33 Brownian motion and fluctuations

33.1 Brownian motion 390
33.2 Johnson noise 393
33.3 Fluctuations 394
33.4 Fluctuations and the availability 395
33.5 Linear response 397
33.6 Correlation functions 400
Chapter summary 406
Further reading 407
Exercises 407

Our treatment of the thermodynamic properties of thermal systems has assumed that we can replace quantities such as pressure by their average values. Even though the molecules in a gas hit the walls of their container stochastically, there are so many of them that the pressure does not *appear* to fluctuate. But with very small systems, these fluctuations can become important. In this chapter, we consider these fluctuations in detail. A useful insight comes from the *fluctuation-dissipation theorem*, which is derived from the assumption that the response of a system in thermodynamic equilibrium to a small external perturbation is the same as its response to a spontaneous fluctuation. This implies that there is a direct relation between the fluctuation properties of a thermal system and what are known as its *linear response* properties.

33.1 Brownian motion

We introduced Brownian motion in Section 19.4. There we showed that the equipartition theorem implies that the translational motion of particles at temperature T fluctuates since each particle must have mean kinetic energy given by $\frac{1}{2}m\langle v^2\rangle = \frac{3}{2}k_{\mathrm{B}}T$. Einstein, in his 1905 paper on Brownian motion, noted that the same random forces that cause Brownian motion of a particle would also cause drag if the particle were pulled through the fluid.

Example 33.1

Find the solution to the equation of motion (known as the **Langevin equation**) for the velocity v of a particle of mass m, which is given by

$$m\dot{v} = -\alpha v + F(t), \tag{33.1}$$

where α is a damping constant (arising from friction), $F(t)$ is a random force whose average value over a long time period, $\langle F\rangle$, is zero.

Solution:

Note first that in the absence of the random force, eqn 33.1 becomes

$$m\dot{v} = -\alpha v, \tag{33.2}$$

which has solution

$$v(t) = v(0)\exp[-t/(m\alpha^{-1})], \tag{33.3}$$

so that any velocity component dies away with a time constant given by m/α. The random force $F(t)$ is necessary to give a model in which the particle's motion does not die away.

To solve eqn 33.1, write $v = \dot{x}$ and premultiply both sides by x. This leads to $mx\ddot{x} = -\alpha x\dot{x} + xF(t)$. A useful identity is

$$\frac{\mathrm{d}}{\mathrm{d}t}(x\dot{x}) = x\ddot{x} + \dot{x}^2, \tag{33.4}$$

and using this we can express our equation of motion as

$$m\frac{\mathrm{d}}{\mathrm{d}t}(x\dot{x}) = m\dot{x}^2 - \alpha x\dot{x} + xF(t). \tag{33.5}$$

We now average this result over time. We note that x and F are uncorrelated, and hence $\langle xF\rangle = \langle x\rangle\langle F\rangle = 0$. We can also use the equipartition theorem, which here states that

$$\frac{1}{2}m\langle\dot{x}^2\rangle = \frac{1}{2}k_{\mathrm{B}}T. \tag{33.6}$$

Hence, using eqn 33.6 in eqn 33.5, we have

$$m\frac{\mathrm{d}}{\mathrm{d}t}\langle x\dot{x}\rangle = k_{\mathrm{B}}T - \alpha\langle x\dot{x}\rangle, \tag{33.7}$$

or equivalently

$$\left(\frac{\mathrm{d}}{\mathrm{d}t} + \frac{\alpha}{m}\right)\langle x\dot{x}\rangle = \frac{k_{\mathrm{B}}T}{m}, \tag{33.8}$$

which has a solution

$$\langle x\dot{x}\rangle = C\mathrm{e}^{-\alpha t/m} + \frac{k_{\mathrm{B}}T}{\alpha}. \tag{33.9}$$

Putting the boundary condition that $x = 0$ when $t = 0$, one can find that the constant $C = -k_{\mathrm{B}}T/\alpha$, and hence

$$\langle x\dot{x}\rangle = \frac{k_{\mathrm{B}}T}{\alpha}(1 - \mathrm{e}^{-\alpha t/m}). \tag{33.10}$$

