1 Newton’s Equation and Langevin’s Equation

In this section we assume that the constituents of matter can be described classically. We are interested in reaction processes occurring in the bulk, either in physiological liquids, membranes or proteins. The atomic motion of these materials is described by the Newtonian equation of motion

\[ m_i \frac{d^2 r_i}{dt^2} = -\frac{\partial}{\partial r_i} V(r_1, \ldots, r_N) \]  

(1)

where \( r_i \) \( (i = 1, 2, \ldots, N) \) describes the position of the \( i \)-th atom. The number \( N \) of atoms is, of course, so large that solutions of Eq. (1) for macroscopic systems are impossible. In microscopic systems like proteins the number of atoms ranges between \( 10^3 \) to \( 10^5 \), i.e., even in this case the solution is extremely time consuming.

However, most often only a few of the degrees of freedom are involved in a particular biochemical reaction and warrant an explicit theoretical description or observation. For example, in the case of transport one is solely interested in the position of the center of mass of a molecule. It is well known that molecular transport in condensed media can be described by phenomenological equations much simpler than Eq. (1), e.g., by the Einstein diffusion equation. The same holds true for reaction processes in condensed media. In this case one likes to focus onto the reaction coordinate, e.g., on a torsional angle.

In fact, there exist successful descriptions of a small subset of degrees of freedom by means of Newtonian equations of motion with effective force fields and added frictional as well as (time dependent) fluctuating forces. Let us assume we like to consider motion along a small subset of the whole coordinate space defined by the coordinates \( q_1, \ldots, q_M \) for \( M \ll N \). The equations which model the dynamics in this subspace are then (\( j = 1, 2, \ldots, M \))

\[ \mu_j \frac{d^2 q_j}{dt^2} = -\frac{\partial}{\partial q_j} W(q_1, \ldots, q_M) - \gamma_j \frac{d}{dt} q_j + \sigma_j \xi_j(t). \]  

(2)

This equation is known as Langevin equation. The first term on its r.h.s. describes the force field derived from an effective potential \( W(q_1, \ldots, q_M) \), the second term describes the velocity \( (\frac{d}{dt} q_j) \) dependent frictional forces, and the third term the fluctuating forces \( \xi_j(t) \) with coupling constants \( \sigma_j \). \( W(q_1, \ldots, q_M) \) includes the effect of the thermal motion of the remaining \( n - M \) degrees of freedom on the motion along the coordinates \( q_1, \ldots, q_M \).

One example of applications of Langevin equation is to model damping, known in physics as an effect that reduces the amplitude of oscillations in an oscillatory system, particularly the harmonic oscillator, in viscous medium. Let us consider a one-dimensional harmonic oscillator whose Langevin equation reads

\[ m\ddot{X} = -m\omega_0^2 X - \gamma m\dot{X} + \xi(t). \]  

(3)
We like to model the motion of an ensemble of such oscillators described through average
\( x(t) = n^{-1} \sum_{j=1}^{n} X_j(t) \) where \( X_j(t) \) is governed by Eq. (3). For an ensemble with large \( n \), the average of fluctuating forces \( \xi(t) \) over the ensemble should be close to the statistical average \( \langle \xi(t) \rangle \). Assuming \( \langle \xi(t) \rangle = 0 \), the ensemble average of \( \xi(t) \) vanishes. Thus, \( x(t) \) obeys
\[
\ddot{x} + \gamma \dot{x} + \omega_0^2 x = 0. \tag{4}
\]
The solutions to Eq. (4) have general forms
\[
x(t) = A e^{r_- t} + B e^{r_+ t}, \tag{5}
\]
with
\[
r_{\pm} = \frac{1}{2} (-\gamma \pm \sqrt{\gamma^2 - 4 \omega_0^2}), \tag{6}
\]
and with \( A \) and \( B \) being determined by initial conditions \( x(0) \) and \( \dot{x}(0) \),
\[
A = x(0) - \frac{r_- x(0) - \dot{x}(0)}{r_- - r_+}, \tag{7}
B = \frac{r_- x(0) - \dot{x}(0)}{r_- - r_+}. \tag{8}
\]
For the overdamped oscillators, i.e., \( \gamma^2 > 4 \omega_0^2 \), both \( r_{\pm} \) are real and negative. The oscillators governed by Eq. (5) cannot oscillate. Instead, they go asymptotically to the equilibrium \( x = 0 \). For the underdamped oscillators \( (\gamma^2 < 4 \omega_0^2) \), \( r_{\pm} \) are complex. The solution Eq. (5) turns into
\[
x(t) = e^{-(\gamma/2)t}[A \cos(\beta t) + B \sin(\beta t)], \tag{9}
\]
with \( \beta = 1/2 \sqrt{4 \omega_0^2 - \gamma^2} \). When \( \gamma = 0 \) the response is sinusoid. When \( \gamma \) is small we would expect the system to still oscillate, but with decreasing amplitude. Over time it should come to rest at equilibrium.

Equations of type (2) will be studied in detail further below. We will not “derive” these equations from the Newtonian equations (1) of the bulk material, but rather show by comparison of the predictions of Eq. (1) and Eq. (2) to what extent the suggested phenomenological descriptions apply. To do so and also to study further the consequences of Eq. (2) we need to investigate systematically the solutions of stochastic differential equations.

2 Stochastic Differential Equations

We consider stochastic differential equations in the form of a first order differential equation
\[
\partial_t x(t) = A[x(t), t] + B[x(t), t] \cdot \eta(t) \tag{10}
\]
subject to the initial condition
\[
x(0) = x_0. \tag{11}
\]
In this equation $A[x(t), t]$ represents the so-called drift term and $B[x(t), t] \cdot \eta(t)$ the noise term. Without the noise term, the resulting equation

$$\partial_t x(t) = A[x(t), t]. \quad (12)$$

describes a deterministic drift of particles along the field $A[x(t), t]$.

