DIRECT MONTE CARLO SIMULATION OF THE CHEMICAL EQUILIBRIUM COMPOSITION OF DETONATION PRODUCTS

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A new Monte Carlo simulation method has been developed by the author which gives the equilibrium chemical composition of a molecular fluid directly. The usual NPT ensemble (isothermal-isobaric) is implemented with N being the number of atoms instead of molecules. Changes in chemical composition are treated as correlated spatial moves of atoms. Given the interaction potentials between molecular products, "exact" (with statistical error $\approx 1\%$) EOS points including the equilibrium chemical composition can be determined from the simulations. This method is applied to detonation products at conditions in the region near the Chapman-Jouget state. For the example of NO, it is shown that the CJ detonation velocity can be determined to a few meters per second. A rather small change in cross potentials is shown to shift the chemical equilibrium and the CJ conditions significantly.

INTRODUCTION

The equation of state (EOS) of high explosives detonation products is a crucial part of any calculation of the behavior of reacting explosives and its effect on adjacent inert materials. In principle, one could calculate an *ab initio* EOS by first using quantum mechanics methods for the potentials between molecular products and second using statistical mechanics for the resulting EOS given these potentials. The first step is limited by the accuracy of available quantum mechanics methods and the required computer time. Where available, these potentials are qualitatively accurate rather than quantitative. Given an accurate method for the second step of statistical mechanics, however, the potentials can be refined from the evaluation of experimental data.

This second step is typically evaluated using thermodynamic perturbation theories. For a single molecular species interacting through a spherical potential, there are several quantitative methods in use. The precision for these methods is not well characterized for multiple species mixtures such as occur in detonation products. In particular, equilibrium chemical composition and possible fluid-fluid phase segregations can have substantial influence on the total EOS of these mixtures. In addition to approximate perturbation theories, there are simulation methods such as Monte Carlo and molecular dynamics which are essentially exact except for small (less than 1%) statistical error. These methods are well established for P, V, T, and E. However, quantities such as free energies, entropy, and chemical potentials are much more difficult to calculate. By standard simulation methods, the chemical equilibrium composition of a multi-component mixture would be nearly intractable.

The Metropolis Monte Carlo method[1] has been the basis for a wide variety of simulation methods for statistical mechanics. Some of the properties requiring the most effort to evaluate accurately are those related to free energies, e. g. chemical potentials, phase equilibrium, and chemical equilibrium. Recently, Panagiatopoulos[2,3] has introduced the Gibbs-ensemble Monte Carlo which allows for the evaluation of gas liquid phase equilibria directly without the intermediate calculation of chemical potentials. Coker and Watts[4] and Kofke and Glandt[5] have used modifications of Grand Canonical ensemble Monte Carlo to determine the chemical equilibrium composition of molecular fluid mixture. Sindzingre *et. al.*[6,7] have shown that chemical potential differences [illegible] individual chemical potentials through their 'difference method'. This generalization of a method by Shing[8,9] involves an interchange of one particle type for another rather than the addition or removal of a particle.

The author has recently developed a Monte Carlo simulation method[10,11] which allows for chemical equilibration as a natural part of a single simulation. (This method is designated $N_{atoms}PT$ ensemble Monte Carlo since the number of atoms is held constant). Starting from an atomic rather than a molecular viewpoint, the equilibrium chemical composition of a molecular fluid mixture is evaluated without explicit calculation of chemical potentials. The partition function for this collection of atoms is rewritten as a sum over all molecular partition functions consistent with this set of atoms. That is, each set of atoms can be grouped into a variety of sets of molecules. Each set of molecules has its own molecular partition function which contributes to the total atomic partition function. That part of the atomic partition function which does not match up atoms into molecular groups is completely negligible for the region of interest.

