Escape from a Metastable Well: The Kramers Turnover Problem

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The thermally activated escape from a metastable well is studied in a region where both recrossing and depletion effects are important. It is shown that the relevant variable for the escape dynamics is the energy in the unstable normal mode at the barrier. In terms of this quantity the theory becomes easily perceptible and allows for a calculation of the escape rate in the turnover region between the low damping and strong damping Kramers limits.

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Almost half a century ago Kramers[1] studied the influence of dissipation on the rate of thermally activated escape from metastable well. In the early description of escape processes by simple transition-state theory, the passage over the barrier was pictured as a free flight of a thermally activated particle. This leads to the well-known rate formula

$$\Gamma_{\mathrm{TST}} = (\omega_0/2\pi)\exp(-\Delta U/k_{\mathrm{B}}T),$$

where ΔU is the height of the potential barrier and ω_0 is the frequency of small undamped oscillations about the metastable minimum of the potential well. While the heat bath is needed to activate the particle, the coupling strength does not appear in this simplified theory. Based on a model where the heat-bath coupling causes a frictional force proportional to the velocity of the particle, Kramers[1] showed that the escape rate Γ is diminished by a transmission factor κ, i.e.,

$$\Gamma = \kappa(\omega_0/2\pi)\exp(-\Delta U/k_{\mathrm{B}}T), \quad \kappa < 1. \tag{1}$$

There are two physical mechanisms leading to this reduction of the pre-exponential factor of the rate. First, a particle having crossed the barrier may be scattered back into the metastable well. This recrossing effect is particularly important for moderate-to-large damping. Second, the flow across the barrier leads to an underpopulation of the upper energy states in the well. This depletion effect dominates for very weakly damped systems where the small coupling to the heat bath admits deviations from the Boltzmann distribution in the well. Kramers calculated the transmission factor κ under conditions where one of the two mechanisms prevails. The turnover between the Kramers limits has attracted considerable interest recently,[2] in particular since rate experiments are now approaching the high accuracy needed to test theories predicting the influence of damping on the pre-exponential factor of the rate.

A first attempt to improve the low-damping Kramers result was made by Büttiker, Harris, and Landauer.[3] Afterwards, various authors[4,5] have provided formulas bridging between the Kramers limits. It is a common feature of these approaches that the transmission factor is calculated by *two* theories valid for weak and strong damping, respectively, and then the results are combined to yield an interpolating formula for the full damping range. In the simplest cases this is achieved by additive or multiplicative combinations of the two transmission factors. A truly unified theory of the Kramers turnover problem avoiding *ad hoc* assumptions is still lacking.

The conventional description of escape processes examines the motion of a principal degree of freedom, the reaction coordinate q, which may be conceptualized as the coordinate of a particle of mass M moving in a metastable potential $U(q)$ while coupled to a heat bath. Frequently, the particle then undergoes a stochastic process described by a Fokker-Planck equation. There is a remarkable range of applicability of Fokker-Planck equations or the stochastically equivalent Langevin equations.[6] In particular, an analog of a particle in a metastable well that follows these equations almost precisely can be built with a current-biased Josephson junction.[7] Previous authors studied the Fokker-Planck process of q and $\dot{q}$ in the phase space of the particle or the stochastic motion of the particle energy $E_p = \frac{1}{2}M\dot{q}^2 + U(q)$. Here I will show that the relevant quantity is not purely a particle variable. The escape process is governed by the energy E in the unstable normal mode at the barrier. Specifically, I shall consider a system described by the Langrangian

$$L = \tfrac{1}{2}M\dot{q}^2 - U(q) + \sum_i \tfrac{1}{2}m_i\left[\dot{q}_i^2 - \omega_{i0}^2\left(q_i - \frac{c_i}{m_i\omega_{i0}^2}q\right)^2\right], \tag{2}$$

which, in the limit of an infinite set of weakly coupled bath oscillators, is known to yield for the reaction coordinate q exactly an equation of motion in the form of a generalized Langevin equation[8] with a time-dependent damping kernel

$$\gamma(t) = \frac{1}{M}\sum_i \frac{c_i^2}{m_i\omega_{i0}^2}\cos(\omega_{i0}t). \tag{3}$$

Note that the combined effect of all bath modes can lead to strong damping of the particle's motion. The

