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A THEORETICAL EQUATION OF STATE FOR
DETONATION PRODUCTS

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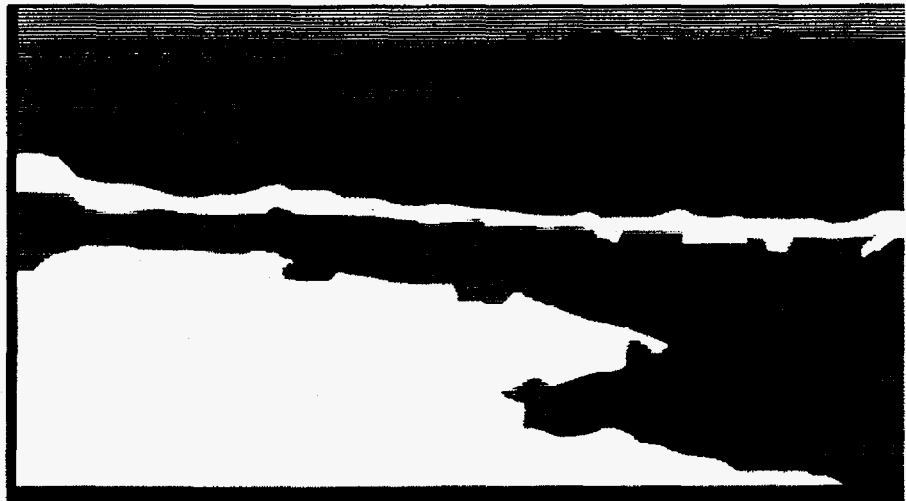
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A THEORETICAL EQUATION OF STATE FOR DETONATION PRODUCTS

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A theoretical equation of state for detonation products is described that places particular emphasis on the characterization of small carbon clusters (20Å- 50Å in diameter) in the products. Diamond clusters are modeled with the dangling bonds on the surface atoms (up to 30% of the cluster) capped by various radicals composed of C, H, N, and O from the background molecular fluid mixture. Free energy methods for the surface groups are used to determine the chemical equilibrium composition of the cluster surface as well as the surrounding molecular fluid mixture. The surface composition shows dramatic changes in composition over some regions and varies slowly in others. A perturbation theory approach is used for the mixture of molecular fluids that also includes features based on Monte Carlo simulations.

INTRODUCTION

The equation of state (EOS) for the detonation products of high explosives is an essential part of any model of explosives behavior. At first glance, the system of products looks relatively simple. The energetically favorable products are CO₂, N₂, H₂O, and solid carbon. At the extreme conditions present due to the high energy density (pressure \approx 30 GPa and $T \approx$ 3000 K), the molecular fluid mixture is far from ideal gas, however ($PV/NkT \approx$ 20). An accurate theoretical treatment must not only handle well the extreme conditions for a single molecular fluid, but also the mixture of species and the thermodynamic chemical equilibrium composition of the products. The solid carbon adds new and different complications. Most EOS methods treat the carbon as either bulk graphite or bulk diamond, depending on the state. Recovery experiments reveal a much more complicated situation where extremely small clusters are found. In particular, the diamond occurs as spherical clusters ranging from 20 - 50 Å in diameter. The corresponding fraction of atoms on the surface is as much as 30 %. Each surface atom has one or more dangling bonds that are energetically unfavorable. Restructuring of the surface can regain some of this energy

penalty, but an attractive alternative is to cap the dangling bonds with various combinations of the C, H, N, and O atoms readily available from the surrounding molecular fluid mixture. Just as the chemical composition of the molecular fluid mixture depends on the thermodynamic state, so will the surface composition of the capping groups.

In the present work, we present a multipronged approach incorporating benchmark simulation methods, approximate analytic methods, and perturbation theory methods to determine the EOS. A nonlinear least squares approach is used to determine effective parameters, characterizing carbon clusters and non-ideal mixing, which cannot be independently determined by available data.

