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Jump statistics, sojourn times, fluctuation dynamics and ergodic behavior for Markov processes in continuous time with a finite number of states

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Abstract

A general approach is introduced for describing the time evolution of a Markov process in continuous time and with a finite number of states. The total number of transition events from one state to other states and of the total sojourn times of the system in the different states are used as additional state variables. The large time behavior of these two types of stochastic state variables is investigated analytically by using a stochastic Liouville equation. It is shown that the cumulants of first and second order of the state variables increase asymptotically linearly in time. A set of scaled sojourn times is introduced which in the limit of large times have a Gaussian behavior. For long times, the total average sojourn times are proportional to the stationary state probability of the process and, even though the relative fluctuations decrease to zero, the relative cross correlation functions tend towards finite values. The results are used for investigating the connections with Van Kampen's approach for investigating the ergodic properties of Markov processes. The theory may be applied for studying fluctuation dynamics in stochastic reaction diffusion systems and for computing effective rates and transport coefficients for non-equilibrium processes in systems with dynamical disorder.

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1. Introduction

Usually the time-dependent behavior of Markov processes is described in terms of a set of suitable random variables characterizing the properties of the system investigated. In some cases, however, the knowledge of the stochastic properties of these variables is not enough for the complete characterization of the system. For instance, this is the case of Markovian rate processes occurring in systems with dynamical disorder. For such systems, the knowledge of the stochastic properties of the time intervals spent by the system in one state or another (the sojourn times, [1–3]) is more important than the knowledge of the probability of occurrence of the different possible states. The knowledge of the stochastic properties of the sojourn times is also important for investigating the ergodic properties of Markov processes [4–6]. Random variables similar to the sojourn times attached to the different states of a Markov process are the numbers of transitions experienced by the system from one state to other possible states. In the particular case of unimolecular reactions, the numbers of transitions have been used by Solc [7] for developing a microscopic description of stochastic reaction dynamics.

The purpose of this article is to investigate the stochastic correlated behavior of the numbers of transition events and of the sojourn times for a Markov process in continuous time with a finite number of discrete state variables. The study is of importance both from the theoretical and applied points of view. In addition to the possible applications for the analysis of the rate and transport processes in systems with dynamical disorder, another possible application is related to the evaluation of relative stability of stochastic reaction–diffusion systems far from equilibrium. From the theoretical point of view such a study is intimately connected with Van Kampen's description of composite stochastic processes and to the ergodic behavior of Markov processes [1,2]. The present paper focuses mainly on the theoretical aspects of our approach. As suggested by a referee, the application of the theory to the evaluation of effective rate and transport coefficients for systems with dynamical disorder is presented in a following paper.

The structure of the paper is as follows. In Section 2 a description of the continuous-time Markov processes with a finite number of discrete state variables is given in terms of the total times spent by the system in the different possible states and of the numbers of jump events corresponding to these states and a stochastic Liouville equation for the corresponding joint probability density is derived. In Section 3 we suggest a procedure of solving the stochastic equations and we evaluate the moments of the random variables. In Section 4 the asymptotic behavior of the moments is analyzed; the analysis shows the existence of certain ergodic properties for a Markov process with a finite state space and continuous time. Finally, in Section 5 some open questions and possible applications of the theory are outlined.

2. Formulation of the problem

Our approach can be applied to any system which can be described by a Markovian master equation

$$\frac{dP_j(t)}{dt} = \sum_{j' \neq j} P_{j'}(t) W_{j'j} - P_j(t)\Omega_j, \quad j,j' = 1,\dots,M\,, \tag{2.1}$$

with

$$\Omega_j = \sum_{j' \neq j} W_{jj'}, \quad j = 1,\dots,M\,, \tag{2.2}$$

where $j = 1,\dots,M$ is a label attached to the different possible M states of the system, $W_{jj'}$ is the transition rate from the state j to the state j', Ω_j is the total transition rate from the state j to other states and $P_j(t)$ is the probability that at time the state of the system is j. We assume that the Markov process described by Eq. (2.1) is time homogeneous, that is, the rates $W_{jj'}$ depend only on the states j and j' and are independent of time. We also assume that the total number M of states is possibly very large but finite, and that all states are connected [8] in the sense that given two arbitrary states j,j' there are at least two ways

$$j_1 \to j_2 \to \cdots \to j' \quad \text{and} \quad j' \to j'_1 \to j'_2 \to \cdots \to j \tag{2.3),(2.4}$$

for which the corresponding rates are different from zero.

By introducing the matrix notations

$$\mathbf{P}(t) = [P_1(t),\dots,P_M(t)]\,, \tag{2.5}$$

$$\mathbf{W} = [W_{jj'}], \qquad W_{jj} = 0\,; \tag{2.6}$$

$$\mathbf{\Omega} = [\delta_{jj'}\Omega_j]\,. \tag{2.7}$$

Eq. (2.1) becomes

$$d\mathbf{P}(t)/dt = \mathbf{P}(t)(\mathbf{W} - \mathbf{\Omega})\,. \tag{2.8}$$

The formal solution of Eq. (2.8) is

$$\mathbf{P}(t) = \mathbf{P}(0)\mathbf{G}(t)\,, \tag{2.9}$$

where the Green function $\mathbf{G}(t)$ is given by

$$\mathbf{G}(t) = \exp[t(\mathbf{W} - \mathbf{\Omega})]\,. \tag{2.10}$$

By considering a large time interval of length t we attach to each of the M states of the system the following random variables (a) the total time θ_j spent by the system in the state j in the time interval of length t; (b) the total number q_j of transition (jump) events from the state j to other states occurring in the same time interval.

Although these variables have been used at times in the literature for describing some random processes of physical or chemical interest, the knowledge of their stochastic properties is still incomplete. The variables θ_j have been called cumulative residence or sojourn times. Some of their properties have been analyzed by Van Kampen by using the theory of composite stochastic processes [1,2]. The motivation of Van Kampen's research has been the theory of chromatography and the theory of anomalous diffusion. His approach is based on a path summation formula which was originally used in the theory of continuous-time random walks. By applying this method he has succeeded in evaluating the asymptotic behavior of average values $\langle\theta_j\rangle$, $j=1,\dots,M$ corresponding to the general master equation (2.1). He has also attempted to evaluate the second moments $\langle\Delta\theta_j\Delta\theta_{j'}\rangle$ of the sojourn times; unfortunately, his equation for the second moments is wrong. An alternative approach is that of Van den Broeck [3,9]; it has been introduced in connection with the generalized Taylor problem and is less general than the one of Van Kampen: it only applies to the case where the rates $W_{jj'}$ are different from zero only for $j'=j\pm 1$. The numbers of events q_j have been introduced by Solc [7] in connection with the stochastic description of the unimolecular reactions. Random variables similar to q_j have also been used in the theory of nuclear reactions [10]. As far as we know, no attempts have been made in the literature to study the stochastic correlations between the total sojourn times and the numbers of transition events.

The method used in this paper for the study of the stochastic properties of the random variables θ_j and q_j is different from the methods used by Van Kampen, Van den Broeck or Solc. It is based on the use of a stochastic Liouville equation. The following analysis based on a stochastic Liouville equation is not limited to the systems obeying the Van den Broeck restriction $W_{jj'}=0$ for $j'\neq j\pm 1$ and avoids the difficulties related to the evaluation of the complicated path sums entering Van Kampen's approach [1,2].

