Escape rate and diffusion of a random walker

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(Dated: September 5, 2016)

We determine the rate of escape from a potential well, and the diffusion coefficient in a periodic potential, of a random walker that moves under the influence of the potential in between successive collisions with the heat bath. In the overdamped limit, both the escape rate and the diffusion coefficient coincide with those of a Langevin particle. Conversely, in the underdamped limit the two dynamics have a different temperature dependence. In particular, at low temperature the random walk has a smaller escape rate, but a larger diffusion coefficient.

The evaluation of the rate of escape of a particle from a one dimensional potential well, and of the diffusion coefficient of a particle moving in a one dimensional periodic potential, are classical problems in statistical physics that are relevant to the physical, chemical, engineering and biological sciences. When the timescale of interaction of the particle with the heat bath is the smallest timescale of the problem, escape and diffusion can be investigated within a Langevin formalism. In this context, solutions have been obtained in both the overdamped, $\tau_{\text{vis}} \ll \tau_{\text{cross}}$, and underdamped limits, $\tau_{\text{vis}} \gg \tau_{\text{cross}}$. Here $\tau_{\text{vis}} = m/\gamma$ is the viscous relaxation timescale, with $m$ mass of the particle and $\gamma$ the viscous friction coefficient, and $\tau_{\text{cross}} = 1/\omega_b$ is a timescale related to the exchange between kinetic and potential energy during barrier crossing fixed by the shape of the potential $V(x)$ on the top of the barrier, $\omega_b^2 = \frac{1}{m} (\partial^2 V/\partial x^2)|_b$. In a variety of different contexts including research strategies in biology, transport in electronics, market evolution models, supercooled liquids, diffusion of atoms in optical lattices, diffusion of molecules at liquid/solid interfaces, the time scale on interaction with the heat bath is not the smallest one, and the Langevin approach is no longer justified. In these cases one should adopt a random walk formalism, allowing the particle to move under the influence of the potential in between successive collisions with the heat bath.

In this Letter we report on the first investigation of escape and diffusion problems within this formalism. We consider a simple model in which a walker interacts with the heat bath with a constant rate $t_c$, the interactions instantaneously randomizing the walker’s velocity according to the Maxwell-Boltzmann distribution at the considered temperature. When not interacting with the heat bath, the walker moves according to Newton’s equation within the potential. As a model potential, we have considered a periodic $x^4$ potential, $V(x)$, with period $L$ and energy barrier $V(\pm L/2) = \Delta U$, but our results are easily generalizable. Thus in the period $-L/2 \leq x \leq L/2$, the potential is $V(x) = \frac{1}{2}m\omega_0^2 x^2 - \frac{m\Delta U}{\omega_0^2} x^4$. The energy barrier is $\Delta U = \omega_0^2 L^2/16$, while $\omega_0^2 = 2m\omega_b^2$. We have determined the escape rate and the diffusion coefficient in both the overdamped, $t_c^{-1} \ll \tau_{\text{cross}}$, and the underdamped limits, $t_c^{-1} \gg \tau_{\text{cross}}$, validating our theoretical results against numerical simulations. We show that in the overdamped limit the random walk and the Langevin dynamics give consistent results. Conversely, the two dynamics differ in the underdamped limit, the Langevin dynamics having an higher escape rate but, surprisingly, a smaller diffusion coefficient.

The escape rate is conventionally defined as the rate with which a particle irreversibly escapes from a well in a given direction. The rate can be determined considering that the escaping process occurs through three uncorrelated steps, as a particle first crosses the energy barrier in the considered direction, then recrosses the barrier an even number of times, and finally moves away from the top of the barrier decorrelating, without the occurrence of any further recrossing. We indicate the probabilities of these events with $P_c/2$, $p$ and $P_d$, respectively, so that $P_c$ is the probability that a thermalized particle performs a barrier crossing jump, regardless of its direction. Accordingly, the escape rate is given by $\Gamma_{\text{RW}} = P_c p P_d/(2t_c)$. Since the probability that a particle recrosses a barrier an even number of times is $p = \sum_{n=0}^{\infty} P_d(1-P_d)^{2n} = (2-P_d)^{-1}$, one finally gets

$$\Gamma_{\text{RW}}(t_c) = \frac{P_c(t_c)P_d(t_c)}{2t_c(2-P_d(t_c))}. \quad (1)$$

