

# Chapter 4: Crystal Lattice Dynamics

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A crystal lattice is special due to its long range order. As you explored in the homework, this yields a sharp diffraction pattern, especially in 3-d. However, lattice vibrations are important. Among other things, they contribute to

- the thermal conductivity of insulators is due to dispersive lattice vibrations, and it can be quite large (in fact, diamond has a thermal conductivity which is about 6 times that of metallic copper).
- in scattering they reduce of the spot intensities, and also allow for inelastic scattering where the energy of the scatterer (i.e. a neutron) changes due to the absorption or creation of a phonon in the target.
- electron-phonon interactions renormalize the properties of electrons (make them heavier).
- superconductivity (conventional) comes from multiple electron-phonon scattering between time-reversed electrons.

## 1 An Adiabatic Theory of Lattice Vibrations

At first glance, a theory of lattice vibrations would appear impossibly daunting. We have  $N \approx 10^{23}$  ions interacting strongly (with energies of about  $(e^2/\mathbf{A})$ ) with  $N$  electrons. However, there is a natural expansion parameter for this problem, which is the ratio of the electronic to the

ionic mass:

$$\frac{m}{M} \ll 1 \quad (1)$$

which allows us to derive an accurate theory.

Due to Newton's third law, the forces on the ions and electrons are comparable  $F \sim e^2/a^2$ , where  $a$  is the lattice constant. If we imagine that, at least for small excursions, the forces binding the electrons and the ions to the lattice may be modeled as harmonic oscillators, then

$$F \sim e^2/a^2 \sim m\omega_{electron}^2 a \sim M\omega_{ion}^2 a \quad (2)$$

This means that

$$\frac{\omega_{ion}}{\omega_{electron}} \sim \left(\frac{m}{M}\right)^{1/2} \sim 10^{-3} \text{ to } 10^{-2} \quad (3)$$

Which means that the ion is essentially stationary during the period of the electronic motion. For this reason we may make an adiabatic

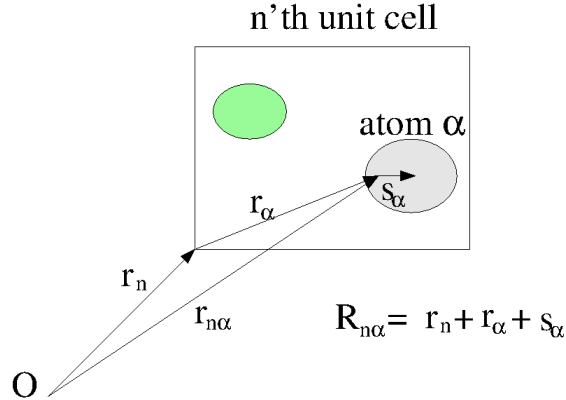


Figure 1: *Nomenclature for the lattice vibration problem.*  $\mathbf{s}_{n,\alpha}$  is the displacement of the atom  $\alpha$  within the  $n$ -th unit cell from its equilibrium position, given by  $\mathbf{r}_{n,\alpha} = \mathbf{r}_n + \mathbf{r}_\alpha$ , where as usual,  $\mathbf{r}_n = n_1\mathbf{a}_1 + n_2\mathbf{a}_2 + n_3\mathbf{a}_3$ .

approximation:

- we treat the ions as stationary at locations  $\mathbf{R}_1, \dots, \mathbf{R}_N$  and determine the electronic ground state energy,  $E(\mathbf{R}_1, \dots, \mathbf{R}_N)$ . This may be done using standard ab-initio band structure techniques (DFT, GGA, etc.).
- we then use this as a potential for the ions; i.e.. we recalculate  $E$  as a function of the ionic locations, always assuming that the electrons remain in their ground state.

