Appendix N

Theory of the Scattering of Neutrons by a Crystal

Let a neutron with momentum $\mathbf{p}$ be scattered by a crystal and emerge with momentum $\mathbf{p}'$ We assume that the only degrees of freedom of the crystal are those associated with ionic motion, that before the scattering the ions are in an eigenstate of the crystal Hamiltonian with energy E_i, and that after the scattering the ions are in an eigenstate of the crystal Hamiltonian with energy E_f. We describe the initial and final states and energies of the composite neutron-ion system as follows:

Before scattering:

$$\Psi_i = \psi_{\mathbf{p}}(\mathbf{r})\Phi_i, \qquad \psi_{\mathbf{p}} = \frac{1}{\sqrt{V}} e^{i\mathbf{p}\cdot\mathbf{r}/\hbar},$$
$$\mathcal{E}_i = E_i + p^2/2M_n;$$

After scattering:

$$\Psi_f = \psi_{\mathbf{p}'}(\mathbf{r})\Phi_f, \qquad \psi_{\mathbf{p}'} = \frac{1}{\sqrt{V}} e^{i\mathbf{p}'\cdot\mathbf{r}/\hbar},$$
$$\mathcal{E}_f = E_f + p'^2/2M_n. \tag{N.1}$$

It is convenient to define variables ω and $\mathbf{q}$ in terms of the neutron energy gain and momentum transfer:

$$\hbar\omega = \frac{p'^2}{2M_n} - \frac{p^2}{2M_n},$$
$$\hbar\mathbf{q} = \mathbf{p}' - \mathbf{p}. \tag{N.2}$$

We describe the neutron-ion interaction by

$$V(\mathbf{r}) = \sum_{\mathbf{R}} v(\mathbf{r} - \mathbf{r}(\mathbf{R})) = \frac{1}{V}\sum_{\mathbf{k},\mathbf{R}} v_{\mathbf{k}} e^{i\mathbf{k}\cdot[\mathbf{r}-\mathbf{r}(\mathbf{R})]}. \tag{N.3}$$

Because the range of v is of order 10^{-13} cm (a typical nuclear dimension), its Fourier components will vary on the scale of $k \approx 10^{13}$ cm^{-1}, and therefore be essentially independent of k for wave vectors of order 10^8 cm^{-1}, the relevant range for experiments that measure phonon spectra. The constant v_0 is conventionally written in terms of a length a, known as the scattering length, defined so that the total cross section for scattering of a neutron by a single isolated ion is given in Born approximation by $4\pi a^2$.[1] Eq. (N.3) is thus written

$$V(\mathbf{r}) = \frac{2\pi\hbar^2 a}{M_n V}\sum_{\mathbf{k},\mathbf{R}} e^{i\mathbf{k}\cdot[\mathbf{r}-\mathbf{r}(\mathbf{R})]}. \tag{N.4}$$

[1] We assume that the nuclei have spin zero and are of a single isotope. In general, one must consider the possibility of a depending on the nuclear state. This leads to two types of terms in the cross section: a *coherent* term, which has the form of the cross section we derive below, but with a replaced by its mean value, and an additional piece, known as the *incoherent* term, which has no striking energy dependence and contributes, along with the multiphonon processes, to the diffuse background.

The probability per unit time for a neutron to scatter from $\mathbf{p}$ to $\mathbf{p}'$ by virtue of its interaction with the ions is almost always calculated with the "golden rule" of lowest-order time-dependent perturbation theory:[2]

$$\begin{aligned} P &= \sum_f \frac{2\pi}{\hbar}\delta(\mathcal{E}_i - \mathcal{E}_f)|(\Psi_i, V\Psi_f)|^2 \\ &= \sum_f \frac{2\pi}{\hbar}\delta(E_f - E_i + \hbar\omega)\left|\frac{1}{V}\int d\mathbf{r}\, e^{i\mathbf{q}\cdot\mathbf{r}}(\Phi_i, V(\mathbf{r})\Phi_f)\right|^2 \\ &= \frac{(2\pi\hbar)^3}{(M_n V)^2} a^2 \sum_f \delta(E_f - E_i + \hbar\omega)\left|\sum_{\mathbf{R}}(\Phi_i, e^{i\mathbf{q}\cdot\mathbf{r}(\mathbf{R})}\Phi_f)\right|^2. \end{aligned} \tag{N.5}$$

