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LETTER TO THE EDITOR

Thermally activated escape of driven systems: the activation energy

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Abstract.

Thermally activated escape in the presence of periodic external field is investigated theoretically and through analog experiments and digital simulations. The observed variation of the activation energy for escape with driving force parameters is accurately described by the *logarithmic susceptibility* (LS). The frequency dispersion of the LS is shown to differ markedly from the standard linear susceptibility. Experimental data on the dispersion are in quantitative agreement with the theory. Switching between different branches of the activation energy is demonstrated for a nonsinusoidal (biharmonic) force.

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Thermally activated escape plays a fundamentally important role in a variety of phenomena, ranging from diffusion in solids and on solid surfaces to chemical reactions. It is therefore important to find ways of controlling escape rates. One possible approach is through the application of an ac field, which can sometimes give rise to a very strong response. The underlying mechanism is readily understood for low frequency (adiabatically slow) driving, where the system remains in quasi-equilibrium under the instantaneous value of the driving force. For a system in thermal equilibrium, the probability of a large fluctuation is given by

$$W \propto \exp[-R/kT]. \tag{1}$$

We will be specifically interested in activated escape, in which case R is the activation energy of escape. The driving force modulates the value of R quasistatically and, even where the modulation amplitude A is small compared to R, it may still substantially exceed kT, in which case W will be changed exponentially strongly. We emphasize that the change of the activation energy is *linear* in the field amplitude in this case.

A different picture might be expected for higher field frequencies, where the driving becomes nonadiabatic. One might suppose that any change in R would depend on the *intensity* I of the driving field rather than just be linear in the field *amplitude* $A \propto I^{1/2}$, i.e. that the field would give rise to an effective "heating" of the system. Such an effect has indeed been discussed and observed for low field intensities [1, 2, 3, 4]. A complete theoretical analysis is significantly more complicated in this case, since one may no longer assume that the system is in thermal equilibrium, so that the activation energy R in Eq. (1) may not be set equal to the height of the free-energy barrier. Numerical results in relation to this problem have been obtained for different models: see Ref. [5] and references therein.

For high-frequency driving, the quantity of primary interest is the period-averaged escape rate $\bar{W}$. Recently it was suggested theoreticallly [6, 7] that, for high-frequency driving $\ln \bar{W}$ should still be linear in the field amplitude A, i.e. that the activation energy R in the equation (1) for $\bar{W}$ should – quite counterintuitively – be linear in A. The proportionality coefficient was called the *logarithmic susceptibility* (LS).

Just like the conventional linear susceptibility, the LS relates the response of the system in the presence of external driving to the system dynamics in thermal equilibrium in the absence of the driving field. Also, in common with the conventional susceptibility, the LS should display frequency dispersion. This dispersion provides a means for selective control of escape rates.

The goals of this Letter are to test the very idea of the LS, thereby providing a solid experimental basis for understanding the effect of the ac field on escape rates, and to develop a general theory of the *frequency dispersion* of the LS. The theory exploits acausal character of the LS for escape. The measurements are done through analog electronic experiments [8] and digital simulations [9] of the escape rate in a driven system. Results of such experiments are reported below for a broad range of frequencies and amplitudes of the driving field, as well as for a nonsinusoidal field. We provide detailed comparisons of the data with the theory. An additional important goal of the paper is to show that, given the system, the LS can be measured directly by experiment. This paves the way for using ac fields for selective control of escape rates (and also of diffusion and nucleation [6, 7]), even where the dynamics of the system are not known and have to be determined experimentally.

We consider fluctuations of an overdamped Brownian particle driven by a periodic (but not necessarily sinusoidal) force $F(t)$ and white Gaussian noise $\xi(t)$,

$$\dot{q} = K(q,t) + \xi(t), \quad K(q,t) = -U'(q) + F(t), \tag{2}$$

where $\langle \xi(t)\xi(t')\rangle = 2D\delta(t-t')$. The noise intensity $D = kT$ if relaxation and fluctuations are due to coupling to a thermal bath at temperature T.

The model (2) is used in many scientific contexts (see e.g. [10, 11, 12] and references therein). We assume that the potential $U(q)$ in (2) has a metastable minimum from which the system can escape. For convenience, experimental data are obtained for a potential with two wells, so that for $F(t) = 0$ the system is bistable and can switch between the stable states due to fluctuations.

