Chapter 4

Smoluchowski Diffusion Equation

Look at Eq. 4.120

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We want to apply now our derivation to the case of a Brownian particle in a force field $\boldsymbol{F}(\boldsymbol{r})$. The corresponding Langevin equation is

$$m\ddot{\boldsymbol{r}} \;=\; -\gamma\,\dot{\boldsymbol{r}} \;+\; \boldsymbol{F}(\boldsymbol{r}) \;+\; \sigma\,\xi(t) \tag{4.1}$$

for scalar friction constant γ and amplitude σ of the fluctuating force. We will assume in this section the *limit of strong friction*. In this limit the magnitude of the frictional force $\gamma\dot{\boldsymbol{r}}$ is much larger than the magnitude of the force of inertia $m\ddot{\boldsymbol{r}}$, i.e.,

$$|\gamma\,\dot{\boldsymbol{r}}| \;\gg\; |m\,\ddot{\boldsymbol{r}}| \tag{4.2}$$

and, therefore, (4.1) becomes

$$\gamma\,\dot{\boldsymbol{r}} \;=\; \boldsymbol{F}(\boldsymbol{r}) \;+\; \sigma\,\xi(t) \tag{4.3}$$

To (4.1) corresponds the Fokker-Planck equation (cf. Eqs. (2.138) and (2.148)

$$\partial_t\, p(\boldsymbol{r}, t|\boldsymbol{r}_0, t_0) \;=\; \left(\boldsymbol{\nabla}^2\,\frac{\sigma^2}{2\gamma^2} \;-\; \boldsymbol{\nabla}\cdot\frac{\boldsymbol{F}(\boldsymbol{r})}{\gamma}\right) p(\boldsymbol{r}, t|\boldsymbol{r}_0, t_0) \tag{4.4}$$

In case that the force field can be related to a scalar potential, i.e., in case $\boldsymbol{F}(\boldsymbol{r}) = -\boldsymbol{\nabla}U(\boldsymbol{r})$, one expects that the Boltzmann distribution $\exp[-U(\boldsymbol{r})/k_BT]$ is a stationary, i.e., time-independent, solution and that, in fact, the system asymptotically approaches this solution. This expectation should be confined to force fields of the stated kind, i.e., to force fields for which holds $\boldsymbol{\nabla}\times\boldsymbol{F} = 0$. Fokker-Planck equations with more general force fields will be considered further below.

4.1 Derivation of the Smoluchoswki Diffusion Equation for Potential Fields

It turns out that the expectation that the Boltzmann distribution is a stationary solution of the Smoluchowski equation has to be introduced as a postulate rather than a consequence of (4.4). Defining the parameters $D = \sigma^2/2\gamma^2$ [cf. (3.12)] and $\beta = 1/k_B T$ the *postulate* of the stationary behaviour of the Boltzmann equation is

$$\left(\boldsymbol{\nabla} \cdot \boldsymbol{\nabla} \, D(\boldsymbol{r}) \; - \; \boldsymbol{\nabla} \cdot \frac{\boldsymbol{F}(\boldsymbol{r})}{\gamma(\boldsymbol{r})} \right) e^{-\beta U(\boldsymbol{r})} \quad = \quad 0 \; . \tag{4.5}$$

We have included here the possibility that the coefficients σ and γ defining the fluctuating and dissipative forces are spatially dependent. In the following we will not explicitly state the dependence on the spatial coordinates $\boldsymbol{r}$ anymore.
Actually, the postulate (4.5) of the stationarity of the Boltzmann distribution is not sufficient to obtain an equation with the appropriate behaviour at thermal equilibrium. Actually, one needs to require the more stringent postulate that at equilibrium there does not exist a net flux of particles (or of probability) in the system. This should hold true when the system asymptotically comes to rest as long as there are no particles generated or destroyed, e.g., through chemical reactions. We need to establish the expression for the flux before we can investigate the ramifications of the indicated postulate.
An expression for the flux can be obtained in a vein similar to that adopted in the case of free diffusion [cf. (3.17–3.21)]. We note that (4.4) can be written

$$\partial_t \, p(\boldsymbol{r}, t|\boldsymbol{r}_0, t_0) \quad = \quad \boldsymbol{\nabla} \cdot \left(\boldsymbol{\nabla} \, D \; - \; \frac{\boldsymbol{F}(\boldsymbol{r})}{\gamma} \right) p(\boldsymbol{r}, t|\boldsymbol{r}_0, t_0) \; . \tag{4.6}$$

Integrating this equation over some arbitrary volume Ω, with the definition of the particle number in this volume

$$N_\Omega(t|\boldsymbol{r}_0, t_0) \quad = \quad \int_\Omega d\boldsymbol{r} \; p(\boldsymbol{r}, t|\boldsymbol{r}_0, t_0) \tag{4.7}$$

and using (4.6), yields

$$\partial_t \, N_\Omega(t|\boldsymbol{r}_0, t_0) \quad = \quad \int_\Omega d\boldsymbol{r} \; \boldsymbol{\nabla} \cdot \left(\boldsymbol{\nabla} \, D \; - \; \frac{\boldsymbol{F}(\boldsymbol{r})}{\gamma} \right) p(\boldsymbol{r}, t|\boldsymbol{r}_0, t_0) \tag{4.8}$$

and, after applying Gauss' theorem (3.19),

$$\partial_t \, N_\Omega(t|\boldsymbol{r}_0, t_0) \quad = \quad \int_{\partial\Omega} d\boldsymbol{a} \cdot \left(\boldsymbol{\nabla} \, D \; - \; \frac{\boldsymbol{F}(\boldsymbol{r})}{\gamma} \right) p(\boldsymbol{r}, t|\boldsymbol{r}_0, t_0) \; . \tag{4.9}$$

The l.h.s. of this equation describes the rate of change of the particle number, the r.h.s. contains a surface integral summing up scalar products between the vector quantity

$$\boldsymbol{j}(\boldsymbol{r}, t|\boldsymbol{r}_0, t_0) \quad = \quad \left(\boldsymbol{\nabla} \, D \; - \; \frac{\boldsymbol{F}(\boldsymbol{r})}{\gamma} \right) p(\boldsymbol{r}, t|\boldsymbol{r}_0, t_0) \tag{4.10}$$

and the surface elements $d\boldsymbol{a}$ of $\partial\Omega$. Since particles are neither generated nor destroyed inside the volume Ω, we must interpret $\boldsymbol{j}(\boldsymbol{r}, t|\boldsymbol{r}_0, t_0)$ as a particle flux at the boundary $\partial\Omega$. Since the volume

and its boundary are arbitrary, the interpretation of $\boldsymbol{j}(\boldsymbol{r},t|\boldsymbol{r}_0,t_0)$ as given by (4.10) as a flux should hold everywhere in Ω.
We can now consider the ramifications of the postulate that at equilibrium the flux vanishes. Applying (4.10) to the Boltzmann distribution $p_o(\boldsymbol{r}) = N \exp[-\beta U(\boldsymbol{r})]$, for some appropriate normalization factor N, yields the equilibrium flux

$$\boldsymbol{j}_o(\boldsymbol{r}) \;=\; \left(\boldsymbol{\nabla} D \;-\; \frac{\boldsymbol{F}(\boldsymbol{r})}{\gamma}\right) N\, e^{-\beta U(\boldsymbol{r})} \,. \tag{4.11}$$

