

Now, by virtue of the distribution (20), we obtain

$$\langle \mathbf{r}(t) \rangle = 0; \quad \langle r^2(t) \rangle = \frac{1}{N} \int_0^\infty n(\mathbf{r}, t) 4\pi r^4 dr = 6Dt \propto t^1, \quad (22)$$

in complete agreement with our earlier results, namely

$$\overline{x(t)} = 0; \quad \overline{x^2(t)} = l^2 t / \tau^* = 2Dt \propto t^1. \quad (23)$$

Thus, the “ensemble” of the Brownian particles, initially concentrated at the origin, “diffuses out” as time increases, the nature and the extent of its spread at any time  $t$  being given by equations (20) and (22), respectively. The diffusion process, which is clearly *irreversible*, gives us a fairly good picture of the statistical behavior of a single particle in the ensemble. However, the important thing to bear in mind is that, whether we focus our attention on a single particle in the ensemble or look at the ensemble as a whole, the ultimate source of the phenomenon lies in the incessant, and more or less random, impacts received by the Brownian particles from the molecules of the fluid. In other words, the irreversible character of the phenomenon ultimately arises from the random, fluctuating forces exerted by the fluid molecules on the Brownian particles. This leads us to another systematic theory of the Brownian motion, namely the theory of Langevin (1908). For a detailed analysis of the problem, see Uhlenbeck and Ornstein (1930), Chandrasekhar (1943, 1949), MacDonald (1948–1949), and Wax (1954).

## 15.3 The Langevin theory of the Brownian motion

We consider the simplest case of a “free” Brownian particle, surrounded by a fluid environment; the particle is assumed to be free in the sense that it is not acted on by any other force except the one arising from the molecular bombardment. The equation of motion of the particle will then be

$$M \frac{d\mathbf{v}}{dt} = \mathcal{F}(t), \quad (1)$$

where  $M$  is the particle mass,  $\mathbf{v}(t)$  the particle velocity, and  $\mathcal{F}(t)$  the force acting on the particle by virtue of the impacts received from the fluid molecules. Langevin suggested that the force  $\mathcal{F}(t)$  may be written as a sum of two parts: (i) an “averaged-out” part, which represents the *viscous drag*,  $-\mathbf{v}/B$ , experienced by the particle (accordingly,  $B$  is the *mobility* of the system, that is, the drift velocity acquired by the particle by virtue of a unit “external” force)<sup>5</sup> and (ii) a “rapidly fluctuating” part  $\mathbf{F}(t)$  which, over long intervals of

<sup>5</sup>If Stokes’s law is applicable, then  $B = 1/(6\pi\eta a)$ , where  $\eta$  is the coefficient of viscosity of the fluid and  $a$  the radius of the particle (assumed spherical).

time (as compared to the characteristic time  $\tau^*$ ), averages out to zero; thus, we may write

$$M \frac{d\mathbf{v}}{dt} = -\frac{\mathbf{v}}{B} + \mathbf{F}(t); \quad \overline{\mathbf{F}(t)} = 0. \quad (2)$$

Taking the ensemble average of (2), we obtain<sup>6</sup>

$$M \frac{d}{dt} \langle \mathbf{v} \rangle = -\frac{1}{B} \langle \mathbf{v} \rangle, \quad (3)$$

which gives

$$\langle \mathbf{v}(t) \rangle = \mathbf{v}(0) \exp(-t/\tau) \quad (\tau = MB). \quad (4)$$

Thus, the mean drift velocity of the particle decays, at a rate determined by the *relaxation time*  $\tau$ , to the ultimate value zero. We note that this result is typical of the phenomena governed by *dissipative* properties such as the viscosity of the fluid; the *irreversible* nature of the result is also evident.

Dividing (2) by the mass of the particle, we obtain an equation for the *instantaneous* acceleration, namely

$$\frac{d\mathbf{v}}{dt} = -\frac{\mathbf{v}}{\tau} + \mathbf{A}(t); \quad \overline{\mathbf{A}(t)} = 0. \quad (5)$$

We now construct the scalar product of (5) with the *instantaneous* position  $\mathbf{r}$  of the particle and take the ensemble average of the product. In doing so, we make use of the facts that (i)  $\mathbf{r} \cdot \mathbf{v} = \frac{1}{2} (dr^2/dt)$ , (ii)  $\mathbf{r} \cdot (d\mathbf{v}/dt) = \frac{1}{2} (d^2r^2/dt^2) - v^2$ , and (iii)  $\langle \mathbf{r} \cdot \mathbf{A} \rangle = 0$ .<sup>7</sup> We obtain

$$\frac{d^2}{dt^2} \langle r^2 \rangle + \frac{1}{\tau} \frac{d}{dt} \langle r^2 \rangle = 2 \langle v^2 \rangle. \quad (6)$$

