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Lecture 7-8: Stochastic Processes, Applications, References

I am neither a man of skills nor a man of knowledge but only a seeker.
Albert Einstein
Chapter 7

Brownian Motion

7.1 Einstein’s concept of Brownian motion

This and the following Chapters extend the material presented in Chapter 2, Section 2.5, where we presented already different approaches to stochastic processes.

In the case of Brownian motion all the approaches work equally well and are essentially equivalent, however, each of them has its own area of application and its own domain of validity outside of the case of diffusion processes: they apply to different cases of the so-called anomalous diffusion as well. Therefore we do not hesitate to discuss the same issue from different points of view and to present different derivations of the same results. Such a deep understanding always pays off.

Motivated mostly by description of Brownian motion several different but strongly interconnected approaches were devised for the description of phenom-
Brownian Motion

ena where the stochastic nature of systems plays a considerable role. The ingenious microscopic derivation of the diffusion equation by A. Einstein (which contained, in a nutshell, several different approaches) and the discussion by P. Langevin marked the two main ways of description of fluctuation phenomena, one based on the discussion of the deterministic equations for the probability densities, another one based on the discussion of a particular stochastic realizations of the process. These approaches, refined both from physical and from the mathematically point of view build now the main instrument of description of both equilibrium and nonequilibrium processes on a mesoscopic scale.

Einstein, in his analysis of the situation has connected the motion of suspended particles with diffusion and showed that this diffusive behavior follows from the three postulates. First, the particles considered are assumed not to interact with each other: their trajectories are independent. Second, one assumes that the motion of the particles lacks long-time memory: one can choose such a time interval $\tau$, that the displacements of the particle during two subsequent intervals are independent. Third, the distribution of a particle’s displacements $s$ during the subsequent time intervals $\phi(s)$ possesses at least two
lower moments. Moreover, for the force-free situation \( \phi(s) \) is symmetric. The displacement of the particle can thus be considered as a result of many tiny, independent, equally distributed steps.

The further line of his reasoning is very close to what we will call now a Kramers-Moyal expansion, see Chapter 2. For the simplicity, following Einstein, we analyze a one-dimensional problem:

The concentration of particles \( n \) in vicinity of point \( x \) is proportional to the probability density \( f(x, t) \) to find one particle at this point. Comparing the probabilities at time \( \tau \) and at time \( t + \tau \) we get (due to the independence of the new displacement of the previous position and to the fact that \( x(t + \tau) = x(t) + s \))

\[
f(x, t + \tau) = \int f(x - s, t) \phi(s) ds. \quad (7.1)
\]

Now, since both \( \tau \) and \( s \) are both small compared to the time- and space-scales of interest, one can expand the function \( f \) in Taylor series on both sides of the equation. On the left-hand side it is enough to expand up to the first order in \( t \), on the right-hand side we need the second order in \( s \). We get:

\[
f + \left( \frac{\partial f}{\partial t} \right) \tau + \ldots = f + \left( \frac{\partial f}{\partial x} \right) \int s \phi(s) ds + \frac{1}{2} \left( \frac{\partial^2 f}{\partial x^2} \right) \int s^2 \phi(s) ds + \ldots \quad (7.2)
\]
Brownian Motion

The integral \( \int s \phi(s) ds \) vanishes due to the symmetry. In the lowest order we thus get:

\[
\frac{\partial f}{\partial t} = \frac{\sigma^2}{2\tau} \frac{\partial^2}{\partial x^2} f, \tag{7.3}
\]

where \( \sigma^2 = \int s^2 \phi(s) ds \). Here we recognize a diffusion equation, and associate \( \sigma^2/2\tau \) with the diffusion coefficient \( D \). The solution of Eq.(7.3) is, clearly, a Gaussian

\[
f(x, t) = \frac{1}{\sqrt{4\pi Dt}} \exp \left( -\frac{x^2}{4Dt} \right), \tag{7.4}
\]

so that the root-mean-square displacement of the particle along the \( x \)-axis would be \( \lambda_x = \sqrt{\langle x^2 \rangle} = \sqrt{2Dt} \), which gives the direct way of experimental measurement of \( D \).

The derivation of the diffusion equation by A. Einstein was the very first step of statistical physics into the new domain of non-equilibrium phenomena. Note however, that it was not the derivation of the diffusion equation, which seemed to Einstein to be the main topic of this work: The discussion of the diffusion of particles in the solution gave the way to determine the Avogadro number \( N_A \) through the macroscopic measurements on large particles, the measurement performed by Perrin some 3 years later. Such measurements were necessary to provide solid
basement for atomistic theory of matter. The corresponding theoretical considerations were summarized in Einstein’s PhD thesis ”Eine neue Bestimmung der Moleküldimensionen” (New method for determination of molecular sizes) presented on April 30, 1906 to the University of Zürich.

7.2 The Langevin equation: theme and variations

7.2.1 The Langevin equation

In his article published in Comptes Rendus in 1908 Paul Langevin proposed another approach to description of Brownian motion, than one of Einstein and Smoluchowski. This one was assumed to be "infinitely simpler" than the Einstein’s one and seemed to be based only on the equipartition theorem. Here we repeat the main argumentation of the original work (Langevin, 1908).

Let us consider the motion of the Brownian particle in fluid. On the average this motion is governed by the Newtonian dynamics under friction, \( m\dot{v} = -\gamma v \), where \( \gamma \) is the friction coefficient (for a macroscopic spherical particle this friction follows the Stokes law, so that \( \gamma = 6\pi \eta r \), where \( r \) is the particle’s radius). However, this equation, leading to the continuous decay of the particle’s velocity, holds only on the average. In order to describe the erratic motion of
the particle, resulting from random, uncompensated impacts of the molecules of surrounding fluid, we have to introduce additional, fluctuating force $\xi(t)$ (“noise”). We assume only that this force has zero mean (so that it does not lead to the overall motion on average), and that it is independent on $x$, which mirrors the homogeneity of the whole system. We thus write

$$m \dot{v} = -\gamma v + \xi(t). \quad (7.5)$$

Our first task will be to find the mean squared displacement of the particle. Let us now multiply both sides of Eq. (7.5) by $x(t)$ and use the evident fact that $x\dot{v} = x\ddot{x} = \frac{d}{dt} (x\dot{x}) - \dot{x}^2$. We thus get

$$m \frac{d}{dt} (x\ddot{x}) = m\ddot{x}^2 - \gamma x\dot{x} + x\xi. \quad (7.6)$$

Let us now average this equation over the realizations of the process. Dividing both parts of the equation by $m$ we get:

$$\frac{d}{dt} \langle x\ddot{x} \rangle = -\frac{\gamma}{m} \langle x\dot{x} \rangle + \langle \dot{x}^2 \rangle + \frac{1}{m} \langle x\xi \rangle. \quad (7.7)$$

The last mean value vanishes due to the independence of $x$ and $\xi$ and to the fact that the mean value of $\xi$ is zero: $\langle x\xi \rangle = \langle x \rangle \langle \xi \rangle = 0$. Moreover, due to the equipartition theorem, the mean squared velocity of the particle in our one-dimensional model is so
that $m \langle \dot{x}^2 \rangle /2 = kT /2$, i.e.

$$\langle \dot{x}^2 \rangle = \frac{kT}{m}. \quad (7.8)$$

Thus, for the mean $\langle x \dot{x} \rangle$ one has

$$\frac{d}{dt} \langle x \dot{x} \rangle = -\frac{\gamma}{m} \langle x \dot{x} \rangle + \frac{kT}{m}. \quad (7.9)$$

Let us now assume that the initial particle’s position is taken to be at the origin of coordinates. Then $\langle x(0) \dot{x}(0) \rangle = 0$. Under this initial condition Eq. (7.9) can easily be solved and delivers

$$\langle x(t) \dot{x}(t) \rangle = \int_0^t \exp \left[ -\frac{\gamma}{m} (t - t') \right] \frac{kT}{m} dt' = \frac{kT}{\gamma} \left[ 1 - \exp \left( -\frac{\gamma}{m} t \right) \right]. \quad (7.10)$$

As a next step, we note that $\langle x(t) \dot{x}(t) \rangle = \frac{1}{2} \frac{d}{dt} \langle x^2(t) \rangle$, so that the mean squared displacement of the particle can be found by an additional integration of Eq. (7.10):

$$\langle x^2(t) \rangle = 2 \int_0^t \langle x(t') \dot{x}(t') \rangle dt' = \frac{2kT}{\gamma} \left[ t - \frac{m}{\gamma} \left( 1 - \exp \left( -\frac{\gamma}{m} t \right) \right) \right]. \quad (7.11)$$

For large time the leading term corresponds to

$$\langle x^2(t) \rangle = 2 \frac{kT}{\gamma} t, \quad (7.12)$$
i.e. to the diffusive behavior with the diffusion coefficient \( D = kT/\gamma \).

7.2.2 Thermalization of the velocity: The fluctuation-dissipation theorem

From our previous discussion it may seem that no properties of the force except for its symmetry are of importance. However, the assumption of the thermalization of the velocity, so that \( \langle v^2 \rangle = kT/m \), poses rather tight conditions on the behavior of the force. In order to show this let us examine the Langevin equation more carefully.

From the Langevin equation we immediately have:

\[
\dot{v} = -\frac{\gamma}{m} v + \frac{1}{m} \xi(t).
\] (7.13)

This is the simplest linear differential equation of the form we have already seen in the previous paragraph, so that its solution can be put down immediately:

\[
v(t) = v(0) \exp \left( -\frac{\gamma}{m} t \right) + \frac{1}{m} \int_0^t dt' \xi(t-t') \exp \left[ -\frac{\gamma}{m} t' \right].
\] (7.14)

Now it is easy to calculate the velocity squared:

\[
v^2(t) = v^2(0) \exp \left( -2\frac{\gamma}{m} t \right) + 2v(0) \exp \left( -\frac{\gamma}{m} t \right) \int_0^t dt' \xi(t-t') \exp \left[ -\frac{\gamma}{m} t' \right] \exp \left[ -\frac{\gamma}{m} t \right] + \left\{ \frac{1}{m} \int_0^t dt' \xi(t-t') \exp \left[ -\frac{\gamma}{m} t' \right] \right\}^2.
\]
Averaging this expression, we see that the first term is not changed since it is deterministic, the second one gives on the average zero since the averaging is the linear operation and as those can be permuted with the integration, and since moreover \( \langle \xi(t - t') \rangle = 0 \). To average the third term we first rewrite the square of the integral as a repeated integral,

\[
\left[ \int_0^t \xi(t - t') \exp \left( -\frac{\gamma t'}{m} \right) \right]^2 =
\left[ \int_0^t dt' \xi(t - t') \exp \left( -\frac{\gamma t'}{m} \right) \right] \left[ \int_0^t dt'' \xi(t - t'') \exp \left( -\frac{\gamma t''}{m} \right) \right] =
\int_0^t \int_0^t dt' dt'' \exp \left( -\frac{\gamma t'}{m} \right) \exp \left( -\frac{\gamma t''}{m} \right) \xi(t - t') \xi(t - t'').
\]

Performing now the averaging we get:

\[
v^2(t) = v^2(0) \exp \left( -2 \frac{\gamma t}{m} \right) \tag{7.17}
+ \frac{1}{m^2} \int_0^t \int_0^t dt' dt'' \exp \left[ -\frac{\gamma}{m} (t' + t'') \right] \langle \xi(t - t') \xi(t - t'') \rangle.
\]

If we now assume the noise to be a stationary random process, then its correlation function depends only on the difference of the arguments, \( \langle \xi(t - t') \xi(t - t'') \rangle = C(t' - t''). \) Thus, we can put down

\[
v^2(t) = v^2(0) \exp \left( -2 \frac{\gamma t}{m} \right) \tag{7.18}
+ \frac{1}{m^2} \int_0^t \int_0^t dt' dt'' \exp \left[ -\frac{\gamma}{m} (t' + t'') \right] C(t' - t'').
\]

Let us now consider the thermalization process. If
the overall integration time is much larger than both the correlation time of the force and the characteristic time \( m/\gamma \) of decay of deterministic motion, the limits of integration can be extended to infinity. We can now change to the sum and to the difference variables: \( s = (t' + t'') / 2 \) and \( q = (t' - t'') \) (the absolute value of the Jakobian of this transformation is 1). If the correlation function decays fast compared to the deterministic motion, \( \tau_c \ll m/\gamma \), the integrations in \( s \) and \( q \) may be considered as independent so that

\[
\langle v^2(t) \rangle \approx v^2(0) \exp \left( -\frac{2\gamma t}{m} \right) + \frac{2}{m^2} \int_0^\infty ds \exp \left[ -\frac{2\gamma}{m} \left( s \right) \right] \int_0^\infty C(q) dq,
\]

where \( C = \int_0^\infty C(t) dt \) is the integral of the correlation function \( C(t') \). The first term decays exponentially with time, so that under thermalization we have

\[
\langle v^2 \rangle_{eq} = \frac{C}{m\gamma}.
\]

Comparing this result with the equipartition condition \( \langle v^2 \rangle_{eq} = kT/m \) we see that \( C = kT\gamma \). This result connecting the behavior of the random force to the friction coefficient and thus to the dissipation in the deterministic motion is a special case of the fluctuation-dissipation theorem. Using the previ-
ously established connection between $\gamma$ and the diffusion coefficient $D$ we get $C = D\gamma^2$.

The velocity will thermalize and the Langevin approach will be valid if the integral $\int_0^\infty C(t)dt$ converges. This is violated if the correlation function of the force decays so slow that $\int_0^\infty C(t)dt$ diverges. The overall behavior in this case can be vastly different from one described above and could correspond to the so-called anomalous diffusion, see Section 7.6.

7.2.3 The properties of the noise

Dividing the overall interaction between the Brownian particle and the medium into a deterministic part (friction) and a random part (noise), we already dispensed from the idea to fully describe the system’s dynamics on very short time scales: both the friction and the random force stem essentially from the molecular impacts and follow very complex dynamics. Looking at the situation at very short time scales we would not recognize any constant friction force. The situation gets very clear when we consider, for example, a particle in a rarefied medium, say, a dust particle in the air. In this case it is clear that the interaction between the particle and the air molecules corresponds to a sequence of separated, very short, practically punctual events of momentum transfer.
Brownian Motion

(impacts), and the periods of practically no interaction. The velocities of the gas particles are governed by the Maxwell distribution, so that the components of their momenta are Gaussian. In order to separate between that deterministic and the stochastic component we need to perform a kind of temporal pre-averaging over some physically small time interval $\Delta t$. The friction force appears on the average due to the fact that the particle moving, say, with the positive velocity in $x$-direction meets more gas molecules hitting it from the right (against the its motion direction) than from the left. The velocity of our particle is finite, and momentum transferred in each impact has the finite second moment. The overall change of the particle’s momentum $\Delta p = \Sigma_i \Delta p(t_i)$ where $t_i$ is the instant of $i$-th impact. The mean force is then $f = \Delta p/\Delta t$ and equals to the mean momentum transfer per impact. Subtracting this mean from the actual value of $\Delta p$ we get the noise. Note that since $\Delta p$ is a sum of many (presumably) independent random variables possessing the finite second moment, then distribution of $\Delta p$ at longer times (after many impacts) will tend to a Gaussian, as a consequence of the Central Limit Theorem. Thus, the distribution of the transferred momentum during the
time $\Delta t$ reads

$$P(\Delta p) \simeq \frac{1}{\sqrt{2\pi \sigma(\Delta t)}} \exp \left( -\frac{(\Delta p - f \Delta t)^2}{2\sigma^2(\Delta t)} \right).$$  \hfill (7.21)

Here $f$ is the deterministic force (which was taken $f = -\gamma v$ in our previous considerations) and $\delta p = \Delta p - f \Delta t$ is the random component of the momentum change during the time $\Delta t$. Assuming this change to be due to the random force $\xi$, we get $\delta p = \int_t^{t+\Delta t} \xi(t') dt'$. Then the dispersion $\sigma^2(\Delta t)$ can be connected with the correlation properties of the noise. Since the noise is assumed to be homogeneous in time we can take $t = 0$ without losing the generality. Using the identity

$$\delta p^2(t) = \left[ \int_0^{\Delta t} \xi(t') dt' \right]^2 = \int_0^{\Delta t} \xi(t') dt' \cdot \int_0^{\Delta t} \xi(t'') dt'',$$  \hfill \text{22}

and averaging this result over the realizations of the noise we get

$$\sigma^2(\Delta t) = \langle \delta p^2(\Delta t) \rangle = \int_0^{\Delta t} \int_0^{\Delta t} \langle \xi(t') \xi(t'') \rangle dt' dt''.$$  \hfill (7.23)
Assuming that \( \langle \xi(t')\xi(t'') \rangle = C(|t' - t''|) \) and changing to a new variable \( q = t' - t'' \) we get

\[
\sigma^2(\Delta t) = \int_0^{\Delta t} dt' \int_{-t'}^{t'} C(|q|) dq = 2 \int_0^{\Delta t} dt' \int_0^{t'} C(q) dq.
\] (7.24)

Assume now that \( \int_0^{t'} C(|q|) dq \) converges so fast that

\[
2 \int_0^{\Delta t} dt' \int_0^{t'} C(q) dq \simeq 2 \int_0^{\Delta t} dt' \int_0^{\infty} C(q) dq = 2C\Delta t
\] (7.25)

(this fast convergence is the mathematical expression of the physical assumption that the forces at different \( \Delta t \)-intervals are uncorrelated). Noting that \( C = D\gamma^2 \) and that according to the fluctuation-dissipation theorem one has \( D = kT/\gamma \) we get that the change of the particle’s momentum during the time \( \Delta t \) follows the probability distribution

\[
P(\Delta p) \simeq \frac{1}{\sqrt{4\pi kT\gamma\Delta t}} \exp \left( -\frac{(\Delta p - f\Delta t)^2}{4kT\gamma\Delta t} \right).
\] (7.26)

Thus, we see that in many cases it is reasonable to assume that the noise in the Langevin equation has a Gaussian distribution. Moreover, one can take this noise to be \( \delta \)-correlated, so that

\[
\langle \xi(t)\xi(t') \rangle = 2C\delta(t - t') = 2kT\gamma\delta(t - t'),
\] (7.27)

which exactly corresponds to the behavior assumed by Eq.(7.25) for any \( \Delta t \). Thus, the noise is supposed
to be Gaussian and white. Moreover, since the averaged force value is subtracted, $\langle \xi(t) \rangle = 0$. The process corresponding to the integral of the noise

$$W(t) = \int_0^t \xi(t) dt$$

(7.28)

is called a Wiener process. The curve depicting this process on the $(t, W)$-plane is continuous (in the sense that large jumps are very improbable) but nowhere differentiable. Its fractal dimension is 2. The introduction of a Wiener process gives several mathematical advantages and leads to mathematically firm derivation of many results. Physically one however has be aware, that it corresponds to generalizing the intermediate-scale dynamics to the smallest, microscopic scales, which may be incorrect.

7.3 Taylor-Kubo formula and velocity-velocity correlations

There exists one more method of calculation of the mean squared displacement, which may seem to be even simpler than even the original Langevin’s one. We already used this method implicitly in our previous discussions, however, it is reasonable to discuss it here in some detail. Let us consider a particle moving with the velocity $v(t)$. If the velocity of the particle is know, it is easy to calculate its displacement

$$x(t) = \int_0^t v(t') dt'$$

(7.29)
(we again assume that the particle’s position at \( t = 0 \) is \( x = 0 \)). To calculate the mean squared displacement we use the already familiar trick:

\[
x^2(t) = \left[ \int_0^t v(t')dt' \right]^2 = \int_0^t v(t')dt' \cdot \int_0^t v(t'')dt'' = \int_0^t \int_0^t v(t')v(t'')dt'dt''.
\] (7.30)

Averaging this equation we get

\[
\langle x^2(t) \rangle = \int_0^t \int_0^t \langle v(t')v(t'') \rangle \ dt'dt''.
\] (7.31)

We now assume the stationarity of the random process \( v(t) \) and define the velocity-velocity correlation function \( B(\tau) = \langle v(t)v(t+\tau) \rangle \) (note that this function is an even function of \( \tau \) which follows from its independence on \( t \) for a stationary process). We get:

\[
\langle x^2(t) \rangle = \int_0^t \int_0^t B(|t' - t''|)dt'dt''.
\] (7.32)

Let us first assume that the velocity-velocity correlation decays rather fast, so that it is integrable. This is the case, for example, for the genuine Langevin case, where it decays exponentially, with the characteristic time \( \tau_{br} = m/\gamma \). Let us now change in the double integral, Eq.(7.31), to a new variable \( q = t' - t'' \)

\[
\langle x^2(t) \rangle = \int_0^t dt' \int_{-t'}^{t'} B(|q|)dq = 2 \int_0^t dt' \int_0^{t'} B(|q|)dq.
\] (7.33)
Since integral over $q$ is convergent, for $t \gg \tau_{br}$ the upper limit of integration can be changed for infinity:

$$\langle x^2(t) \rangle = 2 \left[ \int_0^\infty B(|q|) dq \right] t, \quad (7.34)$$

which immediately gives us the value of the diffusion coefficient

$$D = \int_0^\infty \langle v(t)v(0) \rangle \ dt; \quad (7.35)$$

the diffusion coefficient is nothing else than the integral of the velocity-velocity correlation function. This fact was first discovered by G.I. Taylor (in a related but slightly different context of the passive particles’ transport by a random wind, Taylor, 1921) and is typically referred to as a Taylor-Kubo formula.

Let us now turn to the case of a Langevin equation and obtain the value of the diffusion coefficient. To calculate the velocity-velocity correlation function we start from Eqs.(7.13) and (7.14). Averaging the solution of Eq.(7.14) over the realizations of the noise, we get

$$\langle v(t) \rangle_{\text{noise}} = v_0 \exp \left( -\frac{\gamma}{m} t \right) \quad (7.36)$$

so that

$$\langle v(t)v(0) \rangle_{\text{noise}} = v_0^2 \exp \left( -\frac{\gamma}{m} t \right). \quad (7.37)$$

However, an additional averaging over the initial velocity $v_0^2$ is necessary. The equipartition theorem says
that $\langle v_0^2 \rangle_{eq} = kT/m$, so that

$$B(t) = \langle v(t')v(t'') \rangle = \frac{kT}{m} \exp \left( -\frac{\gamma t}{m} \right). \quad (7.38)$$

Evaluating the integral, Eq.(7.35), for our correlation function, Eq.(7.38), we get

$$D = kT/\gamma, \quad (7.39)$$

an already familiar result.

Note that in order to have a long-time diffusive behavior, the convergence of the integral, Eq.(7.35) is necessary. The situation when the integral diverges lead to different kinds of anomalous diffusion. Quite a few examples of such processes are known. If, for example, $B(\tau) \propto \tau^{-\alpha}$ for $\tau$ large, the corresponding integral diverges if $\alpha \geq -1$, leading to superdiffusion. In this case evaluating of Eq.(7.33) gives $\langle x^2(t) \rangle \propto t^{2-\alpha}$ for $\alpha < 1$ and $\langle x^2(t) \rangle \propto t \ln t$ for $\alpha = 1$ and $t$ large. This last situation is physically relevant. In 1968 Alder and Wainwright performed numerical calculations of the velocity autocorrelation function in a system of hard discs and spheres using molecular dynamics (Alder and Wainwright, 1968, 1969). The process here corresponds to a Brownian motion of one (marked) particle in the fluid of the particles of the same mass. They found out that this correlation function decays at long times essentially
as $t^{-d/2}$, with $d$ being the dimension of space, i.e. $d = 2$ for the discs and $d = 3$ for spheres. This work has initiated a vivid discussion. The reason for such a behavior is that the motion of the Brownian particle is in fact a much more complicated process than one assumed by Langevin. The motion of a particle in a fluid creates a velocity field in a fluid itself, which is rather persistent and interacts with the particle motion: Contrary to the Langevin’s assumption the fluid as a whole is not quite quiescent, and its velocity at the particle’s position depends on the particle’s motion prehistory. The corresponding explanation and calculations may be found in the books of Balescu (1975) and of Zwanzig (2001). For us now it is important to note that in 3d the velocity-velocity correlation decays fast enough to be integrable, so that the Einstein’s and Langevin’s picture of the Brownian motion still holds; the behavior in 2d may however be quite different.

The long-lasting correlations and memory effects lead to non-Markovian Langevin constructions, typically of the form

$$m\ddot{x} = -U'(x) - \int_0^t dt' \dot{x}(t')K(t - t') + \xi(t) \quad (7.40)$$

where $K(t)$ is the memory-kernel. The noise $\xi(t)$ is typically taken to be Gaussian but not white. The
corresponding fluctuation-dissipation relation (the Nyquist theorem) connects the memory kernel and the correlation function of the noise. A simple model leading to such equations will be considered in Section ??.

7.4 The overdamped limit

Essentially, for the separation of integrations in $s$ and in $q$ in Eq.(7.19) it is of no importance, which time scale shorter, it is only important that they differ strongly. We now turn to the situation, $m/\gamma \ll \tau_c$, corresponding to the so-called overdamped limit of the Brownian motion.

Let us return to the Langevin equation

$$m\dot{v} = -\gamma v + \xi(t) \quad (7.41)$$

and consider now a very light particle with $m/\gamma \to 0$. In this case the particle’s motion is governed by the Aristotelian dynamics

$$\dot{x} = v = \frac{1}{\gamma} \xi(t), \quad (7.42)$$

so that the velocity of the particle follows immediately the acting force. The solution follows from the Taylor’s result,

$$\langle x^2(t) \rangle = \frac{1}{\gamma^2} \int_0^t dt' \int_{-t'}^{t'} C(q) dq, \quad (7.43)$$
so that \( B(r) = \gamma^{-2}C(\tau) \). Assuming that the integral \( \int_0^\infty B(\tau)d\tau \) converges and considering times \( t \gg \tau_c \) we get

\[
\langle x^2(t) \rangle = 2t \frac{1}{\gamma^2} \int_0^\infty C(q)dq,
\]  
(7.44)

so that \( \langle x^2(t) \rangle \) grows diffusively. Comparing Eq.(7.44) with the definition of the diffusion coefficient

\[
\langle x^2(t) \rangle = 2Dt
\]  
(7.45)

we get in this case

\[
D = \frac{1}{\gamma^2} \int_0^\infty C(r)dr.
\]  
(7.46)

This definition of the diffusion coefficient coincides with the previous one since as we have already seen also in the underdamped situation \( \int_0^\infty C(r)dr = D\gamma^2 \).

We now make a small change in our notation. We namely can dispense from \( \gamma \) in the Eq.(7.42) and introduce a new notation for the noise term:

\[
\dot{x} = \sqrt{2D}\eta(t),
\]  
(7.47)

where the noise \( \eta \) now possess the unit integral of its correlation function:

\[
\int_{-\infty}^{\infty} \langle \eta(0)\eta(t) \rangle dt = 2 \int_0^\infty \langle \eta(0)\eta(t) \rangle dt = 1. \quad (7.48)
\]

Since we are interested only in the times which are much larger than the correlation times of the noise,
we can take the last practically equal to zero and put down

\[ \langle \eta(0)\eta(t) \rangle = \delta(t), \]  

(7.49)

thus assuming the noise to be \textit{white}. We also note that Eq.(7.47) describes the long-time behavior of a massive Langevin particle, now in the long time limit, i.e. for \( t \gg m/\gamma \).

We note that the Langevin motion can also be considered under the action of some external force, say, gravitation, like it is the case in the Perrin’s experiment with colloidal particles in water. In this case the initial Langevin equation reads

\[ m\dot{v} = f - \gamma v + \xi(t) \]  

(7.50)

where \( f \) is the external force (e.g. \( f = -mg \) in the Perrin’s situation). Taking the limit \( m/\gamma \rightarrow 0 \) (and changing to our new notation) we get

\[ \dot{x} = \mu f + \sqrt{2D}\eta(t) \]  

(7.51)

with the mobility \( \mu = 1/\gamma \), which is the form of the Langevin equation of the widest use. Let us now turn to a simple example.

\textbf{7.4.1 Example: The Ornstein-Uhlenbeck process}

There are several good reasons to discuss the behavior of an overdamped particle in a harmonic poten-
The situation was first discussed by Smoluchowski in 1913. His argumentation however was different from one we use here, where the process is considered as an example for using the Langevin scheme.

The corresponding Langevin equation reads

$$\dot{x} = -\frac{\kappa}{\gamma} x + \sqrt{2D}\eta(t). \quad (7.52)$$

The random process governed by the Eq.(7.52) is called the Ornstein-Uhlenbeck process (Uhlenbeck and Ornstein, 1930). The corresponding process is of interest since it is one of the few less trivial situations where the closed analytical solution is possible.

Let us consider the initial condition problem when the particle starts at $t = 0$ at a given coordinate $x(0) = x_0$. We note that this equation for $x$ coincides (up to the notation) with the one governing the velocity of the particle in the classical Langevin problem, so that the correlation function of the particle’s coordinate can be immediately put down. Parallel to §7.2.2 we have

$$\langle x(t) \rangle = x_0 \exp\left(-\frac{\kappa}{\gamma} t\right) \quad (7.53)$$

and

$$\langle x(t)x(0) \rangle = \langle x_0^2 \rangle \exp\left(-\frac{\kappa}{\gamma} t\right). \quad (7.54)$$
We note that $\tau = \gamma/\kappa$ has a dimension of time; this is the typical relaxation time of the process.

Let us now discuss the Ornstein-Uhlenbeck process from the thermodynamical point of view and some of its peculiar properties. Consider a general thermodynamical system under isothermal conditions, and take $x$ to be a relevant thermodynamical variable. According to the Zeroth Law, a system, let evolve freely, will sooner or later achieve an equilibrium. Being perturbed from the equilibrium state, the system returns back to it; this process takes some time and is called relaxation. The thermodynamical potentials (say, the free energy) have at equilibrium their simple, quadratic minima; the corresponding thermodynamic force $f = -\partial F/\partial x$ is thus linear in the variable $x$ describing the deviation from the equilibrium, $f = -\kappa x$, and our problem is equivalent to one of the behavior of an overdamped harmonic oscillator.

Let us now consider fluctuations of $x$ around its equilibrium value (taken to be $x = 0$). According to the Onsager’s regression principle introduced in Chapter 6 (which is a generalization of the primary Langevin’s picture to the case of liner thermodynamic theories), small fluctuations decay on the average in the same way as macroscopic deviations from equilibrium. However, we know, that these fluctua-
tions in equilibrium do not vanish: this fact is taken into account by the additional random force. Thus, the Ornstein-Uhlenbeck process (or its multidimensional generalizations) describes fluctuations within the linear nonequilibrium thermodynamic scheme, and is just as important and universal as the scheme itself.

The probability density of the particle’s position at time $t$ can for this case be found exactly. The approach is based on the linear property of our Langevin process. Using the fact that

$$\dot{x} = -\frac{\kappa}{\gamma} x + \sqrt{2D} \eta(t)$$

(7.55)

we put down the formal solution of this ODE in form:

$$x(t) - x_0 \exp \left(-\frac{\kappa}{\gamma}(t - t_0)\right) = \sqrt{2D} \int_{t_0}^{t} dt' \eta(t-t') \exp \left[-\frac{\kappa}{\gamma}(t' - t_0)\right],$$

(7.56)

which differs only in notation from our Eq.(7.14). Its right hand side corresponds to a weighted sum of independent Gaussian variables, and thus is also normally distributed. To see this, let consider the subdivision of the integral on the right-hand side into non-intersecting intervals $\Delta t$:

$$\int_{t_0}^{t} dt' \eta(t-t') \exp \left[-\frac{\kappa}{\gamma}(t' - t_0)\right]$$

$$= \sum_n \int_{t_0 + n\Delta t}^{t_0 + (n+1)\Delta t} dt' \eta(t-t') \exp \left[-\frac{\kappa}{\gamma}(t' - t_0)\right]$$
\[= \sum_n \exp \left(\frac{-\kappa}{\gamma} t^*_n \right) \int_{t_0+n\Delta t}^{t_0+(n+1)\Delta t} dt' \eta(t-t') \quad (7.57)\]

where, according to the mean value theorem, \( t^*_n \in [t_0 + n\Delta t, t_0 + (n + 1)\Delta t] \). We already know that all integrals \( \int_{t_0+n\Delta t}^{t_0+(n+1)\Delta t} dt' \eta(t-t') \) are Gaussian-distributed and independent and have zero mean. So are also the products of these integrals with the exponential prefactors. Since the sum of independent Gaussian variables also has a Gaussian distribution, we see that the lhs of Eq.(7.56) is distributed according to a symmetric Gaussian law. From the symmetry it follows that the mean value of the right hand side is zero and thus

\[\langle x(t) \rangle = x_0 \exp(-\tau^{-1} t), \quad (7.58)\]

where the characteristic relaxation time \( \tau = \gamma/\kappa \) is introduced. It is not hard to find the dispersion of the distribution of the right-hand side. Using the fact that \( \langle \eta(t)\eta(t') \rangle = \delta(t-t') \) we get

\[
\sigma^2(t) = 2D \left\langle \left( \int_{t_0}^{t} dt' \eta(t-t') e^{\frac{1}{\tau}(t' - t_0)} \right)^2 \right\rangle = 2D \int_{t_0}^{t} \int_{t_0}^{t} dt' dt'' \delta(t-t' - t + t'') e^{\frac{1}{\tau}(t' + t'' - 2t_0)} = 2D \int_{t_0}^{t} dt' e^{\frac{2}{\tau}(t'-t_0)} = D\tau \left(1 - e^{\frac{2(t'-t_0)}{\tau}} \right) (7.59)
\]
Thus, the probability \( p(x, t|x_0, t_0) \) reads
\[
p(x, t|x_0, t_0) = \frac{1}{\sqrt{2\pi D\tau}} \left(1 - e^{-2(t-t_0)/\tau}\right) \exp \left(-\frac{(x - e^{-(t-t_0)/\tau}x_0)^2}{2D\tau(1 - e^{-2(t-t_0)/\tau})}\right)
\]
(7.60)

The first two central moments \( M_1 = \langle x \rangle \), Eq.(7.58), and \( M_2 = \langle (x - \langle x \rangle)^2 \rangle \), Eq.(7.59), relax exponentially to their equilibrium values. After the equilibration (i.e. for the times \( t \gg \tau \)) the process gets stationary and describes equilibrium fluctuations around the value \( x = 0 \). The distribution of fluctuations \( p(x) = p(x, t|x_0, -\infty) \) is Gaussian,
\[
p(x) = \frac{1}{\sqrt{2\pi D\tau}} \exp \left(-\frac{x^2}{2D\tau}\right),
\]
(7.61)

with the mean squared value of \( x \) equal to \( D\tau \). Now, let us remember that, according to the Einstein’s relation \( D = kT/\gamma \) and that \( \tau = \gamma/\kappa \). Thus, we have \( D\tau = kT/\kappa \), so that \( p(x) \) corresponds to the Boltzmann distribution
\[
p(x) = \frac{\kappa}{\sqrt{2\pi kT}} \exp \left(-\frac{\kappa x^2}{2kT}\right),
\]
(7.62)

the equilibrium value of \( \kappa \langle x^2 \rangle = kT \), according to the equipartition theorem.

