

# A STUDY IN MECHANO-CHEMISTRY: PRESSURE INDUCED REACTIONS AND NON-EQUILIBRIUM PHENOMENON

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## 1. Introduction

In an effort to increase the rate of reaction of metal/oxide mixtures, the general approach has been to reduce the particle sizes of reactants. Ivanov<sup>1,2</sup> reported that metallic powders of sub-micron size are preheated sufficiently fast by thermal conduction to contribute to the shock wave itself and the detonation velocity of a 25:15 mixture of  $\text{NH}_4\text{NO}_3/\text{Al}$  ( $D_p$ (particle diameter)  $< 1\mu\text{m}$ ) increases from 4 km/s to 5 km/s. Nanometric aluminum is now used in certain formulations and significant increases in reaction rates have been observed<sup>3</sup>. It has also been recognized that heating by compression (as in a shock wave) is much faster than thermal conduction and some studies have been undertaken to investigate the possibility to ignite pyrotechnic mixtures by impact. Most notably is the work of Nesterenko and Meyers<sup>4-6</sup> and their co-workers. Other important contributions in this regard have been made by Thadhani<sup>7,8</sup>, Krueger et al.<sup>9</sup>, Boslough<sup>10</sup>, Johnson et al.<sup>11</sup>, Bennett et al.<sup>12,13</sup>, Vreeland et al.<sup>14</sup> and Horie and Kipp<sup>15</sup>. Walley et al.<sup>16</sup> did drop tests on samples at normal and oblique angles. In most cases only partial reaction occurred and the study concluded that no evidence was found for enhancement of the shocks by chemical reaction. Davis et al.<sup>17</sup> did flyer plate experiments with mixtures of  $\text{Al}+\text{Fe}_2\text{O}_3$  plus teflon and  $\text{Ti}+\text{teflon}$ . They found that "a detonation like phenomena can occur in the metal-polymer and metal/metal oxide – polymer mixtures under shock conditions." Another distinction between the pyrotechnic mixtures and explosives is found in the heterogeneous nature of the pyrotechnic mixtures. Here the fuel and oxidizer consist of separate particles and they are not as ideally mixed as in the explosives. Thus we note that in contrast to explosives, two additional steps must be present in the rapid reaction of heterogeneous powders: 1) *powders must fracture to generate very fine reactants (most atoms at or near surfaces) and 2) the fine reactants must mix*. If these steps are time costly, it explains the limited success of the impact experiments. Furthermore, by linear thinking it could be inferred that usage of nanometric powders could circumvent step 1, but it has become evident that the fracture process does more than generate high surface areas; it also produces unstable species that react nearly "instantaneously" without activation. This contribution from fracture is probably least understood, but it strongly connects the mechanical and chemical processes. At the end of the next paragraph an anomaly is stated that connects with this role of fracture.

In 1935, Bridgman<sup>18</sup> reported results of combined hydrostatic pressure and shear for a wide variety of materials. Whilst most substances underwent polymorphic transformation, some reacted violently:  $\text{PbO}$  decomposes quiescently to a thin film of lead while  $\text{PbO}_2$  detonates yielding a residue of  $\text{Pb}$ . Reactive mixtures produced even more violent results: a stoichiometric mixture of  $\text{Cu}$  and  $\text{S}$  detonates at an applied, non-shear, axial load of 2 GPa producing  $\text{CuS}$ . More exothermic reactions like  $\text{Al}/\text{Fe}_2\text{O}_3$  proceed in a detonation-like manner<sup>#</sup>,

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<sup>#</sup> Bridgman used "detonation" without reference to formal measurements that would support that, it could be interpreted as anecdotal.

