Contents

Chapter 1

Chapman-Kolmogorov equation for continuous paths: Fokker-Planck equation

If we consider just Markov processes generating continuous paths we have to assume that all the jump probabilities are zero i.e.

$$w(x', t|x, t) = 0 \tag{1.1}$$

In this case we get the partial differential equation:

$$\boxed{\partial_t p(x', t|x_0, t_0) = \sum_{m=1}^{N} (-1)^m \frac{\partial^m}{\partial x'^m} \left[D^{(m)}(x', t) p(x', t|x_0, t_0) \right]} \tag{1.2}$$

This is what is called the *Kramers-Moyal* expansion and $D^{(m)}(x', t)$ are the *Kramers-Moyal* coefficients. In general, all Kramers-Moyal coefficients are non-zero. However, there is a theorem due to Pawula [3] which states that for a positive transition probability $p(x, t|x_0, t_0)$, the expansion (1.2) may stop either after the first term or after the second term. If, on the other hand, it does not stop after the second term it must contain an infinite number of terms. In the words of Pawula, "it is logically inconsistent to retain more than two terms in Kramers-Moyal expansion unless *all* of the terms are retained. If this is the case, the Kramers-Moyal expansion reduces to the so called *Fokker-Planck* equation:

$$\boxed{\partial_t p(x', t|x_0, t_0) = (-1) \frac{\partial}{\partial x'} \left[D^{(1)}(x', t) p(x', t|x_0, t_0) \right] + \frac{\partial^2}{\partial x'^2} \left[D^{(2)}(x', t) p(x', t|x_0, t_0) \right].} \tag{1.3}$$

Remark. It can be shown that, for a continuous Markov process, the Kramers-Moyal coefficients of order 3 and higher are zero and the K-M expansion reduces to the Fokker-Planck equation.

Remark. Remember that, from the definition of $w(x|x', t)$ the assumption of continuity for the paths $x(t)$ is satisfied when $w(x|x', t) = 0$. Hence, the Fokker-Planck equation describes processes that have continuous paths.

The FP equation can be written as

$$\frac{\partial p(x, t|x_0, t_0)}{\partial t} = \hat{L}_{FP} p(x, t|x_0, t_0) \tag{1.4}$$

where $\hat{L}_{\mathrm{FP}}(x, t)$ is the differential operator

$$\boxed{\hat{L}_{FP}(x, t) = -\frac{\partial}{\partial x} D^{(1)}(x, t) + \frac{\partial^2}{\partial x^2} D^{(2)}(x, t)}. \tag{1.5}$$

Remark. 1. The F-P equation is defined by the *drift term* $D^{(1)}(x,t)$ that characterizes a ballistic motion, and by the *diffusion term* $D^{(2)}(x,t)$ characterizing a diffusive motion.

2. The F-P equation is said to be *linear* if the drift and diffusion term do not depend explicitly of time and if

$$D^{(1)}(x,t) = D^{(1)}(x) = D_1^{(1)} + D_2^{(1)}x, \qquad D^{(2)}(x,t) = D^{(2)}(x) = D_2. \tag{1.6}$$

If, on the other hand $D^{(2)}(x) = D_2$ but $D^{(1)}(x)$ is *non linear*, one has a *almost-linear* F-P equation. We will see that, if the equation is linear, the solution is Gaussian. (The notion of linearity is here related to the properties of $D^{(1)}$ and $D^{(2)}$ since the F-P equation itself is always linear with respect to $p(x,t|x_0,t_0)$.

3. A solution of the F-P equation with the initial condition $p(x,t=t_0|x_0,t_0) = \delta(x-x_0)$ (non random initial condition) is called *fundamental solution* and gives the transition probability of the diffusive Markov process. In order to determine completely the process we need to define the one-point distribution function $p(x,t)$ and average over the initial conditions. Indeed by the linearity of the F-P equation we will have

$$p(x,t) = \int_{\mathbb{R}} dx_0 p(x_0,t_0) p(x,t|x_0,t_0). \tag{1.7}$$

Clearly

$$p(x,t)\,|_{t=t_0} = p(x,t_0). \tag{1.8}$$

If we take the time derivative of eq. (1.7) we have

$$\frac{\partial}{\partial t} p(x,t) = \int_{\mathbb{R}} dx_0 p(x_0,t_0) \frac{\partial}{\partial t} p(x,t|x_0,t_0). \tag{1.9}$$

and by using the FK equation for $p(x,t|x_0,t_0)$ we get:

$$\begin{aligned} \frac{\partial}{\partial t} p(x,t) &= \int_{\mathbb{R}} dx_0 \left\{ \hat{L}_{FP}(x,t) p(x,t|x_0,t_0) \right\} p(x_0,t_0) \\ &= \hat{L}_{FP}(x,t) \int_{\mathbb{R}} dx_0 p(x,t|x_0,t_0) p(x_0,t_0) \\ &= \hat{L}_{FP}(x,t) p(x,t). \end{aligned} \tag{1.10}$$

Hence, also the one point density function $p(x,t)$ satisfies the F-P equation with initial condition

$$p(x,t)\,|_{t=t_0} = p(x,t_0) \tag{1.11}$$

that comes from the limit

$$p(x,t)\,|_{t=t_0} = \lim_{t\to t_0} \int_{\mathbb{R}} dx_0 p(x,t|x_0,t_0) p(x_0,t_0) = \int_{\mathbb{R}} dx_0 \delta(x-x_0) p(x_0,t_0) = p(x,t_0). \tag{1.12}$$

Definition (Stationary distribution)**.** A distribution is called *stationary*, and denoted by $p_s(x,t)$, if

$$\frac{\partial}{\partial t} p_s(x,t) = 0 \qquad \forall x \in \Omega. \tag{1.13}$$

If a stationary distribution $p_s(x,t)$ exists, then it will be a solution of the equation

$$\frac{\partial}{\partial x}\left(D^{(2)}(x) p_s(x) \right) = D^{(1)}(x) p_s(x). \tag{1.14}$$

One says that the distribution *converges to the stationary distribution* for sufficiently large times if

$$\lim_{t\to\infty} p(x,t) = p_s(x) \tag{1.15}$$

1.0.1 Multidimensional case

In the case of multidimensional Markov Processes in which the random variable ξ is a vector $\vec{\xi}$ the variable x' becomes a vector that we denote as

$$\vec{z}(t) = \{z_1(t), \cdots, z_M(t)\} \tag{1.16}$$

and the CK differential equation becomes:

$$\begin{aligned} \partial_t \quad & p(\vec{z}, t|\vec{z}_0, t_0) = \\ & -\sum_i \frac{\partial}{\partial z_i}\left[D_i^{(1)}(\vec{z}, t)p(\vec{z}, t|\vec{z}_0, t_0)\right] + \sum_{i,j} \frac{\partial^2}{\partial z_i \partial z_j}\left[D_{ij}^{(2)}(\vec{z}, t)p(\vec{z}, t|\vec{z}_0, t_0)\right] \\ + \quad & \int_{\mathrm{PV}} d\vec{z}\left[w(\vec{z}, t|\vec{z'}, t)p(\vec{z}, t|\vec{z}_0, t_0) - w(\vec{z'}, t|\vec{z}, t)p(\vec{z'}, t|\vec{z}_0, t_0)\right] \end{aligned} \tag{1.17}$$

Again, for continuous paths $\vec{z}(t)$, $w(\vec{z}, t|\vec{z'}, t) = w(\vec{z'}, t|\vec{z}, t) = 0$ and one ends up with the multidimensional F-P equation:

$$\begin{aligned} \partial_t \quad & p(\vec{z}, t|\vec{z}_0, t_0) = \\ & -\sum_i \frac{\partial}{\partial z_i}\left[D_i^{(1)}(\vec{z}, t)p(\vec{z}, t|\vec{z}_0, t_0)\right] + \sum_{i,j} \frac{\partial^2}{\partial z_i \partial z_j}\left[D_{ij}^{(2)}(\vec{z}, t)p(\vec{z}, t|\vec{z}_0, t_0)\right] \end{aligned} \tag{1.18}$$

where the drift term $D^{(1)}(\vec{z}, t)$ is now a vector and the diffusive term $D^{(2)}(\vec{z}, t)$ is a semidefinite positive and symmetric matrix.

1.0.2 Deterministic process: Liouville equation

If the diffusion term $D^{(2)}(\vec{z}, t)$ is identically zero, the F-P equation reduces to the special case of a Liouville equation

$$\partial_t p(\vec{z}, t|\vec{z}_0, t_0) = -\sum_i \frac{\partial}{\partial z_i}\left[D_i^{(1)}(\vec{z}, t)p(\vec{z}, t|\vec{z}_0, t_0)\right] \tag{1.19}$$

that one has in classical statistical mechanics. This equation describes a completely deterministic motion. Indeed, if $\vec{x}(\vec{x}_0, t)$ is the solution of the ordinary differential equation

$$\frac{d\vec{x}(t)}{dt} = \mathbf{D}^{(1)}\left[\vec{x}(t), t\right] \tag{1.20}$$

with $\vec{x}(\vec{x}_0, t) = \vec{x}_0$, the solution of eq. (1.19) with initial condition $p(\vec{z}, t_0|\vec{x}_0, t_0) = \delta(\vec{z} - \vec{x}_0)$ is

$$p(\vec{z}, t|\vec{x}_0, t_0) = \delta\left[\vec{z} - \vec{x}(\vec{x}_0, t)\right]. \tag{1.21}$$

This can be easily seen by a direct insertion of the solution (1.21) in equation (1.19). Indeed, the drift term becomes

$$\begin{aligned} & -\sum_i \frac{\partial}{\partial z_i}\left\{D_i^{(1)}(\vec{z}, t)\delta\left[\vec{z} - \vec{x}(\vec{x}_0, t)\right]\right\} \\ = \quad & -\sum_i \left\{D_i^{(1)}\left(\vec{x}(\vec{x}_0, t), t\right)\frac{\partial}{\partial z_i}\delta\left[\vec{z} - \vec{x}(\vec{x}_0, t)\right]\right\} \end{aligned} \tag{1.22}$$

On the other hand, the left hand side gives:

$$\frac{\partial}{\partial t}\delta\left[\vec{z} - \vec{x}(\vec{x}_0, t)\right] = -\sum_i \frac{\partial}{\partial z_i}\delta\left[\vec{z} - \vec{x}(\vec{x}_0, t)\right]\frac{d\vec{x}(\vec{x}_0, t)}{dt} \tag{1.23}$$

and since

$$\frac{d\vec{x}(t)}{dt} = \mathbf{D}^{(1)}\left[\vec{x}(t), t\right] \tag{1.24}$$

we have that the left hand side of the Liouville equation is equal to its right hand side.

Remark. The fact that the F-P equation has the Liouville equation as a particular case is not surprising given that a deterministic process is a particular case of a continuous Markov process.

1.1 From Langevin to Fokker-Planck equation

It is possible to show that there exists a relation between the description of the fluctuations by using a Langevin equation and the one by the Fokker-Planck. In a very general settings we can say that, from a physics point of view, the evolution equation is governed by the deterministic differential equation

$$\frac{d}{dt}x(t) = F(t, x(t)). \tag{1.25}$$

If, in addition, the system is subjected to random perturbations whose scales of variations are much more rapid than the characteristic times of the evolution $x(t)$, it is natural to use a Langevin kind of model in which a white noise is added to the deterministic equation:

$$\frac{d}{dt}x(t) = F(t, x(t)) + f(t), \qquad \langle f(t_1)f(t_2)\rangle = \Gamma\delta(t_1 - t_2). \tag{1.26}$$

The parameter Γ will be determined by the physics of the problem. In order to establish the corresponding Fokker-Planck equation we have to determine the drift term D^1 and the diffusion term D^2. This can be done by computing the moments of the variable x starting from x_0 at time t_0 directly from the Langevin equation. Those moments will be then identified with the definitions

$$\begin{aligned} D^{(m)}(x', t) &\equiv \frac{1}{m!}\lim_{\Delta t\to 0}\frac{1}{\Delta t}\int_{\mathbb{R}} dx(x - x')^m p(x, t + \Delta t|x', t) \\ &= \frac{1}{m!}\lim_{\Delta t\to 0}\frac{1}{\Delta t}\mathbb{E}\{(x(t + \Delta t) - x(t))^m|x(t) = x'\}. \end{aligned} \tag{1.27}$$

Let us consider the finite difference version of eq. (1.26)

$$\Delta x(t) \equiv x(t + \Delta t) - x(t) = F(t, x(t))\Delta t + \Gamma^{1/2}\Delta W(t) \tag{1.28}$$

where $\Delta W(t) = W(t+\Delta t) - W(t)$ are increments of the Wiener process. By using the properties $\mathbb{E}\{\Delta W(t)\} = 0$, $\mathbb{E}\{(\Delta W(t))^2\} = \Delta t$ and the independence of the increments $\Delta W(t)$ one obtains:

$$\mathbb{E}\{F(t, x(t))\Delta t|x(t) = x'\} = \mathbb{E}\{F(t, x(t))|x(t) = x'\}\Delta t = F(t, x')\Delta t; \tag{1.29}$$

$$\mathbb{E}\{\Gamma^{1/2}\Delta W(t)|x(t) = x'\} = \Gamma^{1/2}\mathbb{E}\{\Delta W(t)|x(t) = x'\} = \Gamma^{1/2}\mathbb{E}\{\Delta W(t)\} = 0; \tag{1.30}$$

$$\begin{aligned} \mathbb{E}\{\Gamma(\Delta W(t))^2|x(t) = x'\} &= \Gamma\mathbb{E}\{(\Delta W(t))^2|x(t) = x'\} \\ &= \Gamma\mathbb{E}\{(\Delta W(t))^2\} = \Gamma\Delta t. \end{aligned} \tag{1.31}$$

By using the above relation one gets

$$\mathbb{E}\{\Delta x(t)|x(t) = x'\} = \mathbb{E}\{F(t, x(t))\Delta t + \Gamma^{1/2}\Delta W(t)|x(t) = x'\} = F(t, x')\Delta t; \tag{1.32}$$

and

$$\begin{aligned} \mathbb{E}\{(\Delta x(t))^2 \quad &| \quad x(t) = x'\} \\ &= \mathbb{E}\{F^2(t, x(t))(\Delta t)^2 + 2F(t, x(t))\Gamma^{1/2}\Delta t\Delta W(t) + \Gamma(\Delta W(t))^2|x(t) = x'\} \\ &= \Gamma\Delta t + O\left((\Delta t)^2\right). \end{aligned} \tag{1.33}$$

Hence

$$\begin{aligned} D^{(1)}(x', t) &= \lim_{\Delta t\to 0}\frac{1}{\Delta t}\int dx(x - x')p(x, t + \Delta t|x', t) \\ &= \lim_{\Delta t\to 0}\frac{1}{\Delta t}\mathbb{E}\{\Delta x(t)|x(t) = x'\} = F(t, x'); \end{aligned} \tag{1.34}$$

and

$$\begin{aligned} D^{(2)}(x',t) &= \lim_{\Delta t\to 0}\frac{1}{\Delta t}\frac{1}{2}\int dx(x-x')^2 p(x,t+\Delta t|x',t) \\ &= \frac{1}{2}\lim_{\Delta t\to 0}\frac{1}{\Delta t}\mathbb{E}\{(\Delta x(t))^2|x(t)=x'\} = \frac{\Gamma}{2}; \end{aligned} \tag{1.35}$$

The corresponding Fokker-Planck equation becomes:

$$\frac{\partial}{\partial t}p(x,t|x_0,t_0) = -\frac{\partial}{\partial x}\left(F(x,t)p(x,t|x_0,t_0)\right) + \frac{\Gamma}{2}\frac{\partial^2}{\partial x^2}p(x,t|x_0,t_0). \tag{1.36}$$

Example (Ornstein- Uhlenbeck process)**.** Let us consider as an example the 1D dynamic the dynamic evolution of the velocity field for a mesoscopic particle in a fluid. As we have seen before the Langevin equation of this problem is given by:

$$\frac{dv}{dt} = -\gamma v(t) + \frac{1}{m}F(t), \qquad \text{with} \quad \langle F(t)\rangle = 0, \quad \langle F(t_1)F(t_2)\rangle = \sigma^2\delta(t_1-t_2). \tag{1.37}$$

Following the procedure of the previous section one gets:

$$D^{(1)}(v,t) = D^{(1)}(v) = -\gamma v, \qquad D^{(2)}(v,t) = D = \frac{\sigma^2}{2m^2} \tag{1.38}$$

and the associated Fokker-Planck equation becomes

$$\frac{\partial}{\partial t}p(v,t|v_0,t_0) = -\frac{\partial}{\partial v}\left[(-\gamma v)\,p(v,t|v_0,t_0)\right] + \frac{\sigma^2}{2m^2}\frac{\partial^2}{\partial v^2}p(v,t|v_0,t_0). \tag{1.39}$$

