Bull. Chem. Soc. Jpn. Vol. 79, No. 10, 1509–1518 (2006)

Analysis of Short-Time Transient Dynamics of a Diffusion-Controlled Reaction in a Hard-Sphere Fluid Based on Fokker–Planck–Kramers Equation

Kazuyasu Ibuki* **and Masakatsu Ueno**

Department of Molecular Science and Technology, Faculty of Engineering,
Doshisha University, Kyotanabe, Kyoto 610-0321

Received April 12, 2006; E-mail: kibuki@mail.doshisha.ac.jp

Molecular dynamics (MD) simulations are performed for a simple diffusion-controlled reaction in a hard-sphere fluid. The short-time transient rate constants are compared with the Markovian Langevin dynamics (LD), two theories based on the Fokker–Planck–Kramers equation (FPKE), and the Smoluchowski–Collins–Kimball (SCK) theory based on the diffusion equation. At $n^* = 0.7856$, where n^* is the total number density reduced by the diameter of the molecules, molecular motions are diffusive and Markovian, and the MD results agree well with the LD results. At $n^* = 0.9428$, the MD results are much larger than the LD ones at short times, and the discrepancy can be explained by non-Markovian effects. Also at $n^* = 0.2000$, where inertia effects are important, the time profile of the MD rate constant is satisfactorily explained by LD, while the MD rate constant shows a smaller decay than at higher densities. FPKE theory with a continuous velocity distribution reproduces the LD results under all conditions indicating that the theory is valid over a wide density range. FPKE theory with a discontinuous velocity distribution cannot explain the simulation results at the lowest density despite taking into account inertia effects. Although SCK theory is expected to be valid only at high densities, the predicted rate constant is close to that from the simulation even at the lowest density, if the intrinsic rate constant is chosen to reproduce the exact value of the initial rate constant.

Diffusion-controlled reactions are an important class of reactions in the study of the dynamics of bimolecular reactions in fluids.[1] For a better understanding of molecular migration processes before reactants are encountered, the analysis of the short-time transient effects on diffusion-controlled reactions is of great importance,[2–7] since the time dependence of the rate constant is directly determined by the evolution of the non-equilibrium distribution of migrating reactants. The rate of diffusion-controlled reactions has usually been analyzed on the basis of the diffusion equation[1,8–10] which is concerned only with diffusive molecular motions. From the theoretical point of view, however, inertia[11–13] and non-Markovian effects[14–16] on molecular motions play a non-negligible role in determining the short-time transient dynamics of diffusion-controlled reactions. In previous papers,[17,18] we have proposed a theory based on the Fokker–Planck–Kramers equation (FPKE), which is one of the most important equations for analyzing reaction dynamics in fluids[19–21] and properly takes into account inertia effects. In Lennard–Jones fluids, we have shown[18,22] that our FPKE theory can explain the reaction dynamics at shorter times and lower densities than earlier theories.[8,9,11,23] In the present paper, we determine the validity of our FPKE theory in a hard-sphere fluid for discussing inertia and non-Markovian effects on the reaction dynamics in fluids.

Hard-sphere fluids are one of the most important model systems in the study of liquids and solutions. In spite of its simpleness, a hard-sphere model explains the essential features of the equilibrium and non-equilibrium properties of real liquids such as the radial distribution function or the velocity autocorrelation function.[24] The hard-sphere system also provides a reasonable basis for the interpretation of chemical reactions such as dimerization reactions.[25] In the case of diffusion-controlled reactions, hard-sphere fluids have been used to examine the validity of theories since the pioneering work by Dong, Baros, and Andre.[26] In hard-sphere systems, all of the parameters necessary for the theoretical calculations can be obtained without any arbitrariness. We can therefore avoid the use of the adjustable parameters which sometimes obscure the reliability of theories. Moreover, we can strictly apply the boundary conditions of collision-induced type[9,27] used in many theories in the hard-sphere systems because the collision radius is well-defined. This is the reason why the hard-sphere model[16,23,26,28–31] is often preferred to the Lennard–Jones fluid model systems[18,22,32–34] in the study of diffusion-controlled reactions. Nearly ten years ago, we examined the validity of an early FPKE theory[11,23] of the dynamics of diffusion-controlled reactions by comparing it with simulations in hard-sphere fluids.[23] We have improved the FPKE theory[17,18] as mentioned above, and its validity is examined in a hard-sphere fluid.

At high densities, non-Markovian effects on the molecular motions are expected to have a non-negligible contribution to the dynamics of diffusion-controlled reactions in the time range where inertia effects are significant.[14,15,30,31] Hard-sphere fluids are suitable for analyzing non-Markovian effects, and further tests of the theory are necessary in hard-sphere fluids as well as in Lennard–Jones fluids. It is well-known that the velocity autocorrelation function (VACF) is different from the exponential one at high densities because of non-Markovian

Published on the web October 10, 2006; doi:10.1246/bcsj.79.1509

effects.[24,35] In the hard-sphere fluid, however, the VACF obeys the Enskog theory at extremely short times irrespective of the density.[24] This means that non-Markovian effects can be discussed by combining the Enskog friction coefficient at short times and the ordinary friction coefficient at long times. Moreover, there is a useful reference condition in which non-Markovian effects are negligible while the density is high enough to assume diffusive molecular motions.[23,30,31] These features makes hard-sphere fluids more suitable than the Lennard–Jones fluids in examining non-Markovian effects.

For a thorough understanding of the validity of the FPKE theory, density effects should be examined over a wide range. Since FPKE theory takes into account inertia effects, the theory can explain the reaction dynamics at low densities as well as at high densities. In a hard-sphere fluid, we can study density effects over a wide range because of the absence of a liquid–gas phase transition. Another purpose of the present study is to validate the new FPKE theory at low densities in a hard-sphere fluid. The reaction dynamics in the medium and low-density regions are of great interest in relation to the supercritical fluids.[36,37] In the area of diffusion-controlled reactions, the effect of local density augmentation near the critical point has been studied extensively,[34,36–40] and the effect of the attractive interaction between molecules is important at medium and low densities. To discuss such an interesting potential effect thoroughly, the behavior of systems without any attractive force, i.e., hard-sphere fluids, can be used as a reference. If validated over a wide density range in a hard-sphere fluid, the new FPKE theory can be used as a guideline to discuss reaction dynamics at medium and low densities.

In order to carry out a reliable and more detailed test of the theories than our previous work on hard-sphere fluids,[23] we have improved the method of the molecular dynamics (MD) simulations. We have employed much lower reactant concentrations in order to lower the effect of the correlation between the reactant motions. We have performed MD simulations with much longer times to clarify the difference between the short-time and the long-time behaviors. We have estimated the time-dependent rate constants from the survival probabilities obtained by MD, since the limitations of the theories can be recognized more clearly by the rate constants than the survival probabilities. The simulations and the theories were compared only using the survival probability in the previous work. In addition to MD, we have carried out Langevin dynamics (LD) simulations to determine the limitations of the FPKE theory itself from those of the approximations used in solving the FPKE. We have shown in our previous work involving Lennard–Jones fluids[18,22] that LD is quite useful for examining the validity of FPKE theories.

In the next section, we explain the methods of MD and LD. The theories considered in the present work are briefly explained in the third section, and compared with the simulations in the fourth section. The last section is the conclusions.

