

CONTROLLING ACTIVATED PROCESSES

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The rates of activated processes, such as escape from a metastable state and nucleation, are exponentially sensitive to an externally applied field. We describe how this applies to modulation by high-frequency fields and illustrate it with experimental observations. The results may lead to selective control of diffusion in periodic potentials, novel control mechanisms for crystal growth, and new separation techniques.

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1. Introduction

Activated processes are responsible for large qualitative changes in broad classes of systems. A well-known example is escape from a potential well, in which fluctuations carry the system over a potential barrier. Activated escape underlies diffusion in crystals, protein folding, and provides a paradigm for activated chemical reactions. Another example is nucleation in phase transitions. It would be advantageous to control the probabilities of activated processes by applying a comparatively weak external force. The idea is that the force need not be solely responsible for driving the system over the barrier; it only must appropriately influence fluctuations.

A familiar phenomenon which has elements of control of activated processes is stochastic resonance (SR) [1]. In SR, an adiabatic modulation of the system parameters by a slowly varying field is usually assumed. The strong effect of the field can be readily understood in this case, if one notices that the probability of a thermally activated process is $W \propto \exp(-R/k_B T)$, where R is the activation energy (the barrier height for escape from a potential well). Even a comparatively small field-induced modulation δR of the activation energy, $|\delta R| \ll R$, greatly affects W provided $|\delta R| > k_B T$, with $\ln W$ being linear in the modulation amplitude.

In contrast, one might expect that a high-frequency field would just “heat up” the system by changing its effective temperature. The rate W would then be incremented by a term proportional to the field intensity I rather than the amplitude

$A \propto I^{1/2}$. This is indeed the case in the weak-field limit [2,3]. However, one may ask what happens if the appropriately weighted field amplitude is not small compared to the fluctuation intensity (temperature).

Recent results [4–7] show that, counter-intuitively, for high-frequency driving the change of $\ln W$ is linear in A , over a broad range of A . The exponential effect of nonadiabatic driving leads to a number of new phenomena not encountered in SR, including resonant (in the field frequency) rate enhancement. This provides the basis for much of the selectivity and flexibility in controlling fluctuations, as we now outline.

2. General formulation

One can effectively control activated processes because, although they happen at random, the trajectories of the system in an activated process are close to a specific trajectory. The latter is called the optimal path for the corresponding process [8]. The effect of the driving field accumulates along the optimal path, giving rise to a linear-in-the-field correction to the activation energy R . It can be calculated if the fluctuational dynamics of the system is known. Alternatively, response to the driving can be found experimentally, and in fact used to investigate the system dynamics away from the metastable state.

A fairly general case in which the field effect can be evaluated and insight gained into the underlying mechanism is a dynamical system driven by a stationary colored Gaussian noise $f(t)$ with a power spectrum $\Phi(\omega)$ of arbitrary shape [9]. The Langevin equation of motion is of the form:

$$\dot{q} = K(q; t) + f(t), \quad K(q; t) = K_0(q) + F(t), \quad F(t + \tau_F) = F(t), \quad (1)$$

where τ_F is the period of the driving force $F(t)$.

For small characteristic noise intensity $D = \max \Phi(\omega)/2$, the system mainly performs small fluctuations about its periodic metastable state $q_a(t)$. Large fluctuations, like those leading to escape from the basin of attraction to q_a , require large bursts of $f(t)$ which would overcome the restoring force K . The probability densities of large bursts of $f(t)$ are exponentially small, $\propto \exp[-(2D)^{-1} \int dt dt' f(t) \hat{\mathcal{F}}(t-t') f(t')]$, and exponentially different depending on the form of $f(t)$ [$\hat{\mathcal{F}}(t)$ is given by the Fourier transform of $2D/\Phi(\omega)$]. Therefore for any state q_f into which the system is brought by the noise at time t_f , there exists a realization $f(t) = f_{\text{opt}}(t|q_f, t_f)$ which is exponentially more probable than the others. This optimal realization and the corresponding optimal path of the system $q_{\text{opt}}(t)$ provide the minimum to the functional

$$\mathcal{R}[q(t), f(t)] = \frac{1}{2} \iint dt dt' f(t) \hat{\mathcal{F}}(t-t') f(t') + \int dt \lambda(t) [\dot{q} - K(q; t) - f(t)] \quad (2)$$

