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Chap IX Thermal Neutron Scattering

Ref: W. Marshall and S. W. Lovesey, Theory of Thermal Neutron Scattering (Oxford. 1971).
S. H. Chen and S. Yip, eds. Spectroscopy in Biology and Chemistry, Neutron, X-ray, and Laser (Academic Press, 1974), chaps. 1 and 2.

Our objective in this chapter is to formulate the calculation of the double differential scattering cross section $d^2\sigma/d\Omega dE$ for the scattering of thermal neutrons, and to consider briefly the use of thermal neutrons to probe the structure and dynamics of liquids and solids.

A. Fermi Approximation

This is the basic approximation in the development of the theory of thermal neutron scattering. It consists of two parts: the first Born approximation and the use of the Fermi pseudopotential. We will see that the pseudopotential is necessary because the actual nuclear potential (see, for example, (7.1)) is too strong for the Born approximation to be applicable, and it is only by using instead the Fermi pseudopotential that one can justify the Born approximation under the low-energy condition. The 'trick' is to show that the scattering problem has not been altered when we switch to a different potential.

We recall from Chap. VI the scattering amplitude is given by (cf. (6.64))

$$f(\theta) = -\frac{m}{2\pi\hbar^2}\int d^3r\,\exp(i\underset{\wedge}{\bar{\underline{k}}}\cdot\underline{r})\;V(\underline{r})\;\psi_k(\underline{r}) \qquad (9.1) \qquad \longleftarrow$$

where m is the neutron mass, $V(\underline{r})$ the neutron-nucleus interaction, and $\psi_k(\underline{r})$ the neutron wave function. In writing (9.1) it is understood that the incident neutron has energy $E = \hbar^2k^2/2m$. For neutrons of thermal energy, the associated deBroglie wavlength is such that the parameter which is a measure of energy is exceedingly small,

$$kr_o < 10^{-4} \qquad (9.2)$$

because the potential range r_o is typically only a few fermis (10^{-13} cm). This fact is essential to the development of the Fermi approximation.

An immediate consequence of the low-energy condition (9.2) is that to calculate the scattering cross section σ, or equivalently the scattering length a, where $\sigma = 4\pi a^2$, one needs only to evaluate

$$a = -f(\theta)|_{k\to 0}$$

$$= \frac{m}{2\pi\hbar^2}\int d^3r\ V(\underline{r})\ \psi_o(\underline{r}) \longrightarrow \frac{2m}{\hbar^2}\, r_o^3 \int_0^1 dx\ x^2\ V(x)\ \psi_o(x) \qquad (9.3)$$

where the arrow means that for $V(\underline{r})$ we take a spherically symmetric potential of range r_o. In order to avoid having to determine the wave function ψ_o we invoke the Born approximation. Because we are working in the low-energy limit (9.2), the approximation is tantamount to taking ψ_o to be unity. Then (9.3) becomes

$$a \simeq \frac{m}{2\pi\hbar^2}\int d^3r\ V(\underline{r}) \longrightarrow \frac{m}{2\pi\hbar^2}\, 4\pi r_o^3\ V_{avg} \qquad (9.4)$$

where

$$V_{avg} = \int_0^1 dx\ x^2\ V(x) \qquad (9.5)$$

If the Born approximation were valid, the scattering cross section σ can be calculated by using (9.4) which gives the scattering length as a volume integral of the interaction potential. However, the matter is not so simple because one can check the condition for the validity of the Born approximation, the low-energy condition (6.74), by using typical values for the well depth V_o and range r_o. What one finds is that $mV_o\hat{r}{}^2/\hbar^2$ is of order unity and therefore does not satisfy the requirement of

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$$mV_o r_o^2/\hbar^2 \ll 1 \qquad (9.6)$$

One may conclude from the foregoing considerations that the Born approximation is simply not applicable to thermal neutron scattering because the nuclear potential is too strong. There is, however, a way to get around this difficulty. It was observed by E. Fermi that because of (9.2) one can remain in the low-energy limit of $kr_o \ll 1$ even if the range r_o is made considerably greater than the actual range of the nuclear potential. This suggests that a fictitious potential be used to describe the neutron-nucleus interaction, one which has a greater range but smaller well depth such that (9.5) is satisfied. In other words, we imagine there is a fictitious potential in the form of a square well with depth V^* and range r_o^* which we will use in place of the actual nuclear square-well potential of depth V_o and range r_o. In order to ensure that we have not changed the problem, we need to make sure that three conditions are satisfied. The first is that we are still dealing with scattering in the low-energy limit, i.e.,

$$kr_o^* \ll 1 \tag{9.7}$$

The second is that

$$r_o^{*3} V^*_{avg} = r_o^3 V_{avg} \tag{9.8}$$

which means that the scattering length, or the cross section σ, calculated is the same. The third condition is that

$$mV_o^* r_o^{*2}/\hbar^2 \ll 1 \tag{9.9}$$

which will allow us to apply the Born approximation in conjunction with the fictitious potential.

In view of (9.2) and the fact that the left hand side of (9.5) is of order unity, we see that by taking $r_o^* = 10^2 r_o$ and $V_o^* = 10^{-6} V_o$ we can simulatneously preserve the scattering length or condition (9.8), maintain the low-energy limit (9.7) with $kr_o^* \sim 10^{-2}$, and satisfy (9.9) since the left hand side is then of order 10^{-2}. Compared to the nuclear potential we have used in the optical model calculation in Chap. VII, the desired fictitious potential has a much longer range and shallower depth. It turns out that the precise shape of the fictitious potential does not enter into the discussion because we are only interested in determining the scattering length a which depends only on the volume integral of the potential,

$$a = \frac{m}{2\pi\hbar^2} \int d^3r \, V^*(r) \tag{9.10}$$

Fermi suggested that since the deBroglie wavelength $2\pi/k$ is so much longer than r_o^*, to a thermal neutron the real or the fictitious interaction is still an impulse (interaction concentrated over a very small region in space). Therefore, one may as well represent the interaction by a delta function and take

$$V^*(\underline{r}) = \frac{2\pi\hbar^2}{m} a \, \delta(\underline{r}) \tag{9.11}$$

Notice the coefficient in (9.11) is chosen such that inserting this V^* into (9.10) produces an identity. This is a way of making sure the scattering length enters correctly into the theory. In other words, we are no longer calculating the scattering length, rather we put in this information through the fictitious potential; we will henceforth call (9.11) the Fermi pseudopotential. In its formulation the scattering length a is regarded as an experimentally determined constant (see Sec. C below).

The pseudopotential (9.11) applies to the problem of scattering by a single nucleus situated at the origin. For a scattering target system composed of N nuclei, the Fermi pseudopotential takes the form (we will henceforth suppress the superscript *)

$$V(\underline{r}) = \frac{2\pi\hbar^2}{m} \sum_{\ell=1}^{N} a_\ell \, \delta(\underline{r} - \underline{R}_\ell) \tag{9.12}$$

where $\underline{r}$ denotes the neutron position and $\underline{R}_\ell$ the position of ℓth nucleus. [The original derivation of the pseudopotential by Fermi appeared in Riccerca Scientifica 13 (1936), AEC Translation NP-2385 (1951).]

B. Derivation of Double Differential Scattering Cross Section

Having developed a suitable potential for use in conjunction with the Born approximation, we now make use of the cross section formulation discussed in detail in Chap. VI. We begin with the wave equation

$$[\frac{p^2}{2m} + H_s + V] \, \Psi(\underline{r},\underline{R}) = \epsilon \, \Psi(\underline{r},\underline{R}) \tag{9.13}$$

where H_s is the Hamiltonian of the target system which will remain unspecified until later when we will treat specific model systems, and $\underline{R}$ represents all the nuclear positions in the target system, $(\underline{R}_1, \ldots, \underline{R}_N)$. We can treat (9.13) in the same manner as the analysis of electron scattering (see Chap. VIII, Sec. A). We expand the total wave function Ψ in terms of the eigenfunctions of the target system, $|n\rangle$, defined formally as

$$H_s \, |n\rangle = \epsilon_n \, |n\rangle \tag{9.14}$$

with $\langle n|n'\rangle = \delta_{nn'}$. Thus,

$$\Psi(\underline{r}, \underline{R}) = \sum_n \psi_n(\underline{r}) \, |n\rangle \tag{9.15}$$

and (9.13) becomes

$$(\nabla^2 + k_n^2) \, \psi_n(\underline{r}) = \frac{2m}{\hbar^2} \sum_{n'} \langle n|V|n'\rangle \, \psi_{n'}(\underline{r}) \tag{9.16}$$

with the neutron wavenumber k_n defined as

$$\hbar^2 k_n^2/2m = \epsilon - \epsilon_n \tag{9.17}$$

As before we can convert (9.16) into an integral equation by making use of the Green's function $G_n(\underline{r} - \underline{r}')$ (see (6.51) and (6.52)) and its asymptotic form for large r (see (6.60) and (6.62)),

$$G_n(\underline{r} - \underline{r}') \simeq \frac{1}{4\pi r} e^{ik_n r} \exp(-ik_n \hat{\underline{r}} \cdot \underline{r}') \tag{9.18}$$

The integral equation in a form suitable for the application of the Born approximation is

$$\psi_n(\underline{r}) \sim \delta_{nn_o} \exp(i\underline{k}_i \cdot \underline{r}) + \frac{e^{ik_n r}}{r} \left[\frac{m}{2\pi\hbar^2}\right] \sum_{n'} \int d^3r' \exp(-i\underline{k}_n \cdot \underline{r}') V_{nn'} \psi_{n'}(\underline{r}') \tag{9.19}$$

where $V_{nn'}$ denotes the matrix elements in the right hand side of (9.16). The Born approximation therefore consists of replacing $\psi_{n'}(\underline{r}')$ in the integral in (9.19) by the first term in (9.19) which represents the unscattered wave. This then leads to the familiar expression for the scattering amplitude $f(\theta)$, namely , the Fourier transform of the potential function

$$f(\theta) = -\frac{m}{2\pi\hbar^2} \int d^3r \exp(i\underline{Q}_n \cdot \underline{r})\, V_{nn_o}(\underline{r}) \tag{9.20}$$

where $\underline{Q}_n = \underline{k}_i - \underline{k}_n$ is the neutron wavevector transfer. Since $V_{nn_o}(\underline{r})$ is the matrix element of the Fermi pseudopotential (9.12) between final and initial target states, $|n\rangle$ amd $|n_o\rangle$ respectively, the $\underline{r}$-integral in (9.20) is immediately doable, and one obtains

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$$f(n_o \rightarrow n) = -\sum_{\ell=1}^{N} a_\ell \langle n| \exp(i\underline{Q}_n \cdot \underline{R}_\ell) |n_o\rangle \tag{9.21}$$

This result can be regarded as the generalization of the scattering amplitude for two-body scattering, where f = -a, to a target system composed of N scattering centers.

Given the scattering amplitude (9.21), the differential scattering cross section follows,

$$\left(\frac{d\sigma}{d\Omega}\right)_{n_o \rightarrow n} = \frac{k_n}{k_i} \frac{1}{N} |f(n_o \rightarrow n)|^2 \tag{9.22}$$

The factor 1/N appears to make $d\sigma/d\Omega$ a cross section per nucleus. Because it is the cross section for the target system to go from initial state $|n_o\rangle$ to final state $|n\rangle$, (9.22) is not the quantity one observes in a normal neutron scattering measurement where neither the initial nor the final states of the target can be specified. The quantity measured in an experiment corresponds to averaging (9.22) over all initial states and summing over all final states. Thus,

$$\frac{d\sigma}{d\Omega} = \frac{1}{N}\sum_{n}\sum_{n_o} P(n_o)\,\frac{k_n}{k_i}\,|f(n_o \rightarrow n)|^2 \qquad (9.23)$$

where P(n) is the probability that the target system, being in thermal equilibrium at temperature T, is in the state $|n\rangle$.

$$P(n) = \exp(-\beta\epsilon_n)\,[\sum_s \exp(-\beta\epsilon_s)]^{-1} \qquad (9.24)$$

where $\beta = 1/k_BT$.

Thus far we have been interested in the angular differential scattering cross section throughout the course. We can also formulate a calculation of the energy differential cross section $d\sigma/dE_f$ which is a measure of the probability of the incident particle leaving with energy E_f after the scattering. If we imagine a general scattering process in which a beam of particles each with incident energy E_i and momentum $h\underline{k}_i$ is scattered at an angle θ with outgoing energy E_f and momentum $h\underline{k}_f$, as shown in Fig. 9.1, then we can associate the scattered intensity measured at the detector with a <u>double differential scattering cross section</u> $d^2\sigma/d\Omega dE_f$.

