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BROWNIAN DYNAMICS
Lecture notes

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Brownian dynamics

Brownian motion is the observed erratic motion of particles suspended in a fluid (a liquid or a gas) resulting from their collision with the rapidly moving atoms or molecules in the gas or liquid.

This transport phenomenon is named after the botanist Robert Brown. In 1827, while examining grains of pollen in water under a microscope, Brown observed that minute particles ejected from the pollen grains executed a continuous erratic motion. He was not able to determine the mechanisms that caused this motion. One suggestion was that it was "life-related", but by observing the same type of erratic motion also for particles of inorganic matter he was able to rule out that possibility.

It took nearly 100 years before Albert Einstein explained in detail how the motion that Brown had observed was a result of the particles being moved by collisions with individual water molecules. The work was published by Einstein 1905, in one of his three famous papers from that year. The paper contained predictions that could be tested experimentally and Jean Babtiste Perrin verified Einsteins predictions experimentally 1908. The same year Paul Langevin presented an alternative way to study Brownian motion, somewhat more straightforward compared with Einsteins treatment.

The theory by Einstein and its experimental verification was important, it served as convincing evidence that atoms and molecules exist, a validity not universally recognized at that time. It also gave considerable insight into the connection between fluctuations and dissipation of energy for systems in thermal equilibrium. Brownian dynamics is an example of a stochastic process and has served as model system for the development of the theory of noise.

Contents

1 Langevin's equation

Consider a particle with mass m moving in a fluid. For simplicity we will consider motion in one dimension. To a first approximation we assume that the interaction with the fluid can be described by a friction or damping force, proportional to the velocity $v(t)$,

$$m\frac{d}{dt}v(t) = -\alpha v(t)$$

This was used by Stokes 1851 to describe the motion of a particle in a viscous fluid. The friction force describes the average effect from the collisions of the molecular fluid particles. Using macroscopic hydrodynamics Stokes showed that for a spherical particle

$$\alpha = 6\pi\nu R \tag{1}$$

where ν is the viscosity of the fluid and R the radius of the particle. By solving the equation of motion an exponential decay for the velocity

$$v(t) = v(0)e^{-(\alpha/m)t}$$

is obtained. This can not be true in the case of Brownian motion, because we do not describe the erratic motion of the particle. This is due that Brown considered quite small particles and fluctuations of the force become important. We therefore add a fluctuation or stochastic part of the force $f(t) = m\ \xi(t)$ to the equation of motion. This defines the **Langevin's equation**

$$\frac{d}{dt}v(t) = -\eta v(t) + \xi(t) \tag{2}$$

where $\eta = \alpha/m$ will be denoted the **friction coefficient**. To proceed we need to give some properties of the stochastic force. It changes in a very erratic and fast way and it depends on the microscopic motions of the surrounding fluid molecules. We introduce a time-average

$$\langle A(t)\rangle = \frac{1}{\tau_0}\int_{t-\tau_0/2}^{t+\tau_0/2} A(s)ds \tag{3}$$

where τ_0 is a short time scale. It is assumed to be long compared with an individual molecular collision time but short compared with the velocity relaxation time $\tau = 1/\eta$,

$$\tau_0 \ll 1/\eta$$

We assume that the average of the stochastic force is zero

$$\langle\xi(t)\rangle = 0 \tag{4}$$

and that for time differences larger than τ_0 the stochastic force is uncorrelated in time

$$\left\langle\xi(t)\xi(t')\right\rangle = 0 \quad \text{for } \mid t - t' \mid > \tau_0$$

The Brownian motion model is not supposed to describe the very rapid motion on the time scale τ_0 and therefore we may take the limit $\tau_0 \to 0$ and write

$$\left\langle \xi(t)\xi(t') \right\rangle = q\delta(t - t') \tag{5}$$

Furthermore, $\xi(t)$ is assumed to be based on the sum of a large number of independent molecular collisions and $\xi(t)$ can be modelled as a Gaussian random variable. We have introduced the averaging as a time-average in Eqn (3). In some situations it is more convenient to view the average $\langle \ldots \rangle$ as an ensemble average, as in the Eqs (4) and (5). We will not make any clear distinction between these two types of averaging procedures.

The Langevin's equation, defined in Eqn (2), together with the properties of the stochastic force in Eqs (4) and (5) can be used to solve for the Brownian dynamics. Consider a particle with the initial velocity v_0 moving according to Eqn (2). Direct solution leads to

$$v(t) = v_0 e^{-\eta t} + \int_0^t ds\ e^{-\eta(t-s)}\xi(s) \tag{6}$$

Consider now an ensemble of particles all with initial velocity v_0. If we now make an average over the ensemble we get

$$\langle v(t) \rangle = v_0 e^{-\eta t}$$

i.e. the average velocity decays exponentially to zero. The information of the initial velocity v_0 fades away and is essentially lost for times larger than the relaxation time $\tau = 1/\eta$. The velocity squared is given by

$$\begin{aligned} v^2(t) &= v_0^2 e^{-2\eta t} + 2v_0 e^{-\eta t} \int_0^t ds\ e^{-\eta(t-s)}\xi(s) \\ &+ \int_0^t ds \int_0^t ds'\ e^{-\eta(t-s)} e^{-\eta(t-s')}\xi(s)\xi(s') \end{aligned}$$

and its average by

$$\begin{aligned} \left\langle v^2(t) \right\rangle &= v_0^2 e^{-2\eta t} + \int_0^t ds \int_0^t ds'\ e^{-\eta(t-s)} e^{-\eta(t-s')} q\delta(s - s') \\ &= v_0^2 e^{-2\eta t} + \frac{q}{2\eta}\left[1 - e^{-2\eta t}\right] \end{aligned}$$

