Chemistry and Phase Transitions from Hypervelocity Impacts

C. T. WHITE, S. B. SINNOTT, J. W. MINTMIRE, and D. W. BRENNER
Naval Research Laboratory, Washington, DC 20375-5000

D. H. ROBERTSON
Indiana University-Purdue University at Indianapolis, Indianapolis, Indiana 46202

Abstract

Molecular dynamics simulations are used to study hypervelocity impacts of an ultrathin flyer plate with a semi-infinite two-dimensional model diatomic molecular solid. We show that these hypervelocity impacts can produce a dissociative phase transition from a molecular to a close-packed solid in the target material. We also show that hypervelocity impacts of ultrathin plates can produce extensive chemical reactions leading to a detonation accompanied by a phase transition in an energetic version of the model.

Introduction

Advances in technology have led to the development of a variety of methods to launch flyer plates, microprojectiles, and pellets at velocities in excess of several kilometers per second [1]. The shock wave that results when these hypervelocity projectiles strike stationary targets typically separates the unperturbed material by only a few lattice spacings from the shocked solid which experiences pressures of several hundred kilobars, temperatures of several thousand degrees kelvin, while flowing at velocities of several kilometers per second [2]. These extreme but ephemeral conditions have been used to uncover new high pressure phases of solids [3] as well as explore synthetic routes to novel materials such as “hexagonal” diamond [4] (lonsdaleite) originally discovered in granular form in meteorites. Indeed, as early as 1956 Bancroft, Peterson, and Minshall reported data from shock loading experiments that proved the existence of a previously undetected high pressure phase of iron [5]. The signature of this transition was the presence of a split shock wave. Since Bancroft, Peterson, and Minshall’s initial observations, shock wave splitting caused by polymorphic phase transitions has been observed in many other systems [3].

A better atomic-scale understanding of the physical and chemical events that occur during shock-wave loading should not only aid in the design of more resilient materials but also in the production of safer and more reliable explosives. However, the shock processes induced by hypervelocity impacts or sustained by detonations...
occur at such short time (subpicosecond) and length scales (subnanometer scales) that they are difficult to probe experimentally. The short time and length scale of these processes, however, make them ideal for classical molecular dynamics simulations \[6\]. In addition, although starting from an atomic-scale description, molecular dynamics simulations have proven able to treat sufficiently many atoms for long enough times to reproduce the continuum behavior of planar shock waves described by hydrodynamic theory \[7,8\]. Hence, molecular dynamics simulations are ideal for modeling atomic-scale processes associated with shock waves and for relating this atomic-scale behavior to the continuum properties of condensed phase shock waves.

Shock loading resulting from hypervelocity impacts can induce chemical as well as physical changes in materials. An extreme example is that of a solid explosive which when struck can undergo catastrophic exothermic chemical reactions. A less spectacular but no less important example is the short-time corrosive chemistry that can occur when nanometer scale clusters strike surfaces at hypervelocities.

We have developed a series of related many-body reactive potentials that allow processes such as adhesion and friction \[9,10\], and shock-induced phase changes and chemistry \[8,11\] to be studied at atomic-scale resolution. Herein, we summarize and relate some of the results we have obtained in using a subset of these potentials to simulate the processes that can occur during the hypervelocity impact of an ultra-thin flyer plate with a model diatomic molecular solid. Specifically, we discuss results of a series of molecular dynamics simulations of the hypervelocity impact of a nanometer thick flyer plate with several model 2-D diatomic molecular solids. We find that even this ultrathin flyer plate—if accelerated to hypervelocities—can have sufficient momentum to induce a polymorphic (dissociative) transition from a molecular to close-packed solid in the target material. In addition, we show how such impacts can lead to extensive chemical reactions—even to the point of producing a detonation in an energetic version of the model. In the next section we briefly review the model used in these simulations. Then a series of our results are discussed. The final section provides a summary.

