Chapter 6

Brownian Motion: Langevin Equation

The theory of Brownian motion is perhaps the simplest approximate way to treat the dynamics of nonequilibrium systems. The fundamental equation is called the Langevin equation; it contain both frictional forces and random forces. The fluctuation-dissipation theorem relates these forces to each other.

The random motion of a small particle (about one micron in diameter) immersed in a fluid with the same density as the particle is called Brownian motion. Early investigations of this phenomenon were made by the biologist Robert Brown on pollen grains and also dust particles or other object of colloidal size.

The modern era in the theory of Brownian motion began with Albert Einstein. He obtained a relation between the macroscopic diffusion constant D and the atomic properties of matter. The relation is

$$D = \frac{RT}{N_A 6\pi\eta a} = \frac{k_B T}{6\pi\eta a}$$

where R is the gas constant, $N_A = 6.06 \times 10^{23}/\text{mol}$ is Avogadros number, T is the temperature, η is the viscosity of the liquid and a is the radius of the Brownan particle. Also $k_B = R/N_A$ is Boltzmanns constant.

The theory of Brownian motion has been extended to situations where the fluctuating object is not a real particle at all, but instead some collective porperty of a macroscopic system. This might be, for example, the instantaneous concentration of any component of a chemically reacting system near thermal equilibrium. Here the irregular fluctuation in time of this concentration corresponds to the irregular motion of the dust particle.

6.1 Langevin equation

Consider a large particle (the Brownian particle) immersed in a fluid of much smaller particles (atoms). Here the radius of the Brownian particle is typically $10^{-9}\text{m} < a < 5 \times 10^{-7}\text{m}$. The agitated motion of the large particle is much slower than that of the atoms and is the result of random and rapid collisions due to density fluctuations in the fluid. There are in general three vastly different timescales in a colloidal system τ_s, τ_B, and τ_r. Here τ_s is the short atomic scale $\tau_s \approx 10^{-12}\text{s}$, τ_B is the Brownian timescale for

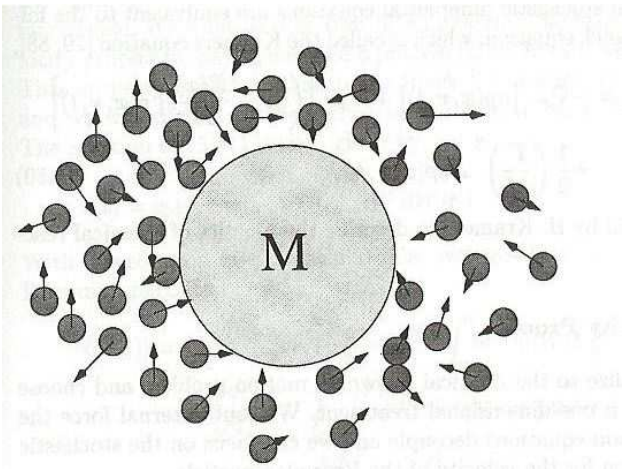

Figure 6.1: *A large Brownian particle with mass M immersed in a fluid of much smaller and lighter particles.*

the relaxation of the particle velocity

$$\tau_B \approx \frac{m}{\gamma} \approx 10^{-3}\mathrm{s}$$

and τ_r is the relaxation time for the Brownian particle, i.e. the time the particle have diffused its own radius

$$\tau_r = \frac{a^2}{D}$$

In general

$$\tau_s \ll \tau_B \ll \tau_r.$$

In dense colloidal suspensions τ_r can become very long of the order of minutes or hours.

While the motion of a dust particle performing Brownian motion appears to be quite random, it must nevertheless be describable by the same equation of motion as is any other dynamical system. In classical mechanics these are Newton's or Hamiltons equations. For simplicity we will consider motion in one dimension. The results can easily be generalised to three dimensions. Newtons equation of motion for the particle (radius a, mass m, position $x(t)$, velocity $v(t)$) in a fluid medium (viscosity η) is

$$m\frac{\mathrm{d}v(t)}{\mathrm{d}t} = F(t) \tag{6.1}$$

where $F(t)$ is the total instantaneous force on the particle at time t. This force is due to the interaction of the Brownian particle with the surrounding medium. If the pssitions of the moelcules in the surrounding medium are known as a function of time, then in principle this force is a known function of time. In this sense it is not a random force at all.

It is usually not practical or even desirable to look for an exact expression for $F(t)$. Experience tells us that in typical cases this force is dominated by a friction force $-\gamma v(t)$,

proportional to the velocity of the Brownian particle. The friction coefficient is given by Stokes law

$$\gamma = 6\pi\eta a \tag{6.2}$$

We also expect a random force $\xi(t)$ due to random density fluctuations in the fluid. The equations of motion of the Brownian particle are:

$$\begin{aligned} \frac{\mathrm{d}x(t)}{\mathrm{d}t} &= v(t) \\ \frac{\mathrm{d}v(t)}{\mathrm{d}t} &= -\frac{\gamma}{m}v(t) + \frac{1}{m}\xi(t) \end{aligned} \tag{6.3}$$

This is the *Langevin equations* of motion for the Brownian particle.

The random force $\xi(t)$ is a stochastic variable giving the effect of background noise due to the fluid on the Brownian particle. If we would neglect this force (6.3) becomes

$$\frac{\mathrm{d}v(t)}{\mathrm{d}t} = -\frac{\gamma}{m}v(t) \tag{6.4}$$

which has the familiar solution

$$v(t) = \mathrm{e}^{-t/\tau_B}v(0), \quad \tau_B = \frac{m}{\gamma} \tag{6.5}$$

According to this, the velocity of the Brownian particle is predicted to decay to zero at long times. This cannot be true since in equilibrium we must have the equipartion theorem

$$\langle v^2(t)\rangle_{\mathrm{eq}} = \frac{k_bT}{m} \tag{6.6}$$

while (6.5) gives

$$\langle v^2(t)\rangle_{\mathrm{eq}} = \mathrm{e}^{-2t/\tau_B}\langle v^2(0)\rangle_{\mathrm{eq}} \to 0 \tag{6.7}$$

The random force in (6.3) is therfore necessary to obtain the correct equilibrium. In the conventional view of the fluctuation force it is supposed to come from occasional impacts of the Brownian particle with molecules of the surrounding medium. The force during an impact is supposed to vary extremely rapidly over the time of any observation. The effect of the fluctuating force can be summarized by giving its first and second moments

$$\langle \xi(t)\rangle_\xi = 0, \quad \langle \xi(t_1)\xi(t_2)\rangle_\xi = g\delta(t_1 - t_2) \tag{6.8}$$

The average $\langle\cdots\rangle_\xi$ is an average with respect to the distribution of the realizations of the stochastic variable $\xi(t)$.

