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General probabilistic approach to the problem of irreversible stochastic transitions

Y A Berlin, D O Drobnitsky and V V Kuz'min

N. N. Semenov Institute of Chemical Physics, Russian Academy of Sciences, ul. Kossygina 4, Moscow 117334, Russia

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Abstract. The consideration of irreversible stochastic transitions (IST) in complex stochastic systems based on the most general probabilistic formalism is performed. The key quantity, transition probability per unit time, α, is strictly introduced without referring to the conventional approach to the IST description. The expressions obtained for transition probabilities and average transition expectation time, $\langle\tau\rangle$, allow one to take into account the influence of interactions between objects undergoing IST and external impacts on probabilities of transitions. The violation of common postulates $\alpha = 1/\langle\tau\rangle = \text{constant}$, as well as of the simple exponential kinetic law for $A \rightarrow B$ transitions, is demonstrated. These postulates are shown to follow from the general consideration performed as a special particular case. The evaluation of statistical characteristics of various complex systems containing objects undergoing IST by means of the approach developed is demonstrated on two model problems.

1. Introduction

Various physical problems concern systems containing objects (atoms, molecules, radicals and other species) undergoing irreversible transitions with random expectation time from a state A to a state B. The most common, 'classical' description of such irreversible stochastic transitions (IST) is based on two major assumptions.

First, for a single object undergoing the $A \rightarrow B$ transition, the waiting (expectation) time distribution is supposed to be exponential with the average waiting time, $\langle\tau\rangle$, being a constant and independent of the observation startout moment, t_0. Such an assumption is mathematically evident when one deals with the $A \rightarrow B$ process which is Markovian in terms of the waiting times.

Second, identical objects are supposed to have equal $\langle\tau\rangle$ values throughout the system. Thus it is *a priori* assumed that the average expectation time is a given constant characterizing the 'reactive system' (Benson 1960, Bharuch-Reid 1960, Goldanskii *et al.* 1962, Kondratiev and Nikitin 1974, Levine and Bernstein 1987 and references therein). In more complicated cases (e.g. complex and multichannel reaction mechanisms, processes in multicomponent systems, etc.) one usually defines the set of constants $\langle\tau\rangle_i$ ($i = 1, 2, \ldots, \mathcal{R}$) being also identical for all objects of the type i (Benson 1960, Goldanskii *et al.* 1962).

Such an approach leads to the exponential evolutionary (kinetic) law, i.e. the law described by an exponential function versus time or (for processes with several $\langle\tau\rangle_i$) by

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a superposition of such functions (Karlin 1968, Feller 1970, Rozanov 1979 and references cited above).

The conventional assumptions mentioned above and the resulting evolutionary law seem particularly reasonable for monomolecular processes. However, numerous experimental data obtained for condensed media (Plonka 1986) and complex biochemical objects (Berlin *et al.* 1992, Frauenfelder *et al.* 1991) provide kinetic curves which cannot be convincingly interpreted using the set of constants describing the reaction rate. This difficulty always appears when one deals with monomolecular processes proceeding under certain external—with respect to the very $A \rightarrow B$ transition—affections.

To overcome the discrepancy between theory and experimental data, several approaches have been proposed (Mikhailov 1972, Agmon and Hopfield 1983, Goldanskii and Kozhushner 1984, Plonka 1986, 1988, 1989, Frauenfelder *et al.* 1991, Sumi 1991, Berlin *et al.* 1990, 1991, 1992, and references therein). For instance, kinetic laws are constructed by using time-dependent rate 'constants' (Plonka 1986, 1988, 1989, Frauenfelder *et al.* 1991, Berlin *et al.* 1990, 1991, 1992) introduced on the basis of the relaxation (Plonka 1986, Berlin *et al.* 1992, Frauenfelder *et al.* 1991) or polychromacity concept (Mikhailov 1972, Goldanskii and Kozhushner 1984). Another group of models (Agmon and Hopfield 1983, Sumi 1991) treats external effects by the method of the 'diffusion perpendicular to the reaction coordinate' (Agmon and Hopfield 1983).

However, all these approaches are based on some qualitative assumptions being distinct for different reaction systems and mechanisms. In addition, they include various mathematical constraints and limitations restricting their applicability. Thus the problem of the general description of IST arises.

