© 2003 The Chemical Society of Japan

Headline Articles

Improved Velocity Distribution Applied to Fokker–Planck–Kramers Equation Treatment for Dynamics of Diffusion-Controlled Reactions in Two Dimensions

Kazuyasu Ibuki,* Fumihiro Nishiguchi, and Masakatsu Ueno

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

(Received August 23, 2002)

The validity of theoretical treatments of short-time dynamics of diffusion-controlled reaction based on the Fokker–Planck–Kramers' equation (FPKE) has been examined using molecular dynamics (MD) simulation in two-dimensional Lennard–Jones fluids. First, we made Langevin dynamics (LD) simulation assuming that the relative diffusion coefficient is given by the sum of the self-diffusion coefficients and that the potential between the reactants is given by the potential of mean force. The LD and the MD simulation results for the time dependence of the survival probabilities of the reactants agree well. This indicates that the FPKE derived from the Langevin equation can be applied to the problem of diffusion-controlled reaction. The time-dependent Harris theory based on the FPKE and the approximation of the half-range Maxwellian velocity distribution showed disagreements with the MD simulation. Such a limitation of the theory has not been recognized in three-dimensional fluids. In the approximation used in the time-dependent Harris theory, the velocity distribution function is not continuous. We have shown that the agreement between the MD simulation and the theory can be improved when we use a new approximation based on a continuous velocity distribution function.

For a better understanding of the dynamics of chemical reaction in solution, it is necessary to study the molecular migration process before the encounter of the reacting pair as well as the electronic process after the encounter. In particular, the rate of diffusion-controlled reaction is determined exclusively by the former process.[1,2] The dynamics of diffusion-controlled reaction has been analyzed by the theories based on the diffusion equation, such as the Smoluchowski–Collins–Kimball (SCK) theory.[3,4] The diffusion equation is valid only when the time of interest is sufficiently longer than the decay time of the velocity auto-correlation function. For shorter times, one may use the Fokker–Planck–Kramers equation (FPKE) for the phase space distribution function. Under the boundary conditions suitable to model chemical reactions,[5] however, the FPKE has not been solved exactly in two- and three-dimensions. Some years ago, Harris[6–9] proposed a simple and mathematically tractable approximation to apply the FPKE to the diffusion-controlled reaction. In a series of papers,[10–13] we have examined the validity of the time-dependent Harris theory[6] by comparing it with computer simulations in three-dimensional fluids after making some straightforward theoretical extensions. When the potential of mean force is used as the potential function, the time-dependent Harris theory successfully explains the short-time dynamics of model reactions in hard-sphere and Lennard–Jones fluids. For a more extensive test of the theory, here we apply the time-dependent Harris theory to two-dimensional systems and propose a new approximation to improve the theory.

Two-dimensional diffusion models have been successfully applied to interpret the reaction dynamics in lipid membranes,[14,15] monolayers,[16] and vesicles.[17] A two-dimensional system is interesting also from the theoretical point of view because the dynamics of two-dimensional diffusion-controlled reaction is considered to be qualitatively different from that in three-dimension. Under the boundary condition that the reactant concentration is always constant at infinite distance, for example, the two-dimensional SCK theory has no solution while the three-dimensional theory has the well-known one.[18–20] This is also the case for the time-dependent Harris theory, because it reduces to the SCK theory in the limit of long time. This indicates that the short-time transient effect may also be qualitatively different in two- and three-dimensions. This is the reason why we make a test of the time-dependent Harris theory in two-dimensional fluids though it is quite successful in three-dimensional fluids.[10,12,13] As we will show later, we have found disagreements between the time-dependent Harris theory and the computer simulations in two-dimensional fluids.

In the FPKE treatment of diffusion-controlled reaction, the time evolution of the velocity and position distributions of reactant molecules around a fixed target is calculated under the boundary condition proposed by Wang and Uhlenbeck.[5] In this boundary condition at the reaction radius, the velocity space is decomposed into two regions with respect to the sign of the radial component of the velocity v_r; the velocity distribution at the reaction radius is zero for $v_r > 0$, while it is positive for $v_r < 0$. In order to apply such a half-ranged boundary condition to the FPKE, Harris proposed a useful approximation.[6–9] In the Harris theory, the velocity space is decomposed into the two regions not only at the reaction radius but also in the entire position space, and the velocity distribution in each region is approximated by a slight modification of the Maxwellian distribution. For the time-dependent problem, Harris used the lowest order approximation of the general half-range method, assuming that the velocity distributions in the two regions are Gaussians with the same half-widths but different heights.[6] The velocity distribution thus defined is not continuous at $v_r = 0$. Even in the higher order half-range method which has been so far developed only for the steady state problems,[8,9] the velocity distribution function is also discontinuous. Although Harris' approximation practically works well in the three-dimensional systems, it is open to question whether the discontinuous velocity distribution can be used in two-dimensional systems, because solutions to the FPKE must in general be continuous. In the present work, we propose a new approximation to improve the theory by using a continuous velocity distribution function; the improved theory shows a better agreement with the computer simulations than the time-dependent Harris theory.

For a critical test of the theory, we need an ideal diffusion-controlled reaction with a well-defined reaction radius and a perfect reactivity for a contact reactant pair. Moreover, all the parameters necessary in the theoretical calculation should be determined independently to avoid the use of any adjustable parameters. Such an ideal system can be attained only by molecular dynamics (MD) simulations,[18,21,22] and here we use two-dimensional Lennard–Jones (LJ) fluids as reference systems. The LJ fluids are more realistic than the hard-sphere fluids used in the previous works,[10–12,21,22] and more suitable for the practical test of the theory. The LJ-disk fluid can be considered as a simple model for lipid membranes or monolayers. Strictly speaking, some difficulties may arise in the application of the diffusion model to the two-dimensional disk fluids because the diffusion coefficient is not well-defined in two-dimension due to the long-time tail in the velocity auto-correlation function.[23,24] Practically, however, the long-time tail is very weak[24] and we can determine the diffusion coefficient by the MD simulation without arbitrariness in the time region of interest. This indicates that the diffusion model can be applied to the two-dimensional disk fluids. Since the diffusion models have been used to interpret experiments in two-dimensional systems as mentioned above, a thorough comparison between the MD simulations and the diffusion theories is very important for practical purposes.

In order to demonstrate the practical validity of the diffusion model in interpreting the dynamics of the two-dimensional disk fluids, we first compare the MD simulation with the Langevin dynamics (LD) simulation based on the Langevin equation with a well defined diffusion coefficient. The applicability of the FPKE to the present problem can also be examined by the comparison between the MD and the LD simulations; the FPKE used here is derived from the Langevin equation. After making such a comparison, we can examine the validity of the theoretical approximations used in the time-dependent Harris theory by comparing the theory with the MD and the LD simulations.

In the next section, we briefly explain the time-dependent Harris theory and propose a new approximation using an improved velocity distribution. The methods of the MD and the LD simulations are explained in the third section. In the fourth section, we discuss the validity of the FPKE treatments by comparing the theoretical results with the simulations.

Theoretical

Model. In this section, we apply the time-dependent Harris theory to a two-dimensional system following the method developed for the three-dimensional problem,[6,10,12] and propose a new approximation.

