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Author(s): Joel D. Kress  
Stephane Mazevet  
Lee A. Collins

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# DENSITY-FUNCTIONAL MOLECULAR DYNAMICS SIMULATIONS OF SHOCKED MOLECULAR LIQUIDS

J. D. Kress, S. Mazevet, and L. A. Collins

*Theoretical Division, Los Alamos National Laboratory, Los Alamos, NM 87545*

**Abstract.** Molecular dynamics (MD) simulations have been performed for highly compressed fluid deuterium, nitrogen, and oxygen, in the density and temperature regime of shock-compression experiments, using density functional (DF) electronic structure techniques to describe the interatomic forces. The Hugoniot derived from the calculated equation-of-state for deuterium does not exhibit the large compression predicted by the recently reported laser-driven experiments. However, the Hugoniot derived for nitrogen and oxygen agree well with explosively-driven and gas-gun experiments. The nature of the fluid along the Hugoniot, as calculated with DF-MD, has been analyzed. All three species ( $D_2$ ,  $N_2$ , and  $O_2$ ) undergo a continuous transition from a molecular to a partially dissociated fluid containing a mixture of atoms and molecules.

Density Functional Molecular Dynamics (DFMD) simulations provide an extremely penetrating probe of a variety of environments in which dense matter at elevated temperatures plays a significant role, including solids, fluids, gases, plasmas, and especially mixtures of these various states of matter. In many circumstances, a quantum ("*ab initio*") treatment of the interaction between electrons and ions provides the only reliable procedure for gaining information and understanding on the state and interaction of matter in these extreme conditions in which experiments remain difficult.

Renewed interest in shocked-compressed nitrogen and oxygen has arisen from an unlikely source, namely, laser-driven shock experiments on deuterium(1). These experiments have indicated that the deuterium Hugoniot appears much softer than originally predicted by a conventional EOS such as the SESAME table(2), allowing a maximum compression ratio ( $\eta_{max} = \rho_{max}/\rho_0$ ) of a factor of six from the liquid state at  $\rho_0$ . This value ( $\eta_{max}=6$ ) more resembles that of an ideal diatomic rigid-rotor molecular fluid than an atomic one ( $\eta_{max}=4$ ). These findings have immense ramifications for many areas of science including the modeling of planetary interiors. As a further complication, considerable disagreement exists among the theoretical methods for

the case of deuterium. While the various *ab initio* simulation approaches (3, 4) now show considerable concurrence, the high compressibility measured experimentally can only be reproduced with fluid theories based on effective pair potentials(5).

Since close parallels exist between deuterium, nitrogen, and oxygen in this compressed-fluid regime, a study using *ab initio* molecular dynamics(MD) simulations might not only elucidate many interesting aspects of compressed nitrogen but also provide further insight into the deuterium dilemma. All three species have natural(cryogenic) fluid states composed of diatomic molecules, and all form molecules with large dissociation energies [4.5, 9.8 and 5.1 eV, respectively, for  $D_2$ ,  $N_2$ , and  $O_2$ ] and moderately high ionization energies [12 – 15 eV]. Since the *ab initio* MD simulations for deuterium show considerable disagreement with laser experiments at high compression ( $\eta_{max} > 4$ ), trials on similar system with established shock data provides a critical test of the theoretical approaches, especially those without tunable parameters.

The past few years have witnessed the development of a variety of large-scale simulation methods to treat fluid systems over a broad range of conditions. In DF methods, the total energy is written as a functional of the electron density, which is

obtained by summing the probability density over the occupied orbitals. Further, for the Generalized Gradient Approximation (GGA), the electronic exchange and correlation energy are approximated using a functional which depends only on the electron density and its spatial derivatives. GGA methods provide a highly accurate means of studying the thermochemistry of chemical bonding by representing the inhomogeneities inherent in the electron charge density relative to the homogeneous electron gas. In addition, the method encompasses all manner of transient effects such as dissociation and association of chemical bonds, quasi-molecular formation, and ionization and recombination. Finally, a semi-empirical tight-binding (TB) electronic structure model for deuterium has been developed(6). The TB method presents an effective compromise, giving a reasonable accurate representation of the principal mechanisms while consuming considerably less computational resources than the DF approaches.

For the DF calculations, we employed the VASP plane-wave pseudopotential code, which was developed at the Technical University of Vienna (7). This code implements the Vanderbilt ultrasoft pseudopotential scheme in a form supplied by G. Kresse and J. Hafner and the Perdew-Wang 91 parameterization of GGA. A finite-temperature density functional procedure (8) is employed by setting the electron and ion temperatures equal (local thermodynamic equilibrium) using a Fermi-Dirac distribution.