Thus the potential energy for the ions

$$\phi(\mathbf{R}_1, \dots, \mathbf{R}_N) = E(\mathbf{R}_1, \dots, \mathbf{R}_N) + \text{the ion-ion interaction} \quad (4)$$

We will define the zero potential such that when all  $\mathbf{R}_n$  are at their equilibrium positions,  $\phi = 0$ . Then

$$H = \sum_n \frac{P_n^2}{2M} + \phi(\mathbf{R}_1, \dots, \mathbf{R}_N) \quad (5)$$

Typical lattice vibrations involve small atomic excursions of the order  $0.1\text{\AA}$  or smaller, thus we may expand about the equilibrium position of the ions.

$$\phi(\{r_{n\alpha i} + s_{n\alpha i}\}) = \phi(\{r_{n\alpha i}\}) + \frac{\partial \phi}{\partial r_{n\alpha i}} s_{n\alpha i} + \frac{1}{2} \frac{\partial^2 \phi}{\partial r_{n\alpha i} \partial r_{m\beta j}} s_{n\alpha i} s_{m\beta j} \quad (6)$$

The first two terms in the sum are zero; the first by definition, and the second is zero since it is the first derivative of a potential being evaluated at the equilibrium position. We will define the matrix

$$\Phi_{n\alpha i}^{m\beta j} = \frac{\partial^2 \phi}{\partial r_{n\alpha i} \partial r_{m\beta j}} \quad (7)$$

From the different conservation laws (related to symmetries) of the system one may derive some simple relationships for  $\Phi$ . We will discuss these in detail later. However, one must be introduced now, that is,

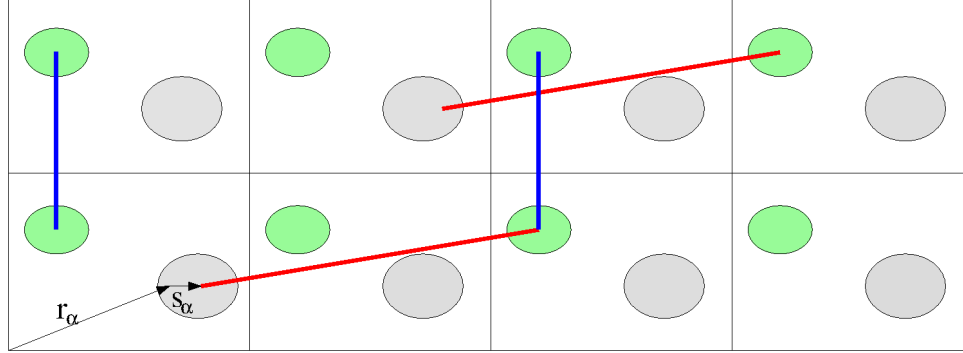


Figure 2: Since the coefficients of potential between the atoms linked by the blue lines (or the red lines) must be identical,  $\Phi_{n\alpha i}^{m\beta j} = \Phi_{0\alpha i}^{(m-n)\beta j}$ .

due to translational invariance.

$$\Phi_{n\alpha i}^{m\beta j} = \Phi_{0\alpha i}^{(m-n)\beta j} = \frac{\partial^2 \phi}{\partial r_{0\alpha i} \partial r_{(n-m)\beta j}} \quad (8)$$

ie, it can only depend upon the distance. This is important for the next subsection.

## 1.1 The Equation of Motion

From the derivative of the potential, we can calculate the force on each site

$$F_{n\alpha i} = - \frac{\partial \phi(\{r_{m\beta j} + s_{m\beta j}\})}{\partial s_{n\alpha i}} \quad (9)$$

so that the equation of motion is

$$-\Phi_{n\alpha i}^{m\beta j} s_{m\beta j} = M_{\alpha} \ddot{s}_{n\alpha i} \quad (10)$$

