

Chapter 7

Dynamics: correlation and response

Much of what we observe in nature is either time- or frequency- dependent. In this chapter, we will introduce language to describe time and frequency dependent phenomena in condensed matter systems near thermal equilibrium. We will focus on dynamic correlations and on linear response to time dependent external fields that are described by time-dependent generalizations of correlation functions and susceptibilities introduced in Chapters 2 and 3. These functions, whose definitions are detailed in Sec. 7.1, contain information about the nature of dynamical modes. To understand how and why, we will consider linear response in damped harmonic oscillators in Secs. 7.2 and 7.3, and in systems whose dynamics are controlled by diffusion in Sec. 7.4. These examples show that complex poles in a complex, frequency-dependent response function determine the frequency and damping of system modes. Furthermore, the imaginary part of this response function is a measure of the rate of dissipation of energy of external forces.

A knowledge of phenomenological equations of motion in the presence of external forces is sufficient to determine dynamical response functions. The calculation of dynamical correlation functions in dissipative systems requires either a detailed treatment of many degrees of freedom or some phenomenological model for how thermal equilibrium is approached. In Sec. 7.5, we follow the latter approach and introduce Langevin theory, in which thermal equilibrium is maintained by interactions with random forces with well-prescribed statistical properties. Frequency-dependent correlation functions for a diffusing particle and a damped harmonic oscillator

are proportional to the imaginary part of a response function. This is the classical version of the very important *fluctuation-dissipation theorem*.

Having discussed correlation and response in simple, phenomenological models, we turn in Sec. 7.6 to a general formal treatment of response and correlation functions. This treatment is valid at all temperatures for both classical and quantum systems, and includes a discussion of symmetry and sum rules and a derivation of the general fluctuation-dissipation theorem. Finally, in Sec. 7.7, we will show how inelastic scattering of neutrons measures dynamic correlation functions.

7.1 Dynamic correlation and response functions

7.1.1 Correlation functions

The time dependence of both classical and quantum mechanical dynamical 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

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

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 and that 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

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

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

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

Equ. (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 $C_{\phi_i\phi_j}(\mathbf{x}, \mathbf{x}', \omega)$.

7.1.2 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:

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

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 $\chi(z)$:

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

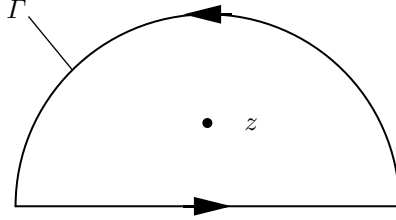


Figure 7.1.1: Contour in the complex plane for the integral in Eq. (7.2.26).

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 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

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

Taking the imaginary part of both sides of this equation, we obtain

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

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 $\tilde{\chi}_{\phi_i\phi_j}(\mathbf{x}, \mathbf{x}', t, t')$ satisfies

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

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

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

where $\chi'_{\phi_i\phi_j}(\mathbf{x}, \mathbf{x}', \omega)$ is related to $\chi''_{\phi_i\phi_j}(\mathbf{x}, \mathbf{x}', \omega)$ by a Kramers-Kronig relation analogous to Eq. (7.1.25). In Sec. 7.6, we will show that $\chi''_{\phi_i\phi_j}(\mathbf{x}, \mathbf{x}', \omega)$

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, $\chi'_{\phi_i\phi_j}(\mathbf{x}, \mathbf{x}', \omega)$ is the real part of and $\chi''_{\phi_i\phi_j}(\mathbf{x}, \mathbf{x}', \omega)$ the imaginary part of the complex response function $\chi_{\phi_i\phi_j}(\mathbf{x}, \mathbf{x}', \omega)$. The zero-frequency limit of Eq. (7.1.31) leads to the thermodynamic sum rule,

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

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

7.2 The harmonic oscillator

7.2.1 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. Detailed 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:

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

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

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 $\pm\omega_0$.

7.2.2 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]. 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

$$\gamma = \alpha/m. \quad (7.2.10)$$

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

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

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.

7.2.3 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

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

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 $\chi(\omega)f_0 e^{-i\omega t}$:

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

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

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

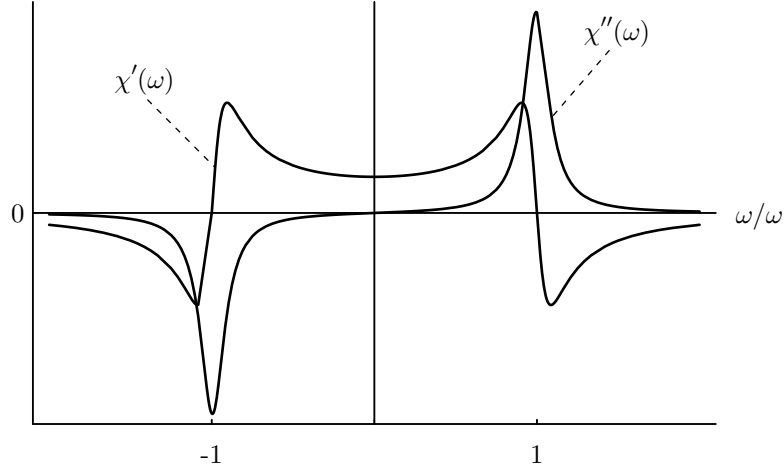


Figure 7.2.1: $\chi''(\omega)$ and $\chi'(\omega)$ for a harmonic oscillator when ω_1 is real.

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 $\omega\tau_f \ll 1$ 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. 7.2.4. 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 powers of $1/z$:

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

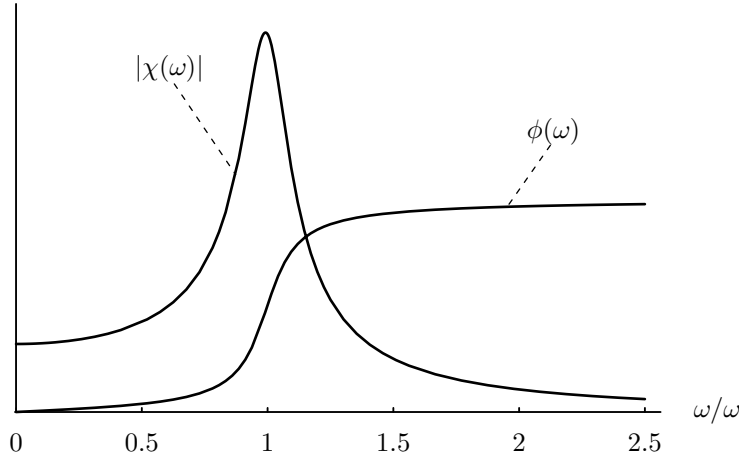
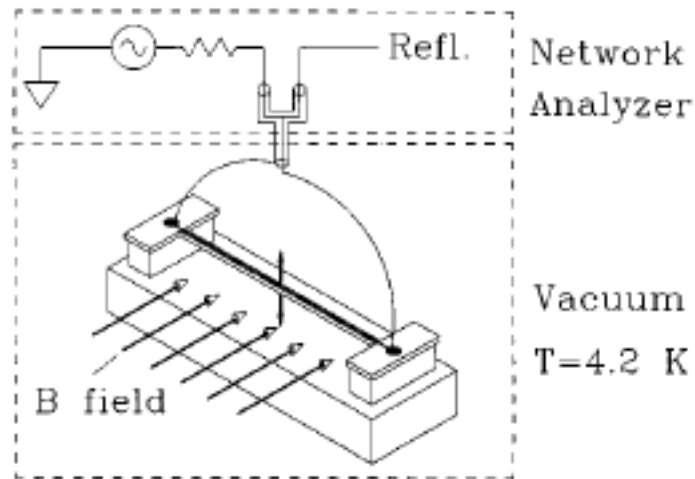


Figure 7.2.2: The amplitude and phase functions $|\chi(\omega)|$ and $\phi(\omega)$ for a harmonic oscillator.

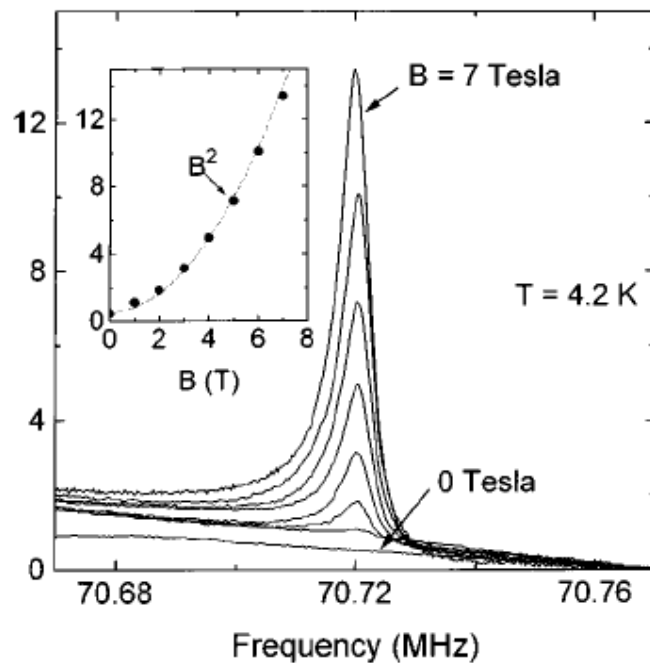
We shall see in Secs. 7.5 and 7.6 that $\chi''(\omega) \equiv \chi''_{xx}(\omega)$ is related via the fluctuation-dissipation theorem to $S(\omega) \equiv S_{xx}(\omega)$ measuring fluctuations in x via $\chi''(\omega)/\omega = S(\omega)/2T$. Frequency moments of $S(\omega)$ are simply equal-time correlation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

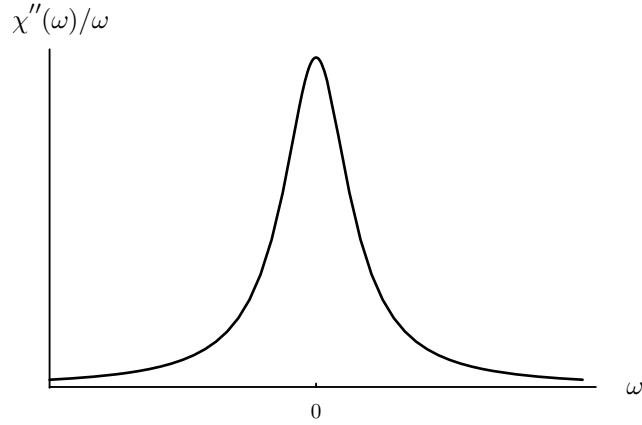


(a)



(b)

Figure 7.2.3: (a) Schematic of a nanometer scale mechanical resonator fabricated from bulk silicon by Cleland and Roukes [Appl. Phys. Lett. **69** 2653 (1996)]. The resonator is a suspended silicon nanobar. There is a magnetic field perpendicular to the bar as shown. An alternating current passes through the bar generating a vertical Lorentz force. The EMF is proportional to the B-field times the velocity, which is proportional to B . Thus the magnitude of the EMF is proportional to B^2 times the displacement. (b) The measured EMF as a function of frequency for different values of B . The curves are proportional to Eq. (7.2.22) times B^2 . Note the resonant frequency is 70 MHz. This high frequency is a direct result of the small size of the resonator.

Figure 7.2.4: $\chi''(\omega)/\omega$ in the overdamped limit when $\tau_f \ll \tau_s$.

7.2.4 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

$$P = \frac{1}{T} \int_0^T dt f(t)\dot{x}(t) = -\frac{1}{T} \int_0^T dt x(t)\dot{f}(t). \quad (7.2.29)$$

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.

7.3 Elastic waves and phonons

7.3.1 Sound waves in an elastic continuum

As we discussed in Chapter 6, an elastic medium in the Eulerian picture is the continuum limit of a collection of mass points connected by Hooke's law springs. The position of each point in the medium relative to its unstretched position is given by the displacement variable $\mathbf{u}(\mathbf{x})$. The velocity of each mass point is therefore $\mathbf{v}(\mathbf{x}, t) = \dot{\mathbf{u}}(\mathbf{x}, t)$, and the kinetic energy of mass motion is

$$K.E. = \frac{1}{2} \int d^d x \rho(\mathbf{x}) v^2(\mathbf{x}), \quad (7.3.1)$$

where $\rho(\mathbf{x})$ is the mass density at \mathbf{x} . In the absence of dissipation, Newton's equation determining the time dependence of the displacement of each mass point is

$$\rho \ddot{u}_i = - \frac{\delta \mathcal{H}_T}{\delta u_i(\mathbf{x})} = \nabla_j \sigma_{ij} + f_i^{\text{ext}}(\mathbf{x}), \quad (7.3.2)$$

where σ_{ij} is the elastic stress tensor of Eq. (??) and $\mathcal{H}_T = \mathcal{H}_{\text{el}} + \mathcal{H}_{\text{ext}}$, with \mathcal{H}_{el} the elastic Hamiltonian of Eq. (??) and $\mathcal{H}_{\text{ext}} = - \int d^d x \mathbf{u}(\mathbf{x}) \cdot \mathbf{f}^{\text{ext}}(\mathbf{x})$ the Hamiltonian arising from an external force density \mathbf{f}^{ext} . Dissipation can be introduced by adding a phenomenological term to the stress tensor proportional to the velocity and thus odd under time reversal. A spatially uniform velocity is equivalent to a Galilean transformation to a moving coordinate system, which will not lead to any dissipation. The dissipative part of the stress tensor is, therefore, proportional to the gradient of the velocity rather than to the velocity itself:

$$\sigma_{ij}^{\text{dis}} = \eta_{ijkl} \nabla_k v_l, \quad (7.3.3)$$

where η_{ijkl} is the viscosity tensor of the solid (viscosity tensors in fluids and solids will be discussed in more detail in Chapter 8). In an isotropic elastic medium, the viscosity tensor, like the elastic tensor, has two independent components,

$$\eta_{ijkl} = \zeta \delta_{ij} \delta_{kl} + \eta \left(\delta_{ik} \delta_{jl} + \delta_{il} \delta_{jk} - \frac{2}{d} \delta_{ij} \delta_{kl} \right), \quad (7.3.4)$$

where ζ is the bulk viscosity and η is the shear viscosity.

The equations of motion for the longitudinal and transverse parts of \mathbf{u} decouple in an isotropic medium. In Fourier space they are

$$[-\omega^2\rho + q^2\mu - i\omega\eta q^2]\mathbf{u}_T(\mathbf{q}, \omega) = \mathbf{f}_T^{\text{ext}}(\mathbf{q}, \omega), \quad (7.3.5)$$

$$[-\omega^2\rho + q^2(\lambda + 2\mu) - i\omega(\zeta + 2(d-1)\eta/d)q^2]u_L = f_L^{\text{ext}}(\mathbf{q}, \omega), \quad (7.3.6)$$

where $\mathbf{u}(\mathbf{q}) = (\mathbf{q}/q)u_L + \mathbf{u}_T$ and similarly for \mathbf{f}^{ext} . These equations yield sound modes whose frequencies go to zero linearly with wave number q and whose widths (imaginary parts) are of order q^2

$$\omega_T = \pm c_T q - i \frac{\eta}{2\rho} q^2, \quad (7.3.7)$$

$$\omega_L = \pm c_L q + \frac{i}{2\rho} \left[\zeta + \frac{2(d-1)}{d} \eta \right] q^2, \quad (7.3.8)$$

where $c_T = (\mu/\rho)^{1/2}$ is the transverse sound velocity and $c_L = [(\lambda + 2\mu)/\rho]^{1/2} > c_T$ is the longitudinal sound velocity. Note there are $2(d-1)$ transverse and two longitudinal modes for each \mathbf{q} . This corresponds to one mode per degree of freedom.

The transverse response function is the ratio of \mathbf{u}_T to $\mathbf{f}_T^{\text{ext}}$:

$$\chi_T(\mathbf{q}, \omega) = \frac{1}{\rho} \frac{1}{-\omega^2 + (\mu - i\omega\eta)q^2/\rho}. \quad (7.3.9)$$

This function reduces to the static susceptibility $1/(\mu q^2)$ [Eq. (??)] when $\omega = 0$. The imaginary part of the response function is

$$\chi_T''(\mathbf{q}, \omega) = \frac{1}{\rho^2} \frac{\omega\eta q^2}{(\omega^2 - \mu q^2/\rho)^2 + (\eta\omega q^2/\rho)^2}. \quad (7.3.10)$$

This function is sketched in Fig. 7.3.1. A similar expression applies for longitudinal sound waves.

7.3.2 Acoustic phonons in a harmonic lattice

The dynamical properties of the classical harmonic lattice described in Sec. 6.6 are easily calculated. The complete Hamiltonian for this system, including the kinetic energy, is

$$\mathcal{H} = \sum_{\mathbf{l}} \frac{\mathbf{p}_{\mathbf{l}}^2}{2m} + \frac{1}{2} \sum_{\mathbf{l}, \mathbf{l}', \mathbf{i}, \mathbf{k}} C_{ik}(\mathbf{R}_{\mathbf{l}} - \mathbf{R}_{\mathbf{l}'}) u_{\mathbf{l}, \mathbf{i}} u_{\mathbf{l}', \mathbf{k}}, \quad (7.3.11)$$

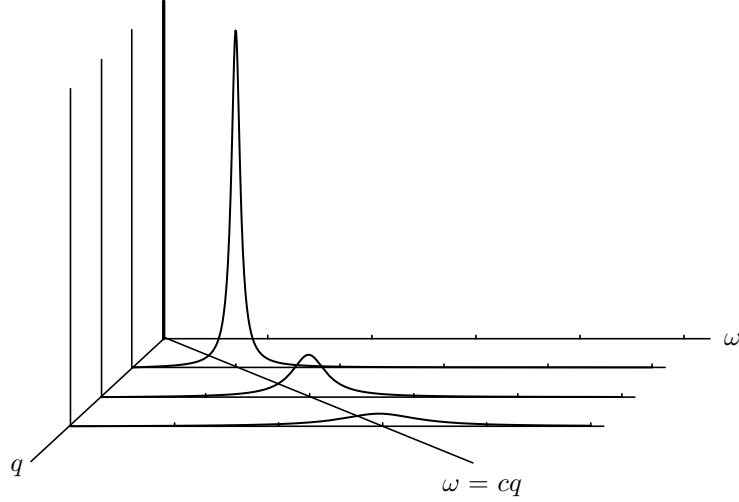


Figure 7.3.1: The imaginary part of the transverse elastic response function showing Lorentzian peaks at frequencies proportional to q .

where m is the mass and $\mathbf{p}_\mathbf{l} = m\dot{\mathbf{u}}_\mathbf{l}$ is the momentum of the particle at site \mathbf{l} . The equations of motion for the displacements $\mathbf{u}_\mathbf{l}$ are

$$m\ddot{\mathbf{u}}_{\mathbf{l},i} = - \sum_{l',k} C_{ik}(\mathbf{R}_\mathbf{l} - \mathbf{R}_{l'}) \mathbf{u}_{l',k} + \mathbf{f}_{\mathbf{l},i}, \quad (7.3.12)$$

where $\mathbf{f}_\mathbf{l}$ is an external force acting at site \mathbf{l} . The spatial part of this equation can be diagonalized by Fourier transforming. Introducing

$$\mathbf{u}_\mathbf{l} = \frac{1}{\sqrt{N}} \sum_{\mathbf{q}} e^{i\mathbf{q}\cdot\mathbf{R}_\mathbf{l}} \mathbf{u}(\mathbf{q}) \quad (7.3.13)$$

and a similar expression for the force and Fourier transforming in time, we have

$$m\omega^2 u_i(\mathbf{q}, \omega) = C_{ik}(\mathbf{q}) u_k(\mathbf{q}, \omega) + f_i(\mathbf{q}, \omega). \quad (7.3.14)$$

where

$$C_{ik}(\mathbf{q}) = \sum_{\mathbf{l}} e^{i\mathbf{q}\cdot\mathbf{R}_\mathbf{l}} C_{ik}(\mathbf{R}_\mathbf{l}). \quad (7.3.15)$$

Finally, we diagonalize $C_{ik}(\mathbf{q})$:

$$C_{ik}(\mathbf{q}) e_k^\lambda(\mathbf{q}) = m\omega_\lambda^2(\mathbf{q}) e_i^\lambda(\mathbf{q}). \quad (7.3.16)$$

$m\omega_\lambda^2(\mathbf{q})$ ($\lambda = 1, \dots, d$) are the d eigenvalues of $C_{ik}(\mathbf{q})$ and $e_i^\lambda(\mathbf{q})$ are the associated orthonormalized eigenvectors satisfying

$$\begin{aligned}\sum_\lambda e_i^{\lambda*}(\mathbf{q})e_j^\lambda(\mathbf{q}) &= \delta_{ij}, \\ \sum_i e_i^{\lambda'*}(\mathbf{q})e_i^\lambda(\mathbf{q}) &= \delta^{\lambda\lambda'}.\end{aligned}\quad (7.3.17)$$

We can now write Eq. (7.3.14) in terms of independent normal modes

$$\omega^2 u_\lambda(\mathbf{q}, \omega) = \omega_\lambda^2(\mathbf{q})u_\lambda(\mathbf{q}, \omega) + f_\lambda(\mathbf{q}, \omega)/m, \quad (7.3.18)$$

where

$$u_\lambda(\mathbf{q}, \omega) = e_i^{\lambda*}(\mathbf{q})u_i(\mathbf{q}, \omega) \quad (7.3.19)$$

and similarly for $f_\lambda(\mathbf{q}, \omega)$. Eq. (7.3.18) is identical to that of the simple harmonic oscillator, Eq. (7.2.9). It implies, therefore, a response function

$$\chi_\lambda(\mathbf{q}, \omega) = \frac{u_\lambda(\mathbf{q}, \omega)}{f_\lambda(\mathbf{q}, \omega)} = \frac{1}{m} \frac{1}{[-\omega^2 + \omega_\lambda^2(\mathbf{q})]}. \quad (7.3.20)$$

This, in turn, implies that the response function for a displacement at \mathbf{l} in response to a force at \mathbf{l}' is

$$\chi_{ij}(\mathbf{l}, \mathbf{l}', \omega) = \frac{1}{N} \sum_{\mathbf{q}} e^{i\mathbf{q}\cdot(\mathbf{R}_i - \mathbf{R}_{i'})} e_i^{\lambda*}(\mathbf{q}) \frac{1}{m} \frac{1}{[-\omega^2 + \omega_\lambda^2(\mathbf{q})]} e_j^\lambda(\mathbf{q}). \quad (7.3.21)$$

The spatial Fourier transform of the imaginary part of this response function is

$$\chi''_{ij}(\mathbf{q}, \omega) = \sum_\lambda e_i^{\lambda*}(\mathbf{q})e_j^\lambda(\mathbf{q}) \frac{\pi}{m} \frac{\omega}{|\omega|} \delta(\omega^2 - \omega_\lambda^2(\mathbf{q})). \quad (7.3.22)$$

Thus, $\chi''_{ij}(\mathbf{q}, \omega)$ provides a direct measure of the phonon spectrum. We will see in Sec 7.7 how neutron scattering determines this function. In an anharmonic lattice where there are interactions among phonons, the plane wave phonon states will generally be damped, and the δ function in Eq. (7.3.22) should be replaced by a Lorentzian.

7.4 Diffusion

7.4.1 Fick's law

Consider particles dissolved or suspended in a fluid. The nature of these particles is, for the moment, arbitrary. They can simply be molecules of

a species different from those composing the fluid, or they can be specks of dust or polystyrene spheres with diameters of order 0.1 microns. The number of these particles does not change with time. Thus, their number density $n(\mathbf{x}, t)$ (represented in terms of particle positions by Eq. (7.1.3)) obeys a conservation law:

$$\frac{\partial n(\mathbf{x}, t)}{\partial t} + \nabla \cdot \mathbf{j}(\mathbf{x}, t) = 0, \quad (7.4.1)$$

where

$$\mathbf{j}(\mathbf{x}, t) = \sum_{\alpha} \mathbf{v}_{\alpha}(t) \delta(\mathbf{x} - \mathbf{x}_{\alpha}(t)) \quad (7.4.2)$$

is the particle current, with $\mathbf{v}_{\alpha}(t) = \dot{\mathbf{x}}_{\alpha}(t)$ the particle velocity. In thermal equilibrium, the particles are distributed uniformly throughout the fluid, and the thermal average $\langle n(\mathbf{x}, t) \rangle$ of the density is independent of both \mathbf{x} and t . What happens, however, if, as a result either of spontaneous fluctuations or of an external force, there exists at some time a spatially non-uniform density, as depicted in Fig. 7.4.1? If external forces are turned off, the density must eventually tend to the spatially uniform equilibrium state. This can only occur as a result of particle motion. Thus, we expect a spatially non-uniform density to give rise to a non-zero current \mathbf{j} . If the density varies very slowly in space, then the density is nearly in equilibrium at each point in space, and currents should be very small. These considerations lead one to expect the current to be proportional to gradients of the density. The current \mathbf{j} must transform like a vector so that the simplest relation between \mathbf{j} and ∇n is

$$\mathbf{j} = -D\nabla n. \quad (7.4.3)$$

This equation is known as *Fick's law*. It is a phenomenological relation analogous to that of Eq. (7.2.7) relating the viscous force to the velocity. It says that a spatially non-uniform density will lead to currents in directions opposite to the direction of changes in densities, i.e., to currents tending to reestablish spatial uniformity of $n(\mathbf{x}, t)$. The coefficient D is a *diffusion constant*. It has units of $[\text{length}]^2/[\text{time}]$. The current \mathbf{j} is odd under time reversal, whereas $n(\mathbf{x}, t)$ and its gradient are even. Thus, the two sides of Eq. (7.5.2) have opposite signs under time reversal, and the diffusion constant is a type of dissipative coefficient.

