Chapter 7

Brownian Motion: Fokker-Planck Equation

The Fokker-Planck equation is the equation governing the time evolution of the probability density of the Brownian particla. It is a second order differential equation and is exact for the case when the noise acting on the Brownian particle is Gaussian white noise. A general Fokker-Planck equation can be derived from the Chapman-Kolmogorov equation, but we also like to find the Fokker-Planck equation corresponding to the time dependence given by a Langevin equation.

The derivation of the Fokker-Planck equation is a two step process. We first derive the equation of motion for the probability density 4/varrho(x, v, t)4 to find the Brownian particle in the interval $(x, x+\mathrm{d}x)$ and $(v, v+\mathrm{d}v)$ at time t for one realization of the random force $\xi(t)$. We then obtain an equation for

$$P(x, v, t) = \langle \varrho(x, v, t) \rangle_\xi$$

i.e. the average of $\varrho(x, v, t)$ over many realizations of the random force. The probability density $P(x, v, t)$ is the macroscopically observed probability density for the Brownian particel.

7.1 Probability flow in phase-space

Let us obtain the probability to find the Brownian particle in the interval $(x, x + \mathrm{d}x$ and $(v, v + \mathrm{d}v)$ at time t. We will consider the space of coordiantes $\boldsymbol{x} = (x, v)$. The Brownian particle is located in the infinitesimal ara $\mathrm{d}x\mathrm{d}v$ with probablity $\varrho(x, v, t)\mathrm{d}x\mathrm{d}v$. The velocity of the particle at point (x, v) is given by $\dot{\boldsymbol{x}} = (\dot{x}, \dot{v})$ and the current density is $\dot{\boldsymbol{x}}\varrho$. Since the Brownian particle must lie somewhere in the phase-space $-\infty < x < \infty,_\infty < v < \infty$ we have the condition

$$\int_{-\infty}^{\infty} \mathrm{d}x \int_{-\infty}^{\infty} \mathrm{d}v \varrho(x, v, t) = 1$$

Let us now consider a finite area, or volume, V_0 in this space. Since the Brownian particle cannot be destroyed a change in the probability contained in V_0 must be due to a flow of probability through the surface S_0 surrounding V_0. Thus

$$\frac{\mathrm{d}}{\mathrm{d}t}\int\int_{V_0} \mathrm{d}x\mathrm{d}v\varrho(x,v,t) = -\int_{S_0} \varrho(x,v,t)\dot{\boldsymbol{x}}\cdot \mathrm{d}\boldsymbol{S}$$

We can now use Gauss theorem to change the surface integral into a volume integral.

$$\int\int_{V_0} \mathrm{d}x\mathrm{d}v\frac{\partial}{\partial t}\varrho(x,v,t) = -\int\int_{V_0} \mathrm{d}x\mathrm{d}v\nabla\cdot(\dot{\boldsymbol{x}}\varrho(x,v,t))$$

Since V_0 is fixed and arbitrary we find the continuity equation

$$\frac{\partial}{\partial t}\varrho(x,v,t) = -\nabla\cdot(\dot{\boldsymbol{x}}\varrho(x,v,t)) = -\frac{\partial}{\partial x}\left(\dot{x}\varrho(x,v,t)\right) - \frac{\partial}{\partial v}\left(\dot{v}\varrho(x,v,t)\right) \tag{7.1}$$

This is the continuity equation in phase-space which just state that probability is conserved.

7.2 Probability flow for Brownian particle

In order to write (7.1) explicitly for a Brownian particle we must know the Langevin equation governing the evolution of the particle. For a particle moving in the presence of a potnetial $V(x)$ the Langevin equations are

$$\begin{aligned}\frac{\mathrm{d}x}{\mathrm{d}t} &= v\\ \frac{\mathrm{d}v}{\mathrm{d}t} &= -\frac{\gamma}{m}v + \frac{1}{m}F(x) + \frac{1}{m}\xi(t)\end{aligned} \tag{7.2}$$

where the force $F(x) = -V'(x)$. Inserting (7.2) into (7.1) gives

$$\begin{aligned}\frac{\partial}{\partial t}\varrho(x,v,t) &= -\frac{\partial}{\partial x}\left(v\varrho(x,v,t)\right) + \frac{\gamma}{m}\frac{\partial}{\partial v}\left(v\varrho(x,v,t)\right) - \frac{1}{m}F(x)\frac{\partial}{\partial v}\varrho(x,v,t)\\ &- \frac{1}{m}\xi(t)\frac{\partial}{\partial v}\varrho(x,v,t) = -L_0\varrho(x,v,t) - L_1(t)\varrho(x,v,t)\end{aligned}$$

where the differential operators L_0 and L_1 are defined as

$$\begin{aligned}L_0 &= v\frac{\partial}{\partial x} - \frac{\gamma}{m} - \frac{\gamma}{m}v\frac{\partial}{\partial v} + \frac{1}{m}F(x)\frac{\partial}{\partial v}\\ L_1 &= \frac{1}{m}\xi(t)\frac{\partial}{\partial v}\end{aligned}$$

Since $\xi(t)$ is a stochastic variable the time evolution of ϱ will be different for each realization of $\xi(t)$. However when we observe an actual Brownian particle we are observing the average effect of the random force on it. Therefore we introduce an observable probability density $P(x,v,t) = \langle\xi(t)\rangle_\xi$.

