Chapter 12

Smoluchowski Equation for Potentials: Extremum Principle and Spectral Expansion

Contents

In this section we will consider the general properties of the solution $p(\boldsymbol{r}, t)$ of the Smoluchowski equation in the case that the force field is derived from a potential, i.e., $\boldsymbol{F}(\boldsymbol{r}) = -\nabla U(\boldsymbol{r})$ and that the potential is finite everywhere in the diffusion doamain Ω. We will demonstrate first that the solutions, in case of reaction-free boundary conditions, obey an extremum principle, namely, that during the time evolution of $p(\boldsymbol{r}, t)$ the total free energy decreases until it reaches a minimum value corresponding to the Boltzmann distribution.

We will then characterize the time-evolution through a so-called spectral expansion, i.e., an expansion in terms of eigenfunctions of the Smoluchowski operator $\mathcal{L}(\boldsymbol{r})$. Since this operator is not self-adjoint, expressed through the fact that, except for free diffusion, the adjoint operator $\mathcal{L}^\dagger(\boldsymbol{r})$ as given by (9.22) or (9.38) is not equal to $\mathcal{L}(\boldsymbol{r})$, the existence of appropriate eigenvalues and eigenfunctions is not evident. However, in the present case $[\boldsymbol{F}(\boldsymbol{r}) = -\nabla U(\boldsymbol{r})]$ the operators $\mathcal{L}(\boldsymbol{r})$ and $\mathcal{L}^\dagger(\boldsymbol{r})$ are similar to a self-adjoint operator for which a complete set of orthonormal eigenfunctions exist. These functions and their associated eigenvalues can be transferred to $\mathcal{L}(\boldsymbol{r})$ and $\mathcal{L}^\dagger(\boldsymbol{r})$ and a spectral expansion can be constructed. The expansion will be formulated in terms of projection operators and the so-called propagator, which corresponds to the solutions $p(\boldsymbol{r}, t|\boldsymbol{r}_0, t0)$, will be stated in a general form.

A pointed out, we consider in this chapter specifically solutions of the Smoluchowski equation

$$\partial_t p(\boldsymbol{r}, t) \; = \; \mathcal{L}(\boldsymbol{r})\, p(\boldsymbol{r}, t) \tag{12.1}$$

in case of diffusion in a potential $U(\boldsymbol{r})$, i.e., for a Smoluchowski operator of the form (9.3)

$$\mathcal{L}(\boldsymbol{r}) \; = \; \nabla \cdot D(\boldsymbol{r})\, e^{-\beta U(\boldsymbol{r})}\, \nabla\, e^{\beta U(\boldsymbol{r})} \; . \tag{12.2}$$

We assume the general initial condition

$$p(\boldsymbol{r}, t_o) \;=\; f(\boldsymbol{r}) \tag{12.3}$$

and appropriate boundary conditions as specified by equations (9.4–9.6). It is understood that the initial distribution is properly normalized

$$\int_\Omega d\boldsymbol{r}\; f(\boldsymbol{r}) \;=\; 1 \;. \tag{12.4}$$

The results of the present section are fundamental for many direct applications as well as for a formal approach to the evaluation of observables, e.g., correlation functions, which serves to formulate useful approximations. We have employed already, in Chapter 2, spectral expansions for free diffusion, a casew in which the Smoluchowski operator $\mathcal{L}(\boldsymbol{r}) = D\nabla^2$ is self-adjoint ($\mathcal{L}(\boldsymbol{r}) = \mathcal{L}^\dagger(\boldsymbol{r})$). In the present chapter we consider spectral expansion for diffusion in arbitrary potentials $U(x)$ and demonstrate the expansion for a harmonic potential.

12.1 Minimum Principle for the Smoluchowski Equation

In case of diffusion in a domain Ω with a 'non-reactive' boundary $\partial\Omega$ the total free energy of the system develops toward a minimum value characterized through the Boltzmann distribution. This property will be demonstrated now. The stated boundary condition is according to (9.4)

$$\hat{n}(\boldsymbol{r}) \cdot \boldsymbol{\jmath}(\boldsymbol{r}, t) \;=\; 0 \tag{12.5}$$

where the flux $\boldsymbol{\jmath}(\boldsymbol{r}, t)$ is [c.f. (4.19)]

$$\boldsymbol{\jmath}(\boldsymbol{r}, t) \;=\; D(\boldsymbol{r})\, e^{-\beta U(\boldsymbol{r})}\, \nabla\, e^{\beta U(\boldsymbol{r})}\, p(\boldsymbol{r}, t) \;. \tag{12.6}$$

The total free energy for a given distribution $p(\boldsymbol{r}, t)$, i.e., the quantity which develops towards a minimum during the diffusion process, is a functional defined through

$$G[p(\boldsymbol{r}, t)] \;=\; \int_\Omega d\boldsymbol{r}\; g(\boldsymbol{r}, t) \tag{12.7}$$

where $g(\boldsymbol{r}, t)$ is the free energy density connected with $p(\boldsymbol{r}, t)$

$$g(\boldsymbol{r}, t) \;=\; U(\boldsymbol{r})\, p(\boldsymbol{r}, t) \;+\; k_B T\, p(\boldsymbol{r}, t) \ln \frac{p(\boldsymbol{r}, t)}{\rho_o} \;. \tag{12.8}$$

Here ρ_o is a constant which serves to make the argument of $\ln(\cdots)$ unitless. ρ_o adds effectively only a constant to $G[p(\boldsymbol{r}, t)]$ since, for the present boundary condition (12.5) [use (12.1, 12.2)],

$$\begin{aligned}
\partial_t \int_\Omega d\boldsymbol{r}\, p(\boldsymbol{r}, t) \;&=\; \int_\Omega d\boldsymbol{r}\, \partial_t p(\boldsymbol{r}, t) \;=\; \int_\Omega d\boldsymbol{r}\, \nabla \cdot D(\boldsymbol{r})\, e^{-\beta U(\boldsymbol{r})} \nabla\, e^{\beta U(\boldsymbol{r})}\, p(\boldsymbol{r}, t) \\
&=\; \int_{\partial\Omega} d\boldsymbol{a} \cdot D(\boldsymbol{r})\, e^{-\beta U(\boldsymbol{r})} \nabla\, e^{\beta U(\boldsymbol{r})}\, p(\boldsymbol{r}, t) \;=\; 0 \;.
\end{aligned} \tag{12.9}$$

From this follows that $\int_\Omega d\boldsymbol{r}\, p(\boldsymbol{r}, t)$ is constant and, hence, the contribution stemming from ρ_o, i.e., $-k_B T\, p(\boldsymbol{r}, t) \ln \rho_o$ contributes only a constant to $G[p(\boldsymbol{r}, t)]$ in (12.7). The first term on the r.h.s. of (12.7) describes the local energy density

$$u(\boldsymbol{r}, t) \;=\; U(\boldsymbol{r})\, p(\boldsymbol{r}, t) \tag{12.10}$$

and the second term, written as $-T\, s(\boldsymbol{r},t)$, the local entropy density[1]

$$s(\boldsymbol{r},t) \;=\; -k\, p(\boldsymbol{r},t) \ln \frac{p(\boldsymbol{r},t)}{\rho_o} \;. \tag{12.11}$$

