

CHAPTER 7

Time-dependent Correlation and Response Functions

The next three chapters are devoted to a discussion of the transport properties and microscopic dynamics of simple, dense fluids.¹ The present chapter deals with the general formalism of time-correlation functions and with linear response theory; Chapter 8 is concerned with the behaviour of time-dependent fluctuations in the long-wavelength, low-frequency limit, where contact can be made with the macroscopic equations of hydrodynamics; and Chapter 9 describes methods that allow the explicit calculation of time-correlation functions.

7.1 GENERAL PROPERTIES OF TIME-CORRELATION FUNCTIONS

A dynamical variable, $A(t)$ say, of a system consisting of N structureless particles is a function of some or all of the time-varying coordinates \mathbf{r}_i and momenta \mathbf{p}_i , $i = 1$ to N . We recall from Section 2.1 that the time evolution of A is determined by the equation of motion $A(t) = \exp(i\mathcal{L}t)A(0)$, where \mathcal{L} is the Liouville operator. It follows that A has the signature $\varepsilon_A = +1$ or -1 under time reversal depending on whether or not it changes sign under the transformation $\mathbf{p}_i \rightarrow -\mathbf{p}_i$. Now consider two such variables, A and B , each of which may be either real or complex. Their equilibrium time-correlation function is written as

$$C_{AB}(t', t'') = \langle A(t')B^*(t'') \rangle \quad (7.1.1)$$

with the convention that $t' \geq t''$. The superscript $*$ denotes a complex conjugate and the angular brackets represent either an average over time or an ensemble average over initial conditions. Thus $C_{AB}(t', t'')$ is defined either as

$$\langle A(t')B^*(t'') \rangle = \lim_{\tau \rightarrow \infty} \frac{1}{\tau} \int_0^\tau A(t' + t)B^*(t'' + t) dt \quad (7.1.2)$$

or as

$$\begin{aligned} \langle A(t')B^*(t'') \rangle = & \iint f_0^{[N]}(\mathbf{r}^N, \mathbf{p}^N) B^*(\mathbf{r}^N, \mathbf{p}^N) \\ & \times \exp[i\mathcal{L}(t' - t'')] A(\mathbf{r}^N, \mathbf{p}^N) d\mathbf{r}^N d\mathbf{p}^N \end{aligned} \quad (7.1.3)$$

The average in (7.1.3) is taken over all possible states of the system at time t'' , weighted by the equilibrium probability density $f_0^{[N]}$; for a system characterised by fixed values of N , V and T , $f_0^{[N]}$ is given by the canonical distribution (2.3.1). Equations (7.1.2) and (7.1.3) yield the same result in the thermodynamic limit if the system is ergodic. The most important class of time-correlation functions are the *autocorrelation* functions $C_{AA}(t)$, for which A and B are the same variable.

Since the equilibrium probability density is independent of time, the ensemble average in (7.1.3) is independent of the choice of time origin t'' , and the correlation function $C_{AB}(t', t'')$ is invariant under time translation. If we put $t'' = s$ and $t' = s + t$ the correlation function is a function only of the time difference t and is said to be *stationary* with respect to s . It is therefore customary to set $s = 0$ and use the more compact notation

$$C_{AB}(t) = \langle A(t)B^* \rangle \quad (7.1.4)$$

where $B^* \equiv B^*(0)$. The stationary character of the correlation function means that

$$\frac{d}{ds} \langle A(t+s)B^*(s) \rangle = \langle \dot{A}(t+s)B^*(s) \rangle + \langle A(t+s)\dot{B}^*(s) \rangle = 0 \quad (7.1.5)$$

and hence that

$$\langle \dot{A}(t)B^* \rangle = -\langle A(t)\dot{B}^* \rangle \quad (7.1.6)$$

In particular:

$$\langle \dot{A}A^* \rangle = 0 \quad (7.1.7)$$

Repeated differentiation with respect to s leads to a number of useful relations; these can also be deduced by exploiting the definition (7.1.2). For example:

$$\begin{aligned} \frac{d^2}{dt^2} \langle A(t)B^* \rangle &= \langle \ddot{A}(t)B^* \rangle \\ &= \lim_{\tau \rightarrow \infty} \frac{1}{\tau} \int_0^\tau \ddot{A}(t+t')B^*(t') dt' \\ &= - \lim_{\tau \rightarrow \infty} \frac{1}{\tau} \int_0^\tau \dot{A}(t+t')\dot{B}^*(t') dt' \\ &= -\langle \dot{A}(t)\dot{B}^* \rangle \end{aligned} \quad (7.1.8)$$

The invariance of correlation functions under time translation implies that

$$\begin{aligned} C_{AB}(t) &= \varepsilon_A \varepsilon_B C_{AB}(-t) = \varepsilon_A \varepsilon_B \langle A(-t)B^* \rangle \\ &= \varepsilon_A \varepsilon_B \langle AB^*(t) \rangle = \varepsilon_A \varepsilon_B C_{BA}^*(t) \end{aligned} \quad (7.1.9)$$

where $\varepsilon_A, \varepsilon_B$ are the time-reversal signatures of the two variables.

It is clear that

$$\lim_{t \rightarrow 0} C_{AB}(t) = \langle AB^* \rangle \quad (7.1.10)$$

where $\langle AB^* \rangle$ is a static correlation function. In the limit $t \rightarrow \infty$ the variables $A(t)$ and B become uncorrelated and

$$\lim_{t \rightarrow \infty} C_{AB}(t) = \langle A \rangle \langle B^* \rangle \quad (7.1.11)$$

However, it is usually more convenient to define the dynamical variables in such a way as to exclude their average values and to consider only the time correlation of their fluctuating parts, i.e.

$$C_{AB}(t) = \langle [A(t) - \langle A \rangle][B^* - \langle B^* \rangle] \rangle \quad (7.1.12)$$

With this convention, $C_{AB}(t) \rightarrow 0$ as $t \rightarrow \infty$. Because

$$\langle [A(t) \pm A][A(t) \pm A]^* \rangle \geq 0 \quad (7.1.13)$$

it is also true that

$$-\langle AA^* \rangle \leq C_{AA}(t) \leq \langle AA^* \rangle \quad (7.1.14)$$

The magnitude of an autocorrelation function is therefore bounded above by its initial value. This is to be expected, since an autocorrelation function describes the averaged way in which spontaneous (thermal) fluctuations in a variable A decay in time.

If $C_{AB}(t)$ is defined as in (7.1.12), it is also possible to define its Fourier transform or *power spectrum*:

$$C_{AB}(\omega) = \frac{1}{2\pi} \int_{-\infty}^{\infty} C_{AB}(t) \exp(i\omega t) dt \quad (7.1.15)$$

and its Laplace transform:

$$\tilde{C}_{AB}(z) = \int_0^{\infty} C_{AB}(t) \exp(izt) dt \quad (7.1.16)$$

where z is a complex frequency. Since $C_{AB}(t)$ is bounded, $\tilde{C}_{AB}(z)$ is analytic in the upper half of the complex z plane ($\text{Im } z > 0$); it is also related to $C_{AB}(\omega)$ by a Hilbert transform, i.e.

$$\begin{aligned} \tilde{C}_{AB}(z) &= \int_0^{\infty} dt \exp(izt) \int_{-\infty}^{\infty} C_{AB}(\omega) \exp(-i\omega t) d\omega \\ &= i \int_{-\infty}^{\infty} \frac{C_{AB}(\omega)}{z - \omega} d\omega \end{aligned} \quad (7.1.17)$$

From the results in (7.1.9) it follows that an autocorrelation function $C_{AA}(t)$ and its power spectrum $C_{AA}(\omega)$ are real, even functions of t and ω , respectively. An integral such as

that in (7.1.17) can be evaluated with the help of a standard relation commonly written in short-hand form as

$$\lim_{\varepsilon \rightarrow 0} \frac{1}{x \pm i\varepsilon} \equiv \mathcal{P}\left(\frac{1}{x}\right) \mp i\pi\delta(x) \quad (7.1.18)$$

where \mathcal{P} denotes the principal value. Thus, since $C_{AA}(\omega)$ is necessarily real:

$$\begin{aligned} \lim_{\varepsilon \rightarrow 0} \operatorname{Re} \tilde{C}_{AA}(\omega + i\varepsilon) &= \lim_{\varepsilon \rightarrow 0} \operatorname{Re} \left(i \int_{-\infty}^{\infty} \frac{C_{AA}(\omega')}{\omega - \omega' + i\varepsilon} d\omega' \right) \\ &= \pi C_{AA}(\omega) \end{aligned} \quad (7.1.19)$$

It can also be shown that $C_{AA} \geq 0$ for all ω . Consider an auxiliary variable, $A_T(\omega)$, defined as

$$A_T(\omega) = \frac{1}{\sqrt{2T}} \int_{-T}^T A(t) \exp(i\omega t) dt \quad (7.1.20)$$

The statistical average of $\langle A_T(\omega) A_T^*(\omega) \rangle$ cannot be negative. Hence

$$\langle A_T(\omega) A_T^*(\omega) \rangle = \frac{1}{2T} \int_{-T}^T dt \int_{-T}^T dt' \langle A(t) A^*(t') \rangle \exp[i\omega(t - t')] \geq 0 \quad (7.1.21)$$

If we now make a change of variable from t' to $\tau = t - t'$ and take the limit $T \rightarrow \infty$, we find that

$$\begin{aligned} \lim_{T \rightarrow \infty} \langle A_T(\omega) A_T^*(\omega) \rangle &= \int_{-\infty}^{\infty} C_{AA}(\tau) \exp(i\omega\tau) d\tau \\ &= C_{AA}(\omega) \geq 0 \end{aligned} \quad (7.1.22)$$

The experimental significance of time-correlation functions lies in the fact that the spectra measured by various spectroscopic techniques are the power spectra of well-defined dynamical variables. This connection between theory and experiment will be made explicit in Section 7.5 for the special but important case of inelastic neutron scattering. In addition, as we shall see later, the linear transport coefficients of hydrodynamics are related to time integrals of certain autocorrelation functions. Finally, time-correlation functions provide a quantitative description of the microscopic dynamics in liquids. Computer simulations play a key role here, since they give access to a large variety of correlation functions, many of which are not measurable by laboratory experiments.

Apart from the limitation to classical mechanics, the properties of time-correlation functions given thus far are completely general. We now restrict the discussion to systems of particles for which the interaction potential is continuous; the hamiltonian is therefore differentiable and the Liouville operator has the form given by (2.1.8). An autocorrelation function of such a system is an even function of time and can be expanded in a Taylor

series in even powers of t around $t = 0$. Thus

$$\begin{aligned} C_{AA}(t) &= \sum_{n=0}^{\infty} \frac{t^{2n}}{(2n)!} \langle A^{(2n)} A^* \rangle = \sum_{n=0}^{\infty} \frac{t^{2n}}{(2n)!} (-1)^n \langle A^{(n)} A^{(n)*} \rangle \\ &= \sum_{n=0}^{\infty} \frac{t^{2n}}{(2n)!} (-1)^n \langle (i\mathcal{L})^n A |^2 \rangle \end{aligned} \quad (7.1.23)$$

where the superscript $(2n)$ denotes a $2n$ -fold derivative and repeated use has been made of (7.1.8). Differentiation of the inverse Fourier transform of (7.1.15) $2n$ times with respect to t gives

$$\langle \omega^{2n} \rangle_{AA} \equiv \int_{-\infty}^{\infty} \omega^{2n} C_{AA}(\omega) d\omega = (-1)^n C_{AA}^{(2n)}(t=0) \quad (7.1.24)$$

Thus, apart from a possible change of sign, the frequency moments of the power spectrum are equal to the derivatives of the autocorrelation function taken at $t = 0$; these derivatives are static correlation functions that are expressible as integrals over the particle distribution functions. On expanding the right-hand side of (7.1.17) in powers of $1/z$ it becomes clear that the frequency moments defined by (7.1.24) are also the coefficients in the high-frequency expansion of the Laplace transform:

$$\tilde{C}_{AA}(z) = \frac{i}{z} \sum_{n=0}^{\infty} \frac{\langle \omega^{2n} \rangle_{AA}}{z^{2n}} \quad (7.1.25)$$

Expansions of the type displayed in (7.1.23) cannot be used for systems such as the hard-sphere fluid. The impulsive nature of the forces between particles with hard cores means that the Liouville operator no longer has the form² shown in (2.1.8). As a result, the time-correlation functions are non-analytic at $t = 0$, and their power spectra have frequency moments that are infinite.

The definition of a time-correlation function provided by (7.1.3) has the form of an inner product of the “vectors” $A(t)$ and B in the infinite-dimensional, Hilbert space of dynamical variables, usually called Liouville space. A useful notation based on this identification is one in which a time-correlation function is written as

$$\langle A(t) B^* \rangle \equiv (B, A(t)) \quad (7.1.26)$$

where (\dots, \dots) denotes an inner product. The usual requirements of an inner product are therefore satisfied. In particular, $(A, A) \geq 0$ and $(A, B) = (B, A)^*$. Formal properties of time-correlation functions can then be deduced from the fact that the Liouville operator is hermitian (and hence $i\mathcal{L}$ is anti-hermitian) with respect to the inner product, i.e.

$$(B, \mathcal{L}A) = (A, \mathcal{L}B)^* = (\mathcal{L}B, A) \quad (7.1.27)$$

Because \mathcal{L} is hermitian, the propagator $\exp(i\mathcal{L}t)$ is a unitary operator with an hermitian conjugate given by $\exp(-i\mathcal{L}t)$. It follows that

$$\begin{aligned}\langle A(t)B^* \rangle &\equiv \langle B, \exp(i\mathcal{L}t)A \rangle = \langle B, \exp(-i\mathcal{L}s)A(t+s) \rangle \\ &= \langle A(t+s), \exp(i\mathcal{L}s)B \rangle^* \equiv \langle A(t+s)B^*(s) \rangle\end{aligned}\quad (7.1.28)$$

thereby proving that the correlation function is stationary. Note that the effect of the operation $A(t) = \exp(i\mathcal{L}t)A$ is to “rotate” A through an angle $\mathcal{L}t$ in Liouville space. By exploiting the fact that $i\mathcal{L}A = \dot{A}$, properties of time-correlation functions that involve time derivatives of dynamical variables are also easily derived. For example:

$$\begin{aligned}\langle \dot{A}(t)B^* \rangle &\equiv \langle B, i\mathcal{L}A(t) \rangle \\ &= -\langle A(t), i\mathcal{L}B \rangle^* \equiv -\langle A(t)\dot{B}^* \rangle\end{aligned}\quad (7.1.29)$$

in agreement with (7.1.6).

The proof that the Liouville operator is hermitian requires an integration by parts of the derivatives appearing in the Poisson-bracket representation (2.1.8). The inner product is sometimes defined without the weighting factor $f_0^{(N)}$, but the Liouville operator retains its hermitian character, since $\mathcal{L}f_0^{(N)} = 0$.

