

3.6 Coherent one-phonon scattering may be regarded as elastic scattering in the rest-frame of a moving crystal whose atoms are displaced with a sinusoidal variation. Show that, if the position of atom l in a Bravais crystal is given by

$$\mathbf{R}_l = \mathbf{l} + \mathbf{A} \cos(\mathbf{q} \cdot \mathbf{l}), \quad \text{where } \mathbf{A} \cdot \boldsymbol{\kappa} \ll 1,$$

and the velocity of the crystal is ω_s/q in the direction of \mathbf{q} , this picture leads to the relations

$$\mathbf{k} - \mathbf{k}' = \boldsymbol{\tau} \pm \mathbf{q}, \quad \frac{\hbar^2}{2m} (k^2 - k'^2) = \pm \hbar \omega_s.$$

3.7 The point $\boldsymbol{\tau} = 0$ is always a point on the coherent one-phonon scattering surface. (It corresponds to the undisturbed incident beam.) Show that whether it is an isolated point, or whether the scattering surface for a given polarisation branch exists in the neighbourhood of $\boldsymbol{\tau} = 0$, depends on whether the velocity of the incident neutrons is less or greater than the velocity of sound for the branch. (Assume for simplicity that the velocity of sound c is independent of the direction of propagation.)

3.8 Show from the form of the coherent one-phonon absorption cross-section that for fixed \mathbf{k}' this cross-section is proportional to $1/k$ (i.e. to $1/v$) as k tends to zero. Interpret this result physically.

4

Correlation functions in nuclear scattering

In the present chapter we relate the cross-sections for neutron scattering to thermal averages of operators belonging to the scattering system. The thermal averages can be expressed in terms of what are known as *correlation functions*. These functions are not only useful for calculating various properties of the scattering system, but they also provide insight into the physical significance of the terms that occur in the scattering cross-sections. This formulation of the subject is due primarily to Van Hove (1954). The calculations are quite general and refer to any system, solid, liquid, or gas, for which the scattering can be divided into coherent and incoherent parts.

4.1 Definitions of $I(\boldsymbol{\kappa}, t)$, $G(\mathbf{r}, t)$, and $S(\boldsymbol{\kappa}, \omega)$

We start with the expression (2.68) for the coherent scattering cross-section before we particularised it to a crystal target.

$$\left(\frac{d^2\sigma}{d\Omega dE'} \right)_{\text{coh}} = \frac{\sigma_{\text{coh}}}{4\pi} \frac{k'}{k} \frac{1}{2\pi\hbar} \int \sum_{jj'} \langle \exp\{-i\boldsymbol{\kappa} \cdot \mathbf{R}_j(0)\} \exp\{i\boldsymbol{\kappa} \cdot \mathbf{R}_j(t)\} \rangle \times \exp(-i\omega t) dt. \quad (4.1)$$

We define a function $I(\boldsymbol{\kappa}, t)$, known as the *intermediate function*, by

$$I(\boldsymbol{\kappa}, t) = \frac{1}{N} \sum_{jj'} \langle \exp\{-i\boldsymbol{\kappa} \cdot \mathbf{R}_j(0)\} \exp\{i\boldsymbol{\kappa} \cdot \mathbf{R}_j(t)\} \rangle, \quad (4.2)$$

where N is the number of nuclei in the scattering system.

We next define functions $G(\mathbf{r}, t)$ and $S(\boldsymbol{\kappa}, \omega)$ by

$$G(\mathbf{r}, t) = \frac{1}{(2\pi)^3} \int I(\boldsymbol{\kappa}, t) \exp(-i\boldsymbol{\kappa} \cdot \mathbf{r}) d\boldsymbol{\kappa}, \quad (4.3)$$

$$S(\kappa, \omega) = \frac{1}{2\pi\hbar} \int I(\kappa, t) \exp(-i\omega t) dt. \quad (4.4)$$

From the inverse relations for Fourier transforms (Appendix B.1)

$$I(\kappa, t) = \int G(\mathbf{r}, t) \exp(i\kappa \cdot \mathbf{r}) d\mathbf{r}, \quad (4.5)$$

$$I(\kappa, t) = \hbar \int S(\kappa, \omega) \exp(i\omega t) d\omega. \quad (4.6)$$

Thus

$$G(\mathbf{r}, t) = \frac{\hbar}{(2\pi)^3} \int S(\kappa, \omega) \exp\{-i(\kappa \cdot \mathbf{r} - \omega t)\} d\kappa d\omega, \quad (4.7)$$

$$S(\kappa, \omega) = \frac{1}{2\pi\hbar} \int G(\mathbf{r}, t) \exp\{i(\kappa \cdot \mathbf{r} - \omega t)\} d\mathbf{r} dt. \quad (4.8)$$

$G(\mathbf{r}, t)$ is known as the *time-dependent pair-correlation function* of the scattering system. $S(\kappa, \omega)$ is known as the *scattering function* of the system.[†] It can be seen that, apart from a constant factor, $S(\kappa, \omega)$ is the Fourier transform of $G(\mathbf{r}, t)$ in space and time. The intermediate function $I(\kappa, t)$ is the Fourier transform of $G(\mathbf{r}, t)$ in space, and $S(\kappa, \omega)$ is the Fourier transform of $I(\kappa, t)$ in time. Note that $I(\kappa, t)$ is dimensionless, $G(\mathbf{r}, t)$ has dimensions [volume]⁻¹, and $S(\kappa, \omega)$ has dimensions [energy]⁻¹.

We define the self intermediate function by

$$I_s(\kappa, t) = \frac{1}{N} \sum_j \langle \exp\{-i\kappa \cdot \mathbf{R}_j(0)\} \exp\{i\kappa \cdot \mathbf{R}_j(t)\} \rangle. \quad (4.9)$$

Similarly we define

$$G_s(\mathbf{r}, t) = \frac{1}{(2\pi)^3} \int I_s(\kappa, t) \exp(-i\kappa \cdot \mathbf{r}) d\kappa, \quad (4.10)$$

$$S_i(\kappa, \omega) = \frac{1}{2\pi\hbar} \int I_s(\kappa, t) \exp(-i\omega t) dt. \quad (4.11)$$

$G_s(\mathbf{r}, t)$ is known as the *self time-dependent pair-correlation function*, and $S_i(\kappa, \omega)$ is known as the *incoherent scattering function*.

Eqs. (4.1), (4.2), and (4.4) give

$$\left(\frac{d^2\sigma}{d\Omega dE'} \right)_{\text{coh}} = \frac{\sigma_{\text{coh}}}{4\pi} \frac{k'}{k} NS(\kappa, \omega). \quad (4.12)$$

[†] It is also known as the *scattering law*, though why a function should be called a law is a mystery to the author.

Similarly (2.69), (4.9), and (4.11) give

$$\left(\frac{d^2\sigma}{d\Omega dE'} \right)_{\text{inc}} = \frac{\sigma_{\text{inc}}}{4\pi} \frac{k'}{k} NS_i(\kappa, \omega). \quad (4.13)$$

The functions $S(\kappa, \omega)$ and $S_i(\kappa, \omega)$ are thus closely related to the coherent and incoherent scattering cross-sections.

4.2 Expressions for $G(\mathbf{r}, t)$ and $G_s(\mathbf{r}, t)$

We develop the expression for $G(\mathbf{r}, t)$. The algebra is straightforward though rather formal. From (4.2) and (4.3)

$$G(\mathbf{r}, t) = \frac{1}{(2\pi)^3} \frac{1}{N} \int \exp(-i\kappa \cdot \mathbf{r}) d\kappa \times \sum_{jj'} \langle \exp\{-i\kappa \cdot \mathbf{R}_{j'}(0)\} \exp\{i\kappa \cdot \mathbf{R}_j(t)\} \rangle. \quad (4.14)$$

Put $\langle \exp\{-i\kappa \cdot \mathbf{R}_{j'}(0)\} \exp\{i\kappa \cdot \mathbf{R}_j(t)\} \rangle$

$$= \int \langle \delta\{\mathbf{r}' - \mathbf{R}_{j'}(0)\} \exp(-i\kappa \cdot \mathbf{r}') \exp\{i\kappa \cdot \mathbf{R}_j(t)\} \rangle d\mathbf{r}'. \quad (4.15)$$

Then

$$G(\mathbf{r}, t) = \frac{1}{(2\pi)^3} \frac{1}{N} \sum_{jj'} \int \langle \delta\{\mathbf{r}' - \mathbf{R}_{j'}(0)\} \times \left[\int \exp\{-i\kappa \cdot \mathbf{r} - i\kappa \cdot \mathbf{r}' + i\kappa \cdot \mathbf{R}_j(t)\} d\kappa \right] \rangle d\mathbf{r}'. \quad (4.16)$$

From (A.13) the integral in the square brackets has the value

$$(2\pi)^3 \delta\{\mathbf{r}' + \mathbf{r} - \mathbf{R}_j(t)\}.$$

Thus

$$G(\mathbf{r}, t) = \frac{1}{N} \sum_{jj'} \int \langle \delta\{\mathbf{r}' - \mathbf{R}_{j'}(0)\} \delta\{\mathbf{r}' + \mathbf{r} - \mathbf{R}_j(t)\} \rangle d\mathbf{r}'. \quad (4.17)$$

By similar reasoning we arrive at the result

$$G_s(\mathbf{r}, t) = \frac{1}{N} \sum_j \int \langle \delta\{\mathbf{r}' - \mathbf{R}_j(0)\} \delta\{\mathbf{r}' + \mathbf{r} - \mathbf{R}_j(t)\} \rangle d\mathbf{r}'. \quad (4.18)$$

The operators $\mathbf{R}_{j'}(0)$ and $\mathbf{R}_j(t)$ do not commute, except when $t = 0$. This follows from the definitions

$$\mathbf{R}_{j'}(0) = \mathbf{R}_{j'}, \quad \mathbf{R}_j(t) = \exp(iHt/\hbar) \mathbf{R}_j \exp(-iHt/\hbar). \quad (4.19)$$

The Hamiltonian H , which is a function of the position and momentum operators of all the nuclei in the scattering system, contains the operator $\mathbf{p}_{j'}$ (momentum of nucleus j'). $\mathbf{R}_{j'}$ does not commute with $\mathbf{p}_{j'}$,

and hence it does not commute with $\mathbf{R}_j(t)$. It is therefore necessary to preserve the order of the operators and keep $\mathbf{R}_{j'}(0)$ on the left of $\mathbf{R}_j(t)$. We have done this in the preceding algebra.