Here again the initial information fades away but the average of $v^2(t)$ does not approach zero, but the finite value $q/2\eta$. This is a measure of the erratic motion seen by Brown. We know from the **equipartition theorem** that if the particle is moving in a fluid at the temperature T

$$\left\langle \frac{mv^2}{2} \right\rangle = \frac{k_B T}{2} \tag{7}$$

at thermal equilibrium. This implies that $\langle v^2(t) \rangle$ should approach k_BT/m for large times and

$$q = 2\eta \frac{k_BT}{m} \tag{8}$$

This is a special case of the famous **Fluctuation-Dissipation theorem**. It relates fluctuations, described by q, to dissipation, described by η. Any system that shows dissipative effects will also show fluctuations and there is a relation between the two.

We can now summarize the solution of Langevin's equation for the time dependence of the mean value $\mu(t)$ and the variance $\sigma^2(t)$ of an ensemble of particles all with the initial velocity v_0 as

$$\begin{aligned} \mu(t) &\equiv \langle v(t) \rangle = v_0 e^{-\eta t} && (9) \\ \sigma^2(t) &\equiv \left\langle [v(t) - \langle v(t) \rangle]^2 \right\rangle = \frac{k_BT}{m} \left[1 - e^{-2\eta t}\right] && (10) \end{aligned}$$

Algorithm BD1 A simple algorithm for solving Langevin's equation can be derived by making the direct discretisation of Eqn (2) according to

$$\frac{v_{n+1} - v_n}{\Delta t} = -\eta v_n + \xi_n$$

or

$$v_{n+1} = (1 - \eta \Delta t) v_n + \Delta t \; \xi_n$$

The strength of the stochastic force also has to be determined. Using

$$\delta(t - t') \to \frac{1}{\Delta t} \delta_{n,n'}$$

we have

$$\langle \xi_n \xi_{n'} \rangle = \frac{2\eta k_BT}{m\Delta t} \delta_{n,n'}$$

and

$$v_{n+1} = (1 - \eta \Delta t) v_n + \sqrt{(2\eta k_BT \Delta t/m)} \; \mathcal{G}_n \tag{11}$$

where $\mathcal{G}_n$ is a Gaussian random number with zero mean, unit variance and uncorrelated in time $\langle \mathcal{G}_n \mathcal{G}_{n'} \rangle = \delta_{n,n'}$.

A better algorithm can be derived by using the analytical solution of the Langevin's equation. We have

$$\begin{aligned} v(t + \Delta t) &= v(0) e^{-\eta (t+\Delta t)} + \int_0^{t+\Delta t} ds \; e^{-\eta(t+\Delta t - s)} \xi(s) \\ &= v(t) e^{-\eta \Delta t} + \zeta_v(t) && (12) \end{aligned}$$

with

$$\zeta_v(t) = \int_t^{t+\Delta t} ds \; e^{-\eta(t+\Delta t-s)} \xi(s) \tag{13}$$

This implies that $\langle \zeta_v(t) \rangle = 0$ and

$$\begin{aligned} \langle \zeta_v^2(t) \rangle &= \int_t^{t+\Delta t} ds\ e^{-\eta(t+\Delta t-s)} \int_t^{t+\Delta t} ds'\ e^{-\eta(t+\Delta t-s')} \langle \xi(s)\xi(s') \rangle \\ &= 2\eta \frac{k_B T}{m} \int_t^{t+\Delta t} ds\ e^{-2\eta(t+\Delta t-s)} = \frac{k_B T}{m} \left[1 - e^{-2\eta\Delta t}\right] \end{aligned} \tag{14}$$

Algorithm BD2 The recommended algorithm for solving Langevin's equation is therefore

$$v_{n+1} = c_0 v_n + v_{th}\sqrt{1 - c_0^2}\ \mathcal{G}_n \tag{15}$$

where

$$c_0 = e^{-\eta\Delta t} \quad \text{and} \quad v_{th} = \sqrt{k_B T/m}$$

and $\mathcal{G}_n$ is a Gaussian random number with zero mean, unit variance and uncorrelated in time $\langle \mathcal{G}_n \mathcal{G}_{n'} \rangle = \delta_{n,n'}$.

Notice that in the limit $\eta\Delta t \to 0$ algorithm **BD1** is recovered. Algorithm **BD2** is more accurate for large time steps Δt. In Fig. 1 we show the result for 5 trajectories using the algorithm **BD2**. The initial velocity is $v_0 = 5v_{th}$ and in the figure we also show the mean value $\mu(t)$ and the standarddeviation $\sigma(t)$ according to Eqs (9) and (10).

