LA-UR-97-2939

CONF-970701--5

Title:

# AN EQUATION OF STATE FOR DETONATION PRODUCTS INCORPORATING SMALL CARBON CLUSTERS

RECEIVED
AUG 13 1997
OSTI

Author(s):

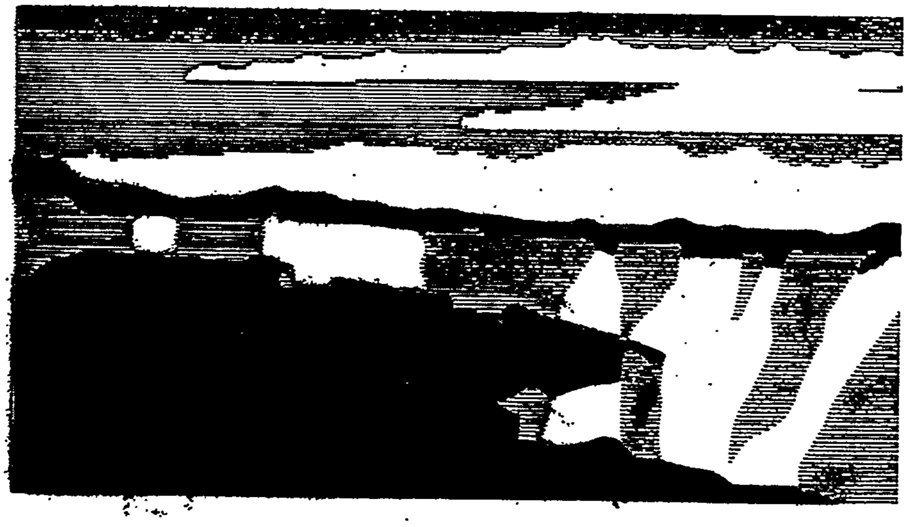
Milton Samuel Shaw T-14

MASTER

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

Submitted to:

1997 APS Topical Conference on Shock Compression of Condensed Matter
July 27-August 1, 1997
University of Massachusetts
Amherst, Massachusetts



**Los Alamos**
NATIONAL LABORATORY

# DISCLAIMER

# AN EQUATION OF STATE FOR DETONATION PRODUCTS INCORPORATING SMALL CARBON CLUSTERS

M. Sam Shaw

*Group T-14 MS B214, Los Alamos National Laboratory, Los Alamos, New Mexico 87545*

A theoretical equation of state for detonation products is presented that incorporates the small cluster behavior of the carbon. For small diamond clusters of the size found in recovery experiments, the fraction of carbon atoms on the surface can be as much as 25%. The composition and properties of the clusters are modeled with the dangling bonds capped by various radicals composed of C, H, N, and O from the background molecular fluid mixture. A perturbation theory approach is used for the mixture of molecular fluids that also includes features based on Monte Carlo simulations. For example, the effect of cross potentials on nonideal mixing in a chemical equilibrium simulations, is shown to be well approximated by an entropy shift and ideal mixing. Comparison is made of the EOS with individual species Hugoniot data and with detonation velocity data for a variety of explosives. In addition, recent data for PBX-9501 is utilized which characterizes sound speed, overdriven Hugoniot, adiabatic $\gamma$, Grüneisen $\gamma$, and a precise thermodynamic CJ state[1].

## I. INTRODUCTION

High explosives detonation products form a very complicated system at rather extreme conditions. Pressures are in the range of several hundred thousand atmospheres at temperatures of a few thousand degrees. Despite the high densitiy (up to 3 g/cm$^3$), the products are primarily a fluid mixture of $H_2O$, $CO_2$, $CO$, $N_2$, and additional minor molecular species. In addition, there are carbon clusters consisting of a few thousand atoms in graphite-like and diamond-like structures with the added complication of a large fraction of the cluster being on the surface.

## II. EQUATION OF STATE

We describe here three interrelated areas of approach being used to develop a theoretical EOS to accurately describe these complicated systems. First, thermodynamic simulation methods (Monte Carlo and molecular dynamics) are developed and implemented to provide a benchmark of "exact" results. These exact results provide computational experiments for thermodynamic results for a given potential. Second, a perturbation theory based method is used for the practical implementation. Particular choices of perturbation theory approximations are made which give accurate thermodynamics and chemical equilibrium for a given set of potentials. Third, data analysis methods are used to extract EOS information from new precision experimental data. These data as well as detonation velocities and Hugoniots for individual species are used to constrain the choices of potentials.