Let

$$\varrho(t) = \mathrm{e}^{-L_0 t}\sigma(t)$$

then

$$\frac{\partial}{\partial t}\sigma(x,v,t) = -\mathrm{e}^{-L_0 t}L_1(t)\mathrm{e}^{-L_0 t}\sigma(x,v,t) = -V(t)\sigma(x,v,t)$$

This equation has the formal solution

$$\sigma(t) = \exp\left[-\int_0^t \mathrm{d}t' V(t')\right]\sigma(0)$$

which follows since formally

$$\begin{aligned}
\sigma(t) &= \sigma(0) - \int_0^t \mathrm{d}t_1 V(t_1)\sigma(t_1) = \sigma(0) - \int_0^t \mathrm{d}t_1 V(t_1)\sigma(0) + \int_0^t \mathrm{d}t_1 \int_0^{t_1} \mathrm{d}t_2 V(t_1)V(t_2)\sigma(0) + \dots \\
&+ (-1)^n \int_0^t \mathrm{d}t_1 \int_0^{t_1} \mathrm{d}t_2 \cdots \int_0^{t_n} \mathrm{d}t_{n-1} V(t_1)V(t_2)\dots V(t_{n-1})\sigma(0) + \dots \\
&= \sum_{n=0}^{\infty} \frac{(-1)^n}{n!}\left[\int_0^t \mathrm{d}t_1 V(t_1)\right]^n \sigma(0) = \exp\left[-\int_0^t \mathrm{d}t' V(t')\right]\sigma(0)
\end{aligned}$$

The third step follows since by changing the order of integration and then varibles

$$\int_0^t \mathrm{d}t_1 \int_0^{t_1} \mathrm{d}t_2 V(t_1)V(t_2) = \int_0^t \mathrm{d}t_2 \int_{t_2}^t \mathrm{d}t_1 V(t_1)V(t_2) = \int_0^t \mathrm{d}t_1 \int_{t_1}^t \mathrm{d}t_2 V(t_1)V(t_2)$$

so that

$$\int_0^t \mathrm{d}t_1 \int_0^{t_1} \mathrm{d}t_2 V(t_1)V(t_2) = \frac{1}{2}\left[\int_0^t \mathrm{d}t_1 V(t_1)\right]^2$$

Also assume that

$$\int_0^t \mathrm{d}t_1 \int_0^{t_1} \mathrm{d}t_2 \cdots \int_0^{t_n} \mathrm{d}t_{n-1} V(t_1)V(t_2)\dots V(t_{n-1}) = \frac{1}{n!}\left[\int_0^t \mathrm{d}t_1 V(t_1)\right]^n \tag{7.3}$$

then by taking the derivative

$$\begin{aligned}
&\frac{\mathrm{d}}{\mathrm{d}t}\int_0^t \mathrm{d}t_1 \int_0^{t_1} \mathrm{d}t_2 \cdots \int_0^{t_{n+1}} \mathrm{d}t_n V(t_1)V(t_2)\dots V(t_n) \\
&= V(t)\int_0^t \mathrm{d}t_2 \int_0^{t_2} \mathrm{d}t_3 \cdots \int_0^{t_n} \mathrm{d}t_{n+1} V(t_1)V(t_2)\dots V(t_n) \\
&= V(t)\frac{1}{n!}\left[\int_0^t \mathrm{d}t_1 V(t_1)\right]^n = \frac{\mathrm{d}}{\mathrm{d}t}\frac{1}{(n+1)!}\left[\int_0^t \mathrm{d}t_1 V(t_1)\right]^{n+1}
\end{aligned}$$

By induction it therefore follows that (7.3) holds. Taking the average $\langle\cdots\rangle_\xi$ over the Gaussian noice $\xi(t)$ we see that $\langle\sigma(t)\rangle_\xi$ is the characteristic function of the random variable $X(t) = \mathrm{i}\int_0^t \mathrm{d}t_1 V(t_1)$. This must again be a Gaussian variable with $\langle X(t)\rangle_\xi = 0$ and the variance is

$$\langle X(t)^2\rangle = \frac{1}{2}\int_0^t \mathrm{d}t_1 \int_0^t \mathrm{d}t_2 \langle V(t_1)V(t_2)\rangle$$

Since the characteristic function for the Gaussian variable $X(t)$ is $\exp(\mathrm{i}X(t)) = \exp\left(\mathrm{i}\mu_X - \langle X(t)^2\rangle/2\right)$ we find

$$\langle\sigma(t)\rangle_\xi = \exp\left(\frac{1}{2}\int_0^t \mathrm{d}t_1 \int_0^t \mathrm{d}t_2 \langle V(t_1)V(t_2)\rangle\right)\sigma(0) \tag{7.4}$$

This formula is just a special case of a cumulant expansion. The integral in (7.4) becomes

$$\begin{aligned}\frac{1}{2}\int_0^t \mathrm{d}t_1 \int_0^t \mathrm{d}t_2 \langle V(t_1)V(t_2)\rangle_\xi &= \frac{1}{2}\int_0^t \mathrm{d}t_1 \int_0^t \mathrm{d}t_2 \langle \mathrm{e}^{L_0 t_1}\frac{1}{m}\xi(t_1)\frac{\partial}{\partial v}\mathrm{e}^{-L_0 t_1}\mathrm{e}^{L_0 t_2}\frac{1}{m}\xi(t_2)\frac{\partial}{\partial v}\mathrm{e}^{-L_0 t_2}\rangle\xi \\ &= \frac{g}{2m^2}\int_0^t \mathrm{d}t_1 \mathrm{e}^{L_0 t_1}\frac{\partial^2}{\partial v^2}\mathrm{e}^{-L_0 t_1}\end{aligned}$$

