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Metastable relaxation times and absorption probabilities for multidimensional stochastic systems

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Abstract. Considering general, discrete stochastic systems, we derive an exact formula expressing the mean exit time from the attraction basin of a metastable state in terms of absorption probabilities. This formula can be applied to reaction–diffusion multidimensional systems, or more generally to the evaluation of the lifetimes of metastable states.

1. Introduction

Estimating the mean exit time of a system from a potential well is an important and almost universal problem in physics and chemistry. For a particle diffusing in a potential well according to a Smoluchowski dynamics, the mean exit time out of the well is, up to a prefactor, $\exp(\beta \Delta\varphi)$, where β is the inverse temperature and $\Delta\varphi$ is the minimal height of the potential barrier (see [1–4]). In microscopic chemical kinetics, this result is known as the transition state theory (see, e.g., [5–7]) and in macroscopic equilibrium chemical kinetics it is also valid, provided that φ is replaced by the free energy divided by the temperature and β is replaced by the volume of the system. More recently, we have generalized this theory to non-equilibrium macroscopic reaction–diffusion systems (see [8]), where the analogue of φ is not known *a priori*, due to the non-equilibrium situation. In this case, the stochastic dynamics of the system is given by a master equation and the problem is to find the mean exit time from the basin of attraction of a locally stable state. More generally, this problem must be solved in order to compute the mean lifetime of the metastable states of any discrete stochastic system.

In the one-dimensional case, and when only jumps to the nearest neighbours are possible, the answer can be derived exactly (see, e.g., [8–10]) using specific methods. On the other hand, for multidimensional kinetics, there seems to be no rigorous, general approach to this problem for a discrete stochastic dynamics, although it has been addressed by many authors (see, for instance, [1, 2]). Certain methods have been developed in the context of the Fokker–Planck equation using partial differential equation methods [11], or probabilistic methods [12], but it has been proved [8] that the mean exit time for a discrete master equation dynamics differs by an exponential factor from the exit time obtained by the Fokker–Planck dynamics. This is related to the fact that a discrete master equation can be approximated by a Fokker–Planck equation only near the macroscopic stationary states, and that this approximation fails completely for extremely large times, which is the case for times of exit from a basin of attraction (see [8]).

This paper provides a new approach to the problem of mean exit time for a multidimensional, discrete stochastic dynamics and it presents detailed proofs of the results used in [8]. Our method uses a resummation over the trajectories of the stochastic process. In section 2, we establish the notation and definitions to be used later. In section 3, we examine the case of a closed system and derive a generalization of the detailed balance condition valid for any discrete stochastic dynamics. In sections 4 and 5 we consider the problem of calculating the absorption probabilities and the first mean exit time from a domain in the state space of the dynamics. In section 6, we deduce various asymptotic results and finally in section 7, we apply our results to reaction–diffusion systems in the large-volume limit.

2. Definition of a transition system

In this section, we establish the notation that we shall use later. For our purposes, it is preferable to work in the most general context. The system we consider is represented by a point in a certain state space X which is assumed to be discrete (finite or infinite). Its dynamic is a jump process, the general theory of which can be found in many works [1–4].

The possible transitions of the system are specified by a collection A of transitions $\alpha \in A$. A transition is by definition a mapping $\alpha : X \rightarrow X$, which is defined only on a subset X_α of X , and which associates a point $\alpha(x)$ to any x in X_α . We shall work in a continuous-time framework. We call $W_\alpha(x)$ the transition rate from x to $\alpha(x)$ (that is, the probability per unit time that the system, being in state x , undergoes the transition α and so jumps in $\alpha(x)$). We define

$$W(x) = \sum_{\alpha} W_{\alpha}(x). \quad (2.1)$$

When the system has reached state x at time t , it stays there during a stochastic waiting time τ obeying an exponential law

$$\text{Prob}(\tau > t) = \exp(-W(x)t) \quad (2.2)$$

and then it jumps at time $t + \tau$, to the state $\alpha(x)$, with probability

$$p_{\alpha}(x) = \frac{W_{\alpha}(x)}{W(x)}. \quad (2.3)$$

We call $p(x, t)$ the probability of finding the system in state x at time t . This probability satisfies the master equation

$$\frac{\partial p(x, t)}{\partial t} = \sum_{\substack{y, \beta \\ \beta(y)=x}} W_{\beta}(y) p(y, t) - \sum_{\alpha} W_{\alpha}(x) p(x, t). \quad (2.4)$$

A sink is a point x , such that $W_{\alpha}(x) = 0$ for all α , so that $W(x) = 0$, in which case we assume that when the system reaches state x , it stays there for ever. Note also that if $W_{\alpha}(x) = 0$, we may as well assume that $\alpha(x)$ is not defined. From equation (2.4), a stationary probability $P(x)$ satisfies

$$W(x) P(x) = \sum_{\substack{y, \beta \\ \beta(y)=x}} W_{\beta}(y) P(y)$$

or using the notation of equation (2.3)

$$W(x) P(x) = \sum_{\substack{y, \beta \\ \beta(y)=x}} p_{\beta}(y) W(y) P(y). \quad (2.5)$$

From this equation, we see immediately that if there are sinks x_s , then the stationary probability is a linear combination of δ -functions at these sinks.

Remark 1. It is important to allow for the possibility that a certain transition is not defined for all x in X . For example, if X is the set of integers ≥ 0 , the transition $x \rightarrow x - 1$ is not defined at $x = 0$.

