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Macroscopic Theory of Activated Decay of Metastable States

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The Brownian motion of a particle over a potential barrier, a problem first solved by Kramers, is reexamined also for the case of "intermediate" friction, to which Kramers' solutions do not apply. The theory is macroscopic and entirely based on the Langevin equation of the particle, but it makes essential use of ideas of a recent microscopic theory of Grabert and of Pollak, Grabert, and Hänggi for a particle coupled to an infinite set of harmonic oscillators. Their result for the escape rate is recovered, but the present method seems more generally applicable. We introduce and use a new theoretical tool—the transformation to a new set of variables mixing the macroscopic and the noise variables of the Langevin equation.

KEY WORDS: Brownian motion; activation rates; intermediate dissipation.

1. INTRODUCTION

The escape of a particle from a potential well via Brownian motion was treated in a classic paper by Kramers.(1) Kramers' theory is macroscopic, being based on the Langevin equation, or the stochastically equivalent Fokker–Planck equation, of a Brownian particle with a phenomenological unretarded friction coefficient and a fluctuating force whose strength is determined by a fluctuation-dissipation relation. In Kramers' work a solution of the escape problem for moderate to large friction and for very weak friction was given, but the turnover from very weak to moderate friction was not treated by his theory. We cannot mention here the immense literature following up on Kramers' work (for reviews see ref. 2), but we mention the generalization of Kramers' work including memory effects by Grote and Hynes(3) and a recent attempt to tackle the turnover problem by

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Mel'nikov.[4] Both developments were made within the macroscopic framework also used by Kramers.

The escape problem can be reformulated within a microscopic model by replacing the phenomenological friction and fluctuation terms by a coupling of the Brownian particle to a reservoir of harmonic oscillatiors.[5] In a remarkable development it was shown in a series of recent papers by Pollak,[6] Grabert,[7] and Pollak *et al.*[8] that the escape problem including memory effects could be solved within the microscopic model also in the turnover region.[7,8] In fact, the final result for the escape rate found in refs. 7 and 8, while differing in certain respects from Mel'nikov's result, is independent of the microscopic details of the model; still, the microscopic formulation of the theory has been indispensable in arriving at this result. This is a strong indication that a completely macroscopic theory including memory effects should exist even in the turnover region. It seems desirable to develop this theory and thereby proove the model independence of the microscopic result.

This is the purpose of the present paper. A further motivation is the hope that one may apply such a macroscopic theory to versions of the escape problem which are not easily modeled on a microscopic level, e.g., in systems far from thermal equilibrium where a simple fluctuation-dissipation theorem does not exist.

For the sake of clarity we treat the case without memory first and include memory effects in the final section. The Langevin equation without memory is formulated in Section 2 and solved near the top of the potential barrier in Section 3. Central notions of the theory, the unstable mode and its energy, are introduced in Section 4 and their relation to the escape rate explained in Section 5. Kramers' results for moderate to large friction are recovered in Section 6. The nonlinear equations of motion for the unstable mode are derived in Section 7 and solved for the escape rate in Section 8. Dissipation with memory is treated in the final section.

2. LANGEVIN EQUATION

We consider a particle of mass one in one dimension with coordinate $q\ (-\infty < q < \infty)$ in a potential well $U(q)$ with a local minimum at $q = q_m < 0$ and a local maximum at $q = 0$. An example is the potential

$$U(q) = -\frac{a}{6} q^2 \left(q - \frac{3}{2} q_m \right) \tag{2.1}$$

with $a > 0$. We assume that the motion of the particle is subject to a frictional force proportional to its velocity. For simplicity, we assume in the following that retardation of the friction is negligible, but we shall completely include retardation effects in Section 9. Furthermore, let the particle be subject to a stochastic force which we assume to be Gaussian and white in the frequency domain of interest. Such a force is inevitably present due to the fluctuation-dissipation theorem if the particle moves in a thermal environment, but in other cases the stochastic force might also have some other physical origin. With the assumptions made, Newton's equation of motion of the particle reads

$$\ddot{q} + \gamma\dot{q} + \frac{\partial U}{\partial q} = \xi(t) \tag{2.2}$$

with the friction rate γ and the stochastic Gaussian force $\xi(t)$ satisfying

$$\begin{aligned} \langle \xi(t) \rangle &= 0 \\ \langle \xi(t)\, \xi(t') \rangle &= Q\delta(t-t') \end{aligned} \tag{2.3}$$

In the case of thermal fluctuations we have

$$Q = 2\gamma k_B T \tag{2.4}$$

In the case of nonthermal fluctuations we may use Eq. (2.4) to define T as the equivalent noise temperature. In the following we shall always assume that the potential well is deep in the sense that

$$\Delta U = U(0) - U(q_m) \gg k_B T \tag{2.5}$$

Kramers posed and to a large extent answered the question of what the average rate is at which a particle injected near the bottom of the potential well escapes from the well over the potential barrier.[1]

In the following we present a new method of solution of this important problem also covering the case of intermediate friction not solved by Kramers, but recently solved[7,8] for a microscopic model[5] from which Eq. (2.2) can be derived. Our method is macroscopic in the sense that only the Langevin equation is used in it. However, it uses in an essential way ideas of the above-mentioned microscopic approach[6–8] to the Kramers problem.