CARBON CLUSTERS

The treatment of the carbon as clusters, rather than bulk solid, adds the significant complication of the surface and what it looks like. For graphite clusters, the majority of the surface is just the plane layer with a van der Waals interaction. So, a small heat of formation shift is adequate for a first cut at incorporating the restructuring of bonds at the edges. Diamond clusters are entirely different. Every part

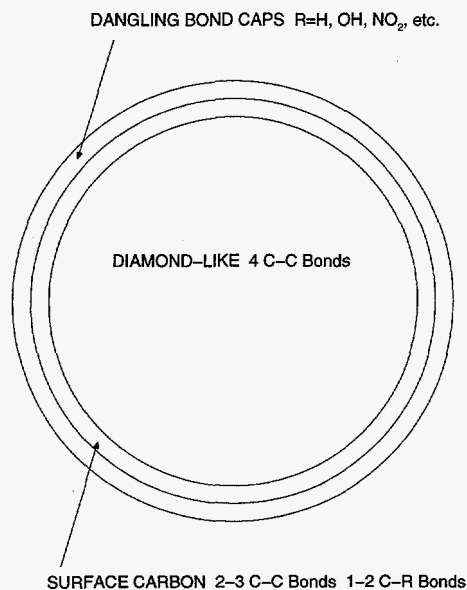


FIGURE 1. A QUALITATIVE DIAGRAM OF THE STRUCTURE OF A 20 Å DIAMETER DIAMOND CLUSTER.

of the surface exposes dangling bonds that cannot be easily restructured because all of the non-surface atoms already have four sp^3 bonds to other atoms. This section describes the treatment of the diamond cluster and its surface. A qualitative picture of a diamond cluster around 20 Å in diameter is shown in Figure 1. In a previous model¹, the surface composition was fixed without a specific characterization of surface groups on the dangling bonds. In this paper, we specifically model the dangling bond caps and the surface carbon atoms as described below. Provision is made for determining the equilibrium composition of the surface groups. A related model by van Thiel and Ree² implemented similar characterization of the surface groups with a fixed choice of surface composition.

A single unit cell of the diamond lattice is shown in Figure 2. The diamond lattice consists of two face-centered cubic (FCC) lattices put together. With respect to a unit cube, the FCC lattice has four atoms at locations $0\ 0\ 0$; $0\ \frac{1}{2}\ \frac{1}{2}$; $\frac{1}{2}\ 0\ \frac{1}{2}$; and $\frac{1}{2}\ \frac{1}{2}\ 0$. All of the rest of the atoms are located by translations of $L\ M\ N$, where L , M , and N are integers. The diamond lattice consists of the FCC lattice plus a copy translated by $\frac{1}{4}\ \frac{1}{4}\ \frac{1}{4}$. Note that each carbon atom is tetrahedrally bonded to its four neighbors. The lattice constant for diamond is about 3.56 Å.

The present model of the structure of a cluster starts with a diamond lattice. All atoms outside of a fixed radius are then eliminated, and the number and

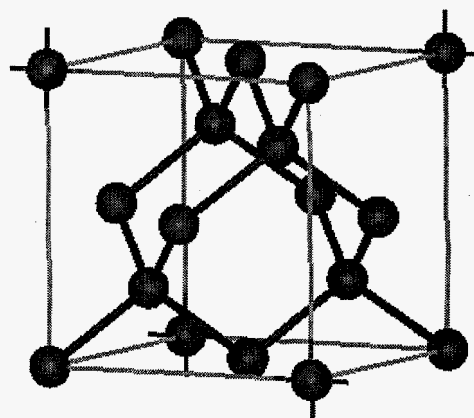


FIGURE 2. A SINGLE UNIT CELL OF THE DIAMOND LATTICE.