Remark 2. In certain applications (in particular in chemistry), the transitions α are such that if $x \neq x'$, $\alpha(x) \neq \alpha(x')$. In this case, one can define an inverse transition α^{-1} such that $\alpha^{-1}(x)$ is the unique y (if it exists) such that $\alpha(y) = x$, and α^{-1} is then partially defined only on the subset $\alpha(X_\alpha)$. In many applications, A is such that if α is a transition in A , then α^{-1} is also in A . In this case, a trajectory $\{x_1, \dots, x_\ell\}$ (so that $x_2 = \alpha_1(x_1), \dots, x_\ell = \alpha_{\ell-1}(x_{\ell-1})$) has an inverse trajectory $\{x_\ell, \dots, x_1\}$.

3. Stationary probability in a finite, closed system

3.1. Equation for stationary probability

We assume here that X is finite and that there exists at least one trajectory of positive probability between any two points in X . In particular, there is no sink. Then the stationary probability is unique and the ergodic theorem is valid. We can iterate equation (2.5), k times, to obtain

$$W(x) P(x) = \sum p_{\beta_k}(x_k) \dots p_{\beta_1}(x_1) W(x_1) P(x_1) \tag{3.1}$$

where the sum is over the set of transitions $(\beta_1, \dots, \beta_k)$ and over the points x_1, \dots, x_k such that

$$\beta_1(x_1) = x_2 \quad \beta_2(x_2) = x_3 \quad \dots \quad \beta_k(x_k) = x. \tag{3.2}$$

We denote by $\gamma_k(x_1 \rightarrow x)$ a trajectory joining x_1 to x in exactly k steps. The probability of such a trajectory is

$$p(\gamma_k(x_1 \rightarrow x)) = p_{\beta_k}(x_k) \dots p_{\beta_1}(x_1) \tag{3.3}$$

and equation (3.1) can be abbreviated as

$$W(x) P(x) = \sum_{x_1} \sum_{\gamma_k(x_1 \rightarrow x)} p(\gamma_k(x_1 \rightarrow x)) W(x_1) P(x_1) \quad \text{for all } k \geq 0. \tag{3.4}$$

3.2. Global balance relation

We now define the following absorption probabilities for two subsets A, B , in X :

$$\bar{p}(y \rightarrow B | A) = \text{the probability, that starting from } y, \text{ the system reaches } B \text{ (at some further time), when the subset } A \text{ is an absorbing set.} \tag{3.5}$$

In other words, this is the probability that starting from y , the system reaches B before reaching A .

A particular case of the definition for $B = \{x\}$, $y = \hat{x}$, $A = \{x_0, x\}$, is the following:

$$\bar{p}(\hat{x} \rightarrow x | x_0, x) = \text{the probability that, starting from } \hat{x}, \text{ the system is absorbed at } x \text{ (rather than at } x_0), \text{ when } x, x_0 \text{ are absorbing points.} \tag{3.6}$$

The first basic result of this paper is the following equation which is obtained from equation (3.4) when k tends to infinity, and is derived in the appendix:

$$W(x) P(x) = W(x) P(x) \bar{p}(x \rightarrow x | x_0, x) + W(x_0) P(x_0) \bar{p}(x_0 \rightarrow x | x_0, x). \quad (3.7)$$

It is clear that equation (3.7) can be rewritten as

$$W(x) P(x) \bar{p}(x \rightarrow x_0 | x_0, x) = W(x_0) P(x_0) \bar{p}(x_0 \rightarrow x | x_0, x). \quad (3.8)$$

This relation is a kind of global balance relation, valid for any transition process.

Using the present notation the usual detailed balance equation, which plays an important role in equilibrium processes in physics and chemistry, would be

$$W_\alpha(x) P(x) = W_{\alpha^{-1}}(\alpha(x)) P(\alpha(x)). \quad (3.9)$$

Clearly, this is satisfied only in special cases, unlike equation (3.8). This global balance relation seems to be a broad generalization of the standard detailed balance condition. The interpretation and applications of this formula will appear in another publication.

4. Stationary probability in a finite, open system

4.1. Finite subset $D \subset X$

Let us now consider a finite subset $D \subset X$ such that between two arbitrary points of D there is at least one trajectory with positive probability which stays in D .

The external boundary D^* of D is the set of points $x \in X$ which are not in D , but which can be reached by a single transition α from a point of D . So D^* is the set of points $x \notin D$ such that there exists $y \in D$ and $\alpha \in A$ with $\alpha(y) = x$. This implies that *any path starting from a point in D which leaves D at some time, must go through a point of D^* .*

4.2. $x \in D$

We fix a point $x \in D$ and apply equation (3.4) and the argument developed in section 3.2, except that x_0 is replaced by D^* . The trajectories $\gamma_k(x_1 \rightarrow x)$ are sorted into two subsets.

- (a) The trajectories from x_1 to x which never go through $\{x\} \cup D^*$ at any intermediary step x_1, \dots, x_{n-1} . This gives a contribution to the second member of equation (3.4)

$$\sum_{\substack{x_1 \neq x \\ x_1 \notin D^*}} W(x_1) P(x_1) \sum_{\bar{\gamma}(x_1 \rightarrow x)} p(\bar{\gamma}_k^*(x_1 \rightarrow x)) \quad (4.1)$$

where $\bar{\gamma}_k^*(x_1 \rightarrow x)$ is a trajectory joining $x_1 \rightarrow x$ in k steps which does not go through x or D^* .

- (b) Trajectories from x_1 to x , which go through $x \cup \{D^*\}$ at an intermediary step. In turn, these trajectories can be split into the following two disjoint subsets.