The reaction considered here is a model of a fluorescence quenching reaction expressed by

$$\mathrm{A} + \mathrm{Q} \rightarrow \mathrm{B} + \mathrm{Q} \tag{1}$$

where A is the fluoropher, B the inert product, and Q the quencher. In the present paper, we consider only the case that the reaction occurs whenever the distance between an A and a Q molecule becomes shorter than the reaction radius R. The reaction rate equation is given by

$$\frac{\mathrm{d}n_\mathrm{A}}{\mathrm{d}t} = -k(t)n_\mathrm{A}n_\mathrm{Q} \tag{2}$$

where $k(t)$ is the time-dependent rate constant and n_A and n_Q are the number densities of A and Q, respectively, in the bulk.

The model system of the time-dependent Harris theory is similar to that of the Smoluchowski–Collins–Kimball (SCK) theory.[1–4] There is a fixed target molecule A at the origin. The quencher molecules Q are migrating with the friction coefficient β on a potential surface $V(r)$ where r is the distance from the A molecule. The mass of a migrating molecule is given by the reduced mass μ of A and Q. The number density of Q in the bulk is $n_\mathrm{Q} = n_\mathrm{o}$. The interactions between the Q molecules are ignored.

This model is the so-called target problem model for reaction based on the reduction of the many-body problem to a simple two-body problem; the molecular migration process is characterized only by the relative diffusion (friction) coefficient of the target and the quencher. If the number of the Q molecules are more than two, the reaction dynamics depends not only on the relative diffusion coefficient but also on the self-diffusion coefficient of the target.[25] Concerning the motion of the reactants, there is another extreme model called the trapping problem model, in which a mobile A reacts with immobile Q molecules distributed at fixed positions. The real systems are intermediates between the target and the trapping problems. For the random walk model, it was shown that the solution to the two problems are practically identical in two-and three-dimensions except at extremely long times.[25] We can expect, therefore, that the present target model is suitable to discuss the reaction dynamics in two-dimensional fluids.

The reaction is regarded as an absorption of a Q molecule by the A molecule. After the reaction begins at the time $t = 0$, the Q molecules at $r = R$ are absorbed and those at $r > R$ flow towards the A molecule in average. The reaction rate constant $k(t)$ can be expressed in terms of the radial component of the flux $j_r(r, t)$ at the reaction radius $r = R$ as

$$k(t)n_o = -2\pi R j_r(R, t) \tag{3}$$

and $j_r(\mathbf{r}, t)$ is given by

$$j_r(\mathbf{r}, t) = \int v_r f(\mathbf{v}, \mathbf{r}, t) d\mathbf{v} \tag{4}$$

where $f(\mathbf{v}, \mathbf{r}, t)$ is the phase space distribution function of Q, $\mathbf{v}$ the velocity, $\mathbf{r}$ the position, and v_r ($= \mathbf{v}\cdot\mathbf{r}/r$) the radial component of the velocity. The distribution and the flux of Q around A are spherically symmetric in position because of the symmetry of the problem.

The survival probability $S(t)$ of A is given by

$$S(t) = \exp\left[-n_o\int_0^t k(t')\mathrm{d}t'\right] \tag{5}$$

The time evolution of the phase space distribution function $f(\mathbf{v}, \mathbf{r}, t)$ is calculated by solving the following Fokker–Planck–Kramers equation[26] (FPKE):

$$\frac{\partial f(\mathbf{v}, \mathbf{r}, t)}{\partial t} + \mathbf{v}\cdot\frac{\partial f(\mathbf{v}, \mathbf{r}, t)}{\partial \mathbf{r}} - \frac{1}{\mu}\frac{\partial V(\mathbf{r})}{\partial \mathbf{r}}\cdot\frac{\partial f(\mathbf{v}, \mathbf{r}, t)}{\partial \mathbf{v}} = \beta\frac{\partial}{\partial \mathbf{v}}\cdot\mathbf{v}f(\mathbf{v}, \mathbf{r}, t) + \beta\frac{k_B T}{\mu}\frac{\partial^2 f(\mathbf{v}, \mathbf{r}, t)}{\partial \mathbf{v}^2} \tag{6}$$

where k_B is the Boltzmann constant and T is the absolute temperature. Because we are dealing with a non-equilibrium problem, we should be careful about the meaning of the temperature; the temperature in Eq. 6 is not defined in terms of the mean kinetic energy calculated from the non-equilibrium distribution function $f(\mathbf{v}, \mathbf{r}, t)$. The FPKE is derived from the Langevin equation with a white noise random force. The temperature appearing in the FPKE is that of the heat bath characterizing the properties of the random force. The average of the square random force is related to the friction coefficient β through the fluctuation-dissipation theorem.

The boundary condition at the reaction radius $r = R$ is important because it characterizes the reaction. In the present case, the absorption occurs whenever the target A and a quencher Q collide. For the phase space distribution function, this condition is expressed by the following equation as proposed by Wang and Uhlenbeck:[5]

$$f(v_r > 0, R, t) = 0 \tag{7}$$

Time-Dependent Harris Theory. In two and three dimensions, the exact solution to the FPKE under the boundary condition given by Eq. 7 has not been derived. To solve the FPKE approximately, Harris employed the method of the half-range Maxwellian distributions.[6–9] In the time-dependent theory,[6] the velocity space is decomposed into two regions: one for $v_r > 0$ and the other for $v_r < 0$. The velocity distribution in each region is approximated by the Maxwellian distribution as follows:

$$f(v_r, r, t) = 2_{n_+}(r, t)\left(\frac{\mu}{2\pi k_B T}\right)^{1/2}\exp\left(-\frac{\mu v_r^2}{2k_B T}\right) \quad \text{for } v_r > 0 \tag{8}$$

and

$$f(v_r, r, t) = 2_{n_-}(r, t)\left(\frac{\mu}{2\pi k_B T}\right)^{1/2}\exp\left(-\frac{\mu v_r^2}{2k_B T}\right) \quad \text{for } v_r < 0 \tag{9}$$

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. The distribution of the tangential velocity is assumed to be the ordinary Maxwellian distribution. In Eqs. 8 and 9, the radial velocity distributions for $v_r > 0$ and for $v_r < 0$ have the same half-widths but different heights; $f(v_r, r, t)$ is not continuous at $v_r = 0$. We will later propose an improved velocity distribution function without the discontinuity because solutions to the FPKE must in general be continuous.

