

# Articles

## Reversible Excited-State Proton Transfer: Effect of the Switching of Interaction Potential by Reaction

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In the reaction  $A + B \rightleftharpoons C$ , where A and B are ionic reactants having opposite charges, a B molecule approaching an A will experience a switching of the interaction potential when the A molecule is captured by one of the other B molecules in the medium. In the reversible case, the former B molecule still has a chance to react with the A, so that one needs to take into account the switched interaction between the reactant B and the product C as well as that between the reactants to treat the kinetics accurately. It is shown that this kind of interaction potential switching affects the relaxation kinetics in an intriguing way as observed in a recent experiment on an excited-state proton transfer reaction.

**Key Words :** Excited-state proton transfer, Reversible diffusion-influenced reaction, Effects of reactant force field

### Introduction

Relaxation kinetics methods have been widely used to measure the forward and reverse reaction rates of very rapid reactions.<sup>1,2</sup> These methods usually assume that the chemical relaxation proceeds exponentially. However, when the molecular diffusion is slow compared to the inherent reaction rate, the long-time relaxation follows power-law decay.<sup>3-5</sup> In addition, the relaxation kinetics at an intermediate time can be quite complicated due to the many-particle effects.

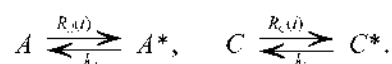
To get a better understanding on the many-particle effects, the reversible association-dissociation reaction,  $A + B \rightleftharpoons C$ , has been studied intensively over the last decade from various theoretical perspective,<sup>3-22</sup> and also via experiments<sup>23-29</sup> and computer simulations.<sup>9,12,30-33</sup> From these efforts, a very accurate analytic theory has finally emerged, which is in almost perfect agreement with computer simulation results over the whole time range,<sup>21</sup> and an exact analytic result has also been obtained for the asymptotic relaxation kinetics.<sup>5</sup> However, when there is a strong interaction potential between the reactants, an accurate theory applicable over the whole time range is still lacking. In this paper, we extend the many-particle kernel (MPK) theory developed in Refs. and to take into account the effect of Coulomb interaction potential between reactants.

The theory will be developed in the context of the reversible excited-state proton transfer reaction, which can be represented schematically as  $AH^* \rightleftharpoons A^{*-} + H^+$ . In a solution, the proton is coordinated with a solvent molecule, which is implicit in the scheme. By lowering the pH value of solution, we may have  $[H^+] \gg [AH^*] - [A^{*-}]$ . The theory can be applied to this pseudo-first-order case as well as the

geminate recombination case. An interesting aspect of this reaction system is that  $H^+$  ions approaching an  $A^{*-}$  will experience a switching of the interaction potential when the  $A^{*-}$  molecule is captured by one of the  $H^+$  ions. None of the previous theories dealt with this dichotomously fluctuating potential field effect. Therefore, the present theoretical extension would help to understand the subtle relaxation kinetic behaviors observed for an excited-state proton transfer reaction system.

### Theory

We will consider a general reaction scheme,  $A^* + B \rightleftharpoons C^*$ , where  $A^*$  and B molecules have opposite charges of the same magnitude. The excited-state molecules  $A^*$  and  $C^*$  are generated from the ground-state molecules A and C by external illumination at appropriate wavelengths, and may undergo unimolecular decays:



$R_A(t)$ ,  $R_C(t)$ ,  $k_A$  and  $k_C$  are the associated rate coefficients. We will assume that  $A^*$  as well as  $C^*$  is immobile. When a mobile B molecule comes into contact with an  $A^*$  at a distance  $\sigma$ , they form a  $C^*$  with an intrinsic bimolecular rate constant  $k_f$ . Then the  $C^*$  molecule may dissociate back into  $A^*$  and B at a separation  $\sigma$  with rate constant  $k_r$ . All molecules are assumed to be spherical.

In the usual experimental situations, the external illumination is weak enough that the concentrations of the excited species are very small compared to those of ground-state species. Then the number densities of ground-state A and C

molecules, denoted by  $C_A$  and  $C_C$ , can be considered to remain constant. We denote the time-dependent number densities of  $A^*$  and  $C^*$  molecules by  $a^*(t)$  and  $c^*(t)$ , while the number density of excess B molecules as  $C_B$ .

The rate equations for  $a^*(t)$  and  $c^*(t)$  was given in Appendix A of Ref. 22. In the Laplace domain [ $\hat{f}(s) \equiv \int_0^\infty dt e^{-st} f(t)$ ], they can be rewritten as

$$(s - k_A)\hat{a}^*(s) - \hat{R}_A(s)C_A = -[(s + k_C)\hat{c}^*(s) - \hat{R}_C(s)C_C] \\ = -\kappa_f \hat{C}_{A^*B}(\sigma, s) + k_r \hat{c}^*(s) \equiv \hat{\alpha}(s). \quad (1)$$

