

1 Correlation functions

The time dependence of both classical and quantum mechanical variables is governed by equations of motion determined by a Hamiltonian \mathcal{H} . A quantum mechanical operator (or field) $\phi_i(\mathbf{x}, t)$ evolves in time in the Heisenberg representation according to

$$\phi_i(\mathbf{x}, t) = e^{i\mathcal{H}t/\hbar} \phi_i(\mathbf{x}, 0) e^{-i\mathcal{H}t/\hbar}. \quad (7.1.1)$$

We will often be interested in the frequency rather than time dependence of operators, and it is useful to introduce the temporal Fourier transforms,

$$\begin{aligned} \phi_i(\mathbf{x}, t) &= \int_{-\infty}^{\infty} \frac{d\omega}{2\pi} e^{-i\omega t} \phi_i(\mathbf{x}, \omega), \\ \phi_i(\mathbf{x}, \omega) &= \int_{-\infty}^{\infty} dt e^{i\omega t} \phi_i(\mathbf{x}, t). \end{aligned} \quad (7.1.2)$$

We will frequently study time-dependent correlations of variables such as the position $\mathbf{x}^\alpha(t)$ of particle α or simple functions of such variables such as the density,

$$n(\mathbf{x}, t) = \sum_{\alpha} \delta(\mathbf{x} - \mathbf{x}^\alpha(t)). \quad (7.1.3)$$

Here, both $n(\mathbf{x}, t)$ and $\mathbf{x}^\alpha(t)$ evolve according to Eq. (7.1.1). Classically, operators such as $\mathbf{x}^\alpha(t)$ evolve according to Newton's equations.

Time-dependent correlation functions can be introduced in strict analogy with the static correlations introduced in Secs. 3.5 and 3.6. Thus, we define

$$C_{\phi_i \phi_j}(\mathbf{x}, \mathbf{x}', t, t') = \langle \phi_i(\mathbf{x}, t) \phi_j(\mathbf{x}', t') \rangle \quad (7.1.4)$$

and

$$\begin{aligned} S_{\phi_i \phi_j}(\mathbf{x}, \mathbf{x}', t, t') &= \langle (\phi_i(\mathbf{x}, t) - \langle \phi_i(\mathbf{x}, t) \rangle) (\phi_j(\mathbf{x}', t') - \langle \phi_j(\mathbf{x}', t') \rangle) \rangle \\ &\equiv C_{\phi_i \phi_j}(\mathbf{x}, \mathbf{x}', t, t') - \langle \phi_i(\mathbf{x}, t) \rangle \langle \phi_j(\mathbf{x}', t') \rangle, \end{aligned} \quad (7.1.5)$$

where, as for the static case, $\langle \rangle$ signifies an average with respect to an equilibrium ensemble. Because the time evolution of the fields $\phi_i(\mathbf{x}, t)$ is governed by the Hamiltonian according to Eq. (7.1.1), there is no ambiguity in the meaning of these averages: for each value of t and t' , they are evaluated by tracing over all points in phase space or all quantum states weighted by the appropriate equilibrium weight function. When $t = t'$, these correlation functions reduce to the static correlation functions discussed in Chapter 3:

$$\begin{aligned} C_{\phi_i \phi_j}(\mathbf{x}, \mathbf{x}', t, t) &\equiv C_{\phi_i \phi_j}(\mathbf{x}, \mathbf{x}'), \\ S_{\phi_i \phi_j}(\mathbf{x}, \mathbf{x}', t, t) &\equiv S_{\phi_i \phi_j}(\mathbf{x}, \mathbf{x'}). \end{aligned} \quad (7.1.6)$$

Unless otherwise specified, we will consider only Hamiltonians that are independent of time so that all thermodynamic averages are invariant under time translations. This implies that $\langle \phi_i(\mathbf{x}, t) \rangle \equiv \langle \phi_i(\mathbf{x}) \rangle$ is independent of time.

the correlation functions $C_{\phi_i\phi_j}(\mathbf{x}, \mathbf{x}', t, t')$ and $S_{\phi_i\phi_j}(\mathbf{x}, \mathbf{x}', t, t')$ depend only on the difference $t - t'$ rather than on t and t' individually. Thus, the correlation function of the temporal Fourier transform variables can be written as

$$\langle \phi_i(\mathbf{x}, \omega) \phi_j(\mathbf{x}', \omega') \rangle = C_{\phi_i\phi_j}(\mathbf{x}, \mathbf{x}', \omega) 2\pi \delta(\omega + \omega'), \quad (7.1.7)$$

where

$$C_{\phi_i\phi_j}(\mathbf{x}, \mathbf{x}', \omega) = \int_{-\infty}^{\infty} dt(t-t') e^{i\omega(t-t')} C_{\phi_i\phi_j}(\mathbf{x}, \mathbf{x}', t-t'). \quad (7.1.8)$$

The correlation function $C_{\phi_i\phi_i}(\mathbf{x}, \mathbf{x}, \omega)$ is often called the power spectrum of $\phi_i(\mathbf{x}, t)$. Eqs. (7.1.7) and (7.1.8) are generalizations of the Wiener-Khintchine theorem relating a power spectrum to the Fourier transform of a time-dependent correlation function. Similarly, we define

$$S_{\phi_i\phi_j}(\mathbf{x}, \mathbf{x}', \omega) = \int_{-\infty}^{\infty} dt(t-t') e^{i\omega(t-t')} S_{\phi_i\phi_j}(\mathbf{x}, \mathbf{x}', t-t'). \quad (7.1.9)$$

Eq. (7.1.5) then implies

$$C_{\phi_i\phi_j}(\mathbf{x}, \mathbf{x}', \omega) = S_{\phi_i\phi_j}(\mathbf{x}, \mathbf{x}', \omega) + \langle \phi_i(\mathbf{x}) \rangle \langle \phi_j(\mathbf{x}') \rangle 2\pi \delta(\omega), \quad (7.1.10)$$

indicating that the $\langle \phi_i(\mathbf{x}) \rangle \langle \phi_j(\mathbf{x}') \rangle$ contributes only to the zero-frequency or static part of $C_{\phi_i\phi_j}(\mathbf{x}, \mathbf{x}', \omega)$.

2 Response functions

Just as the static susceptibilities $\chi_{\phi_i\phi_j}(\mathbf{x}, \mathbf{x}')$ relate changes $\delta \langle \phi_i(\mathbf{x}) \rangle$ in averages of fields to changes in external fields $\delta h_j(\mathbf{x}')$ conjugate to $\phi_j(\mathbf{x})$, the dynamic response function $\tilde{\chi}_{\phi_i\phi_j}(\mathbf{x}, \mathbf{x}', t, t')$ relates changes $\delta \langle \phi_i(\mathbf{x}, t) \rangle$ in averages of time-dependent fields to time-dependent changes $\delta h_j(\mathbf{x}', t')$ in external fields:

$$\delta \langle \phi_i(\mathbf{x}, t) \rangle = \int d^d x' dt' \tilde{\chi}_{\phi_i\phi_j}(\mathbf{x}, \mathbf{x}', t, t') \delta h_j(\mathbf{x}', t'). \quad (7.1.11)$$

It is important to recognize the difference between the temporal and spatial variables in this equation. Disturbances at \mathbf{x}' can lead to changes in $\langle \phi_i(\mathbf{x}, t) \rangle$ at all points \mathbf{x} . Disturbances at time t' can lead to changes in $\langle \phi_i(\mathbf{x}, t) \rangle$ only for times t later than t' , i.e., the response of $\langle \phi_i(\mathbf{x}, t) \rangle$ to $h_j(\mathbf{x}', t')$ is causal. This means that the function $\tilde{\chi}_{\phi_i\phi_j}(\mathbf{x}, \mathbf{x}', t, t')$ can be nonzero only for $t > t'$. It is very useful to incorporate this step-function dependence on time into the definition of the function by writing

$$(7.1.12)$$

the correlation functions $C_{\phi_i\phi_j}(\mathbf{x}, \mathbf{x}', t, t')$ and $S_{\phi_i\phi_j}(\mathbf{x}, \mathbf{x}', t, t')$ depend only on the difference $t - t'$ rather than on t and t' individually. Thus, the correlation function of the temporal Fourier transform variables can be written as

$$\langle \phi_i(\mathbf{x}, \omega) \phi_j(\mathbf{x}', \omega') \rangle = C_{\phi_i\phi_j}(\mathbf{x}, \mathbf{x}', \omega) 2\pi \delta(\omega + \omega'), \quad (7.1.7)$$

where

$$C_{\phi_i\phi_j}(\mathbf{x}, \mathbf{x}', \omega) = \int_{-\infty}^{\infty} dt dt' e^{i\omega(t-t')} C_{\phi_i\phi_j}(\mathbf{x}, \mathbf{x}', t - t'). \quad (7.1.8)$$

The correlation function $C_{\phi_i\phi_i}(\mathbf{x}, \mathbf{x}, \omega)$ is often called the *power spectrum* of $\phi_i(\mathbf{x}, t)$. Eqs. (7.1.7) and (7.1.8) are generalizations of the Wiener-Khintchine theorem relating a power spectrum to the Fourier transform of a time-dependent correlation function. Similarly, we define

$$S_{\phi_i\phi_j}(\mathbf{x}, \mathbf{x}', \omega) = \int_{-\infty}^{\infty} dt dt' e^{i\omega(t-t')} S_{\phi_i\phi_j}(\mathbf{x}, \mathbf{x}', t - t'). \quad (7.1.9)$$

Eq. (7.1.5) then implies

$$C_{\phi_i\phi_j}(\mathbf{x}, \mathbf{x}', \omega) = S_{\phi_i\phi_j}(\mathbf{x}, \mathbf{x}', \omega) + \langle \phi_i(\mathbf{x}) \rangle \langle \phi_j(\mathbf{x}') \rangle 2\pi \delta(\omega), \quad (7.1.10)$$

indicating that the $\langle \phi_i(\mathbf{x}) \rangle \langle \phi_j(\mathbf{x}') \rangle$ contributes only to the zero-frequency or static part of $C_{\phi_i\phi_j}(\mathbf{x}, \mathbf{x}', \omega)$.