The total number density $n(r, t)$ is given by

$$n(r, t) = n_+(r, t) + n_-(r, t) \equiv N(r, t) \tag{10}$$

The radial component of the flux is given by

$$j_r(r, t) = \sqrt{\frac{2k_B T}{\pi\mu}}[n_+(r, t) - n_-(r, t)] \equiv \sqrt{\frac{2k_B T}{\pi\mu}}M(r, t) \tag{11}$$

Substituting Eqs. 8 and 9 into Eq. 6, and calculating the zeroth and the first moments of v_r, we obtain a set of differential equations as follows:

$$\frac{\partial N(r, t)}{\partial t} = -\sqrt{\frac{2k_B T}{\pi\mu}}\frac{1}{r}\frac{\partial}{\partial r}[rM(r, t)] \tag{12}$$

$$\sqrt{\frac{2k_B T}{\pi\mu}}\frac{\partial M(r, t)}{\partial t} = -\frac{k_B T}{\mu}\frac{\partial N(r, t)}{\partial r} - \frac{1}{\mu}\frac{\mathrm{d}V(r)}{\mathrm{d}r}N(r, t) - \beta\sqrt{\frac{2k_B T}{\pi\mu}}M(r, t) \tag{13}$$

Using the notations defined by Eqs. 10 and 11, the boundary condition of Eq. 7 is expressed as

$$N(R, t) = -M(R, t) \tag{14}$$

We assume that the potential is given by the potential of mean force at equilibrium,[12]

$$V(r) = -k_B T \ln g_{AQ}(r) \tag{15}$$

where $g_{AQ}(r)$ is the equilibrium radial distribution function of the A–Q pair. For diffusion-controlled reactions between neutral molecules, the reaction dynamics has often been analyzed using the uniform or direct two-body potentials. The present potential function given by Eq. 15 is much more reasonable than the uniform or direct two-body potentials because the many-body effect is taken into account.[12,18,22,27]

The system is at equilibrium before the reaction begins at $t = 0$, so that the initial condition is given by

$$N(r, 0) = g_{\mathrm{AQ}}(r)n_{\mathrm{o}} \tag{16}$$

$$M(r, 0) = 0 \tag{17}$$

Combining Eqs. 3, 10, 11, and 14, we can calculate the time-dependent rate constant $k(t)$ by the following equation:

$$k(t)n_{\mathrm{o}} = -2\pi R j_{\mathrm{r}}(R, t) = k^{\circ}n(R, t) \tag{18}$$

where k° is defined as

$$k^{\circ} = 2\pi R\sqrt{\frac{2k_{\mathrm{B}}T}{\pi\mu}} \tag{19}$$

At $t = 0$, the rate constant is calculated by the FPKE without approximations as

$$k(0) = \frac{1}{2}g_{\mathrm{AQ}}(R)k^{\circ} = k^{\mathrm{coll}} \tag{20}$$

where k^{coll} is the rate constant at $t = 0$ estimated by the kinetic collision theory. The short-time limiting rate constant $k(0)$ of the time-dependent Harris theory is slightly larger than those given by Eq. 20. In three-dimensional systems for $V(r) = 0$, the analytical solution of the time-dependent Harris theory has been derived,[6] and the $k(0)$ value obtained by the approximation is about 1.1 times as large as that obtained without the approximation.[10]

New Approximation Using Improved Velocity Distribution. Next we propose a new approximation to improve the time-dependent Harris theory. One possible approach is the application of the higher order half-range approximation which has been developed for the steady state problem by Harris.[8] To the authors' knowledge, no one has applied the higher order approximation to the time-dependent problem because of mathematical difficulties. It is to be noted, however, that the distribution function used in the higher order approximation is not continuous at the boundary of the decomposition, although a more elaborate method has been used for the decomposition of the velocity space than in the lowest order approximation. Because solutions to the FPKE must in general be continuous, we do not employ the higher order approximation to improve the time-dependent Harris theory.

Here we take another approach using a continuous distribution function. In order to produce a continuous velocity distribution, we assume that the radial velocity distribution functions for $v_{\mathrm{r}} > 0$ and for $v_{\mathrm{r}} < 0$ are Gaussians with the same heights but different half-widths, i.e., we use the following equations instead of Eqs. 8 and 9:

$$f(v_{\mathrm{r}}, r, t) = n_{\mathrm{r}}(r, t)\left(\frac{\mu}{2\pi k_{\mathrm{B}}T}\right)^{1/2}\exp\left(-\frac{\mu v_{\mathrm{r}}^2}{2k_{\mathrm{B}}T\sigma(r, t)^2}\right) \quad \text{for } v_{\mathrm{r}} > 0 \tag{21}$$

and

$$f(v_{\mathrm{r}}, r, t) = n_{\mathrm{r}}(r, t)\left(\frac{\mu}{2\pi k_{\mathrm{B}}T}\right)^{1/2}\exp\left(-\frac{\mu v_{\mathrm{r}}^2}{2k_{\mathrm{B}}T}\right) \quad \text{for } v_{\mathrm{r}} < 0 \tag{22}$$

Here we use the function $\sigma(r, t)$ to characterizes the asymmetry of the velocity distribution at each position instead of $n_{+}(r, t)$ and $n_{-}(r, t)$ in Eqs. 8 and 9. The half-width of the velocity distribution for $v_{\mathrm{r}} > 0$ is proportional to $\sigma(r, t)$, while that for $v_{\mathrm{r}} < 0$ is assumed to be the same as that at equilibrium because the boundary condition is concerned only for the distribution for $v_{\mathrm{r}} > 0$. The function $n_{\mathrm{r}}(r, t)$ used in both of Eqs. 21 and 22 is proportional to the height of the distribution function. At $v_{\mathrm{r}} = 0$, both Eqs. 21 and 22 give the same values, $n_{\mathrm{r}}(r, t)\sqrt{\mu/2\pi k_{\mathrm{B}}T}$, so that the distribution function is continuous. For the simple method of the decomposition of the velocity space used in the Harris theory, therefore, Eqs. 21 and 22 provide a more reasonable distribution function than Eqs. 8 and 9. In the improved approximation, the number density for $v_{\mathrm{r}} > 0$ at r is given by $\sigma(r, t)n_{\mathrm{r}}(r, t)/2$ and that for $v_{\mathrm{r}} < 0$ is given by $n_{\mathrm{r}}(r, t)/2$.

The total number density $n(r, t)$ is given by

$$n(r, t) = \frac{1}{2}[\sigma(r, t) + 1]n_{\mathrm{r}}(r, t) \tag{23}$$

and the radial component of the flux is given by

$$j_{\mathrm{r}}(r, t) = \frac{1}{2}\sqrt{\frac{2k_{\mathrm{B}}T}{\pi\mu}}[\sigma(r, t)^2 - 1]n_{\mathrm{r}}(r, t) \tag{24}$$

The boundary condition at the reaction radius $r = R$, Eq. 7, is expressed as

$$\sigma(R, t) = 0 \tag{25}$$

and the initial condition is

$$n_{\mathrm{r}}(r, 0) = g(r)n_{\mathrm{o}} \tag{26}$$

$$\sigma(r, 0) = 1 \tag{27}$$

It is to be noted that the present boundary condition, Eq. 25, can be easily extended to the case that the reaction probability α for a collision is less than unity. If the number density for $v_{\mathrm{r}} < 0$ at $r = R$ is $n_{\mathrm{r}}(R, t)/2$, the fraction $\alpha n_{\mathrm{r}}(R, t)/2$ is absorbed and the remaining fraction $(1 - \alpha)n_{\mathrm{r}}(R, t)/2$ rebounds, so that the number density for $v_{\mathrm{r}} > 0$ at $r = R$ is given by $(1 - \alpha)n_{\mathrm{r}}(R, t)/2$. On the other hand, the number density for $v_{\mathrm{r}} > 0$ is given by $\sigma(R, t)n_{\mathrm{r}}(R, t)/2$ in the present model. We obtain, therefore, the following boundary condition:

$$\sigma(R, t) = 1 - \alpha \tag{28}$$

In the present work, we calculate the reaction rate only for $\alpha = 1$, because the reaction dynamics is determined exclusively by the molecular migration process in this case.