3. SOLUTION NEAR THE TOP OF THE POTENTIAL BARRIER

Sufficiently near the potential barrier at $q = 0$ the potential $U(q)$ may be written as

$$U(q) = -\frac{\omega_b^2}{2} q^2 \tag{3.1}$$

Therefore, near $q=0$ the Langevin equation (2.2) becomes linear and is easily solved by

$$q(t)=Ae^{-\gamma_1 t}+Be^{-\gamma_2 t} + \int_0^t dt' \frac{e^{-\gamma_2(t-t')}-e^{-\gamma_1(t-t')}}{\gamma_1-\gamma_2}\xi(t') \tag{3.2}$$

with

$$\gamma_{1,2}=\frac{\gamma}{2}\pm\left(\frac{\gamma^2}{4}+\omega_b^2\right)^{1/2} \tag{3.3}$$

and the constants of integration A, B, which may be expressed in terms of the initial values $q(0)=q_0$, $\dot{q}(0)=\dot{q}_0$, where q_0 must be near $q=0$:

$$\begin{aligned} A&=-(\gamma_2 q_0+\dot{q}_0)/(\gamma_1-\gamma_2)\\ B&=(\gamma_1 q_0+\dot{q}_0)/(\gamma_1-\gamma_2) \end{aligned} \tag{3.4}$$

We note that according to Eq. (3.3), $\gamma_2<0$. Therefore, $q(t)$ as given by Eq. (3.2) contains a growing component which we denote by $q_>(t)$. If for $q_0<0$ the amplitude of the growing component is positive, the particle passes the barrier at $q=0$ and leaves the potential well.

Next we extract the growing part of $q(t)$. This can be done by taking the Laplace transform of $q(t)$,

$$\hat{q}(p)=\int_0^\infty e^{-pt}q(t)\,dt, \qquad \mathrm{Re}(p)>|\gamma_2| \tag{3.5}$$

It is useful to define the Laplace transform of ξ

$$\hat{\xi}(p)=\int_0^\infty e^{-pt}\xi(t)\,dt \tag{3.6}$$

which is in fact a stochastic integral

$$\hat{\xi}(p)=\int_0^\infty e^{-pt}\,dw(t) \tag{3.7}$$

with

$$dw(t)=\xi(t)\,dt, \qquad \langle(dw(t))^2\rangle=Q\,dt \tag{3.8}$$

We note the properties

$$\begin{aligned} &\hat{\xi}(p) \quad \text{Gaussian} \\ &\langle \hat{\xi}(p) \rangle = 0 \\ &\langle \hat{\xi}(p)\, \hat{\xi}(p') \rangle = \frac{Q}{p+p'} \\ &\langle \hat{\xi}(p)\, \xi(t) \rangle = Qe^{-pt}\theta(t) \end{aligned} \tag{3.9}$$

Then we may write the Laplace transform of Eq. (3.2) as

$$\hat{q}(p) = \frac{1}{\gamma_1 + |\gamma_2|} \left\{ -\frac{\gamma_2 q_0 + \dot{q}_0 + \hat{\xi}(p)}{p+\gamma_1} + \frac{\gamma_1 q_0 + \dot{q}_0 + \hat{\xi}(p)}{p - |\gamma_2|} \right\} \tag{3.10}$$

The growing part $q_>(t)$ of $q(t)$ can now be easily identified as the singular part of $\hat{q}(p)$ for $\mathrm{Re}(p) > 0$,

$$\begin{aligned} \hat{q}_>(p) &= \frac{1}{\gamma_1 + |\gamma_2|} \frac{\gamma_1 q_0 + \dot{q}_0 + \hat{\xi}(|\gamma_2|)}{p - |\gamma_2|} \\ q_>(t) &= \frac{\gamma_1 q_0 + \dot{q}_0 + \hat{\xi}(|\gamma_2|)}{\gamma_1 + |\gamma_2|} e^{|\gamma_2| t} \end{aligned} \tag{3.11}$$

Hence, a particle leaves the potential well if and only if

$$\dot{q}_0 + \gamma_1 q_0 + \hat{\xi}(|\gamma_2|) > 0 \tag{3.12}$$

4. THE UNSTABLE MODE AND ITS ENERGY

We now borrow a trick invented in refs. 6 and 7 in the framework of a microscopic description of the present problem. This trick, at first glance, seems much more natural in the microscopic context, but, as we shall see, it is equally useful here. The trick consists in defining the unstable normal mode of the system near the barrier and its energy. This may seem impossible in the present case in view of the dissipative and irreversible behavior of the underlying dynamics. However, we note that a normal mode $u(t)$ with conserved energy E and containing the growing part $q_>(t)$ can be easily defined by writing

$$\alpha u(t) \equiv \tfrac{1}{2}(\gamma_1 q_0 + \dot{q}_0 + \hat{\xi}(|\gamma_2|))\, e^{|\gamma_2| t} + \tfrac{1}{2} C e^{-|\gamma_2| t} \tag{4.1}$$

where α is a positive normalization constant to be fixed later and C

remains presently undetermined. In general C is fixed by the initial condition posed for u. We note that $u(t)$, as defined by Eq. (4.1), satisfies

$$\ddot{u} - |\gamma_2|^2 u = 0 \tag{4.2}$$

with the conserved energy

$$E = \tfrac{1}{2}\dot{u}^2 - \tfrac{1}{2}|\gamma_2|^2 u^2 = \tfrac{1}{2}(\dot{u} + |\gamma_2| u)(\dot{u} - |\gamma_2| u) \tag{4.3}$$

To summarize, the normal mode $u(t)$ has the following remarkable properties:

(i) It satisfies a deterministic equation of motion (i.e., ξ does not appear in its equation of motion).

(ii) It determines uniquely the growing part $q_>(t)$ of the particle coordinate near $q = 0$ by

$$q_>(t) = \frac{\alpha}{\gamma_1 + |\gamma_2|}\left[u(t) + \frac{1}{|\gamma_2|}\dot{u}(t)\right] \tag{4.4}$$

An exponential growth of $q_>(t)$ to positive values corresponds to an exponential growth of $u(t)$ to positive values and vice versa.

(iii) Near the barrier at $q = 0$ the normal mode u is decoupled from the nongrowing part

$$q_<(t) = q(t) - q_>(t) \tag{4.5}$$

(iv) Near $q = 0$ its energy E is conserved.

(v) Its energy E has the usual kinetic part, with the effective mass still normalized to 1 by the choice of α in Eq. (4.1), and a potential energy part which describes a harmonic energy barrier at $u = 0$.

(vi) By (ii) and (v), the region $u > 0$ corresponds to the outside, and the region $u < 0$ corresponds to the inside, of the potential well.