If we ignore the fact that $\mathbf{R}_{j'}(0)$ and $\mathbf{R}_j(t)$ do not commute we can carry out the integration in (4.17). The result, known as the *classical* form of $G(\mathbf{r}, t)$, is

$$G^{\text{cl}}(\mathbf{r}, t) = \frac{1}{N} \sum_{j,j'} \langle \delta\{\mathbf{r} - \mathbf{R}_j(t) + \mathbf{R}_{j'}(0)\} \rangle. \quad (4.20)$$

We could have obtained this result directly from (4.14). If $\mathbf{R}_{j'}(0)$ and $\mathbf{R}_j(t)$ are allowed to commute, we can put

$$\exp\{-i\boldsymbol{\kappa} \cdot \mathbf{R}_{j'}(0)\} \exp\{i\boldsymbol{\kappa} \cdot \mathbf{R}_j(t)\} = \exp[-i\boldsymbol{\kappa} \cdot \{\mathbf{R}_{j'}(0) - \mathbf{R}_j(t)\}] \quad (4.21)$$

in (4.14), and (4.20) follows immediately.

Assume for simplicity that all the nuclei are equivalent. Then, for fixed j' , the sum over j in (4.20) gives the same value whatever the value of j' . So the sum over j' is N times the term with $j' = 0$. Thus

$$G^{\text{cl}}(\mathbf{r}, t) = \sum_j \langle \delta\{\mathbf{r} - \mathbf{R}_j(t) + \mathbf{R}_0(0)\} \rangle. \quad (4.22)$$

We conclude from this equation that $G^{\text{cl}}(\mathbf{r}, t) d\mathbf{r}$ is the probability that, given a particle at the origin at time $t = 0$, any particle (including the origin particle) is in the volume $d\mathbf{r}$ at position \mathbf{r} at time t . Similarly

$$G_s^{\text{cl}}(\mathbf{r}, t) = \langle \delta\{\mathbf{r} - \mathbf{R}_0(t) + \mathbf{R}_0(0)\} \rangle. \quad (4.23)$$

Thus $G_s^{\text{cl}}(\mathbf{r}, t) d\mathbf{r}$ is the probability that, given a particle at the origin at time $t = 0$, the same particle is in the volume $d\mathbf{r}$ at position \mathbf{r} at time t .

From these interpretations of $G^{\text{cl}}(\mathbf{r}, t)$ and $G_s^{\text{cl}}(\mathbf{r}, t)$ it must be the case that

$$\int G^{\text{cl}}(\mathbf{r}, t) d\mathbf{r} = N, \quad \int G_s^{\text{cl}}(\mathbf{r}, t) d\mathbf{r} = 1. \quad (4.24)$$

These results may be verified from the expressions in (4.20) and (4.23). It follows from (4.17) and (4.18) that $G(\mathbf{r}, t)$ and $G_s(\mathbf{r}, t)$ also satisfy the relations

$$\int G(\mathbf{r}, t) d\mathbf{r} = N, \quad \int G_s(\mathbf{r}, t) d\mathbf{r} = 1. \quad (4.25)$$

At $t = 0$

$$\mathbf{R}_{j'}(0) = \mathbf{R}_{j'} \quad \text{and} \quad \mathbf{R}_j(0) = \mathbf{R}_j. \quad (4.26)$$

The two operators commute, and we have

$$\begin{aligned} G(\mathbf{r}, 0) &= \sum_j \langle \delta(\mathbf{r} - \mathbf{R}_j + \mathbf{R}_0) \rangle \\ &= \delta(\mathbf{r}) + g(\mathbf{r}), \end{aligned} \quad (4.27)$$

where

$$g(\mathbf{r}) = \sum_{j \neq 0} \langle \delta(\mathbf{r} - \mathbf{R}_j + \mathbf{R}_0) \rangle. \quad (4.28)$$

$g(\mathbf{r})$ is known as the *static pair-distribution function*. It gives the average particle-density with respect to any particle as the origin. Similarly

$$G_s(\mathbf{r}, 0) = \delta(\mathbf{r}). \quad (4.29)$$

It should be noted that the expression for the cross-section in (4.1) is valid only when there is no correlation between the scattering length and the nuclear site. When there is such a correlation, for example for a crystal composed of more than one element, the scattering lengths have to be included in the expressions for $I(\boldsymbol{\kappa}, t)$ and the other functions. The resulting expression for $G^{\text{cl}}(\mathbf{r}, t)$ does not then have the simple probability interpretation of the expression in (4.22), owing to the presence of the scattering lengths, which act as weighting factors. We shall confine the discussion to simple systems where the mean value of the scattering length is the same for all the nuclear sites.

4.3 Analytic properties of the correlation functions

It is not possible to derive exact expressions for the functions $I(\boldsymbol{\kappa}, t)$, $G(\mathbf{r}, t)$, $S(\boldsymbol{\kappa}, \omega)$, except for the very simplest scattering systems. Approximations have to be made. It is therefore important to establish the basic analytic properties of the functions in order to check that the approximate functions have these properties.

We define an operator

$$\rho(\mathbf{r}, t) = \sum_j \delta\{\mathbf{r} - \mathbf{R}_j(t)\}. \quad (4.30)$$

It gives the number density of particles at position \mathbf{r} at time t and is known as the *particle-density operator*. From (A.13) we can express the operator in terms of its Fourier transform

$$\rho(\mathbf{r}, t) = \frac{1}{(2\pi)^3} \int \rho_{\boldsymbol{\kappa}}(t) \exp(i\boldsymbol{\kappa} \cdot \mathbf{r}) d\boldsymbol{\kappa}, \quad (4.31)$$

where

$$\rho_{\boldsymbol{\kappa}}(t) = \sum_j \exp\{-i\boldsymbol{\kappa} \cdot \mathbf{R}_j(t)\}. \quad (4.32)$$

The integral in (4.31) is over all reciprocal space. Since $\mathbf{R}_j(t)$ is a Hermitian operator

$$\rho^+(\mathbf{r}, t) = \rho(\mathbf{r}, t), \quad (4.33)$$

$$\rho_{\kappa}^+(t) = \rho_{-\kappa}(t). \quad (4.34)$$

From (4.2) and (4.32)

$$I(\kappa, t) = \frac{1}{N} \langle \rho_{\kappa}(0) \rho_{-\kappa}(t) \rangle, \quad (4.35)$$

and from (4.17) and (4.30)

$$G(\mathbf{r}, t) = \frac{1}{N} \int \langle \rho(\mathbf{r}', 0) \rho(\mathbf{r}' + \mathbf{r}, t) \rangle d\mathbf{r}'. \quad (4.36)$$

We may use the properties of the particle-density operator $\rho(\mathbf{r}, t)$ to prove the following results:

$$I(\kappa, t) = I^*(\kappa, -t), \quad (4.37)$$

$$G(\mathbf{r}, t) = G^*(-\mathbf{r}, -t), \quad (4.38)$$

$$S(\kappa, \omega) = S^*(\kappa, \omega), \quad (4.39)$$

$$I(\kappa, t) = I(-\kappa, -t + i\hbar\beta), \quad (4.40)$$

$$G(\mathbf{r}, t) = G(-\mathbf{r}, -t + i\hbar\beta), \quad (4.41)$$

$$S(\kappa, \omega) = \exp(\hbar\omega\beta) S(-\kappa, -\omega). \quad (4.42)$$

From (C.21) the complex conjugate of $I(\kappa, t)$ is obtained by reversing the two operators in (4.35) and taking their Hermitian conjugates. Eqs. (4.34) and (D.13) then give

$$I^*(\kappa, -t) = \frac{1}{N} \langle \rho_{\kappa}(0) \rho_{-\kappa}(t) \rangle = I(\kappa, t).$$

Eq. (4.38) follows from (4.3) and (4.37), and (4.39) from (4.4) and (4.37).

