

## Chapter 5

# Fluctuations and Dynamics

The traditional subject of *thermodynamics* is wrongly named. It deals, essentially, with equilibrium states and the relations between these states. The existence of states of equilibrium is essential to our understanding of the macroscopic world at the quantitative level. Although macroscopic systems must be described, at the microscopic level, by a very large number of variables, the *equilibrium* states of such systems are specified in terms of only a few thermodynamic parameters. The existence of equilibrium states is thus a fortunate aspect of nature; and it is upon this aspect that the discipline of thermodynamics is based.

Classical thermodynamics relates different equilibrium states of a system. One state might be transformed into another by passing “quasi-statically” through a sequence of intermediate (almost) equilibrium states. Or the process might be completely irreversible, such as the Joule-Kelvin throttling, where all one can speak of are the initial and final equilibrium states. In the former case we can draw an “indicator diagram” showing the variation of thermodynamic variables in the process. In the latter case all we can plot are the initial and final points. Classical thermodynamics and its microscopic underpinning of equilibrium statistical mechanics recognizes the existence of initial and final states, but it can tell nothing about the *dynamics* of the transformation processes. Thus the designation *thermodynamics* is a misnomer.

Equilibrium systems have no dynamics, almost by definition. This is true “on the average”, but of course there are fluctuations. By contrast, non-equilibrium systems do have dynamics. Common experience (and indeed the Second Law of thermodynamics) tells us that a non-equilibrium system will evolve towards a state of equilibrium. The subject of non-equilibrium statistical mechanics deals with this *approach* to equilibrium.

Before making direct appeal to the microscopics of particular systems it

is of interest to ask what deductions can be made from specifically macroscopic considerations. As with equilibrium “thermodynamics” the macroscopic approach can relate different properties of a system, but it cannot go much further than this. Adkins’s *Equilibrium Thermodynamics* [1] discusses thermoelectricity from this perspective and the limitations of the approach are clearly discussed. Further progress in the macroscopic approach can be made through the addition of some new “laws”. Traditionally Onsager’s “reciprocity law” is used. More modern is the use of the law of minimum entropy production. Both of these are discussed in Kondepundi and Prigogine’s *Modern Thermodynamics* [2].

The behaviour of specific systems must be treated, as in the equilibrium case, by looking at the microscopics, and applying statistical arguments. In particular this is necessary if we want to study the time dependence of thermodynamic variables in non-equilibrium systems and their variation as the system evolves towards equilibrium. MacDonald [3] coined the phrase “time dependent statistical mechanics” for this.

## 5.1 Fluctuations

### 5.1.1 Probability distribution functions

When a thermodynamic property is fixed its conjugate variable fluctuates about its mean value. Thus we saw, in Section 1.4.6, that when the temperature was fixed there were fluctuations in energy. In a small region of a system there will be fluctuations in all extensive variables. Here we are regarding the small region as a subsystem in equilibrium with a reservoir comprising the remainder of the system. Thus the conditions for the equilibrium of the subsystem are that all intensive variables are fixed: temperature, pressure, chemical potential etc.

To examine the fluctuations in the subsystem we must consider the appropriate thermodynamic potential, here it is the Gibbs free energy  $G(T, p, \mu)$ , since  $T$ ,  $p$ , and  $\mu$  are fixed. We ask the question: What is the probability of the occurrence of a fluctuation of magnitude  $X$  ?

When considering an *isolated* system we saw that the Boltzmann relation  $S = k \ln \Omega$  could be inverted, following Einstein, to give the probability of observing a fluctuation of magnitude  $X$  as

$$P(X) \propto e^{S(X)/k}. \quad (5.1.1)$$

An *open system*, that is, one having fixed values of its intensive variables (our subsystem) is specified by its Gibbs free energy and the probability of

a fluctuation of magnitude  $X$  is

$$P(X) \propto e^{-G(X)/kT}. \quad (5.1.2)$$

(The probability would be given by  $P(X) \propto e^{S(X)/k}$  where  $S(X)$  is the total entropy of the system *plus* reservoir. It becomes  $P(X) \propto e^{-G(X)/kT}$  where  $G(X)$  is the Gibbs free energy of the system alone)

In equilibrium  $G$  is a minimum; let us specify this to occur at  $X = X_0$ . Here  $X$  could be a general extensive variable or an order parameter of a phase

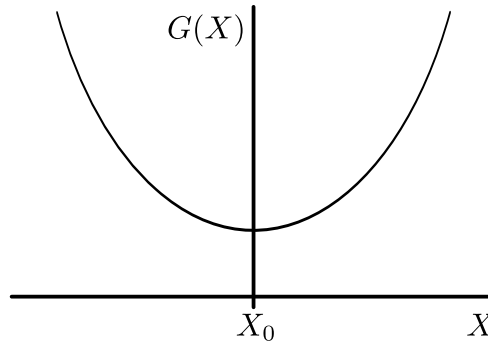


Figure 5.1: Equilibrium value of Gibbs free energy

transition. For convenience we shall put  $X_0 = 0$  so that now the variable  $X$  measures the *deviation* from the mean (equilibrium) value.

For small deviations of  $X$  from its equilibrium value we may expand

$$G(X) = G(0) + X \left. \frac{\partial G}{\partial X} \right|_0 + \frac{X^2}{2} \left. \frac{\partial^2 G}{\partial X^2} \right|_0 + \dots \quad (5.1.3)$$

Since the equilibrium position is a minimum the linear term vanishes. The leading term in  $X$  is thus the quadratic. To leading order in  $X$  the probability is then

$$P(X) \propto \exp - \left\{ G(0)/kT + G''(0) X^2/2kT \right\} \quad (5.1.4)$$

or

$$P(X) \propto e^{-G''(0)X^2/2kT}. \quad (5.1.5)$$

This is a Gaussian probability distribution, which has the general form

$$P(X) \propto e^{-X^2/2\langle X^2 \rangle}. \quad (5.1.6)$$

And from this we can identify the mean square measure of the fluctuations of  $X$  as

$$\langle X^2 \rangle = kT \left. \frac{\partial^2 G}{\partial X^2} \right|_{X=X_0}^{-1} \quad (5.1.7)$$

We see that the *broader* the minimum in  $G$  the greater the magnitude of the fluctuations. So, in particular, at a *critical point* where we saw that  $G'' \rightarrow 0$  the fluctuations become infinite. This is an important property of a critical point. We also note that the fluctuations will diverge at the *spinodal point* of a first order transition.

### 5.1.2 Average behaviour of fluctuations

The mean value of a thermodynamic quantity  $X$  is constant for a system in equilibrium; this is essentially the definition of equilibrium. However the *instantaneous* value of  $X$  will fluctuate with time as dictated by the equations of motion of the system; a typical example is shown in Fig. 5.2. The devia-

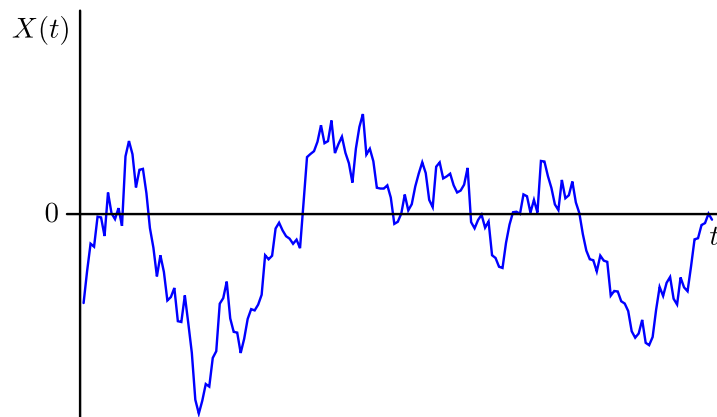


Figure 5.2: Fluctuations in  $X$  as a function of time

tions of  $X$  from its mean will average to zero (indeed this is embodied in the definition of the mean), since the deviations are equally likely to be positive or negative. But the *square* of the deviations of  $X$  from its mean will have a non-zero average; moreover this can be calculated within the framework of standard equilibrium thermodynamics/statistical mechanics. For convenience let us re-scale  $X$  by subtracting off its mean value; our newly scaled  $X$  has zero mean:  $\langle X \rangle = 0$ . But as mentioned above,  $\langle X^2 \rangle \neq 0$ , and in general, certainly for even  $n$ , we will have  $\langle X^n \rangle \neq 0$ . These “moments” can often be calculated without too much difficulty, as treated in Problem 1.13. These moments tell us about the likelihood of fluctuations of different sizes, but they give no indication about the *time-dependence* of the fluctuations.

**Ensembles and averages:** It is not immediately obvious what is meant by taking an average in this case. If many copies of the system are imagined, each having the same values for the macroscopic observables, then one can consider the average evaluated over this collection of copies. The imaginary collection of such copies is referred to as an *ensemble*, the Gibbs ensemble of Chapter 1, and the average is called an *ensemble average*.

What can we say about the time variation of the fluctuations without completely solving the equations of motion for the system? Can we specify a quantity that describes the typical time evolution of the variations?

**Mean value:** At a particular time  $t_0$  we may observe that the variable  $X$  has the value  $a^i$ :

$$X(t_0) = a^i. \quad (5.1.8)$$

This will subsequently develop in time so that the observed mean becomes zero. We can talk of the mean time dependence of  $X$  from this value  $a^i$  by taking a sub-ensemble from a complete ensemble – the sub-ensemble consisting of all those elements that at time  $t_0$  have the value  $a^i$ , that is, the elements of the sub-ensemble obey

$$X_j^i(t_0) = a^i. \quad (5.1.9)$$

The upper index of  $X$  labels the sub-ensemble and the lower index indicates which element within the sub-ensemble. We can then define the mean regression from the initial value  $a^i$  at time  $t_0$  by the average

$$f^i(t_0 + t) = \frac{1}{n_i} \sum_{j=1}^{n_i} X_j^i(t_0 + t) \quad (5.1.10)$$

where  $n_i$  is the number of elements in the  $i^{\text{th}}$  sub-ensemble.

For sufficiently long times  $t$ , the value of  $f^i(t_0 + t)$  will go to zero since there will then be no means of distinguishing that this sub-ensemble is not a representative one. Thus we expect the function  $f^i(t_0 + t)$  to behave as in Fig. 5.3. This function describes “on the average” how  $X$  varies if at time  $t_0$  it had the value  $a^i$ . However since we are considering a system in equilibrium – that is, it has time translation invariance – it follows that the time evolution of  $f^i(t_0 + t)$  is not peculiar to the time  $t_0$ . Whenever  $X$  is observed to take on the value  $a^i$  the subsequent mean time dependence will be given by  $f^i$ . So we may ignore  $t_0$  and we shall put it to zero in our future discussions.

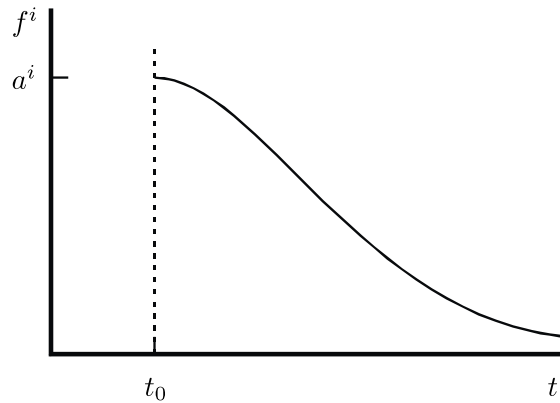


Figure 5.3: Mean regression of a random fluctuation from an initial value

The behaviour does, however, refer specifically to the particular value  $a_i$ . To find the mean regression of any fluctuation we may think of averaging over all the initial values  $a_i$  with appropriate weights. But this is simply an average over the complete ensemble and this, we know, must give zero. Physically we can see that this is so since there will be many positive and negative values of  $f^i$  which will average to zero, as in Fig. 5.4.

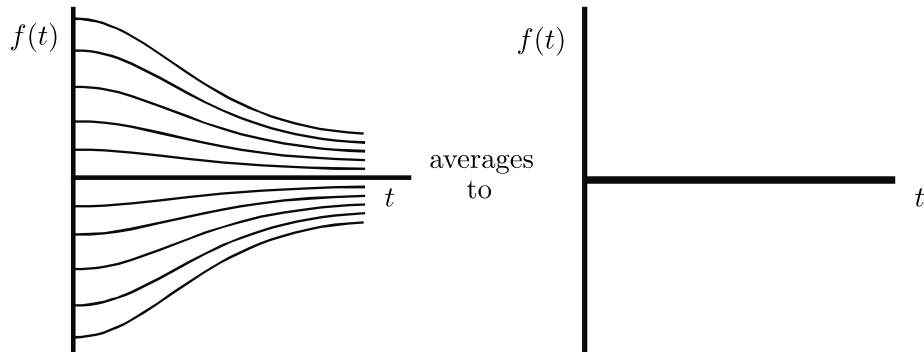


Figure 5.4: Average regression of many different initial states

Mathematically this follows since

$$\langle f(t) \rangle = \sum_i w_i f^i(t) = \sum_i \frac{w_i}{n_i} \sum_j X_j^i(t) \quad (5.1.11)$$

where  $w_i$  is the weight factor for the  $i^{\text{th}}$  sub-ensemble. Now this weight factor is the proportion of the whole ensemble that the  $i^{\text{th}}$  sub-ensemble

represents, that is  $n_i/N$  where  $N$  is the total number of elements in the ensemble:  $N = \sum_i n_i$ . Thus

$$\begin{aligned}\langle f(t) \rangle &= \sum_i \frac{n_i}{N n_i} \sum_j X_j^i(t) \\ &= \frac{1}{N} \sum_{i,j} X_j^i(t),\end{aligned}\tag{5.1.12}$$

the common mean over the full ensemble which is zero.

**Mean square:** Instead of the direct mean we could evaluate the mean of the squares of the regressions of the sub-ensembles. In this way positive and negative variations will all contribute without cancelling each other. We then have

$$\begin{aligned}\langle f^2(t) \rangle &= \sum_i w_i \{f^i(t)\}^2 \\ &= \sum_i \frac{w_i}{n_i} \left\{ \sum_j X_j^i(t) \right\}^2 \\ &= \sum_i \frac{w_i}{n_i} \sum_{j,k} X_j^i(t) X_k^i(t) \\ &= \frac{1}{N} \sum_{i,j,k} X_j^i(t) X_k^i(t)\end{aligned}\tag{5.1.13}$$

but this involves cross terms between members of the ensemble. The idea of correlations between different elements of an ensemble is completely unphysical, the mathematics is becoming complicated, so we shall reject this approach.

