1

Brownian Motion and Langevin Equations

1.1 Langevin Equation and the Fluctuation-Dissipation Theorem

The theory of Brownian motion is perhaps the simplest approximate way to treat the dynamics of nonequilibrium systems. The fundamental equation is called the Langevin equation; it contains both frictional forces and random forces. The fluctuation-dissipation theorem relates these forces to each other. This theorem has many important and far-reaching generalizations. For the present, we focus on the most elementary version of the theorem.

The random motion of a small particle immersed in a fluid is called *Brownian motion*. Early investigations of this phenomenon were made on pollen grains, dust particles, and various other objects of colloidal size. Later it became clear that the theory of Brownian motion could be applied successfully to many other phenomena, for example, the motion of ions in water or the reorientation of dipolar molecules.

In particular, the theory of Brownian motion has been extended to situations where the "Brownian particle" is not a real particle at all, but instead some collective property of a macroscopic system. This might be, for example, the instantaneous concentration of any component of a chemically reacting system near thermal equilibrium. Here the irregular fluctuation in time of this concentration corresponds to the irregular motion of the dust particle. This kind of extension is of the greatest importance and will be discussed in depth later.

While the motion of a dust particle performing Brownian motion appears to be quite random, it must nevertheless be describable by the same equations of motion as is any other dynamical system. In classical mechanics, these are Newton's or Hamilton's equations.

Consider the one-dimensional motion of a spherical particle (radius a, mass m, position x, velocity v) in a fluid medium (viscosity η). Newton's equation of motion for the particle is

$$m\frac{dv}{dt} = F_{\text{total}}(t), \tag{1.1}$$

where $F_{\text{total}}(t)$ is the total instantaneous force on the particle at time t. This force is due to the interaction of the Brownian particle with the surrounding medium. If the positions of the molecules in the surrounding medium are known as functions of time, then in principle, this force is a known function of time. In this sense, it is not a "random force" at all. An example that illustrates this point, a Brownian particle coupled to a heat bath of harmonic oscillators, will be discussed later.

It is usually not practical or even desirable to look for an exact expression for $F_{\text{total}}(t)$. Experience teaches us that in typical cases, this force is dominated by a frictional force $-\zeta v$, proportional to the velocity of the Brownian particle. The friction coefficient is given by Stokes' law, $\zeta = 6\pi\eta a$. If this is the whole story, the equation of motion for the Brownian particle becomes

$$m\frac{dv}{dt} \cong -\zeta v, \tag{1.2}$$

and, as a linear first-order differential equation, it has the familiar solution

$$v(t) = e^{-\zeta t/m} v(0). \tag{1.3}$$

According to this, the velocity of the Brownian particle is predicted to decay to zero at long time. This cannot be strictly true because the mean squared velocity of the particle at thermal equilibrium is $\langle v^2 \rangle_{\text{eq}} = KT/m$, so that the actual velocity cannot remain at zero. Evidently, the assumption that $F_{\text{total}}(t)$ is dominated by the frictional force must be modified.

The appropriate modification, suggested by the observed randomness of an individual trajectory, is to add a "random" or "fluctuating" force $\delta F(t)$ to the frictional force, so that the equation of motion becomes

$$m\frac{dv}{dt} = -\zeta v + \delta F(t). \tag{1.4}$$

This is the *Langevin equation* for a Brownian particle. In effect, the total force has been partitioned into a systematic part (or friction) and a fluctuating part (or noise). Both friction and noise come from the interaction of the Brownian particle with its environment (called, for convenience, the "heat bath"). Because of this, one should not be surprised to find that there is a fundamental relation between friction and noise; this will be demonstrated shortly.

There are two basic views of the nature of the fluctuating force. In the more-commonly presented view, the fluctuating force is supposed to come from occasional impacts of the Brownian particle with molecules of the surrounding medium. The force during an impact is supposed to vary with extreme rapidity over the time of any observation, in fact, in any infinitesimal time interval. This clearly cannot be strictly true in any real system. Then the effects of the fluctuating force can be summarized by giving its first and second moments, as time averages over an infinitesimal time interval,

$$\langle \delta F(t) \rangle = 0, \qquad \langle \delta F(t) \delta F(t') \rangle = 2B\delta(t-t'). \tag{1.5}$$

B is a measure of the strength of the fluctuating force. The delta function in time indicates that there is no correlation between impacts in any distinct time intervals dt and dt'. The remaining mathematical specification of this dynamical model is that the fluctuating force has a Gaussian distribution determined by these moments.

The other view can be illustrated by the analogy of random number generators in computers. These algorithms are deterministic; that is, if the same seed in used in repetitions of the algorithm, the same sequence of numbers is generated. Yet the sequence generated by a good algorithm is "random" in the sense that it satisfies various statistical requirements of randomness for almost all choices of seed. The output of a random number generator is used as input to other programs, for example, Monte Carlo integration. The results are generally independent of the initial seed; only the statistical distribution of random numbers is important. In the same way, the randomness of Brownian noise is fully determined by the initial state of the heat bath. The results of a calculation using the Langevin equation are expected to be independent of the initial state and to involve only the statistical distribution of the noise. In this view, the averages in eq. (1.5) come from averages over initial states. A later section shows how all this can come from a simple harmonic oscillator model of a Brownian heat bath.

As remarked earlier, the particle's velocity decays to zero in the absence of noise, but this cannot be so. At thermal equilibrium, we must require that $\langle v^2 \rangle_{\text{eq}} = kT/m$. The Langevin equation, which is a

linear, first-order, inhomogeneous differential equation, can be solved to give

$$v(t) = e^{-\zeta t/m} v(0) + \int_0^t dt' e^{-\zeta(t-t')/m}\, \delta F(t')/m. \tag{1.6}$$

(Appendix 1 deals with solutions of equations of this kind.) The first term gives the exponential decay of the initial velocity, and the second term gives the extra velocity produced by the random noise. Let us use this to get the mean squared velocity. There are three contributions to $v(t)^2$; the first one is

$$e^{-2\zeta t/m} v(0)^2 \tag{1.7}$$

and clearly decays to zero at long times. There are two cross terms, each first order in the noise,

$$2v(0) e^{-\zeta t/m} \int_0^t dt' e^{-\zeta(t-t')/m}\, \delta F(t')/m. \tag{1.8}$$

On averaging over noise, these cross terms vanish. The final term is second order in the noise:

$$\int_0^t dt' e^{-\zeta(t-t')/m} \delta F(t') \int_0^t dt'' e^{-\zeta(t-t'')/m}\, \delta F(t'')/m^2 . \tag{1.9}$$

Now the product of two noise factors is averaged, according to eq. (1.5), and leads to

$$\int_0^t dt' e^{-\zeta(t-t')/m} \int_0^t dt'' e^{-\zeta(t-t'')/m}\, 2B\, \delta(t'-t'')/m^2 . \tag{1.10}$$

The delta function removes one time integration, and the other can be done directly. The resulting mean squared velocity is

$$\left\langle v(t)^2 \right\rangle = e^{-2\zeta t/m} v(0)^2 + \frac{B}{\zeta m}\left(1 - e^{-2\zeta t/m}\right). \tag{1.11}$$

In the long time limit, the exponentials drop out, and this quantity approaches $B/\zeta m$. But in the long time limit, the mean squared velocity must approach its equilibrium value kT/m. Consequently we find

$$B = \zeta kT. \tag{1.12}$$

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

variations on the fluctuation-dissipation theorem will be encountered in the following pages.

