Short time-scales in the Kramers problem

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Abstract. Escape from a metastable potential is considered on time-scales less than are needed for the creation of quasi-equilibrium within the well. It is shown that the escape flux may then depend exponentially strongly, and in a complicated way, on friction and time.

INTRODUCTION

In his celebrated paper [1], Kramers considered the flux from a metastable potential well (Fig. 1(a)) induced by weak noise. Over the last 60 years, there have been many developments and generalizations of the Kramers problem (see [2,3] for major reviews). However both Kramers and most of those who followed him considered the *quasi-stationary* flux, i.e. the flux that occurs on a time-scale exceeding the time needed for the formation of a quasi-stationary distribution within the metastable well. But what happens on shorter time-scales?

The process of formation of the quasi-equilibrium differs markedly depending on whether there are, or are not, internal barriers within the metastable part of the potential: c.f. Figs. 1(b) and (a) respectively. In the latter case, the formation time is of the order of an *optimal fluctuation duration* t_{opt} (equal to the characteristic relaxation time) whereas, in the former case, the formation proceeds via two distinct stages: first, quasi-equilibrium is formed within the initial well, much as in the single-well case; secondly, equilibrium between different wells is established, which

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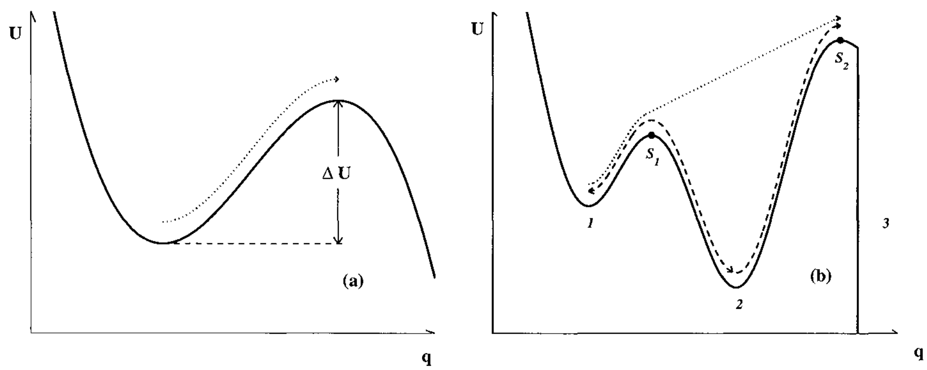

FIGURE 1. Single-well (a) and double-well (b) metastable potentials.

is an exponentially longer process. Correspondingly, escapes for these two cases occur quite differently.

ESCAPE ON DIFFERENT TIME-SCALES

Fig. 2 presents some typical results from a computer simulation of the escape flux from the potential shown in Fig. 1(b). The system is put initially into the bottom of well-1, and then it follows the stochastic equation

$$\begin{aligned} &\ddot{q} + \Gamma\dot{q} + dU/dq = f(t), \\ &\langle f(t)\rangle = 0, \quad \langle f(t)f(t')\rangle = 2\Gamma T\delta(t-t'), \\ &U(q) = \begin{cases} 0.06(q+1.5)^2 - \cos(q) & \text{at} \quad q<q_l=4.5, \\ -\infty & \text{at} \quad q>q_l, \end{cases} \end{aligned} \tag{1}$$

until either the coordinate limit q_l or a (rather arbitrary) time limit $t_l = 1000$ is reached, after which the system is reset to the bottom of the well-1 and everything is repeated. Once the statistics are deemed adequate, the flux

$$J(t) \equiv \frac{1}{N_{\rm reset}} \frac{\Delta N(t)}{\Delta t} \tag{2}$$

is computed as a function of time. Here, $N_{\rm reset}$ is the overall number of resettings and $\Delta N(t)$ is the number of escapes that occur in the interval $[t, t+\Delta t]$ where Δt is chosen to be much larger than the typical interval between two successive escapes, but much smaller than characteristic time-scales at which the flux may change significantly.

One can resolve in Fig. 2 all the stages mentioned above: an initial rapid growth of J on a time-scale $\sim t_{\rm opt}$; then a slow decay over a time t_s (related to the formation of quasi-equilibrium between wells 1 and 2); and finally an even slower exponential (quasi-stationary) decay with a time-scale $t_{qs} \gg t_s$.

