

LARGE EMISSION REGIME IN MEAN FIELD LUMINESCENCE

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In memory of our friend Robert A. Minlos

ABSTRACT. We study a class of random processes on N particles which can be interpreted as stochastic model of luminescence. Each particle can stay in one of two states: Excited state or ground state. Any particle at ground state is excited with a constant rate (pumping). The number of excited particles decreases by means of photon emission through interactions of the particles. We analyse the rare event of flashes, i.e., the emission of a very large number of photons B during a fixed time interval T . We employ the theory of large deviations to provide the asymptotics of the probability of such event when the total number of particles N tends to infinity. This theory gives us also the optimal trajectory of scaled process corresponding to this event. The stationary regime of this process we call the large emission regime. In several cases we prove that in the large emission regime a share of excited particles in a system is stable under the changes of the pumping and emission rates.

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1. INTRODUCTION

We study large fluctuations in a family Θ of continuous-time Markov processes which are mean field models of luminescence where N atoms (or, more generally, some species of particles) can be either in the ground state 0 or in an excited state 1 and where the transition from the excited state to the ground state is accompanied

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by the emission of light. Our interest is in the luminescence distribution, i.e., in the probability of the event that the cumulative number of the transitions from 1 to 0 during a finite time-interval T is at least B . We use the rate function found by large deviation theory on the path level to evaluate the asymptotics of the probability of some functionals that quantify the asymptotic properties of the luminescence distribution when B, N are large. In addition we are interested in the asymptotic behaviour of some functionals of the process trajectories under the large fluctuations.

We consider several scenarios of luminescence. In our setting all possible configurations form the state space $\mathbb{C} = \{0, 1\}^N$, and the Markov processes Θ we consider describe the random transitions within the state space \mathbb{C} , when a single particle or a group of particles changes its state. In order to change their states the particles interact with each other. To this end the particles create groups of some specific size with some specific relations of their states within the group as defined below. For any Markov process $\theta \in \Theta$ we study there exist at least two groups and therefore two types of reaction. One of the groups consists of only a single molecule with state 0. This particle changes its state from 0 to 1 spontaneously. We call this transition an *excitation*. An interpretation of this transition can be conceived as actions of an external medium, for example, *pumping*. Beside, there are other reactions involving groups of particles. In these reactions some amount of excited particles transit simultaneously to 0. Physically, we assume this transition to be accompanied by a emission of light (radiation). Hence the interpretation of our model is describing luminescence.

Our goal is to find statistical properties of the luminescence in some scaling limits. The first limit is the thermodynamic limit $N \rightarrow \infty$ with a suitable scaling of the variables. This limit brings us to the area of the large deviation theory. We consider the large deviations on the path level providing a corresponding *rate function*. Having the rate function we can study rare events. Our interest is an event for which the cumulative number of the transitions from 1 to 0 during a finite time-interval is at least B . Then the second limit is when $B \rightarrow \infty$. We study the density of excited particles conditioned so that B is very large. In the interpretation as emission of light the large deviation describe a bright flash on the time interval. The result we have obtained is rather unexpected:

The average density of the excited molecules conditioned on very large B does not depend on the rates of the transitions of the Markov process.

This statement means for example that no matter how small is the rate of the pumping (the transitions $0 \rightarrow 1$), for any values of the rates of the reactions the density of the excited molecules is equal to the same value. For example, for the particular case of process θ published in [12] this value is equal $\frac{1}{2}$.

The stochastic processes we consider in this article are extremely simple. Our efforts are concentrated on the large deviation theory for these processes. More complete presentations of the stochastic chemical kinetics theory see in [1], [2], [5], [7], [8], [9], [11], [15]. We also mention an intriguing duality of the pumping to one-dimensional diffusion-limited pair-annihilation [14].

The next section contains all definitions.

2. DEFINITIONS

Here we formally describe the set Θ of the Markov processes. We define $\mathcal{N} = \{1, \dots, N\}$. The elements of \mathcal{N} are called particles (or the molecules as in the Introduction). We also define the function

$$c: \mathcal{N} \rightarrow \{0, 1\},$$

where the value $c(i)$ is called a *state* of the particle $i \in \mathcal{N}$. All processes $\theta \in \Theta$ have the same set \mathbb{C} of states, which is the set of all configurations $\mathbb{C} = \{0, 1\}^N$.

The configuration set can be presented as the union

$$\mathbb{C} = \bigcup_{m=0}^N \mathbb{C}(m), \quad (2.1)$$

where

$$\mathbb{C}(m) = \left\{ c \in \mathbb{C} : \sum_{i=1}^N c(i) = m \right\}.$$

is a set of all configurations having the same number m of the particles in state 1. Every configuration c splits the set $\mathcal{N} = \mathcal{N}_0(c) \cup \mathcal{N}_1(c)$, where

$$\mathcal{N}_0(c) = \{i: c(i) = 0\}, \quad \mathcal{N}_1(c) = \mathcal{N} \setminus \mathcal{N}_0(c). \quad (2.2)$$

In other words, for a given configuration c , the set $\mathcal{N}_\alpha(c)$ is the set of atoms in state $\alpha \in \{0, 1\}$. It is clear that $m = |\mathcal{N}_1(c)|$.

In order to define the transitions of the processes $\theta \in \Theta$ we introduce the triplet

$$\tau_0 := (1, 0, -1)$$

and the set of integer triplets

$$\mathcal{K} := \{(k, r, s): k, r, s \in \mathbb{N} \text{ such that } N \geq k \geq r \geq s\} \cup \tau_0.$$

Observe that in any given triplet the third parameter is either a positive integer or -1 . In the latter case only the triplet τ_0 belongs to \mathcal{K} . The transitions of a given process θ are then defined by $d+1$ intensities $\mu_0, \tilde{\mu}_i, i = 1, \dots, d$ and a finite subset

$$\mathcal{K}_\theta = \{\tau_i = (k_i, r_i, s_i) \in \mathcal{K}, i = 1, \dots, d: \text{such that } \tau_i \neq \tau_j, \text{ if } i \neq j\} \cup \{\tau_0\} \subset \mathcal{K} \quad (2.3)$$

of $d+1$ distinct triples from \mathcal{K} , where each triplet encodes an allowed transition as follows.