Leaving the detailed comparison of the above-mentioned methods for a separate paper, in the present work we carry out a consideration of IST based on the most general probabilistic formalism. Such a consideration does not use the propositions mentioned above and provides means to treat the general IST situation regardless of the nature of objects and their environment. From the mathematical point of view, the present consideration does not use assumptions concerning Markovian or non-Markovian, stationary or non-stationary characteristics of the transition process. This advantage makes the proposed theory different from those mentioned above and free from the necessity to introduce special 'memory' terms into the description of IST in the case when the process is non-Markovian.

The origin of the main mathematical quantity of the problem—the transition probability per unit time, α—is considered in section 2. In the following section we investigate properties of α using the most general assumptions and derive expressions for α and $\langle\tau\rangle$. These results are used in section 4 to show how the description of the entire system with elements undergoing transition $A \rightarrow B$ can be performed in the general case. Two important particular situations are considered in detail, i.e. a system with a set of deterministic parameters affecting IST and a system with a set of stochastic parameters. The main conclusions following from our investigation are summarized in section 5.

2. Transition probability per unit time

Here we consider the simplest case when, at $t=0$, the system contains N identical

objects undergoing IST $A \rightarrow B$. The extension to more-complicated cases including, for example, several types of objects and a large number of states, is straightforward. We assume that states A and B differ in some parameter (or the set of parameters), so that the transition $A \rightarrow B$ is defined as the change of this particular parameter. Changes in all other parameters do not refer to the transition between states in the above-mentioned sense, although they can have an influence on the transition.

Let us choose one of the objects. Consider the conditional probability $p(t, \Delta t)$ that this object will undergo the transition during the interval $(t, t+\Delta t)$, if the transition has not occurred before the time t. Regarding this probability, we shall assume that for any $t>0$ there exists $\Delta t>0$ such that the $p(t, \Delta t)$, as a function of Δt, increases on $(-\Delta t, \Delta t)$. This means that the object may undergo the transition into B, no matter how long it has been in A. Because of this assumption, for $\Delta t \rightarrow 0$ the Taylor expansion of $p(t, \Delta t)$ yields

$$p(t, \Delta t) \equiv P\{A \rightarrow B, \Delta t | A \not\rightarrow B, t\} = \alpha(t)\Delta t + o(\Delta t) \tag{1}$$

with $\alpha(t)>0$ for any $t>0$.

The quantity $\alpha(t)$ is called the transition probability per unit time (Kolmogorov 1931, Feller 1970). As follows from our consideration this quantity is, generally speaking, time dependent and is not necessarily equal for all objects under consideration. However, the unusual approach to the IST description includes (1) as a *postulate* (Kolmogorov 1931, Bharuch-Reid 1960, Karlin 1968, Feller 1970, Rozanov 1979) and is restricted to the case $\alpha(t) = \alpha = 1/\langle\tau\rangle = \text{constant}$. This immediately gives the exponential evolutionary law for the probability $p(t)$ for each object to undergo the transition by the time t:

$$p(t) \equiv P\{A \rightarrow B, t\} = 1 - \exp(-\alpha t). \tag{2}$$

In the present work we eliminate this postulate to carry out a more general analysis. In particular, in the next section we elucidate what mathematical values $\alpha(t)$ depends on and deduce general rules for the calculation of this quantity.

3. Basic mathematical analysis: α and $\langle\tau\rangle$

Consider the probability for a chosen object to remain in the state A by the time $t+\Delta t$

$$P\{A \not\rightarrow B, t+\Delta t\} \equiv 1 - p(t+\Delta t) = P\{A \not\rightarrow B, \Delta t | A \not\rightarrow B, t\} P\{A \not\rightarrow B, t\}$$
$$\equiv (1 - p(t, \Delta t)(1 - p(t))$$

i.e.

$$p(t, \Delta t) = 1 - (1 - p(t+\Delta t)(1 - p(t))^{-1}. \tag{3}$$

The right-hand side contains the total probabilities of the transition. Obviously, they depend only on time variables, t and Δt and on initial conditions assumed for the system at $t=0$. Hence $p(t, \Delta t)$ in the left-hand side is a function of the same factors. In turn, the value $\alpha(t)$ in (1), being a coefficient of the Taylor expansion for $p(t, \Delta t)$ in terms of Δt, depends on the time variable t and initial conditions.

