

# A Stochastic Theory of Chemical Reaction Rates. I. Formalism

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A class of stochastic processes is studied that can be used to model elementary and complex chemical reactions composed of a series of several distinct steps. Formal correlation function expressions are directly computed for the stochastic model to yield the overall rate constant for the reaction. One of the main results is a formula connecting the overall rate constant to the rate constants characterizing the elementary steps of the reaction.

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**KEY WORDS:** Stochastic models; chemical reactions; rate constants; barrier crossings.

## 1. INTRODUCTION

The conversion of reactants to products in a chemical reaction is frequently an indirect process that consists of a series of dynamically distinct events. A simple example that possesses these features is a diffusion-influenced reaction. Here the approach of reactants toward each other from large distances is diffusive in character, while the intrinsic reactive event leading to products is governed by short-range forces and the dynamics is non-diffusive. Other examples are provided by isomerization and dissociation reactions that involve potential wells separated by barriers; in these cases the energy relaxation in a potential energy well has a different character

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from the barrier-crossing dynamics. One goal of a theory of chemical reaction rates is to take into account the presence of the different dynamical events that contribute to the overall rate of the reaction.

These features have been recognized and accounted for in many of the classic theories of reaction dynamics. Examples are Lindemann's<sup>(1)</sup> treatment of the contributions of collisions and internal dynamics to unimolecular decay processes, Kramers'<sup>(2)</sup> treatment of barrier-crossing dynamics where different dynamical regimes are recognized, and Smoluchowski's<sup>(3)</sup> and Noyes'<sup>(4)</sup> studies of diffusion-influenced reactions. This latter case provides a clear illustration of some of the features of reaction rates that are the focus of this paper. Following Smoluchowski, many approaches to this problem incorporate the short-range dynamical effects through a boundary condition on the diffusive dynamics, or through a sink term (see, e.g., ref. 5). In a more general context it has been shown that the overall rate constant for a diffusion-influenced reaction  $k$  can be written in the form<sup>(6)</sup>

$$\frac{1}{k} = \frac{1}{k_s} + \frac{1}{k_D} \quad (1.1)$$

where  $k_s$  is the rate constant that characterizes the short-range events and  $k_D = 4\pi RD$  is the Smoluchowski result for a diffusion-controlled reaction, with  $R$  the radius of the perfectly absorbing spherical sink and  $D$  the diffusion coefficient. The derivation of this result from a microscopic kinetic theory involves many subtle features.<sup>(7)</sup>

Addition formulas like (1.1) are found to arise in a number of different contexts<sup>(8-14)</sup> and, while their molecular origin is not always clear, they provide a convenient way to account for and interpolate between contributions arising from widely differing kinds of dynamics. The present paper considers a class of chainlike (non-Markovian) stochastic models for chemical rate processes, in which the transition from reactants to products occurs through a series of intermediate regimes, whose solution yields addition formulas for the overall rate that are generalizations of (1.1). The assumptions of the stochastic model that lead to this result can be analyzed to provide insight into the features of the microscopic dynamics that are necessary in order to obtain simple addition formulas. While the stochastic model is not completely general, it has the attractive and unusual feature that exact rate coefficient results can be obtained. In addition, the formulation has potential applications in the context of reactions occurring far from equilibrium that are driven by external noise sources with simple statistical properties.<sup>(15)</sup>

The general stochastic model is presented in Section 2 and a number

of results are derived that relate the transmission coefficient between the reactant and product states of the model to transmission coefficients between intermediate states.<sup>5</sup> The formulas derived in this section constitute the stochastic basis of the addition formulas. The rate coefficients are calculated in Section 3, starting from the stable-states-picture<sup>(10)</sup> correlation function expression. The results are discussed in Section 4.

The results presented in this paper are general in character and apply to any type of (non-Markovian) process in the intermediate regimes. In the companion paper<sup>(17)</sup> we illustrate this formalism by considering a number of explicit stochastic models for barrier-crossing dynamics.

## 2. CHAINLIKE STOCHASTIC MODELS AND ADDITION FORMULAS

The transition between a reactant  $R$  and a product  $P$  can be described by the motion of a set of coordinates ("particle") on a potential energy surface, with the  $R$  and  $P$  regions typically separated by potential barriers. The coordinates describing the reaction could represent the internuclear separation between atoms or some internal degrees of freedom in a molecule.