Here,  $C_{A^*B}(r, t)$  is the two-particle reduced distribution function (RDF) that represents the product of the average number densities of  $A^*$  and B molecules at the two locations separated by  $r$ . Its time evolution is governed by the following equation,<sup>22</sup>

$$s\hat{C}_{A^*B}(r, s) = L_{A^*B}(r)\hat{C}_{A^*B}(r, s) \\ - k_A \hat{C}_{A^*B}(r, s) + \hat{R}_A(s)C_A C_B g_{AB}(r) \\ - \frac{\partial(r - \sigma)}{4\pi\sigma^2} \hat{\alpha}(s) - \kappa_f \hat{C}_{A^*BB}(r, \sigma, s) - k_r \hat{C}_{C^*B}(r, s). \quad (2)$$

$L_{A^*B}$  denotes the Smoluchowski operator governing the thermal motion of B under the interaction potential of  $A^*$ . Its explicit expression is given by

$$L_{A^*B}(r)f(r) = D\left(\frac{\partial}{\partial r} - \frac{2}{r}\right)\left(\frac{\partial f}{\partial r} + f\frac{\partial U}{\partial r}\right),$$

where  $D$  is the diffusion constant of B's and  $U$  is the interaction potential in units of thermal energy  $k_B T$ . The second and the third terms on the right hand side of Eq. (2) describe the unimolecular decay and generation process of  $A^*$ -B pairs, while the fourth term describes the bimolecular process between the pairs.  $g_{AB}(r)$  is the equilibrium pair correlation function given by  $e^{-U}$ . The last two terms bring in the many-particle effects on the mean-field pair dynamics. If we neglect these many-particle competition terms in Eq. (2), the problem becomes easily solvable but the applicable range of the solution is limited to the very low  $C_B$  case.  $\hat{C}_{A^*BB}(r, \sigma, s)$  denotes the three-particle RDF between  $A^*$  and two B molecules separated by  $r$  and  $\sigma$ , while  $\hat{C}_{C^*B}(r, s)$  denotes the two-particle RDF between  $C^*$  and B molecules. The evolution equation for  $\hat{C}_{C^*B}(r, s)$  is given by<sup>22</sup>

$$s\hat{C}_{C^*B}(r, s) = L_{C^*B}(r)\hat{C}_{C^*B}(r, s) \\ - k_C \hat{C}_{C^*B}(r, s) - \hat{R}_C(s)C_C C_B g_{CB}(r) \\ - \kappa_f \hat{C}_{A^*BB}(r, \sigma, s) + k_r \hat{C}_{C^*B}(r, s). \quad (3)$$

$L_{C^*B}$  is the Smoluchowski operator governing the thermal motion of B against the uncharged product molecule  $C^*$ ,

$$L_{C^*B}(r)f(r) = D\left(\frac{\partial^2}{\partial r^2} + \frac{2}{r}\frac{\partial}{\partial r}\right)f(r),$$

and  $g_{CB}(r) = 1$ . The boundary conditions associated with Eqs. (2) and (3) are given by  $\lim_{r \rightarrow \infty} \hat{C}_{A^*B}(r, s) = \hat{a}^*(s)C_B g_{AB}(r)$ , and  $\lim_{r \rightarrow \infty} \hat{C}_{C^*B}(r, s) = \hat{c}^*(s)C_B g_{CB}(r)$ , respectively.

Equations (2) and (3) involve the three-particle RDF  $\hat{C}_{A^*BB}$ , whose evolution equation again involves the higher order RDF functions in a hierarchical manner. The difference between  $L_{A^*B}$  and  $L_{C^*B}$  renders the complicated many-particle problem even more difficult to solve. To tackle this formidable problem, we choose to employ the simpler version of the MPK theory as presented in Ref. 22. This version of the MPK theory, which we called the MPK2 theory, is mathematically much simpler, though less accurate, than the full MPK theory developed in Ref. 21. It was shown that, for a reaction between the neutral reactants, the MPK2 theory gives quite accurate results unless  $K_{eq}C_B$  is very large ( $K_{eq}$  is the equilibrium constant of the reaction). And we note that the parameters of the experimental system that we are concerned with are well in the applicable range of the MPK2 theory.

We will first present *exact* relations that can be derived in the framework of MPK theory. The rate equation given in Eq. (1) can be put into a non-Markovian rate equation:

$$\hat{\alpha}(s) \equiv -\kappa_f \hat{C}_{A^*B}(\sigma, s) + k_r \hat{c}^*(s) \\ = -\hat{k}_f(s)C_B \hat{a}^*(s) + \hat{k}_r(s)\hat{c}^*(s). \quad (4)$$

where  $\hat{\alpha}(s)$  is the quantity defined in Eq. (1). The rate kernels  $\hat{k}_f(s)$  and  $\hat{k}_r(s)$ , associated with the forward association and the reverse dissociation reactions respectively, are given by

$$\frac{\hat{k}_f(s)}{k_f^{eq}} = \frac{\hat{k}_r(s)}{k_r^{eq}} = \frac{1}{\hat{F}(s)}; \\ \hat{F}(s) = 1 + \kappa_f \Delta \hat{C}_{A^*B}(\sigma, s) / \hat{\alpha}(s), \quad (5)$$

