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A HYBRID MONTE CARLO METHOD FOR EQUILIBRIUM EQUATION OF STATE OF DETONATION PRODUCTS *

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Abstract. A new hybrid Monte Carlo method has been developed 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. The method is called a hybrid because the solid carbon phases (bulk and/or cluster) are encorporated 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. Preliminary results are presented for HMX products including the effects of cross potentials on EOS and equilibrium composition.

INTRODUCTION

The equation of state (EOS) of detonation products has been modeled with a variety of approximate methods, particularly thermodynamic perturbation theory methods. These methods are generally very accurate for the special case of spherical potentials in a single species fluid. The mixing of several species is not as well characterized even for spherical potentials and is much more uncertain for more complicated potentials. Using a recently developed Monte Carlo method(1-3), the chemical equilibrium composition has been shown to be sensitive to the assumed cross potentials for fluids. Most explosives have solid carbon in the products, however.

I have developed a new hybrid Monte Carlo method 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 called a hybrid because the solid carbon is encorporated as an analytic model, while the fluid components are explicitly included in the Monte Carlo simulation. Although Monte Carlo simulation of a solid is straightforward for a fixed number of particles in a lattice, there is not a convenient way to add a single particle and preserve the lattice. Preliminary results for HMX products with carbon in the graphite phase are presented.

HYBRID MONTE CARLO METHOD

The hybrid Monte Carlo method is a generalization of the $N_{atoms}PT$ ensemble Monte Carlo(1-3), which treats a molecular fluid mixture from an atomistic picture. The Gibbs ensemble treatment of fluid-fluid phase separation(4) is readily encorporated.

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

$$Q(N,V,T) = \left[\frac{V^N}{N!\Lambda^{3N}}\right] \int e^{-\beta U} d\mathbf{s}_1 \cdots d\mathbf{s}_N \quad (1)$$

where the scaled coordinates, $\mathbf{s}_i$, are over a unit volume and the total potential energy, U, is evaluated

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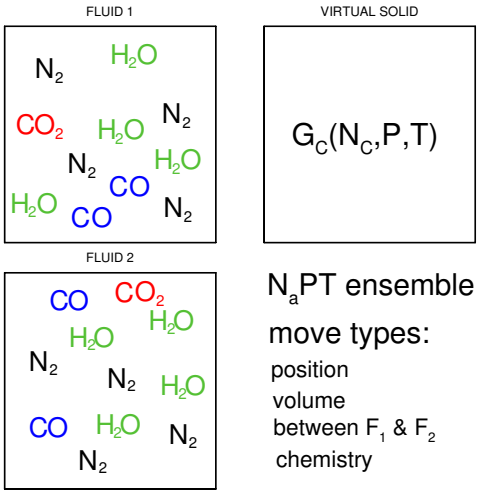

FIGURE 1. Illustration of the three simulation boxes

for the actual coordinates in a volume V. For the isothermal-isobaric ensemble

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

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

$$\Delta(A_1,...,A_I,P,T) = \qquad (3)$$

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

which can be rewritten as

$$\int\int {\sum}' e^{-\beta G_c(N_c,P,T)} e^{-\beta P(V_1+V_2)} Q_1 Q_2 dV_1 dV_2$$

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 $Q_k({}^kM_1,...,{}^kM_J,V_k,T)$ 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

$$Q_k({}^kM_1,...,{}^kM_J,V_k,T) = \qquad (4)$$

$$\frac{{V_k}^{M_k} {q_k}^{{}^kM_1} \cdots {q_k}^{{}^kM_J}}{{}^kM_1! \cdots {}^kM_J! \Lambda_1^{3\,{}^kM_1} \cdots \Lambda_J^{3\,{}^kM_J}}$$

$$\times \int e^{-\beta U_k} d^{\mathbf{k}}\mathbf{s}_1 \cdots d^{\mathbf{k}}\mathbf{s}_{M_k}$$

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

$$\Delta(P,T) = \int_0^\infty \int_0^\infty \int\int {\sum}' \Big[e^W dV_1 dV_2$$

$$d^{\mathbf{1}}\mathbf{s}_1 \cdots d^{\mathbf{1}}\mathbf{s}_{M_1} d^{\mathbf{2}}\mathbf{s}_1 \cdots d^{\mathbf{2}}\mathbf{s}_{M_2} \Big] \qquad (5)$$

where

$$W = -\beta G_c(N_c,P,T) - \beta[U_1+PV_1] - \beta[U_2+PV_2]$$

$$+M_1 lnV_1 + M_2 lnV_2 \qquad (6)$$

$$+\sum_{j=1}^{J}\sum_{k=1}^{2}\Big[{}^kM_j(lnq_j - 3\Lambda_j) - ln({}^kM_j!)\Big]$$

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

$$P_{r\to s} = Min[1, exp(W_s - W_r) p_{s\to r}/p_{r\to s}] \qquad (7)$$

where $p_{r\to s}$ is the unweighted probability of a move from r to s.