**Magnitude:** Another possibility is to take the average of the magnitude of the  $f^i(t)$ , defining

$$\begin{aligned}\langle f(t) \rangle_{\text{mag}} &= \sum_i w_i |f^i(t)| \\ &= \frac{1}{N} \sum_i \left| \sum_j X_j^i(t) \right|.\end{aligned}\tag{5.1.14}$$

Unfortunately there are mathematical difficulties in manipulating modulus functions, but this approach gives a good lead. In fact this method of defining

an average is equivalent to taking a mean with a weight function  $\varepsilon_i$  which is positive for positive  $a^i$  and negative for negative  $a^i$ :

$$\begin{aligned}\langle f(t) \rangle_{\text{mag}} &= \frac{1}{N} \sum_i \varepsilon_i \sum_j X_j^i(t) \\ &= \frac{1}{N} \sum_{i,j} \varepsilon_i X_j^i(t).\end{aligned}\tag{5.1.15}$$

Written in this form the expression for the average behaviour of the regression seems promising. The only difficulty is with the strange weight function

$$\begin{aligned}\varepsilon_i &= +1 \quad \text{if} \quad a^i > 0 \\ &= -1 \quad \text{if} \quad a^i < 0.\end{aligned}\tag{5.1.16}$$

**Autocorrelation:** Instead of this discontinuous function  $\varepsilon$  multiplying the components, there is a much more straightforward weight function that satisfies the fundamental requirement of respecting the sign of the  $a^i$ : we could use the  $a^i$  themselves. In other words, in evaluating the average behaviour of the natural fluctuations we weight each element of the ensemble by its initial value. We have then

$$\frac{1}{N} \sum_{i,j} a^i X_j^i(t)\tag{5.1.17}$$

or, since  $X_j^i(0) = X^i(0) = a^i$ , it can be written as

$$\frac{1}{N} \sum_{i,j} X_j^i(0) X_j^i(t)\tag{5.1.18}$$

and in this form we have achieved an important progress in that the average is over the complete ensemble (with no cross terms) and we can write it as

$$\langle X(0)X(t) \rangle.\tag{5.1.19}$$

This is our chosen expression for the ‘‘average’’ regression of a fluctuation from some initial value back to the mean.

### 5.1.3 The autocorrelation function

The above expression is the mean over the ensemble where each element is weighted in proportion to its initial value. This function of the randomly varying quantity  $X(t)$  is known as the *autocorrelation function*. We shall denote it by the symbol  $G(t)$ :

$$G = \langle X(0)X(t) \rangle.\tag{5.1.20}$$



In Fig. 5.5 we show the fluctuations of Fig 5.2,  $X(t)$ , together with the corresponding autocorrelation function,  $G(t)$ .

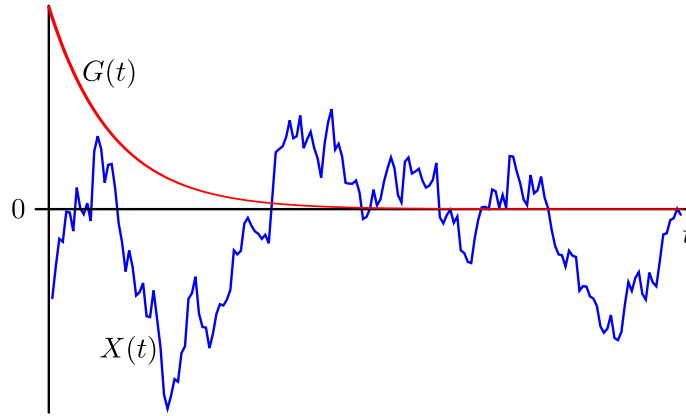


Figure 5.5: Fluctuations in  $X$  together with the autocorrelation function

In the sense described above, the function  $G(t)$  describes the mean time variation of the fluctuations in  $X(t)$ . Observe the smooth behaviour of the autocorrelation function. In a sense this function has distilled the fundamental essence of the random function  $X(t)$  without its wealth of unimportant fine detail.

The zero time value of  $G(t)$  has an immediate interpretation. From the definition of  $G(t)$  we have

$$G(0) = \langle X^2 \rangle, \quad (5.1.21)$$

the mean square value of the fluctuating variable. For long times, as we have argued above,  $G(t)$  should go to zero.

If  $X$  is not defined so that its average  $\langle X \rangle$  is zero then we must modify the definition of the autocorrelation function to

$$\begin{aligned} G(t) &= \langle (X(0) - \langle X \rangle) (X(t) - \langle X \rangle) \rangle \\ &= \langle X(0)X(t) \rangle - \langle X(0) \langle X \rangle \rangle - \langle \langle X \rangle X(t) \rangle + \langle X^2 \rangle \\ &= \langle X(0)X(t) \rangle - \langle X^2 \rangle \end{aligned}$$

since

$$\langle X(0) \langle X \rangle \rangle = \langle \langle X \rangle X(t) \rangle = \langle X^2 \rangle.$$

The time-translation invariance property, which we stated to be a property of equilibrium systems now becomes the stationarity principle:

$$\langle X(\tau) X(t + \tau) \rangle = \langle X(0) X \rangle : \quad (5.1.22)$$

i.e.

$$\text{equilibrium} \Rightarrow \text{stationarity.} \quad (5.1.23)$$

And stationarity implies the time-reversal behaviour. From stationarity we have:

$$\langle X(-\tau) X(0) \rangle = \langle X(0) X(\tau) \rangle \quad (5.1.24)$$

but classically the  $X$  commute, so that

$$\langle X(-\tau) X(0) \rangle = \langle X(\tau) X(0) \rangle \quad (5.1.25)$$

or

$$G(t) = G(-t). \quad (5.1.26)$$

**A paradox:** The correlation function  $G(t)$  has the physical significance that a “large” fluctuation will be expected on average to die out according to  $G(t)$ . A large fluctuation will occur infrequently and on the “large” scale  $X$  may be assumed to decay to its equilibrium value.

We say that  $G(t)$  traces the mean decay of a fluctuation. Now according to this view one would expect  $G(-t)$  to tell us of the past history of the fluctuation. But we have the time-reversal rule  $G(t) = G(-t)$ . Our zero of time always seems to coincide with the peak value of the fluctuation – but how can this be consistent with time-translation invariance? There seems to be a paradox; the time origin is important. The resolution is that the zero of time *is* unique because according to the values of  $X$  at *this* time are the sub-ensembles selected. That is, the weighting factors of the averaging procedure are selected at the zero of time.

#### 5.1.4 The correlation time

The autocorrelation function, as we have seen, starts at a finite value and it decays to zero as the time argument increases. This function indicates to us the average way that a fluctuation dies out. In other words the correlation function indicates the time scale of the variations of the random variable. We shall quantify this time scale by introducing a *correlation time*  $\tau_c$  such that for times much shorter than this  $G(t)$  will hardly have changed, while for times much longer than this  $G(t)$  will have gone to zero.

$$\begin{aligned} G(t) &\approx G(0) & t \ll \tau_c \\ &\approx 0 & t \gg \tau_c. \end{aligned} \quad (5.1.27)$$

(Note: this is not a *definition* of what  $\tau_c$  *is*; it is the essential condition that any suitably-defined  $\tau_c$  must satisfy.)

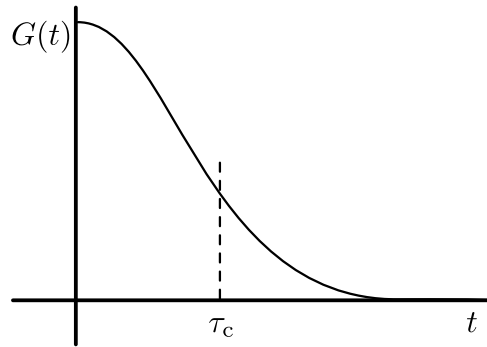


Figure 5.6: correlation time of an autocorrelation function

The correlation time is indicated in Fig. 5.6. It is convenient to have a precise mathematical specification and we shall see that the definition we adopt will make direct connection with future considerations.

The correlation time is a “rough measure” of the *width* of the correlation function. Now we may regard the area of the correlation function is a rough measure of its width multiplied by a rough measure of its height. A rough measure of the height of the correlation function is its initial height  $G(0)$ . And its area is most conveniently expressed as the integral. Thus we are saying

$$\int_0^{\infty} G(t) dt = \tau_c G(0) \quad (5.1.28)$$

or

$$\tau_c = \frac{1}{G(0)} \int_0^{\infty} G(t) dt. \quad (5.1.29)$$

This expression is taken as the definition of the correlation time.

The autocorrelation function is an important function of a random variable. We will encounter autocorrelation functions frequently in what follows. We will see also that the area under the autocorrelation function is an important quantity and, because of this, we will make frequent use of the correlation time as defined above.

### 5.1.5 Spectral Density – the Wiener-Khintchine Theorem

Let us now consider the fluctuating variable in the frequency domain. We would *like* to introduce the Fourier transform of  $X(t)$ , which would be defined

by

$$x(\omega) = \int_{-\infty}^{\infty} X(t)e^{i\omega t} dt. \quad (5.1.30)$$

If, however,  $X(t)$  is a continually-varying function (statistically time-translationally invariant) then this integral will diverge and the Fourier transform will not exist. In that case it is expedient to consider a “truncated” version of  $X(t)$  defined by

$$\begin{aligned} X_T(t) &= X(t) & |t| < T/2 \\ &= 0 & \text{otherwise.} \end{aligned} \quad (5.1.31)$$

The Fourier transform of this *does* exist:

$$\begin{aligned} x_T(\omega) &= \int_{-\infty}^{\infty} X_T(t)e^{i\omega t} dt \\ &= \int_{-T/2}^{T/2} X(t)e^{i\omega t} dt \end{aligned} \quad (5.1.32)$$

and the inverse transform is then

$$X_T(t) = \frac{1}{2\pi} \int_{-\infty}^{\infty} x_T(\omega)e^{-i\omega t} d\omega. \quad (5.1.33)$$

In terms of this Fourier decomposition, the autocorrelation function  $G(t)$  is given by

$$\begin{aligned} G(t) &= \frac{1}{T} \int_{-T/2}^{T/2} X^*(s)X(s+t) ds \\ &= \frac{1}{T} \frac{1}{(2\pi)^2} \int_{-T/2}^{T/2} ds \left\{ \int_{-\infty}^{\infty} x_T^*(\omega_1)e^{i\omega_1 s} d\omega_1 \right\} \left\{ \int_{-\infty}^{\infty} x_T(\omega_2)e^{-i\omega_2(s+t)} d\omega_2 \right\}. \end{aligned} \quad (5.1.34)$$

This can be simplified to

$$G(t) = \frac{1}{T} \frac{1}{(2\pi)^2} \int_{-T/2}^{T/2} ds \int_{-\infty}^{\infty} d\omega_1 \int_{-\infty}^{\infty} d\omega_2 x_T^*(\omega_1)x_T(\omega_2) e^{i(\omega_1-\omega_2)s} e^{-i\omega_2 t}. \quad (5.1.35)$$

We may perform the integral over  $s$ ; and here we may extend the limits of the integral to infinity. Then:

$$\int_{-\infty}^{\infty} e^{i(\omega_1 - \omega_2)s} ds = 2\pi \delta(\omega_1 - \omega_2). \quad (5.1.36)$$

We use the sifting property of the delta function, and so the expression for  $G(t)$  becomes

$$G(t) = \frac{1}{T} \frac{1}{2\pi} \int_{-\infty}^{\infty} d\omega x_T^*(\omega) x_T(\omega) e^{-i\omega t}. \quad (5.1.37)$$

This is a Fourier transform expression; we may write it as

$$G(t) = \frac{1}{2\pi} \int_{-\infty}^{\infty} J(\omega) e^{-i\omega t} d\omega \quad (5.1.38)$$

where

$$J(\omega) = \frac{1}{T} |x_T(\omega)|^2. \quad (5.1.39)$$

Just as  $x_T(\omega)$  is the Fourier transform of  $X_T(x)$ , so  $J(\omega) = |x_T(\omega)|^2/T$  is the Fourier transform of  $G(t)$ .

The quantity  $J(\omega) = |x_T(\omega)|^2/T$  is the *power spectrum* or *spectral density* of the fluctuating variable  $X(t)$ . It should be noted that in the limit of large  $T$ ,  $|x_T(\omega)|^2/T$  will tend to a constant value.

The above result, Eqs. (5.1.38) and (5.1.39), is the essence of the Wiener-Khintchine theorem: the spectral density  $J(\omega)$  is the Fourier transform of the autocorrelation function  $G(t)$ .

## 5.2 Brownian Motion

In 1828 Robert Brown observed that tiny grains of pollen suspended in water underwent a perpetual random motion. He went on to observe this effect in a whole range of powdered substances including house dust and pulverised rock. Brown's (erroneous) conclusion was that the motion was due to some "life force" in all inorganic matter. Today the importance of his work is in the *universality* of the effect. It was Einstein in 1905 [4], who explained the origin of the motion as arising from the continual bombardment of the particles by the atoms or molecules of the fluid in which it is immersed.

The key point about Brownian motion is that it is the motion of a *macroscopic* body arising from *microscopic* impacts from atoms/molecules of the surrounding fluid.

The macroscopic body, which nevertheless might be quite small, may be a pollen grain in water, a smoke particle in air, a flake of ink pigment in water, even the mirror of a traditional galvanometer. The random motion of all these may be observed; Fig. 5.7 shows a typical example. For the present we shall not consider examples such as the galvanometer mirror where there is a “restoring force” acting on the Brownian particle.

