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Vasyl Stefanyk Precarpathian National University

ФІЗИКА І ХІМІЯ ТВЕРДОГО ТІЛА
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V.I. Teslenko, O.L. Kapitanchuk

Average decayed dynamics of one-step transformation process with randomly varying return transition rate

Bogolyubov Institute for Theoretical Physics, National Academy of Sciences of Ukraine, Kyiv, Ukraine,
alkapt@bitp.kiev.ua; vtes@bitp.kiev.ua

The problem of stochastic averaging of the decayed dynamics of the output state population of a one-step transformation process with constant deterministic forward transition rate and randomly varying return transition rate is solved in approximation where random variation is modeled as a dichotomous stochastic process. The form of the obtained solution represented as a product between bimodal sigmoid rise of average population and its unimodal exponential decay is shown to largely be dependent on the stochastic frequency and amplitude parameters. For example, at high stochastic frequency, the behavior of population is reduced to that of a decayed one-step deterministic system. However, for resonance stochastic amplitude at low stochastic frequency, such behavior coincides with that of three-exponential rise-decay kinetics typical rather of a three-step deterministic slowly decaying process. Thus, there is an equivalence between using a more complex deterministic kinetic model and a less complex stochastic kinetic model for describing decayed dynamics of irreversible systems.

Keywords: decayed dynamics, one-step transformation process, randomly varying transition rate.

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Introduction

Many processes in physical, chemical and biological systems, such as inelastic energy transfer in solids, monomolecular reactions in liquids, biomacromolecular conformational transformations in organisms, etc., are one-step transformation processes which occur between the input and the output states of the system and can be described without using explicit knowledge of the laws governing their specific physical behavior. In simple cases, these processes can be depicted by state transition diagrams of two states, one input and one output, between which they take place [1, 2]. In complex cases, however, both the input and the output states can be not steady but irreversibly decaying with some constant rates, whereas return transition rate be not constant but randomly varying [2-4]. This complicates the description of the temporal behavior of output state of the system for the need of an averaging over the stochastic fluctuations involved in a random process.

The corresponding two problems for describing the average dynamics of output state of a one-step transformation process with single decay rate constant and dichotomous fluctuations in forward and return transition rate constants have been solved by the authors in papers [2] and [4], respectively. In this paper, we consider the problem of averaging the decayed dynamics in the case where both an input and an output states of a one-step transformation process are assumed to be decaying with the same rate constants, while the return transformation rate constant be augmented with a dichotomous stochastic process. In section I, we formulate the statement of the problem and present a solution to it in the time domain. The limiting cases are analyzed in section II. Finally, in section III the results obtained are discussed and concluded.

I. Statement of the problem

Consider a pair of unstable excited states of one-step transformation system, that is, input state $|I>$ to which the system is initially activated with probability 1, and output state $|O>$ which transforms from and to corresponding input state with, respectively, a constant forward transition rate f and a random return transition rate $r(t) = r + \alpha(t)$ represented as a combination of a constant in time part r and a zero-mean stochastic part $\alpha(t)$ so that $\overline{\alpha(t)} = 0$ and $\overline{r(t)} = r$, where the overbar designates temporal average. In addition, each state is regarded to be irreversibly decaying with a constant rate k Then the kinetic scheme for such a decayed one-step transformation system is as follows

$$\underset{k}{\longleftarrow} \left| I > \underset{r+\alpha(t)}{\overset{f}{\rightleftarrows}} \right| O > \overset{k}{\longrightarrow} \quad (1)$$

This scheme can serve as a useful template for many processes. For example, different optically active solid-state systems, composed of two and more qubits, suffer from unstable and fluctuating excited states that are poorly defined and need adequate kinetic schemes to describe their average behavior [5]. Also, for photoassisted transformations in polyimides, polymer chains are scissioned, similarly to transformation processes in scheme (1), so leading to the appearance of unstable free radicals that in turn undergo decay processes to more stable groups [6]. More else, by acting on the biomolecular systems via changing the inner volume of allowed conformations subject to thermal fluctuations, the high compressive tension may increase the population of unstable excited states and allow the modulation of biochemical processes [7], such as the breakdown of chemical bonds in the protein backbone and side groups to form high-energy free radicals [6, 8]. Therefore, solving the kinetic scheme (1) for different values of involved rate constant parameters in analytical terms can help understand main mechanisms underlying the randomly modulated decayed dynamics of one-and multistep transformation systems.