For some purposes (e.g., in Section 6) it is convenient to fix the constant C in Eq. (4.1) by demanding that $u(t)$ transforms even under time reversal,

$$t \to -t$$

$$q \to q$$

$$\dot{q} \to -\dot{q}$$

To implement this requirement, we decompose the Gaussian noise $\xi(t)$ into two independent noise sources ξ_+, ξ_- of equal strength,

$$\xi(t) = \xi_+(t) + \xi_-(t) \tag{4.6}$$

$$\langle \xi_+(t)\, \xi_+(t') \rangle = \langle \xi_-(t)\, \xi_-(t') \rangle = \tfrac{1}{2} Q\delta(t-t'); \qquad \langle \xi_+(t)\, \xi_-(t' \rangle = 0 \tag{4.7}$$

which transform even and odd under time reversal, respectively,

$$t \to -t, \qquad \xi_+ \to \xi_+, \qquad \xi_- \to -\xi_-$$

Then the Laplace transforms $\hat{\xi}_+(p)$, $\hat{\xi}_-(p)$ of ξ_+, ξ_- are statistically independent and transform odd and even under time reversal, respectively.

With these prescriptions C is completely fixed and we may write, with $u(0) = u_0$, $\dot{u}(0) = \dot{u}_0$,

$$\begin{aligned} \alpha u_0 &= \gamma_1 q_0 + \hat{\xi}_-(|\gamma_2|) \\ \alpha \dot{u}_0 &= |\gamma_2|\, [\dot{q}_0 + \hat{\xi}_+(|\gamma_2|)] \end{aligned} \tag{4.8}$$

with

$$\begin{aligned} \langle \hat{\xi}_+(|\gamma_2|) \rangle &= \langle \hat{\xi}_-(|\gamma_2|) \rangle = 0 \\ \langle \xi_+(|\gamma_2|)\, \xi_-(|\gamma_2|) \rangle &= 0 \\ \langle \xi_+^2(|\gamma_2|) \rangle &= \langle \xi_-^2(|\gamma_2|) \rangle = \frac{Q}{4\, |\gamma_2|} \end{aligned} \tag{4.9}$$

5. A GENERAL FORMULA FOR THE ESCAPE RATE

Our goal is the determination of the average rate of the escape of the particle over the potential barrier.

If each particle crossing the barrier at $q = 0$ with positive velocity $\dot{q} > 0$ would actually escape, the average rate of escape would be simply given by the average current (number of particles per time) across $q = 0$ with $\dot{q} > 0$,

$$\tilde{\Gamma} = \int_0^\infty P(0, \dot{q})\, \dot{q}\, d\dot{q} \tag{5.1}$$

where $P(q, \dot{q})$ is the phase-space density of the particle. However, due to the action of stochastic forces, there is a certain probability that even after a particle has passed $q = 0$ with $\dot{q} > 0$ it suffers a random kick which sends it back to the potential well. This recrossing probability in general invalidates (5.1) as a rigorous equation and makes the actual escape rate Γ smaller than $\tilde{\Gamma}$.

As first noted in ref. 7, the recrossing problem has a very elegant solution if Γ is expressed in terms of the probability current of the unstable normal mode u. The reason is that near the top of the potential barrier, u satisfies a deterministic equation. Hence, if u has passed the top of the barrier at $u = 0$ in positive direction ($\dot{u} \geqslant 0$), it is impossible, within the linearized description valid near the top of the barrier, that recrossing occurs. Therefore, up to exponentially small terms due to recrossings from positive values of u outside the interval of linearity, we have

$$\Gamma = \int_0^\infty P_u(0, \dot{u})\, \dot{u}\, d\dot{u} \tag{5.2}$$

where $P_u(u, \dot{u})$ is the phase-space density of the unstable mode.

Following Kramers,[1] we are only interested in the case where particles are continuously supplied near the bottom of the potential well in such a way that the particle escape is precisely balanced on the average. Then a time-independent steady state results in which also $P_u(0, \dot{u})$ must be expressed by the single constant of the motion E, $P_u(u, \dot{u}) = P(E)$.

Hence, in the steady state, Eq. (5.2) is reduced to

$$\Gamma = \int_0^\infty P(E)\, dE \tag{5.3}$$

From our present point of view this simple expression is the main motivation for the definition of the unstable normal mode u in addition to $q_>$.

It is interesting to note that the expression (5.3) does not depend on the normalization constant α introduced in Eq. (4.1), as $P(E)\, dE$ is invariant under rescaling of E. Hence, α may be chosen arbitrarily for the purposes of calculating Γ.

6. KRAMER'S ESCAPE TIME FOR SUFFICIENTLY LARGE DAMPING

For sufficiently large damping we may assume that the probability density of the particle within the potential well comes into equilibrium with the noise source. For a sufficiently deep potential well this will always be the case for values of $q < 0$ sufficiently far away from $q = 0$, but the assumption breaks down for small dissipation, which therefore requires separate treatment in Section 8. Ignoring this difficulty in the present section, we assume that for $q<0$ we have the Maxwell–Boltzmann distribution

$$P_{\text{th}}(q, \dot{q}) = N \exp\left\{-\beta\left[\frac{\dot{q}^2}{2} + U(q)\right]\right\}, \qquad q<0 \tag{6.1}$$

with $\beta = 1/k_{\text{B}}T$, whose normalization factor N is determined by evaluating the normalization integral by steepest descent

$$N = \frac{\omega_0\beta}{2\pi} e^{+\beta U(q_m)} \tag{6.2}$$

where $U(q) = U(q_m) + \frac{1}{2}\omega_0^2(q-q_m)^2 + \cdots$ near the bottom of the potential well. In order to compute Γ, we have to determine the distribution $P_u(u, \dot{u})$. For this purpose we first specialize $P_{\text{th}}(q, \dot{q})$ to a small neighborhood of $q=0$, where it takes the form

$$P_{\text{th}}(q, \dot{q})\, dq\, d\dot{q} = \frac{\omega_0\beta}{2\pi} \exp(-\beta\Delta U) \exp\left[-\frac{\beta}{2}(\dot{q}^2 - \omega_b^2 q^2)\right] dq\, d\dot{q} \tag{6.3}$$

