Chapter 7

Adjoint Smoluchowski Equation

Contents

7.1 The Adjoint Smoluchowski Equation

The *adjoint* or *backward Smoluchowski equation* governs the $\boldsymbol{r}_0$-dependence of the solution $p(\boldsymbol{r}, t|\boldsymbol{r}_0, t_0)$ of the Smoluchowski equation also referred to as the *forward equation*. The backward equation complements the forward equation and it often useful to determine observables connected with the solution of the Smoluchowski equation.

Forward and Backward Smoluchowski Equation

The Smoluchowski equation in a diffusion domain Ω can be written

$$\partial_t\, p(\boldsymbol{r}, t|\boldsymbol{r}_0, t_0) \;=\; \mathcal{L}(\boldsymbol{r})\; p(\boldsymbol{r}, t|\boldsymbol{r}_0, t_0) \tag{7.1}$$

where

$$\mathcal{L}(\boldsymbol{r}) \;=\; \boldsymbol{\nabla}\cdot D\left(\boldsymbol{\nabla} \;-\; \beta\,\boldsymbol{F}(\boldsymbol{r})\right) . \tag{7.2}$$

For $\boldsymbol{F}(\boldsymbol{r}) = -\boldsymbol{\nabla} U(\boldsymbol{r})$ one can express

$$\mathcal{L}(\boldsymbol{r}) \;=\; \boldsymbol{\nabla}\cdot D\; e^{-\beta\, U(\boldsymbol{r})}\,\boldsymbol{\nabla}\; e^{\beta\, U(\boldsymbol{r})} . \tag{7.3}$$

With the Smoluchowski equation (7.1) are associated three possible spatial boundary conditions for $h(\boldsymbol{r}) = p(\boldsymbol{r}, t|\boldsymbol{r}_0, t_0)$ on the surface $\partial\Omega$ of the diffusion domain Ω with local normal $\hat{\boldsymbol{a}}(\boldsymbol{r})$:

$$\text{(i)}\quad \hat{\boldsymbol{a}}(\boldsymbol{r})\cdot D\left(\boldsymbol{\nabla} \;-\; \beta\,\boldsymbol{F}(\boldsymbol{r})\right) h(\boldsymbol{r}) \;=\; 0\,, \qquad \boldsymbol{r} \in \partial\Omega \tag{7.4}$$

$$\text{(ii)}\quad h(\boldsymbol{r}) \;=\; 0\,, \qquad \boldsymbol{r} \in \partial\Omega \tag{7.5}$$

$$\text{(iii)}\quad \hat{\boldsymbol{a}}(\boldsymbol{r})\cdot D\left(\boldsymbol{\nabla} \;-\; \beta\,\boldsymbol{F}(\boldsymbol{r})\right) h(\boldsymbol{r}) \;=\; w(\boldsymbol{r})\; h(\boldsymbol{r})\,, \qquad \boldsymbol{r} \in \partial\Omega \tag{7.6}$$

where, in the latter equation, $w(\boldsymbol{r})$ is a continuous function which describes the effectivity of the surface $\partial\Omega$ to react locally. In case of $\boldsymbol{F}(\boldsymbol{r}) = -\boldsymbol{\nabla} U(\boldsymbol{r})$ one can express (7.4)

$$\text{(i)} \quad \hat{\boldsymbol{a}}(\boldsymbol{r}) \cdot D\, e^{-\beta U(\boldsymbol{r})} \boldsymbol{\nabla}\, e^{\beta U(\boldsymbol{r})}\, h(\boldsymbol{r}) \;=\; 0\;, \qquad\qquad \boldsymbol{r} \in \partial\Omega\;. \tag{7.7}$$

Similarly, one can write (7.6) in the form

$$\text{(iii)} \quad \hat{\boldsymbol{a}}(\boldsymbol{r}) \cdot D\, e^{-\beta U(\boldsymbol{r})} \boldsymbol{\nabla}\, e^{\beta U(\boldsymbol{r})}\, h(\boldsymbol{r}) \;=\; w(\boldsymbol{r})\, h(\boldsymbol{r})\;, \quad \boldsymbol{r} \in \partial\Omega\;. \tag{7.8}$$

