Chapter 3

Einstein Diffusion Equation

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In this chapter we want to consider the theory of the Fokker-Planck equation for molecules moving under the influence of random forces in force-free environments. Examples are molecules involved in Brownian motion in a fluid. Obviously, this situation applies to many chemical and biochemical system and, therefore, is of great general interest. Actually, we will assume that the fluids considered are viscous in the sense that we will neglect the effects of inertia. The resulting description, referred to as Brownian motion in the *limit of strong friction*, applies to molecular systems except if one considers very brief time intervals of a picosecond or less. The general case of Brownian motion for arbitrary friction will be covered further below.

3.1 Derivation and Boundary Conditions

Particles moving in a liquid without forces acting on the particles, other than forces due to random collisions with liquid molecules, are governed by the Langevin equation

$$m\,\ddot{\boldsymbol{r}} \;=\; -\gamma\,\dot{\boldsymbol{r}} \;+\; \sigma\,\boldsymbol{\xi}(t) \tag{3.1}$$

In the *limit of strong friction* holds

$$|\gamma\,\dot{\boldsymbol{r}}| \;\gg\; |m\,\ddot{\boldsymbol{r}}| \tag{3.2}$$

and, (3.1) becomes

$$\gamma\,\dot{\boldsymbol{r}} \;=\; \sigma\,\boldsymbol{\xi}(t)\;. \tag{3.3}$$

To this stochastic differential equation corresponds the Fokker-Planck equation [c.f. (2.138) and (2.148)]

$$\partial_t \, p(\boldsymbol{r}, t|\boldsymbol{r}_0, t_0) \;=\; \nabla^2 \, \frac{\sigma^2}{2\gamma^2} \, p(\boldsymbol{r}, t|\boldsymbol{r}_0, t_0) \; . \tag{3.4}$$

We assume in this chapter that σ and γ are spatially independent such that we can write

$$\partial_t \, p(\boldsymbol{r}, t|\boldsymbol{r}_0, t_0) \;=\; \frac{\sigma^2}{2\gamma^2} \, \nabla^2 \, p(\boldsymbol{r}, t|\boldsymbol{r}_0, t_0) \; . \tag{3.5}$$

This is the celebrated *Einstein diffusion equation* which describes microscopic transport of material and heat.

In order to show that the Einstein diffusion equation (3.5) reproduces the well-known diffusive behaviour of particles we consider the mean square displacement of a particle described by this equation, i.e., $\left\langle \left(\boldsymbol{r}(t) - \boldsymbol{r}(t_0) \right)^2 \right\rangle \sim t$. We first note that the mean square displacement can be expressed by means of the solution of (3.5) as follows

$$\left\langle \left(\boldsymbol{r}(t) - \boldsymbol{r}(t_0) \right)^2 \right\rangle \;=\; \int_{\Omega_\infty} d^3r \, \left(\boldsymbol{r}(t) - \boldsymbol{r}(t_0) \right)^2 \, p(\boldsymbol{r}, t|\boldsymbol{r}_0, t_0) \; . \tag{3.6}$$

Integration over Eq. (3.5) in a similar manner yields

$$\frac{d}{dt} \left\langle \left(\boldsymbol{r}(t) - \boldsymbol{r}(t_0) \right)^2 \right\rangle \;=\; \frac{\sigma^2}{2\gamma^2} \int_{\Omega_\infty} d^3r \, \left(\boldsymbol{r}(t) - \boldsymbol{r}(t_0) \right)^2 \, \nabla^2 \, p(\boldsymbol{r}, t|\boldsymbol{r}_0, t_0) \; . \tag{3.7}$$

Applying Green's theorem for two functions $u(\boldsymbol{r})$ and $v(\boldsymbol{r})$

$$\int_{\Omega_\infty} d^3r \, \left(u \nabla^2 v \,-\, v \nabla^2 u \right) \;=\; \int_{\partial\Omega_\infty} d\boldsymbol{a} \cdot \left(u \boldsymbol{\nabla} v \,-\, v \boldsymbol{\nabla} u \right) \tag{3.8}$$

for an infinite volume Ω and considering the fact that $p(\boldsymbol{r}, t|\boldsymbol{r}_0, t_0)$ must vanish at infinity we obtain

$$\frac{d}{dt} \left\langle \left(\boldsymbol{r}(t) - \boldsymbol{r}(t_0) \right)^2 \right\rangle \;=\; \frac{\sigma^2}{2\gamma^2} \int_{\Omega_\infty} d^3r \; p(\boldsymbol{r}, t|\boldsymbol{r}_0, t_0) \; \nabla^2 \left(\boldsymbol{r} - \boldsymbol{r}_0 \right)^2 \; . \tag{3.9}$$

With $\nabla^2 \, (\boldsymbol{r} - \boldsymbol{r}_0)^2 = 6$ this is

$$\frac{d}{dt} \left\langle \left(\boldsymbol{r}(t) - \boldsymbol{r}(t_0) \right)^2 \right\rangle \;=\; 6 \, \frac{\sigma^2}{2\gamma^2} \int_{\Omega_\infty} d^3r \; p(\boldsymbol{r}, t|\boldsymbol{r}_0, t_0) \; . \tag{3.10}$$

We will show below that the integral on the r.h.s. remains constant as long as one does not assume the existence of chemical reactions. Hence, for a reaction free case we can conclude

$$\left\langle \left(\boldsymbol{r}(t) - \boldsymbol{r}(t_0) \right)^2 \right\rangle \;=\; 6 \, \frac{\sigma^2}{2\,\gamma^2} \; t \; . \tag{3.11}$$

For diffusing particles one expects for this quantity a behaviour $6D(t - t_0)$ where D is the diffusion coefficient. Hence, the calculated dependence describes a diffusion process with diffusion coefficient

$$D = \frac{\sigma^2}{2\,\gamma^2} \; . \tag{3.12}$$

One can write the *Einstein diffusion equation* accordingly

$$\partial_t\, p(\boldsymbol{r},t|\boldsymbol{r}_0,t_0) \;=\; D\,\nabla^2\, p(\boldsymbol{r},t|\boldsymbol{r}_0,t_0)\;. \tag{3.13}$$

We have stated before that the Wiener process describes a diffusing particle as well. In fact, the three-dimensional generalization of (2.47)

$$p(\boldsymbol{r},t|\boldsymbol{r}_0,t_0) \;=\; \big(4\pi\,D\,(t-t_0)\big)^{-\frac{3}{2}}\;\exp\!\left[-\frac{(\boldsymbol{r}-\boldsymbol{r}_0)^2}{4\,D\,(t-t_0)}\right] \tag{3.14}$$

is the solution of (3.13) for the initial and boundary conditions

$$p(\boldsymbol{r},t\to t_0|\boldsymbol{r}_0,t_0) \;=\; \delta(\boldsymbol{r}-\boldsymbol{r}_0)\;, \qquad p(|\boldsymbol{r}|\to\infty,t|\boldsymbol{r}_0,t_0) \;=\; 0\;. \tag{3.15}$$

One refers to the solution (3.14) as the *Green's function*. The Green's function is only uniquely defined if one specifies spatial boundary conditions on the surface $\partial\Omega$ surrounding the diffusion space Ω. Once the Green's function is available one can obtain the solution $p(\boldsymbol{r},t)$ for the system for any initial condition, e.g. for $p(\boldsymbol{r},t\to 0) = f(\boldsymbol{r})$

$$p(\boldsymbol{r},t) \;=\; \int_{\Omega_\infty} d^3r_0\; p(\boldsymbol{r},t|\boldsymbol{r}_0,t_0)\, f(\boldsymbol{r}_0)\;. \tag{3.16}$$

We will show below that one can also express the observables of the system in terms of the Green's function. We will also introduce Green's functions for different spatial boundary conditions. Once a Green's function happens to be known, it is invaluable. However, because the Green's function entails complete information about the time evolution of a system it is correspondingly difficult to obtain and its usefulness is confined often to formal manipulations. In this regard we will make extensive use of Green's functions later on.
The system described by the Einstein diffusion equation (3.13) 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 on $\partial\Omega$. In order to formulate these boundary conditions we consider the flux of particles through consideration of the total number of particles diffusing in Ω defined through

$$N_\Omega(t|\boldsymbol{r}_0,t_0) \;=\; \int_\Omega d^3r\; p(\boldsymbol{r},t|\boldsymbol{r}_0,t_0)\;. \tag{3.17}$$

Since there are no terms in the diffusion equation (3.13) which affect the number of particles (we will introduce such terms later on) 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. In fact, taking the time derivative of (3.17) yields, using (3.13) and $\nabla^2 \;=\; \boldsymbol{\nabla}\cdot\boldsymbol{\nabla}$,

$$\partial_t N_\Omega(t|\boldsymbol{r}_0,t_0) \;=\; \int_\Omega d^3r\; D\;\boldsymbol{\nabla}\cdot\boldsymbol{\nabla}\, p(\boldsymbol{r},t|\boldsymbol{r}_0,t_0)\;. \tag{3.18}$$

Gauss' theorem

$$\int_\Omega d^3r\;\boldsymbol{\nabla}\cdot\boldsymbol{v}(\boldsymbol{r}) \;=\; \int_{\partial\Omega} d\boldsymbol{a}\cdot\boldsymbol{v}(\boldsymbol{r}) \tag{3.19}$$

for some vector-valued function $\boldsymbol{v}(\boldsymbol{r})$, allows one to write (3.18)

$$\partial_t\, N_\Omega(t|\boldsymbol{r}_0,t_0) \;=\; \int_{\partial\Omega} d\boldsymbol{a}\cdot D\,\boldsymbol{\nabla}\, p(\boldsymbol{r},t|\boldsymbol{r}_0,t_0)\;. \tag{3.20}$$

Here

$$\boldsymbol{j}(\boldsymbol{r},t|\boldsymbol{r}_0,t_0) \quad = \quad D\ \boldsymbol{\nabla}\, p(\boldsymbol{r},t|\boldsymbol{r}_0,t_0) \tag{3.21}$$

must be interpreted as the flux of particles which leads to changes of the total number of particles in case the flux does not vanish at the surface $\partial\Omega$ of the diffusion space Ω. Equation (3.21) is also known as Fick's law. We will refer to

$$\boldsymbol{\mathcal{J}}_0(\boldsymbol{r}) \quad = \quad D(\boldsymbol{r})\,\boldsymbol{\nabla} \tag{3.22}$$

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

The flux operator $\boldsymbol{\mathcal{J}}_0(\boldsymbol{r})$ governs the spatial boundary conditions since it allows one 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 diffusion equation exists. Such solution cannot exist if it has to satisfy in an infinitesimal neighbourhood entailing $\partial\Omega$ two different boundary conditions.

The first type of boundary condition is specified by

$$\hat{\boldsymbol{a}}(\boldsymbol{r}) \cdot \boldsymbol{\mathcal{J}}_0(\boldsymbol{r})\ p(\boldsymbol{r},t|\boldsymbol{r}_0,t_0) \quad = \quad 0\ , \quad \boldsymbol{r} \in \partial\Omega_i\ , \tag{3.23}$$

which obviously implies that particles do not cross the boundary, i.e., are reflected. Here $\hat{\boldsymbol{a}}(\boldsymbol{r})$ denotes a unit vector normal to the surface $\partial\Omega_i$ at $\boldsymbol{r}$ (see Figure 3.1). We will refer to (3.23) as the *reflection boundary condition*.

The second type of boundary condition is

$$p(\boldsymbol{r},t|\boldsymbol{r}_0,t_0) \quad = \quad 0\ , \quad \boldsymbol{r} \in \partial\Omega_i\ . \tag{3.24}$$

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 (3.24) as the *reaction boundary condition*.

