

# Accelerated Dynamics Simulations of Nanotubes

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## ABSTRACT

We report on the application of accelerated dynamics techniques to the study of carbon nanotubes. We have used the parallel replica method and temperature accelerated dynamics simulations are currently in progress. In the parallel replica study, we have stretched tubes at a rate significantly lower than that used in previous studies. In these preliminary results, we find that there are qualitative differences in the rupture of the nanotubes at different temperatures. We plan on extending this investigation to include nanotubes of various chiralities. We also plan on exploring unique geometries of nanotubes.

**Keywords:** carbon nanotubes, AIREBO, accelerated dynamics, TAD, parallel replica dynamics

## INTRODUCTION

Since its discovery in 1991 by Iijima [1], the nanotube form of carbon has been the subject of intense research. This interest is due to the novel properties of nanotubes, including their extremely high tensile strength and unique electronic characteristics. As researchers gain a greater understanding of these properties, nanotubes will be used in more extensive and varied applications. An important research tool in illuminating the properties of nanotubes is molecular dynamics simulation, a tool which allows the study of the atomistic motion of the tubes versus time.

A large stumbling block in the simulation of systems such as nanotubes is the time scale problem. To understand many systems, the kinetics governing the behavior of the system must be followed for long times. Often, these long simulations are characterized by relatively uninteresting thermal vibrations confined to a local energy basin punctuated by rare, but extremely important, thermal events which take the system from one basin to another. These rare events govern the time evolution of the system, and are the events of interest, but, for many systems, they are so rare as to be practically non-existent during the simulation time achievable using molecular dynamics on today's computers.

One approach to solving this time scale problem is to apply one of the recently developed accelerated dy-

namics techniques. The idea behind these methods is to accelerate the sampling of phase space in some way: either by running several concurrent simulations that each independently examine the phase space of a given energy basin (parallel replica)[2]; by increasing the temperature, forcing the system to explore higher energy regions faster, but in such a way as to follow the correct dynamics at the lower temperature of interest (temperature accelerated dynamics) [3]; or by "filling in" regions of low energy so that the system is not trapped by them (hyperdynamics) [4].

In this work, we apply two such accelerated dynamics techniques to the study of carbon nanotubes. Parallel replica simulations have already been conducted and are reported in this paper. Temperature accelerated dynamics (TAD) simulations are in progress at the time of this writing. Both methods are discussed in more detail in other papers in these proceedings [5], [6].

## CALCULATIONS

We are currently using the AIREBO potential by Stuart et al.[7]. It has some advantages over other empirical potentials for carbon. This potential includes the treatment of nonbonded interactions and a torsional potential term. Nonbonded interactions are important for the study of bundles of nanotubes, as these are precisely the interactions that exist between two neighboring nanotubes. They are also relevant in describing the tube-tube interactions that can lead to van der Waals collapse of large-diameter tubes. The torsional term describes rotations about a bond in a molecule, which play an important role in small hydrocarbon molecules. It also includes descriptions of the interaction between hydrogen and carbon, allowing for the future study of hydrocarbons interacting with carbon nanotubes.

Carbon nanotubes are characterized by their chirality. The chirality of a tube is described by a pair of indices that represent the graphite lattice vector corresponding to the circumference of the tube [8]. Various properties of a nanotube depend greatly upon its chirality, an important example of this being the electronic conductance. Some chiralities result in a metallic nanotube, while others give a semiconductor. One aspect of this work is to look at the dependence of other proper-

ties on the chirality.

We have used the parallel replica method to stretch tubes uniformly versus time at two different temperatures. The basic idea behind parallel replica is to sample the phase space associated with a given energy basin more quickly by releasing a number ( $m$ ) of independent trajectories in the basin. These trajectories are allowed to explore the basin until one of them escapes (i.e., makes a transition). Exploiting the fact that the first passage time is exponentially distributed, we can describe the exact state-to-state dynamics in roughly  $1/m$  as much waiting time. For these preliminary results, a transition is defined as when the trajectory, upon energy minimization, maps to a different energy minimum than that characterizing the previous basin. Here, by different, we mean that the geometry of this new minimum is greater than some distance away from the previous one. This definition can be problematic, especially at high temperatures, as long wavelength distortions occurring on the surface of the nanotube take much longer to fully minimize out. Alternatively, a transition can be defined as a change of coordination upon minimization. This criterion is more natural for nanotubes, as it is a more local definition for a basin and thus circumvents some of the issues with using an absolute distance between states. We are currently exploring this.

Once a transition is detected, the time that all of the trajectories have spent sampling the basin is summed. This is the effective time spent in the basin, or the time at which this transition occurred. This transition is accepted and this whole process is then repeated in the next basin, *ad infinitum*. For more details on parallel replica, see [2], [5].

This work represents the first time that parallel replica has been applied to a driven system. The nanotubes are being stretched versus time. This means that the strain rate each processor sees is  $m$  times greater than the effective strain rate. We have worked out the condition for which such a situation still gives correct dynamics, which we will present elsewhere.