1.1.1 Smoluchowski equation for the position: adiabatic elimination of the velocity process

Let us consider the motion of a mesoscopic particle in a fluid and in presence of an external force field $F(x)$. In the one dimensional case the deterministic motion is described by the equations

$$\begin{aligned} \frac{dx}{dt} &= v(t) \\ \frac{dv}{dt} &= -\gamma v(t) + F(x)/m. \end{aligned} \tag{1.40}$$

In the limit of very viscous fluid (*strong friction limit*) the inertial force dv/dt is much smaller than the frictional force $-\gamma v$. In this limit the velocity is a dumped variable whose variations occur in time intervals that are very small with respect to the ones over which the position varies in an appreciate way. We can then neglect the inertial term dv/dt in the equations, i.e.

$$\begin{aligned} \frac{dx}{dt} &= v(t) \\ v(t) &= \frac{F(x)}{\gamma m} \end{aligned} \tag{1.41}$$

In this approximation the *fast* variable v relaxes very rapidly and it follows almost instantaneously the *slow* variable x. One usually says that v is the slave variable of the order parameter x. The deterministic equation reduces to

$$\frac{dx}{dt} = \frac{F(x(t))}{\gamma m}. \tag{1.42}$$

We can perform a similar approximation for the stochastic version of the motion:

$$\begin{aligned} \Delta x &= v(t)\Delta t \\ \Delta v(t) &= -\gamma v(t)\Delta t + (F(x)/m)\,\Delta t + \frac{\sigma}{m}\Delta t^{1/2}\Delta\hat{W} \end{aligned} \tag{1.43}$$

giving

$$v(t) = \frac{F(x)}{m\gamma} + \frac{\sigma}{\gamma m}\Delta t^{-1/2}\Delta\hat{W} \tag{1.44}$$

and the *overdamped* Langevin equation

$$\boxed{\Delta x(t) = \frac{F(x(t))}{\gamma m}\Delta t + \frac{\sigma}{\gamma m}\Delta\hat{W}(t)} \tag{1.45}$$

where $\Delta W(t)$ are the increments of a Wiener process. In this case $D^{(1)}(x,t) = \frac{F(x(t))}{\gamma m}$ and $D^{(2)}(x,t) = \sigma^2/(2\gamma^2 m^2)$ and the Fokker-Planck equation for the random variable x:

$$\frac{\partial}{\partial t}p(x,t|x_0,t_0) = -\frac{\partial}{\partial x}\left[\frac{F(x)}{\gamma m}p(x,t|x_0,t_0)\right] + \frac{\sigma^2}{2\gamma^2 m^2}\frac{\partial^2}{\partial x^2}p(x,t|x_0,t_0). \tag{1.46}$$

This equation is known as the *Smoluchowski* equation. Note that for $F(x) = 0$ the Smoluchowski equation simplifies to:

$$\frac{\partial}{\partial t}p(x,t|x_0,t_0) = \frac{\sigma^2}{2\gamma^2 m^2}\frac{\partial^2}{\partial x^2}p(x,t|x_0,t_0). \tag{1.47}$$

that describes a diffusion process for the variable x (Einstein's). This is the so-called *diffusion equation* also known as *Fick's equation* when usually $p(x,t)$ is replaced by concentrations.

Note. The approximation we have used above at the level of the deterministic equation is known as *direct adiabatic elimination.* In general this is a quite rough approximation and one can doubt about its validity in presence of a stochastic term. One indeed has to be careful in using it and the best way to do it is, in general, at the level of Fokker-Plack equation. In the case explained above, for example, Kramers has shown rigorously that it is possible to obtain the Smoluchowski equation as a high viscosity limit of the Fokker Planck equations for the two variables (x,v), i.e., the so called Kramers equations (Ref. TODO)

1.1.2 Fokker-Planck equation for the 2D (x,v) process.

If the stochastic Markov diffusive process considered is a n-component vector $\vec{z}(t) = (z_1(t), z_2(t), \cdots, z_n(t))$ process we have seen that the one dimensional Fokker-Planck equation generalizes to

$$\begin{aligned}&\partial_t p(\vec{z},t|\vec{z}_0,t_0) = \\ &-\sum_i \frac{\partial}{\partial z_i}\left[D^{(1)}(\vec{z},t)p(\vec{z},t|\vec{z}_0,t_0)\right] + \sum_{i,j}\frac{\partial^2}{\partial z_i \partial z_j}\left[D^{(2)}_{ij}(\vec{z},t)p(\vec{z},t|\vec{z}_0,t_0)\right]\end{aligned} \tag{1.48}$$

where $D^{(1)}(\vec{z},t)$ is a vector and $D^{(2)}(\vec{z},t)$ a semidefinite positive and symmetric matrix. Perhaps the simplest vectorial stochastic process is related to the one dimensional motion of a mesoscopic particle in a fluid. The motion is described by the position x and by the velocity v of the mesoscopic particle. Since x and v are obviously coupled and they are both stochastic we can see the whole process as a bidimensional stochastic process $\vec{z}(t) = (x(t), v(t))$ whose Langevin equation is given by:

$$\begin{aligned}\Delta x(t) &= v(t)\Delta t \\ \Delta v(t) &= \left[-\gamma v(t) + F(x(t))/m\right]\Delta t + \frac{\sigma}{m}\Delta t^{1/2}\Delta\hat{W}(t).\end{aligned} \tag{1.49}$$

In order to establish the corresponding Fokker Planck equation one has to determine the vector

$$D^{(1)}(\vec{z},t) = \begin{pmatrix} D^{(1)}_x(x,v,t) \\ D^{(1)}_v(x,v,t)\end{pmatrix} \tag{1.50}$$

and the matrix

$$D^{(2)}(\vec{z},t) = \begin{pmatrix} D^{(2)}_{xx}(x,v,t) & D^{(2)}_{xv}(x,v,t) \\ D^{(2)}_{vx}(x,v,t) & D^{(2)}_{vv}(x,v,t) \end{pmatrix} \quad (1.51)$$

with $D^{(2)}_{vx}(x,v,t) = D^{(2)}_{xv}(x,v,t)$. By following the method presented above we can say that, as $t \to t_0$

$$\begin{aligned}
\mathbb{E}\{\Delta x(t)|x(t)=x',v(t)=v'\} &= v'\Delta t & (1.52)\\
\mathbb{E}\{\Delta v(t)|x(t)=x',v(t)=v'\} &= \left(-\gamma v' + \frac{F(x')}{m}\right)\Delta t + O\left((\Delta t)^2\right) & (1.53)\\
\mathbb{E}\{(\Delta x(t))^2|x(t)=x',v(t)=v'\} &= (v'\Delta t)^2 = O\left((\Delta t)^2\right) & (1.54)\\
\mathbb{E}\{\Delta x(t)\Delta v(t)|x(t)=x',v(t)=v'\} &= v'\left(-\gamma v' + \frac{F(x')}{m}\right)(\Delta t)^2 & (1.55)\\
\mathbb{E}\{(\Delta v(t))^2|x(t)=x',v(t)=v'\} &= \frac{\sigma^2}{m^2}\Delta t + O\left((\Delta t)^2\right). & (1.56)
\end{aligned}$$

Dividing by Δt and letting $\Delta t \to 0$ we get

$$\begin{aligned}
D^{(1)}_x(x,v,t) &= v\\
D^{(1)}_v(x,v,t) &= -\gamma v + \frac{F(x)}{m}\\
D^{(2)}_{xx}(x,v,t) &= 0\\
D^{(2)}_{vv}(x,v,t) &= \frac{\sigma^2}{2m^2}\\
D^{(2)}_{xv}(x,v,t) &= 0. \quad (1.57)
\end{aligned}$$

The 2D Fokker-Planck equation is then

$$\begin{aligned}
&\partial_t p(x,v,t|x_0,v_0,t_0) = \\
&-\frac{\partial}{\partial x}\left[vp(x,v,t|x_0,v_0,t_0)\right] - \frac{\partial}{\partial v}\left[\left(\frac{F}{m} - \gamma v\right)p(x,v,t|x_0,v_0,t_0)\right]\\
&+\frac{\sigma^2}{2^2}\frac{\partial^2}{\partial v^2}\left[p(x,v,t|x_0,v_0,t_0)\right] \quad (1.58)
\end{aligned}$$

In general $F(x) = -\frac{\partial U}{\partial x}$.

Remark. If we rewrite the above equation as:

$$\begin{aligned}
&\partial_t p(x,v,t|x_0,v_0,t_0) + v\frac{\partial}{\partial x}p(x,v,t|x_0,v_0,t_0) + \frac{F(x)}{m}\frac{\partial}{\partial v}p(x,v,t|x_0,v_0,t_0)\\
=\ &\gamma\left(\frac{\partial}{\partial v}\left(vp(x,v,t|x_0,v_0,t_0)\right) + \frac{\sigma^2}{2\gamma m^2}\frac{\partial^2}{\partial v^2}p(x,v,t|x_0,v_0,t_0)\right) \quad (1.59)
\end{aligned}$$

one can notice that it has a structure typical of a *kinetic equation*, i.e. of the form

$$\partial_t p(x,v,t|x_0,v_0,t_0) + v\frac{\partial}{\partial x}p(x,v,t|x_0,v_0,t_0) + \frac{F(x)}{m}\frac{\partial}{\partial v}p(x,v,t|x_0,v_0,t_0) = I_p(x,v,t) \quad (1.60)$$

where the linear operator $I_p(x,v,t)$ is a *collision operator* that represents the effects of the collisions of the mesoscopic particle with its environment. If $I_p(x,v,t) = 0$ the knowledge of the flux of the system of differential equations $\dot{x}(t) = v(t)$, $m\dot{v}(t) = F(x(t))$ allows to solve the FP equation. Indeed by taking $\omega = (x,v)$, $t \to \phi_0(\omega_0,t) = \omega(t)$ as a trajectory with initial condition ω_0 and $P(\omega_0)$ the distribution of the initial conditions ω_0, the distribution at times t defined as

$$P(\omega,t) = \int_{\mathbb{R}^2} d\omega_0 P(\omega_0)\delta(\omega - \phi(\omega_0,t)) = P\left(\phi^{-1}(\omega,t)\right) \quad (1.61)$$

can be shown to verify the equation

$$\frac{\partial}{\partial t}P(\omega,t)+v\frac{\partial}{\partial x}P(\omega,t)+\frac{F(x)}{m}\frac{\partial}{\partial v}P(\omega,t)=0. \tag{1.62}$$

For $I_p(x,v,t)\neq 0$ equation (1.58) cannot be resolved analytically in its generality and one has to rely on some approximations suggested by the physical problem under investigation.

1.1.3 Kramer's model

Historically, the 2D Fokker- Planck equation of the form given in (1.58) was first introduced by Kramers in 1940 to study the kinetic of the chemical reactions [4]. It is also a good starting point to study the problem of the transitions between two minima of a double- well potential. Let us consider the following system of equations:

$$\begin{aligned}\frac{dx}{dt} &= v(t)\\ \frac{dv}{dt} &= -\lambda v(t)-\frac{dU(x)}{dx}+F(t)\end{aligned} \tag{1.63}$$

where $F(t)$ is the usual white noise force. This model described, for example, the Brownian motion of a particle in a fluid that experiences a potential $U(x)$. Suppose to consider a double well potential .i.e. a potential having two minima in, say, x_A and x_B and a maximum in x_C with $x_A<x_C<x_B$. With this kind of potential the system (1.63) can describe chemical reactions where the value of the abscissa (x) represents the reaction coordinate. The reaction would then correspond to the transition between the well of the reagents (A) and the well of products (B). This is the so called Kramers model whose Fokker-Planck equation is given by

$$\begin{aligned}&\partial_t p(x,v,t|x_0,v_0,t_0)=\\ &-\frac{\partial}{\partial x}\left[vp(x,v,t|x_0,v_0,t_0)\right]-\frac{\partial}{\partial v}\left[\left(-\frac{dU}{dx}-\lambda v\right)p(x,v,t|x_0,v_0,t_0)\right]\\ &+D\frac{\partial^2}{\partial v^2}p(x,v,t|x_0,v_0,t_0)\end{aligned} \tag{1.64}$$

For $U(x)=ax^2+bx^4$ eq. (1.64) is non linear and an analytical solution is hopeless. A first simplification can be performed in the limit of high viscosity i.e. when $v(t)$ relaxes more rapidly than $x(t)$. We can then use the adiabatic elimination of the variable v by putting $dv/dt=0$ is the second equation. This gives

$$\frac{dx}{dt}=-\frac{1}{\lambda}\frac{dU}{dx}+\frac{1}{2}F(t) \tag{1.65}$$

As before, the corresponding Fokker Planck equation would be a Smoluchowski equation :

$$\partial_t p(x,t|x_0,t_0)+\frac{\partial}{\partial x}\left(-\frac{1}{\lambda}\frac{dU}{dx}p(x,t|x_0,t_0)\right)=\frac{D}{\lambda^2}\frac{\partial^2}{\partial x^2}p(x,t|x_0,t_0). \tag{1.66}$$

We will see later how to compute the stationary solution of this equation in the case of double well potential.

1.2 Probability current and probability conservation law.

It is interesting to rewrite the Fokker-Planck equation as a continuity equation for the probability density $p(x,t)$. Let us focus on the one dimensional case. From remark (1) we know that the FP equation can be written as

$$\frac{\partial p(x,t|x_0,t_0)}{\partial t}=\hat{L}_{FP}p(x,t|x_0,t_0) \tag{1.67}$$

where $\hat{L}_{FP}$ is the differential operator

$$\hat{L}_{FP} = -\frac{\partial}{\partial x} D^{(1)}(x,t) + \frac{\partial^2}{\partial x^2} D^{(2)}(x,t). \tag{1.68}$$

The initial condition is

$$\lim_{t \to t_0} p(x,t|x_0,t_0) = \delta(x - x_0). \tag{1.69}$$

The FP can be written also for the one point probability density $p(x,t)$(see remark (1):

$$\frac{\partial p(x,t)}{\partial t} = \hat{L}_{FP} p(x,t) \tag{1.70}$$

with initial condition

$$p(x,t)|_{t=t_0} = p(x,t_0). \tag{1.71}$$

In analogy with what one does for the Schrodinger equation, eq. (1.70) can be written as

$$\frac{\partial p(x,t)}{\partial t} + \frac{\partial}{\partial x} j(x,t) = 0 \tag{1.72}$$

where

$$\boxed{j(x,t) = \left[D^{(1)}(x,t) - \frac{\partial}{\partial x} D^{(2)}(x,t) \right] p(x,t).} \tag{1.73}$$

Eq. (1.72) is in the form of a continuity equation for the probability density $p(x,t)$ where $j(x,t)$ is the probability current. Indeed if we integrate equation (1.72) for $x \in [a,b]$ we get:

$$\frac{\partial}{\partial t} \int_a^b p(x,t) dx = -\int_a^b \frac{\partial}{\partial x} j(x,t) dx = j(a,t) - j(b,t) \tag{1.74}$$

i.e. a change in probability density in the interval $[a,b]$, is compensated by a change of flux in that region.

The above argument can be generalized to the Fokker-Planck equation of several variables

$$\frac{\partial}{\partial t} p(\vec{z},t|\vec{z}_0,t_0) = \hat{L}_{FP}(\vec{z},t) p(\vec{z},t|\vec{z}_0,t_0), \tag{1.75}$$

where

$$\hat{L}_{FP}(\vec{z},t) = -\sum_{i=1}^{n} \frac{\partial}{\partial z_i} D_i(\vec{z},t) + \sum_{ij} \frac{\partial^2}{\partial z_i \partial z_j} D_{ij}(\vec{z},t). \tag{1.76}$$

In this case the continuity equation becomes

$$\frac{\partial}{\partial t} p(\vec{z},t) + \vec{\nabla} \cdot \vec{j} = 0 \tag{1.77}$$

where

$$j_i(\vec{z},t) = D_i^{(1)}(\vec{z},t) p(\vec{z},t) - \sum_j \frac{\partial}{\partial z_j} D_{ij}^{(2)}(\vec{z},t) p(\vec{z},t) \tag{1.78}$$

As for the 1D case, the local form of the continuity equation has an integral counterpart that can be obtained in the following way. Let Ω be the domain of integration (where the stochastic process lives) whose boundary is given by $\partial\Omega$. The n dimensional version of equation (1.74) is then

$$\frac{\partial}{\partial t} \int_\Omega p(\vec{z},t) d\vec{z} = -\int_{\partial\Omega} \hat{n} \cdot \vec{j}(\vec{z},t) dS \tag{1.79}$$

where $\hat{n}$ is the unit normal to the boundary $\partial\Omega$ (pointing out). If the probability current vanishes on the $\partial\Omega$, the continuity equation implies that the total probability remains constant (in time) inside the boundary. If $p(\vec{z},t)$ is then normalized at time $t = t_0$, it will remain so for any later times, i.e,

$$\int_\Omega p(\vec{z},t) d\vec{z} = 1 \qquad \forall t > t_0. \tag{1.80}$$

1.3 Boundary conditions for the Fokker-Planck equation

The continuity equation in its integral form (eq. (1.74) and eq. (1.79)) suggests that, in order to have a well defined problem, boundary conditions (BC) for the Fokker-Planck equation have to be specified. Let us consider first the $1D$ case. Different BC can be taken into account

1. **Natural boundary conditions** In this case the process is defined on $\mathbb{R}$ and the condition is the one in which the probability current vanishes at the boundaries $x = x_{min} = -\infty$ and $x_{max} = +\infty$. This would imply the conservation of the normalization for $p(x, t)$ since

$$\int_{-\infty}^{+\infty} p(x,t)dx = \text{const.} \tag{1.81}$$

Clearly the decay must be sufficiently rapid to ensure the normalization of the integral above.

