The fluctuation–dissipation theorem

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Abstract. The linear response theory has given a general proof of the fluctuation–dissipation theorem which states that the linear response of a given system to an external perturbation is expressed in terms of fluctuation properties of the system in thermal equilibrium. This theorem may be represented by a stochastic equation describing the fluctuation, which is a generalization of the familiar Langevin equation in the classical theory of Brownian motion. In this generalized equation the friction force becomes retarded or frequency-dependent and the random force is no more white. They are related to each other by a generalized Nyquist theorem which is in fact another expression of the fluctuation–dissipation theorem. This point of view can be applied to a wide class of irreversible process including collective modes in many-particle systems as has already been shown by Mori. As an illustrative example, the density response problem is briefly discussed.

1. Introduction

Let us begin with a very simple example of the Brownian motion of colloidal particles floating in a liquid medium or of a small mirror suspended in a rarefied gas. Under an ultramicroscope one can observe irregular motion of colloidal particles or, by reflection of a light beam, an irregular oscillation of the mirror. Such a random motion of colloidal particles, or of the suspended mirror, is well known as direct evidence of thermal molecular motion, which is, of course, the very basis of the microscopic theory of the structure of matter, because the random force driving the particles or the mirror is apparently due to the impacts exerted by the liquid molecules or the gas molecules. These are classical examples of the Brownian motion which always exists, even in thermal equilibrium, as a fluctuation.

Now suppose an external force is applied as a driving force. The Brownian particles, if they are charged, can be driven by an external electric field. The

mirror is driven by a suitable electromagnetic device such as is used for galvano-meters. Such a forced motion always suffers from a friction or a resistive force. It results from impacts of molecules on the particle or the mirror. Although molecular collisions are random, a number of the collisions produce a systematic result proportional to the velocity of the particle or the angular velocity of the mirror.

Thus random impacts of surrounding molecules generally cause two kinds of effect: firstly, they act as a random driving force on the Brownian particle or the mirror to maintain its incessant irregular motion, and, secondly, they give rise to the frictional force for a forced motion. The first is the *systematic* part of the effect and the second is the *random* part. This in turn means that the frictional force and the random force must be related, because both come from the same origin. This internal relationship between the systematic and the random parts of *microscopic forces* is, in fact, a very general matter, which is manifested in the so-called *fluctuation–dissipation theorem.*

As we shall see in the following, this theorem states a general relationship between the response of a given system to an external disturbance and the internal fluctuation of the system in the absence of the disturbance. Such a response is characterized by a response function or equivalently by an admittance, or an impedance. The internal fluctuation is characterized by a correlation function of relevant physical quantities of the system fluctuating in thermal equilibrium, or equivalently by their fluctuation spectra. The fluctuation–dissipation theorem can thus be used in two ways: it can predict the characteristics of the fluctuation or the noise intrinsic to the system from the known characteristics of the admittance or the impedance, or it can be used as the basic formula to derive the admittance from the analysis of thermal fluctuations of the system. The Nyquist theorem is a classical example of the first category (Nyquist 1928), whereas, perhaps, Onsager's proof of the symmetry of kinetic coefficients is the oldest example of the second (Onsager 1931).

It is somewhat surprising that, in spite of a long history of the basic idea of the fluctuation–dissipation theorem, the importance of this theorem has only recently been realized to the full extent as fundamental to the statistical mechanics of non-equilibrium states or of irreversible processes in general (Kubo 1957, 1959). This is partly because, in non-equilibrium theory, the traditional methods such as the Boltzmann equation had been believed to be the only tool to use. There had been, of course, various attempts along the lines of the fluctuation–dissipation theorem by Einstein, Nyquist and Onsager in the old days, but it was some years before a new development was started by Callen and Welton (1951), Callen and Greene (1952), Takahashi (1952), Kubo and Tomita (1954), Green (1952, 1954), Mori (1956), Nakano (1956), Kubo (1957) and by some others. Thus, in the last ten years or so, a great number of papers appeared on this and related subjects. The present article is not intended, however, to be a comprehensive review of these recent developments, for which the reader is referred to the articles by Chester (1963) and Zwanzig (1965) particularly for extensive lists of literature, but it is meant to be an introduction to a modern aspect of the fluctuation–dissipation theorem with a complementary nature to a previous review article of the author (Kubo 1965) and with an emphasis on the viewpoint of stochastic considerations which has recently been studied by Mori (1965 a) and the author (Kubo 1966).

2. Einstein relation

Many years ago Einstein (1905) noticed that the viscous friction of a Brownian particle must be related to the diffusion constant of the particle by the equation

$$D = kT/m\gamma \tag{2.1}$$

where D is the diffusion constant and $m\gamma$ is the friction constant. In the presence of a given potential field $V(x)$, particles flow with the drift velocity

$$u_\mathrm{d} = -\frac{dV/dx}{m\gamma} \tag{2.2}$$

which is opposed by the diffusion current, so that the net current is given by

$$j(x) = -D\frac{\partial f(x)}{\partial x} + u_\mathrm{d} f(x) \tag{2.3}$$

where $f(x)$ is the concentration at the position x. Vanishing of this net current in equilibrium requires the Einstein relation (2.1), because $f(x)$ then must have the form $f(x) \propto \exp(-V/kT)$.

Diffusion processes are observed in the presence of a non-uniformity in the concentration of the colloidal particles, but it is an obvious result of random migration of particles which is actually observed under a microscope as the Brownian motion. If a marked particle covers a distance x in one-dimensional projection, in a given time t, we may talk of the probability distribution of x, which (as is well known) is given by the solution of a diffusion equation; the diffusion constant D is identified with that which governs the diffusion process in a non-uniform colloidal solution. Therefore we may assume that

$$D = \lim_{t\to\infty} \frac{1}{2t} \langle \{x(t)-x(0)\}^2 \rangle \tag{2.4}$$

where the average $\langle\,\rangle$ is taken over an ensemble in thermal equilibrium. Since we have

$$x(t) - x(0) = \int_0^t u(t')\,dt'$$

equation (2.4) is transformed as

$$
\begin{aligned}
D &= \lim_{t\to\infty} \frac{1}{2t} \int_0^t dt_1 \int_0^t dt_2 \langle u(t_1)\,u(t_2)\rangle \\
&= \lim_{t\to\infty} \frac{1}{t} \int_0^t dt_1 \int_0^{t-t_1} dt' \langle u(t_1)\,u(t_1+t')\rangle \\
&= \int_0^\infty \langle u(t_0)\,u(t_0+t)\rangle\,dt
\end{aligned}
\tag{2.5}
$$

where we assumed that

$$\lim_{t\to\infty} \langle u(t_0)\,u(t_0+t)\rangle = 0. \tag{2.6}$$

Therefore the Einstein relation (2.1) is written as

$$\mu = \frac{1}{m\gamma} = \frac{D}{kT} = \frac{1}{kT}\int_0^\infty \langle u(t_0)\,u(t_0+t)\rangle\,dt \tag{2.7}$$

which means that the mobility, or the inverse of the friction constant, is related to the fluctuation of the velocity of the Brownian motion, which is certainly a manifestation of the fluctuation–dissipation theorem.

3. Classical Langevin equation and the random force

In the classical theory of Brownian motion we usually start from a phenomenological stochastic equation such as

$$m\dot{u}(t) = -m\gamma u + R(t) \tag{3.1}$$

which is the simplest example of the Langevin equation for a free Brownian particle in one dimension. The frictional force exerted by the medium is represented by the first term on the right-hand side, and the second term, $R(t)$, is the random force due to the random collisions of the surrounding molecules.

For the sake of simplicity and idealization, the random force is usually assumed to satisfy the two conditions (Uhlenbeck and Ornstein 1930, Chandrasekhar 1943, Wang and Uhlenbeck 1945), that (i) the process $R(t)$ is a Gaussian process, and (ii) its correlation time is infinitely short, namely the autocorrelation function of $R(t)$ has the form

$$\langle R(t_1) R(t_2) \rangle = 2\pi G_R \, \delta(t_1 - t_2) \tag{3.2}$$

where G_R is a constant. The Gaussian assumption is quite reasonable for a Brownian particle having a mass much larger than the colliding molecules, because then its motion is, so to speak, a result of a great number of successive collisions, which is a condition for the central limit theorem to work. This situation also justifies the second assumption, because correlation between successive impacts remains only for the time of such molecular motion, which is short compared with the time scale of the Brownian motion. Mathematically, these are nice assumptions defining our problem completely in a very simple manner.

Brownian motion theory then derives the required stochastic information for the process $u(t)$ as defined by the stochastic equation (3.1). It turns out then that, by virtue of the assumption (i), it is Gaussian, and also, by the assumption (ii), it is Markoffian (Wang and Uhlenbeck 1945). Therefore complete information is provided by the transition probability $W(u_0, t_0; u, t)$ from the velocity u_0 at the time t_0 to another velocity u at time t. This transition probability is found to be the fundamental solution of the following Fokker–Planck equation:

$$\frac{\partial}{\partial t} W = \frac{\partial}{\partial u} \left(D_u \frac{\partial}{\partial u} + \gamma u \right) W$$

$$W(u_0, t_0; u, t_0) = \delta(u - u_0) \tag{3.3}$$

which is easily derived from the Langevin equation (3.1). It is then found that the diffusion constant D_u in the velocity space is determined by the random force, namely

$$D_u = \frac{1}{m^2} \int_0^\infty \langle R(t_0) R(t_0 + t) \rangle \, dt. \tag{3.4}$$

Since we assume that the Brownian motion is taking place in the medium in *thermal equilibrium*, we ought to have

$$\lim_{t\to\infty} W(u_0, t_0; u, t) = C \exp\left(-\frac{1}{2}\frac{mu^2}{kT}\right). \tag{3.5}$$

In other words, the stationary solution of equation (3.4) must coincide with the Maxwellian distribution. This requires that the relation

$$D_u = \frac{\gamma}{m} kT \tag{3.6}$$

holds between the friction and the diffusion constants. Combining this with equation (3.4), we obtain

$$m\gamma = \frac{m^2 D_u}{kT} = \frac{1}{kT}\int_0^\infty \langle R(t_0)\, R(t_0+t)\rangle\, dt. \tag{3.7}$$

The above considerations apply also to Brownian motion in a potential field. The Langevin equation is then given by the set of equations

$$\dot{x} = u$$

$$m\dot{u} = -m\gamma u - \frac{\partial V}{\partial x} + R(t). \tag{3.8}$$

Under assumptions (i) and (ii), the Fokker–Planck equation for the transition probability $W(x, u, t; x_0, u_0, t_0)$ becomes

$$\left(\frac{\partial}{\partial t} + u\frac{\partial}{\partial x} - \frac{1}{m}\frac{\partial V}{\partial x}\frac{\partial}{\partial u}\right) W = \frac{\partial}{\partial u}\left(D_u\frac{\partial}{\partial u} + \gamma u\right) W$$

$$W(x, u, t_0; x_0, u_0, t_0) = \delta(x - x_0)\, \delta(u - u_0). \tag{3.9}$$

If we require that the stationary solution of this equation coincides with the canonical distribution, i.e.

$$\lim_{t\to\infty} W(x, u, t; x_0, u_0, t) = C \exp\left[-\frac{1}{kT}\{\tfrac{1}{2}mu^2 + V(x)\}\right] \tag{3.10}$$

we again obtain the relations (3.6) and (3.7). In fact, our assumptions imply that the nature of the random force is independent of the presence of the force field.