The third type of boundary condition,

$$\hat{\boldsymbol{a}}(\boldsymbol{r}) \cdot \boldsymbol{\mathcal{J}}_0\ p(\boldsymbol{r},t|\boldsymbol{r}_0,t_0) \quad = \quad w\, p(\boldsymbol{r},t|\boldsymbol{r}_0,t_0)\ , \quad \boldsymbol{r}\ \text{on}\ \partial\Omega_i\ , \tag{3.25}$$

describes the case of intermediate reactivity at the boundary. The reactivity is measured by the parameter w. For $w = 0$ in (3.25) $\partial\Omega_i$ corresponds to a non-reactive, i.e., reflective boundary. For $w \to \infty$ the condition (3.25) 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 (3.25) as the *radiation boundary condition*.

In the following we want to investigate some exemplary instances of the Einstein diffusion equation for which analytical solutions are available.

3.2 Free Diffusion in One-dimensional Half-Space

As a first example we consider a particle diffusing freely in a one-dimensional half-space $x \geq 0$. This situation is governed by the Einstein diffusion equation (3.13) in one dimension

$$\partial_t\, p(x,t|x_0,t_0) \quad = \quad D\ \partial_x^2\, p(x,t|x_0,t_0)\ , \tag{3.26}$$

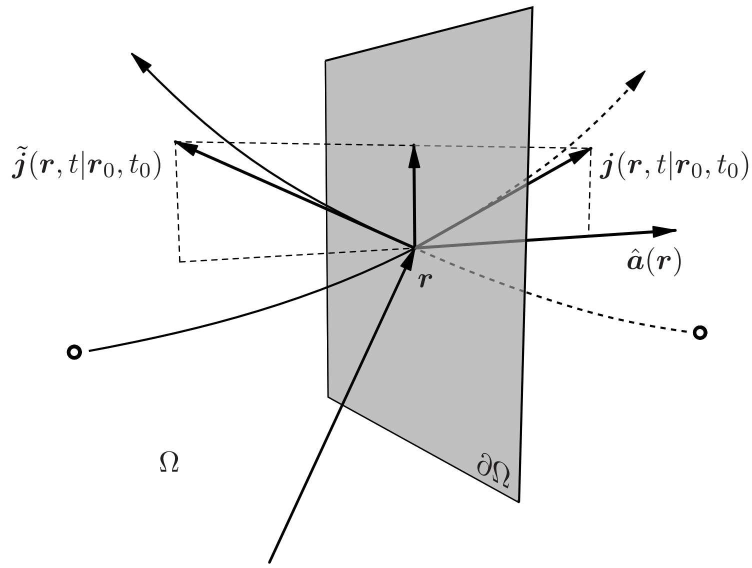

Figure 3.1: depicts the reflection of a partilcle at $\partial\Omega$. After the reflection the particle proceeds on the trajectory of it's mirror image. The probability flux $\boldsymbol{j}(\boldsymbol{r}, t|\boldsymbol{r}_0, t_0)$ of the particle prior to relfection and the probability flux $\tilde{\boldsymbol{j}}(\boldsymbol{r}, t|\boldsymbol{r}_0, t_0)$ of it's mirror image amount to a total flux vector parallel to the surface $\partial\Omega$ and normal to the normalized surface vector $\hat{\boldsymbol{a}}(\boldsymbol{r})$ which results in the boundary condition (3.23).

where the solution considered is the Green's function, i.e., satisfies the initial condition

$$p(x, t \to 0|x_0, t_0) \quad = \quad \delta(x - x_0) \; . \tag{3.27}$$

One-Dimensional Half-Space with Reflective Wall

The transport space is limited at $x = 0$ by a reflective wall. This wall is represented by the boundary condition

$$\partial_x \, p(x, t|x_0, t_0) \quad = \quad 0 \; . \tag{3.28}$$

The other boundary is situated at $x \to \infty$. Assuming that the particle started diffusion at some finite x_0 we can postulate the second boundary condition

$$p(x \to \infty, t|x_0, t_0) \quad = \quad 0 \; . \tag{3.29}$$

Without the wall at $x = 0$, i.e., if (3.28) would be replaced by $p(x \to -\infty, t|x_0, t_0) = 0$, the solution would be the one-dimensional equivalent of (3.14), i.e.,

$$p(x, t|x_0, t_0) \quad = \quad \frac{1}{\sqrt{4\pi \, D \, (t - t_0)}} \, \exp\!\left[-\frac{(x - x_0)^2}{4 \, D \, (t - t_0)} \right] \; . \tag{3.30}$$

In order to satisfy the boundary condition one can add a second term to this solution, the Green's function of an imaginary particle starting diffusion at position $-x_0$ behind the boundary. One obtains

$$p(x,t|x_0,t_0) = \frac{1}{\sqrt{4\pi\, D\,(t-t_0)}}\,\exp\left[-\frac{(x-x_0)^2}{4\,D\,(t-t_0)}\right] + \frac{1}{\sqrt{4\pi\, D\,(t-t_0)}}\,\exp\left[-\frac{(x+x_0)^2}{4\,D\,(t-t_0)}\right]\,, \quad x \geq 0\,, \tag{3.31}$$

which, as stated, holds only in the available half-space $x \geq 0$. Obviously, this function is a solution of (3.26) since both terms satisfy this equation. This solution also satisfies the boundary condition (3.29). One can easily convince oneself either on account of the reflection symmetry with respect to $x = 0$ of (3.31) or by differentiation, that (3.31) does satisfy the boundary condition at $x = 0$.
The solution (3.31) bears a simple interpretation. The first term of this solution describes a diffusion process which is unaware of the presence of the wall at $x = 0$. In fact, the term extends with non-vanishing values into the unavailable half-space $x \leq 0$. This "loss" of probability is corrected by the second term which, with its tail for $x \geq 0$, balances the missing probability. In fact, the $x \geq 0$ tail of the second term is exactly the mirror image of the "missing" $x \leq 0$ tail of the first term. One can envision that the second term reflects at $x = 0$ that fraction of the first term of (3.31) which describes a freely diffusing particle without the wall.

One-Dimensional Half-Space with Absorbing Wall

We consider now a one-dimensional particle which diffuses freely in the presence of an absorbing wall at $x = 0$. The diffusion equation to solve is again (3.26) with initial condition (3.27) and boundary condition (3.29) at $x \to \infty$. Assuming that the absorbing wall, i.e., a wall which consumes every particle impinging on it, is located at $x = 0$ we have to replace the boundary condition (3.28) of the previous problem by

$$p(x=0,t|x_0,t_0) = 0\,. \tag{3.32}$$

One can readily convince oneself, on the ground of a symmetry argument similar to the one employed above, that

$$p(x,t|x_0,t_0) = \frac{1}{\sqrt{4\pi\, D\,(t-t_0)}}\,\exp\left[-\frac{(x-x_0)^2}{4\,D\,(t-t_0)}\right] - \frac{1}{\sqrt{4\pi\, D\,(t-t_0)}}\,\exp\left[-\frac{(x+x_0)^2}{4\,D\,(t-t_0)}\right]\,, \quad x \geq 0 \tag{3.33}$$

is the solution sought. In this case the $x \leq 0$ tail of the first term which describes barrierless free diffusion is not replaced by the second term, but rather the second term describes a *further* particle loss. This contribution is not at all obvious and we strongly encourage the reader to consider the issue. Actually it may seem "natural" that the solution for an absorbing wall would be obtained if one just left out the $x \leq 0$ tail of the first term in (3.33) corresponding to particle removal by the wall. It appears that (3.33) removes particles also at $x \geq 0$ which did not have reached the absorbing wall yet. This, however, is not true. Some of the probability of a freely diffusing particle in a barrierless space for $t > 0$ at $x > 0$ involves Brownian trajectories of that particle which had visited the half-space $x \leq 0$ at earlier times. These instances of the Brownian processes are removed by the second term in (3.33) (see Figure 3.2).

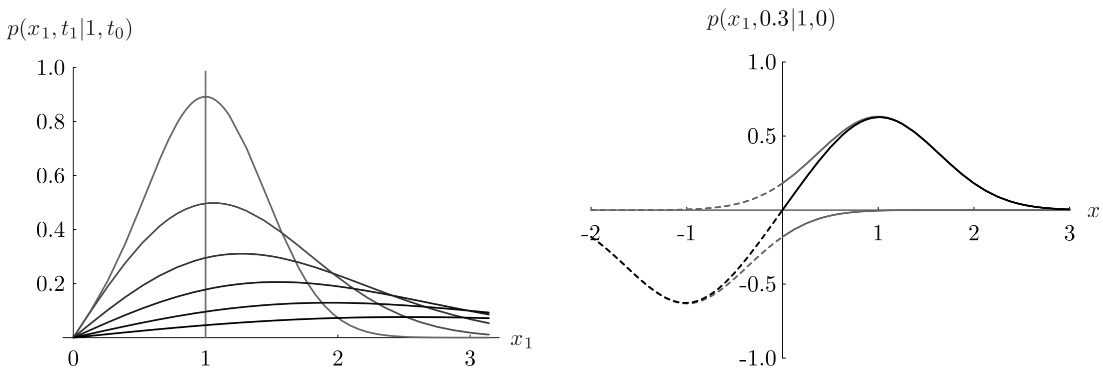

Figure 3.2: Probability density distribution of a freely diffusing particle in half-space with an absobing boundary at $x = 0$. The left plot shows the time evolution of equation (3.33) with $x_0 = 1$ and $(t_1 - t_0) = 0.0, 0.1, 0.3, 0.6, 1.0, 1.7$, and 3.0 for $D = 1$ in arbitrary temporal and spatial units. The right plot depicts the assembly of solution (3.33) with two Gaussian distributions at $(t_1 - t_0) = 0.3$.

Because of particle removal by the wall at $x = 0$ the total number of particles is not conserved. The particle number corresponding to the Greens function $p(x, t|x_0, t_0)$ is

$$N(t|x_0, t_0) \;=\; \int_0^\infty dx\; p(x, t|x_0, t_0)\;. \tag{3.34}$$

Introducing the integration variable

$$y \;=\; \frac{x}{\sqrt{4\,D\,(t - t_0)}} \tag{3.35}$$

(3.34) can be written

$$\begin{aligned} N(t|x_0, t_0) &= \frac{1}{\sqrt{\pi}} \int_0^\infty dy\; \exp\big[-(y - y_0)^2\big] \;-\; \frac{1}{\sqrt{\pi}} \int_0^\infty dy\; \exp\big[-(y - y_0)^2\big] \\ &= \frac{1}{\sqrt{\pi}} \int_{-y_0}^\infty dy\; \exp\big[-y^2\big] \;-\; \frac{1}{\sqrt{\pi}} \int_{y_0}^\infty dy\; \exp\big[-y^2\big] \\ &= \frac{1}{\sqrt{\pi}} \int_{-y_0}^{y_0} dy\; \exp\big[-y^2\big] \qquad (3.36) \\ &= \frac{2}{\sqrt{\pi}} \int_0^{y_0} dy\; \exp\big[-y^2\big]\;. \qquad (3.37) \end{aligned}$$

Employing the definition of the so-called error function

$$\mathrm{erf}(z) \;=\; \frac{2}{\sqrt{\pi}} \int_0^z dy\; \exp\big[-y^2\big] \tag{3.38}$$

leads to the final expression, using (3.35),

$$N(t|x_0, t_0) \;=\; \mathrm{erf}\left[\frac{x_0}{\sqrt{4\,D\,(t - t_0)}}\right]\;. \tag{3.39}$$

The particle number decays to zero asymptotically. In fact, the functional property of erf(z) reveal

$$N(t|x_0, t_0) \sim \frac{x_0}{\sqrt{\pi D(t-t_0)}} \quad \text{for } t \to \infty \,. \tag{3.40}$$

This decay is actually a consequence of the ergodic theorem which states that one-dimensional Brownian motion with certainty will visit every point of the space, i.e., also the absorbing wall. We will see below that for three-dimensional Brownian motion not all particles, even after arbitrary long time, will encounter a reactive boundary of finite size.
The rate of particle decay, according to (3.39), is

$$\partial_t\, N(t|x_0, t_0) = -\frac{x_0}{\sqrt{2\pi\, D\,(t-t_0)}\,(t-t_0)} \exp\left[-\frac{x_0^2}{4\,D\,(t-t_0)} \right] \,. \tag{3.41}$$

An alternative route to determine the decay rate follows from (3.21) which reads for the case considered here,

$$\partial_t\, N(t|x_0, t_0) = -D\; \partial_x\, p(x, t|x_0, t_0)\Big|_{x=0} \,. \tag{3.42}$$

Evaluation of this expression yields the same result as Eq. (3.41). This illustrates how useful the relationship (3.21) can be.

