Inertial dynamic effects on diffusion-influenced reactions: Approach based on the diffusive Cattaneo system

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Sangyoub Lee[a] (ID) and Sergey D. Traytak[b] (ID)

AFFILIATIONS

Department of Chemistry, Seoul National University, Seoul 08826, South Korea and N.N. Semenov Federal Research Center for Chemical Physics, Russian Academy of Sciences, 4 Kosygina St., 119991 Moscow, Russian Federation

[a]Author to whom correspondence should be addressed: sangyoub@snu.ac.kr
[b]Electronic mail: sergtray@mail.ru

ABSTRACT

We investigate the inertial dynamic effects on the kinetics of diffusion-influenced reactions by solving the linear diffusive Cattaneo system with the reaction sink term. Previous analytical studies on the inertial dynamic effects were limited to the bulk recombination reaction with infinite intrinsic reactivity. In the present work, we investigate the combined effects of inertial dynamics and finite reactivity on both bulk and geminate recombination rates. We obtain explicit analytical expressions for the rates, which show that both bulk and geminate recombination rates are retarded appreciably at short times due to the inertial dynamics. In particular, we find a distinctive feature of the inertial dynamic effect on the survival probability of a geminate pair at short times, which can be manifested in experimental observations.

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I. INTRODUCTION

The theoretical description of the diffusion-influenced reaction rates has usually been based on the Smoluchowski diffusion equation.[1–6] This description captures explicitly two essential components of the reaction process: the diffusive motion toward the reaction surface and finite intrinsic reactivity on it. It has provided an adequate explanation of many experimental observations and computer simulation results, but it fails to give an exact account of the short-time scale reaction dynamics.[7] In the Smoluchowski description, the value of the classical diffusive flux at a given spatial point at a given time is assumed to depend only on the values at the same point and the same moment. In reality, however, relaxation processes have a certain finite duration, i.e., they are inertial.

The validity of the diffusion-equation description has been assessed by molecular dynamics simulations[8–11] or Langevin dynamics simulations (that is Brownian dynamics simulations with inertial effects included).[12,13] The molecular dynamics simulations revealed the effects of nondiffusive dynamic behavior in two aspects. The first is the non-Markovian dynamic effect arising from the finite relaxation times of the solvent motions, and the second is the inertial

dynamic effect (also called the memory effect[3]) arising from the finite velocity relaxation time of the reactant molecules. Therefore, to assess the inertial dynamic effect separately, the use of Langevin dynamics simulations is more appropriate.

Analytic theories that dealt with the inertial dynamic effect were proposed by using the Fokker–Planck–Klein–Kramers equation (FPKKE). Unfortunately, analytical solutions to the FPKKE are available only for a few simple cases.[14–20] In the present work, we will take into account inertial dynamic effects by developing a theory based on the linear diffusive Cattaneo system[21–25] with the reaction sink term.

It is customary to distinguish two different cases of recombination with respect to time ranges: (a) first-order geminate recombination (several nanoseconds) and (b) second-order homogeneous recombination (10^3–10^4 ns).[3] Physically, the first case corresponds to the recombination of original pairs, whereas the second case describes the diffusion of reactants belonging to members of different pairs and their subsequent recombination. Previously, it was argued that "...the results given for the times less than 1 ps must be considered as having mathematical meaning only."[26] However, considerable progress in experimental methods leads to the

possibility of measurements within the range from 10^{-4} ns and even less. Readers interested in experimental aspects of the problem at issue are encouraged to refer to the recent review of Kumpulainen *et al.*[27] This renews the interest in the theoretical investigations of the inertial dynamic effects in various applications of diffusion-influenced processes (see, e.g., Refs. 28–32).

We obtain formally exact expressions for the kinetics of both bulk and geminate recombination. The rate expressions reveal the role of inertial dynamic effects at short times. The time-dependent rate expression for the bulk recombination reactions obtained in the present theory agree with the rate expression of Harris[16] that was obtained from an approximate solution of the FPKKE, when the equilibrium rate constant is set equal to that expected from the kinetic theory of dilute gases. On the other hand, when the reactivity at contact distance becomes infinity, our rate expression agrees with that obtained by Rice [Eq. (289) of Ref. 3]. To the knowledge of the authors, the inertial effect on the geminate recombination reaction is first investigated in the present work based on the diffusive Cattaneo system approach.

II. THEORY

We first consider the irreversible bimolecular reaction, $A + B \rightarrow product(s)$, between reactants A and B in the bath of solvent molecules for the low reactant concentration limit. We assume that the reactants are spherical and interact via a centrosymmetric potential $U(r)$ in the units of $k_B T$; k_B and T are the Boltzmann constant and the absolute temperature, respectively. For the sake of simplicity, we will neglect the hydrodynamic interaction between the reactants. Thus, the problem under consideration may be reduced to study spherically symmetric diffusion toward a test sphere with the reaction radius σ. Therefore, it is expedient to use here an appropriate spherical coordinate system.

