Revised: 7/19/2002

MOLECULAR DYNAMICS SIMULATIONS OF DETONATION IN DEFECTIVE EXPLOSIVE CRYSTALS

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Large-scale molecular dynamics simulations using a REBO (reactive empirical bond-order) model potential have been performed in order to investigate the detonation process in condensed phase explosives at a microscopic scale. Starting from a diatomic AB molecular crystal, shock initiation of the exothermic chemical reaction $2AB \rightarrow A_2 + B_2$ can lead to a steady detonation wave for sufficiently strong shock impacts. Perfect crystals are remarkably insensitive, requiring shock compressions of 25% (nearly 100 kbar) before delayed (homogeneous) initiation occurs in the shock-compressed (and heated) AB liquid. Point defects, such as vacancies or isolated A· or B· radical atoms, have no observable effect on this threshold, except in some cases to cause a few localized reactions that fail to propagate. On the other hand, extended structural defects can be quite effective at lowering the detonation threshold by providing heterogeneous initiation sites (hot spots). We report studies of void collapse in two-dimensional AB solids, focusing on the effect of void geometry (circular vs. elliptical) and size.

INTRODUCTION

Detonation of condensed-phase explosives involves a complicated energy transfer process, from delocalized lattice modes excited by shock compression, to internal molecular vibrations and rotations and eventually promotion of chemical reactions. Even for the ideal homogeneous detonation of fluids or defect-free crystals, differing points of view about this process have been put forth.[1-3] The challenge of directly probing a dynamic detonation wave traveling at several km/s suggests that a definitive experimental resolution of the situation is not to be expected anytime soon, despite great advances in ultrafast probes of shocked molecular solids.[4]

The situation becomes even murkier for heterogeneous detonation, which is the case in real-world (i.e., defective and polycrystalline or plastic-bonded) solid explosives. Here the initiation and growth of a detonation wave is largely dominated by the formation of localized "hot spot" regions of elevated temperature and reactivity.[5,6] Candidates for hot spots include cracks, voids, grain boundaries, shear bands, and other density inhomogeneities.[6]

Molecular dynamics simulations, in which the classical equations of motion are evolved on a specified potential energy surface, provide a possible insight into the underlying dynamics. In recent years, multimillion-atom simulations have been used to study shock-induced plasticity[7,8] and polymorphic phase transformations[9] in single-crystal metals. Samples containing 10^7 to 10^9 atoms, although still sub-micron in size (for a roughly cubic simulation cell), are large enough to study not only perfect single crystals, but also to introduce and study the effects of specific defects, such as grain boundaries, voids, dislocations, or combinations thereof, including nanocrystalline samples.

Karo and Hardy[10] appear to have carried out the first molecular dynamics simulations of shock-induced exothermic reactions. They followed shock waves through square lattices bonded by a predissociative pair potential. After the shock wave traversed the small length of the sample (consisting of less than 100 atoms), spallation was observed. This bond stretching resulted in a release of energy back into the crystal, which initiated a chain reaction of atoms being ejected from free surfaces until the crystal was completely destroyed.

A greater degree of realism was introduced by Carter White and his colleagues at the Naval Research Laboratory, who developed a many-body interatomic potential capable of describing a molecular solid.[11] Two-dimensional simulations of a reactive diatomic solid containing several thousand atoms exhibited a chemically sustained shock wave (as in Figures 1 and 2), with properties consistent with the continuum theory of unsupported planar detonations.[12]

REBO POTENTIAL

The empirical interatomic potential function which we have used is the REBO (reactive empirical bond-order) potential introduced by Brenner et al.[11,12] to describe a simple AB molecular system. The form consists of a short-ranged intramolecular Morse-like term

$$V_{bond}(r_{ij}) = V_r(r_{ij}) - \overline{B}_{ij} V_a(r_{ij}) \qquad (1)$$

and an intermolecular van der Waals attraction $V_{vdW}(r_{ij})$. The bond-order function $\overline{B}_{ij}$, first introduced by Tersoff[13] for covalent solids, goes monotonically from 1 to 0 with increasing coordination of atoms i and j. This smoothly transforms $V_{bond}(r_{ij})$ from a Morse potential (for $\overline{B}_{ij} = 1$) between two free radical atoms, to a purely repulsive interaction (for $\overline{B}_{ij} = 0$) between already bound (coordination 1) atoms. The detonation behavior of this model system (see Figures 1 and 2 for examples of unsupported detonations) has recently been reviewed.[14,15]