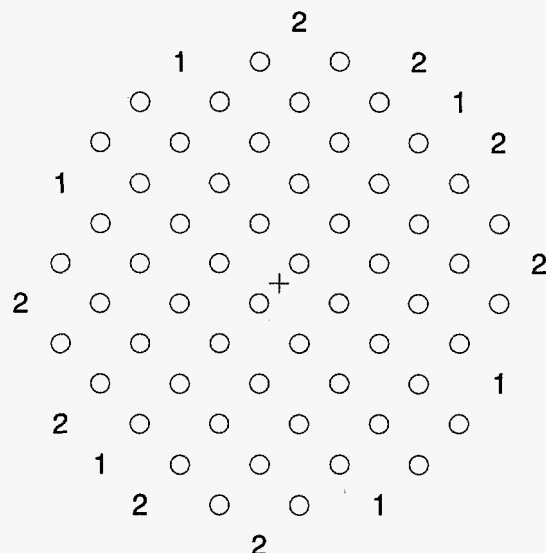


FIGURE 3. THE $z=1/4$ PLANE OF A 23 Å CLUSTER. SINGLE (1) AND DOUBLE (2) DANGLING BONDS.

type of surface atoms are counted. A typical result is illustrated in Figure 3. This shows an x - y plane of the cluster at $z=\frac{1}{4}$. The surface atoms are denoted by a number indicating the associated number of dangling bonds. That is, the number of dangling bonds is the number of nearest neighbor carbon atoms sites that are outside of the cluster radius. Nonsurface atoms, denoted 'core carbon atoms', are indicated by a circle and the origin is given by a plus. The pattern of each layer is the same as the bottom face shown in Figure 2, but with a properly shifted origin. Also note that the tetrahedral bonds are all out of the plane. Each

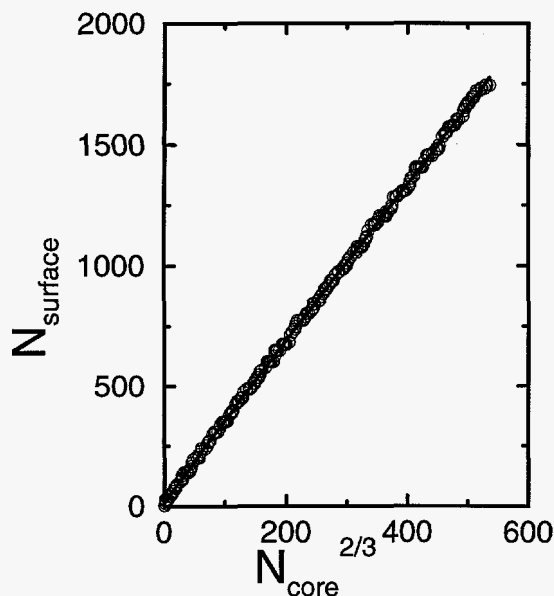


FIGURE 4. NUMBER OF SURFACE ATOMS (O) AND FIT (LINE) VERSUS $2/3$ POWER OF THE NUMBER OF CORE ATOMS.

layer, for a given radius, shows a different pattern of surface groups. The surface of a sphere depends on radius as r^2 and should be approximately proportional to the number of surface atoms, n_s . Likewise, the volume goes as r^3 and corresponds to the total number of core atoms n_c . In Figure 4, we plot n_s versus $n_c^{2/3}$ for clusters ranging up to around 50 Å in diameter (over 10,000 atoms). Letting $x = n_c^{2/3}$, the data are very well fit by the function

$$n_s = f_0 + f_1x + f_2x^2 + f_3x^3, \quad (1)$$

where $f_0 = 14.5353823$, $f_1 = 3.4644895$, $f_2 = -0.0005789$, and $f_3 = 0.0000004438$.

