9

Topics in non-equilibrium statistical mechanics

We have given in two previous chapters a first introduction to non-equilibrium phenomena. The present chapter is devoted to a presentation of more general approaches, in which time dependence will be made explicit, whereas in practice we had to limit ourselves to stationary situations in Chapters 6 and 8. In the first part of the chapter, we examine the relaxation toward equilibrium of a system that has been brought out of equilibrium by an external perturbation. The main result is that, for small deviations from equilibrium, this relaxation is described by *equilibrium* time correlation functions, called Kubo (or relaxation) functions: this result is also known as 'Onsager's regression law'. The Kubo functions turn out to be basic objects of non-equilibrium statistical mechanics. First they allow one to compute the dynamical susceptibilities, which describe the response of the system to an external time dependent perturbation: the dynamical susceptibilities are, within a multiplicative constant, the time derivatives of Kubo functions. A second crucial property is that transport coefficients can be expressed in terms of time integrals of Kubo functions. As we limit ourselves to small deviations from equilibrium, our theory is restricted to a linear approximation and is known as *linear response theory*.[1] The classical version of linear reponse is somewhat simpler than the quantum one, and will be described first in Section 9.1. We shall turn to the quantum theory in Section 9.2, where one of our main results will be the proof of the fluctuation-dissipation theorem. In Section 9.3 we shall describe the projection method, restricting ourselves to the simplest case, the Mori projection method. The idea that underlies this method is that one is not interested in the full dynamics of an N-body system, but only in that of slow modes, for example hydrodynamic modes. One is led to project the full dynamics on that of its slow modes. The back action of fast modes on slow modes can be described thanks to memory effects. The projection

[1] The validity of linear response theory has been challenged by van Kampen in *Physica Norvegica* **5**, 279 (1971). For an answer to van Kampen's arguments, see for example Dorfman [33] Chapter 6.

method leads in a natural way to a description of the dynamics in Section 9.4 by a stochastic differential equation, the Langevin equation. It will be shown in Section 9.5 that the probability distribution associated with the Langevin equation obeys a partial differential equation, the Fokker–Planck equation, whose solutions will be obtained by using an analogy with the Schrödinger equation in imaginary time. Finally numerical studies of the Langevin equation will be examined in Section 9.6.

9.1 Linear response: classical theory

9.1.1 Dynamical susceptibility

Our goal is to study small deviations from equilibrium driven by a (small) perturbation applied to the system, when the equilibrium situation is described by an unperturbed classical Hamiltonian $H(\boldsymbol{p}, \boldsymbol{q})$. As in Section 3.2.1, $(\boldsymbol{p}, \boldsymbol{q})$ is a shorthand notation for the full set of canonical variables $(p_1, \ldots, p_N; q_1, \ldots, q_N)$, N being the number of degrees of freedom, and the partition function is

$$Z(H) = \int \mathrm{d}\boldsymbol{p}\, \mathrm{d}\boldsymbol{q}\, \mathrm{e}^{-\beta H(\mathbf{p},\mathbf{q})} \tag{9.1}$$

The equilibrium average A_i of a classical dynamical variable $\mathcal{A}_i(\boldsymbol{p}, \boldsymbol{q})$ is given from (3.43) by

$$A_i \equiv \langle \mathcal{A}_i \rangle \equiv \langle \mathcal{A}_i \rangle_{\mathrm{eq}} = \int \mathrm{d}\boldsymbol{p}\, \mathrm{d}\boldsymbol{q}\; D_{\mathrm{eq}}(\boldsymbol{p}, \boldsymbol{q}) \mathcal{A}_i(\boldsymbol{p}, \boldsymbol{q}) \tag{9.2}$$

where the probability density D_{eq} is the normalized Boltzmann weight

$$D_{\mathrm{eq}}(\mathbf{p}, \mathbf{q}) = \frac{1}{Z(H)}\, \mathrm{e}^{-\beta H(\mathbf{p},\mathbf{q})} \tag{9.3}$$

In the present chapter, the notation $\langle \bullet \rangle$ will always stand for an average value computed with the equilibrium probability density (9.3), or its quantum analogue (9.55). Let us perturb the Hamiltonian H by applying a perturbation $\mathcal{V}$ of the form

$$\mathcal{V} = -\sum_j f_j \mathcal{A}_j$$

so that

$$H \to H_1 = H + \mathcal{V} = H - \sum_j f_j \mathcal{A}_j \tag{9.4}$$

Comparing with (2.64), we see that the rôle of the Lagrange multipliers λ_j is now played by βf_j. In the present context, the f_js are often called the *external forces*, or simply the forces. This terminology is borrowed from the forced

one-dimensional harmonic oscillator (Exercise 9.7.1), where the perturbation may be written in terms of the dynamical variable $x(t)$ as $\mathcal{V} = -f(t)x(t)$. We denote by $\overline{\mathcal{A}_i}$ the average of the dynamical variable $\mathcal{A}_i$ *computed with the perturbed Hamiltonian* H_1. The response of the average $\overline{\mathcal{A}_i}$ to a variation of the Lagrange multiplier f_j is given by the fluctuation-response theorem, which we may use in the form (2.70) since the classical variables $\mathcal{A}_i$ commute

$$\frac{\partial \overline{\mathcal{A}_i}}{\partial f_j} = \beta \, \overline{(\mathcal{A}_i - \overline{\mathcal{A}_i})(\mathcal{A}_j - \overline{\mathcal{A}_j})} \tag{9.5}$$

If we restrict ourselves to small deviations from the equilibrium Hamiltonian H, we can take the limit $f_j \to 0$ in (9.5), which becomes, since the average values are now computed with D_{eq},

$$\begin{aligned} \frac{\partial \overline{\mathcal{A}_i}}{\partial f_j}\Big|_{f_k=0} &= \beta \langle (\mathcal{A}_i - \langle \mathcal{A}_i \rangle)(\mathcal{A}_j - \langle \mathcal{A}_j \rangle) \rangle \\ &= \beta \langle \delta\mathcal{A}_i \, \delta\mathcal{A}_j \rangle = \langle \mathcal{A}_i \, \mathcal{A}_j \rangle_{\text{c}} \end{aligned} \tag{9.6}$$

where we have defined $\delta\mathcal{A}_i$ by

$$\delta\mathcal{A}_i = \mathcal{A}_i - \langle \mathcal{A}_i \rangle = \mathcal{A}_i - A_i \tag{9.7}$$

so that its (equilibrium) average value vanishes: $\langle \delta\mathcal{A}_i \rangle = 0$. The subscript c stands for 'cumulant' or 'connected'. In the *linear approximation* (9.6) implies at once

$$\overline{\mathcal{A}_i} = \langle \mathcal{A}_i \rangle + \beta \sum_j f_j \langle \delta\mathcal{A}_i \, \delta\mathcal{A}_j \rangle = \langle \mathcal{A}_i \rangle - \beta \langle \mathcal{A}_i \mathcal{V} \rangle_{\text{c}} \tag{9.8}$$

Thus, within this approximation, the deviation from equilibrium is linearly related to the perturbation.

So far we have limited ourselves to static situations: the perturbed Hamiltonian H_1 is time-independent and has been used to define a new probability density D_1

$$D_1 = \frac{1}{Z(H_1)} \, \mathrm{e}^{-\beta H_1}$$

We now assume that the Hamiltonian is equal to H_1 for $t < 0$ during which the system is at equilibrium with a probability density D_1, but we introduce an explicit time dependence by switching off suddenly the perturbation $\mathcal{V}$ at $t = 0$. The Hamiltonian $\tilde{H}_1(t)$ is now

$$\tilde{H}_1(t) = H - \sum_i f_j \mathcal{A}_j = H_1 \quad \text{if} \quad t < 0 \qquad \tilde{H}_1(t) = H \ \text{ if } \ t \geq 0 \tag{9.9}$$

Another equivalent way to proceed is to switch on adiabatically[2] the perturbation at $t = -\infty$ and to switch it off suddenly at $t = 0$,[3]

$$\tilde{H}_1(t) = H - \theta(-t)\mathrm{e}^{\eta t} \sum_j f_j \mathcal{A}_j \qquad \eta \to 0^+ \tag{9.10}$$

where $\theta(-t)$ is a step function. Note that the perturbation $\mathcal{V}$ is a *mechanical perturbation* and the time evolution is Hamiltonian. Energy flows into and out of the system in the form of work only, and we assume that the system remains thermally isolated. We expect that the system will relax for $t \to +\infty$ to an equilibrium situation described by H. It is very difficult to characterize this relaxation in a general way. However, if the deviation from equilibrium is not large, we may work in the framework of the *linear* approximation, and the analysis is straightforward. For $t \leq 0$, $\overline{\mathcal{A}_i}$ takes the time-independent value (9.8), and in particular at $t = 0$

$$\begin{aligned}\overline{\delta\mathcal{A}_i}(t=0) &= \overline{\mathcal{A}_i}(t=0) - \langle \mathcal{A}_i \rangle = \beta \sum_j f_j \langle \mathcal{A}_i(t=0)\mathcal{A}_j \rangle_{\mathrm{c}} \\ &= \beta \sum_j f_j \langle \delta\mathcal{A}_i(t=0)\delta\mathcal{A}_j \rangle\end{aligned}$$

The non-equilibrium ensemble average is obtained by integrating over all possible initial conditions at $t = 0$ with the weight $D_1 = \exp(-\beta H_1)/Z(H_1)$. It is convenient to write the dynamical variable $\mathcal{A}_i$ for positive t as a function of the initial conditions at $t = 0$, $\boldsymbol{p} = \boldsymbol{p}(t=0)$, $\boldsymbol{q} = \boldsymbol{q}(t=0)$, and of t: $\mathcal{A}_i(t) = \mathcal{A}_i(t; \boldsymbol{p}, \boldsymbol{q})$. Contrary to the $t \leq 0$ case, $\overline{\mathcal{A}_i}$ will be time dependent for $t \geq 0$ because the time evolution of $\mathcal{A}_i$ for positive t is governed by H

$$t > 0: \qquad \partial_t \mathcal{A}_i = \{\mathcal{A}_i, H\}$$

while the probability density at $t = 0$ is determined by H_1 (9.4)

$$H_1 = H - \sum_j f_j \mathcal{A}_j = H - \sum_j f_j \mathcal{A}_j(0)$$

Then the non-equilibrium ensemble average of $\mathcal{A}_i(t)$ is

$$\overline{\mathcal{A}_i}(t) = \int \mathrm{d}\boldsymbol{p}\, \mathrm{d}\boldsymbol{q}\; D_1(\boldsymbol{p}, \boldsymbol{q}) \mathcal{A}_i(t; \boldsymbol{p}, \boldsymbol{q})$$

[2] In the present context, adiabatically means infinitely slowly. The relation between this meaning of adiabatic and the thermodynamic one is complex, and is discussed for example in Balian [5], Chapter 5.

[3] In all that follows, η will denote a positive infinitesimal number.

and we get from (9.8)[4]

$$\boxed{\overline{\delta\mathcal{A}_i}(t) = \overline{\mathcal{A}_i}(t) - \langle\mathcal{A}_i\rangle = \beta\sum_j f_j\langle\mathcal{A}_i(t)\mathcal{A}_j(0)\rangle_{\rm c} = \beta\sum_j f_j\langle\delta\mathcal{A}_i(t)\delta\mathcal{A}_j(0)\rangle} \tag{9.11}$$

Equation (9.11) has introduced the *Kubo function* (or relaxation function) $C_{ij}(t)$

$$\boxed{C_{ij}(t) = \langle\mathcal{A}_i(t)\mathcal{A}_j(0)\rangle_{\rm c} = \langle\delta\mathcal{A}_i(t)\delta\mathcal{A}_j(0)\rangle} \tag{9.12}$$

which is the time correlation function of $\delta\mathcal{A}_i(t)$ and $\delta\mathcal{A}_j(0)$ *computed at equilibrium* with the probability density (9.2). Equation (9.11) is often called *Onsager's regression law*: for small deviations from equilibrium, the relaxation toward equilibrium is governed by equilibrium fluctuations. Physically, this result can be understood as follows. One may obtain deviations from equilibrium by applying an external perturbation, as described above, but such deviations may also occur as the result of spontaneous fluctuations, and in both cases the relaxation toward equilibrium should be governed by the same laws.

The Kubo function (9.12) is directly linked to the *dynamical susceptibility* $\chi_{ij}(t)$, which is defined by writing the most general formula for the dynamical linear response to an external time-dependent perturbation $\sum_j f_j(t)\mathcal{A}_j$

$$\overline{\delta\mathcal{A}_i}(t) = \sum_j \int_{-\infty}^{t} {\rm d}t'\,\chi_{ij}(t-t')f_j(t') \tag{9.13}$$

In Fourier space, and supposing that $\chi_{ij}(t-t')$ vanishes for $t' > t$, the convolution in (9.13) is transformed into a product

$$\overline{\delta\mathcal{A}_i}(\omega) = \sum_j \chi_{ij}(\omega)f_j(\omega) \tag{9.14}$$

In the case of a sudden switching off of a constant external perturbation at $t = 0$, as in (9.9), Equation (9.13) becomes

$$\overline{\delta\mathcal{A}_i}(t) = \sum_j f_j \int_{-\infty}^{0} {\rm d}t'\chi_{ij}(t-t') = \sum_j f_j \int_{t}^{\infty} \chi_{ij}(\tau)\,{\rm d}\tau$$

[4] One may wonder why $\delta\mathcal{A}_j$ in (9.11) is taken at $t' = 0$, while any $t' < 0$ would be *a priori* possible. Indeed, any $t' < 0$ would be fine, because $\tilde{H}_1(t')$ in (9.9) is time independent for $t' < 0$, but $H(t')$ and $\mathcal{V}(t')$ are not *separately* time independent. In (9.11) H is taken implicitly at $t' = 0$, which implies that $\mathcal{V}$ should also be taken at $t' = 0$. Note that the correct boundary condition (9.8) is ensured at $t = 0$

$$\overline{\delta\mathcal{A}_i}(t=0) = \beta\sum_j f_j\langle\mathcal{A}_i(0)\mathcal{A}_j(0)\rangle_{\rm c}$$

Differentiating this equation with respect to t and comparing with (9.11) yields

$$\frac{\mathrm{d}}{\mathrm{d}t}\,\overline{\delta\mathcal{A}_i}(t) = -\sum_j f_j\,\chi_{ij}(t) = \beta\sum_j f_j\theta(t)\dot{C}_{ij}(t)$$

so that the dynamical susceptibility is nothing other than minus the time derivative of the Kubo function times β

$$\boxed{\chi_{ij}(t) = -\beta\,\theta(t)\dot{C}_{ij}(t)} \tag{9.15}$$

9.1.2 Nyquist theorem

As a simple application of the preceding considerations, let us derive the Nyquist theorem, which relates the electrical conductivity σ_{el} to the equilibrium fluctuations of the electric current. Since we need consider only two dynamical variables, we simplify the notations by setting $\mathcal{A}_i = \mathcal{B}$ and $\mathcal{A}_j = \mathcal{A}$. Using time-translation invariance at equilibrium yields

$$\dot{C}_{BA}(t) = \langle\dot{\mathcal{B}}(t)\mathcal{A}(0)\rangle_{\mathrm{c}} = -\langle\mathcal{B}(t)\dot{\mathcal{A}}(0)\rangle_{\mathrm{c}} \tag{9.16}$$

From (9.13) and (9.15) we can write the Fourier transform $\overline{\delta\mathcal{B}}(\omega)$ as

$$\overline{\delta\mathcal{B}}(\omega) = \beta f_A(\omega)\int_0^\infty \mathrm{d}t\;\mathrm{e}^{\mathrm{i}\omega t}\,\langle\mathcal{B}(t)\dot{\mathcal{A}}(0)\rangle_{\mathrm{c}} \tag{9.17}$$

In case of convergence problems, ω should be understood as $\lim_{\eta\to 0^+}(\omega + \mathrm{i}\eta)$ (see Section 9.1.3). Let us use this result in the following case. We consider charge carriers with charge q and mass m in a one-dimensional conductor and take as dynamical variables the following $\mathcal{A}$ and $\mathcal{B}$

$$\mathcal{A} = q\sum_i x_i \qquad \mathcal{B} = \dot{\mathcal{A}} = q\sum_i \dot{x}_i = V j_{\mathrm{el}} \tag{9.18}$$

where x_i is the position of carrier i, j_{el} the current density and V the volume of the conductor. The external force is an external (uniform) time dependent electric field $E(t)$ and the perturbation $\mathcal{V}(t)$ is

$$\mathcal{V}(t) = -qE(t)\sum_i x_i = -E(t)\mathcal{A}$$

so that from (9.17)

$$\overline{\delta\mathcal{B}}(\omega) = V j_{\rm el}(\omega) = \beta V^2 E(\omega) \int_0^\infty {\rm d}t\, {\rm e}^{{\rm i}\omega t}\, \langle j_{\rm el}(t)\, j_{\rm el}(0)\rangle|_{E=0}$$
$$= \beta q^2 E(\omega) \int_0^\infty {\rm d}t\, {\rm e}^{{\rm i}\omega t} \sum_{i,k} \langle \dot{x}_i(t)\dot{x}_k(0)\rangle|_{E=0}$$

Since the average equilibrium (or $E = 0$) current density vanishes, we may write $j_{\rm el}$ instead of $\delta j_{\rm el}$. This equation is nothing other than the time dependent Ohm's law $j_{\rm el}(\omega) = \sigma_{\rm el}(\omega)E(\omega)$. We have thus shown that the electrical conductivity $\sigma_{\rm el}(\omega)$ is given by the Fourier transform of the time correlation of the current density in the absence of an external electric field

$$\boxed{\sigma_{\rm el}(\omega) = \beta V \int_0^\infty {\rm d}t\, {\rm e}^{{\rm i}\omega t}\, \langle j_{\rm el}(t)\, j_{\rm el}(0)\rangle|_{E=0}} \tag{9.19}$$

In the zero frequency limit $\omega = 0$ we get the following formula for the static conductivity $\sigma_{\rm el}$

$$\sigma_{\rm el} = \beta V \int_0^\infty {\rm d}t\, \langle j_{\rm el}(t)\, j_{\rm el}(0)\rangle|_{E=0} \tag{9.20}$$

It may be necessary to include a factor $\exp(-\eta t)$ in (9.20) in order to ensure the convergence of the integral. Equation (9.20) is one version of the *Nyquist theorem*, and is typical of a *Green–Kubo formula*, which gives a transport coefficient (in the present case the static electrical conductivity) in terms of the integral of a time correlation function. Let us give a rough estimate of (9.19). As we have seen in Section 3.3.2, velocities of different particles are uncorrelated in classical statistical mechanics. Introducing a microscopic relaxation (or collision) time $\tau^* \sim 10^{-14}$ s

$$\langle \dot{x}_i(t)\dot{x}_k(0)\rangle = \delta_{ik}\langle \dot{x}(t)\dot{x}(0)\rangle \sim \delta_{ik}\frac{kT}{m}{\rm e}^{-|t|/\tau^*}$$

leads to the familiar result, already obtained in (6.59) in the case $\omega = 0$

$$\boxed{\sigma_{\rm el}(\omega) = \frac{nq^2\tau^*}{m(1 - {\rm i}\omega\tau^*)}} \tag{9.21}$$

where n is the density of carriers. Of course, (9.21) may be obtained by much more elementary methods, but the point is that (9.19) and (9.20) are *exact* results, and at least one knows where to start from if one wishes to derive better approximations.

9.1.3 Analyticity properties

In this subsection,[5] we shall work for simplicity with a single dynamical variable $\mathcal{A}$, $\chi_{AA}(t) = \chi(t)$, but the results generalize immediately to any $\chi_{ij}(t)$, provided $\mathcal{A}_i$ and $\mathcal{A}_j$ have the same parity under time reversal (see (9.67)). One very important property of $\chi(t)$ is *causality*: $\chi(t) = 0$ if $t < 0$, which reflects the obvious requirement that the effect must follow the cause. This property allows us to define the Laplace transform of $\chi(t)$

$$\chi(z) = \int_0^\infty \mathrm{d}t\, \mathrm{e}^{\mathrm{i}zt}\chi(t) \tag{9.22}$$

for any complex value of z such that $\mathrm{Im}z > 0$. Indeed, if we write $z = z_1 + \mathrm{i}z_2$, $z_2 > 0$, causality provides in (9.22) a convergence factor $\exp(-z_2 t)$ and this equation defines an analytic function of z in the half plane $\mathrm{Im}z > 0$. Following standard notations, we define $\chi''(t)$ by

$$\chi''(t) = \frac{\mathrm{i}}{2}\beta\dot{C}(t) \tag{9.23}$$

or, equivalently, from (9.15), $\chi''(t) = -(\mathrm{i}/2)\chi(t)$ for $t > 0$; note that $\chi''(t)$ is an odd function of t, as the Kubo function $C_{AA}(t) = C(t)$ is an even function of t. Furthermore, $\chi''(t)$ is pure imaginary, so that its Fourier transform $\chi''(\omega)$ is an odd and real function of ω. Now, for $t > 0$

$$\chi(t) = 2\mathrm{i}\chi''(t) = 2\mathrm{i}\int \frac{\mathrm{d}\omega}{2\pi}\,\mathrm{e}^{-\mathrm{i}\omega t}\chi''(\omega)$$

Plugging this expression for $\chi(t)$ in (9.22) and exchanging the t and ω integrations leads to a *dispersion relation*[6] for $\chi(z)$

$$\chi(z) = \int_{-\infty}^{\infty} \frac{\mathrm{d}\omega'}{\pi}\,\frac{\chi''(\omega')}{\omega' - z} \tag{9.24}$$

[5] The reader is strongly advised to solve the example of the forced harmonic oscillator of Exercise 9.7.1, in order to get some familiarity with the results of this section in an elementary case.

[6] We have assumed in (9.24) that the ω'-integral is convergent at infinity. If this is not the case, one uses subtracted dispersion relations, for example the once-subtracted dispersion relation

$$\chi(z) - \chi(z=0) = z\int_{-\infty}^{\infty} \frac{\mathrm{d}\omega'}{\pi}\,\frac{\chi''(\omega')}{\omega'(\omega' - z)}$$

However, this subtraction is done at the expense of introducing an unknown parameter $\chi(z = 0)$.

The existence of a dispersion relation is of course directly linked to causality. Since $\chi(z)$ is analytic in the upper half plane, $\chi(\omega)$ is the limit $\eta \to 0^+$ of $\chi(\omega + \mathrm{i}\eta)$ and $\chi''(\omega)$ is the imaginary part of $\chi(\omega)$

$$\mathrm{Im}\,\chi(\omega) = \chi''(\omega) \tag{9.25}$$

where we have used in (9.24) $z = \omega + \mathrm{i}\eta$ and

$$\frac{1}{\omega' - \omega - \mathrm{i}\eta} = P\frac{1}{\omega' - \omega} + \mathrm{i}\pi\,\delta(\omega' - \omega)$$

where P indicates the Cauchy principal value. A more elementary derivation uses a periodic external force

$$f(t) = f_\omega \cos\omega t$$

so that from (9.13), writing

$$\chi(\omega) = \chi'(\omega) + \mathrm{i}\chi''(\omega)$$

we get

$$\overline{\delta\mathcal{A}}(t) = f_\omega\left[\chi'(\omega)\cos\omega t + \chi''(\omega)\sin\omega t\right]$$

In this simple case, the reactive part of the response, in phase with the force, is controlled by the real part $\chi'(\omega)$ of $\chi(\omega)$, while the dissipative part, in quadrature with the force (i.e. out of phase by $\pi/2$ with the force), is controlled by its imaginary part $\chi''(\omega)$.[7]

The susceptibility $\chi(z)$ may also be expressed in terms of the Kubo function and of the static susceptibility $\chi = \lim_{\omega\to 0}\chi(\omega + \mathrm{i}\eta)$[8]

$$\chi(z) = -\beta\int_0^\infty \mathrm{d}t\,\mathrm{e}^{\mathrm{i}zt}\dot{C}(t) = \beta C(t=0) + \mathrm{i}z\beta\int_0^\infty \mathrm{d}t\,\mathrm{e}^{\mathrm{i}zt}C(t) = \chi + \mathrm{i}z\beta C(z)$$

Solving for $C(z)$ and using the fact that $\overline{\delta A}(t=0) = \chi f_A$ allows us to derive an expression for $\overline{\delta A}(z)$ that depends on $\overline{\delta A}(t=0)$ (and not on f_A)

$$\overline{\delta A}(z) = \frac{1}{\mathrm{i}z}\Big(\frac{\chi(z)}{\chi} - 1\Big)\overline{\delta A}(t=0) \tag{9.26}$$

[7] However remember our warning: this is only true if $\mathcal{A}_i$ and $\mathcal{A}_j$ have the same parity under time reversal.

[8] The static susceptibility χ is in general different from the isothermal susceptibility χ_T, which is related to the Kubo function by $\chi_T = \beta C(t=0)$. The two susceptibilities coincide if the integral in the second expression of $\chi(z)$ converges at infinity. If the integral does not converge, one writes

$$\chi(z) = \beta[C(0) - C(\infty)] + \mathrm{i}z\beta\int_0^\infty \mathrm{d}t\,\mathrm{e}^{\mathrm{i}zt}\,[C(t) - C(\infty)]$$

and $\chi = \beta[C(0) - C(\infty)]$.

