0.1 Diffusion with obstacles

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Consider a particle in a potential $U(x)$ (fig. 1), with a local minimum separated by a *barrier*. In the classical case, if the particle's energy is sufficiently low, it can become *forever* trapped inside the minimum. However, in the presence of *thermal fluctuations* there may be a possibility of escape - a sort of classical tunnelling.

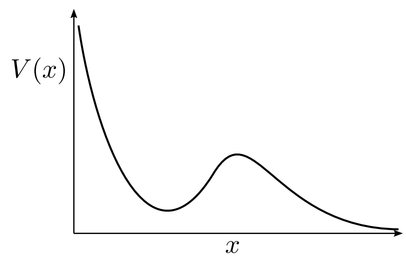

Figure (1) – Potential graph

We first consider an easier problem, that of the diffusion process on a compact domain $[a, b]$, representing the *boundaries* of the potential well of fig. 1. We then suppose that the particle cannot escape from the left side a, but it can do so - and always does - from the right one b. This means that a is a "reflecting" boundary - i.e. if the particle hits $x = a$ it "bounces back"), while $x = b$ is an *absorbing* boundary, that is a particle reaching b can be "absorbed by the environment" and disappear from the system. In the more general case, the probability of reflection at $x = a$ or absorption at $x = b$ will not be certain, but will depend on the particle's energy.

Recall the Langevin equation:

$$\mathrm{d}x(t) = \underbrace{\frac{F(x,t)}{\gamma}}_{f(x,t)}\mathrm{d}t + \sqrt{2D(x,t)}\,\mathrm{d}B \qquad F(x) = -U'(x);\ x \in [a, b]$$

This is equivalent to the Fokker-Planck equation:

$$\begin{aligned}\frac{\partial}{\partial t}W(x,t|x_0,0) &= -\frac{\partial}{\partial x}\left[f(x,t)W(x,t|x_0,0) - \frac{\partial}{\partial x}(D(x,t)W(x,t|x_0,0))\right] = \\ &= -\frac{\partial}{\partial x}\overbrace{\left[-\underbrace{\frac{U'(x)}{\gamma}}_{A(x)}W(x,t|x_0,0) - \frac{\partial}{\partial x}\Big(\underbrace{\frac{k_BT}{\gamma}}_{D}W(x,t|x_0,0)\Big)\right]}^{J(x,t)} = \qquad (1)\\ &= -\partial_x[A(x)W(x,t|x_0,0)] + \partial_x^2[D(x)W(x,t|x_0,0)] \qquad (2)\end{aligned}$$

where we inserted $D(x,t) \equiv D = k_BT/\gamma$ (derived from the equilibrium limit). $J(x,t)$ is the probability flux coming out from x at instant t.
To solve (1) we need a precise mathematical description for the *reflecting* and *absorbing* boundaries:

- In $x = a$, the *reflecting* boundary condition means that:

$$J(a,t) = A(a)W(a,t|x_0,0) - [\partial_x D(x)W(x,t|x_0,0)]|_{x=a} \stackrel{!}{=} 0 \qquad \forall t \tag{3}$$

  As every particle that goes in a immediately comes out after being reflected, the *inward* flux and *outward* one are the same, and so their sum is 0.

- In b, however, the *absorbing* boundary condition means that the probability to find the particle here is exactly 0:

$$W(b,t|x_0,0) \stackrel{!}{=} 0 \tag{4}$$

As $x \in [a,b]$, the domain of equation (1) is not isotropic anymore - meaning that the solution $W(x,t|x_0,0)$ will depend on x_0, making the problem much difficult. The idea is then to translate the problem from finding the full transition probability $W(x,t|x_0,0)$ to finding a simpler, but still interesting, function, that depends on less parameters.
One possible choice is given by the **survival probability**, i.e. the probability that a particle starting at a given point x will still be inside the interval $[a,b]$ at a later time t:

$$G(x,t) = \int_a^b \mathrm{d}y \, W(y,t|x,0)$$

Note that we keep the starting time fixed at 0, and integrate over all the possible *destinations* of the particle - reducing the number of variables from 4 to 2.
Note that generally $G(x,t) \neq 1$, as the boundary in b offers a possibility of escape, leading to a *violation* of the conservation of probability. In fact the condition (4) $W(b,t|x_0,t_0) = 0$ does not mean that the flux here is null. Recalling the definition of $J(x,t)$ from (1):

$$\begin{aligned} J(b,t) &= \cancel{A(b)W(b,t|x_0,t_0)} - \partial_x(D(x)W(x,t|x_0,t_0))|_{x=b} = \\ &= \cancel{-(\partial_x D)W(b,t|x_0,t_0)} - D(b)\partial_x W(x,t|x_0,t_0)|_{x=b} \neq 0 \end{aligned}$$