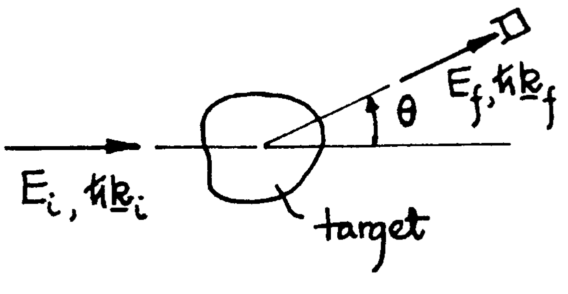

Fig. 9.1 Scattering arrangement for defining the double differential scattering cross section.

In terms of the scattering amplitude $f(n_o \rightarrow n)$ we have derived, the double differential scattering cross section can be written as

$$\frac{d^2\sigma}{d\Omega dE_f} = \frac{1}{N}\frac{k_f}{k_i}\sum_{nn_o} P(n_o)\,|f(n_o\to n)|^2\,\delta(E_f + \epsilon_n - E_i - \epsilon_{n_o}) \tag{9.25}$$

The delta function ensures that energy is conserved in the system of neutron plus target. Notice that (9.25) obviously satisfies the general relation between single and double differential cross sections,

$$\frac{d\sigma}{d\Omega} = \int dE_f\,\frac{d^2\sigma}{d\Omega dE_f} \tag{9.26}$$

We will see below that it is useful to regard (9.25) as essentially a function of two variables, the neutron energy and momentum transfers, or the frequency ω and wave vector $\underline{Q}$,

$$\hbar\omega = E_i - E_f \tag{9.27}$$

$$\hbar\underline{Q} = \hbar(\underline{k}_i - \underline{k}_f) \tag{9.28}$$

As a result we will denote the double differential scattering cross section as $(1/\hbar)d^2\sigma/d\Omega d\omega$.

Space-time Representation

For purposes of interpretation as well as later calculations, we will cast (9.25), a function of wavenumber and frequency, into a space- and time-dependent form. We begin by noting the integral representation of the delta function,

$$\delta(x) = \frac{1}{2\pi}\int_{-\infty}^{\infty} dt\; e^{itx} \tag{9.29}$$

Applying this result to (9.25) we find

$$\frac{d^2\sigma}{d\Omega d\omega} = \frac{k_f}{k_i}\frac{1}{2\pi N}\int_{-\infty}^{\infty} dt\; e^{-it(E_f - E_i)/\hbar}\,\Lambda(Q,t) \tag{9.30}$$

with

$$\Lambda(Q,t) = \sum_{nn_o} P(n_o)\, e^{-it(\epsilon_n - \epsilon_{n_o})/\hbar}\,|f(n_o\to n)|^2 \tag{9.31}$$

Using (9.21) we can rearrange $\Lambda(Q,t)$ to read

$$\Lambda(Q,t) = \sum_{\ell\ell'} a_\ell a_{\ell'} \sum_{n_o} p(n_o)$$

$$\sum_n \langle n_o|\exp(-i\underline{Q}\cdot\underline{R}_{\ell'})\exp(-itH_s/\hbar)|n\rangle\langle n|\exp(i\underline{Q}\cdot\underline{R}_\ell)\exp(itH_s/h)|n_o\rangle \qquad (9.32)$$

where we have eliminated ϵ_n by using the property (9.14). The advantage of doing this is that the n-sum in (9.32) then can be carried out, by invoking the closure property of the states $|n\rangle$,

$$\sum_n \langle n'|A|n\rangle\langle n|B|n''\rangle = \langle n'|AB|n''\rangle \qquad (9.33)$$

to give

$$\langle n_o|e^{itH_s/h}\exp(-i\underline{Q}\cdot\underline{R}_{\ell'})\, e^{-itH_s/h}\exp(i\underline{Q}\cdot\underline{R}_\ell)|n_o\rangle$$

$$= \langle n_o|\exp(-i\underline{Q}\cdot\underline{R}_{\ell'}(t))\exp(i\underline{Q}\cdot\underline{R}_\ell)|n_o\rangle \qquad (9.34)$$

where $\underline{R}_{\ell'}(t)$ is the Heisenberg operator (see (5.88)). Then (9.32) becomes

$$\Lambda(Q,t) = \sum_{\ell\ell'} a_\ell a_{\ell'} \langle\exp(\overset{-i\underline{Q}\cdot\underline{R}_{\ell'}(t)}{\underset{-}{i}\underline{Q}\cdot\underline{R}_{\underset{\ell'}{\ell}}})\exp(\overset{i\underline{Q}\cdot\underline{R}_\ell}{-i\underline{Q}\cdot\cancel{\underline{R}_{\ell'}(t)}})\rangle \qquad (9.35)$$

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where the angular brackets < > denote a thermal average (cf. (5.75)),

$$\langle A\rangle = \sum_n P(n)\langle n|A|n\rangle \qquad (9.36)$$

Combining these results, we have for the double differential cross section

$$\frac{d^2\sigma}{d\Omega d\omega} = \left[\frac{E_f}{E_i}\right]^{1/2} a^2\, S(Q,\omega) \qquad (9.37)$$

where

$$S(Q,\omega) = \frac{1}{2\pi}\int_{-\infty}^{\infty} dt\, e^{i\omega t}\,\frac{1}{N}\langle\sum_{\ell'}\exp(\overset{-i}{\cancel{i}}\underline{Q}\cdot\underline{R}_{\underset{\ell'}{\boxed{\ell}}}^{(t)})\sum_{\ell}\exp(\cancel{-}i\underline{Q}\cdot\underline{R}_{\ell}\cancel{(t)})\rangle \qquad (9.38)$$

In writing (9.37) we have assumed the target system is monoisotopic and the nuclei have no spin, in which case the scattering length a_ℓ is the same for all nuclei so we can put $a_\ell = a$.

The function $S(Q,\omega)$ is called the dynamic structure factor; it is perhaps the single most important quantity in the discussion of inelastic scattering of thermal neutrons. We will have much opportunity to investigate its significance in the following. For the moment we note that this function depends only on a wave vector $\underset{\sim}{Q}$ and a frequency ω, and it is purely a property of the target system. It is useful that the double differential cross section is separable into a product of factors, $(E_f/E_i)^{1/2}$ a, which explicitly refer to neutron scattering, and $S(Q,\omega)$, which represents the generalized response of the target to a density fluctuation. One can expect that $S(Q,\omega)$ is a fundamental structural and dynamical property of the traget that is of more general interest than in the ccontext of neutron scattering. It turns out that neutron scattering is just one of several different methods of studying $S(Q,\omega)$, and through $S(Q,\omega)$ one can relate the information provided by neutron and other experimental techniques, as well as results obtained by theoretical calculations and computer simulations. We will have more to say about this point of view in Sec. D when we discuss time-dependent correlation functions.

C. Coherent and Incoherent Scattering

Before we proceed with further theoretical discussions, it is necessary to recognize the existence of two types of scattering processes known as coherent and incoherent. [For readable overviews without the complexitites of inelastic scattering, see G. E. Bacon, Neutron Diffraction (Clarendon Press, Oxford, 1975), 3rd ed., G. E. Bacon, Neutron Scattering in Chemistry (Butterworths, London, 1977), and D. J. Hughes, Neutron Optics (Interscience, New York, 1954).] The distinction between coherent and incoherent neutron scattering refers to whether the scattered intensity has contribution from different scattering centers. To explain what is meant by this we will consider a simple illustration. Fig. 9.2 shows that the incident wave scattered at nuclei ℓ and ℓ' gives rise to spherical outgoing waves which are observed at the detector. Since the observed intensity is the absolute value square of the scattered wave and the scattered wave is a sum of waves originating from different scattering centers, we can express the scattered intensity as the sum of direct scattering contributions and

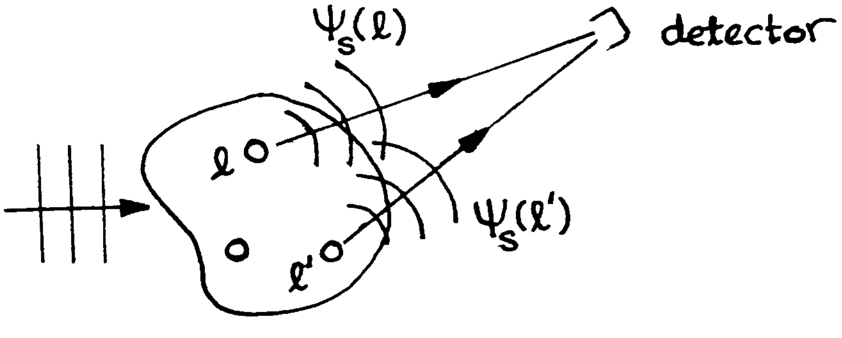


Fig. 9.2 Neutron scattering from a system of target nuclei giving rise to direct scattering and interference effects.

interference terms,

$$I \sim |\sum_{\ell} \psi_s(\ell)|^2$$

$$= \sum_{\ell} |\psi_s(\ell)|^2 + \sum_{\ell,\ell'}{}' \psi_s^*(\ell)\ \psi_s(\ell') \tag{9.39}$$

where $\psi_s(\ell)$ is the scattered wave originating at target nucleus ℓ, and the prime on the summation symbol in (9.39) means that terms for which $\ell = \ell'$ are to be omitted.

In (9.39) the two types of contributions clearly can be intergreted as direct (or single-particle) scattering from the individual nuclei and interference (or collective) scattering from pairs of nuclei. The direct scattering part of (9.39) is called <u>incoherent</u>, whereas the sum of direct and interference contributions is called <u>coherent</u>. It is natural to wonder at this point why one would want to give the direct scattering contribution a distinct name if the observed intensity is always the sum of both contributions. The answer lies in the fact that it is possible in neutron scattering to measure only the direct scattering part, and this is because of the presence of the scattering length a which can vary from one nucleus to another.

There are two reasons why the scattering length of a nucleus can fluctuate in a target system. One is that scattering lengths are known to vary from one isotope to another (because neutron scattering is nuclear interaction and different isotopes can have different nuclear configurations), and the other is that neutron-nuclear interaction is spin-dependent such that if the target nuclei have nonzero spin $\underline{I}$, then different nuclei can couple to the neutron in different spin orientations. In both cases, the variation of a from one nucleus to another has to be taken into account in separating the observed intensity.

Instead of (9.39) we now write the observed intensity as an average over the distribution of isotopes in the target and over the possible oreintations of the coupled neutron-nuclear spins,

$$I \sim \sum_{\ell,\ell'} \overline{a_{\ell} a_{\ell'}}\ \psi_s^*(\ell)\ \psi_s(\ell') \tag{9.40}$$

where the bar denotes both isotope and spin-orientation averages. We note that in separating out the $\ell = \ell'$ and $\ell \neq \ell'$ terms, one has

$$\overline{a_{\ell} a_{\ell'}} = \overline{a_{\ell}^2} = \overline{a^2}, \qquad \ell = \ell' \tag{9.41}$$

$$\overline{a_{\ell} a_{\ell'}} = \overline{a}_{\ell}\, \overline{a}_{\ell'} = (\overline{a})^2, \qquad \ell \neq \ell' \tag{9.42}$$

Because each nucleus is treated equally (the implicit assumption here is that nuclei have random distributions in the target), the $\ell = \ell'$ term gives the average of the square while the $\ell \neq \ell'$ terms gives the square of the average. Combining (9.41) and (9.42) we can write in general,

$$\overline{a_{\ell} a_{\ell'}} = a^2_{inc}\, \delta_{\ell\ell'} + a^2_{coh} \tag{9.43}$$

with

$$a^2_{inc} = \overline{a^2} - (\bar{a})^2 \tag{9.44}$$

and

$$a_{coh} = \bar{a} \tag{9.45}$$

The appearance of the incoherent and coherent scattering lengths a_{inc} and a_{coh} in (9.43) is seen to be consistent with our foregoing definitions of incoherent and coherent processes, namely, incoherence is associated with direct scattering, the contributions from $\ell = \ell'$, and coherent is the contribution from both $\ell = \ell'$ and $\ell \neq \ell'$. It is important to note that in the definitions (9.44) and (9.45) a_{coh} is simply the average scattering length, whereas a_{inc} only exists if there are fluctuations in the scattering length, the condition for which the variance is nonzero.

In view of (9.43) - (9.45) we can now write out explicitly what we mean by the isotope and spin-orientation averages. Suppose our target system has a distribution of isotopes, each labeled by an index p, and let I_p be the nuclear spin of isotope p, then

$$\overline{a^2} = \sum_p C_p \left[(I_p+1)(a^p_+)^2 + I_p(a^p_-)^2\right] / (2I_p+1) \tag{9.46}$$

$$\bar{a} = \sum_p C_p \left[(I_p+1)a^p_+ + I_p a^p_-\right] / (2I_p+1) \tag{9.47}$$

where C_p is the relative abundance of isotope p in the target, and a^p_+ (or a^p_-) is the scattering length for the neutron and nuclear spins in the parallel (or antiparallel) orientation. [Recall that in the case of neutron scattering by a proton, the parallel and antiparallel spin oriuentationns give rise to triplet (total spin 1 and therefore 3 possible orientations) and singlet (total spin zero) scattering lengths.]