The Ornstein-Uhlenbeck process is one of a few situations when the probability density can be immediately deduced from the Langevin picture and from
the properties of the noise. In all other cases the Fokker-Planck approach providing us with the partial differential equation for this probability density is more appropriate.
Chapter 8

Fokker-Planck and Master Equations

8.1 Equations for the probability density

We note that the initial approach of Einstein was based on the discussion of the deterministic equations for the probability densities, while the Langevin’s one emphasized the stochastic nature of single realizations. The generalization of the Einstein’s approach leads to what is now known as a Fokker-Planck equation. Phenomenologically, the equation can be derived along the lines of the Fick’s approach, by combining the linear response assumption and the continuity equation (Fick, 1855). The diffusion-like equation essentially for the overdamped motion with drift was first proposed by A. Fokker in his dissertation in 1914, and discussed by M. Planck in 1918. The work of Planck starts from the note that Fokker published only the equation itself, without any derivation. Such derivation was promised but never published. The same equation was proposed by Smolu-
Thus, the particle’s density $n(x, t)$ or the probability to find a particle $p(x, t)$ fulfills the equation

$$\frac{\partial p}{\partial t} + \text{div} J = 0$$

where $J$ is the probability current. On the other hand, this current may appear due to the two factors: the concentration gradient and the external force $\mathbf{f}$:

$$J = -D \nabla p + \mu \mathbf{f} p$$

where $\mu$ is the particle’s mobility. Combining the equations we get the diffusion equation with drift:

$$\frac{\partial p}{\partial t} = \nabla (-\mu \mathbf{f} p + D \nabla p).$$

The standard derivation of the Fokker-Planck equation due to Smoluchowski, Kolmogorov et al. follows the lines of the Einstein’s discussion and starts from the general Markovian assumption. One considers the process characterized by the transition probabilities $p(x, t|x', t')$, the probability for a particle to be at $x$ at time $t$ provided it started at $x'$ at time $t' < t$. We note that $x$ here has not necessarily to be considered as a scalar, but for the simplicity we use the
Equations for the probability density

Our initial considerations are the ones already discussed in the end of Chapter 2. The Markovian property leads us to the assumption that probability to be at \( x \) at time \( t \) haven started at \( x_0 \) at time \( t_0 \) can be expressed through the integral

\[
p(x, t|x_0, 0) = \int dx' p(x, t|x', t')p(x', t'|x_0, 0) \quad \text{(8.4)}
\]

which essentially doesn’t mean anything else than the statement of the fact that at time \( t' \) the particle has to be found at some place it really could get to. Depending on the community, this equation is termed as a Smoluchowski, or as a Chapman-Kolmogorov equation. We now consider the time \( t' \) as being close enough to \( t \): subtracting \( p(x', t'|x_0, 0) \) from the both parts of the integral equation we get

\[
p(x, t|x_0, 0) - p(x', t'|x_0, 0) = \int dx' p(x, t|x', t')p(x', t'|x_0, 0) - p(x', t')p(x', t'x_0, 0) - p(x', t'
\quad \text{(8.5)}
\]

We now discuss the situation when the difference \( \Delta t = t - t' \) can be considered as small. The left-hand side can be approximated through \( \frac{\partial}{\partial t} p(x, t'|x_0, 0) \Delta t \). We shall assume that typical changes in the coordinates during this short time are also to some extent small. Let us denote \( r = x - x' \) and introduce the transition probabilities \( w(y, r; t, \Delta t) = p(y + r, t + \Delta t|x_0, 0) \)
\[ \Delta t \mid y, t \). Now we rewrite Eq.(8.5) in the form

\[
\frac{\partial}{\partial t} p(x, t \mid x_0, t_0) \Delta t = \int drw(x-r, r; t, \Delta t) p(x-r, t \mid x_0, 0) - p(x, t \mid x_0, t_0) \]

and start expanding the integrand in powers of \( r \). We namely use the fact that

\[
w(x-r, r; t, \Delta t) p(x-r, t \mid x_0, 0) = w(x, r; t, \Delta t) p(x, t \mid x_0, 0) - r \frac{\partial}{\partial x} w(x, r; t, \Delta t) p(x, t \mid x_0, 0) + \frac{1}{2} r^2 \frac{\partial^2}{\partial x^2} w(x, r; t, \Delta t) p(x, t \mid x_0, 0) + \ldots
\]

which lets us rewrite the first integral in the form

\[
\frac{\partial}{\partial t} p(x, t \mid x_0, t_0) \Delta t = p(x, t \mid x_0, t_0) \int drw(x-r, r; t, \Delta t) - \frac{\partial}{\partial x} p(x, t \mid x_0, t_0) \int drw(x-r, r; t, \Delta t) + \frac{\partial^2}{\partial x^2} p(x, t \mid x_0, t_0) \int drw(x-r, r; t, \Delta t) + \ldots
\]

Noting that due to the normalization \( \int drw(y, r; t, \Delta t) = 1 \) we see that the first and the last terms of the expression in the right-hand side cancel. Performing
the limiting transition $\Delta t \to 0$ one has
\[
\frac{\partial}{\partial t} p(x, t|x_0, t_0) = \sum_{n=1}^{\infty} \frac{(-1)^n}{n!} \frac{\partial^n}{\partial x^n} K_n(x, t)p(x, t|x_0, t_0)
\]
(8.9)

where the transition moments
\[
K_n(x, t) = \lim_{\Delta t \to 0} \frac{1}{\Delta t} \int dr r^n w(x, r; t, \Delta t).
\]
(8.10)

The expression Eq.(8.9) corresponds to the Kramers-Moyal expansion. For the case of the Brownian motion and other diffusive processes one finds that only 2 first transition moments are different from zero: there are
\[
A(x, t) = \lim_{\Delta t \to 0} \frac{1}{\Delta t} \int dr r w(x, r; t, \Delta t)
\]
(8.11)

and
\[
B(x, t) = \lim_{\Delta t \to 0} \frac{1}{\Delta t} \int dr r^2 w(x, r; t, \Delta t).
\]
(8.12)

All higher moments vanish under the limiting transition $\Delta t \to 0$ since
\[
\int dr r^n w(x, r; t, \Delta t) = O(\Delta t^2) \text{ for } n \geq 3.
\]
(8.13)

In this case the Kramers-Moyal expansion of the Chapman-Kolmogorov equation leads to the Fokker-Planck equa-
tion for \( p(x, t|x_0, t_0) \)

\[
\frac{\partial}{\partial t} p(x, t|x_0, t_0) = -\frac{\partial}{\partial x} A(x, t)p(x, t|x_0, t_0) + \frac{1}{2} \frac{\partial^2}{\partial x^2} B(x, t)p(x, t|x_0, t_0)
\]

Comparing this general equation with our phenomenological equation, Eq.(8.3), we see that it also has a form of a continuity equation,

\[
\frac{\partial}{\partial t} p = \frac{\partial}{\partial x} \left[ -Ap + \frac{1}{2} \frac{\partial}{\partial x} Bp \right].
\]  

(8.15)

Note that the transition probability \( p(x, t|y, s) \) is essentially a function of two spatial variables, \( x \) and \( y \), the initial and the final particle’s positions, and two times \( t \) and \( s \). It is often desirable to have the equation which defines the function \( p(x, t|y, s) \) with respect to its initial position and to the time \( s = t_0 \). This can be easily done by considering the increment \( p(x, t|y, s) - p(x, t|y', s') \) and repeating the steps leaving to the Fokker-Planck equation, we get (under the same assumptions)

\[
-\frac{\partial}{\partial s} p(x, t|y, s) = A(y, s) \frac{\partial}{\partial y} p(x, t|y, s) + B(y, s) \frac{\partial^2}{\partial y^2} p(x, t|y, s).
\]

(8.16)

Eq.(8.16) is called the backward Kolmogorov equation, while the Fokker-Planck equation in this context is called the forward one. The differential operator
\( \mathbf{L}^+ \) acting on \( p(x, t|y, s) \) in the right-hand side of this equation is adjoint to the differential operator in the right-hand side of the forward (Fokker-Planck) equation \( \mathbf{L} \) with respect to the scalar product of two function \( (f, g) = \int (f(x)g(x)dx \) in the sense that \( (f, \mathbf{L}g) = (\mathbf{L}^+f, g) \).

We also note that the Pawula’s theorem states that either the first two moments (having exactly the behavior described by Eqs.(8.11) and (8.12)) are enough for the full description, or the whole infinite series has to be used. Truncating the series after any other term than the second one leads to equations which do not guarantee the non-negativity of their solutions, which therefore cannot be interpreted as probability density functions. In this case the integral equation representations cannot be reduced to anything considerably more simple.

In the case of the overdamped motion the coefficients \( A \) and \( B \) can be easily obtained from the discussion of the overdamped Langevin motion, Eq.(7.51). From Eq.(??) we get the transition probability density \( w(x, r; t, \Delta t) \) to be Gaussian

\[
 w(x, r; t, \Delta t) = \frac{1}{\sqrt{4\pi D\Delta t}} \exp \left( -\frac{(r - \mu f \Delta t)^2}{4D\Delta t} \right)
\]  
(8.17)
from which we get that $A(t) = \mu f$ and $B = \Delta t^{-1} \left[ (\mu f \Delta t)^2 + 2D\Delta t \right]$. $2D$ for $\Delta t \to 0$, and that the higher transition moments (being the combinations of the two lower ones) are of a higher order in $\Delta t$. Hence, the resulting Fokker-Planck equation reads

$$\frac{\partial}{\partial t}p = \frac{\partial}{\partial x} \left[ -\mu fp + D \frac{\partial}{\partial x} p \right], \quad (8.18)$$

(with $D$ and $\mu$ connected by the fluctuation-dissipation relation $D = kT\mu$). Eq.(8.18) is exactly the one following from our initial phenomenological considerations. The Fokker-Planck equation for the overdamped situation is often called the Smoluchowski equation.

We note that taking the limits in Eq.(8.11) and (8.12) corresponds essentially to the derivatives of the corresponding transition moments. The first one can be then interpreted as the mean velocity at point $x$, $\langle v(x) \rangle$, and the second one as the time derivative of the mean squared displacement from $x$, connected to a local diffusion coefficient.

The form of the Fokker-Planck equation stays the same if one considers the variable $x$ as a vector in the coordinate or in the phase space: The only important assumptions are the Markovian nature of transitions and the existence of transition moments. The vector form of the Fokker-Planck equation reads (compare
Special stochastic processes

8.2 Special stochastic processes

8.2.1 Example 1: The Ornstein-Uhlenbeck process revisited

Let us return to the Ornstein-Uhlenbeck process describing the behavior of an overdamped particle in the harmonic potential under the influence of white noise. The Smoluchowski equation is

\[
\frac{\partial}{\partial t} p = \sum_i \frac{\partial}{\partial x_i} \left[ -A_i p + \frac{1}{2} \sum_j D_{ij} \frac{\partial}{\partial x_j} p \right].
\]  

(8.19)

There are several methods to solve Smoluchowski equations; many of them are discussed in detail in Risken’s book (Risken, 1988, 1994).

Note that a Smoluchowski equation (with coordinate-independent \(D\)) in a field of a potential force \(f = -\nabla U\) can be reduced to a Schrödinger equation by taking \(p(x, t) = \sqrt{p_{eq}(x)} g(x, t)\), where \(p_{eq}(x)\) is the equilibrium solution, \(p_{eq}(x) = \exp \left[ -U(x) / kT \right]\). The equation for \(g(x, t)\) then reads

\[
-\frac{\partial}{\partial t} g = D \left[ -\frac{\partial^2}{\partial x^2} + U_{eff}(x) \right] g,
\]

(8.21)
with the effective potential
\[ U_{\text{eff}}(x) = \left( \frac{1}{2kT} \frac{\partial U}{\partial x} \right)^2 - \frac{1}{2kT} \frac{\partial^2 U}{\partial x^2}. \] (8.22)

The advantage of putting the Smoluchowski equation in this form is the fact that the operator in the right-hand side of Eq.(8.21) is now Hermitian, and the equation itself allows for a much simpler analytical treatment. For example, it is a great convenience, that the right and left eigenfunctions of this operator coincide, so that the simple eigenfunction decomposition approach, known from the quantum mechanics, works:
\[ g(x, t) = \sum_n \phi_n(x)\Phi_n(t) \] (8.23)
where the temporal functions are governed by ordinary differential equations of the type
\[ \frac{d\Phi_n(t)}{dt} = -\lambda_n \Phi_n(t); \] (8.24)
\(\lambda_n\) are the eigenvalues of the Schrödinger operator on the right-hand side. Moreover, the potential \(U_{\text{eff}}(x)\) has an additional symmetry (it corresponds to a so-called supersymmetric quantum mechanics, Gendenstein and Krive, 1985) so that it immediately follows that one of the eigenvalues is zero, which corresponds to a steady (equilibrium) state, and that this state is non-degenerate.
For the quadratic potential corresponding to the Ornstein-Uhlenbeck process, the effective potential given by Eq. (8.22) is quadratic again. Thus, the Fokker-Planck equation describing the Ornstein-Uhlenbeck process is reduced to the Schrödinger equation for a harmonic oscillator. No wonder that all properties of the solutions are known. As a solution of the initial-value problem we get of course an already known result,

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

It is interesting to note, that the Ornstein-Uhlenbeck process (essentially the process with the exponentially decaying covariation) is the only diffusive process (with continuous trajectories) that is Gaussian and Markovian at the same time.

Let us consider a homogeneous Gaussian process, corresponding to the system at equilibrium. The joint probability density \(p(x, t, x_0, t_0) = p(x, x_0, t - t_0)\) is fully defined by the dispersion \(\sigma\) and by the covariance \(g(t - t') = \langle x(t)x(t') \rangle / \sigma^2\) and reads

\[
p(x, t, x_0, t_0) = \frac{1}{2\pi \sigma^2 \sqrt{1 - g^2}} \exp\left(-\frac{(x^2 - 2gxx_0 + x_0^2)}{2\sigma^2(1 - g^2)}\right).
\]

(8.26)
We note that since \( \lim_{dt \to 0} \langle x(t + dt)x(t) \rangle = \langle x(t)x(t) \rangle = \sigma^2 \), one has \( g(0) = 1 \). To obtain the transition probability, which is the conditional probability for a particle to be at \( x \) at time \( t \) provided it was in \( x_0 \) at time \( t_0 \) we use a Bayes theorem, according to which

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

and take \( p(x_0,t_0) \) to be a one-point, equilibrium probability density,

\[
p(x_0,t_0) = \frac{1}{\sqrt{2\pi\sigma^2}} \exp \left( -\frac{x_0^2}{2\sigma^2} \right).
\]

Combining Eqs.(8.26) and (8.27) we get:

\[
p(x,t|x_0,t_0) = \sqrt{\frac{1}{2\pi\sigma^2(1 - g^2)}} \exp \left( -\frac{(x - gx_0)^2}{2\sigma^2(1 - g^2)} \right).
\]  

Inserting this transition probability into a Chapman-Kolmogorov equation

\[
p(x,t|x_0,0) = \int dx' p(x,t|x',t)p(x',t'|x_0,0)
\]

and performing the integrations we get that

\[
\frac{1}{\sqrt{2\pi\sigma^2(1 - g(t)^2)}} \exp \left( -\frac{(x - g(t)x_0)^2}{2\sigma^2(1 - g(t)^2)} \right) = \frac{1}{\sqrt{2\pi\sigma^2(1 - g(t-t')^2g(t')^2)}} \exp \left( -\frac{(x - g(t-t')g(t')x_0)^2}{2\sigma^2(1 - g(t-t')^2g(t')^2)} \right)
\]
from which for any $t' \in [0, t]$ it follows that
\[ g(t) = g(t - t')g(t'). \quad (8.31) \]

The only differentiable solution of this functional equation is an exponential: taking $dt = t - t'$ to be small we get:
\[ g(t) = g(t') + \frac{dg(t')}{dt'} dt = g(dt)g(t'). \quad (8.32) \]

We thus get:
\[ \frac{1}{g(t')} \frac{dg(t')}{dt'} dt = g(dt) - 1. \quad (8.33) \]

Noting that $g(0) = 1$ and denoting $\tau^{-1} = -g'(0)$ we get
\[ \frac{1}{g(t')} \frac{dg(t')}{dt} dt = -\tau^{-1} dt \quad (8.34) \]

so that
\[ \frac{d}{dt} \log g(t) = -\tau^{-1} \quad (8.35) \]

and thus $g(t) = \exp(-t/\tau)$. The corresponding derivation can be generalized to multidimensional case as well.

8.2.2 Example 2: The Klein-Kramers equation

As an example of multivariate Fokker-Planck equation let us consider an underdamped case, correspond-
ing to the genuine Langevin treatment. The mechanical state of the system is now characterized by a pair \((v, x)\) of phase variables so that the probability density \(p\) depends on these two variables and on the time: \(p(v, x, t)\). The overall equations for \(v\) and \(x\) read:

\[
\begin{align*}
    m \dot{v} &= f(x) - \gamma v + \xi(t) \\
    \dot{x} &= v
\end{align*}
\] (8.36)

The coefficients \(A\) and \(B\) are no more scalars: Thus, \(A\) is now a vector and \(B\) is a 2 \(\times\) 2 matrix. The transition probabilities for the vector

\[
\mathbf{r} = \begin{pmatrix}
    \Delta v \\
    \Delta x
\end{pmatrix} = \begin{pmatrix}
    v(t + \Delta t) - v(t) \\
    x(t + \Delta t) - x(t)
\end{pmatrix}
\] (8.37)

can be found by noting that \(\Delta v = \frac{1}{m} \int_t^{t+\Delta t} [f(x) - \gamma v + \xi(t)] \, dt \approx \frac{1}{m} [f(x) - \gamma v] \Delta t + O(\Delta t^2) + \frac{1}{m} \int_t^{t+\Delta t} \xi(t) \, dt\). The first two terms are deterministic, distribution of the last term is given by Eq.(7.26). The development of \(\Delta x\) is also deterministic, so that in the lowest order we have \(\Delta x = v \Delta t\). Thus,

\[
w(\Delta v, \Delta x, x, v, t, \Delta t) = \frac{1}{\sqrt{2\pi kT\gamma \Delta t}} \exp \left\{ -\frac{\left[ \Delta v - \frac{1}{m} (f(x) - \gamma v) \Delta t \right]^2}{2kT\gamma \Delta t} \right\} \delta(\Delta x - v \Delta t).
\] (8.38)
The transition moments are:

$$A(x) = \frac{1}{\Delta t} \left( \langle \Delta v \rangle \right) = \left( \frac{1}{m} f(x) - \frac{\gamma}{m} v \right), \quad (8.39)$$

and

$$B = \frac{1}{\Delta t} \left( \begin{array}{c} \langle \Delta v^2 \rangle \\ \langle \Delta x \Delta v \rangle \\ \langle \Delta x^2 \rangle \\ \end{array} \right) \rightarrow \left( \begin{array}{ccc} kT \gamma & 0 \\ 0 & 0 \end{array} \right) \quad (8.40)$$

since the averages $\langle \Delta x \Delta v \rangle$ and $\langle \Delta x^2 \rangle$ are both proportional to $\Delta t^2$ and moreover $\langle \Delta v^2 \rangle = \langle \Delta v \rangle^2 + \sigma^2(\Delta t) = m^{-1} \left( f(x) - \gamma v \right)^2 \Delta t^2 + 4kT \gamma \Delta t \rightarrow 4kT \gamma \Delta t$.

The overall Fokker-Planck equation for the probability density $p(v, x, t)$ now reads:

$$\frac{\partial}{\partial t} p = -\frac{\partial}{\partial x} vp - \frac{\partial}{\partial v} \frac{1}{m} (f - \gamma v) p + kT \gamma \frac{\partial^2}{\partial v^2} p. \quad (8.41)$$

This equation is often referred to as a Klein-Kramers equation (Klein, 1922, Kramers, 1940). Assuming that the force $f(x)$ is a potential one, $f(x) = -\frac{\partial}{\partial x} U(x)$, it is not hard to show that for the case when $p(v, x)$ is given by

$$p(v, x) = \frac{1}{Z} \exp \left( -\frac{mv^2/2 + U(x)}{kT} \right) \quad (8.42)$$

with

$$Z = \int \int \exp \left( -\frac{mv^2/2 + U(x)}{kT} \right) dvdx, \quad (8.43)$$
the right-hand side of the equation vanishes independently on the value of $\gamma$. Of course, Eq.(8.42) is a canonical distribution, and the absence of $\gamma$ in this equation underlines the fact that the equilibrium properties of a system do not depend on the assumptions on its kinetic behavior. Note that the equilibrium distribution $p(v, x)$ factorizes into a product of the Maxwell distribution of the velocities and of the "barometric" distribution,

$$\frac{1}{\sqrt{2\pi kT}} \exp\left(-\frac{mv^2}{2kT}\right) \cdot \frac{1}{Q} \exp\left(-\frac{U(x)}{kT}\right) \quad (8.44)$$

with $Q = \int \exp\left(-\frac{U(x)}{kT}\right) dx$. This may not be the case for steady states other than the equilibrium. We note that Fokker-Planck equation, Eq.(8.41) can be presented in its usual form of the continuity of the probability current

$$\frac{\partial}{\partial t} p(x, t) = -\frac{\partial}{\partial x} J_x - \frac{\partial}{\partial v} J_v \quad (8.45)$$

with the probability current

$$J = \begin{pmatrix} J_x \\ J_v \end{pmatrix} = \begin{pmatrix} vp \\ \frac{1}{m}(f - \gamma v)p + kT \frac{\partial}{\partial v} p(v, t) \end{pmatrix} \quad (8.46)$$

Note that the probability current (which is the current in the phase space, corresponding to the fact that the phase coordinates of the system continu-
ously change under its Hamiltonian evolution) does not vanish in the equilibrium, while the particles’ current $I(x) = \langle J_x(x) \rangle = \int v p(x, v) dv$ definitely does.

We note that Eq. (8.41) for the joint probability distribution of the coordinate and the velocity can be considered as a combination of the continuity equation for the coordinate,

$$\frac{\partial}{\partial t} p(x, t) = -\frac{\partial}{\partial x} v(x, t) p(x, t)$$

(8.47)

and the ordinary Fokker-Planck equation for the velocity

$$\frac{\partial}{\partial t} p(v, t) = -\frac{\partial}{\partial v} \left( f - \gamma v \right) p(v, t) + kT \gamma \frac{\partial^2}{\partial v^2} p(v, t).$$

(8.48)

which are coupled by the fact that the force $f$ appearing in the last one may be $x$-dependent.

8.3 The Fokker-Planck equation and the Liouville equation

The phenomenological derivation of the diffusion equation by Fick (and our phenomenological derivation of the Fokker-Planck equation as a diffusion equation with drift) was based on the local continuity equation for the probability density (i.e. on the Liouville equation in the broader sense). The relation between the Fokker-Planck equation and the Liouville equation may be made clearer by the discussion of the
immediate derivation of the first from the last. In our discussion we closely follow the book Zwanzig, 2000. We use here a one-dimensional, scalar notation, making more clear the main steps. The trivial generalization to the multivariate case will be discussed at the end of the paragraph.

Let us consider the random process \( x(t) \) governed by the equation of motion

\[
\frac{dx}{dt} = v(x) + \xi(t)
\]  

(8.49)

where \( \xi(t) \) is a Gaussian random variable (noise), so that \( \langle \xi(t) \rangle = 0 \) and \( \langle \xi(t)\xi(t') \rangle = 2D\delta(t - t') \). We are looking for the probability distribution function of the values of \( x_i \) at time \( t \). This probability density \( P(x, t) \) may be obtained from the one for a special realization of the noise \( \xi(t) \), i.e. from the solution of the Liouville (continuity) equation. Assuming the local conservation law (the continuity equation) for \( P \) we can write that

\[
\frac{\partial P}{\partial t} + \sum_i \frac{\partial}{\partial x} \left( \frac{\partial x}{\partial t} P \right) = 0.
\]  

(8.50)

Replacing the time derivative of \( x \) on the right-hand side of this equation by the expression given by Eq.(8.49) we get:

\[
\frac{\partial P}{\partial t} = - \frac{\partial}{\partial x} \left[ (v(x) + \xi(t)) P \right].
\]  

(8.51)
This is a stochastic differential equation giving $P(x, t)$ in a particular realization of the process.

Eq.(8.51) is a linear differential equation, whose formal solution can be obtained as follows. Let us introduce the linear operator $L$ corresponding to the deterministic part of the behavior:

$$\hat{L}P = \frac{\partial}{\partial x} (f(x)P). \quad (8.52)$$

Eq.(8.51) then reads:

$$\frac{\partial P}{\partial t} = -\hat{L}P - \frac{\partial}{\partial x} \left[ \xi(t)P \right]. \quad (8.53)$$

The formal solution of this system is a generalization of the solution of a linear differential equation (say, Eq.(7.14)) and reads:

$$P(x, t) = e^{-\hat{L}t}P(x, 0) - \int_0^t ds e^{-\hat{L}(t-s)} \frac{\partial}{\partial x} \left[ \xi(s)P(x, s) \right]. \quad (8.54)$$

This solution shows explicitly that $P(x, t)$ depends on the noise at all times $s < t$. We now substitute this result into the last term in the right-hand side of Eq.(8.53) and get:

$$\frac{\partial}{\partial t} P(x, t) = -\hat{L}P(x, t) - \frac{\partial}{\partial x} \xi(t)e^{-\hat{L}t}P(x, 0) + \frac{\partial}{\partial x} \xi(t) \int_0^t ds e^{-\hat{L}(t-s)} \frac{\partial}{\partial x} \left[ \xi(s)P(x, s) \right]. \quad (8.55)$$

Now, the ensemble average of this probability density, $p(x, 0) = \langle P(x, 0) \rangle$ follows. The first term in
the right-hand side, containing the $P(x, t)$ only is averaged easily. The second one, containing only the initial condition (independent on the realization of the noise) and $\xi(t)$ vanishes under the averaging, so that only the third one, with the paired noise factors, needs to be averaged explicitly:

$$\frac{\partial}{\partial t} p(x, t) = -\hat{L} p(x, t) + \nabla \int_0^t dse^{-\hat{L}(t-s)} \nabla [\langle \xi(t)\xi(s)P(x, s) \rangle].$$

(8.56)

Now, for $s \neq t$ $\xi(t)$ is uncorrelated with $\xi(s)$ for all $s < t$ and thus with the state of the system $P(x, s)$ (given by the values of the noise at earlier times). Due to the symmetry of the noise, the integrand is zero for all $s \neq t$, so that $\langle \xi(t)\xi(s)P(x, s) \rangle = 0$ for $s \neq t$. On the other hand, $P(x, s)$ given by an integral Eq.(8.54) over the times $s' < s = t$, is dominated by the values of the noise at the previous times, and thus can be considered as independent from $\xi(t)$ exactly at time $t$, so that $\langle \xi(t)\xi(s)P(x, s) \rangle = \langle \xi(t)\xi(s) \rangle \langle P(x, s) \rangle \equiv 2D\delta(t - s)p(x, t)$.

Thus,

$$\frac{\partial}{\partial t} p(x, t) = -\hat{L} p(x, t) + \frac{\partial}{\partial x} \int_0^t dse^{-\hat{L}(t-s)} \frac{\partial}{\partial x} 2D\delta(t - s)p(x, s)$$

$$= \frac{\partial}{\partial x} (f(x)p) + \frac{\partial^2}{\partial x^2} Dp$$

(8.57)

which is a Fokker-Planck equation we looked for. We
note that this is a typical derivation on the physical degree of the accuracy: we didn’t bother too much about the properties of $e^{-L(t-s)}$, the mathematician should do this.

The generalizations to the multidimensional case is trivial: we consider the multidimensional random process \( \{x_i(t)\} \) governed by the equations of motion

\[
\frac{dx_i}{dt} = v_i(x_1, ..., x_n) + \xi_i(t) \quad (8.58)
\]

where \( \xi(t) = (\xi_1(t), ..., \xi_n(t)) \) is the vector of Gaussian random variables (noises) whose correlation properties are \( \langle \xi_i(t) \rangle = 0 \) and

\[
\langle \xi(t)\xi(t') \rangle = 2B \delta(t - t'). \quad (8.59)
\]

We are looking for the probability distribution function of the values of \( x_i \) at time \( t \). The local conservation law now reads

\[
\frac{\partial P}{\partial t} + \sum_i \frac{\partial}{\partial x_i} \left( \frac{\partial x_i}{\partial t} P \right) = 0. \quad (8.60)
\]

Replacing the time derivative of \( x_i \) on the right-hand side of this equation by the expression given by Eq.(8.49) we get:

\[
\frac{\partial P}{\partial t} = -\sum_i \frac{\partial}{\partial x_i} \left[ (v_i(x_1, ..., x_n) + \xi_i(t)) P \right]. \quad (8.61)
\]

This is a stochastic differential equation giving \( p(x, t) \) in a particular realization of the process.
The linear operator $L$ corresponding to the deterministic part of the behavior reads

$$
\dot{L}P = \sum_i \frac{\partial}{\partial x_i} \left( v_i(x_1, \ldots, x_n) P \right),
$$

so that performing the same steps as before we get

$$
\frac{\partial p}{\partial t} = -\nabla v(x)p + \nabla B(x) \nabla p.
$$

### 8.4 Transition rates and master equations.

The Kramers-Moyal expansion used in §8.1 is a formal trick which allows for mathematically rigorous derivation of a Fokker-Planck equation; this trick however is physically not quite transparent. Therefore we discuss here another variant of the approach, which has immediate thermodynamical implications and connects our discussion of Brownian motion with the canonical formalism of statistical physics.

Let us assume the following structure for the transition probability during the time $\Delta t$, $w(x, r; t, \Delta t) = p(x + r, t + \Delta t | x, t)$:

$$
w(x, r; t, \Delta t) = \left[ 1 - \Delta t \int dx' w(x' | x + r) \right] \delta(\dot{8.64}) + w(x + r | x) \Delta t + O(\Delta t^2).
$$

The meaning of the assumption is as follows: Imagine that at time $t$ the system was in state $x$; during the time $\Delta t$ it made a transition to a state $x + r$. 
The probability of such a transition is now expressed through the transition rate \( w(x + r|x) \); the function \( w(x|y) \) is the probability of transition from \( y \) to \( x \) per unit time. The first term follows from the normalization condition \( \int dr w(x, r; t, \Delta t) = 1 \) which must be fulfilled for any \( \Delta t \). Its interpretation is that at time \( t \) the system could already have been in state \( x + r \); this probability of not changing the state is assumed to decay as \( \Delta t \) grows.

Assuming the form, Eq.(8.64) we get instead of Eq.(8.6) the following equation:

\[
\frac{\partial}{\partial t}p(x, t|x_0, t_0)\Delta t = \left[ -\int dx'w(x'|x)p(x, t|x_0, t_0) + \int dr w(x|x - r)p(x - r, t|x_0, t_0) \right] \Delta t + O(\Delta t^2)
\]

Taking the limit \( \Delta t \to 0 \), we get after evident transformations, the following equation for \( p(x, t|x_0, 0) \):

\[
\frac{\partial}{\partial t}p(x, t|x_0, 0) = \int dx'w(x'|x)p(x', t|x_0, 0) \quad (8.66)
\]

\[
- \int dx'w(x'|x)p(x, t|x_0, 0)
\]

Eq.(8.66) is called a master equation, and has a transparent physical meaning: The change in the probability \( p(x, t|x_0, 0) \) per unit time is due to the two competing processes: to the inflow due to the fact that the system may changed its state from some
other state $x'$ to the state $x$ and to the outflow, due to the fact that it may have already been in state $x$ and may have left it for another state. Of course, we can obtain further a Fokker-Planck equation from the master equation, assuming that the transitions are only very-short-ranged, so that at least the two first moments of $\Delta x$ are finite. Using Eq.(8.64) we get

$$A(x) = \int dr \, rw(x + r|x) \quad (8.67)$$

and

$$B(x) = \int dr \, r^2 w(x + r|x). \quad (8.68)$$

If these two moments are finite, the Fokker-Planck equation follows from the master equation in a usual way, and reads

$$\frac{\partial}{\partial t} p = \frac{\partial}{\partial x} \left[ -vp + D \frac{\partial}{\partial x} p \right] \quad (8.69)$$

with $D = B/2$ and $v = A - \frac{1}{2} \frac{\partial}{\partial x} B$. If these lower two moments diverge, we have to do with a genuine jump-process, whose description lies outside of the range of applicability of standard Fokker-Planck equations, see Chapter 12, but still can be treated within the master equation formalism.