In the following we shall identify q, $\dot{q}$ in Eq. (6.3) with q_0, $\dot{q}_0$ in Eq. (4.8), which is permitted because P_{th} is time independent. In order to determine the distribution of u, $\dot{u}$, we need the joint distribution of q_0, $\dot{q}_0$ and $\hat{\xi}_+(|\gamma_2|)$, $\hat{\xi}_-(|\gamma_2|)$. As $\hat{\xi}_\pm(|\gamma_2|)$ depend on $\xi(t)$ only for $t>0$, these quantities are assumed to be statistically independent from q_0, $\dot{q}_0$ and we have the joint distribution

$$\begin{aligned} &P_{\text{th}}(q_0, \dot{q}_0, \hat{\xi}_+(|\gamma_2|), \hat{\xi}_-(|\gamma_2|)) \\ &\qquad = P_{\text{th}}(q_0, \dot{q}_0)\, W(\hat{\xi}_+(|\gamma_2|))\, W(\hat{\xi}_-(|\gamma_2|)) \end{aligned} \tag{6.4}$$

where $W(\xi)$ is a normalized Gaussian with mean square $\gamma/(2\,|\gamma_2|\,\beta)$.

Now we can write

$$\begin{aligned} P_{u\text{th}}(u, \dot{u}) = \int dq\, d\dot{q}\, d\hat{\xi}_+\, d\hat{\xi}_-\, P_{\text{th}}(q, \dot{q}, \hat{\xi}_+, \hat{\xi}_-) \\ \times \delta\left(u - \frac{\gamma_1 q + \hat{\xi}_-}{\alpha}\right) \cdot \delta\left(\dot{u} - \frac{|\gamma_2|}{\alpha}(\dot{q} + \hat{\xi}_+)\right) \end{aligned} \tag{6.5}$$

The integrals are easily carried out using the δ-functions and well-known properties of Gaussian integrals. The result is

$$P_{u\text{th}}(u, \dot{u}) = \frac{\omega_0\beta}{2\pi} \frac{2\alpha^2}{\omega_b(\gamma_1 + |\gamma_2|)} \exp(-\beta\Delta U) \exp\left[-\frac{2\beta\alpha^2 E}{|\gamma_2|\,(\gamma_1 + |\gamma_2|)}\right] \equiv P_{\text{th}}(E) \tag{6.6}$$

From Eq. (5.3) we obtain for the escape rate

$$\Gamma = \frac{\omega_0}{2\pi} \frac{|\gamma_2|}{\omega_b} e^{-\beta \Delta U} \tag{6.7}$$

which, as noted earlier, is independent of the choice of α. However, we note that $P_{u\text{th}}(u, \dot{u})$ is a Maxwell–Boltzmann distribution at the noise temperature T only if we choose α^2 as

$$\alpha^2 = \tfrac{1}{2} |\gamma_2| (\gamma_1 + |\gamma_2|) \tag{6.8}$$

Equation (6.7) is, of course, Kramers' result[1] valid for sufficiently large damping. In Kramers' treatment the result (6.7) does not follow from a thermal distribution (6.3). In fact, using a thermal distribution in Eq. (5.1) yields $\tilde{\Gamma} = (\omega_0/2\pi) \exp(-\beta \Delta U)$ (transition state theory), which is not correct if $|\gamma_2|$ and ω_b differ appreciably. Rather, Kramers' result is obtained from

$$\Gamma = \int_{-\infty}^{+\infty} P_K(0, \dot{q})\, \dot{q}\, d\dot{q} \tag{6.9}$$

with the nonthermal phase-space distribution he derived[1] for the region close to the top of the barrier

$$P_K(q, \dot{q}) = N \left(\frac{|\gamma_2|\, \beta}{2\pi\gamma} \right)^{1/2} \left\{ \exp\left[-\frac{\beta}{2} (\dot{q}^2 - \omega_b^2 q^2) \right] \right\} \times \int_{-\infty}^{\dot{q} - \gamma_1 q} dv \exp\left(-\frac{\beta}{2} \frac{|\gamma_2|}{\gamma} v^2 \right) \tag{6.10}$$

where N is given by Eq. (6.2). Below we shall give an alternative derivation of this distribution. In P_K particle velocities $\dot{q} < \gamma_1 q$ are strongly suppressed compared to the thermal distribution, which accounts for the fact that particles are mainly concentrated at negative values of q and cross the barrier primarily with positive velocities. In our preceding treatment this fact is automatically taken into account by Eqs. (5.2), (5.3), where only positive velocities $\dot{u} > 0$ enter for $u = 0$. The generalization of the latter statement for $u < 0$ (but small) is the restriction $\dot{u} \geqslant |\gamma_2|\, u$. This inequality specifies the smallest domain of phase space $(u, \dot{u})$ near the top of the potential barrier which contains the interior of the well $(u < 0, |\dot{u}| < |\gamma_2|\, u)$ and its boundaries and all trajectories coming in from negative values of $u(u < 0, \dot{u} > 0)$. Due to the boundary conditions of the escape problem all other domains of phase space must be empty. Thus, instead of Eq. (6.6) it is more appropriate to use in thermal equilibrium

$$P_u(u, \dot{u}) = P_{\text{th}}(E)\, \theta(\dot{u} - |\gamma_2|\, u) \tag{6.11}$$

where θ is the step function and $P_{\text{th}}(E)$ remains defined by Eq. (6.6). The result (6.7) for Γ remains, of course, unchanged by this modification. The argument of the step function appearing in Eq. (6.11) may be rewritten in q_0, $\dot{q}_0$, ξ_+, ξ_- with the help of Eq. (4.8). In fact, it is easy to see that Eq. (6.11) is a consequence of Eq. (6.5) if there we use, instead of P_{th}, the modified joint distribution

$$P_K(q_0, \dot{q}_0, \xi_+, \xi_-) = \theta(\dot{q}_0 - \gamma_1 q_0 + \xi_+ - \xi_-)\, P_{\text{th}}(q_0, \dot{q}_0, \xi_+, \xi_-) \tag{6.12}$$

which is the thermal joint distribution modified by the same step function as in Eq. (6.11). On the other hand, integrating the joint distribution (6.12) over ξ_+, ξ_- and identifying $v = \xi_- - \xi_+$, we immediately recover Kramers' distribution (6.10). Thus, apart from rederiving Kramers' distribution, we have found the corresponding joint distribution of q_0, $\dot{q}_0$ and the fluctuating forces $\xi_+(|\gamma_2|)$, $\xi_-(|\gamma_2|)$.