Note that from the physics point of view the afore-introduced input and output states represent the one-particle states of a nonequilibrium two-state excited system coupled weakly to an equilibrium environment and interacting with an external stochastic field [2, 3]. For weak system-environment coupling strengths it is possible to use the reduced description of the dynamics of these states and be restricted in considering the temporal behavior of their populations $p_{I,O}(t)$ −only. Leaving aside the details of this approach (cf. [2-4]) reduces the kinetic equations for state populations of system (1) to the following master equation

$$\begin{cases} \dot{p}_I(t) = -(f+k)p_I(t) + [r+\alpha(t)]p_O(t); \\ \dot{p}_O(t) = f p_I(t) - [r+\alpha(t)+k]p_O(t). \end{cases} \quad (2)$$

As this equation as well as scheme (1) is symmetrical with respect to the decay rate constant k it is constructive to use an exponentially decaying representation of the form

$$p_{I,O}(t) = \pi_{I,O}(t)\exp(-kt) \quad (3)$$

which reduces the system (2) to the master equation

$$\begin{cases} \dot{\pi}_I(t) = -f\pi_I(t) + [r+\alpha(t)]\pi_O(t); \\ \dot{\pi}_O(t) = f\pi_I(t) - [r+\alpha(t)]\pi_O(t). \end{cases} \quad (4)$$

for the stochastic steady-state populations $\pi_{I,O}(t)$ obeying the normalization condition

$$\pi_I(t) + \pi_O(t) = 1 \quad (5)$$

Using this condition reduces system of two equations (4) to a one equation for only the population of output state

$$\dot{\pi}_O(t) = f - [f + r + \alpha(t)]\pi_O(t) \quad (6)$$

As population $\pi_O(t)$ is stochastic, integration of Eq.(6) requires averaging over a stochastic process and solving the result with respect to averages. However, this demands the specification of the form of a stochastic process $\alpha(t)$.

For definiteness, but without loss of generality, let $\alpha(t)$ be a dichotomous stochastic process which is exponentially correlated $\overline{\alpha(0)\alpha(t)} = \sigma^2 exp(-2vt)$ and performs random jumps between the two amplitude values $\pm\sigma$ at a mean frequency v Then $\alpha(t)$ must obey the equations (see, e.g. [2, 4])

$$[\alpha(t)]^2 = \sigma^2; \quad \dot{\alpha}(t) = -2v\alpha(t), \quad \dot{\overline{\alpha(t)y(t)}} = \overline{\alpha(t)\dot{y}(t)} + \overline{\dot{\alpha}(t)y(t)} = \overline{\alpha(t)\dot{y}(t)} - 2v\overline{\alpha(t)y(t)} \quad (7)$$

where $y[\alpha(t)] \equiv y(t)$ is the stochastic functional, for example, population $p_{I,O}(t)$ or $\pi_{I,O}(t)$.