If the Brownian particle has already attained thermal equilibrium with the molecules of the fluid, then the quantity  $\langle v^2 \rangle$  in this equation may be replaced by its *equipartition value*  $3kT/M$ . The equation is then readily integrated, with the result

$$\langle r^2 \rangle = \frac{6kT\tau^2}{M} \left\{ \frac{t}{\tau} - (1 - e^{-t/\tau}) \right\}, \quad (7)$$

<sup>6</sup>The process of “averaging over an ensemble” implies that we are imagining a large number of systems similar to the one originally under consideration and are taking an average over this collection at *any* time  $t$ . By the very nature of the function  $\mathbf{F}(t)$ , the ensemble average  $\langle \mathbf{F}(t) \rangle$  must be zero at all times.

<sup>7</sup>This is so because we have no reason to expect a statistical correlation between the position  $\mathbf{r}(t)$  of the Brownian particle and the force  $\mathbf{F}(t)$  exerted on it by the molecules of the fluid; see, however, Manoliu and Kittel (1979). Of course, we do expect a correlation between the variables  $\mathbf{v}(t)$  and  $\mathbf{F}(t)$ ; consequently,  $\langle \mathbf{v} \cdot \mathbf{F} \rangle \neq 0$  (see Problem 15.7).

where the constants of integration have been so chosen that at,  $t = 0$ , both  $\langle r^2 \rangle$  and its first time-derivative vanish. We observe that, for  $t \ll \tau$ ,

$$\langle r^2 \rangle \simeq \frac{3kT}{M} t^2 = \langle v^2 \rangle t^2, \quad (8)^8$$

which is consistent with the reversible equations of motion whereby one would simply have

$$\mathbf{r} = \mathbf{v}t. \quad (9)$$

On the other hand, for  $t \gg \tau$ ,

$$\langle r^2 \rangle \simeq \frac{6kT\tau}{M} t = (6BkT)t, \quad (10)^9$$

which is essentially the same as the Einstein–Smoluchowski result (15.2.22); incidentally, we obtain here a simple, but important, relationship between the coefficient of diffusion  $D$  and the mobility  $B$ , namely

$$D = BkT, \quad (11)$$

which is generally referred to as the *Einstein relation*.

The irreversible character of equation (10) is self-evident; it is also clear that it arises essentially from the viscosity of the medium. Moreover, the Einstein relation (11), which connects the coefficient of diffusion  $D$  with the mobility  $B$  of the system, tells us that the ultimate source of the viscosity of the medium (as well as of diffusion) lies in the random, fluctuating forces arising from the incessant motion of the fluid molecules; see also the fluctuation–dissipation theorem of Section 15.6.

In this context, if we consider a particle of charge  $e$  and mass  $M$  moving in a viscous fluid under the influence of an external electric field of intensity  $E$ , then the “coarse-grained” motion of the particle will be determined by the equation

$$M \frac{d}{dt} \langle \mathbf{v} \rangle = -\frac{1}{B} \langle \mathbf{v} \rangle + e\mathbf{E}; \quad (12)$$

compare this to equation (3). The “terminal” drift velocity of the particle would now be given by the expression  $(eB)\mathbf{E}$ , which prompts one to define  $(eB)$  as the “mobility” of the system and denote it by the symbol  $\mu$ . Consequently, one obtains, instead of (11),

$$D = \frac{kT}{e} \mu, \quad (13)$$

which, in fact, is the original version of the Einstein relation; sometimes this is also referred to as the *Nernst relation*.

<sup>8</sup>Note that the limiting solution (8) corresponds to “dropping out” the second term on the left side of equation (6).

<sup>9</sup>Note that the limiting solution (10) corresponds to “dropping out” the first term on the left side of equation (6).

So far we have not felt any *direct* influence of the rapidly fluctuating term  $\mathbf{A}(t)$  that appears in the equation of motion (5) of the Brownian particle. For this, let us try to evaluate the quantity  $\langle v^2(t) \rangle$  which, in the preceding analysis, was assumed to have already attained its “limiting” value  $3kT/M$ . For this evaluation we replace the variable  $t$  in equation (5) by  $u$ , multiply both sides of the equation by  $\exp(u/\tau)$ , rearrange and integrate over  $du$  between the limits  $u = 0$  and  $u = t$ ; we thus obtain the formal solution

$$\mathbf{v}(t) = \mathbf{v}(0)e^{-t/\tau} + e^{-t/\tau} \int_0^t e^{u/\tau} \mathbf{A}(u) du. \quad (14)$$