Simulations

Reaction Model. The reaction model is a general fluorescence quenching reaction of the type $A + Q \to B + Q$ where A is the target molecule, Q the quencher, and B the inert product. A, B, Q, and the solvent molecules S are physically identical hard-spheres distinguished only by their labels. Before the the reaction is initiated, the system is in equilibrium. After instantaneous initiation at $t = 0$, the reaction occurs whenever A and Q collide. The reaction rate equation is given by

$$\frac{dS(t)}{dt} = -k(t)S(t)n_Q, \tag{1}$$

where $S(t)$ is the survival probability of A, $k(t)$ the time-dependent rate constant, and n_Q the number density of Q in the bulk.

Molecular Dynamics. The model used for the MD simulations is the same as that proposed by Dong, Baros, and Andre.[26] In a cubic cell with a periodic boundary, there are $N(=500)$ identical hard-spheres. At an arbitrary moment after the system is equilibrated, the time is set to $t = 0$ and N_Q molecules of Q and N_A molecules of A are chosen randomly. The remaining N_S $(=N - N_Q - N_A)$ molecules are solvent molecules S. In practice, we usually use $N_Q = 1$, $N_A = 499$, and $N_S = 0$ for the reasons explained later. Then, the trajectory calculation is restarted. The survival probability $S(t)$ of A is calculated by the following equation:

$$S(t) = \frac{1}{N_A}\sum_{j=1}^{N_A}\theta(t_j - t), \tag{2}$$

where t_j is the reaction time of j-th A molecule at which it collides with one of the Q molecules for the first time and $\theta(x)$ is the Heaviside step function, which is zero for $x \leq 0$ and unity for $x > 0$. We average $S(t)$ for 1×10^5 runs at each condition unless otherwise indicated. A large number of accumulations is necessary to obtain a reliable rate constant $k(t)$ by a numerical differentiation of $S(t)$.

The MD simulations are performed at three densities, $n^* = n\sigma^3 = 0.9428$, 0.7856, and 0.2000 where n is the total number density of the N molecules and σ the diameter of the rigid spheres. The source code is a modification of that given by Allen and Tildesley.[41] The self-diffusion coefficients D_s and the radial distribution functions $g(r)$, which are necessary in the theoretical calculations, were determined by independent non-reactive MD runs. The self-diffusion coefficients were estimated from the slopes of the mean square displacements at sufficiently long times. The contact values of the radial distribution function $g(\sigma)$ were estimated from the virial. The parameters obtained by the non-reactive MD simulations are listed in Table 1.

In order to determine the appropriate values of N_A and N_Q, we examine the dependences of the rate constant on N_A and N_Q. It should be noted that the rate constant obtained by the

Table 1. Parameters Obtained from MD Simulations in a Hard-Sphere Fluid

	n^*		
	0.200	0.7856	0.9428
$\frac{D_s}{\sigma}\sqrt{\frac{m}{k_BT}}$	0.872	0.0706	0.0212
D_s/D_E	1.09	1.03	0.550
$g(R)$	1.33	3.92	5.82
R_{eff}	1.06	1.07	1.01
k_D/k°	1.64	0.134	0.0380
k_C/k°	0.664	1.96	2.91

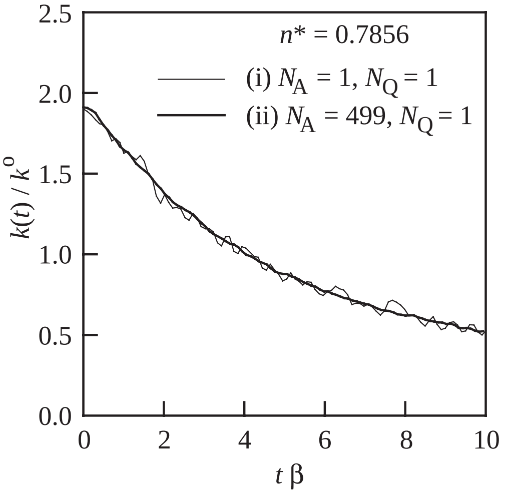

Fig. 1. Time dependence of the rate constants for different initial concentrations of A at $n^* = 0.7856$. Thick and thin lines indicate (i) $N_A = 1$, $N_Q = 1$, $N_S = 498$, and (ii) $N_A = 499$, $N_Q = 1$, $N_S = 0$ at $t = 0$, respectively.

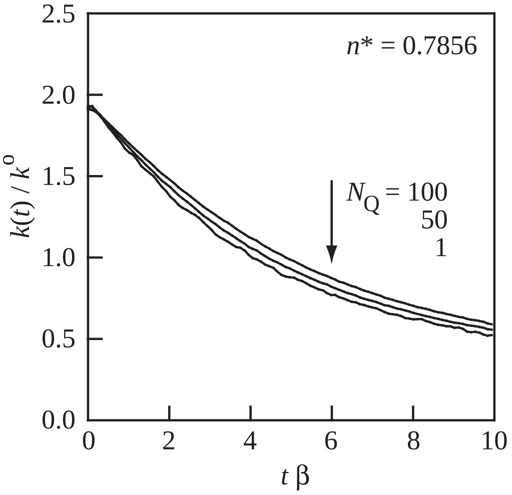

Fig. 2. Time dependence of the rate constants for different concentrations of Q at $n^* = 0.7856$. $N_Q = 1$, 50, and 100. For all the cases, $N_A = 500 - N_Q$ and $N_S = 0$.

present MD simulation did not depend on the initial concentration of A.[18] In the present model, the molecules of Q reacted repeatedly while the molecules of A reacted irreversibly. Since the trajectory of the molecules were determined only by their physical properties and did not depend on their labels, the reaction time of a given A molecule was not altered by exchanging labels between other molecules of A, the molecules of S, and the products B. This means that if we simulate with $N_A = N - N_Q$ and $N_S = 0$, the resultant survival probability and the rate constant correspond to the averages for $(N - N_Q)$ ways of choosing one A molecule from $(N - N_Q)$ possibilities. This can be easily verified by examining the dependence of the rate constant on N_A by actual MD simulations. In Fig. 1, the time dependent rate constants are shown at $n^* = 0.7856$: (i) $N_A = 1$, $N_Q = 1$, and $N_S = 498$, and (ii) $N_A = 499$, $N_Q = 1$, and $N_S = 0$. For cases (i) and (ii), we accumulate the survival probabilities for 3×10^6 and 1×10^5 runs, respectively. The rate constants were normalized by k° defined by

$$k^\circ = 4\pi R^2 \sqrt{\frac{2k_B T}{\pi\mu}}. \tag{3}$$

As shown in Fig. 1, the rate constants for the two conditions agree within the statistical fluctuations as expected. We therefore carry out the remaining simulations in this work for $N_A = N - N_Q$ and $N_S = 0$.

Although the rate constant is independent of the initial concentration of A, it depends on the concentration of Q. In Fig. 2, the rate constants for $N_Q = 1, 50, 100$ obtained by using MD with $n^* = 0.7856$ are shown for comparison. The rate constant increased slightly with increasing concentrations of Q. This is qualitatively the same behavior as a similar model reaction in Lennard–Jones fluids at long times.[18] Since the theories considered in the present work do not take into account the interaction between Q molecules, we carry out the remaining simulations only for $N_Q = 1$.

Langevin Dynamics. Langevin dynamics (LD) simulation is important for determining the validity of theories based on FPKE as shown in our previous work involving Lennard–Jones fluids,[17,18,22] since it provides the numerical but exact solutions to the FPKE, and agreement with LD is the first criterion for validating the approximations used in the theories.