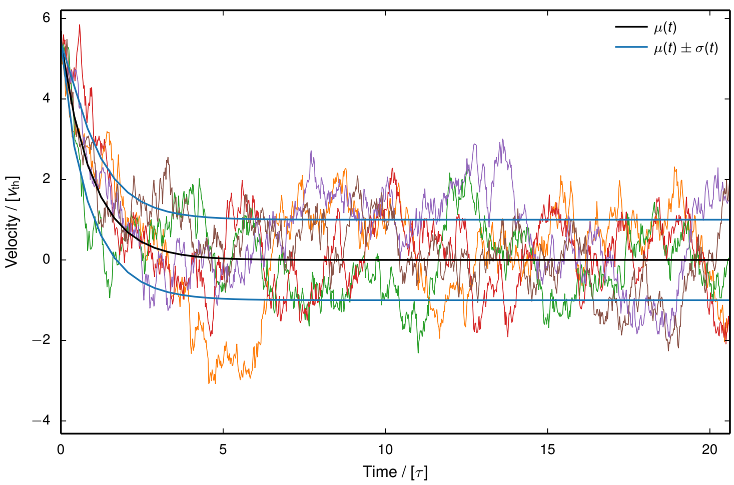

Figure 1: Five trajectories $v(t)$, all with the same initial velocity $v_0 = v_{th}$, together with the analytical result for the mean value $\mu(t)$ and the standarddeviation $\sigma(t)$.

We can also obtain an expression for the time-dependence of the position of the Brownian particle $x(t)$. We still restrict ourselves to motion in one dimension. Consider a particle with the initial conditions $x(0) = x_0$ and $v(0) = v_0$. By direct integration using the result in Eqn (6) we get

$$\begin{aligned} x(t) &= x_0 + \int_0^t ds\ v(s) \\ &= x_0 + \int_0^t ds\ v_0 e^{-\eta s} + \int_0^t ds \int_0^s ds'\ e^{-\eta(s-s')}\xi(s') \\ &= x_0 + \frac{v_0}{\eta}\left[1 - e^{-\eta t}\right] + \int_0^t ds' \int_{s'}^t ds\ e^{-\eta(s-s')}\xi(s') \\ &= x_0 + \frac{v_0}{\eta}\left[1 - e^{-\eta t}\right] + \frac{1}{\eta}\int_0^t ds'\ \left[1 - e^{-\eta(t-s')}\right]\xi(s') \end{aligned}$$

with the average

$$\langle [x(t) - x_0] \rangle = \frac{v_0}{\eta}\left[1 - e^{-\eta t}\right]$$

We can also study the fluctuations from the average value

$$\begin{aligned} \left\langle [x(t) - x_0]^2 \right\rangle &= \frac{v_0^2}{\eta^2}\left[1 - e^{-\eta t}\right]^2 + \frac{2}{\eta}\frac{k_B T}{m}\int_0^t ds\ \left[1 - e^{-\eta(t-s)}\right]^2 \\ &= \frac{v_0^2}{\eta^2}\left[1 - e^{-\eta t}\right]^2 + \frac{2}{\eta}\frac{k_B T}{m}\left[t - \frac{2}{\eta}(1 - e^{-\eta t}) + \frac{1}{2\eta}(1 - e^{-2\eta t})\right] \end{aligned}$$

Here, the initial condition for the velocity is fixed at v_0. We can also consider a system in equilibrium. The initial condition for the velocity is then $\langle v_0 \rangle^{eq} = 0$ and

$$\sqrt{\langle v_0^2 \rangle^{eq}} \equiv v_{th} = \sqrt{\frac{k_B T}{m}} \tag{16}$$

The mean squared displacement $\Delta_{MSD}(t)$ is then given by

$$\Delta_{MSD}(t) \equiv \left\langle [x(t) - x_0]^2 \right\rangle^{eq} = \frac{k_B T}{m}\frac{2}{\eta^2}\left[\eta t - \left(1 - e^{-\eta t}\right)\right] \tag{17}$$

where the superscript *eq* indicates that we have taken an equilibrium average for the initial velocity. For large times $\Delta_{MSD}(t)$ becomes proportional to time. This is the diffusive limit. Below we will show that if the Langevin's equation should be consistent with the ordinary diffusion equation in the long time limit, the diffusion coefficient D has to be equal to

$$D = \frac{k_B T}{m\eta} \tag{18}$$

We can therefore write the **mean squared displacement** as

$$\Delta_{MSD}(t) \equiv \left\langle [x(t) - x_0]^2 \right\rangle^{eq} = 2D\left[t - \frac{1}{\eta}\left(1 - e^{-\eta t}\right)\right] \tag{19}$$

For short times the particle is moving as a free particle with the thermal velocity given by Eqn (16)

$$\Delta_{MSD}(t) = (v_{th}t)^2 \quad t \ll \eta^{-1}$$

while for large times it diffuses with the diffusion coefficient D given by Eqn (18)

$$\Delta_{MSD}(t) = 2Dt \quad t \gg \eta^{-1}$$

2 Fokker-Planck equation

By solving the Langevin's equation we get information on the trajectory of the particle. It is a stochastic differential equation so if we repeat the calculation with the same initial conditions we will get another trajectory. We may then ask for the more detailed information what the probability is to obtain a certain velocity v at time t. Therefore, we introduce the **probability distribution function** $f(v,t)dv$, which is equal to the probability to find the particle at time t with velocity between v and $v+dv$.

