

## Ordinary chemical reaction process induced by a unidimensional map

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In this paper we show the results of the numerical simulation of a “standard” reaction process obtained by a “non standard” system: a reactant oscillator (a harmonic oscillator with an energy threshold) weakly interacting with a unidimensional tent map. According to the paper by M. Bianucci, R. Mannella, B.J. West, and P. Grigolini [Phys. Rev. E **51**, 3002 (1995)], the action of such a map on the reactant system should be equivalent, in some sense, to that of a thermal bath, where the values of the temperature and of the friction depend on the normalized correlation function and on the response function of the map. Here this prediction is confirmed by the numerical simulation. The numerical results are fitted very well by an Arrhenius law with the predicted temperature and friction values. Notice that this is a strict test of the theory because the reaction rate strongly depends on the fine level statistics, i.e., a small deviation in the cue of the distribution would result in a large deviation in the value of the rate.

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### I. INTRODUCTION

The rate of a real standard chemical reaction process in a solvent is well described by the Arrhenius-like structure

$$k = A \exp\left\{-\frac{E_b}{k_B T}\right\}, \quad (1)$$

where  $E_b$  is the minimum energy required for the reaction to take place,  $T$  the solvent temperature, and  $k_B$  the Boltzmann constant. This “transition state structure” is essentially derived by establishing a contact with equilibrium statistical mechanics [1] and by assuming, according to the transition state theory, that the population of all reactants can be described by the canonical equilibrium ensemble.

The usual picture of a reaction process is that of a particle (the reactant) in a potential well that reacts escaping from the well by jumping over a barrier of height  $E_b$  (see Fig. 1). The solvent is assumed to be a thermostat, which is the source of the temperature  $T$  and of the statistical properties that give rise to the Arrhenius-like structure of Eq. (1).

Kramers, in a well-known work [2], obtained Eq. (1) starting from the Langevin dynamical picture:

$$\begin{aligned} \dot{x} &= v, \\ m\dot{v} &= -\frac{\partial U(x)}{\partial x} - m\gamma v + f(t), \end{aligned} \quad (2)$$

where  $U(x)$  is a reaction potential characterized by the barrier  $E_b$  (Fig. 1) and  $f(t)$  is a Gaussian white noise, with vanishing statistical mean value, defined by

$$\langle f(t)f(s) \rangle = 2m\gamma k_B T \delta(t-s). \quad (3)$$

Kramers demonstrates [2] that when the temperature  $k_B T$  of Eq. (3) is low if compared with the value of the energy

barrier  $E_b$ , then the reaction rate is well described by Eq. (1).

In the limit of low friction or viscosity, where Brownian forces do not alter substantially the energy of the reactants during the course of the reaction, Kramers predicts that the constant “A,” and then the rate, will increase proportionally with viscosity. In contrast, in the limit of high viscosity, Kramers predicts that reaction rates are inversely proportional to  $\gamma$ .

The Kramers theory applies to a very large variety of cases, stemming from physics, chemical-physics, biology, etc., e.g., photoisomerization reactions like trans-stilbene and related compounds in liquid  $n$ -alkanes and  $n$ -alkanols over a wide pressure range [3], diffusional barrier crossing in two-state protein folding reactions, like the folding dynamics of the cold shock protein CspB [4] or the formation of  $\beta$  sheet or  $\alpha$  helix [5], catalytic reaction rates at solid surfaces [6,7], etc.

Kramers also obtained the analytical explicit value of the constant “A” for the case of low friction and the case of intermediate and strong friction. He could not obtain the analytical solution for the turnover regime between these two

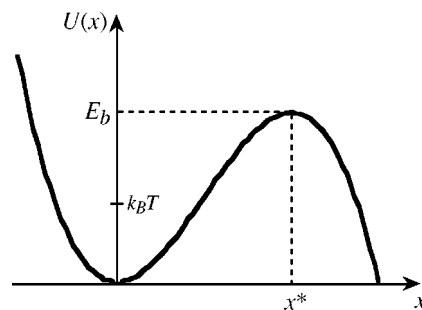


FIG. 1. Schematic drawing of a typical reaction potential in arbitrary units. The reactants are the particles with “coordinate”  $x$  less than  $x^*$ . The reactants move under the influence of the potential  $U(x)$  and of the thermal bath. When a reactant reaches the point  $x^*$  the chemical reaction takes place and it disappears. Thus  $x^*$  is an absorbing point and  $E_b$  is the corresponding energy barrier.