7.2 AN ILLUSTRATION: THE VELOCITY AUTOCORRELATION FUNCTION AND SELF-DIFFUSION

The ideas introduced in Section 7.1 can be usefully illustrated by considering one of the simplest but most important examples of a time-correlation function, namely the autocorrelation function of the velocity $\mathbf{u} = \mathbf{p}/m$ of a tagged particle moving through a fluid. The velocity autocorrelation function, defined as

$$Z(t) = \frac{1}{3} \langle \mathbf{u}(t) \cdot \mathbf{u} \rangle = \langle u_x(t)u_x \rangle \quad (7.2.1)$$

is a measure of the projection of the particle velocity onto its initial value, averaged over initial conditions. Its value at $t = 0$ is given by the equipartition theorem:

$$Z(0) = \frac{1}{3} \langle u^2 \rangle = \frac{k_B T}{m} \quad (7.2.2)$$

At times long compared with any microscopic relaxation time the initial and final velocities will be completely uncorrelated. Thus $Z(t \rightarrow \infty) = 0$. The results of computer simulations of argon-like liquids show that the velocities are already largely decorrelated after times of order 10^{-12} s, but in general $Z(t)$ also has a weak, slowly decaying part. The detailed behaviour at long times varies with thermodynamic state, as is evident from the examples plotted in Figure 7.1. We shall return later to a discussion of the main features of curves such as these, but first we show that there exists a general relationship between the self-diffusion coefficient D and the time integral of $Z(t)$.

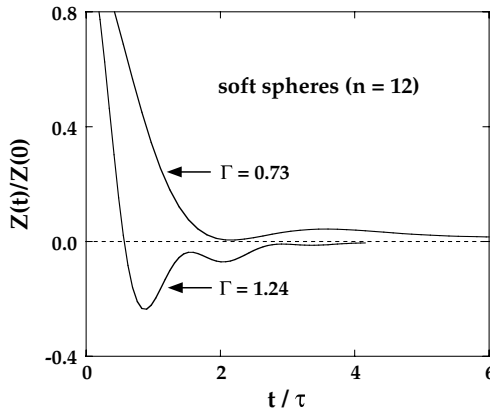


FIG. 7.1. Normalised velocity autocorrelation function of the r^{-12} -fluid at two different values of the dimensionless coupling parameter Γ defined by (5.3.13). The higher value of Γ represents a thermodynamic state close to the fluid–solid transition and the unit of time is $\tau = (m\sigma^2/48\varepsilon)^{1/2}$. After Heyes *et al.*³

Consider a set of identical, tagged particles having initial positions $\{\mathbf{r}_i(0)\}$. If the particles diffuse in time t to positions $\{\mathbf{r}_i(t)\}$, the self-diffusion coefficient is given by a well-known relation due to Einstein:

$$D = \lim_{t \rightarrow \infty} \frac{\langle |\mathbf{r}_i(t) - \mathbf{r}_i(0)|^2 \rangle}{6t} \quad (7.2.3)$$

This result is a direct consequence of Fick’s law of diffusion, as we shall see in Section 8.2. It is also a relation characteristic of a “random walk”, in which the mean-square displacement of the walker becomes a linear function of time after a sufficiently large number of random steps. The nature of the limiting process involved in (7.2.3) highlights the general importance of taking the thermodynamic limit before the limit $t \rightarrow \infty$. For a system of finite volume V , the diffusion coefficient defined by (7.2.3) is strictly zero, since the maximum achievable mean-square displacement is of order $V^{2/3}$. In practice, for a system of macroscopic dimensions, the ratio on the right-hand side of (7.2.3) will reach a plateau value at times much shorter than those required for the diffusing particles to reach the boundaries of the system; it is the plateau value that provides the definition of D for a finite system.

We now rewrite the Einstein relation in terms of the velocity autocorrelation function. The displacement in a time interval t of any tagged particle is

$$\mathbf{r}(t) - \mathbf{r}(0) = \int_0^t \mathbf{u}(t') dt' \quad (7.2.4)$$

When squared and averaged over initial conditions, (7.2.4) becomes

$$\langle |\mathbf{r}(t) - \mathbf{r}(0)|^2 \rangle = \left\langle \int_0^t \mathbf{u}(t') dt' \cdot \int_0^t \mathbf{u}(t'') dt'' \right\rangle$$

$$\begin{aligned}
&= 2 \int_0^t dt' \int_0^{t'} dt'' \langle \mathbf{u}(t') \cdot \mathbf{u}(t'') \rangle \\
&= 6 \int_0^t dt' \int_0^{t'} dt'' Z(t' - t'') \quad (7.2.5)
\end{aligned}$$

A change of variable from t'' to $s = t' - t''$ followed by an integration by parts with respect to t' shows that

$$\begin{aligned}
\langle |\mathbf{r}(t) - \mathbf{r}(0)|^2 \rangle &= 6 \int_0^t dt' \int_0^{t'} ds Z(s) \\
&= 6t \int_0^t \left(1 - \frac{s}{t}\right) Z(s) ds \quad (7.2.6)
\end{aligned}$$

and substitution of (7.2.5) in (7.2.3) gives the required result:

$$D = \int_0^\infty Z(t) dt \quad (7.2.7)$$

Equation (7.2.7) is an example of a *Green-Kubo formula*, an important class of relations in which a macroscopic dynamical property is written as the time integral of a microscopic time-correlation function.

If the interparticle potential is continuous, the short-time expansion of $Z(t)$ starts as

$$Z(t) = \frac{k_B T}{m} \left(1 - \Omega_0^2 \frac{t^2}{2} + \dots \right) \quad (7.2.8)$$

Equation (7.1.23) shows that the coefficient of $\frac{1}{2}t^2$ is

$$\Omega_0^2 = \frac{m}{3k_B T} \langle \dot{\mathbf{u}} \cdot \dot{\mathbf{u}} \rangle = \frac{\langle |\mathbf{F}|^2 \rangle}{3mk_B T} \quad (7.2.9)$$

where \mathbf{F} is the total force exerted on the diffusing particle by its neighbours. If the tagged particle is identical to all other particles in the fluid, $\mathbf{F} = -\nabla V_N$, where V_N is the total potential energy. When V_N is a sum of pair terms, Ω_0^2 can be expressed in terms of the equilibrium pair distribution function and the interparticle potential. To show this, we first derive a useful, general result. Let $A(\mathbf{r}^N)$ be some function of the particle coordinates. Then

$$\begin{aligned}
&\left\langle A(\mathbf{r}^N) \frac{\partial V_N}{\partial x_i} \right\rangle \\
&= \frac{1}{Z_N} \int \dots \int A(\mathbf{r}^N) \frac{\partial V_N}{\partial x_i} \exp(-\beta V_N) d\mathbf{r}_1 \dots dx_i dy_i dz_i \dots d\mathbf{r}_N \\
&= \frac{k_B T}{Z_N} \int \dots \int \frac{\partial A(\mathbf{r}^N)}{\partial x_i} \exp(-\beta V_N) d\mathbf{r}_1 \dots dx_i dy_i dz_i \dots d\mathbf{r}_N \quad (7.2.10)
\end{aligned}$$

or

$$\left\langle A(\mathbf{r}^N) \frac{\partial V_N}{\partial x_i} \right\rangle = k_B T \left\langle \frac{\partial A(\mathbf{r}^N)}{\partial x_i} \right\rangle \quad (7.2.11)$$

The second equality in (7.2.10) follows from an integration by parts with respect to x_i . Equation (7.2.11) is called the Yvon theorem. When applied to the current problem it shows that the mean-square force on a particle is

$$\langle |\mathbf{F}|^2 \rangle = k_B T \langle \nabla^2 V_N \rangle \quad (7.2.12)$$

With the assumption of pairwise additivity, manipulations similar to those used in Section 2.5 now allow (7.2.9) to be rewritten in the form

$$\Omega_0^2 = \frac{(N-1)}{3m} \langle \nabla^2 v(r) \rangle = \frac{\rho}{3m} \int \nabla^2 v(r) g(r) d\mathbf{r} \quad (7.2.13)$$

The quantity Ω_0 is called the Einstein frequency, since it represents the frequency at which the tagged particle would vibrate if it were undergoing small oscillations in the potential well produced by the surrounding particles when maintained at their mean equilibrium positions around the tagged particle. Numerically, Ω_0 is of order 10^{13} s^{-1} for liquid argon near its triple point.

Equation (7.2.8) does not apply to systems of hard spheres because the hard-sphere potential is not differentiable.⁴ The short-time behaviour of $Z(t)$ now takes the form

$$\langle \mathbf{u}(t) \cdot \mathbf{u} \rangle = \langle u^2 \rangle + t \left(\frac{d}{dt} \langle \mathbf{u}(t) \cdot \mathbf{u} \rangle \right)_{t=0} + \dots \quad (7.2.14)$$

where the differentiation with respect to time must be carried out after the ensemble averaging. Thus

$$Z(t) = \frac{1}{3} \langle u^2 \rangle (1 - \Omega_0' t + \dots) \quad (7.2.15)$$

where the frequency Ω_0' is

$$\Omega_0' = -\frac{1}{\langle u^2 \rangle} \lim_{\Delta t \rightarrow 0} \frac{\langle \Delta \mathbf{u} \cdot \mathbf{u} \rangle}{\Delta t} \quad (7.2.16)$$

Consider a tagged hard sphere of diameter d moving in a fluid of untagged but otherwise identical hard spheres.⁵ Over a sufficiently short time interval the tagged sphere will suffer at most one collision with a sphere from the bath. To evaluate Ω_0' from its definition (7.2.16), let us suppose that the tagged sphere, of momentum \mathbf{p} , collides with a sphere of momentum \mathbf{p}' , as pictured in Figure 7.2. Because the collision is elastic, the momentum gained by the tagged particle is $\Delta \mathbf{p} = -(\mathbf{p} \cdot \hat{\mathbf{r}} - \mathbf{p}' \cdot \hat{\mathbf{r}}) \hat{\mathbf{r}}$, where $\hat{\mathbf{r}} = \mathbf{r}/r$ is a unit vector along the line joining the two centres of mass. Thus $-\Delta \mathbf{p} \cdot \mathbf{p} = p(p - p')$ where p, p' are the components of \mathbf{p} and \mathbf{p}' , respectively, along $\hat{\mathbf{r}}$. If $p > p'$, the separation of the two spheres will decrease in a short time Δt by an amount $\Delta r = (p - p') \Delta t / m$. On average, given

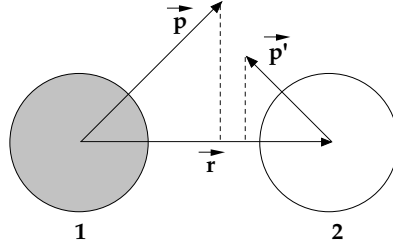


FIG. 7.2. A collision between a tagged hard sphere, (1), and a sphere from the bath, (2).

that Δr is small, the number of spheres that initially lie within a distance d to $d + \Delta r$ of the tagged sphere will be $n(\Delta r) \approx 4\pi d^2 g(d)(p - p')\Delta t/m$, where $g(d)$ is the pair distribution function at contact, and the probability that the tagged sphere will suffer a collision with a sphere having a component of momentum p' along $\hat{\mathbf{r}}$ is $P(p') = n(\Delta r) f_M(p') dp'$, where f_M is the maxwellian distribution (2.1.26) in its component form. The statistical average of $-\Delta \mathbf{p} \cdot \mathbf{p}$ is therefore obtained by multiplying $P(p')$ by $p(p - p') f_M(p) dp$ and integrating over p and p' . Bringing these results together we find that

$$\begin{aligned} \Omega'_0 &= -\frac{1}{3mk_B T} \lim_{\Delta t \rightarrow 0} \frac{\langle \Delta \mathbf{p} \cdot \mathbf{p} \rangle}{\Delta t} \\ &= \frac{4\pi d^2 g(d)}{3m^2 k_B T} \iint_{p > p'} p(p - p')^2 f_M(p) f_M(p') dp dp' \end{aligned} \quad (7.2.17)$$

or, on changing variables from p, p' to $p_+ = (p + p')/\sqrt{2}$, $p_- = (p - p')/\sqrt{2}$:

$$\Omega'_0 = \frac{4\sqrt{2}\pi d^2 g(d)}{3m^2 k_B T} \int_{-\infty}^{\infty} dp_+ \int_0^{\infty} dp_- p_-^3 f_M(p_-) f_M(p_+) \quad (7.2.18)$$

The double integral is now easily evaluated to give

$$\Omega'_0 = \frac{8\rho d^2 g(d)}{3} \left(\frac{\pi k_B T}{m} \right)^{1/2} = \frac{2\Gamma_E}{3} \quad (7.2.19)$$

where Γ_E is the Enskog collision rate introduced in Section 2.5.

The derivation of (7.2.19) shows that the Enskog approximation makes allowance for static correlations in the fluid, but the key assumption underlying the Boltzmann equation is retained, namely that successive collisions are completely uncorrelated. The velocity of a tagged particle immediately following a collision is therefore dependent on its velocity immediately prior to the collision, but not on its velocity at earlier times. Because collisions between hard spheres are instantaneous events, this is tantamount to saying that the “memory” associated with the tagged-particle velocity is of infinitesimally short duration, with the consequence, as we shall see in later sections, that the velocity autocorrelation function is exponential in time. By identifying the right-hand side of (7.2.14) with the

leading terms in the expansion of an exponential function, we do in fact recover Enskog's approximation⁶ for the velocity autocorrelation function of hard spheres:

$$Z_E(t) = \frac{k_B T}{m} \exp(-2\Gamma_E |t|/3) \quad (7.2.20)$$

where the absolute value of t appears because $Z(t)$ must be an even function of t . The corresponding approximation for the diffusion coefficient is obtained by substitution of (7.2.20) in (7.2.7):

$$D_E = \frac{3k_B T}{2m\Gamma_E} = \frac{3}{8\rho d^2 g(d)} \left(\frac{k_B T}{\pi m} \right)^{1/2} \quad (7.2.21)$$

This expression is nearly exact in the low-density limit⁷ while its applicability at higher densities has been thoroughly tested in molecular dynamics calculations.⁸ From Figure 7.3 we see that the diffusion coefficient obtained by simulation exceeds the Enskog value at intermediate densities, but falls below it at densities close to crystallisation.⁹ The high-density deviations arise from back-scattering effects, corresponding to the fact that collisions lead, on average, to the reversal of the velocity of a tagged particle into a comparatively narrow range of angles. This gives rise to an extended negative region in $Z(t)$; the same effect is seen for other potential models, as exemplified in Figure 7.1. The increase in the ratio D/D_E at intermediate densities is attributable in large part to an enhancement of velocity correlations due to the excitation of slowly decaying, collective motions in the fluid. The motion of the tagged particle induces a backflow pattern in the surrounding fluid that reacts on the particle at later times, giving rise to persistence (or “memory”) effects and an unexpectedly slow ($\sim t^{-3/2}$) decay of $Z(t)$ at very long times; this behaviour is again not specific to hard spheres. We shall return to the question of the “long-time tails”

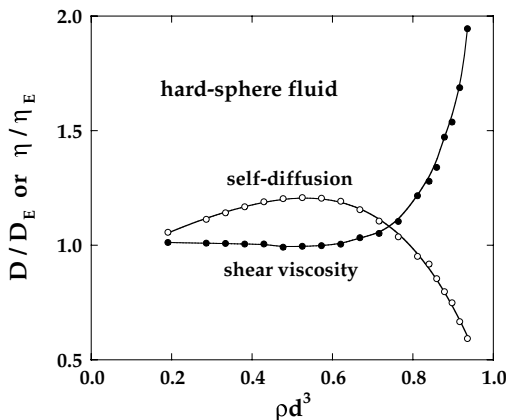


FIG. 7.3. Molecular-dynamics results for the self-diffusion coefficient D and shear viscosity η of the hard-sphere fluid relative to their values in the Enskog approximation. The curves are drawn as a guide to the eye. After Sigurgeirsson and Heyes.^{8(b)}

of correlation functions in Section 8.7. Figure 7.3 also shows the corresponding results for the shear viscosity of the hard-sphere fluid, but we postpone discussion of these until Section 8.4.