Substituting Eqs. 21 and 22 into Eq. 6, and calculating the zeroth and the first moments of v_{r}, we obtain the following set of differential equations:

$$\frac{\partial}{\partial t}\{[\sigma(r, t) + 1]n_{\mathrm{r}}(r, t)\} = -\sqrt{\frac{2k_{\mathrm{B}}T}{\pi\mu}}\frac{1}{r}\frac{\partial}{\partial r}\{r[\sigma(r, t)^2 - 1]n_{\mathrm{r}}(r, t)\} \tag{29}$$

$$\begin{aligned}\sqrt{\frac{2k_\mathrm{B}T}{\pi\mu}}\frac{\partial}{\partial t}\{[\sigma(r,t)^2-1]n_\mathrm{r}(r,t)\} &= -\frac{k_\mathrm{B}T}{\mu}\frac{1}{r}\frac{\partial}{\partial r}\{r[\sigma(r,t)^3+1]n_\mathrm{r}(r,t)\}\\ &+\frac{k_\mathrm{B}T}{\mu}\frac{1}{r}[\sigma(r,t)+1]n_\mathrm{r}(r,t)\\ &-\frac{1}{\mu}\frac{\mathrm{d}V(r)}{\mathrm{d}r}[\sigma(r,t)+1]n_\mathrm{r}(r,t)\\ &-\beta\sqrt{\frac{2k_\mathrm{B}T}{\pi\mu}}[\sigma(r,t)^2-1]n_\mathrm{r}(r,t)\end{aligned} \tag{30}$$

Although Eqs. 29 and 30 are somewhat more complicated than Eqs. 12 and 13, we can solve them by the same simple numerical method as used for the time-dependent Harris theory. The rate constant is calculated by Eq. 18.

Numerical Calculation. Both for the Harris theory and for our improved treatment, we solve the sets of the equations numerically by the Lax–Wendroff explicit method;[28] we cannot solve them analytically for a general potential. The outer boundary distance r_out is chosen so that the functions appearing in the equations remain constant against time during the calculation. The distance Δr and time Δt steps used in the calculations are

$$\Delta r = \frac{1.0\times10^{-2}}{\beta}\sqrt{\frac{2k_\mathrm{B}T}{\pi\mu}},\ \Delta t = \frac{1.0\times10^{-3}}{\beta} \tag{31}$$

The typical values in the usual units are $\Delta r = 8.1\times10^{-13}$ m and $\Delta t = 4.6\times10^{-13}$ s for the Ar–Ar system explained in the next section. Because the inner boundary condition is singular at $t = 0$, the numerical solution vibrates for initial several hundred time steps. In order to obtain the short time solutions with sufficient precision, we also calculate the numerical solutions at $1 \geq t\beta$ using the following distance and time steps:

$$\Delta r = \frac{1.0\times10^{-4}}{\beta}\sqrt{\frac{2k_\mathrm{B}T}{\pi\mu}},\ \Delta t = \frac{1.0\times10^{-5}}{\beta} \tag{32}$$

At $t = 1/\beta$, the differences between the rate constants obtained by using Eqs. 31 and 32 are less than 0.07% for all the cases studied. We estimate the rate constant in the short time limit by extrapolating the stable solution after the 1000-th step using Eq. 32.

For the numerical calculations, we use the radial distribution functions and the friction coefficients obtained by the MD simulation described in the next section. Our theoretical calculation, therefore, employs no adjustable parameters. The friction coefficient is estimated by the following equation:

$$\beta = \frac{k_\mathrm{B}T}{\mu D_\mathrm{r}} \tag{33}$$

where D_r is the relative diffusion coefficient for the A–Q pair. In the present work we simply assume that the relative diffusion coefficient is given by the sum of the self-diffusion coefficients. The diffusion coefficients thus obtained are independent of position and time.

Simulations

Molecular Dynamics. The reaction model used here is a simple extension of the early studies by Fehder et al.[18] and Dong, Baros, and Andre.[21] The interactions between the molecules are assumed to be pairwise additive Lennard–Jones (LJ) potential interactions,

$$V_\mathrm{LJ}(r) = 4\varepsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right] \tag{34}$$

where r is the intermolecular distance, ε the depth of the potential minimum, and σ the diameter parameter. We assume that the physical properties of A and B molecules are identical and can be characterized by the LJ parameters for argon. The physical properties of Q are either the same as or different from those of A and B. Here we made simulations for the following three cases: Q = Ne, Ar, and Xe. The interaction parameters between like molecules are taken from Bernardes,[29] and those between unlike molecules are assumed to obey the Lorentz–Belthelot relations.[30]

We briefly explain the method of the MD simulation. In a square cell with the cell constant L, we put N°_A (= 462) of A molecules and N°_Q (= 50) of Q molecules. At an arbitrary moment after the system is equilibrated under the periodic boundary condition, we set the time $t = 0$. If some of the A molecules are located within the reaction distance R from any of the Q molecules at this moment, we label them as B, and count the number N'_A of the remaining A molecules. Then we continue the simulation and record the reaction time t_j for each A molecule; t_j is the time when the j-th A molecule reacts. An A molecule reacts and becomes B when any one of the Q molecules approaches the A molecule within the reaction distance. The Q molecule remains unchanged after the collision. The reaction radius R is set equal to σ for A–Q pair (σ_AQ). The survival probability $S(t)$ of an A particle is calculated by

$$S(t) = \frac{1}{N'_\mathrm{A}}\sum_{j=1}^{N'_\mathrm{A}}\theta(t_\mathrm{j} - t) \tag{35}$$

where $\theta(x)$ is the Heaviside step function, which is zero for $x \leq 0$ and unity for $x > 0$. We average $S(t)$ for 100 runs at each condition. For a certain A molecule, other A and B molecules can be assumed as solvents, so that the survival probability thus obtained is independent of the concentration of A molecules. In order to examine the effect of the concentration of Q molecules, we also made simulations for $N^\circ_\mathrm{Q} = 10$ ($N^\circ_\mathrm{A} = 502$), $N^\circ_\mathrm{Q} = 100$ ($N^\circ_\mathrm{A} = 412$) and $N^\circ_\mathrm{Q} = 250$ ($N^\circ_\mathrm{A} = 262$) in the Ar–Ar system; we indicate the system by the type of the A–Q pair.

The leap-frog algorithm[30] with the time step of 0.5 fs is employed in an *NVE*-ensemble. The reduced number density is chosen to be $\rho^* = 0.6319$ where ρ^* is defined using σ for A–A pair (σ_AA) as

$$\rho^* = \rho\sigma_\mathrm{AA}^2 = \frac{N^\circ_\mathrm{A} + N^\circ_\mathrm{Q}}{L^2}\sigma_\mathrm{AA}^2 \tag{36}$$

The reduced temperature is $T^* = 1.0$ where T^* is defined as

$$T^* = \frac{k_B T}{\varepsilon_{AA}} \tag{37}$$

The radial distribution functions and the self-diffusion coefficients used in the theoretical calculations and the LD simulations are determined by independent runs of the non-reactive MD simulation. The self-diffusion coefficients are estimated from the slopes of the mean square displacements (MSD) at times up to 25 ps. We obtained good straight lines of MSD for all the species studied, so that we can practically determine the self-diffusion coefficients without arbitrariness.

