

Tight-Binding Molecular Dynamics of Shock Waves in Hydrocarbons

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Hydrocarbons are found in various extreme environments in the solar system. Benzene has been detected in the atmosphere of Jupiter, and methane is an important constituent of the middle ice layers of the outer gas giants Uranus and Neptune. Determining the transformations induced in hydrocarbons by nonequilibrium phenomena such as shock waves and detonations presents a challenging problem. The accepted interpretation of shock wave experiments holds that these materials ultimately decompose into elemental carbon (probably amorphous carbon and diamond powder), molecular hydrogen and perhaps other gases. There is clearly interest in determining what chemical transformations occur on intermediate timescales, as well as examining the formation of transient species under nonequilibrium conditions.

Analyses of shock-compression experiments are based on the Rankine-Hugoniot relations of measured kinematic parameters to thermodynamic variables. The equation of state can then be determined from the pressure-volume trajectory of the shock adiabat; however, such an approach does not shed light on the dynamical processes in the shock-compressed material. In this work we study shock-compression directly with nonequilibrium molecular dynamics. We follow the evolution of the hydrocarbons as they dissociate and decompose at high

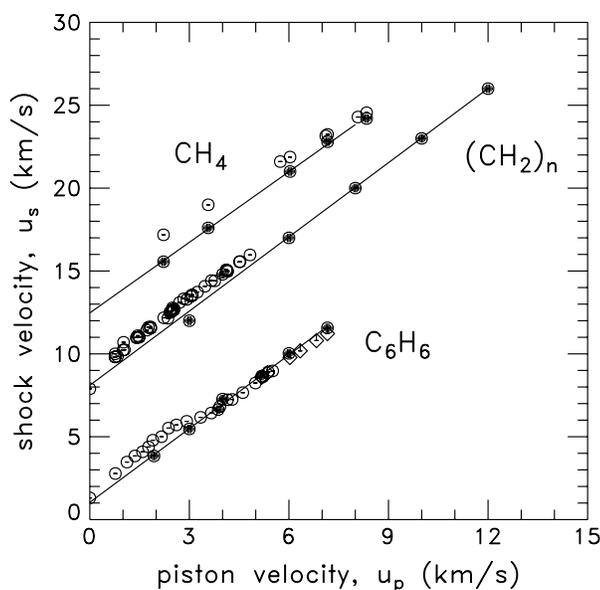


Figure 1: Shock velocity as a function of piston velocity. Bullet = simulation. Opening symbols = experiment. u_s is shifted by 6 and 12 km/s, respectively, for polyethylene $[(CH_2)_n]$, and methane (CH_4).

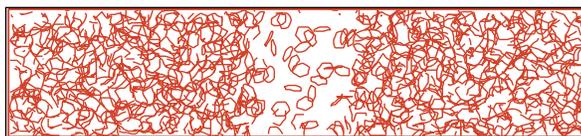


Figure 2: Snapshot from simulation cell containing 576 benzene molecules.

pressures and temperatures. We used a recently developed Order(N) tight-binding algorithm [1] to describe the interatomic forces, where the computational work scales linearly with the number of atoms N. The valence electrons are treated quantum mechanically, with the electronic state of the system calculated at each molecular dynamics timestep to obtain the interatomic forces directly. The Order(N) algorithm leads naturally to a very efficient parallel implementation; the present calculations have been performed on up to 126 processors on the Advanced Strategic Computing Initiative computer at Los Alamos.

In Figure 1, we compare the results of our simulations [2] with the results of single shock gas-gun and high-explosive driven experiments. Initial states were prepared using simulation cells containing 432 methane (CH_4) molecules, up to 576 benzene (C_6H_6) molecules, and two chains of $C_{432}H_{868}$ (amorphous

polyethylene). Shock velocity u_s as a function of piston velocity u_p is shown in Figure 1, where u_s is shifted by 6 and 12 km/s for polyethylene and methane, respectively, for clarity. As u_p increases and the fluid, liquid, or polymer begins to dissociate, experiment and simulation agree, attesting to the accuracy of the quantum mechanical treatment of the valence electrons for the breaking and making of chemical bonds.