The relation which matches (9.24) for $C(z)$ is

$$C(z) = -\frac{\mathrm{i}}{\beta} \int_{-\infty}^{\infty} \frac{\mathrm{d}\omega'}{\pi} \frac{\chi''(\omega')}{\omega'(\omega' - z)} \tag{9.27}$$

Furthermore, from (9.23) and from our conventions (9.22) for Fourier transforms: $\partial_t \to -i\omega$

$$\chi''(\omega) = \frac{1}{2} \beta\omega\, C(\omega) \tag{9.28}$$

This is the classical version of the *fluctuation-dissipation theorem*. On the right hand side of (9.28), $C(\omega)$, being the Fourier transform of $\langle \mathcal{A}(t)\mathcal{A}(0)\rangle$, is clearly a measure of the equilibrium fluctuations of $\mathcal{A}$, but we have still to justify that $\chi''(\omega)$ does describe dissipation: this is shown formally in Section 9.2.4 and Exercise 9.7.6. However, from experience with the forced harmonic oscillator and other systems, we already know that dissipation is governed by that part of the response which is in quadrature of phase with the driving force. As already mentioned, and as is shown explicitly in Exercise 9.7.1, the real part of $\chi(\omega)$ gives the reactive component of the response, while its imaginary part gives the dissipative component (see, however, the comments following (9.68)).

9.1.4 Spin diffusion

As an illustration of the preceding considerations, let us consider, following Kadanoff and Martin [61], a fluid of particles carrying a spin 1/2 aligned in a fixed direction (or, equivalently, an Ising spin) with which is associated a magnetic moment μ. A practical example would be helium-3. We assume that all spin flip processes may be neglected. To the magnetization density

$$n(\vec{r}, t) = \mu[n_+(\vec{r}, t) - n_-(\vec{r}, t)]$$

where n_+ (n_-) is the density of particles with spin up (down), corresponds a magnetization current $\vec{j}(\vec{r}, t)$ such that magnetization is locally conserved

$$\partial_t n(\vec{r}, t) + \vec{\nabla} \cdot \vec{j}(\vec{r}, t) = 0 \tag{9.29}$$

Equation (9.29) is exact under the no spin flip assumption. It implies that the magnetization can change in a volume of space only because particles move into and out of this volume. As a consequence, a local magnetization imbalance cannot disappear locally, but only by slowly spreading over the entire system. The second relation we need is a phenomenological one and is inspired by Fick's law (6.26).

It relates the magnetization current to the density gradient

$$\vec{j}(\vec{r},t) = -D\vec{\nabla}n(\vec{r},t) \tag{9.30}$$

where D is the spin diffusion coefficient. Combining (9.29) and (9.30) leads, of course, to a diffusion equation (6.21) for n

$$\left(\frac{\partial}{\partial t} - D\nabla^2\right) n = 0 \tag{9.31}$$

or, in Fourier space

$$(\omega + \mathrm{i}Dk^2)n(\vec{k},\omega) = 0 \tag{9.32}$$

Note that our convention for space-time Fourier transforms is

$$\begin{aligned} f(\vec{k},\omega) &= \int \mathrm{d}t\, \mathrm{d}^3 r\, \mathrm{e}^{-\mathrm{i}(\vec{k}\cdot\vec{r}-\omega t)} f(\vec{r},t) \\ f(t,\vec{r}) &= \int \frac{\mathrm{d}\omega}{2\pi} \frac{\mathrm{d}^3 k}{(2\pi)^3}\, \mathrm{e}^{\mathrm{i}(\vec{k}\cdot\vec{r}-\omega t)} f(\vec{k},\omega) \end{aligned} \tag{9.33}$$

A mode with a dispersion law $\omega = -i\,Dk^2$ is called a *diffusive mode* and is characteristic of the relaxation of a conserved quantity. Indeed, let us consider a fluctuation of the magnetization density with wavelength λ. Since the relaxation occurs via diffusion, the characteristic time τ is linked to λ through $\lambda^2 \sim D\tau$ so that $\tau \sim \lambda^2/D$ or $\omega \sim Dk^2$.

Let us assume that we have created at $t = 0$ an off-equilibrium magnetization density $n(\vec{r}, t = 0)$, or, in Fourier space, $n(\vec{k}, t = 0)$. Then, for positive times, the evolution of $n(\vec{r}, t)$ is governed by the diffusion equation (9.31), which we write in $(\vec{k}, t)$ space

$$\partial_t n(\vec{k},t) = -Dk^2 n(\vec{k},t) \tag{9.34}$$

Taking the Laplace transform of both sides of (9.34) gives

$$n(\vec{k},z) = \frac{\mathrm{i}}{z + \mathrm{i}Dk^2}\, n(\vec{k}, t = 0) \tag{9.35}$$

Let us now make the link with linear response. If our magnetic fluid is placed in a time-independent, but space-dependent magnetic field, the perturbed Hamiltonian reads (we set for simplicity $\mu = 1$)

$$H_1 = H - \int \mathrm{d}^3 r\, n(\vec{r}) B(\vec{r}) \tag{9.36}$$

Using invariance under space translations, the fluctuation-response theorem gives

$$\overline{\delta n}(\vec{r}) = \int \mathrm{d}^3 r' \, \chi(\vec{r} - \vec{r}\,') B(\vec{r}\,') \tag{9.37}$$

where the static susceptibility $\chi(\vec{r} - \vec{r}\,')$ is given from (4.28) by the space correlations of the density

$$\chi(\vec{r} - \vec{r}\,') = \beta \langle n(\vec{r}) n(\vec{r}\,') \rangle_c$$

Then, in Fourier space, (9.37) becomes

$$\overline{\delta n}(\vec{k}) = \chi(\vec{k}) B(\vec{k}) \tag{9.38}$$

In Fourier space, the Fourier components are decoupled, so that all preceding results on the static suceptibility χ or on the dynamic susceptibility $\chi(t)$ apply without modification to $\chi(\vec{k})$ and $\chi(\vec{k}, t)$ respectively. Of course, this simplicity is a consequence of space translation invariance: the equations would be much more complicated in the absence of this invariance. Comparing (9.35) and (9.26), which reads in the present case

$$\overline{\delta n}(\vec{k}, z) = \frac{1}{\mathrm{i}z} \left(\frac{\chi(\vec{k}, z)}{\chi(\vec{k})} - 1 \right) \overline{\delta n}(\vec{k}, t = 0)$$

one derives the following expression for the dynamical susceptibility

$$\chi(\vec{k}, z) = \frac{\mathrm{i}Dk^2}{z + \mathrm{i}Dk^2} \chi(\vec{k}) \tag{9.39}$$

One notes that the susceptibility depends on a thermodynamic quantity $\chi(\vec{k})$ and on a transport coefficient D. Taking the imaginary part of both sides of (9.39), we obtain $\chi''(\vec{k}, \omega)$

$$\chi''(\vec{k}, \omega) = \frac{\omega D k^2}{\omega^2 + D^2 k^4} \chi(\vec{k}) \tag{9.40}$$

This last expression leads to a Green–Kubo formula. Defining $\chi = \chi(\vec{k} = 0)$, one verifies that

$$D\chi = \lim_{\omega \to 0} \lim_{k \to 0} \frac{\omega}{k^2} \chi''(k, \omega) \tag{9.41}$$

where the order of limits is crucial. The result can be transformed into (see Exercise 9.7.3)

$$D\chi = \frac{1}{3}\beta \int_0^\infty \mathrm{d}t \int \mathrm{d}^3 r \, \mathrm{e}^{-\eta t} \left\langle \vec{j}(t, \vec{r}) \cdot \vec{j}(0, \vec{0}) \right\rangle_{\mathrm{eq}} \tag{9.42}$$

where the factor $\exp(-\eta t)$ has been added in case convergence problems are encountered for $t \to \infty$. One can show that the correct way to proceed to evaluate expressions like (9.42) is to keep η finite for a finite volume, perform the t integral, and then take the thermodynamic limit $V \to \infty$.

The fluctuation-dissipation theorem (9.28) joined to (9.40) gives the Kubo function $C(\vec{k}, \omega)$

$$C(\vec{k}, \omega) = S(\vec{k}, \omega) = \frac{2}{\beta} \frac{Dk^2}{\omega^2 + D^2 k^4} \chi(\vec{k}) \tag{9.43}$$

We have defined a new function $S(\vec{k}, \omega)$, which is called the *dynamical structure factor*. It is the space-time Fourier transform of the (connected) density–density correlation function $\langle n(\vec{r}, t)\, n(\vec{0}, 0)\rangle_c$

$$S(\vec{k}, \omega) = \int \mathrm{d}t \, \mathrm{d}^3 r \, \mathrm{e}^{-\mathrm{i}(\vec{k}\cdot\vec{r} - \omega t)} \langle n(\vec{r}, t)\, n(\vec{0}, 0)\rangle_c \tag{9.44}$$

In the classical case, the structure factor is identical to the Kubo function, but we shall see shortly that the two functions are different in the quantum case. The dynamical structure factor generalizes the static structure factor introduced in Section 3.4.2, and it may also be measured in (inelastic) neutron scattering experiments: see Problem 9.8.1 for an analogous case, that of inelastic light scattering by a suspension of particles in a fluid.

In the case of light scattering by a simple fluid, the dynamical structure factor, plotted as a function of ω, displays three peaks instead of the single peak of width Dk^2 at $\omega = 0$ found in (9.43): see Figure 9.1 and Problem 9.8.2. The central peak at $\omega = 0$ is called the *Rayleigh peak*, and its width $D_{\mathrm{T}} k^2$ is determined by the coefficient of thermal conductivity κ, because it corresponds to light scattering by heat diffusion. The other two peaks are the *Brillouin peaks*: they are centred at $\omega = \pm ck$, where c is the sound speed, and they correspond to light scattering by sound waves. Their width $\Gamma k^2/2$ depends also on the shear viscosity η and the bulk viscosity ζ defined in (6.88)

$$D_{\mathrm{T}} = \frac{\kappa}{mnc_P} \qquad \Gamma = D_T\left(\frac{c_P}{c_V} - 1\right) + \left(\frac{4}{3}\eta + \zeta\right)\frac{1}{mn} \tag{9.45}$$

where mc_P and mc_V are the specific heat per particle at constant pressure and volume, m is the mass of the particles and n the fluid density. As in the spin diffusion

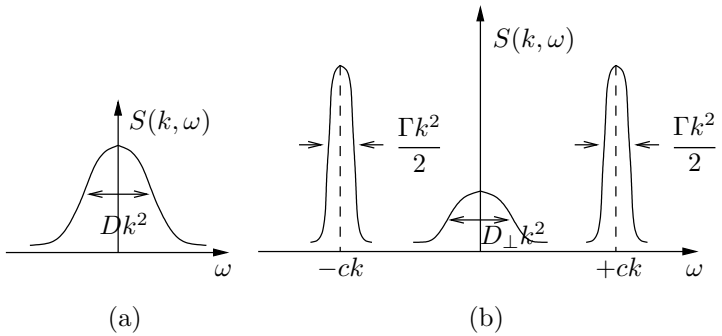

Figure 9.1 Dynamical structure factors. (a) Spin diffusion, (b) light scattering by a simple fluid.

case, the susceptibilities depend on thermodynamic quantities and on transport coefficients. It can also be shown that the transport coefficients κ, η and ζ may be written in the form of Green–Kubo formulae analogous to (9.42).

9.2 Linear response: quantum theory

9.2.1 Quantum fluctuation response theorem

Let us first recall from Chapter 2 that the equilibrium density operator $D \equiv D_{\mathrm{B}}$ is given as a function of the relevant observables A_j by (2.64)

$$D_{\mathrm{B}} \equiv D = \frac{1}{Z}\exp(\lambda_j \mathsf{A}_j) \qquad Z = \mathrm{Tr}\,\exp(\lambda_j A_j) \tag{9.46}$$

where we adopt from now on the summation convention over repeated indices. Let B be an observable that may or may not be a member of the set $\{\mathsf{A}_j\}$; its expectation value $\langle \mathsf{B}\rangle_D$ is

$$\langle \mathsf{B}\rangle_D = \mathrm{Tr}\,(\mathsf{B}D) = \frac{1}{Z}\,\mathrm{Tr}\left[\mathsf{B}\exp(\lambda_j \mathsf{A}_j)\right]$$

We now compute $\partial\langle \mathsf{B}\rangle_D/\partial\lambda_i$

$$\frac{\partial\langle \mathsf{B}\rangle_D}{\partial\lambda_i} = \frac{1}{Z}\frac{\partial}{\partial\lambda_i}\,\mathrm{Tr}\left[\mathsf{B}\exp(\lambda_j \mathsf{A}_j)\right] - \langle \mathsf{A}_i\rangle_D\langle \mathsf{B}\rangle_D \tag{9.47}$$

To compute the λ_i-derivative in (9.47), we use the identity (2.120) for an operator A which depends on a parameter α

$$\frac{\partial}{\partial\alpha}\,\mathrm{e}^{\mathsf{A}(\alpha)} = \int_0^1 \mathrm{d}x\,\mathrm{e}^{x\mathsf{A}(\alpha)}\,\frac{\partial \mathsf{A}(\alpha)}{\partial\alpha}\,\mathrm{e}^{(1-x)\mathsf{A}(\alpha)} \tag{9.48}$$

and obtain

$$\frac{\partial}{\partial\lambda_i}\mathrm{Tr}\left[\mathsf{B}\exp(\lambda_j\mathsf{A}_j)\right]=\int_0^1 \mathrm{d}x\,\mathrm{Tr}\Big(\mathsf{B}\,\mathrm{e}^{x\lambda_j\mathsf{A}_j}\mathsf{A}_i\,\mathrm{e}^{(1-x)\lambda_j\mathsf{A}_j}\Big)$$

so that

$$\frac{\partial\langle\mathsf{B}\rangle_D}{\partial\lambda_i}=\int_0^1 \mathrm{d}x\,\mathrm{Tr}\left[\delta\mathsf{B}\,D^x\,\delta\mathsf{A}_i\,D^{1-x}\right] \tag{9.49}$$

where $\delta\mathsf{B}=\mathsf{B}-\langle\mathsf{B}\rangle_D$ and $\delta\mathsf{A}_i=\mathsf{A}_i-\langle\mathsf{A}_i\rangle_D$. The preceding equation gives the quantum generalization of the fluctuation-response theorem (9.5), and it suggests that it is useful to introduce the following combination of two operators A and B

$$\boxed{\langle\mathsf{B};\mathsf{A}\rangle_D=\int_0^1 \mathrm{d}x\,\mathrm{Tr}\left[\mathsf{B}\,D^x\,\mathsf{A}^\dagger\,D^{1-x}\right]} \tag{9.50}$$

It is easily checked (Exercise 9.7.4) that Equation (9.50) defines on the vector space of operators a positive definite scalar product of the two operators A and B, called *Mori's scalar product*. Note that $\langle\mathsf{B};\mathsf{A}\rangle_D^*=\langle\mathsf{A};\mathsf{B}\rangle_D$ and that, in the classical limit, Mori's scalar product is simply an equilibrium average of two classical variables $\mathcal{B}$ and $\mathcal{A}$

$$\langle\mathcal{B};\mathcal{A}\rangle_D^{\text{classical}}=\langle\mathcal{B}\,\mathcal{A}^*\rangle_D$$

Using the definition (9.50), the quantum fluctuation-response theorem (9.49) may be written in the following equivalent forms

$$\boxed{\frac{\partial\langle\mathsf{B}\rangle_D}{\partial\lambda_i}=\langle\delta\mathsf{B};\delta\mathsf{A}_i^\dagger\rangle_D=\langle\delta\mathsf{B};\mathsf{A}_i^\dagger\rangle_D=\langle\mathsf{B};\delta\mathsf{A}_i^\dagger\rangle_D=\langle\mathsf{B};\mathsf{A}_i^\dagger\rangle_{D,c}} \tag{9.51}$$

From now on we restrict ourselves to Hermitian A_is, leaving the non-Hermitian case to Exercise 9.7.4. Setting $\mathsf{B}=\mathsf{A}_j$ in (9.51) we recover (2.121)

$$\frac{\partial\langle\mathsf{A}_j\rangle_D}{\partial\lambda_i}=\frac{\partial^2\ln Z}{\partial\lambda_i\partial\lambda_j}=\langle\delta\mathsf{A}_j;\delta\mathsf{A}_i\rangle_D=C_{ji} \tag{9.52}$$

The matrix C_{ji} is symmetric and positive definite for Hermitian A_is (Exercise 2.7.8) and has thus an inverse C_{ji}^{-1}. We may write

$$\mathrm{d}\langle\mathsf{A}_j\rangle_D=C_{ji}\,\mathrm{d}\lambda_i\quad\text{or}\quad\mathrm{d}\lambda_i=C_{ij}^{-1}\mathrm{d}\langle\mathsf{A}_j\rangle_D$$

so that

$$\mathrm{d}\langle \mathsf{B}\rangle_D = \langle \delta\mathsf{B};\, \delta\mathsf{A}_i\rangle_D \mathrm{d}\lambda_i = C_{ij}^{-1}\langle \delta\mathsf{B};\, \delta\mathsf{A}_i\rangle_D\, \mathrm{d}\langle \mathsf{A}_j\rangle_D \tag{9.53}$$

It is important to understand the meaning of (9.53). The average value $\langle \mathsf{B}\rangle_D$ is a function of the $\langle \mathsf{A}_j\rangle$s, since it is the set of $\langle \mathsf{A}_j\rangle_D$s which determines the density operator D through the requirement

$$\langle \mathsf{A}_i\rangle_D = \mathrm{Tr}(D\mathsf{A}_i) = A_i$$

Then (9.53) controls the variation of the average value $\langle \mathsf{B}\rangle_D$ when the $\langle \mathsf{A}_j\rangle_D$s are modified. Although we shall not use it, the preceding structure turns out to play an important rôle because it may be generalized to non-equilibrium situations, and it underlies more general approaches to the projection method than that which will be described in this book. Note also that, for the time being, we have not used any linear approximation. The linear approximation will come shortly.

9.2.2 Quantum Kubo function

As in the classical case, we perturb a Hamiltonian H

$$H \to H_1 = H - f_i\mathsf{A}_i \qquad \exp(-\beta H) \to \exp(-\beta H_1) = \exp[-\beta(H - f_i\mathsf{A}_i)] \tag{9.54}$$

One of the observables of the preceding subsection, A_0, is identified with the Hamiltonian H, and the corresponding Lagrange multiplier λ_0 is identified with $-\beta$. As in the previous section, the other Lagrange multipliers $\lambda_i, i = 1, \ldots, N$ are identified with βf_i, and, as we are interested in linear response, we set $\lambda_i = f_i = 0$, $i = 1, \ldots, N$ once the derivatives have been taken. The equilibrium density matrix to be used in the computation of the average values is

$$D_{\mathrm{eq}} = \frac{1}{Z(H)}\exp(-\beta H) \qquad Z(H) = \mathrm{Tr}\,\exp(-\beta H) \tag{9.55}$$

and, as in (9.2), we shall use the convention $\langle \bullet\rangle \equiv \langle \bullet\rangle_{\mathrm{eq}} = \mathrm{Tr}\,(\bullet\, D_{\mathrm{eq}})$. As in the classical case we take external forces of the form

$$f_i(t) = \mathrm{e}^{\eta t}\theta(-t) f_i$$

and in (9.51) we choose as observable B the observable A_j in the Heisenberg picture, setting from now on $\hbar = 1$,

$$\mathsf{A}_{j\mathrm{H}}(t) \equiv \mathsf{A}_j(t) = \mathrm{e}^{\mathrm{i}Ht}\,\mathsf{A}_j\mathrm{e}^{-\mathrm{i}Ht} \tag{9.56}$$

$\mathsf{A}_i = \mathsf{A}_i(0)$ is the observable in the Schrödinger picture; we have written $\mathsf{A}_i(t)$ instead of $\mathsf{A}_{i\mathrm{H}}(t)$, as the explicit time dependence implies that the observable $\mathsf{A}_i(t)$

is taken in the Heisenberg picture. From (9.49) with $\delta\mathsf{B} = \delta\mathsf{A}_j(t)$, the ensemble average $\overline{\delta\mathsf{A}_j}(t)$ is given in the linear approximation by

$$\boxed{\overline{\delta\mathsf{A}_j}(t) = \beta f_i \big\langle \delta\mathsf{A}_j(t); \delta\mathsf{A}_i(0) \big\rangle} \tag{9.57}$$

It is customary to make in (9.50) the change of variables $\alpha = \beta x$ and to write (9.57) as

$$\overline{\delta\mathsf{A}_j}(t) = f_i \int_0^\beta \mathrm{d}\alpha \left\langle \delta\mathsf{A}_j(t)\, \mathrm{e}^{-\alpha H}\, \delta\mathsf{A}_i(0)\, \mathrm{e}^{\alpha H} \right\rangle \tag{9.58}$$

Comparing with (9.11) and (9.12), we see that the Kubo function $C_{ji}(t)$ is now

$$\boxed{C_{ji}(t) = \big\langle \delta\mathsf{A}_j(t); \delta\mathsf{A}_i(0) \big\rangle = \frac{1}{\beta} \int_0^\beta \mathrm{d}\alpha \left\langle \mathsf{A}_j(t)\, \mathrm{e}^{-\alpha H}\, \mathsf{A}_i(0)\, \mathrm{e}^{\alpha H} \right\rangle_{\mathrm{c}}} \tag{9.59}$$

Note that, at equilibrium, the matrix C_{ji} introduced in (9.52) is nothing other than the Kubo function taken at $t = 0$: $C_{ji} = C_{ji}(t = 0)$. In the classical limit, all operators commute and one recovers (9.12). The Kubo function may be written in a different form, using the property that the inverse temperature generates translations in imaginary time as already explained in Chapter 7. We may write from (1.58), with $t = \mathrm{i}\beta$

$$\mathrm{e}^{\mathrm{i}(\mathrm{i}\beta H)} \mathsf{A}_i(0) \mathrm{e}^{-\mathrm{i}(\mathrm{i}\beta H)} = \mathsf{A}_i(\mathrm{i}\beta)$$

so that

$$C_{ji}(t) = \frac{1}{\beta} \int_0^\beta \mathrm{d}\alpha \left\langle \mathsf{A}_j(t) \mathsf{A}_i(\mathrm{i}\alpha) \right\rangle_{\mathrm{c}} \tag{9.60}$$

The dynamical susceptibility is related to the Kubo function exactly as in the classical case

$$\begin{aligned} \chi_{ij}(t) &= -\beta\theta(t)\dot{C}_{ij}(t) \\ \chi''_{ij}(t) &= \frac{\mathrm{i}}{2}\, \beta\, \dot{C}_{ij}(t) \end{aligned} \tag{9.61}$$

All the analyticity properties derived in Section 9.1.3 are also valid in the quantum case, since they depend only on causality.

9.2.3 Fluctuation-dissipation theorem

The susceptibility and its imaginary part are given from (9.61) by the time derivative of the Kubo function, and it turns out that this derivative has a much simpler expression than the function itself. Using time translation invariance, we write the time derivative of $C_{ij}(t)$ as follows

$$\dot{C}_{ij}(t) = -\frac{1}{\beta}\int_0^\beta \mathrm{d}\alpha \left\langle \mathsf{A}_i(t)\mathrm{e}^{-\alpha H}\frac{\mathrm{d}\mathsf{A}_j}{\mathrm{d}t}\Big|_{t=0}\mathrm{e}^{\alpha H}\right\rangle_{\mathrm{c}}$$

From $\partial_t \mathsf{A} = i[H, \mathsf{A}]$

$$\dot{C}_{ij}(t) = \frac{i}{\beta}\int_0^\beta \mathrm{d}\alpha \left\langle \mathsf{A}_i(t)\,\frac{\mathrm{d}}{\mathrm{d}\alpha}\left(\mathrm{e}^{-\alpha H}\mathsf{A}_j\mathrm{e}^{\alpha H}\right)\right\rangle_{\mathrm{c}}$$

The α-integrand is then a total derivative, the integration is trivial and leads to the important result

$$\boxed{\chi''_{ij}(t) = \frac{1}{2}\langle[\mathsf{A}_i(t), \mathsf{A}_j(0)]\rangle} \tag{9.62}$$

The function $\chi''_{ij}(t)$ is given by the average value of a commutator.[9] Similarly, the susceptibility is given by the average value of a *retarded* commutator

$$\boxed{\chi_{ij}(t) = \mathrm{i}\theta(t)\left\langle[\mathsf{A}_i(t), \mathsf{A}_j(0)]\right\rangle} \tag{9.63}$$

As in the classical case, this equation shows that $\chi_{ij}(t)$ is a real function of t if A_i and A_j are Hermitian operators. Let us now evaluate (9.62) by inserting complete sets of states $|n\rangle$ of the Hamiltonian, $H|n\rangle = E_n|n\rangle$. The first term in the commutator on the right hand side of (9.62) is the dynamical structure factor $S_{ij}(t) = \langle \mathsf{A}_i(t)\mathsf{A}_j(0)\rangle_{\mathrm{c}}$

$$S_{ij}(t) = \frac{1}{Z}\sum_{n,m}\exp(-\beta E_n + \mathrm{i}(E_n - E_m)t)\langle n|\delta\mathsf{A}_i|m\rangle\langle m|\delta\mathsf{A}_j|n\rangle$$

and, taking the time Fourier transform

$$S_{ij}(\omega) = \frac{1}{Z}\sum_{n,m}\exp(-\beta E_n)\delta(\omega + E_n - E_m)\langle n|\delta\mathsf{A}_i|m\rangle\langle m|\delta\mathsf{A}_j|n\rangle$$

The second term in the commutator is computed by noting that it may be written as $S_{ji}(-t)$, so that its Fourier transform is $S_{ji}(-\omega)$; exchanging the indices n and

[9] Note that $\chi''(\omega)$ is the imaginary part of $\chi(\omega)$, but that $\chi''(t)$ is *not* the imaginary part of $\chi(t)$. We have kept this standard notation, which is admittedly somewhat confusing.

m in the expression of this second term, one readily finds

$$\boxed{\chi''_{ij}(\omega) = \frac{1}{2\hbar}(1 - \exp(-\beta\omega\hbar))S_{ij}(\omega)} \tag{9.64}$$

where we have for once written explicitly the Planck constant $\hbar$. This is the quantum version of the fluctuation-dissipation theorem, and one recovers its classical version (9.28) in the limit $\hbar \to 0$. As was already mentioned, the structure factor $S_{ij}(t)$ and the Kubo function $C_{ij}(t)$ are identical in the classical case. However, they are *different* in the quantum case. Adding space dependence as in Section 9.1.4, we get a structure factor $S_{ij}(\vec{k}, \omega)$, which may be measured in inelastic scattering experiments (light, X-rays, neutrons, electrons ...), while $\chi''_{ij}(\vec{k}, \omega)$ describes dissipation.

