Chapter 5 Fluctuations and Dynamics

1.4.5 (Energy) Fluctuations

- Isolated system – fixed energy – temperature fluctuates
- System + heat bath – fixed temperature – energy fluctuates

Calculate the *average* energy:

$$\langle E \rangle = kT^2 \left. \frac{\partial \ln Z}{\partial T} \right|_{V,N} = \frac{1}{Z} \sum_i E_i e^{-E_i/kT} = \sum_i E_i p_i$$

but the *instantaneous* energy in the system will *fluctuate*.

- Magnitude of the fluctuations ???

MacDonald: Noise & Fluctuations
Uhlenbeck & Ornstein 1930
Wang & Uhlenbeck 1945
Wax: Dover reprint

- Magnitude of the fluctuations ???

RMS (root mean square) of the energy fluctuations σ_E, defined by

$$\sigma_E = \left\langle \left(E - \langle E \rangle \right)^2 \right\rangle^{1/2} . \qquad (1.36)$$

By expanding this out we obtain

$$\begin{aligned} \sigma_E^2 &= \langle E^2 \rangle - 2\langle E \rangle^2 + \langle E \rangle^2 \\ &= \langle E^2 \rangle - \langle E \rangle^2 . \end{aligned} \qquad (1.37)$$

So we need these two ↑ ↑

Use the "β trick" (twice) where $\beta = 1/kT$.

Start from the expression for $\langle E \rangle$ as

$$\langle E \rangle = \frac{1}{Z}\sum_j E_j e^{-\beta E_j} = -\frac{1}{Z}\frac{\partial}{\partial\beta}\sum_j e^{-\beta E_j} \quad \text{so} \quad Z\langle E \rangle = -\frac{\partial Z}{\partial\beta}.$$

Get at $\langle E^2 \rangle$ by differentiating with respect to β *again*

$$\langle E^2 \rangle = \frac{1}{Z}\sum_j E_j^2 e^{-\beta E_j} = \frac{1}{Z}\frac{\partial^2}{\partial\beta^2}\sum_j e^{-\beta E_j} \quad \text{so} \quad Z\langle E^2 \rangle = \frac{\partial^2 Z}{\partial\beta^2}.$$

so that *another* E_j comes down in the sum.

Evaluate the *second* derivative:

$$\frac{\partial^2 Z}{\partial \beta^2} = \frac{\partial}{\partial \beta}\left(-Z\langle E\rangle\right) = -\frac{\partial Z}{\partial \beta}\langle E\rangle - Z\frac{\partial \langle E\rangle}{\partial \beta} = Z\langle E\rangle^2 - Z\frac{\partial \langle E\rangle}{\partial \beta}$$

so that

$$\frac{1}{Z}\frac{\partial^2 Z}{\partial \beta^2} = \langle E\rangle^2 - \frac{\partial \langle E\rangle}{\partial \beta}.$$

This is $\langle E^2\rangle$, so that

$$\langle E^2\rangle = \langle E\rangle^2 - \frac{\partial \langle E\rangle}{\partial \beta}.$$

This means

$$\sigma_E^2 = -\frac{\partial \langle E\rangle}{\partial \beta}.$$

Now convert from β back to $1/kT$:

$$\frac{\partial}{\partial\beta} = \frac{\partial}{\partial T} \Big/ \frac{\mathrm{d}\beta}{\mathrm{d}T} \quad \text{and} \quad \frac{\mathrm{d}\beta}{\mathrm{d}T} = -1/kT^2,$$

or

$$\sigma_E^2 = kT^2 \frac{\partial \langle E \rangle}{\partial T} = kT^2 C_V$$

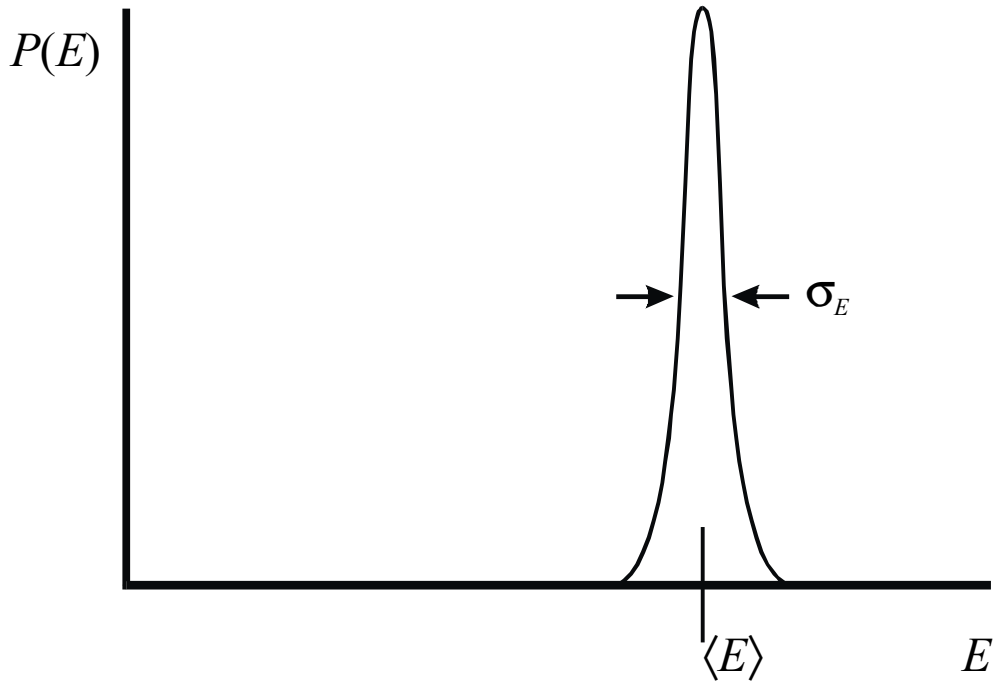
Thus the RMS variation in the energy is given by