Thus, the drift velocity  $\mathbf{v}(t)$  of the particle is also a fluctuating function of time; of course, since  $\langle \mathbf{A}(u) \rangle = 0$  for all  $u$ , the *average* drift velocity is given by the first term alone, namely

$$\langle \mathbf{v}(t) \rangle = \mathbf{v}(0)e^{-t/\tau}, \quad (15)$$

which is the same as our earlier result (4). For the mean square velocity  $\langle v^2(t) \rangle$ , we now obtain from (14)

$$\begin{aligned} \langle v^2(t) \rangle &= v^2(0)e^{-2t/\tau} + 2e^{-2t/\tau} \left[ \mathbf{v}(0) \cdot \int_0^t e^{u/\tau} \langle \mathbf{A}(u) \rangle du \right] \\ &\quad + e^{-2t/\tau} \int_0^t \int_0^t e^{(u_1+u_2)/\tau} \langle \mathbf{A}(u_1) \cdot \mathbf{A}(u_2) \rangle du_1 du_2. \end{aligned} \quad (16)$$

The second term on the right side of this equation is identically zero, because  $\langle \mathbf{A}(u) \rangle$  vanishes for all  $u$ . In the third term, we have the quantity  $\langle \mathbf{A}(u_1) \cdot \mathbf{A}(u_2) \rangle$ , which is a measure of the “statistical correlation between the value of the fluctuating variable  $\mathbf{A}$  at time  $u_1$  and its value at time  $u_2$ ”; we call it the *autocorrelation function* of the variable  $\mathbf{A}$  and denote it by the symbol  $K_A(u_1, u_2)$  or simply by  $K(u_1, u_2)$ . Before proceeding with (16) any further, we place on record some of the important properties of the function  $K(u_1, u_2)$ .

- (i) In a stationary ensemble (i.e., one in which the overall macroscopic behavior of the systems does not change with time), the function  $K(u_1, u_2)$  depends only on the time interval  $(u_2 - u_1)$ . Denoting this interval by the symbol  $s$ , we have

$$K(u_1, u_1 + s) \equiv \langle \mathbf{A}(u_1) \cdot \mathbf{A}(u_1 + s) \rangle = K(s), \text{ independently of } u_1. \quad (17)$$

- (ii) The quantity  $K(0)$ , which is identically equal to the mean square value of the variable  $\mathbf{A}$  at time  $u_1$ , must be *positive definite*. In a stationary ensemble, it would be a constant, independent of  $u_1$ :

$$K(0) = \text{const.} > 0. \quad (18)$$

- (iii) For any value of  $s$ , the magnitude of the function  $K(s)$  cannot exceed  $K(0)$ .

*Proof:* Since

$$\begin{aligned}\langle |\mathbf{A}(u_1) \pm \mathbf{A}(u_2)|^2 \rangle &= \langle A^2(u_1) \rangle + \langle A^2(u_2) \rangle \pm 2\langle \mathbf{A}(u_1) \cdot \mathbf{A}(u_2) \rangle \\ &= 2\{K(0) \pm K(s)\} \geq 0,\end{aligned}$$

the function  $K(s)$  cannot go outside the limits  $-K(0)$  and  $+K(0)$ ; consequently,

$$|K(s)| \leq K(0) \quad \text{for all } s. \quad (19)$$

(iv) The function  $K(s)$  is symmetric about the value  $s = 0$ , that is,

$$K(-s) = K(s) = K(|s|). \quad (20)$$

*Proof:*

$$\begin{aligned}K(s) &\equiv \langle \mathbf{A}(u_1) \cdot \mathbf{A}(u_1 + s) \rangle = \langle \mathbf{A}(u_1 - s) \cdot \mathbf{A}(u_1) \rangle^{10} \\ &= \langle \mathbf{A}(u_1) \cdot \mathbf{A}(u_1 - s) \rangle \equiv K(-s).\end{aligned}$$

(v) As  $s$  becomes large in comparison with the characteristic time  $\tau^*$ , the values  $\mathbf{A}(u_1)$  and  $\mathbf{A}(u_1 + s)$  become *uncorrelated*, that is

$$K(s) \equiv \langle \mathbf{A}(u_1) \cdot \mathbf{A}(u_1 + s) \rangle \xrightarrow{s \gg \tau^*} \langle \mathbf{A}(u_1) \rangle \cdot \langle \mathbf{A}(u_1 + s) \rangle = 0. \quad (21)$$

In other words, the “memory” of the molecular impacts received during a given interval of time, say between  $u_1$  and  $u_1 + du_1$ , is “completely lost” after a lapse of time large in comparison with  $\tau^*$ . It follows that the magnitude of the function  $K(s)$  is significant only so long as the variable  $s$  is of the same order of magnitude as  $\tau^*$ .

