DIRECT SIMULATION OF DETONATION PRODUCTS EQUATION OF STATE BY A COMPOSITE MONTE CARLO METHOD

M. Sam Shaw
Group T-14 Mailstop B214
Los Alamos National Laboratory
Los Alamos, New Mexico 87545

Computer simulations are presented for a Composite Monte Carlo method, which allows direct simulation of 'real' explosives such as HMX and TATB. Chemical equilibrium, solid carbon, fluid-fluid phase separation, and the like, are all included in a single simulation method. Now, the entire detonation products equation of state can be simulated instead of isolated portions for limited benchmarks. The solid carbon phases (bulk and/or cluster) are incorporated using analytic models, while the fluid components are explicitly included in the Monte Carlo simulation. Chemical reactions are treated by a correlated interchange of atoms between species. Solid carbon enters as virtual particles with an associated Gibbs free energy. Simulations for HMX, PBX 9501 and PBX 9502 products cover a range of pressures up to 80 GPa and temperatures up to 5000 K. Starting with potentials chosen for good agreement with single fluid EOS data, the strong dependence of the EOS on cross potentials is demonstrated. This includes chemical equilibrium composition and shifts in the fluid-fluid phase separation lines. Detonation velocity versus density, overdriven Hugoniot, and isentropes are determined from interpolation of a tabulation over a dense set of states in the independent variables P and T.

INTRODUCTION

The detonation products equation of state (EOS) involves a complicated reactive mixture of molecular fluids (e.g. CO_2, N_2, H_2O, and CO) and carbon clusters consisting of a few thousand atoms. The conditions are extreme with pressures on the order of 30 GPa, temperatures around 3000 K, and densities 2-3 times normal liquid values. The products EOS is very sensitive to changes in the equilibrium chemical composition, details of mixing, fluid-fluid phase separation, phases of the carbon, and chemistry on the surface of the carbon clusters.

Current theoretical treatments of detonation products equation of state are primarily based on thermodynamic perturbation theory using spherical potentials. Although very accurate for single species fluids,

mixing procedures are less accurate and are based on limited benchmarking. For more complicated potentials, the mixing theory is even less certain. These uncertainties are amplified by the strong dependence of the chemical equilibrium composition on these details and also possible fluid-fluid phase separation. In addition, most explosives are oxygen poor resulting in solid carbon. The treatment of the carbon involves phase changes as well as surface effects (including surface chemistry) from the small cluster size.

Monte Carlo and molecular dynamics simulation methods have often been used to benchmark various approximations mentioned above. Unfortunately, they have been limited to special cases investigated separately. For example, Gibbs ensemble Monte Carlo has been used to determine fluid-fluid phase separation. My previously developed $N_{atoms}PT$ ensemble Monte Carlo[1-3] has been used to study the chemical equilibrium composition, but only in a fluid mixture (no solid carbon). In this case, the chemical equilibrium composition has been shown to be sensitive to the assumed cross potentials for fluids.

A new Composite Monte Carlo method is presented here that allows the direct simulation of detonation products for 'real' explosives such as HMX, TATB, PBX 9501, and PBX 9502. Chemical equilibrium composition, solid carbon, and phase separation are included. Now, the entire problem of interest can be simulated instead of just isolated portions as benchmarks for approximate perturbation methods. The method is a composite of several types of Monte Carlo simulation methods with more general features added. In particular the solid carbon is implemented as an analytic model embedded in the Monte Carlo method. This solves the problem of how to
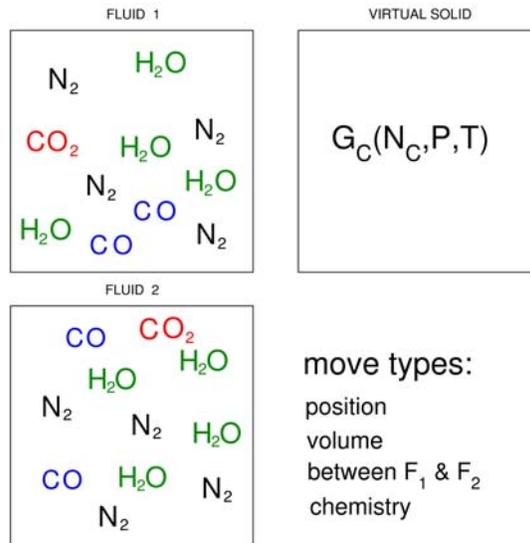
FIGURE 1. SIMULATION BOXES

include carbon phases that react with the molecular fluid mixture. That is, a direct simulation of the carbon phase would not allow for the straightforward addition and subtraction of single carbon atoms while preserving the symmetry of the solid.