$$\sigma_E = \sqrt{kT^2 C_V}\,. \tag{1.40}$$

Since C_V and $\langle E \rangle$ are both proportional to the number of particles in the system, the *fractional* fluctuations in energy vary as

$$\frac{\sigma_E}{\langle E \rangle} \sim \frac{1}{\sqrt{N}} \tag{1.41}$$

This gets smaller and smaller as N increases.



We thus see that the importance of fluctuations vanishes in the thermodynamic limit $N \to \infty$, $V \to \infty$ N/V remains constant. And it is in this limit that statistical mechanics has its greatest applicability.

Chapter 5 Fluctuations and Dynamics

5.1 (General) fluctuations

5.1.1 Probability distribution functions

When a thermodynamic property is fixed its conjugate fluctuates.

- When temperature is fixed, energy fluctuates.
- In ‘small region’ all extensive variables will fluctuate.

‘Small region’ is subsystem in equilibrium with a reservoir comprising the rest of the system. Conditions of the equilibrium: all *intensive* variables are fixed: temperature, pressure, chemical potential etc.

Must consider the appropriate thermodynamic potential:

- Gibbs free energy $G(T, p, \mu)$, since T, p, and μ are fixed.

Question: What is probability of occurrence of a fluctuation X ?

Isolated system: invert Boltzmann relation $S = k\ln\Omega$, to give the probability of observing a fluctuation of magnitude X as

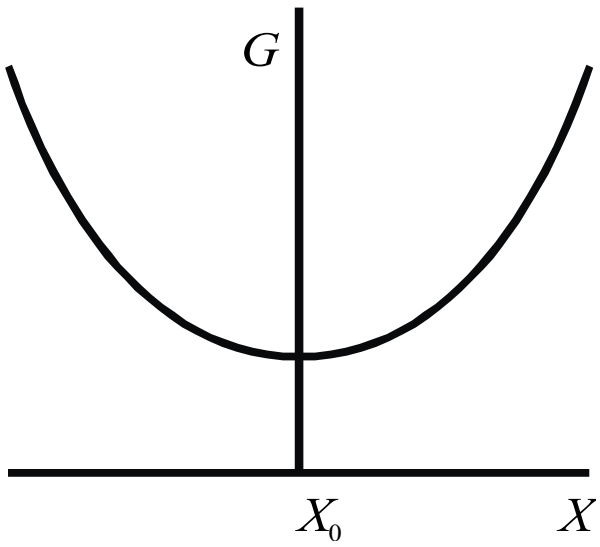
$$P(X) \propto e^{S(X)/k}. \tag{5.1}$$

Open system: probability of a fluctuation of magnitude X is then

$$P(X) \propto e^{-G(X)/kT}. \tag{5.2}$$

(Probability is $P(X) \propto e^{S(X)/k}$ where $S(X)$ is the *total* entropy: system *plus* reservoir. It becomes $P(X) \propto e^{-G(X)/kT}$ where $G(X)$ is the Gibbs free energy of the system.)

In equilibrium G is a minimum.



Here X could be a general extensive variable or an order parameter of a phase transition. For convenience we shall put $X_0 = 0$ so that the variable X measures the *deviation* from the mean (equilibrium) value.

For small deviations of X from its equilibrium value we may write

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

- minimum: the linear term vanishes. So leading term is thus *quadratic*. To leading order in X the probability is then

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

or

$$P(X) \propto e^{-G''(0)X^2/2kT} . \qquad (5.3)$$

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

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

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

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

$$\langle X^2 \rangle = kT \left(\left. \frac{\partial^2 G}{\partial X^2} \right|_{X=X_0} \right)^{-1} \tag{5.4}$$

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 $G'' \rightarrow 0$ (anomalous flattening) 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 Mean behaviour of fluctuations

Moments $\langle X^n \rangle$ give 'static' information about fluctuations.

But what about dynamical information – time dependence?

-- Averages are problematic!!