From (4.35), (D.13), and (D.14)

$$\begin{aligned} I(\kappa, t) &= \frac{1}{N} \langle \rho_{\kappa}(0) \rho_{-\kappa}(t) \rangle = \frac{1}{N} \langle \rho_{-\kappa}(t) \rho_{\kappa}(i\hbar\beta) \rangle \\ &= \frac{1}{N} \langle \rho_{-\kappa}(0) \rho_{\kappa}(-t + i\hbar\beta) \rangle = I(-\kappa, -t + i\hbar\beta). \end{aligned}$$

Eq. (4.41) follows from (4.3) and (4.40). From (4.4) and (4.40)

$$\begin{aligned} S(\kappa, \omega) &= \frac{1}{2\pi\hbar} \int I(-\kappa, -t + i\hbar\beta) \exp(-i\omega t) dt \\ &= \exp(\hbar\omega\beta) \frac{1}{2\pi\hbar} \int I(-\kappa, t') \exp(i\omega t') dt' \\ &= \exp(\hbar\omega\beta) S(-\kappa, -\omega). \end{aligned}$$

It may be noted that it is the quantum properties of the scattering system that cause $G(\mathbf{r}, t)$ to be complex. To obtain $G^*(\mathbf{r}, t)$ we simply reverse the order of the two Hermitian operators in (4.36). For a classical system these two operators commute, and $G(\mathbf{r}, t)$ is real.

We next define three new functions $\tilde{I}(\kappa, t)$, $\tilde{G}(\mathbf{r}, t)$, $\tilde{S}(\kappa, \omega)$ as follows

$$\tilde{I}(\kappa, t) = I(\kappa, t + \frac{1}{2}i\hbar\beta), \quad (4.43)$$

$$\tilde{G}(\mathbf{r}, t) = \frac{1}{(2\pi)^3} \int \tilde{I}(\kappa, t) \exp(-i\kappa \cdot \mathbf{r}) d\kappa, \quad (4.44)$$

$$\tilde{S}(\kappa, \omega) = \frac{1}{2\pi\hbar} \int \tilde{I}(\kappa, t) \exp(-i\omega t) dt. \quad (4.45)$$

Note that the functions $\tilde{G}(\mathbf{r}, t)$ and $\tilde{S}(\kappa, \omega)$ are defined in terms of $\tilde{I}(\kappa, t)$ in exactly the same way as $G(\mathbf{r}, t)$ and $S(\kappa, \omega)$ are defined in terms of $I(\kappa, t)$. The object in defining the new functions is that, as will be shown, $\tilde{G}(\mathbf{r}, t)$ is a real function and serves as a link between $G^{\text{cl}}(\mathbf{r}, t)$, which is also real and which may be calculated from some physical model of the scattering system, and the complex $G(\mathbf{r}, t)$.

The following results are readily proved:

$$\tilde{G}(\mathbf{r}, t) = G(\mathbf{r}, t + \frac{1}{2}i\hbar\beta), \quad (4.46)$$

$$\tilde{S}(\kappa, \omega) = \exp(-\frac{1}{2}\hbar\omega\beta) S(\kappa, \omega), \quad (4.47)$$

$$\tilde{I}(\kappa, t) = \tilde{I}(-\kappa, -t) = \tilde{I}^*(\kappa, -t), \quad (4.48)$$

$$\tilde{G}(\mathbf{r}, t) = \tilde{G}(-\mathbf{r}, -t) = \tilde{G}^*(\mathbf{r}, t), \quad (4.49)$$

$$\tilde{S}(\kappa, \omega) = \tilde{S}(-\kappa, -\omega) = \tilde{S}^*(\kappa, \omega). \quad (4.50)$$

Eqs. (4.46) and (4.47) follow from the definitions of $\tilde{I}(\kappa, t)$, $\tilde{G}(\mathbf{r}, t)$, and $\tilde{S}(\kappa, \omega)$. In deriving (4.47) the variable for the time integration is changed as in the derivation of (4.42). From (4.37), (4.40), and (4.43)

$$\begin{aligned} \tilde{I}(\kappa, t) &= I(\kappa, t + \frac{1}{2}i\hbar\beta) = I(-\kappa, -t + \frac{1}{2}i\hbar\beta) = \tilde{I}(-\kappa, -t) \\ &= I^*(\kappa, -t + \frac{1}{2}i\hbar\beta) = \tilde{I}^*(\kappa, -t). \end{aligned}$$

Eqs. (4.49) and (4.50) then follow from (4.44) and (4.45).

For many scattering systems

$$G(\mathbf{r}, t) = G(-\mathbf{r}, t). \quad (4.51)$$

This relation is true for all disordered systems – gases and liquids. It is also true for polycrystals, and single crystals with a centre of symmetry. If we assume (4.51), the previous equations, together with

(4.4) and (4.5) give

$$I(\kappa, t) = I(-\kappa, t), \quad (4.52)$$

$$S(\kappa, \omega) = S(-\kappa, \omega), \quad (4.53)$$

$$\tilde{I}(\kappa, t) = \tilde{I}(-\kappa, t) = \tilde{I}(\kappa, -t), \quad (4.54)$$

$$\tilde{G}(\mathbf{r}, t) = \tilde{G}(-\mathbf{r}, t) = \tilde{G}(\mathbf{r}, -t), \quad (4.55)$$

$$\tilde{S}(\kappa, \omega) = \tilde{S}(-\kappa, \omega) = \tilde{S}(\kappa, -\omega). \quad (4.56)$$

Eq. (4.53) is the complement of (4.51). If the correlation function for the particles in the scattering system is the same when \mathbf{r} is reversed, then the scattering properties of the system must be the same when κ is reversed.

For all scattering systems, the functions $\tilde{G}(\mathbf{r}, t)$ and $\tilde{S}(\kappa, \omega)$ are real. If the relation (4.51) holds, then $\tilde{I}(\kappa, t)$ is also real, and the three functions $\tilde{I}(\kappa, t)$, $\tilde{G}(\mathbf{r}, t)$, and $\tilde{S}(\kappa, \omega)$ are even in each of their two variables. Further, from (4.38) and (4.51)

$$G(\mathbf{r}, t) = G^*(\mathbf{r}, -t). \quad (4.57)$$

Thus the real part of $G(\mathbf{r}, t)$ is even in t , while the imaginary part is odd in t .

4.4 Principle of detailed balance

Eq. (4.42) is known as the *principle of detailed balance*. It is an important result, and we give an alternative derivation, which shows more clearly its physical significance.

If the δ -function expressing conservation of energy in (2.40) is retained and not expressed as a time integral, the coherent scattering cross-section has the form

$$\left(\frac{d^2\sigma}{d\Omega dE'} \right)_{\text{coh}} = \frac{\sigma_{\text{coh}}}{4\pi} \frac{k'}{k} \sum_{\lambda} p_{\lambda} \sum_{\lambda'} \left| \sum_j \langle \lambda' | \exp(i\kappa \cdot \mathbf{R}_j) | \lambda \rangle \right|^2 \delta(E_{\lambda} - E_{\lambda'} + \hbar\omega). \quad (4.58)$$

Comparing this equation with (4.12) and using the explicit form of p_{λ} in (2.51) we obtain

$$S(\kappa, \omega) = \frac{1}{NZ} \sum_{\lambda\lambda'} \exp(-E_{\lambda}\beta) \left| \sum_j \langle \lambda' | \exp(i\kappa \cdot \mathbf{R}_j) | \lambda \rangle \right|^2 \delta(E_{\lambda} - E_{\lambda'} + \hbar\omega). \quad (4.59)$$

To make the discussion definite let ω be a positive quantity, i.e. let the neutron lose energy in the scattering process. For every transition

of the system that contributes to $S(\kappa, \omega)$, the initial state λ has energy $\hbar\omega$ less than the final state λ' (Fig. 4.1a).

Consider now the function $S(-\kappa, -\omega)$ where ω is the same positive quantity. This represents a process in which the neutron gains energy. The transitions of the system are between the same pairs of levels as for the previous process, but now λ' is the initial state and λ is the final state (Fig. 4.1b). Thus

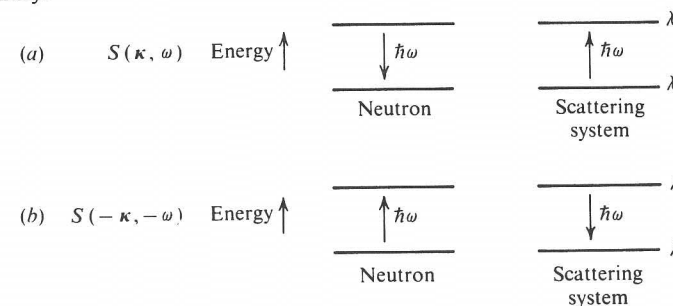
$$\begin{aligned} S(-\kappa, -\omega) &= \frac{1}{NZ} \sum_{\lambda\lambda'} \exp(-E_{\lambda'}\beta) \left| \sum_j \langle \lambda | \exp(-i\kappa \cdot \mathbf{R}_j) | \lambda' \rangle \right|^2 \delta(E_{\lambda'} - E_{\lambda} - \hbar\omega) \\ &= \exp\{-(E_{\lambda'} - E_{\lambda})\beta\} \frac{1}{NZ} \sum_{\lambda\lambda'} \exp(-E_{\lambda}\beta) \left| \sum_j \langle \lambda' | \exp(i\kappa \cdot \mathbf{R}_j) | \lambda \rangle \right|^2 \\ &\quad \times \delta(E_{\lambda} - E_{\lambda'} + \hbar\omega) \\ &= \exp(-\hbar\omega\beta) S(\kappa, \omega). \end{aligned} \quad (4.60)$$

In the middle line of the last equation we have used (C.3), which in the present context expresses the physical result that, for a pair of states in the scattering system, the *a priori* probabilities that the neutron will bring about a transition in either direction are the same. The probability of the system being initially in the higher energy state is lower by the factor $\exp(-\hbar\omega\beta)$ than its probability of being in the lower energy state. Hence the function $S(-\kappa, -\omega)$ is less than $S(\kappa, \omega)$ by this factor.