If there are  $N$  unit cells, each with  $r$  atoms, then this gives  $3Nr$  equations of motion. We will take advantage of the periodicity of the lattice by using Fourier transforms to achieve a significant decoupling of these equations. Imagine that the coordinate  $s$  of each site is decomposed into its Fourier components. Since the equations are linear, we may just consider one of these components to derive our equations of motion in Fourier space

$$s_{n\alpha i} = \frac{1}{\sqrt{M_\alpha}} u_{\alpha i}(\mathbf{q}) e^{i(\mathbf{q} \cdot \mathbf{r}_n - \omega t)} \quad (11)$$

where the first two terms on the rhs serve as the polarization vector for the oscillation,  $u_{\alpha i}(\mathbf{q})$  is independent of  $n$  due to the translational invariance of the system. In a real system the real  $s$  would be composed

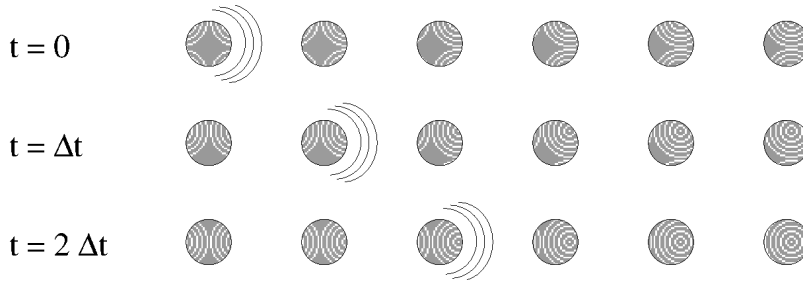


Figure 3:  $u_{\alpha i}(\mathbf{q})$  is independent of  $n$  so that a lattice vibration can propagate and respect the translational invariance of the lattice.

of a sum over all  $\mathbf{q}$  and polarizations. With this substitution, the equations of motion become

$$\omega^2 u_{\alpha i}(\mathbf{q}) = \frac{1}{\sqrt{M_\alpha M_\beta}} \Phi_{n\alpha i}^{m\beta j} e^{i\mathbf{q} \cdot (\mathbf{r}_m - \mathbf{r}_n)} u_{\beta j}(\mathbf{q}) \quad \text{sum repeated indices.} \quad (12)$$

Recall that  $\Phi_{n\alpha i}^{m\beta j} = \Phi_{0\alpha i}^{(m-n)\beta j}$  so that if we identify

$$D_{\alpha i}^{\beta j} = \frac{1}{\sqrt{M_\alpha M_\beta}} \Phi_{n\alpha i}^{m\beta j} e^{i\mathbf{q}\cdot(\mathbf{r}_m - \mathbf{r}_n)} = \frac{1}{\sqrt{M_\alpha M_\beta}} \Phi_{0\alpha i}^{p\beta j} e^{i\mathbf{q}\cdot(\mathbf{r}_p)} \quad (13)$$

where  $\mathbf{r}_p = \mathbf{r}_m - \mathbf{r}_n$ , then the equation of motion becomes

$$\omega^2 u_{\alpha i}(\mathbf{q}) = D_{\alpha i}^{\beta j} u_{\beta j}(\mathbf{q}) \quad (14)$$

or

$$\left( D_{\alpha i}^{\beta j} - \omega^2 \delta_{\alpha i}^{\beta j} \right) u_{\beta j}(\mathbf{q}) = 0 \quad (15)$$

which only has nontrivial ( $u \neq 0$ ) solutions if  $\det(\mathbf{D}(\mathbf{q}) - \omega^2 \mathbf{I}) = 0$ .

For each  $\mathbf{q}$  there are  $3r$  different solutions (branches) with eigenvalues  $\omega^{(n)}(\mathbf{q})$  (or rather  $\omega^{(n)}(\mathbf{q})$  are the root of the eigenvalues). The dependence of these eigenvalues  $\omega^{(n)}(\mathbf{q})$  on  $\mathbf{q}$  is known as the dispersion relation.