Equations like (12) can actually describe a wide variety of phenomena, like chemical kinetics or the firing of neurons. Since such systems are often subject to random perturbations, noise is added to the deterministic equations to yield associated stochastic differential equations. In such cases as well as in the case of classical Brownian particles, the noise term $B[x(t), t] \cdot \eta(t)$ needs to be specified on the basis of the underlying origins of noise.

We like to demonstrate that the one-dimensional Langevin equation (2) of a classical particle, written here in the form

$$\mu \ddot{q} = f(q) - \gamma \dot{q} + \sigma \xi(t) \quad (13)$$

is a special case of (10). In fact, defining $x \in \mathbb{R}^2$ with components $x_1 = m \dot{q}$, $x_2 = m q$ reproduces Eq. (10) if one defines

$$A[x(t), t] = \begin{pmatrix} f(x_2/m) - \gamma x_1/m \\ x_1 \end{pmatrix}, \quad B[x(t), t] = \begin{pmatrix} \sigma & 0 \\ 0 & 0 \end{pmatrix}, \quad \text{and} \quad \eta(t) = \begin{pmatrix} \xi(t) \\ 0 \end{pmatrix}. \quad (14)$$

The noise term represents a stochastic process. We consider only the factor $\eta(t)$ which describes the essential time dependence of the noise source in the different degrees of freedom. The matrix $B[x(t), t]$ describes the amplitude and the correlation of noise between the different degrees of freedom.

### 3 How to Describe Noise

We are now embarking on an essential aspect of our description, namely, how stochastic aspects of noise $\eta(t)$ are properly accounted for. Obviously, a particular realization of the time-dependent process $\eta(t)$ does not provide much information. Rather, one needs to consider the probability of observing a certain sequence of noise values $\eta_1, \eta_2, \ldots$ at times $t_1, t_2, \ldots$. The essential information is entailed in the conditional probabilities

$$p(\eta_1, t_1; \eta_2, t_2; \ldots | \eta_0, t_0; \eta_{-1}, t_{-1}; \ldots) \quad (15)$$

when the process is assumed to generate noise at fixed times $t_i$, $t_i < t_j$ for $i < j$. Here $p(\ | \ )$ is the probability that the random variable $\eta(t)$ assumes the values $\eta_1, \eta_2, \ldots$ at times $t_1, t_2, \ldots$, if it had previously assumed the values $\eta_0, \eta_{-1}, \ldots$ at times $t_0, t_{-1}, \ldots$.

An important class of random processes are so-called Markov processes for which the conditional probabilities depend only on $\eta_0$ and $t_0$ and not on earlier occurrences of noise values. In this case holds

$$p(\eta_1, t_1; \eta_2, t_2; \ldots | \eta_0, t_0; \eta_{-1}, t_{-1}; \ldots) = p(\eta_1, t_1; \eta_2, t_2; \ldots | \eta_0, t_0). \quad (16)$$
This property allows one to factorize $p(\mid )$ into a sequence of consecutive conditional probabilities.

\[
p(\eta_1, t_1; \eta_2, t_2; \ldots | \eta_0, t_0) = p(\eta_2, t_2; \eta_3, t_3; \ldots | \eta_1, t_1) p(\eta_1, t_1 | \eta_0, t_0) \\
= p(\eta_3, t_3; \eta_4, t_4; \ldots | \eta_2, t_2) p(\eta_2, t_2 | \eta_1, t_1) p(\eta_1, t_1 | \eta_0, t_0) \\
\vdots
\]

(17)

The unconditional probability for the realization of $\eta_1, \eta_2, \ldots$ at times $t_1, t_2, \ldots$ is

\[
p(\eta_1, t_1; \eta_2, t_2; \ldots) = \sum_{\eta_0} p(\eta_0, t_0) p(\eta_1, t_1 | \eta_0, t_0) p(\eta_2, t_2 | \eta_1, t_1) \cdots
\]

(18)

where $p(\eta_0, t_0)$ is the unconditional probability for the appearance of $\eta_0$ at time $t_0$. One can conclude from Eq. (18) that a knowledge of $p(\eta_0, t_0)$ and $p(\eta_i, t_i | \eta_{i-1}, t_{i-1})$ is sufficient for a complete characterization of a Markov process.

**Wiener Process**

We will now furnish concrete, analytical expressions for the probabilities characterizing important Markov processes. We begin with the so-called Wiener process. This process, described by $\omega(t)$ for $t \geq 0$, is characterized by the probability distributions

\[
p(\omega_0, t_0) = \frac{1}{\sqrt{4\piDt_0}} \exp\left(-\frac{\omega_0^2}{4Dt_0}\right),
\]

(19)

\[
p(\omega_1, t_1 | \omega_0, t_0) = \frac{1}{\sqrt{4\pi D \Delta t}} \exp\left(-\frac{(\Delta \omega)^2}{4D \Delta t}\right),
\]

(20)

where $\Delta \omega = (\omega_1 - \omega_0)$, $\Delta t = t_1 - t_0$.

The probabilities (see Figure 1) are parameterized through the constant $D$, referred to as the diffusion constant, since the probability distributions $p(\omega_0, t_0)$ and $p(\omega_1, t_1 | \omega_0, t_0)$ are solutions of the diffusion equation (60) discussed extensively below. The Wiener process is homogeneous in time and space, which implies that the conditional transition probability $p(\omega_1, t_1 | \omega_0, t_0)$ depends only on the relative variables $\Delta \omega$ and $\Delta t$. Put differently, the probability $p(\Delta \omega, \Delta t)$ for an increment $\Delta \omega$ to occur is independent of the current state of the Wiener process $\omega(t)$.

