Chapter 2
Microscopic Reversibility

The *Principle of Microscopic Reversibility* was formulated by Richard Tolman [14] who stated that, at equilibrium, "any molecular process and the reverse of that process will be taking place on the average at the same rate". Applying this concept to macroscopic systems at local equilibrium leads to the rule of *detailed balances* (Sect. 2.2) and then, assuming linear relations between thermodynamic forces and fluxes, to the formulation of the celebrated reciprocity relations (Sect. 2.3) derived by Lars Onsager in 1931, and the fluctuation-dissipation theorem, (Sect. 2.4) proved by Herbert Callen and Theodore Welton in 1951. In this chapter, this vast subject matter is treated with a critical attitude, stressing all the hypotheses and their limitations.

2.1 Probability Distributions

Define:

- The simple probability $\Pi(\mathbf{x}, t)$ that the random variable $\mathbf{x}(t)$ has a certain value $\mathbf{x}$ at time t.[1]
- The joint probability $\Pi(\mathbf{x}_2, t_2; \mathbf{x}_1, t_1)$ that the random variable $\mathbf{x}(t)$ has a certain value $\mathbf{x}_2 = \mathbf{x}(t_2)$ at time t_2 and, also, that it has another value $\mathbf{x}_1 = \mathbf{x}(t_1)$ at time t_1.
- The conditional probability $\Pi(\mathbf{x}_2, t_2 | \mathbf{x}_1, t_1)$ that a random variable $\mathbf{x}$ has a certain value $\mathbf{x}_2 = \mathbf{x}(t_2)$ at time t_2, provided that at another (i.e. previous) time t_1 it has a value $\mathbf{x}_1 = \mathbf{x}(t_1)$.

By definition, when $t_2 > t_1$,

$$\Pi(\mathbf{x}_2, t_2; \mathbf{x}_1, t_1) = \Pi(\mathbf{x}_2, t_2 | \mathbf{x}_1, t_1)\, \Pi(\mathbf{x}_1, t_1). \tag{2.1}$$

[1] Here and in the following, we use the same notation, $\mathbf{x}$, to indicate both the random variable and the value that it can assume. Whenever this might be confusing, different symbols will be used.

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In a stationary process all probability distributions are invariant under a time translation $t \to t+\tau$. Therefore for stationary processes the three distribution functions simplify as follows.

- $\Pi(\mathbf{x},t) = \Pi(\mathbf{x})$ independent of t;
- $\Pi(\mathbf{x}_2,t_2;\mathbf{x}_1,t_1) = \Pi(\mathbf{x}_2,\tau;\mathbf{x}_1,0)$;
- $\Pi(\mathbf{x}_2,t_2|\,\mathbf{x}_1,t_1) = \Pi(\mathbf{x}_2,\tau|\,\mathbf{x}_1,0)$,

where $\tau = t_1 - t_2$. In the following, when there is no ambiguity, the time 0 will be omitted.

If the process is also homogeneous, then all probability distributions are invariant under a space translation $\mathbf{x} \to \mathbf{x}+\mathbf{z}$. Therefore for stationary homogeneous processes the three distribution functions simplify as follows.

- $\Pi(\mathbf{x}) = \Pi$ independent of $\mathbf{x}$ and t;
- $\Pi(\mathbf{x}_1,\tau;\mathbf{x}_0,0) = \Pi(\mathbf{z},\tau)$;
- $\Pi(\mathbf{x}_1,\tau|\,\mathbf{x}_0,0) = \Pi(\mathbf{z},\tau)$,

where $\mathbf{z} = \mathbf{x}_1 - \mathbf{x}_0$. Note that for stationary and homogeneous processes the joint probability and the conditional probability are equal to each other; in fact, the ratio between them is given by the simple probability, which in this case is a constant.

Now, let us consider a stationary process. Its probability distribution functions are normalized as follows:

$$1 = \int \Pi(\mathbf{x})\,d\mathbf{x} = \int\int \Pi(\mathbf{x},\tau;\mathbf{x}_0,0)\,d\mathbf{x}\,d\mathbf{x}_0. \tag{2.2}$$

Consequently,

$$1 = \int \Pi(\mathbf{x},\tau|\,\mathbf{x}_0,0)\,d\mathbf{x}, \tag{2.3}$$

showing that, since $\mathbf{x} = \mathbf{x}_0$ at $\tau = 0$, we have

$$\lim_{\tau\to 0} \Pi(\mathbf{x},\tau|\,\mathbf{x}_0,0) = \delta(\mathbf{x}-\mathbf{x}_0). \tag{2.4}$$