Averaging of Eq.(6) leads to the unknown stochastic correlation functional $\overline{\alpha(t)\pi_0(t)}$. Therefore, this equation is not closed with respect to the average population of output state $\overline{\pi_0(t)}$ and cannot be solved without using of (7). Moreover, after differentiating of the averaged equation (6) and then applying to it the formulae of differentiation (7), we arrive to the one more unknown correlation functional $\overline{\alpha(t)\dot{\pi}_O(t)}$. However, multiplying by $\alpha(t)$ the non-averaged equation (6) and averaging the result with the use of (7), for that unknown functional we obtain

$$\overline{\alpha(t)\dot{\pi}_O(t)} = -(f+r)\overline{\alpha(t)\pi_O(t)} - \sigma^2\overline{\pi_O(t)} \quad (8)$$

After some algebra this yields

$$\ddot{\overline{\pi_O(t)}} + 2(f+r+v)\dot{\overline{\pi_O(t)}} + [(f+r)(f+r+2v) - \sigma^2]\overline{\pi_O(t)} = f(f+r+2v) \quad (9)$$

Eq.(9) basically represents the equation governing the evolution of a steady-state population $\overline{\pi_O(t)}$ of harmonic oscillator under the influence of external force $f(f+r+2v)$. This force defined with respect to output state $|O>$ of (1) guarantees of reaching the stochastic equilibrium at $t\to\infty$ with the population

$$\overline{\pi_O^\infty} \equiv \overline{\pi_O(t\to\infty)} = f(f+r+2v)[(f+r)(f+r+2v)-\sigma^2]^{-1} \quad (10)$$

The corresponding equilibrium population attained due to the action of force $r(f+r+2v)-\sigma^2$ on input state $|I>$, respectively, is

$$\overline{\pi_O^\infty} = [r(f+r+2v)-\sigma^2][(f+r)(f+r+2v)-\sigma^2]^{-1} \quad (11)$$

For the initial conditions $\dot{\overline{\pi_O(0)}} = \overline{\pi_O(0)}$=0, Eq. (9) is trivially solved yielding, due to (3) and (9), the following solution of kinetic scheme (1) for the desired average decaying population $\overline{p_O(t)}$ of output state

$$\overline{p_O(t)} = \frac{f(f+r+2v)}{(f+r)(f+r+2v)-\sigma^2}\left[1-\frac{\lambda_1\exp(\lambda_2 t)-\lambda_2\exp(\lambda_1 t)}{\lambda_1-\lambda_2}\right]\exp(-kt) \quad (12)$$

where $\lambda_{1,2} = -(f+r+v)\mp\sqrt{v^2+\sigma^2}$. A 3D graph of this solution is shown in Fig. 1(a). As we see, endowing the return rate constant with a stochastic process substantially modifies the behavior of decayed output population in (1), particularly in the region of low stochastic frequencies v (Fig. 1(b)). Hence it is constructive to analyze the limiting cases of (12).

II. Limiting cases

First of all, in the case of very high stochastic frequency $v \gg \sigma; f; r$, expression (12) reproduces the well-known deterministic two-state decayed kinetics

$$\overline{p_O(t)} = \frac{f}{f+r}\left[1-e^{-(f+r)t}\right]e^{-kt} \quad (13)$$

This corresponds to the limit of negligibly small intensity of dichotomous stochastic fluctuations

$$\gamma = (\sigma^2/v) \to 0 \quad (14)$$

However, in the case of nearly zero stochastic frequency $v\to 0$, which formally corresponds to the opposite limit of extremely high stochastic intensity