The time-dependent bimolecular rate coefficient $k_f(t)$ is given by[5,33,34]

$$k_f(t) = \int d\mathbf{r} S(r) \rho(r,t). \tag{2.1}$$

Here, $S(r)$ is the reaction sink function, which was first introduced by Wilemski and Fixman[35] to account for the effect of reaction on the time-evolution equations of the reactant concentration fields. $\rho(r,t)$ denotes the nonequilibrium pair correlation function.[5,33] We assume that the reaction occurs at a contact distance σ, and thus, the effect of the reaction is modeled by the δ-function reaction sink term

$$S(r) = \kappa \frac{\delta(r - \sigma)}{4\pi\sigma^2}, \tag{2.2}$$

where κ is an intrinsic rate constant. When the δ-function reaction sink term is used, it is implicitly assumed that the infinitely stiff potential wall is located at $\sigma - \varepsilon$ with vanishingly small ε. Hence, the reactants can approach the reaction surface at $r = \sigma$. We then have

$$k_f(t) = \kappa \rho(\sigma,t). \tag{2.3}$$

Together with the non-penetrating boundary condition at the reaction surface $r = \sigma$ and the condition at infinity,

$$J_r(r = \sigma, t) = 0 \text{ and } \lim_{r \to \infty} \rho(r,t) = \lim_{r \to \infty} g(r) = 1, \tag{2.4}$$

the reaction model using the δ-function reaction sink in Eq. (2.2) can be shown to be equivalent to using the following radiation or partially reflecting boundary conditions:[3,35]

$$-4\pi\sigma^2 J_r(r = \sigma, t) = \kappa \rho(\sigma,t). \tag{2.5}$$

Particularly, if $\kappa = 0$, Eq. (2.5) describes the case when no reaction occurs. On the other hand, the $\kappa \to \infty$ limit corresponds to the perfectly absorbing case, and then, (2.5) is called the Smoluchowski boundary condition. We emphasize here that any three-dimensional domain is termed a partially bounded domain if some point of its boundary belongs to infinity. Hence, consequently, e.g., an annual domain $\{\sigma < r < R_0\}$ turns into the partially bounded domain $\{\sigma < r\}$ as $R_0 \to \infty$. In this way, for any function given on the domain $\{\sigma < r\}$ condition at infinity will be treated as a boundary condition.

To include the inertial dynamic effect, we employ the linear diffusive Cattaneo system.[21–25] To include the effects of the reaction, the equation of continuity for $\rho(r,t)$ is modified as

$$\frac{\partial \rho(r,t)}{\partial t} = -\frac{1}{r^2} \frac{\partial}{\partial r} \left[r^2 J_r(r,t) \right] - \kappa \frac{\delta(r - \sigma)}{4\pi\sigma^2} \rho(r,t). \tag{2.6}$$

The equation for the radial flux $J_r(r,t)$ is given by the so-called constitutive relation[18,21–25]

$$J_r(r,t) + \tau_D \frac{\partial}{\partial t} J_r(r,t) = -D\left[\frac{\partial}{\partial r} \rho(r,t) + \frac{\partial U(r)}{\partial r} \rho(r,t) \right], \tag{2.7}$$

where τ_D is the velocity relaxation time, and the relative translational diffusion coefficient D is assumed to be a constant. The second term on the left-hand side of Eq. (2.7), $\tau_D \partial J_r/\partial t$, is called the diffusion-flux relaxation term,[23] which takes account of the relaxation to the local equilibrium of the diffusion flux. The significance of including this term was discussed in detail, for instance, in Ref. 25. When $\tau_D = 0$, Cattaneo diffusive flux law (2.7) reduces to the classical Fick's first law. It must be noted that the constitutive relation (2.7) may involve a coupling term due to the reaction in general. For example, if the full reaction model involves some degrees of freedom other than the positions of reactants, the elimination of these variables leaves a reaction coupling term in the time evolution equation of the reactant probability distribution function in the position space; see Appendix A of Ref. 34. In the present work, we neglect such complications for the sake of simplicity.

For the relative diffusion of the reactant pair, it is given by $\tau_D = \mu/\xi_r$ with μ and ξ_r denoting the reduced mass and the reduced friction coefficient, respectively; that is

$$\mu = \frac{m_A m_B}{m_A + m_B} \text{ and } \xi_r = \frac{\xi_A \xi_B}{\xi_A + \xi_B}, \tag{2.8}$$

where m_α and ξ_α are the mass and the friction coefficient of molecule α, respectively. Hence, the diffusion-flux relaxation term can also be regarded diffusion inertia, responsible for the inertial effects.

The system of continuity Eq. (2.6) and constitutive relation (2.7) can be called the diffusive linear Cattaneo system. By the known Kac's trick,

$$(\rho, J_r) \rightarrow (\rho, \partial\rho/\partial t), \tag{2.9}$$

the Cattaneo system may be reduced to the following hyperbolic diffusion equation:

$$\tau_D \frac{\partial^2 \rho(r,t)}{\partial t^2} + \frac{\partial \rho(r,t)}{\partial t} = D \frac{1}{r^2} \frac{\partial}{\partial r}\left\{ r^2\left[\frac{\partial}{\partial r}\rho(r,t) + \frac{\partial U(r)}{\partial r}\rho(r,t) \right] \right\}$$
$$- \kappa \frac{\delta(r-\sigma)}{4\pi\sigma^2}\left[\rho(r,t) + \tau_D \frac{\partial \rho(r,t)}{\partial t} \right]. \quad (2.10)$$

We emphasize that by performing transition (2.9), some information may be lost (see discussion in Ref. 22). Therefore, it is preferable to use the Cattaneo system (2.6) and (2.7) rather than Eq. (2.10).