2. **Reflecting boundary conditions** For a reflecting boundary condition at $x = a$ the flux at a must be zero

$$j(a,t) = 0 \qquad \forall t. \tag{1.82}$$

This gives:

$$D^{(1)}(a,t)p(a,t) - \frac{\partial}{\partial x} D^{(2)}(x,t)p(x,t)\bigg|_{x=a} = 0 \quad \forall t \tag{1.83}$$

Note that the natural boundary conditions can be seen as a particular case of reflecting BC. A physical example is the case of a Brownian particles near an impenetrable wall at $x = a$.

3. **Absorbing boundary conditions** An absorbing wall at $x = a$ means that the particles are removed from the interval $(-\infty, a]$ as soon as they first hit $x = a$. This can occur for example when a chemical reaction at the wall causes molecule to be absorbed or changed to a different chemical species. Another more mathematical reason of using absorbing BC is when one is interested in looking at the *first passage time* of a process as we will see later. The appropriate BC for an absorbing wall at $x = a$ is

$$p(a,t) = 0 \quad \forall t \tag{1.84}$$

i.e. there is a zero probability of finding particles at the wall, since they are immediately absorbed.

The above classification can be easily generalized to the multidimensional case of eq. (1.79). For example for natural boundary conditions $\vec{j}$ vanishes at infinity giving

$$\int_{\mathbb{R}^n} p(\vec{z},t)d\vec{z} = 1 \qquad \forall t > t_0. \tag{1.85}$$

An example of reflecting boundary in two dimensions ($\vec{z} = (x, y)$) could be the following. Suppose there is an impenetrable wall at $y = a$. Writing $\hat{n}$ as the (outward) unit normal vector at the wall, the no flux condition becomes

$$\hat{n} \cdot \vec{j} = 0 \tag{1.86}$$

i.e. (in components)

$$\begin{aligned} \Bigg[& n_x D_x(\vec{z},t)p(\vec{z},t) + n_x D_x(\vec{z},t)p(\vec{z},t) \\ - & n_x \left(\frac{\partial}{\partial x} D_{xx}(\vec{z},t)p(\vec{z},t) + \frac{\partial}{\partial y} D_{xy}(\vec{z},t)p(\vec{z},t) \right) \\ - & n_y \left(\frac{\partial}{\partial x} D_{yx}(\vec{z},t)p(\vec{z},t) + \frac{\partial}{\partial y} D_{yy}(\vec{z},t)p(\vec{z},t) \right) \Bigg]_{y=a} = 0 \end{aligned} \tag{1.87}$$

1.4 Stationary solutions of the Fokker-Planck equation

We now exploit how the Fokker-Planck equation can be applied to compute the probability density distribution of some Markovian process. Before facing the problem of calculating the time dependence solution one can first focuss on finding the long time limit solution i.e. the stationary solution of the process. This is defined as the probability density p_s that satisfies

$$\boxed{\frac{\partial}{\partial t} p_s(x,t|x_0,t_0) = 0.} \tag{1.88}$$

Let us first consider homogeneous Markov processes.

1.4.1 Homogeneous case with reflecting boundary conditions on a finite domain

For homogeneous Markov diffusive processes, $D^{(1)}(x,t)$ and $D^{(2)}(x,t)$ do not depend explicitly on time i.e.

$$\boxed{D^{(1)}(x,t) = D_1(x), \qquad D^{(2)}(x,t) = D_2(x).} \tag{1.89}$$

In this case eq. (1.88), specialized to the one-point probability density $p(x,t)$, becomes

$$\frac{d}{dx}\left[D_1(x)p_s(x)\right] - \frac{d^2}{dx^2}\left[D_2(x)p_s(x)\right] = 0 \tag{1.90}$$

that, written as a continuity equation becomes:

$$\frac{dj_s(x)}{dx} = 0 \quad \text{with} \quad j_s(x) = \left[D_1(x) - \frac{d}{dx}D_2(x)\right]p_s(x) \tag{1.91}$$

The obvious solution is $j_s(x) = \text{const} \equiv j^*, \quad \forall x$. Clearly, if the process occurs within an interval $[a,b]$, we have :

$$j_s(a) = j_s(b) = j^* \tag{1.92}$$

Suppose, for example, that one of the BC (say a) is **reflecting**. This means zero flux trough the surface $x = a$ implying $j_s(a) = 0$. On the other hand, from eq. (1.92) $j_s(a) = j_s(b) = j^*$ implying $j_s(b) = 0$. Hence,

$$\boxed{j_s(x) = 0 \qquad \forall x \in [a,b].} \tag{1.93}$$

From (1.91) one gets

$$D_1(x)p_s(x) = \frac{d}{dx}\left[D_2(x)p_s(x)\right]. \tag{1.94}$$

By rewriting the left hand side of the above equation as $\frac{D_1(x)}{D_2(x)}D_2(x)p_s(x)$ one ends up with a differential equation of the form

$$\frac{dg}{dx} = A(x)g(x) \quad \text{where} \quad g(x) = D_2(x)p_s(x) \quad \text{and} \quad \frac{D_1(x)}{D_2(x)} = A(x) \tag{1.95}$$

whose formal solution is $g = e^{\int A(x)dx}$ i.e.

$$\boxed{p_s(x) = \frac{\mathcal{N}_0}{D_2(x)}\exp\left(\int_a^x \frac{D_1(x')}{D_2(x')}dx'\right) \equiv \mathcal{N}_0 e^{-\Phi(x)}.} \tag{1.96}$$

It is important to stress that eq. (1.96) is valid only when the boundary $x = a$ is reflecting. The normalization constant $\mathcal{N}_0$ is chosen to satisfy

$$\int_a^b p_s(x)dx = 1. \tag{1.97}$$

Eq. (1.96) is often called *potential solution* since one introduces the notion of *potential* as:

$$\Phi(x) = \ln D_2(x) - \int_a^x \frac{D_1(x')}{D_2(x')}dx'. \tag{1.98}$$

Let us know consider some examples in which solution (1.96) occurs.

1.4.2 Examples

Ornstein-Uhlenbeck process The Langevin equation for the random velocity $v(t)$ is

$$\Delta v(t) = -\gamma v(t)\Delta t + \sigma \Delta W(t) \tag{1.99}$$

and the linear operator $\hat{L}_{FP}$ is obtained from the relations

$$D_1(v) = -\gamma v, \qquad D_2(v) = \frac{\sigma^2}{2}. \tag{1.100}$$

From eq. (1.96) the stationary solution is then given by

$$\begin{aligned} p_s(v) &= \frac{2\mathcal{N}_0}{\sigma^2}\exp\left(\int_{v_a}^{v} dv' \left(-\frac{2\gamma v'}{\sigma^2}\right)\right) \\ &= \frac{2\mathcal{N}_0}{\sigma^2}\exp\left[-\frac{\gamma}{\sigma^2}(v^2 - v_a^2)\right] \\ &= \mathcal{N}\exp\left(-\frac{\gamma v^2}{\sigma^2}\right). \end{aligned} \tag{1.101}$$

Note. If $\gamma > 0$ the stationary solution $p_s(v)$ can be normalized on $(-\infty, +\infty)$ since

$$\mathcal{N}\int_{-\infty}^{+\infty} \exp\left(-\frac{\gamma v^2}{\sigma^2}\right) dv = \mathcal{N}\sqrt{\frac{\pi}{\gamma}\sigma^2}. \tag{1.102}$$

and by assuming $\sigma\mathcal{N}\sqrt{\frac{\pi}{\gamma}} = 1$ one gets

$$\mathcal{N} = \sqrt{\frac{\gamma}{\pi\sigma^2}}. \tag{1.103}$$

In this respect the boundary conditions are the natural ones and the stationary solution exists laos for the process defined in $\mathbb{R}$.

The normalized solution is then

$$p_s(v) = \sqrt{\frac{\gamma}{\pi\sigma^2}}\exp\left(-\frac{\gamma v^2}{\sigma^2}\right). \tag{1.104}$$

Remembering the relation $\boxed{\sigma^2 = 2\gamma^2 D}$ one gets

$$p_s(x) = \sqrt{\frac{1}{2\pi\gamma D}}\exp\left(-\frac{v^2}{2\gamma D}\right). \tag{1.105}$$

or, since $\boxed{D = k_b T/m\gamma}$,

$$\boxed{p_s(v) = \sqrt{\frac{m}{2\pi k_b T}}\exp\left(-\frac{v^2 m}{2k_b T}\right) \qquad \text{Maxwell distribution.}} \tag{1.106}$$

Note. Clearly, if $\gamma < 0$ a stationary solution does not exist any more in $\mathbb{R}$ since, in order to have a normalizable solution, the interval (a, b) must be finite.

Brownian motion in presence of an external force: the over-damped limit. We have previously seen that if the damping coefficient γ is sufficiently big, the velocity variable can be considered essentially as a *slave variable* and the system of two equations can be reduced to a single Langevin equation for the position, i.e.,

$$\Delta x(t) = \frac{F(x)}{m\gamma}\Delta t + \frac{\sigma}{\gamma}\Delta W(t). \tag{1.107}$$

In the Fokker-Planck picture this corresponds to

$$D_1(x) = F(x)/m\gamma, \quad D_2(x) = \sigma^2/(2\gamma^2). \tag{1.108}$$

giving the Smoluchowky equation (see eq. 1.46)

$$\frac{\partial}{\partial t}p(x,t) = -\frac{\partial}{\partial x}\left[\frac{F(x)}{m\gamma}p(x,t)\right] + \frac{\sigma^2}{2\gamma^2}\frac{\partial^2}{\partial x^2}p(x,t). \tag{1.109}$$

From eq. (1.96) the stationary solution becomes

$$p_s(x) = \frac{2\mathcal{N}_0}{\sigma^2}\exp\left(\frac{2\gamma}{m\sigma^2}\int_a^x F(x')dx'\right). \tag{1.110}$$

Clearly an explicit solution would depend on the form of the function $F(x)$. A simple example is the problem of a

Brownian particle moving in a gravitational field. In this case $F = -mg$ and the integration in (1.110) is trivial and one obtains

$$\begin{aligned} p_s(x) &= \frac{2\gamma^2\mathcal{N}_0}{\sigma^2}\exp\left(-\frac{2g\gamma}{\sigma^2}\int_a^x dx'\right) \\ &= \mathcal{N}\exp\left(-\frac{2g\gamma(x-a)}{\sigma^2}\right). \end{aligned} \tag{1.111}$$

This solution can be normalized on (a, b) only if a is finite, although b can be infinite.

Note. Eq. (1.111) simply says that particles diffusing, for example, in a glass of fluid will eventually fall down and if the glass is infinitely deep they never will stop (no existence of $p_s(x)$).

Force field from a potential A very interesting case is when the force field is related to a scalar potential, i.e., in the case $\vec{F}(\vec{r}) = -\vec{\nabla}U(\vec{r})$ (i.e. to force field for which $\vec{\nabla} \times \vec{F} = 0$). For the one dimensional case the starting point is eq. 1.110 that for conservative forces simplifies to

$$p_s(x) = \frac{2\gamma^2\mathcal{N}_0}{\sigma^2}\exp\left(-\frac{2\gamma}{m\sigma^2}(U(x) - U(a))\right) = \mathcal{N}\exp\left(-\frac{2\gamma}{m\sigma^2}U(x)\right). \tag{1.112}$$

Is important to notice that eq. (1.112) is the result of the condition $j(x,t) = 0$, that corresponds to the equilibrium condition. In this respect we should expect that the fluctuation dissipation relation $m\sigma^2 = 2\kappa_B T\gamma$ holds. Inserting this relation in eq. (1.112) we get

$$p_s(x) = \mathcal{N}e^{-\beta U(x)}, \tag{1.113}$$

i.e. the expected equilibrium Boltzmann distribution. In general we can say that if $p_0(\vec{r}) = \mathcal{N}\exp[-\beta U(\vec{r})]$ is the equilibrium distribution with corresponding probability density current

$$\vec{j}(\vec{r}) = \left(\nabla D(\vec{r}) - \frac{\vec{F}(\vec{r}}{m\gamma}\right)\mathcal{N}\exp[-\beta U(\vec{r})], \tag{1.114}$$

(where we have also considered the more general case of a diffusion diffusion coefficient depending on $\vec{r}$), the equilibrium condition becomes

$$\left(\vec{\nabla} D(\vec{r}) - \frac{\vec{F}(\vec{r})}{m\gamma}\right) \mathcal{N} \exp[-\beta U(\vec{r})] = 0. \tag{1.115}$$

By using the identity $\vec{\nabla} D(\vec{r}) \exp[-\beta U(\vec{r})] = \exp[-\beta U(\vec{r})] \left(\vec{\nabla} D(\vec{r}) + \beta \vec{F}(\vec{r})\right)$ we have

$$e^{-\beta U(\vec{r})} \left(D(\vec{r}) \beta \vec{F}(\vec{r}) + \vec{\nabla} D(\vec{r}) - \frac{\vec{F}(\vec{r})}{m\gamma} \right) = 0 \tag{1.116}$$

and finally

$$\vec{\nabla} D(\vec{r}) = \vec{F}(\vec{r}) \left((m\gamma)^{-1} - D(\vec{r})\beta \right), \tag{1.117}$$

that is a more general version of the fluctuation-dissipation theorem. In the form given by (1.117) the fluctuation-dissipation relation allows to reformulate the Fokker-Planck equation as follows. For an arbitrary function $f(\vec{r})$ the following identity holds

$$\begin{aligned} \vec{\nabla} \cdot \vec{\nabla} D(\vec{r}) f(\vec{r}) &= \vec{\nabla} \cdot D(\vec{r}) \vec{\nabla} f(\vec{r}) + \vec{\nabla} \cdot f(\vec{r}) \vec{\nabla} D(\vec{r}) \\ &= \vec{\nabla} \cdot D(\vec{r}) \vec{\nabla} f(\vec{r}) + \vec{\nabla} \cdot \vec{F}(\vec{r}) \left(\frac{1}{\gamma m} - D(\vec{r})\beta \right) f(\vec{r}). \end{aligned} \tag{1.118}$$

where we have used eq. (1.117) for the second line. Since $f(\vec{r})$ the above identity holds also for the probability distribution $p(\vec{r}, t|\vec{r}_0, t_0)$. This identity, once inserted in the Fokker-Planck equation gives

$$\begin{aligned} \partial_t p(\vec{r}, t|\vec{r}_0, t_0) &= \vec{\nabla} \cdot D(\vec{r}) \vec{\nabla} p(\vec{r}, t|\vec{r}_0, t_0) + \vec{\nabla} \cdot \vec{F}(\vec{r}) \left(\frac{1}{\gamma m} - D(\vec{r})\beta \right) p(\vec{r}, t|\vec{r}_0, t_0) - \vec{\nabla} \cdot \frac{F(\vec{r})}{\gamma m} p(\vec{r}, t|\vec{r}_0, t_0) \\ &= \vec{\nabla} \cdot D(\vec{r}) \vec{\nabla} p(\vec{r}, t|\vec{r}_0, t_0) - \vec{\nabla} \cdot \left(\vec{F}(\vec{r}) D(\vec{r}) \beta p(\vec{r}, t|\vec{r}_0, t_0) \right) \\ &= \vec{\nabla} \cdot D(\vec{r}) \left(\vec{\nabla} - \beta \vec{F}(\vec{r}) \right) p(\vec{r}, t|\vec{r}_0, t_0) \end{aligned} \tag{1.119}$$

If we now consider $\vec{F}(\vec{r}) = -\vec{\nabla} U(\vec{r})$ we can finally write

$$\begin{aligned} \partial_t p(\vec{r}, t|\vec{r}_0, t_0) &= \vec{\nabla} \cdot D(\vec{r}) \left(\vec{\nabla} + \beta \vec{\nabla} U(\vec{r}) \right) p(\vec{r}, t|\vec{r}_0, t_0) \\ &= \vec{\nabla} \cdot D(\vec{r}) \left(e^{-\beta U(\vec{r})} \vec{\nabla} e^{\beta U(\vec{r})} \right) p(\vec{r}, t|\vec{r}_0, t_0), \end{aligned} \tag{1.120}$$

where the second line is obtained by the identity

$$\vec{\nabla} e^{\beta U(\vec{r})} p(\vec{r}, t|\vec{r}_0, t_0) = e^{\beta U(\vec{r})} \vec{\nabla} p(\vec{r}, t|\vec{r}_0, t_0) + \beta e^{\beta U(\vec{r})} \vec{\nabla} U(\vec{r}) p(\vec{r}, t|\vec{r}_0, t_0) \tag{1.121}$$

when is multiplied from the left by $e^{-\beta U(\vec{r})}$. In summary, a Fokker-Planck equation, with an external force that can be expressed as the gradient of a potential, can be written in the following form

$$\boxed{\partial_t p(\vec{r}, t|\vec{r}_0, t_0) = \vec{\nabla} \cdot D(\vec{r}) e^{-\beta U(\vec{r})} \vec{\nabla} e^{\beta U(\vec{r})} p(\vec{r}, t|\vec{r}_0, t_0).} \tag{1.122}$$

In this form it is immediately clear that the distribution $p(\vec{r}, t|\vec{r}_0, t_0) = e^{-\beta U(\vec{r})}$ is stationary solution of the F-P equation. From eq. (1.122) the probability current becomes

$$\vec{j}(\vec{r}, t|\vec{r}_0, t_0) == D(\vec{r}) e^{-\beta U(\vec{r})} \vec{\nabla} e^{\beta U(\vec{r})} p(\vec{r}, t|\vec{r}_0, t_0) \tag{1.123}$$

Eqs. (1.122) and (1.123) are often the starting points of many problems of diffusion with an external potential (see section on Diffusion Problems).

