we obtain

$$zd_z^2 Q_\lambda + (1 - z)d_z Q_\lambda + (\lambda/2\gamma)Q_\lambda = 0 . \qquad (5.2.132)$$

This is the differential equation for the *Laguerre polynomials* [5.6] provided

$$\lambda = 2n\gamma . \qquad (5.2.133)$$

We can write

$$Q_\lambda(x) = L_n(\gamma x^2/2\mu) \qquad (5.2.134)$$

which is normalised. Hence, the conditional probability is

$$p(x, t\,|\,x_0, 0) = \sum_{n=0}^{\infty} \frac{\gamma x}{\mu} \exp\left(-\frac{\gamma x^2}{2\mu}\right) L_n\left(\frac{\gamma x_0^2}{2\mu}\right) L_n\left(\frac{\gamma x^2}{2\mu}\right) e^{-2n\gamma t} . \qquad (5.2.135)$$

We can compute the autocorrelation function by the method of (5.2.90):

$$\langle x(t)x(0)\rangle = \sum_{n=0}^{\infty} \left[\int_0^{\infty} x\,dx\,\frac{\gamma x}{\mu} \exp\left(\frac{-\gamma x^2}{2\mu}\right) L_n\left(\frac{\gamma x^2}{2\mu}\right)\right]^2 \exp(-2n\gamma t) \qquad (5.2.136)$$

and using

$$\int_0^{\infty} dz\, z^\alpha e^{-z} L_n(z) = (-1)^n \Gamma(\alpha + 1)\binom{\alpha}{n} , \qquad (5.2.137)$$

we find for the autocorrelation function

$$\langle x(t)x(0)\rangle = \frac{2\mu}{\gamma} \sum_{n=0}^{\infty} \frac{\pi}{4}\binom{\frac{1}{2}}{n}^2 \exp(-2n\gamma t). \qquad (5.2.138)$$

5.2.7 First Passage Times for Homogeneous Processes

It is often of interest to know how long a particle whose position is described by a Fokker-Planck equation remains in a certain region of x. The solution of this problem can be achieved by use of the *backward Fokker-Planck equation*, as described in Sect. 3.6.

a) Two Absorbing Barriers
Let the particle be initially at x at time $t = 0$ and let us ask how long it remains in the interval (a, b) which is assumed to contain x:

$$a \leqslant x \leqslant b \qquad (5.2.139)$$

We erect absorbing barriers at a and b so that the particle is removed from the system when it reaches a or b. Hence, if it is still in the interval (a, b), it has never left that interval.

Under these conditions, the probability that at time t the particle is still in (a, b) is

$$\int_a^b dx' p(x', t\,|\,x, 0) \equiv G(x, t) \,. \tag{5.2.140}$$

Let the time that the particle leaves (a, b) be T. Then we can rewrite (5.2.140) as

$$\text{Prob}(T \geqslant t) = \int_a^b dx' p(x', t\,|\,x, 0) \tag{5.2.141}$$

which means that $G(x, t)$ is the same as $\text{Prob}(T \geqslant t)$. Since the system is time homogeneous, we can write

$$p(x', t\,|\,x, 0) = p(x', 0\,|\,x, -t) \tag{5.2.142}$$

and the backward Fokker-Planck equation can be written

$$\partial_t p(x', t\,|\,x, 0) = A(x)\partial_x p(x', t\,|\,x, 0) + \tfrac{1}{2} B(x)\partial_x^2 p(x', t\,|\,x, 0) \tag{5.2.143}$$

and hence, $G(x, t)$ obeys the equation

$$\partial_t G(x, t) = A(x)\partial_x G(x, t) + \tfrac{1}{2} B(x)\partial_x^2 G(x, t) \,. \tag{5.2.144}$$

The boundary conditions are clearly that

$$p(x', 0\,|\,x, 0) = \delta(x - x')$$

and hence,

$$G(x, 0) = 1 \qquad a \leqslant x \leqslant b \tag{5.2.145}$$
$$\quad\;\; = 0 \qquad \text{elsewhere}$$

and if $x = a$ or b, the particle is absorbed immediately, so

$$\text{Prob}(T \geqslant t) = 0 \qquad \text{when } x = a \text{ or } b \,, \qquad \text{i.e.,}$$
$$G(a, t) = G(b, t) = 0. \tag{5.2.146}$$

Since $G(x, t)$ is the probability that $T \geqslant t$, the mean of any function of T is

$$\langle f(T) \rangle = -\int_0^\infty f(t) dG(x, t) \,. \tag{5.2.147}$$

Thus, the *mean first passage time*

$$T(x) = \langle T \rangle \tag{5.2.148}$$

is given by

$$T(x) = -\int_0^\infty t\, \partial_t G(x, t) dt \tag{5.2.149}$$

$$= \int_0^\infty G(x, t)dt \tag{5.2.150}$$

after integrating by parts.