Generally, the power spectrum of a stationary process $y(t)$ is defined by

$$G_y(\omega) = \frac{1}{2\pi}\int_{-\infty}^\infty \langle y(t_0+t)\, y(t_0)\rangle\, e^{-i\omega t}\, dt \tag{3.11}$$

namely by the Fourier transform of the correlation function of $y(t)$. This means that the Fourier components of $y(t)$ defined by the expression

$$y(t) = \int_{-\infty}^\infty y(\omega)\, e^{i\omega t}\, d\omega$$

have the correlation

$$\langle y(\omega) y(\omega')\rangle = G_y(\omega)\, \delta(\omega + \omega') \tag{3.12}$$

which yields

$$\langle y(t_1) y(t_2) \rangle = \iint_{-\infty}^{\infty} \langle y(\omega) y(\omega') \rangle \exp(i\omega t_1 + i\omega' t_2)\, d\omega\, d\omega'$$

$$= \int_{-\infty}^{\infty} G_y(\omega) \exp\{i\omega(t_1 - t_2)\}\, d\omega \tag{3.13}$$

in accordance with equation (3.11).

Now, the assumption (3.2) means that the power spectrum of the random force $R(t)$ is just a constant equal to G_R. Thus the random force is said to have a white spectrum. Equation (3.7) then is written as

$$G_R = \frac{mkT}{\pi}\gamma \tag{3.14}$$

or

$$\langle R(\omega)\, R(\omega') \rangle = \frac{kTm\gamma}{\pi}\, \delta(\omega + \omega'). \tag{3.15}$$

Equation (3.7) is another manifestation of the fluctuation–dissipation theorem which states that the systematic part of the microscopic force appearing as the friction is actually determined by the correlation of the random force. Conversely, the random force has to satisfy this condition. The relation (3.15) means much more. Namely, it states that the random force must have the power spectrum determined by the friction. This last theorem was first discovered by Nyquist, who obtained this relation by thermodynamic considerations supplemented with the principle of microscopic balance. The friction, or more generally the resistance of a given system, represents the method by which the external work is dissipated into microscopic thermal energy. The reverse process is the generation of random force as the result of thermal fluctuation. Nyquist thus showed that the random electromotive force appearing across a resistor is determined by its impedance.

4. Generalized Langevin equation

As we have seen in the previous section, the classical theory of Brownian motion (3.1) assumes a white noise for the random force (see equations (3.2) and (3.15)) and accordingly a constant friction γ in the Langevin equation. Thus the velocity correlation function in equilibrium is given by

$$\langle u(t_0)\, u(t_0 + t) \rangle = \langle u^2 \rangle \exp(-\gamma |t|) \tag{4.1}$$

as one easily finds from the equation

$$\frac{d}{dt}\langle u(t_0)\, u(t_0 + t) \rangle = -\gamma \langle u(t_0)\, u(t_0 + t) \rangle, \quad t > 0 \tag{4.2}$$

which is obtained from equation (3.1) by noticing that

$$\langle u(t_1)\, R(t_2) \rangle = 0, \quad t_1 < t_2. \tag{4.3}$$

On the other hand, the velocity correlation function must satisfy the condition

$$\frac{d}{dt_0}\langle u(t_0)\, u(t_0 + t) \rangle = 0 \tag{4.4}$$

since in equilibrium $u(t)$ is a stationary process. It follows that

$$\langle u(t)\,\dot{u}(t)\rangle = 0. \tag{4.5}$$

Thus we note that equation (4.1) is in contradiction to equation (4.5). This contradiction obviously arises from the idealization in the classical theory and shows the need of modification for a more realistic treatment. It is a general feature of any dynamical system that the dynamical coherence becomes predominant in short times or at high frequencies, as short or as high as are characteristic of the molecular motion. Equation (4.1) is no longer valid for the very short time $|t|$ in which the Brownian particle suffers only a few or no impacts.

Let us now consider generalization of the Brownian motion theory to random motion of a particle which is *not* necessarily heavier than the particles interacting with it. This means that the time scale of the molecular motion is no longer very much shorter than that of the motion of the particle under observation, so that the assumption (3.2) must be abandoned for the random force. In order to meet the requirement (4.5), we have at the same time to abandon the assumption of a constant friction and to introduce generally a frequency-dependent friction.

Thus we are led to a natural extension of the Langevin equation in the form (Mori 1965 a, Kubo 1966),

$$\dot{u}(t) = -\int_{t_0}^{t}\gamma(t-t')\,u(t')\,dt' + \frac{1}{m}R(t) + \frac{1}{m}K(t), \quad t > t_0 \tag{4.6}$$

where the function $\gamma(t)$ represents a retarded effect of the frictional force and $R(t)$ is the random force. The external force $K(t)$ is also included in this equation. For the random force we may generally assume that it averages to zero, i.e.

$$\langle R(t)\rangle = 0 \tag{4.7}$$

that it is not correlated with the velocity $u(t_0)$, i.e.

$$\langle u(t_0)\,R(t)\rangle = 0, \quad t > t_0 \tag{4.8}$$

and that it does not depend on the external force K, because we consider only the linear effect of K. The random force may have other properties, for example the Gaussian property, depending on the nature of the system under consideration, but they are not assumed in the following discussion.

If a periodic external force

$$K = K_0 \cos \omega t, \quad -\infty < t$$

is applied, equation (4.6) gives the response

$$\langle u(t)\rangle = \mathscr{R}\mu(\omega)\,K_0\,e^{i\omega t}$$

where the complex admittance or the mobility $\mu(\omega)$ is given by

$$\mu(\omega) = \frac{1}{m}\frac{1}{i\omega + \gamma[\omega]} \tag{4.9}$$

$\gamma[\omega]$ being the Fourier–Laplace transform† of the function $\gamma(t)$, i.e.

$$\gamma[\omega] = \int_0^{\infty} e^{-i\omega t}\gamma(t)\,dt. \tag{4.10}$$

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† In the following we use the notation $f[\omega]$ to indicate the Fourier–Laplace transform of $f(t)$.

In the absence of the external force, the velocity correlation function is obtained from equation (4.6) using the assumption (4.8). Its Fourier–Laplace transform is found to be

$$\int_0^\infty e^{-i\omega t} \langle u(t_0)\, u(t_0+t)\rangle\, dt = \langle u^2\rangle \frac{1}{i\omega + \gamma[\omega]} \tag{4.11}$$

so that the admittance $\mu(\omega)$ satisfies the relation

$$\mu(\omega) = \frac{1}{m\langle u^2\rangle} \int_0^\infty \langle u(t_0)\, u(t_0+t)\rangle\, e^{-i\omega t}\, dt \tag{4.12}$$

which may be written as

$$\mu(\omega) = \frac{1}{kT} \int_0^\infty \langle u(t_0)\, u(t_0+t)\rangle\, e^{-i\omega t}\, dt \tag{4.13}$$

if the equipartition law

$$m\langle u^2\rangle = kT$$

is assumed.

From equation (4.6), with $K(t) = 0$, it can also be shown that the relation

$$m\gamma[\omega] = \frac{1}{m\langle u^2\rangle} \int_0^\infty \langle R(t_0)\, R(t_0+t)\rangle\, e^{-i\omega t}\, dt \tag{4.14}$$

holds under the assumption (4.3). Again assuming the equipartition law we can write equation (4.14) as

$$m\gamma[\omega] = \frac{1}{kT} \int_0^\infty \langle R(t_0)\, R(t_0+t)\rangle\, e^{-i\omega t}\, dt \tag{4.15}$$

which implies the relation

$$\langle R(\omega)\, R(\omega')\rangle = \frac{kT}{\pi} m\gamma[\omega]\, \delta(\omega+\omega') \tag{4.16}$$

for the power spectrum of the random force. Equation (4.14) is proved as follows. Noticing that

$$\langle u(t_0)\, \dot u(t_0)\rangle = 0 \quad \text{and} \quad \langle \dot u(t_0)\, u(t_0+t)\rangle = -\langle u(t_0)\, \dot u(t_0+t)\rangle$$

by the stationarity condition, we obtain

$$\int_0^\infty \langle \dot u(t_0)\, \dot u(t_0+t)\rangle\, e^{-i\omega t}\, dt = i\omega \int_0^\infty \langle u(t_0)\, u(t_0+t)\rangle\, e^{-i\omega t}\, dt$$

$$= -i\omega \int_0^\infty \langle \dot u(t_0)\, \dot u(t_0+t)\rangle\, e^{-i\omega t}\, dt$$

$$= \frac{i\omega\gamma[\omega]}{i\omega + \gamma[\omega]} \langle u(t_0)^2\rangle \tag{4.17}$$

where we have used equation (4.11). From equation (4.6) with $K = 0$, we now have

$$\int_0^\infty \langle R(t_0)\, R(t_0 + t)\rangle\, e^{-i\omega t}\, dt$$

$$= m^2 \int_0^\infty \left\langle \dot{u}(t_0) \left\{ \dot{u}(t_0 + t) + \int_0^t \gamma(t - t')\, u(t_0 + t')\, dt' \right\} \right\rangle e^{-i\omega t}\, dt$$

$$= m^2 \left[\int_0^\infty \langle \dot{u}(t_0)\, \dot{u}(t_0 + t)\rangle\, e^{-i\omega t}\, dt + \gamma[\omega] \int_0^\infty \langle \dot{u}(t_0)\, u(t_0 + t)\rangle\, e^{-i\omega t}\, dt \right]$$

which gives equation (4.14) by equation (4.17).

Equation (4.12) is a generalized form of equation (2.7) and represents the most fundamental expression of the fluctuation–dissipation theorem, as will be discussed in the following sections. When it is necessary to distinguish this from another expression of the fluctuation–dissipation theorem, we shall call this the *first* fluctuation–dissipation theorem. Equations (4.15) and (4.16) are generalizations of equations (3.7) and (3.15) and so represent the Nyquist theorem for the thermal noise in a resistor with a frequency-dependent impedance. This theorem may be called the *second* fluctuation–dissipation theorem. This may be regarded as a corollary of the first theorem, as we have seen by the above derivation. The two theorems are unified, so to speak, by the generalized Langevin equation (4.6), which may also be regarded as the definition of the random force.

Mori has shown that a dynamical equation of motion can generally be transformed into the form of equation (4.6) or a more general form such as is given later by equation (9.4). For the derivation, the reader is referred to his original paper (Mori 1965 a).