7. NONLINEAR COUPLING OF STABLE AND UNSTABLE DYNAMICS

As the escape rate is determined completely by the distribution of the energy in the unstable normal mode near the top of the potential barrier, it is desirable to introduce the normal mode amplitude u into the equation of motion of the Brownian particle. This can be done by separating $q(t)$ into an unstable part $q_>(t)$ and a stable part $q_<(t)$ as in Section 3, Eq. (4.5). Let us also split the particle's momentum in the same manner,

$$p(t) = \dot{q}(t) = p_>(t) + p_<(t) \tag{7.1}$$

We now wish to construct the linear coordinate transformation from q, p to $q_>$, $q_<$ which applies in the region close to the top of the barrier and which is then defined to hold unchanged throughout the particle's phase space. This linear transformation will be constructed explicitly in Section 9 for the case which includes friction with memory. Here we shall give only the final result for the special case of friction without memory. It is given by Eq. (7.1) with

$$\begin{aligned} p_>(t) &= |\gamma_2|\, q_>(t) \\ p_<(t) &= -\gamma_1 q_< - \int_t^{\infty} d\tau\, e^{|\gamma_2|(t-\tau)} \xi(\tau) \end{aligned} \tag{7.2}$$

It may be seen from Eqs. (7.2) that $q_<(t)$ and $p_<(t)$, just as $q_>(t)$ and $p_>(t)$ are correlated with the fluctuating force in the future. This should not be surprising: whether a particle eventually escapes ($q_> > 0$) or not ($q_> < 0$) depends on the fluctuating force in the future.

The next goal is to express the equations of motion in $q_>, q_<$,

$$\dot{q} = p$$
$$\dot{p} + \gamma p - \omega_b^2 q = -\frac{\partial U_1}{\partial q} + \xi \tag{7.3}$$

with $U_1(q)$ defined by

$$U(q) = U(0) - \tfrac{1}{2}\omega_b^2 q^2 + U_1(q) \tag{7.4}$$

Again, details of the calculation can be found in Section 9. We obtain

$$\dot{q}_> - |\gamma_2|\, q_> = -U_1'(q_> + q_<)/(\gamma_1 + |\gamma_2|)$$
$$\dot{q}_< + \gamma_1 q_< = U_1'(q_> + q_<)/(\gamma_1\, |\gamma_2|) - \int_t^\infty d\tau\, e^{|\gamma_2|(t-\tau)}\xi(\tau) \tag{7.5}$$

Let us now introduce the unstable mode u and a new stable variable $\bar{q}$ by

$$q_> = \bar{\alpha}(u + \dot{u}/|\gamma_2|)$$
$$q_< = \bar{q} + \bar{\alpha}(u - \dot{u}/|\gamma_2|) \tag{7.6}$$

with

$$\bar{\alpha} = \alpha/(\gamma_1 + |\gamma_2|) \tag{7.7}$$

Then Eqs. (7.5) take the form

$$\ddot{u} - |\gamma_2|^2\, u = -\frac{|\gamma_2|}{\alpha}\, U_1'(2\bar{\alpha}u + \bar{q}) \tag{7.8}$$

$$\dot{\bar{q}} + \gamma_1 \bar{q} = -\gamma\bar{\alpha}(u - \dot{u}/|\gamma_2|) - \int_t^\infty e^{|\gamma_2|(t-\tau)}\xi(\tau) \tag{7.9}$$

We can solve Eqs. (7.8), (7.9) iteratively for weak coupling between u and $\bar{q}$. Here weak coupling means that

$$(\gamma/2\gamma_1)(d \ln |U_1'(2\bar{\alpha}u + \bar{q})|/d \ln \bar{q}) \ll 1$$

i.e., we assume the damping to be sufficiently small and the potential to be sufficiently smooth for this condition to be satisfied. To zeroth order we take $\bar{q} = 0$ in Eq. (7.8) and obtain the first integral,

$$\frac{1}{2}(\dot{u}^2 - |\gamma_2|\, u^2) + \frac{|\gamma_2|}{2\alpha\bar{\alpha}}\, U_1(2\bar{\alpha}u) = E \tag{7.10}$$

We note that this expression for E reduces to Eq. (4.3) near the top of the barrier, where U_1 vanishes. From Eq. (7.10), $u(t)$ for given initial conditions can be determined by quadrature. This zeroth-order solution is inserted on the right-hand side of Eq. (7.9) and we obtain to first order

$$\begin{aligned}\bar{q}(t) &= C_1 e^{-\gamma_1 t} + C_2 e^{-|\gamma_2| t} \\ &+ \frac{1}{\gamma_1 + |\gamma_2|} \int_0^t d\tau (e^{-\gamma_1 (t-\tau)} - e^{-|\gamma_2|(t-\tau)})\, U_1'(2\bar{\alpha} u(\tau)) \\ &- \int_0^t d\tau \int_\tau^\infty d\tau'\, e^{-\gamma_1 (t-\tau) + |\gamma_2| (\tau - \tau')} \xi(\tau')\end{aligned} \tag{7.11}$$

with

$$C_2 = \bar{\alpha} \left(\frac{\dot{u}_0}{|\gamma_2|} - u_0 \right), \qquad C_1 + C_2 = \bar{q}(0) \tag{7.12}$$

For sufficiently weak coupling, higher order contributions will not be needed.

