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Initiation of detonations in three-dimensional crystals with defects

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Abstract. We examine shock-induced detonation in a three-dimensional model of a nitromethane crystal. The crystal may contain a defect in the form of a vacancy cluster, or small void. Three regimes are identified: the shock can be weak enough that no chemical bonds are broken; the shock can be so strong that a detonation front is established in the perfect crystal; or the shock can be of intermediate strength, where chemical activity is dependent on the existence of the defect. In all regimes, the defect increases the reaction rate and causes a hot spot to appear.

1. Introduction

The purpose of the work reported in this paper is to understand some of the peculiar properties of the initiation of detonations in solid chemical explosives. A detonation, as the term is usually used in these contexts, is a physico-chemical process with a characteristic structure [1]. This structure consists, in a solid, liquid or gas, of a shock wave followed by an induction zone, where endothermic chemical processes may begin, and a reaction front, where chemical energy is converted to particle motion. The mutual influences among these travelling interfaces is a complex process whose nature has been the subject of many investigations. For now we should merely point out that, on the one hand, the shock is the cause of the reaction front, for in its passage it creates the conditions which lead to a particular series of reactions, while, on the other hand, in a developed detonation the exothermic reaction front maintains the shock by supplying energy.

In the liquid and gas phases, those properties governing the nature of the detonation process are the chemical composition of the material along with its intensive thermodynamic variables, and the details of the method used to initiate the detonation. In a solid, even when all of these quantities are held constant, there may still be significant variability in the responses of a series of samples. For example, in an experiment in which crystals are detonated by mechanical impact, the variability may take the form of a wide range of impact energies necessary for detonation in apparently identical samples. A possible source of this variable response might be some uncontrolled variation in the experimental conditions, presenting different samples with an unknown variation in initial conditions. However, a sample of solid material, unlike a fluid, is characterized not only by its chemical composition and its thermodynamic state, but also by its particular spatial arrangement of molecules. The fact that the shock, or other mechanical disturbance taking part in the detonation, is a mechanical mode of vibration of the molecular lattice, whose nature is

dependent on the details of the structure of that lattice, implies that the spatial arrangement of molecules must influence the detonation process, including its initiation. What may be more surprising than this modest insight is the suggestion [2] investigated here, that certain minute changes in the molecular arrangement, otherwise known as lattice defects, may have a large, even determining, effect on the initiation of a macroscopic detonation. The idea that minute details of the lattice structure are relevant becomes more reasonable if we consider that the transfer of kinetic energy from a molecule to its neighbours in the direction of shock propagation involves the participation of only a few molecules (along the wavevector direction) in a particular vibrational mode at any one time, since the thickness of the shock front may be only a few lattice planes [3].

One traditional theoretical approach to understanding detonations, and the initiation of a detonation by a shock wave, involves a description in terms of thermodynamic variables that are related by an equation of state for the material [1]. The application of such equations of state depends on an often implicit assumption that thermodynamic equilibrium is achieved in the induction zone, and that through an equipartition process the energy in the lattice vibrations is shared with the chemical bonds. After these bonds have absorbed sufficient energy, they begin to break, and the chain of chemical reactions that comprise a detonation begins. This has been a fruitful model. However, because of the extremely small length and time scales involved in the detonation process in a solid, the applicability of the concept of thermodynamic equilibrium, and the equation of state approach that follows from it, has been called into question [4, 5, 6, 7, 8].

In previous work [9, 10, 11], we performed molecular dynamics simulations of the passage of a shock through a two-dimensional crystal containing various types of defect. We found that the shock's encounter with certain defects led to the rapid creation of a large fluid region within the crystal, and that the collision rate in the region was so high that an equilibrium distribution of molecular speeds was achieved on a very fast time scale, when the shock was still in the neighbourhood of the original defect location. This led us to speculate that in a reacting solid, an understanding in terms of thermal equilibrium may be relevant after all, since the thermalized fluid regions would presumably be the sites of chemical reactions, if their temperatures were high enough, and energy from detonation reactions could be available to accelerate the nearby shock.

Further exploration of these ideas required more realistic simulations, upon which we report in this paper.