9.2.4 Symmetry properties and dissipation

Before showing explicitly that χ''_{ij} describes dissipation, we need to derive its symmetry properties. They follow from various invariances.

(*i*) From time translation invariance

$$\chi''_{ij}(t) = -\chi''_{ji}(-t) \qquad \text{or} \qquad \chi''_{ij}(\omega) = -\chi''_{ji}(-\omega) \tag{9.65}$$

(*ii*) From the Hermiticity of the A_is (see Exercise 9.7.5 for non-Hermitian operators)

$$\chi''^{*}_{ij}(t) = -\chi''_{ij}(t) \qquad \text{or} \qquad \chi''^{*}_{ij}(\omega) = -\chi''_{ij}(-\omega) \tag{9.66}$$

Then $\chi''_{ij}(t)$ is pure imaginary and $\chi_{ij}(t)$ is real from (9.61).

(*iii*) From time reversal invariance

$$\chi''_{ij}(t) = -\varepsilon_i\varepsilon_j\chi''_{ij}(-t) \qquad \text{or} \qquad \chi''_{ij}(\omega) = -\varepsilon_i\varepsilon_j\chi''_{ij}(-\omega) \tag{9.67}$$

In (9.67), ε_i is the parity under time reversal of the observable A_i

$$\Theta\,\mathsf{A}_i(t)\Theta^{-1} = \varepsilon_i\mathsf{A}_i(-t) \tag{9.68}$$

where Θ is the (antiunitary) time reversal operator. We have assumed that the observables have, as is generally the case, a definite parity ε_i under time reversal. The proof of (9.67) is immediate in the classical case, where one first derives the parity property of the Kubo function $C_{ij}(t) = \varepsilon_i\varepsilon_j C_{ij}(-t)$, from which (9.67) follows. The most common case is $\varepsilon_i\varepsilon_j = +1$, for example if $\mathsf{A}_i = \mathsf{A}_j = \mathsf{A}$, then $\chi''_{ij}(\omega)$ is a real and odd function of ω. If $\varepsilon_i\varepsilon_j = -1$, $\chi''_{ij}(\omega)$ is imaginary and even in ω. The symmetry properties under time reversal are, of course, intimately related to the symmetry properties (6.38) of Onsager's coefficients of irreversible thermodynamics.

Let us now justify that χ'' does describe dissipation. Instead of Heisenberg's picture, it is slightly more convenient to use Schrödinger's picture, labelled by a superscript S. Let $D_1^{\mathrm{S}}(t)$ denote the perturbed density operator in the presence of a time-dependent pertubation $\mathsf{V}^{\mathrm{S}}(t) = -\sum_i f_i(t)\mathsf{A}_i$, $\mathsf{A}_i = \mathsf{A}_i^{\mathrm{S}}$. The time evolution of D_1^{S} is governed from (2.14) by

$$i\partial_t D_1^{\mathrm{S}}(t) = [H_1^{\mathrm{S}}(t), D_1^{\mathrm{S}}(t)] = [H + \mathsf{V}^{\mathrm{S}}(t), D_1^{\mathrm{S}}(t)] \tag{9.69}$$

The system is driven by external forces $f_i(t)$, which we assume to be periodic. As a simple example, it is useful to recall the damped mechanical harmonic oscillator driven by an external force: energy is dissipated in the viscous medium which damps the oscillations. The rate $\mathrm{d}W/\mathrm{d}t$ at which the external forces do work on the system is equal to the variation per unit time of the energy $E(t)$ of the system

$$\frac{\mathrm{d}W}{\mathrm{d}t} = \frac{\mathrm{d}E}{\mathrm{d}t} = \frac{\mathrm{d}}{\mathrm{d}t}\,\mathrm{Tr}\Big(D_1^{\mathrm{S}}(t)H_1^{\mathrm{S}}(t)\Big) = \mathrm{Tr}(D_1^{\mathrm{S}}\dot{H}_1^{\mathrm{S}}) + \mathrm{Tr}(\dot{D}_1^{\mathrm{S}}H_1^{\mathrm{S}}) \tag{9.70}$$

The last term in (9.70) vanishes because of (9.69) and of $\mathrm{Tr}\Big([H_1^{\mathrm{S}}, D_1^{\mathrm{S}}]H_1^{\mathrm{S}}\Big) = 0$. Then

$$\frac{\mathrm{d}W}{\mathrm{d}t} = -\sum_i \mathrm{Tr}[D_1^{\mathrm{S}}(t)\mathsf{A}_i]\,\dot{f}_i(t) = -\sum_i \overline{A_i}(t)\,\dot{f}_i(t) \tag{9.71}$$

Let us choose periodic $f_i(t)$s

$$f_i(t) = \frac{1}{2}\Big(f_i^{\omega}\mathrm{e}^{-\mathrm{i}\omega t} + f_i^{\omega *}\mathrm{e}^{\mathrm{i}\omega t}\Big) = \mathrm{Re}\Big(f_i^{\omega}\mathrm{e}^{-\mathrm{i}\omega t}\Big) \tag{9.72}$$

and take a time average of $\mathrm{d}W/\mathrm{d}t$ over a time interval $T \gg \omega^{-1}$. We may use $\overline{\delta\mathsf{A}_i}$ instead of $\overline{\mathsf{A}_i}$ in (9.71) because $\langle \mathsf{A}_i \rangle$ gives a vanishing contribution to a time average. As $\overline{\delta\mathsf{A}_i}(t)$ is given by (9.13), plugging (9.13) in (9.70) and taking the time average gives after an elementary calculation (see Exercises 9.7.1 and 9.7.6)

$$\boxed{\left\langle \frac{\mathrm{d}W}{\mathrm{d}t} \right\rangle_T = \frac{1}{2}\,\omega f_i^{\omega *}\chi_{ij}''(\omega) f_j^{\omega}} \tag{9.73}$$

It is easy to check that the right hand side of (9.73) is a real quantity, even if $\chi_{ij}''(\omega)$ is imaginary, because combining (9.65) and (9.66), which are independent of time reversal, gives $(\chi_{ij}''(\omega))^* = \chi_{ji}''(\omega)$. From the second law of thermodynamics, the right hand side of (9.73) must always be positive, otherwise one would obtain work from a single source of heat, which implies that the matrix $\omega\chi_{ij}''(\omega)$ must be positive. The proof is left to Exercise 9.7.6.

To conclude this subsection, let us write the most general form of linear response, including space-dependent terms, which we have already introduced in

Section 9.1.4. The generalization of (9.13) is

$$\overline{\delta A_i}(\vec{r},t) = \int \mathrm{d}t'\,\mathrm{d}^3r'\,\chi_{ij}(\vec{r},\vec{r}\,',t-t')\,f_j(\vec{r}\,',t') \tag{9.74}$$

In general, space translation invariance holds and χ depends only on the difference $\vec{r}-\vec{r}\,'$. Then one may take the space Fourier transform of (9.73) to cast the convolution into a product

$$\overline{\delta A_i}(\vec{k},t) = \int \mathrm{d}t'\,\chi_{ij}(\vec{k},t-t')\,f_j(\vec{k},t') \tag{9.75}$$

so that all Fourier components are decoupled, and the preceding results can be immediately transposed to each individual Fourier component. However, in using the symmetry property (9.66), one must be careful that $\mathsf{A}_i(\vec{k},t)$ is not Hermitian, even though $\mathsf{A}_i(\vec{r},t)$ is Hermitian since

$$[\mathsf{A}_i(\vec{k},t)]^\dagger = \mathsf{A}_i(-\vec{k},t)$$

9.2.5 Sum rules

The dynamical susceptibility obeys sum rules that are very useful to constrain phenomenological expressions such as those written in Section 9.1.4. Let us start from the representation (9.24) of $\chi_{ij}(z)$

$$\chi_{ij}(\vec{k},z) = \int_{-\infty}^{\infty} \frac{\mathrm{d}\omega'}{\pi}\,\frac{\chi''_{ij}(\vec{k},\omega')}{\omega'-z} \tag{9.76}$$

and assume that $\chi''_{ij}(\vec{k},\omega)$ is odd and real ($\varepsilon_i\varepsilon_j=+1$). The so-called *thermodynamic sum rule* is obtained in the static limit z or $\omega\to 0$

$$\chi_{ij}(\vec{k},\omega=0) = \int_{-\infty}^{\infty} \frac{\mathrm{d}\omega'}{\pi}\,\frac{\chi''_{ij}(\vec{k},\omega')}{\omega'} \tag{9.77}$$

$\chi_{ij}=\lim_{k\to 0}\chi_{ij}(\vec{k},\omega=0)$ is a thermodynamic quantity, hence the terminology 'thermodynamic sum rule'.

By examining the high frequency limit, we obtain the so-called *f-sum rule* (or *Nozières–Pines sum rule*). Let us look at the behaviour $|z|\to\infty$ of (9.76)

$$\frac{1}{\omega-z} = -\frac{1}{z}\left(1+\frac{\omega}{z}+\frac{\omega^2}{z^2}+\cdots\right)$$

Since χ''_{ij} is an odd function of ω

$$\chi_{ij}(\vec{k}, z) = -\frac{1}{z^2} \int_{-\infty}^{\infty} \frac{\mathrm{d}\omega}{\pi}\, \omega \chi''_{ij}(\vec{k}, \omega) + \mathcal{O}\Big(\frac{1}{z^4}\Big) \tag{9.78}$$

This equation gives the leading term in an expansion in $1/z$ of $\chi_{ij}(\vec{k}, z)$. We remark that $\omega\chi''_{ij}(\vec{k}, \omega)$ is the time-Fourier transform of $\mathrm{i}\partial_t \chi''(\vec{k}, \omega)$

$$\omega \chi''_{ij}(\vec{k}, \omega) = \int \mathrm{d}t\, \mathrm{e}^{\mathrm{i}\omega t} \Big[\mathrm{i}\partial_t \chi''_{ij}(\vec{k}, t)\Big]$$

so that, from (9.62), generalized to space-dependent observables $\mathsf{A}_i(\vec{r}, t)$, we get after a Fourier transformation

$$\Big[\mathrm{i}\partial_t \chi''_{ij}(\vec{k}, t)\Big]_{t=0} = \int_{-\infty}^{\infty} \frac{\mathrm{d}\omega}{\pi}\, \omega \chi''_{ij}(\vec{k}, \omega) = \frac{\mathrm{i}}{V} \big\langle \big[\dot{\mathsf{A}}_i(\vec{k}, t), \mathsf{A}_j(-\vec{k}, 0)\big]\big\rangle\Big|_{t=0}$$

where V is the total volume of the sample. By using the commutation relation

$$\dot{\mathsf{A}}_i(\vec{k}, t) = \mathrm{i}[\mathsf{A}_i(t), H]$$

we finally get

$$\int_{-\infty}^{\infty} \frac{\mathrm{d}\omega}{\pi}\, \omega \chi''_{ij}(\vec{k}, \omega) = \frac{1}{V} \big\langle \big[\big[\mathsf{A}_i(\vec{k}), H\big], \mathsf{A}_j(-\vec{k})\big]\big\rangle \tag{9.79}$$

The most important example is that of the density–density correlation function χ''_{nn}. Let us perform the calculation in the classical limit, leaving the quantum case to Exercise 9.7.7. From the classical fluctuation-dissipation theorem

$$\chi''(\vec{k}, \omega) = \frac{1}{2}\beta\omega S(\vec{k}, \omega)$$

and the integral to be computed is

$$I = \beta \int \frac{\mathrm{d}\omega}{2\pi}\, \omega^2 S_{nn}(\vec{k}, \omega)$$

Using time translation invariance leads to

$$V S_{nn}(\vec{k}, t - t') = \big\langle n(\vec{k}, t) n(-\vec{k}, t')\big\rangle_{\mathrm{c}}$$

and the integral I is

$$I = \frac{\beta}{V} \big\langle \dot{n}(\vec{k}, t)\, \dot{n}(-\vec{k}, t)\big\rangle_{\mathrm{c}}$$

Using the spatial Fourier transform of the continuity equation (9.29) $\partial_t n + \mathrm{i}k_l j_l = 0$ finally yields

$$I = \frac{\beta}{V} k_l k_m \langle j_l(\vec{k}, t)\, j_m(\vec{k}, t)\rangle$$

The current density $\vec{j}$ is given by a sum over the N particles of the system as a function of their velocities $\vec{v}^{\,\alpha}$

$$j_l(\vec{r}, t) = \sum_{\alpha=1}^{N} v_l^{\alpha} \delta(\vec{r} - \vec{r}^{\,\alpha}(t)) \tag{9.80}$$

or, in Fourier space

$$j_l(\vec{k}, t) = \sum_{\alpha=1}^{N} v_l^{\alpha} \exp[-\mathrm{i}\vec{k} \cdot \vec{r}^{\,\alpha}(t)] \tag{9.81}$$

In the classical limit, the velocities of different particles are uncorrelated

$$\langle v_l^{\alpha} v_m^{\gamma}\rangle = \frac{1}{3} \delta_{\alpha\gamma}\delta_{lm} \langle \vec{v}^{\,2}\rangle = \delta_{\alpha\gamma}\delta_{lm} \frac{1}{m\beta}$$

and we get the f-sum rule

$$\boxed{\int_{-\infty}^{\infty} \frac{\mathrm{d}\omega}{\pi}\, \omega \chi''_{nn}(\vec{k}, \omega) = \frac{n k^2}{m}} \tag{9.82}$$

where $n = N/V$ is the density.

9.3 Projection method and memory effects

In this section, we first give a phenomenological introduction to memory effects, and then we show that these effects can be accounted for by using the so-called *projection method*. The idea which underlies the projection method is that it is often possible to distinguish between macroscopic variables, which vary slowly in time, and microscopic variables, which, on the contrary, exhibit fast variation with time. The former variables will be called slow modes and the latter fast modes. In general, we are not interested in the fast modes, associated with the microscopic behaviour of the system. For example, in the case of Brownian motion, we are not interested in the fast motion of the fluid molecules, but only in the slow motion of the Brownian particle. The idea is then to project the dynamics onto a subspace spanned by the slowly varying observables, in order to keep only the modes we are interested in. The success of the method will depend on our ability to identify all the slow modes and to restrict the dynamics to that of the slow modes only, which

is called the *reduced dynamics*. The presence of slow modes can usually be traced back to the following sources.

(*i*) Existence of local conservation laws: we have seen an example in Section 9.1.4. In general, the corresponding slow modes are called *hydrodynamic modes*.
(*ii*) Existence of one heavy particle: this is the example of Brownian motion, where a heavy particle of mass M is put in a fluid of particles of mass m, with $M/m \gg 1$. This example will be studied at the end of the present section and in Problem 9.8.3.
(*iii*) Existence of Goldstone modes, associated with a broken continuous symmetry, for example in magnets, superfluids and liquid crystals. These slow modes will not be examined in this book, and we refer to the literature for an account of this very interesting case.

Of course, one cannot completely eliminate the fast modes, and the reduced dynamics cannot be described by a closed set of differential (or partial differential) equations. The back action of the fast modes on the reduced dynamics will appear through a memory term and a stochastic force.

9.3.1 Phenomenological introduction to memory effects

Our hydrodynamic theory of Section 9.1.4 suffers from a major failure: the f-sum rule (9.82) does not converge, since from (9.40) $\chi''(\omega) \sim 1/\omega$ for $\omega \to \infty$. As the continuity equation (9.29) is exact, the weak link of the hydrodynamic description must be Fick's law (9.30). Let us try to correct it, in a heuristic manner, by allowing for memory effects in such a way that the current does not instantaneously follow the density gradient

$$\vec{j}(\vec{r}, t) = -\int_0^t \mathrm{d}t' \gamma(t - t') \vec{\nabla} n(\vec{r}, t') \tag{9.83}$$

$\gamma(t)$ is called the *memory function*. One could also introduce a spatial dependence in the memory function; this generalization is easily handled by going to Fourier space and is left as an exercise for the reader. Let us try the simple parametrization

$$\gamma(t) = \frac{D}{\tau^*} \mathrm{e}^{-|t|/\tau^*} \tag{9.84}$$

where τ^* is a *microscopic* time ($\tau^* \sim 10^{-12} - 10^{-14}$ s), characteristic of relaxation towards *local equilibrium* (let us recall that a hydrodynamic description assumes that a situation of local equilibrium has been reached). If $\vec{\nabla} n$ varies slowly

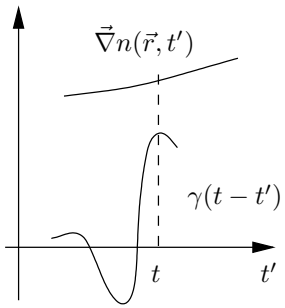

Figure 9.2 A slowly varying density distribution.

on a time scale $\sim \tau^*$, one recovers Fick's law (9.30) for $t \gg \tau^*$ (Figure 9.2)

$$\int_0^t \mathrm{d}t' \gamma(t - t') \vec{\nabla} n(\vec{r}, t') \simeq \vec{\nabla} n(\vec{r}, t) \int_0^\infty \mathrm{d}t' \frac{D}{\tau^*} \mathrm{e}^{-t'/\tau^*} = D \vec{\nabla} n(\vec{r}, t) \tag{9.85}$$

so that (9.30) is recovered. With memory effects included, the continuity equation reads in Fourier space

$$\partial_t n(\vec{k}, t) = -k^2 \int_0^t \mathrm{d}t' \gamma(t - t') n(\vec{k}, t') \tag{9.86}$$

We take the Laplace transform of (9.86) and note that the Laplace transform of the convolution is transformed into a product

$$\int_0^\infty \mathrm{d}t \int_0^t \mathrm{d}t' \, \mathrm{e}^{\mathrm{i}z(t-t')} \mathrm{e}^{\mathrm{i}zt'} \gamma(t - t') \, n(\vec{k}, t') = \gamma(z) \, n(\vec{k}, z)$$

so that

$$n(\vec{k}, t = 0) + \mathrm{i}z n(\vec{k}, z) = k^2 \gamma(z) n(\vec{k}, z)$$

Solving for $n(\vec{k}, z)$ and using (9.26) allows us to identify the new expression for the susceptibility

$$\chi(\vec{k}, z) = \frac{\mathrm{i}k^2 \gamma(z)}{z + \mathrm{i}k^2 \gamma(z)} \chi(\vec{k}) \tag{9.87}$$

while $\gamma(z)$ becomes in the approximation (9.84)

$$\gamma(z) = \frac{D}{\tau^*} \int_0^\infty \mathrm{d}t \, \mathrm{e}^{\mathrm{i}zt - t/\tau^*} = \frac{D}{1 - \mathrm{i}z\tau^*} \tag{9.88}$$

This yields the Laplace transform of the dynamical susceptibility

$$\chi(\vec{k}, z) = \frac{\mathrm{i}k^2 D/(1 - \mathrm{i}z\tau^*)}{z + \mathrm{i}k^2 D/(1 - \mathrm{i}z\tau^*)}\, \chi(\vec{k}) \tag{9.89}$$

and its imaginary part

$$\chi''(\vec{k}, \omega) = \frac{\omega k^2 D}{\omega^2 + D^2(k^2 - \omega^2\tau^*/D)^2}\, \chi(\vec{k}) \tag{9.90}$$

As $\chi''(\omega) \sim 1/\omega^3$ for $\omega \to \infty$, the f-sum rule is now convergent. Since the integral in the sum rule is given by the coefficient of $-1/z^2$ in an expansion of $\chi(\vec{k}, z)$ for $|z| \to \infty$, and since from (9.89)

$$\chi(\vec{k}, z) \sim -\frac{k^2 D}{z^2 \tau^*}\, \chi(\vec{k}) \quad \text{for} \quad |z| \to \infty$$

Equation (9.82) leads to an interesting relation between the diffusion coefficient and the microscopic time τ^*

$$D = \frac{n\tau^*}{m\chi(\vec{k})} \tag{9.91}$$

Incidentally, this equation shows that D (or the memory function) must depend on k. In the example of polarized helium-3 at low temperatures, one may prove that $\tau^* \sim 1/T^2$ because of the Pauli principle, and (9.91) predicts that the same behaviour should be observed for D, which is experimentally verified. However, our approximation (9.84) for the memory function $\gamma(t)$ cannot be the last word, as sum rules with factors of ω^{2n+1} instead of ω remain divergent.

9.3.2 Projectors

We now turn to a formal derivation of memory effects. We shall need the *Liouvillian*, which is an operator acting on the vector space of observables A_i. The definition of the Liouvillian $\mathcal{L}$ follows from Heisenberg's equation of motion for an observable A

$$\boxed{\partial_t \mathsf{A} = \mathrm{i}[H, \mathsf{A}] = \mathrm{i}\mathcal{L}\mathsf{A}} \tag{9.92}$$

The operators acting in the vector space of observables will be denoted by script letters: $\mathcal{L}$, $\mathcal{P}$, $\mathcal{Q}$. Equation (9.92) can be integrated formally as

$$\mathsf{A}(t) = \mathrm{e}^{\mathrm{i}\mathcal{L}t}\, \mathsf{A}(0) \tag{9.93}$$

An explicit expression for the Liouvillian can be obtained by choosing a basis in the Hilbert space of states in which (9.92) reads

$$\mathrm{i}\partial_t \mathsf{A}_{mn}(t) = \mathsf{A}_{m\nu}(t)H_{\nu n} - H_{m\nu}\mathsf{A}_{\nu n}(t)$$

As the observables may be considered as elements of a vector space with components labelled by two indices (m, n) or (μ, ν), the matrix elements of the Liouvillian are then labelled by couples of indices

$$\mathcal{L}_{mn;\mu\nu} = H_{m\mu}\delta_{n\nu} - H_{\nu n}\delta_{m\mu} \tag{9.94}$$

As explained in the introduction to the present section, we want to project the dynamics on the subspace $\mathcal{E}$ spanned by a set of slowly varying observables A_i and the identity operator $\mathcal{I}$: $\mathcal{E} \equiv \{\mathcal{I}, \mathsf{A}_i\}$. Actually the equations we are going to derive in this subsection are valid for any set of observables, but they are physically useful only if $\mathcal{E}$ is a set of slow variables. We are looking for a projector $\mathcal{P}$ ($\mathcal{P}^2 = \mathcal{P}$) on the subspace $\mathcal{E}$ such that

$$\mathcal{P}B = B \qquad \text{if} \qquad B \in \mathcal{E} \equiv \{\mathcal{I}, \mathsf{A}_i\} \tag{9.95}$$

The complementary projector will be denoted by $\mathcal{Q}$: $\mathcal{Q} = \mathcal{I} - \mathcal{P}$. One should be aware that the set $\{\mathsf{A}_i\}$ is defined at $t = 0$ and in general the observables $\mathsf{A}_i(t)$ at a time $t \neq 0$ do *not* belong to the subspace $\mathcal{E}$: only the *projected* operators $\mathcal{P}\mathsf{A}_i(t)$ belong to $\mathcal{E}$.