For this particular study we will concentrate on a common approximation to the molecular partition function which treats each molecule as a single particle with internal degrees of freedom such as vibration and rotation. Instead of restricting this simulation to a given set of molecules, we allow for changes of in the set of molecules corresponding to an exchange of atoms. In the $N_{atoms}PT$ ensemble Monte Carlo simulation, the chemical reaction steps are for an interchange of atoms between molecules. This step is treated like any other Monte Carlo step except that the acceptance probability is more complicated to evaluate. Note that this correlated move is like a "teleporter" from one likely configuration to another likely configuration. For most chemical reactions, the barrier between these two configurations is so high that a direct route involving a series of small changes in configuration would pass through very unlikely states. Hence the correlated move allows for efficient sampling of a configuration space that has islands of locally high probability separated by regions of low probability. A further complication is that of reactions involving a change in the number of molecules. The bookkeeping is simplified by fixing the total number of particles in the simulation but allowing for a variable number of them to be noninteracting.

In this paper the new method is applied to example is that of $N_2 + O_2 \rightleftharpoons 2NO$ at 30GPa and 3000K. Variations in the cross-potentials (i.e. between unlike species) are shown to cause significant shifts in the equilibrium composition. For a 50/50 mix of N and O, a few percent shift in the distance scale of cross potentials leads to an equilibrium mole fraction of NO varying from 8-40%. On the other hand, the Lorentz-Berthelot rules for choosing cross potentials gives chemical equilibrium that is almost exactly reproduced by the ideal mixing approximation.

Another example is the accurate determination of the CJ state. This involves the simulation of $N_2 + O_2 \rightleftharpoons 2NO$ for a variety of P and T near the CJ point. The Hugoniot is constructed by interpolation of appropriate EOS points. The Hugoniot is ploted in u_s vs. u_p space to search for the minimum shock velocity. The uncertainty of the detonation velocity from this method is shown to be a few meters per second. The effect of the cross potentials on the detonation velocity is shown to be significant.

METHOD

The classical partition function for the atomic canonical ensemble, with all atoms identical, is just

$$Q(N,V,T) = \frac{\Lambda^{-3N}}{N!} Z(N,V,T), \qquad (1)$$

where N is the number of atoms, Λ is the de Broglie thermal wavelength and Z(N,V,T) is the configuration integral given by

$$Z(N,V,T) = \int \exp(-\beta U(\mathbf{r}_1, \ldots, \mathbf{r}_N))\, d\mathbf{r}_1 \ldots d\mathbf{r}_N. \qquad (2)$$

With A different types of atoms, N_i atoms of type i, and a total of $N = \sum_i N_i$ atoms of all types the partition function becomes

$$Q(N_1, N_2, \ldots, N_A, V, T) = \frac{\Lambda_1^{-3N_1}}{N_1!} \cdots \frac{\Lambda_A^{-3N_A}}{N_A!} Z(N_1, \ldots, N_A, V, T) \qquad (3)$$

Likewise the partition function for a molecular mixture within the approximation of separable molecular internal degrees of freedom can be written as

$$Q(M_1, \ldots, M_B, V, T) = Z(M_1, \ldots, M_B, V, T) \ldots \qquad (4)$$

tion, such a vibration and rotation, which correspond to an isolated molecule. Eq. (4) is the restriction (e.g. the rigid rotor-harmonic oscillator approximation) of Eq. (3) to those atomic coordinates which correspond to the chosen molecular mixture composition. Now we can relax this restriction slightly to include any set of atomic coordinates which corresponds to any set of M_i's which preserves the atomic compositions. Those atomic coordinates associated with each set of M_i's can be separately approximated by Eq. (4) and the integral over all coordinates allowed by the relaxed restriction becomes a sum of the form

$$Q(N_1,\cdots,N_A,V,T) = \sum{}' Q(M_1,\cdots,M_n,V,T), \tag{5}$$

where $\sum'$ indicates only those sets of M_i's which preserve the set of N_i's. Note that each set of M_i's samples a different nonoverlapping region of atomic coordinate space due to the different sets of atomic correlations which define the molecules. The atomic isothermal-isobaric ensemble partition function is

$$\Delta(N_1,\cdots,N_A,P,T) = \int_0^\infty \exp(-\beta PV)\,Q(N_1,\cdots,N_A,V,T)\,dV. \tag{6}$$