When Fick's law for the current is substituted into the conservation law, the result is the diffusion equation,

$$\frac{\partial n}{\partial t} = D\nabla^2 n. \quad (7.4.4)$$

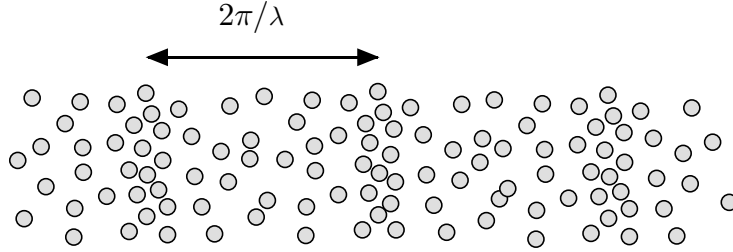


Figure 7.4.1: Spatially modulated distribution of particles. Random motion of these particles will restore spatial homogeneity in times that diverge as the square of the wavelength of the spatial modulation.

The modes predicted by this equation are again obtained by assuming $n(\mathbf{x}, t) \sim e^{-i\omega t}$. The resulting mode frequency is

$$\omega = -iDq^2, \quad (7.4.5)$$

where $q = 2\pi/\lambda$ is the wave number of the spatial modulation of the density. This frequency is purely imaginary, implying, as for the overdamped oscillator, that the response of $n(\mathbf{x}, t)$ to external forces or non-equilibrium boundary conditions will decay exponentially to zero in times of order $D^{-1}\lambda^2$. There will be no oscillatory part to this decay.

7.4.2 The Green function and dynamic response

The density at position \mathbf{x} and time t is related to the density at position \mathbf{x}' and time t' via

$$n(\mathbf{x}, t) = \int d^d x' G(\mathbf{x} - \mathbf{x}', t - t') n(\mathbf{x}', t'), \quad (7.4.6)$$

where $G(\mathbf{x}, t)$ is the diffusion Green function satisfying the boundary condition

$$G(\mathbf{x}, t = 0) = \delta(\mathbf{x}). \quad (7.4.7)$$

For times $t > 0$, $G(\mathbf{x}, t)$ satisfies the same equation as $n(\mathbf{x}, t)$:

$$\frac{\partial G(\mathbf{x}, t)}{\partial t} - D\nabla^2 G(\mathbf{x}, t) = 0. \quad (7.4.8)$$

The solution to this equation subject to the boundary condition Eq. (7.4.7) can be obtained via Laplace transformation in time and Fourier transformation in space. The results are

$$G(\mathbf{q}, z) = \frac{1}{-iz + Dq^2} \quad (7.4.9)$$

and

$$G(\mathbf{q}, t) = \int_{-\infty+i\epsilon}^{\infty+i\epsilon} \frac{dz}{2\pi} e^{-izt} G(\mathbf{q}, z) = e^{-Dq^2|t|}, \quad (7.4.10)$$

$$G(\mathbf{x}, t) = \int \frac{d^d q}{(2\pi)^d} e^{i\mathbf{q}\cdot\mathbf{x}} G(\mathbf{q}, t) = \frac{1}{(4\pi D |t|)^{d/2}} e^{-|\mathbf{x}|^2/(4D|t|)}.$$

This says that particle density initially localized at the origin will spread out with time, occupying a region with mean square radius

$$\langle |\mathbf{x}|^2 \rangle = 2dD |t|, \quad (7.4.11)$$

where as usual d is the dimension of space. The diffusion constant, therefore, measures the mean-square displacement per unit time interval.

7.4.3 The response function

The Green function allows us to determine the density at time t if we know the density at some earlier time t' . It does not, however, give us directly the density response function. To obtain the response function, we create a spatially non-uniform density at time $t < 0$ that is in equilibrium with an external chemical potential with a small spatially varying part $\delta\mu(\mathbf{x})$. We then turn off the external chemical potential at time $t = 0$. For $t > 0$, the equilibrium state is again spatially uniform, and the decay to equilibrium is controlled by the Green function. The external Hamiltonian creating the spatially varying $\langle n(\mathbf{x}, t = 0) \rangle$ is

$$\mathcal{H}_{\text{ext}} = - \int d^d x n(\mathbf{x}, t) \delta\mu(\mathbf{x}) \eta(-t) e^{\epsilon t}, \quad (7.4.12)$$

where ϵ is an infinitesimal. The Fourier transform of the change in the density at $t = 0$ brought about by this external Hamiltonian is

$$\langle \delta n(\mathbf{q}, t = 0) \rangle = \chi(\mathbf{q}) \delta\mu(\mathbf{q}), \quad (7.4.13)$$

where $\chi(\mathbf{q})$ is the static density response function discussed in Chapter 3. The density for $t > 0$ is then determined by its Laplace-Fourier transform satisfying

$$\langle \delta n(\mathbf{q}, z) \rangle = G(\mathbf{q}, z) \langle \delta n(\mathbf{q}, t = 0) \rangle = \frac{\chi(\mathbf{q}) \delta\mu(\mathbf{q})}{-iz + Dq^2}. \quad (7.4.14)$$

Our next step is to determine how $\langle \delta n(\mathbf{q}, z) \rangle$ is related to the dynamic susceptibility $\chi_{nn}(\mathbf{q}, z) \equiv \chi(\mathbf{q}, z)$. From the definition of $\tilde{\chi}(\mathbf{x}, \mathbf{x}', t, t')$ [Eq.

(7.1.11)], and the fact that $\delta\mu(\mathbf{x}, t) = \eta(-t)e^{\epsilon t}\delta\mu(\mathbf{x})$, we have

$$\delta\langle n(\mathbf{q}, t) \rangle = \int_{-\infty}^0 dt' \tilde{\chi}(\mathbf{q}, t-t')e^{\epsilon t'}\delta\mu(\mathbf{q}), \quad (7.4.15)$$

from which we obtain

$$\begin{aligned} \delta\langle n(\mathbf{q}, z) \rangle &= \int_0^\infty dt e^{izt} \int_{-\infty}^0 dt' \int \frac{d\omega}{2\pi} 2i\chi''(\mathbf{q}, \omega) e^{-i\omega(t-t')} e^{\epsilon t'} \delta\mu(\mathbf{q}) \\ &= \int \frac{d\omega}{\pi i} \frac{\chi''(\mathbf{q}, \omega)}{(\omega-z)(\omega-i\epsilon)} \delta\mu(\mathbf{q}) \\ &= \int \frac{d\omega}{\pi i} \chi''(\mathbf{q}, \omega) \frac{1}{z} \left(\frac{1}{\omega-z} - \frac{1}{\omega} \right) \delta\mu(\mathbf{q}) \\ &= \frac{1}{iz} [\chi(\mathbf{q}, z) - \chi(\mathbf{q})] \delta\mu(\mathbf{q}). \end{aligned} \quad (7.4.16)$$

This equation and Eq. (7.4.14) then imply

$$G(\mathbf{q}, z) = \frac{1}{iz} \left[\frac{\chi(\mathbf{q}, z)}{\chi(\mathbf{q})} - 1 \right] \quad (7.4.17)$$

and

$$\chi(\mathbf{q}, z) = \chi(\mathbf{q}) \frac{Dq^2}{-iz + Dq^2}. \quad (7.4.18)$$

This response function has exactly the same form as that of the overdamped oscillator [Eq. (7.2.24)] except that the inverse decay time Dq^2 now depends on wave number. The imaginary part of $\chi(\mathbf{q}, \omega)$ is

$$\frac{\chi''(\mathbf{q}, \omega)}{\omega} = \chi(\mathbf{q}) \frac{Dq^2}{\omega^2 + (Dq^2)^2}. \quad (7.4.19)$$

This is a Lorentzian with integrated intensity $\chi(\mathbf{q})$, height $\chi(\mathbf{q})/Dq^2$, and a width that goes to zero as $q \rightarrow 0$, as shown in Fig. 7.4.2.

As in the case of the harmonic oscillator discussed in the preceding section, the high-frequency moments of $\chi''(\omega)/\omega$ must all be finite. As for the harmonic oscillator, the dissipative function $\chi''(\mathbf{q}, \omega)$ is related to the correlation function $S_{nn}(\mathbf{q}, \omega)$ via the fluctuation-dissipation theorem, which in the classical limit is

$$\frac{\chi''(\mathbf{q}, \omega)}{\omega} = \frac{S_{nn}(\mathbf{q}, \omega)}{2T}. \quad (7.4.20)$$

The second moment of $\chi''(\mathbf{q}, \omega)/\omega$ is thus

$$\begin{aligned} \int \frac{d\omega}{\pi} \omega^2 \frac{\chi''(\mathbf{q}, \omega)}{\omega} &= \frac{1}{T} \int \frac{d\omega}{2\pi} \omega^2 S_{nn}(\mathbf{q}, \omega) = -\frac{1}{VT} \left\langle \frac{\partial^2}{\partial t^2} n(\mathbf{q}, t) n(-\mathbf{q}, t) \right\rangle \\ &= \frac{1}{VT} q^2 \langle \mathbf{j}(\mathbf{q}, t) \cdot \mathbf{j}(-\mathbf{q}, t) \rangle = \frac{1}{VT} \sum_{\alpha} \langle v_{\alpha}^2 \rangle \\ &= \frac{nq^2}{m}, \end{aligned} \quad (7.4.21)$$

where m is the mass of the diffusing particles. This is the f -sum rule, which, as we shall see in Sec. 7.6, is always valid for both classical and quantum systems.

Only the zeroth moment of Eq. (7.4.19) is finite. In order to make all moments finite and to reproduce Eq. (7.4.18) at low frequency, we can introduce a frequency-dependent diffusion constant $D(z)$ that tends to zero faster than any power of $1/z$ at large z and reduces to D at $z = 0$. $D(z)$ will have an integral representation similar to Eq. (7.1.17) for $\chi(z)$ (see Problem 7.4). The phenomenological expression $D(z) = D/(1 - iz\tau)$ produces a finite second moment but infinite higher moments. Following Eq. (7.2.26), the second moment of $\chi''(\mathbf{q}, \omega)/\omega$ is the coefficient of $-1/z^2$ in the high-frequency expansion of $\chi(\mathbf{q}, z)$, which for the above form for $D(z)$ is $-\chi D q^2/\tau$. Identifying this result with the f -sum rule, we find $D = n\tau/m\chi$. This provides a phenomenological connection between the diffusion constant, the susceptibility, and a “microscopic” collision time τ . We will obtain this result in a different way in shortly.

7.4.4 External potentials and the Einstein relation

Fick’s law is appropriate to situations when there is no external potential, such as that of a gravitational field. When there are external potentials, it must be modified. To see why, consider, as Einstein did, densities of diffusing particles sufficiently dilute that interactions between them can be neglected. In this case, the only forces acting on a given particle are those arising from external potentials and from collisions with molecules comprising the fluid. We have already argued [Eq. (7.2.7)] that the effect of the latter is to introduce a friction force on a particular particle proportional to its velocity. In steady state, this force must equal any external forces, implying particles will drift with velocity

$$\mathbf{v}_D = \frac{1}{\alpha} \mathbf{f}^{\text{ext}} \equiv -\frac{1}{\alpha} \nabla U, \quad (7.4.22)$$

where α is the friction constant introduced in Eq. (7.2.7) and U is the external potential determining the force $\mathbf{f}^{\text{ext}} = -\nabla U$. The coefficient $1/\alpha$

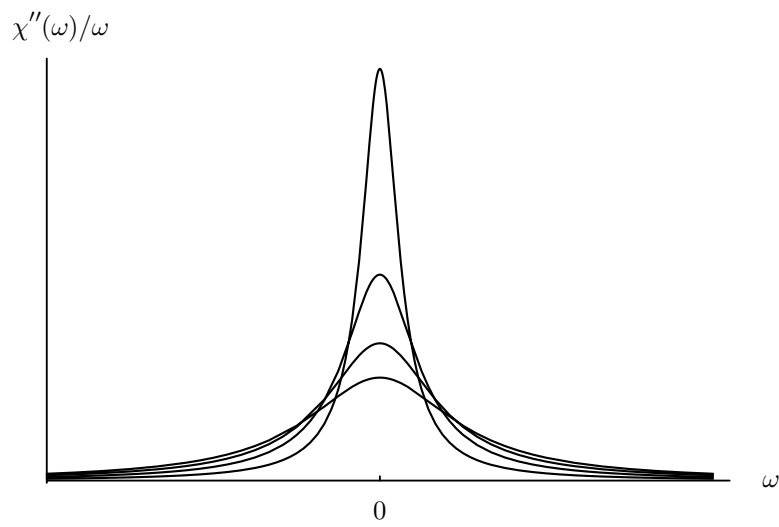


Figure 7.4.2: The imaginary part of the diffusive response function over ω [Eq. (7.5.19)] at different values of q . The half width at half maximum is Dq^2 , so that a measurement of this quantity as a function of q gives the diffusion constant D . The static susceptibility is the area under this curve, or alternatively Dq^2 times its height.

is also referred to as a mobility. This drift gives rise to a drift current $\mathbf{j}_D = n\mathbf{v}_D$, in addition to the diffusion current, about any average flow predicted by Fick's law. The total current is, therefore,

$$\mathbf{j}_{\text{tot}} = -D\nabla n + \mathbf{j}_D = -D\nabla n - \alpha^{-1}n\nabla U. \quad (7.4.23)$$

In thermodynamic equilibrium, the total particle current must be zero, and the density must satisfy the Boltzmann relation

$$n_{\text{eq}} \sim e^{-U(\mathbf{x})/T}. \quad (7.4.24)$$

These two conditions can only be satisfied if

$$D = \frac{T}{\alpha} = \frac{T}{6\pi\eta a}. \quad (7.4.25)$$

This is the Einstein relation published in his famous 1905 paper on Brownian motion. It is the first of the *fluctuation-dissipation* relations expressing an equilibrium average

$$\begin{aligned} D &= \lim_{t \rightarrow \infty} \frac{\langle [x(t) - x(0)]^2 \rangle}{2dt} \\ &= \lim_{t \rightarrow \infty} \frac{1}{2d} \frac{d}{dt} \langle [\mathbf{x}(t) - \mathbf{x}(0)]^2 \rangle \end{aligned} \quad (7.4.26)$$

in terms of a dissipative quantity α .

The total current can be expressed as a coefficient times a gradient of a scalar:

$$\mathbf{j}_{\text{tot}} = -\alpha^{-1}n\nabla(T \ln n + U). \quad (7.4.27)$$

Apart from unimportant constants, $T \ln n$ is just the equilibrium chemical potential $\mu(n) = \delta F / \delta n$ of a non-interacting gas of particles at density n [Eq. (??)]. The external potential U is equivalent to minus the externally fixed chemical potential $\mu^{\text{ext}}(\mathbf{x}) \equiv \mu(\mathbf{x})$ appearing in \mathcal{H}_{ext} [Eq. (7.4.12)]. The total current can, therefore, be written as

$$\mathbf{j}_{\text{tot}} = -\Gamma(n)\nabla[\mu(n) - \mu^{\text{ext}}(\mathbf{x})] = -\Gamma(n)\nabla[\delta F_T / \delta n(\mathbf{x})], \quad (7.4.28)$$

where $F_T = F[n(\mathbf{x})] - \int d^d x \mu^{\text{ext}}(\mathbf{x})n(\mathbf{x})$ and

$$\Gamma(n) = \frac{n}{\alpha} = \frac{n}{m\gamma} \quad (7.4.29)$$

is a density-dependent dissipative coefficient. Note the appearance of the “total” free energy F_T in Eq. (7.4.28). This is similar to the appearance of

the total Hamiltonian in Eqs. (7.2.15) and (7.3.2). F_T is identical to the function W introduced in Eq. (??). In equilibrium, the equation of state,

$$\frac{\delta F}{\delta n(\mathbf{x})} = \mu^{\text{ext}}(\mathbf{x}), \quad (7.4.30)$$

is satisfied, and there is no current. Current only flows when the function $\mu(n)$ differs from the externally imposed chemical potential μ^{ext} .

When $n(\mathbf{x}, t)$ differs from its equilibrium value n_{eq} determined by the equation of state, there will be a current, which for small and slowly varying $\delta n(\mathbf{x}, t) = n(\mathbf{x}, t) - n_{\text{eq}}$ is

$$\begin{aligned} \mathbf{j} &= -\Gamma(n)\nabla[(\partial\mu(n)/\partial n)\delta n] \\ &= -\Gamma(n)(\partial\mu/\partial n)\nabla n. \end{aligned} \quad (7.4.31)$$

This leads to an alternative expression for the diffusion constant:

$$D = \Gamma/\chi = \Gamma/(\partial n/\partial\mu). \quad (7.4.32)$$

This is exactly the result for D we obtained using sum and a phenomenological frequency-dependent $D(z)$ with the identification γ with τ^{-1} . Though Eq. (7.4.27) was motivated by considerations of a dilute gas of diffusing particles, it and Eq. (7.4.32) for D are also applicable to denser systems when interactions between particles become important. In this case, the dissipative coefficient Γ is not simply a linear function of n , and the chemical potential $\mu(n)$ is that appropriate to the interacting system.

7.4.5 Brownian motion

As just discussed, particles do not interact with each other in the dilute limit. In this case, we can focus on an individual diffusing particle. It is constantly subjected to collisions with the molecules of the fluid, and it describes an erratic trajectory in space. Such erratic motion was first reported in 1828 by the botanist Robert Brown, who used a microscope to observe particles of pollen floating on the surface of water. He found that the pollen particles would appear to jump some distance in a random direction, then remain at rest for a period, then jump again in another direction. He subsequently observed similar motion of very fine particles of a number of substances including minerals and fragments of the Sphinx. He concluded that this motion occurred independently of the composition and origin of the particle. The explanation of the origin of this phenomenon of Brownian motion is due to Einstein, who apparently was unaware of

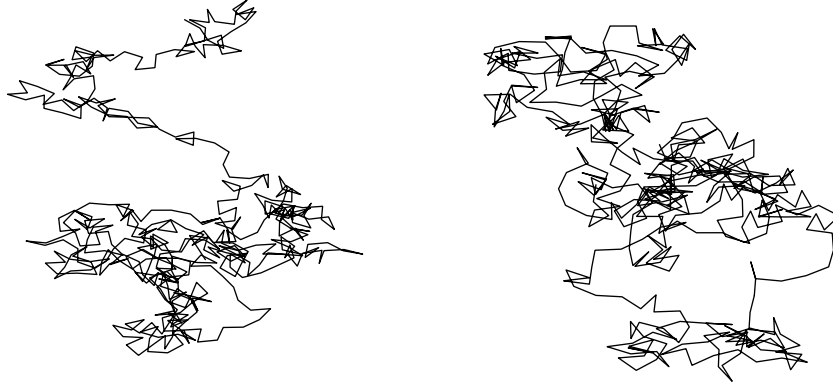


Figure 7.4.3: Schematic representation of two trajectories of a Brownian particle.

Brown's observations. Random motion consisting of a sequence of apparently discrete steps is often referred to as a *random walk* or more colorfully as a *drunkard's walk* (see Sec. 2.12).

The position $\mathbf{x}(t)$ of the Brownian particle is a random function of time. Such a randomly fluctuating variable is called a *stochastic* variable. The series of values of a random variable as a function of time is generally called a *stochastic process*. The conditional probability $P(\mathbf{x}, t | \mathbf{x}_0, t_0)$ that the particle is at position \mathbf{x} at time t , given that it was at position \mathbf{x}_0 at time t_0 , can be expressed as

$$P(\mathbf{x}, t | \mathbf{x}_0, t_0) = \langle \delta(\mathbf{x} - \mathbf{x}(t)) \rangle_{\mathbf{x}_0, t_0}, \quad (7.4.33)$$

where $\mathbf{x}(t)$ is the instantaneous position of the particle moving under the influence of a random force originating from collisions with fluid particles. The brackets in the above equation signify an average over this random force, and the condition that the particle was at position \mathbf{x}_0 at t_0 is implemented by the boundary condition $\mathbf{x}(t_0) = \mathbf{x}_0$.

In the dilute limit, the probability $\langle \delta(\mathbf{x} - \mathbf{x}^\alpha(t)) \rangle_{\mathbf{x}_0^\alpha, t_0}$ that particle α is at \mathbf{x} at time t , given that it was at \mathbf{x}_0^α at time t_0 , is simply $P(\mathbf{x}, t | \mathbf{x}_0^\alpha, t_0)$. The average density of particles at \mathbf{x} at time t , given that the density was $n(\mathbf{x}, t_0) = \sum_\alpha \delta(\mathbf{x} - \mathbf{x}_0^\alpha)$ at $t = t_0$, is, therefore,

$$\begin{aligned} \langle n(\mathbf{x}, t) \rangle &= \sum_\alpha \langle \delta(\mathbf{x} - \mathbf{x}^\alpha(t)) \rangle_{\mathbf{x}_0^\alpha, t_0} = \sum_\alpha P(\mathbf{x}, t | \mathbf{x}_0^\alpha, t_0) \\ &= \int d^d x_0 P(\mathbf{x}, t | \mathbf{x}_0, t_0) \sum_\alpha \delta(\mathbf{x}_0 - \mathbf{x}_0^\alpha) \end{aligned}$$

$$= \int d^d x_0 P(\mathbf{x}, t | \mathbf{x}_0, t_0) n(\mathbf{x}_0, t_0). \quad (7.4.34)$$

This equation is identical to Eq. (7.4.6) and allows us to identify $P(\mathbf{x}, t | \mathbf{x}_0, t_0)$ with the diffusion Green function in the dilute limit:

$$P(\mathbf{x}, t | \mathbf{x}_0, t_0) = G(\mathbf{x} - \mathbf{x}_0, t - t_0). \quad (7.4.35)$$

The mean-square displacement of a single Brownian particle, therefore, satisfies Eq. (7.4.11) with $d = 3$ and with the diffusion constant Eq. (7.4.25) appropriate to non-interacting particle diffusing in a fluid with viscosity η :

$$\langle (\Delta \mathbf{x})^2 \rangle = \langle [\mathbf{x}(t) - \mathbf{x}_0]^2 \rangle = 6Dt = \frac{k_B T}{\pi \eta a} t, \quad (7.4.36)$$

where we have explicitly displayed Boltzmann's constant k_B . This equation was used in one of the early determinations of k_B . The fluid viscosity and radius of a diffusing particle can be measured with reasonable accuracy. Measurements of $\mathbf{x}(t)$ by observations under a microscope then yield $\langle (\Delta \mathbf{x})^2 \rangle$ as a function of time. It is then straightforward to determine k_B from Eq. (7.4.36). A typical fluid such as water has a viscosity of order 0.1 poise. Eq. (7.4.36) then predicts that a particle with a radius of order 0.1 microns will diffuse a distance of order one micron in one second. Thus, diffusion of a particle of this size is observable in laboratory times.

7.4.6 Cooperative diffusion versus self-diffusion

We have considered diffusion of both the average density of particles and of an individual particle. These two processes are referred to, respectively, as *cooperative diffusion* and *self-diffusion*. They are different and are controlled by different diffusion constants D_c and D_s that become equal only when interactions between diffusing particles can be ignored (as they can in the dilute limit discussed above). Both constants can be measured experimentally. As just discussed, self-diffusion can be detected in dilute systems by observations under a microscope. It can also be observed by more sophisticated techniques in which individual particles are tagged, either by rendering them radioactive or by treating them with a photochromic dye that changes from transparent to opaque when exposed to ultraviolet light. In the latter case, quantitative measurements can be made by "forced Rayleigh" scattering experiments in which a suspension is first irradiated with spatially modulated ultraviolet light. Light from a second source is then diffracted from the sample. Its diffracted intensity determines D_s .

Self-diffusion can also be detected, as we shall see in Sec. 7.8, via incoherent neutron scattering, which measures the function

$$S_{\text{self}}(\mathbf{x}, \mathbf{x}', t - t') = \sum_{\alpha} \langle \delta(\mathbf{x} - \mathbf{x}^{\alpha}(t)) \delta(\mathbf{x}' - \mathbf{x}^{\alpha}(t')) \rangle. \quad (7.4.37)$$

This is a self-correlation function because it involves temporal and spatial correlations of a single particle rather than a collection of particles. It can be related to the conditional probability of Eq. (7.4.33) using

$$P_{\alpha}(\mathbf{x}t | \mathbf{x}'t') = \frac{\langle \delta(\mathbf{x} - \mathbf{x}^{\alpha}(t)) \delta(\mathbf{x}' - \mathbf{x}^{\alpha}(t')) \rangle}{\langle \delta(\mathbf{x}' - \mathbf{x}^{\alpha}(t')) \rangle}, \quad (7.4.38)$$

where we have indicated the possibly different behavior for different particles by the subscript α . For translationally invariant systems with volume V , $\langle \delta(\mathbf{x}' - \mathbf{x}^{\alpha}(t')) \rangle = V^{-1}$, P_{α} is independent of α , and from Eqs. (7.4.38) and (7.4.37)

$$S_{\text{self}}(\mathbf{x}, \mathbf{x}', t - t') = nP(\mathbf{x}t | \mathbf{x}'t'), \quad (7.4.39)$$

implying

$$\begin{aligned} S_{\text{self}}(\mathbf{q}, \omega) &= n \int_{-\infty}^{\infty} dt e^{i\omega t} e^{-D_s q^2 |t|} \\ &= 2n \frac{D_s q^2}{\omega^2 + (D_s q^2)^2} \end{aligned} \quad (7.4.40)$$

is a Lorentzian with a width determined by the self-diffusion constant.