A treatment of self-diffusion by kinetic theory that goes beyond the Enskog approximation must take account of the correlated sequences of binary collisions that a tagged particle experiences. In such a sequence the tagged particle collides initially with a particle from the bath, then diffuses through the fluid, suffering collisions with other bath particles, before colliding either with the same particle it met initially or with another particle whose motion is correlated in some way with that of the initial collision partner. Examples of collision sequences are illustrated in Figure 7.4; in each case the tagged particle is labelled 1 and A, B represent two different space-time points. In example (a), the two collisions are uncorrelated. In (b) and (c), particles 1 and 2 first meet at A, then recollide at B; in (b) the recollision involves one intermediate collision between 2 and 3 (a three-body event) and in (c) it involves intermediate collisions between 1 and 4 and between 2 and 3 (a four-body event). Example (d) is a different type of four-body event in which the initial (at A) and final (at B) collision partners are different but the collisions suffered by 1 at A and B are nonetheless correlated. Sequences (b), (c) and (d) are all examples of “ring-collision” events.

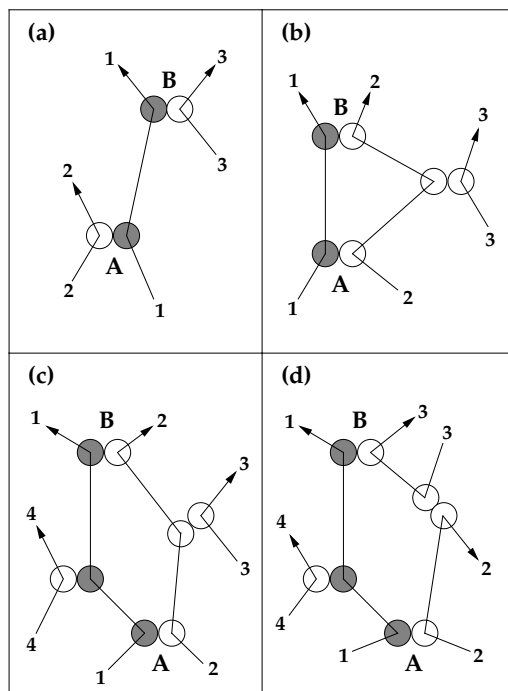


FIG. 7.4. Examples of uncorrelated (a) and correlated (b, c, d) sequences of binary collisions. A and B represent two different space-time points. See text for details.

7.3 BROWNIAN MOTION AND THE GENERALISED LANGEVIN EQUATION

Calculations of the velocity autocorrelation function either by the Enskog method or by other, more sophisticated versions of kinetic theory are largely limited to hard-sphere systems, though efforts have been made to apply similar techniques in calculations for continuous potentials. In this section we describe a different approach that is more phenomenological in character, but has found wide application in the theory of transport processes in liquids. Its basis is the stochastic theory used by Langevin to describe the brownian motion of a large and massive particle in a bath of particles that are much smaller and lighter than itself. The problem is characterised by two very different timescales, one associated with the slow relaxation of the initial velocity of the brownian particle and another linked to the frequent collisions that the brownian particle suffers with particles of the bath. Langevin assumed that the force acting on the brownian particle consists of two parts: a systematic, frictional force proportional to the velocity $\mathbf{u}(t)$, but acting in the opposite sense, and a randomly fluctuating force, $\mathbf{R}(t)$, which arises from collisions with surrounding particles. The equation of motion of a brownian particle of mass m is therefore written as

$$m\dot{\mathbf{u}}(t) = -m\xi\mathbf{u}(t) + \mathbf{R}(t) \quad (7.3.1)$$

where ξ is the *friction coefficient*. The random force is assumed to vanish in the mean:

$$\langle \mathbf{R}(t) \rangle = 0 \quad (7.3.2)$$

to be uncorrelated with the velocity at any earlier time:

$$\langle \mathbf{R}(t) \cdot \mathbf{u} \rangle = 0, \quad t > 0 \quad (7.3.3)$$

and to have an infinitesimally short correlation time, i.e.

$$\langle \mathbf{R}(t+s) \cdot \mathbf{R}(s) \rangle = 2\pi R_0 \delta(t) \quad (7.3.4)$$

which in turn means that the power spectrum of the random force is a constant, R_0 (a “white” spectrum):

$$\frac{1}{2\pi} \int_{-\infty}^{\infty} \langle \mathbf{R}(t) \cdot \mathbf{R} \rangle \exp(i\omega t) dt = R_0 \quad (7.3.5)$$

These are reasonable assumptions when the brownian particle is much larger than its neighbours, because even on a short timescale its motion will be determined by a very large number of essentially uncorrelated collisions. When all particles are of the same size, the assumptions are less well justified, and a generalisation of a type to be described later is required.

The two terms on the right-hand side of the Langevin equation (7.3.1) are not independent. To see the connection between them we first write the solution to (7.3.1) in the form

$$m\mathbf{u}(t) = m\mathbf{u}(0) \exp(-\xi t) + \exp(-\xi t) \int_0^t \exp(\xi s) \mathbf{R}(s) ds \quad (7.3.6)$$

On squaring and taking the statistical average we find, using (7.3.3) and (7.3.4), that

$$\begin{aligned}
 m^2 \langle |\mathbf{u}(t)|^2 \rangle &= m^2 \langle |\mathbf{u}(0)|^2 \rangle \exp(-2\xi t) \\
 &\quad + \exp(-2\xi t) \int_0^t ds \int_0^t ds' \exp[\xi(s+s')] 2\pi R_0 \delta(s-s') \\
 &= m^2 \langle |\mathbf{u}(0)|^2 \rangle \exp(-2\xi t) + \frac{\pi R_0}{\xi} [1 - \exp(-2\xi t)]
 \end{aligned} \tag{7.3.7}$$

We now take the limit $t \rightarrow \infty$; the brownian particle will then be in thermal equilibrium with the bath regardless of the initial conditions. Hence $\langle |\mathbf{u}(\infty)|^2 \rangle = 3k_B T/m$ and (7.3.7) can be rearranged to give an expression for the friction coefficient:

$$\xi = \frac{\pi \beta R_0}{3m} = \frac{\beta}{3m} \int_0^\infty \langle \mathbf{R}(t) \cdot \mathbf{R} \rangle dt \tag{7.3.8}$$

From a physical point of view it is not surprising to find a link between the frictional and random forces. If the brownian particle were to be drawn through the bath by an external field, random collisions suffered by the particle would give rise to a systematic retarding force proportional to the particle velocity. Equation (7.3.8) is a further illustration of the fluctuation-dissipation theorem already discussed in Section 3.5 and which we shall establish more generally in Section 7.6.

The friction coefficient is also related to the diffusion coefficient. Consider the case when the brownian particle is initially ($t = 0$) situated at the origin ($\mathbf{r} = 0$). We wish to calculate the mean-square displacement of the particle after a time t . By multiplying through (7.3.1) by $\mathbf{r}(t)$ and using the results

$$\mathbf{r} \cdot \mathbf{u} = \mathbf{r} \cdot \dot{\mathbf{r}} = \frac{1}{2} \frac{d}{dt} r^2 \tag{7.3.9}$$

$$\mathbf{r} \cdot \dot{\mathbf{u}} = \mathbf{r} \cdot \ddot{\mathbf{r}} = \frac{1}{2} \frac{d^2}{dt^2} r^2 - u^2 \tag{7.3.10}$$

we find that

$$\frac{1}{2} m \frac{d^2}{dt^2} |\mathbf{r}(t)|^2 + \frac{1}{2} \xi m \frac{d}{dt} |\mathbf{r}(t)|^2 = m |\mathbf{u}(t)|^2 + \mathbf{r}(t) \cdot \mathbf{R}(t) \tag{7.3.11}$$

In the statistical mean (7.3.11) becomes

$$\frac{d^2}{dt^2} \langle |\mathbf{r}(t)|^2 \rangle + \xi \frac{d}{dt} \langle |\mathbf{r}(t)|^2 \rangle = \frac{6k_B T}{m} \tag{7.3.12}$$

The solution to (7.3.12) that satisfies the boundary conditions $\langle |\mathbf{r}(0)|^2 \rangle = 0$ and

$$\left. \frac{d}{dt} \langle |\mathbf{r}(t)|^2 \rangle \right|_{t=0} = 2 \langle \mathbf{r}(0) \cdot \mathbf{u}(0) \rangle = 0 \tag{7.3.13}$$

is

$$\langle |\mathbf{r}(t)|^2 \rangle = \frac{6k_B T}{\xi m} \left(t - \frac{1}{\xi} + \frac{1}{\xi} \exp(-\xi t) \right) \quad (7.3.14)$$

At very short times, such that $\xi t \ll 1$, the solution becomes

$$\langle |\mathbf{r}(t)|^2 \rangle \approx \left(\frac{3k_B T}{m} \right) t^2 = \langle u^2 \rangle t^2 \quad (7.3.15)$$

which corresponds to free-particle motion. At very large times ($\xi t \gg 1$), (7.3.14) reduces to

$$\langle |\mathbf{r}(t)|^2 \rangle \approx \left(\frac{6k_B T}{\xi m} \right) t \quad (7.3.16)$$

and comparison with (7.2.3) leads to Einstein's expression for the diffusion coefficient:

$$D = \frac{k_B T}{\xi m} \quad (7.3.17)$$

An estimate of ξ can be obtained from a hydrodynamic calculation of the frictional force on a sphere of diameter d moving with constant velocity \mathbf{u} in a fluid of shear viscosity η . This leads to a famous result due to Stokes, the precise form of which depends on the assumptions made about the behaviour at the surface of the sphere of the velocity field created by the fluid. If the "stick" boundary condition is used, the fluid velocity at the surface is everywhere taken equal to \mathbf{u} ; in the "slip" approximation, the normal component of the fluid velocity is set equal to the normal component of \mathbf{u} , thereby ensuring that no fluid can enter or leave the sphere, and the tangential force acting on the sphere is assumed to vanish. The stress tensor at the surface is then obtained by solving the linearised Navier–Stokes equation (see Section 8.3) subject to one of these boundary conditions, supplemented by the requirement that the fluid velocity must vanish at infinite distance from the sphere. When the stress tensor is known, the total frictional force \mathbf{F} can be calculated by integration over the surface. The final result has the form $\mathbf{F} = -\xi \mathbf{u}$, with

$$\xi = \frac{3\pi\eta d}{m} \quad (\text{stick}), \quad \xi = \frac{2\pi\eta d}{m} \quad (\text{slip}) \quad (7.3.18)$$

Combination of (7.3.17) with (7.3.18) leads to the two familiar forms of Stokes's law:

$$D\eta = \frac{k_B T}{3\pi d} \quad (\text{stick}), \quad D\eta = \frac{k_B T}{2\pi d} \quad (\text{slip}) \quad (7.3.19)$$

It is a remarkable feature of Stokes's law that although it is derived from purely macroscopic considerations, and is apparently limited to brownian particles, it also provides a good, empirical correlation of experimental data on simple liquids, use of the slip boundary condition generally leading to more reasonable values of the effective diameter d .

The form of the velocity autocorrelation function of the brownian particle is easily deduced. If we multiply through (7.3.1) by $\mathbf{u}(0)$ and take the thermal average we find that

$$Z(t) = \frac{1}{3} \langle \mathbf{u}(t) \cdot \mathbf{u}(0) \rangle = \left(\frac{k_B T}{m} \right) \exp(-\xi t) \quad (7.3.20)$$

where $t \geq 0$. The expression for the diffusion coefficient given by (7.3.17) is then recovered by inserting (7.3.20) in (7.2.7). Note that the autocorrelation function is of the same, exponential form as the Enskog result for the hard-sphere fluid. This is to be expected, since a markovian hypothesis underlies both calculations. In practice, as is evident from Figure 7.1, the velocity autocorrelation function of a simple liquid may be very far from exponential. Moreover, the power spectrum of an exponential correlation function has an infinite second moment, which for continuous potentials is not consistent with the result shown in (7.2.8). The inconsistency arises because the applicability of (7.3.20) does not extend to very short times. In a time interval t such that $\xi t \ll 1$ the brownian particle experiences very few collisions and the basic assumptions of the Langevin theory are no longer valid.

When the dimensions of the diffusing particle are similar to those of its neighbours, the weakest part of the theory is the markovian approximation whereby the frictional force on the particle at a given time is assumed to be proportional only to its velocity at the same time. The implication of this assumption is that the motion of the particle adjusts itself instantaneously to changes in the surrounding medium. It would obviously be more realistic to suppose that the frictional force acting on a particle reflects the previous history of the system. In other words, we should associate a certain “memory” with the motion of the particle. This can be achieved by introducing a friction coefficient $\xi(t-s)$ that is non-local in time and determines the contribution to the systematic force at time t coming from the velocity at earlier times s . Mathematically this amounts to writing the frictional force as a convolution in time, giving rise to a non-markovian generalisation of the Langevin equation, which we write as

$$m \dot{\mathbf{u}}(t) = -m \int_0^t \xi(t-s) \mathbf{u}(s) ds + \mathbf{R}(t) \quad (7.3.21)$$

The properties of $\mathbf{R}(t)$ expressed by (7.3.2) and (7.3.3) are assumed to be unaltered. If, therefore, we multiply through (7.3.21) by $\mathbf{u}(0)$ and take the thermal average, we arrive at an equation for the velocity autocorrelation function in the form

$$\dot{Z}(t) = - \int_0^t \xi(t-s) Z(s) ds \quad (7.3.22)$$

The quantity $\xi(t)$ is called the *memory function* for the autocorrelation function $Z(t)$. An equation analogous to (7.3.22) can be written down for the autocorrelation function of an arbitrary dynamical variable, A say. Such an expression may be regarded as a generalised Langevin equation in which the random “force” is proportional to that part of $A(t)$ which is uncorrelated with $A(0)$ (cf. (7.3.3)). All that is lost in extending the use of the generalised

Langevin equation to other dynamical variables is a feeling for the physical meaning of the “friction” coefficient and random “force”.