The benchmark simulation methods provide the testing ground for the various approximations that are used in the practical implementations. Initially, we used molecular dynamics simulations to characterize the thermodynamics of individual molecular fluids (at pressures and temperatures characteristic of detonation products) with very nonspherical interactions[2] (e.g. $N_2$ and $CO_2$). The simulations demonstrated that these nonspherical molecules were not freely rotating under typical conditions in detonation products. A density of states tranformation Monte Carlo method[3] was developed that efficiently simulates a large range of states from a single reference simulation. Most important, we have developed the $N_aPT$ ensemble Monte Carlo method[4]. This method incorporates the chemical equilibrium of a molecular mixture as a natural extension of standard Monte Carlo methods. From an atomic simulation perspective, correlated moves are attempted which interchange atoms between molecules. With a proper accounting of the acceptance probability of these type moves, chemical reactions are allowed in a manner such that the chemical equilibrium composition is determined by an average over states sampled by the simulation. The effect of cross potentials on nonideal mixing was studied by this method. The shift in chemical equilibrium (resulting from a shift in cross potential) had a larger effect on the EOS than the shift in cross potential at fixed composition. A related consequence is that nonideal mixing can be well approximated by ideal mixing plus a constant entropy shift of each constituent that results in shift in chemical equilibrium. In Fig. 1, we illustrate the effect of a small shift in cross potential on the chemical equilibrium composition. In this case, the simulation is for a mixture of $N_2$, $O_2$, and $NO$ at 30 GPa and 3000 K. The potentials are those described previously[5]. The only difference in the two simulations is that the scaled radius of the $N_2 - O_2$ potential for the set designated X is expanded by about 2% to get the set O. Now, using the perturbation theory outlined below, ideal mixing (lower solid line) goes right through the set X. That is, ideal mixing corresponds to a particular choice of cross potential. This simulation method can even be used to find the CJ state of a molecular fluid mixture. With the increased speed of workstations, the direct construction of a tabular EOS for detonation products may be a practical alternative to the perturbation methods discussed below.

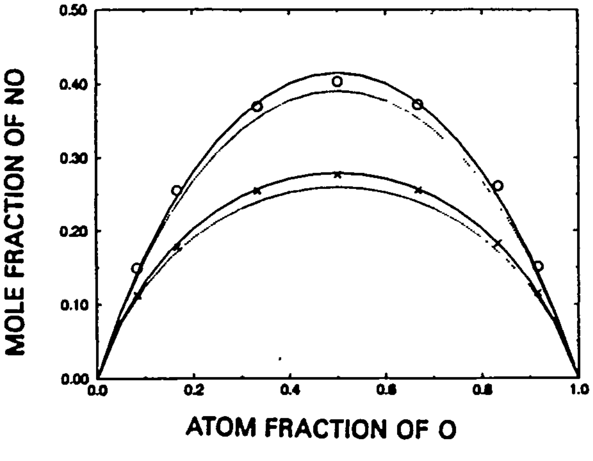


**Figure 1.** Simulation for two different cross potentials, X and O (see text). Lines are perturbation theory with ideal mixing and entropy shifts.

The goal of the practical EOS implementation is to have an accurate, predictive, and physically based method. For the molecular fluid components, we use Ross's perturbation theory method[6] for spherical potentials that is accurate to 1% for single species fluids in this regime. In some cases, we have used an effective spherical potential to characterize the very nonspherical interaction. The effective potential is determined through an equally accurate perturbation theory approach that we have developed and tested against simulation benchmarks. The constant entropy shift approximation mentioned above is used to include nonideal mixing effects from the largely uncharacterized cross potentials. The solid carbon is treated as a cluster rather than a bulk solid. Recovery experiments have found residual diamond-like clusters on the order of 20 Å diameter. With roughly 1000 carbon atoms in a cluster, around 20-30% of the carbon atoms are on the surface in the diamond phase. We allow for the surface dangling bonds to be capped with $H, OH, NH_2, NO_2$, and the like. A qualitative picture of a diamond cluster of around 20 Å diameter is shown in Fig. 2. In the current model, only the net composition of the surface is prescribed along with an effective density and Debye temperature. Future implementations will allow for the surface equilibrium composition to vary according to free energy contributions of individual capping groups. The detonation products EOS is strongly dependent of the carbon phase and on the surface composition. Because of the cluster nature of the carbon and the difference in composition between phases, both graphite and diamond clusters can exist over a limited range (typically a few GPa). These shifts