3.3 Fluorescence Microphotolysis

Fluorescence microphotolysis is a method to measure the diffusion of molecular components (lipids or proteins) in biological membranes. For the purpose of measurement one labels the particular molecular species to be investigated, a membrane protein for example, with a fluorescent marker. This marker is a molecular group which exhibits strong fluorescence when irradiated; in the method the marker is chosen such that there exists a significant probability that the marker is irreversibly degraded through irradiation into a non-fluorescent form.
The diffusion measurement of the labelled molecular species proceeds then in two steps. In the first step at time t_o , a small, circular membrane area of diameter a (some μm) is irradiated by a short, intensive laser pulse of 1-100 mW, causing the irreversible change (photolysis) of the fluorescent markers within the illuminated area. For all practical purposes, this implies that no fluorescent markers are left in that area and a corresponding distribution $w(x, y, t_o)$ is prepared.
In the second step, the power of the laser beam is reduced to a level of 10-1000 nW at which photolysis is negligible. The fluorescence signal evoked by the attenuated laser beam,

$$N(t|t_o) = c_o \int_{\Omega_{\text{laser}}} dx\, dy\; w(x, y, t) \tag{3.43}$$

is then a measure for the number of labelled molecules in the irradiated area at time t. Here Ω_{laser} denotes the irradiated area (assuming an idealized, homogenous irradiation profile) and c_o is a suitable normalization constant. $N(t|t_o)$ is found to increase rapidly in experiments due diffusion of unphotolysed markers into the area. Accordingly, the fluorescence recovery can be used to determine the diffusion constant D of the marked molecules.
In the following, we will assume that the irradiated area is a stripe of thickness $2a$, rather than a circular disk. This geometry will simplify the description, but does not affect the behaviour of the system in principle.

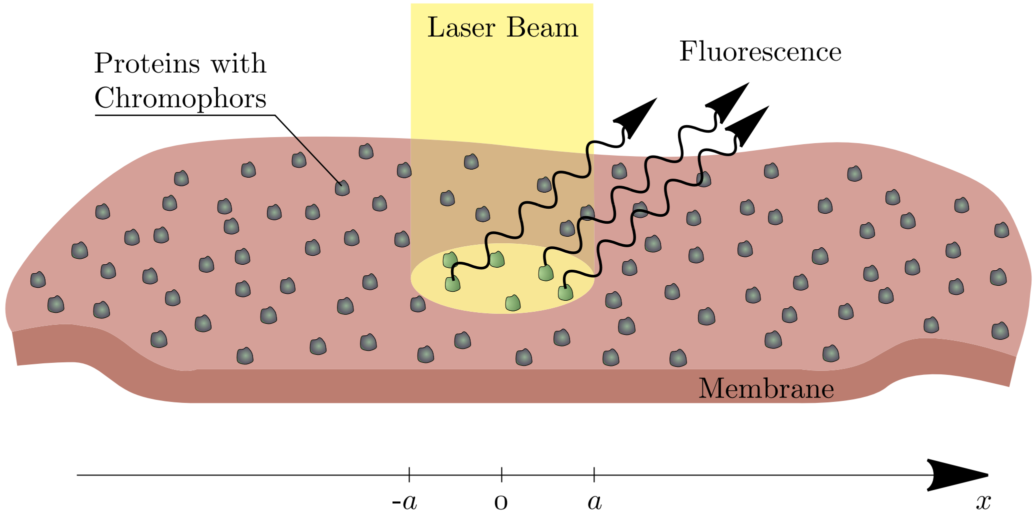

Figure 3.3: Schematic drawing of a fluorescence microphotolysis experiment.

For $t < t_0$ the molecular species under consideration, to be referred to as particles, is homogeneously distributed as described by $w(x,t) = 1$. At $t = t_0$ photolysis in the segment $-a < x < a$ eradicates all particles, resulting in the distribution

$$w(x,t_0) \quad = \quad \theta(a-x) \; + \; \theta(x-a) \; , \tag{3.44}$$

where θ is the Heavisides step function

$$\theta(x) \quad = \quad \begin{cases} 0 & \text{for } x \, < \, 0 \\ 1 & \text{for} x \, \geq \, 0 \end{cases} \; . \tag{3.45}$$

The subsequent evolution of $w(x,y,t)$ is determined by the two-dimensional diffusion equation

$$\partial_t \, w(x,y,t) \quad = \quad D \, \left(\partial_x^2 \, + \, \partial_y^2 \right) \, w(x,y,t) \; . \tag{3.46}$$

For the sake of simplicity, one may assume that the membrane is infinite, i.e., large compared to the length scale a. Since the initial distribution (3.44) does not depend on y, once can assume that $w(x,y,t)$ remains independent of y since distribution, in fact, is a solution of (3.46). However, one can eliminate consideration of y and describe teh ensuing distribution $w(x,t)$ by means of the one-dimensional diffusion equation

$$\partial_t \, w(x,t) \quad = \quad D \, \partial_x^2 \, w(x,t) \; . \tag{3.47}$$

with boundary condition

$$\lim_{|x| \to \infty} \, w(x,t) \quad = \quad 0 \; . \tag{3.48}$$

The Green's function solution of this equation is [c.f. (3.14)]

$$p(x,t|x_0,t_0) \quad = \quad \frac{1}{\sqrt{4\pi D(t-t_0)}} \; \exp\left[-\frac{(x-x_0)^2}{4D(t-t_0)} \right] \; . \tag{3.49}$$

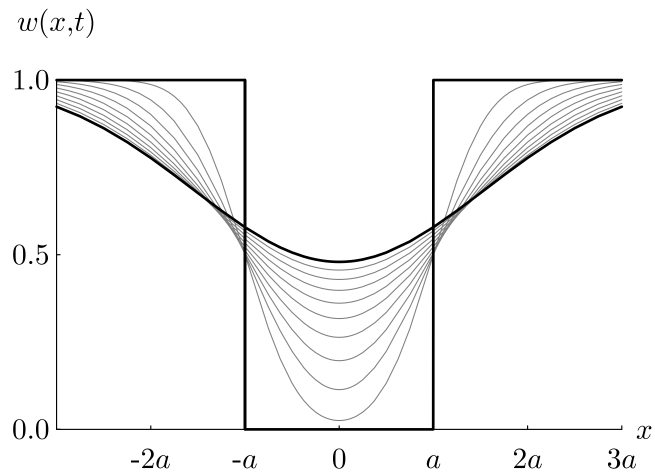

Figure 3.4: Time evolution of the probability distribution $w(x,t)$ for $D = \frac{1}{a^2}$ in time steps $t = 0, 0.1, 0.2, \ldots, 1.0$.

which satisfies the initial condition $p(x,t_0|x_0,t_0) = \delta(x-x_0)$. The solution for the initial probability distribution (3.44), according to (3.16), is then

$$w(x,t) \quad = \quad \int_{-\infty}^{+\infty} dx_o \; p(x,t|x_o,t_o) \; \left(\theta(a-x) + \theta(x-a)\right) \; . \tag{3.50}$$

This can be written, using (3.49) and (3.45),

$$\begin{aligned} w(x,t) \quad &= \quad \int_{-\infty}^{-a} dx_0 \; \frac{1}{\sqrt{4\pi D(t-t_0)}} \; \exp\left[-\frac{(x-x_0)^2}{4D(t-t_0)}\right] \\ &\quad + \int_{a}^{\infty} dx_0 \; \frac{1}{\sqrt{4\pi D(t-t_0)}} \; \exp\left[-\frac{(x-x_0)^2}{4D(t-t_0)}\right] \; . \end{aligned} \tag{3.51}$$

Identifying the integrals with the error function $\operatorname{erf}(x)$ one obtains

$$\begin{aligned} w(x,t) \quad &= \quad \frac{1}{2}\operatorname{erf}\left[\frac{x-x_0}{2\sqrt{D(t-t_0)}}\right]\Bigg|_{-\infty}^{-a} \; + \; \frac{1}{2}\operatorname{erf}\left[\frac{x-x_0}{2\sqrt{D(t-t_0)}}\right]\Bigg|_{a}^{\infty} \\ &= \quad \left(\frac{1}{2}\operatorname{erf}\left[\frac{x+a}{2\sqrt{D(t-t_0)}}\right] + \frac{1}{2}\right) \; - \; \left(\frac{1}{2}\operatorname{erf}\left[\frac{x-a}{2\sqrt{D(t-t_0)}}\right] - \frac{1}{2}\right) \end{aligned}$$

and, finally,

$$w(x,t) \quad = \quad \frac{1}{2}\left(\operatorname{erf}\left[\frac{x+a}{2\sqrt{D(t-t_0)}}\right] \; - \; \operatorname{erf}\left[\frac{x-a}{2\sqrt{D(t-t_0)}}\right]\right) \; + \; 1 \; . \tag{3.52}$$

The time evolution of the probability distribution $w(x,t)$ is displayed in Figure 3.4 for $D = \frac{1}{a^2}$ in time steps $t = 0, 0.1, 0.2, \ldots, 1.0$.
The observable $N(t,|t_o)$, given in (3.43) is presently defined through

$$N(t|t_o) \quad = \quad c_o \int_{-a}^{+a} dx \; w(x,t) \tag{3.53}$$

Comparision with (3.52) shows that the evaluation requires one to carry out integrals over the error function which we will, hence, determine first. One obtains by means of conventional techniques

$$\begin{aligned} \int dx \;\operatorname{erf}(x) &= x\;\operatorname{erf}(x) \;-\; \int dx\; x\,\frac{d}{dx}\;\operatorname{erf}(x) \\ &= x\;\operatorname{erf}(x) \;-\; \frac{1}{\sqrt{\pi}}\int 2x\,dx\;\exp(-x^2) \\ &= x\;\operatorname{erf}(x) \;-\; \frac{1}{\sqrt{\pi}}\int d\xi\;\exp(-\xi) \quad ,\text{ for } \xi = x^2 \\ &= x\;\operatorname{erf}(x) \;+\; \frac{1}{\sqrt{\pi}}\exp(-\xi) \\ &= x\;\operatorname{erf}(x) \;+\; \frac{1}{\sqrt{\pi}}\exp(-x^2)\;. \end{aligned} \tag{3.54}$$

