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DIRECT MONTE CARLO SIMULATION OF CHEMICAL EQUILIBRIUM COMPOSITION OF MOLECULAR FLUID MIXTURES UNDER SHOCK CONDITIONS

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A new Monte Carlo simulation method is implemented which holds the number and kind of atoms constant rather than the number and kind of molecules for a molecular fluid mixture. Chemical reactions are allowed as a correlated move of atoms such as an interchange of atoms between molecules. Equilibrium chemical composition is determined as an average over the simulation along with equation of state quantities. Results are presented for $N_2 + O_2 \rightleftharpoons 2NO$ at 30GPa and 3000K. The equilibrium composition is shown to be sensitive to the potentials between unlike species.

1. INTRODUCTION

Under shock conditions of high temperature and pressure, many types of small molecules undergo chemical reactions that are incomplete in the sense that both reactants and products are present in significant amounts at chemical equilibrium. For high explosive detonation products, energetically unfavorable species such as CO and NO are present due to competition between energy, entropy, and volume at high temperature and pressure ($G = E - TS + PV$). Finding the chemical equilibrium composition is very important for determining the equation of state of such molecular fluid mixtures under these extreme conditions.

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[2 – 9], e. g. chemical potentials, phase equilibrium, and chemical equilibrium. Recently, the author developed a new Monte Carlo simulation method[10] which can handle the extra complexity of chemical equilibrium in a direct fashion. 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 a mixture of molecules can be derived by grouping that for the constituent atoms. That is, several atoms are treated in a correlated fashion as a single particle with internal degrees of freedom such as vibration and rotation. Instead of restricting these correlations to a given set of molecules, we allow for changes of correlations. These changes of correlations are just those of chemical reactions. The partition function is now the sum of those for allowed molecular mixtures. In a Monte Carlo simulation, the chemical reaction steps are for an interchange of atoms between molecules. In this paper, the new method is applied to the test case 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.

2. METHOD

A summary of the new method[10] is given here. The classical partition function for the atomic-canonical ensemble, with all atoms identical, is just

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

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

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

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

$$Q(M_1,\cdots,M_B,V,T) = \frac{Z(M_1,\cdots,M_B,V,T)}{M_1!\cdots M_B!\Lambda_1^{3M_1}\cdots\Lambda_B^{3M_B}} q_1^{M_1}\cdots q_B^{M_B}. \quad (3)$$

The $q_i's$ are those parts of the partition function, such a vibration and rotation, which correspond to an isolated molecule. Eq. (3) is the restriction 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. (3) and the integral over all coordinates allowed by the relaxed restriction becomes a sum of the form

$$Q(N_1,\cdots,N_A,V,T) = \sum{}' Q(M_1,\cdots,M_B,V,T), \quad (4)$$

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 given by the transformation

$$\Delta(P,T) = \int_0^\infty exp(-\beta PV)Q(V,T)dV. \quad (5)$$

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, but we will restrict the current discussion to the case of reactions which conserve the number of molecules. Let M denote the number of molecules of all types, i.e. $M = \sum_{i=1}^{B} M_i$. Then Eq. (4) can be expanded to

$$Q(N_1,\cdots,N_A,V,T) = \quad (6)$$
$$\int \sum{}' exp(W(\mathbf{r}_1,\ldots,\mathbf{r}_M,M_1,\cdots,M_B))d\mathbf{r}_1\cdots d\mathbf{r}_M,$$

where

$$W(\mathbf{r}_1,\ldots,\mathbf{r}_M,M_1,\cdots,M_B) = -\beta U(\mathbf{r}_1,\ldots,\mathbf{r}_M) + \sum_{i=1}^{B}[M_i(lnq_i - 3ln\Lambda_i) - ln(M_i!)]. \quad (7)$$

