Retrapping and velocity inversion in jump diffusion

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A method for the solution of the Kramers problem in periodic potentials is proposed in the general case of a tilted periodic potential. The method is then applied to the Fokker-Planck equation with a cosine potential without tilt, and the results for the jump-length probability distribution are compared to simulation data concerning the lengths crossed by a hopping particle before its first velocity inversion. It is shown that, at high dissipation, the diffusing particle thermalizes in most cases in the cell where it inverts the velocity for the first time. On the contrary, at low dissipation the actual length of the jump and the length crossed before the first velocity inversion display significant differences, showing that the first velocity inversion is not a good criterion for the length of the jump, just in the case where long jumps are more important.

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I. INTRODUCTION

A common feature of noise-assisted dynamics of multistable, spatially periodic classical systems is the jump character of the long-time motion when the potential barriers (E_a) between nearest-neighbor sites of local stability are sufficiently high. This can be understood in terms of some typical time scales. For instance, in the case of Brownian motion of a single classical particle subjected to thermal, Gaussian white noise [Fokker-Planck (FP) dynamics] in a one-dimensional (1D) cosine potential [1], at least three different time scales must be taken into account: the period of small oscillations at the well bottom ($\tau_{\rm osc}$), the time needed to cross a unit cell traveling at the thermal energy ($\tau_{\rm th}$), and the inverse friction or velocity relaxation time (τ_v). Different ratios between these time scales lead to different dynamical regimes [2,3]. In particular a localization (or high-barrier) condition is $\tau_{\rm osc} < \tau_{\rm th}$; in this regime the particle spends most of its time by performing a damped or oscillatory damped motion around a well bottom, rarely escapes, and it is finally retrapped in another well, not necessarily in a nearest-neighbor cell. Jumps longer than a unit lattice spacing (in the following referred to as multiple jumps) are only possible at low friction where the dissipation over the unit cell is small, i.e., when τ_v is longer than $\tau_{\rm osc}$ and $\tau_{\rm th}$. Thus, while at high barriers and strong friction the long-time dynamics can be characterized as a discretized random walk between adjacent lattice cells and the only quantity to be calculated is the jump rate r_j, in the underdamped limit jumps of any discretized length are allowed and also the complete jump-length probability distribution (JLPD) must be evaluated [2,4]. Therefore the low-friction jump problem is a multibarrier crossing problem [5,6]. In the extreme case of vanishing friction the particle gets activated very rarely (r_j vanishes linearly with the friction) but once it has escaped from the well jumps of all lengths are allowed with practically the same probabilities; in this limit jumps of a single lattice spacing have a vanishing probability and all the hopping events are multiple jumps. This can be seen by considering the 1D diffusion coefficient D in the jump regime:

$$D = \tfrac{1}{2} r_j \langle l^2 \rangle , \tag{1}$$

where $\langle l^2 \rangle$ is the mean-square jump length. As the friction η vanishes, r_j shows the usual Kramers behavior [2,4,7] $r_j \propto \eta$, but D diverges as $1/\eta$ [1,8,9], with the consequence that $\langle l^2 \rangle$ must diverge [2,9] as $1/\eta^2$.

The previous picture of the hopping mechanism is based on the solution of the jump problem in the case of the FP dynamics with 1D cosine potential [2–4], but essentially holds also for a linearized Boltzmann equation [9] and (with the differences due to the symmetry of the problem) for FP dynamics in a fourfold potential with cyclic boundary conditions [6] and in a tilted periodic potential [5,10].

The increasing attention recently devoted to the jump problem is mainly connected to two topics: the Kramers problem in periodic potentials [2,4,5,11] (theory of multibarrier crossing) and the dynamical theory of adatom diffusion on crystal surfaces [2,3,12–14]. A phenomenological jump description [15] is not at all a novelty in surface diffusion [16]; however, the phenomenological approach is essentially kinetic as the time evolution is calculated assuming the validity of some discrete master equation where the entering quantities, r_j and the JLPD, are free parameters. What is new in the FP approach is the possibility to obtain a quantitative characterization (both at short and long times [3,12]) of the motion of the adatom, starting from the underlying FP dynamics [17,18]. In fact, in the latter case, r_j and the JLPD are not free parameters, but they can be computed starting from the knowledge of the static and dynamical couplings (adiabatic potential and friction coefficient, respectively) between the diffusing particle and the thermal bath, i.e., the substrate.

