Quantum Mechanics and Molecular Dynamics Calculations Provide New Evidence for a Free-Radical Shock Initiation Model

F. E. Walker

Lawrence Livermore National Laboratory, University of California, Livermore, California 94550 (USA)

Quantenmechanische und molekular-dynamische Berechnungen liefern einen neuen Beweis für das Modell der freien Radikale bei Stoßzündung

Der Unterschied zwischen einem hydrodynamischen Modell für die Stoßzündung von Sprengstoffen und einem neueren mikroskopischen Modell der freien Radikale wird aufgezeigt. Die grundlegende Betrachtungsweise beim Modell der freien Radikale ist, daß die Stoßenergie sehr kohärent ist und daß diese stark genug ist, den mechanischen Bruch der kovalenten Bindungen herbeizuführen. Die Stoßfront bei der mikroskopischen Betrachtungsweise ist sehr schmal (~ 5 Å – 15 Å), ein thermisches Gleichgewicht an der Frontseite existiert nicht. Die freien Atome und Radikale, die gebildet werden in der Stoßfront durch Scher- und Beschleunigungskräfte, leiten die chemische Reaktion ein, die zur Entstehung von Hot-spots und zur möglichen Zersetzung des Sprengstoffs führt. Die Geschwindigkeit der Energiefreisetzung und die Schwingungsintensität der kovalent gebundenen Atome sind Faktoren, die die Detonationsgeschwindigkeit festlegen. Zahlreiche Sprengstoffeigenschaften werden diskutiert, soweit das neue Modell dafür Erklärungen liefert. Neue Erkenntnisse aus molekular-dynamischen und quantenmechanischen Berechnungen für Stoßwellen in kondensierten Systemen und frühere experimentelle Daten werden zur Stützung des Modells der freien Radikale aufgeführt.

Calculs de mécanique quantique et de dynamique moléculaire apportant une nouvelle preuve de la validité du modèle des radicaux libres pour l'amorçage par onde de choc

On rappelle la différence entre un modèle hydrodynamique décrivant l'amorçage des explosifs par onde de choc et un modèle microscopique plus récent, qui fait appel aux radicaux libres. Dans le modèle des radicaux libres on admet essentiellement que l'énergie du choc est très cohérente et qu'elle suffit pour provoquer la rupture mécanique des liaisons covalentes. A l'échelle microscopique, le front de choc est très mince (~ 5 Å – 15 Å) et il n'existe pas d'équilibre thermique au niveau du front. Les atomes et radicaux libres qui se forment dans le front de choc sous l'effet des forces de cisaillement et d'accélération, déclenchent la réaction chimique qui conduit à l'apparition de points chauds et éventuellement à la décomposition de la substance explosive. Le taux d'énergie libérée et la fréquence de vibration des atomes à liaison covalente, sont des facteurs qui déterminent la vitesse de détonation. A la lumière des explications que peut en fournir ce nouveau modèle, on examine différents comportements des explosifs. Pour confirmer le modèle des radicaux libres, on fait appel à de nouvelles connaissances acquises dans le domaine des calculs de dynamique moléculaire et de mécanique quantique sur la propagation des ondes de choc dans les milieux condensés, ainsi qu'à des données expérimentales antérieures.

Summary

The contrast between a hydrodynamic model for shock initiation of explosives and a newer microscopic free-radical model is presented. The primary considerations of the free-radical model are that shock energy is very coherent and that it is strong enough to cause mechanical fracture of covalent bonds. The shock front on a microscopic scale is very narrow (~ 5 Å to 15 Å) and thermal equilibrium does not exist in the front. The free atoms and radicals formed by the shear and acceleration forces in the shock front initiate the chemical reaction that leads to hot spots and the eventual decomposition of the explosive materials. Energy-release rates and vibrational velocities of the covalently bound atoms are factors in establishing detonation velocities. A number of explosives phenomena are discussed as the new model provides explanations for them. New information from molecular dynamics and quantum mechanical calculations on shock waves in condensed systems and recent experimental data are shown to support the free-radical model.

1. Introduction

Computer-generated movies from molecular dynamics calculations[1–5] have provided new insight into the microscopic processes that lead to initiation and appear to be relevant to detonation of explosives. Additionally, the analogy of a shock barrier[6, 7] and a different perception of the temporal and dynamic aspects of these microscopic processes[7] suggest that one could take a different view of the importance of energy-release rates and other physical and chemical factors in initiation and detonation.

