Appendix A3

A3.1 PHONONS—COHERENT AND INCOHERENT INELASTIC SCATTERING

We will now turn to a brief discussion of phonons in solids and their influence on neutron scattering. For further details the reader is referred to one of the comprehensive texts on neutron scattering (Turchin 1965, Lovesey 1984). Our main goals in this discussion are to emphasize the physics involved in coherent and incoherent inelastic neutron scattering from phonons and to present some results which we will use in the text.

For simplicity we will confine the discussion to ideal crystals with only one atom per unit cell. We write the position R_i of the ith atom in the crystal as

$$R_i = \rho_i + u_i(t) \tag{A3.1}$$

where ρ_i represents the equilibrium position of the ith atom in the crystal and $u_i(t)$ represents the motion of the atom about its equilibrium position. It is a basic assumption of our approach that $u_i \ll \rho_i$.

The kinetic energy of the crystal is the sum of the kinetic energies of all the atoms in the crystal

$$T = \sum_i \frac{m_i}{2} \left(\dot{u}_i \right)^2 \tag{A3.2}$$

and the potential energy is, in general, a function, $V(R_i)$, of all the R_i. We take the zero of potential energy to be at the equilibrium position ($R_i = \rho_i$ for all i) and consider that the potential energy is expanded in a power series in u_i. The leading term in this expansion can be written as

$$V = \tfrac{1}{2} \sum_{i,j} \sum_{\mu,\nu} \alpha_{i,j}^{\mu\nu} u_i^\mu u_j^\nu \tag{A3.3}$$

where the $\alpha_{i,j}^{\mu,\nu}$ are called the force constants of the crystal. The superscripts μ and ν label the three components of the vector u_i. Much of the work with

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neutron scattering is devoted to studying these force constants in different materials.

The neglect of higher order terms in the potential energy, (A3.3), is called the harmonic approximation. We will see that the Hamiltonian of the system (given by the sum of (A3.2) and (A3.3)) can be written as the sum of a set of harmonic oscillator Hamiltonians which, when quantized, will each have an energy $\hbar\omega(n + \frac{1}{2})$ where n is a quantum number. We will speak of the system in an eigenstate with quantum number n as containing n phonons of frequency ω. The neglected higher order terms in the potential energy will result in these phonon eigenstates not being exact eigenstates of the actual Hamiltonian. Thus the system will not remain in a given phonon state for an infinite time. We describe this by saying that the neglected terms result in interactions between the phonons with the result that each phonon has a finite lifetime. In addition these higher order terms result in the thermal expansion of solids and the fact that thermal conductivities are finite. These phonon energies are also temperature-dependent due to these terms.

The equations of motion of the system follow from (A3.2) and (A3.3):

$$m_i \ddot{u}_i^\mu = - \sum_{j,\nu} \alpha_{i,j}^{\mu\nu} u_j^\nu. \qquad (A3.4)$$

For a crystal of N atoms there are $3N$ such equations of motion. We see that these equations are coupled—that is the motion of u_i^μ depends in general on all the other u_j^ν except that we expect the coupling to diminish as the atoms i and j are further apart. To simplify these equations we introduce the 'normal modes', that is we introduce new coordinates—linear combinations of the u_i—so that the equation of motion of each of the new coordinates only depends on the new coordinate itself. This is always possible in the case of equations like (A3.4) (Goldstein 1950).

To search for the normal modes we assume the u_i can be written (for the case that all the atoms have mass, $m_i = M$):

$$u_i(t) = \frac{\gamma(q)}{\sqrt{MN}} e^{i(q \cdot \rho_i - \omega t)} \qquad (A3.5)$$

and substitute this into (A3.4). After some manipulation this reduces to

$$\omega^2 \gamma^\mu(q) = \sum_\nu \lambda^{\mu\nu}(q) \gamma^\nu(q) \qquad (A3.6)$$

where the $\lambda(q)$ are linear combinations of $\alpha_{i,j}$. Equation (A3.6) represents three equations, one for each value of μ, and since these equations are linear homogeneous equations for the γ^μ they will only have a solution if the 3×3 determinant:

$$\det \left\| \omega^2 \delta_{\mu\nu} - \lambda^{\mu\nu}(q) \right\| = 0 \qquad (A3.7)$$