A Monte Carlo simulation can be made in these ensembles if a type of move between nonoverlapping regions can be found which is reasonably likely. This can be accomplished by interchanging atoms between molecules. In the general case, the number of molecules could change. Let M denote the total number of molecules, i.e. $M = \sum_{i=1}^{n} M_i$. A change of variables to a reduced distance s given by

$$\mathbf{s}_i = V^{-1/3}\mathbf{r}_i \tag{7}$$

which has the normalization

$$\int d\mathbf{s}_i = 1 \tag{8}$$

Each molecular Q can be rewritten as

$$Q(M_1,\cdots,M_n,V,T) = \frac{V^M q_1^{M_1}\cdots q_n^{M_n}}{M_1!\cdots M_n!\,\Lambda_1^{3M_1}\cdots\Lambda_n^{3M_n}} \int [illegible] \tag{9}$$

that $M' \geq M$ for all molecular compositions of interest. Then Eq. (6) becomes

$$\Delta(N_1, \cdots, N_A, P, T) = \int_0^\infty \int \sum{}' e^{W} dV d\mathbf{s}_1 \cdots d\mathbf{s}_M \cdots d\mathbf{s}_{M'}, \tag{10}$$

where

$$\begin{aligned} W(\mathbf{s}_1, \ldots, \mathbf{s}_M, M_1, \cdots, M_B) = \\ -\beta\{U(\mathbf{s}_1, \ldots, \mathbf{s}_M) + PV\} + M\,lnV \\ + \sum_{i=1}^{B} [M_i(ln q_i - 3 ln \Lambda_i) - ln(M_i!)]. \end{aligned} \tag{11}$$

Note that the first two terms on the righthand side are just those of an NPT ensemble with fixed molecular composition.

A Markov chain giving a limiting distribution proportional to e^{W} is then obtained[1] by accepting a move from state r to states s with the probability $P_{r\to s}$ given by

$$P_{r\to s} = Min[1, exp(W_s - W_r)]. \tag{12}$$

This assumes the usual condition $p_{r\to s} = p_{s\to r}$ where the p's indicate the unweighted probability of a move. It is sometimes convenient to relax this condition so that a low probability move is tried less often with a higher chance of being accepted when it is tried. We still want the net flow from $r \to s$ to be the same as $s \to r$ at the required distribution. The condition

$$exp(W_r) p_{r\to s} P_{r\to s} = exp(W_s) p_{s\to r} P_{s\to r} \tag{13}$$

leads to the choice

$$P_{r\to s} = Min[1, exp(W_s - W_r) p_{s\to r}/p_{r\to s}]. \tag{14}$$

We now have to evaluate the unweighted probabilities of moves for a specific scheme of choosing chemical reactions. The bookkeeping is somewhat easier to follow if we do not keep track of labels for a particular molecule. That is, only the set of positions $\mathbf{s}_i$ and corresponding molecule types t_i at each position are used to characterize a state. The indistinguishability of molecules of any given type cancels the $ln M_i!$ term from Eq. (11) which were originally included to take into account indistinguishability in molecules allowed in the simulation. let each positive integer through m denote one molecule type. Also. let $i=0$ be a null particle which keeps track of the extra integration variables introduced in Eq. (9). A given chemical reaction can be written in the form

$$\sum_{i=0}^{m} \nu_i F_i \rightleftharpoons \sum_{i=0}^{m} \xi_i F_i, \tag{15}$$