1.2 Time Correlation Functions

The Langevin equation can be used to calculate various time correlation functions. This section provides an introduction to these important quantities.

Equilibrium statistical mechanics is based on the idea of a statistical ensemble. We learn that the thermodynamic properties of a gas, for example, can be found by calculating the partition function of a statistical ensemble. We learn that the spatial structure of a liquid can be described statistically by a pair correlation function.

Nonequilibrium statistical mechanics is based on the same idea of a statistical ensemble. A fundamental difference, however, is that while there is only one equilibrium state, there are many nonequilibrium states. There is no unique "partition function" to use as a starting point for calculating transport properties. Time correlation functions play the same role as partition functions and spatial pair correlation functions in nonequilibrium statistical mechanics. Many properties of systems out of equilibrium, for example, coefficients of viscosity, thermal conductivity, diffusion, and conductivity, are determined by time correlation functions. They also provide a useful way to interpret experiments on neutron and light scattering, optical spectroscopy, and nuclear magnetic resonance.

We encounter a time correlation function whenever we analyze the statistical behavior of some time-dependent quantity $A(t)$ measured over a long time. The quantity $A(t)$ could be, for example, the intensity of light scattered by fluctuations in a liquid, or it could be the velocity of a single particle followed in a computer simulation of a liquid. The first stage in the analysis is to time-average the quantity itself,

$$\langle A \rangle = \frac{1}{\tau} \int_0^\tau dt A(t). \tag{1.13}$$

Then we subtract the average to get the fluctuation δA,

$$\delta A(t) = A(t) - \langle A \rangle. \tag{1.14}$$

One often observes that fluctuations at different times are correlated (in the same way that molecules in a liquid are spatially correlated). The time-averaged product of two fluctuations at different times,

$$C(t) = \frac{1}{\tau} \int_0^\tau ds \delta A(s)\, \delta A(t+s), \tag{1.15}$$

is called the *time correlation function* (TCF) of δA. The conventional mean squared fluctuation, the time average of fluctuations at the same time, is $C(0)$.

If the system under investigation is ergodic (generally assumed without proof), a long time average is equivalent to an equilibrium ensemble average. This is where the methods of statistical mechanics come in. Just as we get a pressure by calculating the partition function of a statistical ensemble instead of making a long time average of a single sample, we get a time correlation function by calculating an ensemble average of the product of two fluctuations instead of its long time average. In an equilibrium ensemble, there is no special initial time, and $C(t)$ depends only on the difference t between the two times.

While we based the definition of $C(t)$ on a record of the time dependence of $A(t)$, of the sort that might be produced, for example, by a computer simulation, many experiments actually generate the Fourier transform of the time correlation function directly. Generally, the Fourier transform of any time correlation function,

$$C_\omega = \int_{-\infty}^{\infty} dt e^{-i\omega t} C(t), \tag{1.16}$$

is called its *spectral density*. If we know the spectral density, we can recover the time dependence of the correlation function by Fourier inversion. For example, the optical absorption spectrum of a system as a function of frequency is related to the time correlation function of its total electric dipole moment. This connection will be treated later.

Velocity Correlation Function

Perhaps the simplest example of a time correlation function is the velocity correlation function of a single particle in a fluid, $\langle v(t)v(t')\rangle$, where $v(t)$ is the velocity of that particle at time t. One reason for interest in this time correlation function is its connection with the self-diffusion coefficient D. There are many ways to show this connection. A particularly easy one starts with the one-dimensional diffusion equation for the space (x) and time (t) dependence of the concentration $C(x, t)$ of a tagged particle,

$$\frac{\partial}{\partial t} C(x,t) = D \frac{\partial^2}{\partial x^2} C(x,t). \tag{1.17}$$

Suppose that the tagged particle starts out initially at $x = 0$. Then the concentration will change from an initial delta function in x to a spread-out Gaussian function of x. By symmetry, the mean displacement is zero. The mean squared displacement at time t can be found by multiplying the diffusion equation by x^2 and integrating over x,

$$\frac{\partial}{\partial t}\langle x^2\rangle = \int dx x^2 \frac{\partial}{\partial t} C(x,t)$$

$$= D\int dx x^2 \frac{\partial^2}{\partial x^2} C(x,t)$$

$$= 2D\int dx C(x,t) = 2D. \tag{1.18}$$

The last line comes from integrating by parts and by recognizing that the concentration is normalized to unity. On integrating over time, this result leads to the well-known Einstein formula for diffusion in one dimension, $\langle x^2\rangle = 2Dt$.

Now we make a statistical mechanical theory of the same quantity. The net displacement of the particle's position during the interval from 0 to t is

$$x(t) = \int_0^t ds v(s), \tag{1.19}$$

where $v(s)$ is the velocity of the particle at time s. The ensemble average of the mean squared displacement is

$$\langle x^2\rangle = \left\langle \int_0^t ds_1 v(s_1) \int_0^t ds_2 v(s_2) \right\rangle = \int_0^t ds_1 \int_0^t ds_2 \langle v(s_1) v(s_2)\rangle. \tag{1.20}$$

Note that the integral contains the correlation function of the velocity at times s_1 and s_2. Next, take the time derivative and combine two equivalent terms on the right-hand side,

$$\frac{\partial}{\partial t}\langle x^2\rangle = 2\int_0^t ds \langle v(t) v(s)\rangle. \tag{1.21}$$

The velocity correlation function is an equilibrium average and cannot depend on any arbitrary origin of the time axis. It can depend only on the time difference $t - s = u$, so that

$$\frac{\partial}{\partial t}\langle x^2\rangle = 2\int_0^t ds \langle v(t-s) v(0)\rangle = 2\int_0^t du \langle v(u) v(0)\rangle. \tag{1.22}$$

The velocity correlation function generally decays to zero in a short time; in simple liquids, this may be of the order of picoseconds. The diffusion equation is expected to be valid only at times much longer than a molecular time. In the limit of large t, the left-hand side approaches $2D$, and the right-hand side approaches a time integral from zero to infinity, so we have derived the simplest example of the relation of a transport coefficient to a time correlation function,

$$D = \int_0^\infty dt \langle v(t) v(0)\rangle. \tag{1.23}$$

The three-dimensional version can be obtained by summing over x, y, and z displacements and is

$$D = \frac{1}{3}\int_0^\infty dt\langle \mathbf{V}(t)\cdot\mathbf{V}(0)\rangle, \tag{1.24}$$

where $\mathbf{V}$ is the vector velocity.

1.3 Correlation Functions and Brownian Motion

The Langevin equation and the fluctuation-dissipation theorem can be used to find expressions for various time correlation functions.

Velocity Correlation Function

The first example is to obtain the velocity correlation function of a Brownian particle. In this example, it is instructive to calculate both the equilibrium ensemble average and the long-time average.