We assume that before the reaction is initiated at $t = 0$, the reactants are distributed in equilibrium. Then, the initial conditions for $\rho(r,t)$ and $J_r(r,t)$ are given by

$$\rho(r, t = 0) = g(r) = e^{-U(r)}, \quad (2.11)$$

$$J_r(r, t = 0) = 0. \quad (2.12)$$

With these initial conditions, Laplace transformations of Eqs. (2.6) and (2.7) give

$$s\hat{\rho}(r,s) - g(r) = -\frac{1}{r^2}\frac{\partial}{\partial r}[r^2 \hat{J}_r(r,s)] - \kappa \frac{\delta(r-\sigma)}{4\pi\sigma^2}\hat{\rho}(r,s), \quad (2.13)$$

$$\hat{J}_r(r,s) + \tau_D s\hat{J}_r(r,s) = -De^{-U(r)}\frac{\partial}{\partial r}e^{U(r)}\hat{\rho}(r,s). \quad (2.14)$$

Hereafter, we denote the Laplace transformation of a function $f(r,t)$ as $\mathcal{L}\{f(r,t)\} = \hat{f}(r,s)$. Then, by solving Eq. (2.14) for $\hat{J}_r(r,s)$ and substituting the resulting expression into Eq. (2.13), we obtain

$$s\hat{\rho}(r,s) - g(r) = D_s\frac{1}{r^2}\frac{\partial}{\partial r}r^2 e^{-U(r)}\frac{\partial}{\partial r}e^{U(r)}\hat{\rho}(r,s)$$
$$- \kappa \frac{\delta(r-\sigma)}{4\pi\sigma^2}\hat{\rho}(r,s). \quad (2.15)$$

Here, we introduced the effective diffusion coefficient D_s, which depends on the Laplace transform variable s as follows:

$$D_s \equiv D/(1 + \tau_D s). \quad (2.16)$$

We note that with definition (2.16), the above Laplace-transformed equation for $\hat{\rho}(r,s)$ formally has exactly the same form as the usual reaction-diffusion equation without the inertial dynamic effect taken into account.

Therefore, we can express the reaction kinetic expressions in terms of the Green's function $\hat{G}(r,s|r_0)$ that satisfies the equation[3,5]

$$s\hat{G}_I(r,s|r_0) - \frac{\delta(r-r_0)}{4\pi r_0^2} = L_I(r)\hat{G}_I(r,s|r_0), \quad (2.17)$$

where

$$L_I(r) \equiv \frac{D_s}{r^2}\frac{\partial}{\partial r}r^2 e^{-U(r)}\frac{\partial}{\partial r}e^{U(r)}. \quad (2.18)$$

In these equations, the subscript "I" denotes that these quantities take into account the inertial dynamic effects through D_s defined by Eq. (2.16). The boundary conditions associated with Eq. (2.17) are

$$\frac{\partial}{\partial r}e^{U(r)}\hat{G}_I(r,s|r_0)\bigg|_{r=\sigma} = 0 \text{ and } \lim_{r\to\infty}\hat{G}_I(r,s|r_0) = 0. \quad (2.19)$$

The inner boundary condition at the contact distance σ corresponds to the reflecting boundary condition in Eq. (2.4). Some accurate expressions of $\hat{G}_I(r,s|r_0)$ for arbitrary interaction potentials $U(r)$ were given in Refs. 5, 36, and 37.

In terms of the Green's function, the formal expression for $\hat{\rho}(r,s)$ is given as

$$\hat{\rho}(r,s) = \frac{1}{s}g(r) - \kappa \hat{G}_I(r,s|\sigma)\hat{\rho}(\sigma,s). \quad (2.20)$$

In deriving Eq. (2.20), we have noted that $L_I(r)g(r) = 0$. We thus obtain

$$\hat{\rho}(\sigma,s) = \frac{1}{s}\frac{g(\sigma)}{1 + \kappa\hat{G}_I(\sigma,s|\sigma)}. \quad (2.21)$$

Finally, from Eqs. (2.3) and (2.21), we obtain the Laplace transform of the bimolecular rate coefficient in the low reactant concentration limit:[5]

$$\hat{k}_f(s) = \frac{1}{s}\frac{\kappa g(\sigma)}{1 + \kappa\hat{G}_I(\sigma,s|\sigma)}. \quad (2.22)$$

Explicit expressions for the rate coefficient will be presented in Sec. III.