2 Response functions

Just as the static susceptibilities $\chi_{\phi_i\phi_j}(\mathbf{x}, \mathbf{x}')$ relate changes $\delta \langle \phi_i(\mathbf{x}) \rangle$ in averages of fields to changes in external fields $\delta h_j(\mathbf{x}')$ conjugate to $\phi_j(\mathbf{x})$, the dynamic response function $\tilde{\chi}_{\phi_i\phi_j}(\mathbf{x}, \mathbf{x}', t, t')$ relates changes $\delta \langle \phi_i(\mathbf{x}, t) \rangle$ in averages of time-dependent fields to time-dependent changes $\delta h_j(\mathbf{x}', t')$ in external fields:

$$\delta \langle \phi_i(\mathbf{x}, t) \rangle = \int d^d x' dt' \tilde{\chi}_{\phi_i\phi_j}(\mathbf{x}, \mathbf{x}', t, t') \delta h_j(\mathbf{x}', t'). \quad (7.1.11)$$

It is important to recognize the difference between the temporal and spatial variables in this equation. Disturbances at \mathbf{x}' can lead to changes in $\langle \phi_i(\mathbf{x}, t) \rangle$ at all points \mathbf{x} . Disturbances at time t' can lead to changes in $\langle \phi_i(\mathbf{x}, t) \rangle$ only for times t later than t' , i.e., the response of $\langle \phi_i(\mathbf{x}, t) \rangle$ to $h_j(\mathbf{x}', t')$ is *causal*. This means that the response function $\tilde{\chi}_{\phi_i\phi_j}(\mathbf{x}, \mathbf{x}', t, t')$ can be nonzero only for $t > t'$. It is very useful to incorporate this step-function dependence on time into the definition of the response function by writing

$$\tilde{\chi}_{\phi_i\phi_j}(\mathbf{x}, \mathbf{x}', t, t') = 2i\eta(t - t') \tilde{\chi}_{\phi_i\phi_j}''(\mathbf{x}, \mathbf{x}', t, t'), \quad (7.1.12)$$

where

$$\eta(t - t') = \begin{cases} 1 & \text{if } t > t'; \\ 0 & \text{if } t < t' \end{cases} \quad (7.1.13)$$

is the Heaviside unit step function. The factor of $2i$ ($i = \sqrt{-1}$) is at this stage arbitrary, but it will make comparisons with our later more formal development more straightforward. Eq. (7.1.12) can be viewed as a definition of $\tilde{\chi}_{\phi_i\phi_j}''(\mathbf{x}, \mathbf{x}', t, t')$.

which is pure imaginary if ϕ_i and ϕ_j are both real. Time translational invariance again implies that $\tilde{\chi}(\mathbf{x}, \mathbf{x}', t, t')$ and $\tilde{\chi}_{\phi_i \phi_j}''(\mathbf{x}, \mathbf{x}', t, t')$ depend only on $t - t'$.

We will now discuss some of the analytic properties of the response function and its Fourier transform with respect to time. In order to keep notation compact, we will consider the response of a single position independent field $\phi(t)$ to its conjugate external field $h(t)$. In this case, we have

$$\langle \delta\phi(t) \rangle = \int_{-\infty}^{\infty} dt' \tilde{\chi}(t - t') \delta h(t'), \quad (7.1.14)$$

where $\tilde{\chi}(t) = 2i\eta(t)\tilde{\chi}''(t)$. Both $\langle \phi(t) \rangle$ and $h(t)$ are real so that $\tilde{\chi}''(t)$ is pure imaginary. We will be interested in response as a function of frequency rather than time. We therefore need to calculate the temporal Fourier transform of $\tilde{\chi}(t)$. Because of the causal step-function prefactor in $\tilde{\chi}(t)$, it is useful to introduce the Laplace transform as a function of complex frequency z :

$$\chi(z) = \int_{-\infty}^{\infty} e^{izt} \tilde{\chi}(t) dt = \int_0^{\infty} e^{izt} \tilde{\chi}(t) dt. \quad (7.1.15)$$

The function $\tilde{\chi}''(t)$ is bounded as $t \rightarrow \infty$ because a disturbance at time $t = 0$ will only produce a finite change in $\phi(t)$ at later times. Thus, because t is positive in the above integral, $\chi(z)$ is *analytic in the upper half z-plane* ($\text{Im}z > 0$). The function $\tilde{\chi}''(t, t') = \tilde{\chi}''(t - t')$ is bounded, and we can define its Fourier transform with respect to a real frequency variable,

$$\begin{aligned} \tilde{\chi}''(t) &= \int_{-\infty}^{\infty} \frac{d\omega}{2\pi} e^{-i\omega t} \chi''(\omega) \\ \chi''(\omega) &= \int_{-\infty}^{\infty} dt e^{i\omega t} \tilde{\chi}''(t). \end{aligned} \quad (7.1.16)$$

If $\tilde{\chi}''(t)$ approaches a constant as $t \rightarrow \infty$, then $\chi''(\omega)$ will have *delta-function parts*. Quite general arguments to be discussed in Sec. 7.6 show that $\tilde{\chi}''(t) = -\tilde{\chi}''(-t)$. This, along with the fact that $\tilde{\chi}''(t)$ is pure imaginary, implies that $\chi''(\omega)$ is *real* and *odd* in ω . Eqs. (7.1.12), (7.1.15) and (7.1.16) imply

$$\begin{aligned} \chi(z) &= \int_0^{\infty} dt e^{izt} 2i \int_{-\infty}^{\infty} \frac{d\omega}{2\pi} e^{-i\omega t} \chi''(\omega) \\ &= \int_{-\infty}^{\infty} \frac{d\omega}{\pi} \frac{\chi''(\omega)}{\omega - z} \end{aligned} \quad (7.1.17)$$

for z in the upper half plane. This representation of $\chi(z)$ shows clearly that it only has singularities on the real axis and is, therefore, analytic in the upper half plane. The time-dependent response function $\tilde{\chi}(t)$ is the inverse Laplace transform of $\chi(z)$, which in the present case is an integral along a contour in the upper half plane:

$$\tilde{\chi}(t) = \int_{-\infty+ic}^{\infty+ic} \frac{dz}{2\pi} e^{-itz} \chi(z), \quad (7.1.18)$$

where c is any real number. This result is most easily derived using Eq. (7.1.17). If $t > 0$, the contour $[-\infty + ic, \infty + ic]$ can be closed in the lower half plane, and there is a contribution to the integral at $z = \omega$. If $t < 0$, the contour can be

closed in the upper half plane where $\chi(z)$ is zero. Thus $\tilde{\chi}(t)$ is zero for $t < 0$ and equal to $2i\tilde{\chi}''(t)$ for $t > 0$.

The response function $\chi(\omega)$ relating $\langle \delta\phi(\omega) \rangle$ to $\delta h(\omega)$ can be obtained by using the Fourier representation,

$$\eta(t) = \lim_{\epsilon \rightarrow 0} \int_{-\infty}^{\infty} \frac{d\omega}{2\pi i} e^{i\omega t} \frac{1}{\omega - i\epsilon}, \quad (7.1.19)$$

for the step function. From this and Eq. (7.1.14) we obtain

$$\begin{aligned} \langle \delta\phi(\omega) \rangle &= \int_{-\infty}^{\infty} dt e^{i\omega t} \int_{-\infty}^{\infty} dt' 2i\eta(t-t') \tilde{\chi}''(t-t') \delta h(t') \\ &= \chi(\omega) \delta h(\omega), \end{aligned} \quad (7.1.20)$$

with

$$\chi(\omega) \equiv \lim_{\epsilon \rightarrow 0} \chi(\omega + i\epsilon), \quad (7.1.21)$$

where $\chi(\omega + i\epsilon)$ is given by Eq. (7.1.17) with $z = \omega + i\epsilon$. Thus the response function $\chi(\omega)$ is the limit as z approaches the real axis of the function $\chi(z)$, which is analytic in the upper half plane. When the frequency of the external perturbation tends to zero, $\chi(\omega)$ must reduce to the static susceptibility:

$$\lim_{\omega \rightarrow 0} \chi(\omega) = \int_{-\infty}^{\infty} \frac{d\omega'}{\pi} \frac{\chi''(\omega')}{\omega'} = \frac{\partial \langle \phi \rangle}{\partial h} = \chi. \quad (7.1.22)$$

This is a *sum rule* relating an integral over $\chi''(\omega)$ to a static quantity, the static susceptibility. Because the static quantity is a thermodynamic derivative, this is often called the *thermodynamic sum rule*. It is one of a hierarchy of sum rules which we will discuss in more detail in Sec. 7.6.

