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Reaction probability derived from an interpolation formula for diffusion processes with an absorptive boundary condition

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The present article focuses on a dynamical simulation of molecular motion in liquids. In the simulation involving diffusion-controlled reaction with discrete time steps, lack of information regarding the trajectory within the time step may result in a failure to count the number of reactions of the particles within the step. In order to rectify this, an interpolated diffusion process is used. The process is derived from a stochastic interpolation formula recently developed by the first author [J. Math. Phys. **34**, 775 (1993)]. In this method, the probability that reaction has occurred during the time step given the initial and final positions of the particles is calculated. Some numerical examples confirm that the theoretical result corresponds to an improvement over the Clifford-Green work [Mol. Phys. **57**, 123 (1986)] on the same matter.

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I. INTRODUCTION

Many reactions in solution dealt with in radiation chemistry are diffusion controlled [1–3]. They are determined by the rate at which reaction particles encounter each other in the course of diffusion. Hence, in chemical reaction models, diffusion processes are implemented to determine the trajectories of the particles, which are often assumed to be governed by the following (one-dimensional) stochastic differential equation:

$$dX(t)=b(X(t),t)dt+\sigma(X(t),t)dw(t)\ ,\quad X(0)=x_0\ , \tag{1}$$

where $b=b(x,t)$ is a dynamical variable of the particles called the "drift velocity," $\sigma(x,t)$ is a nondynamical variable called the "diffusion function," and $w(t)$ is a given standard statistical trajectory called the Brownian process (Wiener process). Moreover, "an infinitesimal increment" $dw(t)=w(t+dt)-w(t)$ of process $w(t)$ for a small time interval $dt>0$ is a Gaussian random variable with mean 0 and variance $E[dw(t)dw(t)]=dt$, where $E[\cdot]$ denotes the expectation. Equation (1) tells us that the infinitesimal increment in position $dX(t)=X(t+dt)-X(t)$ consists of two parts; a smooth dynamic part $b(X(t),t)dt$ and a random part $\sigma(X(t),t)dw(t)$. This last term may be understood as a fluctuation of particles. For a precise meaning of the stochastic differential equation, see, for example, Ref. [4]. In this framework, reactions are combined with reactive boundary conditions—either a perfectly absorbing boundary condition or an elastic one. However, it is difficult to find a solution analytically to Eq. (1) under such conditions, and hence one needs to perform a numerical simulation for the stochastic equation by using a finite difference approximation to Eq. (1). For example, in the Euler-Maruyama scheme, the difference equation to Eq. (1) is given by [5]

$$X_{n+1}=X_n+b(X_n,n\delta t)\delta t+\sigma(X_n,n\delta t)\gamma_n\sqrt{\delta t} \quad (n=0,1,\dots) \tag{2}$$

$$X_0=x_0\ ,$$

where δt is the discrete time step, $X_n=X(n\delta t)$, and γ_n is a random variable drawn from a normal distribution $N(0,1)$. Through Eq. (2), an approximate trajectory for the true solution to Eq. (1) with a boundary condition is built up over successive time steps.

Clifford and Green simulated reactions in radiation-induced spurs on the basis of Eq. (2) with an absorbing boundary [1–3]. Their simulation is outlined as follows: The evolution of interparticle distances in the spurs is described by Eq. (2). If the distance of a pair of particles in the spur is within the reaction distance during the course of their random flight, reaction occurs and the particles are removed. Thus the reaction distance plays the role of an absorbing boundary for the diffusion process of the interparticle distance. However, in this framework, one may fail to count the number of the reactions which would have occurred within the time step, since we only know the positions of the particles at the beginning and end of each step. This failure can be reduced by decreasing the size of the time step δt; but this exceedingly consumes computer time in the simulation mentioned above. Therefore, Clifford and Green proposed a method of interpolating the initial and final positions of the particles by a pinned Brownian process [4]: By using the interpolation process, they calculated the probability that a reaction has occurred at the absorbing boundary during the time step, and thereby they counted the number of reactions that would have been missed in the simulation.

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This idea is very appealing, but the method seems to be a bit rough. Indeed, the connection between the original diffusion process (1) and the pinned Brownian process is ambiguous.

Recently, the first author has derived a formula which expresses an interpolation process for the diffusion process satisfying Eq. (1) [6]. The formula is based on a pinned process which is defined by using the original diffusion process (1) in a way analogous to that in the derivation of the pinned Brownian process from the standard Brownian process. The first purpose of the present article is to derive the reaction probability by using the process obtained through this interpolation formula. Then such a pinned diffusion process must yield a better interpolation to the original process than the pinned Brownian process. Therefore, one may expect to improve Clifford and Green's reaction probability by using the formula, and it is our second purpose to show this through some numerical examples.

This article is organized as follows.

Section II is devoted to a review of the interpolation formula mentioned above. Section III is concerned with the derivation of the reaction probability on the basis of the interpolation formula, in a way analogous to that in Clifford and Green's work [1]. In Sec. IV, it is indicated through some simple numerical experiments that the reaction probability reduces the failure of counting the number of the reactions, and that our theoretical result corresponds to an improvement over Clifford and Green's work. Finally, in Sec. V, some concluding remarks are given.