Then

$$\frac{\partial}{\partial t}\langle \sigma(x,v,t)\rangle_\xi = \frac{g}{2m^2}\mathrm{e}^{L_0 t}\frac{\partial^2}{\partial v^2}\mathrm{e}^{-L_0 t}\langle \sigma(x,v,t)\rangle_\xi$$

This gives for $\langle \varrho(x,v,t)\rangle_\xi$

$$\frac{\partial}{\partial t}\langle \varrho(x,v,t)\rangle_\xi = -L_0\langle \varrho(x,v,t)\rangle_\xi + \frac{g}{2m^2}\frac{\partial^2}{\partial v^2}\langle \varrho(x,v,t)\rangle_\xi$$

and for the probability distribution

$$\frac{\partial}{\partial t}P(x,v,t) = -v\frac{\partial}{\partial x}P(x,v,t) - \frac{\partial}{\partial v}\left[\left(\frac{\gamma}{m}v - \frac{1}{m}F(x)\right)P(x,v,t)\right] + \frac{g}{2m^2}\frac{\partial^2}{\partial v^2}P(x,v,t) \tag{7.5}$$

This is the Fokker-Planck equation for the probability $P\mathrm{d}x\mathrm{d}v$ to find the Brownian particle in the interval $(x, x+\mathrm{d}x, (v, v+\mathrm{d}v)$ at time t.

We can write the Fokker-Planck equation as a continuity equation

$$\frac{\partial}{\partial t}P(x,v,t) = -\nabla\cdot\boldsymbol{j}$$

where $\nabla = \boldsymbol{e}_x\partial/\partial x + \boldsymbol{e}_v\partial/\partial v$ and the probability current is

$$\boldsymbol{j} = \boldsymbol{e}_x vP - \boldsymbol{e}_v\left[\left(\frac{\gamma}{m}v - \frac{1}{m}F(x)\right)P + \frac{g}{2m^2}\frac{\partial}{\partial v}P\right]$$

7.3 General Fokker-Planck equation

We can obtain the Fokker-Planck equation for a quite general Langevin equation for the dynamics of a set of fluctuating variables

$$\boldsymbol{a} = \{a_1, a_2, \ldots\}$$

We assume a general friction term $\nu_j(a_1, a_2, \ldots) = \nu_j(\boldsymbol{a})$ and assume a Gaussian noise $\xi_j(t)$ where

$$\begin{aligned}\langle \xi_j(t)\rangle &= 0 \\ \langle \xi_i(t_2)\xi_j(t_1)\rangle &= g_{ij}\delta(t_2 - t_{1)}\end{aligned}$$

The Langevin equation becomes

$$\frac{\mathrm{d}}{\mathrm{d}t}a_j(t) = \nu_j(\boldsymbol{a}) + \xi_j(t)$$

or in vector form

$$\frac{\mathrm{d}}{\mathrm{d}t}\boldsymbol{a}(t) = \nu(\boldsymbol{a}) + \xi(t)$$

We ask for the probability distribution

$$P(\boldsymbol{a}, t) = \langle \varrho(\boldsymbol{a}, t) \rangle_\xi$$

Again from conservation of probability

$$\frac{\partial}{\partial t}\varrho(\boldsymbol{a}, t) + \frac{\partial}{\partial \boldsymbol{a}} \cdot \left[\frac{\mathrm{d}\boldsymbol{a}}{\mathrm{d}t}\varrho(\boldsymbol{a}, t)\right] = 0$$

Usin the Langevin equation to solve for $\mathrm{d}\boldsymbol{a}/\mathrm{d}t$ we find

$$\frac{\partial}{\partial t}\varrho(\boldsymbol{a}, t) = \frac{\partial}{\partial \boldsymbol{a}} \cdot (\nu(\boldsymbol{a})\varrho(\boldsymbol{a}, t)) - \frac{\partial}{\partial \boldsymbol{a}} \cdot (\xi(t)\varrho(\boldsymbol{a}, t)) = -\left[L_0 + L_1(t)\right]\varrho(\boldsymbol{a}, t)$$

where

$$\begin{aligned} L_0 &= \left(\frac{\partial}{\partial \boldsymbol{a}} \cdot \nu(\boldsymbol{a})\right) + \nu(\boldsymbol{a}) \cdot \frac{\partial}{\partial \boldsymbol{a}} \\ L_1(t) &= \xi(t) \cdot \frac{\partial}{\partial \boldsymbol{a}} \end{aligned}$$

Following the steps as above we find

$$\frac{\partial}{\partial t}P(\boldsymbol{a}, t) = -\frac{\partial}{\partial \boldsymbol{a}} \cdot (\nu(\boldsymbol{a})P(\boldsymbol{a}, t)) + \frac{1}{2}\frac{\partial}{\partial \boldsymbol{a}} \cdot \boldsymbol{g} \cdot \frac{\partial}{\partial \boldsymbol{a}}P(\boldsymbol{a}, t) \tag{7.6}$$

Here $\boldsymbol{g}$ is a tensor with elements g_{ij}.