For a discrete system, where the states are numbered by whole numbers $n$ instead of a continuous
variable $x$ the situation gets even more transparent:

$$
\frac{\partial}{\partial t} p(n, t|n_0, 0) = \sum_{n'} w_{n'\to n} p(n', t|n_0, 0) - \sum_{n'} w_{n\to n'} p(n, t|n_0, 0) 
$$

(8.70)

where $w_{n'\to n}$ is the transition rate from the state $n'$ to the state $n$. The coefficients $w_{n'\to n}$ form a matrix $W$. Such discrete equations are in many cases more reasonable instruments of description than the continuous ones, especially in the cases when $n$ can be interpreted not as a coordinate, but as a number of particles (birth-death processes, chemical reactions, etc.).

### 8.5 Energy diffusion and detailed balance

Master equations are often introduced on a quite formal basis, and are intimately connected with the thermodynamical formalism. Let us assume a closed system in a contact with the heat bath at temperature $T$. According to the Zeroth Law, whatever nonequilibrium the initial state of the system is, in course of the time the system will tend to an equilibrium one, if all external perturbations are switched off. Let $\nu$ enumerate the states of this system. Let moreover $E_\nu$ be the energy of the state $\nu$. Then, the final, equilibrium state of the system will be charac-
characterized by the Boltzmann distribution
\[ p_{eq}(\nu) = \frac{1}{Z} \exp \left( -\frac{E_{\nu}}{kT} \right). \] (8.71)

We now consider the relaxation of our system from a nonequilibrium state characterized by the some distribution function \( p(\nu) \) to the equilibrium state. We note that during this evolution the states themselves (which depend on the external conditions which are assumed not to change) do not change; the relaxation is fully due to the change of the probabilities for a system to be in a state \( \nu \). Let us assume these probabilities to follow the master equation with constant transition rates. This assumption follows from the one of the time-independent nature of the states and of the heat bath.

We note that the assumption of the time-independent states fully characterized by their energy may have quite different physical implications. The simplest situation is that the states \( E_{\nu} \) are the localized quantum states (say of an electron at different impurities in a doped semiconductor), and the incoherent transitions between them are caused by the interaction with the heat bath. Just as simple are the Ising-like systems without any internal dynamics. Here the only possible changes are the flips of single spins or their clusters. Each such discrete event may (or
may not) change the energy of the system. A similar situation takes place at a coarse-grained level of description in a classical system corresponding to a particle in a rugged energy landscape (see Ebeling et al., 1984; Engel and Ebeling, 1987, Haus and Kehr, 1987). An underdamped situation corresponds to a much more complex situation: Here, even at a constant energy, a complex dynamics corresponding to the ”microcanonical” (i.e. purely Hamiltonian) evolution of the system takes place. In order to be able to assume that the state is fully characterized by the value of its energy, we have to consider a ”state” as a microcanonical ensemble of systems, equally populating the energy surface \( H(x, p) = E\nu \). The interaction of the system with the heat bath introduces the transitions between different energy surfaces, the rates of such transitions are \( w\nu'\rightarrow\nu \).

The equilibrium state is a stationary (time-independent) solution of the master equation:

\[
0 = \sum_{\nu'} w_{\nu'\rightarrow\nu} p_{eq}(\nu') - \sum_{\nu'} w_{\nu\rightarrow\nu'} p_{eq}(\nu'). 
\] (8.72)

Thus, the Zeroth Law requires that

\[
\sum_{\nu'} [w_{\nu'\rightarrow\nu} p_{eq}(\nu') - w_{\nu\rightarrow\nu'} p_{eq}(\nu)] = 0. 
\] (8.73)

This requirement is tightened by the Second Law: one namely has to assume that not only the sum,
but each term separately vanishes, so that
\[ w_{\nu' \to \nu} p_{eq}(\nu') - w_{\nu \to \nu'} p_{eq}(\nu) = 0. \]  
(8.74)

It follows that
\[ \frac{w_{\nu \to \nu'}}{w_{\nu' \to \nu}} = \frac{p_{eq}(\nu')}{p_{eq}(\nu)} \equiv \exp \left( - \frac{E_{\nu'} - E_{\nu}}{kT} \right). \]  
(8.75)

This assumption is called the **principle of detailed balance**. If the external conditions are time-dependent, the detailed balance principle has to hold at each time for time-dependent rates, as long as Markovian dynamics holds. The same assumptions are of course valid in the continuous case.

The meaning of the principle is as follows: Imagine that the transition rates between the states 1 and 2 of the system do not follow Eq.(8.74), so that the number of the transitions from state 1 to the state 2 is not balanced by the backwards transitions. For example, let us assume that in equilibrium more transitions take place immediately from 1 to 2 than back from 2 to 1: the back flow from 2 to 1 follows through some intermediate state(s) 3, so that a perpetual current \(1 \to 2 \to 3 \to 1\) flows. (The perpetual superconductive currents or the probability currents discussed above are not the currents between the states, but currents within a state; they are not forbidden by the following consideration). If
the energy of the state 2 is lower than the energy of state 1, then at first step the energy is dissipated to the heat bath, and the second step, $2 \rightarrow 3 \rightarrow 1$, is thermally activated: the energy is taken from the bath. The equilibrium state is stable, so that small external perturbation wouldn’t change the state considerably. Thus, if an ingenious gadgeteer would be able to use the unbalanced $1 \rightarrow 2$ current for producing work against small external force, this work will be produced on the cost of cooling the only one heat reservoir, which is explicitly forbidden by the second law. We refrain here from the discussion of possible constructions of such perpetual mobile. The discussion of the thermodynamical implications of detailed balance was given in Bridgman, 1928.

Now let us return to our master equation in the case when it can be reduced to a Fokker-Planck one and show that the Einstein’s relation follows in general from the detailed-balance principle (essentially the initial discussion by Perrin about the exact equilibration of the two currents was a kind of use of it!). Note that in the case when the master equation can be reduced to a Fokker-Planck one, i.e. in the case when $w(x+r|x)$ decays sufficiently fast as a function of $r$, the detailed balance requires the connection between the transition moments: In the overdamped
case one can assume $E(x) = U(x) = -\int f(x)dx$, so that the energy difference between the state $x + r$ and the state $x$ is $E(x + r) - E(x) = -\int f(x)dx$, and the transition rates between these states are connected by

$$w(x+r|x) = w(x|x+r)\exp\left(\int_{x}^{x+r} \frac{f(x)}{kT}dx\right). \quad (8.76)$$

Let us now assume that our system is homogeneous, so that $w(x + r|x) = w(x|x - r)$. (The inhomogeneous situation will be considered in some detail later on). Combining the homogeneity with Eq.(8.76) we get:

$$w(x - r|x) = w(x + r|x)\exp\left(\int_{x}^{x+r} \frac{f(x)}{kT}dx\right). \quad (8.77)$$

Furthermore, we assume that also for the case $f = 0$ the corresponding moments exist, so that the situation is characterized by a constant diffusion coefficient and by a constant mobility. We moreover consider the force as so weak, that the lowest-order (linear) approximation in $f(x)$ is sufficient. The integrals for $A$ and $B$ then read

$$A(x) = \int_{-\infty}^{\infty} dr \, r w(x + r|x) = \int_{0}^{\infty} r \left[ w(x + r|x) - w(x - r|x) \right] dr$$

$$= \int_{0}^{\infty} r w(x + r|x) \left[ 1 - \exp\left(\int_{x}^{x+r} \frac{f(x)}{kT}dx\right) \right] \approx$$
Energy diffusion and detailed balance

\begin{equation}
\approx \int_0^\infty w(x + r|x)r \left[ 1 - 1 - r\frac{f(x)}{kT} \right]
= -\frac{f(x)}{kT} \int_0^\infty w(x + r|x)r^2 dr.
\end{equation}

Note that the term of the zeroth order vanishes. The lowest-order approximation for the coefficient \( B \) is zeroth order in \( f \) and reads

\begin{align}
B &= \int_{-\infty}^{\infty} dr \, r^2 w(x + r|x) = \int_0^\infty r \left[ w(x + r|x) - w(x - r|r) \right] dr \\
&= \int_0^\infty w(x + r|x)r^2 \left[ 1 + \exp \left( \frac{\int_x^{x+r} f(x) \, dx}{kT} \right) \right] \approx \\
&\approx 2 \int_0^\infty w(x + r|x)r^2 dr.
\end{align}

Thus, one readily infers that \( A(x) = -\frac{f(x)}{2kT} B \). Remembering that \( B/2 \) is exactly the diffusion coefficient \( D \) we get

\begin{equation}
\frac{\partial}{\partial t} p = \frac{\partial}{\partial x} \left[ -\frac{D}{kT} f(x)p + D \frac{\partial}{\partial x} p \right],
\end{equation}

i.e. the particles’ mobility \( \mu \) is connected to \( D \) via \( D = kT \mu \).

8.5.1 System in contact with several heat baths

The detailed balance principle guarantees that in equilibrium the distribution over the energy states in the isothermic system is the Boltzmann one. It thus connects the forwards and the backwards rates of the
transitions taking place in presence of the heat bath. However, in many cases, at least not too far from the equilibrium, the rates of different transitions can be considered as independent from each other, and can be taken to depend only on the local temperature at which the transition takes place. This allows us for discussion systems in a contact with several heat baths. A very simple toy model of such a system is considered in what follows.

As an example we consider here a simple system with three energy levels 1, 2, and 3, see Fig.8.1. The results discussed here can easily be generalized to more complex situations or to continuous systems. The discrete system considered here is a very simple one and allows for full mathematical descriptions. The potential differences between states 1 and 2, 3 and 2, and 1 and 3 are $U_{12}$ and $U_{32}$, respectively, both of them positive (the energy difference between 3 and 1 is then $U_{31} = U_{12} - U_{32}$). If the system is kept at a constant temperature, the currents through whatever bond vanish. Moreover, the probabilities to find a particle on the site $i$ does not depend on whether the bond 31 is present or absent. This is the consequence of the transitivity of thermodynamical equilibrium.

Let us now consider the system in contact with two
heat baths, so that the bond 1-2 is kept at temperature $T_1$, and the transition 2-3 at temperature $T_2$. In what follows we assume $T_1 > T_2$ and $U_{12} > U_{32}$, so that the difference $U_{31} = U_{12} - U_{32}$ is positive. Physically, it can be considered as a minimalistic model of a thermocouple (state 1: “electron in the conductor 1”, state 2 – “electron in the conductor 2”, state 3 – electron in the conductor 3”) or as a model for the water circulation in the atmosphere (state 1: ”water molecule on the surface of the ocean”, state 2 – ”water molecule in the rain cloud”, state 3 – ”water molecule in the mountain lake”). However in all these cases the potential energies are essentially the chemical potentials, which themselves depend on temperature and other parameters, so that the whole thermodynamics of the system gets extremely involved. Here we dispense from thermodynamics and fully concentrate on the dynamics of the system. For simplicity, we take all downhill transition rates to be equal to $w_{ij}^- = w$ (the so-called Metropolis prescription, often used in numerical Monte-Carlo simulations of thermodynamical system), the uphill rates will then be $w_{ij}^+ = w_\pm \exp(-U_{ij}/k_B T)$.

Then, the probabilities (or the particle densities) in states 1, 2, and 3 are given by the stationary solution
of the Master equation
\[
\begin{align*}
\frac{d}{dt}p_1 &= wp_2 + wp_3 - w \left( e^{-\frac{U_{12}}{k_B T_1}} + e^{-\frac{U_{13}}{k_B T_2}} \right) p_1 \\
\frac{d}{dt}p_2 &= we^{-\frac{U_{12}}{k_B T_1}} p_1 + we^{-\frac{U_{32}}{k_B T_2}} p_3 - 2wp_2 \quad (8.81) \\
\frac{d}{dt}p_3 &= we^{-\frac{U_{13}}{k_B T_1}} p_1 + wp_2 - w \left( 1 + e^{-\frac{U_{32}}{k_B T_2}} \right) p_3.
\end{align*}
\]

where \( p_i \) is the probability to find the particle on the site \( i \). Note that the sum of the probabilities
\( p_1 + p_2 + p_3 = 1 \) is the integral of the motion, so that the three equations are not independent. Let us consider the stationary situation. The corresponding solutions for \( p_1 \) and \( p_2 \) then read
\[
p_1 = \frac{1}{1 + e^{-\frac{U_{12}}{k_B T_1}} + e^{-\frac{U_{13}}{k_B T_2}}}, \quad (8.82)
\]
Energy diffusion and detailed balance

\[ p_2 = \frac{e^{-\frac{U_{12}}{k_B T_1}} + e^{-\frac{U_{12}}{k_B T_1}} e^{-\frac{U_{32}}{k_B T_2}} + e^{-\frac{U_{32}}{k_B T_2}} e^{-\frac{U_{13}}{k_B T_1}}}{\left(1 + e^{-\frac{U_{12}}{k_B T_1}} + e^{-\frac{U_{13}}{k_B T_1}}\right) \left(2 + e^{-\frac{U_{32}}{k_B T_2}}\right)}, \]

and

\[ p_3 = \frac{e^{-\frac{U_{12}}{k_B T_1}} + 2 e^{-\frac{U_{13}}{k_B T_2}}}{\left(1 + e^{-\frac{U_{12}}{k_B T_1}} + e^{-\frac{U_{13}}{k_B T_1}}\right) \left(2 + e^{-\frac{U_{32}}{k_B T_2}}\right)}. \]

Knowing \( p_i \) we can also calculate the currents through the bonds, \( I_{ij} = w_{ij} p_i - w_{ji} p_j \). For example,

\[ I_{12} = \frac{e^{-\frac{U_{13}}{k_B T_1}} e^{-\frac{U_{32}}{k_B T_2}} - e^{-\frac{U_{12}}{k_B T_1}}}{\left(1 + e^{-\frac{U_{12}}{k_B T_1}} + e^{-\frac{U_{13}}{k_B T_1}}\right) \left(2 + e^{-\frac{U_{32}}{k_B T_2}}\right)}. \]

Of course, the stationary currents through all three bonds are the same. We see that due to the fact that \( U_{13} + U_{32} = U_{12} \) the current vanishes exactly for \( T_1 = T_2 \) and is nonzero if the temperatures of the transitions are different. In our discrete model this is exactly the thermocurrent. Now, we can in principle tap the 31 bond to win energy from this current. However, the efficiency of our system will depend on the particular mechanism of how do we win the energy from the current.

In order to avoid complications let us consider a
system shown in Fig. 8.2. It is a cascade of $N$ such systems switched in series, so that now the site 3 of the previous system is exactly the site 1 of the next one. The existence of the overall current means now that particles injected in the left-hand side of the system are transported uphill (the corresponding model is simply a discrete variant of one discussed by Buttiker, 1987). When reaching the top, the particles are used to produce useful work, say, to charge the battery or to rotate the wheel. Since the energy difference between the upper right and the lower left site is very large, the spontaneous backward transitions may be neglected, so that we really don’t need to think about how do the thermal fluctuations of the battery’s voltage really look like. (The impossibility of backward transitions in the working medium of the system is a rather typical case, since, say, the way
from the ocean to the lake is only possible through evaporation, but not through swimming up the river. The mechanism forbidding this is, however, different, and has to do with the properties of collective motion, an aspect which is absent in our simple model). Under stationary conditions, due to the periodicity, we have, as an equation for $p_1$,

$$0 = 2wp_2 - w\left(e^{\frac{U_{12}}{k_BT_1}} + e^{\frac{U_{32}}{k_BT_2}}\right)p_1$$

which is complemented by the fact that $p_1 + p_2 = 1$. We thus have

$$p_1 = \frac{2}{2 + e^{\frac{U_{12}}{k_BT_1}} + e^{\frac{U_{32}}{k_BT_2}}}$$

and

$$p_2 = \frac{e^{\frac{U_{12}}{k_BT_1}} + e^{\frac{U_{32}}{k_BT_2}}}{2 + e^{\frac{U_{12}}{k_BT_1}} + e^{\frac{U_{32}}{k_BT_2}}}.$$ 

We can also calculate the stationary current through the system (as a current through the 12-bond),

$$I = p_1 e^{\frac{U_{12}}{k_BT_1}} - p_2 = \frac{e^{\frac{U_{12}}{k_BT_1}} - e^{\frac{U_{32}}{k_BT_2}}}{2 + e^{\frac{U_{12}}{k_BT_1}} + e^{\frac{U_{32}}{k_BT_2}}}.$$ 

We see that for the case $U_{12} > U_{32}$ and $e^{\frac{U_{12}}{k_BT_1}} -
\[ e^{-\frac{U_{32}}{k_BT_2}} > 0 \text{ i.e. for} \]
\[ \frac{T_2}{T_1} < \frac{U_{32}}{U_{21}} \]  
(8.90)

the system indeed pumps particles uphill, against the overall potential difference.

Now, imagine that the current between 3 and 1 produces a useful work. The useful power then is \( P = \dot{A} = I N U_{31} \). We also can calculate the heat taken from the hot reservoir (at temperature \( T_1 \)). Since the energy of the particle at sites 1 and 2 differ by exactly \( U_{12} \), this energy is the one that has to be dissipated to the bath when a downhill transition from 2 to 1 takes place, and the one which has to be gained from the bath under the uphill transition. The corresponding heat power then reads

\[ \dot{Q} = N U_{12} I, \]  
(8.91)

and the efficiency \( \eta \) of the system reads

\[ \eta = \frac{\dot{A}}{\dot{Q}} = \frac{U_{31}}{U_{12}} = \frac{U_{12} - U_{32}}{U_{12}} = 1 - \frac{U_{32}}{U_{12}}. \]  
(8.92)

The efficiency of our system is thus independent on temperature. According to Eq.(8.90) we thus have

\[ \eta \leq 1 - \frac{T_2}{T_1} \]  
(8.93)
and moreover we see that the Carnot value is achieved when \( \frac{T_2}{T_1} = \frac{U_{32}}{U_{21}} \), so that the current vanishes (stalling conditions, work at zero power) which exactly corresponds to the quasistatic situation in usual, cyclically working heat engines. It is also interesting to calculate the efficiency at largest power. Let us now fix \( T_1 \) and \( T_2 \) and \( U_{12} \) and tune \( U_{32} \) until the maximum power

\[
P = N(U_{12} - U_{32}) \frac{e^{-\frac{U_{12}}{k_B T_1}} - e^{-\frac{U_{32}}{k_B T_2}}}{2 + e^{-\frac{U_{12}}{k_B T_1}} + e^{-\frac{U_{32}}{k_B T_2}}} = \max.
\]

is achieved. We note that in this case the maximal efficiency is not only the function of the quotient between the temperatures of the heat baths, but depend on their relation to potentials. If the temperatures are low, the overall efficiency stays close to the Carnot one since the currents are small. However, when both temperatures, \( T_1 \) and \( T_2 \) are high compared to the energetic barriers, another result appears, and the maximal efficiency tends to exactly one half of the Carnot value. We note that no general expression for the efficiency at maximal power exists, which would be valid for all systems. The well-known expressions like the celebrated Novikov-Curzon-Ahlborn formula \( \eta = 1 - \sqrt{T_2/T_1} \) Novikov, 1958; Curzon and
Ahlborn, 1975 are pertinent to rather special situations. In application to cyclically working machines these problems are the issue of the so-called ”finite time thermodynamics” (see Andersen, 1984).

Several other systems with different heat baths were considered in the literature, mostly inspired by the Feynman’s ratchet-and-pawl device or by an earlier ”thermal fluctuation rectifier” by L. Brillouin (Brillouin, 1950). The diode thermal fluctuation rectifier (Sokolov, 1998; Sokolov, 1999) is only a slightly more complicated machine than our simple discrete ratchet. It unveils, however, the important property of all realistic devices of such kind, namely the possibility of heat transport through the fluctuations of ”mechanical” degrees of freedom, which makes them intrinsically irreversible and lowers the efficiency even under stalling conditions in comparison with the Carnot’s value. The genuine Feynman’s device (consisting of a vane at temperature $T_1$ and of a ratchet-and-pawl mechanism at temperature $T_2$ connected by a solid axle) is a much more intricate system. Feynman himself assumed its efficiency to be a Carnot one; however Parrondo and Espanol (1996) have shown that it is not the case.

The simplest model system illustrating such mechanism of heat transport is an ”adiabatic piston” in
contact with two gases at temperatures $T_1$ and $T_2$ (conceptually, but not mathematically the simplest situation here corresponds to a frictionless piston of mass $M$ which moves in a cylinder, separating two gases. The walls of the cylinder and the piston itself do not conduct heat), see Kestemont (2000), van der Broeck, (2001). The fluctuations of the piston’s velocity transfer energy from one gas to another. On the average no work is performed, so that the effect we have to do here with is exactly heat conduction through mechanical degree of freedom. The corresponding works of the Belgian groups also discuss the limits of applicability of Langevin approach to such systems, which seems to perform reasonably if the piston is heavy enough.

The more general issue of thermodynamics of ratchet-like devices under different types of forcing has found much attention in the last decade, since their way of functioning is closely related to the one of many biological ”molecular motors”, see Astumian and Hänggi, 2002. Rather exhaustive review of different aspects of such motors can be found in Reiman (2002), Frey (2002), Parrondo and De Cisneros (2002).
Fokker-Planck and Master Equations
Chapter 9

Escape and first passage problems

The possibility to calculate the probability density function or its moments, like the mean square displacement, does not exhaust the whole class of problems of stochastic theory. One of the most important classes of other problem settings are the first passage problems for a stochastic process. Mathematically, the task is to calculate the probability density $\phi(t)$ (as a function of time) for a process $x(t)$ to reach for the first time a point $x$, or a set of points (a typical one-dimensional problem position), or to cross a boundary of a spatial domain in spatial dimension more than one. Physical problems leading to this mathematical formulation are abundant. The genuine first-passage problems are often pertinent to reaction kinetics, where the two particles interact if they approach each other at distance $a$. These situations correspond to crossing the boundary, so to say, from the outside. An opposite situation of the cross-
ing a boundary from inside, emerges when describing a decay of a bounded state in some given potential (a problem emerging by the description of, say, dissociation of a complex molecule, Ebeling, Schimansky-Geier and Romanivsky, 2002). This situation is often termed as an escape problem. In ecology, the first passage through some prescribed value, might mean the extinction of the population, or the start of the epidemic outbreak. The literature discussing the first passage problems both from the mathematical, and from the physical point of view, is abundant. A simple introduction into the topic is given in the book Redner, 2001. In this Chapter we consider only some simple situations. Understanding these situations is, however, necessary for understanding fluctuation effects in chemical reactions, Chapter 10, or the emergence of anomalous diffusion in complex potential landscapes, Chapter 11.

9.1 General considerations

In this chapter we first concentrate on one-dimensional problems. Let us first look at the realizations of the corresponding random process and try to find a mathematical formalization of the problem. The physical situation here can be formulated as follows: At time $t = 0$ a particle is introduced into a system
at \( x = 0 \). As soon as particle reaches the place \( x_0 \) the realization is stopped, the time necessary to reach the boundary (the first passage time) is recorded. Then, we can obtain the distribution of these times, and use it for further calculations. It is important to note that we are interested in the frequencies of the realizations of a random process, i.e. in the trajectories (paths) of the particle. In order to get the distribution of the first passage times, we have to know, in how many realizations the path of the particle crossed the point \( x = x_0 \) at times \( t' < t \). In order to count them, it is enough to assume an absorbing boundary condition at \( x = x_0 \): Particles having touched the point disappear and their trajectories are disregarded at future times. We assume the overdamped regime of motion, where the probability density to find a particle’s at point \( x \) is governed by Smoluchowski equation

\[
\frac{\partial p(x, t)}{\partial t} = -\mu f \frac{\partial p(x, t)}{\partial x} + D \frac{\partial^2 p(x, t)}{\partial x^2}. \tag{9.1}
\]

Here the force \( f = -dU/dx \). In cases corresponding to the systems considered in thermodynamics (i.e. ones possessing true thermodynamical equilibrium) the mobility \( \mu \) and the diffusion coefficient \( D \) are connected to each other through the Einstein’s relation \( D = \mu k_B T \). The equation, Eq.(9.1) has to be solved under the boundary condition \( p(x_0, t) = 0 \) and
for the initial condition $p(x, 0) = \delta(x)$, so that the corresponding solutions are essentially the Green’s functions of the Fokker-Planck equation, $p(x, t) = G(x, t|0, 0)$. It is important to stress here that the equivalence of our assumption that all particles touching $x_0$ disappear and the actual condition that the trajectories crossing $x_0$ have to be disregarded at larger times assumes the continuity of the trajectories, which is the case for Brownian motion, but might be violated for some processes described by generalizations of a Fokker-Planck equation (Chechkin et al., 2003), so that care has to be taken when generalizing the results discussed here to the processes other than Fickian diffusion.

After solving the equation for all times, we can calculate the overall probability for the particle to stay within the interval, which is

$$P(t) = \int_{-\infty}^{x_0} p(x, t) dt \quad (9.2)$$

and note that the change in $P(t)$ between the times $t$ and $t + dt$ is exactly the probability to leave the interval during $dt$. This is,

$$\psi(t) = -\frac{dP(t)}{dt}. \quad (9.3)$$
By noting that

\[ \frac{dP(t)}{dt} = \int_{-\infty}^{x_0} \frac{\partial p(x,t)}{\partial t} \, dx \tag{9.4} \]

and using Eq.(9.1) we get

\[ \psi(t) = \int_{-\infty}^{x_0} \left[ -\mu f \frac{\partial p(x,t)}{\partial x} + D \frac{\partial^2 p(x,t)}{\partial x^2} \right] \, dx. \tag{9.5} \]

Applying partial integration, and using the natural boundary condition \( p(x,t) \to 0 \) and for \( x \to -\infty \) we get:

\[ \psi(t) = -D \frac{\partial p(x,t)}{\partial x} \bigg|_{x=x_0}, \tag{9.6} \]

i.e. that the first passage time probability density is equal to the diffusion current through the absorbing boundary. If we are interested in the case of two absorbing boundaries at the ends of an interval the corresponding currents give us the probability per unit time to leave the interval through the corresponding end.

This approach based on the solution of the forward equation assumes the knowledge of its time-dependent solution, and is the typical "physicist’s" approach to the problem, which is not necessarily the simplest or the most elegant one. However, this is the one which works and, moreover, the one which works
reliably even when the coefficients in the Fokker-Planck equation are time-dependent.

9.2 The renewal approach.

The renewal approach to the first passage problem uses explicitly the continuity of sample paths and the Markovian nature of the problem. It reduces the solution of a problem with absorbing boundary condition to one for the free problem, one with natural boundary conditions, which is sometimes much simpler. The deficiency of the approach is however that it is only effective in the one-dimensional case.

Let us start from the simple case of a single boundary situated at \( x = x_0 \). We consider the process starting at \( t = 0 \) at \( x = 0 \). Imagine that at some time \( t_f > 0 \) the particle is found to the right of the boundary, at some point \( x_f > x_0 \). The probability of this event is given by the transition probability density function of the "free" process \( p(x_f, t_f|0, 0) \).

Due to the continuity of trajectories, the process has to have passed the point \( x_0 \) before reaching \( x \) at some time \( t < t_f \) (and might have passed the point \( x_0 \) one or several times after this). Thus the realizations of the process leading from \( x \) to \( x_f \) may be uniquely classified with respect to the time they first crossed \( x_0 \). Let us denote \( \psi(t, x_0) \) the first passage time dis-
The renewal approach.

tribution through point \( x_0 \), and concentrate on all realizations of the process contributing to \( \psi(t, x_0) \).

Here the Markovian nature of the process comes in play. The probability that the particle reaches \( x = x_f \) at \( t = t_f \) provided it was at \( x_0 \) at time \( t \) depends only on \( x_0 \) and \( t \) but not on the history of the process at \( t < t_0 \) and is given by the transition probability density function of the free process \( p(x_f, t_f | x_0, t_0) \). This means that the probability density to cross the point \( x_0 \) at time \( t \) and then to reach \( x_f \) at time \( t_f \) is simply a product \( p(x_f, t_f | x_0, t) \psi(t, x_0) \). Summing over all possible times \( t < t_f \) one gets

\[
p(x_f, t_f | 0, 0) = \int_0^{t_f} p(x_f, t_f | x_0, t) \psi(t, x_0) dt. \tag{9.7}
\]

This is an exact equation determining the first passage time for a Markovian process.

A next step can be done if the process \( x(t) \) in a "free" motion is stationary (i.e. whenever the coefficients in our Fokker-Planck equation are time-independent). In this case the transition probability density depend only on the difference between its time arguments: \( p(x_2, t_2 | x_1, t_1) = G(x_2, x_1, t_2 - t_1) \) and is equal to the Green’s function solution of the Fokker-Planck equation with time-independent coefficients. The integral in the r.h.s. of Eq.(9.7) has now a form of a convolution. Another simplification
stems from the fact that for diffusion processes one can take a limit $x_f \to x_0$ (since the corresponding Green’s function is nonsingular in this limit), so that

$$G(x_0, 0, t_f) = \int_0^{t_f} G(x_0, x_0, t_f - t)\psi(t, x_0)dt. \quad (9.8)$$

This is a Volterra integral equation, which easily can be solved numerically. The simplest way to its analytical solution is to take Laplace transforms of the both sides of the equation, so that \( \tilde{G}(x_2, x_1, u) = \int_0^\infty G(x_1, x_2, t)e^{-ut}d\tau \). Applying this transform we get \( \tilde{G}(x_0, 0, u) = \tilde{G}(x_0, x_0, u)\tilde{\psi}(u, x_0) \), i.e.

$$\tilde{\psi}(u, x_0) = \frac{\tilde{G}(x_0, 0, u)}{G(x_0, x_0, u)}. \quad (9.9)$$

Of course, in many situations, the inverse Laplace transform has to be performed numerically. However, the expression for the mean first passage \( \tau = \int_0^\infty t\psi(t, x_0)dt = \frac{d}{du} \tilde{\psi}(u, x_0)\bigg|_{u=0} \) follows easily.

The renewal approach can also be applied for calculating splitting probabilities. Let us consider a particle moving between the two absorbing boundaries. Here the two first passage probabilities, \( \psi(t, x_L) \) for first crossing the left boundary situated at \( x_L \) and \( \psi(t, x_R) \) of first crossing the right boundary situated at \( x_R \). Parallel to our previous consideration one can say that if the particle which started at \( x = 0 \) at \( t = 0 \) is found at time \( t \) to the right from the
right boundary (at some $x_f > x_R$) it might either have first crossed the right boundary without touching the left one at some time $t' < t$ and then made the way from $x_R$ to $x_f$ or crossed first the left boundary and then made the way from $x_L$ to $x_f$. The probability to touch the left boundary for the first time without previously touching the right one between times $t$ and $t + dt$ is given by the function $\psi(t, x_L) dt$ and the probability to first touch the right boundary (without touching the left one before) is given by $\psi(t, x_R) dt$. Note that $\psi(t, x_L)$ and $\psi(t, x_R)$ are not proper probability density functions: both integrals $P_L = \int_0^\infty \psi(t, x_L) dt$ and $P_R = \int_0^\infty \psi(t, x_R) dt$ (representing the probabilities to leave the interval through its left or through its right boundary, the so-called splitting probabilities) are in general less than unity. The normalization condition for the splitting probabilities is given by $P_L + P_R = 1$. Following the same scheme as before we obtain

$$G(x_f, t|0, 0) = \int_0^t G(x_f, t|x_R, t')\psi(t', x_R) dt' + \int_0^t G(x_f, t|x_L, t')\psi(t', x_L) dt'$$

(9.10)

This is an equation determining both $\psi(t, x_L)$ and $\psi(t, x_R)$ since it has to be valid for any $x_f$. To obtain the explicit equations we take another $x_f$ to lie to the left from the left boundary, and then make the limiting transition, taking the corresponding $x_f$'s to
tend to the boundaries of the interval from the outside. Since for stationary case the integrals in both such equations are of the convolution type we can make the Laplace-transform of the both and get

\[ G_{RR} \psi_R + G_{RL} \psi_L = G_{R0} \]  
\[ G_{LR} \psi_R + G_{LL} \psi_L = G_{L0}, \]  

where the following shorthand notation is introduced for the Green’s functions: \( G_{RR} = \tilde{G}(x_R, x_R; u), G_{LL} = \tilde{G}(x_L, x_L; u), G_{RL} = \tilde{G}(x_R, x_L; u), G_{LR} = \tilde{G}(x_L, x_R; u), G_{R0} = \tilde{G}(x_R, 0; u), \) and \( G_{L0} = \tilde{G}(x_L, 0; u). \) Moreover, \( \psi_L = \tilde{\psi}(u, x_L) \) and \( \psi_R = \tilde{\psi}(u, x_R). \) The solution of the system of equations (9.11) is

\[ \psi_L = \frac{G_{R0} G_{LL} - G_{L0} G_{RL}}{G_{RR} G_{LL} - G_{LR} G_{RL}} \]  
\[ \psi_R = \frac{G_{RR} G_{L0} - G_{LR} G_{R0}}{G_{RR} G_{LL} - G_{LR} G_{RL}} \]  

so that the probabilities can be found explicitly. The splitting probabilities \( P_L \) and \( P_R \) are simply given by the limiting values of the corresponding functions at \( u \to 0. \)

For non-Markovian processes Eq.(9.8) might or might not hold, depending on the exact nature of the process. Thus it still holds for ”semi-Markovian” situations like continuous-time random walk models dis-
The renewal approach.

cussed in Chapter 11. In this case the renewal approach is effective and preferable because the probability density for free motion might be obtained by the alternative methods, without explicitly solving corresponding (non-Markovian, fractional) Fokker-Planck equations. Eq.(9.8) does not in general hold for the processes described by non-Markovian Langevin equations or by moving averages. However, for a stationary non-Markovian process Eq.(9.8) might still be a reasonable approximation: it simply assumes that having arrived to a position of the absorbing boundary, the particle has practically forgotten initial conditions, so that its further behavior can be described by a new initial condition problem. Of course it does not imply that the corresponding solution of the initial-value problem resembles to any extent the Green’s function of any Markovian process. In this case the renewal approximation based on Eq.(9.8) is equivalent to the so-called Wilemski-Fixman approximation (Wilemski and Fixman, 1974, Sokolov, 2003) being widely used for description of reactions involving polymers.