The function $\chi(\omega)$, unlike its static limit, has a real part and an imaginary part, as can be seen using the identity

$$\frac{1}{\omega' - \omega - i\epsilon} = \mathcal{P} \frac{1}{\omega' - \omega} + i\pi\delta(\omega - \omega') \quad (7.1.23)$$

(\mathcal{P} signifies the principal part) in Eqs. (7.1.17) and (7.1.20). The result is

$$\chi(\omega) = \chi'(\omega) + i\chi''(\omega), \quad (7.1.24)$$

where

$$\chi'(\omega) = \mathcal{P} \int_{-\infty}^{\infty} \frac{d\omega'}{\pi} \frac{\chi''(\omega')}{\omega' - \omega}. \quad (7.1.25)$$

Since $\chi''(\omega)$ is a real function, $\chi'(\omega)$ is also. Thus, $\chi'(\omega)$ and $\chi''(\omega)$ are, respectively, the real and imaginary parts of the complete response function $\chi(\omega)$. Eq. (7.1.25) is a Kramers-Kronig relation between the real and imaginary parts of $\chi(\omega)$. There is also a complementary expression relating $\chi''(\omega)$ to $-\chi'(\omega)$. This is most easily derived by using the Cauchy representation for $\chi(z)$:

$$\chi(z) = \oint_{\Gamma} \frac{d\zeta}{2\pi i} \frac{\chi(\zeta)}{\zeta - z}, \quad (7.1.26)$$

where the contour Γ is the semicircle shown in Fig. 7.1.1. This equation follows because $\chi(z)$ is analytic in the upper half plane. As we shall see in Sec. 7.7, $\chi(z)$ tends to zero faster than $1/z$, as $z \rightarrow \infty$ in most cases of interest. In this case, the



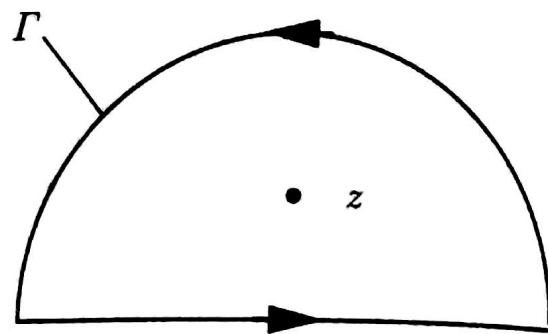


Fig. 7.1.1. Contour in the complex plane for the integral in Eq. (7.1.26).

integral in Eq. (7.1.26) reduces to an integral along a line just above the real axis, i.e., from $-\infty + i\epsilon'$ to $\infty + i\epsilon'$. Then, setting $z = \omega + i\epsilon$ with $\epsilon' < \epsilon$, we obtain

$$\chi(\omega + i\epsilon) = \mathcal{P} \int \frac{d\omega'}{2\pi i} \frac{\chi(\omega' + i\epsilon')}{\omega' - \omega} + \frac{1}{2} \chi(\omega + i\epsilon). \quad (7.1.27)$$

Using Eqs. (7.1.24) and (7.1.25), we obtain

$$\chi''(\omega) = -\mathcal{P} \int \frac{d\omega'}{\pi} \frac{\chi'(\omega')}{\omega' - \omega}. \quad (7.1.28)$$

Because $\chi'(\omega)$ is real and $\chi''(\omega)$ is imaginary, we could also have obtained this result simply by taking the imaginary part of Eq. (7.1.27). The real part of Eq. (7.1.27) yields Eq. (7.1.25). Eqs. (7.1.25) and (7.1.28) are the usual Kramers-Kronig relations. They require slight modification if $\chi(z)$ does not fall off more rapidly than $1/z$ at infinity. Often it is easier to measure $\chi''(\omega)$ (say by an absorption experiment) than $\chi'(\omega)$. If the measurements of $\chi''(\omega)$ are made over a sufficiently large frequency range, the real response can be obtained via Eq. (7.1.25).

The above analysis of the response of a single scalar field applies without change to more general response functions. Thus, the Laplace transform of $\tilde{\chi}_{\phi_i\phi_j}(x, x', t, t')$ satisfies

$$\chi_{\phi_i\phi_j}(x, x', z) = \int_{-\infty}^{\infty} \frac{d\omega}{\pi} \frac{\chi''_{\phi_i\phi_j}(x, x', \omega)}{\omega - z}. \quad (7.1.29)$$

Following Eqs. (7.1.21) and (7.1.24), we have

$$\chi_{\phi_i\phi_j}(x, x', \omega) = \chi'_{\phi_i\phi_j}(x, x', \omega) + i\chi''_{\phi_i\phi_j}(x, x', \omega), \quad (7.1.30)$$

where $\chi'_{\phi_i\phi_j}(x, x', \omega)$ is related to $\chi''_{\phi_i\phi_j}(x, x', \omega)$ by a Kramers-Kronig relation analogous to Eq. (7.1.25). In Sec. 7.6, we will show that $\chi''_{\phi_i\phi_j}(x, x', \omega)$ is real provided ϕ_i and ϕ_j have the same sign under time reversal and there are no external fields or order parameters that break time reversal symmetry. In this case, $\chi'_{\phi_i\phi_j}(x, x', \omega)$ is the real part of and $\chi''_{\phi_i\phi_j}(x, x', \omega)$ the imaginary part of the complex response function $\chi_{\phi_i\phi_j}(x, x', \omega)$. The zero-frequency limit of Eq. (7.1.30) leads to the thermodynamic sum rule,

$$\chi_{\phi_i\phi_j}(x, x') = \frac{\delta \langle \phi_i(x) \rangle}{\delta h_j(x')} = \int_{-\infty}^{\infty} \frac{d\omega}{\pi} \frac{\chi''_{\phi_i\phi_j}(x, x', \omega)}{\omega}. \quad (7.1.31)$$

The spatial Fourier transform in the zero-wavenumber limit of this equation gives, as before, the usual static susceptibility.

7.2 The harmonic oscillator

1 The undamped oscillator

The dynamical properties of condensed matter systems are very often dominated by harmonic oscillator-like modes. These modes include sound waves in fluids, elastic waves and phonons in solids, and spin waves in magnets. Information about the frequency and damping of these modes is contained in both dynamical response and correlation functions. In this section, we will explore in detail the response function of a simple damped harmonic oscillator. Its properties generalize directly to any system with well defined modes at finite frequency.

The Hamiltonian for an undamped oscillator of mass m and spring constant k is

$$\mathcal{H} = \frac{p^2}{2m} + \frac{1}{2}kx^2. \quad (7.2.1)$$

The equations of motion for position $x(t)$ and momentum $p(t)$ are calculated by taking their Poisson brackets with the Hamiltonian:

$$\dot{x} \equiv v = \{\mathcal{H}, x\} = \left(\frac{\partial \mathcal{H}}{\partial p} \frac{\partial x}{\partial x} - \frac{\partial \mathcal{H}}{\partial x} \frac{\partial p}{\partial p} \right) = \frac{p}{m}, \quad (7.2.2)$$

$$\dot{p} = \{\mathcal{H}, p\} = -\frac{\partial \mathcal{H}}{\partial x} = -kx. \quad (7.2.3)$$

The mode structure implied by these equations is obtained by assuming that both $x(t)$ and $p(t)$ are proportional to $e^{-i\omega t}$ and solving the resulting characteristic equation

$$\det \begin{bmatrix} -i\omega & -1/m \\ k & -i\omega \end{bmatrix} = -\omega^2 + k/m = 0. \quad (7.2.4)$$

There are two solutions to this equation:

$$\omega = \pm\omega_0 \equiv \pm\sqrt{k/m}. \quad (7.2.5)$$

Each of these solutions corresponds to a mode of the harmonic oscillator. Note that there is one mode per degree of freedom (x and p). The time dependence of each degree of freedom is governed by a first-order differential equation in time. Thus, there is one mode per first-order differential equation in the equations of motion. This property is quite general and will be encountered again in our study of hydrodynamics of conserved and broken symmetry variables.

The variables $x(t)$ and $p(t)$ have opposite signs under the operation of time reversal (i.e., under change in the sign of time t): $x(-t) = +x(t)$, whereas $p(-t) = -p(t)$. The Hamiltonian [Eq. (7.2.1)] and its associated equations of motion [Eqs. (7.2.2) and (7.2.3)] are invariant under time reversal. The equations of motion relate the time derivative of a variable with one sign under time reversal

to the variable with the opposite sign. These relations lead to the off-diagonal terms in the characteristic determinant and to *real* and *non-zero* solutions to the characteristic equation. This property is again quite general: modes at non-zero real frequency invariably arise from the coupling of variables with opposite sign under time reversal via first-order differential equations in time.

We have taken the trouble to discuss the undamped oscillator in terms of the first-order differential equations determined by the Poisson bracket relations with the Hamiltonian to point out features of such equations that will generalize to more complicated dynamical problems. The first-order Poisson bracket relations can of course be converted into the second-order differential equation of Newton's second law by substituting Eq. (7.2.2) into Eq. (7.2.3). The result is

$$\ddot{x} + \omega_0^2 x = 0. \quad (7.2.6)$$

This equation, like Eqs. (7.2.2) and (7.2.3), is invariant under time reversal and predicts modes with frequencies $\pm\omega_0$.

2 The damped oscillator

To introduce damping in an intuitive way, we place the particle of mass m into a viscous fluid. In constant motion, it experiences a friction force proportional to its velocity at small velocities. This force can be written as

$$f_{\text{vis}} = -\alpha v, \quad (7.2.7)$$

where α is a friction constant with units of [mass]/[time]. Alternatively, $v = -(1/\alpha)f_{\text{vis}}$, and α^{-1} is a *mobility*. For a sphere of radius a moving in a fluid with shear viscosity η , α is given by Stokes's law

$$\alpha = 6\pi\eta a. \quad (7.2.8)$$

We will discuss the meaning of the shear viscosity in the next chapter. The viscosity η has units of [energy \times time]/[volume] (poise) and is of order $n_{\text{fl}}\tau_c T$ in a fluid with number density n_{fl} at temperature T in which the average time between molecular collisions is τ_c . For the moment, both α and η can be regarded as phenomenological parameters. The viscous force law, Eq. (7.2.7), is strictly speaking only valid for a time-independent (i.e., zero frequency) velocity. It must approach zero, as we shall see in Sec. 7.7, at frequencies greater than τ_c^{-1} . For low frequencies or for masses with densities much larger than that of the surrounding fluid (see Problem 7.6), however, it is a very good approximation to the exact force, and we will use it without further apology.