Cooperative diffusion gives rise to density changes and can be probed by inelastic light scattering that, as we shall see at the end of this chapter, measures the density correlation function $S_{nn}(q, t)$ related to $\chi''_{nn}(\mathbf{q}, \omega)$ via the fluctuation-dissipation theorem,

$$S_{nn}(\mathbf{q}, t) = \int \frac{d\omega}{\pi} \frac{\chi''_{nn}(\mathbf{q}, \omega)}{\beta\omega} e^{-i\omega t} = T\chi(\mathbf{q}) e^{-D_c q^2 |t|}. \quad (7.4.41)$$

Various data for both D_c and D_s in suspensions of polystyrene spheres (polyballs) with varying interaction strengths are shown in Figs. 7.4.4 and 7.4.5. These data confirm the general time dependence of correlations predicted by Fick's law. They also show that the self-diffusion constant invariably decreases as interactions between particles are increased, either because the diffusing particle is trapped in a cage by repulsive interactions or because it is attracted to other particles. Cooperative diffusion increases for repulsive interactions (repulsion strongly favors uniform density) or decreases for attractive interactions where higher density may be favored by

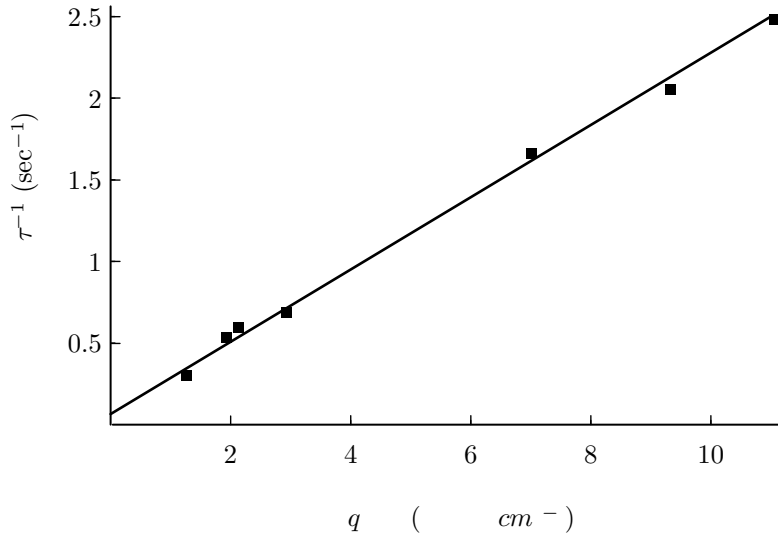


Figure 7.4.4: Inverse decay time as a function of q^2 for self-diffusion measured by forced Rayleigh scattering. (W.D. Dozier, Thesis, UCLA 1986)

an approaching phase separation. The case for repulsive interactions is shown in Fig. 7.4.5 from experiments in which the electrostatic interaction between particles is decreased by increasing the concentration of acid (HCl), which leads to an increase in screening.

7.4.7 Master equation for diffusion on a lattice

Diffusion is not limited to particles in solution. It often occurs when there are processes whose time dependence is controlled by random processes. Here we will consider diffusion on a lattice. We imagine that sites \mathbf{l} on a lattice can be occupied by an atom or some localized excitation. The probability that site \mathbf{l} is occupied at time t is $P(\mathbf{l}, t)$. As time progresses, the atom can hop to other sites. Let $P(\mathbf{l}, t + \Delta t | \mathbf{l}', t) \equiv R(\mathbf{l}, \mathbf{l}', \Delta t)$ be the probability that the atom is at site \mathbf{l} at time $t + \Delta t$, given that it was at site \mathbf{l}' at time t . Then the probability that the atom is at site \mathbf{l} at time $t + \Delta t$ is

$$P(\mathbf{l}, t + \Delta t) = \sum_{\mathbf{l}'} R(\mathbf{l}, \mathbf{l}', \Delta t) P(\mathbf{l}', t). \quad (7.4.42)$$

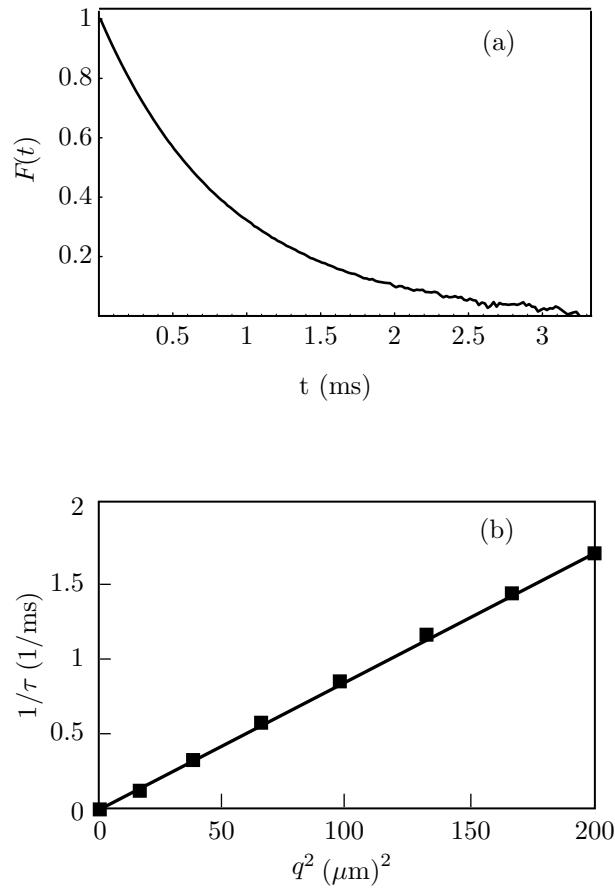


Figure 7.4.5: (a) Intensity correlation function $F(t) = (\langle I(q, 0)I(q, t) \rangle / \langle I(q) \rangle^2) - 1$ where $I(q, t)$ is the intensity of scattered light and (b) characteristic decay time as a function of q^2 for polystyrene spheres in methanol. (Courtesy of J. Xue)

Because $R(\mathbf{l}, \mathbf{l}', \Delta t)$ is a probability, it must satisfy

$$\sum_{\mathbf{l}} R(\mathbf{l}, \mathbf{l}', \Delta t) = \mathbf{1}. \quad (7.4.43)$$

As the time difference Δt goes to zero, the probability that an atom initially at site \mathbf{l}' is at a site different from \mathbf{l}' must go to zero. Thus, for small Δt , we can write

$$R(\mathbf{l}, \mathbf{l}', \Delta t) = \begin{cases} 1 - \sum_{\mathbf{l}_1} w_{\mathbf{l}' \rightarrow \mathbf{l}_1} \Delta t & \text{if } \mathbf{l} = \mathbf{l}'; \\ w_{\mathbf{l}' \rightarrow \mathbf{l}} \Delta t & \text{if } \mathbf{l} \neq \mathbf{l}', \end{cases} \quad (7.4.44)$$

where $w_{\mathbf{l}' \rightarrow \mathbf{l}}$ is a transition rate (with units of 1/[time]) from site \mathbf{l}' to \mathbf{l} defined to be zero for $\mathbf{l} = \mathbf{l}'$. Eqs. (7.4.42) and (7.4.44) lead to a differential equation for $P(\mathbf{l}, t)$:

$$\frac{\partial P(\mathbf{l}, t)}{\partial t} = \sum_{\mathbf{l}'} w_{\mathbf{l}' \rightarrow \mathbf{l}} P(\mathbf{l}', t) - \left(\sum_{\mathbf{l}_1} w_{\mathbf{l} \rightarrow \mathbf{l}_1} \right) P(\mathbf{l}, t). \quad (7.4.45)$$

This equation has a simple interpretation: $P(\mathbf{l}, t)$ increases as a result of hops, which occur at rates $w_{\mathbf{l}' \rightarrow \mathbf{l}}$, from sites $\mathbf{l}' \neq \mathbf{l}$ to the site \mathbf{l} , and it decreases as a result of hops, which occur at rates $w_{\mathbf{l} \rightarrow \mathbf{l}_1}$, from \mathbf{l} to sites $\mathbf{l}_1 \neq \mathbf{l}$.

There are no restrictions on the hopping rates $w_{\mathbf{l}' \rightarrow \mathbf{l}}$ in Eq. (7.4.45). They can connect any sites on the lattice, and the rate $w_{\mathbf{l}' \rightarrow \mathbf{l}}$ does not necessarily have to equal $w_{\mathbf{l} \rightarrow \mathbf{l}'}$. A simplified model is one in which there is hopping only between nearest neighbor sites on a lattice and in which the rate for hopping from \mathbf{l} to \mathbf{l}' is equal to that for hopping from \mathbf{l}' to \mathbf{l} . In this case,

$$w_{\mathbf{l}' \rightarrow \mathbf{l}} = w_{\mathbf{l} \rightarrow \mathbf{l}'} = \tau^{-1} \gamma_{\mathbf{l}, \mathbf{l}'}, \quad (7.4.46)$$

where τ is a hopping time and $\gamma_{\mathbf{l}, \mathbf{l}'}$ is unity if \mathbf{l}' and \mathbf{l} are nearest neighbor sites on the lattice and zero otherwise. The equation governing $P(\mathbf{l}, t)$ then becomes

$$\frac{\partial P(\mathbf{l}, t)}{\partial t} = \frac{1}{\tau} \sum_{\mathbf{l}'} \gamma_{\mathbf{l}, \mathbf{l}'} [P(\mathbf{l}', t) - P(\mathbf{l}, t)]. \quad (7.4.47)$$

Thus, if the Fourier transform of $P(\mathbf{l}, t = 0)$ is $P(\mathbf{q}, t = 0)$, it will decay to zero as

$$P(\mathbf{q}, t) = e^{-t/\tau(\mathbf{q})} P(\mathbf{q}, t = 0) \quad (7.4.48)$$

with

$$\begin{aligned} \tau^{-1}(\mathbf{q}) &= \tau^{-1}[\gamma(0) - \gamma(\mathbf{q})] = \tau^{-1} \sum_{\boldsymbol{\delta}} (1 - e^{i\mathbf{q} \cdot \boldsymbol{\delta}}) \\ &\sim \frac{a^2}{\tau} q^2 \quad \text{for } \mathbf{q} \rightarrow 0, \end{aligned} \quad (7.4.49)$$

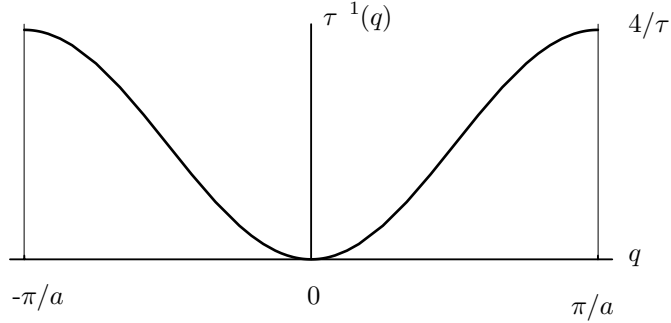


Figure 7.4.6: $\tau^{-1}(q)$ for a one-dimensional lattice. Its maximum $4/\tau$ is at $q = \pm\pi/a$.

where δ is a nearest neighbor vector of magnitude a of the lattice and where the numerical coefficient of q^2 in the last equation is that appropriate to a hypercubic lattice. Thus, at long wavelengths, $P(\mathbf{q}, t)$ decays diffusively [see Eq. (7.4.10)] with diffusion constant

$$D = a^2/\tau. \quad (7.4.50)$$

This is the form of D that one might have predicted simply on the basis of dimensional analysis. The value of $\tau(\mathbf{q})$ at higher values of \mathbf{q} depends on the lattice in question. In one dimension,

$$\tau^{-1}(\mathbf{q}) = 2\tau^{-1}(1 - \cos qa). \quad (7.4.51)$$

This function is plotted in Fig. 7.4.6

The decay time τ can vary widely from system to system. It is often determined by processes involving thermal activation over some barrier. In this case,

$$\tau^{-1} \sim e^{-\Delta E/T}, \quad (7.4.52)$$

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 $\sigma_{\mathbf{l},\mathbf{l}'}$ with capacitance to ground C . The equation for the voltage $V(\mathbf{l}, t)$ at site \mathbf{l} ,

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

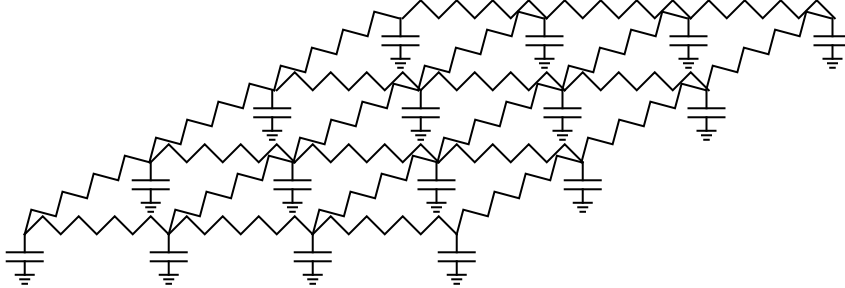


Figure 7.4.7: Schematic representation of a resistor network with capacitances to ground.

is determined by Kirchhoff's laws. When resistors connect only nearest neighbor sites, $\sigma_{1,1'} = \sigma\gamma_{1,1'}$, 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

7.5.1 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). 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

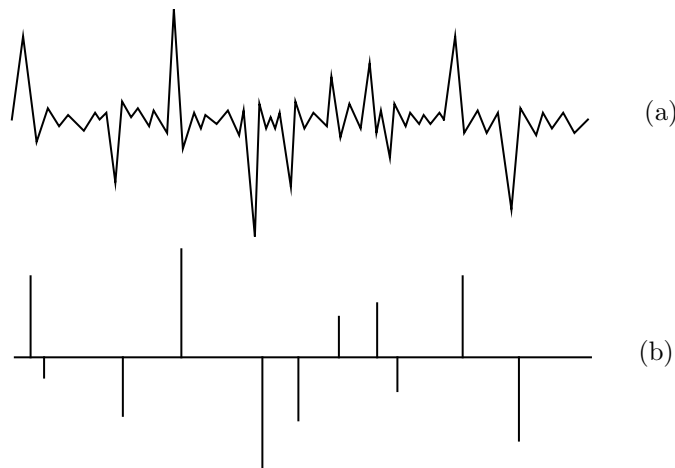


Figure 7.5.1: (a) Schematic representation of the random force $\zeta(t)$ as a function of time. (b) $\zeta(t)$ approximated by a series of random impulses.

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):

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

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.

7.5.2 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

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

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

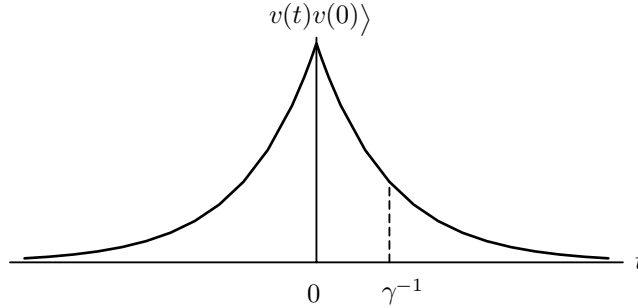


Figure 7.5.2: The velocity correlation function $\langle v(t)v(0) \rangle$ showing exponential decay to zero.

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

$$A = 2\alpha T = 2m\gamma T. \quad (7.5.9)$$

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

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 equations 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 $\langle [x(t) - x(t')]^2 \rangle \equiv \langle [\Delta x(t - t')]^2 \rangle$ 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

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

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 $D = T/(m\gamma)$.

7.5.3 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

$$\langle v(t) \rangle = v_0 e^{-\gamma t}. \quad (7.5.19)$$

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 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

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

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,

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

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.

7.5.4 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.

7.5.5 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

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

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.

7.6 Formal properties of response functions

7.6.1 Response to external fields

In Sec. 7.2, we defined the dynamic response function $\tilde{\chi}_{\phi_i\phi_j}(\mathbf{x}, \mathbf{x}', t, t')$ relating the deviation $\delta\langle\phi_i(\mathbf{x}, t)\rangle$ of the average of the field $\phi_i(\mathbf{x}, t)$ from its equilibrium value to first-order changes in the time-dependent external field $h_j(\mathbf{x}', t')$ thermodynamically conjugate to $\phi_j(\mathbf{x}', t')$. We then showed how this function could be calculated from phenomenological equations of motion. We also found that the imaginary part of the frequency dependent response function for a classical harmonic oscillator was related in a simple way to an equilibrium correlation function [Eq. (7.5.29)]. In this section, we will develop a general formalism for describing dynamic response functions. The important result of this general treatment is that response functions can be expressed in terms of equilibrium expectation values of commutators of operators. From this follow a number of general symmetry properties of response functions and the general quantum mechanical fluctuation dissipation theorem relating the the dissipative part of the susceptibility to an equilibrium correlation function. Our development will be fully quantum-mechanical. Classical results follow simply from the classical limit of quantum mechanics.

The Hamiltonian of a system in the presence of an external field $h_j(\mathbf{x}, t)$ can be expressed as

$$\mathcal{H}_T = \mathcal{H} + \mathcal{H}_{\text{ext}}, \quad (7.6.1)$$

where \mathcal{H} is the Hamiltonian describing the system when h_j is zero, and

$$\mathcal{H}_{\text{ext}} = - \int d^d x \sum_j \phi_j(\mathbf{x}) h_j(\mathbf{x}, t), \quad (7.6.2)$$

expressed in the Schrödinger representation where the field $\phi_j(\mathbf{x})$ is independent of time. \mathcal{H}_{ext} is a perturbation introduced to measure response. There can, of course, be terms in \mathcal{H} linear in $\phi_j(\mathbf{x})$ that look like \mathcal{H}_{ext} . We will be interested in the limit $h_j(\mathbf{x}, t) \rightarrow 0$, and we will assume that $h_j(\mathbf{x}, t)$ is zero for times less than some time t_0 , which we will eventually allow to

go to $-\infty$. Expectation values of operators in the presence of the external field can be expressed as

$$\langle \phi_i(\mathbf{x}, t) \rangle_h = \text{Tr} \rho_h(t, t_0) \phi_i(\mathbf{x}, t_0) \quad (7.6.3)$$

where $\rho_h(t, t_0)$ is the time-dependent density matrix for nonzero $h_j(\mathbf{x}, t)$ that reduces to the statistical equilibrium density matrix $\rho_{\text{eq}}(h = 0)$ for times less than t_0 . The time evolution of $\rho_h(t, t_0)$ is governed by the Schrödinger equation,

$$i\hbar \frac{\partial \rho_h}{\partial t} = [\mathcal{H} + \mathcal{H}_{\text{ext}}, \rho_h], \quad (7.6.4)$$

with the boundary condition $\rho_h(t_0, t_0) = \rho_{\text{eq}} \equiv \rho$. Thus

$$\rho_h(t, t_0) = U(t, t_0) \rho U^{-1}(t, t_0) \quad (7.6.5)$$

where

$$i\hbar \frac{dU(t, t_0)}{dt} = (\mathcal{H} + \mathcal{H}_{\text{ext}}) U(t, t_0) \quad (7.6.6)$$

with $U(t_0, t_0) = 1$ and $U(t, t_0) U^{-1}(t, t_0) = 1$. Because of the cyclic invariance property of the trace, Eq. (7.6.3) can also be expressed as

$$\langle \phi_i(\mathbf{x}, t) \rangle_h = \text{Tr} \rho_h(t, t_0) \phi_i(\mathbf{x}, t_0) = \text{Tr} \rho U^{-1}(t, t_0) \phi_i(\mathbf{x}, t_0) U(t, t_0). \quad (7.6.7)$$

The final form puts time variation in the field operator, expressed in the Heisenberg representation, rather than in the density matrix.

In order to discuss the time dependence of $\phi_i(\mathbf{x}, t)$ when h_j is nonzero, it is convenient to introduce the interaction representation for $U(t, t_0)$ via

$$U(t, t_0) = U_0(t, t_0) U'(t, t_0), \quad (7.6.8)$$

where $U'(t_0, t_0) = 1$ and

$$i\hbar \frac{dU_0}{dt} = \mathcal{H} U_0. \quad (7.6.9)$$

From this and Eqs. (7.6.6) and (7.6.8), it follows that

$$i\hbar \frac{dU'}{dt} = [U_0^{-1} \mathcal{H}_{\text{ext}} U_0] U' \equiv \mathcal{H}_{\text{ext}}^I U', \quad (7.6.10)$$

where the superscript on $\mathcal{H}_{\text{ext}}^I$ indicates that it is expressed in the interaction representation where time evolution is determined by \mathcal{H} rather than

by the total Hamiltonian $\mathcal{H} + \mathcal{H}_{\text{ext}}$. Equation (7.6.10) can be integrated perturbatively to yield $U'(t, t_0)$ as a power series in $\mathcal{H}_{\text{ext}}^I$. The result is

$$\begin{aligned} U'(t, t_0) &= 1 + \frac{1}{i\hbar} \int_{t_0}^t \mathcal{H}_{\text{ext}}^I(t') dt' \\ &+ \left(\frac{1}{i\hbar}\right)^2 \int_{t_0}^t \mathcal{H}_{\text{ext}}^I(t') \int_{t_0}^{t'} \mathcal{H}_{\text{ext}}^I(t'') dt' dt'' + \dots \quad (7.6.11) \\ &\equiv \left[\exp \left(\frac{1}{i\hbar} \int_{t_0}^t \mathcal{H}_{\text{ext}}^I(t') dt' \right) \right]_+, \end{aligned}$$

where $[]_+$ indicates that all operators within the brackets are to be ordered from right to left according to increasing time t . Defining $\phi_i^I(\mathbf{x}, t)$ to be the operator $\phi_i^I(\mathbf{x}, t) = U_0^{-1}(t, t_0) \phi_i(\mathbf{x}, t_0) U_0(t, t_0)$ in the interaction representation, we can write

$$\begin{aligned} \langle \phi_i(\mathbf{x}, t) \rangle_h &= \text{Tr} \rho U'^{-1}(t, t_0) \phi_i^I(\mathbf{x}, t) U'(t, t_0) \\ &\approx \text{Tr} \rho \left[\left(1 - \frac{1}{i\hbar} \int_{t_0}^t \mathcal{H}_{\text{ext}}^I(t') dt' \right) \phi_i^I(\mathbf{x}, t) \right. \\ &\quad \left. \times \left(1 + \frac{1}{i\hbar} \int_{t_0}^t \mathcal{H}_{\text{ext}}^I(t') dt' \right) \right] \quad (7.6.12) \\ &\approx \text{Tr} \rho \phi_i^I(\mathbf{x}, t) + \text{Tr} \rho \left(\frac{1}{i\hbar} \int_{t_0}^t dt' [\phi_i^I(\mathbf{x}, t), \mathcal{H}_{\text{ext}}^I(t')] \right) \end{aligned}$$

where $[\phi_i^I, \mathcal{H}_{\text{ext}}^I]$ is the commutator of ϕ_i^I with $\mathcal{H}_{\text{ext}}^I$. The first term in this equation is merely the equilibrium expectation value $\langle \phi_i(\mathbf{x}, t) \rangle$ in the absence of the external field h_j , and the second term reflects the effects of the external potential to lowest (i.e., linear) order in $h_j(\mathbf{x}, t)$. Allowing the initial time t_0 to go to $-\infty$, we obtain

$$\begin{aligned} \delta \langle \phi_i(\mathbf{x}, t) \rangle &= \langle \phi_i(\mathbf{x}, t) \rangle_h - \langle \phi_i(\mathbf{x}, t) \rangle \\ &= - \int_{-\infty}^t dt \frac{1}{i\hbar} \int d^d \mathbf{x}' \langle [\phi_i(\mathbf{x}, t), \phi_j(\mathbf{x}', t')] \rangle h_j(\mathbf{x}', t') \\ &= \int_{-\infty}^{\infty} dt \int d^d \mathbf{x}' \frac{i}{\hbar} \eta(t - t') \langle [\phi_i(\mathbf{x}, t), \phi_j(\mathbf{x}', t')] \rangle h_j(\mathbf{x}', t'), \end{aligned} \quad (7.6.13)$$

where we have dropped the now superfluous superscript I and where, as usual, $\langle \rangle$ signifies as average with respect to the equilibrium density matrix ρ . The field $\phi_i(\mathbf{x}, t)$ is the Heisenberg operator, evolving in time according

to the Hamiltonian \mathcal{H} . Comparing Eqs. (7.1.11), (7.1.12), and (7.6.13), we obtain

$$\begin{aligned}\tilde{\chi}_{\phi_i\phi_j}(\mathbf{x}, \mathbf{x}', t - t') &= \eta(t - t') \frac{i}{\hbar} \langle [\phi_i(\mathbf{x}, t), \phi_j(\mathbf{x}', t')] \rangle, \\ \tilde{\chi}''_{\phi_i\phi_j}(\mathbf{x}, \mathbf{x}', t - t') &= \frac{1}{2\hbar} \langle [\phi_i(\mathbf{x}, t), \phi_j(\mathbf{x}', t')] \rangle,\end{aligned}\quad (7.6.14)$$

where we have indicated explicit dependence on the time difference $t - t'$. This equation gives us the desired expressions for $\tilde{\chi}''_{\phi_i\phi_j}(\mathbf{x}, \mathbf{x}', t - t')$ and $\chi_{\phi_i\phi_j}(\mathbf{x}, \mathbf{x}', t - t')$ in terms of average values of products of operators evaluated in an equilibrium ensemble.