Example

Our previous result can be obtained as a special case of (7.6). The Langevin equations are

$$\begin{aligned} \frac{\mathrm{d}x}{\mathrm{d}t} &= v \\ \frac{\mathrm{d}v}{\mathrm{d}t} &= -\frac{\gamma}{m}v + \frac{1}{m}F(x) + \frac{1}{m}\xi(t) \end{aligned}$$

where

$$\langle \xi(t_2)\xi(t_{1)}\rangle = 2\gamma k_{\mathrm{B}}T\delta(t_2 - t_1)$$

Then

$$\begin{aligned} \boldsymbol{a} &= \begin{pmatrix} x \\ y \end{pmatrix}, \qquad \nu(\boldsymbol{a}) = \begin{pmatrix} v \\ -\frac{\gamma}{m}v + \frac{1}{m}F(x) \end{pmatrix} \\ \xi(t) &= \begin{pmatrix} 0 \\ \frac{1}{m}\xi(t) \end{pmatrix}, \qquad \boldsymbol{g} = \begin{pmatrix} 0 & 0 \\ 0 & \frac{2\gamma k_{\mathrm{B}}T}{m^2} \end{pmatrix} \end{aligned}$$

The Fokker-Planck equation becomes

$$\frac{\partial}{\partial t}P(x, v, t) = -\frac{\partial}{\partial x}\left[vP(x, v, t)\right] - \frac{\partial}{\partial v}\left[\left(-\frac{\gamma}{m}v + \frac{1}{m}F(x)\right)P(x, v, t)\right] + \frac{\gamma k_{\mathrm{B}}T}{m^2}\frac{\partial^2}{\partial v^2}P(x, v, t)$$

The equilibrium distribution $\partial/\partial t P(x,v,t)=0$ is the solution to

$$-\frac{\partial}{\partial x}\left[vP(x,v,t)\right]-\frac{\partial}{\partial v}\left[\left(-\frac{\gamma}{m}v+\frac{1}{m}F(x)\right)P(x,v,t)\right]+\frac{\gamma k_{\mathrm{B}}T}{m^2}\frac{\partial^2}{\partial v^2}P(x,v,t)=0$$

The Hamiltonian of the Brownian particle is

$$H=\frac{1}{2}mv^2+V(x)$$

i.e we can write the equilibrium condition as

$$-\frac{\partial}{\partial x}\left[\frac{\partial H}{\partial v}P(x,v,t)\right]+\frac{1}{m}\frac{\partial}{\partial v}\left[\frac{\partial H}{\partial x}P(x,v,t)\right]+\frac{\gamma}{m}\frac{\partial}{\partial v}\left[\frac{\partial H}{\partial v}P(x,v,t)+\frac{k_{\mathrm{B}}T}{m}\frac{\partial}{\partial v}P(x,v,t)\right]=0$$

Assuming that

$$P=f(H)$$

we find

$$-\frac{\partial}{\partial x}\left[\frac{\partial H}{\partial v}f(H)\right]+\frac{1}{m}\frac{\partial}{\partial v}\left[\frac{\partial H}{\partial x}f(H)\right]+\frac{\gamma}{m}\frac{\partial H}{\partial v}\left[\frac{\partial H}{\partial v}f(H)+\frac{k_{\mathrm{B}}T}{m}\frac{\partial H}{\partial v}f'(H)\right]=0$$

This equation is satisfied if

$$\begin{aligned}\frac{\partial^2 H}{\partial x\partial v}&=0\\ f(H)+k_{\mathrm{B}}Tf'(H)&=0\end{aligned}$$

with the solution

$$f(h)=\frac{1}{Z}\mathrm{e}^{-\beta H},\quad \beta=\frac{1}{k_{\mathrm{B}}T}$$

The Fokker-Planck equation is therefore consistent with a Boltzmann equilibrium distribution.

7.4 Averages and adjoint operators

Sometimes we want the full solution of a Fokker-Planck equation, but sometimes we are interested only in certain averages. These can be found by two distinct but equivalent procedures analogous to the Schrödinger- Heisenberg duality in quantum mechanics.

First we can follow the evolution of some initial state $P(\boldsymbol{a},0)$ by solving the Fokker-Planck equation

$$\frac{\partial}{\partial t}P(\boldsymbol{a},t)=-LP(\boldsymbol{a},t)$$

where the operator L is given by

$$L=\frac{\partial}{\partial\boldsymbol{a}}\cdot\boldsymbol{v}(\boldsymbol{a})-\frac{\partial}{\partial\boldsymbol{a}}\cdot\boldsymbol{D}\cdot\frac{\partial}{\partial\boldsymbol{a}}$$

with $\boldsymbol{v}$ a streaming term and $\boldsymbol{D}$ a diffusion tensor. The Fokker-Planck equation has the formal operator solution

$$P(\boldsymbol{a},t)=\mathrm{e}^{-Lt}P(\boldsymbol{a},0)$$

This can be used to obtain the average of any dynamical property $A(\boldsymbol{a})$

$$\langle A(t)\rangle = \int \mathrm{d}\boldsymbol{a} A(\boldsymbol{a}) P(\boldsymbol{a},t) = \int \mathrm{d}\boldsymbol{a} A(\boldsymbol{a}) \mathrm{e}^{-Lt} P(\boldsymbol{a},0) \tag{7.7}$$