Langevin Dynamics. The model system used in the Langevin dynamics corresponds to that in the time-dependent Harris theory. In a potential field $V(r)$, there is a fixed A molecule at the origin of the coordinate and a migrating Q molecule. The mass and the friction coefficient of the Q molecule are set equal to the reduced mass and the relative friction coefficient of the A–Q pair obtained by the MD simulations and Eq. 33. The β values used in the LD simulations are 2.78×10^{12}, 2.19×10^{12}, and 1.85×10^{12} s^{-1} for the Ar–Ne, Ar–Ar, and Ar–Xe systems, respectively; we indicate the system by the type of the A–Q pair. The potential $V(r)$ is given by the potential of mean force (PMF) calculated from the equilibrium radial distribution function for the A–Q pair $g_{AQ}(r)$ obtained by the MD simulations.

At $t = 0$, we put the Q molecule at the point where the distance from the fixed A molecule is r_{ini}. The initial velocity is randomly chosen to obey the Maxwellian distribution. Then the trajectory of the Q molecule is calculated by the numerical integration of the Langevin equation with the potential and the inertia terms using the algorism by Turq et al.[31] Use of an inertialess algorism is not suitable for the present purpose, because the FPKE is derived from the Langevin equation with the inertia term; we have already discussed the importance of the inertia effect on the Brownian dynamics of diffusion-controlled reactions in detail in a previous paper.[11] The time step is chosen to be 0.5 fs which is the same as that of the MD simulations. When the Q molecule approaches the A molecule within the distance of R for the first time, we assume that the Q is absorbed by the A and record the reaction time. We produce 50000 trajectories for each r_{ini} and determined the reaction probability $P(r_{\text{ini}}, t)\mathrm{d}t$, which is the probability that a molecule started at $r = r_{\text{ini}}$ at $t = 0$ reacts at the time between $t = t$ and $t = t + \mathrm{d}t$. The rate constant is obtained by the following equation:

$$k(t) = \int_R^{r_{\max}} 2\pi r_{\text{ini}} P(r_{\text{ini}}, t) g(r_{\text{ini}}) \mathrm{d}r_{\text{ini}} \tag{38}$$

We use $r_{\max} = R + 10\sigma_{AA}$ to calculate $k(t)$ at $0 < t < 10$ ps. The interval of r_{ini} is chosen to be $0.02\sigma_{AA}$.

Results and Discussion

MD and LD Simulations. First, we compare the results of the MD and the LD simulations. Figure 1 shows the time dependence of the survival probabilities in the Ar–Ne, Ar–Ar, and Ar–Xe systems. For all the systems studied here, the agreements between the MD and the LD results are excellent. This clearly indicates that in a practical sense, the two-dimensional diffusion model can be applied to interpret the dynamics

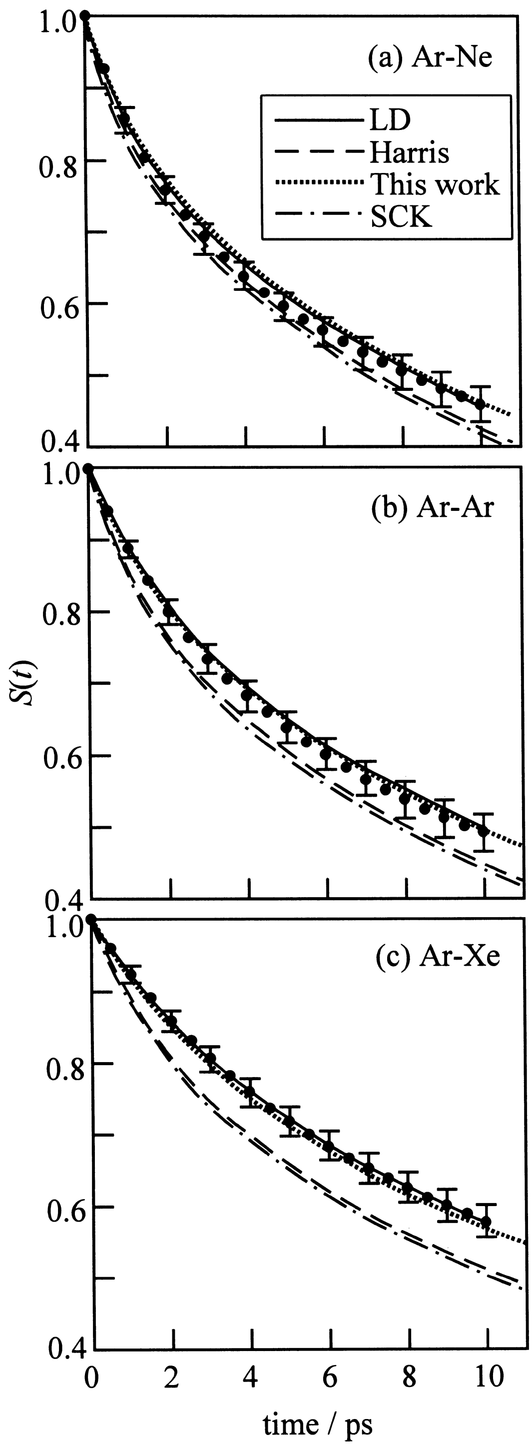

Fig. 1. Time dependences of the survival probabilities for a target of the model diffusion-controlled reaction in two-dimensional Lennard–Jones fluids at $\rho^* = 0.6319$ and $T^* = 1.0$. (a) A = Ar and Q = Ne, (b) A = Ar and Q = Ar, and (c) A = Ar and Q = Xe. Closed circles indicate the average values of the MD simulation results and the heights of the error bars are two times as large as the standard deviations for 100 runs. Solid lines indicate the results of the LD simulation, broken lines the time-dependent Harris theory, dotted lines the present work, and broken-dotted lines the SCK theory.

of the LJ-disk fluids, and that the dynamics of the diffusion-controlled reaction in two dimensions can be explained by the FPKE at least in the present condition; the FPKE used in the present work is derived from the Langevin equation.

In the study of the diffusion-controlled reaction, the relative diffusion coefficient is often assumed to depend on the distance between the reactants[18,27] to incorporate the correlation between the motions of neighboring molecules arising from the many-body effect. Fehder et al.[18] reported that neighboring molecules show a tendency to move together for some duration in the two-dimensional Lennard–Jones fluids; the present simulation condition is the same as one of the conditions in which Fehder et al. observed the strong correlations. In the present LD simulation, on the other hand, we assumed that the relative diffusion coefficient is position-independent and is simply given by the sum of the self-diffusion coefficients. The agreements between the MD and the LD results indicate that the distance dependence of the diffusion coefficient is not necessary in explaining the dynamics of the present model reaction. The present results suggest that such a strong correlation can be explained by the effect of the potential of mean force.

It has been shown theoretically that the diffusion coefficient depends on time if the non-Markovian effect on molecular motions is important.[10,32–35] The observed agreements between the LD and the MD results indicate, however, that the non-Markovian effect is not important in the present model reaction.

The time dependent rate constants obtained by the LD simulation are shown in Fig. 2. At $t = 0$, the LD rate constants are identical to those estimated by Eq. 20. At $t > 0$, the rate constant decreases monotonously with time. We do not calculate the rate constant from the MD results because the uncertainties in the survival probabilities are too large to estimate the rate constant by their numerical differentiation. The excellent agreements in the survival probabilities suggest that the MD rate constant can be assumed to agree with the LD rate constants.