Recent experiments [19–22] and molecular dynamics (MD) simulations [23–25] have demonstrated the importance of long jumps in the mass transport on many different flat surfaces and along surface steps.

In a recent Letter, Pollak *et al.* [13] perform a simulation of diffusion in a 1D cosine potential based on a Langevin equation with white noise, which, as it is well known [1], is fully equivalent to a FP equation. In this simulation they compute the number of lattice cells that are crossed by the diffusing particle before its first velocity inversion. With decreasing the dissipation on the lattice cell Δ (which is proportional to the friction and to the square root of the potential barrier), the diffusing particle crosses a larger number of cells before inverting its velocity. This is clearly evidence for long jumps. However, as we will show in the following, the number of cells crossed before the first velocity inversion is in general not the same thing as the length of the jump; once the particle has inverted its velocity for the first time over a given cell, it may thermalize in that cell or fly in the opposite direction and finally (maybe after many other velocity inversions) get trapped in another cell. The purpose of this paper is to determine if the first velocity inversion can be used as an estimate of the length of the jump; this will be achieved by comparing the results of the Langevin simulations [13] with the exact numerical solution of the jump-length problem [2,4] in the corresponding Fokker-Planck equation (FPE).

In Sec. II the exact numerical method for the solution of the Kramers problem is generalized to the case of a tilted periodic potential; in Sec. III the method is applied to the FPE in the case of zero tilt and cosine potential and the results for the jump lengths are compared to those concerning the first velocity inversion. In Sec. IV the conclusions are outlined.

II. GENERAL METHOD FOR THE SOLUTION OF THE KRAMERS PROBLEM

Let us consider a particle in a tilted periodic potential with local minima in the positions $\ldots, -a, 0, a, \ldots$. At sufficiently high barriers the characteristic function $\Sigma_s(q,t)$,

$$\Sigma_s(q,t)=\langle \exp\{iq[x(t)-x(0)]\}\rangle , \tag{2}$$

can be factorized by separating intracell and intercell motion [2], i.e., by setting

$$x(t)=al(t)+x_c(t) , \tag{3}$$

where the cell index l is integer and $-a/2<x_c<a/2$. At times larger than $1/\eta$, the intracell motion relaxes and Σ_s can be written as

$$\Sigma_s(q,t)=h(q)\Sigma_s^D(q,t) , \tag{4}$$

where Σ_s^D is related to the motion in the discretized lattice:

$$\Sigma_s^D(q,t)=\langle \exp\{iqa[l(t)-l(0)]\}\rangle . \tag{5}$$

Σ_s^D can be obtained by solving a proper master equation on the lattice [2]. In a tilted periodic potential, the particle can hop from the lth cell with a rate r_j to any other cell in the position $(l+n)a$, with n integer and $n\neq 0$, with a probability π_n; in general $\pi_n\neq\pi_{-n}$, as the tilt favors hopping towards one direction.

After solving the master equation Σ_s^D results in the form

$$\Sigma_s^D(q,t)=\exp[-f(q)t] . \tag{6}$$

In the presence of a tilt the function $f(q)$ contains also an imaginary part

$$f(q)=\mathrm{Re}\{f(q)\}+i\,\mathrm{Im}\{f(q)\} , \tag{7}$$

with

$$\mathrm{Re}\{f(q)\}=r_j\sum_{n(\neq 0)}^{\infty}\pi_n[1-\cos(naq)] , \tag{8}$$

$$\mathrm{Im}\{f(q)\}=r_j\sum_{n(\neq 0)}^{\infty}\pi_n\sin(naq) . \tag{9}$$

From Eqs. (6) and (7) an expression for the Laplace transform $\tilde{S}_s(q,z)$ of Σ_s can be obtained; at $z=i\omega$ the result is

$$\tilde{S}_s(q,i\omega)=\frac{h(q)}{i\omega+f(q)} . \tag{10}$$

If $\tilde{S}_s$ is calculated by solving the kinetic equation of the continuous model (for instance, the FPE [2,4]), $f(q)$ can be extracted by

$$f(q)=\lim_{\omega\to 0} i\omega\left[\frac{\tilde{S}_s(q,0)}{\tilde{S}_s(q,\omega)}-1\right]^{-1} . \tag{11}$$