with  $\Delta \hat{C}_{A^*B}(r, s) \equiv \hat{C}_{A^*B}(r, s) - a^*(s)C_B g_{AB}(r)$ . When the molecular diffusion occurs very rapidly, the diffusion effect function  $\hat{F}(s)$  becomes unity, and the rate kernels reduce to the equilibrium rate constants,  $k_f^{eq}$  and  $k_r^{eq}$ . The usual experimental observable is the probability  $Y_C(t|C)$  that a  $C^*$  molecule created at  $t = 0$  will be found as the  $C^*$  at the time  $t$ . Its Laplace transform is given as

$$\hat{Y}_C(s|C) \\ = [s_A + \hat{k}_f(s)C_B] / [s_A s_C + s_C \hat{k}_f(s)C_B + s_A \hat{k}_r(s)], \quad (6)$$

where  $s_A = s + k_A$  and  $s_C = s + k_C$ . It can be seen that  $\hat{Y}_C(s|C)$  can be calculated once  $\hat{F}(s)$  has been determined.

To find an expression for  $\hat{F}(s)$ , we need to solve the coupled Eqs. (2) and (3). At this point, we introduce the truncation approximation of the MPK2 theory,<sup>22</sup>

$$-\kappa_f \hat{C}_{A^*BB}(r, \sigma, s) + k_r \hat{C}_{C^*B}(r, s) \\ \cong -\hat{k}_f(s)C_B \hat{C}_{A^*B}(r, s) + \hat{k}_r(s)\hat{C}_{C^*B}(r, s). \quad (7)$$

Equation (7) is an higher-order analogue of Eq. (4). The

situation considered in Eq. (7) differs from that considered in Eq. (4) in that there is a third  $B$  molecule at the location separated by  $r$  from  $A^*$  (or  $C^*$ ) molecule in addition to the  $B$  molecule that is in contact and undergoing reaction with  $A^*$  molecule. Hence, Eq. (7) implies that the forward and reverse reaction rate kernels are little affected by the presence of the  $B$  molecule at the separation  $r$ . With this approximation, we can solve Eqs. (2) and (3) to obtain  $\Delta\hat{C}_{A^*B}(r, s) = \hat{\alpha}(s)\hat{G}_T(r, \sigma, s)$  (see Appendix for details of derivation). Substituting this relation into Eq. (5), we get

$$\hat{F}(s) = 1 - \kappa_f \hat{G}_T(\sigma, \sigma, s), \quad (8)$$

where  $\hat{G}_T$  is the reaction Green's function that is defined as

$$\begin{aligned} \hat{G}_T(r, r_0, s) &= \{ [s_C + \hat{k}_r(s) - L_0][s_A - \hat{k}_r(s)C_B - L_0 - \Delta L] \\ &- \hat{k}_r(s)\hat{k}_r(s)C_B \}^{-1} [s_C - \hat{k}_r(s) - L_0] \frac{\delta(r-r_0)}{4\pi r_0^2} \\ &= \left[ 1 - \left( \frac{\mu_1}{s_- - L_0} + \frac{\mu_2}{s_- - L_0'} \right) \Delta L \right]^{-1} \left( \frac{\mu_1}{s_- - L_0} - \frac{\mu_2}{s_- - L_0'} \right) \frac{\delta(r-r_0)}{4\pi r_0^2}. \end{aligned} \quad (9)$$

Here,  $L_0 = L_{C^*B}$ ,  $\Delta L = L_{A^*B} - L_{C^*B}$ ,  $\mu_1 = \{\chi_+ - [k_C + \hat{k}_r(s)]\} / (\chi_+ - \chi_-)$ ,  $\mu_2 = 1 - \mu_1$ , and  $s_{\pm} = s - \chi_{\pm}$  with

$$\begin{aligned} \chi_{\pm} &= \{v(s) \pm [v(s)^2 - 4z(s)]^{1/2}\} / 2, \\ v(s) &= k_A + k_C - \hat{k}_r(s)C_B - \hat{k}_r(s), \\ z(s) &= k_A k_C - k_C \hat{k}_r(s)C_B + k_A \hat{k}_r(s). \end{aligned}$$

Now the remaining task is to obtain an explicit expression for the reaction Green's function  $\hat{G}_T$ . Using the relation,  $(1 - X)^{-1} = \sum_{n=0}^{\infty} X^n$ , we can expand the operator on the right side of Eq. (9) to obtain the following Dyson-like series:

$$\begin{aligned} \hat{G}_T(r, r_0, s) &= \sum_{n=0}^{\infty} \left[ \left( \frac{\mu_1}{s_- - L_0} - \frac{\mu_2}{s_- - L_0'} \right) \Delta L \right]^n \\ &\times \left( \frac{\mu_1}{s_- - L_0} - \frac{\mu_2}{s_- - L_0'} \right) \frac{\delta(r-r_0)}{4\pi r_0^2}. \end{aligned} \quad (10)$$