### 2.1. Formal Description of Chainlike Models

For a many-body system the dynamics of the reaction coordinate is, in general, extremely complicated. In this paper, we consider a class of systems that retains some of the main features of this dynamics and yet are exactly solvable. These systems have a linear or chainlike dynamical structure in the following sense: they are models of an overall reaction  $R \rightarrow P$  which is composed of a certain number of elementary steps  $0, 1, 2, \dots, i, \dots, n$ , which we call regimes, such that  $R \rightarrow P$  is achieved if and only if  $1, \dots, n$  are achieved, and moreover step  $i$  cannot occur before the preceding steps  $0, 1, \dots, i-1$ .

Each step or regime  $i$  represents a certain evolution (deterministic or stochastic) which is simpler than the overall reaction. Our purpose is to combine these regimes to obtain the overall reaction  $R \rightarrow P$  and to compute the overall evolution in terms of the simpler evolution within each step.

We begin by specifying the structure of the model in more detail. In

<sup>5</sup> Similar ideas were introduced by Bellman and Wing<sup>(16)</sup> in a study of reflection and transmission coefficients associated with a linear differential equation on a segment. We thank P. Bertrand (ONERA) for pointing out this reference.

each regime  $i$ , the state space of the degree of freedom is denoted  $X_i$ . The particle moves in the linear chain of the  $X_i$  in the following way (cf. Fig. 1): suppose that at some time  $t$ , the particle is in regime  $X_i$ ; then it wanders a certain amount of time inside  $X_i$  and finally finds its way out of  $X_i$  to enter either regime  $X_{i-1}$  or  $X_{i+1}$ . If it enters  $X_{i+1}$ , we suppose that there is a common boundary state  $a_{i+1}^+$  in  $X_i$  and  $X_{i+1}$  such that when the particle leaves  $X_i$  to enter  $X_{i+1}$  it has to pass through  $a_{i+1}^+$ . If instead the particle leaves  $X_i$  to enter  $X_{i-1}$ , we suppose that there is a common boundary state  $a_i^-$  in  $X_i$  and  $X_{i-1}$  such that when the particle leaves  $X_i$  to enter  $X_{i-1}$  it has to pass through  $a_i^-$ .

We have represented this situation very schematically in Fig. 1. The  $X_i$  are represented by boxes;  $X_i$  and  $X_{i+1}$  have two common states, namely  $a_{i+1}^+$  and  $a_i^-$ , which are represented by large dots with an arrow to indicate the "direction" of the motion: when the particle is in  $a_{i+1}^+$ , the motion is necessarily from  $X_i$  to  $X_{i+1}$ , and when the particle is in  $a_i^-$ , the motion is necessarily from  $X_{i+1}$  to  $X_i$ . In this picture, the dotted lines with their arrows indicate possible trajectories of the particle inside  $X_i$ ; for example, a particle coming from  $X_{i-1}$  and entering  $X_i$  through  $a_i^+$  may wander to some extent in  $X_i$  and finally exit from  $X_i$  either by  $a_i^-$  or  $a_{i+1}^+$  as indicated by the two arrows issuing from  $a_i^+$ . We can think of the  $\pm$  indices as the sign of a speed  $\pm v$  of the particle. The distinction between states corresponding to  $\pm v$  is essential for the definition of fluxes in Section 2.5 and of rate constants in Section 3.

The regimes  $X_0$  and  $X_n$  are clearly special; they are respectively connected only to  $X_1$  by  $a_1^\pm$  and to  $X_{n-1}$  by  $a_n^\pm$ . We specify the particle's fate when it arrives in  $a_0^-$  or  $a_n^+$  by assuming absorption there. Subsequently we shall identify the special  $X_0$  and  $X_n$  regimes as the stable reactant ( $R$ ) and product ( $P$ ) states, respectively.

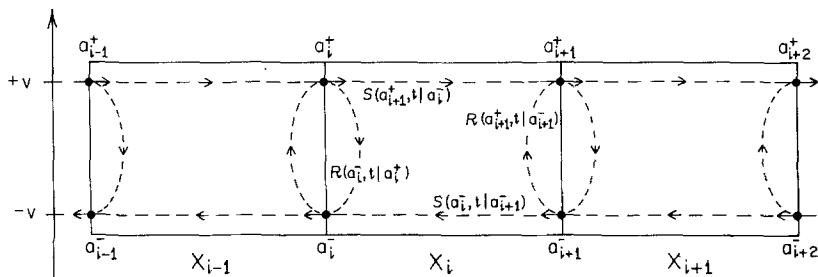


Fig. 1. A schematic diagram of the state space of the stochastic model. Shown are the different types of transitions among the entrance and exit states, and their total probabilities (see the text).