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which has three solutions for ω for each q . We denote these solutions as $\omega_s(q)$, $s = 1, 2, 3$. Once the frequencies $\omega_s(q)$ are known one can solve (A3.6) for the amplitudes $\gamma_s(q)$. The general solution of equations (A3.4) will be a superposition of terms like (A3.5).

$$u_i(t) = \sum_{s,q} \frac{A_{s,q}(t)}{\sqrt{N}} \frac{\gamma_s(q)}{\sqrt{M}} e^{iq \cdot \rho_i}. \tag{A3.8}$$

Substitution of (A3.8) into (A3.2) and (A3.3) yields the Hamiltonian as a function of the $A_{s,q}$

$$H = T + V = \tfrac{1}{2} \sum_{s,q} \left(\dot{A}_{s,q} \dot{A}_{s,q}^* + \omega_s^2(q) A_{s,q} A_{s,q}^* \right) \tag{A3.9}$$

which we recognize as a sum of harmonic oscillator Hamiltonians. Proceeding as in the quantization of the simple harmonic oscillator we introduce the harmonic oscillator raising, $a_{s,q}^+$, and lowering, $a_{s,q}$, operators by setting

$$A_{s,q} = \sqrt{\frac{\hbar}{2\omega_s(q)}} \left[a_{s,q} + a_{s,q}^+ \right]. \tag{A3.10}$$

Substituting this into (A3.9) gives

$$H = \sum_{s,q} \hbar \omega_s(q) \left[a_{s,q}^+ a_{s,q} + \tfrac{1}{2} \right]. \tag{A3.11}$$

The eigenvalues of $\left(a_{s,q}^+ a_{s,q} \right)$ are integers, $n_{s,q}$, and

$$\begin{aligned} a_{s,q}^+ |n_{s,q}\rangle &= \sqrt{n_{s,q} + 1} \, |n_{s,q} + 1\rangle \\ a_{s,q} |n_{s,q}\rangle &= \sqrt{n_{s,q}} \, |n_{s,q} - 1\rangle \end{aligned} \tag{A3.12}$$

where the $|n_{s,q}\rangle$ are the eigenstates of $\left(a_{s,q}^+ a_{s,q} \right)$. Since the energy is a sum of terms, $\hbar \omega_s(q)$, multiplied by integers we speak of the system as if it was composed of excitations each with energy $\hbar \omega_s(q)$ and we call these excitations phonons. $n_{s,q}$ is then the number of (s, q) phonons present in the system. Since a and a^+ change the numbers of phonons we refer to them as phonon annihilation and creation operators. By substituting (A3.10) into (A3.8) we see that we can write

$$u_i(t) = \sum_{s,q} \left[\xi_i(s, q) \, a_{s,q} + \xi_i^*(s, q) \, a_{s,q}^+ \right] \tag{A3.13}$$

where

$$\xi_i(s, q) = \sqrt{\frac{\hbar}{2NM\omega_s(q)}} \gamma_s(q) \, e^{iq \cdot \rho_i} \tag{A3.14}$$

that is the displacements $u_i(t)$ are now quantum mechanical operators.

In order to calculate the scattering cross sections we return to (A2.11) and (A2.12). In the matrix element we will use the expression for R_i given by (A3.1) and A3.13):

$$\langle n_{\mathrm{f}} | e^{i\boldsymbol{Q}\cdot\boldsymbol{R}_i} | n_{\mathrm{i}} \rangle = e^{i\boldsymbol{Q}\cdot\boldsymbol{\rho}_i}$$
$$\times \prod_{s,q} \langle n_{\mathrm{f}} | \exp\left\{ i\boldsymbol{Q}\cdot\left[\boldsymbol{\xi}_i(s,q)\,a_{s,q} + \boldsymbol{\xi}_i^*(s,q)\,a_{s,q}^+\right]\right\} | n_{\mathrm{i}} \rangle$$