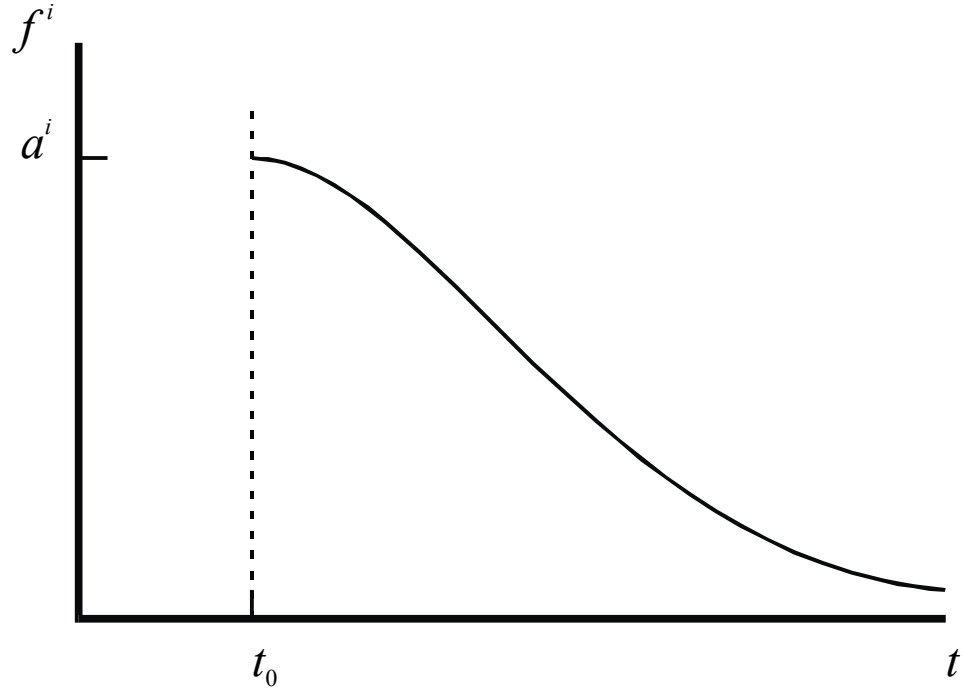


Fig. 5.2 *Mean regression of a random fluctuation from an initial value*

This function describes “on the average” how X varies if at time t_0 it had the value a^i.