Bistable potential An example in which the force $F(x)$ is given by the gradient of a potential is the problem of the stochastic dynamic of a particle in a bistable potential $U(x) = \frac{x^4}{4} - \frac{x^2}{2}$. The corresponding Langevin equation (overdamped limit) would be

$$\Delta x = \frac{-x^3 + x}{m\gamma}\Delta t + \frac{\sigma}{\gamma}\Delta W(t). \tag{1.124}$$

The deterministic problem has critical points at $x = -1$ and $x = 1$ (both stable) and an unstable point at $x = 0$. Mapping to the FP equation gives a drift coefficient $D^{(1)} = D_1(x) = -U'(x) = (-x^3 + x)/(m\gamma)$ and a diffusion term $D_2 = \sigma^2/(2\gamma^2)$. From equation (1.96) the stationary solution of the corresponding Fokker-Planck equation is then

$$p_s(x) = \frac{2\gamma^2 \mathcal{N}_0}{\sigma^2} \exp\left(-\frac{2\gamma}{m\sigma^2}\int_a^x U'(y)dy\right) = \mathcal{N} \exp\left(-\frac{2\gamma}{m\sigma^2}(U(x) - U(a))\right). \tag{1.125}$$

If $U(a) = 0$ (this is true for $a = \pm\sqrt{2}$ in this particular case) we finally get

$$\boxed{p_s(x) = \mathcal{N} \exp\left[-\frac{x^2\gamma}{2m\sigma^2}\left(\frac{x^2}{2} - 1\right)\right].} \tag{1.126}$$

This is a bimodal distribution for small noise strength σ^2: most of the time is spent near the stable points of the deterministic system.

1.4.3 A micro electrode recessed into a surface: an example of diffusion with absorbing boundary condition

In the previous section we have computed the stationary solutions for homogeneous process with *reflecting boundary conditions*. We have seen that in particular cases these conditions reduce to consider the more stringent (equilibrium) condition $j(x,t) = 0$. In this section we give an example of a diffusion equation (i.e. $D_1 = 0$ and $D_2(x) = D$ with absorbing boundary conditions. The physical problem is the one of a microelectrode recessed into a surface. The concentration of ions in the bulk is c_b, the electrode is fixed at $z = 0$, with a flat surface at $z = L$. The Langevin equation for the freely diffusing ions (we consider a quasi 1D motion) with vertical position $z(t)$ is given by a simple Wiener process

$$\Delta z = \sigma \Delta W \tag{1.127}$$

whose corresponding FP equation is a diffusion equation

$$\frac{\partial c(z,t)}{\partial t} = \frac{\sigma^2}{2}\frac{\partial^2 c(z,t)}{\partial z^2} \tag{1.128}$$

where we have considered the concentration $c(z,t) \equiv p(z,t)$. This corresponds to take $D^{(1)}(z) = 0$ and $D^{(2)}(z) = \sigma^2/s$. Physically is reasonable to assume absorbing boundary condition at $z = 0$,

$$c(0,t) = 0. \tag{1.129}$$

Moreover, assuming the concentration at the mouth of the recess is equal to the bulk concentration one has

$$c(L,t) = c_b \tag{1.130}$$

The goal consists in finding the *steady-state current at the electrode* in terms of c_b and L. In this case the probability current is simply

$$j(z,t) = -\frac{\sigma^2}{2}\frac{\partial c(z,t)}{\partial z} \tag{1.131}$$

On the other hand, since the current is proportional to the flux of ions onto electrode, it will be proportional to the probability current at $z = 0$, i.e.,

$$I(t) = Kj(z,t)|_{z=0} = K\frac{\sigma^2}{2}\frac{\partial c(z,t)}{\partial z}\bigg|_{z=0} \tag{1.132}$$

The steady state concentration satisfies the differential equation

$$\frac{d^2}{dz^2}c_s(z) = 0 \tag{1.133}$$

whose solution is

$$c_s(z) = Az + B \tag{1.134}$$

The constants A and B are determined by imposing the BC. This gives $B = 0$ and $A = c_b/L$. Hence

$$c_s(z) = \frac{c_b}{L}z. \tag{1.135}$$

The steady state electrode current is then given by

$$\boxed{I_s = K\frac{\sigma^2}{2}\frac{dc_s(z)}{dz}\bigg|_{z=0} = K\frac{\sigma^2}{2}\frac{c_b}{L}.} \tag{1.136}$$

Note that $c_s(z)$ exists (i.e. is a normalizable solution) because we are considering a problem defined within a closed interval $[0, L]$. In $\mathbb{R}$ the solution (1.135) is not normalizable.

Chapter 2

Fundamental solutions (or Green's functions) of the Fokker-Planck equation

The non stationary solutions of the Fokker-Planck are in general quite difficult to compute and general analytical expressions can be found only when the coefficients $D^{(1)}$ and $D^{(2)}$ assume a particular forms. In general one is interested first in solving the *fundamental solution* or *Green's fucntion* of the FP equation. This is the solution of the equation

$$\partial_t p(\vec{r}, t|\vec{r}_0, t_0) = \hat{L}_{FP} p(\vec{r}, t|\vec{r}_0, t_0) \tag{2.1}$$

with initial conditions

$$p(\vec{r}, t \to t_0|\vec{r}_0, t_0) = \delta(\vec{r} - \vec{r}_0). \tag{2.2}$$

The boundary conditions depend instead on the problem and may be *natural*, *adsorbing*, *reflecting* or a mixture. Clearly the fundamental solution will depend on the form of the coefficient $D^{(1)}(x, t)$ and $D^{(2)}(x, t)$. The simplest situation (but also one of the well studied in physics) is the one in which the drift term $D^{(1)}(x, t)$ is zero and the diffusion term $D^{(2)}(x, t) = D$ i.e. a constant. In this case the Fokker-Planck equation reduces to the well known *diffusion equation* and the underlying process is a *Wiener process*. As discussed before this situation may arises from the full Langevin problem (i.e. the evolution of both $\vec{v}(t)$ and $\vec{r}(t)$) in which the adiabatic approximation has been considered. Given the importance of this case we will devote a full section to it.

2.1 The Diffusion equation: $D^{(1)} = 0$, $D^{(2)} = D$

If $D^{(1)}(x, t) = 0$ and $D^{(2)}(x, t) = D$ the Fokker-Planck equation reduces to the diffusion equation

$$\partial_t p(\vec{r}, t|\vec{r}_0, t_0) = D\nabla^2 p(\vec{r}, t|\vec{r}_0, t_0) \tag{2.3}$$

and the fundamental solution is given by assuming as initial condition

$$p(\vec{r}, t \to t_0|\vec{r}_0, t_0) = \delta(\vec{r} - \vec{r}_0). \tag{2.4}$$

Depending on the boundary conditions we will have different solutions. Let us start first from the case in which *natural* BC are considered i.e. when

$$p(|\vec{r}| \to \infty, t|\vec{r}_0, t_0) = 0. \tag{2.5}$$

In this case since the domain is R^d we can use the Fourier transform approach i.e. we consider

$$\tilde{p}(\vec{k}, t|\vec{r}_0, t_0) = \int_{\mathbb{R}^d} p(\vec{r}, t|\vec{r}_0, t_0) e^{i\vec{k}\cdot\vec{r}} d\vec{r}. \tag{2.6}$$

As $t \to t_0$, because of the initial condition, eq. (2.6) becomes

$$\tilde{p}(\vec{k}, t_0|\vec{r}_0, t_0) = \int_{\mathbb{R}^d} p(\vec{r}, t \to t_0|\vec{r}_0, t_0) e^{i\vec{k}\cdot\vec{r}} d\vec{r} = \int_{\mathbb{R}^d} \delta(\vec{r} - \vec{r}_0) e^{i\vec{k}\cdot\vec{r}} d\vec{r} = e^{i\vec{k}\cdot\vec{r}_0}. \tag{2.7}$$

By Fourier transforming the diffusion equation we get, for each value of $\vec{k}$, the differential equation

$$\frac{\partial}{\partial t}\tilde{p}(\vec{k}, t|\vec{r}_0, t_0) = -D|\vec{k}|^2 \tilde{p}(\vec{k}, t|\vec{r}_0, t_0) \tag{2.8}$$

whose solution in logarithmic form is

$$\ln \tilde{p}(\vec{k}, t|\vec{r}_0, t_0) = -D|\vec{k}|^2 (t - t_0) \tag{2.9}$$

and inverting the log we have

$$\boxed{\tilde{p}(\vec{k}, t|\vec{r}_0, t_0) = \exp\left[-D|\vec{k}|^2 (t - t_0)\right] \tilde{p}(\vec{k}, t_0|\vec{r}_0, t_0).} \tag{2.10}$$

Finally, from the initial condition $\tilde{p}(\vec{k}, t_0|\vec{r}_0, t_0) = \exp(i\vec{k}\cdot\vec{r}_0)$ one gets

$$\tilde{p}(\vec{k}, t) = \exp\left[i\vec{k}\cdot\vec{r}_0 - D|\vec{k}|^2 (t - t_0)\right]. \tag{2.11}$$

By antitrasforming one obtains

$$\boxed{p(\vec{r}, t|\vec{r}_0, t_0) = \frac{1}{(2\pi)^d}\int_{\mathbb{R}^d} \tilde{p}(\vec{k}, t|\vec{r}_0, t_0) e^{-i\vec{r}\cdot\vec{r}} d\vec{k} = (4\pi D(t - t_0))^{-d/2}\, e^{-\frac{(\vec{r}-\vec{r}_0)^2}{4D(t-t_0)}}}. \tag{2.12}$$

Given the Green's function (2.12) it is possible to obtain the solution $p(\vec{r}, t)$ for the system for any initial condition, e.g. for $p(\vec{r}, t \to t_0) = f(\vec{r}_0)$,

$$p(\vec{r}, t) = \int_{\mathbb{R}} d\vec{r}_0 p(\vec{r}, t|\vec{r}_0, t_0) f(\vec{r}_0). \tag{2.13}$$

In general one can write

$$p(\vec{r}_2, t_2|\vec{r}_1, t_1) = (4\pi D(t_2 - t_1))^{d/2}\, e^{-\frac{(\vec{r}_2-\vec{r}_1)^2}{4D(t_2-t_1)}} \qquad t_2 > t_1. \tag{2.14}$$

Note. The process just found is the *Wiener-Levy process* i.e. a Markov process that is homogeneous (but not stationary), Gaussian and with zero average. The realizations of such process are the Brownian paths starting at the origin. It is interesting to verify the well know result:

$$C(t_1, t_2) = \mathbb{E}\{\vec{r}(t_1)\vec{r}(t_2)\} = 2D\min(t_1, t_2) \tag{2.15}$$

by using the solution of the FP equation found above. Indeed by considering first $t_2 > t_1$ we have:

$$\begin{aligned}
\mathbb{E}\{\vec{r}(t_1)\vec{r}(t_2)\} &= \int_{\mathbb{R}^{2d}} d\vec{r}_1 d\vec{r}_2 \vec{r}_1 \vec{r}_2 p(\vec{r}_1, t_1; \vec{r}_2, t_2) \\
&= \int_{\mathbb{R}^{2d}} d\vec{r}_1 d\vec{r}_2 \vec{r}_1 \vec{r}_2 p(\vec{r}_1, t_1) p(\vec{r}_2, t_2|\vec{r}_1, t_1) \\
&= \int_{\mathbb{R}^d} d\vec{r}_1 \vec{r}_1 \left(4\pi D t_1\right)^{d/2} e^{-\frac{\vec{r}_1^2}{4Dt_1}} \int_{\mathbb{R}^d} d\vec{r}_2 \vec{r}_2 \left(4\pi D(t_2 - t_1)\right)^{d/2} e^{-\frac{(\vec{r}_2-\vec{r}_1)^2}{4D(t_2-t_1)}} \\
&= \int_{\mathbb{R}^d} d\vec{r}_1 \vec{r}_1^2 \left(4\pi D t_1\right)^{d/2} e^{-\frac{\vec{r}_1^2}{4Dt_1}} \\
&= 2dDt_1.
\end{aligned} \tag{2.16}$$

Since $\mathbb{E}\{\vec{r}(t_1)\vec{r}(t_2)\}$ is a symmetric function we find (2.15).

We now consider solutions in which different BC are taken into account.

2.1.1 Free diffusion in one-dimensional Half-space: method of images

As a first example we consider a particle diffusing freely in a one-dimensional half-space $x \geq 0$. This problem is governed by the diffusion equation in one dimension

$$\partial_t p(x, t|x_0, t_0) = D\partial_x^2 p(x, t|x_0, t_0). \tag{2.17}$$

If we look for the fundamental solution we should consider the initial condition

$$p(x, t \to t_0|x_0, t_0) = \delta(x - x_0). \tag{2.18}$$

Reflective Wall

The region Ω is here limited by a reflective wall at $x = 0$. This is described by the boundary condition

$$j(x, t|x_0, t_0) = \partial_x p(x, t|x_0, t_0) = 0. \tag{2.19}$$

Assuming that the particle started diffusion at some finite x_0 we can assume a natural boundary condition at $x \to \infty$, i.e.

$$p(x \to \infty, t|x_0, t_0) = 0. \tag{2.20}$$

Without the wall the BC (2.19) would be replaced by a natural BC for $x \to -\infty$, $p(x \to -\infty, t|x_0, t_0) = 0$ and the solution is

$$p(x, t|x_0, t_0) = \frac{1}{\sqrt{4\pi D(t - t_0)}} \exp\left[-\frac{(x - x_0)^2}{4D(t - t_0)}\right]. \tag{2.21}$$

To satisfy the BC at $x = 0$ the idea consists in introducing a sink, or *negative image* at position $-x_0$ and extending the problem to the entire space. This gives

$$\begin{aligned} p(x, t \to t_0|x_0, t_0) &= \frac{1}{\sqrt{4\pi D(t - t_0)}} \exp\left[-\frac{(x - x_0)^2}{4D(t - t_0)}\right] \\ &+ \frac{1}{\sqrt{4\pi D(t - t_0)}} \exp\left[-\frac{(x + x_0)^2}{4D(t - t_0)}\right], \qquad x \geq 0. \end{aligned} \tag{2.22}$$

This solution holds only in the half-space $x \geq 0$. Clearly, this function is a solution of (2.17) since both terms satisfy this equation. By differentiating (2.25) it is easy to show that it satisfies the BC (2.19). Clearly also the natural BC condition at $x \to \infty$ is satisfied. A simple interpretation of (2.25) is the following: the first term describes a diffusion vanishing which is unaware of the wall at $x = 0$ (it travels into the non available half space $x < 0$). This *loss of probability* is corrected by the second term which, with its tail for $x \geq 0$, balances the missing probability. In fact the $x \geq 0$ tail of the second term is exactly the mirror image of the missing $x \geq 0$ tail of the second term. This problem can be easily generalized in d dimensions supposing a freely-diffusing particle in d space with a reflecting boundary at $z = 0$. With the initial condition $p(\vec{r}, t \to t_0|\vec{r}_0 = \hat{z}a, t_0) = \delta(\vec{r} - \hat{z}a)$ (starting point at a distance $z = a$ away from the wall) and the reflecting boundary at $z = 0$ we have:

$$p(\vec{r}, t \to t_0|\hat{z}a, t_0) = (4\pi D(t - t_0))^{d/2} \left[e^{-\frac{(\vec{r} - \hat{z}a)^2}{4D(t - t_0)}} + e^{-\frac{(\vec{x} + \hat{z}a)^2}{4D(t - t_0)}}\right] \tag{2.23}$$

Absorbing Wall

We now consider the case in which the wall is *absorbing* (i.e. a wall which consumes every particle imping on it). In this case the boundary condition (2.19) must be replaced by

$$p(x, t|x_0, t_0) = 0. \tag{2.24}$$

Also in this case it is useful to think in terms of images although here the image must be *negative*. This gives

$$\begin{aligned} p(x, t \to t_0 | x_0, t_0) &= \frac{1}{\sqrt{4\pi D(t-t_0)}} \exp\left[-\frac{(x-x_0)^2}{4D(t-t_0)}\right] \\ &- \frac{1}{\sqrt{4\pi D(t-t_0)}} \exp\left[-\frac{(x+x_0)^2}{4D(t-t_0)}\right], \qquad x \geq 0. \end{aligned} \tag{2.25}$$