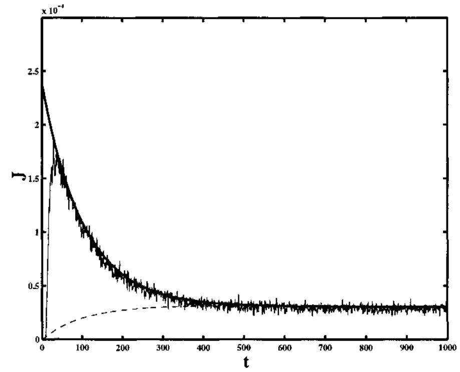

FIGURE 2. Simulations of the escape flux $J(t)$ (2) (thin jagged line) for the model (1) (see $U(q)$ in Fig. 1(b)) with $\Gamma = 0.15$, $T = 0.4$, compared with approximations of $J(t)$ by Eq. (3) in which α_{12}, α_{21} and α_{qs} are calculated by the Kramers-Melnikov formula [3]. The thick full line is for $\alpha_{13,23} = \alpha_{qs}(1+(\Omega_1\Omega_2^{-1}\exp((U_1-U_2)/T))^{\pm 1})/(1+(m^{-1}\exp(kS_{S_2\to S_1}/T))^{\pm 1})$, where Ω_1 and Ω_2 are frequencies of eigenoscillation in the bottom of wells 1 and 2 respectively; k is equal to 1 and -1 for ranges Γ providing noise-free trajectories $S_2 \xrightarrow{nf} 2$ and $S_2 \xrightarrow{nf} 1$ respectively; the action $S_{S_2\to S_1}$ for the transition $S_2 \to S_1$ is calculated from the theory [5]; m is the only adjustable parameter, related to the prefactor in (4) (here, $m \approx 0.9$). For comparison, the dashed line is for: $\alpha_{13} = 0$, $\alpha_{23} = \alpha_{qs}(1 + \alpha_{21}/\alpha_{12})$.

The flux $J(t)$ can be well-described in terms of kinetic equations for the well populations, using the concept of inter-attractor[1] transition rates α_{ij} (c.f. [4]):

$$\begin{aligned} &J(t) = \alpha_{13}e^{-\frac{t}{t_s}} + \alpha_{qs}(e^{-\frac{t}{t_{qs}}} - e^{-\frac{t}{t_s}}), \\ &t_s \approx \alpha_{12}^{-1}, \qquad t_{qs} \approx \alpha_{qs}^{-1} \approx \alpha_{12}/(\alpha_{12}\alpha_{23} + \alpha_{21}\alpha_{13}), \\ &T \ll U_{S_1} - U_1, \qquad t \gg t_{\mathrm{opt}}. \end{aligned} \tag{3}$$

The significance of the two terms in (3) is easily understood (c.f. Fig. 2). The first one, corresponding to *direct* escapes (i.e. not via the bottom of well-2), dominates during the first and second stages; whereas the second term, corresponding to indirect escapes, dominates in the third stage. The asymptotic part of this latter flux, $\alpha_{qs}\exp(-t/t_{qs})$, is called the *quasi-stationary* flux.

Although the coefficients $\alpha_{12}, \alpha_{21}, \alpha_{qs}$ can readily be obtained from the Kramers-Melnikov theory [3] [2], α_{13}, α_{23} cannot be found [3] in this way. One of us [5] has developed a theory of α_{13}, α_{23} based on the concept of *optimal fluctuation*. The latter suggests seeking the escape rate, e.g. α_{13}, in the form

$$\alpha_{13} = P\mathrm{e}^{-\frac{S}{T}}. \tag{4}$$

Here the action S does not depend on T, whereas the prefactor P depends relatively weakly both on T and on other parameters.

1) For the sake of brevity, we refer to region 3 as an "attractor" too.
2) Note that they (as well as a quasi-stationary flux) depend on friction *weakly*.

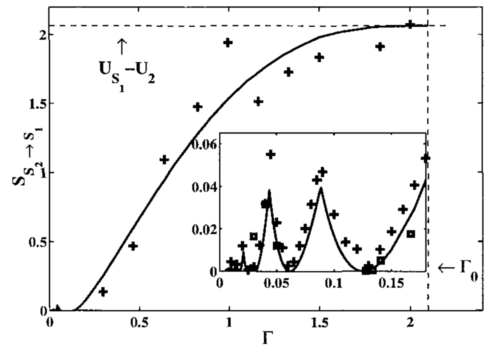

FIGURE 3. Dependence of the action for the transition $S_2 \to S_1$ on the damping constant Γ, at time-scales $t \gg t_{\rm opt}$, in the system (1) (see $U(q)$ in Fig. 1(b)). The solid line is calculated numerically from the theory [5]. The horizontal and vertical dashed lines indicate respectively the upper limit for $S_{S_2 \to S_1}$ and the value of Γ at which the cutoff of direct transitions $S_2 \to S_1$ and escapes $1 \to S_2$ occurs. The crosses and squares represent digital and analogue simulation data respectively. The inset shows an expanded plot of the region of small damping.

The physics and theory of the direct escape process are essentially different on time scales $t \gg t_{\rm opt}$, $t \sim t_{\rm opt}$ and $t \ll t_{\rm opt}$. We consider these in turn.

Long time-scale: $t \gg t_{\rm opt}$. On this time-scale, α_{13} does not depend on time, but its dependence on friction is exponentially strong at sufficiently small temperatures (c.f. Fig. 3). Moreover, it undergoes oscillations[3] in the underdamped range, and can have a cutoff at certain friction Γ_0 from the moderate-to-high friction range (i.e. $\alpha_{13} = 0$ at $\Gamma \geq \Gamma_0$). The oscillations are related to an alternation between ranges of friction in which a noise-free trajectory from the external saddle S_2 goes into either well-1 or well-2. The cutoff at large Γ is related to the absence of turning points in the noise-free trajectories $S_2 \stackrel{nf}{\to} 2$, $S_1 \stackrel{nf}{\to} 2$. Our experimental technique enables α_{13} to be measured with sufficient accuracy to observe these interesting features, and experiment and theory are (Fig. 3) in satisfactory agreement.