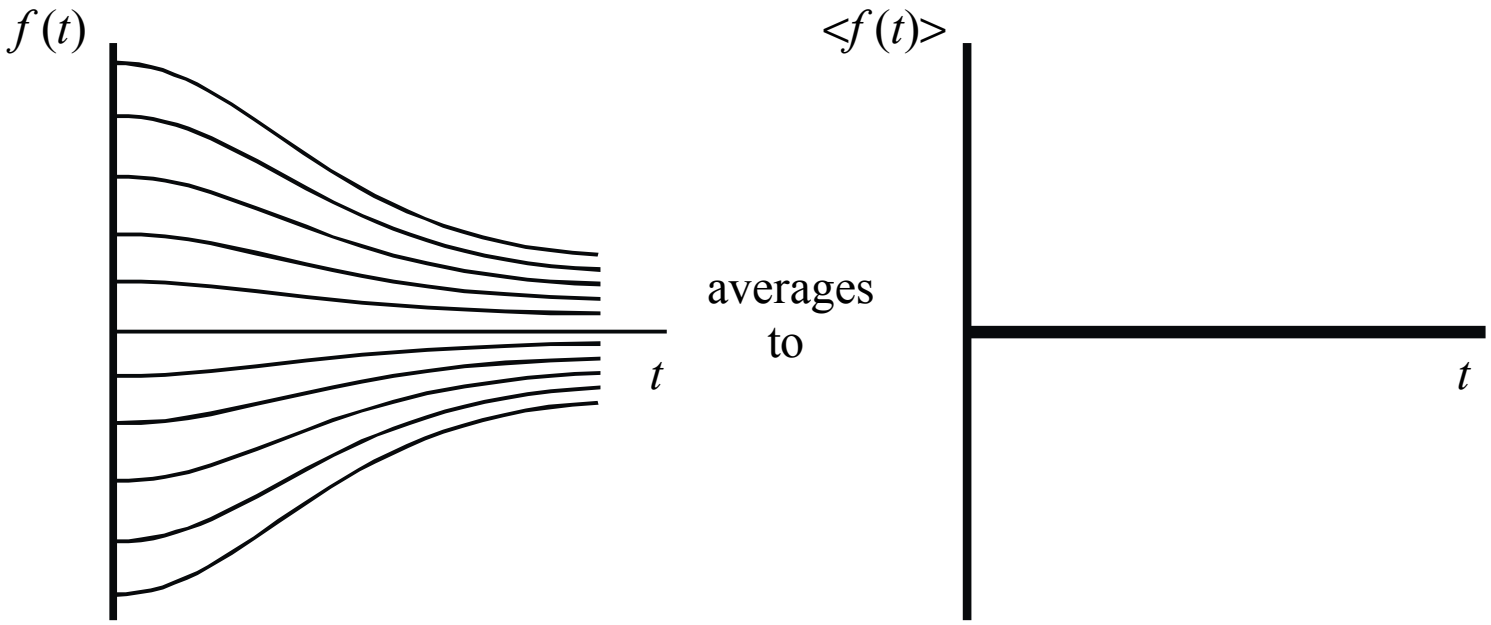


Fig. 5.3 *Average behaviour of many different initial states*

Possible averaging procedures

1. Average the squares of the fluctuations

2. Average the *magnitude* of fluctuations (weight function ±1)

3. Average using a clever weight function.
   - weight with initial value:

$$\langle X(0)X(t)\rangle .$$

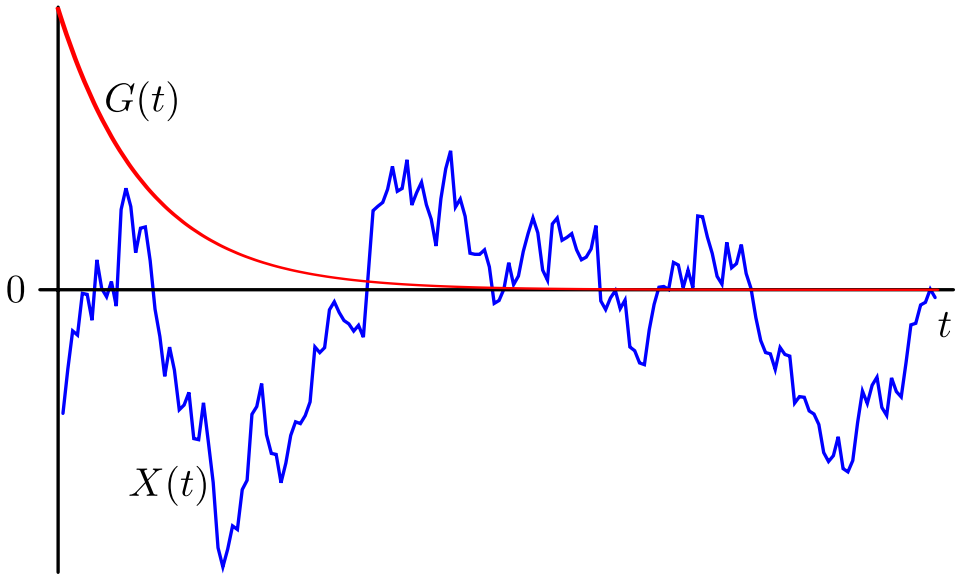
This is our preferred expression for the "average" regression of a fluctuation from some initial value back to the mean.

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 $G(t)$:

$$G(t) = \langle X(0)X(t) \rangle . \tag{5.5}$$

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 mass of unimportant fine detail.



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

$$G(0) = \langle X^2 \rangle \tag{5.6}$$

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

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

$$\left\langle X(\tau)X(t+\tau)\right\rangle = \left\langle X(0)X(t)\right\rangle .$$

i.e. equilibrium $\Rightarrow$ stationarity.

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

$$\left\langle X(-\tau)X(0)\right\rangle = \left\langle X(0)X(\tau)\right\rangle$$

but classically the *X* commute, so that

$$\left\langle X(-\tau)X(0)\right\rangle = \left\langle X(\tau)X(0)\right\rangle$$

or

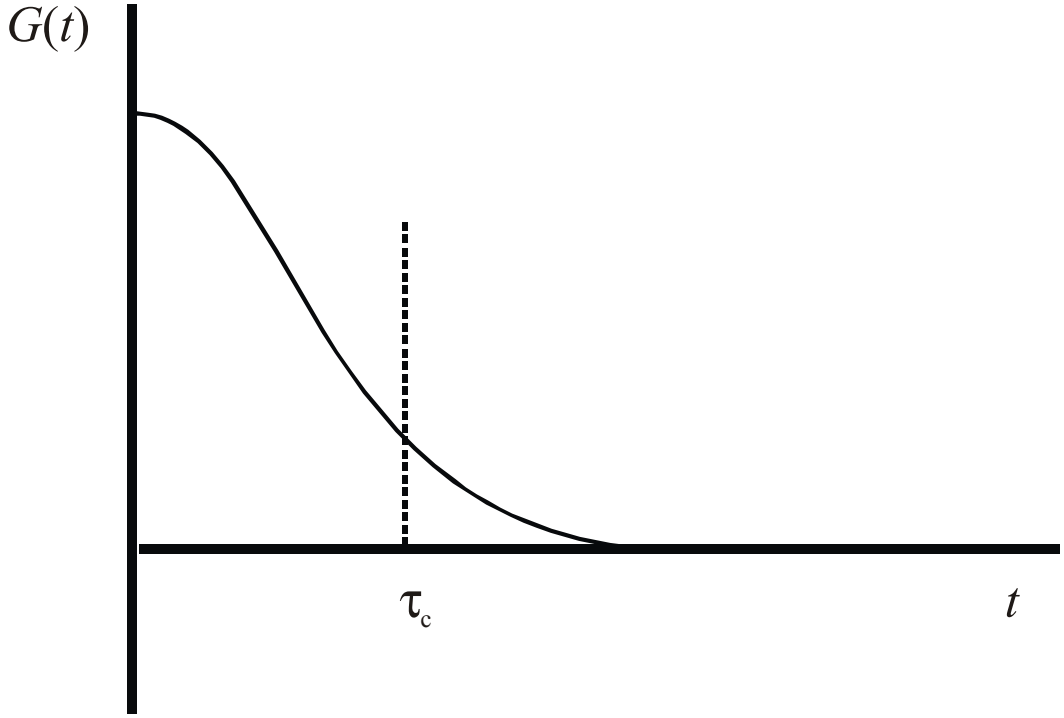
$$G(t) = G(-t). \qquad (5.7)$$

5.1.4 The correlation time

The correlation function indicates the time scale of the variations of the random variable. Quantify this by introducing a *correlation time* τ_c

$$G(t) \approx G(0) \qquad t << \tau_c$$

$$G(t) \approx 0 \qquad t >> \tau_c$$



The correlation time is a 'rough measure' of the width of the correlation function. Now a rough measure of 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

$$\int_0^\infty G(t)\,\mathrm{d}t = \tau_c G(0)$$

or

$$\tau_c = \frac{1}{G(0)}\int_0^\infty G(t)\,\mathrm{d}t \,. \qquad (5.8)$$

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

5.5 Relaxation to equilibrium

5.5.1 Onsager's hypothesis

- How does a non-equilibrium system relax to its equilibrium state?
  — time variation, time scale etc.
- This is outside the framework of "equilibrium" Statistical Mechanics.
- Once again we will use "clever arguments" to extend the applicability of SM.
- Original formulation was a *hypothesis* of Onsager.
- But now justified from *microscopic first principles*. (linear response theory)

