with diffusion constants D_{θ} , D_{a} , and D_{b} . Experiments have observed the complex two-dimensional spatial diffusion at short times ($t \leq \tau_{\theta} = 1/(2D_{\theta})$), as predicted by the Langevin theory. The long-time ($t \gg \tau_{\theta}$) spatial diffusion is isotropic with diffusion constant $\overline{D} = (D_{a} + D_{b})/2$.

15.3.A Brownian motion of a harmonic oscillator

An analysis similar to the one for a diffusing Brownian particle can also be performed for a particle in a harmonic oscillator potential that prevents the particle from diffusing away from the origin and allows a more general analysis of the relationship between the position and velocity response functions and the power spectra of the fluctuations; see Kappler (1938) and Chandrasekhar (1943). The one-dimensional equation of motion for a Brownian particle of mass *M* in a harmonic oscillator potential with spring constant $M\omega_0^2$ is

$$\frac{d^2x}{dt^2} + \gamma \frac{dx}{dt} + \omega_0^2 x = \frac{F(t)}{M},\tag{33}$$

where $\gamma (= 6\pi \eta a/M)$ is the damping coefficient of a spherical particle in a fluid with viscosity η . Just as in the case of diffusive Brownian motion, the force F(t) can be a time-dependent external force designed to explore the response function or a time-dependent random force due to collisions with molecules in the fluid to analyze the equilibrium fluctuations. Assuming the system was in equilibrium in the distant past, the position at time *t* is given by

$$x(t) = \int_{-\infty}^{t} \chi_{xx}(t - t')F(t')dt',$$
(34)

where

$$\chi_{XX}(s) = \frac{1}{M\omega_1} e^{-\frac{\gamma s}{2}} \sin(\omega_1 s)$$
(35)

is the *xx* response function and $\omega_1 = \sqrt{\omega_0^2 - \frac{\gamma^2}{4}}$.¹² The velocity response is given by

$$\nu(t) = \int_{-\infty}^{t} \chi_{\nu x}(t - t') F(t') dt',$$
(36)

¹²This form of the response function assumes that the oscillator is underdamped. The notation χ_{xx} refers to the notation used in Section 15.6.A in which the response of the position coordinate *x* depends on the applied field *F* that couples to the Hamiltonian via a term -F(t)x(t).

where

$$\chi_{\nu x}(s) = \frac{1}{M} e^{-\frac{\gamma s}{2}} \left(\cos\left(\omega_1 s\right) - \frac{\gamma}{2\omega_1} \sin\left(\omega_1 s\right) \right).$$
(37)

The response of the system can be decomposed into a sum of independent terms involving a sinusoidal applied force $\hat{F}(\omega)e^{i\omega t}$. This takes the form

$$\hat{x}(\omega) = \tilde{\chi}_{xx}(\omega)\hat{F}(\omega), \tag{38}$$

where the frequency-dependent response function can be decomposed into real and imaginary parts $\hat{\chi}'_{xx}(\omega)$ and $\hat{\chi}''_{xx}(\omega)$:

$$\tilde{\chi}_{xx}(\omega) = \int_{0}^{\infty} \chi_{xx}(s) e^{i\omega s} ds = \hat{\chi}'_{xx}(\omega) + i\hat{\chi}''_{xx}(\omega), \qquad (39a)$$

$$\hat{\chi}'_{XX}(\omega) = \frac{\omega_0^2 - \omega^2}{M[(\omega_0^2 - \omega^2)^2 + \gamma^2 \omega^2]},$$
(39b)

$$\hat{\chi}_{xx}^{"}(\omega) = \frac{\gamma\omega}{M[(\omega_0^2 - \omega^2)^2 + \gamma^2 \omega^2]}.$$
(39c)

The real part here describes the dispersion and the imaginary part describes the dissipation, that is, it sets the average rate of energy dissipation due to the sinusoidal external force.

