Verification of Kinetic Theoretical Prediction of Diffusion-influenced Reversible Reaction by Molecular Dynamics Simulation

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A diffusion-influenced pseudo-first order reversible reaction $A + B \leftrightarrow C + B$ is investigated by the molecular dynamics (MD) simulation method. Theoretical finding that the temporal evolution of reactants [conditional probabilities] in the reversible system can be expressed by the irreversible survival probability with an effective rate parameter is confirmed even in the presence of solvent particles. We carry out molecular dynamics simulations for both the irreversible and the reversible cases to evaluate the survival and the conditional probabilities for each cases. When the resultant irreversible survival probability is inserted into the proposed relation, the conditional probabilities given by the simulation are exactly reproduced.

Introduction

Recently, a particular type of diffusion-influenced reversible reaction $A + B \leftrightarrow C + B$ has been studied by Gopich, Kipriyanov, and Doktorov (GKD1[1] and GKD2[2]) and by Yang, Lee, and Shin (YLS).[3] In GKD1, the many-particle kinetics in the above reaction was shown to be reduced to a single particle kinetics under certain conditions. Also they found a relation between the reversible and the irreversible descriptions for this reaction system, effectively reducing the former problem to the latter for which exactly solvable models are available. A modified encounter theory of the partially non-Markovian nature was applied in GKD2 to investigate the pseudo-first-order reversible system, in which $[A]$ or $[C] << [B]$, and the results were compared with those of the renormalized kinetic theory of YLS. The same relation between the reversible and irreversible systems obtained by GKD1 was also presented by YLS for the pseudo-first-order system in their kinetic theoretical formulation which incorporates the many-body dynamical correlation effects.

In this work, we carry out the molecular dynamics (MD) simulation for both the pseudo-first-order reversible and irreversible reaction systems and verify the proposed relation between them even in the presence of solvent particles whose influence have not been considered before.

Theoretical Background

Theoretically interesting quantities in the reversible reaction kinetics are conditional probabilities $S_A(t \mid A)$ and $S_A(t \mid C)$ that a reactant be found in A species at time t if it was A or C species at time zero, respectively. First, we discuss a simple probabilistic relation between those.[4] When the concentrations of A and C at time zero are $[A]_0$ and $[C]_0$, the concentration of A at time t can be written in terms of the conditional probabilities as follows:

$$[A(t)] = S_A(t \mid A)[A]_0 + S_A(t \mid C)[C]_0. \quad (1)$$

If $[A]_0 = [A]_{eq}$ and $[C]_0 = [C]_{eq}$, where the subscript eq denotes the equilibrium value, then $[A(t)]$ must be $[A]_{eq}$ for all t and Eq. (1) becomes

$$[A]_{eq} = S_A(t \mid A)[A]_{eq} + S_A(t \mid C)[C]_{eq}. \quad (2)$$

Dividing Eq. (2) by $[A]_{eq}$, we obtain the generalized mass action law (GMA) as follows:

$$1 = S_A(t \mid A) + K_{eq}S_A(t \mid C), \quad (3)$$

where $K_{eq} = k_f^{eq}/k_r^{eq} = [C]_{eq}/[A]_{eq}$ is the equilibrium constant. Rearranging Eq. (1) by use of Eq. (3) and introducing the concentration deviation $\xi(t) \equiv ([A(t)]-[A]_{eq})/([A]_0-[A]_{eq})$, we get the relation

$$\xi(t) = S_A(t|A)-S_A(t|C) = 1-\frac{S_A(t|A)}{S_A^{eq}}, \quad (4)$$

where $S_A^{eq} \equiv [1 + K_{eq}]^{-1}$. This was also derived from our kinetic theory.[3]