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(5,6). 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 are easily determined from counting

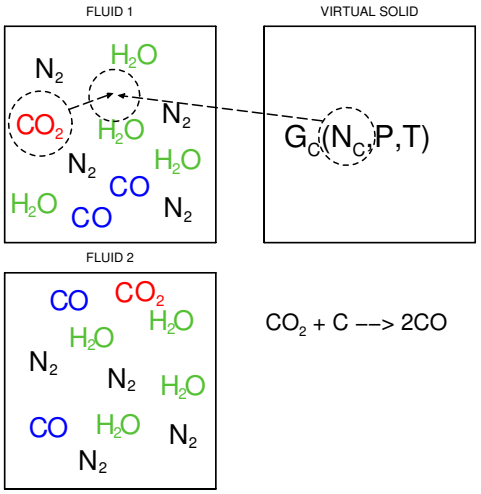

FIGURE 2. Choose the reactants: CO_2+C

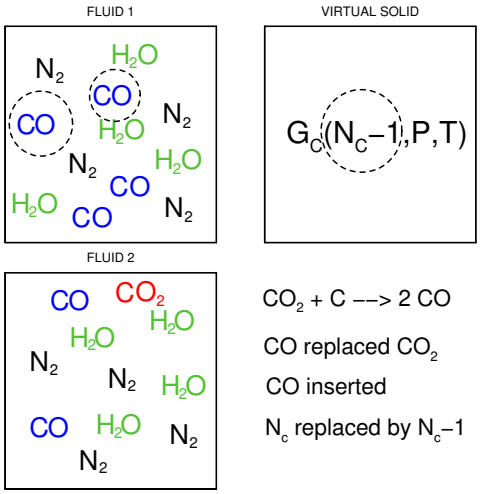

FIGURE 3. Replace with products: 2CO

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(4). 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 a 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 Eq. 5 to a state in a different term in the summation, corresponding to a different correlation of atoms into molecules.

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.

RESULTS

Monte Carlo simulations have been made with the hybrid method for equilibrium products of HMX. The products are restricted to N_2, H_2O, CO_2, CO, and bulk graphite for this demonstration. (The importance of surface chemistry on diamond clusters has been shown previously(7,8). Extension of the Monte Carlo code to include these options are in progress.) With this set of products, the composition reduces to

$$C_4H_8N_8O_8 \rightarrow$$

$$4N_2 + 4H_2O + (4-2x)CO + xCO_2 + xC \quad (8)$$

where x is a parameter that characterizes the equilibrium composition for this restricted set of products. Note that for this case, there are equal concentrations of C and CO_2.

The statistical fluctuation of composition within a simulation is illustrated in Fig. 4. With P=7.5 GPa and T=3000K, a simulation of 10^6 steps is divided into bins of 10^4 steps each. The distribution is essentially uncorrelated and the standard deviation of the average over the full simulation is about 0.05 of the variation seen in Fig. 4.

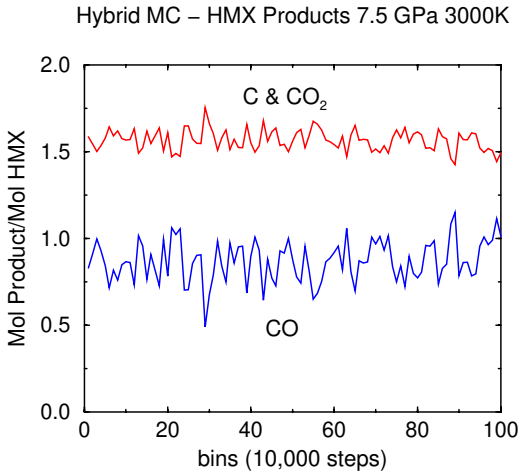

FIGURE 4. HMX products for P=7.5 GPa and T=3000K

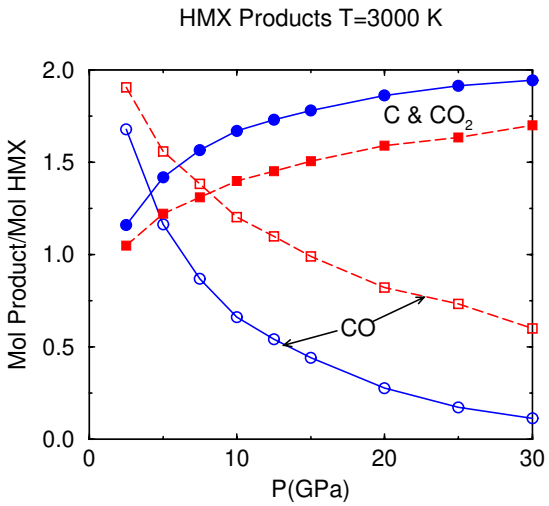

FIGURE 5. HMX products as a function of P at T=3000K. See text for description of symbols.

For a fixed temperature of 3000K, the variation in composition with pressure and with the choice of cross potentials is shown in Fig. 5. The potentials between the same species (e.g. $N_2 - N_2$) are effective spherical potentials that have been used in detonation products modeling(7,8). The solid lines with circles for symbols (filled symbols for C and CO_2, and open symbols for CO) are composition results for cross-potentials (e.g. $N_2 - CO_2$) chosen by simple combining rules from the pure species potential parameters. The dashed lines with square symbols show the sensitivity to variations of around 3% in the radius scale r* of cross-potentials only. (These variations are comparable in magnitude to those used by Ree(9) leading to fluid-fluid phase separation at high pressure.)

CONCLUSIONS

A hybrid 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 practical interest such as HMX and TATB. With current high speed workstations, a tabular EOS with hundreds or even thousands of points can be 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.

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