Recent quantum mechanical studies of anharmonic oscillators[8] and representative explosives bonds[9], along with new experimental evidence of shock-induced intramolecular bond fracture in RDX, TNT, ammonium nitrate[10], and polymeric solids[11] have shown that shock energy is very coherent, and it is probable that a substantial amount of mechanical bond fracture occurs in moderately shocked condensed systems. It has been reported that the Soviets have obtained experimental evidence of shock-induced chemical reaction in both liquids and solids[12]. Graham has stated, "The recent electrical work on polymers and the Soviet solid state chemistry work provide further support for the 'catastrophic shock' concept rather than 'benign shock' concept as the appropriate description for the state of shock-loaded solids. The catastrophic shock concept appears to offer the appropriate framework for explanation of many of the outstanding anomalies of shock wave physics"[12].

Owens and Sharma have written, "Only very recently has there been discussion of possible microscopic mechanisms which address the question of how a shock impulse can initiate rapid exothermic chemical reactions that lead to detonation in explosive solids. One plausible proposal envisions the shock wave breaking molecular bonds of the constituent molecules of the condensed explosive producing radicals, highly reactive molecular fragments with net unpaired electron spin"[10]. They further conclude in their discussion, "The results of these experiments provide direct evidence that a shock of peak pulse less than that necessary to cause detonation can break or alter internal molecular bonds of the constituent molecules of an

explosive solid . . . . These results then show that the first step in the initiation process is an endothermic breaking of the internal bonds of the molecules or molecular ions that constitute the lattice."

Dremin and Klimenko have presented the results of their molecular dynamics calculations of shock waves in both solids and liquids[13] and have reached the same conclusions presented in our earlier work[1–5]. These are:

(1) the shock energy stays very coherent in a shock-front region approximately 10-Å to 15-Å wide;

(2) the material in the shock-front zone is not in thermal equilibrium, and in fact, the normal concept of temperature in this region is not applicable;

(3) the transit of the shock across complex molecules (e.g., explosive molecules) causes destruction of some of the molecules and the formation of active molecular fragments;

(4) these active particles give rise to chemical reactions in individual centers.

Dremin and Breusov have stated that shock-induced chemical and physical processes are different from those that occur from solely thermal effects[14]. The carbon skeletons of benzene, naphthalene, and anthracene, which are very stable to thermal decomposition, are destroyed by shock waves. Different types of polymers, including those with higher molecular weights, can be formed by shock-induced processes in contrast to the chemical methods generally used. A new, very dense form of boron nitride with properties similar to diamond has been produced. Chloroform and chlorobenzene have been made by shocking mixtures of benzene and carbon tetrachloride. Many other reactions of polymeric monomers and small organic molecules are reported in this and other Soviet literature[12].

Other studies[15–24] further show an acceptable rationale and evidence for the importance of free-radical and chain reactions, particularly in early phases of the chemistry of initiation to explosion and detonation.

2. The Free-Radical Shock Initiation Model

A more complete free-radical model for shock initiation and detonation of explosives is proposed here. This model has been developed as an extension of a free-radical model derived from our early experiments[25] and new insights obtained through our recent experimental and calculational studies[1–5]. Our early studies provided substantial evidence for the acceleration of a non-initiating shock front by the release of a significant amount of energy at or very near the front. We observed initiation in nitromethane at much shorter times (10^{-5} s versus 10^{-1} s) and by an apparently different mechanism than had been generally presumed[26]. We also obtained photographs of the initiation patterns in both homogeneous and heterogeneous explosives at relatively low pressures that suggested new initiation models might be required[26, 27]. The new model is constructed from the following concepts and observations.

First, a shock wave in a condensed explosive fractures explosive molecules within a non-equilibrium zone in the shock front. This fracture, which occurs within one or a few tens of vibration periods, is a mechanical process that yields free atoms and radicals. The fracture occurs mechanically from the acceleration and shear forces in the shock front and from the conservation of momentum. The initial bond breaking in the shock front is not a thermal process resulting from

the compression heating or pressure-volume (PdV) work in the explosive.

Second, the number of free atoms and radicals produced is a function of the peak pressure and rise time of the shock wave and, thus, of the energy release rate in or very near the shock front. The steepness of the shock front is a direct function of the energy release rate dE/dt. The rapid reactions of the somewhat randomly produced free atoms and radicals have very low activation energies and yield hot spots or random centers of exothermic reaction. The number of these centers is then a function of the peak pressure and the shock rise time. Multiple shocks cause increased reaction in some systems.