$$(A3.15)$$

and expand the operator in a series

$$\exp\left\{ i\boldsymbol{Q}\cdot\left[\boldsymbol{\xi}_i(s,q)\,a_{s,q} + \boldsymbol{\xi}_i^*(s,q)\,a_{s,q}^+\right]\right\} = 1 + i\boldsymbol{Q}\cdot\left[\boldsymbol{\xi}_i(s,q)\,a + \boldsymbol{\xi}_i^*(s,q)\,a^+\right]$$
$$- \frac{1}{2}\left[(\boldsymbol{Q}\cdot\boldsymbol{\xi}_i)^2\,a^2 + (\boldsymbol{Q}\cdot\boldsymbol{\xi}_i^*)^2\,(a^+)^2\right.$$
$$\left. + |\boldsymbol{Q}\cdot\boldsymbol{\xi}_i|^2\,(aa^+ + a^+a)\right] + \cdots$$

$$(A3.16)$$

where we have omitted the subscripts.

We see that the second term changes the phonon number by one while the third term changes the phonon number by two or zero. Thus the second term will result in scattering processes in which a single phonon is emitted or absorbed while the third term will result in processes in which either two phonons are emitted or absorbed or the phonon number does not change. Concentrating, for the moment, on processes of the latter type—these correspond to elastic scattering—we see that

$$\beta = \langle n_{\mathrm{f}} | e^{i\boldsymbol{Q}\cdot\boldsymbol{R}_i} | n_{\mathrm{i}} \rangle$$
$$= e^{i\boldsymbol{Q}\cdot\boldsymbol{\rho}_i} \prod_{s,q}\left[1 - \frac{1}{2}|\boldsymbol{Q}\cdot\boldsymbol{\xi}_i|^2\,(2n_{s,q}+1)\right]$$

$$(A3.17)$$

(the eigenvalue of $(aa^+ + a^+a)$ is $(2n+1)$ from (A3.12)).

Since the second term in the square bracket is much less than one we can write

$$\beta_i = e^{i\boldsymbol{Q}\cdot\boldsymbol{\rho}_i}e^{-W(Q)}$$

$$(A3.18)$$

where

$$W(Q) = \tfrac{1}{2} \sum_{s,q} \left[|Q \cdot \xi_i|^2 (2n_{s,q} + 1) \right]$$

$$= \tfrac{1}{2} \sum_{s,q} \frac{\hbar}{2M\omega_s(q)N} |Q \cdot \gamma(s,q)|^2 (2n_{s,q} + 1). \qquad (A3.19)$$

If we introduce

$$g(\omega) = \frac{1}{3N} \sum_{s,q} \delta(\omega - \omega_s(q)) \qquad (A3.20)$$

we see that $g(\omega)$ is normalized, i.e.

$$\int d\omega \, g(\omega) = 1 \qquad (A3.21)$$

and that $g(\omega) \, d\omega$ represents the probability of finding a state with energy given by $\hbar\omega$ where ω is in the range ω to $\omega + d\omega$. Since in thermal equilibrium

$$\langle 2n + 1 \rangle = \coth\left(\frac{\hbar\omega}{2k_B T}\right) \qquad (A3.22)$$

we can write (A3.19) as:

$$W(Q) = \frac{3\hbar}{4M} \int d\omega \frac{g(\omega)}{\omega} \left\langle |Q \cdot \gamma|^2 \right\rangle \coth\left(\frac{\hbar\omega}{2k_B T}\right) \qquad (A3.23)$$

where the average of $|Q \cdot \gamma|^2$ is taken over a surface in Q with constant ω and $e^{-2W(Q)}$ is called the Debye–Waller factor and represents the reduction in scattering caused by the vibrations of the atoms around their equilibrium positions. It is important in X-ray and Mössbauer scattering as well as in neutron scattering.