The equations (7.1–7.6) allow one to determine the probability $p(\boldsymbol{r}, t|\boldsymbol{r}_0, t_0)$ to find a particle at position $\boldsymbol{r}$ at time t, given that the particle started diffusion at position $\boldsymbol{r}_0$ at time t_0. It holds

$$p(\boldsymbol{r}, t_0|\boldsymbol{r}_0, t_0) \;=\; \delta(\boldsymbol{r} - \boldsymbol{r}_0)\;. \tag{7.9}$$

For the Smoluchowski equation (7.1) exists an alternative form

$$\partial_t p(\boldsymbol{r}, t|\boldsymbol{r}_0, t_0) \;=\; \mathcal{L}^\dagger(\boldsymbol{r}_0)\; p(\boldsymbol{r}, t|\boldsymbol{r}_0, t_0)\;, \tag{7.10}$$

the so-called *adjoint* or *backward* equation, which involves a differential operator that acts on the $\boldsymbol{r}_0$-dependence of $p(\boldsymbol{r}, t|\boldsymbol{r}_0, t_0)$. The latter operator $\mathcal{L}^\dagger(\boldsymbol{r}_0)$ is the adjoint of the operator $\mathcal{L}(\boldsymbol{r})$ defined in (7.2) above.

Below we will determine the operator $\mathcal{L}^\dagger(\boldsymbol{r}_0)$ as well as the boundary conditions which the solution $p(\boldsymbol{r}, t|\boldsymbol{r}_0, t_0)$ of (7.10) must obey when $p(\boldsymbol{r}, t|\boldsymbol{r}_0, t_0)$ obeys the boundary conditions (7.4–7.6) in the original, so-called *forward* Smoluchowski equation (7.1).

Before proceeding with the derivation of the *backward* Smoluchowski equation we need to provide two key properties of the solution $p(\boldsymbol{r}, t|\boldsymbol{r}_0, t_0)$ of the *forward* Smoluchowski equation (7.1) connected with the time translation invariance of the equation and with the Markov property of the underlying stochastic process.

Homogeneous Time

In case that the Smoluchowski operator $\mathcal{L}(\boldsymbol{r})$ governing (7.1) and given by (7.3) is time-independent, one can make the substitution $t \to \tau = t - t_0$ in (7.1). This corresponds to the substitution $t_0 \to \tau_0 = 0$. The Smoluchowski equation (7.1) reads then

$$\partial_\tau\, p(\boldsymbol{r}, \tau|\boldsymbol{r}_0, 0) \;=\; \mathcal{L}(\boldsymbol{r})\, p(\boldsymbol{r}, \tau|\boldsymbol{r}_0, 0) \tag{7.11}$$

the solution of which is $p(\boldsymbol{r}, t - t_0|\boldsymbol{r}_0, 0)$, i.e., the solution of (7.1) for $p(\boldsymbol{r}, 0|\boldsymbol{r}_0, 0) = \delta(\boldsymbol{r} - \boldsymbol{r}_0)$. It follows

$$p(\boldsymbol{r}, t|\boldsymbol{r}_0, t_0) \;=\; p(\boldsymbol{r}, t - t_0|\boldsymbol{r}_0, 0)\;. \tag{7.12}$$

Chapman-Kolmogorov Equation

The solution $p(\boldsymbol{r}, t|\boldsymbol{r}_0, t_0)$ of the Smoluchowski equation corresponds to the initial condition (7.9). The solution $p(\boldsymbol{r}, t)$ for an initial condition

$$p(\boldsymbol{r}, t_0) \;=\; f(\boldsymbol{r}) \tag{7.13}$$

can be expressed

$$p(\boldsymbol{r}, t) \;=\; \int_\Omega d\boldsymbol{r}_0\; p(\boldsymbol{r}, t|\boldsymbol{r}_0, t_0)\; f(\boldsymbol{r}_0) \tag{7.14}$$

as can be readily verified. In fact, taking the time derivative yields

$$\begin{aligned} \partial_t\, p(\boldsymbol{r},t) &= \int_\Omega d\boldsymbol{r}_0\ \partial_t\, p(\boldsymbol{r},t|\boldsymbol{r}_0,t_0)\ f(\boldsymbol{r}_0) \\ &= \mathcal{L}(\boldsymbol{r}) \int_\Omega d\boldsymbol{r}_0\ p(\boldsymbol{r},t|\boldsymbol{r}_0,t_0)\ f(\boldsymbol{r}_0) \;=\; \mathcal{L}(\boldsymbol{r})\ p(\boldsymbol{r},t)\ . \end{aligned} \tag{7.15}$$