Now let's consider the natural fluctuations of the position and the velocity of the particle *in equilibrium* due to the random collisions with the atoms in the fluid. We will use the same Langevin formalism as was used earlier with Brownian motion of a free particle. The random force averages to zero and is assumed to be delta-function correlated in time:

$$\langle F \rangle = 0, \tag{40a}$$

$$\langle F(t)F(t')\rangle = \Gamma\delta(t-t'),$$
(40b)

where $\Gamma = 2\gamma MkT$. With this choice, the long-time average position and velocity of the particle are both zero,

$$\langle x(t) \rangle = \langle v(t) \rangle = 0, \tag{41}$$

and the average of the squares of the position and velocity both obey the equipartition theorem:

$$\langle x^2(t)\rangle = \frac{kT}{M\omega_0^2}, \quad \langle v^2(t)\rangle = \frac{kT}{M}.$$
 (42a,b)

The xx correlation function is given by

$$G_{xx}(t-t') = \langle x(t)x(t') \rangle$$

= $\frac{kT}{M\omega_0^2} \exp\left(\frac{-\gamma |t-t'|}{2}\right) \left(\cos\left(\omega_1 |t-t'|\right) + \frac{\gamma}{2\omega_1}\sin\left(\omega_1 |t-t'|\right)\right),$ (43)

and the xx power spectrum by

$$S_{XX}(\omega) = \int_{-\infty}^{\infty} G_{XX}(s) e^{i\omega s} ds = \frac{2\gamma kT}{M} \frac{1}{\left(\omega_0^2 - \omega^2\right)^2 + \gamma^2 \omega^2}.$$
 (44)

Note that the imaginary part of the response function, $\hat{\chi}''_{xx}(\omega)$, in equation (39c) is proportional to the power spectrum $S_{xx}(\omega)$:

$$\hat{\chi}_{XX}^{\prime\prime}(\omega) = \frac{\omega}{2kT} S_{XX}(\omega). \tag{45}$$

This result indicates that the dissipation that results from driving a system out of equilibrium by an external force is proportional to the power spectrum of the natural fluctuations that occur in equilibrium. While this result was derived here for a very specific model, it constitutes an example of the very general fluctuation–dissipation theorem we will derive in Section 15.6.A.

15.4 Approach to equilibrium: the Fokker–Planck equation

In our analysis of the Brownian motion we have considered the behavior of a dynamical variable, such as the position $\mathbf{r}(t)$ or the velocity $\mathbf{v}(t)$ of a Brownian particle, from the point of view of fluctuations in the value of the variable. To determine the average behavior of such a variable, we sometimes invoked an "ensemble" of Brownian particles immersed in identical environments and undergoing diffusion. A treatment along these lines was carried out toward the end of Section 15.2, and the most important results of that treatment are summarized in equation (15.2.20) for the density function $n(\mathbf{r}, t)$ and in equation (15.2.22) for the mean square displacement $\langle \mathbf{r}^2(t) \rangle$.

A more generalized way of looking at "the manner in which, and the rate at which, a given distribution of Brownian particles approaches a state of thermal equilibrium" is provided by the so-called *Master Equation*, a simplified version of which is known as the Fokker–Planck equation. For illustration, we examine the displacement, x(t), of the given set of particles along the *x*-axis. At any time *t*, let f(x, t)dx be the probability that an arbitrary particle in the ensemble may have a displacement between *x* and x + dx. The function

f(x, t) must satisfy the normalization condition

$$\int_{-\infty}^{\infty} f(x,t)dx = 1.$$
 (1)

The Master Equation then reads:

$$\frac{\partial f(x,t)}{\partial t} = \int_{-\infty}^{\infty} \{-f(x,t)W(x,x') + f(x',t)W(x',x)\}dx',\tag{2}$$

where $W(x, x')dx'\delta t$ denotes the probability that, in a short interval of time δt , a particle having displacement *x* makes a "transition" to having a displacement between *x*' and x' + dx'.¹³