Calculating the equilibrium ensemble average involves both an average over noise and an average over the initial velocity. The noise average leads to

$$\langle v(t)\rangle_{\text{noise}} = e^{-(\zeta/m)t}v(0). \tag{1.25}$$

Now we multiply by $v(0)$ and average over initial velocity,

$$\langle v(t)v(0)\rangle_{\text{eq}} = \frac{kT}{m}e^{-(\zeta/m)t}. \tag{1.26}$$

This holds only for $t > 0$ because the Langevin equation is valid only for positive times.

We expect that the velocity correlation function is actually a function of the absolute value of t, but to see this from the Langevin equation we have to go to the long time average. This calculation starts with a record of the time dependence of the velocity $v(t)$ over a very long time interval τ. Then the velocity correlation function can be obtained from the long time average,

$$\langle v(t)v(t')\rangle_{\text{time}} = \frac{1}{\tau}\int_0^\tau ds\, v(t+s)v(t'+s). \tag{1.27}$$

The instantaneous velocity at time t is determined by its initial value and by an integral over the noise. We assume that the initial time is the infinite past, so that the contribution from the initial value of the velocity has decayed to zero, and the instantaneous velocity is determined

only by the noise. Then with a slight rearrangement of the time integral, we obtain

$$v(t) = \int_0^\infty e^{-(\zeta/m)u}\,\delta F(t-u)\,du/m. \tag{1.28}$$

Now the velocity correlation function is the triple integral,

$$\begin{aligned}\langle v(t)v(t')\rangle_{\text{time}} &= \int_0^\infty du_1 \int_0^\infty du_2 e^{-(\zeta/m)(u_1+u_2)}\,\frac{1}{\tau}\int_0^\tau ds\,\frac{1}{m^2}\delta F(t-u_1+s)\delta F(t-u_2+s)\\ &= \int_0^\infty du_1 \int_0^\infty du_2 e^{-(\zeta/m)(u_1+u_2)}\,\frac{1}{\tau}\int_0^\tau ds\,\frac{1}{m^2}2B\delta(t-u_1-t'+u_2).\end{aligned} \tag{1.29}$$

The product of two random force factors has been replaced by its average. The integral over s can be done immediately. The delta function removes another integral, and the last one can be done explicitly, leading to

$$\langle v(t)v(t')\rangle = \frac{m}{2\zeta}e^{-\zeta|t-t'|/m}\,\frac{2B}{m^2}. \tag{1.30}$$

Note that when the time correlation function is calculated this way, the absolute value of the time difference comes in automatically. On using the fluctuation-dissipation theorem, this leads to the final expression for the velocity correlation function,

$$\langle v(t)v(t')\rangle_{\text{time}} = \frac{kT}{m}e^{-\zeta|t-t'|/m}. \tag{1.31}$$

The time average of the product of two velocities is the same as the equilibrium ensemble average. This is what one expects of an ergodic system. One point of this derivation is to show that observation of time dependent fluctuations over a long time interval can be used to learn about friction.

Mean Squared Displacement

Another application of the general solution of the Langevin equation is to find the mean squared displacement of the Brownian particle. The actual displacement is

$$\Delta x(t) = \int_0^t dt' v(t'). \tag{1.32}$$

To find $\langle \Delta x(t)^2\rangle_{\text{eq}}$, we start with

$$v(t) = e^{-\zeta t/m} v(0) + \int_0^t dt' e^{-\zeta(t-t')/m} \delta F(t')/m \tag{1.33}$$

and then do the averages. Since the calculation is just like earlier ones, it will be left for the reader. The result is

$$\left\langle \Delta x(t)^2 \right\rangle_{\text{eq}} = 2\frac{kT}{\zeta}\left[t - \frac{m}{\zeta} + \frac{m}{\zeta} e^{-\zeta t/m} \right]. \tag{1.34}$$

At short times, the mean squared displacement increases quadratically with time. This is the inertial behavior that comes from the initial velocity. At long times, the effects of the noise are dominant, and the mean squared displacement increases linearly with time,

$$\left\langle \Delta x(t)^2 \right\rangle \to 2\frac{kT}{\zeta} t. \tag{1.35}$$

Einstein's formula for the mean squared displacement of a diffusing particle is $2Dt$ where D is the self-diffusion coefficient of the Brownian particle. Thus we obtain Einstein's expression for the self-diffusion coefficient,

$$D = \frac{kT}{\zeta}. \tag{1.36}$$

When Stokes' law is used for the friction coefficient, the result is called the Stokes-Einstein formula. This also is a prototype of may similar expressions to be encountered later.

Dipole-Dipole Correlation Function

Many time correlation functions are related to spectroscopic measurements. For example, the frequency dependence of the optical absorption coefficient of a substance is determined by the time correlation function of its electric dipole moment. The derivation of this connection, which will be presented in Section 3.2, is an exercise in applying the quantum mechanical "Golden Rule". The result of the derivation is quite simple, especially in the classical limit where $\hbar\omega/kT << 1$.

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

$$\alpha(\omega) = \frac{2\pi\omega^2\beta}{3nc} \int_{-\infty}^{\infty} dt e^{-i\omega t} \langle \mathbf{M}(0) \cdot \mathbf{M}(t) \rangle_{\text{eq}}. \tag{1.37}$$

In the coefficient, c is the velocity of light in vacuum, and n is the index of refraction. $\mathbf{M}(t)$ is the total electric dipole moment of the system at time t. The absorption coefficient is proportional to the spectral density of the dipole-dipole time correlation function.

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

$$\langle \mathbf{M} \cdot \mathbf{M}(t) \rangle_{\text{eq}} = \mu^2 \langle \mathbf{u}(0) \cdot \mathbf{u}(t) \rangle_{\text{eq}}. \tag{1.38}$$

If the motion is constrained to the xy plane, then it is convenient to represent the orientational vector by the angle θ,

$$\mathbf{u}(t) = (\cos\theta(t), \sin\theta(t)) \rightarrow e^{i\theta(t)}, \tag{1.39}$$

and the time correlation function of the orientations $\mathbf{u}(0)$ and $\mathbf{u}(t)$ in two dimensions can be written as

$$\langle \mathbf{u}(0) \cdot \mathbf{u}(t) \rangle_{\text{eq}} \rightarrow \langle e^{-i\theta(0)} e^{i\theta(t)} \rangle_{\text{eq}}. \tag{1.40}$$

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

$$\frac{d\theta}{dt} = \Omega, \qquad I\frac{d\Omega}{dt} = -\zeta\Omega + \delta F(t) \tag{1.41}$$

and

$$\langle \delta F(t) \delta F(t') \rangle = 2\zeta kT \delta(t - t'). \tag{1.42}$$

Then, as in eq. (1.34), the equilibrium mean squared change in angle as a function of time is

$$\langle \Delta\theta(t)^2 \rangle_{\text{eq}} = 2\frac{kT}{\zeta}\left[t - \frac{I}{\zeta} + \frac{I}{\zeta} e^{-(\zeta/I)t} \right]. \tag{1.43}$$

The orientational time correlation function is

$$C(t) = \langle e^{-i\theta(0)} e^{i\theta(t)} \rangle_{\text{eq}} = \langle e^{i\Delta\theta(t)} \rangle_{\text{eq}}. \tag{1.44}$$

