



Power-law Fokker–Planck equation of unimolecular reaction based on the approximation to master equation



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HIGHLIGHTS

- We obtain a generalized expression of the Fokker–Planck equation of the unimolecular reaction.
- The steady-state solution of FPE and microscopic dynamics Ito–Langevin equation of concentration variables are given.
- Two unimolecular reactions are taken as examples.

ARTICLE INFO

Article history:

Received 23 March 2016

Received in revised form 18 June 2016

Available online 30 July 2016

Keywords:

Master equation

Chemical kinetics

Power-law distribution

ABSTRACT

The Fokker–Planck equation (FPE) of the unimolecular reaction with Tsallis distribution is established by means of approximation to the master equation. The memory effect, taken into transition probability, is relevant and important for lots of anomalous phenomena. The Taylor expansion for large volume is applied to derive the power-law FPE. The steady-state solution of FPE and microscopic dynamics Ito–Langevin equation of concentration variables are therefore obtained and discussed. Two unimolecular reactions are taken as examples and the concentration distributions with different power-law parameters are analyzed, which may imply strong memory effect of hopping process.

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1. Introduction

The master equation is one of the most significant equations in statistical physics, which is a stochastic differential equation of the “Markov” type and has a wide range of applicability in chemical, physical, biological systems [1,2],

$$\frac{\partial P_i(t)}{\partial t} = \sum_j w_{j \rightarrow i} P_j(t) - \sum_j w_{i \rightarrow j} P_i(t), \quad (1)$$

here $P_i(t)$ is the probability of finding the system (molecule) in state i at time t and $w_{i \rightarrow j}$ is the probability per unit time of a transition from state i to state j . “Markov” type means that the transition probability does not depend explicitly on time or past history of the populations. So the master equation specifies how this probability distribution evolves in time due to such short-memory transitions between states. If the transition probabilities are appropriately adopted, the master equation can reduce to linear Fokker–Planck equation (FPE) under certain approximations. For more details about the forms of transition probabilities, please see Ref. [3].

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In the past, the linear FPEs were very useful to describe the normal diffusion behaviors and their steady-state distributions follow thermal equilibrium distribution. However, lots of anomalous diffusion behaviors different from normal ones appear, such as biological membrane channel proteins exhibit subdiffusion behavior [4]; the transport of particles by molecular motors in the crowded environment of living cells is superdiffusion [5,6]; the particle concentration is accompanied with subdiffusion features in very porous solids if the particle's steps are restricted to nearest neighbors [7]; in the vicinity of the transition, the local magnetization fluctuations for the many-body localized phase relax subdiffusively and the distribution of resistivity approaches a power law in the zero-frequency limit [8]; the phase diffusion of a harmonically driven undamped pendulum shows anomalous in the strong sense [9] and so on. Simultaneously, plenty of observations in the experiments show non-thermal equilibrium distribution or power-law distributions in complex systems, such as the displacement distributions of green fluorescence protein labeled avian reovirus protein μ NS under both untreated and DNP (2,4-dinitrophenol)-treated conditions diverge from the expected Gaussian distribution [10]; according to the different transportation modes, such as Walk/Run, Bike, Train/Subway or Car/Taxi/Bus, human mobility shows the power-law distribution [11]; the power-law probability distribution of column densities is shown in molecular clouds [12], etc. These power-law distributions lead to anomalous behaviors different from normal ones in the realm governed by Boltzmann–Gibbs statistics with thermal equilibrium distribution and much attention has been paid. A class of statistical mechanical theories studying the power-law distributions in complex systems has been constructed, for instance, by generalizing Boltzmann entropy to Tsallis entropy [13], by generalizing Gibbsian theory [14] to a system away from thermal equilibrium and so forth. Under these theories, the nonlinear FPEs have been established, which are phenomenological generalization of linear FPEs and their steady-state solutions follow Tsallis q -distribution and satisfy maximum Tsallis' entropy form [13]; some other nonlinear FPEs are generalized based on fractal theory [15]. Nowadays, there is a growing tendency that the nonlinear FPEs have become suitable theoretical candidates for describing anomalous phenomena. Therefore, in this paper the nonlinear FPE with Tsallis distribution, which may describe microscopic chemical reaction, is established according to the master equation.

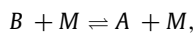
This paper is organized as follows. In Section 2, theoretical derivation of nonlinear FPE with Tsallis distribution is made by means of master equation. The memory effect is taken into transition probability and the Taylor expansion for large volume is used. The steady-state solution of FPEs and microscopic dynamics Ito–Langevin equation of concentration variables are discussed. In Section 3, we apply our result into two unimolecular reactions and analyze the concentration distribution with different power-law parameters. Finally the conclusion is got.

2. Theoretical derivations and analyses

Master equation can be used to model chemical reaction dynamics [1,2]. In this paper, the unimolecular reaction is considered. Unimolecular reaction is in principle the simplest type of chemical reactions that can occur in the gas phase since the reactions formally involve only one molecule. The theory of unimolecular reaction in the gas phase is a classical topic in physical chemistry [16]. When a molecule is supplied with an amount of energy that exceeds some threshold energy, the unimolecular reaction can take place, that is, dissociation or isomerization. In chemical kinetics, it is learned that an elementary reversible unimolecular reaction



has the following scheme [16,17],



where M is an (inert) buffer gas, or any molecule that does not react with the molecule A , which could be A itself. We now consider a particular case, when M is A itself. Thus the above scheme could be expressed as,



where k_1 and k_2 are forward and backward rate constants respectively. Suppose the number of A molecules is m , and the number of B molecules is n . Because the reaction consists of converting between B and A , the total number $N = m + n$ is conserved. A state of the system is specified by $[m, n]$. Transitions are made only in neighboring states, for example, $[m, n]$ to $[m + 1, n - 1]$ or $[m, n]$ to $[m - 1, n + 1]$, in which B is converted to A or A is converted to B . So, the master equation of Eq. (1) becomes,

$$\frac{\partial P_m(t)}{\partial t} = w_{m-1 \rightarrow m} P_{m-1}(t) + w_{m+1 \rightarrow m} P_{m+1}(t) - w_{m \rightarrow m-1} P_m(t) - w_{m \rightarrow m+1} P_m(t). \quad (4)$$

In the traditional theory, the transition rate of this process is only expected to be the forward rate constant k_1 times the number of A s times the concentration of B [2]. However, the noise randomness of surrounding environment would induce random waiting time distribution of particles which are to be spent on a given site before the next jump event occurs. It is expected that this distribution may be related to the probability distribution $P(t)$ [3] and thus owns past memory. The transition probability for a jump between two given states not only depends on the probability distribution of the given

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