Equiped with this result one can evaluate (3.53). For this purpose we adopt the normalization factor $c_o = \frac{1}{2a}$ and obtain

$$\begin{aligned} N(t|t_0) &= \frac{1}{2a}\int_{-a}^{+a} dx\;\frac{1}{2}\left(\operatorname{erf}\left[\frac{x+a}{2\sqrt{D(t-t_0)}}\right] \;-\; \operatorname{erf}\left[\frac{x-a}{2\sqrt{D(t-t_0)}}\right] \;+\; 2\right) \\ &= \frac{1}{4a}\left(\frac{2\sqrt{D\,(t-t_0)}}{\pi}\;\exp\left[\frac{(x+a)^2}{4\,D\,(t-t_0)}\right] \;+\; (x+a)\;\operatorname{erf}\left[\frac{x+a}{2\sqrt{D\,(t-t_0)}}\right]\right. \\ &\quad - \left.\frac{2\sqrt{D\,(t-t_0)}}{\pi}\;\exp\left[\frac{(x-a)^2}{4\,D\,(t-t_0)}\right] \;+\; (x-a)\;\operatorname{erf}\left[\frac{x-a}{2\sqrt{D\,(t-t_0)}}\right] \;+\; 2x\right)\Bigg|_{-a}^{a} \\ &= \frac{\sqrt{D(t-t_0)}}{a\sqrt{\pi}}\left(\exp\left[-\frac{a^2}{D\,(t-t_0)}\right] \;-\; 1\right) \;+\; \operatorname{erf}\left[\frac{a}{\sqrt{D\,(t-t_0)}}\right] \;+\; 1\,. \end{aligned} \tag{3.55}$$

The fluorescent recovery signal $N(t|t_o)$ is displayed in Figure 3.5. The result exhibits the increase of fluorescence in illuminated stripe $[-a,a]$: particles with a working fluorescent marker diffuse into segment $[-a,a]$ and replace the bleached fluorophore over time. Hence, $N(t|t_o)$ is an increasing function which approaches asymptotically the value 1, i.e., the signal prior to photolysis at $t = t_0$. One can determine the diffusion constant D by fitting normalized data of fluorescence measurements to $N(t|t_o)$. Values for the diffusion constant D range from 10 μm^2 to 0.001 μm^2. For this purpose we simplify expression (3.55) introducing the dimensionless variable

$$\xi \;=\; \frac{a}{\sqrt{D\,(t-t_0)}}\;. \tag{3.56}$$

One can write then the observable in teh form

$$N(\xi) \;=\; \frac{1}{\xi\sqrt{\pi}}\left(\exp\left[-\xi^2\right] \;-\; 1\right) \;+\; \operatorname{erf}\left[\xi\right] \;+\; 1\;. \tag{3.57}$$

A characteristic of the fluorescent recovery is the time t_h, equivalently, ξ_h, at which half of the fluorescence is recovered defined through $N(\xi_h) = 0.5$. Numerical calculations, using the *regula falsi* or *secant method* yields ξ_h provide the following equations.

$$\xi_h \;=\; 0.961787\;. \tag{3.58}$$

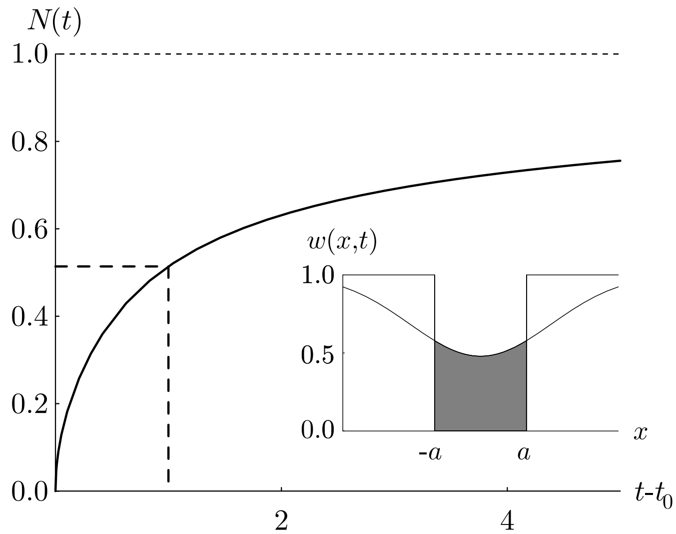

Figure 3.5: Fluorescence recovery after photobleaching as described by $N(t|t_o)$. The inset shows the probability distribution $w(x,t)$ for $t = 1$ and the segment $[-a, a]$. ($D = \frac{1}{a^2}$)

the definition (3.56) allows one to determine teh relationship between t_h and D

$$D \;=\; 0.925034\,\frac{a^2}{t_h - t_0}\;. \tag{3.59}$$

Since a is known through the experimental set up, measurement of $t_h - t_o$ provides the value of D.

3.4 Free Diffusion around a Spherical Object

Likely the most useful example of a diffusion process stems from a situation encountered in a chemical reaction when a molecule diffuses around a target and either reacts with it or vanishes out of its vicinity. We consider the idealized situation that the target is stationary (the case that both the molecule and the target diffuse is treated in Chapter **??**. Also we assume that the target is spherical (radius a) and reactions can arise anywwhere on its surface with equal likelyhood. Furthermore, we assume that the diffusing particles are distributed initially at a distance r_0 from the center of the target with all directions being equally likely. In effect we describe an ensemble of reacting molecules and targets which undergo their reaction diffusion processes independently of each other.

The probability of finding the molecule at a distance r at time t is then described by a spherically symmetric distribution $p(r,t|r_0,t_0)$ since neither the initial condition nor the reaction-diffusion condition show any orientational preference. The ensemble of reacting molecules is then described by the diffusion equation

$$\partial_t\, p(r,t|r_0,t_0) \;=\; D\,\nabla^2\, p(r,t|r_0,t_0) \tag{3.60}$$

and the initial condition

$$p(r,t_0|r_0,t_0) \;=\; \frac{1}{4\pi\, r_0^2}\,\delta(r - r_0)\;. \tag{3.61}$$

The prefactor on the r.h.s. normalizes the initial probability to unity since

$$\int_{\Omega_\infty} d^3\boldsymbol{r}\; p(\boldsymbol{r},t_0|\boldsymbol{r}_0,t_0) \;=\; \int_0^\infty 4\pi\, r^2 dr\; p(r,t_0|r_0,t_0)\;. \tag{3.62}$$

We can assume that the distribution vanishes at distances from the target which are much larger than r_0 and, accordingly, impose the boundary condition

$$\lim_{r\to\infty} p(r,t|r_0,t_0) \;=\; 0\;. \tag{3.63}$$

The reaction at the target will be described by the boundary condition (3.25), which in the present case of a spherical boundary, can be written

$$D\,\partial_r\, p(r,t|r_0,t_0) \;=\; w\; p(r,t|r_0,t_0)\;, \qquad \text{for } r = a\;. \tag{3.64}$$

As pointed out above, w controls the likelyhood of encounters with the target to be reactive: $w = 0$ corresponds to an unreactive surface, $w \to \infty$ to a surface for which every collision leads to reaction and, hence, to a diminishing of $p(r,t|r_0,t_0)$. The boundary condition for arbitrary w values adds significantly to the complexity of the solution, i.e., the following derivation would be simpler if the limits $w = 0$ or $w \to \infty$ would be considered. However, a closed expression for the general case can be provided and, in view of the frequent applicability of the example we prefer the general solution.

We first notice that the Laplace operator ∇^2, expressed in spherical coordinates (r,θ,ϕ), reads

$$\nabla^2 \;=\; \frac{1}{r^2}\left[\partial_r\left(r^2\,\partial_r\right) \;+\; \frac{1}{\sin^2\theta}\,\partial_\phi^2 \;+\; \frac{1}{\sin\theta}\,\partial_\theta\left(\sin\theta\,\partial_\theta\right)\right]\;. \tag{3.65}$$

Since the distribution function $p(r,t_0|r_0,t_0)$ is spherically symmetric, i.e., depends solely on r and not on θ and ϕ, one can drop, for all practical purposes, the respective derivatives. Employing furthermore the identity

$$\frac{1}{r^2}\,\partial_r\left(r^2\,\partial_r\, f(r)\right) \;=\; \frac{1}{r}\,\partial_r^2\left(r\;\, f(r)\right)\;. \tag{3.66}$$

one can restate the diffusion equation (3.60)

$$\partial_t\; r\; p(r,t|r_0,t_0) \;=\; D\,\partial_r^2\; r\; p(r,t|r_0,t_0)\;. \tag{3.67}$$

For the solution of (3.61, 3.63, 3.64, 3.67) we partition

$$p(r,t|r_0,t_0) \;=\; u(r,t|r_0,t_0) \;+\; v(r,t|r_0,t_0), \tag{3.68}$$

$$\text{with}\;\; u(r,t\to t_0|r_0,t_0) \;=\; \frac{1}{4\pi\, r_0^2}\,\delta(r-r_0) \tag{3.69}$$

$$v(r,t\to t_0|r_0,t_0) \;=\; 0\;. \tag{3.70}$$

The functions $u(r,t|r_0,t_0)$ and $v(r,t|r_0,t_0)$ are chosen to obey individually the radial diffusion equation (3.67) and, together, the boundary conditions (3.63, 3.64). We first construct $u(r,t|r_0,t_0)$ without regard to the boundary condition at $r = a$ and construct then $v(r,t|r_0,t_0)$ such that the proper boundary condition is obeyed.

The function $u(r,t|r_0,t_0)$ has to satisfy

$$\partial_t\left(r\; u(r,t|r_0,t_0)\right) \;=\; D\,\partial_r^2\,\left(r\; u(r,t|r_0,t_0)\right) \tag{3.71}$$

$$r\; u(r,t\to t_0|r_0,t_0) \;=\; \frac{1}{4\pi\, r_0}\,\delta(r-r_0)\;. \tag{3.72}$$

An admissable solution $r\,u(r,t|r_0,t_0)$ can be determined readily through Fourier transformation

$$\tilde{U}(k,t|r_0,t_0) \;=\; \int_{-\infty}^{+\infty} dr\; r\; u(r,t|r_0,t_0)\; e^{-i\,k\,r}\;, \tag{3.73}$$

$$r\; u(r,t|r_0,t_0) \;=\; \frac{1}{2\pi}\int_{-\infty}^{+\infty} dk\; \tilde{U}(k,t|r_0,t_0)\; e^{i\,k\,r}\;. \tag{3.74}$$

Inserting (3.74) into (3.67) yields

$$\frac{1}{2\pi}\int_{-\infty}^{\infty} dk \left[\partial_t\,\tilde{U}(k,t|r_0,t_0) \;+\; D\,k^2\,\tilde{U}(k,t|r_0,t_0)\right] e^{ikr} \;=\; 0\;. \tag{3.75}$$

The uniqueness of the Fourier transform allows one to conclude that the coefficients $[\cdots]$ must vanish. Hence, one can conclude

$$\tilde{U}(k,t|r_0,t_0) \;=\; C_u(k|r_0)\;\exp\!\big[-D\,(t-t_0)\,k^2\big]\;. \tag{3.76}$$

The time-independent coefficients $C_u(k|r_0)$ can be deduced from the initial condition (3.72). The identity

$$\delta(r-r_0) \;=\; \frac{1}{2\pi}\int_{-\infty}^{+\infty} dk\; e^{i\,k\,(r-r_0)} \tag{3.77}$$

leads to

$$\frac{1}{4\pi\,r_0}\,\delta(r-r_0) \;=\; \frac{1}{8\pi^2\,r_0}\int_{-\infty}^{+\infty} dk\; e^{i\,k\,(r-r_0)} \;=\; \frac{1}{2\pi}\int_{-\infty}^{+\infty} dk\; C_u(k|r_0)\; e^{i\,k\,r} \tag{3.78}$$

and, hence,

$$C_u(k|r_0) \;=\; \frac{1}{4\pi\,r_0}\; e^{-i\,k\,r_0}\;. \tag{3.79}$$

This results in the expression

$$r\; u(r,t|r_0,t_0) \;=\; \frac{1}{8\,\pi^2\,r_0}\int_{-\infty}^{\infty} dk\;\; \exp\!\big[-D\,(t-t_0)\,k^2\big]\; e^{i\,(r-r_0)\,k} \tag{3.80}$$