## PRELIMINARY RESULTS

Using parallel replica, we can watch for qualitative differences in how a tube might break versus temperature and chirality. We can also determine what effect the presence of defects, such as vacancies, might have on how the tube breaks. Some studies of this sort have been done in the past (see, e.g., [9]–[11]). However, with the accelerated dynamics techniques, we are able to achieve slower, and hence more realistic, strain rates.

Simulations were performed at 300 K and 2000 K. These tubes were stretched at a strain rate of  $10^7/s$ , about 20 times slower than in [9]. Both of these simulations were run on 12 processors. The first event seen in the 300 K case occurs at 30.6 ns. At 2000 K, the first

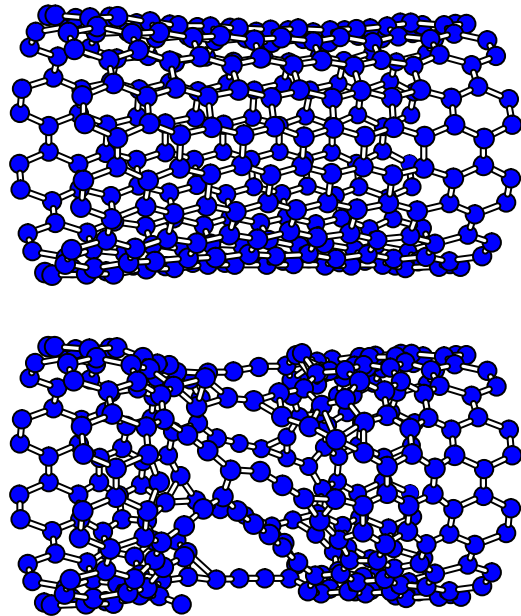


Figure 1: Nanotube stretched at 300 K. The top figure shows the tube after 31.2 ns. At this temperature, nothing has happened during this time. During the next 0.5 ps, however, a critical event occurs that causes a cascade of correlated dynamic events which result in the structure in the bottom figure, a structure characterized by long tendrils of carbon atoms connecting the two halves of the nanotube.

event occurs in about half that time, at 15.1 ns. The simulations had near-perfect efficiency up to the time of the first event (about 12 times in both cases). Both nanotubes were of chirality (10,10) and contained 300 atoms. In the preliminary simulations shown here, 30 atoms were frozen on each end of the nanotube. Because in this approach the tube diameter at the ends is not allowed to shrink as the tube stretches, it is probably less realistic than a fully periodic treatment, which we are presently investigating.

Figures 1 and 2 show preliminary results of this work. There is a qualitative difference in the nature of the first event at the different temperatures. The nanotube stretched at 300 K breaks more suddenly, briefly heating up to thousands of degrees as the initial breakage triggers a cascade of dynamically correlated atomic events. It goes from a perfect, albeit stretched by a factor of 1.37, tube at 30.6 ns to a nearly fragmented tube 0.6 ns later, with two halves connected by long carbon tendrils. This is similar to behavior that has been seen before [9], [10]. Stretching at 2000 K, however, allows the atoms more opportunities to find favorable positions. Events begin occurring relatively soon, at about 15 ns after being stretched by only a factor of 1.16. After that, the

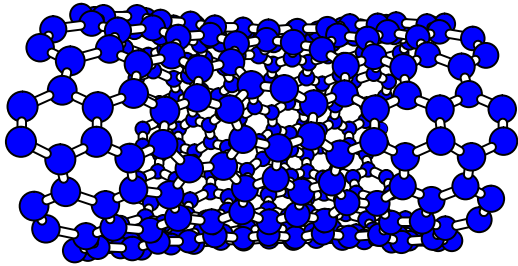
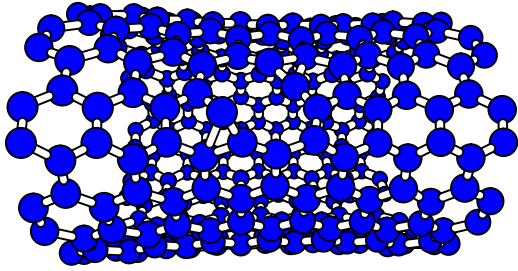


Figure 2: Nanotube stretched at 2000 K. In contrast to the situation at 300 K, events occur much sooner and do not result in such catastrophic damage. The top figure is tube after 15.1 ns, the time at which the first event occurs. This event is the creation of a topological defect, a void with a three member ring next to it. The bottom figure is the tube about 1 ns later, after 10 similar events have taken place. The tube is seen to bow in slightly at the middle, as the defects rearrange to accomodate the strain in the tube.

atoms continue to rearrange as they form topological defects which are able to accomodate some of the strain in the system. This is manifested in the bowing in of the sides of the tube near the midsection. These conclusions are based on only one set of preliminary simulations and may change as our understanding of this system increases.

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