3.1. Rules for calculations of $\alpha(t)$

Let an arbitrary chosen object be in the state A at $t=0$ and the probability of its transition to B be governed by a quantity $\alpha(t)$, so tha (1) is satisfied. Assume that this

object and its environment at $t=0$ is completely characterized by sets of deterministic and stochastic parameters denoted as $\zeta=\{\zeta_1, \zeta_2, \ldots, \zeta_K\}$ and $\eta=\{\eta_1, \eta_2, \ldots, \eta_M\}$, respectively. The set η is distributed due to the total probability $P(\eta', t)$ of η being equal to η' at the time t and the conditional probability $P(\eta', t|\eta(0))$ of η being equal to η' at the time t if at $t=0$ it has been equal $\eta(0)$. The dynamic variable $\zeta(\zeta_0, t)$ is defined by its time evolution and initial conditions $\zeta_0=\zeta(0)$.

Consider the conditional probability,

$$p(t, \Delta t, \zeta, \eta) \equiv P\{A \to B, \Delta t | \zeta(t)=\zeta, \eta(t)=\eta; A -/\to B, t\}.$$

Using Taylor expansion similar to that performed in section 2 one obtains

$$p(t, \Delta t, \zeta, \eta) = \mathcal{T}(\zeta, \eta, t)\Delta t + o(\Delta t) \tag{4}$$

where $\mathcal{T}$ is a certain function.

Due to the total probability formula, $p(t, \Delta t, \zeta, \eta)$ and $p(t, \Delta t)$ are related by

$$p(t, \Delta t) = \int p(t, \Delta t, \zeta(t), \eta) P(\eta, t|\eta(0))\, \mathrm{d}\eta. \tag{5}$$

By substituting (4) into (5) and comparing the result with (1) one obtains

$$\alpha(t) = \int \mathcal{T}(\zeta(t), \eta, t) P(\eta, t|\eta(0))\, \mathrm{d}\eta \tag{6}$$

where the integration over η is, generally speaking, implied in the Lebegue sense.

Now one can mathematically define the 'identify' of objects under consideration. Objects are identical if:

(i) their $\mathcal{T}$ functions have the same forms as well as definition ranges;
(ii) their $\zeta(\zeta_0, t)$, as functions of two variables, coincide;
(iii) their $P(\eta, t|\eta(0))$ distributions are the same together with probabilistic measures defined for η.

Note, however, that, the identity of objects $i=1, \ldots, N$ does not imply that $\alpha^{(i)}$s adopt equal values at a given t, since $\alpha(t)$ depends on the set of initial conditions $\{\zeta(0), \eta(0)\}$ which, in general, can vary from object to object. Moreover, as follows from (6), $\alpha^{(i)}(t)$ are composite functions of t due to the time dependence of the integrand. Thus it becomes obvious that expression (2) represents only a very special particular case of (6) with $\mathcal{T}=$ constant.

Summing up, we come to the following rules for the calculation of the transition probability per unit time, $\alpha(t)$, in IST processes of the general type. Starting with some initial physical model, one should account for all interactions between objects and external influences in terms of $\zeta(\zeta_0, t)$, η and $p(\eta, t|\eta(0))$. The influence of these factors on the IST process are expressed by the function $\mathcal{T}(\zeta, \eta, t)$. Finally, $\alpha(t)$ should be calculated by means of equation (6).

3.2. Average expectation time

To derive $\langle\tau\rangle$ for a chosen object we consider the probability $P\{A \not\to B, t; A \to B, \mathrm{d}t\}$ of its transition within the time interval ranging from t up to $t+\mathrm{d}t$. This quantity constitutes the joint probability of two events, namely the survival of the object in the state A by the time t and its transition to the state B during the time interval $(t, t+\mathrm{d}t)$. By definition of the conditional probability, one can write

$$P\{A \not\to B, t; A \to B, \mathrm{d}t\} = p(t, \mathrm{d}t) P\{A \not\to B, t\}. \tag{7}$$

Noting (1) and the differential order of smallness of $\mathrm{d}t$, one obtains

$$P\{A \not\to B, t; A \to B, \mathrm{d}t\} = \alpha(t) P\{A \not\to B, t\}\,\mathrm{d}t. \tag{8}$$

The probability $P\{A \not\to B, t\}$ can be found from (1) and (3) in the form

$$P\{A \not\to B, t\} = \exp\left(-\int_0^t \alpha(s)\,\mathrm{d}s\right). \tag{9}$$

