However, we have just said that the equipartition theorem is only valid at high temperature. Thus we see that the temperature must be high enough that we can safely ignore the quantum nature of the energy spectrum, but not so high that we invalidate the approximation of treating the relevant potential wells as perfectly quadratic. Fortunately there is plenty of room between these two extremes.

19.4 Brownian motion

We close this chapter with one example in which the effect of the equipartition of energy is encountered.

Example 19.3

Brownian motion:
In 1827, Robert Brown used a microscope to observe pollen grains jiggling about in water. He was not the first to make such an observation (any small particles suspended in a fluid will do the same, and are very apparent when looking down a microscope), but this effect has come to be known as **Brownian motion**.

The motion is very irregular, consisting of translations and rotations, with grains moving independently, even when moving close to each other. The motion is found to be more active the smaller the particles. The motion is also found to be more active the less viscous the fluid. Brown was able to discount a 'vital' explanation of the effect, i.e. that the pollen grains were somehow 'alive', but he was not able to give a correct explanation. Something resembling a modern theory of Brownian motion was proposed by Wiener in 1863, though the major breakthrough was made by Einstein in 1905.

We will postpone a full discussion of Brownian motion until Chapter 33, but using the equipartition theorem, the origin of the effect can be understood in outline. Each pollen grain (of mass m) is free to move translationally and so has mean kinetic energy $\frac{1}{2}m\langle v^2\rangle = \frac{3}{2}k_BT$. This energy is very small, as we have seen, but leads to a measurable amplitude of vibration for a small pollen grain. The amplitude of vibration is greater for smaller pollen grains because a mean kinetic energy of $\frac{3}{2}k_BT$ gives more mean square velocity $\langle v^2\rangle$ to less massive grains. The thermally excited vibrations are resisted by viscous damping, so the motion is expected to be more pronounced in less viscous fluids.

Chapter summary

- The equipartition theorem states that if the energy of a system is the sum of n quadratic modes, and that the system is in contact with a heat reservoir of temperature T, the mean energy of the system is given by $n \times \frac{1}{2}k_BT$.
- The equipartition theorem is a high–temperature result and gives incorrect predictions at low temperature, where the discrete nature of the energy spectrum cannot be ignored.

Exercises

(19.1) What is the mean kinetic energy in eV at room temperature of a gaseous (a) He atom, (b) Xe atom, (c) Ar atom and (d) Kr atom. [Hint: do you have to do four separate calculations?]

(19.2) Comment on the following values of molar heat capacity in $\mathrm{J\,K^{-1}\,mol^{-1}}$, all measured at constant pressure at 298 K.

Al	24.35	Pb	26.44
Ar	20.79	Ne	20.79
Au	25.42	N_2	29.13
Cu	24.44	O_2	29.36
He	20.79	Ag	25.53
H_2	28.82	Xe	20.79
Fe	25.10	Zn	25.40

[Hint: express them in terms of R; which of the substances is a solid and which is gaseous?]

(19.3) A particle at position r is in a potential well $V(r)$ given by

$$V(r) = \frac{A}{r^n} - \frac{B}{r}, \tag{19.28}$$

where A and B are positive constants and $n > 2$. Show that the bottom of the well is approximately quadratic in r. Hence find the particle's mean thermal energy at temperature T above the bottom of the well assuming the validity of the equipartition theorem in this situation.

(19.4) In example 19.1, show that

$$\langle x_i^2 \rangle = \frac{k_BT}{2\alpha_i}. \tag{19.29}$$

(19.5) If the energy E of a system is not quadratic, but behaves like $E = \alpha|x|$ where $\alpha > 0$, show that $\langle E \rangle = k_BT$.

(19.6) If the energy E of a system behaves like $E = \alpha|x|^n$, where $n = 1, 2, 3 \ldots$ and $\alpha > 0$, show that $\langle E \rangle = \xi k_BT$, where ξ is a numerical constant.

(19.7) A simple pendulum with length ℓ makes an angle θ with the vertical, where $\theta \ll 1$. Show that it oscillates with a period given by $2\pi\sqrt{\ell/g}$. The pendulum is now placed at rest and allowed to come into equilibrium with its surroundings at temperature T. Derive an expression for $\langle \theta^2 \rangle$.

33 Brownian motion and fluctuations

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 $\frac{1}{2}m\langle v^2\rangle = \frac{3}{2}k_BT$. Einstein, in his 1905 paper on Brownian motion, noted that the same random forces which 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

$$mx\ddot{x} = -\alpha x\dot{x} + xF(t). \tag{33.4}$$

Now

$$\frac{\mathrm{d}}{\mathrm{d}t}(x\dot{x}) = x\ddot{x} + \dot{x}^2, \tag{33.5}$$

and hence we have that

$$m\frac{\mathrm{d}}{\mathrm{d}t}(x\dot{x}) = m\dot{x}^2 - \alpha x\dot{x} + xF(t). \tag{33.6}$$

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

$$\frac{1}{2}m\langle\dot{x}^2\rangle = \frac{1}{2}k_BT. \tag{33.7}$$

Hence, using eqn 33.7 in eqn 33.6, we have

$$m\frac{\mathrm{d}}{\mathrm{d}t}\langle x\dot{x}\rangle = k_BT - \alpha\langle x\dot{x}\rangle, \tag{33.8}$$

or equivalently

$$\left(\frac{\mathrm{d}}{\mathrm{d}t} + \frac{\alpha}{m}\right)\langle x\dot{x}\rangle = \frac{k_BT}{m}, \tag{33.9}$$

which has a solution

$$\langle x\dot{x}\rangle = Ce^{-\alpha t/m} + \frac{k_BT}{\alpha}. \tag{33.10}$$