To estimate the escape rate, we thus need to estimate the barrier crossing probability $P_c(t_c)$, and the decorrelating probability $P_d$. $P_c$ is simply obtained from an equilibrium average over the jumps. Indeed, each jump is characterized by three variables, the coordinate of the starting point, $x_s$, the initial velocity $v_s$, and the time of flight $t$. $x_s$ and $v_s$ have a Boltzmann and Maxwellian equilibrium distribution, respectively, while $t$ is exponentially distributed with time constant $t_c$. Alternatively, each jump can be characterized by $x_s$, by the coordinate of the final point, $x_f$, and by the total energy $E$. Assuming with no loss of generality $|x_s| < L/2$, $P_c$ is the probability that $|x_f| > L/2$, which is found to be
The predicted flight time equals the time needed to travel from $x_t \to 0$, limits can be rationalized. In the $t_e \to 0$ limit, the above triple integral can be carried out, and one finds $P_{\tau} = \omega_b t_e \pi^{-1} \exp(-\Delta U/T)$. In the $t_e \to \infty$ limit all jumps with enough energy cross the barrier and $P_{\tau}$ approaches a constant, whose weak temperature dependence is neglected in the following.

The decorrelation probability $P_{\tau}$ is estimated considering that, if a particle reaches a position which is at a far enough distance from the top of the barrier without recrossing, then it decorrelates as its dynamics becomes dominated by the potential. We assume $l_T$ to be the distance at which the potential significantly affects the velocity $v(x,E) = \sqrt{(2/m)(E-V(x))}$ of a particle crossing the barrier with energy $E$, and estimate $l_T \simeq \sqrt{T/m\omega_b^2}$ through a Taylor expansion of $v(x,E)$ around the top of an energy barrier. In the overdamped limit $\omega_b t_e \ll 1$, $P_{\tau}$ is given by the probability that a barrier crossing event is followed by a sequence of jumps (of typical size $\propto \sqrt{T}$) able to drive the particle at distance $l_T \propto \sqrt{T}$ from the top, before a recrossing occurs. It is easy to show in a mean first passage time formalism [12] that in this regime $P_{\tau}(t_e) \simeq 2\omega_b t_e$. In the underdamped limit, $\omega_b t_e \gg 1$, jumps are long and the barrier crossing events can be considered irreversible, so that $P_{\tau} = 1$. The numerical measure of $P_{\tau}(t_e)$ confirms our predictions for the overdamped and underdamped limits of $P_{\tau}$, as illustrated in Fig. 1. We approximate in the following $P_{\tau}$ with a simple functional form able to capture the crossover between the $\omega_b t_e \ll 1$ and the $\omega_b t_e \gg 1$ limits, $P_{\tau}(t_e) = \frac{2\omega_b t_e}{k+2\omega_b t_e}$. We fix $k = \omega_b/\omega_b$ exploiting an analogy with the Langevin dynamics in the overdamped low temperature limit, we will detail below.

Having determined $P_{\tau}(t_e)$ and $P_{\tau}(t_e)$, we can compute the escape rate $\Gamma_{RW}(t_e)$ at all $t_e$ through Eq. 4. The overdamped and the underdamped limits result $\Gamma_{RW} = (1/2)\omega_b \pi^{-1} (\omega_b t_e)^{-1} \exp(-\Delta U/T)$ and $\Gamma_{RW} \propto t_e^{-1} e^{-\Delta U/T}$, respectively. Fig. 2 shows that our theoretical prediction (full line) well compares with numerical simulations of the model (open squares), at all $t_e$. In the figure, we also illustrate numerical results (full circles) for the escape rate of the Langevin dynamics, $\Gamma_L$. We remind that in the medium/high damping regime, and in the low temperature limit, $\Gamma_L$ is the celebrated Kramers' escape rate $\Gamma_{K}$, $\Gamma_L = \frac{2\pi}{\omega_b} \sqrt{\frac{1}{2\omega_b^2} + \frac{\Delta U}{2\omega_b^2}} e^{-\Delta U/T}$, and that finite temperature corrections have been determined by Lifson-Jackson [13]. In the overdamped limit, Kramer's result coincides with our prediction for $\Gamma_{RW}$ provided that $k = \omega_b/\omega_b$ in our functional form for $P_{\tau}$. In the underdamped limit, $\Gamma_L$ is known to scale as $\Gamma_L \propto \frac{\Delta U}{T} \pi^{-1} t_e^{-1} e^{-\Delta U/T}$ [2]. This result clarifies that, as
concern the escape rate, the two dynamics markedly differ in the underdamped limit. The Langevin dynamics has a much higher escape rate, being $t_{L}/t_{RW} \propto \Delta U/T$.