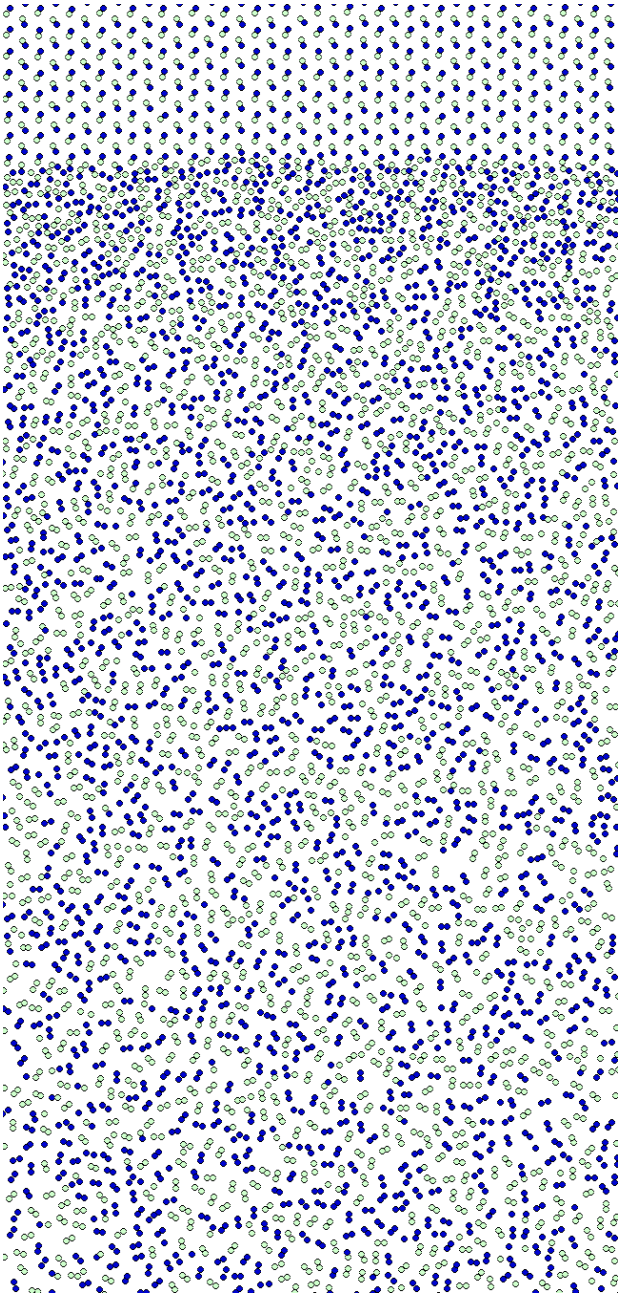

FIGURE 1. UNSUPPORTED DETONATION WAVE TRAVELING FROM BOTTOM TO TOP IN A TWO-DIMENSIONAL AB SOLID INITIATED BY A THIN INERT A_2 FLYER PLATE IMPACT. THE ATOMS ARE COLORED ACCORDING TO THEIR IDENTITY (EITHER A OR B). PERIODIC BOUNDARY CONDITIONS ARE APPLIED IN THE TRANSVERSE DIRECTION.