We introduce the probability

$$B_j(\boldsymbol{\theta},\mathbf{q};t)\,d\boldsymbol{\theta} \quad \text{with } \boldsymbol{\theta}=[\theta_j], \quad \mathbf{q}=[q_j] \quad \text{and} \quad \sum_j\sum_{\mathbf{q}}\int B_j(\boldsymbol{\theta},\mathbf{q};t)\,d\boldsymbol{\theta}=1\,, \tag{2.11}$$

that at time t the state of the system is j and that the cumulative sojourn times corresponding to a total time interval of length t have values between θ_j and $\theta_j+d\theta_j$, $j=1,\dots,M$ and that the corresponding numbers of transition events are $q_j, j=1,\dots,M$. This probability is the solution of a stochastic Liouville equation of the type

$$\left(\frac{\partial}{\partial t}+\frac{\partial}{\partial\theta_j}\right)B_j(\boldsymbol{\theta},\mathbf{q};t)=\sum_{j\neq j'}W_{j'j}B_j(\boldsymbol{\theta},q_1,\dots,q_{j'}-1,\dots,q_M;t)-\Omega_jB_j(\boldsymbol{\theta},\mathbf{q};t)\,. \tag{2.12}$$

Together with the initial and boundary conditions

$$B_j(\boldsymbol{\theta},\mathbf{q};t=0)=P_j(t=0)\delta_{\mathbf{q}0}\delta(\boldsymbol{\theta})\,, \tag{2.13}$$

$$B_j\left(\text{at least one } \theta_j\leqslant 0 \text{ or } \sum\theta_j>t;\ t\neq 0\right)=0\,, \tag{2.14}$$

Eq. (2.12) completely determines the time evolution of the state probability density $B_j(\boldsymbol{\theta}, \mathbf{q}; t)$. The model given by Eqs. (2.12)–(2.14) includes the master equation (2.1) as a particular case. We have

$$P_j(t) = \sum_{\mathbf{q}} \int \cdots \int B_j(\boldsymbol{\theta}, \mathbf{q}; t)\, d\boldsymbol{\theta}\,. \tag{2.15}$$

By summing in Eq. (2.12) over $q_1, \ldots, q_M$, integrating over $\theta_1, \ldots, \theta_M$ and using Eq. (2.15) we recover Eq. (2.1), as expected.

3. Integration of evolution equations. Moments

In order to integrate the stochastic Liouville equation (2.12) we introduce the multiple Laplace–Fourier and z-transform of the state probability density $B_j(\boldsymbol{\theta}, \mathbf{q}; t)$

$$\overline{B}_j(\boldsymbol{\omega}; \mathbf{z}; s) = \int_{t=0}^{\infty} \int \cdots \int \sum_{\mathbf{q}} \prod_j (z_j)^{q_j} \exp\left(-st + \sum_j \theta_j \omega_j\right) B_j(\boldsymbol{\theta}, \mathbf{q}; t)\, d\boldsymbol{\theta}\, dt\,, \tag{3.1}$$

where

$$\boldsymbol{\omega} = [\delta_{jj'} \omega_j], \qquad \mathbf{z} = [\delta_{jj'} z_j]\,, \tag{3.2}$$

ω_j is the frequency conjugate to the sojourn time θ_j, z_j is the z-variable conjugate to q_j, and $\underline{s}$ is the Laplace variable conjugate to the time variable t. We assume that

$$\operatorname{Re} s < 0, \quad |z_j| \leqslant 1, \quad \operatorname{Im} \omega_j = 0\,. \tag{3.3}$$

These conditions ensure the convergence of the sums and integrals in Eq. (3.1). Strictly speaking, the integration limits for θ_j are given by

$$\theta_j \geqslant 0, \quad \sum_j \theta_j = t\,. \tag{3.4),(3.5}$$

We note that these restrictions are implicitly included in Eqs. (2.12)–(2.14) and thus we can formally extend the integration limits for θ_j, $j = 1, \ldots, M$ from $-\infty$ to $+\infty$.

In matrix notation the transform of Eq. (2.12) is

$$s\overline{\mathbf{B}} - \mathbf{P}(0) - \overline{\mathbf{B}} i\boldsymbol{\omega} = \overline{\mathbf{B}}(\mathbf{W} + \mathbf{E} - \boldsymbol{\Omega})\,, \tag{3.6}$$

where

$$\overline{\mathbf{B}} = (\overline{B}_1, \ldots, \overline{B}_M)\,, \tag{3.7}$$

$$\boldsymbol{\omega} = [\delta_{jj'} \omega_j]\,, \tag{3.8}$$

$$\mathbf{E} = [W_{jj'}(z_j - 1)], \quad E_{jj} = 0\,. \tag{3.9}$$

From Eq. (3.6) we can express $\overline{\mathbf{B}}$ by a relationship similar to Eq. (2.9)

$$\overline{\mathbf{B}}(\boldsymbol{\omega},\mathbf{z};s)=\mathbf{P}(0)\overline{\mathfrak{G}}(\boldsymbol{\omega},\mathbf{z};s)\,, \tag{3.10}$$

where

$$\overline{\mathfrak{G}}(\boldsymbol{\omega},\mathbf{z};s)=(\mathbf{I}s+\boldsymbol{\Omega}-i\boldsymbol{\omega}-\mathbf{W}-\mathbf{E})^{-1}\,, \tag{3.11}$$

is the Laplace, Fourier and z-transform of a Green's function similar to the Green's function $\mathbf{G}(t)$ of the master equation (2.1).

Eqs. (3.10) and (3.11) formally solve the problem of determining the stochastic properties of the sojourn times θ_j and of the numbers of transition events q_j. They may be used to evaluate both the state probability density $B_j(\boldsymbol{\theta};\mathbf{q};t)$ and the corresponding moments of θ_j and q_j. To do that we use two different series expansions of the matrix $\overline{\mathfrak{G}}(\boldsymbol{\omega},\mathbf{z};s)$.

A first scheme is based on the separation of the diagonal matrices in Eq. (3.11)

$$\overline{\mathfrak{G}}(\boldsymbol{\omega},\mathbf{z};s)=[\mathbf{I}-(\mathbf{I}s+\boldsymbol{\Omega}-i\boldsymbol{\omega})^{-1}(\mathbf{W}+\mathbf{E})]^{-1}(\mathbf{I}s+\boldsymbol{\Omega}-i\boldsymbol{\omega})^{-1}\,. \tag{3.12}$$

Here the inverse of the matrix $(\mathbf{I}s+\boldsymbol{\Omega}-i\boldsymbol{\omega})$ is equal to

$$(\mathbf{I}s+\boldsymbol{\Omega}-i\boldsymbol{\omega})^{-1}=[\delta_{jj'}/(s+\Omega_j-i\omega_j)]\,. \tag{3.13}$$

By expanding Eq. (3.12) in a matrix geometric series we have

$$\overline{\mathfrak{G}}(\boldsymbol{\omega},\mathbf{z};s)=\sum_{q=0}^{\infty}[(\mathbf{I}s+\boldsymbol{\Omega}-i\boldsymbol{\omega})^{-1}(\mathbf{W}+\mathbf{E})]^{q}(\mathbf{I}s+\boldsymbol{\Omega}-i\boldsymbol{\omega})^{-1}\,. \tag{3.14}$$

From Eq. (3.14) it is easy to express the Green's function $\mathfrak{G}(\boldsymbol{\theta},\mathbf{q};t)$ corresponding to the matrix $\overline{\mathfrak{G}}(\boldsymbol{\omega},\mathbf{z};s)$ in the form of an infinite sum of multiple convolution products over the variables $\boldsymbol{\theta}$, $\mathbf{q}$ and t. The resulting expression is cumbersome and in order to save space we do not give it here. More important is the physical significance of such expansions: they express the contribution to $\mathfrak{G}(\boldsymbol{\theta},\mathbf{q};t)$ or $\mathbf{B}(\boldsymbol{\theta},\mathbf{q};t)$ of the different paths $j_1\to j_2\to\cdots$ of variable length in the state space. The expansion (3.14) or the corresponding formula for the Green's function $\mathfrak{G}(\boldsymbol{\theta},\mathbf{q};t)$ are similar to the path summation formula of Van Kampen [1,2]. The approach presented here includes that of Van Kampen as a particular case. Van Kampen does not discuss the stochastic properties of the numbers q_j of transition events and thus for a comparison we should introduce the marginal probability density of the state of the system and of the sojourn times

$$R_j(\boldsymbol{\theta};t)=\sum_{\mathbf{q}}B_j(\boldsymbol{\theta},\mathbf{q};t)\,. \tag{3.15}$$