In this case the $x \geq 0$ tail of the first term which describes free diffusion is not cancelled by the second term, but rather the second term describes a further particle loss. Because of particle removal by the wall at $x = 0$, the total number of particles is not conserved. It is interesting to compute the number of particles at time t by using the fundamental solution

$$N(t|x_0, t_0) = \int_{\mathbb{R}} p(x, t|x_0, t_0) dx. \tag{2.26}$$

To perform the integral let us introduce the variable

$$y = \frac{x}{\sqrt{4D(t-t_0)}}. \tag{2.27}$$

The integral becomes

$$\begin{aligned} N(t|x_0, t_0) &= \frac{1}{\sqrt{\pi}} \int_{\mathbb{R}} \exp\left[-(y-y_0)^2\right] - \frac{1}{\sqrt{\pi}} \int_{\mathbb{R}} \exp\left[-(y+y_0)^2\right] \\ &= \frac{1}{\sqrt{\pi}} \int_{-y_0}^{\infty} \exp\left[-(y-y_0)^2\right] - \frac{1}{\sqrt{\pi}} \int_{y_0}^{\infty} \exp\left[-(y+y_0)^2\right] \\ &= \frac{1}{\sqrt{\pi}} \int_{-y_0}^{y_0} \exp\left[-(y-y_0)^2\right] \\ &= \frac{2}{\sqrt{\pi}} \int_{0}^{y_0} \exp\left[-(y-y_0)^2\right] \\ &= erf(y_0). \end{aligned} \tag{2.28}$$

This gives

$$N(t|x_0, t_0) = erf\left[\frac{x_0}{\sqrt{4D(t-t_0)}}\right]. \tag{2.29}$$

From the property of $erf(z)$ we have

$$N(t|x_0, t_0) \sim \frac{x_0}{\sqrt{4D(t-t_0)}} \qquad \text{for} \quad t \to \infty. \tag{2.30}$$

In other words the particle number decays to zero asymptotically. This is because one-dimensional Brownian motion will visit almost surely every point of the space and in particular the absorbing wall. The rate of particle decay is given by

$$\partial_t N(t|x_0, t_0) = -\frac{x_0}{\sqrt{2\pi D(t-t_0)}(t-t_0)} \exp\left[-\frac{x_0^2}{4D(t-t_0)}\right]. \tag{2.31}$$

2.1.2 Free diffusion in a 1d finite domain

A particle diffusing freely (no potential U) within a one dimensional interval

$$\Omega = [x_1, x_2] \tag{2.32}$$

is governed by the Fokker-Planck equation

$$\partial_t p(x,t|x_0,t_0) = D\partial_x^2 p(x,t|x_0,t_0). \tag{2.33}$$

Note that the above equation may be written ad

$$\partial_t p(x,t|x_0,t_0) = \partial_x j(x,t|x_0,t_0) \tag{2.34}$$

where

$$j(x,t|x_0,t_0) = D\left[\partial_x p(x,t|x_0,t_0)\right]. \tag{2.35}$$

A general set of BC conditions can then be written as

$$\begin{aligned} j(x_1,t|x_0,t_0) &= k_1 p(x_1,t|x_0,t_0) \\ j(x_2,t|x_0,t_0) &= k_2 p(x_2,t|x_0,t_0) \end{aligned} \tag{2.36}$$

that in this case simplify to

$$\begin{aligned} D\partial_x p(x,t|x_0,t_0)|_{x=x_1} - k_1 p(x_1,t|x_0,t_0) &= 0 \\ D\partial_x p(x,t|x_0,t_0)|_{x=x_2} - k_2 p(x_2,t|x_0,t_0) &= 0 \end{aligned} \tag{2.37}$$

This equation can be easily solved with the method of the *separation of variables*. The idea is to assume the solution $p(x,t|x_0,t_0)$ to be separable in x and t. This gives:

$$p(x,t|x_0,t_0) = X(x)T(t) \tag{2.38}$$

so that eq. (**??**) becomes

$$X''T = D^{-1}X\dot{T} \tag{2.39}$$

or, by diving by $X(x)T(t)$

$$\frac{X''}{X} = D^{-1}\frac{\dot{T}}{T} = k, \tag{2.40}$$

where k is the separation constant. The two equations must to be solved independently. The time equation

$$\dot{T} = DkT, \tag{2.41}$$

has solution

$$T(t) = T(t_0)e^{Dk(t-t_0)}. \tag{2.42}$$

Clearly $T(t)$ will increase in time if k is positive while it will decrease in time only if k is negative. Let us take

$$k = -\lambda^2. \tag{2.43}$$

This gives the spatial equation

$$\boxed{\frac{d^2X}{dx^2} + \lambda^2 X = 0.} \tag{2.44}$$

The BC (2.37) become in this case

$$\begin{aligned} -k_1X(x_1) + D\frac{dX}{dx}|_{x=x_1} &= 0 \\ -k_2X(x_2) + D\frac{dX}{dx}|_{x=x_2} &= 0 \end{aligned} \tag{2.45}$$

$$\tag{2.46}$$

Equation (2.44) with the associated BC (2.46) is an example of the so-called *Sturm-Liouville* problem discussed in many textbooks of mathematical physics and quantum mechanics (eigenvalues problem) and that here we recall for completeness.

Sturm-Liouville problem

In general the Sturm-Liouville problem associated to eq. such as (2.44), defined on the closed interval $x_1 \leq x \leq x_2$, will satisfy satisfying the following mixed BC

$$\alpha_1 X + \beta_1 \frac{dX}{dx} = 0 \qquad (x = x_1) \tag{2.47}$$

$$\alpha_2 X + \beta_2 \frac{dX}{dx} = 0 \qquad (x = x_2), \tag{2.48}$$

with real coefficients α_1, β_1, α_2, β_2, and λ^2, has the general solution

$$X(x) = \sum_\lambda X_\lambda(x). \tag{2.49}$$

The eigenfunctions $X_\lambda(x)$ depend on the sign of $\lambda's$.

$\lambda^2 > 0$ The eigenfunctions are periodic,

$$X_\lambda(x) = A_\lambda \sin(\lambda x) + B_\lambda \cos(\lambda x) \tag{2.50}$$

$\lambda^2 = 0$ Linear,

$$X_0(x) = A_0 x + B_0 \tag{2.51}$$

$\lambda^2 < 0$ The eigenfunctions are exponential,

$$X_\lambda(x) = A_\lambda \exp(\lambda x) + B_\lambda \exp(-\lambda x) \tag{2.52}$$

In our case λ^2 is positive and the eigenfuctions are the periodic ones. The BC conditions (2.48) require that the coefficients A_λ and B_λ satisfy the constraints

$$\begin{aligned} \alpha_1 \left(A_\lambda \sin(\lambda x_1) + B_\lambda \cos(\lambda x_1)\right) + \beta_1 \left(\lambda A_\lambda \cos(\lambda x_1) - \lambda B_\lambda \sin(\lambda x_1)\right) &= 0 \\ \alpha_2 \left(A_\lambda \sin(\lambda x_2) + B_\lambda \cos(\lambda x_2)\right) + \beta_2 \left(\lambda A_\lambda \cos(\lambda x_2) - \lambda B_\lambda \sin(\lambda x_2)\right) &= 0. \end{aligned} \tag{2.53}$$

To simplify a little bit these conditions let us consider the following change of variables

$$\begin{aligned} z &= x - x_1 \\ L &= x_2 - x_1. \end{aligned} \tag{2.54}$$

In this case the interval is $z \in [0, L]$ and the BC simplify to:

$$\alpha_1 B_\lambda + \beta_1 A_\lambda = 0, \tag{2.55}$$

$$\alpha_2 \left(A_\lambda \sin(\lambda L) + B_\lambda \cos(\lambda L)\right) + \beta_2 \left(\lambda A_\lambda \cos(\lambda L) - \lambda B_\lambda \sin(\lambda L)\right) = 0, \tag{2.56}$$

leading to a homogeneous system of two linear equations for A_λ and B_λ which requires the determinant of the system to be zero. This requirement results in a transcendental equation for λ^2,

$$\left(\alpha_1\alpha_2 + \lambda^2 \beta_1\beta_2\right) \frac{\sin(\lambda L)}{\lambda L} = (\alpha_2\beta_1 - \alpha_1\beta_2)\cos(\lambda L), \tag{2.57}$$

which can be written as

$$\lambda \cot(\lambda L) = a\lambda^2 + b \tag{2.58}$$

with

$$a = \frac{\beta_1\beta_2}{\alpha_2\beta_1 - \alpha_1\beta_2}, \quad b = \frac{\alpha_1\alpha_2}{\alpha_2\beta_1 - \alpha_1\beta_2}. \tag{2.59}$$

Notice that eq. (2.57) and (2.58) are the eigenvalues equations for $\lambda^2 \in \mathbb{R}$ and not for λ.

Two absorbing BC

If both extremities are absorbing i.e. if $k_1 = k_2 = \infty$ or *zero boundary conditions* we have $p(0, t|z_0, t_0) = p(L, t|z_0, t_0) = 0$. In the general formalism above this corresponds to take $\beta_1 = \beta_2 = 0$ and $\alpha_1 = \alpha_2 = 1$ and eq. (2.55) (2.56) simplify to

$$B_\lambda = 0, \tag{2.60}$$

and

$$\sin(\lambda L) = 0 \tag{2.61}$$

whose possible solutions are given by the eigenvalues

$$\lambda_n = n\pi/L. \tag{2.62}$$

For each value of n the complete solution is

$$A_n T_0 \sin\left(\frac{n\pi}{L} z\right) e^{-Dn^2\pi^2(t-t_0)/L^2} \tag{2.63}$$

and the general solution is obtained by summing over n

$$p(z, t|z_0, t_0) = T_0 \sum_{n=1}^{\infty} A_n \sin\left(\frac{n\pi}{L} z\right) e^{-Dn^2\pi^2(t-t_0)/L^2} \tag{2.64}$$

Exercise. Find the expression for $p(z, t|z_0, t_0)$ when the boundary at $z = 0$ is absorbing while the boundary at $z = L$ is reflecting.

Initial condition

The final step is to apply the initial conditions, namely

$$p(z, t \to t_0|z_0, t_0) = \sum_{n=1}^{\infty} A'_n \sin\left(\frac{n\pi}{L} z\right) = \delta(z - z_0) \tag{2.65}$$

where $A'_n \equiv T(t_0)A_n$. This can be obtained by inverting the Fourier series

$$A'_n = \frac{2}{L}\int_0^L \delta(z - z_0) \sin\left(\frac{n\pi}{L} z\right) dz, \tag{2.66}$$

for all positive integers, n. This gives

$$A'_n = \frac{2}{L} \sin\left(\frac{n\pi}{L} z_0\right) \tag{2.67}$$

Finally we get

$$p(z, t|z_0, t_0) = \frac{2}{L} \sum_{n=1}^{\infty} \sin\left(\frac{n\pi}{L} z\right) \sin\left(\frac{n\pi}{L} z_0\right) e^{-D\lambda_n^2(t-t_0)}, \tag{2.68}$$

where

$$\lambda_n^2 = \left(\frac{n\pi}{L}\right)^2 \tag{2.69}$$

are the eigenvalues. Going back to the original problem where $x \in [x_1, x_2]$ we finally get

$$p(x, t|x_0, t_0) = \frac{2}{L} \sum_{n=1}^{\infty} \sin\left(\frac{n\pi}{(x_2 - x_1)}(x - x_1)\right) \sin\left(\frac{n\pi}{(x_2 - x_1)}(x_0 - x_1)\right) e^{-\frac{Dn^2\pi^2}{(x_2-x_1)^2}(t-t_0)}, . \tag{2.70}$$

Laplace transform solution

The above problem can also be solved by using the Laplace transform on the time coordinate. This allow us to obtain $p(x,t|x_0,t_0)$ as a single function instead than an infinite Fourier series. The problem will be then to invert the Laplace transform and getting back the solution in real time. If we perform a Laplace transform of the diffusion equation (2.33) we get

$$-s\tilde{p}(x,s|x_0,t_0) + \delta(x-x_0) + D\frac{d^2}{dx^2}\tilde{p}(x,s|x_0,t_0) = 0 \tag{2.71}$$

where

$$\tilde{p}(x,s|x_0,t_0) = \int_{\mathbb{R}+} e^{-st}p(x,t|x_0,t_0) \tag{2.72}$$

and the δ function reflects the initial condition $p(x,t_|x_0,t_0) = \delta(x-x_0)$. To simplify the notation let us consider the following change of variable: $y = x\sqrt{\frac{s}{D}}$ and re-write the equation as follows:

$$D\frac{d^2}{dy^2}\tilde{p}(y,s|y_0,t_0) - \tilde{p}(y,s|y_0,t_0) = -\delta(y-y_0)\sqrt{\frac{1}{sD}} \tag{2.73}$$

The above equation must be solved in two distinct domains: $y_1 < y < y_0$ and $y_0 < y < y_2$. In each subinterval equation (2.73) becomes

$$D\frac{d^2}{dy^2}\tilde{p}(y,s|y_0,t_0) - \tilde{p}(y,s|y_0,t_0) = 0 \tag{2.74}$$

whose general solution is of the form

$$\tilde{p}(y,s|y_0,t_0) = Ae^{y} + Be^{-y} \tag{2.75}$$

Let us denote by $\tilde{p}_<(y,s|y_0,t_0)$ and $\tilde{p}_>(y,s|y_0,t_0)$ the solution of (2.74) respectively for $y \in [y_1,y_0]$ and $y \in [y_0,y_2]$. We can now impose the BC in y_1 and y_2. These are

$$\begin{aligned}
\tilde{p}(x_1,s|x_0,t_0) &= 0 = \tilde{p}\left(y_1\sqrt{\frac{D}{s}}, s|y_0\sqrt{\frac{D}{s}}, t_0\right) = 0 \\
\tilde{p}(x_2,s|x_0,t_0) &= 0 = \tilde{p}\left(y_2\sqrt{\frac{D}{s}}, s|y_0\sqrt{\frac{D}{s}}, t_0\right) = 0
\end{aligned} \tag{2.76}$$

giving

$$B_< = -A_<e^{2y_1} \qquad B_> = -A_>e^{2y_2} \tag{2.77}$$

Hence

$$\begin{aligned}
\tilde{p}_<(y,s|y_0,t_0) &= A_<e^{y_1}\left(e^{y-y_1} - e^{y_1-y}\right) = 2A_<e^{y_1}\sinh(y-y_1) = C_<\sinh(y-y_1) \\
\tilde{p}_<(y,s|y_0,t_0) &= A_>e^{y_2}\left(e^{y_2-y} - e^{y-y_2}\right) = 2A_>e^{y_2}\sinh(y_2-y) = C_>\sinh(y_2-y).
\end{aligned} \tag{2.78}$$

The constants C can be now determined by imposing the continuity of the two solutions and the discontinuity of their first derivatives (because of the delta) at $y = y_0$ i.e.

$$\begin{aligned}
\tilde{p}_>(y_0,s|y_0,t_0) - \tilde{p}_<(y_0,s|y_0,t_0) &= 0 \\
\left(\frac{d}{dy}\tilde{p}_>(y,s|y_0,t_0) - \tilde{p}_<(y,s|y_0,t_0)\right)\Bigg|_{y=y_0} &= -\frac{1}{\sqrt{sD}}
\end{aligned} \tag{2.79}$$

where the second condition has been obtained by integrating equation 2.33 around y_0. The first condition is satisfied if

$$\tilde{p}(y,s|y_0,t_0) = K\sinh(y_< - y_1)\sinh(y_2 - y_>), \tag{2.80}$$

where $y_< = \min(y, y_0)$ and $y_> = \max(y, y_0)$. The second condition is used to get the constant K. Finally

$$\tilde{p}(y, s|y_0, t_0) = \frac{1}{\sqrt{sD}} \frac{\sinh(y_< - y_1)\sinh(y_2 - y_>)}{\sinh(y_0 - y_1)\sinh(y_2 - y_0) + \sinh(y_0 - y_1)\sinh(y_2 - y_0)}. \tag{2.81}$$

Note that in the case in which $x_1 = 0$ and $x_2 = L$ we have $y_1 = 0$ and $y_2 = L\sqrt{s/D}$ giving

$$\tilde{p}(x, s|x_0, t_0) = \frac{1}{2\sqrt{sD}} \frac{\sinh(\sqrt{s/D}x_<)\sinh(\sqrt{s/D}(L - x_>))}{\sinh(\sqrt{s/D}x_0)\sinh(\sqrt{s/D}(L - x_0))}. \tag{2.82}$$