- **Pumping:** Consider a configuration $c \in \mathbb{C}(m)$ with $0 \leq m < N$, which means that $N - m$ particles are in the ground state. Then the transition corresponding to the triplet $\tau_0 = (1, 0, -1)$ means that one of the particles in the ground state, which is chosen uniformly, becomes excited. In our notation the first entry 1 in the triplet means that one particle takes part in the transition, the second 0 means that this particle is in the ground state before the transition takes place, and -1 denotes that this particle is being excited. Physically, this transition is due to external pumping and occurs with intensity μ_0 .

- **Radiation:** The triplets τ_i with $i \in \{1, \dots, d\}$ denote transitions of a configuration $c \in \mathbb{C}(m)$ with $0 < m \leq N$ where the number of the excited particles decreases as follows. The first parameter k_i is the *cluster size*, i.e., the number of the particles involved in the transition τ_i . A cluster is chosen uniformly from all possible clusters of $k_i \leq N$ particles. If r_i of the particles in the selected cluster are excited then s_i uniformly chosen particles from this set relax to their ground state. Otherwise nothing happens. We call this event radiation and denote its intensity by $\tilde{\mu}_i$. Physically, this process is a spontaneous emission of s_i photons that occurs as a result of a collective interaction of k atoms.

Notice that these processes induce transitions between the sets $\mathbb{C}(m)$. Pumping increases the number of excited by one. Since there are $N - m$ ground state particles that can turn excited the intensity of the transition from $c \in \mathbb{C}(m)$ to the set $\mathbb{C}(m + 1)$ is equal to $\mu_0(N - m)$. Radiation defined by some triplet τ_i moves the configuration c from the set $\mathbb{C}(m)$ to the set $\mathbb{C}(m - s_i)$. Since for a fixed m the number clusters with k_i particles of which r_i are excited is given by

$$q_i(N, m) = \binom{m}{r_i} \binom{N - m}{k_i - r_i}$$

the intensity of the transition $\mathbb{C}(m)$ to $\mathbb{C}(m - s_i)$ is $\tilde{\mu}_i q_i(N, m)$. Below, the rates $\tilde{\mu}_i$ will be chosen to depend on N , $\tilde{\mu}_i \equiv \tilde{\mu}_i(N)$. We define this functional dependence when we determine the Markov process of functionals of the process θ .

Let us introduce some auxiliary objects corresponding to these d transitions. Let S, R, K be the following three subsets associated to the configuration c :

$$S, R \subseteq \mathcal{N}_1(c), K \subseteq \mathcal{N} \text{ such that } \emptyset \neq S \subseteq R \subseteq K$$

We call these sets *three-set- c* and denote as $\langle S, R, K \rangle^c$ or by the shorter notation $\mathbf{t}^c = \langle S, R, K \rangle^c$. We use also the equivalent presentation $\mathbf{t}^c = \langle \mathbf{s}(\mathbf{t}^c), \mathbf{r}(\mathbf{t}^c), \mathbf{k}(\mathbf{t}^c) \rangle^c$ with the obvious notations.

We say that the three-set- c \mathbf{t}^c represents the triplet $\tau_i = (k_i, r_i, s_i) \in \mathcal{K}_\theta$ and write $\mathbf{t}^c \rightarrow \tau_i$ if $|S| = s_i, |R| = r_i, |K| = k_i$. The index i in this representation we denote as $i(\mathbf{t}^c)$. Let $\mathbf{s}(\mathbf{t}^c) = S$. Every three-set- c $\mathbf{t}^c = \langle S, R, K \rangle^c$ representing the reaction $\tau_i = (k_i, r_i, s_i)$ realizes the transition $c \rightarrow c' = c_{S_i}^-$, where

$$c_{S_i}^-(j) = \begin{cases} 0, & \text{if } j \in S_i, \\ c(j), & \text{otherwise.} \end{cases}$$

On the other hand, the process represented by the triplet τ_0 realizes the transition $c \rightarrow c' = c_{j_0}^+(j)$, where

$$c_{j_0}^+(j) = \begin{cases} 1, & \text{if } j = j_0, \\ c(j), & \text{otherwise.} \end{cases}$$

Thus, the infinitesimal generator of the process θ described informally above is

$$\mathbf{L}_\theta f(c) = \mu_0 \sum_{j_0 \in \mathcal{N}_0(c)} [f(c_{j_0}^+) - f(c)] + \sum_{S \subseteq \mathcal{N}_1(c)} \sum_{\tau \in \mathcal{K}_\theta} \sum_{\substack{\mathbf{t}^c: \mathbf{t}^c \rightarrow \tau \\ \mathbf{s}(\mathbf{t}^c) = S}} \mu_{i(\mathbf{t}^c)} [f(c_S^-) - f(c)].$$

Functionals. Introduce some functionals of the processes θ we deal with in this work. The first functional is simply defined as the number of 1's in a current configuration

$$m(t) = |\mathcal{N}_1(\theta(t))|.$$

We consider the processes on time interval $[0, T]$. Let $0 \equiv t_0 < t_1 < \dots < t_n < T$ be the sequence of the moments on the time interval $[0, T]$ where the process θ changes its configuration. That is, the sequence $\theta(t_0) = c_0, \theta(t_1) = c_1, \dots, \theta(t_n) = c_n$ is the path of the θ on $[0, T]$: assuming $\theta(t) = c_i, t_i \leq t < t_{i+1}$, where $t_{n+1} \equiv T$, i.e., the process θ is continuous from the right, therefore $\theta(t_k)$ is the configuration c_k which the process takes after the random event occurred at t_k .