If we take the Laplace transform of (7.3.22), we obtain a simple, algebraic relation between $\tilde{Z}(z)$ and $\tilde{\xi}(z)$:

$$\tilde{Z}(z) = \frac{k_B T/m}{-iz + \tilde{\xi}(z)} \quad (7.3.23)$$

On replacing the frequency-dependent friction coefficient in (7.3.23) by a constant, ξ , and inverting the transform, we recover the exponential form of $Z(t)$ given by (7.3.20); this amounts to choosing a purely local (markovian) memory function, $\xi(t) = \xi\delta(t)$, which leads back to the original Langevin equation (7.3.1). Similarly, the Enskog approximation (7.2.20) corresponds to taking $\xi(t) = (3/2\Gamma_E)\delta(t)$. Equation (7.3.22) is exact, however, since it acts as a definition of the unknown function $\xi(t)$. What is lacking at this stage is any statistical-mechanical definition of either $\mathbf{R}(t)$ or $\xi(t)$, nor is it obvious that $\xi(t)$ is a simpler object to understand than $Z(t)$ itself; if it were not, (7.3.22) would be of little value. The interpretation of the generalised Langevin equation and the memory-function equation in terms of statistical mechanics is described in detail in Chapter 9. Here it is sufficient to say that $\xi(t)$ is expected to decay much faster than $Z(t)$. If this is so, it suggests that a phenomenological model of a complicated dynamical process can be devised by postulating a rather simple form for the appropriate memory function that satisfies, in particular, the low-order sum rules on the autocorrelation function. For example, to describe the diffusion process, we could suppose that the memory function decays exponentially¹⁰ with a characteristic time τ :

$$\xi(t) = \xi(0) \exp(-|t|/\tau) \quad (7.3.24)$$

If we differentiate (7.3.22) with respect to time, set $t = 0$ and use (7.2.9), we find that

$$\dot{\xi}(0) = -\frac{\ddot{Z}(0)}{Z(0)} = \Omega_0^2 \quad (7.3.25)$$

Then, by taking the Laplace transform of (7.3.24) and substituting the result in (7.3.23), we obtain the expression

$$\tilde{Z}(z) = \frac{k_B T/m}{-iz + \frac{\Omega_0^2}{-iz + \tau^{-1}}} \quad (7.3.26)$$

It follows from (7.2.7) that the diffusion coefficient is

$$D = \tilde{Z}(0) = \frac{k_B T}{m\Omega_0^2\tau} \quad (7.3.27)$$

and inverse Laplace transformation of (7.3.26) shows that the velocity autocorrelation function is given by

$$Z(t) = \left(\frac{k_B T/m}{\alpha_+ - \alpha_-} \right) [\alpha_+ \exp(-\alpha_-|t|) - \alpha_- \exp(-\alpha_+|t|)] \quad (7.3.28)$$

where α_+, α_- are the two poles of $\tilde{Z}(z = i\alpha)$:

$$\alpha_{\pm} = \frac{1}{2\tau} [1 \mp (1 - 4\Omega_0^2 \tau^2)^{1/2}] \quad (7.3.29)$$

If $\tau < 1/2\Omega_0$, the poles are real and positive and $Z(t)$ decays monotonically with the correct curvature (Ω_0^2) at the origin. On the other hand, if $\tau > 1/2\Omega_0$, which from (7.3.27) is equivalent to the condition

$$\frac{mD\Omega_0}{k_B T} < 2 \quad (7.3.30)$$

then the poles are a complex-conjugate pair and the velocity autocorrelation function behaves as

$$Z(t) = \left(\frac{k_B T}{m} \right) \exp(-|t|/2\tau) [\cos \Omega_1 |t| + (1/2\Omega_1 \tau) \sin \Omega_1 |t|] \quad (7.3.31)$$

where $\Omega_1^2 = \Omega_0^2 - 1/4\tau^2$. The function defined by (7.3.31) exhibits a negative region at intermediate times, in qualitative agreement with simulation results on simple liquids at low temperatures and high densities (see Figure 7.1), where the condition (7.3.30) is indeed well satisfied. The argument that leads to (7.3.28) is nonetheless inadequate in certain respects. First, it provides no prescription for the relaxation time τ , though the value of τ can be derived from (7.3.27) if D is known. Secondly, use of the simple memory function (7.3.24) yields a spectrum $Z(\omega)$ for which the even frequency moments beyond the second are all infinite. Both defects can be overcome by postulating a gaussian rather than an exponential memory function and forcing agreement with the fourth frequency moment of $Z(\omega)$, which in turn requires a knowledge of the equilibrium triplet distribution function. However, none of the phenomenological memory-function calculations that use as their basic ingredients only the short-time behaviour of the correlation function are capable of reproducing the observed slow ($\sim t^{-3/2}$) decay at long times ($\Omega_0 t \gg 1$).

7.4 CORRELATIONS IN SPACE AND TIME

A detailed description of the time evolution of spatial correlations in liquids requires the introduction of time-dependent generalisations of the static distribution functions defined in Sections 2.5 and 2.6. The relevant dynamical variable is the microscopic particle density (3.1.2), where account must now be taken of the time-dependence of the particle coordinates \mathbf{r}_i . More generally, we define a microscopic dynamical variable as

$$A(\mathbf{r}, t) = \sum_{i=1}^N a_i(t) \delta[\mathbf{r} - \mathbf{r}_i(t)] \quad (7.4.1)$$

where a_i is some physical quantity such as the mass, velocity or energy of particle i . The spatial Fourier components of $A(\mathbf{r}, t)$ are

$$A_{\mathbf{k}}(t) = \int A(\mathbf{r}, t) \exp(-i\mathbf{k} \cdot \mathbf{r}) d\mathbf{r} = \sum_{i=1}^N a_i(t) \exp[-i\mathbf{k} \cdot \mathbf{r}_i(t)] \quad (7.4.2)$$

A microscopic dynamical variable is said to be *conserved* if it satisfies a continuity equation of the form

$$\frac{\partial A(\mathbf{r}, t)}{\partial t} + \nabla \cdot \mathbf{j}^A(\mathbf{r}, t) = 0 \quad (7.4.3)$$

where \mathbf{j}^A is the *current* associated with the variable A . Equation (7.4.3) is a local expression of the fact that $\int A(\mathbf{r}, t) d\mathbf{r} = \sum_i a_i(t)$ is independent of time; the corresponding equation for the Fourier components of A is

$$\frac{\partial A_{\mathbf{k}}(t)}{\partial t} + i\mathbf{k} \cdot \mathbf{j}_{\mathbf{k}}^A(t) = 0 \quad (7.4.4)$$

which shows that spontaneous fluctuations in a conserved variable decay very slowly at long wavelengths.

The time-dependent, microscopic particle density

$$\rho(\mathbf{r}, t) = \sum_{i=1}^N \delta[\mathbf{r} - \mathbf{r}_i(t)] \quad (7.4.5)$$

corresponds to the case when $a_i = 1$ and is a particularly important example of a conserved local variable. The associated particle current is

$$\mathbf{j}(\mathbf{r}, t) = \sum_{i=1}^N \mathbf{u}_i(t) \delta[\mathbf{r} - \mathbf{r}_i(t)] \quad (7.4.6)$$

with Fourier components

$$\mathbf{j}_{\mathbf{k}}(t) = \sum_{i=1}^N \mathbf{u}_i(t) \exp[-i\mathbf{k} \cdot \mathbf{r}_i(t)] \quad (7.4.7)$$

where \mathbf{u}_i is the velocity of particle i . Each Fourier component may be separated into longitudinal (l) and transverse (t) parts, the two parts being parallel and perpendicular, respectively, to the wavevector \mathbf{k} . The longitudinal component, $\mathbf{j}_{\mathbf{k}l}$, is related to the microscopic density via the continuity equation (7.4.4).

The time-correlation function of two space-dependent dynamical variables is defined as in (7.1.2) or (7.1.3) but is now, in general, non-local in space:

$$C_{AB}(\mathbf{r}', \mathbf{r}''; t', t'') = \langle A(\mathbf{r}', t') B^*(\mathbf{r}'', t'') \rangle \quad (7.4.8)$$

while the correlation functions of the Fourier components are defined as

$$C_{AB}(\mathbf{k}', \mathbf{k}''; t', t'') = \langle A_{\mathbf{k}'}(t') B_{\mathbf{k}''}^*(t'') \rangle = \langle A_{\mathbf{k}'}(t') B_{-\mathbf{k}''}(t'') \rangle \quad (7.4.9)$$

These correlation functions have all the properties given in Section 7.1, in particular those associated with stationarity. In addition, for homogeneous liquids, translational invariance in space means that the correlation function (7.4.8) depends only on the relative coordinates $\mathbf{r} = \mathbf{r}' - \mathbf{r}''$. Thus

$$C_{AB}(\mathbf{r}', \mathbf{r}''; t', t'') = C_{AB}(\mathbf{r}' - \mathbf{r}'', t' - t'') \quad (7.4.10)$$

Translational invariance also implies that correlations between Fourier components $A_{\mathbf{k}'}(t')$ and $B_{\mathbf{k}''}(t'')$ are non-zero only if $\mathbf{k}' = \mathbf{k}''$, i.e.

$$C_{AB}(\mathbf{k}', \mathbf{k}''; t) = \langle A_{\mathbf{k}'}(t) B_{-\mathbf{k}''} \rangle \delta_{\mathbf{k}', \mathbf{k}''} \quad (7.4.11)$$

Clearly $C_{AB}(\mathbf{k}, t)$ is the spatial Fourier transform of $C_{AB}(\mathbf{r}, t)$:

$$C_{AB}(\mathbf{k}, t) = \int C_{AB}(\mathbf{r}, t) \exp(-i\mathbf{k} \cdot \mathbf{r}) d\mathbf{r} \quad (7.4.12)$$

If the fluid is also isotropic, the correlation functions (7.4.10) and (7.4.11) share with their static counterparts the property that they are functions, respectively, of the scalar quantities r and k . The frequency moments of the power spectrum of an autocorrelation function $C_{AA}(k, t)$ are again given by (7.1.24), but are now wavenumber-dependent. The continuity equation for conserved variables leads to simple expressions for the second frequency moments, called f -sum rules. From (7.1.24) and (7.4.4) it follows that

$$\langle \omega^2 \rangle_{AA} = \langle \dot{A}_{\mathbf{k}} \dot{A}_{-\mathbf{k}} \rangle = k^2 \langle |\mathbf{j}_{\mathbf{k}}^A|^2 \rangle \quad (7.4.13)$$

The memory function, M_{AA} say, associated with a space-dependent autocorrelation function C_{AA} must allow for non-local effects in space as well as in time. The memory-function equation satisfied by C_{AA} is therefore written as

$$\dot{C}_{AA}(\mathbf{r}, t) + \int_0^t dt' \int d\mathbf{r}' M_{AA}(\mathbf{r} - \mathbf{r}', t - t') C_{AA}(\mathbf{r}', t') = 0 \quad (7.4.14)$$

or, by exploiting the convolution theorem:

$$\dot{C}_{AA}(\mathbf{k}, t) + \int_0^t dt' M_{AA}(\mathbf{k}, t - t') C_{AA}(\mathbf{k}, t') = 0 \quad (7.4.15)$$

We now focus specifically on the way in which time-dependent correlations in the microscopic density and particle current are described. A convenient starting point is provided by the space and time-dependent distribution function introduced by van Hove. The van

Hove function for a uniform fluid is defined as

$$G(\mathbf{r}, t) = \left\langle \frac{1}{N} \sum_{i=1}^N \sum_{j=1}^N \int \delta[\mathbf{r} - \mathbf{r}_j(t) + \mathbf{r}_i(0)] \right\rangle \quad (7.4.16)$$

which can be rewritten successively as

$$\begin{aligned} G(\mathbf{r}, t) &= \left\langle \frac{1}{N} \int \sum_{i=1}^N \sum_{j=1}^N \delta[\mathbf{r}' + \mathbf{r} - \mathbf{r}_j(t)] \delta[\mathbf{r}' - \mathbf{r}_i(0)] d\mathbf{r}' \right\rangle \\ &= \left\langle \frac{1}{N} \int \rho(\mathbf{r}' + \mathbf{r}, t) \rho(\mathbf{r}', 0) d\mathbf{r}' \right\rangle = \frac{1}{\rho} \langle \rho(\mathbf{r}, t) \rho(\mathbf{0}, 0) \rangle \end{aligned} \quad (7.4.17)$$

The van Hove function therefore has the meaning of a density–density time-correlation function which for $t = 0$ is closely related to the static correlation function (3.1.6). It separates naturally into two terms, usually called the “self” (s) and “distinct” (d) parts, i.e.

$$G(\mathbf{r}, t) = G_s(\mathbf{r}, t) + G_d(\mathbf{r}, t) \quad (7.4.18)$$

where

$$G_s(\mathbf{r}, t) = \left\langle \frac{1}{N} \sum_{i=1}^N \delta[\mathbf{r} - \mathbf{r}_i(t) + \mathbf{r}_i(0)] \right\rangle \quad (7.4.19a)$$

$$G_d(\mathbf{r}, t) = \left\langle \frac{1}{N} \sum_{i=1}^N \sum_{j \neq i}^N \delta[\mathbf{r} - \mathbf{r}_j(t) + \mathbf{r}_i(0)] \right\rangle \quad (7.4.19b)$$

Hence $G_s(\mathbf{r}, 0) = \delta(\mathbf{r})$ and (from (2.5.15)) $G_d(\mathbf{r}, 0) = \rho g(\mathbf{r})$. The physical interpretation of the van Hove function is that $G(\mathbf{r}, t) d\mathbf{r}$ is the number of particles j in a region $d\mathbf{r}$ around a point \mathbf{r} at time t given that there was a particle i at the origin at time $t = 0$; the division into self and distinct parts corresponds to the possibilities that i and j may be the same particle or different ones. As t increases, G_s broadens into a bell-shaped curve and the peaks in G_d gradually disappear. In the limit $t \rightarrow \infty$, both functions become independent of r , with $G_s(\mathbf{r}, t \rightarrow \infty) \sim 1/V$ and $G_d(\mathbf{r}, t \rightarrow \infty) \sim \rho$; the behaviour at large r is the same as that at large t .