We want to assume for some t

$$p(\boldsymbol{r},t) \;>\; 0 \qquad \forall \boldsymbol{r},\, \boldsymbol{r} \in \Omega \;. \tag{12.12}$$

This assumption can be made for the initial condition, i.e., at $t = t_o$, since a negative initial distribution could not be reconciled with the interpretation of $p(\boldsymbol{r},t)$ as a probability. We will see below that if, at any moment, (12.12) does apply, $p(\boldsymbol{r},t)$ cannot vanish anywhere in Ω at later times.
For the time derivative of $G[p(\boldsymbol{r},t)]$ can be stated

$$\partial_t G[p(\boldsymbol{r},t)] \;=\; \int_\Omega d\boldsymbol{r}\; \partial_t g(\boldsymbol{r},t) \tag{12.13}$$

where, according to the definition (12.8),

$$\partial_t g(\boldsymbol{r},t) \;=\; \left[U(\boldsymbol{r}) \;+\; k_B T \ln \frac{p(\boldsymbol{r},t)}{\rho_o} \;+\; k_B T \right] \partial_t p(\boldsymbol{r},t) \;. \tag{12.14}$$

Using the definition of the local flux density one can write (12.14)

$$\partial_t g(\boldsymbol{r},t) \;=\; \left[U(\boldsymbol{r}) \;+\; k_B T \ln \frac{p(\boldsymbol{r},t)}{\rho_o} \;+\; kT \right] \nabla \cdot \boldsymbol{\jmath}(\boldsymbol{r},t) \tag{12.15}$$

or, employing $\nabla \cdot w(\boldsymbol{r}) \boldsymbol{v}(\boldsymbol{r}) \;=\; w(\boldsymbol{r}) \nabla \cdot \boldsymbol{v}(\boldsymbol{r}) \;+\; \boldsymbol{v}(\boldsymbol{r}) \cdot \nabla w(\boldsymbol{r})$,

$$\begin{aligned} \partial_t g(\boldsymbol{r},t) \;&=\; \nabla \cdot \left\{ \left[U(\boldsymbol{r}) \;+\; k_B T \ln \frac{p(\boldsymbol{r},t)}{\rho_o} \;+\; k_B T \right] \boldsymbol{\jmath}(\boldsymbol{r},t) \right\} \\ &\qquad -\, \boldsymbol{\jmath}(\boldsymbol{r},t) \,\cdot\, \nabla \left[U(\boldsymbol{r}) \;+\; k_B T \ln \frac{p(\boldsymbol{r},t)}{\rho_o} \;+\; k_B T \right] . \end{aligned} \tag{12.16}$$

Using

$$\begin{aligned} \nabla \left[U(\boldsymbol{r}) \;+\; k_B T \ln \frac{p(\boldsymbol{r},t)}{\rho_o} \;+\; k_B T \right] \;&=\; -\,\boldsymbol{F}(\boldsymbol{r}) \;+\; \frac{k_B T}{\boldsymbol{p}(\boldsymbol{r},t)} \nabla p(\boldsymbol{r},t) \\ &=\; +\,\frac{k_B T}{\boldsymbol{p}(\boldsymbol{r},t)} \left[\, \nabla p(\boldsymbol{r},t) \;-\; \beta\, \boldsymbol{F}(\boldsymbol{r})\, p(\boldsymbol{r},t) \,\right] \\ &=\; \frac{k_B T}{\boldsymbol{p}(\boldsymbol{r},t)}\, \boldsymbol{\jmath}(\boldsymbol{r},t) \end{aligned} \tag{12.17}$$

one can write (12.16)

$$\partial_t g(\boldsymbol{r},t) \;=\; -\,\frac{k_B T}{\boldsymbol{p}(\boldsymbol{r},t)}\, \boldsymbol{\jmath}^2(\boldsymbol{r},t) \;+\; \nabla \cdot \left\{ \left[U(\boldsymbol{r}) \;+\; k_B T \ln \frac{p(\boldsymbol{r},t)}{\rho_o} \;+\; k_B T \right] \boldsymbol{\jmath}(\boldsymbol{r},t) \right\} \;. \tag{12.18}$$

[1]For a definition and explanation of the entropy term, often referred to as mixing entropy, see a textbook on Statistical Mechanics, e.g., "Course in Theoretical Physics, Vol. 5, Statistical Physics, Part 1, 3rd Edition", L.D. Landau and E.M. Lifshitz, Pergamon Press, Oxford)

For the total free energy holds then, according to (12.13),

$$\partial_t G[p(\boldsymbol{r},t)] \;=\; -\int_\Omega d\boldsymbol{r}\,\frac{k_BT}{p(\boldsymbol{r},t)}\,\boldsymbol{\jmath}^2(\boldsymbol{r},t) \;+\; \int_{\partial\Omega} d\boldsymbol{a}\cdot\left\{\left[U(\boldsymbol{r}) \;+\; k_BT\ln\frac{p(\boldsymbol{r},t)}{\rho_o} \;+\; k_BT\right]\boldsymbol{\jmath}(\boldsymbol{r},t)\right\}\,. \tag{12.19}$$

Due to the boundary condition (12.5) the second term on the r.h.s. vanishes and one can conclude

$$\partial_t G[p(\boldsymbol{r},t)] \;=\; -\int_\Omega d\boldsymbol{r}\,\frac{k_BT}{p(\boldsymbol{r},t)}\,\boldsymbol{\jmath}^2(\boldsymbol{r},t) \;\le\; 0\,. \tag{12.20}$$

According to (12.20) the free energy, during the time course of Smoluchowski dynamics, develops towards a state $p_o(\boldsymbol{r})$ which minimizes the total free energy G. This state is characterized through the condition $\partial_t G \;=\; 0$, i.e., through

$$\boldsymbol{\jmath}_o(\boldsymbol{r}) \;=\; D(\boldsymbol{r})\,e^{-\beta U(\boldsymbol{r})}\,\nabla\,e^{\beta U(\boldsymbol{r})}\,p_o(\boldsymbol{r}) \;=\; 0\,. \tag{12.21}$$

The Boltzmann distribution

$$p_o(\boldsymbol{r}) \;=\; N\,e^{-\beta U(\boldsymbol{r})}\,, \qquad N^{-1} \;=\; \int_\Omega d\boldsymbol{r}\,p_o(\boldsymbol{r}) \tag{12.22}$$

obeys this condition which we, in fact, enforced onto the Smoluchowski equation as outlined in Chapter 3 [cf. (4.5–4.19)]. Hence, the solution of (12.1–12.3, 12.5) will develop asymptotically , i.e., for $t \;\to\; \infty$, towards the Boltzmann distribution.