In the presence of a viscous force and an external force f , Newton's equation for a one-dimensional harmonic oscillator becomes

$$\ddot{x} + \omega_0^2 x + \gamma \dot{x} = f/m, \quad (7.2.9)$$

where

$$\gamma = \alpha/m.$$

The characteristic decay time $\gamma^{-1} = m/(6\pi\eta a)$ is of order $m/(an_f\tau_c T)$. If the average interparticle spacing $d = n_f^{-1/3}$ and the mean free path $v\tau_c = (2T/m_f)^{1/2}\tau_c$, where m_f is the mass of a fluid particle, are of the same order, then $\gamma^{-1} \sim (m/m_f)(d/a)\tau_c$. Thus, for all but the most microscopic of particles, $m \gg m_f$ and $\gamma^{-1} \gg \tau_c$.

The viscous force breaks time-reversal invariance in Eq. (7.2.9). Any microscopic Hamiltonian and its associated equations of motion must be invariant under time reversal. In the present case, the microscopic Hamiltonian is that describing the harmonic oscillator *and* all of the degrees of freedom of the fluid in which it moves. The viscous force describes the average effect on the harmonic oscillator of interactions with the many incoherent degrees of freedom of the fluid. In general, any energy in the harmonic oscillator will tend to flow irreversibly into the many modes of the fluid. This is reflected in the sign of the viscous force which leads to the decay of $x(t)$ with time. The irreversible flow of energy into incoherent degrees of freedom is called *dissipation*, and f_{vis} is a dissipative force. We will return in Sec. 7.5 to a description of the harmonic oscillator when it is in thermal equilibrium with the fluid so that it receives energy from as well as transmits energy to the fluid.

The mode structure of the damped harmonic oscillator is determined by the equation

$$-\omega^2 + \omega_0^2 - i\gamma\omega = 0 \quad (7.2.11)$$

with solutions

$$\omega = \pm[\omega_0^2 - (\gamma^2/4)]^{1/2} - i\gamma/2 \equiv \pm\omega_1 - i\gamma/2. \quad (7.2.12)$$

If $\omega_0^2 > \gamma^2/4$, ω_1 is real, and solutions for $x(t)$ will oscillate with frequency ω_1 and decay in time with time constant $\tau = 2/\gamma$. If $\omega_0^2 < \gamma^2/4$, ω_1 is imaginary, and there will be no oscillatory component to $x(t)$. In this case, the oscillator is said to be *overdamped*, with inverse decay times

$$\begin{aligned} \tau_f^{-1} &= \frac{1}{2}\gamma[1 + (1 - 4\omega_0^2\gamma^{-2})^{1/2}] \xrightarrow{\omega_0 \ll \gamma/2} \gamma, \\ \tau_s^{-1} &= \frac{1}{2}\gamma[1 - (1 - 4\omega_0^2\gamma^{-2})^{1/2}] \xrightarrow{\omega_0 \ll \gamma/2} \omega_0^2/\gamma = k/\alpha. \end{aligned} \quad (7.2.13)$$

When $\omega_0^2 \ll \gamma^2/4$, the fast decay time τ_f is much shorter than the slow decay time τ_s . Thus for times long compared to τ_f , the first mode can be neglected. This corresponds in the original equations of motion to neglecting the *inertial* term $m\ddot{x}$. The resulting equation of motion is

$$a\dot{x} = -kx + f. \quad (7.2.14)$$

This approximate equation of motion is often written as

$$\dot{x} = -\frac{k}{\alpha}x + \frac{1}{\alpha}f = -\Gamma \frac{\partial \mathcal{H}_T}{\partial x}, \quad (7.2.15)$$

where $\Gamma = \alpha^{-1}$ and $\mathcal{H}_T = \mathcal{H} - fx$ is the total Hamiltonian including $\mathcal{H}_{\text{ext}} = -fx$. It is very useful in describing the dynamics of systems, such as polymers in solution, dominated by viscous effects.

3 The response function

The frequency-dependent response of x to an external force is easily calculated using Eqs. (7.1.20) and (7.2.9):

$$\chi(\omega) = \frac{x(\omega)}{f(\omega)} = \frac{1}{m} \frac{1}{-\omega^2 + \omega_0^2 - i\omega\gamma}. \quad (7.2.16)$$

The denominator of this equation is precisely the characteristic equation [Eq. (7.2.11)] determining the mode structure. Thus, *there are poles in $\chi(\omega)$ at complex mode frequencies of the oscillator*. This result is quite general. A static external force f will lead to an equilibrium displacement of $x = f/k$. This result is correctly described by the zero-frequency limit of Eq. (7.2.16):

$$\lim_{\omega \rightarrow 0} \chi(\omega) = \frac{1}{m\omega_0^2} = \frac{1}{k} = \frac{\partial x}{\partial f} = \chi. \quad (7.2.17)$$

At high frequency, $\chi(\omega)$ is negative and falls off as ω^{-2} with a coefficient that depends only on the mass:

$$\lim_{\omega \rightarrow \infty} \chi(\omega) = -\frac{1}{m\omega^2}. \quad (7.2.18)$$

We will reconsider this result in Sec. 7.6.

The imaginary part of the response function is

$$\begin{aligned} \chi''(\omega) &= \frac{1}{m} \frac{\omega\gamma}{(\omega^2 - \omega_0^2)^2 + (\omega\gamma)^2} \\ &= \frac{1}{2m\omega_1} \left[\frac{\gamma/2}{(\omega - \omega_1)^2 + (\gamma/2)^2} - \frac{\gamma/2}{(\omega + \omega_1)^2 + (\gamma/2)^2} \right] \\ &\xrightarrow{\gamma \rightarrow 0} \frac{\pi\omega}{m|\omega|} \delta(\omega^2 - \omega_0^2) = \frac{\pi}{2m\omega_0} [\delta(\omega - \omega_0) - \delta(\omega + \omega_0)]. \end{aligned} \quad (7.2.19)$$

We see from this that $\chi''(\omega)$ is *real* and *odd* in ω , and it has peaks with Lorentzian line shapes centered at $\omega = \pm\omega_1$ (when ω_1 is real) with half-width at half-maximum equal to $\gamma/2$. Furthermore, when the viscous damping is set to zero, $\chi''(\omega)$ has delta-function spikes at the frequencies $\pm\omega_0$ of the undamped oscillator. The real part of the response function is

$$\chi'(\omega) = \frac{1}{m} \frac{\omega_0^2 - \omega^2}{(\omega^2 - \omega_0^2)^2 + \omega^2\gamma^2}. \quad (7.2.20)$$

$\chi'(\omega)$ is positive for $\omega < \omega_0$, tending to $1/k$ as $\omega \rightarrow 0$; it is negative for $\omega > \omega_0$, tending to $-1/(m\omega^2)$ as $\omega \rightarrow \infty$; and it is zero at exactly $\omega = \omega_0$. $\chi''(\omega)$ and $\chi'(\omega)$ are plotted in Fig. 7.2.1.

The steady-state time dependence of $x(t)$ in the presence of a force $f(t) = f_0 \cos \omega t$ is obtained from the real part of $\chi(\omega)f_0 e^{-i\omega t} = |\chi(\omega)| f_0 e^{-i(\omega t - \phi)}$:

$$x(t) = f_0 |\chi(\omega)| \cos[\omega t - \phi(\omega)], \quad (7.2.21)$$

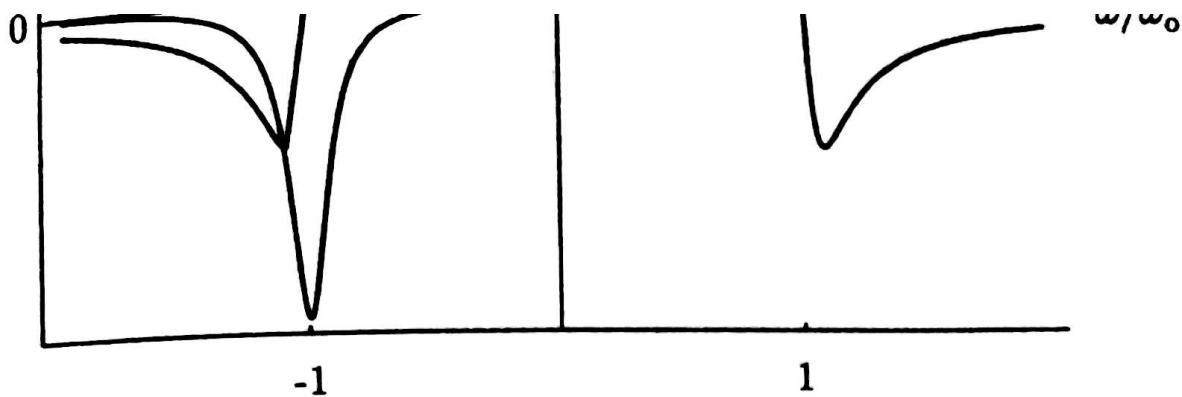


Fig. 7.2.1. $\chi''(\omega)$ and $\chi'(\omega)$ for a harmonic oscillator when ω_1 is real.

where

$$|\chi(\omega)| = \frac{1}{m} \frac{1}{[(\omega^2 - \omega_0^2)^2 + \omega^2 \gamma^2]^{1/2}} \quad (7.2.22)$$

and

$$\tan \phi(\omega) = \frac{\chi''(\omega)}{\chi'(\omega)} = \frac{\omega \gamma}{\omega_0^2 - \omega^2}. \quad (7.2.23)$$

Thus, the amplitude of $x(t)$ reaches a maximum for driving frequencies in the vicinity of the natural frequency ω_0 of the oscillator. Furthermore, the phase shift describing the degree to which $x(t)$ lags behind $f(t)$ passes through $\pi/2$ at precisely ω_0 . $|\chi(\omega)|$ and $\phi(\omega)$ are plotted in Fig. 7.2.2.