COMPOSITE MONTE CARLO

The Composite Monte Carlo Method is constructed as a generalization of the $N_{atoms}PT$ ensemble Monte Carlo Method[1-3]. The preliminary extension to include solid carbon[4] is expanded here. The total number of atoms is preserved, but different collections of atoms into molecules are allowed. The Gibbs ensemble treatment of fluid-fluid phase separation[5] is readily incorporated.

In order to include solid products as well, the partition function is formally separated into three parts where the phase denoted by the subscripts are given by: 0=solid, 1=fluid1, and 2=fluid2. The corresponding three simulation boxes are illustrated in Fig. 1. The total volume is just the sum of the parts, i.e. $V=V_0+V_1+V_2$

The classical partition function for a canonical ensemble with identical atoms is just

$$Q(N,V,T) = \frac{V^N}{N!\Lambda^{3N}} \int e^{-\beta U} ds_1 \cdots ds_2 \quad (1)$$

where the scaled coordinates, ds_i, are over a unit volume and the total potential energy, U, is evaluated for the actual coordinates in a volume V. For the isothermal-isobaric ensemble

$$\Delta(N,P,T) = \int_0^\infty e^{-\beta PV} Q(N,V,T) dV \quad (2)$$

Let A_i be the total number of atoms of type i out of I types of atoms, and ^kM_j the number of molecules of type j in box k. Then the generalization is

$$\Delta(N,P,T) = \quad (3)$$

$$\iiint e^{-\beta P(V_0+V_1+V_2)_1} \sum{}' Q_0 Q_1 Q_2 dV_0 dV_1 dV_2$$

which can be rewritten as

$$\iint \sum{}' e^{-\beta G_C(N_C,P,T)} e^{-\beta P(V_1+V_2)} Q_1 Q_2 dV_1 dV_2 \quad (4)$$

where $e^{-\beta G_C(N_C,P,T)} = e^{W_0} = \Delta_C(N_C,P,T)$ will be evaluated directly using an approximate analytic scheme for solid carbon, combining a cold curve and a Debye model. Q_k denotes $Q_k(^kM_1,\cdots,^kM_J,V_k,T)$ and the prime on the summation indicates only those sets of molecules in the three boxes such that the total number of atoms of each type over the whole is conserved.

Each of the fluid Q_k's take into account the distinguishability and mass of each

molecule. Also, internal degrees of freedom, such as vibrational modes, for each molecule are treated as separable quantum partition functions for the isolated molecule. The product of all these contributions are denoted q_j for a molecule of the jth type. For a given set of molecules in the kth fluid box, the partition function becomes

$$Q_k(^kM_1,\cdots,^kM_J,V_k,T) = \quad (5)$$

$$\frac{V_k^{M_k} q_1^{^kM_1} \cdots q_J^{^kM_J}}{^kM_1! \cdots ^kM_J! \Lambda_1^{3^kM_1} \cdots \Lambda_J^{3^kM_J}}$$

$$\times \int e^{-\beta U_k} d^k s_1 \cdots d^k s_{M_k}$$

where M_k is the total number of molecules in box k and U_k is the total potential energy of the molecules in box k. The full partition function is

$$\Delta(P,T) = \int_0^\infty \int_0^\infty \iint \sum{}' \quad (6)$$

$$\left[e^W dV_1 dV_2 d^1 s_1 \cdots d^1 s_{M_1} d^2 s_1 \cdots d^2 s_{M_2} \right]$$

where

$$W = -\beta G_C(N_C,P,T) - \beta[U_1 + PV_1] \quad (7)$$

$$-\beta[U_2 + PV_2] + M_1 \ln(V_1) + M_2 \ln(V_2)$$

$$\sum_{j=1}^J \sum_{k=1}^2 \left[^kM_j(\ln(q_j) - 3\Lambda_j) - \ln(^kM_j!) \right]$$

For the Monte Carlo simulation, we want a Markov chain with a limiting distribution proportional to e^W. A trial move from a

state r to a state s should be accepted[5,6] with a probability

$$P_{r \to s} = Min\big[1, \exp(W_s - W_r) p_{s \to r} / p_{s \to r}\big] \quad (8)$$

where $p_{r \to s}$ is the probability of a move from r to s, without taking into account the weighting factor. In addition, the $\ln(^k M_j!)$ terms are included only if the particles are treated as distinguishable. For the case where a state is characterized by a set of positions, without regard to order, and the corresponding particle type at each position, then that term is dropped because the particles are already treated as indistinguishable.