In classical systems, the commutators in Eq. (7.6.14) become Poisson brackets:

$$\begin{aligned}\tilde{\chi}''_{\phi_i\phi_j}(\mathbf{x}, \mathbf{x}', t - t') &= -\frac{i}{2} \langle \{\phi_i(\mathbf{x}, t), \phi_j(\mathbf{x}', t')\} \rangle \\ &\equiv \frac{i}{2} \sum_{\alpha} \left\langle \frac{\partial \phi_i(\mathbf{x}, t)}{\partial q^{\alpha}(t)} \frac{\partial \phi_j(\mathbf{x}', t')}{\partial p^{\alpha}(t')} - \frac{\partial \phi_i(\mathbf{x}, t)}{\partial p^{\alpha}(t)} \frac{\partial \phi_j(\mathbf{x}', t')}{\partial q^{\alpha}(t')} \right\rangle\end{aligned}\quad (7.6.15)$$

where (q^{α}, p^{α}) is a complete set of canonically conjugate coordinates.

7.6.2 Symmetry properties of response functions

There are a number of symmetry properties of $\tilde{\chi}''_{\phi_i\phi_j}(\mathbf{x}, \mathbf{x}', t - t')$ that follow directly because it is an equilibrium average of a commutator. It must be anti-symmetric under interchange of all indices:

$$\begin{aligned}\tilde{\chi}''_{\phi_i\phi_j}(\mathbf{x}, \mathbf{x}', t - t') &= -\tilde{\chi}''_{\phi_j\phi_i}(\mathbf{x}', \mathbf{x}, t' - t) \\ \chi''(\mathbf{x}, \mathbf{x}', \omega) &= -\chi''_{\phi_j\phi_i}(\mathbf{x}', \mathbf{x}, -\omega).\end{aligned}\quad (7.6.16)$$

The fields $\phi_i(\mathbf{x}, t)$ are observables and thus Hermitian operators. Therefore,

$$\begin{aligned}[\tilde{\chi}''_{\phi_i\phi_j}(\mathbf{x}, \mathbf{x}', t - t')]^* &= \left(\frac{1}{2\hbar} \langle [\phi_i(\mathbf{x}, t), \phi_j(\mathbf{x}', t')] \rangle \right)^* \\ &= \frac{1}{2\hbar} \langle [\phi_j(\mathbf{x}', t'), \phi_i(\mathbf{x}, t)] \rangle,\end{aligned}\quad (7.6.17)$$

and

$$[\tilde{\chi}''_{\phi_i\phi_j}(\mathbf{x}, \mathbf{x}', t - t')]^* = \tilde{\chi}''_{\phi_j\phi_i}(\mathbf{x}', \mathbf{x}, t' - t).\quad (7.6.18)$$

Or from Eq. (7.6.16),

$$[\tilde{\chi}''_{\phi_i\phi_j}(\mathbf{x}, \mathbf{x}', t - t')]^* = -\tilde{\chi}''_{\phi_i\phi_j}(\mathbf{x}, \mathbf{x}', t - t').\quad (7.6.19)$$

Hence, $\tilde{\chi}''_{\phi_i\phi_j}(\mathbf{x}, \mathbf{x}', t - t')$ is pure imaginary and $\tilde{\chi}_{\phi_i\phi_j}(\mathbf{x}, \mathbf{x}', t - t')$ is pure real as they should be. Finally, using Eq. (7.6.18), we obtain

$$[\chi''(\mathbf{x}, \mathbf{x}', \omega)]^* = \chi''_{\phi_j\phi_i}(\mathbf{x}', \mathbf{x}, \omega). \quad (7.6.20)$$

It follows from Eqs. (7.6.16) and (7.6.20) that if $\chi''(\mathbf{x}, \mathbf{x}', \omega)$ is *even* under interchange of (\mathbf{x}, i) and (\mathbf{x}', j) , it is *real* and *odd* in ω . If it is odd under the same interchange, it is imaginary and even in ω . The former case is the most common, but the latter can occur.

The behavior of the fields $\phi_i(\mathbf{x}, t)$ and the density matrix ρ under time reversal determine further symmetry properties of $\tilde{\chi}''_{\phi_i\phi_j}(\mathbf{x}, \mathbf{x}', t, t')$. The time-reversal operator θ applied to an operator ϕ_i leads to a new operator $\phi'_i = \theta\phi_i\theta^{-1}$. Fields $\phi_i(\mathbf{x}, t)$ can be classified according to their signature $\epsilon_{\phi_i} = \pm 1$ under time reversal:

$$\phi'_i(\mathbf{x}, t) = \theta\phi_i(\mathbf{x}, t)\theta^{-1} = \epsilon_{\phi_i}\phi_i(\mathbf{x}, -t). \quad (7.6.21)$$

Operators such as mass and energy density are even ($\epsilon = +1$) whereas those such as momentum density and magnetization are odd ($\epsilon = -1$) under time reversal. The density matrix depends on externally applied fields (such as magnetic fields) and the nature of order in the system. Thus, in the absence of external fields breaking time-reversal symmetry and in states with no order parameter breaking time reversal, ρ is invariant under θ . If, however, there are external fields or order parameters, which we represent by B , breaking time reversal, then ρ will change under θ : $\theta\rho(B)\theta^{-1} = \rho(-B)$. The time-reversal operator θ is anti-unitary. Let $|m'\rangle = (\theta|m\rangle)$ and $\langle m'| = (\langle m|\theta)$ be, respectively, the images of $|m\rangle$ and $\langle m|$ under time reversal. Then for any operator A , $\langle m'|A|n\rangle = \langle m|\theta A|n\rangle = [\langle m'|(\theta A|n\rangle)]^* = \langle m'|A'|n'\rangle^* = \langle n'|A^\dagger|m'\rangle$ where $A' = \theta A\theta^{-1}$. Applying this relation to $A = \rho\phi_i\phi_j$ and noting that if $\{|m\rangle\}$ is a complete set of states, then $\{|m'\rangle\}$ is also, we obtain

$$\begin{aligned} \tilde{\chi}''_{\phi_i\phi_j}(\mathbf{x}, \mathbf{x}', t - t', B) &= -\epsilon_{\phi_i}\epsilon_{\phi_j}\tilde{\chi}''_{\phi_i\phi_j}(\mathbf{x}, \mathbf{x}', t' - t, -B) \\ &= \epsilon_{\phi_i}\epsilon_{\phi_j}\tilde{\chi}_{\phi_j\phi_i}(\mathbf{x}', \mathbf{x}, t - t', -B) \\ \chi''(\mathbf{x}, \mathbf{x}', \omega, B) &= -\epsilon_{\phi_i}\epsilon_{\phi_j}\chi''(\mathbf{x}, \mathbf{x}', -\omega, -B) \\ &= \epsilon_{\phi_i}\epsilon_{\phi_j}\chi''_{\phi_j\phi_i}(\mathbf{x}', \mathbf{x}, \omega, -B). \end{aligned} \quad (7.6.22)$$

In a classical system, these results follow from Eq. (7.1.21) and the fact that Poisson brackets change sign under time-reversal because $\partial/\partial p^\alpha(t) \rightarrow -\partial/\partial p^\alpha(-t)$. When there is no external field or order parameter breaking time-reversal invariance, Eqs. (7.6.16), (7.6.18), and (7.6.22) imply that $\chi''(\mathbf{x}, \mathbf{x}', \omega)$ is real, odd in ω , and symmetric under interchange of (\mathbf{x}, i) and

(\mathbf{x}', j) when ϕ_i and ϕ_j have the same sign under time reversal and imaginary, even in ω , and antisymmetric under interchange of (\mathbf{x}, i) and (\mathbf{x}', j) when they have the opposite sign. Symmetry properties of $\chi'_{\phi_i \phi_j}(\mathbf{x}, \mathbf{x}', \omega)$ follow from

$$\chi'_{\phi_i \phi_j}(\mathbf{x}, \mathbf{x}', \omega) = \mathcal{P} \int_{-\infty}^{\infty} \frac{d\omega'}{\pi} \frac{\chi''(\mathbf{x}, \mathbf{x}', \omega')(\omega' + \omega)}{\omega'^2 - \omega^2}. \quad (7.6.23)$$

For example, when $B = 0$, $\chi'_{\phi_i \phi_j}(\mathbf{x}, \mathbf{x}', \omega)$ is real, even in ω , and symmetric under interchange of (\mathbf{x}, i) and (\mathbf{x}', j) when $\epsilon_{\phi_i} = \epsilon_{\phi_j}$.

In addition to the symmetries involving time coordinates, there are also symmetries involving spatial coordinates. For example in homogeneous, isotropic systems, $\chi''(\mathbf{x}, \mathbf{x}', t - t')$ must be a function only of $|\mathbf{x} - \mathbf{x}'|$ and its spatial Fourier transform a function only of $q = |\mathbf{q}|$. In more complicated crystalline systems, point and space group symmetries lead to other spatial symmetries for $\chi''(\mathbf{x}, \mathbf{x}', \omega)$.

7.6.3 Dissipation

In our discussion of the harmonic oscillator, we found that power dissipated was proportional to $\omega\chi''(\omega)$. We will now show that this result is more generally valid. The rate at which work is done on the system can be calculated using a generalization of Eq. (7.2.28). The rate dW/dt at which the external field $h_i(\mathbf{x}, t)$ does work on the system is equal to the rate of change of the total energy of the system: $dE/dt = (d/dt)\text{Tr}\rho(t)\mathcal{H}_T = \text{Tr}\rho(t)d\mathcal{H}_T/dt + \text{Tr}(d\rho(t)/dt)\mathcal{H}_T$. In the Schrödinger representation, the fields $\phi_i(\mathbf{x})$ are independent of time, and $d\mathcal{H}_T/dt = d\mathcal{H}_{\text{ext}}/dt$. In addition, $\text{Tr}(d\rho/dt)\mathcal{H}_T = (1/i\hbar)\text{Tr}[\mathcal{H}_T, \rho]\mathcal{H}_T = (1/i\hbar)\text{Tr}\rho[\mathcal{H}_T, \mathcal{H}_T] = 0$. Therefore, the rate at which work is done on the system is

$$\begin{aligned} \frac{dW}{dt} &= - \sum_i \int d^d x \langle \phi_i(\mathbf{x}, t) \rangle_h \dot{h}_i(\mathbf{x}, t) \\ &= - \sum_i \int d^d x \langle \phi_i(\mathbf{x}, t) \rangle_0 \dot{h}_i(\mathbf{x}, t) \\ &\quad - \sum_{ij} \int d^d x d^d x' \int_{-\infty}^t [dt' \dot{h}_i(\mathbf{x}, t) 2i\eta(t-t') \\ &\quad \times \tilde{\chi}''_{\phi_i \phi_j}(\mathbf{x}, \mathbf{x}', t-t') h_j(\mathbf{x}', t')] + O(\hbar^3). \end{aligned} \quad (7.6.24)$$

Now, consider an external field oscillating at a single frequency ω :

$$h_i(\mathbf{x}, t) = \text{Re} h_i(\mathbf{x}) e^{-i\omega t} = \frac{1}{2} [h_i(\mathbf{x}) e^{-i\omega t} + h_i^*(\mathbf{x}) e^{i\omega t}] \quad (7.6.25)$$

Then

$$\begin{aligned} \frac{dW}{dt} = & -\sum_{ij} \int d^d x d^d x' \frac{1}{2} \left\{ \int_{-\infty}^t dt' i\omega [h_i^*(\mathbf{x})e^{i\omega t} - h_i(\mathbf{x})e^{-i\omega t}] \right. \\ & \left. \times 2i\tilde{\chi}''_{\phi_i\phi_j}(\mathbf{x}, \mathbf{x}', t-t') [h_j^*(\mathbf{x}')e^{i\omega t'} + h_j(\mathbf{x}')e^{-i\omega t'}] \right\} \end{aligned} \quad (7.6.26)$$

where the first term in Eq. (7.6.24) has been dropped because it will disappear on averaging over a cycle of the external potential. Upon performing this average, we obtain

$$\begin{aligned} \overline{\frac{dW}{dt}} = & -\frac{1}{4}i\omega \int_{-\infty}^t \int d^d x d^d x' [2ih_i^*(\mathbf{x})\tilde{\chi}''_{\phi_i\phi_j}(\mathbf{x}, \mathbf{x}', t-t')h_j(\mathbf{x}')e^{i\omega(t-t')} \\ & - 2ih_i(\mathbf{x})\tilde{\chi}''_{\phi_i\phi_j}(\mathbf{x}, \mathbf{x}', t-t')h_j^*(\mathbf{x}')e^{-i\omega(t-t')}] \end{aligned} \quad (7.6.27)$$

since the terms proportional to $e^{\pm i\omega(t+t')}$ disappear on averaging. Changing variables to $t_1 = t - t'$, we obtain

$$\begin{aligned} \overline{\frac{dW}{dt}} = & \frac{1}{2}\omega \sum_{ij} \int d^d x d^d x' \int_0^\infty dt_1 [h_i^*(\mathbf{x})\tilde{\chi}''_{\phi_i\phi_j}(\mathbf{x}, \mathbf{x}', t_1)h_j(\mathbf{x}')e^{i\omega t_1} \\ & - h_i(\mathbf{x})\tilde{\chi}''_{\phi_i\phi_j}(\mathbf{x}, \mathbf{x}', t_1)h_j^*(\mathbf{x}')e^{-i\omega t_1}]. \end{aligned} \quad (7.6.28)$$

Then interchanging (\mathbf{x}, i) and (\mathbf{x}, j) and letting $t_1 \rightarrow -t_1$ in the second term of this expression and using the symmetry property of Eq. (7.6.16), we obtain

$$\overline{\frac{dW}{dt}} = \frac{1}{2}\omega \sum_{ij} \int d^d x d^d x' h_i^*(\mathbf{x})\chi''(\mathbf{x}, \mathbf{x}', \omega)h_j(\mathbf{x}'). \quad (7.6.29)$$

For systems in thermal equilibrium, power is absorbed from external sources, and \overline{dW}/dt must be positive definite. Thus, $\omega\chi''(\mathbf{x}, \mathbf{x}', \omega)$ is a *positive definite* matrix. This in turn implies that the real part of the response function $\chi'_{\phi_i\phi_j}(\mathbf{x}, \mathbf{x}', \omega)$ is positive for small ω and negative for large ω when ρ is invariant under time reversal and $\epsilon_{\phi_i} = \epsilon_{\phi_j}$:

$$\begin{aligned} \chi'_{\phi_i\phi_j}(\mathbf{x}, \mathbf{x}', \omega) &= \mathcal{P} \int_{-\infty}^{\infty} \frac{d\omega'}{\pi} \frac{\chi''(\mathbf{x}, \mathbf{x}', \omega')}{\omega' - \omega} \\ &= \mathcal{P} \int_{-\infty}^{\infty} \frac{d\omega'}{\pi} \frac{\omega' \chi''(\mathbf{x}, \mathbf{x}', \omega')}{\omega'^2 - \omega^2} \\ &\rightarrow \mathcal{P} \int_{-\infty}^{\infty} \frac{d\omega'}{\pi} \frac{1}{\omega'^2} \omega' \chi''(\mathbf{x}, \mathbf{x}', \omega') > 0 \quad \omega \rightarrow 0, \\ &\rightarrow -\frac{1}{\omega^2} \mathcal{P} \int_{-\infty}^{\infty} \frac{d\omega'}{\pi} \omega' \chi''(\mathbf{x}, \mathbf{x}', \omega') < 0 \quad \omega \rightarrow \infty. \end{aligned} \quad (7.6.30)$$

The simple harmonic oscillator discussed in Sec. 7.3 demonstrated a simple example of this behavior.

7.6.4 Spectral representations of χ''

It is instructive to express $\chi''(\mathbf{x}, \mathbf{x}', \omega)$ in terms of the matrix elements of $\phi_i(\mathbf{x}, t)$ with respect to energy eigenstates of the system. Let $|n\rangle$ be an eigenstate of \mathcal{H} with energy $\hbar\omega_n$, and assume that ρ is diagonal in the eigenstate basis with matrix elements $\langle n | \rho | m \rangle = \rho_n \delta_{nm}$. Then we can write

$$\begin{aligned} \langle [\phi_i(\mathbf{x}, t), \phi_j(\mathbf{x}', 0)] \rangle &= \text{Tr} \rho [e^{i\mathcal{H}t/\hbar} \phi_i(\mathbf{x}, 0) e^{-i\mathcal{H}t/\hbar}, \phi_j(\mathbf{x}', 0)] \\ &= \sum_{nm} \rho_n [e^{i(\omega_n - \omega_m)t} \langle n | \phi_i(\mathbf{x}, 0) | m \rangle \langle m | \phi_j(\mathbf{x}', 0) | n \rangle \\ &\quad - e^{-i(\omega_n - \omega_m)t} \langle n | \phi_j(\mathbf{x}', 0) | m \rangle \langle m | \phi_i(\mathbf{x}, 0) | n \rangle]. \end{aligned} \quad (7.6.31)$$

This then implies

$$\begin{aligned} \chi''(\mathbf{x}, \mathbf{x}', \omega) &= \frac{\pi}{\hbar} \sum_{nm} \rho_n \{ \langle n | \phi_i(\mathbf{x}, 0) | m \rangle \langle m | \phi_j(\mathbf{x}', 0) | n \rangle \delta(\omega + \omega_n - \omega_m) \\ &\quad - \langle n | \phi_j(\mathbf{x}', 0) | m \rangle \langle m | \phi_i(\mathbf{x}, 0) | n \rangle \delta(\omega - \omega_n + \omega_m) \}. \end{aligned} \quad (7.6.32)$$

If $\phi_i(\mathbf{x}, t) = \phi(t)$ is independent of \mathbf{x} and i , Eq. (7.6.32) reduces in the canonical ensemble to

$$\chi''(\omega) = \frac{\pi}{\hbar} \sum_{nm} \frac{e^{-\beta\hbar\omega_n}}{Z} |\langle n | \phi | m \rangle|^2 [\delta(\omega + \omega_n - \omega_m) - \delta(\omega - \omega_n + \omega_m)], \quad (7.6.33)$$

where $Z = \sum_n e^{-\beta\hbar\omega_n}$ is the partition function.

Thus, χ'' consists of a series of delta function spikes with weights determined by the equilibrium density matrix and the matrix elements $\langle n | \phi_i(\mathbf{x}, 0) | m \rangle$. This in turn implies that the complex response function has poles along the real axis at frequencies $\pm(\omega_n - \omega_m)$ corresponding to the possible excitation frequencies of the system. Using Eqs. (7.1.29) and (7.6.32), we obtain

$$\begin{aligned} \chi_{\phi_i \phi_j}(\mathbf{x}, \mathbf{x}', z) &= \frac{1}{\hbar} \sum_{nm} \rho_n \left\{ \frac{\langle n | \phi_i(\mathbf{x}, 0) | m \rangle \langle m | \phi_j(\mathbf{x}', 0) | n \rangle}{\omega_m - \omega_n - z} \right. \\ &\quad \left. - \frac{\langle n | \phi_j(\mathbf{x}', 0) | m \rangle \langle m | \phi_i(\mathbf{x}, 0) | n \rangle}{\omega_n - \omega_m - z} \right\}. \end{aligned} \quad (7.6.34)$$

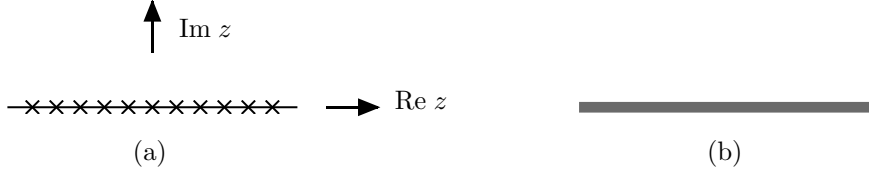


Figure 7.6.1: (a) Pole structure for $\chi(z)$ for finite systems. There are poles along the real axis separated by a minimum distance. $\chi(z)$ is analytic everywhere in the complex z plane except at these poles and is in particular analytic in the upper half plane as required by the considerations of Sec. 7.2. (b) Singularity structure for an infinite system. The poles merge together to form a branch cut separating the upper and lower half planes. $\chi(z)$ remain analytic in the upper half plane.

For a finite system, there is a minimum excitation energy, and thus a minimum distance between poles of $\chi(z)$ as shown in Fig. 7.6.1. This means that $\chi(z)$ can be analytically continued to the negative half plane directly using Eq. (7.6.34). As the characteristic length L of the system tends to infinity, as it does in most systems of interest in condensed matter physics, the energy level spacing goes to zero as L^{-2} . In this case, the poles in $\chi(z)$ push closer and closer together until, finally, when $L \rightarrow \infty$, the discrete set of poles becomes a branch cut. $\chi(z)$ defined by the spectral representation of Eq. (7.1.29) is analytic function for z in the upper half plane or in the lower half plane. It, however, reaches different values on opposite sides of the cut

$$\lim_{\eta \rightarrow 0} \chi(\omega + i\eta) \neq \lim_{\eta \rightarrow 0} \chi(\omega - i\eta). \quad (7.6.35)$$

Each pole in $\chi(z)$ corresponds to a delta function in $\chi''(\omega)$. Thus in a finite system, $\chi''(\omega)$ will consist of separated spikes with intensities determined by the matrix elements in Eq. (7.6.34) as shown in Fig. 7.6.2a. When $L \rightarrow \infty$, the spikes merge into a continuous curve as shown in Fig. 7.6.2b that can, for example, have the Lorentzian shape discussed in Sec. 7.3. This illustrates how dissipation characterized by a finite width in $\chi''(\omega)$ results when $L \rightarrow \infty$.

7.6.5 The fluctuation-dissipation theorem

In the preceding section, we saw that there is a simple relation between the dissipation function $\chi''_{xx}(\omega)$ and the correlation function $S_{xx}(\omega)$ for the classical harmonic oscillator. We will now use the formalism developed in this section to show that an obvious generalization of this result applies to

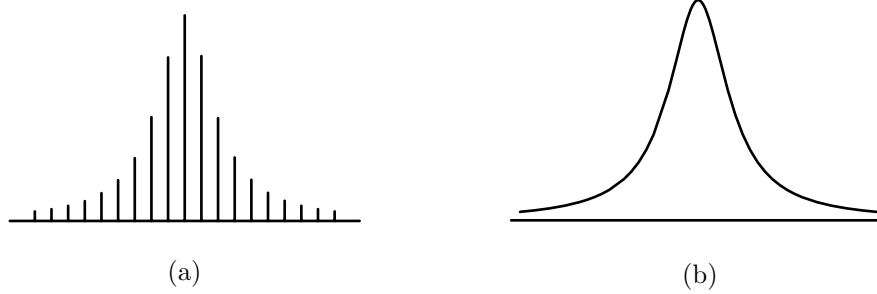


Figure 7.6.2: (a) $\chi''(\omega)$ consisting of a set of discrete delta-function spikes corresponding to the pole structure of Fig. 7.6.1a. (b) $\chi''(\omega)$ when $L \rightarrow \infty$ (corresponding to the branch cut of Fig. 7.6.1b).

all systems in thermal equilibrium. For simplicity, we will consider only systems described by the canonical density matrix,

$$\rho = \frac{1}{Z} e^{-\beta\mathcal{H}}, \quad Z = \text{Tr} e^{-\beta\mathcal{H}}. \quad (7.6.36)$$

A proof of the theorem rests on the observation that $e^{-\beta\mathcal{H}}$ is an imaginary time translation operator. Thus, we can write

$$\begin{aligned} \text{Tr} e^{-\beta\mathcal{H}} \phi_i(\mathbf{x}, t) \phi_j(\mathbf{x}', t') &= \text{Tr} e^{-\beta\mathcal{H}} \phi_i(\mathbf{x}, t) e^{\beta\mathcal{H}} e^{-\beta\mathcal{H}} \phi_j(\mathbf{x}', t') \\ &= \text{Tr} \phi_i(\mathbf{x}, t + i\beta\hbar) e^{-\beta\mathcal{H}} \phi_j(\mathbf{x}', t'), \\ &= \text{Tr} e^{-\beta\mathcal{H}} \phi_j(\mathbf{x}', t') \phi_i(\mathbf{x}, t + i\beta\hbar). \end{aligned} \quad (7.6.37)$$

where the last step follows from the cyclic invariance property of the trace. We can use this result to express the correlation function $S_{\phi_i\phi_j}(\mathbf{x}, \mathbf{x}', \omega)$ in terms of $S_{\phi_j\phi_i}(\mathbf{x}', \mathbf{x}, -\omega)$:

$$\begin{aligned} S_{\phi_i\phi_j}(\mathbf{x}, \mathbf{x}', \omega) &= \int_{-\infty}^{\infty} dt e^{i\omega t} S_{\phi_i\phi_j}(\mathbf{x}, \mathbf{x}', t, 0) \\ &= \int_{-\infty}^{\infty} dt S_{\phi_j\phi_i}(\mathbf{x}', \mathbf{x}, -t - i\beta\hbar, 0) e^{i\omega t} \\ &= e^{\beta\hbar\omega} \int_{-\infty}^{\infty} dt S_{\phi_j\phi_i}(\mathbf{x}', \mathbf{x}, t, 0) e^{-i\omega t}. \end{aligned} \quad (7.6.38)$$

Thus

$$S_{\phi_i\phi_j}(\mathbf{x}, \mathbf{x}', \omega) = e^{\beta\hbar\omega} S_{\phi_j\phi_i}(\mathbf{x}', \mathbf{x}, -\omega). \quad (7.6.39)$$

By definition,

$$\chi''(\mathbf{x}, \mathbf{x}', \omega) = \frac{1}{2\hbar} [S_{\phi_i \phi_j}(\mathbf{x}, \mathbf{x}', \omega) - S_{\phi_j \phi_i}(\mathbf{x}', \mathbf{x}, -\omega)] \quad (7.6.40)$$

so that

$$\chi''(\mathbf{x}, \mathbf{x}', \omega) = \frac{1}{2\hbar} (1 - e^{-\beta\hbar\omega}) S_{\phi_i \phi_j}(\mathbf{x}, \mathbf{x}', \omega). \quad (7.6.41)$$

Note that this result reduces to the classical result $\chi''(\mathbf{x}, \mathbf{x}', \omega) = \frac{1}{2}\beta\omega S_{\phi_i \phi_j}(\mathbf{x}, \mathbf{x}', \omega)$ when $\hbar \rightarrow 0$ and agrees with the harmonic oscillator result of the preceding section.

