6.8.2 reaction controlled limit

If on the other hand $k_2 \ll k_{\pm 1}$ an equilibrium between reactands and reactive complex will be established

$$A + B \leftrightharpoons \{A\,B\} \qquad \frac{c_{\{AB\}}}{c_A c_B} = K = \frac{k_1}{k_{-1}}$$

Now the overall reaction rate is

$$\dot{c}_c = k_2 c_{\{AB\}} = k_2 K c_A c_B$$

determined by the reaction rate k_2 and the constant of the diffusion equilibrium

7 kinetic theory - Fokker-Planck equation

We consider a model system (protein) interacting with a surrounding medium which is only taken implicitly into account. We are interested in the dynamics on a slower time scale than the medium fluctuations. Then the interaction with the medium can be approximately substituted by the sum of an average force and a stochastic force.

7.1 stochastic differential equation for Brownian motion

The simplest example describes 1-dimensional Brownian motion of a big particle in a sea of small particles. The average interaction leads to damping of the motion which is described in terms of a velocity dependent damping term

$$\frac{dv(t)}{dt} = -\gamma v(t)$$

This equation alone leads to exponential relaxation $v = v(0)e^{-\gamma t}$ which is not compatible with thermodynamics, since the average kinetic energy should be $\frac{m}{2}v^2 = \frac{kT}{2}$ in equilibrium. Therefore we add a randomly fluctuating force which represents the collisions with many solvent molecules during a finite time interval τ . The result is the Langevin equation

$$\frac{dv(t)}{dt} = -\gamma v(t) + F(t)$$

with the formal solution

$$v(t) = v_0 e^{-\gamma t} + \int_0^t e^{\gamma(t'-t)} F(t') dt'$$

The average of the stochatic force has to be zero to because the equation of motion for the average velocity should be

$$\frac{d < v(t) >}{dt} = -\gamma < v(t) >$$

We assume that during τ many collisions occur and therefore forces at different times are not correlated

$$< F(t)F(t') >= C\delta(t - t')$$

The velocity correlation function is

$$< v(t)v(t') >= e^{-\gamma(t+t')}\left(v_0^2 + \int_0^t dt_1 \int_0^{t'} dt_2 \quad e^{\gamma(t_1+t_2)} < F(t_1)F(t_2) >\right)$$

without loosing generality we assume $t' > t$ and substitute $t_2 = t_1 + s$

$$= v_0^2 e^{-\gamma(t+t')} + e^{-\gamma(t+t')} \int_0^t dt_1 \int_{-t_1}^{t'-t_1} ds\, e^{\gamma(2t_1+s)} < F(t_1)F(t_1+s) >$$

$$= v_0^2 e^{-\gamma(t+t')} + e^{-\gamma(t+t')} \int_0^t dt_1 e^{2\gamma t_1} C dt$$

$$v_0^2 e^{-\gamma(t+t')} + e^{-\gamma(t+t')} \frac{e^{2\gamma t} - 1}{2\gamma} C$$

The exponential terms vanish very quickly and we find

$$< v(t)v(t') > \to e^{-\gamma|t'-t|}\frac{C}{2\gamma}$$

Now C can be determined from the average kinetic energy as

$$\frac{m < v^2 >}{2} = \frac{kT}{2} = \frac{m}{2}\frac{C}{2\gamma} \to C = \frac{2\gamma kT}{m}$$

The mean square displacement of a particle starting at x_0 with velocity v_0 is

$$< (x(t) - x(0))^2 >=< \left(\int_0^t dt_1 v(t_1)\right)^2 >= \int_0^t \int_0^t < v(t_1)v(t_2) > dt_1 dt_2$$

$$= \int_0^t \int_0^t \left(v_0^2 e^{-\gamma(t_1+t_2)} + \frac{kT}{m} e^{-\gamma|t_1-t_2|}\right) dt$$

and since

$$\int_0^t \int_0^t e^{-\gamma(t_1+t_2)} dt_1 dt_2 = \left(\frac{1-e^{-\gamma t}}{\gamma}\right)^2$$