There are four types of moves used in the simulation: position, volume, between fluids, and chemistry. Position moves are precisely those of standard NVT ensemble Monte Carlo[6,7]. In this case, the only part of W that changes are the $-\beta U$ terms and $p_{r \to s} = p_{s \to r}$. Volume changes are made by uniform scaling and are just those of the NPT ensemble. For the next two types of moves, $p_{r \to s} \neq p_{s \to r}$ in general, but the ratio is easily determined from counting the number of ways to choose particles for that type of move. Moves between fluids can occur by interchange of particles or by moving a single particle from one box to another as in the Gibbs ensemble[5].

The chemistry moves in the hybrid method are generalizations of the $N_{atoms}PT$ ensemble[1-3] to include solids. The virtual solid box in Fig. 1 represents the analytic contribution of the solid to W, rather than an actual simulation cell.

Figure 2 represents the initial state of the forward reaction $CO_2 + C \Rightarrow 2CO$, where the CO_2 molecule and the C involved in the chemistry step are selected. Also, the random position for a particle insertion is represented as the empty circle. In atomistic terms, there is a correlated move of one O from the CO_2 and one C from the solid carbon to the chosen location for particle insertion. In molecular terms, a move is made from a state in one term of the summation in Eqn. 5 to a state in a different term in the summation, corresponding to a different correlation of atoms into molecules.
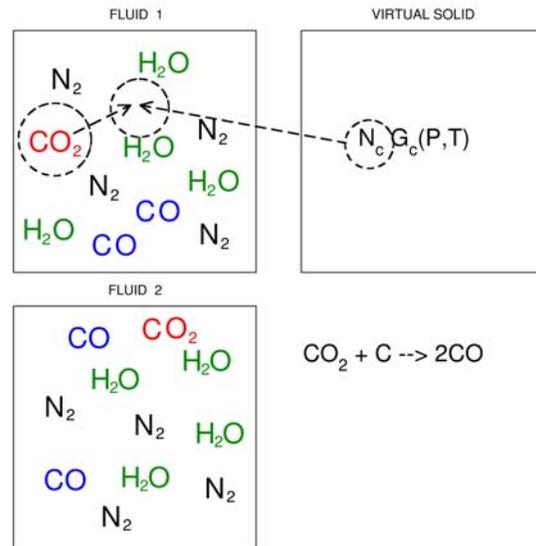
FIGURE 2. CHOOSE THE REACTANTS: $CO_2 + C$
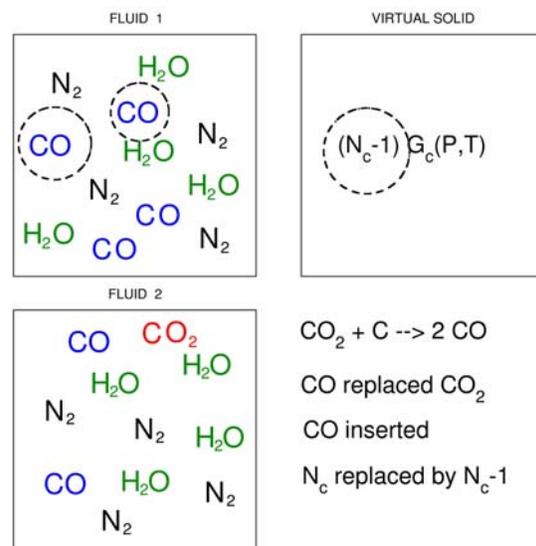
FIGURE 3. REPLACE WITH PRODUCTS: 2CO