The FPKE used here was derived from the following Langevin equation:[19,42]

$$\mu \frac{d\boldsymbol{v}(t)}{dt} = -\mu\beta\boldsymbol{v}(t) - \frac{dV(\boldsymbol{r})}{d\boldsymbol{r}} + \boldsymbol{R}(t), \tag{4}$$

where μ is the reduced mass of A and Q, $\boldsymbol{v}(t)$ the relative velocity at t, β the friction coefficient, $V(\boldsymbol{r})$ the potential, and $\boldsymbol{R}(t)$ the Gaussian random force. β and $\boldsymbol{R}(t)$ satisfy the fluctuation-dissipation theorem.

The model system used in the LD simulations is the so-called target-problem model. In a potential field $V(r)$, there is a molecule of A fixed at the origin of the coordinate and a migrating molecule of Q. At $t = 0$, the molecule of Q is set at a point with the initial distance r_{ini} from the fixed molecule of A. The initial velocity is randomly chosen to obey the Maxwellian distribution. Then the trajectory of the Q molecule is calculated by the numerically integrating Eq. 4 using the algorithm proposed by Turq et al.[43] In this algorithm, inertia effects are properly taken into account. When the Q molecule approaches the A molecule within a distance R $(=\sigma)$ for the first time, reaction occurs. We produced 50000 trajectories for each r_{ini} and determined the reaction probability $P(r_{\text{ini}}, t)dt$, which is the probability that a molecule started from r_{ini} reacts at a time between t and $t + dt$. The rate constant was obtained by the following equation:

$$k(t) = \int_R^{r_{\max}} 4\pi r_{\text{ini}}^2 P(r_{\text{ini}}, t) g(r_{\text{ini}}) dr_{\text{ini}}. \tag{5}$$

The potential $V(r)$ is given by the potential of mean force (PMF) calculated from the equilibrium radial distribution function $g(r)$ obtained from the MD simulations.

$$V(r) = -k_B T \ln g(r), \tag{6}$$

where k_B is the Boltzmann constant, and T is the temperature. Although the present model for the LD simulation contains only two molecules, a two-body potential is not suitable; the effective potential in a real system is determined by many-body effect including the solvent molecules, and the equilibrium PMF has been expected to be a good approximation even in the reaction dynamics problem.[44]

The friction coefficients β used in the LD simulations were estimated from the relative diffusion coefficients D_r through the Einstein relation.

$$\beta = \frac{k_B T}{\mu D_r}. \tag{7}$$

We simply assumed that D_r is given by the sum of the self-diffusion coefficients obtained from the MD simulations.

The time step Δt for the integration of Eq. 4 was $1 \times 10^{-2}\beta^{-1}$ except for the short-time run ($t\beta < 10$) at $n^* = 0.2000$ where we used $\Delta t = 1 \times 10^{-3}\beta^{-1}$. The intervals of r_{ini} ranged from 0.0025σ to 0.1σ depending on the friction coefficient and the duration of the LD run. The $r_{\max}$ values in Eq. 5 were chosen to be large enough to guarantee that no reaction occurs for $r_{\mathrm{ini}} \geq r_{\max}$ within the duration of the LD runs. The rate constants were estimated at every $1 \times 10^{-1}\beta^{-1}$ for the short-time runs up to $t\beta = 10$ and at every β^{-1} for the long-time runs up to $t\beta = 100$.

Theoretical

In this work, we compare three theories with the simulations: the FPKE theory with a continuous velocity distribution (FPKE-C), the FPKE theory with a discontinuous velocity distribution (FPKE-D), and the Smoluchowski–Collins–Kimball (SCK) theory based on the diffusion equation. All three theories are based on the target-problem model used in the LD simulation.

FPKE-C Theory. The main purpose of the present study is to test the FPKE-C theory using a hard-sphere fluid. The starting equation of the FPKE theories is the following Fokker–Planck–Kramers equation:[19,42]

$$\frac{\partial f(\boldsymbol{v},\boldsymbol{r},t)}{\partial t} + \boldsymbol{v}\cdot\frac{\partial f(\boldsymbol{v},\boldsymbol{r},t)}{\partial \boldsymbol{r}} - \frac{1}{\mu}\frac{\partial V(\boldsymbol{r})}{\partial \boldsymbol{r}}\cdot\frac{\partial f(\boldsymbol{v},\boldsymbol{r},t)}{\partial \boldsymbol{v}} = \beta\frac{\partial}{\partial \boldsymbol{v}}\cdot\boldsymbol{v}f(\boldsymbol{v},\boldsymbol{r},t) + \beta\frac{k_B T}{\mu}\frac{\partial^2 f(\boldsymbol{v},\boldsymbol{r},t)}{\partial \boldsymbol{v}^2}, \tag{8}$$

where $f(\boldsymbol{v},\boldsymbol{r},t)$ is the distribution function of Q relative to A.

Before the initiation of the reaction at $t = 0$, the distribution was in equilibrium. At $t > 0$, Eq. 8 was solved with the boundary condition at $r = R$ proposed by Wang and Uhlenbeck[27] as

$$f(v_r > 0, R, t) = 0, \tag{9}$$

where v_r is the radial component of the velocity given by

$$v_r = \boldsymbol{v}\cdot\frac{\boldsymbol{r}}{r}. \tag{10}$$

The condition of Eq. 9 expresses that the Q molecules are absorbed by A whenever they collide at distance $r = R$. The reaction rate constant was determined by

$$k(t)n_{\mathrm{Q}} = -4\pi R^2 j_r(R,t), \tag{11}$$

$$j_r(\boldsymbol{r},t) = \int v_r f(\boldsymbol{v},\boldsymbol{r},t)\mathrm{d}\boldsymbol{v}, \tag{12}$$

where $j_r(\boldsymbol{r},t)$ is the radial component of the flux of Q and $j_r(R,t)$ characterizes the reactive flux. The number density of Q at infinite distance n_{Q} remains constant even after the initiation of the reaction.

At $t = 0$, the rate constant $k(0)$ can be calculated exactly since the distribution function for $v_r < 0$ is still the same as that in the equilibrium while that for $v_r < 0$ is zero at $r = R$ because a reaction occurs. In this case, $k(0)$ agrees with the rate constant derived from the equilibrium collision frequency k_{C} given by

$$k_{\mathrm{C}} = \frac{1}{2}g(R)k^{\circ} = k(0). \tag{13}$$

At $t > 0$, the exact solution of Eq. 8 with Eq. 9 has not been determined except for the uniform force field in one dimension. We therefore used an approximate method to solve it. For the FPKE-C theory, the distribution function was assumed to be the following:[17,18]

$$f(\boldsymbol{v},r,t) = n_r(r,t)\left(\frac{\mu}{2\pi k_B T}\right)^{3/2} \times \exp\left[-\frac{\mu}{2k_B T}\left(\frac{v_r^2}{\sigma(r,t)^2} + v_\theta^2 + v_\phi^2\right)\right] \quad \text{for } v_r > 0, \tag{14}$$

$$f(\boldsymbol{v},r,t) = n_r(r,t)\left(\frac{\mu}{2\pi k_B T}\right)^{3/2} \times \exp\left[-\frac{\mu}{2k_B T}\left(v_r^2 + v_\theta^2 + v_\phi^2\right)\right] \quad \text{for } v_r < 0, \tag{15}$$

where v_θ and v_ϕ are the velocity components perpendicular to v_r. The function $n_r(r,t)$ characterizes the distribution in position and $\sigma(r,t)$ the asymmetry of the distribution of v_r at each position. Since the reactive flux of Q towards A is produced by the asymmetry of the velocity distribution, the appropriate choice of its functional form is of great importance. The function used here was continuous in the whole velocity space, had a maximum at $v_r = 0$, and had different half-widths for $v_r > 0$ and $v_r < 0$. These features are qualitatively the same as those actually observed for the reactive MD using the Lennard–Jones fluids.[17,18]

Since the temperature is related to the half-widths of the equilibrium velocity distribution, the meaning of the temperature in the present non-equilibrium problem is important. The temperature T in Eqs. 14 and 15 indicates that of the heat bath, and it corresponds to the temperature of the whole $N(=500)$ particle system in the MD simulations. The distribution given by Eqs. 14 and 15 is, on the other hand, that of the non-equilibrium partial system concerning only with the relative velocity between A and Q.