Eq.(9.43) is result we need to separate the coherent and incoherent scattering. Upon inserting it into (9.30) with $\Lambda(Q,t)$ given by (9.35), we find the double differential cross section in the form,

$$\frac{d^2\sigma}{d\Omega d\omega} = (E_f/E_i)^{1/2}\,[\,a_{inc}^2\,S_s(Q,\omega) + a_{coh}^2\,S(Q,\omega)] \qquad (9.48)$$

where

$$S_s(Q,\omega) = \frac{1}{2\pi}\int_{-\infty}^{\infty} dt\; e^{i\omega t}\,\frac{1}{N}\sum_{\ell} \langle \exp(\overset{(-}{i}\underline{Q}\cdot\underline{R}_{\ell}^{(t)})\exp(\overset{q}{-}i\underline{Q}\cdot\underline{R}_{\underset{\ell}{\cancel{\ell'}}}\overset{q}{\boxed{(t)}})\rangle \qquad (9.49) \leftarrow$$

$$S(Q,\omega) = \frac{1}{2\pi}\int_{-\infty}^{\infty} dt\; e^{i\omega t}\,\frac{1}{N}\sum_{\ell,\ell'} \langle \exp(\overset{(-}{i}\underline{Q}\cdot\underset{\underline{R}_{\ell'}(t)}{\boxed{\underline{R}_{\ell}}})\exp(\overset{q}{-}i\underline{Q}\cdot\underline{R}_{\ell'}\overset{q}{\boxed{(t)}})\rangle \qquad (9.50)$$

The separation of the cross section into incoherent and coherent contributions is useful because these two processes can be measured separately. [In principle, one can imagine making up scattering samples such that either a_{inc} or a_{coh} is appreciably larger than the other; in practice such selective sample preparations are not always possible, so one has to live with whatever scattering process nature dictates for a particular element in the periodic table.] The new quantity $S_s(Q,\omega)$ is sometimes called the single-particle (or test-particle) dynamic structure factor because it represents structural and dynamical effects involving correlations of a nucleus in speace and time with itself. An example of such effects is the diffusional motion of atoms in a liquid. From (9.49) and (9.50) it is clear that the correlations observed in thermal neutron scattering involve the positions of two target particles, one at time t and the other at t = 0 (implicit). Although S_s and S differ only in the identity of the particles, these two functions can represent very different physical properties of the system, as we will see below.

We have previously implied that the scattering lengths in the Fermi pseudopotential are to be regarded as experimentally determined quantities. Indeed there exist tables of a_{inc} and a_{coh} for many isotopes which have been compiled from measurements (mostly total reflection or critical scattering, see Hughes and the first Bacon reference mentionned above). One such table is shown in Table 9.1 which compares neutron and X-ray scattering cross sections. As an illustration of how these data may be used, we consider again the two sources of incoherent scattering, spin and isotope averaging.

Spin Incoherence

This effect may be present only in nuclei with nonzero spin; the most most overwhelmingly important case is the hydrogen nucleus H^1, with other notable examples being Na^{23}, Cl^{35}, V^{51}, and Co^{59}. In the case of a monoisotopic target, (9.44), in view of (9.46) and (9.47), becomes

$$a_{inc}^2 = \frac{I(I+1)}{(2I+1)^2}\,(a_+ - a_-)^2 \qquad (9.51)$$

In the case of hydrogen, the proton has a spin of I = 1/2, and the triplet and singlet scattering lengths are, respectively

$$a_+ = 1.08 \times 10^{--12} \text{ cm},, \quad a_{--} = --4.74 \times 10^{--12} \text{ cm}$$

so that

$$a_{inc} = 2,52 \times 10^{--12} \text{ cm},, \quad a_{coh} = --0.375 \times 10^{--12} \text{ cm}$$

The corresponding scattering cross sections are $\swarrow$ — $\leftarrow$

$$\sigma_{inc} = 4\pi\underset{a}{\alpha}^2_{inc} = 79.8 \times 10^{\overset{-}{\downarrow}24} \text{ cm}^2 \qquad (9.52)$$

$$\sigma_{coh} = 4\pi\underset{a}{\alpha}^2_{coh} = 1.8 \times 10^{--24} \text{ cm}^2 \qquad (9.53) \leftarrow$$

and the total cross section is $\sigma = \sigma_{inc} + \sigma_{coh}$ = 81.6 barns. There are two noteworthy points here. First is the value of σ which is the largest cross scattering among all known nuclei, and second is the fact that the incoherent cross section is 45 times greater than the coherent contribution. Since there are many physical systems which have significant hydrogen content, this special property of the proton makes it a particularly important nucleus for thermal neutron scattering investigations.

The relatively small coherent cross section of the proton also means that neutron diffraction from hydrogenous samples is difficult. Fortunately, as shown in Table 9.1, the deutron has cross sections σ_{inc} = 2.2 barns and σ_{coh} = 5.4 barns. For crystal structure studies it is often advantageous to 'deuterate' (chemical substitution of hydrogen atoms by deuterium atoms) the sample in order to enhance the diffraction intensities which depend on interference effects (and are therefore proportional to σ_{coh}) relative to background intensities which are governed by σ_{inc}.

It should be noted that the scattering length values given in Table 9.1 are bound--atom scattering lengths. In the literature sometimes one will encounter the quantity called free--atom scattering length. The relation between the two is

$$a(\text{bound}) = \frac{m + M}{\cancel{m}\,M} a(\text{free}) \qquad (9.54)$$

where m is the neutron mass and M the scatterer mass. Thus, for a proton, the bound--atom cross section is a factor 4 greater than the free--atom value. In the Fermi pseudopotential (9.11) and (9.12), the quantity which appears is the bound-atom scattering length (one should beware of the convention, not adopted here, of labeling this as b, and using a for the free--atom scattering length). One may ask, why we should be concerned with

Table 9.1 Neutron and X-ray scattering data for elements and isotopes (b denotes the bound-atom coherent scattering length a_{coh}, script S the bound-atom coherent scattering cross section $\sigma_{coh} = 4\pi a_{coh}^2$, and σ the total cross section, $\sigma_{inc} + \sigma_{coh}$).[from G. E. Bacon, Neutron Diffraction, p.31.]

					Neutrons			*X-rays*	
								f_x, 10^{-12} *cm.*	
Element	*Atomic number*	*Atomic weight of natural element*	*Specific nucleus*	*Nuclear spin*	b (10^{-12} *cm.*)	$\mathcal{S}$ (*barns*)	σ (*barns*)	$\sin\theta = 0$	$(\sin\theta)/\lambda = 0{\cdot}5$ Å^{-1}
H	1	..	H^{1}	$\frac{1}{2}$	−0·378	1·79	81·5	0·28	0·02
			H^{2}	1	0·65	5·4	7·6	0·28	0·02
He	2	..	He^{4}	0	0·30	1·1	1·1	0·56	0·15
Li	3	6·94	..	..	−0·18	0·47	1·2	0·84	0·28
			Li^{6}	1	0·18$^{(2)}$	0·4	..	0·84	0·28
			Li^{7}	$\frac{3}{2}$	−0·21$^{(2)}$	0·6	1·4	0·84	0·28
Be	4	..	Be^{9}	$\frac{3}{2}$	0·774	7·53	7·54	1·13	0·39
B	5	..	..	..	..	..	4·4	1·41	0·42
C	6	..	C^{12}	0	0·661	5·50	5·51	1·69	0·48
			C^{13}	$\frac{1}{2}$	0·60	4·5	5·5	1·69	0·48
N	7	..	N^{14}	1	0·940	11·0	11·4	1·97	0·53
O	8	..	O^{16}	0	0·577	4·2	4·24	2·25	0·62
F	9	..	F^{19}	$\frac{1}{2}$	0·55	3·8	4·0	2·53	0·75
Ne	10	..	..	..	..	..	2·9	2·82	0·96
Na	11	..	Na^{23}	$\frac{3}{2}$	0·351	1·55	3·4	3·09	1·14
Mg	12	24·3	..	..	0·54	3·60	3·70	3·38	1·35
Al	13	..	Al^{27}	$\frac{5}{2}$	0·35	1·5	1·5	3·65	1·55
Si	14	28·06	..	..	0·42	2·16	2·2	3·95	1·72
P	15	..	P^{31}	$\frac{1}{2}$	0·53	3·5	3·6	4·23	1·83
S	16	..	S^{32}	0	0·31	1·2	1·2	4·5	1·9
Cl	17	35·5	..	..	0·99	12·2	15	4·8	2·0
A	18	..	A^{40}	0	0·20	0·5	0·9	5·07	2·2
K	19	39·1	..	..	0·35	1·5	2·2	5·3	2·2
Ca	20	40·1	..	..	0·49	3·0	3·2	5·6	2·4
			Ca^{40}	0	0·49	3·0	3·1	5·6	2·4
			Ca^{44}	0	0·18	0·4	..	5·6	2·4
Sc	21	..	Sc^{45}	$\frac{7}{2}$	1·18	17·5	24	5·9	2·5
Ti	22	47·9	..	..	−0·34	1·45	4·4	6·2	2·7
			Ti^{46}	0	0·48$^{(3)}$	2·90	..	6·2	2·7
			Ti^{47}	$\frac{5}{2}$	0·33$^{(3)}$	1·37	..	6·2	2·7
			Ti^{48}	0	−0·58$^{(3)}$	4·23	..	6·2	2·7
			Ti^{49}	$\frac{7}{2}$	0·08$^{(3)}$	0·08	..	6·2	2·7
			Ti^{50}	0	0·55$^{(3)}$	3·80	..	6·2	2·7
V	23	..	V^{51}	$\frac{7}{2}$	−0·051	0·033	5·1	6·5	2·8
Cr	24	52·0	..	..	0·352	1·56	4·1	6·8	3·0
			Cr^{52}	0	0·490	3·02	..	6·8	3·0
Mn	25	..	Mn^{55}	$\frac{5}{2}$	−0·36	1·6	2·0	7·0	3·1
Fe	26	55·8	..	..	0·96	11·4	11·8	7·3	3·3
			Fe^{54}	0	0·42	2·2	2·5	7·3	3·3
			Fe^{56}	0	1·01	12·8	12·8	7·3	3·3
			Fe^{57}	..	0·23	0·64	2	7·3	3·3
Co	27	..	Co^{59}	$\frac{7}{2}$	0·25$^{(2)}$	0·78	6	7·6	3·4
Ni	28	58·7	..	..	1·03	13·4	18·0	7·9	3·6
			Ni^{58}	0	1·44	25·9	..	7·9	3·6
			Ni^{60}	0	0·30	1·1	..	7·9	3·6
			Ni^{62}	0	−0·87	9·5	..	7·9	3·6
Cu	29	63·6	..	..	0·79$^{(2)}$	7·8	8·5	8·2	3·8
			Cu^{63}	$\frac{3}{2}$	0·67$^{(2)}$	5·7	..	8·2	3·8
			Cu^{65}	$\frac{3}{2}$	1·11$^{(2)}$	15·3	..	8·2	3·8
Zn	30	65·4	..	..	0·59	4·3	4·2	8·5	3·9
Ga	31	69·7	..	..	..	..	7·5	8·8	4·1
Ge	32	72·6	..	..	0·84	8·8	9·0	9·0	4·2
As	33		As^{75}	$\frac{3}{2}$	0·63	5·0	8	9·3	4·4

Table 9.1 (contd.)

