

A Soluble Model for Diffusion in a Bistable Potential

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After a general discussion of diffusion in a potential field having two minima, an explicit solution is obtained for a special form of the potential. The potential is symmetric, but the diffusing particle is initially at an arbitrary point near the potential maximum. Various suggested approximation schemes are tested, with the following conclusions. (i) In linear approximation around the maximum the probability distribution is Gaussian. A two-peaked distribution emerges only through nonlinear terms. (ii) The chances for the particle to go to the right or the left valley cannot be found from the linear approximation. Matching the linear approximation with a macroscopic description far away from the maximum is therefore wrong. (iii) Kramers' treatment of the escape across a potential barrier yields a practically exact result for this model.

KEY WORDS: Fluctuations; diffusion; instability.

1. INTRODUCTION

Experience has taught us that the behavior of most many-body systems can be described by macroscopic laws. These laws are not exact: Their validity is limited by the existence of fluctuations. As a rule, the fluctuations are small and their influence on the behavior tends to zero when the size of the system goes to infinity. This is the basis of the usual approximation methods⁽¹⁻⁶⁾ and has been called "propagation of the extensive property of macrovariables."⁽³⁾ However, there are exceptions to this rule. When the system is in an unstable situation its macroscopic future will be determined by the initial fluctuations. Hence the distinction between macroscopic behavior and small fluctuations is no longer possible. This paper investigates such a situation on the basis of a simple model.

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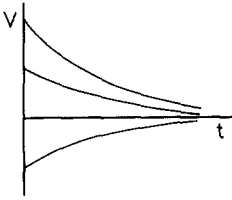


Fig. 1. The macroscopic behavior of the velocity of a Brownian particle.

To specify the problem more fully, it is useful to distinguish three situations.

(i) The macroscopic equations have one stationary solution and all other solutions converge to it. Thus, all solutions are asymptotically stable (Fig. 1). The effect of any random fluctuation occurring at an arbitrary time will ultimately die out. The fluctuations will not build up, but remain small at all times. In particular, in the stationary state the effect of the fluctuations is balanced by the macroscopic tendency to return to the stationary value. Equilibrium fluctuations are the outcome of such a balance; the resulting relation is the fluctuation-dissipation theorem. The classic example of this situation is the *velocity* V of a Brownian particle (in this connection often called Rayleigh particle), which obeys the macroscopic equation $\dot{V} = -\gamma V$.

(ii) The solutions of the macroscopic equations are stable but not asymptotically stable, i.e., two neighboring solutions remain near to each other but do not converge (Fig. 2). The *position* X of a Brownian particle is an example, the macroscopic equation being $\dot{X} = 0$. Another example is provided by systems with a limit cycle: The phase of the periodic solution is not asymptotically stable.^(7,8) The fluctuations are not damped by the macroscopic motion, nor magnified, but by accumulation in the course of time their effect grows proportionally with \sqrt{t} . When the system starts out in a definite state the distinction between macroscopic motion and fluctuations is meaningful only for a limited period. Although this period is longer for larger systems, it is impossible to compute the long-time behavior by any approximation method based on the smallness of fluctuations.

(iii) The macroscopic equations have a stationary solution that is unstable: From any neighborhood around it different solution curves emerge, which end up by being far apart (Fig. 3). When the system is in that unstable

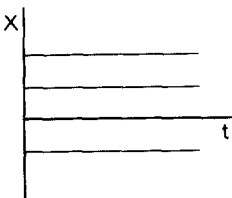


Fig. 2. The position of a Brownian particle macroscopically.

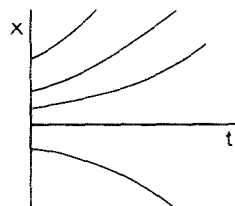


Fig. 3. The stationary solution $x = 0$ is unstable.

stationary state at $t = 0$ the initial fluctuations will determine whether it will evolve along one or the other macroscopic trajectory. Regardless of how large one chooses the system, in the course of time the effect of the early fluctuations magnifies into macroscopic size. An example of this situation will be treated in the present paper.