Since we have extracted the average force $-\gamma v(t)$ in the Langevin equation the average of the fluctuating force must by definition be zero. g is a measure of the strength of the fluctuation force. The delta function in time indicates that there is no correlation between impacts in any distinct time intervals $\mathrm{d}t_1$ and $\mathrm{d}t_2$. This loss of correlation is a consequence of the separation of time scales discussed above. During a short time interval $\mathrm{d}t$ on scale $\tau_B = 10^{-3}$s, say $\mathrm{d}t = 10^{-5}$s, there are still roughly $\mathrm{d}t/\tau_s \approx 10^7$ collisons with the atoms in the liquid. Therefore any memory between forces at different times will be lost due to these frequent collisions.

The remaining mathematical specification of this dynamical model is that the fluctuating force has a Gaussian distribution determined by the moments in (6.8).

The property (6.8) imply that $\xi(t)$ is a wildly fluctuating function, and it is not at all obvious that the differential equation (6.3) has a unique solution for a given initial condition, or even that $\mathrm{d}v/\mathrm{d}t$ exists. There is a standard existence theorem for differential equations which guarantee the existence of a *local* solution if $\xi(t)$ is continous. A local solution is one which exists in some neighborhood of the point at which the initial value is given. But even if a solution exists it may be only local, or it may not be unique, unless some stronger conditions are imposed on $\xi(t)$.

We can obtain an explicit formal solution of (6.3) as

$$v(t) = \mathrm{e}^{-t/\tau_B} v(0) + \frac{1}{m}\int_0^t \mathrm{d}s \mathrm{e}^{-(t-s)/\tau_B}\xi(s) \tag{6.9}$$

but this only transfers the problem elsewhere. How do we know that the integral in (6.9) exists, that it is more than just a formal symbol?

To obtain a meaning to (6.3) and (6.9) we write (6.3) as

$$\mathrm{d}v(t) = -\frac{\gamma}{m}v(t)\mathrm{d}t + \frac{1}{m}\mathrm{d}U(t) \tag{6.10}$$

where

$$\mathrm{d}U(t) = \xi(t)\mathrm{d}t \tag{6.11}$$

For an arbitrary nonstochastic continous function $f(t)$ we then find

$$\int_0^t f(s)\mathrm{d}v(s) = -\frac{\gamma}{m}\int_0^t f(s)v(s)\mathrm{d}s + \frac{1}{m}\int_0^t f(s)\,\mathrm{d}U(s) \tag{6.12}$$

In particular $f(t) = 1$ gives

$$\begin{aligned} v(t) - v(0) &= -\frac{\gamma}{m}\int_0^t v(s)\mathrm{d}s + \frac{1}{m}\left[U(t) - U(0)\right] \\ &= -\frac{\gamma}{m}\left[x(t) - x(0)\right] + \frac{1}{m}\left[U(t) - U(0)\right] \end{aligned} \tag{6.13}$$

We now discuss the integral noice $U(t)$ for long times t. Dividing t into intervals we have

$$U(t) - U(0) = \sum_{k=1}^{n}\left[U(t_k) - U(t_{k-1})\right] \tag{6.14}$$

with $0 = t_0 < t_1 < t_2 < \cdots < t_n = t$.

$U(t)$ is a continous Markov process with zero mean. The continuity follows from (6.10) since

$$U(t) = U(0) + \int_0^t \xi(s)\mathrm{d}s \tag{6.15}$$

and we must require that the integral be a continous function of its upper limit, as for ordinary integrals. The Markov property follows since a Brownian particle in a liquid solution undergoes something of the order of 10^{12} random collisions per second with the particles of the environment. Therefore, we can make each interval $t_i - t_{i-1}$ macroscopically

very small even though during it very many collisions occur. These numerous impacts destroy all correlations between what happens during the time interval (t_i, t_{i-1}) and what has happended before t_{i-1}. This implies that $U(t)$ is a Markov process, i.e. $U(t_n)$ depends only on $U(t_{n-1})$ etc.

On account of the randomness of the motion the random force $\xi(t)$ must average to zero, which is also implied by the separation in (6.3). If we now choose our time origin so that $U(0) = 0$ we must have $\langle U(t_k)\rangle = 0$.

From the discussion above about the random collisions we also argue that the increments

$$U(t_1) - U(0), U(t_2) - U(t_1), \cdots, U(t_n) - U(t_{n-1}) \tag{6.16}$$

are independent. For long times we suppose that the random motion of the medium has attained a steady state. Then the increments (6.16) are also stationary and identically distributed with zero mean. Applying the central limit theorem to (6.14) we deduce that $U(t)$ is Gaussian with zero mean. Therefore, it has all the requirements for a Wiener process, i.e.

$$U(t) = W(t) \tag{6.17}$$

We can now write (6.10) as

$$\mathrm{d}v(t) = -\frac{\gamma}{m} v(t)\mathrm{d}t + \frac{1}{m}\mathrm{d}W(t) \tag{6.18}$$

and the solution in (6.9) becomes

$$v(t) = \mathrm{e}^{-t/\tau_B} v(0) + \frac{1}{m}\int_0^t \mathrm{e}^{-(t-s)/\tau_B}\mathrm{d}W(s) \tag{6.19}$$