The transition rate P is related to the measured cross section, $d\sigma/d\Omega\, dE$, by the fact that the cross section, transition rate, and incident neutron flux, $j = (p/M_n)|\psi_{\mathbf{p}}|^2 = (1/V)(p/M_n)$ satisfy[3]

$$\begin{aligned} j\frac{d\sigma}{d\Omega\, dE}\, d\Omega\, dE &= \frac{p}{M_n V}\frac{d\sigma}{d\Omega\, dE}\, d\Omega\, dE = \frac{PV\, d\mathbf{p}'}{(2\pi\hbar)^3} \\ &= \frac{PVp'^2\, dp'\, d\Omega}{(2\pi\hbar)^3} = \frac{PVM_n p'\, dE\, d\Omega}{(2\pi\hbar)^3}. \end{aligned} \tag{N.6}$$

For a given initial state i (and all final states f compatible with the energy-conserving δ-function), Eqs. (N.5) and (N.6) give

$$\frac{d\sigma}{d\Omega\, dE} = \frac{p'}{p}\frac{Na^2}{\hbar} S_i(\mathbf{q}, \omega), \tag{N.7}$$

where

$$S_i(\mathbf{q}, \omega) = \frac{1}{N}\sum_f \delta\left(\frac{E_f - E_i}{\hbar} + \omega\right)\left|\sum_{\mathbf{R}}(\Phi_i, e^{i\mathbf{q}\cdot\mathbf{r}(\mathbf{R})}\Phi_f)\right|^2. \tag{N.8}$$

To evaluate S_i we use the representation

$$\delta(\omega) = \int_{-\infty}^{\infty}\frac{dt}{2\pi} e^{i\omega t}, \tag{N.9}$$

and note that any operator A obeys the relation $e^{i(E_f - E_i)t/\hbar}(\Phi_f, A\Phi_i) = (\Phi_f, A(t)\Phi_i)$, where $A(t) = e^{iHt/\hbar}Ae^{-iHt/\hbar}$. Furthermore for any pair of operators A and B,

$$\sum_f (\Phi_i, A\Phi_f)(\Phi_f, B\Phi_i) = (\Phi_i, AB\Phi_i). \tag{N.10}$$

Therefore

$$S_i(\mathbf{q}, \omega) = \frac{1}{N}\int\frac{dt}{2\pi} e^{i\omega t}\sum_{\mathbf{R}\mathbf{R}'} e^{-i\mathbf{q}\cdot(\mathbf{R}-\mathbf{R}')}(\Phi_i, \exp\left[i\mathbf{q}\cdot\mathbf{u}(\mathbf{R}')\right]\exp\left[-i\mathbf{q}\cdot\mathbf{u}(\mathbf{R}, t)\right]\Phi_i). \tag{N.11}$$

[2] See, for example, D. Park *Introduction to the Quantum Theory* McGraw-Hill, New York, 1964, p. 244. The analysis of neutron scattering data relies heavily on this use of lowest-order perturbation theory—i.e., on the Born approximation. Higher order perturbation theory produces so-called *multiple scattering* corrections.

[3] We use the fact that a volume element $d\mathbf{p}'$ contains $V\, d\mathbf{p}'/(2\pi\hbar)^3$ neutron states of a given spin. (The argument is identical to that given in Chapter 2 for electrons.)

Generally the crystal will be in thermal equilibrium, and we must therefore average the cross section for the given i over a Maxwell-Boltzmann distribution of equilibrium states. This requires us to replace S_i by its thermal average

$$\boxed{S(\mathbf{q}, \omega) = \frac{1}{N}\sum_{\mathbf{R}\mathbf{R}'} e^{-i\mathbf{q}\cdot(\mathbf{R}-\mathbf{R}')} \int \frac{dt}{2\pi} e^{i\omega t} \langle \exp[i\mathbf{q}\cdot\mathbf{u}(\mathbf{R}')] \exp[-i\mathbf{q}\cdot\mathbf{u}(\mathbf{R}, t)]\rangle,} \tag{N.12}$$

where

$$\langle A \rangle = \frac{\sum e^{-E_i/k_BT}(\Phi_i, A\Phi_i)}{\sum e^{-E_i/k_BT}}. \tag{N.13}$$

Finally,

$$\boxed{\frac{d\sigma}{d\Omega\, dE} = \frac{p'}{p}\frac{Na^2}{\hbar} S(\mathbf{q}, \omega).} \tag{N.14}$$

$S(\mathbf{q}, \omega)$ is known as the *dynamical structure factor* of the crystal, and is entirely determined by the crystal itself without reference to any properties of the neutrons.[4] Furthermore, our result (N.14) has not even exploited the harmonic approximation, and is therefore quite general, applying (with the appropriate changes in notation) even to the scattering of neutrons by liquids. To extract the peculiar characteristics of neutron scattering by a lattice of ions, we now make the harmonic approximation.