It was also found from the kinetic theory that the conditional probabilities can be predicted via the relation[3]

$$\frac{S_A(t|A)}{S_A^{eq}} = 1 + K_{eq}S_{irr,\,eff}(t), \quad (5a)$$

$$\frac{S_A(t|C)}{S_A^{eq}} = 1-S_{irr,\,eff}(t), \quad (5b)$$

where $S_{irr,\,eff}(t)$ is the effective irreversible survival probability of A. The expression of $S_{irr,\,eff}(t)$ can be obtained within the framework of the kinetic theory, if the bimolecular reaction undergoes *irreversibly* with the effective equilibrium rate constant k_{eff}^{eq} ($\equiv k_f^{eq} + k_r^{eq}$), where k_f^{eq} and k_r^{eq} are the equilibrium forward and reverse rate constants, respectively. In fact, Eq. (5b) can be directly obtained from Eq. (5a) by use of the GMA given by Eq. (3). These relations tell us that the reversible reaction kinetics could be predicted once one knows the information of the irreversible reaction dynamics. In other words, the reverse reaction can not

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change the reaction dynamics itself (including the pair dynamics and the many-body competitive reaction for a reactant) but merely introduces an alternative probabilistic argument reflecting the various initial conditions induced by the reverse reaction. When $K_{eq} \to \infty$, the relations given in Eqs. (5) yield the survival probability of the irreversible reaction as it should be. We can see that these equations satisfy the GMA given by Eq. (3). Inserting Eq. (5b) into Eq. (4), one gets

$$\xi(t) = S_{irr,eff}(t). \tag{6}$$

Despite the complication associated with the different molecular histories embedded in the reversible reaction, it is very interesting that there still exist such simple relations.

All physical effects (potential of mean force, non-diffusive motion, many-body competitive reaction, *etc*.) on the reversible reaction kinetics are included in the expression of the survival probability of irreversible reaction for the system. Any tractable theory introduces some approximations regarding the reactant dynamics in liquid and thus the expressions of the irreversible survival probability can not be exact for a real system. Therefore, we do not expect Eq. (6) with the irreversible survival probability exactly produces the concentration deviation (or conditional probabilities) of a real system or an MD simulation. However, the purpose of this paper is to test whether the general relations, Eqs. (5) and (6), are exact in the description of the many-body effects associated with various initial conditions at different times induced by the reverse reactions. These should be reflected in the expression of concentration deviation (conditional probabilities). One of the available tests may be to perform a model computer simulation for a system for which the exact irreversible survival probability is known and to compare the result with Eqs. (5) and (6). A more general test would be to perform MD simulations for both irreversible and reversible reactions and to confirm the exactness of those relations by comparing the irreversible survival probability and the concentration deviation of the reversible reaction obtained by the simulation. In this paper we choose the latter test.

MD Simulation

Molecular dynamics simulations have been carried out for diffusion-influenced *irreversible* bimolecular and fluorescence quenching reactions.[5,6] We extend a similar MD simulation method to the pseudo-first-order *reversible* reaction of type $A + B \leftrightarrow C + B$ in this work. Since the main features of diffusion-influenced reactions can be quite well characterized by the hard sphere model, we also choose this model for the description of reactant and solvent molecules in liquid. A canonical ensemble of N (= 512) identical hard spheres in a cubic cell with the reduced volume 1 is chosen for our MD simulations. The value of the reduced diameter b of a hard sphere is taken to be $b = 0.114$ to get the number density value of $Nb^3 = 0.76$ which corresponds to a normal liquid density.

Initial configuration was randomly chosen avoiding the overlapping among the hard spheres and the initial velocities are chosen from the Maxwell-Boltzmann distribution. The starting configuration of the system is brought to an equilibrium state by running the MD. The equations of motion for the hard spheres must be solved in a way which is qualitatively different from the MD for a continuous potential. The standard method for this is well known.[7] The ordinary periodic boundary condition in the x-, y-, and z-directions and the minimum image convention are used. After the equilibration, we run the MD and generate trajectories of all particles, which are stored at every collision time for further analyses up to the total collision number of 200,000. From stored configurations of all particles, we analyze the reaction events. For the pseudo-first-order case, every A or C reactant is assumed to be independent of each other. Then we consider only one tagged reactant of these species in the simulation cell.