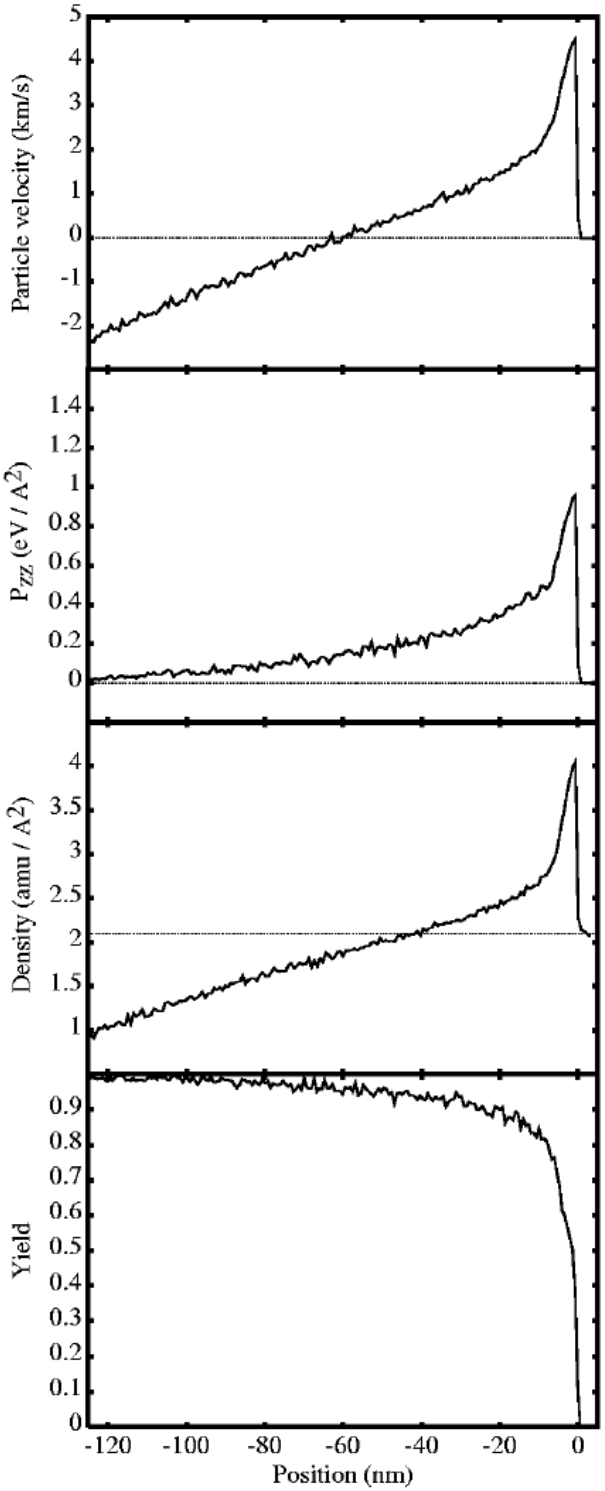

FIGURE 2. 2-D UNSUPPORTED DETONATION PROFILES. THE (PERIODIC) CROSS-SECTION IS 124 NM WIDE AND THE ENTIRE SAMPLE CONTAINS 234,200 ATOMS. YIELD IS DEFINED AS THE FRACTION OF ATOMS IN PRODUCT (A_2 OR B_2) MOLECULES.

In the present study, we use the functional form and parameters given in Ref. 12 (as corrected in the erratum), with a Morse well depth of 2.0 eV for reactant AB molecules and 5.0 eV for product A_2 and B_2 molecules, all with equilibrium bond lengths of 1.2 Å. The van der Waals well depth of 5.0 meV stabilizes a molecular crystal at low temperatures (below roughly 50 K), in a herringbone lattice (see Figure 1) in 2-D and the α-N_2 structure in 3-D. A more gradual cutoff of $V_{bond}(r_{ij})$ leads to a dissociative phase transformation,[11,14,15] and variation of the activation energy or exothermicity can have dramatic effects on the detonation velocity, reaction zone thickness, and the critical width of finite two-dimensional strips.[16,17]

VOID COLLAPSE STUDIES

Collapsing voids are key sources of local hot spots, an important step in the shock-to-detonation transition of condensed-phase energetic materials.[6,18] Fluid dynamics simulations by Mader[6] show a convergent jet impacting the downstream void wall, leaving behind a hot spot approximately the size of the original void. Molecular dynamics simulations have been used to study void collapse in three-dimensional inert atomic[19] and diatomic[20] solids. In the latter work,[20] a critical shock strength was found, below which the void wall remains intact as it collapses, and above which ejection of material into the void leads to a turbulent collapse and significantly greater vibrational excitation.