7.6.6 Sum rules and moment expansions

The representation of χ'' as the expectation value of a commutator, allows us to express the high-frequency moments of χ'' in terms of expectation values of equilibrium commutators. At high frequency, we can expand in powers of $1/z$:

$$\begin{aligned} \chi_{\phi_i \phi_j}(\mathbf{x}, \mathbf{x}', z) &= \int \frac{d\omega}{\pi} \frac{\chi''(\mathbf{x}, \mathbf{x}', \omega)}{\omega - z} \\ &= - \sum_{p=1}^{\infty} \frac{1}{z^p} \int_{-\infty}^{\infty} \frac{d\omega}{\pi} \omega^p \frac{\chi''(\mathbf{x}, \mathbf{x}', \omega)}{\omega} \\ &\equiv - \sum_{p=1}^{\infty} \frac{1}{z^p} [\omega_{ij}^p(\mathbf{x}, \mathbf{x}')] \chi_{\phi_i \phi_j}(\mathbf{x}, \mathbf{x}', 0), \end{aligned} \quad (7.6.42)$$

where we introduced the p^{th} frequency moment of $\chi''(\mathbf{x}, \mathbf{x}', \omega)$ defined as

$$[\omega_{ij}^p(\mathbf{x}, \mathbf{x}')] \chi_{\phi_i \phi_j}(\mathbf{x}, \mathbf{x}', 0) \equiv \int_{-\infty}^{\infty} \frac{d\omega}{\pi} \omega^p \frac{\chi''(\mathbf{x}, \mathbf{x}', \omega)}{\omega} \quad (7.6.43)$$

These frequency moments are defined so that the zeroth moment is one. They can be evaluated in terms of commutators of the time derivatives of the field $\phi_i(\mathbf{x}, t)$. It follows directly from Eq. (7.6.17) that

$$\begin{aligned} \frac{1}{\hbar} \langle [(id/dt)^n \phi_i(\mathbf{x}, t), \phi_j(\mathbf{x}', 0)] \rangle &= \int_{-\infty}^{\infty} \frac{d\omega}{\pi} \omega^n \chi''(\mathbf{x}, \mathbf{x}', \omega) \\ &= \frac{1}{\hbar} \langle [[\dots[\phi_i(\mathbf{x}, t), \mathcal{H}/\hbar], \mathcal{H}/\hbar] \dots], \phi_j(\mathbf{x}', t)] \rangle. \end{aligned} \quad (7.6.44)$$

Thus, the high-frequency moments can be obtained from equal-time commutators. Note that since the left hand side of Eq. (7.6.44) is bounded, all

moments of $\chi''(\mathbf{x}, \mathbf{x}', \omega)$ for $p \geq 0$ must exist, and as a result $\chi''(\mathbf{x}, \mathbf{x}', \omega)$ must die off at large ω faster than any power of ω .

One particularly important sum rule is the f -sum rule for the particle density. We first note that

$$\begin{aligned} \int \frac{d\omega}{\pi} \omega \chi''_{nn}(\mathbf{x}, \mathbf{x}', \omega) &= \frac{1}{\hbar} \langle [\partial n(\mathbf{x}, t) / \partial t, n(\mathbf{x}', t)] \rangle \\ &= \frac{1}{\hbar} \nabla_i \langle [j_i(\mathbf{x}, t), n(\mathbf{x}', t)] \rangle, \end{aligned} \quad (7.6.45)$$

where $n(\mathbf{x}, t)$ is the density operator and $j_i(\mathbf{x}, t) = \sum_{\alpha} p_i^{\alpha} \delta(\mathbf{x} - \mathbf{x}_{\alpha}(t)) / m$ is the current operator. The current-density commutator is easily calculated to be

$$\int \frac{d\omega}{\pi} \omega \chi''_{nn}(\mathbf{x}, \mathbf{x}', \omega) = \frac{1}{m} \nabla \cdot \nabla' \langle n(\mathbf{x}) \rangle \delta(\mathbf{x} - \mathbf{x}'). \quad (7.6.46)$$

The Fourier transform of this is Eq. (7.4.21).

7.7 Memory Functions and Kubo Formulae

7.7.1 Current Response

Until now, we have assumed that transport coefficients like Γ [Eq. (7.4.29)] in the diffusion problem or the friction coefficient α for a particle in a fluid are constants. In fact in general, these coefficients like dynamic response functions are frequency or equivalently time dependent. Thus, we should rewrite the relationship between current and chemical potential gradient in the diffusion problem as

$$\mathbf{j}(\mathbf{x}, t) = \int_{-\infty}^{\infty} dt' \tilde{\Gamma}(t - t') \nabla \mu(\mathbf{x}, t'), \quad (7.7.1)$$

where $\tilde{\Gamma}(t)$ is the dynamic response of the current to gradients in the chemical potential. $\tilde{\Gamma}$ could also depend on distance, but we will restrict our attention to slow spatial variations where such dependence is unimportant. The response of the current to chemical potential gradients must be causal, and $\tilde{\Gamma}(t)$ like the response function $\tilde{\chi}(t)$ is proportional to a step function. For reasons that will become more clear shortly, we will define $\tilde{\Gamma}(t)$ without the factor of i that appeared in our definition of $\tilde{\chi}(t)$ [Eq. (7.1.12)]:

$$\tilde{\Gamma}(t) = 2\eta(t) \tilde{\Gamma}'(t). \quad (7.7.2)$$

As already indicated, there is no i in this equation, and it contains $\tilde{\Gamma}'(t)$ rather than $\tilde{\Gamma}''(t)$. We can Fourier-Laplace transform $\tilde{\Gamma}(t)$ exactly as we transformed $\tilde{\chi}(t)$. The result is

$$\begin{aligned}\Gamma(z) &= \int_0^\infty dt e^{izt} \tilde{\Gamma}(t) \\ &= \int_{-\infty}^\infty \frac{d\omega}{\pi i} \frac{\Gamma'(\omega)}{\omega - z}\end{aligned}\quad (7.7.3)$$

where $\text{Im}z > 0$ and $\Gamma'(\omega)$ is the Fourier transform of $\tilde{\Gamma}(t)$. Setting $z = \omega + i\epsilon$, we obtain

$$\Gamma(\omega) \equiv \Gamma(\omega + i\epsilon) = \Gamma'(\omega) + i\Gamma''(\omega), \quad (7.7.4)$$

where

$$\Gamma''(\omega) = -P \int_{-\infty}^\infty \frac{d\omega'}{\pi i} \frac{\Gamma'(\omega')}{\omega' - \omega}. \quad (7.7.5)$$

The correlation and response functions for the density are identical in form to what we calculated previously [Eq. (7.4.28)], except that D should be replaced by $D(z) = \Gamma(z)/\chi$.

The functions $\Gamma'(\omega)$ and $\Gamma(z)$ can be expressed in terms of commutators/correlation functions of the particle current \mathbf{j} , much as the density response can be expressed in terms of commutators of the density. The resulting formula, particularly in the zero-frequency limit is called a Kubo formula. From Eq. (7.4.28), we see that Γ is simply the response of \mathbf{j} to $\nabla\mu^{\text{ext}}$ in the spatially uniform equilibrium state with n a constant and $\nabla\mu(n) = 0$.¹ We, therefore, consider

$$\delta\langle j_i(\mathbf{q}, \omega) \rangle = \chi_{j_i n}(\mathbf{q}, \omega) \mu^{\text{ext}}(\mathbf{q}, \omega) = \int \frac{d\omega'}{\pi} \frac{\chi''_{j_i n}(\mathbf{q}, \omega')}{\omega' - \omega - i\epsilon} \mu^{\text{ext}}(\mathbf{q}, \omega). \quad (7.7.6)$$

Since \mathbf{j} is the current associated with the conserved density n , we have

$$\partial'_t \tilde{\chi}_{j_i n}(\mathbf{x}, \mathbf{x}', t, t') = -\partial'_k \tilde{\chi}_{j_i j_k}(\mathbf{x}, \mathbf{x}', t, t') \quad (7.7.7)$$

$$i\omega \chi''_{j_i n}(\mathbf{q}, \omega) = iq_k \chi_{j_i j_k}(\mathbf{q}, \omega), \quad (7.7.8)$$

Where $\partial'_t = \partial/\partial t'$ and $\partial'_k = \partial/\partial x'_k$. Thus

$$\langle j_i(\mathbf{q}, \omega) \rangle = \int \frac{d\omega'}{\pi} \frac{\chi''_{j_i j_k}(\mathbf{q}, \omega')}{i\omega'(\omega' - \omega - i\epsilon)} iq_k \delta\mu^{\text{ext}}(\mathbf{q}, \omega). \quad (7.7.9)$$

¹We continue to use the convention, which is common in the physics community, in which the temporal Fourier transform of a field $\phi(t)$ is defined with a $-i\omega t$ in the exponent: $\phi(t) = \int (d\omega/(2\pi)) e^{-i\omega t} \phi(\omega)$. In the engineering and rheology literature the opposite convention is usually used. As a result, the signs of some of the equations that follow will differ from those often encountered in the literature.

The spatial Fourier transform of $\partial_k \mu^{\text{ext}}(\mathbf{x}, \omega)$ is $i q_k \mu^{\text{ext}}(\mathbf{q}, \omega)$. The response to the gradient of the external chemical potential μ^{ext} when the density is spatially uniform is just the negative of the response to the gradient of the internal chemical potential μ [See Eq. (7.4.28)] when the external gradient is zero, and we conclude that in the limit of slow spatial variations in which $\partial_k \mu^{\text{ext}}(\mathbf{x}, \omega)$ is essentially constant that

$$\langle j_i(\mathbf{x}, \omega) \rangle = -\Gamma_{ik}(\omega) \partial_k \mu(\mathbf{x}, \omega), \quad (7.7.10)$$

where

$$\Gamma_{ik}(\omega) = \int \frac{d\omega'}{\pi} \frac{\chi''_{j_i j_k}(\mathbf{q} = 0, \omega')}{i\omega'(\omega' - \omega - i\epsilon)}. \quad (7.7.11)$$

Comparing this equation with Eq. (7.7.3), we obtain

$$\Gamma'_{ik}(\omega) = \frac{\chi''_{j_i j_k}(\mathbf{q} = 0, \omega)}{\omega} \quad (7.7.12)$$

$$= \frac{1 - e^{-\hbar\omega/T}}{2\hbar\omega} S_{j_i j_k}(\mathbf{q} = 0, \omega) \quad (7.7.13)$$

$$\rightarrow \frac{1}{2T} S_{j_i j_k}(\mathbf{q} = 0, \omega), \quad (7.7.14)$$

where we used the fluctuation-dissipation theorem [Eq. (7.6.41)] and the last form is valid in the classical limits, $\hbar \rightarrow 0$. The zero-frequency transport coefficient $\Gamma_{ik} = \delta_{ik} \Gamma$ is

$$\Gamma_{ik} = \frac{1}{2T} S_{j_i j_k}(0, 0) \quad (7.7.15)$$

$$= \frac{1}{T} \int d^d x \int_0^\infty dt \langle j_i(\mathbf{x}, t) j_k(\mathbf{0}, 0) \rangle, \quad (7.7.16)$$

where we used $S_{j_i j_k}(\mathbf{x}, \mathbf{x}', \omega) = S_{j_i j_k}(\mathbf{x}, \mathbf{x}', -\omega)$. This is the Kubo formula for the static transport coefficient. Because of the zero-frequency limit, it is valid for both quantum and classical systems.

Kubo formulae can be derived for any transport coefficients. They have formal value in that they express these coefficients in terms of correlation functions whose symmetry properties we know and understand. Using them, we can prove symmetry relations among transport coefficients. For example in a two-component fluid, a gradient in the chemical potential difference $\tilde{\mu}$ between the two species produces a heat current \mathbf{Q} in addition to a relative diffusion current \mathbf{J} , and a gradient in the temperature produces a diffusion current in addition to heat current: $\mathbf{Q} = -\kappa \nabla T - T \gamma_{Tn} \tilde{\mu}$ and $\mathbf{J} = -\Gamma \nabla \tilde{\mu} - \gamma_{nT} \nabla T$. The Kubo relations guarantee that $\gamma_{Tn} = \gamma_{nT}$.

7.7.2 Shear Viscosity and Complex Shear Modulus

Of particular interest is the Kubo formula for the shear viscosity. In a fluid, the momentum is a conserved quantity, and the momentum density $\mathbf{g}(\mathbf{x}, t)$ satisfies a conservation law,

$$\frac{\partial g_i}{\partial t} = \nabla_j \sigma_{ij}, \quad (7.7.17)$$

where the stress tensor σ_{ij} is the negative of the momentum current. The momentum density is the mass density ρ times the local velocity \mathbf{v} , which is the field conjugate to \mathbf{g} (just as the chemical potential is the field conjugate to the number density n). The dissipative part of the stress tensor is proportional to the gradient of the local velocity:

$$\sigma_{ij} = \eta(\delta_{ik}\delta_{jl} + \delta_{il}\delta_{jk} - \frac{2}{3}\delta_{ij}\delta_{lk})\partial_k v_l + \zeta\nabla \cdot \mathbf{v}, \quad (7.7.18)$$

where η is the shear viscosity and ζ is the bulk viscosity. The shear viscosity η like Γ_{ij} depends on frequency, and it has a Kubo-like expression in terms of correlations of the stress tensor:

$$\eta(\omega) = \int \frac{d\omega'}{\pi i} \frac{\chi''_{\sigma_{xy}\sigma_{xy}}(\mathbf{q} = 0, \omega')}{\omega'(\omega' - \omega - i\epsilon)} \quad (7.7.19)$$

$$= \frac{1}{T} \int d^3x \int_0^\infty e^{i\omega t} \langle \sigma_{xy}(\mathbf{x}, t) \sigma_{xy}(\mathbf{0}, 0) \rangle \quad (7.7.20)$$

$$= \eta'(\omega) + i\eta''(\omega). \quad (7.7.21)$$

In simple fluids, we are normally interested in very low frequencies for which $\eta'(\omega) = \eta$ is a constant and $\eta''(\omega) = 0$. If the fluid is characterized by a single relaxation time τ , then

$$\eta(\omega) = \frac{\eta_0}{1 - i\omega\tau} \quad (7.7.22)$$

$$\eta'(\omega) = \eta_0 \frac{1}{1 + \omega^2\tau^2} \quad (7.7.23)$$

$$\eta''(\omega) = \eta_0 \frac{\omega\tau}{1 + \omega^2\tau^2}, \quad (7.7.24)$$

where η_0 is the zero-frequency viscosity. These relations define the Maxwell model for a fluid. Note that both the real and the imaginary parts of the viscosity vanish at high frequencies.

An isotropic elastic solid is characterized by a zero-frequency shear modulus μ . The stress tensor is μ times gradients of the displacement vector

u. The velocity vector is the time derivative of the displacement: $\partial_t \mathbf{u} = \mathbf{v}$ and

$$\sigma_{xy} = (\mu - i\omega\eta)\partial_y u_x \equiv G^*(\omega)\partial_y u_x \quad (7.7.25)$$

if $\partial_y u_x$ is the only non-vanishing component of $\partial_i u_j$. $G^*(\omega)$ is the complex shear modulus, which is usually represented as

$$G^*(\omega) = -i\omega\eta(\omega) = G'(\omega) + iG''(\omega) \quad (7.7.26)$$

where $G'(\omega)$ is the storage modulus and $G''(\omega)$ is the loss modulus. This equation expresses $G^*(\omega)$ in terms of the frequency-dependent viscosity. If there is a non vanishing shear modulus, then $\eta(\omega)$ has a part equal to $\mu/(-i\omega)$ at low frequency. In the Maxwell model,

$$G^*(\omega) = \eta_0 \frac{-i\omega}{1 - i\omega\tau} \quad (7.7.27)$$

$$G'(\omega) = \eta_0 \frac{\omega^2\tau}{1 + \omega^2\tau^2} \quad (7.7.28)$$

$$G''(\omega) = -\eta_0 \frac{\omega}{1 + \omega^2\tau^2}. \quad (7.7.29)$$

Thus, $G''(\omega) \rightarrow \eta_0/\tau \equiv \mu_\infty$ as $\omega \rightarrow \infty$. μ_∞ is a high-frequency shear modulus. Note that the sign $G''(\omega)$ is negative as it should be with our sign convention for Fourier transforms. $G^*(\omega)$ is really the inverse response of the strain (i.e., displacement) to stress (i.e., force). The imaginary part of $\omega G^{*-1}(\omega)$ must, therefore, be positive definite as it is.

With the above definitions, we can express $\sigma_{xy} \equiv \sigma$ in terms of the strain $\gamma = \partial_y u_x$ or strain rate $\dot{\gamma} = \partial_y v_x$ as

$$\sigma(\omega) = G^*(\omega)\gamma(\omega) = \eta(\omega)\dot{\gamma}(\omega) \quad (7.7.30)$$

$$\sigma(t) = \int_{-\infty}^{\infty} dt' \tilde{G}^*(t-t')\gamma(t') = \int_{-\infty}^t dt' \tilde{\eta}(t-t') \frac{d\gamma(t')}{dt'}. \quad (7.7.31)$$

A common experimental condition is to apply a specific strain γ at time $t = 0+$. This will set up a time-dependent stress

$$\sigma(t) = \tilde{\eta}(t)\gamma. \quad (7.7.32)$$

7.8 Microrheology

Recall from Sec. 7.2 that a particle in a fluid experiences a friction force proportional to its velocity times the viscosity of fluid. Thus, measurements of the particle's motion can be used to determine the viscosity of the fluid, for

example via $\langle r^2(t) \rangle = 6Dt = [T/(\pi\eta a)]t$, where $\mathbf{r}(t)$ is the particle displacement. Measurements of the response or fluctuations of particles embedded in complex media such as gels, polymer solutions, colloidal dispersions of both isotropic and anisotropic particles, and even living cells can provide information about the complex shear modulus $G^*(\omega)$ of the medium[5]. If the radius a of a particle is large compared to any characteristic length of the medium with a complex shear modulus in which it moves, its equation of motion can be shown to be

$$m \frac{\partial v_i}{\partial t} + \int_{-\infty}^t dt' \tilde{\alpha}(t-t') v_i(t') = f_i(t) + \zeta_i(t), \quad (7.8.1)$$

where $\tilde{\alpha}(t) = 6\pi a \tilde{\eta}(t)$, f_i is the external force, and $\zeta_i(t)$ is the Langevin noise. From this, we can calculate directly the response of the velocity to the external force:

$$\chi_{v_i r_j}(z) = \delta_{ij} \frac{1}{-izm + \alpha(z)}. \quad (7.8.2)$$

From this we can calculate $\chi_{r_i r_j}(z)$

$$\chi_{r_i r_j}(z) = \int \frac{d\omega}{\pi} \frac{\chi''_{r_i r_j}(\omega)}{\omega - z} \quad (7.8.3)$$

$$= \int \frac{d\omega}{\pi} \frac{\chi''_{v_i r_j}(\omega)}{-i\omega(\omega - z)} \quad (7.8.4)$$

$$= \frac{1}{-iz} \int \frac{d\omega}{\pi} \left(\frac{1}{\omega - z} - \frac{1}{\omega} \right) \chi''_{v_i r_j}(\omega) \quad (7.8.5)$$

$$= \frac{1}{-iz} \chi_{v_i r_j}(z) = \delta_{ij} \frac{1}{-iz(-izm + 6\pi a \eta(z))} \quad (7.8.6)$$

$$\approx \delta_{ij} \frac{1}{6\pi a G^*(z)}, \quad (7.8.7)$$

where we used the fact that $\chi''_{v_i r_j}(\omega)$ is even in ω so that the second term in Eq. (7.8.5) is zero, and where in the final form [Eq. (7.8.7)], we assume that frequencies are low enough that the inertial term $-z^2 m$ can be neglected. A similar analysis yields

$$\chi_{v_i v_j}(z) = \delta_{ij} \frac{iz}{-izm + 6\pi a \eta(z)} \quad (7.8.8)$$

$$\chi''_{v_i v_j}(\omega) = \delta_{ij} \frac{\omega \alpha'(\omega)}{|-i\omega m + \alpha(\omega)|^2}. \quad (7.8.9)$$

Thus a measurement of the response $\chi_{r_i r_j}(\omega)$ of the particle displacement to an external force yields the complex shear modulus $G^*(\omega)$, which is

measured directly in more macroscopic rheology experiments. Equivalently, the Laplace transform of the response $\chi_{r_i r_j}(is)$ yields the Laplace transform $G^*(is)$ of the complex shear modulus. As usual, the response function can be determined experimentally by measuring the amplitude and phase of the displacement in response to a frequency-dependent external force.

Rather than measuring the response to an external force, it is often easier experimentally to measure directly the Brownian motion of a particle in a complex medium, i.e. to measure $\langle \Delta r^2(t) \rangle = \langle (\mathbf{r}(t) - \mathbf{r}(0)) \cdot (\mathbf{r}(t) - \mathbf{r}(0)) \rangle$ or its Laplace transform $\langle \Delta r^2(s) \rangle$. The Laplace transform

$$C_{v_i v_j}(s) = \int_0^\infty e^{-st} C_{v_i v_j}(t, 0) \quad (7.8.10)$$

of the velocity can be calculated directly from Eq. (7.8.1):

$$C_{v_i v_j}(s) = \frac{1}{ms + 6\pi a \eta(s)} m \langle v_i(0) v_j(0) \rangle = \delta_{ij} \frac{T}{ms + 6\pi a \eta(s)}. \quad (7.8.11)$$

Then, using

$$\langle \Delta r_i(t) \Delta r_j(t) \rangle = \int_0^t dt_1 \int_0^t dt_2 \langle v_i(t_1) v_j(t_2) \rangle = 2 \int_0^t dt' (t - t') C_{v_i v_j}(t', 0), \quad (7.8.12)$$

we obtain

$$\langle \Delta r^2(s) \rangle = \frac{2}{s^2} C_{v_i v_i}(s) \quad (7.8.13)$$

$$= \frac{6T}{ms^2 + 6\pi a s^2 \eta(s)} \approx \frac{T}{\pi a G^*(s)}. \quad (7.8.14)$$

Thus, the Laplace transform of the displacement correlation function yields the Laplace transform $G^*(s)$ of the the complex shear modulus. The conversion $G^*(s)$ to $G^*(\omega)$ is in principal straightforward, but it does require some care. One approach is to fit $G^*(s)$ with a functional form, and merely replace s by $-i\omega$.

Figures 7.8.1 to 7.8.3 show $\langle \Delta r^2(t) \rangle$, $G^*(s)$, and $G'(\omega)$ and $G''(\omega)$ for microrheological measurements in solutions of F-actin taken by Gisler and Weitz [Phys. Rev. Lett. **82**, 1606 (1999)]. F-actin is a long semi-flexible polymer. The data show that the system has a nearly constant storage modulus $G'(\omega)$ and that the reactive (storage) part of G^* dominates over the dissipative (loss) part at low frequency. At high frequency, both $G'(\omega)$ and $G''(\omega)$ are proportional to $\omega^{3/4}$.

Our analysis above of a system in which the dissipative coefficient is a memory function rather than simply a constant did not consider the noise.

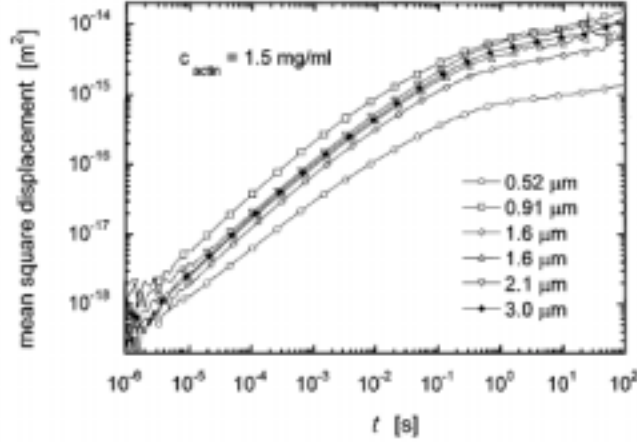


Figure 7.8.1: Mean-square displacements $\langle \Delta r^2(t) \rangle$ of polystyrene latex beads in 1.5 mg/ml phalloidin-stabilized F-actin measured with diffusing-wave spectroscopy; symbols denote different bead sizes.

