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STOCHASTIC BEHAVIOR IN NONEQUILIBRIUM SYSTEMS

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A system caught in a metastable state will ultimately escape as a result of thermal fluctuations. The situation may be modelled by a Brownian particle caught in a potential trough, obeying either a Smoluchowski diffusion equation or a Kramers equation. The escape time can be identified with a mean first passage time, which obeys the Dynkin equation. Unless this equation can be solved exactly, it has to be treated by singular perturbation theory. The calculation is demonstrated for the case of diffusion and for the one-dimensional Kramers equation.

1. Introduction

Figure 1 shows half an ellipsoid of solid material resting on a table. A marble is at rest in the unstable equilibrium position. The random collisions of the air molecules will start it rolling down and we ask the probability distribution of the point where it hits the table. It is easy to write the stochastic equations of motion for the marble, but as there is no hope for an explicit solution, we have to find an approximation method.

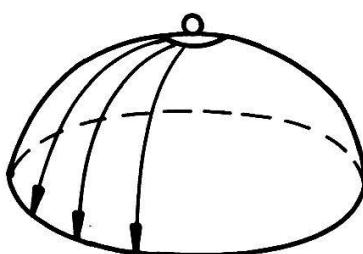


FIGURE 1

The obvious idea is to select a small cap around the top in such a way that: (a) inside the cap the equations of motion can be linearized, so that they can be solved including the random force; (b) outside the cap the effect of the random force is negligible and the nonlinear deterministic equations suffice. Thus the linearized stochastic equations serve to find the probabili-

ty distribution along the edge of the cap, which is then translated by the subsequent deterministic motion into a distribution along the equator. The result must be independent of the precise size of the cap.

This is precisely what is done in singular perturbation theory [1], of which the classic example is the calculation of Prandtl's boundary layer for fluids with small viscosity [2]. We want to emphasize that *singular perturbation theory is the appropriate tool for dealing with fluctuations in unstable situations*. The many ad hoc approximation methods in the literature are merely this method in various disguises. Admittedly, the method is less cut and dry than regular perturbation theory; one still needs some ingenuity in applying it, but less than in reinventing it.

This lecture is confined to the problem of computing the decay time of a metastable state. Other problems of interest are: the decay time of unstable states; the probability distribution of their decay products, illustrated by Fig. 1; the behavior near critical points where stable states become unstable; and finally the evolution of the probability itself, which contains all other information.

An apology: I am talking about *mathematical* methods applied to *given* equations. The equations are suggested by physical systems and are often used to describe them. However, they are customarily obtained by adding *ad hoc* a fluctuating force with assumed properties, rather than by actually describing the actual physical mechanisms that cause the fluctuations. I find this approach unsatisfactory and it has caused many difficulties [3], culminating in the grotesque Itô-Stratonovich controversy [4].

## 2. One-dimensional diffusion

Brownian particle in a field of force:

$$\frac{\partial P(x,t)}{\partial t} = \frac{\partial}{\partial x} U'(x)P + \theta \frac{\partial^2 P}{\partial x^2} \quad (-\infty < x < \infty) . \quad (1)$$

$U(x)$  is the force potential and  $\theta$  the absolute temperature; the mobility is absorbed in  $t$ . This equation does not just apply to Brownian particles, but is also used for chemical reactions, nuclear diffusion, nucleation and population statistics. We are interested in potentials of the shape in Fig. 2. The question is: when at  $t = 0$  the particle resides in the potential trough

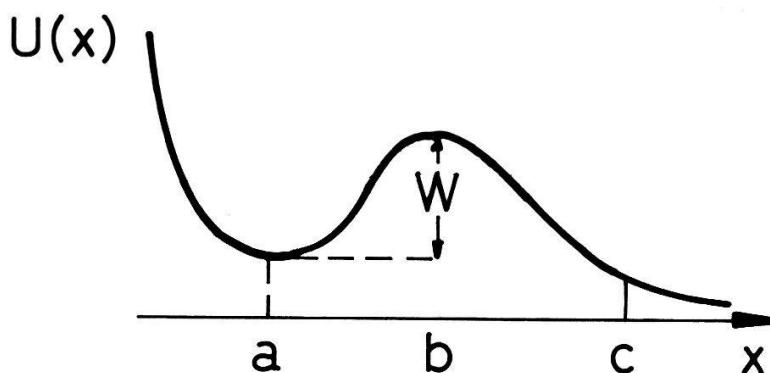


FIGURE 2

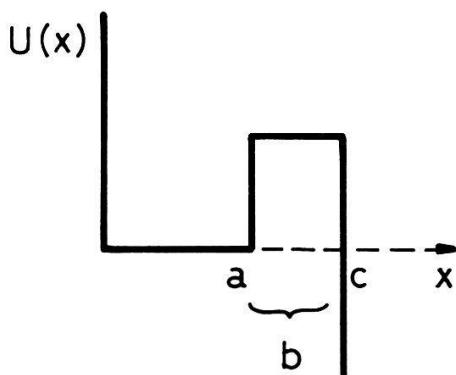
around a, how long does it take on the average to fluctuate across the barrier  $W$  at  $b$ ?