But $\Delta\theta(\tau)$ is linear in the noise and in the initial angular velocity, and both of these have a Gaussian distribution. (This is explained further in Appendix 2, which surveys some properties of Gaussian distributions.) Then $\Delta\theta(\tau)$ has a Gaussian distribution with a zero mean value and a second moment given by eq. (1.43), and we can use the general formula for any Gaussian average,

$$\langle \exp(iax) \rangle = \exp\left(ia\bar{x} - \frac{1}{2} a^2 \left\langle (x - \bar{x})^2 \right\rangle \right). \tag{1.45}$$

Then the time correlation function is

$$C(t) = \exp - \frac{1}{2} \left\langle \Delta\theta(t)^2 \right\rangle_{\text{eq}}. \tag{1.46}$$

At long times this decays exponentially,

$$C(t) \to \exp\left(-\frac{kT}{\zeta} t \right). \tag{1.47}$$

1.4 Brownian Motion of Other Variables

The preceding discussion started with the Brownian motion of a heavy particle, but the ideas have a much wider applicability. Another example is the kinetics of a first-order isomerization reaction between two species called A and B. For convenience, we use the same symbols, A and B, for the total number of molecules of each species that are present in a unit volume of the system. In a laboratory experiment, these are macroscopic quantities, perhaps of the order of Avogadro's number. The basic rate equations are

$$\begin{aligned} \frac{dA}{dt} &= -k_1 A + k_2 B \\ \frac{dB}{dt} &= -k_2 B + k_1 A, \end{aligned} \tag{1.48}$$

and they have the equilibrium solutions A_{eq}, B_{eq}. The sum $A + B$ is constant in time, so that we can replace the two equations with a single one. The deviation of A from equilibrium is denoted by C, and because of conservation, the deviation of B from equilibrium is $-C$,

$$A = A_{\text{eq}} + C, \qquad B = B_{\text{eq}} - C. \tag{1.49}$$

We use the equilibrium condition,

$$k_1 A_{\text{eq}} = k_2 B_{\text{eq}} \tag{1.50}$$

so that the deviation C satisfies

$$\frac{dC}{dt} = -(k_1 + k_2) C. \tag{1.51}$$

A macroscopic deviation from equilibrium decays exponentially. Now we use the "regression hypothesis" of L. Onsager (1931); this asserts that small fluctuations decay on the average in exactly the same way as macroscopic deviations from equilibrium. (This is not really a hypothesis—it seems to always be true.) Then the time correlation function of the equilibrium fluctuations in particle number is

$$\langle C(t)C(t')\rangle_{\text{time}} = \langle C^2\rangle_{\text{eq}} e^{-(k_1+k_2)|t-t'|}. \tag{1.52}$$

Equation (1.51) requires that C must decay to zero at long times; but we know that if this reacting system comes to thermal equilibrium, there are still thermal fluctuations in C, and in particular the mean squared deviation (determined by statistical thermodynamics) $\langle C^2\rangle_{\text{eq}}$ is of the order of Avogadro's number and cannot vanish. This situation is exactly like what we saw in connection with the Brownian particle. To account for the fluctuations, a "random force" or noise term $\delta F(t)$ must be added to the basic kinetic equation,

$$\frac{dC}{dt} = -(k_1 + k_2)C + \delta F(t), \tag{1.53}$$

and to have the correct equilibrium behavior, we must impose the condition

$$\langle \delta F(t)\delta F(t')\rangle = 2(k_1 + k_2)\langle C^2\rangle_{\text{eq}}\,\delta(t - t'). \tag{1.54}$$

This is evidently another version of the fluctuation-dissipation theorem. Observation of particle number fluctuations over a very long time can be used to find a rate constant.

Several Variables

At this point, it should be clear than any linear dissipative equation will lead to a similar Langevin equation and a corresponding fluctuation-dissipation theorem. The general treatment is more complex because of the possibility of both dissipative and oscillatory behavior and will be handled using a vector-matrix notation. The general treatment will be followed by an illustrative example, the Brownian motion of a harmonic oscillator.

We consider a set of dynamical variables $\{a_1, a_2, \ldots\}$ denoted by the vector $\mathbf{a}$, and the Langevin equation

$$\frac{\partial a_j}{\partial t} = \sum_k \Theta_{jk} a_k + F_j(t), \tag{1.55}$$

or in matrix form,

$$\frac{\partial \mathbf{a}}{\partial t} = \Theta \cdot \mathbf{a} + \mathbf{F}(t), \tag{1.56}$$

in which Θ is a matrix and $\mathbf{F}(t)$ is a random force vector. (To save space, the extra δ will be dropped from $\delta\mathbf{F}$.) The strength of the noise is given by

$$\langle F_j(t)F_k(t')\rangle = 2B_{jk}\delta(t-t') \tag{1.57}$$

or

$$\langle \mathbf{F}(t)\mathbf{F}(t')\rangle = 2\mathbf{B}\delta(t-t'), \tag{1.58}$$

where $\mathbf{B}$ is by definition a symmetric matrix.

Θ can be diagonalized by a similarity transformation. If it has a zero eigenvalue, the corresponding eigenvector corresponds to a dynamical constant of the motion. We assume that all such quantities have been removed from the set $\mathbf{a}$. For a system that approaches equilibrium at long times, all eigenvalues of Θ must have negative real parts; however, they can be complex.

To obtain the analog of the fluctuation-dissipation theorem for this Langevin equation, we integrate, omitting the initial value term that decays to zero at long times. The result is

$$\mathbf{a}(t) = \int_0^t ds e^{(t-s)\Theta} \cdot \mathbf{F}(s). \tag{1.59}$$

Now we form the matrix $\langle \mathbf{a}(t)\mathbf{a}(t)\rangle$, giving proper attention to the transpose (denoted by †),

$$\begin{aligned}\langle \mathbf{a}(t)\mathbf{a}(t)\rangle &= \int_0^t ds \int_0^t ds' e^{(t-s)\Theta} \cdot \langle \mathbf{F}(s)\mathbf{F}(s')\rangle \cdot e^{(t-s')\Theta^\dagger} \\ &= \int_0^t ds e^{(t-s)\Theta} \cdot 2\mathbf{B} \cdot e^{(t-s)\Theta^\dagger}.\end{aligned} \tag{1.60}$$

In the limit of very large time, this second moment must approach its equilibrium value, denoted by $\mathbf{M}$,

$$\langle \mathbf{aa}\rangle_{\text{eq}} = \mathbf{M} = 2\int_0^\infty dt e^{t\Theta} \cdot \mathbf{B} \cdot e^{t\Theta^\dagger}. \tag{1.61}$$

To evaluate the time integral, we first construct the symmetrized quantity $\Theta \cdot \mathbf{M} + \mathbf{M} \cdot \Theta^\dagger$ and then use the integral representation of $\mathbf{M}$,

$$\begin{aligned}\Theta \cdot \mathbf{M} + \mathbf{M} \cdot \Theta^\dagger &= 2\int_0^\infty dt \Theta \cdot e^{t\Theta} \cdot \mathbf{B} \cdot e^{t\Theta^\dagger} + 2\int_0^\infty dt e^{t\Theta} \cdot \mathbf{B} \cdot e^{t\Theta^\dagger} \cdot \Theta^\dagger \\ &= 2\int_0^\infty dt \frac{d}{dt} e^{t\Theta} \cdot \mathbf{B} \cdot e^{t\Theta^\dagger} \\ &= \left(2e^{t\Theta} \cdot \mathbf{B} \cdot e^{t\Theta^\dagger}\right)_{t=\infty} - 2\mathbf{B}.\end{aligned} \tag{1.62}$$