Kramers model of frequency-independent damping corresponds to a specific choice of the spectral density of bath oscillators.[8,9] Here, I shall treat the general case of frequency-dependent damping. It is convenient to have the origin of q and U at the barrier top. Then near the barrier $U(q)=-\frac{1}{2}M\omega_b^2q^2$, while near the metastable minimum $U(q)=-\Delta U+\frac{1}{2}M\omega_0^2(q-q_0)^2$. Following Pollak,[10] I make an orthogonal transformation which diagonalizes the Lagrangian in the vicinity of the barrier. The standard procedure gives

$$L=\tfrac{1}{2}\dot{u}^2+\tfrac{1}{2}\omega_R^2u^2+\sum_i\tfrac{1}{2}(\dot{s}_i^2-\omega_i^2s_i^2)-V(u,s_i), \quad (4)$$

where u and s_i are mass-weighted coordinates reducing to normal-mode coordinates in the barrier region. The unstable mode u has an effective barrier frequency ω_R which is just the Grote-Hynes frequency appearing in the theory of non-Markovian rate processes.[2,11] For frequency-independent damping one has $\omega_R=(\omega_b^2+\frac{1}{4}\gamma^2)^{1/2}-\frac{1}{2}\gamma$. The ω_i are renormalized bath frequencies and $V(u,s_i)$ describes the nonlinear interaction between the modes outside the barrier region. Since the reaction coordinate may be written as a linear combination of the normal-mode coordinates

$$q=M^{-1/2}g_u\left(u+\textstyle\sum_i g_is_i\right), \quad (5)$$

we have $V(u,s_i)=U(q)+\frac{1}{2}M\omega_b^2q^2$, which contains cubic and higher-order nonlinearities. The following analysis is fairly independent of the explicit form of the coefficients characterizing the relation between (3) and (4) and I shall defer details to a forthcoming paper.

In order to escape from the metastable well, the system has to traverse the barrier region. There the total energy of the system becomes the sum of the energies in the normal modes. The probability to escape is completely determined by the energy E in the unstable mode. When the system approaches the barrier with $E<0$, the u component of the trajectory will go through a turning point and the particle returns to the well. For $E>0$ the particle will escape with probability 1. Note that the dynamics of the particle coordinate q near the barrier top is stochastic and it may cross $q=0$ several times, because q contains contributions of all the stable coordinates s_i. The behavior of the u coordinate, however, is always smooth and regular.

Now imagine injecting particles at a constant rate near the bottom of the well.[1] Then the system will approach a steady-state probability with a constant flux across the barrier. The flux equals the escape rate Γ when the probability is normalized to one particle in the well. For $E\lesssim 0$ let $f(E)dE$ be the probability to find within one unit of time the system in the barrier region at a turning point of the u mode (at $u=0$) with a mode energy between E and $E+dE$. In terms of this quantity, the escape rate reads

$$\Gamma=\int_0^\infty dE\,f(E) \quad (6)$$

since all particles with $E>0$ escape. When $E<0$ the particle returns to the well where all modes are coupled and exchange energy. Let $P(E\,|\,E')dE$ be the conditional probability that a system leaving the barrier region with normal-mode energy E' will return with an energy between E and $E+dE$. For a bath in thermal equilibrium, this probability satisfies the condition of detailed balance

$$P(E\,|\,E')\exp(-\beta E')=P(E'\,|\,E)\exp(-\beta E) \quad (7)$$

and it tends to thermalize the distribution $f(E)$. Assuming a Boltzmann distribution of the coupled system (particle and bath) normalized to one particle in the well one finds

$$f_{\rm eq}(E)=\frac{1}{2\pi k_BT}\frac{\omega_0\omega_R}{\omega_b}\exp\left(-\frac{\Delta U+E}{k_BT}\right). \quad (8)$$

The algebra necessary to derive (8) is provided by Pollak.[10] Because of the flow across the barrier, the steady-state probability $f(E)$ deviates from (8) and satisfies

$$f(E)=\int_{-\infty}^0 dE'\,P(E\,|\,E')f(E'). \quad (9)$$

The lower limit of integration can be shifted to $-\infty$ since for $E\ll 0$ the probability $f(E)$ approaches $f_{\rm eq}(E)$ as a consequence of (7). Near $E=0$ deviations from (8) may arise from the absence of inflowing particles with $E'>0$.

What remains to be done is to calculate the conditional probability $P(E\,|\,E')$. Fortunately, this quantity is needed explicitly only when the unstable mode and stable modes are coupled weakly in the well region, because otherwise the mode energy is thermalized and $P(E\,|\,E')$ has a Boltzmann tail near $E=0$. In that case the solution of (9) is very accurately given by (8). Only when E remains close to E' will deviations from $f_{\rm eq}(E)$ become important.