8. ESCAPE RATE FOR SMALL AND INTERMEDIATE DAMPING

Equations (7.8), (7.9) are similar in form to equations of motion recently derived for a Brownian particle coupled to a bath of oscillators by Grabert.[7] The main difference consists in the fact that our Eqs. (7.8), (7.9) are expressed entirely in terms of the parameters of the basic Langevin equation, while Grabert's equations (apart from treating a more general model including memory effects, which we shall consider in Section 9) contain the parameters of the microscopic model. In ref. 7 it was shown how a formula for $P(E)$ for a weak and intermediate damping can be obtained from the weak-coupling solutions, in our case Eqs. (7.10)–(7.12). The method of ref. 7 was invented by Mel'nikov[4] for the calculation of the distribution of the total energy of the particle for weak damping and noise. We now give a short account of this method and present the final result. Consider a particle which comes close to the top of the barrier, but without escaping. Let its u energy (7.10) there be E'. After one further round trip through the well, let its u energy be E and the conditional probability to find that value of E be $P(E/E')$. In the steady state the distribution $P(E)$ must be invariant,

$$P(E) = \int_{-\infty}^{0} P(E/E')\, P(E')\, dE' \tag{8.1}$$

Following Grabert,[7] we show below [Eqs. (8.8)–(8.15)] that $P(E/E')$ takes the form of a Gaussian valid for E, E' close to zero

$$P(E/E') = \frac{1}{(2\pi\sigma_E)^{1/2}} \exp\left[-\frac{(E - E' + \Delta E)^2}{2\sigma_E}\right] \tag{8.2}$$

where ΔE is the average loss of u energy after one round trip and σ_E is the mean-square of the fluctuations of that energy loss. It should be noted that the Gaussian form (8.2) was already used by Mel'nikov,[4] but it was assumed as an ansatz and not derived in ref. 4. The solution of Eq. (8.1) with Eq. (8.2) for E sufficiently far below 0 ($E \ll -\sqrt{\sigma_E}$) approaches the thermal form,

$$P_{\text{th}}(E) = \text{const} \cdot e^{-(2\Delta E/\sigma_E)E} \tag{8.3}$$

This form should coincide with the thermal distribution (6.6), i.e., we should have

$$\sigma_E = \frac{|\gamma_2|\,(\gamma_1 + |\gamma_2|)}{\alpha^2 \beta} \Delta E \tag{8.4}$$

which must be verified below, and the normalization constant in Eq. (8.3) must be chosen as

$$\text{const} = \frac{\omega_0 \beta}{2\pi} \frac{2\alpha^2 e^{-\beta \Delta U}}{\omega_b(\gamma_1 + |\gamma_2|)} \tag{8.5}$$

With the boundary condition (8.3), (8.5) the integral equation can be solved[4,7] and the result be substituted in Eq. (5.3). All E integrals are carried out by steepest descent. The resulting escape rate is then obtained in the form first given by Grabert,[7]

$$\Gamma = \frac{\omega_0\,|\gamma_2|}{2\pi\omega_b} \exp\left[\frac{1}{\pi}\int_{-\infty}^{+\infty} \frac{dy}{1+y^2} \ln(1 - e^{-\delta(1+y^2)/4})\right] \tag{8.6}$$

with

$$\delta = \frac{\Delta E}{k_B T} \frac{2\alpha^2}{|\gamma_2|\,(\gamma_1 + |\gamma_2|)} \tag{8.7}$$

For $\delta \gg 1$ and $\delta \ll 1$ the result (8.6) approaches Kramers' results[1] for sufficiently large and sufficiently small damping, but it also applies to the intermediate region, which was not covered by Kramers' theory.

It remains to calculate ΔE and to verify Eq. (8.4).

By Eq. (7.10) the time-dependent energy of the u mode is defined by

$$E(t)=\frac{1}{2}\left[\dot{u}^2(t)-|\gamma_2|^2 u^2(t)\right]+\frac{|\gamma_2|}{2\alpha\bar{\alpha}} U_1(2\bar{\alpha}u(t)+\bar{q}(t)) \tag{8.8}$$

Its change ΔE over one period t_p of the u mode is given by the work done by the $\bar{q}$ mode,

$$\Delta\varepsilon=\frac{|\gamma_2|}{2\alpha\bar{\alpha}}\int_0^{t_p} d\tau\, \dot{\bar{q}}(\tau)\, U_1'(2\bar{\alpha}u(\tau)+\bar{q}(\tau)) \tag{8.9}$$

We evaluate this expression to first order in the $(u, \bar{q})$ coupling, i.e., we neglect $\bar{q}$ in the argument of U_1' and insert the zeroth-order result for $u(\tau)$. Furthermore, assuming that ΔE does not change rapidly with E', we evaluate ΔE for $E'=0$, i.e., for the u trajectory with $t_p=\infty$ starting (at $t\to -\infty$) with $u_0=0$, $\dot{u}_0=0$ and coming back near the top of the barrier for $t\to +\infty$. Then $\Delta\varepsilon$ is obtained as the sum of a systematic part (the average ΔE) and a Gaussian noise term, which enters in Eq. (8.9) via the additive noise in $\dot{\bar{q}}$ Eq. (7.9). This proves the Gaussian form (8.2) with the average

$$\Delta E=-\langle\Delta\varepsilon\rangle=\frac{1}{2}\int_{-\infty}^{+\infty} d\tau \int_{-\infty}^{+\infty} d\tau'\, K(|\tau-\tau'|) \times U_1'(2\bar{\alpha}u(\tau))\, U_1'(2\bar{\alpha}u(\tau')) \tag{8.10}$$

where

$$K(|\tau|)=\frac{|\gamma_2|}{2\alpha^2}\left(\gamma_1 e^{-\gamma_1|\tau|}-|\gamma_2|\, e^{-|\gamma_2|\tau}\right) \tag{8.11}$$