In a harmonic crystal the position of any ion at time t is a linear function of the positions and momenta of all the ions at time zero. It can be proved,[5] however, that if A and B are operators linear in the $\mathbf{u}(\mathbf{R})$ and $\mathbf{P}(\mathbf{R})$ of a *harmonic crystal*, then

$$\langle e^A e^B \rangle = e^{(1/2)\langle A^2 + 2AB + B^2\rangle}. \tag{N.15}$$

This result is directly applicable to (N.12):

$$\langle \exp[i\mathbf{q}\cdot\mathbf{u}(\mathbf{R}')] \exp[-i\mathbf{q}\cdot\mathbf{u}(\mathbf{R}, t)]\rangle = \exp\left(-\tfrac{1}{2}\langle[\mathbf{q}\cdot\mathbf{u}(\mathbf{R}')]^2\rangle - \tfrac{1}{2}\langle[\mathbf{q}\cdot\mathbf{u}(\mathbf{R}, t)]^2\rangle + \langle[\mathbf{q}\cdot\mathbf{u}(\mathbf{R}')][\mathbf{q}\cdot\mathbf{u}(\mathbf{R}, t)]\rangle\right). \tag{N.16}$$

This can be further simplified from the observation that the operator products depend only on the relative positions and times

$$\begin{aligned}\langle[\mathbf{q}\cdot\mathbf{u}(\mathbf{R}')]^2\rangle &= \langle[\mathbf{q}\cdot\mathbf{u}(\mathbf{R}, t)]^2\rangle = \langle[\mathbf{q}\cdot\mathbf{u}(0)]^2\rangle \equiv 2W,\\ \langle[\mathbf{q}\cdot\mathbf{u}(\mathbf{R}')][\mathbf{q}\cdot\mathbf{u}(\mathbf{R}, t)]\rangle &= \langle[\mathbf{q}\cdot\mathbf{u}(0)][\mathbf{q}\cdot\mathbf{u}(\mathbf{R}-\mathbf{R}', t)]\rangle,\end{aligned} \tag{N.17}$$

and therefore:

$$S(\mathbf{q}, \omega) = e^{-2W}\int \frac{dt}{2\pi} e^{i\omega t} \sum_{\mathbf{R}} e^{-i\mathbf{q}\cdot\mathbf{R}} \exp\langle[\mathbf{q}\cdot\mathbf{u}(0)][\mathbf{q}\cdot\mathbf{u}(\mathbf{R}, t)]\rangle. \tag{N.18}$$

Equation (N.18) is an *exact* evaluation of $S(\mathbf{q}, \omega)$, Eq. (N.12), *provided that the crystal is harmonic.*

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4 It is simply the Fourier transform of the density autocorrelation function.

5 N. D. Mermin, *J. Math. Phys.* **7**, 1038 (1966) gives a particularly compact proof.

In Chapter 24 we classified neutron scatterings according to the number, m, of phonons emitted and/or absorbed by the neutron. If one expands the exponential occurring in the integrand of S,

$$\exp\langle[\mathbf{q}\cdot\mathbf{u}(0)][\mathbf{q}\cdot\mathbf{u}(\mathbf{R}, t)]\rangle = \sum_{m=0}^{\infty}\frac{1}{m!}\left(\langle[\mathbf{q}\cdot\mathbf{u}(0)][\mathbf{q}\cdot\mathbf{u}(\mathbf{R}, t)]\rangle\right)^m, \tag{N.19}$$

then it can be shown that the mth term in this expansion gives precisely the contribution of the m-phonon processes to the total cross section. We limit ourselves here to showing that the $m = 0$ and $m = 1$ terms give the structure we deduced on less precise grounds for the zero- and one-phonon processes of Chapter 24.