The final state of this chemistry step is illustrated in Fig. 3. The number of carbon atoms in the virtual solid is reduced by one, a CO molecule is inserted, and the CO_2 is replaced by CO. For the reverse reaction, $2CO \Rightarrow CO_2 + C$, one of the chosen CO molecules is replaced by CO_2 and the other is eliminated. The number of carbon atoms in the virtual solid is increased by one. Then Fig. 3 shows reactants and Fig. 2, products. The unweighted probability of choosing a reaction move from state r to state s depends on how a move is chosen. For example, two particles are chosen at random. If these two particles lead to an allowed reaction, then a reactive move is attempted. Otherwise, a new pair is selected. For the forward reaction, it doesn't matter which particle is chosen first since the final state consists of indistinguishable CO molecules at the two chosen positions. So, there are two choices that lead to the same final state for each of N_C carbon atoms. The reverse reaction, for the case where the first choice becomes CO_2 and the second choice C, leads to only a single choice leading to a particular final state. Neglecting a minor correction due to slightly different numbers of total choices available in the two states, the forward reaction gives the ratio $p_{s \rightarrow r} / p_{r \rightarrow s} = \dfrac{1}{2N_C}$ and the inverse for reverse reaction steps. Other scheme for choosing a reaction lead to different ratios, but are as readily determined. For example, a reaction could be chosen at random and then the reactants from the set of particles of the type of each reactant. Then the number of particles of each type enters into the unweighted probabilities explicitly rather than implicitly as in the previous method.

RESULTS

Monte Carlo simulations have been made with the composite method for equilibrium products of HMX, PBX 9501, and PBX 9502. In the current study, the products are restricted to N_2, H_2O, CO_2, CO, graphite, and diamond (with the addition of HCl and CF_4 for the case of PBX 9502). The importance of surface chemistry on diamond clusters has been shown previously[8,9]. Extension of the Monte Carlo code to include these options are in progress. In the present work, the bulk diamond EOS has been modified to mock up the effects of diamond clusters as seen in the thermodynamic perturbation theory treatment. Quantitative results for these clusters will require the Monte Carlo treatment of clusters with surface chemistry.
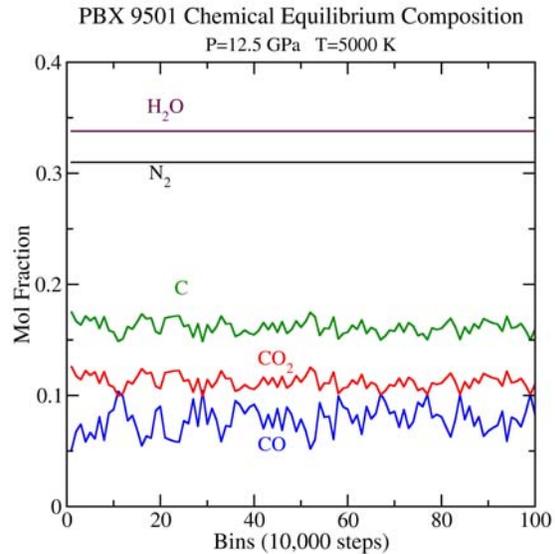
FIGURE 4. FLUCTUATIONS IN PBX 9501 PRODUCTS FOR A SINGLE FLUID MIXTURE SIMULATION

In the Composite Monte Carlo simulations, the chemical composition is sampled in the same fashion as other quantities such and energy and volume. Typical fluctuations are shown in Figure 4 for the case of PBX 9501 at pressure 12.5 GPa and temperature 5000 K. This state

was chosen to avoid overlap of the fluctuations of the individual components and is simulated with a single fluid box. The potentials for interactions of like molecules were chosen from a set found to give good results[8,9] for thermodynamic perturbation theory calculations of detonation products. Two sets of cross-potentials (the potentials between unlike species) are studied here. The first case is the usual Lorentz-Berthelot (LB) combining rules as modified by Ree[10] for exponential six potentials. The second is an arbitrary shift of around 3% in some of the cross potentials to illustrate the sensitivity of the EOS to the choice of cross potentials.
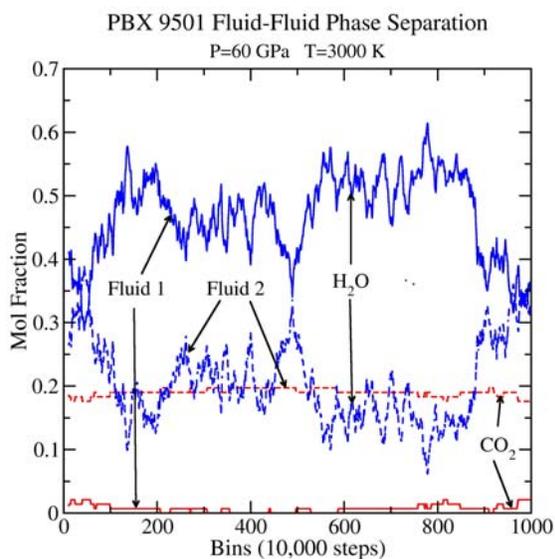
FIGURE 5. HMX PRODUCTS FOR TWO FLUID BOXES WITH FLUID-FLUID PHASE SEPARATION

The inclusion of two fluid boxes is required to include the option of fluid-fluid phase separation. Typical fluctuation in the regime where this fluid-fluid phase separation occurs are illustrated in Figure 5. The shifted cross potentials are used in this case and the pressure is 60GPa and the temperature is 3000K. Only CO_2 and H_2O are shown and the composition from box 1 are solid lines and the results from box 2 are dashed lines.