**Model**

The model potentials used in our studies are based on empirical bond order potentials such as those used by Tersoff to describe silicon \[12\] but tailored by us to treat reactive diatomic molecular solids \[8\]. Within this approach the total potential energy, \( E_B \), of a collection of \( N \) atoms is represented by,

\[
E_B = \sum_{i<j}^{N} \sum_{i}^{N} \{ f_c(r_{ij})[V_R(r_{ij}) - \tilde{B}_{ij}V_A(r_{ij})] + V_{vdW}(r_{ij}) \},
\]

where the molecular bonding portion of the potential consists of a repulsive term, \( V_R(r) \), and an attractive term, \( V_A(r) \), both modeled by exponentials. A Lennard–Jones potential, \( V_{vdW} \), is used to describe the weak long-ranged van der Waals interaction. This Lennard–Jones potential is truncated not only at large distances but also at close-range bonding separations to allow for covalent bonding. The bond
order function, $\tilde{B}_{ij} = (B_{ij} + B_{ji})/2$, introduces many-body effects into the potential by modifying $V_{a}(r)$ according to the local bonding environment. These many-body effects arise from the hidden electronic degrees of freedom that are not treated explicitly in the model. For an isolated diatomic molecule $\tilde{B}_{ij}$ is unity and the potential reduces to a generalized Morse function familiar in the description of diatomic bonding [13]. For more highly coordinated structures $\tilde{B}_{ij}$ is no longer unity, but rather decreases with the increasing number and strength of competing bonds the atoms $i$ and $j$ form. This decrease in $\tilde{B}_{ij}$ reflects the finite number of valence electrons these atoms have available for bonding. Hence $\tilde{B}_{ij}$ represents an effective valence which can be tailored through its dependence on environment to describe either highly coordinated metals [14], tetrahedrally bonded semiconductors [15] and insulators or low coordination molecular solids with a few strong bonds [8].

In what follows the functions and associated parameters entering Eq. (1) have been chosen to describe a diatomic molecular solid at ambient conditions as described in detail elsewhere [8]. The diatomic molecules that make up this model solid can be composed of either like ($A_2$ or $B_2$) or unlike ($AB$) molecules. These diatomic molecules all have reasonable physical and chemical characteristics including binding energies, bond lengths, vibrational frequencies, and barriers to chemical reaction [8]. In addition, the diatomic molecular solids formed from these diatomic molecules have reasonable physical characteristics including densities, solid-state sound speeds, and high pressure phase transitions [8].

The $A_2$ and $B_2$ molecules entering this model are taken to have identical binding energies of 5 eV while the binding energy of each $AB$ molecule is set to 2 eV. Hence simulations starting from an $AB$ molecular solid allow for the possibility of exothermic chemical reactions from the higher energy $AB$ molecules to the more stable $A_2$ and $B_2$ molecular products. In contrast, simulations starting from either $A_2$ or $B_2$ molecular solids do not have the possibility of any net release of energy. This model then allows simulations of hypervelocity impacts with target materials composed of either energetic or nonenergetic diatomic molecules.

**Results and Discussion**

Hypervelocity impact simulations are initiated by slamming an ultrathin thin flyer plate composed of 20 layers or less of the target material into the edge of the semi-infinite model diatomic molecular crystal initially at rest. Both the flyer plate and the molecular crystal are initially taken to have near-zero temperature and pressure. The dynamics of the system resulting from this hypervelocity impact is then studied by integrating Hamiltonian's equations of motion using a Nordsieck predictor-corrector method [15]. During these simulations periodic boundary conditions are imposed perpendicular to the direction of shock propagation.

A series of studies were first carried out assuming an all $A_2$ or equivalently an all $B_2$ diatomic molecular solid. A sequence of snapshots for a simulation beginning with the 15 km/sec velocity plate is shown in Figure 1. At 0.8 ps [Fig. 1(a)] only a single compressional shock wave is visible. Across this shock front the diatomic
molecular solid (DMS) transforms directly to a close-packed solid (CPS). Although the density of this CPS, $\rho_{\text{CPS}}$, is approximately 2.4 times larger than the density of the DMS, $\rho_{\text{DMS}}$, the average nearest-neighbor interatomic separation in this phase, $d_{\text{NN}}$, is actually 20% larger due to an increase in the interatomic coordination. These properties of the CPS make this DMS to CPS transition similar to the dissociative transition reported in diatomic molecular solids of iodine [16] and bromine [17]. This transition occurs at 21 GPa in I$_2$ and 81 GPa in Br$_2$ leading to an increase in the overall relative density, $\rho_{\text{CPS}}/\rho_{\text{DMS}}$, of 1.7 for I$_2$ and 2.3 for Br$_2$, and an increase in $d_{\text{NN}}$ of around 15% for both materials.