To obtain the solution as a function of time one needs to perform the inverse Laplace transform, keeping in mind that $\tilde{p}(y, s|y_0, t_0)$ depends on s also through y:

$$p(x, t|x_0, t_0) = \int_{\gamma - i\infty}^{\gamma + i\infty} ds \frac{e^{ts}}{2\sqrt{sD}} \frac{\sinh(\sqrt{s}(y_< - y_1)\sinh(\sqrt{s}(y_2 - y_>)}{\sinh(\sqrt{s}(y_0 - y_1))\sinh(\sqrt{s}(y_2 - y_0))}. \tag{2.83}$$

where $y_{<,>} = \frac{x_{<,>}}{\sqrt{D}}$. The integral must be evaluated along a line parallel to the imaginary axis. In order to apply the residue theorem we should chose a contour made by two semi-circles. Indeed, since the function $\sqrt{s}$ is a multi-valued function and has $s = 0$ as a branch cut point, we should choose a path as the one skectched in figure **??**, use Jordan theorem for the external circle and the fact that being $\lim_{s\to 0} sp(x, s|x_0, t_0) = 0$, also the integral along the small semi-circle vanishes. We then have to evaluate the integral along the full closed curve that is related to the sum of the residues of the poles inside the curve. Since e^{st} is rapidly growing, the only pole to be considered is the one with the largest real part. TODO

Exercise. Show that for mixed boundary conditions i.e. when

$$\begin{aligned} \partial_x p(x, t|x_0, t_0)\,|_{x=L} &= 0 \qquad \forall t \\ p(x = 0, t|x_0, t_0) &= 0 \end{aligned} \tag{2.84}$$

the solution in the Laplace space is given by

$$\tilde{p}(x, s|x_0, t_0) = \frac{1}{\sqrt{sD}} \frac{\sinh(\sqrt{s/D}x_<)\cosh(\sqrt{s/D}(L - x_>))}{\sinh(\sqrt{s/D}x_0)\sinh(\sqrt{s/D}(L - x_0)) + \cosh(\sqrt{s/D}x_0)\cosh(\sqrt{s/D}(L - x_0))}. \tag{2.85}$$

2.1.3 Free diffusion around a spherical object

One of the most useful example of a diffusion process is the one in which a molecule diffuses around a target and either reacts with it or vanishes out of its vicinity. Suppose for simplicity that the target is stationary and spherical with radius a. Moreover let us suppose that the reaction may occur anywhere on the surface of the target with the same probability. We consider an initial condition in which the molecule are uniformly distributed at a distance $\vec{r}_0$ from the center of the target

$$p(\vec{r}, t_0|\vec{r}_0, t_0) = \frac{1}{4\pi\vec{r}_0^2}\delta(|\vec{r}| - |\vec{r}_0|). \tag{2.86}$$

Since neither the initial condition nor the reaction-diffusion condition have any orientation preference, we should expect a spherically symmetric distribution $p(r, t|r_0, t_0)$ that follows the diffusion equation

$$\partial_t p(r, t|r_0, t_0) = D\nabla^2 p(r, t|r_0, t_0). \tag{2.87}$$

Let us now consider the boundary conditions of the problem. If we assume that the distribution vanishes at distances from the target which are much larger than r_0 the following *natural boundary condition* can be consider

$$\lim_{r\to\infty} p(r, t|r_0, t_0) = 0. \tag{2.88}$$

The reaction at the target may be described by a *radiation boundary condition* (known also as *Robin BC*) which for a spherical boundary, may be described by

$$\hat{n} \cdot j_r(r,t|r_0,t_0) = D\partial_t p(r,t|r_0,t_0) = kp(r,t|r_0,t_0), \qquad \text{for} \quad r = a. \tag{2.89}$$

Clearly $k = 0$ corresponds to non reactive surface (reflecting BC), whereas the limit $k >> 1$ to a surface for which every collision leads to reaction that diminishes $p(r,t|r_0,t_0)$ (in the $k \to \infty$ limit we have absoring BC). For this problem it is easier to write the diffusion equation in spherical coordinates remembering that

$$\nabla^2 = \frac{1}{r^2}\left[\partial_r\left(r^2\partial_r\right) + \frac{1}{\sin^2\theta}\partial_\phi^2 + \frac{1}{\sin\theta}\partial_\theta\left(\sin\theta\partial_\theta\right)\right]. \tag{2.90}$$

Since the probability distribution is spherically symmetric it depends only on r. Moreover,from the identity

$$\frac{1}{r^2}\partial_r\left(r^2\partial_r f(r)\right) = \frac{1}{r}\partial_r^2\left(rf(r)\right), \tag{2.91}$$

we get

$$\partial_t rp(r,t|r_0,t_0) = D\partial_r^2 rp(r,t|r_0,t_0). \tag{2.92}$$

Because of the mixed BC (2.89) it is convenient to partition the solution into two terms

$$p(r,t|r_0,t_0) = u(r,t|r_0,t_0) + v(r,t|r_0,t_0), \tag{2.93}$$

with initial condition

$$\begin{aligned} u(r,t\to t_0|r_0,t_0) &= \frac{1}{4\pi r_0^2}\delta(r-r_0) \\ v(r,t\to t_0|r_0,t_0) &= 0. \end{aligned} \tag{2.94}$$

Each function has to satisfy the diffusion equation and their sum must satisfy the mixed BC. Let us first compute $u(r,t\to t_0|r_0,t_0)$. It must satisfy

$$\begin{aligned} \partial_t ru(r,t|r_0,t_0) &= D\partial_r^2\left(ru(r,t|r_0,t_0)\right) \\ ru(r,t\to t_0|r_0,t_0) &= \frac{1}{4\pi r_0^2}\delta(r-r_0). \end{aligned} \tag{2.95}$$

Let us consider the Fourier transform

$$\tilde{u}(k,t|r_0,t_0) = \int_{\mathbb{R}} ru(r,t|r_0,t_0)e^{-ikr}dr. \tag{2.96}$$

By Fourier transforming equation (2.95) we get

$$\partial_t\tilde{u}(k,t|r_0,t_0) = -Dk^2\tilde{u}(k,t|r_0,t_0) \tag{2.97}$$

and integrating with respect to t gives

$$\tilde{u}(k,t|r_0,t_0) = A(k|r_0)e^{-D(t-t_0)k^2} \tag{2.98}$$

where $A(k|r_0)$ can be obtained from the initial condition in (2.95). Indeed, from the identity

$$\delta(r-r_0) = \frac{1}{2\pi}\int_{\mathbb{R}} dk e^{ik(r-r_0)} \tag{2.99}$$

we have

$$\begin{aligned} u(r,t\to t_0|r_0,t_0) &= \frac{1}{2\pi r}\int_{\mathbb{R}} dk\tilde{u}(k,t\to t_0|r_0,t_0)e^{ikr} \\ &= \frac{1}{2\pi r}\int_{\mathbb{R}} dk A(k|r_0)e^{ikr} \\ &= \frac{1}{4\pi r_0}\delta(r-r_0) \\ &= \frac{1}{8\pi^2 r_0}\int_{\mathbb{R}} dk e^{ik(k-k_0)} \end{aligned} \tag{2.100}$$

giving

$$A(k|r_0) = \frac{1}{4\pi r_0} e^{-ikr_0}. \tag{2.101}$$

This results in the expression

$$ru(r,t|r_0,t_0) = \frac{1}{8\pi^2 r_0} \int_{\mathbb{R}} dk \exp\left[-D(t-t_0)k^2\right] e^{ik(r-r_0)} \tag{2.102}$$

and from the identity

$$\int_{\mathbb{R}} dk e^{-\alpha k^2} e^{ixk} = \left(\frac{\pi}{\alpha}\right)^{1/2} e^{-\frac{x^2}{4\alpha}} \tag{2.103}$$

we finally get

$$ru(r,t|r_0,t_0) = \frac{1}{4\pi r_0} \frac{1}{\sqrt{4\pi D(t-t_0)}} \exp -\frac{(r-r_0)^2}{4D(t-t_0)}. \tag{2.104}$$

We now consider the solution $v(r,t|r_0,t_0)$ that must satisfy

$$\partial_t \left(rv(r,t|r_0,t_0)\right) = D\partial_r^2 \left(rv(r,t|r_0,t_0)\right) \tag{2.105}$$

with initial condition

$$rv(r,t \to t_0|r_0,t_0) = 0. \tag{2.106}$$

If we apply the Laplace transform

$$\tilde{v}(r,s|r_0,t_0) = \int_{\mathbb{R}} e^{-st} v(r,t|r_0,t_0) dt \tag{2.107}$$

to eq. (2.105) we get an expression, that integrated by parts, gives

$$-rv(r,t_0 t_0|r_0,t_0) + sr\tilde{v}(r,s|r_0,t_0). \tag{2.108}$$

Because of the initial condition (2.106) the first term vanishes and we obtain

$$\frac{s}{D}\left(r\tilde{v}(r,s|r_0,t_0)\right) = \partial_r^2 \left(r\tilde{v}(r,s|r_0,t_0)\right) \tag{2.109}$$

A solution that satisfies the natural BC (2.88) is

$$r\tilde{v}(r,s|r_0,t_0) = A(s|r_0) \exp\left[-\sqrt{\frac{s}{D}} r\right]. \tag{2.110}$$

Where the constant $A(s|r_0)$ will be determined by imposing the BC (2.89). We now take the Laplace transform of the BC (2.89). Denoting by $\tilde{p}(r,s|r_0,t_0)$ the Laplace transform of the full solution $p(r,t|r_0,t_0)$ one may verify that

$$D\partial_r \left(r\tilde{p}(r,s|r_0,t_0)\right) = D\tilde{p}(r,s|r_0,t_0) + rD\partial_r \tilde{p}(r,s|r_0,t_0). \tag{2.111}$$

Using this identity in (2.89) we get

$$\partial_r r\tilde{p}(r,s|r_0,t_0)|_{r=a} = \frac{ka+D}{Da} a\tilde{p}(a,s|r_0,t_0). \tag{2.112}$$

We now need the Laplace transform of $u(r,t|r_0,t_0)$. By using the identity

$$\int_{\mathbb{R}} e^{-st} \frac{1}{\sqrt{4\pi Dt}} \exp\left[-\frac{(r-r_0)^2}{4Dt}\right] = \frac{1}{\sqrt{4\pi Ds}} \exp\left[-\sqrt{\frac{s}{D}}|r-r_0|\right] \tag{2.113}$$

we get

$$r\tilde{p}(r,s|r_0,t_0) = \frac{1}{4\pi r_0} \frac{1}{\sqrt{4\pi Ds}} \exp\left[-\sqrt{\frac{s}{D}}|r-r_0|\right] + A(s|r_0) \exp\left[-\sqrt{\frac{s}{D}} r\right]. \tag{2.114}$$

The BC condition (2.112) for $r = a < r_0$ becomes

$$\sqrt{\frac{s}{D}} \left(\frac{1}{4\pi r_0}\frac{1}{\sqrt{4\pi Ds}}\exp\left[-\sqrt{\frac{s}{D}}(r_0-a)\right] - A(s|r_0)\exp\left[-\sqrt{\frac{s}{D}}a\right]\right) \tag{2.115}$$

$$= \frac{ka+D}{Da}a\left(\frac{1}{4\pi r_0}\frac{1}{\sqrt{4\pi Ds}}\exp\left[-\sqrt{\frac{s}{D}}(r_0-a)\right] + A(s|r_0)\exp\left[-\sqrt{\frac{s}{D}}a\right]\right). \tag{2.116}$$

This gives

$$A(s|r_0) = \frac{(s/D)^{1/2}-(ka+D)/(Da)}{(s/D)^{1/2}+(ka+D)/(Da)}\frac{1}{4\pi r_0}\frac{1}{\sqrt{4\pi Ds}}\exp\left[-\sqrt{\frac{s}{D}}(r_0-2a)\right], \tag{2.117}$$

and we finally get

$$\begin{aligned} r\tilde{p}(r,s|r_0,t_0) &= \\ &= \frac{1}{4\pi r_0}\frac{1}{\sqrt{4\pi Ds}}\exp\left[-\sqrt{\frac{s}{D}}|r-r_0|\right] \\ &+ \frac{(s/D)^{1/2}-(ka+D)/(Da)}{(s/D)^{1/2}+(ka+D)/(Da)}\frac{1}{4\pi r_0}\frac{1}{\sqrt{4\pi Ds}}\exp\left[-\sqrt{\frac{s}{D}}(r+r_0-2a)\right] \\ &= \frac{1}{4\pi r_0}\frac{1}{\sqrt{4\pi Ds}}\left(\exp\left[-\sqrt{\frac{s}{D}}|r-r_0|\right]+\exp\left[-\sqrt{\frac{s}{D}}(r+r_0-2a)\right]\right) \\ &- \frac{(ka+D)/(Da)}{\sqrt{\frac{s}{D}}+(ka+D)/(Da)}\frac{1}{4\pi r_0}\frac{1}{\sqrt{Ds}}\exp\left[-\sqrt{\frac{s}{D}}(r+r_0-2a)\right]. \end{aligned} \tag{2.118}$$

By applying the inverse Laplace transform we obtain the final result

$$\begin{aligned} rp(r,t|r_0,t_0) &= \\ &= \frac{1}{4\pi r_0}\frac{1}{\sqrt{4\pi D(t-t_0)}}\left(\exp\left[-\frac{(r-r_0)^2}{4D(t-t_0)}\right]+\exp\left[-\frac{(r+r_0-2a)^2}{4D(t-t_0)}\right]\right) \\ &- \frac{1}{4\pi r_0}\frac{ka+D}{Da}\exp\left[\left(\frac{ka+D}{Da}\right)^2 D(t-t_0)+\frac{ka+D}{Da}(r+r_0-2a)\right] \\ &\times Erfc\left[\frac{ka+D}{Da}\sqrt{D(t-t_0)}+\frac{r+r_0-2a}{\sqrt{4D(t-t_0)}}\right]. \end{aligned} \tag{2.119}$$

Reflective boundary

If the boundary at $r = a$ is reflective we have $k = 0$ and the solution (2.119) simplifies to

$$\begin{aligned} p(r,t|r_0,t_0) &= \\ &= \frac{1}{4\pi rr_0}\frac{1}{\sqrt{4\pi D(t-t_0)}}\left(\exp\left[-\frac{(r-r_0)^2}{4D(t-t_0)}\right]+\exp\left[-\frac{(r+r_0-2a)^2}{4D(t-t_0)}\right]\right) \\ &- \frac{1}{4\pi arr_0}\exp\left[\frac{D}{a^2}(t-t_0)+\frac{r+r_0-2a}{a}\right] \\ &\times Erfc\left[\frac{\sqrt{D(t-t_0)}}{a}+\frac{r+r_0-2a}{\sqrt{4D(t-t_0)}}\right]. \end{aligned} \tag{2.120}$$

Absorbing boundary

This condition is equivalent to take $k \to \infty$. We need to look at the asymptotic behaviour of the error function i.e.

$$\sqrt{\pi}z\exp z^2 Erfc(z) \sim 1 + O\left(\frac{1}{z^2}\right). \tag{2.121}$$

If we consider the substitutions $\gamma = (ka + D)/(Da)$ $z = \gamma z_1 + z_2$, $z_1 = \sqrt{D(t - t_0)}$ and $z_2 = (r + r_0 - 2a)/\sqrt{4D(t - t_0)}$ we have

$$\begin{aligned} &\gamma \exp\left[\gamma^2 D(t - t_0) + \gamma(r + r_0 - 2a)\right] Erfc\left[\gamma\sqrt{D(t - t_0)}\right] \\ = \; &\gamma e^{z^2} e^{-z_2^2} Erfc(z) \sim \frac{\gamma}{\sqrt{\pi} z} e^{-z_2^2}\left(1 + O\left(\frac{1}{\gamma^2}\right)\right) \end{aligned} \tag{2.122}$$

in the asymptotic limit $\gamma \to \infty$. Hence, at leading order

$$\begin{aligned} &\gamma \exp\left[\gamma^2 D(t - t_0) + \gamma(r + r_0 - 2a)\right] Erfc\left[\gamma\sqrt{D(t - t_0)}\right] \\ \sim \; &\left(\frac{2}{\sqrt{4\pi D(t - t_0)}} + O\left(\frac{1}{\gamma^2}\right)\right) \exp\left[-\frac{(r + r_0 - 2a)^2}{4D(t - t_0)}\right]. \end{aligned} \tag{2.123}$$

The full solution becomes, in the limit $k \to \infty$,

$$p(r, t|r_0, t_0) = \frac{1}{4\pi r r_0} \frac{1}{\sqrt{4\pi D(t - t_0)}} \left(\exp\left[-\frac{(r - r_0)^2}{4D(t - t_0)}\right] - \exp\left[-\frac{(r + r_0 - 2a)^2}{4D(t - t_0)}\right]\right). \tag{2.124}$$