Putting the boundary condition that $x = 0$ when $t = 0$, one can find that the constant $C = -k_BT/\alpha$, and hence

$$\langle x\dot{x}\rangle = \frac{k_BT}{\alpha}(1 - e^{-\alpha t/m}). \tag{33.11}$$

Using the identity

$$\frac{1}{2}\frac{\mathrm{d}}{\mathrm{d}t}\langle x^2\rangle = \langle x\dot{x}\rangle, \tag{33.12}$$

we then have

$$\langle x^2\rangle = \frac{2k_BT}{\alpha}\left[t - \frac{m}{\alpha}(e^{-\alpha t/m})\right]. \tag{33.13}$$

When $t \ll m/\alpha$,

$$\langle x^2\rangle = \frac{k_BTt^2}{m}, \tag{33.14}$$

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

$$\langle x^2\rangle = \frac{2k_BTt}{\alpha}. \tag{33.15}$$

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

[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_BT and also to the mobility α^{-1}. Note that the diffusion constant $D = k_BT/\alpha$ is independent of mass. The mass only enters in the transient term in eqn 33.13 (see also eqn 33.14) 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 $D = k_BT/\alpha$ 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

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

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

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

and hence

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

This example shows that the velocity correlation function decays to zero as time increases at exactly the same rate that the velocity itself relaxes (see eqn 33.3).

33.2 Johnson noise

We now consider another fluctuating system: the noise voltage which is generated across a resistor of resistance R by thermal fluctuations. Let us suppose that the resistor is connected to a transmission line of length L which is correctly terminated at each end, as shown in Fig. 33.1.[2] Because the transmission line is matched, it should not matter whether it is connected or not. The transmission line can support modes of wave vector $k = n\pi/L$ and frequency $\omega = ck$, and therefore there is one mode per frequency interval $\Delta\omega$ given by

$$\Delta\omega = \frac{c\pi}{L}. \tag{33.22}$$

By the equipartition theorem, each mode has mean energy k_BT, and hence the energy per unit length of transmission line, in an interval $\Delta\omega$, is given by

$$k_BT\frac{\Delta\omega}{c\pi}. \tag{33.23}$$

Half this energy is travelling from left to right, and half from right to left. Hence, the mean power incident on the resistor is given by

$$\frac{1}{2\pi}k_BT\Delta\omega, \tag{33.24}$$

and in equilibrium this must equal the mean power dissipated by the resistor, which is given by

$$\langle I^2R\rangle. \tag{33.25}$$

In the circuit, we have $I = V/(2R)$ and hence

$$\frac{\langle V^2\rangle}{4R} = \langle I^2R\rangle = \frac{1}{2\pi}k_BT\Delta\omega, \tag{33.26}$$

and hence

$$\langle V^2\rangle = \frac{2}{\pi}k_BTR\Delta\omega, \tag{33.27}$$

which, using $\Delta\omega = 2\pi\Delta f$, can be written in the form

$$\boxed{\langle V^2\rangle = 4k_BTR\Delta f.} \tag{33.28}$$

This expression is known as the **Johnson noise** produced across a resistor in a frequency interval Δf. It is another example of the connection between fluctuations and dissipation, since it relates fluctuating noise power ($\langle V^2\rangle$) to the dissipation in the circuit (R).

We can derive a quantum mechanical version of the Johnson noise formula by replacing k_BT by $\hbar\omega/(e^{\beta\hbar\omega} - 1)$, which yields

$$\langle V^2\rangle = \frac{2R}{\pi}\frac{\hbar\omega\Delta\omega}{e^{\beta\hbar\omega} - 1}. \tag{33.29}$$

[2] We will give a method of calculating the noise voltage that may seem a little artificial at first, but provides a convenient way of calculating how the resistor can exchange energy with a thermal reservoir. A more elegant approach will be done in Example 33.9.

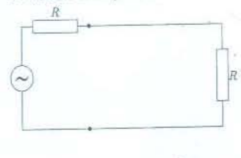

Fig. 33.1 The equivalent circuit to consider the Johnson noise across a resistor. The resistor is connected to a matched transmission line which is correctly terminated, hence the presence of the second resistor; one can consider the noise voltage as being an alternating voltage source which is connected in series with the second resistor.

33.3 Fluctuations

In this section, we will consider the origin of fluctuations and show how much freedom a system has to allow the functions of state to fluctuate. We will focus on one such function of state, which we will call x, and ask the question: if the system is in equilibrium, what is the probability distribution of x? Let us suppose that the number of microstates associated with a system characterised by this parameter x and having energy E (which we will consider fixed[3]) is given by

$$\Omega(x, E). \tag{33.30}$$

[3] This part of the argument assumes that we are working in the microcanonical ensemble (see Section 4.6).