We then consider the geminate recombination reaction occurring in the low reactant concentration limit. We assume that the initial separation between the geminate reactants is r_0. The probability density $P(r, t|r_0)$ that the pair of geminate reactants has not reacted by time t and at the separation r satisfies the following equation:

$$\frac{\partial}{\partial t}P(r,t|r_0) = -\frac{1}{r^2}\frac{\partial}{\partial r}[r^2 J_g(r,t|r_0)] - \kappa\frac{\delta(r-\sigma)}{4\pi\sigma^2}P(r,t|r_0). \quad (2.23)$$

The relative flux $J_g(r,t|r_0)$ of the geminate pair in the radial direction satisfies the following constitutive relation:[18,21–25]

$$J_g(r,t|r_0) + \tau_D\frac{\partial}{\partial t}J_g(r,t|r_0) = -De^{-U(r)}\frac{\partial}{\partial r}e^{U(r)}P(r,t|r_0). \quad (2.24)$$

Because the geminate recombination reaction starts at $t = 0$, the initial conditions are given by

$$P(r, t = 0|r_0) = \frac{\delta(r-r_0)}{4\pi r_0^2} \text{ and } J_g(r, t = 0|r_0) = 0. \quad (2.25)$$

The boundary conditions are

$$J_g(\sigma,t|r_0) = 0 \text{ and } \lim_{r\to\infty}P(r,t|r_0) = 0. \quad (2.26)$$

The survival probability $W(r_0,t)$ that the geminate pair has not reacted until time t is

$$W(r_0,t) = \int d\mathbf{r}P(r,t|r_0). \quad (2.27)$$

Integrating Eq. (2.23) over the whole space of **r** with the boundary conditions in Eq. (2.26), we obtain

$$\frac{\partial}{\partial t} W(r_0, t) = -\kappa P(\sigma, t|r_0) \equiv -R(r_0, t), \quad (2.28)$$

where $R(r_0, t)$ denotes the time-dependent geminate recombination rate.

With the initial conditions in Eq. (2.25), Laplace transformations of Eqs. (2.23) and (2.24) give

$$s\hat{P}(r, s|r_0) - \frac{\delta(r - r_0)}{4\pi r_0^2} = -\frac{1}{r^2}\frac{\partial}{\partial r}[r^2 \hat{J}_g(r, s|r_0)]$$
$$- \kappa \frac{\delta(r - \sigma)}{4\pi\sigma^2}\hat{P}(r, s|r_0), \quad (2.29)$$

$$\hat{J}_g(r, s|r_0) + \tau_D s \hat{J}_g(r, s|r_0) = -D e^{-U(r)}\frac{\partial}{\partial r}e^{U(r)}\hat{P}(r, s|r_0). \quad (2.30)$$

Solving Eq. (2.30) for $\hat{J}_g(r, s|r_0)$ and substituting the resulting expression into Eq. (2.28), we obtain

$$s\hat{P}(r, s|r_0) - \frac{\delta(r - r_0)}{4\pi r_0^2} = L_I(r)\hat{P}(r, s|r_0) - \kappa\frac{\delta(r - \sigma)}{4\pi\sigma^2}\hat{P}(r, s|r_0), \quad (2.31)$$

where the operator $L_I(r)$ is defined by Eq. (2.18).

In terms of the Green's function defined by Eq. (2.17), the formal expression for $\hat{P}(r, s|r_0)$ is given by

$$\hat{P}(r, s|r_0) = \hat{G}_I(r, s|r_0) - \kappa\hat{G}_I(r, s|\sigma)\hat{P}(\sigma, s|r_0), \quad (2.32)$$

with

$$\hat{P}(\sigma, s|r_0) = \frac{\hat{G}_I(\sigma, s|r_0)}{1 + \kappa\hat{G}_I(\sigma, s|\sigma)}. \quad (2.33)$$

From Eqs. (2.28) and (2.33), the Laplace transform expressions for the geminate recombination rate and the survival probability are then given, respectively, by

$$\hat{R}(r_0, s) = \frac{\kappa\hat{G}_I(\sigma, s|r_0)}{1 + \kappa\hat{G}_I(\sigma, s|\sigma)}, \quad (2.34)$$

$$\hat{W}(r_0, s) = s^{-1}[1 - \hat{R}(r_0, s)]. \quad (2.35)$$

Explicit expressions for these quantities will be presented in Sec. III.

It is worth noting that Eqs. (2.22), (2.34), and (2.35) for $\hat{k}_f(s)$, $\hat{R}(r_0, s)$, and $\hat{W}(r_0, s)$, respectively, satisfy the general relations between the bulk and geminate recombination rates given by[5]

$$k_f(t) = \int d\mathbf{r}_0 R(r_0, t)g(r_0) = \kappa g(\sigma)W(\sigma, t). \quad (2.36)$$

This relation was first obtained by Tachiya.[38]

III. RESULTS AND DISCUSSION

In this paper, we now restrict the discussion to the reaction between interaction-free hard spherical reactants. When $U(r) = 0$ for $r \geq \sigma$, the Green's function is given by[5,39]

$$\hat{G}_I^0(r, s|r_0) = \frac{1}{8\pi D_s \zeta r r_0}\left[e^{-\zeta|r - r_0|} + \frac{\zeta\sigma - 1}{\zeta\sigma + 1}e^{-\zeta(r + r_0 - 2\sigma)}\right], \quad (3.1)$$

where the superscript "0" to the Green's function denotes an expression in this special case, and

$$\zeta = (s/D_s)^{1/2} = [s(1 + \tau_D s)/D]^{1/2}. \quad (3.2)$$

To get the explicit expressions for $\hat{k}_f(s)$ and $\hat{W}(r_0, s)$, we just need simpler expressions:

$$\hat{G}_I^0(\sigma, s|\sigma) = \frac{1}{4\pi D_s \sigma}\frac{1}{1 + \zeta\sigma} \quad (3.3)$$

and

$$\hat{G}_I^0(\sigma, s|r_0) = \frac{1}{4\pi D_s r_0}\frac{e^{-\zeta(r_0 - \sigma)}}{1 + \zeta\sigma}. \quad (3.4)$$