From Eqs. 8, 14, and 15, we derived a set of equations for $n_r(r,t)$ and $\sigma(r,t)$. We numerically solved it by using the Lax–Wendroff explicit method.[45] The potential and the friction coefficient used in the theoretical calculations were the same as those used in the LD simulation.

FPKE-D Theory. In the previous work,[23] we discussed the validity of the FPKE-D theory by comparing it with simulations using a hard-sphere fluid. The FPKE-D theory[11,23] is an early theory based on the FPKE using following functional form instead of Eqs. 14 and 15:

$$f(\boldsymbol{v},r,t) = 2n_+(r,t)\left(\frac{\mu}{2\pi k_B T}\right)^{3/2}$$

$$\times \exp\left(-\frac{\mu v^2}{2k_B T}\right) \quad \text{for } v_r > 0, \tag{16}$$

$$f(\boldsymbol{v}, r, t) = 2n_-(r, t)\left(\frac{\mu}{2\pi k_B T}\right)^{3/2}$$
$$\times \exp\left(-\frac{\mu v^2}{2k_B T}\right) \quad \text{for } v_r < 0. \tag{17}$$

Here, $n_+(r,t)$ and $n_-(r,t)$ are the number density of the molecules with the velocity $v_r > 0$ and $v_r < 0$, respectively. From Eqs. 8, 16, and 17, we derived a set of equations for $[n_+(r,t) + n_-(r,t)]$ and $[n_+(r,t) - n_-(r,t)]$. We numerically solved it by the same method as the FPKE-C theory.

In this theory, the asymmetry of the velocity distribution is characterized by the difference between the heights for $v_r > 0$ and $v_r < 0$. As a result, the distribution function was not continuous at $v_r = 0$. Since solutions of the FPKE should be continuous, the approximation used in the FPKE-D theory is unrealistic. This is why we proposed the improved approximation based on the continuous distribution explained in the previous subsection. As far as the survival probability is concerned, the FPKE-D theory reasonably agrees with MD in a hard-sphere fluid at high densities.[23] In the present paper, we discuss the validity of the FPKE theories in more detail by using the rate constant.

From the theoretical point of view, the most significant difference between the results of the two FPKE theories is that the FPKE-D theory reduces to the SCK theory based on the diffusion equation while the FPKE-C theory does not unless the system is quite close to the equilibrium. In the present problem of the reaction dynamics, the distribution at short distances is far from the equilibrium even in the long-time limit.

SCK Theory. The Smoluchowski–Collins–Kimball (SCK) theory[8–10] is the most widely used theory for studying diffusion-controlled reactions. The SCK theory is based on the following diffusion equation:

$$\frac{\partial n(\boldsymbol{r},t)}{\partial t} = D_r \frac{\partial}{\partial \boldsymbol{r}} \cdot \left[\frac{\partial n(\boldsymbol{r},t)}{\partial \boldsymbol{r}} + \frac{1}{k_B T}\frac{\partial V(\boldsymbol{r})}{\partial \boldsymbol{r}} n(\boldsymbol{r},t)\right], \tag{18}$$

where $n(\boldsymbol{r},t)$ is the position distribution of Q relative to A. Since inertia effects are neglected in the diffusion equation, the SCK theory is only valid at times much longer than the inverse of β.

The boundary condition at $r = R$ is given by[9]

$$k_{\text{int}} n(R,t) = 4\pi R^2 D_r \left[\left.\frac{\partial n(r,t)}{\partial r}\right|_{r=R} + \frac{1}{k_B T}\left.\frac{dV(r)}{dr}\right|_{r=R} n(R,t)\right], \tag{19}$$

where k_{int} is the intrinsic rate constant which characterizes the rate process at contact.

The reaction rate constant is given by

$$k(t) n_Q = k_{\text{int}} n(R,t). \tag{20}$$

At finite times, we numerically solved Eq. 18 with Eq. 19 by the Crank–Nicolson method.[45]

In the long-time limit, the SCK rate constant is given by

$$k(\infty) = \frac{k_{\text{int}} g(R) k_D}{k_{\text{int}} g(R) + k_D}, \tag{21}$$

where k_D is the steady-state rate constant derived from the Smoluchowski theory[8,10] which is the limiting case of the SCK theory with an infinite k_{int}.[9] The Smoluchowski rate constant k_D is given by the following equations:

$$k_D = 4\pi R_{\text{eff}} D_r, \tag{22}$$

$$R_{\text{eff}} = \left[\int_R^\infty \frac{dr}{r^2 g(r)}\right]^{-1}. \tag{23}$$

In the short-time limit, the SCK rate constant is given by

$$k(0) = g(R) k_{\text{int}}. \tag{24}$$

The SCK theory itself provides no explanation how to determine k_{int}. It is well-known that the infinite k_{int} used in the Smoluchowski theory is unrealistic since it leads to an infinite initial rate constant.[1,9] As mentioned in the previous subsection, the FPKE-D theory reduces to the SCK theory in the steady state. In this case, k_{int} is given by k° of Eq. 3.[23] If we apply $k_{\text{int}} = k^\circ$ to the SCK theory, however, the resultant $k(0)$ value is two times as large as the exact value given by Eqs. 3 and 13. In order to adjust the initial rate constant of the SCK theory to the exact one, Zhou and Szabo[28] proposed the following intrinsic rate constant:

$$k_{\text{int}} = 2\pi R^2 \sqrt{\frac{2k_B T}{\pi\mu}} = \frac{1}{2} k^\circ. \tag{25}$$

Here, we used this k_{int} value.

Results and Discussion

Velocity Autocorrelation Functions. In this work, we performed simulations using three densities, $n^* = 0.9428$, 0.7856, and 0.2000, to discuss the situations that the molecular motions are (1) diffusive and non-Markovian, (2) diffusive and Markovian, and (3) inertial and Markovian, respectively. Inertia effects are usually considered to be important at low densities while the molecular motions are diffusive at high densities. At very high densities, moreover, non-Markovian effects become significant. The classification of the conditions studied here can be qualitatively understood in this way. In order to confirm the classification, it is better to examine the velocity autocorrelation functions (VACF) and the steady-state rate constants derived from simple theories.