From Eqs. (3.10)–(3.14) it follows that the Fourier and Laplace transform of $R_j(\boldsymbol{\theta};t)$

$$\overline{R}_j(\boldsymbol{\omega};s)=\int_0^{\infty}\int_0^{\infty}\cdots\int\exp\left(-st+\sum_j\theta_j\omega_j\right)R_j(\boldsymbol{\theta};t)\,d\boldsymbol{\theta}\,dt\,,$$

is equal to

$$\bar{R}_j(\boldsymbol{\omega}; s) = [\mathbf{P}(0)\overline{\mathfrak{G}_1}(\boldsymbol{\omega}; s)]_j\,, \tag{3.16}$$

where

$$\overline{\mathfrak{G}_1}(\boldsymbol{\omega}; s) = \overline{\mathfrak{G}}(\boldsymbol{\omega}, \forall z_j = 1; s) = [\mathbf{I} - (\mathbf{I}s + \boldsymbol{\Omega} - i\boldsymbol{\omega})^{-1}\mathbf{W}]^{-1}(\mathbf{I}s + \boldsymbol{\Omega} - i\boldsymbol{\omega})^{-1}\,. \tag{3.17}$$

By expanding Eq. (3.17) in a geometric series and coming back to the real time variables θ_j and t, we obtain

$$\begin{aligned}\mathfrak{G}_{1j_0j}(\boldsymbol{\theta}; t) = {} & \delta_{jj_0}\gamma_{j_0}(t)\delta(\theta_{j_0} - t) + \int_0^t \psi_{j_0j}(t_0)\gamma_j(t_0 - t)\,dt_0 \\ & + \sum_{q=2}^{\infty}\sum_{j_1,\ldots,j_{q-1}}\cdots\sum \int_{t_{q-1}=0}^{t}\cdots\int_{t_0=0}^{t_1} \psi_{j_0j_1}(t_0)\psi_{j_1j_2}(t_1 - t_0)\cdots \\ & \times \psi_{j_{q-1}j}(t_{q-1} - t_{q-2})\gamma_j(t - t_{q-1})\delta(\theta_{j_0} - t_0) \\ & \times \delta(\theta_{j_1} - (t_1 - t_0))\cdots\delta(\theta_j - (t - t_{q-1}))\,dt_0\cdots dt_{q-1}\,,\end{aligned} \tag{3.18}$$

where

$$\psi_{jj'}(t)\,dt = W_{jj'}\exp(-t\Omega_j)\,dt \tag{3.19}$$

is the probability that a given jump occurs from a given state j to the state j' after a waiting time in the state j between t and $t + dt$ and

$$\gamma_j(t) = \sum_{j'}\int_t^{\infty}\psi_{jj'}(t)\,dt = \exp(-t\Omega_j) \tag{3.20}$$

is the probability that the system stays in the state j in a time interval of length t. The product

$$\psi_{j_0j_1}(t_0)\psi_{j_1j_2}(t_1 - t_0)\cdots\psi_{j_{q-1}j}(t_{q-1} - t_{q-2})\gamma_j(t - t_{q-1})\,dt_0\cdots dt_{q-1} \tag{3.21}$$

is the probability of occurrence of a path $j_0 \to j_1 \to \cdots \to j_{q-1} \to j$ which is made up of a transition $j_0 \to j_1$ occurring at a time between t_0 and $t_0 + dt_0, \ldots$ and from a transition $j_{q-1} \to j$ occurring at a time between t_{q-1} and $t_{q-1} + dt_{q-1}$ and that from the time t_{q-1} to the current time t the system stays in the state j. From Eq. (3.18) we see that the Green's function $\mathfrak{G}_{1j_0j}(\boldsymbol{\theta}; t)$ is the average of a product of delta functions

$$\delta(\theta_{j_0} - t_0)\delta(\theta_{j_1} - (t_1 - t_0))\cdots\delta(\theta_j - (t - t_{q-1})) \tag{3.22}$$

which expresses the probability that the sojourn times between the different transitions are equal to

$$\theta_{j_0} = t_0, \qquad \theta_{j_1} = (t_1 - t_0), \ldots, \theta_j = (t - t_{q-1})\,. \tag{3.23}$$

The average is evaluated by means of the probability distribution (3.21) of a path of a given length q; finally, the contributions of paths of different lengths are added. Eq. (3.18) is the same as Van Kampen's summation formula [1,2] which has been recovered as a particular case of our approach. In particular, if the integrals over $\theta_{j_0}, \theta_{j_1}, \ldots, \theta_j$ are carried out then Eq. (3.18) gives a path expansion of the Green function $\mathbf{G}(t)$ connected to the master equation (2.1); similar expansions have been used in connection with the theory of continuous-time random walks (CTRW, [11]) and of age-dependent master equations (ADME, [12]).

The moments of the total sojourn times θ_j and of the total numbers q_j of transition events can be evaluated by using a different type of expansion. The moments of qth order of these random variables depend on the derivatives of qth order of $\overline{\mathfrak{G}}(\boldsymbol{\omega}, \mathbf{z}; s)$ evaluated in the point $\boldsymbol{\omega} = \mathbf{0}$, $\forall z_j = 1$. That is why we shall try to find an expansion of $\overline{\mathfrak{G}}(\boldsymbol{\omega}, \mathbf{z}; s)$ in which the qth term is a homogeneous function of qth order of the variables ω_j and $z_j - 1$. If such an expansion can be computed analytically, thus, at least in principle, all moments of θ_j and q_j can be evaluated exactly.

We try to express $\overline{\mathfrak{G}}(\boldsymbol{\omega}, \mathbf{z}; s)$ in terms of the Laplace transform of the Green's function $\mathbf{G}(t)$

$$\overline{\mathbf{G}}(s) = \int_0^\infty \mathbf{G}(t) \exp(-st)\, dt = (\mathbf{I}s - \mathbf{W} + \boldsymbol{\Omega})^{-1} . \tag{3.24}$$

From Eqs. (3.11) and (3.24) we come to

$$\begin{aligned} \overline{\mathfrak{G}}(\boldsymbol{\omega}, \mathbf{z}; s) &= (\overline{\mathbf{G}}^{-1}(\mathbf{s}) - i\boldsymbol{\omega} - \mathbf{E})^{-1} = [\mathbf{I} - \overline{\mathbf{G}}(\mathbf{s})(i\boldsymbol{\omega} + \mathbf{E})]^{-1}\overline{\mathbf{G}}(\mathbf{s}) \\ &= \overline{\mathbf{G}}(\mathbf{s}) + \sum_{q=1}^{\infty} [\overline{\mathbf{G}}(\mathbf{s})(i\boldsymbol{\omega} + \mathbf{E})]^q \overline{\mathbf{G}}(\mathbf{s}) . \end{aligned} \tag{3.25}$$

As $i\boldsymbol{\omega}$ and $\mathbf{E}$ are linear homogeneous functions of ω_j and $z_j - 1$, respectively, it follows that the qth term of Eq. (3.25) is a homogeneous function of qth order in ω_j and $z_j - 1$. It turns out that (3.25) is the expansion sought for.