In addition to these closed (i.e., finite) void studies, elongated gaps, or "nanocracks," normal to the shock direction have been studied. Maffre and Peyrard[21] considered a detonation wave approaching a gap, and found that reinitiation occurs on the downstream side. More intriguing is the recent work of White and colleagues,[15] showing that a nonreactive shock wave can lead to ignition and growth of a stable detonation after crossing a gap, depending on the width of the gap (see Figure 8, below). Only recently has it been demonstrated[22] that the source of this width dependence is the PV work available from recompression of an expanding ejecta spray. (The traditional "gap test" involves a slab of inert material rather than a vacuum in the gap; this type of simulation has also been performed.[23])

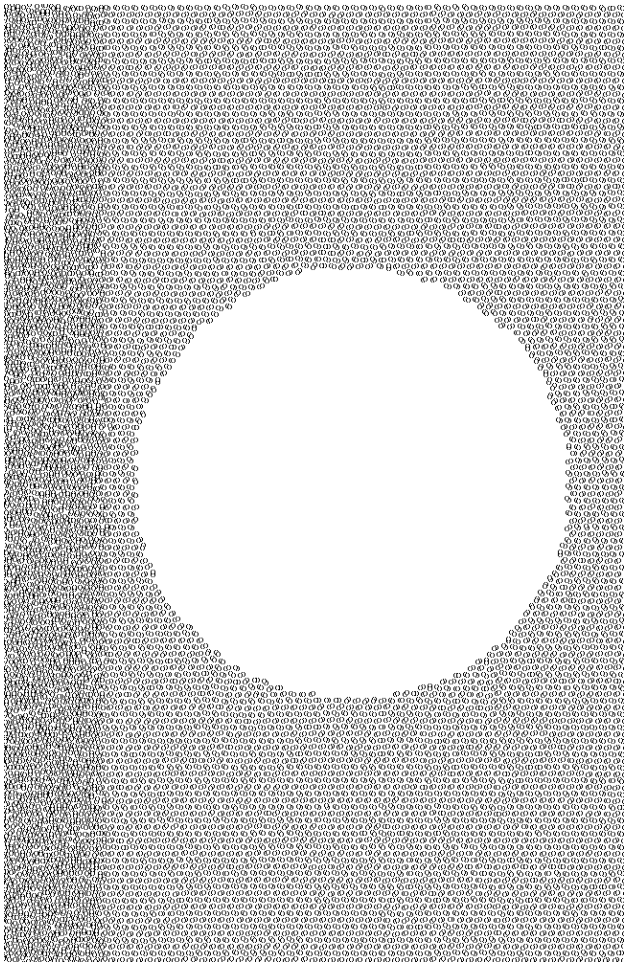

FIGURE 3. SUPPORTED NONREACTIVE SHOCK WAVE (WITH PARTICLE VELOCITY u_p = 1.38 KM/S) APPROACHING A 20 NM DIAMETER VOID, 0.25 PS BEFORE IMPACT. ONLY A CLOSE-UP PORTION OF THE ENTIRE (129 NM X 45 NM) SIMULATION CELL ARE SHOWN IN THIS AND FOLLOWING FIGURES.

Using large-scale simulations, we can now study the collapse of closed voids in an energetic solid; snapshots from one such simulation

are shown in Figures 3-5. As the (nonreactive) shock wave encounters the upstream side of the void, molecules are ejected and are focused towards the center of the downstream wall, as shown in Figure 4. The leading molecules of the ejecta spray are not sufficient to cause reaction upon impact in this simulation (Figure 4); only after the void is nearly closed does reaction occur and an expanding pressure wave develop (Figure 5). Further reactions occur until the product molecules occupy a circle roughly the size of the original void.

