Non-Equilibrium Zeldovich-Von Neumann-Doring Theory and Reactive Flow Modeling of Detonation

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This paper discusses the Non-Equilibrium Zeldovich - von Neumann - Doring (NEZND) theory of self-sustaining detonation waves and the Ignition and Growth reactive flow model of shock initiation and detonation wave propagation in solid explosives. The NEZND theory identified the non-equilibrium excitation processes that precede and follow the exothermic decomposition of a large high explosive molecule into several small reaction product molecules. The thermal energy deposited by the leading shock wave must be distributed to the vibrational modes of the explosive molecule before chemical reactions can occur. The induction time for the onset of the initial endothermic reactions can be calculated using high pressure, high temperature transition state theory. Since the chemical energy is released well behind the leading shock front of a detonation wave, a physical mechanism is required for this chemical energy to reinforce the leading shock front and maintain its overall constant velocity. This mechanism is the amplification of pressure wavelets in the reaction zone by the process of de-excitation of the initially highly vibrationally excited reaction product molecules. This process leads to the development of the three-dimensional structure of detonation waves observed for all explosives. For practical predictions of shock initiation and detonation in hydrodynamic codes, phenomenological reactive flow models have been developed. The Ignition and Growth reactive flow model of shock initiation and detonation in solid explosives has been very successful in describing the overall flow measured by embedded gauges and laser interferometry. This reactive flow model uses pressure and compression dependent reaction rates, because time resolved experimental temperature data is not yet available. Since all chemical reaction rates are ultimately controlled by temperature, the next generation of reactive flow models will use temperature dependent reaction rates. Progress on a statistical hot spot ignition and growth reactive flow model with multistep Arrhenius chemical reaction pathways is discussed.

INTRODUCTION

The Non-Equilibrium Zeldovich - von Neumann – Doring (NEZND) theory was developed to identify the non-equilibrium chemical processes that precede and follow exothermic chemical energy release within the reaction zones of self-sustaining detonation waves in gaseous, liquid and solid explosives (1-10). Prior to the development of the NEZND model, the chemical energy released was merely treated as a heat of reaction in the conservation of energy equation in the Chapman-Jouguet (C-J) (11,12), Zeldovich – von Neumann-Doring (ZND) (13-15), and curved detonation wave front theories (16). NEZND theory has explained many experimentally determined detonation wave properties. These include: the induction time delays for the onset of chemical reaction; the rapid rates of the chain reactions that form the reaction product molecules, the de-excitation rates of the initially highly vibrationally excited products; the feedback mechanism that allows the chemical energy to sustain the leading shock wave front at an overall constant detonation velocity; and the establishment of the complex three-dimensional Mach stem structure of the leading shock wave fronts common to all detonation waves. The current status of the NEZND theory is discussed in this paper.

Along with a physical understanding of the processes that occur within the reaction zone of a detonation wave, it is also necessary to have a practical reactive flow model that can be used to

predict shock initiation and detonation wave propagation in one-, two-, and three-dimensional hydrodynamic computer codes. The Ignition and Growth model (17) has been very successful in this regard. It was formulated using compression and pressure dependent reaction rate laws, because the computers were not large enough to handle temperature dependent rates, and there was little or no time resolved temperature data. The current status of the Ignition and Growth model is discussed in this paper. While there is still very little time resolved temperature data, several new experimental efforts have been started to obtain such data. Computers are now large and fast enough to handle mesoscopic models, so temperature dependent reactive flow model development has begun at several laboratories. Its current status is discussed.

NEZND THEORY OF DETONATION

Figure 1 illustrates the various processes that occur in the NEZND model of detonation in condensed explosives. At the head of every detonation wave is a three-dimensional Mach stem shock wave front. There has long been a debate concerning the definition of the width of a shock wave. Zeldovich and Raizer (18) defined shock wave width as the distance at which the viscosity and heat conduction become negligible. Behind the shock front in solid explosives, the phonon modes are first excited, followed by multi-phonon excitation of the lowest frequency vibrational (doorway) modes and then excitation of the higher frequency modes by multi-phonon up-pumping and internal vibrational energy redistribution (IVR)(19). Internal energy equilibration is being studied in shocked liquid and solid explosives by Dlott et al. (20) and Fayer et al. (21). Only after the explosive molecules become vibrationally excited can chemical reactions begin.