The moments of the sojourn times

$$\langle \theta_{u_1}(t) \cdots \theta_{u_q}(t) \rangle = \sum_j \sum_{\mathbf{q}} \int \cdots \int \theta_{u_1} \cdots \theta_{u_q} B_j(\boldsymbol{\theta}, \mathbf{q}; t)\, d\boldsymbol{\theta} , \tag{3.26}$$

may be evaluated by means of the equation

$$\langle \theta_{u_1}(t) \cdots \theta_{u_q}(t) \rangle = i^{-q} \mathscr{L}^{-1} \left\{ \sum_{j_0} \sum_j \left[\frac{\partial^q \overline{\mathfrak{G}}_{j_0 j}(\boldsymbol{\omega}, \forall z_j = 1; s)}{\partial \omega_{u_1} \cdots \partial \omega_{u_q}} \right]_{\boldsymbol{\omega} = 0} \right\} , \tag{3.27}$$

which can be derived by combining Eqs. (3.10), (3.15), (3.16) and (3.26). In Eq. (3.26) $\mathscr{L}^{-1}$ denotes the inverse Laplace transformation with respect to the s-variable. Only the qth term from the expansion (3.25) gives a contribution to Eq. (3.27). We emphasize that in Eq. (3.27) some of the labels $u_1, u_2, \ldots, u_q$ may have the same values and thus this equation can be used to evaluate all moments of the sojourn times, θ_j, including the ones having the form $\langle \theta_1^{m_1} \cdots \theta_M^{m_M} \rangle$, where $m_1 \geqslant 1, m_2 \geqslant 1, \ldots, m_M \geqslant 1$. After some calculations, Eqs. (3.25) and (3.27) lead to the following expressions for the moments of the sojourn times:

$$\langle \theta_{u_1}(t) \cdots \theta_{u_q}(t) \rangle = \sum_{\alpha} \int_0^1 P_{u_{\alpha_1}}(t) \otimes G_{u_{\alpha_1} u_{\alpha_2}}(t) \otimes \cdots \otimes G_{u_{\alpha_{q-1}} u_{\alpha_q}}(t)\, dt\,, \tag{3.28}$$

where $\otimes$ denotes the temporal convolution product:

$$f(t) \otimes g(t) = \int_0^t f(t-t') f(t')\, dt\,, \tag{3.29}$$

$P_j(t)$ is the solution of the master equation (2.1):

$$P_j(t) = \sum_{j_0} P_{j_0}(0) G_{j_0 j}(t)\,, \tag{3.30}$$

and

$$\boldsymbol{\alpha} = (\alpha_1, \ldots, \alpha_q) \tag{3.31}$$

is a permutation of $(1, \ldots, q)$ and the sum runs over all possible permutations $(1, \ldots, q)$. From Eq. (3.28), we get the following expressions for the average values of the sojourn times and for the elements of their covariance matrix:

$$\langle \theta_u(t) \rangle = \int_0^t P_u(t')\, dt'\,, \tag{3.32}$$

$$\langle \Delta\theta_{u_1}(t) \Delta\theta_{u_2}(t) \rangle = \int_0^t \int_0^{t'} [P_{u_1}(t') G_{u_1 u_2}(t'-t'') + P_{u_2}(t') G_{u_2 u_1}(t'-t'')]\, dt' dt''$$
$$- \int_0^t \int_0^t P_{u_1}(t') P_{u_2}(t'')\, dt'\, dt''\,. \tag{3.33}$$

The other moments of the sojourn times θ_j and of the numbers of transition events q_j can be computed in a similar way (see Appendix A). We get the following expressions for the mean values of q_j and of the covariances of q_j and of q_j and θ_j:

$$\langle q_u(t) \rangle = \Omega_u \int_0^t P_u(t')\, dt'\,, \tag{3.34}$$

$$\langle \Delta q_{u_1}(t) \Delta q_{u_2}(t) \rangle = \left[\Omega_{u_1} \int_0^t P_{u_1}(t')\,dt' \right] \left[\delta_{u_1 u_2} - \Omega_{u_2} \int_0^t P_{u_2}(t'')\,dt'' \right]$$

$$+ \int_0^t \int_0^{t'} \left[P_{u_1}(t') \sum_j W_{u_1 j} G_{j u_2}(t' - t'') \Omega_{u_2} \right.$$

$$\left. + P_{u_2}(t') \sum_j W_{u_2 j} G_{j u_1}(t' - t'') \Omega_{u_1} \right] dt'\,dt'' , \qquad (3.35)$$

$$\langle \Delta \theta_{u_1}(t) \Delta q_{u_2}(t) \rangle = - \int_0^t \int_0^t P_{u_1}(t') \Omega_{u_2} P_{u_2}(t'')\,dt'\,dt''$$

$$+ \int_0^t \int_0^{t'} \left[P_{u_1}(t') G_{u_1 u_2}(t' - t'') \Omega_{u_2} \right.$$

$$\left. + P_{u_2}(t') \sum_j W_{u_2 j} G_{j u_1}(t' - t'') \right] dt'\,dt'' . \qquad (3.36)$$

Eqs. (3.28) and (3.32)–(3.36) for the moments of the sojourn times and of the numbers of the transition events are new. They are valid for any time interval of length t, short or long. Although exact, these equations are rather difficult to be used in the general case. In the asymptotic regime they turn into simpler forms which are easy to use. The analysis of the asymptotic behavior of Eqs. (3.28) and (3.32)–(3.36) is the subject of the next section.

4. Asymptotic behavior. Ergodic properties

It is known that for a Markov processes with a finite number of connected states the probability vector $\mathbf{P}(t)$ and the Green's matrix $\mathbf{G}(t)$ tend towards stationary values which are independent of the initial state of the system:

$$\lim_{t\to\infty} \mathbf{P}(t) = [P_1^{st} \cdots P_M^{st}] \quad \text{and} \quad \lim_{t\to\infty} \mathbf{G}(t) = \begin{bmatrix} P_1^{st} & \cdot & \cdot & \cdot & P_M^{st} \\ \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot \\ P_1^{st} & \cdot & \cdot & \cdot & P_M^{st} \end{bmatrix} , \qquad (4.1)$$

where $\mathbf{P}^{st} = [P_1^{st} \cdots P_M^{st}]$ is the stationary solution of the master equation (2.1). In order to evaluate the asymptotic behavior of the moments of the sojourn times and of the numbers of transition events we need to know also the properties of the functions

$$\Gamma^{(1)}_{j_0 j}(t) = \int_0^t G_{j_0 j}(t')\, dt' , \tag{4.2}$$

$$\Gamma^{(2)}_{j_0 j}(t) = \int_0^t \Gamma^{(1)}_{j_0 j}(t'')\, dt'' . \tag{4.3}$$

In Appendix B we show that

$$\Gamma^{(1)}_{j_0 j}(t) = tP_j^{st} + C_{j_0 j} + \Lambda^{(1)}_{j_0 j}(t) , \tag{4.4}$$

$$\Gamma^{(2)}_{j_0 j}(t) = \tfrac{1}{2} t^2 P_j^{st} + tC_{j_0 j} + \Lambda^{(0)}_{j_0 j} + \Lambda^{(1)}_{j_0 j}(t) , \tag{4.5}$$

where $C_{j_0 j}$ and $\Lambda^{(0)}_{j_0 j}$ are constants and $\Lambda^{(1,2)}_{j_0 j}(t)$ are combinations of exponentials with constant or polynomial coefficients of t which decay exponentially to zero as $t \to \infty$

$$\Lambda^{(1,2)}_{j_0 j}(t) \to 0 \quad \text{as } t \to \infty . \tag{4.6}$$

For the analysis of the asymptotic behavior we need only the values of P_u^{st} and $C_{j_0 j}$. The stationary state probabilities P_u^{st} are determined by the stationary form of the master equation (2.1):

$$\sum_{j' \neq j} W_{j'j} P_j^{st} = \Omega_j P_j^{st}, \quad j = 1, \ldots, M , \tag{4.7}$$

and by the normalization condition

$$\sum_j P_j^{st} = 1_j^{st} . \tag{4.8}$$

In Appendix B we derive a system of linear equations for $C_{j_0 j}$ which is similar to Eqs. (4.7), (4.8):

$$P_j^{st} - \delta_{jj'} = \sum_{u \neq j} C_{ju} W_{uj'} - C_{jj'} \Omega_{j'}, \quad j, j' = 1, \ldots, M , \tag{4.9}$$

$$\sum_{j'} C_{jj'} = 0, \quad j = 1, \ldots, M . \tag{4.10}$$

The system (4.9), (4.10) has only one non-trivial solution.