damaging parts of the press - this occurs at hydrostatic pressures between 1-3 GPa. In the case of Al/CuSO<sub>4</sub>, detonation only occurs after application of a shear force. The Bridgman results indicate that in the presence of mechanical loading, surface area is rapidly generated. Enikolopyan and co-workers have studied many systems, both endothermic and exothermic, with Bridgman anvils and high pressure extruders<sup>19-27</sup>. They expanded Bridgman's compound list, e.g. CuSO<sub>4</sub>•5H<sub>2</sub>O decomposes violently at 700MPa (no external shear) with elemental Cu in the residue<sup>20,22</sup>. Their experiments lend further proof to the existence of structural collapse. Enikolopyan provided evidence of mechanically enhanced reactions. Al/Fe<sub>2</sub>O<sub>3</sub> mixtures, pressed into 4mm thick discs, reacted completely within 100 nanoseconds.<sup>9,11</sup> The anvil was destroyed and the lack of plastic deformation in its fracture zones points to detonation. Particles were ejected from cylindrical pre-forms (samples not radially contained) at velocities up to 2,000 m/s<sup>23</sup>. Reactions were accompanied by high-energy electrons, sound and electromagnetic radiation<sup>22</sup>. Enikolopyan<sup>26</sup> found the following anomalous result. *The intensity of explosion of thermite mixtures under hydrostatic pressure increases when larger particle sizes are used and Al+Fe<sub>2</sub>O<sub>3</sub> detonated for the particle size ranges:  $300\mu\text{m} \leq \phi_{Al} \leq 1,000\mu\text{m}; \phi_{Fe_2O_3} \approx 1,000\mu\text{m}$ .* (Mixtures of these sizes would normally not react by thermal ignition.)

The work of Enikolopyan<sup>26</sup> lends further proof to a surface generating mechanism. Batsanov<sup>28</sup> noted that, with increased pressure, ionic compounds rearrange valence electron density distributions and the Szegeti charges are reduced (decrease in long range forces) until a state of decomposition is reached. The reactants exist in a state of higher chemical reactivity. Upon fracture reactive species are ejected from crack fronts and rapid chemical reaction leads to high- energy products that could induce fracture of adjacent materials – this would explain the feedback mechanism between mechanical and chemical processes. State variable formulations become questionable in this region because time scales shorten to the point where thermal equilibrium is disturbed and the concept of temperature is not defined. To study ultra-fast mechanisms of mass and energy transfer, mechanisms are needed that enhance Fourier conduction and diffusion - mechanisms related to structural collapse of crystals initiated by mechanical/thermal means. We posit that ultra-fast surface-area generation holds the key to this problem.

These phenomena are not limited to chemically reactive systems. Mechanical interaction with phase transformations could play a similar role as mechano-chemical reactions. Explosive recrystallization<sup>29</sup> has been observed in phase transformations of SiC. Sornette<sup>30</sup> proposes that metastable states of silica could transform to stable phases in the relaxation zone of an earthquake. He builds his model around the coesite → quartz transformation. Very interesting results have been reported by Fortov<sup>31</sup> who has measured supersonic wave speeds for phase transformations from the super-conducting mode to normal mode in intermetallic wires.

## 2. Experimental Procedures

The experiments have been performed in a hydraulic press (custom built by ROCKLAND RESEARCH CORPORATION, West Nyack N.Y.) and a picture of it is shown in Fig. 1. The material systems which have been investigated include polymethyl methacrylate (PMMA), hydrated copper (II) sulfate (ACS, 98.0-102%), sulfur powder (-325 mesh, 99.5% metal basis), mixtures of sulfur powder and zinc powder (median 6-9 micron, 97.5% metal basis) in the ratio of 10% Zn of stoichiometry of ZnS, bismuth (III) oxide powder (99%) and mixtures of bismuth