With this definition the postulate discussed above is

$$\left(\boldsymbol{\nabla} D \;-\; \frac{\boldsymbol{F}(\boldsymbol{r})}{\gamma}\right) N\, e^{-\beta U(\boldsymbol{r})} \;\equiv\; 0 \,. \tag{4.12}$$

The derivative $\boldsymbol{\nabla} D \exp[-\beta U(\boldsymbol{r})] = \exp[-\beta U(\boldsymbol{r})] \left(\boldsymbol{\nabla} D + \beta \boldsymbol{F}(\boldsymbol{r})\right)$ allows us to write this

$$e^{-\beta U(\boldsymbol{r})} \left(D\, \beta\, \boldsymbol{F}(\boldsymbol{r}) \;+\; \boldsymbol{\nabla} D \;-\; \frac{\boldsymbol{F}(\boldsymbol{r})}{\gamma}\right) \;\equiv\; 0 \,. \tag{4.13}$$

From this follows

$$\boldsymbol{\nabla} D \;=\; \boldsymbol{F}(\boldsymbol{r}) \left(\gamma^{-1} \;-\; D\,\beta\right) \,. \tag{4.14}$$

an identity which is known as the so-called *fluctuation - dissipation theorem.*
The fluctuation - dissipation theorem is better known for the case of spatially independent D in which case follows $D\,\beta\,\gamma = 1$, i.e., with the definitions above

$$\sigma^2 \;=\; 2\, k_B\, T\, \gamma \,. \tag{4.15}$$

This equation implies a relationship between the amplitude σ of the fluctuating forces and the amplitude γ of the dissipative (frictional) forces in the Langevin equation (4.1), hence, the name *fluctuation - dissipation theorem.* The theorem states that the amplitudes of fluctuating and dissipative forces need to obey a temperature-dependent relationship in order for a system to attain thermodynamic equilibrium. There exist more general formulations of this theorem which we will discuss further below in connection with response and correlation functions.
In its form (4.14) the fluctuation - dissipation theorem allows us to reformulate the Fokker-Planck equation above. For any function $f(\boldsymbol{r})$ holds with (4.14)

$$\boldsymbol{\nabla}\cdot\boldsymbol{\nabla}\, D f \;=\; \boldsymbol{\nabla}\cdot D\, \boldsymbol{\nabla} f \;+\; \boldsymbol{\nabla}\cdot f\, \boldsymbol{\nabla} D \;=\; \boldsymbol{\nabla}\cdot D\, \boldsymbol{\nabla} f \;+\; \boldsymbol{\nabla}\cdot \boldsymbol{F} \left(\frac{1}{\gamma} - D\,\beta\right) f \tag{4.16}$$

From this follows finally for the Fokker-Planck equation (4.4)

$$\partial_t\, p(\boldsymbol{r},t|\boldsymbol{r}_0,t_0) \;=\; \boldsymbol{\nabla}\cdot D \left(\boldsymbol{\nabla} \;-\; \beta \boldsymbol{F}(\boldsymbol{r})\right) p(\boldsymbol{r},t|\boldsymbol{r}_0,t_0) \,. \tag{4.17}$$

One refers to Eq. (4.17) as the *Smoluchowski equation.*
The Smoluchowski equation (4.17), in the case $\boldsymbol{F}(\boldsymbol{r}) = -\boldsymbol{\nabla} U(\boldsymbol{r})$, can be written in the convenient form

$$\partial_t\, p(\boldsymbol{r},t|\boldsymbol{r}_0,t_0) \;=\; \boldsymbol{\nabla}\cdot D\; e^{-\beta U(\boldsymbol{r})}\, \boldsymbol{\nabla}\, e^{\beta U(\boldsymbol{r})}\; p(\boldsymbol{r},t|\boldsymbol{r}_0,t_0) \,. \tag{4.18}$$

This form shows immediately that $p \propto \exp[-\beta U(\boldsymbol{r})]$ is a stationary solution. The form also provides a new expression for the flux $\boldsymbol{j}$, namely,

$$\boldsymbol{j}(\boldsymbol{r},t|\boldsymbol{r}_0,t_0) \;=\; D\; e^{-\beta U(\boldsymbol{r})}\, \boldsymbol{\nabla}\, e^{\beta U(\boldsymbol{r})}\; p(\boldsymbol{r},t|\boldsymbol{r}_0,t_0) \quad . \tag{4.19}$$

Boundary Conditions for Smoluchowski Equation

The system described by the Smoluchoswki (4.17) or Einstein (3.13) diffusion equation may either be closed at the surface of the diffusion space Ω or open, i.e., $\partial\Omega$ either may be impenetrable for particles or may allow passage of particles. In the latter case, $\partial\Omega$ describes a reactive surface. These properties of Ω are specified through the boundary conditions for the Smoluchoswki or Einstein equation at $\partial\Omega$. In order to formulate these boundary conditions we consider the flux of particles through consideration of $N_\Omega(t|\boldsymbol{r}_0, t_0)$ as defined in (4.7). Since there are no terms in (4.17) which affect the number of particles the particle number is conserved and any change of $N_\Omega(t|\boldsymbol{r}_0, t_0)$ must be due to particle flux at the surface of Ω, i.e.,

$$\partial_t \, N_\Omega(t|\boldsymbol{r}_0, t_0) \;\; = \;\; \int_{\partial\Omega} d\boldsymbol{a} \cdot \boldsymbol{j}(\boldsymbol{r}, t|\boldsymbol{r}_0, t_0) \tag{4.20}$$

where $\boldsymbol{j}(\boldsymbol{r}, t|\boldsymbol{r}_0, t_0)$ denotes the particle flux defined in (4.10). The fluctuation - dissipation theorem, as stated in (4.14), yields

$$\boldsymbol{\nabla} D \, f \;\; = \;\; D \, \boldsymbol{\nabla} f \; + \; f \, \boldsymbol{F}(\boldsymbol{r}) \left(\gamma^{-1} \, - \, D \, \beta \right) \tag{4.21}$$

and with (4.10) and (3.12) follows

$$\boldsymbol{j}(\boldsymbol{r}, t|\boldsymbol{r}_0, t_0) \;\; = \;\; D \left(\boldsymbol{\nabla} \; - \; \beta \, \boldsymbol{F}(\boldsymbol{r}) \right) \, p(\boldsymbol{r}, t|\boldsymbol{r}_0, t_0) \tag{4.22}$$

We will refer to

$$\boldsymbol{\mathcal{J}}(\boldsymbol{r}) \;\; = \;\; D \left(\boldsymbol{\nabla} \; - \; \beta \, \boldsymbol{F}(\boldsymbol{r}) \right) \tag{4.23}$$

as the flux operator. This operator, when acting on a solution of the Smoluchowski equation, yields the local flux of particles (probability) in the system.