For scattering systems for which reversal of κ has no effect, the principle of detailed balance is

$$S(\kappa, -\omega) = \exp(-\hbar\omega\beta) S(\kappa, \omega). \quad (4.61)$$

Fig. 4.1 Principle of detailed balance: diagram showing transitions for (a) $S(\kappa, \omega)$, where ω is positive, and (b) $S(-\kappa, -\omega)$, where ω is the same positive quantity.



Schofield's prescription for $G(r, t)$

We have mentioned that in general it is not possible to calculate $G(r, t)$ exactly from the atomic properties of the scattering system. Instead, we proceed by setting up a physical model and deriving $G^{\text{cl}}(r, t)$, the classical form of $G(r, t)$, from it. However, this calculated $G^{\text{cl}}(r, t)$ is not a good approximation for $G(r, t)$, because for many systems $G^{\text{cl}}(r, t)$ is real and even in r and t . If we take $G(r, t)$ to be real and even in r and t , then from (4.8)

$$S(\kappa, \omega) = S(-\kappa, -\omega). \quad (4.62)$$

The result violates the principle of detailed balance.

Schofield (1960) suggested that a better approximation is to assume

$$\tilde{G}(r, t) = G^{\text{cl}}(r, t). \quad (4.63)$$

We know that the correct $\tilde{G}(r, t)$ is real and even in r and t . So if we put $\tilde{G}(r, t)$ equal to the calculated $G^{\text{cl}}(r, t)$ and then use the result

$$G(r, t) = \tilde{G}(r, t - \frac{1}{2}i\hbar\beta), \quad (4.64)$$

the resulting $S(\kappa, \omega)$ will satisfy the detailed balance condition.

4.5 Scattering from a single free nucleus

To illustrate the various functions defined in the present chapter we consider the simplest possible case, namely scattering by a single free nucleus of mass M . By this we do not mean an isolated nucleus, but one that is a member of an ensemble at temperature T .

We start with the expression for the cross-section obtained from (2.40)

$$\frac{d^2\sigma}{d\Omega dE'} = b^2 \frac{k'}{k} \sum_{\lambda} p_{\lambda} \sum_{\lambda'} |\langle \lambda' | \exp(i\kappa \cdot \mathbf{R}) | \lambda \rangle|^2 \delta(E_{\lambda} - E_{\lambda'} + \hbar\omega). \quad (4.65)$$

b is the scattering length of the nucleus, and \mathbf{R} is its position vector. The first point to note is that the matrix element $\langle \lambda' | \exp(i\kappa \cdot \mathbf{R}) | \lambda \rangle$ is zero unless momentum is conserved in the scattering process. To see this we suppose the neutrons and the nuclei in the scattering system to be confined to a box of volume Y . Since the nuclei are free, their state functions are plane waves, i.e.

$$|\lambda\rangle = \frac{1}{\sqrt{Y}} \exp(i\xi \cdot \mathbf{R}), \quad (4.66)$$

where ξ is the wavevector of the nucleus. ξ like k (the wavevector of

the neutron) is periodic in the box. Then

$$\langle \lambda' | \exp(i\kappa \cdot \mathbf{R}) | \lambda \rangle = \frac{1}{Y} \int_{\text{box}} \exp\{i(\kappa + \xi - \xi') \cdot \mathbf{R}\} d\mathbf{R}. \quad (4.67)$$

The integral is zero unless

$$\kappa = k - k' = \xi' - \xi. \quad (4.68)$$

(The reasoning is the same as in (A.15).) Multiplication of this equation by \hbar gives conservation of momentum. If the condition is satisfied

$$\langle \lambda' | \exp(i\kappa \cdot \mathbf{R}) | \lambda \rangle = 1. \quad (4.69)$$

$$\text{Thus} \quad \sum_{\lambda'} |\langle \lambda' | \exp(i\kappa \cdot \mathbf{R}) | \lambda \rangle|^2 = 1, \quad (4.70)$$

$$\text{and} \quad \xi' = \kappa + \xi. \quad (4.71)$$

$$\text{Then} \quad E_{\lambda} - E_{\lambda'} = \frac{\hbar^2}{2M} (\xi^2 - \xi'^2) = -\frac{\hbar^2}{2M} (\kappa^2 + 2\kappa \cdot \xi). \quad (4.72)$$

The function $S(\kappa, \omega)$ is obtained from (4.12) and (4.65).

$$\begin{aligned} S(\kappa, \omega) &= \sum_{\lambda\lambda'} p_{\lambda} |\langle \lambda' | \exp(i\kappa \cdot \mathbf{R}) | \lambda \rangle|^2 \delta(E_{\lambda} - E_{\lambda'} + \hbar\omega) \\ &= \sum_{\xi} p_{\xi} \delta\left\{ \hbar\omega - \frac{\hbar^2}{2M} (\kappa^2 + 2\kappa \cdot \xi) \right\}. \end{aligned} \quad (4.73)$$

The initial energy of the nucleus is $\hbar^2 \xi^2 / 2M$. The probability p_{ξ} of the nucleus having wavevector ξ is therefore proportional to $\exp(-\hbar^2 \xi^2 \beta / 2M)$. Thus

$$S(\kappa, \omega) = \frac{\int \exp(-\hbar^2 \xi^2 \beta / 2M) \delta\{\hbar\omega - (\hbar^2 / 2M)(\kappa^2 + 2\kappa \cdot \xi)\} d\xi}{\int \exp(-\hbar^2 \xi^2 \beta / 2M) d\xi} \quad (4.74)$$

$$= \left(\frac{\beta}{4\pi E_r} \right)^{1/2} \exp\left\{ -\frac{\beta}{4E_r} (\hbar\omega - E_r)^2 \right\}, \quad (4.75)$$

where

$$E_r = \frac{\hbar^2 \kappa^2}{2M}. \quad (4.76)$$

The integrals in (4.74) are evaluated by taking cartesian coordinates in ξ space, with one of the axes in the direction of κ .

The expressions for $I(\kappa, t)$ and $G(r, t)$ follow from (4.3), (4.6), (B.6), and (B.7). They are

$$I(\kappa, t) = \exp\{-\kappa^2 \sigma^2(t)/2\}, \quad (4.77)$$

$$G(r, t) = \{2\pi\sigma^2(t)\}^{-3/2} \exp\{-r^2/2\sigma^2(t)\}, \quad (4.78)$$

$$\text{where} \quad \sigma^2(t) = t(t - i\hbar\beta)/M\beta. \quad (4.79)$$

The functions $\tilde{I}(\kappa, t)$, $\tilde{G}(\mathbf{r}, t)$, and $\tilde{S}(\kappa, \omega)$ are obtained from (4.43), (4.46), and (4.47). The results are

$$\tilde{I}(\kappa, t) = \exp\{-\kappa^2 \tilde{\sigma}^2(t)/2\}, \quad (4.80)$$

$$\tilde{G}(\mathbf{r}, t) = \{2\pi\tilde{\sigma}^2(t)\}^{-3/2} \exp\{-r^2/2\tilde{\sigma}^2(t)\}, \quad (4.81)$$

$$\tilde{S}(\kappa, \omega) = \left(\frac{\beta}{4\pi E_r}\right)^{1/2} \exp\left\{-\frac{\beta}{4E_r}(\hbar^2\omega^2 + E_r^2)\right\}, \quad (4.82)$$

where
$$\tilde{\sigma}^2(t) = (t^2 + \frac{1}{4}\hbar^2\beta^2)/M\beta. \quad (4.83)$$

Eq. (4.75) shows that, for a fixed value of κ , $S(\kappa, \omega)$ is a Gaussian function of ω , centred on $\hbar\omega = E_r$. From the results in Appendix I.2

$$\int S(\kappa, \omega) d(\hbar\omega) = 1, \quad (4.84)$$

$$\int S(\kappa, \omega) \hbar\omega d(\hbar\omega) = E_r, \quad (4.85)$$

$$\int S(\kappa, \omega) (\hbar\omega)^2 d(\hbar\omega) = \frac{2E_r}{\beta} + E_r^2. \quad (4.86)$$

The following points may be noted:

(i) For a single nucleus the functions $G(\mathbf{r}, t)$, $I(\kappa, t)$, and $S(\kappa, \omega)$ are identical with their self counterparts. Although we have been considering scattering from a single nucleus, the results apply also to a perfect gas of identical atoms. For such a system $G_s(\mathbf{r}, t)$, $I_s(\kappa, t)$, and $S_s(\kappa, \omega)$ are the same as for a single nucleus, and $G(\mathbf{r}, t)$ differs from $G_s(\mathbf{r}, t)$ only by a constant independent of \mathbf{r} and t . It follows that for a perfect gas the functions $I(\kappa, t)$ and $I_s(\kappa, t)$ are essentially the same. They differ only by a term proportional to $\delta(\kappa)$. The same is true for the functions $S(\kappa, \omega)$ and $S_s(\kappa, \omega)$.