II. SUMMARY OF A STOCHASTIC INTERPOLATION FORMULA

In this section, we give a brief summary of the first author's stochastic interpolation formula. Since the result already appears in Ref. [6], we will review it with stress on the technical ideas.

We first touch on a pinned Brownian process (Brownian bridge) [4], which is useful for interpolating between the given two-boundary values [1–3]. Suppose that x and y are given random variables on s and t, respectively, where s and t are given values on $\mathbb{R}^1$. Then the pinned Brownian process $\hat{B}(u)$ on the time interval $[s,t]$ is defined through the original Brownian process $B(t)$ as follows [4]:

$$\begin{aligned}\hat{B}(u)= &\left[\frac{t-u}{t-s}\right]x+\left[\frac{u-s}{t-s}\right]y\\ &+\left[\frac{t-u}{t-s}\right][B(u)-B(s)]\\ &-\left[\frac{u-s}{t-s}\right][B(t)-B(u)]-\infty<s\le u\le t<\infty\ .\end{aligned} \tag{3}$$

It is easy to see that this process satisfies $\hat{B}(t)=y$ and $\hat{B}(s)=x$, respectively. That is, $\hat{B}(u)$ coincides with the given variables at the two end points of the time interval. Moreover, if x and y are compatibly given for $B(s)$ and $B(t)$, respectively, the right-hand side of Eq. (3) determines an exact value of the Brownian motion B on each u in $[s,t]$. Hence we may regard this process as a sort of stochastic interpolation process between x on s and y on t.

Our stochastic interpolation formula is derived on the basis of a pinned process which corresponds to an extension of this pinned Brownian process. The pinned process is obtained as follows: Let $X(t)$ be a one-dimensional diffusion process satisfying Eq. (1). Then, replacing the Brownian process B by this diffusion process X in the above equation, we obtain a pinned process $\hat{X}(u)$ on a given time interval $[s,t]$ as follows:

$$\begin{aligned}\hat{X}(u)= &\left[\frac{t-u}{t-s}\right]x+\left[\frac{u-s}{t-s}\right]y\\ &+\left[\frac{t-u}{t-s}\right][X(u)-X(s)]\\ &-\left[\frac{u-s}{t-s}\right][X(t)-X(u)]-\infty<s\le u\le t<\infty\ ,\end{aligned} \tag{4}$$

where x and y are given values on s and t satisfying $\hat{X}(t)=y$ and $\hat{X}(s)=x$, respectively. Our process X reduces to the Brownian process B, if we set b and σ in Eq. (1) as 0 and 1, respectively. Hence $\hat{X}(u)$ is a pinned process which corresponds to an extension of the pinned Brownian process $\hat{B}(u)$.

Since the original process X is governed by the stochastic differential equation (1), we may expect that this process is also written by the drift function b and the diffusion function σ given in the equation; and our stochastic interpolation formula is just derived through such a procedure. Then, in view of the interpolation, it is assumed that the increments $X(u)-X(s)$ and $X(t)-X(u)$ in the right-hand side of Eq. (4) are forward and backward in time, respectively. This assumption is essential: Indeed, if both of the increments in Eq. (4) are forward, they may be given approximately for the diffusion process under $t-s\ll 1$ by

$$\begin{aligned}X(u)-X(s)\approx\, &b(X(s),s)(u-s)\\ &+\sigma(X(s),s)[w(u)-w(s)]\end{aligned} \tag{5}$$

and

$$\begin{aligned}X(t)-X(u)\approx\, &b(X(u),u)(t-u)\\ &+\sigma(X(u),u)[w(t)-w(u)]\ ,\end{aligned} \tag{6}$$

respectively, since dX in Eq. (1) arises as a limit of the finite forward increment $\Delta X(t)=X(t+\Delta t)-X(t)$ $(\Delta t>0)$. Then Eq. (4) is approximately rewritten in a form containing b and σ by substituting Eqs. (5) and (6) into the right-hand side of Eq. (4). However, the equation is not suitable as an interpolation formula. Indeed, it seems natural that one may determine the value of $\hat{X}$ on u through an interpolation formula from x, y, and the two boundary values of $b(X(\tau),\tau)$ and

$\sigma(X(\tau),\tau)$ at $\tau=s$ and $\tau=t$; however, through the above equation we may not carry out such a procedure, since Eq. (6) does not contain $b(X(t),t)$ and $\sigma(X(t),t)$. Such a failure is caused by looking upon $X(t)-X(u)$ as a forward increment; therefore, one needs the assumption mentioned above.