Similarly, defining

$$T_n(x) = \langle T^n \rangle , \tag{5.2.151}$$

we find

$$T_n(x) = \int_0^\infty t^{n-1} G(x, t)dt . \tag{5.2.152}$$

We can derive a simple ordinary differential equation for $T(x)$ by using (5.2.150) and integrating (5.2.144) over $(0, \infty)$. Noting that

$$\int_0^\infty \partial_t G(x, t)dt = G(x, \infty) - G(x, 0) = -1 , \tag{5.2.153}$$

we derive

$$A(x)\partial_x T(x) + \tfrac{1}{2} B(x)\partial_x^2 T(x) = -1 \tag{5.2.154}$$

with the boundary condition

$$T(a) = T(b) = 0 . \tag{5.2.155}$$

Similarly, we see that

$$- nT_{n-1}(x) = A(x)\partial_x T_n(x) + \tfrac{1}{2} B(x)\partial_x^2 T_n(x) \tag{5.2.156}$$

which means that all the moments of the first passage time can be found by repeated integration.

Solutions of the Equations. Equation (5.2.154) can be solved directly by integration. The solution, after some manipulation, can be written in terms of

$$\psi(x) = \exp\left\{\int_a^x dx'[2A(x')/B(x')]\right\} . \tag{5.2.157}$$

We find

$$T(x) = \frac{2\left[\left(\int_a^x \dfrac{dy}{\psi(y)}\right)\int_x^b \dfrac{dy'}{\psi(y')}\int_a^{y'} \dfrac{dz\psi(z)}{B(z)} - \left(\int_x^b \dfrac{dy}{\psi(y)}\right)\int_a^x \dfrac{dy'}{\psi(y')}\int_a^{y'} \dfrac{dz\psi(z)}{B(z)}\right]}{\int_a^b \dfrac{dy}{\psi(y)}} . \tag{5.2.158}$$

b) One Absorbing Barrier

We consider motion still in the interval (a, b) but suppose the barrier at a to be reflecting. The boundary conditions then become

$$\partial_x G(a, t) = 0 \qquad\qquad (5.2.159a)$$

$$G(b, t) = 0 \qquad\qquad (5.2.159b)$$

which follow from the conditions on the backward Fokker-Planck equation derived in Sect.5.2.4. We solve (5.2.154) with the corresponding boundary condition and obtain

$$T(x) = 2 \int_x^b \frac{dy}{\psi(y)} \int_a^y \frac{\psi(z)}{B(z)} dz \qquad \begin{array}{l} a \quad \text{reflecting} \\ b \quad \text{absorbing} \\ a < b \end{array} \qquad\qquad (5.2.160)$$

Similarly, one finds

$$T(x) = 2 \int_a^x \frac{dy}{\psi(y)} \int_y^b \frac{\psi(z)}{B(z)} dz \qquad \begin{array}{l} b \quad \text{reflecting} \\ a \quad \text{absorbing} \\ a < b \end{array} \qquad\qquad (5.2.161)$$

c) Application—Escape Over a Potential Barrier

We suppose that a point moves according to the Fokker-Planck equation

$$\partial_t p(x, t) = \partial_x[U'(x)p(x, t)] + D\partial_x^2 p(x, t) . \qquad\qquad (5.2.162)$$

The potential has maxima and minima, as shown in Fig. 5.3. We suppose that motion is on an infinite range, which means the stationary solution is

$$p_s(x) = \mathcal{N} \exp \left[-U(x)/D\right] \qquad\qquad (5.2.163)$$

which is bimodal (as shown in Fig. 5.3) so that there is a relatively high probability of being on the left or the right of b, but not near b. What is the mean escape time from the left hand well? By this we mean, what is the mean first passage time from a to x, where x is in the vicinity of b? We use (5.2.160) with the substitutions

$$b \rightarrow x_0$$
$$a \rightarrow -\infty \qquad\qquad (5.2.164)$$
$$x \rightarrow a$$