We want to determine now the difference between the free energy density $g(\boldsymbol{r},t)$ and the equilibrium free energy density. For this purpose we note

$$U(\boldsymbol{r})\,p(\boldsymbol{r},t) \;=\; -k_BT\,p(\boldsymbol{r},t)\ln\left[e^{-\beta U(\boldsymbol{r})}\right] \tag{12.23}$$

and, hence, according to (12.8)

$$g(\boldsymbol{r},t) \;=\; k_BT\,p(\boldsymbol{r},t)\ln\frac{p(\boldsymbol{r},t)}{\rho_o e^{-\beta U(\boldsymbol{r})}}\,. \tag{12.24}$$

Choosing $\rho_o^{-1} \;=\; \int_\Omega d\boldsymbol{r}\,\exp[-\beta U(\boldsymbol{r})]$ one obtains, from (12.22)

$$g(\boldsymbol{r},t) \;=\; k_BT\,p(\boldsymbol{r},t)\ln\frac{p(\boldsymbol{r},t)}{p_o(\boldsymbol{r})}\,. \tag{12.25}$$

For $p(\boldsymbol{r},t) \;\to\; p_o(\boldsymbol{r})$ this expression vanishes, i.e., $g(\boldsymbol{r},t)$ is the difference between the free energy density $g(\boldsymbol{r},t)$ and the equilibrium free energy density.

We can demonstrate now that the solution $p(\boldsymbol{r},t)$ of (12.1–12.3, 12.5) remains positive, as long as the initial distribution (12.3) is positive. This follows from the observation that for positive distributions the expression (12.25) is properly defined. In case that $p(\boldsymbol{r},t)$ would then become very small in some region of Ω, the free energy would become $-\infty$, except if balanced by a large positive potential energy $U(\boldsymbol{r})$. However, since we assumed that $U(\boldsymbol{r})$ is finite everywhere in Ω, the distribution cannot vanish anywhere, lest the total free energy would fall below the zero equilibrium value of (12.25). We conclude that $p(\boldsymbol{r},t)$ cannot vanish anywhere, hence, once positive everywhere the distribution $p(\boldsymbol{r},t)$ can nowhere vanish or, as a result, become negative.

12.2 Similarity to Self-Adjoint Operator

In case of diffusion in a potential $U(\boldsymbol{r})$ the respective Smoluchowski operator (12.2) is related, through a similarity transformation, to a self-adjoint or Hermitean operator $\mathcal{L}_h$. This has important ramifications for its eigenvalues and its eigenfunctions as we will demonstrate now.
The Smoluchowski operator $\mathcal{L}$ acts in a function space with elements $f, g, \ldots$. We consider the following transformation in this space

$$f(\boldsymbol{r}),\ g(\boldsymbol{r}) \quad \rightarrow \quad \tilde{f}(\boldsymbol{r}) \ = \ e^{\frac{1}{2}\beta U(\boldsymbol{r})}\, f(\boldsymbol{r}),\ \tilde{g}(\boldsymbol{r}) \ = \ e^{\frac{1}{2}\beta U(\boldsymbol{r})}\, g(\boldsymbol{r})\ .$$

Note that such transformation is accompanied by a change of boundary conditions.
A relationship

$$g \ = \ \mathcal{L}(\boldsymbol{r})\, f(\boldsymbol{r}) \tag{12.26}$$

implies

$$\tilde{g} \ = \ \mathcal{L}_h(\boldsymbol{r})\, \tilde{f}(\boldsymbol{r}) \tag{12.27}$$

where $\mathcal{L}_h$,

$$\mathcal{L}_h(\boldsymbol{r}) \ = \ e^{\frac{1}{2}\beta U(\boldsymbol{r})}\, \mathcal{L}(\boldsymbol{r})\, e^{-\frac{1}{2}\beta U(\boldsymbol{r})} \tag{12.28}$$

is connected with $\mathcal{L}$ through a similarity transformation. Using (12.2) one can write

$$\mathcal{L}_h(\boldsymbol{r}) \ = \ e^{\frac{1}{2}\beta U(\boldsymbol{r})}\, \nabla \cdot D(\boldsymbol{r})\, e^{-\beta U(\boldsymbol{r})}\, \nabla\, e^{\frac{1}{2}\beta U(\boldsymbol{r})}\ . \tag{12.29}$$

We want to prove now that $\mathcal{L}_h(\boldsymbol{r})$, as given by (12.29), is a self-adjoint operator for suitable boundary conditions restricting the elements of the function space considered. Using, for some scalar test function f, the property $\nabla \exp[\frac{1}{2}\beta U(\boldsymbol{r})]\, f \ = \ \exp[\frac{1}{2}\beta U(\boldsymbol{r})] \nabla f \ - \ \frac{1}{2}\beta \boldsymbol{F}\, f$ yields

$$\mathcal{L}_h(\boldsymbol{r}) \ = \ e^{\frac{1}{2}\beta U(\boldsymbol{r})}\, \nabla \cdot D(\boldsymbol{r})\, e^{-\frac{1}{2}\beta U(\boldsymbol{r})} \left[\nabla \ - \ \frac{1}{2}\boldsymbol{F} \right]\ . \tag{12.30}$$

Employing the property $\nabla \cdot \exp[-\frac{1}{2}\beta U(\boldsymbol{r})]\, \boldsymbol{v} \ = \ \exp[-\frac{1}{2}\beta U(\boldsymbol{r})]\, (\nabla \cdot \boldsymbol{v} \ + \ \frac{1}{2}\beta \boldsymbol{F} \cdot \boldsymbol{v})$, which holds for some vector-valued function $\boldsymbol{v}$, leads to

$$\mathcal{L}_h(\boldsymbol{r}) \ = \ \nabla \cdot D\, \nabla \ - \ \frac{1}{2}\beta \nabla \cdot D\, \boldsymbol{F} \ + \ \frac{1}{2}\beta \boldsymbol{F} \cdot (\, D\nabla \ - \ \frac{1}{2}\beta \boldsymbol{F}\,)\ . \tag{12.31}$$

The identity $\nabla D\boldsymbol{F} f \ = \ D\boldsymbol{F} \cdot \nabla f \ + \ f\, \nabla \cdot D\boldsymbol{F}$ allows one to express finally

$$\mathcal{L}_h(\boldsymbol{r}) \ = \ \nabla \cdot D\, \nabla \ + \ \frac{1}{2}\beta((\nabla \cdot \boldsymbol{F})) \ - \ \frac{1}{4}\beta^2 \boldsymbol{F}^{\,2} \tag{12.32}$$

where $((\cdots))$ indicates a multiplicative operator, i.e., indicates that the operator inside the double brackets acts solely on functions within the bracket. One can write the operator (12.32) also in the form

$$\mathcal{L}_h(\boldsymbol{r}) \ = \ \mathcal{L}_{oh}(\boldsymbol{r}) \ + \ U(\boldsymbol{r}) \tag{12.33}$$

$$\mathcal{L}_{oh}(\boldsymbol{r}) \ = \ \nabla \cdot D\, \nabla \tag{12.34}$$

$$U(\boldsymbol{r}) \ = \ \frac{1}{2}\beta((\nabla \cdot \boldsymbol{F})) \ - \ \frac{1}{4}\beta^2 \boldsymbol{F}^{\,2} \tag{12.35}$$

where it should be noted that $U(\boldsymbol{r})$ is a multiplicative operator.
One can show now, using (9.20–9.23), that Eqs. (12.33–12.35) define a self-adjoint operator. For this purpose we note that the term (12.35) of $\mathcal{L}_h$ is self-adjoint for any pair of functions $\tilde{f}, \tilde{g}$, i.e.,

$$\int_\Omega d\boldsymbol{r}\, \tilde{g}(\boldsymbol{r})\, U(\boldsymbol{r})\, \tilde{f}(\boldsymbol{r}) \;=\; \int_\Omega d\boldsymbol{r}\, \tilde{f}(\boldsymbol{r})\, U(\boldsymbol{r})\, \tilde{g}(\boldsymbol{r})\,. \tag{12.36}$$