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cases, and we had to wait more than 50 years to have a quite general unified treatment [8].

In the present paper we limit ourself to the underdamped limit (low friction), for which the Kramers result is

$$A = \gamma \frac{I(E_b)}{k_B T} \frac{\omega_0}{2\pi}, \quad (4)$$

where  $I(E)$  is the action, defined by

$$I(E) \equiv \oint m v dx, \quad (5)$$

and  $\omega_0/2\pi$  is the frequency at the bottom of the potential well:

$$\frac{\omega_0}{2\pi} \equiv \left. \frac{\omega(I)}{2\pi} \right|_{I=0}, \quad \text{with} \quad \frac{\omega(I)}{2\pi} \equiv \frac{\partial E}{\partial I}. \quad (6)$$

Actually, from Eq. (2), in the underdamped regime, a more accurate expression for the reaction rate  $k$  can be obtained [9] [ $\beta \equiv 1/k_B T, I_b \equiv I(E_b)$ ]:

$$k = \gamma k_B T \left[ \int_0^{I_b} dI \exp[-\beta E(I)] \int_I^{I_b} dI' \frac{\omega(I') \exp[\beta E(I')]}{2\pi I'} \right], \quad (7)$$

which reduces to the Kramers expression in the limit of high activation energy ( $\beta E_b \gg 1$ ).

In substance, the Langevin picture consists of a way of representing a thermostat. In fact in Eq. (2) the thermostat is represented by the two forces that act on the reactant oscillator: the friction  $-m\gamma v$  and the Gaussian stochastic force  $f(t)$ . The Gaussianity of the stochastic force ensures the “correct” fluctuation properties of the system, the friction is responsible for its relaxation behavior, and the intensity of the stochastic force, assigned by the relaxation-fluctuation relation in Eq. (3), introduces *by hand* the temperature in the system. Therefore the stochastic Langevin picture rests on a phenomenological (not microscopic) description of the thermostat. We could also say that the Langevin equation defines what a thermostat is. Thus any “real” microscopic description of a thermostat must be statistically equivalent to the Langevin picture from the point of view of the system of interest (here the reactant). With the present paper we want to check how good the microscopic model for the thermostat proposed in paper [10] is by studying the reaction process induced by the action of such a model over a reactant oscillator.

Notice that about 20 years ago it was shown that if we let interact in a special way the system of interest with variables whose dynamics depends in a proper way on the kinetic energy of the system, we have (in the ergodic case) that the distribution of the system of interest “relaxes” (in some sense) to the canonical equilibrium distribution [11–13]. Moreover, the relaxation process follows the “standard” fluctuations dissipation rules. Thus these artificial deterministic systems, now called Nosé-Hoover systems, are very important in the field of molecular dynamics, where they can efficiently replace the action of a thermostat [14]. More recently a number of modifications to the Nosé-Hoover systems have

been proposed [15–21]. Moreover, in [22] a generalization to non-Hamiltonian systems of the usual Hamiltonian phase space analysis has been applied to these models, to include them in the general framework of the standard statistical mechanics theory.

However, though these systems are very useful in molecular simulations, it is a difficult task to link them to what should be a real microscopic model, for two main reasons:

(1) the temperature is still inserted by hand, and

(2) in the “extended” phase space, where we can recover a Hamiltonian structure, the dynamics of the “thermal bath” depends directly on the kinetic energy of the relevant system, instead of depending on the coordinate variables as in real systems.

Our approach here and in [10] is quite different: our task is not to find a competitive model to be used in computer molecular dynamics simulations, but to contribute to shedding a light on understanding the link between the dynamical properties of the deterministic microscopic systems and the dynamical and equilibrium properties emerging when observing them at a macroscopic scale. More precisely, we are looking for the key properties of the microscopic “irrelevant” system, and of the interaction of it with the variables of interest, necessary for the setup of a standard fluctuation-dissipation process. A first step toward this goal was already done in papers [23–25], where, however, two main points make them weak:

(1) the dynamics of the “thermal bath” depends on the velocity variable of the system of interest (instead of depending on the coordinate, as in any reasonable interaction potential); and

(2) there is not a defined time scale for the system of interest.