The first part of the integral in equation (2) corresponds to all those transitions that remove particles from the displacement x at time t to some other displacement x' and, hence, represent a net *loss* to the function f(x, t); similarly, the second part of the integral corresponds to all those transitions that bring particles from some other displacement x' at time t to the displacement x and, hence, represent a net *gain* to the function f(x, t).¹⁴

The structure of the Master Equation is thus founded on very simple and straightforward premises. Of course, under certain conditions, this equation, or any generalization thereof (such as the one including velocity, or momentum, coordinates in the argument of f), can be reduced to the simple form

$$\frac{\partial f}{\partial t} = -\frac{f - f_0}{\tau},\tag{3}$$

which has proved to be a very useful first approximation for studying problems related to *transport phenomena*. Here, f_0 denotes the *equilibrium distribution function* (for $\partial f/\partial t = 0$ when $f = f_0$), while τ is the *relaxation time* that determines the rate at which the fluctuations in the system drive it to a state of equilibrium.

In studying Brownian motion on the basis of equation (2), we can safely assume that it is only transitions between "closely neighboring" states x and x' that have an appreciable probability of occurring; in other words, the transition probability function W(x, x') is sharply peaked around the value x' = x and falls rapidly to zero away from x. Denoting the interval (x' - x) by ξ , we may write

$$W(x, x') \to W(x;\xi), \ W(x', x) \to W(x'; -\xi) \tag{4}$$

¹³We are tacitly assuming here a "Markovian" situation where the *transition probability function* W(x,x') depends *only* on the present position *x* (and, of course, the subsequent position *x'*) of the particle but *not* on the previous history of the particle.

¹⁴In the case of fermions, an account must be taken of the *Pauli exclusion principle*, which controls the "occupation of single-particle states in the system"; for instance, we cannot, in that case, consider a transition that tends to transfer a particle to a state that is already occupied. This requires an appropriate modification of the Master Equation.

where $W(x;\xi)$ and $W(x';-\xi)$ have sharp peaks around the value $\xi = 0$ and fall rapidly to zero elsewhere.¹⁵ This enables us to expand the right side of (2) as a Taylor series around $\xi = 0$. Retaining terms up to second order only, we obtain

$$\frac{\partial f(x,t)}{\partial t} = -\frac{\partial}{\partial x} \{\mu_1(x)f(x,t)\} + \frac{1}{2}\frac{\partial^2}{\partial x^2} \{\mu_2(x)f(x,t)\},\tag{5}$$

where

$$\mu_1(x) = \int_{-\infty}^{\infty} \xi W(x;\xi) d\xi = \frac{\langle \delta x \rangle_{\delta t}}{\delta t} = \langle v_x \rangle$$
(6)

and

$$\mu_2(x) = \int_{-\infty}^{\infty} \xi^2 W(x;\xi) d\xi = \frac{\langle (\delta x)^2 \rangle_{\delta t}}{\delta t}.$$
(7)

Equation (5) is the so-called Fokker–Planck equation, which occupies a classic place in the field of Brownian motion and fluctuations.

We now consider a specific system of Brownian particles (of negligible mass), each particle being acted on by a linear restoring force, $F_x = -\lambda x$, and having mobility *B* in the surrounding medium; the assumption of negligible mass implies that the relaxation time τ (= *MB*) of equation (15.3.4) is very small, so the time *t* here may be regarded as very large in comparison with that τ . The mean viscous force, $-\langle v_x \rangle / B$, is then balanced by the linear restoring force, with the result that

$$-\frac{\langle v_x \rangle}{B} + F_x = 0 \tag{8}$$

and hence

$$\langle v_x \rangle \equiv \mu_1(x) = -\lambda B x.$$
 (9)

