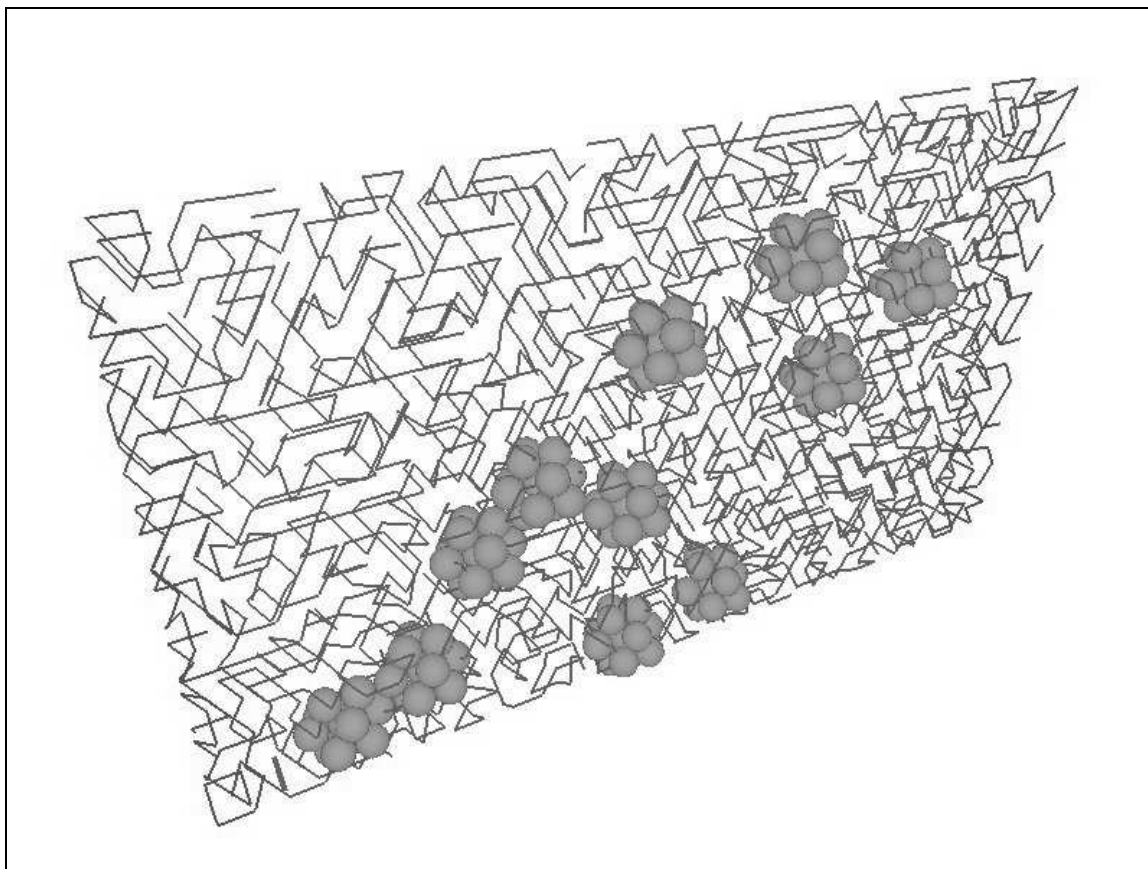


Figure 2. Two-phase computer-generated material. The rigid phase is present in the form of quasi-spherical islands, forming a similar structure to that of a polymer liquid crystal (PLC). The chains in the material are represented by lines, with rigid segments being represented as spheres. Overall LC phase concentration is 21 %.

One of the main advantages of OpenGL is that it allows us to represent each chain in a different color, to show or hide different chains, to change the size of the spheres, and to move or rotate the structure on the screen, all this in real time with simple commands.