The importance of this problem for many questions in physics, chemistry, and biology has become clear in recent years and has given rise to a vast literature. No approximation scheme based on a separation of macroscopic behavior and small fluctuations will be able to handle this process of magnifying fluctuations. Kramers⁽⁹⁾ studied the motion of a particle in a potential field, subjected to viscous damping and to a fluctuating force. Starting from an equation for the probability distribution of both position and momentum, he derived for the case of strong damping a diffusion equation for the position alone. This equation for the overdamped case will be our starting point. His further results, however, are of no avail to us, because he was interested in the escape over a potential barrier rather than in the approach to equilibrium in a bistable potential. Other treatments of the escape problem were given by Montroll and Shuler⁽¹⁰⁾ and Griffiths *et al.*⁽¹¹⁾

More recently the problem of fluctuations near an unstable equilibrium has received much attention, since it was realized that it occurs in a large variety of phenomena of the type of phase transitions.⁽¹²⁾ Of the abundant literature we can only quote a selection. One such phenomenon is the decay of metastable states⁽¹³⁾ or spinodal decomposition (see Ref. 14 for a survey). This case, however, is complicated by the fact that one is dealing with a continuous system and therefore an infinity of variables rather than our single one. The theory has therefore so far been restricted mainly to studying what is here called the macroscopic equation,⁽¹⁵⁾ even when it starts with a master equation formulation,⁽¹⁶⁾ but some attention has been given to fluctuations as well.^(17,18)

More directly related to our problem are tunnel diodes and other switching devices.⁽¹⁹⁾ Much work has been done with respect to the laser, which above pumping threshold may operate in either one of two (or more) stable modes.^(20,5) Chemical reactions in open systems may also have two stable stationary regimes separated by an unstable stationary solution.⁽²¹⁾ Other instabilities can be found in the attitudes of interacting social groups.⁽²²⁾

The equations for bistable systems have also been studied from a general point of view.^(23,24)

It must be said, however, that the Fokker–Planck or diffusion approximation, which is very popular in these fields, is subject to serious objections. The reason is that in many-body systems the only way to make the individual jumps small is by increasing the size of the system, which, however, at the same time reduces the influence of nonlinearity on the fluctuations.^(1,8) In particular, near a point of instability the master equation cannot be replaced with a Fokker–Planck equation, because the finite size of the individual jumps is decisive. For this reason we shall here resort to a model in which the instability is due to an external mechanical force.

2. DIFFUSION IN A BISTABLE POTENTIAL

As a stochastic description of a bistable system we shall use the one-variable Fokker–Planck equation

$$\frac{\partial P(x, t)}{\partial t} = \frac{\partial}{\partial x} U'(x)P + \vartheta \frac{\partial^2 P}{\partial x^2} \quad (1)$$

where $U'(x)$ is the derivative of a potential function U with two minima as sketched in Fig. 4. As a physical model one may take the unstable pendulum of Fig. 5, immersed in a viscous medium whose temperature is given by ϑ . Our reason for choosing (1) is merely that it seems to be the mathematically simplest example of bistability, and can be solved for a suitable choice of U .

The range of x may be either $(-\infty, \infty)$, or x may be bounded at one or at both ends. The probability flow is

$$J(x, t) = -(U'P + \vartheta P') \quad (2)$$

As boundary condition we require J to vanish at the boundaries, which means that the system has no other states outside the range of x . One then has for any solution of (1) the identity

$$\frac{d}{dt} \frac{\vartheta}{2} \int e^{U/\vartheta} P(x, t)^2 dx = - \int e^{U/\vartheta} (U'P + \vartheta P')^2 dx \quad (3)$$

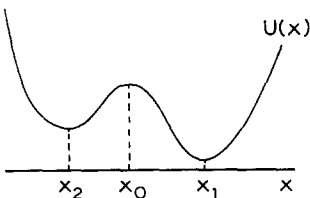


Fig. 4. A bistable potential.

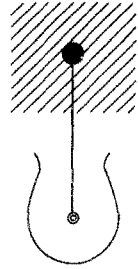


Fig. 5. A physical realization of Eq. (1).

This implies that at a boundary at infinity, or at a boundary where U is infinite, the boundary condition is taken to be

$$e^{U/\vartheta}PJ \equiv \vartheta P \frac{d}{dx} e^{U/\vartheta}P \rightarrow 0 \tag{4}$$

It follows from (3) that all solutions of (1) obeying the boundary conditions will ultimately satisfy the equation $U'P + \vartheta P' = 0$. The only solution of this equation with the boundary conditions is the stationary solution

$$P_0(x) = e^{-U(x)/\vartheta} \tag{5}$$

It also follows that for given initial $P(x, 0)$ only a single solution of (1) exists. Of course it suffices to take

$$P(x, 0) = \delta(x - y) \tag{6}$$

with arbitrary y in the range. The solutions of (1) with this initial value will be denoted by $P(x, t|y)$.