When the dissipative coefficient is a constant α , the noise fluctuation in an equilibrium systems is simply $\langle \zeta_i(t)\zeta_j(t') \rangle = 2\alpha T\delta(t-t')$. When the dissipative coefficient $\tilde{\alpha}(t)$ depends on time, the noise spectrum must be modified to drive the system to equilibrium. To determine what the noise spectrum must be, we calculate the response of v_i to the noise from Eq. (7.8.1) from which we obtain

$$v_i(\omega) = \frac{\zeta_i(\omega)}{-i\omega m + \alpha(\omega)}. \quad (7.8.15)$$

Then setting

$$\langle \zeta_i(t)\zeta_j(t') \rangle = A(t-t')\delta_{ij} \quad (7.8.16)$$

we obtain

$$C_{v_i v_j}(\omega) = \delta_{ij} \frac{A(\omega)}{|-i\omega m + \alpha(\omega)|^2} \quad (7.8.17)$$

$$= \frac{A(\omega)}{\alpha'(\omega)} \frac{\chi_{v_i v_j}(\omega)}{\omega} \quad (7.8.18)$$

$$= \frac{A(\omega)}{\alpha'(\omega)} \frac{1}{2T} C_{v_i v_j}(\omega), \quad (7.8.19)$$

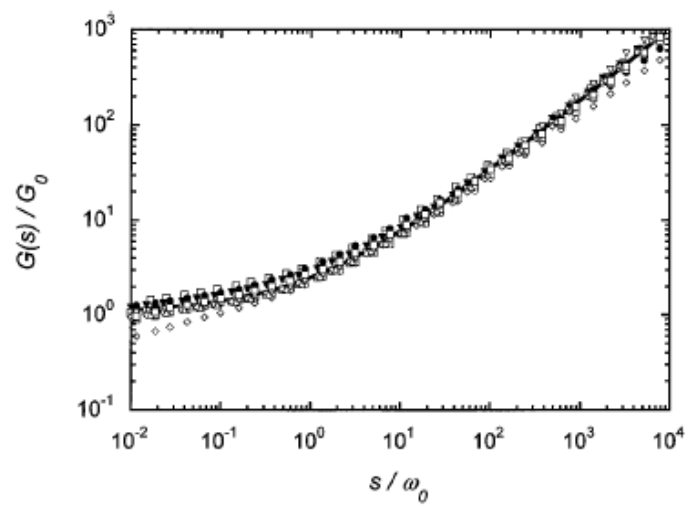


Figure 7.8.2: $G(s)$ scaled with low-frequency value $G_0(s)$ as a function of the normalized frequency s/ω_0 . Symbols correspond to actin monomer concentrations between 1 and 2 mg/ml and bead diameters between 0.52 and 3 μm . The solid line is a fit of the ansatz $G(s)/G_0 = 1 + c_1(s/\omega_0)^{1/3} + c_2(s/\omega_0)^{3/4}$ to the averaged data. Best-fit parameters are $c_1 = 0.5$ and $c_2 = 1.0$.

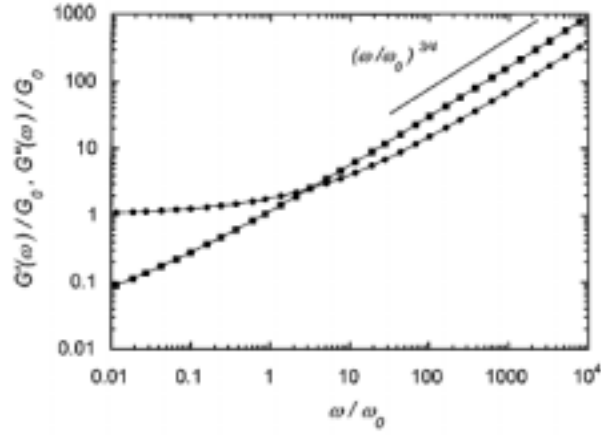


Figure 7.8.3: Storage modulus $G'(\omega)$ (closed circles) and loss modulus $G''(\omega)$ (closed squares) calculated from the light scattering data. The crossover regions is broadened by a term scaling as $\omega^{1/3}$.

where we used Eq. (7.8.9) for $\chi''_{v_i v_j}(\omega)$. From this we conclude that

$$A(\omega) = 2T\alpha'(\omega) \tag{7.8.20}$$

and

$$\langle \zeta_i(t)\zeta_j(t') \rangle = \delta_{ij}2T\tilde{\alpha}'(t - t'). \tag{7.8.21}$$

This is relation between noise and the time-dependent dissipative memory coefficient generalizes to more complex situations.

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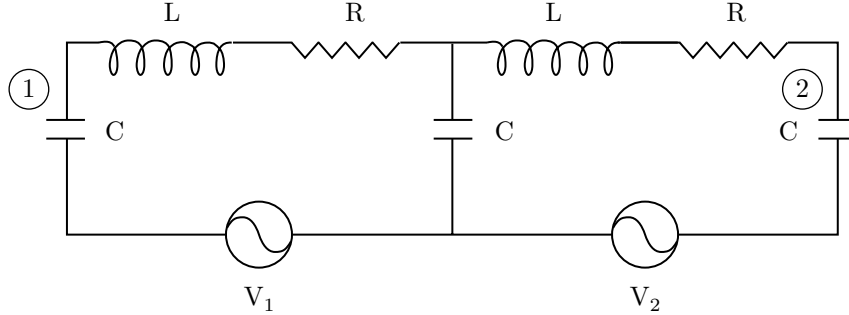
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Problems

7.1 Consider the coupled *LRC* electrical circuit shown in Fig 7P.1.

- (a) Calculate the frequency-dependent response function $\chi_{ij}(\omega)$ for the charge q_i on capacitor $i = 1, 2$ produced by a voltage at source $j = 1, 2$ at frequency ω .
- (b) Calculate $\chi''_{11}(\omega)$ and plot it as a function of frequency. Discuss the limit $R \rightarrow 0$.
- (c) Calculate $\lim_{\omega \rightarrow 0} \chi_{ij}(\omega)$ and $\lim_{\omega \rightarrow \infty} \chi_{ij}(\omega)$ and compare these results with sum rules that can be calculated independently (you may assume $R = 0$ here).
- (d) Calculate the thermal equilibrium charge correlation function $S_{q_i q_j}(\omega)$.

7.2 Calculate the transverse position-velocity and velocity-velocity response functions for the harmonic continuum elastic model of Sec. 7.3. Determine, in particular, the low-frequency form of $\chi_{vv}(\mathbf{q}, z)$ and the long-wavelength form for $\chi''_{vv}(\mathbf{q}, \omega)$.

Figure 7P.1: *LRC* circuit for Prob. 7.1

- 7.3 Calculate the density-density response function using Eq. (7.4.28) for the current and a time-dependent external chemical potential $\mu^{\text{ext}}(\mathbf{x}, t)$.
- 7.4 If the diffusion constant depends on frequency, then

$$\chi(\mathbf{q}, z) = \chi(\mathbf{q}) \frac{D(\mathbf{q}, z)q^2}{-iz + D(\mathbf{q}, z)q^2}.$$

Express $D(\mathbf{q}, z)$ in terms of $\chi(\mathbf{q}, z)$ and then, using the analyticity properties of $\chi(\mathbf{q}, z)$, show that $D(\mathbf{q}, z)$ is analytic in the upper half plane and can be written as

$$D(\mathbf{q}, z) = \int \frac{d\omega}{\pi} \frac{D'(\mathbf{q}, \omega)}{\omega - z},$$

where $D'(\mathbf{q}, \omega)$ is the real part of $D(\mathbf{q}, \omega + i\epsilon)$.

- 7.5 Generalize the resistor network equation [Eq. (7.4.47)] to include a current $I(t)$ inserted at the origin and a current $-I(t)$ extracted at site \mathbf{x} . Show that the complex impedance for current flowing from the origin to \mathbf{x} is

$$Z(\mathbf{x}, \omega) = \int \frac{d^d q}{(2\pi)^d} \frac{2(1 - \cos \mathbf{q} \cdot \mathbf{x})}{-i\omega C + \sigma[\gamma(0) - \gamma(\mathbf{q})]}.$$

From this, calculate the time-dependent impedance $Z(\mathbf{x}, t)$ for $t > 0$ and express your result in the continuum limit in terms of the diffusion Green function [Eq. (7.4.10)].

- 7.6 (a) Show that the equilibrium displacement correlation function for a damped harmonic oscillator is

$$C_{xx}(t) = \frac{T}{m\omega_0^2} \left(\cos \omega_1 t \frac{\gamma}{2\omega_1} + \sin \omega_1 t \right) e^{-\gamma t/2}.$$

Use this function to calculate the velocity-velocity correlation function $C_{vv}(t)$ and the velocity-displacement correlation functions $C_{xv}(t)$ and $C_{vx}(t)$.

- (b) Calculate the frequency-dependent correlation functions $C_{vv}(\omega)$, $C_{xv}(\omega)$, and $C_{vx}(\omega)$. Then use the fluctuation-dissipation theorem to calculate $\chi''_{vv}(\omega)$, $\chi''_{xv}(\omega)$, and $\chi''_{vx}(\omega)$. Discuss the symmetry properties of these response functions.
- 7.7 (Memory effects) In our treatment of a Brownian particle in a viscous fluid, we assumed that the friction force was simply a constant friction coefficient times the velocity. In general, however, the dissipative force at time t should depend on the velocity at earlier times, and the dissipative coefficient γ should be a time-dependent memory function $\tilde{\gamma}(t) = 2\eta(t)\tilde{\gamma}'(t)$. In the presence of an external force $F(t)$, the velocity equation then becomes

$$\frac{\partial v}{\partial t} = - \int_{-\infty}^{\infty} \tilde{\gamma}(t-t')v(t')dt' + \frac{1}{m}F(t) + \frac{1}{m}\zeta(t).$$

- (a) Using arguments similar to those used to derive Eq. (7.1.17), show that

$$\gamma(z) = \int_0^{\infty} dt e^{izt} \tilde{\gamma}(t) = \int \frac{d\omega}{\pi i} \frac{\gamma'(\omega)}{\omega - z}$$

and that $\gamma(\omega) = \lim_{\epsilon \rightarrow 0} \gamma(\omega + i\epsilon) = \gamma'(\omega) + i\gamma''(\omega)$, where the imaginary part $\gamma''(\omega)$ is related to the real part $\gamma'(\omega)$ by a Kramers-Kronig relation. Show also that $\gamma^*(\omega) = \gamma(-\omega)$

- (b) Calculate the mobility $\mu(\omega)$ relating the velocity to the external force via $v(\omega) = \mu(\omega)F(\omega)$ in terms of $\gamma(\omega)$. What is the complex electrical conductivity of a system with a density n , of non-interacting Brownian particles, each carrying a charge e .
- (c) Show that noise correlations must satisfy

$$C_{\zeta\zeta}(\omega) = I(\omega) = 2Tm\gamma'(\omega)$$

to produce thermal equilibrium. Then show that the velocity correlation function is

$$C_{vv}(\omega) = \frac{2T}{m} \frac{\gamma'(\omega)}{|-i\omega + \gamma(\omega)|^2}.$$

You may wish to use the fact that $\gamma(\omega)$ is analytic in the upper half plane to obtain this result.

- (d) (difficult) If a particle of radius a and density ρ_0 moves with a time-dependent velocity in a fluid of density ρ , it will excite viscous shear waves in the fluid with frequency $\omega_v = -i\eta q^2/\rho$ (see the next chapter). This leads to a singular memory function

$$\gamma(\omega) = -2i\omega\rho/\rho_0 + \gamma[(-i\omega\tau_v)^{1/2} + 1],$$

where $\tau_v = \rho a^2/\eta$ is the viscous relaxation time (the time for a shear wave to diffuse across a particle radius). Show that

$$C_{vv}(t) = \frac{T}{m^*} F(\tau),$$

where $m^* = m[1 + \rho/(2\rho_0)]$, $\tau = (m/m^*)\gamma t$,

$$F[\tau] = \frac{\sigma}{\pi} \tau^{-3/2} \int_0^\infty \frac{e^{-u^2} u^2 du}{(\tau^{-1}u^2 - 1)^2 + \sigma^2 \tau^{-1}u^2},$$

where $\sigma^2 = (m/m^*)(\gamma\tau_v) = (9/2)\rho/[\rho_0 + (\rho/2)]$. This implies that $F(\tau) \rightarrow \sigma\tau^{-3/2}/(2\sqrt{\pi})$ as $\tau \rightarrow \infty$. Such algebraic rather than exponential fall-off of correlation functions at long times is often referred to as a long-time tail. Use the above expression for $C_{vv}(t)$ and Eq. (7.5.16) to show that

$$D(t) \rightarrow D[1 - (\tau_v/t)^{1/2}]$$

as $t \rightarrow \infty$, where $D = T/m\gamma$ is the diffusion constant. Thus, the Einstein relation is satisfied even though the approach to this result at long time is algebraic rather than exponential. Note that when the density of the Brownian particle is much greater than the fluid density, $\sigma \rightarrow 0$, $m^* \rightarrow m$, and $F(t) \rightarrow e^{-\gamma|t|}$, and Eq. (7.5.10) is regained.

- 7.8 (a) Show that the conditional probability function $P(v, t|v_0, t_0)$ defined in Eq. (7.5.32) satisfies

$$\int dv P(v, t|v_0, t_0) = 1, \quad \int dv F(v) P(v, t|v_0, t_0) = \langle F(v(t)) \rangle.$$

- (b) Show that

$$P(v, t|v_0, t_0) = \int_{-\infty}^{\infty} d\lambda \left\langle e^{i\lambda(v-v(t))} \right\rangle_{v_0, t_0}.$$

Then use Eq. (7.5.18) and the fact that

$$\left\langle \exp \left[i\lambda \int_0^t f(t')\zeta(t')dt' \right] \right\rangle = \exp \left[-m\gamma T\lambda^2 \int_0^t f^2(t')dt' \right]$$

for any function $f(t)$ to show that

$$P(v, t|v_0, t_0) = \frac{1}{\sqrt{2\pi\Delta_v(t)}} e^{-(v-\langle v(t) \rangle)^2/2\Delta_v(t)}.$$

(c) The function

$$P(x, t|x_0, v_0, t_0) = \langle \delta(x - x(t)) \rangle_{x_0, v_0, t_0}$$

is the probability that $x = x(t)$ at time t , given that $x = x_0$ and $v = v_0$ at time t_0 . Using Eqs. (7.5.18) and (7.5.22), show that

$$x(t) - \langle x(t) \rangle = \int_0^t dt' \left(1 - e^{\gamma(t'-t)} \right) \zeta(t')/m,$$

where $\langle x(t) \rangle$ is given in Eq. (7.5.23). Then, following the same reasoning as in part (a), show that

$$P(x, t|x_0, v_0, t_0) = \frac{1}{\sqrt{2\pi\Delta_x(t)}} e^{-(x-\langle x(t) \rangle)^2/2\Delta_x(t)},$$

where $\Delta_x(t)$ is given in Eq. (7.5.26). Finally, average the probability $P(x, t|x_0, v_0, t_0)$ over a Maxwell-Boltzmann distribution for v_0 to obtain

$$P(x, t|x_0) = \frac{1}{\sqrt{2\pi\langle [\Delta x(t)]^2 \rangle}} e^{-(x-x_0)^2/2\langle [\Delta x(t)]^2 \rangle},$$

where $\langle [\Delta x(t)]^2 \rangle$ is given by Eq. (7.5.13).

7.9 (Diffusion in an external force field)

(a) Show that the stochastic equation for a three dimensional position $\mathbf{x}(t)$ for a Brownian particle in an external force \mathbf{F} for times long compared to $1/\gamma$ where inertial effects can be ignored is

$$\frac{\partial \mathbf{x}}{\partial t} = \Gamma \mathbf{F} + \boldsymbol{\eta} = -\Gamma \nabla_{\mathbf{x}} \mathcal{H} + \boldsymbol{\eta},$$

where $\Gamma = 1/\alpha$ and $\boldsymbol{\eta} = \boldsymbol{\zeta}/\gamma$ is a vector noise.

- (b) Now consider a particle of mass density ρ in a fluid of density ρ_0 in a gravitational field $\mathbf{g} = g\mathbf{e}_z$. Show that the Smoluchowski equation for the probability $P(\mathbf{x}, t)$ that the particle is at position \mathbf{x} at time t satisfies the equation

$$\frac{\partial P}{\partial t} = D\nabla^2 P + \mathbf{c} \cdot \nabla P \equiv -\nabla \cdot \mathbf{j},$$

where $D = T\Gamma = T/(\gamma m)$, $\mathbf{c} = \mathbf{g}[1 - (\rho/\rho_0)]/\gamma$, and $\mathbf{j} = -(D\nabla P + \mathbf{c}P)$ is the current. This defines a directed diffusion problem in which there is an average drift along \mathbf{e}_z .

- (c) Show that the solution to this equation in an infinite system subject to the boundary condition $P(\mathbf{x}, 0) = \delta(\mathbf{x} - \mathbf{r}_0)$ is

$$P(\mathbf{r}, t) = \frac{1}{(4\pi D|t|)^{3/2}} e^{-|\mathbf{x} - \mathbf{x}_0 + \mathbf{c}t|^2/(4D|t|)}.$$

This shows that there is an average drift in the direction of the applied force. As a result diffusion in an external field is often referred to as directed diffusion

- (d) (Sedimentation: difficult) A physical container is not infinite, and no current can flow through the boundaries of the container. Assume $P(\mathbf{x}, t) = P(z, t)$ does not depend on x or y and solve the directed diffusion equation for $P(z, t)$ subject to the boundary condition $P(z, 0) = \delta(z - z_0)$ and $j_z = 0$ at $z = 0$.

- 7.10 Show that the probability $P(x, p, t|x_0, p_0, t_0)$ that a particle has position x and momentum p at time t , given that it had position x_0 and momentum p_0 at time t_0 , satisfies Kramer's equation

$$\frac{\partial P}{\partial t} = \alpha T \frac{\partial}{\partial p} \left[\frac{1}{T} \frac{\partial \mathcal{H}}{\partial p} + \frac{\partial}{\partial p} \right] P + \frac{\partial}{\partial p} \left(\frac{\partial \mathcal{H}}{\partial x} P \right) - \frac{\partial}{\partial x} \left(\frac{\partial \mathcal{H}}{\partial p} P \right),$$

where $\mathcal{H} = p^2/2m + U(x)$ is the Hamiltonian for a particle in an external potential $U(x)$. Show that a stationary solution to this equation is $P = e^{-\mathcal{H}/T}$.

- 7.11 Calculate the high-frequency moments $\int (d\omega/\pi) \omega^n \chi''_{xx}(\omega)$ for $n = 1$ and $n = 3$ for the quantum anharmonic oscillator with Hamiltonian

$$\mathcal{H} = \frac{p^2}{2m} + \frac{1}{2}kx^2 + ux^4.$$

- 7.12 Use the spectral representations for $\chi''_{\phi_i \phi_j}(\mathbf{x}, \mathbf{x}', \omega)$ and $S_{\phi_i \phi_j}(\mathbf{x}, \mathbf{x}', \omega)$ to derive the fluctuation-dissipation theorem.

Chapter 8

Hydrodynamics

Thermodynamics provides a description of the equilibrium states of systems with many degrees of freedom. It focuses on a small number of macroscopic degrees of freedom, such as internal energy, temperature, number density, or magnetization, needed to characterize a homogeneous equilibrium state. In systems with a broken continuous symmetry, thermodynamics can be extended to include slowly varying elastic degrees of freedom and to provide descriptions of spatially nonuniform states produced by boundary conditions or external fields. Since the wavelengths of the elastic distortions are long compared to any microscopic length, the departure from ideal homogeneous equilibrium is small. In this chapter, we will develop equations governing dynamical disturbances in which the departure from ideal homogeneous equilibrium of each point in space is small at all times.

8.1 Conserved and broken-symmetry variables

Thermodynamic equilibrium is produced and maintained by collisions between particles or elementary excitations that occur at a characteristic time interval τ . In classical fluids, τ is of order 10^{-10} to 10^{-14} seconds. In low-temperature solids or in quantum liquids, τ can be quite large, diverging as some inverse power of the temperature T . The mean distance λ between collisions (mean free path) of particles or excitations is a characteristic velocity v times τ . In fluids, v is determined by the kinetic energy, $v \sim (T/m)^{1/2}$, where m is a mass. In solids, v is typically a sound velocity. Imagine now a disturbance from the ideal equilibrium state that varies periodically in time and space with frequency ω and wave number q . If $\omega\tau \ll 1$ and $q\lambda \ll 1$, the disturbance varies slowly on time and length scales set by τ

and λ , and there will be many equilibrating collisions in each of its temporal and spatial cycles. Thus, each point in space is close to thermodynamic equilibrium at each instant of time, and one would expect to be able to treat such disturbances as perturbations from thermodynamic equilibrium even though they vary in time. Most disturbances in many body systems have characteristic frequencies that are of order τ^{-1} . If excited, they decay rapidly to equilibrium. There are, however, certain classes of variables that are guaranteed to have slow temporal variations at long wavelengths. These are

- (1) densities of conserved variables, and
- (2) broken-symmetry elastic variables.

A conserved density such as the number density n obeys a conservation law of the form

$$\frac{\partial n}{\partial t} + \nabla \cdot \mathbf{j} = 0, \quad (8.1.1)$$

where \mathbf{j} is the particle current. When Fourier transformed, such equations imply frequencies ω that go to zero with wave number q . Indeed, in the preceding chapter, we found that the characteristic frequency associated with the conserved density of particles suspended in a fluid was $-iDq^2$. In Chapter 6, we saw that the free energy is invariant with respect to the spatially uniform displacement of broken-symmetry elastic variables such as the angle θ in the xy -model. Thus, spatially uniform changes in elastic variables lead to new equilibrium states that are stationary in time. This implies that the frequency associated with zero wave number displacements of broken-symmetry elastic variables is zero. Spatially non-uniform displacements will, however, have nonzero characteristic frequencies.

Historically, the first system whose long-wavelength, low-frequency dynamics was given serious attention was water. The dynamics of water in motion is called *hydrodynamics*. Today, the term hydrodynamics is used for the long-wavelength, low-frequency dynamics of conserved and broken-symmetry variables in any system. Thus, for example, spin systems and crystalline solids as well as water have a well defined hydrodynamics. They will be the subject of this chapter.

The time dependence of each conserved variable is determined by a current as in Eq. (8.1.1). Currents for broken-symmetry variables can, as we shall see, also be introduced. For slowly varying disturbances, these currents are local functions of the fields thermodynamically conjugate to the hydrodynamical variables. Thus, as we saw in the Chapter 7, the current for particles suspended in a fluid is proportional to the gradient of their chemical potential. The equations relating currents to thermodynamic fields are

called *constitutive relations*. The hydrodynamics of a given system is determined by its hydrodynamical variables and their currents and associated constitutive relations. As we discussed in the preceding chapter, fields can be classified according to their sign under time reversal. Currents have the opposite sign under time reversal from their associated hydrodynamical variables. Coefficients relating a current and a field with the same sign under time reversal are *nondissipative* and are ultimately responsible for propagating modes such as sound waves. These nondissipative coefficients can usually be determined by straightforward invariance arguments. For example, the time derivative $\partial\mathbf{u}/\partial t$ of the displacement variable \mathbf{u} in a crystal in motion at constant velocity \mathbf{v} must be equal to \mathbf{v} . In addition, the momentum density \mathbf{g} must be equal to the mass density times \mathbf{v} . The equation $\partial\mathbf{u}/\partial t = \mathbf{v}$ provides a coupling between the hydrodynamical variables \mathbf{u} and \mathbf{g} that does not involve any dissipation since it applies to a steady state situation. Relations between a current and a field with the opposite sign under time reversal are necessarily irreversible. They imply entropy production and are thus *dissipative*.

Our program for obtaining hydrodynamical equations is the following. First, since hydrodynamics is basically a perturbation about thermodynamic equilibrium, we have to generalize our treatment of thermodynamics and statistical mechanics to include all conserved and broken-symmetry variables, including for example the momentum in fluids. Second, we must identify the time dependence induced in hydrodynamical variables of one sign under time reversal by nonzero values of variables of the opposite sign, i.e., we must identify reactive couplings. Finally, we must derive irreversible dissipative couplings.

The hydrodynamics of water is quite complicated because there are five hydrodynamical variables arising from the five conservation laws (mass, energy and momentum) in a one-component fluid. The imposition of a broken symmetry, as in a liquid crystal, leads to even greater complexity. We will, therefore, study first the hydrodynamics of a simple model with only two conserved variables and a single broken-symmetry variable in the low-temperature, ordered phase. This model will introduce all of the ingredients essential to the understanding of hydrodynamics, including generalization of thermodynamics to include variables describing states of nonzero motion, derivation of reactive and dissipative constitutive relations, determination of the linearized mode structure, and calculation of response functions. We will then derive and discuss the hydrodynamics of spin systems, one- and two-component fluids, liquid crystals, crystalline solids and superfluids.