In order to compute $\mathcal{P}$, let us recall an elementary example. Assume that we are given in $\mathbb{R}^N$ a set of M ($M < N$) non-orthogonal, non-normalized vectors $\vec{e}_1, \ldots, \vec{e}_M$. The action on a vector $\vec{V}$ of the projector $\mathcal{P}$ that projects on the subspace spanned by these vectors is

$$\mathcal{P}\vec{V} = C_{ij}^{-1}(\vec{V} \cdot \vec{e}_i)\vec{e}_j \qquad \text{where} \qquad C_{ij} = \vec{e}_i \cdot \vec{e}_j \tag{9.96}$$

Equation (9.96) is generally valid provided one is given a scalar product C_{ij} of two vectors $\vec{e}_i$ and $\vec{e}_j$. In particular we can use (9.96) in the space of observables and choose Mori's scalar product (9.51) to define the projector $\mathcal{P}$ on the subspace $\mathcal{E}$,[10]

$$\boxed{\mathcal{P} = \delta\mathsf{A}_j C_{jk}^{-1}\delta\mathsf{A}_k \qquad C_{jk} = \langle\delta\mathsf{A}_j; \delta\mathsf{A}_k\rangle} \tag{9.97}$$

[10] Strictly speaking, there is one term missing in (9.97), because one must have $\mathcal{P}I = I$. Setting $\delta\mathsf{A}_0 = I$, we may write

$$\mathcal{P} = \sum_{j,k=0} \delta\mathsf{A}_j C_{jk}^{-1}\delta\mathsf{A}_k$$

where we have used $\langle\delta\mathsf{A}_0; \delta\mathsf{A}_0\rangle = 1$ and $\langle\delta\mathsf{A}_0; \delta\mathsf{A}_i\rangle = 0$ for $i \neq 0$.

and the average $\langle\bullet\rangle$ is computed with the *equilibrium density operator* (9.55); recall that $\delta\mathsf{A}_i = \mathsf{A}_i - A_i$. The explicit action of $\mathcal{P}$ on an observable B is

$$\mathcal{P}\mathsf{B} = \delta\mathsf{A}_j\, C^{-1}_{jk}\langle\delta\mathsf{A}_k; \mathsf{B}\rangle = \frac{\partial B}{\partial A_j}\,\delta\mathsf{A}_j$$

where the last equation follows from (9.53) and Hermiticity of A_k and B. It is easily checked that $\mathcal{P}^2 = \mathcal{P}$ and that $\mathcal{P}^\dagger = \mathcal{P}$. Moreover we also note that the Liouvillian is Hermitian with respect to Mori's scalar product (Exercise 9.7.4)

$$\langle\mathsf{A}; \mathcal{L}\mathsf{B}\rangle = \langle\mathcal{L}\mathsf{A}; \mathsf{B}\rangle \tag{9.98}$$

An important consequence of (9.98) is the antisymmetry property deduced from $\partial_t = \mathrm{i}\mathcal{L}$

$$\langle\mathsf{A}; \dot{\mathsf{B}}\rangle = -\langle\dot{\mathsf{A}}; \mathsf{B}\rangle \tag{9.99}$$

where $\dot{\mathsf{A}} = \partial_t\mathsf{A}$, from which $\langle\mathsf{A}; \dot{\mathsf{A}}\rangle = 0$ follows.

9.3.3 Langevin–Mori equation

We now wish to derive equations of motion for the observables of the set A_i.[11] Let us start from the trivial identity $\mathcal{P} + \mathcal{Q} = \mathcal{I}$ and write

$$\dot{\mathsf{A}}_i(t) = \mathrm{e}^{\mathrm{i}\mathcal{L}t}\mathcal{Q}\dot{\mathsf{A}}_i + \mathrm{e}^{\mathrm{i}\mathcal{L}t}\mathcal{P}\dot{\mathsf{A}}_i \tag{9.100}$$

It is easy to evaluate the second term in (9.100)

$$\begin{aligned}\mathrm{e}^{\mathrm{i}\mathcal{L}t}\mathcal{P}\dot{\mathsf{A}}_i &= \mathrm{e}^{\mathrm{i}\mathcal{L}t}\delta\mathsf{A}_j C^{-1}_{jk}\langle\delta\mathsf{A}_k; \mathrm{i}\mathcal{L}\mathsf{A}_i\rangle \\ &= \Omega_{ji}\,\mathrm{e}^{\mathrm{i}\mathcal{L}t}\,\delta\mathsf{A}_j\end{aligned} \tag{9.101}$$

the frequencies Ω_{ji} being defined by

$$\Omega_{ji} = C^{-1}_{jk}\langle\delta\mathsf{A}_k; \mathrm{i}\mathcal{L}\mathsf{A}_i\rangle \tag{9.102}$$

Note that $\Omega_{ji} = 0$ if all observables in $\mathcal{E}$ have the same parity under time reversal (see Exercise 9.7.4). In this case $\langle\dot{\mathsf{A}}_i; \mathsf{A}_j\rangle = 0\,\forall(i, j)$ and $\dot{\mathsf{A}}_i \in \mathcal{E}_\perp$. In particular $\Omega = 0$ if there is only one slow observable.

In order to deal with the first term in (9.100) we use the operator identity (2.118), which can be cast into the form

$$\mathrm{e}^{\mathrm{i}\mathcal{L}t} = \mathrm{e}^{\mathrm{i}\mathcal{Q}\mathcal{L}t} + \mathrm{i}\int_0^t \mathrm{d}t'\,\mathrm{e}^{\mathrm{i}\mathcal{L}(t-t')}\mathcal{P}\mathcal{L}\mathrm{e}^{\mathrm{i}\mathcal{Q}\mathcal{L}t'} \tag{9.103}$$

[11] We are going to derive Mori's version of the projection method. There exist many other versions of the projection method, but Mori's turns out to be the easiest to derive and the most useful close to equilibrium.

We then transform (9.103) by introducing operators $\mathsf{f}_i(t)$, which are called *stochastic forces* for reasons that will become clear in Section 9.3.5, through

$$\boxed{\mathsf{f}_i(t) = \mathrm{e}^{\mathrm{i}\mathcal{Q}\mathcal{L}\mathcal{Q}t}\,\mathcal{Q}\dot{\mathsf{A}}_i} \tag{9.104}$$

The stochastic forces live entirely in the space $\mathcal{E}_\perp$ orthogonal to $\mathcal{E}$. First $\mathcal{Q}$ projects $\dot{\mathsf{A}}_i$ on this subspace,[12] and then the operator $\mathcal{Q}\mathcal{L}\mathcal{Q}$, which has non-zero matrix element only in $\mathcal{E}_\perp$, is the evolution operator in $\mathcal{E}_\perp$: $\exp(\mathrm{i}\mathcal{Q}\mathcal{L}\mathcal{Q}t)\mathcal{Q}\dot{\mathsf{A}}_i$ does not leave $\mathcal{E}_\perp$. The stochastic forces may thus vary with a time scale entirely different from that characteristic of $\mathcal{P}\mathsf{A}_i(t)$, which should evolve slowly with time. Note also that the stochastic forces have zero equilibrium average values, $\langle \mathsf{f}_i(t)\rangle = 0$, and that they are orthogonal by construction to the A_is: $\langle \mathsf{A}_i; \mathsf{f}_i(t)\rangle = 0$. Given the definition (9.104), the first term in (9.103) yields, when applied to $\mathcal{Q}\dot{\mathsf{A}}_i$

$$\mathrm{e}^{\mathrm{i}\mathcal{Q}\mathcal{L}t}\mathcal{Q}\dot{\mathsf{A}}_i = \mathrm{e}^{\mathrm{i}\mathcal{Q}\mathcal{L}\mathcal{Q}t}\mathcal{Q}\dot{\mathsf{A}}_i = \mathsf{f}_i(t)$$

where we have used

$$\begin{aligned}&\left(I + \mathrm{i}\mathcal{Q}\mathcal{L}t + \frac{\mathrm{i}^2}{2!}\mathcal{Q}\mathcal{L}\mathcal{Q}\mathcal{L}t^2 + \cdots\right)\mathcal{Q}\\ &= \left(I + \mathrm{i}\mathcal{Q}\mathcal{L}\mathcal{Q}t + \frac{\mathrm{i}^2}{2!}(\mathcal{Q}\mathcal{L}\mathcal{Q})(\mathcal{Q}\mathcal{L}\mathcal{Q})t^2 + \cdots\right)\mathcal{Q}\end{aligned}$$

because $\mathcal{Q}^2 = \mathcal{Q}$. The last contribution comes from the second term in (9.103)

$$\begin{aligned}&\int_0^t \mathrm{d}t'\,\mathrm{e}^{\mathrm{i}\mathcal{L}(t-t')}\,\delta\mathsf{A}_j\,C^{-1}_{jk}\left\langle \delta\mathsf{A}_k;\,\mathcal{L}\mathrm{e}^{\mathrm{i}\mathcal{Q}\mathcal{L}\mathcal{Q}t'}\mathcal{Q}\,\delta\dot{\mathsf{A}}_i\right\rangle\\ &= \int_0^t \mathrm{d}t'\,\mathrm{e}^{\mathrm{i}\mathcal{L}(t-t')}\delta\mathsf{A}_j\,C^{-1}_{jk}\left\langle \delta\mathsf{A}_k;\,\mathrm{i}\mathcal{L}\,\mathsf{f}_i(t')\right\rangle\end{aligned}$$

Using the Hermiticity (9.98) of $\mathcal{L}$, we transform the scalar product

$$\left\langle \delta\mathsf{A}_k;\,\mathrm{i}\mathcal{L}\,\mathsf{f}_i(t')\right\rangle = -\left\langle \mathrm{i}\mathcal{L}\,\delta\mathsf{A}_k;\,\mathcal{Q}\,\mathsf{f}_i(t')\right\rangle = -\left\langle \mathsf{f}_k;\,\mathsf{f}_i(t')\right\rangle$$

and cast the second term coming from (9.103) into the form

$$-\int_0^t \mathrm{d}t'\,\delta\mathsf{A}_j(t-t')C^{-1}_{jk}\left\langle \mathsf{f}_k;\,\mathsf{f}_i(t')\right\rangle = -\int_0^t \mathrm{d}t'\,\delta\mathsf{A}_j(t-t')\gamma_{ji}(t')$$

[12] If all slow observables have the same parity under time reversal, $\mathcal{Q}\dot{\mathsf{A}}_i = \dot{\mathsf{A}}_i$.

where we have defined the *memory matrix* $\gamma_{ji}(t)$

$$\boxed{\gamma_{ji}(t) = C^{-1}_{jk}\langle \mathsf{f}_k; \mathsf{f}_i(t)\rangle} \tag{9.105}$$

Gathering all terms in the preceding discussion leads to the *Langevin–Mori equations*, which are the promised equations of motion for the slow observables A_i

$$\boxed{\partial_t \mathsf{A}_i(t) = \dot{\mathsf{A}}_i(t) = \Omega_{ji}\,\delta\mathsf{A}_j(t) - \int_0^t \mathrm{d}t'\,\gamma_{ji}(t')\delta\mathsf{A}_j(t-t') + \mathrm{e}^{\mathrm{i}\mathcal{Q}\mathcal{L}\mathcal{Q}t}\,\mathsf{f}_i} \tag{9.106}$$

The Langevin–Mori equations contain a frequency term, a memory term and a stochastic force. We emphasize that no approximations have been made in deriving (9.106), and *the Langevin–Mori equations are exact*. As already mentioned, they are valid for any set of observables $\{\mathsf{A}_i\}$, but they are useful only if this is a set of slow observables. Note that $\dot{\mathsf{A}}_i(t) = \delta\dot{\mathsf{A}}_i(t)$ as A_i is time independent. Other exact equations can be obtained if we assume a time-dependent situation given by the quantum version of (9.9). If D is the density operator at $t = 0$, we can compute the average value of (9.106) with D, and using the same notation as in (9.11), $\overline{\mathsf{A}_i} = \langle \mathsf{A}_i\rangle_D$, we obtain for $t > 0$

$$\partial_t\,\overline{\delta\mathsf{A}_i}(t) = \Omega_{ji}\,\overline{\delta\mathsf{A}_j}(t) - \int_0^t \mathrm{d}t'\,\gamma_{ji}(t')\overline{\delta\mathsf{A}_i}(t-t') + \left\langle \mathrm{e}^{\mathrm{i}\mathcal{Q}\mathcal{L}\mathcal{Q}t}\,\mathsf{f}_i\right\rangle_D \tag{9.107}$$

In the absence of the last term in (9.107), we would have a simple linear integro-differential equation for the average values $\overline{\delta\mathsf{A}_i}(t)$. The complexity of the dynamics lies in the average value of the stochastic force, which reflects the dynamics of the fast modes.

The stochastic forces may be eliminated if we restrict ourselves to equations of motion for the Kubo functions. Indeed, taking the scalar product of the Langevin–Mori equation (9.106) with $\delta\mathsf{A}_k$ we get

$$\boxed{\dot{C}_{ki}(t) = \Omega_{ji}\,C_{kj}(t) - \int_0^t \mathrm{d}t'\,\gamma_{ji}(t')C_{kj}(t-t')} \tag{9.108}$$

In the case of a single slow mode, this equation simplifies to

$$\boxed{\dot{C}(t) = -\int_0^t \mathrm{d}t'\,\gamma(t')C(t-t')} \tag{9.109}$$

Using (9.57) and (9.108), we can derive equations of motion for the average values $\overline{\delta \mathsf{A}_i}(t)$, which are then given by (9.107), but *without the stochastic term*. We thus have a closed sytem of integro-differential equations of motion for the $\overline{\delta \mathsf{A}_i}(t)$s. However, *this system of equations is only valid close to equilibrium*, because we have used (9.57), which implies linear response, and thus small deviations from equilibrium. In the case of a single observable, this system reduces to

$$\partial_t \overline{\delta \mathsf{A}}(t) = -\int_0^t \mathrm{d}t' \gamma(t') \overline{\delta \mathsf{A}(t-t')} \tag{9.110}$$

These equations can also be derived directly, by using in (9.107) the linear approximation to the density operator D which follows from (2.119)

$$D \simeq D_{\mathrm{eq}} \Big(I - f_i \int_0^\beta \mathrm{d}\alpha \, \mathrm{e}^{\alpha H} \, \mathsf{A}_i \, \mathrm{e}^{-\alpha H} \Big)$$

and observing that $\langle \mathsf{f}_i(t) \rangle = \langle I; \mathsf{f}_i(t) \rangle = 0$ and $\langle \mathsf{A}_i; \mathsf{f}_j(t) \rangle = 0$. Comparing (9.110) with (9.83), we clearly see the connection with our previous heuristic approach to memory effects.

9.3.4 Brownian motion: qualitative description

We consider in classical mechanics a Brownian particle, namely a 'heavy' (by microscopic standards) particle of mass M in a heat bath of light molecules of mass m: $m/M \ll 1$. The first effect one can think of is viscosity. If the heavy particle has a velocity $\vec{v}$ in the positive x direction, the fluid molecules coming from the right will appear to have a larger velocity than those coming from the left, and because of its collisions with the fluid molecules and of this simple Doppler effect, the particle will be submitted to a force directed toward the left

$$\vec{\mathcal{F}} = -\alpha \vec{v} \tag{9.111}$$

where α is the friction coefficient; $\tau = M/\alpha = 1/\gamma$ defines a characteristic *macroscopic* time scale for the particle. However, there is another time scale in the problem, a *microscopic* time scale τ^*. Due to the random character of the collisions with the fluid molecules, one observes fluctuations of the force on a time scale $\sim 10^{-12} - 10^{-14}$ s on the order of the duration of a collision. The separation of time scales relies on the inequality $m/M \ll 1$: compare on Figure 9.3 the behaviour of the velocity of a Brownian particle and that of a ^{17}O molecule in a gas of ^{16}O molecules. In the latter case the velocity changes suddenly on a time

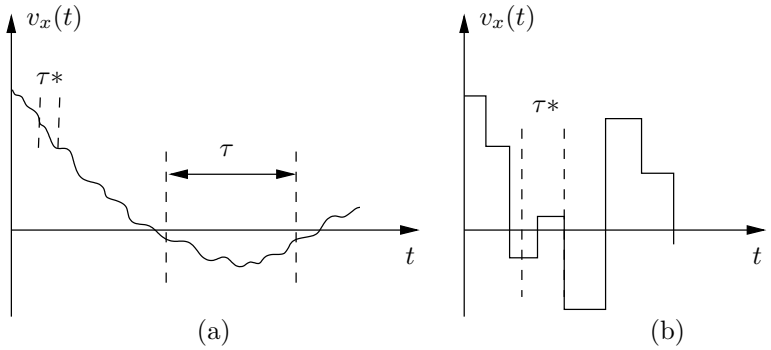

Figure 9.3 x-component of the velocity. (a) Heavy (Brownian) particle in a bath of light particles, (b) ^{17}O molecules in a gas of ^{16}O molecules.

scale τ^* (it may even change sign), while in the case of the Brownian particle, the time scale for velocity changes is τ because of its large inertia, although a short time scale τ^* is superimposed on this average motion. Although the Brownian particle may suffer large accelerations, the mean velocity varies very little on a time scale τ^*, and the average motion is a smooth one.

Let $\mathcal{A} = v$ be the velocity of a one-dimensional Brownian particle (or B-particle for short) which we identify with the (classical) observable in (9.110). From the preceding qualitative analysis, we may hope that v (but not $\dot{v}$!) is a slow variable, and we note that $\delta v = v$ since $\langle v \rangle = 0$. In the classical limit

$$\langle v(0); v(t) \rangle \to \langle v(0) v(t) \rangle = C_{vv}(t)$$

$C_{vv}(t)$ is the velocity autocorrelation function. Equation (9.109) becomes in this case

$$\dot{C}_{vv}(t) = -\int_0^t \mathrm{d}t' \, \gamma(t') \, C_{vv}(t - t')$$

If the characteristic time scale of $\gamma(t)$ is much shorter than that of $C_{vv}(t)$, we may use a Markovian approximation as in (9.85), and we get an ordinary differential equation

$$\dot{C}_{vv}(t) = -\gamma \, C_{vv}(t) \qquad \text{with} \qquad \gamma = \int_0^\infty \mathrm{d}t \, \gamma(t)$$

whose solution, taking into account the parity property of C, leads to an exponential decrease of the correlation function

$$C_{vv}(t) = \mathrm{e}^{-\gamma |t|} C_{vv}(0) = \mathrm{e}^{-|t|/\tau} \, C_{vv}(0) \tag{9.112}$$

9.3.5 Brownian motion: the $m/M \to 0$ limit

Since the friction force $\vec{\mathcal{F}}$ in (9.111) is due to the collisions with the fluid molecules, it should be related to the stochastic force. In this subsection, we shall derive this relation in the limit $m/M \to 0$.[13] Let us write a classical Hamiltonian for the system composed of the fluid and Brownian particle

$$H = \sum_\alpha \frac{p_\alpha^2}{2m} + \frac{1}{2}\sum_{\alpha\neq\beta} V(\vec{r}_{\alpha\beta}) + \frac{P^2}{2M} + \sum_\alpha U(\vec{R}-\vec{r}_\alpha) \tag{9.113}$$

where p_α and m denote the momenta and mass of the fluid molecules, V their potential energy, P and M the momentum and mass of the B-particle and U its potential energy in the fluid. The Liouvillian $\mathcal{L}$ corresponding to (9.113) may be written as $\mathcal{L} = \mathcal{L}_\mathrm{f} + \delta\mathcal{L}$, where $\mathcal{L}_\mathrm{f}$ is the fluid Liouvillian corresponding to the first two terms in (9.113)

$$\mathrm{i}\mathcal{L}_\mathrm{f} = \sum_\alpha \frac{\vec{p}_\alpha}{m}\cdot\frac{\partial}{\partial\vec{r}_\alpha} - \frac{1}{2}\sum_{\alpha\neq\beta}\vec{\nabla}V(\vec{r}_{\alpha\beta})\cdot\Big(\frac{\partial}{\partial\vec{p}_\alpha} - \frac{\partial}{\partial\vec{p}_\beta}\Big) \tag{9.114}$$

and

$$\mathrm{i}\delta\mathcal{L} = \frac{\vec{P}}{M}\cdot\frac{\partial}{\partial\vec{R}} - \sum_\alpha \vec{\nabla}U(\vec{R}-\vec{r}_\alpha)\cdot\frac{\partial}{\partial\vec{P}} + \sum_\alpha \vec{\nabla}U(\vec{R}-\vec{r}_\alpha)\cdot\frac{\partial}{\partial\vec{p}_\alpha} \tag{9.115}$$

In (9.115), the first term, denoted by $\mathcal{L}_\mathrm{B}$, is the Liouvillian of a free B-particle, the second $\mathcal{L}_{\mathrm{f}\to\mathrm{B}}$ represents the action of the fluid molecules on the B-particle and the third $\mathcal{L}_{\mathrm{B}\to\mathrm{f}}$ the action of the B-particle on the fluid molecules. Our slow variables are the components P_i of the momentum $\vec{P}$; remember that $\dot{P}_i$ is *not* a slow variable, as is clear from Figure 9.3, and does not belong to $\mathcal{E}$. Let $C_{ij}(t)$ be the equilibrium time correlation function of the components of $\vec{P}$

$$C_{ij}(t) = \langle P_i; \mathrm{e}^{\mathrm{i}\mathcal{L}t}P_j\rangle \to \langle P_i(0)P_j(t)\rangle \tag{9.116}$$

From rotational invariance (no summation over i in (9.117) and (9.118))

$$C_{ij}(t) = \delta_{ij}C(t) \qquad C_{ii}(0) = \langle P_i^2\rangle = MkT \tag{9.117}$$

The memory matrix γ_{ij} is also proportional to δ_{ij}: $\gamma_{ij} = \delta_{ij}\gamma(t)$

$$\gamma(t) = \frac{1}{MkT}\,\langle\dot{P}_i; \mathrm{e}^{\mathrm{i}\mathcal{Q}\mathcal{L}\mathcal{Q}t}\dot{P}_i\rangle \tag{9.118}$$

Since $\langle\vec{P}\rangle = 0$, the projector $\mathcal{Q}$ is, from (9.97) and (9.117),

$$Q = \mathcal{I} - \vec{P}\,\frac{1}{MkT}\,\vec{P} \tag{9.119}$$

[13] Our derivation follows closely Foerster [43], Section 6.1.

We now use the property that $p \sim \sqrt{mkT}$ and $P \sim \sqrt{MkT}$ to remark that in (9.114) and (9.115)

$$\frac{P/M}{p/m} \sim \left(\frac{m}{M}\right)^{1/2} \qquad \frac{\partial/\partial P}{\partial/\partial p} \sim \left(\frac{m}{M}\right)^{1/2}$$

so that

$$\frac{\mathcal{L}_{\mathrm{B}} + \mathcal{L}_{\mathrm{f}\to\mathrm{B}}}{\mathcal{L}_{\mathrm{f}} + \mathcal{L}_{\mathrm{B}\to\mathrm{f}}} \sim \left(\frac{m}{M}\right)^{1/2}$$

and $\mathcal{L} \to \mathcal{L}_0 = \mathcal{L}_{\mathrm{f}} + \mathcal{L}_{\mathrm{B}\to\mathrm{f}}$ in the limit $m/M \to 0$. But $\mathcal{L}_0$ does not act on the B-particle: $\mathcal{L}_0 \vec{P} = 0$, so that

$$\lim_{m/M\to 0} \gamma(t) = \gamma_\infty(t) = \frac{1}{MkT} \langle \dot{P}_i ; \mathrm{e}^{\mathrm{i}\mathcal{L}_0 t} \dot{P}_i \rangle$$

Now,

$$\frac{\mathrm{d}}{\mathrm{d}t} \vec{P} = \mathrm{i}\mathcal{L}\vec{P} = -\sum_\alpha \vec{\nabla} U(\vec{R} - \vec{r}_\alpha) = \vec{F}$$

where $\vec{F}$ is the *instantaneous* force that the fluid molecules exert on the B-particle, not to be confused with the friction force $\vec{\mathcal{F}}$ (9.111), which represents a mean effect. Thus we get our final result for the memory function

$$\gamma_\infty(t) = \frac{1}{3MkT} \langle \vec{F}_\infty(t) \cdot \vec{F}_\infty(0) \rangle \tag{9.120}$$

where $\vec{F}_\infty(t)$ is the force on an *infinitely heavy* B-particle, namely a B-particle *at rest* in the fluid, so that we are in an equilibrium situation. This force, which has zero average value, $\langle \vec{F}_\infty \rangle = 0$, varies randomly in time with a characteristic scale τ^*, which justifies the terminology 'stochastic force' in the definition (9.104). In a Markovian approximation, the viscosity parameter $\gamma = \alpha/M$, where α is defined in (9.111), is given by

$$\gamma = \frac{1}{6MkT} \int_{-\infty}^{\infty} \mathrm{d}t \, \langle \vec{F}_\infty(t) \cdot \vec{F}_\infty(0) \rangle \tag{9.121}$$

This is a Green–Kubo formula; another derivation of this result is proposed in Exercise 9.7.2. To summarize, we have derived a stochastic differential equation for the B-particle

$$\frac{\mathrm{d}}{\mathrm{d}t} \vec{P} = -\gamma \vec{P} + \vec{F}_\infty(t) \tag{9.122}$$

where γ is given by (9.121) and $\vec{F}_\infty(t)$ is the stochastic force acting on a B-particle *at rest* in the fluid.