Applying (9.20–9.23) for the operator $\mathcal{L}_{oh}(\boldsymbol{r})$, i.e., using (9.20–9.23) in the case $\boldsymbol{F} \equiv 0$, implies

$$\begin{aligned} \int_\Omega d\boldsymbol{r}\, \tilde{g}(\boldsymbol{r})\, \mathcal{L}_{oh}(\boldsymbol{r})\, \tilde{f}(\boldsymbol{r}) &= \int_\Omega d\boldsymbol{r}\, \tilde{f}(\boldsymbol{r})\, \mathcal{L}^\dagger_{oh}(\boldsymbol{r})\, \tilde{g}(\boldsymbol{r}) \;+\; \int_{\partial\Omega} d\boldsymbol{a} \cdot \boldsymbol{P}(\tilde{g}, \tilde{f}) && (12.37) \\ \mathcal{L}^\dagger_{oh}(\boldsymbol{r}) &= \nabla \cdot D(\boldsymbol{r})\, \nabla && (12.38) \\ \boldsymbol{P}(\tilde{g}, \tilde{f}) &= \tilde{g}(\boldsymbol{r}) D(\boldsymbol{r}) \nabla \tilde{f}(\boldsymbol{r}) \;-\; \tilde{f}(\boldsymbol{r}) D(\boldsymbol{r}) \nabla \tilde{g}(\boldsymbol{r})\,. && (12.39) \end{aligned}$$

In the present case holds $\mathcal{L}_{oh}(\boldsymbol{r}) = \mathcal{L}^\dagger_{oh}(\boldsymbol{r})$, i.e., in the space of functions which obey

$$\hat{n}(\boldsymbol{r}) \cdot \boldsymbol{P}(\tilde{g}, \tilde{f}) \;=\; 0 \qquad \text{for } \boldsymbol{r} \in \partial\Omega \tag{12.40}$$

the operator $\mathcal{L}_{oh}$ is self-adjoint. The boundary condition (12.40) implies

$$\begin{aligned} &(\tilde{\imath}) & \hat{\mathrm{n}}(\boldsymbol{r}) \cdot \mathrm{D}(\boldsymbol{r}) \nabla \tilde{\mathrm{f}}(\boldsymbol{r}) &= 0, & \boldsymbol{r} &\in \partial\Omega && (12.41) \\ &(\widetilde{\imath\imath}) & \tilde{\mathrm{f}}(\boldsymbol{r}) &= 0, & \boldsymbol{r} &\in \partial\Omega && (12.42) \\ &(\widetilde{\imath\imath\imath}) & \hat{\mathrm{n}}(\boldsymbol{r}) \cdot \mathrm{D}(\boldsymbol{r}) \nabla \tilde{\mathrm{f}}(\boldsymbol{r}) &= w(\boldsymbol{r})\, \tilde{f}(\boldsymbol{r}), & \boldsymbol{r} &\in \partial\Omega && (12.43) \end{aligned}$$

and the same for $\tilde{g}(\boldsymbol{r})$, i.e., $(\tilde{\imath})$ must hold for both $\tilde{f}$ and $\tilde{g}$, or $(\widetilde{\imath\imath})$ must hold for both $\tilde{f}$ and $\tilde{g}$, or $(\widetilde{\imath\imath\imath})$ must hold for both $\tilde{f}$ and $\tilde{g}$.
In the function space characterized through the boundary conditions (12.41–12.43) the operator $\mathcal{L}_h$ is then also self-adjoint. This property implies that eigenfunctions $\tilde{u}_n(\boldsymbol{r})$ with real eigenvalues exists, i.e.,

$$\mathcal{L}_h(\boldsymbol{r})\, \tilde{u}_n(\boldsymbol{r}) \;=\; \lambda_n \tilde{u}_n(\boldsymbol{r})\,, n \;=\; 0, 1, 2, \ldots\,, \qquad \lambda_n \in \mathbb{R} \tag{12.44}$$

a property, which is discussed at length in textbooks of quantum mechanics regrading the eigenfunctions and eigenvalues of the Hamiltonian operator[2]. The eigenfunctions and eigenvalues in (12.44) can form a discrete set, as indicated here, but may also form a continuous set or a mixture of both; continuous eigenvalues arise for diffusion in a space Ω, an infinite subspace of which is accessible. We want to assume in the following a discrete set of eigenfunctions.
The volume integral defines a scalar product in the function space

$$\langle f | g \rangle_\Omega \;=\; \int_\Omega d\boldsymbol{r}\, f(\boldsymbol{r})\, g(\boldsymbol{r})\,. \tag{12.45}$$

With respect to this scalar product the eigenfunctions for different eigenvalues are orthogonal, i.e.,

$$\langle \tilde{u}_n | \tilde{u}_m \rangle_\Omega \;=\; 0 \qquad \text{for } \lambda_n \neq \lambda_m. \tag{12.46}$$

This property follows from the identity

$$\langle \tilde{u}_n | \mathcal{L}_h\, \tilde{u}_m \rangle_\Omega \;=\; \langle \mathcal{L}_h\, \tilde{u}_n | \tilde{u}_m \rangle_\Omega \tag{12.47}$$

[2] See also textbooks on Linear Alegebra, e.g., "Introduction to Linear Algebra", G. Strang (Wellesley-Cambridge Press, Wellesley, MA, 1993)

which can be written, using (12.44),

$$(\lambda_n - \lambda_m) \langle \tilde{u}_n | \tilde{u}_m \rangle_\Omega = 0 . \tag{12.48}$$

For $\lambda_n \neq \lambda_m$ follows $\langle \tilde{u}_n | \tilde{u}_m \rangle_\Omega = 0$. A normalization condition $\langle \tilde{u}_n | \tilde{u}_n \rangle_\Omega = 1$ can be satisfied for the present case of a finite diffusion domain Ω or a confining potential in which case discrete spectra arise. The eigenfunctions for identical eigenvalues can also be chosen orthogonal, possibly requiring a linear transformation[3], and the functions can be normalized such that the following orthonormality property holds

$$\langle \tilde{u}_n | \tilde{u}_m \rangle_\Omega = \delta_{nm} . \tag{12.49}$$

Finally, the eigenfunctions form a complete basis, i.e., any function f in the respective function space, observing boundary conditions (12.41–12.43), can be expanded in terms of the eigenfunctions

$$\tilde{f}(\boldsymbol{r}) = \sum_{n=0}^{\infty} \alpha_n \tilde{u}_n(\boldsymbol{r}) \tag{12.50}$$

$$\alpha_n = \langle \tilde{u}_n | \tilde{f} \rangle_\Omega . \tag{12.51}$$

The mathematical theory of such eigenfunctions is not trivial and has been carried out in connection with quantum mechanics for which the operator of the type $\mathcal{L}_h$, in case of constant D, plays the role of the extensively studied Hamiltonian operator. We will assume, without further comments, that the operator $\mathcal{L}_h$ gives rise to a set of eigenfunctions with properties (12.44, 12.49–12.51)[4].