Based on these definitions, for any functions $f(\mathbf{x})$ and $g(\mathbf{x})$ we can define the averages,

$$\langle f(\mathbf{x})\rangle = \int f(\mathbf{x})\Pi(\mathbf{x})\,d\mathbf{x}, \tag{2.5}$$

and

$$\langle f(\mathbf{x}_1)g(\mathbf{x}_0)\rangle = \int\int f(\mathbf{x}_1)g(\mathbf{x}_0)\Pi(\mathbf{x}_1,t_1;\mathbf{x}_0,t_0)\,d\mathbf{x}_1\,d\mathbf{x}_0, \tag{2.6}$$

where $\mathbf{x}_1 = \mathbf{x}(t_1)$ and $\mathbf{x}_0 = \mathbf{x}(t_0)$. Obviously, while the first average is a constant, the second is a function of $\tau = t_1 - t_0$.

We can also define the conditional average of any functions $f(\mathbf{x})$ of the random variable $\mathbf{x}(t)$ as the mean value of $f(\mathbf{x})$ at time τ, assuming that $\mathbf{x}(0) = \mathbf{x}_0$, i.e.,

$$\big\langle f(\mathbf{x})\big\rangle_{\tau}^{\mathbf{x}_0} = \int f(\mathbf{x})\, \Pi[\mathbf{x}, \tau\,|\,\mathbf{x}_0, 0]\, d\mathbf{x}. \tag{2.7}$$

This conditional average depends on τ and on $\mathbf{x}_0$.

Now, substituting (2.1) into (2.6), we obtain the following equality,

$$\big\langle f(\mathbf{x}) g(\mathbf{x}_0)\big\rangle = \int\int f(\mathbf{x}) g(\mathbf{x}_0) \Pi(\mathbf{x}, \tau|\mathbf{x}_0, 0) \Pi(\mathbf{x}_0)\, d\mathbf{x}\, d\mathbf{x}_0, \tag{2.8}$$

that is:

$$\big\langle f(\mathbf{x}) g(\mathbf{x}_0)\big\rangle = \big\langle\big\langle f(\mathbf{x})\big\rangle_{\tau}^{\mathbf{x}_0} g(\mathbf{x}_0)\big\rangle. \tag{2.9}$$

2.2 Microscopic Reversibility

For a classical N-body system with conservative forces, microscopic reversibility is a consequence of the invariance of the equations of motion under time reversal and simply means that for every microscopic motion reversing all particle velocities also yield a solution. More precisely, the equations of motion of an N particle system are invariant under the transformation

$$\tau \to -\tau; \qquad \mathbf{r} \to \mathbf{r}; \qquad \mathbf{v} \to -\mathbf{v}, \tag{2.10}$$

where $\mathbf{r} \equiv \mathbf{r}^N$ and $\mathbf{v} \equiv \mathbf{v}^N$ are the positions and the velocities of the N particles. This leads to the so-called *principle of detailed balance*, stating that in a stationary situation each possible transition $(\hat{\mathbf{r}}, \hat{\mathbf{v}}) \to (\mathbf{r}, \mathbf{v})$ balances with the time reversed transition $(\mathbf{r}, -\mathbf{v}) \to (\hat{\mathbf{r}}, -\hat{\mathbf{v}})$, so that,

$$\Pi\big[\mathbf{r}(\tau), \mathbf{v}(\tau);\ \hat{\mathbf{r}}(0), \hat{\mathbf{v}}(0)\big] = \Pi\big[\hat{\mathbf{r}}(\tau), -\hat{\mathbf{v}}(\tau);\ \mathbf{r}(0), -\mathbf{v}(0)\big]. \tag{2.11}$$

As we saw in Sect. 1.1, this same condition can be applied when we deal with thermodynamic, coarse grained variables at local equilibrium, i.e. when $\tau \le \tau_{fluct}$, where τ_{fluct} is the typical fluctuation time. In fact, for such very short times, forward motion is indistinguishable from backward motion, as they both are indistinguishable from fluctuations.

First, let us consider variables $x_i(t)$ that are invariant under time reversal, e.g. they are even functions of the particle velocities. In this case, another, perhaps more intuitive, way to write the principle of detailed balance is to assume that the conditional mean values of a variable at times τ and $-\tau$ are equal to each other, which means,

$$\langle \mathbf{x}\rangle_{\tau}^{\mathbf{x}_0} = \langle \mathbf{x}\rangle_{-\tau}^{\mathbf{x}_0} \tag{2.12}$$

or, equivalently,

$$\Pi(\mathbf{x}, \tau\,|\,\mathbf{x}_0, 0) = \Pi(\mathbf{x}, -\tau\,|\,\mathbf{x}_0, 0). \tag{2.13}$$

Multiplying this last equation by $\Pi(\mathbf{x}_0)$, it can be rewritten as

$$\Pi(x_i, \tau; x_{0k}, 0) = \Pi(x_i, -\tau; x_{0k}, 0) = \Pi(x_i, 0; x_{0k}, \tau), \tag{2.14}$$

where we have applied the stationarity condition. As expected, this equation is identical to (2.11), with $\mathbf{x} = \mathbf{r}$.