5. Linear response theory

We now give a brief derivation of equation (4.12) by statistical mechanics (Kubo 1957). Consider a system the natural motion of which is governed by the Hamiltonian $\mathcal{H}$. An external force $K(t)$ is applied to it from the infinite past, $t = -\infty$, when the system was at thermal equilibrium. If ρ is the distribution function or the density matrix representing the statistical ensemble, one has the equation of motion

$$\frac{\partial \rho(t)}{\partial t} = i\mathcal{L}_t\, \rho(t) \tag{5.1}$$

where $i\mathcal{L}_t$ is the Liouville operator corresponding to the perturbed Hamiltonian

$$\mathcal{H}_t = \mathcal{H} + \mathcal{H}_{\text{ext}}(t)$$

$$= \mathcal{H} - AK(t) \tag{5.2}$$

A being the dynamical quantity conjugate to the applied force K. In classical mechanics the Liouville operator is given by

$$i\mathcal{L}_t = -\sum \left(\frac{\partial \mathcal{H}_t}{\partial p}\, \frac{\partial}{\partial q} - \frac{\partial \mathcal{H}_t}{\partial q}\, \frac{\partial}{\partial p} \right) \equiv i\mathcal{L} + i\mathcal{L}_{\text{ext}} \tag{5.3}$$

where p and q represent the set of canonical momenta and coordinates and $i\mathscr{L}$ and $i\mathscr{L}_{\text{ext}}$ are the Liouville operators corresponding to $\mathscr{H}$ and $\mathscr{H}_{\text{ext}}$ respectively. In quantum mechanics the Liouville operators $i\mathscr{L}$, $i\mathscr{L}_t$ and $i\mathscr{L}_{\text{ext}}$ are defined by commutators of ρ with the corresponding Hamiltonians, for example,

$$i\mathscr{L}\rho = \frac{1}{i\hbar}(\mathscr{H}\rho - \rho\mathscr{H}). \tag{5.4}$$

Equation (5.1) is solved under the initial condition

$$\rho(-\infty) = \rho_e = C\exp(-\beta\mathscr{H}), \quad \beta = \frac{1}{kT} \tag{5.5}$$

to the first order of the external force to give

$$\rho(t) = \rho_e + \Delta\rho(t) + \dots$$

with

$$\Delta\rho(t) = \int_{-\infty}^t dt' \exp\{i(t-t')\mathscr{L}\} i\mathscr{L}_{\text{ext}}(t')\rho_e. \tag{5.6}$$

The response of the system to the force is now observed in the change of a certain physical quantity B, which is given by

$$\Delta\bar{B}(t) = \operatorname{Tr} B(p,q)\Delta\rho(t) \tag{5.7}$$

where Tr means the phase space integration

$$\operatorname{Tr}\dots = \int dp\dots dq\dots$$

in classical mechanics and the well-known trace operation in quantum mechanics. The expression (5.7) is easily transformed into the form

$$\Delta\bar{B}(t) = \int_{-\infty}^t dt' K(t') \operatorname{Tr}\rho_e(A(0), B(t-t')). \tag{5.8}$$

Here

$$B(t) = e^{-i\mathscr{L}t} B = B(p_t, q_t) \tag{5.9}$$

$$= e^{it\mathscr{H}/\hbar} B e^{-it\mathscr{H}/\hbar} \quad \text{(quantal)} \tag{5.10}$$

represents the dynamical change of the phase function B; namely, in classical mechanics $B(p_t, q_t)$ is its value as the phase point moves according to Hamilton's equations of motion

$$\dot{p}_t = -\frac{\partial\mathscr{H}}{\partial q_t}, \quad \dot{q}_t = \frac{\partial\mathscr{H}}{\partial p_t}$$

with the initial conditions $p_0 = p$, $q_0 = q$, whereas it is the Heisenberg operator in quantum mechanics as defined by equation (5.10). The bracket in equation (5.8) is the Poisson bracket

$$(A(0), B(t)) = \sum \left\{\frac{\partial A(p,q)}{\partial q}\frac{\partial B(p_t, q_t)}{\partial p} - \frac{\partial A(p,q)}{\partial p}\frac{\partial B(p_t, q_t)}{\partial q}\right\} \tag{5.11}$$

in classical mechanics, and the quantal Poisson bracket

$$(A(0), B(t)) = \frac{1}{i\hbar}\{A(0)B(t) - B(t)A(0)\} \tag{5.12}$$

in quantum mechanics. Equation (5.8) is obtained by performing partial integrations or by using the cyclic property of trace.

Now we define the *response function*

$$\phi_{BA}(t) = \mathrm{Tr}\, \rho_e(A(0), B(t)) = \langle (A(0), B(t)) \rangle \tag{5.13}$$

which may also be written as

$$\phi_{BA}(t) = \mathrm{Tr}\, (\rho_e, A(0))\, B(t) \tag{5.14}$$

and write equation (5.8) as

$$\Delta \bar{B}(t) = \int_{-\infty}^{t} dt'\, K(t')\, \phi_{BA}(t - t'). \tag{5.15}$$

Equation (5.15) expresses the response $\Delta \bar{B}(t)$ as linear in the external force K, as superposition of the delayed effects. The response function represents the response of the system at the time t to an impulsive force $K(t) \propto \delta(t)$ exerted on the system at $t = 0$. That the Poisson bracket has this meaning is seen by the following consideration. If the phase point is (p, q) at $t = 0$ when a unit impulsive force is applied, the displacement $(\Delta p, \Delta q)$ is given by

$$\Delta p = -\int \frac{\partial \mathscr{H}_{\mathrm{ext}}}{\partial q}\, dt = \frac{\partial A}{\partial q}, \quad \Delta q = \int \frac{\partial \mathscr{H}_{\mathrm{ext}}}{\partial p}\, dt = -\frac{\partial A}{\partial p}$$

for every set of canonical variables. The phase function $B(t) = B(p_t, q_t)$ at the time t changes as a result of these shifts by the amount

$$\Delta B(t) = \Sigma \left(\frac{\partial B}{\partial p} \Delta p + \frac{\partial B}{\partial q} \Delta q \right)$$

$$= \Sigma \left\{ \frac{\partial A(0)}{\partial q} \frac{\partial B(t)}{\partial p} - \frac{\partial A(0)}{\partial p} \frac{\partial B(t)}{\partial q} \right\}.$$

Thus $\phi_{BA}(t)$ given by equation (5.12) is just equal to this change averaged over the initial distribution of the phase. The corresponding quantum expression, namely the commutator, means in the same way the effect of an impulsive force conjugate to a quantity A on another quantity $B(t)$ at a later time.

The expression (5.14) is obtained from (5.13) by using the cyclic property of trace or by partial integrations. Its meaning is also clear. It is the average of $B(t)$ over the change of distribution at $t = 0$ induced by the impulsive force. For a periodic force

$$K = \mathscr{R}\, K_0\, e^{i\omega t}$$

the response (5.15) is expressed as

$$\Delta \bar{B}(t) = \mathscr{R}\, \chi_{BA}(\omega)\, K_0\, e^{i\omega t}$$

where the admittance χ_{BA} is given by

$$\chi_{BA}(\omega) = \int_0^\infty \phi_{BA}(t)\, e^{-i\omega t}\, dt \tag{5.16a}$$

$$= \int_0^\infty \langle (A(0), B(t)) \rangle\, e^{-i\omega t}\, dt \tag{5.16b}$$

$$= \int_0^\infty \mathrm{Tr}\, (\rho_e, A)\, B(t)\, e^{-i\omega t}\, dt. \tag{5.16c}$$

In classical mechanics we find that

$$(\rho_e, A) = -\beta\rho_e(\mathscr{H}, A) = \beta\rho_e \dot{A} \tag{5.17}$$

by equation (5.5). The corresponding quantal equation is (Kubo 1957)

$$(\rho_e, A) = \int_0^\beta d\lambda\, \rho_e\, e^{\lambda\mathscr{H}} \dot{A}\, e^{-\lambda\mathscr{H}}$$

$$= \int_0^\beta d\lambda\, \rho_e \dot{A}(-i\hbar\lambda) \tag{5.18}$$

where $\dot{A}$ is the time derivative of A at $t = 0$, i.e.

$$\dot{A} = (A, H) = \frac{1}{i\hbar}(A\mathscr{H} - \mathscr{H}A)$$

and $\dot{A}(-i\hbar\lambda)$ is a Heisenberg operator with an imaginary time.

Here we introduce the notation

$$\langle X;\, Y\rangle = \frac{1}{\beta}\int_0^\beta d\lambda\, \mathrm{Tr}\, \rho_e\, e^{\lambda\mathscr{H}} X\, e^{-\lambda\mathscr{H}}\, Y. \tag{5.19}$$

Then equation (5.18) yields the relation

$$\langle(X(0), Y(t))\rangle = \beta\langle \dot{X}(0);\, Y(t)\rangle \tag{5.20}$$

so that equation (5.16) may be written as

$$\chi_{BA}(\omega) = \beta\int_0^\infty \langle \dot{A}(0);\, B(t)\rangle\, e^{-i\omega t}\, dt. \tag{5.21}$$

6. Correlations and correlation spectra

The expression $\langle X;\, Y\rangle$ defined by equation (5.19) will be called hereafter the *canonical* correlation of X and Y in order to distinguish it from other definitions of correlation such as

$$\langle XY\rangle = \mathrm{Tr}\,\rho_e\, XY \tag{6.1}$$

$$\langle\{XY\}\rangle = \mathrm{Tr}\,\rho_e(XY + YX)/2 \tag{6.2}$$

the latter being the symmetrized correlation. This discrimination is necessary only in quantal cases where physical quantities do not necessarily commute.

We note here some properties of the canonical and the symmetrized correlations (see Kubo 1957, or Kubo 1959 for the proof):

(i) They are stationary, i.e.

$$\langle X(0);\, Y(t)\rangle = \langle X(t_0);\, Y(t_0+t)\rangle$$
$$\langle\{X(0)\, Y(t)\}\rangle = \langle\{X(t_0)\, Y(t_0+t)\}\rangle. \tag{6.3}$$

(ii) They are real if X and Y are real (Hermitian). In particular, it follows that

$$\langle X;\, X\rangle \geqslant 0 \quad \langle X^2\rangle \geqslant 0. \tag{6.4}$$

(iii) Generally

$$\langle X;\, Y\rangle = \langle Y;\, X\rangle, \quad \langle\{XY\}\rangle = \langle\{YX\}\rangle \tag{6.5}$$

so that we have

$$\langle X(0); \, Y(t)\rangle = \langle Y(t); \, X(0)\rangle = \langle Y(0); \, X(-t)\rangle$$

$$\langle\{X(0) \, Y(t)\}\rangle = \langle\{Y(0) \, X(-t)\}\rangle \tag{6.6}$$

and in particular

$$\langle X(0); \, X(t)\rangle = \langle X(0); \, X(-t)\rangle$$

$$\langle\{X(0) \, X(t)\}\rangle = \langle\{X(0) \, X(-t)\}\rangle. \tag{6.7}$$

(iv) Time reversal symmetry yields

$$\langle X(0); \, Y(t)\rangle_H = \epsilon_X \epsilon_Y \langle X(0); \, Y(-t)\rangle_{-H} = \epsilon_X \epsilon_Y \langle Y(0); \, X(t)\rangle_{-H}$$

$$\langle\{X(0) \, Y(t)\}\rangle_H = \epsilon_X \epsilon_Y \langle\{X(0) \, Y(-t)\}\rangle_{-H} = \epsilon_X \epsilon_Y \langle\{Y(0) \, X(t)\}\rangle_{-H} \tag{6.8}$$

where H is the external magnetic field and ϵ_X takes the value $+1$ or -1, depending on whether X is even or odd with respect to the momenta.

