Reaction ensemble molecular dynamics: Direct simulation of the dynamic equilibrium properties of chemically reacting mixtures

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A molecular simulation method to study the dynamics of chemically reacting mixtures is presented. The method uses a combination of stochastic and dynamic simulation steps, allowing for the simulation of both thermodynamic and transport properties. The method couples a molecular dynamics simulation cell (termed dynamic cell) to a reaction mixture simulation cell (termed control cell) that is formulated upon the reaction ensemble Monte Carlo (RxMC) method, hence the term reaction ensemble molecular dynamics. Thermodynamic and transport properties are calculated in the dynamic cell by using a constant-temperature molecular dynamics simulation method. RxMC forward and reverse reaction steps are performed in the control cell only, while molecular dynamics steps are performed in both the dynamic cell and the control cell. The control cell, which acts as a sink and source reservoir, is maintained at reaction equilibrium conditions via the RxMC algorithm. The reaction ensemble molecular dynamics method is analogous to the grand canonical ensemble molecular dynamics technique, while using some elements of the osmotic molecular dynamics method, and so simulates conditions that directly relate to real, open systems. The accuracy and stability of the method is assessed by considering the ammonia synthesis reaction $N_2+3H_2 \Leftrightarrow 2NH_3$. It is shown to be a viable method for predicting the effects of nonideal environments on the dynamic properties (particularly diffusion) as well as reaction equilibria for chemically reacting mixtures.

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I. INTRODUCTION

Predicting and understanding the physical effects of nonideal conditions (strong intermolecular forces, nanostructured media, etc.) on chemical reaction equilibria is critical in many fields of science including mixture separation and purification using porous solids, catalysis, plasma physics, and shock physics. The reaction ensemble Monte Carlo method (RxMC) [1–3] is a powerful simulation tool for studying reaction mixtures and is uniquely capable of predicting shifts of reaction equilibria caused by such highly nonideal environments. The RxMC method requires as input only the intermolecular potentials and the ideal-gas partition functions for the reaction species that are present. Furthermore, the method does not require a reactive-type potential that mimics bond breakage and formation. Applications of the RxMC simulation method include reactive systems confined in porous materials [4–10], reactions of plasmas [11,12], reactions in supercritical fluid solvents [10], reactions under shock [13], and still others [14–17]. Deviations from the ideal-gas phase reaction equilibria caused by nonideal conditions can be determined for quantities such as the fluid density, pressure, and species concentrations.

However, dynamic properties such as diffusion coefficients cannot be determined using the RxMC method. In this work, we introduce a simulation method that can determine the dynamic properties of reaction mixtures at equilibrium. The method is akin to the grand canonical molecular dynamics method [18–20] and the osmotic molecular dynamics method [21,22]. These methods use a control cell to maintain the desired chemical potential while a dynamic cell is used to determine the dynamic properties. For the method introduced here, termed the reaction ensemble molecular dynamics (RxMD) method, the control cell is used to maintain the system at the reaction equilibrium conditions [1–3]. RxMC forward and reverse reaction steps are performed in the control cell only, while constant-temperature molecular dynamics steps are performed in both the dynamic cell and the control cell. The dynamic cell is in direct contact with the control cell so that particles are able to move freely between the cells. Since the entire simulation box (consisting of the control cell and the dynamic cell) is in thermodynamic equilibrium due to the molecular dynamics steps, reaction equilibrium conditions are established in the dynamic cell as a consequence of the physical contact between the control and dynamic cell. In this scenario, fluid properties in the dynamic cell are unaffected by the stochastic reaction steps occurring in the control cell. Therefore, dynamic quantities of reaction mixtures such as the velocity autocorrelation functions and the diffusion coefficients can be accurately determined in the dynamic cell. These dynamic properties are more precisely *dynamic equilibrium properties* since they describe correlations at different times along an equilibrium trajectory [23].

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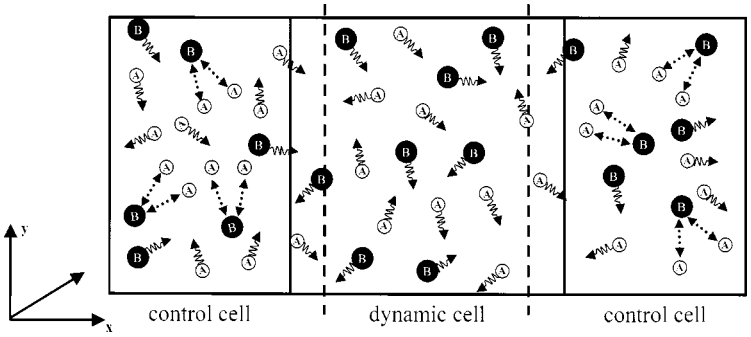

FIG. 1. Schematic of the reaction ensemble molecular dynamics method. The model reaction $2A \Leftrightarrow B$ is occurring. Molecular dynamics particle displacement steps ( ) occur in all cells, while reaction ensemble Monte Carlo reaction steps ( ) occur only in the control cell. The dashed lines denote the portion of the dynamic cell in which the dynamic properties are calculated.