The flux operator $\boldsymbol{\mathcal{J}}(\boldsymbol{r})$ governs the spatial boundary conditions since it allows to measure particle (probability) exchange at the surface of the diffusion space Ω. There are three types of boundary conditions possible. These types can be enforced simultaneously in disconnected areas of the surface $\partial\Omega$. Let us denote by $\partial\Omega_1, \partial\Omega_2$ two disconnected parts of $\partial\Omega$ such that $\partial\Omega = \partial\Omega_1 \cup \partial\Omega_2$. An example is a volume Ω lying between a sphere of radius R_1 ($\partial\Omega_1$) and of radius R_2 ($\partial\Omega_2$). The separation of the surfaces $\partial\Omega_i$ with different boundary conditions is necessary in order to assure that a continuous solution of the Smoluchowski equation exists. Such solution cannot exist if it has to satisfy in an infinitesimal neighborhood entailing $\partial\Omega$ two different boundary conditions.

The first type of boundary condition is specified by

$$\hat{\boldsymbol{a}}(\boldsymbol{r}) \cdot \boldsymbol{\mathcal{J}}(\boldsymbol{r}) \; p(\boldsymbol{r}, t|\boldsymbol{r}_0, t_0) \;\; = \;\; 0 \; , \quad \boldsymbol{r} \, \in \, \partial\Omega_i \tag{4.24}$$

which, obviously, implies that particles do not cross the boundary, i.e., that particles are reflected there. Here $\hat{\boldsymbol{a}}(\boldsymbol{r})$ denotes a unit vector normal to the surface $\partial\Omega_i$ at $\boldsymbol{r}$. We will refer to (4.24) as the *reflection boundary condition.*

The second type of boundary condition is

$$p(\boldsymbol{r}, t|\boldsymbol{r}_0, t_0) \;\; = \;\; 0 \; , \quad \boldsymbol{r} \, \in \, \partial\Omega_i \; . \tag{4.25}$$

This condition implies that all particles arriving at the surface $\partial\Omega_i$ are taken away such that the probability on $\partial\Omega_i$ vanishes. This boundary condition describes a reactive surface with the highest degree of reactivity possible, i.e., that *every* particle on $\partial\Omega_i$ reacts. We will refer to (4.25) as the *reaction boundary condition.*

The third type of boundary condition,

$$\hat{\boldsymbol{a}}(\boldsymbol{r}) \cdot \boldsymbol{\mathcal{J}}(\boldsymbol{r})\, p(\boldsymbol{r}, t|\boldsymbol{r}_0, t_0) \;=\; w\, p(\boldsymbol{r}, t|\boldsymbol{r}_0, t_0)\;, \quad \boldsymbol{r} \text{ on } \partial\Omega_i\;, \tag{4.26}$$

describes the case of intermediate reactivity at the boundary. The reactivity is measured by the parameter w. For $w = 0$ in (4.26) $\partial\Omega_i$ corresponds to a non-reactive, i.e., reflective boundary. For $w \to \infty$ the condition (4.26) can only be satisfied for $p(\boldsymbol{r}, t|\boldsymbol{r}_0, t_0) = 0$, i.e., every particle impinging onto $\partial\Omega_i$ is consumed in this case. We will refer to (4.26) as the *radiation boundary condition*.

4.2 One-Dimensional Diffuson in a Linear Potential

We consider now diffusion in a linear potential

$$U(x) \;=\; c\, x \tag{4.27}$$

with a position-independent diffusion coefficient D. This system is described by the Smoluchowski equation

$$\partial_t\, p(x, t|x_0, t_0) \;=\; \left(D\, \partial_x^2 \;+\; D\, \beta\, c\, \partial_x \right) p(x, t|x_0, t_0)\;. \tag{4.28}$$

This will be the first instance of a system in which diffusing particles are acted on by a non-vanishing force. The techniques to solve the Smoluchowski equation in the present case will be particular for the simple force field, i.e., the solution techniques adopted cannot be generalized to other potentials.

4.2.1 Diffusion in an infinite space $\Omega_\infty =]-\infty, \infty[$

We consider first the situation that the particles diffusing under the influence of the potential (4.27) have available the infinite space

$$\Omega_\infty \;=\;]-\infty, \infty[\;. \tag{4.29}$$

In this case hold the boundary conditions

$$\lim_{x \to \pm\infty} p(x, t|x_0, t_0) \;=\; 0\;. \tag{4.30}$$

The initial condition is as usual

$$p(x, t_0|x_0, t_0) \;=\; \delta(x - x_0)\;. \tag{4.31}$$

In order to solve (4.28, 4.30, 4.31) we introduce

$$\tau \;=\; D\, t \quad , \qquad b \;=\; \beta\, c\;. \tag{4.32}$$

The Smoluchowski equation (4.28) can be written

$$\partial_\tau\, p(x, \tau|x_0, \tau_0) \;=\; \left(\partial_x^2 \;+\; b\, \partial_x \right) p(x, \tau|x_0, \tau_0)\;. \tag{4.33}$$

We introduce the time-dependent spatial coordinates

$$y \;=\; x \;+\; b\, \tau \quad , \qquad y_0 \;=\; x_0 \;+\; b\, \tau_0 \tag{4.34}$$

and express the solution

$$p(x, \tau | x_0, \tau_0) \quad = \quad q(y, \tau | y_0, \tau_0) \; . \tag{4.35}$$

Introducing this into (4.33) yields

$$\partial_\tau \, q(y, \tau | y_0, \tau_0) \; + \; b \; \partial_y \, q(y, \tau | y_0, \tau_0) \quad = \quad \left(\partial_y^2 \; + \; b \, \partial_y \right) \, q(y, \tau | y_0, \tau_0) \tag{4.36}$$

or

$$\partial_\tau \, q(y, \tau | y_0, \tau_0) \quad = \quad \partial_y^2 \, q(y, \tau | y_0, \tau_0) \; . \tag{4.37}$$

This equation has the same form as the Einstein equation for freely diffusing particles for which the solution in case of the diffusion space Ω_∞ is

$$q(y, \tau | y_0, \tau_0) \quad = \quad \frac{1}{\sqrt{4\pi \, (\tau - \tau_0)}} \, \exp\left[- \frac{(y - y_0)^2}{4 \, (\tau - \tau_0)} \right] \; . \tag{4.38}$$

Expressing the solution in terms of the original coordinates and constants yields

$$p(x, t | x_0, t_0) \quad = \quad \frac{1}{\sqrt{4\pi \, D \, (t - t_0)}} \, \exp\left[- \frac{\left(x - x_0 + D \, \beta \, c \, (t - t_0) \right)^2}{4 \, D \, (t - t_0)} \right] \; . \tag{4.39}$$

This solution is identical to the distribution of freely diffusing particles, except that the center of the distribution drifts down the potential gradient with a velocity $-D \, \beta \, c$.