(the integrals are taken from $-\infty$ to ∞). The Lagrange multiplier $\lambda(t)$ relates $f_{\text{opt}}(t)$ and $q_{\text{opt}}(t)$ to each other [cf. Eq. (1); $\lambda(t) = 0$ for $t > t_f$]. The activation rate has the form

$$W = C \exp[-R/D], \quad R = \min \mathcal{R}. \quad (3)$$

The exponent R can be obtained for an arbitrary noise spectrum and an arbitrary periodic driving by solving the variational problem (2) numerically, with appropriate boundary conditions [4,9].

We now turn to the case where the driving force $F(t)$ is comparatively weak, so that the field-induced correction $|\delta R| \ll R$. Nonetheless, $|\delta R|$ may exceed D and thus strongly change the rate W (3). To first order, δR can be obtained by evaluating the term $\propto F(t)$ in (2) along the path $q_{\text{opt}}^{(0)}(t), f_{\text{opt}}^{(0)}(t), \lambda^{(0)}(t)$ calculated for $F = 0$. Special care has to be taken when activated escape and nucleation are analyzed. Here in the absence of driving, the optimal path is an instanton, the optimal fluctuation may occur at any time t_c . The field $F(t)$ lifts the time degeneracy of escape paths. It synchronizes optimal escape trajectories, selecting one per period, so as to minimize the activation energy of escape R [4, 5]. The correction δR should be evaluated along the appropriate trajectory,

$$\delta R = \min_{t_c} \delta R(t_c), \quad \delta R(t_c) = \int_{-\infty}^{\infty} dt \chi(t - t_c) F(t), \quad \chi(t) = -\lambda^{(0)}(t). \quad (4)$$

Eq. (4) provides a closed-form expression for the change of the time-averaged activation rate \bar{W} , for an arbitrary spectrum of the driving field $F(t)$. Clearly $\ln \bar{W}$ is linear in F , and the corresponding coefficient χ is therefore called the logarithmic susceptibility (LS) [4]. Because of minimization over t_c , the change of $\ln \bar{W}$ is nonanalytic in $F(t)$, which leads to a number of observable consequences. The LS has been evaluated for overdamped and underdamped white-noise driven systems [4]. Extensive numerical and analog simulations of the escape rate in driven systems [6] are in excellent qualitative and quantitative agreement with the theory, including the prefactor [4, 5, 10], over a broad range of field amplitudes.

3. Dynamical symmetry breaking in an optical trap

A simple physical system which embodies a number of activated phenomena is a mesoscopic dielectric Brownian particle trapped by a strongly focused laser beam creating an optical gradient trap, i.e. “optical tweezers” [11]. Techniques based on optical tweezers have found broad applications in contactless manipulation of objects such as atoms, colloidal particles, and biological materials. Activated escape can be studied using a dual optical trap generated by two closely spaced parallel light beams. This was used initially to investigate the synchronization of interwell transitions by low-frequency (adiabatic) sinusoidal forcing [12].

Quantitative characterization of activated processes requires that the double-well confining potential of a dual trap $U(\mathbf{r})$ be adequately determined. The corresponding measurement, for a transparent spherical silica particle of diameter $2R = 0.6 \mu\text{m}$ optically trapped in water, was reported recently [14].

In the experiment [14], all three coordinates of the particle are determined simultaneously. The double-well potential $U(\mathbf{r})$ is found directly from the measured stationary distribution $\rho(\mathbf{r}) = Z^{-1} \exp[-U(\mathbf{r})/k_B T]$. From the Kramers theory [13], it is possible then to calculate the rates W_{ij} ($i, j = 1, 2$) of activated transitions between the minima of $U(\mathbf{r})$. For the range of $U(\mathbf{r})$ in which W_{ij} vary by nearly 3 orders of magnitude, the calculated values of W_{ij} are in excellent quantitative agreement with the results of direct measurements. This provides a direct model-free test of the multidimensional Kramers rate theory, with no adjustable parameters.