Furthermore, we note using (7.9)

$$p(\boldsymbol{r},t_0) \;=\; \int_\Omega d\boldsymbol{r}_0\ \delta(\boldsymbol{r}-\boldsymbol{r}_0)\ f(\boldsymbol{r}_0) \;=\; f(\boldsymbol{r})\ . \tag{7.16}$$

One can apply identity (7.14) to express $p(\boldsymbol{r},t|\boldsymbol{r}_0,t_0)$ in terms of the probalities $p(\boldsymbol{r},t|\boldsymbol{r}_1,t_1)$ and $p(\boldsymbol{r}_1,t_1|\boldsymbol{r}_0,t_0)$

$$p(\boldsymbol{r},t|\boldsymbol{r}_0,t_0) \;=\; \int_\Omega d\boldsymbol{r}_1\ p(\boldsymbol{r},t|\boldsymbol{r}_1,t_1)\ p(\boldsymbol{r}_1,t_1|\boldsymbol{r}_0,t_0)\ . \tag{7.17}$$

This latter identity is referred to as the *Chapman-Kolmogorov equation*. Both (7.14) and (7.17) state that knowledge of the distribution at a single instance t, i.e., $t=t_0$ or $t=t_1$, allows one to predict the distributions at all later times. The *Chapman-Kolmogorov equation* reflects the Markov property of the stochastic process assumed in the derivation of the Smoluchowski equation.
We like to state finally the *Chapman-Kolmogorov equation* (7.17) for the special case $t_1 = t-\tau$. Employing identity (7.12) one obtains

$$p(\boldsymbol{r},t|\boldsymbol{r}_0,t_0) \;=\; \int_\Omega d\boldsymbol{r}_1\ p(\boldsymbol{r},\tau|\boldsymbol{r}_1,0)\ p(\boldsymbol{r}_1,t-\tau|\boldsymbol{r}_0,t_0)\ . \tag{7.18}$$

Taking the time derivative yields, using (7.1),

$$\partial_t\, p(\boldsymbol{r},t|\boldsymbol{r}_0,t_0) \;=\; \int_\Omega d\boldsymbol{r}_1\ p(\boldsymbol{r},\tau|\boldsymbol{r}_1,0)\ \mathcal{L}(\boldsymbol{r}_1)\ p(\boldsymbol{r}_1,t-\tau|\boldsymbol{r}_0,t_0)\ . \tag{7.19}$$

The Adjoint Smoluchowski Operator

We want to determine now the operator $\mathcal{L}^\dagger$ in (7.10). For this purpose we prove the following identity [46]:

$$\int_\Omega d\boldsymbol{r}\ g(\boldsymbol{r})\ \mathcal{L}(\boldsymbol{r})\ h(\boldsymbol{r}) \;=\; \int_\Omega d\boldsymbol{r}\ h(\boldsymbol{r})\ \mathcal{L}^\dagger(\boldsymbol{r})\ g(\boldsymbol{r}) \;+\; \int_{\partial\Omega} d\boldsymbol{a}\cdot\boldsymbol{P}(g,h) \tag{7.20}$$

$$\mathcal{L}(\boldsymbol{r}) \;=\; \boldsymbol{\nabla}\cdot D\,\boldsymbol{\nabla} \;-\; \beta\,\boldsymbol{\nabla}\cdot D\,\boldsymbol{F}(\boldsymbol{r}) \tag{7.21}$$

$$\mathcal{L}^\dagger(\boldsymbol{r}) \;=\; \boldsymbol{\nabla}\cdot D\,\boldsymbol{\nabla} \;+\; \beta\, D\,\boldsymbol{F}(\boldsymbol{r})\cdot\boldsymbol{\nabla} \tag{7.22}$$

$$\begin{aligned} \boldsymbol{P}(g,h) &= g(\boldsymbol{r})\ D\,\boldsymbol{\nabla}\, h(\boldsymbol{r}) \;-\; h(\boldsymbol{r})\ D\,\boldsymbol{\nabla}\, g(\boldsymbol{r}) \\ &\qquad -\; \beta\, D\,\boldsymbol{F}(\boldsymbol{r})\ g(\boldsymbol{r})\ h(\boldsymbol{r})\ . \end{aligned} \tag{7.23}$$