oxide powder and aluminum powder (spherical, 3.0-4.5 micron, 97.5% metal basis) in ratio of 50% Al of stoichiometry of  $\text{Bi}_2\text{O}_3 + 2\text{Al} \rightarrow \text{Al}_2\text{O}_3 + 2\text{Bi}$ . A high-speed video camera (PHOTRON FASTCAM-ultima 1024) has been used to record the events of the blasts. A one-centimeter grid background has been placed next to the anvil to serve as a scale to determine displacements of particles over sequential frames. Samples of the materials have been prepared in the form of thin discs. The discs are placed between anvil heads as shown in Fig. 1 (b) and a uniaxial load is applied. The powders are compressed to axial loads that vary between 5 and 8 kbar. During this stage some deformation occurs and porosity is reduced to negligible levels. When the axial load reaches a level that exceeds the mechanical stability of the compact, a fracture wave develops. Gordopolov and Viljoen<sup>32</sup> and Viljoen, Gordopolov and van Rensburg<sup>33</sup> have analyzed the stress distributions in particulate systems under uniaxial loading. One of their major results is the formation of a local maximum in particle density near the periphery. The locus of the maximum is in the shape of a convex arch. Particles that compose the arch are called voussoirs and they exert compressive forces on the voussoir at the midway plane. Particles to the interior (i.e. behind) the arch also exert compressive forces on the center voussoir. The state of compression on all particles in the arch is necessary to maintain stability.



(a)



(b)

**Figure 1: (a) Bridgman anvil. (b) Close-up of platens.**

The fracture wave causes the ejection of a very fine dust. Systems that contain metal powders have been associated with bright photo-emissions, this is due to the combustion of the metal powder, following their ejection from the anvil. A frame-by-frame analysis of the high-speed video allows us to determine the average velocities of dust particles (cf. Fig.2). In some cases the particle sizes can be estimated from the video.

### **3. Experimental results and discussion.**

Several experiments have been performed for each material system. The experiments with PMMA, bismuth (III) oxide, and mixtures of bismuth (III) oxide + 50% aluminum have exhibited

single explosions during compression. In the latter case (bismuth (III) oxide + 50% aluminum) the lattice collapse has been associated with a violent explosion. We can speculate that non-equilibrium fracture products are very reactive and the fracture wave is accompanied by a reaction front. The combined effects of lattice failure and chemical reaction lead to a violent explosion. The time sequence of frames proceeds from the top of the picture towards the bottom. The white areas in Figure 2 are photo-emission.