6.2 Examples

Ornstein-Uhlenbeck process

In the Ornstein-Uhlenbeck process we study a Brownian particle where the equation of motion is given by (6.3) or

$$\begin{aligned} x(t) &= x_0 + \int_0^t v(s)\mathrm{d}s \\ v(t) &= \mathrm{e}^{-t/\tau_B} v_0 + \frac{1}{m}\int_0^t \mathrm{e}^{-(t-s)/\tau_B}\mathrm{d}W(s) \end{aligned} \tag{6.20}$$

where $x_0 = x(0)$ and $v_0 = v(0)$. Since $\mathrm{d}W$ is a Gaussian process this is also the case for $v(t)$ and $x(t)$. We can therefore obtain the distribution functions for these variables knowing the first and second moments. Taking the average of the second eq. in (6.20) and using $\langle \mathrm{d}W(t)\rangle = 0$ we find

$$\langle v(t)\rangle = v_0 \mathrm{e}^{-t/\tau_B} \tag{6.21}$$

From (6.20) we can also calculate the correlation function

$$\begin{aligned} & C_v(t_2, t_1) = \langle [v(t_2) - \langle v(t_2)\rangle]\,[v(t_1) - \langle v(t_1)\rangle]\rangle \\ = \;& \frac{1}{m^2}\int_0^{t_2}\int_0^{t_1} \mathrm{e}^{-(t_2-s_2)/\tau_B}\mathrm{e}^{-(t_1-s_1)/\tau_B}\langle \mathrm{d}W(s_2)\mathrm{d}W(s_1)\rangle \end{aligned} \tag{6.22}$$

But $W(s)$ is a Wiener process and we have

$$\langle \mathrm{d}W(s_2)\mathrm{d}W(s_1)\rangle = g(\mathrm{d}s_2 \cap \mathrm{d}s_1) \tag{6.23}$$

where g denotes the variance of $W(t)$. Therefore the only contribution to the integral in (6.22) comes when $s_1 = s_2$, and

$$\begin{aligned} C_v(t_2,t_1) &= \frac{g}{m^2}\int_0^{\min(t_2,t_1)} \mathrm{d}s_1 \mathrm{e}^{-(t_2+t_1-2s_1)/\tau_B} \\ &= \frac{g\tau_B}{2m^2}\left[\mathrm{e}^{-(t_2+t_1-2\min(t_2,t_1))/\tau_B} - \mathrm{e}^{-(t_2+t_1)/\tau_B}\right] \\ &= \frac{g\tau_B}{2m^2}\left[\mathrm{e}^{-(|t_2-t_1|))/\tau_B} - \mathrm{e}^{-(t_2+t_1)/\tau_B}\right] \end{aligned} \tag{6.24}$$

From the correlation function we also directly get the second moment of $v(t)$

$$\langle v(t_2)v(t_1)\rangle_\xi = \left[v_0^2 - \frac{g\tau_B}{2m^2}\right]\mathrm{e}^{-(t_2+t_1)/\tau_B} + \frac{g\tau_B}{2m^2}\mathrm{e}^{-(|t_2-t_1|))/\tau_B} \tag{6.25}$$

Here we can also average over the initial velocity distribution where in equilibrium $\langle v_0^2\rangle_{\mathrm{eq}} = k_BT/m$. For such a system the second moment can only depend on the time difference $|t_2 - t_1|$ and the first term has to vanish. We can also see this when $t_2 = t_1 = t$, then

$$\langle\langle v^2(t)\rangle_\xi\rangle_{\mathrm{eq}} = \left[\langle v_0^2\rangle_{\mathrm{eq}} - \frac{g\tau_B}{2m^2}\right]\mathrm{e}^{-2t/\tau_B} + \frac{g\tau_B}{2m^2} \tag{6.26}$$

The condition for equilibrium is that $\langle\langle v^2(t)\rangle_\xi\rangle_{\mathrm{eq}} = k_BT/m$. This requires

$$g = 2mk_BT/\tau_B = 2\gamma k_BT \tag{6.27}$$

This important result is known as the Fluctuation dissipation theorem. It relates the strength g of the random noise or fluctuating force to the magnitude γ of the friction or dissipation. It expresses the balance between friction which tends to drive any system to a completely dead state and noise which tends to keep the system alive. This balance is required to have a thermal equilibrium state at long times.

The variance of $v(t)$ is obtained from (6.24) for $t_2 = t_1 = t$ and with $g = 2\gamma k_BT$ as

$$\sigma_v^2(t) = \langle\langle\left[v(t) - v_0\mathrm{e}^{-t/\tau_B}\right]^2\rangle_\xi\rangle_{\mathrm{eq}} = \frac{k_BT}{m}\left[1 - \mathrm{e}^{-2t/\tau_B}\right] \tag{6.28}$$

We can now obtain the conditional probability distribution function for the velocity

$$\varrho_v(vt|v_00) = \left(\frac{1}{2\pi\sigma_v^2(t)}\right)^{1/2}\mathrm{e}^{-\frac{(v-\mu_v(t))^2}{2\sigma_v^2(t)}} \tag{6.29}$$

where $\mu_v(t) = v_0\mathrm{e}^{-t/\tau_B}$.

From (6.20) we can also get an expression for the displacement of the particle

$$\begin{aligned} x(t) &= x_0 + \int_0^t \mathrm{d}s v_0\mathrm{e}^{-s/\tau_B} + \frac{1}{m}\int_0^t \mathrm{d}s\int_0^s \mathrm{e}^{-(s-u)/\tau_B}\mathrm{d}W(u) \\ &= x_0 + v_0\tau_B\left[1 - \mathrm{e}^{-t/\tau_B}\right] + \frac{1}{m}\int_0^t \mathrm{d}W(u)\int_u^t \mathrm{d}s\mathrm{e}^{-(s-u)/\tau_B} \\ &= x_0 + v_0\tau_B\left[1 - \mathrm{e}^{-t/\tau_B}\right] + \frac{\tau_B}{m}\int_0^t \left[1 - \mathrm{e}^{-(t-u)/\tau_B}\right]\mathrm{d}W(u) \end{aligned} \tag{6.30}$$

where we in step two changed the order of integration. The average displacement is then

$$\mu_x(t) = \langle x(t)\rangle_\xi = x_0 + v_0\tau_B\left[1 - \mathrm{e}^{-t/\tau_B}\right] \tag{6.31}$$