9.4 Langevin equation

Equation (9.122) is the prototype of a stochastic differential equation and is called a Langevin equation. We have just seen that it is able to describe Brownian motion, but its importance lies in the fact that it has many other applications in physics, due to its versatility in the description of noise in general physical systems. One important particular case of the Langevin equation corresponds to the so-called Ornstein–Uhlenbeck process, where, in addition to the stochastic force, the Brownian particle is submitted to an harmonic force in the strong friction limit.

9.4.1 Definitions and first properties

We have derived in the case of Brownian motion a stochastic differential equation (9.122). In order to encompass more general situations, we rewrite it in one dimension as

$$\boxed{\dot{V}(t) = -\gamma V(t) + f(t) \qquad f(t) = \frac{1}{m} F_\infty(t)} \tag{9.123}$$

where, from now on, we denote by m the mass of the B-particle. In (9.123), $V(t)$ is a *random function*, which we write with an upper case letter V in order to make the distinction with the *number* $v(t)$, which is the value of the velocity for a particular realization of $f(t)$. The function $f(t)$ is a random function with zero average value, $\overline{f}(t) = 0$, and with a characteristic time scale τ^* much smaller than the characteristic time scale $\tau = 1/\gamma$ of the velocity: $\tau^* \ll \tau$. In general, $\overline{X}$ denotes an average of the random variable X taken over all the realizations of the random function $f(t)$, while $\langle X \rangle$ denotes as before an equilibrium average. In the case of Brownian motion with a B-particle at equilibrium, $\overline{X} = \langle X \rangle$ and (9.121) becomes in the one-dimensional case

$$\gamma = \frac{m}{2kT} \int_{-\infty}^{\infty} \mathrm{d}t \, \langle f(t) f(0) \rangle \qquad \langle f(t) \rangle = 0 \tag{9.124}$$

In order to write the Langevin equation in a precise form, we must define the time autocorrelation function of $f(t)$ in (9.123). Since $\tau^* \ll \tau$, we shall approximate the time autocorrelation of $f(t)$ by a δ-function

$$\boxed{\overline{f(t) f(t')} = 2A \, \delta(t - t')} \tag{9.125}$$

In the case of Brownian motion, the coefficient A is then given from (9.124) by

$$\boxed{A = \gamma \frac{kT}{m}} \tag{9.126}$$

Since $f(t)$ is the result of a large number of random collisions, it is customary to assume (but we shall not need this assumption), that in addition to $\overline{f}(t) = 0$ and (9.125), $f(t)$ is a Gaussian random function. These assumptions on $f(t)$ specify completely the stochastic differential equation (9.123).

Equation (9.123) may be solved as a function of the initial velocity $v_0 = V$ $(t = 0)$ as

$$V(t) = v_0 \mathrm{e}^{-\gamma t} + \mathrm{e}^{-\gamma t} \int_0^t \mathrm{d}t' \, \mathrm{e}^{\gamma t'} f(t') \tag{9.127}$$

from which we derive, by taking an average over all realizations of $f(t)$,[14]

$$\begin{aligned} \overline{\left(V(t) - v_0 \mathrm{e}^{-\gamma t}\right)^2} &= \mathrm{e}^{-2\gamma t} \int_0^t \mathrm{d}t' \, \mathrm{d}t'' \, \mathrm{e}^{2\gamma(t'+t'')} \overline{f(t') f(t'')} \\ &= 2A \, \mathrm{e}^{-2\gamma t} \int_0^t \mathrm{d}t' \, \mathrm{e}^{2\gamma t'} = \frac{A}{\gamma} \left(1 - \mathrm{e}^{-2\gamma t}\right) \end{aligned} \tag{9.128}$$

If $t \gg 1/\gamma$ we reach an equilibrium situation

$$\left\langle \left(V(t) - v_0 \mathrm{e}^{-\gamma t}\right)^2 \right\rangle \to \langle V^2 \rangle = \frac{A}{\gamma} = \frac{kT}{m}$$

and we recover (9.126). We can also compute the position $X(t)$ of the Brownian particle from

$$X(t) = x_0 + \int_0^t \mathrm{d}t' V(t')$$

An elementary, but somewhat tedious, calculation leads to

$$\overline{(X(t) - x_0)^2} = \left(v_0^2 - \frac{kT}{m}\right) \frac{1}{\gamma^2} \left(1 - \mathrm{e}^{-\gamma t}\right)^2 + \frac{2kT}{m\gamma} \left(t - \frac{1}{\gamma} \left[1 - \mathrm{e}^{-\gamma t}\right]\right)$$

[14] We cannot use an equilibrium average because the B-particle is not at equilibrium if it is launched in the thermal bath with a velocity $v_0 \gg \sqrt{kT/m}$.

For large values of t, $t \gg 1/\gamma$, one recovers a diffusive behaviour (see Exercise 9.7.8 for another derivation of (9.129))

$$\langle (X(t) - x_0)^2 \rangle = 2 \frac{kT}{m\gamma} t = 2D\, t \tag{9.129}$$

The *diffusion coefficient* D is given by Einstein's relation (6.61)

$$\boxed{D = \frac{kT}{m\gamma} = \frac{1}{\beta m \gamma}} \tag{9.130}$$

For $t \ll 1/\gamma$, one observes a ballistic behaviour: $\overline{(X(t) - x_0)^2} = v_0^2 t^2$.

9.4.2 Ornstein–Uhlenbeck process

We are now interested in writing down a Langevin equation for the position $X(t)$ of a Brownian particle submitted to an external (deterministic) force $F(x)$. We assume that we may use a *strong friction limit*,[15] where the Brownian particle takes almost instantaneously its limit velocity v_{L}. Neglecting diffusion for the time being

$$\dot{v} = -\gamma v + \frac{F(x)}{m} \tag{9.131}$$

and the limit velocity is given by $\dot{v} = 0$, or $v_{\mathrm{L}}(x) = F(x)/(m\gamma)$. Then one adds to $\dot{x} = v_{\mathrm{L}}$ a random force $b(t)$

$$\dot{X}(t) = \frac{F(x)}{m\gamma} + b(t) \tag{9.132}$$

In the absence of $F(x)$, one should recover the diffusive behaviour (9.129), and this is satisfied if

$$\overline{b(t)b(t')} = 2D\, \delta(t - t') \tag{9.133}$$

A more rigorous derivation of (9.132) is proposed in Exercise 9.7.9 in the case of the harmonic oscillator, and in Problem 9.8.4, where one first writes an exact system of coupled equations for X and V (Kramer's equation). The strong friction limit is then obtained as a controlled approximation to this equation. The Ornstein–Uhlenbeck (O–U) process is obtained if one chooses $F(x)$ to be a harmonic force,

[15] The strong friction limit was introduced in Section 6.2.2.

$F(x) = -m\,\omega_0^2\,x$

$$\frac{F(x)}{m\gamma} = -\overline{\gamma}\,x \qquad \overline{\gamma} = \frac{\omega_0^2}{\gamma} \tag{9.134}$$

The O–U process is thus defined by the stochastic differential equation

$$\boxed{\dot{X}(t) = -\overline{\gamma}\,X(t) + b(t)} \tag{9.135}$$

where $b(t)$ is a Gaussian random function of zero mean that obeys (9.133). Since the Fourier tranform of $\overline{b(t)b(t')}$ is a constant, $b(t)$ is also called a *Gaussian white noise*.

We now wish to compute the *conditional* probability $P(x, t|x_0, t_0)$ of finding the particle at point x at time t, knowing that it was at point x_0 at time t_0. We shall take for simplicity $t_0 = 0$, and write $P(x, t|x_0, t_0) = P(x, t|x_0)$. From (9.127) we can solve (9.135) for $X(t)$

$$Y = X(t) = x_0 \mathrm{e}^{-\overline{\gamma}t} + \mathrm{e}^{-\overline{\gamma}t} \int_0^t \mathrm{d}t'\, \mathrm{e}^{\overline{\gamma}t'} b(t') \tag{9.136}$$

Equation (9.136) defines a random variable Y. We are going to show that the probability distribution of Y is Gaussian. Let us divide the $[0, t]$ interval in N small intervals of length $\varepsilon = t/N,\ N \gg 1$, with $t_i = i\varepsilon$ and define the random variable B_ε^i by

$$B_\varepsilon^i = \int_{t_i}^{t_i+\varepsilon} \mathrm{d}t'\, b(t')\,\mathrm{d}t' \tag{9.137}$$

B_ε^i is time independent due to time translation invariance. We note that $\overline{B_\varepsilon^i} = 0$ and that from (9.133)

$$\overline{B_\varepsilon^i\, B_\varepsilon^j} = \int \mathrm{d}t'\,\mathrm{d}t''\, \overline{b(t')b(t'')} = 2\varepsilon D\,\delta_{ij} \tag{9.138}$$

The definition (9.137) allows us to write a Riemann approximation to the integral in (9.136)

$$Y \simeq \mathrm{e}^{-\overline{\gamma}\,t} \sum_{i=0}^{N-1} \mathrm{e}^{\overline{\gamma}t_i}\, B_\varepsilon^i$$

which shows that Y is the sum of a large number of independent random variables. From the central limit theorem, the probability distribution of Y is Gaussian with

a variance given by $\overline{Y^2}$

$$\overline{Y^2} = \mathrm{e}^{-2\overline{\gamma}t} \sum_{i,j=0}^{N-1} \mathrm{e}^{\overline{\gamma}t_i}\, \mathrm{e}^{\overline{\gamma}t_j}\, \overline{B_\varepsilon^i B_\varepsilon^j}$$

$$= \varepsilon \mathrm{e}^{-2\overline{\gamma}t} \sum_{i=0}^{N} \mathrm{e}^{2\overline{\gamma}t_i} \;\to\; \mathrm{e}^{-2\overline{\gamma}t} \int_0^t \mathrm{d}t'\, \mathrm{e}^{2\overline{\gamma}t'} = \frac{D}{\gamma}\left(1 - \mathrm{e}^{-2\overline{\gamma}t}\right)$$

This gives the probability distribution of Y, or equivalently of $X(t)$

$$\boxed{P(x,t|x_0) = \left[\frac{\overline{\gamma}}{2\pi D(1-\mathrm{e}^{-2\overline{\gamma}t})}\right]^{1/2} \exp\left[-\frac{\overline{\gamma}(x - x_0\mathrm{e}^{-\overline{\gamma}t})^2}{2D(1-\mathrm{e}^{-2\overline{\gamma}t})}\right]} \tag{9.139}$$

The final result (9.139) has a simple interpretation: as is clear from the previous derivation, it is a Gaussian distribution for the centred variable $y = (x - x_0\mathrm{e}^{\overline{\gamma}t})$ with a variance $\sigma^2(t) = (D/\overline{\gamma})(1 - \exp(-2\overline{\gamma}t))$.

It is instructive to look at the short and long time limits of (9.139). In the long time limit $t \gg 1/\overline{\gamma}$, one reaches an equilibrium situation governed by a Boltzmann distribution

$$P(x,t|x_0) \to \left(\frac{\overline{\gamma}}{2\pi D}\right)^{1/2} \exp\left(-\frac{\overline{\gamma}\,x^2}{2D}\right) = P_{\mathrm{eq}}(x) \propto \exp\left(-\frac{m\,\omega_0^2\,x^2}{2k_{\mathrm{B}}T}\right) \tag{9.140}$$

Equation (9.140) gives another derivation of Einstein's relation (9.130), since it leads to

$$\frac{\overline{\gamma}}{D} = \frac{m\,\omega_0^2}{k_{\mathrm{B}}T} \qquad \text{with} \qquad \overline{\gamma} = \frac{\omega_0^2}{\gamma}$$

The limit $t \ll 1/\overline{\gamma}$

$$P(x,t|x_0) \to \frac{1}{(4\pi Dt)^{1/2}} \exp\left[\frac{(x-x_0)^2}{4Dt}\right] \tag{9.141}$$

shows that *the short time limit is dominated by diffusion*

$$\langle (x - x_0)^2 \rangle \sim 2D\,t$$

As one can write $\langle |X(t+\varepsilon) - x(t)| \rangle \propto \sqrt{t}$, one sees that the trajectory $x(t)$ is a continuous, but non-differentiable function of t (see also Exercise 9.7.12).

Of course (9.139) may also be used to obtain $P(v,t|v_0)$ from (9.132): one has only to make in (9.139) the substitutions $x \to v$, $D \to A$ and $\overline{\gamma} \to \gamma$ to get

$$P(v,t|v_0) = \left[\frac{\gamma}{2\pi A(1-\mathrm{e}^{-2\gamma t})}\right]^{1/2} \exp\left[-\frac{\gamma(v - v_0\mathrm{e}^{-\gamma t})^2}{2A(1-\mathrm{e}^{-2\gamma t})}\right] \tag{9.142}$$

The long time limit of (9.143) gives the Maxwell distribution $\exp[-mv^2/(2k_BT)]$, and comparison of the Maxwell distribution with the long time limit of (9.143) leads once more to (9.126).

9.5 Fokker–Planck equation

The probability distribution (9.141) derived from the Langevin equation obeys a partial differential equation, the Fokker–Planck equation. This equation displays a remarkable analogy with a Schrödinger equation in imaginary time, an analogy that we shall use to study convergence to equilibrium.

9.5.1 Derivation of Fokker–Planck from Langevin equation

We wish to derive a partial differential equation (PDE) for the conditional probability $P(x, t|x_0)$, when $x(t)$ obeys a Langevin equation of the form

$$\dot{X}(t) = a(x) + b(t) \tag{9.143}$$

where we have set $a(x) = F(x)/(m\gamma)$. This PDE is the Fokker–Planck (F–P) equation. Note that (9.143) is a generalization of the O–U equation (9.135), where $a(x) = -\overline{\gamma}\, x$; the random function $b(t)$ has the same properties as in the preceding section, and in particular it obeys (9.133). Equation (9.143) defines a Markovian process, because it is first order in time and because of the delta function in (9.133): if $b(t)$ had a finite (microscopic) autocorrelation time τ^*, or, in other words, if $b(t)$ was not strictly a white noise, then (9.133) would not define a Markovian process. Having a Markovian process allows us to write down a Chapman–Kolmogorov equation for P

$$P(x, t+\varepsilon|x_0) = \int \mathrm{d}y\, P(x, t+\varepsilon|y, t) P(y, t|x_0) \tag{9.144}$$

and integrating (9.143) over an infinitesimal time ε gives the random trajectory $X_y^{[b]}(t+\varepsilon; t)$ for a particular realization of the random force $b(t)$ and of the initial position $X(t) = y$

$$X_y^{[b]}(t+\varepsilon; t) = y + \varepsilon a(y) + \int_t^{t+\varepsilon} \mathrm{d}t'\, b(t') = y + \varepsilon a(y) + B_\varepsilon$$

where we have used the definition (9.137) of B_ε. From this equation follows, to order ε

$$\begin{aligned} P(x, t+\varepsilon|y, t) &= \overline{\delta(x - y - \varepsilon a(y) - B_\varepsilon)} \\ &\simeq (1 - \varepsilon a'(x))\, \overline{\delta(x - y - \varepsilon a(x) - B_\varepsilon)} \end{aligned}$$

Indeed, at order ε, we may write $a(x) = a(y) + \mathcal{O}(\varepsilon)$; we have also used the standard identity

$$\delta(f(y)) = \frac{1}{|f'(y)|}\, \delta(y - y_0) \qquad f(y_0) = 0$$

We expand formally the δ-function in powers of ε,[16] noting that one must expand to order B_ε^2, because B_ε is in fact of order $\sqrt{\varepsilon}$

$$\begin{aligned} &\delta(x - y - \varepsilon a(x) - B_\varepsilon) = \delta(x - y) + [\varepsilon a(x) + B_\varepsilon]\delta'(x - y) \\ &+\frac{1}{2}[\varepsilon a(x) + B_\varepsilon]^2 \delta''(x - y) + \cdots \end{aligned}$$

and plug the result in the Chapman–Kolmogorov equation, keeping only terms of order $\sqrt{\varepsilon}$ and ε. This leads to the integral

$$\begin{aligned} &\int \mathrm{d}y\, P(y, t|x_0) \\ &\times \overline{\big[(1 - \varepsilon a'(x))\delta(y - x) + (\varepsilon a(x) + B_\varepsilon)\delta'(y - x) + (B_\varepsilon^2/2)\delta''(y - x)\big]} \end{aligned}$$

which is evaluated thanks to $\overline{B_\varepsilon} = 0$ and $\overline{B_\varepsilon^2} = 2D\varepsilon$. Performing the now trivial integrations gives to order ε

$$\begin{aligned} P(x, t+\varepsilon|x_0) &= P(x, t|x_0) + \varepsilon \frac{\partial P}{\partial t} \\ &= P(x, t|x_0) + \varepsilon \bigg[-a'(x) P(x, t|x_0) - a(x) \frac{\partial}{\partial x} P(x, t|x_0) \\ &\quad + D \frac{\partial^2}{\partial x^2} P(x, t|x_0) \bigg] + \mathcal{O}(\varepsilon^2) \end{aligned}$$

[16] This is simply a shorthand notation; for example

$$\begin{aligned} \int \mathrm{d}x f(x) \delta(x - (x_0 + \varepsilon)) &= f(x_0 + \varepsilon) = f(x_0) + \varepsilon f'(x_0) \\ \int \mathrm{d}x f(x)[\delta(x - x_0) - \varepsilon \delta'(x - x_0)] &= f(x_0) + \varepsilon f'(x_0) \end{aligned}$$

and we obtain the Fokker–Planck equation

$$\boxed{\frac{\partial}{\partial t}\,P(x,t|x_0) = -\frac{\partial}{\partial x}\Big[a(x)P(x,t|x_0)\Big] + D\frac{\partial^2}{\partial x^2}\,P(x,t|x_0)} \tag{9.145}$$

The clearest physical interpretation of the F–P equation follows from writing it in the form of a continuity equation. Defining the current $j(x,t)$

$$j(x,t) = a(x)P(x,t) - D\frac{\partial P(x,t)}{\partial x} = \frac{F(x)}{m\gamma}\,P(x,t) - D\frac{\partial P(x,t)}{\partial x} \tag{9.146}$$

where we have used the shorthand notation $P(x,t) = P(x,t|x_0)$, (9.145) becomes a continuity equation

$$\frac{\partial P(x,t)}{\partial t} + \frac{\partial j(x,t)}{\partial x} = 0 \tag{9.147}$$

We find the important physical result that the current is the sum of the usual deterministic part $a(x)P = \dot{x}P$ in the absence of diffusion, and of a diffusive part $-D\partial P/\partial x$. Another useful expression of the current is obtained by introducing the potential $V(x)$: $F(x) = -\partial V/\partial x$ and using Einstein's relation (9.130)

$$j(x,t) = -D\Big(\beta P\frac{\partial V}{\partial x} + \frac{\partial P}{\partial x}\Big) \tag{9.148}$$

9.5.2 Equilibrium and convergence to equilibrium

There is a remarkable correspondence between the F–P equation and the Schrödinger equation in imaginary time.[17] Let us write the Schrödinger equation for a particle moving in one dimension in a potential $U(x)$ ($\hbar = 1$)

$$\mathrm{i}\frac{\partial\psi(x,t')}{\partial t'} = -\frac{1}{2m}\frac{\partial^2\psi(x,t')}{\partial x^2} + U(x)\psi(x,t') = H\psi(x,t')$$

and make the change of variables $t' = -\mathrm{i}t$

$$\frac{\partial\psi(x,t)}{\partial t} = \frac{1}{2m}\frac{\partial^2\psi(x,t)}{\partial x^2} - U(x)\psi(x,t) = -H\psi(x,t) \tag{9.149}$$

Taking $U = 0$ in (9.149), one recognizes the diffusion equation (6.21) if one identifies $D = 1/(2m)$. The F–P equation (9.145) is not yet in the form of (9.149), but it will not be difficult to find the transformation that casts (9.145) in the form

[17] In other words, the F–P equation is related to the Schrödinger equation by the Wick rotation already encountered in Chapter 7.

of (9.149). Let us first find the equilibrium distribution; we set $\beta = 1$ in order to simplify the notations and use (9.147) and (9.148)

$$\frac{\partial P}{\partial t} = D\frac{\partial}{\partial x}\Big(P\frac{\partial V}{\partial x} + \frac{\partial P}{\partial x}\Big) = -\frac{\partial j}{\partial x}$$

A sufficient condition for equilibrium is that $j = 0$,[18] leading to the Boltzmannn distribution (with $\beta = 1$)

$$P_{\rm eq}(x) \propto \exp(-V(x))$$

Let us define $\rho(x,t)$ by

$$P(x,t) = \exp\Big(-\frac{1}{2}V(x)\Big)\rho(x,t) \tag{9.150}$$

so that

$$\frac{\partial P}{\partial x} + P\frac{\partial V}{\partial x} = \exp\Big(-\frac{1}{2}V(x)\Big)\left[\frac{\partial \rho}{\partial x} + \frac{1}{2}\rho\,\frac{\partial V}{\partial x}\right]$$

A straightforward calculation shows that the unwanted terms of (9.149) cancel out, leaving us with the desired result

$$\begin{aligned} \frac{\partial \rho(x,t)}{\partial t} &= D\,\frac{\partial^2 \rho(x,t)}{\partial x^2} - U(x)\rho(x,t) = -H\rho(x,t) \\ H &= -D\frac{\partial^2}{\partial x^2} + U(x) \qquad U(x) = \frac{D}{4}\Big(\frac{\partial V}{\partial x}\Big)^2 - \frac{D}{2}\,\frac{\partial^2 V}{\partial x^2} \end{aligned} \tag{9.151}$$

Let us define $\psi_0(x) = \mathcal{N}\exp(-\frac{1}{2}V(x))$, where $\mathcal{N}$ is a normalization constant such that

$$\int \mathrm{d}x\,|\psi_0(x)|^2 = 1$$

The result $P_{\rm eq}(x) \propto \exp(-V(x))$ is equivalent to $H\psi_0 = 0$; indeed

$$\Big[\frac{\partial}{\partial x} + \frac{1}{2}\,\frac{\partial V}{\partial x}\Big]\psi_0(x) = 0$$

which corresponds to $j = 0$. Since $\psi_0(x)$ has no nodes (zeroes), one knows from a standard theorem in quantum mechanics that $\psi_0(x)$ is the ground state wave function, and it has energy $E_0 = 0$. All excited states have energies $E_n > 0$. In order to obtain the time evolution, we expand the initial condition at time $t = 0$ on a complete set of eigenfunctions $\psi_n(x) = \langle x|n\rangle$ of H

$$H\psi_n(x) = E_n\psi_n(x) \tag{9.152}$$

[18] In one dimension $j = \text{const}$ implies $j = 0$, but one may have stationary non-equilibrium currents in higher dimensions.

which can be chosen to be real. Then

$$\rho(x,0|x_0) = \sum_n c_n \psi_n(x)$$
$$c_n = \int \mathrm{d}x\ \psi_n(x)\rho(x,0|x_0) = \psi_n(x_0)\mathrm{e}^{\frac{1}{2}V(x_0)} = \langle n|x_0\rangle \mathrm{e}^{\frac{1}{2}V(x_0)}$$

since $\rho(x,0|x_0) = \exp(\frac{1}{2}V(x_0))\delta(x-x_0)$ and we have intoduced Dirac's bra and ket notation. We get $\rho(x,t|x_0)$ from the time evolution of the ψ_ns: $\psi_n(x,t) = \exp(-E_n t)\psi_n(x)$

$$\begin{aligned}\rho(x,t|x_0) &= \sum_n c_n \mathrm{e}^{-E_n t}\psi_n(x)\\ &= \sum_n \mathrm{e}^{\frac{1}{2}V(x_0)}\langle x|n\rangle \mathrm{e}^{-E_n t}\langle n|x_0\rangle\\ &= \mathrm{e}^{\frac{1}{2}V(x_0)}\langle x|\mathrm{e}^{-tH}|x_0\rangle\end{aligned}$$

Summarizing

$$\boxed{P(x,t|x_0) = \mathrm{e}^{-\frac{1}{2}(V(x)-V(x_0))}\langle x|\mathrm{e}^{-tH}|x_0\rangle} \tag{9.153}$$

For large times

$$\mathrm{e}^{-tH} \simeq |0\rangle\langle 0| + \mathrm{e}^{-E_1 t}|1\rangle\langle 1|$$

so that the approach to equilibrium is controlled by the energy E_1 of the first excited state $\psi_1(x)$: $H\psi_1(x) = E_1\psi_1(x)$.[19] One checks from (9.153) that

$$\lim_{t\to\infty} P(x,t|x_0) = \mathcal{N}^2 \mathrm{e}^{-V(x)}$$

9.5.3 Space-dependent diffusion coefficient

It is possible to generalize the F–P equation (9.145) to a space-dependent diffusion coefficient $D(x)$

$$\boxed{\frac{\partial}{\partial t}P(x,t|x_0) = -\frac{\partial}{\partial x}\Big[a(x)P(x,t|x_0)\Big] + \frac{\partial^2}{\partial x^2}\Big[D(x)P(x,t|x_0)\Big]} \tag{9.154}$$

Note that we have written *a priori* $D(x)$ *inside* the x-derivative. Further comments on this apparently arbitrary choice will be given later on, but for the time being let us use (9.154) as it stands to compute the first and second moments of the trajectory. Let us expand $P(x,t+\varepsilon|x_0,t)$ in powers of ε and use (9.154) to express

[19] The reader will remark the analogy with Equation (7.188) of Problem 7.9.8.