where F_i is the formula for molecule i. For example, the reaction $2CO + O_2 \rightleftharpoons 2CO_2$ would be characterized by F_0 =null, $F_1 = CO$, $F_2 = O_2$, $F_3 = CO_2$, $\nu_0 = 0$, $\nu_1 = 2$, $\nu_2 = 1$, $\nu_3 = 0$, $\xi_0 = 1$, $\xi_1 = 0$, $\xi_2 = 0$, $\xi_3 = 2$. Likewise, $N_2 + O_2 \rightleftharpoons 2NO$ would be characterized by F_0 =null, $F_1 = N_2$, $F_2 = O_2$, $F_3 = NO$, $\nu_0 = 0$, $\nu_1 = 1$, $\nu_2 = 1$, $\nu_3 = 0$, $\xi_0 = 0$, $\xi_1 = 0$, $\xi_2 = 0$, $\xi_3 = 2$.

For a given simulation, one or more chemical reactions can be included at fixed or random intervals in the same way that occasional volume changes are included in a standard NPT ensemble simulation. For convenience, we pick a reaction at random after a fixed number of Monte Carlo steps. For a given state r, the number of ways to choose a forward reaction is given by

$$N_f(r) = \prod_{i=0}^{m} \binom{M_i}{\nu_i}. \tag{16}$$

Similarly, the backward reaction has a number of choices given by

$$N_b(r) = \prod_{i=0}^{m} \binom{M_i}{\xi_i}. \tag{17}$$

For a given chemical reaction step, we choose the forward path with probability $\frac{N_f}{N_f+N_b}$ and the backward reaction with probability $\frac{N_b}{N_f+N_b}$. Then the reactants are chosen randomly from the available molecules of the proper type. This is equivalent to choosing $\nu = \sum \nu_i$ particles at random and proceeding with the trial reaction if the set of molecules is that of either side of Eq. (15). Otherwise, the process is repeated with another set of ν particles chosen at random until an acceptable set of particles is found.

Let s denote a specific final state for the forward reaction and t a specific final state for the reverse reaction. The final state molecule types are assigned randomly over the chosen ν particles for the reaction. The number of distinct final states for the process is $\nu! \prod \xi_i!$ for the forward reaction and $\xi! \prod \nu_i$ for

[illegible]
state r to state s is given by

$$p_{r\rightarrow s} = \frac{\prod_{t=0}^{m} \xi_t!}{\nu!(N_f(r) + N_b(r))}. \qquad (18)$$

Similarly,

$$p_{s\rightarrow r} = \frac{\prod_{t=0}^{m} \nu_t!}{\xi!(N_f(s) + N_b(s))}. \qquad (19)$$

and consequently

$$\frac{p_{s\rightarrow r}}{p_{r\rightarrow s}} = \frac{\prod_{t=0}^{m} \nu_t!((N_f(r) + N_b(r))}{\prod_{t=0}^{m} \xi_t!(N_f(s) + N_b(s))} \qquad (20)$$

and likewise for the reverse reaction

$$\frac{p_{t\rightarrow r}}{p_{r\rightarrow t}} = \frac{\prod_{t=0}^{m} \xi_t!(N_f(r) + N_b(r))}{\prod_{t=0}^{m} \nu_t!(N_f(t) + N_b(t))}. \qquad (21)$$

The acceptance probabilities for a chemical reaction move are obtained from a combination of Eq.(11), Eq.(14), Eq(20), and Eq.(21). These can be compared with a specific case given in reference 10. For spatial moves not involving a chemical reaction, the usual canonical ensemble probabilities are used. In the isothermal isobaric ensemble, moves in volume are also allowed in the standard fashion.

RESULTS

Monte Carlo simulations have been performed in the atomic isothermal-isobaric ensemble using the method described above. A series of simulations have been made with nitrogen/oxygen mixtures at high P and T. Allowed molecular species are N_2, O_2, and NO. The contribution to W from q_i's and Λ_i's is given using molecular constants and expressions found in McQuarrie[12] and supplemented with electronic level constants [13,14]. The molecular constants used for this evaluation are given in Table 1. M is the molecular weight, Θ_r is the characteristic rotational temperature, σ is the symmetry number, Θ_v is the vibrational temperature, D_0 is the energy difference between the lowest vibrational level and the dissociated molecule, ϵ_i is the ith electronic energy level, and g_i is the degeneracy of the ith level. Only those electronic levels which contribute at $T = 5000K$ are included. Note that conversion factors for the units include kcal/mole = 503.22K and 1K = 0.695036cm^{-1}.