A3.1.1   One-phonon coherent inelastic scattering

For inelastic scattering we concentrate on the one-phonon case so only the second term in (A3.16) will contribute. The states $|n_i\rangle$, $|n_f\rangle$ will differ in that the quantum numbers of one particular phonon mode (s, q) will differ by ± 1. The operators for all the other modes (except s, q) will be diagonal and since the removal of a single mode from the sum (A3.19) will have no perceptible effect there will be a contribution $e^{-W(Q)}$ from all these diagonal modes. Hence (A3.15) becomes, using (A3.16), (A3.12) and (A3.14):

$$\beta_i = \left\langle n_{\rm f} \left| {\rm e}^{{\rm i}\boldsymbol{Q}\cdot\boldsymbol{R}_i} \right| n_{\rm i} \right\rangle = {\rm e}^{-W(Q)} \left(\frac{\hbar}{2MN\omega_s(\boldsymbol{q})} \right)^{1/2} {\rm i}\boldsymbol{Q}\cdot\boldsymbol{\gamma}(s,\boldsymbol{q})$$

$$\times \begin{cases} {\rm e}^{{\rm i}\boldsymbol{\rho}_i\cdot(\boldsymbol{Q}+\boldsymbol{q})}\sqrt{n_{s,\boldsymbol{q}}} \\ {\rm e}^{{\rm i}\boldsymbol{\rho}_i\cdot(\boldsymbol{Q}-\boldsymbol{q})}\sqrt{n_{s,\boldsymbol{q}}+1} \end{cases} \qquad (A3.24)$$

for $\begin{cases} \text{absorption} \\ \\ \text{emission} \end{cases}$ of a phonon.

For coherent scattering we require $\left|\sum_i \beta_i\right|^2$ (see (A2.11)) which is proportional to

$$\alpha_{\pm} = \frac{1}{N} \left| \sum_i {\rm e}^{{\rm i}\boldsymbol{\rho}_i\cdot(\boldsymbol{Q}\pm\boldsymbol{q})} \right|^2. \qquad (A3.25)$$

Now we can see that if, in a perfect crystal, the exponent in (A3.25) is an integer multiple of 2π for every $\boldsymbol{\rho}_i$ the sum will be very large. If this condition does not hold the sum will tend to zero. It turns out (see Turchin 1965, ch 3) that we can write

$$\alpha_{\pm} = \frac{(2\pi)^3}{B} \delta^{(3)}(\boldsymbol{Q}\pm\boldsymbol{q}-\boldsymbol{\tau}) \qquad (A3.26)$$

where $\boldsymbol{\tau}$ is a reciprocal lattice vector and B is the volume of a unit cell in the crystal. If $\boldsymbol{\tau}$ were absent from (A3.26) the δ-function would represent the condition of conservation of momentum. The presence of $\boldsymbol{\tau}$ means that the neutron can be diffracted by the periodic crystal lattice during the inelastic scattering process. Using (A3.24)–(A3.26) in (A2.11) we finally obtain the coherent one-phonon inelastic scattering cross section:

$$\left(\frac{{\rm d}^2\sigma}{{\rm d}\Omega\,{\rm d}\omega}\right) = a_{\rm coh}^2 \left(\frac{k_{\rm f}}{k_{\rm i}}\right) {\rm e}^{-2W(Q)} \frac{(2\pi)^3\hbar}{NB2M} \sum_{s,\boldsymbol{q}} \frac{|\boldsymbol{Q}\cdot\boldsymbol{\gamma}(s,\boldsymbol{q})|^2}{\omega_s(\boldsymbol{q})}$$

$$\times \begin{cases} \frac{\delta^{(3)}(\boldsymbol{Q}+\boldsymbol{q}-\boldsymbol{\tau})\delta(\hbar\omega_{s,\boldsymbol{q}}+\hbar\omega)}{\left({\rm e}^{\hbar\omega/k_{\rm B}T}-1\right)} \\ \frac{\delta^{(3)}(\boldsymbol{Q}-\boldsymbol{q}-\boldsymbol{\tau})\delta(\hbar\omega_{s,\boldsymbol{q}}-\hbar\omega)}{\left(1-{\rm e}^{-\hbar\omega/k_{\rm B}T}\right)} \end{cases} \qquad (A3.27)$$

for $\begin{cases} \text{absorption} \\ \\ \text{emission} \end{cases}$ of a phonon.