2. Method

2.1. *The physical model*

In order to investigate the question of the effects of the details of the lattice structure on the initiation of a detonation, we have exploited as realistic a microscopic model as is now practical for three-dimensional calculations. The basic method used is computational molecular dynamics, where the forces between particles are calculated from additive classical potentials. The form of the potential between two particles depends only on the types of the particles, which determines the type of bond between them. The potentials were not adjusted in order to enforce the stability of a predetermined lattice structure. For the purpose of avoiding discontinuous force transitions, the potentials were truncated smoothly at a distance where the force magnitude is insignificant. This assists in energy conservation and numerical stability, but does not affect the results.

There are two classes of potentials employed. The intermolecular interactions are

governed by Morse potentials that are similar in form to the Lennard-Jones potentials used in some previous molecular dynamics calculations of solid detonations [12]. The intramolecular interactions, or the chemical bonds, are represented by a predissociative potential formed by the difference between two Morse potentials. This type of chemical bond model has been used successfully to model detonations in solids in several previous studies [13, 8]. Its use has a basis in the theoretical chemistry of the subject, where it is believed in some theories that the detonation of many energetic solids depends on the population of an excited state of the molecules in the lattice, followed by the breaking of a key molecular ('predissociative') bond [14]. According to this theory, the molecules can be considered to act as diatoms. Whether or not these ideas are correct, the predissociative diatomic model is useful in three dimensions, where more elaborate many-body chemical models, used sometimes in one- or two-dimensional simulations [15, 16], have not yet been attempted and may be too expensive.

Our model system is a diatomic, predissociative representation of crystalline nitromethane in a simple cubic configuration [12]. The nitromethane molecule consists of a CH₃ group, with a mass of 15 amu, bonded to an NO₂ group, with a mass of 46 amu. The bond is between C and N. The diatomic model treats each group as an unbreakable molecular unit; following common practice, we refer to the CH₃ group as 'C' and the NO₂ group as 'N', and the predissociative bond between them as the 'C-N bond' (the C and N groups are also often referred to as 'atoms').

The particular values of the parameters used in the potentials that we adopt here are due to the recent work of Maffre and Peyrard [17, 18], where the nitromethane potentials were scaled in order to produce an accurate sound speed. The intermolecular potential is given by

$$V(r - r_0) = E (e^{-S(r-r_0)} - 1)^2 - E$$

where the values of E , S , and r_0 depend on whether this is an N-N, N-C, or C-C interaction. The N-C intramolecular potential is given by

$$W(r - r_0) = E_a (e^{-S_a(r-r_0)} - 1)^2 - E_a - (e^{-S_b(r-r_0)} - 1)^2 - E_b.$$

Here r is the length of the chemical bond, and r_0 is its equilibrium length. The values of all the parameters are given in table 1. Also following [18] we use a mass of 15 amu for the C group and a mass of 47 amu for the N system.

Table 1. Parameters used in the intermolecular and intramolecular potentials.

	V_{N-N}	V_{C-C}	V_{C-N}	V_a	V_b
E (eV)	0.004	0.001	0.00075	7.93467	8.93467
S (\AA^{-1})	2.1	1.3	1.4	1.8650	1.5749
r_0 (\AA)	5.022	5.022	4.09	1.48	1.48

Preliminary calculations with results very similar to the results reported in this paper have been presented elsewhere [19]. The methods were the same, but the nitromethane model was less accurate, involving arbitrary values for some of the potential parameters. In addition, free crystal boundaries were used in all directions, which somewhat obscured the role of the lattice defects. These deficiencies have been corrected in this paper, but this experience shows that the essential character of the results do not depend in detail on the forms of the potentials used, nor on all the details of the model.

2.2. The numerical method

Some of the calculations reported here were performed on NRL's Cray-XMP, using a vectorized version of the monotonic Lagrangian grid (MLG) [20] algorithm. The use of these techniques for molecular dynamics calculations on Cray-type machines has been discussed in detail elsewhere [12]. Here we shall merely mention that the advantage of the MLG is that, at each timestep, a particle's neighbours can be identified quickly by cycling over a predetermined sub-region of an index space, rather than by searching through coordinate space with an expensive comparison of particle separations.

The bulk of the work reported here was performed on a Connection Machine CM-200 installed at NRL. This computer consists of 16384 separate processors, which can be divided into two completely independent banks of 8192 processors each. The hardware configuration used includes 64 bit floating point accelerators.