In the limit $\vartheta \rightarrow 0$, Eq. (1) reduces to the first-order equation

$$\frac{\partial P}{\partial t} - \frac{\partial}{\partial x} U'(x)P = 0 \tag{7}$$

The characteristics are determined by the first-order differential equation

$$\dot{x} = -U'(x) \tag{8}$$

This is the macroscopic equation corresponding to the Fokker-Planck equation (1). Notice that the *velocity* is proportional to the force because (1) describes the overdamped case. U is the potential of the mechanical force, divided by the friction constant, and may be called “viscous potential.” Let the solution of (8) with initial value y be

$$x = \varphi(y, t), \quad y = \psi(x, t) \tag{9}$$

Then the solution of (7) is

$$P(x, t) = P(\psi(x, t), 0) \frac{\partial \psi(x, t)}{\partial x}$$

In particular for the initial condition (6)

$$P(x, t|y) = \delta\{x - \varphi(y, t)\} \tag{10}$$

However, the limit $\vartheta \rightarrow 0$ does not commute with the limit $t \rightarrow \infty$. In any *finite* time interval $0 < t < T$ it is true that the solution of (1) with initial condition (6) tends to (9). More precisely, for any smooth test function $f(x)$ one has for fixed t

$$\lim_{\vartheta \rightarrow 0} \int f(x)P(x, t|y) dx = \int f(x) \delta\{x - \varphi(y, t)\} dx = f\{\varphi(y, t)\}$$

But it is not true that the asymptotic behavior of $P(x, t|y)$ for $t \rightarrow \infty$ can be found from (10), not even when ϑ is very small. This will now be demonstrated.

The behavior of the solutions (9) can be gleaned from Fig. 6. When $y > x_0$ the motion is in the direction of x_1 , and x will end up by crawling toward x_1 according to

$$x - x_1 = \text{const} \times \exp[-U''(x_1)t] \tag{11}$$

Thus we have found for $y > x_0$

$$\lim_{t \rightarrow \infty} \lim_{\vartheta \rightarrow 0} P(x, t|y) = \delta(x - x_1) \tag{12}$$

Similarly, when $y < x_0$ one sees that x approaches x_2 and

$$\lim_{t \rightarrow \infty} \lim_{\vartheta \rightarrow 0} P(x, t|y) = \delta(x - x_2) \tag{13}$$

On the other hand, if one first takes the limit $t \rightarrow 0$ one knows that $P(x, t|y)$ tends to (5). The subsequent limit $\vartheta \rightarrow 0$ can be taken again by means of a test function. For small ϑ one finds

$$\int f(x)P_0(x) dx = a_1 f(x_1) + a_2 f(x_2)$$

where $a_1 + a_2 = 1$ and

$$a_1/a_2 = \exp\{-[U(x_1) - U(x_2)]/\vartheta\}$$

Hence, when $U(x_1) < U(x_2)$ as in Fig. 4, one has

$$\lim_{\vartheta \rightarrow 0} \lim_{t \rightarrow \infty} P(x, t|y) = \delta(x - x_1) \tag{14}$$

regardless of the initial y . Thus, as long as the fluctuations are not yet

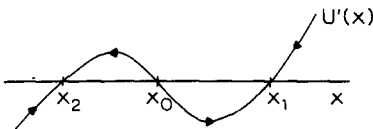


Fig. 6. The behavior of the macroscopic solutions in the bistable viscous potential of Fig. 4.

entirely neglected, the system will end up in its lowest energy state. Moreover, when $U(x_1) = U(x_2)$ one obtains

$$\lim_{\vartheta \rightarrow 0} \lim_{t \rightarrow \infty} P(x, t | y) = \frac{1}{2} \delta(x - x_1) + \frac{1}{2} \delta(x - x_2) \quad (15)$$

Physically the former limiting process means that one ignores fluctuations and describes the evolution of the system macroscopically. The distribution is a delta function at all times and tends to either (12) or (13) for $t \rightarrow \infty$. The latter limiting process, however, means that one allows the system to reach its ultimate state in the presence of fluctuations, and subsequently studies systems with smaller and smaller temperatures ϑ . The existence of fluctuations allows the system to probe the entire space of states x and search for the lowest potential minimum. When the fluctuations are small this may take a very long time, but that does not show up in the result, because the limit $t \rightarrow \infty$ is taken first. In the case $U(x_1) < U(x_2)$ the subsequent lowering of ϑ always reaches a stage where $\vartheta \ll U(x_2) - U(x_1)$, so that the minimum at x_2 is depleted during the evolution of the system and the result (14) emerges. In the case $U(x_1) = U(x_2)$ the two minima are always equally probable, no matter how small ϑ , and the result is (15).

The physicist, however, is dealing with time periods that may be long but are never infinite, and with a ϑ that is usually small, but never zero. The question is therefore: Which of the two mathematical limiting procedures is appropriate to describe the actual system and may serve as a starting point for successive approximations? The obvious answer is that in almost all cases occurring in practice the macroscopic description is very good. Both situations (i) and (ii) in Section 1 can be handled by taking the macroscopic description as lowest approximation, and subsequently adding corrections for the fact that ϑ is not quite zero.