We will now derive the corresponding partial differential equation for probability distribution function $f(v,t)$. The probability can increase in time if the particle velocity is changed to v or decrease in time if the particle velocity is changed from v. This is described by the **Master equation**

$$\frac{\partial}{\partial t} f(v,t) = \int_{-\infty}^{\infty} dv' \left[\tilde{W}(v,v') f(v',t) - \tilde{W}(v',v) f(v,t) \right] \tag{20}$$

where $\tilde{W}(v,v')$ is the probability per unit time for a transition from v' to v. The critical assumption made in the Master equation is that the transition probability $\tilde{W}(v,v')$ is independent of time, *i.e.* memory effects are neglected. We introduce the notation

$$y = v - v'$$

for the change of velocity and write

$$\tilde{W}(v,v') = W(v-v',v') = W(y,v')$$

We will later assume that y is small, but first we rewrite the Master equation as

$$\begin{aligned}
\frac{\partial}{\partial t} f(v,t) &= \int_{-\infty}^{\infty} dv' \left[W(v-v',v') f(v',t) - W(v'-v,v) f(v,t) \right] \\
&= \int_{-\infty}^{\infty} dy \left[W(y,v') f(v',t) - W(-y,v) f(v,t) \right] \\
&= \int_{-\infty}^{\infty} dy \left[W(y,v') f(v',t) - W(y,v) f(v,t) \right]
\end{aligned}$$

where we in the last line as made the change $y \to -y$ in the second term. We then expand $f(v',t)$ and $W(y,v')$ in terms of v' around v, *i.e.* for small values of y

$$f(v',t) = f(v,t) + (v'-v)\frac{\partial f(v,t)}{\partial v} + \frac{1}{2}(v'-v)^2 \frac{\partial^2 f(v,t)}{\partial v^2} + \ldots$$

and

$$W(y,v') = W(y,v) + (v'-v)\frac{\partial W(y,v)}{\partial v} + \frac{1}{2}(v'-v)^2 \frac{\partial^2 W(y,v)}{\partial v^2} + \ldots$$

which implies to lowest order in y that

$$
\begin{aligned}
W(y,v')f(v',t) &= W(y,v)f(v,t) \\
&- y\frac{\partial}{\partial v}\left[W(y,v)f(v,t)\right] + \frac{y^2}{2}\frac{\partial^2}{\partial v^2}\left[W(y,v)f(v,t)\right]
\end{aligned}
$$

If we insert this into the Master equation we obtain

$$
\frac{\partial}{\partial t}f(v,t) = \int_{-\infty}^{\infty} dy \left\{ -y\frac{\partial}{\partial v}\left[W(y,v)f(v,t)\right] + \frac{y^2}{2}\frac{\partial^2}{\partial v^2}\left[W(y,v)f(v,t)\right] \right\}
$$

$$
= -\frac{\partial}{\partial v}\left\{ \left[\int_{-\infty}^{\infty} dy\ yW(y,v)\right] f(v,t) \right\} + \frac{1}{2}\frac{\partial^2}{\partial v^2}\left\{ \left[\int_{-\infty}^{\infty} dy\ y^2W(y,v)\right] f(v,t) \right\}
$$

or

$$
\frac{\partial}{\partial t}f(v,t) = -\frac{\partial}{\partial v}\left[A(v)f(v,t)\right] + \frac{1}{2}\frac{\partial^2}{\partial v^2}\left[B(v)f(v,t)\right] \tag{21}
$$

where

$$
\begin{aligned}
A(v) &= \int_{-\infty}^{\infty} dy\ yW(y,v) \\
B(v) &= \int_{-\infty}^{\infty} dy\ y^2W(y,v)
\end{aligned}
$$

This is the Fokker-Planck equation. It is based on the assumption that the velocity only changes by small amounts, y is small. This is justified in the case of Brownian dynamics. In other cases where one can not assume that the change of the velocity is small, as for instance in collisions of neutral atoms with the same mass, a more appropriate transport equation is the Boltzmann equation. In the present case we can use the solution to Langevin's equation in Eqs (12)-(14) to obtain explicit expressions for the two coefficients $A(v)$ and $B(v)$. We get

$$
\begin{aligned}
A(v) &\equiv \lim_{\Delta t\to 0}\frac{1}{\Delta t}\left\langle v(t+\Delta t) - v(t)\right\rangle = -\eta v \\
B(v) &\equiv \lim_{\Delta t\to 0}\frac{1}{\Delta t}\left\langle [v(t+\Delta t) - v(t)]^2\right\rangle = 2\eta\frac{k_BT}{m}
\end{aligned}
$$

and the **Fokker-Planck equation** can now be written as

$$
\frac{\partial}{\partial t}f(v,t) = \eta\frac{\partial}{\partial v}\left[v + \frac{k_BT}{m}\frac{\partial}{\partial v}\right]f(v,t) \tag{22}
$$