## 1.2 Example, a Linear Chain

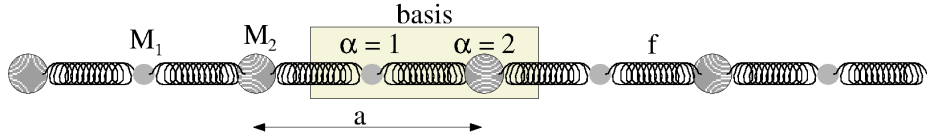


Figure 4: A linear chain of oscillators composed of a two-element basis with different masses,  $M_1$  and  $M_2$  and equal strength springs with spring constant  $f$ .

Consider a linear chain of oscillators composed of a two-element basis with different masses,  $M_1$  and  $M_2$  and equal strength springs with spring constant  $f$ . It has the potential energy

$$\phi = \frac{1}{2} f \sum_n (s_{n,1} - s_{n,2})^2 + (s_{n,2} - s_{n+1,1})^2. \quad (16)$$



We may suppress the indices  $i$  and  $j$ , and search for a solution

$$s_{n\alpha} = \frac{1}{\sqrt{M_\alpha}} u_\alpha(\mathbf{q}) e^{i(\mathbf{q}\cdot\mathbf{r}_n - \omega t)} \quad (17)$$

to the equation of motion

$$\omega^2 u_\alpha(\mathbf{q}) = D_\alpha^\beta u_\beta(\mathbf{q}) \quad \text{where} \quad D_\alpha^\beta = \frac{1}{\sqrt{M_\alpha M_\beta}} \Phi_{0\alpha}^{p,\beta} e^{i\mathbf{q}\cdot(\mathbf{r}_p)} \quad (18)$$

and,

$$\Phi_{n,\alpha}^{m,\beta} = \frac{\partial^2 \phi}{\partial r_{0,\alpha} \partial r_{(n-m),\beta}} \quad (19)$$

where nontrivial solutions are found by solving  $\det(\mathbf{D}(\mathbf{q}) - \omega^2 \mathbf{I}) = 0$ .

The potential matrix has the form

$$\Phi_{n,1}^{n,1} = \Phi_{n,2}^{n,2} = 2f \quad (20)$$

$$\Phi_{n,1}^{n,2} = \Phi_{n,2}^{n,1} = \Phi_{n,1}^{n-1,2} = \Phi_{n,2}^{n+1,1} = -f. \quad (21)$$

This may be Fourier transformed on the space index  $n$  by inspection, so that

$$\begin{aligned} D_\alpha^\beta &= \frac{1}{\sqrt{M_\alpha M_\beta}} \Phi_{0\alpha}^{p,\beta} e^{i\mathbf{q}\cdot(\mathbf{r}_p)} \\ &= \begin{pmatrix} \frac{2f}{M_1} & -\frac{f}{\sqrt{M_1 M_2}} (1 + e^{-iqa}) \\ -\frac{f}{\sqrt{M_1 M_2}} (1 + e^{+iqa}) & \frac{2f}{M_2} \end{pmatrix} \end{aligned} \quad (22)$$

Note that the matrix  $\mathbf{D}$  is hermitian, as it must be to yield real, physical, eigenvalues  $\omega^2$  (however,  $\omega$  can still be imaginary if  $\omega^2$  is negative, indicating an unstable mode). The secular equation  $\det(\mathbf{D}(\mathbf{q}) - \omega^2 \mathbf{I}) = 0$  becomes

$$\omega^4 - \omega^2 2f \left( \frac{1}{M_1} + \frac{1}{M_2} \right) + \frac{4f^2}{M_1 M_2} \sin^2(qa/2) = 0, \quad (23)$$

with solutions

$$\omega^2 = f \left( \frac{1}{M_1} + \frac{1}{M_2} \right) \pm f \sqrt{\left( \frac{1}{M_1} + \frac{1}{M_2} \right)^2 - \frac{4}{M_1 M_2} \sin^2(qa/2)} \quad (24)$$

This equation simplifies significantly in the  $q \rightarrow 0$  and  $q/a \rightarrow \pi$  limits.