and

$$\int_0^t \int_0^t e^{-\gamma|t_1-t_2|} dt_1 dt_2 = 2\int_0^t dt_1 \int_0^{t_1} e^{-\gamma(t_1-t_2)} dt_2 = \frac{2}{\gamma}t - \frac{2}{\gamma^2}(1-e^{-\gamma t})$$

we obtain

$$< (x(t) - x(0))^2 >= (v_0^2 - \frac{kT}{m})\frac{(1-e^{-\gamma t})^2}{\gamma^2} + \frac{2kT}{m\gamma}t - \frac{2kT}{m\gamma^2}(1-e^{-\gamma t})$$

If we started with an initial velocity distribution for the stationary state $< v_0^2 >= kT/m$ and the first term vanishes. For very large times the leading term is [10]

$$< (x(t) - x(0))^2 >= 2Dt \qquad D = \frac{kT}{m\gamma}$$

[10] This is the well known Einstein result for the diffusion constant D

7.2 probability distribution

We discuss now the probability distribution $W(v)$. The time evolution can be described as

$$W(v,t+\tau) = \int P(v,t+\tau|v',t)W(v',t)dv'$$

To derive an expression for the differential $\partial W(v,t)/\partial t$ we need the transition probability $P(v,t+\tau|v',t)$ for small τ . Introducing $\Delta = v - v'$ we expand the integrand in a Taylor series

$$P(v,t+\tau|v',t)W(v',t) = P(v,t+\tau|v-\Delta,t)W(v-\Delta,t)$$

$$= \sum_{n=0}^{\infty} \frac{(-1)^n}{n!}\Delta^n \left(\frac{\partial}{\partial v}\right)^n P(v+\Delta,t+\tau|v,t)W(v,t)$$

Inserting this into the integral gives

$$W(v,t+\tau) = \sum_{n=0}^{\infty} \frac{(-1)^n}{n!} \left(\frac{\partial}{\partial v}\right)^n \left(\int \Delta^n P(v+\Delta,t+\tau|v,t)d\Delta\right) W(v,t)$$

and assuming that the moments exist which are defined by

$$M_n(v',t,\tau) =< (v(t+\tau)-v(t))^n >_{|v(t)=v'} = \int (v-v')^n P(v,t+\tau|v',t)dv$$

we find

$$W(v,t+\tau) = \sum_{n=0}^{\infty} \frac{(-1)^n}{n!} \left(\frac{\partial}{\partial v}\right)^n M_n(v,t,\tau)W(v,t)$$

Expanding the moments into a Taylor series

$$\frac{1}{n!}M_n(v,t,\tau) = \frac{1}{n!}M_n(v,t,0) + D^{(n)}(v,t)\tau + \cdots$$

we have finally[11]

$$W(v,t+\tau) - W(v,t) = \sum_{1}^{\infty} \left(-\frac{\partial}{\partial v}\right)^n D^{(n)}(v,t)W(v,t)\tau + \cdots$$

which gives the equation of motion for the probability distribution[12]

$$\frac{\partial W(v,t)}{\partial t} = \sum_{1}^{\infty} \left(-\frac{\partial}{\partial v}\right)^n D^{(n)}(v,t)W(v,t)$$

If this expansion stops after the second term[13] the general form of the 1-dimensionsal Fokker-Planck equation results, written now with the more conventional argument x

$$\frac{\partial W(x,t)}{\partial t} = \left(-\frac{\partial}{\partial x}D^{(1)}(x,t) + \frac{\partial^2}{\partial x^2}D^{(2)}(x,t)\right) W(x,t)$$