Initial conditions are a random set of positions for 120 molecules. Only N_2 and O_2 molecules are

symbol	N_2	O_2	NO
M	28.0134	31.988	30.0007
$\Theta_r(K)$	2.88	2.07	2.45
σ	2	2	1
$\Theta_V(K)$	3374	2256	2719
D_0 (kcal/mol)	225.1	118.0	150.0
ω_1	1	3	2
$\epsilon_1(cm^{-1})$	0	0	0
ω_2	3	2	2
$\epsilon_2(cm^{-1})$	49754.78	7882.39	119.82
ω_3		1	8
$\epsilon_3(cm^{-1})$		13120.91	38440.
ω_4		1	
$\epsilon_4(cm^{-1})$		32664.1	

TABLE 2. EXPONENTIAL-SIX POTENTIAL PARAMETERS FOR THE BASE CASE.

#	Species	ϵ (K)	r^* (Å)	α
1	$N_2 - N_2$	75.	4.251	13.474
2	$N_2 - O_2$	75.	4.1805	13.2955
3	$N_2 - NO$	93.715	4.123	12.777
4	$O_2 - O_2$	75.	4.110	13.117
5	$O_2 - NO$	93.715	4.0525	12.5985
6	$NO - NO$	117.1	3.995	12.08

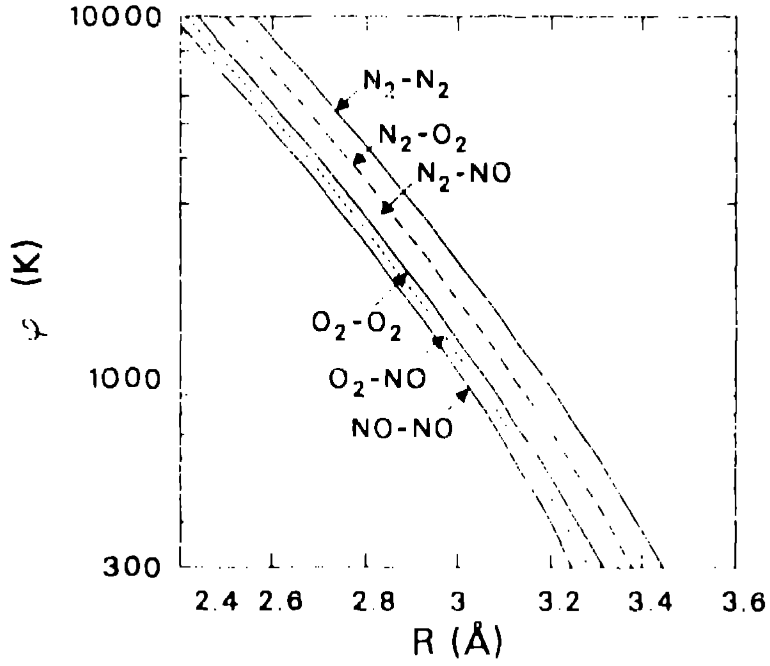

FIGURE 1
POTENTIALS φ(K) VERSUS RADIUS R(Å) FOR THE BASE CASE

allowed in the initial configuration. The potentials are of the exponential six form, $\phi = \epsilon(6exp(\alpha(1 - r/r^*)) - \alpha(r/r^*)^{-6})/(\alpha - 6)$, with parameters given [illegible] molecules are chosen to fit shock wave data[15]. The cross potentials for the baseline case are given by the Lorentz-Berthelot rules and the arithmetic mean for α's. Variations in the cross potentials are labeled in Table 3. Runs of 10^6 steps were made with the first 2×10^5 steps ignored for the purpose of evaluating averages of quantities. Atomic exchanges were attempted every 37 steps and volume changes every 120 steps.