Rather than considering the density–density correlation in real space, it is often more convenient to focus attention on the correlation function of the Fourier components $\rho_{\mathbf{k}}$:

$$F(\mathbf{k}, t) = \frac{1}{N} \langle \rho_{\mathbf{k}}(t) \rho_{-\mathbf{k}} \rangle \quad (7.4.20)$$

The function $F(\mathbf{k}, t)$ is called the *intermediate scattering function*; as we shall see later, $F(\mathbf{k}, t)$ is closely related to the cross-section measured in an inelastic scattering experiment. By following steps almost identical to those that establish the relation (4.1.3) between the static structure factor and the pair distribution function it is easy to show that

$F(\mathbf{k}, t)$ is the spatial Fourier transform of the van Hove function, i.e.

$$F(\mathbf{k}, t) = \int G(\mathbf{r}, t) \exp(-i\mathbf{k} \cdot \mathbf{r}) d\mathbf{r} \quad (7.4.21)$$

The power spectrum of the intermediate scattering function:

$$S(\mathbf{k}, \omega) = \frac{1}{2\pi} \int_{-\infty}^{\infty} F(\mathbf{k}, t) \exp(i\omega t) dt \quad (7.4.22)$$

is called the *dynamic structure factor*. Combination of (4.1.1) and (7.1.24) shows that the static and dynamic structure factors are related by

$$\int_{-\infty}^{\infty} S(\mathbf{k}, \omega) d\omega = F(\mathbf{k}, 0) = S(\mathbf{k}) \quad (7.4.23)$$

The physical significance of this sum rule will become clear in the next section. Finally, we define the autocorrelation function of the Fourier components (7.4.7) of the current associated with the microscopic density. Because $\mathbf{j}_{\mathbf{k}}$ is a vector, the corresponding correlation function is a second-rank tensor, but rotational invariance implies that the longitudinal and transverse projections of the particle current are uncorrelated if the fluid is isotropic. When that is so, the correlation-function tensor has only two independent components and may therefore be written in the form

$$\begin{aligned} C_{\alpha\beta}(\mathbf{k}, t) &= \frac{k^2}{N} \langle j_{\mathbf{k}}^{\alpha}(t) j_{-\mathbf{k}}^{\beta} \rangle \\ &= \hat{k}_{\alpha} \hat{k}_{\beta} C_l(k, t) + (\delta_{\alpha\beta} - \hat{k}_{\alpha} \hat{k}_{\beta}) C_t(k, t) \end{aligned} \quad (7.4.24)$$

where $\alpha, \beta = x, y$ or z and $\hat{k}_{\alpha}, \hat{k}_{\beta}$ are cartesian components of the unit vector $\hat{\mathbf{k}} = \mathbf{k}/k$. If the z -axis is chosen parallel to \mathbf{k} , the longitudinal and transverse current autocorrelation functions are given by

$$C_l(k, t) = \frac{k^2}{N} \langle j_{\mathbf{k}}^z(t) j_{-\mathbf{k}}^z \rangle \quad (7.4.25a)$$

$$C_t(k, t) = \frac{k^2}{N} \langle j_{\mathbf{k}}^x(t) j_{-\mathbf{k}}^x \rangle \quad (7.4.25b)$$

The continuity equation (7.4.4) (with $A = \rho$) and the general property (7.1.8) imply that the density and longitudinal-current correlation functions are not independent, since

$$C_l(k, t) = \frac{1}{N} \langle \dot{\rho}_{\mathbf{k}}(t) \dot{\rho}_{\mathbf{k}} \rangle = -\frac{d^2}{dt^2} F(k, t) \quad (7.4.26)$$

Written in terms of Laplace transforms, (7.4.26) becomes

$$\tilde{C}_l(k, z) = z^2 \tilde{F}(k, z) - izS(k) \quad (7.4.27)$$

or, on taking the real part and making use of (7.1.19):

$$C_l(k, \omega) = \omega^2 S(k, \omega) \quad (7.4.28)$$

The function $C_l(k, \omega)$ describes the spectrum of longitudinal-current fluctuations in the liquid. Fluctuations in density are therefore intimately related to fluctuations in longitudinal current, but are independent of the transverse current.

In classical statistical mechanics, positions and velocities at a given instant are uncorrelated. Thus the definitions of the current autocorrelation functions show that their zero-time values are the same and given by

$$C_{l,t}(k, 0) = k^2 \left(\frac{k_B T}{m} \right) = \omega_0^2, \quad \text{say} \quad (7.4.29)$$

From (7.4.26) and the general f -sum rule (7.4.13) it follows that the second frequency moment of the dynamic structure factor is given by

$$\langle \omega^2 \rangle_{\rho\rho} = \int_{-\infty}^{\infty} \omega^2 S(k, \omega) d\omega = -\ddot{F}(k, 0) = \omega_0^2 \quad (7.4.30)$$

Since the f -sum rule is a consequence of the continuity equation, the second moment is purely kinetic in origin, but higher-order moments depend on the interparticle potential. If the potential is continuous, the general results contained in (7.1.23) and (7.1.24) imply that the odd frequency moments of $S(k, \omega)$ are all zero and the fourth moment is equal, by virtue of the relation (7.4.28), to the second moment of $C_l(k, \omega)$. We may therefore base a calculation of the fourth moment on the short-time expansion of $C_l(k, t)$, which we write as

$$C_l(k, t) = \omega_0^2 \left(1 - \omega_{ll}^2 \frac{t^2}{2!} + \dots \right) \quad (7.4.31)$$

Equations (7.1.8) and (7.4.31) show that

$$\omega_0^2 \omega_{ll}^2 = - \frac{d^2}{dt^2} C_l(k, t) \Big|_{t=0} = \frac{d^4}{dt^4} F(k, t) \Big|_{t=0} = \frac{1}{N} \langle \ddot{\rho}_{\mathbf{k}} \ddot{\rho}_{-\mathbf{k}} \rangle \quad (7.4.32)$$

If again we take the z -axis along the direction of \mathbf{k} and make the substitution $\dot{u}_{iz} = -(1/m)(\partial V_N / \partial z_i)$, (7.4.32) becomes

$$\omega_0^2 \omega_{ll}^2 = k^4 \langle u_{iz}^4 \rangle + k^2 \left(\frac{k_B T}{m} \right) \left\langle \sum_{i=1}^N \sum_{j=1}^N \frac{\partial V_N}{\partial z_i} \frac{\partial V_N}{\partial z_j} \exp[ik(z_i - z_j)] \right\rangle \quad (7.4.33)$$

For a maxwellian distribution of velocities, $\langle u_{iz}^4 \rangle = 3\langle u_{iz}^2 \rangle^2$, and the statistical average in (7.4.33) can be simplified with the help of Yvon's theorem (7.2.11) to give

$$\begin{aligned} & \left\langle \sum_{i=1}^N \sum_{j=1}^N \frac{\partial V_N}{\partial z_i} \frac{\partial V_N}{\partial z_j} \exp[ik(z_i - z_j)] \right\rangle \\ &= k_B T \left\langle N \frac{\partial^2 V_N}{\partial z_1^2} + N(N-1) \frac{\partial^2 V_N}{\partial z_1 \partial z_2} \exp[ik(z_1 - z_2)] \right\rangle \end{aligned} \quad (7.4.34)$$

where 1 and 2 are the labels of two, arbitrarily chosen particles. Hence, if V_N is a sum of pair terms:

$$\omega_{1l}^2 = 3\omega_0^2 + \frac{\rho}{m} \int (1 - \cos kz) \frac{\partial^2 v(r)}{\partial z^2} g(r) \, \mathbf{dr} \quad (7.4.35)$$

where $v(r)$ is the pair potential. At large k , the kinetic contribution dominates, corresponding to free-particle behaviour. From (7.4.28) we see that ω_{1l}^2 is related to the second and fourth frequency moments of $S(k, \omega)$ by $\omega_{1l}^2 = \langle \omega^4 \rangle_{\rho\rho} / \langle \omega^2 \rangle_{\rho\rho}$.

A similar calculation can be made for the transverse current. The short-time expansion of the correlation function is now

$$C_t(k, t) = \omega_0^2 \left(1 - \omega_{1t}^2 \frac{t^2}{2!} + \dots \right) \quad (7.4.36)$$

with

$$\omega_0^2 \omega_{1t}^2 = - \frac{d^2}{dt^2} C_t(k, t) \Big|_{t=0} \quad (7.4.37)$$

By pursuing the methods already used in the longitudinal case we find that the analogue of (7.4.35) is

$$\omega_{1t}^2 = \omega_0^2 + \frac{\rho}{m} \int (1 - \cos kz) \frac{\partial^2 v(r)}{\partial x^2} g(r) \, \mathbf{dr} \quad (7.4.38)$$

Higher-order moments of $C_l(k, \omega)$ and $C_t(k, \omega)$ involve correlations between increasingly large numbers of particles and rapidly become very tedious to evaluate.

7.5 INELASTIC NEUTRON SCATTERING

We now show how the Fourier transforms of the van Hove functions $G(\mathbf{r}, t)$ and $G_s(\mathbf{r}, t)$ are related to measurements of the inelastic scattering of slow (or "thermal") neutrons. To do so, we require a generalisation of the calculation of Section 4.1 that allows for the exchange of energy between the neutrons and the target.¹¹ Neutrons are particularly useful as probes of the microscopic dynamics of liquids because their momentum $\hbar\mathbf{k}$ and energy $E = \hbar\omega$ are related by $E = \hbar^2 k^2 / 2m$, where m is the neutron mass. It follows that when E is of order $k_B T$, and therefore comparable with the thermal energies of particles in the

liquid, the wavelength $\lambda = 2\pi/k$ associated with the neutron is approximately 2 \AA , which is similar to the distance between neighbouring particles.

In a typical scattering event a neutron of momentum $\hbar\mathbf{k}_1$ and energy $\hbar\omega_1$ is scattered into a solid angle $d\Omega$. Let the momentum and energy of the neutron after the event be $\hbar\mathbf{k}_2$ and $\hbar\omega_2$ and let the momentum and energy transfer from neutron to sample be $\hbar\mathbf{k}$ and $\hbar\omega$. The dynamical conservation laws require that

$$\hbar\omega = E_2 - E_1 \equiv \hbar\omega_{12} \quad (7.5.1)$$

$$\hbar\mathbf{k} = \hbar\mathbf{k}_1 - \hbar\mathbf{k}_2 \quad (7.5.2)$$

where E_1 and E_2 are the initial and final energies of the sample. The probability per unit time, W_{12} , for the transition $|1, \mathbf{k}_1\rangle \rightarrow |2, \mathbf{k}_2\rangle$, where $|1\rangle$ and $|2\rangle$ denote the initial and final states of the sample, is given by Fermi's "golden rule":

$$W_{12} = \frac{2\pi}{\hbar} |\langle 1, \mathbf{k}_1 | \mathcal{V} | 2, \mathbf{k}_2 \rangle|^2 \delta(\hbar\omega - \hbar\omega_{12}) \quad (7.5.3)$$

where \mathcal{V} represents the perturbation, i.e. the interaction between the neutron and the atomic nuclei. For the sake of simplicity we have ignored the spin state of the neutron. The partial differential cross-section for scattering into the solid angle $d\Omega$ in a range of energy transfer $\hbar d\omega$ is calculated by averaging W_{12} over all initial states $|1\rangle$ with their statistical weights $P_1 \propto \exp(-\beta E_1)$, summing over all final states $|2\rangle$ allowed by energy conservation, multiplying by the density of final states of the neutron, namely

$$d\mathbf{k}_2 / (2\pi)^3 = k_2^2 dk_2 d\Omega / (2\pi)^3 = (m/\hbar^2) \hbar k_2 d\omega d\Omega / (2\pi)^3 \quad (7.5.4)$$

and dividing by the flux $\hbar k_1 / m$ of incident neutrons, with the final result having the form

$$\frac{d^2\sigma}{d\Omega d\omega} = \frac{k_2}{k_1} \left(\frac{m}{2\pi\hbar^2} \right)^2 \sum_{\{1\}} \sum_{\{2\}} P_1 |\langle 1, \mathbf{k}_1 | \mathcal{V} | 2, \mathbf{k}_2 \rangle|^2 \delta(\omega - \omega_{12}) \quad (7.5.5)$$

The differential cross-section (4.1.9) is obtained by integrating over all energy transfers:

$$\frac{d\sigma}{d\Omega} = \int \frac{d\sigma}{d\Omega d\omega} d\omega \quad (7.5.6)$$

The structure and dynamics of the liquid enter the calculation through the interaction of the neutron with the atomic nuclei. We assume again that \mathcal{V} is given by the sum (4.1.12) of δ -function pseudopotentials between a neutron located at \mathbf{r} and nuclei at positions \mathbf{r}_i . If the initial and final states of the neutron are taken as plane-wave states of the form (4.1.6), the matrix element in (7.5.5) may be rewritten as

$$\langle 1, \mathbf{k}_1 | \mathcal{V} | 2, \mathbf{k}_2 \rangle = \frac{2\pi\hbar^2}{m} \sum_{i=1}^N \langle 1 | b_i \exp(-i\mathbf{k} \cdot \mathbf{r}_i) | 2 \rangle \quad (7.5.7)$$

where $\hbar \mathbf{k}$ is the momentum transfer already defined and b_i is the scattering length of nucleus i .

Consider first the case when all nuclei in the sample have the same scattering length. By incorporating (7.5.7) into (7.5.5), exploiting the definition (4.1.2) and introducing the integral representation of the δ -function, we obtain an expression for the cross-section in terms of the Fourier components of the microscopic density:

$$\begin{aligned} \frac{d^2\sigma}{d\Omega d\omega} &= b^2 \left(\frac{k_2}{k_1} \right) \sum_{\{1\}} \sum_{\{2\}} P_1 |\langle 1 | \rho_{\mathbf{k}} | 2 \rangle|^2 \delta(\omega - \omega_{12}) \\ &= b^2 \left(\frac{k_2}{k_1} \right) \sum_{\{1\}} \sum_{\{2\}} P_1 \frac{1}{2\pi} \int_{-\infty}^{\infty} |\langle 1 | \rho_{\mathbf{k}} | 2 \rangle|^2 \exp[i(\omega - \omega_{12})t] dt \end{aligned} \quad (7.5.8)$$

Equation (7.5.8) can be simplified by recognising that

$$\begin{aligned} &\exp(-i\omega_{12}t) |\langle 1 | \rho_{\mathbf{k}} | 2 \rangle|^2 \\ &= \exp(-iE_2t/\hbar) \exp(iE_1t/\hbar) \langle 1 | \rho_{\mathbf{k}} | 2 \rangle \langle 2 | \rho_{-\mathbf{k}} | 1 \rangle \\ &= \langle 1 | \exp(iE_1t/\hbar) \rho_{\mathbf{k}} \exp(-iE_2t/\hbar) | 2 \rangle \langle 2 | \rho_{-\mathbf{k}} | 1 \rangle \\ &= \langle 1 | \exp(i\mathcal{H}t/\hbar) \rho_{\mathbf{k}} \exp(-i\mathcal{H}t/\hbar) | 2 \rangle \langle 2 | \rho_{-\mathbf{k}} | 1 \rangle \\ &= \langle 1 | \rho_{\mathbf{k}}(t) | 2 \rangle \langle 2 | \rho_{-\mathbf{k}} | 1 \rangle \end{aligned} \quad (7.5.9)$$

where \mathcal{H} is the hamiltonian of the sample.

It remains only to sum over the initial states of the sample, which is equivalent to taking an ensemble average, and over the final states, which is done by exploiting the closure property, $\sum_j |j\rangle \langle j| = 1$, of a complete set of quantum states $|j\rangle$. The final result for the cross-section is

$$\begin{aligned} \frac{d^2\sigma}{d\Omega d\omega} &= b^2 \left(\frac{k_2}{k_1} \right) \frac{1}{2\pi} \int_{-\infty}^{\infty} \langle \rho_{\mathbf{k}}(t) \rho_{-\mathbf{k}} \rangle \exp(i\omega t) dt \\ &= Nb^2 \left(\frac{k_2}{k_1} \right) S(\mathbf{k}, \omega) \end{aligned} \quad (7.5.10)$$

where $S(\mathbf{k}, \omega)$ is the dynamic structure factor defined by (7.4.22). Equation (7.5.10) shows that a measurement of the experimental cross-section as a function of \mathbf{k} and ω is equivalent, at least in principle, to a determination of the van Hove correlation function $G(\mathbf{r}, t)$. The connection with the elastic cross-section is made via (7.5.6); comparison of (4.1.23) with (7.5.10), taken for the case $k_1 = k_2$, shows that (7.5.6) provides the physical content of the so-called “elastic” sum rule (7.4.23).