This equation can be rewritten as (see Appendix for details of derivation)

$$\begin{aligned} G_T(r, r_0, s) &= [\hat{M} + \hat{N} + \hat{M} \bullet \hat{N} - \hat{N} \bullet \hat{M} \\ &- \hat{M} \bullet \hat{N} \bullet \hat{M} - \hat{N} \bullet \hat{M} \bullet \hat{N} + \dots] \frac{\delta(r-r_0)}{4\pi r_0^{d-1}}, \end{aligned} \quad (11)$$

where  $\bullet \equiv \Delta L$ , and  $\hat{M}$  and  $\hat{N}$  are the propagation operators defined by

$$\hat{M} \equiv \sum_{n=0}^{\infty} \left( \frac{\mu_1}{s_- - L_0} \Delta L \right)^n \frac{\mu_1}{s_- - L_0} = \frac{\mu_1}{s_- - L_0 - \mu_1 \Delta L} \quad (12)$$

$$\hat{N} \equiv \sum_{n=0}^{\infty} \left( \frac{\mu_2}{s_- - L_0} \Delta L \right)^n \frac{\mu_2}{s_- - L_0} = \frac{\mu_2}{s_- - L_0 - \mu_2 \Delta L}. \quad (13)$$

For the sake of clarity, we present detailed derivation procedures of Eqs. (9) and (11) in Appendix. Because  $\mu_1$  and  $\mu_2$  have values between 0 and 1, the series in Eq. (11) converges. Especially when either  $\mu_1$  or  $\mu_2$  is close to 0, the series converges quite rapidly. This is the case when the reactant density is very low so that  $\sigma^2 C_B \ll 1$ . By keeping only the first four terms in Eq. (11), we get

$$\begin{aligned} \hat{G}_T(r, r_0, s) &\cong \mu_1 \hat{G}_M(r, r_0, s) + \mu_2 \hat{G}_N(r, r_0, s) \\ &- 4\pi r_C D \mu_1 \mu_2 \int_{\sigma}^{\infty} dr_1 \hat{G}_M(r, r_1, s) \frac{\partial}{\partial r_1} \hat{G}_N(r_1, r_0, s) \\ &- 4\pi r_C D \mu_1 \mu_2 \int_{\sigma}^{\infty} dr_1 \hat{G}_N(r, r_1, s) \frac{\partial}{\partial r_1} \hat{G}_M(r_1, r_0, s). \end{aligned} \quad (14)$$

where  $\mu_1 \hat{G}_M(r, r_0, s) \equiv \hat{M} \frac{\delta(r-r_0)}{4\pi r_0^2}$  and  $\mu_2 \hat{G}_N(r, r_0, s) = \hat{N} \frac{\delta(r-r_0)}{4\pi r_0^2}$ . We then make the following approximations which are basically assuming weak interaction potential:  $\hat{G}_M(r, r_1, s) \approx \hat{G}_M(r_1, r, s)$  and  $\hat{G}_N(r, r_1, s) \approx \hat{G}_N(r_1, r, s)$ . This helps us to rewrite Eq. (14) in a much simpler form. When  $r = r_0$ , we have

$$\begin{aligned} \hat{G}_T(r, r, s) &\cong \mu_1 \hat{G}_M(r, r, s) + \mu_2 \hat{G}_N(r, r, s) \\ &+ 4\pi r_C D \mu_1 \mu_2 \hat{G}_M(r, \sigma, s) \hat{G}_N(\sigma, r, s) \end{aligned} \quad (15)$$

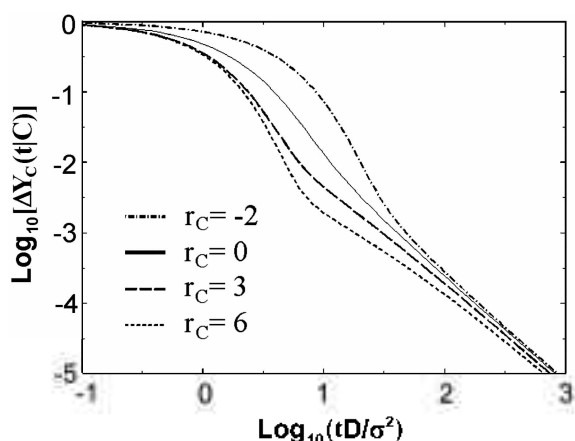
From the definitions of the operators,  $\hat{M}$  and  $\hat{N}$ , given in Eqs. (12) and (13), we can easily see that  $\hat{G}_M(r, r, s) = \hat{G}^{DS}(r, r, s; \mu_1)$  and  $\hat{G}_N(r, r, s) = \hat{G}^{DS}(r, r, s; \mu_2)$  are the Green's function for the Debye-Smoluchowski equation with the potential of mean force scaled by  $\mu_i U(r)$ . When  $U(r) = -r_C/r$ , with  $r_C$  denoting the Onsager distance at which the Coulomb energy is equal to the thermal energy, explicit expression for  $\hat{G}^{DS}(r, r_0, s; 1)$  was derived by Hong and Noolandi.<sup>34</sup>