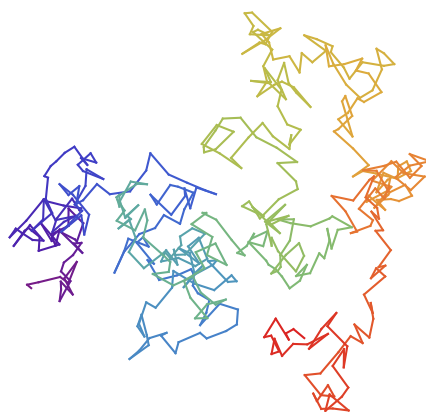


Figure 5.7: Typical Brownian motion of a particle in two dimensions. The colour changes with advancing time.

### 5.2.1 Kinematics of a Brownian particle

For simplicity we shall consider motion of a Brownian particle in one dimension; the generalization to two and three dimensions is straightforward. The location of the particle is not bounded and as time increases it will travel further and further from the origin. The square of the displacement for a typical trajectory is shown in Fig. 5.8. We see that the mean square displacement increases (even though in one dimension there is always a finite probability of the particle returning to its starting point).

We shall investigate the mean square displacement of the particle. At this stage we consider the *kinematics* of the particle. That is, we will treat things at a descriptive (but quantitative) level without delving into the dynamics and the forces involved.

The distance travelled by the Brownian particle in a time  $t$  may be found

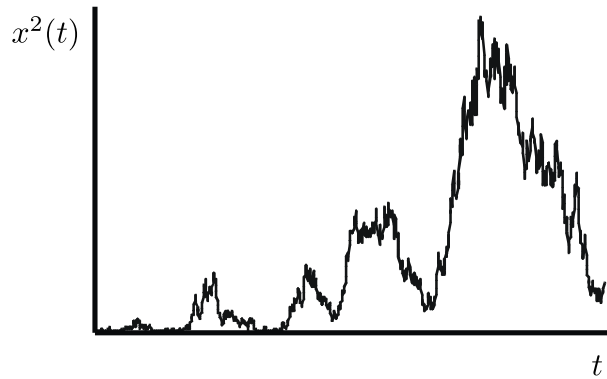


Figure 5.8: Typical squared displacement of Brownian particle

by integrating up its velocity:

$$x = \int_0^t v(\tau) d\tau. \quad (5.2.1)$$

Here  $v(\tau)$  is the particle's velocity at time  $\tau$ .

The square of the displacement is then

$$\begin{aligned} x^2(t) &= \left\{ \int_0^t v(\tau) d\tau \right\}^2 \\ &= \int_0^t v(\tau_1) d\tau_1 \int_0^t v(\tau_2) d\tau_2 \\ &= \int_0^t d\tau_1 \int_0^t d\tau_2 v(\tau_1) v(\tau_2), \end{aligned}$$

so the mean square displacement is

$$\langle x^2 \rangle = \int_0^t d\tau_1 \int_0^t d\tau_2 \langle v(\tau_1) v(\tau_2) \rangle. \quad (5.2.2)$$

We see that the mean square displacement is given in terms of the velocity autocorrelation function.

$$G_v(\tau_1 - \tau_2) = \langle v(\tau_1) v(\tau_2) \rangle \quad (5.2.3)$$

Here we have used the subscript  $v$  to indicate that it is the autocorrelation function of the *velocity*. The stationarity of the random velocity (a consequence of thermal equilibrium) is indicated in the argument  $(\tau_1 - \tau_2)$ . This allows us to take a further step in the expression for the mean square displacement. We may change variables in the double integral to

$$\begin{aligned}\tau &= \tau_1 - \tau_2 \\ T &= \tau_1 + \tau_2\end{aligned}\tag{5.2.4}$$

whereupon we may integrate over the variable  $T$ . This is a nontrivial procedure, detailed in Appendix 4; the result is

$$\langle x^2 \rangle = 2 \int_0^t (t - \tau) G_v(\tau) d\tau.\tag{5.2.5}$$

This is a remarkably useful expression, as we shall see. It is worthwhile to re-emphasize what has been achieved at this stage. Using only kinematics we have found an expression for the mean square displacement of the Brownian particle in terms of the particle's velocity autocorrelation function. This also reinforces the idea that autocorrelation functions are useful quantities when considering random processes.

Pursuing the kinematical arguments further we will see that the above expression for the mean square displacement can be simplified in two limiting cases.

## 5.2.2 Short time limit

The natural time scale for the process we are considering (the only time scale we have at this stage) is the velocity correlation time, which we shall denote by  $\tau_v$ . The specification of  $\tau_v$  is such that

$$G_v(\tau) \approx G_v(0) \quad \text{when} \quad \tau \ll \tau_v;\tag{5.2.6}$$

at these short times the autocorrelation function will have changed negligibly from its initial value. So when we consider times much shorter than  $\tau_v$ , we may replace  $G_v(\tau)$  by  $G_v(0)$  in the integral expression for  $\langle x^2 \rangle$ . But in this case  $G_v(0)$  comes out of the integral and we have

$$\langle x^2 \rangle = 2G_v(0) \int_0^t (t - \tau) d\tau.\tag{5.2.7}$$



Now the integral may be evaluated simply, giving

$$\begin{aligned}\langle x^2 \rangle &= 2G_v(0) \left[ t \int_0^t d\tau - \int_0^t \tau d\tau \right] \\ &= 2G_v(0) [t^2 - t^2/2] \\ &= G_v(0)t^2.\end{aligned}\tag{5.2.8}$$

The mean square displacement is proportional to the square of the time interval. We may write our result as

$$\langle x^2 \rangle = \langle v^2 \rangle t^2.\tag{5.2.9}$$

This indicates that the Brownian particle is moving essentially freely; at these short times there have not been sufficient atomic impacts to have any significant effect on the particle. This is referred to as the *ballistic* régime.

### 5.2.3 Long time limit

The other statement about the correlation time is

$$G_v(\tau) \approx 0 \quad \tau \gg \tau_v;\tag{5.2.10}$$

the autocorrelation function will have decayed to zero at long times. So when we consider times much longer than  $\tau_v$ ,  $G_v(\tau)$  will be zero and in the expression for  $\langle x^2 \rangle$  we will make no error by extending the upper limit of the integral to infinity.

$$\langle x^2 \rangle = 2 \int_0^\infty (t - \tau) G_v(\tau) d\tau.\tag{5.2.11}$$

The integral may be rearranged as

$$\langle x^2 \rangle = 2t \int_0^\infty G_v(\tau) d\tau - 2 \int_0^\infty \tau G_v(\tau) d\tau.\tag{5.2.12}$$

The second term (independent of time) is negligible compared with the first at long times, so we conclude that in the long time limit

$$\langle x^2 \rangle = 2t \int_0^\infty G_v(\tau) d\tau.\tag{5.2.13}$$

Now we see that the mean square displacement of the Brownian particle is proportional to time (rather than the  $t^2$  of the ballistic régime).

You should recall that a mean square displacement proportional to time is characteristic of a *diffusive* process. And in fact in 1d the solution of the diffusion equation gives directly

$$\langle x^2 \rangle = 2Dt \quad (5.2.14)$$

where  $D$  is the diffusion coefficient.

Thus we conclude that in the long time limit the motion of the Brownian particle is diffusive, and its diffusion coefficient is given by

$$D = \int_0^{\infty} G_v(t) dt \quad (5.2.15)$$

or

$$D = \int_0^{\infty} \langle v(0)v(t) \rangle dt. \quad (5.2.16)$$

The diffusion coefficient is given by the area under the velocity autocorrelation function. The long time limit, when  $t \gg \tau_v$ , is called the *diffusive* régime.

Recall that the definition of the correlation time was given in terms of the area under the autocorrelation function, Eq. (5.1.29):

$$\tau_v = \frac{1}{G_v(0)} \int_0^{\infty} G_v(t) dt. \quad (5.2.17)$$

From this it follows that we may write the diffusion coefficient as

$$D = G_v(0)\tau_v \quad (5.2.18)$$

or

$$D = \langle v^2 \rangle \tau_v. \quad (5.2.19)$$

Again we emphasize that the preceding discussion is purely kinematical. All the quantities we have considered are properties of the Brownian particle. The random atomic bombardment causes the velocity of the particle to vary randomly but we have not, as yet, considered the dynamics of the collision processes.

### 5.2.4 Equipartition

Although we shall not consider the dynamics of the collision processes in this section, since the system of Brownian particle plus surrounding fluid is regarded as being in thermal equilibrium, we may apply the equipartition theorem to the Brownian particle. The objection might be raised that equipartition is a classical result which becomes invalid when issues of indistinguishability and multiple occupation of states becomes important. However we will apply equipartition specifically to the Brownian particle, not to the surrounding medium. And since the Brownian particle is a macroscopic object its behaviour may be understood purely in classical terms. As it is in thermal equilibrium with a bath at a temperature  $T$  the equipartition theorem tells us that

$$\frac{1}{2}M \langle v^2 \rangle = \frac{1}{2}kT \quad (5.2.20)$$

in one dimension, where  $M$  is the mass of the Brownian particle. The mean square velocity is then

$$\langle v^2 \rangle = \frac{kT}{M}. \quad (5.2.21)$$

This is a *consequence* of the microscopic atomic bombardment from the surrounding fluid, but the expression is a purely thermodynamic result independent of the details of the interaction. It is sufficient that there is thermal equilibrium.

Equipartition allows us to write the diffusion coefficient of the Brownian particle as

$$D = \frac{kT}{M} \tau_v. \quad (5.2.22)$$

This does not mean that the diffusion coefficient is proportional to temperature since the velocity correlation time will, in general, depend on temperature. At a certain level this is still a kinematical result about the Brownian particle since  $\tau_v$  is also a property of the Brownian particle. What we really want to know is how the interactions with the atoms of the surrounding medium affect the particle's motion. For this we need to consider the dynamics of the process.

## 5.3 Langevin's Equation

### 5.3.1 Introduction

The task of studying the *dynamics* of Brownian motion was initiated by Langevin in 1908. Langevin wrote down an equation of motion for the Brow-

nian particle. Essentially this was an equation of the form  $F = ma$ , but Langevin's special insight was in the way he viewed the force acting on the Brownian particle. Our treatment is inspired by the papers of Uhlenbeck and Ornstein [5], Wang and Uhlenbeck [6] and MacDonald's book[3].

Langevin wrote the force acting on the particle as

$$F = f(t) - \frac{1}{\mu}v(t). \quad (5.3.1)$$

He regarded the force  $F$  acting on the particle as being made up of two contributions: a random part  $f(t)$  and a systematic or friction force proportional to and opposing the particle's velocity  $v(t)$ . The constant  $\mu$  in the friction force is known as the *mobility*. This view of the forces acting is eminently sensible; we know that there will be random atomic bombardments and that a body moving in a fluid will experience friction.

Langevin's equation of motion is then

$$M \frac{dv(t)}{dt} = f(t) - \frac{1}{\mu}v(t), \quad (5.3.2)$$

solution of which will give the time variation of the velocity  $v(t)$ .

Considering the specific problem of Brownian motion as outlined in the previous sections, it is to be expected that from the solution of the Langevin equation, an expression for the velocity autocorrelation function of the Brownian particle may be found in terms of the random force  $f(t)$  acting upon it. This will be done below.

The Langevin equation is, however, capable of much more. In particular, it will show how the random force and the friction force are related. This is a result of considerable generality and importance since it relates in a fundamental way the random fluctuations in the system  $f(t)$  and the dissipation characterized by the friction (or the mobility). This connection, in its general form, is known as the *fluctuation dissipation theorem*.

### 5.3.2 Separation of forces

It is commonly stated that it is a *hypothesis* of Langevin's approach that the force on the Brownian particle may be decomposed as the sum of a random part and a systematic friction part proportional to velocity. We shall see that this decomposition may actually be justified and understood in terms of the different centre of mass frames of the fluid and the Brownian particle [7].

A Brownian particle at rest in the centre of mass frame of the fluid medium suffers bombardments from the atoms of the fluid. These bombardments will result in a random force. On average there will be as many impacts in each direction so the average of the force will be zero.

Now consider the particle moving with respect to the centre of mass frame of the fluid. Then the impacts from the front will be at a greater relative velocity and the impacts from the rear will be at a lesser relative velocity. This will result in a mean force acting on the particle in opposition to its motion. We can see this from a simple model calculation. Let us consider two impacts, one from the rear and one from the front, where the atoms are moving with velocities  $+v$  and  $-v$  with respect to the fluid centre of mass.

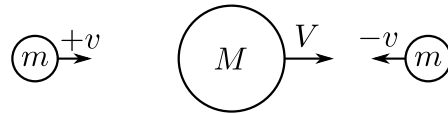


Figure 5.9: Bombardment of Brownian particle

The impact from the atom to the left transfers momentum  $m\Delta v$  to the Brownian particle. Assuming the atom mass  $m$  is very much less than that of the Brownian particle  $M$ , its velocity will be reversed. Its change of velocity is then twice the relative velocity,  $2(v - V)$ , so the momentum transferred is then

$$\Delta p_{\text{left}} = 2m(v - V). \quad (5.3.3)$$

In the impact from the right the change of velocity of the atom will similarly be twice the relative velocity, in this case  $2(v + V)$ . So the momentum transferred from this impact is

$$\Delta p_{\text{right}} = 2m(v + V) \quad (5.3.4)$$

The net momentum transfer is the difference between these

$$\Delta p = -4mV, \quad (5.3.5)$$

independent of  $v$ . Then if there are  $n$  impacts per unit time the net force on the Brownian particle will be

$$-4nmV. \quad (5.3.6)$$

On average, in the centre of mass frame of the fluid, there will be equal impacts from the left and right, leading to an average force of the above form.

It is of interest to observe that we have *derived* a force of frictional proportional to velocity. This is in contrast to elementary discussions which state that the friction force is *assumed* to be proportional to velocity. The

hidden assumption in our treatment is that the motion of the Brownian particle does not disturb the atomic motions of the fluid. This should be true if the velocity is small or of the fluid is not too dense. This is, essentially, a “linear” approximation since if the motion does affect the fluid then that will feed back as an additional force on the particle, changing its motion, which will feed back to the fluid and . . . round and round.

We have seen that Langevin’s decomposition of the forces acting on the Brownian particle may be understood in terms of the different centre of mass frames of the fluid and the particle. The random force  $f(t)$ , whose mean value is zero, is supplemented by a mean force proportional to and opposing the velocity of the particle. Thus we have justified writing the force as

$$F = f(t) - \frac{1}{\mu}v(t) \quad (5.3.7)$$

and we then expect that the mobility  $\mu$  should be related to  $f(t)$  in a fundamental way. This relation will follow from our consideration of the solution of the Langevin equation.