9.2.1 Example: Free diffusion in presence of boundaries

As an example let us consider the first passage time distribution for free diffusion (Brownian motion), where
Escape and first passage problems

\[ G(x_2, x_1, t) = (4\pi Dt)^{-1/2} \exp \left[ -\left( \frac{x_2 - x_1}{2\sqrt{Dt}} \right)^2 \right], \]

so that

\[ \tilde{G}(x_2, x_1, u) = \frac{1}{\sqrt{4Du}} \exp \left( |x_2 - x_1| \sqrt{\frac{u}{D}} \right). \quad (9.14) \]

This delivers \( \tilde{\psi}(u, x_0) = \exp( |x_0| \sqrt{u/D} ) \) from which it follows that

\[ \psi(t, x_0) = \frac{|x_0|}{\sqrt{4\pi Dt}^{3/2}} \exp \left( \frac{x_0^2}{4Dt} \right). \quad (9.15) \]

This distribution of the first passage time to a boundary is called Smirnov, Lévy-Smirnov or sometimes "inverse Gaussian" distribution, and decays for long times as \( \psi(t, x_0) \propto t^{-3/2} \) so that it does not have the first moment: the mean first passage time diverges. Note that the function \( \psi(t, x_0) \) is a proper probability density function, so that \( \int_0^\infty \psi(t, x_0) dt = 1 \). This means that the particle in 1d is eventually captured at the boundary. This fact has to do with the recurrence of the one-dimensional Wiener process, which visits any point on the line with probability 1 at longer times.

We note that our consideration here based on the fact that the trajectories of the process are continuous. The result that at long times \( \psi(t, x_0) \propto t^{-3/2} \) is, however, valid also for a large class of jump processes, i.e. the ones with discontinuous trajectories.
Mean life time in a potential well

However in the case $\psi(t, x_0)$ has to be considered not as the distribution of first passage times, but as the distribution of times at which the particle is for the first time found on the other side of $x_0$ than its initial position $x = 0$ was, see Chechkin et al., 2003. This statement is one of the important consequences of the Sparre-Andersen theorem from the theory of random walks, see Feller, 1991.

Let us now consider splitting probabilities for a particle starting at $X = 0$ on the interval with absorbing boundaries at $x_L < 0 < x_R$. Using equations (9.12) and (9.13) and our Laplace-transformed Green’s function, Eq.(9.14) we get after expanding the exponential up to the first order in their arguments:

$$P_R = 1 - P_L = \frac{1}{2} + \frac{|x_L| - |x_R|}{2|x_R - x_L|}.$$  (9.16)

9.3 Mean life time in a potential well

One of the most important results following from the theory based on the Fokker-Planck equation is the typical life-time in a potential well, i.e. the time necessary to overcome a potential barrier. Since this result will be repeatedly used in what follows, we shall discuss it here in some detail.

The situation considered here is depicted in Fig.9.1.
Imagine, a particle starts at the minimum of the potential, at point $x = 0$. We say that the particle overcame a barrier if it arrived for the first time at a maximum of the potential curve at $x = x_0$. The value of the potential energy of the particle there is $U(x_0)$ while the minimum of the potential energy at $x = 0$ is taken for the reference point, $U(0) = 0$.

9.3.1 The flow-over-population approach

In order to find the mean first passage time, we don’t need to solve the whole time-dependent problem.

Let us return to the physical formulation of the problem, and again discuss the experiment with putting the particles into a system. However, in order to ob-
tain the result, it is not necessary to put the particles one by one, and wait until the corresponding realization terminates. Let us imagine that at the point \( x = 0 \) a constant current of strength \( I \) is flowing into the system, see Fig.9.2. At the beginning, after switching on such current, the concentration of particles in the system will grow, and the output current, leaving the system at point \( x_0 \), will be smaller than the input current \( I \). Eventually, the steady state is reached, the input and the output currents equilibrate, and the steady-state concentration profile establishes itself. Now, if the mean first passage time, i.e. the time a particle on the average spends within the system, is \( \tau \), the mean number of particles within the system will be exactly \( I \tau \).

This mean number is nothing else than the integral over the steady-state concentration of the particles over the whole system (in our case over the semi-infinite interval \( -\infty < x < x_0 \)). Thus, we have:

\[
\tau = I^{-1} \int_{-\infty}^{x_0} p(x) dx
\]  

(9.17)

where \( p(x) \) is the steady-state solution of the Fokker-Planck equation (9.1). Note that the Fokker-Planck equation is essentially the continuity equation for the
probability current, and that

\[ I = \mu(x)f(x)p(x, t) - D(x)\frac{d}{dx}p(x, t). \quad (9.18) \]

Here we remind that \( f = -\frac{dU}{dx} \). This is an ordinary linear differential equation, which can be rewritten in the form:

\[ \frac{dp(x)}{dx} + p(x)\frac{\mu(x)}{D} \frac{d}{dx}U(x) = -\frac{I}{D(x)} \quad (9.19) \]

Eq.(9.19) is a linear differential equation, whose for-
Mean life time in a potential well

The solution reads:

\[ p(x) = \exp(-V(x)) \left[ p(0) - \int_0^x \frac{I}{D(x)} \exp(V(x')) dx' \right] \]

with \( V(x) = \mu(x)U(x)/D(x) = U(x)/k_B T \). The boundary condition \( p(x_0) = 0 \) leads to the expression for \( p(0) \):

\[ p(0) = \exp(-V(0)) \int_0^{x_0} \frac{I}{D(x)} \exp(V(x')) dx'. \]

From here on we assume for simplicity that the mobility and the temperature are constant throughout the whole system. According to our choice of the reference energy in Fig.9.2 we have \( \exp(-V(0)) = 1 \), which simplifies the expressions. Note that the probability current to the left from point \( x = 0 \) vanishes, so that to the left of this point the steady-state solution coincides with the equilibrium solution \( p(x) = p(0) \exp(-V(x)) \). We thus have:

\[ N(x) = \begin{cases} 
\frac{I}{D} \exp(-V(x)) \int_0^{x_0} \exp(V(x')) dx' & \text{for } x \leq 0 \\
\frac{I}{D} \exp(-V(x)) \int_x^{x_0} \exp(V(x')) dx' & \text{for } 0 < x < x_0 
\end{cases}. \]

We thus have the following expression for the mean
first passage time in the system:

\[ \tau = \frac{1}{D} \int_{-\infty}^{0} \exp(-V(x')) dx' \int_{0}^{x_0} \exp(V(x')) dx' + \]
\[ + \frac{1}{D} \int_{0}^{x_0} \left[ \exp(-V(x'')) \int_{x''}^{x_0} \exp(V(x')) dx' \right] \, dx'' \]  
(9.23)

the expression that can be rewritten in a form

\[ \tau = \frac{1}{D} \int_{0}^{x_0} dy' \int_{-\infty}^{y'} dy'' \exp[V(y') - V(y'')] \]  
(9.24)

Let us now concentrate on the case of a deep well or small temperatures. In this case we can make simple estimates for our integrals which now depend only on the properties of the potential close to points \( x = 0 \) and \( x = x_0 \).

9.3.2 The Arrhenius law

Let us assume that close to the maximum at point \( x = x_0 \) one has \( V(x) \simeq V(x_0) - (2k_B T)^{-1}U''(x_0)(x_0 - x)^2 \) and evaluate Eq.(9.23). In this case the integral \( \int_{0}^{x_0} \exp(V(x')) dx' \) in the first line of the last expression and the integral \( \int_{x}^{x_0} \exp(V(x')) dx' \) (which, for \( x'' \) not too close to \( x_0 \), is practically a constant) are approximately equal to each other and are given by the saddle-point approxi-
Mean life time in a potential well

\[ \int_0^{x_0} \exp(V(x'))dx' \simeq \frac{\sqrt{\pi k_B T}}{\sqrt{2|U''(x_0)|}} \exp[V(x_0)]. \] (9.25)

If we assume that the potential has a simple quadratic minimum close to \( x = 0 \), i.e. that \( V(x) \simeq (2k_B T)^{-1}U''(0)x^2 \), the same type of an approximation for \( \int_{-\infty}^0 \exp(-V(x'))dx' \) and for \( \int_0^{x_0} \exp(-V(x'))dx' \) again shows that the integrals are approximately equal to each other and can be approximated by

\[ \int_0^{x_0} \exp(-V(x'))dx' \simeq \frac{\sqrt{\pi k_B T}}{\sqrt{2U''(0)}} \exp[-V(0)] \] (9.26)

(in our case we have \( V(0) = 0 \)). The overall expression for \( \tau \) the reads

\[ \tau \simeq \frac{\pi k_B T}{D\sqrt{U''(x_0)U''(0)}} \exp \left( \frac{U(x_0)}{k_B T} \right) : \] (9.27)

the mean first passage time depends exponentially on the height of the barrier relative to the thermal energy of particles. This exponential growth is often termed as the Arrhenius law.

9.3.3 Diffusion in a double-well

As the next example let us consider the behavior of a particle in a double-well potential consisting of two
wells of depths $U_1$ and $U_2$ measured with respect to the top of potential barrier. Then the mean first passage time from one well to another one is determined by the corresponding well’s depths. Fig.9.3 shows a symmetric potential well $U(x) = x^4 - 2x^2 + 1$ (having two minima at $x = \pm 1$ separated by a barrier of height 1 with the maximum at $x = 1$). A trajectory of the diffusive process $x(t)$ for $\mu = 1$ and for $T = 0.15$ is shown in Fig.9.4. Note that the behavior of the trajectory shown in Fig.9.4 suggests its possible description as a sequence transitions between the two well-defined states, in which the particle is localized either in the left well (around $x = -1$) or in the right one (around $x = 1$). Let us now identify the position of the particle to the left from the top of the barrier with the $L$-state of the system, and the
position to the right from the top with the $R$-state. The average life-time in either state is $2\tau$ (since after reaching the top of the potential barrier the particle can either change the well or return to the initial one, with equal probability), which defines the transition rate between the wells, $k$, which corresponds to the mean number of transitions in either direction per unit time. For the wells of different depth, two different rates, $k_+$ for the transition in positive direction and $k_-$ for the transition in negative direction; each of them being equal to a half of the inverse of the corresponding mean first passage time to the top of the barrier.

The transition between the $L$- and the $R$ states of
the system can be considered as a simplest reversible isomerization reaction,

\[ L \rightleftharpoons R. \quad (9.28) \]

and the probabilities \( P_L \) and \( P_R \) to find a system in either state are given by the system of ordinary differential equations,

\[ \frac{dP_L}{dt} = -k_- P_L + k_- P_R \]
\[ \frac{dP_R}{dt} = -k_+ P_R + k_+ P_L. \quad (9.29) \]

This coarse-grained approximation corresponds to the approach known as formal kinetics. If we consider the ensemble of such two-level systems, then the number of systems being in states \( R \) and \( L \) are proportional to the corresponding probabilities, and their sum equals to the overall number of systems \( N \).

The equilibrium probabilities following from Eq.(9.29) are \( P_L = k_-/(k_+ + k_-) \) and \( P_L = k_+/(k_+ + k_-) \) so that

\[ \frac{P_L}{P_R} = \frac{k_-}{k_+}. \quad (9.30) \]

Expressing the transition rates through the first passage times and using the expression for the first pas-
Moments of the first passage time

9.4 Moments of the first passage time

In the previous section we have seen how much information is contained even in the first moment of the first passage time distribution, i.e. in the mean
first passage time. Sometimes one also needs higher moments of the distribution. The trivial way of obtaining $\psi(t, x_0)$ and then integrating it to obtain

$$\langle t^n \rangle = \int_0^\infty t^n \psi(t, x_0) dt$$

might be too complicated, so that it is reasonable to derive equations which give us these moments immediately. Here we first return to the potential shown in Fig.9.1 where the particle leaves the potential well through the point $x_0$. Let us consider now a general initial condition, i.e. let the particle start at some point $y$ within the well and obtain the first passage time probability density $\phi(t, y) = \psi(t, x_0|y)$ as a function of $y$. We have

$$\phi(t, y) = -\frac{\partial}{\partial t} \int_{-\infty}^{x_0} p(x, t|y, 0) dx.$$  

(9.35)

We now can interchange the sequence of temporal differentiation and integration over $x$. Moreover, if the coefficients in the Fokker-Planck equation are time-independent, the probability density $p(x, t|y, t')$ depends only on the difference $t - t'$ and thus as a function of $y$ is given by the backward Kolmogorov equation

$$\frac{\partial}{\partial t} p(x, t|y, 0) = \left[ \mu f(y) \frac{\partial}{\partial y} + D \frac{\partial^2}{\partial y^2} \right] p(x, t|y, 0),$$

(9.36)
so that

$$\phi(t, y) = - \left[ \mu f(y) \frac{\partial}{\partial y} + D(x) \frac{\partial^2}{\partial y^2} \right] \int_{-\infty}^{x_0} G(x, t|y, 0) dx. \quad (9.37)$$

where we have interchanged the sequence of integration over $x$ and differentiation over $y$. Taking the temporal derivative from both parts of this equation and using the definition of $\phi(t, y)$, Eq.(9.35) we get the closed equation for $\phi(t, y)$ in form of a backward equation

$$\frac{\partial}{\partial t} \phi(t, y) = - \left[ \mu f(y) \frac{\partial}{\partial y} + D \frac{\partial^2}{\partial y^2} \right] \phi(t, y). \quad (9.38)$$

The corresponding initial and boundary conditions follow from those for the backward Kolmogorov equation, but can be easily put down also from the purely physical considerations: $\phi(0, y) = 0$ for $y \neq x_0$ (the particle needs finite time to reach the boundary from any point inside the well) and $\phi(t, x_0) = \delta(t)$, since the particle needs zero time to rich the boundary in the case it was there from the very beginning. Now, we use the definition of the moments, i.e. multiply both sides of Eq.(9.38) by $t^n$ and perform the inte-
gration over $t$ to get

$$\left[ \mu(y)f(y) \frac{d}{dy} + D \frac{d^2}{dy^2} \right] \langle t^n(y) \rangle = -n \langle t^{n-1}(y) \rangle \phi(t, y)$$

(9.39)

giving the recursive hierarchy of equations for moments. The boundary condition $\langle t^n(x_0) \rangle = 0$ ($n < 0$) follows from those for the $\delta$-functional form of $\phi(t, x_0)$. Note that $\langle t^0 \rangle = 1$ due to normalization. For the mean first-passage time we thus get

$$\left[ \mu(y)f(y) \frac{d}{dy} + D(y) \frac{d^2}{dy^2} \right] \langle t(y) \rangle = -1.$$  

(9.40)

This equation was first derived by Pontryagin, Andronov and Witt (1933). The splitting probabilities can be, of course, discussed by introducing the corresponding boundary conditions at two ends of the interval.

Note that Eq.(9.40) can be easily integrated (by introducing first $z(y) = \frac{d\langle t(y) \rangle}{dy}$ and assuming that this function vanishes for $y \to -\infty$) and leads to the same results as the flow over population method: The general solution of the equation reads

$$\tau = \langle t(y) \rangle = \int_y^{x_0} dy' \int_{-\infty}^{y'} dy'' \frac{exp[V(y') - V(y'')]}{D(y'')}$$

(9.41)
An underdamped situation

where

\[ V(x) = - \int_{-\infty}^{x} \frac{\mu(z)f(z)}{D(z)} \, dz = \frac{U(x)}{k_B T} \]  

(9.42)

is the same as in section 9.3.1. The overall scheme however allows for obtaining the higher moments as well.

The corresponding results may also be obtained from the immediate discussion of the trajectories of the process, see van Kampen, 1992, which approach is a bit less formal, but needs starting again from the general Master equation for the whole process.

9.5 An underdamped situation

This is only the overdamped motion in 1d (described by the Smoluchowski equation) for which many beautiful exact solutions are readily available. For more general cases, say the ones described by the Klein-Kramers equation, exact expressions are not known (in the sense that you have first to solve equation to get the result). Here a lot of nice numerical work is done, and several approximations based on special properties of the process are known, see Risken, 1988; Hänggi, Talkner and Borkovec, 1990.

However, the limiting case of extremely low friction is also amenable for theoretical investigation. The treatment here might be based on the idea of energy
diffusion discussed in Chapter 8. For \( \mu \to \infty \) (small friction) the Klein-Kramers equation is reduced to the Liouville equation: We have now to do with the microcanonical ensemble with conserved energy \( E = mv^2/2 + U(x) \), defining the states of the system. The external noise causes the transitions between the different states. In this case we can approximately reduce the two-dimensional Klein-Kramers equation to a one-dimensional one. From formal reasons it is better to characterize the states not by the energy itself but by the action \( I(E) \) being the function of energy.

The relation between the energy and the action

\[
I = \int p \, dx = 2 \int_{x_{\min}}^{x_{\max}} \sqrt{2m (E - U(x))} \, dx \quad (9.43)
\]

follows from the Hamiltonian dynamics of the system; \( x_{\min} \) and \( x_{\max} \) are the turning points of the corresponding trajectory.

The instantaneous probability of transitions between the two states depends on where the phase point is situated during the transition. The next step is then averaging over all such transitions to get the corresponding second moment giving the diffusion coefficient in the corresponding Smoluchowski equation. This procedure, introduced by Kramers (see Kramers, 1940 and Zwanzig, 1959) leads to the
following expression for the probability density in $I$:

$$\frac{\partial p(I,t)}{\partial t} = \gamma \frac{\partial}{\partial I} I \left[ 1 + \frac{2\pi k_B T}{\omega(I)} \frac{\partial}{\partial I} \right] p(I,t)$$  \hspace{1cm} (9.44)

where $\omega(I)$ is the frequency corresponding to the action $I$:

$$\omega(I) = 2\pi \frac{\partial E}{\partial I}.$$  \hspace{1cm} (9.45)

Eq.(9.44) is a one-dimensional equation for which the discussions of our previous section hold. Using the method based on the backward equation, Eqs.(9.40), we can get an explicit result for the mean life time in a well.

The main difference between the over- and the underdamped situation can, however, be grasped without really solving Eq.(9.44). Let us consider, for example, the motion in a harmonic potential with a cut-off at $E = E_{\text{max}}$. For this case $\omega(I) = \omega_0 = \sqrt{k/m}$, where $k$ is the elasticity constant of the spring, and $I(E) = 2\pi E/\omega_0$. Eq.(9.44) now reads *:

$$\frac{\partial p(I,t)}{\partial t} = \gamma \frac{2\pi}{\omega_0} \frac{\partial}{\partial I} \left[ \frac{\omega_0}{2\pi} I + k_B T \frac{\partial}{\partial I} \right] p(I,t)$$  \hspace{1cm} (9.46)

*The simplification consisting the assumption that the maximum of the potential corresponds to a cusp at $E_{\text{max}}$, is not always realistic. Typically, the escape escape takes place through a saddle point of the potential (quadratic maximum). The frequency on the trajectory passing through this saddle point vanishes, so that the diffusion coefficient $2\pi k_B T \gamma I/\omega(I)$ formally diverges. Thus, in the underdamped problem the behavior close to the separatrix is much less important than for the overdamped case. Estimates show that our simple result is not too far from the reality, see van Kampen, 1988
Comparing this equation with a typical overdamped form

$$\frac{\partial}{\partial t} p(x, t) = \mu \frac{\partial}{\partial x} \left[ -f(x) + k_B T \frac{\partial}{\partial x} \right] p(x, t)$$ (9.47)

we see that the situation is equivalent to the overdamped case with $\mu$ changed for $2\pi \gamma / \omega_0$ and the force being $-\omega_0 I / 2\pi$. Therefore we can immediately say that the corresponding rate (proportional to $\mu$) will linearly grow with friction coefficient $\gamma$, a situation opposite to the overdamped case, where it decays as $\gamma^{-1}$. Thus, the overall situation corresponds to a nonmonotonous $\gamma$-dependence: For initial energies below $E_{\text{max}}$ the rate, as a function of $\gamma$ first grows and then starts to decay. The crossover between these two types of behavior at moderate damping was discussed almost half a century later, in the works by Melnikov and Meshkov, 1986, and by Pollak, Grabert and Hänggi, 1989, see Hänggi, Talkner and Borkovec, 1990 for a review.
Chapter 10

Reaction kinetics

One of the typical and important cases pertinent to the domain of nonequilibrium thermodynamics or statistical physics corresponds to the reaction kinetics. One has to stress that what we call the "reactions" has a much broader meaning than a real chemical reaction in a gas or liquid phase, but includes many "physical" phenomena such as recombination of ions and electrons in plasma, the recombination of electrons and holes in semiconductors, different classes of processes leading to luminescence in solids and liquids, to creation and healing of the radiation defects, etc. Some special examples of these reactions will be discussed in the following chapters. Here we start from what is called the classical kinetic theory, the approach based on the assumption that there exist well defined reaction rates, i.e. the probabilities of reaction per particle per unit time. Before going into details of kinetics, let us say a few words about
the thermodynamics of reactions.

10.1 The mass action law

The typical chemical reaction

\[ \text{adducts} \rightleftharpoons \text{products} \quad (10.1) \]

eventually leads to establishing equilibrium between the adducts and the products of the reaction; their equilibrium concentrations depend on the thermodynamical properties of adducts and products and on the reaction heat, and is given by the mass action law, being a law of equilibrium thermodynamics. For example, if our reaction is a simple bimolecular one,

\[ A + B \rightleftharpoons C \quad (10.2) \]

(say, simple dissociation \( H + H \rightleftharpoons H_2 \), or ionization in plasma \( H^+ + e^- \rightleftharpoons H \) or in electrolytes, or electron-hole recombination on a semiconductor, or recombination of Frenkel defects in an irradiated solid) the equilibrium concentration of the product \( C \) and its dependence on temperature and pressure are prescribed by thermodynamics, Landau and Lifshitz, 1990. The concentration of the reactant \( A \) will throughout this chapter be denoted by the italic \( A \).

Each reaction equation of the type above can be put
The mass action law

down in a form

\[ n_1 R_1 + n_2 R_2 + \cdots + n_n R_n \rightleftharpoons n_{n+1} R_{n+1} + \cdots + n_M R_M \]  
(10.3)

where \( R_i \) with \( i = 1, \ldots, n \) are the adducts and \( R_i \) with \( i > n \) are the products of the reaction. In our example above we had \( \nu_1 = \nu_2 = \nu_3 = 1 \). Eq.(10.3) can be rewritten as

\[ \nu_1 R_1 + \nu_2 R_2 + \cdots + \nu_n R_n + \nu_{n+1} R_{n+1} + \cdots + \nu_M R_M = 0, \]  
(10.4)

where the numbers \( \nu_i \) are the stoichiometric coefficients. Here we have \( \nu_i = n_i \) for the adducts and \( \nu_i = -n_i \) for the products of the reaction. Let us concentrate on the case when only one reaction is possible in the system. The reaction equation dictates then that the changes in the numbers of corresponding species are not independent: the reaction equation, Eq.(10.4) represents a conservation law for a given combination of the particle numbers \( N_1, N_2, \ldots, N_M \). Thus, if the number of particles of the sort \( R_1 \) changed by \( \delta N_1 \), then the number of particles \( R_2 \) has to change by \( \delta N_2 = (\nu_2/\nu_1)\delta N_1 \), etc. The changes in the numbers of the corresponding particles \( N_1, N_2, \ldots, N_M \) are connected via

\[ \frac{\delta N_1}{\nu_1} = \frac{\delta N_1}{\nu_1} = \cdots = \frac{\delta N_M}{\nu_M} = \delta \alpha. \]  
(10.5)
The equilibrium state of the system is then characterized by the minimum of Gibbs potential $G$ being the function of $N_1, N_2, ..., N_M$, of the pressure $p$, and of the temperature $T$. The change in this potential is

$$\delta G = \sum_{i=1}^{M} \frac{\partial G}{\partial N_i} \delta N_i = \delta \alpha \sum_{i=1}^{M} \nu_i \frac{\partial G}{\partial N_i}$$  \hspace{1cm} (10.6)$$

In equilibrium, the Gibbs potential is minimal, so that

$$\sum_{i=1}^{M} \nu_i \frac{\partial G}{\partial N_i} = 0.$$ \hspace{1cm} (10.7)$$

Let us now turn to the simplest situation which emerges when the reaction takes place in well-mixed gaseous phase or in dilute solutions. In this case the overall value of $G$ can be put into the form

$$G = \sum_{i=1}^{M} \left( N_i \mu_i - k_B T N_i \ln \frac{N_i}{N} \right),$$ \hspace{1cm} (10.8)$$

where $\mu_i$ is the chemical potential of the pure component, and the second term corresponds to the mixing entropy. This last one is taken in a form it has in ideal gases or in dilute solutions. Here $N$ denotes the overall number of particles $N = N_1 + N_2 + ... + N_M$. Using Eqs. (10.7) and (10.8) we get:

$$\sum_{i=1}^{M} \nu_i \left[ \mu_i - k_B T \left( \ln \frac{N_i}{N} + 1 \right) \right] = 0,$$ \hspace{1cm} (10.9)$$
The mass action law which equation can be rewritten in the form
\[
\sum_{i=1}^{M} \nu_i \ln \frac{N_i}{N} = \sum_{i=1}^{M} \nu_i \left( \frac{\mu_i}{k_B T} - 1 \right).
\] (10.10)

Introducing the relative concentrations \(c_i = N_i/N\) we get
\[
c_1^{\nu_1} \cdot \cdots \cdot c_M^{\nu_M} = K_c
\] (10.11)
where \(K_c\) is the reaction equilibrium constant,
\[
K_c = \exp \left[ \sum_{i=1}^{M} \nu_i \left( \frac{\mu_i}{k_B T} - 1 \right) \right].
\] (10.12)

Note that \(K_c\) is the function of the pressure \(p\) and the temperature \(T\) being the natural variables of chemical potentials. This is the mass action law, formulated by Guldenberg and Waage in 1867. This law connects the relative equilibrium concentrations of the particles with chemical potentials of reacting components. The dependence of the equilibrium constant dependence on the temperature and pressure was examined by van’t Hoff, whose investigations brought him the (very first!) Nobel prize in chemistry in 1901. The volume concentrations \(R_i = c_i N/V = c_i p/(k_B T)\) of the products satisfy the similar equation,
\[
R_1^{\nu_1} \cdot \cdots \cdot R_M^{\nu_M} = K_c(T, p) \left( \frac{p}{k_B T} \right)^\nu
\] (10.13)
with $\nu = \nu_1 + ... + \nu_M$. In our simple bimolecular reaction taken as an example the combination in the l.h.s. would correspond to $A B / C$. The mass action law and the corresponding van’t Hoff’s equations are the consequences of thermodynamics, and do not depend on the exact dynamical mechanism of the reaction. Note however, that here the condition of ”well-mixedness” is explicitly assumed. The Gibbs potential (the free enthalpy) of the system depends, through the entropic contribution, on the correlations between the particle’s positions, which might appear either through interactions or dynamically, through the reaction itself. Thus, the mass action law might be violated, which doesn’t mean the violation of any thermodynamical principles. Note that some correlations might be destroyed by effective mixing: this is how mixing procedures may influence chemical equilibria.

10.2 Classical kinetics

Let us now turn to the kinetics of the reaction. In many cases both the forward and the backward reaction can be described by the rates $k_+$ and $k_-:$

$$A + B \Leftrightarrow C$$

$$k_+$$

$$k_-$$

(10.14)
so that the kinetic equations for the corresponding concentrations (denoted by the same symbols, now in italic) follows a system of ordinary differential equations:

\[
\begin{align*}
\frac{d}{dt} A &= \frac{d}{dt} B = -k_+ AB + k_- C \\
\frac{d}{dt} C &= k_+ AB - k_- C.
\end{align*}
\]  

Here we assume that the two adduct molecules A and B have a well-defined probability to meet and to react per unit time, and that the product molecule C has a well-defined probability to dissociate per unit time. The first probability is assumed to be proportional to the product of concentrations A and B (which means that for a given one A-molecule the number of reactive encounters with B is proportional to the actual B-concentration in the system; this probability per unit time is exactly \(k_+\)); the second probability is assumed to be constant and is exactly \(k_-\).

The system of equations of classical reaction kinetics can be easily solved, and shows a relaxation to an equilibrium state given by the situation when the time-derivatives in the left hand sides vanish. In this case

\[
\frac{AB}{C} = \frac{k_-}{k_+}.
\]  

(10.16)
We note that \( \frac{AB}{C} \) is exactly the combination whose value is prescribed by the mass action law. Thus, if the reaction rate coefficients \( k_+ \) and \( k_- \) exist, they are not independent, but connected to each other via the constant of the mass action law. However, as we hasten to note, the existence of well-defined, time-independent reaction rates is essentially an additional hypothesis which is often violated, so that the real kinetics of the reaction hardly resembles the one prescribed by the system of first-order ordinary equations of the formal kinetics, or even the reaction-diffusion equations.

Van Kampen summarizes typical conditions under which the reaction rate approach applies (see van Kapmen, 1992):

1. The mixture must be homogeneous, so that the density at each point is the same. If the reaction is sufficiently slow, such homogeneity might be achieved by stirring.
2. The non-reactive elastic collisions must be sufficiently frequent to ensure the Maxwell velocity distribution at temperature \( T \). Otherwise the collision frequency could not be proportional to the product of densities. This assumption is typically satisfied in the presence of a solvent or inert gas. It is, of course, always the case if
the transport process can be approximated by diffusion.

(3) The internal degrees of freedom of the molecules are supposed to be in thermal equilibrium, at the same temperature $T$.

(4) The temperature must be constant in space and time so that one may treat the reaction rates as constants even though they depend strongly on temperature.

In many cases, the homogeneity of the system as a whole might be violated. However, just in spirit of non-equilibrium thermodynamics, in many cases one can still assume local equilibrium, so that the reaction can be described by concentrations, temperatures, etc., which are coordinate-dependent. This approach assumes that the characteristic size of inhomogeneities is large compared with the interparticle distance and with their mean free path. Moreover, the approach assumes that some "microscopic" reaction rate constants exist, which govern the local course of the reaction, so that all inhomogeneities may be considered on the "mesoscopic" level, i.e. assuming that the reaction takes place in a locally homogeneous medium, however, the local concentrations or temperatures may differ from place to place. This assumption leads to the reaction-diffusion or
reaction-diffusion-advection equations, being mesoscopic approximations. The corresponding continuous-medium approximations (e.g. reaction-diffusion equations) describe a large variety of effects. However, these approaches fail whenever the clear-cut scale separation gets impossible.

10.3 The Smoluchowski approximation

It is important to stress that real kinetics of chemical reactions depends both on the properties of the elementary act of the reaction (through the probability of forwards / backwards reactions) and on the transport process, bringing the reacting particles together. The last one depends strongly on the properties of the reaction medium, and may be different for example for the cases when this medium is stirred or not. Note that the chemical equilibrium, depending essentially on the thermodynamic (i.e. static) properties of products and adducts is typically determined solely by the nature of the products and adducts, but not by transport.

The first theory taking into account the properties of the transport process stems again from Smoluchowski, whose model was the coagulation of diffusing particles in absence and in presence of flows (Smoluchowski, 1917).
The approach of Smoluchowski was rather simple but effective. Let us consider a bimolecular reaction of particles A and B in a quiescent medium. Let at the beginning imagine that only particles A diffuse, and the B-particles are immobile (fixed). The physical picture exactly corresponding to this situation will be discussed in the next paragraph.

Let us first consider the reaction taking place with probability 1 on contact between A and B particles. The reaction rate $k$ of the forward reaction can then be interpreted as a current (Berg 1994, Rice, 1985) of A-particles onto the surface of a B one: This is a number of encounters of A’s and a chosen B per unit time. Imagine, the motion of A’s is pure diffusion, and the reaction takes place when the A particle approaches the B one at a distance $a$, called the reaction radius. The overall situation is assumed to be spherically symmetric. The reaction rate of such purely diffusion-controlled reaction can be obtained through the solution of the diffusion equation for the concentration $n$ of the A-particles surrounding the chosen B. To get the number of such encounters per unit time it is the enough to calculate the overall current of A’s onto the surface of the chosen B. This is a diffusion current, which in three dimensions is given
Reaction kinetics

by

\[ J_{\text{diff}} = -4\pi a^2 D \nabla n(r \to a_+, t); \]  \quad (10.17)

the reaction rate is nothing else as \( k = J_{\text{diff}}/A \). Here the concentration \( n(r, t) \) is a solution of the diffusion equation

\[ \frac{\partial}{\partial t} n(r, t) = D \Delta n(r, t). \]  \quad (10.18)

There are no A-particle within the reaction sphere, so that the boundary condition \( n(a, t) = 0 \) applies. The initial condition corresponds to a well-premixed system, in which the A-concentration is constant, so that \( n(r, 0) = A \theta(r - a) \).