The jump rate r_j and the jump probabilities π_n are obtained by inverting Eqs. (8) and (9), i.e., by the Fourier analysis of $f(q)$:

$$r_j=\frac{a}{\pi}\int_0^{\pi/a}\mathrm{Re}\{f(q)\}dq , \tag{12}$$

$$\pi_n=\frac{a}{\pi r_j}\left[-\int_0^{\pi/a}\mathrm{Re}\{f(q)\}\cos(naq)dq + \int_0^{\pi/a}\mathrm{Im}\{f(q)\}\sin(naq)dq\right] . \tag{13}$$

These formulas show that the jump rate and the jump-length distribution can be extracted from the analysis of the complex dynamic structure factor $\tilde{S}_s$ even in the presence of a tilt; from this point of view this method is completely equivalent to that by Jung and Berne [5], based on the Fourier analysis of the lowest-lying eigenvalue band. In fact, at high barriers, $f(q)$ and the lowest-lying eigenvalue band coincide.

Finally, at zero tilt (the case which will be considered in the following section), the periodic potential is symmetric and therefore the probability P_n of a jump of length $|n|a$ satisfies $P_n=2\pi_n=2\pi_{-n}$; from this fact it follows that $\mathrm{Im}\{f(q)\}=0$ and the formulas (11)–(13) reduce to those of Refs. [2,4] [where $S_s(q,\omega)=\mathrm{Re}\{\tilde{S}_s(q,i\omega)\}/\pi$]. At zero tilt and high barriers, $f(q)$ is equal to the half-width at half maximum of the quasielastic peak of S_s [4].

III. FIRST VELOCITY INVERSION AND RETRAPPING

The general method outlined in Sec. II is applied here to the Langevin equation with Gaussian white noise.

This equation is completely equivalent to the FPE for the probability density in the phase space of the particle. The case of zero tilt is of interest, for instance, in the applications to surface diffusion [2,4,12,13]. The FPE can be numerically solved by the matrix-continued-fraction method [1] and $\tilde{S}$ calculated. A detailed account of the method applied to the computation of $\tilde{S}$ may be found, for instance, in Ref. [3]. From $\tilde{S}$, $f(q)$ and then the jump rate and the jump probabilities P_n are extracted as explained in Sec. II.

As stated in the Introduction, P_n is the probability that the particle, starting from the cell in $n=0$, will be retrapped in the nth cell, where it will spend a time which is much longer with respect to the characteristic times τ_v, $\tau_{\rm th}$, and $\tau_{\rm osc}$. This definition of the jump probabilities is that of the jump-diffusion theory which is usually employed in the interpretation of the experimental data [19,20]. The probabilities P_n can be compared with the probabilities $P(n)$, as defined in Ref. [13]. We recall that there $P(n)$ is defined as the probability that an activated particle crossing barrier 0 (which is, for instance, the barrier on the right of the cell 0, i.e., the cell of departure) will reverse its velocity for the first time while traveling from barrier n to barrier $n+1$. Thus the probability of inverting the velocity for the first time on the first cell is $P(0)$. This has to be compared with the probability of retrapping in the nearest-neighbor cell, which is P_1; in general P_n is to be compared to $P(n-1)$.

Let us consider a cosine potential $U(x)$:

$$U(x)=-A\cos\left[\frac{2\pi x}{a}\right] . \tag{14}$$

In this case the solutions of the FPE depend on the couple of dimensionless parameters (γ,g) [2,3]:

$$\gamma=\frac{a}{2\pi}\left[\frac{m}{k_BT}\right]^{1/2}\eta, \quad g=\frac{A}{2k_BT} , \tag{15}$$

γ is the normalized friction.

Another parameter which is of particular significance at high barriers ($g>1$) is the dissipation Δ on the lattice cell, defined by

$$\Delta=\frac{\eta}{k_BT}\int_{-a/2}^{a/2}\sqrt{2m\,[U_M-U(x)]}\,dx , \tag{16}$$

where U_M is the maximum value of the potential [$U_M=A$ for the potential of Eq. (14)]; in our case Δ is related to γ and g simply by

$$\Delta=8\gamma\sqrt{2g} . \tag{17}$$

In fact, at large g, the solutions of the FPE tend to be functions of Δ only and not of γ and g separately [10]. This fact can be seen in Fig. 1. In this figure the probability of multiple jumps $P_{\rm MJ}$ (i.e., the probability of being retrapped in a cell which is not a nearest-neighbor of the cell of departure),

$$P_{\rm MJ}=1-P_1 , \tag{18}$$

is plotted as a function of $\log_{10}(\Delta)$ in two cases corresponding to different g: $g=1.25$ (black dots) and $g=4$ (open circles). From these results it is evident that $P_{\rm MJ}$ depends on two parameters, which can be chosen in the triplet (γ,g,Δ); the same happens for all the P_n. However, if the couple (Δ,g) is chosen (as in the figure), the dependence on g at fixed Δ is weak at $g>1$.