## 2.2. Evolution inside a Regime

Within each regime, the evolution of the particle can be deterministic, stochastic, Markovian, or non-Markovian, but we shall assume that it can be computed so that the segment rate constant for  $X_i$  can ultimately be found. As a necessary preliminary, we need to characterize the dynamics in each regime. We first consider a given regime  $X_i$  as isolated: when the particle leaves  $X_i$  either by  $a_i^-$  or  $a_{i+1}^+$ , it never returns. We need to define the following quantities:

$S(a_{i+1}^+, t | a_i^+)$  is the probability to be in  $a_{i+1}^+$  at time  $t$ , knowing that the particle started from  $a_i^+$  at time 0, i.e., entered  $X_i$ , and remained inside  $X_i$  during  $[0, t]$ .

$R(a_i^-, t | a_i^+)$  is the probability to be in  $a_i^-$  at time  $t$ , knowing that the particle started from  $a_i^+$  at time 0 and remained inside  $X_i$  during  $[0, t]$ .

In a similar way, we also define  $S(a_i^-, t | a_{i+1}^-)$  and  $R(a_{i+1}^+, t | a_{i+1}^-)$ . These probabilities are the weights of the dotted paths shown in Fig. 1.

The main quantities of interest are the long-time limits of the probabilities defined above:

$$\begin{aligned}
 S_{i,i+1} &= \lim_{t \rightarrow \infty} S(a_{i+1}^+, t | a_i^+) \\
 R_{i,i+1} &= \lim_{t \rightarrow \infty} R(a_i^-, t | a_i^+) \\
 S_{i+1,i} &= \lim_{t \rightarrow \infty} S(a_i^-, t | a_{i+1}^-) \\
 R_{i+1,i} &= \lim_{t \rightarrow \infty} R(a_{i+1}^+, t | a_{i+1}^-)
 \end{aligned}
 \tag{2.1}$$

$S_{i,i+1}$  is the probability of leaving regime  $X_i$  by the state  $a_{i+1}^+$ , knowing that the particle entered regime  $X_i$  by the state  $a_i^+$  and stayed the entire time in  $X_i$ . The term  $R_{i,i+1}$  describes the other possibility; it is the probability of leaving regime  $X_i$  by the state  $a_i^-$ , knowing that the particle entered regime  $X_i$  by the state  $a_i^+$  and stayed the entire time in  $X_i$ . The other two quantities  $S_{i+1,i}$  and  $R_{i+1,i}$ , have similar interpretations. With these definitions, we have the obvious conservation equations

$$\begin{aligned}
 S_{i,i+1} + R_{i,i+1} &= 1 \\
 S_{i+1,i} + R_{i+1,i} &= 1
 \end{aligned}
 \tag{2.2}$$

Later we relate these quantities to the rate constant for the regime  $X_i$

[see formula (3.6)]. If we define in a standard way the Laplace transform of a function  $f(t)$  by

$$\hat{f}(s) = \int_0^\infty e^{-st} f(t) dt$$

we see that

$$\begin{aligned} S_{i,i+1} &= \lim_{s \rightarrow 0} s \hat{S}(a_{i+1}^+, s | a_i^+) \\ R_{i,i+1} &= \lim_{s \rightarrow 0} s \hat{R}(a_i^-, s | a_i^+) \end{aligned} \tag{2.3}$$

and so forth for  $S_{i+1,i}$  and  $R_{i+1,i}$ .

### 2.3. Combination of Two Successive Regimes

Having completed the formal description of the particle evolution in a single regime, we now consider the evolution of the particle in two successive regimes,  $X_i \cup X_{i+1}$ ; for this combined system, the particle can enter by the state  $a_i^+$  or  $a_{i+2}^-$  and leave by the states  $a_i^-$  or  $a_{i+2}^+$  (cf. Fig. 1). Our main assumption is that each time the particle changes its regime, it begins an independent evolution in the next regime. Nevertheless, the *total* evolution can be non-Markovian.