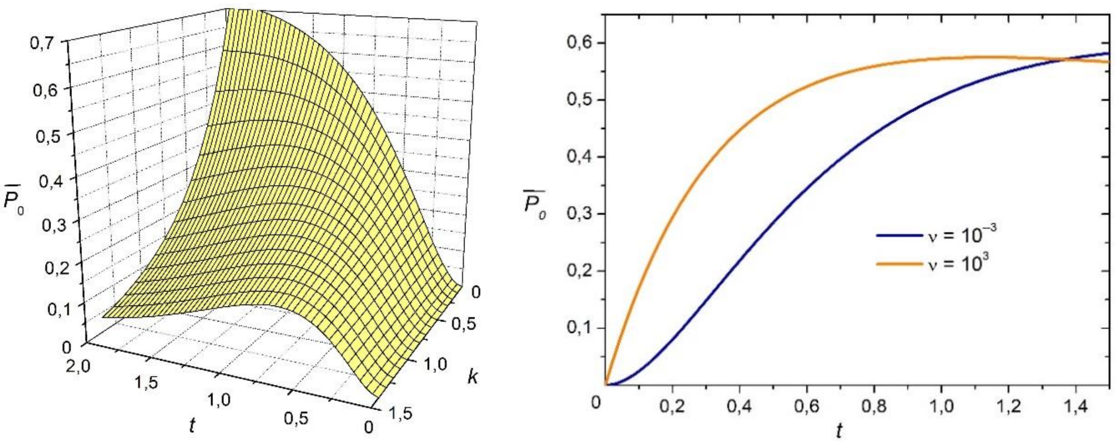
$$\gamma = (\sigma^2/v) \to \infty \quad (15)$$

there is the difference between using of the corresponding relation (15) in the case of almost zero stochastic amplitude $\sigma\approx 0$ and in the case of resonant stochastic amplitude $\sigma \approx r$, respectively, provided that generally $0\le\sigma\le r$. Indeed, in the first case, it is straightforward to arrive at the deterministic decayed dynamics (13). On the contrary, in the second case, the distinctly decaying behavior of output state of a one-step system (1) emerges

$$\overline{p_O(t)} = \frac{f(f+r)}{\lambda_1\lambda_2}\left(1-\frac{\lambda_1 e^{\lambda_2 t}-\lambda_2 e^{\lambda_1 t}}{\lambda_1-\lambda_2}\right)e^{-kt} \quad (16)$$

This signifies a type of a stochastic resonance observed, for example, in few-level atomic systems and two-dimensional excitable lattices in high intensity fluctuating fields [2, 4, 9, 10].

At the same time, in the low decay rate constant limit $k \ll |\lambda_{1,2}|$ for resonant in amplitude $\sigma = r$ and zero in frequency $v=0$ stochastic process, when



a) *b)*

Fig. 1. Evolution of the average population $\overline{p_O(t)}$ (12) of the output state of a decayed one-step process (1) depending on the control parameters: (a) 3D graph of the population (12) as a function of time t and rate k at fixed parameters of stochastic amplitude and frequency, deterministic rate constants $f=2, r=1, \sigma=1, v=10^{-3}$ (in the inverse of time units); (b) curves of population (12) calculated at fixed rate parameters $f=2, r=1, \sigma=1$, $k=0.1$ for two different values of the stochastic frequency $v=10^{-3}$and $v=10^3$ illustrating limiting cases.

$\lambda_1 = -(f + 2r)$ and $\lambda_2 = -f$, solution (16) can be represented as

$$\overline{p_O(t)} = f(f + r)\left[\frac{e^{-kt}}{f(f+2r)} + \frac{e^{-(f+2r)t}}{2r(f+2r)} + \frac{e^{-ft}}{2fr}\right] \qquad (17)$$

It is noteworthy that such solution exactly coincides with the solution for population of output state of the following three-step decayed deterministic kinetic scheme (cf. [3])

$$\left|A > \underset{\overleftarrow{r-b}}{\overset{f}{\longrightarrow}}\right| I > \underset{\overleftarrow{b}}{\overset{f+r}{\longrightarrow}}\left| O > \overset{k}{\rightarrow}\right. \qquad (18)$$

This scheme, consisted of three states, that is, initially activated state $|A>$, intermediate state $|I>$ and output state $|O>$, and containing the particular forward rate constants f and $f + r$, as well as return rate constants b and $r - b$, and decay rate constant k, is typical of modeling the three-stage decay processes in many physical, chemical and biological systems, such as optoelectronic systems, ceramic composites and ionic channels [3, 11-13]. Therefore, in situation when some rate constants in a three-step decaying system (18) are incomplete or uncertain, which is often the case, instead of a complex slowly decayed three-step scheme (18) we can use a far simpler slowly decayed one-step kinetic scheme (1) with a return transition rate showing high intense random variability in stochastic resonance regime.