Effect of Quencher Concentration. We examined the effect of the quencher concentration by the MD simulations in the Ar–Ar system. The effect of the interaction between the Q molecules can be discussed more directly using the Ar–Ar system than the other two systems, because the diffusion coefficient and the radial distribution function do not depend on the Q concentration in the former system. The MD results of the survival probabilities in Ar–Ar system for $N_Q = 10$, 50, 100, and 250 are shown in Fig. 3 together with the LD results neglecting the interaction between Q molecules; the LD results are calculated by Eq. 5 with the same rate constant as shown in Fig. 2 and with different n_0. At $N_Q = 10$ and 50, the MD results are well reproduced by the LD simulations. This means that the reaction rate constant does not depend on the quencher concentration for $N_Q \leq 50$. It is interesting to note that the reaction dynamics of the present MD simulation can be explained without taking account of the interaction between the quenchers even at a relatively high quencher concentration, the mole fraction about 0.1 ($N_Q = 50$). This indicates that the effect of the interactions between the Q molecules is implicitly taken into account in part by the use of the potential of mean force. At larger quencher concentrations, the LD simulation tends to underestimate the reaction rate.

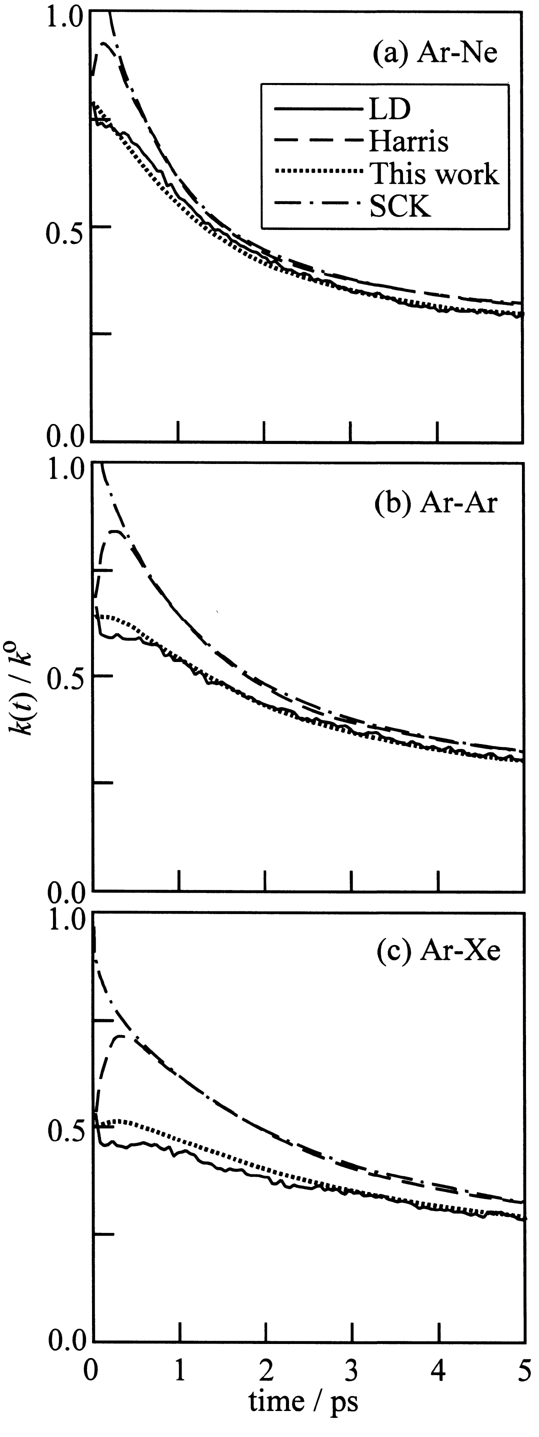

Fig. 2. Time dependences of the rate constants of the model diffusion-controlled reaction in two-dimensional Lennard–Jones fluids at $\rho^* = 0.6319$ and $T^* = 1.0$. (a) A = Ar and Q = Ne, (b) A = Ar and Q = Ar, and (c) A = Ar and Q = Xe. Solid lines indicate the results of the LD simulation, broken lines the time-dependent Harris theory, dotted lines the present work, and broken-dotted lines the SCK theory.

Although the deviation of the LD result from the MD one at $N_Q = 100$ is not so significant considering the simulation uncertainties, the deviation at $N_Q = 250$ is obvious. The underes-

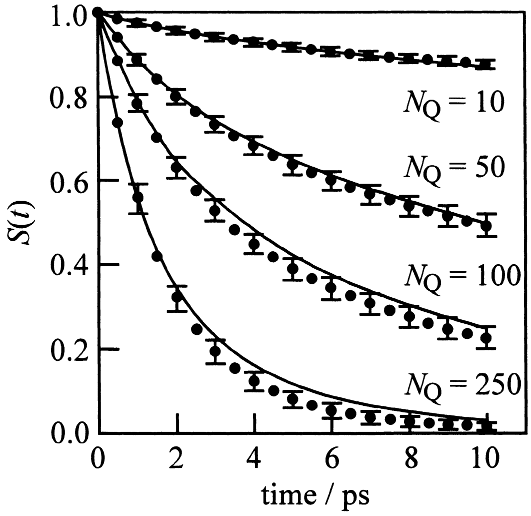

Fig. 3. Time dependences of the survival probabilities for a target of the model diffusion-controlled reaction in two-dimensional Lennard–Jones fluids at $\rho^* = 0.6319$ and $T^* = 1.0$. A = Ar and Q = Ar. N_Q = 10, 50, 100, 250. Closed circles indicate the average values of the MD simulation results and the heights of the error bars are two times as large as the standard deviations for 100 runs. Solid lines indicate the LD results.

timation of the LD simulation at large quencher concentrations may be due to the neglect of the hydrodynamic interaction. Here we restrict our discussion on the reaction dynamics at low quencher concentration where the interaction between the quencher molecules are negligible.

Time-Dependent Harris Theory and Simulations. Next we examine the validity of the time-dependent Harris theory based on the lowest order approximation of the half-range method by comparing the theoretical results with the results of the LD and the MD simulations. The survival probabilities obtained by the time-dependent Harris theory are exhibited in Fig. 1 by the broken lines. For the Ar–Ne system, the differences between the time-dependent Harris theory and the simulations are not so significant. For the Ar–Xe system, on the other hand, the disagreements are obvious. Even for the Ar–Ar system, for which we had shown a good agreement between the time-dependent Harris theory and the MD results in a three-dimensional LJ fluid,[13] the limitation of the theory in two-dimensional systems can be recognized.

The limitation of the time-dependent Harris theory is more clearly observed in the rate constants shown in Fig. 2; the rate constants are plotted only at $t < 5$ ps to clarify the differences between the results. As mentioned above, the rate constants obtained by the LD simulation decay monotonously with time for all the three systems studied. However, the rate constants calculated from the time-dependent Harris theory show a maximum against time. For a larger quencher system, the maximum in the rate constant becomes larger and the difference in the survival probabilities between the simulations and the theory becomes larger. Since the FPKE given by Eq. 6 corresponds to the Langevin equation used in the LD simulation, the disagreement between the theory and the LD simulation is due to the approximation used in the theory.