The *average escape time*  $\tau$  involves the Arrhenius factor  $e^{W/\theta}$ . This was first suggested by the transition state theory for chemical reactions [5], according to which the process from  $a$  to  $c$  requires an excitation into the 'activated complex'  $b$ . Apart from  $e^{W/\theta}$  there is another factor; our aim is to compute this factor on the basis of (1).

In order that  $\tau$  is well-defined it has to be much longer than the local relaxation inside the trough, so that the precise initial location in the trough is immaterial. Also the particle has clearly escaped only when it has reached a location  $c$  from where the return probability (per unit time) is negligible. These conditions require  $e^{W/\theta}$  to be large. The escape time  $\tau$  is *defined* only up to order 1, that is, relative order  $e^{-W/\theta}$ .

As a preliminary exercise consider the potential in Fig. 3. (The letters  $a$ ,  $c$  and  $b = c-a$  have a slightly different meaning than in Fig. 2). The equations are

FIGURE 3



$$\frac{\partial P(x,t)}{\partial t} = \theta \frac{\partial^2 P}{\partial x^2} \quad \text{for } 0 < x < a \quad \text{and } a < x < c ,$$

$$P(a+o,t) = e^{-W/\theta} P(a-o,t) .$$

at  $x = c$ .

Reflection at  $x = 0$  and absorption

$$[P(x,t)/\partial x]_{x=0} , \quad P(c,t) = 0 .$$

The solution can be expressed as an eigenfunction expansion

$$P(x, t) = \sum_{\lambda} c_{\lambda} P_{\lambda}(x) e^{-\lambda t},$$

where the eigenvalues  $\lambda$  are given by

$$\lambda = \theta k^2, \quad \tan ka = e^{-W/\theta} \cot kb.$$

For  $W/\theta \gg 1$  there is one low lying eigenvalue, which is the transition probability per unit time,

$$\lambda_0 = (\theta/ab)e^{-W/\theta} = 1/\tau. \quad (2)$$

The factors  $a$  and  $b$ , being the widths of the trough and the thickness of the barrier, will appear in every case.

Back to the potential of Fig. 2. Let  $T_c(x)$  denote the average time it takes a particle starting at  $x$  to reach  $c$  for the first time. This *mean first passage time* is a precisely defined quantity. The *escape time*  $\tau$  may be identified with  $T_c(a)$  within the margin of its definition.  $T_c(x)$  obeys the Dynkin equation [6,7]

$$-U'(x) \frac{dT_c}{dx} + \theta \frac{d^2T_c}{dx^2} = -1, \quad T_c(c) = 0. \quad (3)$$

Thus one can find the mean first passage time from an ordinary differential equation without having to solve the partial differential equation (1) (as we did in the previous example). The left-hand side of (3) is the adjoint of the operator in (1).

The solution of (3) is

$$T_c = \frac{1}{\theta} \int_x^c e^{U(x')/\theta} dx' \int_{-\infty}^{x'} e^{-U(x'')/\theta} dx''. \quad (4)$$

If one takes  $x$  anywhere near  $a$  and approximates the integrals for small  $\theta$

$$\tau = 2\pi [U''(a) |U''(b)|]^{-1/2} e^{-W/\theta}.$$

$[U''(a)]^{-1/2}$  is a measure for the width of the trough and  $|U''(b)|^{-1/2}$  measures the thickness of the barrier. Higher orders in  $\theta$  may be added to the pre-

factor; they are not very interesting, but they are not inconsistent with the inherent margin in the definition of  $\tau$ , which is of relative order  $e^{-W/\theta}$ . It would be *inconsistent*, however, to evaluate the integrals in (4) with more precision than is provided by these expansions in  $\theta$ .