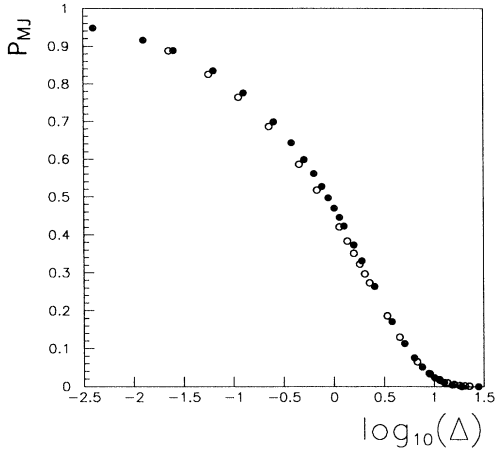

FIG. 1. Probability of multiple jump $P_{\rm MJ}$ as a function of the dissipation Δ [see Eqs. (16) and (17)]. The black dots and the open circles refer to potential barriers of $5k_BT$ ($g=1.25$) and $16k_BT$ ($g=4$), respectively.

In general $P_{\rm MJ}$ tends to 0 at $\Delta\to\infty$ and to 1 at $\Delta\to 0$. Clearly, at high dissipation, the probability of crossing the first cell without being trapped becomes vanishingly small; this holds essentially for $\Delta>10$. At vanishing dissipation the reverse happens: longer and longer jumps become important; all the P_n tend to become equal and small and therefore $P_1\to 0$. This fact may be understood by comparing the average energy of the particle (denoted as $\langle E\rangle$) when it exits from the cell of departure and the dissipation on the first cell. At low friction [26], $\langle E\rangle\propto\eta^{1/2}$, but the dissipation Δ is proportional to η; therefore the ratio between $\langle E\rangle$ and the dissipation on the first cell behaves as $\eta^{-1/2}$. A smaller and smaller fraction of the initial energy is thus dissipated on the first cell as the friction vanishes and therefore the probability of being retrapped in that cell tends to zero; correspondingly $P_{\rm MJ}$ tends to unity [10].

The comparison between P_n (black dots) and $P(n-1)$ (open squares) is shown in Figs. 2 and 3. The P_n are obtained by the method outlined in Sec. II, applied to the FPE with a cosine potential; the $P(n-1)$ are taken from Ref. [13] where a Langevin simulation of the same model has been performed. In Fig. 2 the case of $g=1.25$ and $\gamma=3.162\times10^{-1}$, corresponding to $\Delta=4$, is considered; in Fig. 3 we show the case of $g=1.25$ with $\gamma=3.162\times10^{-4}$, which gives a very low dissipation ($\Delta=4\times10^{-3}$).

At high dissipation, both the retrapping probabilities and the first velocity inversion probabilities behave as perfect exponentials depending on n. Figure 2 shows that P_n and $P(n-1)$ practically coincide, at least in the range where simulation data are available ($n\le 6$). This means that, at high dissipation, a particle is always trapped in

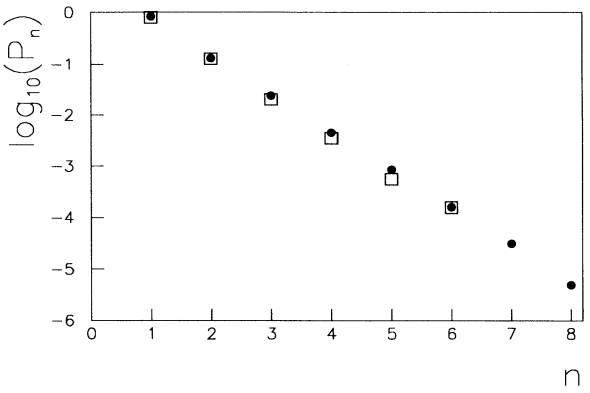

FIG. 2. Logarithmic plot of the jump-length probabilities P_n (black dots) in the case of $g=1.25$ and $\gamma=3.162\times10^{-1}$, corresponding to $\Delta=4$. The open squares are the simulation data for the probability $P(n-1)$ of having the first velocity inversion in the nth cell. The simulation data are taken from Ref. [13].