At 1.6 ps [Fig. 1(b)] a second leading compressional shock wave has appeared in the 15 km/sec simulation. Across this new front the diatomic molecules are compressed and rotated from their initial positions in the undisturbed crystal but
HYPERVELOCITY IMPACTS

retain their molecular identity. Once the second shock front is clearly visible it rapidly separates from the dissociative front, as can be seen by comparing Figure 1(b) to Figure 1(c). Although both the compressional and dissociative shock fronts propagate at velocities in excess of the speed of sound in the undisturbed crystal, the velocity of the dissociative front rapidly decreases from more than 12 km/sec at 0.5 ps to about 3 km/sec at 2.4 ps. In contrast, the velocity of the leading compressional shock remains pinned around 12 km/sec while the dissociative front exists, only gradually beginning to slow after the CPS disappears. As the dissociative front slows the accompanying dissociative zone also narrows as this region is consumed from behind by the rarefaction wave [Fig. 1(a)--Fig. 1(d)]. Figures 1 and 2 show that (Fig. 2) this front also begins to smear with the material behind entering a mixed phase region by 2.4 ps [Fig. 1(c)] as the velocity of the dissociative front approaches 3 km/sec. This mixed phase is clearly present at 3.2 ps [Fig. 1(d)] just prior to the complete disappearance of the dissociative zone.

A dissociative phase together with an accompanying split shock wave such as shown in Figure 1(b) is also present in all the other simulations begun with flyer plate velocities between 10 to 20 km/sec. Although the appearance of the leading compressional wave is delayed for higher impact plate velocities, once formed this front always exhibits a velocity near but slightly less than 12 km/sec, provided the dissociative region remains well-defined. In all simulations exhibiting a split shock wave, the dissociative zone begins to lose its identity only after the particle flow velocity behind the dissociative front slows to near 3 km/sec.

![Figure 2. Scatter plot of $u_{pc}$ 3.0 Å behind the dissociative front for the hypervelocity impact simulation depicted in Figure 1.](image-url)
The general properties of these hypervelocity impact simulations as well as the explicit behavior shown in Figure 1 are all consistent with continuum predictions of a shock induced phase transition. An important property of these phase transitions is the compressional shock wave splitting that might occur. If split compressional shock waves are present, then continuum theory predicts [18] that the leading shock front starts material flow bringing it to the point of transition while the transition occurs across the second compressional shock front. A split shock wave with the transition occurring across the second front is just what is observed in Figure 1(b) and 1(c).

The continuum theory of planar shock waves also predicts [18] that a shock wave propagates into a medium (assumed at rest and characterized by a pressure $P_0$ and a specific volume $V_0$) with a velocity $D$ given by:

$$D = (1 - V/V_0)^{-1} u_p,$$

where the particle flow velocity behind this shock front, $u_p$, is given by:

$$u_p = \sqrt{(V_0 - V)(P - P_0)},$$

with $V$ the specific volume and $P$ the pressure of the shocked material. Therefore, because the leading shock front carries the pressure, $P_T$, and specific volume, $V_T$, of the phase transition, its velocity from Eqs. (2) and (3) is given by $D_1 = (P_T - P_0)/(\sqrt{V_0 - V_T})$, and hence is predicted as pinned at a constant value determined by the properties of the phase transition and the undisturbed molecular crystal. In addition, the second front can only exist as a shock front so long as the particle flow velocity behind this front exceeds the particle flow velocity in the leading compressional zone, $u_{p1} = \sqrt{(V_0 - V_T)(P_T - P_0)}$. Hence $u_{p1}$ is also a constant determined by the properties of the phase transition and the initial state. Continuum theory therefore explains why when two shock waves are present in the system—regardless of the impact plate velocity—the first shock propagates at a near constant velocity $D_1$, while the second always fragments as the particle velocity behind this front, $u_{p2}$, approaches a fixed value, $u_{p1}$. Elsewhere we have shown [8] that for the present model: $V_T \approx 4.5$ Å$^2$/atom; $P_T \approx 0.813$ eV/Å$^2$; $V_0 \approx 6.14$ Å$^2$/atom; and $P_0 \approx 0.00$ eV/Å$^2$; results which imply that $D_1 \approx 11.5$ km/sec and $u_{p1} \approx 3.0$ km/sec. These predictions differ no more than 5% from the corresponding near-constant values of $D_1$ and $u_{p1}$ observed in all of these flyer plate simulations confirming the consistency of the continuum interpretation.