The Fourier integral

$$\int_{-\infty}^{\infty} dk\; e^{-a\,k^2}\; e^{i\,x\,k} \;=\; \sqrt{\frac{\pi}{a}}\;\exp\!\left[\frac{-x^2}{4\,a}\right] \tag{3.81}$$

yields

$$r\; u(r,t|r_0,t_0) \;=\; \frac{1}{4\,\pi\,r_0}\,\frac{1}{\sqrt{4\pi\,D\,(t-t_0)}}\;\exp\!\left[-\frac{(r-r_0)^2}{4\,D\,(t-t_0)}\right]\;. \tag{3.82}$$

We want to determine now the solution $v(r,t|r_0,t_0)$ in (3.68, 3.70) which must satisfy

$$\partial_t\,\big(\,r\;v(r,t|r_0,t_0)\,\big) \;=\; D\;\partial_r^2\;\big(\,r\;v(r,t|r_0,t_0)\,\big) \tag{3.83}$$

$$r\;v(r,t\to t_0|r_0,t_0) \;=\; 0\;. \tag{3.84}$$

Any solution of these homogeneous linear equations can be multiplied by an arbitrary constant C. This freedom allows one to modify $v(r,t|r_0,t_0)$ such that $u(r,t|r_0,t_0) + C\,v(r,t|r_0,t_0)$ obeys the desired boundary condition (3.64) at $r = a$.
To construct a solution of (3.83, 3.84) we consider the Laplace transformation

$$\check{V}(r,s|r_0,t_0) \;=\; \int_0^\infty d\tau\; e^{-s\tau}\; v(r,t_0+\tau|r_0,t_0)\;. \tag{3.85}$$

Applying the Lapace transform to (3.83) and integrating by parts yields for the left hand side

$$-r\; v(r,t_0|r_0,t_0) \;+\; s\; r\;\check{V}(r,s|r_0,t_0)\;. \tag{3.86}$$

The first term vanishes, according to (3.84), and one obtains

$$\frac{s}{D}\,\big(r\;\check{V}(r,s|r_0,t_0)\big) \;=\; \partial_r^2\,\big(r\;\check{V}(r,s|r_0,t_0)\big)\;. \tag{3.87}$$

The solution with respect to boundary condition (3.63) is

$$r\;\check{V}(r,s|r_0,t_0) \;=\; C(s|r_0)\;\exp\Big[-\sqrt{\frac{s}{D}}\;r\Big]\;. \tag{3.88}$$

where $C(s|r_0)$ is an arbitrary constant which will be utilized to satisfy the boundary condition(3.64). Rather than applying the inverse Laplace transform to determine $v(r,t|r_0,t_0)$ we consider the Laplace transform $\check{P}(r,s|r_0,t_0)$ of the complete solution $p(r,t|r_0,t_0)$. The reason is that boundary condition (3.64) applies in an analogue form to $\check{P}(r,s|r_0,t_0)$ as one sees readily applying the Laplace transform to (3.64). In case of the function $r\,\check{P}(r,s|r_0,t_0)$ the extra factor r modifies the boundary condition. One can readily verify, using

$$D\;\partial_r\,\big(r\;\check{P}(r,s|r_0,t_0)\big) \;=\; D\,\check{P}(r,s|r_0,t_0) \;+\; r\,D\;\partial_r\,\check{P}(r,s|r_0,t_0)\big) \tag{3.89}$$

and replacing at $r = a$ the last term by the r.h.s. of (3.64),

$$\partial_r\; r\,\check{P}(r,s|r_0,t_0)\Big|_{r=a} \;=\; \frac{w\,a \,+\, D}{D\,a}\;\; a\;\check{P}(a,s|r_0,t_0)\;. \tag{3.90}$$

One can derive the Laplace transform of $u(r,t|r_0,t_0)$ using the identity

$$\int_0^\infty dt\; e^{-s\tau}\;\frac{1}{4\pi\,r_0}\;\frac{1}{\sqrt{4\pi\,D\,\tau}}\;\exp\Big[-\frac{(r-r_0)^2}{4\,D\,\tau}\Big] \;=\; \frac{1}{4\pi\,r_0}\;\frac{1}{\sqrt{4\,D\,s}}\;\exp\Big[-\sqrt{\frac{s}{D}}\;|r-r_0|\Big] \tag{3.91}$$

and obtains for $r\,\check{P}(r,s|r_0,t_0)$

$$r\,\check{P}(r,s|r_0,t_0) \;=\; \frac{1}{4\pi\,r_0}\;\frac{1}{\sqrt{4\,D\,s}}\;\exp\Big[-\sqrt{\frac{s}{D}}\;|r-r_0|\Big] \;+\; C(s|r_0)\;\exp\Big[-\sqrt{\frac{s}{D}}\;r\Big]\;. \tag{3.92}$$

Boundary condition (3.90) for $r = a < r_0$ is

$$\begin{aligned}
&\sqrt{\frac{s}{D}}\left(\frac{1}{4\pi\,r_0}\;\frac{1}{\sqrt{4\,D\,s}}\;\exp\Big[-\sqrt{\frac{s}{D}}\;(r_0-a)\Big] \;-\; C(s|r_0)\;\exp\Big[-\sqrt{\frac{s}{D}}\;a\Big]\right) \\
&\quad=\; \frac{w\,a\,+\,D}{D\,a}\left(\frac{1}{4\pi\,r_0}\;\frac{1}{\sqrt{4\,D\,s}}\;\exp\Big[-\sqrt{\frac{s}{D}}\;(r_0-a)\Big] \;+\; C(s|r_0)\;\exp\Big[-\sqrt{\frac{s}{D}}\;a\Big]\right)
\end{aligned} \tag{3.93}$$

or

$$\left(\sqrt{\frac{s}{D}} \;-\; \frac{w\,a \,+\, D}{D\,a} \right)\; \frac{1}{4\,\pi\,r_0}\; \frac{1}{\sqrt{4\,D\,s}}\; \exp\!\left[-\sqrt{\frac{s}{D}}\; (r_0 - a) \right] \tag{3.94}$$
$$= \left(\frac{w\,a \,+\, D}{D\,a} \;+\; \sqrt{\frac{s}{D}} \right)\; C(s|r_0)\; \exp\!\left[-\sqrt{\frac{s}{D}}\; a \right] \;.$$

This condition determines the appropriate factor $C(s|r_0)$, namely,

$$C(s|r_0) \;=\; \frac{\sqrt{s/D} \;-\; (w\,a \,+\, D)/(D\,a)}{\sqrt{s/D} \;+\; (w\,a \,+\, D)/(D\,a)}\; \frac{1}{4\,\pi\,r_0}\; \frac{1}{\sqrt{4\,D\,s}}\; \exp\!\left[-\sqrt{\frac{s}{D}}\; (r_0 - 2\,a) \right] \;. \tag{3.95}$$

Combining (3.88, 3.91, 3.95) results in the expression

$$\begin{aligned}
& r\; \check{P}(r, s|r_0, t_0) \\
&\quad = \frac{1}{4\,\pi\,r_0}\; \frac{1}{\sqrt{4\,D\,s}}\; \exp\!\left[-\sqrt{\frac{s}{D}}\; |r - r_0| \right] \\
&\quad\quad + \frac{\sqrt{s/D} \;-\; (w\,a \,+\, D)/(D\,a)}{\sqrt{s/D} \;+\; (w\,a \,+\, D)/(D\,a)}\; \frac{1}{4\,\pi\,r_0}\; \frac{1}{\sqrt{4\,D\,s}}\; \exp\!\left[-\sqrt{\frac{s}{D}}\; (r + r_0 - 2\,a) \right] \\
&\quad = \frac{1}{4\,\pi\,r_0}\; \frac{1}{\sqrt{4\,D\,s}} \left(\exp\!\left[-\sqrt{\frac{s}{D}}\; |r - r_0| \right] \;+\; \exp\!\left[-\sqrt{\frac{s}{D}}\; (r + r_0 - 2\,a) \right] \right) \\
&\quad\quad - \frac{(w\,a \,+\, D)/(D\,a)}{\sqrt{s/D} \;+\; (w\,a \,+\, D)/(D\,a)}\; \frac{1}{4\,\pi\,r_0}\; \frac{1}{\sqrt{D\,s}}\; \exp\!\left[-\sqrt{\frac{s}{D}}\; (r + r_0 - 2\,a) \right]
\end{aligned} \tag{3.96}$$

Application of the inverse Laplace transformation leads to the final result

$$\begin{aligned}
& r\; p(r, t|r_0, t_0) \\
&\quad = \frac{1}{4\,\pi\,r_0}\; \frac{1}{\sqrt{4\pi\,D\,(t - t_0)}} \left(\exp\!\left[-\frac{(r - r_0)^2}{4\,D\;(t - t_0)} \right] \;+\; \exp\!\left[-\frac{(r + r_0 - 2\,a)^2}{4\,D\;(t - t_0)} \right] \right) \\
&\quad - \frac{1}{4\,\pi\,r_0}\; \frac{w\,a \,+\, D}{D\,a}\; \exp\!\left[\left(\frac{w\,a \,+\, D}{D\,a} \right)^2 D\,(t - t_0) \;+\; \frac{w\,a \,+\, D}{D\,a}\; (r + r_0 - 2\,a) \right] \\
&\quad \times\; \mathrm{erfc}\!\left[\frac{w\,a \,+\, D}{D\,a}\; \sqrt{D\,(t - t_0)} \;+\; \frac{r + r_0 - 2\,a}{\sqrt{4\,D\,(t - t_0)}} \right] \;.
\end{aligned} \tag{3.97}$$

The substituion

$$\alpha \;=\; \frac{w\,a \,+\, D}{D\,a} \tag{3.98}$$

simplifies the solution slightly

$$\begin{aligned}
p(r, t|r_0, t_0) \;&=\; \frac{1}{4\,\pi\,r\,r_0}\; \frac{1}{\sqrt{4\pi\,D\,(t - t_0)}} \left(\exp\!\left[-\frac{(r - r_0)^2}{4\,D\;(t - t_0)} \right] + \exp\!\left[-\frac{(r + r_0 - 2\,a)^2}{4\,D\;(t - t_0)} \right] \right) \\
&\quad - \frac{1}{4\,\pi\,r\,r_0}\; \alpha\; \exp\!\left[\alpha^2\,D\,(t - t_0) \;+\; \alpha\;(r + r_0 - 2\,a) \right] \\
&\quad \times\; \mathrm{erfc}\!\left[\alpha\; \sqrt{D\,(t - t_0)} \;+\; \frac{r + r_0 - 2\,a}{\sqrt{4\,D\,(t - t_0)}} \right] \;.
\end{aligned} \tag{3.99}$$

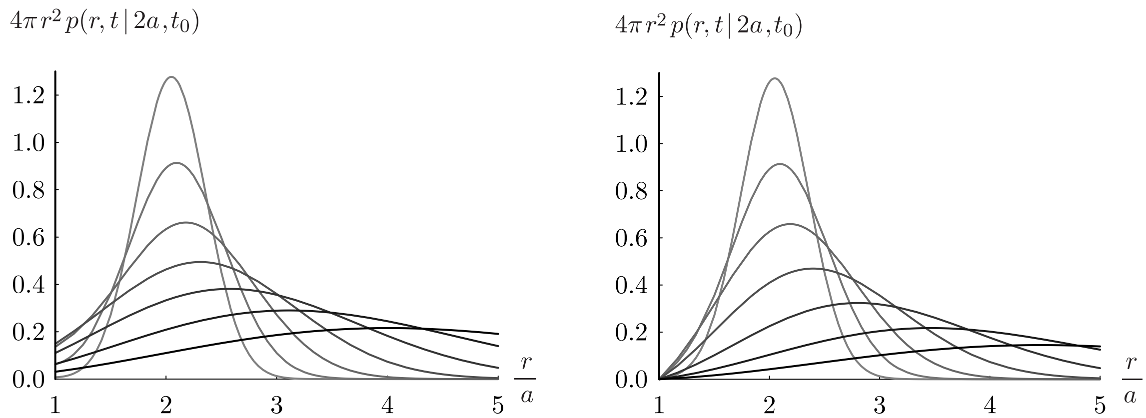

Figure 3.6: Radial probability density distribution of freely diffusing particles around a spherical object according to equation (3.99). The left plot shows the time evolution with $w = 0$ and $(t_1 - t_0) = 0.05, 0.1, 0.2, 0.4, 0.8, 1.6, 3.2$. The right plot depicts the time evolution of equation (eq:fdso27) with $w = \infty$ and $(t_1 - t_0) = 0.05, 0.1, 0.2, 0.4, 0.8, 1.6, 3.2$. The time units are $\frac{a^2}{D}$.