[11] The zero order moment doe not depend on τ

[12] This is knwon as the Kramers-Moyal expansion

[13] It can be shown that this is the case for all Markov processes

7.3 Diffusion

Consider a particle performing a random walk in one dimension due to collisions. We use the stochastic differential equation[14]

$$\frac{dx}{dt} = v_0 + f(t)$$

where the velocity has a drift component v_0 and a fluctuating part $f(t)$ with

$$< f(t) >= 0 \qquad < f(t)f(t') >= q\delta(t-t')$$

The formal solution is simply

$$x(t) - x(0) = v_0 t + \int_0^t f(t')dt'$$

The first moment is

$$M_1(x_0, t, \tau) =< x(t+\tau) - x(t) >_{|x(t)=x_0}= v_0\tau + \int_0^\tau < f(t') > dt'0$$

$$D^{(1)} = v_0$$

The second moment is

$$M_2(x_0, t, \tau) = v_0^2\tau^2 + v_0\tau\int_0^\tau < f(t') > dt' + \int_0^\tau\int_0^\tau < f(t_1)f(t_2) > dt_1 dt_2$$

The second term vanishes and the only linear term in $\tau comes$from the double integral

$$\int_0^\tau\int_0^\tau < f(t_1)f(t_2) > dt_1 dt_2 = \int_0^\tau dt_1 \int_{-t_1}^{\tau - t_1} q\delta(t')dt' = q\tau$$

hence

$$D^{(2)} = \frac{q}{2}$$

and the corresponding Fokker-Planck equation is the diffusion equation

$$\frac{\partial W(x,t)}{\partial t} = -v_0\frac{\partial W(x,t)}{\partial x} + D\frac{\partial^2 W(x,t)}{\partial x^2}$$

with the diffusion constant $D = D^{(2)}$.

We can easily find the solution for a sharp initial distribution $W(x,0) = \delta(x - x_0)$ by taking the Fourier transform

$$\widetilde{W}(k,t) = \int_{-\infty}^{\infty} dx\, W(x,t)\, e^{-ikx}$$

We obtain

$$\frac{\partial\widetilde{W}(k,t)}{\partial t} = (-Dk^2 + iv_0k)\widetilde{W}(k,t) \to \widetilde{W}(k,t) = \widetilde{W}_0 \exp\left\{(-Dk^2 + iv_0k)t + ikx_0\right\}$$

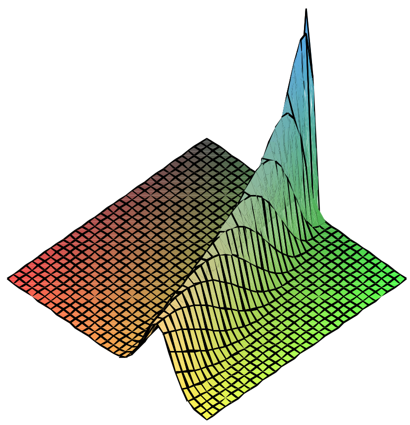
[14] This is a so called Wiener process

and the Fourier back transformation gives[15]

$$W(x,t) = \frac{1}{\sqrt{4\pi Dt}} \exp\left\{-\frac{(x-x_0-v_0t)^2}{4Dt}\right\}$$

which is a Gaussian distribution centered at $x_c = x_0 + v_0 t$ with a variance of $<(x-x_c)^2>= 4Dt$

Figure 58: solution of the diffusion equation for sharp initial conditions



example: absorbing boundary

Consider a particle from species A which can undergo a chemical reaction with a particle from species B at position $x_A = 0$

$$A + B \rightarrow AB$$

If the reaction rate is very fast, then the concentration of A vanishes at $x = 0$ which gives an additional boundry condition

$$W(x=0,t) = 0$$

Starting again with a localized particle at time zero with $W(x,0) = \delta(x - x_0)$ $v_0 = 0$ the probability distribution

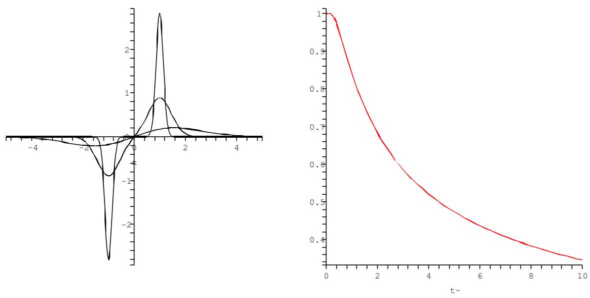
$$W(x,t) = \frac{1}{\sqrt{4\pi Dt}} \left(e^{-\frac{(x-x_0)^2}{4Dt}} - e^{-\frac{(x+x_0)^2}{4Dt}} \right)$$