Now, we need to translate (1) to a differential equation for $G(x,t)$. We can start by evaluating the time derivative of $G(x,t)$:

$$\frac{\partial}{\partial t} G(x,t) = \int_a^b \mathrm{d}x' \, \frac{\partial}{\partial t} W(x',t|x,0) \tag{5}$$

We could use (2) to expand the $\partial_t W(x',t|x,0)$ term - but this does not really work:

$$\frac{\partial}{\partial t} G(x,t) = \int_a^b \mathrm{d}x' \, [-\partial_{x'}(A(x')W(x',t|x,0)) + \partial^2_{x'}(D(x')W(x',t|x,0))]$$

To reconstruct derivatives of $G(x,t)$ in the right side, we would need to bring the $\partial_{x'}$ out of the integrals - but this is not possible, as x' is the variable of integration. One way to solve this would be to somehow move the derivative from $\partial_{x'}$ to ∂_x.

To do this, we start from the ESCK relation:

$$\int_a^b \mathrm{d}x_1\, W(x_2,t_2|x_1,t_1)W(x_1,t_1|x_0,t_0) = W(x_2,t_2|x_0,t_0) \qquad t_0 < t_1 < t_2$$

Differentiating with respect to the middle time t_1:

$$\int_a^b \mathrm{d}x_1\, [W(x_1,t_1|x_0,t_0)\partial_{t_1}W(x_2,t_2|x_1,t_1) + W(x_2,t_2|x_1,t_1)\, \partial_{t_1}W(x_1,t_1|x_0,t_0)] = 0$$

We then use (2) to expand the highlighted term:

$$\begin{aligned}&\int_a^b \mathrm{d}x_1\, W(x_1,t_1|x_0,t_0)\partial_{t_1}W(x_2,t_2|x_1,t_1)+\\ &+\int_a^b \mathrm{d}x_1\, W(x_2,t_2|x_1,t_1)[-\partial_{x_1}A(x_1)W(x_1,t_1|x_0,t_0) + \partial^2_{x_1}D(x_1)W(x_1,t_1|x_0,t_0)] = 0\end{aligned}$$

And then we integrate by parts the second term, to move the ∂_{x_1} and $\partial^2_{x_1}$ derivatives:

$$\begin{aligned}&\int_a^b \mathrm{d}x_1\, W(x_1,t_1|x_0,t_0)\partial_{t_1}W(x_2,t_2|x_1,t_1)+\\ &-A(x_1)W(x_1,t_1|x_0,t_0)W(x_2,t_2|x_1,t_1)\Big|_{x_1=a}^{x_1=b} + W(x_2,t_2|x_1,t_1)[\partial_{x_1}D(x_1)W(x_1,t_1|x_0,t_0)]\Big|_{x_1=a}^{x_1=b}\\ &-D(x_1)W(x_1,t_1|x_0,t_0)[\partial_{x_1}W(x_2,t_2|x_1,t_1)]\Big|_{x_1=a}^{x_1=b}\\ &+\int_a^b \mathrm{d}x_1\, [A(x_1)W(x_1,t_1|x_0,t_0)\partial_{x_1}W(x_2,t_2|x_1,t_1) + D(x_1)W(x_1,t_1|x_0,t_0)]\partial^2_{x_1}W(x_2,t_2|x_1,t_1) = 0\end{aligned}$$

In the limit $t_1 \to 0$, $W(x_1,t_1|x_0,t_0) = \delta(x_1 - x_0)\delta(t_1 - t_0)$. This makes all the boundary terms vanish (given that $x_0 \neq a, b$), and allows to compute the other integrals (with $x_1 = x_0$ and $t_1 = t_0$), leading to:

$$\frac{\partial}{\partial t_0}W(x_2,t_2|x_0,t_0) + A(x_0)\frac{\partial}{\partial x_0}W(x_2,t_2|x_0,t_0) + D(x_0)\frac{\partial^2}{\partial x_0^2}W(x_2,t_2|x_0,t_0) = 0$$