Any jump-moment $t_k, k = 1, \dots, n$ corresponds to some of the triplets $\tau \in \mathcal{K}_\theta$. For any $i = 1, \dots, d$ introduce $I^i(t)$ the number of jumps of the process θ occurred thanks the triplet τ_i . Define the following d functionals:

$$y^i(t) = s_i I^i(t), \quad i = 1, \dots, d.$$

All $d + 1$ functionals can be considered as vector paths $(m(t), y^1(t), \dots, y^d(t))$.

Note that the vector of functional $(m(t), y^1(t), \dots, y^d(t))$ is indeed Markov process on the state space $\{0, 1, \dots, N\} \times \mathbb{Z}_+^d$. We denote it as $\zeta = (\xi, \eta_1, \dots, \eta_d)$. The continuous time Markov process ζ is defined by a given set of triples \mathcal{K}_θ and its dynamics governed by the generator

$$\begin{aligned} \mathbf{L}g(m, y_1, \dots, y_d) &= \mu_0(N - m)[g(m + 1, y_1, \dots, y_d) - g(m, y_1, \dots, y_d)] \\ &+ \sum_{i=1}^d \tilde{\mu}_i \binom{m}{r_i} \binom{N - m}{k_i - r_i} [g(m - s_i, y_1, \dots, y_i + s_i, \dots, y_d) - g(m, y_1, \dots, y_d)], \end{aligned} \quad (2.4)$$

acting on the set of functions $g: \mathfrak{N} \times \mathbb{Z}_+^d \rightarrow \mathbb{R}$, where the parameter μ_0 is the rates of the jumps $+1$ of the process component ξ , and $\tilde{\mu}_i, i = 1, \dots, d$, are rates of the jumps $-s_i$ of the process ξ . When ξ changes its value by $-s_i$, simultaneously the component η_i increases its value by s_i : every component η_i jumps by the non-random number s_i , defined by the triplet (k_i, r_i, s_i) .

Except for the case $\mathcal{K}_\theta = \{\tau_1 = (1, 1, 1), \tau_0 = (1, 0, -1)\}$ (the linear case) all processes describe the mean field behavior. Thus the intensity of the emissions $\tilde{\mu}_i \equiv \tilde{\mu}_i(N)$ are scaled in the limit $N \rightarrow \infty$

$$\mu_i = \lim_{N \rightarrow \infty} \tilde{\mu}_i(N) N^{k_i - 1}, \quad (2.5)$$

where μ_i is some positive constant, or we can simply define

$$\tilde{\mu}_i \equiv \tilde{\mu}_i(N) = \frac{\mu_i}{N^{k_i - 1}}. \quad (2.6)$$

This type of mean field scaling sometimes is called *canonical* scaling, see for example [11], or it refers to the stochastic analog of the *law of mass actions*, see for example [4, Chapter 10, p. 454]. Moreover, such rate scaling brings our process defined by the generator (2.4) to the class of the processes known as *density dependent processes*,

see [4, Chapter 10]. Indeed, with (2.6) the generator (2.4) can be represented in the following way

$$\begin{aligned} \mathbf{L}g(m, y_1, \dots, y_d) &= N\mu_0\left(1 - \frac{m}{N}\right)[g(m+1, y_1, \dots, y_d) - g(m, y_1, \dots, y_d)] \\ &\quad + \sum_{i=1}^d N\left(\mu_i \frac{(m/N)^{r_i}}{r_i!} \frac{(1-m/N)^{k_i-r_i}}{(k_i-r_i)!} + O\left(\frac{1}{N}\right)\right) \\ &\quad \times [g(m-s_i, y_1, \dots, y_i+s_i, \dots, y_d) - g(m, y_1, \dots, y_d)]. \end{aligned} \quad (2.7)$$

Thus, our process will belong to the *density dependent family* of processes introduced [4], if for any $i = 1, \dots, d$ we define $\tilde{\mu}_i(N)$ such that

$$\tilde{\mu}_i(N) \binom{m}{r_i} \binom{N-m}{k_i-r_i} = N\mu_i \frac{(m/N)^{r_i}}{r_i!} \frac{(1-m/N)^{k_i-r_i}}{(k_i-r_i)!} \quad (2.8)$$

for any N . This scaling avoids $O(1/N)$ in (2.7). It provides finally the generator for the process ζ we will deal with in this paper:

$$\begin{aligned} \mathbf{L}g(m, y_1, \dots, y_d) &= N\mu_0\left(1 - \frac{m}{N}\right)[g(m+1, y_1, \dots, y_d) - g(m, y_1, \dots, y_d)] \\ &\quad + N \sum_{i=1}^d \mu_i \frac{(m/N)^{r_i}}{r_i!} \frac{(1-m/N)^{k_i-r_i}}{(k_i-r_i)!} \\ &\quad \times [g(m-s_i, y_1, \dots, y_i+s_i, \dots, y_d) - g(m, y_1, \dots, y_d)]. \end{aligned} \quad (2.9)$$

Further, the \mathbf{L} stands for the generator defined by (2.9).

3. PROBLEMS AND THE APPROACH

We study the large deviations as the following. Namely, we want to find the asymptotics of

$$\ln \Pr\left(\sum_{i=1}^d \eta_i(T) > BN\right)$$

as $N \rightarrow \infty$, where $B > 0$. Or, equivalently,

$$\ln \Pr\left(\frac{1}{N} \sum_{i=1}^d \eta_i(T) > B\right). \quad (3.1)$$

Since the problem belongs to the branch of the probability theory called the large deviations we have to find the rate function corresponding to the large deviation principle related to the problem ([3], [6], [13], see also [10], where the large deviation principle is studied for a model that is close to our model in some respect).

