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Long-time kinetics of the excited-state association–dissociation reaction with different lifetimes

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Abstract

We consider the long-time behaviour of the reversible diffusion-influenced reaction $A + B \rightleftharpoons C$ when A and C are immobile electronically excited states and B particles are in excess. A and C have different lifetimes. When C decays faster than A , the two leading terms of the asymptotic behaviour are obtained analytically by mapping this problem onto an effective irreversible reaction. The first term is exponential, and it coincides with that obtained from conventional rate equations with steady-state diffusion-influenced rate constants. The second term in the exponent is \sqrt{t} , as in the Smoluchowski irreversible kinetics.

1. Introduction

Bimolecular reversible reactions in solution approach equilibrium not exponentially but as a power law ($t^{-3/2}$ in three dimensions). This behaviour for $A + B \rightleftharpoons C$ was first predicted [1] using physical arguments based on spatial concentration fluctuations. The basic idea is that the final approach to equilibrium is determined by the diffusion of the particles. The power law decay was subsequently obtained in various ways [2–4]. The amplitude of this decay remained elusive until recently. Analytical expressions for the amplitude of the relaxation were obtained in a few special cases [5–9] and later a complete rigorous solution of the problem for arbitrary concentrations and diffusion coefficients of the reactants was presented in [10, 11].

The problem becomes more complicated when the reaction involves excited states, A and C , with different decay rates:



One example of such a reaction is excited-state proton transfer to solvent [12, 13]. In the geminate limit (an isolated A or C), the kinetics of the above reaction can be found exactly

for arbitrary decay rates [14, 15]. Depending on the reactants' lifetimes, the concentration relaxation switches from $t^{-3/2} \exp(-k_A t)$ (when $k_A < k_C + k_r$ where $k_r = \kappa_f k_D / (\kappa_f + k_D)$ and k_D is the diffusion-controlled rate constant) to pure exponential behaviour (when $k_A > k_C + k_r$) [14, 16]. In the transition point ($k_A = k_C + k_r$), the asymptotic decay follows $t^{-1/2} \exp(-k_A t)$.

The situation changes if finite concentration of reactants is taken into account. Only when the lifetimes of A and C are equal do the concentrations decay as $t^{-3/2} \exp(-k_A t)$. The simplest generalization of the geminate case to finite concentration is the pseudo-first-order limit in which B molecules are in excess. For this case, several approximate theories have been developed [17–24]. Using ‘kinetic theory’ [18], Kwac *et al* [21] suggested that the long-time behaviour of the excited-state reversible reaction is always purely exponential (except when $k_A = k_C$). This has been tested using Brownian dynamics simulations [25]. However, the exponent of the decay was found only numerically.

In this paper we will show how to determine the leading terms of the long-time kinetics analytically for the case when C decays faster than A . In the derivation we exploit the analogy of this reversible reaction with an effective irreversible reaction $A + B \rightarrow C$ ($[B] \gg [A]$) for which the exact solution is available when A is static [26, 27].

In the following section, after formulating the problem, we give, as our main result, the long-time kinetics of the reaction and an explicit expression for the two leading terms of the asymptotics. Section 3 gives details of the derivation based on a many-particle formulation of the problem.

2. Formulation and results

Consider a static A particle surrounded by randomly distributed diffusing B s (with diffusion constant D). When a B particle approaches an A particle at distance R , they can react with the forward intrinsic rate constant κ_f to form a static C . The latter may dissociate into a contact A – B pair with the reverse intrinsic rate constant κ_r . Both A and C decay to their ground states with the rate constants k_A and k_C (see (1)). It is assumed that $k_C > k_A$. The key idea is that this process (i.e., when an A particle turns into the short-lived C after reaction with B s) can be represented as an effective irreversible reaction at long times. The irreversible reaction is exactly described by the Smoluchowski kinetics.

