0.1 Title

(Lesson ? of 25/11/19) Compiled: November 25, 2019

We were dealing with a particle subject to a potential with a local minimum at $x = c$, a local maximum at $x = d$ and going to ∞ at $x \to -\infty$ and to 0 for $x \to +\infty$. We wrote the Langevin equation:

$$\dot{x} = -\frac{\partial_x U}{\gamma} + \sqrt{2D}\xi$$

and we expect the equilibrium distribuion to be:

$$\mathbb{P}_{\text{eq}}(x) = \frac{e^{-\beta U(x)}}{z}$$

The Fokker-Planck equation is then:

$$\dot{\mathbb{P}}(x', t|x, 0) = \partial_x[-A(x')\mathbb{P}(x', t|x, 0) + \partial_x(D(x')\mathbb{P}(x', t|x, 0))] \qquad A(x) = \partial_x U(x) \quad D(x) = D$$

Before solving this problem, however, it is convenient to consider the *simpler* situation of a particle confined to an interval $[a, b]$, with *reflective* boundary conditions at $x = a$, and *absorbing* bc at $x = b$. We already found that:

$$\int_a^b \mathbb{P}(x', t|x, 0)\,\mathrm{d}x' = G(x, t) = \mathbb{P}(T_b > t|x) \tag{1}$$

where T_b is the *survival time* of the particle, given it started in x at time 0.
We then wrote the *backward* F-P equation by differentiating F-P wrt t_0:

$$\partial_{t_0} P(x', t|x, t_0) = -A(x)\partial_x P(x', t|x, t_0) - D(x)\partial_x^2 P(x', t|x, t_0)$$

Note that, because $A(x)$ and $D(x)$ **do not** depend on time, transitional probabilities depend only on *temporal differences*:

$$P(x', t|x, t_0) = P(x', t - t_0|x, 0)$$

So we can make a change of variables and substitute ∂_{t_0} with $-\partial_t$.
Then, the *absorbing* bc is expressed in terms of probability:

$$P(x', t|x, 0)\Big|_{x'=b} = 0$$

and the reflective bc in terms of *flux*:

$$J(x', t) = A(x')P(x', t|x, 0) - \partial_{x'}(D(x')P(x', t|x_0, 0))\Big|_{x_0=a} = 0$$

We want now to express this relation using the survival probability $G(x, t)$. Note that, if we differentiate (1) wrt t:

$$\partial_t G(x, t) = A(x)\partial_x G(x, t) + D(x)\partial_x^2 G(x, t)$$

Recall the ESCK relation:

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

As the right side is independent of τ, the derivative wrt τ will be 0:

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

$$= \int_a^b [(\partial_\tau \bar{P})P + \bar{P}\partial_\tau P]\,\mathrm{d}y =$$

Substituting in the Backward and Forward F-P:

$$= \int_a^b [(-A(y)\partial_y \bar{P} - D(y)\partial_y^2 \bar{P})P + \bar{P}\partial_y(-A(y)P + \partial_y(D(y)P))]$$

By performing multiple *integrations by parts*, several terms cancel out, and only boundary terms remain, leading to:

$$0 = \bar{P}(-A(y)P + \partial_y(D(y)P))\Big|_a^b - (\partial_y \bar{P}) \cdot (D(y)P)\Big|_a^b$$

Recall that:

$$\bar{P} = P(x', t|y, 0)$$

As the flux vanishes at $y = a$, and $\bar{P}$ vanishes at $y = b$, the first term is 0, leading to:

$$-(\partial_y \bar{P})D(y)P(y, \tau|x, 0)\Big|_{y=a}^{y=b} = 0$$

which is again 0 at $y = b$, so the only remaining expression is:

$$\partial_y P(x', t|y, \tau)\Big|_{y=a} = 0\ \forall\tau \quad \vee \quad \partial_y \bar{P}\Big|_{y=a} = 0$$