Exercise 4.1:
Apply this to the case (i) of an ion moving between two electrodes at a distance of 1cm in water with a potential of 1 Volt. Estimate how long the ion needs to drift from one electrode to the other. (ii) an ion moving through a channel in a biological membrane of 40Å at which is applied a typical potential of 0.1eV. Assume the ion experiences a diffusion coefficient of $D = 10^{-5} cm^2/s$. Estimate how long the ion needs to cross the membrane.
Answer i) Let's assume that at the moment $t_0 = 0$ the ion is at $x_0 = 0$ with

$$p(x_0, t_0) \quad = \quad \delta(x_0) \; . \tag{4.40}$$

Then, according to (4.39) we have

$$p(x, t) \quad = \quad p(x, t | 0, 0) \quad = \quad \frac{1}{\sqrt{4\pi \, D \, t}} \, \exp\left[- \frac{\left(x + D \, \beta \, c \, t \right)^2}{4 \, D \, t} \right] \; . \tag{4.41}$$

Calculate now the mean value of x:

$$\left\langle x(t) \right\rangle \quad = \quad \int_{-\infty}^{\infty} dx \; x \, p(x, t) \quad = \quad \frac{1}{\sqrt{4\pi \, D \, t}} \int_{-\infty}^{\infty} dx \; x \; \exp\left[-(x + \beta \, c \, D \, t)^2 / 4 \, D \, t \right] \; . \tag{4.42}$$

In order to solve this integral add and substract a $\beta \, c \, D \, t$ term to x and make the change of variable $z = x + \beta \, D \, c \, t$. This yields

$$\left\langle x(t) \right\rangle \quad = \quad -D \, \beta \, c \, t \quad = \quad v_d \, t \tag{4.43}$$

where $v_d = -D\,\beta\,c$ is the drift velocity of the ion. Taking into consideration that the electrical force that acts on the ion is $c = q\,E$, $E = U/d$, $\beta = 1/k_b T$ and $\langle x(\tau)\rangle = d$ we obtain for the time τ needed by the ion to drift from one electrod to another

$$\tau = \frac{k_b\,T\,d^2}{D\,q\,U} \ . \tag{4.44}$$

For $d = 1\,\mathrm{cm}$, $k_B = 1.31 \times 10^{-23}\,\mathrm{J/K}$, $T = 300\,\mathrm{K}$, $D = 1.545 \times 10^{-5}\,\mathrm{cm^2/sec}$, $q = 1.6 \times 10^{-19}\,\mathrm{C}$, $U = 1\,\mathrm{V}$ we obtain $\tau = 1674\,\mathrm{sec}$.
ii) Applying the same reasoning to the ion moving through a membrane one gets $\tau = 4.14 \times 10^{-9}$ sec.

Diffusion and exponential growth

The above result (4.39) can be used for a stochastic processes with exponential growth by performing a simple substitution.
Comparing the Fokker-Planck equation (2.148) with the Smoluchowski equation (4.28) of the previous example one can easily derive within Ito calculus the corresponding stochastic differential equation

$$\partial_t\, x(t) = -D\,\beta\,c + \sqrt{D}\,\xi(t) \ , \tag{4.45}$$

or equivalently

$$dx = -D\,\beta\,c\;dt + \sqrt{D}\;d\omega \ . \tag{4.46}$$

Equation (4.46) displays the mechanism that generates the stochastic trajectories within a linear potential (4.27) . The increment dx of a trajectory $x(t)$ is given by the drift term $-D\,\beta\,c\;dt$, which is determined by the force c of the lineare potential and the friction $\gamma = D\,\beta$. Furthermore the increment dx is subject to Gaussian noise $d\omega$ scaled by $\sqrt{D}$.
We now consider a transformation of the spatial variable x. Let $x \mapsto y = \exp x$. This substitution and the resulting differential $dy/y = dx$ render the stochastic differential equation

$$dy = -D\,\beta\,c\;y\;dt + \sqrt{D}\;y\;d\omega \ . \tag{4.47}$$

Equation (4.47) describes a different stochastic process $y(t)$. Just considering the first term on the r.h.s. of (4.47), one sees that $y(t)$ is subject to exponential growth or decay depending on the sign of c. Neglecting the second term on the r.h.s of (**??**) one obtains the deterministic trajectory

$$y(t) = y(0)\;\exp\left[-\,D\,\beta\,c\;t\right] \ . \tag{4.48}$$

This dynamic is typical for growth or decay processes in physics, biology or economics. Furthermore, $y(t)$ is subject to Gaussian noise $d\omega$ scaled by $y\,\sqrt{D}$. The random fluctuation are consequently proportional to y, which is the case when the growth rate and not just the increment are subject to stochastic fluctuations.
Since (4.46) and (4.47) are connected via the simple mapping $y = \exp x$ we can readily state the solution of equation (4.47) by substituting $\log y$ for x in (4.39) .

$$
\begin{aligned}
p(y,t|y_0,t_0) &= p(x(y),t|x(y_0),t_0)\,\frac{dx}{dy} \\
&= \frac{1}{\sqrt{4\pi\,D\,(t-t_0)}\,y}\,\exp\left[-\frac{\left(\log\left(\frac{y}{y_0}\right)+D\,\beta\,c\,(t-t_0)\right)^2}{4\,D\,(t-t_0)}\right] . \qquad (4.49)
\end{aligned}
$$

4.2.2 Diffusion in a Half-Space $\Omega_\infty = [0,\infty[$

We consider now diffusion in a half-space $\Omega_\infty = [0,\infty[$ under the influence of a linear potential with a reflective boundary at $x = 0$. To describe this system by a distribution function $p(x,t|x_0,t_0)$ we need to solve the Smoluchowski equation (4.28) subject to the boundary conditions

$$
\begin{aligned}
D\,(\partial_x + \beta\,c)\;p(x,t|x_0,t_0) &= 0\,, \quad \text{at } x = 0 \qquad (4.50)\\
p(x,t|x_0,t_0) &\underset{x\to\infty}{\asymp} 0\,. \qquad (4.51)
\end{aligned}
$$

The solution has been determined by Smoluchowski ([45], see also [21]) and can be stated in the form

$$
\begin{aligned}
p(x,t|x_0,0) &= \sum_{j=1}^{3} p_j(x,t|x_0,0) \qquad (4.52)\\
p_1(x,t|x_0,0) &= \frac{1}{\sqrt{4\pi\,D\,t}}\,\exp\left[-(x-x_0+\beta\,c\,D\,t)^2/4\,D\,t\right] \qquad (4.53)\\
p_2(x,t|x_0,0) &= \frac{1}{\sqrt{4\pi\,D\,t}}\,\exp\left[\beta\,c\,x_0-(x+x_0+\beta\,c\,D\,t)^2/4\,D\,t\right] \qquad (4.54)\\
p_3(x,t|x_0,0) &= \frac{\beta\,c}{2}\,\exp[-\beta\,c\,x]\;\operatorname{erfc}\left[(x+x_0-\beta\,c\,D\,t)/\sqrt{4\,D\,t}\right] . \qquad (4.55)
\end{aligned}
$$