An important quantity is the mean squared displacement of the particle from the starting point. This is obtained as

$$\begin{aligned}
&\langle [x(t) - x_0]^2\rangle_\xi = v_0^2\tau_B^2\left[1 - \mathrm{e}^{-t/\tau_B}\right]^2 \\
+ \;& \frac{\tau_B^2}{m^2}\int_0^t\int_0^t \left[1 - \mathrm{e}^{-(t-u)/\tau_B}\right]\left[1 - \mathrm{e}^{-(t-v)/\tau_B}\right]\langle \mathrm{d}W(u)\mathrm{d}W(v)\rangle_\xi \\
= \;& v_0^2\tau_B^2\left[1 - \mathrm{e}^{-t/\tau_B}\right]^2 + \frac{g\tau_B^2}{m^2}\int_0^t \left[1 - \mathrm{e}^{-(t-u)/\tau_B}\right]^2 \\
= \;& \tau_B^2\left[1 - \mathrm{e}^{-t/\tau_B}\right]^2\left[v_0^2 - \frac{g}{2m\gamma}\right] + \frac{g}{\gamma^2}\left[t - \tau_B\left(1 - \mathrm{e}^{-t/\tau_B}\right)\right]
\end{aligned} \tag{6.32}$$

In equilibrium the first term vanishes as before. From the remaining second term we get for short and long times

$$\langle\langle (x(t) - x_0)^2\rangle\rangle = \begin{cases} \frac{k_BT}{m}t^2 & t \to 0 \\ \frac{2k_BT}{\gamma}t & t \to \infty \end{cases} \tag{6.33}$$

The result for short times is the free particle term, where for short times $x(t) - x_0 = v_0 t$. The result for long times can be compared with the diffusion result

$$\langle\langle (x(t) - x_0)^2\rangle\rangle = 2Dt \tag{6.34}$$

which gives the Stokes-Einstein result

$$D = \frac{k_BT}{\gamma} = \frac{k_BT}{6\pi\eta a} \tag{6.35}$$

The second moment of the displacemnet becomes

$$\sigma_x^2(t) = \langle (x(t) - \mu_x(t))^2\rangle = \frac{2k_BT\tau_B^2}{m}\left[t/\tau_B - \frac{3}{2} + 2\mathrm{e}^{-t/\tau_B} - \frac{1}{2}\mathrm{e}^{-2t/\tau_B}\right]. \tag{6.36}$$

The conditional distribution function for the displacement is then

$$\varrho_x(xt|x_0 0) = \left(\frac{1}{2\pi\sigma_x^2(t)}\right)^{1/2} \mathrm{e}^{-\frac{(x-\mu_x(t))^2}{2\sigma_x^2(t)}} \tag{6.37}$$

From the relation between the position and velocity we can also get a general Kubo relation

$$x(t) - x(0) = \int_0^t \mathrm{d}s\, v(s) \tag{6.38}$$

which for a stationary process gives

$$\begin{aligned}
\langle (x(t)-x(0))^2\rangle &= \int_0^t \mathrm{d}s_1 \int_0^t \mathrm{d}s_2 \langle v(s_2)v(s_1)\rangle \\
&= \int_0^t \mathrm{d}s_2 \int_0^{s_2} \mathrm{d}s_1 \langle v(s_2)v(s_1)\rangle + \int_0^t \mathrm{d}s_2 \int_{s_2}^t \mathrm{d}s_1 \langle v(s_2)v(s_1)\rangle \\
&= \int_0^t \mathrm{d}s_2 \int_0^{s_2} \mathrm{d}s_1 \langle v(s_2-s_1)v(0)\rangle + \int_0^t \mathrm{d}s_1 \int_0^{s_1} \mathrm{d}s_2 \langle v(s_1-s_2)v(0)\rangle \\
&= 2\int_0^t \mathrm{d}s \int_0^s \mathrm{d}u \langle v(u)v(0)\rangle = 2\int_0^t \mathrm{d}u \langle v(u)v(0)\rangle \int_u^t \mathrm{d}s \\
&= 2\int_0^t \mathrm{d}u (t-u)\langle v(u)v(0)\rangle
\end{aligned}$$

For $t \to \infty$ we then find

$$\langle (x(t)-x(0))^2\rangle = 2t\int_0^\infty \mathrm{d}u \langle v(u)v(0)\rangle = 2Dt$$

which gives the Kubo relation

$$D = \int_0^\infty \mathrm{d}u \langle v(u)v(0)\rangle \tag{6.39}$$

Brownian motion in a harmonic potential

Consider a Brownian particle of mass m which is constrained to move in one dimension in a harmonic potential $V(x) = kx^2/2$. The corresponding force on the particle is $F_h = -kx$.

The Langevin equations are

$$\begin{aligned}
\frac{\mathrm{d}x}{\mathrm{d}t} &= v \\
\frac{\mathrm{d}v}{\mathrm{d}t} &= -\frac{\gamma}{m}v - \omega_0^2 x + \frac{1}{m}\xi(t)
\end{aligned}$$

where $\omega_0^2 = k/m$. Here the random force is a Gaussian random process with moments

$$\begin{aligned}
\langle \xi(t_1)\rangle &= 0 \\
\langle \xi(t_1)\xi(t_2)\rangle &= 2\gamma k_\mathrm{B} T \delta(t_1 - t_2)
\end{aligned}$$

The spectral density is the Fourier transform of the correlation function

$$S_\xi(\omega) = \int_{-\infty}^\infty \mathrm{d}t \mathrm{e}^{\mathrm{i}\omega t}\langle \xi(t)\xi(0)\rangle = 2\gamma k_\mathrm{B} T$$

which is white noise. We can Fourier transform the Langevin equations

$$\begin{aligned}
-\mathrm{i}\omega x(\omega) &= v(\omega) \\
-\mathrm{i}\omega v(\omega) &= -\frac{\gamma}{m}v(\omega) - \omega_0^2 x(\omega) + \frac{1}{m}\xi(\omega)
\end{aligned}$$