The probability is

\[
p(\Delta \omega, \Delta t) = p(\omega_0 + \Delta \omega, t_0 + \Delta t | \omega_0, t_0) = \frac{1}{\sqrt{4\pi D \Delta t}} \exp\left(-\frac{(\Delta \omega)^2}{4D \Delta t}\right).
\]

(21)

A Taylor expansion allows one to identify the moments\(^1\)

\[
\langle \omega^n(t) \rangle = \begin{cases} 
0 & \text{for odd } n, \\
(n-1)!! \cdot (2D)^{n/2} & \text{for even } n,
\end{cases}
\]

(22)

\(^1\)The double factorial $n!!$ for positive $n \in \mathbb{N}$ denotes the product $n(n-2)(n-4) \ldots 1$ for odd $n$ and $n(n-2)(n-4) \ldots 2$ for even $n.$
Figure 1: The probability density distribution (20) of a Wiener process for $D = 1$ in arbitrary temporal and spatial units. The distribution (20) is shown for $\omega_0 = 0$ and $(t_1 - t_0) = 0.1, 0.3, 0.6, 1.0, 1.7, 3.0, \text{ and } 8.0$.

The correlation functions of the Wiener process read

$$\left\langle \omega^{n_1}(t_1) \omega^{n_0}(t_0) \right\rangle = \begin{cases} 0 & \text{for odd } (n_0 + n_1), \\ 2 D \min(t_1, t_0) & \text{for } n_0 = 1 \text{ and } n_1 = 1, \\ 12 D^2 t_0 \min(t_1, t_0) & \text{for } n_0 = 1 \text{ and } n_1 = 3, \\ 4 D^2 \left( t_0 t_1 + 2 \min^2(t_1, t_0) \right) & \text{for } n_0 = 2 \text{ and } n_1 = 2, \\ \ldots & \end{cases} \quad (23)$$

**White Noise Process**

An important idealized stochastic process is the so-called ‘Gaussian white noise’. This process, denoted by $\xi(t)$, is not characterized through conditional and unconditional probabilities, but through the following statistical moment and correlation function

$$\left\langle \xi(t) \right\rangle = 0 \ , \quad (24)$$

$$\left\langle \xi(t_1) \xi(t_0) \right\rangle = \zeta^2 \delta(t_1 - t_0) \ . \quad (25)$$

The reason why this process is termed ‘white’ is connected with its correlation function (25), the Fourier transform of which is constant, i.e., entails all frequencies with equal amplitude just as white radiation. The importance of the process $\xi(t)$ stems from the fact that many other stochastic processes are described through stochastic differential equations with a (white) noise term $\xi(t)$. For example, there is an important relationship between white noise $\xi(t)$ and the
Wiener process $\omega(t)$,

$$\omega(t) = \int_0^t ds \xi(s) , \quad (26)$$

for $2D = \zeta^2 = 1$.

### 4 Fokker-Planck Equations

We consider the stochastic differential equation (10) with a noise term characterized through white noise, i.e., Eq. (25)

$$\partial_t x(t) = A[x(t), t] + B[x(t), t] \cdot \eta(t) \quad (27)$$

assuming $\eta(t) = \xi(t)$ with

$$\left\langle \xi_i(t) \right\rangle = 0 \quad (28)$$

$$\left\langle \xi_i(t_1) \xi_j(t_0) \right\rangle (dt)^2 = \delta_{ij} \delta(t_1 - t_0) dt \quad (29)$$

First, we express the above stochastic differential equation as an integral equation,

$$x(t) = \int_0^t ds A[x(s), s] + \int_0^t ds \xi(s) \cdot B^T [x(s), s] . \quad (30)$$

Since $x(t)$ is continuous, the first integral on the r.h.s. is well defined, e.g., in the sense of a Riemann integral. However, the second integral poses problems. Let us consider the simple one-dimensional case with an arbitrary function or stochastic process $G[t]$.

$$I(t) = \int_0^t ds \xi(s) G[s] . \quad (31)$$

One can rewrite the integral (31) in terms of a normalized Wiener process $\omega(t)$ with $D = 1/2$. One substitutes $d\omega(s)$ for $ds\xi(s)$, since $\int_0^t ds \xi(s) = \omega(t) = \int_0^t d\omega(s)$ and obtains

$$I(t) = \int_0^t d\omega(s) G[s] . \quad (32)$$

It can be shown that ordinary calculus cannot be applied to Eq. (32) due to stochastic variable $\omega(s)$. Therefore, alternative approaches are needed. One popular approach, known as Ito calculus, has the following rules,

$$d\omega_i(t) d\omega_j(t) = \delta_{ij} dt , \quad (33)$$

$$[d\omega(t)]^N = 0 , \text{ for } N > 2 , \quad (34)$$

$$d\omega(t)^N dt = 0 , \text{ for } N \geq 1 , \quad (35)$$

$$dt^N = 0 , \text{ for } N > 1 . \quad (36)$$
As with distributions, like the Dirac delta function $\delta(x)$, these rules (33-36) have to be seen in the context of integration. Furthermore the integration has to be over so-called non-anticipating functions or processes $G(t)$ which are statistically independent of $(\omega(s) - \omega(t))$ for any $s > t$.