With the expression for the reaction Green's function  $\hat{G}_T(\sigma, \sigma, s)$  given by Eq. (15), we can calculate the diffusion-effect function  $\hat{F}(s)$  from Eq. (8), and in turn the rate kernels and the survival probability from Eqs. (5) and (6), respectively. It should be noted that, in the limit of  $C_B \rightarrow 0$ , the present solution recovers the exact result for the isolated-pair problem. Although an exact expression for  $\hat{G}^{DS}$  is available, the following simpler approximate expression will be used:

$$\begin{aligned} \hat{G}^{DS}(\sigma, \sigma, s; r_C) &\cong \hat{G}_{DS}^0(\sigma, \sigma, s; r_C) \\ &= \frac{\exp(r_C/\sigma)}{4\pi\sigma_{eff}D} \frac{1}{1 + \sigma_{eff}\sqrt{s/D}} \end{aligned} \quad (16)$$

where the effective contact distance  $\sigma_{eff}$  is given by

$$\begin{aligned} \sigma_{eff}(r_C) &= \left\{ \int_{\sigma}^{\infty} dr \exp[-r_C/r] r^{-2} \right\}^{-1} \\ &= r_C [1 - \exp(-r_C/\sigma)]^{-1}. \end{aligned}$$

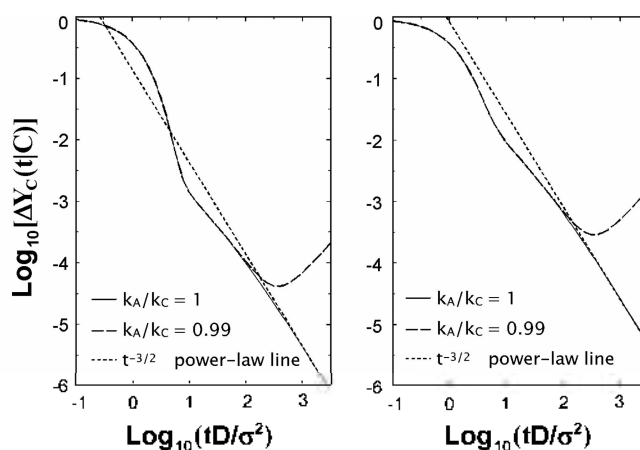


**Figure 1.** Dependence of the  $\Delta Y_C(t|C)$  curves on the magnitudes of Coulombic interaction.

### Results and Discussion

When  $k_A = k_C$ , the number density of  $C^*$  decays as  $K_{eq}C_B(1 + K_{eq}C_B)^{-1}\exp(-k_C t)$  at long times. Therefore,  $\Delta Y_C(t|C) = Y_C(t|C)\exp(k_C t) - K_{eq}C_B(1 + K_{eq}C_B)$  is the usual quantity reported in experiment to characterize the relaxation behavior of the reversible association reactions. In Figure 1, we compare the  $\Delta Y_C(t|C)$  curves for systems with different magnitudes of Coulombic interaction. The values of parameters used in Figure 1 are  $k_A^{0q}/4\pi\sigma D = 1$ ,  $k_r\sigma^2/D = 1$ , and  $4\pi\sigma^3 C_B = 0.1$ . We see that when there is an attractive Coulombic interaction between  $A^*$  and  $B$ , after the initial fast decaying phase, there emerges an intermediate phase in which the relaxation curve shows a slower decay than the asymptotic  $t^{-3.2}$  power-law decay. The relaxation curve at this intermediate time interval cannot be described by either of the exponential and the power-law function with a single exponent, but follows  $t^{-\beta(t)}$  with time-dependent exponent  $\beta(t)$  that is an increasing function and converges to at long times. In contrast, when there is a repulsive Coulomb interaction between  $A^*$  and  $B$ ,  $\beta(t)$  is a decreasing function that converges to . This intermediate phase is absent in the relaxation curve for the reaction between neutral reactant for which  $r_C = 0$ . In addition, one can see that the amplitude of the asymptotic  $t^{-3.2}$  power-law depends on the value of  $r_C$ . For the reversible association reaction between neutral molecules, the linearized enhanced superposition approximation (LESA)-based RDF theory is known to give an exact asymptotic solution.<sup>3-5</sup> The LESA results for the reactions between ionic reactants can be obtained simply by replacing  $y(s)$  and  $z(s)$  in Eq. (9) with  $y^{LESA}(s) = k_A - k_C - k_A^0 C_B + k_r$  and  $z^{LESA}(s) = k_A k_C + k_C k_A^0 C_B + k_A k_r$ , respectively. Therefore, for the case with  $k_A = k_C$ , the asymptotic behavior of  $Y_C(t|C)$  can be obtained as

$$Y_C^{LESA}(t|C)\exp(k_C t) \approx \frac{K_{eq}C_B}{1 + K_{eq}C_B} + \frac{K_{eq}\exp(-\mu_1^0 r_C / \sigma)}{(1 + K_{eq}C_B)^3} \times \left[ 1 - \frac{1 - \exp(-\mu_1^0 r_C / \sigma)}{1 + \sqrt{2\sigma_M^2/D}} \right] (4\pi D t)^{-3/2}, \quad (17)$$