In this expression $\operatorname{erfc}(z)$ is the complementary error function

$$
\operatorname{erfc}(z) = \frac{2}{\sqrt{\pi}}\int_z^\infty dx\; e^{-x^2} \qquad (4.56)
$$

for which holds

$$
\begin{aligned}
\operatorname{erfc}(0) &= 1 \qquad (4.57)\\
\operatorname{erfc}(z) &\underset{z\to\infty}{\asymp} \frac{1}{\sqrt{\pi}\,z}\;e^{-z^2} \qquad (4.58)\\
\partial_z\operatorname{erfc}(z) &= -\frac{2}{\sqrt{\pi}}\;e^{-z^2}\,. \qquad (4.59)
\end{aligned}
$$

Plots of the distributions p_1, p_2 and p_3 as functions of x for different t's are shown in Figure 4.1. In Figure 4.2 the total distribution function $p(x,t) = p_1(x,t)+p_2(x,t)+p_3(x,t)$ is ploted as a function of x for three consecutive instants of time, namely for $t = 0.0, 0.025, 0.05, 0.1, 0.2, 0.4, 0.8, \infty$. The contribution (4.53) to the solution is identical to the solution derived above for diffusion in $]-\infty,\infty[$, i.e., in the absence of a boundary at a finite distance. The contribution (4.54) is analogous to the second term of the distribution (3.31) describing free diffusion in a half-space with reflective boundary; the term describes particles which have impinged on the boundary and have been carried away from the boundary back into the half-space Ω. However, some particles which impinged on

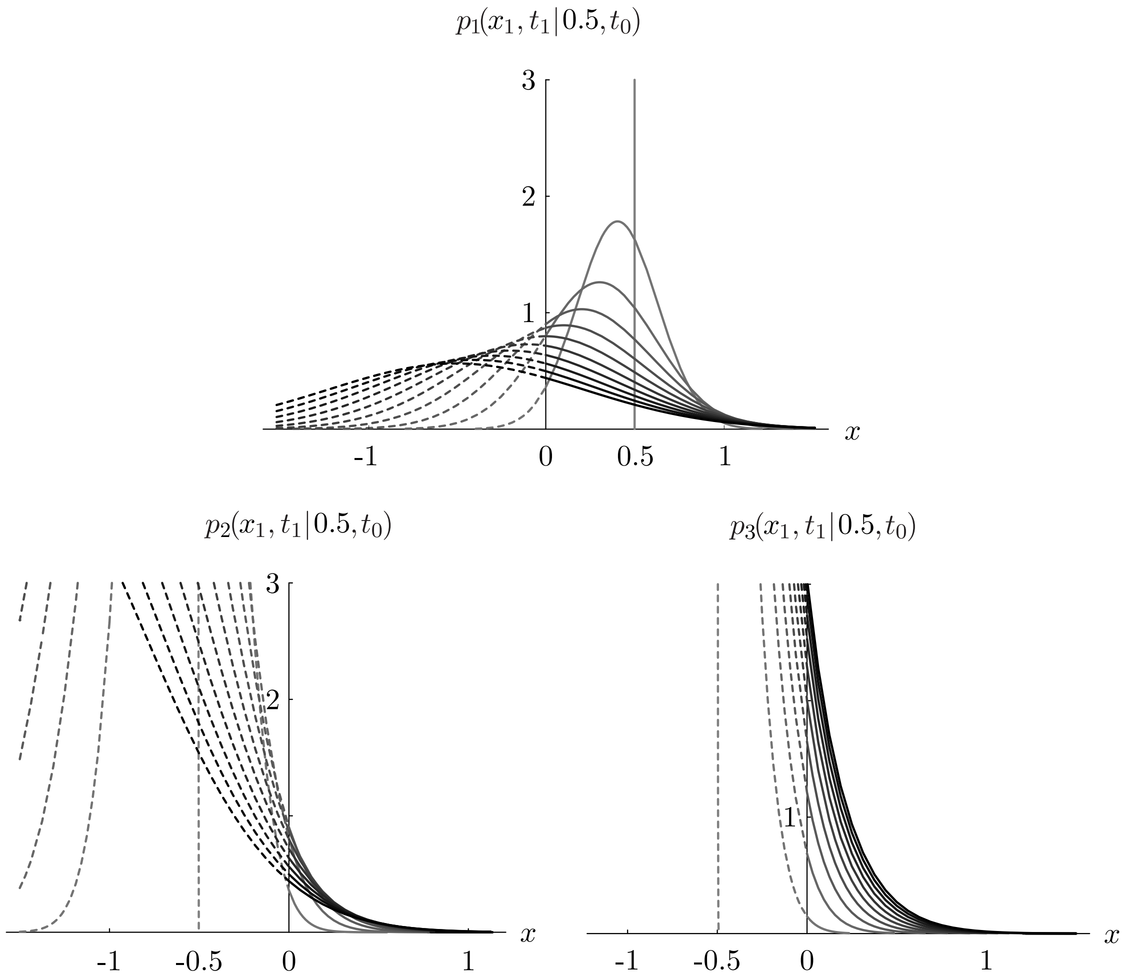

Figure 4.1: These three plots show p_1, p_2 and p_3 as a function of x for consecutive times $t = 0.0, 0.1, \ldots, 1.0$ and $x_0 = 0.5$; the length unit is $L = \frac{4}{\beta\, c}$, the time unit is $T = \frac{4}{D\, \beta^2\, c^2}$ while p_i $(i = 1, 2, 3)$ is measured in $\frac{1}{L}$.

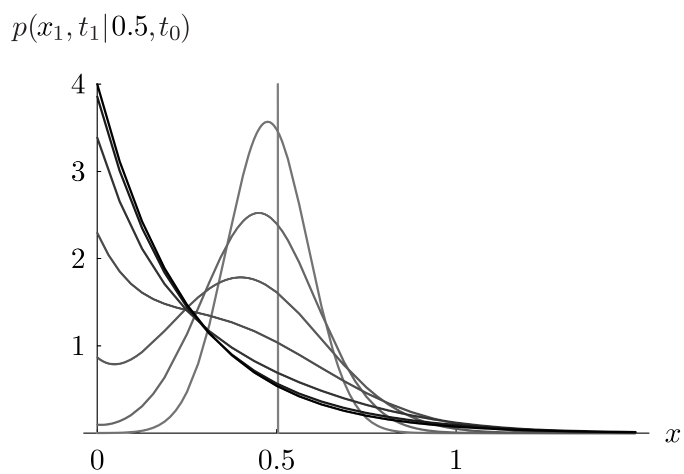

Figure 4.2: Plot of $p(x,t|0.5,0) = p_1(x,t|0.5,0) + p_2(x,t|0.5,0) + p_3(x,t|0.5,0)$ vs. x for $t = 0.0, 0.025, 0.05, 0.1, 0.2, 0.4, 0.8, \infty$. Same units as in Figure 4.1.

the boundary equilibrate into a Boltzmann distribution $\exp(-\beta\, c\, x)$. These particles are collected in the term (4.55). One can intuitively think of the latter term as accounting for particles which impinged onto the surface at $x = 0$ more than once.