Figures 15.7 through 15.9 later in this chapter show the  $s$ -dependence of certain typical correlation functions  $K(s)$ ; they fully conform to the properties listed here.

We now evaluate the double integral appearing in (16):

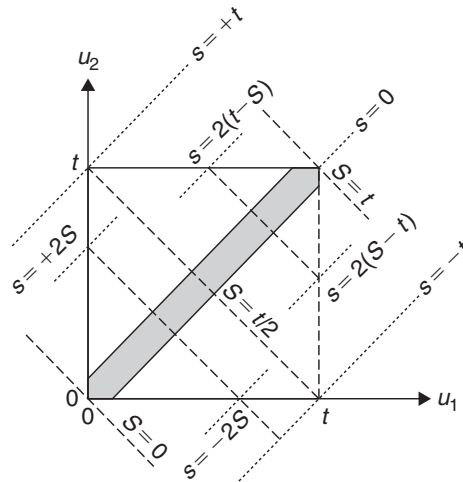
$$I = \int_0^t \int_0^t e^{(u_1+u_2)/\tau} K(u_2 - u_1) du_1 du_2. \quad (22)$$

Changing over to the variables

$$S = \frac{1}{2}(u_1 + u_2) \quad \text{and} \quad s = (u_2 - u_1), \quad (23)$$

the integrand becomes  $\exp(2S/\tau)K(s)$ , the element  $(du_1 du_2)$  gets replaced by the corresponding element  $(dS ds)$  while the limits of integration, in terms of the variables  $S$  and  $s$ ,

<sup>10</sup>This is the only crucial step in the proof. It involves a “shift,” by an amount  $s$ , in both instants of the measurement process; the equality results from the fact that the ensemble is supposed to be stationary.



**FIGURE 15.2** Limits of integration, of the double integral  $I$ , in terms of the variables  $S$  and  $s$ .

can be read from [Figure 15.2](#); we find that, for  $0 \leq S \leq t/2$ ,  $s$  goes from  $-2S$  to  $+2S$  while, for  $t/2 \leq S \leq t$ , it goes from  $-2(t-S)$  to  $+2(t-S)$ . Accordingly,

$$I = \int_0^{t/2} e^{2S/\tau} dS \int_{-2S}^{+2S} K(s) ds + \int_{t/2}^t e^{2S/\tau} dS \int_{-2(t-S)}^{+2(t-S)} K(s) ds. \quad (24)$$

In view of property (v) of the function  $K(s)$ , see [equation \(21\)](#), the integrals over  $s$  draw significant contribution only from a very narrow region, of the order of  $\tau^*$ , around the value  $s = 0$  (i.e., from the shaded region in [Figure 15.2](#)); contributions from regions with larger values of  $|s|$  are negligible. Thus, if  $t \gg \tau^*$ , the limits of integration for  $s$  may be replaced by  $-\infty$  and  $+\infty$ , with the result

$$I \simeq C \int_0^t e^{2S/\tau} dS = C \frac{\tau}{2} (e^{2t/\tau} - 1), \quad (25)$$

where

$$C = \int_{-\infty}^{\infty} K(s) ds. \quad (26)$$

Substituting [\(25\)](#) into [\(16\)](#), we obtain

$$\langle v^2(t) \rangle = v^2(0) e^{-2t/\tau} + C \frac{\tau}{2} (1 - e^{-2t/\tau}). \quad (27)$$

Now, as  $t \rightarrow \infty$ ,  $\langle v^2(t) \rangle$  must tend to the equipartition value  $3kT/M$ ; therefore,

$$C = 6kT/M\tau \quad (28)$$

and hence

$$\langle v^2(t) \rangle = v^2(0) + \left\{ \frac{3kT}{M} - v^2(0) \right\} (1 - e^{-2t/\tau}). \quad (29)^{11}$$

We note that if  $v^2(0)$  were itself equal to the equipartition value  $3kT/M$ , then  $\langle v^2(t) \rangle$  would always remain the same, which shows that statistical equilibrium, once attained, has a natural tendency to persist.