Let $f[x(t)]$ be an arbitrary function of a process $x(t)$ that satisfies the one-dimensional stochastic differential equation

$$dx(t) = \left( a[x(t), t] + b[x(t), t] \xi(t) \right) dt = a[x(t), t] dt + b[x(t), t] d\omega(t). \quad (37)$$

To determine the change of $f[x(t)]$ with respect to $dx$ and $dt$ we perform a Taylor expansion

$$df[x(t)] = f'[x(t)] a[x(t), t] \, dt + f'[x(t)] b[x(t), t] \, d\omega(t) + \frac{1}{2} f''[x(t)] \, dx^2(t) + O(dx^3(t)).$$

Substituting equation (37) for $dx$ we can write

$$df[x(t)] = f'[x(t)] a[x(t), t] \, dt + f'[x(t)] b[x(t), t] \, d\omega(t) + \frac{1}{2} f''[x(t)] \left( b[x(t), t] \, d\omega(t) \right)^2 + O(d\omega^3(t)) \, O(dt^2). \quad (38)$$

We can neglect higher orders of $d\omega(t)$ and $dt$ due to Ito’s rules (34 - 36). We can also substitute $d\omega^2(t)$ by $dt$ due to (33) and obtain

$$df[x(t)] = f'[x(t)] a[x(t), t] \, dt + f'[x(t)] b[x(t), t] \, d\omega(t) + \frac{1}{2} f''[x(t)] \left( b[x(t), t] \right)^2 \, dt. \quad (39)$$

The resulting equation is so-called Ito’s formula. Ito’s formula in more than one-dimension reads

$$df[x(t)] = \sum_i A_i \left( \partial_i f[x(t)] \right) dt + \sum_{i,j} B_{ij} \left( \partial_i f[x(t)] \right) d\omega_j(t) \quad + \frac{1}{2} \sum_{i,j,k} B_{ik} B_{jk} \left( \partial_i \partial_j f[x(t)] \right) dt \quad (39)$$

Let us further consider the average of Ito’s formula (39).

$$\left< df[x(t)] \right> = \sum_i \left< A_i \left( \partial_i f[x(t)] \right) dt \right> + \sum_{i,j} \left< B_{ij} \left( \partial_i f[x(t)] \right) d\omega_j(t) \right> + \frac{1}{2} \sum_{i,j,k} \left< B_{ik} B_{jk} \left( \partial_i \partial_j f[x(t)] \right) dt \right> \quad (40)$$
The second sum on the r.h.s. vanishes, since $B_i(x(t), t)$ and $\partial_i f(x(t))$ are non-anticipating functions and therefore statistically independent of $d\omega_j(t)$, and because of equation (28) considering $d\omega_j(t) = \xi_j(t) dt$.

$$\langle B_{ij} \left( \partial_i f[x(t)] \right) d\omega_j(t) \rangle = \langle B_{ij} \left( \partial_i f[x(t)] \right) \rangle \langle \xi_j(t) \rangle dt = 0.$$  \hfill (41)

One is left with equation

$$\left\langle \frac{d}{dt} f[x(t)] \right\rangle = \sum_i \left\langle A_i \left( \partial_i f[x(t)] \right) \right\rangle + \frac{1}{2} \sum_{i,j} \left\langle [B \cdot B^T]_{ij} \left( \partial_i \partial_j f[x(t)] \right) \right\rangle .$$  \hfill (42)

$\langle f[x(t)] \rangle$ can be expressed as

$$\left\langle f[x(t)] \right\rangle = \int d\mathbf{x} \ f[\mathbf{x}] \ p(\mathbf{x}, t|\mathbf{x}_0, t_0) .$$  \hfill (43)

The reader should note that the initial value of $\langle f[x(t)] \rangle$ defined through (43) is $f[x_0]$ in accordance with the initial condition assumed for Eq. (10). Applying the time derivative to the r.h.s. of (43) and comparing with (42) yields

$$\int d\mathbf{x} \ f[\mathbf{x}] \ \partial_t p(\mathbf{x}, t|\mathbf{x}_0, t_0) =$$  \hfill (44)

$$\int d\mathbf{x} \ \left( \sum_i A_i \left( \partial_i f[\mathbf{x}] \right) + \frac{1}{2} \sum_{i,j} [B \cdot B^T]_{ij} \left( \partial_i \partial_j f[\mathbf{x}] \right) \right) p(\mathbf{x}, t|\mathbf{x}_0, t_0) .$$

Partial integration assuming a volume $\Omega$ with a surface $\partial \Omega$ allows one to change the order of the partial differential operators. For example, the first sum becomes

$$\int_{\Omega} d\mathbf{x} \ \sum_i A_i \left( \partial_i f[\mathbf{x}] \right) p(\mathbf{x}, t|\mathbf{x}_0, t_0) = - \int_{\Omega} d\mathbf{x} \ f[\mathbf{x}] \ \left( \sum_i \partial_i A_i \ p(\mathbf{x}, t|\mathbf{x}_0, t_0) \right)$$

$$+ \int_{\Omega} d\mathbf{x} \ \left( \sum_i \partial_i A_i \ f[\mathbf{x}] \ p(\mathbf{x}, t|\mathbf{x}_0, t_0) \right)$$

$$= - \int_{\Omega} d\mathbf{x} \ f[\mathbf{x}] \ \left( \sum_i \partial_i A_i \ p(\mathbf{x}, t|\mathbf{x}_0, t_0) \right)$$

$$+ \int_{\partial \Omega} d\mathbf{a} \cdot A \ f[\mathbf{x}] \ p(\mathbf{x}, t|\mathbf{x}_0, t_0) .$$ \hfill (45)