The rate function $I(\cdot)$ is defined on the space of paths

$$\gamma(\cdot) = (x_0(\cdot), x_1(\cdot), \dots, x_d(\cdot))$$

mapping $[0, T] \rightarrow [0, 1] \times \mathbb{R}_+^d$, where the paths $x_1(\cdot), \dots, x_d(\cdot)$ start from 0 at $t = 0$, are non-decreasing, and

$$\Pr\left(\frac{\zeta(\cdot)}{N} \approx \gamma(\cdot)\right) \approx \exp(-NI(\gamma(\cdot))).$$

We define the rate function via non-linear Hamiltonian

$$\begin{aligned} H_{\mathcal{K}_\theta}(x_0(\cdot), x_1(\cdot), \dots, x_d(\cdot), \sigma(\cdot), \varkappa_1(\cdot), \dots, \varkappa_d(\cdot)) \\ = \mu_0(1 - x_0(\cdot))[e^{\sigma(\cdot)} - 1] + \sum_{i=1}^d \mu_i \frac{x_0^{r_i}}{r_i!} \frac{(1 - x_0)^{k_i - r_i}}{(k_i - r_i)!} [e^{-s_i \sigma(\cdot) + s_i \varkappa_i(\cdot)} - 1]. \end{aligned} \quad (3.2)$$

The Hamiltonian $H_{\mathcal{K}_\theta}$ is defined by the generator \mathcal{H} of a non-linear semigroup acting on the functions f on $[0, 1] \times \mathbb{R}_+^d$. Let $\underline{x} \in [0, 1] \times \mathbb{R}_+^d$; then

$$H_{\mathcal{K}_\theta}(\underline{x}, \nabla f) := (\mathcal{H}f)(\underline{x}) := \lim_{N \rightarrow \infty} \frac{1}{N} e^{-Nf(\underline{x})} (\mathbf{L}e^{Nf})(\underline{x})$$

The rate function is defined as the integral of the Legendre transform of the Hamiltonian.

$$\begin{aligned} I(x_0(\cdot), x_1(\cdot), \dots, x_d(\cdot)) = \int_0^T \sup_{\sigma(t), \varkappa_1(t), \dots, \varkappa_d(t)} \left[\sigma(t) \dot{x}_0(t) + \sum_{i=1}^d \varkappa_i(t) \dot{x}_i(t) \right. \\ \left. - H_{\mathcal{K}_\theta}(x_0(t), x_1(t), \dots, x_d(t), \sigma(t), \varkappa_1(t), \dots, \varkappa_d(t)) \right] dt. \end{aligned} \quad (3.3)$$

The asymptotics of the probability in (3.1) is

$$\lim_{N \rightarrow \infty} \frac{1}{N} \ln \Pr \left(\frac{1}{N} \sum_{i=1}^d \eta_i(T) \geq B \right) = - \inf \left\{ I(x_0, x_1, \dots, x_d) : \sum_{i=1}^d x_i(T) \geq B \right\}.$$

Finding this asymptotics we have to solve the following system

$$\begin{cases} \dot{x}_0 = \mu_0(1 - x_0) \exp\{\sigma\} - \sum_{i=1}^d \mu_i s_i Q(x_0, r_i) Q(1 - x_0, k_i - r_i) \exp\{-(s_i \sigma - s_i \varkappa_i)\}, \\ \dot{x}_1 = \mu_1 s_1 \exp\{-(s_1 \sigma - s_1 \varkappa_1)\}, \\ \dots \\ \dot{x}_d = \mu_d s_d \exp\{-(s_d \sigma - s_d \varkappa_d)\}, \\ \dot{\sigma} = \mu_0 [\exp\{\sigma\} - 1] - \sum_{i=1}^d \mu_i [\exp\{-(s_i \sigma - s_i \varkappa_i)\} - 1] \\ \quad \times [Q(x_0, r_i - 1) Q(1 - x_0, k_i - r_i) - Q(x_0, r_i) Q(1 - x_0, k_i - r_i - 1)], \\ \dot{\varkappa}_1 = 0, \\ \dots \\ \dot{\varkappa}_d = 0, \end{cases} \quad (3.4)$$

where $Q(z, q) = \frac{z^q}{q!}$, if $z \in [0, 1]$, $q \in \mathbb{Z}_+$ and $Q(z, q) = 0$ elsewhere. The first $d + 1$ equations of (3.4) are to find the supremum in the integrand (3.3). The remaining $d + 1$ equations are the system of Euler–Lagrange equations.

The explicit solution of the Hamiltonian system (3.4) is either very difficult or impossible for the case general initial conditions $x_0(0)$. The problem appears from the expression $Q(x_0, r_i - 1) Q(1 - x_0, k_i - r_i)$ and $Q(x_0, r_i) Q(1 - x_0, k_i - r_i - 1)$

in the equation for σ . There exists perhaps only exclusion for the case studied in [12], where the exact solution is found (see also the examples below).

However there exist initial conditions $x_0(0) = \hat{x}_0$ for which the solution can be found. This solution is such that $x_0(t) \equiv \hat{x}_0$, $t \in [0, T]$.

The main result in this note is about the existence of such solution. The main goal of our studies is to understand what happens on level $B \rightarrow \infty$. A general conjecture is

Theorem 3.1. *There exists only one $i_0 \in \{1, \dots, d\}$ such that*

$$x_0(t) \equiv \hat{x}_0 = \frac{r_{i_0}}{k_{i_0} + s_{i_0}}$$

for $0 \leq t \leq T$.

Of course, some assumption are required. Later only particular cases are considered.

4. PROOF

We split the proof in several steps corresponding different values of d .