In our problem, we need not follow the detailed motion inside  $X_i$  or  $X_{i+1}$ , but we must concern ourselves with the way that the particle changes its regime. We can then consider that the particle exists only on a reduced six-point state space  $\{a_i^\pm, a_{i+1}^\pm, a_{i+2}^\pm\}$  on which it performs a non-Markovian motion. The allowed transitions are shown by the arrows on the dotted edges of the oriented graph of Fig. 1. We call  $P(a_{i+2}^+, t | l)$  the probability to be in the absorbing boundary state  $a_{i+2}^+$  at time  $t$ , starting from state  $l = a_i^+, a_{i+1}^+, a_{i+1}^-$  at time 0 and remaining during the entire time  $[0, t]$  on the reduced state space  $\{a_i^\pm, a_{i+1}^\pm, a_{i+2}^\pm\}$ . From the definitions introduced in Section 2.2, we obtain the following evolution equations:

$$P(a_{i+2}^+, t | a_i^+) = \int_0^t P(a_{i+2}^+, t - \tau | a_{i+1}^+) \frac{d}{d\tau} S(a_{i+1}^+, \tau | a_i^+) d\tau \tag{2.4a}$$

$$\begin{aligned} P(a_{i+2}^+, t | a_{i+1}^+) &= S(a_{i+2}^+, t | a_{i+1}^+) + \int_0^t P(a_{i+2}^+, t - \tau | a_{i+1}^-) \\ &\quad \times \frac{d}{d\tau} R(a_{i+1}^-, \tau | a_{i+1}^+) d\tau \end{aligned} \tag{2.4b}$$

$$P(a_{i+2}^+, t | a_{i+1}^-) = \int_0^t P(a_{i+2}^+, t - \tau | a_{i+1}^+) \frac{d}{d\tau} R(a_{i+1}^+, \tau | a_{i+1}^-) d\tau \tag{2.4c}$$

The interpretation of these equations is straightforward. For example, Eq. (2.4b) states that the total probability to be at  $a_{i+2}^+$  at time  $t$ , starting from  $a_{i+1}^+$ , is composed of two contributions: (1) the probability of being absorbed at time  $t$  starting from  $a_{i+1}^+$  and staying in  $X_{i+1}$  without entering  $X_i$ , which is just  $S(a_{i+2}^+, t | a_{i+1}^+)$ , and (2) the probability of being absorbed at  $a_{i+2}^+$  at time  $t$  starting from  $a_{i+1}^+$  and entering  $X_i$  at least one time  $\tau$ . This probability is itself composed of the product of  $(d/d\tau) R(a_{i+1}^-, \tau | a_{i+1}^+) d\tau$  (which is the probability of arriving at  $a_{i+1}^-$  in the time interval  $[\tau, \tau + d\tau]$  and staying in  $X_{i+1}$  during  $[0, t]$ ), and  $P(a_{i+2}^+, t - \tau | a_{i+1}^-)$  (which is the probability of starting from  $a_{i+1}^-$  at  $\tau$  and arriving at  $a_{i+2}^+$  at time  $t$ ).

After Laplace transformation, Eqs. (2.4a)–(2.4c) can easily be solved for the Laplace transforms  $\hat{P}(a_{i+2}^+, s | l)$  to give

$$\hat{P}(a_{i+2}^+, s | a_i^+) = \hat{S}(a_{i+2}^+, s | a_{i+1}^+) s \hat{S}(a_{i+1}^+, s | a_i^+) D(s)^{-1} \quad (2.5a)$$

$$\hat{P}(a_{i+2}^+, s | a_{i+1}^+) = \hat{S}(a_{i+2}^+, s | a_{i+1}^+) D(s)^{-1} \quad (2.5b)$$

$$\hat{P}(a_{i+2}^+, s | a_{i+1}^-) = \hat{S}(a_{i+2}^+, s | a_{i+1}^+) s \hat{R}(a_{i+1}^+, s | a_{i+1}^-) D(s)^{-1} \quad (2.5c)$$

where

$$D(s) = 1 - s \hat{R}(a_{i+1}^+, s | a_{i+1}^-) s \hat{R}(a_{i+1}^-, s | a_{i+1}^+)$$

With these equations we can calculate the probabilities of absorption at the boundaries for  $X_i \cup X_{i+1}$ : we define  $S_{i,i+2}$  = the probability to be absorbed by the right boundary  $a_{i+2}^+$ , knowing that the particle started at time 0 from the left boundary  $a_i^+$  and remained in  $X_i \cup X_{i+1}$  the entire time. We have

$$S_{i,i+2} = \lim_{t \rightarrow \infty} P(a_{i+2}^+, t | a_i^+) = \lim_{s \rightarrow 0} s \hat{P}(a_{i+2}^+, s | a_i^+) \quad (2.6)$$