When we begin to put real groups on the dangling bonds, it is very important what type of bond is available. In Figure 5, we plot the fraction of the surface atoms that are of each type as a function of the number of core atoms to the $-1/3$ power. This choice of variable is convenient because the large n_c limit is a small extrapolation from the covered range and the behavior of the function is nearly linear. For practical use, the fraction of double bonds is represented by a fit, $F_{double} = 0.29594 + 0.41873N_{core}^{-1/3}$. The number of triple dangling bonds is relatively small and sometimes zero. However, each triple dangling bond can be replaced by a single dangling bond with a capping group that has a carbon atom with three bonds capped. For example, three hydrogen caps on a triple dangling bond is equivalent to a single dangling bond

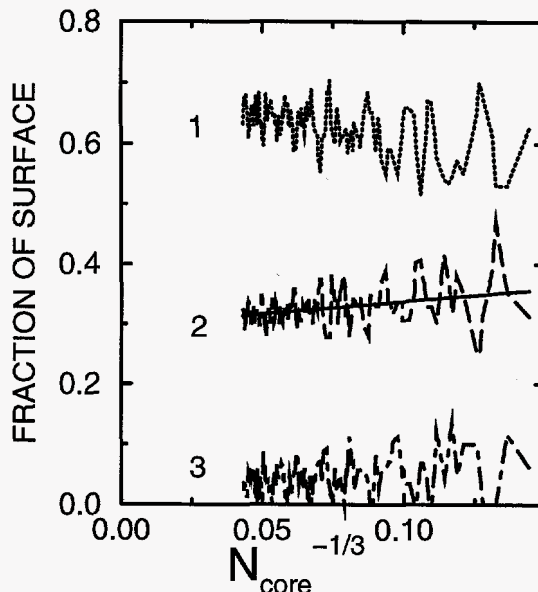


FIGURE 5. THE FRACTION OF SURFACE ATOMS WITH SINGLE (1, DOT), DOUBLE (2, DASH), AND TRIPLE (3, CHAIN DASH) DANGLING BONDS, VERSUS THE $-1/3$ POWER OF THE NUMBER OF CORE ATOMS.

with a CH_3 group as the cap. So, the triple dangling bond surface atoms are effectively added to the single bond atoms and $F_{single} = 1 - F_{double}$.

Now we turn our attention from the surface dangling bond sites, per se, to the surface groups that cap the bonds and how to characterize the free energy of the total cluster. Remember that the goal is to include equilibrium composition on the surface, so we have to explicitly give the free energy as a function of the surface composition. The total partition function Q is factored into separate parts for which the cross interactions can be ignored. Each of these isolated components contributes additively (in this approximation) to the total Helmholtz free energy $A = -kT \ln(Q) = U - TS$. Eventually, we will use the Gibbs free energy $G = A + PV$ since the various components of the mixture are at the same P and T .

Some definitions of notation are necessary to keep track of the relevant variables. For this model, the number of core atoms in a cluster n_c is taken as a constant for all clusters although the average over a distribution will give the same results. The number of moles of clusters is denoted x_c and the number of atoms in the core of all the clusters is given by $N_c = N_A n_c x_c$, where N_A is Avogadro's number. From the previous discussion, the total number of surface atoms in a cluster, n_s , is given by Equation 1 and the

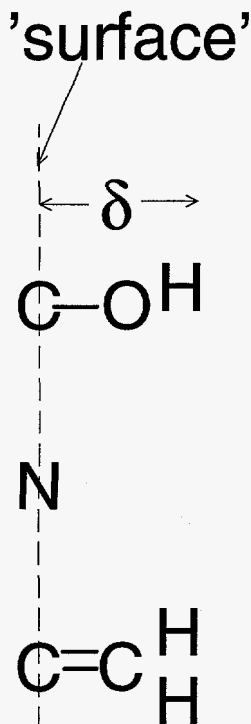


FIGURE 6. TYPICAL GROUPS ON THE SURFACE OF A CLUSTER. THE EFFECTIVE THICKNESS OF A SURFACE GROUP IS DENOTED δ .

total number of surface atoms in all of the clusters is given by $N_s = n_s x_c N_A$. Likewise, the number of single and double bond surface groups are $N_1 = n_1 x_c N_A$ and $N_2 = n_2 x_c N_A$, respectively. Again from the previous discussion, $n_1 = F_1 n_c$ and $n_2 = F_2 n_c$. Let $N_i^{(1)}$ denote the total number of groups of type i that are on single bond surface sites and $x_i^{(1)}$ the corresponding number of moles. The number of atoms of type j in a group i is given by a_{ij} and the same notation will be used for the composition of molecules in the fluid.