In order to prove that (4.52–4.55) provides a solution of (4.28, 4.31, 4.50, 4.51) we note

$$\lim_{t\to 0} p_1(x,t|x_0,0) \;=\; \delta(x - x_0) \tag{4.60}$$

$$\lim_{t\to 0} p_2(x,t|x_0,0) \;=\; e^{\beta\, c\, x_0}\, \delta(x + x_0) \tag{4.61}$$

$$\lim_{t\to 0} p_3(x,t|x_0,0) \;=\; 0 \tag{4.62}$$

where (4.60, 4.61) follow from the analogy with the solution of the free diffusion equation, and where (4.62) follows from (4.59). Since $\delta(x + x_0)$ vanishes in $[0,\infty[$ for $x_0 > 0$ we conclude that (4.31) holds.

The analogy of $p_1(x,t|x_0,0)$ and $p_2(x,t|x_0,0)$ with the solution (4.39) reveals that these two distributions obey the Smoluchowski equation and the boundary condition (4.51), but individually not the boundary condition (4.50). To demonstrate that p_3 also obeys the Smoluchowski equation we introduce again $\tau = D\,t$, $b = \beta\, c$ and the function

$$f \;=\; \frac{1}{\sqrt{4\pi\tau}}\, \exp\left[-\,b\,x \;-\; \frac{(x + x_0 - b\,\tau)^2}{4\,\tau}\right] \;. \tag{4.63}$$

For $p_3(x,\tau/D|x_0,0)$, as given in (4.55), holds then

$$\partial_\tau\, p_3(x,\tau|x_0,0) \;=\; f\,b\,\frac{x + x_0 + b\,\tau}{2\,\tau} \tag{4.64}$$

$$\partial_x\, p_3(x,\tau|x_0,0) \;=\; -\frac{1}{2}\,b^2\,e^{-b\,x}\,\operatorname{erfc}\left[\frac{x + x_0 - b\,\tau}{\sqrt{4\,\tau}}\right] \;-\; f\,b \tag{4.65}$$

$$\partial_x^2\, p_3(x,\tau|x_0,0) \;=\; \frac{1}{2}\,b^3\,e^{-b\,x}\,\operatorname{erfc}\left[\frac{x + x_0 - b\,\tau}{\sqrt{4\,\tau}}\right] \;+\; f\,b\,\frac{x + x_0 - b\,\tau}{2\,\tau} \;+\; f\,b^2 \;. \tag{4.66}$$

It follows for the r.h.s. of the Smoluchowski equation

$$\left(\partial_x^2 \;+\; b\,\partial_x\right)\, p_3(x,\tau|x_0,0) \;=\; f\,b\,\frac{x + x_0 + b\,\tau}{2\,\tau} \;. \tag{4.67}$$

Since this is identical to (4.64), i.e., to the l.h.s. of the Smoluchowski equation, $p_3(x,t|,x_0,0)$ is a solution of this equation.
We want to demonstrate now that $p(x,t|,x_0,0)$ defined through (4.52–4.55) obey the boundary condition at $x = 0$, namely, (4.50). We define for this purpose the function

$$g \;=\; \frac{1}{\sqrt{4\pi\,\tau}}\,\exp\left[-\frac{(x_0 - b\,\tau)^2}{4\,\tau}\right]\;. \tag{4.68}$$

It holds then at $x = 0$

$$\begin{aligned}
b\,p_1(0,\tau|,x_0,0) &= g\,b && (4.69)\\
b\,p_2(0,\tau|,x_0,0) &= g\,b && (4.70)\\
b\,p_3(0,\tau|,x_0,0) &= \frac{1}{2}\,b^2\ \mathrm{erfc}\left[\frac{x_0 - b\,\tau}{\sqrt{4\,\tau}}\right] && (4.71)\\
\partial_x\,p_1(x,\tau|,x_0,0)\Big|_{x=0} &= g\,b\,\frac{x_0 - b\,\tau}{2\,\tau} && (4.72)\\
\partial_x\,p_2(x,\tau|,x_0,0)\Big|_{x=0} &= g\,b\,\frac{-x_0 - b\,\tau}{2\,\tau} && (4.73)\\
\partial_x\,p_3(x,\tau|,x_0,0)\Big|_{x=0} &= -\,g\,b\;-\;\frac{1}{2}\,b^3\ \mathrm{erfc}\left[\frac{x_0 - b\,\tau}{\sqrt{4\,\tau}}\right] && (4.74)
\end{aligned}$$

where we used for (4.70, 4.73) the identity

$$b\,x_0 \;-\; \frac{(x_0 + b\,\tau)^2}{4\,\tau} \;=\; -\frac{(x_0 - b\,\tau)^2}{4\,\tau}\;. \tag{4.75}$$

From (4.69–4.74) one can readily derive the boundary condition (4.50).
We have demonstrated that (4.52–4.55) is a proper solution of the Smoluchowski equation in a half-space and in a linear potential. It is of interest to evaluate the fraction of particles which are accounted for by the three terms in (4.52). For this purpose we define

$$N_j(t|x_0) \;=\; \int_0^\infty dx\ p_j(x,t|x_0,0)\;. \tag{4.76}$$

One obtains then

$$\begin{aligned}
N_1(t|x_0) &= \frac{1}{\sqrt{4\pi\,\tau}}\int_0^\infty dx\ \exp\left[-\frac{(x - x_0 + b\,\tau)^2}{4\,\tau}\right]\\
&= \frac{1}{\sqrt{4\pi\,\tau}}\int_{-x_0+b\tau}^\infty dx\ \exp\left[-\frac{x^2}{4\,\tau}\right]\\
&= \frac{1}{2}\,\frac{2}{\sqrt{\pi}}\int_{\frac{-x_0+b\tau}{\sqrt{4\tau}}}^\infty dx\ \exp\left[-x^2\right] \;=\; \frac{1}{2}\,\mathrm{erfc}\left[\frac{-x_0 + b\,\tau}{\sqrt{4\,\tau}}\right] && (4.77)
\end{aligned}$$

Similarly one obtains

$$N_2(t|x_0) \;=\; \frac{1}{2}\,\exp[b\,x_0]\ \mathrm{erfc}\left[\frac{x_0 + b\,\tau}{\sqrt{4\,\tau}}\right]\;. \tag{4.78}$$

For $N_3(t|x_0)$ one derives, employing (4.56),

$$N_3(t|x_0) \;=\; \frac{1}{2}\,b\int_0^\infty dx\ \exp[-b\,x]\,\frac{2}{\sqrt{\pi}}\int_{\frac{x+x_0-b\tau}{\sqrt{4\tau}}}^\infty dy\ \exp\left[-y^2\right] \tag{4.79}$$

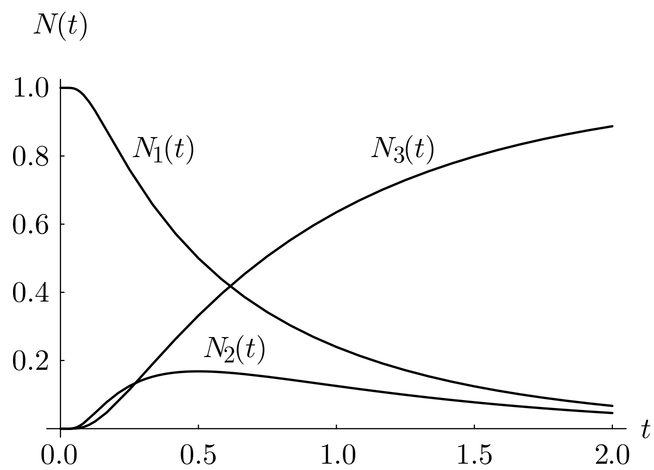

Figure 4.3: Plots of N_1, N_2 and N_3 vs. t, for $x_0 = 0$. The length and time units are the same as in Figure 4.1. For all $t > 0$ holds $N_1 + N_2 + N_3 = 1$.