There are many advantages in using colorful 3D representation for education²⁵; on one hand, students are receptive to such visual techniques. At the same time, many phenomena cannot be easily understood from two-dimensional figures. In fact, trying to explain 3D phenomena based on 2D representation can lead to erroneous concepts being acquired by the student.

4. ANIMATION

In order to represent the evolution of the simulation along time, a different file is created for each time step. Thus, by reading from sequential result files, we can update the information being represented on screen, creating an animation. Snapshots from an animation are shown in Figure 3.

The possibilities of this method of representation are broad, starting from the generation of the materials, which can be used to teach about polymerization - in this case the step-wise polymerization process. The coiled structure of polymeric chains can also be more

easily understood from 3D representation, as well as structures with high degree of orientation. Using this type of graphical representation, it also becomes quite simple to teach about physical entanglements between chains. Moreover, one can see how the molecular weight and conformation of the chains influences the number of entanglements.

Some of the animations we made available show the structure of polymeric materials, others represent molecular phenomena, and others are more related to the mechanical and tribological properties of these materials. They can be found at <http://www.unt.edu/LAPOM/resources.html> or by following the “Resources for Education” link from our main page <http://www.unt.edu/LAPOM> on the menu to the right. On this web page we included animations of the following:

- The triangular lattice used to build the polymeric materials on the computer.
- The structure of highly oriented PLCs consisting only of chains aligned with the direction of force application. We know PLCs can be highly oriented by the use of magnetic fields^{26, 27} and that the level of orientation will affect their mechanical properties.
- The structure of coiled polymer chains. This is a common representation of a polymeric system, where there is no preferential direction of growth of the chains during polymerization. Here we can also see a distribution of molecular weight of the chains.
- Entanglements between chains. These affect the mechanical properties and the behavior of the material during deformation, as reported by Solovyov and Goldman²⁸. The number of entanglements is dependent on the molecular weight of the chains, as well as on their orientation. This animation shows also how some chains are highly oriented in the material and others are coiled around themselves, depending on the random nature of the generation/polymer-ization process.

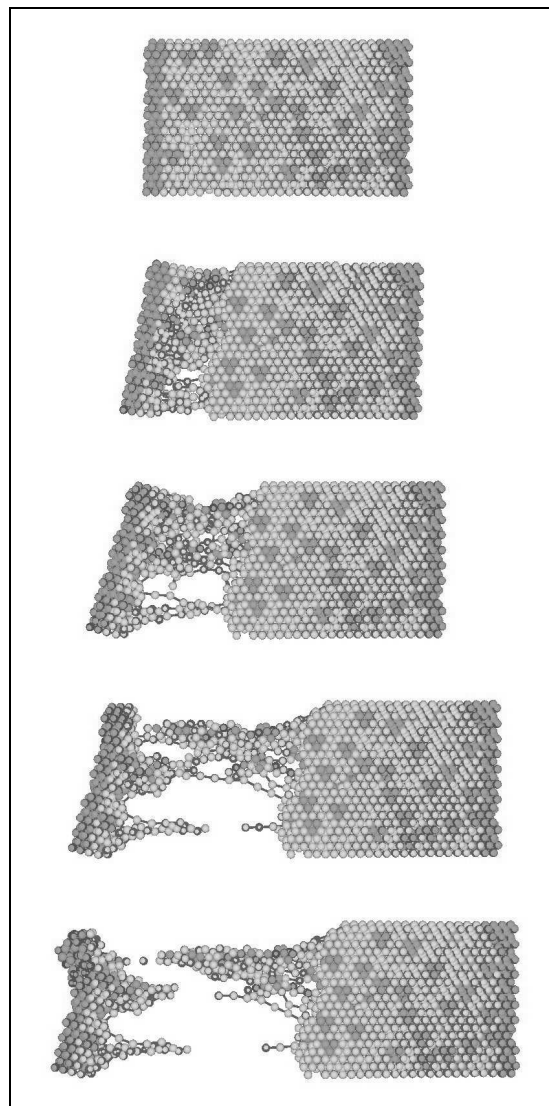


Figure 3. Snapshots taken from a simulation of the cracking phenomena in PLCs under uniaxial tensile deformation. Rigid segments are represented as dark spheres and flexible segments as light spheres.