We introduce the adjoint operator $L^\dagger$ defined by

$$\int \mathrm{d}\boldsymbol{a} \phi^*(\boldsymbol{a}) L \psi(\boldsymbol{a}) = \left(\int \mathrm{d}\boldsymbol{a} \psi^*(\boldsymbol{a}) L^\dagger \phi(\boldsymbol{a}) \right)^*$$

or $\langle \phi | L \psi \rangle = \langle L^\dagger \phi | \psi \rangle^*$. By partial integration we find

$$L^\dagger = -\boldsymbol{v}(\boldsymbol{a}) \cdot \frac{\partial}{\partial \boldsymbol{a}} - \frac{\partial}{\partial \boldsymbol{a}} \cdot \boldsymbol{D} \cdot \frac{\partial}{\partial \boldsymbol{a}}$$

The average in (7.7) can be obtained by partial integration

$$\begin{aligned} \langle A(t)\rangle &= \int \mathrm{d}\boldsymbol{a} A(\boldsymbol{a}) \mathrm{e}^{-Lt} P(\boldsymbol{a},0) = \sum_{n=0}^{\infty} \frac{(-t)^n}{n!} \int \mathrm{d}\boldsymbol{a} A(\boldsymbol{a}) L^n P(\boldsymbol{a},0) \\ &= \sum_{n=0}^{\infty} \frac{(-t)^n}{n!} \int \mathrm{d}\boldsymbol{a} \left[(L^\dagger)^n A(\boldsymbol{a}) \right] P(\boldsymbol{a},0) = \int \mathrm{d}\boldsymbol{a} \left[\mathrm{e}^{-L^\dagger t} A(\boldsymbol{a}) \right] P(\boldsymbol{a},0) \end{aligned}$$

This defines the time-dependent variable

$$A(\boldsymbol{a},t) = \mathrm{e}^{-L^\dagger t} A(\boldsymbol{a})$$

The equation of motion for the dynamical variable $A(\boldsymbol{a},t)$ becomes

$$\frac{\partial}{\partial t} A(\boldsymbol{a},t) = -L^\dagger A(\boldsymbol{a},t) = \left(-\boldsymbol{v}(\boldsymbol{a}) \cdot \frac{\partial}{\partial \boldsymbol{a}} - \frac{\partial}{\partial \boldsymbol{a}} \cdot \boldsymbol{D} \cdot \frac{\partial}{\partial \boldsymbol{a}} \right) A(\boldsymbol{a},t) \tag{7.8}$$

7.5 Green's function

A formal solution of the Fokker-Planck equation uses the operator e^{-Lt}. A somewhat more explicit solution uses the Green's function $G(\boldsymbol{a},t|\boldsymbol{a}_0)$

$$P(\boldsymbol{a},t) = \int \mathrm{d}\boldsymbol{a}_0 G(\boldsymbol{a},t) P(\boldsymbol{a}_0,0)$$

The Green's function is the conditional probability to find the systems in state $\boldsymbol{a}$ at time t when is started at $\boldsymbol{a}_0$ at time $t=0$. It satisfies the equation

$$\begin{aligned} \frac{\partial}{\partial t} G(\boldsymbol{a},t|\boldsymbol{a}_0) &= -LG(\boldsymbol{a},t|\boldsymbol{a}_0) \\ G(\boldsymbol{a},0|\boldsymbol{a}_0) = \delta(\boldsymbol{a}-\boldsymbol{a}_0) & \end{aligned}$$

When the streaming term $\boldsymbol{v}(\boldsymbol{a})$ is linear in $\boldsymbol{a}$

$$\boldsymbol{v}(\boldsymbol{a}) = \boldsymbol{C} \cdot \boldsymbol{a}$$

and the diffusion tensor $\boldsymbol{D}$ is constant independent of $\boldsymbol{a}$, the Green function can be found explicitly by the Fourier transform

$$\hat{G}(\boldsymbol{k},t|\boldsymbol{a}_0) = \int \mathrm{d}\boldsymbol{a} \mathrm{e}^{\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{a}} G(\boldsymbol{a},t|\boldsymbol{a}_0)$$

Then

$$\frac{\partial}{\partial t}\hat{G}(\boldsymbol{k},t|\boldsymbol{a}_0) = \boldsymbol{k}\cdot\boldsymbol{C}\cdot\frac{\partial}{\partial \boldsymbol{k}}\hat{G}(\boldsymbol{k},t|\boldsymbol{a}_0) - \boldsymbol{k}\cdot\boldsymbol{D}\cdot\boldsymbol{k}\hat{G}(\boldsymbol{k},t|\boldsymbol{a}_0)$$

which follows since a derivatives of $\boldsymbol{a}$ gives a factor $-\mathrm{i}\boldsymbol{k}$ and multiplication by $\boldsymbol{a}$ gives a derivative with repsect ot . Dividing by $\hat{G}(\boldsymbol{k},t|\boldsymbol{a}_0)$ gives

$$\frac{\partial}{\partial t}\ln\hat{G}(\boldsymbol{k},t|\boldsymbol{a}_0) = \boldsymbol{k}\cdot\boldsymbol{C}\cdot\frac{\partial}{\partial \boldsymbol{k}}\ln\hat{G}(\boldsymbol{k},t|\boldsymbol{a}_0) - \boldsymbol{k}\cdot\boldsymbol{D}\cdot\boldsymbol{k}$$