Third, the important initial chemical reactions are the direct (immediate) reactions and the early chain reactions of the atoms and radicals that lead to the final products CO_2, H_2O, CO, N_2, NO_2, etc. The velocity of an initiating shock front can be accelerated or decelerated by the addition of chemicals that influence the initial free atom or radical reactions and the chain reactions. Increased chain branching and added lighter atoms or radicals can accelerate the initiation reactions, whereas chain-termination steps or the addition of heavy atoms or radicals can slow the chemistry. Obviously, many other factors have an effect, also. Thus, it is proposed here that the kinetics or energy release rates can influence both shock velocity and detonation velocity; however, very large changes in the reaction rates are required to produce small changes in detonation velocities because of a shock barrier[6].

Fourth, the factor that controls the detonation velocity of an explosive is primarily the combination of the vibration velocities of the atoms in the explosive molecules. This combination provides a shock messenger system, and it sets the maximum shock velocity under the initiation or detonation conditions. It has been indicated experimentally that large increases in energy content or energy release rate provide only small increases in detonation velocity. Hugoniot calculations indicate that large increases in shock energy (produced by a flying plate) cause only relatively small increases in shock velocity, as has been observed in Hugoniot experiments. Secondary considerations are then energy content, energy release rate, density, and temperature of the explosive.

Fifth, there is a critical energy fluence[25, 28–32] that determines whether an initiation process will proceed to explosion or detonation. (Obviously, there are minimum sizes required[30] for each explosive to allow the explosion or detonation to fully develop, particularly at low pressures.) Energy fluence is important because the shock energy stays very coherent in the shock front[1–5, 15], and it is this flow of coherent energy across or through the explosive molecules that fractures them to begin the initiation process. The equation for the critical energy fluence is derived from the conservation and Hugoniot relationships as substituted in the kinetic energy equation. It represents the kinetic energy in the shock wave[25]:

$$E_c = \frac{t \cdot P^2}{\varrho \cdot U_s} \tag{1}$$

The value E_c is the total number of joules per square centimeter transferred through the shocked surface of the explosive, which will lead to an explosion or detonation.

It is seen that the critical energy is a function of the square of the pressure, and the pressure is related directly to the shock velocity, which is the important factor in mechanically fracturing the molecules. The time width of the pulse is a first-order effect. This shows that it is not PdV work[33] that is most

important in initiation, but energy fluence. The PdV work is not really a piston action but a summation of the microscopic kinematic processes. The critical time width of the pulse allows the reactions to proceed until the exothermic reaction is irrevocably initiated. That is, cooling caused by arrival of the rarefaction will not extinguish the reaction centers or hot spots.

3. Evidence and Considerations

There are new insights from experimental and calculational work that give credence to the new free-radical model. Considerations of X-ray and infrared examination, initiation experiments, molecular dynamics, quantum mechanics, solid state physics, and other calculations will be reviewed below.

3.1. X-ray and infrared studies

From infrared studies of HMX[34] and RDX[35], it is seen that the higher vibrational frequencies are for the C-H bonds, and the values at or near standard conditions are in the range of 3000 cm^{-1} to 3100 cm^{-1}. The X-ray crystallography for HMX[36] shows that the H atoms bonded to C atoms travel about 0.5 Å in each one-half vibration (as calculated from the major axis of the thermal motion ellipsoid). From these observations, it is easily found[37] that the nominal velocity with which the H atoms are moving in their vibrational modes is about 9 Å in 10^{-13} s or 9 mm/μs.

Infrared examination of nitromethane under very high pressure (~5 GPa) and elevated temperatures[38] has shown that there is very little shift in the IR absorption from the ambient values. Other work[39] has shown that vibrational frequencies increase relatively slowly with increasing temperature. These considerations lead one to the conclusion that without radiation or some electronic process, there is no energy transport system available[40] to transmit or carry the vibrational energy in condensed organic explosives faster than about 9 mm/μs to 10 mm/μs. This strongly suggests there is a shock barrier that limits detonation velocities. The shock barrier would also limit the transfer of heat or activation energy for high-temperature reactions so that for first-order kinetics the log of the apparent rate constant would reach a maximum of about six[41].

3.2. Molecular dynamics calculations

A number of factors germane to the free-radical model are clearly apparent in our molecular dynamics calculations[1-5] and the movies generated therefrom.