Two scenarios:

1. Look at the *equilibrium fluctuations* in a system (perhaps through a microscope). The observed quantity (perhaps density) will vary randomly 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.

2. Apply a disturbance to this system, driving it from equilibrium. Then remove the disturbance. The system will then return to equilibrium. The observed quantity will fluctuate while — on average, returning to its mean (equilibrium) value.

Onsager made the remarkable hypothesis that one would not be able to distinguish between the two situations.

Onsager's hypothesis: The relaxation of a system following a disturbance is the same as the average regression of a fluctuation in an equilibrium system.

- The behaviour of a *non-equilibrium* system may be understood by studying the properties of the corresponding *equilibrium* system.
- At the *microscopic* level there is no distinction between equilibrium and non-equilibrium. But then, of course, equilibrium is a thoroughly *macroscopic* concept.
- A large excursion in an *equilibrium* system is indistinguishable from an imposed excursion in a *non-equilibrium* system.

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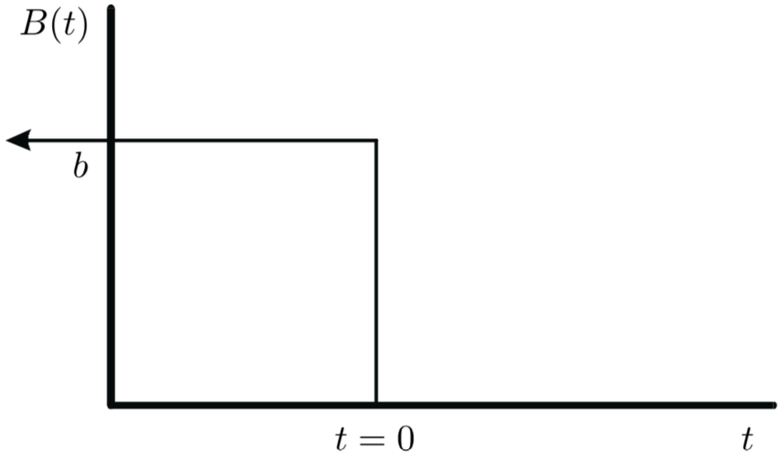
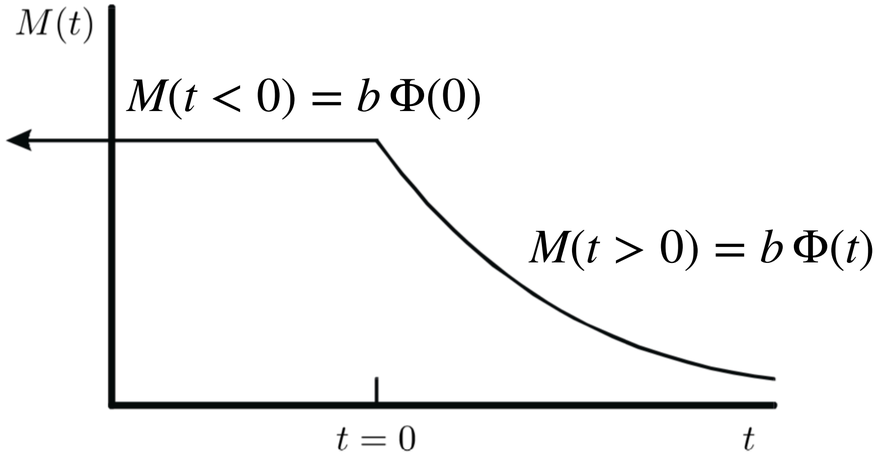
Relaxation of a non-equilibrium system to equilibrium.

(Use M, B variables — measure M from its equilibrium value)

- System is “held” in a non-equilibrium state by applying a “force” b.
- This non-equilibrium “displacement” will be denoted by $M(0)$.
- The “force” B is removed — then M relaxes from $M(0)$ to zero.