We now proceed to obtain an explicit form of our interpolation formula under the above assumption; that is, we put Eq. (4) for the pinned process $\hat{X}(u)$ into a form containing values of functions b and σ on s and t. As was mentioned, if $t-s \ll 1$ holds, the increment $X(u)-X(s)$ is approximately rewritten by Eq. (5) containing the values of the functions b and σ on s. In contrast to this, to rewrite the increment $X(t)-X(u)$ in a similar fashion, we need the backward stochastic calculus proposed in Refs. [7] and [8], since the increment is backward. According to the references, under weaker conditions on b, σ, and the probability density function ρ of X, the diffusion process $X(t)$ governed by Eq. (1) satisfies the following backward stochastic differential equation:

$$d_*X(t)=b_*(X(t),t)d_*t+\sigma_*(X(t),t)d_*w_*(t)\ , \tag{7}$$

where

$$b_*(x,t)=b(x,t)-\frac{1}{\rho}\frac{\partial}{\partial x}(\sigma^2\rho)\ ,\quad \sigma(x,t)=\sigma_*(x,t)\ , \tag{8}$$

and $d_*X(t)$ arises as a limit of finite backward increment $\Delta X(t)=X(t)-X(t-\Delta t)$ $(\Delta t>0)$. Moreover, in Eq. (7), w_* is a backward standard Wiener process identified through

$$d_*w_*=dw+\frac{1}{\rho}\frac{\partial}{\partial x}(\rho\sigma)dt\ . \tag{9}$$

Hence, on account of the meaning of $d_*X(t)$, the backward increment $X(t)-X(u)$ in Eq. (4) is given approximately by

$$X(t)-X(u)\approx b_*(X(t),t)(t-u)$$
$$+\sigma_*(X(t),t)[w_*(t)-w_*(u)]\ . \tag{10}$$

Note that the right-hand side of this equation contains the values of functions b and σ on t in terms of Eqs. (8). Hence, substituting Eqs. (5) and (10) into Eq. (4) together with Eqs. (8) and (9), we rewrite the pinned process $\hat{X}(u)$ in the form containing b and σ as follows:

$$\hat{X}(u)=\left[\frac{t-u}{t-s}\right]x+\left[\frac{u-s}{t-s}\right]y+\left[\frac{(t-u)(u-s)}{t-s}\right]\left[b(X(s),s)-b(X(t),t)+\sigma\frac{\partial}{\partial x}\sigma(X(t),t)\right]$$
$$+\left[\frac{t-u}{t-s}\right]\sigma(X(s),s)[w(u)-w(s)]-\left[\frac{u-s}{t-s}\right]\sigma(X(t),t)[w(t)-w(u)]\ ,\quad -\infty<s\le u\le t<\infty\ . \tag{11}$$

This is just the stochastic interpolation formula (its approximate version under $t-s\ll 1$) we want. For the precise procedure for the deviation of the stochastic interpolation formula or for the exact version of it, see Ref. [6].

Finally, we remark again that the above formula (11) is an extension of a pinned Brownian motion (3) which is used by Clifford and Green to derive the reaction probability [1]. Hence we may expect to improve their result by using this formula, and in Sec. III, we will carry out this attempt in a way analogous to that in Clifford and Green's work.

III. REACTION PROBABILITY

In this section, by using our interpolation formula (11), we will find the probability that passage to a reactive boundary (absorbing boundary), at separation R, occurs during the time interval δt, given the discrete positions X_n and X_{n+1} through a difference scheme for the original process X.

Let us consider a difference scheme, e.g., Eq. (2), having the discrete time step δt for the diffusion process $X(t)$ described by Eq. (1). Then we denote the discrete times $n\delta t$ and $(n+1)\delta t$ by s and t, respectively. In what follows, we further modify our interpolation formula (11) to derive the reaction probability from it. First we assign $x=X(s)=X_n$ and $y=X(t)=X_{n+1}$ in Eq. (11), since the discrete values X_n and X_{n+1} determined through the difference scheme are regarded as the values of X at s and t. Next, for each u on $[s,t]$, we replace the terms containing the differences $w(u)-w(s)$ and $w(t)-w(u)$ in Eq. (11) as a random variable by

$$\left[\left[\frac{t-u}{t-s}\right]\sigma^2(X(s),s)+\left[\frac{u-s}{t-s}\right]\sigma^2(X(t),t)\right]^{1/2}$$
$$\times(t-u)B\left[\frac{(u-s)}{(t-u)(t-s)}\right]\ , \tag{12}$$

where B is another Wiener process, because of the Gaussian nature of the Wiener process W. Moreover, we rewrite u as $s+\nu\delta t$, where $\delta t\equiv t-s(\ll 1)$ and $\nu\equiv(u-s)/(t-s)(0\le\nu\le 1)$. Then Eq. (11) is put into the following equation:

$$\hat{X}(s+\nu\delta t)=(1-\nu)x+\nu y+\nu(1-\nu)\delta t(b_1-b_2+c)+\sqrt{\tilde{\sigma}^2(\nu)}\delta t(1-\nu)B\left[\frac{\nu}{(1-\nu)\delta t}\right]\ ,\quad 0\le\nu\le 1\ , \tag{13}$$