If x were constrained to this value, the entropy S of the system would be

$$S(x, E) = k_B \ln \Omega(x, E), \tag{33.31}$$

which we could write equivalently as $\Omega(x, E) = e^{S(x,E)/k_B}$. If x were not constrained, its probability distribution function would then follow the function $p(x)$, where

$$p(x) \propto \Omega(x, E) = e^{S(x,E)/k_B}. \tag{33.32}$$

At equilibrium the system will maximize its entropy, and let us suppose that this occurs when $x = x_0$. Hence

$$\left(\frac{\partial S(x, E)}{\partial x}\right) = 0 \quad \text{when } x = x_0. \tag{33.33}$$

Let us now write a Taylor expansion of $S(x, E)$ around the equilibrium point $x = x_0$:

$$S(x, E) = S(x_0, E) + \left(\frac{\partial S}{\partial x}\right)_{x=x_0}(x-x_0) + \frac{1}{2}\left(\frac{\partial^2 S}{\partial x^2}\right)_{x=x_0}(x-x_0)^2 + \cdots. \tag{33.34}$$

which with eqn 33.33 implies that

$$S(x) = S(x_0) + \frac{1}{2}\left(\frac{\partial^2 S}{\partial x^2}\right)_{x=x_0}(x-x_0)^2 + \cdots \tag{33.35}$$

Hence, defining $\Delta x = x - x_0$, we can write the probability function as a Gaussian,

$$p(x) \propto \exp\left(-\frac{(\Delta x)^2}{2\langle(\Delta x)^2\rangle}\right), \tag{33.36}$$

where

$$\boxed{\langle(\Delta x)^2\rangle = -\frac{k_B}{\left(\frac{\partial^2 S}{\partial x^2}\right)_E}.} \tag{33.37}$$

This equation shows that if the entropy S changes rapidly as a function of x, we are more likely to find the system with x close to x_0. This makes sense.

Example 33.3

Let x be the internal energy U for a system with fixed volume. Using $T = (\partial U/\partial S)_V$, we have that

$$\left(\frac{\partial^2 S}{\partial U^2}\right)_V = \left(\frac{\partial(1/T)}{\partial U}\right)_V = -\frac{1}{T^2 C_V}, \tag{33.38}$$

and hence

$$\langle(\Delta U)^2\rangle = -\frac{k_B}{\left(\frac{\partial^2 S}{\partial U^2}\right)_V} = k_B T^2 C_V. \tag{33.39}$$

So if a system is in contact with a bath at temperature T, there is a non-zero probability that we may find the system away from the equilibrium internal energy: thus U can fluctuate. The size of the fluctuations is larger if the heat capacity is larger.

Both the heat capacity C_V and the internal energy U are extensive parameters and therefore they scale with the size of the system. The r.m.s. fluctuations of U scale with the square root of the size of the system, so the *fractional* r.m.s. fluctuations scale with the size of the system to the power $-\frac{1}{2}$. Thus if the system has N atoms, then

$$C \propto N, \quad U \propto N \quad \sqrt{\langle(\Delta U)^2\rangle} \propto \sqrt{N}, \tag{33.40}$$

and

$$\frac{\sqrt{\langle(\Delta U)^2\rangle}}{U} \propto \frac{1}{\sqrt{N}}. \tag{33.41}$$

Hence as $N \to \infty$, we can ignore fluctuations. Fluctuations are more important in small systems. However, note that at a critical point for a first-order phase transition, $C \to \infty$ and hence

$$\frac{\langle(\Delta U)^2\rangle}{U} \to \infty. \tag{33.42}$$

Hence fluctuations become divergent at the critical point and cannot be ignored, even for large systems.

33.4 Fluctuations and the availability

We now generalize an argument presented in Section 16.5 to the case in which numbers of particles can fluctuate. Consider a system in contact with a reservoir. The reservoir has temperature T_0, pressure p_0 and chemical potential μ_0. Let us consider what happens when we transfer energy dU, volume dV and dN particles from the reservoir to the system. The internal energy of the reservoir changes by dU_0, where

$$dU_0 = -dU = T_0\, dS_0 - p_0(-dV) + \mu_0(-dN), \tag{33.43}$$

where the minus signs express the fact that the energy, volume and number of particles in the reservoir are *decreasing*. We can rearrange this expression to give the change of entropy in the reservoir as

$$\mathrm{d}S_0 = \frac{-\mathrm{d}U - p_0\mathrm{d}V + \mu_0\mathrm{d}N}{T_0}. \tag{33.44}$$

If the entropy of the system changes by $\mathrm{d}S$, then the total change of entropy $\mathrm{d}S_{\mathrm{tot}}$ is

$$\mathrm{d}S_{\mathrm{tot}} = \mathrm{d}S + \mathrm{d}S_0, \tag{33.45}$$

and the second law of thermodynamics implies that $\mathrm{d}S_{\mathrm{tot}} \geq 0$. Using eqn 33.44, we have that

$$\mathrm{d}S_{\mathrm{tot}} = -\frac{\mathrm{d}U - T_0\mathrm{d}S + p_0\mathrm{d}V - \mu_0\mathrm{d}N}{T_0}, \tag{33.46}$$

which can be written as

$$\mathrm{d}S_{\mathrm{tot}} = -\frac{\mathrm{d}A}{T_0}, \tag{33.47}$$

where $A = U - T_0S + p_0V - \mu_0N$ is the **availability** (this generalizes eqn 16.32).

We now apply the concept of availability to fluctuations. Let us suppose that the availability depends on some variable x, so that we can write a function $A(x)$. Equilibrium will be achieved when $A(x)$ is minimized (so that S_{tot} is maximized, see eqn 33.47) and let us suppose that this occurs when $x = x_0$. Hence we can similarly write $A(x)$ in a Taylor expansion around the equilibrium point and hence

$$A(x) = A(x_0) + \frac{1}{2}\left(\frac{\partial^2 A}{\partial x^2}\right)_{x=x_0}(\Delta x)^2 + \cdots, \tag{33.48}$$

so that we can recover the probability distribution in eqn 33.36 with

$$\langle(\Delta x)^2\rangle = -\frac{k_{\mathrm{B}}T_0}{\left(\frac{\partial^2 A}{\partial x^2}\right)}. \tag{33.49}$$

Example 33.4

A system with a fixed number N of particles is in thermal contact with a reservoir at temperature T. It is surrounded by a tensionless membrane so that its volume is able to fluctuate. Calculate the mean square volume fluctuations. For the special case of an ideal gas, show that $\langle(\Delta V)^2\rangle = V^2/N$.