These relations show that either the canonical correlations or the symmetrized correlations can be used in quantal stochastic processes as the quantal generalization of the correlations of classical variables. We have already seen, however, that the response is more directly related to the canonical correlations rather than to other sorts of correlation functions.

The power spectrum of a process $X(t)$ may be defined either as a canonical or a symmetrized power spectrum, namely

$$G_X{}^c(\omega) = \frac{1}{2\pi} \int_{-\infty}^{\infty} \langle X(t_0); \, X(t_0+t)\rangle \, \mathrm{e}^{-i\omega t} \, dt \tag{6.9}$$

or

$$G_X{}^s(\omega) = \frac{1}{2\pi} \int_{-\infty}^{\infty} \langle\{X(t_0) \, X(t_0+t)\}\rangle \, \mathrm{e}^{-i\omega t} \, dt. \tag{6.10}$$

The correlation of the Fourier components of $X(t)$

$$X(\omega) = \frac{1}{2\pi} \int_{-\infty}^{\infty} X(t) \, \mathrm{e}^{-i\omega t} \, dt \tag{6.11}$$

is then given by

$$\langle X(\omega); \, X(\omega')\rangle = G_X{}^c(\omega) \, \delta(\omega + \omega') \tag{6.12}$$

or by

$$\langle\{X(\omega) \, X(\omega')\}\rangle = G_X{}^s(\omega) \, \delta(\omega + \omega'). \tag{6.13}$$

The power spectrum by either definition is real and positive.

For two given quantal quantities X and Y, the time correlation functions $\langle X(0) \, Y(t)\rangle$ and $\langle Y(t) \, X(0)\rangle$ are not generally equal. Their Fourier transforms, or the correlation spectra, are related to each other by the equation

$$\int_{-\infty}^{\infty} \langle X(0) \, Y(t)\rangle \, \mathrm{e}^{-i\omega t} \, dt = \mathrm{e}^{\beta\hbar\omega} \int_{-\infty}^{\infty} \langle Y(t) \, X(0)\rangle \, \mathrm{e}^{-i\omega t} \, dt. \tag{6.14}$$

This is seen most easily by writing down each expression in terms of the matrix elements in the representation diagonalizing the Hamiltonian $\mathscr{H}$. Equation (6.14) gives the relation

$$\int_{-\infty}^{\infty} \langle(X(0), \, Y(t))\rangle \, \mathrm{e}^{-i\omega t} \, dt = \frac{1}{i\hbar} (1 - \mathrm{e}^{-\beta\hbar\omega}) \int_{-\infty}^{\infty} \langle X(0) \, Y(t)\rangle \, \mathrm{e}^{-i\omega t} \, dt \tag{6.15}$$

or

$$\int_{-\infty}^{\infty} \langle (X(0), Y(t)) \rangle \, \mathrm{e}^{-i\omega t} \, dt = \frac{\omega}{iE_\beta(\omega)} \int_{-\infty}^{\infty} \langle \{X(0) \, Y(t)\} \rangle \, \mathrm{e}^{-i\omega t} \, dt \qquad (6.16)$$

where

$$E_\beta(\omega) = \tfrac{1}{2}\hbar\omega \coth \tfrac{1}{2}\beta\hbar\omega \qquad (6.17)$$

is the average energy of a harmonic oscillator with frequency ω at $T = 1/k\beta$. Using the relation (5.20), we may rewrite equation (6.16) in the form

$$\int_{-\infty}^{\infty} \langle X(0); Y(t) \rangle \, \mathrm{e}^{-i\omega t} \, dt = \frac{1}{\beta E_\beta(\omega)} \int_{-\infty}^{\infty} \langle \{X(0) \, Y(t)\} \rangle \, \mathrm{e}^{-i\omega t} \, dt. \qquad (6.18)$$

In particular, when $Y = X$, this gives the relation

$$G_X{}^{\mathrm{c}}(\omega) = \frac{1}{\beta E_\beta(\omega)} G_X{}^{\mathrm{s}}(\omega) \qquad (6.19)$$

between the power spectra (6.9) and (6.10).

7. The fluctuation–dissipation theorem

Equation (6.16) or (6.18) generally gives a relation between the dissipative part of the admittance function $\chi_{BA}(\omega)$ and the correlation spectra of the relevant physical quantities. Using equation (6.16), we obtain from (5.16)

$$\chi_{BA}{}'(\omega) = \frac{\omega}{2iE_\beta(\omega)} \int_{-\infty}^{\infty} \langle \{A(0) \, B(t)\} \rangle \, \mathrm{e}^{-i\omega t} \, dt \qquad (7.1)$$

if $\phi_{BA}(t)$ is even in t and $\chi_{BA}{}'$ is dissipative and

$$\chi_{BA}{}''(\omega) = \frac{\omega}{2E_\beta(\omega)} \int_{-\infty}^{\infty} \langle \{A(0) \, B(t)\} \rangle \, \mathrm{e}^{-i\omega t} \, dt \qquad (7.2)$$

if $\phi_{BA}(t)$ is odd and $\chi_{BA}{}''$ is dissipative where $\chi_{BA} = \chi_{BA}{}' - i\chi_{BA}{}''$.

This sort of relationship between dissipation and correlation spectra is commonly called the *fluctuation–dissipation* theorem. The present form (7.1) or (7.2) includes the quantum effect through the factor $E_\beta(\omega)$. In this article we have been, however, using the phrase 'fluctuation–dissipation' theorem in a wider sense including non-dissipative parts of admittance and so speaking of the time correlation itself rather than the correlation spectra. Thus we regard equation (5.16) or equation (5.21) as the exact expression of the fluctuation–dissipation theorem, which is generalized to apply to quantal systems as well as classical systems. A formal generalization in quantal cases is just the use of a canonical correlation (5.21) in place of a classical one. Let us illustrate the general theory again for the simple example of a Brownian particle.

When a driving force K is applied periodically, the velocity of the Brownian particle is determined on average by the mobility $\mu(\omega)$, which is given by

$$\mu(\omega) = \beta \int_0^{\infty} \langle u(0); u(t) \rangle \, \mathrm{e}^{-i\omega t} \, dt. \qquad (7.3)$$

This is obtained directly from equation (5.21) by inserting $B = u$ and $A = x$, since we should put

$$\mathscr{H}_{\text{ext}}(t) = -xK(t)$$

in equation (5.2). Equation (7.3) is the generalized form of the first fluctuation–dissipation theorem and coincides with equation (4.12) in the classical limit. Note that equation (7.3) may be written in the form of equation (4.12), i.e.

$$\mu(\omega) = \frac{1}{m\langle u; u\rangle} \int_0^\beta \langle u(0); u(t)\rangle \, e^{-i\omega t} \, dt \qquad (7.4)$$

where we have used the *equipartition* law

$$\langle u; mu\rangle = \langle \dot{x}; p\rangle = \frac{1}{\beta}\langle (x,p)\rangle = \frac{1}{\beta} \qquad (7.5)$$

which is obtained from equation (5.20).

Now we consider $u(t)$ as a stochastic process just in the same way as we did in §4. Quantal generalization requires the use of canonical correlations. First, we write the equation of motion for the average motion of u under an external force K in the form

$$m\frac{d}{dt}\langle u(t)\rangle = -m\int_{-\infty}^t dt' \gamma(t-t')\langle u(t')\rangle + K(t) \qquad (7.6)$$

which yields, under a periodic force, a forced motion

$$\langle u(t)\rangle = \mathscr{R}\,\mu(\omega)\,K_0\,e^{-i\omega t}$$

where $\mu(\omega)$ must be identified with equation (4.9), i.e.

$$\mu(\omega) = \frac{1}{m}\frac{1}{i\omega + \gamma[\omega]}. \qquad (7.7)$$

Conversely the function γ in equation (7.6) is determined when the mobility $\mu(\omega)$ is given.

Now let us suppose that the process $u(t)$, stationary in equilibrium, is generated by a random force $R'(t)$. As a force, it should appear in place of $K(t)$ in equation (7.6) when the equation is replaced by a stochastic equation of motion. Thus we may assume

$$m\dot{u}(t) = -m\int_{-\infty}^t \gamma(t-t')\,u(t')\,dt' + R'(t) \qquad (7.8)$$

in the absence of external force. Since $u(t)$ is stationary, $R'(t)$ must also be stationary. Equation (7.8) yields the relation

$$u[\omega] = \frac{1}{m}\frac{1}{i\omega + \gamma[\omega]}R'[\omega] \qquad (7.9)$$

between the Fourier components of $u(t)$ and $R'(t)$. By the Rice method (see Wang and Uhlenbeck 1945), we then have

$$G_u{}^c(\omega) = \frac{1}{m^2}\frac{1}{|i\omega + \gamma[\omega]|^2}G_R{}^c(\omega) \qquad (7.10)$$

for the canonical spectra of u and R'.

Since the function $\langle u(0); u(t) \rangle$ is even in t, we have from equation (7.3)

$$\mathscr{R}\,\mu(\omega) = \frac{\beta}{2} \int_{-\infty}^{\infty} \langle u(0), u(t) \rangle\, \mathrm{e}^{i\omega t}\, dt = \frac{\beta}{2} G_u{}^{c}(\omega) \tag{7.11}$$

which yields, by equations (7.7) and (7.10),

$$m\mathscr{R}\,\gamma[\omega] = \mathscr{R}\,\mu(\omega)^{-1}$$

$$= \frac{\beta}{2} G_{R'}{}^{c}(\omega)$$

$$= \frac{\beta}{2} \int_{-\infty}^{\infty} \langle R'(0); R'(t) \rangle\, \mathrm{e}^{-i\omega t}\, dt. \tag{7.12}$$

If the function $\gamma[\omega]$ is assumed to be expressed as a Fourier–Laplace transform of a real function, equation (7.12) implies that

$$m\gamma[\omega] = \int_{0}^{\infty} \langle R'(0); R'(t) \rangle\, \mathrm{e}^{-i\omega t}\, dt \tag{7.13}$$

or

$$m\gamma(t) = \beta \langle R'(0); R'(t) \rangle. \tag{7.14}$$

Thus, the retarded friction $\gamma(t)$ is related to the canonical correlation of the random force $R'(t)$.