where b_1, b_2, and c are constants on s and t given by $b_1 \equiv b(x,s)$, $b_2 \equiv b(y,t)$, and $c \equiv [\sigma(\partial\sigma/\partial x)](y,t)$, respectively (note that x and y are given values at s and t). The function $\tilde{\sigma}^2(\nu)$ in Eq. (13) is given by

$$\tilde{\sigma}^2(\nu)=(1-\nu)\sigma_1^2+\nu\sigma_2^2 , \tag{14}$$

where σ_1 and σ_2 are also constants on s and t given by $\sigma_1 \equiv \sigma(x,s)$ and $\sigma_2 \equiv \sigma(y,t)$, respectively. Here we note that Eq. (13) corresponds to Eq. (10) in Clifford and Green's paper [1], which is the basic equation for finding the reaction probability we want. Therefore, in a way similar to that in their work, we change the variables ν and $\hat{X}$ in Eq. (13) as

$$\tau=\frac{\nu}{(1-\nu)\delta t} , \quad 0 \le \tau < \infty , \tag{15}$$

$$Z(\tau)=(1+\tau\delta t)\hat{X}(s+\nu\delta t)-x-(\tau\delta t)R . \tag{16}$$

Then, inserting Eqs. (13)–(15) into Eq. (16), we see that $Z(\tau)$ with the initial condition $Z(0)=0$ forms a diffusion process whose transition probability density $\rho(\tau,z,0)$ can be shown to obey the following "Fokker-Planck equation" with absorbing boundary condition $\rho(R-x)=0$ [9,10]:

$$\frac{\partial\rho}{\partial\tau}=-\frac{\partial}{\partial z}(\hat{b}\rho)+\frac{\hat{\sigma}^2}{2}\frac{\partial^2\rho}{\partial z^2} , \tag{17}$$

where

$$\hat{b}(z,\tau)=\frac{[(\sigma_2/\sigma_1)^2-1]\delta t}{2[1+\tau(\sigma_2/\sigma_1)^2\delta t](1+\tau\delta t)}z+\left[1-\frac{\tau[(\sigma_2/\sigma_1)^2-1]\delta t}{2[1+\tau(\sigma_2/\sigma_1)^2\delta t](1+\tau\delta t)}\right](y-R)\delta t$$
$$+\left[1-\frac{\tau[(\sigma_2/\sigma_1)^2-1]\delta t}{2[1+\tau(\sigma_2/\sigma_1)^2\delta t]}\right]\frac{(b_1-b_2+c)(\delta t)^2}{(1+\tau\delta t)^2} \tag{18}$$

and

$$\hat{\sigma}^2(\tau)=\tilde{\sigma}^2(\nu(\tau))(\delta t)^2=\frac{\sigma_1^2+\sigma_2^2\tau\delta t}{1+\tau\delta t}(\delta t)^2 . \tag{19}$$

Now we proceed to obtain the reaction probability. The probability we seek is just the probability that $\hat{X}$ reaches the reactive boundary at the separation R during the time interval $\delta t = t-s$. Then transformations (15) and (16) indicate that this is equivalent to the probability that the process $Z(\tau)$ with $Z(0)=0$ reaches $R-x$ during the span in time. To calculate such a probability, we need the transition probability density of $Z(\tau)$ with the absorbing boundary condition [9]; that is, we must find the solution of Eq. (17) with (18) and (19) under the condition $\rho(R-x)=0$. It is difficult, however, to solve the equation with the boundary condition exactly, since $\hat{b}$ and $\hat{\sigma}^2$ depend on variables z and τ. Moreover, in view of practical simulations, it is desirable that the functional form of the transition probability density be simple, even if it is somewhat inexact as to the solution of Eq. (17). Indeed, if the form is so complex, the reaction probability derived from the density can also be given in a complex form, so that the numerical calculation for the probability may consume computer time in practical simulations. On account of these facts, we approximate $\hat{b}$ and $\hat{\sigma}^2$ by "constants," respectively, and thereby we obtain an approximate solution to Eq. (17) with the absorbing boundary condition. First, we are concerned with $\hat{\sigma}^2(\tau)$. Equation (19) indicates that $\hat{\sigma}^2$ become a function depending on τ because $\tilde{\sigma}^2$, given by Eq. (14), is a function with respect to ν. Therefore, replacing $\tilde{\sigma}^2(\nu)$ by an approximate value, we may transform function $\hat{\sigma}^2(\tau)$ to a certain constant. In view of this, as such a constant for $\tilde{\sigma}^2(\nu)$, we choose the following average value of the function with respect to the original time variable ν $(0 \le \nu \le 1)$:

$$\bar{\sigma}^2=\frac{1}{1-0}\int_0^1\tilde{\sigma}^2(\nu)d\nu=\left[\frac{\sigma_2^2+\sigma_1^2}{2}\right] . \tag{20}$$

If the function $\tilde{\sigma}^2(\nu)$ turns into the constant $\bar{\sigma}^2$, then it is easy to see that $\hat{\sigma}^2(\tau)$ is given by the following constant:

$$\hat{\sigma}^2(\tau)=\bar{\sigma}^2(\delta t)^2=\left[\frac{\sigma_2^2+\sigma_1^2}{2}\right](\delta t)^2 . \tag{21}$$