					Neutrons			*X-rays*	
								f_x, 10^{-12} cm	
Element	*Atomic number*	*Atomic weight of natural element*	*Specific nucleus*	*Nuclear spin*	b (10^{-12} *cm.*)	$\mathcal{S}$ (*barns*)	σ (*barns*)	$\sin\theta = 0$	$(\sin\theta)/\lambda = 0·5$ Å^{-1}
Rb	37	85·5	..	..	0·55	3·8	5·5	10·4	5·0
Sr	38	87·6	..	..	0·57	4·1	10	10·7	5·2
Y	39	..	Y^{89}	$\frac{1}{2}$	0·80(10)	..	..	11·0	5·4
Zr	40	91·2	..	..	0·62	4·9	6·3	11·3	5·5
Nb	41	..	Nb^{93}	$\frac{9}{2}$	0·691	6·0	6·6	11·5	5·7
Mo	42	95·9	..	..	0·661	5·5	6·1	11·8	5·9
Tc	43	..	..	..	..	..	..	..	..
Ru	44	101·7	..	..	0·73(4)	6·68	6·31	12·5	6·2
Rh	45	..	Rh^{103}	$\frac{1}{2}$	0·60	4·5	5·6	12·8	6·4
Pd	46	106·7	..	..	0·59(11)	4·4	4·8	12·9	6·5
Ag	47	107·9	..	..	0·61	4·6	6·5	13·3	6·7
			Ag^{107}	$\frac{1}{2}$	0·83	8·7	10	13·3	6·7
			Ag^{109}	$\frac{1}{2}$	0·43	2·3	6	13·3	6·7
Cd	48	112·4	..	..	0·38+i0·12(7)	..	..	13·6	6·9
In	49	114·8	..	..	0·36(4)	1·63	..	13·9	7·1
Sn	50	118·7	..	..	0·61	4·6	4·9	13·9	7·1
Sb	51	121·8	..	..	0·54	3·7	4·2	14·2	7·3
Te	52	127·5	..	..	0·56	4·0	4·5	14·7	7·6
			Te^{120}	..	0·52	3·4	..	14·7	7·6
			Te^{123}	$\frac{1}{2}$	0·57	4·2	..	14·7	7·6
			Te^{124}	..	0·55	3·9	..	14·7	7·6
			Te^{125}	$\frac{1}{2}$	0·56	4·0	..	14·7	7·6
I	53	..	I^{127}	$\frac{5}{2}$	0·52	3·4	3·8	15·0	7·7
Xe	54	130·2	..	..	..	..	..	15·3	8·0
Cs	55	..	Cs^{133}	$\frac{7}{2}$	0·49	3·0	7	15·5	8·1
Ba	56	137·4	..	..	0·52	3·4	6	15·8	8·3
La	57	..	La^{139}	$\frac{7}{2}$	0·83	8·7	9·3	16·1	8·4
Ce	58	140·25	..	..	0·46	2·7	2·7	16·3	8·6
			Ce^{140}	..	0·47	2·8	2·6	16·3	8·6
			Ce^{142}	..	0·45	2·6	2·6	16·3	8·6
Pr	59	..	Pr^{141}	$\frac{5}{2}$	0·44	2·4	4·0	16·6	8·8
Nd	60	144·3	..	..	0·72	6·5	16	16·9	9·0
			Nd^{142}	..	0·77	7·5	7·5	16·9	9·0
			Nd^{144}	..	0·28	1·0	1·0	16·9	9·0
			Nd^{146}	..	0·87	9·5	9·5	16·9	9·0
Il	61	..	..	..	..	..	..	17·3	9·2
Sm	62	150·4	..	..	..	..	..	17·5	9·3
			Sm^{152}	..	−0·5	3	..	17·5	9·3
			Sm^{154}	..	0·8	8	..	17·5	9·3
Eu	63	152·0	..	..	..	..	..	17·8	9·5
Gd	64	157·3	..	..	..	..	..	18·2	9·7
Tb	65	..	Tb^{159}	$\frac{3}{2}$	0·76(10)	..	..	18·5	9·8
Dy	66	162·5	..	..	..	..	..	18·6	10·0
Ho	67	..	Ho^{165}	$\frac{7}{2}$	0·85(1)	9·1	~13	18·9	10·2
Er	68	167·6	..	..	0·79	7·8	15	19·2	10·3
Tm	69	..	Tm^{169}	$\frac{1}{2}$	..	..	..	19·5	10·5
Yb	70	173·0	..	..	1·26(10)	..	..	19·8	10·7
Lu	71	175·0	..	..	0·73(10)	..	..	20·0	10·9
Hf	72	178·6	..	..	0·88	9·7	..	20·3	11·1
Ta	73	..	Ta^{181}	$\frac{7}{2}$	0·70	6·1	6	20·5	11·3
W	74	183·9	..	..	0·466	2·74	5·7	20·8	11·4
Re	75	186·2	..	..	0·92(6)	10·6	..	21·1	11·6
Os	76	190·2	..	..	1·08(5)	14·7	14·9	21·4	11·8
Ir	77	192·2	..	..	0·36(4)	1·63	1·66	21·7	12·0
Pt	78	195·2	..	..	0·95	11·2	12	22·0	12·1
Au	79	..	Au^{197}	$\frac{3}{2}$	0·76	7·3	9	22·2	12·3
Hg	80	200·6	..	..	1·3	22	26·5	22·5	12·5

Table 9.1 (contd.)

					Neutrons			*X-rays*	
								f_x, 10^{-12} *cm.*	
Element	*Atomic number*	*Atomic weight of natural element*	*Specific nucleus*	*Nuclear spin*	b (10^{-12} *cm.*)	$\mathscr{S}$ (*barns*)	σ (*barns*)	$\sin\theta = 0$	$(\sin\theta)/\lambda = 0{\cdot}5$ Å^{-1}
Bi	83	..	Bi^{209}	$\frac{9}{2}$	0·864	9·35	9·37	23·3	13·1
Po	84	210	..	..	..	..	..	23·7	13·3
At	85	..	..	..	..	..	..	24·0	13·5
Rn	86	222	..	..	..	..	..	24·3	13·7
Fr	87	..	..	..	..	..	..	24·5	13·9
Ra	88	226	..	..	..	..	..	24·8	14·1
Ac	89	227	..	..	..	..	..	25·1	14·2
Th	90	..	Th^{232}	0	1·01	12·8	12·6	25·3	14·4
Pa	91	231	..	..	..	..	..	25·7	14·6
U	92	..	U^{238}	..	0·85	9·0	..	25·9	14·8
Np	93	..	..	..	..	..	..	..	..
Pu	94	..	..	..	..	..	..	..	..

Values are taken mainly from earlier compilations together with recent additions indicated by numbered superscripts as follows:

1. Koehler, Wilkinson, and Wollan (unpublished).
2. Keating *et al.*, *Phys. Rev.* **111**, 261 (1958).
3. Wilkinson and Shull (unpublished).
4. Sidhu, Le Roy Heaton, and Mueller, ANL Paper No. 1196 (1958).
5. Le Roy Heaton and Sidhu, *Phys. Rev.* **105**, 216 (1957).
6. Wilkinson *et al.*, unpublished.
7. Peterson, S. W., and Smith, H. G., unpublished, for a wavelength $\lambda = 1{\cdot}075$ Å
8. A modified value from W. L. Roth, *Phys. Rev.* **110**, 1333 (1958).
9. Peterson and Smith, *J. Phys. Soc. Japan* (1962).
10. Atoji, M., ibid.
11. Bergsma and Goedkoop, *Physica*, **26**, 744 (1960).

b is the coherent scattering amplitude, in units of 10^{-12} cm.

$\mathscr{S}$ is the coherent scattering cross-sections in barns (i.e. 10^{-24} cm.^{2}).

σ is the total scattering cross-section in barns.

the free-atom cross section? The answer is that if we consider potential scattering in the energy range of eV and higher, we often find the cross section is a constant, and if we set this constant equal to $4\pi a^2$, then the scattering length a turns out to have the value of the free-atom scattering length. Put in another way, if we used the bound-atom scattering length in (9.12) as we should and then calculate the scattering cross section σ in the energy range of around 1 - 100 eV where σ is typically a constant, we would find the value is $4\pi a^2(m/m+M)^2$.

M

Isotope Incoherence

To illustrate the second source of incoherence, that arising from isotope distribution, we consider neutron scattering from naturally occurring Ni which has a measured coherent (bound-atom) scattering length of 1.03×10^{-12} cm. Because natural Ni is composed of three isotopes, all even-even and therefore have zero spin, the scattering length is an isotope average in the sense of (9.46) and (9.47) with $I_p = 0$. Using the following data,

p	C_p	a_p [10^{-12} cm]
Ni^{58}	.68	1.47
Ni^{60}	.26	.28
Ni^{62}	.04	-.85

one finds $\bar{a} = \Sigma C_p a_p = 1.038 \times 10^{-12}$ cm, and $\sigma_{inc}^2 = \overline{a^2} - (\bar{a})^2 = 0.437$ barns. Thus, for this element we would predict, on the basis of the above data for the three isotopes, $\sigma_{coh} = 13.5$ barns and $\sigma_{inc} = 5.5$ barns. Experimentally, the corresponding values are 13.2 and 4.8 ± .2, respectively.

D. Time-Dependent Density Correlation Functions

In this section we will take up further discussions of the significance of the dynamic structure factor $S(\underline{Q},\omega)$ which one can measure by means of inelastic thermal neutron scattering. We will show that $S(\underline{Q},\omega)$ can be expressed as the four-dimensional (space-time) Fourier transform of the quantity known as the density correlation function $G(\underline{r},t)$. Our interest in $G(\underline{r},t)$ stems from the fact that it has a rather simple and useful physical interpretation, and the fact that the concept of a time-dependent correlation function is fundamental in study of statistical mechanics of a many-body system. [A classic reference on this topic is L. van Hove, Phys. Rev. 95, 249 (1954).]

Since we are not concerned here so much with coherent versus incoherent neutron scattering, we will begin with (9.38) in the form of a Fourier time transform,

$$S(\underline{Q},\omega) = \frac{1}{2\pi}\int_{-\infty}^{\infty} dt\; e^{i\omega t}\, F(\underline{Q},t) \tag{9.55}$$

where

$$F(\underline{Q},t) = \frac{1}{N}\sum_{\ell,\ell'} \langle \exp(-i\underline{Q}\cdot\underline{R}_{\ell'}(t))\exp(i\underline{Q}\cdot\underline{R}_{\ell})\rangle \tag{9.56}$$

is called the intermediate scattering. If we denote the Fourier transform of $F(\underline{Q},t)$ as the function $G(\underline{r},t)$,

$1/(2\pi)^3$ 4/29/91

$$\frac{1}{(2\pi)^3} \qquad G(\underline{r},t) = \cancel{\frac{1}{2\pi}}\int d^3Q\, \exp(i\underline{Q}\cdot\underline{r})\, F(\underline{Q},t) \tag{9.57}$$

✓

then we would have, upon combining (9.55) and (9.57),

✓

$$S(\underline{Q},\omega) = \frac{1}{2\pi}\int_{-\infty}^{\infty} dt \int d^3r\, \exp[i(\omega t - \underline{Q}\cdot\underline{r})]\, G(\underline{r},t) \tag{9.58}$$

which is the result mentioned above.

Since Fourier transformation is a mathematical operation, we can regard $S(\underline{Q},\omega)$, $F(\underline{Q},t)$, and $G(\underline{r},t)$ as a group of functions all having essentially the same physical content, and when one is known the other two can be obtained, if necessary by numerical integration. Inspite of their equivalence, it is also true that sometimes one function is more accessible than the others. For example, whereas $S(\underline{Q},\omega)$ is the quantity directly proportional to the observed scattered distribution, from the standpoint of physical interpretation or theoretical calculation, it is more convenient to work with $G(\underline{r},t)$ or $F(\underline{Q},t)$, as we will show in this section and the next.

Since $S(\underline{Q},\omega)$ is defined by (9.38), we can combine this definition with (9.58) to obtain an expression for $G(\underline{r},t)$. It can be shown that $G(\underline{r},t)$ can be written as [the derivation is left as an excercise for the reader]

$$\boxed{(2\pi)^3} \quad G(r,t) = \frac{1}{N}\sum_{\ell,\ell'}\int d^3r'\, \langle\delta(\underline{r}+\underline{r}'-\underline{R}_{\ell'}(t))\;\delta(\underline{r}'-\underline{R}_{\ell})\rangle \tag{9.59}$$

✓

✓ Notice that because $\underline{R}_{\ell'}(t)$ and $\underline{R}_{\ell}$ do not in general commute, we cannot carry out the $\underline{r}'$-integral by using the property of the delta function. If our system is translationally invariant (homogeneous), such as in a simple fluid. then the thermal average < > is independent of $\underline{r}'$ and one obtains

$$G(\underline{r},t) = \frac{1}{n}\sum_{\ell,\ell'} <\delta(\underline{r} - \underline{R}_{\ell'}(t))\ \delta(\underline{R}_{\ell})> \tag{9.60}$$

where n is the overall number density of the system, V/N, with V being the system volume. This result can be given a simple interpretation because each sum over delta function defines a time-denendent, local number density operator. For example,

$$\rho(\underline{r},t) = \sum_{\ell} \delta(\underline{r} - \underline{R}_{\ell}(t)) \tag{9.61}$$

is the operator whose expectation value gives the density at position $\underline{r}$ and time t. Thus (9.60) becomes.

$$G(\underline{r},t) = \frac{1}{n} <\rho(\underline{r},t)\rho(0,0)> \tag{9.62}$$

This shows why $G(\underline{r},t)$ is called the density correlation function; it is simply the average of two density operators displaced in space and time from each other, one at position $\underline{r}$ and time t and other at the origin and t=0. Notice that the space and time dependence of G is the spatial and temporal separation of the argument of the density operators. More generally, (9.62) can be written as

$$G(\underline{r} - \underline{r}',t - t') = \frac{1}{n} <\rho(\underline{r},t)\rho(\underline{r}',t')> \tag{9.63}$$

A similar transformation can be carried out for the single-particle dynamic structure factor $S_s(\underline{Q},\omega)$ (cf. (9.49)). One finds

$$S_s(\underline{Q},\omega) = \frac{1}{2\pi}\int_{-\infty}^{\infty} dt \int d^3r\ \exp[-i(\underline{Q}\cdot\underline{r} - \omega t)]\ G_s(\underline{r},t) \tag{9.64}$$

with

$$G_s(\underline{r},t) = V <\delta(\underline{r} - \underline{R}(t))\delta(\underline{R})> \tag{9.65}$$

which is sometimes called the van Hove self correlation function. In (9.65) it is assumed that the system is homogeneous so that $\underline{R}$ denotes the position of a target nucleus which can be any of the N nuclei.