Rearranging, and dropping some subscripts:

$$\partial_{t_0}W(x,t|x_0,t_0) = -A(x_0)\partial_{x_0}W(x,t|x_0,t_0) - D(x_0)\partial^2_{x_0}W(x,t|x_0,t_0) \qquad (6)$$

This is the **backward Fokker-Planck equation**, as all derivatives are with respect to the starting time or position - meaning that it can be use to “retrodict” the past given the future. This could be used for computing $\partial_t G(x,t)$ - but first we need to express the derivative ∂_{t_0} in terms of the derivative ∂_t that appears in $\partial_t G(x,t)$.
Supposing that $A(x)$ and $D(x)$ are time-independent (as we implicitly did in the previous notation), then (2) is an *autonomous* differential equation, meaning that the solution does not change after a time translation:

$$W(x,t|x_0,t_0) = W(x,t-t_0|x_0,0)$$

Differentiating with respect to t_0:

$$\partial_{t_0} W(x,t|x_0,t_0) = \partial_{t'} W(x,t'|x_0,0)|_{t'=t-t_0} \partial_{t_0}(t-t_0) = -\partial_t W(x,t-t_0|x_0,0) = -\partial_t W(x,t|x_0,t_0)$$

Substituting this relation in (6) we get:

$$\partial_t W(x,t|x_0,t_0) = A(x_0)\partial_{x_0} W(x,t|x_0,t_0) + D(x_0)\partial^2_{x_0} W(x,t|x_0,t_0) \tag{7}$$

Finally, we can use (7) in (5):

$$\begin{aligned}\frac{\partial}{\partial t} G(x,t) &= \int_a^b \mathrm{d}x'\, \partial_t W(x',t|x,0) = &(8)\\ &\underset{(7)}{==} \int_a^b \mathrm{d}x'\, [A(x)\partial_x W(x',t|x,0) + D(x)\partial^2_x W(x',t|x,0)] = \\ &= A(x)\partial_x \underbrace{\int_a^b \mathrm{d}x'\, W(x',t|x,0)}_{G(x,t)} + D(x)\partial^2_x \underbrace{\int_a^b \mathrm{d}x'\, W(x',t|x,0)}_{G(x,t)} = \\ &= A(x)\partial_x G(x,t) + D(x)\partial^2_x G(x,t) &(9)\end{aligned}$$

We have now a differential equation for $G(x,t)$, and we need to translate the appropriate boundary conditions (3) and (4). The latter is immediate:

$$W(b,t|x_0,0) = 0 \qquad \forall t\, \forall x_0 \in [a,b] \Rightarrow G(x,t)|_{x=b} = 0 \tag{10}$$

However, the analogous of (3) requires a bit more work. So we start again from the ESCK relation, and differentiate with respect to the mid-time:

$$\partial_\tau \int_a^b \mathrm{d}y\, W(x',t|y,\tau)W(y,\tau|x,0) = \partial_\tau W(x',t|x,0) = 0$$

Expanding the left side:

$$\int_a^b \mathrm{d}y\, [W(y,\tau|x,0)\, \partial_\tau W(x',t|y,\tau) + W(x',t|y,\tau)\, \partial_\tau W(y,\tau|x,0)\,] = 0$$

We can now use (6) for the term highlighted in yellow, and (2) (also called **forward Fokker-Planck equation**) for the term in green, leading to:

$$\begin{aligned}&\int_a^b \mathrm{d}y\, [-A(y)\partial_y W(x',t|y,\tau) - D(y)\partial^2_y W(x',t|y,\tau)] W(y,\tau|x,0) + \\ &\int_a^b \mathrm{d}y\, [-\partial_y A(y) W(y,\tau|X,0) + \partial^2_y D(y) W(y,\tau|x,0)] W(x',t|y,\tau)\end{aligned}$$