**Figure 2.** Dependence of the  $\Delta Y_C(t|C)$  curves on the relative magnitude of the unimolecular decay rate constants of  $A^*$  and  $C^*$ .

where  $\sigma_M = \sigma_{eff}(\mu_1 r_C)$  and  $\mu_1^0 = K_{eq}C_B(1 + K_{eq}C_B)^{-1}$ . Eq. (17) indicates that the amplitude of the asymptotic power-law decay is a decreasing function of  $\mu_1^0 r_C$ , so that the dependence of the power-law amplitude on  $r_C$  becomes more noticeable as  $K_{eq}C_B$  increases. This reflects the fact that the Coulombic interaction plays its role not through the dissociation reaction but through the association reaction. For  $r_C = 0$ , Eq. (17) reduces to the exact result known for the reaction between neutral reactants.<sup>5</sup>

Figure 2 shows that the amplitude of the asymptotic power-law predicted by the LESA theory is practically the same as that predicted by the MPK2 theory for the system with Coulombic interaction, when  $K_{eq}C_B$  is not too large. However, when  $K_{eq}C_B \gg 1$ , there is a noticeable discrepancy between the power-law amplitudes predicted by the two theories. The parameters used for Figure 2 has the same order of magnitude with those for typical excited-state proton transfer reaction in acidified water:  $k_r\sigma^2/D = 1$ ,  $4\pi\sigma^3 C_B = 1.26 \times 10^{-2}$ ,  $r_C = 6\sigma$ ,  $k_C = 10^{-3}\sigma^2/D$ . The value of  $k_A^{0q}/4\pi\sigma D$  is 0.5 in (a) and 4 in (b). Note that even a very small difference in the lifetimes of  $A^*$  and  $C^*$  prevents the  $\Delta Y_C(t|C)$  curve from reaching the asymptotic  $t^{-3.2}$  power-law relaxation phase ultimately, which is one of the characteristics of the reversible association reactions in the absence of the reactant decay. For the time region where  $t > O(|k_A - k_C|^{-1})$  the time-dependence of is mostly determined by the different rate of uni-molecular decaying processes of  $A^*$  and  $C^*$ . Therefore, one should not neglect just mentioned effects in analyzing the experimental data obtained after  $t = |k_A - k_C|^{-1}$ .

Figure 2(a) also shows that, for a small value of  $k_A^{0q}$ , the  $\Delta Y_C(t|C)$  curve first goes above the asymptotic power-law line at short times, then it goes below the line due to the presence of the reaction-driven fluctuation of interaction potential and approaches the asymptotic power-law line from below. However, for a large value of  $k_A^{0q}$ , it is possible that such cross between the  $\Delta Y_C(t|C)$  curve and the asymptotic power-law line does not occur. In any case, the  $\Delta Y_C(t|C)$  curve cannot go above the power-law line at asymptotic region when the lifetimes of  $A^*$  and  $C^*$  are

identical.

In summary, we have presented a theory dealing with the effects of reaction-driven fluctuation of interaction potential on the diffusion-influenced kinetics of reversible reactions. We have found that the relaxation curve displays an interesting non-monotonous power-law relaxation behavior in the intermediate time region that follows  $t^{-\beta(t)}$  with the time-dependent exponent  $\beta(t)$ , before  $t^{-3/2}$  asymptotic power-law relaxation phase is reached. The value of  $\beta(t)$  is less than 3/2 for the system with attractive Coulomb potential, while it is larger than 3/2 for the system with repulsive Coulomb potential, but in either case it converges to 3/2. We expect that the present theory would help to disclose the effects of various reaction parameters on the  $\Delta Y_C(t/C)$  curve that may be observed in experiments.

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Appendix

Here we present the details of derivation of Eqs. (9) and (11). Invoking the truncation approximation, Eq. (7), of the MPK2 theory, one can rewrite Eqs. (2) and (3) as

$$s_{\pm} \Delta \hat{C}_{\pm}^{A^*B}(r, s) = L_{\pm}^{A^*B}(r) \Delta \hat{C}_{\pm}^{A^*B}(r, s) + \frac{\delta(r - \sigma)}{4\pi\sigma^2} \hat{\alpha}(s) - \hat{k}_{\pm}(s) C_B \Delta \hat{C}_{\pm}^{A^*B}(r, s) + \hat{k}_{\pm}(s) \Delta \hat{C}_{C^*B}(r, s) + \hat{k}_{\pm}(s) \hat{\alpha}^*(s) C_B [g_{C^*B}(r) - g_{LB}(r)] \quad (A1)$$