The operator $\mathcal{L}^\dagger(\boldsymbol{r})$ is called the *adjoint* to the operator $\mathcal{L}(\boldsymbol{r})$, and $\boldsymbol{P}(g,h)$ is called the *concomitant* of $\mathcal{L}(\boldsymbol{r})$.
To prove (7.20–7.23) we note, using $\boldsymbol{\nabla}\cdot w(\boldsymbol{r})\,\boldsymbol{q}(\boldsymbol{r}) \;=\; \boldsymbol{q}(\boldsymbol{r})\cdot\boldsymbol{\nabla}\,w(\boldsymbol{r}) + w(\boldsymbol{r})\,\boldsymbol{\nabla}\cdot\boldsymbol{q}(\boldsymbol{r})$

$$\begin{aligned} \boldsymbol{\nabla}\cdot\big(\,g\,D\,\boldsymbol{\nabla}\,h \;-\; h\,D\,\boldsymbol{\nabla}\,g\,\big) &= ((\boldsymbol{\nabla} g))\,D\,((\boldsymbol{\nabla} h)) \;+\; g\,\boldsymbol{\nabla}\cdot D\,\boldsymbol{\nabla}\,h \\ &\qquad -\; ((\boldsymbol{\nabla} h))\,D\,((\boldsymbol{\nabla} g)) \;-\; h\,\boldsymbol{\nabla}\cdot D\,\boldsymbol{\nabla}\,g \\ &= g\,\boldsymbol{\nabla}\cdot D\,\boldsymbol{\nabla}\,h \;-\; h\,\boldsymbol{\nabla}\cdot D\,\boldsymbol{\nabla}\,g \end{aligned} \tag{7.24}$$

or

$$g\,\nabla \cdot D\,\nabla h \;=\; h\,\nabla \cdot D\,\nabla g \;+\; \nabla \cdot (\,g\,D\,\nabla h \;-\; h\,D\,\nabla g\,)\,. \tag{7.25}$$

The double brackets $(\!(\ldots)\!)$ limit the scope of the differential operators.
Furthermore, one can show

$$\nabla \cdot D\,\boldsymbol{F}\,g\,h \;\;=\;\; g\,\nabla \cdot D\,\boldsymbol{F}\,h \;+\; h\,D\,\boldsymbol{F} \cdot \nabla\,g \tag{7.26}$$

or

$$-g\,\nabla \cdot \beta D\,\boldsymbol{F}\,h \;\;=\;\; h\,\beta\,D\,\boldsymbol{F} \cdot \nabla\,g \;-\; \nabla \cdot \beta\,D\,\boldsymbol{F}\,g\,h\,. \tag{7.27}$$

Equations (7.26, 7.27) can be combined, using (7.21–7.23),

$$g\;\mathcal{L}\;h \;\;=\;\; h\;\mathcal{L}^{\dagger}\;g \;+\; \nabla \cdot \boldsymbol{P}(g,h) \tag{7.28}$$

from which follows (7.20).
In case

$$\boldsymbol{P}(g,h) \;\;=\;\; 0\;,\;\text{for}\;\boldsymbol{r}\,\in\,\partial\Omega\;, \tag{7.29}$$

which implies a condition on the functions $g(\boldsymbol{r})$ and $h(\boldsymbol{r})$, (7.20) corresponds to the identity

$$\langle g|\mathcal{L}(\boldsymbol{r})\,h\rangle_{\Omega} \;\;=\;\; \langle \mathcal{L}^{\dagger}(\boldsymbol{r})\,g|h\rangle_{\Omega}\;, \tag{7.30}$$

a property which is the conventional definition of a pair of adjoint operators. We like to determine now which conditions $g(\boldsymbol{r})$ and $h(\boldsymbol{r})$ must obey for (7.30) to be true.
We assume that $h(\boldsymbol{r})$ obeys one of the three conditions (7.4–7.6) and try to determine if conditions for $g(\boldsymbol{r})$ on $\partial\Omega$ can be found such that (7.29) and, hence, (7.30) hold. For this purpose we write (7.29) using (7.23)

$$g(\boldsymbol{r})\,D\left[\,\nabla\,f(\boldsymbol{r}) \;-\; \beta\,\boldsymbol{F}(\boldsymbol{r})\,f(\boldsymbol{r})\right] \;-\; h(\boldsymbol{r})\,D\,\nabla\,g(\boldsymbol{r}) \;\;=\;\; 0\;, \quad \boldsymbol{r}\,\in\,\partial\Omega\,. \tag{7.31}$$