Assuming a $p(\mathbf{x}, t|\mathbf{x}_0, t_0)$ of finite spatial extent, such that it vanishes on the boundary $\partial \Omega$, we can neglect the surface term. Applying the same calculation twice to the second term in (44) leads to

$$\int d\mathbf{x} \ f[\mathbf{x}] \ \partial_t p(\mathbf{x}, t|\mathbf{x}_0, t_0) =$$  \hfill (46)

$$\int d\mathbf{x} \ f[\mathbf{x}] \ \left( - \sum_i \partial_i A_i \ p(\mathbf{x}, t|\mathbf{x}_0, t_0) + \frac{1}{2} \sum_{i,j} \partial_i \partial_j [B \cdot B^T]_{ij} \ p(\mathbf{x}, t|\mathbf{x}_0, t_0) \right) .$$
Since \( f[x(t)] \) is arbitrary we can conclude

\[
\partial_t p(x, t|x_0, t_0) = -\sum_i \partial_i A_i p(x, t|x_0, t_0) + \frac{1}{2} \sum_{i,j} \partial_i \partial_j [B \cdot B^T]_{ij} p(x, t|x_0, t_0).
\] (47)

This is the celebrated Fokker-Planck equation which describes the time evolution of the probability that the stochastic process determined by (10) assumes the value \( x \) at time \( t \) when it had assumed the value \( x_0 \) at time \( t_0 \).

5 Einstein Diffusion Equation

Now 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.

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

\[
m \ddot{r} = -\gamma \dot{r} + \sigma \xi(t)
\] (48)

In the limit of strong friction holds

\[|\gamma \dot{r}| \gg |m \ddot{r}| \] (49)

and, (48) becomes

\[
\gamma \dot{r} = \sigma \xi(t).
\] (50)

To this stochastic differential equation corresponds the Fokker-Planck equation [c.f. (27) and (47)]

\[
\partial_t p(r, t|r_0, t_0) = \nabla^2 \frac{\sigma^2}{2\gamma^2} p(r, t|r_0, t_0).
\] (51)

We assume in this chapter that \( \sigma \) and \( \gamma \) are spatially independent such that we can write

\[
\partial_t p(r, t|r_0, t_0) = \frac{\sigma^2}{2\gamma^2} \nabla^2 p(r, t|r_0, t_0).
\] (52)

This is the celebrated Einstein diffusion equation which describes microscopic transport of material and heat.
In order to show that the Einstein diffusion equation (52) reproduces the well-known diffusive behaviour of particles we consider the mean square displacement of a particle described by this equation, i.e., \( \langle (r(t) - r(t_0))^2 \rangle \sim t \). We first note that the mean square displacement can be expressed by means of the solution of (52) as follows

\[
\langle (r(t) - r(t_0))^2 \rangle = \int_{\Omega_\infty} d^3r (r(t) - r(t_0))^2 p(r, t| r_0, t_0).
\]  \(\text{(53)}\)

Integration over Eq. (52) in a similar manner yields

\[
\frac{d}{dt} \langle (r(t) - r(t_0))^2 \rangle = \frac{\sigma^2}{2\gamma^2} \int_{\Omega_\infty} d^3r (r(t) - r(t_0))^2 \nabla^2 p(r, t| r_0, t_0).
\]  \(\text{(54)}\)

Applying Green’s theorem for two functions \( u(r) \) and \( v(r) \)

\[
\int_{\Omega_\infty} d^3r (u \nabla^2 v - v \nabla^2 u) = \int_{\partial\Omega_\infty} d\mathbf{a} \cdot (u \nabla v - v \nabla u)
\]  \(\text{(55)}\)

for an infinite volume \( \Omega \) and considering the fact that \( p(r, t| r_0, t_0) \) must vanish at infinity we obtain

\[
\frac{d}{dt} \langle (r(t) - r(t_0))^2 \rangle = \frac{\sigma^2}{2\gamma^2} \int_{\Omega_\infty} d^3r p(r, t| r_0, t_0) \nabla^2 (r - r_0)^2.
\]  \(\text{(56)}\)

With \( \nabla^2 (r - r_0)^2 = 6 \) this is

\[
\frac{d}{dt} \langle (r(t) - r(t_0))^2 \rangle = 6 \frac{\sigma^2}{2\gamma^2} \int_{\Omega_\infty} d^3r p(r, t| r_0, t_0).
\]  \(\text{(57)}\)

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

\[
\langle (r(t) - r(t_0))^2 \rangle = 6 \frac{\sigma^2}{2\gamma^2} t.
\]  \(\text{(58)}\)

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

\[
D = \frac{\sigma^2}{2\gamma^2}.
\]  \(\text{(59)}\)

One can write the Einstein diffusion equation accordingly

\[
\partial_t p(r, t| r_0, t_0) = D \nabla^2 p(r, t| r_0, t_0).
\]  \(\text{(60)}\)

The solution to Eq. (60) is actually the three-dimensional generalization of the Wiener process (20)

\[
p(r, t| r_0, t_0) = (4\pi D(t - t_0))^{-\frac{3}{2}} \exp\left[-\frac{(r - r_0)^2}{4D(t - t_0)}\right]
\]  \(\text{(61)}\)
for the initial and boundary conditions

\[ p(r, t \to t_0 | r_0, t_0) = \delta(r - r_0) , \quad p(|r| \to \infty, t | r_0, t_0) = 0 . \] (62)

The system described by the Einstein diffusion equation (60) may either be closed at the surface of the diffusion space \( \Omega \) 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 \( \Omega \) 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 \( \Omega \) defined through

\[ N_\Omega(t | r_0, t_0) = \int \Omega d^3r p(r, t | r_0, t_0) . \] (63)