The macroscopic approach is even to a certain extent applicable to our diffusion in a bistable potential, because in macroscopic systems the probability to fluctuate from one potential valley into the other across the barrier is extremely small; the time required may easily exceed the age of the universe. All memory devices rely on this fact.⁽¹⁹⁾ However, the situation is different if the initial value y is taken at the maximum x_0 . Then the macroscopic equation (8) simply yields $x(t) = x_0$ for all $t \geq 0$, while in reality it is the fluctuations that determine how the system is going to evolve and whether it will end up near x_1 or near x_2 . Clearly the macroscopic description is no longer a suitable first approximation. Similarly, when y is close to x_0 the macroscopic value moves away very slowly, and in the meantime the fluctuations may carry the system across the maximum so as to render the macroscopic solution spurious. The problem of finding $P(x, t | y)$ starting from a value of y close to x_0 is the subject of this paper.

3. LINEARIZATION AROUND THE UNSTABLE STATE

Any approximation method that starts from the macroscopic equation and subsequently adds fluctuations as small corrections breaks down when y is close to x_0 . For, the initial fluctuations magnify into macroscopic consequences. As a remedy several authors have suggested the following alternative approximation scheme.

(a) For the region near x_0 replace U' in (1) by its linear term and solve the resulting equation exactly.

(b) Use the result for $P(x, t|y)$ up till a time t_s , after which fluctuations across the maximum are negligible. Thus this linearized solution already determines the probabilities for ending up in x_1 and x_2 , respectively.

(c) To find $P(x, t|y)$ for $t > t_s$, take the $P(x, t_s|y)$ found above as initial distribution and match it with the macroscopic approximation method for the subsequent evolution.

The crucial question is whether a t_s can be found sufficiently small for the errors made in (a) by linearizing to be harmless, and sufficiently large for the approximations made in (b) and (c) to be valid. One test, of course, is that the result must be insensitive to the precise choice of t_s , but the actual verification requires an estimate of the errors made. For the Malthus–Verhulst problem of population growth^(25,8) I have found that, if the errors are measured in terms of the size of the system, no consistent choice of t_s is possible. The failure is due to the fact that the error made in (a) is magnified by (c) owing to the diverging of the macroscopic paths. The present soluble model will allow us to verify this conclusion explicitly.

We start by computing the solution of (1) with linearized U' . Take $x_0 = 0$ and set

$$U(x) \approx U(0) - \vartheta K^2 x^2 \quad (16)$$

The coefficient of x^2 has been called ϑK^2 to facilitate comparison with the calculation in Section 4. Now (1) reduces to the linear Fokker–Planck equation

$$\frac{\partial P}{\partial t} = -2\vartheta K^2 \frac{\partial}{\partial x} xP + \vartheta \frac{\partial^2 P}{\partial x^2} \quad (17)$$

The solution is of course a Gaussian:

$$P(x, t|y) = \frac{K}{[\pi(e^{2\tau} - 1)]^{1/2}} \exp\left[-\frac{K^2(x - ye^\tau)^2}{e^{2\tau} - 1}\right] \quad (18)$$

where we have set $2\vartheta K^2 t = \tau$ for typographical reasons. The center moves away exponentially according to

$$x = y \exp \tau = y \exp(2\vartheta K^2 t) \quad (19)$$

which is the solution of the linearized macroscopic equation associated with (17). The width, however, grows at the same rate. When $y = 0$ the center remains at $x = 0$, and only the width grows as $\exp(2\vartheta K^2 t)$.

A first conclusion is that *it is not true that P develops two separate peaks*. The intuitively appealing idea that one probability maximum emerges on each side of the potential maximum is not correct in the linear approximation. Two peaks can only originate by the nonlinearity of $U(x)$, as may be understood as follows. When the rapidly expanding wings of the Gaussian (18) reach the values of x where $U(x)$ begins to curve upward, they are slowed down and later even reflected by the rising potential wall. Thus on each side the probability is trapped between that wall and the central barrier and settles down as a peak around the minimum of U . We conclude that the representation of the P as a sum of two Gaussians^(18,24) is unfit for describing the neighborhood of the unstable point.