Using the expression of the $\hat{G}_I^0(\sigma, s|\sigma)$ in Eq. (3.3), Eq. (2.22) gives the Laplace transform of the bimolecular rate coefficient as

$$\frac{\hat{k}_f(s)}{k_D} = \frac{\kappa}{k_D}\frac{1}{s}\frac{1 + \zeta\sigma}{1 + \zeta\sigma + (\kappa/k_D)(1 + \tau_D s)}, \quad (3.5)$$

where k_D is the steady-state diffusion-controlled rate constant given by

$$k_D = 4\pi D\sigma. \quad (3.6)$$

When the reaction probability is unity on the collision of the reactant pair, it can be shown that the bimolecular rate coefficient in the low-density limit is given by[9,10,18,40,41]

$$\kappa_{kin} = \pi\sigma^2\left(\frac{8k_B T}{\pi\mu}\right)^{1/2} = \sigma^2\left(\frac{8\pi D}{\tau_D}\right)^{1/2}, \quad (3.7)$$

where the subscript "kin" denotes a result of the kinetic theory of gases. When the value of κ is set equal to $2\kappa_{kin}$, Eq. (3.5) coincides with the rate expressions of Harris[16] and Ibuki and Ueno[42] that were obtained from approximate solutions of the FPKKE; see also Eq. (4.3) of Ref. 18. As noted in Ref. 42, Eq. (15) of Ref. 16 must be multiplied by $1/s$ to get the correct result.

When κ goes to infinity, Eq. (3.5) gives the same result as that obtained by Rice [Eq. (289) of Ref. 3], who solved the hyperbolic diffusion equation with the Smoluchowski absorbing boundary condition:

$$\frac{k_f(t)}{k_D} = \left(1 - e^{-t/\tau_D}\right) + \left(\frac{t_D}{\tau_D}\right)^{1/2}e^{-t/(2\tau_D)}I_0\left(\frac{t}{2\tau_D}\right), \quad (3.8)$$

where $t_D = \sigma^2/D$, and $I_0(z)$ is the modified Bessel function of the first kind. Note in passing that Rice did not give any derivation of Formula (3.8), referring only to his unpublished result. We emphasize that this Formula (3.8) differs from the similar result given in Ref. 21 by term $(t_D/\tau_D)^{1/2}e^{-t/\tau_D}$, which rapidly vanishes in course of time for $t > \tau_D$.

We see that $k_f(t)$ coincides with the Smoluchowski rate expression at long times. On the other hand, the value of the rate coefficient $k_f(t)$ at $t = 0+$ is given by

$$k_f(t = 0+) = \lim_{s \to \infty} s\hat{k}_f(s) = \kappa\left[1 + (\kappa/k_D)(\tau_D/t_D)^{1/2}\right]^{-1}. \quad (3.9)$$

We note that the value drops immediately from $k_f(0) = \kappa$. This sudden drop is due to the quick depletion of reactants in contact and manifests the inertial dynamic effect that retards the inward diffusive flux. In the particular case of $\kappa \to \infty$, Eq. (3.9) reduces to $k_f(t = 0+) = 4\pi\sigma^2 c_D$ where $c_D\left[= (D/\tau_D)^{1/2}\right]$ is the speed of the diffusive wave.[21] Taking account of Eq. (3.7), one can also recast this formula as $k_f(t = 0+) = \sqrt{2\pi}\kappa_{kin}$. This corresponds to the so-called ballistic regime of the reaction kinetics occurring for time values $0 < t \ll \tau_D$.[43] It is significant that a similar formula for $k_f(t = 0+)$ was derived by Berezhkovskii *et al.*[7] with the help of a path-integral approach, without using solution to the FPKKE. Note that to compare our result with that obtained there, one should keep in mind that the particle mass is taken to be unity in Ref. 7.

In the case of finite κ, we do not have an explicit expression for $k_f(t)$. However, when $\tau_D = 0$, the inverse Laplace transformation of Eq. (3.5) gives the well-known Collins–Kimball–Smoluchowski rate coefficient that will be denoted by $k_f^0(t)$:[3]

$$\frac{k_f^0(t)}{k_D} = \frac{\kappa/k_D}{1 + \kappa/k_D}\left\{1 + \frac{\kappa}{k_D}\Omega\left[\frac{\sqrt{Dt}}{\sigma}\left(1 + \frac{\kappa}{k_D}\right)\right]\right\}. \quad (3.10)$$

Here, $\Omega(z) = \exp(z^2)\mathrm{erfc}(z)$, which reduces to $1/(\pi^{1/2}z)$ for large z. Therefore, the ratio $k_f(t)/k_f^0(t)$ represents the inertial dynamic effects on the time-dependent bimolecular rate coefficient.

For the case with infinite κ, which corresponds to the Smoluchowski absorbing boundary condition, the time-dependent bimolecular rate coefficient $k_f(t)$ is given by Eq. (3.8). Figure 1 displays the calculated results of the ratio $k_f(t)/k_f^0(t)$ for the three values of τ_D. The two values of τ_D, 0.004 and 0.028 in units of t_D, correspond to the parameters used in a paper by Rice *et al.*,[26] who investigated the reaction rates of ions, based on the Debye–Smoluchowski equation. The third value 0.1 is an arbitrarily chosen one to examine the case involving more pronounced inertial dynamic effects.

