

Chapter 11

The Brownian Oscillator

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The one-dimensional Smoluchowski equation, in case that a stationary flux-free equilibrium state $p_o(x)$ exists, can be written in the form

$$\partial_t p(x, t) = \frac{k_B T}{\gamma} \partial_x p_o(x) \partial_x [p_o(x)]^{-1} p(x, t) . \quad (11.1)$$

where we employed $D = \sigma^2/2\gamma^2$ [c.f. (3.12)], the fluctuation-dissipation theorem in the form $\sigma^2 = 2k_B T \gamma$ [c.f. (4.15)], the Onsager form of the Smoluchowski equation (4.18) applied to one dimension, and $p_o(x) = N \exp[-\beta U(x)]$. The form (11.1) of the Smoluchowski equation demonstrates most clearly that it describes a stochastic system characterized through an equilibrium state $p_o(x)$ and a single constant γ governing the relaxation, the friction constant. The equation also assumes that the underlying stochastic process

$$\gamma \dot{x} = k_B T p_o(x) \partial_x \ln[p_o(x)] + \sqrt{2k_B T \gamma} \xi(t) \quad (11.2)$$

alters the variable x continuously and not in discrete jumps.

One is inclined to invoke the Smoluchowski equation for the description of stochastic processes for which the equilibrium distribution is known. Underlying such description is the assumption that the process is governed by a single effective friction constant γ . For the sake of simplicity and in view of the typical situation that detailed information regarding the relaxation process is lacking, the Smoluchowski equation serves on well with an approximate description.

The most prevalent distribution encountered is the Gaussian distribution

$$p_o(x) = \frac{1}{\sqrt{2\pi\Sigma}} \exp \left[-\frac{(x - \langle x \rangle)^2}{\Sigma} \right] . \quad (11.3)$$

The reason is the fact that many properties x are actually based on contributions from many constituents. An example is the overall dipole moment of a biopolymer which results from stochastic motions of the polymer segments, each contributing a small fraction of the total dipole moment. In such case the *central limit theorem* states that for most cases the resulting distribution of x is Gaussian. This leads one to consider then in most cases the Smoluchowski equation for an effective quadratic potential

$$U_{\text{eff}}(x) = \frac{k_B T}{\Sigma} (x - \langle x \rangle)^2 . \quad (11.4)$$

Due to the central limit theorem the Smoluchowski equation for a Brownian oscillator has a special significance. Accordingly, we will study the behaviour of the Brownian oscillator in detail.

11.1 One-Dimensional Diffusion in a Harmonic Potential

We consider again the diffusion in the harmonic potential

$$U(x) = \frac{1}{2} f x^2 \quad (11.5)$$

applying in the present case spectral expansion for the solution of the associated Smoluchowski equation

$$\partial_t p(x, t|x_0, t_0) = D(\partial_x^2 + \beta f \partial_x x) p(x, t|x_0, t_0) \quad (11.6)$$

with the boundary condition

$$\lim_{x \rightarrow \pm\infty} x^n p(x, t|x_0, t_0) = 0, \quad \forall n \in \mathbb{N} \quad (11.7)$$

and the initial condition

$$p(x, t_0|x_0, t_0) = \delta(x - x_0). \quad (11.8)$$

Following the treatment in Chapter 3 we introduce dimensionless variables

$$\xi = x/\sqrt{2\delta}, \quad \tau = t/\tilde{\tau}, \quad (11.9)$$

where

$$\delta = \sqrt{k_B T/f}, \quad \tilde{\tau} = 2\delta^2/D. \quad (11.10)$$

The Smoluchowski equation for the normalized distribution in ξ given by

$$q(\xi, \tau|\xi_0, \tau_0) = \sqrt{2\delta} p(x, t|x_0, t_0) \quad (11.11)$$

is then again

$$\partial_\tau q(\xi, \tau|\xi_0, \tau_0) = (\partial_\xi^2 + 2\partial_\xi \xi) q(\xi, \tau|\xi_0, \tau_0) \quad (11.12)$$

with the initial condition

$$q(\xi, \tau_0|\xi_0, \tau_0) = \delta(\xi - \xi_0) \quad (11.13)$$

and the boundary condition

$$\lim_{\xi \rightarrow \pm\infty} \xi^n q(\xi, \tau|\xi_0, \tau_0) = 0, \quad \forall n \in \mathbb{N}. \quad (11.14)$$