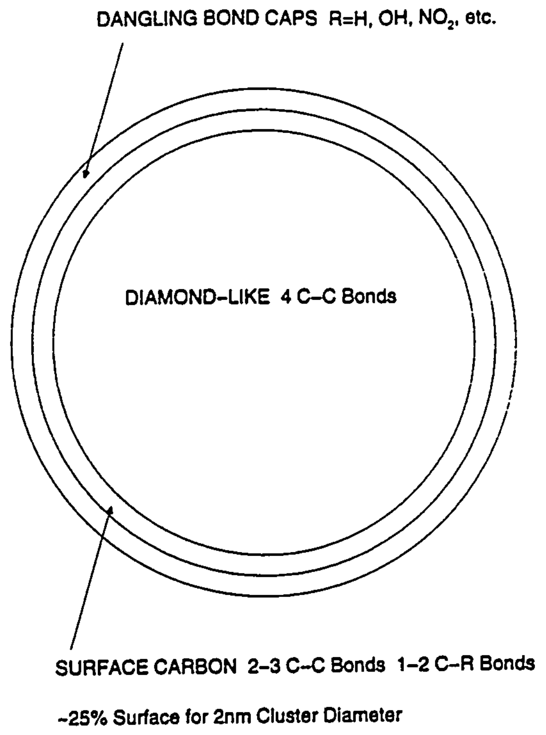


**Figure 2.** A qualitative diagram of the structure of a 20 Å diameter diamond cluster.

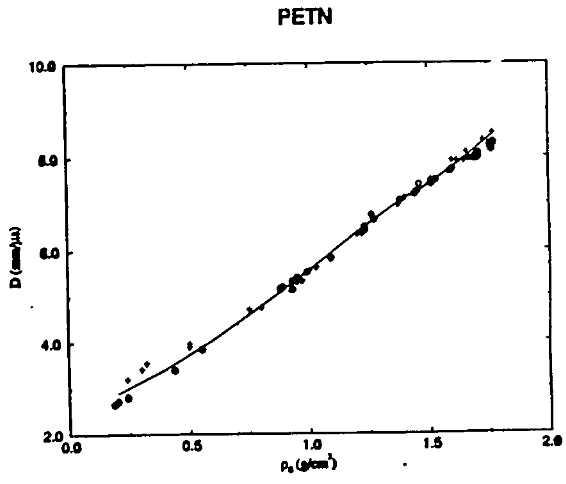


**Figure 3.** Detonation velocity of PETN versus $\rho_0$. Comparison of experiment (symbols) and theory (line).

in the phase of carbon are reflected by small, but significant changes in the CJ detonation velocity as a function of initial density, $\rho_0$, as seen in Fig. 3 for PETN. The current theory has no solid carbon for $\rho_0$ below 1.0 $g/cm^3$, a graphite-like phase up to ≈ 1.4, a mixed phase up to ≈ 1.5, and a diamond-like phase at higher values of $\rho_0$. The individual potential for a given species is primarily determined from Hugoniot data and where available, spectroscopy measurements leading to a temperature[7]. Constants affecting nonideal mixing and carbon are determined in a coupled manner from detonation velocity data for various compositions and initial densities. In addition, new data from group DX-1, discussed below, provides a more precise constraint[1,8].

The two types of experiments discussed here have in common that the initial state in the detonation products is overdriven. This has the advantage of minimizing the reaction zone effects and any coupling of hydrodynamics to the EOS. The combination of Lagrange sound speed and overdriven Hugoniot data allows for the precise determination of the CJ state. The sonic condition is readily found from the intersection of the two curves. With a combination of a well chosen local EOS form and some statistical analysis, we have determined the CJ state for PBX-9501 to about 1% accuracy. In addition, derivative quantities such as the adiabatic $\gamma$ and the Grüneisen $\gamma$ are determined from the data. These provide a much stronger constraint on the detonation