## II. A SHORT REVIEW

In paper [10], which reports and generalizes the results of papers [26–29], the Fokker-Planck or Langevin type transport equation from the underlying microscopic dynamics is explored, exploiting the simple case of a system composed of a relevant one degree of freedom oscillator coupled to an irrelevant multidegree of freedom system through a weak interaction of strength  $\Delta$  [10]:

$$\dot{x} = v,$$

$$m\dot{v} = -\frac{\partial V(x)}{\partial x} - \Delta \xi,$$

$$\dot{\xi} = F(\xi, \boldsymbol{\pi}, -\Delta x),$$

$$\dot{\boldsymbol{\pi}} = \mathbf{G}(\xi, \boldsymbol{\pi}, -\Delta x), \quad (8)$$

where  $V(x)$  is the potential of the oscillator of interest [as we will show later, it is practically indistinguishable from  $U(x)$  of Eq. (2)] and  $\xi, \boldsymbol{\pi} (= \pi_1, \dots, \pi_{n-1})$  are the variables of the  $n$ -dimensional irrelevant system that we call “booster” [10,26–29] (the “thermostat”).

From Eq. (8) we see that the booster exerts an action on the oscillator of interest through the term  $-\Delta\xi/m$  (action). The oscillator reacts back (reaction), and this is expressed by the dependence of  $F$  and  $\mathbf{G}$  on the term  $-\Delta x$ . If the third argument of the functions  $F$  and  $\mathbf{G}$  is equal to zero we say that the booster is “unperturbed,” otherwise we say that the booster is “perturbed.” Thus in Eq. (8) the perturbation is given by the term  $-\Delta x$ .

The general structure of Eq. (8) includes the case of Hamiltonian boosters weakly interacting with the system of interest, where the interaction potential is expanded in Taylor series up to the first term in the coupling parameter  $\Delta$  (linear interaction). Of course, the Hamiltonian case is the most interesting one and it was analyzed in paper [10]. Following a procedure close to that in [10], this case is also explored in more recent papers [30–32].

The structure of Eq. (8) is also compatible with non-Hamiltonian dynamical systems, often used to model the dynamics at “mesoscopic” scale. Given a specific non-Hamiltonian system compatible with Eq. (8), it could be also possible to apply the procedure of paper [22] to construct the distribution function sampled by the variables of interest, and verify the emergence of standard equilibrium statistical properties. Note, however, that our approach is quite general but perturbative, this means that the distribution function of the booster (that depends on the position in the phase space of the variables of the system of interest) must be always close to the unperturbed one. This condition must be checked case by case in the phase space analysis of the equilibrium distribution.

The booster, to act as a thermostat, has to fulfill two important dynamical properties [10]:

(i) Its correlation function, in the unperturbed case, must decay in a finite time, i.e., if  $\varphi(t)$  is the normalized unperturbed autocorrelation function of the variable  $\xi$ ,

$$\varphi(t) \equiv \frac{\langle \xi(t)\xi(0) \rangle_0}{\langle \xi^2 \rangle_0}, \quad (9)$$

we need to have

$$\tau \equiv \int_0^\infty \varphi(t) dt < \infty; \quad (10)$$

where the symbol  $\langle \cdots \rangle_0$  indicates the average over the unperturbed ( $\Delta=0$ ) equilibrium distribution of the booster. Throughout this paper we assume, without any loss of generality, that the unperturbed average of the variable  $\xi$  of the booster vanishes, i.e.,  $\langle \xi \rangle_0=0$ .

(ii) The booster responds linearly (in a statistical sense) to a weak perturbation. More precisely, we assume that if at time  $t=0$  we perturb the booster with an external field  $K(t)$  [ $K(t)$  is in place of the perturbation  $-\Delta x$  in Eq. (8)], the average of  $\xi$  moves from zero to a value that can be well approximated by a linear function of the perturbation, i.e.,

$$\langle \xi \rangle_K(t) \approx \int_0^t S(u)K(t-u)du \quad (11)$$

where  $S(u)$  is the response function and  $\langle \cdots \rangle_K(t)$  indicates the average at time  $t$  over the distribution of the perturbed booster, starting from the unperturbed ( $K=0$ ) equilibrium distribution at  $t=0$ . This means that if we perturb the booster with a *constant* field of intensity  $K$  (i.e.,  $K$  does not depend on time), we can write  $\langle \xi \rangle_K(t)=K\chi(t)$ , where  $\chi(t) \equiv \int_0^t S(u)du$ . The susceptibility  $\chi(t)$  is a function that goes from zero, at the initial time  $t=0$ , to a value  $\chi \equiv \chi(\infty)$  at time  $t=\infty$ . Introducing the function  $c(t)$ , defined by

$$\chi(t) = [1 - c(t)]\chi, \quad (12)$$

it is evident that  $c(0)=1$ ,  $c(\infty)=0$ , and  $S(t)=-\chi\partial c(t)/\partial t$ .