The idea underlying the theory of the LS [6, 7] is that, although the motion of the fluctuating system is random, in a large rare fluctuation from a metastable state to a remote state, or in a fluctuation resulting in escape, the system is most likely to move along a particular trajectory known as the optimal, or most probable path (see [13, 14, 15, 16, 17] and references therein). This path provides a minimum to the functional

$$R[q] = \frac{1}{4}\int_{-\infty}^{\infty} dt\,[\dot{q} - K(q,t)]^2 \tag{3}$$

The minimum is taken over all instanton-type [18] trajectories which start for $t \to -\infty$ from the stable periodic state $q_a(t)$ of the dynamical system $\dot{q} = K(q,t)$, and approach as $t \to \infty$ the unstable periodic state of this system $q_b(t)$.

In the absence of driving ($F = 0$) the variational problem has a simple solution $q^{(0)}(t)$, which is given by the equation

$$\dot{q}^{(0)} = U'(q) \tag{4}$$

Clearly, the most probable escape path (4) is just the time-reversed path from the unstable steady state at the top q_b of the potential barrier $U(q)$ down to the potential minimum at q_a [19, 20]. The value of $R[q]$ in this case is equal $U(q_b) - U(q_a)$.

If the periodic driving force $F(t) = \sum_k F_k \exp(ik\omega t)$ is comparatively weak, the leading-order correction δR to the activation energy of escape can be evaluated along the unperturbed most probable escape path $q^{(0)}(t)$

$$\delta R = \min_{t_c} \delta R(t_c),\ \delta R(t_c) = \sum_k F_k \tilde{\chi}(k\omega) e^{ik\omega t_c},$$
$$\tilde{\chi}(\omega) = -\int_{-\infty}^{\infty} dt\, \dot{q}^{(0)}(t) e^{i\omega t}. \tag{5}$$

Here, $\tilde{\chi}(\omega)$ is the LS for escape. It is given [6, 7] by the Fourier transform of the velocity along the most probable escape path $q^{(0)}(t)$ in the absence of driving ($F(t) = 0$).

Eq. (5) can be understood in terms of the *work* that the field does on the system as it moves along the optimal path. One may expect this work to be related to the field-induced change in the activation energy R for the corresponding large fluctuation. This change is *linear* in the field, provided that the field-induced change of the optimal path itself remains small.

An important feature of Eq. (5) is the minimization over t_c. It corresponds to choosing the position of the center of the instantonic escape path $q^{(0)}(t - t_c)$ so as to maximize the work the field $F(t)$ does on the system along it.

Unlike the standard linear susceptibility [21] which, on causality arguments, is given by a Fourier integral over time from 0 to ∞, the LS $\tilde{\chi}(\omega)$ is given by an integral from $-\infty$ to ∞. The analytic properties of $\tilde{\chi}(\omega)$ therefore differ from those of the standard susceptibility, and in particular their high-frequency asymptotics are *qualitatively* different. The standard susceptibility for damped dynamical systems decays as a power law for large ω (e.g., as $1/[U''(q_a) - i\omega]$, for the model (2)). In contrast, from (5), the LS decreases *exponentially* fast.

Asymptotic behavior of $\tilde{\chi}(\omega)$ for large positive ω can be found by shifting the contour of integration in (5) over t from the real axis to the upper half of the complex t plane, as shown in Fig. 1. The function $\dot{q}^{(0)}(t)$ (4) has poles or branching points at Im $t \neq 0$, which correspond to the singularities of $U'(q)$ in the complex q-plane, i.e. for Im $q \neq 0$. For large ω, the major contribution to $\tilde{\chi}(\omega)$ is determined by the parts of the integration contour in Fig. 1 near the singularity of $\dot{q}^{(0)}(t)$ with the smallest value of Im $t = \tau_p$. Near the singular point one can change from integrating over t to integrating over q, which gives for $\exp(\omega\tau_p) \gg 1$

$$\tilde{\chi}(\omega) = Me^{-|\omega|\tau_p}, \quad \tau_p = \min\left|\mathrm{Im}\int dq/U'(q)\right|. \tag{6}$$

Here, the integral is taken from any point in the interval (q_a, q_b) to the (complex) position q_p of the appropriate singularity of $U'(q)$ corresponding to the singularity of $\dot{q}^{(0)}(t - t_c)$ at Im $t = \tau_p$. The prefactor M depends on the form of $U(q)$ near q_p. In particular, for a polynomial potential ($|q_p| \to \infty$) with $U(q) = Cq^n/n$ for $|q| \to \infty$, we have

$$|M| = 2\pi|\omega/C|^{\nu}|\nu|^{\nu+1}/\nu!, \ \nu = 1/(n-2). \tag{7}$$

This expression applies also for finite $|q_p|$, with $U(q) \approx C/\mu(q - q_p)^{\mu}$ for $q \to q_p$, if n in (7) is replaced by $-\mu$: note that $|M|$ then decreases with increasing ω.