The composition of particular choices of surface groups is conveniently characterized in the form Y-R, where Y is the atom that occupies the given surface site, normally C. However, the option of substituting another atom (e.g. N or O) in its place is allowed. R denotes the rest of the surface group. For example, Y=C and R=OH (single bond site) is the top case in Figure 6. Next is Y=N and R=none for a substitutional group (single bond site) and then Y=C and R=CH₂ on a double bond site. Each of the surface bond sites can be occupied by one of several choices of surface group types.

As we will see, the separate free energy terms for a given group type on a given bond site type is independent of the location of the site. That independence gives an entropy contribution due to counting of states. We have included a dangling bond among the possible surface group types (i.e. Y=C and R=none, treated as a separate group type for single and for double), so all of the surface sites are occupied. That is, $N^{(1)} = \sum' N_i^{(1)}$ and $N^{(2)} = \sum' N_i^{(2)}$, where the prime on the summation means to only include terms of the same bond site type. The surface sites can in principle be labeled in the same way as lattice sites in a crystal. Taking into account identical surface groups, the total number of ways to occupy all of the surface single bond sites is given by

$$N_{count}^{(1)} = \frac{N^{(1)}!}{N_1^{(1)}! N_2^{(1)}! \dots N_i^{(1)}!} \quad (2)$$

The contribution of this factor in the partition function to the free energy is given by

$$-\beta A_{count} = \ln(N^{(1)}!) - \sum' \ln(N_i^{(1)}!) \quad (3)$$

Using Stirling's formula and substituting numbers of moles,

$$\frac{A}{NkT} = \sum' x_i^{(1)} \ln(x_i^{(1)}/x^{(1)}) \quad (4)$$

and similarly for the double bond sites.

The vibrational terms are determined with a hybrid model. The core atoms are all taken together using a Debye model³ with the volume dependence of the Debye temperature chosen to give a constant Grüneisen gamma. The surface group vibrational modes are assumed to not couple too strongly to the core vibrations. An Einstein model is used for each vibrational frequency (with the same volume dependence). The vibrational modes on the surface are estimated from isolated molecules of the form Z-R where Z=CH₃ in place of a single bond site and Z=CH₂ for the double bond. Not all of the frequencies can be estimated this way. An arbitrary low frequency is chosen for the bending of the R group as a whole against the nearly fixed surface.

The cold curve is taken from bulk diamond with minor modifications allowed. The volume of each surface group is estimated by the geometric extension of the surface (δ in Figure 6) times an effective surface area for each surface site. The value of δ is estimated from bond distances and angles in the model molecule Z-R. An effective standoff distance from the geometric

surface is chosen to take into account that the occupied volume (i.e. volume excluded from the molecular fluid) is not identical to the geometric volume. Notice for substitutional cases, δ will be small or even negative. In particular, this will be very important for N. The PV term in the Gibbs free energy is very favorable, but only at high enough pressure. The volume of surface group is scaled with the diamond cold curve.

The heat of formation for a cluster is given by additive bond strengths. Starting from the bulk values, the surface is created by breaking bonds and half the total is added to the energy of the cluster. The ΔH_f for R in the gas phase is added. The Z-R bond strength is subtracted to estimate the actual surface bond strength. The net Gibbs free energy is a strong function of surface composition.