Solution:

Fixing T and N means that U can fluctuate. Fixing N implies that $\mathrm{d}N = 0$ and hence we have that

$$\mathrm{d}U = T\mathrm{d}S - p\mathrm{d}V. \tag{33.50}$$

Changes in the availability therefore follow:

$$\mathrm{d}A = \mathrm{d}U - T_0\mathrm{d}S + p_0\mathrm{d}V = (T - T_0)\mathrm{d}S + (p_0 - p)\mathrm{d}V, \tag{33.51}$$

and hence

$$\left(\frac{\partial A}{\partial V}\right)_{T,N} = p_0 - p \tag{33.52}$$

and

$$\left(\frac{\partial^2 A}{\partial V^2}\right)_{T,N} = -\left(\frac{\partial p}{\partial V}\right)_{T,N}. \tag{33.53}$$

Hence

$$\langle(\Delta V)^2\rangle = -k_{\mathrm{B}}T_0\left(\frac{\partial V}{\partial p}\right)_{T,N}. \tag{33.54}$$

For an ideal gas, $(\partial V/\partial p)_{T,N} = -Nk_{\mathrm{B}}T/p^2 = -V/p$, and hence

$$\langle(\Delta V)^2\rangle = \frac{V^2}{N}. \tag{33.55}$$

Equation 33.55 implies that the *fractional* volume fluctuations follow

$$\frac{\sqrt{\langle(\Delta V)^2\rangle}}{V} = \frac{1}{N^{1/2}}. \tag{33.56}$$

Thus for a box containing 10^{24} molecules of gas (a little over a mole of gas), the fractional volume fluctuations are at the level of one part in 10^{12}.

We can derive other similar expressions for other fluctuating variables, including

$$\langle(\Delta T)^2\rangle = \frac{k_{\mathrm{B}}T^2}{C_V}, \tag{33.57}$$

$$\langle(\Delta S)^2\rangle = k_{\mathrm{B}}C_p, \tag{33.58}$$

$$\langle(\Delta p)^2\rangle = \frac{k_{\mathrm{B}}T\kappa_S}{C_V}, \tag{33.59}$$

where κ_S is the adiabatic compressibility (see eqn 16.72).

33.5 Linear response

In order to understand in more detail the relationship between fluctuations and dissipation, it is necessary to consider how systems respond to external forces in a rather more general way. We consider a displacement variable $x(t)$ that is the result of some force $f(t)$, and require that the product xf has the dimensions of energy. (We will say that x and f are **conjugate variables** if their product has the dimensions of energy.) We assume that the response of x to a force f is linear (so that, for example, doubling the force doubles the response), but there could be

some delay in the way in which the system responds. The most general way of writing this down is as follows: we say that the average value of x at time t is denoted by $\langle x(t)\rangle_f$ (the subscript f reminds us that a force f has been applied) and is given by

$$\langle x(t)\rangle_f = \int_{-\infty}^{\infty} \chi(t-t')f(t')\,\mathrm{d}t', \tag{33.60}$$

where $\chi(t-t')$ is a **response function**. This relates the value of $x(t)$ to a sum over values of the force $f(t')$ at all other times. Now it makes sense to sum over past values of the force, but not to sum over future values of the force. This will force the response function $\chi(t-t')$ to be zero if $t<t'$. Before seeing what effect this has, we need to Fourier transform eqn 33.60 to make it simpler to deal with. The Fourier transform of $x(t)$ is given by the function $\tilde{x}(\omega)$ given by

$$\tilde{x}(\omega) = \int_{-\infty}^{\infty} \mathrm{d}t\, \mathrm{e}^{-\mathrm{i}\omega t} x(t). \tag{33.61}$$

The inverse transform is then given by

$$x(t) = \frac{1}{2\pi}\int_{-\infty}^{\infty} \mathrm{d}\omega\, \mathrm{e}^{\mathrm{i}\omega t}\tilde{x}(\omega). \tag{33.62}$$

The expression in eqn 33.60 is a convolution of the functions χ and f, and hence by the convolution theorem we can write this equation in Fourier transform form as

$$\langle \tilde{x}(\omega)\rangle_f = \tilde{\chi}(\omega)\tilde{f}(\omega). \tag{33.63}$$

This is much simpler than eqn 33.60 as it is a product, rather than a convolution. Note that the response function $\tilde{\chi}(\omega)$ can be complex. The real part of the response function gives the part of the displacement which is in phase with the force. The imaginary part of the response function gives a displacement with is $\frac{\pi}{2}$ out of phase with the force. It corresponds to dissipation because the external force does work on the system at a rate given by the force multiplied by the velocity, i.e. $f(t)\dot{x}(t)$, and this work is dissipated as heat. For $f(t)$ and $\dot{x}(t)$ to be in phase, and hence give a non-zero average, $f(t)$ and $x(t)$ have to be $\frac{\pi}{2}$ out of phase (see Exercise 33.2).