Note that $P\{A -/\to B, t; A \to B, \mathrm{d}t\}$ is the probability of the expectation time to be within the interval $(t, t+\mathrm{d}t)$. Therefore substituting (9) into (8), multiplying the result by t and finally integrating over t one obtains

$$\langle\tau\rangle = \int_0^\infty \alpha(t) t \exp\left(-\int_0^t \alpha(s)\,\mathrm{d}s\right)\mathrm{d}t. \tag{10}$$

After integrating (10) by parts we obtain

$$\langle\tau\rangle = \int_0^\infty \exp\left(-\int_0^t \alpha(s)\,\mathrm{d}s\right)\mathrm{d}t \tag{11}$$

where the lower integration limit represents the expectation startout moment which has been set at $t_0 = 0$ for the sake of convenience.

Up to now we have been examining a single object undergoing IST. However, the solution of the majority of physical problems involving IST requires the estimation of statistical characteristics of the entire system. They are given by probabilities $P_m(t)$ of observing $m = 1, 2, \ldots, N$ transitions $A \to B$ by the time t. In the next section we show how the results obtained above can be used for the calculation of $P_m(t)$.

4. Description of the entire system

One of the key problems for the mathematical consideration of the system with objects undergoing IST—in particular, for the derivation of master equations and differential equations for $P_m(t)$—is the estimation of the order of smallness of probabilities, $P_k(t, \Delta t)$, of k transitions occurring $(k>1)$ during the time interval $\Delta t \to 0$. Therefore this section starts with the investigation of this item. After that we illustrate the exploitation of the approach developed by solving two model problems: the first concerns IST dynamics governed only by the set of deterministic parameters, ζ, while the second deals with IST evolution influenced only by the set of stochastic parameters, η. Their solutions yield expressions for $P_m(t)$ which completely define all statistical characteristics of the system.

4.1. Orders of smallness

Let the system contain $n \leq N$ objects in the state A by a certain time t. Due to the above results their transition probabilities are given by

$$p^{(i)}(t, \Delta t) = \alpha^{(i)}(t)\Delta t + o(\Delta t) \tag{12}$$

where $\alpha^{(i)}(t) = O(1), i = 1, 2, \ldots, n$.

The probability of any two transitions during the time interval $\Delta t \to 0$ can be expressed using the total probability formula as follows

$$P_2(t, \Delta t) = \sum_{\substack{i,j=1 \\ i \neq j}}^{n} [p(i, \Delta t|j)(\alpha^{(j)}(t)\Delta t + o(\Delta t))]. \tag{13}$$

Here $p(i, \Delta t|j, \Delta t)$ is the conditional probability of the transition of the object i during Δt if the object j undergoes transition during the same time interval. Similarly to $p(t, \Delta t)$, the function $p(i, \Delta t|j)$ increases with Δt and hence its Taylor expansion in the vicinity of $\Delta t = 0$ provides

$$p(i, \Delta t|j) = \gamma(t)\Delta t + o(\Delta t) \tag{14}$$

where a certain function γ satisfies the condition $\gamma(t) = O(1)$. Combining (13) and (14) we have

$$P_2(t, \Delta t) = O(\Delta t^2) = o(\Delta t).$$

Similarly the estimation for any $k > 1$ yields

$$P_k(t, \Delta t) = o(\Delta t), \Delta t \to 0 \qquad \text{for any } k > 1. \tag{15}$$

Usually the property (15) is postulated for systems which contain objects undergoing IST (Kolmogorov 1931, Karlin 1968, Feller 1970). Here it has been derived on the base of quite general assumptions discussed above.

4.2. Example of IST governed by a set of deterministic parameters

As an example we consider the system with IST proceses affected by some 'driving force' which induces the same $\xi(t)$ values for all objects undergoing transitions. Because of such an affection

$$\mathcal{T}^{(i)}(t) = \mathcal{T}(\xi(\xi_0, t))$$

where, obviously,

$$\xi_0^{(1)} = \xi^{(1)}(0) = \xi_0^{(2)} = \ldots \xi_0^{(N)}.$$

Then (6) provides

$$\alpha^{(i)}(t) = \alpha(t) = \int \mathcal{T}(\xi(\xi_0, t))P(\eta, t|\eta(0))\, d\eta$$

$$= \mathcal{T}(\xi(\xi_0, t)) \int P(\eta, t|\eta(0))\, d\eta = \mathcal{T}(\xi(\xi_0, t) \tag{16}$$

and because of (1), one obtains

$$p^{(i)}(t, \Delta t) = p(t, \Delta t) = \mathcal{T}(\xi(\xi_0, t))\Delta t + o(\Delta t) \tag{17}$$

for each object.