and

$$s_C \Delta \hat{C}_{C^*B}(r, s) = L_{C^*B}(r) \Delta \hat{C}_{C^*B}(r, s) + \hat{k}_C(s) C_B \Delta \hat{C}_{\pm}^{A^*B}(r, s) - \hat{k}_C(s) \Delta \hat{C}_{C^*B}(r, s) + \hat{k}_C(s) C_B \hat{\alpha}^*(s) [g_{C^*B}(r) - g_{CB}(r)] \quad (A2)$$

respectively. Throughout this work we assume that interaction potential between A and B is so weak that the last terms on the right side of Eqs. (A1) and (A2) are negligible. From Eq. (A2), we get the following relation between  $\Delta C_{C^*B}$  and  $\Delta C_{\pm}^{A^*B}$ :

$$\Delta \hat{C}_{C^*B}(r, s) = \hat{k}_C(s) C_B [s_C + \hat{k}_C(s) - L_0(r)]^{-1} \Delta \hat{C}_{\pm}^{A^*B}(r, s) \quad (A3)$$

Substituting Eq. (A3) into Eq. (A1), we get

$$\Delta \hat{C}_{\pm}^{A^*B}(r, s) = \hat{\alpha}(s) \{ [s_C + \hat{k}_C(s) - L_0] [s_{\pm} + \hat{k}_{\pm}(s) C_B - L_0 - \Delta L] - \hat{k}_{\pm}(s) \hat{k}_C(s) C_B \}^{-1} \cdot [s_{\pm} + \hat{k}_{\pm}(s) - L_0] \frac{\delta(r - \sigma)}{4\pi\sigma^2} \quad (A4)$$

In Eqs. (A3) and (A4),  $L_0$  and  $\Delta L$  are given by  $L_0 = L_{C^*B}$ ,  $\Delta L = L_{\pm}^{A^*B} - L_{C^*B}$ . If we define  $\hat{G}_{\pm}(r, r_0, s)$  as

$$\hat{G}_{\pm}(r, r_0, s) = \{ [s_C + \hat{k}_C(s) - L_0] [s_{\pm} + \hat{k}_{\pm}(s) C_B - L_0 - \Delta L] - \hat{k}_{\pm}(s) \hat{k}_C(s) C_B \}^{-1} \cdot [s_{\pm} + \hat{k}_{\pm}(s) - L_0] \frac{\delta(r - r_0)}{4\pi r_0^2} \quad (A5)$$

Eq. (A4) reads as

$$\Delta \hat{C}_{\pm}^{A^*B}(r, s) = \hat{\alpha}(s) \hat{G}_{\pm}(r, \sigma, s) \quad (A6)$$

Substituting Eq. (A6) into the exact equation, Eq. (5),<sup>21,22</sup> we get Eq. (9).

Equation (10) can be obtained straightforwardly from Eq. (9). Let us define X and Y as  $X = \mu_1/(S - L_0)$  and  $Y = \mu_2/(S - L_0)$ , where we use the same notations as in Eq. (10). In terms of X and Y, Eq. (10) can be written as

$$\hat{G}_{\pm}(r, r_0, s) = [(X+Y) + (X-Y) \bullet (X-Y) - (X+Y) \bullet (X-Y) \bullet (X-Y) \bullet \dots] \frac{\delta(r-r_0)}{4\pi r_0^2} \quad (A7)$$

where  $\bullet$  represents  $\Delta L$ . The operator in the bracket in the R.H.S. of Eq. (A7) can be rewritten as follows:

$$[(X+Y) - (X-Y) \bullet (X-Y) - (X-Y) \bullet (X+Y) \bullet (X+Y) + \dots] = (X+X \bullet X - X \bullet X \bullet X - \dots) - (Y+Y \bullet Y + Y \bullet Y \bullet Y - \dots) + (X-X \bullet X + X \bullet X \bullet X - \dots) \bullet (Y-Y \bullet Y + Y \bullet Y \bullet Y - \dots) - (Y+Y \bullet Y + Y \bullet Y \bullet Y - \dots) \bullet (X+X \bullet X + X \bullet X \bullet X - \dots) - (X+X \bullet X - X \bullet X \bullet X - \dots) \bullet (Y+Y \bullet Y + Y \bullet Y \bullet Y - \dots) \bullet (X+X \bullet X + X \bullet X \bullet X - \dots) - (Y-Y \bullet Y + Y \bullet Y \bullet Y - \dots) \bullet (X+X \bullet X + X \bullet X \bullet X - \dots) - (Y-Y \bullet Y + Y \bullet Y \bullet Y - \dots) \bullet (X+X \bullet X - X \bullet X \bullet X - \dots) \bullet (Y+Y \bullet Y - Y \bullet Y \bullet Y + \dots) + \dots \quad (A8)$$

Noting that

$$(X - X \bullet X + X \bullet X \bullet X + \dots) = \sum_{n=0}^{\infty} \left( \frac{\mu_1}{s_- - L_0} \Delta L \right)^n \frac{\mu_1}{s_- - L_0} = \frac{\mu_1}{s_- - L_0 - \mu_1 \Delta L} \equiv \bar{M} (Y - Y \bullet Y + Y \bullet Y \bullet Y + \dots) = \sum_{n=0}^{\infty} \left( \frac{\mu_2}{s_- - L_0} \Delta L \right)^n \frac{\mu_2}{s_- - L_0} = \frac{\mu_2}{s_- - L_0 - \mu_2 \Delta L} \equiv \bar{N} \quad (A9)$$

one can identify Eq. (A8) with Eq. (11).