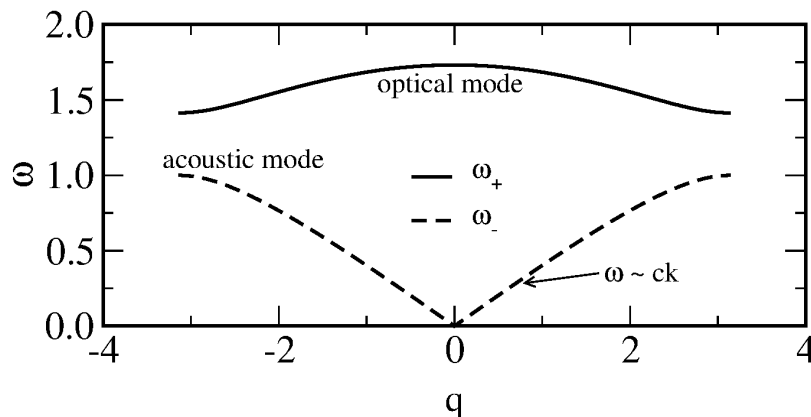


Figure 5: *Dispersion of the linear chain of oscillators shown in Fig. 4 when  $M_1 = 1$ ,  $M_2 = 2$  and  $f = 1$ . The upper branch  $\omega_+$  is called the optical and the lower branch is the acoustic mode.*

In units where  $a = 1$ , and where the reduced mass  $1/\mu = \left( \frac{1}{M_1} + \frac{1}{M_2} \right)$ ,

$$\lim_{q \rightarrow 0} \omega_-(q) = qa \sqrt{\frac{f\mu}{2M_1 M_2}} \quad \lim_{q \rightarrow 0} \omega_+(q) = \sqrt{\frac{2f}{\mu}} \quad (25)$$

and

$$\omega_-(q = \pi/a) = \sqrt{2f/M_2}. \quad \omega_+(q = \pi/a) = \sqrt{2f/M_1} \quad (26)$$

As a result, the  $+$  mode is quite flat; whereas the  $-$  mode varies from zero at the Brillouin zone center  $q = 0$  to a flat value at the edge of the zone. This behavior is plotted in Fig. 5.

It is also instructive to look at the eigenvectors, since they will tell us how the atoms vibrate. Let's look at the optical mode at  $q = 0$ ,  $\omega_+(0) = \sqrt{2f/\mu}$ . Here,

$$\mathbf{D} = \begin{pmatrix} 2f/M_1 & -2f/\sqrt{M_1M_2} \\ -2f/\sqrt{M_1M_2} & 2f/M_2 \end{pmatrix}. \quad (27)$$

Eigenvectors are non-trivial solutions to  $(\omega^2\mathbf{I} - \mathbf{D})\mathbf{u} = 0$ , or

$$0 = \begin{pmatrix} 2f/\mu - 2f/M_1 & 2f/\sqrt{M_1M_2} \\ 2f/\sqrt{M_1M_2} & 2f/\mu - 2f/M_2 \end{pmatrix} \begin{pmatrix} u_1 \\ u_2 \end{pmatrix}. \quad (28)$$

with the solution  $u_1 = -\sqrt{M_2/M_1}u_2$ . In terms of the actual displacements Eqs.11

$$\frac{s_{n1}}{s_{n2}} = \sqrt{\frac{M_2}{M_1}} \frac{u_1}{u_2} \quad (29)$$

or  $s_{n1}/s_{n2} = -M_2/M_1$  so that the two atoms in the basis are moving out of phase with amplitudes of motion inversely proportional to their masses. These modes are described as optical modes since these atoms,

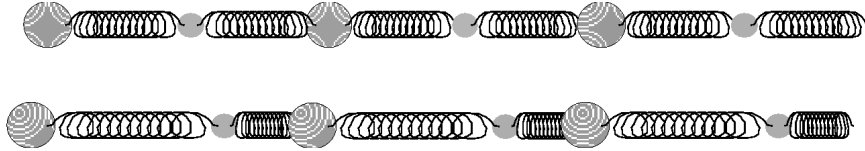


Figure 6: *Optical Mode (bottom) of the linear chain (top).*

if oppositely charged, would form an oscillating dipole which would couple to optical fields with  $\lambda \sim a$ . Not all optical modes are optically active.