For the case with infinite κ, $k_f^0(t)$ diverges as $t \to 0+$, which is a rather unphysical result. On the other hand, for the case with finite values of τ_D, we have a finite value of $k_f(t = 0+)$ as given by Eq. (3.9). Figure 1 shows that the inertial dynamic effects are pronounced at very short times that are comparable with τ_D.

Figure 2 displays the inertial dynamic effects on the time-dependent bimolecular rate coefficient when κ is given by the collision-limited rate constant in low-pressure gases, κ_{kin} in Eq. (3.7). We calculate $k_f(t)$ by the numerical inverse Laplace transformation of Eq. (3.5) by using the Stehfest algorithm.[44] We observe a similar trend as in the case of Fig. 1, but the magnitude of the inertial dynamic effects is considerably diminished. Another difference is that $k_f(t)$ approaches $k_f^0(t)$ almost monotonically.

Using the expressions for the Green's function in Eqs. (3.3) and (3.4), the Laplace transform of the geminate recombination rate can be obtained from Eq. (2.34) as

$$\hat{R}(r_0, s) = \frac{\sigma}{r_0}\frac{(\kappa/k_D)(1 + \tau_D s)}{1 + \zeta\sigma + (\kappa/k_D)(1 + \tau_D s)}e^{-\zeta(r_0 - \sigma)}, \quad (3.11)$$

where ζ and k_D were defined by Eqs. (3.2) and (3.6), respectively. The usual experimental observable is the survival probability of the geminate reactant pair, which is given by Eqs. (2.35) and (3.11).
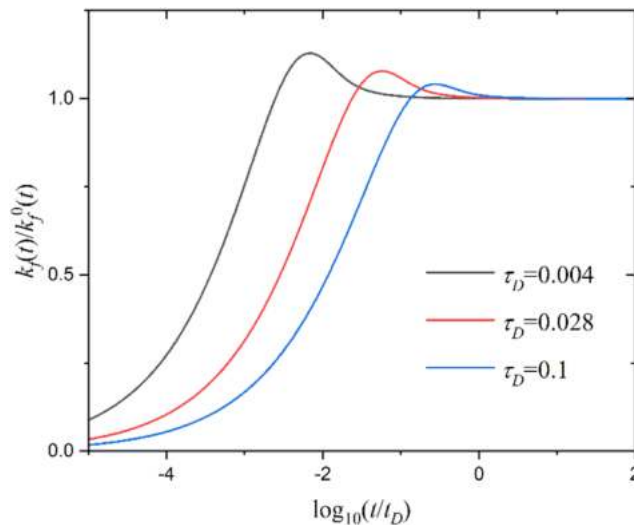

FIG. 1. Inertial dynamic effects on the time-dependent bimolecular rate coefficient $k_f(t)$ for the case with infinite κ. $k_f^0(t)$ denotes the Smoluchowski result given by Eq. (3.10), which neglects the inertial dynamic effect. The values of τ_D in the legend are given in units of $t_D(= \sigma^2/D)$.
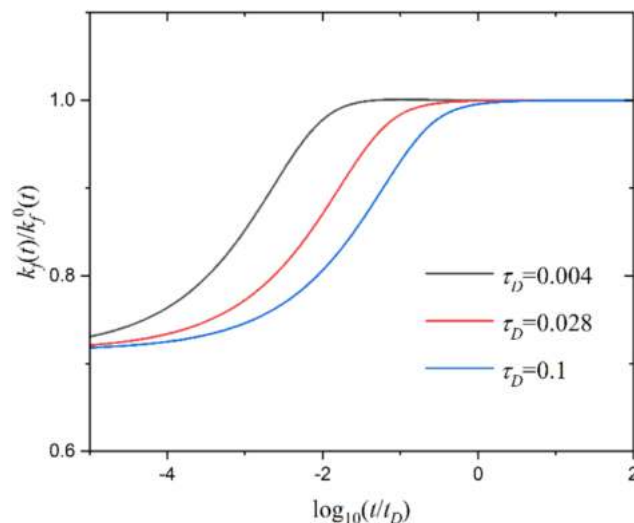

FIG. 2. Inertial dynamic effects on the time-dependent bimolecular rate coefficient $k_f(t)$ when $\kappa = \kappa_{kin}$; see Eq. (3.7). $k_f^0(t)$ denotes the Smoluchowski result given by Eq. (3.10), which neglects the inertial dynamic effect. The values of τ_D in the legend are given in the units of $t_D(= \sigma^2/D)$.