Now, define the correlation function for a stationary process as:

$$\langle x_i x_k \rangle(\tau) = \left\langle x_i(\tau) x_k(0) \right\rangle = \int\int x_i x_{0k} \Pi(\mathbf{x}, \tau; \mathbf{x}_0, 0)\, d\mathbf{x}\, d\mathbf{x}_0, \tag{2.15}$$

for $\tau > 0$. Applying (2.14), we see that from microscopic reversibility we obtain:

$$\langle x_i x_k \rangle(\tau) = \langle x_i x_k \rangle(-\tau), \tag{2.16}$$

that is,

$$\left\langle x_i(\tau)\, x_k(0) \right\rangle = \left\langle x_i(0)\, x_k(\tau) \right\rangle. \tag{2.17}$$

From this expression, applying Eq. (2.9), we see that another formulation of microscopic reversibility is:

$$\left\langle x_{0k}\, \langle x_i \rangle_\tau^{\mathbf{x}_0} \right\rangle = \left\langle x_{0i}\, \langle x_k \rangle_\tau^{\mathbf{x}_0} \right\rangle. \tag{2.18}$$

Now, consider the general case where x_i is an arbitrary variable which, under time reversal, transforms into the reversed variable according to the rule,

$$x_i \to \epsilon_i x_i, \tag{2.19}$$

where $\epsilon_i = +1$, when the variable is even under time reversal and $\epsilon_i = -1$, when it is odd.[2] At this point, Eq. (2.18) can be generalized as:

$$\left\langle x_{0k}\, \langle x_i \rangle_\tau^{\mathbf{x}_0} \right\rangle = \epsilon_i \epsilon_k \left\langle x_{0i}\, \langle x_k \rangle_\tau^{\mathbf{x}_0} \right\rangle. \tag{2.20}$$

In the following, we will denote by x those variables having $\epsilon = +1$, i.e. those remaining invariant under time reversal, and by y those variables having $\epsilon = -1$, i.e. those changing sign under time reversal, (e.g. velocity or angular momentum).[3]

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[2]Note that, since $\Pi(x_i) = \Pi(\epsilon_i x_i)$, then $\langle x_i \rangle = \epsilon_i \langle x_i \rangle$, implying that all odd variables have zero stationary mean.

[3]In most of the literature, x- and y-variables are generally referred to as α- and β-variables.

2.3 Onsager's Reciprocity Relations

Assume the following linear phenomenological relations: (i.e. neglecting fluctuations)

$$\dot{x}_i = \sum_{j=1}^{n} L_{ij} X_j, \tag{2.21}$$

where the dot denotes time derivative, $\dot{\mathbf{x}}$ are referred to as thermodynamic fluxes, while $\mathbf{X}$ are the generalized forces defined in (1.16). That means that this equation holds when we apply it to its conditional averages,

$$\langle \dot{x}_i \rangle_\tau^{\mathbf{x}_0} = \sum_{j=1}^{n} L_{ij} \langle X_j \rangle_\tau^{\mathbf{x}_0}. \tag{2.22}$$

The coefficients L_{ij} are generally referred to as Onsager's, or phenomenological, coefficients. Now take the time derivative of Eq. (2.18), considering that $\mathbf{x}_0$ is constant:

$$\sum_{j=1}^{n} L_{ij} \big\langle x_{0k} \langle X_j \rangle_\tau^{\mathbf{x}_0} \big\rangle = \sum_{j=1}^{n} L_{kj} \big\langle x_{0i} \langle X_j \rangle_\tau^{\mathbf{x}_0} \big\rangle. \tag{2.23}$$

Considering that $\langle X_j \rangle_{\tau=0}^{\mathbf{x}_0} = X_{0j}$ and $\langle x_{0i} X_{0j} \rangle = -\delta_{ij}$, we obtain:

$$L_{ik} = L_{ki}. \tag{2.24}$$

These are the celebrated reciprocity relations, derived by Lars Onsager [12, 13] in 1931.