Since there are no terms in the diffusion equation (60) which affect the number of particles the particle number is conserved and any change of \( N_\Omega(t | r_0, t_0) \) must be due to particle flux at the surface of \( \Omega \). In fact, taking the time derivative of (63) yields, using (60) and \( \nabla^2 = \nabla \cdot \nabla \),

\[ \partial_t N_\Omega(t | r_0, t_0) = \int \Omega d^3r D \nabla \cdot p(r, t | r_0, t_0) . \] (64)

**Gauss’ theorem**

\[ \int \Omega d^3r \nabla \cdot v(r) = \int _{\partial \Omega} da \cdot v(r) \] (65)

for some vector-valued function \( v(r) \), allows one to write (64)

\[ \partial_t N_\Omega(t | r_0, t_0) = \int _{\partial \Omega} da \cdot D \nabla p(r, t | r_0, t_0) . \] (66)

Here

\[ j(r, t | r_0, t_0) = D \nabla p(r, t | r_0, t_0) \] (67)

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 \( \Omega \). Equation (67) is also known as Fick’s law. We will refer to

\[ \mathbf{J}_0(r) = D(r) \nabla \] (68)

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 \( \mathbf{J}_0(r) \) governs the spatial boundary conditions since it allows one to measure particle (probability) exchange at the surface of the diffusion space \( \Omega \). There are three types of boundary conditions possible.

The first type of boundary condition is specified by

\[ \hat{a}(r) \cdot \mathbf{J}_0(r) p(r, t | r_0, t_0) = 0 , \quad r \in \partial \Omega_i , \] (69)
which obviously implies that particles do not cross the boundary, i.e., are reflected. Here \( \hat{a}(\mathbf{r}) \) denotes a unit vector normal to the surface \( \partial \Omega_i \) at \( \mathbf{r} \). We will refer to (69) as the reflection boundary condition.

The second type of boundary condition is

\[
p(\mathbf{r}, t|\mathbf{r}_0, t_0) = 0, \quad \mathbf{r} \in \partial \Omega_i.
\]

(70)

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 (70) as the reaction boundary condition.

The third type of boundary condition,

\[
\hat{a}(\mathbf{r}) \cdot \mathbf{J}_0 p(\mathbf{r}, t|\mathbf{r}_0, t_0) = w p(\mathbf{r}, t|\mathbf{r}_0, t_0), \quad \mathbf{r} \in \partial \Omega_i,
\]

(71)

describes the case of intermediate reactivity at the boundary. The reactivity is measured by the parameter \( w \). For \( w = 0 \) in (71) \( \partial \Omega_i \) corresponds to a non-reactive, i.e., reflective boundary. For \( w \to \infty \) the condition (71) can only be satisfied for \( p(\mathbf{r}, t|\mathbf{r}_0, t_0) = 0 \), i.e., every particle impinging onto \( \partial \Omega_i \) is consumed in this case. We will refer to (71) 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.

**One-Dimensional Half-Space with Reflective Wall**

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 (60) in one dimension

\[
\partial_t p(x, t|x_0, t_0) = D \partial_x^2 p(x, t|x_0, t_0),
\]

(72)

where the solution considered satisfies the initial condition

\[
p(x, t \to 0|x_0, t_0) = \delta(x - x_0).
\]

(73)

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

\[
\partial_x p(x, t|x_0, t_0) = 0.
\]

(74)

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

\[
p(x \to \infty, t|x_0, t_0) = 0.
\]

(75)

Without the wall at \( x = 0 \), i.e., if (74) would be replaced by \( p(x \to -\infty, t|x_0, t_0) = 0 \), the solution would be the one-dimensional equivalent of (61), i.e.,

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

(76)
In order to satisfy the boundary condition one can add a second term to this solution for an imaginary particle starting diffusion at position $-x_0$ behind the boundary. One obtains

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

(77)

which, as stated, holds only in the available half-space $x \geq 0$. Obviously, this function is a solution of (72) since both terms satisfy this equation. This solution also satisfies the boundary condition (75). One can easily convince oneself either on account of the reflection symmetry with respect to $x = 0$ of (77) or by differentiation, that (77) does satisfy the boundary condition at $x = 0$.

The solution (77) 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 (77) 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 (72) with initial condition (73) and boundary condition (75) 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 (74) of the previous problem by

$$
p(x = 0, t|x_0, t_0) = 0.
$$

(78)

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

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

(79)

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 (79) corresponding to
Figure 2: Probability density distribution of a freely diffusing particle in half-space with an absorbing boundary at $x = 0$. The left plot shows the time evolution of equation (79) with $x_0 = 1$ and $(t_1 - t_0) = 0.0, 0.1, 0.3, 0.6, 1.0, 1.7, \text{ and } 3.0$ for $D = 1$ in arbitrary temporal and spatial units. The right plot depicts the assembly of solution (79) with two Gaussian distributions at $(t_1 - t_0) = 0.3$.

particle removal by the wall. It appears that (79) 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 (79) (see Figure 2).

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

$$N(t|x_0,t_0) = \int_0^\infty dx \, p(x,t|x_0,t_0) \, .$$

(80)

Introducing the integration variable

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

(81)

(80) can be written

$$N(t|x_0,t_0) = \frac{2}{\sqrt{\pi}} \int_0^{y_0} dy \, \exp[-y^2] \, ,$$

(82)

leading to the final expression, using (81),

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

(83)

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

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

(84)
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.

The rate of particle decay, according to (83), is

\[
\frac{\partial_t N(t|x_0, t_0)}{N(t|x_0, t_0)} = - \frac{x_0}{\sqrt{2\pi D (t - t_0)}} \frac{x_0^2}{4D (t - t_0)} \exp\left[ - \frac{x_0^2}{4D (t - t_0)} \right].
\](85)

An alternative route to determine the decay rate follows from (67) which reads for the case considered here,

\[
\frac{\partial_t N(t|x_0, t_0)}{N(t|x_0, t_0)} = -D \left. \partial_x p(x, t|x_0, t_0) \right|_{x=0}.
\](86)

Evaluation of this expression yields the same result as Eq. (85). This illustrates how useful the relationship (67) can be.