Notice that the linear response of a “chaotic” booster to a weak perturbation is a quite general property and, as shown in papers [33,34], the response function can usually be evaluated following an approach “a la Kubo” [35].

There are three cases where the procedure of paper [10] yields to a standard statistical mechanics:

(1) Large separation between the time scale of the booster (order of  $\tau$ ) and the typical oscillation time ( $1/\omega$ ) of the system of interest, i.e.,  $\omega\tau \ll 1$ ;  $V(x)$ : any; number of degree of freedom of the booster: any.

(2)  $V(x)=\omega^2 x^2/2$ , i.e., the system of interest is a harmonic oscillator;  $\omega$  and  $\tau$ : any (notice, however, that a resonance  $\omega \equiv \tau$  could break the assumption of weak interaction between the booster and the system of interest); number of degree of freedom of the booster: any.

(3) Large number of degree of freedom of the booster;  $\omega$  and  $\tau$ : any;  $V(x)$ : any.

In this paper we assume to be in the first case. This means that the present procedure could be applied to a wide variety of complex reaction dynamics, with real potentials, such as, for example, protein folding reactions. However, for the sake of simplicity, we will limit ourself considering only the case of harmonic potentials.

At this point, as it is shown in [10], at large times, for small  $\Delta$  and from a “macroscopic point of view” ( $t \gg \tau$ ) we can replace the initial system of Eq. (8) with the following stochastic one:

$$\begin{aligned} \dot{x} &= v, \\ m\dot{v} &= -\frac{\partial V(x)}{\partial x} + \Delta^2 \chi x - \Delta^2 \chi \vartheta v + f(t), \end{aligned} \quad (13)$$

where  $f(t)$  plays the role of an “effective” Gaussian stochastic force with zero average and autocorrelation function given by

$$\langle f(t)f(s) \rangle = 2\Delta^2 \langle \xi^2 \rangle_0 \tau \delta(t-s), \quad (14)$$

while  $\vartheta$  is the response time of the booster:

$$\vartheta \equiv \int_0^\infty c(u)du. \quad (15)$$

Thus, making the following identifications:

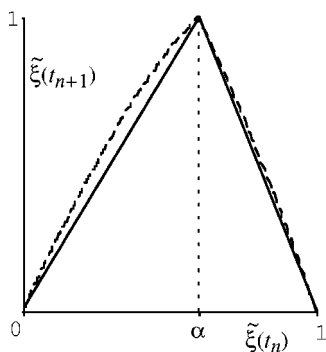


FIG. 2. The tent map (solid line) and the perturbed tent map (dashed line). The booster dynamics is given by a shift of this map:  $\xi = \tilde{\xi} - 0.5$ .

$$U(x) \equiv V(x) - \Delta^2 \chi \frac{x^2}{2}, \quad (16)$$

$$m\gamma \equiv \Delta^2 \chi \vartheta, \quad (17)$$

we recover the Langevin system of Eq. (2), with a temperature given by

$$k_B T \equiv m \langle v^2 \rangle_{eq} = \frac{\langle \xi^2 \rangle_0 \tau}{\chi \vartheta}. \quad (18)$$

At this point we have to choose a proper booster and the reaction rate can be predicted by inserting Eqs. (16)–(18) in Eqs. (1) and (4), or in the more accurate expression of Eq. (7).