If we make the Gaussian ansatz

$$\ln\hat{G}(\boldsymbol{k},t|\boldsymbol{a}_0) = \mathrm{i}\boldsymbol{m}(t)\cdot\boldsymbol{k} - \frac{1}{2}\boldsymbol{k}\cdot\boldsymbol{S}(t)\cdot\boldsymbol{k}$$

with the unknown vector $\boldsymbol{m}(t)$ and tensor $\boldsymbol{S}(t)$ we find

$$\mathrm{i}\frac{\mathrm{d}}{\mathrm{d}t}\boldsymbol{m}(t)\cdot\boldsymbol{k} - \frac{1}{2}\boldsymbol{k}\cdot\frac{\mathrm{d}}{\mathrm{d}t}\boldsymbol{S}(t)\cdot\boldsymbol{k} = \mathrm{i}\boldsymbol{k}\cdot\boldsymbol{C}\cdot\boldsymbol{m}(t) - \frac{1}{2}\boldsymbol{k}\cdot\boldsymbol{C}\cdot\boldsymbol{S}(t)\cdot\boldsymbol{k} - \frac{1}{2}\boldsymbol{k}\cdot\boldsymbol{S}(t)\cdot\boldsymbol{C}^T\cdot\boldsymbol{k} - \boldsymbol{k}\cdot\boldsymbol{D}\cdot\boldsymbol{k}$$

Identifying equal powers of $\boldsymbol{k}$ this gives

$$\begin{aligned}\frac{\mathrm{d}}{\mathrm{d}t}\boldsymbol{m}(t) &= \boldsymbol{C}\cdot\boldsymbol{m}(t)\\ \frac{\mathrm{d}}{\mathrm{d}t}\boldsymbol{S}(t) &= \boldsymbol{C}\cdot\boldsymbol{S}(t) + \boldsymbol{S}(t)\cdot\boldsymbol{C}^T + 2\boldsymbol{D} \qquad (7.9)\end{aligned}$$

From the initial value $\ln\hat{G}(\boldsymbol{k},0|\boldsymbol{a}_0) = \mathrm{i}\boldsymbol{k}\cdot\boldsymbol{a}_0$ we find

$$\boldsymbol{m}(0) = \boldsymbol{a}_0, \quad \boldsymbol{S}(0) = 0$$

The solution to (7.9) can then be written

$$\begin{aligned}\boldsymbol{m}(t) &= \mathrm{e}^{\boldsymbol{C}t}\cdot\boldsymbol{a}_0 \qquad (7.10)\\ \boldsymbol{S}(t) &= 2\int_0^t \mathrm{d}s\mathrm{e}^{\boldsymbol{C}(t-s)t}\cdot\boldsymbol{D}\cdot\mathrm{e}^{\boldsymbol{C}^T(t-s)t} \qquad (7.11)\end{aligned}$$

which one can easily verify by substitution. These quantities have a simple interpretation in terms of averages and mean squared fluctuations since

$$\left(\frac{\partial}{\partial \boldsymbol{k}}\hat{G}(\boldsymbol{k},t|\boldsymbol{a}_0)\right)_{\boldsymbol{k}=0} = \int \mathrm{d}\boldsymbol{a}\mathrm{i}\boldsymbol{a}G(\boldsymbol{a},t|\boldsymbol{a}_0) = \mathrm{i}\langle\boldsymbol{a}\rangle = \mathrm{i}\boldsymbol{m}(t)$$

and

$$\left(\frac{\partial}{\partial \boldsymbol{k}}\frac{\partial}{\partial \boldsymbol{k}}\hat{G}(\boldsymbol{k},t|\boldsymbol{a}_0)\right)_{\boldsymbol{k}=0} = -\int \mathrm{d}\boldsymbol{a}\boldsymbol{a}\boldsymbol{a}G(\boldsymbol{a},t|\boldsymbol{a}_0) = -\langle\boldsymbol{a}\boldsymbol{a}\rangle = -\boldsymbol{m}(t)\boldsymbol{m}(t) - \boldsymbol{S}(t)$$

and

$$\boldsymbol{S}(t) = \langle \boldsymbol{a}\boldsymbol{a}\rangle - \langle \boldsymbol{a}\rangle\langle \boldsymbol{a}\rangle = \langle [\boldsymbol{a} - \langle \boldsymbol{a}\rangle]\,[\boldsymbol{a} - \langle \boldsymbol{a}\rangle]\rangle$$

Since $G(\boldsymbol{k}, t|\boldsymbol{a}_0)$ is a Gaussian the inverse transform also give a Gaussian and follows the same lines as we did before in connection with the multivariate Gaussian distribution and we find

$$G(\boldsymbol{a}, t|\boldsymbol{a}_0) = \left[\frac{1}{2\pi \det \boldsymbol{S}(t)} =\right]^{1/2} \exp\left(-\frac{1}{2}\,[\boldsymbol{a} - \boldsymbol{m}(t)]\cdot \boldsymbol{S}^{-1}(t)\cdot [\boldsymbol{a} - \boldsymbol{m}(t)]\right) \tag{7.12}$$