**Free Diffusion in a Finite Domain**

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

\[ \Omega = [0, a]. \] (87)

The boundaries of \( \Omega \) 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

\[
\frac{\partial_t p(x, t|x_0, t_0)}{p(x, t|x_0, t_0)} = D \frac{\partial_x^2 p(x, t|x_0, t_0)}{p(x, t|x_0, t_0)}
\] (88)

subject to the initial condition

\[ p(x, t_0|x_0, t_0) = \delta(x - x_0) \] (89)

and to the boundary conditions

\[ D \left. \partial_x p(x, t|x_0, t_0) \right|_{x=0} = 0, \quad \text{for } x = 0, \text{ and } x = a. \](90)

In order to solve (88–90) we expand \( p(x, t|x_0, t_0) \) in terms of eigenfunctions of the diffusion operator

\[ L_0 = D \partial_x^2. \] (91)

where we restrict the function space to those functions which obey (90). The corresponding functions are

\[ v_n(x) = A_n \cos\left( n \frac{\pi x}{a} \right), \quad n = 0, 1, 2, \ldots . \] (92)

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

\[
L_0 v_n(x) = \lambda_n v_n(x)
\] (93)

\[ \lambda_n = - D \left( \frac{n \pi}{a} \right)^2. \] (94)
We can define, in the present case, the scalar product for functions \( f, g \) in the function space considered

\[
\langle g \mid f \rangle_\Omega = \int_0^a dx \, g(x) \, f(x).
\] (95)

For the eigenfunctions (92) we choose the normalization

\[
\langle v_n \mid v_n \rangle_\Omega = 1.
\] (96)

This implies

\[
A_n = \begin{cases} \sqrt{1/a} & \text{for } n = 0, \\ \sqrt{2/a} & \text{for } n = 1, 2, \ldots. \end{cases}
\] (97)

On the other hand, one can show that the functions \( v_n \) are orthogonal with respect to the scalar product (95), i.e.,

\[
\langle v_m \mid v_n \rangle_\Omega = \delta_{mn}.
\] (98)

Without proof we note that the functions \( v_n \), defined in (92), form a complete basis for the function space considered. Together with the scalar product (95) this basis is orthonormal. We can, hence, readily expand \( p(x,t \mid x_0, t_0) \) in terms of \( v_n \)

\[
p(x,t \mid x_0, t_0) = \sum_{n=0}^\infty \alpha_n(t \mid x_0, t_0) \, v_n(x).
\] (99)

Inserting this expansion into (88) and using (93) yields

\[
\sum_{n=0}^\infty \partial_t \alpha_n(t \mid x_0, t_0) \, v_n(x) = \sum_{n=0}^\infty \lambda_n \, \alpha_n(t \mid x_0, t_0) \, v_n(x).
\] (100)

Taking the scalar product \( \langle v_m \mid \) leads to

\[
\partial_t \, \alpha_m(t \mid x_0, t_0) = \lambda_m \, \alpha_m(t \mid x_0, t_0)
\] (101)

from which we conclude

\[
\alpha_m(t \mid x_0, t_0) = e^{\lambda_m(t-t_0)} \beta_m(x_0, t_0).
\] (102)

Here, \( \beta_m(x_0, t_0) \) are time-independent constants which are determined by the initial condition (89)

\[
\sum_{n=0}^\infty \beta_n(x_0, t_0) \, v_n(x) = \delta(x-x_0).
\] (103)

Taking again the scalar product \( \langle v_m \mid \) results in

\[
\beta_m(x_0, t_0) = v_m(x_0).
\] (104)
Altogether holds then

\[ p(x,t|x_0,t_0) = \sum_{n=0}^{\infty} e^{\lambda_n(t-t_0)} v_n(x_0) v_n(x) . \]  

(105)

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

\[ p(x,t) = \int_0^a dx_0 \ p(x,t|x_0,t_0) f(x_0) . \]  

(106)

Employing the expansion (105) this can be written

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

(107)

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

\[ p(x,t) \underset{t \to \infty}{\sim} \frac{1}{a} . \]  

(108)

This asymptotic behaviour, indeed, follows from (107). We note from (94)

\[ e^{\lambda_n(t-t_0)} \underset{t \to \infty}{\sim} \begin{cases} 1 & \text{for } n = 0 \\ 0 & \text{for } n = 1, 2, \ldots \end{cases} \]  

(109)

From (92, 97) follows \( v_0(x) = \frac{1}{\sqrt{a}} \) and, hence,

\[ p(x,t) \underset{t \to \infty}{\sim} \frac{1}{a} \int_0^a dx \ v(x_0) . \]  

(110)

The property \( \langle 1 | f \rangle_\Omega = 1 \) implies then (108).

The solution presented here [cf. (87–110)] provides in a nutshell 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 later modules.