(1) A shock moving at about 8 mm/μs is also transiting 8 Å in 10^{-13} s or, in a more significant context, the shock front is crossing about one to three layers of interatomic bonds per atomic vibrational period.

(2) The shock energy is very coherent, and it does not couple to any substantial degree to the thermal energy of a shocked, condensed system until long after the passage of the shock front (perhaps 150 vibrations later).

(3) Thus the energy in the shock front is highly non-ergodic, and thermal equilibrium, particularly between the translational and vibrational energy modes, does not exist in the front. No realistic temperature can be ascribed to this zone.

(4) The shock-front energy remains remarkably coherent within this non-equilibrium zone, which appears to be about 5-Å to 15-Å wide depending on the shock strength and the material properties of the condensed system. This factor is pertinent to the description of shock rise times, where the intensity of the shock pressure and the properties of the interatomic potentials are the important parameters.

(5) The shock strength in the range of shocks that will initiate explosive reaction in condensed explosives is sufficient to mechanically fracture the covalent bonds in organic systems. This was first shown by hand calculations[25] and corroborated by the molecular dynamics calculations[1-5, 13], and verified by experiments with plastics[11, 42], explosives[10, 43, 44], and other small organic molecules[14].

(6) The extent of the initial mechanical bond fracture appears to be a function of the shock pressure and rise time, and, thus, it is coupled to the energy release rate dE/dt.

(7) A series of experiments was completed in a 10-cm-diameter air gun in which thin metal plates were propelled against disks of explosives (Table 1 and Fig. 1). The explosive samples were instrumented so that the transit time of the shock across the sample could be measured. The samples consisted of a standard TNT charge that had 5 wt.% of selected chemicals added for the testing. A TNT control set was examined at various densities to prepare a very sensitive density parameter study. Then four control additives were used to screen out the effects of adding more sensitive explosives such as PETN and hexanitrostilbene (HNS) or hard, inert materials (SiO$_2$ and BN). None of these additives provided a significant change in shock velocity; however, two
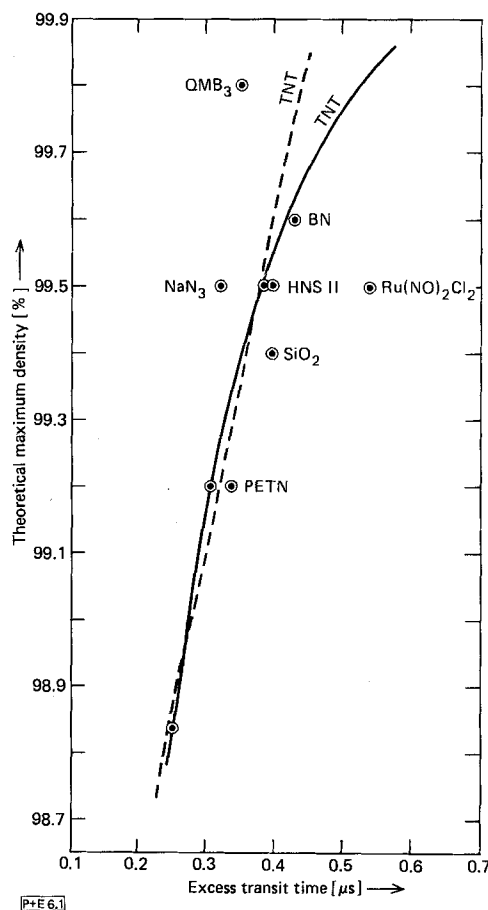
Figure 1. Air gun shock-velocity tests of TNT with additives.

Table 1. Excess Transit Time Measurements from the Air Gun Shock-Velocity Tests of TNT with Additives .

Sample[a]	Density [% TMD][b]	Excess-transit time [μs]
TNT	98.9	0.250
TNT	99.2	0.307
TNT	99.5	0.382
TNT + PETN	99.2	0.338
TNT + SiO$_2$	99.4	0.396
TNT + NaN$_3$	99.5	0.323
TNT + HNS II	99.5	0.396
TNT + Ru(NO)$_2$Cl$_2$	99.5	0.540
TNT + BN	99.6	0.430
TNT + QMB[c]	99.8	0.351

[a] All additives are 5wt.% of total.
[b] Theoretical maximum density.
[c] Tetramethylammonium triborohydride.

chemicals selected as free-radical reagents did change the shock velocity by significant amounts. Tetramethylammonium triborohydride, which had been shown to sensitize a number of materials (explosives and non-explosives) in drop-hammer tests, accelerated the shock in TNT. Ruthenium nitroso chloride, which had markedly reduced the sensitivity of TNT in gap tests, caused a significant deceleration.