Physical Interpreation of G(r,t) in the Classical Limit

It is difficult to give physical meaning to the density correlation functions $G(\underline{r},t)$ and $G_s(\underline{r},t)$ because of noncommuting operators and the fact that these quantities are in general complex. These difficulties are not present in the classical limit where the dynamical variables commute, the functions are real and have straightforward physical interpretations. When $G(\underline{r},t)$ is treated classically [this limit can be taken properly as the limit of $\hbar \rightarrow 0$, although we will not go into the details here, see M. Rosenbaum and P. F. Zweifel, Phys. Rev. 137, B271 (1965).], (9.59) becomes

$$G(\underline{r},t) = \frac{1}{N}\sum_{\ell,\ell'} \langle\delta(\underline{r} + \underline{R}_{\ell}(0) - \underline{R}_{\ell'}(t)\rangle \qquad (9.66)$$

To interpret this expression, we can choose a coordinate with the origin at $\underline{R}_{\ell}(0)$. Then the physical meaning of (9.66) is

$G(\underline{r},t) \equiv$ average density of atoms at $\underline{r}$ at time t, given that at t=0 an atom was located at the origin.

Notice that $G(\underline{r},t)$ is more than just the density of particles at $(\underline{r},t)$; it is essentially a correlation of two densities (aside from dimensionality factors), one at the origin at time 0 and the other at the position $\underline{r}$ and time t later. In the same manner the van Hove self correlation function (9.65) becomes in the classical limit,

$$G_s(\underline{r},t) = \langle\delta(\underline{r} + \underline{R}(0) - \underline{R}(t)\rangle \qquad (9.67)$$

and its physical meaning is that of a conditional probability,

$G_s(\underline{r},t) \equiv$ probability per unit volume of finding an atom at $\underline{r}$ at time t, given that this atoms was at the origin at t = 0.

Fig. 9.3 shows that the particle initially localized at the origin can move to $\underline{r}$ after a time t. This is the only contribution to $G_s(\underline{r},t)$, whereas for $G(\underline{r},t)$ there is another contribution from other particles in the system who can move to $\underline{r}$ from their intial positions after a time t. In other words, we can write

$$G(\underline{r},t) = G_s(\underline{r},t) + G_d(\underline{r},t) \qquad (9.68)$$

where $G_d(\underline{r},t)$ is called the distinct density correlation function.

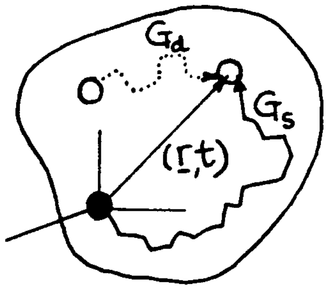


Fig. 9.3 Different contributions to $G(\underline{r},t)$, $G_s(\underline{r},t)$ and $G_d(\underline{r},t)$.

✓

The initial values of $G_s(\underline{r},t)$ and $G(\underline{r},t)$ also reveal the physical content of these correlation functions,

$$G_s(\underline{r},0) = \delta(\underline{r}) \tag{9.69}$$

$$G(\underline{r},0) = d(\underline{r}) + n\, g(\underline{r}) \tag{9.70}$$

δ

where

$$n\, g(\underline{r}) = \frac{1}{N}\sum_{\ell,\ell'}{}' \langle \delta(\underline{r} + \underline{R}_\ell - \underline{R}_{\ell'})\rangle \tag{9.71}$$

The quantity $g(\underline{r})$ is called the radial distribution function or pair distribution function; it is the quantity the Fourier transform of which is measured directly in a neutron or X-ray diffraction experiment [see, for example, P. A. Egelstaff, <u>An Introduction to the Liquid State</u> (Academic Press, London, 1967), p. 15.]

The integrals of the correlation functions are quite simple.

$$\int d^3r\, G(\underline{r},t) = N \tag{9.72}$$

$$\int d^3r\, G_s(\underline{r},t) = 1 \tag{9.73}$$

For the dynamic structure factor we have

$$\begin{aligned} S(\underline{Q}) &\equiv \int_{-\infty}^{\infty} d\omega\, S(\underline{Q},\omega) \\ &= F(\underline{Q},\, t=0) \\ &= \int d^3r\, \exp(-i\underline{Q}\cdot\underline{r})\, G(\underline{r},0) \\ &= 1 + n\int d^3r\, \exp(-i\underline{Q}\cdot\underline{r})\, [g(\underline{r}) - 1] \end{aligned} \tag{9.74}$$

The quantity $S(\underline{Q})$ is called the <u>static structure factor</u>; it is directly proportional to the angular differential scattering cross section $d\sigma/d\Omega$. Eq.(9.74) shows clearly that the measurement of $d\sigma/d\Omega$ in a diffraction experiment provides information (through the Fourier transform) of the spatial correlation between pairs of atoms in the target system. The basic objective in the study of equilibrium properties of liquids is to determine $g(\underline{r})$ or $S(\underline{Q})$. [In addition to the Egelstaff reference, interested readers may see D. A. McQuarrie, <u>Statistical Mechanics</u> (Harper & Row, New York, 1973), chaps. 13 and 14, or J.-P. Hansen and I. R. McDonald, <u>Theory of Simple Liquids</u> (Academic Press, London, 1976), chap. 2.]

E. Model Systems in Neutron Inelastic Scattering

There are two simple models for which we can evaluate the quantum mechanical expression for $S(\underline{Q},\omega)$ exactly, the ideal gas and the harmonic oscillator. (The system of free rotator is also exactly soluble, but it is less relevant in the present context.) The analysis of these two models is instructive, and the results are useful for interpreting neutron scattering experiments on liquids and solids.

Dilute Monatomic Gas

Consider a system of N particles, each of mass M, which do not interact with each other, although the system itself is in thermal equilibrium at temperature T. The Hamiltonian for this system is

$$H_s = \sum_{\ell=1}^{N} \underline{P}^2_{\ell}/2M \qquad (9.75)$$ ←

and its eigenfunctions and eigenvalues are well-known.

$$H_s\,|n\rangle = \epsilon_n\,|n\rangle \qquad (9.76)$$

$$|n\rangle = \prod_{\ell=1}^{N} [(2\pi)^{-3/2}\exp(i\underline{k}_\ell\cdot\underline{R}_\ell)] \equiv \prod_{\ell=1}^{N} |\underline{k}_\ell\rangle \qquad (9.77)$$

$$\epsilon_n = \sum_{\ell=1}^{\nu} \hbar^2 k_\ell^{\,2}/2M \qquad (9.78)$$

In the limit of low particle density we can ignore the contributions in $F(\underline{Q},t)$ [cf.(9.56)] for which $\ell \neq \ell'$. This means that $F(\underline{Q},t) = F_s(\underline{Q},t)$, and

$$F_s(\underline{Q},t) = \langle\exp(-i\underline{Q}\cdot\overset{(t)}{\underline{R}})\,\exp(i\underline{Q}\cdot\underline{R}\boxed{(t)})\rangle \qquad (9.79)$$ ←

For a free particle, its position at time t is simply

$$\underline{R}(t) = \underline{R}(0) + \underline{P}(0)t/M \qquad (9.80)$$

T to deal with the two exponential operators in (9.79) we make use of the operator identity [see Merzbacher, Quantum Mechanics] ←

$$e^{A+B} = e^{A}\,e^{B}\,e^{-[A,B]/2} \qquad (9.81)$$

which holds if operators A and B both commute with [A,B], This is applicable in the present problem because the two noncommuting operators R_α and P_β commute with their commutator, $[R_\alpha,P_\beta] = i\hbar\delta_{\alpha\beta}$, which is a constant.

Thus,

$$\exp[i\underline{Q}\cdot\underline{R}(t)] = \exp[i\underline{Q}\cdot\underline{R}(0)]\ \exp[it\underline{P}(0)\cdot\underline{Q}/M]\ e^{-it\hbar Q^2/2M} \tag{9.82}$$

and upon inserting this into (9.79) we get

$$F_s(\underline{Q},t) = e^{-it\hbar Q^2/2M} \sum_k P(k)\ \langle k|\exp[it\underline{P}(0)\cdot\underline{Q}/M]|k\rangle \tag{9.83}$$

The states $|k\rangle$, the eigenfunctions of H_s, are also eigfunctions of $\underline{P}$, so the expectation value in (9.83) is just $\exp(it\hbar\underline{k}\cdot\underline{Q}/M)$. To carry out the thermal average we replace the k-sum by a velocity integral through the relation $\underline{P} = \hbar\underline{k} = M\underline{V}$,

$$F_s(\underline{Q},t) = e^{-it\hbar Q^2/2M}\ (\beta M/2\pi)^{3/2} \int d^3V\ e^{-\beta MV^2/2}\ e^{itQ\cdot V} \tag{9.84}$$

$$= \exp[-\frac{Q^2}{2M}\ (it\hbar + t^2/\beta)] \tag{9.85}$$

The dynamic structure factor $S_s(\underline{Q},\omega)$ is the Fourier transform of $F_s(\underline{Q},t)$. Since F_s in this case is a function only of the magnitude of $\underline{Q}$, S_s will be likewise a function only of Q. One obtains

$$S_s(Q,\omega) = (\beta/4\pi E_R)^{1/2} \exp[-\beta(\hbar\omega - E_R)^2/4E_R] \tag{9.86}$$

where $E_R = \hbar^2Q^2/2M$ is the recoil energy of the target nucleus. Because the double differential scattering cross section is propoertional to the dynamic structure factor, (9.86) shows that in the case of scattering by a dilute gas target, the energy distribution of the scattered neutrons is simply the Doppler line shape, a skew Gaussian with peak position at approximately $E_f = E_i - E_R$. A spectrum of this type is of limited interest since it only depends on the mass of the scattering nucleus and the temperature of the medium. It can be shown that this is the limiting behavior of scattering from any physical system at sufficiently high incident neutron energies or momentum transfers, and its physical significance is that at such energies and momentum transfers one is probing the motions of the target system over very short times and distances such that all particles move in a linear trajectory no matter what is the state of the system.

It is useful to cast the dynamic structure factor $S_s(Q,\omega)$ for a dilute gas into a different form. Writing out the square in the exponent in (9.86) one has

$$S_s(Q,\omega) = e^{-\beta E_R/4}\, e^{\beta \hbar\omega/2}\, S_s^{cl}(Q,\omega) \tag{9.87}$$

where

$$S_s^{cl}(Q,\omega) = (\sqrt{2\pi}\, Qv_o)^{-1} \exp[-\tfrac{1}{2}(\tfrac{\omega}{Qv_o})^2] \tag{9.88}$$

and $v_o = (\beta M)^{-1/2}$ is the thermal speed of the target particles. The first exponential in (9.87) is known as the recoil factor for rather obvious reasons. The second is called the detailed balance factor; its presence signifies that S_s is not an even function of ω. The remaining function in (9.87) is the classical limit ($h \rightarrow 0$) of the dynamic structure factor, hence the superscript cl. In this form (9.87) shows the relation between the quantum mechanical and classical dynamic structure factors, derived for the case of an ideal gas target. One may wonder whether the same relation holds for other models of scattering systems. The answer is yes, but only to first order in h.

In Fig. 9.4 we show a sketch of (9.86) as a function of outgoing neutron energy. Notice that the energy spectrum has its peak <u>lower</u> than the incident energy. This means that the probability for the neutron to lose energy is <u>greater</u> than the probability to gain energy, or down scattering is more likely than up scattering. This asymmetry, present in the quantum mechanical result and not in the classical limit, is a consequence of a property of the cross section called detailed balance. Its origin lies in the fact that for a system to remain in thermal equilibrium the transition between any two states must be equal (otherwise one state will build up and the system is not in equilibrium). It turns out that all classical correlation functions are even functions in frequency and do not have the recoil factor mentioned above. Therefore any approximation involving a classical calculation of the dynamic structure factor (such as through atomistic simulation) will not correctly describe the recoil of the target and also violate the condition of detailed balance. In practice a partial correction of this error can be made by multiplying the classical result by the two exponential factors in (9.87).