This is an approximate constant for $\hat{\sigma}^2(\tau)$. Next, we turn to function $\hat{b}$: As was seen in Eq. (18), the functional form is so complicated that we directly take a long-term average for it. Then we obtain the following simple constant:

$$\bar{b}=\lim_{T\to\infty}\frac{1}{T}\int_0^T\hat{b}(z,\tau)d\tau=(y-R)\delta t . \tag{22}$$

Hence we choose this constant as an approximation for $\hat{b}$

Replacing $\hat{b}$ and $\hat{\sigma}^2$ in Eq. (17) by $\bar{b}$ and $\bar{\sigma}^2(\delta t)^2$, respectively, we finally find an approximate solution (transition probability density) of Eq. (17) with absorbing boundary $\rho(R-x)=0$ and initial condition $Z(0)=0$ as

$$\rho(\tau,z,0)=q(\tau,z,0)-\exp\left[-\frac{4(y-R)(x-R)}{(\sigma_1^2+\sigma_2^2)\delta t}\right]\times q(\tau,z,2(R-x)) , \tag{23}$$

where

$$q(\tau,z,\hat{z})=\frac{1}{\sqrt{\pi(\sigma_1^2+\sigma_2^2)\delta t^2\tau}}\times\exp\left[-\frac{[z-\hat{z}-\tau(y-R)\delta t]^2}{(\sigma_1^2+\sigma_2^2)\delta t^2\tau}\right] . \tag{24}$$

For this solution, our reaction probability, denoted by W, is calculated by [1,9]

$$W=\int_0^{+\infty}\left\{\int_{R-x}^{+\infty}\left[-\frac{d\rho}{d\tau}\right]dz\right\}d\tau . \tag{25}$$

Hence, inserting (23) with (24) into this equation, we finally obtain the reaction probability that $Z(\tau)$ reacts at $R-x$ during the whole time; that is, $\hat{X}$ reacts at R in the time interval $\delta t=t-s$ under the conditions $\hat{X}(t)=y$ and $\hat{X}(s)=x$ as follows:

$$W=\exp\left[-\frac{4(y-R)(x-R)}{(\sigma_1^2+\sigma_2^2)\delta t}\right]. \tag{26}$$

This is the desired result.

Remark. As mentioned in Sec. I, Clifford and Green obtained the following reaction probability [1]:

$$W_{\mathrm{CG}}=\exp\left[-\frac{2(y-R)(x-R)}{\sigma^2\delta t}\right], \tag{27}$$

where σ is a single value of the diffusion coefficient $\sigma(x,t)$ in Eq. (1) at initial time $s=n\delta t$. In contrast, our reaction probability (26) contains two values of $\sigma(x,t)$ at initial time $s=n\delta t$ and final time $t=(n+1)\delta t$. This indicates that the present result is more precise than Clifford and Green's. Of course, such a difference between Eqs. (26) and (27) are reduced by decreasing the size of δt. Moreover, in the case of $\sigma(x,t)=\text{const}$ in Eq. (1), two results just coincide with each other. In Sec. IV, our result Eq. (26) will be compared with Eq. (27) through a concrete numerical simulation.

IV. NUMERICAL SIMULATIONS

In this section, through some numerical experiments, we show that (i) the reaction probability (26) is useful for a more accurate count of the number of reactions in the diffusion problem with the absorbing boundary, and (ii) the result corresponds to an improvement over Clifford and Green's. For these purposes, we give the following equations as examples of the stochastic differential equation (1):

$$dX(t)=\left[\frac{2}{X(t)}+\frac{c}{X(t)}\right]dt+\sqrt{2}\,dW(t), \tag{28}$$

$$dX(t)=\left[6+\frac{c}{X(t)}\right]dt+2\sqrt{2X(t)}\,dW(t), \tag{29}$$

where c is a constant. The former is often used in the ion pair recombination model [3]: In this model, the equation represents the distance of a pair of particles which diffuse under a potential c/x in three-dimensional space. The latter is the equation which describes the diffusion process for the square value of the distance process (28).

On the basis of these equations, we perform numerical experiments in a similar way to that in Clifford and Green's work, as was mentioned in Sec. I. First, we set an initial value $X(0)$ and an absorbing boundary value R, which corresponds to an interparticle distance and a reaction distance in the chemical reaction model, respectively. Moreover, we prepare two numerical schemes for the above stochastic differential equations: One is the Euler-Maruyama scheme and the other is the second order Runge-Kutta scheme [5,11]. They are given for a scalar autonomous stochastic differential equation

$$dX(t)=b(X(t))dt+\sigma(X(t))dW(t)$$

[of course, Eqs. (28) and (29) are of this type] as follows:

(a) Euler-Maruyama scheme

$$X_{n+1}=X_n+b(X_n)\delta t+\sigma(X_n)\gamma_n\sqrt{\delta t}, \tag{30}$$

where δt is the discrete time step, and γ_n is the $N(0,1)$ random variable.