### III. THE CASE UNDER STUDY

As already specified above, we use here, for the reactant system, a quadratic potential with an absorbing (reaction) point at  $x=x^*$ :  $V(x) = \omega^2 x^2 / 2$  ( $m=1$ ),  $E_b = \omega^2 (x^*)^2 / 2$ . Moreover, due to the usual large reaction times (compared with the relaxation time due to the friction), we use a booster very “fast” to integrate: a shifted one-dimensional “tent” map, i.e.,  $\xi = \tilde{\xi} - 0.5$ , where  $\tilde{\xi}(t_{n+1}) = g(\tilde{\xi}(t_n))$ , with (see Fig. 2)

$$g(\tilde{\xi}) = \begin{cases} \frac{\tilde{\xi}}{\alpha} & \text{for } 0 \leq \tilde{\xi} \leq \alpha \\ -\frac{\tilde{\xi} - \alpha}{1 - \alpha} + 1 & \text{for } \alpha < \tilde{\xi} \leq 1. \end{cases} \quad (19)$$

For such a booster it is easy to obtain analytically [36] both the correlation function and the susceptibility [that depend on the  $\alpha$  parameter in Eq. (19)]. The correlation function is given by

$$\varphi(t) = e^{-t/\tau}, \quad (20)$$

$$\tau \equiv -1/\log(2\alpha - 1). \quad (21)$$

In the numerical simulations we choose  $\alpha = 0.9917$  which leads to  $\tau = 60$ . This value for the relaxation time, much larger than one, let us to avoid the problems due to the discrete time evolution of this booster.

The reactive oscillator frequency ( $\omega$ ) used in the simulation is equal to  $5/3 \times 10^{-3}$ , this ensures a large enough separation between the time scale of the booster and that of the system of interest ( $\omega\tau = 0.1$ ). The invariant distribution of the unperturbed variable  $\tilde{\xi}$  is the uniform distribution in the interval  $[0, 1]$ , thereby resulting in  $\langle \tilde{\xi} \rangle_0 = 0.5$ , i.e.,  $\langle \xi \rangle_0 = 0$ , and  $\langle \xi^2 \rangle_0 = \langle \tilde{\xi}^2 \rangle_0 - (0.5)^2 = 1/12$ .

The perturbation of strength  $K(t)$  of this booster is here defined as in [36], i.e., by the following additive quadratic term to the tent map (see Fig. 2):  $K(t) \delta g(\tilde{\xi})$ , with

$$\delta g(\tilde{\xi}) \equiv \begin{cases} \tilde{\xi}(\alpha - \tilde{\xi}) & \text{for } 0 \leq \tilde{\xi} \leq \alpha \\ (\tilde{\xi} - \alpha)(1 - \tilde{\xi}) & \text{for } \alpha < \tilde{\xi} \leq 1. \end{cases} \quad (22)$$

The corresponding response function  $S(t)$  has been evaluated in [36] and it is proportional to the correlation function:

$$S(t) = \frac{\alpha^3 + (1 - \alpha)^3}{6} \varphi(t), \quad (23)$$

from which we obtain

$$\chi \equiv \int_0^\infty S(u) du = \frac{\alpha^3 + (1 - \alpha)^3}{6} \tau \quad (24)$$

and

$$\vartheta = \tau. \quad (25)$$

Applying a constant perturbation  $K$  to the booster, we find that it responds linearly for  $|K| < 10^{-3}$ , thus characterizing the region of linear behavior.

The coupling of the booster with the system of interest is realized by setting  $K(t) = -\Delta x(t)$  [see Eq. (8)].

Substituting Eqs. (24) and (25) in Eqs. (16)–(18) we obtain:

$$U(x) = V(x) - \Delta^2 \frac{\alpha^3 + (1 - \alpha)^3}{6} \tau \frac{x^2}{2}, \quad (26)$$

$$\gamma = \Delta^2 \tau^2 \frac{\alpha^3 + (1 - \alpha)^3}{6}, \quad (27)$$

$$k_B T = \frac{\langle \xi^2 \rangle_0}{\tau} \frac{6}{\alpha^3 + (1 - \alpha)^3}. \quad (28)$$

By inserting in Eq. (28) the values  $\langle \xi^2 \rangle_0 = 1/12$  and  $\alpha = 0.9917$  (from which  $\tau = 60$ ), we obtain a temperature given by  $k_B T = 8.544 \times 10^{-3}$ . The friction and the renormalization of the reactive oscillator frequency depend on the coupling constant  $\Delta$ . The range of the allowed values for the coupling constant  $\Delta$  is evaluated in the following way: the booster responds linearly for  $K(t) < 10^{-3} \equiv K_M$ , thus, after the coupling with the system of interest, the condition  $(\Delta x)^2 < (K_M)^2 = 10^{-6}$  must be fulfilled. Using  $x^2 \approx k_B T / \omega^2$ , where  $k_B T = 8.544 \times 10^{-3}$ , this condition is rewritten as  $\Delta^2 / \omega^2 < 10^{-4}$ . The numerical calculations fulfill this condition. Notice that from this condition it follows that the renormalization of the frequency of the reactive oscillator intro-