The snapshots shown in Figure 1 also suggest that hypervelocity impacts sufficient to induce a local dissociative transition should also be capable of causing substantial chemical rearrangement of the atoms in the dissociative zone. To explore the possibility of chemistry induced by hypervelocity impacts we have used the energetic AB version of our model diatomic molecular solid. Hence, rather than starting with an all $A_2$ molecular solid we now start with an all AB molecular solid which when shocked might undergo exothermic chemical reactions to yield the more stable $A_2$ and $B_2$ molecules. As noted in the “Model” section the exothermic gas-phase half reactions, $AB + B \rightarrow B_2 + A$ and $BA + A \rightarrow A_2 + B$—taken as identical
in the model—are each assumed to liberate 3.0 eV. This 3.0 eV is similar to the 3.3 eV of energy liberated in the exothermic reaction \( \text{N} + \text{NO} \rightarrow \text{N}_2 + \text{O} \) thought important in the detonation of NO. Also, the transition states for these two identical reactions occur in a collinear geometry with an early barrier to reaction which is typical of atom–diatom exothermic reactions. In addition, the barrier for these two model reactions is 0.11 eV. This barrier is greater than but similar to the barrier reported for the exothermic reaction \( \text{F} + \text{H}_2 \rightarrow \text{FH} + \text{F} \) [19].

Figure 3 depicts a snapshot of a simulation begun by the impact of a four-layer, 6.0 km/sec flyer plate with the AB model molecular solid. As in Figure 1(b), four distinct regions are present: the unreacted molecular solid, a leading compressional region, a close packed solid (CPS) phase, and a product region. Hence, the AB molecular solid also exhibits a split shock wave structure and associated polymorphic phase transition similar to that found in the A₂ simulations. However, in contrast to the all-A₂ model, the CPS phase does not shrink but rather grows at a constant rate as the simulation progresses. The work necessary to maintain and increase this CSP is supplied by the exothermic chemical reactions induced by the shock wave. These exothermic reactions almost completely convert the AB molecular solid to the lower energy A₂ and B₂ molecular products clearly visible to the far left of Figure 3. In this way, the simulation depicted in Figure 3 has become a chemically sustained shock wave with the velocities of the three interfaces separating the four distinct regions soon reaching constant but different values as shown in Figure 4. As we will discuss in detail elsewhere, many properties of this chemically sustained shock wave such as peak pressure, particle flow velocity, and power generation are all consistent with a detonation. Hence, Figure 3 demonstrates that hypervelocity impacts are not only capable of causing chemical reactions but also catastrophic chemical reactions leading to a detonation.

Whether or not a chemically sustained shock wave occurs depends on the mass and impact velocity of the flyer plate. Specifically, as the number of layers in the flyer plate is increased the minimum impact velocity for initiation decreases approaching an asymptotic value of about 4.5 km/sec. Thus, even macroscopically thick flyer plates must impact at hypervelocities to cause a chemically sustained shock wave in the model material. This result agrees with the observed insensitivity of crystalline explosives to initiation.
Summary

In summary, we have reported the results of a series of molecular dynamics simulations of hypervelocity impacts of an ultra-thin plate with a model diatomic molecular solid. At these high impact velocities even this ultra-thin plate is found able to induce a dissociative phase transition to a close-packed solid with accompanying complex behavior such as shock wave splitting. Although this close-packed phase persists for less than 10 ps and is confined to a domain less than 10 nm wide it still behaves in a manner consistent with continuum theory. Additional simulations of hypervelocity impacts of an ultrathin flyer plate with a model diatomic energetic material not only produce a dissociative phase transition but also extensive chemical reactions leading to a chemically sustained shock wave.

Acknowledgments

This work was supported in part by the Office of Naval Research both at NRL and at IUPUI. One of us (SBS) acknowledges a NRC/NRL Postdoctoral Research Associateship.

Bibliography


Received June 15, 1994