### 5.3.3 The Langevin equation

We write the Langevin equation as

$$M \frac{dv(t)}{dt} + \frac{1}{\mu}v(t) = f(t), \quad (5.3.8)$$

which emphasizes its structure as an inhomogeneous linear first order ordinary differential equation with source  $f(t)$ . It is convenient to make a simplification by the substitutions

$$\begin{aligned} A(t) &= \frac{f(t)}{M} \\ \gamma &= \frac{1}{M\mu}. \end{aligned} \quad (5.3.9)$$

Then the Langevin equation becomes

$$\frac{dv(t)}{dt} + \gamma v(t) = A(t); \quad (5.3.10)$$

and  $\gamma$  is identified as the dissipation rate. This equation has solution

$$v(t) = v(0)e^{-\gamma t} + \int_0^t e^{-\gamma(t-\tau)} A(\tau) d\tau. \quad (5.3.11)$$

The first term represents the transient part of the solution: that which depends on the initial conditions and which arises from the solution to the corresponding homogeneous equation. This is the *complementary function*. The second term represents the steady state response to the source “force”  $A(t)$ . This is the *particular integral* and this part persists when all memory of the initial condition has gone.

It is conventional to enunciate properties of the (scaled) random force  $A(t)$  [5]. These are listed as:

1.  $\langle A(t) \rangle = 0$ . The mean of  $A$  is zero. This follows, in our treatment, from the considerations of the centre of mass frame of the fluid.
2.  $\langle A(t_1)A(t_2) \rangle = 0$  unless  $t_1$  is close to  $t_2$ . In other words, the correlation time of the random force,  $\tau_f$ , is short.
3.  $\langle A(t)^2 \rangle$  has some definite value (independent of  $t$ ).

We may develop property 2 by approximating

$$\langle A(t_1)A(t_2) \rangle = \mathcal{A}^2 \delta(t_1 - t_2). \quad (5.3.12)$$

If we integrate this we obtain

$$\mathcal{A}^2 = \int_{-\infty}^{\infty} \langle A(0)A(t) \rangle dt \quad (5.3.13)$$

so that  $\mathcal{A}^2$  is the area under the (scaled) random force correlation function. Then

$$\mathcal{A} = \langle A(t)^2 \rangle \tau_f, \quad (5.3.14)$$

in terms of the force correlation time  $\tau_f$ .

As a simple application of the above results we can examine the mean value of  $v(t)$ . We find for a given initial condition

$$\langle v \rangle = v(0)e^{-\gamma t} \quad (5.3.15)$$

since by property 1,  $\langle A \rangle = 0$ . This tends to zero as time proceeds and memory of the initial condition fades.

### 5.3.4 Velocity autocorrelation function

In our kinematical analysis of Brownian motion we saw that the motion of the Brownian particle was conveniently expressed in terms of the velocity autocorrelation function. From Eq. (5.3.11) we have

$$\begin{aligned} \langle v(t)v(t+\tau) \rangle &= \langle v^2(0) \rangle e^{-\gamma(2t+\tau)} + \\ &+ e^{-\gamma(2t+\tau)} \left\{ \int_0^t + \int_0^{t+\tau} \right\} du \langle v(0)A(u) \rangle \\ &+ e^{-\gamma(2t+\tau)} \int_0^t du \int_0^{t+\tau} dw e^{\gamma(u+w)} \langle A(u)A(w) \rangle. \end{aligned} \quad (5.3.16)$$

The first term is the transient response which dies away at long times; it is of no interest. The second term vanishes since there is no correlation between  $v(t)$  and  $A(t)$ . The third term is of interest since it describes the equilibrium state of the particle, independent of the initial conditions.

In order to evaluate this term we make use of property 2, that  $\tau_f$  is small, and approximate the force autocorrelation function by the delta function expression, Eq. (5.3.12). This forces  $w = u$  when the integral over  $w$  is performed. Thus we obtain

$$\langle v(t)v(t+\tau) \rangle = \frac{\mathcal{A}^2}{2\gamma} e^{-\gamma\tau} \quad (5.3.17)$$

or

$$G_v = \langle v^2(0) \rangle e^{-\gamma t}. \quad (5.3.18)$$

We conclude that the correlation time for the velocity autocorrelation function is simply the damping time associated with the friction force

$$\tau_v = \gamma^{-1}. \quad (5.3.19)$$

We should note that in reality the force correlation time will have a finite size and the approximation of the force autocorrelation function by a delta function, Eq. (5.3.12), must be questioned. The approximation is valid whenever the velocity correlation time  $\tau_v$  is much greater than  $\tau_f$ . This condition:

$$\tau_v \gg \tau_f, \quad (5.3.20)$$

is known as the *separation of timescales*. It underlies many of the results connected with the Langevin method; it is saying that although the random force and the friction force are *related*, they are not *correlated*. Moreover the



emergence of the irreversible behaviour of macroscopic quantities from the reversible dynamics at the microscopic level is intimately connected with this separation of timescales.

### 5.3.5 Mean square velocity and equipartition

The mean square velocity is the zero time value of the velocity autocorrelation function. We set  $\tau = 0$  in Eq. (5.3.17), giving

$$\langle v^2(t) \rangle = \mathcal{A}^2 / 2\gamma \quad (5.3.21)$$

independent of time.

The importance of this expression becomes apparent when we exploit the equipartition theorem. This tells us, as we have seen,

$$\langle v^2 \rangle = \frac{kT}{M} \quad (5.3.22)$$

so that

$$\gamma = \frac{M}{2kT} \mathcal{A}^2 \quad (5.3.23)$$

which provides us with a relation between the mobility (contained in  $\gamma$ ) and the random force (contained in  $A(t)$ ). From the definition of  $\gamma$ , that for  $\mathcal{A}^2$  and that for  $A(t)$ , we can then express the mobility as

$$\frac{1}{\mu} = \frac{1}{2kT} \int_{-\infty}^{\infty} \langle f(0)f(t) \rangle dt. \quad (5.3.24)$$

This expression achieves the objective of relating the two forces in the Langevin equation, the mobility or friction force and the random force of atomic bombardment. The structure of this expression is that the systematic/dissipative force is expressed in terms of the autocorrelation function of the random/fluctuation force. This is a very general result, called *the fluctuation dissipation theorem*. The  $kT$  factor that appears in the relation between the macroscopic and the microscopic force is, recall, a consequence of equipartition.

### 5.3.6 Diffusion Coefficient

We saw that the diffusion coefficient of the Brownian particle was given in terms of  $\tau_v$  by

$$D = \frac{kT}{M} \tau_v, \quad (5.3.25)$$

which we can now re-express as

$$D = \frac{kT}{M\gamma} \quad (5.3.26)$$

or

$$D = \mu kT. \quad (5.3.27)$$

This connection between the diffusion coefficient and the mobility is known as the *Einstein relation*.

That is fine; it is purely kinematical and descriptive. But the real advance is that the fluctuation dissipation theorem of the previous section allows us to express this in terms of the fluctuating microscopic forces. That is the true content of the Einstein relation.

**A paradox:** Thermal equilibrium is intimately connected with time translation invariance. And on general grounds one can argue that correlation functions such as that for the velocity must then decay exponentially (in any time interval of a given duration the function decreases by the same factor). Our calculation above for  $G_v(t)$  conforms to this. This general result is known as Doob's theorem [8]. However, we have a problem. Such behaviour is incompatible with microscopic reversibility which implies that  $G_v(t) = G_v(-t)$ , so that assuming  $G_v(t)$  is analytic at the origin, all its odd derivatives would have to vanish. The paradox is resolved, however, when we recall we used the delta function approximation for the force autocorrelation time. This causes the bad behaviour at  $t = 0$ . For a smoothed  $G_f(t)$  we would find that  $G_v(t)$  was exponential over most of its range, but for very short times it would flatten off. Doob's theorem would not apply at very short times; it is a thermodynamic/hydrodynamic result so that is no problem.

### 5.3.7 Harmonically bound particle

To study the Brownian motion of a harmonically bound particle we add a restoring force  $Kx(t)$  to Eq. (5.3.8), giving

$$M \frac{d^2x(t)}{dt^2} + \frac{1}{\mu} \frac{dx(t)}{dt} + Kx(t) = f(t). \quad (5.3.28)$$

Here  $K$  is the spring constant. As previously,  $M$  is the mass of the Brownian particle,  $\mu$  its mobility and  $f(t)$  the random force acting on the particle. And

as previously we make the simplifications, through the substitutions

$$\begin{aligned} A(t) &= \frac{f(t)}{M} \\ \gamma &= \frac{1}{M\mu}. \end{aligned} \quad (5.3.29)$$

To these we now add the substitution

$$\omega_z = \sqrt{\frac{K}{M}}; \quad (5.3.30)$$

here  $\omega_z$  is the oscillation (angular) frequency (that would occur for zero damping).

Now the equation of motion is

$$\frac{d^2x(t)}{dt^2} + \gamma \frac{dx(t)}{dt} + \omega_z^2 x(t) = A(t). \quad (5.3.31)$$

With an oscillator it is often convenient to express the damping in terms of the Q-factor

$$Q = \omega_z / \gamma. \quad (5.3.32)$$

Eq. (5.3.31) has solution for the displacement  $x(t)$

$$\begin{aligned} x(t) &= \frac{\gamma x(0) + 2v(0)}{2\omega_f} e^{-\gamma t/2} \sin \omega_f t + x(0) e^{-\gamma t/2} \cos \omega_f t + \\ &+ \frac{1}{\omega_f} \int_0^t e^{-\gamma(t-u)/2} \sin \omega_f(t-u) A(u) du \end{aligned} \quad (5.3.33)$$

and for the velocity  $v(t) = dx(t)/dt$

$$\begin{aligned} v(t) &= -\frac{2\omega_z^2 x(0) + \gamma v(0)}{2\omega_f} e^{-\gamma t/2} \sin \omega_f t + v(0) e^{-\gamma t/2} \cos \omega_f t + \\ &+ \frac{1}{\omega_f} \int_0^t e^{-\gamma(t-u)/2} \left\{ -\frac{\gamma}{2} \sin \omega_f(t-u) + \omega_f \cos \omega_f(t-u) \right\} A(u) du \end{aligned} \quad (5.3.34)$$

where  $\omega_f$  is the free-ringing frequency, slightly lower than the zero damping frequency  $\omega_z$ :

$$\omega_f^2 = \omega_z^2 - \frac{\gamma^2}{4} = \omega_z^2 \left( 1 - \frac{1}{4Q^2} \right). \quad (5.3.35)$$

The autocorrelation functions for the displacement and the velocity are then found to be

$$\begin{aligned} G_x(\tau) = \langle x(t)x(t+\tau) \rangle &= \frac{\mathcal{A}^2}{\pi} \int_0^\infty \frac{\cos \omega\tau}{(\omega_z^2 - \omega^2)^2 + \gamma^2\omega^2} d\omega \\ &= \frac{\mathcal{A}^2}{2\gamma\omega_z^2} e^{-\gamma\tau/2} \left( \cos \omega_f\tau + \frac{\gamma}{2\omega_f} \sin \omega_f\tau \right) \end{aligned} \quad (5.3.36)$$

and

$$\begin{aligned} G_v(\tau) = \langle v(t)v(t+\tau) \rangle &= \frac{\mathcal{A}^2}{\pi} \int_0^\infty \frac{\omega^2 \cos \omega\tau}{(\omega_z^2 - \omega^2)^2 + \gamma^2\omega^2} d\omega \\ &= \frac{\mathcal{A}^2}{2\gamma} e^{-\gamma\tau/2} \left( \cos \omega_f\tau - \frac{\gamma}{2\omega_f} \sin \omega_f\tau \right). \end{aligned} \quad (5.3.37)$$

These have the form of a Fourier transform, so we can immediately write down the corresponding spectral density functions by inspection:

$$\begin{aligned} J_x(\omega) &= \mathcal{A}^2 \frac{1}{(\omega_z^2 - \omega^2)^2 + \omega_z^2\omega^2/Q^2} \\ J_v(\omega) &= \mathcal{A}^2 \frac{\omega^2}{(\omega_z^2 - \omega^2)^2 + \omega_z^2\omega^2/Q^2}. \end{aligned} \quad (5.3.38)$$

The spectral densities have the conventional Lorentzian resonance profiles, centred at  $\omega_z$  with quality factor  $Q$ . These are plotted in Fig. 5.10 for the case  $Q = 10$ . At this low  $Q$  value the small difference between the displacement and the velocity spectra can be discerned.

### 5.3.8 Equipartition and mean-square values

When the equipartition theorem is applied to the harmonic oscillator we must remember that both the the velocity and the displacement have their equipartition contributions since both the kinetic energy and the potential energy give quadratic terms to the hamiltonian. Thus we have

$$\begin{aligned} \langle v^2 \rangle &= \frac{kT}{M} \\ \langle x^2 \rangle &= \frac{kT}{K} = \frac{kT}{M\omega_z^2}. \end{aligned} \quad (5.3.39)$$

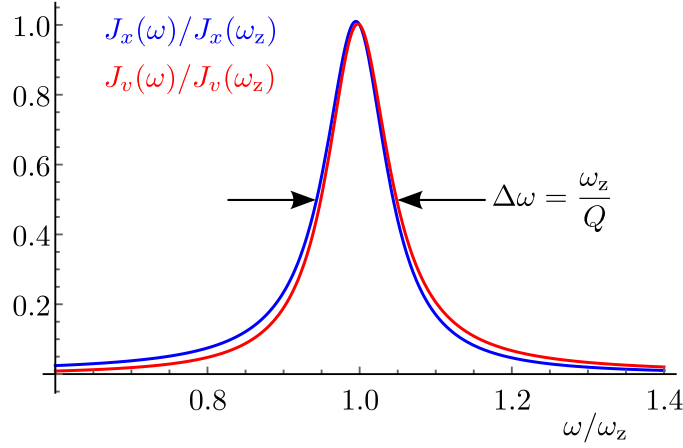


Figure 5.10: Displacement and velocity power spectrum. Plot corresponds to an oscillator with a  $Q$  factor of 10.