The upper limit, at infinite time, vanishes because the eigenvalues of Θ all have negative real parts. So we have derived the fluctuation-dissipation theorem:

$$\Theta \cdot \mathbf{M} + \mathbf{M} \cdot \Theta^{\dagger} = -2\mathbf{B}. \tag{1.63}$$

Note that by their definition as second moments, $\mathbf{B}$ and $\mathbf{M}$ are symmetric, but Θ is not. According to the last equation, the product $\Theta \cdot \mathbf{M}$ has a symmetric part that is related to $\mathbf{B}$. But it can also have an antisymmetric part that has no relation to $\mathbf{B}$. It has become conventional to write Θ in the form

$$\Theta = i\Omega - \mathbf{K}. \tag{1.64}$$

The fluctuation-dissipation theorem requires both a symmetry, involving $\mathbf{K}$, and an antisymmetry, involving Ω,

$$\mathbf{B} = \mathbf{K} \cdot \mathbf{M} = \mathbf{M} \cdot \mathbf{K}^{\dagger}, \tag{1.65}$$

and

$$i\Omega \cdot \mathbf{M} = -\mathbf{M} \cdot i\Omega^{\dagger}. \tag{1.66}$$

The reason for including the factor i in $i\,\Omega$ is that Ω itself typically represents a frequency, so that $i\,\Omega$ describes oscillatory motion. The quantity $\mathbf{K} \cdot \mathbf{M}$ is real and symmetric and describes decaying motion. The symmetry of $\mathbf{K} \cdot \mathbf{M}$ is a statement of the "reciprocal relations" found by L. Onsager (1931).

A good illustration of the many-variable Langevin equation is the Brownian motion of a harmonic oscillator. We extend the earlier treatment of Langevin equations by adding an elastic force to the frictional force. The position and momentum of the oscillator are x and p, and the explicit equations of motion are

$$\begin{aligned} \frac{dx}{dt} &= \frac{p}{m} \\ \frac{dp}{dt} &= -m\omega^2 x - \zeta \frac{p}{m} + F_p(t). \end{aligned} \tag{1.67}$$

The noise in the momentum equation is labeled by a subscript p. Then the various vectors and matrices are

$$\mathbf{a} = \begin{pmatrix} x \\ p \end{pmatrix}, \qquad \mathbf{F} = \begin{pmatrix} 0 \\ F_p(t) \end{pmatrix} \tag{1.68}$$

$$\mathbf{M} = \begin{pmatrix} \langle x^2 \rangle & 0 \\ 0 & \langle p^2 \rangle \end{pmatrix} = \begin{pmatrix} kT/m\omega^2 & 0 \\ 0 & mkT \end{pmatrix} \tag{1.69}$$

$$i\Omega = \begin{pmatrix} 0 & 1/m \\ -m\omega^2 & 0 \end{pmatrix}, \qquad \mathbf{K} = \begin{pmatrix} 0 & 0 \\ 0 & \zeta/m \end{pmatrix}. \tag{1.70}$$

On multiplying out the various matrices, it is easy to see that all the consequences of the fluctuation-dissipation theorem are met.

1.5 Generalizations of Langevin Equations

Nonlinear Langevin Equations

Up to now we have discussed only linear Langevin equations. They have the great practical advantage that finding analytic solutions is easy. For example, this is how the fluctuation-dissipation theorem was derived. But one often encounters nonlinear Langevin equations in modeling physical problems. A typical example is Brownian motion of a molecular dipole in a periodic potential $U(x) = u\cos 2x$. It is customary, when constructing nonlinear Langevin equations, to assume that the friction is still linear in the velocity, and that the noise is related to the friction by the same fluctuation-dissipation theorem as in the linear case. Then the equations of motion are

$$\begin{aligned} \frac{dx}{dt} &= \frac{p}{m} \\ \frac{dp}{dt} &= -U'(x) - \zeta\frac{p}{m} + \delta F(t), \end{aligned} \tag{1.71}$$

where the force is $F(x) = -U'(x)$, and we have restored the δ in the noise term. An explicit derivation of these equations, starting with a Hamiltonian describing interaction of a system with a harmonic oscillator heat bath, is presented in the following section.

In the linear case, the first moments $\langle x\rangle$ and $\langle p\rangle$ obey exactly the same equations as the unaveraged variables, except that the noise term is absent. But if the force $F(x)$ is not linear in x, this is no longer true and the problem is much more difficult. The average equation of motion for the average momentum $\langle p\rangle$ is

$$\frac{d\langle p\rangle}{dt} = \langle F(x)\rangle - \zeta\frac{\langle p\rangle}{m} \tag{1.72}$$

and contains the average of the force. It is generally not safe to replace the average of a nonlinear function by the same function of the average,

$$\langle F(x)\rangle \neq F(\langle x\rangle). \tag{1.73}$$

This would require, for example, that the mean squared fluctuation of x must be negligible, and that is not necessarily so. A solution of the

nonlinear Langevin equation will generally involve *all* moments of x and p, $\langle x^m p^n \rangle$, and these will all be coupled together.

While nonlinear Langevin equations have a pleasant pictorial character and are amenable to easy computer simulation (where the noise is modeled using random number generators), they are very hard to treat analytically. The most practical approach is to convert the Langevin equation into a Fokker-Planck equation. This will be discussed in chapter 2.

Markovian and Non-Markovian Langevin Equations

The Langevin equations considered up to now are called "Markovian." This word, familiar in the theory of probability, has a somewhat different usage in nonequlibrium statistical mechanics. It is used here to indicate that the friction at time t is proportional to the velocity at the same time, and that the noise is delta-function correlated or "white." ("White" means that the Fourier transform of the correlation function of the noise, or its spectral density, is independent of frequency.) Real problems are often not Markovian. The friction at time t can depend on the history of the velocity $v(s)$ for times s that are earlier than t. That is, the friction may have a "memory." The friction coefficient ζ is replaced by a memory function $K(t)$, sometimes called an aftereffect function, so that the frictional force at time t becomes

$$-\zeta v(t) \to -\int_{-\infty}^{t} ds K(t-s)v(s), \tag{1.74}$$

or, on changing variables from s to $t - s$,

$$-\zeta v(t) \to -\int_{0}^{\infty} ds K(s)v(t-s). \tag{1.75}$$

If a system of this sort approaches equilibrium at long times, the fluctuation-dissipation theorem must be modified; the noise is no longer white. Problems of this kind are called non-Markovian.