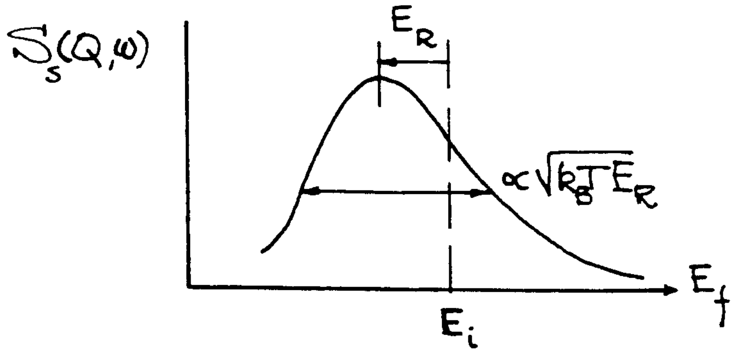


fig. 9.4 **Energy distribution of neutrons scattered by an ideal gas target, particle mass M and system temperature T.**

To show that (9.87) is indeed the classical expression for the single-particle dynamic structure factor we will derive it directly using the definition of $G_s(\underline{r},t)$, (9.65). In a classical calculation, the thermal average becomes an average over the position and momentum of the target particles,

$$G_s(\underline{r},t) = V \int d^3R \, d^3P \, f(\underline{R},\underline{P}) \, \delta(\underline{r} - \underline{R} - t\underline{P}/M) \, \delta(\underline{R}) \tag{9.89}$$

where $f(\underline{R},\underline{P})$ is an equilibrium distribution of particle position and momentum. For a classical dilute gas, we will take the particles to be uniformly distributed in space and have a Maxwellian momentum distribution. Thus,

$$G_s^{cl}(\underline{r},t) = \int d^3V \, f_o(\underline{V}) \, \delta(\underline{r} - \underline{V}t) \tag{9.90}$$

with

$$f_o(\underline{V}) = (\sqrt{2\pi}\, v_o)^{-3} \exp[-\tfrac{1}{2}(\tfrac{V}{v_o})^2] \tag{9.91}$$

Carrying out the indicated integration in (9.90) we obtain

$$G_s^{cl}(\underline{r},t) = (\sqrt{2\pi}\, v_o t)^{-3} \exp[-\tfrac{1}{2}(\tfrac{r}{v_o t})^2] \tag{9.92}$$

So the van Hove self correlation function for an ideal gas particle is a Gaussian with width proportional to $v_o t$; the motion of the particle generates a spherical thermal cloud which spreads at a speed v_o. In the limit of $t \rightarrow 0$, $G_s^{cl}(\underline{r},t) \rightarrow \delta(\underline{r})$, which verifies the initial condition that at $t = 0$ a particle is localized at the origin. Taking the Fourier transform (the inverse of (9.57)) of (9.92), the classical intermediate scattering function is seen to be

$$\begin{aligned} F_s^{cl}(\underline{Q},t) &= \int d^3r \, \exp(-i\underline{Q}\cdot\underline{r}) \, G_s^{cl}(r,t) \\ &= \exp[-\tfrac{1}{2}\,(Qv_o t)^2] \end{aligned} \tag{9.93}$$

Notice that $F_s^{cl}(\underline{Q},0) = 1$ for any Q which is a convenient initial value, and that $F_s^{cl}(0,t) = 1$ for any t, a statement of particle conservation. Taking the Fourier transform of (9.93) in time one finds that the classical dynamic structure factor S_s^{cl} is indeed given by (9.88). It is significant that all three functions, G_s, F_s, and S_s are Gaussian functions in r, Q, and ω repsectively. In addition, F_s is also a Gaussian in t. We will come back later to this property of the correlation functions.

It is instructive to examine the low-temperature limit of the double differential cross section, (9.37), in the context of the dilute gas model. In the limit of stationary target particles, one has

$$\frac{d^2\sigma}{d\Omega dE_f} \xrightarrow[T\to 0]{} (E_f/E_i)^{1/2}\, a^2\, \delta(E_i - E_f + E_R) \qquad (9.94)$$

where we have made use of another representation of the delta function,

$$\lim_{\gamma\to\infty} (\gamma/\sqrt{4\pi})\, \exp[-\frac{\gamma^2}{4}(x-y)] = \delta(x-y) \qquad (9.95)$$

We can carry out the angular integration of (9.94) to obtain the energy differential cross section,

$$a_f \equiv a\left(\frac{M}{m+M}\right)$$

$$\frac{d\sigma}{dE_f} = \begin{cases} 4\pi\, a_f^2\, \dfrac{1}{E_i(1-\alpha)}, & \alpha E_i \le E_f \le E_i \\ 0, & \text{otherwise} \end{cases} \qquad (9.96)$$

which is a well-known expression used in reactor physics to describe the process of neutron slowing down. One can derive (9.56) directly by invoking three assumptions (cf. 22.111 Lecture Notes), elastic scattering, scattering is isotropic in CMCS, and target nucleus is at rest. The first is equivalent to saying that one is considering only potential scattering. The second corresponds to treating only s-wave scattering. The third is the same as our taking the T → 0 limit above. From this standpoint, we can regard the dynamic structure factor (9.86) as the generalization to include the effects of particle motions in a gas target.

At finite tempeature, the integration of $(E_f/E_i)^{1/2}S(\underline{Q},\omega)$, with S given by (9.86), to obtain $d\sigma/dE_f$ can be carried out analytically [see, for example, M. M. R. Williams, <u>Slowing Down and Thermalization of Neutrons</u> (North-Holland, 1966), chap. II, sec. 5; or G. I. Bell and S. Glasstone, <u>Nuclear Reactor Theory</u> (van Nostrand, 1970), sec. 7.3.], It is worthwhile to see a little of what is involved. We have

$$\frac{d\sigma}{dE_f} = \int d\Omega\, \frac{d^2\sigma}{d\Omega dE_f}$$

$$= a^2\, (E_f/E_i)^{1/2}\, (\beta\pi)^{1/2} \int_{-1}^{1} d\mu\, \frac{1}{E_R}\, e^{-(E_i-E_f-E_R)^2\beta/4E_R} \qquad (9.97)$$

where $E_R = (m/M)(E_i+E_f-2\mu\sqrt{E_iE_f})^{1/2}$. This integral can be expressed in terms of the error function,

$$\mathrm{erf}(x) = \frac{2}{\sqrt{\pi}} \int dt\ e^{-t^2} \tag{9.98}$$

and the result depends on whether E_i is greater or less than E_f. One obtains

$$\frac{d\sigma}{dE_f} = a^2 \frac{A}{2E_i} \otimes \tag{9.99}$$

where

$$\begin{aligned} \otimes = e^{-(\epsilon_f-\epsilon_i)}[&\mathrm{erf}(\theta\sqrt{\epsilon_i} - \zeta\sqrt{\epsilon_f}) \pm \mathrm{erf}(\theta\sqrt{\epsilon_i} + \zeta\sqrt{\epsilon_f}) \\ &\mathrm{erf}(\theta\sqrt{\epsilon_f} - \zeta\sqrt{\epsilon_i}) \mp \mathrm{erf}(\theta\sqrt{\epsilon_f} + \zeta\sqrt{\epsilon_i})] \end{aligned} \tag{9.100}$$

In (9.100) we have defined reduced energies $\epsilon = E/k_BT$ and several mass parameters, $A = M/m$, $\theta = (A+1)/2\sqrt{A}$, $\zeta = (A-1)/2\sqrt{A}$. Also one should take the upper sign if $\epsilon_f > \epsilon_i$, or the lower sign if $\epsilon_i > \epsilon_f$. This result is known as the Wigner-Wilkins scattering kernel; its general behavior is sketched in Fig. 9.5. Notice that the energy distribution becomes increasingly asymmetric as the incident energy increases. In the limit of large E_i, or equivalently zero T, only down-scattering is possible and the distribution becomes uniform within the energies E_f that can be reached from E_i (cf. (9.96). We can next integrate (9.99) over E_f to obtain $\sigma(E_i)$, the total scattering cross section,

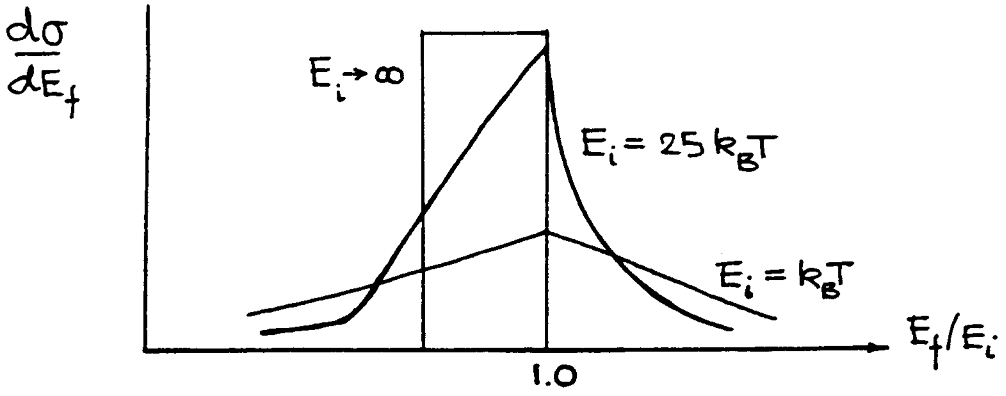


Fig. 9.5 Energy distribution of neutrons scattered by a dilute gas target at temperature T at different incident energies.

$$\sigma(E) = 4\pi a^2 \left(\frac{A}{A+1}\right)^2 \frac{1}{2A\epsilon} [(1+2A\epsilon)\mathrm{erf}(\sqrt{A\epsilon}) + \sqrt{4A\epsilon/\pi}\, e^{-A\epsilon}] \qquad (9.101)$$

Notice that $\sigma(E)$ varies like $1/\sqrt{E}$ as $A\epsilon \longrightarrow 0$, and as $A\epsilon >> 1$,

$$\sigma(E) \longrightarrow 4\pi a^2 \left(\frac{A}{A+1}\right)^2 \equiv \sigma(\text{free atom}) \qquad (9.102)$$

Eq.(9.102) shows that at high energies such that $AE >> k_BT$, the cross section is a constant defined to be $4\pi a^2$, where a is the free-atom scattering length and not the bound-atom scattering length [recall our discussion in connection with (9.54)].

Turning our attention to the angular differential cross section $d\sigma/d\Omega$, we find that it cannot be obtained by analytical integration in the case of the dilute gas target. The best one can do is to generate a power series in v_o/v_i, where v_i is the speed of the incident neutron, so that at sufficiently high incident energies, $E_i > (m/M)k_BT$, only a few terms will need to be calculated [see A. C. Zemach and R. J. Glauber, Phys. Rev. 101, 118 and 129 (1956)].

System of Indpendent Oscillators

The simplest dynamical model of a crystal is the Einstein model; it consists of a system of uncoupled oscillators, each of mass M and vibrating at fundamental frequency ω_o. Because the oscillator Hamiltonian is separable in the three Cartesian components, we can work with the one-dimensional system, (5.90), and generalize the results to three-dimensions at the appropriate stage,

$$H_s = \frac{P^2}{2M} + \frac{1}{2} M\omega_o X^2 \qquad (9.103)$$

2 ←

As in Chap. V, Sec. E we introduce normal coordinates a and $a^\dagger$ by writing

$$X = (\hbar/2M\omega_o)^{1/2} (a + a^\dagger) \qquad (9.104)$$

$$P = i(\hbar M\omega_o/2)^{1/2} (a^\dagger - a) \qquad (9.105)$$

The Hamiltonian then becomes

$$H_s = \hbar\omega_o(a^\dagger a + \tfrac{1}{2}) \qquad (9.106)$$

To evaluate the intermediate scattering function for incoherent scattering,

$$F_s(Q,t) = \langle e^{-iQ\overset{X(t)}{\boxed{X}}} e^{iQX\boxed{(t)}} \rangle \tag{9.107}$$

where

$$X(t) = X(0)\cos\omega_o t + \frac{P(0)}{M\omega_o}\sin\omega_o t$$

$$= (\hbar/2M\omega_o)^{1/2}\,(a^\dagger e^{i\omega_o t} + a\, e^{-i\omega_o t}) \tag{9.108}$$

we can use again the operator identity (9.81) to write

$$F_s(Q,t) = e^{\frac{Q^2}{2}[\overset{X(t),\,X}{\boxed{X,X(t)}}]} \langle e^{-iQ[\overset{X(t)-X}{\boxed{X-X(t)}}]} \rangle \qquad \leftarrow$$

$$= e^{-Q^2[\langle X^2\rangle - \langle X(t)X\rangle]} \tag{9.109}$$

where in the second step we have used another operator property,

$$\langle e^A \rangle = e^{\frac{1}{2}\langle A^2\rangle} \tag{9.110}$$

which holds if A is any linear combination of oscillator coordinates and momenta [for proof, see Zemach and Glauber, Phys. Rev. 101, 129 (1956)]. Thus $F_s(Q,t)$ is the product of two factors,

$$F_s(Q,t) = e^{-2W} e^{Q^2 \langle X(t)X\rangle} \tag{9.111}$$

where $\exp(-2W) = \exp[-Q^2\langle X^2\rangle]$ is known as the Debye-Waller factor, a quantity first studied in the context of attenuation effects in X-ray diffraction due to thermal vibrations of the atoms. The two thermal averages which have to be evaluated are the mean square amplitude $\langle X^2\rangle$ of the oscillator, and the time-displaced position coorelation $\langle X(t)X\rangle$.