In case that $h(\boldsymbol{r})$ obeys (7.4) follows

$$\text{(i')} \qquad \hat{\boldsymbol{a}}(\boldsymbol{r}) \cdot D\,\nabla\,g(\boldsymbol{r}) \;\;=\;\; 0\;, \qquad \boldsymbol{r}\in\partial\Omega\,. \tag{7.32}$$

In case that $h(\boldsymbol{r})$ obeys (7.5), follows

$$\text{(ii')} \qquad g(\boldsymbol{r}) \;\;=\;\; 0\;, \qquad \boldsymbol{r}\in\partial\Omega \tag{7.33}$$

and, in case that $h(\boldsymbol{r})$ obeys (7.6), follows

$$\text{(iii')} \qquad w\,g(\boldsymbol{r}) \;-\; \hat{\boldsymbol{a}}(\boldsymbol{r}) \cdot D\,\nabla\,g(\boldsymbol{r}) \;\;=\;\; 0\;, \qquad \boldsymbol{r}\in\partial\Omega\,. \tag{7.34}$$

From this we can conclude:

1. $\langle g|\mathcal{L}(\boldsymbol{r})\,h\rangle_{\Omega} \;=\; \langle \mathcal{L}^{\dagger}(\boldsymbol{r})\,g|h\rangle_{\Omega}$ holds if h obeys (i), i.e., (7.4), and g obeys (i′), i.e., (7.32);
2. $\langle g|\mathcal{L}(\boldsymbol{r})\,h\rangle_{\Omega} \;=\; \langle \mathcal{L}^{\dagger}(\boldsymbol{r})\,g|h\rangle_{\Omega}$ holds if h obeys (ii), i.e., (7.5), and g obeys (ii′), i.e., (7.33);
3. $\langle g|\mathcal{L}(\boldsymbol{r})\,h\rangle_{\Omega} \;=\; \langle \mathcal{L}^{\dagger}(\boldsymbol{r})\,g|h\rangle_{\Omega}$ holds if h obeys (iii), i.e., (7.6), and g obeys (iii′), i.e., (7.34).

Derivation of the Adjoint Smoluchowski Equation

The Chapman-Kolmogorov equation in the form (7.19) allows one to derive the adjoint Smoluchowski equation (7.10). For this purpose we replace $\mathcal{L}(\boldsymbol{r}_0)$ in (7.19) by the adjoint operator using (7.30)

$$\partial_t p(\boldsymbol{r}, t|\boldsymbol{r}_0, t_0) = \int_\Omega d\boldsymbol{r}_1 \; p(\boldsymbol{r}, \tau|\boldsymbol{r}_1, 0) \; \mathcal{L}(\boldsymbol{r}_1) \; p(\boldsymbol{r}_1, t-\tau|\boldsymbol{r}_0, t_0) \tag{7.35}$$

$$= \int_\Omega d\boldsymbol{r}_1 \; p(\boldsymbol{r}_1, t-\tau|\boldsymbol{r}_0, t_0) \; \mathcal{L}^\dagger(\boldsymbol{r}_1) \; p(\boldsymbol{r}, \tau|\boldsymbol{r}_1, 0) \; . \tag{7.36}$$

Note that $\mathcal{L}(\boldsymbol{r}_1)$ in (7.35) acts on the *first* spatial variable of $p(\boldsymbol{r}_1, t-\tau|\boldsymbol{r}_0, t_0)$ whereas $\mathcal{L}^\dagger(\boldsymbol{r}_1)$ in (7.36) acts on the *second* spatial variable of $p(\boldsymbol{r}, \tau|\boldsymbol{r}_1, 0)$. Taking the limit $\tau \to (t - t_0)$ yields, with $p(\boldsymbol{r}_1, t-\tau|\boldsymbol{r}_0, t_0) \to \delta(r_1 - r_0)$,

$$\partial_t \, p(\boldsymbol{r}, t|\boldsymbol{r}_0, t_0) = \mathcal{L}^\dagger(\boldsymbol{r}_0) \; p(\boldsymbol{r}, t-t_0|\boldsymbol{r}_0, 0) \; , \tag{7.37}$$

i.e., the *backward* Smoluchowski equation (7.10).