(ii) $I(\kappa, t)$ and $G(\mathbf{r}, t)$ are complex functions, while $\tilde{I}(\kappa, t)$ and $\tilde{G}(\mathbf{r}, t)$ are real and even in both their arguments. $S(\kappa, \omega)$ and $\tilde{S}(\kappa, \omega)$ are both real, and the latter is even in κ and ω .

(iii) In Example 4.1 it is shown that for a perfect gas the classical form of $G_s(\mathbf{r}, t)$ is

$$G_s^{\text{cl}}(\mathbf{r}, t) = \{2\pi\sigma_{\text{cl}}^2(t)\}^{-3/2} \exp\{-r^2/2\sigma_{\text{cl}}^2(t)\}, \quad (4.87)$$

where
$$\sigma_{\text{cl}}^2(t) = t^2/M\beta, \quad (4.88)$$

which we see is the limiting form of $G(\mathbf{r}, t)$ and $\tilde{G}(\mathbf{r}, t)$ for a single nucleus as $\hbar \rightarrow 0$ or $\beta \rightarrow 0$ ($T \rightarrow \infty$).

(iv) $S(\kappa, \omega)$ may be calculated from $G(\mathbf{r}, t)$ by means of (4.8). If we put $G(\mathbf{r}, t) = G_s^{\text{cl}}(\mathbf{r}, t)$, the resulting expression for $S(\kappa, \omega)$ is

$$S(\kappa, \omega) = \left(\frac{\beta}{4\pi E_r}\right)^{1/2} \exp\left(-\frac{\beta\hbar^2\omega^2}{4E_r}\right). \quad (4.89)$$

It can be seen that this violates the principle of detailed balance. If we adopt the Schofield prescription and put $\tilde{G}(\mathbf{r}, t) = G_s^{\text{cl}}(\mathbf{r}, t)$, the resulting expression for $S(\kappa, \omega)$ is

$$S(\kappa, \omega) = \left(\frac{\beta}{4\pi E_r}\right)^{1/2} \exp\left\{-\frac{\beta}{4E_r}(\hbar^2\omega^2 - 2\hbar\omega E_r)\right\}. \quad (4.90)$$

This expression does satisfy the principle of detailed balance and is a good approximation (for $E_r \ll \hbar\omega$) to the correct expression in (4.75).

4.6 Moments of the scattering function

The energy moments of the scattering function $S(\kappa, \omega)$ may be obtained experimentally and often provide a useful check on the measurements. We define the n th moment by

$$S_n(\kappa) = \int_{-\infty}^{\infty} S(\kappa, \omega) (\hbar\omega)^n d(\hbar\omega). \quad (4.91)$$

From (4.2), (4.5), (4.6), and (4.27) we have the following results for the zeroth moment

$$S_0(\kappa) = \int_{-\infty}^{\infty} S(\kappa, \omega) d(\hbar\omega) = I(\kappa, 0) \quad (4.92)$$

$$= \frac{1}{N} \sum_{j,j'} \langle \exp\{i\kappa \cdot (\mathbf{R}_j - \mathbf{R}_{j'})\} \rangle \quad (4.93)$$

$$= 1 + \int g(\mathbf{r}) \exp(i\kappa \cdot \mathbf{r}) d\mathbf{r}. \quad (4.94)$$

For the incoherent scattering function

$$\int_{-\infty}^{\infty} S_i(\kappa, \omega) d(\hbar\omega) = I_s(\kappa, 0) = 1. \quad (4.95)$$

An expression for the higher moments of $S(\kappa, \omega)$ is obtained from (4.6)

$$S_1(\kappa) = \int_{-\infty}^{\infty} S(\kappa, \omega) \hbar\omega d(\hbar\omega) = \frac{\hbar}{i} \left\{ \frac{\partial}{\partial t} I(\kappa, t) \right\}_{t=0}, \quad (4.96)$$

and in general

$$S_n(\kappa) = \left(\frac{\hbar}{i}\right)^n \left\{ \frac{\partial^n}{\partial t^n} I(\kappa, t) \right\}_{t=0}. \quad (4.97)$$

We consider the first moment. From (4.35), (4.96), and (D.6)

$$\begin{aligned} \int_{-\infty}^{\infty} S(\kappa, \omega) \hbar \omega d(\hbar \omega) &= \frac{\hbar}{iN} \left\langle \rho_{\kappa}(0) \left\{ \frac{\partial}{\partial t} \rho_{-\kappa}(t) \right\}_{t=0} \right\rangle \\ &= -\frac{1}{N} \langle \rho_{\kappa}(0) [\rho_{-\kappa}(0), H] \rangle, \end{aligned} \quad (4.98)$$

where H is the Hamiltonian of the scattering system. In Section 4.5 we showed that for a perfect gas of identical atoms

$$\int S(\kappa, \omega) \hbar \omega d(\hbar \omega) = \frac{\hbar^2 \kappa^2}{2M}, \quad (4.99)$$

where M is the mass of an atom. The usefulness of this result is that it is true, not only for a perfect gas, but for any system, provided the interactions between the atoms depend only on their positions \mathbf{R}_i and not on their momenta. This result follows from the form of (4.98). The additional term in the Hamiltonian due to the interatomic forces commutes with $\rho_{-\kappa}(0)$ – since the latter depends only on the positions \mathbf{R}_i – and hence contributes nothing to the right-hand side of (4.98).

Eq. (4.99) has a simple physical interpretation for a perfect gas. Consider a neutron scattered with change of wavevector κ due to a collision with a single nucleus. Then by conservation of momentum

$$\hbar \kappa = \mathbf{p}' - \mathbf{p}, \quad (4.100)$$

where \mathbf{p} and \mathbf{p}' are the momenta of the nucleus before and after the collision. The gain in the kinetic energy of the nucleus is

$$\frac{1}{2M} (p'^2 - p^2) = \frac{1}{2M} (\hbar^2 \kappa^2 + 2\hbar \mathbf{p} \cdot \kappa). \quad (4.101)$$

For fixed κ , the average of $\mathbf{p} \cdot \kappa$ is zero. Therefore the average gain of energy of a nucleus, sometimes termed the *recoil energy*, is

$$E_r = \frac{\hbar^2 \kappa^2}{2M}. \quad (4.102)$$

Thus $S_1(\kappa)$ is the mean energy transferred from the neutron to the nucleus.

The result (4.99) applies also to the incoherent scattering function $S_i(\kappa, \omega)$. This follows because, for a perfect gas, the coherent and incoherent scattering functions are essentially the same, and by the previous reasoning $\int S_i(\kappa, \omega) \hbar \omega d(\hbar \omega)$ is the same for all systems with velocity-independent interactions.

The expressions for higher moments have been derived by Placzek (1952). He showed that for an isotropic system the second moment of

the incoherent scattering function is

$$\int_{-\infty}^{\infty} S_i(\kappa, \omega) (\hbar \omega)^2 d(\hbar \omega) = \frac{4}{3} E_r \bar{K} + E_r^2, \quad (4.103)$$

where \bar{K} is the mean kinetic energy of a nucleus. For a classical system

$$\bar{K} = \frac{3}{2\beta}, \quad (4.104)$$

and (4.103) becomes

$$\int_{-\infty}^{\infty} S_i(\kappa, \omega) (\hbar \omega)^2 d(\hbar \omega) = \frac{2E_r}{\beta} + E_r^2, \quad (4.105)$$

which is the same as the result (4.86) for a perfect gas. The general expression for the second moment of the coherent scattering function is more complicated. The leading terms are the same as for the incoherent scattering function, but there are additional quantum terms arising from correlations between the momenta of different nuclei. Expressions for the second and higher moments of the two scattering functions may be found in Placzek (1952) and in Rahman *et al.* (1962). The results for the moments of the scattering functions are known as *sum rules*.

4.7 Relation between elastic scattering and $I(\kappa, \infty)$, $G(r, \infty)$

We now show that elastic scattering is directly related to the functions $I(\kappa, t)$, $G(r, t)$ evaluated at $t = \infty$. The relations lead to some useful results. Elastic scattering does not occur for liquids or gases (see Chapter 5) so the present discussion refers to scattering by a solid.

We consider the functions $I(\kappa, t)$ and $S(\kappa, \omega)$ for some fixed κ and drop the symbol κ . The function $I(t)$ tends to the same limit as t tends to $\pm\infty$. Put

$$I(t) = I(\infty) + I'(t), \quad (4.106)$$

where $I(\infty)$ is the limiting value of $I(t)$, and $I'(t)$ is the time-dependent part which tends to zero as $t \rightarrow \pm\infty$. This is indicated schematically in Fig. 4.2a, where $I(t)$ is taken as real for the purpose of illustration. Then from (4.4)

$$\begin{aligned} S(\omega) &= \frac{1}{2\pi\hbar} \int_{-\infty}^{\infty} \{I(\infty) + I'(t)\} \exp(-i\omega t) dt \\ &= \frac{1}{\hbar} \delta(\omega) I(\infty) + \frac{1}{2\pi\hbar} \int_{-\infty}^{\infty} I'(t) \exp(-i\omega t) dt. \end{aligned} \quad (4.107)$$

Since $\hbar\omega$ is the change in energy of the neutron, the first term on the right-hand side of (4.107) represents elastic scattering and the second term inelastic scattering (Fig. 4.2b). Note that the second term is not zero at $\omega = 0$, but it is completely swamped by the first term.