7.6 Examples

Free Brownian particle

For a free Brownian particle we have the Langevin equation

$$m\frac{\mathrm{d}v}{\mathrm{d}t} = -\gamma v + \xi(t)$$

Then with vector notation

$$\boldsymbol{a}\boldsymbol{e}_v, \quad \boldsymbol{v}(\boldsymbol{a}) = -\frac{\gamma}{m}v\boldsymbol{e}_v, \quad \Xi = \frac{1}{m}\xi(t)\boldsymbol{e}_v, \quad \boldsymbol{g} = \frac{2\gamma k_\mathrm{B}T}{m^2}\boldsymbol{I}$$

The general Fokker-Planck equation (7.6)

$$\frac{\partial}{\partial t}P(\boldsymbol{a}, t) = -\frac{\partial}{\partial \boldsymbol{a}}\cdot(\nu(\boldsymbol{a})P(\boldsymbol{a}, t)) + \frac{1}{2}\frac{\partial}{\partial \boldsymbol{a}}\cdot \boldsymbol{D}\cdot\frac{\partial}{\partial \boldsymbol{a}}P(\boldsymbol{a}, t)$$

becomes

$$\frac{\partial}{\partial t}P(v, t) = -\frac{\partial}{\partial v}\left(-\frac{\gamma}{m}vP(v, t)\right) + \frac{\gamma k_\mathrm{B}T}{m^2}\frac{\partial^2}{\partial v^2}P(v, t) \tag{7.13}$$

This is a linear equation and we can directly obtain the solution for the Green function from (7.12). The moments are obtained from (7.11) with $\boldsymbol{C} = -\gamma/m\boldsymbol{I}$. Therefore

$$\boldsymbol{m}(t) = \mathrm{e}^{\boldsymbol{C}t}\cdot v_0\boldsymbol{e}_v = \mathrm{e}^{-t/\tau_B}v_0\boldsymbol{e}_v = m(t)\boldsymbol{e}_v, \quad \tau_B = \frac{m}{\gamma}$$

Also

$$\boldsymbol{S}(t) = 2\int_0^t \mathrm{d}s\mathrm{e}^{\boldsymbol{C}(t-s)}\cdot\boldsymbol{D}\cdot\mathrm{e}^{\boldsymbol{C}^T(t-s)t} = 2\int_0^t \mathrm{d}s\mathrm{e}^{-2(t-s)/\tau_B}\frac{\gamma k_\mathrm{B}T}{m^2}\boldsymbol{I} = \frac{k_\mathrm{B}T}{m}\boldsymbol{I}\left[1 - \mathrm{e}^{-2t/\tau_B}\right] = S(t)\boldsymbol{I}$$

The Green function is then

$$G(v, t|v_0) = \left[\frac{1}{2\pi S(t)}\right]^{1/2}\exp\left(-\frac{(v - m(t))^2}{2S(t)}\right) = \sqrt{\frac{\beta m}{2\pi\left[1 - \mathrm{e}^{-2t/\tau_B}\right]}}\exp\left(-\frac{\beta m}{2}\frac{\left(v - v_0\mathrm{e}^{-t/\tau_B}\right)^2}{\left[1 - \mathrm{e}^{-2t/\tau_B}\right]}\right)$$

We see that

$$G(v, t|v_0) \to \left(\frac{\beta m}{2\pi}\right)^{1/2}\mathrm{e}^{-\beta m v^2/2}, \quad t \to \infty$$

i.e a Maxwell-Boltzmann distribution as expected.

Diffusion controlled reactions

The rate of chemical reactions in condensed phases is often determined by the rate at which the reacting species get close enough together to react. Once they get within some critical distance of each other, the making and breaking of chemical bonds takes place rapidly. The process by which the reactive particles reach that critical distance is the brownian motion of the particles themselves. Such reactions are called *diffusion controlled reactions* since the diffusive Brownian motion of the species is the rate determining step.

There are two reacting species A and B in solution. At first we consider B to be stationary and species A to diffuse with diffusion constant D_A. When an A particle comes within a distance R of a B particle the particles react and effectively disappear from the problem. For simplicity the particles are assumed to be spherical. We also assume that there are no forces between A and B when they are farther apart than R.

Let the concentration of A and B particles be n_A and n_B respectively. The rate at which A particles disappear is then n_B times the flux of A particles across the sphere of radius R surrounding a B particle. If $\boldsymbol{j}$ be the current density of A particles we have

$$\text{rate} = -n_B \int \boldsymbol{j} \cdot \mathrm{d}\boldsymbol{S} = 4\pi R^2 n_B j_r(R,t)$$

where j_r is the radial component of $\boldsymbol{j}$. The integration is over the surface of a sphere of radius R about the stationary B particle, and the current $\boldsymbol{j}$ is supposd not to vary on the surface $\boldsymbol{S}$.

The current is given by Ficks law

$$\boldsymbol{j} = -D_A \nabla n_A$$

and the continuity equation for n_A leads to the diffusion equation

$$\frac{\partial n_A}{\partial t} = D_A \nabla^2 n_A = D_A \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2 \frac{\partial n_A}{\partial r}\right)$$

In the last step we have expressed the Laplacian in terms of spherical coordinates and used the spherical symmetry in the problem. The initial and boundary conditions are

$$\begin{aligned} n_A(r,t=0) &= n_A^0 \\ n_A(r,t) &\rightarrow n_A^0, \quad r \rightarrow \infty \\ n_A(R,t) &= 0, \quad r = R \end{aligned}$$

The second condition requires that the concentration very far from the sink (B particle) is not perturbed by the sink. The last condition insures that the sphere of radius R is a sink. At $r = R$ the A particle reacts and it is then no longer an A particle.

