Physica A 391 (2012) 3093–3101

Contents lists available at SciVerse ScienceDirect

Physica A

journal homepage: www.elsevier.com/locate/physa

Explicit propagators for a random walker and unidirectionality on linear chains

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ARTICLE INFO

Article history:
Received 21 November 2011
Received in revised form 29 December 2011
Available online 25 January 2012

Keywords:
Diffusion
Propagators
Perturbation
Nanomachines
Short-range potentials
Unidirectionality

ABSTRACT

Explicit propagators are given for a diffusing particle (motor) moving on a linear chain of either infinity or finite length with reflecting ends. Each chain contains a number of thermally accessible barriers and/or potential wells (active sites). All particle interactions with its environment are considered to be short-range and are described by repulsive/attractive delta function potentials. By employing perturbation expansion, closed analytical expressions for the spatio-temporal evolution of the probability density function of the motor are derived, and are valid up to second order with respect to the expansion parameter u, which denotes the strength of interaction between motor and active sites. The mean displacement for two different chains is calculated indicating in both cases that the organization of the motion is done through the interplay of interaction intensities and their positions.

1. Introduction

The spatio-temporal evolution of many systems in Physics, Chemistry, and Biology are described either by Green's functions or by Master Equations depending on the frame of description, continuous or discrete space [1]. In both cases, most of system's properties are expressed through the propagator, which describes the probability density function and contains all the information for the evolution of a system. However, the explicit form of the propagator for a real system is a task difficult or impossible, and simplifications and assumptions must be made in order to obtain it. Recently, a new technique applicable in systems with small number of available states has been provided [2], however, as the number of states increases alternative approximations are needed.

A field of great technological importance in which the knowledge of the propagator is necessary is this of artificial nanomachines. Artificial molecular machines are nano-structured systems consisting of coupled components, which, under suitable conditions, may manifest mechanical functions [3]. The simplest form of them consists of a linear chain on which the motor walks, and they can be viewed as one-dimensional system. Motor is the part of the machine moving regarding the other parts, and it walks within an area that contains potential wells and/or barriers (active sites or stations), whose existence is to constraint it to unidirectional movements. It is generally accepted that the design of a molecular machine necessitates spatio-temporal asymmetry and conditions far from equilibrium. The latter is achieved driving the motor out of its initial equilibrium state under the influence of an external stimulus, e.g. photon absorption, charge transfer, pH variation, and so on. The newly established energy difference combined with environment's fluctuations can lead the motor to a specific functionality. All the supplied work is dissipated and it cannot be used for other tasks, as a systematic external load does not exist but is only present at specific sites of the environment. In these cases, the walker transits from random either to partially or to fully ordered motion [4], and of interest is the interplay between local inhomogeneities (stations) towards achieving

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0378-4371/$ – see front matter
doi:10.1016/j.physa.2012.01.029

directionality [4,5]. Thus far, linear artificial molecular systems consisting of two or more potential wells and/or barriers have been synthesized [6–9]. Recently, a two state rotaxane-based system has been studied both theoretically [10] and experimentally [11] revealing useful information about the direction of the force exerted by the motor on its environment. In a simplified version, the structure of a nanomachine is a linear chain with active sites, stations, distributed on it. The conditions of the machine's function are encoded into the propagator, and properties such as the mean and the mean square displacement, the flux, the force exerted by the motor on its environment, and the motor's entropy production can be expressed through it. Every structure associated with different interactions and/or different boundary conditions corresponds to a different propagator.

In this work, the spatio-temporal evolution of the motor's distribution function, which moves on a linear chain of infinity/finite length containing active sites whose interaction intensity is described by attractive/repulsive delta function potentials, is given, and it is valid up to second order with respect to the interaction parameter. Furthermore, the mean displacement, for two different chains, is calculated revealing that the directionality of the motion is governed by the interplay of the characteristics of the active sites (interaction intensities and positions).

2. The theoretical framework

In continuous space and for the ideal case, the motor walks randomly on a linear chain exploiting thermal collisions with the molecules of its environment, and maybe interacts with boundaries if are present. In this case, the propagator satisfies the well-known diffusion equation

$$\frac{\partial G_0(x, x_0; t)}{\partial t} - D\frac{\partial^2 G_0(x, x_0; t)}{\partial x^2} = P(x; 0)\delta(t). \tag{1}$$

In Eq. (1), $P(x; 0)\delta(t)$ gives the initial distribution of the walker, $G_0(x, x_0; t)$ defines the probability density function of the walker to be at x at time t given that it started from x_0 at $t = 0$, and D is the diffusion coefficient of the medium in which the motion evolves. Eq. (1) is modified to a generalized diffusion equation when additional interactions are present, and it reads as

$$\frac{\partial G(x, x_0; t)}{\partial t} - D\frac{\partial^2 G(x, x_0; t)}{\partial x^2} + UG(x, x_0; t) = P(x; 0)\delta(t) \tag{2}$$

where, the term U expresses the rate of visits (in units of inverse time), and accounts for the extra interactions, which the presence of barriers/potential energy minima brings on the random motion. It can take positive/negative values reflecting the decrease/increase of the number of visits of the motor to the area of the local inhomogeneity. This frequency is always determined in comparison with the frequency of visits of the motor to a prescribed area in the absence of barrier/potential energy well where the interaction potential is nil, and Eq. (2) returns to Eq. (1). U has the form

$$U = \sum_{i=1}^{n} u_i\delta(x - x_i) \tag{3}$$

where, x_i denotes the position of the active sites, u_i expresses a mean field interaction between the walker with the ith active site and it is equal to $u_i = \int_0^\infty \mathrm{d}x\,(1 - \exp[-V(x_i)/k_BT])$, $V(x_i)$ is the real potential at the position x_i, and k_BT is the Boltzmann's constant times the temperature of the bath. This approximation is reasonable for the description of short-range interactions [12,13], while there are synthesized artificial systems where the interaction sites have width of the order of a chemical bond (a fraction of an Ångstrom) [14–16].

Inserting Eq. (3) into Eq. (2) we write

$$\frac{\partial G(x, x_0; t)}{\partial t} - D\frac{\partial^2 G(x, x_0; t)}{\partial x^2} + \sum_{i=1}^{n} u_i\delta(x - x_i)G(x, x_0; t) = P(x; 0)\delta(t). \tag{4}$$

A closed analytical solution satisfying Eq. (4) can be extracted only in the presence of a single-site [17–19]. Approximate solutions, when more than one sites are present, have been given in some specific regimes, e.g. long time limit, early time moments, infinity repulsions or attractions [4], infinity chain consisting of equally spaced barriers of the same height and for uniform initially distribution of walkers [20]. Herein, by using perturbation expansion regarding the interaction parameter a closed analytical expression for the probability density function valid up to second order in u_i is given. Assuming that the initial distribution of the walker is a delta function spike, $P(x, 0) = \delta(x - x_0)$, and by using the equation $G(x, x_0; t) = G_0(x, x_0; t) - \sum_{i=1}^{n} u_i \int_0^t \mathrm{d}\tau \int \mathrm{d}x_i G_0(x_i, x_0; \tau)U(x)G(x, x_i; t - \tau)$ [21,22], Eq. (4) in time Laplace domain, $(f(s) = L\{f(t)\} = \int_0^\infty \mathrm{e}^{-st} f(t)\mathrm{d}t)$, reads as

$$G(x, x_0; s) = G_0(x, x_0; s) - \sum_{i=1}^{n} u_i G_0(x_i, x_0; s)G(x, x_i; s). \tag{5}$$