In the overdamped case, the imaginary part of $\chi(\omega)$ is peaked at the origin rather than at nonzero frequencies. In the extreme overdamped limit at frequencies $\omega_{rf} \ll 1$ where inertial terms can be ignored,

$$\chi(\omega) = \frac{1}{m} \frac{1}{\omega_0^2 - i\omega\gamma} = \chi \frac{1}{1 - i\omega\tau_s} \quad (7.2.24)$$

and

$$\frac{\chi''(\omega)}{\omega} = \chi \frac{\tau_s^{-1}}{\omega^2 + \tau_s^{-2}}. \quad (7.2.25)$$

Thus, $\chi''(\omega)/\omega$ is a Lorentzian centered at the origin with width $\tau_s^{-1} = \Gamma\chi$, as shown in Fig. 7.2.3. Its integral over ω trivially satisfies the thermodynamic sum rule, Eq. (7.1.22).

The high frequency behavior of $\chi(z)$ is determined by the frequency moments of $\chi''(\omega)$, as can be seen by expanding the integral representation [Eq. (7.1.17)] in

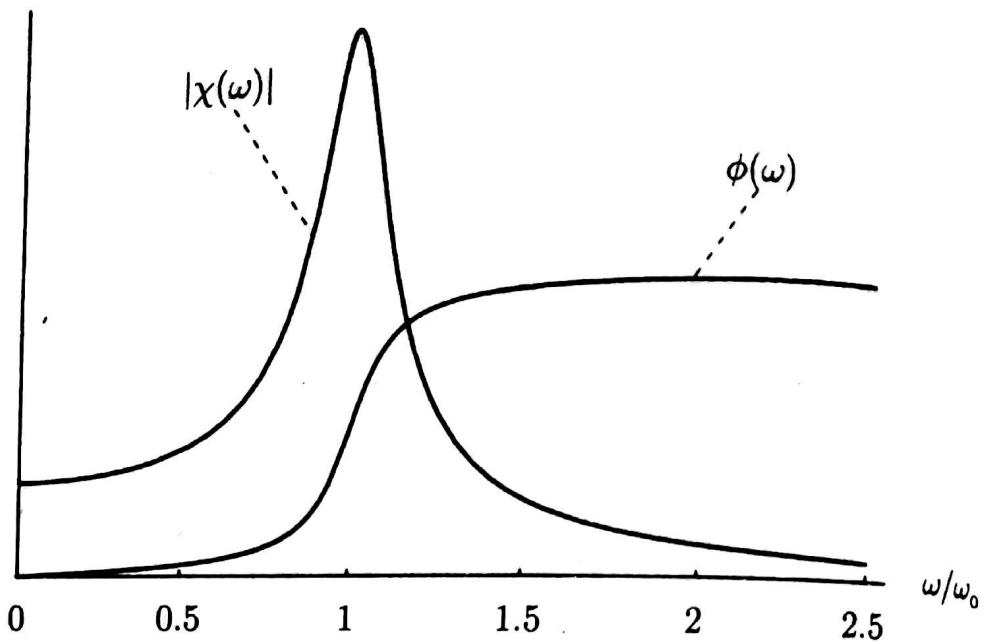


Fig. 7.2.2. The amplitude and phase functions $|\chi(\omega)|$ and $\phi(\omega)$ for a harmonic oscillator.

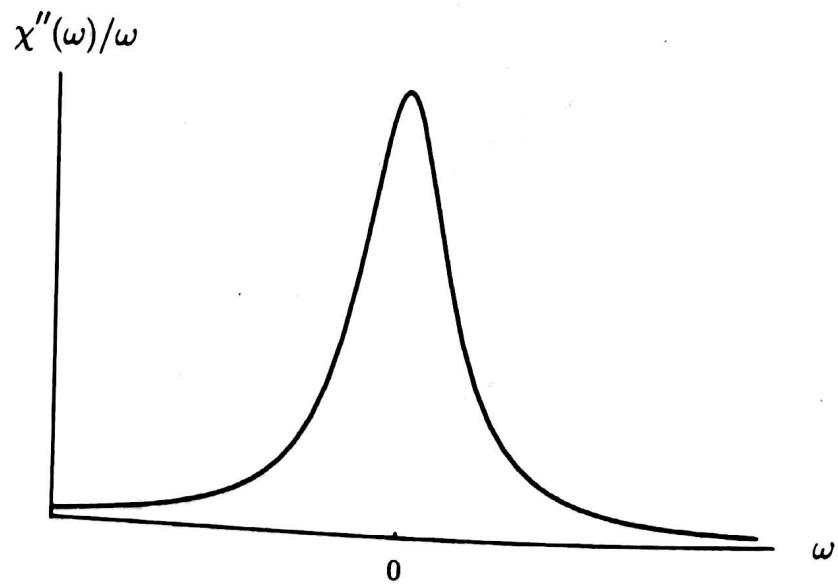


Fig. 7.2.3. $\chi''(\omega)/\omega$ in the overdamped limit when $\tau_f \ll \tau_s$.

powers of $1/z$:

$$\begin{aligned} \chi(z) &= -\frac{1}{z} \int \frac{d\omega}{\pi} \frac{\chi''(\omega)}{1 - \omega/z} \\ &= -\frac{1}{z} \int \frac{d\omega}{\pi} \omega \frac{\chi''(\omega)}{\omega} - \frac{1}{z^2} \int \frac{d\omega}{\pi} \omega^2 \frac{\chi''(\omega)}{\omega} + \dots \end{aligned} \quad (7.2.26)$$

We shall see in Secs. 7.5 and 7.6 that $\chi''(\omega) \equiv \chi''_{xx}(\omega)$ is related via the fluctuation-dissipation theorem to $S(\omega) \equiv S_{xx}(\omega)$ measuring fluctuations in x via $\chi''(\omega)/\omega = S(\omega)/2T$. Frequency moments of $S(\omega)$ are simply equal-time correlation functions of $x(t)$ and its time derivatives, which are all finite:

$$\int \frac{d\omega}{2\pi} \omega^n S(\omega) = i^n \left\langle \left(\frac{d}{dt} \right)^n x(t)x(t') \right\rangle_{t=t'} = T \int \frac{d\omega}{2\pi} \omega^n \frac{\chi''(\omega)}{\omega}. \quad (7.2.27)$$

This equation says that all moments of $\chi''(\omega)/\omega$ exist and are finite. The odd n moments are all zero because $\chi''(\omega)$ is odd in ω . The first two nonzero moments of the phenomenological form for $\chi''(\omega)$ in Eq. (7.2.19) are finite. The zeroth moment is simply χ , as required by the thermodynamic sum rule. The second moment is $-\langle \dot{x}(t)x(t) \rangle / T = \langle (\dot{x}(t))^2 \rangle / T = 1/m$ because the average kinetic energy $m\langle v^2 \rangle / 2$ is $T/2$. This agrees with Eq. (7.2.18) and the high-frequency expansion Eq. (7.2.27). The higher moments of Eq. (7.2.19) are infinite. The problem is that the phenomenological damping parameter γ does not provide a correct description of high-frequency behavior. In order for all moments of $\chi''(\omega)/\omega$ to exist, γ must be replaced by a function $\gamma(z)$ of complex z that tends to zero more rapidly than any power of z . An often-used phenomenological form for γ is $\gamma(z) = \gamma/(1 - iz\tau)$, where τ is some microscopic collision time. This form leads to a finite fourth moment of $\chi''(\omega)/\omega$ but to infinite higher moments.

4 Dissipation

In steady state, the external force does work on the oscillator that is eventually dissipated as heat in the viscous fluid. The rate at which the external force does work is

$$\frac{dW}{dt} = f(t)\dot{x}(t). \quad (7.2.28)$$

Since in the steady state, both $f(t)$ and $\dot{x}(t)$ are periodic functions of t with period $T = 2\pi/\omega$, the average power dissipated is

$$P = \frac{1}{T} \int_0^T dt f(t)\dot{x}(t) = -\frac{1}{T} \int_0^T dt x(t)f'(t). \quad (7.2.29)$$

Using Eq. (7.2.21) for $x(t)$, we obtain

$$\begin{aligned} P &= -\frac{f_0^2}{T} \int_0^T dt \omega |\chi(\omega)| \cos \omega t \sin [\omega t - \phi(\omega)] \\ &= \frac{1}{2} \omega f_0^2 |\chi(\omega)| \sin \phi(\omega) = \frac{1}{2} f_0^2 \omega \chi''(\omega). \end{aligned} \quad (7.2.30)$$

Thus, we arrive at the very important result that the rate of energy dissipation is proportional to $\omega \chi''(\omega)$. For this reason, $\chi''(\omega)$ is sometimes referred to as the dissipation. Note that $\chi''(\omega)$ is odd in ω so that $\omega \chi''(\omega)$ is even. In thermodynamic equilibrium, the power dissipation must be positive, implying that $\omega \chi''(\omega)$ must be positive. The positivity of $\omega \chi''(\omega)$ in the present case is associated with the positivity of the dissipative coefficient γ . Its sign was chosen so that the viscous force opposes motion of the oscillator mass. This sign is consistent with energy transfer to the incoherent degrees of freedom of the fluid and to positive power absorption.