When κ goes to infinity, Eq. (3.11) reduces to

$$\hat{R}(r_0, s) = \frac{\sigma}{r_0}e^{-\zeta(r_0 - \sigma)}. \quad (3.12)$$

From Eqs. (2.35) and (3.12), the time-dependent survival probability is given by[45]

$$
W(r_0, t) = 1 - \Theta(t - \chi) \frac{\sigma}{r_0} \left\{ \exp\left(-\frac{r_0 - \sigma}{2\sqrt{D\tau_D}} \right) \right.
$$
$$
\left. + \frac{r_0 - \sigma}{2\sqrt{D\tau_D}} \int_\chi^t d\tau \, \exp\left(-\frac{\tau}{2\tau_D} \right) \frac{I_1\left(\sqrt{\tau^2 - \chi^2}/(2\tau_D) \right)}{\sqrt{\tau^2 - \chi^2}} \right\}.
$$
(3.13)

Here, $\Theta(z)$ and $I_1(z)$ are the Heaviside step function and the modified Bessel function of the first kind, respectively. χ is an important kinetic parameter defined by

$$
\chi = (\tau_D/D)^{1/2}(r_0 - \sigma) = (r_0 - \sigma)/c_D.
$$
(3.14)

It measures the time required for the geminate pair to approach the contact distance σ starting from the initial distance r_0 and depends significantly on the velocity relaxation time τ_D. In other words, χ is the time for passing the distance $r_0 - \sigma$ by the diffusive wave. This time is zero when $\tau_D = 0$. This reflects a known paradox that the classical diffusion equation predicts an infinite propagation velocity of a diffusive perturbation.[46]

When $\tau_D = 0$, from Eqs. (2.35) and (3.12), the time-dependent survival probability is given by[3]

$$
W(r_0, t) = 1 - \frac{\sigma}{r_0} \mathrm{erfc}\left(\frac{r_0 - \sigma}{2\sqrt{Dt}} \right).
$$
(3.15)

Figure 3 displays the results calculated from Eqs. (3.13) and (3.15) for the three values of τ_D, 0, 0.028, and 0.1 in units of t_D. The initial distance r_0 between the geminate reactants is set to 2σ. From Eqs. (3.13) and (3.14), we see that the survival probability starts to decay when $t > \chi$. When $\tau_D = 0$, the geminate recombination starts too early, considering the physical time required for the reactants to arrive at the contact distance starting from the initial distance r_0. The inertial dynamic effects are manifested distinctively at short times. However, for $t > t_D$, the inertial dynamic effects die out rapidly.

In the case with finite values of κ and τ_D, we do not have an explicit time-domain expression for the survival probability. When $\tau_D = 0$, the inverse Laplace transformation of Eq. (2.35) with Eq. (3.11) gives the following expression:[3,45]

$$
W(r_0, t) = 1 - \frac{\sigma}{r_0} \frac{\kappa/k_D}{1 + \kappa/k_D} \left\{ \mathrm{erfc}\left[\frac{r_0 - \sigma}{2(Dt)^{1/2}} \right] \right.
$$
$$
\left. - \exp\left[-\frac{(r_0 - \sigma)^2}{4Dt} \right] \Omega\left[\frac{r_0 - \sigma}{2(Dt)^{1/2}} + \left(1 + \frac{\kappa}{k_D} \right) \frac{(Dt)^{1/2}}{\sigma} \right] \right\},
$$
(3.16)

where $\Omega(z) = \exp(z^2)\mathrm{erfc}(z)$. At large s values, Eq. (3.11) behaves as

$$
\hat{R}(r_0, s) \cong \frac{\sigma}{r_0} \frac{\kappa/k_D}{(D\tau_D)^{-1/2}\sigma + (\kappa/k_D)} e^{-\zeta(r_0 - \sigma)}.
$$
(3.17)

Comparing Eq. (3.17) with Eq. (3.12), we expect that $W(r_0, t)$ drops abruptly at $t \cong \chi$ also in the case with finite values of κ and τ_D.
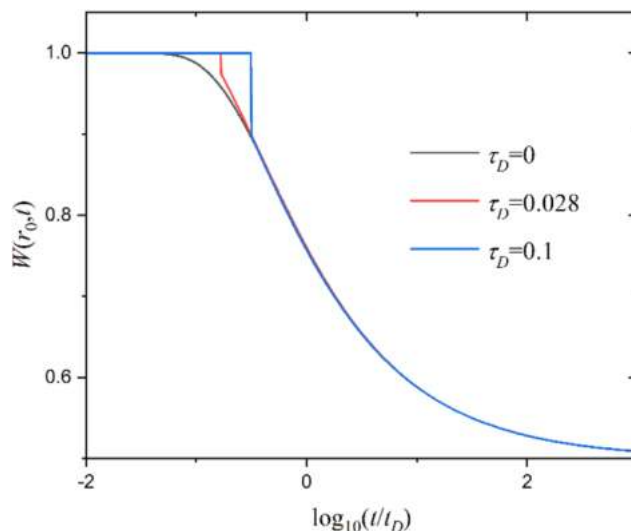

FIG. 3. Inertial dynamic effects on the time-dependent survival probability $W(r_0, t)$ for the case with infinite κ. The initial distance r_0 between the geminate reactants is set to 2σ. The values of τ_D in the legend are given in units of $t_D(= \sigma^2/D)$.

Because most numerical methods of inverse Laplace transformation do not produce the step function behavior faithfully, we take the approximation that $W(r_0, t \le \chi) = 1$. For $t > \chi$, the numerical inverse Laplace transformation works beautifully.