It is important to note further that, analogous to the RxMC method, the RxMD method predicts the *physical* effects on reaction equilibria, as opposed to predicting *chemical* effects. The RxMD method does not provide reaction rate information; separate methods must be used for this purpose (for a review of these methods see Santiso and Gubbins [24]. Despite these limitations, the RxMD method can provide unique insight into the molecular-level dynamic behavior of a wide variety of reacting systems. In particular, it enables the simultaneous study of the influence of nonideality and nanostructure on both diffusion and reaction equilibria.

II. METHODOLOGY

The reaction ensemble molecular dynamics method provides insight into the dynamic phenomena of reaction mixtures by combining a stochastic simulation method (RxMC) with a deterministic method (constant-T MD). The RxMC method can be performed at constant-volume or at constant-pressure conditions. The constant-volume version requires two types of Monte Carlo moves: (1) particle displacements and (2) forward and reverse reaction steps. Multiple reactions can be simulated simultaneously by including the forward and reverse reaction steps for each reaction in order to maintain stoichiometry. The constant-pressure version of the RxMC method requires the additional step of fluctuating the simulation cell volume to achieve the desired pressure. Further details of the RxMC method can be found elsewhere [1–3]. In this work, we demonstrate the RxMD method at constant-volume conditions; extension to constant-pressure conditions is straightforward.

The reaction ensemble molecular dynamics method is a direct extension of the reaction ensemble Monte Carlo method. In the RxMD method, Monte Carlo displacements steps are replaced by molecular dynamics time steps, while forward and reverse reaction steps are still performed in a Monte Carlo fashion. Reaction steps in the RxMC method require particle insertion, particle deletion, and/or particle identity exchange in the simulation cell. Such conditions are typically not suitable for the molecular dynamics technique since the deterministic pathway of the particle trajectories will be disrupted by such events. To avoid these adverse effects to the particle trajectories, the control cell and dynamic cell simulation setup described above is implemented. In practice, this entails positioning one-half of the control cell on each side of the dynamic cell. Such an arrangement allows for the use of periodic boundary conditions in all directions. Moreover, total momentum is inherently conserved due to symmetry of the total simulation box. A schematic of the RxMD method is given in Fig. 1, where the model reaction $2A \Leftrightarrow B$ is occurring. In Fig. 1, molecular dynamics time steps are performed in both the control and dynamic cells while reaction steps are performed in the control cell only. Since the control cell is in direct contact with the dynamic cell, the particles are able to move freely between both cells. To minimize interface effects, the properties of the fluid in the dynamic cell are determined from an interior portion of the cell, which is away from the control-cell–dynamic-cell interface; i.e., at any time step only particles that reside within the interior portion are included in the properties calculation. The dashed lines in Fig. 1 are intended to illustrate this procedure. Last, particle velocities for newly inserted particles are drawn from a Maxwell-Boltzmann distribution at the appropriate temperature [23,25].

III. VERIFICATION: APPLICATION TO AMMONIA SYNTHESIS

We demonstrate the RxMD method using the ammonia synthesis reaction $N_2 + 3H_2 \Leftrightarrow 2NH_3$ at constant volume. Due to the illustrative nature of this work, the reacting species are modeled as simple spherical particles interacting through an exponential-6 potential, where electrostatics contributions are ignored [26]. The potential was truncated and shifted at 1.05 nm. The potential parameters are given in Table I, where the Lorentz-Berthelot combining rules [27] were used for unlike-pair interactions. Molecular partition functions were determined using JANAF thermochemical data tables [28]. All simulations were initiated from an initial mixture of 600 H_2 molecules and 200 N_2 molecules. For the state conditions simulated here, these relatively large system sizes result in large simulation cell volumes that help to minimize any interface effects caused by the dynamic-cell–control-cell boundary. The interior two-thirds of the dynamic cell were

TABLE I. Exponential-6 potential parameters [26].

Species	r_{core} (Å)	r_m (Å)	ε/k_B (K)	α
NH_3	1.12	3.72	244.9	12.0
N_2	1.03	4.17	97.1	13.0
H_2	1.25	3.49	30.4	11.2

TABLE II. Comparison of properties calculated by the reaction ensemble molecular dynamics method (RxMD) with the reaction ensemble Monte Carlo (RxMC) and molecular dynamics (MD) methods at various temperatures.[a]