The algorithms described in [11] for two-dimensional nonreactive molecular dynamics calculations on the Connection Machine were readily adapted to the current three-dimensional reactive calculations. The parallelized MLG data structure fits naturally onto a space of any dimensionality. The only significant changes needed were an increase in book-keeping demanded by the multiple potentials used in the predissociative model. Rather than the one Lennard-Jones potential, there are now four distinct potentials. Also, in order to determine, in analysing the results, when a bond is broken, each particle (N or C group) must be assigned a unique index.

3. Results

The reference configuration used for all of the numerical experiments described here is identical, in form, with the 'type-1' stable lattice described in [12]. It is a simple cubic lattice of N groups, to each of which is bonded a C group. The position of each C group is obtained by adding the identical displacement to the x , y , and z coordinates of each N group; the displacements are chosen so that the length of the N-C bond is r_0 , given in table 1.

Our experience in previous calculations in two dimensions [10, 11] suggests that, of all the possible crystallographic defects, the most important in a shocked crystal are the small voids (also called 'vacancy clusters', because a single missing lattice site is called a vacancy). We use the term 'void', but it must be understood that these are voids on a molecular length scale, and their stability depends on a rigid lattice structure. These are not to be confused with the macroscopic or micron-sized voids that are known to be important in the shock initiation of, for example, liquids, where the voids are actually gas bubbles that can be heated by compression by a passing shockwave. The earlier molecular dynamics calculations of Karo, Hardy and Walker [21, 22] also suggested, indirectly, the importance of voids in a (two-dimensional) crystal, by demonstrating that a shock's encounter with a free surface results in spalling from the surface. This is relevant because a void involves free surfaces parallel to the shock front, but, as was shown elsewhere [9, 10, 11], the effect of a complete void interior to a crystal is completely different from a free surface or a gap.

A defective crystal is created by removing a contiguous handful of molecules from the reference crystal described above, leaving behind a slightly distorted lattice with an embedded void.

The method of driving a shock into the crystal is the same in all cases. The leftmost (referring to the orientation in the figures) plane of molecules is assigned a relatively large mass of 800 amu per group, and given an initial velocity to the right. The system is

then allowed to evolve freely under the action of its internal interparticle forces. Periodic boundaries are maintained transverse to the initial velocity direction, with a 75 Å periodicity length, while the left and right boundaries are free surfaces 156 Å apart. No moving computational window is employed; no particles are removed from or added to the system. These initial conditions simulate the action of a piston, in that a nearly planar left free surface is maintained, with a nearly constant velocity, but avoids the continual addition of energy to the system. Shocks of different strengths are produced by varying the initial 'piston' velocity. The shock speed itself is a characteristic of the material.

As is well known [12], it is possible to establish a detonation structure, in a simulation, in a three-dimensional crystal without defects. A detonation structure is a characteristic set of moving interfaces that delineate the shock, an induction zone, and a plastic or fluid reaction zone of reaction products. A detonation of a bulk solid is thought to consist of such detonation structures in each crystal domain of the solid, and simulations such as the ones reported on here are attempts to model the detonation structure in a part of one of the domains. Such a detonation structure can be simulated with the model and method we have described above, using a piston velocity greater than 2.0 km s^{-1} . As such results have appeared in the literature before [12] they will not be discussed in detail here. If a small void is added to the crystal lattice in such a simulation, we observe that the detonation front proceeds as before, with some distortion near the void site, and that a hot spot is formed as the front passes the defect. In addition, the defect is a region of enhanced early bond breaking, increasing the reactivity, or proportion of dissociated molecules to intact molecules, somewhat.