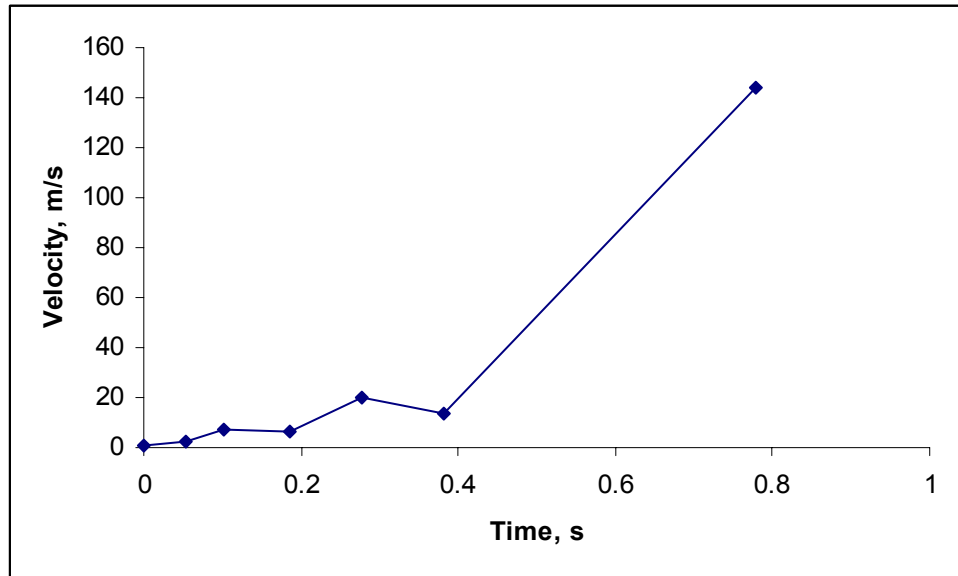


**Figure 2: Six consecutive frames of the  $\text{Bi}_2\text{O}_3$ + 50% Al at 8000 frames/sec**

The first frame (top) shows the profile of the anvil just prior to failure. In the next frame the darker cloud of unreacted materials that have been ejected from the midway plane of the anvil is clearly visible and some photo-emission from reaction of material closer to the top and bottom anvil plates is also noticeable. The third frame shows a distinct demarcation between chemical reaction at the top and bottom regions, whilst unreacted dust cloud fills the bulk of the center and ahead of the bright regions. From the fourth slide onwards, the chemical reaction has caught up with the dust cloud.

Experiments with copper (II) sulfate and sulfur powders have shown double blasts during compression (the first explosion is weak and the main blast is strong). In the case of mixtures of sulfur + 10% zinc powder, we have observed multiple (up to seven) blasts during compression. In Figure 3 we relate the sequence of events during the seven blasts. Three observations are worth mentioning. The particle velocities increase with each explosion and the time delays between consecutive explosions increase as well. The severity of the final explosion is substantially higher than the others, since it is accompanied by photo-emission. Therefore it is reasonable to conclude that chemical reaction has played a role in the final event. It is interesting to note that the time delay between the last two explosions is

approximately 400ms.



**Figure 3: Velocity of consecutive blasts of Zn/S system.**

The particle velocities that have been measured by high-speed video vary for the same experiment, but the general trend is that finer particles have higher velocities. We associate the fastest particle velocities with the finest particles which are still discernible on the video clips. A comparison of the fine particle velocities of the main blasts shows that the presence of a metal phase in the mixture reduces the velocity of the main blast by approximately 40%. However, the fine particle velocities of the preliminary blasts for mixtures with and without a metal phase do not show any significant differences. Several factors play a role in the mitigating effect of a metal phase on particle velocity. First consider arguments based on the allocation of energy. The energy which is added to the system by uniaxial compression is stored in the lattice of crystalline structure (i.e. oxides or sulfur) as elastic potential energy and as plastic deformation in the metal phases (aluminum and zinc). The elastic potential is released at the moment of lattice collapse. event of blast. The plastic deformation is an irreversible process and the energy that is stored in distorted lattices cannot be directly recovered as kinetic energy (it is retrievable as chemical potential energy). Therefore less elastic potential energy is stored in crystalline/metal mixtures than in pure crystalline samples. Consequently less energy is released during the blast and the kinetic energy of the particles is lower. The preliminary blasts occur at lower pressures. At lower pressures the plastic deformation of the metal phase is smaller and it is only a small fraction of the total energy of the system. Other arguments pertain to the crystalline/metal system during the loading stage, prior to explosion. We have observed that a migration occurs of the plastic deformable phase to the anvil platens. The separation of phases may have an effect on the stress distribution in the compact. It is quite feasible that the metal phases that concentrate near the platens could reduce the total load before failure, due to slip failure between the metal phases and the platen surfaces.

The particle velocities are measures of the amount of energy that is released in a collapse of stable compact. The estimate is complicated by additional energy consuming processes: fracture and electron excitation. Thus the lattice collapse is a path dependent process and

when experiments are repeated, the outcome is not necessarily the same. It is not surprising since the fracture wave is a non-equilibrium process. The fracture wave propagates from the periphery towards the center of the disc. If the fracture wave reaches the center of the compact before the load increases enough to stabilize the residual compact in a new arch structure, the next blast does not occur.