so that

$$T(a \rightarrow x_0) = \frac{1}{D} \int_a^{x_0} dy \, \exp\left[U(y)/D\right] \int_{-\infty}^y \exp\left[-U(z)/D\right]dz . \qquad\qquad (5.2.165)$$
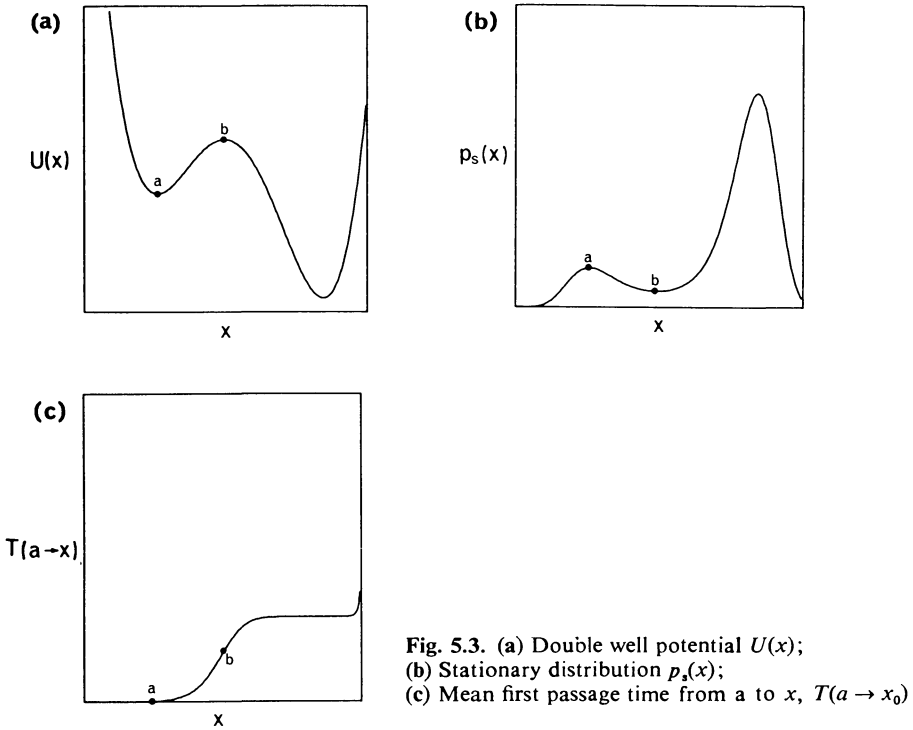
(a)

(b)

(c)

Fig. 5.3. (a) Double well potential $U(x)$;
(b) Stationary distribution $p_s(x)$;
(c) Mean first passage time from a to x, $T(a \rightarrow x_0)$

If the central maximum of $U(x)$ is large and D is small, then $\exp[U(y)/D]$ is sharply peaked at $x = b$, while $\exp[-U(z)/D]$ is very small near $z = b$. Therefore, $\int_{-\infty}^{y} \exp[-U(z)/D]dz$ is a very slowly varying function of y near $y = b$. This means that the value of the integral $\int_{-\infty}^{y} \exp[-U(z)/D]dz$ will be approximately constant for those values of y which yield a value of $\exp[U(y)/D]$ which is significantly different from zero. Hence, in the inner integral, we can set $y = b$ and remove the resulting constant factor from inside the integral with respect to y. Hence, we can approximate (5.2.165) by

$$T(a \rightarrow x_0) \simeq \left\{ \frac{1}{D} \int_{-\infty}^{b} dy \, \exp[-U(z)/D] \right\} \int_{a}^{x_0} dy \, \exp[U(y)/D]. \qquad (5.2.166)$$

Notice that by the definition of $p_s(x)$ in (5.2.163), we can say that

$$\int_{-\infty}^{b} dy \, \exp[-U(z)/D] = n_a/\mathcal{N} \qquad (5.2.167)$$

which means that n_a is the probability that the particle is to the left of b when the system is stationary.

A plot of $T(a \rightarrow x_0)$ against x_0 is shown in Fig. 5.3 and shows that the mean first passage time to x_0 is quite small for x_0 in the left well and quite large for x_0 in the

right well. This means that the particle, in going over the barrier to the right well, takes most of the time in actually surmounting the barrier. It is quite meaningful to talk of the *escape time* as that time for the particle, initially at a, to reach a point near c, since this time is quite insensitive to the exact location of the initial and final points. We can evaluate this by further assuming that near b we can write

$$U(x) \simeq U(b) - \frac{1}{2}\left(\frac{x - b}{\delta}\right)^2 \tag{5.2.168}$$

and near a

$$U(x) \simeq U(a) + \frac{1}{2_s}\left(\frac{x - a}{\alpha}\right)^2 . \tag{5.2.169}$$