Figure 3 exhibits single molecule VACFs normalized at $t = 0$. In addition to the results from MD, the exponential decays with time constant $1/\beta$ are plotted, since the VACF of an exponential type, $\exp(-t\beta)$, is derived from the Markovian Langevin equation, Eq. 4. The exponential decays with the Enskog friction coefficient β_E are also exhibited for comparison. The Enskog friction coefficient β_E and the diffusion coefficient D_E are given as follows:

$$\beta_E = \frac{8}{3} n\sigma^2 g(\sigma)\sqrt{\pi m k_B T}, \tag{26}$$

$$D_E = \frac{k_B T}{m\beta_E}, \tag{27}$$

where m is the mass of a rigid sphere. Although the macroscopic diffusion coefficient can be explained by the Enskog theory only at sufficiently low densities, it has been known that the initial slope of the VACF in a hard-sphere fluid is always

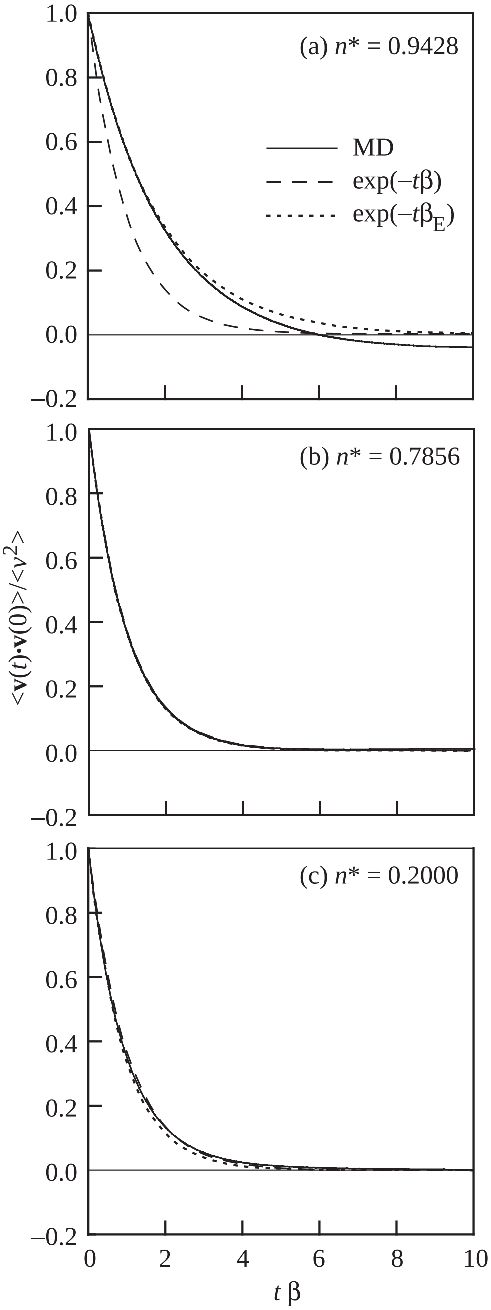

Fig. 3. Velocity autocorrelation functions at (a) $n^* = 0.9428$, (b) 0.7856, and (c) 0.2000. Solid lines indicate the MD results, broken lines the exponential decay with β and dotted lines the exponential decay with β_E.

determined by the collision frequency derived from the Enskog theory even at high densities.[24,46]

At $n^* = 0.9428$, the initial decay of the VACF from MD is much slower than that of $\exp(-t\beta)$.[46] This clearly indicates the significance of non-Markovian effects. It is to be noted that the VACF from MD coincides with the exponential function using β_E at short times up to about $t\beta = 4$, though β_E is much larger than the observed one at this density as shown in Table 1. We will later use this property to discuss non-Markovian effects on the reaction dynamics. At $n^* = 0.7856$ and 0.2000, on the other hand, results of the VACF from MD are almost exponential. At the former density, β obtained from MD is very close to β_E.[46,47] Although there is a tail at long times[24,35,48] at $n^* = 0.2000$, the discrepancy between the results from MD and $\exp(-t\beta)$ is very small. It has been shown from theoretical analysis based on a generalized diffusion equation[49] that the effect of the long-time tail on the rate of diffusion-controlled reactions is small. These results indicate that the Markovian approximation can be used at $n^* = 0.7856$ and 0.2000.

The importance of inertia effects is now discussed on the basis of the steady-state rate constant derived from the Smoluchowski theory k_D and the kinetic collision theory k_C. At $t = 0$, the rate constant $k(0)$ is equal to k_C irrespective of the density. At high densities, where the molecular motions are diffusive, k_D is much smaller than k_C, and the rate constant is expected to decay with time towards close to k_D. In the low-density limit, where the inertial motions determine the dynamics of the system, k_C is much smaller than k_D, and the rate constant is expected to be independent of time. This suggests that $k_\mathrm{D}/k_\mathrm{C}$ is a convenient criterion to distinguish between diffusive and inertial conditions. As shown in Table 1, $k_\mathrm{D}/k_\mathrm{C}$ is much smaller than unity at $n^* = 0.7856$ while it is more than 2 at $n^* = 0.2000$. Therefore, the difference between the diffusive and the inertial cases can be discussed by comparing the results at $n^* = 0.7856$ and 0.2000.

Diffusive and Markovian Case. The results for $n^* = 0.7856$ are discussed first since the diffusive and Markovian system is an important reference system for examining inertia and non-Markovian effects. The time dependent rate constants at $n^* = 0.7856$ are shown in Fig. 4.

The results from MD and LD at $n^* = 0.7856$ agree over the entire time range studied up to $t\beta = 100$. Although there is a small discrepancy between them at $t\beta < 10$ as shown in Fig. 4a, the agreement at longer times is remarkable. This indicates that the target-problem model with the Markovian Langevin equation and the equilibrium PMF provides a good explanation for the reaction dynamics in this condition. So far we have no clear explanation for the origin of the small discrepancy between the results from MD and LD at short times. Since non-Markovian effects and the interaction between Q molecules are absent under the present conditions, the possible sources of the discrepancy are the PMF and the relative diffusion coefficient. Although there has been no definite theories to treat these problems, the potential suitable for a non-equilibrium system might be different from the equilibrium PMF used here, and the correlated motion of A and Q would violate the assumption that the relative diffusion coefficient is given by the sum of the self-diffusion coefficients. The small discrepancy between the results from MD and LD indicates, however, that these effects are not significant in high-density fluids.

The rate constant derived from the FPKE-C theory agrees well with the results from LD over the entire time range. In other words, the approximation used in the theory is valid. Although $k(0)$ from the FPKE-C theory is larger than the exact one because of the approximate nature of the theory,[17,18] the deviation is small and is only observed in the extremely short-time region. In a practical sense, therefore, the FPKE-C theory well reproduces the results from LD and MD at the high density.

The FPKE-D theory predicts a rate constant that is some-

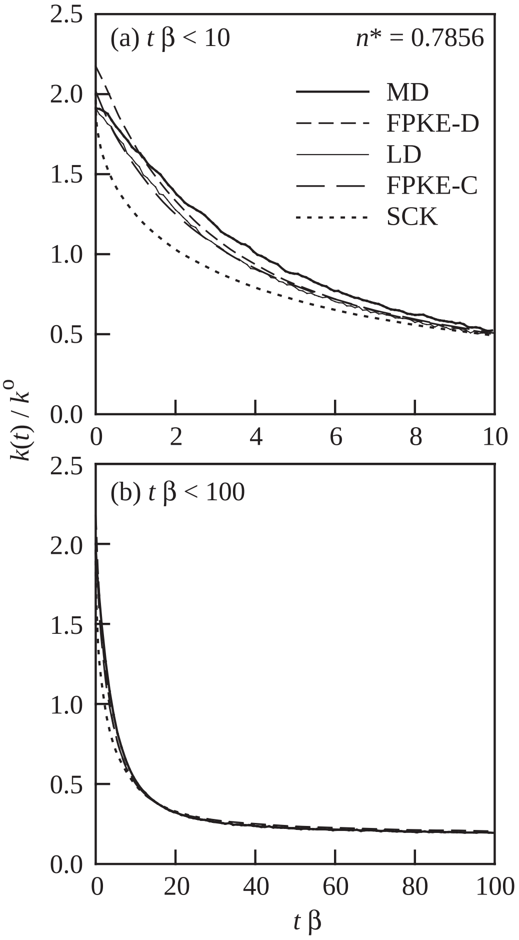

Fig. 4. Time dependence of rate constant at $n^* = 0.7856$ for (a) $0 < t\beta < 10$ and (b) $0 < t\beta < 100$. Thick solid line indicates MD, thin solid line LD, long broken line FPKE-C, short broken line FPKE-D, and dotted line SCK. In (b), the LD results are almost identical to those of the FPKE-C theory and omitted to avoid confusion.