By analogy with (7.4.21) and (7.4.22), it is customary to define a *self dynamic structure factor* $S_s(\mathbf{k}, \omega)$ as the double Fourier transform of the self part of the van Hove function, i.e.

$$S_s(\mathbf{k}, \omega) = \frac{1}{2\pi} \int_{-\infty}^{\infty} dt \exp(i\omega t) \int G_s(\mathbf{r}, t) \exp(-i\mathbf{k} \cdot \mathbf{r}) d\mathbf{r} \quad (7.5.11)$$

together with a self intermediate scattering function $F_s(\mathbf{k}, t)$, defined through the transform

$$S_s(\mathbf{k}, \omega) = \frac{1}{2\pi} \int_{-\infty}^{\infty} F_s(\mathbf{k}, t) \exp(i\omega t) dt \quad (7.5.12)$$

with $F_s(\mathbf{k}, 0) = 1$. The self functions are important for the discussion of inelastic scattering in situations where more than one scattering length is involved. As in Section 4.1, the averaging over scattering lengths can be carried out independently of the thermal average over nuclear coordinates. A generalisation of the result in (4.1.21) allows the inelastic cross-section to be written as the sum of incoherent and coherent parts in the form

$$\frac{d^2\sigma}{d\Omega d\omega} = \left(\frac{d^2\sigma}{d\Omega d\omega} \right)_{\text{inc}} + \left(\frac{d^2\sigma}{d\Omega d\omega} \right)_{\text{coh}} \quad (7.5.13)$$

with

$$\begin{aligned} \left(\frac{d^2\sigma}{d\Omega d\omega} \right)_{\text{inc}} &= N b_{\text{inc}}^2 \left(\frac{k_2}{k_1} \right) S_s(\mathbf{k}, \omega) \\ \left(\frac{d^2\sigma}{d\Omega d\omega} \right)_{\text{coh}} &= N b_{\text{coh}}^2 \left(\frac{k_2}{k_1} \right) S(\mathbf{k}, \omega) \end{aligned} \quad (7.5.14)$$

By varying the isotopic composition of the sample, or by using polarised neutrons, it is possible to measure separately the coherent and incoherent cross-sections and thereby, again in principle, to separate G_s and G_d .

For systems with inversion symmetry, which includes all fluids, the dynamic structure factor is invariant under a change of sign of \mathbf{k} . In the classical limit, $S(\mathbf{k}, \omega)$ is also an even function of ω , but a measured cross-section cannot be strictly even with respect to ω ; if that were the case, thermal equilibrium between radiation and sample would never be reached. The principle of detailed balance requires that the cross-sections for the scattering processes $|\mathbf{k}_1, 1\rangle \rightarrow |\mathbf{k}_2, 2\rangle$ and $|\mathbf{k}_2, 2\rangle \rightarrow |\mathbf{k}_1, 1\rangle$ be equal to the ratio of the statistical weights of the states $|1\rangle$ and $|2\rangle$, i.e. $S(\mathbf{k}, \omega)/S(\mathbf{k}, -\omega) = \exp(\beta\hbar\omega)$. Experimental scattering data are therefore frequently reported in the form of a “symmetrised” dynamic structure factor, $\bar{S}(\mathbf{k}, \omega)$, defined as

$$\bar{S}(\mathbf{k}, \omega) = \exp\left(-\frac{1}{2}\beta\hbar\omega\right) S(\mathbf{k}, \omega) \quad (7.5.15)$$

This is an even function of frequency for both classical and quantum systems.

In the limit $\mathbf{r}, t \rightarrow 0$, particles in a fluid move freely at constant velocity. These conditions correspond to the limit $k, \omega \rightarrow \infty$, where $S(k, \omega)$ behaves in the manner appropriate to an ideal gas. The limiting form of $S(k, \omega)$ is easily derived, since positions of different particles are uncorrelated in an ideal gas ($G_d = \rho$); the calculation of $S(k, \omega)$ is therefore equivalent to a calculation of $G_s(r, t)$. The probability that an ideal-gas particle will move a distance r in a time t is equal to the probability, given by the Maxwell distribution (2.1.28), that the particle has a velocity in the range \mathbf{u} to $\mathbf{u} + d\mathbf{u}$, where $\mathbf{u} = \mathbf{r}/t$. Thus

$$G_s(\mathbf{r}, t) = \left(\frac{\beta m}{2\pi t^2} \right)^{3/2} \exp(-\beta m r^2 / 2t^2) \quad (7.5.16)$$

where the form of the pre-exponential factor is determined by the requirement that $\int G_s(\mathbf{r}, t) d\mathbf{r} = 1$. The corresponding result for $S(k, \omega)$ is

$$S(k, \omega) = \left(\frac{\beta m}{2\pi k^2} \right)^{1/2} \exp(-\beta m \omega^2 / 2k^2) \quad (7.5.17)$$

Equation (7.5.17) provides a reasonable fit to data on simple liquids at wavelengths significantly shorter than the spacing between particles, typically for k greater than about 10 \AA^{-1} ; small deviations from the free-particle result can be allowed for by calculating the correction to $S(k, \omega)$ due to a single, binary collision. At longer wavelengths correlations between particles become increasingly important and the ideal-gas model is no longer valid. Very small values of k correspond to the hydrodynamic regime, where thermodynamic equilibrium is brought by frequent collisions between particles; this is the opposite extreme to the free-particle limit represented by (7.5.17).

Inelastic neutron-scattering experiments designed for the study of both single-particle and collective dynamical properties have been carried out for a number of monatomic liquids. These experiments have been complemented by simulations of the Lennard-Jones and hard-sphere fluids and a variety of models of the liquid alkali metals. Most of the interest lies in the behaviour of the dynamic structure factor as a function of k and all the existing experiments and simulations reveal broadly the same features. At reduced wavenumbers $kd \approx 1$ or smaller, where d is the atomic diameter, $S(k, \omega)$ has a sharp peak at zero frequency and two more or less well defined side peaks, one on each side of the central peak. As k increases, the peaks shift to higher frequencies with a dispersion that is approximately linear. We shall see in Chapter 8 that the side peaks observed at long wavelengths correspond to propagating sound waves; they are clearly visible in the results of neutron scattering experiments on liquid caesium, some of which are plotted in Figure 7.5. At shorter wavelengths the sound waves are strongly damped and disappear when $kd \approx 2$, leaving only a central, lorentzian-like peak. The width of the central peak first increases with k , but then shows a marked decrease at wavenumbers close to the peak in the static structure factor (see curve (d) in Figure 7.5). This last effect is called “de Gennes narrowing”; it corresponds to a dramatic slowing down in the decay of the density autocorrelation function $F(k, t)$, which in turn has its origins in the strong spatial correlations existing at these wavelengths. At still larger values of k , the spectrum broadens again, going over finally to its free-particle limit. The behaviour of $S_s(k, \omega)$ is much simpler; this has only a single, central peak, the width of which increases smoothly with k .

Measurements of $S(k, \omega)$ can also be made by the inelastic scattering of light or x-rays. Both techniques measure only the coherent cross-section and cannot be used as probes of the single-particle motion, though this also simplifies analysis of the experimental data. In thermal-neutron scattering experiments the smallest momentum transfers correspond to wavelengths of the order of the nearest-neighbour spacing, but in light scattering the wavelengths involved are much larger, of order 5000 \AA . It is therefore possible to calculate the spectral distribution of scattered light from the macroscopic equations of hydrodynamics, which are discussed in detail in Chapter 8. Light is scattered by fluctuations in the local dielectric constant of the sample, but for most liquids these are directly proportional to the fluctuations in density and the measured spectrum is proportional to $S(k, \omega)$. Inelastic x-ray

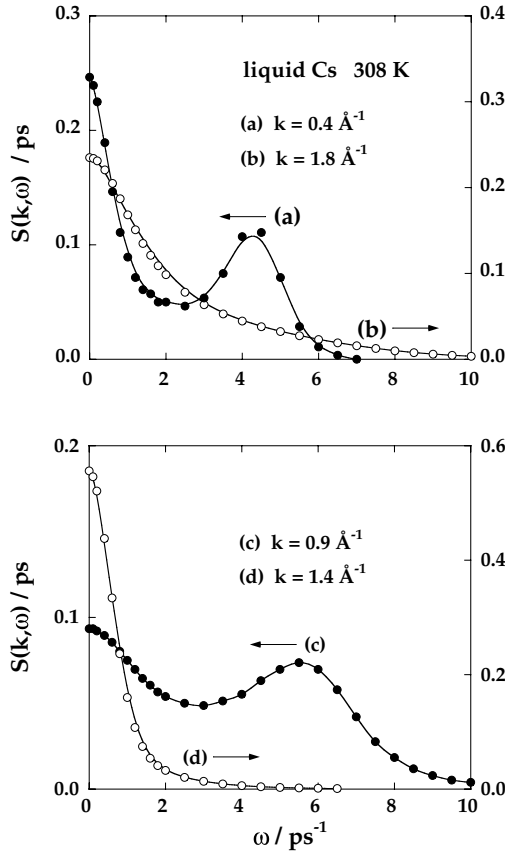


FIG. 7.5. Results from inelastic neutron-scattering experiments for the dynamic structure factor of liquid caesium near the normal melting temperature. The spectra have been normalised to unit area and only the energy-gain side is shown. The main peak in $S(k)$ is at $k \approx 1.4 \text{ \AA}^{-1}$. After Bodensteiner *et al.*¹²

scattering experiments have become feasible only with the development of high-resolution synchrotron radiation facilities. The momentum-energy relation for the neutron means that there exists a maximum possible energy transfer for a given momentum transfer, with a value determined by the velocity of the incoming neutron. This constraint does not apply in the case of x-ray scattering, thereby allowing measurements of $S(k, \omega)$ to be made over a wider range of the frequency-wavenumber plane.

7.6 LINEAR-RESPONSE THEORY

We turn now to an investigation of the behaviour of a system under the perturbing influence of an external field to which the system is weakly coupled. As we shall see, the response of the system can be described entirely in terms of time-correlation functions characteristic of

the system at equilibrium, i.e. in the *absence* of the field; the expression already obtained for the inelastic neutron-scattering cross-section in terms of the dynamic structure factor is an example of this relationship. The derivation of the general result requires only a straightforward calculation of the change produced in a dynamical variable B by an applied space and time-dependent field \mathcal{F} conjugate to a variable A . Both A and B are to be regarded in general as functions of the coordinates and momenta of all particles in the system. The mean value of B in the equilibrium state is assumed to be zero.

The hamiltonian of the system in the presence of the external field is

$$\mathcal{H} = \mathcal{H}_0 + \mathcal{H}'(t) \quad (7.6.1)$$

where \mathcal{H}_0 characterises the unperturbed system and $\mathcal{H}'(t)$ represents the perturbation:

$$\mathcal{H}'(t) = - \int A(\mathbf{r}) \mathcal{F}(\mathbf{r}, t) d\mathbf{r} \quad (7.6.2)$$

The external field can always be treated as a superposition of monochromatic plane waves. Since we are interested in the linear response of the system, it is sufficient to consider a single plane wave:

$$\mathcal{F}(\mathbf{r}, t) = \frac{1}{V} \mathcal{F}_{\mathbf{k}} \exp[i(\mathbf{k} \cdot \mathbf{r} - \omega t)] \quad (7.6.3)$$

in which case (7.6.2) becomes

$$\mathcal{H}'(t) = -A_{-\mathbf{k}} \mathcal{F}_{\mathbf{k}} \exp(-i\omega t) \quad (7.6.4)$$

As a further simplification we shall temporarily suppose that the external field is spatially homogeneous and ignore the dependence on \mathbf{k} ; the latter is trivially reintroduced at a later stage. We also assume that the system was in thermal equilibrium in the infinite past ($t \rightarrow -\infty$). Then $\mathcal{H}'(t)$ may be written as

$$\mathcal{H}'(t) = -A\mathcal{F}(t) = -A\mathcal{F}_0 \exp[-i(\omega + i\varepsilon)t] \quad (7.6.5)$$

where A and B are now taken to be real. The factor $\exp(\varepsilon t)$ ($\varepsilon > 0$) is included to ensure that $\mathcal{F} \rightarrow 0$ as $t \rightarrow -\infty$; the limit $\varepsilon \rightarrow 0$ is taken at the end of the calculation. The time evolution of the phase-space probability density $f^{[N]}(t) \equiv f^{[N]}(\mathbf{r}^N, \mathbf{p}^N; t)$ in the presence of the perturbation is determined by the Liouville equation (2.1.9). Thus

$$\begin{aligned} \frac{\partial f^{[N]}(t)}{\partial t} &= -i\mathcal{L}f^{[N]}(t) = \{\mathcal{H}_0 + \mathcal{H}', f^{[N]}(t)\} \\ &= -i\mathcal{L}_0 f^{[N]}(t) - \{A, f^{[N]}(t)\}\mathcal{F}(t) \end{aligned} \quad (7.6.6)$$

where \mathcal{L}_0 is the Liouville operator corresponding to the unperturbed hamiltonian. Equation (7.6.6) must be solved subject to the initial condition that $f^{[N]}(-\infty) = f_0^{[N]}$.

We are interested only in the response to a weak external field. We may therefore write the probability density as

$$f^{[N]}(t) = f_0^{[N]} + \Delta f^{[N]}(t) \quad (7.6.7)$$

and linearise (7.6.6) in the form

$$\frac{\partial \Delta f^{[N]}(t)}{\partial t} = -i\mathcal{L}_0 \Delta f^{[N]}(t) - \{A, f_0^{[N]}\} \mathcal{F}(t) \quad (7.6.8)$$

The solution to (7.6.8) is

$$\Delta f^{[N]}(t) = - \int_{-\infty}^t \exp[-i(t-s)\mathcal{L}_0] \{A, f_0^{[N]}\} \mathcal{F}(s) ds \quad (7.6.9)$$

That this is the solution for all t is easily checked by differentiation, since it is obviously correct for $t = -\infty$. In the canonical ensemble, $f_0^{[N]} \propto \exp(-\beta\mathcal{H}_0)$, and the Poisson bracket appearing in (7.6.9) can be re-expressed as

$$\begin{aligned} \{A, f_0^{[N]}\} &= \sum_{i=1}^N \left(\frac{\partial A}{\partial \mathbf{r}_i} \cdot \frac{\partial f_0^{[N]}}{\partial \mathbf{p}_i} - \frac{\partial A}{\partial \mathbf{p}_i} \cdot \frac{\partial f_0^{[N]}}{\partial \mathbf{r}_i} \right) \\ &= -\beta \sum_{i=1}^N \left(\frac{\partial A}{\partial \mathbf{r}_i} \cdot \frac{\partial \mathcal{H}_0}{\partial \mathbf{p}_i} - \frac{\partial A}{\partial \mathbf{p}_i} \cdot \frac{\partial \mathcal{H}_0}{\partial \mathbf{r}_i} \right) f_0^{[N]} \\ &= -\beta(i\mathcal{L}_0 A) f_0^{[N]} = -\beta \dot{A} f_0^{[N]} \end{aligned} \quad (7.6.10)$$

The mean change in the variable $B(\mathbf{r}^N, \mathbf{p}^N)$ arising from the change in the distribution function is therefore

$$\begin{aligned} \langle \Delta B(t) \rangle &= \iint B(\mathbf{r}^N, \mathbf{p}^N) \Delta f^{[N]}(t) d\mathbf{r}^N d\mathbf{p}^N \\ &= \beta \int_{-\infty}^t \mathcal{F}(s) ds \iint f_0^{[N]} B \exp[-i(t-s)\mathcal{L}_0] \dot{A} d\mathbf{r}^N d\mathbf{p}^N \\ &= \beta \int_{-\infty}^t \mathcal{F}(s) ds \iint f_0^{[N]} \dot{A} \exp[i(t-s)\mathcal{L}_0] B d\mathbf{r}^N d\mathbf{p}^N \end{aligned} \quad (7.6.11)$$

where we have used a result contained in (7.1.28). The response of the system can therefore be written in the form

$$\langle \Delta B(t) \rangle = \int_{-\infty}^t \Phi_{BA}(t-s) \mathcal{F}(s) ds \quad (7.6.12)$$

in terms of an *after-effect function* $\Phi_{BA}(t)$, defined as

$$\Phi_{BA}(t) = \beta \langle B(t) \dot{A} \rangle = -\beta \langle \dot{B}(t) A \rangle \quad (7.6.13)$$

The thermal averages in (7.6.13) are taken over the unperturbed system because in the linear approximation represented by (7.6.11) the variable B evolves in time under the influence of the reference-system propagator $\exp(i\mathcal{L}_0 t)$. It is sometimes convenient to use as an alternative definition of the after-effect function the expression

$$\theta_{BA}(t) = -\beta \langle \dot{B}(t) A \rangle \theta(t) \quad (7.6.14)$$

where $\theta(t)$ is the Heaviside step-function. Since $\theta_{BA}(t) = 0$ for $t < 0$, the upper limit of the integral in (7.6.12) can then be extended to $+\infty$.