Relaxation function $\Phi(t)$:

$$M(t) = b\,\Phi(t) \quad \text{when } t > 0$$

($M(t)$ and $M(0)$ are "macroscopic/hydrodynamic" quantities)

Onsager's hypothesis $\Longrightarrow \Phi(t) \propto \langle m(0)\, m(t)\rangle$. ($m$ is microscopic/instantaneous)

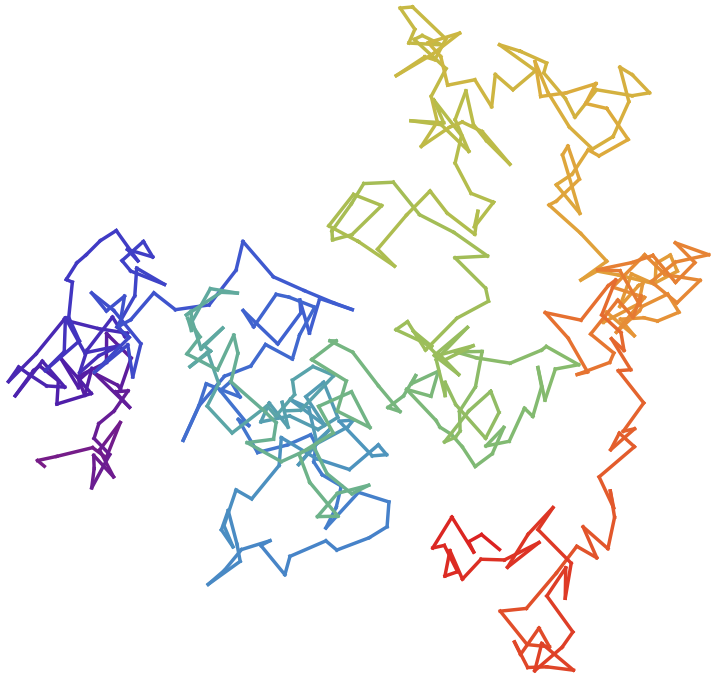
Include constant of proportionality: $\Phi(t) = \dfrac{1}{kT}\langle m(0)\, m(t)\rangle$.

The pre-factor comes from equipartition/microscopic calculation (linear response).

- This is a simplified version of the treatment in the book.

5.2 Brownian Motion

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



5.2.1 Kinematics of a Brownian particle

(Brownian particle in one dimension) Kinematics!!

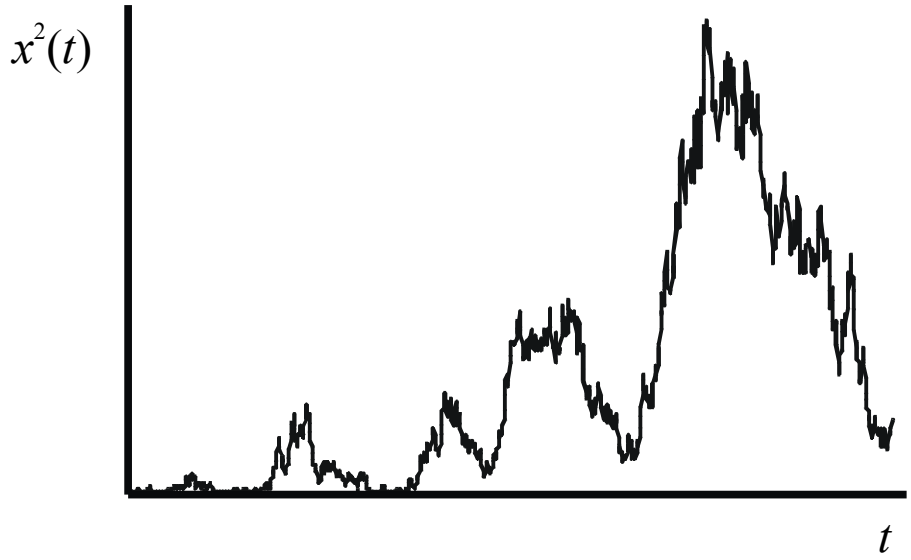


Fig. 5.8 Typical squared displacement of Brownian particle

The distance travelled by the Brownian particle in a time t may be found by integrating up its velocity:

$$x(t)=\int_0^t v(\tau)\mathrm{d}\tau \ .$$

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

The square of the displacement is then

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

so the mean square displacement is

$$\left\langle x^2(t)\right\rangle = \int_0^t \mathrm{d}\tau_1 \int_0^t \mathrm{d}\tau_2 \left\langle v(\tau_1) v(\tau_2)\right\rangle .$$

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

$$G_v(\tau_1 - \tau_2) = \left\langle v(\tau_1) v(\tau_2)\right\rangle$$

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

$$\tau = \tau_1 - \tau_2$$

$$T = \tau_1 + \tau_2$$

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

$$\left\langle x^2(t) \right\rangle = 2\int_0^t (t-\tau) G_v(\tau) \mathrm{d}\tau \,. \qquad (5.9)$$

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

Two limiting cases – still kinematics

5.2.2 Short time limit

The natural time scale for the process is the velocity correlation time, which we shall denote by τ_v. Recall we have the definition, Eq. (5.8):

$$\tau_v = \frac{1}{G_v(0)} \int_0^\infty G_v(t)\,\mathrm{d}t \,.$$

More particularly, we have the statement that

$$G_v(t) \approx G_v(0) \qquad t << \tau_v \,.$$

So when we consider times much shorter than τ_v, we may replace $G_v(t)$ by $G_v(0)$ in the integral expression for $\langle x^2(t)\rangle$. But in this case $G_v(0)$ comes out of the integral and we have

$$\left\langle x^2(t)\right\rangle = 2G_v(0)\int_0^t (t-\tau)\,\mathrm{d}\tau \,.$$

Now the integral may be evaluated simply, giving

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

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

$$\left\langle x^2(t)\right\rangle = \left\langle v^2\right\rangle t^2. \tag{5.10}$$

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* regime.