The random force $R(t)$ defined by equation (4.6) is not the same as $R'(t)$ in equation (7.8) but they are related by

$$R(t) = R'(t) - m \int_{-\infty}^{t_0} dt'\gamma(t - t')\, u(t').$$

Although $R'(t)$ is stationary, $R(t)$ is not stationary because it depends on t_0, the arbitrarily chosen initial time. However, we have seen that equation (4.15) is derived from equation (4.6), which means that the relation

$$\langle R(t_0); R(t_0 + t) \rangle = \langle R'(t_1); R'(t_1 + t) \rangle \tag{7.15}$$

holds. Therefore we may write equation (7.13) as

$$m\gamma[\omega] = \beta \int_{0}^{\infty} \langle R(t_0); R(t_0 + t) \rangle\, \mathrm{e}^{-i\omega t}\, dt. \tag{7.16}$$

Summarizing, we may say that the generalized Langevin equation (4.6) can be regarded as a representation of the basic theorem (7.3) for linear responses through a stochastic equation with the random force $R(t)$ which satisfies equation (7.16), the *second* fluctuation–dissipation theorem. This representation is not a mere change of wording since the random force is a physical reality observable, for instance, as the thermal voltage across a resistor.

8. Force correlations

The random force $R(t)$ defined through the equation

$$m\dot{u}(t) = - \int_{t_0}^{t} m\gamma(t - t')\, u(t')\, dt' + R(t), \quad t > t_0$$

$$\langle u(t_0); R(t) \rangle = 0 \tag{8.1}$$

is a part of the total force

$$F(t) = m\dot{u}(t) = -\int_{t_0}^{t} m\gamma(t-t')\, u(t')\, dt' + R(t) \tag{8.2}$$

the systematic or frictional part being subtracted. We now show that a very simple relation holds between the correlation functions of $F(t)$ and $R(t)$; namely

$$\gamma[\omega] = \frac{i\omega\gamma_{\mathrm{t}}[\omega]}{i\omega - \gamma_{\mathrm{t}}[\omega]}, \quad \gamma_{\mathrm{t}}[\omega] = \frac{i\omega\gamma[\omega]}{i\omega + \gamma[\omega]} \tag{8.3}$$

or more simply

$$\frac{1}{\gamma[\omega]} = \frac{1}{\gamma_{\mathrm{t}}[\omega]} - \frac{1}{i\omega} \tag{8.4}$$

where

$$\gamma_{\mathrm{t}}[\omega] = \frac{\beta}{m} \int_0^{\infty} \langle F(t_0);\, F(t_0+t)\rangle\, \mathrm{e}^{-i\omega t}\, dt \tag{8.5}$$

is the Fourier–Laplace transform of the total force correlation.

Equation (8.3) is proved as follows. Carrying out a partial integration of the expression (7.3), we obtain

$$m\mu(\omega) = \frac{1}{i\omega} - \frac{1}{(i\omega)^2}\gamma_{\mathrm{t}}[\omega] \tag{8.6}$$

where we used the relations

$$\langle u(t_0);\, \dot{u}(t_0)\rangle = 0, \quad \langle u(t_0);\, \ddot{u}(t)\rangle = -\langle \dot{u}(t_0);\, \dot{u}(t)\rangle.$$

Equating the expression (8.6) to (7.7), we find equation (8.3). An alternative proof has already been given by equation (4.17) which also holds for canonical correlations, i.e.

$$\int_0^{\infty} \langle F(t_0);\, F(t_0+t)\rangle\, \mathrm{e}^{-i\omega t}\, dt = m\langle u(t_0);\, u(t_0)\rangle\frac{i\omega\gamma[\omega]}{i\omega + \gamma[\omega]}. \tag{8.7}$$

This becomes equation (8.3) when the equipartition law (7.5) is inserted.

Equations (8.3) and (8.4) show explicitly how the force correlations behave differently from each other. At low frequencies we generally expect that

$$\gamma[\omega] \sim \text{finite} \quad \text{and} \quad \gamma_{\mathrm{t}}[\omega] \sim i\omega \tag{8.8}$$

whereas at high frequencies

$$\gamma[\omega] \simeq \gamma_{\mathrm{t}}[\omega]. \tag{8.9}$$

The low-frequency limit is in accordance with the theorem which generally states that

$$\int_0^{\infty} \langle \dot{X}(0);\, \dot{X}(t)\rangle\, dt = 0 \tag{8.10}$$

if the random variable $X(t)$ is bounded in the sense that its variation in any given time interval is finite. Then we have

$$0 = \lim_{t\to\infty}\frac{1}{2t}\langle X(t)-X(0);\, X(t)-X(0)\rangle$$

$$= \lim_{t\to\infty}\frac{1}{2t}\int_0^{t} dt_1\int_0^{t} dt_2\langle \dot{X}(t_1);\, \dot{X}(t_2)\rangle = \int_0^{\infty} \langle \dot{X}(0);\, \dot{X}(t)\rangle\, dt.$$

In many practical cases we have two characteristic times, or frequencies, the relaxation time τ_{r} and the microscopic (or collision duration) time τ_{c}, which differ greatly in the order of magnitude, i.e.

$$\tau_{\mathrm{r}} \gg \tau_{\mathrm{c}}. \tag{8.11}$$

For instance, if the particle is scattered occasionally by dilute scatterers, the relaxation time τ_{r} is much longer than τ_{c} which then is the time spent in a single process of scattering. The same is true for a nearly ideal Brownian particle because a single impact by surrounding particles changes the velocity of the heavy particle by only a small fraction. The above examples illustrate very typical cases where the condition (8.11) holds. The first is for strong but localized or instantaneous collisions, whereas the second is for weak but continuous interactions.
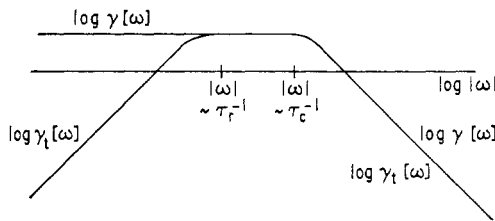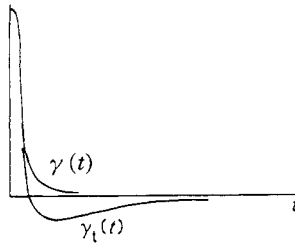

Figure 1.

Figure 2.

If the condition (8.11) holds, we have

$$1/\tau_{\mathrm{r}} = \gamma[0] \equiv \gamma \tag{8.12}$$

and

$$\gamma_t[\omega] \sim \gamma \quad \text{for} \quad \gamma \ll \omega \ll \omega_{\mathrm{c}} = \tau_{\mathrm{c}}^{-1}. \tag{8.13}$$

For very high frequencies, $\omega \gg \omega_{\mathrm{c}}$, equation (8.5) gives

$$\gamma_t[\omega] \sim \gamma[\omega] \sim \frac{\beta \langle F; F \rangle}{mi\omega}. \tag{8.14}$$

Figure 1 illustrates this situation for real values of $i\omega = s$. Figure 2 shows the corresponding time correlations. The correlation function of the random force R will decay in a time interval of τ_{c}, whereas that of the total force F has two parts, the short time part or the fast part similar to that of the random force and the slow part which should just cancel the fast part in the time integral.

The above considerations show that we may put

$$\gamma[0] = \frac{1}{\tau_{\mathrm{r}}} = \frac{\beta}{m} \int_0^\tau \langle F(t_0); F(t_0+t)\rangle \, dt \tag{8.15}$$

if the upper limit is so chosen that

$$\tau_{\mathrm{c}} \ll \tau \ll \tau_{\mathrm{r}} \tag{8.16}$$

because the slow tail of the correlation function is cut off. The time integral in equation (8.15) then attains a plateau value for τ satisfying (8.16). This fact was noticed by Kirkwood (1946) who first gave equation (8.15) as the microscopic expression for the friction constant of a Brownian particle.

9. Correlation matrix formulation

Here we generalize the foregoing treatment of correlation functions to many variables. We consider a set of physical quantities $X_1, \ldots, X_n$, which are regarded as stationary stochastic variables fluctuating in equilibrium of the system. It is convenient to normalize the matrix of canonical correlations in such a way that

$$\langle X_j(t); X_k(t)\rangle = \delta_{jk} \tag{9.1}$$

or

$$\langle \mathbf{X}(t); \tilde{\mathbf{X}}(t)\rangle = 1 \tag{9.2}$$

where $\mathbf{X}(t)$ is a column vector, and $\tilde{\mathbf{X}}(t)$ the corresponding row vector, i.e.

$$\mathbf{X}(t) = \begin{bmatrix} X_1(t) \\ \vdots \\ X_n(t) \end{bmatrix}, \quad \tilde{\mathbf{X}}(t) = (X_1(t), \ldots, X_n(t)).$$

Thus $\langle \mathbf{X}; \tilde{\mathbf{X}}\rangle$ represents the correlation matrix. This normalization is achieved by diagonalizing the correlation matrix and then changing the norms.

By the stationarity condition of the process $\mathbf{X}(t)$ we may define a Hermitian matrix $\mathbf{\Omega}$ by

$$i\Omega_{jk} = \langle \dot{X}_j(t); X_k(t)\rangle = -\langle X_j(t); \dot{X}_k(t)\rangle. \tag{9.3}$$

Then the Langevin equation for $\mathbf{X}(t)$ is written as a matrix equation

$$\dot{\mathbf{X}}(t) = i\mathbf{\Omega}\mathbf{X}(t) - \int_{t_0}^t \mathbf{\Gamma}(t-t')\,\mathbf{X}(t')\,dt' + \mathbf{R}(t), \quad t > t_0 \tag{9.4}$$

which generalizes equation (4.6) to many variables.

For the random force we assume

$$\langle \mathbf{R}(t)\rangle = 0 \quad \text{and} \quad \langle \mathbf{R}(t); \tilde{\mathbf{X}}(t_0)\rangle = 0 \tag{9.5}$$

corresponding to equations (4.7) and (4.8). Thus, the Fourier–Laplace transforms of canonical correlation functions

$$\Lambda_{jk}[\omega] = \int_0^\infty dt \, e^{-i\omega t}\langle X_j(t+t_0); X_k(t_0)\rangle \tag{9.6}$$

are found from equation (9.4) to be given by the matrix

$$\mathbf{\Lambda}[\omega] = \frac{1}{i(\omega - \mathbf{\Omega}) + \mathbf{\Gamma}[\omega]} \tag{9.7}$$

where

$$\mathbf{\Gamma}[\omega] = \int_0^\infty dt \, e^{-i\omega t} \mathbf{\Gamma}(t). \tag{9.8}$$

Corresponding to equation (4.14), the correlation matrix of the random force will satisfy the relation

$$\mathbf{\Gamma}[\omega] = \int_0^\infty dt \, e^{-i\omega t} \langle \mathbf{R}(t + t_0); \, \tilde{\mathbf{R}}(t_0) \rangle \tag{9.9}$$

or

$$\mathbf{\Gamma}(t) = \langle \mathbf{R}(t + t_0); \, \tilde{\mathbf{R}}(t_0) \rangle. \tag{9.10}$$

This can be proved in the same way as was done for equation (4.14), only those alterations necessary for matrix formalism being made.