If we multiply Eqs. (2.5) by  $s$  and take the  $s=0$  limit, taking into account Eqs. (2.3) and (2.6), we obtain the relations

$$S_{i,i+2} = P(a_{i+2}^+, \infty | a_i^+) = S_{i,i+1} S_{i+1,i+2} D(0)^{-1} \quad (2.7a)$$

$$P(a_{i+2}^+, \infty | a_{i+1}^+) = S_{i+1,i+2} D(0)^{-1} \quad (2.7b)$$

$$P(a_{i+2}^+, \infty | a_{i+1}^-) = S_{i+1,i+2} R_{i+1,i} D(0)^{-1} \quad (2.7c)$$

with

$$D(0) = 1 - R_{i+1,i+2} R_{i+1,i}$$

From (2.7a) and (2.2) we then obtain the fundamental formula

$$\frac{1}{S_{i,i+2}} - 1 = \frac{1}{S_{i,i+1}} - 1 + \frac{S_{i+1,i}}{S_{i,i+1}} \left( \frac{1}{S_{i+1,i+2}} - 1 \right) \tag{2.8}$$

This equation provides a relationship between  $S_{i,i+2}$  (related to the combined evolution in  $X_i \cup X_{i+1}$ ) and  $S_{i,i+1}$ ,  $S_{i+1,i}$  (related to  $X_j$ ) and  $S_{i+1,i+2}$  for  $X_{i+1}$ .

At this point, it is interesting to rewrite Eq. (2.8) in a more symmetric form by defining overall equilibrium probabilities  $q_i$  satisfying the detailed balance conditions

$$q_i S_{i,i+1} = q_{i+1} S_{i+1,i} \tag{2.9}$$

These quantities may be computed by starting from any  $q_0$  and defining the successive quotients

$$\frac{q_{i+1}}{q_i} = \frac{S_{i,i+1}}{S_{i+1,i}}$$

and normalizing by

$$\sum_{i=0}^{n+1} q_i = 1$$

Using (2.9), we can rewrite the fundamental formula (2.8) as the addition formula

$$\frac{1}{q_i} \left( \frac{1}{S_{i,i+2}} - 1 \right) = \frac{1}{q_i} \left( \frac{1}{S_{i,i+1}} - 1 \right) + \frac{1}{q_{i+1}} \left( \frac{1}{S_{i+1,i+2}} - 1 \right) \tag{2.10}$$

### 2.4. Combination of the $n + 1$ Regimes $X_j$

We consider now dynamics in the whole system  $X_0 \cup X_1 \cup \dots \cup X_n$ . We define  $P(a_{n+1}^+, t | a_k^+) =$  the probability to be absorbed by the extreme right boundary state  $a_{n+1}^+$  at time  $t$ , starting from  $a_k^+$  at time 0 (and remaining the entire time in  $X_0 \cup \dots \cup X_n$ ). For the entire system  $a_0^-$  and  $a_{n+1}^+$  are absorbing states and  $a_0^+$  and  $a_{n+1}^-$  are entrance states. Recall also that the particle loses memory each time it crosses the boundary  $a_k^\pm$  of any of the  $X$  regimes. As shown in Appendix A, the result Eq. (2.10) for two regimes may be generalized easily for the whole system. We first define

$$S_{0,n+1} = \lim_{t \rightarrow \infty} P(a_{n+1}^+, t | a_0^+) \tag{2.11}$$



which is the probability to be absorbed by the extreme right boundary state  $a_{n+1}^+$  (forming stable product  $P$ ) at some time, knowing that the particle started from  $a_0^+$  at time 0, i.e., entered the system from the left (from the stable reactant  $R$ ). Then Eq. (2.10) can be generalized as

$$\frac{1}{q_0} \left( \frac{1}{S_{0,n+1}} - 1 \right) = \sum_{h=0}^n \frac{1}{q_h} \left( \frac{1}{S_{h,k+1}} - 1 \right) \quad (2.12)$$

## 2.5. Definition of the Fluxes

We define the probability flux to be absorbed at some time in the extreme right boundary state  $a_{n+1}^+$  to form  $P$  (rather than  $a_0^-$  to form  $R$ ) in the system  $X_0 \cup \dots \cup X_n$ , starting from  $a_k^+$  with speed  $+$  and  $a_k^-$  with speed  $-$ . This is, by definition,

$$\Phi(k) = P(a_{n+1}^+, \infty | a_k^+) - P(a_{n+1}^+, \infty | a_k^-) \quad (2.13)$$