MOLECULAR MIXTURES

Benchmark simulation methods provide the testing ground for the various approximations that are used in calculating the contributions of the molecular fluid mixture. 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 interactions⁴ (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 transformation Monte Carlo method⁵ was developed that efficiently simulates a large range of states from a single reference simulation. Most important, we have developed the $N_{atoms}PT$ ensemble Monte Carlo method⁶. 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 Figure 7, we illustrate the effect of a small shift in cross potential on the chemical equilibrium composition. In

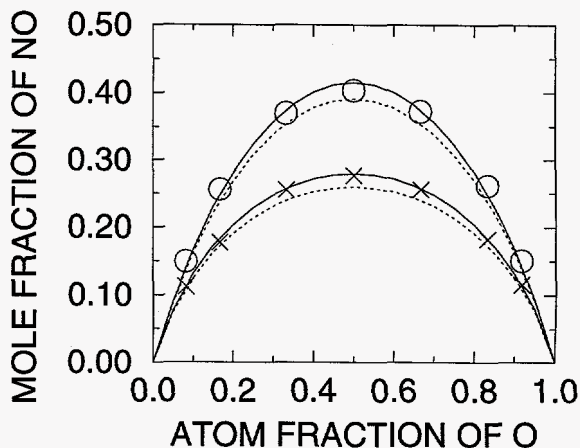


FIGURE 7. SIMULATION FOR TWO DIFFERENT CROSS POTENTIALS, X AND O (SEE TEXT). LINES ARE PERTURBATION THEORY WITH IDEAL MIXING AND ENTROPY SHIFTS.

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 previously⁷. 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.

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 method⁸ 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 individual potential for a given species is primarily determined from Hugoniot data and where available, spectroscopy measurements leading to a temperature⁹. Constants affecting nonideal mixing

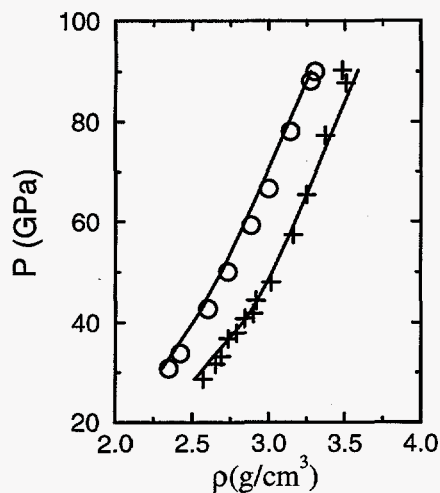


FIGURE 8. PRESSURE VERSUS DENSITY ON THE OVERDRIVEN HUGONIOT FOR PBX-9501 (O) AND PBX-9502 (+). THEORY (LINE).

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 constraint¹⁰.

The total Gibbs free energy for a molecular fluids mixture plus small carbon clusters is then used to calculate the thermodynamic chemical equilibrium composition. The Gibbs free energy is minimized with respect to all molar concentrations consistent with the net atomic composition. Not only are the molecular fluid components dependent on the state and the net composition, but also the chemical composition of the surface of the diamond clusters now varies.

CALIBRATION

Not all parameters used to describe the total detonation products EOS are well determined. On the other hand, there is often a physically meaningful choice over a limited range. For example, the Debye temperature used to characterize the diamond cluster core is going to be softer than for bulk diamond due to the large surface effect. Lacking measurements on 20 Å diamond clusters this can be adjusted to better fit detonation data, but there is a limit. One way to handle this limited constraint is within a modified nonlinear least squares fit to data. Let y_i be the calculated value for a measurement y_i^0 with a standard deviation σ_i . Let z_j be the value of a parameter for

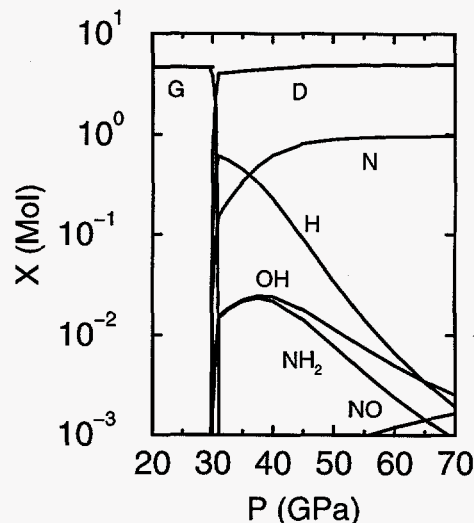


FIGURE 9. MOLAR CONCENTRATION OF ATOMS IN GRAPHITE CLUSTERS (G) AND DIAMOND CLUSTERS (D) VERSUS PRESSURE. N SUBSTITUTED FOR A SURFACE CARBON (N) AND OTHER CAP GROUPS AS LABELED.