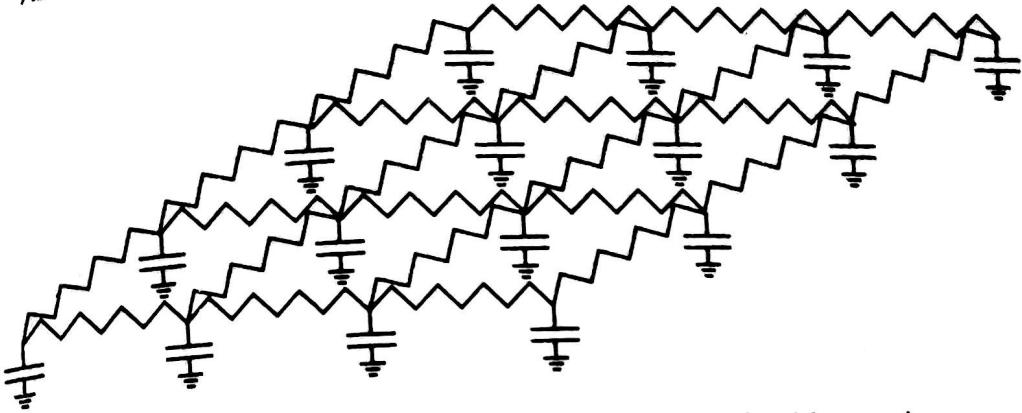


Fig. 7.4.7. Schematic representation of a resistor network with capacitances to ground.

where ΔE is the barrier energy. For temperatures much less than ΔE , τ becomes very long. In some situations, it can be so long that the probability that a hop occurs in the time scale of a laboratory experiment can be vanishingly small.

It is interesting to observe that Eq. (7.4.47) is precisely the equation governing the voltage in a resistor network consisting of sites connected by resistances of conductance $\sigma_{l'}$ with capacitance to ground C . The equation for the voltage $V(l, t)$ at site l ,

$$C \frac{\partial V(l, t)}{\partial t} = \sum_{l'} \sigma_{l'} [V(l', t) - V(l, t)], \quad (7.4.53)$$

is determined by Kirchhoff's laws. When resistors connect only nearest neighbor sites, $\sigma_{l'} = \sigma \gamma_{l'}$, and Eq. (7.4.53) reduces to Eq. (7.4.47) with $\tau = (C/\sigma)$. Resistor networks are often used to model diffusive transport problems (see Fig. 7.4.7).

7.5 Langevin theory

1 Random forces and thermal equilibrium

The erratic motion of a Brownian particle is due to collisions with molecules in the fluid in which it moves. These collisions allow an exchange of energy between the fluid at temperature T and the Brownian particle and for the establishment of thermal equilibrium between the degrees of freedom of the particle and those of the fluid. This means that the mean-square of each component of the velocity of the Brownian particle averaged over a sufficiently long time must have the value T/m predicted by Boltzmann statistics. This average is maintained through constant collisions.

To understand how thermal equilibrium can be brought about by random forces, let us focus on a particle diffusing in one dimension. Individual molecules of the fluid collide with the diffusing particle in a random fashion and exert a force whose time average is simply the viscous force $-\alpha v$ introduced in Eq. (7.2.7).

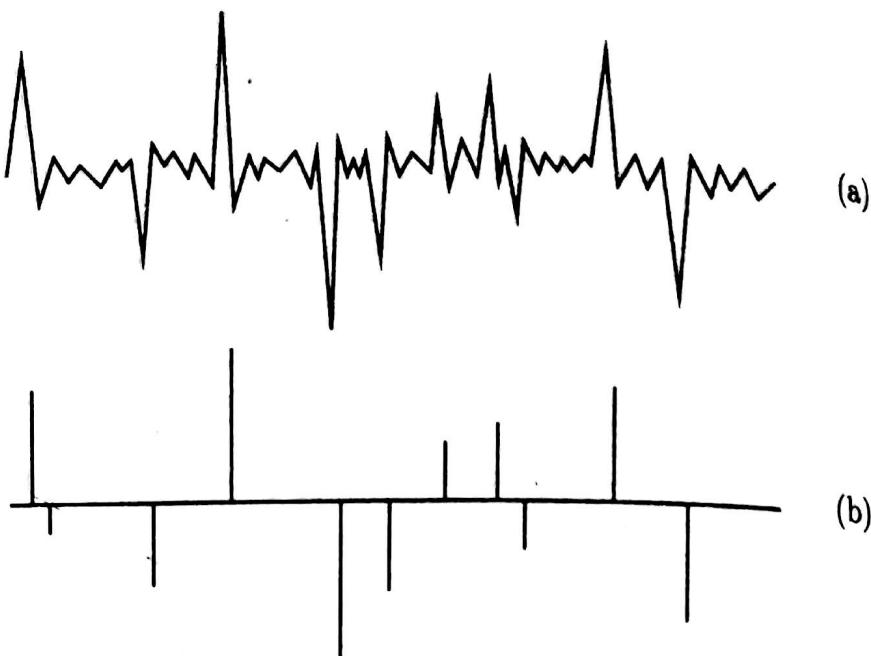


Fig. 7.5.1. (a) Schematic representation of the random force $\zeta(t)$ as a function of time. (b) $\zeta(t)$ approximated by a series of random impulses.

We can, therefore, break the force exerted on the particle by the fluid into two parts: the average viscous force $-\alpha v$ and a random force $\zeta(t)$ whose time average is zero.

This random force is well approximated by a sequence of independent impulses of random sign and magnitude as shown in Fig. 7.5.1; it is a stochastic process whose time average is zero. Rather than considering averages over time, we will consider averages over the ensemble of possible random forces and represent averages over this ensemble with brackets, $\langle \rangle$, in the same way that we represented averages over equilibrium thermodynamic ensembles. We will choose the ensemble of random forces so that averages over it are identical to averages over an equilibrium ensemble. Thus, we have

$$\langle \zeta(t) \rangle = 0. \quad (7.5.1)$$

If each impulse is considered an independent random event, then the probability distribution for $\zeta(t)$ is independent of $\zeta(t')$ for $t' \neq t$. This implies

$$\langle \zeta(t) \zeta(t') \rangle = A \delta(t - t') \quad (7.5.2)$$

is local in time. A is a constant that remains to be determined. Finally, $\zeta(t)$ in the independent impulse approximation is the sum of a large number of independent functions. The central limit theorem then implies that the probability distribution for $\zeta(t)$ is Gaussian with a width determined by its variance, Eq. (7.5.2):

$$P[\zeta(t)] = \frac{1}{\sqrt{2\pi A}} e^{-\frac{1}{A} \int dt \zeta^2(t)}. \quad (7.5.3)$$

Random forces such as $\zeta(t)$ give rise to erratic or *noisy* behavior of observables and are often referred to as *noise sources*, especially in the context of electrical circuits.

Eqs. (7.5.1) to (7.5.3) provide a sufficiently precise characterization of the stochastic collision force $\zeta(t)$ to allow us to discuss the establishment of thermal equilibrium. The detailed form of $\zeta(t)$ is determined by the temporal statistics of the molecules of the fluid. Thus, one expects the approximation of independent random events to break down for time differences $t - t'$ less than a characteristic collision time τ_c of the fluid. As discussed in Sec. 7.3, however, the characteristic time γ^{-1} for motion of the Brownian particle is much larger than τ_c , and the independent collision approximation will be very good for times of interest.

The power spectrum of $\zeta(t)$, or the Fourier transform of $\langle \zeta(t)\zeta(t') \rangle$,

$$I(\omega) \equiv C_{\zeta\zeta}(\omega) = A \quad (7.5.4)$$

is independent of ω in the independent collision approximation. A noise source with a frequency-independent power spectrum is called a *white noise source*.

2 Correlation functions for diffusion

We will now show how knowledge of statistics of the stochastic force allows us to calculate correlation functions rather than response functions (Langevin 1908). In the absence of external forces, the equation of motion of a diffusing particle is

$$m\ddot{v} + \alpha v = \zeta(t). \quad (7.5.5)$$

The solution to this equation for $v(t)$ has a homogeneous part determined by initial conditions and an inhomogeneous part proportional to $\zeta(t)$. Since the homogeneous part, which depends on initial conditions, will decay to zero in a time of order γ^{-1} , the long-time properties of $v(t)$ will be determined entirely by the inhomogeneous part and be independent of initial conditions. In Fourier space the inhomogeneous part of v is simply

$$v(\omega) = \frac{\zeta(\omega)}{-i\omega m + \alpha}. \quad (7.5.6)$$

Using Eqs. (7.1.7) and (7.5.4), we can calculate $C_{vv}(\omega)$ by averaging $v(\omega)v(-\omega)$ over the random forces:

$$C_{vv}(\omega) = \frac{I(\omega)}{|-i\omega m + \alpha|^2} = \frac{A}{m^2[\omega^2 + \gamma^2]}. \quad (7.5.7)$$

The constant A characterizing the variance of the random force is as yet unspecified. We can now use Eq. (7.5.7) to calculate the instantaneous mean-square velocity in terms of A and thereby determine the value of A needed to ensure thermal equilibrium:

$$\langle v^2 \rangle = \int \frac{d\omega}{2\pi} C_{vv}(\omega) = \frac{A}{2m\alpha}. \quad (7.5.8)$$

In thermal equilibrium $\langle v^2 \rangle = T/m$, and we conclude

$$A = 2\alpha T = 2m\gamma T \quad \text{and} \quad \langle \zeta(t)\zeta(t') \rangle = 2\alpha T \delta(t - t'). \quad (7.5.9)$$

Thus, the amplitude of white noise fluctuations is fixed by the requirements of thermal equilibrium.