This equation is not too hard to solve. Applying the Laplace-transform in time (changing to \( n(r, u) = \int_0^\infty n(r, t)e^{-ut}dt \)) and using the spherical symmetry of the problem we get:

\[ u n(r, u) - A \theta(r - a) = D \frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial n(r, u)}{\partial r} \right) \]  \quad (10.19)

with boundary conditions \( n(a, u) = 0, n(r, u) \to A \) for \( r \to \infty \). The change of variables \( n(r, u) = \psi(r, u)/r \) reduces this equation to one with constant coefficients, which is readily solved. The inverse Laplace
transform then gives
\[ n(r, t) = A \left[ 1 - \frac{a}{r} \text{erfc} \left( \frac{r - a}{2\sqrt{Dt}} \right) \right]. \]  
(10.20)

Note that for \( t \to \infty \) the solution tends to a stationary one,
\[ n(r, u) = A \left( 1 - \frac{a}{r} \right), \]  
(10.21)
i.e. to the solution of the three-dimensional Laplace equation fulfilling the boundary conditions. Equation (10.20) gives us the current onto the reaction surface
\[ J_{\text{diff}} = 4\pi Da \left( 1 + \frac{a}{2\sqrt{Dt}} \right) \]  
(10.22)
which after a transient tends to a constant giving the famous result
\[ k_{\text{diff}} = 4\pi Da \]  
(10.23)
for the reaction rate constant (Smoluchowski, 1917). If both reactants are mobile, the diffusion coefficient \( D \) is changed for the mutual diffusion coefficient \( \tilde{D} = D_A + D_B \) being the sum of the diffusion coefficients of reactants. The same approach was used by Debye (Debye, 1942) to get the effective rates of recombination in electrolytes, see also Falkenhagen, 1971, Rice, 1985.
The fact that the reaction takes place not with the probability 1 on encounter can be taken into account by using a partially reflecting (von Neuman) boundary condition and leads to a simple result

$$k^{-1} = (k_{diff} + k_r)^{-1}$$  \hspace{1cm} (10.24)

where $k_r$ is the reaction-controlled contribution, connected with the reaction probability (see Rice, 1985, Ovchinnikov, Timashev and Belyi, 1986). Since many real chemical reactions in fluid or solid phases are not ”fast” (i.e. purely diffusion-controlled) so that the probabilities of the reactions on a contact are small, the effective rate is mostly governed by the reaction probability (Kramers rate), and therefore the deficiencies of the Smoluchowski’s approach are not relevant. However, in the cases with slow diffusion and rather fast reaction these deficiencies get evident. Such cases are often pertinent to luminescent energy transport or to interactions of radiation defects in solids. Interestingly enough, here the theorists were first to discuss the situation; the results were then experimentally proved. The reason why the effects were not paid much attention are typically as follows: The systems are anyhow complex. The exact reaction schemes may include intermediate stages about which nothing is known. Including such
stages allows to fit whatever experimental curve. On the other hand, theoretical approaches starting from simple models have clearly shown that the deviations might be strong and that they might persist asymptotically.

Considering the physical meaning of $n(r, t)$ in Eq. (10.18), it is easy to understand that it is proportional to $c_{AB}(r, t)$, the two-point correlation function of the positions of A and B-particles, so that the equation of formal kinetics,

$$\frac{\partial}{\partial t}c_A = -kc_A c_B$$  \hspace{1cm} (10.25)

with

$$k = -4\pi a^2 D \nabla c_{AB}(r, t)$$  \hspace{1cm} (10.26)

for the one-point concentrations $c_A = A$ and $c_B = B$ and the Smoluchowski’s diffusion equation

$$\frac{\partial}{\partial t}c_{AB}(r, t) = D \Delta c_{AB}(r, t)$$  \hspace{1cm} (10.27)

with boundary condition $c_{AB}(a, t) = 0$, and initial condition $c_{AB}(r, 0) = \theta(r - a)$ are essentially the first and the second equation in the BBGKY-hierarchy, with a truncation of the second one. (The correct second equation should also contain a functional of the three-point correlation function in its r.h.s., Kuzovkov and Kotomin, 1988; 1996. This means, that
the Smoluchowski equation is clearly a two-particle approximation, fully disregarding higher correlations. So are also many of the reaction-diffusion schemes in use. The relative importance of many-particles effects in nonequilibrium dynamics of such reactions may be assessed by means of more accurate theories, or by numerical simulations. Note that although the characteristic scale of the change in A-concentration, which might be considered as the effective range of the "interaction" caused by chemical reaction, given by Eq.(10.21) is the reaction radius \(a\), i.e. is microscopic, the "interaction" itself is long-range. This indicates that the situations might occur in which the two-particle picture by Smoluchowski, as well as other two-particle approximations lose their validity. By now, several classes of reactions are known, in which the approximations dramatically fail to predict kinetics; three ones will be considered in what follows.

We note that, as it is often the case, the BBGKY-hierarchy itself, although being formally the universal theoretical instrument, does not provide a comfortable base for practical calculations, so that only few effects (like Ovchinnikov-Zeldovich slowing-down, \textit{vide infra}) can be reasonably described within these schemes; moreover even here the description relies on uncon-
trolled approximations like Kirkwood decomposition or equivalent. On the other hand, several special cases can be discussed with high degree of rigor using alternative (probabilistic or field-theoretical) approaches, see e.g. Mattis and Glasser, 1998. We would like to stress that for the quantitative description of such cases the random-walks approaches based on the picture put forward by Elliot Montroll and Georges Weiss were proved superior to Langevin schemes or continuous approximations. However, it is not our aim here to discuss the modern theory of diffusion-controlled reactions in full depth: For us it is only valuable as an example of how surprising non-equilibrium effects emerge from in the situations, in which the equilibrium behavior is clear and boring. The interested reader finds a lot of material in a book by Kuzovkov and Kotomin, 1996.

These are not only the multiparticle effects that may lead to failure of the reaction rate approximation. The notion of the constant reaction rates is intrinsically inappropriate in lower dimensions (capillaries, surfaces, involved fractal geometries of porous media, see Kopelman 1988, Blumen, Klafter and Zumofen, 1986).

Let us consider as an example a purely one-dimensional situation (the coordinate is now denoted by $x$, the B-
Reaction kinetics

particle is placed in the origin). Once again the concentration of A is given by Eqs.(10.25-10.27). In one dimension, however, Eq.(10.27) does not possess any stationary solution, to which the actual solution of the initial-value problem would tend at longer times. The solution of Eq.(10.27) in one dimension is given by

\[ c_{AB}(x, t) = \text{erfc} \left( -\frac{|x| - a}{2\sqrt{Dt}} \right) \]  

(10.28)

and is not a stationary, but a self-similar one. The corresponding reaction rate \( k(t) \) is a function of time and continuously decays, indicating the ineffectiveness of the one-dimensional transport:

\[ k(t) = -2D \frac{d}{dx} c_{AB}(x, t) \big|_{x=a} = \frac{2\sqrt{D}}{\sqrt{\pi t}} \]  

(10.29)

(note that the dimension of the reaction rate in \( d \) dimensions is \( [L^d/T] \), so that in 1d it has the dimension of velocity).

In two-dimensions situation the reaction rate also decays, and goes as \( 1/\ln t \). The behavior is 1d and 2d is intrinsically connected with the recurrence of random walks in these dimensions, which leads to a compact exploration of the reaction volume. We return to this discussion in Chapter 11, devoted to the random walk approaches to nonequilibrium pro-
10.4 Fluctuation effects in chemical kinetics

In many cases considered in thermodynamics fluctuations play a subordinated role, and are typically neglected. One of such cases is pertinent to the theory of chemical reactions, where one often uses classical reaction schemes as if they were immediately following from the mass action law. However, one has to be aware that such schemes may be very week and crude approximations, which are valid only for restricted values of parameters (say, homeopathic concentrations or high temperatures) or under special additional conditions (say, vigorous mixing).

Let us consider a few simple examples illustrating the deficiencies of the classical concept of reaction rates. We consider a few classes of reactions which are especially "popular" due to their relevance for physics. Thus we consider

\[ A + B \rightarrow B \]

with B immobile ("trapping"), showing strongly non-classical kinetics, as compared to

\[ A + B \rightarrow B \]

with A immobile ("scavenging"), whose kinetics fol-
low a classical pattern,

\[ A + B \rightarrow 0 \]

(”annihilation”, nonclassical) as compared to

\[ A + A \rightarrow 0 \]

(”quenching”, classical, at least at small concentrations), as well as

\[ A + B \rightarrow 2B, \]

being the simplest autocatalytic reaction. Some effects considered here are discussed in much more detail in the review article Mikhailov, 1989 and in the book by Kotomin and Kuzovkov, 1996.

FOR ADDITIONAL MATERIAL READ THE ORIGINAL BOOK
Chapter 11

Random Walk Approaches

The diffusion behavior governing fluctuations close to equilibrium and the time evolution of many nonequilibrium systems is ubiquitous, and the description of this diffusive behavior within the Langevin or Fokker-Planck schemes is a commonplace. However, as already said, these approaches are based on extrapolating mesoscopic type of behavior to microscopic scales, which is not always advantageous. It might be reasonable to start from a simple microscopic kinematic model (the one very close to the multiple scattering picture proposed by P. Drude in his electronic theory of metals), and to build the theory along slightly different lines. Although the approaches considered in this chapter are very close in idea to the ones proposed by Einstein and Smoluchowski, they are not always even mentioned in books on nonequilibrium thermodynamics. However, random walks approaches are one of the methods of the widest use
at least in the discussion of simplified nonequilibrium models, and give clues to understanding of such complex phenomena as dispersive transport in amorphous solids or aging in glass-like materials. Thus, up to the time these lines were written, the original work by Harvey Scher and Elliot Montroll explaining the dispersive transport in amorphous semiconductors within the continuous-time random walk model was referred to more than 1000 times (Scher and Montroll, 1975)! The versatility of random walk models and the possibility to adapt them to a variety of essentially non-Markovian situations make them an extremely valuable tool in the investigation of kinetic phenomena in the cases when the approaches based on the Markovian dynamics fail. The weakness of the approach in its classical form, put forwards by Elliot Montroll and George Weiss, is that it strongly relies on the homogeneity of the system: It is not always easy to adapt this approach to the case of motion in the external fields; however, this is sometimes possible and leads to beautiful mathematics (fractional Fokker-Planck equations). General information about the random walk approaches to different physical problems can be bound in the review articles by Haus and Kehr (1987), by Bouchaud and Georges (1990) and by Isichenko (1992).
11.1 The random walk approach to transport processes.

Parallel to the Einstein’s treatment of the Brownian motion, let us consider the motion of a particle as a sequence of independent steps. Each of these steps takes some time $\tau$ and brings a particle some distance $s$ away from its initial position. The step’s duration $\tau$ and length $s$ may be correlated or uncorrelated and are taken from some probability distribution $\psi(\tau, s)$. At the beginning we assume the step lengths and times to be independent on the particle’s position and on the actual time: As one can anticipate, the random walk approach reduces our transport problem to the mathematical problem of the distributions of the sums of independent, equally distributed increments. For example, the situation discussed in the Einstein’s work on Brownian motion is really very close to a genuine random walk picture put forward by Bachelier, Rayleigh and Pearson, see Chapter 1.

To stress the connection of random walks with our previous approaches let us return to the Einstein’s discussion of the Brownian motion as following from the independence of the particles’ motion and from the two additional postulates, namely the ones that the displacements of a particle during two subsequent intervals of the duration $\tau$ are independent and that the distribution of these displacements, $\phi(s)$, pos-
Random Walk Approaches

sesses the finite dispersion. The displacement of the particle can be considered as a result of many small, independent, equally distributed steps. The displacement of the particle after \( n \) such steps is:

\[
X_n = s_1 + s_2 + \ldots + s_n. \tag{11.1}
\]

In order to find the distribution of the sum of independent random variables, a useful instrument is provided by characteristic functions: A characteristic function of a probability distribution given by the probability density \( p(x) \) is defined as the mathematical expectation of \( e^{ikx} \), i.e. it is simply the Fourier-transform of \( p(x) \). Note that the Fourier-transform can be inverted, so that the density of a probability distribution can be found through its characteristic function via the inverse Fourier-transform (under the well-known conditions and restrictions). Note also that since

\[
\frac{d^n}{dk^n}f(k) = \int_{-\infty}^{\infty} (-ix)^n e^{ikx} p(x) dx, \tag{11.2}
\]

the characteristic function of a distribution is a generating function of its moments: if the \( n \)-the derivative of the characteristic function exists then

\[
M_n = \int x^n p(x) dx = (-i)^n \frac{d^n}{dk^n}f(k) \bigg|_{k=0}. \tag{11.3}
\]

Now let us consider the characteristic function of
the sum of $n$ independent random variables. Let us start from $n = 2$. The probability $p(y)$ that the sum of two independent random variables $x_1$ and $x_2$ having the probability densities $p_1(x_1)$ and $p_2(x_2)$ is equal to $y$ is given by

$$p(y) = \int dx_1 p_1(x_1)p_2(y - x_1) \quad (11.4)$$

(i.e. is a convolution of the probability distributions $p_1$ and $p_2$). To see this it is enough to note that for any value of $x_1$ the value of the sum $y = x_1 + x_2$ is attained for the well-prescribed value of $x_2 = y - x_1$, with the probability $p_2(y - x_1)dx_1$, which has to weighted over all possible values of $x_1$. A characteristic function of $p(y)$ is, of course, the Fourier-transform of this convolution, i.e. the product of the corresponding characteristic functions:

$$f(y) = \int e^{iky}p(y)dy = f_1(k) \cdot f_2(k). \quad (11.5)$$

For the sum of $n$ independent, equally distributed variables we can proceed recursively and show that the characteristic function of the distribution of a random variable $X$ given by Eq.(11.1) will be

$$f_X(k) = f_1(k) \cdot f_2(k) \cdot ... \cdot f_n(k). \quad (11.6)$$

If all $f_i(k) = f(k)$ are the same, we simply have

$$f_X(k) = [f(k)]^n. \quad (11.7)$$
Thus, the characteristic function of the distribution of the sum of \( n \) identically distributed, independent variables is the \( n \)-th power of the characteristic function of the distribution of each of them. We also note that if the corresponding variable \( s \) is nonnegative, the Laplace-transform of the probability density, \( L\{p(X)\} \) will have the same property, namely,

\[
\hat{L}\{p_X(X)\} = [\hat{L}\{p_s(s)\}]^n. \quad (11.8)
\]

Let us remind that the Laplace transform is defined as

\[
\hat{f}(u) \equiv \hat{L}\{f(y)\} \equiv \int_0^\infty e^{-uy} f(y) dy. \quad (11.9)
\]

Let us first discuss the genuine Einstein’s (or Pearson’s) problem. The random walk approach allows us for finding the probability distribution of the particle’s position \( p(x) \) immediately through \( \phi(s) \), without the intermediate step of putting down the corresponding differential equation for it. Let us assume that \( \phi(s) \) possesses at least two finite moments. Then one has

\[
\hat{\phi}(k) = 1 + M_1 k + \frac{1}{2} M_2 k^2 + o(k^2). \quad (11.10)
\]

After \( n \) steps we then have

\[
\hat{f}(k) = \hat{\phi}(k)^n = \left[ 1 + i M_1 k - \frac{1}{2} M_2 k^2 + o(k^2) \right]^n. \quad (11.11)
\]
Let us now concentrate on the case $n \to \infty$ and use the well-known limiting relation
\[ (1 + x)^{1/x} \to e \]  
for $x \to 0$. One thus has for $k$ small:
\[ f(k) \approx \left\{ [1 + (\phi(k) - 1)]^{1/(\phi(k) - 1)} \right\}^{(\phi(k) - 1)n} \to e^{n(\phi(k) - 1)}. \]  
Thus, for $k$ small enough we have
\[ f(k) \approx \exp \left[ n \left(iM_1k - \frac{1}{2}M_2k^2\right)\right] \]  
which is a characteristic function of a Gaussian distribution
\[ p(x) = \frac{1}{\sqrt{2\pi n\sigma}} \exp \left[ - \frac{(x - nM_1)^2}{2n\sigma^2} \right] \]  
with $\sigma = M_2 - M_1^2$. Since in the Einstein’s treatment the distribution $\phi(s)$ was supposed to be symmetric, $M_1 = 0$ and
\[ p(x) = \frac{1}{\sqrt{2\pi n\sigma}} \exp \left[ - \frac{x^2}{2n\sigma^2} \right]. \]  
Again, as in the Einstein’s approach we can take $n = [t/\tau]$, where $[...]$ denotes the whole part of the number. For $t$ large enough we can simply take $n = t/\tau$. Inserting this expression in Eq.(11.16) we
get
\[ p(x, t) = \frac{1}{\sqrt{4\pi Dt}} \exp \left[ -\frac{x^2}{4Dt} \right] \] (11.17)

with \( D = \sigma^2/2\tau \), as already discussed. Due to the assumed homogeneity in space and time we can also immediately put down the transition probability (the Green’s function)
\[ p(x, t|x_0, t_0) = \frac{1}{\sqrt{4\pi D(t-t_0)}} \exp \left[ -\frac{(x-x_0)^2}{4D(t-t_0)} \right]. \] (11.18)

Of course, what we did up to now, is nothing else than a hand waving derivation of the Central Limit Theorem first stated by Gauss and Laplace; its full mathematical formulation is due to Lévy and Cramér; the criteria of convergence and the possibility to drop out an \( o(k^2) \)-term in Eq.(11.11) are given by the Berry-Esseen theorem and its generalizations (see Feller, 1991).

### 11.1.1 Random walks on lattices

Let us discuss random walks on lattices, which are often considered as \textit{the} random walk model. A vast mathematical literature is devoted to precisely this subject; the already mentioned books by Spitzer (1976), by Feller (1991) as well as one by Georges Weiss
(1994) are the examples. However, also physically the model is quite reasonable for description of, say, energy transfer in crystals (say luminescent reactions in molecular crystals as exemplified by trapping, see Montroll and Weiss (1965), Montroll (1969)). The model follows by allowing the particle to jump only to next-neighboring lattice sites, i.e. to fixing the function \( \phi(x) = C^{-1} \sum_j \delta(x - r_j), \) where \( j = 1, ..., C \) numbers the nearest neighbors of the corresponding site and \( C \) is the coordination number of the lattice.

Of course, using the general scheme of a Master equation one can immediately describe the particles’ displacements either exactly or within the Fokker-Planck approximation. However, there are other approaches which might be more suitable for calculation of some special properties. We concentrate here first on random walks with discrete time (fixed time needed to perform a step). The continuous-time results follow then by the subordination procedure, as discussed in the next section.

Let \( P_N(r) \) be the probability for a particle starting at 0, to be at the point \( r \) after \( N \) steps. Many useful results for random walks are obtained using the generation function formalism. The idea here is as follows: The values of \( P_N(r) \) for given \( r \) and given initial conditions form a number sequence. Let us represent
this sequence as a sequence of Taylor-coefficients of
a function

\[ P(r; z) = \sum_{N=0}^{\infty} P_N(r) z^N \]  \hspace{1cm} (11.19)

which is said to be a generating function for the se-
quence \( P_N(r) \). If the generation function exists, it
contains the whole information about \( P_N(r) \), and al-


tows for obtaining many results in a closed, analytical
form.

Let us first consider a general situation. Imagine
that \( f(z) = \sum_{N=0}^{\infty} f_N z^N \) is a generating function of a
sequence \( f_N \) (here we assume that the series converge
at least in some range of \( z \)). The \( z \)-transformation
leading from the sequence \( f_N \) to its generating func-
tion is a discrete analogue of the Laplace-transform:
taking \( z = \exp(u) \), one recognizes in Eq.(11.19) an
integral sum for the corresponding Laplace integral.
The \( z \)-transformation shears with the Laplace trans-
form some important properties: thus, it is linear,
\( Z(\{f_n\} + \{g_n\}) = Z \{f_n\} + Z \{g_n\} \), and the \( Z \)-
transform of a discrete convolution of two sequences
\( \{f_n\} \) and \( \{g_n\} \), i.e. of a sequence \( \{h_n\} = \{f_n\} \ast \{g_n\} \)
with the elements \( h_n = \sum_{i=0}^{n} f_i g_{n-i} \) is a product
of the corresponding generating functions: \( h(z) = f(z)g(z) \). Moreover, under some regularity condi-
tions the generating function can even be approxi-
mated by a Laplace transform.

Now let us say a few words about the back transformation. Of course we can use the tables, or approximate the back z-transform by a back Laplace transform. However, for a special class of functions we meet in what follows (i.e. those which asymptotically behave as power-laws), we will not need it. The back transform is essentially given by so-called Tauberian theorems, Feller (1991), vol.2 Chap. XIII, §5.

Imagine \( g(y) = \sum_{N=0}^{\infty} g_n e^{-y_n} \) with \( g_n > 0 \) (note that \( y = \ln z \)). Let us consider the functions which behave essentially as power laws, so that for \( y \) small \( g(y) \sim y^{-\gamma} L(1/y) \) and \( L(x) \) is a slowly changing function of \( x \), i.e. \( \lim_{x \to \infty} \frac{L(Cx)}{L(x)} = 1 \) for any positive constant \( C \). An example of a slowly changing function are not only functions tending to a finite limit when \( x \to \infty \), but also, say, \( \log(x) \) or any powers of the logarithm. Let us introduce now a new function \( \varphi(y) \) so that \( g(y) = \varphi(1/y) \). Then that the partial sum of the series can be approximated as

\[
g_1 + g_2 + \ldots + g_n \approx \frac{\varphi(n)}{\Gamma(\gamma + 1)}. \tag{11.20}
\]
If the sequence \( \{g_n\} \) is monotonous,

\[
g_n \simeq \frac{\varphi'(n)}{\Gamma(\gamma + 1)}. \tag{11.21}
\]

The quality of approximation is typically very good.

Having the instrument, we can start discussing some important results connected with the first passage probabilities and with the overall number of visited sites.

Let us discuss for example the probability \( F_N(r) \) of visiting the site \( r \) for the first time at step \( N \). We can use here the discrete analogue of the renewal approach based on the relation between \( P_N(r) \) and \( F_N(r) \). Let us consider a random walk starting at \( 0 \). The probability to be at step \( N \) at site \( r \) is then given by:

\[
P_N(r) = \delta_{N,0}\delta_{r,0} + \sum_{j=0}^{N} P_{N-j}(0)F_j(r). \tag{11.22}
\]

The particle starting from \( 0 \) and being at \( r \) after \( N \) steps might have first visited the site \( r \) for the first time at step \( j \) and then returned to it. The probability of such return after \( N - j \) steps is \( P_{N-j}(0) \) due to the homogeneity of the lattice. Applying the \( z \)-transformation to this equation we get: \( P(r, z) = \)
The random walk approach to transport processes.

\[ \delta_{\mathbf{r}, 0} + P(\mathbf{0}, z) F(\mathbf{r}, z), \text{ from which} \]

\[ F(\mathbf{r}; z) = \frac{P(\mathbf{r}; z) - \delta_{\mathbf{r}, 0}}{P(\mathbf{0}; z)}. \] (11.23)

The overall probability to visit the site \( \mathbf{r} \) is thus

\[ F(\mathbf{r}) = \sum_{n=0}^{\infty} F(\mathbf{r}, N). \]

Let us calculate for example the overall return probability \( F(\mathbf{0}) \). Note that \( F(\mathbf{r}) = F(\mathbf{r}; 1), \) and thus

\[ F(\mathbf{0}) = 1 - \frac{1}{P(\mathbf{0}; 1)}. \] (11.24)

Thus, the random walk returns to the origin with probability 1 if \( P(\mathbf{0}; 1) \) diverges, and the return probability is finite if \( P(\mathbf{0}; 1) \) is finite. Now, using the characteristic function of the random walk, \( f_N(\mathbf{k}) = \lambda^n(\mathbf{k}), P_N(\mathbf{0}) \) can be easily found by back Fourier-transform: \( P_N(\mathbf{0}) = \left( \frac{1}{2\pi} \right)^d \int_\Omega f_N(\mathbf{k}) d\mathbf{k} \) (integration over the Wigner-Seitz cell of the lattice), so that \( P(\mathbf{0}; z) \) may be obtained by integration the geometric series. Interchanging integration and summation we obtain

\[ P(\mathbf{0}; z) = \left( \frac{1}{2\pi} \right)^d \int_\Omega \frac{d\mathbf{k}}{1 - z f(\mathbf{k})}. \] (11.25)

The integral for \( P(\mathbf{0}; 1) \) can only diverge if for some \( \mathbf{k} \)-vectors one has \( f(\mathbf{k}) = 1. \) For example, for hy-
percubic lattices $f(k) = \frac{1}{d} \sum_{j=1}^{d} \cos(k_j a)$ and divergence can take place only for $k = 0$. For small $k$, $f(k) \approx 1 - \frac{1}{2} a^2 k^2 + \ldots$, so that

$$P(0; 1) \approx \left(\frac{1}{2\pi}\right)^d \int_{\Omega} \frac{k^2 dk}{1 - (1 - \frac{1}{2} a^2 k^2)} \approx 2 \left(\frac{1}{2\pi}\right)^d a^{-2} \int_{\Omega} k^{d-3} dk.$$  

(11.26)

The corresponding integral diverges for $d = 1$ and 2: the simple random walks in one and two dimensions are recurrent. In $d = 3$ the integral converges, so that the random walk does not necessarily return to the origin (is transient). Some known return probabilities are:

$$F(0) = \begin{cases} 0.3405 \text{ for SC lattice} \\ 0.2822 \text{ for BCC lattice} \\ 0.2563 \text{ for FCC lattice} \end{cases}$$  

(11.27)

(Here SC denotes the simple cubic lattice, and BCC and FCC the body-centered and the face-centered cubic lattices, respectively). A more important property of the lattice random walk is the number of different sites visited. Indeed, it is a property which is intimately connected with the rates of diffusion-controlled reactions on such lattices. Let $\langle S_N \rangle$ be the mean number of different sites visited by a particle A.

Let moreover consider a scavenging reaction where single mobile A-particle removes immobile B’s met
on its way. The mean number of B removed during $N$ steps is connected with $\langle S_N \rangle$ via $N_B = c_B \langle S_N \rangle$ where $c_B$ is the concentration of $B$ (a probability that a lattice site is occupied by B). Thus, the rate of scavenging reaction on a lattice is proportional to the increase in $S_N$ per unit time. Of course, the corresponding picture can be translated to the continuous limit and gives rise to the visited-volume approach to chemical reactions (stemming from Montroll and Weiss) as opposed to the Smoluchowski approach.

Let us now calculate $\langle S_N \rangle$ following Dvoretzky and Erdös (1951). One first notes that

$$\langle S_N \rangle = 1 + \sum_{j=1}^{N} \Delta_j$$

(11.28)

where $\Delta_j$ is the mean number of the sites visited for the first time on step $j$: $\Delta_j = \sum_r F(r, j)$. For $\Delta(z)$, the generating function of $\Delta_j$, we thus have

$$\Delta(z) = \frac{z}{(1 - z)P(0; z)}$$

(11.29)

(Note that $F(r; z) = P(r; z)/P(0; z) - \delta_{r,0}/P(0; z)$ and that $\sum_r P(r; z) = 1 + z + z^2 + ... = 1/(1 - z)$ since $\sum_r P(r, N) = 1$). The generating function of $\langle S_N \rangle - 1$ thus equals to

$$\frac{z}{(1 - z)^2P(0; z)}.$$
Random Walk Approaches

The back transform gives (for $N \gg 1$):

$$\langle S_N \rangle \simeq \begin{cases} \sqrt{\frac{2}{\pi}} N & \text{in } d = 1 \\ \pi N / \ln N & \text{in } d = 2 \\ N / P(0;1) & \text{in } d = 3 \end{cases} . \quad (11.31)$$

In $d = 1$ and 2 the number of different visited places grows slower than $N$, which is a consequence of the fact that each of them is visited repeatedly. On the other hand, in $d = 3$ the number of different visited places grows as $N$: the sites visited are visited only once or a few times.

These results are also of great importance for the continuous-time lattice random walks, since the subordination transformation, see §11.1.2 makes it possible to translate physical time $t$ into $N$, see the next section.

The Vaks-Balagurov slowing down in trapping can also be reproduced in the approach and has to do with fluctuations in $S_N$, which are mirrored by the higher moments of this quantity. We refrain here from the detailed discussion of the mathematical approach to the problem.

11.1.2 The continuous-time random walks (CTRW)

The situation of the fixed step time $\tau$ corresponds to the so-called simple random walks. This time may however be itself a random variable. For example, the
random walk may result from a series of scattering events (in which case the time $\tau$ and the displacement $s$ will be strongly correlated). Another situation is exactly the one we discuss in this paragraph: the particle is trapped in some bounded state. From time to time it is released (due to the thermal excitation) and makes a random motion until it gets trapped again. This is exactly the situation Scher and Montroll confronted with when describing the transport in disordered semiconductors. Having this situation in mind, we shall consider $s$ and $\tau$ as independent random variables*.

Thus, let us consider $\psi(\tau, s)$ as a product of the two functions, $\psi(\tau, s) = \psi(\tau)\phi(s)$. The spatial aspect of the problem corresponds to a simple random walk, however, the number of steps now fluctuates: the number of steps performed up to the time $\tau$ is no more the whole part of $t/\tau$, but may in principle take any value from 0 to $\infty$. We note that such a situation corresponds to the case of subordinated Markovian processes: A discrete-time Markovian process $X_n$, a simple random walk, depends on its number of steps $n$, which may be called the operational time of the

*Although we use the one-dimensional notation here, this decoupling is not exactly what happens in a real one-dimensional system. One may much more consider the situation as a projection of a three-dimensional motion on the $x$-axis. The genuine one-dimensional situation with its additional correlations introduced by geometrical restrictions is considered e.g. by Bouchaud and Georges (1990)
process. The operational time itself is a random process with positive increments which depends on the physical time $t$. A resulting process may be Markovian or not, depending on the properties of $\psi(\tau)$.

Now, let us suppose that the probability to arrive at point $x$ after $n$ steps is known and is given by a probability density $p_n(x)$. In order to obtain the probability to be at $x$ at time $t$ we have to average $p_n(x)$ over the probability distribution $\chi_n(t)$ to make exactly $n$ steps up to the time $t$:

$$p(x, t) = \sum_{n=0}^{\infty} p_n(x)\chi_n(t). \quad (11.32)$$

The probability density $p_n(x)$ is known and is given by its characteristic function

$$f(k) = \tilde{\phi}(k)^n. \quad (11.33)$$

Our task is now to find the distribution $\chi_n(t)$ of making exactly $n$ steps up to $t$. We note that the step times $\tau$ are assumed to be independent and identically distributed. The probability to make no steps after beginning is

$$\chi_0(t) = 1 - F_1(t) = 1 - \int_0^t \psi_1(\tau) d\tau, \quad (11.34)$$

where $\psi_1(\tau)$ is the probability density to make the first step during the time $\tau$, and $F_1(t)$ is the corresponding cumulative distribution function. We have
to reserve the possibility that the waiting time distribution for the first step may differ from ones of the subsequent steps, Tunaley (1974); this gives us a clue for understanding some aging phenomena in systems showing the glass-like dynamics (*vide infta*). The probability to make no steps during time $t$ after a step was made is

$$
\chi(t) = 1 - F(t) = 1 - \int_0^t \psi(\tau) d\tau. \quad (11.35)
$$

Now, the probability that exactly one step was made up to the time $t$ is the one that the first step followed at some time $\tau$ and afterwards no steps followed:

$$
\chi_1(t) = \int_0^t \psi_1(\tau) \chi(t - \tau) d\tau. \quad (11.36)
$$

The probability to make exactly 2 steps is

$$
\chi_2(t) = \int_0^t \int_0^t \psi_1(\tau_1) \psi(\tau_2) \chi(t - \tau_1 - \tau_2) d\tau_1 d\tau_2, \quad (11.37)
$$

etc., so that

$$
\chi_n(t) = \int_0^t \cdots \int_0^t \psi_1(\tau_1) \psi(\tau_2) \cdots \psi(\tau_n) \chi(t - \tau_1 - \cdots - \tau_n) d\tau_1 \cdots d\tau_n. \quad (11.38)
$$

A multiple convolution structure of these expressions leads to simple structures under the Laplace transform:

$$
\hat{\chi}_0(u) = \frac{1 - \hat{\psi}_1(u)}{u} \quad ...
$$
Random Walk Approaches

\[
\hat{\chi}_n(u) = \hat{\psi}_1(u) \hat{\varphi}^{n-1}(u) \frac{1 - \hat{\psi}(u)}{u}. \quad (11.39)
\]

The Fourier-Laplace-transform of Eq.(11.32) thus reads:

\[
\hat{f}(k, u) = \sum_{n=0}^{\infty} \phi(k)^n \hat{\chi}_n(u)
= \frac{1 - \hat{\psi}_1(u)}{u} + \frac{1 - \hat{\psi}(u) \hat{\psi}_1(u)}{u} \sum_{n=1}^{\infty} \left( \phi(k) \hat{\varphi}(k) \right)^n
\]

In the second term one easily recognizes the geometric series, so that the closed form for the Fourier-Laplace transform follows:

\[
\hat{f}(k, u) = \frac{1 - \hat{\psi}_1(u)}{u} + \frac{1 - \hat{\psi}(u) \phi(k) \hat{\psi}_1(u)}{u} \left( \frac{1}{1 - \phi(k) \hat{\psi}(u)} \right).
\quad (11.41)
\]

In the case when \(\phi_1(\tau) = \psi(\tau)\) (Markovian situation, as well as non-Markovian situations when the time count starts together with the first step, corresponding to the so-called ordinary renewal processes, see Cox (1967)) the result, Eq.(11.42) is further simplified:

\[
\hat{f}(k, u) = \frac{1 - \hat{\psi}(u)}{u} \frac{1}{1 - \phi(k) \hat{\psi}(u)}.
\quad (11.43)
\]

The corresponding \(p(x, t)\) follows by an inverse Fourier and Laplace-transforms.
Let us now discuss the overall behavior of this probability density and concentrate first on the situation when \( \phi(s) \) is symmetric and possesses the finite second moment, as it was the case in the Einstein’s discussion. Differentiating Eq.\((11.43)\) twice with respect to \( k \) we get (assuming that \( \phi(k) = 1 - \frac{1}{2}\sigma^2k^2 + o(k^2) \))

\[
\langle x^2(u) \rangle = \frac{\hat{\psi}(u)}{u[1 - \hat{\psi}(u)]}\sigma^2, \quad (11.44)
\]

and \( \langle x^2(t) \rangle \) is given by the inverse Laplace transform of this expression. We note now that the behavior of \( \langle x^2(t) \rangle \) for \( t \) large is governed by one of \( \langle x^2(u) \rangle \) for small values of \( u \) and that, just parallel to Eq.\((11.3)\), we have

\[
\hat{\psi}(u) = 1 - \langle \tau \rangle u + \langle \tau^2 \rangle u^2 + ... \quad (11.45)
\]

(provided the corresponding moments exist) so that for \( u \to \infty \) we have

\[
\langle x^2(u) \rangle \simeq \frac{\sigma^2}{\langle \tau \rangle}u^{-2}. \quad (11.46)
\]

The inverse Laplace transform immediately gives:

\[
\langle x^2(t) \rangle = \frac{\sigma^2}{\langle \tau \rangle}t. \quad (11.47)
\]

The prefactor can be associated with the diffusion coefficient: \( D = \sigma^2/2 \langle \tau \rangle \) and is finite as long as the
first moment of the waiting time exists. A simple random walk is just one of the situations when this is the case.