which we have some estimate of a physically meaningful value z_j^0 with an estimated uncertainty δ_j . For a limited number of parameters, the function

$$f = \sum_i \left(\frac{y_i - y_i^0}{\sigma_i} \right)^2 + \sum_j \left(\frac{z_j - z_j^0}{\delta_j} \right)^2 \quad (5)$$

can be minimized for a 'best' choice of z_j 's. This method was used over a limited set of data and constants. Further refinement is planned, in particular using more of the new types of measurements such as sound speeds¹⁰ and temperatures⁹.

RESULTS

The calculations presented here are focused on two examples that are strongly dependent on the chemical equilibrium of clusters and surface groups. The first case is the overdriven Hugoniot^{10,12} data for PBX-9501 and PBX-9502. In Figure 8, the PBX-9501 data of pressure versus density is smoothly varying. For PBX-9502, however, there is a noticeable slope change in the data. The present theory is able to reproduce both features of the data at the same time. The slope change in the theory is due to an interesting chemical equilibrium effect on the surface of the diamond clusters. The concentrations of several species are shown in Figure 9. Note that the concentrations for graphite and diamond clusters have

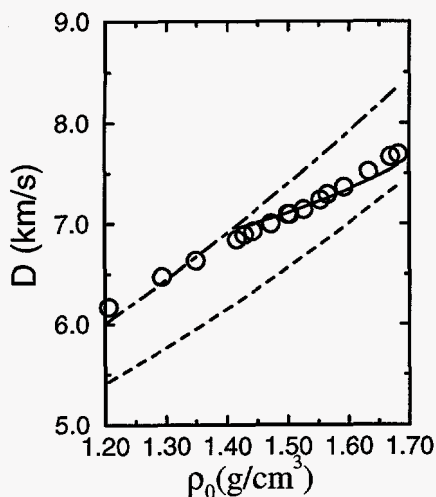


FIGURE 10. DETONATION VELOCITY OF 50/50 RDX/TNT VERSUS INITIAL DENSITY. THEORY: EQUILIBRIUM (LINE), GRAPHITE ONLY (CHAIN DASH), AND DIAMOND ONLY (DASH).

been multiplied by the number of carbon atoms in the core of the cluster. That is, the concentration is of C atoms, not of clusters. The curve labeled N is the case $Y=N$ and $R=\text{none}$, a substitutional N atom. At high pressure, almost the entire set of single dangling bond sites is occupied by N atoms. The PV term in the free energy gives preference to smaller volumes. At lower pressures, the case $Y=C$ and $R=H$ takes over with a larger volume but a lower energy. A few of the minor surface species are also shown. Note that the graphite-diamond transition is spread over 1-2 GPA and is below the range of the data. The surface chemical composition shift from 30-50 GPa is enough to make a significant shift in the slope. In the same region for PBX-9501, the total concentration of carbon clusters is much smaller and so is the effect.