In the presence of a magnetic field $\mathbf{B}$ or when the system rotates with angular velocity $\boldsymbol{\Omega}$, the operation of time reversal implies, besides the transformation (2.10), the reversal of $\mathbf{B}$ and $\boldsymbol{\Omega}$ as well. Therefore, the Onsager reciprocity relations become:

$$L_{ik}(\mathbf{B}, \boldsymbol{\Omega}) = L_{ki}(-\mathbf{B}, -\boldsymbol{\Omega}). \tag{2.25}$$

In the following, we will assume that $\mathbf{B} = \mathbf{0}$ and $\boldsymbol{\Omega} = \mathbf{0}$; however, we should keep in mind that in the presence of magnetic fields or overall rotations, the Onsager relations can be applied only when $\mathbf{B}$ and $\boldsymbol{\Omega}$ are reversed.

A clever way to express the Onsager coefficients L_{ij} can be obtained by multiplying Eq. (2.22) by x_{0k} and averaging:

$$\big\langle x_{0k} \langle \dot{x}_i \rangle_\tau^{\mathbf{x}_0} \big\rangle = \sum_{j=1}^{n} L_{ij} \big\langle x_{0k} \langle X_j \rangle_\tau^{\mathbf{x}_0} \big\rangle. \tag{2.26}$$

Now take $\tau = 0$ and apply Eq. (2.9) to obtain:

$$L_{ik} = -\langle \dot{x}_i x_k \rangle_0^{sym}, \tag{2.27}$$

where the superscript "sym" indicates the symmetric part of a tensor, i.e. $A_{ij}^{sym} = \frac{1}{2}(A_{ij} + A_{ji})$. This is one of the many forms 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. Although it was formulated by Nyquist in 1928 to determine the voltage fluctuations in electrical impedances [11], the fluctuation-dissipation theorem was first proven in its general form by Callen and Welton [3] in 1951.

In (2.27), $\dot{\mathbf{x}}$ is the velocity of the random variable as it relaxes to equilibrium. Therefore, considering that $\mathbf{x}$ tends to $\mathbf{0}$ for long times, we see that $\mathbf{x}(0) = -\int_0^\infty \dot{\mathbf{x}}(t)\, dt$ and therefore the fluctuation-dissipation theorem can also be formulated through the following Green-Kubo relation:[4]

$$L_{ik} = \int_0^\infty \left\langle \dot{x}_i(0)\dot{x}_k(t)\right\rangle^{sym} dt, \tag{2.28}$$

showing that the Onsager coefficients can be expressed as the time integral of the correlation function between the velocities of the random variables at two different times.

Now, consider the opposite process, where the random variable evolves out of its equilibrium position $\mathbf{x} = \mathbf{0}$. Therefore, applying again Eq. (2.27), but with negative times, we obtain:

$$L_{ik} = \frac{1}{2}\frac{d}{dt}\langle x_i x_k\rangle_0^{sym}, \tag{2.29}$$

showing that the Onsager coefficients can be expressed as the temporal growth of the mean square displacements of the system variables from their equilibrium values.

These results are easily extended to the case where we have both x and y-variables, i.e. even and odd variables under time reversal. In this case, the phenomenological equations (2.21) can be generalized as:

$$\dot{x_i} = \sum_{j=1}^{n} L_{ij}^{(xx)} X_j + \sum_{j=1}^{n} L_{ij}^{(xy)} Y_j, \tag{2.30}$$

$$\dot{y_i} = \sum_{j=1}^{n} L_{ij}^{(yx)} X_j + \sum_{j=1}^{n} L_{ij}^{(yy)} Y_j, \tag{2.31}$$

where

$$X_i = \frac{1}{k}\frac{\partial \Delta S}{\partial x_i}; \qquad Y_i = \frac{1}{k}\frac{\partial \Delta S}{\partial y_i} \tag{2.32}$$

are the thermodynamic forces associated with the x and y-variables, respectively. With the help of these quantities, the reciprocity relations (2.24) were generalized

[4]The Green-Kubo relation is also called the fluctuation-dissipation theorem of the second kind. See [7, 8].

by Casimir in 1945 as [4]:

$$L_{ij}^{(xx)} = L_{ji}^{(xx)}; \qquad L_{ij}^{(xy)} = -L_{ji}^{(yx)}; \qquad L_{ij}^{(yy)} = L_{ji}^{(yy)}. \tag{2.33}$$