We can build causality into our problem by writing the response function as

$$\chi(t) = y(t)\theta(t), \tag{33.64}$$

where $\theta(t)$ is a Heaviside step function (see Fig. 30.1) and $y(t)$ is a function which equals $\chi(t)$ when $t>0$ and can equal anything at all when $t<0$. For the convenience of the following derivation, we will set $y(t) = -\chi(|t|)$ when $t<0$, making $y(t)$ an odd function (and, importantly, making $\tilde{y}(\omega)$ purely imaginary). By the inverse convolution theorem, the Fourier transform of $\chi(t)$ is given by the convolution

$$\tilde{\chi}(\omega) = \frac{1}{2\pi}\int_{-\infty}^{\infty} \mathrm{d}\omega'\tilde{\theta}(\omega'-\omega)\tilde{y}(\omega'). \tag{33.65}$$

Writing the Heaviside step function as

$$\theta(t) = \begin{cases} \mathrm{e}^{-\epsilon t} & t>0 \\ 0 & t<0 \end{cases}, \tag{33.66}$$

in the limit in which $\epsilon \to 0$ its Fourier transform is given by

$$\tilde{\theta}(\omega) = \int_0^{\infty} \mathrm{d}t\, \mathrm{e}^{-\mathrm{i}\omega t}\mathrm{e}^{-\epsilon t} = \frac{1}{\mathrm{i}\omega+\epsilon} = \frac{\epsilon}{\omega^2+\epsilon^2} - \frac{\mathrm{i}\omega}{\omega^2+\epsilon^2}. \tag{33.67}$$

Thus, taking the limit $\epsilon\to 0$, we have that

$$\tilde{\theta}(\omega) = \pi\delta(\omega) - \frac{\mathrm{i}}{\omega}. \tag{33.68}$$

Substituting this into eqn 33.65 yields[4]

$$\tilde{\chi}(\omega) = \frac{1}{2}\tilde{y}(\omega) - \frac{\mathrm{i}}{2\pi}\mathcal{P}\int_{-\infty}^{\infty}\frac{\tilde{y}(\omega')\,\mathrm{d}\omega'}{\omega'-\omega}. \tag{33.69}$$

We now write $\tilde{\chi}(\omega)$ in terms of its real and imaginary parts:

$$\tilde{\chi}(\omega) = \tilde{\chi}'(\omega) + \mathrm{i}\tilde{\chi}''(\omega), \tag{33.70}$$

and since $\tilde{y}(\omega)$ is purely imaginary, eqn 33.69 yields

$$\mathrm{i}\tilde{\chi}''(\omega) = \frac{1}{2}\tilde{y}(\omega), \tag{33.71}$$

and hence

$$\boxed{\tilde{\chi}'(\omega) = \mathcal{P}\int_{-\infty}^{\infty}\frac{\mathrm{d}\omega'}{\pi}\frac{\tilde{\chi}''(\omega')}{\omega'-\omega}}. \tag{33.72}$$

This is one of the **Kramers–Kronig relations** which connects the real and imaginary parts of the response function.[5] Note that our derivation has only assumed that the response is linear (eqn 33.60) and causal, so that the Kramers-Kronig relations are very general.

By putting $\omega=0$ into eqn 33.72, we obtain another very useful result:

$$\boxed{\tilde{\chi}'(0) = \mathcal{P}\int_{-\infty}^{\infty}\frac{\mathrm{d}\omega'}{\pi}\frac{\tilde{\chi}''(\omega')}{\omega'}}. \tag{33.73}$$

Sometimes the response function is called a **generalized susceptibility**, and the zero frequency real part, $\tilde{\chi}'(0)$, is called the **static susceptibility**. As discussed above, the imaginary part of the response function, $\tilde{\chi}''(\omega)$, corresponds to the dissipation of the system. Equation 33.73 therefore shows that the static susceptibility (the response at zero frequency) is related to an integral of the total dissipation of the system.

[4] The symbol $\mathcal{P}$ denotes the **Cauchy principal value** of the integral. This means that an integral whose integrand blows up at some value is evaluated using an appropriate limit. For example, $\int_{-1}^{1}\mathrm{d}x/x$ is undefined since $1/x\to\infty$ at $x=0$, but

$$\mathcal{P}\int_{-1}^{1}\frac{\mathrm{d}x}{x} = \lim_{\epsilon\to 0^+}\left(\int_{-1}^{-\epsilon}\frac{\mathrm{d}x}{x} + \int_{\epsilon}^{1}\frac{\mathrm{d}x}{x}\right) = 0.$$

[5] The other Kramers-Kronig relation is derived in Exercise 33.3.

Example 33.5

Find the reponse function for the damped harmonic oscillator (mass m, spring constant k, damping α) whose equation of motion is given by

$$m\ddot{x} + \alpha\dot{x} + kx = f \qquad (33.74)$$

and show that eqn 33.73 holds.

Solution:

Writing the resonant frequency $\omega_0^2 = k/m$, and writing the damping $\gamma = \alpha/m$, we have

$$\ddot{x} + \gamma\dot{x} + \omega_0^2 x = \frac{f}{m}, \qquad (33.75)$$

and Fourier transforming this gives immediately that

$$\tilde{\chi}(\omega) = \frac{\tilde{x}(\omega)}{\tilde{f}(\omega)} = \frac{1}{m}\left[\frac{1}{\omega_0^2 - \omega^2 - i\omega\gamma}\right]. \qquad (33.76)$$

Hence, the imaginary part of the response function is

$$\tilde{\chi}''(\omega) = \frac{1}{m}\left[\frac{\omega\gamma}{(\omega^2-\omega_0^2)^2 + (\omega\gamma)^2}\right], \qquad (33.77)$$

and the static susceptibility is

$$\tilde{\chi}'(0) = \frac{1}{m\omega_0^2} = \frac{1}{k}. \qquad (33.78)$$

The real and imaginary parts of $\tilde{\chi}(\omega)$ are plotted in Fig. 33.2(a). The imaginary part shows a peak near ω_0. Equation 33.77 shows that $\tilde{\chi}''(\omega)/\omega = (\gamma/m)[(\omega^2-\omega_0^2)+(\omega\gamma)^2]$ and straightforward integration shows that $\int_{-\infty}^{\infty}(\tilde{\chi}''(\omega)/\omega)\,d\omega = \pi/(m\omega_0^2) = \pi\tilde{\chi}'(0)$ and hence that eqn 33.73 holds. This is illustrated in Fig. 33.2(b).