In the expression for  $\langle x^2 \rangle$  we have also given the formula in terms of  $M$ , so that

$$\langle v^2 \rangle = \omega_z^2 \langle x^2 \rangle. \quad (5.3.40)$$

The expressions for the autocorrelation functions above are written in terms of  $\mathcal{A}$ , defined in Eq. (5.3.13). Now, using equipartition, and taking the zero-time values of  $G_x(\tau)$  and  $G_v(\tau)$  we can write the  $\mathcal{A}^2$  prefactor as

$$\mathcal{A}^2 = 2\gamma \frac{kT}{M} = \frac{2\omega_z kT}{QM}. \quad (5.3.41)$$

The autocorrelation functions are then

$$\begin{aligned} G_x(\tau) &= \frac{kT}{M\omega_z^2} e^{-\gamma\tau/2} \left( \cos \omega_f \tau + \frac{\gamma}{2\omega_f} \sin \omega_f \tau \right) \\ G_v(\tau) &= \frac{kT}{M} e^{-\gamma\tau/2} \left( \cos \omega_f \tau - \frac{\gamma}{2\omega_f} \sin \omega_f \tau \right) \end{aligned} \quad (5.3.42)$$

and the corresponding spectral density functions are

$$\begin{aligned} J_x(\omega) &= \frac{2\omega_z kT}{QM} \frac{1}{(\omega_z^2 - \omega^2)^2 + \omega_z^2 \omega^2 / Q^2} \\ J_v(\omega) &= \frac{2\omega_z kT}{QM} \frac{\omega^2}{(\omega_z^2 - \omega^2)^2 + \omega_z^2 \omega^2 / Q^2}. \end{aligned} \quad (5.3.43)$$

From the zero-time value of Eq. (5.1.38) we have  $G(0)$  in terms of the area under the spectral density function:

$$\int_0^{\infty} J(\omega) d\omega = \pi G(0), \quad (5.3.44)$$

so that the “total power” in the displacement and the velocity fluctuations are

$$\begin{aligned} \int_0^{\infty} J_x(\omega) d\omega &= \pi \langle x^2 \rangle = \pi \frac{kT}{M\omega_z^2} \\ \int_0^{\infty} J_v(\omega) d\omega &= \pi \langle v^2 \rangle = \pi \frac{kT}{M}. \end{aligned} \quad (5.3.45)$$

The on-resonance values of  $J_x(\omega)$  and  $J_v(\omega)$  are

$$\begin{aligned} J_x(\omega_z) &= \frac{2kT}{M} \frac{Q}{\omega_z^3} \\ J_v(\omega_z) &= \frac{2kT}{M} \frac{Q}{\omega_z} \end{aligned} \quad (5.3.46)$$

so for both

$$\int_0^{\infty} J_{x/v}(\omega) d\omega = \frac{\pi\omega_z}{2Q} J_{x/v}(\omega_z). \quad (5.3.47)$$

This is telling us that the power in the thermal fluctuations is spread over a bandwidth of order  $\omega_z/Q$ . This is indicated in Fig. 5.10 above.

### 5.3.9 Electrical analogue of the Langevin equation

The Langevin equation, Eq. (5.3.8):

$$M \frac{dv(t)}{dt} + \frac{1}{\mu} v(t) = f(t)$$

describes the velocity  $v(t)$  of the Brownian particle of mass  $M$  in terms of the mobility  $\mu$  (inverse friction) and the random force  $f(t)$ . However the real achievement of the approach was in relating the mobility to the random force, Eq. (5.3.24). In this section we shall explore an electrical analogue of this.

Imagine an electrical circuit comprising an inductor of inductance  $L$  connected in series with a resistor of resistance  $R$ . The current  $I$  flowing in the

circuit results from the motion of a very large number of electrons; in this respect we regard  $I$  as a *macroscopic* quantity. The voltage  $V$  across the circuit is given by

$$L \frac{dI(t)}{dt} + RI(t) = V(t). \quad (5.3.48)$$

The random motion of the electrons will result in a randomly fluctuating voltage  $V(t)$ . Then the analogy between the two above equations is quite clear. We can follow the analogy through the arguments of the previous sections. The equipartition expression, Eq.(5.3.12), now becomes

$$\langle I^2 \rangle = \frac{kT}{L} \quad (5.3.49)$$

and the analogue of the fluctuation-dissipation result, Eq. (5.3.24) gives

$$R = \frac{1}{2kT} \int_{-\infty}^{\infty} \langle V(0)V(t) \rangle dt. \quad (5.3.50)$$

This shows how the resistance (dissipation) is related to the fluctuations of voltage. This will be explored further in Section 5.5.2 where we shall consider Nyquist's theorem.

In Problem 5.9 you will examine a different electrical analogue of the Langevin equation which results in relating resistance to *current* fluctuations:

$$\frac{1}{R} = \frac{1}{2kT} \int_{-\infty}^{\infty} \langle I(0)I(t) \rangle dt. \quad (5.3.51)$$

## 5.4 Linear Response I – Phenomenology

### 5.4.1 Definitions and assumptions

In this section we turn to the question of the response of a system to an externally applied disturbance. This is fundamentally a non-equilibrium problem and so it is outside the area of applicability of *equilibrium* statistical mechanics. A special case of this question is the way a system relaxes to its equilibrium state from an initial non-equilibrium configuration. The general case involves the introduction of the concept of the dynamic susceptibility; for magnetic systems this is a generalization of the magnetic susceptibility discussed in Chapter 2.

We consider an arbitrary system, to which we apply a generalized force  $B$ . And we observe the response  $M$  to this force. In the magnetic case  $B$

could be an applied magnetic field and  $M$  the magnetization response. But the discussion will remain more general than this.

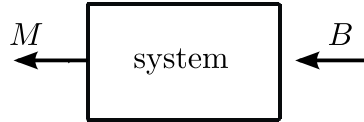


Figure 5.11: Excitation  $B$  and its response  $M$

The response depends on the force:  $M$  is a function of  $B$ . Thus we write

$$M = f(B). \quad (5.4.1)$$

We shall now assume that our system obeys the following three rules:

**A: Linearity** If  $M_1$  is the response to the force  $B_1$  and  $M_2$  is the response to the force  $B_2$  then the response to the force  $\alpha B_1 + \beta B_2$  is given by  $\alpha M_1 + \beta M_2$ . In other words the response function  $f(B)$  obeys the rule

$$f(\alpha B_1 + \beta B_2) = \alpha f(B_1) + \beta f(B_2). \quad (5.4.2)$$

Physically we would expect the response to be linear for sufficiently small excitation  $B$ .

If we now consider time variation, then (very generally) we expect that  $M$  at a given time will depend on  $B$  at other times. The condition of linearity means that  $M$  at a given time will depend *linearly* on  $B$  at other times. Thus  $M(t)$  will be a linear *functional* of  $B(t)$ :

$$M(t) = \int X(t, \tau) B(\tau) d\tau. \quad (5.4.3)$$

The function  $X()$  is known as the time domain dynamical susceptibility or simply the response function.

**B: Stationarity** If the time variation of  $B(t)$  is shifted by an amount  $t'$  then the response  $M(t)$  will be shifted by the same amount  $t'$ . This is the physical requirement of time translation invariance. If we apply this time shift to Eq. (5.4.3) we find that time translation invariance requires that

$$X(t + t', \tau + t') = X(t, \tau) \quad (5.4.4)$$



for any time  $t'$ . If, in particular, we set  $t' = -\tau$  then we find

$$X(t - \tau, 0) = X(t, \tau). \quad (5.4.5)$$

This indicates that the response function  $X$  depends only on the time difference  $t - \tau$ . And then Eq. (5.4.3) can be written as

$$M(t) = \int X(t - \tau)B(\tau) d\tau \quad (5.4.6)$$

or, by change of variable as

$$M(t) = \int X(\tau)B(t - \tau) d\tau. \quad (5.4.7)$$

In many respects the response function  $X(\tau)$  describes the *memory* of the system.  $M(t)$  will depend strongly on excitations  $B(t)$  when  $t$  is close to  $\tau$ , and less so as  $t$  becomes more distant from  $\tau$ , as indicated in Fig. 5.12.

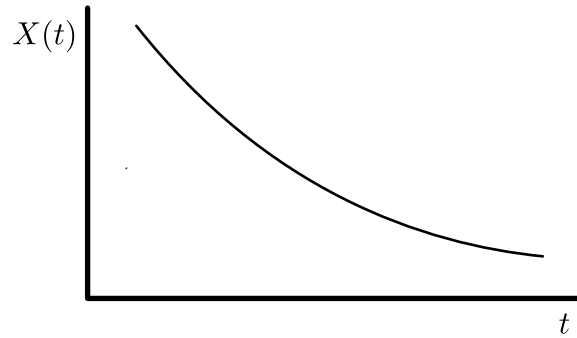


Figure 5.12: General form of the response function

**C: Causality** It is a fundamental principle of Physics that effect cannot precede cause. Thus in Eqs. (5.4.6) and (5.4.7) we see that this requires that  $X(t)$  be zero for negative  $t$ :

$$X(t) = 0 \quad t < 0. \quad (5.4.8)$$

This requirement also means that the domain of integration in Eq. (5.4.6) may be taken to be  $-\infty < \tau < t$ :

$$M(t) = \int_{-\infty}^t X(t - \tau)B(\tau) d\tau, \quad (5.4.9)$$

and in Eq. (5.4.7) to be  $0 < \tau < \infty$ :

$$M(t) = \int_0^{\infty} X(\tau)B(t - \tau) d\tau. \quad (5.4.10)$$

These equations give the general expression for the linear response of  $M$  to the excitation  $B$ .

### 5.4.2 Response to a harmonic excitation

Many experimental techniques are based upon observing the response of a system to a harmonic excitation. This is the method of conventional *spectroscopy*.

We shall consider our system to be excited by a cosine of frequency  $\omega$ :

$$B(t) = b \cos(\omega t). \quad (5.4.11)$$

Then the response, from Eq. (5.4.9), will be

$$M(t) = b \int_0^{\infty} X(\tau) \cos \omega(t - \tau) d\tau. \quad (5.4.12)$$

Upon expanding the cosine we have

$$M(t) = b \cos(\omega t) \int_0^{\infty} X(\tau) \cos \omega(\tau) d\tau + b \sin(\omega t) \int_0^{\infty} X(\tau) \sin \omega(\tau) d\tau. \quad (5.4.13)$$

This is telling us that the response to the monochromatic excitation  $b \cos(\omega t)$  will be monochromatic at the same frequency  $\omega$ . However in general the phase of the response will *lag behind* that of the excitation; particularly at higher frequencies the response will not be able to “keep up” with the excitation. We shall define:

$$\chi'(\omega) = \int_0^{\infty} X(t) \cos(\omega t) dt \quad (5.4.14)$$

and

$$\chi''(\omega) = \int_0^{\infty} X(t) \sin(\omega t) dt. \quad (5.4.15)$$

Then the response is expressed as a component  $b\chi'(\omega)$  in phase with the excitation and a component  $b\chi''(\omega)$  in quadrature ( $90^\circ$  out of phase):

$$M(t) = b\chi'(\omega) \cos(\omega t) + b\chi''(\omega) \sin(\omega t). \quad (5.4.16)$$

We see that  $\chi'(\omega)$  and  $\chi''(\omega)$  correspond to the Fourier cosine and sine transforms of  $X(t)$ .

Since the system is linear, it will prove mathematically convenient to consider the response to the un-physical complex exponential excitation<sup>1</sup>

$$B_c(t) = be^{-i\omega t} = b \cos(\omega t) - i b \sin(\omega t). \quad (5.4.17)$$

Linearity, Eq. (5.4.2), means that the mathematical response will be a complex  $M_c(t)$ , the real part of which is the response to  $b \cos(\omega t)$ , Eq. (5.4.16). (The imaginary part is the response to  $b \sin(\omega t)$ ). The complex representation proves particularly convenient since it obviates the need to keep track of the sines and cosines. Note, however, that this simplification cannot be used in the case of a *nonlinear* response.

The response to the complex sinusoidal excitation will be, from Eq. (5.4.7)

$$\begin{aligned} M_c(t) &= b \int_{-\infty}^{\infty} X(\tau) e^{-i\omega(t-\tau)} d\tau \\ &= be^{-i\omega t} \int_{-\infty}^{\infty} X(\tau) e^{i\omega\tau} d\tau. \end{aligned} \quad (5.4.18)$$

Here we have written the integration range  $-\infty < \tau < \infty$  so the integral is the complex Fourier transform; we must therefore account for causality in the response function  $X(\tau)$ , as in Eq. (5.4.8), separately. So now we see that the response to the (hypothetical) complex monochromatic excitation  $be^{-i\omega t}$  is a complex response proportional to the same complex sinusoid  $e^{-i\omega t}$ . And the proportionality factor is the Fourier transform of  $X(t)$ , which we denote by  $\chi(\omega)$ :

$$\chi(\omega) = \int_{-\infty}^{\infty} X(t) e^{i\omega t} dt. \quad (5.4.19)$$

---

<sup>1</sup>We write the elementary complex harmonic oscillation as  $e^{-i\omega t}$  (with a  $-$  sign), consistent with the usual expression for a propagating wave:  $e^{i(kx-\omega t)}$ . This conforms with the physicist's usual Fourier transform convention, Eq. (5.4.26), but it contrasts with engineering practice. Engineers prefer to express the elementary oscillation with a  $+$  sign as  $e^{j\omega t}$ .

Thus

$$M_c(t) = be^{-i\omega t} \chi(\omega). \quad (5.4.20)$$

The real (physical) response is then found by taking the real part of this equation

$$\begin{aligned} M(t) &= \Re M_c(t) \\ &= b \cos(\omega t) \int_{-\infty}^{\infty} X(\tau) \cos(\omega\tau) d\tau + b \sin(\omega t) \int_{-\infty}^{\infty} X(\tau) \sin(\omega\tau) d\tau \end{aligned} \quad (5.4.21)$$

since  $X(t)$  is real. However since causality requires the domain of integration to be restricted to  $0 < \tau < \infty$ , the integrals here correspond to the  $\chi'(\omega)$  and  $\chi''(\omega)$  of Eqs. (5.4.14) and (5.4.15). Thus we have precisely the result obtained in Eq. (5.4.13), where now  $\chi'(\omega)$  and  $\chi''(\omega)$  may be regarded as the real and imaginary parts of the (complex) Fourier transform of  $X(t)$ .