Reflective Boundary at $r = a$ We like to consider now the solution (3.99) in case of a reflective boundary at $r = a$, i.e., for $w = 0$ or $\alpha = 1/a$. The solution is

$$\begin{aligned} p(r,t|r_0,t_0) \;&=\; \frac{1}{4\,\pi\,r\,r_0}\;\frac{1}{\sqrt{4\pi\,D\,(t-t_0)}}\left(\exp\!\left[-\frac{(r-r_0)^2}{4\,D\;(t-t_0)}\right] + \exp\!\left[-\frac{(r+r_0-2\,a)^2}{4\,D\;(t-t_0)}\right]\right) \\ &\quad -\;\frac{1}{4\,\pi\,a\,r\,r_0}\;\exp\!\left[\frac{D}{a^2}\,(t-t_0) \;+\; \frac{r+r_0-2\,a}{a}\right] \\ &\quad\times\;\operatorname{erfc}\!\left[\frac{\sqrt{D\,(t-t_0)}}{a} \;+\; \frac{r+r_0-2\,a}{\sqrt{4\,D\,(t-t_0)}}\right]\,. \end{aligned} \tag{3.100}$$

Absorptive Boundary at $r = a$ In case of an absorbing boundary at $r = a$, one has to set $w \to \infty$ and, hence, $\alpha \to \infty$. To supply a solution for this limiting case we note the asymptotic behaviour[1]

$$\sqrt{\pi}\;z\;\exp\!\left[z^2\right]\;\operatorname{erfc}[z] \;\;\sim\;\; 1 \;+\; \mathcal{O}\!\left(\frac{1}{z^2}\right)\,. \tag{3.101}$$

[1]Handbook of Mathematical Functions, Eq. 7.1.14

This implies for the last summand of equation (3.99) the asymptotic behaviour

$$\begin{aligned}
&\alpha\ \exp\left[\alpha^2 D\,(t-t_0)\ +\ \alpha\ (r+r_0-2\,a)\right]\ \operatorname{erfc}\left[\alpha\ \sqrt{D\,(t-t_0)}\ +\ \frac{r+r_0-2\,a}{\sqrt{4\,D\,(t-t_0)}}\right] \\
&= \alpha\ \exp\left[z^2\right]\ \exp\left[-z_2^2\right]\ \operatorname{erfc}[z]\ , \quad \text{with}\ \ z\ =\ \alpha\, z_1\ +\ z_2\ , \\
&\qquad\qquad\qquad\qquad\qquad\qquad z_1\ =\ \sqrt{D\,(t-t_0)}\ ,\ \text{and} \\
&\qquad\qquad\qquad\qquad\qquad\qquad z_2\ =\ (r+r_0-2\,a)/\sqrt{4\,D\,(t-t_0)}\ . \\
&\sim \frac{\alpha}{\sqrt{\pi}\,z}\ \exp\left[-z_2^2\right]\ \left(1\ +\ \mathcal{O}\left(\frac{1}{\alpha^2}\right)\right) \qquad (3.102) \\
&= \frac{1}{\sqrt{\pi}}\ \frac{\alpha\sqrt{4\,D\,(t-t_0)}}{2\,\alpha\,D\,(t-t_0)+r+r_0-2a}\ \exp\left[-\frac{(r+r_0-2\,a)^2}{4\,D\,(t-t_0)}\right]\ \left(1\ +\ \mathcal{O}\left(\frac{1}{\alpha^2}\right)\right) \\
&= \left(\frac{1}{\sqrt{\pi\,D\,(t-t_0)}}\ -\ \frac{r+r_0-2\,a}{\sqrt{4\pi}\ \alpha\,\big(D\,(t-t_0)\big)^{3/2}}\ +\ \mathcal{O}\left(\frac{1}{\alpha^2}\right)\right)\ \exp\left[-\frac{(r+r_0-2\,a)^2}{4\,D\,(t-t_0)}\right]\ .
\end{aligned}$$

One can conclude to leading order

$$\begin{aligned}
&\alpha\ \exp\left[\alpha^2 D\,(t-t_0)\ +\ \alpha\ (r+r_0-2\,a)\right]\ \operatorname{erfc}\left[\alpha\sqrt{D\,(t-t_0)}\ +\ \frac{r+r_0-2\,a}{\sqrt{4\,D\,(t-t_0)}}\right] \\
&\qquad \sim\ \left(\frac{2}{\sqrt{4\pi\,D\,(t-t_0)}}\ +\ \mathcal{O}\left(\frac{1}{\alpha^2}\right)\right)\ \exp\left[-\frac{(r+r_0-2\,a)^2}{4\,D\,(t-t_0)}\right]\ . \qquad (3.103)
\end{aligned}$$

Accordingly, solution (3.99) becomes in the limit $w \to \infty$

$$p(r,t|r_0,t_0)\ =\ \frac{1}{4\,\pi\,r\,r_0}\ \frac{1}{\sqrt{4\pi\,D\,(t-t_0)}}\left(\exp\left[-\frac{(r-r_0)^2}{4\,D\ (t-t_0)}\right]\ -\ \exp\left[-\frac{(r+r_0-2\,a)^2}{4\,D\ (t-t_0)}\right]\right). \qquad (3.104)$$

Reaction Rate for Arbitrary w We return to the general solution (3.99) and seek to determine the rate of reaction at $r = a$. This rate is given by

$$K(t|r_0,t_0)\ =\ 4\pi\ a^2\ D\ \partial_r\ p(r,t|r_0,t_0)\Big|_{r=a} \qquad (3.105)$$

where the factor $4\pi a^2$ takes the surface area of the spherical boundary into account. According to the boundary condition (3.64) this is

$$K(t|r_0,t_0)\ =\ 4\pi\ a^2 w\ p(a,t|r_0,t_0)\ . \qquad (3.106)$$

One obtains from (3.99)

$$\begin{aligned}
K(t|r_0,t_0)\ =\ \frac{a\,w}{r_0}\ &\left(\frac{1}{\sqrt{\pi\,D\,(t-t_0)}}\ \exp\left[-\frac{(r_0-a)^2}{4\,D\,(t-t_0)}\right]\right. \qquad (3.107) \\
&\left.-\ \alpha\ \exp\left[\alpha\,(r_0-a)+\alpha^2\,D\,(t-t_0)\right]\ \operatorname{erfc}\left[\frac{r_0-a}{\sqrt{4\,D\,(t-t_0)}}+\alpha\sqrt{D\,(t-t_0)}\right]\right).
\end{aligned}$$

Reaction Rate for $w \to \infty$ In case of an absorptive boundary ($w, \alpha \to \infty$) one can conclude from the asymptotic behaviour (3.102) with $r = a$

$$K(t|r_0, t_0) = \frac{a\,w}{r_0} \left(\frac{r_0 - a}{\sqrt{4\pi}\,\alpha\,\big(D\,(t-t_0)\big)^{3/2}} + \mathcal{O}\Big(\frac{1}{\alpha^2}\Big) \right) \exp\Big[-\frac{(r_0-a)^2}{4\,D\,(t-t_0)} \Big] .$$

Employing for the limit $w, \alpha \to \infty$ equation (3.98) as $w/\alpha \sim D$ one obtains the reaction rate for a completely absorptive boundary

$$K(t|r_0, t_0) = \frac{a}{r_0} \frac{1}{\sqrt{4\pi\,D\,(t-t_0)}} \frac{r_0 - a}{t - t_0} \exp\Big[-\frac{(r_0-a)^2}{4\,D\,(t-t_0)} \Big] . \qquad (3.108)$$

This expression can also be obtained directly from (3.104) using the definition (3.105) of the reaction rate.

Fraction of Particles Reacted for Arbitrary w One can evaluate the fraction of particles which react at the boundary $r = a$ according to

$$N_{\mathrm{react}}(t|r_0, t_0) = \int_{t_0}^{t} dt'\, K(t'|r_0, t_0) . \qquad (3.109)$$

For the general case with the rate (3.107) one obtains

$$N_{\mathrm{react}}(t|r_0, t_0) = \frac{a\,w}{r_0} \int_{t_0}^{t} dt' \left(\frac{1}{\sqrt{\pi\,D\,(t'-t_0)}} \exp\Big[-\frac{(r_0-a)^2}{4\,D\,(t'-t_0)} \Big] \right. \qquad (3.110)$$
$$\left. -\ \alpha\ \exp\big[\,\alpha(r_0 - a) + \alpha^2 D\,(t'-t_0)\,\big]\,\mathrm{erfc}\Big[\frac{r_0 - a}{\sqrt{4D(t'-t_0)}} + \alpha\sqrt{D\,(t'-t_0)} \Big] \right)$$

To evaluate the integral we expand the first summand of the integrand in (3.110). For the exponent one can write

$$-\underbrace{\frac{(r_0-a)^2}{4\,D\,(t'-t_0)}}_{=x^2(t')} = \underbrace{(r_0 - a)\,\alpha\ +\ D\,(t'-t_0)\,\alpha^2}_{=y(t')} - \underbrace{\frac{(r_0 - a\ +\ 2\,D\,(t'-t_0)\,\alpha)^2}{4\,D\,(t'-t_0)}}_{=z^2(t')} . \qquad (3.111)$$

We introduce the functions $x(t')$, $y(t')$, and $z(t')$ for notational convenience. For the factor in front of the exponential function we consider the expansion

$$\frac{1}{\sqrt{\pi\,D\,(t'-t_0)}} \qquad (3.112)$$
$$= \frac{2}{\sqrt{\pi}\,D\,\alpha} \left(\frac{D\,(r_0-a)}{4\,\big(D\,(t'-t_0)\big)^{3/2}} - \frac{D\,(r_0-a)}{4\,\big(D\,(t'-t_0)\big)^{3/2}} + \frac{D^2\,(t'-t_0)\,\alpha}{2\,\big(D\,(t'-t_0)\big)^{3/2}} \right)$$
$$= \frac{2}{\sqrt{\pi}\,D\,\alpha} \left(\underbrace{\frac{D\,(r_0-a)}{4\,\big(D\,(t'-t_0)\big)^{3/2}}}_{=dx(t')/dt'} \underbrace{- \frac{(r_0-a)}{2\,(t'-t_0)\,\sqrt{4\,D\,(t'-t_0)}} + \frac{D\,\alpha}{\sqrt{4\,D\,(t'-t_0)}}}_{=dz(t')/dt'} \right) .$$

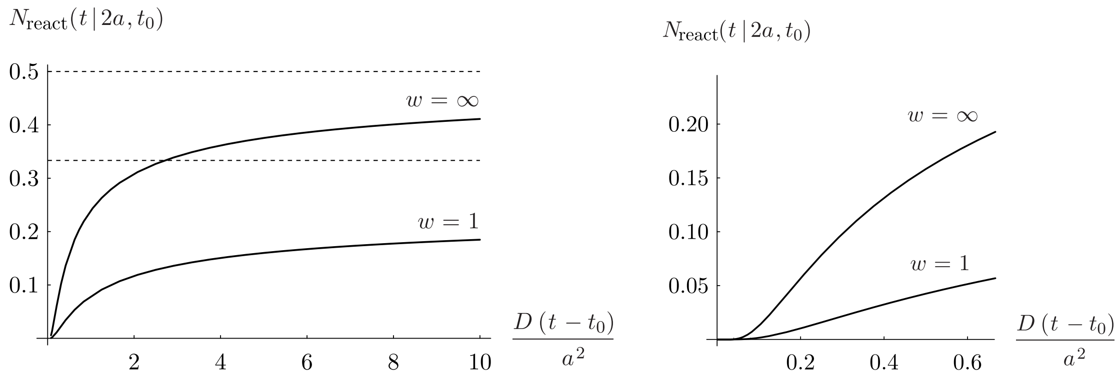

Figure 3.7: The left plot shows the fraction of particles that react at boundary $r = a$. The two cases $w = 1$ and $w = \infty$ of equation (3.114) are displayed. The dotted lines indicate the asymptotic values for $t \to \infty$. The right plot depicts the time evolution of equation (3.114) for small $(t - t_0)$.