From the Lagrangian (4) and the representation (5) of the reaction coordinate q, the equations of motion for the stable modes may be written as

$$\ddot{s}_i(t)+\omega_i^2s_i(t)=g_iF(t), \quad (10)$$

where $F(t)=\ddot{u}(t)-\omega_R^2u(t)$ is a "force pulse" which is nonvanishing only during a traversal of the well region. For the case of small coupling between the unstable and the stable modes, $F(t)$ may be treated as a weak external force driving the stable modes. The $s_i(t)$ trajectories may then be calculated explicitly as linear functionals of $F(t)$ for arbitrary initial conditions $s_i,\dot{s}_i$ at $t=0$ when the u mode goes through the turning point. The energy absorbed by the stable modes is easily worked out. This energy is a stochastic quantity since it depends on the initial conditions for the stable modes. When the initial coordinates $s_i, \dot{s}_i$ are thermally distributed, the u mode is found to return to the barrier region with an energy E distributed as

$$P(E \mid E') = (4\pi k_B T \Delta E)^{-1/2} \exp[-(E-E'+\Delta E)^2/4k_B T \Delta E], \tag{11}$$

where

$$\Delta E = \tfrac{1}{2} \textstyle\sum_i g_i^2 \displaystyle\int_0^\infty ds \int_0^\infty ds' \cos[\omega_i(s-s')] F(s) F(s') \tag{12}$$

is the average energy loss which may be evaluated for the $E=0$ trajectory.

Since the distribution (11) satisfies the detailed balance condition (7), Eq. (9) has a solution $f(E)$ approaching $f_{\rm eq}(E)$ for $\beta E \ll 0$. It is convenient to make the *Ansatz* $f(E) = f_{\rm eq}(E) \exp(\frac{1}{2}\beta E)\phi(\beta E)$ which transforms (9) into a Wiener-Hopf equation with a symmetric kernel that can be solved by standard methods.[12] From (6) the escape rate is then found to be of the form (1) with the transmission factor

$$\kappa = \frac{\omega_R}{\omega_b} \exp\left[\frac{1}{\pi}\int_{-\infty}^{+\infty} \frac{dy}{1+y^2} \ln(1-e^{-\delta(1+y^2)/4})\right], \tag{13}$$

where $\delta = \Delta E/k_B T$. For the Kramers model, Melnikov[5] has obtained a related result which differs, however, in two respects. The factor ω_R/ω_b is absent and ΔE is defined differently. Melnikov considers the stochastic process of the particle energy E_p. Because of recrossing effects his rate expression [corresponding to Eq. (6)] is only approximately valid and the rate approaches the transition-state theory result for $\Delta E \gg k_B T$. The correct rate in the moderate-to-large damping regime can only be obtained by an *ad hoc* multiplication with the corresponding transmission factor. In the normal-mode representation recrossing effects are strictly absent. Further, the energy loss of the unstable mode is very accurately given by (12) as long as $\Delta E \ll \Delta U$, because the u mode decouples from the other modes in the region of slow motion near the barrier.

For $\delta \gg 1$, the transmission factor (13) approaches $\kappa = \omega_R/\omega_b$ exponentially fast [corrections are of order $\exp(-\delta/4)$]. In this region $f(E)$ is very close to $f_{\rm eq}(E)$ and the escape rate is given by the Grote-Hynes theory result[2,10,11] which is independent of the precise form of $P(E \mid E')$. Nonequilibrium effects in $f(E)$ are only important for δ of order 1 or smaller. Because of $k_B T \ll \Delta U$, we then have $\Delta E \ll \Delta U$ and the approximation (10) for $P(E \mid E')$ is sufficient. For $\delta \ll 1$, the transmission factor (13) approaches $\kappa = \omega_R \Delta E/\omega_b k_B T$. A small energy loss always arises in the limit of weak damping. Using explicit expressions for the coefficients g_i and partial integrations, one can show that to second order in the coupling constants c_i the expression (12) for ΔE coincides with the energy loss of the energy diffusion equation which is usually employed to treat the weak damping limit.[2]

For frequency-independent damping the result (13) thus describes the turnover between the weak damping and the moderate-to-large damping Kramers results.

In the general case of frequency-dependent damping, deviations from the Grote-Hynes theory transmission factor, $\kappa = \omega_R/\omega_b$, we are not restricted to the weak damping limit. For instance, consider a system with an exponential damping kernel, $\gamma(t) = a\exp(-at/\gamma_0)$, where $\gamma_0 = \int_0^\infty dt \gamma(t)$ is the low-frequency damping coefficient. When $a < \omega_R^2$, the energy loss ΔE becomes small for $\gamma_0 \to 0$ and also for $\gamma_0 \to \infty$ leading to strong deviations from the Grote-Hynes theory result in both limits.[13] This and other cases will be discussed in detail elsewhere. In summary, I have shown that the energy in the unstable normal near the barrier is the relevant variable for the escape problem. In the entire range of damping parameters, the escape rate can be calculated from the probability distribution of this quantity in a unified way.

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