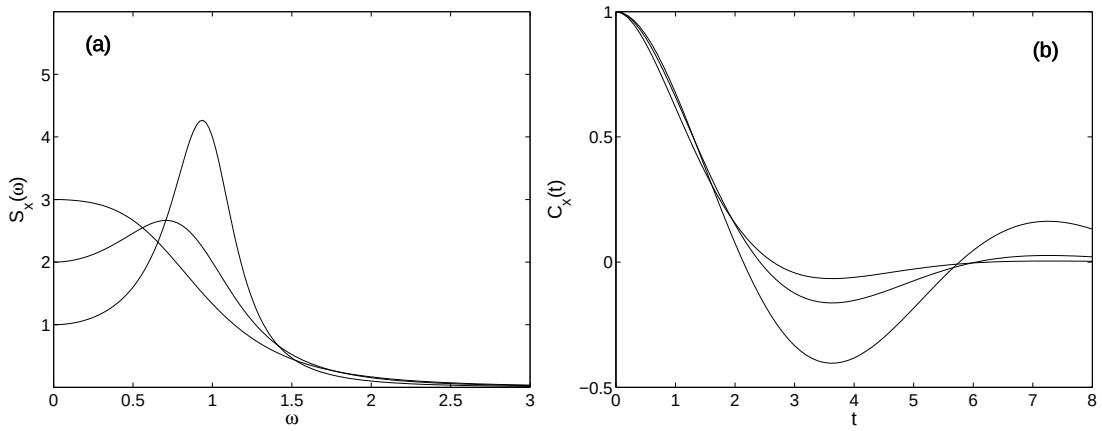

Figure 6.2: *(a) The spectrum $S_x(\omega)/\langle x_0^2\rangle$ for a Brownian particle in a harmonic potential plotted versus ω/ω_0 for $\gamma/m = 0.5, 1.0$ and $1.5\omega_0$ (b) The correspondning results for the normalized correlation function $C_x(t)/C_x(t=0)$ plotted versus $t\omega_0$.*

Then we can solve for $x(\omega)$ in terms of the fluctuating force to obtain

$$x(\omega) = \frac{1}{m}\frac{\xi(\omega)}{\omega_0^2 - \omega^2 - \frac{\gamma}{m}\mathrm{i}\omega}$$

The spectral density is proportional to $|x(\omega)|^2$ and so

$$S_x(\omega) = \frac{1}{m^2}\frac{S_\xi(\omega)}{\left|\omega_0^2 - \omega^2 - \frac{\gamma}{m}\mathrm{i}\omega\right|^2} = \frac{2\gamma k_\mathrm{B}T}{m^2}\frac{1}{\left[(\omega_0^2-\omega^2)^2 + \frac{\gamma^2}{m^2}\omega^2\right]}$$

For the corresponding time dependent correlation function we have

$$C_x(t) = \frac{1}{2\pi}\int_{-\infty}^{\infty}\mathrm{d}\omega \mathrm{e}^{-\mathrm{i}\omega t}S_x(\omega) = \frac{2\gamma k_\mathrm{B}T}{2\pi m^2}\int_{-\infty}^{\infty}\mathrm{d}\omega \mathrm{e}^{-\mathrm{i}\omega t}\frac{1}{\left[(\omega_0^2-\omega^2)^2 + \frac{\gamma^2}{m^2}\omega^2\right]}$$

The integral can be calculated as a contour integral in the complex plane by taking the residues at the poles. These are located at

$$\omega_0^2 - \omega^2 = \pm\frac{\gamma}{m}\mathrm{i}\omega, \Rightarrow \omega = \pm\mathrm{i}\frac{\gamma}{2m} \pm \sqrt{\omega_0^2 - \frac{\gamma^2}{4m^2}} = \pm\mathrm{i}\frac{\gamma}{2m} \pm \omega_1$$

with $\omega_1 = \sqrt{\omega_0^2 - \gamma^2/4m^2}$. For $t > 0$ and $\omega = x + \mathrm{i}y$ we see that the exponent $-\mathrm{i}\omega t = -\mathrm{i}xt + yt$, and the contour in the complex ω-plane have to be closed by a semicircle in the lower half plane. The poles are then at $\omega = \pm\omega_1 - \mathrm{i}\gamma/2m$. By working out the residues one find

$$\begin{aligned}
C_x(t) &= \frac{2\gamma k_\mathrm{B}T}{2\pi m^2}\int_{-\infty}^{\infty}\mathrm{d}\omega\frac{\mathrm{e}^{-\mathrm{i}\omega t}}{(\omega-\omega_1-\mathrm{i}\frac{\gamma}{2m})(\omega-\omega_1+\mathrm{i}\frac{\gamma}{2m})(\omega+\omega_1-\mathrm{i}\frac{\gamma}{2m})(\omega+\omega_1+\mathrm{i}\frac{\gamma}{2m})} \\
&= -2\pi\mathrm{i}\frac{2\gamma k_\mathrm{B}T}{2\pi m^2}\left[\frac{\mathrm{e}^{-\mathrm{i}(\omega_1-\mathrm{i}\frac{\gamma}{2m})t}}{(-\mathrm{i}\frac{\gamma}{m})(2\omega_1-\mathrm{i}\frac{\gamma}{m})(2\omega_1)} + \frac{\mathrm{e}^{-\mathrm{i}(-\omega_1-\mathrm{i}\frac{\gamma}{2m})t}}{(-2\omega_1-\mathrm{i}\frac{\gamma}{m})(-2\omega_1)(-\mathrm{i}\frac{\gamma}{m})}\right] \\
&= \frac{k_\mathrm{B}T}{m\omega_0^2}\mathrm{e}^{-\frac{\gamma}{2m}t}\left\{\cos\omega_1 t + \frac{\gamma}{2m\omega_1}\sin\omega_1 t\right\}
\end{aligned}$$

We notice that at $t = 0$ we have $C_x(t = 0) = \langle x_0^2 \rangle = k_\mathrm{B}T/m\omega_0^2$ which is just the equipartiton theorem

$$\frac{1}{2}\omega_0^2\langle x_0^2\rangle = \frac{1}{2}k_\mathrm{B}T$$

Similarly we find the spectral density for the velocity correlatons

$$S_v(\omega) = \omega^2 S_x(\omega)$$

and from this we can get the velocity correlation function $C_v(t)$.