5.2.3 Long time limit

The other statement about the correlation time is

$$G_v(t) \approx 0 \qquad t >> \tau_v ;$$

the autocorrelation function will have decayed to zero at long times. So when we consider times much longer than τ_v, $G_v(t)$ will be zero and in the expression for $\langle x^2(t) \rangle$ we will make negligible error by extending the upper limit of the integral to infinity.

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

The integral may be rearranged as

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

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

$$\left\langle x^2(t)\right\rangle = 2t\int_0^\infty G_v(\tau)\,\mathrm{d}\tau \,. \qquad (5.11)$$

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

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

$$\left\langle x^2(t)\right\rangle = 2Dt \qquad (5.12)$$

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

$$D = \int_0^\infty G_v(t)\,\mathrm{d}t$$

or

$$D = \int_0^\infty \langle v(0)v(t)\rangle\,\mathrm{d}t\ .$$

The diffusion coefficient is given by the *area under* the velocity autocorrelation function.

The long time limit, when $t >> \tau_v$, is called the diffusive regime.

Recall that the definition of the correlation time was given in terms of the area under the autocorrelation function, Eq. (5.8):

$$\tau_v = \frac{1}{G_v(0)} \int_0^\infty G_v(t)\,\mathrm{d}t \,.$$

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

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

or

$$D = \langle v^2 \rangle \tau_v \,. \qquad (5.13)$$

Again we re-emphasise 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.

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. Since it is in thermal equilibrium with a bath at a temperature T the equipartition theorem tells us that

$$\frac{1}{2} M \langle v^2 \rangle = \frac{1}{2} kT \tag{5.14}$$

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

$$\langle v^2 \rangle = \frac{kT}{M} . \tag{5.15}$$

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 thermal equilibrium is established.

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

$$D = \frac{kT}{M}\tau_v . \qquad (5.16)$$

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 τ_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 examining the *dynamics* of Brownian motion was initiated by Langevin in 1908. Langevin wrote down an equation of motion for the Brownian particle. Essentially this was an equation of the form $F = ma$, but Langevin's important contribution was in the way he viewed the force acting on the Brownian particle. Our treatment is inspired by the papers of Uhlenbeck and Ornstein, and Wang and Uhlenbeck.

Langevin wrote the force acting on the particle as

$$F(t) = f(t) - \frac{1}{\mu} v \,. \tag{5.17}$$

He regarded the force $F(t)$ 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. The constant μ 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 a body moving in a fluid is known to experience friction.

The Langevin equation is written

$$M\frac{\mathrm{d}v(t)}{\mathrm{d}t} = f(t) - \frac{1}{\mu}v(t) \qquad (5.18)$$

and this must be solved for the velocity $v(t)$.

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

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

k

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.

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 on the particle in opposition to its motion.

We can see this from a simple model. 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.

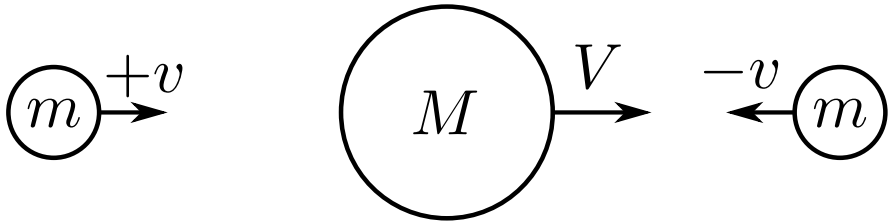


Fig. 5.9 Bombardment of Brownian particle

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

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

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

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

The net momentum transfer is the difference between these

$$\Delta p = -4mV.$$

The net momentum transfer is the difference between these

$$\Delta p = -4mV .$$

Then if there are *n* impacts per unit time the net force on the Brownian particle will be

$$-4nmV .$$

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 proportional to *V*.

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

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

and we see that the mobility μ 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

$$M\frac{\mathrm{d}v(t)}{\mathrm{d}t}+\frac{1}{\mu}v(t)=f(t), \tag{5.19}$$

which emphasises 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

$$A(t)=\frac{f(t)}{M}$$

$$\gamma=\frac{1}{M\mu}.$$

Then the Langevin equation becomes

$$\frac{\mathrm{d}v(t)}{\mathrm{d}t}+\gamma v(t)=A(t).$$

This has solution

$$v(t)=v(0)e^{-\gamma t}+\int_0^t e^{\gamma(u-t)}A(u)\mathrm{d}u.$$

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 $A(t)$. These are listed as

1 $\langle A(t) \rangle = 0$. 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 'almost identical with' t_2. We understand this to mean that the correlation time of the random force is short.

3 $\langle A^2(t) \rangle$ has some definite value (independent of t).

We may develop property 2 by *approximating*

$$\left\langle A\left(t_1\right)A\left(t_2\right)\right\rangle = A^2\delta\left(t_1 - t_2\right). \tag{5.20}$$

If we integrate this we obtain

$$A^2 = \int_{-\infty}^{\infty} \left\langle A(0)\,A(t)\right\rangle \mathrm{d}t \tag{5.21}$$

so that A^2 is the area under the (scaled) random force correlation function.