- Trajectories which go from x_1 to x in $k-h$ steps and then from x to x without reaching $x \cup \{D^*\}$ in the last h steps. They give the contribution

$$\sum_h' \sum_{x_1} W(x_1) P(x_1) \sum_{\gamma_{k-h}(x_1 \rightarrow x)} p(\gamma_{k-h}(x_1 \rightarrow x)) \sum_{\bar{\gamma}_h^*(x \rightarrow x)} p(\bar{\gamma}_h^*(x \rightarrow x)). \quad (4.2)$$

- Trajectories which go from x_1 to $x^* \in D^*$, in $k - h$ steps and then from x^* to x , without reaching $x \cup \{D^*\}$ again in the last h steps. They give the contribution

$$\sum_h' \sum_{x_1} W(x_1) P(x_1) \sum_{\substack{\gamma_{k-h}(x_1 \rightarrow x^*) \\ x^* \in D^*}} p(\gamma_{k-h}(x_1 \rightarrow x^*)) \sum_{\bar{\gamma}_h^*(x^* \rightarrow x)} p(\bar{\gamma}_h^*(x^* \rightarrow x)). \quad (4.3)$$

We add the contributions given by equations (4.1)–(4.3) to obtain

$$\begin{aligned} W(x) P(x) &= \sum_{\substack{x_1 \neq x \\ x_1 \notin D^*}} W(x_1) P(x_1) \sum_{\bar{\gamma}_k^*(x_1 \rightarrow x)} p(\bar{\gamma}_k^*(x_1 \rightarrow x)) \\ &+ W(x) P(x) \sum_h' \sum_{\bar{\gamma}_h^*(x_1 \rightarrow x)} p(\bar{\gamma}_h^*(x_1 \rightarrow x)) \\ &+ \sum_{x^* \in D^*} W(x^*) P(x^*) \sum_h' \sum_{\bar{\gamma}_h^*(x_1 \rightarrow x)} p(\bar{\gamma}_h^*(x_1 \rightarrow x)). \end{aligned} \quad (4.4)$$

In equations (4.2)–(4.4), \sum_h' is the sum over $1 \leq h \leq k - 1$.

4.3. Limit $k \rightarrow \infty$

We go to the limit $k \rightarrow \infty$ in equation (4.4). The first term in the second member tends to zero (it is the probability of going from x_1 to x with $\{x\} \cup D^*$ as an absorbing condition). So we obtain, for x in D

$$W(x) P(x) = W(x) P(x) \bar{p}(x \rightarrow x | x, D^*) + \sum_{x^* \in D^*} W(x^*) P(x^*) \bar{p}(x^* \rightarrow x | x, D^*) \quad (4.5)$$

where we have used the notation of equation (3.6), so that $\bar{p}(\hat{x} \rightarrow x | x, D^*)$ is the probability, starting from \hat{x} , to be absorbed by x at any further time, with $\{x, D^*\}$ as the absorbing conditions. In particular, $\bar{p}(x \rightarrow x | x, D^*)$ is the probability starting from x , to hit x again, before leaving D .

We shall assume the following hypothesis:

Any trajectory joining a point outside D , to a point inside D must hit D^* . (4.6)

This hypothesis is fulfilled if for any permitted transition α , the inverse transition α^{-1} is also permitted. If hypothesis (4.6) is realized, $\bar{p}(x^* \rightarrow x | x, D^*)$ is the probability, starting from x^* , to hit x again, while staying all the time in D , except at the initial point, so that

$$\bar{p}(x^* \rightarrow x | x, D^*) = \sum_{\substack{\beta \\ \beta(x^*) \in D}} p_\beta(x^*) \bar{p}(\beta(x^*) \rightarrow x | x, D^*). \quad (4.7)$$

Then using equation (4.7) we can rewrite (4.5), for any x in D ,

$$W(x) P(x) \bar{p}(x \rightarrow D^* | x, D^*) = \sum_{x^* \in D^*} \sum_{\substack{\beta \in A \\ \beta(x^*) \in D}} W_\beta(x^*) P(x^*) \bar{p}(\beta(x^*) \rightarrow x | x, D^*). \quad (4.8)$$

Equation (4.8) is one of the main results of this paper.

The quantity $W_\beta(x^*) P(x^*)$ is a part of the probability current for the transition β from x^* to $\beta(x^*)$. It is the entrance current for β at x^* . The full (algebraic) current for the transition β at x is

$$J_\beta(x) = -J_{\beta^{-1}}(\beta(x)) = W_\beta(x) P(x) - W_{\beta^{-1}}(\beta(x)) P(\beta(x)). \quad (4.9)$$

All currents are zero for the stationary distribution P if and only if detailed balance holds.

Equation (4.8) is valid even if the master equation (2.1) is not valid outside $D \cup D^*$, and it involves only the mechanism of the transitions inside $D \cup D^*$. Moreover, D is coupled to D^* only via the entrance currents $W_\beta(x^*) P(x^*)$, and when the asymptotic transmission probabilities \bar{p} are known, equation (4.8) determines the stationary probability inside D as a linear combination of these entrance currents. It is clear that equation (4.8) is just a balance equation. Its formulation in terms of entrance currents can be useful in practical problems, since the entrance currents are directly related to physical fluxes entering the system.

Equation (4.8) will be used in the approximations developed in sections 6 and 7.

5. Mean exit time from D

5.1. Equation for mean exit time

Given a point x in D , the exit time of a trajectory starting from x (i.e. the first time such that a trajectory hits D^* and thus leaves D) is a certain functional $\tau(\gamma)$ of the trajectory. We call $T_D(x)$ the mean exit time, i.e. the average over the set of all trajectories γ starting from x , stopped at their first hitting of D^* . Because $1/W(x)$ is the mean waiting time at x , it is clear that

$$\begin{aligned} T_D(x) &= \frac{1}{W(x)} + \sum_{\beta} p_{\beta}(x) T_D(\beta(x)) \\ T_D(x) &= 0 \quad \text{for } x \notin D. \end{aligned} \quad (5.1)$$

We shall define $\theta(x)$ by

$$\theta(x) = \begin{cases} \frac{1}{W(x)} & \text{for } x \in D \\ 0 & \text{for } x \notin D \end{cases} \quad (\text{in particular if } x \in D^*) \quad (5.2)$$

and write

$$q_{\beta}(x) = \begin{cases} p_{\beta}(x) & \text{for } x \in D \\ 0 & \text{for } x \notin D. \end{cases} \quad (5.2')$$

Thus equation (5.1) can be rewritten for any x in X ,

$$T_D(x) = \theta(x) + \sum_{\beta} q_{\beta}(x) T_D(\beta(x)) \quad \text{for all } x \in X \quad (5.3)$$

an equation that can also be obtained from the adjoint master equation [1].

