of an argument involving the second law of thermodynamics and the exchange of energy between two resistances in thermal equilibrium.[19]

15.6 The fluctuation–dissipation theorem

In Section 15.3 we obtained a result of considerable importance, namely

$$\frac{1}{B} \equiv \frac{M}{\tau} = \frac{M^2}{6kT} C = \frac{M^2}{6kT} \int_{-\infty}^{\infty} K_{\boldsymbol{A}}(s) ds$$
$$= \frac{1}{6kT} \int_{-\infty}^{\infty} K_{\boldsymbol{F}}(s) ds; \tag{1}$$

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

$$K_{\boldsymbol{A}}(s) = \langle \boldsymbol{A}(0) \cdot \boldsymbol{A}(s) \rangle = \frac{1}{M^2} \langle \boldsymbol{F}(0) \cdot \boldsymbol{F}(s) \rangle = \frac{1}{M^2} K_{\boldsymbol{F}}(s). \qquad (2)^{20}$$

Equation (1) establishes a fundamental relationship between the coefficient, $1/B$, of the "averaged-out" part of the total force $\boldsymbol{\mathcal{F}}(t)$ 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*

[19] We note that the foregoing results are essentially equivalent to Einstein's original result for charge fluctuations in a conductor, namely

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

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

[20] We note that the functions $K_{\boldsymbol{A}}(s)$ and $K_{\boldsymbol{F}}(s)$, which are nonzero only for $s = O(\tau^*)$, see equation (15.3.21), may, for certain purposes, be written as

$$K_{\boldsymbol{A}}(s) = \tfrac{6kT}{M^2 B} \delta(s) \quad \text{and} \quad K_{\boldsymbol{F}}(s) = \tfrac{6kT}{B} \delta(s).$$

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

$$\frac{1}{D} = \frac{1}{6(kT)^2} \int_{-\infty}^{\infty} K_{\boldsymbol{F}}(s)ds. \tag{3}$$

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

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

which gives

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

Proceeding in the same manner as for the integral in equation (15.3.22), one obtains

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

compare this to equation (15.3.24).

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

$$K_{\boldsymbol{v}}(s) = \begin{cases} v^2(0)e^{-(2t+s)/\tau} + \dfrac{3kT}{M}e^{-s/\tau}(1-e^{-2t/\tau}) & \text{for} \quad s>0 \qquad (7) \\ v^2(0)e^{-(2t+s)/\tau} + \dfrac{3kT}{M}e^{s/\tau}(1-e^{-2(t+s)/\tau}) & \text{for} \quad s<0; \qquad (8) \end{cases}$$

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

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

compare this to equation (15.3.29). In the case of a "stationary ensemble,"

$$K_{\boldsymbol{v}}(s) = \frac{3kT}{M} e^{-|s|/\tau}, \tag{10}$$

which is consistent with property (15.3.20). It should be noted that the time scale for the correlation function $K_{\boldsymbol{v}}(s)$ is provided by the *relaxation time* τ of the Brownian motion, which is many orders of magnitude larger than the *characteristic time* τ^* that provides the time scale for the correlation functions $K_{\boldsymbol{A}}(s)$ and $K_{\boldsymbol{F}}(s)$.

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,

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

In the same limit, equation (6) reduces to

$$\langle r^2 \rangle \simeq \int_0^t dS \int_{-\infty}^{\infty} K_{\boldsymbol{v}}(s) ds = t \int_{-\infty}^{\infty} K_{\boldsymbol{v}}(s) ds. \tag{12}$$

Comparing the two results, we obtain the desired relationship:

$$D = \frac{1}{6} \int_{-\infty}^{\infty} K_{\boldsymbol{v}}(s) ds. \tag{13}$$

In passing, we note, from equations (3) and (13), that

$$\int_{-\infty}^{\infty} K_{\boldsymbol{v}}(s) ds \int_{-\infty}^{\infty} K_{\boldsymbol{F}}(s) ds = (6kT)^2; \tag{14}$$

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 $\boldsymbol{\mathcal{B}}(t)$. In the spirit of the Langevin theory, this e.m.f. may be split into two parts: (i) an "averaged-out" part, $-R\boldsymbol{I}(t)$, which represents the resistive (or dissipative) aspect of the situation, and (ii) a "rapidly fluctuating" part, $\boldsymbol{V}(t)$, which, over long intervals of time, averages out to zero. The "spontaneous" current in the resistor is then given by the equation

$$L\frac{d\boldsymbol{I}}{dt} = -R\boldsymbol{I} + \boldsymbol{V}(t); \quad \langle \boldsymbol{V}(t) \rangle = 0. \tag{15}$$

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 $\boldsymbol{V}(t)$. In view of equations (1) and (13), this relationship would be

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

or, equivalently,

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

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* $\boldsymbol{j}(t)$ is given by the expression

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

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

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

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

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

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

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

Taking the inverse of (21), we get

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

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

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

see footnote 20. A reference to equations (15.5.17) shows that, in the present approximation, thermal fluctuations in the electric current are charaterized 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

$$H(t) = H_0 - h(t)B, \tag{24}$$

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

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

where equilibrium averages involve traces over the density matrix:

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

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