To derive differential equations for $P_m(t)$ let us consider the conditional probabilities, $P_k(m, t, \Delta t)$, of $k = 0, 1, \ldots, N-m$ transitions occurring in the system during the time interval $\Delta t \to 0$ if m transitions have proceeded during the time interval t before Δt. Since the probabilities of $k > 1$ transitions occurring have the order of smallness $o(\Delta t)$ (see subsection 4.1), one obtains

$$P_0(m, t, \Delta t) = 1 - P_1(m, t, \Delta t) + o(\Delta t)$$

$$P_1(m, t, \Delta t) = \sum_{i=1}^{N-m} p^{(i)}(t, \Delta t) + o(\Delta t) = w_m(t)\Delta t + o(\Delta t) \tag{18}$$

$$P_k(m, t, \Delta t) = o(\Delta t) \qquad \forall k > 1$$

where

$$w_m(t) = (N-m)\alpha(t) \tag{19}$$

with $\alpha(t)$ given by (16).

Using the total probability formula for the probability, $P_m(t+\Delta t)$, of m transitions occurring during the time interval $t+\Delta t$, we have

$$P_m(t+\Delta t) = P_m(t)P_0(m, t, \Delta t) + P_{m-1}(t)P_1(m, t, \Delta t)$$

$$+ \sum_{i=2}^{m} P_{m-i}(t)P_m(m, t, \Delta t). \tag{20}$$

Substituting (18) into (20) and setting $\Delta t \to 0$, we derive differential equations for $P_m(t)$ as follows:

$$\frac{dP_m(t)}{dt} = -w_m(t)P_m(t) + w_{m-1}(t)P_{m-1}(t). \tag{21}$$

For initial conditions

$$P_0(0) = 1 \qquad \text{and } P_m(0) = 0 \qquad \text{for any } m > 0$$

the solution to (21) is given by

$$P_m(t) = C_N^m (p(t))^m (1-p(t))^{N-m} \tag{22}$$

where

$$C_N^m = \frac{N!}{m!(N-m)!}, \tag{23}$$

and

$$p(t) = 1 - \exp\left(-\int_0^t \alpha(\tau)\, d\tau\right) \tag{24}$$

with $\alpha(t)$ given by (16).

The derivation of statistical characteristics of the system under consideration, i.e.

the moments of the distribution $P_m(t)$, is straightforward. For example, from (22)–(24), the average, $\langle m(t)\rangle \equiv \Sigma\, mP_m(t)$, can be written as

$$\langle m(t)\rangle = Np(t) = N\left(1-\exp\left(-\int_0^t \alpha(\tau)\,\mathrm{d}\tau\right)\right) \tag{25}$$

while for the dispersion $D(t) \equiv \sum_t (m^2 - \langle m(t)\rangle^2)P_m(t)$ one obtains

$$D(t) = N\left(1-\exp\left(-\int_0^t \alpha(\tau)\,\mathrm{d}\tau\right)\right)\exp\left(-\int_0^t \alpha(\tau)\,\mathrm{d}\tau\right). \tag{26}$$

Finally we note that the expression for the average lifetime of an object in the state A is defined by (11) with α given by (16). Namely

$$\langle\tau\rangle = \int_0^\infty \exp\left(-\int_0^t \mathcal{T}(\zeta\to(\xi_0, s))\,\mathrm{d}s\right)\mathrm{d}t \tag{27}$$

being the same for all objects of the system.

4.3. Example of an IST governed by a set of stochastic parameters

Now we turn to another model situation when the system contains N identical and statistically independent objects, each being characterized by an internal stochastic process, so that (4) and (6) for ith object reduce to

$$p(t, \Delta t, \zeta, \boldsymbol{\eta}) = p(t, \Delta t, \boldsymbol{\eta}) = \mathcal{T}(\boldsymbol{\eta}, t)\Delta t + o(\Delta t) \tag{28}$$

and

$$\alpha^{(i)}(t) = \int \mathcal{T}(\boldsymbol{\eta}, t)P(\boldsymbol{\eta}, t|\boldsymbol{\eta}^{(i)}(0))\,\mathrm{d}\boldsymbol{\eta} \tag{29}$$

respectively.