Dipole-dipole correlation function

Many time correlation functions are related to spectroscopic measurements. For example the frequency dependence of the optical absorption coefficient of a substance is determined by the time correlation of its electric dipole moment.

The absorption coefficient $\alpha(\omega)$ at frequency ω is

$$\alpha(\omega) = \frac{2\pi\omega^2\beta}{3nc}\int_{-\infty}^{\infty} \mathrm{d}t \mathrm{e}^{-\mathrm{i}\omega t}\langle \boldsymbol{M}(t)\cdot\boldsymbol{M}(0)\rangle_\mathrm{eq}$$

where c is the speed of light in vacuum, $\beta = 1/k_\mathrm{B}T$ and n is the index of refraction. $\boldsymbol{M}(t)$ is the total electric dipole moment of the system at time t.

Suppose the system being investigated is a single dipolar molecule. Then $\boldsymbol{M}$ is just its permanent dipole moment. It has a constant magnitude μ and a time dependent orientation specified by the unit vector $\boldsymbol{u}(t)$ so that

$$\langle \boldsymbol{M}(t)\cdot\boldsymbol{M}(0)\rangle_\mathrm{eq} = \mu^2\langle \boldsymbol{u}(t)\cdot\boldsymbol{u}(0)\rangle_\mathrm{eq}$$

For a planar rotor with $\theta(t)$ the instantaneous angle with the x-axis

$$\boldsymbol{u}(t) = (\cos\theta(t), \sin\theta(t))$$

and

$$\begin{aligned}\langle \boldsymbol{u}(t)\cdot\boldsymbol{u}(0)\rangle_\mathrm{eq} &= \langle \cos\theta(t)\cos\theta(0) + \sin\theta(t)\sin\theta(0)\rangle_\mathrm{eq} = \langle\cos(\theta(t)-\theta(0))\rangle \\ &= \mathrm{Re}\langle \mathrm{e}^{\mathrm{i}\theta(t)}\mathrm{e}^{-\mathrm{i}\theta(0)}\rangle_\mathrm{eq}\end{aligned}$$

We can calculate this quantity using the Langevin equation for rotational Brownian motion. The position x is replaced by the angle θ and the velocity v by the angular velocity Ω, and the mass m by the moment of inertia I

$$\begin{aligned}\frac{\mathrm{d}\theta}{\mathrm{d}t} &= \Omega \\ I\frac{\mathrm{d}\Omega}{\mathrm{d}t} &= -\gamma\Omega + \xi(t)\end{aligned}$$

where the fluctuating torque has correlation function

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

Then with $\tau_R = I/\gamma$

$$\Omega(t) = \Omega(0)\mathrm{e}^{-t/\tau_R} + \frac{1}{I}\int_0^t \mathrm{d}s\, \mathrm{e}^{-(t-s)/\tau_R}\xi(s)$$

and

$$\begin{aligned}\theta(t) &= \theta(0) + \int_0^t \mathrm{d}s\Omega(0)\mathrm{e}^{-s/\tau_R} + \frac{1}{I}\int_0^t \mathrm{d}s \int_0^s \mathrm{d}u\mathrm{e}^{-(s-u)/\tau_R}\xi(u) \\ &= \theta(0) + \tau_R\Omega(0)\left(1-\mathrm{e}^{-t/\tau_R}\right) + \frac{1}{\gamma}\int_0^t \mathrm{d}s\left(1-\mathrm{e}^{-(t-s)/\tau_R}\right)\xi(s)\end{aligned}$$

As before in the Ornstein-Uhlenbeck process we now get

$$\langle(\theta(t)-\theta(0))^2\rangle = \frac{2k_\mathrm{B}TI}{\gamma^2}\left[t/\tau_R - \left(1-\mathrm{e}^{-t/\tau_R}\right)\right]$$

The orientational time correlation function is

$$C_R(t) = \mathrm{Re}\langle \mathrm{e}^{\mathrm{i}(\theta(t)-\theta(0))}\rangle = \mathrm{Re}\langle \mathrm{e}^{\mathrm{i}\Delta\theta(t)}\rangle$$

But $\Delta\theta(t) = \theta(t) - \theta(0)$ is linear in the noise and in the initial angular velocity, and both these have a Gaussian distribution. Then $\Delta\theta(t)$ also has a Gaussian distribution with a zero mean value and a second moment $\langle(\Delta\theta(t))^2\rangle$. For a Gaussian vaiable X with mean value μ_X and variance σ_X^2 we have the characteristic function

$$\langle \mathrm{e}^{\mathrm{i}kX}\rangle = \mathrm{e}^{\mathrm{i}k\mu_X - k^2\sigma_X^2/2}$$

Therefore

$$C_R(t) = \mathrm{e}^{-\langle(\Delta\theta(t))^2\rangle/2} = \exp\left(-\frac{2k_\mathrm{B}TI}{\gamma^2}\left[t/\tau_R - \left(1-\mathrm{e}^{-t/\tau_R}\right)\right]\right)$$

For short and long times we then have

$$\begin{aligned}C_R(t) &= \exp\left(-\frac{1}{2}\frac{k_\mathrm{B}T}{I}t^2\right), \quad t \ll \tau_R \\ C_R(t) &= \exp\left(-\frac{k_\mathrm{B}T}{\gamma}t\right), \quad t \gg \tau_R \end{aligned} \tag{6.40}$$

The rotational correlation function is directly related to the dielectric susceptibility which is measured in dielectric relaxation measurements. The relation is

$$\begin{aligned}\epsilon(\mathrm{i}\omega) &= \epsilon_\infty + (\epsilon_0 - \epsilon_\infty)\int_0^\infty \mathrm{e}^{-\mathrm{i}\omega t}\left(-\frac{\mathrm{d}C_R(t)}{\mathrm{d}t}\right)\mathrm{d}t \\ &= \epsilon_\infty + (\epsilon_0 - \epsilon_\infty)\left[1 - \mathrm{i}\omega C_R(\mathrm{i}\omega)\right]\end{aligned} \tag{6.41}$$

Here ϵ_0 is the static dielectric constant for $\omega = 0$ and ϵ_∞ the corresponding one for high frequencies. An exponential relaxation for long times, as obtained above, is seen for single molecules or low densities. For high densities the relaxation is more complex and one often observes a so called Kohlrausch- Williams-Watts form for $C_R(t)$

$$C_R(t) = \mathrm{e}^{-(t/\tau)^\beta}, \quad 0 < \beta < 1$$

with the relaxation time τ increasing rapidly with decreasing temperature or increasing density. The corresponding imaginary part of the dielectric susceptibility $\epsilon''(\omega)$ has then a much broader peak than the Lorentzian shape obtained for an exponential function.