By equation (5.21) of the linear response theory, $\mathbf{\Lambda}(\omega)$ as given by equation (9.6) is the admittance matrix defining the linear response

$$\langle \mathbf{X}(t) \rangle = \mathcal{R} \, \mathbf{\Lambda}[\omega] \, \mathbf{K}_0 \, e^{i\omega t} \tag{9.11}$$

where $\mathbf{K} = (K_1, \ldots, K_n)$ is the force, the lth component K_l being conjugate to the variable A_l defined by

$$\dot{A}_l = X_l. \tag{9.12}$$

Thus equation (9.6) with equation (9.11) represents the first fluctuation–dissipation theorem, whereas equation (9.9) or (9.10) represents the second fluctuation–dissipation theorem. The Langevin equation (9.4) is extended to

$$\dot{\mathbf{X}}(t) = i\mathbf{\Omega}\mathbf{X}(t) - \int_{t_0}^t \mathbf{\Gamma}(t - t') \, \mathbf{X}(t') \, dt' + \mathbf{R}(t) + \mathbf{K}(t) \tag{9.13}$$

by including the external force $\mathbf{K}(t)$. This is the equation of motion of the system in the framework of linear response theory.

We may also define the *total* force $\mathbf{F}$ by

$$\dot{\mathbf{X}} = i\mathbf{\Omega}\mathbf{X}(t) + \mathbf{F}(t) \tag{9.14}$$

or

$$\mathbf{F}(t) = - \int_{t_0}^t \mathbf{\Gamma}(t - t') \, \mathbf{X}(t') \, dt' + \mathbf{R}(t) \tag{9.15}$$

in the absence of external forces. In equation (9.14), $i\mathbf{\Omega}\mathbf{X}$ is regarded as the restoring force for the modes $\mathbf{X} = (X_1, \ldots, X_n)$ and $\mathbf{F}(t)$ is the microscopic force, which consists of the systematic and the random parts. The above terminology is, however, rather conventional, because the normal mode frequencies are determined not only by the matrix $\mathbf{\Omega}$ but also by some part of $\mathbf{\Gamma}(\omega)$.

The relation (8.3) or (8.4) is easily generalized to correlation matrices of the total force and the random force. If we define

$$\mathbf{\Gamma}_{\mathrm{t}}[\omega] = \int_0^\infty dt \, e^{-i\omega t} \langle \mathbf{F}(t_0 + t); \, \tilde{\mathbf{F}}(t_0) \rangle \tag{9.16}$$

we then have

$$\frac{1}{\mathbf{\Gamma}[\omega]} = \frac{1}{\mathbf{\Gamma}_t[\omega]} - \frac{1}{i(\omega - \mathbf{\Omega})} \tag{9.17}$$

corresponding to equation (8.4). This shows that $\mathbf{\Gamma}[\omega]$ and $\mathbf{\Gamma}_t[\omega]$ behave very differently around the proper frequencies of $\mathbf{\Omega}$, but they approach the same limit at very high frequencies. Generally the situation will be more complex than that discussed in the previous section because there may be more than two characteristic time constants, so that we may have to distinguish, for instance, the adiabatic, the non-adiabatic or the intermediate effects.

We add here some remarks on the symmetry of the correlation matrices. By combining the properties (6.6) and (6.8) we have, in general,

$$\Lambda_{jk}(\omega, \mathbf{H}) = \epsilon_j \, \epsilon_k \, \Lambda_{kj}(\omega, -\mathbf{H}) \tag{9.18}$$

where ϵ_j is plus or minus one depending on whether X_j is even or odd by time reversal. In particular, if all ϵ_j's are equal, equation (9.18) gives the symmetry of Λ for transposition

$$\Lambda(\omega, \mathbf{H}) = \tilde{\Lambda}(\omega, -\mathbf{H}). \tag{9.19}$$

Since a canonical correlation function of real quantities is real, we have the symmetry

$$\mathscr{R} \, \Lambda(\omega) = \mathscr{R} \, \Lambda(-\omega) \tag{9.20}$$

and

$$\mathscr{I} \, \Lambda(\omega) = - \mathscr{I} \, \Lambda(-\omega). \tag{9.21}$$

Combined with (9.19), the above-mentioned symmetry implies that

$$\mathscr{R} \, \Lambda_s(\omega, \mathbf{H}) = \mathscr{R} \, \Lambda_s(-\omega, \mathbf{H}) = \mathscr{R} \, \Lambda_s(\omega, -\mathbf{H})$$

$$\mathscr{I} \, \Lambda_s(\omega, \mathbf{H}) = - \mathscr{I} \, \Lambda_s(-\omega, \mathbf{H}) = \mathscr{I} \, \Lambda_s(\omega, -\mathbf{H})$$

$$\mathscr{R} \, \Lambda_a(\omega, \mathbf{H}) = \mathscr{R} \, \Lambda_a(-\omega, \mathbf{H}) = - \mathscr{R} \, \Lambda_a(\omega, -\mathbf{H})$$

$$\mathscr{I} \, \Lambda_a(\omega, \mathbf{H}) = - \mathscr{I} \, \Lambda_a(-\omega, \mathbf{H}) = - \mathscr{I} \, \Lambda_a(\omega, -\mathbf{H}) \tag{9.22}$$

for the symmetric and the antisymmetric parts of the matrix Λ defined by

$$\Lambda_s = \tfrac{1}{2}(\Lambda + \tilde{\Lambda}), \quad \Lambda_a = \tfrac{1}{2}(\Lambda - \tilde{\Lambda}).$$

The same symmetry holds for $\mathbf{\Gamma}[\omega]$ and $\mathbf{\Gamma}_t[\omega]$ because they are related to $\Lambda(\omega)$ by equations (9.7) and (9.17). If we write

$$\mathbf{\Gamma}_s{}' = \mathscr{R} \, \mathbf{\Gamma}_s, \quad \mathbf{\Gamma}_s{}'' = \mathscr{I} \, \mathbf{\Gamma}_s$$

$$\mathbf{\Gamma}_a{}' = i \, \mathscr{I} \, \mathbf{\Gamma}_a, \quad \mathbf{\Gamma}_a{}'' = -i \, \mathscr{R} \, \mathbf{\Gamma}_a$$

and

$$\mathbf{\Gamma}_s = \mathbf{\Gamma}_s{}' + i \mathbf{\Gamma}_s{}'', \quad \mathbf{\Gamma}_a = \mathbf{\Gamma}_a{}' + i \mathbf{\Gamma}_a{}''.$$

$\mathbf{\Gamma}_s{}'$, $\mathbf{\Gamma}_s{}''$, $\mathbf{\Gamma}_a{}'$ and $\mathbf{\Gamma}_a{}''$ are all Hermitian. $\mathbf{\Gamma}_s{}'$ and $\mathbf{\Gamma}_a{}'$ act as damping coefficients, whereas $\mathbf{\Gamma}_s{}''$ and $\mathbf{\Gamma}_a{}''$ result in frequency shifts. Each term has its own even–odd symmetry with respect to ω and $\mathbf{H}$ as indicated by (9.22).

10. Moments, sum rules and continued fraction expansion

We have seen in §5 that an admittance is generally expressed in the form

$$\chi(\omega) = \int_0^\infty \phi(t)\, e^{-i\omega t}\, dt = \chi'(\omega) - i\chi''(\omega). \tag{10.1}$$

Depending on whether $\phi(t)$ is even or odd in t, this equation is inverted as

$$\phi(t) = \frac{1}{\pi}\int_{-\infty}^\infty \chi'(\omega)\, e^{i\omega t}\, d\omega \tag{10.2}$$

or as

$$\phi(t) = \frac{1}{\pi i}\int_{-\infty}^\infty \chi''(\omega)\, e^{i\omega t}\, d\omega. \tag{10.3}$$

If the time derivatives exist for $\phi(t)$ at $t = 0$, we then have

$$\frac{1}{\pi}\int_{-\infty}^\infty \chi'(\omega)\, \omega^{2n}\, d\omega = (-)^n\, \phi^{(2n)}(0) \tag{10.4}$$

for an even ϕ and

$$\frac{1}{\pi}\int_{-\infty}^\infty \chi''(\omega)\, \omega^{2n+1}\, d\omega = (-)^n\, \phi^{(2n+1)}(0) \tag{10.5}$$

for an odd ϕ, in which case another equation

$$\frac{1}{\pi}\int_{-\infty}^\infty \frac{\chi''(\omega)}{\omega}\, d\omega = \chi'(0) = \int_0^\infty \phi(t)\, dt \tag{10.6}$$

should also be quoted. This last equation is obtained as a particular case of the well-known Kramers–Kronig relation or by applying equation (10.4) to

$$\Phi(t) = \int_t^\infty \phi(t')\, dt'.$$

Generally, $\chi'(\omega)$ or $\chi''(\omega)$ in these equations is positive because it represents the dissipative part of the admittance. On the right-hand sides of the equations we have the derivatives of a response function evaluated at $t = 0$, which are canonical correlations such as

$$\phi_{BA}(0) = \beta\langle \dot{A}(0); B(0)\rangle = \langle (A(0), B(0))\rangle$$

$$\dot{\phi}_{BA}(0) = \beta\langle \dot{A}(0); \dot{B}(0)\rangle = \langle (A(0), \dot{B}(0))\rangle$$

$$\ddot{\phi}_{BA}(0) = \beta\langle \dot{A}(0); \ddot{B}(0)\rangle = -\langle (\dot{A}(0), \dot{B}(0))\rangle$$

$$\dddot{\phi}_{BA}(0) = -\beta\langle \ddot{A}(0); \ddot{B}(0)\rangle = -\langle (\dot{A}(0), \ddot{B}(0))\rangle \tag{10.7}$$

and so forth.

This is summarized by the general *sum-rule* theorem (Kubo 1957, 1959) which states that the moments of the frequency distribution of dissipative intensities sum-rule moments are determined by the *equilibrium* (static) fluctuation of relevant physical quantities. The right-hand sides of equation (10.7) may be just a universal constant determined by the commutation rules of dynamical variables, in which case the sum rule becomes most impressive and useful.

Equation (10.1) may be transformed by partial integration to

$$\chi(\omega) = \frac{\phi(0)}{i\omega} + \frac{\dot{\phi}(0)}{(i\omega)^2} + \ldots + \frac{\phi^{(n)}(0)}{(i\omega)^{n+1}} + \frac{1}{(i\omega)^{n+1}} \int_0^\infty \phi^{(n+1)}(t) \, e^{-i\omega t} \, dt \qquad (10.8)$$

which is useful at high frequencies. If the expansion is carried out to infinite order, this becomes an asymptotic expansion expressed only in terms of the sum-rule moments, or the sum-rule quantities. This may be called a *sum-rule expansion*.