### 5.4.3 Fourier representation

Any excitation  $B(t)$  can be made up from a superposition of sinusoids:

$$B(t) = \frac{1}{2\pi} \int_{-\infty}^{\infty} b(\omega) e^{-i\omega t} d\omega. \quad (5.4.22)$$

Now the response to  $b(\omega)e^{-i\omega t}$  is given by Eq. (5.4.20). Let us call this  $m(\omega)e^{-i\omega t}$ . Then clearly

$$m(\omega) = \chi(\omega)b(\omega) \quad (5.4.23)$$

so that on multiplying by  $e^{i\omega t}$  and integrating over  $\omega$  we obtain

$$\int_{-\infty}^{\infty} m(\omega) e^{i\omega t} d\omega = \int_{-\infty}^{\infty} \chi(\omega) b(\omega) e^{i\omega t} d\omega \quad (5.4.24)$$

where the left hand side of this equation is the Fourier transform of  $M(t)$ , that is,

$$M(t) = \frac{1}{2\pi} \int_{-\infty}^{\infty} m(\omega) e^{-i\omega t} d\omega. \quad (5.4.25)$$

Thus Eq. (5.4.23) expresses the relation between the Fourier transform of the excitation and the response.

$$m(\omega) = \int_{-\infty}^{\infty} M(t)e^{i\omega t} dt$$

$$M(t) = \frac{1}{2\pi} \int_{-\infty}^{\infty} m(\omega)e^{-i\omega t} d\omega. \quad (5.4.26)$$

The *same* Fourier transform relations hold also for  $\{b(\omega), B(t)\}$  and  $\{\chi(\omega), X(t)\}$ .

#### 5.4.4 Response to a step excitation

Let us consider the response to a step excitation. We imagine a constant excitation to have been applied back into the past and we remove this at time  $t = 0$ . Clearly for negative times the response  $M(t)$  will be a constant. And the interest then focuses on how  $M(t)$  relaxes to its new equilibrium value when  $B$  drops to zero.

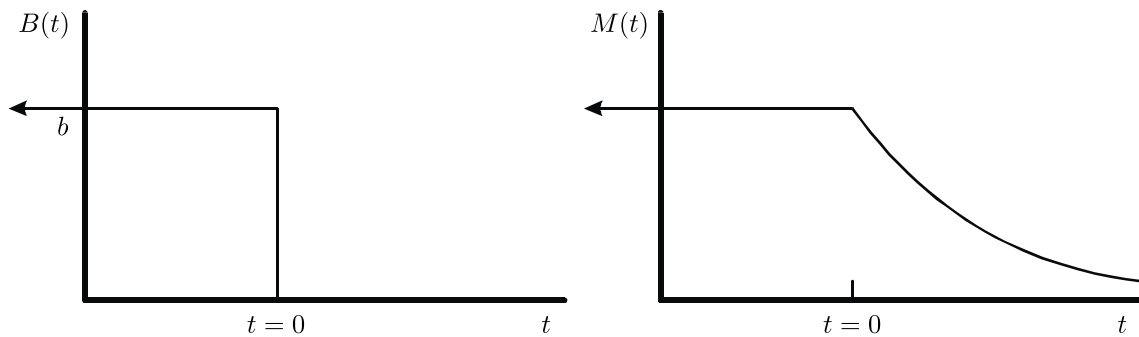


Figure 5.13: Step excitation and its response

Here the excitation is specified to be

$$B(t) = b \quad t < 0$$

$$= 0 \quad t > 0 \quad (5.4.27)$$

or

$$B(t) = b\theta_-(t) \quad (5.4.28)$$

where  $\theta_-(t)$  is the unit step (off) function. Then the response, according to Eq. (5.4.6), is given by

$$M_{\text{step}}(t) = b \int_{-\infty}^0 X(t - \tau) d\tau \quad (5.4.29)$$

or, upon change of variables

$$M_{\text{step}}(t) = b \int_t^{\infty} X(\tau) d\tau. \quad (5.4.30)$$

Of course this holds only for times  $t > 0$ .

### 5.4.5 Response to a “shock” or delta function excitation

Let us now consider the response to a delta function, or spike, excitation. Now  $B(t)$  is specified as

$$B(t) = b \delta(t) \quad (5.4.31)$$

where  $\delta(t)$  is the Dirac delta function.

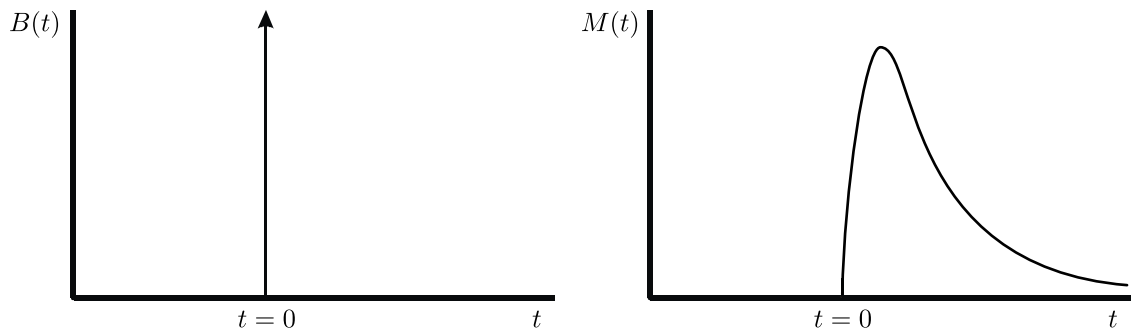


Figure 5.14: Delta function excitation and its response

Then the response, according to Eq. (5.4.6) is given by

$$M_{\delta}(t) = b \int_{-\infty}^{\infty} X(t - \tau) \delta(\tau) d\tau \quad (5.4.32)$$

and, upon using the properties of the delta function, this becomes

$$M_{\delta}(t) = bX(t). \quad (5.4.33)$$

This is just the response function  $X(t)$  introduced above. In other words  $X(t)$  may be regarded as the response to a delta function of unit strength.

The delta function is minus the derivative of the unit step function. The linearity condition relates the responses to these excitations. And indeed directly from Eqs. (5.4.30) and (5.4.33) we see that

$$M_\delta = -\frac{d}{dt}M_{\text{step}}. \quad (5.4.34)$$

It will prove useful to define the function  $\Phi(t)$  as the response to a unit step excitation, just as  $X(t)$  is the response to a delta function excitation. Then

$$X(t) = -\frac{d}{dt}\Phi(t). \quad (5.4.35)$$

Conventional spectroscopy, as discussed in Section 5.4.2 observes the response of a system to a succession of pure sinusoids. Making such measurements can be time-consuming. A delta-function excitation, however, contains spectral components at *all* frequencies. So if we were to excite our system with such a shock its response would contain the responses at all frequencies. As an example, one may measure the harmonic characteristics of a concert hall by carefully recording the response to sinusoidal excitations of different frequencies. Alternatively one may simply fire off a gun: the fourier transform of the response to this excitation gives the frequency response over the entire spectrum (almost instantaneously)!

### 5.4.6 \*Response to a Noise Excitation

There is an alternative to a delta-function excitation in order to excite at all frequencies simultaneously. White noise, also, contains spectral components at *all* frequencies. So if we were to excite our system with such noise its response would contain the responses at all frequencies. In this case we need to know how to “disentangle” all these responses.

We shall express the system’s response to an excitation as in Eq. (5.4.9), writing the excitation as  $n$  to indicate that it is noise:

$$M_n(t) = \int_0^\infty X(\tau)n(t-\tau) d\tau. \quad (5.4.36)$$

The details of the response  $M_n(t)$  depend on the details of the noise excitation. In other words, we might say that the  $M_n(t)$  response is *correlated*

with the  $n(t)$  excitation. We would study this correlation through the  $M_n - n$  cross-correlation function  $\langle M_n(t)n(T) \rangle$ :

$$\langle M_n(t)n(T) \rangle = \int_0^{\infty} X(\tau) \langle n(T)n(t-\tau) \rangle d\tau. \quad (5.4.37)$$

Inside the integral we observe the noise *autocorrelation* function. If the noise is regarded as “white” then its correlation is a delta function, as in Eq. (5.3.12),

$$\langle n(T)n(t-\tau) \rangle = a^2 \delta(t-\tau-T). \quad (5.4.38)$$

Here  $a$ , a measure of the strength of the noise, is to be determined. The effect of the delta function is to select out the  $\tau = t - T$  value from the integral so that

$$\langle M_n(t)n(T) \rangle = a^2 X(t-T) \quad (5.4.39)$$

then invoking stationarity (time-translation invariance) we obtain

$$\langle M_n(t)n(0) \rangle = a^2 X(t). \quad (5.4.40)$$

Thus the  $M_n - n$  cross-correlation function gives the response function directly.

In order to determine  $a$  we write the area under the noise autocorrelation function as

$$\int_{-\infty}^{\infty} \langle n(t)n(0) \rangle dt = \langle n^2 \rangle \tau_n \quad (5.4.41)$$

where  $\langle n^2 \rangle$  is the mean-square strength of the noise excitation and  $\tau_n$  is its correlation time. Then by comparing Eq. (5.4.38) with Eq. (5.4.41) we identify

$$a^2 = \langle n^2 \rangle \tau_n \quad (5.4.42)$$

so that

$$\langle M_n(t)n(0) \rangle = \langle n^2 \rangle \tau_n X(t). \quad (5.4.43)$$

This is telling us that the dynamical response function  $X(t)$  may be determined by exciting the system with noise and cross-correlating the resultant response with the driving noise

$$X(t) = \frac{\langle M_n(t)n(0) \rangle}{\langle n^2 \rangle \tau_n}. \quad (5.4.44)$$



There appears to be a contradiction. Although we regarded the noise to be *white*, we then referred to its correlation time  $\tau_n$ . But, by definition, the correlation time of white noise is zero. In reality there is no such thing as truly white noise; its spectrum cannot extend to infinite frequencies! The resolution of the contradiction is in the *separation of timescales*. The timescale for the noise fluctuations,  $\tau_n$  must be much less than the timescale for the response function, that is

$$\frac{X(t + \tau_n) - X(t)}{X(t)} \ll 1. \quad (5.4.45)$$

When this condition is satisfied the noise is *effectively* white and the arguments above are valid.

The shock excitation and the white noise excitation, both applying all frequencies simultaneously, provide the same information. The relative advantages of these methods involve signal-to-noise considerations; unfortunately these are beyond the scope of this book.

### 5.4.7 Consequence of the reality of $X(t)$

In the next few sections we shall revisit the use of complex quantities in linear response questions. The response to a real time-dependent excitation  $B(t)$  is a real quantity  $M(t)$ . And these are related by the integral expression, Eq. (5.4.3). Thus we conclude that the kernel  $X(t)$  must be a real function. However its Fourier transform,  $\chi(\omega)$ , the dynamical susceptibility, can be complex. We shall see that the reality of the time function has important consequences for the frequency function.

In Eq. (5.4.19):

$$\chi(\omega) = \int_{-\infty}^{\infty} X e^{i\omega t} dt \quad (5.4.46)$$

let us take the complex conjugate. This gives

$$\chi^*(\omega) = \int_{-\infty}^{\infty} X e^{-i\omega t} dt \quad (5.4.47)$$

since the real  $X(t)$  remains unchanged. And if we now replace  $\omega$  by  $-\omega$  we have

$$\chi^*(-\omega) = \int_{-\infty}^{\infty} X e^{i\omega t} dt = \chi(\omega) \quad (5.4.48)$$

so we conclude that

$$\chi^*(-\omega) = \chi(\omega). \quad (5.4.49)$$

This is the consequence of the reality of  $X(t)$ .

In terms of the real and imaginary parts of the susceptibility this gives the pair of relations

$$\begin{aligned} \chi'(\omega) &= \chi'(-\omega) \\ \chi''(\omega) &= -\chi''(-\omega). \end{aligned} \quad (5.4.50)$$

Thus  $\chi'(\omega)$  is an even function and  $\chi''(\omega)$  is an odd function. This means that  $\chi''(0)$  must be zero; obviously there cannot be a quadrature response at zero frequency, the static case.

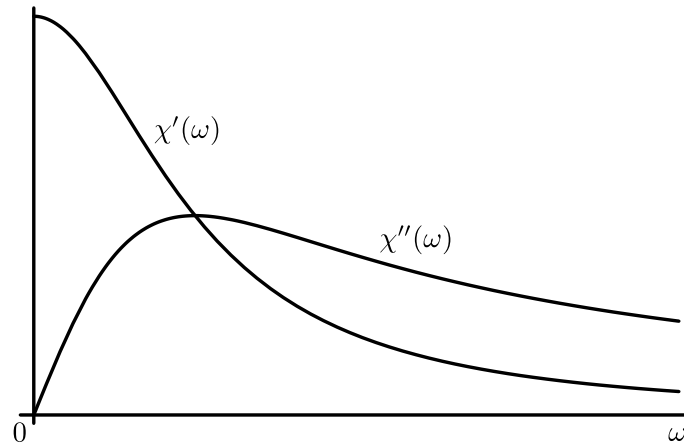


Figure 5.15: Real and imaginary part of the dynamical susceptibility

### 5.4.8 Consequence of causality ?????

The definition of  $\chi'(\omega)$  and  $\chi''(\omega)$  was given in Eqs. (5.4.14) and (5.4.15):

$$\chi'(\omega) = \int_0^{\infty} X(t) \cos(\omega t) dt \quad [5.4.14]$$

$$\chi''(\omega) = \int_0^{\infty} X(t) \sin(\omega t) dt. \quad [5.4.15]$$

The requirement of causality was expressed in Eq. (5.4.8), that  $X(t)$  be zero for negative times. We see this is reflected directly in the domains of

integration. Now these real Fourier transforms may be inverted; we see that  $X(t)$  may be found equivalently from either  $\chi'(\omega)$  or  $\chi''(\omega)$ :

$$X(t) = \frac{2}{\pi} \int_0^{\infty} \chi'(\omega) \cos(\omega t) d\omega \quad (5.4.51)$$

$$X(t) = \frac{2}{\pi} \int_0^{\infty} \chi''(\omega) \sin(\omega t) d\omega. \quad (5.4.52)$$

The point about this is that  $\chi'(\omega)$  and  $\chi''(\omega)$  are not independent; they both come (invertibly) from  $X(t)$ . So, in particular,  $\chi'(\omega)$  may be found from  $\chi''(\omega)$  or *vice versa*.