is a solution which fullfills the boundary conditions. This solution is similar to the mirror principle known from electrostatics. The total concentration of species A in solution is then given by

$$\int_0^\infty dx\, W(x,t) = erf\left(\frac{x_0}{\sqrt{4Dt}}\right)$$

[15] with the proper normalization factor

Figure 59: solution from the mirror principle



7.4 Fokker-Planck equation for Brownian motion

For Brownian motion we have from the formal solution

$$v(\tau) = v_0(1 - \gamma\tau + \cdots) + \int_0^\tau (1 + \gamma(t_1 - \tau) + \cdots)F(t_1)dt_1$$

The first moment is[16]

$$M_1(v_0, t, \tau) = < v(\tau) - v(0) > = -\gamma\tau v_0 + \cdots$$

$$D^{(1)}(v, t) = -\gamma v$$

The second moment follows from

$$< (v(\tau) - v_0)^2 > = (v_0\gamma\tau)^2 + \int_0^\tau \int_0^\tau (1 + \gamma(t_1 + t_2 - 2\tau \cdots))F(t_1)F(t_2)dt_1 dt_2$$

The double integral gives

$$\int_0^\tau dt_1 \int_{-t_1}^{\tau - t_1} dt'(1 + \gamma(2t_1 + t' - 2\tau + \cdots)\frac{2\gamma kT}{m}\delta(t')$$

$$= \int_0^\tau dt_1 \frac{2\gamma kT}{m}(1 + \gamma(2t_1 - 2\tau + \cdots)$$

$$= \frac{2\gamma kT}{m}\tau + \cdots$$

and we have

$$D^{(2)} = \frac{\gamma kT}{m}$$

The higher moments have no contributions linear in τ and the resulting Fokker-Planck equation is

$$\frac{\partial W(v,t)}{\partial t} = \gamma \frac{\partial}{\partial v}(vW(v,t)) + \frac{\gamma kT}{m}\frac{\partial^2}{\partial v^2}W(v,t)$$

[16] here and in the following we use $< F(t) > = 0$

7.5 stationary solution of the FP equation

The Fokker-Planck equation can be written in the form of a continuity equation

$$\frac{\partial W(v,t)}{\partial t} = -\frac{\partial}{\partial v} S(v,t)$$

with the probability current

$$S(v,t) = -\frac{\gamma kT}{m}\left(\frac{mv}{kT} W(v,t) + \frac{\partial}{\partial v} W(v,t)\right)$$

For a stationary solution (with open boundaries $-\infty < v < \infty$) the probability current has to vanish

$$\frac{\partial}{\partial v} W(v,t) = -\frac{mv}{kT} W(v,t)$$

which has as its solution the Maxwell distribution

$$W_{stat}(v,t) = \sqrt{\frac{m}{2\pi kT}} e^{-mv^2/2kT}$$

Therefore we conclude that the Fokker-Planck equation describes systems, that reach thermal equilibrium starting from a non equilibrium distribution. We want to look at the relaxation process itself in the following.We start with

$$\frac{\partial W(v,t)}{\partial t} = \gamma W(v,t) + \gamma v \frac{\partial W(v,t)}{\partial v} + \frac{\gamma kT}{m} \frac{\partial^2 W(v,t)}{\partial v^2}$$

and introduce the new variables

$$\rho = v e^{\gamma t} \qquad y(\rho,t) = W(\rho e^{-\gamma t}, t)$$

which transforms the differentials

$$\frac{\partial W}{\partial v} = \frac{\partial y}{\partial \rho}\frac{\partial \rho}{\partial v} = e^{\gamma t}\frac{\partial y}{\partial \rho}$$

$$\frac{\partial^2 W}{\partial v^2} = e^{2\gamma t}\frac{\partial^2 y}{\partial \rho^2}$$

$$\frac{\partial W}{\partial t} = \frac{\partial y}{\partial t} + \frac{\partial y}{\partial \rho}\frac{\partial \rho}{\partial t} = \frac{\partial y}{\partial t} + \gamma \rho \frac{\partial y}{\partial \rho}$$