The presence of the two δ-functions indicates that in one-phonon coherent inelastic scattering, energy and momentum are both conserved. As a result of this the scattering cross section will show peaks at values of ω, $\boldsymbol{Q}$ satisfying

$$\omega = \pm\omega_s\left(\boldsymbol{Q}\right) = \frac{\hbar}{2m}\left(k_i^2 - k_f^2\right) \tag{A3.28}$$

although these peaks will be broadened to a finite width because of the anharmonic forces which we have neglected. Thus coherent inelastic scattering can be used to measure the functional dependence $\omega_s\left(\boldsymbol{q}\right)$ called the dispersion curve— and there is a vast amount of research effort devoted to measuring dispersion curves in various materials and relating these curves to the force constants in the material. At small Q we have

$$\omega_s = c_s Q \tag{A3.29}$$

these are the acoustic modes—the phonons representing sound waves. The Debye model assumes that (A3.29) holds up to some maximum value of Q. In the following discusson we shall make this assumption and concentrate on a single mode (single value of s).

From (2.30) we can write

$$Q = \sqrt{k_i^2 + k_f^2 - 2k_i k_f \cos\theta} \tag{A3.30}$$

where θ is the angle between $\boldsymbol{k}_i$ and $\boldsymbol{k}_f$. Thus Q lies in the range

$$|\boldsymbol{k}_i - \boldsymbol{k}_f| \le Q \le k_i + k_f \tag{A3.31}$$

corresponding to θ lying between $\theta = 0$ and $\theta = \pi$. Using (A3.29) and (A3.31) we can plot ω against k_f for different values of θ and for fixed k_i. Every point within the shaded region of figure A3.1 corresponds to some value of θ. On the same graph we can plot the magnitude of ω from (A3.28). Scattering is allowed for those values of k_f where the parabolae (A3.28) lie within the shaded region. For the case shown, corresponding to the initial neutron velocity, $v_i = \hbar k_i/m > c_s$ both phonon emission ($k_f < k_i$) and phonon absorption ($k_f > k_i$) are possible. In the case when this condition does not hold only phonon absorption is possible. We will have occasion to refer to this figure in our discussions of the scattering of UCN.

A3.1.2   Incoherent one-phonon inelastic scattering

For incoherent inelastic scattering we see from (A2.12) and (A3.24) that the cross section depends on

$$\alpha' = \sum_i |\beta_i|^2 = \sum_i \frac{\hbar}{2MN\omega_s\left(\boldsymbol{q}\right)} e^{-2W(Q)} |\boldsymbol{Q}\cdot\boldsymbol{\gamma}_s\left(\boldsymbol{q}\right)|^2 \left\{ \begin{array}{c} n_s\left(\boldsymbol{q}\right) \\ n_s\left(\boldsymbol{q}\right) + 1 \end{array} \right\}.$$
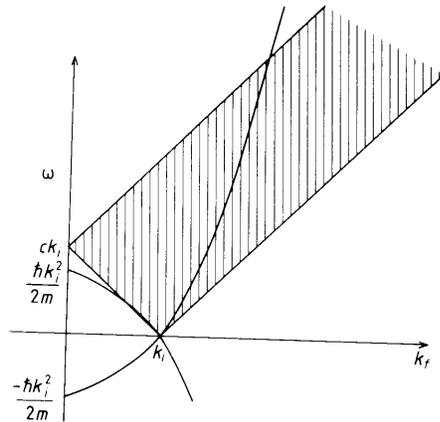$$\tag{A3.32}$$

Figure A3.1 One-phonon coherent scattering. Energy transfer ω against final neutron wavenumber, k_f, for fixed incident neutron wavenumber k_i. (A3.29) and (A3.31) allow all points within the shaded region. Conservation of energy (A3.28) gives the parabola. Adapted from Turchin (1965).