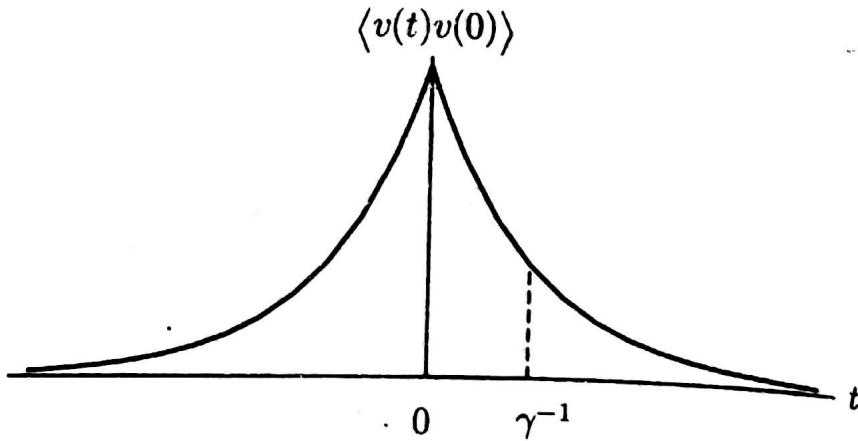


Fig. 7.5.2. The velocity correlation function $\langle v(t)v(0) \rangle$ showing exponential decay to zero.

The correlation function $C_{vv}(\omega)$ determines $C_{vv}(t, t') = \langle v(t)v(t') \rangle$ as well as the instantaneous average $\langle v^2 \rangle$. Neglect of the homogeneous term in the solution for $v(\omega)$ is only valid for times long compared to γ^{-1} . The Fourier transform of $C_{vv}(\omega)$ in Eq. (7.5.7) therefore gives the function $C_{vv}(t) = \lim_{\tau \rightarrow \infty} C_{vv}(\tau + t, \tau)$:

$$C_{vv}(t - t') = \int \frac{d\omega}{2\pi} e^{-i\omega(t-t')} C_{vv}(\omega) = \frac{T}{m} e^{-\gamma|t-t'|}. \quad (7.5.10)$$

This equation shows that $v(t)$ and $v(0)$ become decorrelated for times greater than γ^{-1} , and that $\langle v(t)v(0) \rangle$ is of order the equal-time thermal average T/m for times less than γ^{-1} , as shown in Fig. 7.5.2.

The Fourier transform $x(\omega)$ of position is $v(\omega)/(-i\omega)$. Thus, we can determine the position correlation function,

$$C_{xx}(\omega) = \frac{2\gamma T}{m\omega^2(\omega^2 + \gamma^2)}, \quad (7.5.11)$$

from Eq. (7.5.7) for $C_{vv}(\omega)$. The integral of $C_{xx}(\omega)$ over ω gives the mean-square displacement $\langle x^2(t) \rangle$. This integral is divergent because of the extra factor of ω^2 in the denominator of $C_{xx}(\omega)$, and we correctly conclude that $\langle x^2(t) \rangle$ is infinite. This result is analogous to the result, discussed in Chapter 6, that the mean-square of an elastic variable is infinite below its lower critical dimension. The average $\langle [\Delta x(t) - x(t')]^2 \rangle \equiv \langle [\Delta x(t - t')]^2 \rangle$ is, however, finite. Using Eq. (7.5.11), we obtain

$$\begin{aligned} \langle [\Delta x(t)]^2 \rangle &= \int \frac{d\omega}{2\pi} 2C_{xx}(\omega)[1 - e^{-i\omega t}] \\ &= \frac{4T}{m\gamma} \int \frac{d\omega}{2\pi} \left(\frac{1}{\omega^2} - \frac{1}{\omega^2 + \gamma^2} \right) (1 - e^{-i\omega t}). \end{aligned} \quad (7.5.12)$$

The second term in this expression is easily evaluated by contour integration; the first term, which is proportional to $|t|$, can be obtained from the second by taking the limits $\gamma \rightarrow 0$. The result is

$$\langle [\Delta x(t)]^2 \rangle = 2D \left(|t| - \frac{1 - e^{-\gamma|t|}}{\gamma} \right), \quad (7.5.13)$$

where we used the Einstein relation $D = T/m\gamma$. For times $t \gg \gamma^{-1}$, this equation reduces to the result, Eq. (7.4.11), predicted by the diffusion equation in one spatial dimension. At short times,

$$\langle [\Delta x(t)]^2 \rangle \sim D\gamma t^2 = \langle v^2 \rangle t^2, \quad (7.5.14)$$

indicating that the Brownian particle moves ballistically in this limit.

The Einstein relation [Eq. (7.4.26)] can be reexpressed in various ways in terms of the velocity correlation function. First we have

$$\begin{aligned} \langle [\Delta x(t)]^2 \rangle &= \left\langle \left(\int_0^t dt' v(t') \right)^2 \right\rangle = \int_0^t dt_1 \int_0^t dt_2 C_{vv}(t_1 - t_2) \\ &= 2 \int_0^t dt_1 \int_0^{t_1} dt_2 C_{vv}(t_1 - t_2) = 2 \int_0^t dt_1 \int_0^{t_1} d\tau C_{vv}(\tau) \\ &= 2 \int_0^t (t - \tau) C_{vv}(\tau) d\tau, \end{aligned} \quad (7.5.15)$$

where the final expression in this equation can be obtained from the preceding line by integrating by parts. From this, we can easily calculate a time-dependent diffusion constant,

$$\begin{aligned} D(t) &= \frac{1}{2} \frac{d}{dt} \langle (\Delta x(t))^2 \rangle, \\ &= \int_0^t d\tau C_{vv}(\tau), \end{aligned} \quad (7.5.16)$$

that approaches the diffusion constant,

$$D = \int_0^\infty d\tau C_{vv}(\tau) = \frac{1}{2} C_{vv}(\omega = 0), \quad (7.5.17)$$

in the infinite time limit. The last expression could have been obtained directly from Eqs. (7.5.7), (7.5.9), and the relation $D = T/(m\gamma)$.

3 Short-time behavior

In the above analysis, we argued we could neglect initial conditions if we are interested in long-time limits and thermal equilibrium. Initial conditions are, however, often of interest and can be treated almost as easily as the long-time limits. The solution to Eq. (7.5.5) for $v(t)$ subject to the boundary condition that $v(t = 0) = v_0$ is

$$v(t) = v_0 e^{-\gamma t} + \int_0^t dt_1 e^{-\gamma(t-t_1)} \zeta(t_1)/m. \quad (7.5.18)$$

The average velocity is then

$$\langle v(t) \rangle = v_0 e^{-\gamma t}.$$

The velocity correlation function is

$$\begin{aligned}\langle v(t)v(t') \rangle &= v_0^2 e^{-\gamma(t+t')} + \int_0^t dt_1 \int_0^{t'} dt_2 e^{-\gamma(t-t_1)-\gamma(t'-t_2)} \frac{2\gamma T}{m} \delta(t_1 - t_2) \\ &= \left(v_0^2 - \frac{T}{m} \right) e^{-\gamma(t+t')} + \frac{T}{m} e^{-\gamma|t-t'|},\end{aligned}\quad (7.5.20)$$

and the variance of the velocity is

$$\Delta_v(t) = \langle [v(t) - \langle v(t) \rangle]^2 \rangle = \frac{T}{m} (1 - e^{-2\gamma|t|}), \quad (7.5.21)$$

where we used Eq. (7.5.2) for $\langle \zeta(t)\zeta(t') \rangle$ with $A = 2m\gamma T$. These equations show that the velocity correlation function tends to the thermal equilibrium result of Eq. (7.5.10) for times t and/or t' much greater than the decay time γ^{-1} , regardless of the initial velocity v_0 . Furthermore, if the initial velocity is averaged over an equilibrium Maxwell-Boltzmann distribution at temperature T , then $\langle v(t)v(t') \rangle$ has its thermal equilibrium form at all times.

The displacement variable $x(t)$ can be obtained from the velocity by simple integration:

$$x(t) = x_0 + \int_0^t v(t_1) dt_1, \quad (7.5.22)$$

where $x(t=0) = x_0$. From this and Eq. (7.5.19), we can calculate the average displacement as a function of time:

$$\langle x(t) \rangle = x_0 + (v_0/\gamma)(1 - e^{-\gamma t}). \quad (7.5.23)$$

Similarly, we can calculate correlations in the displacement at different times $t > 0$ and $t' > 0$:

$$\langle [x(t) - x(t')]^2 \rangle = \left\langle \left(\int_{t'}^t dt_1 v(t_1) \right)^2 \right\rangle. \quad (7.5.24)$$

Using Eq. (7.5.20) for the velocity correlation function, we obtain

$$\begin{aligned}\langle [x(t) - x(t')]^2 \rangle &= \left(v_0^2 - \frac{T}{m} \right) \frac{1}{\gamma^2} \left(e^{-\gamma t'} - e^{-\gamma t} \right)^2 \\ &\quad + \frac{2T}{\gamma m} \left[|t - t'| - \frac{1}{\gamma} (1 - e^{-\gamma|t-t'|}) \right].\end{aligned}\quad (7.5.25)$$

If both t and t' are much greater than γ^{-1} , this reduces to Eq. (7.5.13) independent of v_0 . If, on the other hand, both t and t' are much less than γ^{-1} , $\langle [x(t) - x(t')] \rangle = v_0^2(t - t')^2$, i.e., the Brownian particle moves ballistically with the specified initial velocity. The average of Eq. (7.5.25) over an equilibrium ensemble of initial velocities also reduces to Eq. (7.5.13). The average $\langle [x(t) - x_0]^2 \rangle$ is obtained from Eq. (7.5.25) by setting $t' = 0$ so that $x(t') = x_0$. Finally, we can calculate the variance of the position,

$$\begin{aligned}\Delta_x(t) &= \langle [x(t) - \langle x(t) \rangle]^2 \rangle \\ &= 2 \frac{T}{\gamma m} \left[t - \frac{1}{\gamma} (1 - e^{-\gamma t}) - \frac{1}{2\gamma} (1 - e^{-\gamma t})^2 \right].\end{aligned}\quad (7.5.26)$$

Note that $\Delta_x(t)$ is not equal to $\langle [\Delta x(t)]^2 \rangle$ in Eq. (7.5.13) because it explicitly retains the memory that initial motion was ballistic rather than diffusive. The variance, $\langle [x(t) - x(t') - \langle x(t) - x(t') \rangle]^2 \rangle$ does not, and is in fact identical to $\langle [\Delta x(t - t')]^2 \rangle$.