This leads to the new differential equation

$$\frac{\partial y}{\partial t} = \gamma y + D e^{2\gamma t}\frac{\partial^2 y}{\partial \rho^2}$$

To solve this equation we introduce new variables again

$$y = \chi e^{\gamma t}$$

which results in

$$\frac{\partial \chi}{\partial t} = D e^{2\gamma t}\frac{\partial^2 \chi}{\partial \rho^2}$$

Now we introduce a new time scale

$$\theta = \frac{1}{2\gamma}(e^{2\gamma t} - 1)$$

$$d\theta = e^{2\gamma t} dt$$

satisfying the initial condition $\theta(t = 0) = 0$. Now we have to solve a diffusion equation

$$\frac{\partial \chi}{\partial \theta} = D \frac{\partial^2 \chi}{\partial \rho^2}$$

which gives

$$\chi(\rho, \theta, \rho_0) = \frac{1}{\sqrt{4\pi D\theta}} \exp(-\frac{(\rho - \rho_0)^2}{4\pi D\theta})$$

After backsubstitution of all variables we find

$$W(v,t) = \sqrt{\frac{m}{2\pi kT(1 - e^{-2\gamma t})}} \exp\left\{-\frac{m}{2kT}\frac{(v - v_0 e^{-\gamma t})^2}{(1 - e^{-2\gamma t})}\right\}$$

This solution shows that the system behaves for small times like

$$W(v,t) \approx \frac{1}{\sqrt{4\pi Dt}} \exp\left\{-\frac{(v - v_0)^2}{4Dt}\right\}$$

and relaxes to the Maxwell distribution with a time constant $\Delta t = 1/2\gamma$.

7.6 Diffusion in an external potential - Kramers equation

We consider motion of a particle under the influence of an external (mean) force $K(x) = -\frac{d}{dx}U(x)$. The stochastic differential euation for position and velocity is

$$\dot{x} = v$$

$$\dot{v} = -\gamma v + \frac{1}{m}K(x) + F(t)$$

We will calculate the moments for the Kramers-Moyal expansion. For small τ we have

$$M_x =< x(\tau) - x(0) >= \int_0^\tau v(t)dt = v_0\tau + \cdots$$

$$M_v =< v(\tau) - v(0) >= \int_0^\tau (-\gamma v(t) + \frac{1}{m}K(x(t)) + < F(t) >)dt = (-\gamma v_0 + \frac{1}{m}K(x_0))\tau + \cdots$$

$$M_{xx} =< (x(\tau) - x(0))^2 >= \int_0^\tau \int_0^\tau v(t_1)v(t_2)dt_1 dt_2 = v_0^2\tau^2 + \cdots$$

$$M_{vv} =< (v(\tau) - v(0))^2 >= (-\gamma v_0 + \frac{1}{m}K(x_0))^2\tau^2 + \int_0^\tau \int_0^\tau F(t_1)F(t_2)dt_1 dt_2 = \frac{2\gamma kT}{m}\tau + \cdots$$

hence the drift and diffusion coefficients are

$$D^{(x)} = v$$

$$D^{(v)} = -\gamma v + \frac{1}{m}K(x)$$

$$D^{(xx)} = 0$$
$$D^{(vv)} = \frac{\gamma kT}{m}$$

which leads to the Klein-Kramers equation

$$\frac{\partial W(x,v,t)}{\partial t} = \left[-\frac{\partial}{\partial x} D^{(x)} - \frac{\partial}{\partial v} D^{(v)} + \frac{\partial^2}{\partial v^2} D^{(vv)} \right] W(x,v,t)$$

$$\frac{\partial W(x,v,t)}{\partial t} = \left[-\frac{\partial}{\partial x} v + \frac{\partial}{\partial v} (\gamma v - \frac{K(x)}{m}) + \frac{\gamma kT}{m} \frac{\partial^2}{\partial v^2} \right] W(x,v,t)$$