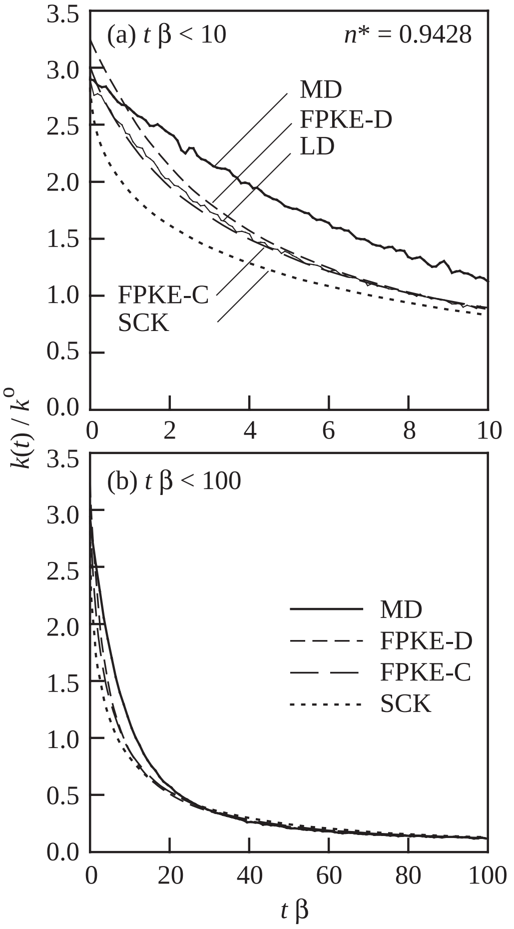

Fig. 5. Time dependence of rate constant at $n^* = 0.9428$ for (a) $0 < t\beta < 10$ and (b) $0 < t\beta < 100$. Lines have the same meanings as in Fig. 4. In (b), the LD results are almost identical to those of the FPKE-C theory and omitted to avoid confusion.

what larger than that from LD at $t\beta < 10$ as shown in Fig. 4a. Initial rate constant $k(0)$ is also larger than that from the FPKE-C theory,[18,23] and the deviation persists for some duration. It is interesting to note that the rate constant from the FPKE-D theory is much closer to that from MD than those from LD and the FPKE-C theory at short-times. We pointed out in our previous paper[23] that the FPKE-D theory reasonably reproduces the time dependence of the survival probability in a hard-sphere fluid under this condition. The present results disclose that this is merely a consequence of the cancellation between the underestimation using LD and the overestimation using FPKE-D theory. Since the FPKE theories are based on the Langevin equation, they are considered to be valid if they agree with the results from LD. In a practical sense, however, the difference between the results from the FPKE-D theory and LD is small, and so the limitations of the FPKE-D theory are not clearly observed at the high density.

The SCK rate constant is distinctively smaller than the others at $t\beta < 10$. The rapid initial decay of the rate constant is a characteristic of the inertialess approximation.[16] In the previous papers,[18,23,30,31] we concluded due to the rapid initial decay that the SCK theory is invalid. The inertialess approximations is, however, expected to be valid only in the long-time region in which the VACF vanishes, so that it is not so fair to judge the SCK theory invalid due to the limitation at extremely short times. It can be seen from Fig. 4b that all of the simulated and theoretical rate constants become virtually identical at $t\beta > 10$. This indicates that the reaction dynamics in the diffusive and Markovian system can be explained by using the SCK theory at long times as usually expected. Moreover, the steady-state rate constant is very close to the Smoluchowski rate constant k_D as can be seen from Eq. 21; note that $k_{int}g(R) = k_C \gg k_D$. This explains the reason why the steady-state rate constants of diffusion-controlled reactions can be reasonably interpreted in many cases in terms of the simple Smoluchowski theory in spite of its limitations at short times.

Diffusive and Non-Markovian Case. Next non-Markovian effects are discussed. Figure 5 exhibits the simulation and the theoretical rate constants at $n^* = 0.9428$. At $t\beta < 30$, there is a discrepancy between the MD and LD results which is significantly larger and persists until longer times than that with $n^* = 0.7856$. We examine whether or not the discrepancy can be attributed to non-Markovian effects.

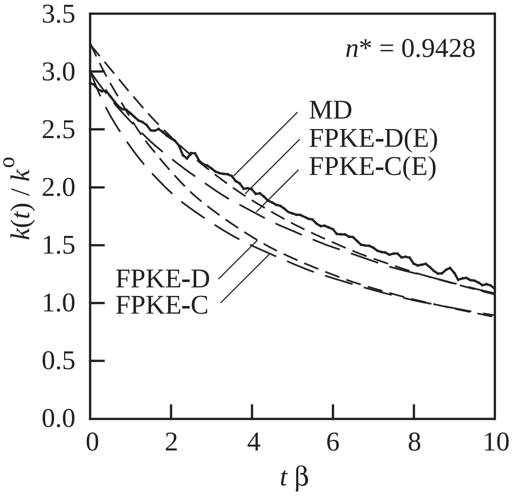

Fig. 6. Time dependence of rate constant at $n^* = 0.9428$ for $0 < t\beta < 10$. Lines have the same meanings as in Fig. 4. FPKE-C and FPKE-D indicate the theoretical results calculated with β, and FPKE-C(E) and FPKE-D(E) those calculated with β_E.

Non-Markovian effects on the dynamics of diffusion-controlled reactions have been discussed on the basis of the generalized Fokker–Planck equation[30] (GFPE) and the generalized diffusion equation[14,15,29,31] (GDE) both of which are derived from the generalized Langevin equation.[50,51] The GFPE and the GDE have been derived only for the uniform potential and the harmonic oscillators, and therefore, realistic systems with a large potential effect, such as the present one, cannot be treated by them. Furthermore, the GFPE is not suitable for numerical calculations since the coefficients in the GFPE diverge at times where the VACF crosses the zero level.[30] We therefore carry out a semi-quantitative discussion of non-Markovian effects based on the ordinary FPKE in a somewhat intuitive way.[23]

As mentioned earlier, the VACF obtained using MD at $n^* = 0.9428$ coincides with the exponential function with the Enskog friction coefficient β_E at $t\beta < 4$. This means that in a hard-sphere fluid, the effect of the non-Markovian friction on the dynamics of diffusion-controlled reactions can be examined quantitatively up to at least $t\beta = 4$ by using β_E instead of the macroscopic friction coefficient β. Thus, hard-sphere fluids are appropriate models for studying non-Markovian effects.