More interesting is the regime where the piston speed is small enough that a nonreacting shock is created in the defect-free crystal, but where the presence of a defect causes reactions to begin. Such a regime was found with a piston speed of 1 km s^{-1} and a defect consisting of 50 missing atoms. The evolution of the system containing the defect is illustrated in figure 1. This figure shows the atom positions, in a perspective view, with the slowest 24% of $(\text{speed})^2$ removed to show the internal structure, and with darker shades indicating higher speeds. The defect is buried in the interior of the system, so a plot of all the atoms obscures the details of interest. As the shock velocity is greater than the piston velocity, we can see the shock front running away from the left edge into the crystal in the first frame of the figure (figure 1(a)), which shows the configuration at 0.72 ps. The front is visible as the rightmost plane of displayed atoms; the leftmost two planes comprise the 'piston'; the planes visible between them are oscillating due to the passage of the shock. A small disordered region can be seen where the shock front has passed the defect, and a jet of atoms can be seen protruding from the void. The jet continues to grow until, in the second frame (figure 1(b)), at 1.4 ps, it has reached the free surface at the right. Further examination of the data shows that the fastest particles in the system are in this filament, and that the reason it progresses beyond the shock is that it consists of dissociated atoms that have absorbed the chemical energy stored originally in the C-N bond. The shock itself is purely mechanical, all bond breaking originating at the defect site.

Figure 2 is a plot of the number of free atoms (which is twice the number of broken C-N bonds) as a function of time, from close to the time of the shock-void encounter to the time at the end of figure 1, 1.4 ps. At the end of the simulation 300 atoms have become dissociated.

Their positions are shown in figure 3, which is a plot of the actual particle positions, but showing only dissociated atoms. Intact molecules are made invisible. Atoms are shaded according to their speed squared, with darker shades indicating higher speeds. The angle of view is identical to that in figure 1. We can see here, at 1.4 ps, a cluster of free atoms on the