#### 4. Mathematical model

First consider the steady propagation of a fracture wave into a solid material. For the sake of simplicity, we consider a one-dimensional description. Let the speed of the fracture wave be denoted by  $D$ , then a transformation of coordinates from the laboratory to the wave front:  $z=x-Dt$  leads to the following conservation equations for mass and momentum across the fracture front.

$$\begin{aligned} D(\rho_0 - \rho) &= -\rho u \\ D(\rho u) &= -P_0 + \rho u^2 \end{aligned} \tag{1a,b}$$

Remark: The subscript 0 denotes conditions ahead of the front.

The particle velocity and density behind the front is  $u$  and  $\rho$ , ahead of the front the particle velocity is zero and the density is  $\rho_0$ . The pressure is zero behind the front, but there are two contributions to pressure ahead of the front. The first component of pressure is the so-called cold pressure or elastic pressure,  $P_{el}$ . It describes the huge internal pressures caused by repulsive nuclei and much weaker forces in a tensile state. The elastic pressure is directly related to the elastic part of internal energy:

$$U_{el} = -\int P_{el} dv \tag{2}$$

Strictly speaking, the integral must be evaluated at absolute zero where no thermal expansion is present, but the difference between the specific volume at absolute zero ( $v_{oo}$ ) and room temperature ( $v_k$ ) is so small for most materials that  $v = v_k$  is mostly used as the lower bound of the integral. The expression for cold pressure that we prefer to use is:

$$P_{el} = K_{T_0} / \chi [e^{\chi(1-v/v_k)} - 1] \tag{3}$$

The isothermal bulk modulus is  $K_{T_0}$  (defined as  $v \left( \frac{\partial P}{\partial v} \right)_T$  evaluated at room temperature) and

the first derivative of the isothermal bulk modulus  $\chi$  (defined as  $1 + \frac{\partial K_T}{\partial P}$ , evaluated at room temperature). Eq.(3) forms part of the equation of state (together with thermal and electron pressure terms) and  $P_{el}$  and  $\rho_0$  are related through eq.(3).

The second component of pressure is due to chemical pressure. Some readers may find the usage of the term chemical pressure instead of thermal pressure unorthodox, but it all reduces to a competition between different time scales. If the solid consists of a reactive mixture, the internal energy of the solid has additional chemical potential energy. If the chemical energy is released on a time scale that is slow enough to allow the product species to adopt a Maxwell distribution, it is correct to describe the second term as thermal pressure,  $P_T = K_{T_0} \alpha_T T$  defined in terms of the isothermal bulk modulus  $K_{T_0}$ , the volumetric thermal expansion coefficient  $\alpha_T$  and the absolute temperature  $T$ . The important point is that chemical

potential energy is converted into kinetic energy. In the case of "slow release" it results in the transfer of the chemical potential energy into kinetic energy that is randomly distributed amongst the different degrees of freedom. For simplicity we could consider products with vibrational and translational degrees of freedom. Equilibrium between the different modes of energy storage implies  $T_{\text{vib}} = T_{\text{tr}}$ . Let  $f$  denote the distribution of product particles in the six-dimensional space of velocity, position and time,  $[\bar{\xi}, \bar{r}, t]$ . The velocity vector consists of two parts: the drift component  $\mathbf{u}$  and the peculiar component  $\mathbf{c}$ . The moment of the distribution  $f$  with respect to  $\mathbf{c}$  taken over velocity space is zero:

$$\int c f d\xi = 0, \quad (4)$$

but the following integral is not zero; it is customary to refer to it as a stress tensor:

$$\int c_i c_j f d\xi = -\sigma_{ij}. \quad (5)$$

Furthermore, the second moment relates the peculiar velocity with the thermal component of the internal energy:

$$\int c \cdot c f d\xi = 2\rho U_{\text{th}} \quad (6)$$

Therefore, if the chemical potential energy is converted into kinetic energy with peculiar velocity vector, that energy is given by eq. (6). The negative trace of  $\sigma$  is related to the thermal pressure and a linear relation exists between thermal pressure and the thermal component of internal energy. When equilibrium is not established during reaction, the picture is different.