We want the acceptance probablities for Monte Carlo steps such that we obtain a limiting distribution with probability e^W. Let $P_{r\to s}$ be the acceptance probability for a step from state r to state s and $p_{r\to s}$ the probability of trying that step. In order to have equal net flow from r→s and from s→r we have the condition

$$exp(W_r)p_{r\to s}P_{r\to s} = exp(W_s)p_{s\to r}P_{s\to r}, \quad (8)$$

which is satisfied by the choice

$$P_{r\to s} = Min[1, exp(W_s - W_r)p_{s\to r}/p_{r\to s}] \quad (9)$$

For simplicity, we will restrict the current discussion to the reaction $N_2 + O_2 \rightleftharpoons 2NO$. For a given state r we can choose two molecules at random. If one is N_2 and the other is O_2, then we can try the forward reaction. If both are NO, then we can try the reverse reaction. Other cases are not allowed. The bookkeeping is somewhat easier to follow if we do not keep track of labels for a particular molcule. That is, only the set of positions and corresponding molecule type at each position are used to characterize a state. This indistinguishability of molecules of any given type removes the $lnM_i!$ terms from Eq. (7) which were originally included to take into account indistinguishability in the usual labeled representation. Let s denote a specific final state for the forward reaction. For the initial state r, there are $M_3(M_3-1)+2M_1M_2$ allowed choices of pairs of molecules leading to a reaction. For the forward reaction, the order of choosing an N_2 and an O_2 does not effect the final state s and therefore gives two allowed choices leading to a particular state s. Taking into account the different number of molecules of each type in states r and s, we have

$$p_{r\to s} = \frac{2}{M_3(M_3-1)+2M_1M_2} \quad (10)$$

and likewise

$$p_{s\to r} = \frac{1}{(M_3+2)(M_3+1)+2(M_1-1)(M_2-1)}. \quad (11)$$

The acceptance probabilities for Monte Carlo steps for the forward reaction are then

$$P_{r\rightarrow s} = Min[1, exp(-\beta(U_s - U_r) - \sum_{i=1}^{B}[\nu_i(lnq_i - 3ln\Lambda_i)] + \frac{1}{2}\delta M_{r\rightarrow s})], \tag{12}$$

where

$$\delta M_{r\rightarrow s} \equiv \frac{M_3(M_3-1)+2M_1M_2}{(M_3+2)(M_3+1)+2(M_1-1)(M_2-1)} \tag{13}$$

which is very nearly 1 even for M≈100. Similar results are obtained for the reverse reaction. For moves not involving a chemical reaction, the usual isothermal-isobaric ensemble method is used.

3. RESULTS

Monte Carlo simulations have been performed in the atomic-isothermal-isobaric ensemble as described above. The system chosen for testing the method was a series of nitrogen/oxygen mixtures at T=3000K and P=30GPa. Allowed molecular species are N_2, O_2, and NO. The change in that part of W from q_i's and Λ_i's was determined[11 – 13] to be 4.2548 for the forward reaction. Initial conditions are a random set of positions for 120 molecules. Only N_2 and O_2 molecules are 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 in Table I. The repulsive part of these potentials are shown in Fig. 1. The interactions between like molecules are chosen to fit shock wave data[14]. 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 II. 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.

Fig. 2 shows equilibrium mole fraction of NO as a function of atomic fraction of O for the various sets of potentials. Comparison is made with perturbation theory results[14] employing ideal mixing. The relatively small differences in potentials leads to an accurate representation with ideal mixing for the baseline set of

Table I. Exponential-six potential parameters for the baseline 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