We now integrate by parts the first term, moving the ∂_y and ∂^2_y derivatives away from $W(x',t|y,\tau)$:

$$\begin{aligned}&- A(y)W(x',t|y,\tau)W(y,\tau|x,0)\Big|_{y=a}^{y=b} + \int_a^b \mathrm{d}y\, [\partial_y A(y) W(y,\tau|x,0)] W(x',t|y,\tau) + \\ &- D(y)W(y,\tau|x,0)[\partial_y W(x',t|y,\tau)]\Big|_{y=a}^{y=b} + W(x',t|y,\tau)[\partial_y D(y) W(y,\tau|x,0)]\Big|_{y=a}^{y=b} + \\ &- \int_a^b \mathrm{d}y\, [\partial^2_y D(y) W(y,\tau|x,0)] W(x',t|y,\tau) - \int_a^b \mathrm{d}y\, \partial_y [A(y) W(y,\tau|x,0)] W(x',t|y,\tau) + \\ &+ \int_a^b \mathrm{d}y\, \partial^2_y [D(y) W(y,\tau|x,0)] W(x',t|y,\tau) = 0\end{aligned}$$

The highlighted terms cancel out, leaving only boundaries:

$$-A(y)W(x',t|y,\tau)W(y,\tau|x,0)\Big|_{y=a} - D(y)W(y,\tau|x,0)[\partial_y W(x',t|y,\tau)]\Big|_{y=a}^{y=b} +$$
$$+W(x',t|y,\tau)[\partial_y D(y)W(y,\tau|x,0)]\Big|_{y=a}^{y=b} = 0$$

Now $W(b,t|x_0,0) = 0$ (4), and also $W(x',t|b,\tau) = 0$, as a particle starting in b escapes immediately from $[a,b]$. This makes all the boundary terms vanish at $y=b$, leaving only:

$$+A(a)W(x',t|a,\tau)W(a,\tau|x,0) + D(a)W(a,\tau|x,0)[\partial_y W(x',t|y,\tau)]|_{y=a} +$$
$$-W(x',t|a,\tau)[\partial_y D(y)W(y,\tau|x,0)]|_{y=a} = 0$$

Collecting $W(x',t|a,\tau)$ allows to recognize a $J(x,t)$ term:

$$D(a)W(a,\tau|x,0)[\partial_y W(x',t|y,\tau)]|_{y=a} +$$
$$+W(x',t|a,\tau)\Big[\underbrace{A(a)W(a,\tau|x,0) - [\partial_y D(y)W(y,\tau|x,0)]|_{y=a}}_{J(a,\tau)}\Big] = 0$$

But recall that $J(a,\tau) = 0\ \forall\tau$ as per (4). So only a term remains:

$$D(a)W(a,\tau|x,0)[\partial_y W(x',t|y,\tau)]|_{y=a} = 0 \Rightarrow W(a,\tau|x,0) = 0 \ \vee\ \partial_y W(x',t|y,\tau)|_{y=a} = 0 \quad \forall\tau$$

Finally, by integrating the second term:

$$\int_a^b \mathrm{d}x'\, \partial_y W(x',t|y,\tau) = \partial_y \int_a^b \mathrm{d}x'\, W(x',t|y,\tau) = \partial_y G(y,\tau)$$

And evaluating at $y = a$ leads to:

$$\partial_x G(x,t)|_{x=a} = 0 \tag{11}$$

which is the last boundary condition we needed for $G(x,t)$.
So, the problem now becomes:

$$\begin{cases} \partial_t G(x,t) = A(x)\partial_x G(x,t) + D(x)\partial_x^2 G(x,t) \\ \partial_x G(x,t)|_{x=a} = 0 \\ G(x,t)|_{x=b} = 0 \end{cases}$$

We can make one last simplification by *removing* the time coordinate. Let's introduce $T(x)$ as being the *lifetime* of a particle starting at x - meaning the amount of time needed for that particle to "disappear" by reaching b (so, in this case, $T(x)$ coincides with $T_{\text{ftv}}(b,x)$, i.e. the *time to the first visit* of b). The exact value of $T(x)$ will depend on the particle's path, making $T(x)$ a random variable. Note that:

$$G(x,t) = \mathbb{P}(T(x) > t)$$

That is, the survival probability is the probability that the particle *has not yet reached* b during the time interval $[0, t]$, which is equivalent to saying that its lifetime is greater than t. Denoting with $\mathbb{P}_{\text{ftv}}(T_b)\,\mathrm{d}T_b$ the probability that a particle will visit b in the time range $[T_b, T_b + \mathrm{d}T_b]$, we have:

$$G(x,t) = \mathbb{P}(T(x) > t) = \int_t^{+\infty} \mathbb{P}_{\text{ftv}}(T_b)\,\mathrm{d}T_b = -\int_{+\infty}^{t} \mathbb{P}_{\text{ftv}}(T_b)\,\mathrm{d}T_b$$