2.1.4 Free diffusion in a cylinder

Let us now consider the problem of a particle diffusion within a cylinder of radius ρ and $z \in [0, L_0]$. The diffusion equation can be written as

$$\partial_t p(x, y, z, t|x_0, y_0, z_0, t_0) = D_\perp \left(\partial_x^2 + \partial_y^2\right) ip(x, y, z, t|x_0, y_0, z_0, t_0) + D_{||}\partial_z^2 p(x, y, z, t|x_0, y_0, z_0, t_0) \tag{2.125}$$

where we have supposed $D_\perp \neq D_{||}$. It is clearly convenient to pass to cylindrical coordinates (r, ϕ, z):

$$\partial_t p(r, \phi, z, t|r_0, \phi_0, z_0, t_0) = D_\perp \left[\frac{1}{r}\frac{\partial}{\partial r}\left(r\frac{\partial p}{\partial r} + \frac{1}{r}\frac{\partial^2 p}{\partial \phi^2}\right)\right] + D_{||}\partial_z^2 p(r, \phi, z, t|r_0, \phi_0, z_0, t_0). \tag{2.126}$$

If we restrict ourselves to solutions that are cylindrically symmetric i.e. to solutions $p(r, \phi, z, t|r_0, \phi_0, z_0, t_0) = p(r, z, t|r_0, z_0, t_0)$ equation above simplifies to

$$\partial_t p(r, z, t|r_0, z_0, t_0) = D_\perp \frac{1}{r}\frac{\partial}{\partial r}\left(r\frac{\partial p}{\partial r}\right) + D_{||}\partial_z^2 p(r, z, t|r_0, z_0, t_0). \tag{2.127}$$

Note that eq. (2.127) holds also for $D_\perp = D_\perp(t)$, $D_{||} = D_{||}(t)$. Let us look first to the stationary solutions. These are given by imposing the condition $\partial_t p = 0$ i.e.

$$D_\perp \frac{1}{r}\frac{\partial}{\partial r}\left(r\frac{\partial p_s(r, z|r_0, z_0, t_0)}{\partial r}\right) + D_{||}\partial_z^2 p_s(r, z|r_0, z_0, t_0) = 0, \tag{2.128}$$

or

$$D_\perp \frac{\partial^2}{\partial r^2} p_s(r, z|r_0, z_0, t_0) + D_\perp \frac{1}{r}\frac{\partial}{\partial r} p_s(r, z|r_0, z_0, t_0) + D_{||}\frac{\partial^2}{\partial z^2} p_s(r, z|r_0, z_0, t_0) = 0. \tag{2.129}$$

If $D_\perp > 0, D_{||} > 0$ we can divide the above equation by $D_\perp$ obtaining

$$\frac{\partial^2}{\partial r^2} p_s(r, z|r_0, z_0, t_0) + \frac{1}{r}\frac{\partial}{\partial r} p_s(r, z|r_0, z_0, t_0) + \alpha^2 \frac{\partial^2}{\partial z^2} p_s(r, z|r_0, z_0, t_0) = 0. \tag{2.130}$$

where

$$\alpha^2 = \frac{D_{||}}{D_\perp}. \tag{2.131}$$

To obtain a stationary solution it is necessary to define the boundary conditions. Suppose that the cylindrical surface is a reflecting boundary (no flux trough this surface) i.e.

$$\left.\frac{\partial}{\partial r} p_s(r, z|r_0, z_0, t_0)\right|_{r=\rho} = 0. \tag{2.132}$$

In addition suppose that the disk ($z = 0, r \leq R$) is an absorbing boundary i.e. $p_s(r, 0|r_0, z_0, t_0) = 0$ whereas the disk at $z = L_0$ is at constant value p_b. This is a reasonable assumption if, for example, L_0 is large enough and p_b can be seen as a molecule concentration in the bulk, i.e. far away from the exit at $z = 0$. Equation (2.130) can be integrated by method of separation of variables, i.e. by assuming that the stationary solution $p_s(r, z|r_0, z_0, t_0)$ can be written as

$$p_s(r, z) = R(r)Z(z) \tag{2.133}$$

where we have omitted the conditional initial conditions (r_0, z_0) for simplicity. Inserting in equation (2.130) we get

$$R''Z + \frac{1}{r}R'Z + \alpha^2 RZ'' = 0 \tag{2.134}$$

Hence

$$\frac{R''}{R} + \frac{1}{r}\frac{R'}{R} = -\alpha^2 \frac{Z''}{Z} = -\lambda^2. \tag{2.135}$$

The two equations above must be solved independently. Let us consider first the radial part

$$r^2 R'' + rR' + r^2 \lambda R = 0 \tag{2.136}$$

This equation in the form of a *Bessel equation* $x^2 y'' + xy' + (x^2 - n^2)y = 0$ with $x = \lambda r$ and $n = 0$ (i.e. order zero). We the expect a general solution of the form

$$R(r) = C_1 J_0(\lambda r) + C_2 Y_0(\lambda r) \tag{2.137}$$

where J_0 and Y_0 are the zero order Bessel functions of, respectively, the first and second kind. Clearly the full solution is a sum of two solutions since we have a second order differential equation. A plot of $J_0(x)$ and $Y_0(x)$ are reported in figure. To determine the constants C_1 and C_2 we should consider the BC. Since $Y_0(0) = -\infty$ and we expect instead $R(0) < \infty$, we should put $C_2 = 0$. We then have

$$R(r) = C_1 J_0(\lambda r). \tag{2.138}$$

The second BC is given by the no flux condition at the cylinder surface , i.e.

$$\left.\frac{dR}{dr}\right|_{R=\rho} = 0, \tag{2.139}$$

i.e.

$$\left.\frac{dJ_0(x)}{dx}\right|_{x=\lambda\rho} = 0. \tag{2.140}$$

Since $C_1 \neq 0$, we have to find the values of λ for which condition (2.140) is satisfied i.e. the values λ_m such that

$$\left.\frac{dJ_0(x)}{dx}\right|_{x=\lambda_m\rho} = 0. \tag{2.141}$$

On the other hand, from the properties of the Bessel functions J_p we know that

$$\frac{d}{dr} J_p(\lambda r) = -\lambda J_{p+1}(\lambda r) + \frac{p}{r} J_p(\lambda r) \tag{2.142}$$

and in our specific case

$$\frac{d}{dr} J_0(\lambda r) = -\lambda J_1(\lambda r). \tag{2.143}$$

Hence the BC condition (2.140) can be re-casted as follows: find the values of λ_m such that

$$J_1(\lambda\rho) = 0. \tag{2.144}$$

Denoting by j_{1m} the m-th zero of $J_1(\lambda_m \rho)$ we have

$$R(r) = C_1 J_0(\lambda_m r), \qquad \text{with} \qquad \lambda_m = j_{1m}/\rho. \tag{2.145}$$

For any fixed value λ_m we now solve the equation for $Z(z)$:

$$Z'' - \frac{\lambda_m^2}{\alpha^2} Z = 0. \tag{2.146}$$

A general solution is the well known sum

$$Z_m(z) = A \sinh\left(\frac{\lambda_m}{\alpha} z\right) + B \cosh\left(\frac{\lambda_m}{\alpha} z\right) \tag{2.147}$$

From the absorbing boundary condition at $z = 0$ we have $Z(0) = 0$ giving

$$Z(z) = A \sinh\left(\frac{\lambda_m}{\alpha} z\right). \tag{2.148}$$

For fixed λ_m we then have the eigenfunction

$$p_{sm}(r, z) = A_m \sinh\left(\frac{\lambda_m}{\alpha} z\right) J_0(\lambda_m r), \qquad \lambda_m = j_{1m}/\rho, \qquad m = 1, 2, \cdots \tag{2.149}$$

The general solution is then

$$p_s(r, z) = \sum_{m=1}^{\infty} A_m \sinh\left(\frac{\lambda_m}{\alpha} z\right) J_0(\lambda_m r). \tag{2.150}$$

Since $p(z = L_0, r) = p_b$ we have

$$p_b = \sum_{m=1}^{\infty} A_m \sinh\left(\frac{\lambda_m}{\alpha} L_0\right) J_0(\lambda_m r) \tag{2.151}$$

Multiplying both sides by $r J_0(\lambda_m r)$ and integrating in $[0, 1]$ we have

$$p_b \int_0^1 r J_0(\lambda_m r) dr = \sum_{m=1}^{\infty} A_m \sinh\left(\frac{\lambda_m}{\alpha} L_0\right) \int_0^1 r J_0(\lambda_m r) J_0(\lambda_m r) dr. \tag{2.152}$$

On the other hand since (see appendix)

$$\int_0^1 x J_0(ax) dx = \left[\frac{x}{a} J_1(ax)\right]_0^1 = J_1(a)/a \tag{2.153}$$

and from the orthogonality properties

$$\int_0^1 x J_\alpha(x\lambda_{\alpha,m}) J_\alpha(x\lambda_{\alpha,n}) dx = \frac{\delta_{m,n}}{2} \left[J_{\alpha+1}(x\lambda_{\alpha,m})\right]^2, \tag{2.154}$$

we have

$$p_b \frac{J_1(\lambda_m)}{\lambda_m} = A_m \sinh\left(\frac{\lambda_m}{\alpha} L_0\right) \frac{1}{2} \left[J_1^2(\lambda_m)\right] \tag{2.155}$$

giving

$$A_m = \frac{2 p_b}{\lambda_m J_1(\lambda_m) \sinh\left(\frac{\lambda_m}{\alpha} L_0\right)} \tag{2.156}$$

The steady state solution is then

$$p_s(r, z) = \sum_{m=1}^{\infty} \frac{2 p_b}{\lambda_m J_1(\lambda_m) \sinh\left(\frac{\lambda_m}{\alpha} L_0\right)} \sinh\left(\frac{\lambda_m}{\alpha} z\right) J_0(\lambda_m r). \tag{2.157}$$

Full solution

We now consider the solution of the full problem i.e.

$$\partial_t p(r,z,t|r_0,z_0,t_0) = \frac{\partial^2}{\partial r^2} p(r,z,t|r_0,z_0,t_0) + \frac{1}{r}\frac{\partial}{\partial r} p(r,z,t|r_0,z_0,t_0) + \alpha^2 \frac{\partial^2}{\partial z^2} p(r,z,t|r_0,z_0,t_0), \tag{2.158}$$

where

$$\alpha^2 = \frac{D_{||}}{D_{\perp}}. \tag{2.159}$$

Since we are looking for a full solution, in addition to the boundary conditions

$$\begin{aligned} \frac{\partial}{\partial r} p(r,z,t|r_0,z_0,t_0)\bigg|_{r=\rho} &= 0 \\ p(r,0,t|r_0,z_0,t_0) = 0, \qquad & p(r,L_0,t|r_0,z_0,t_0) = p_b \end{aligned} \tag{2.160}$$

we have to consider the initial condition

$$p(r,z,t \to t_0|r_0,z_0,t_0) = p(r_0,z_0) \tag{2.161}$$

As before we can use the separation of variables trick by assuming

$$p(r,z,t|r_0,z_0,t_0) = R(r)Z(z)T(\tau). \tag{2.162}$$

Inserting this assumption in (2.158) we get

$$\frac{R''}{R} + \frac{1}{r}\frac{R'}{R} + \alpha^2 \frac{Z''}{Z} = \frac{T'}{T} = -\lambda^2 \tag{2.163}$$

and we can write

$$T(\tau) = T_1 \exp(-\lambda^2 \tau) \tag{2.164}$$

and

$$\frac{R''}{R} + \frac{1}{r}\frac{R'}{R} + \lambda^2 = -\alpha^2 \frac{Z''}{Z} = \mu_2 \tag{2.165}$$

The above equations would give a trivial solution unless $\mu_2 > 0$. we can then take $\mu_2 = \mu^2$ and the above equations become

$$\frac{R''}{R} + \frac{1}{r}\frac{R'}{R} + \lambda^2 = -\alpha^2 \frac{Z''}{Z} = \mu^2 \tag{2.166}$$

that is

$$R'' + \frac{1}{r}R' + (\lambda^2 - \mu^2)R = 0 \tag{2.167}$$

and

$$Z'' + \frac{\mu^2}{\alpha^2} Z = 0 \tag{2.168}$$

From the first equation

$$r^2 R'' + rR' + (\lambda^2 - \mu^2) r^2 R = 0 \tag{2.169}$$

we should look for a general solution of the form

$$R(r) = C_1 J_0(\gamma r) + C_2 Y_0(\gamma r), \qquad \gamma^2 = \lambda^2 - \mu^2 \tag{2.170}$$

with BC

$$R'(0) = 0, Y_0(0) = -\infty, \quad \text{giving} \quad C_2 = 0 \tag{2.171}$$

and

$$R'(\rho) = 0..... \tag{2.172}$$

TODO

2.1.5 Appendix

Let us consider the indefinite integrals

$$S_n = \int x^n J_0(ax)dx. \tag{2.173}$$

They can be solved by recursion as follows. By inserting the following properties of the Bessel functions $J_0(ax)$:

$$\frac{d}{dx}\left(xJ_1(ax)\right) = axJ_0(ax) \tag{2.174}$$

and

$$\frac{d}{dx}J_0(ax) = -axJ_1(ax) \tag{2.175}$$

we have

$$\begin{aligned}
S_n &= \int x^n J_0(ax)d = \frac{1}{a}\int x^{n-1}axJ_0(ax)dx = \frac{1}{a}\int x^{n-1}\frac{d}{dx}\left(xJ_1(ax)\right)dx \\
&= \frac{1}{a}\left[x^{n-1}xJ_1(ax) - \int (n-1)x^{n-2}xJ_1(ax)dx\right] = \\
&= \frac{x^n}{a}J_1(ax) + \frac{n-1}{a^2}\int x^{n-1}\left(-aJ_1(ax)\right)dx = \frac{x^n}{a}J_1(ax) + \frac{n-1}{a^2}\int x^{n-1}\left(\frac{dJ_0(ax)}{dx}\right)dx = \\
&= \frac{x^n}{a}J_1(ax) + \frac{n-1}{a^2}\left[x^{n-1}J_0(ax) - \int (n-1)x^{n-2}J_0(ax)dx\right] = \\
&= \frac{x^n}{a}J_1(ax) + \frac{n-1}{a^2}x^{n-1}J_0(ax) - \frac{(n-1)^2}{a^2}\int x^{n-2}J_0(ax)dx
\end{aligned} \tag{2.176}$$

Hence

$$S_n = \frac{x^n}{a}J_1(ax) + \frac{n-1}{a^2}x^{n-1}J_0(ax) - \frac{(n-1)^2}{a^2}S_{n-2} \tag{2.177}$$

For $n = 1$ we have

$$S_1 = \int xJ_0(ax)dx = \frac{1}{a}\int axJ_0(ax)dx = \frac{x}{a}J_1(ax). \tag{2.178}$$

Orthogonality

$$\int_0^1 xJ_\alpha(xu_{\alpha,m})J_\alpha(xu_{\alpha,n})dx = \frac{\delta_{m,n}}{2}\left[J_{\alpha+1}(u_{\alpha,m})\right]^2 \tag{2.179}$$

2.2 Processes with drift and diffusion terms depending on time: $D_1(t)$, $D_2(t)$.

If the drift and diffusion terms depend on t, i.e. $D^{(1)}(x,t) = D_1(t)$ and $D^{(2)}(x,t) = D_2(t)$, the FP equation becomes:

$$\partial_t p(x,t|x_0,t_0) = -D_1(t)\frac{\partial}{\partial x}p(x,t|x_0,t_0) + D_2(t)\frac{\partial^2}{\partial x^2}p(x,t|x_0,t_0). \tag{2.180}$$

Following the previous case we look first for solutions in Fourier space where eq. (2.180) becomes

$$\frac{\partial}{\partial t}\tilde{p}(k,t) = \left(ikD_1(t) - k^2D_2(t)\right)\tilde{p}(k,t). \tag{2.181}$$

The solution in logarithmic form is then

$$\ln\tilde{p}(k,t) - \ln\tilde{p}(k,t_0) = ik\int_{t_0}^t D_1(\tau)d\tau - k^2\int_{t_0}^t D_2(\tau)d\tau, \tag{2.182}$$

giving

$$\tilde{p}(k,t) = \exp\left[ik\int_{t_0}^{t} D_1(\tau)d\tau - k^2\int_{t_0}^{t} D_2(\tau)d\tau\right]\tilde{p}(k,t_0), \tag{2.183}$$

and since $\tilde{p}(k,t_0) = \exp(ikx_0)$, one gets

$$\boxed{\tilde{p}(k,t) = \exp\left[ik\left(x_0 + \int_{t_0}^{t} D_1(\tau)d\tau\right) - k^2\int_{t_0}^{t} D_2(\tau)d\tau\right]}. \tag{2.184}$$

By antitransforming the above equation one finally gets that $p(x,t|x_0,t_0)$ follows a Normal distribution with

$$\mathbb{E}\{x(t)\} = x_0 + \int_{t_0}^{t} D_1(\tau)d\tau \tag{2.185}$$

$$\mathbb{E}\{x(t)^2\} = 2\int_{t_0}^{t} D_2(\tau)d\tau. \tag{2.186}$$

2.3 Ornstein-Uhlenbeck process

Let us now look at the Ornstein-Uhlenbeck process where D_2 is still constant but $D^{(1)} = D_1(v)$. In this case

$$D^{(1)}(v) = -\gamma v(t) \qquad \text{and} \qquad D^{(2)}(v) = \frac{\sigma^2}{2} = \text{const.} \tag{2.187}$$