Our main result is that the survival probability of A in the reversible reaction, $S_{AA}(t) = [A(t)]/[A(0)]$ provided initially there were only A particles, is proportional at long times to the Smoluchowski kinetics with an effective rate coefficient:

$$S_{AA}(t) \sim \alpha \exp\left(-[B] \int_0^t k_{\text{irr}}(t') dt' - k_A t\right) \quad (2)$$

$$\alpha = \frac{k_C - k + k_r}{[B]k_f + k_r + k_A + k_C - 2k},$$

where

$$k_f = \frac{\kappa_f 4\pi DR}{\kappa_f + 4\pi DR}, \quad k_r = k_f / K_{\text{eq}} \quad (3)$$

are the steady-state rate constants (which differ from the intrinsic rate constants κ_f and κ_r), $K_{\text{eq}} = \kappa_f / \kappa_r$. The effective rate coefficient $k_{\text{irr}}(t)$ has the following Laplace transform ($\hat{\phi}(s) = \int_0^\infty \phi(t) \exp(-st) dt$):

$$\frac{1}{s\hat{k}_{\text{irr}}(s)} = \frac{1}{\kappa_f \hat{f}(-k)} + \frac{1}{s\hat{k}_D(s)} \quad (4)$$

where $s\hat{k}_D(s) = 4\pi DR(1 + \sqrt{sR^2/D})$. It differs from the well-known Collins–Kimball rate coefficient for the irreversible reaction only by the factor $\hat{f}(-k)$ in the intrinsic rate constant, where $\hat{f}(s)$ is given by

$$\hat{f}(s) = \frac{s + k_C}{s + k_C + \kappa_r} \quad (5)$$

and k is defined as the least square root of the following self-consistency relation:

$$k = [B] \frac{\kappa_f \hat{f}(-k) 4\pi DR}{\kappa_f \hat{f}(-k) + 4\pi DR} + k_A. \quad (6)$$

This equation can be readily solved:

$$k = (k_0 + k_A + k_C)/2 - \sqrt{(k_C - k_A - k_0)^2/4 + \mu k_0(k_C - k_A)} \quad (7)$$

where $k_0 = [B]k_f + k_r$ and $\mu = (1 + [B]K_{\text{eq}})^{-1}$. In the irreversible limit ($\kappa_r \rightarrow 0$ or $k_C \rightarrow \infty$), $\hat{f}(-k) = 1$, $\alpha = 1$ and equation (2) reduces to the exact result for the irreversible reaction.

At long times, the exponent in equation (2) can be further simplified by using

$$k_{\text{irr}}(t) \sim k_{\text{ss}} + \frac{k_{\text{ss}}^2}{4\pi D} \frac{1}{\sqrt{\pi Dt}}, \quad (8)$$

where $k_{\text{ss}} = k_{\text{irr}}(\infty)$ is the long-time limit of the effective rate coefficient,

$$k_{\text{ss}} = \frac{\kappa_f \hat{f}(-k) 4\pi DR}{\kappa_f \hat{f}(-k) + 4\pi DR}. \quad (9)$$

Substituting this in equation (2) we get the leading terms of the asymptotic behaviour,

$$S_{AA}(t) \sim \exp\left(-kt - \frac{(k - k_A)^2 \sqrt{t}}{2[B](\pi D)^{3/2}}\right). \quad (10)$$

It is interesting that the first leading term, $\exp(-kt)$, can be obtained from conventional rate equations with the steady-state forward and reverse rate constants k_f and k_r (see equation (3)). The exponential decay is corrected by the square root term. Being in the exponent, this term may significantly decrease $S_{AA}(t)$ at long times.

The kinetics of the reaction that starts from C particles, $S_{AC}(t) = [A(t)]/[C(0)]$, can be found by using the relation for the Laplace transforms which extends the result for the problem without lifetimes [28] and was derived in [22]:

$$(s + k_A)\hat{S}_{AA}(s) + K_{\text{eq}}[B](s + k_C)\hat{S}_{AC}(s) = 1. \quad (11)$$

The kinetics of C provided initially there were only A particles, $S_{CA}(t) = [C(t)]/[A(0)]$, is obtained using conservation law extended to the unimolecular decay

$$(s + k_A)\hat{S}_{AA}(s) + (s + k_C)\hat{S}_{CA}(s) = 1. \quad (12)$$

An analogous equation is used to get $S_{CC}(t) = [C(t)]/[C(0)]$. As a result we find

$$\begin{aligned} S_{AC}(t) &\sim \frac{k - k_A}{K_{\text{eq}}[B](k_C - k)} S_{AA}(t) \\ S_{CA}(t) &\sim \frac{k - k_A}{k_C - k} S_{AA}(t) \\ S_{CC}(t) &\sim \frac{(k - k_A)^2}{K_{\text{eq}}[B](k_C - k)^2} S_{AA}(t) \end{aligned} \quad (13)$$

where $S_{AA}(t)$ is given by equation (2). Thus the leading terms of the long-time kinetics of both A and C do not depend on the initial conditions.