4.1. $d = 1$. We prove the theorem for the processes with one reaction. Let $\mathcal{K}_\theta = \{(k, r, s), (1, 0, -1)\}$. The Hamiltonian is

$$H(x_0, x_1, \sigma, \varkappa) = \mu_0(1 - x_0)[e^\sigma - 1] + Q(x_0, r)Q(1 - x_0, k - r)[e^{-s\sigma + s\varkappa} - 1]. \quad (4.1)$$

The Hamiltonian system (3.4) for this case is

$$\begin{cases} \dot{x}_0 = \mu_0(1 - x_0)e^\sigma - sQ(x_0, r)Q(1 - x_0, k - r)e^{-s\sigma + s\varkappa}, \\ \dot{x}_1 = sQ(x_0, r)Q(1 - x_0, k - r)e^{-s\sigma + s\varkappa}, \\ \dot{\sigma} = \mu_0(e^\sigma - 1) - (Q(x_0, r - 1)Q(1 - x_0, k - r) - Q(x_0, r)Q(1 - x_0, k - r - 1)) \\ \quad \times [e^{-s\sigma + s\varkappa} - 1], \\ \dot{\varkappa} = 0. \end{cases} \quad (4.2)$$

Recall that $Q(1 - x_0, k - r - 1) = 0$ in the case $k = r$.

Assume that there exists \hat{x}_0 such that $x_0(t) \equiv \hat{x}_0$, is a constant. Assume that \dot{x}_1 is also a constant. Then $\dot{x}_1 = B$. Then, assuming $T = 1$, we obtain

$$e^{-s\sigma + s\varkappa} = \frac{B}{sQ(\hat{x}_0, r)Q(1 - \hat{x}_0, k - r)}.$$

Since $\dot{x}_0 = 0$ we obtain

$$\mu_0 e^\sigma = \frac{sQ(\hat{x}_0, r)Q(1 - \hat{x}_0, k - r)e^{-s\sigma + s\varkappa}}{1 - \hat{x}_0} = \frac{B}{1 - \hat{x}_0}.$$

Because $\dot{\sigma} = 0$ we have

$$\begin{aligned} \mu_0 e^\sigma = \mu_0 + (Q(\hat{x}_0, r - 1)Q(1 - \hat{x}_0, k - r) \\ - Q(\hat{x}_0, r)Q(1 - \hat{x}_0, k - r - 1))[e^{-s\sigma + s\varkappa} - 1]. \end{aligned}$$

From three above relations we obtain

$$\frac{1}{1 - \widehat{x}_0} = \frac{Q(\widehat{x}_0, r - 1)Q(1 - \widehat{x}_0, k - r)}{sQ(\widehat{x}_0, r)Q(1 - \widehat{x}_0, k - r)} - \frac{Q(\widehat{x}_0, r)Q(1 - \widehat{x}_0, k - r - 1)}{sQ(\widehat{x}_0, r)Q(1 - \widehat{x}_0, k - r)} + o(1)$$

for $B \rightarrow \infty$. This is equivalent to

$$1 = \frac{r}{s} \frac{1 - \widehat{x}_0}{\widehat{x}_0} - \frac{k - r}{s},$$

which finally gives

$$x_0(t) \equiv \widehat{x}_0 = \frac{r}{k + s}. \quad (4.3)$$

We consider several examples for the demonstration of the result.

4.1.1. *Linear case.* It is the case when $\mathcal{K}_\theta = \{(1, 1, 1), (1, 0, -1)\}$. The Hamiltonian is

$$H_{\mathcal{K}_\theta}(x_0(\cdot), x_1(\cdot), \sigma(\cdot), \varkappa(\cdot)) = \mu_0(1 - x_0(\cdot))[e^{\sigma(\cdot)} - 1] + \mu_1 x_0(\cdot)[e^{-\sigma(\cdot) + \varkappa(\cdot)} - 1].$$

The corresponding Hamiltonian system (4.2) is

$$\begin{cases} \dot{x}_0 = \mu_0(1 - x_0) \exp\{\sigma\} + \mu_1 x_0 \exp\{-\sigma + \varkappa\}, \\ \dot{x}_1 = \mu_1 \exp\{-(\sigma - \varkappa)\}, \\ \dot{\sigma} = \mu_0[\exp\{\sigma\} - 1] - \mu_1[\exp\{-(\sigma - \varkappa)\} - 1], \\ \dot{\varkappa} = 0. \end{cases} \quad (4.4)$$

This system can be solved analytically for the following initial and boundary conditions

$$\begin{aligned} x_0(0) &= \widehat{x}_0 \in [0, 1], \\ x_1(0) &= 0, \\ x_1(T) &= B, \\ \sigma(T) &= 0. \end{aligned} \quad (4.5)$$

There is no the mean field actions in this case therefore the parameter $\tilde{\mu}_1 = \mu_i$ is not scaled. According to (4.3)

$$x_0(t) = \frac{1}{2}.$$

This case has been studied in [12].

4.1.2. *Quadratic potentials.* In this section we consider the following three examples: $\tau_1 = (2, 2, 2)$, $\tau_1 = (2, 2, 1)$, and $\tau_1 = (2, 1, 1)$.

The Hamiltonian equations (3.4) of these examples cannot be solved explicitly for any initial condition $x_0(0)$ (as we assume). However there exists a special $x_0(0) = \widehat{x}_0$ such that the solution $x_0(t)$ is a constant, $x_0(t) \equiv \widehat{x}_0$ if $x_0(0) = \widehat{x}_0$. We obtain the value of \widehat{x}_0 in the course of the solution.

The following Hamiltonians correspond to the processes considered here.