### 3. Diffusion in more dimensions

The diffusion equation in a potential  $U(\mathbf{r})$  is

$$\partial P(\mathbf{r}, t) / \partial t = \nabla \cdot (\nabla U) P + \theta \nabla^2 P.$$

We take two dimensions and assume that  $U(x, y)$  is shaped as in Fig. 4, with a minimum at  $a$  and a pass in the crater ridge at  $b$ , of height  $W$ . The trough

covers a region  $\Omega$  in the  $x, y$  plane and the projection of the ridge is a closed curve  $\partial\Omega$ . Let  $T(\mathbf{r})$  be the mean time for first arrival at the ridge. The escape time is  $\tau = 2T(a)$ , because on the ridge the particle has a fifty-fifty chance to return. The Dynkin equation is

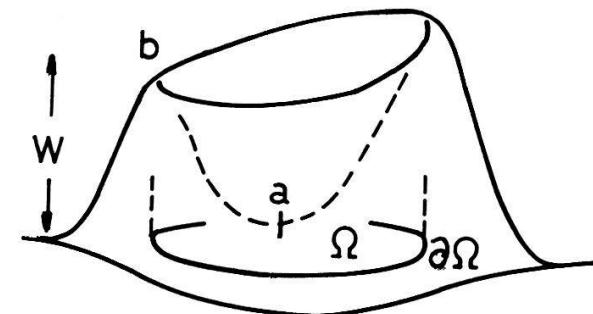


FIGURE 4

$$-\nabla U(\mathbf{r}) \cdot \nabla T(\mathbf{r}) + \theta \nabla^2 T(\mathbf{r}) = -1 \quad (\mathbf{r} \in \Omega) , \quad T(\mathbf{r}) = 0 \quad (\mathbf{r} \in \partial\Omega) . \quad (5)$$

An explicit solution is no longer possible and singular perturbation theory is needed. I give a simplified version of the calculation of Schuss and Matkowsky [8, 7].

Inside  $\Omega$ , away from the boundary,  $T(\mathbf{r})$  is nearly constant and contains the factor  $e^{W/\theta}$ . We suppose again  $W/\theta \gg 1$  and set

$$T(\mathbf{r}) = e^{W/\theta} w(\mathbf{r}) , \quad w(\mathbf{r}) = 0 \quad (\mathbf{r} \in \partial\Omega) , \quad w(\mathbf{r}) = C \text{ inside } \Omega .$$

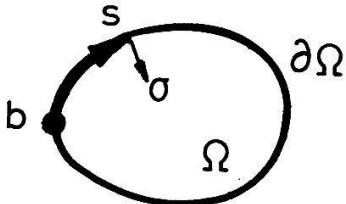
$$-\nabla U(\mathbf{r}) \cdot \nabla w(\mathbf{r}) + \theta \nabla^2 w(\mathbf{r}) = e^{-W/\theta} . \quad (6)$$

To determine  $C$  we have to study the vicinity of the pass at  $b$ .

Introduce coordinates  $s, \sigma$  as in Fig. 5, so that near  $b$

$$U(\underline{r}) = u(s) - \frac{1}{2}\sigma^2 v(s) + \mathcal{O}(\sigma^3) .$$

FIGURE 5



Equation (6) transforms into

$$-u'(s) \frac{\partial w}{\partial s} + \sigma v(s) \frac{\partial w}{\partial \sigma} + \theta \left( \frac{\partial^2 w}{\partial s^2} + \frac{\partial^2 w}{\partial \sigma^2} \right) = \mathcal{O}\left(e^{-W/\theta}\right).$$

For brevity we have omitted some terms which will disappear in the next step

anyway. The next step consists in rescaling:  $\sigma = \theta^{1/2} \xi$ , so that to lowest order

$$-u'(s) \frac{\partial w}{\partial s} + \xi v(s) \frac{\partial w}{\partial \xi} + \frac{\partial^2 w}{\partial \xi^2} = 0 . \quad (7)$$

At the pass  $u'(s) = 0$ ; as a consequence the first term may be omitted, as will be verified presently. Then the solution, involving two integration constants  $A(s)$ ,  $B(s)$ , is

$$w = A(s) \int_0^\xi e^{-v(s)\eta^2/2\theta} d\eta + B(s) .$$

But  $B = 0$  since  $w$  must vanish on  $\partial\Omega$ . For large  $\xi$

$$w \rightarrow A(s) [\pi\theta/2v(s)]^{1/2} .$$

This must be the value  $C$  of  $w$  inside  $\Omega$ . Hence we have in the vicinity of  $b$

$$T(s, \sigma) = e^{W/\theta} C \sqrt{\frac{2v(s)}{\pi\theta}} \int_0^{\sigma/\sqrt{\theta}} e^{-\frac{1}{2}v(s)\eta^2} d\eta .$$