**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

\[ P_3 = P_0 \cos \theta \]  

(111)

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
\[
\partial_t p(r, t| r_0, t_0) = D \nabla^2 p(r, t| r_0, t_0) \tag{112}
\]
for the condition \(|r| = |r_0| = 1\). In order to obey this condition one employs the Laplace operator \(\nabla^2\) in terms of spherical coordinates \((r, \theta, \phi)\), i.e.,
\[
\nabla^2 = \frac{1}{r^2} \left[ \partial_r \left( r^2 \partial_r \right) + \frac{1}{\sin^2 \theta} \partial_\phi^2 + \frac{1}{\sin \theta} \partial_\theta \left( \sin \theta \partial_\theta \right) \right], \tag{113}
\]
and sets \(r = 1\), dropping also derivatives with respect to \(r\). This yields the rotational diffusion equation
\[
\partial_t p(\Omega, t| \Omega_0, t_0) = \tau_r^{-1} \left[ \frac{1}{\sin \theta} \partial_\theta \left( \sin \theta \partial_\theta \right) + \frac{1}{\sin^2 \theta} \partial_\phi^2 \right] p(\Omega, t| \Omega_0, t_0). \tag{114}
\]
We have defined here \(\Omega = (\theta, \phi)\). We have also introduced, instead of the diffusion constant, the rate constant \(\tau_r^{-1}\) since the replacement \(r \to 1\) altered the units in the diffusion equation; \(\tau_r\) 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.,
\[
p(\Omega, t| \Omega_0, t_0) = \sum_{\ell=0}^{\infty} \sum_{m=-\ell}^{+\ell} A_{\ell m}(t| \Omega_0, t_0) Y_{\ell m}(\Omega). \tag{115}
\]
In addition, one can exploit the eigenfunction property
\[
\left[ \frac{1}{\sin \theta} \partial_\theta \left( \sin \theta \partial_\theta \right) + \frac{1}{\sin^2 \theta} \partial_\phi^2 \right] Y_{\ell m}(\Omega) = -\ell (\ell + 1) Y_{\ell m}(\Omega). \tag{116}
\]
Inserting (115) into (114) and using (116) results in
\[
\sum_{\ell=0}^{\infty} \sum_{m=-\ell}^{+\ell} \partial_t A_{\ell m}(t| \Omega_0, t_0) Y_{\ell m}(\Omega) = -\sum_{\ell=0}^{\infty} \sum_{m=-\ell}^{+\ell} \ell (\ell + 1) \tau_r^{-1} A_{\ell m}(t| \Omega_0, t_0) Y_{\ell m}(\Omega), \tag{117}
\]
The orthonormality property
\[
\int d\Omega \, Y_{\ell_m'}(\Omega) Y_{\ell m}(\Omega) = \delta_{\ell \ell'} \delta_{m'm} \tag{118}
\]
leads one to conclude
\[
\partial_t A_{\ell m}(t| \Omega_0, t_0) = -\ell (\ell + 1) \tau_r^{-1} A_{\ell m}(t| \Omega_0, t_0), \tag{119}
\]
and, accordingly,
\[
A_{\ell m}(t| \Omega_0, t_0) = e^{-\ell (\ell+1)(t-t_0)/\tau_r} a_{\ell m}(\Omega_0), \tag{120}
\]
or
\[ p(\Omega, t|\Omega_0, t_0) = \sum_{\ell=0}^{\infty} \sum_{m=-\ell}^{\ell} e^{-\ell(\ell+1)(t-t_0)/\tau_r} a_{\ell m}(\Omega_0) Y_{\ell m}(\Omega) . \]  

(121)

The coefficients \( a_{\ell m}(\Omega_0) \) are determined through the condition
\[ p(\Omega, t_0|\Omega_0, t_0) = \delta(\Omega - \Omega_0) . \]  

(122)

The completeness relationship of spherical harmonics states
\[ \delta(\Omega - \Omega_0) = \sum_{\ell=0}^{\infty} \sum_{m=-\ell}^{\ell} Y_{\ell m}^*(\Omega_0) Y_{\ell m}(\Omega) . \]  

(123)

Equating this with (121) for \( t = t_0 \) yields
\[ a_{\ell m}(\Omega_0) = Y_{\ell m}^*(\Omega_0) \]  

(124)

and, hence,
\[ p(\Omega, t|\Omega_0, t_0) = \sum_{\ell=0}^{\infty} \sum_{m=-\ell}^{\ell} e^{-\ell(\ell+1)(t-t_0)/\tau_r} Y_{\ell m}^*(\Omega_0) Y_{\ell m}(\Omega) . \]  

(125)

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
\[ \lim_{t \to \infty} p(\Omega, t|\Omega_0, t_0) = \frac{1}{4\pi} , \]  

(126)

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
\[ p_0(\Omega) = \frac{1}{4\pi} . \]  

(127)

The equilibrium average of the polarization expressed in (111) is
\[ \langle P_3 \rangle = \int d\Omega P_0 \cos \theta \ p_0(\Omega) . \]  

(128)

One can readily show
\[ \langle P_3 \rangle = 0 . \]  

(129)

Another quantity of interest is the so-called equilibrium correlation function
\[ \langle P_3(t) P_3^*(t_0) \rangle = P_0^2 \int d\Omega \int d\Omega_0 \ \cos \theta \ \cos \theta_0 \ p(\Omega, t|\Omega_0, t_0) p_0(\Omega_0) . \]  

(130)
Using

\[ Y_{10}(\Omega) = \sqrt{\frac{3}{4\pi}} \cos \theta \]  

(131)

and expansion (125) one obtains

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

(132)

where

\[ C_{10,\ell m} = \int d\Omega \ Y_{10}^*(\Omega) \ Y_{\ell m}(\Omega) . \]  

(133)

The orthonormality condition of the spherical harmonics yields immediately

\[ C_{10,\ell m} = \delta_{\ell 1} \delta_{m0} \]  

(134)

and, therefore,

\[ \langle P_3(t) P_3^*(t_0) \rangle = \frac{4\pi}{3} P_0^2 e^{-2(t-t_0)/\tau_r} . \]  

(135)

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.

References