It is possible for variables other than conserved or broken-symmetry variables to have characteristic frequencies that are much slower than the

inverse collision time. For example, decay times of a nonconserved order parameter diverge as a second-order phase transition is approached. In Sec. 8.6, we will discuss dynamic scaling of correlation functions and characteristic frequencies near second-order critical points. This is a natural generalization of the static scaling discussed in Chapter 5. We will then discuss stochastic dynamical equations for both hydrodynamical and slow critical variables. These are the natural generalizations to continuous fields of the Langevin equations discussed in Sec. 7.5.

8.2 A tutorial example – rigid rotors on a lattice

The hydrodynamics of real physical systems is either quite complicated because of the large number of hydrodynamic variables (e.g., fluids, liquid crystals and solids) or confusing because of possibly unfamiliar time evolution (e.g., spin systems). We will, therefore, study a simple model system that has no known physical realization but that will illustrate all of the essential features of hydrodynamics. The study of real systems will then be almost straightforward though sometimes tedious.

8.2.1 Description of the model

The model we will investigate is one with a symmetric rigid rotor or bar at each of N sites \mathbf{l} on a d -dimensional lattice as shown, in Fig. 8P.1. Each rotor can rotate frictionlessly in the two-dimensional xy -plane. The direction of the rotor at site \mathbf{l} can be specified by the unit vector

$$\boldsymbol{\nu}_{\mathbf{l}} = (\cos \vartheta_{\mathbf{l}}, \sin \vartheta_{\mathbf{l}}), \quad (8.2.1)$$

where $\vartheta_{\mathbf{l}}$ is the angle of the rotor relative the x -axis. Neighboring rotors do not touch, but there is an exchange-like interaction potential favoring parallel alignment. At high temperature, the rotors are randomly oriented like spins in the paramagnetic phase. At low temperature, they align along a common axis like the molecules of a nematic liquid crystal, as shown in Fig. 8P.1b. The ordered phase, like the nematic phase of liquid crystals, is characterized by a symmetric, traceless tensor order parameter,

$$\begin{aligned} \langle Q_{ij}(\mathbf{x}) \rangle &= \left\langle \sum_{\mathbf{l}} \left(\nu_{i\mathbf{l}} \nu_{j\mathbf{l}} - \frac{1}{2} \delta_{ij} \right) \delta(\mathbf{x} - \mathbf{R}_{\mathbf{l}}) \right\rangle \\ &= (N/V) S \left(n_i n_j - \frac{1}{2} \delta_{ij} \right) \quad (i, j = x, y), \end{aligned} \quad (8.2.2)$$

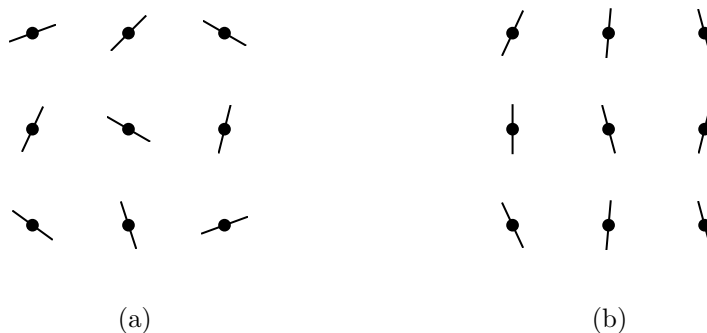


Figure 8P.1: (a) Disordered phase of the rigid rotor model. Rigid rotors at lattice sites \mathbf{l} rotate freely about a fixed axis. The direction of the rotors is random. (b) Ordered phase of the rigid rotor model. Rotors align along a common axis as in a nematic liquid crystal. The order parameter $\langle Q_{ij} \rangle$ is nonzero.

where V is the volume and $\mathbf{n}(\mathbf{x}) = [\cos \theta(\mathbf{x}), \sin \theta(\mathbf{x})]$ is the director specifying the direction of average alignment at \mathbf{x} . The distinction between the microscopic angle $\vartheta_{\mathbf{l}}$ specifying the direction of the local rotor at site \mathbf{l} and the coarse-grained angle $\theta(\mathbf{x})$ specifying the direction of the director $\mathbf{n}(\mathbf{x})$ is identical to that introduced in Sec. 6.1 in our discussion of fluctuations in the xy -model. A potential energy favoring parallel rotors which is invariant under the inversion operation $\nu_{\mathbf{l}} \rightarrow -\nu_{\mathbf{l}}$ ($\vartheta_{\mathbf{l}} \rightarrow \vartheta_{\mathbf{l}} + \pi$) is

$$U[\vartheta_{\mathbf{l}}] = -J \sum_{\langle \mathbf{l}, \mathbf{l}' \rangle} \cos[2(\vartheta_{\mathbf{l}} - \vartheta_{\mathbf{l}'})]. \quad (8.2.3)$$

Except for the factor of two in the cosine assuring inversion symmetry, this is identical to the classical xy -Hamiltonian of Eq. (??).

Because the lattice is rigidly fixed and the rotors rotate without friction, the rotational angular momentum of the rotors about the z -axis is conserved. Thus, there are two, and only two, conserved variables in this system: the energy E and the angular momentum L . The energy density and angular momentum density operators (in the sense of Chapter 3), $\hat{\varepsilon}(\mathbf{x}, t)$ and $\hat{l}(\mathbf{x}, t)$, obey local conservation laws,

$$\frac{\partial \hat{\varepsilon}}{\partial t} + \nabla \cdot \hat{\mathbf{j}}^{\varepsilon} = 0, \quad \frac{\partial \hat{l}}{\partial t} + \nabla \cdot \hat{\boldsymbol{\tau}} = 0, \quad (8.2.4)$$

where $\hat{\mathbf{j}}^{\varepsilon}$ and $\hat{\boldsymbol{\tau}}$ are, respectively, the energy and angular momentum current operators. Ensemble or coarse-grained averages of the above conser-

vation equations lead to identical equations relating the averaged densities, $\varepsilon(\mathbf{x}, t) = \langle \hat{\varepsilon}(\mathbf{x}, t) \rangle$ and $l(\mathbf{x}, t) = \langle \hat{l}(\mathbf{x}, t) \rangle$, to the averaged currents, $\mathbf{j}^\varepsilon(\mathbf{x}, t) = \langle \hat{\mathbf{j}}^\varepsilon(\mathbf{x}, t) \rangle$ and $\boldsymbol{\tau}(\mathbf{x}, t) = \langle \hat{\boldsymbol{\tau}}(\mathbf{x}, t) \rangle$. It is important to remember that ε and $\boldsymbol{\tau}$ are even under time reversal whereas l and \mathbf{j}^ε are odd under the same operation.

In the ordered phase, the angle $\theta(\mathbf{x})$ is an elastic variable with associated free energy [Eq. (??)],

$$F_{\text{el}} = \frac{1}{2} \int d^d x \rho_s (\nabla \theta)^2 \equiv \frac{1}{2} \int d^d x \rho_s \mathbf{v}_\theta^2, \quad \mathbf{v}_\theta \equiv \nabla \theta. \quad (8.2.5)$$

If $\theta = 0$ in the equilibrium state, then $\mathbf{n} = (1, 0)$, $\langle Q_{xx} \rangle = -\langle Q_{yy} \rangle = (N/V)S/2$, and $\langle Q_{xy} \rangle = 0$. Small changes of θ produce a non-vanishing $\langle Q_{xy} \rangle = 2\langle Q_{xx} \rangle \delta\theta$. Thus, for small deviations from the ground state, $\theta = \langle Q_{xy} \rangle / (2\langle Q_{xx} \rangle)$. As in a nematic liquid crystal, the bars are inversion invariant, and all physical quantities must be invariant under the transformation $\mathbf{n} \rightarrow -\mathbf{n}$. θ is even under time reversal.

8.2.2 The disordered phase

In the disordered phase, the only hydrodynamic variables are ε and l . Before we can study the hydrodynamics of this system, we must first include the angular momentum in its statistical mechanics and thermodynamics. We begin by constructing the Lagrangian, from which we can obtain the Hamiltonian that controls statistical averages. If each rod has a moment of inertia I , then the Lagrangian is

$$\mathcal{L} = \frac{1}{2} \sum_{\mathbf{1}} I \dot{\vartheta}_{\mathbf{1}}^2 - U[\vartheta_{\mathbf{1}}], \quad (8.2.6)$$

where U is the potential energy like that of Eq. (8.2.3). From this, we can construct the angular momentum of each site,

$$p_{\mathbf{1}} = \frac{\partial \mathcal{L}}{\partial \dot{\vartheta}_{\mathbf{1}}} = I \dot{\vartheta}_{\mathbf{1}}, \quad (8.2.7)$$

and the Hamiltonian,

$$\mathcal{H} = \sum_{\mathbf{1}} \frac{p_{\mathbf{1}}^2}{2I} + U. \quad (8.2.8)$$

Since U depends only on $\vartheta_{\mathbf{1}} - \vartheta_{\mathbf{1}'}$, it is straightforward to verify that the total angular momentum,

$$L = \sum_{\mathbf{1}} p_{\mathbf{1}}, \quad (8.2.9)$$

is independent of time, i.e., a conserved quantity. The associated angular momentum density is

$$\hat{l}(\mathbf{x}, t) = \sum_{\mathbf{l}} p_{\mathbf{l}} \delta(\mathbf{x} - \mathbf{R}_{\mathbf{l}}). \quad (8.2.10)$$

Since L is conserved, it is possible to have stationary states (i.e., states that do not vary in time) in which $\langle L \rangle = V \langle \hat{l} \rangle$ is nonzero. Thus, stationary states are characterized by their angular momentum density $l = \langle \hat{l} \rangle$ as well as by their energy density ε . If $\langle \hat{l}(\mathbf{x}, t) \rangle$ is independent of \mathbf{x} , then the average angular velocity of each rotor is the same, and we can introduce an angular velocity Ω via

$$l = \langle \hat{l} \rangle = \tilde{I} \Omega, \quad (8.2.11)$$

where $\tilde{I} = NI/V$ is the moment of inertia per unit volume. The angular frequency $\Omega(l)$ is determined completely by the value of the stationary angular momentum density. More generally, \tilde{I} could be a function of l and ε , and $\Omega(l, \varepsilon)$ would be a function of both l and ε .

Having established that stationary states with a nonzero l are possible, we next need to identify ensembles that lead to equilibrium nonzero values of l . Clearly, the canonical ensemble constructed from the Hamiltonian of Eq. (8.2.8) will lead to $l = 0$ because it is a minimum at $p_{\mathbf{l}} = 0$ for every \mathbf{l} and it is an even function of $p_{\mathbf{l}}$. To create an ensemble favoring $l \neq 0$, we need only add a term $-\Omega_e L = -\Omega_e \sum_{\mathbf{l}} p_{\mathbf{l}}$ to \mathcal{H} . Rather than adding such a term directly, we will show how it arises naturally from a Lagrangian expressed in terms of angular velocities relative to a coordinate system rotating with angular velocity Ω_e . Define the relative angle $\vartheta'_{\mathbf{l}}$ and its angular velocity $\omega_{\mathbf{l}} = \dot{\vartheta}'_{\mathbf{l}}$ via

$$\begin{aligned} \vartheta_{\mathbf{l}} &= \Omega_e t + \vartheta'_{\mathbf{l}} \\ \dot{\vartheta}_{\mathbf{l}} &= \Omega_e + \omega_{\mathbf{l}}. \end{aligned} \quad (8.2.12)$$

Then, because $\vartheta_{\mathbf{l}} - \vartheta_{\mathbf{l}'} = \vartheta'_{\mathbf{l}} - \vartheta'_{\mathbf{l}'}$, the Lagrangian as a function of $\vartheta'_{\mathbf{l}}$ is

$$\mathcal{L} = \frac{1}{2} I \sum_{\mathbf{l}} (\Omega_e + \omega_{\mathbf{l}})^2 - U[\vartheta'_{\mathbf{l}}]. \quad (8.2.13)$$

This Lagrangian differs by a total time derivative from one in which the kinetic energy is $\frac{1}{2} I \sum_{\mathbf{l}} \omega_{\mathbf{l}}^2$ rather than $\frac{1}{2} I \sum_{\mathbf{l}} (\Omega_e + \omega_{\mathbf{l}})^2$. The equations of motion for $\vartheta'_{\mathbf{l}}$ predicted by these two Lagrangians are thus identical. Either can be used to construct momentum conjugate to $\omega_{\mathbf{l}}$ and a Hamiltonian. The Lagrangian of Eq. (8.2.13) will be more useful to us. The momentum

conjugate to ω_1 is

$$p_1 = \frac{\partial \mathcal{L}}{\partial \omega_1} = I(\Omega_e + \omega_1) = I \sum_1 \dot{\vartheta}_1. \quad (8.2.14)$$

Thus, the value of the canonical momentum p_1 is $I\dot{\vartheta}_1$, independent of the value of Ω_e . The Hamiltonian associated with the Lagrangian of Eq. (8.2.13) is then

$$\begin{aligned} \mathcal{H}_T &= \sum_1 p_1 \omega_1 - \mathcal{L} \\ &= \frac{1}{2} \sum_1 (p_1^2 / I) + U[\theta_1] - \Omega_e L \\ &\equiv \mathcal{H} - \Omega_e L, \end{aligned} \quad (8.2.15)$$

where \mathcal{H} is the Hamiltonian in the frame with $\Omega_e = 0$ and $L = \sum_1 p_1 = \sum_1 I(\Omega_e + \omega_1)$ is the total angular momentum. It is a straightforward exercise to verify the Poisson bracket relation, $\{H, L\} = 0$, and that L is conserved. Note that L is the rest frame angular momentum regardless of the value of Ω_e . Note also that the Ω_e is thermodynamically conjugate to the angular momentum (see Chapter 2).

Thermodynamic functions can now be determined via the partition function,

$$\begin{aligned} \Xi(T, \Omega_e) &= \text{Tr} e^{-(\mathcal{H} - \Omega_e L)/T} \equiv e^{S - (E - \Omega_e \langle L \rangle)/T} \\ &= \frac{1}{N!} (2\pi IT)^{dN/2} e^{NI\Omega_e^2/(2T)} \prod_1 \int d\vartheta_1 e^{-U[\vartheta_1]/T}, \end{aligned} \quad (8.2.16)$$

where S is the entropy and $E = \langle \mathcal{H} \rangle$ is the internal energy. From this, the average angular momentum in thermal equilibrium is easily found to be

$$\langle L \rangle = \frac{\partial \ln \Xi}{\partial \beta \Omega_e} = NI\Omega_e. \quad (8.2.17)$$

Thus, in thermal equilibrium, the frequency Ω introduced in Eq. (8.2.11) is equal to Ω_e . This is really just the statement that when there is an equilibrium angular momentum, the average angular velocity of each rotor will be $\langle \dot{\vartheta}_1 \rangle = \Omega = l/\tilde{I}$, and the average angular velocity measured relative to the frame rotating with frequency $\Omega_e = \Omega$ will be zero, since by Eq. (8.2.12)

$$\langle \omega_1 \rangle = \Omega - \Omega_e. \quad (8.2.18)$$

In what follows, we will generally measure all angular velocities in the rest frame so that Ω_e will be zero. It is useful, however, to remember that there is the same distinction between Ω and Ω_e that there is between the equilibrium and external chemical potential μ and μ^{ext} that we encountered in our discussion of diffusion in Sec. 7.4.

The thermodynamic potential associated with the partition function of Eq. (8.2.16) is

$$W(T, \Omega) = -T \ln \Xi(T, \Omega) = E - \Omega \langle L \rangle - TS. \quad (8.2.19)$$

It satisfies the differential thermodynamic relation

$$dW = -SdT - \langle L \rangle d\Omega. \quad (8.2.20)$$

Here, since we are considering only relations valid in thermodynamic equilibrium, we have dropped the distinction between Ω and Ω_e ; they are equal in this case. This equation implies a relation (the volume V is constant),

$$Tds = d\varepsilon - \Omega dl, \quad (8.2.21)$$

between intensive densities ε , l and $s = S/V$ of extensive quantities. This equation is the analog of Eq. (??) for isotropic fluids. The entropy density s is a thermodynamic potential that is a function of the variables ε and l . The variables Ω and T are also functions of ε and l via the relations

$$\Omega(\varepsilon, l) = -T \left(\frac{\partial s}{\partial l} \right)_{\varepsilon}, \quad T^{-1}(\varepsilon, l) = \left(\frac{\partial s}{\partial \varepsilon} \right)_{l}. \quad (8.2.22)$$

We will be principally interested in states near the equilibrium state with $l = 0$. In this case, the entropy density can be expanded in powers of l as

$$s(\varepsilon, l) = s_0(\varepsilon) - \frac{1}{2T\tilde{I}} l^2, \quad (8.2.23)$$

where $\tilde{I}^{-1} = \partial \Omega / \partial l$.

The fundamental thermodynamic identity, Eq. (8.2.21), and the continuity equations (8.2.4) can now be used to tell us how the entropy changes in response to changes in the conserved hydrodynamical variables:

$$\begin{aligned} T \frac{\partial s}{\partial t} &= \frac{\partial \varepsilon}{\partial t} - \Omega \frac{\partial l}{\partial t} = -\nabla \cdot \mathbf{j}^{\varepsilon} + \Omega \nabla \cdot \boldsymbol{\tau} \\ &= -\nabla \cdot (\mathbf{j}^{\varepsilon} - \Omega \boldsymbol{\tau}) - \boldsymbol{\tau} \cdot \nabla \Omega. \end{aligned} \quad (8.2.24)$$

Then, using the identity

$$\nabla \cdot \mathbf{Q} = T \nabla \cdot (\mathbf{Q}/T) + \mathbf{Q} \cdot (\nabla T/T), \quad (8.2.25)$$

we obtain

$$T \left(\frac{\partial s}{\partial t} + \nabla \cdot (\mathbf{Q}/T) \right) = -\mathbf{Q} \cdot (\nabla T/T) - \boldsymbol{\tau} \cdot \nabla \Omega, \quad (8.2.26)$$

where

$$\mathbf{Q} = \mathbf{j}^\varepsilon - \Omega \boldsymbol{\tau} \quad (8.2.27)$$

is the *heat current*. Integrating Eq. (8.2.26) over a large volume subject to the boundary condition that the heat current is zero at its outer surface, we obtain an expression for the total rate of entropy production,

$$T \frac{dS}{dt} = \int d^d x [-\mathbf{Q} \cdot (\nabla T/T) - \boldsymbol{\tau} \cdot \nabla \Omega], \quad (8.2.28)$$

which must be non-negative.

In reversible, non-dissipative processes, the entropy remains constant, i.e., dS/dt is zero. Thus, *in the absence of dissipation*, the currents $\boldsymbol{\tau}$ and \mathbf{Q} must be zero:

$$\boldsymbol{\tau} = 0; \quad \mathbf{Q} = \mathbf{j}^\varepsilon - \Omega \boldsymbol{\tau} = 0. \quad (8.2.29)$$

Since by the second law of thermodynamics, the entropy always increases when constraints are removed from the system, the rate of entropy production must be strictly positive when dissipation is allowed. When T and Ω are spatially uniform, the currents are zero. We therefore expect $\boldsymbol{\tau}$ and \mathbf{Q} to be linearly proportional to ∇T and $\nabla \Omega$. The *constitutive relations* between these variables must be chosen so that dS/dt is positive. In addition, dissipative currents of one sign under time reversal must be proportional to variables of the opposite sign. These constraints imply

$$\mathbf{Q} = -\kappa \nabla T, \quad \boldsymbol{\tau} = -\Gamma \nabla \Omega, \quad (8.2.30)$$

with $\kappa > 0$ and $\Gamma > 0$ because

$$T \frac{dS}{dt} = \int d^d x [\kappa (\nabla T)^2 / T + \Gamma (\nabla \Omega)^2] > 0. \quad (8.2.31)$$

κ and Γ are *transport coefficients*; κ is the *thermal conductivity*. Eqs. (8.2.30) are constitutive relations expressing the currents in terms of a spatial derivative of the fields T and Ω conjugate to E and $\langle L \rangle$. There is no term relating $\boldsymbol{\tau}$ to ∇T because they have the same signs under time reversal (or l and T have opposite signs). Similarly, there is no term coupling \mathbf{Q} to $\nabla \Omega$.

The equations for the energy and angular momentum densities linearized about the state with zero angular momentum and $\Omega = 0$ are, therefore,

$$\begin{aligned}\frac{\partial \varepsilon}{\partial t} &= -\nabla \cdot \mathbf{j}^\varepsilon = \kappa \nabla^2 T, \\ \frac{\partial l}{\partial t} &= -\nabla \cdot \boldsymbol{\tau} = \Gamma \nabla^2 \Omega.\end{aligned}\quad (8.2.32)$$

These equations can be closed with the aid of the thermodynamic relations

$$d\Omega = \tilde{I}^{-1} dl, \quad dT = C_l^{-1} d\varepsilon, \quad (8.2.33)$$

where C_l is the specific heat at constant l . C_l and \tilde{I} are particular realizations of a susceptibility relating changes of conjugate variables. We now obtain

$$\frac{\partial \varepsilon}{\partial t} = D_\varepsilon \nabla^2 \varepsilon, \quad \frac{\partial l}{\partial t} = D_l \nabla^2 l, \quad (8.2.34)$$

where

$$D_\varepsilon = \kappa / C_l, \quad D_l = \Gamma / \tilde{I} \quad (8.2.35)$$

are, respectively, the thermal and angular momentum diffusion constants. Thus, both ε and l relax diffusively. D_ε and D_l , like the diffusion constant [Eq. (7.4.32)] for particles in a fluid, are the ratio of a transport coefficient Γ to a susceptibility χ . This form is quite general. The dissipative parts of the response functions can be obtained directly using the methods introduced in Sec. 7.4:

$$\frac{\chi''_{\varepsilon\varepsilon}(\mathbf{q}, \omega)}{\omega} = C_l \frac{D_\varepsilon q^2}{\omega^2 + (D_\varepsilon q^2)^2}, \quad (8.2.36)$$

$$\frac{\chi''_{ll}(\mathbf{q}, \omega)}{\omega} = \tilde{I} \frac{D_l q^2}{\omega^2 + (D_l q^2)^2}. \quad (8.2.37)$$

From this we see that there is one mode (one peak in a response function) for each of the conserved variables ε and l . This result is quite general. There is always one mode associated with each conserved variable and, as we shall see shortly, with each broken-symmetry variable.

Eqs. (8.2.34) are the phenomenological diffusive dynamical equations for the conserved densities ε and l . Identical equations control the time development of the conjugate fields T and Ω as long as the linear thermodynamic relations of Eqs. (8.2.33) hold. Thus, for example, $\partial T / \partial t = D_\varepsilon \nabla^2 T$. This is the equation of thermal diffusion. We regard the equations in terms of ε and l as more fundamental than those for T and Ω because the former variables obey microscopic conservation laws.

8.2.3 The ordered phase

The free energy of the ordered phase is completely independent of the spatially uniform angle variable θ . Gradients of θ do, however, increase the free energy, and $\mathbf{v}_\theta = \nabla\theta$ must be included as an independent thermodynamic variable. \mathbf{v}_θ is also a broken-symmetry hydrodynamical variable whose characteristic excitation frequencies go to zero with wave number q . ε , l and \mathbf{v}_θ are the only hydrodynamic variables. All other variables relax to equilibrium values determined by local values of ε , l and \mathbf{v}_θ in microscopic times τ ; they do not need to be considered at any stage in the derivation of hydrodynamical equations. It is possible, however, to include non-hydrodynamical variables in a non-rigorous way by a slight generalization of the methods presented here.