12.3 Eigenfunctions and Eigenvalues of the Smoluchowski Operator

The eigenfunctions $\tilde{u}_n(\boldsymbol{r})$ allow one to obtain the eigenfunctions $v_n(\boldsymbol{r})$ of the Smoluchowski operator $\mathcal{L}$. It holds, inverting the transformation (12.2),

$$v_n(\boldsymbol{r}) = e^{-\beta U/2} \, \tilde{u}_n(\boldsymbol{r}) \tag{12.52}$$

For this function follows from (12.2, 12.28, 12.44)

$$\begin{aligned} \mathcal{L}\, v_n &= e^{-\beta U/2} \, e^{\beta U/2} \nabla \cdot D(\boldsymbol{r}) \, e^{-\beta U(\boldsymbol{r})} \, \nabla \, e^{\beta U(\boldsymbol{r})/2} \, \tilde{u}_n \\ &= e^{-\beta U/2} \, \mathcal{L}_h \tilde{u}_n = e^{-\beta U/2} \, \lambda_n \, \tilde{u}_n , \end{aligned} \tag{12.53}$$

i.e.,

$$\mathcal{L}(\boldsymbol{r}) \, v_n(\boldsymbol{r}) = \lambda_n v_n(\boldsymbol{r}) . \tag{12.54}$$

The eigenfunctions w_n of the adjoint Smoluchowski operator $\mathcal{L}^\dagger$ (9.38) are given by

$$w_n(\boldsymbol{r}) = e^{\beta U(\boldsymbol{r})/2} \, \tilde{u}_n(\boldsymbol{r}) \tag{12.55}$$

and can be expressed equivalently, comparing (12.55) and (12.52),

$$w_n(\boldsymbol{r}) = e^{\beta U(\boldsymbol{r})} \, v_n(\boldsymbol{r}) . \tag{12.56}$$

[3] A method to obtain orthogonal eigenfunctions is the Schmitt orthogonalization.
[4] see also "Advanced Calculus for Applications, 2nd Ed." F.B.. Hildebrand, Prentice Hall 1976, ISBN 0-13-011189-9, which contains e.g., the proof of the orthogonality of eigenfunctions of the Smoluchowski operator.

In fact, using (9.38, 12.2, 12.54), one obtains

$$\mathcal{L}^\dagger w_n \;=\; e^{\beta U} \nabla \cdot D\, e^{-\beta U}\, \nabla\, e^{\beta U}\, v_n \;=\; e^{\beta U}\, \mathcal{L}\, v_n = e^{\beta U}\, \lambda_n\, v_n \tag{12.57}$$

or

$$\mathcal{L}^\dagger(\boldsymbol{r})\, w_n(\boldsymbol{r}) \;=\; \lambda_n\, w_n(\boldsymbol{r}) \tag{12.58}$$

which proves the eigenfunction property.
The orthonormality conditions (12.49) can be written

$$\begin{aligned} \delta_{nm} &= \langle \tilde{u}_n | \tilde{u}_m \rangle_\Omega \;=\; \int_\Omega d\boldsymbol{r}\, \tilde{u}_n(\boldsymbol{r})\, \tilde{u}_m(\boldsymbol{r}) \\ &= \int_\Omega d\boldsymbol{r}\, e^{-\beta U(\boldsymbol{r})/2}\, \tilde{u}_n(\boldsymbol{r})\, e^{\beta U(\boldsymbol{r})/2}\, \tilde{u}_m(\boldsymbol{r})\, . \end{aligned} \tag{12.59}$$

or, using (12.52, 12.55),

$$\langle w_n | v_m \rangle_\Omega \;=\; \delta_{nm}\, . \tag{12.60}$$

Accordingly, the set of eigenfunctions $\{w_n, n = 0, 1, \dots\}$ and $\{v_n, n = 0, 1, \dots\}$, defined in (12.55) and (12.52), form a so-called *bi-orthonormal system*, i.e., the elements of the sets $\{w_n, n = 0, 1, \dots\}$ and $\{v_n, n = 0, 1, \dots\}$ are mutually orthonormal.
We want to investigate now the boundary conditions obeyed by the functions $e^{\beta U/2}\, \tilde{f}$ and $e^{-\beta U/2}\, \tilde{g}$ when $\tilde{f}, \tilde{g}$ obey conditions (12.41–12.43). According to (12.2) holds, in case of $e^{\beta U/2}\, \tilde{f}$,

$$e^{\beta U/2}\, \tilde{f} \;=\; e^{\beta U}\, f\, . \tag{12.61}$$

According to (12.41–12.43), the function f obeys then

$$\begin{aligned} &\text{(i)} & \hat{n}(\boldsymbol{r}) \cdot D(\boldsymbol{r}) \nabla\, e^{\beta U}\, f(\boldsymbol{r}) &= 0, & \boldsymbol{r} &\in \partial\Omega & (12.62)\\ &\text{(ii)} & e^{\beta U}\, f(\boldsymbol{r}) &= 0, & \boldsymbol{r} &\in \partial\Omega & (12.63)\\ &\text{(iii)} & \hat{n}(\boldsymbol{r}) \cdot D(\boldsymbol{r}) \nabla\, e^{\beta U}\, f(\boldsymbol{r}) &= w(\boldsymbol{r})\, e^{\beta U}\, f(\boldsymbol{r}), & \boldsymbol{r} &\in \partial\Omega & (12.64) \end{aligned}$$

which is equivalent to the conditions (9.7, 9.5, 9.8) for the solutions of the Smoluchowski equation. We have established, therefore, that the boundary conditions assumed for the function space connected with the self-adjoint Smoluchowski operator $\mathcal{L}_h$ are consistent with the boundary conditions assumed previously for the Smoluchowski equation. One can veryfy similarly that the functions $e^{-\beta U/2}\, \tilde{g}$ imply the boundary conditions (9.7, 9.5, 9.8) for the adjoint Smoluchowski equation.