Figure 2 shows results from a previous paper[11] for P=30GPa and T=3000K to illustrate the substantial effect of cross potentials on the equilibrium composition. Comparison is made with perturbation theory[15] using ideal mixing. The relatively small differences in potentials leads to an accurate representation with ideal mixing for the baseline set of potentials. Other choices for cross potentials lead to significantly different equilibrium compositions. Note that since the potentials between like molecules are not changed, the ideal mixing composition is also unchanged.

In this study we have expanded the set of calculated states to include the region near the CJ conditions for the detonation of liquid NO. This is the first time a CJ state has been calculated by an (essentially) exact method such as a Monte Carlo simulation. The simulation results for the base set of potentials is given in Table 4. The same set of P and T points for the A set of potentials is given in Table 5. Units used in the tables are P(Mbar), T(K), V(cm^3/g), E(Mbar cm^3/g), and u(m/s). Statistical uncertainties from the Monte Carlo simulations are E ± .00007, V ± .00040, u_s ± 7, u_p ± 2, and x_{NO} ± .002 where x_{NO} is the mole fraction of NO in the products. Note that in these tables the difference between the specific internal energy of a state and the corresponding energy on a Hugoniot ($E_H = E_0 + \frac{1}{2}P(V_0 - V)$) is given. The initial conditions are taken as $\rho_0 = 1.294$ g/cm^3 and $E_0 = 19.03$ kcal/mol relative to N_2 and O_2 at T = 0 and P = 0. The simulation data is plotted in Figure 3 in the form V versus T. With the help of the tables, groupings of data at a given value of P are readily identified. Note that the base case and the A case are significantly shifted relative to one another. Some of the apparent similar values between sets are actually from different values of P.

The interpolations to give the Hugoniot are shown in Table 6 and Table 7. The results include the conversion of P,V to u_s, u_p from the standard formulae $u_s = V_0\sqrt{\frac{P - P_0}{V_0 - V}}$ and $u_p = \sqrt{(P - P_0)(V_0 - V)}$ and conversion to units of meters per second. The

TENTIALS

Label	$N_2 - O_2$	$N_2 - NO$	$O_2 - NO$
base	2	3	5
A	1	3	5
B	2	6	6
C	2	6	5
D	*	3	5
E	4	3	5
F	2	1	4

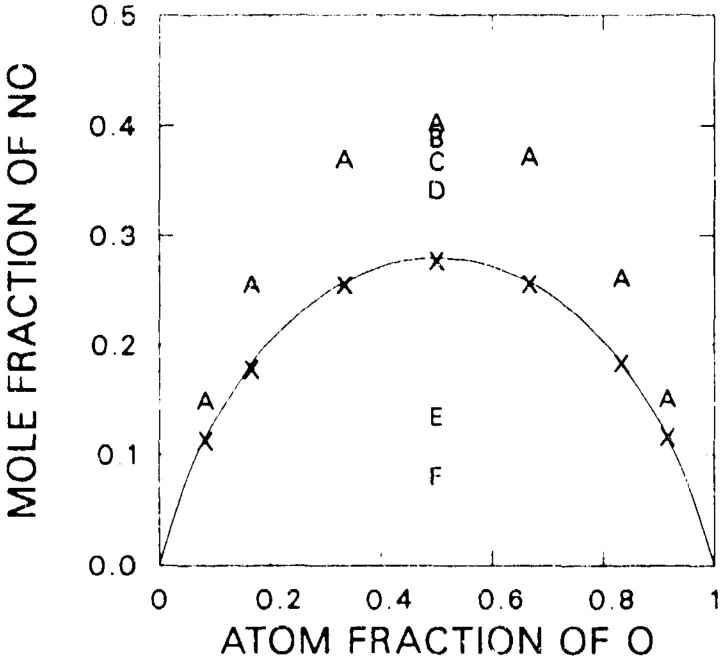

FIGURE 2
EQUILIBRIUM MOLE FRACTION OF NO VS. THE ATOMIC FRACTION OF O AT 3000K AND 30GPA. BASE SET OF POTENTIALS X, SETS A-F AS LABELED, AND PERTURBATION THEORY.