We may substitute  $X(t)$  from Eq. (5.4.52) into Eq. (5.4.14); this gives  $\chi'(\omega)$  in terms of  $\chi''(\omega)$

$$\chi'(\omega) = \frac{2}{\pi} \int_0^{\infty} d\omega' \left[ \int_0^{\infty} dt \cos \omega t \sin \omega' t \right] \chi''(\omega') \quad (5.4.53)$$

or we may substitute  $X(t)$  from Eq. (5.4.51) into Eq. (5.4.15); this gives  $\chi''(\omega)$  in terms of  $\chi'(\omega)$

$$\chi''(\omega) = \frac{2}{\pi} \int_0^{\infty} d\omega' \left[ \int_0^{\infty} dt \sin \omega t \cos \omega' t \right] \chi'(\omega'). \quad (5.4.54)$$

In evaluating the integrals in the square brackets we must take the upper limit to infinity carefully. Let's put the upper limit as  $T$  to start with. Then we find

$$\begin{aligned} \int_0^T \cos \omega t \sin \omega' t dt &= \int_0^T \frac{1}{2} \left\{ \sin(\omega + \omega')t - \sin(\omega - \omega')t \right\} dt \\ &= -\frac{1}{2} \left\{ \frac{\cos(\omega + \omega')t}{\omega + \omega'} - \frac{\cos(\omega - \omega')t}{\omega - \omega'} \right\} \Big|_0^T \\ &= \frac{1}{2} \left\{ \frac{1 - \cos(\omega + \omega')T}{\omega + \omega'} - \frac{1 - \cos(\omega - \omega')T}{\omega - \omega'} \right\}. \end{aligned} \quad (5.4.55)$$

Now we argue that as  $T \rightarrow \infty$  the cosines vary very fast: so rapidly that they average to zero. This means that effectively, when the limit of the integral

goes to zero, we have

$$\begin{aligned} \int_0^{\infty} \cos \omega t \sin \omega' t dt &= \frac{1}{2} \left\{ \frac{1}{\omega + \omega'} - \frac{1}{\omega - \omega'} \right\} \\ &= \frac{\omega'}{\omega'^2 - \omega^2}. \end{aligned} \quad (5.4.56)$$

Using this result in Eqs. (5.4.53) and (5.4.54) then gives

$$\begin{aligned} \chi'(\omega) &= \frac{2}{\pi} \int_0^{\infty} \frac{\omega' \chi''(\omega')}{\omega'^2 - \omega^2} d\omega' \\ \chi''(\omega) &= -\frac{2}{\pi} \int_0^{\infty} \frac{\omega \chi'(\omega')}{\omega'^2 - \omega^2} d\omega'. \end{aligned} \quad (5.4.57)$$

These are known as the Kramers-Kronig relations; they are purely a consequence of causality. They tell us that the real and imaginary parts of the susceptibility are not independent; the real part may be found from knowledge of the imaginary part *at all frequencies* and *vice versa*.

### 5.4.9 Consequence of causality

The requirement of causality was expressed in Eq. (5.4.8), that  $X(t)$  be zero for negative times. We can express this condition by

$$\theta_+(t)X(t) = X(t) \quad (5.4.58)$$

where  $\theta_+(t)$  is the unit step (on) function. We also have the result

$$\theta_-(t)X(t) = 0. \quad (5.4.59)$$

These equations put an important restriction on the dynamic susceptibility  $\chi(\omega)$ . This is most easily seen from the convolution theorem for Fourier transforms:

$$\int_{-\infty}^{\infty} F(t) G(t) e^{i\omega t} dt = \frac{1}{2\pi} \int_{-\infty}^{\infty} f(\omega') g(\omega - \omega') d\omega' \quad (5.4.60)$$

where  $\{F(t), f(\omega)\}$  and  $\{G(t), g(\omega)\}$  are Fourier transform pairs, as defined by Eq. (5.4.26).

Now the Fourier transform of the two step functions is

$$\left. \begin{aligned} \mathcal{F}\{\theta_+\} &= \frac{i}{\omega + i\varepsilon} \\ \mathcal{F}\{\theta_-\} &= \frac{-i}{\omega - i\varepsilon} \end{aligned} \right\} \varepsilon \rightarrow 0_+. \quad (5.4.61)$$

So the Fourier transforms of Eqs. (5.4.58) and (5.4.59), using the convolution expression, Eq. (5.4.60) are:

$$\frac{i}{2\pi} \int_{-\infty}^{\infty} \frac{\chi(\omega') d\omega'}{\omega - \omega' + i\varepsilon} = \chi(\omega) \quad (5.4.62)$$

and

$$\frac{i}{2\pi} \int_{-\infty}^{\infty} \frac{\chi(\omega') d\omega'}{\omega - \omega' - i\varepsilon} = 0. \quad (5.4.63)$$

We define the *principal part* of the integral along the real line by

$$\mathcal{P} \int_{-\infty}^{\infty} \frac{f(\omega') d\omega'}{\omega - \omega'} = \lim_{\delta \rightarrow 0} \left\{ \int_{-\infty}^{\omega - \delta} \frac{f(\omega') d\omega'}{\omega - \omega'} + \int_{\omega + \delta}^{\infty} \frac{f(\omega') d\omega'}{\omega - \omega'} \right\} \quad (5.4.64)$$

and we shall accept this as equal to

$$\frac{1}{2} \left\{ \int_{-\infty}^{\infty} \frac{f(\omega') d\omega'}{\omega - \omega' + i\varepsilon} + \int_{-\infty}^{\infty} \frac{f(\omega') d\omega'}{\omega - \omega' - i\varepsilon} \right\}. \quad (5.4.65)$$

Then from Eqs. (5.4.62) and (5.4.63) we obtain

$$\chi(\omega) = \frac{i}{\pi} \mathcal{P} \int_{-\infty}^{\infty} \frac{\chi(\omega') d\omega'}{\omega - \omega'}. \quad (5.4.66)$$

The appearance of the  $i$  in this equation means that if we separate the real and imaginary parts,  $\chi'$  is given in terms of  $\chi''$  and *vice versa*.

$$\begin{aligned} \chi'(\omega) &= -\frac{1}{\pi} \mathcal{P} \int_{-\infty}^{\infty} \frac{\chi''(\omega') d\omega'}{\omega - \omega'} \\ \chi''(\omega) &= \frac{1}{\pi} \mathcal{P} \int_{-\infty}^{\infty} \frac{\chi'(\omega') d\omega'}{\omega - \omega'} \end{aligned} \quad (5.4.67)$$

These are known as the Kramers-Kronig relations; they are purely a consequence of causality. They tell us that the real and imaginary parts of the susceptibility are not independent; the real part may be found from knowledge of the imaginary part *at all frequencies* and *vice versa*.

### 5.4.10 Energy considerations

If we regard the excitation  $B(t)$  as a force and the response  $M(t)$  as a displacement, then the element of work done *on* the system is given by

$$dW = -B dM. \quad (5.4.68)$$

And the power dissipated, the rate of doing work *by* the system is then

$$B \frac{dM}{dt}. \quad (5.4.69)$$

For a periodic excitation we can find the mean power dissipated by averaging this expression over a cycle.

$$P = \left\langle B \frac{dM}{dt} \right\rangle \quad (5.4.70)$$

From Eq. (5.4.16) we see that the response to an excitation  $B = b \cos \omega t$  is

$$M = b(\chi'(\omega) \cos \omega t + \chi''(\omega) \sin \omega t). \quad (5.4.71)$$

The mean power dissipated is then

$$P = \omega b^2 (-\chi'(\omega) \langle \cos \omega t \sin \omega t \rangle + \chi''(\omega) \langle \cos^2 \omega t \rangle). \quad (5.4.72)$$

The  $\cos \times \sin$  average is zero and the  $\cos^2$  average is  $1/2$ . Thus we find

$$P = \frac{1}{2} b^2 \omega \chi''(\omega); \quad (5.4.73)$$

the power dissipated depends solely on the imaginary part of the dynamical susceptibility. In other words, dissipation occurs in the response that is  $90^\circ$  out of phase with the excitation. Since the energy dissipation must be positive, a requirement of the Second Law of thermodynamics, this puts a further general restriction on the dynamical response:  $\omega \chi''(\omega)$  must be positive at all frequencies (in conformity with Eq. (5.4.50)).

There is, of course, a certain arbitrariness in what we choose to call a generalized force or excitation and in what we call a generalized displacement

or response. However we shall use Eq. (5.4.68) as a paradigmatic relation in that, in general, the excitation  $B$  and the response  $M$  are related by

$$B = \frac{\partial \text{energy}}{\partial M}. \quad (5.4.74)$$

In other words they comprise the regular extensive-intensive conjugate pairs of thermodynamics.

We can use this result to examine the dimensions of the generalized susceptibility. The defining equation for the dynamical response function gives us the result

$$[M] = [\chi][B] \quad (5.4.75)$$

and the energy expression above tells us that

$$[B] = [\text{energy}] / [M]. \quad (5.4.76)$$

By eliminating  $[B]$  we then find that

$$[\chi] = [M^2] / [\text{energy}]; \quad (5.4.77)$$

the dynamical susceptibility thus has the dimensions of the square of the response divided by energy. In a similar way we see that the dimensions of the dynamical response function are

$$[X] = [M^2] / [\text{energy}][\text{time}] \quad (5.4.78)$$

and the dimensions of the step response function are

$$[\Phi] = [M^2] / [\text{energy}]. \quad (5.4.79)$$

### 5.4.11 Static susceptibility

The static susceptibility is the response to a constant excitation. This may be regarded as the zero-frequency limit of the frequency-dependent susceptibility  $\chi(\omega)$ . We denote the static susceptibility by  $\chi_0$ . Thus

$$\chi_0 = \chi(\omega \rightarrow 0). \quad (5.4.80)$$

We can relate the static susceptibility to the time domain response function through the Fourier transform relation, Eq. (5.4.19), taking the zero-frequency limit. Then we find

$$\chi_0 = \int_0^{\infty} X(t) dt; \quad (5.4.81)$$

the static susceptibility is the area under the time response function. We also note that the static susceptibility is equal to the zero-time value of the step response function, defined in Section 5.4.5.

$$\Phi(0) = \chi_0 \quad (5.4.82)$$

This may be seen from Eq. (5.4.35).

We know that the imaginary part of  $\chi$  vanishes at zero frequency. So the static susceptibility may be expressed as the zero-time value of the real part of the susceptibility:

$$\chi_0 = \chi'(\omega \rightarrow 0). \quad (5.4.83)$$

Now the zero-frequency value of  $\chi'$  may be found from the Kramers-Kronig relation:

$$\chi_0 = \frac{1}{\pi} \int_{-\infty}^{\infty} \frac{\chi''(\omega)}{\omega} d\omega. \quad (5.4.84)$$

This is the basis of resonance methods used to measure very small static susceptibilities in terms of power absorption. Observe that there is no need to take the principal part of the integral as  $\chi''$  vanishes (sufficiently fast) at  $\omega = 0$ , so that there is no pole in the integral.

We conclude this section by making connection between the generalized susceptibility discussed here and the magnetic susceptibility treated in Chapter 2. The magnetic susceptibility is defined, in the SI system of units, as the ratio of the magnetization per unit volume to the applied magnetic  $H$  field. It is not our place here to discuss the rights and wrongs of this definition. But we note two points that follow. Firstly, since it is magnetization *per unit volume*, this is an intensive quantity. The magnetic field is an intensive quantity and this means that the magnetic susceptibility is *intensive*. Secondly, since the magnetization per unit volume and the  $H$  field have the same dimensions, this means that the magnetic susceptibility is dimensionless. These are the consequences of the SI definition of electromagnetic units. Now let us look at the generalized susceptibility of this chapter, in the magnetic case. The response here is the total magnetization – an extensive quantity. The magnetic field is intensive so this means that the generalized susceptibility is *extensive*. And here the appropriate magnetic field is the  $B$  field, to ensure the product of the excitation and the response has the dimensions of energy. We then conclude that the electromagnetic susceptibility and the generalized susceptibility are related by

$$\chi_{\text{gen}} = \frac{V}{\mu_0} \chi_{\text{em}}. \quad (5.4.85)$$



In Chapter 2 we found the Curie law static magnetic susceptibility of an assembly of  $N$  magnetic moments  $\mu$ . We can now recast the results expressed in Eq. (2.9.12) as the generalized static susceptibility of this chapter, using Eq. (5.4.85). The result is

$$\chi_0 = \frac{N}{kT} \mu^2 = \frac{1}{kT} \langle M^2 \rangle. \quad (5.4.86)$$

### 5.4.12 Relaxation time approximation

The memory of a system to a disturbance is most directly specified in the step response function,  $\Phi(t)$ , schematically displayed in Fig. 5.13. This is a decaying function and the more rapidly it decays, the less memory the system has of distantly occurring excitations. Indeed the characteristic time of this relaxation may be regarded as the “memory time” of the system. Subsequent discussion will relate the step response function to the autocorrelation function of the response variable. Thus the memory time is also the correlation time, introduced in Section 5.1.4.

It is often observed that the relaxation of the step response function follows (at least approximately) a decaying exponential

$$\Phi(t) = \chi_0 e^{-t/\tau}; \quad (5.4.87)$$

we write the  $\chi_0$  pre-factor since we know that the zero-time value of the step response function is the static susceptibility. In this section we shall explore the consequences of this exponential form.

The dynamical response function is minus the derivative of  $\Phi(t)$ .

$$X = \chi_0 \frac{1}{\tau} e^{-t/\tau} \quad (5.4.88)$$

And the frequency domain susceptibility is given by the Fourier transform. Thus

$$\chi(\omega) = \frac{\chi_0}{1 - i\omega\tau}, \quad (5.4.89)$$

its real and imaginary parts being given by

$$\chi'(\omega) = \chi_0 \frac{1}{1 + \omega^2\tau^2} \quad (5.4.90)$$

$$\chi''(\omega) = \chi_0 \frac{\omega\tau}{1 + \omega^2\tau^2}$$

It is these functions that are plotted in Fig. 5.14.