We define a new function

$$n_A(r,t) = \frac{u(r,t)}{r}$$

then

$$r^2 \frac{\partial n_A}{\partial r} = -u(r,t) + r\frac{\partial}{\partial r}u(r,t)$$

and so $u(r,t)$ satisfies the simple diffusion equation

$$\frac{\partial}{\partial t}u(r,t) = D_A \frac{\partial^2}{\partial r^2}u(r,t) \tag{7.14}$$

and the boundary conditions are

$$\begin{aligned} u(r,t) &\rightarrow n_A^0 r \quad r \rightarrow \infty \\ u(R,t) &= 0 \end{aligned}$$

The solution to (7.15) with the initial condition $U(r,0) = n_A^0 r, r > R$ is

$$u(r,t) = \int_R^\infty \mathrm{d}r' G(r,t|r',0) n_A^0 r'$$

where the Green function$G$ satisfies (7.14) with a $\delta(r - r')$ initial condition and boundary condition

$$G(R,t|r') = 0$$

For a homogeneous medium the diffusion equation has the solution

$$G_0(r,t|r',0) = \left(\frac{1}{4\pi Dt}\right)^{1/2} \mathrm{e}^{-(r-r\,')^2/2Dt}$$

To satisfy the boundary condition we introduce a mirror source in $= s$ and choose s so that the boundary condition is satisfied, i.e.

$$G(r,t|r',0) = G_0(r,t|r',0) - G_0(r,t|s,0)$$

Then $G(R,t|r\,',0) = 0$ provided

$$(R - r')^2 = (R - s)^2, \quad \Rightarrow \quad s = \begin{cases} r\,' \\ 2R - r\,' \end{cases}$$

Therefore the Green-function which satisfies the boundary condition at $r = R$ is

$$G(r,t|r',0) = \left(\frac{1}{4\pi Dt}\right)^{1/2} \left[\mathrm{e}^{-(r-r')^2/2Dt} - \mathrm{e}^{-(r+r'-2R)^2/2Dt}\right]$$

The solution for the density of A particles $n_A(r,t)$ in the region $r > R$ therefore becomes

$$n_A(r,t) = \frac{n_A^0}{r}\left(\frac{1}{4\pi Dt}\right)^{1/2} \int_R^\infty \mathrm{d}r' \left[\mathrm{e}^{-(r-r')^2/2Dt} - \mathrm{e}^{-(r+r'-2R)^2/2Dt}\right] r'$$

Then by a change of variables

$$\begin{aligned} n_A(r,t) &= \frac{n_A^0}{\sqrt{2\pi} r}\left[\int -\infty^{\frac{r-R}{\sqrt{2Dt}}} \mathrm{d}\xi \mathrm{e}^{-\xi^2}\left(r - \sqrt{2Dt}\xi\right) - \int \frac{r-R}{\sqrt{2Dt}}^\infty \mathrm{d}\xi \mathrm{e}^{-\xi^2}\left(\sqrt{2Dt}\xi + 2R - r\right)\right] \\ &= n_A^0\left[1 - \frac{2R}{r}\frac{1}{\sqrt{2\pi}}\int \frac{r-R}{\sqrt{2Dt}}^\infty \mathrm{d}\xi \mathrm{e}^{-\xi^2}\right] = n_A^0\left[1 - \frac{R}{r} + \frac{R}{r}\frac{2}{\sqrt{2\pi}}\int 0^{\frac{r-R}{\sqrt{2Dt}}} \mathrm{d}\xi \mathrm{e}^{-\xi^2}\right] \end{aligned}$$

The radial component of the current for particle A then becomes

$$j_r(r,t) = -D_A \frac{\partial}{\partial r} n_A(r,t) = -D_A n_A^0 \left[\frac{R}{r^2} + \frac{R}{r} \frac{1}{\sqrt{\pi D t}} \mathrm{e}^{-(r-R)^2/2Dt} - \frac{R}{r^2} \frac{2}{\sqrt{2\pi}} \int 0^{\frac{r-R}{\sqrt{2Dt}}} \mathrm{d}\xi \mathrm{e}^{-\xi^2} \right]$$

and so

$$j_r(R,t) - D_A n_A^0 \left[\overline{R} + \frac{1}{\sqrt{\pi D t}} \right]$$

This gives the rate

$$\text{rate} = D_A n_A n_B 4\pi R \left[\overline{R} + \frac{1}{\sqrt{\pi D t}} \right] = k_{AB} n_A n_B$$

with the rate constant

$$k_{AB} = D_A 4\pi R \left[\overline{R} + \frac{1}{\sqrt{\pi D t}} \right]$$

The time dependent correction is of little interest experimentally.

In reality the B particles move around just as do the A particles. We can take account of this motion by replacing D_A with $D_A + D_B$. Then wth the Stokes-Einstein relation

$$D_i = \frac{k_{\mathrm{B}} T}{6\pi\eta Ri}$$

we find

$$k_{AB} = 4\pi R(D_A + D_B) = \frac{2k_{\mathrm{B}} T}{3\eta} \frac{(R_A + R_B)^2}{R_A R_B}$$