From (4.12) and (4.107)

$$\left(\frac{d^2\sigma}{d\Omega dE'}\right)_{\text{coh el}} = \frac{\sigma_{\text{coh}}}{4\pi} \frac{N}{\hbar} \delta(\omega) I(\kappa, \infty). \quad (4.108)$$

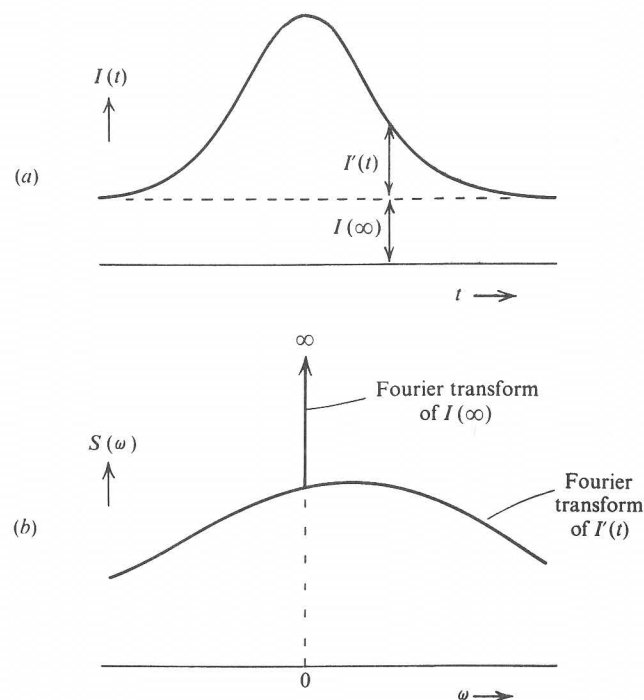
Integrating this with respect to E' gives

$$\left(\frac{d\sigma}{d\Omega}\right)_{\text{coh el}} = \frac{\sigma_{\text{coh}}}{4\pi} NI(\kappa, \infty). \quad (4.109)$$

By definition

$$I(\kappa, \infty) = \frac{1}{N} \sum_{ij'} \langle \exp\{-i\kappa \cdot \mathbf{R}_{j'}(0)\} \exp\{i\kappa \cdot \mathbf{R}_j(\infty)\} \rangle. \quad (4.110)$$

Fig. 4.2 (a) Schematic representation of $I(t)$. (The function is actually complex.) (b) $S(\omega)$, the Fourier transform of $I(t)$.



But as $t \rightarrow \infty$ the correlation between $\mathbf{R}_{j'}(0)$ and $\mathbf{R}_j(t)$ becomes independent of t , and we have

$$I(\kappa, \infty) = \frac{1}{N} \sum_{ij'} \langle \exp(-i\kappa \cdot \mathbf{R}_{j'}) \rangle \langle \exp(i\kappa \cdot \mathbf{R}_j) \rangle. \quad (4.111)$$

Note that

$$\langle \exp\{i\kappa \cdot \mathbf{R}_j(t)\} \rangle = \langle \exp\{i\kappa \cdot \mathbf{R}_j(0)\} \rangle = \langle \exp\{i\kappa \cdot \mathbf{R}_j\} \rangle. \quad (4.112)$$

This may be verified formally by writing $\langle \exp\{i\kappa \cdot \mathbf{R}_j(t)\} \rangle$ in terms of the definition of a Heisenberg operator. But it is obvious on physical grounds, since the origin of t is arbitrary. From (4.109) and (4.111)

$$\left(\frac{d\sigma}{d\Omega}\right)_{\text{coh el}} = \frac{\sigma_{\text{coh}}}{4\pi} \sum_{ij'} \langle \exp(-i\kappa \cdot \mathbf{R}_{j'}) \rangle \langle \exp(i\kappa \cdot \mathbf{R}_j) \rangle. \quad (4.113)$$

It may be verified that for a Bravais crystal this is the same as (3.48): see Example 4.3.

The same reasoning may be used to obtain an expression for $G(\mathbf{r}, \infty)$. From (4.17)

$$G(\mathbf{r}, t) = \frac{1}{N} \sum_{ij'} \int \langle \delta\{\mathbf{r}' - \mathbf{R}_{j'}(0)\} \delta\{\mathbf{r}' + \mathbf{r} - \mathbf{R}_j(t)\} \rangle d\mathbf{r}'. \quad (4.114)$$

Therefore

$$\begin{aligned} G(\mathbf{r}, \infty) &= \frac{1}{N} \sum_{ij'} \int \langle \delta(\mathbf{r}' - \mathbf{R}_{j'}) \rangle \langle \delta(\mathbf{r}' + \mathbf{r} - \mathbf{R}_j) \rangle d\mathbf{r}' \\ &= \frac{1}{N} \int \langle \rho(\mathbf{r}') \rangle \langle \rho(\mathbf{r}' + \mathbf{r}) \rangle d\mathbf{r}', \end{aligned} \quad (4.115)$$

where $\rho(\mathbf{r})$ is the particle density operator at $t = 0$. The function $G(\mathbf{r}, \infty)$ is known as the *Patterson function* and is used as an aid to structure determination in X-ray scattering by crystals.[†]

The coherent elastic cross-section may be expressed in terms of the Fourier transform of $\langle \rho(\mathbf{r}) \rangle$. From (4.5)

$$\begin{aligned} NI(\kappa, \infty) &= N \int G(\mathbf{r}, \infty) \exp(i\kappa \cdot \mathbf{r}) d\mathbf{r} \\ &= \int \langle \rho(\mathbf{r}') \rangle \langle \rho(\mathbf{r}' + \mathbf{r}) \rangle \exp(i\kappa \cdot \mathbf{r}) d\mathbf{r}' d\mathbf{r} \end{aligned} \quad (4.116)$$

$$= \int \langle \rho(\mathbf{r}') \rangle \langle \rho(\mathbf{r}'') \rangle \exp\{i\kappa \cdot (\mathbf{r}'' - \mathbf{r}')\} d\mathbf{r}' d\mathbf{r}'' \quad (4.117)$$

$$= \left| \int \langle \rho(\mathbf{r}) \rangle \exp(i\kappa \cdot \mathbf{r}) d\mathbf{r} \right|^2. \quad (4.118)$$

[†] See for example Woolfson (1970), Section 8.3.

In taking the step from (4.116) to (4.117) we have put $\mathbf{r}'' = \mathbf{r}' + \mathbf{r}$. Since the integrals with respect to \mathbf{r} and \mathbf{r}'' are over all space and are taken with \mathbf{r}' constant, integrating with respect to \mathbf{r}'' gives the same result as integrating with respect to \mathbf{r} . From (4.109) and (4.118)

$$\left(\frac{d\sigma}{d\Omega}\right)_{\text{coh el}} = \frac{\sigma_{\text{coh}}}{4\pi} \left| \int \langle \rho(\mathbf{r}) \rangle \exp(i\mathbf{\kappa} \cdot \mathbf{r}) d\mathbf{r} \right|^2. \quad (4.119)$$

For the incoherent elastic cross-section, the result corresponding to (4.109) is

$$\begin{aligned} \left(\frac{d\sigma}{d\Omega}\right)_{\text{inel}} &= \frac{\sigma_{\text{inc}}}{4\pi} N I_s(\mathbf{\kappa}, \infty) \\ &= \frac{\sigma_{\text{inc}}}{4\pi} N \int G_s(\mathbf{r}, \infty) \exp(i\mathbf{\kappa} \cdot \mathbf{r}) d\mathbf{r}, \end{aligned} \quad (4.120)$$

where

$$I_s(\mathbf{\kappa}, \infty) = \frac{1}{N} \sum_j \langle \exp(-i\mathbf{\kappa} \cdot \mathbf{R}_j) \rangle \langle \exp(i\mathbf{\kappa} \cdot \mathbf{R}_j) \rangle, \quad (4.121)$$

and

$$G_s(\mathbf{r}, \infty) = \frac{1}{N} \sum_j \langle \delta(\mathbf{r}' - \mathbf{R}_j) \rangle \langle \delta(\mathbf{r}' + \mathbf{r} - \mathbf{R}_j) \rangle d\mathbf{r}'. \quad (4.122)$$

Comparison of (3.128) and (4.120) shows that

$$\begin{aligned} \exp(-2W) &= I_s(\mathbf{\kappa}, \infty) \\ &= \int G_s(\mathbf{r}, \infty) \exp(i\mathbf{\kappa} \cdot \mathbf{r}) d\mathbf{r}, \end{aligned} \quad (4.123)$$

i.e. the Debye-Waller factor is the Fourier transform of $G_s(\mathbf{r}, \infty)$.

4.8 Static approximation

We return to the discussion of the scattering by a general physical system and consider an important limiting case known as the *static approximation*.