(b) The second order Runge-Kutta scheme

$$X_{n+1}=X_n+\tfrac{1}{2}\delta t(f_1+f_2)+\tfrac{1}{2}\sqrt{\delta t}\,(g_1+g_2)\gamma_{n1}, \tag{31}$$

where

$$f_1=b(X_n),$$
$$g_1=\sigma(X_n),$$
$$f_2=b(X_n+f_1\delta t+g_1\sqrt{\delta t}\,\gamma_{n2}),$$
$$g_2=\sigma(X_n+f_1\delta t+g_1\sqrt{\delta t}\,\gamma_{n2}),$$

and γ_{n1} and γ_{n2} are mutually independent $N(0,1)$ random variables.

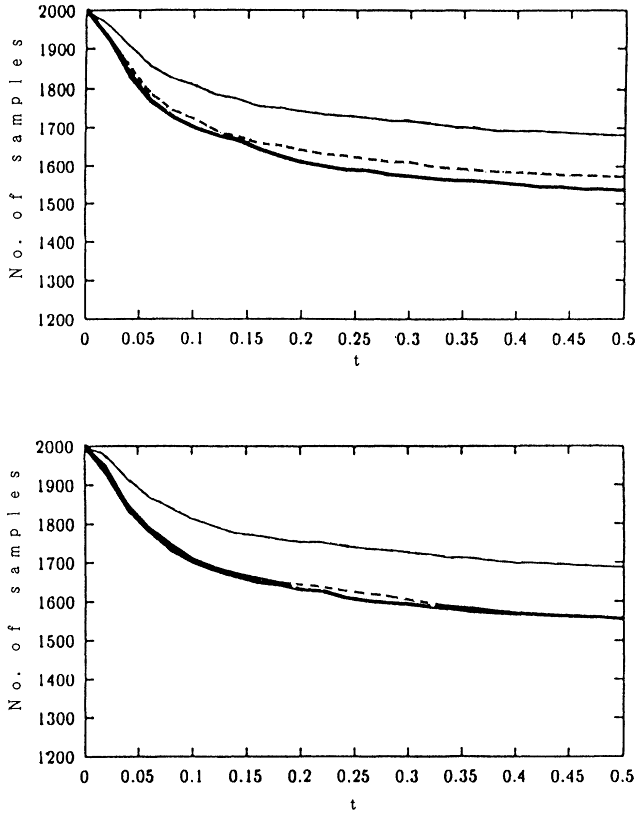

FIG. 1. (a) Comparison of the number of survival samples under $\delta t=2.0\times10^{-3}$ (——), $\delta t=2.0\times10^{-5}$ (——), and $\delta t=2.0\times10^{-3}$ with the reaction probability (26) (— —) in the Euler-Maruyama scheme (30) for Eq. (28). t $(=n\delta t)$ is dimensionless. (b) Comparison of the number of survival samples under $\delta t=2.0\times10^{-3}$ (——), $\delta t=2.0\times10^{-5}$(——), and $\delta t=2.0\times10^{-3}$ with the reaction probability (26) (— — —) in the Runge-Kutta scheme (31) for Eq. (28). t $(=n\delta t)$ is dimensionless.

On the basis of these difference equations for Eqs. (28) or (29), we move 2000 samples which correspond to interparticle distances or to their square values in the chemical reaction model, on successive time steps $n=1,2,\ldots$. Then the reaction occurs, and the sample is removed when the sample is within the reaction distance at the end of a time step. When it is determined that the reaction would have occurred within the time step, this latter reaction probability is given by Eqs. (26) or (27). Thus the history of the number of the survival samples is built up, and this is the result we want. Indeed, we compare between results obtained by using the reaction probabilities (26) and (27), and the result without using such reaction probabilities, and thereby we confirm facts (i) and (ii) mentioned in the introductory part of this section.

We are to observe the numerical results. In the following simulations, we set the initial value $X(0)$, the constant c in Eqs. (28) and (29), and the reaction distance R as 0.5, 0.2, and 0.2, respectively. Moreover, the normal pseudorandom number sequences γ_n which are used here are given by [5,12]

$$\gamma_n=\xi_{n_1}+\xi_{n_2}+\cdots+\xi_{n_{12}}-6\ ,$$

where ξ_m's are the pseudorandom number sequences generated by the following congruence method:

$$\xi_{m+1}\equiv a\xi_m \quad (\bmod 2^{31}-1\ ,\ \ a=16\,807)\ .$$

As to the check of the statistical quality for the above pseudorandom number sequences, Coveyou-MacPherson's k-dimensional spectral tests ($k=2$, 3, 4, 5 and 6) and Knuth's criterion (Refs. [12] and [13]) are used; that is, the pseudorandom number sequences roughly satisfy the following condition [12]:

$$\ln_2 \nu_k \geq 30/k \quad (k=2,3,4,5,6)\ ,$$

where ν_k is the so-called minimum of k-dimensional wave numbers for pseudorandom number sequences [13]. In the case of our random numbers, for $k=2,3,4,5$, and 6, the values of $\ln_2 \nu_k$ are given by about 14.0, 9.3, 7.2, 6.1, and 4.9, respectively; hence it seems that the random numbers satisfy the above criterion.