5.2. Mean exit time in terms of absorption probabilities

One can iterate equation (5.3) using the previous conventions, to obtain

$$T_D(x) = \theta(x) + \sum_{\beta} q_{\beta_1}(x) \theta(x_1) + \cdots + \sum_{\beta_1, \dots, \beta_k} q_{\beta_1}(x) q_{\beta_2}(x_1) \cdots q_{\beta_k}(x_{k-1}) \theta(x_k) + \cdots \quad (5.4)$$

where $x_1 = \beta_1(x), \dots, x_j = \beta_j(x_{j-1})$.

This can be resummed as

$$T_D(x) = \theta(x) + \sum_{x' \in D} \theta(x') \sum_{k \geq 1} \sum_{\substack{\beta_1, \dots, \beta_k \\ x_k = x'}} q_{\beta_1}(x) q_{\beta_2}(x_1) \cdots q_{\beta_k}(x_{k-1}). \quad (5.5)$$

The product $q_{\beta_1}(x) q_{\beta_2}(x_1) \dots q_{\beta_k}(x_{k-1})$ is the probability of a trajectory $(x, x_1, \dots, x_{k-1}, x_k = x')$ joining x to x' in k transitions, without leaving D . Such a trajectory hits x' m times, where $m \geq 1$, at steps $k_1, \dots, k_m = k$.

Thus the quantity

$$\sum_{k \geq 1} \sum_{\substack{\beta_1, \dots, \beta_k \\ x_k = x'}} q_{\beta_1}(x) q_{\beta_2}(x_1) \dots q_{\beta_k}(x_{k-1})$$

is the total probability of all trajectories joining x to x' staying all the time in D , and is given by

$$\bar{p}(x \rightarrow x' | x, D^*) \sum_{m \geq 1} [(\bar{p}(x' \rightarrow x' | \{x', D^*\}))]^{m-1} = \frac{\bar{p}(x \rightarrow x' | x', D^*)}{\bar{p}(x' \rightarrow D^* | x', D^*)}$$

where we have used the notation (3.6). Then equation (5.5) becomes

$$T_D(x) = \theta(x) + \sum_{x' \in D} \frac{\bar{p}(x \rightarrow x' | x', D^*)}{\bar{p}(x' \rightarrow D^* | x', D^*)} \theta(x'). \tag{5.6}$$

This result is the basis of the lifetime evaluation for a locally stable state, presented in section 6. Here again, as defined in equation (3.6), $\bar{p}(a \rightarrow b | x', D^*)$ is the probability, starting from a , to reach b when x' and D^* are absorbing.

6. Approximation in the neighbourhood of a probability maximum

In this section, we shall assume that D contains only a single sharp maximum x_0 , of the stationary probabilities $P(x)$. We shall also assume that on D^* , P has a sharp maximum at x_0^* , but still

$$P(x_0^*) \ll P(x_0). \tag{6.1}$$

6.1. Estimation of the absorption probabilities

In equation (4.8), all quantities $W_\beta(x^*)$ have the same order of magnitude, and we suppose that the quantities $\bar{p}(\beta(x^*) \rightarrow x' | D^*)$ also have the same order of magnitude for all x^* in D^* and β .

Using equation (6.1), we see that the main term in the second member of (4.8) is

$$\left(\sum_{\substack{\beta \in A \\ \beta(x_0^*) \in D}} W_\beta(x_0^*) \bar{p}(\beta(x_0^*) \rightarrow x | x, D^*) \right) P(x_0^*).$$

But the quantities $\bar{p}(\beta(x_0^*) \rightarrow x | x, D^*)$ are essentially $\bar{p}(x_0^* \rightarrow x | x, D^*)$, so that (4.8) becomes, using (6.1),

$$W(x) P(x) \bar{p}(x \rightarrow D^* | x, D^*) \sim \left(\sum_{\substack{\beta \in A \\ \beta(x_0^*) \in D}} W_\beta(x_0^*) \right) \bar{p}(x_0^* \rightarrow x | x, D^*) P(x_0^*). \tag{6.2}$$

It is clear that the probability $\bar{p}(x_0^* \rightarrow x \mid x, D^*)$, that starting from x_0^* , the particle is absorbed by $x \in D$ before reaching D^* , is less than the probability of making a first transition from x_0^* to a point in D ,

$$\bar{p}(x_0^* \rightarrow x \mid x, D^*) \leq \frac{\sum_{\beta, \beta(x_0^*) \in D} W_\beta(x_0^*)}{W(x_0^*)} \tag{6.3}$$

and so from equations (6.2) and (6.3), we obtain the inequality

$$\frac{1}{\bar{p}(x \rightarrow D^* \mid x, D^*)} \geq \frac{W(x) W(x_0^*)}{\left(\sum_{\beta, \beta(x_0^*) \in D} W_\beta(x_0^*)\right)^2} \frac{P(x)}{P(x_0^*)} \geq \frac{W(x)}{\sum_{\beta, \beta(x_0^*) \in D} W_\beta(x_0^*)} \frac{P(x)}{P(x_0^*)}. \tag{6.4}$$

In general, the upper bound given by equation (6.4) is not effective and $\bar{p}(x_0^* \rightarrow x \mid x, D^*)$ is indeed much smaller than the upper bound given in the second member of equation (6.4).