We have found how the function  $T(x, y)$ , which is constant inside  $\Omega$ , is dented near the escape pass  $b$ . The constant  $C$  is still undetermined because we have not yet utilized the right-hand side of (5). Multiply (5) with  $e^{-U/\theta}$  and integrate

$$-\theta \int_{\partial\Omega} e^{-U/\theta} \frac{\partial T}{\partial \sigma} ds = - \int_{\Omega} e^{-U/\theta} dx dy .$$

The main contribution to the integral on the left comes from the vicinity of  $b$

and with the usual approximations for the integrals one obtains

$$\tau = 2e^{W/\theta} \quad C = 2e^{W/\theta} \sqrt{\frac{u''(o)}{v(o)}} \int_{\Omega} e^{-U/\theta} dx dy .$$

$[u''(o)]^{-1/2}$  measures the width of the pass,  $v(o)$  the thickness of the barrier. The integral can again be evaluated by expanding around the minimum  $a$ . Notice that only values of  $s$  enter for which  $u''(o)s^2 \sim \theta$ , which a posteriori justifies the omission of the first term of (7).

The method can be modified for other cases: more than one pass; ridge of constant height; sharp arête as in Fig. 6. More serious is the case where the deterministic part of the diffusion equation *has no potential*. This may occur in physical systems that are kept far from equilibrium by some external agency, and also in nonphysical systems such as populations. Then the boundary  $\partial\Omega$  is the separatrix between two domains of attraction [9]. Yet almost the same calculation can be performed.

#### 4. The Kramers equation

If the Brownian particle is *not* overdamped the inertial term in its equation of motion must be taken into account, so that the velocity or momentum  $p$  enters as a variable in addition to  $x$ . The stochastic behavior is described by the Kramers equation [10,11,12] for the probability density in  $(x,p)$ -space

$$\frac{\partial P(x,p,t)}{\partial t} = -p \frac{\partial P}{\partial x} + U'(x) \frac{\partial P}{\partial p} + \gamma \left( \frac{\partial}{\partial p} pP + \theta \frac{\partial^2 P}{\partial p^2} \right) . \quad (8)$$

It contains a second parameter, the friction coefficient  $\gamma$ . We are again interested in the escape from the potential trough in Fig. 2.

(i) For large  $\gamma$  (8) reduces to the one-variable Smoluchowski case (1). To show this [11,13,14,15] one eliminates the fast variable  $p$  by a singular perturbation technique akin to the Chapman-Enskog method in kinetic gas theory.

(ii) For small  $\gamma$  the zeroth approximation is the deterministic motion  $\dot{x} = p$ ,  $\dot{p} = -U'(x)$ . For the motion inside the trough one transforms to action-angle variables, or to energy and phase angle [11,16]. The terms with  $\gamma$  are averaged over the phase so as to obtain a single-variable Smoluchowsky equation for the energy distribution. However, near  $b$  the motion is too slow

for phase averaging; hence this equation cannot be used to compute the escape, unless the potential maximum is peaked as in Fig. 6.

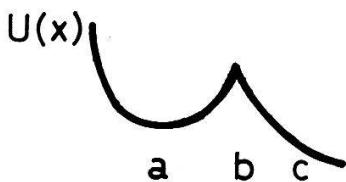


FIGURE 6

(iii) If  $\gamma$  is fixed but  $\theta$  small the zeroth approximation is the damped motion

$$\dot{x} = p, \quad \dot{p} = -U'(x) - \gamma p.$$

Let  $x = \varphi(t)$ ,  $p = \psi(t)$  be a solution. The fluctuations are obtained by substituting in (8)

$$x = \varphi(t) + \theta^{1/2} \xi, \quad p = \psi(t) + \theta^{1/2} \eta.$$

The result is an equation for the probability  $\Pi(\xi, \eta, t)$ , which can be solved by ordinary perturbation theory in powers of  $\theta^{1/2}$ . Hence one finds the deterministic behavior with small fluctuations tagged on to it. Condition is that there is a single point attractor, otherwise the fluctuations may grow to make the approximation spurious. Limit cycles can be treated to a certain extent [17], but not our escape problem.