$\partial P/\partial t$

$$P(x, t+\varepsilon|x_0, t) = \delta(x-x_0) + \varepsilon\frac{\partial P}{\partial t} + O(\varepsilon^2)$$
$$= \delta(x-x_0) - \varepsilon\frac{\partial}{\partial x}[a(x)P] + \varepsilon\frac{\partial^2}{\partial x^2}[D(x)P] + \mathcal{O}(\varepsilon^2)$$

The first moment is

$$\lim_{\varepsilon\to 0}\frac{1}{\varepsilon}\overline{X(t+\varepsilon)-x_0} = \int \mathrm{d}x\,(x-x_0)\Big[-\frac{\partial}{\partial x}[(a(x)P] + \frac{\partial^2}{\partial x^2}[D(x)P)]\Big] \tag{9.155}$$

where we have used $(x-x_0)\,\delta(x-x_0) = 0$. We integrate (9.155) by parts and use $\lim_{|x|\to\infty} P(x, t|x_0) = 0$, so that only the first term in the square bracket of (9.155) contributes and

$$\boxed{\lim_{\varepsilon\to 0}\frac{1}{\varepsilon}\overline{X(t+\varepsilon)-x_0} = a(x_0)} \tag{9.156}$$

The second moment $(1/\varepsilon)\overline{(X(t+\varepsilon)-x_0)^2}$ is also given by an integration by parts, but it is now the second term in the square bracket of (9.155) that contributes

$$\boxed{\lim_{\varepsilon\to 0}\frac{1}{\varepsilon}\overline{(X(t+\varepsilon)-x_0)^2} = 2D(x_0)} \tag{9.157}$$

Thus, given the first two moments of the trajectory (9.156) and (9.157), one can write the corresponding F–P equation (9.154). These results are easily generalized to multivariate F–P equations (Exercise 9.7.11).

From these results, one would be tempted to conclude that $X(t)$ obeys a Langevin equation

$$\dot{X}(t) = a(x) + \sqrt{D(x)}\,b(t) \qquad \overline{b(t)b(t')} = 2\delta(t-t') \tag{9.158}$$

However, because of the delta function in (9.158), the function $b(t)$ is singular, and the product $\sqrt{D(x)}\,b(t)$ is not defined: this leads to the famous Itô vs. Stratonovitch dilemma (see Problem 9.8.4 for more details). Let us define $C(x) = \sqrt{D(x)}$ and try to integrate Equation (9.158) over a small time interval ε

$$X(t+\varepsilon) - x(t) = \varepsilon a(x(t)) + \int_t^{t+\varepsilon} \mathrm{d}t'\, C(x(t'))b(t')$$

There are many possible prescriptions for handling the product $C(x(t'))b(t')$, and each of them leads to a different F–P equation. One can show that giving a finite width τ^* to the time autocorrelation function of $b(t)$ leads to the Stratonovitch

prescription

$$\int_t^{t+\varepsilon} \mathrm{d}t'\, C(x(t'))b(t') \to C\Big[\frac{x(t)+x(t+\varepsilon)}{2}\Big] \int_t^{t+\varepsilon} \mathrm{d}t'\, b(t')$$

and a corresponding F–P equation

$$\frac{\partial}{\partial t} P(x,t|x_0) = -\frac{\partial}{\partial x}\Big[a(x)P(x,t|x_0)\Big] + \frac{\partial}{\partial x}\Big[C(x)\,\frac{\partial}{\partial x}\,C(x)P(x,t|x_0)\Big] \tag{9.159}$$

while the Itô prescription

$$\int_t^{t+\varepsilon} \mathrm{d}t'\, C(x(t'))b(t') \to C(x(t)) \int_t^{t+\varepsilon} \mathrm{d}t'\, b(t')$$

leads to the F–P equation (9.154). Other prescriptions and the corresponding F–P equations are examined in Problem 9.8.4. One may always write the F–P equation in the form (9.154); however, the various prescriptions correspond to modifying the drift velocity $a(x)$.

9.6 Numerical integration

In this section it will be convenient to work in a system of units with $D = m\gamma = 1$ (and $kT = 1$ from Equation (9.130)). Then as we saw in Section 9.5, the Langevin equation

$$\dot{X}(t) = a(x) + b(t) \tag{9.160}$$

where $a(x) = -\partial V(x)/\partial x$ and $\overline{b(t)b(t')} = 2\delta(t-t')$, admits a stationary solution of the form

$$P(x,t|x_0) \propto \mathrm{e}^{-V(x)} \tag{9.161}$$

In other words, for $t \to \infty$, the configurations are given by the time-independent probability distribution (9.161). It was also shown in the previous section that the approach to this stationary solution is controlled by the spectrum of the Fokker–Planck Hamiltonian, which is not known in general.

It is therefore evident that numerical solutions of the Langevin equation are important in the non-equilibrium case where transient effects are dominant. However, it should be evident from the discussions of Chapter 7 and Equation (9.161) that the Langevin equation can also be used as a tool to perform numerical simulations at equilibrium. In Chapter 7 we discussed how to construct dynamics (for example

Metropolis, Glauber or Wolff) which, in the long time limit, generate configurations with the correct Boltzmann distribution, $P_{\mathrm{B}} = \exp(-\beta E)$. Equations (9.160) and (9.161) give another way with $V = \beta E$. Therefore, the numerical methods that we now discuss may be applied both to equilibrium and non-equilibrium situations. We stress, however, that in the equilibrium case, the Langevin dynamics may or may not describe the actual approach to the stationary state: one may use the Langevin equation even if it does not describe the true dynamics of the system if the interest is only in the equilibrium properties.

In the case of a deterministic differential equation,

$$\frac{\mathrm{d}x(t)}{\mathrm{d}t} = -\frac{\partial V(x)}{\partial x} \tag{9.162}$$

one may use the simplest (Euler) discretization of the time derivative,

$$x(t+\varepsilon) \approx x(t) - \varepsilon \frac{\partial V(x)}{\partial x} + \mathcal{O}(\varepsilon^2) \tag{9.163}$$

The error committed in this case is of the order of ε^2. We shall now apply the same approximation to the Langevin equation (9.160)[20]

$$x(t+\varepsilon) \approx x(t) - \varepsilon \frac{\partial V(x)}{\partial x} + \varepsilon b(t) \tag{9.164}$$

However, care must be taken with the stochastic noise $b(t)$ since t is now discrete and we can no longer have $\overline{b(t)b(t')} = 2\delta(t-t')$. Recalling that the dimension of $\delta(t-t')$ is t^{-1}, we see that the discrete time form of the delta function becomes

$$\overline{b(t)b(t')} = 2\frac{\delta_{tt'}}{\varepsilon} \tag{9.165}$$

We may then rescale the noise, $b(t) \to b(t)\sqrt{2/\varepsilon}$, leading to the discrete time Langevin equation

$$x(t+\varepsilon) \approx x(t) - \varepsilon \frac{\partial V(x)}{\partial x} + \sqrt{2\varepsilon} b(t) \tag{9.166}$$

where we now have

$$\overline{b(t)b(t')} = \delta_{tt'} \tag{9.167}$$

Since the noise term in Equation (9.166) is of the order of $\sqrt{\varepsilon}$, the numerical error due to this discretization is $\mathcal{O}(\varepsilon)$ and not $\mathcal{O}(\varepsilon^2)$ as for the deterministic equation. This may also be seen clearly from the derivation of the Fokker–Planck equation where the same discretization was used for the Langevin equation and where we neglected terms of order ε in the final result.

[20] For the numerical integration of the Langevin equation we make no distinction between $X(t)$ and $x(t)$ and write all variables with lower case.

In the general case, where we may have, say, N variables (for example N B-particles) the Langevin equations are given by

$$x_i(t+\varepsilon) \approx x_i(t) - \varepsilon \frac{\partial V(\{x\})}{\partial x_i} + \sqrt{2\varepsilon} b_i(t) \tag{9.168}$$

with

$$\overline{b_i(t) b_j(t')} = \delta_{tt'} \delta_{ij} \tag{9.169}$$

The numerical integration is now simple to implement: choose an initial configuration, $\{x_i(t_0)\}$, at $t = t_0$, calculate the deterministic force $-\partial V(\{x\})/\partial x_i$, generate N random numbers, $b_i(t_0)$, and use Equation (9.168) to obtain $x_i(t_0 + \varepsilon)$ and repeat for as many time steps as is desired.

It is clear that random numbers $b_i(t)$ satisfying (9.169) may be easily generated using a Gaussian random number generator. However, while this is sufficient, it is not necessary: all one needs for (9.168) is a random number such that $\overline{b_i(t)} = 0$ and whose second moment is given by (9.169) with no conditions given for higher moments. For example, random numbers drawn from a uniform distribution between $-\sqrt{3}$ and $+\sqrt{3}$ satisfy these conditions and are much faster to generate than Gaussian ones.

To obtain higher precision with this algorithm, it is necessary to take smaller time steps. But, in order to keep the same physical time, the number of steps must be increased correspondingly, which might be costly in computer time.

It is therefore desirable to have a higher order algorithm that yields smaller errors for the same time step. A very simple such algorithm is the second order Runge–Kutta discretization. As for deterministic equations, first do a tentative update of the variables using a simple Euler step,

$$x_i'(t+\varepsilon) = x_i(t) - \varepsilon \frac{\partial V(\{x\})}{\partial x_i} + \sqrt{2\varepsilon} b_i(t) \tag{9.170}$$

and then use this $x_i'(t+\varepsilon)$ with $x_i(t)$ to get the final evolution of one time step,

$$x_i(t+\varepsilon) = x_i(t) - \frac{\varepsilon}{2} \left(\frac{\partial V(\{x\})}{\partial x_i}\Big|_{\{x_i(t)\}} + \frac{\partial V(\{x\})}{\partial x_i}\Big|_{\{x_i'(t+\varepsilon)\}} \right) + \sqrt{2\varepsilon} b_i(t) \tag{9.171}$$

For example, taking the simple case of $V(x) = x^2/2$, the tentative update (9.170) becomes

$$x'(t+\varepsilon) = x(t) - \varepsilon x(t) + \sqrt{2\varepsilon} b(t) \tag{9.172}$$

and the final update (9.171) is obtained from

$$\begin{aligned} x(t+\varepsilon) &= x(t) - \frac{\varepsilon}{2}\left(\frac{\partial V(\{x\})}{\partial x}\Big|_{\{x(t)\}} + \frac{\partial V(\{x\})}{\partial x}\Big|_{\{x'(t+\varepsilon)\}}\right) + \sqrt{2\varepsilon}b(t) \\ &= x(t) - \frac{\varepsilon}{2}\left(x(t) + x'(t+\varepsilon)\right) + \sqrt{2\varepsilon}b(t) \\ &= x(t) - \varepsilon\left(1 - \frac{\varepsilon}{2}\right)x(t) + \sqrt{2\varepsilon}\left(1 - \frac{\varepsilon}{2}\right)b(t) \end{aligned} \tag{9.173}$$

Although the Runge–Kutta algorithm is rather simple in general for these stochastic equations, the above particularly simple form is a special case for the quadratic case.

Three very important remarks are in order. First, it is crucial to emphasize that the *same* random number $b_i(t)$ is used in both (9.170) and (9.171): *we do not generate a number for step (9.170) and another for (9.171)*. This condition is required to ensure that the error is $\mathcal{O}(\varepsilon^2)$ and has the additional advantage that it reduces the amount of work. The second remark is that it is no longer sufficient to use a random number uniformly distributed between $-\sqrt{3}$ and $+\sqrt{3}$: in the proof that the error in this algorithm is $\mathcal{O}(\varepsilon^2)$, the fourth moment of the random number is needed. The easiest way to satisfy all the conditions in this case is to use a Gaussian random number generator. The third remark is to note that this algorithm is in fact *not* equivalent to two successive Euler steps, which would still lead to an order $\mathcal{O}(\varepsilon)$ algorithm. The error of the second order Runge–Kutta algorithm just presented is $\mathcal{O}(\varepsilon^2)$. This may be shown with a tedious calculation that follows steps leading to Equation (9.145) but using (9.170) and (9.171) for the discretized Langevin equation [12, 52]. The behaviour of the errors will be studied numerically in the exercises. Higher order Runge–Kutta discretizations are also available but become very complicated.

One final comment concerns the stability of the integration. Consider the one-variable Langevin equation in the Euler discretization (9.164) with $V(x) = ax^2/2$ and with a a constant.[21] Iterating this equation a few times one observes the appearance of a term of the form $(1 - \varepsilon a)^n$ where n is the number of iterations. Clearly, for the iterations to converge, the condition $\varepsilon a < 1$ must be satisfied. In the more general case where $V(\{x_i\}) = x_i M_{ij} x_j/2$ (i and j are summed), the stability condition becomes $\varepsilon\lambda_{\max} < 1$ where $\lambda_{\max}$ is the largest eigenvalue of the matrix M. We therefore arrive at the very important result that the time step is set by the largest eigenvalue, i.e. by the fastest mode. On the other hand, we saw at the end of Section 9.5.2 that the relaxation time is controlled by the lowest excited state, in other words the *smallest* eigenvalue, $\lambda_{\min}$. So the relaxation time

[21] While we present the argument based on the Euler discretization, the conclusions are in fact general and apply for the Runge–Kutta case too.

is $\tau \sim \lambda_{\min}^{-1}$ while the time step is $\varepsilon \sim \lambda_{\max}^{-1}$. Therefore the number of iterations required to decorrelate the configurations is

$$n_{\text{corr}} \sim \lambda_{\max}/\lambda_{\min} \tag{9.174}$$

For this reason, n_{corr} can be very large indeed. When $\lambda_{\max}/\lambda_{\min} \gg 1$, the matrix M is said to be ill-conditioned. This is another example of critical slowing down which was discussed in Chapter 7.

If one is interested only in the stationary solution of the Langevin equation and not in how that solution is approached, one may modify the dynamics to *precondition M* and greatly accelerate the convergence. This topic is beyond our scope; see Reference [12].

9.7 Exercises

9.7.1 Linear response: forced harmonic oscillator

1. Let us consider a forced one-dimensional harmonic oscillator with mass m and damping constant γ

$$\ddot{x} + \gamma \dot{x} + \omega_0^2 x = \frac{f(t)}{m}$$

and define its dynamical susceptibility $\chi(t)$ by

$$x(t) = \int \mathrm{d}t' \, \chi(t - t') f(t')$$

Show that the Fourier transform of $\chi(t)$ is

$$\chi(\omega) = \frac{1}{m[-\omega^2 - \mathrm{i}\omega\gamma + \omega_0^2]}$$

Write the explicit expression of $\chi''(\omega)$. Find the location of the poles $\omega_\pm$ of $\chi(\omega)$ in the complex ω-plane and show that one must distinguish between the cases $\gamma < 2\omega_0$ and $\gamma > 2\omega_0$; $\gamma = 2\omega_0$ is the *critical damping*. When $\gamma \geq 2\omega_0$, one says that *the oscillator is overdamped*.

2. Find the static susceptibility χ

$$\chi = \lim_{\omega \to 0} \chi(\omega) = \frac{1}{m\omega_0^2}$$

and show that in the overdamped case one may write

$$\chi(\omega) = \frac{1}{m} \frac{1}{\omega_0^2 - \mathrm{i}\omega\gamma} = \frac{\chi}{1 - \mathrm{i}\omega\tau} \qquad \tau = \frac{\gamma}{\omega_0^2} \tag{9.175}$$

Write $\chi''(\omega)$ explicitly. Note that working in the strong friction limit amounts to neglecting inertia.

3. Starting from the work per unit of time done by the external force on the oscillator

$$\frac{\mathrm{d}W}{\mathrm{d}t} = f(t)\dot{x}(t)$$

and taking a periodic $f(t)$

$$f(t) = \mathrm{Re}\Big(f_\omega\,\mathrm{e}^{-\mathrm{i}\omega t}\Big) = \frac{1}{2}\Big(f_\omega\,\mathrm{e}^{-\mathrm{i}\omega t} + f_\omega^*\,\mathrm{e}^{\mathrm{i}\omega t}\Big)$$

show that the time average of $\mathrm{d}W/\mathrm{d}t$ over a time interval $T \gg \omega^{-1}$ is

$$\left\langle\frac{\mathrm{d}W}{\mathrm{d}t}\right\rangle_T = \frac{1}{2}\,\omega|f_\omega|^2\int_0^\infty \mathrm{d}t\;\chi(t)\sin\omega t$$

Observing that $\chi(t) = 2\mathrm{i}\,\theta(t)\,\chi''(t)$ and that $\chi''(t) = -\chi''(-t)$, deduce from this equation

$$\left\langle\frac{\mathrm{d}W}{\mathrm{d}t}\right\rangle_T = \frac{1}{2}\,\omega|f_\omega|^2\,\chi''(\omega) \tag{9.176}$$

9.7.2 Force on a Brownian particle

Let us consider a Brownian particle with mass M in a fluid. We call m the mass of the fluid molecules, $m \ll M$ and $\vec{v}$ the velocity of the Brownian particle with respect to the fluid. In the Galilean frame where the Brownian particle is at rest, the Hamiltonian reads

$$H_1 = \sum_{i=1}^{N}\frac{1}{2}m(\vec{v}_i - \vec{v})^2 + \text{potential energy}$$

where $\vec{v}_i$ is the velocity of molecule i. Define the dynamical variable $\vec{\mathcal{A}}$ by

$$\vec{\mathcal{A}} = m\sum_{i=1}^{N}\vec{v}_i$$

In the linear approximation, the perturbation is $\mathcal{V} = -\vec{\mathcal{A}}\cdot\vec{v}$. Use linear response theory to compute $\mathrm{d}\delta\vec{\mathcal{A}}/\mathrm{d}t$, and show that the viscosity coefficient α is given by

$$\alpha = \frac{1}{3kT}\int_0^\infty \mathrm{d}t\;\langle\vec{F}(t)\cdot\vec{F}(0)\rangle$$

where $\vec{F}$ is the force on the particle assumed to be *at rest* in the fluid.

9.7.3 Green–Kubo formula

Starting from

$$D\chi = \lim_{\omega\to 0}\lim_{k\to 0}\frac{\omega}{k^2}\chi''(k,\omega)$$

show that the diffusion coefficient is given by the Green–Kubo formula

$$D\chi = \frac{\beta}{3}\int_0^\infty \mathrm{d}t \int \mathrm{d}^3 r\, \langle \vec{j}(t,\vec{r})\cdot\vec{j}(0,\vec{0})\rangle$$

Hints

(*i*) Using rotational invariance, show that ($l, m = x, y, z$)

$$\int \mathrm{d}^3 r\, \mathrm{e}^{-i\vec{k}\cdot\vec{r}}\langle\vec{\nabla}\cdot\vec{j}(t,\vec{r})\,\vec{\nabla}\cdot\vec{j}(0,\vec{0})\rangle = \sum_{l,m} k_l k_m\Big(H(t,k^2)\delta_{lm} + K(t,k^2)k_l k_m\Big)$$

(*ii*) Study the limit

$$\lim_{\omega\to 0}\lim_{k\to 0}\frac{1}{3}\int_{-\infty}^{\infty}\mathrm{d}t\,\mathrm{e}^{\mathrm{i}\omega t}\int \mathrm{d}^3 r\,\mathrm{e}^{-i\vec{k}\cdot\vec{r}}\langle\vec{j}(t,\vec{r})\cdot\vec{j}(0,\vec{0})\rangle$$

9.7.4 Mori's scalar product

1. One defines for two operators A and B and a density operator D the scalar product

$$\langle \mathsf{B};\mathsf{A}\rangle_D = \int_0^1 \mathrm{d}x\,\mathrm{Tr}\left[\mathsf{B}\,D^x\,\mathsf{A}^\dagger\,D^{1-x}\right]$$

Show that $\langle \mathsf{B};\mathsf{A}\rangle_D$ defines a Hermitian scalar product: it is linear in B, antilinear in A and it obeys

$$\langle \mathsf{A};\mathsf{B}\rangle_D = \langle \mathsf{B};\mathsf{A}\rangle_D^*$$

Hint: $[\mathrm{Tr}(ABC)]^* = \mathrm{Tr}(C^\dagger B^\dagger A^\dagger)$. Furthermore, show that $\langle \mathsf{A};\mathsf{A}\rangle_D \geq 0$ and that $\langle \mathsf{A};\mathsf{A}\rangle_D = 0$ implies that $\mathsf{A} = 0$. These last two results show that Mori's scalar product is positive definite.

2. Show that $\mathcal{L}$ is Hermitian with respect to Mori's scalar product

$$\langle \mathsf{A};\, \mathcal{L}\mathsf{B}\rangle = \langle \mathcal{L}\mathsf{A};\, \mathsf{B}\rangle$$

Hint: First derive

$$\langle \mathsf{A};\, \mathcal{L}\mathsf{B}\rangle = \frac{1}{\beta}\,\langle [\mathsf{A},\, \mathsf{B}]\rangle \tag{9.177}$$

3. Show that

$$\langle \mathsf{A}_i;\, \dot{\mathsf{A}}_j\rangle = -\varepsilon_i \varepsilon_j \langle \mathsf{A}_i;\, \dot{\mathsf{A}}_j\rangle \tag{9.178}$$

where ε_i (ε_j) is the parity of A_i (A_j) under time reversal.

9.7.5 Symmetry properties of χ''_{ij}

1. Show the following properties for Hermitian A_is:

(*i*) from time translation invariance

$$\chi''_{ij}(t) = -\chi''_{ji}(-t) \quad \text{or} \quad \chi''_{ij}(\omega) = -\chi''_{ji}(-\omega)$$

(*ii*) from the Hermiticity of the A_is

$$\chi''^{*}_{ij}(t) = -\chi''_{ij}(t) \quad \text{or} \quad \chi''^{*}_{ij}(\omega) = -\chi''_{ij}(-\omega)$$

(*iii*) from time reversal invariance

$$\chi''_{ij}(t) = -\varepsilon_i \varepsilon_j \chi''_{ij}(-t) \quad \text{or} \quad \chi''_{ij}(\omega) = -\varepsilon_i \varepsilon_j \chi''_{ij}(-\omega)$$

where ε_i (ε_j) is the parity of A_i (A_j) under time reversal. Combine (*i*) and (*ii*) to show that $(\chi''_{ij}(\omega))^* = \chi''_{ji}(\omega)$. Hint for (*iii*): If H is invariant under time reversal, $\Theta H \Theta^{-1} = H$, show that for two operators A_i and A_j

$$\langle \mathsf{A}_i(t)\, \mathsf{A}_j(0)\rangle = \varepsilon_i \varepsilon_j \langle \mathsf{A}_j^{\dagger}(0)\, \mathsf{A}_i^{\dagger}(-t)\rangle$$

by noticing that $|\tilde{n}\rangle = \Theta|n\rangle$ is an eigenvector of H

$$H|\tilde{n}\rangle = E_n|\tilde{n}\rangle$$

if $H|n\rangle = E_n|n\rangle$.