This is a partial differential equation. The stationary solution is given by the Maxwellian velocity distribution

$$
f(v,t\to\infty) = f^{eq}(v) = \sqrt{\frac{m}{2\pi k_BT}}\exp\left[-\frac{mv^2}{2k_BT}\right] \tag{23}
$$

where we have introduced the proper normalisation. If we consider the initial condition with a precisely specified velocity, *i.e.* $f(v, t = 0) = \delta(v - v_0)$, the Fokker-Planck equation has the analytical solution

$$f(v,t) = \sqrt{\frac{m}{2\pi k_B T(1 - e^{-2\eta t})}} \exp\left[-\frac{m(v - v_0 e^{-\eta t})^2}{2k_B T(1 - e^{-2\eta t})}\right] \tag{24}$$

It shows how the initial sharp distribution spreads out in time until the final Maxwellian distribution in Eqn (23) is reached at large times.

The Fokker-Planck equation can also be solved numerically using some standard grid based method. An interesting alternative method is to use the connection with the Langevin's equation. By generating a lot of trajectories, all with the initial condition $v = v_0$, and then making a histogram, $f(v, t)$ in Eqn (24) can be obtained. This is not a competitive numerical method for low dimensional problems. However, for high dimensional problems, where grid based methods become computationally too demanding, "trajectory-based" methods can be used. They are essentially insensitive to the dimensionality of the problem. In Fig. 2 we compare the analytical solution in Eqn (24) with the numerical result obtained by solving Langevin's equation using the algorithm **BD2**. We have generated 10000 trajectories and then made an histogram for five different time extensions. The agreement is excellent.

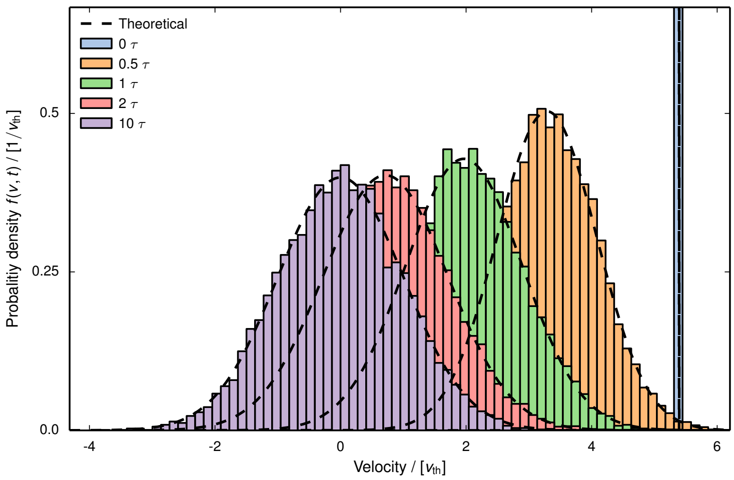

Figure 2: The probability distribution function $f(v, t)$ at 5 different times obtained by generating 10000 trajectories. The numerical solution is compared with the analytical result.

3 Time-correlation functions and the power spectrum

Time-correlation functions are useful in characterising dynamic properties. Consider a system in equilibrium. The velocity $v(t)$ is then stationary in time. We can define the **time-correlation function** as

$$\begin{aligned} C(t) &= \langle v(t)v(0)\rangle^{eq} \\ &= \lim_{\mathsf{T}\to\infty}\frac{1}{\mathsf{T}}\int_0^{\mathsf{T}} v(t+s)v(s)ds \end{aligned}$$

The superscript eq indicates that the time average is taken over a system in equilibrium. We also notice that $\langle v(t)\rangle^{eq}$=0. The correlation function is even in time

$$C(-t) = C(t) \tag{25}$$

This follows from that $v(t)$ is a classical dynamical variable and it commutes with itself at different times. We can also introduce the corresponding **spectral density** using the Fourier transform

$$\begin{aligned} \mathcal{F}[C(t)] &\equiv \hat{C}(\omega) \\ &= \int_{-\infty}^{\infty} dt C(t)e^{i\omega t} \end{aligned}$$

with the corresponding inverse relation

$$\begin{aligned} \mathcal{F}^{-1}[\hat{C}(\omega)] &\equiv C(t) \\ &= \int_{-\infty}^{\infty}\frac{d\omega}{2\pi}\hat{C}(\omega)e^{-i\omega t} \end{aligned}$$

The spectral density is also even in frequency

$$\hat{C}(-\omega) = \hat{C}(\omega) \tag{26}$$

It is instructive to consider the frequency components of $v(t)$ obtained by Fourier analysis as well as the corresponding power spectrum. To avoid convergence problems introduce

$$v_{\mathsf{T}}(t) = \begin{cases} v(t) & -\mathsf{T}/2 < t < \mathsf{T}/2 \\ 0 & \text{otherwise} \end{cases}$$

The frequency components are then obtained from the Fourier transform

$$v_{\mathsf{T}}(\omega) = \int_{-\infty}^{\infty} v_{\mathsf{T}}(t)e^{i\omega t}dt = \int_{-\mathsf{T}/2}^{\mathsf{T}/2} v(t)e^{i\omega t}dt$$

We then define the **power spectrum** as

$$\mathcal{P}(\omega) = \lim_{\mathsf{T}\to\infty}\frac{1}{\mathsf{T}}\left|v_{\mathsf{T}}(\omega)\right|^2 \tag{27}$$