Finite-temperature, fixed-volume molecular dynamics simulations were performed for density and temperature points selected to span the range of the single-shock Hugoniot experiments. A simulation cell with periodic boundary conditions with a fixed number of atoms was employed. For nitrogen and oxygen we used 32 atoms (160 and 192 valence electrons, respectively), while for deuterium, 128 atoms (128 valence electrons) Further details can be found in (3) and (10).

The Rankine-Hugoniot equation

$$(U_1 - U_2) + \frac{1}{2}(V_1 - V_2)(P_1 + P_2) = 0, \quad (1)$$

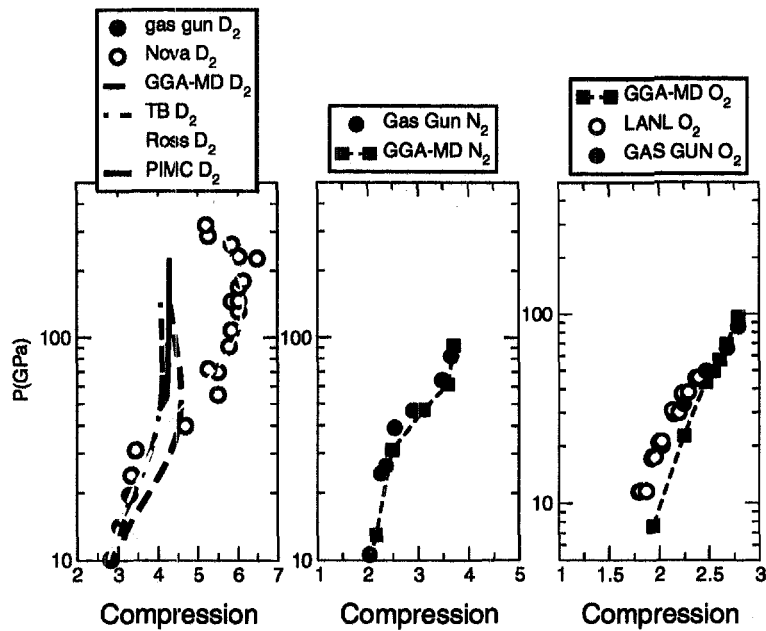
describes the shock adiabat through a relation between initial ( $V_1 = 1/\rho_1$ ,  $U_1$ ,  $P_1$ ) and final ( $V_2 = 1/\rho_2$ ,  $U_2$ ,  $P_2$ ) volume, internal energy, and pressure. The internal energy per atom  $U$  consists of the sum

of the ion kinetic energy ( $\frac{3}{2} k_B T_i$ ) and the time average of the DF potential energy  $E/N$ , where  $k_B$  is the Boltzmann constant. The pressure  $P$  is computed using the Hellmann-Feynman forces derived from the DF potential energy. We have chosen  $P_1 = 0$ , and  $U_1$  so that the energy of the isolated molecule is zero. The initial densities were set to  $\rho_1 = 0.171, 0.808$ , and  $1.2 \text{ g/cm}^3$ , respectively, for  $D_2$ ,  $N_2$ , and  $O_2$ . To find the Hugoniot point for a given  $V_2$ ,  $P$  and  $U$  derived from the DF-MD results were fit by a least-squares prescription to a quadratic function in  $T$ .  $P_2$  and  $T_2$  were found by substituting these functions and solving Eq. 1.

The DF-MD Hugoniot points appear in Fig. 1 along with the experimental data for  $D_2$ ,  $N_2$ , and  $O_2$ . We first focus on the results for deuterium (Fig. 1a). The system starts as a cryogenically-cooled liquid. The points in pressure-density space then follow from the application of the single-shock Rankin-Hugoniot conditions based on the equation-of-state for a given theoretical model. At present, a large difference exists among various methods and the laser-driven NOVA experiments(1). The SESAME(2) (not shown), tight-binding-MD (TB)(6), DF-MD(3), and path integral Monte Carlo (PIMC)(4) approaches all appear in generally good agreement, giving a maximum compression  $\eta = \rho/\rho_o$  of around 4. This value closely matches that for an ideal atomic fluid. However, they differ substantially from the linear-mixing model(5) and the lone experimental (laser-driven) results(1) above  $P = 50 \text{ GPa}$ ; both yield  $\eta=6$  – more like an ideal molecular fluid.

We emphasize a point that appears to cause considerable confusion in the general literature. All the models discussed from SESAME to the DF-GGA and PIMC include dissociation at some level of approximation. The large compressions seen in the laser experiments cannot be solely attributed to dissociation. Some additional mechanism must also be at work. Furthermore, all of these models have a representation, at some level, of the basic physical processes that govern Hydrogen in this regime. Identifying the precise physical mechanisms that lead to such differences in the theoretical models has remained elusive.