A second conclusion is that nonetheless the exchange of probability across the maximum at $x = 0$ decreases rapidly. One has from (18) for $2\vartheta K^2 t \gg 1$

$$P(0, t | y) \simeq \frac{K}{\sqrt{\pi}} \exp(-2\vartheta K^2 t) \exp(-K^2 y^2) \tag{20}$$

which decreases exponentially with time. More relevant is the probability flow

$$J(0, t) \simeq \frac{-2\vartheta K^3 y}{\sqrt{\pi}} \exp(-4\vartheta K^2 t) \exp(-K^2 y^2) \tag{21}$$

but it leads to the same conclusion: for $2\vartheta K^2 t \gg 1$ no probability is exchanged any more across the potential barrier.

Consequently, the probabilities p_+ and p_- to be to the right or the left of the potential maximum must tend to constant values. In fact, one has

$$p_+(t) = \int_0^\infty P(x, t | y) dx = \frac{1}{2} + \frac{1}{2} \operatorname{erf} \left[\frac{Ky e^{\tau}}{(e^{2\tau} - 1)^{1/2}} \right]$$

Thus

$$p_\pm(\infty) = \frac{1}{2} \pm \frac{1}{2} \operatorname{erf}[Ky] \tag{22}$$

When y is small, $|Ky| \ll 1$, this reduces to

$$p_\pm(\infty) = \frac{1}{2} \pm \frac{Ky}{\sqrt{\pi}} \tag{23}$$

The explicit solution in Section 5 will show that this result is incorrect. This condemns step (b) in the above proposed scheme. *It is therefore not possible to approximate the solution of a nonlinear diffusion problem by matching*

at some intermediate t_s the solution of the linearized problem around the instability with a macroscopic approximation for the behavior far from the energy maximum.

4. THE EIGENFUNCTION METHOD

Another approach to solving Eq. (1) consists in splitting off a time factor $e^{-\lambda t}$ and studying the eigenvalue equation

$$\partial P'' + U'P' + (U'' + \lambda)P = 0 \quad (24)$$

with the boundary conditions (4). We know from (3) that there is one eigenvalue $\lambda = 0$ with eigenfunction P_0 given by (5), and that all other λ are positive.

For a further discussion it is convenient to remove the second term, so as to give the equation the form of a time-independent Schrödinger equation for a nonrelativistic particle in a one-dimensional potential field. Set

$$P(x) = e^{-U(x)/2\vartheta} \varphi(x) \quad (25)$$

so that φ obeys

$$\varphi'' + \left[-\frac{U'^2}{4\vartheta^2} + \frac{U''}{2\vartheta} + \frac{\lambda}{\vartheta} \right] \varphi = 0$$

This has the form of a Schrödinger equation

$$\varphi'' + [E - V(x)]\varphi = 0 \quad (26)$$

in which the potential V is related to U by

$$V = U'^2/4\vartheta^2 - U''/2\vartheta + C \quad (27)$$

with arbitrary constant C . To solve this Riccati equation for U' , set

$$U' = -2\vartheta Z'/Z, \quad Z = e^{-U/2\vartheta} \quad (28)$$

Equation (27) then reduces to

$$Z'' + (C - V)Z = 0$$

which is the same as (26). As (28) makes no sense unless $Z > 0$, the only permissible solution for Z is the ground state φ_0 , so that one must take $C = E_0$. The outcome of this algebra is therefore the following.⁽²⁶⁾

Take an arbitrary Schrödinger equation (26). Use its ground state φ_0 to define a viscous potential U through (28), that is,

$$U = -2\vartheta \log \varphi_0 \quad (29)$$

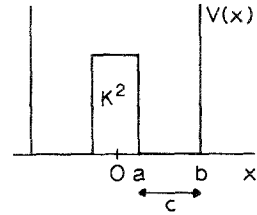


Fig. 7. The rectangular potential chosen as $V(x)$.

The corresponding eigenvalue problem (1) has the eigenfunctions P_n , which are related to the eigenfunctions φ_n of (26) by (25), i.e.,

$$P_n(x) = \varphi_0(x)\varphi_n(x), \quad n = 0, 1, 2, \dots$$

while the eigenvalues are

$$\lambda_n = \vartheta(E_n - E_0)$$

The general solution of (1) is

$$P(x, t) = c_0\varphi_0(x)^2 + \varphi_0(x) \sum_{n=1}^{\infty} c_n\varphi_n(x) \exp[-\vartheta(E_n - E_0)t]$$

We shall take the φ_n normalized in the familiar quantum mechanical norm; then the normalization of P as a probability density is achieved by choosing $c_0 = 1$. The other c_n are found from the initial distribution $P(x, 0)$ in the usual way. In particular

$$P(x, t|y) = \varphi_0(x)^2 + \varphi_0(x) \sum_{n=1}^{\infty} \frac{\varphi_n(y)}{\varphi_0(y)} \varphi_n(x) \exp[-\vartheta(E_n - E_0)t] \quad (30)$$