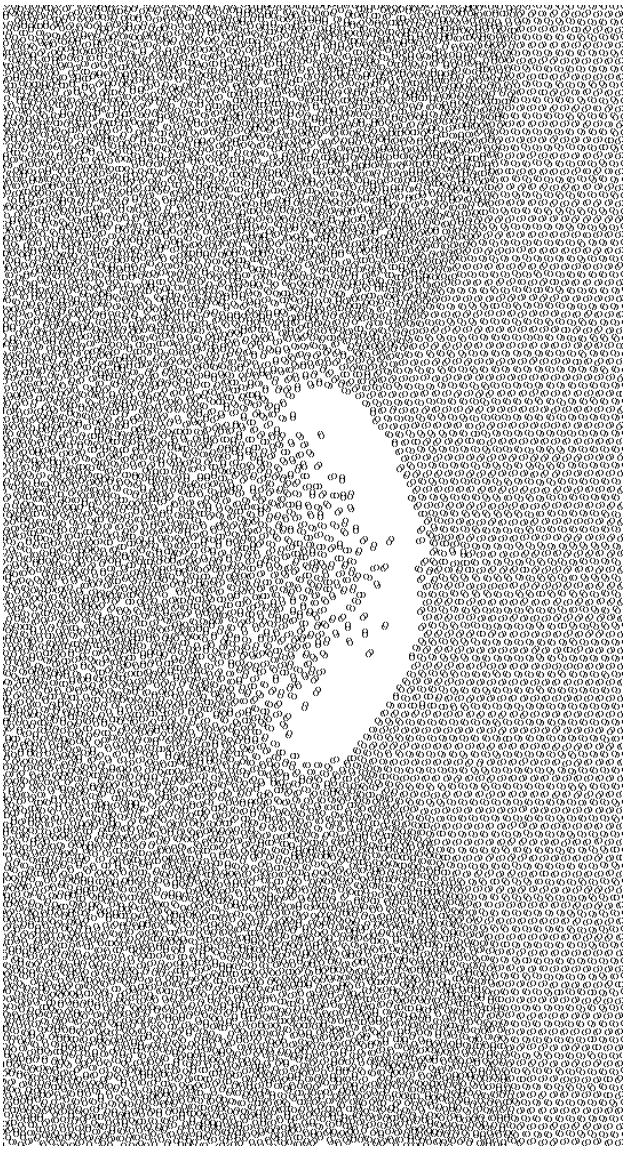

FIGURE 4. SAME AS FIGURE 3, 5.34 PS AFTER IMPACT.

It appears that the burning would be quenched at this point were it not for the periodic images in the transverse direction (the center-to-center distance between voids is 45 nm). Instead, collision of the expanding pressure waves induces a buildup to detonation in this particular simulation.