(8) As previously shown experimentally[25], the number of initiation sites in a shocked explosive is a direct function of the shock pressure, as this is the factor that determines, along with rise time, the number of free atoms and radicals produced.

(9) The attempt to measure microscopic shock rise time is perhaps doomed to failure until gauges capable of measuring angstroms are coupled with clocks capable of measuring tenths of picoseconds. The effort expended to measure macroscopic rise times can give only a measure of surface finish, microcrystalline structure, or void size, even with sub-picosecond instrumentation. Thus, with a shock or detonation wave moving at 5 mm/μs to 9 mm/μs (5 Å to 9 Å in 10^{-13} s) and with defects or structural features from 0.01 μm to 10 μm, an apparent shock rise time of about 1 ns to 2 ns would be the shortest time measurable. Even if the defects or features of microcrystalline structure in the material under study could be kept to ≤ 0.1 μm, the measured rise time, even with sub-picosecond instrumentation, would appear to be about 0.01 ns to 0.02 ns. Our calculations show that microscopic rise times are in a few measured units of 10^{-13} s at all points of contact between irregular surfaces. The overall rise time (macroscopic) in a molecular dynamics problem is determined merely by the linear offset of the impact points.

(10) Hugoniot curves for organic-type materials have been calculated[5, 13] that very satisfactorily match the Hugoniot experimental data for organic plastics and explosives. Calculations are made from only the values of atomic masses, Morse potentials, and the conservation and Newtonian motion equations. In the calculations, the shock energy is increased from an initial value by a factor of nine, while the shock velocity is only increased by a factor of 1.55. This shows that shock velocity is a fundamental property of atomic mass and bonding potential, and it provides a rationale from first principles for the existence of a shock barrier. The calculations also show that the results are very similar whether the lattice is initially quiescent (cold) or has moderate to intense thermal motion.

3.3. Quantum mechanical calculations

Certain concepts and equations of quantum mechanics have been previously applied to the study of shocked condensed systems. Dancz and Rice[8] provide the theoretical basis and the mathematics that support the plausibility of coherent states (minimum-uncertainty wave packets) in systems of anharmonic oscillators with free ends, as described by Morse potentials. The behaviour of shock waves as solitons in these systems, in which the solitary wave forms preserve their shape even upon collision with other solitary wave forms, is shown to be feasible. Both the solitary wave forms and solitonlike behavior are seen in our two-dimensional studies of shocked systems. In fact, Dancz and Rice state that "it is interesting to think about the possibility of inducing reaction at remote sites (relative to the initial excitation) by propagation of large amplitude excitation analogous to a solitary wave."

In Owens' recent quantum mechanical studies he suggests that the rate-controlling process in shock-induced bond scission of energetic materials may be a transfer of lattice phonons to the internal vibrations of the explosive molecules, and bonds that cannot break at atmospheric pressure may be susceptible to unimolecular fracture at higher pressures[9]. This would provide a theoretical justification for the contention that reactions of the slower thermal decomposition may not be the important reactions of shock-induced bond scission. Owens further proposes that, "The model is particularly appropriate to the case of shock-induced temperature rise where the short duration of the temperature rise may not allow the population of the internal vibrational states of the molecule to be in equilibrium with the external lattice modes." This concept was proposed earlier in our work[25].

3.4. Thermal and kinetic considerations

If we now consider that the maximum vibrational velocities in organic explosives are normally about 8 mm/μs to 9 mm/μs and that this is also the range of the maximum detonation velocities observed for these substances, we can develop a clearer concept of the thermal and kinetic factors in detonation. If one were to assume that as a shock front passed over each layer of interatomic bonds the bonds were fractured or the atoms separated in one or two vibration periods, the first-order rate constant locally would be about 10^{13}/s. It seems reasonable to assume that this would be near the maximum microscopic kinetic rate in this mechanically shocked system. However, because the next layer of bonds in a condensed system cannot be broken until the shock energy is transmitted to it by the vibrational motion of the previous layer, the log of the overall or global reaction-rate constant for a large piece of explosive can only be about six.

This is not really a kinetic rate but a rate maximum determined by the maximum rate of advance of vibrational or activating energy through the condensed system. Thus in all the common, condensed explosive systems, a maximum of about 10^6 g of explosive are consumed per second per square centimeter of detonation front surface. This fact shows a direct link between atomic vibration velocities and detonation velocities.