Medium time-scale: $t \sim t_{\rm opt}$. The escape flux then becomes non-stationary because the *most probable escape path* ($MPEP$) now depends on a given escape time t which it should provide, so that action along the $MPEP$ becomes dependant on t, thus, leading to a strong (but smooth) drop of $J(t)$ as t decreases. This is equally relevant both to single-well and multi-well metastable potentials, and to inter-attractor transition rates in multi-well *stable* potentials. In earlier studies, an analytic solution was presented [6] for the overdamped regime in a piece-wise linear potential; and an asymptotic theory was developed [7] for an arbitrary single-well potential in the strongly underdamped and overdamped regimes.

Short time-scales: $t \ll t_{\rm opt}$. Apart from its intrinsic interest and fundamen-

[3] Typically, the scale of oscillation of S is small in comparison with $U_{S_2} - U_1$ (the latter corresponds to the Arrhenius dependence of a conventional quasi-stationary flux on T [1]- [3]) but, in some cases, it can be equal or even greatly exceed $U_{S_2} - U_1$ [5].

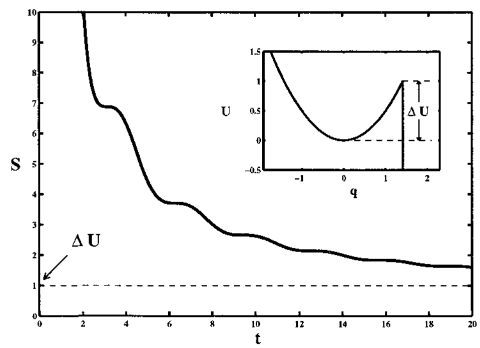

FIGURE 4. Calculated dependence (solid line) of the action S on the time t of escape from the bottom of the (inset) potential well $U(q) = \begin{cases} q^2/2 & \text{at } q<\sqrt{2} \\ -\infty & \text{at } q>\sqrt{2} \end{cases}$ ($\Gamma = 0.05$). The dashed line in the main figure shows the large-time asymptote level, equal to the barrier height ΔU.

tal significance, this limit is also highly topical given the advent of experimental techniques that allow one to study processes related to fluctuations on exceedingly short time-scales: see e.g. [8] in which the dynamics of a chemical reaction is studied on a femtosecond time-scale. We have found explicitly the MPEP and action for a particular model (see inset of Fig. 4). Fig. 4 shows how the action depends on the escape time from the bottom of the well (i.e. from the stable stationary state of the noise-free system) to beyond the barrier. It indicates that the flux should grow with time in a *step-wise* manner (exponentially sharply) until a quasi-stationary value is reached at $t \gg t_{\text{opt}}$. The higher a step is, the larger the number of turning points in the MPEP (at large t, the MPEP coincides with the noise-free trajectory relaxing from the saddle into the well, but reversed in time). The physical origin of the steps lies in the oscillatory character of noise-free trajectories at small and moderate friction. Thus, we expect it to be a general phenomenon, arising in both single-well and multi-well potentials. It is interesting to note also that, in the more formal problem of a transition for a given time between two given states, neither of which is stable, the transition flux $J(t)$ generally undergoes exponentially strong oscillations at $t \ll t_{\text{opt}}$.

CONCLUSIONS AND OPEN PROBLEMS

Escape from a metastable potential differs markedly *after* and *before* the formation of quasi-equilibrium within the metastable part of the potential. The formation process is essentially different for *single-well* and *multi-well* metastable potentials. In the former case (Fig. 1(a)), the formation time is relatively short, namely of the order of an optimal fluctuation duration, whereas it is exponentially longer in the latter case (Fig. 1(b)).

Escape on this latter time-scale has been studied in our work for the first time, both theoretically and experimentally: unlike the conventional quasi-stationary flux, the escape flux on this time-scale depends on friction exponentially sharply, moreover, it can undergo oscillations in the underdamped range and a cutoff in the overdamped range. (Fig. 3).

For $t \ll t_{\rm opt}$, we have demonstrated theoretically for the first time that the escape flux depends exponentially strongly on both friction and time; moreover, if the friction is small or moderate, it grows with time in a step-wise manner (Fig. 4).

Open problems yet to be addressed include –

- To study theoretically and experimentally the dependence of the pre-exponential factor in the escape probability from a multi-well metastable potential on Γ, T and $U(q)$: it is as fundamental a problem as that for the single-well case [1]- [3], but more difficult.
- To test experimentally the prediction that, for small to moderate friction, the escape flux may grow in a step-wise manner for $t \ll t_{\rm opt}$, and to study the problem in a more general context, including an arbitrary potential, a pre-exponential factor, inter-attractor transitions in multi-well stable potentials.

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