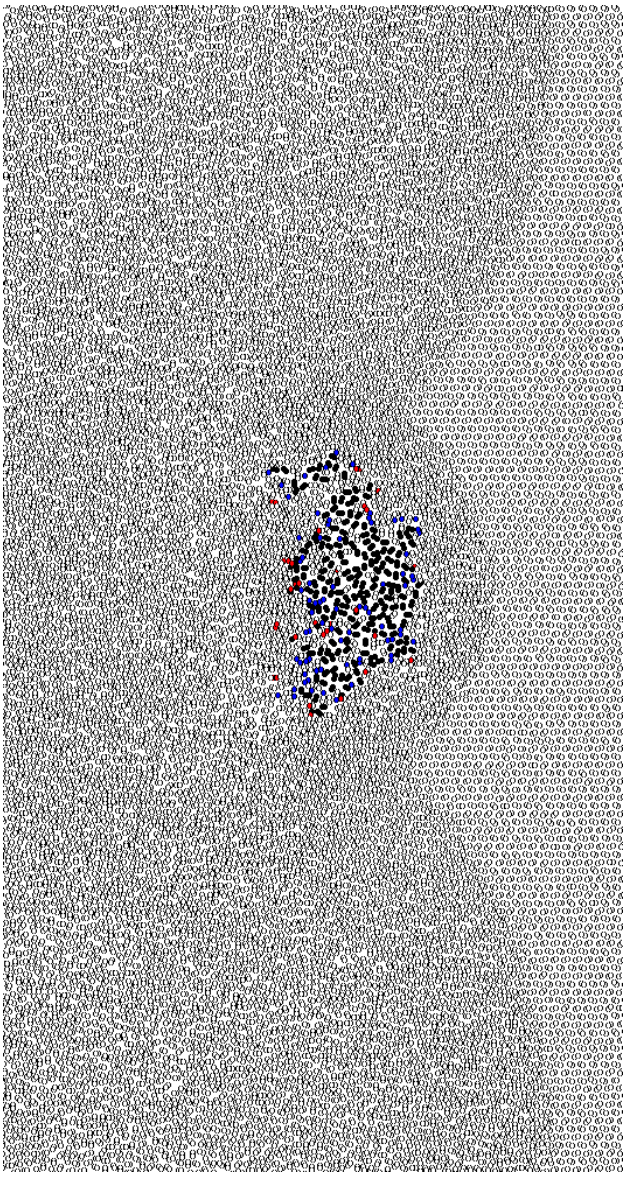

FIGURE 5. SAME AS FIGURE 3, 6.87 PS AFTER IMPACT. BLACK MOLECULES ARE A_2 OR B_2 PRODUCTS; RED AND BLUE ATOMS REPRESENT FREE RADICALS OR MANY-BODY REACTION COMPLEXES.

From simulations such as these, it is evident that the initiation process is not a direct mechanical one, but rather a thermal one which may occur long after the initial ejecta impacts. Whether or not reactions occur basically signal whether or not a critical reaction temperature T^* (dependent on pressure and the observation time) is exceeded locally. After presenting such "go/no go" results for elliptical voids in the next section, we conclude by discussing our nascent attempts to quantitatively predict such behavior.

COLLAPSE OF ELLIPTICAL VOIDS

To study void shape effects, we carried out a systematic series of calculations for elliptical voids having a 2:1 aspect ratio. (Such preferentially oriented voids might be created as a result of uniaxial pressing.) The geometry used is shown in Figure 6; an initially nonreactive shock wave is introduced from the left, travels a distance x_1 (chosen to be 160 unit cells, or approximately 100 nm in the current work) before encountering the void. Once the shock wave passes the void, it travels a further distance x_2 (chosen to be 80 unit cells, or approximately 50 nm in the current work), at which point chemical reactions either have or have not been caused by the void collapse. Because periodic boundaries are used in the transverse dimension, we need to introduce at least a modest spacing between periodically replicated voids (on the short timescale set by the transit time across x_2). This is done by setting the center-to-center distance between images to be equal to 3 times the void height a. (The distance of closest approach is thus 2a.)

The results of a series of such simulations are shown in Figure 7, for void areas ranging from 5 to 800 nm^2. Since initiation is a thermally activated process, the reaction probability varies continuously from 0 to 1 and multiple simulations are required near the "threshold" to determine where the 50% probability occurs. For a perfect crystal, the threshold shock strength, measured by the particle velocity u_p, is approximately 1.6 km/s.

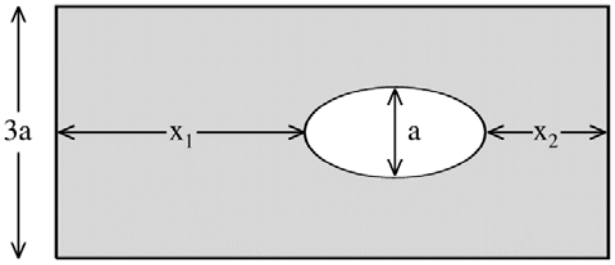

FIGURE 6. SIMULATION GEOMETRY USED FOR TWO-DIMENSIONAL ELLIPTICAL VOID STUDIES.

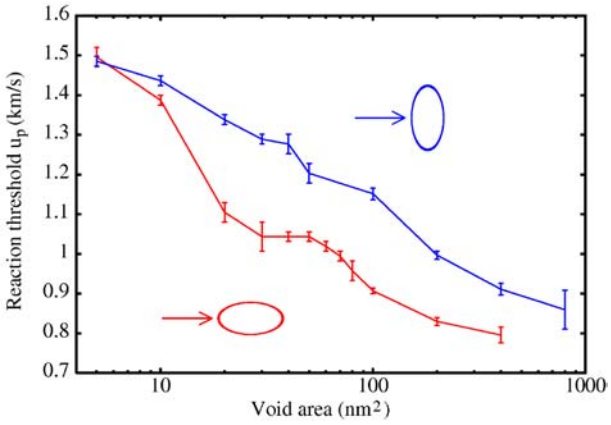

FIGURE 7. SHOCK STRENGTH (IN TERMS OF PARTICLE VELOCITY u_p) REQUIRED TO INITIATE CHEMICAL REACTIONS FOLLOWING COLLAPSE OF ELLIPTICAL VOIDS OF VARIOUS SIZES AND ORIENTATIONS.