The notion of the LS applies not only to escape, but also to the probability of a large fluctuation to any given state, in which case the integral over time in (5) is taken to the moment of arrival in this state, and there is no minimization over t_c [7]. The analytic properties of this LS are similar to those of the standard linear susceptibility.

We have investigated the escape rate for a driven Duffing oscillator with the potential $U(q) = -q^2/2 + q^4/4$. If the state occupied initially is $q_a = -1$, we obtain from (5)

$$\dot{q}^{(0)}(t) = \exp(2t)[1 + \exp(2t)]^{-3/2}. \tag{8}$$

and therefore the LS

$$\tilde{\chi}(\omega) = -\pi^{-1/2}\Gamma(\frac{1-i\omega}{2})\Gamma(\frac{2+i\omega}{2}). \tag{9}$$

It follows from (9) that $\tilde{\chi}(0) = -1$, and the LS decays monotonically with increasing ω, with $\tau_p = \pi/2, M = -(1+i)(\pi\omega)^{1/2}$ in (6). Already for $\omega > 0.7$ the asymptotic behavior of $|\tilde{\chi}(\omega)|$ given by (6) becomes very close to the exact result Eq. (9) which is shown with solid line in the inset of Fig. 2.

The period-averaged rate of escape from the stable state q_a can be found conveniently in experiment from measurements of the mean time $\langle t \rangle$ to reach a point q_e well behind the barrier top (so that the probability of returning to the vicinity of q_a is negligibly small). Our main quantity of interest is the field-dependent correction to $\bar{W} = 1/\langle t \rangle$. It is given by $\exp(-\delta R/D)$ for $|\delta R| \gg D$ [6, 7, 22]. For a sinusoidal driving force, the correction to the activation energy of escape (5) is $\delta R = -2|F_1\tilde{\chi}(\omega)|$.

To test these predictions, we have built an analog electronic model [8] of (2) for the double-well Duffing potential. We drive it with zero-mean quasi-white Gaussian noise from a shift-register noise generator, digitize the response $q(t)$, and analyse it with a digital data processor. We have also carried out a complementary digital simulation, using a high-speed pseudo-random generator [9].

The analogue and digital measurements of R involved noise intensities $0.028 < D < 0.036$ and $0.020 < D < 0.028$ respectively; the lowest (real time [8]) driving frequency used was 460 Hz. The results are plotted in Fig. 2. The major observation is that, as predicted, R is indeed *linear* in the force amplitude ($R = 1/4$ for $F = 0$). The slope yields the absolute value of the LS. Its frequency dependence, a fundamental characteristic of the original equilibrium system, is compared with the theoretical predictions in the inset of Fig. 2.

The results demonstrate that the variation of the activation energy with field can be well described analytically, for a wide range of parameter values, in terms of the LS. We note however a small deviation from the theory at small amplitudes of the external drive, and the consequent systematic shift of the experimental and numerical points above the theory (solid line). This deviation arises as a result of the finite noise intensities used in the experiment, and the fact that the $D \to 0$ limit of the theory breaks down for amplitudes F of the external driving for which $|\chi F|/D$ is small; it can be accounted for by an extension [22] of the theory taking account of changes in the prefactor.

We now discuss some of the new effects that are to be expected [6] when the driving field is non-sinusoidal. They are related to the minimization over t_c in (5), which is what makes the logarithm of the escape rate a nonanalytic function of $F(t)$ in the $D \to 0$ limit. We can apply the theory (5) to describe the dependence of the activation energy on field parameters. In particular, we seek experimentally the *switching* between escape paths that is predicted [6] for a simple form of nonsinusoidal driving: the biharmonic field. We took $F(t) = 0.1\cos(1.2t) + 0.3\cos(2.4t + \phi_0)$ and investigated the effect of altering the phase difference ϕ_0 between the two sinusoidal components. For a field of this kind, $\delta R(t_c)$ (5) may have two local minima; but the activation energy will of course correspond to its *absolute* minimum. Thus, as ϕ_0 is changed, the escape path will switch from being determined by one local minimum to being determined by the other, analogous to a first order phase transition in which δR and t_c play the roles of the free energy and the order parameter, respectively.