We seek to expand $q(\xi, \tau_0|\xi_0, \tau_0)$ in terms of the eigenfunctions of the operator

$$\mathbf{O} = \partial_\xi^2 + 2\partial_\xi \xi, \quad (11.15)$$

restricting the functions to the space

$$\{h(\xi) \mid \lim_{\xi \rightarrow \pm\infty} \xi^n h(\xi) = 0\} . \quad (11.16)$$

We define the eigenfunctions $f_n(\xi)$ through

$$\mathbf{O} f_n(\xi) = -\lambda_n f_n(\xi) \quad (11.17)$$

The solution of this equation, which obeys (11.14), is well known

$$f_n(\xi) = c_n e^{-\xi^2} H_n(\xi) . \quad (11.18)$$

Here, $H_n(x)$ are the Hermite polynomials and c_n is a normalization constant. The negative eigenvalues are

$$\lambda_n = 2n, \quad (11.19)$$

The functions $f_n(\xi)$ do not form the orthonormal basis with the scalar product (3.129) introduced earlier. Instead, it holds

$$\int_{-\infty}^{+\infty} d\xi e^{-\xi^2} H_n(\xi) H_m(\xi) = 2^n n! \sqrt{\pi} \delta_{nm} . \quad (11.20)$$

However, following Chapter 5 one can introduce a bi-orthogonal system. For this purpose we choose for $f_n(\xi)$ the normalization

$$f_n(\xi) = \frac{1}{2^n n! \sqrt{\pi}} e^{-\xi^2} H_n(\xi) \quad (11.21)$$

and define

$$g_n(\xi) = H_n(\xi) . \quad (11.22)$$

One can readily recognize from (11.20) the biorthogonality property

$$\langle g_n | f_m \rangle = \delta_{nm} . \quad (11.23)$$

The functions $g_n(\xi)$ are the eigenfunctions of the adjoint operator

$$\mathbf{O}^+ = \partial_\xi^2 - 2\xi \partial_\xi , \quad (11.24)$$

i.e., it holds

$$\mathbf{O}^+ g_n(\xi) = -\lambda_n g_n(\xi) . \quad (11.25)$$

The eigenfunction property (11.25) of $g_n(\xi)$ can be demonstrated using

$$\langle g | \mathbf{O} f \rangle = \langle \mathbf{O}^+ g | f \rangle . \quad (11.26)$$

or through explicit evaluation.

The eigenfunctions $f_n(\xi)$ form a complete basis for all functions with the property (11.14). Hence, we can expand $q(\xi, \tau | \xi_0, \tau_0)$

$$q(\xi, \tau | \xi_0, \tau_0) = \sum_{n=0}^{\infty} \alpha_n(t) f_n(\xi) . \quad (11.27)$$

Inserting this into the Smoluchowski equation (11.12, 11.15) results in

$$\sum_{n=0}^{\infty} \dot{\alpha}_n(\tau) f_n(\xi) = - \sum_{n=0}^{\infty} \lambda_n \alpha_n(\tau) f_n(\xi). \quad (11.28)$$

Exploiting the bi-orthogonality property (11.23) one derives

$$\dot{\alpha}_m(\tau) = - \lambda_m \alpha_m(\tau). \quad (11.29)$$

The general solution of of this differential equation is

$$\alpha_m(\tau) = \beta_m e^{-\lambda_m \tau}. \quad (11.30)$$

Upon substitution into (11.27), the initial condition (11.13) reads

$$\sum_{n=0}^{\infty} \beta_n e^{-\lambda_n \tau_0} f_n(\xi) = \delta(\xi - \xi_0). \quad (11.31)$$

Taking again the scalar product with $g_m(\xi)$ and using (11.23) results in

$$\beta_m e^{-\lambda_m \tau_0} = g_m(\xi_0), \quad (11.32)$$

or

$$\beta_m = e^{\lambda_m \tau_0} g_m(\xi_0). \quad (11.33)$$

Hence, we obtain finally

$$q(\xi, \tau | \xi_0, \tau_0) = \sum_{n=0}^{\infty} e^{-\lambda_n(\tau - \tau_0)} g_n(\xi_0) f_n(\xi), \quad (11.34)$$

or, explicitly,

$$q(\xi, \tau | \xi_0, \tau_0) = \sum_{n=0}^{\infty} \frac{1}{2^n n! \sqrt{\pi}} e^{-2n(\tau - \tau_0)} H_n(\xi_0) e^{-\xi^2} H_n(\xi). \quad (11.35)$$