For further analysis it is convenient to describe internal stochastic processes in terms of $\mathcal{T}$. This implies the introduction of probability distributions defined by

$$\phi(\mathcal{T}, t) \equiv P\{\mathcal{T}(t) = \mathcal{T}\} = \int \mathrm{d}\boldsymbol{\eta}_0 \int \mathcal{T}(\boldsymbol{\eta}, t)P(\boldsymbol{\eta}, t|\boldsymbol{\eta}_0)P(\boldsymbol{\eta})\,\mathrm{d}\boldsymbol{\eta} \tag{30}$$

and

$$\rho(\mathcal{T}_0, \mathcal{T}, t) = P\{\mathcal{T}(\boldsymbol{\eta}, t) = \mathcal{T}\,|\,\mathcal{T}(0) = \mathcal{T}_0\}$$

$$= \int_{\mathcal{T}(\boldsymbol{\eta}_0)=\mathcal{T}_0} \mathrm{d}\boldsymbol{\eta}_0 \int_{\mathcal{T}(\boldsymbol{\eta})=\mathcal{T}} \mathcal{T}(\boldsymbol{\eta}, t)P(\boldsymbol{\eta}, t|\boldsymbol{\eta}_0)P(\boldsymbol{\eta}_0)\,\mathrm{d}\boldsymbol{\eta}. \tag{31}$$

Obviously, since objects are identical, their distributions ρ and ϕ are the same, while initial conditions $\mathcal{T}(0)$ are, generally speaking, different. Such a difference can be explicated by rewriting (29) for an ith object with $\mathcal{T}^{(i)}(0) = \mathcal{T}_0^{(i)}$ as

$$\alpha^{(i)}(t) = \int \mathcal{T}\rho(\mathcal{T}_0^{(i)}, \mathcal{T}, t)\,\mathrm{d}\mathcal{T}. \tag{32}$$

Taking into account (28)–(32) it is easy to show that for this object the conditional probability, $p_{\mathcal{T}_0}(t, \Delta t)$, of the transition during the interval $\Delta t \to 0$ if it has not undergone the transition by the time t before Δt is given by

$$P_{\mathcal{T}_0}(t, \Delta t) = \Delta t \int \mathcal{T}\, \rho(\mathcal{T}_0, \mathcal{T}, t)\, \mathrm{d}\mathcal{T} + o(\Delta t). \tag{33}$$

Following the total probability formula, one can write the probability, $p_{\mathcal{T}_0}(t + \Delta t)$, of the transition during the time $t + \Delta t$ as follows

$$p_{\mathcal{T}_0}(t + \Delta t) \equiv P\{A \to B, t + \Delta t\} = P\{A \to B, t\}$$

$$+ p_{\mathcal{T}_0}(t, \Delta t) P\{A - / \to B, t\}$$

$$= p_{\mathcal{T}_0}(t) + \left(1 - p_{\mathcal{T}_0}(t)\right) P_{\mathcal{T}_0}(t, \Delta t). \tag{34}$$

The substitution of (33) into (34) yields

$$p_{\mathcal{T}_0}(t + \Delta t) = p_{\mathcal{T}_0}(t) + \left(1 - p_{\mathcal{T}_0}(t)\right) \Delta t \int \mathcal{T}\, \rho(\mathcal{T}_0, \mathcal{T}, t)\, \mathrm{d}\mathcal{T} + o(\Delta t)$$

or

$$\frac{p_{\mathcal{T}_0}(t + \Delta t) - p_{\mathcal{T}_0}(t)}{\Delta t} = \left(1 - p_{\mathcal{T}_0}(t)\right) \int \mathcal{T}\, \rho(\mathcal{T}_0, 0, \mathcal{T}, t)\, \mathrm{d}\mathcal{T} + o(\Delta t).$$

In the limit $\Delta t \to 0$ the latter expression provides the differential equation as follows

$$\frac{\partial p_{\mathcal{T}_0}(t)}{\partial t} = (1 - p_{\mathcal{T}_0}(t)) \int \mathcal{T}\, \rho(\mathcal{T}_0, 0, \mathcal{T}, t)\, \mathrm{d}\mathcal{T}. \tag{35}$$

The solution of (35) is given by

$$p_{\mathcal{T}_0}(t) = 1 - \exp\left(- \int_0^t \mathrm{d}\tau \int \rho(\mathcal{T}_0, \mathcal{T}, \tau) \mathcal{T}\, \mathrm{d}\mathcal{T} \right). \tag{36}$$