There exists another type of moment expansion in the form of a continued fraction which was investigated recently by Mori (1965 b). For simplicity, let us illustrate this for a pair of variables, say X' and X'', which represent an oscillatory mode and so form a set of canonical conjugates. We may then take a complex variable

$$A = X' + iX''.$$

In the absence of a magnetic field, X' and X'' differ under time reversal symmetry, so that correlations of the type $\langle A \, ; A \rangle$ or $\langle A^* \, ; A^* \rangle$ vanish identically. Then the Langevin equation (9.4) may be written as

$$\dot{A}(t) = i\omega_0 A(t) - \int_{t_0}^t \gamma_1(t - t') A(t') \, dt' + A_1(t), \quad t > t_0 \qquad (10.9)$$

where $A_1(t)$ is a complex random force with the same symmetry as $\dot{A}(t)$. The equation of motion of $A_1(t)$ may be put in the same form as equation (10.9) introducing a higher order random force $A_2(t)$. Repeating this process, we have a hierarchy of generalized Langevin equations in the form

$$\dot{A}_n(t) = i\omega_n A_n(t) - \int_{t_0}^t \gamma_{n+1}(t - t') A_n(t') \, dt' + A_{n+1}(t), \quad t > t_0 \qquad (10.10)$$

with

$$A_0(t) \equiv A(t)$$

$$\int_0^\infty dt \, e^{-i\omega t} \langle A_n(t) \, ; A_n{}^*(t) \rangle = \frac{\langle A_n \, ; A_n{}^* \rangle}{i(\omega - \omega_n) + \gamma_{n+1}[\omega]} \qquad (10.11)$$

$$\gamma_{n+1}(t) = \frac{\langle A_{n+1}(t + t_0) \, ; A_{n+1}{}^*(t_0) \rangle}{\langle A_n(t_0) \, ; A_n{}^*(t_0) \rangle} \qquad (10.12)$$

and

$$i\omega_n = \frac{\langle \dot{A}_n \, ; A_n{}^* \rangle}{\langle A_n \, ; A_n{}^* \rangle}. \qquad (10.13)$$

These recurrence formulae define the continued fraction

$$\int_0^\infty dt \, e^{-i\omega t} \langle A(t + t_0) \, ; A^*(t_0) \rangle$$

$$= \frac{\langle A \, ; A^* \rangle}{i(\omega - \omega_0) + \Delta_1 [i(\omega - \omega_1) + \Delta_2 / \{i(\omega - \omega_2) + \ldots\}]^{-1}} \qquad (10.14)$$

where

$$\Delta_n = \frac{\langle A_n \, ; A_n{}^* \rangle}{\langle A_{n-1} \, ; A_{n-1}{}^* \rangle}. \qquad (10.15)$$

The constants appearing in equation (10.14) are expressed in terms of initial values $A_n(t_0)$, $\dot{A}_n(t_0)$, ..., or, by the recurrence formula (10.10), in terms of the initial derivatives of $A(t)$, namely in terms of the sum-rule moments.

The continued fraction expansion of the type (10.14) includes perturbational calculations, but it is not limited to the category of perturbation. Mori (1965 b, 1966) used this method to investigate the anomaly of transport coefficients of a system near the critical transition. This method is closely related to modern aspects of many-body problems.

11. Density response, conduction and diffusion

In order to illustrate the general theory hitherto described, we discuss here the density response and related subjects for a system of interacting particles. The particle density at a given position is defined by

$$n(\mathbf{r}, t) = \sum_l \delta(\mathbf{r} - \mathbf{r}_l(t))$$

$$= \sum_{\mathbf{k}} n_{\mathbf{k}}(t) \exp(i\mathbf{k}.\mathbf{r}) \tag{11.1}$$

where $n_{\mathbf{k}}(t)$ is the Fourier component

$$n_{\mathbf{k}}(t) = L^{-3} \sum_l \exp\{-i\mathbf{k}.\mathbf{r}_l(t)\} \tag{11.2}$$

L^3 being the volume of the space, and similarly the current density and its Fourier components are defined by

$$\mathbf{j}(\mathbf{r}, t) = \sum_{\mathbf{k}} \mathbf{j}_{\mathbf{k}}(t) \exp(i\mathbf{k}.\mathbf{r}) \tag{11.3}$$

$$\mathbf{j}_{\mathbf{k}}(t) = L^{-3} \sum_l \frac{1}{m} [\mathbf{p}_l(t) \exp\{-i\mathbf{k}.\mathbf{r}_l(t)\}]. \tag{11.4}$$

The density and current Fourier components have the Poisson bracket

$$(\mathbf{j}_{-\mathbf{k}}, n_{\mathbf{k}}) = \frac{n}{m} i\mathbf{k} \tag{11.5}$$

where n is the number density of the particle. The continuity equation is written as

$$\dot{n}_{\mathbf{k}}(t) + i\mathbf{k}.\mathbf{j}_{\mathbf{k}}(t) = 0. \tag{11.6}$$

When an external potential $\varphi^{\mathrm{e}}(\mathbf{r}, t)$ is imposed the perturbation is given by the Hamiltonian

$$\mathscr{H}_{\mathrm{ext}}(t) = \sum_{\mathbf{k}} n_{-\mathbf{k}}(t) \varphi_{\mathbf{k}}^{\mathrm{e}}(t) \tag{11.7}$$

where $\varphi_{\mathbf{k}}^{\mathrm{e}}(t)$ is the spatial Fourier component of the external potential. Then the linear response of the system to

$$\varphi_{\mathbf{k}}^{\mathrm{e}}(t) = \mathscr{R}\varphi_{\mathbf{k}}^{\mathrm{e}} \, \mathrm{e}^{i\omega t}$$

is expressed by

$$\langle n_{\mathbf{k}}(t) \rangle = -\mathscr{R}\chi[\mathbf{k}, \omega] \, \varphi_{\mathbf{k}}^{\mathrm{e}} \, \mathrm{e}^{i\omega t} \tag{11.8}$$

for the density, and by

$$\langle \mathbf{j}_{\mathbf{k}}(t) \rangle = -\mathscr{R}\mu[\mathbf{k}, \omega] \, i\mathbf{k}\varphi_{\mathbf{k}}^{\mathrm{e}} \, \mathrm{e}^{i\omega t} \tag{11.9}$$

for the current, where

$$\chi[\mathbf{k}, \omega] = \int_0^\infty dt \, e^{-i\omega t} \langle (n_{-\mathbf{k}}(0), n_{\mathbf{k}}(t)) \rangle \tag{11.10}$$

(see equation (5.16*b*)) is the susceptibility for the density response and

$$\mu^e[\mathbf{k}, \omega] = \beta \int_0^\infty dt \, e^{-i\omega t} \langle \mathbf{j}_{-\mathbf{k}}(0); \mathbf{j}_{\mathbf{k}}(t) \rangle \tag{11.11}$$

is the *external* mobility tensor (see equations (5.21) and (11.6)). This terminology is introduced here in order to discriminate it from the *local* mobility μ which will be defined later. The susceptibility and the external mobility are related with each other by equation (7.3), namely

$$i\omega\chi[\mathbf{k}, \omega] - \mathbf{k} \cdot \mu^e[\mathbf{k}, \omega] \cdot \mathbf{k} = 0 \tag{11.12}$$

which is also obtained from equation (11.10) by performing partial integration.

Now let us consider the canonical correlation of density fluctuation

$$\langle n_{-\mathbf{k}}(0); n_{\mathbf{k}}(t) \rangle$$

and define its Fourier–Laplace transform

$$\Lambda[\mathbf{k}, \omega] = \int_0^\infty dt \, e^{-i\omega t} \langle n_{-\mathbf{k}}(0); n_{\mathbf{k}}(t) \rangle \tag{11.13}$$

which is related to the susceptibility by

$$\Lambda[\mathbf{k}, \omega] = \frac{1}{i\omega\beta}(\chi[\mathbf{k}, 0] - \chi[\mathbf{k}, \omega]) \tag{11.14}$$

as is easily proved by partial integration of the right-hand side of equation (11.13) with the use of equation (5.20). Here $\chi(\mathbf{k}, 0)$ is the *static* density susceptibility to the external potential $\varphi_{\mathbf{k}}^e$, namely

$$\chi[\mathbf{k}, 0] = \beta \langle n_{-\mathbf{k}}(0); n_{\mathbf{k}}(0) \rangle = -\frac{\partial \langle n_{\mathbf{k}} \rangle}{\partial \varphi_{\mathbf{k}}^e} \tag{11.15}$$

which approaches, as $k \to 0$,

$$\lim_{k \to 0} \chi[\mathbf{k}, 0] = \left(\frac{\partial n}{\partial \zeta}\right)_T = -n^2 \kappa \tag{11.16}$$

where ζ is the chemical potential and κ the isothermal compressibility. The first equality in equation (11.16) is obtained by identifying the local change of $-\varphi^e$ with that of the chemical potential. The second equality follows from the Gibbs–Duhem relation.

We now write $\Lambda[\mathbf{k}, \omega]$, equation (11.13), in the form

$$\Lambda[\mathbf{k}, \omega] = \frac{\langle n_{-\mathbf{k}}(0); n_{\mathbf{k}}(0) \rangle}{i\omega + \gamma_{\mathbf{k}}[\omega]} = \frac{\chi[\mathbf{k}, 0]}{\beta(i\omega + \gamma_{\mathbf{k}}[\omega])}. \tag{11.17}$$

As we have seen in §7, equation (11.6) is then regarded as a Langevin equation

$$\dot{n}_{\mathbf{k}}(t) = -i\mathbf{k} \cdot \mathbf{j}_{\mathbf{k}}^0(t) - i\mathbf{k} \cdot \mathbf{j}_{\mathbf{k}}'(t) \tag{11.18}$$

where the systematic current $\mathbf{j}_\mathbf{k}{}^0(t)$ is defined by the equation

$$-i\mathbf{k}.\mathbf{j}_\mathbf{k}{}^0(t) = -\int_0^t \gamma_\mathbf{k}(t-t')\,n_\mathbf{k}(t')\,dt' \qquad (11.19)$$

and

$$\mathbf{j}_\mathbf{k}'(t) = \mathbf{j}_\mathbf{k}(t) - \mathbf{j}_\mathbf{k}{}^0(t) \qquad (11.20)$$

is the random current. The systematic current is the part of the total current $\mathbf{j}_\mathbf{k}(t)$ induced by the density change. Equation (11.18) corresponds to equation (8.1) or (10.9) (with $\omega_0 = 0$), so that the second fluctuation–dissipation theroem, (7.16) or (10.11), tells us that the function $\gamma_\mathbf{k}[\omega]$ in equation (11.17) is determined by the time correlation of the random current. Thus we may write it as

$$\gamma_\mathbf{k}[\omega] = \frac{\mathbf{k}.\mu^*[\mathbf{k},\omega].\mathbf{k}}{\chi[\mathbf{k},0]} = \mathbf{k}.D[\mathbf{k},\omega].\mathbf{k} \qquad (11.21)$$

where the local mobility tensor is defined by

$$\mu^*[\mathbf{k},\omega] = \beta \int_0^\infty dt\, e^{-i\omega t}\langle \mathbf{j}_{-\mathbf{k}}'(0); \mathbf{j}_\mathbf{k}'(t)\rangle \qquad (11.22)$$

and the diffusion constant D by

$$D[\mathbf{k},\omega] = \mu^*[\mathbf{k},\omega]/\chi[\mathbf{k},0]. \qquad (11.23)$$

Equation (8.3) is applied here to obtain the relationship between the external and local mobilities, which amounts to

$$\mu^*[\mathbf{k},\omega] = \frac{\mu^e[\mathbf{k},\omega]}{1 - \mathbf{k}.\mu^e[\mathbf{k},\omega].\mathbf{k}/i\omega\chi[\mathbf{k},0]} \qquad (11.24)$$

or

$$\mu^e[\mathbf{k},\omega] = \frac{\mu^*[\mathbf{k},\omega]}{1 + \mathbf{k}\mu^*[\mathbf{k},\omega]\,\mathbf{k}/i\omega\chi[\mathbf{k},0]} \equiv \frac{\mu^*[\mathbf{k},\omega]}{\epsilon^*[\mathbf{k},\omega]}. \qquad (11.25)$$

In the last equation we introduced the shielding factor $\epsilon^*[\mathbf{k},\omega]$ by the definition

$$\epsilon^*[\mathbf{k},\omega] = 1 + \frac{\mathbf{k}.\mu^*[\mathbf{k},\omega].\mathbf{k}}{i\omega\chi[\mathbf{k},0]} \qquad (11.26)$$

which can be written as

$$\frac{1}{\epsilon^*[\mathbf{k},\omega]} = 1 - \frac{\mathbf{k}.\mu^e[\mathbf{k},\omega]\,\mathbf{k}}{i\omega\chi[\mathbf{k},0]} = 1 - \frac{\chi[\mathbf{k},\omega]}{\chi[\mathbf{k},0]} \qquad (11.27)$$

by virtue of equations (11.24) and (11.12).