The diffusion coefficient of the random walk dynamics is conveniently determined by describing each trajectory as a sequence of barrier crossing jumps, with displacement $\Delta x^i_j$, each one followed by an effective intra-well jump, with displacement $\Delta x^i_{j+1}$. The effective displacement $\Delta x^i_j$ is the total of the intra–well jumps connecting the final jump of position $\Delta x^i_j$, and the initial position of jump $\Delta x^i_{j+1}$. Since the fraction of barrier-crossing jumps in $P_c$, after $N \approx t/t_c$ jumps the overall displacement is $R_N = \sum_{i}^{N} P_c(\Delta x^i_j + \Delta x^i_{j+1})$, and the diffusion coefficient is

$$D = \lim_{t \to \infty} \frac{1}{2Nt_c} \left[ \left( \sum_{j=1}^{N} \Delta x^i_j \right)^2 + \left( \sum_{j=1}^{N} \Delta x^i_{j+1} \right)^2 \right],$$

(3)

the cross product term vanishing for symmetry reasons.

Since only a fraction $P_d$ of the terms appearing in the above sums are uncorrelated, the diffusion coefficient can also be expressed as

$$D = \frac{1}{2t_c} P_d P_c \left[ \langle (\Delta x^i_j)^2 \rangle + \langle (\Delta x^i_{j+1})^2 \rangle \right] = D^i + D^j,$$

(4)

where $\langle \rangle$ indicates averages over uncorrelated jumps.

Thus, we have left with the problem of estimating the mean square jump length of uncorrelated barrier crossing jumps, $\langle (\Delta x^i_j)^2 \rangle$, and of uncorrelated effective intra-well jumps, $\langle (\Delta x^i_{j+1})^2 \rangle$.

In the overdamped $t_c \to 0$ limit all jumps are short, and barrier crossing jumps start and end close to the top of a barrier, where the potential is flat. Accordingly, $\langle (\Delta x^i_j)^2 \rangle_{t_c \to 0} \approx 12Tt_c^2/m$ \cite{12}, and given our results for $P_d$ and $P_c$,

$$D^i_{t_c \to 0} \approx 6TcP_cP_d \propto TL^2 - t_c^3 \Delta UE^{-\Delta U/T}.$$  

(5)

To estimate $\Delta x^i_{j+1} \to 0$ we consider that, since barrier crossing jumps are short, two subsequent barrier crossing jumps are connected by a sequence of jumps whose total displacement is either zero, if the particle recrosses the same barrier, or roughly equal to the period of the potential, if the particle traverses a well and crosses a subsequent barrier. For uncorrelated barrier crossing jumps these two possibilities are equally likely, which implies $\langle (\Delta x^i_{j+1})^2 \rangle_{t_c \to 0} \approx L^2/2$. This allows to estimate

$$D^j_{t_c \to 0} \approx \frac{L^2}{4} \frac{P_d}{P_c} \propto \Delta U t_c e^{-\Delta U/T}.$$  

(6)

In the underdamped $t_c \to \infty$ limit a particle that has enough energy to cross an energy barrier will traverse $\Delta x^i(t, E)/L \approx t/t_E$ wells, where $t$ is the jump duration, and $t_E$ the time the particle needs to cross a single energy well. Thus

$$\langle (\Delta x^i(t, E)^2) \rangle \approx L^2(t^2)/(t_E^2)$$

is evaluated averaging over the waiting time distribution ($\langle t^2 \rangle = 2t_E^2$) and over the energy of the particle. This leads to $\langle (\Delta x^i(t, E)^2) \rangle = 2t_c^2 L^2 \int_{\Delta U}^{\infty} \frac{e^{-\frac{E-E_0}{kT}}}{t_E} dE \left( \int_{\Delta U}^{\infty} e^{-\frac{E-E_0}{kT}} t_E dE \right)^{-1}$, that scales as

$$\langle (\Delta x^i_j)^2 \rangle_{t_c \to \infty} \propto \Delta U t_c^2$$

(7)

since $t_E(\frac{t}{t_E} \to \frac{L}{2}) \propto \frac{\sqrt{\Delta U}}{\Delta U}$ for small $E - \Delta U$. We thus estimate

$$D^j_{t_c \to \infty} \propto \Delta U t_c \exp(\Delta U/T).$$  

(8)

To determine $\langle (\Delta x^i_{j+1})^2 \rangle_{t_c \to \infty}$, we indicate with $p_k$ the probability that a walker interacts $k$ times with the heat bath in a well, before escaping. If $x_s$ is the original position inside the well, and $x_f$ the final one, then

$$\langle (\Delta x^i_{j+1})^2 \rangle_{t_c \to \infty} = \sum_p p_k \int P_c(x_c)P_k^{wh}(x_s|x_c)(x_s - x_f) dx_c dx_s.$$  