Our problem is therefore to calculate the escape time without using these limits, but how is the escape time defined? Of course one must have again  $e^{W/\theta} \gg 1$ , but when is a particle escaped? The position  $x$  alone does not

specify the state and one is not sure whether particles 1 and 2 in Fig. 7 are escaped. One cannot therefore identify the escape time with (twice) the mean time for first arrival on top of the barrier. Rather one should take the time of

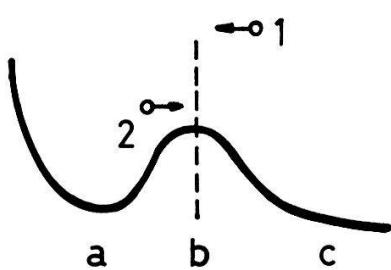


FIGURE 7

first arriving at some  $c$  such that  $c-b$  is large compared to the mean free path  $\theta^{1/2} \gamma$  and the return probability per unit time is negligible (namely of order  $e^{-W/\theta}$ ). The corresponding Dynkin equation is

$$p \frac{\partial T}{\partial x} - U'(x) \frac{\partial T}{\partial p} - \gamma p \frac{\partial T}{\partial p} + \gamma \theta \frac{\partial^2 T}{\partial p^2} = -1 \quad (9)$$

$$T(c, p) = 0 \quad \text{for } p > 0.$$

We solve this equation in the same way as (5) by the Ansatz

$$T(x,p) = e^{W/\theta} w(x,p) \approx e^{W/\theta} C .$$

Near  $b$  we set  $x-b = y$  and

$$U(x) = W - \frac{1}{2}vy^2 + \mathcal{O}(y^3) . \quad (10)$$

Hence

$$p \frac{\partial w}{\partial y} + vy \frac{\partial w}{\partial p} - \gamma p \frac{\partial w}{\partial p} + \gamma \theta \frac{\partial^2 w}{\partial p^2} = 0 .$$

The equation has a traveling wave solution [11]

$$w(y,p) = f(p+\alpha y) , \quad \alpha = \frac{1}{2}\gamma + \sqrt{\frac{1}{4}\gamma^2 + v^2}$$

$$f(z) = A \int_z^{\infty} \exp\left[-\frac{\alpha-\gamma}{2\gamma\theta} z'^2\right] dz' + B . \quad (11)$$

At  $c$  the integral is practically zero, hence  $B = 0$ . For  $y \rightarrow -\infty$

$$w(x,p) \rightarrow A[2\pi\gamma\theta/(\alpha-\gamma)]^{1/2} = C .$$

Finally to find  $C$  multiply (9) with  $\exp[-p^2/2\theta - U/\theta]$  and integrate over  $-\infty < x < b$ ,  $-\infty < p < \infty$ . After partial integration the only surviving terms are

$$\begin{aligned} - \sqrt{\frac{2\pi}{\theta}} \int_{-\infty}^C e^{-U/\theta} dx &= \int_{-\infty}^{\infty} p e^{-p^2/2\theta} dp e^{-U(b)/\theta} \tau(b,p) \\ &= \int_{-\infty}^{\infty} p e^{-p^2/2\theta} dp A \int_p^{\infty} \exp\left[-\frac{\alpha-\gamma}{2\gamma\theta} z^2\right] dz \\ &= \sqrt{\frac{\alpha-\gamma}{2\pi\gamma\theta}} C(-\theta) \int_{-\infty}^{\infty} e^{-p^2/2\theta} \exp\left[-\frac{\alpha-\gamma}{2\gamma\theta} p^2\right] dp \\ &= -\theta \sqrt{\frac{\alpha-\gamma}{\alpha}} C = -\theta C \left[ \sqrt{1 + \frac{\gamma^2}{4v^2}} - \frac{\gamma}{2\sqrt{v}} \right] \end{aligned}$$

This determines  $C$  and hence  $\tau$ . The curious combination of  $\gamma$  and  $v = |U''(b)|$  exhibits the interplay of the mean free path and the width of the potential barrier.

Apart from the condition  $e^{W/\theta} \gg 1$  we have used the parabolic approximation (10). Let  $\ell_b$  be a typical distance over which this holds; in most cases

$$\ell_b \sim |U''(b)/U'''(b)| \text{ or } \ell = |U''(b)/U'''(b)|^{1/2}.$$

On the other hand, we used the asymptotic expressions for the integral in (11); hence the approximation is consistent provided that

$$[(\alpha-\gamma)/\gamma\theta]\ell_b^2 \gg 1 \text{ or } |U''(b)|\ell_b^2 \gg \theta\gamma\{\gamma+|U''(b)|\}.$$

Thus we have shown that, for the Kramers equation in a metastable potential trough, the escape time can be found by a rather straightforward application of singular perturbation theory. In the seminal paper of Kramers the problem was solved by ingenious calculations, but in principle it contains all the ideas that went into our more formal methods.

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