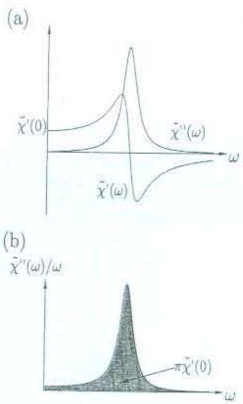

Fig. 33.2 (a) The real and imaginary parts of $\tilde{\chi}(\omega)$ as a function of ω. (b) An illustration of eqn 33.73 for the damped harmonic oscillator.

33.6 Correlation functions

Consider a function $x(t)$. Its Fourier transform[6] is given by

$$\tilde{x}(\omega) = \int_{-\infty}^{\infty} dt\, e^{-i\omega t} x(t), \qquad (33.79)$$

[6] See Appendix C.11.

as before, and we define the **power spectral density** as $\langle|\tilde{x}(\omega)|^2\rangle$. This function shows how much power is associated with different parts of the frequency spectrum. We now define the **autocorrelation function** $C_{xx}(t)$ by

$$C_{xx}(t) = \langle x(0)x(t)\rangle = \int_{-\infty}^{\infty} x^*(t')x(t'+t)\,dt'. \qquad (33.80)$$

The notation here is that the double subscript means we are measuring how much x at one time is correlated with x at another time. (We could also define a cross-correlation function $C_{xy}(t) = \langle x(0)y(t)\rangle$ which measures how much x at one time is correlated with a different variable y at another time.) The autocorrelation function is connected to the power spectral density by the **Wiener–Khinchin theorem**[7] which states that the power spectral density is given by the Fourier transform of the autocorrelation function:

[7] Norbert Wiener (1894–1964); Alexsandr Y. Khinchin (1894–1959). The proof of this theorem is given in Appendix C.11.

$$\boxed{\langle|\tilde{x}(\omega)|^2\rangle = \tilde{C}_{xx}(\omega) = \int_{-\infty}^{\infty} e^{-i\omega t}\langle x(0)x(t)\rangle\,dt} \qquad (33.81)$$

The inverse relation also must hold:

$$\langle x(0)x(t)\rangle = \frac{1}{2\pi}\int_{-\infty}^{\infty} e^{i\omega t}\langle|\tilde{x}(\omega)|^2\rangle\,d\omega, \qquad (33.82)$$

and hence for $t=0$ we have that

$$\langle x(0)x(0)\rangle = \frac{1}{2\pi}\int_{-\infty}^{\infty}\langle|\tilde{x}(\omega)|^2\rangle\,d\omega, \qquad (33.83)$$

or, more succinctly,

$$\boxed{\langle x^2\rangle = \frac{1}{2\pi}\int_{-\infty}^{\infty}\tilde{C}_{xx}(\omega)\,d\omega.} \qquad (33.84)$$

This is a form of **Parseval's theorem** that states that the integrated power is the same whether you integrate over time or over frequency.[8]

[8] Parseval's theorem is actually nothing more than Pythagoras' theorem in an infinite-dimensional vector space. If you think of the function $x(t)$, or its transform $\tilde{x}(\omega)$, as a single vector in such a space, then the square of the length of the vector is equal to the sum of the squares on the 'other sides', which in this case is the sum of the squares of the components (i.e. an integral of the squares of the values of the function).

Example 33.6

A random force $F(t)$ has average value given by

$$\langle F(t)\rangle = 0 \qquad (33.85)$$

and its autocorrelation function is given by

$$\langle F(t)F(t')\rangle = A\delta(t-t'), \qquad (33.86)$$

where $\delta(t-t')$ is a Dirac delta function.[9] Find the power spectrum.

[9] See Appendix C.10.

Solution:

By the Wiener–Khinchin theorem, the power spectrum is simply the Fourier transform of the autocorrelation function, and hence

$$\langle|F(\omega)|^2\rangle = A \qquad (33.87)$$

is a flat power spectrum.

This demonstrates that if the random force $F(t)$ has zero autocorrelation, it must have infinite frequency content.

Example 33.7

Find the velocity autocorrelation for the Brownian motion particle governed by eqn 33.1 where the random force $F(t)$ is as described in the previous example, i.e. with $\langle F(t)F(t')\rangle = A\delta(t-t')$. Hence relate the constant A to the temperature T.
Solution:
Equation 33.1 states that

$$m\dot{v} = -\alpha v + F(t), \tag{33.88}$$

and the Fourier transform of this equation is

$$\tilde{v}(\omega) = \frac{\tilde{F}(\omega)}{\alpha - im\omega}. \tag{33.89}$$

This implies that the Fourier transform of the velocity autocorrelation function is

$$\tilde{C}_{vv}(\omega) = \langle |v(\omega)|^2\rangle = \frac{A}{\alpha^2 + m^2\omega^2}, \tag{33.90}$$

using the result of eqn 33.87. The Wiener–Khinchin theorem states that

$$\tilde{C}_{vv}(\omega) = \int \mathrm{e}^{-\mathrm{i}\omega t}\langle v(0)v(t)\rangle\,\mathrm{d}t, \tag{33.91}$$

and hence

$$\tilde{C}_{vv}(t) = \langle v(0)v(t)\rangle = \langle v^2\rangle \mathrm{e}^{-\alpha t/m}, \tag{33.92}$$

in agreement with eqn 33.21 derived earlier using another method. Parseval's theorem (eqn 33.84) implies that

$$\langle v^2\rangle = \int_{-\infty}^{\infty} \frac{\mathrm{d}\omega}{2\pi}\tilde{C}_{vv}(\omega) = \frac{A}{2m\alpha}. \tag{33.93}$$