A simple illustration of how non-Markovian behavior can arise is by elimination of the momentum in the Brownian motion of a harmonic oscillator. The starting equations are Markovian,

$$\begin{aligned} \frac{dx}{dt} &= \frac{p}{m} \\ \frac{dp}{dt} &= -m\omega^2 x - \zeta \frac{p}{m} + F_p(t). \end{aligned} \tag{1.76}$$

Let us suppose that the momentum vanishes in the infinite past, $p(-\infty) = 0$. We solve the second equation for $p(t)$ by integrating from $-\infty$ to t,

$$p(t) = \int_{-\infty}^{t} ds e^{-\zeta(t-s)/m}(-m\omega^2 x(s) + F_p(s))$$
$$= \int_{-\infty}^{t} ds e^{-\zeta s/m}(-m\omega^2 x(t-s) + F_p(t-s)). \tag{1.77}$$

When this is put back into the equation for dx/dt, we obtain

$$\frac{dx(t)}{dt} = -\int_0^\infty ds K(s)x(t-s) + F_x(t), \tag{1.78}$$

where the memory function $K(s)$ and the new fluctuating force $F_x(t)$ (with a subscript "$_x$" to distinguish it from the old $F_p(t)$) are given by

$$K(t) = \omega^2 e^{-\zeta|t|/m}, \tag{1.79}$$

$$F_x(t) = \frac{1}{m}\int_0^\infty ds e^{-\zeta s/m} F_p(t-s). \tag{1.80}$$

At equilibrium, the second moment of x is

$$\langle x^2 \rangle_{\text{eq}} = \frac{kT}{m\omega^2}. \tag{1.81}$$

Then the second moment of the new random force can be worked out explicitly, using the second moment of the old force. (It is important to remember that t' can be either smaller or larger than t.) The result of this somewhat tedious calculation is

$$\langle F_x(t)F_x(t')\rangle = \langle x^2 \rangle_{\text{eq}} K(|t-t'|). \tag{1.82}$$

This is a non-Markovian version of the fluctuation-dissipation theorem. The correlation function of the new noise is proportional to the memory function for the new friction.

In the limit of very large friction, and if we are concerned only with times much longer than m/ζ, then the memory function $K(s)$ can be approximated by a delta function having the same area,

$$K(s) \cong 2\frac{m\omega^2}{\zeta}\delta(s), \tag{1.83}$$

corresponding to Markovian friction. Then eq. (1.78) becomes an approximately Markovian Langevin equation for the position $x(t)$.

Whenever variables are eliminated from a Markovian system of equations, the result is a non-Markovian system. The converse is useful to keep in mind: If the memory decays exponentially in time, a non-Markovian system can be changed into a Markovian system by adding another variable. In the present example, adding a momentum converts eq. (1.78) into the two-variable Markovian eq. (1.76).

In this treatment of non-Markovian Brownian motion, the "history" began at $t = -\infty$, and the equations reflected that. It often happens, however, that the history begins at some specified time $t = 0$. This could be, for example, because the system has been prepared in some state at that time. Then the standard form of linear non-Markovian equations is very much like those already discussed,

$$\frac{d\mathbf{a}(t)}{dt} = i\Omega \cdot \mathbf{a}(t) - \int_0^t ds \mathbf{K}(s) \cdot \mathbf{a}(t-s) + \mathbf{F}(t), \tag{1.84}$$

and the corresponding fluctuation-dissipation theorem is, in matrix form,

$$\langle \mathbf{F}(t)\mathbf{F}(t') \rangle = \mathbf{K}(t-t') \cdot \langle \mathbf{aa} \rangle_{\text{eq}}. \tag{1.85}$$

1.6 Brownian Motion in a Harmonic Oscillator Heat Bath

It is always instructive to look at simple examples, where everything can be worked out in detail. Here is a derivation of the Langevin equation for the Brownian motion of an arbitrary nonlinear system interacting bilinearly with a harmonic oscillator heat bath. This is a prototype for many statistical mechanical models, both in classical mechanics and in quantum mechanics. It will appear several times in later sections.

The main results are an exact Langevin equation, and an explanation of the way in which averages of the random force are handled. Also we can see how Markovian behavior is an approximation to true non-Markovian behavior.

The system is described by a coordinate x and its conjugate momentum p. The heat bath is described by a set of coordinates $\{q_j\}$ and their conjugate momenta $\{p_j\}$. For simplicity, all oscillator masses are set equal to 1. The system Hamiltonian H_s is

$$H_s = \frac{p^2}{2m} + U(x), \tag{1.86}$$

and the heat bath Hamiltonian H_B includes harmonic oscillator Hamiltonians for each oscillator and a very special coupling to the system,

$$H_B = \sum_j \left(\frac{p_j^2}{2} + \frac{1}{2}\omega_j^2 \left(q_j - \frac{\gamma_j}{\omega_j^2} x \right)^2 \right), \tag{1.87}$$

in which ω_j is the frequency of the jth oscillator and γ_j measures the strength of coupling of the system to the jth oscillator. H_B consists of

three parts: The first is just the ordinary harmonic oscillator Hamiltonian, specified by its frequencies; the second contains a bilinear coupling to the system, $(\Sigma_j \gamma_j q_j)x$, specified by the coupling constants; and the third contains only x and could be regarded as part of the arbitrary $U(x)$. The bilinear coupling is what makes the derivation manageable.

The equations of motion for the combined Hamiltonian $H_S + H_B$ are simple:

$$\frac{dx}{dt} = \frac{p}{m}, \qquad \frac{dp}{dt} = -U'(x) + \sum_j \gamma_j \left(q_j - \frac{\gamma_j}{\omega_j^2} x \right)$$
$$\frac{dq_j}{dt} = p_j, \qquad \frac{dp_j}{dt} = -\omega_j^2 q_j + \gamma_j x. \tag{1.88}$$

Suppose that the time dependence of the system coordinate $x(t)$ is known. Then it is easy to solve for the motion of the heat bath oscillators, in terms of their initial values and the influence of $x(t)$,

$$q_j(t) = q_j(0)\cos\omega_j t + p_j(0)\frac{\sin\omega_j t}{\omega_j} + \gamma_j \int_0^t ds x(s) \frac{\sin\omega_j (t-s)}{\omega_j}. \tag{1.89}$$

Integration by parts leads to a more useful form:

$$q_j(t) - \frac{\gamma_j}{\omega_j^2} x(t) = \left(q_j(0) - \frac{\gamma_j}{\omega_j^2} x(0) \right) \cos\omega_j t + p_j(0) \frac{\sin\omega_j t}{\omega_j}$$
$$- \gamma_j \int_0^t ds \frac{p(s)}{m} \frac{\cos\omega_j (t-s)}{\omega_j^2}. \tag{1.90}$$

When this is put back into the equation for dp/dt, we obtain the formal Langevin equation

$$\frac{dp(t)}{dt} = -U'(x(t)) - \int_0^t ds K(s) \frac{p(t-s)}{m} + F_p(t), \tag{1.91}$$

in which the memory function $K(t)$ is explicitly

$$K(t) = \sum_j \frac{\gamma_j^2}{\omega_j^2} \cos\omega_j t, \tag{1.92}$$

and the "noise" $F_p(t)$ is given explicitly by

$$F_p(t) = \sum_j \gamma_j p_j(0) \frac{\sin\omega_j t}{\omega_j} + \sum_j \gamma_j \left(q_j(0) - \frac{\gamma_j}{\omega_j^2} x(0) \right) \cos\omega_j t. \tag{1.93}$$

By carefully choosing the spectrum $\{\omega_j\}$ and coupling constants $\{\gamma_j\}$, the memory function can be given any assigned form. For example, if

the spectrum is continuous, and the sum over j is replaced by an integral, $\int d\omega\, g(\omega)$, where $g(\omega)$ is a density of states, and if γ is a function of ω, then the memory function $K(t)$ becomes a Fourier integral,

$$K(t) = \int_0^\infty d\omega g(\omega) \frac{\gamma(\omega)^2}{\omega^2} \cos \omega t. \tag{1.94}$$

Further, if $g(\omega)$ is proportional to ω^2 and γ is a constant, then $K(t)$ is proportional to $\delta(t)$ and the resulting Langevin equation is Markovian.