As we are interested in a bistable U , the potential V must be chosen in such a way that φ_0 has two maxima with one minimum in between. One easily convinces oneself that therefore V has to have a maximum enclosed by two minima, i.e., the same general shape as U . A suitable choice is the rectangular V in Fig. 7, because the corresponding equation (26) can be solved rather explicitly. The infinite potential wall at $x = b$ has the effect that $\varphi_n \sim b - x$, and therefore $e^{U/\vartheta} \sim (b - x)^{-2}$ and $P_n \sim (b - x)^2$, so that the P_n obey the boundary condition (4). Although V is discontinuous, U is differentiable and only its second derivative jumps at $x = \pm a$ (see Fig. 8).

The fact that we have chosen V symmetric somewhat restricts the generality but greatly simplifies the calculation and the discussion. The eigen-

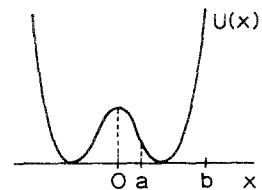


Fig. 8. Sketch of $U(x)$ corresponding to Fig. 7.

functions are alternatively symmetric ($n = 0, 2, 4, \dots$) and antisymmetric (n odd). They can be found by solving the Schrödinger equation for $0 < x < b$ with boundary value $\varphi'(0) = 0$ and $\varphi(0) = 0$, respectively. The probabilities p_+ and p_- to be in the right or the left half are given by

$$\begin{aligned} p_{\pm}(t) &= \frac{1}{2} \pm \frac{1}{2} \int_0^b \{P(x, t|y) - P(-x, t|y)\} dx \\ &= \frac{1}{2} \pm \sum_{m=0}^{\infty} \frac{\varphi_{2m+1}(y)}{\varphi_0(y)} \exp[-\vartheta(E_{2m+1} - E_0)t] \int_0^b \varphi_0(x) \varphi_{2m+1}(x) dx \quad (31) \end{aligned}$$

The solution of (26) is an exercise in elementary quantum mechanics.⁽²⁷⁾ We suppose $Ka \gg 1$, which has the effect that the barrier in U is also high. The following features are easily checked. We set $k = \sqrt{E}$ and $\kappa = (K^2 - k^2)^{1/2}$.

(i) The lowest eigenvalue is

$$k_0 = \frac{\pi}{c} - \frac{\pi}{Kc^2} + \mathcal{O}\left(\frac{1}{(Kc)^2}\right) \quad (32)$$

The corresponding normalized eigenfunction is symmetric and

$$\varphi_0 = \frac{1}{\sqrt{c}} \sin[k_0(b - x)], \quad a < x < b \quad (33)$$

$$\varphi_0 = \frac{2\pi}{Kc} \frac{1}{\sqrt{c}} e^{-\kappa a} \cosh Kx, \quad |x| < a \quad (34)$$

Hence, omitting an irrelevant constant term,

$$U = -2\vartheta \log \sin[k_0(b - x)], \quad a < |x| < b \quad (35)$$

$$U = -2\vartheta \log \cosh 2K + 2\vartheta Ka + 2\vartheta \log(Kc/2\pi), \quad |x| < a \quad (36)$$

Near its maximum at $x = 0$ the potential is given by (16).

(ii) The next eigenvalue corresponds to an antisymmetric eigenfunction and differs from (32) by a very small amount

$$k_1 - k_0 = \frac{4\pi}{Kc^2} e^{-2\kappa a} + \mathcal{O}(e^{-4\kappa a}) \quad (37)$$

The normalized eigenfunction is

$$\varphi_1(x) = \frac{1}{\sqrt{c}} \sin[k_1(b - x)], \quad a < x < b \quad (38)$$

$$\varphi_1(x) = \frac{1}{\sqrt{c}} \frac{2\pi}{Kc} e^{-\kappa a} \sinh Kx, \quad |x| < a \quad (39)$$

For $x > a$, it is practically equal to φ_0 ; for $x < -a$, to $-\varphi_0$.