Velocity Distribution in MD Simulations. As pointed out previously, the velocity distribution function used in the time-dependent Harris theory is not continuous at $v_r = 0$. Because solutions to the FPKE must in general be continuous, the discontinuity is considered to be one of the origins of the disagreements between the simulations and the Harris theory. In order to see the realistic behavior of the radial velocity distributions, we calculated the distribution of the relative velocity between A and Q by the MD simulation. Figure 4 shows the distribution of radial component of the relative velocity at the A–Q distance of $\sigma_{AQ}^2 < r^2 < 1.1\sigma_{AQ}^2$ and at the time $t < 1$ ps; we calculated the radial velocity distributions only for the neighboring A-Q pairs because the non-equilibrium effect is expected to be significant for those pairs. As expected, the distributions obtained by the MD have no discontinuity. It is noted, moreover, that the half-width of the distribution for $v_r < 0$ is almost identical to that of the Maxwellian distribution, while that for $v_r > 0$ is much smaller. These results supports the validity of our improved approximation for the velocity distribution given by Eqs. 21 and 22.

Improved Theory and Simulations. The survival probabilities and the rate constants obtained by the present improved theory are depicted in Figs. 1 and 2 by the dotted lines. The present theory shows a better agreement with the simulations than the time-dependent Harris theory. The survival probabilities obtained by the present theory agree quantitatively with the MD and the LD results for all the cases studied. For the Ar–Ar and Ar–Xe systems, the present rate constants exhibit much smaller maxima against time than the time-dependent Harris theory. The present rate constant for the Ar–Ne system decreases monotonously with time, and agrees excellently with the LD result. We can conclude that the improved approximation reasonably reproduces the time dependence of the rate constants obtained by the LD simulations for all the cases studied.

In order to examine the validity of the improved approximation in the short-time limit, we tabulate the short-time limiting rate constants $k(0)$ in Table 1. As pointed out in the theoretical section, the $k(0)$ values estimated by the time-dependent Harris theory are larger than the exact values estimated by Eq. 20. The improved approximation results in the $k(0)$ values closer to the exact ones than the original approximation.

Smoluchowski–Collins–Kimball Theory. Before closing the present article, we should discuss the relation between the Smoluchowski–Collins–Kimball (SCK) theory,[3,4] the time-dependent Harris theory and the present improved theory. The SCK theory is based on the diffusion equation given by

$$\frac{\partial n(r,t)}{\partial t} = D_r \frac{1}{r}\frac{\partial}{\partial r}\left[r\frac{\partial n(r,t)}{\partial r} + r\frac{n(r,t)}{k_B T}\frac{dV(r)}{dr}\right] \quad (39)$$

The radiation boundary condition at the reaction radius is given by

$$k^{\mathrm{int}} n(R,t) = -2\pi R j_r(R,t) \quad (40)$$

where k^{int} is the intrinsic rate constant. Instead of Eq. 4, $j_r(R,t)$ is given by Fick's law.

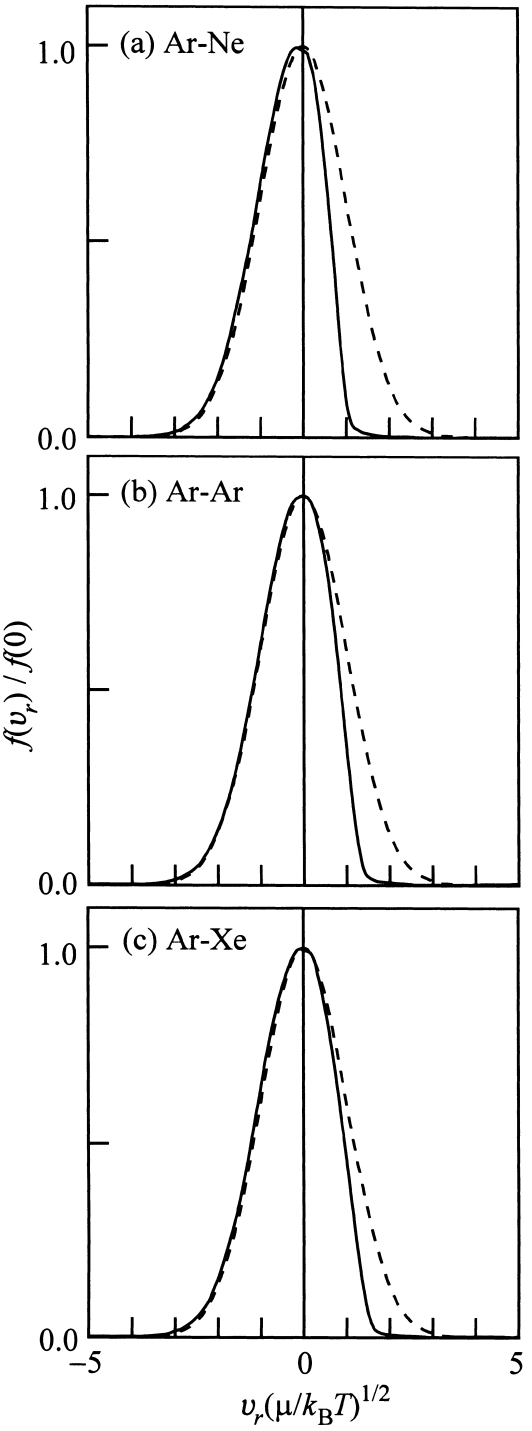

Fig. 4. The normalized distributions of the radial component of the relative velocity between A and Q molecules at the distance $\sigma_{AQ}^2 < r^2 < 1.1\sigma_{AQ}^2$ and at the time $t < 1$ ps in two-dimensional Lennard–Jones fluid at $\rho^* = 0.6319$ and $T^* = 1.0$. (a) A = Ar and Q = Ne, (b) A = Ar and Q = Ar, and (c) A = Ar and Q = Xe. Solid lines indicate the MD simulation results and broken lines the Maxwellian distributions. The distribution functions are normalized by the height at $v_r = 0$.

$$j_r(r,t) = -D_r\left[\frac{\partial n(r,t)}{\partial r} + \frac{n(r,t)}{k_B T}\frac{dV(r)}{dr}\right] \tag{41}$$

Table 1. The Short-Time Limiting Rate Constants

	$k(0)/k°$		
A–Q	Ar–Ne	Ar–Ar	Ar–Xe
Eq. 20	0.764	0.617	0.486
Harris	0.850	0.687	0.541
This work	0.789	0.637	0.501

To compare the SCK theory with other results, we need to determine the value of the intrinsic rate constant that corresponds to the reaction probability of unity, $\alpha = 1$. So far one of the following two values has been used in two-dimensional studies: the first[19,20,36] is that k^{int} is infinite and the other[18] is that k^{int} is given by $k°/2$. For the former, the boundary condition is expressed by the well-known perfect absorbing condition, i.e., $n(R, t) = 0$. For the latter, the SCK theory provides the exact value of the short-time limiting rate constant given by Eq. 20. Both of the $k°$ values are, however, inconsistent with the FPKE treatment.