We need to specify now the boundary conditions which the solution of the adjoint Smoluchowski equation (7.37) must obey. It should be noted here that the adjoint Smoluchowski equation (7.37) considers $p(\boldsymbol{r}, t|\boldsymbol{r}_0, t_0)$ a function of $\boldsymbol{r}_0$, i.e., we need to specify boundary conditions for $\boldsymbol{r}_0 \in \Omega$. The boundary conditions arise in the step (7.35) $\to$ (7.36) above. This step requires:

1. In case that $p(\boldsymbol{r}, t|\boldsymbol{r}_0, t_0)$ obeys (i) for its $\boldsymbol{r}$-dependence, i.e., (7.4) for $\boldsymbol{r} \in \partial\Omega$, then $p(\boldsymbol{r}, t|\boldsymbol{r}_0, t_0)$ must obey (i′) for its $\boldsymbol{r}_0$-dependence, i.e., (7.32) for $\boldsymbol{r}_0 \in \partial\Omega$;

2. In case that $p(\boldsymbol{r}, t|\boldsymbol{r}_0, t_0)$ obeys (ii) for its $\boldsymbol{r}$-dependence, i.e., (7.5) for $\boldsymbol{r} \in \partial\Omega$, then $p(\boldsymbol{r}, t|\boldsymbol{r}_0, t_0)$ must obey (ii′) for its $\boldsymbol{r}_0$-dependence, i.e., (7.33) for $\boldsymbol{r}_0 \in \partial\Omega$;

3. In case that $p(\boldsymbol{r}, t|\boldsymbol{r}_0, t_0)$ obeys (iii) for its $\boldsymbol{r}$-dependence, i.e., (7.6) for $\boldsymbol{r} \in \partial\Omega$, then $p(\boldsymbol{r}, t|\boldsymbol{r}_0, t_0)$ must obey (iii′) for its $\boldsymbol{r}_0$-dependence, i.e., (7.34) for $\boldsymbol{r}_0 \in \partial\Omega$.

We note finally that $\mathcal{L}^\dagger(\boldsymbol{r})$, given by (7.22), in case that the force $\boldsymbol{F}(\boldsymbol{r})$ is related to a potential, i.e., $\boldsymbol{F}(\boldsymbol{r}) = -\boldsymbol{\nabla}\, U(\boldsymbol{r})$, can be written

$$\mathcal{L}^\dagger(\boldsymbol{r}) = e^{\beta\, U(\boldsymbol{r})} \, \boldsymbol{\nabla} \cdot D \; e^{-\beta\, U(\boldsymbol{r})} \, \boldsymbol{\nabla} \; . \tag{7.38}$$

This corresponds to expression (7.3) for $\mathcal{L}$.

7.2 Correlation Functions

Often an experimentalist prepares a system in an initial distribution $B(\boldsymbol{r})\, p_o(\boldsymbol{r})$ at a time t_0 and probes the spatial distribution of the system with sensitivity $A(\boldsymbol{r})$ at any time $t > t_0$. The observable is then the socalled **correlation function**

$$C_{A(\boldsymbol{r})\, B(\boldsymbol{r})}\,(t) = \int_\Omega d\boldsymbol{r} \int_\Omega d\boldsymbol{r}_{\mathbf{o}} \; A(\boldsymbol{r}) \; p(\boldsymbol{r}, t|\boldsymbol{r}_{\mathbf{o}}, t_0) \; B(\boldsymbol{r}_{\mathbf{o}}) \; , \tag{7.39}$$

where $p(\boldsymbol{r}, t|\boldsymbol{r}_{\mathbf{o}}, t_0)$ obeys the backward Smoluchowski equation (7.37) with the initial condition

$$p(\boldsymbol{r}, t_0|\boldsymbol{r}_0, t_0) = \delta(\boldsymbol{r} - \boldsymbol{r}_0) \; . \tag{7.40}$$