(iii) All eigenfunctions φ_{2m} with even index are symmetric, all φ_{2m+1} are antisymmetric. As long as the eigenvalues are small compared to K they come in successive, almost degenerate pairs

$$k_{2m} \approx m\pi/c \tag{40}$$

$$k_{2m+1} - k_{2m} \approx \frac{4\pi m}{Kc^2} e^{-2Ka} \tag{41}$$

The corresponding distance of the “energy levels” is

$$E_{2m+1} - E_{2m} \approx \frac{8\pi^2 m}{Kc^3} e^{-2Ka} \tag{42}$$

Again for $x > a$ each φ_{2m+1} is practically equal to φ_{2m} , while for $|x| < a$ it is practically zero. Hence

$$\int_0^b \varphi_{2m+1}(x)\varphi_{2m'}(x) \approx \frac{1}{2}\delta_{mm'}, \quad k_{2m}, k_{2m'} \ll K \tag{43}$$

It follows that (31) may be written approximately

$$p_{\pm}(t) = \frac{1}{2} \pm \frac{1}{2} \frac{\varphi_1(y)}{\varphi_0(y)} \exp[-\vartheta(E_1 - E_0)t] \\ \pm \sum_{E_{2m} > K^2} \frac{\varphi_{2m+1}(y)}{\varphi_0(y)} \exp[-\vartheta(E_{2m+1} - E_{2m})t] \int_0^b \varphi_0(x)\varphi_{2m+1}(x) dx \tag{44}$$

(iv) The eigenvalues far above K^2 are roughly equidistant; i.e., for $n\pi \gg Kb$

$$k_n \simeq (n + 1)\pi/2b, \quad \varphi_n(x) \simeq (2/b)^{1/2} \sin[k_n(b - x)]$$

It will be clear that the general features of this picture are insensitive to the precise shape of the potential, and that the special choice of our model merely served to make the picture more concrete by supplying some actual figures.

5. THE EVOLUTION OF THE PROBABILITY DISTRIBUTION

We are now in a position to describe the successive stages in the development of $P(x, t|y)$, as given by (30).

$$\text{STAGE I:} \quad \vartheta K^2 t \ll 1 \tag{45}$$

At $t = 0$ the distribution is a delta function, and all terms up to $n = \infty$ are important in the sum (30). As t increases, the higher terms are damped out, resulting in a flattening of the peak. As long as (45) holds, however, the terms

on the second line of (44) still contribute, so that p_+ and p_- vary with time: there is an exchange of probability between the regions $x > 0$ and $x < 0$. This stage ends in an interregnum where $\vartheta^2 K t \sim 1$, during which no general qualitative statements can be made.

$$\text{STAGE II: } 1 \ll \vartheta K^2 t \ll (Kc)^2 \quad (46)$$

The terms on the second line of (44) have been damped out. On the other hand, the exponential on the first line is practically unity due to (41). The separation of the distribution into two separate parts is completed and the share of each is given by

$$p_{\pm} = \frac{1}{2} \pm \frac{1}{2} \frac{\varphi_1(y)}{\varphi_0(y)} \quad (47)$$

The detailed distribution (30) itself, however, still varies: Inside both separate potential valleys the diffusion toward equilibrium is still in progress.

$$\text{STAGE III: } 1 \ll \vartheta t/c^2 \ll Kce^{2Ka} \quad (48)$$

All eigenfunctions are damped out except φ_0 and φ_1 :

$$P(x, t|y) = \varphi_0(x)^2 + \frac{\varphi_1(y)}{\varphi_0(y)} \varphi_0(x)\varphi_1(x) \exp\left(-\vartheta t \frac{8\pi^2}{Kc^3} e^{-2Ka}\right) \quad (49)$$

The distribution has reached equilibrium in each separate valley, but exchange between both valleys is extremely slow.

The share of each valley is given by (47). Inserting the actual values, one finds

$$p_{\pm} = \frac{1}{2} \pm \frac{1}{2} \frac{\sinh Ky}{\cosh Ky} = (1 + e^{\mp 2Ky})^{-1} \quad (50)$$

This demonstrates that the result (22) obtained by linearizing around the maximum of U is erroneous. In particular, for $|Ky| \ll 1$,

$$p_{\pm} = \frac{1}{2} \pm \frac{1}{2} Ky$$

in contrast with (23). The reason for this discrepancy is that for (22) to hold, one must have $\vartheta K^2 t_s \gg 1$. By that time, however, the values of x represented in (18) are so large that $Kx \gg 1$, and therefore the linear approximation (16) of (36) is no longer valid. Thus *there is a gap between the time interval during which U can be linearized and the time when P decomposes into two independent peaks.*

$$\text{STAGE IV: } \vartheta t \sim Kc^3 e^{2Ka} \quad (51)$$

On this time scale the last term in (49) is disappearing through diffusion over the potential barrier. The final distribution is (5), which attributes equal

probabilities to both valleys. The rate at which this happens is given by (49). The relaxation time τ_r is

$$\frac{1}{\tau_r} = \vartheta \frac{8\pi^2}{Kc^3} e^{-2Ka} \tag{52}$$

6. ESCAPE OVER THE BARRIER

The result can be utilized to study the escape over a potential barrier of the form (36). According to (44), (37), and (52), one has during Stage IV

$$p_{\pm}(t) = \frac{1}{2} \pm \frac{1}{2} Ce^{-t/\tau_r}$$

where the constant C is all that is left of the initial distribution. Hence p_+ and p_- obey the simple linear rate equations

$$\frac{dp_+}{dt} = -\frac{p_+ - p_-}{2\tau_r}, \quad \frac{dp_-}{dt} = \frac{p_+ - p_-}{2\tau_r} \tag{53}$$