To calculate $\langle X^2\rangle$ we rewrite it using (9.104) as

$$\langle X^2\rangle = \frac{h}{2M\omega_o}\,[2\langle a^\dagger a\rangle + 1] \tag{9.112}$$

with

$$\langle a^\dagger a\rangle = \sum_n P(n)\,\langle n|a^\dagger a|n\rangle \tag{9.113}$$

For a system of independent oscillators in thermal equilibrium at temperature T, the probability that an oscillator is in state $|n\rangle$ is

$$P(n) = e^{-\beta\epsilon_n} [\sum_s e^{-\beta\epsilon_s}]^{-1} \qquad (9.114)$$

where $\epsilon_n = h\omega_o(n + 1/2)$. The summation in the denominator in (9.114) gives $\exp(-\beta h\omega_o/2)[1 - \exp(-\beta h\omega_o)]^{-1}$, so (9.113) becomes

$$\begin{aligned} \langle a^\dagger a\rangle &= (1 - e^{-\beta\hbar\omega_o}) \sum_n n\, e^{-n\beta\hbar\omega_o} \\ &= e^{-\beta\hbar\omega_o} (1 - e^{-\beta\hbar\omega_o})^{-1} \qquad (9.113) \end{aligned}$$

Thus,

$$\begin{aligned} \langle X^2\rangle &= \frac{\hbar}{2M\omega_o} \frac{1 + e^{-\beta\hbar\omega_o}}{1 - e^{-\beta \underset{\uparrow \hbar}{\lambda} \omega_o}} \qquad \leftarrow \\ &= \frac{\hbar}{2M\omega_o} \coth \frac{\beta\hbar\omega_o}{2} \qquad (9.114) \end{aligned}$$

This result has an interesting high-temperature limit. As T → ∞, (9.114) gives $1/\beta M\omega_o$ which is also the classical limit. Then one has

$$\frac{1}{2} M\omega_o^2\langle X^2\rangle = \frac{1}{2} \langle H_s\rangle = \frac{1}{2\beta} \qquad (9.115)$$

which is the statement of equipartition.

←

Following a similar procedure one can arrive at the result

$$\langle X(t)X\rangle = \frac{\hbar}{2M\omega_o} \operatorname{csch}(z)\, [e^z\, e^{-i\omega_o t} + e^{-z}\, e^{i\omega_o t}] \qquad (9.116)$$

with $z = \beta\hbar\omega_o/2$. Inserting this into (9.111) we see $F_s(Q,t)$ is of the form,

$$F_s(Q,t) = e^{-2W}\, e^{(\gamma/2)(\alpha + 1/\alpha)} \qquad (9.117)$$

if we define $\gamma = (\hbar Q^2/2M\omega_o)\operatorname{csch}(z)$ and $\alpha = \exp(-z+i\omega_o t)$. The second exponential in (9.117) turns out to be the generating function for the modified Bessel function,

$$e^{(\gamma/2)(\alpha + 1/\alpha)} = \sum_{n=-\infty}^{\infty} \alpha^n I_n(\gamma) \tag{9.118}$$

By combining (9.117) and (9.118) we see that the time dependence of $F_s(Q,t)$ appear only in the factor $\exp(in\omega_o t)$ which makes the time Fourier transform a simple matter. Thus, for the independent oscillator model the dynamic structure factor becomes

$$S_s(Q,\omega) = e^{-2W} \sum_{-\infty}^{\infty} e^{-n\beta\hbar\omega_o/2} I_n[(\hbar Q^2/2M\omega_o)\mathrm{csch}(\beta\hbar\omega_o/2)]\ \delta(\omega + n\omega_o) \tag{9.119}$$

A straightforward interpretation of (9.119) can be given to the individual terms in the summation. Since the oscillator can only exist in states of discrete energy, separated by multiples of $\hbar\omega_o$, it is not surprising that the energy-transfer cross section should be given as a series of terms, each corresponding to a particular amount of energy exchange between the neutron and the oscillator. With a quantized lattice vibration being called a phonon, eq.(9.119) is known as a phonon expansion. Writing out the n = 0, ±1 terms, we find

$$S_s(Q,\omega) = e^{-2W}\delta(\omega) + e^{-2W} \frac{\hbar Q^2}{2M\omega_o} \mathrm{csch}(z)[e^{z}\delta(\omega - \omega_o) + e^{-z}\delta(\omega + \omega_o)] \tag{9.120}$$

The first term represents the zero-phonon (no excitation or de-excitation of lattice vibration) contribution which is therefore just elastic scattering. The second and third terms represent the first-phonon contributions, with neutron losing and gaining an amount of energy equal to $\hbar\omega_o$ respectively. Notice that this inelastic scattering intensity is proportional to Q^2, Q being the momentum transfer, and increases with T. The higher-order terms in the series are called multiphonon excitations; they are of little intrinsic interest although in many actual applications they cannot be ignored. One also should notice that in our result neutron energy loss is more probable than energy gain, the ratio again satisfies detailed balance condition.

Coherent Scattering

Thus far we have been concentrating on the $\ell = \ell'$ terms in the intermediate scattering function which make up the incoherent scattering contriubtion. The $\ell \neq \ell'$ terms make up the 'distinct' part of $F(\underline{Q},t)$,

$$F_d(\underline{Q},t) = \frac{1}{N}\sum_{\ell\neq\ell'} \langle \exp[-i\underline{Q}\cdot\underline{R}_{\ell'}(t)]\exp[i\underline{Q}\cdot\underline{R}_{\ell}]\rangle \tag{9.121}$$

✓

To consider the $\ell \neq \ell'$ terms in the gas model we note that because the target Hamiltonian is a sum of single-particle Hamiltonians (cf. (9.75)), there is no coupling in either position or momentum among the particles. This absence of correlation means

$$\langle e^{itH_{\ell'}/\hbar}\exp(-i\underline{Q}\cdot\underline{R}_{\ell'})e^{-itH_{\underset{\ell'}{\cancel{\ell}}}/\hbar}\exp(i\underline{Q}\cdot\underline{R}_{\ell})\rangle = \langle\exp(-i\underline{Q}\cdot\underline{R}_{\ell'})\rangle\langle\exp(i\underline{Q}\cdot\underline{R}_{\ell})\rangle \quad (9.122)$$ ←

when $\ell \neq \ell'$, so F_d becomes independent of time and contributes only to elastic scattering. We can reduce (9.122) further by writing

$$\begin{aligned} F_d(\underline{Q}) &= (N-1)\langle\exp(-i\underline{Q}\cdot\underline{R}_1)\rangle\langle\exp(i\underline{Q}\cdot\underline{R}_2)\rangle \\ &= (N-1)\ |\langle\exp(i\underline{Q}\cdot\underline{R})\rangle|^2 \qquad (9.123) \end{aligned}$$

where

$$\begin{aligned} \langle\exp(i\underline{Q}\cdot\underline{R})\rangle &= \frac{1}{V}\int d^3R\ \exp(i\underline{Q}\cdot\underline{R}) \\ &= \frac{3}{QR_o}\ j_1(QR_o) \qquad (9.124) \end{aligned}$$

In arriving at (9.124) we have taken the gas volume to be a sphere of radius R_o. In the thermodynamic limit of $N \to \infty$, $V \to \infty$, and $N/V \to n$, the gas density, F_d becomes

$$F_d(Q) \longrightarrow 12\pi(n/Q^3)\ \frac{1}{QR_o} = \frac{3}{4\pi^3}\ (n\lambda^3)(\frac{\lambda}{R_o}) \qquad (9.125)$$

Eq.(9.125) shows that F_d vanishes even if at finitie density since the factor $\lambda/R_o \to 0$. This is a consequence of the fact that the particle positions are assumed to be totally uncorrelated. This is physically unrealistic because particles are not point masses; their finite size means there will be an excluded volume effect which is a form of spatial correlation. If we take each particle to be a hard sphere of diameter d, then

$$\begin{aligned} F_d(Q) &= \frac{N-1}{V}\int d^3R\ \theta(R-d)\ \exp(i\underline{Q}\cdot\underline{R}) \\ &= 4\pi n\int_d^{R_o} dR\ R^2\ \frac{\sin QR}{QR} \\ &= -\ nV_{ex}(\frac{3}{Qd})j_1(Qd) \qquad (9.126) \end{aligned}$$

$\theta(x) = 1 \quad x < 0$ ←
$\qquad\ \ 0 \quad x > 0$

where $V_{ex} = (4\pi/3)d^3$ is the 'excluded volume' of a particle. Now the distinct part of the contribution is finite in the thermodynamic limit, and one can still argue that at low densities, $n << V_{ex}^{-1}$, the interference effect is small.

For the Einstein model the $\ell \neq \ell'$ terms also contribute only to elastic scattering since the oscillators are independent. If one is interested in neutron scattering by crystals one can go beyond this model and introduce the effects of the crystal structure into the calculation. We now consider the target to be a crystal lattice where atoms vibrate indpendently about their respective lattice positions. In this case there is spatial correlation among the particles but F_d is still time-independent,

$$F_d(\underline{Q},t) = \frac{1}{N}\sum_{\ell\neq\ell'} \langle\exp(-i\underline{Q}\cdot\underline{R}_{\ell'})\exp(i\underline{Q}\cdot\underline{R}_{\ell})\rangle$$

$$= \frac{1}{N}\sum_{\ell\neq\ell'} \mathrm{epx}[i\underline{Q}\cdot(\underline{X}_{\ell}-\underline{X}_{\ell'})] \ \langle\exp(-i\underline{Q}\cdot\underline{u}_{\ell'})\rangle\langle\exp(i\underline{Q}\cdot\underline{u}_{\ell})\rangle$$

$$= e^{-2W}\frac{1}{N}\sum_{\ell\neq\ell'} \exp[i\underline{Q}\cdot(\underline{X}_{\ell}-\underline{X}_{\ell'})]$$

$$= [\frac{(2\pi)^3}{v_a}\sum_{\tau} \delta(\underline{Q} - \underline{\tau}) \ - \ 1] \ e^{-2W} \tag{9.128}$$

In arriving at this result, we have expressed the particle position $\underline{R}_{\ell}$ as the sum of $\underline{X}_{\ell}$, the lattice site of particle ℓ, and $\underline{u}_{\ell}$, its instantaneous displacement from the lattice site. Also the thermal average $\langle\exp(i\underline{Q}\cdot\underline{u}_{\ell})\rangle$ is set equal to $\exp(-Q^2\langle u^2\rangle/2)$ by virtue of (9.110), and in the last step of (9.128) we have carried out the summations over ℓ and ℓ' which gives the familiar condition for Bragg reflection from crystal planes, with $\underline{\tau}$ being the reciprocal lattice vector such that $\underline{X}\cdot\underline{\tau} = 2\pi$ x (integer) [see, for example, C. Kittel, Introduction to Solid State Physics (Wiley, 1976), chap. 2] and v_a the unit cell volume in the reciprocal lattice.

We can now combine the incoherent and distinct part of the scattering to write the double differential cross section for scattering by a crystal target as

$$\frac{d^2\sigma}{d\Omega d\omega} = (E_f/E_i)^{1/2}\{[(a^2_{inc} + a^2_{coh})I_o(\frac{\hbar Q^2}{2M\omega_o}\mathrm{csch}\frac{\beta\hbar\omega}{2}) - a^2_{coh}]\ \delta(\omega)$$

$$+ \delta(\omega)\ a^2_{coh}\ \frac{(2\pi)^3}{v_a} \sum_{\tau} \delta(\underline{Q} - \underline{\tau})$$

$$+ (a^2_{inc} + a^2_{coh}) \sum_{\substack{n=-\infty \\ n\neq 0}}^{\infty} e^{-\frac{n\beta\hbar\omega_o}{2}}\ I_n(\frac{\hbar Q^2}{2M\omega_o}\mathrm{csch}\frac{\beta\hbar\omega_o}{2})\ \delta(\omega + n\omega_o)\} \qquad (9.129)$$

Although (9.129) is a lengthy result, the various terms have rather direct physical meaning. Keeping in mind that our model applies to a crystal lattice in which the atoms vibrate independently, we regard (9.129) as consisting of four parts, two proportional to $\delta(\omega)$ and two proportional to $\delta(\omega + n\omega_o)$ (n can be positive or negative).