Changing the order of integration yields

$$
\begin{aligned}
N_3(t|x_0) &= \frac{b}{\sqrt{\pi}} \int_{\frac{x_0 - b\tau}{\sqrt{4\tau}}}^{\infty} dy \ \exp\left[-y^2\right] \int_0^{\sqrt{4\tau} y - x_0 + b\tau} dx \ \exp[-b\,x] \\
&= \frac{1}{\sqrt{\pi}} \int_{\frac{x_0 - b\tau}{\sqrt{4\tau}}}^{\infty} dy \ \exp\left[-y^2\right] \ - \ \frac{1}{\sqrt{\pi}} \int_{\frac{x_0 - b\tau}{\sqrt{4\tau}}}^{\infty} dy \ \exp\left[-(y + b\sqrt{\tau})^2 \ + \ b\,x_0\right] \\
&= \frac{1}{2} \ \mathrm{erfc}\left[\frac{x_0 - b\,\tau}{\sqrt{4\tau}}\right] \ - \ \frac{1}{2} \ \exp[b\,x_0] \ \mathrm{erfc}\left[\frac{x_0 + b\,\tau}{\sqrt{4\,\tau}}\right] \ .
\end{aligned}
$$

Employing the identity

$$
\frac{1}{2} \ \mathrm{erfc}(z) \ = \ 1 \ - \ \frac{1}{2} \ \mathrm{erfc}(-z) \tag{4.80}
$$

one can write finally

$$
\begin{aligned}
N_3(t|x_0) &= 1 \ - \ \frac{1}{2} \ \mathrm{erfc}\left[\frac{-x_0 + b\,\tau}{\sqrt{4\,\tau}}\right] \ - \ \frac{1}{2} \ \exp[b\,x_0] \ \mathrm{erfc}\left[\frac{x_0 + b\tau}{\sqrt{4\tau}}\right] \\
&= 1 \ - \ N_1(t|x_0) \ - \ N_2(t|x_0) \ .
\end{aligned} \tag{4.81}
$$

This result demonstrates that the solution (4.52–4.55) is properly normalized. The time dependence of N_1, N_2 and N_3 are shown in Figure 4.3.

4.3 Diffusion in a One-Dimensional Harmonic Potential

We consider now diffusion in a harmonic potential

$$
U(x) = \frac{1}{2}\, f\, x^2 \tag{4.82}
$$

which is simple enough to yield an analytical solution of the corresponding Smoluchowski equation

$$
\partial_t p(x,t|x_0,t_0) = D(\partial_x^2 + \beta f \ \partial_x x)\, p(x,t|x_0,t_0) \ . \tag{4.83}
$$

We assume presently a constant diffusion coefficient D. The particle can diffuse in the infinite space Ω_∞. However, the potential confines the motion to a finite area such that the probability distribution vanishes exponentially for $x \to \pm\infty$ as expressed through the boundary condition

$$\lim_{x\to\pm\infty} x^n\, p(x,t|x_0,t_0) = 0, \quad \forall n \in I\!N\,. \tag{4.84}$$

We seek the solution of (4.83, 4.84) for the initial condition

$$p(x,t_0|x_0,t_0) = \delta(x - x_0)\,. \tag{4.85}$$

In thermal equilibrium, particles will be distributed according to the Boltzmann distribution

$$p_0(x) = \sqrt{f/2\pi k_B T}\, \exp\bigl(-f x^2/2k_B T\bigr) \tag{4.86}$$

which is, in fact, a stationary solution of (4.83, 4.84). We expect that the solution for the initial condition (4.85) will asymptotically decay towards (4.86).
The mean square deviation from the average position of the particle at equilibrium, i.e., from $\langle x\rangle = 0$, is

$$\begin{aligned} \delta^2 &= \int_{-\infty}^{+\infty} dx\, (x - \langle x\rangle)^2\, p_0(x) \\ &= \sqrt{f/2\pi k_B T} \int_{-\infty}^{+\infty} dx\, x^2\, \exp\bigl(-f x^2/2k_B T\bigr)\,. \end{aligned} \tag{4.87}$$

This quantity can be evaluated considering first the integral

$$I_n(\alpha) = (-1)^n \int_{-\infty}^{+\infty} dx\, x^{2n}\, e^{-\alpha x^2}\,.$$

One can easily verify

$$I_1(\alpha) = -\,\partial_\alpha I_0(\alpha) = \frac{\sqrt{\pi}}{2\alpha^{3/2}}\,. \tag{4.88}$$

and, through recursion,

$$I_n(\alpha) = \frac{\Gamma\bigl(n + \frac{1}{2}\bigr)}{\alpha^{n+\frac{1}{2}}}\,, \qquad n = 0, 1, \ldots \tag{4.89}$$

One can express δ^2 in terms of the integral I_1. Defining

$$\kappa = \sqrt{\frac{f}{2k_B T}} \tag{4.90}$$

and changing the integration variable $x \to y = \kappa x$ yields

$$\delta^2 = \frac{1}{\kappa^2}\frac{1}{\sqrt{\pi}} \int_{-\infty}^{+\infty} dy\, y^2\, e^{-y^2} = \frac{1}{\kappa^2}\frac{1}{\sqrt{\pi}}\, I_1(1)\,. \tag{4.91}$$

According to (4.88) holds $I_1(1) = \sqrt{\pi}/2$ and, hence,

$$\delta^2 = \frac{1}{2\kappa^2}\,, \tag{4.92}$$

or

$$\delta \;=\; \sqrt{k_B T / f}\;. \tag{4.93}$$

For a solution of (4.83, 4.84, 4.85) we introduce dimensionless variables. We replace x by

$$\xi \;=\; x/\sqrt{2}\delta \tag{4.94}$$

We can also employ δ to define a natural time constant

$$\tilde{\tau} \;=\; 2\delta^2/D \tag{4.95}$$

and, hence, replace t by

$$\tau \;=\; t/\tilde{\tau}\;. \tag{4.96}$$

The Smoluchowski equation for

$$q(\xi,\tau|\xi_0,\tau_0) \;=\; \sqrt{2}\,\delta\; p(x,t|x_0,t_0) \tag{4.97}$$

reads then

$$\partial_\tau q(\xi,\tau|\xi_0,\tau_0) = (\partial_\xi^2 + 2\,\partial_\xi\;\xi)\,q(\xi,\tau|\xi_0,\tau_0)\;, \tag{4.98}$$