- Step-wise polymerization. We created both two-dimensional (2D) and 3D representations of chain growth during polymerization. In the 2D material the growth of the chains is easier to follow; however, in such materials we cannot have entanglements between chains.
- Crack formation and propagation in PLCs. We used here a 2D material of oriented chains for ease of visualization. In a complex structure in 3D, pinpointing of crack initiation *loci* and following the cracks growing is very

difficult, mainly due to the fact that most phenomena occur internally and the rest of the material blocks them from view.

- The Poisson effect during deformation of polymers. It is expected during deformation of a polymer that as the length of the material increases in the direction of force application, the cross-sectional area perpendicular to that direction will decrease. This is related to the Poisson parameter of the material.
- Several deformation mechanisms at the molecular level. We use different materials to represent the principles of chain separation, chain scission and chemical bond rupture at fracture.
- Geometry of specimens used both in experimental testing and simulations. We have created materials on the computer with geometry similar to tensile testing specimens. This results in the computer-generated material failing in the region of smaller cross-sectional area - as we would expect from experiments.
- Scratch testing. Here we show how we perform simulations of scratching, by moving an indenter along the surface of the material, similar to the way experimental scratch testing is conducted.
- Scratch resistance and recovery. A plot of the surface changing over time as the indenter performs the scratch test shows us how each segment on the material offers a different resistance to scratching, and how each recovers over time, displaying a viscoelastic behavior. The final topography of the surface represents the permanent deformation and allows us to measure scratch recovery. Experimental aspects of scratch resistance determination have been discussed before in this Journal²⁷.
- Development of true stress during tensile deformation of polymers. Although the common procedure when determining experimentally the mechanical properties of polymers is to measure only the engineering

stress, it is possible on the computer to follow the evolution of the true stress, which depends on the actual minimum cross-sectional area along the material.

Obviously, these animations are simply a demonstration of how OpenGL 3D graphical representation can be used as an educational tool. Computer graphics and animations can be used to represent nearly any physical system or phenomenon, and most can be represented using simple coding, following a method similar to ours.

The topic of molecular dynamics simulations has been approached by several authors of instructional packages, including by means of multimedia representation. Some of these instructional packages are commercially available on CD-ROM^{29, 30, 31}. However, those authors have not dealt with the phenomena of large scale deformation in polymers leading to fracture, which is a key aspect of our work.

5. CONCLUDING REMARKS

Computer simulations not only provide us with information about the molecular behavior and properties of polymers but can also be used as an educational tool. Results from simulations in the form of 3D animations help in teaching about complex structures and phenomena. However, obtaining such animations might not be easy for particular topics. In those cases, the lecturer can develop a relatively simple graphics program, using a method similar to ours. Once the code is created, adapting it for teaching different topics requires a much smaller effort.

The animations we have created can be used as a teaching aid for polymer-related topics; however, they cover only a limited and fairly basic overview of structures and properties of polymers. We plan on expanding the animations to cover a wider range of topics and encourage anyone with interest in 3D graphical teaching methods to follow a similar route.

ACKNOWLEDGEMENTS

Parts of our work discussed above have been supported by the Robert A. Welch Foundation, Houston, TX (Grant # B-1203), and by the Fundação para a Ciência e a Tecnologia, 3^o Quadro Comunitário de Apoio, Lisbon. Helpful reviews from Dr. Yves Termonia, E.I. du Pont de Nemours & Co., Wilmington, DE, and Dr. Stephen A. Fossey, US Army Natick Soldier Center, Natick, MA, are appreciated. We also acknowledge the work of our undergraduate student J. Adam Hinze on the tribology simulations.

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