1. *Zero-Phonon Contribution* ($m = 0$) If the exponential on the extreme right of (N.18) is replaced by unity, then the sum over $\mathbf{R}$ can be evaluated with Eq. (L.12), the time integral reduces to a δ-function as in (N.9), and the no-phonon contribution to $S(\mathbf{q}, \omega)$ is just

$$\boxed{S_{(0)}(\mathbf{q}, \omega) = e^{-2W}\,\delta(\omega)\, N \sum_{\mathbf{K}} \delta_{\mathbf{q},\mathbf{K}}.} \tag{N.20}$$

The δ-function requires the scattering to be elastic. Integrating over final energies, we find that:

$$\frac{d\sigma}{d\Omega} = \int dE\, \frac{d\sigma}{d\Omega\, dE} = e^{-2W}(Na)^2 \sum_{\mathbf{K}} \delta_{\mathbf{q},\mathbf{K}}. \tag{N.21}$$

This is precisely what one expects for Bragg-reflected neutrons: The scattering is elastic and occurs only for momentum transfers equal to $\hbar$ times a reciprocal lattice vector. The fact that Bragg scattering is a coherent process is reflected in the cross section being proportional to N^2 times the cross section a^2 for a single scatterer, rather than merely to N times the single ion cross section. Thus the *amplitudes* combine additively (rather than the cross sections). The effect of the thermal vibrations of the ions about their equilibrium positions is entirely contained in the factor e^{-2W}, which is known as the Debye-Waller factor. Since the mean square ionic displacement from equilibrium $\langle[\mathbf{u}(0)]^2\rangle$ will increase with temperature, we find that the thermal vibrations of the ions diminish the intensity of the Bragg peaks but do *not* (as was feared in the early days of X-ray scattering) eliminate the peaks altogether.[6]

2. *One-Phonon Contribution* ($m = 1$) To evaluate the contribution to $d\sigma/d\Omega\, dE$ from the $m = 1$ term in (N.19) one requires the form of

$$\langle[\mathbf{q}\cdot\mathbf{u}(0)][\mathbf{q}\cdot\mathbf{u}(\mathbf{R}, t)]\rangle, \tag{N.22}$$

This is readily evaluated from Eq. (L.14) and the fact that[7]

$$\begin{aligned} a_{\mathbf{k}s}(t) &= a_{\mathbf{k}s}e^{-i\omega_s(\mathbf{k})t}, & a_{\mathbf{k}s}^\dagger(t) &= a_{\mathbf{k}s}^\dagger e^{i\omega_s(\mathbf{k})t},\\ \langle a_{\mathbf{k}'s'}^\dagger a_{\mathbf{k}s}\rangle &= n_s(\mathbf{k})\delta_{\mathbf{k}\mathbf{k}'}\delta_{ss'}, & \langle a_{\mathbf{k}s}^\dagger a_{\mathbf{k}'s'}^\dagger\rangle &= 0,\\ \langle a_{\mathbf{k}s} a_{\mathbf{k}'s'}^\dagger\rangle &= [1 + n_s(\mathbf{k})]\,\delta_{\mathbf{k}\mathbf{k}'}\delta_{ss'}, & \langle a_{\mathbf{k}s}a_{\mathbf{k}'s'}\rangle &= 0.\end{aligned} \tag{N.23}$$

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6 This is a mark of the long-range order that always persists in a true crystal.

7 Here, as in (23.10), $n_s(\mathbf{q})$ is the Bose-Einstein occupation factor for phonons in mode s with wave vector $\mathbf{q}$ and energy $\hbar\omega_s(\mathbf{q})$.

We then find that

$$S_{(1)}(\mathbf{q}, \omega) = e^{-2W} \sum_s \frac{\hbar}{2M\omega_s(\mathbf{q})} [\mathbf{q} \cdot \boldsymbol{\epsilon}_s(\mathbf{q})]^2 \Big([1 + n_s(\mathbf{q})]\, \delta[\omega + \omega_s(\mathbf{q})] + n_s(\mathbf{q})\, \delta[\omega - \omega_s(\mathbf{q})] \Big). \tag{N.24}$$

Substituting this into (N.14) we find that the one-phonon cross section is:

$$\frac{d\sigma}{d\Omega\, dE} = Ne^{-2W} \frac{p'}{p} a^2 \sum_s \frac{1}{2M\omega_s(\mathbf{q})} [\mathbf{q} \cdot \boldsymbol{\epsilon}_s(\mathbf{q})]^2 \Big([1 + n_s(\mathbf{q})]\, \delta[\omega + \omega_s(\mathbf{q})] + n_s(\mathbf{q})\, \delta[\omega - \omega_s(\mathbf{q})] \Big). \tag{N.25}$$

Note that this does indeed vanish unless the one-phonon conservation laws (24.9) or (24.10) are satisfied; thus, as a function of energy, $d\sigma/d\Omega\, dE$ is a series of sharp delta-function peaks at the allowed final neutron energies.