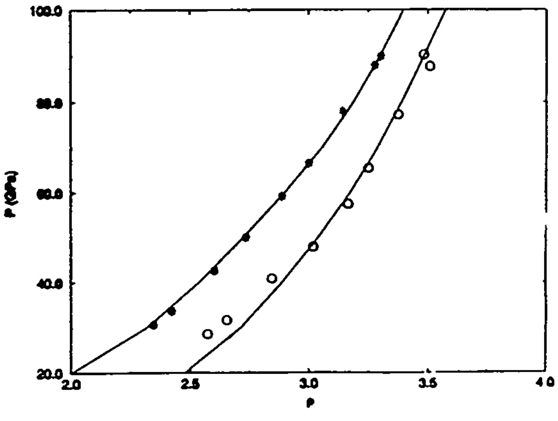


**Figure 4** Overdriven Hugoniot data for PBX-9501 (*) and PBX-9502 (O) compared with theory (line).

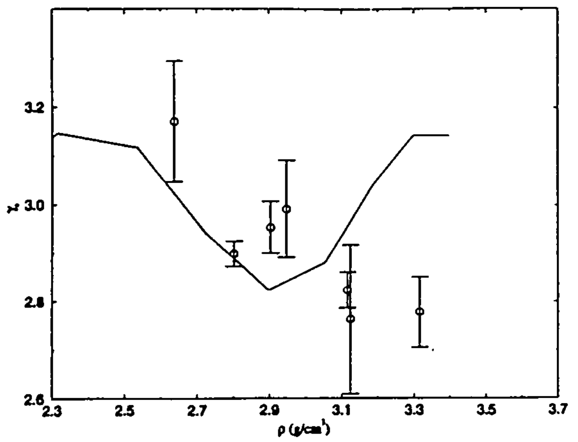


**Figure 5.** Adiabatic $\gamma$ data (O) and theory (line) as a function of density.

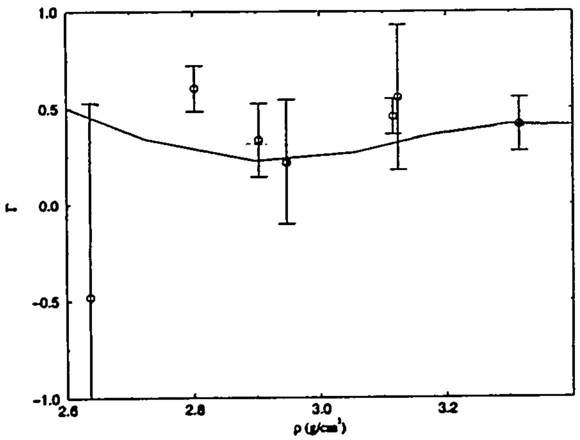


**Figure 6.** Grüneisen $\gamma$ data (O) and theory (line) as a function of density.

products EOS than simple detonation velocities. In Fig. 4, we compare the thoery with the overdriven Hugoniot for PBX-9501 and for PBX-9502 with the carbon constrained to be in the diamond phase. In Figures 5 and 6, we see the comparison with the adiabatic $\gamma$ and the Grüneisen $\gamma$, respectively.

The release isentrope experiments require the inversion of interface velocimetry data. Here we

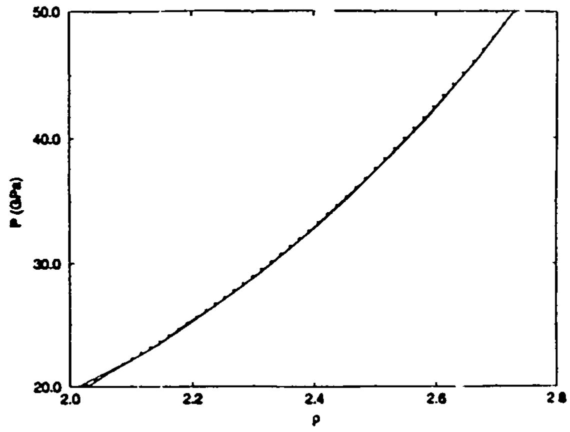


**Figure 7.** Inverted release isentrope from velocimetry data (lines) and theory (O).

use a tabular reference isentrope form and hydrodynamic calculations. A computationally intensive nonlinear least squares procedure is used to extract the best EOS match to the velocity data. The high precision of the data leads to a very accurate isentrope that provides strong constraints on the EOS with the advantage of starting from a well characterized initial state. A comparison of the theory with preliminary results for PBX-9501 are shown in Fig. 7.

## III. DISCUSSION

The calibration of nonideal mixing terms and the model of the diamond-like carbon clusters leads to an very good representation of the detonation products equation of state. Further refinement of the EOS will be made using a nonlinear least squares procedure to simulataneously fit a variety of data. More precision data of the type described above, will be included as available. Allowance for shifts in the chemical composition of the surface of the diamond-like clusters will probably be needed to improve the global accuracy.

[1] J. N. Fritz, R. S. Hixson, M. S. Shaw, C. E. Morris, and R. G. McQueen, J. Appl. Phys. **80**, 6129 (1996).
[2] M. S. Shaw, J. D. Johnson, and J. D. Ramshaw, *J. Chem. Phys.* **84**, 3479 (1986).
[3] M. S. Shaw, *J. Chem. Phys.* **89**, 2312 (1988).
[4] M. S. Shaw, J. Chem. Phys. **94**, 7550 (1991).
[5] M. S. Shaw, Proceedings of the 10th International Detonation Symposium, pp. 401-408 (1995).
[6] M. Ross, J. Chem. Phys.,**71**, 1567 (1979).
[7] S. C. Schmidt, D. S. Moore, and M. S. Shaw, J. Chem. Phys. **107**, 325 (1997).
[8] J. E. Vorthman, R. S. Hixson, and J. N. Fritz, this conference.