Substituting (29) into the right side of (6), we obtain a more representative description of the manner in which the quantity  $\langle r^2 \rangle$  varies with  $t$ ; we thus have

$$\frac{d^2}{dt^2} \langle r^2 \rangle + \frac{1}{\tau} \frac{d}{dt} \langle r^2 \rangle = 2v^2(0)e^{-2t/\tau} + \frac{6kT}{M}(1 - e^{-2t/\tau}), \quad (30)$$

with the solution

$$\langle r^2 \rangle = v^2(0)\tau^2(1 - e^{-t/\tau})^2 - \frac{3kT}{M}\tau^2(1 - e^{-t/\tau})(3 - e^{-t/\tau}) + \frac{6kT\tau}{M}t. \quad (31)$$

Solution (31) satisfies the initial conditions that both  $\langle r^2 \rangle$  and its first time-derivative vanish at  $t = 0$ ; moreover, if we put  $v^2(0) = 3kT/M$ , it reduces to solution (7) obtained earlier. Once again, we note the *reversible* nature of the motion for  $t \ll \tau$ , with  $\langle r^2 \rangle \simeq v^2(0)t^2$ , and its *irreversible* nature for  $t \gg \tau$ , with  $\langle r^2 \rangle \simeq (6BkT)t$ .

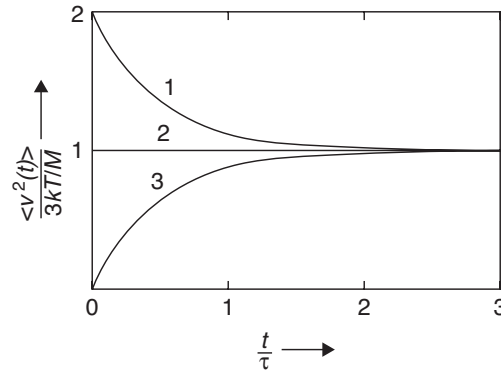
Figures 15.3 and 15.4 show the variation, with time, of the ensemble averages  $\langle v^2(t) \rangle$  and  $\langle r^2(t) \rangle$  of a Brownian particle, as given by equations (29) and (31), respectively. All important features of our results are manifestly evident in these plots.

Brownian motion continues to be a topic of contemporary research nearly 200 years after Brown's discovery and over 100 years after Einstein and Smoluchowski's analysis and early measurements by Perrin. The renewed interest is due to the growth in the technological importance of colloids across a wide range of fields and the development of digital video and computer image analysis. An interesting example is the detailed observation and analysis of rotational and two-dimensional translational Brownian motion of ellipsoidal particles by Han et al. (2006) in a thin microscope slide. The case of rotational Brownian motion was first analyzed by Einstein (1906b) and first measured by Perrin (1934, 1936). Both rotational and translational modes diffuse according to Langevin dynamics but the translational diffusion is coupled to the rotational diffusion since the translational diffusion constant parallel to the longer axis is larger than the diffusion constant perpendicular

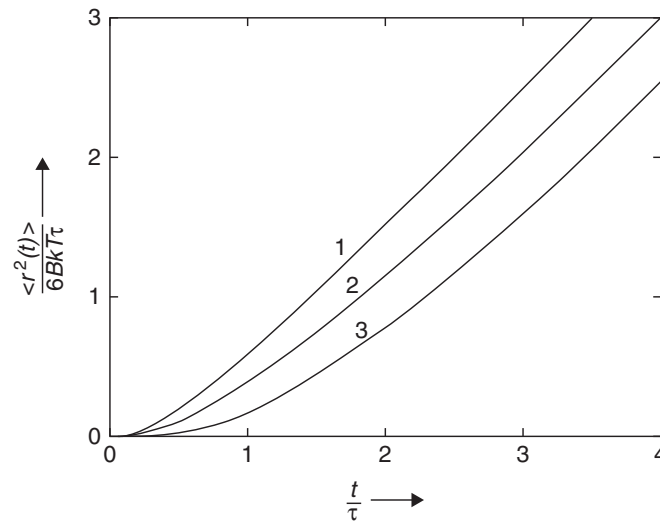
<sup>11</sup>One may check that

$$\frac{d}{dt} \langle v^2(t) \rangle = \frac{2}{\tau} \left[ v^2(\infty) - \langle v^2(t) \rangle \right] = -\frac{2}{\tau} \Delta \langle v^2(t) \rangle,$$

where  $v^2(\infty) = 3kT/M$  and  $\Delta \langle v^2(t) \rangle$  is the "deviation of the quantity concerned from its equilibrium value." In this form of the equation, we have a typical example of a "relaxation phenomenon," with *relaxation time*  $\tau/2$ .



**FIGURE 15.3** The mean square velocity of a Brownian particle as a function of time. Curves 1, 2, and 3 correspond, respectively, to the initial conditions  $v^2(0) = 6kT/M, 3kT/M$ , and 0.