The physical meaning of (7.6.12) and (7.6.13) is that the response, i.e. the change in the variable B at time t , is a superposition of delayed effects and the response to a unit δ -function force applied at $t = 0$ is proportional to the after-effect function itself. The basic result of linear-response theory embodied in these two equations can also be derived by calculating the changes in the phase-space trajectories of the particles to first order in the applied force. That method of derivation emphasises the assumption of mechanical linearity which underlies linear-response theory. Mechanical linearity cannot hold for macroscopic times, however, since it is known that the perturbed and unperturbed phase-space trajectories diverge exponentially on a macroscopic timescale even when the external field is very weak. On the other hand, the corresponding deviation in the phase-space distribution function is expected to behave smoothly as a function of the perturbation. Linearisation of the statistically averaged response should therefore be justified, in agreement with experimental observations. The apparent contradiction between mechanical non-linearity and statistical linearity is resolved by noting that the decay times of the relevant correlations, i.e. the times after which randomisation sets in, are generally quite short, and that use of a linear approximation for the divergence of the trajectories in phase space is valid for time intervals over which the after-effect function differs significantly from zero.

Equation (7.6.12) is easily generalised to the case in which the external field also varies in space. If the unperturbed system is spatially uniform, the response is determined by an after-effect function $\Phi_{BA}(\mathbf{r}, t)$ through the relation

$$\langle \Delta B(\mathbf{r}, t) \rangle = \int_{-\infty}^t ds \int \Phi_{BA}(\mathbf{r} - \mathbf{r}', t - s) \mathcal{F}(\mathbf{r}', s) d\mathbf{r}' \quad (7.6.15)$$

or, in terms of Fourier components, by

$$\langle \Delta B_{\mathbf{k}}(t) \rangle = \int_{-\infty}^t ds \int \Phi_{BA}(\mathbf{k}, t - s) \mathcal{F}_{\mathbf{k}}(s) ds \quad (7.6.16)$$

where

$$\Phi_{BA}(\mathbf{k}, t) = -\frac{\beta}{V} \langle \dot{B}_{\mathbf{k}}(t) A_{-\mathbf{k}} \rangle \quad (7.6.17)$$

Equation (7.6.16) shows that in the linear regime a perturbation of given wavevector induces a response only of the same wavevector; this is a consequence of the assumed uniformity of the unperturbed system and the property (7.4.11).

We now restrict the discussion to the case of isotropic fluids. If the external field has the monochromatic form of (7.6.5), the expression for the response becomes

$$\begin{aligned}
 \langle \Delta B_{\mathbf{k}}(t) \rangle &= \int_{-\infty}^t \Phi_{BA}(k, t-s) \mathcal{F}_{\mathbf{k}} \exp[-i(\omega + i\varepsilon)s] ds \\
 &= \mathcal{F}_{\mathbf{k}} \exp[-i(\omega + i\varepsilon)t] \int_{-\infty}^t \Phi_{BA}(k, t-s) \exp[-i(\omega + i\varepsilon)(s-t)] ds \\
 &= \mathcal{F}_{\mathbf{k}} \exp[-i(\omega + i\varepsilon)t] \int_0^{\infty} \Phi_{BA}(k, t) \exp[i(\omega + i\varepsilon)t] dt \quad (7.6.18)
 \end{aligned}$$

or, taking the limit $\varepsilon \rightarrow 0$:

$$\langle \Delta B_{\mathbf{k}}(t) \rangle = \chi_{BA}(k, \omega) \mathcal{F}_{\mathbf{k}} \exp(-i\omega t) \quad (7.6.19)$$

where $\chi_{BA}(k, \omega)$ is a complex *dynamic susceptibility* or *dynamic response function*:

$$\begin{aligned}
 \chi_{BA}(k, \omega) &= \chi'_{BA}(k, \omega) + i\chi''_{BA}(k, \omega) \\
 &= \lim_{\varepsilon \rightarrow 0+} \int_0^{\infty} \Phi_{BA}(k, t) \exp[i(\omega + i\varepsilon)t] dt \quad (7.6.20)
 \end{aligned}$$

If we substitute for $\Phi_{BA}(k, t)$ from (7.6.17) and integrate by parts, we find that

$$\chi_{BA}(k, \omega) = \frac{\beta}{V} [C_{BA}(k, t=0) + i(\omega + i\varepsilon) \tilde{C}_{BA}(k, \omega + i\varepsilon)] \quad (7.6.21)$$

When A and B are the same, it follows from (7.1.19) that

$$C_{AA}(k, \omega) = \frac{Vk_B T}{\pi\omega} \chi''_{AA}(k, \omega) \quad (7.6.22)$$

The zero-frequency limit of $\chi_{AA}(k, \omega)$, i.e. the static susceptibility $\chi_{AA}(k)$, is obtained from (7.6.21) as

$$\chi_{AA}(k) \equiv \chi_{AA}(k, \omega=0) = \frac{\beta}{V} C_{AA}(k, t=0) \quad (7.6.23)$$

Thus the static version of (7.6.19) for the case when A and B are the same is

$$\langle \Delta A_{\mathbf{k}} \rangle = \frac{\beta}{V} \langle A_{\mathbf{k}} A_{-\mathbf{k}} \rangle \mathcal{F}_{\mathbf{k}} \quad (7.6.24)$$

Equation (7.6.22) is a particular form of the fluctuation–dissipation theorem. Indeed the name is often applied specifically to this relation between the power spectrum of the auto-correlation function of a dynamical variable and the imaginary part of the corresponding response function. Use of the term “dissipation” is connected to the fact, well known in

spectroscopy, that the energy absorbed from the external field and later dissipated as heat is proportional to $\omega\chi''_{AA}(k, \omega)$.

When A is the microscopic density some minor changes are needed to the formulae we have derived. Let $\phi_{\mathbf{k}} \exp(-i\omega t)$ be a Fourier component of an external potential that couples to the component $\rho_{-\mathbf{k}}$ of the density. The term $\mathcal{H}'(t)$ in the hamiltonian (7.6.1) now has the form

$$\mathcal{H}'(t) = \frac{1}{V} \rho_{-\mathbf{k}} \phi_{\mathbf{k}} \exp(-i\omega t) \quad (7.6.25)$$

The resulting change in density is

$$\langle \Delta \rho_{\mathbf{k}}(t) \rangle = \chi_{\rho\rho}(k, \omega) \phi_{\mathbf{k}} \exp(-i\omega t) \quad (7.6.26)$$

which is a generalisation to non-zero frequencies of the static result (3.6.9). The after-effect function is

$$\Phi_{\rho\rho}(k, t) = \frac{\beta}{V} \langle \dot{\rho}_{\mathbf{k}}(t) \rho_{-\mathbf{k}} \rangle = \beta \rho \dot{F}(k, t) \quad (7.6.27)$$

and the imaginary part of the response function is related to the dynamic structure factor by

$$S(k, \omega) = -\frac{k_B T}{\pi \rho \omega} \chi''_{\rho\rho}(k, \omega) \quad (7.6.28)$$

The changes in sign relative to (7.6.17) and (7.6.22) arise from the difference in sign between the hamiltonian terms (7.6.4) and (7.6.25); the density response function is conventionally defined in terms of the response to an external potential rather than an external field. Similarly, the static susceptibility is now

$$\chi_{\rho\rho}(k) = -\frac{\beta}{V} \langle \rho_{\mathbf{k}} \rho_{-\mathbf{k}} \rangle = -\beta \rho S(k) \quad (7.6.29)$$

in agreement with (3.6.9).

The properties of the after-effect function $\Phi_{BA}(k, t)$ follow directly from its definition (7.6.17) and the general properties of time-correlation functions. If A and B are different, we see from (7.1.9) and (7.6.17) that

$$\Phi_{BA}(k, t) = \varepsilon_A \varepsilon_B \dot{\Phi}_{AB}(k, t) = -\varepsilon_A \varepsilon_B \Phi_{AB}(k, t) \quad (7.6.30)$$

Equation (7.6.30) is an expression of the Onsager *reciprocity relations*. If A and B are real, $\Phi_{BA}(k, t)$ is also real, and from (7.6.20) we see that on the real axis

$$\chi_{BA}(k, -\omega) = \chi_{BA}^*(k, \omega) = \chi'_{BA}(k, \omega) - i \chi''_{BA}(k, \omega) \quad (7.6.31)$$

Thus the real and imaginary parts of χ_{BA} are, respectively, even and odd functions of frequency.

The response function $\chi_{BA}(k, \omega)$ can be interpreted as the limit of a Laplace transform $\chi(k, z)$ defined in the entire upper half of the complex plane ($\text{Im } z > 0$):

$$\chi_{BA}(k, z) = \int_0^\infty \Phi_{BA}(k, t) \exp(izt) dt \quad (7.6.32)$$

If we confine ourselves to the important special case when the variables B and A are the same we may discard the subscripts and consider the behaviour of the susceptibility $\chi(k, z) \equiv \chi_{AA}(k, z)$ as a function of the complex variable $z = \omega + i\varepsilon$, with $\varepsilon > 0$. By restricting ε to positive values we ensure that $\chi(k, z)$ is analytic in the upper half-plane, but the function is undefined in the lower half-plane because the integral in (7.6.32) diverges. Since (7.6.13) implies that the after-effect function (with $A = B$) is linear in t at short times, it follows that $\chi(k, z)$ behaves asymptotically as z^{-2} at large z .

Let the contour C in the complex plane be $C = C_1 + C_2$, where C_1 is the real axis and C_2 is the infinite semicircle in the upper half-plane. Application of Cauchy's integral formula shows that

$$\chi(k, z) = \frac{1}{2\pi i} \int_C \frac{\chi(k, z')}{z' - z} dz' \quad (7.6.33)$$

where z is any point inside C . On the other hand, because the conjugate variable z^* lies outside C , the function $\chi(k, z')/(z' - z^*)$ is analytic in and on the contour C . It follows from Cauchy's theorem that

$$\int_C \frac{\chi(k, z')}{z' - z^*} dz' = 0 \quad (7.6.34)$$

The contributions to the integrals (7.6.33) and (7.6.34) from the contour C_2 are both zero, because $\chi(k, z)$ vanishes rapidly as $z \rightarrow \infty$. By adding quantities that are zero to the right-hand side of (7.6.33) and discarding the integral around C_2 , $\chi(k, z)$ can be re-expressed either as

$$\chi(k, z) = \frac{1}{2\pi i} \int_{C_1} \chi(k, z') \left(\frac{1}{z' - z} + \frac{1}{z' - z^*} \right) dz' \quad (7.6.35a)$$

or as

$$\chi(k, z) = \frac{1}{2\pi i} \int_{C_1} \chi(k, z') \left(\frac{1}{z' - z} - \frac{1}{z' - z^*} \right) dz' \quad (7.6.35b)$$

Two further expressions for $\chi(k, z)$ are obtained by adding the real part of (a) to i times the imaginary part of (b) and vice versa:

$$\chi(k, z) = \frac{1}{\pi} \int_{-\infty}^{\infty} \frac{\chi''(k, \omega)}{\omega - z} d\omega \quad (7.6.36a)$$

$$\chi(k, z) = \frac{1}{\pi i} \int_{-\infty}^{\infty} \frac{\chi'(k, \omega)}{\omega - z} d\omega \quad (7.6.36b)$$

We now let $\varepsilon \rightarrow 0$ in (7.6.36a), so that $\chi(k, \omega + i\varepsilon) \rightarrow \chi'(k, \omega) + i\chi''(k, \omega)$, and use the identity (7.1.18). In this way we find that

$$\chi'(k, \omega) = \mathcal{P} \frac{1}{\pi} \int_{-\infty}^{\infty} \frac{\chi''(k, \omega')}{\omega' - \omega} d\omega' \quad (7.6.37)$$

which is the Kramers–Kronig relation for $\chi'(k, \omega)$ in terms of $\chi''(k, \omega)$. The inverse relation, obtained by applying the rule (7.1.18) to (7.6.36b), is

$$\chi''(k, \omega) = -\mathcal{P} \frac{1}{\pi} \int_{-\infty}^{\infty} \frac{\chi'(k, \omega')}{\omega' - \omega} d\omega' \quad (7.6.38)$$

These results show that the real and imaginary parts of $\chi(k, \omega)$ are not independent of each other and a knowledge of one part is sufficient to determine the full response function.

The dispersion and damping of the collective modes associated with a dynamical variable A are governed, respectively, by the real and imaginary parts of the poles (corresponding to resonances) of the analytic continuation of $\chi_{AA}(k, z)$ into the lower half-plane. Much of the early theoretical work on density fluctuations in liquids was based on attempts to modify the density response function of an ideal gas to allow for the effects of particle interactions through a variety of mean-field or “effective-field” approximations. The problem with such approximations is that they account only for static and not for dynamic correlations between particles; they therefore fare badly at densities characteristic of the liquid state.

7.7 APPLICATIONS OF THE LINEAR-RESPONSE FORMALISM

The best known and most important of the applications of linear-response theory is its use in the derivation of expressions for the transport coefficients of hydrodynamics, through which induced fluxes are related to certain gradients within the fluid. The simplest example concerns the mobility of a tagged particle under the action of a constant external force \mathcal{F} that acts only on the tagged particles. We suppose that the force is applied along the x -direction from $t = 0$ onwards. Then the perturbation term in the hamiltonian is $\mathcal{H}'(t) = -\mathcal{F}x(t)\theta(t)$, where $x(t)$ is the x -coordinate of a tagged particle; if the fluid is isotropic, the drift velocity \mathbf{u} of the particle will be in the same direction as the applied force. From (7.6.12) and (7.6.13) it follows that

$$\langle u_x(t) \rangle = \beta \int_{-\infty}^t \langle u_x(t') \dot{x} \rangle \mathcal{F} \theta(t') dt' = \beta \mathcal{F} \int_0^t \langle u_x(t') u_x \rangle dt' \quad (7.7.1)$$

This leads to the Einstein relation for the mobility μ , defined as the ratio of the limiting drift velocity to the applied force:

$$\mu = \lim_{t \rightarrow \infty} \frac{1}{k_B T} \int_0^t \langle u_x(t') u_x \rangle dt' = \frac{D}{k_B T} \quad (7.7.2)$$

where D is the diffusion coefficient. Equation (7.7.2) is a further example of the fluctuation–dissipation theorem: D is a quantity that characterises spontaneous fluctuations in the velocity of a tagged particle and μ is a measure of the response of the tagged particle to an applied force.