The results plotted in Figure 1 illustrate that NEMD and the modified Oxford TB provides a good description of the mechanical properties of fluid methane, liquid benzene, and amorphous polyethylene. The trajectories can also be analyzed to determine the chemical properties at high temperatures and pressures. To mimic a driving “piston” in a shock experiment, the ends of the simulation cell perpendicular to the shock direction move inward, with appropriate periodic velocity boundary conditions. The initial cell for the benzene simulations, of length $L = 213 \text{ \AA}$, contains only rings of unreacted molecules. In Figure 2, a snapshot from the last step ($L = 90 \text{ \AA}$) of a simulation for a shock wave (of $u_p = 7.16 \text{ km/s}$) in benzene is shown as a 2D projection of the C-C bonds. The two shock fronts, visible as a density gradient between the unreacted (benzene rings) and reacted (dense “polymer”) regions, have almost collided in the center. To better characterize the reacted region in Figure 2, the average number of C atoms within a cut-off radius of a given C atom is counted and plotted in Figure 3. (Only one half of the cell is shown for clarity.) The shock and piston are both moving from left to right (from larger to smaller position). The region vacated upon compression was assigned a value that distinguishes it from the unshocked portion of the sample (yellow region), which contains only unreacted benzene (two C-C nearest neighbors per C atom). At the end of the simulation, the average number of C-C bonds has increased to ~ 2.3 . Some of the benzene rings have opened and formed clusters (polymers, see Figure 2) that are diamond-like (three C-C bonds per C atom).

An analysis of the number of C-C nearest neighbors for a simulation of shock-compressed amorphous polyethylene ($u_s = 10 \text{ km/s}$) is plotted in Figure 4. In the uncompressed region, there are two C-C neighbors, corresponding to normal polyethylene chains. After about 100 fs, the number of C-C neighbors decreases to about 1.7, indicating that some polyethylene chains are broken upon compression. The C-C neighbor chemical wave (interface between the region with 2 and 1.7 neighbors) tracks just behind and parallel to the shock front in the time-evolved density profile.

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- [1] J. D. Kress, S. Goedecker, A. Hoisie, H. Wasserman, O. Lubeck, L. A. Collins, and B. L. Holian, *J. Comp.-Aided Mat. Design* **5**, 295 (1998).
 [2] J. D. Kress, S. R. Bickham, L. A. Collins, B. L. Holian, and S. Goedecker, *Phys. Rev. Lett.* **83**, 3896-3900 (1999).

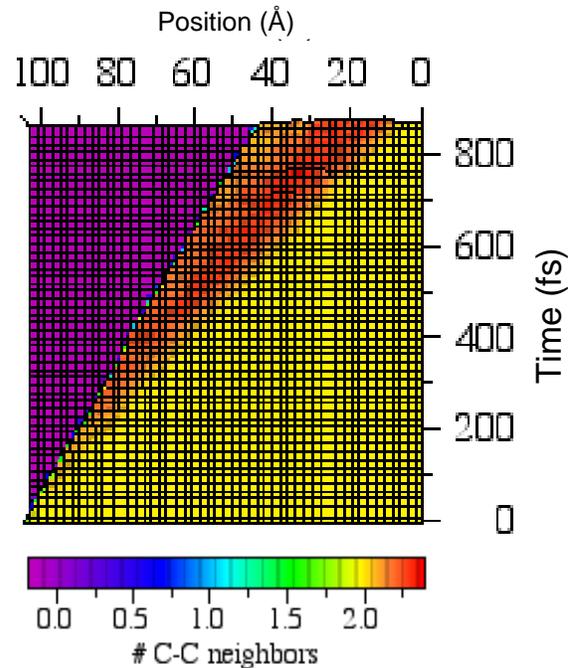


Figure 3: Average number of C neighbors for each C atom during propagation of a shock wave in benzene.

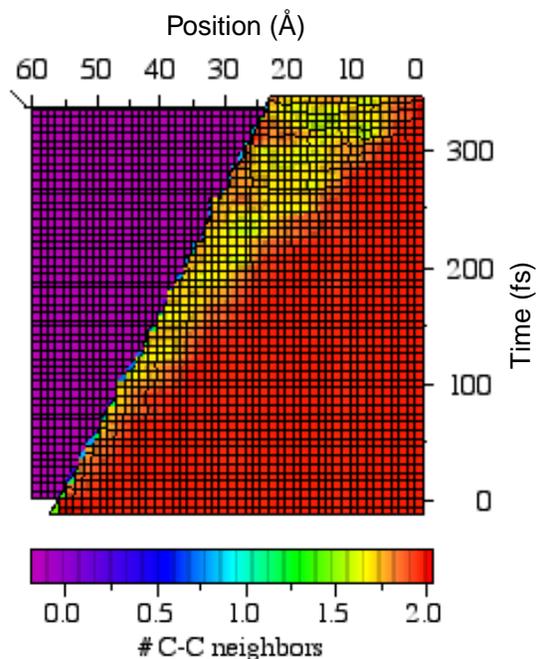


Figure 4: Average number of C neighbors for each C atom during propagation of a shock wave in polyethylene.