The FPKE-C and the FPKE-D rate constants calculated using β and β_E are depicted in Fig. 6 together with the MD result. By using β_E, the degree of the agreement between the MD and the theoretical results was improved to the level of that at $n^* = 0.7856$. This indicates that the large discrepancy between the rate constants from MD and the others at short times at $n^* = 0.9428$ can be explained by non-Markovian effects. As in the case at $n^* = 0.7856$, the FPKE-D theory apparently provides a rate constant closer to the MD result because of a cancellation of errors.

At sufficiently long times, the ordinary friction coefficient β should be used to explain the results from MD. As shown in Fig. 5b, the LD and the theoretical rate constants calculated with β reproduce the results from MD at long times. If β_E is used, the resultant steady-state rate constant becomes about two times as large as that calculated using β, since k_D is proportional to D_r. It should be noted, however, that non-Markovian friction exerts a small but persistent effect on the survival probability $S(t)$ at long times since $S(t)$ is obtained by a time integration of the rate constant. In the present simulations, $S(t) = 0.975$ using MD and 0.978 using LD at $t\beta = 100$. Although the two results appear similar, the decrement of the survival probability $[1 - S(t)]$ differs by more than 10%.

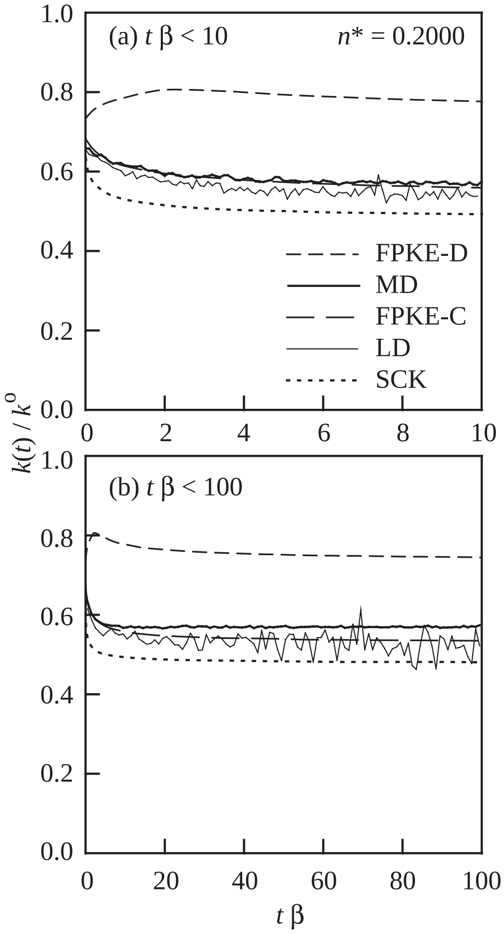

Fig. 7. Time dependence of rate constant at $n^* = 0.2000$ for (a) $0 < t\beta < 10$ and (b) $0 < t\beta < 100$. Lines have the same meanings as in Fig. 4.

Inertial and Markovian Case. We finally discuss the behavior of the low-density fluid in which inertia effects are important. The simulation and the theoretical rate constants at $n^* = 0.2000$ are shown in Fig. 7.

At this density, the magnitudes of the decay in the rate constants are much smaller than those at the higher densities. The agreement between the results from MD and LD is satisfactory also at the low density. However, the LD rate constant is slightly smaller than the MD one even at $t\beta = 100$ at $n^* = 0.2000$ while the difference between them vanishes at long times at higher densities. Since the decay in the rate constant is small, the friction coefficient or the relative diffusion coefficient should not have a large effect at $n^* = 0.2000$. At low densities, where $k_C \ll k_D$, the rate constant at long times depends more directly on k_C than at high densities. The collision rate constant k_C was determined by the contact value of the radial distribution function. This suggests that the small discrepancy between MD and LD might be attributed to non-equilibrium effects on PMF.

The FPKE-C theory agrees well with the LD results also at $n^* = 0.2000$ in particular at long times. In our previous works with Lennard–Jones fluids,[18,22] there was not such excellent agreement between them because the simulations were performed only at times less than about $t\beta = 5$; note the small β values at low densities. At short times, the theory slightly overestimates the rate constant; the FPKE-C results were almost identical to the MD results in Fig. 7a. As mentioned earlier, $k(0)$ based on the FPKE-C theory is larger than the exact value. The effect of the limitation at $t = 0$ does not vanish to some duration at low densities. We have observed a similar tendency in the Lennard–Jones fluids,[22] though we have so far no idea to explain the reason. In a practical sense, however, the discrepancy between the FPKE-C and the LD results is small, and we can conclude that the FPKE-C theory is a good approximation for LD over the entire density range studied here.

The FPKE-D theory significantly overestimates the rate constant at low densities though it takes into account inertia effects. This has been already shown for the FPKE-D theory under the steady-state conditions by Tachiya[52] and under the transient conditions by us.[22] The limitations of the FPKE-D theory are closely related to the fact that it reduces to the SCK theory under the steady-state conditions. In the SCK theory, the Maxwellian velocity distribution is always assumed implicitly, so that only half of the molecules at $r = R$ participate in the collisions. In the FPKE-D theory, on the other hand, the distribution for $v_r > 0$ is absent at $r = R$ as indicated by Eq. 9, so that all the molecules at $r = R$ participate in the collisions. This means that the reaction occurs more efficiently in the FPKE-D theory than in the SCK theory. If such an efficient condition of the FPKE-D theory is applied to the SCK theory without modification, the resultant rate constant will be very large. This is the reason why the FPKE-D theory overestimates the rate constant at low densities and long times where it reduces to the SCK theory. At high densities, such a limitation of the FPKE-D theory due to the collision effects is hidden by a large diffusion effect, i.e., $k_D \ll k_C$. At short distances, the velocity distribution of the reactants is far from the equilibrium irrespective of the density, and so the use of the Maxwellian distribution is not justified even at long times because of the highly non-equilibrium boundary condition, Eq. 9. This suggests that the success of the FPKE-C theory is related to the fact that it does not reduce to the SCK theory if the system is far from equilibrium.

As mentioned earlier, the intrinsic rate constant derived from the FPKE-D theory is $k_{\mathrm{int}} = k^\circ$. If we employ $k_{\mathrm{int}} = k^\circ/2$ in the SCK theory as proposed by Zhou and Szabo,[28] the deviation of the rate constant from the LD results will decrease to some extent. As expected, the SCK theory with $k_{\mathrm{int}} = k^\circ/2$ predicts a rate constant much closer to that from LD as shown in Fig. 7. We have obtained similar results using low-density Lennard–Jones fluids.[22] As pointed out by Bicout et al.,[13] the steady-state rate constant in the low-density limit derived from the SCK theory using Eq. 25 agrees with the exact one, k_C. This may be the reason for the moderate success of the SCK theory at low density. For a qualitative discussion of the rate constant at long times, the SCK theory provides a reasonable guideline over a wide density range.

Conclusion

In the present work, we have examined the validity of the FPKE-C theory by comparing it with MD simulations in a hard-sphere fluid and Markovian LD simulations with inertia effects. The FPKE-C theory reproduced the time profiles of the rate constants obtained from LD under all conditions studied here. This clearly indicates that the theory is valid. The rate constants obtained by using the FPKE-C theory and LD reasonably agreed with those from MD except at short times at the highest density studied. Using the Enskog friction coefficient instead of the ordinary one, we showed that the discrepancy observed at the highest density was explained by non-Markovian effects. At high densities, where the molecular motions are diffusive, the difference between the rate constants derived from the FPKE-C theory, the earlier FPKE-D theory, and the SCK theory based on the diffusion equation was not significant at long times. At low densities, where the molecular motions are inertial, on the other hand, the calculated results from the three theories were markedly different.