(1) $\mathcal{K}_\theta = \{(2, 2, 2), (1, 0, -1)\}$. The corresponding Hamiltonian (4.1) in this case is

$$H_{\mathcal{K}_\theta}(x_0, x_1, \sigma, \varkappa) = \mu_0(1 - x_0)[e^\sigma - 1] + \mu_1 \frac{x_0^2}{2}[e^{-2\sigma + 2\varkappa} - 1].$$

The interpretation of this process emission is the following. The emission occurs when two excited atoms collide each other. Each collided atom emits one photon. Therefore the second term in the Hamiltonian has multiplier $x_0^2/2$. By the same reason, the exponent is $e^{-2\sigma+2\kappa}$ meaning that the number of the excited atoms decreased by two and two photons were emitted. The corresponding Hamiltonian system (4.2) is

$$\begin{cases} \dot{x}_0 = \mu_0(1-x_0)e^\sigma - \mu_1 \frac{x_0^2}{2} e^{-2\sigma+2\kappa}, \\ \dot{x}_1 = \mu_1 x_0^2 e^{-2\sigma+2\kappa}, \\ \dot{\sigma} = \mu_0[e^\sigma - 1] - \mu_1 x_0[e^{-2\sigma+2\kappa} - 1], \\ \dot{\kappa} = 0 \end{cases}$$

with the same boundary conditions (4.5), and according (4.3) in this case

$$x_0(t) \equiv \hat{x}_0 = \frac{1}{2}.$$

(2) $\mathcal{K}_\theta = \{(2, 2, 1), (1, 0, -1)\}$. The corresponding Hamiltonian (4.1) in this case is

$$H_{\mathcal{K}_\theta}(x_0, x_1, \sigma, \kappa) = \mu_0(1-x_0)[e^\sigma - 1] + \mu_1 \frac{x_0^2}{2} [e^{-\sigma+\kappa} - 1].$$

As in the previous process, the emission occurs when two excited atoms collide. However only one of the collided atoms emits photon. Therefore there is the multiplier $x_0^2/2$ as in the previous case. In this case, the exponent is $e^{-\sigma+\kappa}$ meaning that the number of the excited atoms is decreasing by one and one photon is emitted. The Hamiltonian system (4.2) is

$$\begin{cases} \dot{x}_0 = \mu_0(1-x_0)e^\sigma - \mu_1 \frac{x_0^2}{2} e^{-\sigma+\kappa}, \\ \dot{x}_1 = \mu_1 \frac{x_0^2}{2} e^{-\sigma+\kappa}, \\ \dot{\sigma} = \mu_0[e^\sigma - 1] - \mu_1 x_0[e^{-\sigma+\kappa} - 1], \\ \dot{\kappa} = 0 \end{cases}$$

with the same boundary conditions (4.5), but in this case

$$x_0(t) \equiv \hat{x}_0 = \frac{2}{3}.$$

(3) $\mathcal{K}_\theta = \{(2, 1, 1), (1, 0, -1)\}$. The corresponding Hamiltonian (4.1) in this case is

$$H_{\mathcal{K}_\theta}(x_0, x_1, \sigma, \kappa) = \mu_0(1-x_0)[e^\sigma - 1] + \mu_1 x_0(1-x_0)[e^{-\sigma+\kappa} - 1].$$

In this case the reaction due to two atoms, one of them is excited and another one is in the ground state. Therefore the multiplier is $x_0(1-x_0)$. The exponent is

the same as in the previous case: $e^{-\sigma+\varkappa}$. The Hamiltonian system is

$$\begin{cases} \dot{x}_0 = \mu_0(1-x_0)e^\sigma - \mu_1 x_0(1-x_0)e^{-\sigma+\varkappa}, \\ \dot{x}_1 = \mu_1 x_0(1-x_0)e^{-\sigma+\varkappa}, \\ \dot{\sigma} = \mu_0[e^\sigma - 1] - \mu_1(2x_0 - 1)[e^{-\sigma+\varkappa} - 1], \\ \dot{\varkappa} = 0 \end{cases}$$

with the same boundary conditions (4.5) and in this case

$$x_0(t) = \hat{x}_0 = \frac{1}{3}.$$

4.1.3. *Cubic potentials.* In this section we consider a model having cubic potential, which means that the emission occurs when three atoms collide.

If $\mathcal{K}_\theta = \{(333), (1, 0, -1)\}$, then

$$H_{\mathcal{K}_\theta}(x_0, x_1, \sigma, \varkappa) = \mu_0(1-x_0)[e^\sigma - 1] + \mu_1 \frac{x_0^3}{6}[e^{-3\sigma+3\varkappa} - 1].$$

Three photons are emitted if three excited atoms collide. The number of possibilities to choose three excited atoms gives the multiplier $x_0^3/6$ and the exponent is $e^{-3\sigma+3\varkappa}$ meaning that three excited atoms disappear and three photons were emitted. The Hamiltonian system is

$$\begin{cases} \dot{x}_0 = \mu_0(1-x_0)e^\sigma - \mu_1 \frac{x_0^3}{2}e^{-3\sigma+3\varkappa}, \\ \dot{x}_1 = \mu_1 \frac{x_0^3}{2}e^{-3\sigma+3\varkappa}, \\ \dot{\sigma} = \mu_0[e^\sigma - 1] - \mu_1 \frac{x_0^2}{2}[e^{-3\sigma+3\varkappa} - 1], \\ \dot{\varkappa}_2 = 0 \end{cases}$$

with the boundary conditions (4.5) and

$$x_0(t) \equiv \hat{x}_0 = \frac{1}{2}.$$

4.2. $d = 2$. In this section we consider two reactions. Let

$$\mathcal{K}_\theta = \{(k_1, r_1, s_1), (k_2, r_2, s_2), (1, 0, -1)\}$$

and $s_1 \neq s_2$. The Hamiltonian is

$$\begin{aligned} H_{\mathcal{K}_\theta}(x_0, x_1, x_2, \sigma, \varkappa_1, \varkappa_2) \\ = \mu_0(1-x_0)[e^\sigma - 1] + \mu_1 Q(x_0, r_1)Q(1-x_0, k_1-r_1)[e^{-s_1\sigma+s_1\varkappa_1} - 1] \\ + \mu_2 Q(x_0, r_2)Q(1-x_0, k_2-r_2)[e^{-s_2\sigma+s_2\varkappa_2} - 1]. \end{aligned} \quad (4.6)$$