Next, in view of equation (15.3.10), we have

$$\frac{\langle (\delta x)^2 \rangle}{\delta t} \equiv \mu_2(x) = 2BkT; \tag{10}$$

it will be noted that the influence of λ on this quantity is being neglected here. Substituting (9) and (10) into (5), we obtain

$$\frac{\partial f}{\partial t} = \lambda B \frac{\partial}{\partial x} (xf) + BkT \frac{\partial^2 f}{\partial x^2}.$$
(11)

¹⁵Clearly, this assumption limits our analysis to what may be called the "Brownian motion approximation," in which the object under consideration is presumed to be on a very different scale of magnitude than the molecules constituting the environment. It is obvious that if one tries to apply this sort of analysis to "understand" the behavior of molecules *themselves*, one cannot hope for anything but a "crude, semiquantitative" outcome.

Now we apply equation (11) to an "ensemble" of Brownian particles, initially concentrated at the point $x = x_0$. To begin with, we note that, in the absence of the restoring force ($\lambda = 0$), equation (11) reduces to the one-dimensional *diffusion equation*

$$\frac{\partial f}{\partial t} = D \frac{\partial^2 f}{\partial x^2} \quad (D = BkT), \tag{12}$$

which conforms to our earlier results (15.2.19) and (15.3.11). The present derivation shows that the process of diffusion is essentially a "random walk, at the molecular level." In view of equation (15.2.20), the function f(x, t) here would be

$$f(x,t) = \frac{1}{(4\pi Dt)^{1/2}} \exp\left\{-\frac{(x-x_0)^2}{4Dt}\right\},$$
(13)

with

$$\overline{x} = x_0$$
 and $\overline{x^2} = x_0^2 + 2Dt;$ (14)

the last result shows that the mean square distance traversed by the particle(s) increases *linearly* with time, without any upper limit on its value. The restoring force, however, puts a check on the diffusive tendency of the particles. For instance, in the presence of such a force ($\lambda \neq 0$), the terminal distribution f_{∞} (for which $\partial f/\partial t = 0$) is determined by the equation

$$\frac{\partial}{\partial x}(xf_{\infty}) + \frac{kT}{\lambda}\frac{\partial^2 f_{\infty}}{\partial x^2} = 0,$$
(15)

which gives

$$f_{\infty}(x) = \left(\frac{\lambda}{2\pi kT}\right)^{1/2} \exp\left(-\frac{\lambda x^2}{2kT}\right),\tag{16}$$

with

$$\overline{x} = 0$$
 and $\overline{x^2} = kT/\lambda$. (17)

The last result agrees with the fact that the mean square value of *x* must ultimately comply with the *equipartition theorem*, namely $\overline{(\frac{1}{2}\lambda x^2)}_{\infty} = \frac{1}{2}kT$. From the point of view of equilibrium statistical mechanics, if we regard Brownian particles with kinetic energy $p_x^2/2m$ and potential energy $\frac{1}{2}\lambda x^2$ as *loosely coupled* to a thermal environment at temperature *T*, then we may directly write

$$f_{ea}(x,p_x)dxdp_x \propto e^{-(p_x^2/2m + \lambda x^2/2)/kT}dxdp_x.$$
(18)

On integration over p_x , expression (18) leads directly to the distribution function (16).



FIGURE 15.5 The distribution function (19) at times t = 0, $t = 1/(2\lambda B)$, and $t = \infty$.

The general solution of equation (11), relevant to the ensemble under consideration, is given by

$$f(x,t) = \left\{\frac{\lambda}{2\pi kT(1 - e^{-2\lambda Bt})}\right\}^{1/2} \exp\left\{-\frac{\lambda(x - x_0 e^{-\lambda Bt})^2}{2kT(1 - e^{-2\lambda Bt})}\right\},$$
(19)

with

$$\overline{x} = x_0 e^{-\lambda Bt}$$
 and $\overline{x^2} = x_0^2 e^{-2\lambda Bt} + \frac{kT}{\lambda} (1 - e^{-2\lambda Bt});$ (20)

in the limit $\lambda \to 0$, we recover the purely "diffusive" situation, as described by equations (13) and (14), while for $t \gg (\lambda B)^{-1}$, we approach the "terminal" situation, as described by equations (16) and (17). Figure 15.5 shows the manner in which an ensemble of Brownian particles approaches a state of equilibrium under the combined influence of the restoring force and the molecular bombardment; clearly, the relaxation time of the present process is $\sim (\lambda B)^{-1}$.