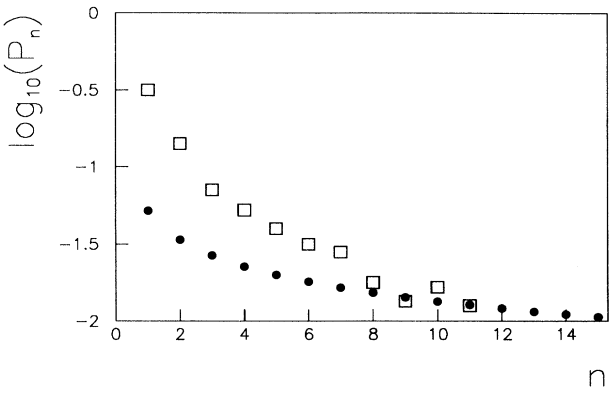

FIG. 3. The same as in Fig. 2, but with $g=1.25$ and $\gamma=3.162\times10^{-4}$, corresponding to the very low dissipation $\Delta=4\times10^{-3}$. Notice the clear deviation from the exponential behavior of both the P_n and the $P(n-1)$.

the cell where it inverts the velocity for the first time; in this parameter range, which has a lower limit around $\Delta=2$ (as may be seen by comparing Fig. 1 here with Fig. 1 in Ref. [13]), the first velocity inversion on a given cell is a good criterion for an actual thermalization in that cell. However, we remark that in this parameter range long jumps are not very important: at $\Delta=2, P_{\rm MJ}$ is about 0.3 and at $\Delta=4$ it is less than 0.2.

On the contrary, at low dissipation (see Fig. 3), the quantitative difference between P_n and $P(n-1)$ is apparent. From the Langevin simulation data [13] it results that the probability $P(0)$ of inverting the velocity for the first time on the first cell is considerably larger than the probability P_1 of thermalizing in that cell. This means that a particle which changes direction for the first time on the first cell has a large probability of spending a short time there, being finally retrapped in another cell. The decrease of the $P(n-1)$ with n is steeper than that of the P_n; in Fig. 3 the two plots cross around $n=10$ [at large n $P(n-1)<P_n$ because of the normalization of probabilities].

In the jump-diffusion regime, the diffusion coefficient D is related to the jump probabilities by Eq. (1), where the mean-square jump length $\langle l^2\rangle$ is given by

$$\langle l^2\rangle = a^2 \sum_{n=1}^{\infty} n^2 P_n \ . \tag{19}$$

An evaluation of $\langle l^2\rangle$ by the sum $a^2\sum n^2P(n-1)$ may lead to a very large underestimation of D at low dissipation, as $P(n-1)>P_n$ for short jumps and $P(n-1)<P_n$ for long jumps. Rather low dissipations have been found in a molecular-dynamics simulation of diffusion of CO on Ni(111) [23]; at a temperature of 200 K a barrier corresponding to $g=1.5$ and a friction corresponding to $\gamma=0.05$ have been calculated. Those values give $\Delta\simeq0.7$, i.e., a dissipation regime where already there are some quantitative discrepancies between P_n and $P(n-1)$.

IV. CONCLUSIONS

In this paper we have shown that the length crossed by a particle without inverting its motion and the actual length of the jump become more and more different as the dissipation decreases, i.e., when long jumps become really important. The computation of the diffusion coefficient by means of the mean-square length crossed before the first velocity inversion may lead to a severe underestimation. Therefore the evaluation of jump lengths in simulations cannot in general be obtained with simplified criteria, especially at dissipations Δ much lower than unity. The motion of the particle has to be completely followed from its departure to its first thermalization. In fact, many velocity inversions may happen before retrapping. The cell where the retrapping occurs may be identified by requiring the particle to spend in that cell a time longer than the characteristic times τ_v, $\tau_{\rm th}$, and $\tau_{\rm osc}$. In fact, only a clear separation of time scales can indicate that the diffusing particle has attained local equilibrium in a metastable potential well.

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