We next return to the principal Hugoniots for  $N_2$  (Fig. 1b) and  $O_2$  (Fig. 1c). (Further DF-MD calculations on double-shocked Hugoniots for  $N_2$  are

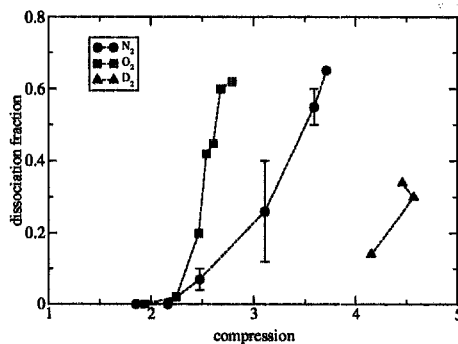


**FIGURE 1.** Hugoniot (compression =  $\rho/\rho_0$ ). (a) Deuterium. DF-MD [purple long-dashed line, Ref. (3)]. PIMC [magenta solid line, Ref. (4)]. Tight-binding (TB) [green dashed-line, Ref. (6)]. Linear-mixing model (Ross) [yellow short-dashed line, Ref. (5)]. Laser-driven experiments (NOVA) [purple open circles, Ref. (1)]. Gas-gun experiments [green closed circles, Ref. (9)]. (b) Nitrogen. DF-MD [orange closed squares, Ref. (10)]. Experiments [black closed circles, Refs. (11), (12) and (13)]. (c) Oxygen. DF-MD [orange closed squares]. Explosively-driven experiments [purple open circles, Ref. (14)]. Gas-gun experiments [green closed circles, Ref. (12)].

ported elsewhere in these proceedings(15).) We find very good agreement between the DF-MD calculations and the explosively-driven and gas-gun experimental results all along the single-shock Hugoniot. In particular, the calculations reproduce the distinctive inflection associated with dissociation, centered about  $\eta = 4, 3,$  and  $2.5,$  respectively, for  $D_2, N_2,$  and  $O_2$ . These comparisons with available experimental results demonstrate that the MD simulations can reasonably reproduce the major trends along the principal Hugoniot. We now explore the explicit nature of the fluid for which the experiments can offer only indirect evidence.

In order to place these results on a more quantitative basis, we have performed a standard cluster analysis of the MD trajectories. An effective radius is selected, and all atoms within this distance are considered bound to a reference atom. This produces, at a selected time step in the MD trajec-

tory, a distribution of monomers, dimers, and larger molecules. We then average the distributions over the extent of the MD trajectory. Figure 2 shows the variation of the dissociation fraction  $\beta$ , the ratio of monomers to the total number of particles, along the principal Hugoniot. For  $N_2$ , the value for  $\beta$  at a fixed density was calculated as an average of two temperatures (approximately 500 K above and below the Hugoniot), with the error bars indicating the spread between these two results. Figure 2 gives clear indications of the general trends in the evolution of the fluid. The system appears to undergo a continuous transition from a molecular to a nearly fully dissociated fluid. As the fluid starts to dissociate (at around  $\eta = 4, 2.2,$  and  $2,$  respectively, for  $D_2, N_2,$  and  $O_2$ ), trimers and larger clusters appear. (Note that this dissociation region coincides with the inflection region in Fig. 1.) However, these trimers survive for less than a vibrational period of the ground state dimer



**FIGURE 2.** Variation of the average dissociation fraction  $\beta$  along the principal Hugoniot as a function of shock compression ( $\eta = \rho/\rho_0$ ).  $D_2$  [triangles, adapted from Ref. (?)];  $N_2$  [circles, Ref. (10)];  $O_2$  (squares).

and are thus highly transient. By contrast, the dimers hold together for many such periods. As the temperature and density increase, the lifetimes of the molecular species will decline since the collisional frequency will likewise rise, facilitating the breaking of the chemical bonds. This behavior becomes even more apparent from movies of the particle motions. The continuous dissociation and the transient character along the principal Hugoniot for  $D_2$ ,  $N_2$ , and  $O_2$  all closely resemble each other.

In summary, we have calculated equation-of-state properties for deuterium, nitrogen, and oxygen using density functional molecular dynamics simulations at the GGA level. We obtain very good agreement (for pressure vs. density) with the gas-gun experiments along the principal Hugoniot. As density and pressure increase along the Hugoniot, the system appears to undergo a continuous transition from a molecular to a partially dissociated fluid containing a mixture of atoms and molecules. A small fraction of clusters larger than dimers were found; however, these larger clusters were of a highly transient nature, with lifetimes of a few femtoseconds.

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