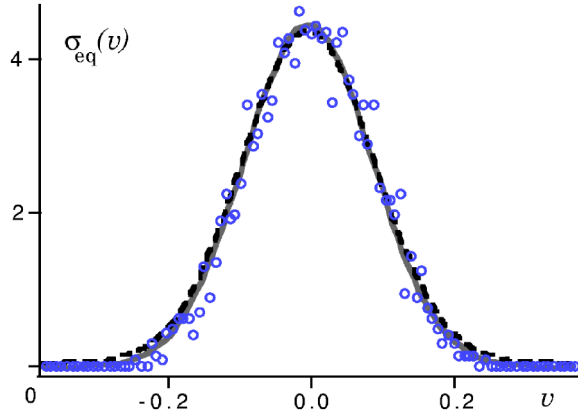


FIG. 3. Equilibrium distribution function of the velocity obtained from the numerical simulation (circles) of the systems in Eq. (30), compared with a Gaussian function with a width equal to  $8.544 \times 10^{-3}$  (dashed line), i.e., the theoretical temperature of Eq. (28). The solid line is a fit from numerical results. In this simulation we used  $\Delta = 4.5 \times 10^{-5}$  and an ensemble of 1000 samples. Notice that we set  $\theta = m = 1$ , thus the units of the variables in the abscissa and ordinate axes are here arbitrary.

duced by Eq. (26) is completely negligible, i.e.,  $U(x) \sim V(x)$ .

#### IV. THE REACTION RATE: NUMERICAL RESULTS

To solve numerically the problem of coupling the system of interest, that evolves with continuity with time, with the booster, that evolves with a discrete times step (that we call  $\theta$ ), we “transform” to a map the oscillator of interest too, integrating the time evolution along the same time step:

$$x(t_{n+1}) = x(t_n) \cos(\omega\theta) + \frac{v(t_n)}{\omega} \sin(\omega\theta),$$

$$v(t_{n+1}) = v(t_n) \cos(\omega\theta) - \omega x(t_n) \sin(\omega\theta). \quad (29)$$

The coupling between this oscillator map and the booster gives the following complete system that we use in the numerical simulation:

$$x(t_{n+1}) = x(t_n) \cos(\omega\theta) + \frac{v(t_n)}{\omega} \sin(\omega\theta)$$

$$v(t_{n+1}) = v(t_n) \cos(\omega\theta) - \omega x(t_n) \sin(\omega\theta) - \frac{\Delta}{m} \xi(t_{n+1})$$

$$\tilde{\xi}(t_{n+1}) = f(\tilde{\xi}(t_n)) - \Delta x(t_{n+1}) \delta f(\tilde{\xi}(t_n)), \quad (30)$$

where we set  $\theta = 1(\theta \ll 1/\omega)$ .

In Fig. 3 we show the equilibrium distribution of the variable  $v$  obtained from the numerical simulation; it is evident that it is a Gaussian function with a width given by the theoretical temperature of Eq. (28). The agreement between the theoretical prediction and the numerical result is quite good. We are now ready to check the realization of the

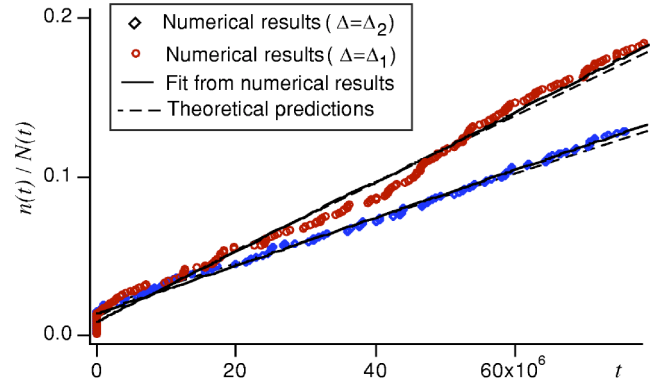


FIG. 4. Comparison between numerical data and theoretical values of the normalized curves of escapes from the barrier. The values of the coupling constant are  $\Delta_1 = \sqrt{2} \times 4.5 \times 10^{-5}$ ,  $\Delta_2 = \Delta_1 / \sqrt{2}$ . The value of the energy barrier is  $E_b = 3k_B T$ , where  $k_B T = 8.544 \times 10^{-3}$ . The average is over an ensemble of 1000 samples. The time  $t$  is the number of iteration of the map of Eq. (30).