3. Derivation

To get the results in section 2 from the many-particle formulation of the problem, consider one A or C particle in the origin and N diffusing B s in a volume V . This system is described by the probability density $F_A(\{r\}, t)$ for the A particle while B s are located at $\{r\} = \{r_1, r_2, \dots, r_N\}$ and the probability density $F_{C_i}(\{r_{\neq i}\}, t)$ for the C which is formed after association of the A with i th B while all the others are located at $\{r_{\neq i}\} = \{r_1, \dots, r_{i-1}, r_{i+1}, \dots, r_N\}$. These obey the following equations:

$$\frac{\partial}{\partial t} F_A = \sum_{i=1}^N [D\nabla_i^2 F_A - W_f(r_i) F_A + W_r(r_i) F_{C_i}] - k_A F_A \quad (14a)$$

$$\frac{\partial}{\partial t} F_{C_i} = \sum_{j \neq i}^N D\nabla_j^2 F_{C_i} + \int d\vec{r}_i W_f(r_i) F_A - (\kappa_r + k_C) F_{C_i} \quad (14b)$$

where the terms with $W_f(r_i) = \kappa_f \delta(r_i - R)/4\pi R^2$ and $W_r(r_i) = \kappa_r \delta(r_i - R)/4\pi R^2$ describe the forward and reverse reactions respectively. Both F_A and F_C obey the reflecting boundary condition at $r = R$. Initially, there is only an A particle, so $F_A(t = 0) = V^{-N}$ and $F_{C_i}(t = 0) = 0$. The survival probability $S_{AA}(t)$ is obtained from $F_A(\{r\}, t)$ by integrating over the coordinates of all B s and taking the thermodynamic limit ($N \rightarrow \infty$ and $V \rightarrow \infty$ with $N/V = c$).

In the absence of dissociation ($W_r = 0$), the many-particle equation for F_A can be solved exactly [26, 27], resulting in the Smoluchowski kinetics:

$$S_{AA}(t) = \exp\left(-[B] \int_0^t k_{\text{irr}}(t') dt' - k_A t\right) \quad (15)$$

where the Laplace transform of $k_{\text{irr}}(t)$ is given in equation (4) with $\hat{f}(-k) = 1$.

To map the equations for the reversible reaction onto those for the effective irreversible reaction, we formally solve the equation for F_{C_i} , equation (14b), and substitute the solution into equation (14a). In this way we get a closed equation for F_A :

$$\frac{\partial}{\partial t} F_A = \sum_{i=1}^N [D\nabla_i^2 F_A - W_f(r_i) \mathcal{K}_i F_A] - k_A F_A. \quad (16)$$

Here \mathcal{K}_i is the time-dependent operator acting on the coordinates of all particles except i :

$$\mathcal{K}_i F_A \equiv \int_0^t f(t-t') e^{(t-t') \sum_{j \neq i} D\nabla_j^2} F_A(\{r\}, t') dt', \quad (17)$$

where $\exp(-t D\nabla_j^2)$ is the free Green's function of the j th B particle and $f(t)$ is defined as

$$f(t) = \delta(t) - \kappa_r e^{-(\kappa_r + k_C)t} \quad (18)$$

whose Laplace transform is given in equation (5). For an irreversible reaction ($\kappa_r = 0$), $f(t) = \delta(t)$ (or $\hat{f}(s) = 1$ in the Laplace space). In the general case we approximate $\hat{f}(s)$ by its value at $s = -k$, where k is defined as the rightmost irregular point (a pole or any other singular point) that determines the long-time behaviour of the kinetics. With this approximation, equation (16) becomes equivalent to the equation for the irreversible reaction with κ_f replaced by $\kappa_f \hat{f}(-k)$. After integrating over the coordinates of B s and taking the thermodynamic limit, we get the survival probability of the irreversible reaction, equation (2), with the redefined forward intrinsic rate constant given in equation (4).

The final step is to define the location of the singular point k . It is found *a posteriori* from the long-time behaviour of the effective irreversible kinetics. Using the fact that at long times

$k_{\text{irr}}(t)$ approaches its steady-state value k_{ss} , equation (9), we find that $k = [B]k_{\text{ss}} + k_A$ and get the self-consistent equation for k , equation (6)

The method described above does not allow one to determine the amplitude α of the long-time behaviour. However, it can be approximated by the amplitude obtained from the conventional rate equations. As a result we get α given in equation (2).

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