11.1.3 CTRW and the master equation

Let us consider an important situation \( \psi(\tau) = \langle \tau \rangle^{-1} \exp(-t/\langle \tau \rangle) \) corresponding to the Markovian case. As we proceed to show, on this case the CTRW exactly corresponds to a master-equation scheme with the transition rates \( w(x'|x) = \phi(x' - x)/\tau_0 \) with \( \tau_0 = \langle \tau \rangle \).

Let us consider the situation when the particle initially starts at \( x = 0 \) at time \( t = 0 \), i.e. for the initial condition \( p(x,0) = \delta(x) \). We moreover denote \( p(x,t) = p(x,t|0,0) \). The Master equation for the case of homogeneous transition rates reads

\[
\frac{\partial}{\partial t} p(x,t) = \frac{1}{\tau_0} \int dx' \phi(x-x')p(x',t) - \frac{1}{\tau_0} \int dx' \phi(x'-x)p(x,t).
\] (11.48)

Note that the second integral in the r.h.s. simplifies due to the homogeneity and to the normalization condition for the step-length distribution \( \phi(s) \),

\[
\int dx' \phi(x' - x)p(x,t) = p(x,t),
\]

so that

\[
\frac{\partial}{\partial t} p(x,t) = \frac{1}{\tau_0} \int dx' \phi(x-x')p(x',t) - \frac{1}{\tau_0} p(x,t).
\] (11.49)
Let us now first make Fourier-transform in the spatial variable $x$ and note that the first integral in the right-hand side has a form of the convolution, so that

$$\frac{\partial}{\partial t} f(k, t) = \frac{1}{\tau_0} \phi(k) f(k, t) - \frac{1}{\tau_0} f(k, t). \quad (11.50)$$

Now, we take the Laplace transform in the temporal variable: we know that $\frac{\partial}{\partial t} f(k, t) = u \hat{f} - f(k, 0)$. The initial condition is $f(k, 0) = 1$, which is a Fourier-transform of the $\delta$-function. Thus,

$$u \hat{f}(k, u) - 1 = \frac{1}{\tau_0} [\phi(k) \hat{f}(k, u) - \hat{f}(k, u)]. \quad (11.51)$$

so that

$$\hat{f}(k, u) = \frac{1}{u - \frac{1}{\tau_0} [\phi(k) - 1]} \quad (11.52)$$

Now we compare this result with the one of the CTRW approach,

$$\hat{f}(k, u) = \frac{1}{u} \frac{1 - \hat{\psi}(u)}{1 - \phi(k) \hat{\psi}(u)} \quad (11.53)$$

The expressions, Eq. (11.51) and Eq. 11.52) are equivalent if we take

$$\hat{\psi}(u) = \frac{1}{u \tau_0 + 1} \quad (11.54)$$

i.e. for the exponential waiting-time probability density $\psi(\tau) = \tau_0^{-1} \exp(-\tau/\tau_0)$. This is the only situ-
ation in which the approaches are equivalent. The exponential waiting time distribution corresponds to a Markovian process in time in which the probability to make a jump during the time interval $\delta t$ equals to $\delta t/\tau_0$. In this case the probability to make a jump to the state $x$ depends only on the actual state of the system, and not on the time, when the previous step was made. In all other cases the probability of the jump depends also on the time of the previous one. However, the CTRW process can be considered as discrete Markovian process in the following sense: At the moment a step is made, the length and the time of the next jump is taken at random, from given probability distributions, independent on the previous history. Such processes are sometimes called semi-Markovian. However, being considered at arbitrary time, the process exhibits memory about the instant of the last jump. In this sense the process is non-Markovian. As we proceed to show, many CTRWs are even non-stationary and exhibit aging.

$^\dagger$In general, decoupled continuous-time random walks can be described by generalized Master equations with a memory kernel introduced by Kenkre and Knox (1974), see Klafter and Silbey (1980). We shall not discuss this approach here, but we shall consider continuous limits of a class of such equations later in §11.3.
11.2 Power-law waiting-time distributions

We first stay stuck to the case of uncorrelated spatial and temporal parts (i.e. decoupling $\psi(x,t) = \phi(x) \psi(t)$) and discuss the situation under which $\psi(t)$ lacks the first moment, i.e. when the integral $\int_0^\infty \tau \psi(\tau) d\tau$ diverges. Such an absence of means is not a too-seldom situation in statistical physics, and it is definitely a one, under which usual, close-to-equilibrium thermodynamics fails. However, the situation is experimentally a wide-spread one, so that we first turn to a short discussion of the experimental results which lead Scher and Montroll to the formulation of the CTRW approach.

By mid seventies several experiments on photoeffect in disordered semiconductors showed a very peculiar time-dependence of the transient photocurrent. A typical experimental setup consists of a slab or a film of material of thickness $L$ kept under voltage between one massive and one thin, semi-transparent electrode. A typical current through the system (at low temperatures) is extremely small, since the thermal activation is not too strong to considerably populate the conduction zone. A strong light flash from the side at which the electrode is semi-transparent produces free charge carriers (electrons), which are then moving towards the massive electrode, giving
a pulse of a current. Essentially we have here to do with a kind of a time-of-flight experiment. One could anticipate (and it is really the case for the temperatures high enough) that a Gaussian pulse of electrons moves with a more or less constant velocity \( v = \mu eE \) where \( \mu \) is the mobility and \( E \) is the electric field, and broadens according to the diffusive law. Thus, the form of the charge pulse \( en(x, t) \) (with \( n \) being the electron density) can be calculated via the solution of the corresponding Fokker-Planck equation (under constant field and an absorbing boundary condition at the position of the massive electrode). The instantaneous value of the photocurrent, being the time derivative of the dipole moment of the charge distribution, is \( I = e \frac{d}{dt} \int_0^L xn(x, t) dx \). This would give us a current which is practically constant before a considerable part of electrons reaches the electrode, and then decays fast, over the time connected with the width of the Gaussian.

However, experiments at lower temperatures done with a variety of non-organic and organic materials showed a very different picture: The "almost constant" part of the photocurrent and a fast subsequent decay are absent. Instead, one encounters a continuous and very slow decay; a current plotted on the double logarithmic scales shows a crossover
between the two linear regimes, denoting the power-laws. Moreover, if the slope of the line at the short-time domain is $\gamma$, the slope of one for the long-time domain is $2 - \gamma$; this simple connection was clearly seen in all corresponding experiments. The explanation of the effect was connected with multiple trapping phenomena.

In a disordered semiconductor (compared to an ideal crystal) the density of states in the conduction band has a tail protruding into the energy gap of the ideal one. One can envisage this tail as connected with the local density fluctuations in a disordered solid. Such states are localized, and do not contribute to the electric conductivity. The typical decay of this tail of the density of states into the gap goes as $\rho(E) \propto E_0^{-1} \exp\left(-E/E_0\right)$, where $E$ is the energy calculated, say from the localization threshold, and $E_0$ is the energetic scale characterizing the "fatness" of the tail, and depending on the degree of disorder (the prefactor $E_0$ is introduced to keep the correct dimension of the density of states). The overall transport process (called "dispersive transport", to stress the difference with the normal diffusive one) can be considered as a sequence of periods during which the particle is trapped and does not move, and ones when it is thermally activated to higher
energies, and moves. Neglecting the possibility of multiple trapping in the same state (which does not change anything in the three-dimensional case considered here but is of importance in lower dimensions, see Bouchaud and Georges (1990)) we can obtain the qualitative behavior of the waiting-time in a trap using the following ”hand waiving” argument:

A typical life-time of an electron in a trap of depth $E$ follows the Arrhenius law,

$$\tau \simeq \tau_0 \exp(-E/kT). \quad (11.55)$$

To get the probability distribution of $\tau$ we note that the probability distribution of the trap’s depth is proportional to the corresponding density of states, $p(E) \propto \rho(E) \propto E_0^{-1} \exp(-E/E_0)$. The probability density of the waiting time $\tau$ can then be obtained by the change of variables in this expression: \[ \psi(\tau) = p(E(\tau)) \frac{dE}{d\tau}, \] where $E(\tau) \simeq kT \ln(\tau/\tau_0)$ according to Eq.\(\text{(11.55)}\). Using this expression we get

$$\psi(\tau) \propto \exp(-kT \ln(\tau/\tau_0)/E_0) \frac{kT}{E_0\tau} \propto \tau_0^\gamma \tau^{-1-\gamma} \quad (11.56)$$

with $\gamma = kT/E_0$. Of course, such arguments only give the asymptotic behavior of $\psi(\tau)$ for very large $\tau$, however, as we proceed to show, the exact form of this distribution is of minor importance for what
follows. It is clear that the presence or the absence of the higher moments of such distribution depends only on the value of $\gamma$: in the low temperature regime (for $T < E_0/k$) the mean value of $\tau$ diverges, so that the change of transport regime from diffusion to something else may take place. One of the forms typically used in calculation examples is

$$\psi(\tau) = \frac{\gamma}{\tau_0 \left[ 1 + \frac{\tau}{\tau_0}\right]^{1+\gamma}}. \quad (11.57)$$

The waiting-time distributions with power-law asymptotics are wide-spread also in other applications, see the review article by Bouchaud and Georges for a detailed discussion. The motion of the particle between the two trapping events is characterized by some displacement probability density $\phi(x)$, and can be adequately modeled through a random walk. In the absence of the external field this walk is unbiased, so that the first moment of $\phi(x)$ vanishes. The field introduces a nonzero bias, which can be taken to be proportional to $E$.

Let us first consider the free diffusion, without external field, in such a system. In this case the mean squared displacement can be obtained from Eq.(11.43) by noting that the second moment of the distribution is given by the second $k$-derivative of $\hat{f}(k, u)$ (whose
first $k$-derivative vanishes). Noting that for small $k$ one has $\dot{\phi}(k) \approx 1 - 2\lambda^2 k^2$ one arrives at

$$\hat{f}(k, u) = \frac{1}{u} \frac{1 - \hat{\psi}(u)}{1 - (1 - 2\sigma^2 k^2) \hat{\psi}(u)}$$

(11.58)

from. In the case of a power-law, Eq.(11.57) one has

$$\psi(u) \approx 1 - Au^\alpha$$

(11.59)

with $A = \Gamma(1 - \alpha)\tau_0^\alpha$ so that

$$\hat{f}(k, u) = \frac{Au^{\alpha - 1}}{1 - (1 - \frac{\lambda^2}{2} k^2)(1 - Au^\alpha)} \approx \frac{1}{Bk^2 u^{1-\alpha} + u}$$

(11.60)

with $B = \lambda^2/2A$. From this form the scaling of the distribution is evident: The whole is a function of $\xi = x/t^{\alpha/2}$. We note that the inverse Fourier-Laplace transforms of such forms can be expressed within the class of special functions known as Meijer G-Functions (Prudnikov et al, 1990) or even more general Fox’s H-Functions (Fox, 1961), see also a MathWorld entry on http://mathworld.wolfram.com/MeijerG-Function.html. In some situations these functions can be reduced to something simpler, however this is typically not the case.

Comparing this situation with the one for the exponential waiting-time distribution, $\psi(t) = \tau^{-1} \exp(-t/\tau)$, whose Laplace-transform is $\hat{\psi}(u) = 1/(1 + u\tau) \approx$
$1 - u\tau$ we get

$$\hat{f}(k, u) \simeq \frac{1}{(\lambda^2/2\tau) k^2 + u} \quad (11.61)$$

where we easily recognize a Fourier-Laplace-transform of the Gaussian Green’s function of the diffusion equation,

$$P(x, t) = \frac{1}{\sqrt{4\pi Dt}} \exp \left(-\frac{x^2}{4Dt}\right) \quad (11.62)$$

with $D = \lambda^2/2\tau$. This distribution scales as a function of $\xi = x/\sqrt{t}$. In Fig.11.1 we compare this Gaussian distribution with $D = 1$ with the one following from Eq.(11.60) with $B = 1$ and $\alpha = 1/2$. Note the overall tent-like form of the function corresponding to the anomalous diffusion with the cusp at $x = 0$. 

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Caption for the figure:

Fig. 11.1. The limiting form of the probability density of a particle performing CTRW (as the inverse Fourier-Laplace transform of Eq.(11.60) (for $B = 1$ and $\alpha = 0.5$). For comparison the Gaussian distribution with the same dispersion is shown as a dashed line.
which mirrors the fact that the initial conditions in such a system never get forgotten.

For biased diffusion (say, in an external field) one has to take \( \phi(k) = 1 + ibk + \lambda^2 k^2/2 + \ldots \), where \( b \) characterizes the strengths of external bias. In this case the characteristic function reads

\[
\hat{f}(k, u) \sim \frac{1}{(ibk/A + Bk^2)u^{1-\alpha} + u}.
\] (11.63)

Using the fact that the characteristic function of a probability distribution is a generating function of its moments, we can calculate for example the mean displacement \( M_1(t) \) of particles, through its Laplace-transform:

\[
M_1(u) = \frac{d}{dk} \hat{f}(k, u)|_{k=0} = \frac{b}{A} u^{-1-\alpha},
\] (11.64)

which corresponds asymptotically to \( M_1(t) \approx t^\alpha \).

This finding allows us to explain the basic features of photoconductivity experiments discussed at the beginning of the paragraph:

At short time after irradiation the charge carriers do not “feel” the absorbing boundary, so that the mean displacement \( \langle X(t) \rangle = M_1(t) \propto t^\alpha \), and \( I(t) \propto dX(t)/dt \propto t^{\alpha-1} \): The slope of the initial part of the curve is \( \alpha_1 = -\alpha + 1 \). This regime (due to the “typical” motion) ends when \( \langle X(t) \rangle \sim l \), i.e. at time \( \tau(l) \propto l^\alpha \). At even longer times the parti-
cles still present within the sample are mostly those which were trapped all the time before. The current due to these particles is proportional to their number, \( I \propto \frac{d}{dt}N(t) \propto \psi(t) \) and goes as \( t^{-1-\alpha} \) (the tail of the first passage distribution), so that \( \alpha_2 = 1 + \alpha \), and thus, \( \alpha_1 + \alpha_2 = 2 \) in full agreement with the experimental findings.

11.2.1 Aging behavior of CTRW systems

The subdiffusive CTRW is an intrinsically nonstationary process, and exhibits many effects typical for nonstationarity. It was first considered as a toy model for aging in glasses by Feigelman and Vinokur (1988), and got to be a popular quantitative model for the description of such phenomena afterwards, see Bouchaud and Montus (1996), Laloux and P. Le Doussal (1998). Here we present some simple considerations elucidating the nature of aging due to Sokolov et al (2001). We concentrate on the linear response of the system to a time-dependent external field, and assume the following: We consider an ensemble of random walkers performing the CTRW. During the trapping period the particle does not move, independently on the strength of the external field. However, when the particle jumps, the field biases the direction of the step, so that the mean displace-
moment per step is proportional to the strength of the external field. We again use the one-dimensional notation.

Let us discuss the linear response of an ensemble of the random walkers performing the CTRW to the changing external field and consider some physically short time interval $dt$. Let $dN$ be the mean number of steps performed during $dt$. Now, the mean displacement during $dt$ is $\overline{dX} = xdN$ (note that for very short times $dt$ the value of $dN$ can be considered as a proportion of the realizations in which a particle has performed just one step) where $x$ is the mean displacement per step depending on the actual value of the external field $E$: $x = \kappa E$ with $\kappa \simeq \lambda/k_B T$. We thus get:

$$\overline{dX} = \kappa E(t) dN.$$  \hspace{1cm} (11.65)

where $dN = N(t + dt) - N(t) \approx dt \sum_{i=0}^{\infty} n \frac{d}{dt} \chi_n(t)$. Thus, the typical particles’ velocity at time $t$ (which is proportional to the particles’ current) is given by:

$$\nabla(t) = \frac{dX}{dt} = \kappa f(t) E(t).$$  \hspace{1cm} (11.66)

where

$$f(t) = \sum_{i=0}^{\infty} n \frac{d}{dt} \chi_n(t).$$  \hspace{1cm} (11.67)

Now, using Eq.(11.39) and Eq.(11.67) we arrive at
the Laplace-transform of $f(t)$, which reads:

$$f(\lambda) = \frac{\psi(\lambda)}{1 - \psi(\lambda)} \quad (11.68)$$

Using Eq.(11.59) and applying the inverse Laplace transform we get the behavior of $f(t)$ for longer times:

$$f(t) = \frac{\sin \pi \alpha}{\pi \tau_0^\alpha} t^{\alpha-1}. \quad (11.69)$$

Thus at longer times one has

$$\overline{V(t)} = \kappa \frac{\sin \pi \alpha}{\pi \tau_0^\alpha} t^{\alpha-1} E(t). \quad (11.70)$$

Note that the current or velocity response of a CTRW-system to the external field is local in time and is explicitly dependent on the time elapsed after the system was prepared. To obtain the particle’s position (or the polarization of the medium) we simply have to integrate Eq.(11.70) over time:

$$\overline{X(t)} = \kappa \frac{\sin \pi \alpha}{\pi \tau_0^\alpha} \int_0^t t_1^{\alpha-1} E(t_1) dt_1. \quad (11.71)$$

Thus, the response of the CTRW-system to a time-dependent field dies out, and its polarization tends to a constant value. Note that the CTRW-system not only ages, but shows a kind of ”Freudistic” response: the polarization at time $t$ is mostly due to the early history of the system, immediately after it
Random Walk Approaches

Fig. 11.2 The response of the CTRW system to an external field. The upper panel shows the mean velocity as a response to two pulses of unit height and duration following at $t = 1$ and at $t = 4$. Note that the response to the second pulse is considerably weaker: The system shows aging. The lower panel shows the response to the sinusoidal field. Here the mean velocity and the mean displacement are shown by a dashed and by a solid line, respectively.

was prepared in a state corresponding to CTRW. The response of the CTRW system to a pulsed and to the sinusoidal external field is shown in Fig. 11.2.

The behavior for a $\theta$-functional field unveils a very important property of the linear response in such systems. This response depends on the time elapsed since the system was prepared (a time of the 1st step): The system displays **aging**. The response to a constant field $E$ switched at $t_w$ behaves as $\overline{V}(t) \propto (t_w + \Delta t)^{-1} E \propto t_w^{-1}(1 + \Delta t/t_w)^{-1} E$, where $\Delta t$ is the time elapsed after switching the field. Thus, the overall strength of response is proportional to $t_w^{-1}$.
and the characteristic time of this response is exactly $t_w$. One says, that the situation corresponds to simple or normal aging. It can happen that the characteristic time of relaxation goes as $t_w^{\mu}$ with some $\mu \neq 1$. The situations with $\mu < 1$ are known and are said to correspond to subaging.

Let us discuss the reason for aging in a CTRW model in some depth. This reason is exactly the difference between the first step forward waiting time distribution $\psi_1(t)$ and the distribution of all other waiting times.

Let $\tau_1$ be the waiting time for the first renewal of the process after starting observation at time $t_w$, see Fig.11.3. The jump immediately preceding $t_w$ (numbered $i-1$), took place at time $t_{i-1} = s$. The forward waiting time distribution $\psi_1(t)$ is

$$\psi_1(t \mid t_w) = \int_0^{t_w} p(x)\psi(t_w - x + \tau_1)ds, \quad (11.72)$$

where $p(s)$ is the probability density to make a jump.
Random Walk Approaches

exactly at time \( s \):

\[
p(s) = \sum_{n=0}^{\infty} p_n(s). \tag{11.73}
\]

Here \( p_n(t) \) is the probability density that it is exactly \( n \)-th jump that takes place at time \( t \). This one is given by an \( n \)-fold convolution of the waiting time probability density \( \psi(t) \) with itself. Under Laplace-transform Eq.(11.73) reads:

\[
\hat{p}(u) = 1 + \hat{\psi}(u) + \hat{\psi}^2(u) + ... = \frac{1}{1 - \hat{\psi}(u)}. \tag{11.74}
\]

The Laplace-transform of \( \psi_1(\tau_1, t_w) \) as a function of \( t_w \) is then:

\[
\hat{\psi}_1(\tau; u) = \frac{e^{u\tau} \left[ \hat{\psi}(u) - \int_0^\tau e^{-ut} \psi(t) dt \right]}{1 - \psi(u)}. \tag{11.75}
\]

The inverse transform of this expression gives for both \( t_w \) and \( \tau_1 \) large

\[
\psi_1(\tau \mid t_w) \simeq C \left( \frac{t_w}{\tau} \right)^\alpha \frac{1}{t_w + \tau}. \tag{11.76}
\]

The longer \( t_w \), the longer is typically \( \tau \) (which is an extreme form of the inspection paradox, see Feller (1991)).

Note that our expression, Eq.(11.76), is only valid for \( 0 < \alpha < 1 \). For \( \alpha > 1 \), when the mean waiting time \( \langle t \rangle \) exists, the distribution of the forward waiting
times is given by
\[ \psi_1(\tau_1) = \frac{1}{\langle t \rangle} [1 - F(\tau_1)] \]  
(11.77)
where \( F \) is the cumulative distribution function of the \( \psi \)-distribution. Note that for power-law distributions \( \langle t \rangle \), if it exists, is the only relevant timescale of the problem, i.e. \( \psi(t) \sim \langle t \rangle^\alpha t^{-1-\alpha} \) (in order to have a correct dimension of the probability density), so that at longer times
\[ \psi_1(\tau) \sim \frac{1}{\langle t \rangle^{1-\alpha}} \tau^{-\alpha} \]  
(11.78)
Thus, for \( t_w > \langle t \rangle \) \( \psi_1(\tau) \) is independent on \( t_w \) (and shows no aging!).

Comparing Eq.(11.76) and Eq.(11.78) one readily infers that for \( \tau < t_w \)
\[ \psi_1(\tau \mid t_w) \sim \frac{1}{t_w^{1-\alpha}} \tau^{-\alpha} \]  
(11.79)
i.e. in this case \( t_w \) is only typical timescale, so that we take here \( t_w \) instead of \( \langle t \rangle \)! For \( \tau \gg t_w \), on the other hand, \( \psi_1(\tau \mid t_w) \) follows the behavior similar to one of \( \psi(t) \) i.e.
\[ \psi_1(\tau \mid t_w) \sim C t_w^\alpha \tau^{-1-\alpha} \]  
(11.80)
but again with the typical timescale of \( t_w \). We note that this type of nonstationarity is typical for three-
dimensional systems for which CTRW is a valid model describing their asymptotic behavior. In the low-dimensional systems, the situation is more complex and may lead to subaging, see Rinn, Maass and Bouchaud, 2000, 2001.

One more note is here at place. CTRW is a powerful scheme, which describes several kinds of physical processes. One of the important applications of CTRW is connected with intermittent dynamics, as generated, for example by maps. As an example one can consider a map

\[ x_{n+1} \equiv F(x_n, z, a) = x_n + ax_n^z, \quad 0 < \tilde{x}_n < \frac{1}{2}, \]

where \( \tilde{x}_n \) is a fractional part of \( x_n \). For \( \frac{1}{2} < \tilde{x}_n < 1 \) the map is defined by the mirror symmetry. Parameter \( z > 1 \) in Eq. (11.81) stands for a degree of nonlinearity and \( a \) is a control parameter, \( a > 1 \). If \( 1 < z < 2 \) the diffusion generated by the map is normal, whereas for \( z > 2 \) the diffusion is anomalous. In this anomalous case, the behavior of the system is excellently described by CTRW, as first shown by Geisel and Thomae (1984), see also the discussion by Zumofen and Klafter (1993). The behavior of such maps shows aging effects typical for CTRW models, which fact was first discussed by Barkai (2003).
11.3 CTRW and fractional Fokker-Planck equations.

The description of transport processes within a framework of deterministic Fokker-Planck equations has considerable analytical advantages compared to stochastic approaches. Is it possible to formulate a Fokker-Planck-like approach to processes more complex than normal, Fickian diffusion? The answer to this question is positive, however the corresponding Fokker-Planck equations are somewhat unusual, since they often involve the derivatives of non-integer order with respect to their temporal or spatial variable. Such equations where first postulated on the basis of purely phenomenological considerations (Balakrishnan, 1985, Schneider und Wyss 1987, 1989); their close relation with CTRW schemes was understood much later, see Metzler and Klafter (2000), Sokolov, Klafter and Blumen (2002). The phenomenological introduction of such equation is based on the following consideration. A usual Fick’s diffusion equation is a partial differential equation of a parabolic type, i.e. has a first-order time derivative on its left-hand side and the second-order derivative in coordinate (or a Laplacian, in a multidimensional case) on its right-hand side. It’s Green’s function solution scales as a function of time: The form of the equation does not change when simultaneously changing the time-scale
by a factor of $\lambda$ and the length-scale by a factor of $\lambda^2$. Therefore, such an equation possesses a scaling solution, $P(x, t) = f(t)P(x/\sqrt{t})$, where $f(t)$ is simply a time-dependent normalization factor of the probability density. The Green’s function of the equation is exactly such a solution: $P(x, t) = G(x, t; 0, 0) = (4\pi Dt)^{-1/2} \exp \left[ -\frac{1}{4D} (x/\sqrt{t})^2 \right]$. From the scaling form of the solution it follows that the characteristic length of the problem scales as a square root of the time, and a characteristic length squared (e.g. the mean squared displacement) grows as the first power of time. Reverting this consideration one can say that the fact that the mean squared displacement scales linearly in time would propose to look for the governing equation being first-order in time and second-order in spatial coordinate, i.e. for a parabolic one. The process, in which the mean squared displacement grows as $t^\alpha$ with $0 < \alpha < 1$ could probably be described by an equation being still of second-order in spatial coordinate but of a fractional $\alpha$-th order in time. Before we discuss the meaning of such equations, we have to be sure that such an operator as a fractional $\alpha$-th derivative can be mathematically reasonably defined and possesses a correct physical interpretation, see Miller and Ross (1993), Oldham and Spanier (1974).
The definition of a fractional derivative is a generalization of a definition of "normal" derivative. As already stated, there are several ways of such generalization. We start here from a definition of a Riemann-Liouville derivative (1832) which starts from the generalization of the repeated integration formula:

\[
\frac{d^{-n}}{dx^{-n}} f(x) = \int_a^x \int_a^{y_1} \cdots \int_a^{y_{n-1}} f(y_n) dy_n \cdots dy_1 = \frac{1}{(n-a)!} \int_a^x (x-y)^{n-1} f(y) dy \quad (11.82)
\]

This allows to define a fractional integral:

\[
(I_{a+}^\alpha f)(x) = \frac{1}{\Gamma(\alpha)} \int_a^x (x-y)^{\alpha-1} f(y) dy \quad (x > a)
\]  

(11.83)

with \(0 < \alpha < 1\), which restriction guarantees the convergence of the integral for nonsingular integrable functions \(f(y)\). The \(\alpha\)-th fractional derivative is then defined through

\[
aD^\alpha_x = \frac{d}{dx} I_{a+}^{1-\alpha} = \frac{d}{dx} \frac{1}{\Gamma(\alpha)} \int_a^x (x-y)^{\alpha-1} f(y) dy.
\]  

(11.84)

The higher derivatives are defined by repeating additional differentiation. We note that the Riemann-Liouville integrals or derivatives behave under Laplace transform behave in the same way as the whole-number repeated integrals or derivatives. For the
integrals we have

\[ \mathcal{L} \{ I_{0+}^{\alpha} f(t) \} = u^{-\alpha} f(t). \]  

(11.85)

For the fractional derivatives we have correspondingly

\[ \mathcal{L} \{ 0D_{t}^{\alpha} f(t) \} = u^{\alpha} f(t) - \sum_{j=0}^{n} u^{j} c_{j} \]  

(11.86)

where \( n = [\alpha] \) and \( c_{j} \) are the ”quasi-initial values”, \( c_{j} = \lim_{t \to 0} 0D_{t}^{\alpha-1-j} f(t) \).

Note also that the Riemann-Liouville definition leads to a trivial generalization of the standard rule for the differentiation of a power: \( \frac{d^{n}}{dx^{n}} x^{m} = \frac{m!}{(m-n)!} x^{m-n} \), so that \( 0D_{x}^{\alpha} x^{\beta} = \frac{\Gamma(\beta+1)}{\Gamma(\beta-\alpha+1)} x^{\beta-\alpha} \).

Interchanging integration and differentiation in Eq.(11.84) introduces a slightly different operator, called a Caputo derivative, (Caputo, 1969). The Riemann-Liouville and Caputo definitions are the most important ones for the description of subdiffusive CTRW behavior.

Several other definitions are common, for example the Weyl definition (1917) starting from

\[ (I_{+}^{\alpha} f)(x) = \frac{1}{\Gamma(\alpha)} \int_{-\infty}^{x} (x-y)^{\alpha-1} f(y) dy \]  

\[ -\infty D_{x}^{\alpha} = \frac{d}{dx} I_{+}^{1-\alpha} \]  

(11.87)

so that \( -\infty D_{x}^{\alpha} = \frac{d}{dx} I_{+}^{1-\alpha} \) and the Riesz definition
(1949) leading to a symmetric form:
\[
(I^\alpha f)(x) = \frac{1}{2 \cos \frac{\alpha \pi}{2}} (I^\alpha_+ + I^\alpha_-) ; \quad D^\alpha = \frac{d}{dx} I^{1-\alpha}.
\]
These ones are often used in fractional equations describing superdiffusion. The Weyl operator preserves the usual rule for the differentiating of the exponential \(-\infty D^\alpha_x e^x = e^x\). The Weyl and Riesz operators are those which reproduce the properties of usual integrals or derivatives under Fourier-transform:
\[
\mathcal{F} \{-\infty D^\alpha_t f(t)\} = (i\omega)^\alpha f(\omega) \quad (11.89)
\]
for a Weyl operator and
\[
\mathcal{F} \{-\infty D^\alpha_t f(t)\} = -\omega^\alpha f(\omega) \quad (11.90)
\]
for a Riesz one. This one is a very special form generalizing the behavior of the second derivative, and is exactly the one appearing on its place in fractional equations for superdiffusion.

Let us now turn to the fractional generalization of the diffusion or of the Fokker-Planck equation of the form
\[
\frac{\partial}{\partial t} P(x, t) = \partial D^{1-\alpha}_t \left[ \nabla (-\mu^* f P + K^* \nabla P) \right],
\]
with the additional Rieman-Liouville fractional derivative operator acting on the ”normal” right-hand side
of a Fokker-Planck equation, see Metzler and Klafter 2000, Sokolov, Klafter and Blumen, 2002. Here \( \mu^* \) denotes the (generalized) mobility and \( K^* \) denotes the (generalized) diffusion coefficient; the change of notation for the diffusion coefficient from \( D \) to \( K \) is necessary in order not to mix it up with the differential operator. Eq.(11.91) represents a by far the most widely used form of the fractional Fokker-Planck equation. We note that the equation discussed belongs therefore to the class of non-Markovian Fokker-Planck equations, and the additional fractional derivative plays the role of the memory kernel. The corresponding non-Markovian Fokker-Planck equations are often considered as a dangerous theoretical instrument, since they in general do not guarantee for the possibility of the solutions which therefore cannot be interpreted as probability density. However, as we proceed to show, the solution of the fractional Fokker-Planck equation, Eq.(11.91) is probability density, and moreover they correspond to the continuous limit of a CTRW scheme with power-law waiting-time distribution.

Let us first assume the external force to be constant and the initial condition to be \( \delta \)-functional. Applying the Laplace-transform in temporal variable to the
both parts of the equation Eq.(11.91) we get:

\[ u \hat{P}(k, u) - P(k, 0) = u^{1-\alpha} \left[ -ik\mu f \hat{P}(k, u) - Kk^2 \nabla \hat{P}(k, u) \right] \]

(11.92)

with \( P(k, 0) = 1 \). The solution of Eq.(11.92) then reads:

\[ \hat{P}(k, u) = \frac{1}{u^{1-\alpha}(ik\mu f + Kk^2) + u}, \]  

(11.93)

exactly the form which immediately follows from the CTRW model, see Eq.(11.63).