This leads to the final expression for the boundary conditions:

$$G(x, t)\Big|_{x=b} = 0 \qquad \partial_x G(x, t)\Big|_{x=a} = 0$$

Recall that we defined $G(x, t)$ to be the probability that a particle has survived for at least t:

$$G(x, t) = \mathbb{P}(T_b > t) = \int_t^\infty \mathbb{P}_{\text{fvt}}(T_b)\,\mathrm{d}T_b$$

where we introduce:

$$\mathbb{P}_{\text{fvt}}(T_b)\,\mathrm{d}T_b$$

being he probability that the particle arrived at $x = b$ (for the first time, as it then disappears) in the time interval $(T_b, T_b + \mathrm{d}T_b)$ (fvt stands for "first time visit"). Differentiating wrt t:

$$\partial_t G(x,t) = -\mathbb{P}_{\text{fvt}}(t) \tag{2}$$

If we consider now the *average survival time*:

$$\begin{aligned} T_b(x) = \langle T_b \rangle &= \int_0^\infty t\mathbb{P}_{\text{fvt}}(t)\,\mathrm{d}t = \\ &= -\int_0^\infty t\partial_t G(x,t)\,\mathrm{d}t = -tG(x,t)\Big|_0^\infty + \underbrace{\int_0^\infty G(x,t)\,\mathrm{d}t}_{\langle G(x)\rangle} \end{aligned}$$

$tG(x,t) = 0$ obviously at $t = 0$. We know that $G(x,t) = 0$ for $t \to \infty$ (the particle will certainly visit $x = b$ given *infinite time* to do so), however it is not clear if $G(x,t) \to 0$ as $t \to \infty$ "fast enough" so that $tG(x,t) \to 0$. For now, we will assume that it does, as it is quite reasonable.
So we found:

$$\langle T_b \rangle = T_b(x) = \int_0^\infty G(x,t)\,\mathrm{d}t$$

Expanding (2):

$$\partial_t G(x,t) = A(x)\partial_x G + D(x)\partial_x^2 G$$

If we then *integrate*:

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

and so:

$$G(x,t)\Big|_{t=0}^{t=\infty} = -G(x,0) = -1$$

as the particle starts at a position *different* from b $(x < b)$. Then:

$$A(x)\partial_x T_b(x) + D(x)\partial_x^2 T_b(x) = -1$$

with the following boundary conditions:

$$T_b(x)\Big|_{x=b} = 0 \qquad \partial_x T_b(x)\Big|_{x=a} = 0$$

Denote $\partial_x T \equiv f$. The second order ODE becomes:

$$Af + Df'' = -1$$

The homogeneous equation (with 0 instead of -1) would have solution:

$$f(x) = \exp\left(-\int_a^x \frac{A(y)}{D(y)}\,\mathrm{d}y\right)c$$

To solve the *inhomogeneous* case, we consider c being a function: $c(x)$. Substituting back $f(x)$ leads to an explicit expression for $c(x)$, allowing to write the general solution:

$$T_b(x) = \int_x^b \mathrm{d}y \int_a^y \mathrm{d}z \, \frac{1}{D(z)} \exp\left(-\int_z^y \frac{A(v)}{D(v)} \, \mathrm{d}v\right)$$

Where we imposed $f(a) = 0 \Rightarrow c(a) = 0$.
Substituting the definitions of $A(x) = -\partial_x U(x)/\gamma$ and $D(x) = D = (\gamma\beta)^{-1}$ ($\beta = 1/(k_B T)$) for our specific case, and setting $a = -\infty$ and $b = d$ (positions of *reflective* and *absorbing*boundaries for the particle in the potential well $U(x)$), we get:

$$T_d(c) = \gamma\beta \int_c^d \mathrm{d}y \, e^{\beta U(y)} \underbrace{\int_{-\infty}^y e^{-\beta U(z)} \, \mathrm{d}z}_{e^{F(y)}}$$

This integral cannot be evaluated in general. However, if β is sufficiently large, meaning that the temperature $T \to 0$, we can use the *saddle point approximation* and compute it.
So, we assume $\beta U(d) \gg 1$ and $\beta U(c) \gg 1$. Note that:

$$\frac{\displaystyle\int_{-\infty}^y e^{-\beta U(z)} \, \mathrm{d}z}{\displaystyle\int_{-\infty}^{+\infty} e^{-\beta U(z)} \, \mathrm{d}z} = \mathbb{P}(x < y)$$

as $e^{-\beta U(z)} \, \mathrm{d}z$ is the probability that the article is in $(z, z + \mathrm{d}z)$ at equilibrium.
Then:

$$T_d(c) = \gamma\beta \int_c^d e^{\beta U(y) + F(y)}$$

Expanding the potential around the local maximum at $y = d$:

$$U(y) = U(d) + \frac{(y-d)^2}{2} \underbrace{U''(d)}_{<0} + \dots$$

we can simplify the integral as:

$$T_d(c) = \gamma\beta e^{\beta U(d)} \int_c^d \mathrm{d}y \exp\left(-\frac{\beta |U''(d)|}{2} (y-d)^2 + \dots + F(y)\right)$$