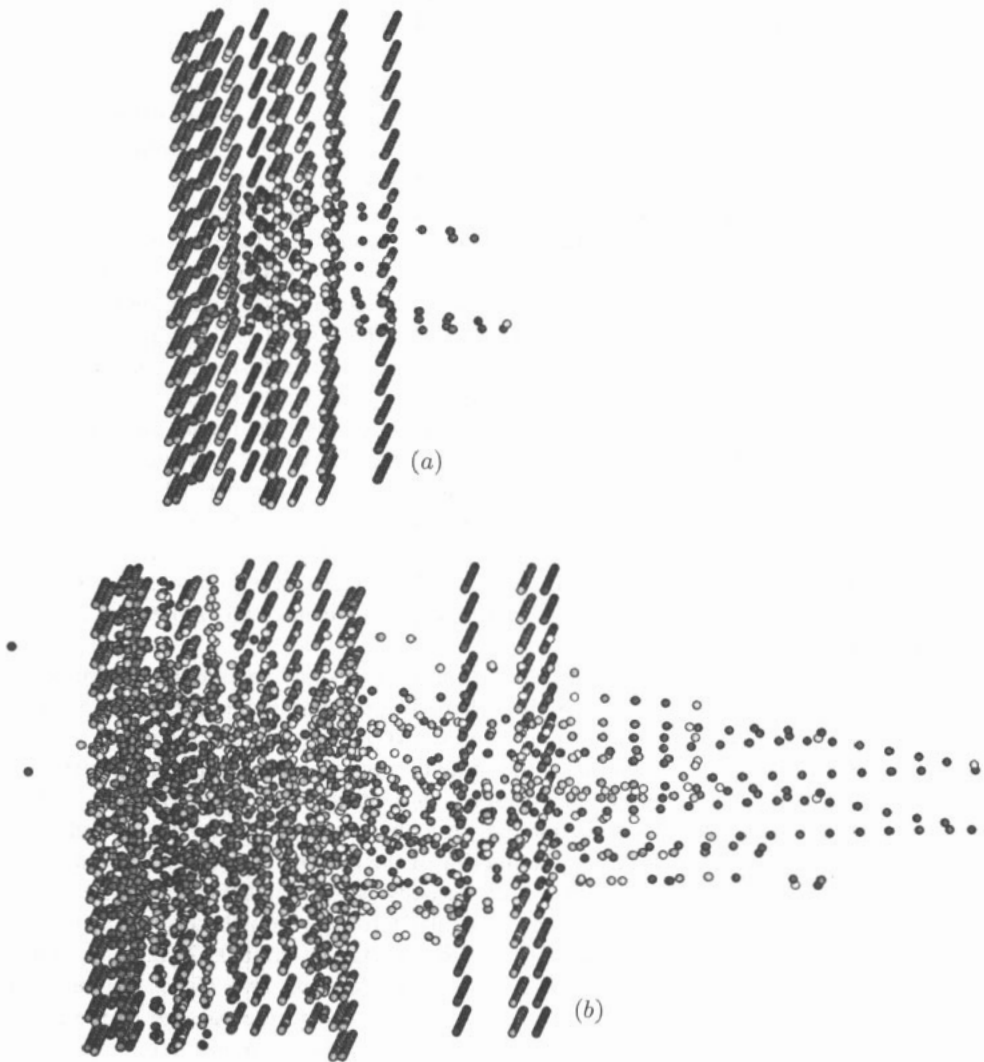


Figure 1. Perspective view of the atom distributions in a nitromethane crystal at (a) 0.72 ps and (b) 1.40 ps as a shock encounters a small void in the crystal lattice. Darker shades indicate higher speeds, and the slowest 24% of $(\text{speed})^2$ has been removed to show the internal structure.

left, at the defect site, and a jet of free atoms that has emerged from the void and extends almost completely through the crystal, showing that the jets seen in figure 1 consist partially of reaction products. A comparison of this figure with figure 1 shows that the tip of the jet of reaction products is accelerating the atoms ahead of it, which have not yet dissociated. In fact the figures show that the chaotic region of energetic molecules and reaction products at the defect site has produced what may be interpreted as the transient, filamentary origins of a detonation structure. Since the average velocity of propagation of this structure is higher than the shock speed, it reaches the end of the system when the shock front has traversed about half that distance. Most of the crystal ahead of the shock is not much affected by the

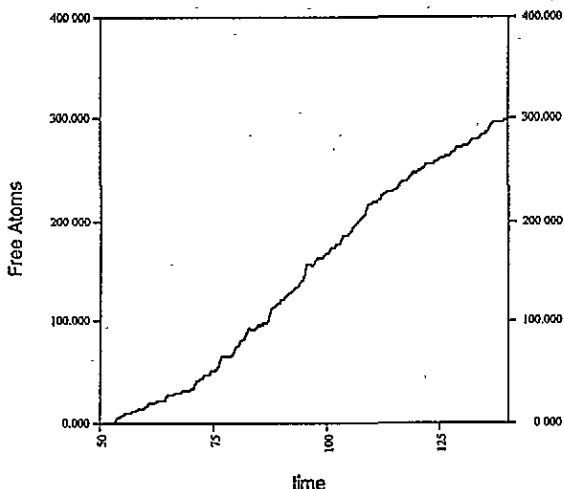


Figure 2. The number of unbonded atoms as a function of time (in hundredths of picoseconds).

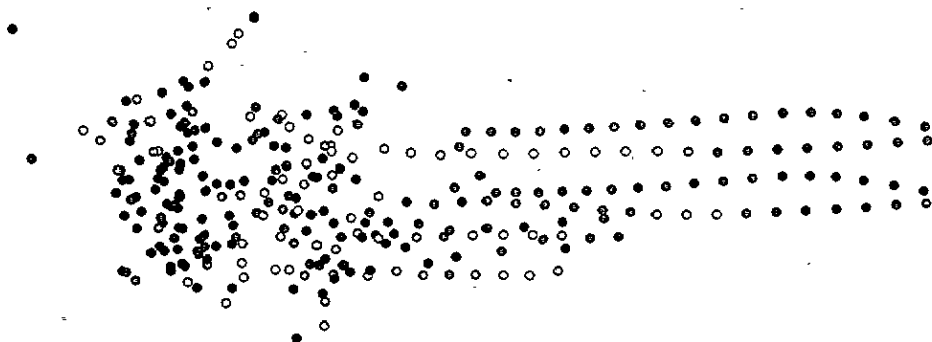


Figure 3. This figure corresponds to figure 1(b). Shown here are the locations of dissociated atoms only, with darker shades indicating higher speeds; a jet of reaction products can be seen extending from the defect site to the free end of the crystal on the right.

passage of this small detonation front, but the figures show a disturbance passing radially outward from the jet.