When the chemical reaction is preceded by a fracture wave, the products could vary from gas molecules to particles and it depends on the amount of energy that is expended during fracture to generate new surfaces. Fine particles would not adopt a Maxwell distribution on the same time scale as a gas molecule would. Therefore we argue that the chemical potential energy may first be converted into translational kinetic energy. The products acquire initial drift velocity that is denoted as  $\mathbf{u}$ . In our one-dimensional description, it reduces to  $u$ , the mass velocity used in eqns. (1a,b). When we need to assign a value to the chemical pressure, we evaluate it in terms of the adiabatic temperature rise:

$$P_{\text{chem}} = K_{T_0} \alpha_T (T_{\text{ad}} - T_k) \quad (7)$$

If chemical potential energy is first converted into translational kinetic energy, a non-Maxwellian distribution exists immediately behind the reaction front. This non-equilibrium distribution changes to a Maxwell distribution as it progresses from the reaction front, primarily due to elastic collisions with ambient gas. In reality the products would be partially equilibrated upon exiting the reaction front, but in the analysis we assume that all the chemical potential energy is first released as translational kinetic energy along the x-axis (i.e.  $z$  in translated coordinates). The reason that the particles would primarily have velocity component along this axis, is based on the fact that the fracture plane is normal to this axis. This argument is widely accepted in shock studies (and for which the majority models are still one-dimensional). Thus the distribution at the reaction front (which lies behind the leading edge of the fracture front) is

$$f = N_0 e^{-\frac{m(\bar{\xi}-u)^2}{2k\theta}} \quad (8)$$

The products may possess a peculiar component of velocity, but their distribution differs from

the Maxwell distribution of the ambient gas:

$$f_A = M_0 e^{\frac{-m_A c^2}{2kT_A}} \quad (9)$$

Matters would become more complicated if we would consider the size distribution of the products. The size of product particles is estimated according to the approach outlined by Cherepanov<sup>35</sup>. First we need to calculate the energy that is available for fracture. The macroscopic energy balance across the fracture/reaction front is

$$U_{dis} = U_{el} + U_{chem} + \frac{P_0}{2} \left[ \frac{1}{\rho_0} - \frac{1}{\rho} \right] \quad (10)$$

The total internal potential energy ahead of the front consists of elastic and chemical components. Correspondingly, the total pressure comprises of the elastic and chemical parts, where the latter part is expressed as an equivalent thermal pressure, eq.(7). In practice, not all the energy  $U_{dis}$  is used to generate new surface and it is reasonable to expect that some energy is expended to excite electrons from the ground state. In this study though, we assign all the dissipation energy to fracture processes. The surface energy is estimated from ground state, orderly packed crystals<sup>35</sup>. Let  $\gamma$  denote the surface energy ( $J/m^2$ ), the average spherical particle size is:

$$\phi = \frac{6\gamma}{\rho U_{dis}} \quad (11)$$

When  $U_{dis}$  approaches the limit of the theoretical strength of the crystalline structure, eq.(11) implies that the material volatilizes. Once this point is crossed, electron states would act as energy buffers. However, as mentioned earlier, the storage of energy in excited states may occur prior to this limit. Different size distributions may be conjectured, as long as the first moment of that distribution corresponds to the average particle size given by eq. (11). In light of the non-equilibrium state of particles exiting the reaction front, the size distribution has further implications.