Had all the molecules been separated so that the activating energy could have reached them all (e.g., by radiation) in 10^{-13} s, then the global rate constant could have been near 10^{13}/s. It appears probable then that the initiating kinetics of

detonation is not controlled as an Arrhenius process, but as a vibratory-energy transmission asymptote.

The atoms in the non-equilibrium shock front have reached the maximum values of vibrational velocities attainable under the detonation conditions, and this puts a physical limit on the transmission of activating energy. In other words, detonating organic explosives have reached the physical kinetic limit of chemical reaction in condensed systems. Thus, it is not energy content alone that limits detonation velocity but also atomic vibratory motion.

4. Discussion

The new insights obtained from the above work have led to a very different initiation model based on first principles. The basic premises are contrasted with those of the generally accepted hydrodynamic models in Table 2.

Obviously, many of the phenomena of explosive performance can be explained by both models discussed above, but there are many items that can be explained or demonstrated satisfactorily only by our free-radical microscopic model. For example, this model shows:

(1) How a free-radical gradient[16] and free-radical chemistry[15] can lead to detonation without an initial shock wave.

(2) How radiation-induced primary free radicals in RDX[46] and HMX[47] can yield high levels of secondary radicals and explosions, even when very cold.

(3) How a hydrogen spray could be produced off the end of a detonating charge[48, 49].

(4) Why cold explosives can be more sensitive than warm[50].

Table 2. Contrasts between the Microscopic Free-Radical Shock Initiation Model and the Zeldovich-von Neuman-Doering (ZND) or Hydrodynamic Model

Microscopic free-radical model	ZND or hydrodynamic model
Shock front is not in thermal equilibrium and not a discontinuity.	Shock front is in thermal equilibrium and considered to be a discontinuity.
There is no von Neuman spike as described in the ZND model, but a gradual rise in pressure and temperature to the maximum[a].	There is an immediate jump to the von Neuman spike condition, with a decrease in pressure to the Chapman-Jouguet state.
Initiation reactions are started by mechanical fracture of molecules.	Initiation reactions are started by compression heating or other thermal processes.
Subsequent chemistry is mainly chain reactions of free atoms and radicals to yield final products.	Subsequent chemistry is mainly ionic to yield final products.
Shock energy stays very coherent in narrow shock front. Near solitonlike behavior exists.	Shock energy is spread across relatively wide shock front.
Detonation velocity is limited primarily by a shock barrier and energy release rates.	Detonation velocity is limited primarily by energy content (cal/g) and density of the explosive.
Kinetics can change detonation velocity as a second-order function. (Energy release rate can be important)	Kinetics cannot change detonation velocity. (Energy release rate is immaterial)

[a] Reference 45.

(5) How a detonation velocity of 6.73 mm/μs could be demonstrated in nitromethane by the addition of 0.05% diethylene triamine[20].

(6) How the failure diameter of nitromethane can be decreased by one-half by the addition of 0.025 mol% triethylamine[51].

(7) Why nitromethane demonstrates a memory effect through large detonating charges.

(8) Why there is a correlation between explosive sensitivity and free-radical stability of the large free radicals of the explosives[22].

(9) Why triaminotrinitrobenzene (TATB) can desensitize HMX significantly[52].

(10) How (with regards to first principles) voids, inclusions, and other defects in explosives lead to increased sensitivity[4, 5].

(11) How massive mechanical fracture of covalent bonds can occur in shocked condensed systems[5, 11].

(12) How the shock-front gradient in initiation or detonation can be determined by chemical reaction, as indicated in particle-velocity gauge studies[45].

5. Conclusions

The new evidence derived from molecular dynamics and quantum mechanical calculations on shock waves in condensed systems, in consort with the experimental results recently reported from studies of shocked polymeric materials and explosives, gives corroborative support to our microscopic free-radical initiation model. The primary elements of this model are that shock energy is very coherent and that it is strong enough to cause mechanical fracture of covalent bonds. The shock front on a microscopic scale is very narrow (~5 Å to 15 Å), and thermal equilibrium does not exist in the front. The free atoms and radicals formed by the shear and acceleration forces in the shock front initiate the chemical reaction that leads to hot spots and the eventual decomposition of the explosive materials, and both energy-release rates and vibrational velocities of the covalently bound atoms are factors in establishing detonation velocities.

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