We shall show in Section 3 that this quantity is intimately connected to the overall  $R \rightarrow P$  rate constant for the process. In (2.13),  $k$  can take the values  $0, 1, 2, \dots, n$ , corresponding to different initial points for the probability flux. If  $k=0$ , then  $P(a_{n+1}^+, \infty | a_0^-) \equiv 0$ ; there is no probability flux of forming  $P$ , since  $R$  is formed. We show in Appendix B that the various fluxes satisfy a flux conservation condition:

$$q_k \Phi(k) = q_l \Phi(l) \quad (2.14)$$

for any  $0 \leq k, l \leq n$  and that they satisfy the fundamental addition formula

$$\frac{1}{q_k} \left( \frac{1}{\Phi(k)} - 1 \right) = \sum_{h=k}^n \frac{1}{q_h} \left( \frac{1}{S_{h,h+1}} - 1 \right) + \sum_{h=k}^l \frac{1}{q_h} \left( \frac{1}{S_{h,h-1}} - 1 \right) \quad (2.15)$$

## 3. RATE CONSTANTS

### 3.1. Definitions of the Rate Constants

In this section we turn to a consideration of the dynamics in the full system,  $\bigcup_{k=0}^n X_k$ , and regard its absorbing states  $a_0^-$  and  $a_{n+1}^+$  as defining the reactants  $R$  and products  $P$ , respectively. The evolution between reactants and products occurs through a series of intermediate steps in the various regimes  $X_i$ , and we shall compute, with the results of Section 2, the overall rate constant for the process in terms of the rate constants characteristic of the different regimes.

The starting point of the analysis is the correlation function expression for the  $R \rightarrow P$  rate constant  $k$  obtained from the stable-states-picture (SSP) of chemical reactions,<sup>(10)</sup>

$$k = k_{i,n+1} = \int_0^\infty dt \langle j_i(0) j_{n+1}(t) \rangle_R \quad (3.1)$$

where  $j_{n+1}(t)$  is the probability current passing through  $a_{n+1}$  at time  $t$  into the product, and  $j_i(0)$  is the initial total probability current through  $a_i$ . The dynamics is subject to absorption at the boundaries 0 and  $n+1$ . The angular brackets  $\langle \dots \rangle_R$  signify an average over the stochastic evolution of the system, normalized by the reactant partition function  $q_0$ , with the initial condition that at time zero the system is in equilibrium at point  $a_i$ . Equation (3.1) for the rate constant hinges on the recognition that the dynamics within the stable reactant and product regions does not contribute significantly to the rate constant and may be replaced by absorbing boundary conditions: only the dynamics in the intermediate regions is relevant. Our stochastic model explicitly incorporates such an assumption since the  $a_0^-$  and  $a_{n+1}^+$  are absorbing states, so the SSP rate constant expression is ideal for our calculations.

In the chainlike stochastic model there is an equal equilibrium probability to have speed  $\pm v$  at any point. If, as earlier, we let  $P(a_{n+1}^+, t|l)$  be the probability to be in the absorbing state  $a_{n+1}^+$  at time  $t$  given that we start from  $l = a_i^\pm$  at time zero and remain in the full system  $\bigcup_{k=0}^n X_k$ , then it follows that the correlation function (3.1) is

$$\langle j_i(0) j_{n+1}(t) \rangle_R = \frac{q_i v}{q_0} \frac{d}{dt} [P(a_{n+1}^+, t|a_i^+) - P(a_{n+1}^+, t|a_i^-)] \quad (3.2)$$

where  $q_i/q_0$  is the ratio of the equilibrium populations in  $a_i$  and in the reactant  $a_0$ . Thus, the  $R \rightarrow P$  rate constant is

$$\begin{aligned} k = k_{i,n+1} &= \frac{q_i v}{q_0} [P(a_{n+1}^+, \infty | a_i^+) - P(a_{n+1}^+, \infty | a_i^-)] \\ &= \frac{q_i v}{q_0} \Phi(i) \end{aligned} \quad (3.3)$$

where Eq. (2.13) has been used. It should be pointed out that this "rate constant" has the dimensions of velocity rather than reciprocal time. In order to recover the standard correlation function of probability and the corresponding rate constants from (3.2) and (3.3),  $q_i$  should be the probability *density* at  $a_i$ , whereas  $q_0$  is the probability at 0. The explicit calculations in paper II,<sup>(17)</sup> which consider specific forms for the absorbing and intermediate states, take this difference into account.

### 3.2. Addition Formulas for Chainlike Models

Using Eq. (2.14), it is clear that  $k_{i,n+1}$  does not depend on the location  $a_i$  where the initial current  $j_i(0)$  is measured. Finally, using Eq. (2.15), we may write a general formula for the total rate constant:

$$\frac{1}{k} = \frac{1}{k_{i,n+1}} = \sum_{h=i}^1 \frac{q_0}{q_n v} \left( \frac{1}{S_{h,h-1}} - 1 \right) + \frac{q_0}{q_i v} \frac{1}{S_{i,i+1}} + \sum_{h=i+1}^n \frac{q_0}{q_h v} \left( \frac{1}{S_{h,h+1}} - 1 \right) \quad (3.4)$$

This equation is a basic result of this section and expresses the overall rate constant in terms of the transmission coefficients for the intermediate regimes.