Note, that the substitutions in (3.112) define the signs of $x(t')$ and $z(t')$. With the above expansions and substitutions one obtains

$$\begin{aligned} N_{\rm react}(t|r_0, t_0) &= \frac{a\,w}{D\,\alpha\,r_0} \int_{t_0}^{t} dt' \left(\frac{2}{\sqrt{\pi}}\,\frac{dx(t')}{dt'}\; e^{-x^2(t')} \right. \\ &\qquad \left. + \frac{2}{\sqrt{\pi}}\,\frac{dz(t')}{dt'}\; e^{y(t')}\; e^{-z^2(t')} \;-\; \frac{dy(t')}{dt'}\; e^{y(t')}\; \mathrm{erfc}[z(t')] \right) \\ &= \frac{a\,w}{D\,\alpha\,r_0} \left(\frac{2}{\sqrt{\pi}} \int_{x(t_0)}^{x(t)} dx\; e^{-x^2} \;-\; \int_{t_0}^{t} dt'\; \frac{d}{dt'} \left(e^{y(t')}\; \mathrm{erfc}[z(t')] \right) \right) \\ &= \frac{a\,w}{D\,\alpha\,r_0} \left(\mathrm{erf}[\,x(t')\,] \;-\; e^{y(t')}\; \mathrm{erfc}[z(t')] \right) \Bigg|_{t_0}^{t} . \end{aligned} \tag{3.113}$$

Filling in the integration boundaries and taking $w\,a = D\,(a\,\alpha - 1)$ into account one derives

$$\begin{aligned} N_{\rm react}(t|r_0, t_0) &= \frac{a\,\alpha - 1}{r_0\,\alpha} \left(1 \;+\; \mathrm{erf}\left[\frac{a - r_0}{\sqrt{4\,D\,(t - t_0)}} \right] \right. \\ &\qquad \left. -\; e^{(r_0 - a)\,\alpha + D\,(t - t_0)\,\alpha^2}\;\; \mathrm{erfc}\left[\frac{r_0 - a + 2\,D\,(t - t_0)\,\alpha}{\sqrt{4\,D\,(t - t_0)}} \right] \right) . \end{aligned} \tag{3.114}$$

Fraction of Particles Reacted for $w \to \infty$ One derives the limit $\alpha \to \infty$ for a completely absorptive boundary at $x = a$ with the help of equation (3.102).

$$\begin{aligned} \lim_{\alpha\to\infty} N_{\rm react}(t|r_0, t_0) &= \frac{a}{r_0} \left(1 \;+\; \mathrm{erf}\left[\frac{a - r_0}{\sqrt{4\,D\,(t - t_0)}} \right] \right. \\ &\qquad \left. -\; \frac{1}{\alpha} \left(\frac{2}{\sqrt{4\pi\,D\,(t - t_0)}} + \mathcal{O}\left(\frac{1}{\alpha^2}\right) \right) \exp\left[-\frac{(r_0 - a)^2}{4\,D\,(t - t_0)} \right] \right) . \end{aligned} \tag{3.115}$$

The second line of equation (3.115) approaches 0 and one is left with

$$\lim_{\alpha\to\infty} N_{\rm react}(t|r_0,t_0) \;=\; \frac{a}{r_0}\;\mathrm{erfc}\left[\frac{r_0-a}{\sqrt{4\,D\,(t-t_0)}}\right]\;. \tag{3.116}$$

Fraction of Particles Reacted for $(t-t_0)\to\infty$ We investigate another limiting case of $N_{\rm react}(t|r_0,t_0)$; the long time behavior for $(t-t_0)\to\infty$. For the second line of equation (3.114) we again refer to (3.102), which renders for $r=a$ and with respect to orders of t instead of α

$$\begin{aligned}&\exp\left[\,\alpha^2\,D\,(t-t_0)\,+\,\alpha\,(r_0-a)\,\right]\;\mathrm{erfc}\left[\alpha\,\sqrt{D\,(t-t_0)}\;+\;\frac{r_0-a}{\sqrt{4\,D\,(t-t_0)}}\right]\\ &\qquad=\;\left(\frac{1}{\sqrt{\pi\,D\,(t-t_0)}}\;+\;\mathcal{O}\left(\frac{1}{t-t_0}\right)\right)\;\exp\left[-\frac{(r_0-a)^2}{4\,D\,(t-t_0)}\right]\;.\end{aligned} \tag{3.117}$$

Equation (3.117) approaches 0 for $(t-t_0)\to\infty$, and since $\mathrm{erf}[-\infty]=0$, one obtains for $N_{\rm react}(t|r_0,t_0)$ of equation (3.114)

$$\lim_{(t-t_0)\to\infty} N_{\rm react}(t|r_0,t_0)\;=\;\frac{a}{r_0}\;-\;\frac{1}{r_0\,\alpha}\;. \tag{3.118}$$

Even for $w,\alpha\to\infty$ this fraction is less than one in accordance with the ergodic behaviour of particles diffusing in three-dimensional space. In order to overcome the a/r_0 limit on the overall reaction yield one can introduce long range interactions which effectively increase the reaction radius a.

We note that the fraction of particles $N(t|r_0)$ not reacted at time t is $1\,-\,N_{\rm react}(t|r_0)$ such that

$$\begin{aligned}N(t|r_0,t_0)\;&=\;1\;-\;\frac{a\,\alpha-1}{r_0\,\alpha}\left(1\;+\;\mathrm{erf}\left[\frac{a-r_0}{\sqrt{4\,D\,(t-t_0)}}\right]\right.\\ &\qquad\left.-\;e^{(r_0-a)\,\alpha\,+\,D\,(t-t_0)\,\alpha^2}\;\mathrm{erfc}\left[\frac{r_0-a+2\,D\,(t-t_0)\,\alpha}{\sqrt{4\,D\,(t-t_0)}}\right]\right)\;.\end{aligned} \tag{3.119}$$

We will demonstrate in a later chapter that this quantity can be evaluated directly without determining the distribution $p(r,t|r_0,t_0)$ first. Naturally, the cumbersome derivation provided here makes such procedure desirable.

3.5 Free Diffusion in a Finite Domain

We consider now a particle diffusing freely in a finite, one-dimensional interval

$$\Omega\;=\;[0,\,a]\;. \tag{3.120}$$

The boundaries of Ω at $x\,=\,0,\,a$ are assumed to be reflective. The diffusion coefficient D is assumed to be constant. The conditional distribution function $p(x,t|x_0,t_0)$ obeys the diffusion equation

$$\partial_t\,p(x,t|x_0,t_0)\;=\;D\;\partial_x^2\,p(x,t|x_0,t_0) \tag{3.121}$$

subject to the initial condition

$$p(x,t_0|x_0,t_0)\;=\;\delta(x\,-\,x_0) \tag{3.122}$$

and to the boundary conditions

$$D\,\partial_x\, p(x,t|x_0,t_0) \;=\; 0\;, \qquad \text{for } x \;=\; 0, \text{ and } x \;=\; a\;. \tag{3.123}$$

In order to solve (3.121–3.123) we expand $p(x,t|x_0,t_0)$ in terms of eigenfunctions of the diffusion operator

$$\mathcal{L}_0 \;=\; D\,\partial_x^2\;. \tag{3.124}$$

where we restrict the function space to those functions which obey (3.123). The corresponding functions are

$$v_n(x) \;=\; A_n\,\cos\Big[n\,\pi\,\frac{x}{a}\Big]\;, \qquad n \;=\; 0,1,2,\ldots\;. \tag{3.125}$$

In fact, for these functions holds for $n = 0,1,2,\ldots$

$$\mathcal{L}_0\, v_n(x) \;=\; \lambda_n\, v_n(x) \tag{3.126}$$

$$\lambda_n \;=\; -\,D\,\left(\frac{n\,\pi}{a}\right)^2\;. \tag{3.127}$$

From

$$\partial_x\, v_n(x) \;=\; -\frac{n\,\pi}{a}\,A_n\,\sin\Big[n\,\pi\,\frac{x}{a}\Big]\;, \qquad n \;=\; 0,1\,2,\ldots \tag{3.128}$$

follows readily that these functions indeed obey (3.123).
We can define, in the present case, the scalar product for functions f, g in the function space considered

$$\langle\, g\,|\,f\,\rangle_\Omega \;=\; \int_0^a dx\;g(x)\,f(x)\;. \tag{3.129}$$

For the eigenfunctions (3.125) we choose the normalization

$$\langle\, v_n\,|\,v_n\,\rangle_\Omega \;=\; 1\;. \tag{3.130}$$

This implies for $n = 0$

$$\int_0^a dx\;A_0^2 \;=\; A_0^2\,a \;=\; 1 \tag{3.131}$$

and for $n \neq 0$, using $\cos^2\alpha = \frac{1}{2}(1 + \cos 2\alpha)$,

$$\int_0^a dx\;v_n^2(x) \;=\; A_n^2\,\frac{a}{2} \,+\, \frac{1}{2}\,A_n^2\,\int_0^a dx\;\cos\Big[2\,n\,\pi\,\frac{x}{a}\Big] \;=\; A_n^2\,\frac{a}{2}\;. \tag{3.132}$$

It follows

$$A_n \;=\; \begin{cases} \sqrt{1/a} & \text{for } n \;=\; 0\;, \\ \sqrt{2/a} & \text{for } n \;=\; 1,2,\ldots\;. \end{cases} \tag{3.133}$$

The functions v_n are orthogonal with respect to the scalar product (3.129), i.e.,

$$\langle v_m|v_n\rangle_\Omega \;=\; \delta_{mn}\;. \tag{3.134}$$

To prove this property we note, using

$$\cos\alpha\,\cos\beta \;=\; \frac{1}{2}\big(\cos(\alpha+\beta) \;+\; \cos(\alpha-\beta)\big)\;, \tag{3.135}$$

for $m \neq n$

$$\begin{aligned}
\langle\, v_m \,|\, v_n \,\rangle_\Omega &= \frac{A_m\,A_n}{2}\left(\int_0^a dx\;\cos\Big[(m+n)\,\pi\,\frac{x}{a}\Big] \;+\; \int_0^a dx\;\cos\Big[(m-n)\,\pi\,\frac{x}{a}\Big]\right) \\
&= \frac{A_m\,A_n}{2\,\pi}\left(\frac{a}{(m+n)}\;\sin\Big[(m+n)\,\pi\,\frac{x}{a}\Big] \;+\; \frac{a}{(m-n)}\;\sin\Big[(m-n)\,\pi\,\frac{x}{a}\Big]\right)\Bigg|_0^a \\
&= 0\;.
\end{aligned}$$