With modern computer power, simulations can be made over a large number of states. Figure 6 illustrates the choice of P, T sampled in this study. More points are readily added as needed for a particular focus.
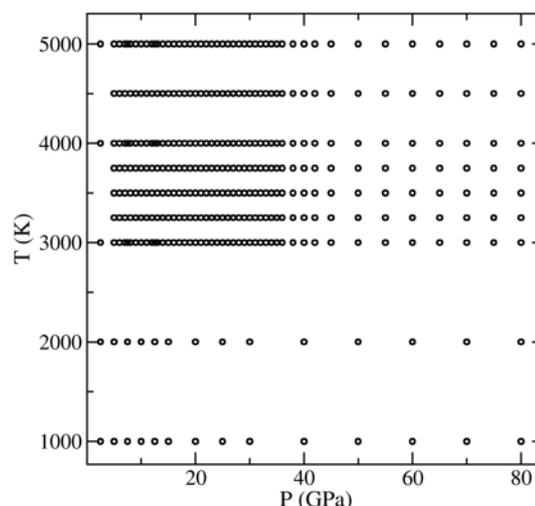
FIGURE 6. MESH OF P, T POINTS SIMULATED

Results are shown in Figure 7 for the variation in concentration of CO (solid blue line) and CO_2 (dash red line) for the LB cross potentials and carbon in the form of graphite as a function of P, T for HMX products.
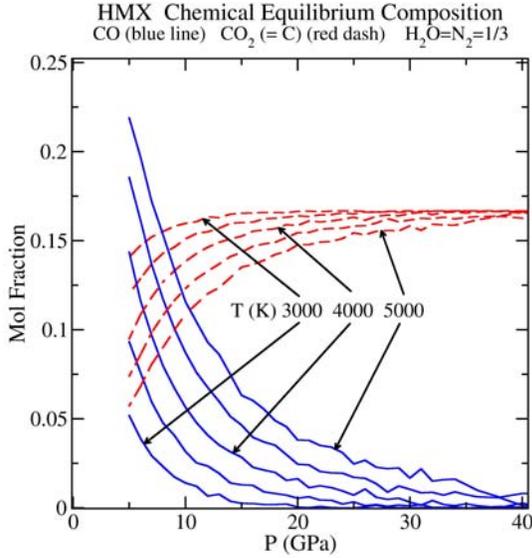
FIGURE 7. HMX CHEMICAL EQUILIBRIUM COMPOSITION

The chemical equilibrium composition is very sensitive to the choice of cross potentials. In Figure 8, the mol fraction of CO is shown for the LB (blue line) and shift (red dash) cross potentials. Note that for HMX with the current choice of products allowed, the total mol fraction for CO, CO_2, and C is 1/3.
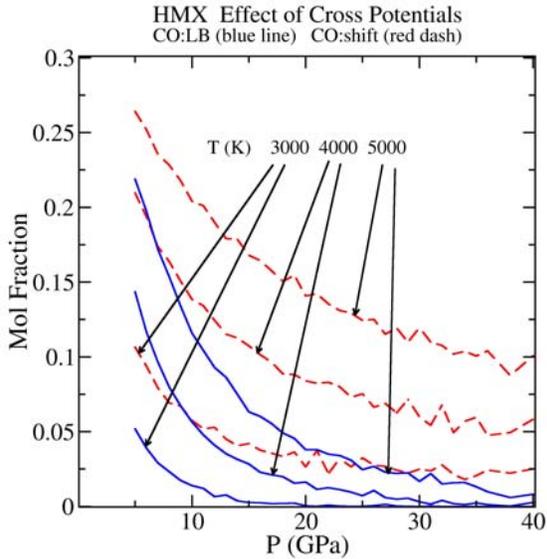
FIGURE 8. VARIATION OF MOL FRACTION OF CO IN HMX DETONATION PRODUCTS WITH CROSS POTENTIAL