There is a direct connection between the power spectrum and the corresponding time-correlation function. It is called the **Wiener-Khintchin's theorem** and it was derived in Appendix F in the lecture notes "Molecular dynamics". It states that the power spectrum for a dynamic variable in an equilibrium system is equal to the Fourier transform of the corresponding time-correlation function,

$$\mathcal{P}(\omega) = \hat{C}(\omega) \tag{28}$$

The total power spectrum is hence given by

$$\int_{-\infty}^{\infty} d\omega \mathcal{P}(\omega) = 2\pi C(t=0) \tag{29}$$

Consider the velocity $v(t)$. Using the solution to Langevin's equation in Eqn (6) we get the time-correlation function

$$C(t) = \frac{k_B T}{m} e^{-\eta|t|}$$

for a system in equilibrium. The corresponding power spectrum

$$\mathcal{P}(\omega) = \int_{-\infty}^{\infty} dt C(t) e^{i\omega t} = \frac{k_B T}{m} \frac{2\eta}{\omega^2 + \eta^2}$$

is a Lorentzian, centered at $\omega = 0$ and with the half width at half maximum equal to η. In Fig. 3 we show a typical spectrum for a damped oscillator. We also notice that $C(t)$ has a cusp at $t = 0$. Using the true microscopic motions $C(t)$ has no cusp, $dC(t)/dt = 0$ for $t = 0$. The reason is that when deriving Langevin's equation we disregarded motion on the very short time scale $t < \tau_0$, and hence the Langevin's equation is only applicable for $t > \tau_0$.

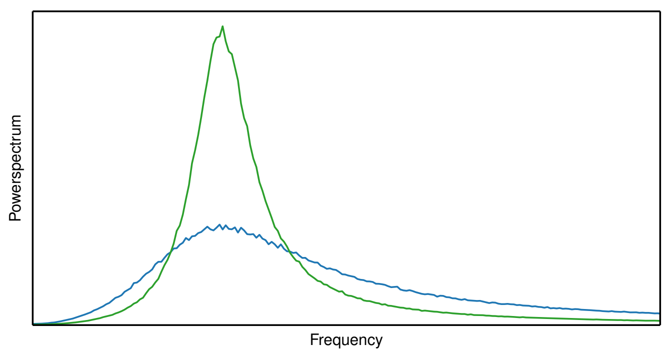

Figure 3: The power spectrum for a damped oscillator with low (green curve) and high (blue curve) damping.

We can also consider the spectrum of the stochastic force $\xi(t)$. Its time-correlation is a delta function in time

$$C_\xi(t) = 2\eta \frac{k_B T}{m} \delta(t)$$

and hence its power spectrum is given by

$$\mathcal{P}_\xi(\omega) = 2\eta \frac{k_B T}{m}$$

This is independent on frequency and is called white noise.

4 Langevin with external force

We can also add an external force to Langevin's equation of motion

$$m\frac{d}{dt}v(t) = -m\eta v(t) + F^{ext} + m\xi(t) \tag{30}$$

For instance, if the particle carries a charge e and is placed in a uniform electric field $\mathcal{E}$ the external force is $F^{ext} = e\mathcal{E}$. If we apply a constant external force on the particle it will achieve a constant drift velocity v^{drift} at equilibrium. The constant of proportionality B is called the **mobility**

$$v^{drift} = BF^{ext} \tag{31}$$

Taking the mean value of Eqn (30) and considering the steady-state situation where $d\langle v((t)\rangle/dt = 0$, yields the relation $m\eta v^{drift} = F^{ext}$. Combining this with the relation between the friction and the diffusion coefficients in Eqn (18) we obtain a relation, the **Einstein relation**, between the mobility and the diffusion coefficient

$$B = \frac{D}{k_B T} \tag{32}$$

If we assume that the external force depend on the position of the particle we have to solve the coupled equations

$$\frac{d}{dt}x(t) = v(t) \tag{33}$$

$$\frac{d}{dt}v(t) = -\eta v(t) + a(x(t)) + \xi(t) \tag{34}$$

where $a(x(t)) = (1/m)F^{ext}(x(t))$ is the acceleration caused by the external force.

As an example, consider the motion of a Brownian particle in an one-dimensional harmonic potential well. The external force is then given by

$$F^{ext}(x) = -kx(t)$$

Using the relation $k = m\omega_0^2$ where ω_0 is the corresponding harmonic frequency, we obtain the equation of motion

$$\frac{d}{dt}v(t) = -\eta v(t) - \omega_0^2 x(t) + \xi(t)$$

or

$$\frac{d^2}{dt^2}x(t) + \eta\frac{d}{dt}x(t) + \omega_0^2 x(t) = \xi(t) \tag{35}$$