For gaseous explosives, the non-equilibrium processes, which precede chemical reaction are easily measured, because they occur in nanosecond or longer time frames. They are easily calculated using the perfect gas law (2). The high initial densities of solids make the measurement and calculation of the states attained behind a shock wave more difficult, because the processes now take tens and hundreds of picoseconds and the perfect gas law does not apply. The distribution of the shock compression energy between the potential (cold compression) energy of the unreacted liquid or solid and its thermal energy is also a complex function of shock strength.
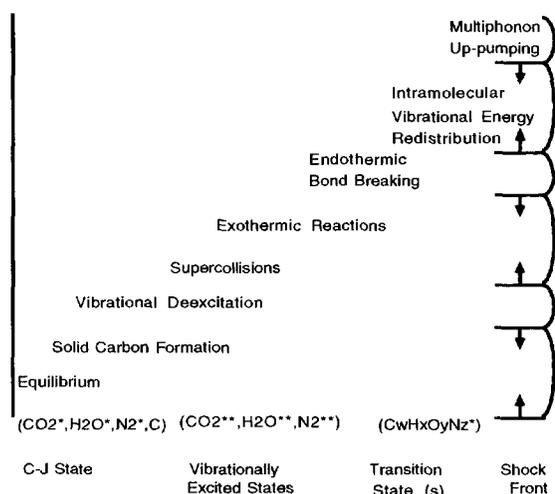

FIGURE 1. The Non-Equilibrium Zeldovich - von Neumann-Doring (NEZND) model of detonation for condensed phase explosives

The induction time for the initial endothermic bond breaking reaction can be calculated using the high pressure, high temperature transition state theory. Experimental unimolecular gas phase reaction rates under low temperature ($<1000°$) shock conditions obey the usual Arrhenius law:

$$K = A\,e^{-E/RT} \qquad (1)$$

where K is the reaction rate constant, A is a frequency factor, E is the activation energy, and T is temperature, at low temperatures, but "fall-off" to less rapid rates of increase at high temperatures (22). Nanosecond reaction zone measurements for solid explosives overdriven to pressures and temperatures exceeding those attained in self-sustaining detonation waves have shown that the reaction rates increase very slowly with shock temperature (23). Eyring (24) attributed this "falloff" in unimolecular rates at the extreme temperature and density states attained in shock and detonation waves to the close proximity of vibrational states, which causes the high frequency mode that becomes the transition state to rapidly equilibrate with the surrounding modes by IVR. These modes form a "pool" of vibrational energy in which the energy required for decomposition is shared. Any large quantity of vibrational energy that a specific mode receives from an excitation process is shared among the modes before reaction can occur.

Conversely, sufficient vibrational energy from the entire pool of oscillators is statistically present in the transition state vibrational mode long enough to cause reaction. When the total energy in the vibrational modes equals the activation energy, the reaction rate constant K is:

$$K = (kT/h) \, e^{-s} \sum_{i=0}^{s-1} (E/RT)^i \, e^{-E/RT} / \, i! \quad (2)$$

where k, h, and R are Boltzmann's, Planck's, and the gas constant, respectively, and s is the number of neighboring vibrational modes interacting with the transition state. The main effect of this rapid IVR among s+1 modes at high densities and temperatures pressures. is to decrease the rate constant dependence on temperature. Reasonable reaction rate constants were calculated for detonating solids and liquids using Eq. (2) with realistic equations of state and values of s (4). For the lower temperatures attained in shock initiation of homogeneous liquid and solid explosives, the reaction rate constants calculated using Eq. (2) are larger than those predicted by Eq. (1). Reaction rate constants from Eqs. (1) and (2) are compared to induction time results for liquid nitromethane, and single crystal PETN in Figs. 2 and 3, respectively (6). Despite uncertainties in the calculated shock temperatures for various equations of state, it is clear that Eq. (2) agrees quite well with both sets of data using reasonable values of s. Thus high pressure, high temperature transition state theory accurately calculates induction times for shock initiation and detonation of homogeneous liquid and heterogeneous solid explosives. Once a sufficient number of radicals form, the action starts.