Substituting (2.30), (2.31) and (2.33) into the generalized form (1.26) of the entropy production term,

$$\frac{1}{k}\frac{dS}{dt} = \sum_{i=1}^{n} \dot{x}_i X_i + \sum_{i=1}^{n} \dot{y}_i Y_i, \tag{2.34}$$

we obtain:

$$\frac{1}{k}\frac{d}{dt}\Delta S = \sum_{i=1}^{n}\sum_{j=1}^{n} L_{ij}^{(xx)} X_i X_j + \sum_{i=1}^{n}\sum_{j=1}^{n} L_{ij}^{(yy)} Y_i Y_j. \tag{2.35}$$

This shows that neither the antisymmetric parts of the Onsager coefficients $\mathbf{L}^{(xx)}$ and $\mathbf{L}^{(yy)}$, nor the coupling terms between x and y-variables, $\mathbf{L}^{(xy)}$ and $\mathbf{L}^{(yx)}$, give any contribution to the entropy production rate.

It should be stressed that, when we apply the Onsager-Casimir reciprocity relations, we must make sure that the n variables (and therefore their time derivatives, or fluxes, as well) are independent from each other, and similarly for the thermodynamic forces.[5]

Comment 2.1 In the course of deriving the reciprocity relations, we have assumed that the same equations (2.21) govern both the macroscopic evolution of the system and the relaxation of its spontaneous deviations from equilibrium. This condition is often referred to as Onsager's postulate and is the basis of the Langevin equation (see Chap. 3).[6] The fluctuation-dissipation theorem, Eqs. (2.29) and (2.41), can be seen as a natural consequence of this postulate.

Comment 2.2 The simplest way to see the meaning of the fluctuation-dissipation theorem is to consider the free diffusion of Brownian particles (see Sect. 3.1). First, consider a homogeneous system, follow a single particle as it moves randomly around[7] and define a coefficient of self-diffusion as (one half of) the time derivative of its mean square displacement. Then, take the system out of equilibrium, and define the gradient diffusivity as the ratio between the material flux resulting from an imposed concentration gradient and the concentration gradient itself. As shown by Einstein in his Ph.D. thesis on Brownian motion [6], when the problem is linear (i.e. when particle-particle interactions are neglected), these two diffusivities are

[5] As shown in [10], when fluxes and forces are not independent, but still linearly related to one another, there is a certain arbitrariness in the choice of the independent variables, so that at the end the phenomenological coefficients can be chosen to satisfy the Onsager relations.

[6] Onsager stated that "the average regression of fluctuations will obey the same laws as the corresponding macroscopic irreversible process". See discussions in [9, 15].

[7] This process is sometimes called Knudsen *effusion*.

equal to each other, thus establishing perhaps the simplest example of fluctuation-dissipation theorem. Although we take this result for granted, it is far from obvious, as it states the equality between two very different quantities: on one hand, the fluctuations of a system when it is macroscopically at equilibrium; on the other hand, its dissipative properties as it approaches equilibrium.

2.4 Fluctuation-Dissipation Theorem

As we saw in the previous section, the *fluctuation-dissipation theorem* (FDT) connects the linear response relaxation of a system to its statistical fluctuation properties at equilibrium and it relies on Onsager's postulate that the response of a system in thermodynamic equilibrium to a small applied force is the same as its response to a spontaneous fluctuation.

First, let us derive the FDT in a very simple and intuitive way, following the original formulation by Callen and Greene [1, 2]. Assume that a constant thermodynamic force $\mathbf{X}_0 = -\mathbf{F}_0/kT$ is applied to the system for an infinite time $t < 0$ and then it is suddenly turned off at $t = 0$. Therefore, at $t = 0$ the system will have a non-zero position of stable equilibrium, $\mathbf{x}_0$, such that

$$\mathbf{F}_0 = \nabla_{\mathbf{x}} W_{min} = kT\mathbf{g}\cdot\mathbf{x}_0, \tag{2.36}$$

where $W_{min} = \frac{1}{2}kT\mathbf{x}_0\cdot\mathbf{g}\cdot\mathbf{x}_0 = \mathbf{F}_0\cdot\mathbf{x}_0$ is the minimum work that the constant force, $\mathbf{F}_0$, has to exert to displace the system to position $\mathbf{x}_0$.