### 1.3 The Constraints of Symmetry

We know a great deal about the dispersion of the lattice vibrations without solving explicitly for them. For example, we know that for each  $q$ , there will be  $dr$  modes (where  $d$  is the lattice dimension, and  $r$  is the number of atoms in the basis). We also expect (and implicitly assumed above) that the allowed frequencies are real and positive. However, from simple mathematical identities, the point-group and translational symmetries of the lattice, and its time-reversal invariance, we can learn more about the dispersion without solving any particular problem.

The basic symmetries that we will employ are

- The translational invariance of the lattice and reciprocal lattice.
- The point group symmetries of the lattice and reciprocal lattice.
- Time-reversal invariance.

#### 1.3.1 Symmetry of the Dispersion

**Complex Properties of the dispersion and Eigenmodes** First, from the symmetry of the second derivative, one may show that  $\omega^2$  is real. Recall that the dispersion is determined by the secular equation  $\det(\mathbf{D}(\mathbf{q}) - \omega^2\mathbf{I}) = 0$ , so if  $\mathbf{D}$  is hermitian, then its eigenvalues,  $\omega^2$ , must be real.

$$D_{\alpha i}^{*\beta j} = \frac{1}{\sqrt{M_\alpha M_\beta}} \Phi_{0\alpha i}^{p\beta j} e^{-i\mathbf{q}\cdot(\mathbf{r}_p)} \quad (30)$$

$$= \frac{1}{\sqrt{M_\alpha M_\beta}} \Phi_{0,\alpha,i}^{-p,\beta,j} e^{i\mathbf{q}\cdot(\mathbf{r}_p)} \quad (31)$$

Then, due to the symmetric properties of the second derivative

$$D_{\alpha i}^{*\beta j} = \frac{1}{\sqrt{M_\alpha M_\beta}} \Phi_{-p,\beta,j}^{0,\alpha,i} e^{i\mathbf{q}\cdot(\mathbf{r}_p)} = \frac{1}{\sqrt{M_\alpha M_\beta}} \Phi_{0,\beta,j}^{p,\alpha,i} e^{i\mathbf{q}\cdot(\mathbf{r}_p)} = D_{\beta j}^{\alpha i} \quad (32)$$

Thus,  $\mathbf{D}^{T*} = \mathbf{D}^\dagger = \mathbf{D}$  so  $\mathbf{D}$  is hermitian and its eigenvalues  $\omega^2$  are real. This means that either  $\omega$  are real or they are pure imaginary. We will assume the former. The latter yields pure exponential growth of our Fourier solution, indicating an instability of the lattice to a second-order structural phase transition.

Time-reversal invariance allows us to show related results. We assume a solution of the form

$$s_{n\alpha i} = \frac{1}{\sqrt{M_\alpha}} u_{\alpha i}(\mathbf{q}) e^{i(\mathbf{q}\cdot\mathbf{r}_n - \omega t)} \quad (33)$$

which is a plane wave. Suppose that the plane wave is moving to the right so that  $\mathbf{q} = \hat{\mathbf{x}}q_x$ , then the plane of stationary phase travels to the right with

$$x = \frac{\omega}{q_x} t. \quad (34)$$

Clearly then changing the sign of  $q_x$  is equivalent to taking  $t \rightarrow -t$ . If the system is to display proper time-reversal invariance, so that the plane wave retraces its path under time-reversal, it must have the same frequency when time, and hence  $\mathbf{q}$ , is reversed, so

$$\omega(-\mathbf{q}) = \omega(\mathbf{q}). \quad (35)$$

Note that this is fully equivalent to the statement that  $D_{\beta j}^{\alpha i}(\mathbf{q}) = D_{\beta j}^{*\alpha i}(-\mathbf{q})$  which is clear from the definition of  $\mathbf{D}$ .