Equation (8.10) can be evaluated if the form of the potential $U(q)$ is known. It can be seen from Eq. (8.11) that δ in Eq. (8.7) and Γ in Eq. (8.6) are independent of the choice of α. The mean square of the Gaussian fluctuations of the u energy

$$\sigma_E=\langle(\Delta\varepsilon)^2\rangle-(\Delta E)^2 \tag{8.12}$$

is obtained in the same approximation. Here only the noise contribution to $\dot{\bar{q}}(\tau)$ in Eq. (7.9) enters. We find

$$\sigma_E=\left(\frac{|\gamma_2|}{2\alpha\bar{\alpha}}\right)^2\int_{-\infty}^{+\infty} d\tau\int_{-\infty}^{+\infty} d\tau'\, C(|\tau-\tau'|)\, U_1'(2\bar{\alpha}u(\tau))\, U_1'(2\bar{\alpha}u(\tau')) \tag{8.13}$$

with

$$C(|\tau-\tau'|)=\frac{d}{d\tau}\frac{d}{d\tau'}\int_{-\infty}^{\tau} d\tau_1 \int_{-\infty}^{\tau'} d\tau_2 \int_{\tau_1}^{\infty} d\tau_3 \int_{\tau_2}^{\infty} d\tau_4 \langle \xi(\tau_3)\,\xi(\tau_4)\rangle$$
$$\times \exp[-\gamma_1(\tau+\tau'-\tau_1-\tau_2)+|\gamma_2|\,(\tau_1+\tau_2-\tau_3-\tau_4)] \qquad (8.14)$$

Using the δ correlation of the noise and evaluating the integrals, we find

$$C(|\tau-\tau'|)=\frac{1}{2\beta(\gamma_1+|\gamma_2|)}\,(\gamma_1 e^{-\gamma_1|\tau-\tau'|}-|\gamma_2|\,e^{-|\gamma_2|\cdot|\tau-\tau'|}) \qquad (8.15)$$

It can now be verified that σ_E is indeed given by Eq. (8.4).

9. FRICTION WITH MEMORY

The method we have presented works also after including dissipation with memory. We briefly indicate the generalizations which are necessary. For an explicit example see ref. 8.

The Langevin equation reads

$$\ddot{q}+\int_0^t d\tau\,\gamma(t-\tau)\,\dot{q}(\tau)+\frac{\partial U}{\partial q}=\xi(t) \qquad (9.1)$$

with

$$\langle \xi(t)\,\xi(t')\rangle = k_B T\gamma(t-t') \qquad (9.2)$$

Near the barrier the Langevin equation can again be linearized and solved by Laplace transformation,

$$\hat{q}(s)=\frac{\hat{\xi}(s)+\dot{q}(0)+[s+\hat{\gamma}(s)]\,q(0)}{s^2+\hat{\gamma}(s)\,s-\omega_b^2} \qquad (9.3)$$

We define $|\gamma_2|$ by the positive root of

$$|\gamma_2|^2+|\gamma_2|\,\hat{\gamma}(|\gamma_2|)-\omega_b^2=0 \qquad (9.4)$$

and γ_1 by $\omega_b^2=\gamma_1\,|\gamma_2|$. Then we decompose

$$\hat{q}(s)=\hat{q}_>(s)+\hat{q}_<(s) \qquad (9.5)$$

with

$$\hat{q}_>(s)=\frac{\hat{\xi}(|\gamma_2|)+\dot{q}(0)+\gamma_1 q(0)}{\lambda(s-|\gamma_2|)}$$
$$\lambda=\gamma_1+|\gamma_2|\,[1+d\hat{\gamma}(|\gamma_2|)/d\,|\gamma_2|] \qquad (9.6)$$

and

$$\hat{q}_<(s) = \frac{\hat{\xi}(s) - \hat{\xi}(|\gamma_2|) + [s + \hat{\gamma}(s) - \gamma_1]\, q(0)}{s^2 + \hat{\gamma}(s)\, s - \omega_b^2} + \hat{K}(s)[\hat{\xi}(|\gamma_2|) + \dot{q}(0) + \gamma_1 q(0)] \tag{9.7}$$

where

$$\hat{K}(s) = \frac{1}{s^2 + \hat{\gamma}(s)\, s - \omega_b^2} - \frac{1}{\lambda(s - |\gamma_2|)} \tag{9.8}$$

The unstable normal mode u is defined by Eq. (4.1) with $q_>, |\gamma_2|, \gamma_1$ redefined as above. In fact, the results of Sections 4–7 can all be taken over using these redefinitions, $\gamma \equiv \hat{\gamma}(|\gamma_2|)$, and the new correlation function of the fluctuating forces

$$\langle \hat{\xi}(s)\, \hat{\xi}(s') \rangle = \frac{1}{\beta} \frac{\hat{\gamma}(s) + \hat{\gamma}(s')}{s + s'} \tag{9.9}$$

Let us now construct a linear transformation from q, p to $q_>$, $q_<$. It is most convenient to consider the Laplace transforms. We have, near the top of the barrier,

$$\hat{q}(s) = \hat{q}_>(s) + \hat{q}_<(s) \tag{9.10}$$

$$\hat{p}(s) = s\hat{q}_>(s) + s\hat{q}_<(s) - q(0) \tag{9.11}$$

Equation (9.11) still contains the constant of integration $q(0)$ and is therefore not yet a transformation of coordinates. However, we can eliminate $q(0)$ by solving Eqs. (9.6), (9.7) for $q(0)$ and $[\gamma_1 q(0) + \dot{q}(0) + \hat{\xi}(|\gamma_2|)]$ in terms of $q_>(s)$, $q_<(s)$ and inserting the result in Eq. (9.11). We obtain, after some algebra,

$$\hat{p}(s) = \frac{|\gamma_2|\, [1 + \hat{\gamma}'(|\gamma_2|)](s - |\gamma_2|)\, \hat{q}_>(s) - \gamma_1(s - |\gamma_2|)\, q_<(s) - \hat{\xi}(|\gamma_2|) + \hat{\xi}(s)}{s + \hat{\gamma}(s) - \gamma_1} \tag{9.12}$$