In the remainder of this section, we rewrite the formula (3.4) in terms of rate constants characteristic of the intermediate regimes. Consider the rate constant for an elementary reaction step in regime  $X_i$ . Its definition is a special case of Eq. (3.1) and, if we let  $k_{i,i+1}$  denote the rate constant for the  $i$ th regime, we have the SSP formula

$$k_{i,i+1} = \int_0^\infty dt \langle j_i(0) j_{i+1}(t) \rangle_R \quad (3.5)$$

where  $a_i^-$  and  $a_{i+1}^+$  are taken to be absorbing states, and the angular brackets denote an average over the stochastic dynamics in  $X_i$ , normalized again by the reactant partition function  $q_0$ . It follows directly from the definitions of Section 2.2 that

$$k_{i,i+1} = \frac{v q_i}{q_0} \lim_{t \rightarrow \infty} P(a_{i+1}^+, t | a_i^+) = \frac{v q_i}{q_0} S_{i,i+1} \quad (3.6)$$

This relation can be used to express (3.4) in terms of the segment rate constants  $k_{i,i+1}$ . However, since the factors

$$\frac{q_0}{q_i v} \left( \frac{1}{S_{i,i+1}} - 1 \right)$$

appear in the formula for the overall rate constant, it is convenient to first interpret these factors and express them in terms of effective rate constants.

The transition state theory (TST) rate constant  $k^{\text{TST}}$  for any reaction is computed from the equilibrium one-way flux across a surface separating

the reactant and product regions. The TST rate constant for regime  $i$  takes the simple form

$$k_{i,i+1}^{\text{TST}} = \frac{q_i v}{q_0} \quad (3.7)$$

i.e., just the speed of the particle  $v$  times the equilibrium probability  $q_i/q_0$  to be at  $a_i$  relative to that of the reactant. If we define an effective rate constant for the  $i$ th regime by

$$\frac{1}{k_{i,i+1}^{\text{eff}}} \equiv \frac{q_0}{q_i v} \left( \frac{1}{S_{i,i+1}} - 1 \right) = \frac{1}{k_{i,i+1}} - \frac{1}{k_{i,i+1}^{\text{TST}}} \quad (3.8)$$

so that  $k_{i,i+1}^{\text{eff}}$  measures the departure from the TST rate, we obtain

$$\frac{1}{k} = \frac{1}{k_{i,n+1}} = \sum_{h=i}^1 \frac{1}{k_{h,h-1}^{\text{eff}}} + \frac{1}{k_{i,i+1}} + \sum_{h=i+1}^n \frac{1}{k_{h,h+1}^{\text{eff}}} \quad (3.9)$$

This formula is a major result of this paper and completely expresses the overall rate constant for the chainlike model in terms of rate coefficients for the individual regimes. Its chief advantage is that it reduces the rate calculation to that for each regime with absorbing boundary conditions; once these simpler dynamical problems are solved, the full rate constant can be constructed from Eq. (3.9).

Equation (3.9) is of the form of the rate constant relation which follows from the general SSP theory.<sup>(10)</sup> The present result is exact for the stochastic model, whereas the SSP result requires certain approximations.<sup>(10)</sup> In addition, (3.8) expresses the rate constants for the individual regimes simply in terms of the transmission probabilities.

#### 4. CONCLUSION

The reciprocal of the overall rate constant for the chainlike stochastic model has been shown to satisfy an addition formula involving the reciprocals of the rate constants characteristic of the intermediate regimes. While the stochastic dynamics of the system is non-Markovian in general, it is the partial Markov assumption whereby the "particle" loses memory when it moves from one regime to the next, in conjunction with the chainlike nature of the model, that gives rise to the addition formula for the rate constant. As such, the general stochastic model provides some insight into the dynamical features that are responsible for the observed approximate validity of the addition formulas for real rate processes. The results are general in that the dynamics in the individual regimes is not specified and

thus the results may be applied to a variety of systems. Because a large class of reacting systems involve a series of intermediate steps of a distinct dynamical nature, the formulas derived here allow the overall rate constant to be constructed from an analysis of the rate constants for the constituent processes, which is a much simpler task.

Some applications to non-Markovian stochastic models for barrier-crossing dynamics are given in the companion paper. It is also shown there that the same techniques can be generalized to treat processes with a branching step that destroys the chainlike character of the model.