Using the identity

$$\frac{1}{2}\frac{\mathrm{d}}{\mathrm{d}t}\langle x^2\rangle = \langle x\dot{x}\rangle, \tag{33.11}$$

we then have

$$\langle x^2\rangle = \frac{2k_{\mathrm{B}}T}{\alpha}\left[t - \frac{m}{\alpha}(\mathrm{e}^{-\alpha t/m})\right]. \tag{33.12}$$

When $t \ll m/\alpha$,

$$\langle x^2\rangle = \frac{k_{\mathrm{B}}Tt^2}{m}, \tag{33.13}$$

while for $t \gg m/\alpha$,

$$\langle x^2\rangle = \frac{2k_{\mathrm{B}}Tt}{\alpha}. \tag{33.14}$$

Writing[1] $\langle x^2\rangle = 2Dt$, where D is the diffusion constant, yields

$$D = k_{\mathrm{B}}T/\alpha. \tag{33.15}$$

[1] See Appendix C.12.

If a steady force F had been applied instead of a random one, then the terminal velocity (the velocity achieved in the steady state, with $\dot{v} = 0$) of the particle could have been obtained from

$$m\dot{v} = -\alpha v + F = 0, \tag{33.16}$$

yielding $v = \alpha^{-1}F$, and so α^{-1} plays the rôle of a **mobility** (the ratio of velocity to force). It is easy to understand that the terminal velocity should be limited by frictional forces, and hence depends on α. However, the previous example shows that the diffusion constant D is proportional to $k_{\mathrm{B}}T$ and also to the mobility α^{-1}. Note that the diffusion constant $D = k_{\mathrm{B}}T/\alpha$ is independent of mass. The mass only enters in the transient term in eqn 33.12 (see also eqn 33.13) that disappears at long times.

Remarkably, we have found that the diffusion rate D, describing the random fluctuations of the particle's position, is related to the frictional damping α. The formula $D = k_{\mathrm{B}}T/\alpha$ is an example of the fluctuation-dissipation theorem, which we will prove later in the chapter (Section 33.6).

As a prelude to what will come later, the following example considers the correlation function for the Brownian motion problem.

Example 33.2

Derive an expression for the velocity **correlation function** $\langle v(0)v(t)\rangle$ for the Brownian motion problem.

Correlation functions are discussed in more detail in Section 33.6. The velocity correlation function $\langle v(0)v(t)\rangle$ is defined by

$$\lim_{T\to\infty} \frac{1}{T}\int_{-T/2}^{T/2} \mathrm{d}t'\, v(t')v(t+t'),$$

and describes how well, on average, the velocity at a certain time is correlated with the velocity at a later time.

Solution:
The rate of change of v is given by

$$\dot{v}(t) = \frac{v(t+\tau) - v(t)}{\tau} \tag{33.17}$$

in the limit in which $\tau \to 0$. Inserting this into eqn 33.1 and premultiplying by $v(0)$ gives

$$\frac{v(0)v(t+\tau) - v(0)v(t)}{\tau} = -\frac{\alpha}{m}v(0)v(t) + \frac{v(0)F(t)}{m}. \tag{33.18}$$

Averaging this equation, and noting that $\langle v(0)F(t)\rangle = 0$ because v and F are uncorrelated, yields

$$\frac{\langle v(0)v(t+\tau)\rangle - \langle v(0)v(t)\rangle}{\tau} = -\frac{\alpha}{m}\langle v(0)v(t)\rangle, \tag{33.19}$$

and taking the limit in which $\tau \to 0$ yields

$$\frac{\mathrm{d}}{\mathrm{d}t}\langle v(0)v(t)\rangle = -\frac{\alpha}{m}\langle v(0)v(t)\rangle, \tag{33.20}$$

and hence

$$\langle v(0)v(t)\rangle = \langle v(0)^2\rangle \mathrm{e}^{-\alpha t/m}. \tag{33.21}$$