**FIGURE 15.4** The mean square displacement of a Brownian particle as a function of time. Curves 1, 2, and 3 correspond, respectively, to the initial conditions  $v^2(0) = 6kT/M, 3kT/M$ , and 0.

to that axis. The rotational diffusion and both long-axis (a) and short-axis (b) body-frame diffusions are all Gaussian:

$$p_{\theta}(\Delta\theta, t) = \frac{1}{\sqrt{4\pi D_{\theta}t}} \exp\left(-\frac{(\Delta\theta)^2}{4D_{\theta}t}\right), \quad (32a)$$

$$p_a(\Delta x_a, t) = \frac{1}{\sqrt{4\pi D_a t}} \exp\left(-\frac{(\Delta x_a)^2}{4D_a t}\right), \quad (32b)$$

$$p_b(\Delta x_b, t) = \frac{1}{\sqrt{4\pi D_b t}} \exp\left(-\frac{(\Delta x_b)^2}{4D_b t}\right), \quad (32c)$$



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

### 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

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

where  $\gamma (= 6\pi\eta a/M)$  is the damping coefficient of a spherical particle in a fluid with viscosity  $\eta$ . 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

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

where

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

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

$$v(t) = \int_{-\infty}^t \chi_{vx}(t-t')F(t')dt', \quad (36)$$

<sup>12</sup>This form of the response function assumes that the oscillator is underdamped. The notation  $\chi_{xx}$  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  $-F(t)x(t)$ .

of an argument involving the second law of thermodynamics and the exchange of energy between two resistances in thermal equilibrium.<sup>19</sup>

## 15.6 The fluctuation–dissipation theorem

In [Section 15.3](#) we obtained a result of considerable importance, namely

$$\begin{aligned} \frac{1}{B} &\equiv \frac{M}{\tau} = \frac{M^2}{6kT} C = \frac{M^2}{6kT} \int_{-\infty}^{\infty} K_A(s) ds \\ &= \frac{1}{6kT} \int_{-\infty}^{\infty} K_F(s) ds; \end{aligned} \quad (1)$$

see [equations \(15.3.4\)](#), [\(15.3.26\)](#), and [\(15.3.28\)](#). Here,  $K_A(s)$  and  $K_F(s)$  are, respectively, the autocorrelation functions of the fluctuating acceleration  $\mathbf{A}(t)$  and the fluctuating force  $\mathbf{F}(t)$  experienced by the Brownian particle:

$$K_A(s) = \langle \mathbf{A}(0) \cdot \mathbf{A}(s) \rangle = \frac{1}{M^2} \langle \mathbf{F}(0) \cdot \mathbf{F}(s) \rangle = \frac{1}{M^2} K_F(s). \quad (2)^{20}$$

[Equation \(1\)](#) establishes a fundamental relationship between the coefficient,  $1/B$ , of the “averaged-out” part of the total force  $\mathcal{F}(t)$  experienced by the Brownian particle due to the impacts of the fluid molecules and the statistical character of the “fluctuating” part,  $F(t)$ , of that force; see Langevin’s [equation \(15.3.2\)](#). In other words, it relates the coefficient of viscosity of the fluid, which represents *dissipative* forces operating in the system, with the temporal character of the molecular *fluctuations*; the content of [equation \(1\)](#) is, therefore, referred to as a *fluctuation–dissipation theorem*.

The most striking feature of this theorem is that it relates, in a fundamental manner, the fluctuations of a physical quantity pertaining to the *equilibrium state* of a given system to a dissipative process which, in practice, is realized only when the system is subject to an external force that drives it *away from equilibrium*. Consequently, it enables us to determine the *nonequilibrium properties* of the given system on the basis of a knowledge of the thermal fluctuations occurring in the system when the system is in one of its *equilibrium*

<sup>19</sup>We note that the foregoing results are essentially equivalent to Einstein’s original result for charge fluctuations in a conductor, namely

$$\langle \delta q^2 \rangle_t = \frac{2kT}{R} t;$$

compare, as well, the Brownian-particle result:  $\langle x^2 \rangle_t = 2Bkt$ .

<sup>20</sup>We note that the functions  $K_A(s)$  and  $K_F(s)$ , which are nonzero only for  $s = O(\tau^*)$ , see [equation \(15.3.21\)](#), may, for certain purposes, be written as

$$K_A(s) = \frac{6kT}{M^2 B} \delta(s) \quad \text{and} \quad K_F(s) = \frac{6kT}{B} \delta(s).$$

In this form, the functions are nonzero only for  $s = 0$ .

states! For an expository account of the fluctuation–dissipation theorem, the reader may refer to Kubo (1966).