## APPENDIX A

Equation (2.12), which is applicable to the system  $X_0 \cup \dots \cup X_n$ , may be obtained as follows: the system may be reduced to the two-regime case by dividing it into two parts:

$$X_0 \cup \dots \cup X_n = X_0 \cup Y \quad (\text{A.1})$$

where  $Y = X_1 \cup \dots \cup X_n$ ; the absorbing states for  $X_0$  are  $a_0^-$  and  $a_1^+$ , and those of  $Y$  are  $a_1^-$  and  $a_{n+1}^+$ . The transmission coefficients for  $X_0$  are  $S_{0,1}$  and  $S_{1,0}$ , while those for  $Y$  are denoted by  $S_{1,n+1}$  and  $S_{n+1,1}$ , and  $S_{1,n+1}$  is defined to be the probability to be absorbed in  $a_{n+1}^+$  at some time, starting from  $a_1^+$  at time 0 and staying in  $Y$  all the time.

Equation (2.8) can be applied to  $X_0 \cup Y$  to yield

$$\frac{1}{S_{0,n+1}} - 1 = \frac{1}{S_{0,1}} - 1 + \frac{S_{1,0}}{S_{0,1}} \left( \frac{1}{S_{1,n+1}} - 1 \right)$$

which can be rewritten, using (2.9) for  $i=0$ ,

$$\frac{1}{q_0} \left( \frac{1}{S_{0,n+1}} - 1 \right) = \frac{1}{q_0} \left( \frac{1}{S_{0,1}} - 1 \right) + \frac{1}{q_1} \left( \frac{1}{S_{1,n+1}} - 1 \right) \quad (\text{A.2})$$

Induction can be applied to the second term on the right-hand side of (A.2) to obtain Eq. (2.12).

## APPENDIX B

To obtain (2.14) and (2.15) we use induction. First we start from the two-regime situation  $X_i \cup X_{i+1}$ . We use notation of Section 2.3, and define the flux for the two-regime system  $X_i \cup X_{i+1}$  as

$$\Phi^{(i,i+1)}(k) = P(a_{i+2}^+, \infty | a_k^+) - P(a_{i+2}^+, \infty | a_k^-) \quad (\text{B.1})$$

where  $k$  takes only the values  $i$  or  $i + 1$ ; more precisely,

$$\Phi^{(i,i+1)}(i) = P(a_{i+2}^+, \infty | a_i^+) = S_{i,i+2} \tag{B.2}$$

$$\begin{aligned} \Phi^{(i,i+1)}(i+1) &= P(a_{i+2}^+, \infty | a_{i+1}^+) - P(a_{i+2}^+, \infty | a_{i+1}^-) \\ &= \frac{S_{i+1,i+2} S_{i+1,i}}{1 - R_{i+1,i+2} R_{i+1,i}} \end{aligned} \tag{B.3}$$

[this last equation has been deduced from Eqs. (2.7b) and (2.7c)]. From (2.7a)–(2.7c) and from the definition (2.9), we obtain easily the flux conservation

$$q_i \Phi^{(i,i+1)}(i) = q_{i+1} \Phi^{(i,i+1)}(i+1) \tag{B.4}$$

and we also obtain from (B.3)

$$\frac{1}{\Phi^{(i,i+1)}(i)} - 1 = \left( \frac{1}{S_{i+1,i+2}} - 1 \right) + \left( \frac{1}{S_{i+1,i}} - 1 \right) \tag{B.5}$$

To prove Eq. (2.15), we split  $X_0 \cup \dots \cup X_n$  into two subsystems:

$$\begin{aligned} Y_0 &= X_0 \cup \dots \cup X_k && \text{(absorbing states } a_{k+1}^+, a_0^-) \\ Y_1 &= X_{k+1} \cup \dots \cup X_n && \text{(absorbing states } a_{k+1}^-, a_{n+1}^+) \end{aligned}$$

We can apply (B.5) to this two-regime situation to obtain

$$\frac{1}{\Phi(k)} - 1 = \left( \frac{1}{S_{k,n+1}} - 1 \right) + \left( \frac{1}{S_{k,0}} - 1 \right) \tag{B.6}$$

Then Eq. (2.15) is obtained from (B.6) after multiplication by  $q_k^{-1}$  and use of Eq. (2.12) to express  $(1/S_{k,n+1} - 1)(1/q_k)$  as a sum and also  $(1/S_{k,0} - 1)(1/q_k)$  as a sum (reversing the motion). The detailed balance equation (2.14) follows from a similar generalization of Eq. (B.4).

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