The noise $\zeta(t)$ is a Gaussian random variable. Both $v(t)$ and $x(t)$ are linear functions of $\zeta(t)$. Since linear functions of Gaussian random variables are also Gaussian random variables, the probability distribution functions for $v(t)$ and $x(t)$ are Gaussian and are completely determined by the expectation values and variances of these variables. We leave a formal derivation of these results to the problems at the end of the chapter.

4 Fluctuation-dissipation theorem for the harmonic oscillator

A harmonic oscillator in a viscous fluid, like a free particle in the same fluid, will reach thermal equilibrium as a result of collisions with the fluid molecules. This means that the average energy per degree of freedom of the oscillator will be $T/2$, or that $\langle x^2(t) \rangle = T/(m\omega_0^2)$ and $\langle v^2(t) \rangle = T/m$. The equation of motion for an oscillator in a random force is Eq. (7.2.9), with f replaced by $\zeta(t)$. In the long-time limit, we need only concern ourselves with the inhomogeneous solution to this equation, which as a function of frequency is

$$x(\omega) = \chi(\omega)\zeta(\omega) = \frac{\zeta(\omega)}{m[-\omega^2 + \omega_0^2 - i\omega\gamma]}, \quad (7.5.27)$$

where $\chi(\omega)$ is the response function of Eq. (7.2.16). The nature of the random force $\zeta(t)$ does not depend on whether our particle is attached to a spring or not. The noise correlation function $C_{\zeta\zeta}(\omega)$ is thus independent of ω_0 and has the same form as for $\omega_0 = 0$. From this, and the correlation function for $\zeta(t)$, we obtain

$$C_{xx}(\omega) = 2m\gamma T |\chi(\omega)|^2 = \frac{2\gamma T}{m} \frac{1}{(\omega^2 - \omega_0^2)^2 + \omega^2\gamma^2}. \quad (7.5.28)$$

We leave it as an exercise to verify that $\langle x^2 \rangle$ obtained by integrating this function over ω is, in fact, $T/(m\omega_0^2)$. Then, using Eq. (7.2.19) and the fact that $\langle x(t) \rangle = 0$ so that $C_{xx}(\omega) = S_{xx}(\omega)$, we obtain the very important result

$$\chi''_{xx}(\omega) = \frac{1}{2}\beta\omega S_{xx}(\omega), \quad (7.5.29)$$

where $\beta \equiv 1/T$. This is the classical *fluctuation-dissipation theorem*, the complete quantum mechanical version of which was originally derived by Callen and Welton (1952). It relates $\chi''_{xx}(\omega)$, which, as we saw in Sec. 7.3, is proportional to the rate at which work done by external forces is dissipated as heat, to the Fourier transform of the mean-square fluctuation $\langle [x(t) - \langle x(t) \rangle][x(0) - \langle x(0) \rangle] \rangle$. Thus, absorption or response experiments that probe $\chi''_{xx}(\omega)$ contain the same information as scattering or related measurements that probe $S_{xx}(\omega)$. Although we derived the fluctuation-dissipation theorem for a single classical oscillator in equilibrium in a viscous fluid, the theorem applies to all response and correlation functions of systems in equilibrium. Furthermore, it is applicable, as we shall

see in the next section, to situations where the classical approximation is not applicable.

5 The Fokker-Planck and Smoluchowski equations

In the preceding discussion, we focused on the correlation functions of velocity and position. The Langevin equations can be used to derive not only these correlation functions but also the equations determining the entire probability distribution function for these variables. The equation for the velocity probability function for a diffusing particle is called the Fokker-Planck equation; its generalization to displacement and other variables is generally called the Smoluchowski equation. These equations show how probability distributions decay to Maxwell-Boltzmann distributions describing thermal equilibrium at long times. They are applicable not only for harmonic Hamiltonians but also for anharmonic Hamiltonians containing other than quadratic terms in the fundamental variables. This latter result is important because it implies that Langevin equations provide a correct phenomenological description of dynamics for all arbitrarily complicated interacting systems as well as for the simple free particles and harmonic oscillator we have considered so far.

We will begin our derivation of the Fokker-Planck equation by rewriting the equation of motion in terms of the momentum p to produce a form that will most easily generalize to other variables:

$$\frac{dp}{dt} = -\gamma p + \zeta = -\Gamma \frac{\partial \mathcal{H}}{\partial p} + \zeta, \quad (7.5.30)$$

where $\Gamma \equiv \alpha = \gamma m$ and

$$\langle \zeta(t)\zeta(t') \rangle = 2\Gamma T \delta(t - t'). \quad (7.5.31)$$

This equation is now in a form that could in general include anharmonicities in the Hamiltonian \mathcal{H} .

We now consider the probability

$$P(p, t | p_0, t_0) = \langle \delta(p - p(t)) \rangle_{p_0, t_0} \quad (7.5.32)$$

that a diffusing particle has momentum p at time t , given that it had momentum p_0 at time t_0 . The probability that the particle has a momentum p at time $t + \Delta t$ is

$$P(p, t + \Delta t | p_0, t_0) = \int dp' P(p, t + \Delta t | p', t) P(p', t | p_0, t_0). \quad (7.5.33)$$

The conditional probability

$$P(p, t + \Delta t | p', t) = \langle \delta(p - p(t + \Delta t)) \rangle_{p', t} \quad (7.5.34)$$

can be calculated from the equation of motion for $p(t)$:

$$p(t + \Delta t) = p' - \Gamma \frac{\partial \mathcal{H}}{\partial p'} \Delta t + \int_t^{t+\Delta t} dt' \zeta(t'). \quad (7.5.35)$$

The average of the third term in this equation is zero; its square, however, is proportional to Δt :

$$\int_t^{t+\Delta t} dt_1 \int_t^{t+\Delta t} dt_2 \langle \zeta(t_1) \zeta(t_2) \rangle = 2\Gamma T \Delta t. \quad (7.5.36)$$

Terms higher order in $\int dt \zeta(t)$ are higher order in Δt because $\zeta(t)$ is a Gaussian random variable and averages of products of $\zeta(t)$ can be expressed as products of the variance $\langle \zeta(t_1) \zeta(t_2) \rangle$. Thus, for example $\langle (\int dt \zeta(t))^4 \rangle \sim (\int dt_1 dt_2 \langle \zeta(t_1) \zeta(t_2) \rangle)^2 \sim (\Delta t)^2$. Using this result, we now expand the left hand side of Eq. (7.5.34) to first order in Δt :

$$\langle \delta(p - p(t + \Delta t)) \rangle_{p', t} = \left[1 + \Delta t \Gamma \frac{\partial \mathcal{H}}{\partial p'} \frac{\partial}{\partial p} + \Delta t \Gamma T \frac{\partial^2}{\partial p'^2} \right] \delta(p - p'). \quad (7.5.37)$$

This result and Eq. (7.5.32) then allow us to calculate

$$\frac{\partial P}{\partial t} = T \Gamma \frac{\partial}{\partial p} \left[\left(\frac{1}{T} \frac{\partial \mathcal{H}}{\partial p} + \frac{\partial}{\partial p} \right) P \right]. \quad (7.5.38)$$

The left hand side of this equation is zero when

$$P = P_{eq} \sim e^{-\mathcal{H}(p)/T}, \quad (7.5.39)$$

i.e., when P has the equilibrium form predicted by Maxwell-Boltzmann statistics. In fact, P decays in time to P_{eq} .

The probability distribution for any variable ϕ satisfying a linear differential equation in time of the form of Eq. (7.5.30) will satisfy Eq. (7.5.38) with p replaced by ϕ . For example, the equation for an overdamped oscillator Eq. (7.2.15) has exactly the same form of Eq. (7.5.30). The equation for $P(x, t)$, which is identical to Eq. (7.5.38) with p replaced by x , is the Smoluchowski equation.

The probability distribution [Eq. (7.5.32)] appearing in the Fokker-Planck equation [Eq. 7.5.38] is for the momentum subject to the boundary condition $p(t = 0) = p_0$. We have calculated both the expectation value $\langle p(t) \rangle = m \langle v(t) \rangle$ and the variance $\Delta_p(t) = m^2 \Delta_v(t)$ of the momentum subject to this boundary condition. The force $\zeta(t)$ is a Gaussian random process governed by the probability distribution of Eq. (7.5.3). Since the velocity is linearly proportional to $\zeta(t)$, it should also be a Gaussian random process with a Gaussian probability distribution (i.e., characterized only by its mean and variance). One can easily verify that

$$P(p, t | p_0, 0) = \frac{1}{(2\pi\Delta_p(t))^{1/2}} e^{-(p - \langle p(t) \rangle)^2 / 2\Delta_p(t)} \quad (7.5.40)$$

satisfies the Fokker-Planck equation.