Remark. It may occur that for a certain x , near x_0 , the quantities $\bar{p}(\beta(x^*) \rightarrow x \mid x, D^*)$ are very different for different x^* in D^* . For example, suppose that the state space X contains two sharp maxima of $P(x)$, x_0, x'_0 , and a saddle point x''_0 , and suppose that D contains x_0, x''_0 , but not x'_0 . Then, if x^* in D^* , is in the basin of attraction of x'_0 , $\bar{p}(x^* \rightarrow x_0 \mid x, D^*)$ will be extremely small, whereas if x_0^* in D^* is in the basin of attraction of x_0 , $\bar{p}(x^* \rightarrow x_0 \mid D^*)$ will be of the order of unity. In these cases one cannot derive any accurate results without further information (see [8]).

6.2. Estimation of the mean exit time

Let us assume again that D contains a single sharp maximum x_0 of $P(x)$ and that the quantities $\bar{p}(\beta(x^*) \rightarrow x_0 \mid x, D^*)$ have the same order of magnitude for all x^* in D^* .

We now consider equation (5.6) giving $T_D(x)$ and the sum

$$\sum_{x' \in D} \frac{\bar{p}(x \rightarrow x' \mid x', D^*)}{\bar{p}(x' \rightarrow D^* \mid x', D^*)} \theta(x'). \tag{6.5}$$

Using the bound of equation (6.4), we see that

$$\frac{1}{\bar{p}(x' \rightarrow D^* \mid x', D^*)}$$

is sharply peaked at $x' = x_0$ in D , and if x is well inside D , $\bar{p}(x \rightarrow x' \mid x', D^*)$ will be $O(1)$ at $x' = x_0$, so that $T_D(x)$ will be very large.

Thus, for x inside D far away from the boundary D^* , we find from equation (5.6) that

$$T_D(x) \sim \frac{\bar{p}(x \rightarrow x_0 \mid x_0, D^*) \theta(x_0)}{\bar{p}(x_0 \rightarrow D^* \mid x_0, D^*)}. \tag{6.6}$$

In fact, in this case, one can write up to terms of order one,

$$\bar{p}(x \rightarrow x_0 \mid x_0, D^*) \sim \bar{p}(x_0 \rightarrow x_0 \mid x_0, D^*) = 1 - \bar{p}(x_0 \rightarrow D^* \mid x_0, D^*) \simeq 1$$

so that

$$T_D(x) \sim T_D(x_0) \sim \frac{\theta(x_0)}{\bar{p}(x_0 \rightarrow D^* \mid x_0, D^*)}. \tag{6.7}$$

Using equation (6.4), we see that, because $\theta(x) = 1/W(x)$

$$T_D \sim \frac{W(x_0^*)}{\left(\sum_{\beta, \beta(x_0^*) \in D} W_\beta(x_0^*)\right)^2} \frac{P(x_0)}{P(x_0^*)} \geq \frac{P(x_0)}{P(x_0^*)}. \tag{6.8}$$

We note that equation (6.8) is a generalization, in our context, of the formula for the inverse of the rate constant given by the transition state theory in chemical systems and mentioned in the introduction (see also [8]).

7. Reaction–diffusion systems in large volumes

7.1. The model

We consider a system of particles which can react or diffuse in a vessel of volume Ω . This can be viewed as a special case of the previous formalism according to the usual methods of reaction–diffusion systems [1, 4, 5]. The vessel is divided into N cells of volume $V = \Omega/N$, which are small enough to be homogeneous, but are also large enough compared with the mean free path of the particles. Thus, V will be very large in microscopic units.

The state space X is formed by collections $x = \{x_i\}_{i=1,\dots,s}$, where s is the total number of species (either true species or species in various spatial cells) and x_i is the concentration of species i , $x_i = n_i/V$, where n_i is the number of particles of species i . The transitions α are the chemical or diffusion processes which take place in the system. Here the state space X is still discrete as in section 2, but we want to determine the asymptotic behaviour of the previous results for large V . So we write

$$dx_i = \frac{1}{V} \tag{7.1}$$

and if $P(x)$ is the stationary probability, it gives a probability density $p(x)$ by the formula

$$P(x) = p(x) \prod_{i=1}^s dx_i = p(x) V^{-s}. \tag{7.2}$$

Moreover, one must rescale the transition rates by

$$W_\alpha(x) = V w_\alpha(x) \tag{7.3}$$

where $w_\alpha(x)$ is the transition rate for the process α , per unit volume, the state of the system being x . We refer to the literature [4, 13–15] for details and explanations. We assume that for large V [8, 13–15] we have

$$p(x) \sim U(x, V) \exp(-V\Phi(x)) \tag{7.4}$$

where $\Phi(x)$ is the ‘information potential’ (per unit volume) and $U(x, V)$ is a prefactor depending of the state x and the volume V . In [8, 14], it is shown that Φ satisfies a Hamilton–Jacobi equation and that U is given by a transport equation. It has been proved that there is a unique, smooth function Φ , up to an additive constant, and a unique, smooth U , up to a multiplicative constant, satisfying these equations. These constants are fixed by the normalization condition for $p(x)$.

Thus, if x is an absolute minimum of Φ , the constants can be given by the conditions

$$U(x, V) \sim U_0(x) \left(\frac{V}{2\pi}\right)^{s/2} \tag{7.5}$$

$$\Phi(x_0) = 0 \tag{7.6}$$

$$U_0(x_0) = \left(\det \frac{\partial^2 \Phi}{\partial x_i \partial x_j}(x_0)\right)^{1/2} \tag{7.7}$$

(provided we are not in a critical case).