We find a significant orientation dependence, with shock compression along the long axis of the void much more efficient (i.e., lower threshold u_p) than along the short axis. Two effects contribute to this; one is the smaller downstream area over which the ejecta spray is focused. The second is the longer transit distance, which allows the spray to expand further and provides more PV work upon recompression (an effect seen more clearly in the next section).

This type of data provides a demanding test of models for the initial void collapse temperature (that is, prior to subsequent heating by any exothermic reactions) as a function of shock strength and void shape and size.

INITIATION ACROSS THIN GAPS

In order to proceed further, it is helpful to eliminate the focusing effects of curved void surfaces, and instead first attempt to understand shock initiation across planar gaps.[15,22] Threshold results, analogous to those for elliptical voids in Figure 7, are shown in Figure 8.

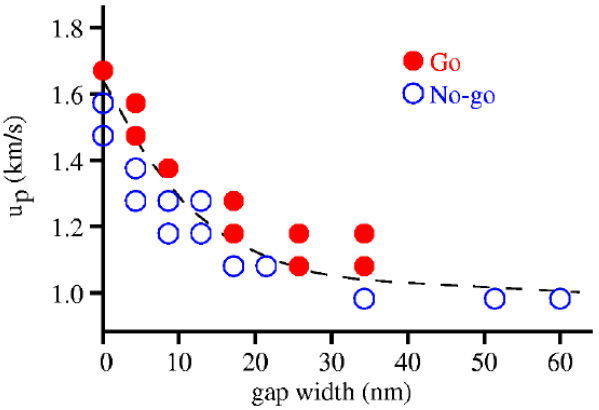

FIGURE 8. SHOCK STRENGTH (IN TERMS OF PARTICLE VELOCITY u_p) REQUIRED TO INITIATE CHEMICAL REACTIONS ACROSS VARYING GAP WIDTHS.

Recently, we have demonstrated that the key to understanding such behavior is the "crush-up" of an expanding ejecta spray.[22] The resulting pressure-volume work leads to a temperature rise across a gap width l equal to

$$T(l) = T(l=0) + \Delta T_{\max}(1 - e^{-l/l_0}), \qquad (2)$$

where the maximum temperature rise $\Delta T_{\max}$ can be estimated from the available PV work, and l_0 is a phenomenological length scale. Further work is needed to be able to predict l_0 and improve the estimate of $\Delta T_{\max}$, but once this is done, Equation (2) can be used along with a reaction threshold T^* value to predict the go/no-go data in Figure 8.

CONCLUDING REMARKS

Assuming that the ejecta crush-up model[22] can be used to predict go/no-go behavior for the simple gap geometry (Figure 8), the logical next step is to try to apply it to circular and elliptical void data such as Figure 7. If focusing effects due to void surface curvatures are minor, rectangular approximations will suffice and the extension to three-dimensional spherical voids would be straightforward. However, we already have a hint that focusing may be important: the planar gap data in Figure 8 approaches a limiting critical particle velocity u_p = 1.0 km/s with increasing gap width, but the ellipse data in Figure 7 is approaching an even lower threshold, 0.8 km/s or less. This suggests that focusing effects may contribute an additional temperature rise beyond that in Equation (2); we are currently analyzing temperature profiles from closed void collapse simulations to better understand this effect.

ACKNOWLEDGEMENTS

We gratefully acknowledge useful discussions with Ed Kober, Laurent Soulard, and Carter White. The work at LANL was supported by the Accelerated Strategic Computing Initiative (ASCI), under the auspices of the U.S. Department of Energy (contract number W-7405-ENG-48). Work at LBNL was supported by the Director, Office of Advanced Scientific Computing Research, Division of Mathematics, Information and Computing Sciences, U.S. Department of Energy (contract number DE-AC03-76SF00098).

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