The integral is *dominated* by *small values* :

$$\beta |U''(d)| (y-d)^2 \lesssim 1$$

And so we write:

$$T_d(x) = \gamma\beta e^{\beta U(d) + F(d)} \int_c^d \mathrm{d}y \exp\left(-\frac{|U''(d)|(y-d)^2 \beta}{2} + \dots\right)$$

Substituting $-d+y=z$:

$$T_d(c) = \gamma\beta e^{\beta U(d)+F(d)} \int_{-d+c}^{0} \exp\left(-z^2|U''(d)|\frac{\beta}{2}\right) \mathrm{d}z \approx \int_{-\infty}^{0} \exp\left(-z^2|U''(d)|\frac{\beta}{2}\right) \mathrm{d}z = \frac{1}{2}\sqrt{2\pi}\frac{1}{\sqrt{\beta U''(d)}}$$

Then only the following is left to evaluate:

$$e^{F(d)} = \int_{-\infty}^{d} e^{-\beta U(z)} \, \mathrm{d}z$$

which is dominated by values around the *minimum* of $U(x)$:

$$U(z) = U(c) + \frac{(z-c)^2}{2} U''(c) + \dots$$

and by substituting $z - c = v$:

$$e^{F(d)} \approx e^{-\beta U(c)} \int_{-\infty}^{+\infty} \mathrm{d}v \exp\left(-\frac{\beta U''(c)}{2} v^2\right) = e^{-\beta U(c)} \sqrt{\frac{2\pi}{\beta U''(c)}}$$

Substituting everything back leads to:

$$T_d(c) = \frac{\beta\gamma}{2} \frac{2\pi}{\sqrt{\beta|U''(d)|\beta U''(c)}} e^{-\beta(U(d)-U(c))}$$

Note that the particle is more likely to overcome the *barrier* and escape the potential well if the temperature is high and the barrier height is low. The *escape* transition rate is the reciprocal:

$$\frac{1}{T_d(c)}$$

0.2 Quantum Mechanics

Recall the Schödinger equation:

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

where H is the *Hamiltonian* operator:

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

If we consider a free particle ($V = 0$), the Schrödinger equation becomes:

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

which is very similar to the diffusion equation:

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

In fact, we can define $D_{QM} = i\hbar/(2m)$.
Recall that the diffusion solution is:

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

So by substituting $D = D_{QM}$ everywhere:

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

We can ask: if $t \to t_0$, does $\psi(x,t) \to \psi(x,0) = \delta(x-x_0)$ (as it happens in the diffusion solution)? In fact, now we have an *imaginary* exponential, meaning that for $t \to t_0$ the wavefunction oscillates *very fast*. The idea is then that, in this case, it is almost everywhere 0. This can be proved by using the *stationary phase* technique, which shows that the integral of $\psi(x,t)$ is dominated by the values with a really small phase.
We can now use what we learned with path integrals:

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

Note that now *trajectories* are weighted by a *complex number*. So we are **not** dealing with a probability measure, and thus we cannot directly use the Kolmogorov extension theorem (which would require non-negative real "weights").
With $\hbar \to 0$, 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 F-P equation:

$$\partial_t P = D\partial_x^2 P - VP$$

We found that, in this case:

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

Leading to the substitutions:

$$D \to D_{QM} = \frac{i\hbar}{2m}$$
$$V \to \frac{i}{\hbar} V$$

And so we can write the solution in the quantum case:

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

Recalling the definition of the action S:

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

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

$$\exp\left(\frac{i}{\hbar} S\left(\{x(\tau)\}_0^t\right)\right)$$

So that the *most contributing trajectory* is the one that *stationarizes* S: $\delta S = 0$, implying:

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