This phenomenon can be demonstrated experimentally by direct observation of the two different escape paths* providing the two local minima of $\delta R(t_c)$. Within a critical range of ϕ_0, the two escape paths should coexist and be observable experimentally: by variation of the phase difference near its critical value within this range, one should observe switching between the two different escape paths. The effect is clearly evident in the analogue data of Fig. 3(a) and (b): a small change in ϕ_0 is sufficient to switch the predominant escape path from $\phi \simeq 1$ in (a) to $\phi \simeq 5$ in (b).

It follows from the above analysis that the absolute value of the logarithmic susceptibility can be recovered from measurements of the correction δR to the escape activation energy at different frequencies of a sinusoidal driving field. The *phase* of the LS $\arg\tilde{\chi}(\omega)$ can be found by measuring δR for a driving field with more than one harmonic. In particular, for biharmonic driving with period $2\pi/\omega$, we see from Eq. (5) that δR depends on the phase of LS in terms of the factor $\Theta(\omega) = 2\arg\tilde{\chi}(\omega) - \arg\tilde{\chi}(2\omega)$. The solution of this functional equation for $\arg\tilde{\chi}(\omega)$, with the boundary condition $\arg\chi(0) = 0$, has the form

$$\arg\tilde{\chi}(\omega) = \omega t_c + \sum_{k=0}^{\infty} 2^{-k-1}\Theta(2^k\omega). \tag{10}$$

This expression relates $\arg\tilde{\chi}(\omega)$ to the values of Θ at the subharmonics $2^{-k}\omega$ of the frequency ω (due to analyticity of $\chi(\omega)$ at $\omega \to 0$, the function $\Theta(\omega)$ is quadratic in ω for $\omega \to 0$, and therefore the series (10) converges).

In conclusion, we have shown experimentally that thermally activated escape under nonequilibrium conditions can be understood in terms of the logarithmic susceptibility, and that the latter is a physically observable quantity: the field-induced change of the activation energy for escape is *linear* in the field amplitude [6, 7] even where the frequency of the field exceeds the reciprocal relaxation time of the system and substantially exceeds the escape rate. The LS relates the probability of large fluctuations in the presence of an external field to the relaxational dynamics in thermal equilibrium. We have shown that the LS for escape displays frequency dispersion which is qualitatively different from that of the conventional linear susceptibility. We have also verified experimentally the predicted [6] switching between different branches of the activation energy as a function of the field parameters for biharmonic driving: adjustment of its phase (alone) is sufficient to select the escape path.

* Coexistence of different escape paths in nonequilibrium systems has been widely discussed. See e.g. [23, 24, 25] for theory, and [20, 26] for theory and experimental tests.

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Figure captions

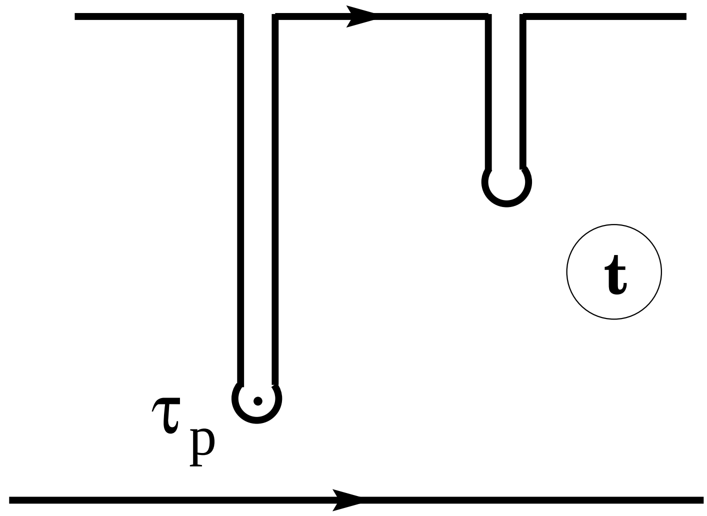

Figure 1. Contour of integration over time in (5) for the analysis of the behavior of the logarithmic susceptibility $\tilde{\chi}(\omega)$ for large positive ω; τ_p is the smallest imaginary value of t where $\dot{q}^{(0)}(t)$ has a singularity.