Without proof we note that the functions v_n, defined in (3.125), form a complete basis for the function space considered. Together with the scalar product (3.129) this basis is orthonormal. We can, hence, readily expand $p(x,t|x_0,t_0)$ in terms of v_n

$$p(x,t|x_0,t_0) \;=\; \sum_{n=0}^{\infty} \alpha_n(t|x_0,t_0)\; v_n(x)\;. \tag{3.136}$$

Inserting this expansion into (3.121) and using (3.126) yields

$$\sum_{n=0}^{\infty} \partial_t\,\alpha_n(t|x_0,t_0)\; v_n(x) \;=\; \sum_{n=0}^{\infty} \lambda_n\;\alpha_n(t|x_0,t_0)\; v_n(x)\;. \tag{3.137}$$

Taking the scalar product $\langle\, v_m \,|$ leads to

$$\partial_t\,\alpha_m(t|x_0,t_0) \;=\; \lambda_m\,\alpha_m(t|x_0,t_0) \tag{3.138}$$

from which we conclude

$$\alpha_m(t|x_0,t_0) \;=\; e^{\lambda_m\,(t-t_0)}\,\beta_m(x_0,t_0)\;. \tag{3.139}$$

Here, $\beta_m(x_0,t_0)$ are time-independent constants which are determined by the initial condition (3.122)

$$\sum_{n=0}^{\infty} \beta_n(x_0,t_0)\,v_n(x) \;=\; \delta(x-x_0)\;. \tag{3.140}$$

Taking again the scalar product $\langle\, v_m \,|$ results in

$$\beta_m(x_0,t_0) \;=\; v_m(x_0)\;. \tag{3.141}$$

Altogether holds then

$$p(x,t|x_0,t_0) \;=\; \sum_{n=0}^{\infty} e^{\lambda_n\,(t-t_0)}\,v_n(x_0)\,v_n(x)\;. \tag{3.142}$$

Let us assume now that the system considered is actually distributed initially according to a distribution $f(x)$ for which we assume $\langle 1 \,|\, f \rangle_\Omega = 1$. The distribution $p(x,t)$, at later times, is then

$$p(x,t) \;=\; \int_0^a dx_0 \; p(x,t|x_0,t_0)\, f(x_0) \; . \tag{3.143}$$

Employing the expansion (3.142) this can be written

$$p(x,t) \;=\; \sum_{n=0}^{\infty} e^{\lambda_n (t-t_0)}\, v_n(x) \int_0^a dx_0 \; v_n(x_0)\, f(x_0) \; . \tag{3.144}$$

We consider now the behaviour of $p(x,t)$ at long times. One expects that the system ultimately assumes a homogeneous distribution in Ω, i.e., that $p(x,t)$ relaxes as follows

$$p(x,t) \;\underset{t\to\infty}{\asymp}\; \frac{1}{a} \; . \tag{3.145}$$

This asymptotic behaviour, indeed, follows from (3.144). We note from (3.127)

$$e^{\lambda_n (t-t_0)} \;\underset{t\to\infty}{\asymp}\; \begin{cases} 1 & \text{for } n \,=\, 0 \\ 0 & \text{for } n \,=\, 1,2,\dots \end{cases} \; . \tag{3.146}$$

From (3.125, 3.133) follows $v_0(x) = 1/\sqrt{a}$ and, hence,

$$p(x,t) \;\underset{t\to\infty}{\asymp}\; \frac{1}{a} \int_0^a dx \; v(x_0) \; . \tag{3.147}$$

The property $\langle 1 \,|\, f \rangle_\Omega = 1$ implies then (3.145).
The solution presented here [cf. (3.120–3.147)] provides in a nutshel the typical properties of solutions of the more general Smoluchowski diffusion equation accounting for the presence of a force field which will be provided in Chapter 4.

3.6 Rotational Diffusion

Dielectric Relaxation

The electric polarization of liquids originates from the dipole moments of the individual liquid molecules. The contribution of an individual molecule to the polarization in the z-direction is

$$P_3 \;=\; P_0 \cos\theta \tag{3.148}$$

We consider the relaxation of the dipole moment assuming that the rotational diffusion of the dipole moments can be described as diffusion on the unit sphere.
The diffusion on a unit sphere is described by the three-dimensional diffusion equation

$$\partial_t \, p(\boldsymbol{r},t|\boldsymbol{r}_0,t_0) \;=\; D\, \nabla^2 \, p(\boldsymbol{r},t|\boldsymbol{r}_0,t_0) \tag{3.149}$$

for the condition $|\boldsymbol{r}| = |\boldsymbol{r}_0| = 1$. In order to obey this condition one employs the Laplace operator ∇^2 in terms of spherical coordinates (r,θ,ϕ) as given in (3.65) and sets $r = 1$, dropping also derivatives with respect to r. This yields the rotational diffusion equation

$$\partial_t \, p(\Omega,t|\Omega_0,t_0) \;=\; \tau_r^{-1} \left[\frac{1}{\sin\theta}\, \partial_\theta \left(\sin\theta \, \partial_\theta \right) \;+\; \frac{1}{\sin^2\theta}\, \partial_\phi^2 \right] p(\Omega,t|\Omega_0,t_0) \; . \tag{3.150}$$

We have defined here $\Omega = (\theta, \phi)$. We have also introduced, instead of the diffusion constant, the rate constant τ_r^{-1}since the replacement $r \to 1$ altered the units in the diffusion equation; τ_r has the unit of time. In the present case the diffusion space has no boundary; however, we need to postulate that the distribution and its derivatives are continuous on the sphere.
One way of ascertaining the continuity property is to expand the distribution in terms of spherical harmonics $Y_{\ell m}(\Omega)$ which obey the proper continuity, i.e.,

$$p(\Omega, t|\Omega_0, t_0) \;=\; \sum_{\ell=0}^{\infty} \sum_{m=-\ell}^{+\ell} A_{\ell m}(t|\Omega_0, t_0)\, Y_{\ell m}(\Omega) \; . \tag{3.151}$$

In addition, one can exploit the eigenfunction property

$$\left[\frac{1}{\sin\theta}\, \partial_\theta \left(\sin\theta\, \partial_\theta \right) \;+\; \frac{1}{\sin^2\theta}\, \partial_\phi^2 \right] Y_{\ell m}(\Omega) \;=\; -\ell\,(\ell+1)\, Y_{\ell m}(\Omega) \; . \tag{3.152}$$

Inserting (3.151) into (3.150) and using (3.152) results in

$$\sum_{\ell=0}^{\infty} \sum_{m=-\ell}^{+\ell} \partial_t\, A_{\ell m}(t|\Omega_0, t_0)\; Y_{\ell m}(\Omega) \;=\; -\sum_{\ell=0}^{\infty} \sum_{m=-\ell}^{+\ell} \ell\,(\ell+1)\; \tau_r^{-1}\; A_{\ell m}(t|\Omega_0, t_0)\; Y_{\ell m}(\Omega) \tag{3.153}$$

The orthonormality property

$$\int d\Omega\; Y^*_{\ell' m'}(\Omega)\; Y_{\ell m}(\Omega) \;=\; \delta_{\ell' \ell}\, \delta_{m' m} \tag{3.154}$$

leads one to conclude

$$\partial_t\, A_{\ell m}(t|\Omega_0, t_0) \;=\; -\ell\,(\ell+1)\; \tau_r^{-1}\; A_{\ell m}(t|\Omega_0, t_0) \tag{3.155}$$

and, accordingly,

$$A_{\ell m}(t|\Omega_0, t_0) \;=\; e^{-\ell\,(\ell+1)\,(t-t_0)/\tau_r}\; a_{\ell m}(\Omega_0) \tag{3.156}$$

or

$$p(\Omega, t|\Omega_0, t_0) \;=\; \sum_{\ell=0}^{\infty} \sum_{m=-\ell}^{+\ell} e^{-\ell\,(\ell+1)\,(t-t_0)/\tau_r}\; a_{\ell m}(\Omega_0)\; Y_{\ell m}(\Omega) \; . \tag{3.157}$$

The coefficients $a_{\ell m}(\Omega_0)$ are determined through the condition

$$p(\Omega, t_0|\Omega_0, t_0) \;=\; \delta(\Omega - \Omega_0) \; . \tag{3.158}$$

The completeness relationship of spherical harmonics states

$$\delta(\Omega - \Omega_0) \;=\; \sum_{\ell=0}^{\infty} \sum_{m=-\ell}^{+\ell} Y^*_{\ell m}(\Omega_0)\; Y_{\ell m}(\Omega) \; . \tag{3.159}$$

Equating this with (3.157) for $t = t_0$ yields

$$a_{\ell m}(\Omega_0) \;=\; Y^*_{\ell m}(\Omega_0) \tag{3.160}$$

and, hence,

$$p(\Omega, t|\Omega_0, t_0) \;=\; \sum_{\ell=0}^{\infty} \sum_{m=-\ell}^{+\ell} e^{-\ell\,(\ell+1)\,(t-t_0)/\tau_r}\; Y^*_{\ell m}(\Omega_0)\; Y_{\ell m}(\Omega)\;. \tag{3.161}$$

It is interesting to consider the asymptotic, i.e., the $t \to \infty$, behaviour of this solution. All exponential terms will vanish, except the term with $\ell = 0$. Hence, the distribution approaches asymptotically the limit

$$\lim_{t\to\infty} p(\Omega, t|\Omega_0, t_0) \;=\; \frac{1}{4\pi}\;, \tag{3.162}$$

where we used $Y_{00}(\Omega) = 1/\sqrt{4\pi}$. This result corresponds to the homogenous, normalized distribution on the sphere, a result which one may have expected all along. One refers to this distribution as the equilibrium distribution denoted by

$$p_0(\Omega) \;=\; \frac{1}{4\pi}\;. \tag{3.163}$$

The equilibrium average of the polarization expressed in (3.148) is

$$\left\langle P_3 \right\rangle \;=\; \int d\Omega P_0\;\cos\theta\; p_0(\Omega)\;. \tag{3.164}$$

One can readily show

$$\left\langle P_3 \right\rangle \;=\; 0\;. \tag{3.165}$$

Another quantity of interest is the so-called equilibrium correlation function

$$\left\langle P_3(t)\, P_3^*(t_0) \right\rangle \;=\; P_0^2 \int d\Omega \int d\Omega_0\;\cos\theta\;\cos\theta_0\; p(\Omega, t|\Omega_0, t_0)\; p_0(\Omega_0)\;. \tag{3.166}$$

Using

$$Y_{10}(\Omega) \;=\; \sqrt{\frac{3}{4\pi}}\;\cos\theta \tag{3.167}$$

and expansion (3.161) one obtains

$$\left\langle P_3(t)\, P_3^*(t_0) \right\rangle \;=\; \frac{4\pi}{3}\; P_0^2 \sum_{m=-\ell}^{+\ell} e^{-\ell\,(\ell+1)\,(t-t_0)/\tau_r}\;|C_{10,\ell m}|^2\;, \tag{3.168}$$

where

$$C_{10,\ell m} \;=\; \int d\Omega\; Y^*_{10}(\Omega)\; Y_{\ell m}(\Omega)\;. \tag{3.169}$$

The orthonormality condition of the spherical harmonics yields immediately

$$C_{10,\ell m} \;=\; \delta_{\ell 1}\;\delta_{m0} \tag{3.170}$$

and, therefore,

$$\left\langle P_3(t)\, P_3^*(t_0) \right\rangle \;=\; \frac{4\pi}{3}\; P_0^2\; e^{-2\,(t-t_0)/\tau_r}\;. \tag{3.171}$$

Other examples in which rotational diffusion plays a role are fluorescence depolarization as observed in optical experiments and dipolar relaxation as observed in NMR spectra.