The double-beam trap can also be used to investigate the effect of ac-modulation on transition rates. An interesting application of this effect is to direct the diffusion

of a particle in a spatially periodic potential [15]. For a generic periodic potential, the ac-induced change of the activation barrier differs depending on the direction in which the particle moves (right or left, for example). This makes the probabilities of transitions to the right and to the left exponentially different and results in diffusion in the direction of more frequent transitions.

An effect closely related to directed diffusion, but more amenable to testing using optical trapping, is ac-field induced localization in one of the wells of a symmetric double-well potential. Both effects should occur if the field breaks the spatio-temporal symmetry of the system. The ratio of the period-averaged stationary populations \bar{w}_1, \bar{w}_2 of the wells is determined by the ratio of the period-averaged transition rates \bar{W}_{ij} ,

$$\bar{w}_1/\bar{w}_2 = \bar{W}_{21}/\bar{W}_{12} \propto \exp([\delta R_1 - \delta R_2]/k_B T), \quad (5)$$

where $\delta R_{1,2}$ are the field-induced corrections (4) to the activation energies of escape from wells 1,2.

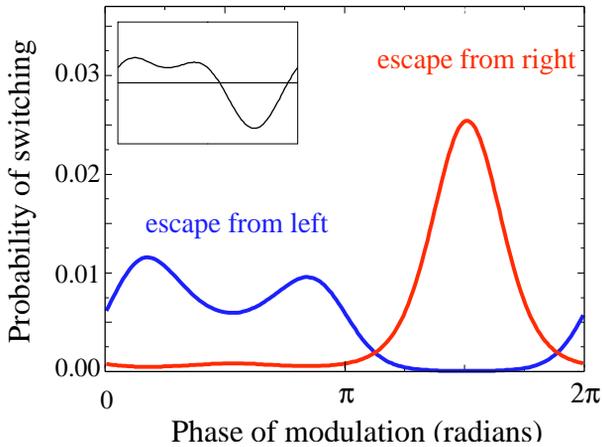


Fig 1. The least-squares fits to the experimentally determined instantaneous time-dependent switching probabilities $W_{ij}(t)$ for a particle in the adiabatically modulated double-beam trap, over a cycle $\omega_F t$ of the modulating waveform. The phase angle between the first and second harmonics is $\phi_{12} = \pi/2$. When the phase angle is incremented by π , the escape rates from the left and right wells interchange. The inset shows the instantaneous difference between the heights of the potential barriers in the two wells.

The experimental data [7] on effective localization due to the field-induced symmetry breaking are shown in Fig. 1. The experiment is conducted with a symmetric double-well potential and barrier height $\approx 7.5 k_B T$. The intensity of the laser beams is then modulated so that the well depths are changed by $\delta U_1(t) = -\delta U_2(t) = \text{const} \times [\sin(\omega_F t) + (1/2) \sin(2\omega_F t + \phi_{12})]$. The modulation amplitude is $\approx 2.5 k_B T$. The frequency $\omega_F/2\pi$ varies between 1 and 100 Hz, which covers the range from adiabatically slow to nonadiabatic modulation. Over this range, field-induced re-population occurs between the wells for a nonsinusoidal modulation waveform, so that $\bar{w}_1 \neq \bar{w}_2$.

It is the breaking of the spatio-temporal symmetry $t \rightarrow t + \pi/\omega_F, \mathbf{r} \rightarrow -\mathbf{r}$ that leads to the escape rate from one of the wells being on average much bigger than from the other, as seen from Fig. 1. In turn, this leads to a higher population in one of the wells. Not only is it observed under slow modulation, as evidenced by Fig. 1, but a population difference of 20% is also observed far into the nonadiabatic regime. This is sufficient to create significant directional diffusion, and demonstrates the onset of *dynamical* symmetry breaking. The effect would not arise if nonadiabatic driving led just to “heating” of the particle.

4. Conclusions

Investigation of methods to control activated processes is currently at a very exciting stage. The importance of the problem and its relevance to many areas, from condensed-matter physics to biophysics, is becoming increasingly appreciated. The results outlined here show that there is a fairly general approach to controlling fluctuations, and the first experiments on overdamped systems show that such control can indeed be exercised. A broad range of problems remains unexplored. They include such issues as a microscopic theory of driven many-body systems and experimental exploration of underdamped driven systems. We also envision practical applications of these results, starting with the development of new highly selective colloidal separation as well as crystal growth techniques.

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