and the adjoint boundary conditions (7.32, 7.33, 7.34).
We like to provide a three examples of correlation functions. A trivial example arises in the case of $A(\boldsymbol{r}) = \delta(\boldsymbol{r} - \boldsymbol{r}')$ and $B(\boldsymbol{r}) = \delta(\boldsymbol{r} - \boldsymbol{r}'')/p_o(\boldsymbol{r})')$ which yields

$$C_{AB}(t) \;=\; p(\boldsymbol{r}', t|\boldsymbol{r}'', t_0)\;. \tag{7.41}$$

In the case one can only observe the total number of particles, i.e. $A(\boldsymbol{r}) = 1$, and for the special case $B(\boldsymbol{r}) = \delta(\boldsymbol{r} - \boldsymbol{r}')/p_o(\boldsymbol{r})')$, the correlation function is equal to the total particle number , customarily written

$$N(t, \boldsymbol{r}') \;=\; C_{1\,\delta(\boldsymbol{r}-\boldsymbol{r}')/p_o(\boldsymbol{r})')}(t) \;=\; \int_\Omega d\boldsymbol{r}\; p(\boldsymbol{r}, t|\boldsymbol{r}', t_0)\;. \tag{7.42}$$

The third correlation function, the so-called Mößbauer Lineshape Function, describes the absorption and re-emissions of γ-quants by ^{57}Fe. This isotope of iron can be enriched in the heme group of myoglobin. The excited state of ^{57}Fe has a lifetime $\Gamma^{-1} \approx 100\,ns$ before te isotope reemits the γ-quant. The re-emitted γ-quants interfere with the incident, affecting the lineshape of the spectrum. In the limit of small motion of the iron the following function holds for the spectral intensity

$$I(\omega) \;=\; \frac{\sigma_0\Gamma}{4}\int_{-\infty}^{\infty} dt\; e^{-i\omega t - \frac{1}{2}\Gamma|t|}\; G(\boldsymbol{k}, t)\;, \tag{7.43}$$

where

$$G(\boldsymbol{k}, t) \;=\; \int d\boldsymbol{r} \int d\boldsymbol{r_0}\; e^{i\boldsymbol{k}\cdot(\boldsymbol{r}-\boldsymbol{r}_0)}\; p(\boldsymbol{r}, t|\boldsymbol{r_0}, 0)\; p_0(\boldsymbol{r}_0) \;=\; C_{e^{i\boldsymbol{k}\cdot\boldsymbol{r}}\; e^{-i\boldsymbol{k}\cdot\boldsymbol{r}_o}}\;. \tag{7.44}$$

The term $-\frac{1}{2}\Gamma|t|$ in the exponent of (7.43) reflects the Lorentzian broadening of the spectral line due to the limited lifetime of the quants.
In order to evaluate a correlation function $C_{A(\boldsymbol{r})\,B(\boldsymbol{r})}(t)$ one can determine first the quantity

$$C_{A(\boldsymbol{r})}(t|\boldsymbol{r}_o) \;=\; \int_\Omega d\boldsymbol{r}\; A(\boldsymbol{r})\, p(\boldsymbol{r}, t|\boldsymbol{r}_o, t_o) \tag{7.45}$$

and evaluate then

$$C_{A(\boldsymbol{r})B(\boldsymbol{r})}(t|\boldsymbol{r}_o) \;=\; \int d\boldsymbol{r}_o\, B(\boldsymbol{r}_o) p(\boldsymbol{r}, t|\boldsymbol{r}_o, t_o)\;. \tag{7.46}$$

$C_{A(\boldsymbol{r})}(t|\boldsymbol{r}_o)$ can be obtained by carrying out the integral in (7.45) over the backward Smoluchowski equation (**??**7.37)). One obtains

$$\partial_t C_{A(\boldsymbol{r})}(t|\boldsymbol{r}_o) \;=\; \mathcal{L}^\dagger(\boldsymbol{r})\, C_{A(\boldsymbol{r})}(t|\boldsymbol{r}_o) \tag{7.47}$$

with the initial condition

$$C_{A(\boldsymbol{r})}(t_0|\boldsymbol{r}_o) \;= A(\boldsymbol{r}_0) \tag{7.48}$$

and the appropriate boundary condition selected from (7.32, 7.33, 7.34).