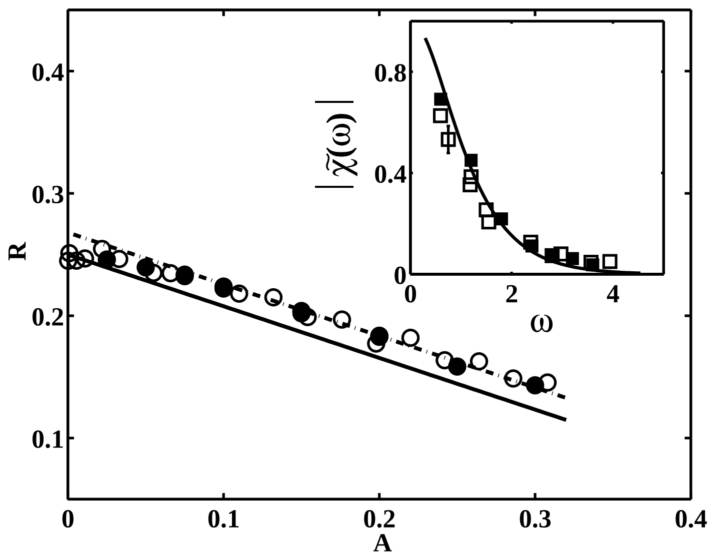

Figure 2. The dependence of the activation energy R on the amplitude A of the harmonic driving force $F(t) = A\cos(1.2t)$ as determined by electronic experiment (open circles), numerical simulations (filled circles) and analytic calculation (solid line) based on (5); the dash-dot line is a guide to the eye. Inset: the absolute value of the LS of the system $|\tilde{\chi}(\omega)|$ (5) measured (open and filled squares for experiment and numerical simulation, respectively) and calculated (full curve) as a function of frequency ω.

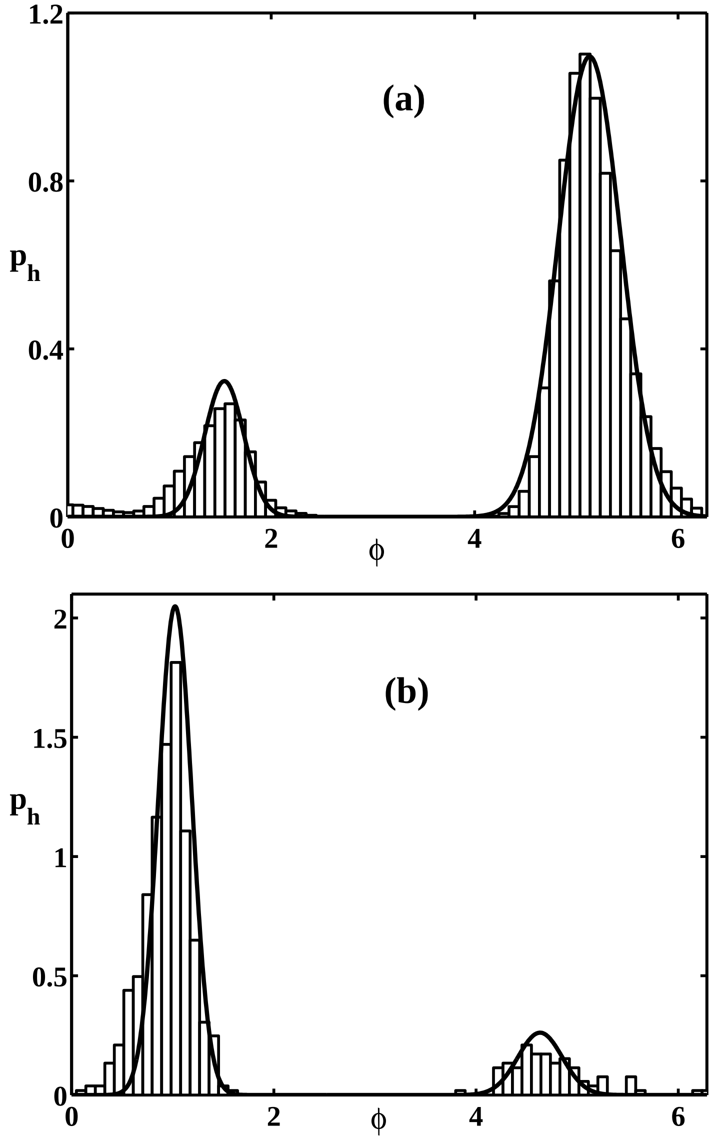

Figure 3. Distributions of the phase ϕ at which escape paths from the attractor at $q = -1$ cross a line at $q = -0.5$, measured in the analogue electronic experiment for two phase differences of the biharmonic driving force close to the critical value: (a) $\phi_0 = 3.04$; and (b) $\phi_0 = 4.04$. It is evident that, wihin the critical range, a tiny change in ϕ_0 is sufficient to cause switching of the dominant escape path.