Given the current tabulation of simulation points, it is straightforward to determine the Hugoniot by interpolation. For a fixed pressure P, the quantity

$$\Delta E = E - E_0 - 0.5P(V_0 - V) \qquad (9)$$

is calculated for each P,T point and the Hugoniot condition is met for the T where it becomes zero (for given initial conditions E_0 and V_0). Then other quantities are interpolated for that value of T. Then auxiliary properties such as shock velocity

$$U_s = V_0 \sqrt{\frac{P - P_0}{V_0 - V}} \qquad (10)$$

and particle velocity

$$U_P = \sqrt{(P - P_0)(V_0 - V)} \qquad (11)$$

are evaluated. Then the CJ condition is readily evaluated from the minimum of the shock velocity for a given initial condition. This evaluation is illustrated in Figure 9 for HMX at several different initial densities, carbon as graphite, and the LB cross potentials. Lines are fit to the points.
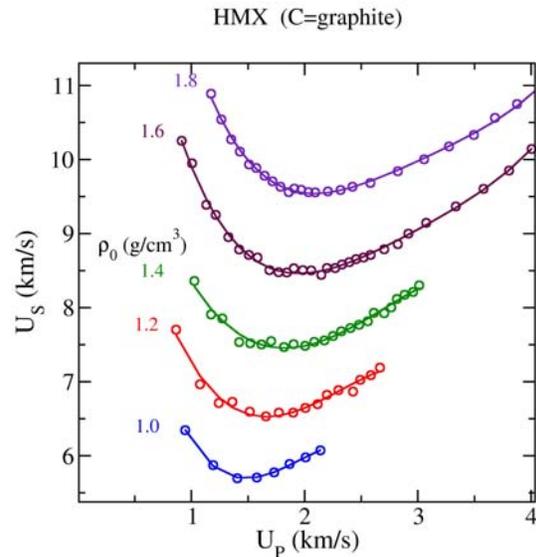
FIGURE 9. U_S VERSUS U_P FOR SEVERAL INITIAL DENSITIES IN HMX

The scale is expanded in Figure 10 for initial density 1.8 g/cm³ (blue line) and the corresponding results for the shift cross potentials (red dash) are shown.
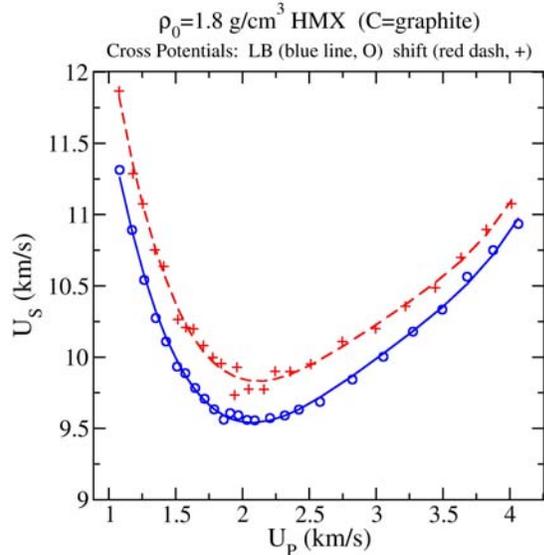
FIGURE 10. LB VERSUS SHIFT

The lines in P, T space covered by the Hugoniots at different initial densities (1.0, 1.2, 1.4, 1.6, and 1.8 from left to right) and different cross potentials (LB - line and shift - dot) are illustrated in Figure 11. The tabulated mesh is shown as the grey background points.
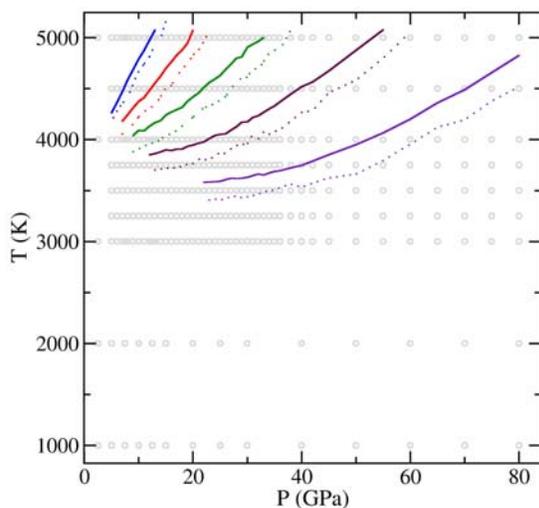
FIGURE 11. HUGONIOT LINES IN P, T SPACE FOR HMX