Projection Operators

We consider now the following operators defined through the pairs of eigenfunctions v_n, w_n of the Smoluchowski operators $\mathcal{L}, \mathcal{L}^\dagger$

$$\hat{J}_n\, f \;=\; v_n\, \langle w_n | f \rangle_\Omega \tag{12.65}$$

where f is some test function. For these operators holds

$$\hat{J}_n \hat{J}_m\, f \;=\; \hat{J}_n v_m\, \langle w_m | f \rangle_\Omega \;=\; v_n\, \langle w_n | v_m \rangle_\Omega\, \langle w_m | f \rangle_\Omega\, . \tag{12.66}$$

Using (12.60) one can write this

$$\hat{J}_n \hat{J}_m f \;=\; v_n \, \delta_{nm} \langle w_m | f \rangle_\Omega \tag{12.67}$$

and, hence, using the definition (12.65)

$$\hat{J}_n \hat{J}_m \;=\; \delta_{nm} \hat{J}_m \; . \tag{12.68}$$

This property identifies the operators $\hat{J}_n$, $n = 0, 1, 2, \ldots$ as mutually complementary projection operators, i.e., each $\hat{J}_n$ is a projection operator ($\hat{J}_n^2 = \hat{J}_n$) and two different $\hat{J}_n$ and $\hat{J}_m$ project onto orthogonal subspaces of the function space.
The completeness property (12.50, 12.51) of the set of eigenfunctions $\tilde{u}_n$ can be expressed in terms of the operators $\hat{J}_n$. For this purpose we consider

$$\alpha_n \;=\; \langle \tilde{u}_n | \tilde{f} \rangle_\Omega \;=\; \int_\Omega d\boldsymbol{r} \; \tilde{u}_n \; \tilde{f} \tag{12.69}$$

Using $\tilde{u}_n = \exp(\beta U/2)\, v_n$ and $\tilde{f} = \exp(\beta U/2)\, f$ [see (12.52, 12.2)] as well as (12.56) one can express this

$$\alpha_n \;=\; \int_\Omega d\boldsymbol{r} \; \exp(\beta U/2)\, v_n \; \exp(\beta U/2)\, f \;=\; \int_\Omega d\boldsymbol{r} \; \exp(\beta U)\, v_n\, f \;=\; \langle w_n | f \rangle_\Omega$$

Equations (12.50, 12.51) read then for $\tilde{f} = \exp(\beta U/2)\, f$

$$f \;=\; \sum_{n=0}^{\infty} e^{\beta U/2} \; u_n \, \langle w_n | f \rangle_\Omega \tag{12.70}$$

and, using again (12.52) and (12.65)

$$f \;=\; \sum_{n=0}^{\infty} \hat{J}_n \, f \tag{12.71}$$

Since this holds for any f in the function space with proper boundary conditions we can conclude that within the function space considered holds

$$\sum_{n=0}^{\infty} \hat{J}_n \;=\; 1\!\!1 \; . \tag{12.72}$$

The projection operators $\hat{J}_n$ obey, furthermore, the property

$$\mathcal{L}(\boldsymbol{r}) \, \hat{J}_n \;=\; \lambda_m \, \hat{J}_n \; . \tag{12.73}$$

This follows from the definition (12.65) together with (12.54).

The Propagator

The solution of (12.1–12.3) can be written formally

$$p(\boldsymbol{r}, t) \;=\; \left[e^{\mathcal{L}(\boldsymbol{r})(t - t_o)} \right]_{\rm bc} f(\boldsymbol{r}) \; . \tag{12.74}$$

The brackets $[\cdots]_{\rm bc}$ indicate that the operator is defined in the space of functons which obey the chosen spatial boundary conditions. The exponential operator $\exp[\mathcal{L}(\boldsymbol{r})(t-t_o)]$ in (12.74) is defined through the Taylor expansion

$$\left[e^{A}\right]_{\rm bc} \;=\; \sum_{\nu=0}^{\infty} \frac{1}{\nu!}\,[A]_{\rm bc}^{\nu} \,. \tag{12.75}$$

The operator $[\exp[\mathcal{L}(\boldsymbol{r})(t-t_o)]\,]_{\rm bc}$ plays a central role for the Smoluchowski equation; it is referred to as the *propagator*. One can write, dropping the argument $\boldsymbol{r}$,

$$\left[e^{\mathcal{L}(t-t_o)}\right]_{\rm bc} \;=\; e^{\mathcal{L}(t-t_o)} \sum_{n=0}^{\infty} \hat{J}_n \tag{12.76}$$

since the projection operators project out the functions with proper boundary conditions. For any function $Q(z)$, which has a convergent Taylor series for all $z \,=\, \lambda_n$, $n = 0, 1, \ldots$, holds

$$Q(\mathcal{L})\, v_n \;=\; Q(\lambda_n)\, v_n \tag{12.77}$$

and, hence, according to (12.73)

$$Q(\mathcal{L})\, \hat{J}_n \;=\; Q(\lambda_n)\, \hat{J}_n \tag{12.78}$$

This property, which can be proven by Taylor expansion of $Q(\mathcal{L})$, states that if a function of $\mathcal{L}$ "sees" an eigenfunction v_n, the operator $\mathcal{L}$ turns itself into the scalar λ_n. Since the Taylor expansion of the exponential operator converges everywhere on the real axis, it holds

$$e^{\mathcal{L}(t-t_o)}\, v_n \;=\; e^{\lambda_n(t-t_o)}\, v_n \,. \tag{12.79}$$

The expansion can then be written

$$\left[e^{\mathcal{L}(t-t_o)}\right]_{\rm bc} \;=\; \sum_{n=0}^{\infty} e^{\lambda_n(t-t_o)}\, \hat{J}_n \,. \tag{12.80}$$

We assume here and in the following the ordering of eigenvalues

$$\lambda_0 \;\geq\; \lambda_1 \;\geq\; \lambda_2 \;\cdots \tag{12.81}$$

which can be achieved by choosing the labels n, $n = 0, 1, \ldots$ in the appropriate manner.

The Spectrum of the Smoluchowski Operator

We want to comment finally on the eigenvalues λ_n appearing in series (12.81). The minimum principle for the free energy $G[p(\boldsymbol{r},t)]$ derived in the beginning of this section requires that for reflective boundary conditions (9.4, 9.32) any solution $p(\boldsymbol{r},t)$ of the Smoluchowski equation (12.1–12.3), at long times, decays towards the equilibrium distribution (12.22) for which holds [cf. (12.21)]

$$\mathcal{L}\, p_o(\boldsymbol{r}) \;=\; \nabla\cdot D(\boldsymbol{r})\, e^{-\beta U(\boldsymbol{r})}\, \nabla\, e^{\beta U(\boldsymbol{r})}\, p_o(\boldsymbol{r}) \;=\; 0 \,. \tag{12.82}$$