Langevin dynamics of a Gaussian polymer chain

Consider a polymer molecule with N beads or particles of mass m connected by springs with force constant k, and moving in a fluid of small molecules. The interaction potential is

$$U = \sum_{\ell=1}^{N} \frac{1}{2} \left[\boldsymbol{r}(\ell, t) - \boldsymbol{r}(\ell - 1, t) \right]^2$$

The equation of motion of bead ℓ reads

$$m \frac{\mathrm{d}^2}{\mathrm{d}t^2} \boldsymbol{r}(\ell, t) = -\gamma \frac{\mathrm{d}}{\mathrm{d}t} \boldsymbol{r}(\ell, t) + k \left[\boldsymbol{r}(\ell + 1, t) - 2\boldsymbol{r}(\ell, t) + \boldsymbol{r}(\ell - 1, t) \right] + \xi(\ell, t)$$

Here γ is the friction constant. Neglecting inertial effects, i.e. the acceleration term this gives

$$\frac{\mathrm{d}}{\mathrm{d}t} \boldsymbol{r}(\ell, t) = \frac{k}{\gamma} \left[\boldsymbol{r}(\ell + 1, t) - 2\boldsymbol{r}(\ell, t) + \boldsymbol{r}(\ell - 1, t) \right] + \frac{1}{\gamma} \xi(\ell, t)$$

Let's consider a ring polymer or a chain with periodic boundary conditions. Then a discrete Fourier transform is

$$\boldsymbol{R}(q, t) = \sum_{\ell=1}^{N} \mathrm{e}^{\mathrm{i}q\ell} \boldsymbol{r}(\ell, t)$$

with the inverse transform

$$\boldsymbol{r}(\ell, t) = \frac{1}{N} \sum_{k=1}^{N} \mathrm{e}^{-\mathrm{i}q_k \ell} \boldsymbol{R}(q, t)$$

and where

$$q_k = -\pi + \frac{2\pi k}{N}, \quad k = 1, \ldots, N$$

This follows since periodic boundary conditions imply $\boldsymbol{r}(\ell, t) = \boldsymbol{r}(\ell + N, t)$ and so $\exp(\mathrm{i}qN) = 1$. We also have the relation

$$\sum_{\ell=1}^{N} \mathrm{e}^{\mathrm{i}(q-q')\ell} = \mathrm{e}^{\mathrm{i}(q-q')} \frac{1 - \mathrm{e}^{\mathrm{i}(q-q')N}}{1 - \mathrm{e}^{\mathrm{i}(q-q')}} = \begin{cases} 0 & q \neq q' \\ N & q = q' \end{cases}$$

and similarly when summing over q_k. For $\boldsymbol{R}(q, t)$ we find the equation

$$\frac{\mathrm{d}}{\mathrm{d}t} \boldsymbol{R}(q, t) = -\frac{2k}{\gamma} \left[1 - \cos q \right] \boldsymbol{R}(q, t) + \frac{1}{\gamma} \xi(q, t)$$

The solution is given by

$$\boldsymbol{R}(q, t) = \frac{1}{\gamma} \int_{-\infty}^{t} \mathrm{d}s \, \mathrm{e}^{-(1 - \cos q)(t-s)/\tau} \xi(q, s)$$

with the relaxation time $\tau = \gamma / 2k$, and so

$$\boldsymbol{r}(\ell, t) = \frac{1}{N\gamma} \sum_{q} \int_{0}^{\infty} \mathrm{d}s \, \mathrm{e}^{-(1 - \cos q)(t-s)/\tau} \mathrm{e}^{-\mathrm{i}q\ell} \xi(q, t - s)$$

We are interested to calculate the correlation function

$$C(\ell,t) = \langle [\boldsymbol{r}(\ell,t) - \boldsymbol{r}(0,0)]^2 \rangle$$

which is a measure of the mean squared displacement for the different beads. Then

$$\begin{aligned} C(\ell,t) &= \frac{1}{N^2\gamma^2} \sum_q \sum_{q'} \int_0^\infty \mathrm{d}s \int_0^\infty \mathrm{d}s' \, \mathrm{e}^{-(1-\cos q)(t-s)/\tau} \mathrm{e}^{-(1-\cos q')(t-s')/\tau} \\ &\times \left\langle \left[\mathrm{e}^{-\mathrm{i}q\ell} \xi(q,t-s)\xi(q,-s) \right] \cdot \left[\mathrm{e}^{-\mathrm{i}q'\ell} \xi(q',t-s')\xi(q',-s') \right] \right\rangle \end{aligned}$$

Now, the fluctuating force ξ is uncorrelated on different beads and at different times

$$\langle \xi^\alpha(\ell,t)\xi^\beta(\ell',t') \rangle = g\delta_{\ell,\ell'}\delta(t-t')\delta_{\alpha,\beta}$$

and so

$$\begin{aligned} \langle \xi^\alpha(q,t)\xi^\beta(q',t') \rangle &= \sum_{\ell=1}^N \sum_{\ell'}^N \mathrm{e}^{\mathrm{i}q\ell} \mathrm{e}^{\mathrm{i}q'\ell'} \langle \xi^\alpha(\ell,t)\xi^\beta(\ell',t') \rangle = g \sum_{\ell=1}^N \mathrm{e}^{\mathrm{i}(q+q')\ell} \delta(t-t')\delta_{\alpha,\beta} \\ &= N g \delta_{q+q',0} \, \delta(t-t')\delta_{\alpha,\beta} \end{aligned}$$