By using Eqs. (4.2), (4.3) we get the following asymptotic expressions for the moments of the sojourn times and of the number of transition events as $t \to \infty$:

$$\langle \theta_u(t) \rangle \sim P_u^{st} t \quad \text{as } t \to \infty , \tag{4.11}$$

$$\langle q_u(t) \rangle \sim P_u^{st} \Omega_u t \quad \text{as } t \to \infty , \tag{4.12}$$

$$\langle \Delta\theta_{u_1}(t) \Delta\theta_{u_2}(t) \rangle \sim (P_{u_1}^{st} C_{u_1 u_2} + P_{u_2}^{st} C_{u_2 u_1}) t \quad \text{as } t \to \infty , \tag{4.13}$$

$$\langle \Delta\theta_{u_1}(t)\Delta q_{u_2}(t)\rangle \sim \left(P_{u_1}^{st}C_{u_1u_2}\Omega_{u_2} + P_{u_2}^{st}\sum_j W_{u_2j}C_{ju_1}\right)t \quad \text{as } t\to\infty\,, \tag{4.14}$$

$$\langle \Delta\theta_{u_1}(t)\Delta q_{u_2}(t)\rangle$$
$$\sim \left(P_{u_1}^{st}\delta_{u_1u_2}\Omega_{u_1} + P_{u_2}^{st}\sum_j W_{u_1j}C_{ju_2}\Omega_{u_2} + P_{u_2}^{st}\sum_j W_{u_2j}C_{ju_1}\Omega_{u_1}\right)t \quad \text{as } t\to\infty\,. \tag{4.15}$$

Eq. (4.11) has already been derived by Van Kampen [1,2] and a particular case of Eq. (4.12) for $M=2$ has been derived by Solc [7]; Eqs. (4.13)–(4.15) are new. For the covariance matrix of the sojourn times Van Kampen gives a different formula [2]

$$\langle \Delta\theta_{u_1}(t)\Delta\theta_{u_2}(t)\rangle \sim P_{u_1}^{st}P_{u_2}^{st}(\Omega_{u_1}^{-1} + \Omega_{u_2}^{-1})t \quad \text{as } t\to\infty\,. \tag{4.16}$$

Although Eq. (4.16) predicts the same time dependence as our Eq. (4.13), it is not correct. As the sum of the sojourn times θ_j is constant and equal to the length t of the time interval considered (see Eq. (3.5)), we should have

$$\sum_{u_1}\sum_{u_2}\langle \Delta\theta_{u_1}(t)\Delta\theta_{u_2}(t)\rangle = \left\langle\left[\sum_u \Delta\theta_u(t)\right]^2\right\rangle = \langle[\Delta t]^2\rangle = 0\,. \tag{4.17}$$

Our Eq. (4.13) fulfills the condition (4.17); this condition is a consequence of the identity $\Sigma_{u_2}C_{u_1u_2} = \Sigma_{u_1}C_{u_2u_1} = 0$ (see Eq. (4.10)). On the other hand, from Van Kampen's formula (4.16) we obtain

$$\left\langle\left[\sum_u \Delta\theta_u(t)\right]^2\right\rangle = 2\sum_u P_u^{st}/\Omega_u > 0\,, \tag{4.18}$$

an expression which is wrong.

Eqs. (4.11)–(4.15) have two important physical consequences. The first consequence is related to ergodicity and has already been noticed by Van Kampen [2]. Considering a physical variable $f(j)$ which depends on the state j of the system but does not depend explicitly on time, from Eqs. (4.11) it is easy to show that

$$\lim_{t\to\infty} t^{-1}\sum_j \langle\theta_j(t)\rangle = \langle f(j)\rangle^{st}\,, \tag{4.19}$$

where

$$\langle f(j)\rangle^{st} = \sum_j P_j^{st} f(j) \tag{4.20}$$

is the stationary ensemble average of the variable $f(j)$. It follows that for $t\to\infty$ the time evolution of a single system passing from one state to another may be represented by a stationary ensemble of systems characterized by the probabilities P_j^{st}, $j=1,\dots,M$. The connections between this property and ergodicity are discussed later in this section.

A second consequence is related to the relative magnitude of fluctuations of the sojourn timers and of the numbers of transition events. From Eqs. (4.11)–(4.15) we can compute the relative fluctuations of θ_u and q_u, $\varepsilon(\theta_u)$ and $\varepsilon(q_u)$, respectively. We obtain

$$\varepsilon(\theta_u) = \sqrt{\langle(\Delta\theta_u(t))^2\rangle}/\langle\theta_u(t)\rangle \sim t^{-1/2}\sqrt{2C_{uu}/P_u^{st}} \quad \text{as } t \to \infty\,, \tag{4.21}$$

$$\varepsilon(q_u) = \sqrt{\langle(\Delta q_u(t))^2\rangle}/\langle q_u(t)\rangle$$
$$\sim t^{-1/2}\sqrt{\left(1 + 2\sum_j W_{uj}C_{ju}\right)\Big/(P_u^{st}\Omega_u)} \quad \text{as } t \to \infty\,. \tag{4.22}$$

As $t \to \infty$, the relative fluctuations of the sojourn times (Eqs. (4.21)) and of the numbers of jump events (Eqs. (4.22)) decrease to zero as $t^{-1/2}$; thus, for large times, the contribution of fluctuations is negligible in comparison with the average values. Here the length t of the time interval plays the role of a large parameter similar to the total number of particles in equilibrium statistical mechanics: Eqs. (4.21) are "$t^{-1/2}$ laws" which justify the use of the average quantities $\langle\theta_u(t)\rangle$ and $\langle q_u(t)\rangle$ for the description of the system, for instance for the evaluation of the rate or transport coefficients. We emphasize that as $t \to \infty$ the fluctuations, although very small, play, however, a certain role in the description of the system. To show that we evaluate the relative correlations between θ_u and q_u.

$$\mathrm{Corr}(\theta_{u_1};\theta_{u_2}) = \langle\Delta\theta_{u_1}\Delta\theta_{u_2}\rangle/\sqrt{\langle[\Delta\theta_{u_1}]^2\rangle\langle[\Delta\theta_{u_2}]^2\rangle}$$
$$\sim [P_{u_1}^{st}C_{u_1u_2} + P_{u_2}^{st}C_{u_2u_1}]/\sqrt{4P_{u_1}^{st}P_{u_2}^{st}C_{u_1u_1}C_{u_2u_2}} \quad \text{as } t \to \infty,\ u_1 \neq u_2\,, \tag{4.23}$$

$$\mathrm{Corr}(\theta_{u_1};q_{u_2}) = \langle\Delta\theta_{u_1}\Delta q_{u_2}\rangle/\sqrt{\langle[\Delta\theta_{u_1}]^2\rangle\langle[\Delta q_{u_2}]^2\rangle}$$
$$\sim \left[P_{u_1}^{st}C_{u_1u_2}\Omega_{u_2} + P_{u_1}^{st}\sum_j W_{u_2j}C_{ju_1}\right]\Big/$$
$$\sqrt{P_{u_1}^{st}C_{u_1u_1}\left(2 + 4\sum_j W_{u_2j}C_{ju_2}\right)} \quad \text{as } t \to \infty\,, \tag{4.24}$$

$$\mathrm{Corr}(q_{u_1};q_{u_2}) = \langle\Delta q_{u_1}\Delta q_{u_2}\rangle/\sqrt{\langle[\Delta q_{u_1}]^2\rangle\langle[\Delta q_{u_2}]^2\rangle}$$
$$\sim \frac{P_{u_1}^{st}\sum_j W_{u_1j}C_{ju_2}\Omega_{u_2} + P_{u_2}^{st}\sum_j W_{u_2j}C_{ju_1}\Omega_{u_1}}{\sqrt{P_{u_1}^{st}P_{u_2}^{st}\Omega_{u_1}\Omega_{u_2}(1 + \sum_j W_{u_1j}C_{ju_2})(1 + \sum_j W_{u_2j}C_{ju_1})}}$$
$$\text{as } t \to \infty,\ u_1 \neq u_2\,. \tag{4.25}$$

The relative correlations do not vanish at $t \to \infty$ but rather tend towards constant values.