At this stage we recall that in [equation \(15.3.11\)](#) we obtained a relationship between the *diffusion coefficient*  $D$  and the *mobility*  $B$ , namely  $D = BkT$ . Combining this with [equation \(1\)](#), we get

$$\frac{1}{D} = \frac{1}{6(kT)^2} \int_{-\infty}^{\infty} K_F(s) ds. \quad (3)$$

Now, the diffusion coefficient  $D$  can be related directly to the autocorrelation function  $K_v(s)$  of the fluctuating variable  $\mathbf{v}(t)$ . For this, one starts with the observation that, by definition,

$$\mathbf{r}(t) = \int_0^t \mathbf{v}(u) du, \quad (4)$$

which gives

$$\langle r^2(t) \rangle = \int_0^t \int_0^t \langle \mathbf{v}(u_1) \cdot \mathbf{v}(u_2) \rangle du_1 du_2. \quad (5)$$

Proceeding in the same manner as for the integral in [equation \(15.3.22\)](#), one obtains

$$\langle r^2(t) \rangle = \int_0^{t/2} dS \int_{-2S}^{+2S} K_v(s) ds + \int_{t/2}^t dS \int_{-2(t-S)}^{+2(t-S)} K_v(s) ds; \quad (6)$$

compare this to [equation \(15.3.24\)](#).

The function  $K_v(s)$  can be determined by making use of expression [\(15.3.14\)](#) for  $\mathbf{v}(t)$  and following exactly the same procedure as for determining the quantity  $\langle v^2(t) \rangle$ , which is nothing but the maximal value,  $K_v(0)$ , of the desired function. Thus, one obtains

$$K_v(s) = \begin{cases} v^2(0)e^{-(2t+s)/\tau} + \frac{3kT}{M}e^{-s/\tau}(1 - e^{-2t/\tau}) & \text{for } s > 0 \\ v^2(0)e^{-(2t+s)/\tau} + \frac{3kT}{M}e^{s/\tau}(1 - e^{-2(t+s)/\tau}) & \text{for } s < 0; \end{cases} \quad (7)$$

compare these results to [equation \(15.3.27\)](#). It is easily seen that formulae (7) and (8) can be combined into a single one, namely

$$K_v(s) = v^2(0)e^{-|s|/\tau} + \left\{ \frac{3kT}{M} - v^2(0) \right\} (e^{-|s|/\tau} - e^{-(2t+s)/\tau}) \quad \text{for all } s; \quad (9)$$

compare this to [equation \(15.3.29\)](#). In the case of a “stationary ensemble,”

$$K_v(s) = \frac{3kT}{M} e^{-|s|/\tau}, \quad (10)$$

which is consistent with property [\(15.3.20\)](#). It should be noted that the time scale for the correlation function  $K_v(s)$  is provided by the *relaxation time*  $\tau$  of the Brownian motion, which is many orders of magnitude larger than the *characteristic time*  $\tau^*$  that provides the time scale for the correlation functions  $K_A(s)$  and  $K_F(s)$ .

It is now instructive to verify that the substitution of expression [\(10\)](#) into [\(6\)](#) leads to formula [\(15.3.7\)](#) for  $\langle r^2 \rangle$ , while the substitution of the more general expression [\(9\)](#) leads to formula [\(15.3.31\)](#); see Problem 15.17. In either case,

$$\langle r^2 \rangle \xrightarrow[t \gg \tau]{} 6Dt. \quad (11)$$

In the same limit, [equation \(6\)](#) reduces to

$$\langle r^2 \rangle \simeq \int_0^t dS \int_{-\infty}^{\infty} K_v(s) ds = t \int_{-\infty}^{\infty} K_v(s) ds. \quad (12)$$

Comparing the two results, we obtain the desired relationship:

$$D = \frac{1}{6} \int_{-\infty}^{\infty} K_v(s) ds. \quad (13)$$

In passing, we note, from [equations \(3\)](#) and [\(13\)](#), that

$$\int_{-\infty}^{\infty} K_v(s) ds \int_{-\infty}^{\infty} K_F(s) ds = (6kT)^2; \quad (14)$$

see also Problem 15.7.

It is not surprising that the equations describing a fluctuation–dissipation theorem can be adapted to any situation that involves a dissipative mechanism. For instance, fluctuations in the motion of electrons in an electric resistor give rise to a “spontaneous” thermal e.m.f., which may be denoted as  $\mathcal{B}(t)$ . In the spirit of the Langevin theory, this e.m.f. may be split into two parts: (i) an “averaged-out” part,  $-RI(t)$ , which represents the resistive (or dissipative) aspect of the situation, and (ii) a “rapidly fluctuating” part,  $V(t)$ , which, over long intervals of time, averages out to zero. The “spontaneous” current in the resistor is then given by the equation

$$L \frac{dI}{dt} = -RI + V(t); \quad \langle V(t) \rangle = 0. \quad (15)$$

Comparing this with the *Langevin equation* (15.3.2) and pushing the analogy further, we infer that there exists a direct relationship between the resistance  $R$  and the temporal character of the fluctuations in the variable  $\mathbf{V}(t)$ . In view of equations (1) and (13), this relationship would be

$$R = \frac{1}{6kT} \int_{-\infty}^{\infty} \langle \mathbf{V}(0) \cdot \mathbf{V}(s) \rangle ds \quad (16)$$

or, equivalently,

$$\frac{1}{R} = \frac{1}{6kT} \int_{-\infty}^{\infty} \langle \mathbf{I}(0) \cdot \mathbf{I}(s) \rangle ds. \quad (17)$$