Method		U_{conf} (J/mol)	P [MPa]	*density* [g/cm^3]	$x(NH_3)$[b]	$x(N_2)$	$x(H_2)$	$D(NH_3)$ (10^8 m^2/s)
				$T=300.0$ K				
	RxMC	-3.9_2	0.0297_6	0.000191_6	0.882_3	0.0294_1	0.0882_1	NA[c]
RxMD	dynamic cell	-3.5_6	0.0303_4	0.000202_8	0.885_4	0.0291_9	0.0852_6	552.1_4
	control cell	-4.1_4	0.0311_8	0.000186_9	0.883_7	0.0301_5	0.0867_2	NA
	MD-NVT	-3.8_4	0.0304_4	0.000191	0.882	0.0294	0.0882	552.8_5
				$T=600.0$ K				
	RxMC	-383.7_{19}	14.83_4	0.0382_7	0.526_1	0.118_4	0.355_2	NA
RxMD	dynamic cell	-384.2_{11}	14.77_5	0.0399_8	0.527_3	0.115_8	0.357_4	3.584_6
	control cell	-381.9_{26}	14.86_6	0.0387_9	0.526_1	0.116_3	0.358_5	NA
	MD-NVT	-382.6_{13}	14.83_5	0.0382	0.526	0.118	0.355	3.578_8
				$T=900.0$ K				
	RxMC	-203.3_{38}	55.9_8	0.0668_7	0.178_1	0.205_2	0.616_3	NA
RxMD	dynamic cell	-201.6_{27}	55.4_5	0.0654_8	0.181_5	0.197_4	0.622_8	2.781_9
	control cell	-202.1_{15}	56.5_6	0.0660_6	0.173_3	0.209_7	0.619_2	NA
	MD-NVT	-202.7_{18}	55.7_4	0.0668	0.178	0.205	0.616	2.788_7

[a]Reported uncertainties determined from block averages where, for example -383.7_{19} implies -383.7 ± 1.9 [23].
[b]$x(i)$: mole fraction of species $i=N_i/N_{\text{total}}$, where N is the number of molecules.
[c]NA=not applicable to method.

used to calculate the fluid properties. Cubic simulation cells were used and periodic boundary conditions were imposed in all three directions for the total system. All reported pressures were calculated using the virial expression [25].

A standard *NVT* molecular dynamics method was employed with the equations of motion solved using the Verlet leapfrog algorithm [25] and implementing the damped force method of Brown and Clark to maintain constant temperature [29]. A time step of $\Delta t=3.0$ fs was used for a total simulation time of 2 ns following an equilibration period. The ratio of attempted reaction steps per molecular dynamics steps was 40:1; this choice was based on a series of short simulation runs that were made during the development of the method, but may vary for different systems.

The ammonia synthesis reaction was simulated at a series of temperatures under known gas-phase conditions [4]. Comparisons of the quantities calculated by the RxMD method are made with two different methods. First, the thermodynamic quantities calculated from the RxMD approach (e.g., density, configurational energy, pressure, and species concentrations) are compared to quantities calculated by the RxMC approach. Second, the dynamic quantities of the RxMD method (e.g., velocity autocorrelation functions) are compared to quantities determined from an *NVT* molecular dynamics mixture simulation.

For a comparison of the thermodynamic properties, a constant-volume RxMC simulation was performed at the same temperature and initial mixture as the RxMD simulation. Table II presents a comparison of results for the RxMD and RxMC approaches, where quantities calculated in both the dynamic cell and the control cell are given. As expected, quantities in the dynamic cell and control cell are the same within statistical uncertainty, ensuring that the RxMD has equilibrated properly. The quantities calculated using the RxMD and the RxMC approaches also agree within statistical uncertainty for all the temperatures considered.

For a comparison of the dynamic properties, *NVT* molecular dynamics simulations were performed at the temperature, volume, and species concentrations that were used or determined in the RxMC simulations. Self-diffusion coefficients (D) for each species were determined from the velocity autocorrelation functions [23] in both the *NVT*-MD simulations and in the dynamic cell of the RxMD simulations. Comparisons of the self-diffusion coefficients determined by both methods for NH_3 are given in Table II. Excellent agreement is evident between the two approaches, with similar agreement found for the self-diffusion coefficients of N_2 and H_2.

IV. DISCUSSION

We have presented a simulation tool, the reaction ensemble molecular dynamics method, to study the dynamics of chemically reacting systems. The RxMD method is capable of predicting the physical effects of nonideal environments on dynamic properties of the equilibrium mixture. The RxMD method combines the reaction ensemble Monte Carlo method with the *NVT* molecular dynamics technique, resulting in a simulation method that mimics real, open systems for many experimental situations. The method as presented here effectively combines two simulation runs into a single simulation, since the same result could be achieved by running an RxMC simulation followed by a mixture *NVT*-MD simulation at the conditions determined from the RxMC result. The value of the RxMD method lies in its potential

application to other scenarios—e.g., where the dynamic cell is modeled as a porous solid and two control cells at different thermodynamic conditions are used. Such an arrangement mimics combined reaction and adsorption phenomena relevant to membrane reactors and fuel cells, as well as to various possible nanochemical devices [30].

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