To evaluate statistical characteristics of the entire system one should take into account all N objects with random initial conditions $\mathcal{T}^{(i)}(0)=\mathcal{T}_0^{(i)}$ distributed due to $P(\mathcal{T}_0^{(1)},\ldots,\mathcal{T}_0^{(N)})$, with upper indexes numbering objects. By virtue of the statistical independence of objects one obtains

$$P(\ldots,\mathcal{T}_0^{(i)},\ldots,\mathcal{T}_0^{(j)},\ldots)=P(\ldots,\mathcal{T}_0^{(j)},\ldots,\mathcal{T}_0^{(i)},\ldots)$$

and

$$P(\mathcal{T}_0^{(1)},\ldots,\mathcal{T}_0^{(N)})=\prod_{i=1}^{N}\phi(\mathcal{T}_0^{(i)},0).$$

Therefore due to the total probability formula we have

$$\begin{aligned}P_m(t)=\int C_N^m\left\{\prod_{i=1}^{m}p_{\mathcal{T}_0^{(i)}}(t)\prod_{j=m+1}^{N}(1-p_{\mathcal{T}_0^{(j)}}(t))\right\}&\\ \times P(\mathcal{T}_0^{(1)},\ldots,\mathcal{T}_0^{(N)})\,\mathrm{d}\mathcal{T}_0^{(1)}\ldots\mathrm{d}\mathcal{T}_0^{(N)}&\\ =\int C_N^m\left\{\prod_{i=1}^{m}p_{\mathcal{T}_0^{(i)}}(t)\prod_{j=m+1}^{N}(1-p_{\mathcal{T}_0^{(j)}}(t)\right\}\prod_{k=1}^{N}(\phi(\mathcal{T}_0^{(k)},0)\,\mathrm{d}\mathcal{T}_0^{(k)})&\\ =C_N^m\prod_{i=1}^{m}\left\{\int p_{\mathcal{T}_0^{(i)}}(t)\phi(\mathcal{T}_0^{(i)},0)\,\mathrm{d}\mathcal{T}_0^{(i)}\right\}&\\ \times\prod_{j=m+1}^{N}\left\{\int(1-p_0^{(j)}(t))\phi(\mathcal{T}_0^{(j)},0)\,\mathrm{d}\mathcal{T}_0^{(j)}\right\}&\\ =C_N^m\left\{\int p_{\mathcal{T}_0}(t)\phi(\mathcal{T}_0,0)\,\mathrm{d}\mathcal{T}_0\right\}^m\left\{\int(1-p_{\mathcal{T}_0}(t))\phi(\mathcal{T}_0,0)\,\mathrm{d}\mathcal{T}_0\right\}^{N-m}.&\end{aligned}\tag{37}$$

Combining (36) and (37) one finally obtains

$$P_m(t)=C_N^m(\tilde{p}(t))^m(1-\tilde{p}(t))^{N-m}\tag{38}$$

where

$$\tilde{p}(t)=\int\left\{1-\exp\left(-\int_0^t\mathrm{d}\tau\int\rho(\mathcal{T}_0,\mathcal{T},\tau)\mathcal{T}\,\mathrm{d}\mathcal{T}\right)\right\}\phi(\mathcal{T}_0,0)\,\mathrm{d}\mathcal{T}_0.\tag{39}$$

As seen from the form of (38) (cf. (22)), expressions for $\langle m(t)\rangle$, $D(t)$ and other moments formally coincide with those obtained in the previous subsection (see (25) and (26)) with $p(t)$ replaced by $\tilde{p}(t)$).

To complete the description we derive the expression for the average lifetime in the state A for an object characterized by $\mathcal{T}(0)=\mathcal{T}_0$. This can be done by substituting (32) into (11), which yields

$$\langle\tau\rangle_{\mathcal{T}_0}=\int_0^\infty\exp\left(-\int_0^t\mathrm{d}s\int\mathcal{T}\rho(\mathcal{T}_0,\mathcal{T},s)\,\mathrm{d}\mathcal{T}\right)\mathrm{d}t\tag{40}$$

varying from object to object.

4.4. Comments on examples

As has already been mentioned above, the expression for $P_m(t)$ obtained for the

example of a system with IST governed by a set of stochastic parameters formally coincides with that for the example of the system with IST governed by a set of deterministic parameters, if one replaces $p(t)$ by $\bar{p}(t)$ (cf. (22) and (38)). It should be noted that the conventional approach (Feller 1970) also provides $P_m(t)$ defined by (22), but with $p(t)$ given by (2).