The probability per unit time for the particle to cross the boundary is therefore $1/2\tau_r$, given by (52) or, using (36),

$$\frac{1}{2\tau_r} = \frac{\vartheta}{c^3} \cdot e^{-U(0)/\vartheta} \cdot Kc \tag{54}$$

The first factor may be understood as roughly the rate at which probability inside the valley diffuses toward the foot of the barrier. The exponential is the probability to reach the top of the barrier. The last factor originates from the matching of the wave functions at $x = a$ and must therefore be interpreted as a coupling effect between the valley and the barrier. This interpretation is only possible when in the exact value $1/2\tau_r = \frac{1}{2}\vartheta(E_1 - E_0)$ the energy difference is replaced with its approximate expression for large K . However, that is a purely algebraic approximation, not based on physical intuition. The result (53) may therefore be utilized to test more intuitive approximation methods.

Kramers⁽⁹⁾ used (2) in the form ($\pm d$ are the positions of the minima of U)

$$\int_{-d}^d J(x, t) e^{U(x)/\vartheta} dx = -\vartheta [e^{U(x)/\vartheta} P(x, t)]_{-d}^d$$

During Stage IV the variation of P is very slow, so that J is practically independent of x . The remaining integral can be approximated using (16):

$$\begin{aligned} \int_{-d}^d \exp[U(x)/\vartheta] dx &\approx \exp[U(0)/\vartheta] \int_{-\infty}^{\infty} \exp(-K^2x^2) dx \\ &= (\sqrt{\pi}/K) \exp[U(0)/\vartheta] \end{aligned} \tag{55}$$

On the right-hand side the value of P at $\pm d$ is related to p_{\pm} by using the Gaussian approximation

$$P(x \approx d, t) = p_+(t)[2\pi\vartheta/U''(d)]^{-1/2} \exp[-U''(d)(x-d)^2/2\vartheta]$$

Then there follows with the aid of (35) and (32)

$$P(d, t) = p_+(t)[2\pi\vartheta/U''(d)]^{-1/2} = (\pi/c^2)^{1/2} p_+(t) \quad (56)$$

Hence the probability flow across the barrier is found to be

$$J = \vartheta \frac{K}{\sqrt{\pi}} e^{-U(0)/\vartheta} \frac{\sqrt{\pi}}{c} (p_- - p_+) \quad (57)$$

Comparison with (53) shows that the constant factor in (57) represents $1/2\tau_+$. Comparison with (54) shows that *Kramers' calculation leads to the correct value*. This is somewhat surprising, because both (55) and (56) differ from the exact value by a factor $\frac{1}{2}\sqrt{\pi}$, but both factors cancel in the final result. That may well be a freak of our special U .

The method of Griffiths *et al.*⁽¹¹⁾ may be paraphrased as follows. Substitute $P = e^{-U/\vartheta} Q$ in (1), so that

$$\frac{\partial Q}{\partial t} = -U'(x) \frac{\partial Q}{\partial x} + \vartheta \frac{\partial^2 Q}{\partial x^2}$$

Replace U by its linearization (16) and suppose again that Q is practically stationary,

$$2K^2 x Q' + \vartheta Q'' = 0$$

The general solution is

$$Q(x) = A + B \operatorname{erf}(Kx)$$

To determine the integration constants, one observes that

$$\begin{aligned} p_+ &= \int_0^b \{A + B \operatorname{erf}(Kx)\} e^{-U/\vartheta} dx \\ &\approx (A + B) \int_0^b e^{-U/\vartheta} dx \\ &\approx (A + B)[2\pi\vartheta/U''(d)]^{1/2} = (A + B)c/\sqrt{\pi} \end{aligned} \quad (58)$$

and similarly for p_- with $-B$ instead of B . Hence

$$A = \sqrt{\pi}/2c, \quad B = (\sqrt{\pi}/2c)(p_+ - p_-) \quad (59)$$

Now the probability flow evaluated at $x = 0$ is

$$J = -\vartheta \left[\frac{\partial P}{\partial x} \right]_{x=0} = -\vartheta e^{-U(0)/\vartheta} B \frac{2}{\sqrt{\pi}} K$$

On substituting (59), one obtains again (57) and hence the correct result.

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