7.2. Large-volume asymptotics of absorption probability

We now consider a macroscopic domain D in the state space X . This means that D contains a number of states of order $O(V^s)$. Then, D^* , the external boundary of D , contains a number of states of the order $O(V^{s-1})$. This is essentially due to the fact that there are only a finite number of transitions $\alpha \in A$ leading from a state x to a neighbouring state in one time step (the boundary of a macroscopic domain is not ‘thick’).

In equation (4.8), the probabilities $P(y)$ rescale like V^{-s} and the rates W rescale like V (equations (7.2) and (7.3)). After division by V^{-s+1} , equation (4.8) becomes

$$w(x) p(x) \bar{p}(x \rightarrow D^* | x, D^*) = \sum_{x^* \in D} \sum_{\substack{\beta \\ \beta(x^*) \in D}} w_\beta(x^*) p(x^*) \bar{p}(\beta(x^*) \rightarrow x | x, D^*). \quad (7.8)$$

This equation is a rescaled version of equation (4.8).

We shall now assume that

- (H1) D contains a single minimum x_0 of Φ and does not contain any other critical points of Φ . Moreover, D^* contains no critical point of Φ .
 (H2) The minimum of Φ on D^* is reached at a point x_0^* which is non-degenerate.

Because of (H1) a typical trajectory of the stochastic process follows, in any finite time, the deterministic trajectory associated with the vector field of the deterministic chemical processes. Moreover, $\bar{p}(\beta(x^*) \rightarrow x | x, D^*)$ is essentially $O(1)$ for all $x^* \in D^*$ and x close to x_0 (see [8] for a justification of these facts). So, the assumption made in section 6 is valid.

Because we are in the large- V limit, the estimation of the sum in the second member of equation (7.8) must take into account the fact that the number of states $x^* \in D^*$, where Φ stays very close to $\Phi(x_0^*)$ is given approximately by

$$(2\pi V)^{(s-1)/2} (\det_{D^*} \Phi''(x_0^*))^{1/2} \quad (7.9)$$

where \det_{D^*} denotes the determinant of the matrix of the second derivatives of Φ at x_0^* but only along tangential directions to D^* (i.e. along the orthonormal directions in the tangent space at x_0^* to D^*).

The asymptotic of equation (7.8) becomes, with equation (7.9)

$$w(x) p(x) \bar{p}(x \rightarrow D^* | x, D^*) \sim (2\pi V)^{(s-1)/2} (\det_{D^*} \Phi''(x_0^*))^{1/2} p(x_0^*) \left(\sum_{\substack{\beta \\ \beta(x_0^*) \in D}} w_\beta(x_0^*) \right) \bar{p}(x_0^* \rightarrow x | x, D^*)$$

(using the fact that $\bar{p}(\beta(x_0^*) \rightarrow x | x, D^*)$ is to leading order $\bar{p}(x_0^* \rightarrow x | x, D^*)$). We deduce that under the hypotheses (H1) and (H2), equation (6.4) should be replaced by

$$\frac{1}{\bar{p}(x \rightarrow D^* | x, D^*)} \sim \frac{w(x)}{\sum_{\beta, \beta(x_0^*) \in D} w_\beta(x_0^*)} \frac{(2\pi V)^{(1-s)/2} (\det_{D^*} \Phi''(x_0^*))^{-1/2} p(x)}{\bar{p}(x_0^* \rightarrow x | x, D^*)} \frac{p(x)}{p(x_0^*)} \quad (7.10)$$

and up to prefactors

$$\frac{p(x)}{p(x_0^*)} \sim \exp(-V(\Phi(x) - \Phi(x_0^*))). \quad (7.11)$$

In critical situations, however, Φ may vanish and the prefactor may become preponderant.

7.3. Large-volume asymptotics of the mean exit time

The same reasoning as in section 6.2, can now be applied to $T_D(X)$ provided hypotheses (H1) and (H2) above hold. For x inside D , $\bar{p}(x \rightarrow x' | x', D^*)$ will be almost equal to one, and so in equation (5.6), the sum in x' is sharply peaked at the point where $(\bar{p}(x' \rightarrow D^* | x', D^*))^{-1}$ is maximal. According to equation (7.10), this is the point $x' = x_0$ in the large-volume limit.

On the other hand,

$$\bar{p}(x \rightarrow x_0 | x_0, D^*) \sim 1. \tag{7.12}$$

The number of states where $p(x')$ attains its maximum at x_0 is of the order

$$(2\pi V)^{s/2} (\det \Phi''(x_0))^{1/2} \tag{7.13}$$

and so using equations (7.10)–(7.13) in (5.6) we obtain our final formula for the mean exit time from the basin of attraction of x_0 in the large-volume limit:

$$T_D(x) \sim \frac{1}{V^{1/2}} \frac{(2\pi)^{1/2}}{\left(\sum_{\beta, \beta(x_0^*) \in D} w_\beta(x_0^*)\right)} \left(\frac{\det \Phi''(x_0)}{\det \Phi''(x_0^*)}\right)^{1/2} \frac{1}{\bar{p}(x_0^* \rightarrow x | x, D^*)} \frac{p(x_0)}{p(x_0^*)}. \tag{7.14}$$

Again we have used the fact that $\theta(x_0) \simeq 1/(Vw(x_0))$.

Here the quantity $\bar{p}(x_0^* \rightarrow x | x, D^*)$ is of $O(1)$, and $p(x_0)/p(x_0^*) \sim \exp(V\Phi(x_0^*))$ (recall that $\Phi(x_0) = 0$ by our convention of equation (7.6)).

In particular, for x in D , we obtain from equation (7.14)

$$T_D(x) \sim T_D(x_0) \tag{7.15}$$

Again the estimations of equations (7.14) and (7.15) are valid under the hypotheses (H1) and (H2).

Equation (7.14) is our main result for physical and chemical applications.