We first consider the irreversible reaction case. The quantity to be obtained from the simulation is the irreversible survival probability $S_{irr}(t)$ that a reactant survives as A species when that molecule was initially A species surrounded by an equilibrium distribution of B's. To prepare the ensemble composed of the microscopic states associated with this macroscopic initial state, we choose the first configuration stored from the trajectory calculation. For that configuration, among N particles, we randomly select one and tag the species label A on it. Among the remaining N–1 particles, N_B particles were selected randomly and labeled as B. The rest of the N–1–N_B molecules make up the solvent. By this labeling of solute molecules to that configuration, we get one of the microscopic reaction states. To save the CPU time for the trajectory calculation, we prepare other 39 initial reaction states from that configuration varying the random selection of the B's to construct the independent 40 ensembles for the selected A molecule. Again, these random selection of the 40 configurations of B's are repeated for other 39 random selections of an A molecule. Then we get the independent 1,600 microscopic reaction states from a species-irrelevant configuration. With the time interval of 5 collisions in the trajectory calculation, we choose 100 species-irrelevant configurations and repeat the above procedure for every configuration to obtain the total N_A^0 (=160,000) microscopic initial reaction states. Since only one A molecule exists in a given microscopic initial reaction state, N_A^0 can be thought to be the number of A's, which are independent of each other, in the macroscopic initial equilibrium state.

For every microscopic initial reaction state, we check the reaction events along the trajectory of the initial species-irrelevant configuration. When the colliding molecules are labeled to be A and B species in the ith microscopic initial reaction state, they react with the probability w_f. If a real value less than w_f is generated by a random number generator, the reaction occurs and the survival time is stored as τ_i for further analysis of the survival probability. This state is excluded in the reaction-checking subroutine for the subsequent time evolution of the trajectory. Here, the time elapsed

between the creation of the molecule *A* and its disappearance upon reaction is called the survival time of the *A* molecule. If there is no reaction until the end of the trajectory, we set the survival time of that initial state to be infinity. After finishing the check of reaction events, the number of unreacted molecules of *A* in the ensemble at time *t* is evaluated by[5]

$$N_A(t) \equiv \sum_{i=1}^{N_A^0} \theta(\tau_i - t), \tag{7}$$

where $\theta(t)$ is the step function. With this quantity, the survival probability of the irreversible reaction can be obtained, in practice for a finite number of initial states, as

$$S_{irr}(t) = \frac{N_A(t)}{N_A^0}. \tag{8}$$

Now we consider the reversible reaction. In this case, we obtain the conditional probability $S_A(t|C)$ that a reactant be *A* species at time *t* if it was *C* species at time zero. In the simulation, the procedure of the preparation of the microscopic initial reaction states is the same as that of the irreversible reaction case except that the species of the tagged molecule in every initial state is not *A* but *C*. Contrary to the irreversible case, we should trace the trajectory by the end for all microscopic initial reaction states since the forward and the reverse reactions can occur consecutively. Along the trajectory evolution, we check the reaction event. When the colliding molecular pair is *A* (or *C*) and *B* in the *i*th microscopic initial reaction state, they will react with the probability w_f (or w_r). If the reaction occurs, the time [elapsed between the preparation of the initial state and the reaction] and the species of the tagged molecule after the reaction are stored into *TIME*(*i*, *j*) and *SPEC*(*i*, *j*) where the indices *i* and *j* denote the *i*th ensemble and the *j*th reaction, respectively. These values of *TIME* and *SPEC* variables stored will be used in the further analysis for the conditional probability. This procedure is repeated until the end of the trajectory. At the end of the trajectory, we set $TIME(i, N_i + 1) = \infty$ and $SPEC(i, N_i + 1) = SPEC(i, N_i - 1)$ where N_i denotes the number of reactions of the tagged molecule in the *i*th ensemble. To remove the outer boundary effect in time, the trajectory calculation should be carried out for a sufficiently long time.