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

$$\left\langle v\left(t\right)\right\rangle = v\left(0\right)e^{-\gamma t} \tag{5.22}$$

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

m

5.3.4 Mean square velocity and equipartition

By similar arguments we can now examine the mean square velocity. A key result then follows when we exploit the equipartition theorem to relate the equilibrium mean square velocity of the Brownian particle to the temperature of its surrounding medium. The expression for the mean square velocity is

$$\left\langle v^2(t)\right\rangle = v^2(0)e^{-2\gamma t} + 2e^{-2\gamma t}\int_0^t e^{\gamma u}\left\langle v(0)A(u)\right\rangle \mathrm{d}u + e^{-2\gamma t}\int_0^t \mathrm{d}u\int_0^t \mathrm{d}w\, e^{\gamma(u+w)}\left\langle A(u)A(w)\right\rangle .$$

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 $v(0)$ and $A(t)$. The third term is of interest since it describes the equilibrium state of the particle, independent of the initial conditions. In this term we make use of property 2 and approximate the force autocorrelation function by the delta function expression, Eq. (5.20):

$$\left\langle A\left(t_1\right)A\left(t_2\right)\right\rangle = A^2\delta\left(t_1 - t_2\right).$$

This forces $w = u$ when the integral over w is performed. Thus we obtain at long times

$$\begin{aligned}\left\langle v^2\left(t\right)\right\rangle &= A^2 e^{-2\gamma t}\int_0^t \mathrm{d}u e^{2\gamma u} \\ &= \frac{A^2 e^{-2\gamma t}}{2\gamma}\left(e^{2\gamma t} - 1\right) \\ &= \frac{A^2 e^{-2\gamma t}}{2\gamma}\left(1 - e^{-2\gamma t}\right).\end{aligned} \tag{5.23}$$

And in the long time limit this takes on the time-independent value

$$\left\langle v^2\right\rangle = \frac{A^2}{2\gamma}.$$

Equipartition

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

$$\left\langle v^2 \right\rangle = \frac{kT}{M} \tag{5.24}$$

so that

$$\gamma = \frac{M}{2kT} A^2 \tag{5.25}$$

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

$$\frac{1}{\mu} = \frac{1}{2kT} \int_{-\infty}^{\infty} \langle f(0) f(t) \rangle \, \mathrm{d}t \,. \qquad (5.26)$$

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.

5.3.5 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. The calculation of this is only slightly more complicated than that of the mean square velocity. We have

$$\left\langle v(t)v(t+\tau)\right\rangle = v^2(0)e^{-\gamma(2t+\tau)} + e^{-\gamma(2t+\tau)}\int_0^t \mathrm{d}u\int_0^{t+\tau}\mathrm{d}w\, e^{\gamma(u+w)}\left\langle A(u)A(w)\right\rangle$$

where the cross term vanishes, as above. And as discussed above, the first term is of no interest since at long times t the memory of the initial state is lost. The steady-state behaviour is contained in the remaining term. To proceed we use property 2 of the force autocorrelation function and the delta function approximation. This forces $w = u$ when the integral over w is

performed. The calculation is identical to that for the mean square velocity, except for the additional $e^{-\gamma\tau}$ prefactor

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

or

$$G_v\left(t\right) = \left\langle v^2\left(0\right)\right\rangle e^{-\gamma t}. \qquad (5.27)$$

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

$$\tau_v = \gamma^{-1}.$$

We saw that the diffusion coefficient of the Brownian particle was given in terms of τ_v by

$$D = \frac{kT}{M}\tau_v ,$$

which we can now re-express as

$$D = \frac{kT}{M\gamma}$$

or

$$D = \mu kT . \qquad (5.28)$$

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.

5.3.6 Electrical analogue of the Langevin equation

The Langevin equation, Eq. (5.19):

$$M\frac{\mathrm{d}v(t)}{\mathrm{d}t}+\frac{1}{\mu}v(t)=f(t) \qquad\qquad L\frac{dI(t)}{dt}+RI(t)=V(t)$$

describes the velocity $v(t)$ of the Brownian particle of mass M in terms of the mobility μ (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. (5.26).

$$\frac{1}{\mu}=\frac{1}{2kT}\int_{-\infty}^{\infty}\langle f(0)f(t)\rangle\,\mathrm{d}t$$

In this section we shall explore an electrical analogue of this.

Imagine an electrical circuit comprising an inductor of inductance L and a resistor of resistance R. The current I flowing in the circuit results from the motion of a very large number of electrons.

The voltage V across the circuit is given by

$$L\frac{dI(t)}{dt}+RI(t)=V(t). \qquad (5.29)$$

The random motion of the electrons will result in a randomly fluctuating voltage $V(t)$.

The analogue of the fluctuation-dissipation result, Eq. (5.26) gives

$$\frac{1}{\mu}=\frac{1}{2kT}\int_{-\infty}^{\infty}\langle f(0)f(t)\rangle\,\mathrm{d}t \quad \Rightarrow \quad R=\frac{1}{2kT}\int_{-\infty}^{\infty}\langle V(0)V(t)\rangle\,\mathrm{d}t$$

This shows how the resistance (dissipation) is related to the fluctuations of voltage.

$$\langle V^2\rangle_{\Delta f}=4kTR\Delta f\,.$$

Frequency domain
Johnson noise
Nyquist theorem