Here $P_c(x) \propto 1/v(x)$ is the probability that a barrier crossing jump ends in $x_s$, one could evaluate from the equilibrium distributions over the barrier-crossing jumps, and $P_k^{wh}(x_s|x_c)$ is the probability that the jump through which the particle escapes from the well starts in $x_s$, being the particle arrived in $x_c$. To a good approximation \cite{11} a particle exits from the well after performing a single collision, so that $x_s - x_f = 0$, or after thermalizing within the well, so that $x_c$ and $x_s$ becomes uncorrelated. Accordingly, $\langle (\Delta x^i_{j+1})^2 \rangle_{t_c \to \infty} = p_1 \cdot 0 + (1 - p_1) \langle (L^2) \rangle$, where

$$\langle (L^2) \rangle_{t_c \to \infty} \approx \int_{-L/2}^{L/2} P_c(x_c) P_k^{wh}(x_s|x_c)(x_s - x_f) dx_c dx_s,$$

(9)

with $P_k^{wh}(x_s|x_c)$ the probability that a barrier crossing jumps of a thermalized state starts from position $x_s$. The evaluation \cite{11} of both $p_1, P_c(x_c), P_k^{wh}(x_s|x_c)$ leads to $\langle (\Delta x^i_{j+1})^2 \rangle_{t_c \to \infty} \propto L^2$. Summarizing, in the $t_c \to \infty$ limit

$$D^j_{t_c \to \infty} \propto \frac{P_c}{2t_c} \langle (\Delta x^i_{j+1})^2 \rangle_{t_c \to \infty} \propto \frac{L^2}{t_c} \exp(-\Delta U/T).$$  

(10)

We finally note that, in both Eq. 8 and Eq. 10, the proportionality constants have a weak temperature dependence we neglect, that is fixed by the shape of the potential \cite{11}.

While we have estimated $D^i_{t_c \to 0}$ and $D^j_{t_c \to \infty}$ in the low temperature regime, it is also possible to estimate $D^\infty(t_c)$ at all $t_c$. To this end we assume the barrier crossing jumps to be always uncorrelated, since they are uncorrelated in the underdamped limit, as jumps are short and particles on the top of the barrier move as free particles, and in the underdamped limit. With this assumption we estimate $P_c(\langle (\Delta x^i_j)^2 \rangle)$ from equilibrium average over the jumps, $P_c(\langle (\Delta x^i_j)^2 \rangle) = 2 \int_{-L/2}^{L/2} dx_s \int_{-L/2}^{L/2} dx_c \int_{-\Delta U}^{\infty} dE f(x_s, x_c, E)(x_s - x_c)^2$, with $f$
given in Eq. 2 and thus get $D^\sigma(t_c) = \frac{1}{2}P_tP_3((\Delta x^2)^2)$. Beside being valid at all $t_c$ in the low temperature regime, this prediction is also valid at all temperature in the underdamped regime, where $P_d = 1$. Fig. 3 illustrates that this theoretical prediction (dashed line) correctly describes the numerical data (full circles), and scales as $t_c^3$ as $t_c$ in the overdamped and in the underdamped limit, as predicted in Eq. 5 and in Eq. 8 respectively. In the figure, we also illustrate numerical results for the contribution to the diffusion coefficient of the intra-well jumps (full diamonds), that behaves as predicted in Eq. 6.

We finally compare the diffusion coefficient of the random walk and of the Langevin dynamics, identifying their characteristic timescales, $\tau_c = \tau_{vis}$. For both dynamics $D = \Gamma L^2$ in the overdamped limit. In this limit, the full van Hove distributions actually coincide at all times. In the underdamped low temperature limit, the diffusivity of the Langevin dynamics is $D_L \propto T\tau_\text{vis}^{-\Delta U/T}$, while that of the random walker is given by Eq. 8.

In conclusion, we put forward an analytical treatment of the escape rate from a well, and of the diffusion coefficient in a periodic potential, of a random walker in both the overdamped and the underdamped limits. The walker behaves as a Langevin particle in the overdamped limit. In the underdamped low temperature limit, conversely, with respect to a Langevin particle a random walker has a smaller escape rate, but a larger diffusion coefficient. An important open question ahead concerns the temporal evolution of the jumps of the van Hove distribution in the underdamped limit, where a transient Fickian not-
Gaussian dynamics is observed, as in many physical systems [9,17].

Support from the Singapore Ministry of Education through the Academic Research Fund (Tier 1) under Projects No. RG104/15 and RG179/15 is gratefully acknowledged.

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