2. In the case of two operators A and B, not necessarily Hermitian, one defines

$$\chi''_{AB}(t) = \frac{1}{2}\,\langle [\mathsf{A}(t),\, B^{\dagger}(0)]\rangle \tag{9.179}$$

Show the following properties:

(*i*) from time translation invariance

$$\chi''^{*}_{AB}(t) = -\chi''_{B^\dagger A^\dagger}(-t)$$

(*ii*) from Hermitian conjugation

$$\chi''_{AB}(t) = -\chi''_{A^\dagger B^\dagger}(t)$$

(*iii*) from time reversal invariance

$$\chi''_{AB}(t) = -\varepsilon_A \varepsilon_B \chi''_{A^\dagger B^\dagger}(-t) = \varepsilon_A \varepsilon_B \chi''_{B^\dagger A^\dagger}(t)$$

9.7.6 Dissipation

Give the detailed proof of

$$\left\langle \frac{\mathrm{d}W}{\mathrm{d}t} \right\rangle_T = \frac{1}{2} \sum_{i,j} f_i^{\omega *} \omega \chi''_{ij}(\omega) f_j^{\omega}$$

Hint: Use (9.13) in the form

$$\overline{\delta \mathsf{A}_i}(t) = \int \mathrm{d}t' \, \chi_{ij}(t') f_j(t - t')$$

and integrate over t in the range $[0, T]$, $T \gg \omega^{-1}$. It is useful to remark that $\chi''_{ij}(t) = -\chi''_{ji}(-t)$. Furthermore, show that $\omega \chi''_{ij}(\omega)$ is a positive matrix. Hint: Study

$$\sum_{i,j} \int_0^T \mathrm{d}t \, \mathrm{d}t' a_i \mathrm{e}^{\mathrm{i}\omega t} a_j^* \mathrm{e}^{-\mathrm{i}\omega t'} \langle \mathsf{A}_i(t) \mathsf{A}_j(t') \rangle$$

9.7.7 Proof of the f-sum rule in quantum mechanics

The particle density operator n is defined as

$$\mathsf{n}(\vec{r}) = \sum_{\alpha=1}^{N} \delta(\vec{r} - \vec{\mathsf{r}}^{\alpha})$$

for a system of N particles of mass m, while the current density operator is ($i = x, y, z$)

$$\mathsf{j}_i(\vec{r}) = \sum_{\alpha=1}^{N} \frac{\mathsf{p}_i^{\alpha}}{m} \delta(\vec{r} - \vec{\mathsf{r}}^{\alpha})$$

More precisely, one should use a symmetrized version of the right hand side in the above definition; $\vec{\mathsf{r}}^{\alpha}$ and $\vec{\mathsf{p}}^{\alpha}$ are the position and momentum of particle α, which

obey the commutation relations ($\hbar = 1$)

$$[\mathsf{x}_i^\alpha, \mathsf{p}_j^\beta] = \mathrm{i}\delta_{ij}\delta_{\alpha\beta} I$$

1. Show that the sum rule (9.79) may be written

$$\int \frac{\mathrm{d}\omega}{\pi}\, \omega \chi''_{nn}(\vec{r}, \vec{r}\,'; \omega) = -\mathrm{i}\nabla_x \cdot \left\langle [\vec{\mathsf{j}}(\vec{r}), \mathsf{n}(\vec{r}\,')] \right\rangle$$

2. Take the Fourier transform of both sides and remark, for example in the case of the density, that

$$\mathsf{n}(\vec{q}) = \sum_{\alpha=1}^{N} \exp(\mathrm{i}\vec{q} \cdot \vec{\mathsf{r}}^{\,\alpha})$$

3. Compute the commutator. For a single variable

$$[\mathsf{p}, \exp(\mathrm{i}q\mathsf{x})] = -\mathrm{i}\frac{\partial}{\partial x} \exp(\mathrm{i}q\mathsf{x}) = q \exp(\mathrm{i}q\mathsf{x})$$

9.7.8 Diffusion of a Brownian particle

1. Let $I(T)$ be the integral

$$I(T) = \int_{-T/2}^{T/2} \mathrm{d}t_1 \int_{-T/2}^{T/2} \mathrm{d}t_2\, g(t)$$

where the function $g(t)$ depends only on the difference $t = t_1 - t_2$. Show that

$$I(T) = T \int_{-T}^{+T} \mathrm{d}t\, g(t) \left(1 - \frac{|t|}{T}\right) \tag{9.180}$$

The second term may be neglected if the function $g(t)$ decreases rapidly on a time scale $\tau \ll T$. Application:

$$\int_{-T/2}^{T/2} \mathrm{d}t_1 \int_{-T/2}^{T/2} \mathrm{d}t_2\, \mathrm{e}^{-|t|/\tau} = 2T \left[\tau \left(1 - \frac{\tau}{T}\right) + \frac{\tau^2}{T}\mathrm{e}^{-T/\tau}\right] \tag{9.181}$$

2. Starting from the *equilibrium* velocity autocorrelation function (9.112) $C_{vv}^{\mathrm{eq}}(t)$, compute

$$\langle (\Delta X(t))^2 \rangle = \langle (X(t) - x(0))^2 \rangle$$

and show that one obtains a diffusive behaviour

$$\langle (\Delta X(t))^2 \rangle = 2Dt$$

when $t \gg 1/\gamma$.

9.7.9 Strong friction limit: harmonic oscillator

We consider again the forced harmonic oscillator of Exercise 9.7.1, assuming that the external force $F(t)$ is a stationary random force

$$\ddot{X} + \gamma \dot{X} + \omega_0^2 X = \frac{F(t)}{m}$$

Let $C_{xx}(t)$ denote the position autocorrelation function

$$C_{xx}(t) = \overline{X(t'+t)X(t')}$$

and $C_{pp}(t)$ the momentum autocorrelation function

$$C_{pp}(t) = \overline{P(t'+t)P(t')}$$

τ_x and τ_p are the characteristic times of $C_{xx}(t)$ and $C_{pp}(t)$.

1. Using the Wiener–Kinchin theorem (9.189), compute the Fourier transform $C_{xx}(\omega)$ as a function of the autocorrelation of the force $C_{FF}(\omega)$. If $C_{FF}(t)$ is given by (9.125)

$$C_{FF}(t) = \overline{F(t'+t)F(t')} = 2A\delta(t)$$

show that

$$C_{xx}(\omega) = \frac{1}{m^2} \frac{2A}{(\omega^2 - \omega_0^2)^2 + \gamma^2 \omega^2} \tag{9.182}$$

2. The strong friction limit corresponds to $\gamma \gg \omega_0$. Draw qualitatively $C_{xx}(\omega)$ in this limit, show that the width of the curve is $\simeq \omega_0^2/\gamma$ and estimate τ_x.

3. What is the relation between $C_{xx}(\omega)$ and $C_{pp}(\omega)$? Draw qualitatively $C_{pp}(\omega)$ in the strong friction limit and determine its width. Deduce from this width that $\tau_p \simeq 1/\gamma$ and that $\tau_x \gg \tau_p$. Discuss the physical significance of this result.

4. Show that taking the strong friction limit amounts to neglecting the inertial term $\ddot{X}$ in the equation of motion and recover the Ornstein–Uhlenbeck equation for $\dot{X}$ as well as τ_x.

9.7.10 Green's function method

Let $G(t)$ be the retarded Green's function of the damped harmonic oscillator ($G(t) = 0$ if $t < 0$)

$$\Big(\frac{\mathrm{d}^2}{\mathrm{d}t^2} + \gamma\frac{\mathrm{d}}{\mathrm{d}t} + \omega_0^2\Big)G(t) = \delta(t)$$

If $\gamma < 2\omega_0$, show that

$$G(t) = \frac{\theta(t)}{\omega_1}\mathrm{e}^{-\gamma t/2}\sin\omega_1 t \qquad \omega_1 = \frac{1}{2}(4\omega_0^2 - \gamma^2)^{1/2}$$

where $\theta(t)$ is the step function. We want to solve the following stochastic differential equation for the random function $X(t)$, with initial conditions $x(0)$ and $\dot{x}(0)$

$$\Big(\frac{\mathrm{d}^2}{\mathrm{d}t^2} + \gamma\frac{\mathrm{d}}{\mathrm{d}t} + \omega_0^2\Big)X(t) = b(t)$$

where $b(t)$ is a stochastic force

$$\overline{b(t)b(t')} = \frac{2A}{m^2}\,\delta(t - t')$$

Show that

$$X(t) - x_0(t) = Y(t) = \int_0^t \mathrm{d}t'\, G(t - t')b(t')$$

where $x_0(t)$ is the solution of the homogeneous equation with initial conditions $x(0)$ and $\dot{x}(0)$. What is the characteristic damping time of $x_0(t)$? Compute $\langle Y(t)Y(t+\tau)\rangle$ for $t \gg 1/\gamma$

$$\overline{Y(t)Y(t+\tau)} \simeq \frac{A\mathrm{e}^{-\gamma\tau/2}}{\gamma\omega_0^2}\Big[\cos\omega_1 t + \frac{\gamma}{2\omega_1}\sin\omega_1 t\Big]$$

9.7.11 Moments of the Fokker–Planck equation

Let $P(x,t)$, $x = (x_1, \ldots, x_N)$ be a multivariate probability distribution that obeys the Fokker–Planck equation

$$\frac{\partial P}{\partial t} = -\sum_{i=1}^{N}\frac{\partial}{\partial x_i}\Big[A_i(x)P\Big] + \sum_{i,j=1}^{N}\frac{\partial^2}{\partial x_i\partial x_j}\Big[D_{ij}(x)P\Big] \tag{9.183}$$

Define $\Delta X_i = X_i(t+\varepsilon) - x_i(t)$. Show that

$$\begin{aligned} \lim_{\varepsilon\to 0} \frac{1}{\varepsilon} \overline{\Delta X_i} &= A_i(x) \\ \lim_{\varepsilon\to 0} \frac{1}{\varepsilon} \overline{\Delta X_i \Delta X_j} &= 2D_{ij}(x) \end{aligned} \tag{9.184}$$

Hint: Integrate by parts. What is the corresponding Langevin equation if D_{ij} is x-independent?

9.7.12 Backward velocity

Let v^+ be the forward velocity

$$v^+ = \lim_{\varepsilon\to 0} \frac{1}{\varepsilon} \overline{X(t+\varepsilon) - x} = a(x)$$

for the Langevin equation

$$\frac{\mathrm{d}X}{\mathrm{d}t} = a(x) + b(t) \qquad \overline{b(t)b(t')} = 2D\delta(t-t')$$

Assume that one *knows* that the particle is at x at time t. One now wishes to determine the backward velocity

$$v^- = \lim_{\varepsilon\to 0} \frac{1}{\varepsilon} \overline{x - X(t-\varepsilon)}$$

Show that

$$v^- = v^+ - 2D \frac{\partial \ln P(x,t|x_0)}{\partial x}$$

Hint: Use $P(x,t|y,t-\varepsilon)$. This result shows clearly that the trajectory is not differentiable.

9.7.13 Numerical integration of the Langevin equation

In this exercise we shall test the Euler and Runge–Kutta integration schemes discussed in Section 9.6.

1. Write a program to implement the Euler approximation (9.166) with $V(x) = x^2/2$. Run your program doing of the order of 10^4 thermalization iterations and then about 10^6 measurement iterations. Measure $\langle x^2 \rangle$ as a function of the discrete time step ε for $0.1 \le \varepsilon \le 0.5$. Compare with the exact result, which you can calculate easily. Time your program and verify that, for the same precision and the same *physical time* $t = n\varepsilon$ where n is the number of iterations, the Runge–Kutta method is much more efficient than Euler's.

Do the same for $V(x) = x^4/4$. In this case, the exact result is unavailable but you will see that both Euler and Runge–Kutta tend to the same value as $\varepsilon \to 0$. In this case do the simulations for $5 \times 10^{-3} \leq \varepsilon \leq 0.1$.

Note: It is important to work in double precision otherwise you will quickly lose accuracy as ε gets smaller.

2. For the case $V(x) = x^2/2$ calculate the autocorrelation function $\langle x(t_0)x(t_0 + t)\rangle$ and verify that it decays exponentially. Use the Runge–Kutta method with $\varepsilon = 0.2$. What is the relaxation time? Does it agree with the prediction of the Fokker–Planck equation? Compare with the exact result. See Equations (9.151) and (9.153) but note that whereas in (9.153) we took $E_0 = 0$, in the numerical integration it is not!

Use this method to determine $E_0 - E_1$ for the case $V(x) = x^4/4$. In this case take $\varepsilon = 0.01$ or smaller.

9.7.14 Metastable states and escape times

In this exercise we shall study the tunneling time τ of a particle trapped in a metastable state (local minimum). We shall assume the particle dynamics to be described by the Langevin equation,

$$\frac{\mathrm{d}x(t)}{\mathrm{d}t} = -\frac{\partial V(x)}{\partial x} + \sqrt{T}b(t) \tag{9.185}$$

where we have introduced the temperature explicitly. The potential

$$V(x) = (ax^2 - b)^2 \tag{9.186}$$

has two degenerate minima at $x = \pm\sqrt{b/a}$ and looks like a section of the Mexican hat potential in Chapter 4. This degeneracy is lifted by the application of an external 'field' h

$$V(x) = (ax^2 - b)^2 - hx \tag{9.187}$$

where, to fix ideas, we take $h > 0$. This lifts the minimum at $-\sqrt{a/b}$ to a higher energy than the minimum at $+\sqrt{a/b}$; it also slightly shifts their positions. So now the minimum at $x < 0$ is a local minimum, and a particle trapped in it will eventually tunnel out into the global minimum.[22] Our goal is to study this tunneling time as a function of temperature.

Take $a = 1$, $b = 1$ and $h = 0.3$, and use the Runge–Kutta discretization with $\varepsilon = 0.01$ to study the escape of the particle. We consider the particle to have

[22] If one waits long enough the particle will tunnel back into the local minimum for a while and then tunnel out of it again.

escaped the local minimum as soon as $x > 0$ since then it will have passed the peak of the barrier.

To determine the average escape time, we place the particle at $x = -1$ and start the Runge–Kutta integration. We stop when $x > 0$ and record the time it took to reach this point. We repeat this, say, 5000 times and calculate the average of the escape times thus found.[23] Of course this is equivalent to taking a population of 5000 particles in the local minimum and observing it decay to the global one.

1. For several temperatures, say $T = 0.075$, 0.08, 0.09, 0.1, make a separate histogram of the escape times recorded for each temperature. Does the shape of the histogram suggest a form for the dependence of the population on time? Calculate the average escape time τ for each of these temperatures and try a fit of the form $\exp(-t/\tau)$ for the histograms.

2. Determine τ for many temperatures $0.075 \leq T \leq 1.5$ and plot τ versus T. Compare your numerical results with the theoretical calculation[24]

$$\tau = \frac{2\pi}{\sqrt{V''(x_A)|V''(x_B)|}} \mathrm{e}^{(V(x_B)-V(x_A))/T} \tag{9.188}$$

where $V''(x)$ is the second derivative of the potential, $x_A < 0$ is the position of the local minimum, $V'(x_A) = 0$, and x_B is the position of the peak separating the two minima, $V'(x_B) = 0$. Is the agreement better at low or at high temperature? At what temperature does the agreement become bad?

In fact, the very definition of escape time τ presupposes that τ is much longer than the time needed to establish local equilibrium in the local minimum. Since as the temperature of the particle increases its energy gets closer to the top of the barrier, this condition is no longer satisfied and the agreement between theory and simulation deteriorates.

9.8 Problems

9.8.1 Inelastic light scattering from a suspension of particles

In this problem we limit ourselves to the classical approximation. When light travels through a dielectric medium, the medium is polarized, and the polarization acts as the source of the electromagnetic field. We split the dielectric response into a component ε independent of space and time and a fluctuation $\delta\varepsilon(\vec{r}, t)$; the polarization is written accordingly

$$\vec{P} = \varepsilon_0(\varepsilon - 1)\vec{E}(\vec{r}, t) + \delta\vec{P}(\vec{r}, t)$$

[23] Although we are always starting the particle at the same initial position, it will not follow the same path since the noise (sequence of random numbers) is different.

[24] See for example van Kampen [119] Chapter XI.

where ε_0 is the vacuum permittivity and $\vec{E}(\vec{r}, t)$ the electric field.

1. Show that in the gauge defined by

$$\frac{\varepsilon}{c^2}\frac{\partial \varphi}{\partial t} + \vec{\nabla} \cdot \vec{A} = 0$$

where φ is the scalar potential, the vector potential $\vec{A}$ obeys

$$\nabla^2 \vec{A} - \frac{\varepsilon}{c^2}\frac{\partial^2 \vec{A}}{\partial t^2} = -\frac{1}{\varepsilon_0 c^2}\frac{\partial \delta \vec{P}}{\partial t}$$

What is the corresponding equation for the scalar potential φ? Note that $c/\sqrt{\varepsilon}$ is the light velocity in the medium.

2. It is convenient to use the Hertz vector $\vec{Z}$

$$\varphi = -\vec{\nabla} \cdot \vec{Z} \qquad \vec{A} = \frac{\varepsilon}{c^2}\frac{\partial \vec{Z}}{\partial t}$$

Write the partial differential equation obeyed by $\vec{Z}$ as a function of $\delta \vec{P}$. Give the expression of $\vec{E}$ as a function of $\vec{Z}$.

3. Show that if the wave is scattered by a fluctuation $\delta \vec{P}$ of frequency ω located around $\vec{r}\,'$, then for $r = |\vec{r}| \gg |\vec{r}\,'|$ (see Figure 9.4 for the geometry of the scattering)

$$\vec{Z}(\vec{r}, \omega) \simeq \frac{1}{4\pi \varepsilon_0 \varepsilon}\frac{\mathrm{e}^{\mathrm{i}kr}}{r}\int \mathrm{d}^3 r'\, \mathrm{e}^{-\mathrm{i}\vec{k}\cdot\vec{r}\,'}\delta \vec{P}(\vec{r}\,', \omega)$$

In the above equation, $\vec{k} = k\hat{r}$ ($\hat{r} = \vec{r}/r$) is the wave vector of the scattered light, $k = \omega\sqrt{\varepsilon}/c$. Obtain from this equation the scattered electric field

$$\vec{E}(\vec{r}, \omega) \simeq \frac{\omega^2}{4\pi \varepsilon_0 c^2}\frac{\mathrm{e}^{\mathrm{i}kr}}{r}\int \mathrm{d}^3 r'\, \mathrm{e}^{-\mathrm{i}\vec{k}\cdot\vec{r}\,'}\hat{k} \times (\delta \vec{P}(\vec{r}\,', \omega) \times \hat{k})$$

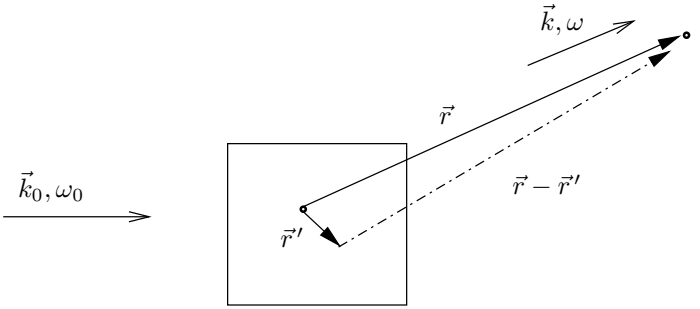

Figure 9.4 Geometry of the scattering.

4. Show the *Wiener–Kinchin theorem*: If $X(t)$ is a stationary random function and $X_T(t)$ is defined by

$$X_T(t) = X(t) \qquad -T \le t \le T, \quad \text{otherwise } X_T(t) = 0$$

where T is a time chosen to be much larger than all the characteristic times of the problem, then

$$\boxed{\langle X_T(\omega) X_T^*(\omega)\rangle \simeq T S_T(\omega)} \tag{9.189}$$

where $S_T(\omega)$ is the Fourier transform of the autocorrelation function of $X_T(t)$

$$\boxed{S_T(\omega) = \int \mathrm{d}t\, \mathrm{e}^{\mathrm{i}\omega t} \langle X_T(t) X_T^*(0)\rangle} \tag{9.190}$$

Hint: Use (9.180). In what follows, the subscript T will be suppressed.

5. We consider light scattering by small particles suspended in a fluid. The fluctuations of the polarization $\delta\vec{P}(\vec{r}, t)$ of the medium submitted to an incident electric field

$$\vec{E}(\vec{r}, t) = \vec{E}_0\, \mathrm{e}^{\mathrm{i}(\vec{k}_0\cdot\vec{r} - \omega_0 t)}$$

are given by

$$\delta\vec{P}(\vec{r}, t) = \alpha\varepsilon_0 \delta n(\vec{r}, t)\vec{E}_0 \mathrm{e}^{\mathrm{i}(\vec{k}_0\cdot\vec{r} - \omega_0 t)}$$

where ε_0 is the vacuum polarizability, α the difference between the particle dielectric constant and that of the fluid and $\delta n(\vec{r}, t)$ the density fluctuations of the particles. One notes the similarity of this problem with the spin diffusion considered in Section 9.1.4: here the rôle of the magnetic field, conjugate to the magnetization density, is played by the chemical potential, conjugate to the density.

Show that the power $\mathrm{d}\mathcal{P}$ radiated in a solid angle $\mathrm{d}\Omega$ and a frequency range $\mathrm{d}\omega$ is

$$\frac{\mathrm{d}\mathcal{P}}{\mathrm{d}\Omega\, \mathrm{d}\omega} = \frac{\varepsilon_0 c}{(4\pi\varepsilon_0)^2}\left(\frac{\omega}{c}\right)^4 \frac{1}{2\pi T}(\hat{e}_0 \times \hat{k})^2 \langle \delta\vec{P}(\vec{k}, \omega)\cdot\delta\vec{P}^*(\vec{k}, \omega)\rangle$$

where $\hat{e}_0 = \vec{E}_0/E_0$ and Ω is the solid angle of $\vec{k}$.

6. Show that

$$\delta\vec{P}(\vec{k}, \omega) = \alpha\varepsilon_0 \vec{E}_0\, \delta n(\vec{k} - \vec{k}_0, \omega - \omega_0)$$

and deduce that per unit volume of the target

$$\frac{\mathrm{d}\mathcal{P}}{\mathrm{d}\Omega\, \mathrm{d}\omega} = \frac{\varepsilon_0 c}{32\pi^3}\left(\frac{\omega}{c}\right)^4 (\hat{e}_0 \times \hat{k})^2\, \alpha^2 \vec{E}_0^2\, S_{nn}(\vec{k}', \omega')$$

where $\vec{k}' = \vec{k} - \vec{k}_0$, $\omega' = \omega - \omega_0$ and $S_{nn}(\vec{r}, t)$ is the density autocorrelation function

$$S_{nn}(\vec{r}, t) = \langle \delta n(\vec{r}, t) \delta n(\vec{0}, 0) \rangle$$

7. One takes for $S_{nn}(\vec{k}', \omega')$ the following expression

$$S_{nn}(\vec{k}', \omega') = \frac{2}{\beta} \chi(\vec{k}') \frac{Dk'^2}{\omega'^2 + (Dk'^2)^2}$$

where D is the diffusion coefficient of the particles in the fluid and $\chi(\vec{k}')$ the Fourier transform of the static susceptibility $\chi(\vec{r} - \vec{r}') = \delta n(\vec{r})/\delta \mu(\vec{r}')$. By appealing to Section 9.1.4, give a justification of this expression.

8. Taking into account that $r^2 \langle \vec{E}(\vec{r}, \omega) \cdot \vec{E}^*(\vec{r}, \omega) \rangle$ is in fact a function of $\vec{k}'$ and ω, one defines $\vec{\mathcal{E}}(\vec{r}, t) = r\vec{E}(\vec{r}, t)$ and $S_{EE}(\vec{k}', \omega)$ as the time autocorrelation function of $\vec{\mathcal{E}}(\vec{r}, t)$

$$S_{EE}(\vec{k}', \omega) = \int \mathrm{d}t \, \mathrm{e}^{\mathrm{i}\omega t} \langle \vec{\mathcal{E}}(\vec{r}, t) \cdot \vec{\mathcal{E}}^*(\vec{r}, 0) \rangle$$

Show that

$$S_{EE}(\vec{k}', \omega) = A \frac{2Dk'^2}{(\omega - \omega_0)^2 + (Dk'^2)^2}$$

and determine the coefficient A. What is the value of $\langle \vec{\mathcal{E}}(\vec{r}, t) \cdot \vec{\mathcal{E}}^*(\vec{r}, 0) \rangle$? One recalls that

$$\int \mathrm{d}t \, \mathrm{e}^{\mathrm{i}\omega t - \gamma |t|} = \frac{2\gamma}{\omega^2 + \gamma^2}$$

Note also that $\omega' \ll \omega_0$: $A(\omega) \simeq A(\omega_0)$.

9. Instead of $\mathrm{d}\mathcal{P}/\mathrm{d}\Omega \, \mathrm{d}\omega$, one can measure experimentally the intensity correlation function $S_{II}(\vec{r}, t)$ of $r^2 I(\vec{r}, t) = \vec{\mathcal{E}}(\vec{r}, t) \cdot \vec{\mathcal{E}}^*(\vec{r}, t)$ whose Fourier transform is $\mathcal{I}(\vec{k}', t)$

$$S_{II}(\vec{k}', \omega) = \int \mathrm{d}t \, \mathrm{e}^{i\omega t} \langle \mathcal{I}(\vec{k}', t) \mathcal{I}(\vec{k}', 0) \rangle$$

Assuming that $\vec{E}(\vec{r}, t)$ is a Gaussian random function, show that $S_{II}(\vec{k}', \omega)$ is proportional to

$$2\pi \delta(\omega) + \frac{4Dk'^2}{\omega^2 + (2Dk'^2)^2}$$

Knowing that $Dk'^2 \simeq 500$ Hz, why is it more advantageous to measure $S_{II}(\vec{k}', \omega)$ rather than $S_{EE}(\vec{k}', \omega)$?

9.8.2 Light scattering by a simple fluid

We consider a simple fluid close to *static equilibrium* and call n, ε and $\vec{g} = 0$ the *equilibrium* particle, energy and momentum densities. The notations are those of Section 6.3. As in Section 9.1, we assume that a non-equilibrium situation has been created at $t = 0$ and we wish to study the relaxation toward equilibrium for $t > 0$. This study will allow us to compute the Kubo function, from which one deduces the dynamical structure factors which govern light scattering by the fluid. We denote the *deviations from equilibrium* by $\overline{n}(\vec{r}, t)$, $\overline{\varepsilon}(\vec{r}, t)$ and $\vec{g}(\vec{r}, t)$: since $\vec{g} = 0$ at equilibrium, there is no need for a bar. We assume that all these deviations are small, so that we may work in the linear approximation and use a linearized form of the hydrodynamic equations of Section 6.3.