Thermodynamic functions describing the ordered phase must be a function either of \mathbf{v}_θ or its conjugate field \mathbf{h}_θ in addition to T and Ω . The function $\tilde{W}'(T, \Omega, \mathbf{h}_\theta) = E - \Omega\langle L \rangle - TS - \int d^d x \mathbf{h}_\theta \cdot \mathbf{v}_\theta$ is a natural function of \mathbf{h}_θ , whereas

$$\tilde{W} = \tilde{W}'(T, \Omega, \mathbf{h}_\theta) + \int d^d x \mathbf{h}_\theta \cdot \mathbf{v}_\theta = E - \Omega\langle L \rangle - TS \quad (8.2.38)$$

is a natural function of T , Ω and \mathbf{v}_θ satisfying

$$d\tilde{W} = -SdT - Ld\Omega + \int d^d x \mathbf{h}_\theta \cdot d\mathbf{v}_\theta. \quad (8.2.39)$$

From this follows the fundamental relation

$$Tds = d\varepsilon - \Omega dl - \mathbf{h}_\theta \cdot d\mathbf{v}_\theta \quad (8.2.40)$$

among intensive quantities. The potential $\tilde{W}(T, \Omega, \mathbf{v}_\theta)$ can be expanded in a power series in \mathbf{v}_θ for small \mathbf{v}_θ . It must reduce to $W(T, \Omega)$ when \mathbf{v}_θ is zero. There is no linear term in \mathbf{v}_θ because \mathbf{v}_θ is zero when \mathbf{h}_θ is zero. The coefficient of v_θ^2 is independent of Ω for small Ω . Thus, for small \mathbf{v}_θ and Ω , we have

$$\tilde{W}(T, \Omega, \mathbf{v}_\theta) = W(T, \Omega) + F_{\text{el}}(T, \mathbf{v}_\theta). \quad (8.2.41)$$

The conjugate field \mathbf{h}_θ satisfies

$$\begin{aligned} h_{\theta i} &= -T \left(\frac{\partial s}{\partial v_{\theta i}} \right)_{\varepsilon, l} = \frac{1}{V} \left(\frac{\partial \tilde{W}}{\partial v_{\theta i}} \right)_{T, \Omega} \\ &= \rho_s v_{\theta i}. \end{aligned} \quad (8.2.42)$$

The first line of Eq. (8.2.42) is generally valid. The second line is valid only to lowest order in \mathbf{v}_θ . Since we will be most interested in modes associated

with the equilibrium state with $\mathbf{v}_\theta = 0$, the latter form will suffice for our purposes. In this case, the entropy density can be expanded about the state with $l = 0$ and $\mathbf{v}_\theta = 0$ as

$$s(\varepsilon, l, \mathbf{v}_\theta) = s_0(\varepsilon) - \frac{1}{2T\tilde{I}}l^2 - \frac{1}{2T}\rho_s \mathbf{v}_\theta \cdot \mathbf{v}_\theta. \quad (8.2.43)$$

To treat the dynamical properties of θ and \mathbf{v}_θ , we define the “current” X via

$$\frac{d\theta}{dt} + X = 0. \quad (8.2.44)$$

We first consider the reactive part of X . In the ordered phase with nonzero $\langle Q_{ij} \rangle$, the director $\mathbf{n}(\mathbf{x}, t)$ will rotate with the average angular frequency of the rotors. Thus, in an ordered stationary state with nonzero angular momentum,

$$\frac{d\theta}{dt} = \Omega = \tilde{I}^{-1}l. \quad (8.2.45)$$

Alternatively, the angle θ' measured with respect to a frame rotating with frequency Ω_e will satisfy $d\theta'/dt = \Omega - \Omega_e$. There is no dissipation in the above relation; it will be satisfied so long as there are no external perturbations. Ω is the *reactive* or *nondissipative* part of the current X . As we have seen, reactive parts of currents always couple the time derivative of one variable to another variable with opposite sign under time reversal. The dissipative parts of currents couple the time derivative of one variable to other variables with the same sign under time reversal. We define the dissipative “current” X' via

$$X = -\Omega + X'. \quad (8.2.46)$$

Since θ is a broken, symmetry hydrodynamic variable, we expect X' to tend to zero with wave number. The equation of motion for \mathbf{v}_θ is

$$\frac{\partial \mathbf{v}_\theta}{\partial t} = -\nabla(X' - \Omega). \quad (8.2.47)$$

Then the thermodynamic relation [Eq. (8.2.40)] and the conservation laws [Eqs. (8.2.4)] for ε and l imply

$$T \frac{\partial s}{\partial t} = -\nabla \cdot \mathbf{j}^\varepsilon + \Omega \nabla \cdot \boldsymbol{\tau} - \mathbf{h}_\theta \nabla \cdot (\Omega - X') \quad (8.2.48)$$

so that the entropy production equation becomes

$$T \left(\frac{\partial s}{\partial t} + \nabla \cdot (\mathbf{Q}/T) \right) = -\mathbf{Q} \cdot (\nabla T/T) - (\boldsymbol{\tau} + \mathbf{h}_\theta) \cdot \nabla \Omega - X' \nabla \cdot \mathbf{h}_\theta, \quad (8.2.49)$$

where

$$\mathbf{Q} = \mathbf{j}^\varepsilon - \Omega\boldsymbol{\tau} - \mathbf{h}_\theta X' \quad (8.2.50)$$

is the heat current.

In the absence of dissipation, entropy production is zero,

$$\boldsymbol{\tau} = -\mathbf{h}_\theta, \quad \mathbf{Q} = 0, \quad X' = 0, \quad (8.2.51)$$

and

$$\frac{\partial l}{\partial t} = \nabla \cdot \mathbf{h}_\theta = \rho_s \nabla^2 \theta, \quad (8.2.52)$$

$$\frac{\partial \theta}{\partial t} = \Omega = \tilde{I}^{-1} l. \quad (8.2.53)$$

These are the equations determining the modes of the system in the absence of dissipation. Note their similarity to Poisson bracket equations [Eq. (7.2.2)] for the harmonic oscillator.

We should pause at this point to assess what our formal manipulations have told us. We began with a statement that $d\theta/dt$ is equal to Ω in steady state situations when there is a nonzero angular momentum. The requirement that there be no entropy production for non-dissipative processes then told us that there must be a reactive term in the angular momentum current equal to $-\mathbf{h}_\theta$. This term could not have been predicted using arguments with spatially uniform fields since \mathbf{h}_θ is nonzero only when there is spatial variation of θ . The end result is that the equations for l and θ , which have opposite signs under time reversal, are coupled. This is analogous to the coupling between p and x in the simple harmonic oscillator discussed in Sec. 7.2. A linear relation between the time derivative of a variable u with one sign under time reversal and a variable v with the opposite sign will invariably lead to a reciprocal linear relation between the time derivatives of v and u . Usually, one relation can be obtained using invariance arguments (such as those used to obtain the relation between θ and Ω); the other then follows from requirement of zero entropy production. The derived relation usually involves more gradients than the fundamental relation following from invariance arguments. The time derivative of either of Eqs. (8.2.52) or (8.2.53) leads to second-order sound-like equations,

$$\frac{\partial^2 l}{\partial t^2} = \rho_s \tilde{I}^{-1} \nabla^2 l \quad \text{or} \quad \frac{\partial^2 \theta}{\partial t^2} = \rho_s \tilde{I}^{-1} \nabla^2 \theta, \quad (8.2.54)$$

and predict undamped propagating modes with a sound-like dispersion relation

$$\omega = \pm \left(\frac{\rho_s}{\tilde{I}} \right)^{1/2} q. \quad (8.2.55)$$

Reactive couplings between variables with opposite sign under time reversal usually lead to propagating modes with linear dispersion in q and a velocity proportional to the square root of a rigidity divided by some measure of inertia. There are cases, as we shall see, however, where these modes can become overdamped and be effectively diffusive.

Constitutive relations for the dissipative parts of the currents can be derived just as in the disordered state. They are

$$\begin{aligned} Q'_i &= -\kappa_{ij}\nabla_j T, \\ \boldsymbol{\tau} &= -\mathbf{h}_\theta + \boldsymbol{\tau}', \quad \tau'_i = -\Gamma_{ij}\nabla_j \Omega, \\ X' &= -\gamma\nabla \cdot \mathbf{h}_\theta = -\gamma\rho_s\nabla^2\theta. \end{aligned} \quad (8.2.56)$$

γ is a new dissipative coefficient not present in the disordered phase. It must be positive for positive entropy production. The ordered phase is anisotropic, and dissipative currents can depend on the direction of spatial variation (∇) relative to the local director $\mathbf{n}(\mathbf{x})$. Thus, the dissipative coefficients κ and Γ of the disordered phase become tensors,

$$\begin{aligned} \kappa_{ij} &= \kappa_{\parallel}n_in_j + \kappa_{\perp}(\delta_{ij} - n_in_j), \\ \Gamma_{ij} &= \Gamma_{\parallel}n_in_j + \Gamma_{\perp}(\delta_{ij} - n_in_j), \end{aligned} \quad (8.2.57)$$

in the ordered phase. X' and \mathbf{Q} have the same sign under time reversal, and in general there could be dissipative cross-couplings of the form

$$X' \sim \nabla T, \quad \mathbf{Q} \sim \nabla \cdot \mathbf{h}_\theta. \quad (8.2.58)$$

Other symmetries, however, prevent such couplings. \mathbf{Q} is a vector. The only possible way to create a vector from $\nabla \cdot \mathbf{h}_\theta$ would be to use the director \mathbf{n} in $\mathbf{n}\nabla \cdot \mathbf{h}_\theta$. This is not permitted because all physical quantities must be invariant under $\mathbf{n} \rightarrow -\mathbf{n}$.

The complete linearized hydrodynamic mode equations in the ordered phase are

$$\begin{aligned} \frac{\partial \varepsilon}{\partial t} &= C_l^{-1}\kappa_{ij}\nabla_i\nabla_j\varepsilon, \\ \frac{\partial \theta}{\partial t} &= \Omega + \gamma\rho_s\nabla^2\theta = \tilde{I}^{-1}l + \gamma\rho_s\nabla^2\theta, \\ \frac{\partial l}{\partial t} &= \rho_s\nabla \cdot \mathbf{v}_\theta + \Gamma_{ij}\nabla_j\Omega = \rho_s\nabla^2\theta + \tilde{I}^{-1}\Gamma_{ij}\nabla_i\nabla_j l. \end{aligned} \quad (8.2.59)$$

The energy mode decouples from the others and remains diffusive as it was in the disordered phase. Its frequency,

$$\omega = -i(\kappa_{\parallel}\cos^2\theta_0 + \kappa_{\perp}\sin^2\theta_0)C_l^{-1}q^2, \quad (8.2.60)$$

depends on the direction of \mathbf{q} relative to \mathbf{n}_0 , the uniform equilibrium direction of \mathbf{n} ($\mathbf{q} \cdot \mathbf{n}_0 = q \cos \theta_0$). The “sound wave” arising from the coupling of θ and l is now damped:

$$\begin{aligned}\omega &= \frac{1}{2} \left[-i(D_\theta + D_l)q^2 \pm [4\rho_s \tilde{I}^{-1}q^2 - (D_\theta - D_l)^2 q^4]^{1/2} \right] \\ &\approx \pm cq - i\frac{1}{2}Dq^2,\end{aligned}\quad (8.2.61)$$

where

$$D_\theta = \gamma\rho_s, \quad D_l = \tilde{I}^{-1}(\Gamma_\parallel \cos^2 \theta_0 + \Gamma_\perp \sin^2 \theta_0) \quad (8.2.62)$$

and

$$D = (D_\theta + D_l) \quad (8.2.63)$$

and where

$$c = (\rho_s/\tilde{I})^{1/2} \quad (8.2.64)$$

is the “sound velocity”. There are in reality two sound modes at positive and negative frequencies. Thus, the ordered phase, which has one more hydrodynamical variable than the disordered phase, has one more mode than the disordered phase, with a total of three.

The response functions for θ and l can be obtained from the equations of motion, Eqs. (8.2.59), via the Laplace transform technique we used to obtain the diffusive response function in Sec. 7.4. The Laplace transform of Eqs. (8.2.59) yields the matrix equation,

$$\begin{pmatrix} \theta(\mathbf{q}, \omega) \\ l(\mathbf{q}, \omega) \end{pmatrix} = \frac{1}{\Delta} \begin{pmatrix} -i\omega + D_l q^2 & \tilde{I}^{-1} \\ -\rho_s q^2 & -i\omega + D_\theta q^2 \end{pmatrix} \begin{pmatrix} \theta(\mathbf{q}, t=0) \\ l(\mathbf{q}, t=0) \end{pmatrix}, \quad (8.2.65)$$

for $\theta(\mathbf{q}, \omega)$ and $l(\mathbf{q}, \omega)$, where

$$\begin{aligned}\Delta &= (-i\omega + D_l q^2)(-i\omega + D_\theta q^2) + \rho_s \tilde{I}^{-1} q^2 \\ &\approx -\omega^2 + c^2 q^2 - i\omega D q^2.\end{aligned}\quad (8.2.66)$$

To calculate response functions from Eq. (8.2.65), we need the matrix generalization of Eqs. (7.4.14) and (7.4.17),

$$\theta_\alpha(\mathbf{q}, \omega) = \frac{1}{i\omega} [\chi_{\alpha\beta}(\mathbf{q}, \omega) - \chi_{\alpha\beta}(\mathbf{q})] \chi_{\beta\gamma}^{-1}(\mathbf{q}) \theta_\gamma(\mathbf{q}, t=0), \quad (8.2.67)$$

where $\theta_\alpha \equiv (\theta, l)$ and summation over repeated indices is understood. Both $\chi''_{\theta\theta}(\mathbf{q}, \omega)$ and $\chi''_{ll}(\mathbf{q}, \omega)$ are real and odd in ω . They can, therefore, be

obtained by taking the real parts of the $\theta - \theta$ and $l - l$ components of Eq. (8.2.65):

$$\begin{aligned}\frac{\chi''_{\theta\theta}(\mathbf{q}, \omega)}{\omega} &= \frac{1}{\rho_s q^2} \frac{\omega^2 D q^2 - (\omega^2 - c^2 q^2) D_l q^2}{(\omega^2 - c^2 q^2)^2 + (\omega D q^2)^2}, \\ \frac{\chi''_{ll}(\mathbf{q}, \omega)}{\omega} &= \tilde{I} \frac{\omega^2 D q^2 - (\omega^2 - c^2 q^2) D_\theta q^2}{(\omega^2 - c^2 q^2)^2 + (D \omega q^2)^2}.\end{aligned}\quad (8.2.68)$$

Note that the same modes appear in both $\chi''_{\theta\theta}$ and χ''_{ll} . The intensity of $\chi''_{\theta\theta}$ is much larger, however, because the susceptibility $\chi_{\theta\theta} = (\rho_s q^2)^{-1}$ diverges at small q . The angular momentum density l and the angle θ have opposite signs under time reversal. Thus, the general symmetry arguments of Sec. 7.6 require that $\chi''_{\theta,l}(\mathbf{q}, \omega)$ be imaginary and even in ω and $\chi'_{\theta,l}(\mathbf{q}, \omega)$ be imaginary and odd in ω . This implies that $\chi''_{\theta,l}(\mathbf{q}, \omega) = -i \text{Re} \chi_{\theta,l}(\mathbf{q}, \omega)$ or, from Eq. (8.2.65):

$$\chi''_{\theta l}(\mathbf{q}, \omega) = i \frac{\omega^2 D q^2}{(\omega^2 - c^2 q^2)^2 + (\omega D q^2)^2}.\quad (8.2.69)$$

When the dissipation goes to zero, the peaks in $\chi''_{\alpha\beta}$ become delta functions at the “sound” wave frequencies

$$\frac{\chi''_{\theta\theta}}{\omega} = \frac{1}{\rho_s q^2 \tilde{I}} \frac{\chi''_{ll}}{\omega} = \frac{1}{\rho_s q^2} \frac{\chi''_{\theta l}}{i} = \frac{1}{\rho_s q^2} \frac{\pi}{2} [\delta(\omega - cq) + \delta(\omega + cq)].\quad (8.2.70)$$

The correlation functions,

$$\begin{aligned}S_{\theta\theta}(\mathbf{q}, \omega) &= \frac{2\hbar}{1 - e^{-\beta\hbar\omega}} \chi''_{\theta\theta}(\mathbf{q}, \omega), \\ S_{\varepsilon\varepsilon}(\mathbf{q}, \omega) &= \frac{2\hbar}{1 - e^{-\beta\hbar\omega}} \chi''_{\varepsilon\varepsilon}(\mathbf{q}, \omega),\end{aligned}\quad (8.2.71)$$

are plotted in Fig. 8P.2. Note that the intensity of the “sound” peak at negative frequency is less than that at positive frequency.

8.2.4 Excitations from the classical ground state

The hydrodynamical equations derived above determine the long wavelength, low frequency dynamics throughout the ordered phase. Near zero temperature, when there is nearly perfect alignment of all spins, the interaction energy between rotors [Eq. (8.2.3)] can be expanded in powers of $\vartheta_{\mathbf{l}} - \vartheta_{\mathbf{l}'}$. The leading term leads to the harmonic Hamiltonian,

$$H = \sum_{\mathbf{l}} p_{\mathbf{l}}^2 / (2I) + J \sum_{\mathbf{l}, \mathbf{l}'} \gamma_{\mathbf{l}, \mathbf{l}'} (\vartheta_{\mathbf{l}} - \vartheta_{\mathbf{l}'})^2 - zJN,\quad (8.2.72)$$

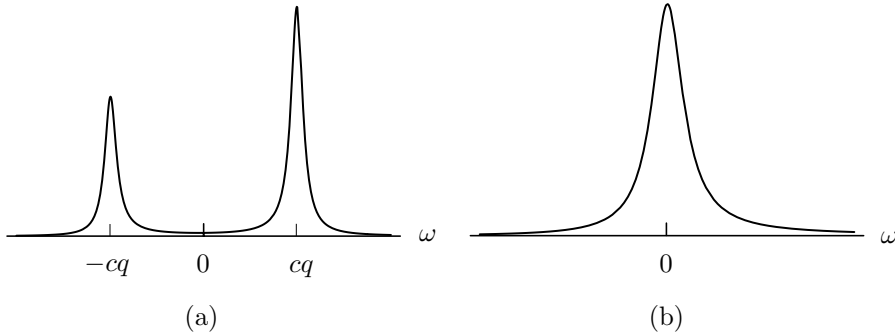


Figure 8P.2: (a) $S_{\theta\theta}(\mathbf{q}, \omega)$ and (b) $S_{\varepsilon\varepsilon}(\mathbf{q}, \omega)$ for fixed q . Note that the thermal factor in $S_{\theta\theta}$ causes the peak at $-cq$ to have a lower intensity for $T > 0$ than the peak at $+cq$. Both the diffusive and propagating peaks have widths proportional to q^2 .

whose mode structure is easily calculated. ($\gamma_{1,\nu}$ is the nearest-neighbor matrix introduced in Eq. (??).) The equation of motion for ϑ_1 is

$$I\ddot{\vartheta}_1 = -2J \sum_{\nu} \gamma_{1,\nu} (\vartheta_1 - \vartheta_{\nu}), \quad (8.2.73)$$

or

$$\omega^2(\mathbf{q}, \omega) = (4J/I)[\gamma(0) - \gamma(\mathbf{q})] \approx (2zJ/dI)a^2q^2. \quad (8.2.74)$$

Thus, the elementary excitations from the ground state are propagating waves with a linear dispersion. The velocity of these modes is $c = (zJ/dIa^2)^{1/2}$. On the other hand, the low temperature rigidity [Eq. (??)] is $\rho_s(T \approx 0) = (zJ/d)a^{2-d}$, and $\tilde{I} = I/a^d$. Thus $c = (\rho_s/\tilde{I})^{1/2}$, in agreement with the hydrodynamical result. The hydrodynamical result is, however, valid throughout the ordered phase, even when thermal (or quantum) fluctuations depress $\rho_s(T)$ considerably below its zero temperature classical value of zJa^{2-d} . In addition, the hydrodynamical equations determine the form of the damping (imaginary part of ω) of modes. In a harmonic theory, each mode is independent and there is no damping. When anharmonic terms are added to the harmonic Hamiltonian, collisions between elementary excitations occur, and there can be damping. The dissipative coefficients κ and Γ can, therefore, be calculated at low temperatures by considering collisions between elementary excitations.

8.2.5 The Goldstone theorem

The existence of a new zero-frequency mode in the ordered phase is intimately connected with the facts that the conserved angular momentum L is a generator of rotations and that rotational symmetry is broken in the ordered phase. The Poisson bracket-commutation relation of ν_l with L is

$$\{\nu_i(t), L\} = \frac{1}{i\hbar}[\nu_i(t), L] = -\epsilon_{ij}\nu_j(t), \quad (8.2.75)$$

where ϵ_{ij} is the two-dimensional antisymmetric matrix with $\epsilon_{xy} = 1$. This equation is valid for any time t because L is a conserved, and thus time-invariant quantity. The commutator of L with the xy -component of the order parameter is thus

$$[Q_{xy}(\mathbf{x}, t), L] = 2i\hbar Q_{xx}(\mathbf{x}, t). \quad (8.2.76)$$

When L is expressed as the integral over \mathbf{x}' of the angular momentum density $l(\mathbf{x}', t')$, this equation implies

$$\int d^d x' \tilde{\chi}''_{Q_{xy}, l}(\mathbf{x}, \mathbf{x}', t, t') = i\langle Q_{xx}(\mathbf{x}, t) \rangle \quad (8.2.77)$$

or

$$\chi''_{Q_{xy}, l}(\mathbf{q} = 0, \omega) = 2\pi i \langle Q_{xx} \rangle \delta(\omega). \quad (8.2.78)$$

There is no factor of $2\hbar$ on the right hand side of Eqs. (8.2.77) and (8.2.78) because of the factor of $1/2\hbar$ in the definition [Eq. (7.6.14)] of $\chi''_{Q_{xy}, l}(\mathbf{x}, \mathbf{x}', t, t')$ in terms of the commutator of $Q_{xy}(\mathbf{x}, t)$ and $l(\mathbf{x}', t')$. Thus, the existence of a broken continuous symmetry implies that there is a zero-frequency pole in the zero wave number order-parameter generator response function, $\chi_{Q_{xy}, l}(\mathbf{q} = 0, z)$, or, equivalently, that there is a zero-frequency mode at zero wave number. This is the content of the *Goldstone theorem* (Goldstone 1961, Nambu 1960). The new mode is generally called the *Goldstone mode*.

The Goldstone theorem, Eq. (8.2.78), strictly speaking applies only at $\mathbf{q} = 0$. In the absence of long range forces, however, one can usually argue that the limit of response functions as $\mathbf{q} \rightarrow 0$ is equal to their value at $\mathbf{q} = 0$. In this case, the Goldstone theorem implies that there is a mode whose frequency goes continuously to zero as the wave number goes to zero. Indeed, our hydrodynamical analysis leads to precisely such a mode. If continuity is assumed, then, with the replacement $\delta\langle Q_{xy} \rangle = 2\langle Q_{xx} \rangle \delta\theta$, Eq. (8.2.78) can be rewritten as

$$\lim_{\mathbf{q} \rightarrow 0} \chi''_{\theta, l}(\mathbf{q}, \omega) = i\pi \delta(\omega), \quad (8.2.79)$$

in agreement with the hydrodynamical predictions of Eq. (8.2.70)

8.2.6 Kubo formulae

The fluctuation-dissipation theorem provides a correspondence between equilibrium correlation functions and response functions that lead, for example, to relations between the static thermodynamic susceptibility of conserved variables and equal time correlation functions [Eqs. (??) and (??)]. There are analogous relations, called *Kubo formulae*, between dissipative transport coefficients and current correlation functions. To see how such relations can be derived, consider the imaginary part of the angular momentum density response function [Eq. (8.2.37)]. It is straightforward to show that

$$\Gamma = D_l \tilde{I} = \lim_{\omega \rightarrow 0} \lim_{q \rightarrow 0} \frac{\omega}{q^2} \chi''_{ll}(\mathbf{q}, \omega) = \lim_{\omega \rightarrow 0} \lim_{q \rightarrow 0} \frac{\beta \omega^2}{2 q^2} S_{ll}(\mathbf{q}, \omega), \quad (8.2.80)$$

where the fluctuation-dissipation theorem [Eq. (7.6.41)] was used to obtain the final formula. The conservation law for angular momentum [Eq. (8.2.4)] implies

$$\begin{aligned} \omega^2 S_{ll}(\mathbf{q}, \omega) &= q_i q_j S_{\tau_i \tau_j}(\mathbf{q}, \omega) \\ &= \frac{1}{dV} q^2 \int d^d x d^d x' \int_{-\infty}^{\infty} dt e^{i\omega t} e^{-i\mathbf{q} \cdot \mathbf{x}} \langle \boldsymbol{\tau}(\mathbf{x}, t) \cdot \boldsymbol{\tau}(\mathbf{x}', 0) \rangle, \end{aligned} \quad (8.2.81)$$

where we used the fact that the disordered state is rotationally isotropic. Combining Eqs. (8.2.80) and (8.2.81), we obtain

$$\begin{aligned} \Gamma &= \frac{\beta}{2} \frac{1}{dV} \int d^d x \int d^d x' \int_{-\infty}^{\infty} dt \langle \boldsymbol{\tau}(\mathbf{x}, t) \cdot \boldsymbol{\tau}(\mathbf{x}', 0) \rangle \\ &= \frac{\beta}{2} \frac{1}{dV} \int d^d x \int d^d x' \int_0^{\infty} dt \langle \{\tau_i(\mathbf{x}, t), \tau_i(\mathbf{x}', 0)\}_+ \rangle, \end{aligned} \quad (8.2.82)$$

where $\{A, B\}_+ = AB + BA$ is the anticommutator of A and B . Thus, the dissipative coefficient Γ is related to the integral over time of the current-current correlation function. Similar expressions apply for the thermal conductivity and, indeed, for any dissipative coefficient associated with a conserved variable (see Problem 8.3). There are also related generalized Kubo formulae for the ordered phase. Often, Kubo formulae provide the best way to calculate dissipative coefficients from microscopic models.

8.2.7 Summary

In this section, we have studied the hydrodynamics of a simple model system. Many of the concepts and results introduced here apply quite generally to the hydrodynamics of all systems. The most important of these are listed below.

- Long-wavelength, low-frequency excitations are associated with conservation laws and broken symmetry.
- There is exactly one mode associated with each conservation law and each broken symmetry.
- Currents of hydrodynamical variables contain reactive and dissipative parts. The reactive parts of currents couple variables of opposite sign under time reversal and lead to propagating modes.
- In the absence of reactive couplings, the hydrodynamical modes are diffusive.
- Diffusion constants are the ratio of a transport coefficient to a susceptibility.
- The velocities of propagating modes are square roots of the ratio of a reactive transport coefficient to a susceptibility.
- Dissipative coefficients are related to current correlation functions via Kubo formulae.
- Elementary excitations from the ground state can be described by a harmonic Hamiltonian. These excitations are sound-like propagating modes with a velocity that agrees with the predictions of the hydrodynamic theory in the low-temperature limit.
- The Goldstone theorem states that there must be a zero-frequency, zero wave number mode in systems with a continuous broken symmetry. The new hydrodynamic mode in the ordered phase is the continuation of the zero-frequency Goldstone mode to nonzero wave number.