u_s vs. u_p data are shown in Figure 4 along with least square fits of a quadratic to the data. Note that the small change in cross potentials leads to almost 100m/s difference in detonation velocities. This change is due to a combination of changes in the EOS per se and changes in the equilibrium composition for the products.

DISCUSSION

We have demonstrated a new method for the calculation of the CJ state of an explosive using a set of Monte Carlo simulations giving directly the equilibrium chemical composition. A general derivation has been given which allows for multiple species, multiple chemical reactions, and reactions involving

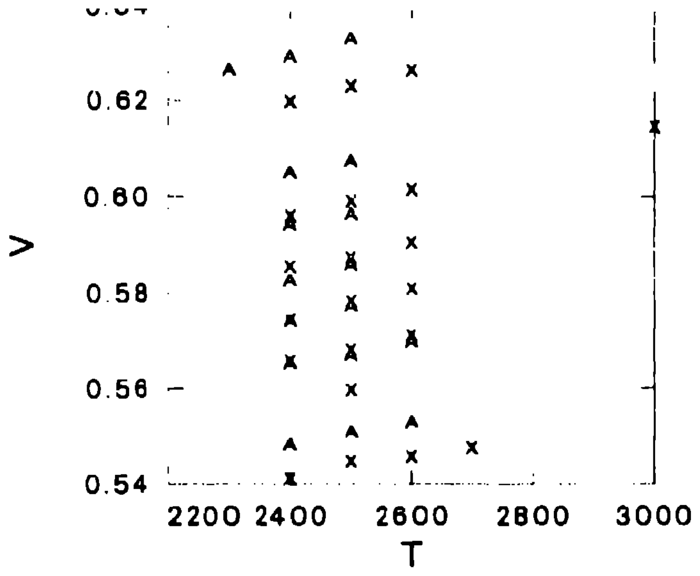

FIGURE 3
VOLUME VS. TEMPERATURE AT VARIOUS VALUES OF P.

a change in the total number of moles. The precision of the detonation velocity is a few meters per second for reasonable length simulations. Future application will be made of the method to more standard explosives. The extension of the method to the inclusion of solid products such as carbon is straightforward. Likewise, the method is easily extended to include fluid-fluid phase segregation (e.g. oil and water) utilizing the Gibbs ensemble method[2] as has already been demonstrated[16]. The net result of this combination of methods will be to allow essentially exact calculation of detonation products EOS and CJ conditions for any given set of intermolecular potentials with a given free energy representation of solid products.

ACKNOWLEDGEMENTS

This work is supported by the U. S. Department of Energy.

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BASE SET OF POTENTIALS.

P	T	E	V	$E-E_{\mu}$	$x_{\gamma\alpha}$
.080	2400	.031918	.61986	-.00074	.056
.080	2500	.033104	.62307	.00058	.059
.080	2600	.034778	.62628	.00238	.079
.090	2400	.033237	.59617	-.00125	.063
.090	2500	.034471	.59918	.00012	.067
.090	2600	.035851	.60159	.00161	.078
.090	3000	.041297	.61444	.00763	.115
.095	2400	.033759	.58553	-.00168	.060
.095	2500	.035219	.58734	-.00013	.072
.095	2600	.036588	.59055	.00139	.083
.100	2400	.034418	.57449	-.00204	.063
.100	2500	.035701	.57830	-.00056	.070
.100	2600	.037034	.58091	.00090	.079
.105	2400	.034761	.56586	-.00264	.058
.105	2500	.036359	.56807	-.00093	.075
.105	2600	.037709	.57128	.00059	.086
.110	2500	.037045	.55964	-.00122	.080
.120	2400	.036815	.54117	-.00362	.070
.120	2500	.038112	.54478	-.00211	.079
.120	2600	.039596	.54579	-.00057	.095
.120	2700	.041065	.54759	.00101	.105