The asymptotic behavior of the joint probability density $B_j(\boldsymbol{\theta}, \mathbf{q}; t)$ cannot be evaluated in a simple way. However, the asymptotic form of the reduced (marginal) probability of the sojourn times

$$\mathfrak{R}(\boldsymbol{\theta}, t) = \sum_j \sum_q B_j(\boldsymbol{\theta}, \mathbf{q}; t), \tag{4.26}$$

can be evaluated analytically by using the expressions (3.28) for the moments $\langle \theta_{u_1}(t) \cdots \theta_{u_q}(t) \rangle$. The asymptotic '$t^{-1/2}$ law' (4.21) suggests the introduction of the scaled sojourn times

$$\tau_j = (\theta_j - \langle \theta_j \rangle) \Big/ \sqrt{\langle \theta_j \rangle}\ , \tag{4.27}$$

in terms of which we define as called probability density

$$\mathfrak{R}^*(\boldsymbol{\tau}; t)\, d\boldsymbol{\tau} = \mathfrak{R}(\boldsymbol{\theta}; t)\, d\boldsymbol{\theta} \tag{4.28}$$

and the corresponding characteristic function

$$\mathfrak{C}^*(\boldsymbol{\omega}^*; t) = \int \cdots \int \exp\left(i \sum_i \omega_j^* \tau_j \right) \mathfrak{R}^*(\boldsymbol{\tau}; t)\, d\boldsymbol{\tau}\,. \tag{4.29}$$

where ω_j^*, $j = 1, \ldots, M$ are the Fourier variables conjugate to the scaled sojourn times τ_j, $j = 1, \ldots, M$.

Our method of evaluating the probability density of the sojourn times in the limit $t \to \infty$ is to compute the asymptotic behavior of the moments $\langle \theta_{u_1}(t) \cdots \theta_{u_q}(t) \rangle$ and to evaluate the characteristic function $\mathfrak{C}^*(\boldsymbol{\omega}^*; t)$ by expressing it as a moment expansion. If the characteristic function $\mathfrak{C}^*(\boldsymbol{\omega}^*; t)$ is known then the probability $\mathfrak{R}^*(\boldsymbol{\tau}; t)\, d\boldsymbol{\tau}$ can be evaluated by means of an inverse Fourier transformation.

The first step is to express the moments of the scaled sojourn times in terms of the non-scaled moments given by Eqs. (3.28). By using Eqs. (4.27) we obtain

$$\langle \tau_{u_1} \cdots \tau_{u_q} \rangle = (-1)^q \sqrt{\prod_{m=1}^{M} \langle \theta_{u_m} \rangle} \left\{ 1 + \sum_{m=1}^{q} \frac{(-1)^m}{m!} \sum_{\alpha_1, \ldots, \alpha_m}^{*} \cdots \sum^{*} \frac{\langle \prod_{\beta=1}^{m} \theta_{u_{\alpha_\beta}} \rangle}{\prod_{\beta=1}^{m} \langle \theta_{u_{\alpha_\beta}} \rangle} \right\}, \tag{4.30}$$

where the star * shows that in the multiple sum over $\alpha_1, \ldots, \alpha_m$ all labels should be distinct. Eq. (4.30) can be easily proven by the direct expansion of the product

$$\prod_{m=1}^{q} [1 - \theta_{u_{\alpha_m}} / \langle \theta_{u_{\alpha_m}} \rangle] \tag{4.31}$$

and by averaging the resulting expansion. We insert Eqs. (3.28) for the moments of the non-scaled sojourn times into Eq. (4.30) and evaluate the asymptotic behavior of the multiple convolution products by using the properties of the Green's functions $G_{jj'}(t)$ derived in Appendix B. The calculations are cumbersome but standard; by keeping the non-vanishing terms in the limit $t \to \infty$ we obtain

$$\langle \tau_{u_1}(t) \cdots \tau_{u_{2q}}(t) \rangle \sim \sum_{\text{all partitions of } 2q} \cdots \sum [C_{u_{\alpha_1} u_{\alpha_2}} \sqrt{P^{st}_{u_{\alpha_1}}/P^{st}_{u_{\alpha_2}}} + C_{u_{\alpha_2} u_{\alpha_1}} \sqrt{P^{st}_{u_{\alpha_2}}/P^{st}_{u_{\alpha_1}}}]$$

$$\times [C_{u_{\alpha_3} u_{\alpha_4}} \sqrt{P^{st}_{u_{\alpha_3}}/P^{st}_{u_{\alpha_4}}} + C_{u_{\alpha_4} u_{\alpha_3}} \sqrt{P^{st}_{u_{\alpha_4}}/P^{st}_{u_{\alpha_3}}}] \times \cdots$$

$$\times [C_{u_{\alpha_{2q-1}} u_{\alpha_{2q}}} \sqrt{P^{st}_{u_{\alpha_{2q-1}}}/P^{st}_{u_{\alpha_{2q}}}} + C_{u_{\alpha_{2q}} u_{\alpha_{2q-1}}} \sqrt{P^{st}_{u_{\alpha_{2q}}}/P^{st}_{u_{\alpha_{2q-1}}}}] \quad \text{as } t \to \infty , \tag{4.32}$$

$$\langle \tau_{u_1}(t) \cdots \tau_{u_{2q+1}}(t) \rangle \sim 0 \quad \text{as } t \to \infty , \tag{4.33}$$

where the sum over the partitions of $2q$ means a division of the integer $2q$ into q pairs $(\alpha_1, \alpha_2), (\alpha_3, \alpha_4), \ldots, (\alpha_{2q-1}, \alpha_{2q})$; the total number of partitions is equal to

$$(2q)!/[2^q q!] . \tag{4.34}$$

In Appendix C we show that the moments (4.32), (4.33) correspond to:

$$\mathfrak{R}^*(\boldsymbol{\tau}; t) = (2\pi)^{-M/2} [\det | \mathfrak{m} + \mathfrak{m}^+ |]^{-1/2} \exp[-\tfrac{1}{2} \boldsymbol{\tau} (\mathfrak{m} + \mathfrak{m}^+)^{-1} \boldsymbol{\tau}^+] \quad \text{as } t \to \infty , \tag{4.35}$$

$$\mathfrak{C}^*(\boldsymbol{\omega}^*; t) = \exp[-\tfrac{1}{2} \boldsymbol{\omega}^* (\mathfrak{m} + \mathfrak{m}^+) \boldsymbol{\omega}^{*+}] \quad \text{as } t \to \infty , \tag{4.36}$$

where the matrix $\mathfrak{m}$ is given by

$$\mathfrak{m} = [C_{uu'} \sqrt{P^{st}_u / P^{st}_{u'}}] . \tag{4.37}$$

If we return to the non-scaled sojourn times θ_j, $j = 1, \ldots, M$ we get a time-dependent Gaussian law which includes as particular cases the other similar Gaussian laws derived for the distribution of sojourn times in different physical and chemical contexts [1–3,9]

$$\mathfrak{R}(\boldsymbol{\theta}; t) \sim (2\pi t)^{-M/2} [\det | \mathbf{bC} + \mathbf{C}^+ \mathbf{b} |]^{-1/2}$$

$$\times \exp\{-\tfrac{1}{2} (\boldsymbol{\theta} - t\mathbf{P}^{st}) [t(\mathbf{bC} + \mathbf{C}^+ \mathbf{b})]^{-1} (\boldsymbol{\theta} - t\mathbf{P}^{st})^+\} \quad \text{as } t \to \infty , \tag{4.38}$$

where the matrices $\mathbf{b}$ and $\mathbf{C}$ are given by

$$\mathbf{b} = [P^{st}_j \delta_{jj'}], \qquad \mathbf{C} = [C_{jj'}] . \tag{4.39}$$

It is easy to check that the moments of first- and second-order corresponding to the Gaussian law (4.39) are the same as the ones given by Eqs. (4.11) and (4.13). The characteristic function

$$\mathfrak{C}(\boldsymbol{\omega}; t) = \int \cdots \int \exp \left(i \sum_j \omega_j \theta_j \right) \mathfrak{R}(\boldsymbol{\theta}; t) \, d\boldsymbol{\theta} \tag{4.40}$$

is also Gaussian,

$$\mathfrak{C}(\boldsymbol{\omega};t) = \exp\left\{it\mathbf{P}^{st}\boldsymbol{\omega}^{+} - \frac{t}{2}\boldsymbol{\omega}(\mathbf{bC} + \mathbf{C}^{+}\mathbf{b})\boldsymbol{\omega}^{+}\right\} \quad \text{as } t \to \infty\,. \tag{4.41}$$