1. *Linearized hydrodynamics.* Show that in the linear approximation, the Navier–Stoke equation (6.91) becomes

$$\partial_t \vec{g} + \vec{\nabla} P - \frac{1}{mn}\left(\zeta + \frac{\eta}{3}\right)\vec{\nabla}(\vec{\nabla}\cdot\vec{g}) - \frac{\eta}{mn}\nabla^2\vec{g} = 0 \tag{9.191}$$

where P is the pressure and we have written the mass densiy $\rho = mn$, m being the mass of the fluid molecules. Note that the advection term $\vec{u}\cdot\vec{\nabla}\vec{u}$ in (6.91), which is quadratic in the fluid velocity $\vec{u}$, has been eliminated in the linear approximation. Show that within the same approximation the energy current $\vec{j}_E$ becomes

$$\vec{j}_E = (\varepsilon + P)\vec{u} - \kappa\vec{\nabla}T \tag{9.192}$$

2. *Decomposition into transverse and longitudinal components.* As for any vector field, the momentum density $\vec{g}$ may be split into a transverse component $\vec{g}_{\mathrm{T}}$ and a longitudinal component $\vec{g}_{\mathrm{L}}$

$$\vec{g} = \vec{g}_{\mathrm{T}} + \vec{g}_{\mathrm{L}} \qquad \vec{\nabla}\cdot\vec{g}_{\mathrm{T}} = 0 \qquad \vec{\nabla}\times\vec{g}_{\mathrm{L}} = 0$$

This terminology reflects a property of the spatial Fourier transforms: $\vec{g}_{\mathrm{T}}(\vec{k}, t)$ is perpendicular to $\vec{k}$ (transverse), $\vec{k}\cdot\vec{g}_{\mathrm{T}}(\vec{k}, t) = 0$ and $\vec{g}_{\mathrm{L}}(\vec{k}, t)$ is parallel to $\vec{k}$ (longitudinal), $\vec{k}\times\vec{g}_{\mathrm{L}}(\vec{k}, t) = 0$. Show that the continuity and Navier–Stokes equations

for $\overline{n}(\vec{r},t)$, $\vec{g}(\vec{r},t)$ and $\overline{\varepsilon}(\vec{r},t)$ take the form

$$\partial_t \overline{n} + \frac{1}{n}\vec{\nabla}\cdot\vec{g}_{\mathrm{L}} = 0 \tag{9.193}$$

$$\left(\partial_t - \frac{\eta}{mn}\nabla^2\right)\vec{g}_{\mathrm{T}} = 0 \tag{9.194}$$

$$\partial_t \vec{g}_{\mathrm{L}} + \vec{\nabla}P - \frac{\zeta'}{mn}\nabla^2\vec{g}_{\mathrm{L}} = 0 \tag{9.195}$$

$$\partial_t \overline{\varepsilon} + \frac{\varepsilon + P}{mn}\vec{\nabla}\cdot\vec{g}_{\mathrm{L}} - \kappa\nabla^2 T = 0 \tag{9.196}$$

where $\zeta' = (4\eta/3 + \zeta)$. Hint: To show (9.195), remember that for a vector field $\vec{V}(\vec{r})$

$$\vec{\nabla}\times\vec{\nabla}\times\vec{V} = \vec{\nabla}(\vec{\nabla}\cdot\vec{V}) - \vec{\nabla}^2\vec{V}$$

From (9.193) and (9.196), show that the continuity equation for the energy may be put into the following form

$$\partial_t \overline{\varepsilon} - \frac{\varepsilon + P}{n}\partial_t\overline{n} - \kappa\nabla^2 T = 0 \tag{9.197}$$

This equation suggests that it is useful to introduce the following quantity

$$q(\vec{r},t) = \overline{\varepsilon}(\vec{r},t) - \frac{\varepsilon + P}{n}\overline{n}(\vec{r},t) \tag{9.198}$$

3. *Transverse component.* Equation (9.194) shows that $\vec{g}_{\mathrm{T}}$ obeys a diffusion equation. Show that this equation implies that the Fourier–Laplace transform (9.22) $\vec{g}_{\mathrm{T}}(\vec{k},z)$ obeys

$$\vec{g}_{\mathrm{T}}(\vec{k},z) = \frac{\mathrm{i}}{z + \mathrm{i}k^2\eta/(mn)}\,\vec{g}(\vec{k},t=0)$$

Discuss the physical interpretation of this equation by comparing with Section 9.1.4 and give the expression for the dynamical structure factor $S_{\mathrm{T}}(\vec{k},\omega)$.

4. *Thermodynamic identities.* The study of the longitudinal component $\vec{g}_{\mathrm{L}}$ is unfortunately somewhat more complicated than that of $\vec{g}_{\mathrm{T}}$. The dynamical variables are $\overline{\varepsilon}$, $\overline{n}$ and $\vec{g}_{\mathrm{L}}$ and they obey a system of *coupled* partial differential equations. Furthermore, we want to use as independent thermodynamic variables n and ε, and we must express $\vec{\nabla}P$ and $\vec{\nabla}T$ as functions of these variables. We consider a subsystem of the fluid containing a fixed number N of molecules (it has of course a variable volume V) and all thermodynamic derivatives will be taken at *fixed* N; note that fixed V is then equivalent to fixed density n. Let us start from

$$\delta P = \left.\frac{\partial P}{\partial n}\right|_{\varepsilon}\delta n + \left.\frac{\partial P}{\partial \varepsilon}\right|_{n}\delta\varepsilon$$

where $(\partial P/\partial n)_\varepsilon$ and $(\partial P/\partial \varepsilon)_n$ are *equilibrium* thermodynamic derivatives. Show that

$$\left.\frac{\partial P}{\partial \varepsilon}\right|_n = \frac{V}{T}\left.\frac{\partial P}{\partial S}\right|_n$$

where S is the entropy of the subsystem. To evaluate $(\partial P/\partial n)_\varepsilon$, start from

$$V\,\mathrm{d}\varepsilon = T\,\mathrm{d}S - (\varepsilon + P)\,\mathrm{d}V$$

and show that

$$\left.\frac{\partial P}{\partial V}\right|_\varepsilon = \frac{\varepsilon + P}{T}\left.\frac{\partial P}{\partial S}\right|_n + \left.\frac{\partial P}{\partial V}\right|_S$$

It is then easy to derive

$$\vec{\nabla} P = \left.\frac{\partial P}{\partial n}\right|_S \vec{\nabla}\overline{n} + \frac{V}{T}\left.\frac{\partial P}{\partial S}\right|_n \vec{\nabla} q$$

The calculation of $\vec{\nabla} T$ follows exactly the same lines: one simply makes the substitution $P \to T$ and obtains

$$\vec{\nabla} T = \left.\frac{\partial T}{\partial n}\right|_S \vec{\nabla}\overline{n} + \frac{V}{T}\left.\frac{\partial T}{\partial S}\right|_n \vec{\nabla} q$$

5. *Equation for* $\vec{g}_\mathrm{L}$. From the results of Question 4, transform the coupled equations for q, $\overline{n}$ and $\vec{g}_\mathrm{L}$ into

$$\left[\partial_t - \frac{\zeta'}{mn}\nabla^2\right]\vec{g}_\mathrm{L} + \left.\frac{\partial P}{\partial n}\right|_S \vec{\nabla}\,\overline{n} + \frac{V}{T}\left.\frac{\partial P}{\partial S}\right|_n \vec{\nabla} q = 0 \tag{9.199}$$

$$\left[\partial_t - \kappa\frac{V}{T}\left.\frac{\partial T}{\partial S}\right|_n \nabla^2\right] q - \kappa\left.\frac{\partial T}{\partial n}\right|_S \nabla^2\overline{n} = 0 \tag{9.200}$$

Show also that δq (9.198) is related to the entropy density

$$\frac{T}{V}\,\delta S = \delta\varepsilon - \frac{\varepsilon + P}{n}\,\delta n = \delta q$$

It is convenient to define the following quantities

$$D_\mathrm{L} = \frac{\zeta'}{mn} = \frac{1}{mn}\left(\frac{4}{3}\eta + \zeta\right)$$

$$mnc_V = \frac{T}{V}\left.\frac{\partial S}{\partial T}\right|_n \qquad mnc_P = \frac{T}{V}\left.\frac{\partial S}{\partial T}\right|_P$$

$$c^2 = \frac{1}{m}\left.\frac{\partial P}{\partial n}\right|_S$$

c is the sound velocity, mc_V and mc_P are the specific heat capacities per fluid molecule.

6. *Relaxation of $\overline{\varepsilon}$, q and $\vec{g}_{\rm L}$.* Equations (9.193), (9.199) and (9.200) define a system of coupled PDE for $\overline{\varepsilon}$, q and $\vec{g}_{\rm L}$. Show that they can be solved by taking the spatial Fourier and time Laplace transforms

$$\begin{pmatrix} z & -\dfrac{k}{m} & 0 \\ -kmc^2 & z+\mathrm{i}k^2 D_{\rm L} & -\dfrac{V}{T}\dfrac{\partial P}{\partial S}\Big|_n k \\ \mathrm{i}k^2\kappa\dfrac{\partial T}{\partial n}\Big|_S & 0 & z+\mathrm{i}k^2\dfrac{\kappa}{mnc_V} \end{pmatrix} \begin{pmatrix} \overline{n}(\vec{k},z) \\ g_{\rm L}(\vec{k},z) \\ q(\vec{k},z) \end{pmatrix} = \mathrm{i} \begin{pmatrix} \overline{n}(\vec{k},t=0) \\ g_{\rm L}(\vec{k},t=0) \\ q(\vec{k},t=0) \end{pmatrix} \tag{9.201}$$

where we have defined $g_{\rm L}(\vec{k},z)$ by $\vec{g}_{\rm L}(\vec{k},z) = \hat{k}\, g_{\rm L}(\vec{k},z)$.

7. *Poles of $\vec{g}_{\rm L}(\vec{k},z)$.* An explicit solution of (9.201) requires the inversion of the 3×3 matrix M in this equation. We shall limit ourselves to finding the poles of the functions $\overline{n}(\vec{k},z)$, $q(\vec{k},z)$ and $\vec{g}_L(\vec{k},z)$, which are given by the zeroes of the determinant of M. First we use a low temperature approximation, where P is essentially a function of n and S essentially a function of T, so that

$$\frac{\partial P}{\partial S}\Big|_n = \frac{\partial T}{\partial n}\Big|_S \simeq 0$$

and $c_P \simeq c_V$. Within this approximation, show that the poles are located at

$$z \simeq -\mathrm{i}\frac{\kappa}{mnc_V}k^2$$
$$z \simeq \pm ck - \frac{\mathrm{i}}{2}D_{\rm L}k^2$$

In the general case, show that the additional term in the determinant is proportional to k^4 with a coefficient X

$$X = \mathrm{i}\frac{\kappa V}{T}\frac{\partial T}{\partial P}\Big|_S \frac{\partial P}{\partial S}\Big|_n$$

and that X may be written as

$$X = \mathrm{i}\frac{\kappa V T}{C_P C_V}\frac{\partial V}{\partial T}\Big|_P \frac{\partial P}{\partial T}\Big|_V$$

Use (1.38) to express the result in terms of $C_P - C_V$. Show that the position of the poles is now

$$z \simeq -\mathrm{i}\frac{\kappa}{mnc_P}k^2$$
$$z \simeq \pm ck - \frac{\mathrm{i}}{2}k^2\left[D_{\rm L} + \frac{\kappa}{mnc_P}\left(\frac{c_P}{c_V}-1\right)\right] = \pm ck - \mathrm{i}\frac{\Gamma}{2}k^2$$

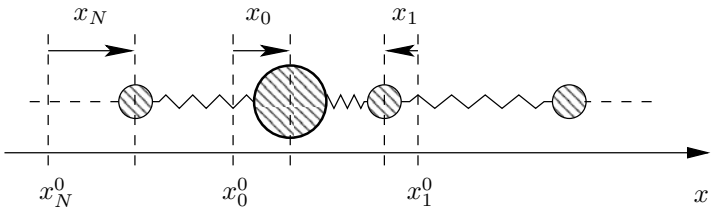

Figure 9.5 Springs and masses.

These equations give the positions of the heat pole and the two sound poles of Figure 9.1. If laser light is scattered from a simple fluid with wave vector transfer $\vec{k}$, the position of the sound poles gives the sound velocity and the width of the poles gives a combination of transport coefficients and thermodynamic quantities. It remains to compute explicitly the Kubo functions and the structure factors describing light scattering. This computation is now straightforward but cumbersome, and we refer the courageous reader who has followed us up to this point to Kadanoff and Martin [61] or Foerster [43].

9.8.3 Exactly solvable model of a Brownian particle

The model considered in this problem is an exactly solvable model, in which one can compute explicitly the memory function and the stochastic force. The model consists of a chain of coupled harmonic oscillators, with N ($N \to \infty$) light oscillators of mass m, and a heavy (Brownian) oscillator of mass M, with $M \gg m$, although the model can be solved for any ratio m/M. The goal of the problem is to compute the memory function, the memory time τ^*, the velocity relaxation time τ, and to show that $\tau^*/\tau \sim m/M$. We use a quantum mechanical treatment, as it is no more complicated than a classical one.

A Preliminary results

Let us consider N identical masses m, linked by identical springs with spring constant K (Figure 9.5). The equilibrium position of mass n is labelled by $x_n^0 = n$, where the lattice spacing is taken to be unity, and $n = 1, \ldots, N$; x_n denotes the deviation with respect to equilibrium of the position of mass n. The extremities of the first and last springs are fixed: $x_0 = x_{N+1} = 0$. Let q_k denote the (lattice) Fourier tranform of x_n

$$q_k = \sum_n C_{kn} x_n$$

with

$$C_{nk} = C_{kn} = \sqrt{\frac{2}{N+1}}\,\sin\Big(\frac{\pi kn}{N+1}\Big)$$

1. Show that C_{nk} is an orthogonal matrix

$$\sum_{k=1}^{N} C_{nk}C_{km} = \delta_{nm}$$

2. The Hamiltonian H of the chain reads

$$H = \sum_{n=1}^{N} \frac{p_n^2}{2m} + \frac{1}{2}K\sum_{n=0}^{N}(x_{n+1} - x_n)^2$$

Show that

$$H = \sum_{k=1}^{N} \frac{r_k^2}{2m} + \frac{1}{2}m\sum_{k=1}^{N}\omega_k^2 q_k^2 \qquad \omega_k = \sqrt{\frac{4K}{m}}\,\sin\frac{\pi k}{2(N+1)}$$

and r_k is the Fourier transform of p_n.

B The model

We use as quantum Hamiltonian of the model

$$H = \frac{\mathsf{p}_0^2}{2M} + \sum_{n=1}^{N}\frac{\mathsf{p}_n^2}{2m} + \frac{1}{2}K\sum_{n=0}^{N}(\mathsf{x}_{n+1} - \mathsf{x}_n)^2$$

Note the periodic boundary condition: $\mathsf{x}_{N+1} = \mathsf{x}_0$. The strategy will be to project the dynamics on the slow variable p_0, namely the momentum of the heavy particle.

3. Using the relation (see Exercise 9.7.4)

$$\langle \mathsf{A};\, \mathcal{L}\mathsf{B}\rangle = \frac{1}{\beta}\langle [\mathsf{A}^\dagger, \mathsf{B}]\rangle$$

where $\langle \bullet;\, \bullet\rangle$ denotes Mori's scalar product and $\mathcal{L}$ the Liouvillian, show that

$$\mathrm{i}\mathcal{L}\mathsf{x}_0 = \frac{\mathsf{p}_0}{M} \qquad \langle \mathsf{p}_0;\, \mathsf{p}_0\rangle = \frac{M}{\beta} \qquad \langle \mathsf{p}_0;\, \mathsf{x}_0\rangle = 0$$

4. Let $\mathcal{P}$ denote the projector on p_0 (with respect to the Mori scalar product), and $\mathcal{Q} = \mathcal{I} - \mathcal{P}$. Show that for any dynamical variable B that is a linear combination of p_n and x_n

$$\mathsf{B} = \sum_{n=0}^{N}(\lambda_n \mathsf{p}_n + \mu_n \mathsf{x}_n)$$

if one defines $\overline{H} = H - \mathsf{p}_0^2/2M$, then

$$\mathcal{Q}\,\mathcal{L}\,\mathsf{B} = [\overline{H}, \mathsf{B}] = \overline{\mathcal{L}}\,\mathsf{B}$$

The potential energy can be re-expressed as a function of the variables $\mathsf{x}'_n = \mathsf{x}_n - \mathsf{x}_0$, and the projected dynamics corresponds to that of a heavy particle at rest.

5. Show that the stochastic force $\mathsf{f}(t) = \exp(\mathrm{i}\overline{\mathcal{L}}\,t)\mathcal{Q}\,\mathrm{i}\,\mathcal{L}\,\mathsf{p}_0$ is given by

$$\mathsf{f}(t) = K\exp(\mathrm{i}\overline{\mathcal{L}}t)\,(\mathsf{x}_1 + \mathsf{x}_N - 2\mathsf{x}_0)$$

6. By going to Fourier space, show that $\mathsf{f}(t)$ is given as a function of the operators x_n and p_n in the Schrödinger picture by

$$\mathsf{f}(t) = K\sum_{k,n=1}^{N}(C_{1k} + C_{Nk})\Big[C_{kn}(\mathsf{x}_n - \mathsf{x}_0)\cos\omega_k t + C_{kn}\frac{\mathsf{p}_n}{m\omega_k}\sin\omega_k t\Big]$$

and the memory function by

$$\gamma(t) = \frac{\beta}{M}\langle\mathsf{f}(0);\mathsf{f}(t)\rangle = \frac{K}{M}\sum_{k,n=1}^{N}C_{kn}(C_{1k} + C_{Nk})\cos\omega_k t$$

7. Compute $\gamma(t)$ in the thermodynamic limit $N \to \infty$

$$\lim_{N\to\infty}\gamma(t) = \frac{m}{M}\alpha^2\frac{J_1(\alpha t)}{\alpha t}$$

with $\alpha = \sqrt{4K/m}$, and where J_1 is a Bessel function. One may use the following representation of the Bessel function

$$\frac{J_1(\alpha t)}{\alpha t} = \frac{1}{\pi}\int_{-\pi/2}^{\pi/2}\cos^2\varphi\cos(\alpha t\sin\varphi)\mathrm{d}\varphi$$

Compute the velocity relaxation time τ and give an estimate of the memory time τ^*. Show that $\tau^*/\tau \sim m/M$ and give a physical discussion of your results.

9.8.4 Itô versus Stratonovitch dilemma

When the diffusion coefficient is x-dependent, the Langevin equation is ambiguous. Let us write

$$\frac{\mathrm{d}X}{\mathrm{d}t} = a(x) + \sqrt{D(x_0)}\,b(t)$$

with

$$\overline{b(t)b(t')} = 2\,\delta(t - t')$$

while, for an infinitesimal time interval $[t, t+\varepsilon]$, x_0 is defined as a function of a parameter q, $0 \leq q \leq 1$, by

$$x_0 = x(t) + (1-q)[X(t+\varepsilon) - x(t)] = y + (1-q)[X(t+\varepsilon) - y]$$

We define as in (9.137)

$$B_\varepsilon = \int_t^{t+\varepsilon} \mathrm{d}t'\, b(t') \qquad \overline{B_\varepsilon} = 0 \qquad \overline{B_\varepsilon^2} = 2$$

1. *Itô prescription.* We first study the Itô prescription, which corresponds to $q = 1$: $x_0 = x(t)$

$$X(t+\varepsilon) = y + \varepsilon a(y) + \sqrt{D(y)} \int_t^{t+\varepsilon} \mathrm{d}t'\, b(t')$$

As in Section 9.5.1, we start from the Chapman–Kolmogorov equation (9.144) with

$$P(x, t+\varepsilon | y, t) = \overline{\delta(x - y - \varepsilon a(y) - \sqrt{D(y)}\, B_\varepsilon)}$$

Show that, to order ε, the δ-function may be written as $f'(x)\delta(y - f(x))$ where

$$f(x) = x - \varepsilon a(x) - B_\varepsilon \sqrt{D(x)} + \frac{1}{2} B_\varepsilon^2 D'(x) \tag{9.202}$$

Taking an average over all realizations of $b(t)$, derive the F–P equation (9.154)

$$\frac{\partial P}{\partial t} = -\frac{\partial}{\partial x}[a(x)P] + \frac{\partial^2}{\partial x^2}[D(x)P]$$

2. *General case.* In the general case, show that

$$\overline{X(t+\varepsilon) - y} = \varepsilon[a(y) + (1-q)D'(y)]$$

and, with respect to the preceding case, one has to make the substitution

$$a(y) \to a(y) + (1-q)D'(y)$$

Derive the F–P equation for arbitrary q

$$\frac{\partial P}{\partial t} = -\frac{\partial}{\partial x}[a(x)P] + \frac{\partial}{\partial x}\left[D^{1-q}(x)\frac{\partial}{\partial x}D^q(x)P\right]$$

The Stratonovitch prescription corresponds to $q = 1/2$. One notes that the various

prescriptions differ by the drift velocities if one wants to write the F–P equation in the form (9.154).

9.8.5 Kramers equation

Consider a particle of mass m, moving in one dimension, which is subjected to a deterministic force $F(x) = -\partial V/\partial x$, a viscous force $-\gamma p$ and a random force $f(t)$

$$\overline{f(t)f(t')} = 2A\,\delta(t - t')$$

The equations of motion are

$$\dot{P} = F(x) - \gamma P + f(t) \qquad \dot{X} = \frac{P}{m}$$

Note that X and P alone are not Markovian variables, but the set (X, P) is Markovian.

1. By examining the moments $\langle \Delta X \rangle$, $\langle \Delta P \rangle$, $\langle (\Delta P)^2 \rangle$, $\langle (\Delta X)^2 \rangle$ and $\langle \Delta P \Delta X \rangle$ and by using (9.183) and (9.184), show that the probability distribution $P(x, p; t)$ obeys the *Kramers equation*

$$\boxed{\left[\frac{\partial}{\partial t} + \frac{p}{m}\frac{\partial}{\partial x} + F(x)\frac{\partial}{\partial p}\right] P = \gamma \left[\frac{\partial}{\partial p}(pP) + mkT\frac{\partial^2 P}{\partial p^2}\right]}$$

with $kT = A/(m\gamma)$. This equation can be simplified in the strong friction limit. Let us define the density

$$\rho(x, t) = \int \mathrm{d}p\, P(x, p; t)$$

and the current

$$j(x, t) = \int \mathrm{d}p\, \frac{p}{m}\, P(x, p; t)$$

2. From the $|p| \to \infty$ behaviour of $P(x, p; t)$, prove the (exact) continuity equation

$$\frac{\partial \rho}{\partial t} + \frac{\partial j}{\partial x} = 0$$

In the strong friction limit, show that one expects

$$P(x, p; t) \simeq \rho(x, t)\sqrt{\frac{1}{2\pi mkT}}\, \exp\left(-\frac{[p - \overline{p}(x)]^2}{2mkT}\right)$$

with $\overline{p}(x) = F(x)/\gamma$.

3. Let us finally define

$$K(x,t) = \int \mathrm{d}p \, \frac{p^2}{m} \, P(x, p; t)$$

What is the physical meaning of K? Prove the (exact) continuity equation

$$m\frac{\partial j}{\partial t} + \frac{\partial K}{\partial x} - F(x)\rho = -\gamma m j(x,t)$$

and show that in the strong friction limit

$$\left|\frac{\partial j}{\partial t}\right| \ll \gamma |j|$$

and that

$$K(x,t) \simeq \rho(x,t)\left[kT + \frac{\overline{p}^2(x)}{m}\right]$$

Using the continuity equation for $K(x,t)$, show that $\rho(x,t)$ obeys a Fokker–Planck equation when $kT \gg \overline{p}^2(x)/m$

$$\frac{\partial \rho}{\partial t} + \frac{\partial}{\partial x}\left[\frac{F(x)}{m\gamma}\rho(x,t) - D\frac{\partial}{\partial x}\rho(x,t)\right] = 0$$

Give the explicit expression of the diffusion coefficient D for x-independent γ and A. Can you generalize to x-dependent γ and A?

4. Show that for $F(x) = 0$, $X(t)$ obeys a diffusion equation with a space-dependent diffusion coefficient. Write this diffusion equation in the form of a Langevin equation and find the prescription (Itô, Stratonovitch or other, see Problem 9.8.4) that must be used in the following two cases (*i*) γ is x-independent and A is x-dependent and (*ii*) vice versa.

9.9 Further reading

An elementary introduction to the topics of this chapter may be found in Chandler [28]. The material in Sections 9.1 and 9.2 is detailed by Foerster [43] (Chapter 2) and by Fick and Sauermann [41] (Chapter 9). Spin diffusion is treated in Foerster [43] (Chapter 2) and in Kadanoff and Martin [61]. Good references on the projection method are: Balian *et al*. [7], Fick and Sauermann [41] (Chapters 14 to 18), Grabert [51], Zubarev *et al*. [126] (Chapter 2) and Rau and Müller [107]. The discussion of Section 9.3.5 follows Foerster [43] (Chapter 6); see also Lebowitz and Résibois [76]. The application of the projection method to Goldstone modes

is discussed in great detail by Foerster [43] (Chapters 7 to 11); see also Chaikin and Lubensky [26] (Chapter 8). Although the articles are some fifty years old, the collection by Wax [121] is still a very useful reference on random functions; see also, e.g. Mandel and Wolff [86] (Chapters 1 and 2). There are many references on the Langevin and Fokker–Planck equations, among them: Parisi [99] (Chapter 19), van Kampen [119], Risken [110], Reichl [108] (Chapter 5).