Expression (11.35) can be simplified using the generating function of a product of two Hermit polynomials

$$\begin{aligned} & \frac{1}{\sqrt{\pi(1-s^2)}} \exp \left[-\frac{1}{2}(y^2 + y_0^2) \frac{1+s^2}{1-s^2} + 2yy_0 \frac{s}{1-s^2} \right] \\ &= \sum_{n=0}^{\infty} \frac{s^n}{2^n n! \sqrt{\pi}} H_n(y) e^{-y^2/2} H_n(y_0) e^{-y_0^2/2}. \end{aligned} \quad (11.36)$$

Using

$$s = e^{-2(\tau - \tau_0)}, \quad (11.37)$$

one can show

$$q(\xi, \tau | \xi_0, \tau_0)$$

$$= \frac{1}{\sqrt{\pi(1-s^2)}} \exp \left[-\frac{1}{2}(\xi^2 + \xi_0^2) \frac{1+s^2}{1-s^2} + 2\xi\xi_0 \frac{s}{1-s^2} - \frac{1}{2}\xi^2 + \frac{1}{2}\xi_0^2 \right]. \quad (11.38)$$

We denote the exponent on the r.h.s. by E and evaluate

$$\begin{aligned} E &= -\xi^2 \frac{1}{1-s^2} - \xi_0^2 \frac{s^2}{1-s^2} + 2\xi\xi_0 \frac{1}{1-s^2} \\ &= -\frac{1}{1-s^2} (\xi^2 - 2\xi\xi_0 s + \xi_0^2 s^2) \\ &= -\frac{(\xi - \xi_0 s)^2}{1-s^2} \end{aligned} \quad (11.39)$$

We obtain then

$$q(\xi, \tau | \xi_0, \tau_0) = \frac{1}{\sqrt{\pi(1-s^2)}} \exp \left[-\frac{(\xi - \xi_0 s)^2}{1-s^2} \right], \quad (11.40)$$

where s is given by (11.37). One can readily recognize that this result agrees with the solution (4.119) derived in Chapter 3 using transformation to time-dependent coordinates.

Let us now consider the solution for an initial distribution $h(\xi_0)$. The corresponding distribution $\tilde{q}(\xi, \tau)$ is ($\tau_0 = 0$)

$$\tilde{q}(\xi, \tau) = \int d\xi_0 \frac{1}{\sqrt{\pi(1-e^{-4\tau})}} \exp \left[-\frac{(\xi - \xi_0 e^{-2\tau})^2}{1-e^{-4\tau}} \right] h(\xi_0). \quad (11.41)$$

It is interesting to consider the asymptotic behaviour of this solution. For $\tau \rightarrow \infty$ the distribution $\tilde{q}(\xi, \tau)$ relaxes to

$$\tilde{q}(\xi) = \frac{1}{\sqrt{\pi}} e^{-\xi^2} \int d\xi_0 h(\xi_0). \quad (11.42)$$

If one carries out a corresponding analysis using (11.34) one obtains

$$\tilde{q}(\xi, \tau) = \sum_{n=0}^{\infty} e^{-\lambda_n \tau} f_n(\xi) \int d\xi_0 g_n(\xi_0) h(\xi_0) \quad (11.43)$$

$$\sim f_0(\xi) \int d\xi_0 g_0(\xi_0) h(\xi_0) \quad \text{as } \tau \rightarrow \infty. \quad (11.44)$$

Using (11.21) and (11.22), this becomes

$$\tilde{q}(\xi, \tau) \sim \frac{1}{\sqrt{\pi}} e^{-\xi^2} \underbrace{H_0(\xi)}_{=1} \int d\xi_0 h(\xi_0) \quad (11.45)$$

in agreement with (11.42). One can recognize from this result that the expansion (11.43), despite its appearance, conserves total probability $\int d\xi_0 h(\xi_0)$. One can also recognize that, in general, the relaxation of an initial distribution $h(\xi_0)$ to the Boltzmann distribution involves numerous relaxation times, given by the eigenvalues λ_n , even though the original Smoluchowski equation (11.1) contains only a single rate constant, the friction coefficient γ .