Equations (9.10), (9.12) now define the desired change of coordinates, which we extend, by definition, to the entire phase space. Equations (7.2) are obtained as special cases for $\hat{\gamma}(p) = \gamma$. Let us next derive the equations of motion satisfied by $q_>, q_<$. From $\dot{q} = p$ we obtain

$$[s^2 + s\hat{\gamma}(s) - \omega_b^2]\, \hat{q}_<(s) + \hat{q}_>(s) = [(s - |\gamma_2|)\, \lambda]\, \hat{q}_>(s) + \hat{\xi}(s) - \hat{\xi}(|\gamma_2|) + [s + \hat{\gamma}(s) - \gamma_1]\, q_0 \tag{9.13}$$

and Eq. (9.1) leads to

$$\begin{aligned}[s^2+s\hat{\gamma}(s)-\omega_b^2][q_>(s)+q_<(s)]\\ = -\hat{U}_1'(s)+\hat{\xi}(s)+\dot{q}_0+[s+\hat{\gamma}(s)]\,q_0\end{aligned} \tag{9.14}$$

with

$$\begin{aligned} U_1(q) &= U(q)+\tfrac{1}{2}\omega_b^2q^2-U(0)\\ \hat{U}_1'(s) &= \int_0^\infty dt\,e^{-st}U_1'(q(t))\\ U_1'(q) &= dU_1(q)/dq\end{aligned} \tag{9.15}$$

From Eqs. (9.13), (9.14), we can derive, in real time,

$$\dot{q}_> - |\gamma_2|\,q_> = -U_1'(q_<+q_>)/\lambda \tag{9.16}$$

where we used

$$\dot{q}(0)+\gamma_1 q(0)+\hat{\xi}(|\gamma_2|)=\lambda q_>(0) \tag{9.17}$$

which follows from Eqs. (9.6), to absorb a constant inhomogeneity in the initial condition for $q_>$. Using Eq. (9.16) in the first or second of Eqs. (9.13), (9.14), we obtain

$$\begin{aligned}\hat{q}_<(s) = &-\left[\frac{1}{s^2+s\hat{\gamma}(s)-\omega_b^2}-\frac{1}{\lambda(s-|\gamma_2|)}\right]\hat{U}_1'(s)\\ &+\frac{\hat{\xi}(s)+\dot{q}_0+[s+\hat{\gamma}(s)]\,q_0}{s^2+s\hat{\gamma}(s)-\omega_b^2}-\frac{\hat{\xi}(|\gamma_2|)+\dot{q}_0+\gamma_1q_0}{\lambda(s-|\gamma_2|)}\end{aligned} \tag{9.18}$$

Equations (7.5) are a special case of Eqs. (9.16), (9.18) for $\hat{\gamma}(s)=\gamma$.

As in Section 7, it is convenient to make the further change (7.6), (7.7), which now read

$$\begin{aligned}\hat{q}_>(s) &= \frac{\alpha[(s+|\gamma_2|)\,\hat{u}(s)-u(0)]}{|\gamma_2|\,\lambda}\\ \hat{q}_<(s) &= \hat{\hat{q}}(s)-\frac{\alpha[(s-|\gamma_2|)\,\hat{u}(s)-u(0)]}{|\gamma_2|\,\lambda}\end{aligned} \tag{9.19}$$

Here $u(0)$ is an arbitrary constant, connected to the arbritrary constant C in Eq. (4.1), which enters because (7.6), (7.7) are differential equations. We obtain the equations of motion

$$\ddot{u} - |\gamma_2|^2 u = -\frac{|\gamma_2|}{\alpha} U_1' \left(\frac{2\alpha u}{\lambda} + \bar{q} \right)$$

$$\begin{aligned} \hat{\bar{q}} = &- \left[\frac{1}{s^2 + s\hat{\gamma}(s) - \omega_b^2} - \frac{2|\gamma_2|}{\lambda(s^2 - |\gamma_2|^2)} \right] \hat{U}_1'(s) \\ &+ \frac{\hat{\xi}(s) + \dot{q}_0 + [s + \hat{\gamma}(s)]\, q_0}{s^2 + s\hat{\gamma}(s) - \omega_b^2} - \frac{\hat{\xi}(|\gamma_2|) + \dot{q}_0 + \gamma_1 q_0}{\lambda(s - |\gamma_2|)} \\ &+ \frac{\alpha[\dot{u}(0) - |\gamma_2|\, u(0)]}{\lambda(s + |\gamma_2|)} \end{aligned} \tag{9.20}$$

The further calculation is carried out most conveniently for the Laplace-transformed variables and using Eq. (9.9), but otherwise it proceeds as in Sections 7 and 8 with essentially the same results, except that now

$$\Delta E = -\langle \Delta \varepsilon \rangle = \frac{1}{2} \int_{-\infty}^{+\infty} d\tau \int_{-\infty}^{+\infty} d\tau'\, K(|\tau - \tau'|)\, U_1'\left(\frac{2\alpha u(\tau)}{\lambda} \right) U_1'\left(\frac{2\alpha u(\tau')}{\lambda} \right)$$

$$K(|\tau|) = \frac{\lambda}{2\alpha^2} \int \frac{ds}{2\pi i} e^{s|\tau|} \left[\frac{s}{s^2 + s\hat{\gamma}(s) - \omega_b^2} - \frac{2|\gamma_2|\, s}{\lambda(s^2 - |\gamma_2|^2)} \right] \tag{9.21}$$

in agreement with the result of refs. 7 and 8.

10. CONCLUDING REMARKS

Equations (8.6)–(8.8), (9.21) constitute the final result, which agrees with the result obtained from a corresponding microscopic model in refs. 7 and 8, but which has been derived here for the first time within a purely macroscopic approach. The essential step was the introduction of a normal mode amplitude in Eq. (4.1) mixing the particle variables q, $\dot{q}$ and the noise source in such a way that a new quantity E appeared which is conserved near the top of the barrier. The same normal mode, mixing particle variables and bath-oscillator variables, also appears in the microscopic calculation.[7,8] Having succeeded in reformulating this idea in a manner which is manifestly independent of microscopic detail, we can now proceed to apply this method to Langevin equations of more general form. In particular, the essential new idea of this paper, the use of variables which mix the macroscopic and the noise variables of the Langevin equation, might be a useful new tool for their analysis.

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