Now, in the absence of any external force, i.e. when $t > 0$, the mean value of the $\mathbf{x}$-variable relaxes in time following Eq. (2.22), with,

$$\langle\dot{\mathbf{x}}\rangle^{\mathbf{x}_0}(t) = -\mathbf{M}\cdot\langle\mathbf{x}\rangle^{\mathbf{x}_0}(t);\quad \text{i.e.,}\quad \langle\mathbf{x}\rangle^{\mathbf{x}_0}(t) = \exp(-\mathbf{M}t)\cdot\mathbf{x}_0, \tag{2.37}$$

where $\mathbf{M} = \mathbf{L}\cdot\mathbf{g}$ is a constant phenomenological relaxation coefficient. Therefore, substituting (2.36) into (2.37) we obtain:

$$\langle\mathbf{x}\rangle^{\mathbf{x}_0}(t) = \boldsymbol{\chi}(t)\cdot\frac{\mathbf{F}_0}{kT}, \tag{2.38}$$

where

$$\boldsymbol{\chi}(t) = \exp(-\mathbf{M}t)\cdot\mathbf{g}^{-1} \tag{2.39}$$

is a time dependent relaxation coefficient.

On the other hand, the function $\boldsymbol{\chi}$ is related to the correlation function at equilibrium, $\langle\mathbf{xx}\rangle$. In fact, from the definition (2.15), substituting (2.37) we see that:

$$\langle\mathbf{xx}\rangle(t) = \left\langle\langle\mathbf{x}\rangle_t^{\mathbf{x}_0}\mathbf{x}_0\right\rangle = \exp(-\mathbf{M}t)\cdot\langle\mathbf{x}_0\mathbf{x}_0\rangle = \exp(-\mathbf{M}t)\cdot\mathbf{g}^{-1}. \tag{2.40}$$

Comparing the last two equations, we conclude:

$$\langle \mathbf{xx} \rangle(t) = \boldsymbol{\chi}(t). \tag{2.41}$$

This relation represents the fluctuation-dissipation theorem.[8]

Note that, when $t = 0$, the relation (2.41) is identically satisfied, since $\langle \mathbf{xx} \rangle(0) = \mathbf{g}^{-1}$, while $\boldsymbol{\chi}(0) = \mathbf{g}^{-1}$.

The fluctuation-dissipation theorem can also be determined assuming a general, time-dependent driving force, $\mathbf{F}(t)$. In this case, due to the linearity of the process, we can write:

$$\big\langle \mathbf{x}(t) \big\rangle = \frac{1}{kT} \int_{-\infty}^{\infty} \boldsymbol{\kappa}\big(t - t'\big) \cdot \mathbf{F}\big(t'\big)\, dt', \tag{2.42}$$

where $\boldsymbol{\kappa}(t)$ is the generalized susceptibility, with $\boldsymbol{\kappa}(t) = 0$ for $t < 0$. Denoting by $\widehat{\mathbf{x}}(\omega)$, $\widehat{\boldsymbol{\kappa}}(\omega)$ and $\widehat{\mathbf{X}}(\omega)$, the Fourier transforms (C.1) of $\langle \mathbf{x}(t) \rangle$, $\boldsymbol{\kappa}(t)$ and $\mathbf{X}(t)$, respectively, we have:

$$\widehat{\mathbf{x}}(\omega) = \frac{1}{kT} \widehat{\boldsymbol{\kappa}}(\omega) \cdot \widehat{\mathbf{F}}(\omega). \tag{2.43}$$

In general, $\widehat{\boldsymbol{\kappa}}(\omega)$ is a complex function, with $\widehat{\boldsymbol{\kappa}} = \widehat{\boldsymbol{\kappa}}^{(r)} + i\widehat{\boldsymbol{\kappa}}^{(i)}$, where the superscripts (r) and (i) indicate the real and imaginary part. Since $\boldsymbol{\kappa}(t)$ is real, we have:

$$\widehat{\boldsymbol{\kappa}}(-\omega) = \widehat{\boldsymbol{\kappa}}^{*}(\omega), \tag{2.44}$$

where the asterisk indicates complex conjugate, showing that $\widehat{\boldsymbol{\kappa}}^{(r)}$ is an even function, while $\widehat{\boldsymbol{\kappa}}^{(i)}$ is an odd function, i.e.,

$$\widehat{\boldsymbol{\kappa}}^{(r)}(-\omega) = \widehat{\boldsymbol{\kappa}}^{(r)}(\omega); \qquad \widehat{\boldsymbol{\kappa}}^{(i)}(-\omega) = -\widehat{\boldsymbol{\kappa}}^{(i)}(\omega). \tag{2.45}$$

Analogous relations exists regarding the correlation function $\langle \mathbf{xx} \rangle(t)$. In fact, considering the microscopic reversibility (2.16) and the reality condition, we obtain:

$$\langle \widehat{\mathbf{xx}} \rangle(\omega) = \langle \widehat{\mathbf{xx}} \rangle^{+}(\omega) = \langle \widehat{\mathbf{xx}} \rangle^{*}(-\omega), \tag{2.46}$$

i.e. the Fourier transform of the correlation function is a real and symmetric matrix.