Fractional Fokker-Planck equations are however a more versatile tool, giving solutions in many cases when the Fourier transform in spatial coordinate would not simplify the situation due to spatial inhomogeneity.

To see this let us consider a general non-Markovian Fokker-Planck equation with memory operator on the right-hand side:

\[ \frac{\partial}{\partial t} P(x, t) = M [ \nabla (-\mu f P + K*\nabla P) ], \]  

(11.94)

where \( \hat{M} \) is an operator of the convolution type acting on the right-hand side of the equation; it is either:

\[ M f(t) = \int_{t_0}^{t} g(t - t') f(t') dt' \]  

(11.95)
or

\[ M f(t) = \frac{d}{dt} \int_{t_0}^{t} g(t - t') f(t') dt'. \quad (11.96) \]

The corresponding integral is assumed to tend to zero for \( t \to t_0 \), i.e. the kernel of the transformation may possess only a weak singularity like one of the fractional integral with \( 0 < p < 1 \), so that under the Laplace-transform the action of the operator \( \hat{M} \) on the function \( f \) can be described by a mononomial \( \hat{LM}f(t) = \hat{M}(u)\hat{f}(u) \) with \( \hat{L} \) denoting the operator of the Laplace transform, i.e. does not introduce additional initial conditions. Note that a fractional derivative is just an operator of the type needed. Let us show now that the formal solution of the non-Markovian Fokker-Planck equation Eq.(11.94) has a following form:

\[ P(x, t) = \int_{0}^{\infty} F(x, \tau) T(\tau, t) d\tau, \quad (11.97) \]

where \( F(x, \tau) \) is a solution of a Markovian Fokker-Planck equation with the same Fokker-Planck operator,

\[ \frac{\partial}{\partial t} F = \nabla (-\mu^* f F + K^* \nabla F), \quad (11.98) \]

and for the same initial and boundary conditions, and the function \( T(\tau, t) \) is connected with the memory kernel \( \hat{M} \) by the following relation: The Laplace-
transform of $T$ in its second variable $t$, $\tilde{T}(\tau, u) = \int_0^\infty T(\tau, t)e^{-ut}dt$ reads:

$$\hat{T}(\tau, u) = \frac{1}{M(u)} \exp \left[ -\tau \frac{u}{M(u)} \right], \quad (11.99)$$

see Barkai, 2001, Sokolov 2001, 2003. To show this let us consider the Laplace-transform of $P(x, t)$ given by Eq.(11.97) with respect to its temporal variable:

$$\hat{P}(x, u) = \int_0^\infty dt e^{-ut} \int_0^\infty d\tau F(x, \tau)T(\tau, t) =$$

$$= \int_0^\infty d\tau F(x, \tau)\hat{T}(\tau, u) =$$

$$= \int_0^\infty d\tau F(x, \tau)\frac{1}{M(u)} \exp \left[ -\tau \frac{u}{M(u)} \right] =$$

$$= \frac{1}{M(u)} \hat{F} \left( x, \frac{u}{M(u)} \right), \quad (11.100)$$

where $\hat{F}(x, u)$ is a Laplace-transform of $F(x, \tau)$ in its second (temporal) variable $\tau$. Let us now note that the Laplace-transform of the non-Markovian FPE, Eq.(11.94) reads:

$$u\hat{P}(x, u) - P(x, 0) = M(u)L\hat{P}(x, u), \quad (11.101)$$

where $L$ denotes the Fokker-Planck operator acting on the probability density $P$ and where $P(x, 0)$ is the initial condition. Inserting the form, Eq.(11.100),
Random Walk Approaches

into Eq. (11.101) one gets:

\[ \frac{u}{K(u)} \hat{F} \left( x, \frac{u}{K(u)} \right) - P(x, 0) = L \hat{F} \left( x, \frac{u}{K(u)} \right). \]  

(11.102)

Introducing a new variable \( s = u/M(u) \) we rewrite Eq. (11.102) in a form

\[ s \hat{F} (x, s) - P(x, 0) = L \hat{F} (x, s), \]  

(11.103)

in which one readily recognizes the Laplace-transform of an ordinary, Markovian FPE, Eq. (11.98), with the same initial condition \( P(x, 0) \). This completes our proof. Thus, the solution of a non-Markovian Fokker-Planck equation of the type of Eq. (11.94) in the Laplace domain is connected with the solution of the regular Fokker-Planck equation through

\[ \hat{P}(x, u) = \frac{1}{M(u)} \hat{F} \left( x, \frac{u}{M(u)} \right). \]  

(11.104)

In time domain the solution of Eqs. (11.91) and (11.98) are connected via Eq. (11.97) where \( T(\tau, t) \) is given by Eq. (11.99). Now, if the function \( T \) can be interpreted as the probability density of the number of steps \( \tau \) of the random walk (in continuous limit) as a function of the "physical" time \( t \), Eq. (11.97) describes exactly the continuous-time version of the Eq. (11.32), i.e describes CTRW. For the memory kernel corresponding
to the fractional derivative of the order between zero and one, i.e. for Eq.(11.91), the Laplace-transform of the memory kernel is $M(u) = u^{1-\alpha}$, so that

$$\hat{T}(\tau, u) = \frac{1}{\hat{M}(u)} \exp \left[ -\tau \frac{u}{\hat{M}(u)} \right] = u^{\alpha-1} \exp(-\tau u^{-\alpha}),$$

(11.105)

Barkai, 2001, Sokolov, 2001. This function is a probability density, which can be expressed through the one-sided Lévy probability density,

$$T(\tau, t) = \frac{t}{(\alpha \tau^{1+1/\alpha})} L\left( \frac{t}{\tau^{1/\alpha}}, \alpha, -\alpha \right)$$

(11.106)

(where the standard notation of Feller (1991) is used). This special case corresponds to the limiting distribution of $\chi_n(t)$ for both $n$ and $t$ large, where a continuous variable $\tau$ is introduced instead of a discrete $n$. This special case was mentioned in Metzler and Klafter 2000 and is discussed in detail in a work of Barkai, 2001. We also note here that the procedure showing the connection between the continuous limit of CTRW schemes with power-law waiting-time distributions and fractional Fokker-Planck equation is not the only way to obtain them from the stochastic random walk schemes. Another approach based on the generalization of Kramers-Moyal expansion is discussed by Barkai, Metzler and Klafter, 2000.
Random Walk Approaches

Fig. 11.4 The time evolution of the probability density in a fractional Ornstein-Uhlenbeck process. The initial condition corresponds to $P(x; t) = \delta(x)$. The parameters are $K = \mu = 1$ and $\alpha = 1/2$. For comparison, the results for the simple diffusion are shown as a dashed line.

The physical picture described by the equation closely corresponds to random traps model: The external force biases the direction of jumps but does not influence the waiting-time distribution. This force now can be inhomogeneous in space, moreover, complex boundary condition problems can be discussed.

As an example we show in Fig. 11.4 the time-development of the corresponding probability density of the particle’s position for a $\delta$-functional initial condition in a fractional generalization of the Ornstein-Uhlenbeck process, described by Eq. (11.91) with $f(x) = -\kappa x$. Note the persisting cusp at the initial position of particles. This cusp is a consequence of the long-time memory typical for CTRW with power-law waiting time distributions.

Although the integral transformation, Eq. (11.97), essentially solves the equation, the expression is not always the best starting point for the further theoretical analysis. Thus, the eigenfunction decomposi-
tion, as used in our second discussion of the Ornstein-Uhlenbeck process may be a better approach. From the form of fractional Fokker-Planck equation it follows that its spatial eigenfunctions are the same as for a normal, Markovian one, so that only the temporal parts differ. The temporal functions are now governed by ordinary fractional differential equations of the type
\[
\frac{d\Phi_n(t)}{dt} = -\lambda_n D_t^{1-\alpha} \Phi_n(t); \tag{11.107}
\]
\(\lambda_n\) are the eigenvalues of the corresponding Fokker-Planck operator, see §8.2.1. The solution of an ordinary fractional differential equation
\[
\frac{d\Phi(t)}{dt} = -\tau^{-\alpha} D_x^{1-\alpha} \Phi(t) \tag{11.108}
\]
is given by a known special function, a Mittag-Leffler function \(E_\alpha (- (t/\tau)^\alpha)\) which is defined through the inverse Laplace transform
\[
E_\alpha (- (t/\tau)^\alpha) = L^{-1} \left\{ \frac{1}{u + \tau^{-\alpha} u^{1-\alpha}} \right\}. \tag{11.109}
\]
Its asymptotic behavior is a stretched exponential \(E_\alpha (- (t/\tau)^\alpha) \approx \exp \left[ - (t/\tau)^\alpha / \Gamma(1 + \alpha) \right]\) for small \(t\) and a power-law \(E_\alpha (- (t/\tau)^\alpha) \approx - (t/\tau)^\alpha / \Gamma(1 - \alpha)\) for large \(t\). The Mittag-Leffler function is a natural generalization of an exponential function, which cor-
responds to $E_1(-t/\tau)$. Note that the solutions $\Phi(t)$, except one for $\alpha = 1$, being an exponential, show at long times slow, power-law decay. The Mittag-Leffler functions are ubiquitous in the relaxation patterns governed by subdiffusion. The behavior of the Mittag-Leffler function $E_{1/2}(- (t/\tau)^{1/2})$ is shown in Fig.11.5.

11.4 Superdiffusion: Lévy flights and Lévy walks.

In what follows we shortly discuss what happens if the third Einstein’s postulate of the ”normal” diffusion is abandoned, namely the one of finite mean free path (i.e. of the finite mean square displacement per step). Here several different models can be discussed.

The simplest one is the uncorrelated simple or continuous-
time random walk with the step lengths distributed according, say, to a power-law, \( p(x) \approx x^{-1-\alpha} \) with \( 0 < \alpha < 2 \). According to the generalized central limit theorem due to P. Lévy, after many steps the distribution of the particle’s coordinate converges to one characterized by a probability density corresponding to one of the so-called infinitely divisible stable laws. Apart from trivial translation, these laws are characterized by a family of the probability densities, whose characteristic functions all have very simple form:

\[
f(k) = \exp \left( -A |k|^\alpha e^{i\pi \gamma /2} \right)
\]

(for \( k > 0 \)), Feller (1991). Since the Fourier-transform of this function represents a probability density, which is a real function, the behavior for negative \( k \) is given by \( f(-k) = f^*(k) \). The parameter \( \gamma \) describes the asymmetry of the distribution; the distributions with \( \gamma = 0 \) are symmetric. The values of \( \gamma \) change between \(-\alpha\) and \( \alpha \) for \( 0 < \alpha \leq 1 \) and between \(-2+\alpha\) and \( 2-\alpha \) for \( 1 < \alpha \leq 2 \). The distributions with \( \gamma \) at either boundaries of the corresponding intervals are called extreme laws. For \( 0 < \alpha \leq 1 \) the corresponding densities vanish identically for all negative (positive) values of \( x \). The Gaussian distribution (the one with \( \alpha = 2 \)) is always symmetric. The parame-
ter $A$ is connected with the width of the distribution, which is proportional to $A^{1/\alpha}$. This can be immediately seen from the overall scaling behavior or from the dimensional arguments. Since all Lévy distributions except for a Gaussian have power-law tails decaying as $x^{-1-\alpha}$, they all have infinite variance, so that the width must be understood either as their interquartile distance or as some fractional moment, $W_q = \langle |x|^q \rangle^{1/q}$ with $q < \alpha$. A simple scaling argument shows, that the parameter $A$ is proportional to the number of steps of the Lévy flight $n$. Indeed, let us compare a flight of $n$ steps with the one of $2n$ steps. The probability density of positions after $2n$ steps is a convolution of the corresponding identical probability densities after $n$ steps, i.e. its characteristic function is a square of the corresponding function for $n$ steps. This, it is given by a function Eq.(11.110) with twice the corresponding coefficient $A$. In general, the function after $\lambda n$ steps is given by the characteristic function

$$f(k) = \exp \left( -\lambda An |k|^\alpha e^{i\pi\gamma/2} \right), \quad (11.111)$$

i.e. $A \propto n$. The width of the corresponding distribution thus grows as $W \propto n^{1/\alpha}$, i.e. superdiffusively.

Note that the Lévy flight is a Markovian jump process. When passing to the continuous time variable,
the corresponding Chapman-Kolmogorov equation of the process can be put down in a form of a fractional Fokker-Planck (diffusion) equation. For symmetric Lévy distribution the form of this equation is extremely simple,

\[
\frac{\partial p(x, t)}{\partial t} = K_\alpha \frac{\partial^\alpha}{\partial |x|^\alpha} p(x, t),
\]

where the corresponding fractional differential operator has to be considered as a symmetrized Riesz-Weyl derivative, and \( K_\alpha \) is the fractional diffusion coefficient having the dimension \([L^\alpha/T]\), \(0 < \alpha < 2\). Noting that under the Fourier-transform this operator corresponds to multiplication by \(-|k|^\alpha\), we see that Eq.(11.112) corresponds to

\[
\frac{\partial f(k, t)}{\partial t} = -K_\alpha |k|^\alpha f(k, t)
\]

so that the Green’s function solution of Eq.(11.112) corresponding to the initial condition \(f(k, t) = 1\), reads

\[
f(k, t) = \exp \left(-K_\alpha |k|^\alpha t\right),
\]

i.e. is a characteristic function of a symmetric Lévy distribution of type Eq.(11.110) with \(\gamma = 0\).

The genuine Lévy flight model might seem unphysical since it allows for indefinitely large jumps, i.e. the
Random Walk Approaches

model does not possess a limiting velocity. However, as long as \( x \) is not a Euclidean coordinate, this is not a real problem. As an example let us consider the following system. Imagine a (quasi)particle (say an exciton) jumping between the monomers of a long polymer chain. The monomers of the chain are numbered consecutively starting from the chain’s beginning, the number \( n \) of the monomer is considered as a coordinate in the one-dimensional chemical space. The jumps of the particle might take place along the chain or between the monomers which are far away in the chemical sequence of the chain, but are by chance close to each other in the Euclidean space under a chain’s particular conformation (Sokolov, 1996). If the conformational changes in a chain are fast enough compared with the typical time between the particle’s jumps, the corresponding process in the chemical space is the genuine Lévy flight. The behavior of such a process in the force-free case is governed by Eq.(11.112). Incorporation of the external forces into a problem was considered by Brockmann and Sokolov, 2002. the corresponding equations was used by Brockmann and Geisel, 2003 for the description of flights in different potential fields. We also note that the theory of the equations like Eq.(11.112) is not fully developed. Thus it is not jet clear how the
boundary condition problems for them have to be uniquely formulated (Chechkin et al., 2003).

Another important model is a Lévy walk, introduced by Shlesinger, West and Klafter (1987). A simplest realization of the Lévy walk is a process in which the particle moves with a constant velocity \( \vec{v} \) during a period of time \( t_i \). After time \( t_i \) the direction of the velocity is chosen anew (a Drude-like model). The duration periods \( t_i \) in given by the waiting-time probability density \( \psi(t) \). If \( \psi(t) \approx t_0^{-1-\alpha} (\tau_0 \text{ is the characteristic time of a step}) \) and the second moment of the waiting-time \( t \) is absent \( (\alpha < 2) \) the mean free path diverges, so that departure from the simple diffusion can be anticipated. The initial model was formulated as a toy model of diffusion in turbulent flows; however in this case the approach seems to be oversimplified. The behavior closely described by this model arises in several physical situations. One of the experimental realizations (a particles’ transport in a flow between two rotating cylinders) and some simulation results can be found on the webpage http://chaos.ph.utexas.edu/research.html. Another realization corresponds to a Hamiltonian system in which a particle moves in a two-dimensional egg-crate potential

\[
V(x, y) = B(\cos x + \cos y) + C \cos x \cos y, \quad (11.115)
\]
at energies above the one at which infinite motion gets possible, Klafter and Zumofen (1993). The difference between the Lévy walk model and the random walk models considered so far is that in the present case the temporal and spatial aspects are coupled: a single motion event is described by a probability density $\psi(r, t)$ to make a step of length $r$ and of duration $t$. In our simple one dimensional case where between the scattering events the particle moves with the constant velocity either to the left or to the right we have, for example $\psi(r, t) = \frac{1}{2} \psi(t) [\delta(r - vt) + \delta(r - vt)]$.

Let $\eta(r, t)$ be the probability density of just arriving at $r$ in time $t$, i.e. the probability density of the particle’s position just after completing the step. This probability density fulfills the following recursion equation

$$
\eta(r, t) = \int dr' \int_0^t d\tau \eta(r', \tau) \psi(r-r', t-\tau) + \delta(t)\delta_{r,0},
$$

(11.116)

where the last term introduces the initial condition. Here we use the fact that our process is semi-Markovian: the probability density of the random walker’s position after completing the next step depends only on its position at the beginning of the step. In the Fourier-Laplace representation $\psi(r, t) \rightarrow \psi(k, u)$, we
have:

\[ \eta(k, u) = \eta(k, u)\psi(k, u) + 1 \]  \hspace{1cm} (11.117)

i.e.

\[ \eta(k, u) = \frac{1}{1 - \psi(k, u)} \left( = \psi^0 + \psi^1 + ... + \psi^n + ... \right). \]  \hspace{1cm} (11.118)

We have also to include the possibility that a walker didn’t complete a full step up to time \( t \). Let us consider the position of a random walker which completed \( n \) steps up to time \( t - \tau \) and is moving freely with a constant velocity during the rest time \( \tau \). The probability density of positions at time \( t \) is given by

\[ P(r, t) = \int dr' \int_0^t d\tau \eta(r - r', t - \tau)\Psi(r', \tau) \]  \hspace{1cm} (11.119)

where \( \Psi(r', \tau) \) the probability to move exactly at the distance \( r' \) at time \( \tau \). For a Lévy walk it reads

\[ \Psi(r, t) = \frac{1}{2} \delta (|r| - vt) \int_t^\infty \psi(t')dt' \]  \hspace{1cm} (11.120)

since it corresponds to the motion with a constant velocity under the condition that no scattering events took place before time \( t \). The Fourier-Laplace-transform of \( P(r, t) \) is thus

\[ P(k, u) = \frac{\Psi(k, u)}{1 - \psi(k, u)}. \]  \hspace{1cm} (11.121)
Random Walk Approaches

From here on we take for simplicity $v = 1$. The back transforms are made with use of Tauberian theorems.

Let us first concentrate of the behavior of the second moment of the displacement. The calculations show that the behavior depends on the range of the parameter $\alpha$ of the distribution of the times of free motion and are summarized as follows

- for $\alpha < 1$ one has $\langle R^2(t) \rangle \propto t^2$ (a ballistic regime)
- for $1 < \alpha < 2$ $\langle R^2(t) \rangle \propto t^{3-\alpha}$ (a subballistic superdiffusion)
- for $\alpha > 2$ $\langle R^2(t) \rangle \propto t^1$ (a normal diffusion).

The asymptotic form of a Lévy-walk-propagator ($v = 1$) for $\alpha > 1$ is

$$P(r, t) \simeq \begin{cases} 
  t^{-\beta} \exp \left[ -c \left( \frac{r}{t^{\beta}} \right)^2 \right] & \text{for } |r| < t^\beta \\
  t/|r|^{1+\alpha} & \text{for } t^\beta < |r| < t \\
  t^{1-\alpha} \delta(|r| - t) & \text{a } \delta\text{-function at } |r| = t \\
  0 & \text{for } |r| > t
\end{cases}$$

with $\beta = 1/\alpha$ for $1 < \alpha < 2$ and $\beta = 1/2$ for $\alpha > 2$ (in this case the middle part is a normal Gaussian; it (very) slowly overweighs a still heavy tail). Here the characteristic time $\tau_0$ is taken as a unit time and $v\tau_0$ as a unit length. One can thus distinguish four characteristic domains in such a distribution:
Superdiffusion: Lévy flights and Lévy walks.

(1) a Gaussian middle part due to multiple scattering
(2) a power-law (Lévy) tail
(3) δ-''horns'' due to particles which never got scattered
(4) cutoff due to the finite velocity

Note that the overall distribution does not scale as a whole.

For $0 < \alpha < 1$ only one exemplary analytical form (namely the arcsine-law for $\alpha = 1/2$) is known, which is exactly

$$P(x, t) = p(x, t) = \frac{1}{\pi \sqrt{(vt + x)(vt - x)}}. \quad (11.123)$$

Numerical simulations show that all distributions look more or less the same (with flat middle part and singularities at $\pm vt$). The corresponding distributions scale as a whole, see Zumofen and Klafter (1993).

Lévy walks can also be described within the framework of fractional kinetic equations. The corresponding equation was derived by Sokolov and Metzler (2003), see also discussion in Uchaikin (2003), Becker-Kern, Meerschaert and Scheffler (2004). The equation (reducing to a telegrapher’s equation for the case of normal diffusion) does not have a form of a Fokker-Planck equation. Other physical situations lead to many other different problems, being combinations or variants of ones considered here. The classifica-
tion of all of them might be a topic of a separate review so that we refrain from giving full details in our introductory discussion.
Chapter 12

Active Brownian Motion

12.1 Self-propelling of Brownian particles

When the British botanist Robert Brown discovered in 1827 the erratic motion of small particles immersed in a liquid, he considered them first as living entities. He addressed even a letter to Charles Darwin, asking him about his opinion concerning these creatures. A legend is saying that Darwin, wise by long experience, answered in a rather indefinite way. Indeed, only after the turn of the century, Einstein, Smoluchowski, Langevin and others have shown that the behaviour of Brownian particles are due to physical effects only. As we have demonstrated in the previous chapters, the behavior of usual Brownian particles is completely due to the (passive) stochastic collisions, the particles suffer from the surrounding medium. There is no active transfer of energy to the particles. The energetic equilibrium between particles and surrounding medium is expressed by the fluctuation-
dissipation theorems.

In this Chapter, we want to generalize the idea of Brownian particles including an energy input from the surrounding. This way we will be able to derive a simplified model of active biological motion. Therefore, we introduce active Brownian particles which are Brownian particles with the ability to take up energy from the environment. Simple models of active Brownian particles were studied already in Chapter 5 of this book and in many earlier works (Schienbein and Gruler, 1993; Steuernagel et al., 1994; Klimontovich, 1995; Derenyi and Viscek, 1995; Bier and Astumian, 1996; Mikhailov & Calenbuhr, 2002; Schweitzer, 2003). Here we will study in a more systematic way models of many Brownian particles with negative friction and will investigate in more details the depot model for particles which are able to store the inflow of energy in an internal depot and to convert internal energy to perform different activities (Schweitzer, Ebeling & Tilch, 1998; Ebeling, Schweitzer & Tilch, 1999). Other previous versions of active Brownian particle models (Schimansky-Geier et al., 1995, 1997; Schweitzer et al., 1997; Schweitzer, 2003) consider more specific activities, such as environmental changes and signal–response behavior. In these models, the active Brownian particles (or active walkers, within
Self-propelling of Brownian particles

A discrete approximation) are able to generate a self-consistent field, which in turn influences their further movement and physical or chemical behavior. This non-linear feedback between the particles and the field generated by themselves results in an interactive structure formation process on the macroscopic level. Hence, these models have been used to simulate a broad variety of pattern formations in complex systems, ranging from physical to biological and social systems (Schweitzer and Schimansky-Geier, 1994; Schimansky-Geier et al., 1995, 1997; Schweitzer et al., 1997; Helbing, 1997, 2001, Mikhailov & Cahlenbuhr, 2002; Schweitzer, 2003).

The plan of the Chapter is in brief as follows: At first we will develop several models of systems of active Brownian particles in 2d-systems including energy input and noise. The energy input is modeled (i) by Rayleigh-Helmholtz-type velocity-dependent friction, (ii) by models of self-propelling based on internal energy depots, (iii) by more general partially negative space-dependent friction laws. The Rayleigh-Helmholtz was originally developed to model the complex energy input in musical instruments. In the framework of depot models, the Brow-
nian particles have explicitly the ability to take up energy from the environment, to store it in an internal depot and to convert internal energy into kinetic energy. Considering also internal dissipation, we consider this as a simplified model of active biological motion. For the take-up of energy several examples we will discuss here only a spatially homogeneous supply of energy. The case of supply of energy at spatially localized sources (food centers) generates a more complicated dynamics (Ebeling et al., 1999).

The motion of the particles is described here by a Langevin equation which includes an acceleration term resulting from the pumping. The corresponding Fokker-Planck equations are derived. Simulations of the Brownian particles are compared with analytical solutions of the Fokker-Planck equation. The velocity distributions show a crater-like shape which strongly deviate from Maxwell distributions. In the presence of external parabolic forces, the system develops a limit cycle in the 4d phase space, the corresponding distribution has the form of a hoop or a tire in the 4d-space.

Summarizing, our basic assumption is to add to the dynamics of simple physical Brownian particles the new mechanism of pumping with free energy, which may be realized in several steps as by energy
take-up, storage and conversion of energy, and energy consuming motion. This way, the particles become more complex, which result in new dynamical features that may resemble active biological motion. Hence, the basic idea can be formulated as follows: how much of physics is needed to achieve a degree of complexity which gives us the impression of motion phenomena found in biological systems? However, we will study here only the physical aspects of the problem. In particular we are interested in the question how known types of Hamiltonian motion or Brownian motion could be extended by mechanisms of energy take-up, storage and conversion. These new elements should contribute to the development of a microscopic theory of active biological motion. In the present model we restrict ourselves to take into account specific aspects of energy balances that are related to the mechanisms of energy pumping and energy dissipation.

We will show, that in comparison with simple Brownian particles, the active particles become much more complex, which result in new dynamical features as e.g.:

(i) New diffusive properties with large mean square displacement,
(ii) Unusual velocity distributions with craterlike shape,
(iii) Formation of limit cycles corresponding to the motion on circles in space. Some of these features may resemble active biological motion. Hence, the basic idea can be formulated as follows: how much of physics is needed to achieve a degree of complexity which gives us the impression of motion phenomena found in biological systems?

In order to avoid misunderstandings we underline again, that we do not intend here to model any particular biological or social object but instead to analyze particular physical nonequilibrium systems which show new types of dynamics which might be interest for a later more concrete approach.

12.2 Equations of motions and depot models

The motion of Brownian particles with general velocity- and space-dependent friction in a space-dependent potential $U(r)$ can be described by the Langevin equation:

$$\frac{dr}{dt} = v; \quad m\frac{dv}{dt} = F - \nabla U(r) + \mathcal{F}(t) \quad (12.1)$$

Here $F$ is a dissipative force which is in the simplest case given by a friction law

$$F = -m\gamma(r, v)v \quad (12.2)$$
where $\gamma(\mathbf{r}, \mathbf{v})$ is the friction function of the particle with mass $m$ at position $\mathbf{r}$, moving with velocity $\mathbf{v}$. The friction $\gamma(\mathbf{r}, \mathbf{v})$ may depend on space and time. $\mathcal{F}(t)$ is a stochastic force with strength $S$ and a $\delta$-correlated time dependence

$$\langle \mathcal{F}(t) \rangle = 0; \quad \langle \mathcal{F}(t) \mathcal{F}(t') \rangle = 2S \delta(t - t') \quad (12.3)$$

The noise strength $S$ for the momentum is connected with the previously used noise strength for the velocities $D_v$ by the simple relation $S = m^2 D_v$. In the case of thermal equilibrium systems, with $\gamma(\mathbf{r}, \mathbf{v}) = \gamma_0 = \text{const.}$, we may assume that the loss of energy resulting from friction, and the gain of energy resulting from the stochastic force, are compensated in the average. In this case the fluctuation-dissipation theorem (Einstein relation) is saying:

$$S = D_v m^2 = m k_B T \gamma_0 \quad (12.4)$$

$T$ is the temperature and $k_B$ is the Boltzmann constant, and $D_v$ is a scaled expression for the strength of the stochastic force in the velocity space. In the following we will choose units in which $m \equiv 1$ what leads to $S = D_v$. We are interested mainly in statistical descriptions, i.e. in the probability $P(\mathbf{r}, \mathbf{v}, t)$ to find the particle at location $\mathbf{r}$ with velocity $\mathbf{v}$ at time $t$. As shown earlier the distribution function, $P(\mathbf{r}, \mathbf{v}, t)$, which corresponds to the Langevin
Active Brownian Motion

equation (12.1), can be described by a Fokker-Planck equation of the form:

\[
\frac{\partial P(r, v, t)}{\partial t} + v \frac{\partial P(r, v, t)}{\partial r} + \nabla U(r) \frac{\partial P(r, v, t)}{\partial v}
\]

(12.5)

\[
= \frac{\partial}{\partial v} \left[ \gamma(r, v) v P(r, v, t) + D_v \frac{\partial P(r, v, t)}{\partial v} \right]
\]

(12.6)

As discussed already previously (see Chapter 5, section 5.1), in the special case \(\gamma(r, v) = \gamma_0\) the stationary solution of eqn. (12.6), \(P_0(r, v)\), is known to be the Boltzmann distribution:

\[
P_0(r, v) = N \exp \left\{ -\frac{1}{k_B T} \left[ \frac{m}{2} v^2 + U(r) \right] \right\}
\]

(12.7)

The major question discussed throughout this Chapter is, how this known picture changes if we add a new activity to the model by considering that Brownian particles can be also pumped with energy from the environment. While for usual Brownian motion the dissipation of energy caused by friction is compensated by the stochastic force, we now discuss the case of an additional influx of energy, which may be used to accelerate the particle’s motion. In our model, this will be considered by a more complex friction function which now can be a space- and/or velocity-dependent function, \(\gamma(r, v)\). To gain more insight,
in the following section we restrict the discussion to cases where the friction depends either on $\mathbf{v}$ or in $\mathbf{r}$.

Let us consider now several models of the self-propelling mechanism, in part repeating and generalizing the results from Chapter 5. First we consider velocity-dependent friction as a mechanism accelerating the Brownian motion. Velocity-dependent friction plays an important role e.g. in certain models of the theory of sound developed by Rayleigh and Helmholtz. In the simplest case we may assume the following friction force of the individual Brownian particle:

$$\gamma(\mathbf{r}, \mathbf{v}) = -\gamma_1 + \gamma_2 \mathbf{v}^2 = \gamma_1 \left( \frac{\mathbf{v}^2}{v_0^2} - 1 \right) = \gamma_2 (\mathbf{v}^2 - v_0^2)$$

(12.8)

This Rayleigh-Helmholtz model is a standard model studied in many papers on Brownian dynamics (Klimontovich, 1995; Erdmann et al., 2000). We note that $v_0^2 = \gamma_1/\gamma_2$ defines a special value of the velocities where the friction is zero. Another standard model for active friction with a zero point $v_0$ was detected empirically in experiments with moving cells and analyzed by Schienbein and Gruler (1973)

$$\gamma(\mathbf{v}) = \gamma_0 \left( 1 - \frac{v_0}{|\mathbf{v}|} \right)$$

(12.9)
Active Brownian Motion

It was shown by the mentioned authors that this model allows to describe the active motion of several cell types as e.g. granulocytes (Schienbein & Gruler, 1993; Erdmann et al., 2000). A disadvantage of this model is the singularity of the friction function at \( v = 0 \). On the other hand we may consider as an advantage that the friction function converges at large \( v \) to the constant of passive friction.

Now we will consider the so-called depot model (see also Chapter 5) for the friction function which is well behaved in the full velocity range. This friction function is based on the idea of an energy depot of the particles (Schweitzer et al., 1998; Ebeling et al., 1999; Schweitzer, 2003). We assume that the Brownian particle itself should be capable of taking up external energy storing some of this additional energy into an internal energy depot, \( e(t) \). This energy depot may be may be altered by three different processes:

1. Take-up of energy from the environment; where \( q(\mathbf{r}) \) is the space-dependent pump rate of energy
2. Internal dissipation, which is assumed to be proportional to the internal energy. Here the rate of energy loss, \( c \), is assumed to be constant.
3. Conversion of internal energy into motion, where \( d(v) \) is the rate of conversion of internal to kinetic degrees of freedom. This means that the
depot energy may be used to accelerate motion on the plane.

This extension of the model is motivated by investigations of active biological motion, which relies on the supply of energy, which is dissipated by metabolic processes, but can be also converted into kinetic energy. The resulting balance equation for the internal energy depot, $e$, of a pumped Brownian particle is then given by:

$$\frac{d}{dt}e(t) = q(r) - ce(t) - d(v) e(t) \quad (12.10)$$

A simple ansatz for $q(r)$ and $d(v)$ reads:

$$q(r) \equiv q_0 \quad d(v) = dv^2 \quad (12.11)$$

where $d > 0$ is the conversion rate of internal into kinetic energy. Under the condition of stationary depots we get

$$e_0 = \frac{q_0}{c + dv^2} \quad (12.12)$$

The energy conversion may result in an additional acceleration of the Brownian particle in the direction of movement. This way we get for the dissipative force including the usual passive friction and the acceleration on the cost of the depot

$$\mathbf{F} = -m\gamma \mathbf{v} + me(t)\mathbf{v} \quad (12.13)$$
Correspondingly we find a Langevin equation, which contains an additional driving force, \(de(t)v\):

\[
m\dot{v} + m\gamma_0 v + \nabla U(r) = mde(t)v + \mathcal{F}(t) \quad (12.14)
\]

Hence, the Langevin eq.\( (12.14) \) is now coupled with the equation for the energy depot, eq.\( (12.10) \). The energy loss of the depot is fully converted into kinetic energy of motion of the Brownian particle. In most cases we will assume in the following that the energy bag is stationary \( \dot{e}(t) = 0 \). This allows the adiabatic elimination of the energy and leads to an effective dissipative force (see Fig. 12.1):

\[
\mathcal{F}(v) = -m \left[ \gamma_0 - \frac{q}{c + d\dot{v}^2} \right] v \quad (12.15)
\]

The corresponding friction function is

\[
\gamma(v) = \gamma_0 - \frac{q}{c + d\dot{v}^2} \quad (12.16)
\]

The behavior of the force and the friction changes qualitatively in dependence on the bifurcation parameter (Erdmann et al., 2000; Erdmann & Ebeling, 2003)

\[
\zeta = \frac{qd}{c\gamma_0} - 1 \quad (12.17)
\]

For positive \( \zeta \) – values we observe that the force disappears for 3 values of the velocity. Let us now consider several special cases in more detail: In the case
that the velocities are rather small we get for the friction law
\[
\gamma(v) = \left( \frac{q_0}{c} - \frac{q_0 d}{c^2} \right) v^2 + \mathcal{O}(v^4) \tag{12.18}
\]
which corresponds with
\[
\begin{align*}
\gamma_1 &= \frac{q_0}{\gamma_0} - \gamma_0; \\
\gamma_2 &= \frac{q_0 d}{c^2}
\end{align*} \tag{12.19}
\]
to the Rayleigh-Helmholtz model discussed above.