The second case shows a very large effect due to the graphite diamond transition. Measurements¹¹ of the detonation velocity of 50/50 mixture (by weight) of RDX/TNT showed a substantial change in slope as a function of initial density, Figure 10. An equilibrium calculation shows all graphite below $\rho_0=1.4 \text{ g/cm}^3$ and all diamond above $\rho_0=1.7 \text{ g/cm}^3$. In the intermediate densities, the equilibrium detonation velocity (line) fits the data very well. In Figure 11, we show the calculated shock velocity versus particle velocity at $\rho_0=1.682$ for equilibrium (line), graphite only (chain dash) and diamond only (dash). A very

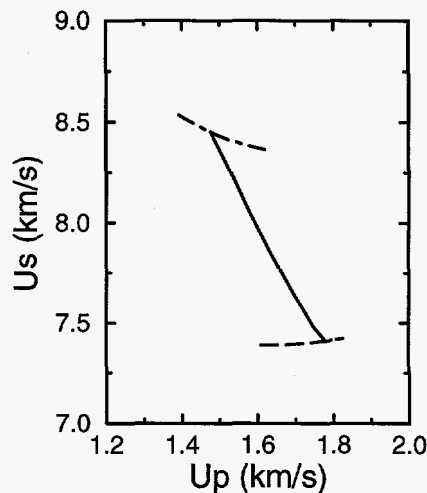


FIGURE 11. SHOCK VELOCITY VERSUS PARTICLE VELOCITY. EQUILIBRIUM (LINE), GRAPHITE ONLY (CHAIN DASH), AND DIAMOND ONLY (DASH).

interesting feature is that the intermediate density regime is not due to the minimum shock velocity occurring in the mixed region. Rather, the equilibrium shock velocity is coincident with the graphite only curve at low velocity and with the diamond only curve at high velocity. The minimum in the shock velocity occurs at the state where the equilibrium has just shifted all the way to diamond. This doesn't occur at the minimum in the pure diamond shock velocity, but at a higher shock velocity. Even though the graphite diamond transition region is narrow, the effect is amplified by this unusual behavior of the shock velocity.

CONCLUSION

The chemical equilibrium treatment of surface chemistry on diamond clusters was started based on the premise that there was too large a fraction of atoms on the surface to treat the carbon as a pure bulk material. The calculations demonstrate that there can be regions with a large shift in the chemical composition on the surface and that the consequences of these shifts are within the range of sensitivity of experiments. These preliminary results suggest that fitting an EOS theory to detonation velocity data is not as straightforward as it seems. Significant portions of the data could be strongly influenced by transition regions in the chemical composition.

This study is essentially a lowest order model of chemical equilibrium on the surface of clusters. Fur-

ther study should include a better evaluation of vibrational frequencies, heats of formation, compressibility of the complex cluster, etc.

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DISCUSSION

Ricardo Mendes
University of Coimbra
Portugal

Do you have results on how the diamond-graphite phase transition is related to the release wave of a detonation?

REPLY BY M. SAM SHAW

If the release wave follows chemical equilibrium, then there would be a region of lower slope connecting the two higher slope regions, forming a steplike structure. Once a diamond phase is formed at high pressure, however, it might persist as a metastable phase down to lower pressure. Then the structure in the release would not be seen.

DISCUSSION

Michael L. Hobbs
Sandia National Laboratories
Albuquerque, New Mexico

Since TNT has a lot of carbon, I expect to see an enhanced influence of the carbon EOS. The data seems smooth with no "kinks". Isn't a single-phase carbon EOS adequate for this system?

REPLY BY M. SAM SHAW

Actually, there is the beginning of a break in the D versus ρ_0 curve at the highest density. Dremine et al.¹¹ show that the kink becomes more pronounced as RDX is added to TNT. This gets the detonation pressure high enough for the effect to be more easily measured.

DISCUSSION

Andrei I Sumin
Mendeleev University of Chemical Technology
Moscow, Russia

What do you say about the form of curve of detonation pressure on the charge density for mixtures of TNT/RDX?

REPLY BY M. SAM SHAW

As the density increases, the detonation pressure makes a large jump at $\rho_0 \approx 1.40 \text{ g/cm}^3$. Throughout the transition region, the detonation condition is determined by where the equilibrium shifts to all diamond. The detonation pressure varies slowly in this region. The slope then increases at high ρ_0 as the detonation condition is then determined by the minimum in shock velocity of the diamond only phase.