(1) Elastic incoherent. Usually the argument of I_o is sufficiently small that I_o is effectively unity and the coherent parts cancel. One can show the contribution to $\sigma(E_i)$ varies like $1/E_i$.

(2) Elastic coherent. This contribution would vanish for E_i below the Bragg cutoff (E_B); it is responsible for the cross section $\sigma(E_i)$ to take on a jagged appearance since σ would rise suddenly whenever a set of planes begins to reflect.

(3) Phonon absorption. Composed of all the $n > 0$ terms, this contribution involves neutron gaining energy from the crystal. Therefore, it can be strongly temperature dependent.

(4) Phonon emission. Composed of all the $n < 0$ terms, this contribution increases with increasing incident energy; it dominates over the other contributions at energies above thermal and is responsible for $\sigma(E_i)$ becoming a constant in the high-energy (~ eV) limit.

These four parts are shown separately in Fig. 9.6. The characteristic variation of the total cross section with energy actually show up in the observed cross sections of polycrystalline solids such as C and Be [see BNL-325]. An application of the Bragg cutoff property is to use such materials as neutron filters. By cooling the solid to increase the cross section difference across the cutoff, one can have a scattering target which allows only the long wavelength neutrons ($E < E_B$) to pass through.

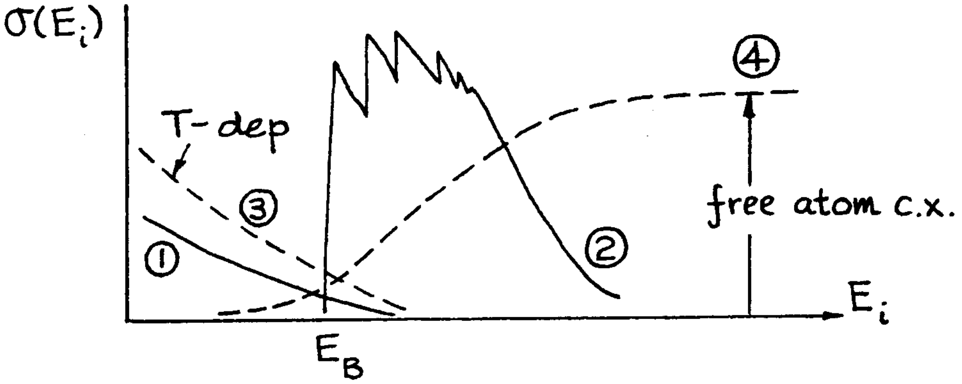


Fig. 9.6 Four contributions to the total neutron scattering cross section of a polcrystalline element.

Diffusing Atoms

The ideal gas and oscillator models we have considered may serve as first approximations to real gases and solids, but they are not applicable to liquids. Since a characteristic dynamical feature of liquids is atomic diffusion, we can introduce the model of diffusing atom as a simple description of incoherent neutron scattering in liquids. Unlike the two preceding models, this is a purely classical calculation.

Recall again the physical interpretation of $G_s(\underline{r},t)$. Over long distances and time intervals (compared to mean free paths and times between successive collisions) the motions of an atom in the liquid may be visualized as a series of small-step diffusion like in a random walk process. In this case one may assume $G_s(\underline{r},t)$ satisfies the time-dependent diffusion equation

$$\frac{\partial G_s(r,t)}{\partial t} = D\,\nabla^2 G_s(\underline{r},t) \tag{9.130}$$

where D is the self-diffusion coefficient of the liquid, with initial condition, $G_s(\underline{r},0) = \delta(\underline{r})$. This equation can be solved to give the following results,

$$G_s(\underline{r},t) = (4\pi Dt)^{-3/2}\, e^{-\frac{r^2}{4Dt}} \tag{9.131}$$

$$F_s(\underline{Q},t) = e^{-DQ^2 t} \tag{9.132}$$

$$S_s(\underline{Q},\omega) = \frac{1}{\pi}\,\frac{DQ^2}{\omega^2 + (DQ^2)^2} \tag{9.133}$$

Compared to the ideal-gas results we see that F_s has a different time expansion at short times; this indicates that the diffusion model is not correct at short times (or large frequencies) where inertial effects dominate.

Gaussian Approximation

We have obtained explicit results for G_s, F_s, and S_s for three physically very different models. One should notice that in all three cases the van Hove self correlation function G_s is a Gaussian function of r, and therefore the intermediate scattering function F_s is Gaussian in Q. This suggests that one may write as a general approximation [G. H. Vineyard, Phys. Rev. 110, 999 (1958)],

$$G_s(\underline{r},t) = [2\pi W(t)(]^{-3/2}\, e^{-\frac{\surd r^2}{2W(t)}} \qquad (\phi 9.134)$$

and

$$F_s(\underline{Q},t) = e^{-Q^2 W(t)/2} \qquad (9.135)$$

This is known as the 'Gaussian approximation'; it can accommodate any wdith function W(t) one wishes to use. For our three models,

$$W(t) = (v_o t)^2 \quad , 2\ ? \qquad \text{gas} \qquad (9.136)$$
$$2(bv_o/\omega_o)(1 - \cos\omega_o t) \qquad \text{oscillator}$$
$$2Dt \qquad \text{diffusing atom}$$

?

The behavior of these width functions is sketched in Fig. 9.7. For further discussions of model calculations applied to neutron inelastic scattering, the reader should consult the literature [see, for example, J.-P. Boon and S. Yip, Molecular Hydrodynamics (McGraw-Hill, 1980)].

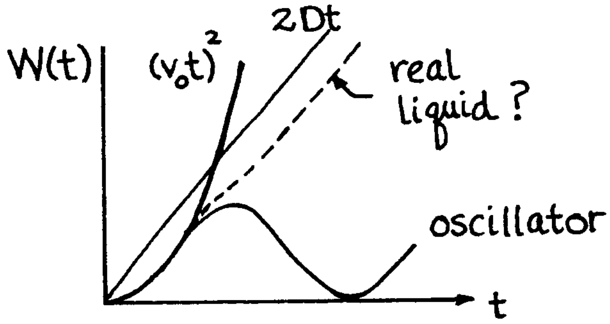
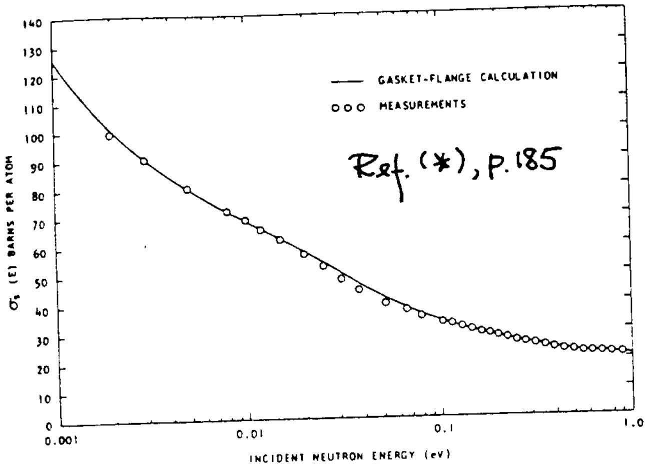
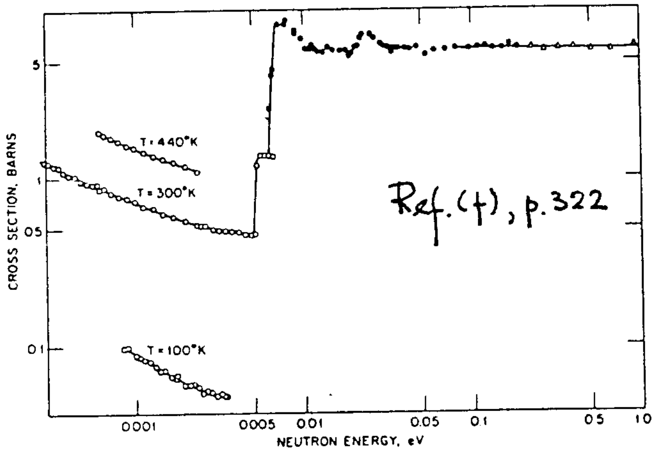


Fig. 9.7 Behavior of width function W(t) for various idealized models.

Neutron scattering cross section results, theory and experiments

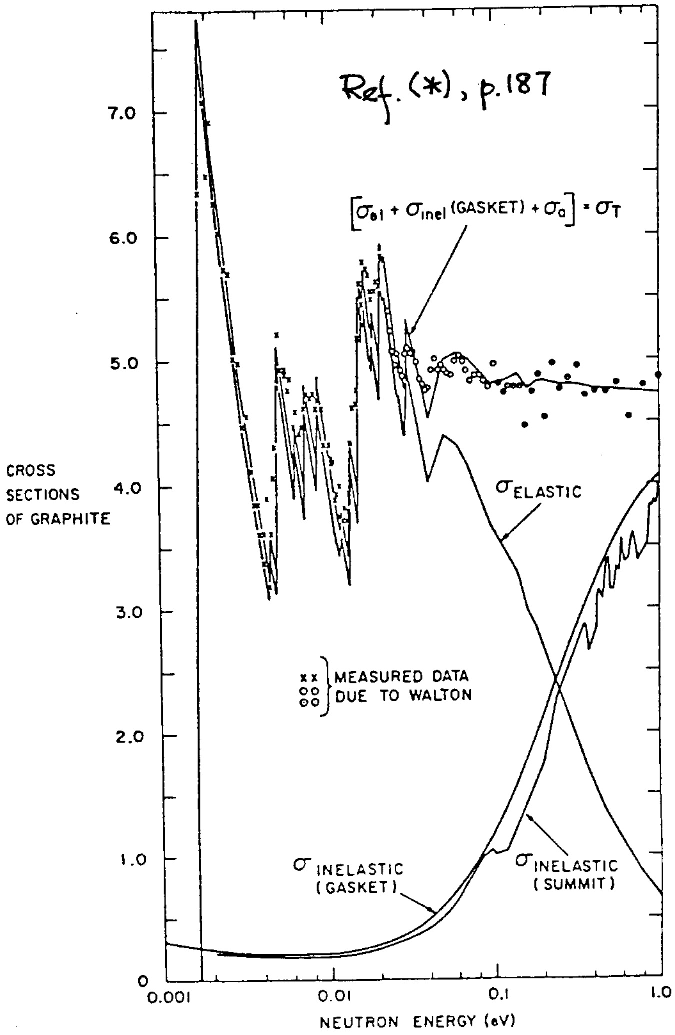


Ref. (*), p.185



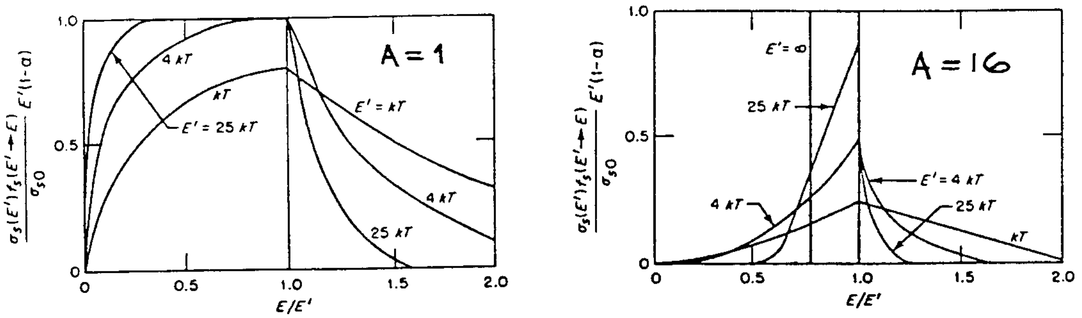
Ref. (†), p.322

FIG. 7.2 ELASTIC SCATTERING CROSS SECTIONS OF BERYLLIUM (AFTER BNL-325).



Ref. (*), p.187

Figure 26. Measured and calculated total scattering cross sections of graphite.



Ref. (†), p.336

FIG. 7.5 ENERGY TRANSFER FUNCTION IN A MONATOMIC GAS WITH $A = 1$

Ref. (*), Reactor Physics in the Resonance & Thermal Regions, A.J. Goodjohn & G.C. Pomeraning, eds. (MIT Press, 1966), vol. 1.

Ref. (†), G.I. Bell & S. Glasstone, Nuclear Reactor Theory (van Nostrand, 1970)