Following the induction and endothermic initial bond breaking processes, exothermic chain reaction processes follow in which reaction product gases are formed in highly vibrationally excited states (2). These excited products either undergo reactive collisions with the surrounding explosive molecules or non-reactive collisions with their neighbors in which one or more quanta of vibrational energy is transferred. Some collisions are "super-collisions"(25) in which several quanta of vibrational energy are transferred. Since reaction rates increase rapidly with each quanta of vibrational energy available, reactive collisions dominate and the main chemical reactions are extremely fast. Once the chain reactions are completed, the remainder of the reaction zone is dominated by vibrational de-excitation of the
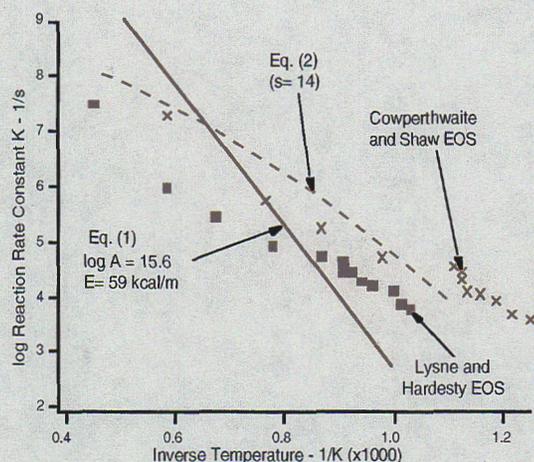

FIGURE 2. Reaction rate constants for nitromethane as functions of shock temperature
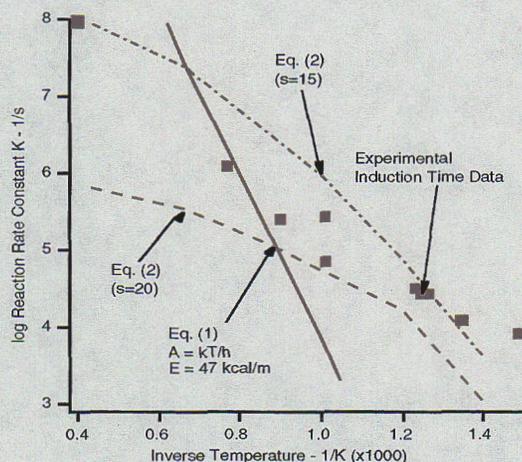

FIGURE 3. Reaction rate constants for single crystal PETN as functions of shock temperature

gaseous molecules and solid carbon formation.

This de-excitation process controls the length of the reaction zone and provides the chemical energy necessary for shock wave amplification during shock-to-detonation transition (SDT) and self-sustaining detonation (7). As pressure wavelets pass through the subsonic reaction zone, they are amplified by vibrational de-excitation processes. The opposite effect – shock wave damping by a non-equilibrium gas that lacks vibrational energy after expansion through a nozzle – is a well-known phenomenon

(18). These pressure wavelets then interact with the main shock front and replace the energy lost during compression, acceleration and heating of the explosive molecules. During shock initiation, this interaction process increases the shock front pressure and velocity. If the initial shock wave is accelerated to a velocity at which chemical reaction occurs close to the front, then self-sustaining detonation occurs. The pressure wavelet amplification process then provides the required chemical energy by developing a three-dimensional Mach stem shock front structure.

IGNITION AND GROWTH MODELING

It has long been known that shock initiation of solid explosives is controlled by ignition of hot spots (26). How large and how hot does a hot spot have to be to react and begin to grow? Critical conditions for the growth or failure of hot spots in HMX- and TATB-based explosives have been calculated using multistep Arrhenius chemical kinetic decomposition models derived from thermal explosion experiments (27). Figure 4 shows the calculated critical spherical hot spot temperatures in HMX and TATB. Once ignited, the growth rates of reacting hot spots into neighboring solid explosive particles and the interactions of several growing hot spots have been calculated for various geometries (28). Figure 5 shows the times required for spherical HMX particles of various radii to complete inward deflagration under various boundary temperature conditions. These relatively long times show that large explosive particles must fragment, producing smaller particles with more reactive surface area for hot gaseous reaction products to ignite. As growing hot spots coalesce at high pressures and temperatures, the transition from shock induced reaction to detonation occurs very rapidly. The buildup of pressure and particle velocity behind the shock wave front during shock initiation has been thoroughly studied using embedded gauge (29,30) and laser interferometric (31,32) techniques.