From (2.40)

$$\begin{aligned} \left(\frac{d^2\sigma}{d\Omega dE'}\right)_{\text{coh}} &= \frac{\sigma_{\text{coh}}}{4\pi} \frac{k'}{k} \sum_{\lambda} p_{\lambda} \sum_{\lambda'} \left| \sum_j \langle \lambda' | \exp(i\mathbf{\kappa} \cdot \mathbf{R}_j) | \lambda \rangle \right|^2 \\ &\quad \times \delta(E_{\lambda} - E_{\lambda'} + E - E'). \end{aligned} \quad (4.124)$$

E is the energy of the incident neutron and E' the energy of the scattered neutron. Suppose we fix \mathbf{k} and the direction of the scattered neutrons, and consider the cross-section as a function of $|\mathbf{k}'|$, see Fig. 4.3. If k' lies in a small range of values, the value of E' is fixed. For a

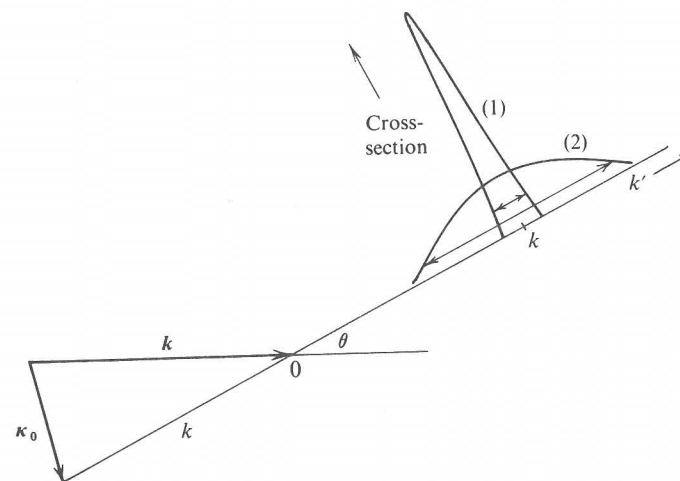
given initial state λ of the scattering system, the δ -function term in the cross-section picks out certain final states λ' , namely, those whose energy is correct for conservation of energy. The sum over λ' is taken only over those states. For each successive interval of k' , a different set of λ' states contribute to the scattering. In the development of the theory in Chapter 2 we changed the operator in the matrix element to a time-dependent one, and summed over all λ' . The result was the same as if we had not changed the operator and summed over the correct limited number of λ' .

The static approximation is to ignore the term $E_{\lambda} - E_{\lambda'}$ in the argument of the δ -function in (4.124). This has two consequences. Firstly, the cross-section becomes a δ -function in $(E - E')$, i.e. the scattering is zero unless $k = k'$. Secondly, in the sum over λ' , instead of the matrix element for each λ' being evaluated at the correct value of $\mathbf{\kappa}$ (determined by the value of k'), all the matrix elements are evaluated at the same value of $\mathbf{\kappa}$, namely $\mathbf{\kappa}_0$, the value of $\mathbf{\kappa}$ when $k' = k$.

If the term $E_{\lambda} - E_{\lambda'}$ is ignored in (4.124) the summation over λ' may be carried out by the closure relation.

$$\begin{aligned} \sum_{\lambda'} \langle \lambda | \exp(-i\mathbf{\kappa}_0 \cdot \mathbf{R}_j) | \lambda' \rangle \langle \lambda' | \exp(i\mathbf{\kappa}_0 \cdot \mathbf{R}_j) | \lambda \rangle \\ = \langle \lambda | \exp[i\mathbf{\kappa}_0 \cdot (\mathbf{R}_j - \mathbf{R}_j)] | \lambda \rangle. \end{aligned} \quad (4.125)$$

Fig. 4.3 Cross-section $d^2\sigma/d\Omega dE'$ as a function of k' for fixed scattering angle. The cross-section is effectively non-zero over a range $\Delta k'$ (shown \leftrightarrow). The static approximation is valid for (1) ($\Delta k' \ll k$), but not for (2).



Thus

$$\left(\frac{d^2\sigma}{d\Omega dE'}\right)_{\text{coh}}^{\text{sa}} = \frac{\sigma_{\text{coh}}}{4\pi} \sum_{\lambda} p_{\lambda} \sum_{jj'} \langle \lambda | \exp\{i\kappa_0 \cdot (\mathbf{R}_j - \mathbf{R}_{j'})\} | \lambda \rangle \delta(E - E'). \quad (4.126)$$

Integration with respect to E' gives

$$\left(\frac{d\sigma}{d\Omega}\right)_{\text{coh}}^{\text{sa}} = \frac{\sigma_{\text{coh}}}{4\pi} \sum_{jj'} \langle \exp\{i\kappa_0 \cdot (\mathbf{R}_j - \mathbf{R}_{j'})\} \rangle \quad (4.127)$$

$$= \frac{\sigma_{\text{coh}}}{4\pi} NI(\kappa_0, 0). \quad (4.128)$$

Alternatively, we may use the formalism of $G(\mathbf{r}, t)$ and $S(\kappa, \omega)$. From (4.8) and (4.12)

$$\left(\frac{d^2\sigma}{d\Omega dE'}\right)_{\text{coh}} = \frac{\sigma_{\text{coh}}}{4\pi} \frac{k'}{k} \frac{N}{2\pi\hbar} \int G(\mathbf{r}, t) \exp\{i(\kappa \cdot \mathbf{r} - \omega t)\} d\mathbf{r} dt. \quad (4.129)$$

Again we keep the scattering angle, i.e. the direction of \mathbf{k}' , fixed and integrate with respect to E' . In the correct calculation κ varies with E' . But in the static approximation the cross-section is a δ -function in $(E' - E)$. So the only contribution to the integral comes from $\kappa = \kappa_0$. Since

$$E - E' = \hbar\omega, \quad dE' = -\hbar d\omega. \quad (4.130)$$

Thus

$$\begin{aligned} \left(\frac{d\sigma}{d\Omega}\right)_{\text{coh}}^{\text{sa}} &= \int \left(\frac{d^2\sigma}{d\Omega dE'}\right)_{\text{coh}}^{\text{sa}} dE' \\ &= \frac{\sigma_{\text{coh}}}{4\pi} \frac{N}{2\pi} \int G(\mathbf{r}, t) \exp\{i(\kappa_0 \cdot \mathbf{r} - \omega t)\} d\mathbf{r} dt d\omega \\ &= \frac{\sigma_{\text{coh}}}{4\pi} N \int G(\mathbf{r}, t) \exp(i\kappa_0 \cdot \mathbf{r}) \delta(t) d\mathbf{r} dt \\ &= \frac{\sigma_{\text{coh}}}{4\pi} N \int G(\mathbf{r}, 0) \exp(i\kappa_0 \cdot \mathbf{r}) d\mathbf{r} \\ &= \frac{\sigma_{\text{coh}}}{4\pi} NI(\kappa_0, 0) \quad \text{as before.} \end{aligned} \quad (4.131)$$

Note that although the static approximation gives elastic scattering, the resulting cross-section is not the same as the cross-section for true elastic scattering. The former – (4.127) – includes scattering for all final states λ' . The latter – (4.113) – contains only terms with $\lambda' = \lambda$.

Condition for validity of static approximation

Since, in the static approximation, κ is replaced by κ_0 in the matrix elements of (4.124), the approximation will be a good one if, for values of k' not close to k , the states λ' specified by conservation of energy give matrix elements $\sum_j \langle \lambda' | \exp(i\kappa \cdot \mathbf{R}_j) | \lambda \rangle$ which are small.

The matrix elements become small as $|E_{\lambda'} - E_{\lambda}|$ increases beyond a certain value, because for most scattering systems there is an upper limit to the amount of energy that can be transferred to the neutron. Call this upper limit E_0 . For a crystal $E_0 \sim \hbar\omega_m$, where ω_m is the maximum frequency of a phonon. For a liquid $E_0 \sim \hbar/t_0$, where t_0 is the relaxation time for a disturbance in the liquid. The values of k' therefore lie between a maximum and minimum value given by

$$\frac{\hbar^2}{2m}(k_{\text{max}}^2 - k^2) \sim E_0, \quad \frac{\hbar^2}{2m}(k^2 - k_{\text{min}}^2) \sim E_0. \quad (4.132)$$

If the maximum and minimum values are not very different from the value of k , (4.132) becomes

$$\frac{\hbar^2}{m} k' \Delta k' \sim E_0, \quad (4.133)$$

where $\Delta k'$ is the range of k' (Fig. 4.3). Putting $E = \hbar^2 k^2 / 2m$ gives

$$\frac{\Delta k'}{k} \sim \frac{E_0}{E}. \quad (4.134)$$

The condition for the validity of the static approximation is $\Delta k' \ll k$. From (4.134) this is equivalent to

$$E_0 \ll E, \quad (4.135)$$

i.e. the energy that can be transferred to and from the scattering system is small compared to the energy of the incident neutron.