Due to the pumping slow particles are accelerated and fast particles are damped. At definite conditions our active friction functions have a zero corresponding to stationary velocities \(v_0\), where the friction function and the friction force disappear. The deterministic trajectory of our system moving on a plane is in both cases attracted by a cylinder in the 4d-space given by
\[
v_1^2 + v_2^2 = v_0^2 \tag{12.20}
\]
where \(v_0\) is the value of the stationary velocity which is for the Rayleigh-model or the depot model respectively
\[
\begin{align*}
v_0^2 &= \frac{\gamma_1}{\gamma_2}; \\
v_0^2 &= \frac{q_0}{\gamma_0} - \frac{c}{d}.
\end{align*} \tag{12.21}
\]
Before we conclude this section let us discuss briefly several other closely related depot models. We may define a second variant of the depot model by the
assumptions:

\[ \mathbf{F}(\mathbf{v}) = m \left[ \frac{\mathbf{v}}{\mathbf{v}} \right] de - \gamma_0 \mathbf{v} \]  

(12.22)

where again e is the energy content of a depot and \( d \) a conversion parameter. In difference to the standard depot model (SET-model) the first term which expresses an acceleration in the direction of \( \mathbf{v} \) is not dependent on the modulus \( |\mathbf{v}| \). The acceleration depends only on the energy content \( e \). The corresponding balance of the depot energy reads

\[ \frac{de}{dt} = q - ce - d|\mathbf{v}|e \]  

(12.23)

Within the new second variant of the depot model we get assuming \( q > 0 \) and requiring that the internal energy depot relaxes fast compared to the motion of
the particle in adiabatic approximation

\[ \mathbf{F} = m \mathbf{v} \left( \frac{dq}{cv + d\mathbf{v}^2} - \gamma_0 \right) \]  \hspace{1cm} (12.24)

Now for any \( q > 0 \) a root \( v_0 > 0 \) exists and the Schienbein-Gruler law follows with the correct derivative in the limit \( |\mathbf{v}| \gg v_0 \). On the other hand the Rayleigh law cannot be obtained from the depot model type B in a simple way. There is one point which seems to be unrealistic in both depot models discussed so far: The dissipative force increases linearly with the energy content. For real systems one would expect a saturation with increasing \( e \). This leads us to a third variant of the depot model:

\[ \mathbf{F}(\mathbf{v}) = m \left[ \frac{\mathbf{v}}{1 + ge} \frac{de}{v} - \gamma_0 \mathbf{v} \right] \]  \hspace{1cm} (12.25)

The parameter \( g \) leads to the wanted saturation for \( ge \gg 1 \). The corresponding balance of the depot energy reads

\[ \frac{de}{dt} = q - ce - d|\mathbf{v}| \frac{de}{1 + ge} \]  \hspace{1cm} (12.26)

Within this third variant of the depot model we get assuming \( q > 0 \) and requiring that the internal energy depot relaxes fast compared to the motion of
the particle in adiabatic approximation

\[ \mathbf{F} = -m \mathbf{v} \left( \frac{G(v)}{2gv^2} - \gamma_0 \right) \]  
(12.27)

where the function \( G(v) \) is defined by

\[ G(v) = dv + c + gq - \sqrt{(dv + c - gq)^2 + 4gq}\]  
(12.28)

The behavior of this third variant of depot models introduced here is not essentially different from the standard depot model (SET-model) or from the Schienbein-Gruler law.

12.3 Force-free motion of active particles and mean square displacement

Let us study first the stationary solutions of the equation. For the -model of active friction. For the case of free motion (no external forces) we get the stationary solution

\[ P_0(v) = N \exp \left[ \frac{\gamma_1}{2D} v^2 - \frac{\gamma_2}{4D} v^4 \right] \]  
(12.29)

The shape of this distribution (eq. 12.29) can be seen in Fig.12.2. With \( \gamma_2 = 1 \) the normalization constant is (Erdmann et al., 2000):

\[ N^{-1} = \pi \sqrt{\pi D} \exp \left( \frac{\gamma_1^2}{4D} \right) \left[ 1 + \text{erf} \left( \frac{\gamma_1}{2\sqrt{D}} \right) \right] \]  
(12.30)
For the Schienbein-Gruler model the solution is of particular simplicity (Schienbein & Gruler, 1993)

\[ P_0(v) = N \exp \left( \frac{\gamma_0}{2D} (|v| - v_0)^2 \right) \]  \hspace{1cm} (12.31)

For the depot-model (SET-model) the stationary solution reads

\[ P_0(v) = N \left( 1 + \frac{d}{c} v^2 \right)^{\frac{\gamma_0}{2D}} \exp \left( -\frac{\gamma_0}{2D} v^2 \right) \]  \hspace{1cm} (12.32)

The Fig.12.2 shows a cross section of the probability distribution for Rayleigh-Helmholtz and Schienbein-Gruler friction function. For strong noise corresponding to high temperatures \( D \sim T \to \infty \) we get by
Fig. 12.3  Velocity distribution function of active Brownian particles for the depot model with overcritical parameter values (active regime $d = 10$).

Using equ.(12.4) the Maxwell distribution

$$P_0(v) = \left( \frac{m}{2\pi k_B T} \right) \exp \left[ -\frac{mv^2}{2k_BT} \right] \quad (12.33)$$

This limit case is well known, it corresponds to the standard Brownian motion. Many characteristic quantities are explicitly known and were given already in earlier Chapters, as e.g. the dispersion of the velocities

$$\langle v^2 \rangle = 2 \frac{k_BT}{m} \quad (12.34)$$
and the most probable value of the modulus of the velocity

\[ \tilde{v} = \sqrt{\frac{k_B T}{m}}. \]  

(12.35)

Further we know the autocorrelation functions

\[ \langle \mathbf{v}_i(t) \mathbf{v}_j(0) \rangle = \delta_{ij} \frac{k_B T}{m} \]  

(12.36)

and the mean square displacement

\[ \langle (\mathbf{r}(t) - \mathbf{r}(0))^2 \rangle = \frac{4kT}{m\gamma_0} \left[ t + \gamma_0^{-1}(\exp(-\gamma_0 t) - 1) \right]. \]  

(12.37)

which gives in the limit \( t \to \infty \) the Einstein formula

\[ \langle (\mathbf{r}(t) - \mathbf{r}(0))^2 \rangle = 2D_r t. \]  

(12.38)

Here

\[ D_r = \frac{2kT}{m\gamma_0} \]  

(12.39)

is the coefficient of spatial diffusion. In the opposite case of weak noise we get a hat-like distribution, see fig.12.3, and in the limit \( D_v \sim T \to 0 \) and strong pumping we find a \( \delta \)-distribution of the velocities

\[ P_0(\mathbf{v}) = \mathcal{N} \delta \left( \mathbf{v}^2 - \mathbf{v}_0^2 \right) \]  

(12.40)

In this case of strong pumping the distribution function is maximal on the cylinder discussed above. The cross-section with the \( v_1 - v_2 \)-plane has the shape
of a hat. Following Schienbein and Gruler (1993) or Mikhailov and Meinköhn (1997) we get in this case the following formula for the mean-square displacement

$$\langle (\mathbf{r}(t) - \mathbf{r}(0))^2 \rangle = \frac{2v_0^4}{D_v} t + \frac{v_0^6}{D_v^2} \left[ \exp \left( -\frac{2D_v t}{v_0^2} \right) - 1 \right].$$

(12.41)

In the following we restrict ourselves to the depot model and will give a formula for the mean square displacement which contains the two limit cases discussed above. Let us consider the mean-square displacement on the plane $d = 2$ for a dynamics according to the depot model. We will apply a procedure which is a generalization of the methods developed by Klimontovich (1982, 1986) and Mikhailov & Meinköhn (1997). A particle starting at $t = 0$ in $\mathbf{r}(0)$ will at time $t$ at the coordinate vector

$$\mathbf{r}(t) = \int_0^t dt_1 \mathbf{v}(t_1)$$

(12.42)

The general expression for the mean square displacement reads

$$\langle (\mathbf{r}(t) - \mathbf{r}(0))^2 \rangle = \int_0^t dt_1 \int_0^t dt_2 \langle \mathbf{v}(t_1) \mathbf{v}(t_2) \rangle,$$

(12.43)

The correlation function of the velocities may be calculated exactly if the velocities are Maxwell distributed or $\delta-$distributed (see above). We will apply here the here more general assumption that the velocities have
a rather narrow distribution around the most probable value $\tilde{v}$. For the depot model the most probable velocity $\tilde{v}$ is the positive root of the bi-quadratic equation

$$\frac{D_v}{\tilde{v}^2} + \frac{qd}{c + d\tilde{v}^2} = \gamma_0$$

(12.44)

Following Klimontovich (1982, 1984) we introduce now radial and angle variables for the velocities

$$v_1(t) = \rho(t) \cos \phi(t); \quad v_2(t) = \rho(t) \sin \phi(t).$$

(12.45)

We consider $\rho(t)$ as a slow variable which is decoupled from the fast dynamics of the angle $\phi(t)$. For the correlation function we find

$$K(t) = \langle v(t_1)v(t_2) \rangle = \langle \rho(t_1)\rho(t_2) \cos(\phi(t_1-t_2)) \rangle$$

(12.46)

Assuming that the dynamics is decoupled we derive

$$K(t) \simeq \langle \rho(t_1)\rho(t_2) \rangle \langle \cos(\phi(t_1-t_2)) \rangle \simeq \tilde{v}^2 \langle \cos(\phi(t_1-t_2)) \rangle$$

(12.47)

Here we assumed that the absolute values of the velocities are always near to the value of maximal probability. Let us now study the correlation of the angles. Following again Klimontovich (1982, 1986) we
have to study the Fokker-Planck equation
\[
\frac{\partial f(\phi, t)}{\partial t} = D_\phi \frac{\partial^2 f}{\partial \phi^2}
\] (12.48)
with the diffusion coefficient \(D_\phi = D_v/(2\rho^2)\). Replacing here \(\rho^2\) by its mean value we get
\[
D_\phi = \frac{D_0}{2\langle v^2 \rangle} = \frac{1}{t_0}
\] (12.49)

The characteristic time \(t_0\) determines the relaxation of the angle-angle correlations. Using the distribution
\[
f(\phi, \tau|0, 0) = \frac{1}{\sqrt{4\pi t/t_0}} \exp \left[ -\frac{t_0\phi^2}{4\tau} \right]
\] (12.50)
we get finally after carrying out the time integration
\[
\langle (r(t) - r(0))^2 \rangle = \tilde{v}^2 \left[ t t_0 - t_0^2 + t_0^2 \exp(-t/t_0) \right]
\] (12.51)

In the limit of passive Brownian motion with Maxwell-distributed velocities \(q = 0\) with \(\tilde{v}^2 = kT/m\) and \(<v^2> = 2kT/m\) this leads us back to the classical formula eq.(12.37). In the opposite case of strong driving \(q \to \infty\) and \(\delta-\)distributed velocities we come back to the Mikhailov-Meinköhn formula eq.(12.41).

This way we have shown that our approximate expression eq.(12.51) is correct in the limits \(q \to 0\) and \(q \to \infty\). For intermediate values of the driving pa-
rameter $q$ our result eq.(12.51) is at least a useful approximation. Going to the limit of infinite time $t \gg t_0$ we find the mean-square displacement

$$\langle (\mathbf{r}(t) - \mathbf{r}(0))^2 \rangle = 2\bar{v}^2 t_0 t$$  \hspace{1cm} (12.52)

In the case of strong noise or weak driving we find in agreement with the Einstein-formula

$$D_{\text{eff}} = \frac{2kT}{m\gamma_0}$$  \hspace{1cm} (12.53)

and accordingly for weak noise or strong driving the effective spatial diffusion coefficient of Mikhailov and
Active Brownian Motion

Meinköhn

\[ D_{\text{eff}} = \frac{v_0^4}{D_v}. \]  (12.54)

We have carried out several simulations for the de- pot model. Then introducing the expression for \( v_0^2 \) the theory provides for large values of the bifurcation parameter \( \zeta \)

\[ D_{\text{eff}} = \frac{1}{D_v} \left( \frac{q}{\gamma_0} - \frac{c}{d} \right)^2 \]  (12.55)

As we see from Fig. 12.5 the points found from nu-

![Graph](image-url)

Fig. 12.5  Effective diffusion coefficient (\( D_{\text{eff}} \)) in dependence on the driving parameter \( q \). The calculated points correspond to \( q = 0.0; 0.4; 0.6; 0.8; 1.0; 1.5; 2.0; 3.0 \). For comparison the asymptotic estimate for large driving corresponding to eq. (12.55) is represented (lower curve given by crosses).

merical experiments correspond in a reasonable way to the asymptotic theory for large \( q \)-values.
12.4 Deterministic motion in parabolic external Potentials

In the following, we continue to discuss the particle’s motion in a two-dimensional space, \( \mathbf{r} = \{x_1, x_2\} \). The case of constant external forces was already treated by Schienbein and Gruler (Schienbein & Gruler, 1993). Here we specify the potential \( U(\mathbf{r}) \) as a symmetric parabolic potential:

\[
U(x_1, x_2) = \frac{1}{2} a (x_1^2 + x_2^2) \quad (12.56)
\]

First, we restrict the discussion to a deterministic motion, which then is described by four coupled first-order differential equations:

\[
\begin{align*}
\dot{x}_1 &= v_1, \\
\dot{x}_2 &= v_2, \\
\dot{v}_1 &= -\gamma (v_1, v_2) v_1 - ax_1 \\
\dot{v}_2 &= -\gamma (v_1, v_2) v_2 - ax_2
\end{align*}
\quad (12.57)
\]

For the one-dimensional Rayleigh-model it is well known that this system processes a limit cycle corresponding to sustained oscillations with the energy \( E_0 = \frac{\gamma_1}{\gamma_2} \). For the 2d case we can show by simulation and theoretical considerations that a limit cycle in the 4d-space is developed (Ebeling et al., 1999). The projection of this periodic motion to the \( \{v_1, v_2\} \) plane is the circle

\[
v_1^2 + v_2^2 = v_0^2 = \text{const.} \quad (12.58)
\]
Active Brownian Motion

The projection to the \( \{x_1, x_2\} \) plane also corresponds to a circle

\[
x_1^2 + x_2^2 = r_0^2 = \text{const.} \tag{12.59}
\]

Due to the condition of equilibrium between centripetal and centrifugal forces on the limit cycle we have

\[
\frac{mv_0^2}{r_0} = mr_0. \tag{12.60}
\]

Therefore the radius of the limit cycle is given by

\[
r_0 = \frac{v_0}{\omega_0} \tag{12.61}
\]

The energy for motions on the limit cycle is

\[
E_0 = \frac{m}{2}(v_1^2 + v_2^2) + \frac{a}{2}(x_1^2 + x_2^2). \tag{12.62}
\]

\[
= \frac{m}{2}v_0^2 + \frac{a}{2}r_0^2 \tag{12.63}
\]

From eq.(12.60) follows

\[
\frac{m}{2}v_0^2 = \frac{m}{2}r_0^2 \tag{12.64}
\]

This means we have equal distribution of potential and kinetic energy on the limit cycle (Ebeling et al., 1999). As for the harmonic oscillator in 1-d, both parts of energy contribute the same amount to the full energy. Therefore the energy of motions on the
Deterministic motion in parabolic external Potentials

limit cycle, which is asymptotically reached, is double the kinetic energy

\[ H \longrightarrow E_0 = m v_0^2. \]  

(12.65)

The energy is a slow (adiabatic) variable which allows a phase average with respect to the phases of the rotation (Ebeling et al., 1999).

In explicit form we may represent one exact solution representing a cycle in the 4d-space by the 4 equations

\[ x_1 = r_0 \cos(\omega t + \Phi) \quad v_1 = -r_0 \omega \sin(\omega t + \Phi) \]
\[ x_2 = r_0 \sin(\omega t + \Phi) \quad v_2 = r_0 \omega \cos(\omega t + \Phi) \]

(12.66)

By insertion into the dynamic equations we can prove easily, that this is an exact solution (for zero noise) if \( \omega = \omega_0 \). The frequency is given by the time the particle needs for one period moving on the circle with radius \( r_0 \) with constant speed \( v_0 \). This leads to the relation

\[ \omega = \frac{r_0}{v_0} = \left( \frac{m}{a} \right)^{1/2} = \omega_0. \]  

(12.67)

This means, the particle rotates even at strong pumping with the frequency given by the linear oscillator frequency \( \omega_0 \). The trajectory defined by the above 4 equations looks like a hoop in the 4d-space. Most projections to the 2d-subspaces are circles or ellipses
however there are to subspaces namely $x_1 - v_2$ and $x_2 - v_1$ where the projection is like a rod.

A second limit cycle is obtained by time reversal

$$t^- > -t; \quad v_1^- > -v_1; \quad v_2^- > -v_2 \quad (12.68)$$

This leads to the solution

$$x_1 = r_0 \cos(\omega t - \Phi) \quad v_1 = -r_0 \omega \sin(\omega t - \Phi)$$
$$x_2 = -r_0 \sin(\omega t - \Phi) \quad v_2 = -r_0 \omega \cos(\omega t - \Phi) \quad (12.69)$$

This second cycle forms also a hula hoop which is different from the first one, however both l.c. have the same projections to the $x_1 - x_2-$ and to the $v_1 - v_2-$ plane. The projection to the $x_1 - x_2-$ plane has the opposite direction of rotation in comparison with the first limit cycle. The projections of the two hula hoops on the $x_1 - x_2-$ plane or on the $v_1 - v_2-$plane are 2d-rings (Fig. 12.6) The hula hoops distribution intersect perpendicular the $x_1 - v_2-$plane and the $x_2 - v_1-$plane (see Fig. 12.6. The projections to these planes are rod-like and the intersection manifold with these planes consists of two ellipses located in the diagonals of the planes (see Fig. 12.6. In order to construct later solutions for stochastic motions we need beside $H = mv_0^2$ other appropriate invariants of motion. Looking at the first solution we see, that
the following relation is valid

\[ v_1 + \omega_0 x_2 = 0; \quad v_2 - \omega_0 x_1 = 0. \quad (12.70) \]

In order to characterize the first l.c. we introduce in accordance with Chapter 5 the invariant

\[ J_+ = H - \omega_0 = \frac{m}{2}(v_1 + \omega_0 x_2)^2 + \frac{m}{2}(v_2 - \omega_0 x_1)^2. \quad (12.71) \]

We see immediately that \( J_+ = 0 \) holds on the first limit cycle which correspond to positive angular momentum. In order to characterize the second l.c. we use the invariant

\[ J_- = H + \omega_0 L = \frac{m}{2}(v_1 - \omega_0 x_2)^2 + \frac{m}{2}(v_2 + \omega_0 x_1)^2. \quad (12.72) \]

Correspondingly on the second l.c., which corresponds to negative angular momentum, holds \( J_- = 0 \).
Active Brownian Motion

As pointed out by Deng and Zhu (2004), there are two other important and simple invariants of motion

\[ H_1 = \frac{m}{2}v_1^2 + \frac{m}{2}\omega_0 x_1^2, \quad H_y = \frac{m}{2}v_2^2 + \frac{m}{2}\omega_0 x_2^2 \]

As shown by the above mentioned authors, these invariants may also be used for deriving explicit solutions for problems of the dynamics in parabolic fields.

12.5 Perturbed and transient limit cycles

The most important result obtained so far, is the existence of limit cycles, corresponding to stable rotational excitations. In the present section we will discuss briefly several extensions of the theory developed in the previous section:

- effects of anharmonicity of the potential,
- effects of rotational asymmetry of the potential,
- effects due to transients to the stationary energy state.

At first we will discuss how anharmonic potentials influence. For the general case of radially symmetric but anharmonic potentials \( U(r) \), the equal distribution between potential and kinetic energy \( mv_0^2 = ar_0^2 \) does not hold. Therefore the relation for the frequencies \( \omega_0 = v_0/r_0 = \omega \) is no more valid. It has to be replaced by the more general condition that on the
Perturbed and transient limit cycles

limit cycle the attracting radial forces are in equilibrium with the centrifugal forces. This condition leads to

$$\frac{mv_0^2}{r_0} = |U'(r_0)|$$  \hspace{1cm} (12.74)

If $v_0$ is given, the equilibrium radius may be found from the implicit relation

$$v_0^2 = \frac{r_0}{m} |U'(r_0)|$$  \hspace{1cm} (12.75)

Then the frequency of the limit cycle oscillations is given by

$$\omega_0^2 = \frac{v_0^2}{r_0^2} = \frac{|U'(r_0)|}{mr_0}$$  \hspace{1cm} (12.76)

In the case of linear oscillators this leads again to $\omega_0 = \sqrt{a/m}$. For the case of quartic oscillators

$$U(r) = \frac{k}{4} r^4$$  \hspace{1cm} (12.77)

we get the limit cycle frequency

$$\omega_0 = \frac{k^{1/4}}{v_0^{1/2}}$$  \hspace{1cm} (12.78)

If the equation (12.75) has several solutions, the dynamics might be much more complicated, e.g. we could find Kepler-like orbits oscillating between the
solutions for $r_0$. In other words we may find then besides driven rotations also driven oscillations between the multiple solutions of eq.(12.75).

An interesting application of the theoretical results given above, is the following: Let us imagine a system of Brownian particles which are pairwise bound by a Lennard-Jones-like potential $U(r_1 - r_2)$ to dumbbell-like configurations. Then the motion consists of two independent parts, the free motion of the center of mass, and the relative motion under the influence of the potential. The motion of the center of mass is described by the equations for free motion and the relative motion is described by the equations given in this section. As a consequence, the center of mass of the dumb-bell will make a driven Brownian motion but in addition the dumb-bells are driven to rotate around there center of mass. What we observe then is a system of pumped Brownian molecules which show driven translations with respect to their center of mass. On the other side the internal degrees of freedom are also excited and we observe driven rotations and in general (if eq.(12.75) has several solutions) also driven oscillations. In this way we have shown that the mechanisms described here may be used also to excite the internal degrees of freedom of Brownian molecules (Erdmann et al., 2000).
Another possible application is to the motion of clusters of active molecules. Similar as in the case of the dumb-bells the clusters will be driven to make spontaneous rotations. Finally a stationary state will be reached which is a mixture of rotating clusters or droplets similar as described by Mikhailov and Calenbuhr (2002) in the framework of a different model. We will come back to the dynamics of clusters in Chapter 13.

Let us study now another interesting effect, connected with broken rotational symmetry of the potential. So far we studied only external potentials depending on the radius $r$. In reality this symmetry might be broken and we should study the more general case of asymmetric external potentials (Erdmann et al. 2000). Let us assume that the former symmetric parabolic potential is a bit stretched, elliptically. Concerning to develop a model what ought to describe natural systems, we introduce a small asymmetry. In nature, exact symmetric systems cannot be found. In the general case of elliptic symmetry we find after turning to the main axis:

$$ U(x_1, x_2) = \frac{1}{2} \left( a_1 x_1^2 + a_2 x_2^2 \right) , \quad (12.79) $$

We introduce the parameter of asymmetry

$$ a_1 - a_2 = \Delta = \omega_1^2 - \omega_2^2 \quad (12.80) $$
what can be understood as small detuning of the frequencies of two oscillators. The deterministic dynamics is then given by the equations

\[
\begin{align*}
\dot{x}_1 &= v_1 \\
\dot{v}_1 &= \left[\alpha - \beta \left(v_1^2 + v_2^2\right)\right] v_1 - \omega_1^2 x_1 \\
\dot{x}_2 &= v_2 \\
\dot{v}_2 &= \left[\alpha - \beta \left(v_1^2 + v_2^2\right)\right] v_2 - \omega_2^2 x_2
\end{align*}
\]

We now investigate the stability of the existing limit cycles in the parameter space \(\{\Delta, \alpha\}\). Apart from the limit cycles described above there exist an infinite number of limit cycles if one starts with symmetric initial conditions. This can be understood if one looks at the system eq.(12.81) in complex representation \((z = x_1 + ix_2 \text{ and } \omega_1 = \omega_2 = \omega_0)\):

\[
\ddot{z} - \beta \left(\frac{\alpha}{\beta} - z^2\right) + \omega_0^2 z = 0 \tag{12.83}
\]

Assuming

\[
z(t) = z e^{i\Omega_0 t} = |z| e^{i\Phi} e^{i\Omega_0 t} \tag{12.84}
\]

one can see that for angles \(\Phi\) between zero and \(2\pi\), stable oscillations are possible. As far as one increases the detuning parameter \(\Delta\), the symmetric cycle will be destroyed. For asymmetric initial conditions one can observe two limit cycles as in the case of the parabolic potential. Compared to the parabolic case, for a detuned potential the two limit cycles are just stable within a region of finite size. In simulations
one can observe a region within the existing limit cycles stay stable even with a relatively high amount of the detuning $\Delta$. Outside that region the limit cycle can go through certain bifurcation scenarios like period doubling of the cycle (Neimark-Sacker bifurcations). More details on the bifurcation scenario may be found in (Erdmann et al., 2002).

Finally we want to discuss the role of transient processes. We studied so far the dynamics in the 4-dimensional space $x_1 - x_2 - v_1 - v_2$ and neglected the dynamics of the depot variable. This however, is already a simplification and sometimes the dynamics of the additional 5th variable $e(t)$ might be complicated (Tilch et al., 1999). As a rule however, this dynamics is smooth, exponentially approaching the limit values. In order to show this we will study here the transition of the energy of the depot to its stationary state. Including the full depot dynamics, we have in addition to the previous 4 dynamic variables an additional variable $e(t)$ which is the content of the depot at time $t$. This variable has of course its own dynamics (Ebeling et al, 1999; Ebeling, 2003). In order to study this dynamics let us assume at first that the depot is full at the initial time $t = 0$ and that there is no feeding $q = 0$. A numerical solution
of the simplified depot equation

$$\frac{d}{dt} e(t) = q_0 - c \, e(t) - dv^2 \, e(t) \quad (12.85)$$

together with the dynamic equations for the coordinates and momenta (for $D = 0$) gives transient limit cycles corresponding to left/right rotations. One of them is shown in Fig. 12.7. We see that in the first period a transient limit cycle is formed which then decays since the depot energy is exhausted. Therefore stationary or quasistationary processes need a permanent energy support. In later applications of the theory we will study for simplicity only an adiabatic approximation for the depot dynamics.
12.6 Stochastic motion in symmetric external potentials

Since the main effect of noise is the spreading of the deterministic attractors we may expect that the two hoop-like limit cycles are converted into a distribution looking like two embracing hoops with finite size, which for strong noise converts into two embracing tires in the 4d-space. In order to get the explicit form of the distribution we may introduce the amplitude–phase representation

\begin{align*}
x_1 &= \rho(t) \cos(\omega_0 t + \phi(t)) \quad v_1 = -\rho(t)\omega_0 \sin(\pm \omega_0 t + \phi(t)) \\
x_2 &= \rho(t) \sin(\omega_0 t + \phi(t)) \quad v_2 = \rho(t)\omega_0 \sin(\pm \omega_0 t + \phi(t))
\end{align*}

(12.86)

where the radius \( \rho(t) \) is now a slow and the phase \( \phi(t) \) is a fast stochastic variable (Erdmann et al., 2000). Again the row signs \( \pm \omega t \) correspond to the two directions of the angular momentum (right or left rotations). On the basis of this 'ansatz' we get for the Hamiltonian

\[ H = \omega_0^2 \cdot \rho(t)^2 \]

(12.87)

The angular momenta \( L = xv_y - yv_x \) corresponding to the two limit cycles are

\[ L = +L_0; \quad L = -L_0; \quad L_0 = v_0^2/\omega_0. \]  

(12.88)

Both limit cycles are located on the sphere \( H = v_0^2 \) where \( H \) is the Hamiltonian. The dynamics may be
treated by using the standard procedure of averaging with respect to the fast phases (Erdmann et al., 2000). A more easy approach is found based on the procedure developed in Section 5.1. Considering harmonic oscillators and using equipartition of potential and kinetic energy (see eq.(12.65) we find for motions on the limit cycle

\[ v^2 = \frac{H}{m} \]  

(12.89)

Assuming that  \( v^2 \approx H/m \) holds also near to the limit cycle, the dynamic system is converted to a canonical dissipative system with

\[ \gamma(v^2) \approx \gamma(H/m). \]  

(12.90)

This way we come to the following solution for the Rayleigh-model

\[ P_0(x_1, x_2, v_1, v_2) = N \exp \left[ \frac{\gamma_1 H - \gamma_2 H^2/2}{D_v} \right] \]  

(12.91)

with the most probable value of the energy

\[ \tilde{H} = H_0 = \frac{\gamma_1}{\gamma_2} = mv_0^2. \]  

(12.92)

Here \( H_0 \) is the energy on the limit cycle.

A different way to derive this distribution is to start
from the relation
\[ \frac{dH}{dt} = -m\gamma(v^2)v^2 + \sqrt{2D_v}v \cdot \xi(t) \quad (12.93) \]

This leads for the Rayleigh model and near to the limit cycle to the linearized Langevin equation
\[ \frac{d\delta H}{dt} = -\gamma_2 v_0^2 \delta H + \sqrt{2D_H} \xi(t) \quad (12.94) \]

with
\[ \delta H = H - H_0; \quad D_H = D_v mv_0^2. \quad (12.95) \]

The stationary distribution of this linearized problem reads
\[ P_0(H) = C \exp \left[ -\frac{\gamma_2}{2m^2D_v} \delta H^2 \right] \quad (12.96) \]

We see that the Langevin method leads to the same stationary distribution of the Hamiltonian, the probability is in fact distributed on the surface of a 4-dimensional sphere.

By using eq. (12.87) we get for the Rayleigh model of pumping in our approximation the following distribution of the radii:
\[ P_0(\rho) \propto \exp \left[ \frac{\gamma_1 \omega_0^2}{D_v} \rho^2 \left( 1 - \frac{\rho^2}{2r_0^2} \right) \right], \quad r_0^2 = \omega^2 v_0^2 = \frac{m\gamma_1}{a\gamma_2} \quad (12.97) \]

We see in Fig. 12.8 that the probability crater is located above the deterministic limit cycles. This way
the maximal probability corresponds indeed to the deterministic limit cycle. So far we represented only

![Probability density for the Rayleigh-model represented over the $x_1 - x_2$ plane.](image)

a projection on the $x_1 - x_2$ plane. The full probability distribution in the 4d-space is not constant on the 4d-sphere $H = mv_0^2$ as suggested by eq.(12.91) but should be concentrated around the limit cycles which are closed curves on the $4-d$ sphere $H = mv_0^2$. This means, only a subspace of this sphere is filled with probability. The correct stationary probability has the form of two noisy distributions in the 4d space, which look like hula hoops. This characteristic form of the distributions was confirmed also by simulations (see Fig. 12.9) The projections of the distribution to the $\{x_1, x_2\}$ plane and to the $\{v_1, v_2\}$ plane are noisy tori in the 4d-space (see Fig. 12.9). The hula hoop distribution intersects perpendicular the $\{x_1, v_2\}$ plane and the $\{x_2, v_1\}$ plane. The projections to these planes are rod-like and the inter-
section manifold with these planes consists of two
circles located in the diagonals of the planes. In or-
der to find the distribution of the angular momenta
we start from the Langevin equation
\[ \frac{dL}{dt} = -\gamma(v^2)L + \sqrt{2}D_L \xi(t) \] (12.98)
with
\[ D_L = m^2 r_0^2 D_v \] (12.99)
This leads for the Rayleigh model to the following
equation for the deviations \( \delta L = L \pm m r_0 v_0 \):
\[ \frac{d\delta L}{dt} = -\gamma_2 v_0^2 \delta L + \sqrt{2D_L} \xi(t) \] (12.100)
The stationary solution reads
\[ P_0(L) = C \exp \left[ -\frac{\gamma_2 \cdot \omega_0^2}{m^2 D_v} (\delta L)^2 \right] \] (12.101)
The given method does not provide a complete solution in the 4d-space, but gives us a good idea about the projections on different planes.

In order to find a distribution in the 4d-space we try the following 'ansatz'.

\[
P_0(x_1, x_2, v_1, v_2) = C \exp \left[ -\frac{\gamma^2}{2m^2D_v}(H - H_0)^2 \right] \\
\cdot \left( \exp \left[ -\frac{\gamma^2\omega_0^2}{m_D^D}(L - H/\omega_0)^2 \right] + \exp \left[ -\frac{\gamma^2\omega_0^2}{m_D^D}(L + H/\omega_0)^2 \right] \right)
\]

We may convince ourselves that this formula agrees with all projections studied above. Furthermore, it is in agreement with the general 'ansatz' derived in Chapter 5 from information theory. We note that in a recent paper Deng and Zhu (2004) derived a different approximative solution.
Chapter 14

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