These reactive flows have been modeled in multidimensional codes by the Ignition and Growth model (17). Figure 6 shows measured and calculated pressure histories obtained for shock initiation of the TATB-based explosive LX-17 (33). Figure 7 shows the measured and calculated interface histories for LX-17 detonating into various salt crystals. Figure 8 shows measured and calculated free surface velocities of 0.267 mm thick tantalum discs driven
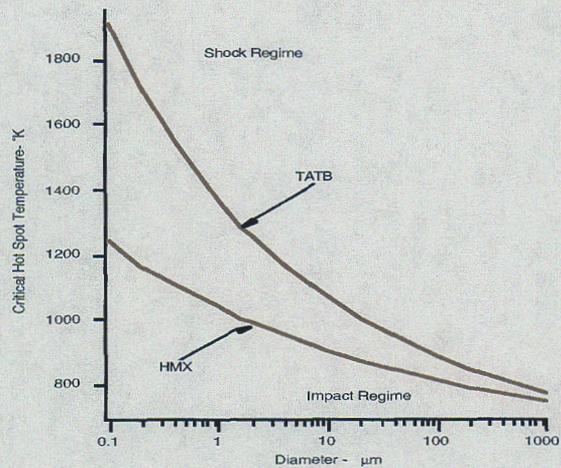

FIGURE 4. Critical spherical hot spot temperatures in HMX and TATB at various diameters
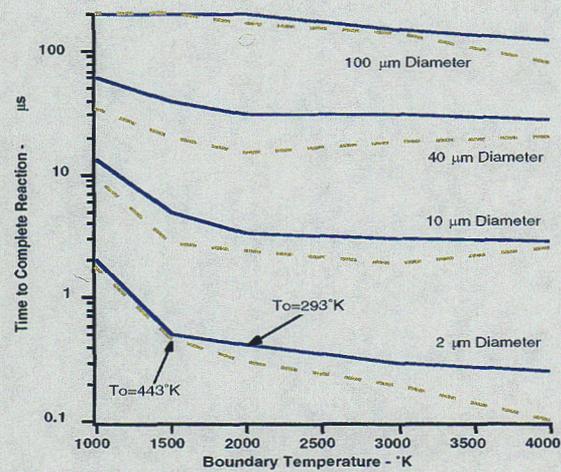

FIGURE 5. Reaction times for HMX particles

by 19.871 mm of detonating LX-17 (34).

The Ignition and Growth model has been applied to a great deal of shock initiation data on short pulses, multiple shocks, ramp waves, colliding shocks, diverging waves, etc. (35) and detonation data on failure diameter, curvature, corner turning, divergence, convergence, etc. (36). However, if used improperly, its reaction rates can overestimate the extent of reaction in multiple shock waves.
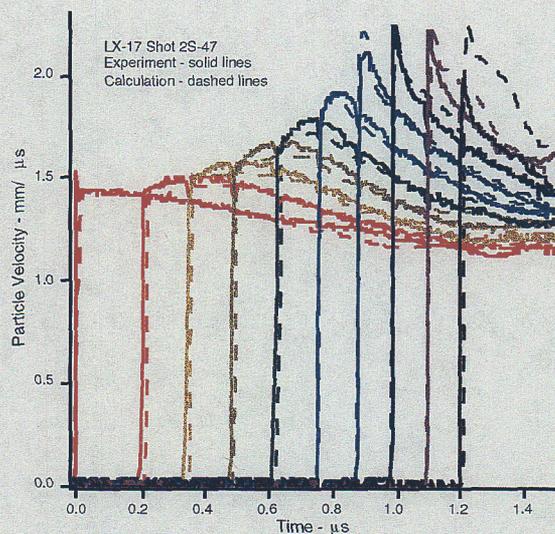
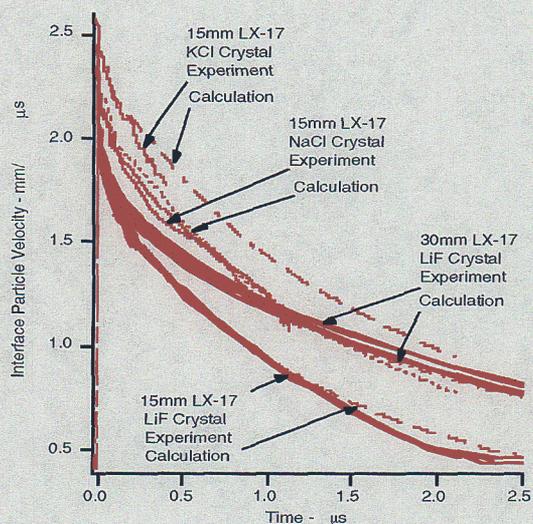FIGURE 6. Pressure histories for ambient temperature LX-17 shock initiated by a Kel-F flyer at 2.951 mm/μs