Again, this result was known and proved only in special cases. Because of the relation $p(x_0)/p(x_0^*) \simeq \exp(V\Phi(x_0^*))$, $T_D(x)$, as given in equation (7.14), displays an Arrhenius factor, with the information potential instead of the classical free energy (see, e.g., [5–7]). Usually, in equilibrium or near-equilibrium situations $V\Phi$ is given (it is the free energy divided by the temperature). In our general setting, Φ is not known *a priori* and is only defined as a stationary solution of a Hamilton–Jacobi equation (of a non-standard type) (see [8, 13–15]).

Usually, results of the type of equations (7.14) and (7.15) are derived for continuous systems using partial differential equations methods (see, e.g., [11]) or the theory of small random perturbations of solutions of deterministic differential equations (see, e.g., [12]). Using these methods, Φ is obtained by solving a Hamilton–Jacobi equation associated with a Fokker–Planck equation (see again [11, 12] for more rigorous derivations). Nevertheless, when one starts from a reaction–diffusion in a discrete space (taking the number of particles rather than the concentrations, as variables) the criterion $P(x) \sim \exp(-V\Phi(x))$ leads to a non-standard Hamilton–Jacobi equation of the Kubo type (see [8, 13–15]) and Φ differs significantly from the corresponding function obtained by the Fokker–Planck equation. As proved on explicit models in [16] this leads to exponentially large errors. This is why the partial differential equations methods or the standard random perturbation of a vector field, applied directly to a discrete master equation do not provide a correct evaluation of the quantity $p(x_0)/p(x_0^*)$ in equations (7.14) or (7.15).

We also note that for one degree of freedom an exact formula for the mean exit time is given in [1], but the method there cannot be extended to many degrees of freedom. Thus we realized in [16] that the Fokker–Planck continuous-space approach is not suitable. By

comparison, our approach is more ‘path-integral’-like (see [8, 17]) and also gives useful new formulae, which are completely general, even for small V .

Near criticality, the information potential Φ can vanish and the prefactor becomes the leading term in the approximation for the mean exit time. The study of the prefactor is a rather delicate point and will be the subject of future publications [18].

Remark. For a domain D that contains more than one critical point of Φ , one can obtain more complex results (see [8]), but in this case $T_D(x)$ will depend on x in general when x moves from one basin of attraction to another.

8. Conclusion

We have given various general formulae for a stochastic transition system. First, for a closed system we present a generalization of the detailed balance condition, which is a global balance condition, equation (3.12). For an open domain, we obtain a relation expressing the absorption probability in terms of quantities on the boundary of the system equation (4.9), which does not need knowledge of the transition system out of an open domain (except through the entrance fluxes). We also obtain an equation for the mean exit time, equation (5.6), in terms of absorption probabilities. Finally, we have examined certain asymptotic approximations, in particular for reaction–diffusion systems in the large-volume limit. Our method does not rely on partial differential equation techniques, or on special circumstances which could make the system exactly solvable. It only uses partial summation over classes of paths. The reason we wanted to have an approach independent of the standard partial differential equation technique (such as Fokker–Planck) is that these techniques do not give correct results for the discrete classical diffusion systems, even for their continuum limits, as we proved in [8, 18]. The general estimation (equation (7.14)) of the mean exit time of a reaction–diffusion system from the basin of attraction of a stable state is very useful for the analysis of physico-chemical systems, since it gives the largest evolution time scale of the system, without solving an eigenvalue problem. It leads to an evaluation of the chemical rate constants and more generally to the estimation of the lifetime of metastable states, which are of great importance in many physico-chemical problems.

Appendix. Derivation of the global balance relation

We adopt the notation of section 3, and consider equation (3.4). Let us now fix a point $x_0 \neq x$ in X . We can sort the trajectories $\gamma_k(x_1 \rightarrow x)$ into two subsets.

- (a) *The trajectories going from x_1 to x in k steps and which do not pass at x_0 nor x in the first $k - 1$ steps, namely x_1, x_2, \dots, x_{k-1} are all different from x and x_0 . We shall denote such a trajectory by $\tilde{\gamma}_k(x_1 \rightarrow x)$.*

The contribution of this set (a) of trajectories to the second member of equation (3.4) is

$$\sum_{x_1 \neq x_0, x} W(x_1) P(x_1) \sum_{\tilde{\gamma}_k(x_1 \rightarrow x)} p(\tilde{\gamma}_k(x_1 \rightarrow x)). \quad (\text{A.1})$$

- (b) *The trajectories going from x_1 to x in k steps and which pass at least once at x_0 or x in one of the intermediate steps. Such a trajectory reaches x_0 or x for the last time (before step k) at an intermediate step $k - h$, $1 \leq h \leq k - 1$, so that the last part is of the type $\tilde{\gamma}_h(x \rightarrow x)$ or $\tilde{\gamma}_h(x_0 \rightarrow x)$, where $\tilde{\gamma}_h$ is as above in (a).*

Now for fixed h , with $1 \leq h \leq k - 1$ and $\hat{x} = x$ or x_0 we see that

$$\sum_{x_1} W(x_1) P(x_1) \sum_{\gamma_{k-h}(x_1 \rightarrow \hat{x})} p(\gamma_{k-h}(x_1 \rightarrow \hat{x})) = W(\hat{x}) P(\hat{x})$$

so that the contribution of this second set (b) of trajectories to the second member of equation (3.4) is

$$W(x) P(x) \sum'_h \sum_{\tilde{\gamma}_h(x \rightarrow x)} p(\tilde{\gamma}_h(x \rightarrow x)) + W(x_0) P(x_0) \sum'_h \sum_{\tilde{\gamma}_h(x_0 \rightarrow x)} p(\tilde{\gamma}_h(x_0 \rightarrow x)) \tag{A.2}$$

where \sum'_h denotes a summation over $1 \leq h \leq k - 1$.