The "noise" $F_p(t)$ is defined in terms of the initial positions and momenta of the bath oscillators and is therefore in principle a known function of time. However, if the bath has a large number of independent degrees of freedom, then the noise is a sum containing a large number of independent terms, and because of the central limit theorem, we can expect that its statistical properties are simple.

Suppose, for example, that a large number of computer simulations of this system are done. In each simulation, the bath initial conditions are taken from a distribution,

$$f_{\text{eq}}(p, q) \propto \exp(-H_B/kT), \tag{1.95}$$

in which the bath is in thermal equilibrium with respect to a frozen or constrained system coordinate $x(0)$. Then the averages of q and p are

$$\left\langle q_j(0) - \frac{\gamma_j}{\omega_j^2} x(0) \right\rangle = 0, \qquad \langle p_j(0) \rangle = 0. \tag{1.96}$$

Since the noise is a linear combination of these quantities, its average value is zero. The second moments are

$$\left\langle \left(q_j(0) - \frac{\gamma_j}{\omega_j^2} x(0) \right)^2 \right\rangle = \frac{kT}{\omega_j^2}, \qquad \left\langle p_j(0)^2 \right\rangle = kT. \tag{1.97}$$

There are no correlations between the initial values for different js. Then by direct calculation, using trigonometric identities, one sees immediately that there is a fluctuation-dissipation theorem,

$$\langle F_p(t) F_p(t') \rangle = kTK(t - t'). \tag{1.98}$$

Because the noise is a linear combination of quantities that have a Gaussian distribution, the noise is itself a Gaussian random variable. If the heat bath has been constructed so that the memory function is a delta function, then the noise is white or Markovian. This model justifies all the assumptions that were made about Langevin equations earlier.

In this example, the fluctuation-dissipation theorem was obtained for a rather specific kind of initial distribution of states. It may not work out so simply for a different initial distribution. One must remember that the distinction between what we call "systematic behavior" and what we call "noise" can be arbitrary; it depends on how we decide to define averages. Noise is not an intrinsic property of a material; it is determined by the experiment used to measure it.

1.7 Heavy Mass in a Harmonic Lattice

Another very instructive model of Brownian motion is due to R. J. Rubin (1960). The model is a one-dimensional harmonic lattice in which one particle is much heavier than the rest. The heavy particle appears to behave like a freely moving Brownian particle with a frictional force proportional to its velocity. This section presents a calculation of the heavy particle's velocity correlation function.

All particles except one have the same mass m. The exceptional particle has mass M. The coordinate and velocity of the jth particle are x_j and v_j, where j goes from 0 to $N-1$. Periodic boundary conditions are used, so that $x_N = x_0$. Later the limit of very large N will be taken. Nearest neighbor particles are connected by harmonic springs so that the energy is

$$E = \frac{M}{2}v_0^2 + \sum_{j=1}^{N-1}\frac{m}{2}v_j^2 + \sum_{j=0}^{N-1}\frac{K}{2}(x_j - x_{j+1})^2. \tag{1.99}$$

The equations of motion are

$$[m + (M-m)\delta_{j0}]\ddot{x}_j = K(x_{j+1} - 2x_j + x_{j-1}). \tag{1.100}$$

The velocity correlation function (VCF), normalized to unity at $t = 0$, is the equilibrium average

$$C(t) = \frac{\langle v_0(t)v_0(0)\rangle}{\langle v_0^2\rangle}. \tag{1.101}$$

Because the equations of motion are linear, the position and velocity at time t are linear combinations of initial positions and velocities. The equilibrium average of the product of a coordinate and a velocity vanishes, and the velocities of different particles are not correlated,

$$\langle x_j v_0\rangle = 0, \qquad \langle v_j v_0\rangle = \frac{k_B T}{M}\delta_{j0}. \tag{1.102}$$

As long as we want only the velocity correlation function, we do not have to solve the equations of motion for an arbitrary initial condition;

it is enough to set all initial coordinates and velocities except $v_0(0)$ equal to zero; their contributions will vanish anyway.

The equations of motion are conveniently solved by taking Laplace transforms (appendix 3). The Laplace transform of the jth coordinate is

$$\hat{x}_j(z) = \int_0^\infty dt e^{-zt} x_j(t), \tag{1.103}$$

and the equations of motion for this special choice of initial condition are

$$[m + (M-m)\delta_{j0}](z^2\hat{x}_j - \delta_{j0}v_0(0)) = K(\hat{x}_{j+1} - 2\hat{x}_j + \hat{x}_{j-1}). \tag{1.104}$$

The structure of the potential energy suggests a normal mode transformation to new coordinates q_k,

$$x_k = \frac{1}{\sqrt{N}} \sum_{j=0}^{N-1} q_j \exp\left(\frac{2\pi i}{N} jk\right), \tag{1.105}$$

which has the inverse transformation

$$q_k = \frac{1}{\sqrt{N}} \sum_{j=0}^{N-1} x_j \exp\left(-\frac{2\pi i}{N} jk\right). \tag{1.106}$$

After some rearrangement, the transformed equations are

$$\hat{q}_k = \frac{1}{\sqrt{N}} \frac{1}{z^2 + \omega_k^2} \left[\frac{M}{m} v_0(0) - \frac{M-m}{m} z^2 \hat{x}_0\right], \tag{1.107}$$

where the normal mode frequencies are

$$\omega_k^2 = \frac{2k}{m}\left(1 - \cos\frac{2\pi k}{N}\right). \tag{1.108}$$

A further summation over k leads to

$$\hat{x}_0 = \frac{1}{N} \sum_k \frac{1}{z^2 + \omega_k^2} \left[\frac{M}{m} v_0(0) - \frac{M-m}{m} z^2 \hat{x}_0\right]. \tag{1.109}$$

The sum will be denoted by

$$\hat{\phi}(z) = \frac{1}{N} \sum_0^{N-1} \frac{1}{z^2 + \omega_k^2}. \tag{1.110}$$

This quantity is particularly simple in the limit of large N. Change variables from k to θ, and replace the sum over k by an integral over θ,

$$\hat{\phi}(z) \cong \frac{1}{2\pi}\int_0^{2\pi} d\theta \frac{1}{z^2 + (2K/m)(1-\cos\theta)}$$
$$= \frac{1}{z}\frac{1}{\sqrt{z^2 + 4K/m}}. \tag{1.111}$$