As shown in Appendix C, using the causality principle, i.e. imposing that $\boldsymbol{\kappa}(t) = 0$ for $t < 0$, we see that the generalized susceptibility is subjected to the Kramers-Kronig relation (C.17), so that $\boldsymbol{\kappa}(t)$ can be related to $\boldsymbol{\chi}(t)$ as [cf. Eq. (C.30)][9]

$$\boldsymbol{\chi}(\omega) = \frac{2}{i\omega} \boldsymbol{\kappa}(\omega). \tag{2.47}$$

[8] The same result can be obtained assuming that the constant thermodynamic force $\mathbf{X}_0$ is suddenly turned on at $t = 0$, so that for long times the system will have a non-zero position of stable equilibrium, $\mathbf{x}_F = -\mathbf{g}^{-1} \cdot \mathbf{X}_0$. In that case, redefining the random variable $\mathbf{x}$ as $\mathbf{x}_F - \mathbf{x}$, we find again Eq. (2.41).

[9] This is a somewhat simplified analysis. For more details, see [5].

Substituting this result into Eq. (2.41) and considering (2.46), we see that the fluctuation-dissipation theorem can be written in the following equivalent form:

$$\langle \widehat{\mathbf{x}\mathbf{x}} \rangle^{(r)}(\omega) = \frac{2}{\omega}\left[\widehat{\boldsymbol{\kappa}}^{(i)}(\omega)\right]^{(s)}, \tag{2.48}$$

where the superscripts (s) denotes the symmetric part of the tensor.

Note that, since

$$\langle \mathbf{x}\mathbf{x} \rangle_0 = \int_{-\infty}^{\infty} \langle \widehat{\mathbf{x}\mathbf{x}} \rangle(\omega) \frac{d\omega}{2\pi} = \frac{1}{\pi}\int_{-\infty}^{\infty} \frac{\widehat{\boldsymbol{\kappa}}^{(i)}(\omega)}{\omega} d\omega, \tag{2.49}$$

using the dispersion equation (C.17) with $u = 0$, we obtain the obvious relation,

$$\langle \mathbf{x}\mathbf{x} \rangle_0 = \widehat{\boldsymbol{\kappa}}^{(r)}(0) = \widehat{\boldsymbol{\kappa}}(0) = \mathbf{g}^{-1}, \tag{2.50}$$

where we have used the fact that $\widehat{\boldsymbol{\kappa}}(0)$ is an even function.

This result can be easily extended to cross correlation functions between x- and y-type variables, considering that $\langle \widehat{\mathbf{x}\mathbf{y}} \rangle(\omega)$ is an imaginary and antisymmetric matrix, i.e.,

$$\langle \widehat{\mathbf{x}\mathbf{y}} \rangle(\omega) = -\langle \widehat{\mathbf{x}\mathbf{y}} \rangle^{+}(\omega) = -\langle \widehat{\mathbf{x}\mathbf{y}} \rangle^{*}(-\omega). \tag{2.51}$$

At the end, the fluctuation-dissipation relation becomes,

$$\langle \widehat{\mathbf{x}\mathbf{y}} \rangle^{(i)}(\omega) = \frac{2}{\omega}\left[\widehat{\boldsymbol{\kappa}}^{(r)}(\omega)\right]^{(a)}, \tag{2.52}$$

where the superscripts (a) denotes the antisymmetric part of the tensor.

To better understand the meaning of the fluctuation-dissipation relation, consider the single variable case,[10]

$$\langle \dot{x} \rangle = -M\left(\langle x \rangle - \frac{F}{gkT}\right). \tag{2.53}$$

Now, Fourier transforming this equation, we obtain (2.43) with,

$$\widehat{\kappa}(\omega) = \frac{M}{g(M - i\omega)} = \frac{1}{g - i\omega L^{-1}} = \frac{g + i\omega L^{-1}}{g^2 + \omega^2 L^{-2}}. \tag{2.54}$$

On the other hand, the correlation function (2.40) gives:

$$\langle xx \rangle(t) = \frac{1}{g} e^{-Mt}, \tag{2.55}$$

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[10]Here, when the applied force F is constant, the equilibrium state will move from $\langle x \rangle = 0$ to $\langle x \rangle = F/(gkT)$.

whose Fourier transform yields:

$$\langle \widehat{xx} \rangle(\omega) = \frac{2M}{g(M^2+\omega^2)} = \frac{2L^{-1}}{g^2+\omega^2 L^{-2}} \tag{2.56}$$

thus showing that the FDT (2.48) is identically satisfied.