A physical system to which the foregoing theory is readily applicable is provided by the oscillating component of a moving-coil galvanometer. Here, we have a coil of wire and a mirror that are suspended by a fine fiber, so they can rotate about a vertical axis. Random, incessant collisions of air molecules with the suspended system produce a succession of torques of *fluctuating* intensity; as a result, the angular position θ of the system continually fluctuates and the system exhibits an *unsteady* zero. This is clearly another example of the Brownian motion! The role of the viscous force in this case is played by the mechanism of air damping (or, else, electromagnetic damping) of the galvanometer, while the restoring torque, $N_{\theta} = -c\theta$, arises from the torsional properties of the fiber. In equilibrium, we

expect that

$$\overline{\left(\frac{1}{2}c\theta^2\right)} = \frac{1}{2}kT$$
, that is, $\overline{\theta^2} = \frac{kT}{c}$; (21)

compare this to equation (17). An experimental determination of the mean square deflection, $\overline{\theta^2}$, of such a system was made by Kappler (1931) who, in turn, applied his results to derive, with the help of equation (21), an empirical value for the Boltzmann constant k (or, for that matter, the Avogadro number N_A). The system used by Kappler had a moment of inertia $I = 4.552 \times 10^{-4} \text{ g cm}^2$ and a time period of oscillation $\tau = 1379 \text{ s}$; accordingly, the constant c of the restoring torque had a value given by the formula $\tau = 2\pi (I/c)^{1/2}$, so that

$$c = 4\pi^2 (I/\tau^2) = 9.443 \times 10^{-9} \text{g cm}^2 \text{s}^{-2}/\text{rad}.$$

The observed value of $\overline{\theta^2}$, at a temperature of 287.1 K, was 4.178×10^{-6} . Substituting these numbers in (21), Kappler obtained: $k = 1.374 \times 10^{-16}$ erg K⁻¹. And, since the gas constant *R* is equal to 8.31×10^7 erg K⁻¹mole⁻¹, he obtained for the Avogadro number: $N_A = R/k = 6.06 \times 10^{23}$ mole⁻¹.

One might expect that by suspending the mirror system in an "evacuated" casing the fluctuations caused by the collisions of the air molecules could be severely reduced. This is not true because even at the lowest possible pressures there still remain a tremendously large number of molecules in the system that keep the Brownian motion "alive." The interesting part of the story, however, is that the mean square deflection of the system, caused by molecular bombardment, is not at all affected by the density of the molecules; for a system *in equilibrium*, it is determined solely by the temperature. This situation is depicted, rather dramatically, in Figure 15.6 where we have two traces of oscillations of the mirror system, the upper one having been taken at the atmospheric pressure and the lower one at a pressure of 10^{-4} mm of mercury. The root-mean-square deviation is very nearly the same in the two cases! Nevertheless, one does note a difference of "quality" between the two traces that relates to the "frequency spectrum" of the fluctuations and arises for the following reason. When the density of the surrounding gas is relatively high, the molecular impulses come in rapid succession, with the result that the *individual* deflections of the system are large in number but small in magnitude. As the pressure is lowered, the time intervals between successive impulses become longer, making the *individual* deflections smaller in number but larger in magnitude. However, the overall deflection, observed over a long interval of time, remains essentially the same.

FIGURE 15.6 Two traces of the thermal oscillations of a mirror system suspended in air; the upper trace was taken at the atmospheric pressure, the lower one at a pressure of 10^{-4} mm of mercury.