When eq. (1.109) is solved for $\hat{x}_0$, one gets

$$\hat{x}_0 = \frac{(1+Q)\hat{\phi}}{1+Qz^2\hat{\phi}} v_0(0), \tag{1.112}$$

where Q is defined as

$$Q = \frac{M-m}{m}. \tag{1.113}$$

The transform of the velocity is $z\hat{x}_0$, so the transform of the normalized velocity correlation function is

$$\hat{C}(z) = \frac{(1+Q)}{1+Qz^2\hat{\phi}(z)} z\hat{\phi}(z). \tag{1.114}$$

In the large N limit, the approximate expression for $\hat{\phi}$ found earlier leads to an algebraic function of z,

$$\hat{C}(z) = \frac{1+Q}{Qz+\sqrt{z^2+4K/m}}. \tag{1.115}$$

The short time behavior of $C(t)$ can be found from the large z expansion,

$$\hat{C}(z) = \frac{1}{z} - \frac{2K}{Mz^3} + \cdots. \tag{1.116}$$

(Note the change from m to M; at short times, the inertial motion of the heavy mass dominates.) Then at short times, C is

$$C(t) = 1 - \frac{K}{M}t^2 + \cdots. \tag{1.117}$$

The quadratic dependence on t is a natural consequence of time-reversal symmetry.

The inverse Laplace transform can be found in tables if $Q = 0$ or 1. Otherwise, there are no known inverse transforms in terms of standard functions. When $Q = 0$, one finds the Bessel function of order 0,

$$C(t) = J_0(2t\sqrt{K/m}) \qquad (M = m). \tag{1.118}$$

When $Q = 1$, the result is another Bessel function, of order 1,

$$C(t) = \frac{J_1(2t\sqrt{K/m})}{t\sqrt{K/m}} \qquad (M = 2m). \tag{1.119}$$

After some algebraic rearrangement, the transform of the velocity correlation function may be written in the memory function form,

$$\hat{C}(z) = \frac{1}{z + \dfrac{m}{M}\hat{k}(z)}, \qquad \hat{k}(z) = \sqrt{z^2 + 4K/m} - z. \tag{1.120}$$

On inverting the transforms, this is equivalent to

$$\frac{d}{dt}C(t) = -\frac{m}{M}\int_0^t dsk(s)C(t-s), \tag{1.121}$$

and the time dependent $k(s)$ (which does not depend on M) is

$$k(s) = \frac{4K}{m}\frac{J_1(2s\sqrt{K/m})}{s}. \tag{1.122}$$

Equations similar to eq. (1.121) occur frequently in nonequilibrium statistical mechanics. There is a convolution, with a memory function that has a short life time, in this case of the order of $(m/K)^{1/2}$. The convolution integral has a coefficient that can be very small, in this case of the order of m/M. In the heavy mass limit, the time derivative of $C(t)$ is small, and this suggests a Markovian approximation to eq. (1.121), where $C(t-s)$ is replaced by $C(t)$ and the integral is extended to infinity,

$$\frac{d}{dt}C(t) \approx -\frac{m}{M}\int_0^\infty dsk(s)C(t). \tag{1.123}$$

The infinite time integral is

$$\int_0^\infty dsk(s) = \sqrt{4K/m} = \frac{1}{t_0}. \tag{1.124}$$

Then the velocity correlation function decays exponentially on a time scale of the order of $M/m\ t_0$,

$$C(t) \approx \exp\left(-\frac{m}{M}\frac{t}{t_0}\right). \tag{1.125}$$

In problems of this sort, with a short memory and a small coefficient, one generally finds approximate exponential decay. But one would like to know what the limitations are on the approximation.

One can always invert a Laplace transform by means of a contour integral in the complex plane,

$$C(t) = \frac{1}{2\pi i}\int_{\varepsilon-i\infty}^{\varepsilon+i\infty} e^{tz}\,\frac{1+Q}{Qz+\sqrt{z^2+4K/m}}. \tag{1.126}$$

Evaluating contour integrals is an exercise in complex variable theory. Rubin has done the complete calculation; we will not repeat it here. He found that there is a small correction to the exponential decay at very long times, which is bounded by

$$\left|C(t) - \exp\left(-\frac{m}{M}\frac{t}{t_0}\right)\right| \le \frac{m}{M}\sqrt{2} \tag{1.127}$$

and which decays more slowly than exponentially. The exponential decay dominates as long as

$$t << \frac{M}{m}\ln\frac{M}{m}t_0. \tag{1.128}$$

If $M = 10^4 m$, the correction to the exponential has the same order of magnitude as the exponential after about nine relaxation times.

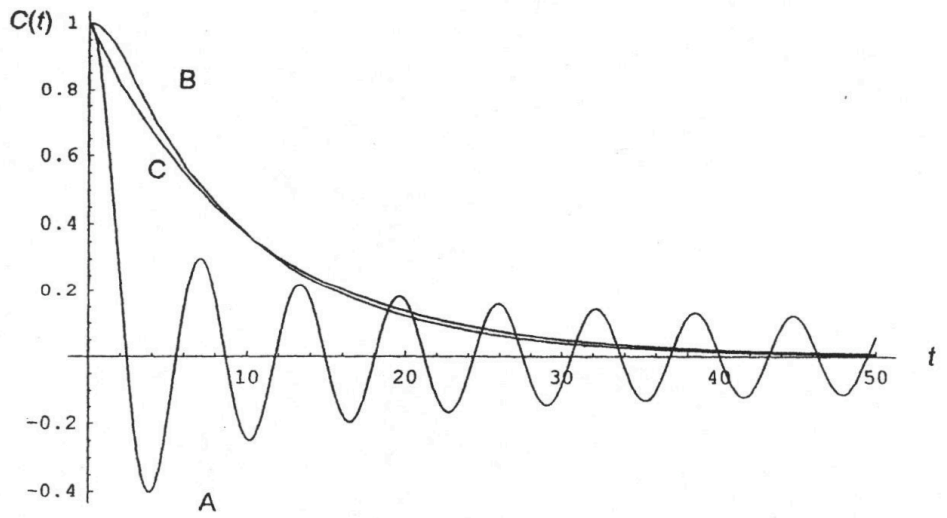

Figure 1.7.1 The velocity correlation function $C(t)$ as a function of time t. Curve A is the Bessel function for equal masses. Curve B is the result of numerical inversion of the Laplace transform when $M = 10m$. Curve C is the exponential $\exp(-t/10)$.

Sometimes one can invert a Laplace transform numerically (see Appendix 3). Figure 1.7.1 shows $C(t)$ for the equal mass case $M = m$, where A is $J_0(t)$, B is the numerical inversion for $M = 10m$, and C is the exponential $\exp(-t/10)$. Note that the asymptotic exponential works quite well except for small t.

The preceding analysis was based on the limit of large N. Two kinds of correction must be made if N is finite. One is that the magnitude of the velocity correlation function is changed by terms of the order of $1/N$. The other correction limits the time over which the large N limit applies. When the particle at $j = 0$ moves, it sends out sound waves that carry away energy and information. With periodic boundary conditions, these sound waves will eventually come back to influence that particle; in mathematical language, the motion is "almost periodic" and has recurrences. If N is large, recurrences occur only at times very much longer than the exponential relaxation time. So it is quite reasonable to take advantage of the large N limit.