References

- Eigen, M.; Kruse, W.; Maass, G.; de Maeyer, L. *Prog. React. Kinet.* **1964**, *2*, 287.
- Bernasconi, C. F. *Relaxation Kinetics*; Academic: New York, 1976.
- Sung, J.; Shin, K. J.; Lee, S. *J. Chem. Phys.* **1997**, *107*, 9418; **1998**, *109*, 9101.
- Naumann, W.; Shokhirev, N. V.; Szabo, A. *Phys. Rev. Lett.* **1997**, *79*, 3074.
- Gopich, I. V.; Agmon, N. *Phys. Rev. Lett.* **2000**, *84*, 2730; Agmon, N.; Gopich, I. V. *J. Chem. Phys.* **2000**, *112*, 2863.
- Zel'dovich, Y. B.; Ovchinnikov, A. A. *JETP Lett.* **1977**, *26*, 440.
- Lee, S.; Karplus, M. *J. Chem. Phys.* **1987**, *86*, 1883; Erratum, *ibid.* **1992**, *96*, 1663.
- Agmon, N.; Szabo, A. *J. Chem. Phys.* **1990**, *92*, 5270.
- Szabo, A.; Zwanzig, R. *J. Stat. Phys.* **1991**, *65*, 1057.
- Szabo, A. *J. Chem. Phys.* **1991**, *95*, 2481.
- Burlatsky, S. F.; Oshanin, G. S.; Ovchinnikov, A. A. *Chem. Phys.* **1991**, *152*, 13.
- Agmon, N.; Schnörer, H.; Blumen, A. *J. Phys. Chem.* **1991**, *95*, 7326.
- Martinho, J. M. G.; Farinha, J. P.; Berberan-Santos, M. N.; Duhamel, J.; Winnik, M. A. *J. Chem. Phys.* **1992**, *96*, 8143.
- Agmon, N. *Phys. Rev. E* **1993**, *47*, 2415.
- Naumann, W.; Molski, A. *J. Chem. Phys.* **1994**, *100*, 1511.
- Molski, A.; Naumann, W. *J. Chem. Phys.* **1994**, *100*, 1520.
- Naumann, W. *J. Chem. Phys.* **1994**, *101*, 10953.
- Gopich, I. V.; Doktorov, A. B. *J. Chem. Phys.* **1996**, *105*, 2320.
- Yang, M.; Lee, S.; Shin, K. J. *Phys. Rev. Lett.* **1997**, *79*, 3783.
- Yang, M.; Lee, S.; Shin, K. J. *J. Chem. Phys.* **1998**, *108*, 9069.
- Sung, J.; Lee, S. *J. Chem. Phys.* **1999**, *111*, 796.
- Sung, J.; Lee, S. *J. Chem. Phys.* **1999**, *111*, 10159; **2000**, *112*, 2128.
- Pines, E.; Huppert, D. *J. Chem. Phys.* **1986**, *84*, 3576.
- Pines, E.; Huppert, D.; Agmon, N. *J. Chem. Phys.* **1988**, *88*, 5620.
- Agmon, N.; Pines, E.; Huppert, D. *J. Chem. Phys.* **1988**, *88*, 5631.
- Agmon, N.; Huppert, D.; Masad, A.; Pines, E. *J. Phys. Chem.* **1991**, *95*, 10407; **1992**, *96*, 2020.

27. Huppert, D.; Goldberg, S. Y.; Masad, A.; Agmon, N. *Phys. Rev. Lett.* **1992**, *68*, 3932.
  28. Solntsev, K. M.; Agmon, N. *Chem. Phys. Lett.* **2000**, *262*, 320.
  29. Solntsev, K. M.; Huppert, D.; Agmon, N. *J. Phys. Chem. A* **2001**, *105*, 5868.
  30. Edelstein, A. L.; Agmon, N. *J. Chem. Phys.* **1993**, *99*, 5396.
  31. Agmon, N.; Edelstein, A. L. *J. Chem. Phys.* **1994**, *100*, 4181.
  32. Edelstein, A. L.; Agmon, N. *J. Mol. Liq.* **1995**, *64*, 241; *J. Phys. Chem.* **1995**, *99*, 5389.
  33. Kim, H.; Yang, M.; Shin, K. J. *J. Chem. Phys.* **1999**, *111*, 1068.
  34. Hong, K. M.; Noolandi, J. *J. Chem. Phys.* **1978**, *68*, 5163, 5172; Rice, S. A.; Butler, P. R.; Pilling, M. J.; Baird, J. K. *J. Chem. Phys.* **1979**, *70*, 4001.
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