Equipartition, which gives that $\frac{1}{2}m\langle v^2\rangle = \frac{1}{2}k_{\mathrm{B}}T$, leads immediately to

$$A = 2\alpha k_{\mathrm{B}}T. \tag{33.94}$$

Let us next suppose that the energy E of a harmonic system is given by $E = \frac{1}{2}\alpha x^2$ (as in Chapter 19). The probability $P(x)$ of the system taking the value x is given by a Boltzmann factor $\mathrm{e}^{-\beta E}$ and hence

$$P(x) = \mathcal{N}\mathrm{e}^{-\beta\alpha x^2/2}, \tag{33.95}$$

where $\mathcal{N}$ is a normalization constant. Now we apply a force f which is conjugate to x so that the energy E is lowered by xf. The probability $P(x)$ becomes

$$P(x) = \mathcal{N}\mathrm{e}^{-\beta(\alpha x^2/2 - xf)}, \tag{33.96}$$

and by completing the square, this can be rewritten as

$$P(x) = \mathcal{N}'\mathrm{e}^{-\frac{\beta\alpha}{2}(x-\frac{f}{\alpha})^2}, \tag{33.97}$$

where $\mathcal{N}'$ is a different normalization constant. This equation is of the usual Gaussian form

$$P(x) = \mathcal{N}'\mathrm{e}^{-(x-\langle x\rangle_f)^2/2\langle x^2\rangle}, \tag{33.98}$$

where $\langle x\rangle_f = f/a$ and $\langle x^2\rangle = 1/\beta\alpha$. Notice that $\langle x\rangle_f$ is telling us about the average value of x in response to the force f, while $\langle x^2\rangle = k_{\mathrm{B}}T/\alpha$ is telling us about fluctuations in x. The ratio of these two quantities is given by

$$\frac{\langle x\rangle_f}{\langle x^2\rangle} = \beta f. \tag{33.99}$$

Now $\langle x\rangle_f$ is the average value x takes when a force f is applied, and we know that $\langle x\rangle_f$ is related[10] to f by the static susceptibility by

$$\frac{\langle x\rangle_f}{f} = \tilde{\chi}'(0), \tag{33.100}$$

so that eqn 33.99 can be rewritten as

$$\boxed{\langle x^2\rangle = k_{\mathrm{B}}T\tilde{\chi}'(0).} \tag{33.101}$$

Equation 33.101 thus relates $\langle x^2\rangle$ to the static susceptibility of the system. Using eqn 33.73, we can express this relationship as

$$\langle x^2\rangle = k_{\mathrm{B}}T\int_{-\infty}^{\infty}\frac{\mathrm{d}\omega'}{\pi}\frac{\tilde{\chi}''(\omega')}{\omega'}, \tag{33.102}$$

and together with eqn 33.84, this motivates

$$\boxed{\tilde{C}_{xx}(\omega) = 2k_{\mathrm{B}}T\frac{\tilde{\chi}''(\omega)}{\omega},} \tag{33.103}$$

which is a statement of the **fluctuation–dissipation theorem**. This shows that there is a direct connection between the autocorrelation function of the *fluctuations*, $\tilde{C}_{xx}(\omega)$, and the imaginary part $\tilde{\chi}''(\omega)$ of the response function which is associated with *dissipation*.

[10] Here we are making the assumption that the linear response function $\tilde{\chi}(\omega)$ governs both fluctuations and the usual response to perturbations.

Example 33.8

Show that eqn 33.103 holds for the problem considered in Example 33.5.
Solution:
Recall from Example 33.7 that

$$\tilde{C}_{xx}(\omega) = \int \mathrm{e}^{-\mathrm{i}\omega t}\langle x(0)x(t)\rangle\,\mathrm{d}t = \langle |\tilde{x}(\omega)|^2\rangle = A|\chi(\omega)|^2, \tag{33.104}$$

and hence using $\tilde{\chi}(\omega)$ from eqn 33.76 and A from eqn 33.94, we have that

$$\tilde{C}_{xx}(\omega) = \frac{2\gamma k_B T}{m}\left[\frac{1}{(\omega^2-\omega_0^2)^2+(\omega\gamma)^2}\right]. \tag{33.105}$$

Equation 33.77 shows that

$$2k_B T\frac{\tilde{\chi}''(\omega)}{\omega} = \frac{2\gamma k_B T}{m}\left[\frac{1}{(\omega^2-\omega_0^2)^2+(\omega\gamma)^2}\right], \tag{33.106}$$

and hence eqn 33.103 holds.

Example 33.9

Derive an expression for the Johnson noise across a resistor R using the circuit in Fig. 33.3 (which includes the small capacitance across the ends of the resistor).