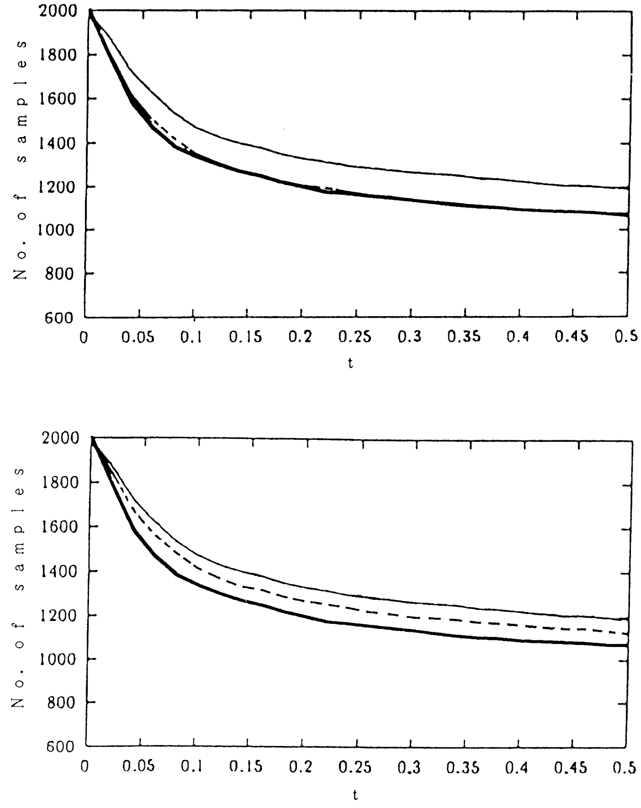

FIG. 2. (a) Comparison of the number of survival samples under $\delta t=2.0\times10^{-3}$ (——), $\delta t=2.0\times10^{-5}$ (——), and $\delta t=2.0\times10^{-3}$ with the reaction probability (26) (— — —) in the Euler-Maruyama scheme (30) for Eq. (29). t ($=n\delta t$) is dimensionless. (b) Comparison of the number of survival samples under $\delta t=2.0\times10^{-3}$ (——), $\delta t=2.0\times10^{-5}$(——), and $\delta t=2.0\times10^{-3}$ with the reaction probability (27) (— — —) in the Euler-Maruyama scheme (30) for Eq. (29). t ($=n\delta t$) is dimensionless.

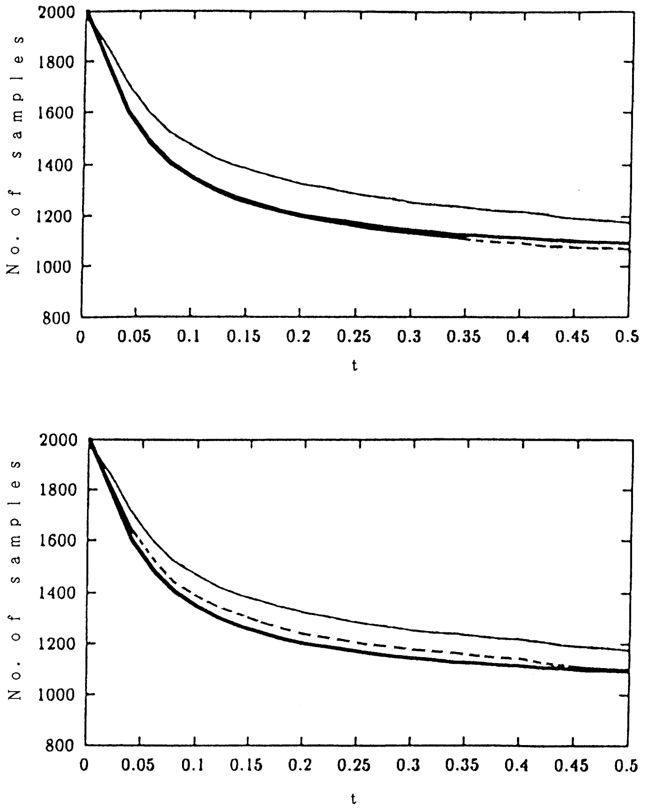

FIG. 3. (a) Comparison of the number of survival samples under $\delta t=2.0\times10^{-3}$ (——), $\delta t=2.0\times10^{-5}$ (——), and $\delta t=2.0\times10^{-3}$ with the reaction probability (26) (— — —) in the Runge-Kutta scheme (31) for Eq. (29). t ($=n\delta t$) is dimensionless. (b) Comparison of the number of survival samples under $\delta t=2.0\times10^{-3}$ (——), $\delta t=2.0\times10^{-5}$ (——), and $\delta t=2.0\times10^{-3}$ with the reaction probability (27) (— — —) in the Runge-Kutta scheme (31) for Eq. (29). t ($=n\delta t$) is dimensionless.