Inserting this into the expression for C we can perform the time integrals and one summation over q, to obtain

$$\begin{aligned} C(\ell,t) &= \frac{3g}{N^2\gamma^2} \sum_q \sum_{q'} \int_0^\infty \mathrm{d}s \int_0^\infty \mathrm{d}s' \mathrm{e}^{-(1-\cos q)(t-s)/\tau} \mathrm{e}^{-(1-\cos q)(t-s')/\tau} \\ &\times \delta_{q+q',0} \left[\delta(s-s') - \mathrm{e}^{-\mathrm{i}q\ell}\delta(t-s+s') - \mathrm{e}^{-\mathrm{i}q'\ell}\delta(t-s+s') + \delta(s-s') \right] \\ &= \frac{3g}{N2k\gamma} \sum_q \frac{1 - \mathrm{e}^{-(1-\cos q)t/\tau} \cos q\ell}{1-\cos q} \end{aligned}$$

In the limit $N \to \infty$, q becomes a continous variable in the interval $(-\pi, \pi$ and

$$C(\ell,t) = \frac{3g}{2k\gamma} \frac{1}{2\pi} \int_{-\pi}^{\pi} \mathrm{d}q \frac{1 - \mathrm{e}^{-(1-\cos q)t/\tau} \cos q\ell}{1-\cos q}$$

For $t = 0$ we have

$$\begin{aligned} C(\ell,0) &= \frac{3g}{2k\gamma} \frac{1}{2\pi} \int_{-\pi}^{\pi} \mathrm{d}q \frac{1-\cos q\ell}{1-\cos q} = \left[\mathrm{e}^{\mathrm{i}q} = z \right] = \frac{3g}{2k\gamma} \frac{1}{2\pi\mathrm{i}} \int_C \mathrm{d}z \frac{1}{z^\ell} \frac{(z^\ell-1)^2}{z-1} \\ &= \frac{3g}{2k\gamma} \frac{1}{2\pi\mathrm{i}} \int_C \mathrm{d}z \frac{1}{z^\ell} \left(\sum_{k=0}^{\ell-1} z^k \right)^2 \end{aligned}$$

where C is a unit-circle in the z-plane. Since

$$\frac{1}{2\pi\mathrm{i}} \int_C \mathrm{d}z \frac{1}{z^m} = \delta_{m,1}$$

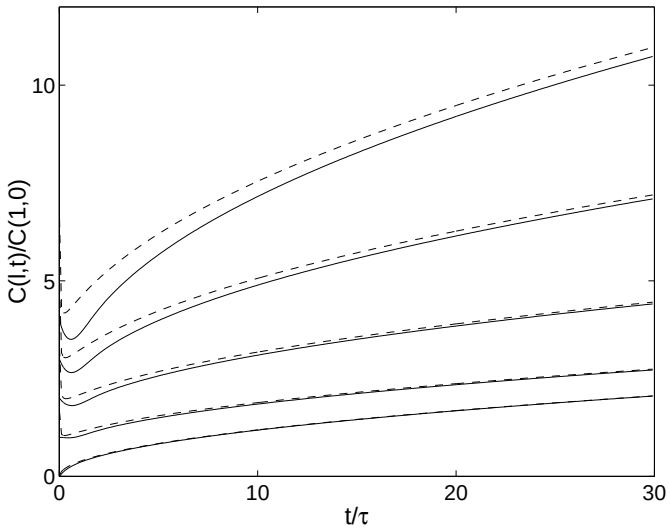

Figure 6.3: *The function $C(\ell,t)/C(1,0)$ versus $t\tau$ for $\ell = 0-4$. The asymptotoc behaviour for $t/\tau \gg 1$is shown as dashed curves.*

we see that there are ℓ terms where $z^k z^p = z^{\ell-1}$ and so

$$C(\ell,0) = \frac{3g}{2k\gamma}\ell = C(1,0)\ell$$

To find a more explicit expression for the timedependence we can take the derivative of $C(\ell,t)$

$$\begin{aligned}\frac{\partial}{\partial t}C(\ell,t) &= \frac{3g}{\gamma^2}\frac{1}{2\pi}\int_{-\pi}^{\pi}\mathrm{d}q\,\mathrm{e}^{-(1-\cos q)t/\tau}\cos q\ell = \frac{3g}{\gamma^2}\mathrm{e}^{-t/\tau}\frac{1}{2\pi}\int_{-\pi}^{\pi}\mathrm{d}q\,\mathrm{e}^{\mathrm{i}q\ell}\mathrm{e}^{\cos q(t/\tau)} \\ &= \frac{3g}{\gamma^2}\mathrm{e}^{-t/\tau}I_\ell\left(t/\tau\right)\end{aligned}$$

where I_ℓ is the modified Bessel function of order ℓ. Integrating we find

$$C(\ell,t) = C(\ell,0) + \frac{g}{2k\gamma}S(\ell,t/\tau)$$

where

$$S(\ell,x) = x\mathrm{e}^{-x}\left[I_0(x)+I_1(x)\right] + \ell\left[\mathrm{e}^{-x}I_0(x)-1\right] + x\mathrm{e}^{-x}\sum_{n=1}^{\ell-1}(\ell-n)I_n(x)$$

In figure 6.3 $C(\ell,t)$ is plotted for $\ell = 0-4$. For $t \gg \tau$ we have the asymptotic expansion

$$I_n(x) = \frac{\mathrm{e}^x}{(2\pi x)^{1/2}}, \quad x \gg 1$$

which gives a $\sqrt{(}t)$ dependence of $C(\ell,t)$ for large times. In particular for $\ell = 0$ this gives the long time behaviour

$$C(0,t) = \frac{g}{\gamma k}\left(\frac{kt}{\pi\gamma}\right)^{1/2}$$

The dashed curves in fig. 6.3 shows this long time behaviour. For small ℓ-values this asymptotic behaviour is reached for rather short times.