Differentiating with respect to t:

$$\partial_t G(x,t) = -\mathbb{P}_{\text{fvt}}(t)$$

As we need a function, and $T(x)$ is a random variable, we consider its *average*, i.e. the *mean time of arrival at* b $T_b(x)$:

$$\begin{aligned} T_b(x) \equiv \langle T(x) \rangle &\equiv \int_0^{+\infty} t\mathbb{P}_{\text{fvt}}(t)\,\mathrm{d}t = -\int_0^{+\infty} t\partial_t G(x,t)\,\mathrm{d}t = \\ &= -tG(x,t)\Big|_{t=0}^{t=+\infty} + \int_0^{+\infty} G(x,t)\,\mathrm{d}t \underset{(a)}{=} \langle G(x) \rangle \end{aligned} \tag{12}$$

In (a) we used that $tG(x,t)$ vanishes at $t = 0$ and also at $t = +\infty$, because the particle will eventually reach $x = b$ if given infinite time to do so. It is not clear if $G(x,t) \xrightarrow[t\to\infty]{} 0$ *faster* than $t \to \infty$, so that $tG(x,t) \xrightarrow[t\to\infty]{} 0$. Here, we will just assume it, as it is physically reasonable.

Then, we need to translate once again everything to expressions involving $T_b(x)$. Fortunately, this time it is much quicker. To get the differential equation, we just integrate (9):

$$\int_0^{+\infty} \mathrm{d}t\,\partial_t G(x,t) = A(x)\partial_x \int_0^{+\infty} G(x,t)\,\mathrm{d}t + D(x)\partial_x^2 \int_0^{+\infty} G(x,t)\,\mathrm{d}t$$

And applying (12) we get:

$$G(x,t)\Big|_{t=0}^{t=+\infty} = G(x,+\infty) - G(x,0) = -1 = A(x)\partial_x T_b(x) + D(x)\partial_x^2 T_b(x)$$

as $G(x,+\infty) = 0$ (no particle lives eternally) and $G(x,0) = 0$ (as a particle does not "disappear" immediately for $x \neq b$). Similarly, integrating (11) and (10) leads to:

$$\begin{cases} A(x)\partial_x T_b(x) + D(x)\partial_x^2 T_b(x) = -1 \\ T_b(x)\big|_{x=b} = 0 \\ \partial_x T_b(x)\big|_{x=a} = 0 \end{cases}$$

This is a linear ordinary differential equation. We start by letting $f(x) = \partial_x T_b(x)$, leading to:

$$f'(x) = -\frac{A(x)}{D(x)} f(x) - \frac{1}{D(x)} \qquad f(a) = 0$$

First consider the *homogeneous* equation:

$$A(x)\Phi(x) + D(x)\Phi'(x) = 0$$

This can be solved by separation of variables:

$$Af + D\frac{\mathrm{d}\Phi}{\mathrm{d}x} = 0 \Rightarrow \frac{\mathrm{d}\Phi}{\Phi} = -\frac{A}{D}\,\mathrm{d}x \Rightarrow \ln|\Phi(x)| = -\int_{x_0}^{x} \frac{A(y)}{D(y)}\,\mathrm{d}y + c$$

where x_0 is a fixed point $\in [a,b]$ (it does not matter which one). Exponentiating:

$$\Phi(x) = \exp\left(-\int_{x_0}^{x} \frac{A(y)}{D(y)}\,\mathrm{d}y\right) k$$

Where $k = e^c$ will be fixed by the boundary condition $f(a) = 0$. First, we need to find the general integral of the inhomogeneous equation - for example by using the method of **variation of parameters**.