III. Discussion and conclusions

In this paper, an analytical solution for the temporal behavior of an average population $\overline{p_O(t)}$ of output state $|O>$ of a decayed one-step transformation process (1), with deterministic forward transition rate constan f, randomly varying return transition rate $r + \alpha(t)$ and deterministic decay rate constant k, is obtained (12) and depicted as a 3D graph in Fig. 1(a) for variable frequencies v of a stochastic process $\alpha(t)$ considered to be dichotomous (7). The form of solution for population appears to be a product between its bimodal sigmoid rise and unimodal exponential decay (12). At high stochastic frequency with respect to stochastic amplitude and rate constants $v \gg \sigma; f; r$, the sigmoid rise of population turns out to be unimodal (Fig. 1(b), orange curve) typical for a decayed one-step deterministic relaxation process [2]. Rather, at low stochastic frequency $v \ll \sigma; f; r$, this sigmoid rise remains bimodal (Fig. 1(b), blue curve), but in such a way that, in condition of resonant stochastic amplitude $\sigma \approx r$, an expression (12) becomes analogous to the three-exponential sigmoid rise and decay kinetics (17) characteristic of a three-stage deterministic decay process (18) (see, e.g. [3, 11,12]).

In conclusion, a decayed one-step transformation kinetic scheme (1) with deterministic forward transition rate constant f and randomly varying return transition rate constant $r + \alpha(t)$ can be regarded to be equivalent to a decayed three-step kinetic scheme (18) with deterministic forward transition rate constants $f; f + r$ and deterministic return transition rate constants $b; d$, provided that conditions of a stochastic resonance and high intensity for fluctuations in return rate constant both hold. This forecasts an alternative in using different kinetic models of various complexity for describing the behavior of irreversible systems slowly decaying in characteristic deterministic and stochastic regimes.

Conflicts of interest

Authors declare that there are no conflicts of interest between them.

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Teslenko V.I. – Doctor of Physical and Mathematical Sciences, Leading researcher;
Kapitanchuk O.L. – Candidate of Physical and Mathematical Sciences, Senior Researcher

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В.І. Тесленко, О.Л. Капітанчук

Усереднена згасаюча динаміка однокрокового процесу перетворення з випадково-змінною швидкістю зворотного переходу

Інститут теоретичної фізики ім. М.М. Боголюбова, Національна Академія Наук України, Київ, Україна,
alkapt@bitp.kiev.ua; vtes@bitp.kiev.ua

Вирішено проблему стохастичного усереднення згасаючої динаміки заселеності вихідного стану для процесу однокрокового перетворення з постійною детерміністичною швидкістю прямого переходу та випадково-змінною швидкістю зворотного переходу у наближенні, де випадкова варіація моделюється дихотомічним стохастичним процесом. Показано, що отриманий розв'язок, який представляється у вигляді добутку бімодального сигмоїдального зросту усередненої заселеності та її унімодального експоненціального спаду, містить значну залежність від параметрів стохастичної частоти й амплітуди. Наприклад, за дуже високої стохастичної частоти поведінка заселеності зводиться до такої для згасаючої однокрокової детерміністичної системи. Однак за низької стохастичної частоти і резонансної стохастичної амплітуди ця поведінка співпадає з такою для трьох-експоненціальної кінетики зросту-спаду, скоріше типовою для трикрокового детерміністичного процесу, що повільно загасає. Тобто існує еквівалентність між складнішою детерміністичною кінетичною моделлю та простішою стохастичною кінетичною моделлю у прикладанні до опису згасаючої динаміки необоротних систем.

Ключові слова: згасаюча динаміка, однокроковий процес перетворення, випадково-змінна швидкість переходу.