A generalization of the foregoing result has been given by Kubo (1957, 1959); see, for instance, Problem 6.19 in Kubo (1965), or Section 23.2 of Wannier (1966). On generalization, the *electric current density*  $\mathbf{j}(t)$  is given by the expression

$$j_i(t) = \sum_l \int_{-\infty}^t E_l(t') \Phi_{li}(t-t') dt' \quad (i, l = x, y, z); \quad (18)$$

here,  $\mathbf{E}(t)$  denotes the applied electric field while

$$\Phi_{li}(s) = \frac{1}{kT} \langle j_l(0) j_i(s) \rangle. \quad (19)$$

Clearly, the quantities  $kT\Phi_{li}(s)$  are the components of the *autocorrelation tensor* of the fluctuating vector  $\mathbf{j}(t)$ . In particular, if we consider the static case  $\mathbf{E} = (E, 0, 0)$ , we obtain for the *conductivity* of the system

$$\begin{aligned} \sigma_{xx} &\equiv \frac{j_x}{E} = \int_{-\infty}^t \Phi_{xx}(t-t') dt' = \int_0^{\infty} \Phi_{xx}(s) ds \\ &= \frac{1}{2kT} \int_{-\infty}^{\infty} \langle j_x(0) j_x(s) \rangle ds, \end{aligned} \quad (20)$$

which may be compared with equation (17). If, on the other hand, we take  $\mathbf{E} = (E \cos \omega t, 0, 0)$ , we obtain instead

$$\sigma_{xx}(\omega) = \frac{1}{2kT} \int_{-\infty}^{\infty} \langle j_x(0) j_x(s) \rangle e^{-i\omega s} ds. \quad (21)$$

Taking the inverse of (21), we get

$$\langle j_x(0)j_x(s) \rangle = \frac{kT}{\pi} \int_{-\infty}^{\infty} \sigma_{xx}(\omega) e^{i\omega s} d\omega. \quad (22)$$

If we now assume that  $\sigma_{xx}(\omega)$  does not depend on  $\omega$  (and may, therefore, be denoted by the simpler symbol  $\sigma$ ), then

$$\langle j_x(0)j_x(s) \rangle = (2kT\sigma)\delta(s); \quad (23)$$

see footnote 20. A reference to equations (15.5.17) shows that, in the present approximation, thermal fluctuations in the electric current are characterized by a “white” noise.

### 15.6.A Derivation of the fluctuation–dissipation theorem from linear response theory

In this section we will show that the nonequilibrium response of a thermodynamic system to a small driving force is very generally related to the time-dependence of equilibrium fluctuations. In hindsight, this is not too surprising since natural fluctuations about the equilibrium state also induce small deviations of observables from their average values. The response of the system to these natural fluctuations should be the same as the response of the system to deviations from the equilibrium state as caused by small driving forces; see Martin (1968), Forster (1975), and Mazenko (2006).

Let us compute the time-dependent changes to an observable  $A$  caused by a small time-dependent external applied field  $h(t)$  that couples linearly to some observable  $B$ . The Hamiltonian for the system then becomes

$$H(t) = H_0 - h(t)B, \quad (24)$$

where  $H_0$  is the unperturbed Hamiltonian in the equilibrium state. Remarkably, the calculation for determining the nonequilibrium response to the driving field is easiest using the quantum-mechanical density matrix approach developed in Section 5.1. The equilibrium density matrix is given by

$$\hat{\rho}_{\text{eq}} = \frac{\exp(-\beta H_0)}{\text{Tr}(\exp(-\beta H_0))}, \quad (25)$$

where equilibrium averages involve traces over the density matrix:

$$\langle A \rangle_{\text{eq}} = \text{Tr}(A\hat{\rho}_{\text{eq}}). \quad (26)$$

When the Hamiltonian includes a small time-dependent field  $h(t)$ , then this additional term drives the system slightly out of equilibrium. We will assume that the field was zero in the distant past so the system was initially in the equilibrium state defined by the