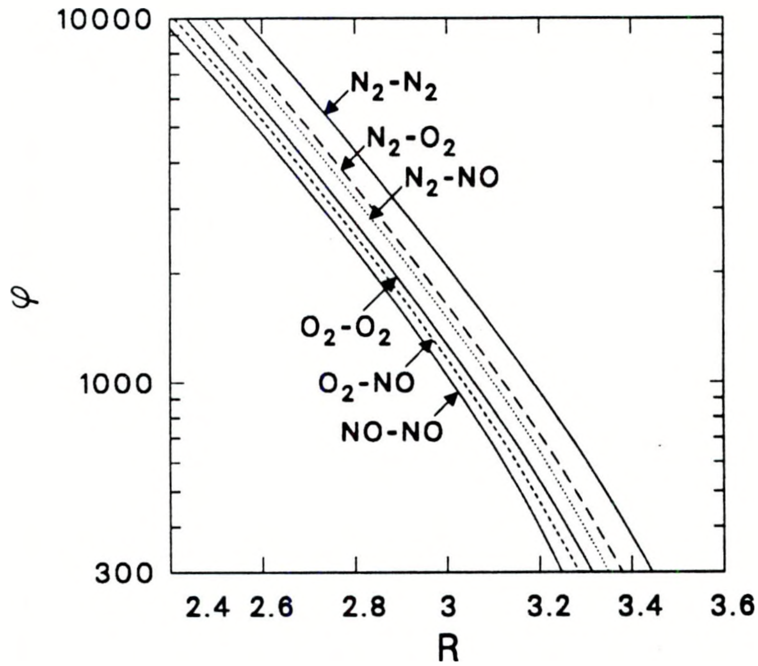

Figure 1. Potentials ϕ(K) versus radius R(Å) for the baseline case.

Table II. Labels for sets of cross potentials. (For label D, * indicates the average of parameters from potentials 1 and 2.)

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

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. The results are given in Table III and Table IV with error bars estimated from the variance of subaverages

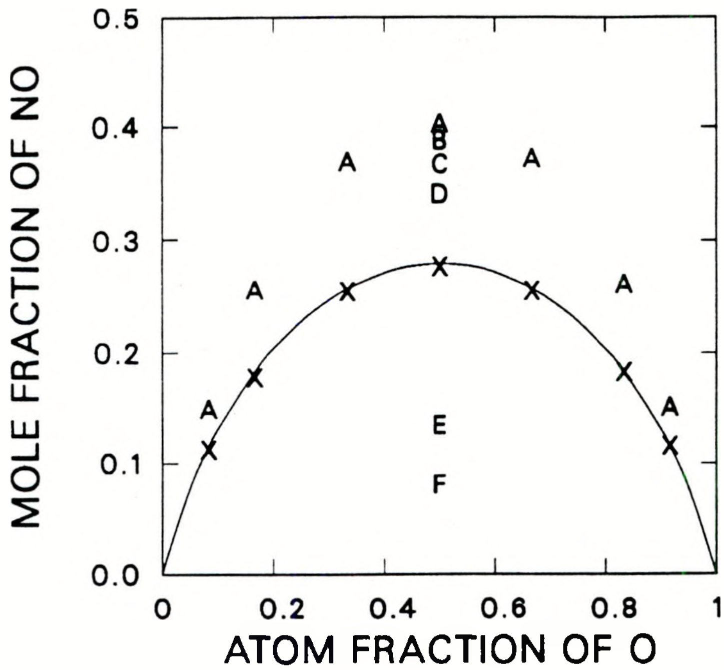

Figure 2. Equilibrium mole fraction of NO vs. atomic fraction of O at 3000K and 30GPa. Baseline set of potentials X, sets A-F as labeled, and perturbation theory (line).

Table III. Equilibrium mole fraction of NO, x_3, as a function of atomic fraction of O, denoted x_O, for perturbation theory (PT), for the baseline set of potentials, and for set A.

x_O	PT	Baseline	A
$\frac{1}{12}$	0.1152	0.1125±.0006	0.1492±.0003
$\frac{1}{6}$	0.1831	0.1776±.0012	0.2555±.0009
$\frac{1}{3}$	0.2574	0.2549±.0016	0.3703±.0015
$\frac{1}{2}$	0.2795	0.2768±.0022	0.4035±.0020
$\frac{2}{3}$	0.2574	0.2555±.0017	0.3725±.0016
$\frac{5}{6}$	0.1831	0.1828±.0013	0.2613±.0009
$\frac{11}{12}$	0.1152	0.1157±.0006	0.1510±.0003

Table IV. Equilibrium mole fraction of NO, x_3, for sets of potentials as described in Table II and atomic composition $x_O = 0.5$.

Potentials	x_3
B	0.3892±.0012
C	0.3683±.0014
D	0.3421±.0017
E	0.1346±.0025
F	0.0808±.0027

4. DISCUSSION

We have demonstrated an effective Monte Carlo method for determining equilibrium chemical composition in a simulation. Application to more molecular species and more chemical reactions is straightforward with the possible exception of reactions with mole number changes. (The creation of a new molecule, for example, can be coupled with a volume change and even a correlated move of other molecules to make room for it.) Implementation for more complicated systems is in progress.

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