Because the diffusion equation is not valid at short times, the relation between the FPKE treatment and the SCK theory should be discussed on the basis of their long-time behaviors. In the time-dependent Harris theory, Eq. 13 reduces to Fick's law in the steady state,[6] and can be assumed to be an extension of Fick's law. In the steady state, therefore, the time-dependent Harris theory is identical to the SCK theory with the intrinsic rate constant given by

$$k^{int} = k° \tag{42}$$

This equation represents the intrinsic rate constant of the SCK theory suitable for the present purpose. The intrinsic rate constant k^{int} thus derived is two times as large as the initial rate constant derived by the kinetic collision theory for $V(r) = 0$; similar results have been derived in three dimensions.[10]

In Figs. 1 and 2, we show the survival probabilities and the rate constants calculated by the SCK theory with the intrinsic rate constant given by Eq. 42. The SCK results were obtained by numerical solutions of Eq. 39 using the Crank–Nicolson method.[28] Since the Harris and the SCK theories become identical in the steady state, we can expect in two-dimensional systems that the results of the SCK theory will approach those of the time-dependent Harris theory at sufficiently long times. As expected, the rate constants obtained by the two theories are almost identical at $t > 1$ ps for all the cases studied.

In our improved theory, Eq. 30 gives the extended Fick's law. If the system is near equilibrium, $\sigma(r, t)$ is close to unity and $(\sigma(r, t)^3 + 1)$ can be approximated by $(\sigma(r, t) + 1)$. For this case, Eq. 30 becomes identical to Eq. 13 and the improved approximation reduces to the original one. This indicates that the approximation given by Eqs. 8 and 9 is valid only near equilibrium and the application limit of the theory is extended towards more non-equilibrium states by using the continuous distribution function given by Eqs. 21 and 22. In the case of diffusion-controlled reaction, the distribution of the relative velocity for neighboring pairs is far from equilibrium as shown in Fig. 4, so that such an extension of the application limit is necessary.

Conclusions

We have tested the validity of the Fokker–Planck–Kramers equation treatments of the dynamics of diffusion-controlled reaction in two-dimensional Lennard–Jones fluids. We first compare the results of Langevin and molecular dynamics simulations. In the LD simulation, we have used the potential of mean force and the diffusion coefficients determined by the MD simulation. The agreements in the survival probabilities between the LD and the MD simulations were excellent. This clearly indicates that the FPKE can be applied to the problem of the dynamics of diffusion-controlled reaction in two-dimensional fluids. Next, we have tested the validity of the time-dependent Harris theory which is based on the FPKE and the lowest order approximation of the half-range Maxwellian velocity distributions. Although the time-dependent Harris theory successfully explains the MD results in three-dimensional fluids, we have found disagreements between the theoretical and simulation results in two-dimensional fluids. We have proposed a new approximation using a continuous velocity distribution function because solutions to the FPKE must be continuous. The improved theory shows a good agreement with the simulation results. The present results tell us that the application limits of the time-dependent Harris theory are different in two dimensions and in three dimensions. In the present paper, we have proposed and tested an approximation suitable for two-dimensional systems. As a next step of our investigation, we will apply the present theoretical approach to three-dimensional systems to discuss the physical meaning of the difference in the application limits. We believe that the present work provides important insight for a deep understanding of the dynamics of chemical reactions on solid surfaces or membranes.

This work was supported by the grant to the research project at Doshisha University entitled “Intelligent Information Science and Its Applications to Problem Solving in Engineering Fields” from the Ministry of Education, Culture, Sports, Science and Technology (MEXT). One of the authors (K. I.) thanks Professor M. Nakahara of Kyoto University for helpful discussions.

References

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

2 J. Keizer, *Chem. Rev.*, **87**, 167 (1987).

3 M. von Smoluchowski, *Z. Phys. Chem.*, **92**, 129 (1917).

4 F. C. Collins and G. E. Kimball, *J. Colloid Sci.*, **4**, 425 (1949).

5 M. C. Wang and G. E. Uhlenbeck, *Rev. Mod. Phys.*, **17**, 323 (1945).

6 S. Harris, *J. Chem. Phys.*, **78**, 4698 (1983).

7 S. Harris, *J. Chem. Phys.*, **75**, 3103 (1981).

8 S. Harris, *J. Chem. Phys.*, **76**, 587 (1981).

9 S. Harris, *J. Chem. Phys.*, **77**, 934 (1982).

10 K. Ibuki and M. Ueno, *Bull. Chem. Soc. Jpn.*, **70**, 543 (1997).

11 K. Ibuki and M. Ueno, *J. Chem. Phys.*, **106**, 10113 (1997).

12 K. Ibuki and M. Ueno, *J. Chem. Phys.*, **107**, 6594 (1997).

13 K. Ibuki and M. Ueno, *J. Mol. Liq.*, **90**, 271 (2001).

14 H.-J. Galla and E. Sackmann, *Ber. Bunsenges. Phys. Chem.*, **78**, 949 (1974).

15 K. Kano, H. Kawaizumi, T. Ogawa, and J. Sunamoto, *J. Phys. Chem.*, **85**, 2204 (1981).

16 F. Caruso, F. Grieser, A. Murphy, P. Thistlethwaite, R. Urquhart, M. Almgren, and E. Wistus, *J. Am. Chem. Soc.*, **113**, 4838 (1991).

17 J. M. Vanderkooi, S. Fischkoff, M. Andrich, F. Podo, and C. S. Owen, *J. Chem. Phys.*, **63**, 3661 (1975).

18 C. A. Emeis and P. L. Fehder, *J. Am. Chem. Soc.*, **92**, 2246 (1970).

19 C. S. Owen, *J. Chem. Phys.*, **63**, 3204 (1975).

20 D. L. Freeman and J. D. Doll, *J. Chem. Phys.*, **78**, 6002 (1983).

21 W. Dong, F. Baros, and J. C. Andre, *J. Chem. Phys.*, **91**, 4643 (1989).

22 H. X. Zhou and A. Szabo, *J. Chem. Phys.*, **95**, 5948 (1991).

23 B. J. Alder and T. E. Wainwright, *Phys. Rev. A*, **1**, 18 (1970).

24 J.-P. Hansen and I. R. McDonald, “Theory of Simple Liquids,” 2nd ed, Academic, London (1986), Chap. 8.

25 A. Szabo, *J. Phys. Chem.*, **93**, 6929 (1989), and references cited therein.

26 H. Risken, “The Fokker–Planck Equation,” 2nd ed, Springer, Berlin (1989).

27 S. H. Northrup and J. T. Hynes, *J. Chem. Phys.*, **71**, 871, 884 (1979).

28 G. D. Smith, “Numerical Solution of Partial Differential Equation: Finite Differential Methods,” 3rd ed, Clarendon Press, Oxford (1985).

29 N. Bernardes, *Phys. Rev.*, **112**, 1534 (1958).

30 M. P. Allen and D. J. Tildesley, “Computer Simulation of Liquids,” Oxford University, Oxford (1987).

31 P. Turq, F. Lantelme, and H. L. Friedman, *J. Chem. Phys.*, **66**, 3039 (1977).

32 S. A. Adelman, *J. Chem. Phys.*, **64**, 124 (1976).

33 R. Mazo, in “Lecture Notes in Physics,” Vol. 84, “Stochastic Process in Nonequilibrium Systems,” ed by L. Garrido, P. Seglar, and P. J. Shepherd, Springer, Berlin (1978), p. 54.

34 W. Dong, F. Baros, and J. C. Andre, *Ber. Bunsenges. Phys. Chem.*, **94**, 269 (1990).

35 W. Dong and J. C. Andre, *J. Chem. Phys.*, **101**, 299 (1994).

36 D. L. Freeman and J. D. Doll, *J. Chem. Phys.*, **79**, 2343 (1983).