Arrhenius law with this system. Each time that a single trajectory reaches the sink in  $x^*$  we increase by one unity the number  $n$  of reactions, and we store it in an array together with the current time. Then we plot the array  $n$  versus the time and we obtain the reaction rate  $k$  as the slope of the resulting straight line divided by the number of samples of our ensemble. In Fig. 4 two curves  $n(t)$  obtained in this way for two different values of the coupling constant  $\Delta$  are compared with straight lines with a slope  $k$  given by Eq. (7) where the friction and the temperature are that given in Eqs. (27) and (28), respectively. The same procedure is repeated changing the reaction point  $x^*$ , i.e., for different barrier energies  $E_b$ . In Fig. 5 we plot these results.

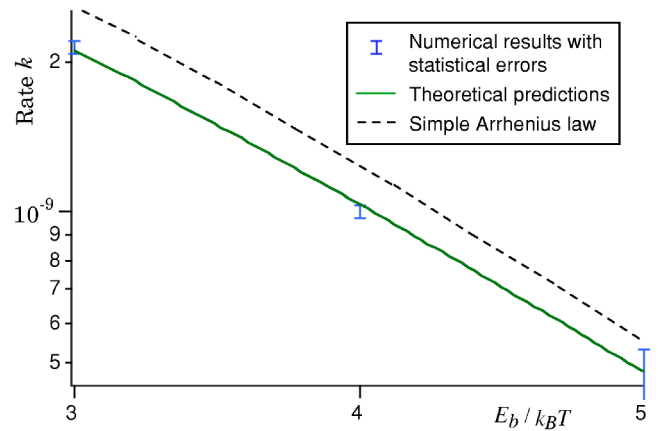


FIG. 5. Numerical and theoretical reaction rates vs the barrier energy. The energy is changed choosing a different reaction point  $x^*$ , according to the formula  $x^* = \sqrt{2E_b}/\omega$ . The value of the coupling constant is  $\Delta = \sqrt{2} \times 4.5 \times 10^{-5}$ . The simple Arrhenius law is that in Eq. (1) with Eq. (4). The average is over an ensemble of 1000 samples. The values in the abscissa axes are dimensionless corresponding to the inverse of the number of the iteration of the map of Eq. (30).

## V. CONCLUSION

The agreement between the theoretical prediction and the simulation is very good. Our few dimensional deterministic booster is almost indistinguishable from a true thermal bath, with a temperature and diffusion coefficient predicted by Eqs. (17) and (18). The result is so good that we had to compare the numerical results with the very accurate expression of Eq. (7) for the reaction rate, rather than the more approximate Arrhenius law of Eq. (1) with Eq. (4).

It should be noted that in a reaction process the local shape of the stationary distribution is important not only where the statistics is high, i.e., in the bottom of the well, but also in the cue of the distribution, near the absorbing point: a small deviation in the cue of the distribution results in a large deviation in the value of the rate. Thus this is a strict test of the theory, the rate depending on a fine level statistics. The agreement between the predicted rate and the numerical data shows how good the identification of our deterministic booster with a thermostat is.

The approach of [10] allow us to shed light on the way to link the regular behavior of macroscopic observables (like the reaction rate) to the “chaotic” dynamics of the underlying microscopic system. To continue to investigate in this direction starting from the general results of [10], in the next paper we will study the reaction rate in the case where there is not a strong scale separation between the relaxation time of the booster ( $\tau$ ) and the typical oscillation time ( $1/\omega$ ) of the reactant system, thus only the long reaction time makes “macroscopic” the reaction process. In this case, according to [10], we will see that a resonance mechanism between the booster and the system of interest is activated and the reaction rate depends strongly on the typical frequency of the reactant system (before the thermodynamics limit, i.e., for a booster with a not too large number of degree of freedom). This fact could contribute to explain some multiple time scale reaction processes occurring in mesoscopic systems, like in protein, the energy transfer in surface catalytic reactions, the selective enzyme reaction kinetics, etc.

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