Adding the contributions (A.1) and (A.2), we obtain

$$\begin{aligned} W(x) P(x) &= W(x) P(x) \sum'_h \sum_{\tilde{\gamma}_h(x \rightarrow x)} p(\tilde{\gamma}_h(x \rightarrow x)) \\ &+ W(x_0) P(x_0) \sum'_h \sum_{\tilde{\gamma}_h(x_0 \rightarrow x)} p(\tilde{\gamma}_h(x_0 \rightarrow x)) \\ &+ \sum_{x_1 \neq x_0, x} W(x_1) P(x_1) \sum_{\tilde{\gamma}_k(x_1 \rightarrow x)} p(\tilde{\gamma}_k(x_1 \rightarrow x)). \end{aligned} \tag{A.3}$$

The quantity

$$\sum_{\tilde{\gamma}_k(x_1 \rightarrow x)} p(\tilde{\gamma}_k(x_1 \rightarrow x))$$

is the total probability of going from x_1 to x in k steps when x and x_0 are absorbing points. It tends to zero when $k \rightarrow \infty$.

The quantity

$$\sum'_h \sum_{\tilde{\gamma}_h(\hat{x} \rightarrow x)} p(\tilde{\gamma}_h(\hat{x} \rightarrow x))$$

(with $\hat{x} = x_0$ or x) is the probability that, starting from \hat{x} , the system is absorbed at x at most k steps, rather than at x_0 , when x_0 and x are absorbing points. When k tends to ∞ , this quantity tends to the absorption probability $\bar{p}(\hat{x} \rightarrow x | x_0, x)$ as defined in equation (3.6). Thus from (A.3) we obtain formula (3.7), as well as the global balance relation (3.8).

From equation (A.5), we see that if x_1, x_2, x_3 are three different states, we have

$$\frac{\bar{p}(x_1 \rightarrow x_2 | \{x_1, x_2\}) \bar{p}(x_2 \rightarrow x_3 | \{x_2, x_3\})}{\bar{p}(x_2 \rightarrow x_1 | \{x_1, x_2\}) \bar{p}(x_3 \rightarrow x_2 | \{x_2, x_3\})} = \frac{\bar{p}(x_1 \rightarrow x_3 | \{x_1, x_3\})}{\bar{p}(x_3 \rightarrow x_1 | \{x_1, x_3\})} \tag{A.4}$$

or

$$\begin{aligned} &\bar{p}(x_1 \rightarrow x_2 | \{x_1, x_2\}) \bar{p}(x_2 \rightarrow x_3 | \{x_2, x_3\}) \bar{p}(x_3 \rightarrow x_1 | \{x_1, x_3\}) \\ &= \bar{p}(x_1 \rightarrow x_3 | \{x_1, x_3\}) \bar{p}(x_3 \rightarrow x_2 | \{x_2, x_3\}) \bar{p}(x_2 \rightarrow x_1 | \{x_1, x_2\}). \end{aligned} \tag{A.5}$$

This relation can also be checked directly from the definition of \bar{p} .

References

[1] Van Kampen N 1981 *Stochastic Processes in Physics and Chemistry* (Amsterdam: North-Holland)
 Gardiner H 1983 *Handbook of Stochastic Methods* (New York: Springer)
 [2] Langer J S 1969 *Ann. Phys., NY* **54** 258
 [3] Hughes B D 1995 *Random Walks and Random Environments* vol 1 (Oxford: Clarendon)
 [4] Nicolis G and Prigogine I 1977 *Self-organization in non equilibrium systems* (New York: Wiley)
 [5] Glasstone S, Laidler K and Eyring H 1941 *The Theory of Rate Processes* (New York: McGraw-Hill)

- Benson S W 1960 *The Foundations of Chemical Kinetics* (New York: McGraw-Hill)
- Steinfeld J I, Francisco J S and Hase W L 1989 *Chemical Kinetics and Dynamics* (Englewood Cliffs, NJ: Prentice Hall)
- [6] Kramers H A 1940 *Physica* **7** 284
- [7] Hynes J T 1985 *Theory of Chemical Reaction Dynamics* vol 4, ed M Baer (Boca Raton, FL: Chemical Rubber Company) p 171
- [8] Gaveau B, Moreau M and Toth J 1999 *J. Chem. Phys.* **111** 7736–48
R Casalbuoni *et al* *Path Integrals and Non Equilibrium Thermodynamics in Path Integrals from peV to TeV* (Singapore: World Scientific) pp 52–8
Gaveau B, Moreau M and Toth J 2000 *Physica A* **277** 455–68
- [9] Gaveau B and Schulman L S 1987 *J. Phys. A: Math. Gen.* **20** 2865
- [10] Gaveau B and Schulman L S 1993 *J. Stat. Phys.* **70** 614
Gaveau B and Schulman L S 1994 *J. Stat. Phys.* **74** 607
- [11] Ludwig D 1975 *SIAM Rev.* **17** 605
- [12] Freidlin M and Ventcell A 1970 *Russian Math. Surv.* **25** 1
- [13] Kubo R, Matsuo K and Kitahara K 1973 *J. Stat. Phys.* **2** 51
- [14] Lemarchand H 1980 *Physica* **101** 518
Lemarchand H and Nicolis G 1984 *J. Stat. Phys.* **57** 609
- [15] Decalzi O and Tirapegui E 1989 *Instantaneous and Non-Equilibrium Structure* vol II (Dordrecht: Kluwer)
- [16] Gaveau B, Moreau M and Toth J 1997 *Lett. Math. Phys.* **40** 101
- [17] Onsager L and Machlup F 1953 *Phys. Rev.* **21** 1505
- [18] Gaveau B, Latrémolière D and Moreau M 2000 *Physica A*, at press