This structure makes it possible to distinguish the one-phonon processes from all the remaining terms in the multiphonon expansion of S or the cross section, all of which can be shown to be smooth functions of the final neutron energy. Note that the intensity in the one-phonon peaks is also modulated by the same Debye-Waller factor that diminishes the intensity of the Bragg peaks. Note also the factor $[\mathbf{q} \cdot \boldsymbol{\epsilon}_s(\mathbf{q})]^2$, which enables one to extract information about the phonon polarization vectors. Finally, the thermal factors $n_s(\mathbf{q})$ and $1 + n_s(\mathbf{q})$ are for processes in which phonons are absorbed or emitted, respectively. These factors are typical for processes involving the creation and absorption of Bose-Einstein particles, and indicate (as is reasonable) that at very low temperatures processes in which phonons are emitted will be the dominant ones (when they are allowed by the conservation laws).

APPLICATION TO X-RAY SCATTERING

Aside from the factor $(p'/p)a^2$, peculiar to the dynamics of neutrons, the inelastic scattering cross section for X rays should have precisely the same form as (N.14). However, one can generally not resolve the small (compared with X-ray energies) energy losses or gains occurring in one-phonon processes, and must therefore, in effect, integrate the cross section over all final energies:

$$\frac{d\sigma}{d\Omega} \propto \int d\omega\, S(\mathbf{q}, \omega) \propto e^{-2W} \sum_{\mathbf{R}} e^{-i\mathbf{q} \cdot \mathbf{R}} \exp \langle [\mathbf{q} \cdot \mathbf{u}(0)][\mathbf{q} \cdot \mathbf{u}(\mathbf{R})] \rangle. \tag{N.26}$$

This result is simply related to our discussion of X-ray scattering in Chapter 6, in which we relied on the static lattice model. In that chapter we found that the scattering for a monatomic Bravais lattice was proportional to a factor:

$$\Big|\sum_{\mathbf{R}} e^{i\mathbf{q} \cdot \mathbf{R}}\Big|^2. \tag{N.27}$$

Equation (N.26) generalizes this result by allowing for the ions to be displaced from their equilibrium positions, $\mathbf{R} \to \mathbf{R} + \mathbf{u}(\mathbf{R})$, and taking a thermal equilibrium average over ionic configurations.

Making the multiphonon expansion in (N.26) will yield the frequency integrals of the individual terms in the multiphonon expansion we made in the neutron case. The no-phonon terms continue to give the Bragg peaks, diminished by the Debye-Waller factor—an aspect of the intensity of the Bragg peaks that was not taken into account in our discussion of Chapter 6. The one-phonon term yields a scattering cross section proportional to

$$\int d\omega\, S_{(1)}(\mathbf{q}, \omega) = e^{-2W} \sum_s \frac{\hbar}{2M\omega_s(\mathbf{q})} (\mathbf{q} \cdot \boldsymbol{\epsilon}_s(\mathbf{q}))^2 \coth \tfrac{1}{2}\beta\hbar\omega_s(\mathbf{q}), \tag{N.28}$$

where $\mathbf{q}$ is the change in X-ray wave vector. Since the change in photon energy is minute, $\mathbf{q}$ is entirely determined by the incident X-ray energy and the direction of observation. The contribution to (N.28) of the terms arising from the various branches of the phonon spectrum may be disentangled, by doing the experiment at several values of $\mathbf{q}$ differing by reciprocal lattice vectors. However the major problem is distinguishing the contribution (N.28) of the one-phonon processes to the total scattering cross section, from the contribution of the multiphonon terms, since the characteristic structure of the one-phonon terms lies entirely in their singular energy dependence, which is lost once the integral over ω has been performed. In practice, one can do little better than to try to estimate the multiphonon contribution from the general result (N.26). Alternatively, one can work at temperatures so low, and momentum transfers q sufficiently small, as to make the expansion (N.19) rapidly convergent. If crystals were strictly classical this would always be possible, since the deviations from equilibrium of the ions would vanish as $T \to 0$. Unfortunately, however, the zero-point ionic vibrations are present even at $T = 0$, and there is therefore an intrinsic limit to the rate at which the multiphonon expansion can converge.