This is often called the Debye form for the dynamical susceptibility. The electric susceptibility of many dielectrics follows this form to a *reasonable* extent.

## 5.5 Linear Response II – Microscopics

### 5.5.1 Onsager's hypothesis

We have discussed many formal aspects of the dynamical response function  $X(t)$  and its Fourier transform, the dynamical susceptibility  $\chi(\omega)$ . These provide a description for the evolution of a system from a non-equilibrium state, following a disturbance and they also give the energy dissipation under the application of a such disturbance. The formalism is quite elegant, but it does not tell us how to calculate any of these things from microscopic first principles. In this respect it is more properly of the nature of thermodynamics rather than of statistical mechanics.

It is possible to calculate such response functions from microscopic first principles, certainly in the linear régime, using statistical-mechanical perturbation theory. However such techniques are fairly complicated; they require methods beyond the scope of this book. The interested reader is referred particularly to the works of Ryogo Kubo [9]. We shall give a flavour of these methods in Sections 5.5.3 and 5.5.4 below.

Fortunately there is another way, perhaps a more intuitive way, of tackling the question; this was pioneered by Lars Onsager. Imagine looking at the equilibrium fluctuations in a system, perhaps observing through a microscope the fluctuations in a fluid. The observed quantity will vary in some random way about its mean value. Sometimes there will be small excursions and sometimes, large excursions from the mean. These excursions return, on the average, to the mean value. Now consider that someone has applied a disturbance to this system, driving it from equilibrium, and then the disturbance is removed. The system will then return to its equilibrium state. Through our microscope we would see the observed quantity fluctuating while it returns, on average, to its equilibrium value. Onsager made the remarkable hypothesis [10] that one would not be able to distinguish between he two situations. In other words he assumed that the relaxation of a system following a disturbance is the same as the average regression of a fluctuation in an equilibrium system.

This is indeed remarkable. It says that the behaviour of a *non-equilibrium* system may be understood by studying the properties of the corresponding *equilibrium* system. Alternatively, one may say that at the *microscopic* level there is no distinction between equilibrium and non-equilibrium. But then, of course, equilibrium is a thoroughly *macroscopic* concept.

The point, for us, is that we already know the average way fluctuations in an equilibrium system regress towards the mean. This is given by the autocorrelation function of the fluctuating quantity,  $\langle M(0)M(t) \rangle$ , discussed

and explained in Section 5.1.2 and 5.1.3. The relaxation following the removal of a disturbance is described by the step response function  $\Phi(t)$ . Thus Onsager's hypothesis may be expressed as

$$\Phi(t) = \beta \langle M(0)M(t) \rangle \quad (5.5.1)$$

where  $\beta$  is a constant to be determined. From the considerations of Section 5.4.8 we know that  $\beta$  has the dimensions of inverse energy.

A full microscopic calculation is needed to determine the value of  $\beta$ . For inspiration we shall look at the zero-time value of Eq. (5.5.1). Since  $\Phi(0)$  is equal to the static susceptibility  $\chi_0$ , we have

$$\chi_0 = \beta \langle M^2 \rangle. \quad (5.5.2)$$

Compare this with the magnetic case, expressed in Eq. (5.4.86). We are thus led to identify  $\beta$  with  $1/kT$ . It is *plausible* that this result is more generally applicable; we assert that it is.

The equation for the step response function

$$\Phi(t) = \frac{1}{kT} \langle M(0)M(t) \rangle, \quad (5.5.3)$$

or, equivalently for the dynamical response function

$$X(t) = -\frac{1}{kT} \frac{d}{dt} \langle M(0)M(t) \rangle \quad (5.5.4)$$

is indeed the correct *classical* result, as could be derived using statistical-mechanical perturbation theory. A quantum-mechanical calculation gives a more complicated temperature dependence, which reduces to the above expression in the high temperature limit. The  $kT$  factor is essentially a reflection of equipartition.

The dynamical susceptibility is then found from the Fourier transform of  $X(t)$ :

$$\chi(\omega) = -\frac{1}{kT} \int_0^{\infty} \langle M(0)\dot{M}(t) \rangle e^{i\omega t} dt \quad (5.5.5)$$

or, upon integration by parts

$$\chi(\omega) = \chi_0 + \frac{i\omega}{kT} \int_0^{\infty} \langle M(0)M(t) \rangle e^{i\omega t} dt. \quad (5.5.6)$$

This shows how the dynamical susceptibility depends on the autocorrelation function of the equilibrium fluctuations in the response variable.

### 5.5.2 Nyquist's Theorem

As early as 1906, Einstein [11] predicted that the random motion of charge carriers in a conductor would lead to fluctuations of voltage or current in any system in thermal equilibrium. This was first observed by Johnson [12] and subsequently explained theoretically by Nyquist [13], who calculated the power spectrum of the fluctuations.

In order to frame this treatment within the discussion of the previous sections, the generalized force will now be taken as the applied voltage  $V$  and the generalized response will be the electric charge  $Q$ . Then the linear response relation between these two will be

$$Q(t) = \int X(t - \tau) V(\tau) d\tau \quad (5.5.7)$$

or, in the frequency domain

$$q(\omega) = \chi(\omega) v(\omega). \quad (5.5.8)$$

Thus in electrical terms we identify the generalized susceptibility in this case as a frequency-dependent capacitance. Then the imaginary part of this will be related to the conductance and thus to the dissipation. Recall we saw in Section 5.4.8 that the imaginary part of the generalized susceptibility was connected with dissipation.

The admittance  $Y(\omega)$  is given by  $i\omega$  multiplied by the capacitance, so that from Eq. (5.5.5), this is

$$Y(\omega) = -\frac{i\omega}{kT} \int_0^{\infty} \langle Q(0) \dot{Q}(t) \rangle e^{i\omega t} dt. \quad (5.5.9)$$

Note, here, that  $\dot{Q}(t)$  is the electric current  $I(t)$ . Let us integrate the above equation by parts in such a way as to differentiate the other  $Q$ . This will give

$$Y(\omega) = \frac{1}{kT} \int_0^{\infty} \langle I(0) I(t) \rangle e^{i\omega t} dt. \quad (5.5.10)$$

This result tells us that the electrical admittance of an object is related to the equilibrium current fluctuations in it. Indeed we can decompose the admittance into its real and imaginary parts: the conductance  $G$  and the susceptance  $S$

$$Y(\omega) = G(\omega) + iS(\omega) \quad (5.5.11)$$

so that

$$G(\omega) = \frac{1}{kT} \int_0^{\infty} \langle I(0)I(t) \rangle \cos \omega t \, dt$$

$$S(\omega) = \frac{1}{kT} \int_0^{\infty} \langle I(0)I(t) \rangle \sin \omega t \, dt.$$
(5.5.12)

The expression for  $G(\omega)$  is a generalization of Eq. (5.3.51) derived through the Langevin equation discussion.

Nyquist's result follows from inverting the expression for the conductance  $G(\omega)$ .

$$\langle I(0)I(t) \rangle = kT \frac{2}{\pi} \int_0^{\infty} G(\omega) \cos \omega t \, d\omega$$
(5.5.13)

If we now let  $t$  tend to zero, then we obtain the mean square value for the current fluctuations

$$\langle I^2 \rangle = \frac{2kT}{\pi} \int_{-\infty}^{\infty} G(\omega) \, d\omega.$$
(5.5.14)

Thus in a frequency band  $\Delta f = \Delta\omega/2\pi$ , there will be a contribution to the mean square current of

$$\langle I^2 \rangle_{\Delta f} = 4kTG\Delta f.$$
(5.5.15)

Alternatively, in a resistance of  $R = 1/G$ , there will be mean square voltage fluctuations of

$$\langle V^2 \rangle_{\Delta f} = 4kTR\Delta f.$$
(5.5.16)

This so-called ‘‘Johnson noise’’ is commonly heard as the hiss from the speakers of a hi-fi amplifier when there is no signal output.

We first encountered Johnson noise as the thermal equilibrium black body radiation in the (one-dimensional) terminated transmission line, in Section 2.8.5. That treatment obtained the full quantum-mechanical result, of which Eqs. (5.5.15) and (5.5.16) are the high temperature / equipartition limit. We then saw it from the perspective of the electrical analogue of the Langevin equation, in Section 5.3.9.

### 5.5.3 Calculation of the step response function

We introduced the step response function in Section 5.4.4. We imagined a constant excitation  $B = b$  to have been applied back into the past, and we

remove this at time  $t = 0$ . For negative times the response  $M(t)$  will be a constant. And interest focuses on how  $M(t)$  relaxes to its new equilibrium value when  $B$  drops to zero.

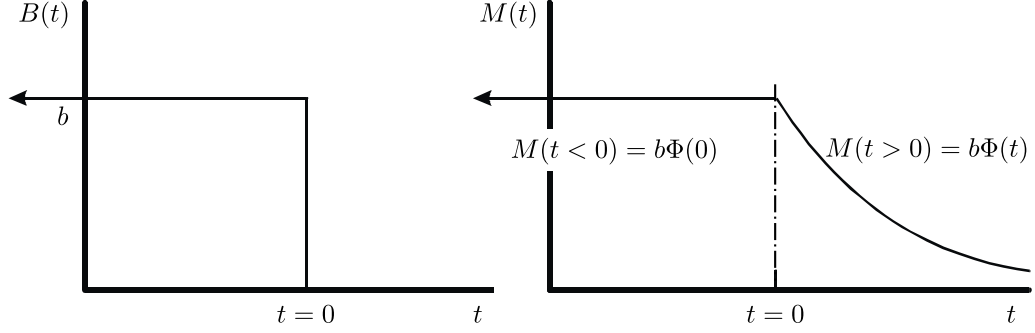


Figure 5.16: Step response

The step response function  $\Phi(t)$  is then defined, for  $t > 0$ , as

$$\Phi(t) = \frac{1}{b}M(t). \quad (5.5.17)$$

And the question is then to (try to) calculate this from first principles. In this section we shall show how  $\Phi(t)$  is related to the autocorrelation function of  $M(t)$ , obtaining the Onsager expression. By no means can the derivation be regarded as rigorous, but it is hoped that the flavour of the procedure will be appreciated. The question of how the autocorrelation function may be calculated will be considered in the following section.

The mean value of the response  $M(t)$  is found by evaluating the average, weighted by the appropriate Boltzmann factor:

$$\langle M \rangle = \frac{1}{Z} \sum_i M_i e^{-E_i/kT}. \quad (5.5.18)$$

Now the system has been *prepared* by applying the “field”  $b$  for negative times. This has the effect of altering the energy levels by adding the term  $bM_i$ . Then in calculating the mean values we must use the appropriately-modified Boltzmann factor

$$\langle M \rangle = \frac{1}{Z} \sum_i M_i e^{-(E_i + bM_i)/kT}. \quad (5.5.19)$$

The point about *linear* response is that we take the excitation  $b$  to be very small. In this case we can make the approximation

$$e^{-(E_i + bM_i)/kT} \sim e^{-E_i/kT} (1 + bM_i/kT) \quad (5.5.20)$$

and then

$$\langle M \rangle = \frac{1}{Z} \sum_i M_i e^{-E_i/kT} + \frac{b}{kT} \frac{1}{Z} \sum_i M_i(0) M_i(t) e^{-E_i/kT}. \quad (5.5.21)$$

The first term is the equilibrium value of  $M$  in the *absence* of the applied field; this will be zero. The second term may be written as an average over the equilibrium ensemble, and then

$$\langle M(t) \rangle = \frac{b}{kT} \langle M(0)M(t) \rangle. \quad (5.5.22)$$

So the step response function is

$$\Phi = \frac{1}{kT} \langle M(0)M(t) \rangle, \quad (5.5.23)$$

as we proposed in Section 5.5.1.

The important point about this result – we have mentioned it before but it is worth repeating it – is that the relaxation from a non-equilibrium state is expressed in terms of the fluctuations in the equilibrium state.

### 5.5.4 Calculation of the autocorrelation function

The calculation of the dynamical susceptibility from microscopic first principles is clearly a very difficult problem. As with our introductory discussion of the foundations of statistical mechanics, some sort of statistical treatment will be needed to solve any real problem. Moreover, almost all calculational procedures will involve the use of approximations.

There are some general methods of approach, often using a Boltzmann equation, to calculate the evolution of a system in phase space from specified initial conditions. Unfortunately this is beyond the scope of this book. However we note that the discussions of Section 5.4. impose various constraints on any autocorrelation function so-calculated. In terms of the dynamical susceptibility  $X(t)$  and its Fourier transform, the frequency-dependent susceptibility  $\chi(\omega)$ , we know that:

1. causality places restrictions on the relationship between the real part  $\chi'(\omega)$  and the imaginary part  $\chi''(\omega)$ ;
2. energy considerations restrict  $\chi''(\omega)$  to be positive for all (positive) frequencies;
3. the reality of  $X(t)$  requires that  $\chi''(0)$  be zero;

4. causality and microscopic reversibility require that the first derivative  $X'(0)$  be zero; the reason for this is explored in Problem 5.3.

So any approximately calculated susceptibility must satisfy these requirements.

Hydrodynamic considerations will often give further information; the long-time behaviour of  $X(t)$  and the low-frequency behaviour of  $\chi(\omega)$  will thereby have further constraints imposed upon them. The way in which such hydrodynamic constraints may be incorporated into the description of correlation functions has been extensively explored by Kadanoff and Martin [14].

In a very few cases a full quantum-mechanical description of the dynamics might be appropriate. Spin diffusion in a paramagnet is a classical example of this [15]. It is then possible to calculate the short-time behaviour of  $X(t)$  as a power series in time. Higher-order derivatives become increasingly difficult to evaluate, but knowledge of the first few derivatives may be combined with long-time hydrodynamic information through the use of an appropriate interpolation procedure. The reader is referred to the author's book on Nuclear Magnetic Resonance [16], particularly the section dealing with solid  $^3\text{He}$ , for further details. Section 6.3.7 of that book shows also how short-time expansions actually place constraints on the behaviour of the correlation functions at long times.