Identical results are obtained in the multi-variable case, where we have:

$$\langle \dot{\mathbf{x}} \rangle = \mathbf{L} \cdot \left(\langle \mathbf{X} \rangle + \frac{1}{kT}\mathbf{F} \right), \tag{2.57}$$

where $\mathbf{L} = \mathbf{M} \cdot \mathbf{g}^{-1}$ is the Onsager phenomenological coefficient, while $\mathbf{X} = -\mathbf{g} \cdot \mathbf{x}$, obtaining:

$$\widehat{\boldsymbol{\kappa}} = \left(\mathbf{g} - i\omega \mathbf{L}^{-1} \right)^{-1}. \tag{2.58}$$

Note that the symmetry of $\widehat{\boldsymbol{\kappa}}$ is a direct consequence of the Onsager reciprocity relation $\mathbf{L} = \mathbf{L}^{+}$.

Sometimes, it is convenient to consider the fluctuations of $\mathbf{x}$ as being caused by a random fictitious force $\mathbf{f}$, so that the instantaneous value of $\mathbf{x}$ (not its mean value, which is identically zero) is linearly related to $\mathbf{f}$ through the same generalized susceptibility $\boldsymbol{\kappa}$ that governs the relaxation of the system far from equilibrium,[11] i.e.,

$$\mathbf{x}(t) = \frac{1}{kT} \int_{-\infty}^{\infty} \boldsymbol{\kappa}\left(t-t'\right) \cdot \mathbf{f}\left(t'\right) dt'. \tag{2.59}$$

In this case, considering that $\widehat{\boldsymbol{\kappa}}(-\omega) = \widehat{\boldsymbol{\kappa}}^*(\omega)$, we have:

$$\langle \widehat{\mathbf{xx}} \rangle(\omega) = (kT)^{-2} \widehat{\boldsymbol{\kappa}}^*(\omega) \cdot \langle \widehat{\mathbf{ff}} \rangle(\omega) \cdot \widehat{\boldsymbol{\kappa}}(\omega); \tag{2.60}$$

then, we obtain:

$$\langle \widehat{\mathbf{ff}} \rangle(\omega) = (kT)^2 \frac{2}{\omega} \widehat{\boldsymbol{\kappa}} \cdot \widehat{\boldsymbol{\kappa}}^{(i)} \cdot \widehat{\boldsymbol{\kappa}}(\omega) = \frac{2}{\omega}(kT)^2 \mathrm{Im}\left\{ \left[\widehat{\boldsymbol{\kappa}}^* \right]^{-1} \right\}. \tag{2.61}$$

Therefore, when the generalized susceptibility can be expressed as Eq. (2.58), we obtain:

$$\langle \widehat{\mathbf{ff}} \rangle(\omega) = 2(kT)^2 \mathbf{L}^{-1} = 2kT\boldsymbol{\zeta}, \tag{2.62}$$

where $\boldsymbol{\zeta} = kT\mathbf{L}^{-1}$. In fact, in this case Eq. (2.57) becomes the Langevin equation (see next chapter),

$$\dot{\mathbf{x}} = -\mathbf{M} \cdot \mathbf{x} + \widetilde{\mathbf{J}}, \tag{2.63}$$

[11] This is clearly equivalent to the Onsager regression hypothesis. Note that here and in the following $\mathbf{x}$ denotes the fluctuation $(\mathbf{x} - \langle \mathbf{x} \rangle)$.

where $\widetilde{\mathbf{J}} = \frac{1}{kT}\mathbf{L}\cdot\mathbf{f}$ is the fluctuating flux, satisfying the following relation:

$$\left\langle \widetilde{\mathbf{J}}(0)\,\widetilde{\mathbf{J}}(t)\right\rangle = 2\mathbf{L}\,\delta(t), \tag{2.64}$$

where $\delta(t)$ is the Dirac delta. This shows that there is no correlation between the particle position $\mathbf{x}$ and the random force $\mathbf{f}$ (see Problem 2.2). In fact, it is this lack of correlation that is at the foundation of the Onsager regression hypothesis, therefore justifying the Langevin equation, as discussed in the next chapter.

2.5 Problems

Problem 2.1 Consider a small particle of arbitrary shape moving in an otherwise quiescent Newtonian fluid. In creeping flow conditions, determine the symmetry relations satisfied by the resistance matrix connecting velocity and angular velocity with the force and the torque that are applied to the particle.

Problem 2.2 Consider a driven 1D oscillator of mass m at frequency ω_0, with damping force $\zeta\dot{x}$, with x denoting the displacement from its equilibrium position, $x = 0$. Determine the spectrum of the random force.

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