Refresher of variation of parameters. Consider the following Cauchy problem:

$$\begin{cases} y' = A(t)y + b(t) \\ y(t_0) = y_0 \end{cases}$$

Suppose we know a solution $\Phi(t)$ of the homogeneous equation $y' = A(t)y$. Then $\Phi' = A\Phi$. We search for a particular solution for the full equation in the form $\tilde{\varphi}(t) = \Phi(t)c(t)$. Substituting in the equation:

$$\Phi'c + c'\Phi = A\Phi c + c'\Phi = A\Phi c + b \Rightarrow c' = \Phi^{-1}b$$

This can be integrated to find c, and then $\tilde{\varphi}$. Then, the general integral will be the sum of the homogeneous solution $\Phi(t)$ and the particular one $\tilde{\varphi}$. Imposing the boundary condition will lead to the general integral:

$$\varphi(t) = \Phi(t)\Phi(t_0)^{-1}y_0 + \Phi(t)\int_{t_0}^{t} \Phi(\tau)^{-1}b(\tau)\,\mathrm{d}\tau \tag{13}$$

Applying formula (13) leads to the desired $f(x)$:

$$\begin{aligned} f(x) &= \Phi(x)\Phi(a)\cdot 0 + \Phi(x)\int_a^x \mathrm{d}z\,\Phi(z)^{-1}\left[-\frac{1}{D(z)}\right] = \\ &= \exp\left(-\int_{x_0}^{x}\frac{A(y)}{D(y)}\,\mathrm{d}y\right)\int_a^x -\frac{\mathrm{d}z}{D(z)}\exp\left(+\int_{x_0}^{z}\frac{A(y)}{D(y)}\,\mathrm{d}y\right) = \\ &= -\int_a^x \frac{\mathrm{d}z}{D(z)}\exp\left(+\int_x^z \frac{A(y)}{D(y)}\,\mathrm{d}y\right) \end{aligned}$$

Recall that $f(x) = \partial_x T_b(x)$, with $T_b(b) = 0$. So, to find $T_b(x)$ we need one last integration:

$$T_b(x) = \int_{x_0}^{x} \mathrm{d}y\, f(y) + c$$

Imposing $T_b(b) = 0$ leads to:

$$T_b(b) = \int_{x_0}^{b} \mathrm{d}y\, f(y) + c \overset{!}{=} 0 \Rightarrow c = -\int_{x_0}^{b} \mathrm{d}y\, f(y)$$

Leading to:

$$T_b(x) = \int_b^x \mathrm{d}y\, f(y) = \int_x^b \mathrm{d}y \int_a^y \frac{\mathrm{d}z}{D(z)} \exp\left(-\int_z^y \mathrm{d}v\, \frac{A(v)}{D(v)}\right) \tag{14}$$

0.1.1 Escape from a potential well

Let's now use (14) to solve the problem we started from. So, suppose to have a potential $U(x)$ with a local minimum at $x = c$, and a local maximum at $x = d$, with $c < d$. Consider a particle starting at $x = c$. We wish to compute the average first visit time of d, denoted with $\langle T(c \to d)\rangle$. This can be done by redefining the system as the half-line $[-\infty, d]$, with $x = -\infty$ being a *reflective* boundary, and $x = d$ an *absorbing* one. We can do this because we are not interested in the behaviour *after* passing d, but just in the mean arrival times.
So $A(x) = -\partial_x U(x)/\gamma$. Supposing to be at equilibrium, $D(x) \equiv D = 1/(\gamma B)$. Letting $a = -\infty$ and $b = d$ leads to:

$$\begin{aligned} T_d(x) &= \int_x^d \mathrm{d}y \int_{-\infty}^{y} \beta\gamma\, \mathrm{d}z \exp\left(-\int_z^y -\mathrm{d}v\, \frac{\partial_v U(v)}{\gamma}\gamma\beta\right) = \\ &= \beta\gamma \int_x^d \mathrm{d}y \int_{-\infty}^{y} \mathrm{d}z \exp(\beta[U(y) - U(z)]) = \\ &= \beta\gamma \int_x^d \mathrm{d}y\, e^{\beta U(y)} \underbrace{\int_{-\infty}^{y} \mathrm{d}z\, e^{-\beta U(z)}}_{e^{F(y)}} = \beta\gamma \int_x^d \mathrm{d}y\, e^{\beta U(y) + F(y)} \end{aligned}$$