The constant factor in (5.2.166) is evaluated as

$$\int_{-\infty}^{b} dz \exp\left[-U(z)/D\right] \sim \int_{-\infty}^{\infty} dz \exp\left[-\frac{U(a)}{D} - \frac{(z - a)^2}{2D\alpha^2}\right] \tag{5.2.170}$$

$$\sim \alpha\sqrt{2\pi D} \exp\left[-U(a)/D\right] \tag{5.2.171}$$

and the inner factor becomes, on assuming x_0 is well to the right of the central point b,

$$\int_{a}^{x_0} dy \exp U(y)/D \sim \int_{-\infty}^{\infty} dy \exp\left[\frac{U(b)}{D} - \frac{(y - b)^2}{2D\delta^2}\right] \tag{5.2.172}$$

$$= \delta\sqrt{2\pi D} \exp\left[U(b)/D\right] . \tag{5.2.173}$$

Putting both of these in (5.2.166), we get

$$T(a \to x_0) \simeq 2\alpha\delta\pi \exp\left\{[U(b) - U(a)]/D\right\} . \tag{5.2.174}$$

This is the classical *Arrhenius formula* of chemical reaction theory. In a chemical reaction, we can model the reaction by introducing a coordinate such that $x = a$ is species A and $x = c$ is species C. The reaction is modelled by the above diffusion process and the two distinct chemical species are separated by the potential barrier at b. In the chemical reaction, statistical mechanics gives the value

$$D = kT , \tag{5.2.175}$$

where k is Boltzmann's constant and T is the absolute temperature. We see that the most important dependence on temperature comes from the exponential factor which is often written

$$\exp\left(\Delta E/kT\right) \tag{5.2.176}$$

and predicts a very characteristic dependence on temperature. Intuitively, the answer is obvious. The exponential factor represents the probability that the energy

will exceed that of the barrier when the system is in thermal equilibrium. Those molecules that reach this energy then react, with a certain finite probability.

We will come back to problems like this in great detail in Chap.9.

5.2.8 Probability of Exit Through a Particular End of the Interval

What is the probability that the particle, initially at x in (a, b), exits through a, and what is the mean exit time?

The total probability that the particle exits through a after time t is given by the time integral of the probability current at a. We thus define this probability by

$$g_a(x, t) = - \int_t^\infty dt' \, J(a, t' \,|\, x, 0) \tag{5.2.177}$$

$$= \int_t^\infty dt' \, \{-A(a)p(a, t' \,|\, x, 0) + \tfrac{1}{2}\partial_a[B(a)p(a, t' \,|\, x, 0)]\} \tag{5.2.178}$$

(the negative sign is chosen since we need the current pointing to the left) and

$$g_b(x, t) = \int_t^\infty dt' \, \{A(b)p(b, t' \,|\, x, 0) - \tfrac{1}{2}\partial_b[B(b)p(b, t' \,|\, x, 0)]\} \,. \tag{5.2.179}$$

These quantities give the probabilities that the particle exits through a or b after time t, respectively. The probability that (given that it exits through a) it exits after time t is

$$\text{Prob}(T_a > t) = g_a(x, t)/g_a(x, 0) \,. \tag{5.2.180}$$

We now find an equation for $g_a(x, t)$. We use the fact that $p(a, t \,|\, x, 0)$ satisfies a backward Fokker-Planck equation. Thus,

$$A(x)\partial_x g_a(x, t) + \tfrac{1}{2}B(x)\partial_x^2 g_a(x, t) = - \int_t^\infty dt'\partial_{t'} J(a, t' \,|\, x, 0)$$

$$= J(a, t \,|\, x, 0)$$

$$= \partial_t g_a(x, t) \,. \tag{5.2.181}$$

The mean exit time, given that exit is through a, is

$$T(a, x) = - \int_0^\infty t\partial_t\text{Prob} \, (T_a > t) \, dt = \int_0^\infty g_a(x, t)dt/g_a(x, \infty) \,. \tag{5.2.182}$$

Simply integrating (5.2.181) with respect to t, we get

$$\boxed{A(x)\partial_x[\pi_a(x)T(a, x)] + \tfrac{1}{2}B(x)\partial_x^2[\pi_a(x)T(a, x)] = -\pi_a(x) \,,} \tag{5.2.183}$$

where we define

$$\pi_a(x) = (\text{probability of exit through } a) = g_a(x, 0) \,. \tag{5.2.184}$$