It is instructive to consider an alternative derivation of (7.7.2). If the tagged particles are subjected to a weak, external force derived from a potential $\exp(\varepsilon t)\phi(\mathbf{r})$ ($\varepsilon > 0$), a concentration gradient is set up. The resulting induced current is

$$\langle \mathbf{j}^{(s)}(\mathbf{r}, t) \rangle = -\mu\rho_s \exp(\varepsilon t) \nabla \phi(\mathbf{r}) - D \nabla \langle \rho^{(s)}(\mathbf{r}, t) \rangle \quad (7.7.3)$$

or, in terms of Fourier components:

$$\langle \mathbf{j}_{\mathbf{k}}^{(s)}(t) \rangle = -i\mu\rho_s \exp(\varepsilon t) \mathbf{k} \phi_{\mathbf{k}} - iD \mathbf{k} \langle \rho_{\mathbf{k}}^{(s)}(t) \rangle \quad (7.7.4)$$

where ρ_s is the number of tagged particles per unit volume. The first term on the right-hand side of (7.7.3) represents the contribution to the current from the drift velocity of the tagged particles and the second term arises from Fick's law of diffusion (see Section 8.2). If the field is turned on sufficiently slowly, i.e. if $\varepsilon \ll Dk^2$, the system will remain in a steady state. The two contributions to the current then cancel and (7.7.4) reduces to

$$\langle \rho_{\mathbf{k}}^{(s)} \rangle = -\frac{\mu\rho_s}{D} \phi_{\mathbf{k}} \quad (7.7.5)$$

If the concentration of tagged particles is sufficiently low for interactions between them to be negligible, it follows from (3.6.9) that $\langle \rho_{\mathbf{k}}^{(s)} \rangle$ and $\phi_{\mathbf{k}}$ are also related by¹³

$$\langle \rho_{\mathbf{k}}^{(s)} \rangle = -\beta\rho_s \phi_{\mathbf{k}} \quad (7.7.6)$$

where $-\beta\rho_s$ is the static susceptibility of a non-interacting system of density ρ_s . Combination of (7.7.5) and (7.7.6) leads back to the Einstein expression (7.7.2).

The calculation of the electrical conductivity provides an example of a different type, in which a collective response of a system to an external field is involved. Suppose that a time-dependent electric field $\mathbf{E}(t)$ is applied to a system of charged particles. The field gives rise to a charge current, defined as

$$e\mathbf{j}^Z(t) = \sum_{i=1}^N z_i e \dot{\mathbf{r}}_i(t) = \dot{\mathbf{M}}(t) \quad (7.7.7)$$

where $z_i e$ is the charge carried by the i th particle (e is the elementary charge) and $\mathbf{M}(t)$ is the total dipole moment of the sample. The interaction with the applied field is described by the hamiltonian

$$\mathcal{H}'(t) = -\sum_{i=1}^N \mathbf{M}(t) \cdot \mathbf{E}(t) \quad (7.7.8)$$

If the system is isotropic and the field is applied, say, along the x -axis, then, in the statistical mean, only the x -component of the induced current will survive. The linear response to a real, periodic field can therefore be written as

$$e\langle j_x^Z(t) \rangle = \text{Re } \sigma(\omega) E_0 \exp(-i\omega t) \quad (7.7.9)$$

where, according to the general formulae (7.6.13) and (7.6.20), the electrical conductivity per unit volume is given by

$$\begin{aligned} \sigma(\omega) &= \frac{\beta e}{V} \int_0^\infty \sum_{i=1}^N \langle j_x^Z(t) z_i e \dot{x}_i \rangle \exp(i\omega t) dt \\ &= \frac{\beta e^2}{V} \int_0^\infty \langle j_x^Z(t) j_x^Z \rangle \exp(i\omega t) dt \end{aligned} \quad (7.7.10)$$

The usual static electrical conductivity σ is then identified as $\sigma = \lim_{\omega \rightarrow 0} \sigma(\omega)$. The statistical average in the second line of (7.7.10) is the autocorrelation function of the fluctuating charge current in the absence of the electrical field. In deriving this result we have ignored any spatial variation of the electric field, thereby avoiding the difficulties which arise when taking the long-wavelength limit for coulombic systems; we shall return to a discussion of this problem in Chapter 10.

Correlation-function formulae for transport coefficients have been obtained by many authors in a variety of ways. The derivation from linear-response theory is not always as straightforward as it is in the case of electrical conductivity, the difficulty being that the dissipative behaviour described by hydrodynamics is generally not induced by external forces but by gradients of local thermodynamic variables, which cannot be represented by a perturbation term in the hamiltonian. The thermal conductivity provides an example; this is the transport coefficient that relates the induced heat flux to an imposed temperature gradient via Fourier's law. A temperature gradient is a manifestation of boundary conditions and cannot be formulated in mechanical terms because temperature is a statistical property of the system. However, a linear-response argument can still be invoked by introducing an inhomogeneous field that couples to the energy density of the system and sets up a heat flow. Einstein's argument relating the diffusion coefficient to the mobility can then be extended to yield a correlation-function expression for the thermal conductivity. We postpone a derivation of the microscopic expressions for thermal conductivity and shear and bulk viscosities to Chapter 8, where it is shown that these coefficients are related to the long-wavelength, low-frequency (or "hydrodynamic") limit of certain space and time-dependent correlation functions.

The response to a weak, applied field can be measured directly in a molecular dynamics simulation in a way that allows the accurate calculation of transport coefficients with relatively modest computational effort.¹⁴ To understand what is involved, we return to the problem of the electrical conductivity. Clearly we could hope to mimic a real experiment by adding to the equations of motion of the particles the force due to a steady electrical field and computing the steady-state charge current to which the field gives rise. The practical

value of such an approach is seriously limited by the fact that a very large field must be applied in order to produce a systematic response that is significantly greater than the natural fluctuations. Use of a large field leads to a rapid heating-up of the system, non-conservation of energy and other undesirable effects.

The problems associated with the use of large fields can be overcome either by imposing constraints that maintain the system at constant kinetic energy or by a “subtraction” technique closely related to linear-response theory. In the subtraction method the response is computed as the difference in the property of interest along two phase-space trajectories; both start from the same phase point at time $t = 0$ but in one case a very small perturbing force is applied. In the example of electrical conductivity the response is the difference in charge current after a time t , given by

$$\Delta j_x^Z(t) = \exp(i\mathcal{L}t)j_x^Z - \exp(i\mathcal{L}_0t)j_x^Z \quad (7.7.11)$$

where \mathcal{L} and \mathcal{L}_0 are the Liouville operators that determine the perturbed and unperturbed trajectories, respectively. The statistical response is obtained by averaging (7.7.11) over initial conditions:

$$\begin{aligned} \langle \Delta j_x^Z(t) \rangle &= \iint f_0^{[N]} [\exp(i\mathcal{L}t) - \exp(i\mathcal{L}_0t)] j_x^Z \, d\mathbf{r}^N \, d\mathbf{p}^N \\ &= \langle j_x^Z(t) \rangle_{\mathcal{L}} - \langle j_x^Z(t) \rangle_{\mathcal{L}_0} \end{aligned} \quad (7.7.12)$$

where the brackets denote averages over the unperturbed equilibrium distribution function and the nature of the mechanical evolution is indicated by the subscripts \mathcal{L} and \mathcal{L}_0 . The success of the method rests mostly on the fact that random fluctuations in the two terms in (7.7.12) are highly correlated and therefore largely cancel, leaving only the systematic part, i.e. the response to the perturbation. It is therefore possible to use a perturbing force that is very small. In principle, because the hamiltonian in the absence of the perturbation is symmetric under reflection ($x_i \rightarrow -x_i$), the second term in (7.7.12) should vanish, but in practice this is not the case because the average is taken over a limited number of trajectories. The form of the statistical response depends on the time-dependence of the applied field. If a constant electric field is applied along the x -axis from $t = 0$ onwards, acting in opposite senses on charges of different sign, the mean response is proportional to the integral of the current autocorrelation function and therefore reaches a plateau value from which the conductivity can be calculated via (7.7.10); if a δ -function force is applied at $t = 0$, the response is proportional to the current autocorrelation function itself. The length of the trajectories must, of course, exceed the relevant relaxation time of the system, in this case the lifetime of spontaneous fluctuations in the electric current.

As a final example we show how the density response function of a non-interacting system can be calculated by a linear-response argument. The time evolution of the single-particle phase-space distribution function $f^{(1)}(\mathbf{r}, \mathbf{p}; t)$ of an ideal gas in an external potential $\phi(\mathbf{r}, t)$ is determined by the Boltzmann equation (2.1.24) with the collision term set equal to zero, i.e.

$$\left(\frac{\partial}{\partial t} + \frac{\mathbf{p}}{m} \cdot \frac{\partial}{\partial \mathbf{r}} - \frac{\partial \phi(\mathbf{r}, t)}{\partial \mathbf{r}} \cdot \frac{\partial}{\partial \mathbf{p}} \right) f^{(1)}(\mathbf{r}, \mathbf{p}; t) = 0 \quad (7.7.13)$$

If we write the distribution function as

$$f^{(1)}(\mathbf{r}, \mathbf{p}; t) = \rho f_M(\mathbf{p}) + \Delta f^{(1)}(\mathbf{r}, \mathbf{p}; t) \quad (7.7.14)$$

where $f_M(\mathbf{p})$ is the Maxwell distribution (2.1.26), the change $\Delta f^{(1)}$ induced by the external potential is linear in ϕ when the potential is weak. Substitution of (7.7.14) in (7.7.13) yields an equation of motion for $\Delta f^{(1)}$:

$$\left(\frac{\partial}{\partial t} + \frac{\mathbf{p}}{m} \cdot \frac{\partial}{\partial \mathbf{r}} - \frac{\partial \phi(\mathbf{r}, t)}{\partial \mathbf{r}} \cdot \frac{\partial}{\partial \mathbf{p}} \right) \Delta f^{(1)}(\mathbf{r}, \mathbf{p}; t) - \rho \frac{\partial \phi(\mathbf{r}, t)}{\partial \mathbf{r}} \cdot \frac{\partial f_M(\mathbf{p})}{\partial \mathbf{p}} = 0 \quad (7.7.15)$$

and a double, Fourier–Laplace transform leads (in an obvious notation) to

$$\left(\omega + i\varepsilon - \frac{\mathbf{p} \cdot \mathbf{k}}{m} \right) \Delta f^{(1)}(\mathbf{k}, \mathbf{p}; \omega + i\varepsilon) + \rho \phi(\mathbf{k}, \omega + i\varepsilon) \mathbf{k} \cdot \frac{\partial f_M}{\partial \mathbf{p}} = 0 \quad (7.7.16)$$

The mean change in microscopic density due to the external potential is

$$\langle \Delta \rho(\mathbf{r}, t) \rangle = \int \Delta f^{(1)}(\mathbf{r}, \mathbf{p}; t) d\mathbf{p} \quad (7.7.17)$$

or, in terms of Fourier components:

$$\langle \rho_{\mathbf{k}}(\omega) \rangle = \int \Delta f^{(1)}(\mathbf{k}, \mathbf{p}; \omega) d\mathbf{p} \quad (7.7.18)$$

Dividing through (7.7.16) by $(\omega + i\varepsilon - \mathbf{p} \cdot \mathbf{k}/m)$ and integrating over \mathbf{p} we find that

$$\langle \rho_{\mathbf{k}}(\omega + i\varepsilon) \rangle = -\rho \phi(\mathbf{k}, \omega + i\varepsilon) \int \frac{\mathbf{k} \cdot (\partial f_M / \partial \mathbf{p})}{\omega + i\varepsilon - \mathbf{p} \cdot \mathbf{k}/m} d\mathbf{p} \quad (7.7.19)$$

Thus the density response function is

$$\begin{aligned} \chi_{\rho\rho}(k, \omega + i\varepsilon) &= -\rho \int \frac{\mathbf{k} \cdot (\partial f_M / \partial \mathbf{p})}{\omega + i\varepsilon - \mathbf{p} \cdot \mathbf{k}/m} d\mathbf{p} \\ &= \beta \rho \int \frac{(\mathbf{p} \cdot \mathbf{k}/m) f_M(\mathbf{p})}{\omega + i\varepsilon - \mathbf{p} \cdot \mathbf{k}/m} d\mathbf{p} \\ &= -\beta \rho + (\omega + i\varepsilon) \beta \rho \int \frac{f_M(\mathbf{p})}{\omega + i\varepsilon - \mathbf{p} \cdot \mathbf{k}/m} d\mathbf{p} \end{aligned} \quad (7.7.20)$$

In the limit $\varepsilon \rightarrow 0$ the imaginary part of (7.7.20) is

$$\chi''_{\rho\rho}(k, \omega) = -\pi \beta \rho \omega \int f_M(\mathbf{p}) \delta(\omega - \mathbf{p} \cdot \mathbf{k}/m) d\mathbf{p} \quad (7.7.21)$$

This result follows immediately from the identity (7.1.18). On substituting for $f_M(\mathbf{p})$ and integrating over \mathbf{p} we find that

$$\chi''_{\rho\rho}(k, \omega) = -\beta\rho\omega \left(\frac{\pi\beta m}{2k^2} \right)^{1/2} \exp(-\beta m\omega^2/2k^2) \quad (7.7.22)$$

which, combined with (7.6.28), is equivalent to the expression (7.5.17) derived earlier for the dynamic structure factor of an ideal gas.

NOTES AND REFERENCES

1. Some of the material discussed in Chapters 7 to 9 is dealt with at greater length in a number of specialised texts. (a) Berne, B.J. and Pecora, R., "Dynamic Light Scattering". John Wiley, New York, 1976. (b) Réisibois, P. and DeLeener, M., "Classical Kinetic Theory of Fluids". John Wiley, New York, 1977. (c) Boon, J.P. and Yip, S., "Molecular Hydrodynamics". Dover Publications, New York, 1991. (d) Mazo, R.M., "Brownian Motion". Clarendon Press, Oxford, 2002.
2. See, e.g., ref. 1(b), p. 240.
3. Heyes, D.M., Powles, J.G. and Rickayzen, G., *Mol. Phys.* **100**, 595 (2002).
4. Lebowitz, J.L., Percus, J.K. and Sykes, J., *Phys. Rev.* **188**, 487 (1969).
5. Longuet-Higgins, H.C. and Pople, J.A., *J. Chem. Phys.* **25**, 884 (1956).
6. See, e.g., ref. 1(b), p. 324.
7. When $g(d) = 1$, (7.2.2) reduces to the result obtained by solution of the Boltzmann equation in a first-order approximation; higher-order corrections are of order 2%. See, e.g., Chapman, S. and Cowling, T.G., "The Mathematical Theory of Non-Uniform Gases", 3rd edn. Cambridge University Press, Cambridge, 1970, p. 258.
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9. Comparison of molecular-dynamics results for the Lennard-Jones fluid with an extended form of Enskog theory reveals a different behaviour at intermediate densities. See Miyazaki, K., Srinivas, G. and Bagchi, B., *J. Chem. Phys.* **114**, 6276 (2001).
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13. Equation (7.7.6) is just the ideal-gas form of (3.6.9).
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