It is not possible to evaluate this integral in the general case. However, in the limit $\beta \to \infty$ ($T \to 0$) we can use the saddle-point approximation.
Recall Laplace's formula:

$$\int_a^b e^{Mf(x)}\, \mathrm{d}x \underset{M\to+\infty}{\approx} \sqrt{\frac{2\pi}{M|f''(x_0)|}} e^{Mf(x_0)}$$

where $f'(x_0) = 0$ and $f''(x_0) < 0$.
For the integral in $\mathrm{d}z$, $f(z) = -U(z)$. We search for a maximum of $f(z)$, i.e. a minimum of $U(z)$, which is $z = c$. So:

$$\int_{-\infty}^{y} e^{-\beta U(z)}\, \mathrm{d}z = \sqrt{\frac{2\pi}{\beta U''(c)}} e^{-\beta U(c)}$$

This is a constant, and can be brought outside the integral over $\mathrm{d}y$. Then, by applying Laplace's formula once again:

$$\int_c^d \mathrm{d}y\, e^{\beta U(y)} = \sqrt{\frac{2\pi}{\beta |U''(d)|}} e^{\beta U(d)}$$

as now $f(y) = U(y)$, and U has a local maximum in $y = d$. Finally, this leads to:

$$T_d(c) \underset{T\to 0}{\approx} \frac{2\pi\gamma}{\sqrt{U''(c)|U''(d)|}} \exp\left(\beta[U(d) - U(c)]\right)$$

Note that the mean transition time from c to d diverges exponentially as the barrier's height $U(d)-U(c)$ rises. Equivalently, the *escape transition rate* $1/T_d(c) \to 0$.

0.2 Feynman Path Integral

We finish our discussion about the diffusion formalism noting several correspondences with quantum processes.
Recall the Schödinger equation:

$$\begin{aligned} i\hbar\frac{\partial}{\partial t}\psi(x,t) &= -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}\psi(x,t) + V(x)\psi(x,t) = \\ &= H(x, \partial_x^2, t)\psi(x,t) \end{aligned}$$

where H is the *Hamiltonian* operator:

$$H(x, \partial_x^2, t) \equiv -\frac{\hbar^2}{2m}\partial_x^2 + V(x,t)$$

If we consider a free particle ($V(x,t) \equiv 0$), the Schrödinger equation becomes:

$$\partial_t \psi = i\frac{\hbar}{2m}\partial_x^2\psi \qquad \psi(x,0) = \delta(x - x_0) \tag{15}$$

which is very similar to the diffusion equation:

$$\partial_t W(x,t) = D\partial_x W(x,t) \qquad W(x,t|x_0,0)\Big|_{t=0} = \delta(x - x_0) \tag{16}$$

In fact, we can map (15) to (16) by defining a *quantum diffusion coefficient* $D_{QM} = i\hbar/(2m)$.

Does this mean that all properties of the diffusion equation - and its solution - can be mapped to the quantum case? Unfortunately, the answer is a bit complex.
Recall that the solution of (16) for a particle initially starting in x_0 at t_0 is:

$$W(x,t|x_0,t_0) = \frac{1}{\sqrt{4\pi D(t-t_0)}} \exp\left(-\frac{(x-x_0)^2}{4D(t-t_0)}\right) \tag{17}$$

By substituting $D \leftrightarrow D_{\text{QM}}$ we can construct the analogous *quantum* solution:

$$\psi(x,t) = \sqrt{\frac{2m}{4\pi(t-t_0)i\hbar}} \exp\left(i\frac{m}{2\hbar}\frac{(x-x_0)^2}{t-t_0}\right) \tag{18}$$

Note that now the exponential argument is *complex*, making basic properties of (17) not-trivial. For example, if $t \to t_0$, the exponential in (17) tends to a δ:

$$\lim_{t\to t_0} W(x,t|x_0,t_0) = \delta(x - x_0)$$

giving back the starting distribution, as expected.
The same, however, does not happen for (18), given the presence of the i. Nonetheless, it is true that in the limit $t \to t_0$, (18) is a *infinitely oscillating function*, meaning that it is 0 *almost* everywhere. This can be proven by using more sophisticated techniques, such as the *stationary phase approximation*.