Figure 4 displays the time dependence of $W(r_0, t)$ for the cases with finite κ. The value of κ_{kin} in Eq. (3.7) depends on the value of τ_D. If we take σ and $t_D(= \sigma^2/D)$ as the units of length and time, respectively, then κ_{kin}/k_D is 2.38 for $\tau_D = 0.028$ and 1.26 for $\tau_D = 0.1$. We thus set the value of κ/k_D to 2. The initial distance r_0 between
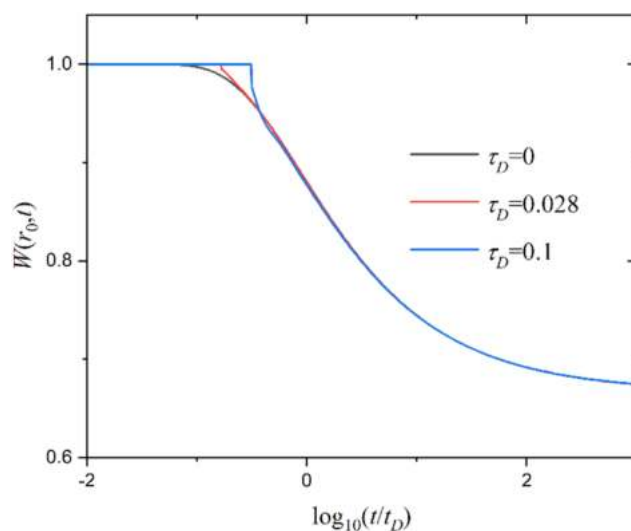

FIG. 4. Inertial dynamic effects on the time-dependent survival probability $W(r_0, t)$ when $\kappa = 2k_D$. The initial distance r_0 between the geminate reactants is set to 2σ. The values of τ_D in the legend are given in units of $t_D(= \sigma^2/D)$.

the geminate reactants is set to 2σ. $W(r_0, t)$ for $\tau_D = 0$ was calculated from Eq. (3.16), whereas those for $\tau_D = 0.028$ and 0.1 were calculated by numerical inverse Laplace transformation by using the Stehfest algorithm with the approximation $W(r_0, t \leq \chi) = 1$. The inertial dynamic effect on the survival probability is qualitatively similar to the cases with infinite κ.

We see that in Figs. 3 and 4, the survival probability at $\tau_D > 0$ has a discontinuity of the first kind. This behavior is similar to that was revealed and reported previously for both heat and diffusion transfer in media with finite times of relaxation τ_D (see, e.g., Refs. 47 and 48).

When $r_0 = \sigma$, the inertial dynamic effects on the survival probability can be easily envisaged from the relation (2.36) and Figs. 1 and 2.

IV. CONCLUDING REMARKS

In this work, we have investigated the inertial dynamic effects on the kinetics of diffusion-influenced reactions. Both bulk and geminate recombination rates are considered in the low reactant concentration limit. When the interaction potential between the reactants can be neglected, we presented exact expressions for the Laplace transforms of the bimolecular rate coefficient [Eq. (3.5)] and the geminate reaction rates [Eq. (3.11)]. When the intrinsic reaction rate constant κ goes to infinity, explicit time-domain expressions were also presented; the time-dependent bimolecular rate coefficient in Eq. (3.8) and the time-dependent survival probability of the geminate reactant pair in Eq. (3.13). The bimolecular rate coefficient expression in Eq. (3.8) coincides with that obtained by Rice without derivation [Eq. (289) of Ref. 3], whereas the survival probability expression in Eq. (3.13) has been first obtained in this work. The Laplace transform expressions for the bimolecular rate coefficient [Eq. (3.5)] and the geminate reaction rates [Eq. (3.11)] have also been obtained for the first time in the present work.

It is of interest that when the value of intrinsic reaction rate constant κ is set equal to twice the kinetic rate constant κ_{kin} of dilute gases [Eq. (3.7)], the Laplace transform expression for the bimolecular rate coefficient in Eq. (3.5) coincides with that obtained by Harris[16] and Ibuki and Ueno[40] from approximate solutions of the Fokker–Planck–Klein–Kramers equation and independently derived with the aid of a path-integral approach by Berezhkovskii et al.[7]

Because of the inertial dynamic effects, both the rates of bulk and geminate recombination are retarded appreciably at short times. An interesting finding in regard to the geminate recombination rate is that in the presence of an inertial effect, the geminate reaction can occur only after time elapsed by χ as defined by Eq. (3.14). When the inertial dynamic effect is neglected, even for the case with $r_0 > \sigma$, the geminate recombination may occur immediately after the reaction is initiated, although the rate may be very small at early times. This reflects a known paradox that the classical diffusion equation predicts an infinite propagation velocity of a diffusive perturbation.[44]

AUTHOR DECLARATIONS

Conflict of Interest

The authors have no conflicts to disclose.

Author Contributions

Sangyoub Lee: Conceptualization (equal); Data curation (lead); Formal analysis (lead); Funding acquisition (equal); Investigation (equal); Methodology (lead); Project administration (equal); Resources (equal); Software (equal); Validation (equal); Visualization (equal); Writing – original draft (equal); Writing – review & editing (equal). **Sergey D. Traytak**: Conceptualization (equal); Formal analysis (supporting); Funding acquisition (equal); Investigation (equal); Methodology (supporting); Project administration (equal); Resources (equal); Validation (equal); Writing – review & editing (equal).

DATA AVAILABILITY

The data that support the findings of this study are available within the article.

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