However, the meanings of quantities $p(t)$ and $\bar{p}(t)$ are quite different. The former is the probability of the transition $A \to B$ of a single object while the latter describes the behaviour of the whole system and cannot be attributed to any chosen object. Such a difference is due to distinct natures of the systems considered.

Nevertheless, as follows from (39), $\bar{p}(t)$ possesses all the mathematical properties of probability referred to some imaginary 'averaged' object, although such an object does not exist in reality. Moreover, the introduction of such an 'averaged' object does not at all lead to the replacement of α in (2) by some average value, $\langle \mathcal{T} \rangle$, of the transition probability per unit time

$$\langle \mathcal{T} \rangle = \int \mathcal{T} \Phi(\mathcal{T}, t) \, \mathrm{d}\mathcal{T}.$$

Thus the only common feature of the two quantities $p(t)$ and $\bar{p}(t)$ is their equality to the ratio of the average number of objects in the state B at time t to the total number of objects in the system.

Another point to be discussed concerns the average transition expectation time. For the case described in subsection 4.2 we have found $\langle \tau \rangle$ equal for all objects of the system (equation (27)). The opposite situation is observed for the system with stochastic IST parameters (subsection 4.3, equation (40)). In the latter case the dependence of $\langle \tau \rangle$ on $\mathcal{T}_0$ may tend one to average $\langle \tau \rangle_{\mathcal{T}_0}$ over the distribution $\phi(\mathcal{T}_0, 0)$. The result of this procedure yields the average transition expectation time reckoned from some initial $t = 0$ for an object to be arbitrarily chosen at this time instant. However, this quantity

$$\langle \tau \rangle = \int \phi(\mathcal{T}_0, 0) \int_0^\infty \exp\left(- \int_0^t \mathrm{d}s \int \mathcal{T} \rho(\mathcal{T}_0, \mathcal{T}, s) \, \mathrm{d}\mathcal{T} \right) \mathrm{d}t \, \mathrm{d}\mathcal{T}_0 \qquad (41)$$

is not related to the statistical characteristics of the entire system as follows from (38) and (39), which do not contain $\langle \tau \rangle$ defined by (41). On the other hand, it is not related to characteristics of a single object either, since objects have different values of average expectation times, $\langle \tau \rangle_{\mathcal{T}_0}$s, due to the random difference in initial conditions, $\mathcal{T}_0$.

5. Conclusions

We have carried out a general analysis of IST processes which is free from the not-so-obvious qualitative assumptions of conventional approaches. This analysis is based on strict mathematical introduction of the transition probability per unit time, α. Our analysis does not refer to the concrete nature of $A \to B$ stochastic transitions and therefore makes the IST description free from separation of Markovian and non-Markovian processes. On the other hand, our approach allows α to be calculated for each concrete physical problem.

It has been shown that in the general case α depends on time and on initial conditions for an object undergoing IST, while the conventional approach implies

α = constant. The latter simple equality is a special particular case of (6), when $\zeta(t)$ = constant $P(\eta, t|\eta(0)) = \delta(\eta - \eta(0))$ and $\eta(0)$ is fixed. Such conditions mean that one neglects the influence of interactions between objects and external impacts on the probability of transitions.

On the contrary, our formalism offers rules for the calculation of α having regard to these factors (equation (4)–(6)). This makes it possible to evaluate the statistical characteristics of transitions. In particular, general expressions for the transition probability and for the average expectation time, $\langle\tau\rangle$, have been obtained. Our results show that, in contrast to the conventional formalism, the IST kinetics is not obliged to be exponential (see (22)–(24) and (38), (39)). In addition, $\langle\tau\rangle$ is found to be governed by the time dependence of α and hence by the expectation startout moment, t_0 ((11), (27) and (40)).

The advantage of the basic expressions (4)–(6) and (11) is that they are exact and universal. This allows one to use them for the evaluation of statistical characteristics of various complex systems containing objects undergoing IST. Such a possibility has been demonstrated in section 4.

The approach developed opens the way to account for and analyse many essential features of systems demonstrating IST processes. Thus these considerations can enrich the physical picture of IST and seems to be useful for broadening insight into the kinetics of complex physical and chemical systems as well as systems of some other nature.

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