We may express this condition another way. If v is the velocity and λ the wavelength of the incident neutron,

$$E = \frac{1}{2}mv^2 \approx \hbar kv \approx \frac{\hbar v}{\lambda}. \quad (4.136)$$

The condition $E_0 \ll E$ therefore becomes

$$\frac{1}{t_0} \ll \frac{v}{\lambda}. \quad (4.137)$$

Now for scattering to occur other than in the forward direction λ must be of the order of or larger than a , the interatomic spacing in the

scattering system. Thus

$$\frac{\lambda}{v} \geq \frac{a}{v} \sim t_1, \quad (4.138)$$

where t_1 is the time taken by the neutron to cross from one atom to the next. So another way of expressing the condition for the validity of the static approximation is

$$t_1 \ll t_0, \quad (4.139)$$

i.e. the time taken for the neutron to cross from one atom to the next is small compared to the characteristic oscillation or relaxation time of the scattering system.

Comments on scattering theory

We bring together the basic results for the coherent cross-sections.

General result:

$$\left(\frac{d^2\sigma}{d\Omega dE'} \right)_{\text{coh}} = \frac{\sigma_{\text{coh}}}{4\pi} \frac{k'}{k} NS(\kappa, \omega), \quad (4.140)$$

$$S(\kappa, \omega) = \frac{1}{2\pi\hbar} \int G(\mathbf{r}, t) \exp\{i(\kappa \cdot \mathbf{r} - \omega t)\} d\mathbf{r} dt. \quad (4.141)$$

Static approximation:

$$\begin{aligned} \left(\frac{d\sigma}{d\Omega} \right)_{\text{coh}}^{\text{sa}} &= \frac{\sigma_{\text{coh}}}{4\pi} N \int G(\mathbf{r}, 0) \exp(i\kappa_0 \cdot \mathbf{r}) d\mathbf{r} \\ &= \frac{\sigma_{\text{coh}}}{4\pi} N \left\{ 1 + \int g(\mathbf{r}) \exp(i\kappa_0 \cdot \mathbf{r}) d\mathbf{r} \right\}. \end{aligned} \quad (4.142)$$

The last line follows from (4.27).

Eq. (4.140) shows that the cross-section is essentially the product of two factors. The first factor σ_{coh} depends on the interaction between the neutron and the individual particles in the scattering system. The second factor $S(\kappa, \omega)$ does not depend on the properties of the neutron at all, neither on its intrinsic properties – mass, energy, etc. – nor on its interaction with the particles in the scattering system. It is a property only of the scattering system and depends on the relative positions and motions of the particles in the system. These depend on the forces between the particles, and on the temperature of the system.

This separation of the cross-section into two factors applies, not only to the scattering of thermal neutrons, but to the scattering of any

particle – X-rays, electrons, etc. – provided the Born approximation is valid for the scattering process, and there is no correlation between scattering length (or the equivalent physical parameter for X-rays, etc.) and atomic site.

The scattering function $S(\kappa, \omega)$ is the Fourier transform in space and time of $G(\mathbf{r}, t)$, the time-dependent pair-correlation function. When the static approximation applies, the cross-section is proportional to the Fourier transform of $G(\mathbf{r}, 0)$, the static pair-correlation function. The relevance of the time variation of the pair-correlation function comes from the interference aspect of scattering. Whatever the nature of the incident particles they may be regarded as waves. The waves scattered by the particles in the scattering system interfere, and their relative phases depend on the relative positions of the particles. Consider the scattering by two particles j' and j . The incident wave reaches j' at time zero and j at time t . The phase difference between the two scattered waves depends on the position of atom j at time t relative to that of j' at time zero. Hence the scattering depends on $G(\mathbf{r}, t)$. When the static approximation applies, the waves travel so fast that in the interval between the two scattering events the particle j has not had time to move. Hence the scattering depends on $G(\mathbf{r}, 0)$.

For most condensed systems the characteristic time for oscillation or relaxation is

$$t_0 \sim 10^{-13} \text{ to } 10^{-12} \text{ s.}$$

The atomic spacing a is $\sim 10^{-10}$ m. For X-rays or light, travelling with velocity c , the time t_1 for the incident radiation to pass from one particle in the scattering system to the next is

$$t_1 \sim \frac{a}{c} \sim 10^{-18} \text{ s.}$$

Thus $t_1 \ll t_0$ and the static approximation is valid. The scattering of light and X-rays can therefore give information only about $G(\mathbf{r}, 0)$, the static pair-correlation function. For thermal neutrons

$$v \sim 10^3 \text{ m s}^{-1}, \text{ and } t_1 \sim 10^{-13} \text{ s.}$$

Thus the static approximation does not apply. The scattering of thermal neutrons gives information about $G(\mathbf{r}, t)$ for all values of t . It is this property that makes it such a useful tool for studying the properties of condensed matter.

Examples

4.1 Prove that for a perfect gas of atoms of mass M at temperature T the classical form of $G_s(\mathbf{r}, t)$ is

$$G_s^{\text{cl}}(\mathbf{r}, t) = \{2\pi\sigma_{\text{cl}}^2(t)\}^{-3/2} \exp\{-r^2/2\sigma_{\text{cl}}^2(t)\},$$

where

$$\sigma_{\text{cl}}^2(t) = t^2/M\beta.$$

4.2 Prove the following results for an isotropic harmonic oscillator of mass M and frequency ω .

$$(a) \quad I_s(\boldsymbol{\kappa}, t) = \exp\{-\kappa^2\sigma^2(t)/2\},$$

$$G_s(\mathbf{r}, t) = \{2\pi\sigma^2(t)\}^{-3/2} \exp\{-r^2/2\sigma^2(t)\},$$

$$\text{where } \sigma^2(t) = \frac{\hbar}{M\omega} \left\{ \coth\left(\frac{1}{2}\hbar\omega\beta\right)(1 - \cos \omega t) - i \sin \omega t \right\}.$$

$$(b) \quad \tilde{I}_s(\boldsymbol{\kappa}, t) = \exp\{-\kappa^2\tilde{\sigma}^2(t)/2\},$$

$$\text{where } \tilde{\sigma}^2(t) = \frac{\hbar}{M\omega} \left\{ \coth\left(\frac{1}{2}\hbar\omega\beta\right) - \text{cosech}\left(\frac{1}{2}\hbar\omega\beta\right) \cos \omega t \right\}.$$

(c) The classical form of $I_s(\boldsymbol{\kappa}, t)$ is

$$I_s^{\text{cl}}(\boldsymbol{\kappa}, t) = \exp\{-\kappa^2\sigma_{\text{cl}}^2(t)/2\},$$

where

$$\sigma_{\text{cl}}^2(t) = \frac{2}{M\omega^2\beta}(1 - \cos \omega t).$$

(d) The classical expression for $\langle r^2(t) \rangle$, the mean-square distance between the positions of the particle at times zero and t , is

$$\langle r_{\text{cl}}^2(t) \rangle = \frac{6}{M\omega^2\beta}(1 - \cos \omega t).$$

Comment. It follows from the above results that, for a cubic Bravais crystal, $I_s(\boldsymbol{\kappa}, t)$ and $G_s(\mathbf{r}, t)$ have the same form as for a single oscillator, with $\sigma^2(t)$ given by

$$\sigma^2(t) = \frac{\hbar}{M} \int_0^{\omega_m} \frac{Z(\omega)}{\omega} \left\{ \coth\left(\frac{1}{2}\hbar\omega\beta\right)(1 - \cos \omega t) - i \sin \omega t \right\} d\omega. \quad (4.143)$$

Similarly, the classical expression for the mean-square distance between the positions of an atom at times zero and t is

$$\langle r_{\text{cl}}^2(t) \rangle = \frac{6}{M\beta} \int_0^{\omega_m} \frac{Z(\omega)}{\omega^2} (1 - \cos \omega t) d\omega. \quad (4.144)$$

4.3 Show that for a Bravais crystal

$$\begin{aligned} \sum_{l'} \langle \exp(-i\boldsymbol{\kappa} \cdot \mathbf{R}_{l'}) \rangle \langle \exp(i\boldsymbol{\kappa} \cdot \mathbf{R}_l) \rangle \\ = N \frac{(2\pi)^3}{v_0} \exp(-2W) \sum_{\boldsymbol{\tau}} \delta(\boldsymbol{\kappa} - \boldsymbol{\tau}). \end{aligned}$$

4.4 (a) The atoms of a cubic Bravais crystal have mean-square displacement $\langle u^2 \rangle$. Show that the thermal average of the particle density operator is

$$\langle \rho(\mathbf{r}) \rangle = (\pi\sigma^2)^{-3/2} \sum_l \exp\{-(\mathbf{r} - \mathbf{l})^2/\sigma^2\},$$

where

$$\sigma^2 = \frac{2}{3}\langle u^2 \rangle.$$

(b) Hence or otherwise show that the self pair-correlation function at $t = \infty$ is

$$G_s(\mathbf{r}, \infty) = (2\pi\sigma^2)^{-3/2} \exp(-r^2/2\sigma^2).$$

(c) If r is the distance between the positions of an atom at two instants a long time apart, show that

$$\langle r^2 \rangle = 2\langle u^2 \rangle.$$

4.5 Show that for incoherent one-phonon scattering from a cubic Bravais crystal at high temperature ($\hbar\omega\beta \ll 1$)

$$S_i(\boldsymbol{\kappa}, \omega) = \frac{\kappa^2}{2M\hbar\beta} \exp(-2W) \frac{Z(\omega)}{\omega^2}.$$