The variation of detonation velocity with initial density is compared with experimental results for HMX and RDX in Figure 12. Note that the net elemental compositions are identical and the initial energies (per gram) are nearly identical. The results for LB (line) are compared with shift (dash). Results for graphite (black) and diamond (blue) are shown.
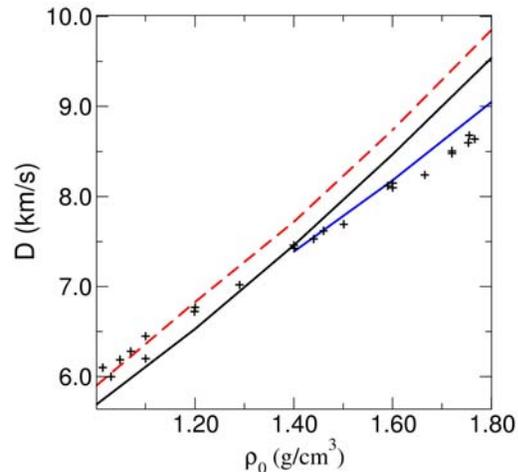
FIGURE 12 DETONATION VELOCITY VERSUS DENSITY FOR HMX

Similar results are shown for PBX 9501. The Hugoniot lines in P, T space are shown in Figure 13 for initial densities 1.0, 1.2, 1.4, 1.6, 1.8, and 1.84. Also shown is the location of the fluid-fluid phase separation line for the shift cross potentials. The LB cross potentials do not show this phase and the location of the line is again very strongly dependent on the choice of cross potentials The difference in detonation velocity results with cross potential set is also shown in Figure 14.

Results for PBX 9502 are also shown in Figures 15 and 16 for initial densities 1.4, 1.5, 1.6, 1.7, and 1.8.

CONCLUSIONS

A Composite Monte Carlo method has been developed that includes solid products in addition to previously developed methods for fluid-fluid phase separation and chemical equilibrium. The equilibrium detonation products EOS can now be simulated directly for explosives of
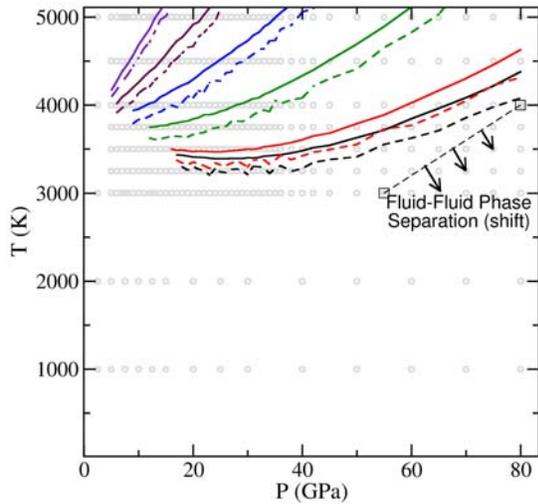
FIGURE 13 HUGONIOT LINES IN P, T SPACE FOR PBX 9501
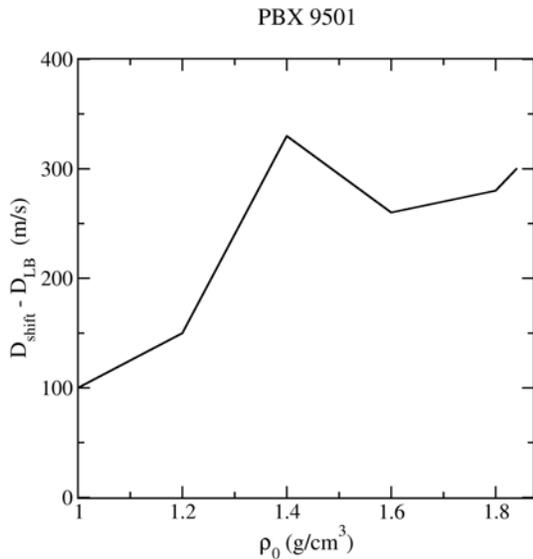
FIGURE 14. EFFECT OF CROSS POTENTIALS ON DETONATION VELOCITY FOR PBX 9501
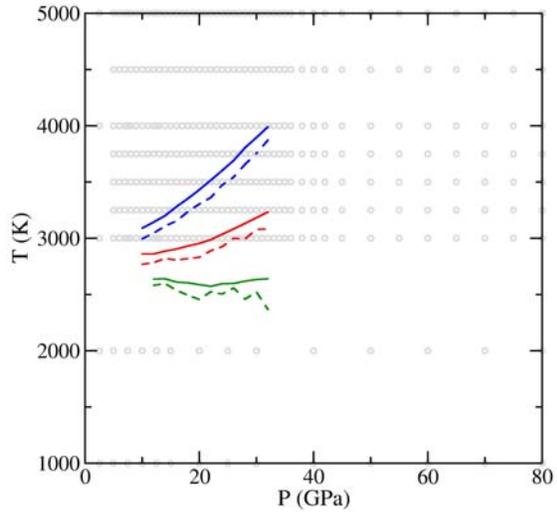
FIGURE 15. HUGONIOT LINES IN P, T SPACE FOR PBX 9502
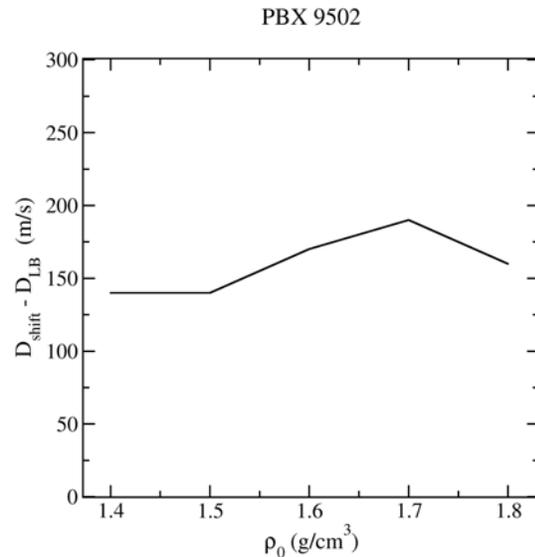
FIGURE 16. EFFECT OF CROSS POTENTIALS ON DETONATION VELOCITY FOR PBX 9502