We see that because of the form of (A3.32) the exponentials have disappeared from the result so that there will be no momentum conservation δ-functions (A3.26) in the incoherent scattering cross section. Thus incoherent scattering does not conserve momentum with an individual phonon in the way coherent scattering does. This is because, as we have seen in the discussion of correlation functions, incoherent scattering essentially takes place from individual atoms. During incoherent scattering the impulse transmitted from the neutron to the crystal displaces a single atom which then excites a superposition of phonon waves travelling in different directions. This does not require a discrete momentum to be transferred from the neutron as would be the case in the excitation of a single phonon.

Putting (A3.32) into (A2.12) we obtain the result for the incoherent scattering cross section:

$$
\left(\frac{\mathrm{d}^2 \sigma}{\mathrm{d}\Omega \, \mathrm{d}\omega} \right)_{\mathrm{inc}} = a_{\mathrm{inc}}^2 \frac{k_f}{k_i} \sum_{s,q} \frac{\hbar}{2MN\omega_s(q)} \mathrm{e}^{-2W(Q)} \left| Q \cdot \gamma_s(q) \right|^2
$$

$$
\times \left\{ \begin{array}{c} \langle n_s(q) \rangle \, \delta(\hbar\omega_{s,q} + \hbar\omega) \\[2mm] \langle n_s(q) + 1 \rangle \, \delta(\hbar\omega_{s,q} - \hbar\omega) \end{array} \right\} \qquad (A3.33)
$$

where, again, the brackets $\langle \ldots \rangle$ refer to thermal averaging.

As in our discussion of the Debye–Waller factor, $W(Q)$, we can replace the summation over s, q by an integral

$$\sum_{s,q} \longrightarrow 3N \int \mathrm{d}\omega'\, g(\omega') \qquad\qquad \text{(A3.34)}$$

where $g(w)$ is given by (A3.20), and we evaluate the integral by means of the δ functions in (A3.33). Further, since

$$\frac{\langle n_s(q)+1 \rangle}{\omega_{s,q}} = \frac{1}{\omega_{s,q}\left(1 - \mathrm{e}^{-\hbar\omega_{s,q}/k_\mathrm{B}T}\right)} = \psi\left(\omega_{s,q}\right)$$

$$\frac{\langle n_s(q) \rangle}{\omega_{s,q}} = \frac{1}{\omega_{s,q}\left(\mathrm{e}^{\hbar\omega_{s,q}/k_\mathrm{B}T} - 1\right)} = \psi\left(-\omega_{s,q}\right) \qquad \text{(A3.35)}$$

we can write the result in a form which applies to both phonon emission and absorption (dropping the subscripts on $\omega_{s,q}$).

$$\left(\frac{\mathrm{d}^2\sigma}{\mathrm{d}\Omega\,\mathrm{d}\omega}\right)_{\mathrm{inc}} = a_{\mathrm{inc}}^2 \frac{k_\mathrm{f}}{k_\mathrm{i}} \mathrm{e}^{-2W(Q)} \left|Q \cdot \gamma\right|_{\mathrm{ave}}^2 \frac{3\hbar}{2M} g(\omega)\psi\left(\omega_{s,q}\right). \qquad \text{(A3.36)}$$

Since all the factors in (A3.36) are known except for $g(\omega)$ one-phonon incoherent inelastic scattering can be used for studying the spectral density of normal modes, $g(\omega)$, in many materials including liquids.

As we shall see the coherent scattering of UCN is usually small because of the restrictions imposed by the momentum conservation conditions (A3.1) and incoherent inelastic scattering is usually the most important.

For applications involving integrals over the double-differential cross sections, (A3.27) or (A3.36), it is sufficient to use what is called the 'incoherent approximation'. This consists of using (A3.36) with a_{inc}^2 replaced by $a_{\mathrm{inc}}^2 + a_{\mathrm{coh}}^2$ as the total double-differential cross section (Turchin 1965).