For the purpose of producing these figures, we needed to adopt a definition of 'dissociation' useful within the predissociative molecular model. An atom is considered dissociated if its current distance from the atom to which it was originally chemically bonded (bonded by the predissociative potential $W(r - r_0)$ given above) is greater than 3.0 Å. The 'breaking point' of the potential (its local maximum) is at about 2.0 Å, but the separation distance at which all the energy absorbed by the bond in stretching has been reconverted to kinetic energy is very close to 3.0 Å. Further separation of the N and C partners beyond 3.0 Å causes an extra conversion of bond energy into kinetic energy, and is the exothermic phase of the reaction. The precise definition of dissociation is somewhat arbitrary, but we have used this definition consistently. A plot of dissociated atoms can then be thought of as a diagram of all of those locations where the energy originally stored in chemical bonds is being supplied to the lattice as kinetic energy.

We believe these figures illustrate processes near a detonation threshold, for the following reasons. As mentioned above, if the piston speed is doubled, a fully developed detonation front is established quickly, without the need for a defect. If, at a piston speed of 1 km s^{-1} , the defect is removed, a reactionless shock traverses the system, leaving it undisturbed. Also, if the void used in the illustrated simulation is replaced by one with a smaller cross-section in the shock-front plane, and a smaller volume (32 missing atoms instead of 50), but the piston speed is not changed, the shock again traverses the system without any reactions occurring, but with some lattice disruption. It is reasonable to assume that there is a boundary for detonations that consists of a surface in a multidimensional space defined by excitation strength, void size and other factors, and it seems as if we have found a point near this surface. However, we do not yet know whether the reactions initiated by the shock-void interaction shown here would grow into a full detonation if given enough time, nor how long this might take.

4. Conclusions

Some intriguing experimental evidence has accumulated [23] (see also the printed discussion following [23]) that seems to show that defects, and perhaps, in particular, microscopic voids, might need to be present in order for single crystals of certain high explosives to be detonable. The evidence that this author has seen involves materials with a more complex molecular structure than nitromethane (which is a liquid at room temperature and pressure) and have therefore less chance of being represented reasonably by a diatomic molecular dynamics model. However, it is hoped that this type of molecular dynamics model captures some of the behaviour of any energetic solid where the detonation reaction always involves an endothermic phase, where the molecules absorb energy, followed by an exothermic phase, where reaction products supply kinetic energy to the crystal lattice and the shock propagating through it. Indeed, it has been shown [24, 12] that a detonation front with the correct structure, obeying local conservation laws, can result from any of a variety of molecular dynamics models. However, the length and time scales involved in the entire process of mechanical excitation of a crystal domain, followed by initiation of chemical reactions, and through to the eventual development of a steady state detonation front, are beyond the range of molecular dynamics simulations, at least using current computers, and probably for the foreseeable future. For this reason it is not yet possible to show, in such a simulation, that a defect will lead to the detonation of a crystal. Nevertheless, we have shown here that a molecular dynamics model that is known to be successful in reproducing many aspects of steady state detonations in solids can also capture the (very-short-time-scale) process of the creation of the first chemical reactions by a shock-void interaction. Since such reactions, and the long transient phase that follows, must occur before a detonation can develop, we believe that we have shown, for the first time, that a standard molecular dynamics model does provide some evidence that a void can enhance the sensitivity of a single crystal of energetic material. We can observe in this simulation a basic mechanism by which a void might initiate the shock-to-detonation transition; the simulation produces a reactionless shock, a chemically active hot spot at a defect site and an incipient detonation front, all of which can be seen simultaneously in a relatively small system of 16384 atoms.

Although it is still possible, with this model, to have a detonation without a defect, the defect always increases the rate of reaction in the initiation phase, and results in a hot spot. There is a regime where the shock is too weak to cause a detonation in the absence of a defect, but in this case a void will be the site of the release of chemical energy. Whether this reaction site is powerful enough to lead to the development of a mature detonation front

is beyond the scope of this study, and will have to wait for simulations on a larger scale, carried out for longer times.

Even if one's exploration of parameter variations is limited to changes in the piston speed, as defined here, and in the void size and shape, the expense of three-dimensional calculations prohibits the visiting of more than a small fraction of even the most important volume of the resulting parameter space. The use of massively parallel computer architectures, which are well suited to the simulation of multiparticle problems with short-range potentials, reduces the turn-around time of these simulations and eases this task, but the difficulty persists. For these reasons we have not attempted to delineate, quantitatively, the initiation threshold as a function of void dimensions.

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