FIGURE 7. Interface particle velocity histories for detonating LX-17 and various salt crystals

FUTURE RESEARCH

Since all chemical reaction rates are controlled by the local temperature in a region of molecules, the most urgent need in explosives is for time resolved
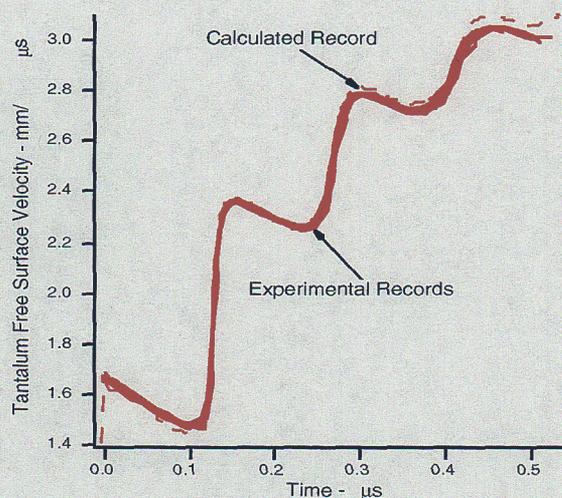

FIGURE 8. Free surface velocities for 0.267 mm thick tantalum disks driven by 19.871 mm of LX-17

experimental measurements of temperature in all regions of reacting explosives: in and around impact produced hot spots; in deflagration waves; in the reactive flows behind shock fronts; and in detonation waves. Assuming that this type of data will soon become available, the next generation of reactive flow models will be based entirely on Arrhenius temperature dependent rate laws. A mesoscale model has been formulated in which individual particles of a solid explosive plus their binders and voids are meshed, shocked, and either react or fail to react using Arrhenius kinetics (37). Zoning of individual particles is still impossible for practical problems even with today's parallel computers, so a continuum statistical hot spot reactive flow model is currently being developed in the ALE3D hydrodynamic computer code (38). In this model, realistic numbers of hot spots of various sizes, shapes, and temperatures based on the original void volume, particle size distribution and temperature of the solid explosive are assumed to be created as the initiating shock front compresses the explosive particles. The hot spots then either react and grow into the surrounding explosive or fail to react and die out based on the multistep Arrhenius kinetics rates used to generate Figs. 4 and 5. The coalescence of growing hot spots at high pressures and temperatures, the creation of additional surface area available to the reacting sites as the pressure rises, and the rapid transition to detonation are three of the

most challenging current problems under investigation. Results from several mesoscale models and the statistical hot spot reactive flow model will be presented at the upcoming Twelfth International Detonation Symposium.

Vibrational de-excitation has been postulated as the physical mechanism by which the chemical energy supports the detonation wave front at an overall constant velocity (2,7). This process seems to be a very general phenomenon that occurs whenever exothermic chemical energy is released as an acoustic or shock wave is propagating through the region. Relaxation of vibrationally excited molecules within wavelets of the correct frequencies is the most likely explanation of acoustic wave amplification, flame acceleration (39), deflagration to detonation transition, shock acceleration in heterogeneous explosives, and detonation wave propagation.

ACKNOWLEDGMENTS

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