The corresponding initial condition is

$$q(\xi,\tau_0|\xi_0,\tau_0) = \delta(\xi-\xi_0)\,, \tag{4.99}$$

and the boundary condition

$$\lim_{\xi\to\pm\infty} \xi^n\, q(\xi,\tau|\xi_0,\tau_0) = 0, \quad \forall n \in I\!N\;. \tag{4.100}$$

The prefactor of $p(x,t|x_0,t_0)$ in the definition (4.97) is dictated by the condition that $q(\xi,\tau|\xi_0,\tau_0)$ should be normalized, i.e.,

$$\int_{-\infty}^{+\infty} dx\, p(x,t|x_0,t_0) \;=\; \int_{-\infty}^{+\infty} d\xi\; q(\xi,\tau|\xi_0,\tau_0) \;=\; 1 \tag{4.101}$$

In the following we choose

$$\tau_0 \;=\; 0\;. \tag{4.102}$$

In order to solve (4.98, 4.99, 4.100) we seek to transform the Smoluchowski equation to the free diffusion equation through the choice of the time-dependent position variable

$$y \;=\; \xi\, e^{2\tau}\;, \qquad y_0 \;=\; \xi_0\;, \tag{4.103}$$

replacing

$$q(\xi,\tau|\xi_0,0) \;=\; v(y,\tau|y_0,0)\;. \tag{4.104}$$

We note that this definition results in a time-dependent normalization of $v(y,\tau|y_0,0)$, namely,

$$1 \;=\; \int_{-\infty}^{+\infty} d\xi\; q(\xi,\tau|\xi_0,0) \;=\; e^{-2\tau}\int_{-\infty}^{+\infty} dy\, v(y,\tau|y_0,0)\;. \tag{4.105}$$

The spatial derivative ∂_y, according to the chain rule, is determined by

$$\partial_\xi \;=\; \frac{\partial y}{\partial \xi}\,\partial_y \;=\; e^{2\tau}\,\partial_y \tag{4.106}$$

and, hence,

$$\partial_\xi^2 \;=\; e^{4\tau}\,\partial_y^2 \tag{4.107}$$

The l.h.s. of (4.98) reads

$$\partial_\tau q(\xi,\tau|\xi_0,0) \;=\; \partial_\tau v(y,\tau|y_0,0) \;+\; \underbrace{\frac{\partial y}{\partial \tau}}_{2y}\,\partial_y v(y,\tau|y_0,0)\;. \tag{4.108}$$

The r.h.s. of (4.98) becomes

$$e^{4\tau}\,\partial_y^2 v(y,\tau|y_0,0) \;+\; 2\,v(y,\tau|y_0,0) \;+\; 2\,\underbrace{\xi e^{2\tau}}_{y}\,\partial_y v(y,\tau|y_0,0)\,, \tag{4.109}$$

such that the Smoluchowski equation for $v(y,\tau|y_0,0)$ is

$$\partial_\tau v(y,\tau|y_0,0) \;=\; e^{4\tau}\,\partial_y^2 v(y,\tau|y_0,0) \;+\; 2\,v(y,\tau|y_0,0)\;. \tag{4.110}$$

To deal with a properly normalized distribution we define

$$v(y,\tau|y_0,0) \;=\; e^{2\tau}\,w(y,\tau|y_0,0) \tag{4.111}$$

which yields, in fact,

$$\int_{-\infty}^{\infty} d\xi\, q(\xi,\tau|\xi_0,0) \;=\; e^{-2\tau}\int_{-\infty}^{\infty} dy\, v(y,\tau|y_0,0) \;=\; \int_{-\infty}^{\infty} dy\, w(y,\tau|y_0,0) \;=\; 1\;. \tag{4.112}$$

The Smoluchowski equation for $w(y,\tau|y_0,0)$ is

$$\partial_\tau w(y,\tau|y_0,0) \;=\; e^{4\tau}\,\partial_y^2\, w(y,\tau|y_0,0) \tag{4.113}$$

which, indeed, has the form of a free diffusion equation, albeit with a time-dependent diffusion coefficient. The initial condition which corresponds to (4.99) is

$$w(y,0|y_0,0) \;=\; \delta(y-y_0)\;. \tag{4.114}$$

It turns out that the solution of a diffusion equation with time-dependent diffusion coefficient $\tilde{D}(\tau)$

$$\partial_\tau w(y,\tau|y_0,\tau_0) \;=\; \tilde{D}(\tau)\;\partial_y^2\; w(y,\tau|y_0,\tau_0) \tag{4.115}$$

in Ω_∞ with

$$w(y,\tau_0|y_0,\tau_0) \;=\; \delta(y\,-\,y_0) \tag{4.116}$$

is a straightforward generalization of the corresponding solution of the free diffusion equation (3.30), namely,

$$w(y,\tau|y_0,\tau_0) \;=\; \left(4\pi\int_0^\tau d\tau'\,\tilde{D}(\tau')\right)^{-\frac{1}{2}}\,\exp\left[-\,\frac{(y-\xi_0)^2}{4\int_0^\tau d\tau'\,\tilde{D}(\tau')}\right]\;. \tag{4.117}$$

This can be readily verified. Accordingly, the solution of (4.113, 4.114) is

$$w(y,\tau|y_0,0) \;=\; \left(4\pi \int_0^\tau d\tau'\, e^{4\tau'}\right)^{-\frac{1}{2}} \exp\left[-\frac{(y-y_0)^2}{4\int_0^\tau d\tau'\, e^{4\tau'}}\right] . \tag{4.118}$$

The corresponding distribution $q(\xi,\tau|\xi_0,0)$ is, using (4.103, 4.104, 4.111),

$$q(\xi,\tau|\xi_0,0) \;=\; \frac{1}{\sqrt{\pi(1-e^{-4\tau})}} \exp\left[-\frac{(\xi-\xi_0 e^{-2\tau})^2}{1-e^{-4\tau}}\right] . \tag{4.119}$$

and, hence, using (4.94, 4.95, 4.96, 4.97), we arrive at

$$p(x,t|x_0,t_0) \;=\; \frac{1}{\sqrt{2\pi k_B T\, S(t,t_0)/f}} \exp\left[-\frac{\left(x \,-\, x_0\, e^{-2(t-t_0)/\tilde{\tau}}\right)^2}{2k_B T S(t,t_0)/f}\right] \tag{4.120}$$

$$S(t,t_0) \;=\; 1 \,-\, e^{-4(t-t_0)/\tilde{\tau}} \tag{4.121}$$

$$\tilde{\tau} \;=\; 2k_B T \,/\, fD\, . \tag{4.122}$$

One notices that this distribution asymptotically, i.e., for $t \to \infty$, approaches the Boltzmann distribution (4.86). We also note that (4.120, 4.121, 4.122) is identical to the conditional probability of the Ornstein-Uhlenbeck process (2.81, 2.82) for $\gamma = 2/\tilde{\tau}$ and $\sigma^2 = 2k_B T$.