practical interest such as HMX and TATB. With current high speed workstations, a tabular EOS with hundreds or even thousands of points is easily made. Simple approximate potentials, mixing rules, and perturbation theory methods are no longer necessary. Alternatively, these approximate schemes can be benchmarked against the

full EOS instead of isolated parts.

As the extension to clusters with surface chemistry is accomplished, the method will be used to calibrate a set of potentials that matches a large body of detonation data.

ACKNOWLEDGEMENTS

REFERENCES

1. Shaw, M. S., "Monte Carlo Simulation of Equilibrium Chemical Composition of Molecular Fluid Mixtures in the $N_{atoms}PT$ Ensemble," J. Chem. Phys. 94, 7550 (1991).
2. Shaw, M. S., "Direct Monte Carlo Simulation of Chemical Equilibrium Composition of Molecular Fluid Mixtures Under Shock Conditions," in Shock Compression of Condensed Matter 1991, edited by S. C. Schmidt et al., North-Holland, Amsterdam, 1992, pp. 131-134.
3. Shaw, M. S., "Direct Monte Carlo Simulation of the Chemical Equilibrium Composition of Detonation Products," in Tenth International Detonation Symposium, edited by J. M. Short, ONR 33395-12, Arlington, 1995, pp401-408.
4. Shaw, M. Sam, "A Hybrid Monte Carlo Method for Equilibrium Equation of State of Detonation Products," in Shock Compression of Condensed Matter 2001, to be published.
5. Panagiotopoulos, A. Z., Quirke, N., Stapleton, M., and Tildesley, D. J., Mol. Phys.63, 527-545 (1988).
6. Metropolis, N., Rosenbluth, A. W., Teller, E. H., and Teller, E., J. Chem. Phys., 21, 1087-1092 (1953).
7. Allen, M. P., and Tildesley, D. J., "Computer Simulation of Liquids", Clarendon Press, Oxford, 1987, pp 110-139.
8. Shaw, M. S., "A Theoretical Equation of State for Detonation Products with Chemical Equilibrium Composition of the Surface of Small Carbon Clusters," in Shock Compression of Condensed Matter - 1999, edited by M. D. Furnish et al., AIP Conference Proceedings 505, New York, 2000, pp. 235-238.
9. Shaw, M. S., "A Theoretical Equation of State for Detonation Products," in Eleventh International Detonation Symposium, edited by J. M. Short, ONR 33300-5, Arlington, 2000, pp. 933-941.
10. Ree, F. H., J. Chem. Phys. 81, pp. 1251 (1983).