The Hamiltonian system is

$$\left\{ \begin{array}{l} \dot{x}_0 = \mu_0(1-x_0)e^\sigma \\ \quad - \mu_1 s_1 Q(x_0, r_1) Q(1-x_0, k_1-r_1) e^{-s_1\sigma+s_1\kappa_1} \\ \quad - \mu_2 s_2 Q(x_0, r_2) Q(1-x_0, k_2-r_2) e^{-s_2\sigma+s_2\kappa_2}, \\ \dot{x}_1 = \mu_1 s_1 Q(x_0, r_1) Q(1-x_0, k_1-r_1) e^{-s_1\sigma+s_1\kappa_1}, \\ \dot{x}_2 = \mu_2 s_2 Q(x_0, r_2) Q(1-x_0, k_2-r_2) e^{-s_2\sigma+s_2\kappa_2}, \\ \dot{\sigma} = \mu_0[e^\sigma - 1] \\ \quad - \mu_1 [Q(x_0, r_1-1) Q(1-x_0, k_1-r_1) \\ \quad \quad - Q(x_0, r_1) Q(1-x_0, k_1-r_1-1)] [e^{-s_1\sigma+s_1\kappa_1} - 1] \\ \quad - \mu_2 [Q(x_0, r_2-1) Q(1-x_0, k_2-r_2) \\ \quad \quad - Q(x_0, r_2) Q(1-x_0, k_2-r_2-1)] [e^{-s_2\sigma+s_2\kappa_2} - 1], \\ \dot{\kappa}_1 = 0, \\ \dot{\kappa}_2 = 0. \end{array} \right. \quad (4.7)$$

The boundary conditions are

$$\begin{aligned} x_0(0) &= \widehat{x}_0, \\ x_1(0) &= 0, \quad x_1(T) = B_1, \\ x_2(0) &= 0, \quad x_2(T) = B_2, \\ \sigma(T) &= 0, \end{aligned}$$

where $B = B_1 + B_2$.

Let $i_0 = \arg(\max\{s_1, s_2\})$. We prove that

$$x_0(t) = \frac{r_{i_0}}{k_{i_0} + s_{i_0}}. \quad (4.8)$$

As in previous case we assume that $x_0(t) \equiv \widehat{x}_0$. Then $\sigma \equiv \text{constant}$, and $\kappa_1 \equiv \text{constant}$ and $\kappa_2 \equiv \text{constant}$. And

$$\begin{aligned} \dot{x}_1 &= B_1 = \mu_1 s_1 Q(x_0, r_1) Q(1-x_0, k_1-r_1) e^{-s_1\sigma+s_1\kappa_1}, \\ \dot{x}_2 &= B_2 = \mu_2 s_2 Q(x_0, r_2) Q(1-x_0, k_2-r_2) e^{-s_2\sigma+s_2\kappa_2}. \end{aligned} \quad (4.9)$$

Recall that (see the first equation in (4.7))

$$\begin{aligned} 0 = \dot{x}_0 &= \mu_0(1-x_0)e^\sigma - \mu_1 s_1 Q(x_0, r_1) Q(1-x_0, k_1-r_1) e^{-s_1\sigma+s_1\kappa_1} \\ &\quad - \mu_2 s_2 Q(x_0, r_2) Q(1-x_0, k_2-r_2) e^{-s_2\sigma+s_2\kappa_2} \end{aligned} \quad (4.10)$$

and (see the fourth equation in (4.7))

$$\begin{aligned} 0 = \dot{\sigma} &= \mu_0[e^\sigma - 1] \\ &\quad - \mu_1 [Q(x_0, r_1-1) Q(1-x_0, k_1-r_1) - Q(x_0, r_1) Q(1-x_0, k_1-r_1-1)] \\ &\quad \quad \times [e^{-s_1\sigma+s_1\kappa_1} - 1] \\ &\quad - \mu_2 [Q(x_0, r_2-1) Q(1-x_0, k_2-r_2) - Q(x_0, r_2) Q(1-x_0, k_2-r_2-1)] \\ &\quad \quad \times [e^{-s_2\sigma+s_2\kappa_2} - 1]. \end{aligned} \quad (4.11)$$

Finding relation between B_1 and B_2 we assume that $B_1 = \alpha B$ and $B_2 = (1-\alpha)B$, where $\alpha \in [0, 1]$.

Using (4.9) we obtain from (4.10) the relation

$$\begin{aligned} \frac{\mu_0 e^\sigma}{B} &= \frac{\alpha}{s_1} \left[\frac{Q(x_0, r_1-1)Q(1-x_0, k_1-r_1)}{Q(x_0, r_1)Q(1-x_0, k_1-r_1)} - \frac{Q(x_0, r_1)Q(1-x_0, k_1-r_1-1)}{Q(x_0, r_1)Q(1-x_0, k_1-r_1)} \right] \\ &\quad + \frac{1-\alpha}{s_2} \left[\frac{Q(x_0, r_2-1)Q(1-x_0, k_2-r_2)}{Q(x_0, r_2)Q(1-x_0, k_2-r_2)} - \frac{Q(x_0, r_2)Q(1-x_0, k_2-r_1-2)}{Q(x_0, r_2)Q(1-x_0, k_2-r_2)} \right] \\ &\quad + o(1) \end{aligned}$$

as $B \rightarrow \infty$. This is

$$\frac{\mu_0 e^\sigma}{B} = \frac{\alpha}{s_1} \left[\frac{r_1}{x_0} - \frac{k_1-r_1}{1-x_0} \right] + \frac{1-\alpha}{s_2} \left[\frac{r_2}{x_0} - \frac{k_2-r_2}{1-x_0} \right] + o(1).$$