What about path integrals? If we start with the usual definition and make the substitution $D \leftrightarrow D_{\text{QM}}$ we get:

$$\begin{aligned}\psi(x,t) &= \langle \delta(x(t)-x)\rangle_W = \\ &= \int_{\mathbb{R}^T} \prod_{\tau=0^+}^{t} \frac{\mathrm{d}x(\tau)}{\sqrt{4\pi D_{\text{QM}}\,\mathrm{d}\tau}} \exp\left(-\frac{1}{4D_{\text{QM}}}\int_0^t \left(\frac{\mathrm{d}x(\tau)}{\mathrm{d}\tau}\right)^2 \mathrm{d}\tau\right)\delta(x(t)-x) = \\ &= \int_{\mathbb{R}^T} \prod_{\tau=0^+}^{t} \frac{\mathrm{d}x(\tau)}{\sqrt{4\pi D_{QM}\,\mathrm{d}t}} \exp\left(\frac{i}{\hbar}\frac{1}{2}m\int_0^t \left[\frac{\mathrm{d}x(\tau)}{\mathrm{d}\tau}\right]^2 \mathrm{d}\tau\right)\delta(x(t)-x)\end{aligned}$$

Note that now *trajectories* are weighted by a *complex number*. This means that they *are not probabilities* - and in particular, we cannot use Kolmogorov extension theorem to prove the existence of such a measure as the *continuum limit* of a measure defined on *discretized paths*.
However, we note that in the limit $\hbar \to 0$, the integral can be approximated with the saddle-point method, which returns the *classical trajectory* - the one where the *phases oscillate slowly*.
In fact, it can be proven that *QM* cannot be derived by statistical mechanics alone: quantum "noise" is very much different from thermal "noise"!

Consider now the more general case of non-zero potential:

$$\frac{\partial}{\partial t}\psi(x,t) = i\frac{\hbar}{2m}\partial_x^2\psi(x,t) - \frac{iV(x)}{\hbar}\psi(x,t)$$

which is just the quantum evaluated version of the Fokker-Planck equation:

$$\partial_t W(x,t) = D\partial_x^2 W(x,t) - V(x)W(x,t)$$

with the substitutions:

$$\begin{aligned}D &\to D_{QM} = \frac{i\hbar}{2m} \\ V &\to \frac{i}{\hbar}V\end{aligned} \tag{19}$$

The solution we obtained from discussing the diffusion process is:

$$\begin{aligned}W(x,t|x_0,t_0) &= \langle \exp\left(-\int_0^t V(x(\tau))\,\mathrm{d}\tau\right)\delta(x(t)-x)\rangle_W = \\ &= \int_{\mathbb{R}^T} \prod_{\tau=0^+}^{t} \frac{\mathrm{d}x(\tau)}{\sqrt{4D\pi}\,\mathrm{d}\tau} \exp\left(-\frac{1}{4D}\int_0^t \dot{x}^2(\tau)\,\mathrm{d}\tau - \int_0^t V(x(\tau))\,\mathrm{d}\tau\right)\delta(x(t)-x)\end{aligned}$$

Applying (19) we arrive to the **Feynman path integral**:

$$\psi(x,t) = \int_{\mathbb{R}^T} \prod_{\tau=0^+}^{t} \frac{\mathrm{d}x(\tau)}{\sqrt{4\pi D_{QM}\,\mathrm{d}\tau}} \exp\left(\frac{i}{\hbar}\int_0^t \mathrm{d}\tau \underbrace{\left[\frac{\dot{x}^2(\tau)}{2} - V(x(\tau))\right]}_{L(\dot{x},x)}\right)\delta(x(t)-x)$$

To compute it we can resort to variational methods. We define the action functional S as:

$$S \equiv \int_0^t \mathrm{d}\tau\, L(\dot{x}(\tau), x(\tau))$$

Note that the Feynman path integral *weights* every trajectory with the following quantity:

$$\exp\left(\frac{i}{\hbar} S\left(\{x(\tau)\}_{\tau\in[0,t]}\right)\right)$$

Then, according to the variational method, we can approximate $\psi(x,t)$ by evaluating it only for the *most contributing trajectory*, i.e. the one that *stationarizes* S: $\delta S = 0$, implying:

$$x_c\colon \frac{\partial L}{\partial x} - \frac{\mathrm{d}}{\mathrm{d}t}\frac{\partial L}{\partial \dot{x}}\bigg|_{x_c} = 0$$