The corresponding FP equation is

$$\frac{\partial}{\partial t}p(v,t|v_0,t_0) = \gamma\frac{\partial}{\partial v}\left(v(t)p(v,t|v_0,t_0)\right) + \frac{\sigma^2}{2}\frac{\partial^2}{\partial v^2}p(v,t|v_0,t_0), \tag{2.188}$$

with initial condition

$$p(v,t_0|v_0,t_0) = \delta(v - v_0). \tag{2.189}$$

By taking the Fourier transform of equation (2.188) one gets

$$\frac{\partial}{\partial t}\tilde{p}(k,t|v_0,t_0) = -\gamma k\frac{\partial}{\partial k}\tilde{p}(k,t|v_0,t_0) - \frac{\sigma^2 k^2}{2}\tilde{p}(k,t|v_0,t_0) \tag{2.190}$$

where the substitutions $\partial/\partial v \to ik$ and $v \to i\partial/\partial k$ have been considered. The initial condition becomes

$$\tilde{p}(k,t_0|v_0,t_0) = e^{ikv_0} \tag{2.191}$$

Eq. (2.190) is a first order PDE whose general form is

$$a(k,t)\frac{\partial\tilde{p}}{\partial k} + b(k,t)\frac{\partial\tilde{p}}{\partial t} + c(k,t)\tilde{p} = 0 \tag{2.192}$$

with initial condition $\tilde{p}(k,t_0|v_0,t_0) = f(k)$. This class of PDE's can be solved with the *method of characteristics*. The idea beyond this method consists in performing a change of coordinates from (k,t) to a new coordinate system, say (k_0,s), in which the PDE becomes an ordinary differential equation (ODE) along a certain curves in the (k,t) plane. These curves $\{[k(s),t(s)] : 0 < s < \infty\}$ are called *characteristic* curves. The new variable s will vary while the new variable k_0 will be constant along the characteristics. The variable k_0 will change along the initial curve (i.e. along the line $t = 0$). The equations determining the characteristic curves can be obtained by the following considerations. If one chooses the differential equations

$$\frac{dt}{ds} = b(k,t) \tag{2.193}$$

$$\frac{dk}{ds} = a(k,t) \tag{2.194}$$

we get

$$\begin{aligned}\frac{d\tilde{p}}{ds} &= \frac{dk}{ds}\frac{\partial\tilde{p}}{\partial k} + \frac{dt}{ds}\frac{\partial\tilde{p}}{\partial t} \\ &= a(k,t)\frac{\partial\tilde{p}}{\partial k} + b(k,t)\frac{\partial\tilde{p}}{\partial t}\end{aligned} \tag{2.195}$$

and along the characteristic curves the PDE becomes the ODE

$$\frac{d\tilde{p}}{ds} + c(k,t)\tilde{p} = 0. \tag{2.196}$$

with initial condition

$$\tilde{p}(k,t_0|v_0,t_0) = \tilde{p}(k_0,s_0|v_0,t_0) = f(k_0). \tag{2.197}$$

The first step consists in solving the characteristic equations (2.193) (2.194) that in this case become

$$\frac{dt}{ds} = 1 \tag{2.198}$$

$$\frac{dk}{ds} = \gamma k \tag{2.199}$$

Eq. (2.198) gives $t = s + A$ and using $t(0) = 0$ one gets $t = s$. In this situation the second equation becomes

$$\frac{dk}{dt} = \gamma k \qquad , k(0) = k_0 \qquad \text{(points along the } t=0 \text{ axis)} \tag{2.200}$$

whose solution is

$$k = k_0 \exp\left(\gamma(t-t_0)\right). \tag{2.201}$$

We now have the transformation from (k,t) to (k_0,s), $k = k(k_0,s)$ and $t = t(k_0,s)$ and we can solve the ODE (2.196)

$$\frac{d\tilde{p}}{ds} = -\frac{\sigma^2 k^2}{2}\tilde{p} \tag{2.202}$$

with initial condition $\tilde{p}(t_0,k|t_0,v_0) = f(k_0) = e^{ik_0v_0}$. We can pass from s to k by using the second characteristic equation (eq. 2.199). This gives $ds = \frac{dk}{\gamma k}$ and plugging into eq. (2.202) one gets

$$\frac{d\tilde{p}}{dk} = -\frac{\sigma^2 k}{2\gamma}\tilde{p} \tag{2.203}$$

whose solution is

$$\tilde{p} = f(k_0)\exp\left(-\frac{\sigma^2}{4\gamma}(k^2-k_0^2)\right) = \exp\left(ik_0v_0 - \frac{\sigma^2}{4\gamma}(k^2-k_0^2)\right). \tag{2.204}$$

The parameter k_0 is then obtained by inverting eq. (2.201). By inserting the expression for k_0 in eq. (2.204) one gets

$$\tilde{p} = \exp\left[ike^{-\gamma(t-t_0)}v_0 - \frac{\sigma^2k^2}{4\gamma}\left(1-e^{-2\gamma(t-t_0)}\right)\right] \tag{2.205}$$

By antitransforming we obtain that the transition probability density $p(v,t|v_0,t_0)$ for the OU process follows a Normal distribution with mean

$$\mathbb{E}\{v|v_0,t_0\} = v_0e^{-\gamma(t-t_0)}, \tag{2.206}$$

and variance

$$\mathbb{E}\{v^2|v_0,t_0\} = \frac{\sigma^2}{2\gamma}\left(1-e^{-2\gamma(t-t_0)}\right), \tag{2.207}$$

namely

$$p(v,t|v_0,t_0) = \sqrt{\frac{\gamma}{\pi\sigma^2\left(1-e^{-2\gamma(t-t_0)}\right)}}\exp\left[-\frac{\gamma\left(v-e^{-\gamma(t-t_0)}v_0\right)^2}{\sigma^2\left(1-e^{-2\gamma(t-t_0)}\right)}\right]. \tag{2.208}$$

In the limit $\gamma \to 0$ the solution for the Wiener process is recovered. Note that the solution is valid either for $\gamma > 0$ or for $\gamma \leq 0$. For $\gamma > 0$ and in the limit $\gamma(t-t_0) >> 1$ (large time scales) the general solution converges to

$$p(v,t|v_0,t_0) \to \sqrt{\frac{\gamma}{\pi\sigma^2}}\exp\left[-\frac{\gamma v^2}{\sigma^2}\right] \tag{2.209}$$

i.e. the stationary solution (1.104) found previously with the method of the probability current.

2.4 Harmonic oscillator

It is interesting to notice that the Ornstein-Uhlenbeck process written in the space of coordinates x furnishes the following Fokker-Planck equation

$$\frac{\partial}{\partial t}p(x,t|x_0,t_0) = \beta\frac{\partial}{\partial x}(x(t)p(x,t|x_0,t_0)) + \frac{\sigma^2}{2}\frac{\partial^2}{\partial x^2}p(x,t|x_0,t_0). \tag{2.210}$$

The above equation is similar to a Smoluchowski equation (1.46) for a Brownian particle that experiences an external harmonic force $F_E(x) = -\beta x$ (i.e. with a potential $U(x) = \frac{1}{2}\beta x^2$ where $\beta = \frac{\omega_0^2}{m}$ is always positive. Hence all the results obtained before for the O-U process apply also to this case with the substitutions $v \to x$, $\gamma \to \beta$.

2.5 Application to problems of metastability

The Fokker- Planck formalism can be applied to study the life time of a particle in a local potential minimum that experiences thermal fluctuations. This is a direct application of the Kramers' equation. Let us consider a particle in a potential $V(x)$ and lat us suppose that the particle occupies the equilibrium position a (local minimum of the potential). Due to thermal fluctuations the particle eventually will overcome the potential gap of amplitude V_0 in $x = b$. The process of overcoming a potential barrier by thermal fluctuation is called *thermal activation*. This effect can be, for example, represent the dissociation of a molecule in a solvent of temperature T. Kramers supposed that the particle experience a random force $f(T)$ due to the fluctuations of the medium. The goal is to compute the first time in which the particle leaves the minimum a $x = a$ given that at $t = 0$ it is in its neighborhood (*leaving time*). The deterministic equation would be

$$\frac{d^2}{dt^2}x(t) = -\frac{V'(x(t))}{m} - \gamma v(t). \tag{2.211}$$

If one switch on the thermal noise and if the thermal energy if weak compared to V_0 (i.e. $\kappa_B T << V_0$) the particle will eventually reach sufficient kinetic energy to overcome the barrier V_0. The case $\kappa_B T >> V_0$ it is clearly not interesting since the particle in this case will overcome the barrier quite easily. Before doing any calculation it is clear that a proper definition of the leaving time is needed. In principle one has to solve the Kramers' equation

$$\begin{aligned}\partial_t p(x,v,t) + v\frac{\partial}{\partial x}p(x,v,t) &+ \frac{F_E}{m}\frac{\partial}{\partial v}p(x,v,t) \\ &= \gamma\left(\frac{\partial}{\partial v}(vp(x,v,t)) + \frac{\kappa_B T}{m}\frac{\partial^2}{\partial v^2}p(x,vt)\right).\end{aligned} \tag{2.212}$$

with initial distribution centered in a and to determine the probability of finding the particle in $x \in \{b,\infty\}$. The leaving time can be the defined as the average of the first passage time of the

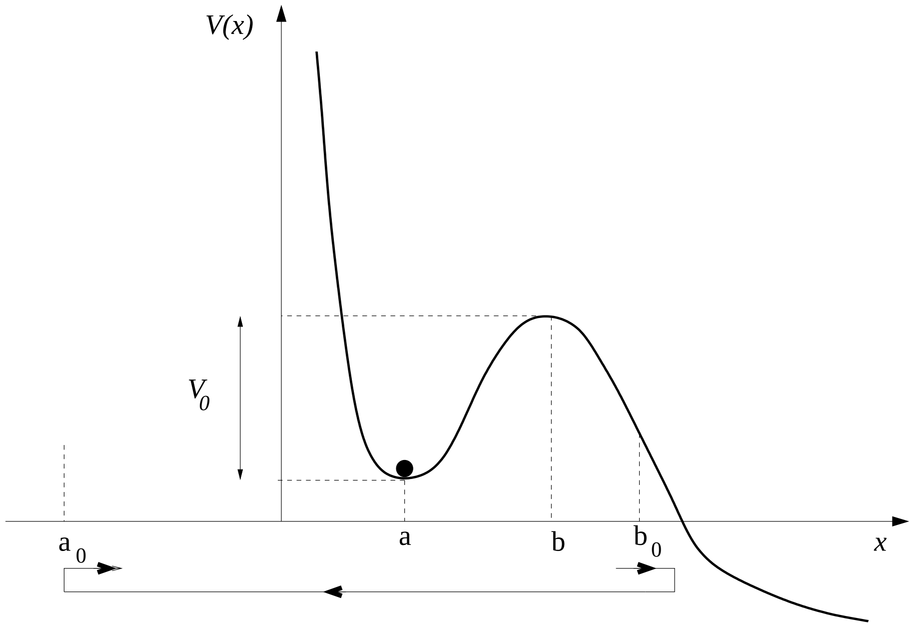

Figure 2.1: Sketch of the potential energy for the problem of the metastability.

particle in $x = b$. Since the potential considered is not a confining potential there are no stationary states to be found and the solution of the Kramers' equation becomes more difficult since it would be a non stationary solution. However one can change slightly the problem in the following way: one can imagine that once the particle has overcomes the point b, say in b_0 it is reinserted in the system with the same velocity to the left of the origin a_0. This effect can be taken into account by adding a term $S(x, t)$ in the Kramers' equation who plays the role of a sink in b_0 (adorbing boundary), of a source in a_0 and that is zero for $x \in [a_0, b_0]$. Under these conditions a stationary state is possible in the system with a stationary current between a_0 and b_0. It is not necessary to make explicit the form for $S(x, t)$ because we will concentrate only on the properties of the stationary state. The effect of the adsorption in b_0 is given by the boundary condition

$$p(x = b_0, v, t) = 0. \tag{2.213}$$

On the other hand, since the potential is confining for $x \to -\infty$ it is possible to consider $a_0 = -\infty$.

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Exercises

1. Let $x = \pm 1$. Show that

$$p(x,t|x',t') = \frac{1}{2}\left(1+e^{-2\gamma(t-t')}\right)\delta_{x,x'} + \frac{1}{2}\left(1-e^{-2\gamma(t-t')}\right)\delta_{x,-x'} \tag{2.214}$$

obeys the Chapman-Kolmogorov equation. Write $p(x,t|x',t')$ as a 2×2 matrix and formulate the Chapman-Kolmogorov equation as a property of that matrix.

2. The conditional probability that a stochastic variable Y takes the value y_2 at time t_2, given it had value y_1 at time t_1 is

$$p(y_2,t_2|y_1,t_1) = \frac{1}{\sqrt{2\pi(t_2-t_1)}}\exp\left[\frac{-\left(y_2-y_1-(t_2-t_1)\right)^2}{2(t_2-t_1)}\right], \tag{2.215}$$

for all $y_1, y_2 \in \mathbb{R}$ and $t_2 > t_1$. Show that $p(y_2,t_2|y_1,t_1)$ satisfies the Chapman-Kolmogorv equation.

3. The 2D deterministic system (with positive constants ν and Ω

$$\begin{aligned}\frac{dx_1}{dt} &= \nu(1-x_1^2-x_2^2)x_1 - \Omega x_2\\ \frac{dx_2}{dt} &= \nu(1-x_1^2-x_2^2)x_2 - \Omega x_1\end{aligned} \tag{2.216}$$

can be expressed in polar coordinates $r = \sqrt{x_1^2+x_2^2}$, $\theta = \tan^{-1}\frac{x_1}{x_2}$ as

$$\begin{aligned}\frac{dr}{dt} &= \nu(1-r^2)r\\ \frac{d\theta}{dt} &= \Omega\end{aligned} \tag{2.217}$$

(to see that consider $x_1 = r\cos\theta$ and $x_2 = r\sin\theta$). This represents a nonlinear oscillator with an asymptotically stable limit cycle at $r = 1$. The rotation frequency Ω is constant. The steady-state deterministic solution in the original variables x_1 and x_2 is

$$\begin{aligned}x_1(t) &= \cos(\Omega t+\theta_0)\\ x_2(t) &= \sin(\Omega t+\theta_0)\end{aligned} \tag{2.218}$$

Since this system is asymptotically stable it is interesting to understand the effect of noise upon the system (Risken chapt 12). Let us consider additive noise with independent equal intensity noise source $\eta_1(t)$ and $\eta_2(t)$ in the two directions respectively. The Langevin equation are

$$\begin{aligned}\frac{dx_1}{dt} &= \nu(1-x_1^2-x_2^2)x_1 - \Omega x_2 + \eta_1(t)\\ \frac{dx_2}{dt} &= \nu(1-x_1^2-x_2^2)x_2 - \Omega x_1 + \eta_2(t)\end{aligned} \tag{2.219}$$

with

$$\langle \eta_i(t)\eta_j(t')\rangle = 2\kappa\delta_{ij}\delta(t-t'). \tag{2.220}$$

(A) Write the FP equation for the joint PDF $p(x_1,x_2,t)$.

(B) Rewrite the FP in cylindrical polar coordinates (r, θ).

(C) Find a stationary solution $p_s(r, \theta)$.

4. Consider the two dimensional stochastic process $(X(t), V(t))$ whose evolution is described by the Langevin equations

$$\begin{aligned} \Delta x &= v(t)\Delta t \\ \Delta v &= -\gamma v(t)\Delta t - \omega_0^2 x(t)\Delta t + \Delta W \end{aligned} \tag{2.221}$$

A Write the corresponding 2D Fokker-Planck equation by first computing the coefficients

$$\begin{aligned} D_x^{(1)} &= \lim_{\Delta t \to 0} \frac{1}{\Delta t}\langle \Delta x \rangle \\ D_v^{(1)} &= \lim_{\Delta t \to 0} \frac{1}{\Delta t}\langle \Delta v \rangle \\ D_{xx}^{(2)} &= \lim_{\Delta t \to 0} \frac{1}{\Delta t}\langle (\Delta x)^2 \rangle \\ D_{xv}^{(2)} &= \lim_{\Delta t \to 0} \frac{1}{\Delta t}\langle (\Delta x)(\Delta v) \rangle \\ D_{vv}^{(2)} &= \lim_{\Delta t \to 0} \frac{1}{\Delta t}\langle (\Delta v)^2 \rangle. \end{aligned} \tag{2.222}$$

B Solve the Fokker-Planck equation with the initial condition

$$p(x, v, t \to 0) = \delta(x - x_0)\delta(v - v_0). \tag{2.223}$$

Hint: for the solution it is simpler to work with the independent variables

$$z_1 = v + ax, \qquad z_2 = v + bx, \tag{2.224}$$

where

$$a = \frac{\gamma}{2} + i\omega_1 \quad \text{and} \quad b = \frac{\gamma}{2} - i\omega_1. \tag{2.225}$$