This equation can be divided into a reversible and an irreversible part

$$\frac{\partial W}{\partial t} = (\mathfrak{L}_{rev} + \mathfrak{L}_{irrev}) W$$

$$\mathfrak{L}_{rev} = \left[-v \frac{\partial}{\partial x} + \frac{1}{m} \frac{\partial U}{\partial x} \frac{\partial}{\partial v} \right] \qquad \mathfrak{L}_{irrev} = \left[\frac{\partial}{\partial v} \gamma v + \frac{\gamma kT}{m} \frac{\partial^2}{\partial v^2} \right]$$

The reversible part corresponds to the Liouville operator for a particle moving in the potential without friction

$$\mathfrak{L} = \left[\frac{\partial \mathfrak{H}}{\partial x} \frac{\partial}{\partial p} - \frac{\partial \mathfrak{H}}{\partial p} \frac{\partial}{\partial x} \right] \qquad \mathfrak{H} = \frac{p^2}{2m} + U(x)$$

obviously

$$\mathfrak{L}\mathfrak{H} = 0$$

and

$$\mathfrak{L}_{irrev} \exp\left\{ -\frac{\mathfrak{H}}{kT} \right\} = \exp\left\{ -\frac{\mathfrak{H}}{kT} \right\} \left[\gamma - \gamma v \frac{mv}{kT} + \frac{\gamma kT}{m} ((\frac{mv}{kT})^2 - \frac{m}{kT}) \right] = 0$$

Therefore the Klein-Kramers equation has the stationary solution

$$W_{stat}(x,v,t) = Z^{-1} e^{-(mv^2/2 + U(x))/kT}$$

$$Z = \int \int dv dx \, e^{-(mv^2/2 + U(x))/kT}$$

The Klein-Kramers equation can be written in the form of a continuity equation

$$\frac{\partial}{\partial t} W = -\frac{\partial}{\partial x} S_x - \frac{\partial}{\partial v} S_v$$

with the probability current

$$S_x = vW$$

$$S_v = -\left[\gamma v + \frac{1}{m} \frac{\partial U}{\partial x} \right] W - \frac{\gamma kT}{m} \frac{\partial W}{\partial v}$$

7.7 large friction limit - Smoluchowski equation

For large friction constant γ we may neglect the second derivative with time and obtain the stochastic differential equation

$$\dot{x} = \frac{1}{m\gamma}K(x) + \frac{1}{\gamma}F(t)$$

and the corresponding Fokker-Planck equation is the Smoluchowski equation

$$\frac{\partial W(x,t)}{\partial t} = \left[-\frac{1}{m\gamma}\frac{\partial}{\partial x}K(x) + \frac{kT}{m\gamma}\frac{\partial^2}{\partial x^2} \right] W(x,t)$$

which can be written with the mean force potential $U(x)$as

$$\frac{\partial W(x,t)}{\partial t} = \frac{1}{m\gamma}\frac{\partial}{\partial x}\left[kT\frac{\partial}{\partial x} + \frac{\partial U}{\partial x} \right] W(x,t)$$

7.8 Master equation

A very general linear equation for the probability density is the master equation. If the variable x takes on only integer values, it has the form

$$\frac{\partial W_n}{\partial t} = \sum_m \left(w_{m\to n}W_m - w_{n\to m}W_n \right)$$

where W_n is the probability to find the integer value n and $w_{m\to n}$is the transition probability. For a continuous variable summation has to be replaced by integration

$$\frac{\partial W(x,t)}{\partial t} = \int \left(w_{x'\to x}W(x',t) - w_{x\to x'}W(x,t) \right) dx'$$

The Fokker-Planck equation is a special form of the master equation with

$$w_{x'\to x} = \left(-\frac{\partial}{\partial x}D^{(1)}(x) + \frac{\partial^2}{\partial x^2}D^{(2)}(x) \right) \delta(x - x')$$

So far we only discussed Markov processes where the change of probability at time t only depends on the probability at time t. If memory effects are included the generalized Master equation results.

7.9 Kramers theory

The model undelying Kramers theory for the description of chemical activation is shown in the following figure.