### **Fokker-Planck approximation**

Therefore let us keep focused on the non-equilibrium and assume a delta-function distribution in size. Also note that  $M_A \int f_A d\bar{\xi} = \rho_A$  is the ambient density ( $M_A$  is a conversion factor from number density to mass density). The Boltzmann equation in translated coordinates is:

$$\frac{\partial f}{\partial t} - D \frac{\partial f}{\partial z} + \xi_z \frac{\partial f}{\partial z} = \left( \frac{\delta f}{\delta \mathbf{a}} \right)_{coll} \quad (12)$$



Whilst  $f_A$  satisfies the l.h.s. of eq.(12) identically, the non-equilibrium distribution  $f$  has a drift velocity component that depends on position and time. The collision term describes the interaction between the product particles and the ambient gas. We will treat this interaction in two ways. The decay rate of the drift velocity is parameterized and this information is used in the generalized Fokker-Planck equation. The collision integral is approximated by two linear terms in the Fokker-Planck equation; diffusion in velocity space and advection in velocity space. The generalized Fokker-Planck equation approximates the collision integral with a diffusion term in velocity space and an advection term in velocity space. The equation, in laboratory reference frame, is:

$$\frac{\partial f}{\partial t} + \xi_z \frac{\partial f}{\partial z} = D_\xi \frac{\partial^2 f}{\partial \xi^2} + R \frac{\partial(\xi f)}{\partial \xi} \quad (13)$$

The second term on the r.h.s differs from typical generalized Fokker-Planck equations, insofar they use the peculiar velocity instead:  $R \frac{\partial(cf)}{\partial \xi}$ . Of course, the main argument to use the peculiar velocity is to conserve kinetic energy and momentum during collisions. In our case, only the number density is conserved during collision. When the collisions occur with the background gas, momentum and energy is only conserved for the combined system. The zeroth moment of eq.(13) over velocity space is the conservation equation for particle number density:

$$\frac{\partial \rho}{\partial t} + \frac{\partial \rho u}{\partial z} = 0. \quad (14)$$

After we have defined the function  $\theta(t, z)$  (a measure of thermal energy) as follows:

$$\theta = \frac{\int (c \cdot c) f d\xi}{\int f d\xi} = \frac{\int (c \cdot c) f d\xi}{\rho},$$

the next two moments are:

$$\frac{\partial \rho u}{\partial t} + \frac{\partial[\rho u^2 + \rho \theta]}{\partial z} = -R \rho u \quad (15)$$

$$\frac{\partial[\rho u^2 + \rho \theta]}{\partial t} + \frac{\partial[\rho u^3 + 3\rho u \theta]}{\partial z} = 2D_\xi \rho - 2R[\rho \theta + \rho u^2]. \quad (16)$$

Eqns.(15-16) describe the changes in momentum and thermal energy as a result of interaction between the pdf and the background; the interaction is completely defined by the parameters  $D_\xi$  and  $R$ .

## 5. Conclusions

- Non-reactive materials such as PMMA, copper (II) sulfate, sulfur powder and bismuth (III) oxide powder explode under uniaxial loading and particle velocities are average 180-190 m/s, with maximum values of 280 m/s.

- Mixtures of crystalline and metal powders such as sulfur and zinc, bismuth oxide and aluminum, exhibit lower particle velocities. Velocities range from 80 m/s to 160 m/s (110 m/s average), but chemical reaction occurs in the region directly behind the ejected particles. These reactions are associated with photo-emission. It is most likely reactions between fine metal powders and ambient air.
- Some systems exhibit multiple explosive ejections of particles from the anvil. Copper (II) sulfate and sulfur produce double explosions. The sulfur/zinc mixture exhibits as many as seven distinct explosions during a single experiment.
- The use of finer metal powders should increase the rate of reaction and it would be interesting to use nano powders. If the reaction could occur closer to the fracture front, the possibility to provide feedback strengthens. Under these conditions it becomes possible to contemplate the direct conversion of chemical energy into kinetic energy of products.
- In our experiments we have found particle velocities that have been substantially lower (more than one order of magnitude) compared to the velocities that Enikolopyan<sup>23</sup> has claimed.
- A modified Fokker-Planck equation has been derived to describe the non-equilibrium state. Since the particles interact with a background medium (surrounding atmosphere) only particle number density is conserved, but momentum and energy changes and eventually equilibrate with the background.

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