Now we discuss the general relationship between the relation (4.19) and ergodicity. Given a time interval of length t we introduce the time average

$$\widetilde{f[j(t')]}(t) = t^{-1}\int_0^t f[j(t')]\,dt'\,. \tag{4.42}$$

By observing that the sojourn time $\theta_j(t)$ of the state j corresponding to a time interval of length t can be expressed as the time average of a Kronecker symbol

$$\theta_j(t) = \int_0^t \delta_{(j)[j(t')]}\,dt'\,, \tag{4.43}$$

the time average (4.42) can be expressed as the weighted sum of the sojourn times θ_j corresponding to the different states of the system

$$\widetilde{f[j(t')]}(t) = t^{-1}\sum_{j=1}^{M}\theta_j(t)f(j)\,. \tag{4.44}$$

If a system is ergodic then in the limit $t \to \infty$ the time average $\widetilde{f[j(t')]}\,(\infty)$ is equal to the corresponding ensemble average

$$\widetilde{f[j(t')]}(\infty) = \langle f(j)\rangle^{st}\,, \tag{4.45}$$

where the statistical ensemble average $\langle f(j)\rangle^{st}$ is given by Eq. (4.20). In general, since the sojourn times $\theta_j(t)$, $j = 1,\ldots,M$ are random the time average $\widetilde{f[j(t')]}(t)$ is also random and then we can introduce the statistical ensemble average of a time average

$$\langle\widetilde{f[j(t')]}\rangle(t) = \left\langle t^{-1}\sum_{j=1}^{M}\theta_j(t)f(j)\right\rangle = t^{-1}\sum_{j=1}^{M}\langle\theta_j(t)\rangle f(j)\,, \tag{4.46}$$

where the average $\langle\cdots\rangle$ is given by

$$\langle\cdots\rangle = \int\cdots\mathfrak{R}(\boldsymbol{\theta};t)\,d\boldsymbol{\theta}\,. \tag{4.47}$$

In particular, Eq. (4.19) can be expressed as

$$\langle\widetilde{f[j(t')]}\rangle(\infty) = \langle f(j)\rangle^{st}\,. \tag{4.48}$$

By comparing Eq. (4.45) with Eq. (4.48), we notice that for the ergodic property to be valid it is necessary that

$$\langle\widetilde{f[j(t')]}\rangle(\infty) = \widetilde{f[j(t')]}\,(\infty)\,, \tag{4.49}$$

i.e., for an ergodic process in the limit $t \to \infty$ the ensemble average of a time average should be equal to the time average itself. In other words for the ergodic property to be valid it is necessary that in the limit $t \to \infty$ the time average $\widetilde{f[j(t')]}(\infty)$ should be non-random. The non-randomness condition can be expressed for instance by requiring that all cumulants of the time average $\widetilde{f[j(t')]}(\infty)$ of order bigger than one vanish

$$\langle\langle \widetilde{f[j(t')]} \rangle\rangle(t) \to 0 \quad \text{as } t \to \infty, \quad m \geqslant 2\,, \tag{4.50}$$

where $\langle\langle \cdots \rangle\rangle$ denotes the cumulant average. In general, it is very hard to check whether all cumulants of order bigger than one vanish. That is why we use a non-randomness condition in the mean square sense commonly used in the mathematical literature by requiring that only the second cumulant of the time average vanishes

$$\begin{aligned}\langle \Delta[\widetilde{f[j(t')]}]^2 \rangle &= \langle [\widetilde{f[j(t')]}]^2 \rangle - \langle \widetilde{f[j(t')]} \rangle^2 \\ &= \langle\langle [\widetilde{f[j(t')]}]^2 \rangle\rangle \to 0 \quad \text{as } \to \infty\,. \end{aligned} \tag{4.51}$$

The cumulant of second order of the time average can be easily computed by combining Eqs. (4.44) and (4.51) with the expressions (4.11) and (4.13) for the asymptotic behavior of the moments of the sojourn times θ_j, $j = 1, \ldots, M$. After some calculations we come to

$$\begin{aligned}\langle\langle [\widetilde{f[j(t')]}]^2 \rangle\rangle(t) &= t^{-2} \sum_{u_1} \sum_{u_2} f(u_1) f(u_2) \langle \Delta\theta_{u_1} \Delta\theta_{u_2} \rangle(t) \\ &\sim 2t^{-1} \left\langle f(u) \sum_{u'} C_{uu'} f(u') \right\rangle^{st} \to 0 \quad \text{as } t \to \infty\,, \end{aligned} \tag{4.52}$$

where the averages $\langle \cdots \rangle^{st}$ are computed in terms of the steady-state probability P_u^{st}. From Eq. (4.52) it follows that in the limit $t \to \infty$ the time average $\widetilde{f[j(t')]}\ (t)$ is non-random in the mean square sense and thus the ergodic property (4.45) holds [13].

5. Conclusions

In this article, a new description of the evolution of Markov processes in continuous time and with a finite number of states has been suggested by using the total sojourn times and the numbers of jump events as random variables. In terms of these variables the dynamics of the process can be described by using a stochastic Liouville equation. Two infinite-order perturbation approaches have been developed for evaluating the stochastic properties of the sojourn times and of the total numbers of transition events; these approaches lead to exact expressions for the moments and the cumulants of the random variables. The asymptotic stochastic behavior has been investigated in the limit of very large times. In this limit, the sojourn times become Gaussian random variables and their cumulants of first- and second-order increase linearly in time.

This linear time-dependence of the cumulants ensures the ergodicity of the Markov process.

The computations presented in this article are more than a simple academic exercise. They may serve as a basis for a systematic approach for computing transport coefficients and effective rate constants for rate and transport processes in systems with dynamical disorder and for the study of fluctuation dynamics in reaction–diffusion processes. Such an approach for computing rate coefficients is a direct generalization of Van den Broeck's approach to the problem of Taylor diffusion [3–9]. Possible applications include the study of exotic (dispersive or enhanced) diffusion, the stochastic theory of line shape, the propagation of non-linear chemical waves in random media, etc. Moreover, the theory can be used for making a connection between the stochastic theories and the thermodynamic description of non-equilibrium steady states. Other possibilities of application are related to the study of relative stability in reaction–diffusion systems far from equilibrium. Work on these problems is in progress and the results are going to be presented in other articles. In the next paper we are going to discuss the connections between our approach and the thermodynamic description of a non-equilibrium convection–diffusion process in an external force field [13].

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Appendix A

We introduce the one-time mixed factorial moments

$$\begin{aligned}&\langle q_1(q_1-1)\cdots(q_1-m_1+1)\cdots q_M(q_M-1)\cdots(q_M-m_M+1)\theta_{u_1}\cdots\theta_{u_p}\rangle\\&\quad=\sum_j\sum_{q_1}\cdots\sum_{q_M} q_1(q_1-1)\cdots(q_1-m_1+1)\cdots\\&\quad\quad\times q_M(q_M-1)\cdots(q_M-m_M+1)\\&\quad\quad\times\int\cdots\int\theta_{u_1}\cdots\theta_{u_p}B_j(\boldsymbol{\theta};\mathbf{q};t)\,d\boldsymbol{\theta}\,.\end{aligned} \tag{A.1}$$

From Eq. (3.1) we notice that the mixed factorial moments (A.1) can be computed from $\overline{B}_j(\boldsymbol{\omega}; \mathbf{z}; s)$ by repeated differentiation

$$\langle q_1(q_1-1)\cdots(q_1-m_1+1)\cdots q_M(q_M-1)\cdots(q_M-m_M+1)\theta_{u_1}\cdots\theta_{u_p}\rangle$$
$$= (-i)^p \mathscr{L}^{-1}\left[\frac{\partial^{m_1+\cdots+m_M+p}\overline{B}_j(\boldsymbol{\omega}; \mathbf{z}; s)}{\partial z_1^{m_1}\cdots\partial z_M^{m_M}\partial\omega_{u_1}\cdots\partial\omega_{u_p}}\right]\Bigg|_{\forall z_j=1;\ \boldsymbol{\omega}=\mathbf{0}} . \tag{A.2}$$

We use the identity

$$q^m = \sum_{\rho=0}^{m} \mathfrak{S}_m^{(\rho)} q(q-1)\cdots(q-m+1) , \tag{A.3}$$

where

$$\mathfrak{S}_m^{(\rho)} = \sum_{k=0}^{\rho} \frac{(-1)^\rho k^m}{k!(\rho-k)!} \tag{A.4}$$

are the Stirling numbers of second kind. From Eqs. (A.2)–(A.4) we can compute all central moments $\langle q_1^{m_1}\cdots q_M^{m_M}\theta_{u_1}\cdots\theta_{u_p}\rangle$ and the corresponding cumulants. In particular, for $m_{1;2}=1;2$ after some calculations we come to Eqs. (3.34)–(3.36).