Solution:

Simple circuit theory yields

$$V + IR = \frac{Q}{C}. \tag{33.107}$$

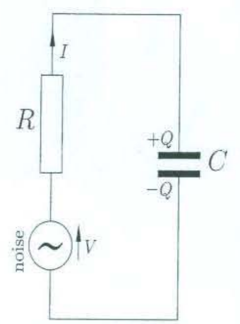

Fig. 33.3 Circuit for analysing Johnson noise across a resistor.

The charge Q and voltage V are conjugate variables (their product has dimensions of energy) and so we write

$$\tilde{Q}(\omega) = \tilde{\chi}(\omega)\tilde{V}(\omega), \tag{33.108}$$

where the response function $\tilde{\chi}(\omega)$ is given for this circuit by

$$\tilde{\chi}(\omega) = \frac{1}{C^{-1} - \mathrm{i}\omega R}. \tag{33.109}$$

Hence $\tilde{\chi}''(\omega)$ is given by

$$\tilde{\chi}''(\omega) = \frac{\omega R}{C^{-2}+\omega^2 R^2}. \tag{33.110}$$

At low frequency ($\omega \ll 1/RC$, and since the capacitance will be small, $1/RC$ will be very high so that this is not a severe resistriction) we have that $\tilde{\chi}''(\omega) \to \omega RC^2$. Thus the fluctuation–dissipation theorem (eqn 33.103) gives

$$\tilde{C}_{QQ}(\omega) = 2k_B T\frac{\tilde{\chi}''(\omega)}{\omega} = 2k_B TRC^2. \tag{33.111}$$

Because $Q = CV$ for a capacitor, correlations in Q and V are related by

$$\tilde{C}_{VV}(\omega) = \frac{\tilde{C}_{QQ}(\omega)}{C^2}, \tag{33.112}$$

and hence

$$\tilde{C}_{VV}(\omega) = 2k_B TR. \tag{33.113}$$

Equation 33.84 implies that

$$\langle V^2\rangle = \frac{1}{2\pi}\int_{-\infty}^{\infty}\tilde{C}_{VV}(\omega)\,\mathrm{d}\omega, \tag{33.114}$$

and hence if this integral is carried out, not over all frequencies, but only in a small interval $\Delta f = \Delta\omega/(2\pi)$ about some frequency $\pm\omega_0$ (see Fig. 33.4),

$$\langle V^2\rangle = 2C_{VV}(\omega)\Delta f = 4k_B TR\Delta f, \tag{33.115}$$

in agreement with eqn 33.28.

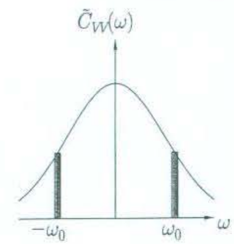

Fig. 33.4 The voltage fluctuations $\langle V^2\rangle$ in a small frequency interval $\Delta f = \Delta\omega/(2\pi)$ centred on $\pm\omega_0$ are due to the part of the $\tilde{C}_{VV}(\omega)$ shown by the shaded boxes. One can imagine that the noise is examined through a filter which only allows these frequencies through, so that the integral in eqn 33.114 only picks up the regions shown by the shaded boxes.

We close this chapter by remarking that our treatment so far applies only to classical systems. The quantum mechanical version of the fluctuation–dissipation theorem can be evaluated by replacing $k_B T$, the mean thermal energy in a classical system, by

$$\hbar\omega\left(n(\omega)+\frac{1}{2}\right) \equiv \frac{\hbar\omega}{2}\coth\frac{\beta\hbar\omega}{2}, \tag{33.116}$$

which is the mean energy in a quantum harmonic oscillator. In eqn 33.116,

$$n(\omega) = \frac{1}{e^{\beta\hbar\omega}-1} \tag{33.117}$$

is the Bose factor, which is the mean number of quanta in the harmonic oscillator at temperature T. Hence, in the quantum mechanical case, eqn 33.103 is replaced by

$$\tilde{C}_{xx}(\omega) = \hbar\tilde{\chi}''(\omega)\coth\frac{\beta\hbar\omega}{2}. \tag{33.118}$$

At high temperature, $\coth(\beta\hbar\omega/2) \to 2/(\beta\hbar\omega)$ and we recover eqn 33.103. The quantum mechanical version of eqn 33.102 is

$$\langle x^2\rangle = \frac{\hbar}{2}\int_{-\infty}^{\infty}\mathrm{d}\omega'\,\tilde{\chi}''(\omega')\coth\frac{\beta\hbar\omega}{2}. \tag{33.119}$$

Chapter summary

- The fluctuation–dissipation theorem implies that there is a direct relation between the fluctuation properties of the thermal system (e.g. the diffusion constant) and its linear response properties (e.g. the mobility). If you've characterised one, you've characterised the other.
- Fluctuations are more important for small systems than for large systems, though are always dominant near the critical point of a phase transition, even for large systems.
- Fluctuations in a variable x are given by

$$\langle (\Delta x)^2 \rangle = -k_B T_0 / (\partial^2 A / \partial x^2).$$

- A response function is defined by

$$\langle x(t) \rangle_f = \int_{-\infty}^{\infty} \chi(t-t') f(t')\, dt',$$

  and causality implies the Kramers–Kronig relations.
- The Fourier transform of the correlation function gives the power spectrum. This allows us to show that

$$\langle x^2 \rangle = \frac{1}{2\pi} \int_{-\infty}^{\infty} \tilde{C}_{xx}(\omega)\, d\omega.$$

- The fluctuation–dissipation theorem states that

$$\tilde{C}_{xx}(\omega) = 2 k_B T \frac{\tilde{\chi}''(\omega)}{\omega},$$

  and relates the autocorrelation function to the dissipations via the imaginary part of the response function.