From (4.10) we obtain

$$\frac{\mu_0 e^\sigma}{B} = \frac{\alpha}{1-x_0} + \frac{1-\alpha}{1-x_0}. \quad (4.12)$$

Finally

$$\frac{\alpha}{s_1} \left[r_1 \frac{1-x_0}{x_0} - (k_1-r_1) \right] + \frac{\alpha}{s_1} \left[r_1 \frac{1-x_0}{x_0} - (k_1-r_1) \right] = 1.$$

Then

$$\frac{1-x_0}{x_0} = \frac{1 + \frac{\alpha}{s_1}(k_1-r_1) + \frac{(1-\alpha)}{s_2}(k_2-r_2)}{\frac{\alpha}{s_1}r_1 + \frac{(1-\alpha)}{s_2}r_2}. \quad (4.13)$$

Finding α we minimise the rate function $I(x_0, x_1, x_2)$ over α (see (3.3)). From (4.12) and (4.9) we obtain

$$\begin{aligned} \sigma &= \ln B + O(1), \\ \varkappa_1 &= \frac{1}{s_1} \ln B_1 + O(1) = \left(1 + \frac{1}{s_1}\right) \ln B + O(1), \\ \varkappa_2 &= \frac{1}{s_2} \ln B_2 + O(1) = \left(1 + \frac{1}{s_2}\right) \ln B + O(1). \end{aligned}$$

The functions $\dot{x}_0, \dot{x}_1, \dot{x}_2$ and $\sigma, \varkappa_1, \varkappa_2$ are constants. Therefore the rate function can be represented as

$$I(x_0, x_1, x_2) = \sup_{\sigma, \varkappa_1, \varkappa_2} \{ \dot{x}_1 \varkappa_1 + \dot{x}_2 \varkappa_2 - H_{\mathcal{K}_\theta}(x_0, x_1, x_2, \sigma, \varkappa_1, \varkappa_2) \}. \quad (4.14)$$

Recall that $\dot{x}_0 = 0$. Thus

$$\frac{I(x_0, x_1, x_2)}{B \ln B} = \alpha \left(1 + \frac{1}{s_1}\right) + (1-\alpha) \left(1 + \frac{1}{s_2}\right) + o(1) \quad (4.15)$$

since

$$\frac{H_{\mathcal{K}_\theta}(x_0, x_1, x_2, \sigma, \varkappa_1, \varkappa_2)}{B} = o(\ln B).$$

The result (4.10) follows from (4.15).

REFERENCES

- [1] R. Aris, *Prolegomena to the rational analysis of systems of chemical reactions*, Arch. Rational Mech. Anal. **19** (1965), 81–99. MR [0174284](#)
- [2] J. C. Baez and B. S. Pollard, *A compositional framework for reaction networks*, Rev. Math. Phys. **29** (2017), no. 9, 1750028, 41. MR [3694082](#)
- [3] A. Dembo and O. Zeitouni, *Large deviations techniques and applications*, Stochastic Modelling and Applied Probability, vol. 38, Springer-Verlag, Berlin, 2010. MR [2571413](#). Corrected reprint of the 2nd (1998) edition.
- [4] S. N. Ethier and T. G. Kurtz, *Markov processes. Characterization and convergence*, Wiley Series in Probability and Mathematical Statistics: Probability and Mathematical Statistics, John Wiley & Sons, Inc., New York, 1986. MR [838085](#)
- [5] M. Feinberg, *Complex balancing in general kinetic systems*, Arch. Rational Mech. Anal. **49** (1972/73), 187–194. MR [0413930](#)
- [6] J. Feng and T. G. Kurtz, *Large deviations for stochastic processes*, Mathematical Surveys and Monographs, vol. 131, Amer. Math. Soc., Providence, RI, 2006. MR [2260560](#)
- [7] F. Horn, *Necessary and sufficient conditions for complex balancing in chemical kinetics*, Arch. Rational Mech. Anal. **49** (1972/73), 172–186. MR [0413929](#)
- [8] F. Horn, *The dynamics of open reaction systems*, SIAM-AMS Proceedings, Vol. VIII, pp. 125–137, Amer. Math. Soc., Providence, RI, 1974. MR [0468667](#)
- [9] F. Horn and R. Jackson, *General mass action kinetics*, Arch. Rational Mech. Anal. **47** (1972), 81–116. MR [0400923](#)
- [10] R. Kraaij, *Large deviations for finite state Markov jump processes with mean-field interaction via the comparison principle for an associated Hamilton-Jacobi equation*, J. Stat. Phys. **164** (2016), no. 2, 321–345. MR [3513255](#)
- [11] V. A. Malyshev, S. A. Pirogov, and A. N. Rybko, *Random walks and chemical networks*, Mosc. Math. J. **4** (2004), no. 2, 441–453, 535. MR [2108444](#)
- [12] E. Pechersky, S. Pirogov, G. M. Schütz, A. Vladimirov, and A. Yambartsev, *Large fluctuations of radiation in stochastically activated two-level systems*, J. Phys. A **50** (2017), no. 45, 455203, 20. MR [3718895](#). Preprint version: [arXiv:1702.05475](#) [cond-mat.stat-mech].
- [13] F. Rezakhanlou, *Lectures on the large deviation principle*, Department of Mathematics, UC Berkeley. Available as <https://math.berkeley.edu/~rezakhan/LD.pdf>.
- [14] G. M. Schütz, *Diffusion-annihilation in the presence of a driving field*, J. Phys. A **28** (1995), no. 12, 3405–3415. MR [1344373](#)
- [15] J. Weiner and P. T. Ho, *Light-matter interaction: Fundamentals and applications*, Wiley, 2008.

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