We first focus on the result for the stochastic differential equation (28). Here we remark that our reaction probability (26) is agreed with Clifford and Green's, Eq. (27), for this stochastic differential equation, since the diffusion function in Eq. (28) is a constant (see the *Remark* in Sec. III). Hence in this case we examine only fact (i) through the numerical result.

Figures 1(a) and 1(b) show a comparison between the numerical results under $\delta t = 2.0 \times 10^{-3}$ and 2.0×10^{-5} without a consideration of reaction probability (26), and the revised result under $\delta t = 2.0 \times 10^{-3}$ by (26): the former is obtained under the Euler-Maruyama scheme (30) and the latter is obtained under the Runge-Kutta scheme (31). In each figure, we see that the revised data for $\delta t = 2.0 \times 10^{-3}$ nearly agree with those for $\delta t = 2.0 \times 10^{-5}$. Obviously, by decreasing the size of the time step δt, we obtain a more accurate numerical result for our diffusion problem, and hence the above fact indicates that reaction probability (26) improves the accuracy of the numerical data for $\delta t = 2.0 \times 10^{-3}$. Thus we confirm the utility of our reaction probability for counting the number of reactions in the numerical simulation of a diffusion process with the absorbing boundary.

Next we turn to numerical simulations for the stochastic differential equation (29). Through the results, we can compare the utility of our reaction probability with that of Clifford and Green's, since the diffusion function in Eq. (29) is not constant. The numerical data are given by Figs. 2(a) and 2(b) and 3(a) and 3(b): They indicate the number of survival samples under $\delta t = 2.0 \times 10^{-3}$ and 2.0×10^{-5} together with the revised data for $\delta t = 2.0 \times 10^{-3}$ by the reaction probabilities (26) and (27). From these figures, we find that data revised by (26) are more similar to data for $\delta t = 2.0 \times 10^{-5}$ than those revised by (27) in the Euler-Maruyama or Runge-Kutta schemes. This fact means that probability (26) gives a more accurate approximation of the number of reactions in our diffusion problem than (27), and hence we confirm that the theoretical result obtained in Sec. III is an improvement over that of Clifford and Green. Thus we have observed the utility of our reaction probability (26), and its superiority to (27) in the numerical simulations for the reaction model mentioned above.

V. CONCLUDING REMARKS

In this paper, we obtain an alternative reaction probability (26) by using the first author's stochastic interpolation formula (11); it rectifies a failure to count the number of reactions in the numerical simulation for the chemical reaction model described by a diffusion process with the absorbing boundary. Moreover, through some numerical examples, we confirm the utility of our result and its superiority to Clifford and Green's. Finally, as concluding remarks, we will comment on the following.

(1) As numerical examples in Sec. IV we treated only the simple reaction model to examine the utility of Eq. (26). However, even in the case of more complicated reaction models, it may be useful for the reduction of failure to count the number of reactions, as Clifford-Green's works dealt within such models [1–3].

(2) We have focused on a reaction model with an absorbing boundary condition, but do not treat a model with an elastic boundary condition. In a similar way to that in this paper, the reaction probability may also be obtained for such a model on the basis of the interpolation formula (11).

We will come back to these problems in a future paper.

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[1] P. Clifford and N. J. B. Green, Mol. Phys. **57**, 123 (1986).

[2] P. Clifford, N. J. B. Green, M. J. Oldfield, M. J. Pilling, and S. M. Pimblott, J. Chem. Soc. Faraday Trans. I **82**, 2673 (1986).

[3] P. Clifford, N. J. B. Green, and M. J. Pilling, J. R. Stat. Soc. B **49**, 266 (1987).

[4] N. Ikeda and S. Watanabe, *Stochastic Differential Equations and Diffusion Processes,* 2nd ed. (North-Holland, Amsterdam, 1989).

[5] P. E. Kloeden and E. Platen, *Numerical Solution of Stochastic Differential Equations* (Springer-Verlag, Berlin, 1992).

[6] T. Misawa, J. Math. Phys. **34**, 775 (1993).

[7] K. Itô, in *Proceedings of the International Symposium on Stochastic Differential Equations, Kyoto 1976,* edited by K. Itô (Wiley, New York, 1978), p. 95.

[8] U. G. Haussmann and E. Pardoux, Ann. Prob. **14**, 1188 (1986).

[9] H. Riskin, *The Fokker Planck Equation: Methods of Solution and Applications,* 2nd ed. (Springer-Verlag, Berlin, 1989).

[10] S. Karlin and H. M. Taylor, *A Second Course in Stochastic Processes* (Academic, Orlando, 1981).

[11] J. R. Klauder and W. P. Petersen, SIAM J. Numer. Anal. **22**, 1153 (1985).

[12] D. E. Knuth, *The Art of Computer Programming,* 2nd ed. (Addison-Wesley, Reading, MA, 1981), Vol. 2.

[13] R. R. Coveyou and R. D. MacPherson, J. Assoc. Comput. Mach. **14**, 100 (1967).