The present work indicates that the FPKE-C theory is useful for interpreting reaction dynamics over a wide density range. It is a good reference theory for discussing specific problems in individual systems such as the intermolecular interactions and the non-Markovian friction.

This work was supported in part by Grant-in-Aid for Scientific Research (C), No. 16550023, 2004–2005 from the Ministry of Education, Culture, Sports, Science and Technology (MEXT). K. I. thanks Prof. Ph. A. Bopp of Université Bordeaux 1 for this work was finished at his laboratory.

References

1 S. A. Rice, *Diffusion-Limited Reactions* in *Comprehensive Chemical Kinetics*, ed. by C. H. Bamford, C. F. H. Tipper, R. G. Compton, Elsevier, New York, **1985**, Vol. 25.

2 W. R. Ware, T. L. Nemzek, *Chem. Phys. Lett.* **1973**, *23*, 557; T. L. Nemzek, W. R. Ware, *J. Chem. Phys.* **1975**, *62*, 477.

3 G. C. Joshi, R. Bhatnagar, S. Doraiswamy, N. Periasamy, *J. Phys. Chem.* **1990**, *94*, 2908.

4 S. Nishikawa, T. Asahi, T. Okada, N. Mataga, T. Kakitani, *Chem. Phys. Lett.* **1991**, *185*, 237.

5 A. D. Scully, S. Hirayama, K. Fukushima, T. Tominaga, *J. Phys. Chem.* **1993**, *97*, 10524.

6 C. F. Shannon, D. D. Eads, *J. Chem. Phys.* **1995**, *103*, 5208.

7 S. Iwai, S. Murata, M. Tachiya, *J. Chem. Phys.* **1998**, *109*, 5963.

8 M. von Smoluchowski, *Z. Phys. Chem.* **1917**, *92*, 129.

9 F. C. Collins, G. E. Kimball, *J. Colloid Sci.* **1949**, *4*, 425.

10 P. Debye, *Trans. Electrochem. Soc.* **1942**, *82*, 265.

11 S. Harris, *J. Chem. Phys.* **1983**, *78*, 4698.

12 A. Morita, *J. Math. Chem.* **1994**, *16*, 49.

13 D. J. Bicout, A. M. Berezhkovskii, A. Szabo, *J. Chem. Phys.* **2001**, *114*, 2293.

14 W. Dong, F. Baros, J. C. Andre, *Ber. Bunsen-Ges. Phys.*

Chem. **1990**, *94*, 269.

15 W. Dong, J. C. Andre, *J. Chem. Phys.* **1994**, *101*, 299.

16 W. Naumann, *J. Chem. Phys.* **2003**, *118*, 9297.

17 K. Ibuki, F. Nishiguchi, M. Ueno, *Bull. Chem. Soc. Jpn.* **2003**, *76*, 261.

18 K. Ibuki, M. Ueno, *J. Chem. Phys.* **2003**, *119*, 7054.

19 H. Risken, *The Fokker-Planck Equation*, 2nd ed., Springer, Berlin, **1989**, Chap. 10.

20 H. A. Kramers, *Physica* **1940**, *7*, 284.

21 M. Nagaoka, T. Okamoto, Y. Maruyama, *J. Chem. Phys.* **2002**, *117*, 5594, and references cited therein.

22 K. Ibuki, M. Ueno, *J. Chem. Phys.* **2006**, *124*, 134506.

23 K. Ibuki, M. Ueno, *J. Chem. Phys.* **1997**, *107*, 6594.

24 J.-P. Hansen, I. R. McDonald, *Theory of Simple Liquids*, 2nd ed., Academic, London, **1986**, Chap. 8.

25 Y. Yoshimura, Y. Kimura, M. Nakahara, *Ber. Bunsen-Ges. Phys. Chem.* **1988**, *92*, 1095.

26 W. Dong, F. Baros, J. C. Andre, *J. Chem. Phys.* **1989**, *91*, 4643.

27 M. C. Wang, G. E. Uhlenbeck, *Rev. Mod. Phys.* **1945**, *17*, 323.

28 H. X. Zhou, A. Szabo, *J. Chem. Phys.* **1991**, *95*, 5948.

29 H. Van Beijeren, W. Dong, L. Bocquet, *J. Chem. Phys.* **2001**, *114*, 6265.

30 K. Ibuki, M. Ueno, *Bull. Chem. Soc. Jpn.* **1997**, *70*, 543.

31 K. Ibuki, M. Ueno, *J. Chem. Phys.* **1997**, *106*, 10113.

32 K. Ibuki, M. Ueno, *J. Mol. Liq.* **2001**, *90*, 271.

33 C. A. Emeis, P. L. Fehder, *J. Am. Chem. Soc.* **1970**, *92*, 2246.

34 S. Ganapathy, J. A. O'Brien, T. W. Randolph, *AIChE J.* **1995**, *41*, 346.

35 J. P. Boon, S. Yip, *Molecular Hydrodynamics*, McGraw-Hill, New York, **1980**, Chap. 3.

36 O. Kajimoto, *Chem. Rev.* **1999**, *99*, 355, and references cited therein.

37 J. F. Brennecke, J. E. Chateauneuf, *Chem. Rev.* **1999**, *99*, 433.

38 S. C. Tucker, *Chem. Rev.* **1999**, *99*, 391.

39 M. Okamoto, H. Nagashima, F. Tanaka, *Phys. Chem. Chem. Phys.* **2002**, *4*, 5627.

40 T. Arita, O. Kajimoto, *J. Phys. Chem. A* **2003**, *107*, 1770.

41 M. P. Allen, D. J. Tildesley, *Computer Simulation of Liquids*, Oxford University, Oxford, **1987**, Chap. 3.

42 N. G. van Kampen, *Stochastic Processes in Physics and Chemistry*, North-Holland, Amsterdam, **1981**, Chap. 8.

43 P. Turq, F. Lantelme, H. L. Friedman, *J. Chem. Phys.* **1977**, *66*, 3039.

44 S. H. Northrup, J. T. Hynes, *J. Chem. Phys.* **1979**, *71*, 871; **1979**, *71*, 884.

45 G. D. Smith, *Numerical Solution of Partial Differential Equation: Finite Differential Methods*, 3rd ed., Clarendon Press, Oxford, **1985**, Chap. 2.

46 B. J. Alder, D. M. Gass, T. E. Wainwright, *J. Chem. Phys.* **1970**, *53*, 3813.

47 A. J. Easteal, L. A. Woolf, D. L. Jolly, *Physica A* **1983**, *121*, 286.

48 B. J. Alder, T. E. Wainwright, *Phys. Rev. A* **1970**, *1*, 18.

49 W. Dong, *J. Chem. Phys.* **1997**, *107*, 9890.

50 S. A. Adelman, *J. Chem. Phys.* **1976**, *64*, 124.

51 R. Mazo, *Stochastic Process in Nonequilibrium Systems* in *Lecture Notes in Physics*, ed. by L. Garrido, P. Seglar, P. J. Shepherd, Springer, Berlin, **1978**, Vol. 84, p. 54.

52 M. Tachiya, *J. Chem. Phys.* **1986**, *84*, 6178.