This identifies the equilibrium (Botzmann) distribution as the eigenfunction of $\mathcal{L}$ with vanishing eigenvalue. One can argue that this eigenvalue is, in fact, the largest eigenvalue of $\mathcal{L}$, i.e., for the "reflective" boundary condition (9.4)

$$\lambda_0 \;=\; 0 \;>\; \lambda_1 \;\geq\; \lambda_2 \;\cdots \tag{12.83}$$

The reason is that the minimum principle (12.20) for the free energy $G[p(\boldsymbol{r},t)]$ implies that any solution of the Smoluchowski equation with reflective boundary condition must asymptotically, i.e., for $t \to \infty$, decay towards $p_o(\boldsymbol{r})$ [cf. (12.21, 12.22)].
One can identify $p_o(\boldsymbol{r})$ with an eigenfunction $v_{n_o}(\boldsymbol{r})$ of $\mathcal{L}$ since $\mathcal{L}v_o = 0$ implies that $p_o(\boldsymbol{r})$ is an eigenfunction with vanishing eigenvalue. According to (12.22) and (12.57) holds that $w_{n_o}(\boldsymbol{r})$, the respective eigenfunction of $\mathcal{L}^\dagger$, is a constant which one may choose

$$w_{n_o} \equiv 1 \,. \tag{12.84}$$

Adopting the normalization $\langle w_{n_o} | v_{n_o} \rangle_\Omega = 1$ implies

$$v_{n_o}(\boldsymbol{r}) = p_o(\boldsymbol{r}) \,. \tag{12.85}$$

One can expand then any solution of the Smoluchowski equation, using (12.74, 12.80) and $\lambda_{n_o} = 0$,

$$\begin{aligned} p(\boldsymbol{r},t) &= \sum_{n=0}^{\infty} e^{\lambda_n (t-t_o)} \hat{J}_n \, f(\boldsymbol{r}) \\ &= \hat{J}_{n_o} \, f(\boldsymbol{r}) + \sum_{n \neq n_o} e^{\lambda_n (t-t_o)} \hat{J}_n \, f(\boldsymbol{r}) \,. \end{aligned} \tag{12.86}$$

The definition of $\hat{J}_{n_o}$ yields with (12.84, 12.85) and (12.4),

$$p(\boldsymbol{r},t) = p_o(\boldsymbol{r}) + \sum_{n \neq n_o} e^{\lambda_n (t-t_o)} v_n(\boldsymbol{r}) \langle w)n | f \rangle_\Omega \,. \tag{12.87}$$

The decay of $p(\boldsymbol{r},t)$ towards $p_o(\boldsymbol{r})$ for $t \to \infty$ implies then

$$\lim_{t\to\infty} e^{\lambda_n (t-t_o)} = 0 \tag{12.88}$$

from which follows $\lambda_n < 0$ for $n \neq n_o$. One can conclude for the spectrum of the Smuluchowski operator

$$\lambda_0 = 0 > \lambda_1 \geq \lambda_2 \geq \cdots \tag{12.89}$$

12.4 Brownian Oscillator

We want to demonstrate the spectral expansion method, introduced in this chapter, to the case of a Brownian oscillator governed by the Smoluchowski equation for a harmonic potential

$$U(x) = \frac{1}{2} f \, x^2 \,, \tag{12.90}$$

$$namely, by \partial_t p(x,t|x_0,t_0) = D(\partial_x^2 + \beta f \; \partial_x x) \, p(x,t|x_0,t_0) \tag{12.91}$$

with the boundary condition

$$\lim_{x\to\pm\infty} x^n \, p(x,t|x_0,t_0) = 0, \quad \forall n \in I\!N \tag{12.92}$$

and the initial condition

$$p(x,t_0|x_0,t_0) = \delta(x - x_0) \,. \tag{12.93}$$

In order to simplify the analysis we follow the treatment of the Brownian oscillator in Chapter 3 and introduce dimensionless variables

$$\xi \;=\; x/\sqrt{2}\delta\,, \qquad \tau \;=\; t/\tilde{\tau}\,, \tag{12.94}$$

where

$$\delta = \sqrt{k_B T/f}\,, \qquad \tilde{\tau} \;=\; 2\delta^2/D\,. \tag{12.95}$$

The Smoluchowski equation for the normalized distribution in ξ, given by

$$q(\xi,\tau|\xi_0,\tau_0) \;=\; \sqrt{2}\,\delta\, p(x,t|x_0,t_0)\,, \tag{12.96}$$

is then again [c.f. (4.98)]

$$\partial_\tau q(\xi,\tau|\xi_0,\tau_0) = (\partial_\xi^2 + 2\,\partial_\xi\;\xi)\,q(\xi,\tau|\xi_0,\tau_0) \tag{12.97}$$

with the initial condition

$$q(\xi,\tau_0|\xi_0,\tau_0) \;=\; \delta(\xi-\xi_0) \tag{12.98}$$

and the boundary condition

$$\lim_{\xi\to\pm\infty} \xi^n\,q(\xi,\tau|\xi_0,\tau_0) = 0, \quad \forall n \in I\!N\,. \tag{12.99}$$

This equation describes diffusion in thepotential $\tilde{U}(\xi) \;=\; \xi^2$. Using (13.9, 13.9, 12.90) one can show $\tilde{U}(\xi) \;=\; \beta U(x)$.
We seek to expand $q(\xi,\tau_0|\xi_0,\tau_0)$ in terms of the eigenfunctions of the operator

$$\mathcal{L}(\xi) \;=\; \partial_\xi^2 + 2\partial_\xi\xi\,, \tag{12.100}$$

restricting the functions to the space

$$\{h(\xi)\,|\,\lim_{\xi\to\pm\infty}\xi^n\,h(\xi) = 0\}\,. \tag{12.101}$$

The eigenfunctions $f_n(\xi)$ of $\mathcal{L}(\xi)$ are defined through

$$\mathcal{L}(\xi) f_n(\xi) \;=\; \lambda_n f_n(\xi) \tag{12.102}$$

Corresponding functions, which also obey (13.14), are

$$f_n(\xi) = c_n\,e^{-\xi^2}\,H_n(\xi)\,. \tag{12.103}$$

where $H_n(x)$ is the n-th Hermite polynomials and where c_n is a normalization constant chosen below. The eigenvalues are

$$\lambda_n \;=\; -\,2n, \tag{12.104}$$

As demonstrated above, the eigenfunctions of the Smoluchowski operator do not form an orthonormal basis with the scalar product (3.129) and neither do the functions $f_n(\xi)$ in (13.18). Instead, they obey the orthogonality property

$$\int_{-\infty}^{+\infty} d\xi\,e^{-\xi^2} H_n(\xi) H_m(\xi) \;=\; 2^n n!\sqrt{\pi}\delta_{nm}\,. \tag{12.105}$$

which allows one to identify a bi-orthonormal system of functions. For this purpose we choose for $f_n(\xi)$ the normalization

$$f_n(\xi) \;=\; \frac{1}{2^n n! \sqrt{\pi}}\, e^{-\xi^2}\, H_n(\xi) \tag{12.106}$$

and define

$$g_n(\xi) \;=\; H_n(\xi)\,. \tag{12.107}$$

One can readily recognize then from (13.20) the biorthonormality property

$$\langle g_n | f_n \rangle = \delta_{nm}\ . \tag{12.108}$$

The functions $g_n(\xi)$ can be identified with the eigenfunctions of the adjoint operator