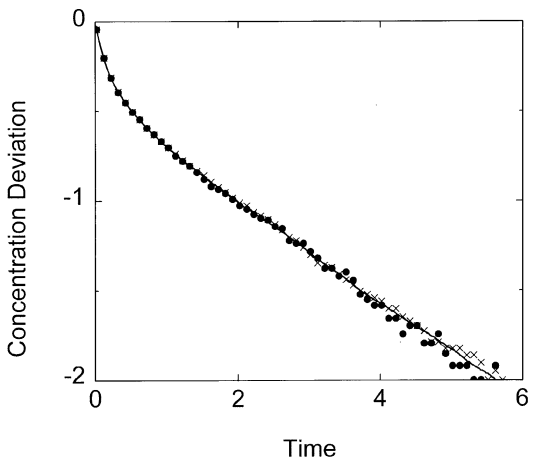

Figure 1. Irreversible survival probability when $w_f = 1$ and the concentration deviation of reversible reaction with the values of (a) $w_f = w_r = 0.5$ (●●●) and (b) $w_f = 0.2$ and $w_r = 0.8$ (×××). The time is in the reduced unit of $\sqrt{m/k_BT}$.

After finishing the check of reaction events for all microscopic initial reaction states, we evaluate the number of *A* molecules in the ensemble at time *t* by the values of *SPEC* and *TIME* stored from the following relation:

$$N_A(t \mid C) \equiv \sum_{i=1}^{N_A^0} \sum_{j=1}^{N_i} \{\theta[t - TIME(i,j)] \cdot \theta[TIME(i,j+1) - t]\} \delta_{SPEC(i,j),A}. \tag{9}$$

With this quantity, the conditional probability $S_A(t \mid C)$ can be obtained as

$$S_A(t|C) = \frac{N_A(t|C)}{N_A^0}. \tag{10}$$

Results and Discussion

The relations given by Eqs. (5) and (6) are closely related to each other via the GMA and thus we confine our discussion in this paper to the conditional probability $S_A(t|C)$. First, we perform the molecular dynamic simulation for the irreversible reaction system with the reaction probability $w_f = 1$. We consider the number of *B*'s, $N_B = 54$, which corresponds to the moderately high concentration of *B* species, $4\pi\sigma^3 N_B = 1.0$. For convenience, the reaction distance σ is assumed to be equivalent to the reduced hard sphere diameter *b*. The time dependence of the irreversible survival probability $S_{irr}(t;\ w_f = 1)$ is displayed by the solid line in Figure 1. The time is in the reduced unit, $\sqrt{m/k_BT}$ (k_B is the Boltzmann constant, T the absolute temperature, and m molecular mass).

To verify the relation of Eq. (5b), we should perform the simulation for the reversible reaction system with the sum of the equilibrium rate constants $k_f^{eq} + k_r^{eq}$ corresponding to the above irreversible simulation. In the present simulation, the intrinsic reactivities are characterized by the forward and reverse reaction probabilities, w_f and w_r. Then the equilibrium rate constant k_f^{eq} (or k_r^{eq}) will be the product of the reaction probability w_f (or w_r) and the equilibrium collision frequency. So, the equilibrium rate constant is linearly proportional to the reaction probability. We choose two sets of the reaction probabilities, (a) $w_f = w_r = 0.5$ and (b) $w_f = 0.2$ and $w_r = 0.8$, which satisfy the condition $w_f + w_r = 1$ which corresponds to the above irreversible reaction simulation. The equilibrium constants K_{eq} for these cases are (a) 1 and (b) 0.25 to give the equilibrium values of the conditional probability S_A^{eq} of (a) 0.5 and (b) 0.8, respectively. With these values, we plot the concentration deviation $\xi = 1 - S_A(t \mid C)/S_A^{eq}$ in Figure 1 and compare those with the irreversible survival probability obtained earlier. The coincidence between the reversible and the irreversible kinetics is

perfect for two sets of the reactivity of reversible reaction. From this comparison, we can conclude that the relations given by Eqs. (5) and (6) are essentially exact in the description of the reverse reaction even in the presence of solvent particles.

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