TABLE 5. MONTE CARLO RESULTS FOR THE A SET OF POTENTIALS

P	T	E	V	$E-E_{\mu}$	$x_{\gamma\alpha}$
.080	2300	.031517	.62648	.00088	.072
.080	2400	.032775	.62929	.00049	.078
.080	2500	.034277	.63310	.00215	.093
.090	2400	.034110	.60520	.00003	.085
.090	2500	.035482	.60761	.00151	.095
.095	2400	.034770	.59436	.00025	.090
.095	2500	.036189	.59657	.00128	.100
.100	2400	.035626	.58272	.00042	.098
.100	2500	.036777	.58593	.00089	.101
.105	2400	.036117	.57429	.00085	.097
.105	2500	.037536	.57730	.00073	.108
.110	2400	.036862	.56526	.00109	.102
.110	2500	.038068	.56706	.00021	.109
.110	2600	.039716	.56987	.00202	.127
.120	2400	.038268	.54839	.00174	.115
.120	2500	.039615	.55100	.00023	.125
.120	2600	.041025	.55301	.00130	.135

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P	T	E	V	u_s	u_p
.080	2456	.03259	.62167	5623	1100
.090	2488	.03438	.59854	5554	1252
.095	2509	.03531	.58827	5545	1324
.100	2539	.03566	.57894	5550	1392
.105	2561	.03719	.57003	5561	1459
.110	2581	.03815	.56174	5579	1524
.120	2636	.04012	.54643	5627	1648

TABLE 7. INTERPOLATED HUGONIOT FOR THE A SET OF POTENTIALS.

P	T	E	V	u_s	u_p
.080	2370	.03233	.62815	5747	1076
.090	2398	.03408	.60515	5662	1228
.095	2416	.03500	.59472	5644	1301
.100	2432	.03599	.58374	5620	1375
.105	2454	.03688	.57590	5643	1438
.110	2470	.03787	.56688	5648	1505
.120	2516	.03982	.55140	5690	1630

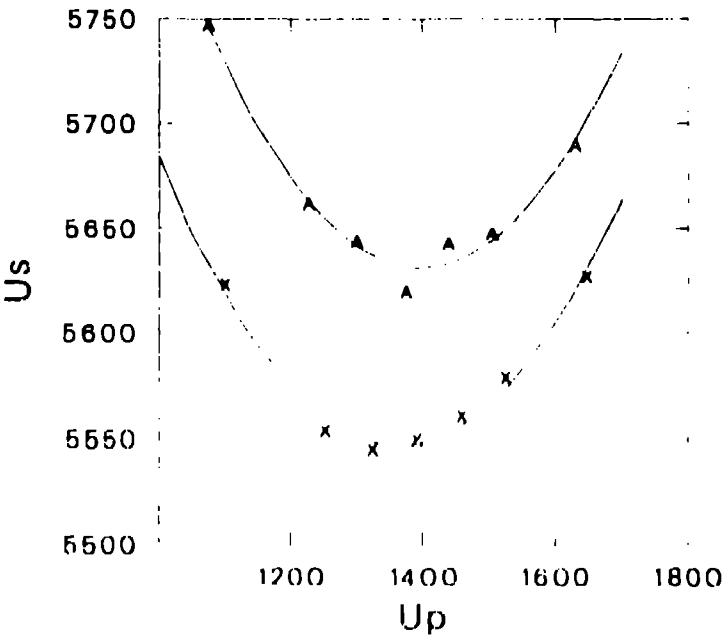

FIGURE 1
Shock velocity vs. particle velocity

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