$$\mathcal{L}^+(\xi) = \partial_\xi^2 - 2\xi\partial_\xi\ , \tag{12.109}$$

obeying

$$\mathcal{L}^+(\xi) g_n(\xi) \;=\; \lambda_n g_n(\xi)\ . \tag{12.110}$$

Comparing (13.18) and (13.22) one can, in fact, discern

$$g_n(\xi) \;\sim\; e^{\xi^2}\, g_n(\xi). \tag{12.111}$$

and, since $\xi^2 \;=\; f x^2/2k_B T$ [c.f. (13.9, 13.11)], the functions $g_n(\xi)$, according to (12.56), are the eigenfunctions of $\mathcal{L}^+(\xi)$.
The eigenfunctions $f_n(\xi)$ form a complete basis for all functions with the property (13.14). Hence, we can expand $q(\xi, \tau|\xi_0, \tau_0)$

$$q(\xi, \tau|\xi_0, \tau_0) = \sum_{n=0}^{\infty} \alpha_n(t) f_n(\xi)\ . \tag{12.112}$$

Inserting this into the Smoluchowski equation (13.12, 13.15) results in

$$\sum_{n=0}^{\infty} \dot{\alpha}_n(\tau) f_n(\xi) \;=\; \sum_{n=0}^{\infty} \lambda_n\, \alpha_n(\tau)\, f_n(\xi)\,. \tag{12.113}$$

Exploiting the bi-orthogonality property (13.23) one derives

$$\dot{\alpha}_m(\tau) \;=\; \lambda_m\, \alpha_m(\tau)\,. \tag{12.114}$$

The general solution of of this differential equation is

$$\alpha_m(\tau) = \beta_m\, e^{\lambda_m \tau}\ . \tag{12.115}$$

Upon substitution into (13.27), the initial condition (13.13) reads

$$\sum_{n=0}^{\infty} \beta_n\, e^{\lambda_n \tau_0}\, f_n(\xi) \;=\; \delta(\xi - \xi_0)\ . \tag{12.116}$$

Taking again the scalar product with $g_m(\xi)$ and using (13.23) results in

$$\beta_m \, e^{\lambda_m \tau_0} = g_m(\xi_0) \,, \tag{12.117}$$

or

$$\beta_m = e^{-\lambda_m \tau_0} \, g_m(\xi_0) \,. \tag{12.118}$$

Hence, we obtain finally

$$q(\xi, \tau|\xi_0, \tau_0) \;=\; \sum_{n=0}^{\infty} e^{\lambda_n (\tau - \tau_0)} \, g_n(\xi_0) \, f_n(\xi) \,, \tag{12.119}$$

or, explicitly,

$$q(\xi, \tau|\xi_0, \tau_0) \;=\; \sum_{n=0}^{\infty} \frac{1}{2^n n! \sqrt{\pi}} \, e^{-2n(\tau-\tau_0)} \, H_n(\xi_0) \, e^{-\xi^2} \, H_n(\xi) \,. \tag{12.120}$$

Expression (13.35) can be simplified using the generating function of a product of two Hermit polynomials

$$\frac{1}{\sqrt{\pi(1-s^2)}} \, \exp\left[-\tfrac{1}{2}(y^2+y_0^2)\,\tfrac{1+s^2}{1-s^2} \;+\; 2yy_0\,\tfrac{s}{1-s^2}\right]$$

$$= \sum_{n=0}^{\infty} \frac{s^n}{2^n n! \sqrt{\pi}} \, H_n(y) \, e^{-y^2/2} \, H_n(y_0) \, e^{-y_0^2/2} \,. \tag{12.121}$$

Using

$$s = e^{-2(\tau-\tau_0)} \,, \tag{12.122}$$

one can show

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

$$= \;\frac{1}{\sqrt{\pi(1-s^2)}} \exp\left[-\frac{1}{2}(\xi^2+\xi_0^2)\,\frac{1+s^2}{1-s^2} \;+\; 2\xi\xi_0\,\frac{s}{1-s^2} \;-\; \frac{1}{2}\xi^2 \;+\; \frac{1}{2}\xi_0^2\right] \,. \tag{12.123}$$

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

$$\begin{aligned} E &= -\xi^2 \frac{1}{1-s^2} \;-\; \xi_0^2 \frac{s^2}{1-s^2} \;+\; 2\xi\xi_0 \frac{1}{1-s^2} \\ &= -\frac{1}{1-s^2}(\xi^2 \;-\; 2\xi\xi_0 s \;+\; \xi_0^2 s^2) \\ &= -\frac{(\xi-\xi_0 s)^2}{1-s^2} \end{aligned} \tag{12.124}$$

We obtain then

$$q(\xi, \tau|\xi_0, \tau_0) \;=\; \frac{1}{\sqrt{\pi(1-s^2)}} \exp\left[-\frac{(\xi-\xi_0 s)^2}{1-s^2}\right] \,, \tag{12.125}$$

where s is given by (13.37). 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 $f(\xi_0)$. The corresponding distribution $\tilde{q}(\xi,\tau)$ is ($\tau_0 = 0$)

$$\tilde{q}(\xi,\tau) \;=\; \int d\xi_0 \, \frac{1}{\sqrt{\pi(1-e^{-4\tau})}} \exp\left[-\frac{(\xi - \xi_0 e^{-2\tau})^2}{1-e^{-4\tau}} \right] f(\xi_0) \, . \tag{12.126}$$

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

$$\tilde{q}(\xi) \;=\; \frac{1}{\sqrt{\pi}} \, e^{-\xi^2} \int d\xi_0 \, f(\xi_0) \, . \tag{12.127}$$

If one carries out a corresponding analysis using (13.34) one obtains

$$\tilde{q}(\xi,\tau) \;=\; \sum_{n=0}^{\infty} e^{\lambda_n \tau} \, f_n(\xi) \int d\xi_0 \, g_n(\xi_0) \, f(\xi_0) \tag{12.128}$$

$$\sim \; f_0(\xi) \int d\xi_0 \, g_n(\xi_0) \, f(\xi_0) \quad \text{as } \tau \to \infty \, . \tag{12.129}$$

Using (13.21) and (13.22), this becomes

$$\tilde{q}(\xi,\tau) \;\sim\; \frac{1}{\sqrt{\pi}} \, e^{-\xi^2} \underbrace{H_0(\xi)}_{=1} \int d\xi_0 \, \underbrace{H_0(\xi_0)}_{=1} \, f(\xi_0) \tag{12.130}$$

in agreement with (13.42) as well as with (12.87). One can recognize from this result that the expansion (13.43), despite its appearance, conserves total probability $\int d\xi_0 \, f(\xi_0)$. One can also recoginze that, in general, the relaxation of an initial distribution $f(\xi_0)$ to the Boltzmann distribution involves numerous relaxation times $\tau_n = -1/\lambda_n$, even though the original Smoluchowski equation (13.1) contains only a single rate constant, the friction coefficient γ.