It is remarked incidentally that the shielding factor $\epsilon^*[\mathbf{k},\omega]$ or the susceptibility $\chi[\mathbf{k},\omega]$ has a close relation with the thermodynamic property of the particle system. If the particles interact with a pair potential

$$v(r-r') = \int dk\, v_\mathbf{k} \exp\{i\mathbf{k}.(\mathbf{r}-\mathbf{r}')\} \qquad (11.28)$$

the total interaction energy is

$$E_{\text{int}} = \tfrac{1}{2}L^3 \sum_\mathbf{k} v_\mathbf{k}\, n_{-\mathbf{k}}\, n_\mathbf{k}.$$

Then we have for the free energy F of the system the relationship

$$2\frac{\partial}{\partial v_\mathbf{k}}\frac{F}{L^3} = \langle n_{-\mathbf{k}} n_\mathbf{k}\rangle = \frac{1}{\pi}\int_{-\infty}^{\infty} d\omega\, \frac{\hbar\chi[\mathbf{k},0]}{1-\mathrm{e}^{-\beta\hbar\omega}}\,\mathscr{I}\!\left(\frac{1}{\epsilon^*[\mathbf{k},\omega]}\right). \tag{11.29}$$

This is an example of application of the fluctuation–dissipation theorem in the form of equation (6.15), which gives for $\chi[\mathbf{k},\omega]$ the equation

$$2\mathscr{I}\chi[\mathbf{k},\omega] = -\frac{1-\mathrm{e}^{-\beta\hbar\omega}}{\hbar}\int_{-\infty}^{\infty}\langle n_{-\mathbf{k}}(0)\,n_\mathbf{k}(t)\rangle\,\mathrm{e}^{-i\omega t}\,dt. \tag{11.30}$$

Reversing the transformation for $t = 0$ and using equation (11.27), we arrive at equation (11.29). This equation is sometimes called the dielectric formula† (Nozieres and Pines 1958, Englert and Brout 1960), and it allows computation of the free energy, or the ground-state energy in particular, using a certain approximation for the shielding function $\epsilon^*[\mathbf{k},\omega]$. As an additional remark, we note that the integral on the right-hand side of equation (11.30) is known as the dynamic form factor $S[\mathbf{k},\omega]$, which is thus expressed in terms of the shielding factor or the susceptibility function. It is essentially the real part of $\Lambda[\mathbf{k},\omega]$. The generalized diffusion constant $D[\mathbf{k},\omega]$ is thus related to the dynamic form factor which is observable, for instance, by neutron inelastic measurements.

The current response (11.9) may be written as

$$\langle \mathbf{j}_\mathbf{k}(t)\rangle = -\mathscr{R}\mu^*[\mathbf{k},\omega]\,i\mathbf{k}\varphi_\mathbf{k}^*\mathrm{e}^{i\omega t} \tag{11.31}$$

where the potential $\varphi_\mathbf{k}^*(t)$ of the *local* field is introduced by the definition

$$\varphi_\mathbf{k}^*(t) = \frac{1}{\epsilon^*[\mathbf{k},\omega]}\,\varphi_\mathbf{k}^\mathrm{e}(t). \tag{11.32}$$

This can be written, with the use of equations (11.27), (11.8) and (11.15), as

$$\varphi_\mathbf{k}^*(t) = \varphi_\mathbf{k}^\mathrm{e}(t) - \frac{\chi[\mathbf{k},\omega]}{\chi[\mathbf{k},0]}\varphi_\mathbf{k}^\mathrm{e}(t) = \varphi_\mathbf{k}^\mathrm{e}(t) + \frac{\langle n_\mathbf{k}(t)\rangle}{\chi[\mathbf{k},0]} \tag{11.33}$$

which shows that the local field is the resultant of the external field and the effective field induced by the density change. The latter causes the shielding of the applied field. The current may be supposed to be driven either by the external field with the external mobility $\mu^\mathrm{e}[\mathbf{k},\omega]$ or by the local field with the local mobility $\mu^*[\mathbf{k},\omega]$ (Luttinger 1964, Martin 1965).

As long as the particle interaction is short-ranged, it can generally be proved that the static susceptibility $\chi[\mathbf{k},0]^{-1}$ is non-singular at $\mathbf{k}=0$, so that the local field correction vanishes in the long wavelength limit $k\to0$, i.e.

$$\lim_{k\to0}\epsilon^*[\mathbf{k},\omega] = 1 \tag{11.34}$$

if the particles are not bound, and so the local mobility should remain finite at $k = 0$ and $\omega = 0$. Therefore the external and local mobilities become equal in the limit $k\to0$, and equation (11.23) gives the Einstein relation

$$D \equiv D[0,0] = \mu^*[0,0]\Big/\frac{\partial n}{\partial \zeta}. \tag{11.35}$$

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† Usually the dielectric formula is written in terms of the dielectric function $\epsilon[\mathbf{k},\omega]$ defined by equation (11.40) rather than the shielding factor.

For small non-zero k's, equation (11.33) may be approximated by

$$\varphi_{\mathbf{k}}^*(t) = \varphi_{\mathbf{k}}^e(t) - \frac{\partial \zeta}{\partial n} \langle n_{\mathbf{k}}(t) \rangle \tag{11.36}$$

which means that the local field correlation is nothing but the chemical potential change induced by the density change. This appears as the diffusion force or the pressure gradient.

For charged particles the function $\chi[\mathbf{k}, 0]^{-1}$ is singular at $k = 0$ in such a way that

$$\chi[\mathbf{k}, 0]^{-1} \sim \frac{4\pi e^2}{k^2} \tag{11.37}$$

is the dominant term for small k's, e being the charge on each particle. This comes from the Coulomb interaction energy which contributes a part of the free energy change when a density fluctuation is induced with a wave number k. If we take only this term of $\chi[\mathbf{k}, 0]^{-1}$ to define the local field

$$\varphi_{\mathbf{k}}(t) = \varphi_{\mathbf{k}}^e(t) + \frac{4\pi e^2}{k^2} \langle n_{\mathbf{k}}(t) \rangle \tag{11.38}$$

the shielding factor becomes equal to the usual dielectric constant $\epsilon[\mathbf{k}, \omega]$. It should be remembered, however, that the shielding factor $\epsilon^*[\mathbf{k}, \omega]$ as defined by (11.25) generally differs from the dielectric constant because the local field in equation (11.33) contains, in principle, all sorts of local effects such as diffusion, pressure gradient and even thermoelectric force.

For charged particles it is customary to talk about the conductivity defined by

$$\sigma[\mathbf{k}, \omega] = e^2 \mu^*[\mathbf{k}, \omega] \tag{11.39}$$

in terms of which equation (11.26) is written as

$$\epsilon[\mathbf{k}, \omega] = 1 + \frac{4\pi}{i\omega k^2} \mathbf{k} . \sigma[\mathbf{k}, \omega] . \mathbf{k} \tag{11.40}$$

which is a familiar expression for the dielectric constant in terms of the conductivity. The conductivity tensor σ is therefore given by equation (11.22), namely

$$\sigma[\mathbf{k}, \omega] = e^2 \beta \int_0^\infty dt \, e^{-i\omega t} \langle \mathbf{j}_{-\mathbf{k}}'(0); \mathbf{j}_{\mathbf{k}}'(t) \rangle \tag{11.41}$$

in terms of the correlation function of the random current. This should be discriminated from the expression of the external conductivity

$$\sigma^e[\mathbf{k}, \omega] = e^2 \beta \int_0^\infty dt \, e^{-i\omega t} \langle \mathbf{j}_{-\mathbf{k}}(0); \mathbf{j}_{\mathbf{k}}(t) \rangle \tag{11.42}$$

which is related to $\sigma[\mathbf{k}, \omega]$ by

$$\sigma^e[\mathbf{k}, \omega] = \frac{\sigma[\mathbf{k}, \omega]}{\epsilon[\mathbf{k}, \omega]} = \frac{\sigma[\mathbf{k}, \omega]}{1 + 4\pi\sigma[\mathbf{k}, \omega]/i\omega}. \tag{11.43}$$

Note, however, that these equations may fail for large k's for which the approximation (11.37) is no longer valid.

The sum-rule consideration can be applied to both kinds of conductivity, although it becomes more complicated for the local conductivity. The lowest-order sum rule equally applies to both, for the random current is initially equal to the total current. Therefore we have

$$\frac{1}{\pi} \int_{-\infty}^{\infty} \mathscr{R}\sigma[\mathbf{k}, \omega] \, d\omega = \frac{1}{\pi} \int_{-\infty}^{\infty} \mathscr{R}\sigma^{\mathrm{e}}[\mathbf{k}, \omega] \, d\omega = \frac{ne^2}{m}. \qquad (11.44)$$

Within the framework of the linear response theory, all the necessary information about the system is contained in the function $\Lambda[\mathbf{k}, \omega]$ or $\chi[\mathbf{k}, \omega]$ or any of the related quantities. In the spirit of the fluctuation–dissipation theorem this means that any one of these functions tells us all possible modes of collective oscillation, individual excitations around the equilibrium states, etc. In particular, at low frequencies and for long wavelengths the macroscopic or hydrodynamical laws governing the motion of the system are directly reflected in the structure of these response functions (Kadanoff and Martin 1963). This means that the transport or the kinetic coefficients appearing in the hydrodynamic equations can be identified with proper microscopic expressions when the response functions are calculated by statistical mechanics. A simple example has been given here for the conductivity. Such expressions are very fundamental for the statistical–mechanical theory of irreversible processes and have proved very useful for practical computations. The great advantage is that they are valid even when the traditional kinetic equation method is questionable or cannot be used. On the other hand, one should, of course, appreciate the great power of kinetic equations within their own limitations as they are able to cover a large area of non-linear phenomena. Extension of the present approach to the non-linear régime is possible (Bernard and Callen 1959) but it has not been explored to any great extent. Further discussion of applications and extensions is out of place in the present article.

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