By Fourier transforming we obtain

$$\left[-\omega^2 - i\eta\omega + \omega_0^2\right] x_{\mathsf{T}}(\omega) = \xi_{\mathsf{T}}(\omega)$$

and hence the power spectrum is given by

$$\begin{aligned}\mathcal{P}_x(\omega) &= \lim_{\mathsf{T}\to\infty}\frac{1}{2\mathsf{T}}\frac{|\xi_{\mathsf{T}}(\omega|^2}{\left|-\omega^2 - i\eta\omega + \omega_0^2\right|^2} \\ &= \frac{k_B T}{m}\frac{2\eta}{(\omega^2-\omega_0^2)^2+\eta^2\omega^2} \end{aligned} \tag{36}$$

which describes a damped harmonic oscillator. By noticing that $v_{\mathsf{T}}(\omega) = -i\omega x_{\mathsf{T}}(\omega)$ the power spectrum for the velocity is given by

$$\mathcal{P}_v(\omega) = \frac{k_B T}{m}\frac{2\eta\omega^2}{(\omega^2-\omega_0^2)^2+\eta^2\omega^2} \tag{37}$$

The Fokker-Planck equation in Eqn (22) can be generalized to include the effect from an external force. We have to obtain the equation for the probability distribution function $f(x,v,t)$. It is given by

$$\left[\frac{\partial}{\partial t} + v\frac{\partial}{\partial x} + \frac{F^{ext}}{m}\frac{\partial}{\partial v}\right] f(x,v,t) = \eta\frac{\partial}{\partial v}\left[v + \frac{k_B T}{m}\frac{\partial}{\partial v}\right] f(x,v,t) \tag{38}$$

We will now consider the formal solution of Eqn (38) using the Liouville formulation and use this to derive an efficient numerical scheme. We assume that the external force can depend on the position of the Brownian particle $F^{ext}(x)$ and we introduce the acceleration caused by the external force, $a(x) = F^{ext}(x)/m$. The Fokker-Planck can now be written as

$$\frac{\partial}{\partial t} f(x,v,t) = -i\mathcal{L}\ f(x,v,t)$$

with the formal solution

$$f(x,v,t) = e^{-i\mathcal{L}t} f(x,v,t=0)$$

and where

$$i\mathcal{L} = i\mathcal{L}_x + i\mathcal{L}_v + i\mathcal{L}_\eta$$

and

$$\begin{aligned} i\mathcal{L}_x &= v\frac{\partial}{\partial x} \\ i\mathcal{L}_v &= a(x)\frac{\partial}{\partial v} \\ i\mathcal{L}_\eta &= -\eta\frac{\partial}{\partial v}\left[v + \frac{k_B T}{m}\frac{\partial}{\partial v}\right] \end{aligned}$$

We split the time evolution into small time steps of size Δt and approximate the propagator as

$$\begin{aligned} e^{-\Delta t i\mathcal{L}} f(x,v,t) &= e^{-\Delta t[i\mathcal{L}_x + i\mathcal{L}_v + i\mathcal{L}_\eta]} f(x,v,t) \\ &= e^{-\left[\frac{\Delta t}{2}i\mathcal{L}_\eta + \frac{\Delta t}{2}i\mathcal{L}_v + \Delta t\, i\mathcal{L}_x + \frac{\Delta t}{2}i\mathcal{L}_v + \frac{\Delta t}{2}i\mathcal{L}_\eta\right]} f(x,v,t) \\ &\approx e^{-\frac{\Delta t}{2}i\mathcal{L}_\eta} e^{-\frac{\Delta t}{2}i\mathcal{L}_v} e^{-\Delta t\, i\mathcal{L}_x} e^{-\frac{\Delta t}{2}i\mathcal{L}_v} e^{-\frac{\Delta t}{2}i\mathcal{L}_\eta} f(x,v,t) \end{aligned}$$

The symmetric decomposition with $\Delta t/2$ in the end and in the beginning reduces the error from $\mathcal{O}(\Delta t^2)$ to $\mathcal{O}(\Delta t^3)$. The two operators $\Delta t\mathcal{L}_x$ and $\Delta t\mathcal{L}_v$ were discussed in appendix B in the lecture notes "Molecular dynamics". The first of these operators translate the position coordinate with $v\Delta t$ and the second the velocity with $a\Delta t$. The third operator $\Delta t\mathcal{L}_\eta$ corresponds to the Langevin's equation Eqn (2)and for that the algorithm **BD2** will be used. The solution of Eqs (33)-(34) can now be written as

$$
\begin{aligned}
&v(t^+) = \sqrt{c_0}v(t) + v_{th}\sqrt{1-c_0}\ \mathcal{G}_1 \\
&v(t+\Delta t/2) = v(t^+) + \frac{1}{2}a(t)\Delta t \\
&x(t+\Delta t) = x(t) + v(t+\Delta t/2)\Delta t \\
&\texttt{calculate new (external) accelerations/forces} \\
&v(t^- + \Delta t) = v(t+\Delta t/2) + \frac{1}{2}a(t+\Delta t)\Delta t \\
&v(t+\Delta t) = \sqrt{c_0}v(t^-+\Delta t) + v_{th}\sqrt{1-c_0}\ \mathcal{G}_2
\end{aligned}
$$

where the notation form algorithm **BD2** has been used. We notice that in the limit $\eta \to 0$ the velocity Verlet algorithm is recovered. Finally:

Algorithm BD3 The Langevin's equation with an external force (acceleration) that depends on the position can be numerically solved using the following algorithm (that reduces to the velocity Verlet in the limit $\eta \to 0$):

$$
\begin{aligned}
&\tilde{v}_{n+1} = \frac{1}{2}a_n\Delta t + \sqrt{c_0}v_n + v_{th}\sqrt{1-c_0}\ \mathcal{G}_{1,n} \\
&x_{n+1} = x_n + \tilde{v}_{n+1}\Delta t \\
&\texttt{calculate new external accelerations/forces} \\
&v_{n+1} = \frac{1}{2}\sqrt{c_0}a_{n+1}\Delta t + \sqrt{c_0}\tilde{v}_{n+1} + v_{th}\sqrt{1-c_0}\ \mathcal{G}_{2,n}
\end{aligned}
$$

where

$$c_0 = e^{-\eta\Delta t} \quad \text{and} \quad v_{th} = \sqrt{k_BT/m}$$

and $\mathcal{G}_1$ and $\mathcal{G}_2$ are two independent Gaussian random numbers with zero mean, unit variance and uncorrelated in time $\langle \mathcal{G}_{1,n}\mathcal{G}_{1,n'} \rangle = \delta_{n,n'}$ and $\langle \mathcal{G}_{2,n}\mathcal{G}_{2,n'} \rangle = \delta_{n,n'}$.

5 Diffusion equation

If the friction coefficient η is large the velocity will thermalize quite rapidly and a more slow diffusive motion in ordinary space will then take over. Consider the Langevin's equation

$$m\frac{d^2}{dt^2}x(t) = -m\eta\frac{d}{dt}x(t) + F^{ext}(x) + m\xi(t)$$

and assume that the friction term is large compared with the inertial term

$$\mid m\eta\frac{d}{dt}x(t) \mid \gg \mid m\frac{d^2}{dt^2}x(t) \mid$$

This leads to the stochastic differential equation

$$\frac{d}{dt}x(t) = \frac{1}{m\eta}F^{ext}(x) + \frac{1}{\eta}\xi(t) \tag{39}$$

Algorithm BD4 The stochastic diffusion equation can be solved using the following algorithm

$$x_{n+1} = x_n + \frac{\Delta t}{m\eta}F_n^{ext} + \sqrt{\frac{2k_BT\Delta t}{m\eta}}\,\mathcal{G}_n \tag{40}$$

where $\mathcal{G}_n$ is a Gaussian random number with zero mean, unit variance and uncorrelated in time $\langle \mathcal{G}_n \mathcal{G}_{n'} \rangle = \delta_{n,n'}$.

A corresponding Fokker-Planck equation can be derived for the probability distribution $\rho(x,t)dx$ to find the particle at time t with position between x and $x+dx$. In this case the coefficients $A(x)$ and $B(x)$ are given by

$$\begin{aligned} A(x) &\equiv \lim_{\Delta t\to 0}\frac{1}{\Delta t}\langle x(t+\Delta t) - x(t)\rangle = \frac{1}{m\eta}F_n^{ext} \\ B(x) &\equiv \lim_{\Delta t\to 0}\frac{1}{\Delta t}\left\langle [x(t+\Delta t) - x(t)]^2\right\rangle = \frac{2}{\eta}\frac{k_BT}{m} \end{aligned}$$

The corresponding Fokker-Planck equation is called **the Smoluchowski equation**

$$\frac{\partial}{\partial t}\rho(x,t) = \frac{1}{m\eta}\frac{\partial}{\partial x}\left[-F^{ext}(x) + k_BT\frac{\partial}{\partial x}\right]\rho(x,t) \tag{41}$$

This is a diffusion equation in the presence of an external force $F^{ext}(x)$. The corresponding stationary distribution is given by

$$\rho(x, t\to\infty) \equiv \rho^{eq}(x) \propto \exp\left[-\frac{V(x)}{k_BT}\right] \tag{42}$$

where $V(x)$ is the potential defined by the external force

$$F^{ext}(x) \equiv -\frac{dV(x)}{dx} \tag{43}$$

In the absence of an external force we recover the ordinary **diffusion equation**

$$\frac{\partial}{\partial t}\rho(x,t) = D\frac{\partial^2}{\partial x^2}\rho(x,t) \tag{44}$$

where we have used the relation $D = k_B T/m\eta$ between the **diffusion coefficient** D and the friction coefficient η, introduced in Eqn (18). With the initial condition $\rho(x, t = 0) = \delta(x - x_0)$ we have the solution

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

which shows how an initial localized distribution spreads out in time. The Smoluchowski equation can also be written as

$$\frac{\partial}{\partial t}\rho(x,t) = D\frac{\partial}{\partial x}\left[-\frac{F^{ext}(x)}{k_B T} + \frac{\partial}{\partial x}\right]\rho(x,t) \tag{45}$$

Algorithm BD5 Algorithm for the Smoluchowski equation (45)

$$x_{n+1} = x_n + \frac{D\Delta t}{k_B T}F_n^{ext} + \sqrt{2D\Delta t}\,\mathcal{G}_n \tag{46}$$

where $\mathcal{G}_n$ is a Gaussian random number with zero mean, unit variance and uncorrelated in time $\langle \mathcal{G}_n \mathcal{G}_{n'} \rangle = \delta_{n,n'}$.