Appendix B

We express the matrix Greens function $\mathbf{G}(t)$ of Eq. (2.1) as an inverse Laplace transform

$$\mathbf{G}(t) = \mathscr{L}^{-1}(\mathbf{I}s - \mathbf{W} + \boldsymbol{\Omega})^{-1} . \tag{B.1}$$

From Eq. (B.1) it follows that the time dependence of $\mathbf{G}(t)$ is determined by the roots of the secular equation

$$\det|\mathbf{I}s - \mathbf{W} + \boldsymbol{\Omega}| = 0 . \tag{B.2}$$

Since the matrix elements $G_{jj'}(t)$ obey the normalization condition $\sum_{j'} G_{jj'}(t)=1$ it follows that $s_0=0$ is a simple root of Eq. (B.2). The other roots $s_1, s_2, \ldots$ are either real and negative or complex with negative real parts. If the roots of Eq. (B.2) are $s_0 = 0, s_1, s_2, s_3, \ldots$ with multiplicities $m_0 = 1, m_1, m_2, m_3, \ldots$, then $\mathbf{G}(t)$ can be expressed as

$$\mathbf{G}(t) = \sum_\beta \sum_{k=1}^{m_\beta} \frac{t^{k-1}\exp(s_\beta t)}{(k-1)!(m_\beta-k)!}\mathbf{G}_{\beta k} , \tag{B.3}$$

where

$$\mathbf{G}_{\beta k} = \frac{d^{m_\beta-k}}{ds^{m_\beta-k}}\left\{\left[\frac{\operatorname{Adj}(\mathbf{I}s-\mathbf{W}+\boldsymbol{\Omega})}{\det|\mathbf{I}s-\mathbf{W}+\boldsymbol{\Omega}|}\right](s-s_\beta)^{m_\beta}\right\}\Bigg|_{s=s_\beta} . \tag{B.4}$$

By inserting Eq. (B.3) into Eqs. (4.2) and (4.3) we obtain Eqs. (4.4) and (4.5) where the constant terms C_{j_0j} and $\Lambda_{j_0j}^{(0)}$ come from the time-independent parts of the integrals:

$$\int_0^t t^{k-1}\exp(-s_\beta t)\,dt \quad \text{and} \quad \int_0^t\int_0^{t'} t^{k-1}\exp(-s_\beta t)\,dt\,dt' . \tag{B.5}$$

A possible way of computing the matrix elements $C_{jj'}$ would be to express Eq. (4.2) for $\Gamma_{j_0j}^{(1)}(t)$ in terms of Eq. (B.3) for the matrix Green's function $\mathbf{G}(t)$ and to keep the time-independent terms. This method is cumbersome because for applying it we need to know the solutions $s_0 = 0, s_1, s_2, s_3, \ldots$ of the secular equation (B.2). A more advantageous way of evaluating C_{j_0j} is to integrate term by term the evolution equation for the Green's function $\mathbf{G}(t)$

$$d\mathbf{G}(t)/dt = \mathbf{G}(t)(\mathbf{W}-\boldsymbol{\Omega}), \qquad \mathbf{G}(t=0) = \mathbf{I} , \tag{B.6}$$

and the normalization conditions

$$\sum_j G_{jj'}(t) = 1, \quad j = 1,\ldots,M , \tag{B.7}$$

resulting in

$$\mathbf{G}(t) - \mathbf{I} = \int_0^t \mathbf{G}(t)(\mathbf{W}-\boldsymbol{\Omega})\,dt , \tag{B.8}$$

$$\sum_j \int_0^t G_{jj'}(t)\,dt = t, \quad j = 1,\ldots,M . \tag{B.9}$$

By inserting Eq. (4.4) into Eqs. (B.8) and (B.9) and keeping the constant terms in the limit $t\to\infty$, we come to Eqs. (4.9) and (4.10).

By summing in Eqs. (4.9) over j' we come to M identities $0 = 0$ and thus of the M^2 equations only $M(M-1)$ are linearly independent. The M supplementary conditions (4.19) provide the necessary additional information for the determination of the M^2 unknown matrix elements $C_{jj'}$, $j, j' = 1,\ldots,M$.

Appendix C

We express the scaled characteristic function $\mathfrak{C}^*(\boldsymbol{\omega}^*;t)$ in terms of a moment expansion:

$$\mathfrak{C}^*(\boldsymbol{\omega}^*;t) = 1 + \sum_{q=1}^{\infty}\frac{(-1)^q}{(2q)!}\sum_{u_1}\cdots\sum_{u_{2q}}\omega_{u_1}^*\cdots\omega_{u_{2q}}^*\,\langle\tau_{u_1}(t)\cdots\tau_{u_{2q}}(t)\rangle . \tag{C.1}$$

We insert the expressions (4.32) of the even moments $\langle \tau_{u_1}(t) \cdots \tau_{u_{2q}}(t) \rangle$ into Eq. (C.1) and evaluate the multiple sums in two steps. In a first step we use the expression (4.34) of the total number of partitions in Eq. (4.32) and express the sum

$$\sum_{u_1} \cdots \sum_{u_{2q}} \sum_{\text{all partitions of } 2q} \cdots \sum \omega^*_{u_1} \cdots \omega^*_{u_{2q}} \langle \tau_{u_1}(t) \cdots \tau_{u_{2q}}(t) \rangle , \tag{C.2}$$

as a multinomial expansion. Eq. (C.1) becomes

$$\mathfrak{C}^*(\boldsymbol{\omega}^*; t) = \sum_{q=0}^{\infty} \frac{(-1)^q}{(q)!} \left\{ \frac{1}{2} \sum_{u_1, u_2 = 1}^{M} \omega^*_{u_1} \omega^*_{u_2} [C_{u_1 u_2} \sqrt{P^{st}_{u_1} / P^{st}_{u_2}} + C_{u_2 u_1} \sqrt{P^{st}_{u_2} / P^{st}_{u_1}}] \right\}^q . \tag{C.3}$$

The sum over q in Eq. (C.3) can be easily evaluated, resulting in Eq. (4.36). The probability $\mathfrak{R}^*(\boldsymbol{\tau}; t) d\boldsymbol{\tau}$ of the scaled sojourn times $\tau_1, \ldots, \tau_M$ can be evaluated from the characteristic function $\mathfrak{C}^*(\boldsymbol{\omega}^*; t)$ by means of an inverse Fourier transformation

$$\mathfrak{R}^*(\boldsymbol{\tau}; t) = (2\pi)^{-M} \int \cdots \int \mathfrak{C}^*(\boldsymbol{\omega}^*; t) \exp\left(-i \sum_j \omega^*_j \tau_j \right) d\boldsymbol{\omega}^* . \tag{C.4}$$

By inserting Eq. (4.36) into Eq. (C.4) and evaluating the integrals over $\boldsymbol{\omega}^*$ we come to Eq. (4.35).

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