Now, return to the secular equation, Eq. 15.

$$\left( D_{\alpha i}^{\beta j}(\mathbf{q}) - \omega^2(\mathbf{q})\delta_{\alpha i}^{\beta j} \right) \epsilon_{\beta j}(\mathbf{q}) = 0 \quad (36)$$

Lets call the (normalized) eigenvectors of this equation  $\epsilon$ . They are the elements of a unitary matrix which diagonalizes  $\mathbf{D}$ . As a result, they have orthogonality and completeness relations

$$\sum_{\alpha, i} \epsilon_{\alpha, i}^{*(n)}(\mathbf{q}) \epsilon_{\alpha, i}^{(m)}(\mathbf{q}) = \delta_{m, n} \quad \text{orthogonality} \quad (37)$$

$$\sum_n \epsilon_{\alpha, i}^{*(n)}(\mathbf{q}) \epsilon_{\beta, j}^{(n)}(\mathbf{q}) = \delta_{\alpha, \beta} \delta_{i, j} \quad (38)$$

If we now take the complex conjugate of the secular equation

$$\left( D_{\alpha i}^{\beta j}(-\mathbf{q}) - \omega^2(-\mathbf{q})\delta_{\alpha i}^{\beta j} \right) \epsilon_{\beta j}^*(\mathbf{q}) = 0 \quad (39)$$

Then it must be that

$$\epsilon_{\beta j}^*(\mathbf{q}) \propto \epsilon_{\beta j}(-\mathbf{q}). \quad (40)$$

Since the  $\{\epsilon\}$  are normalized the constant of proportionality may be chosen as one

$$\epsilon_{\beta j}^*(\mathbf{q}) = \epsilon_{\beta j}(-\mathbf{q}). \quad (41)$$

**Point-Group Symmetry and the Dispersion** A point group operation takes a crystal back to an identical configuration. Both the original and final lattice must have the same dispersion. Thus, since the reciprocal lattice has the same point group as the real lattice, the dispersion relations have the same point group symmetry as the lattice.

For example, the dispersion must share the periodicity of the Brillouin zone. From the definition of  $\mathbf{D}$

$$D_{\alpha i}^{\beta j}(\mathbf{q}) = \frac{1}{\sqrt{M_\alpha M_\beta}} \Phi_{0\alpha i}^{p\beta j} e^{i\mathbf{q}\cdot(\mathbf{r}_p)} \quad (42)$$

it is easy to see that  $D_{\alpha i}^{\beta j}(\mathbf{q} + \mathbf{G}) = D_{\alpha i}^{\beta j}(\mathbf{q})$  (since  $\mathbf{G} \cdot \mathbf{r}_p = 2\pi n$ , where  $n$  is an integer). I.e.,  $\mathbf{D}$  is periodic in  $\mathbf{k}$ -space, and so its eigenvalues (and eigenvectors) must also be periodic.

$$\omega^{(n)}(\mathbf{k} + \mathbf{G}) = \omega^{(n)}(\mathbf{k}) \quad (43)$$

$$\epsilon_{\beta j}(\mathbf{k} + \mathbf{G}) = \epsilon_{\beta j}(\mathbf{k}). \quad (44)$$

### 1.3.2 Symmetry and the Need for Acoustic modes

Applying basic symmetries, we can show that an elemental lattice (that with  $r = 1$ ) must have an acoustic model. First, look at the transla-

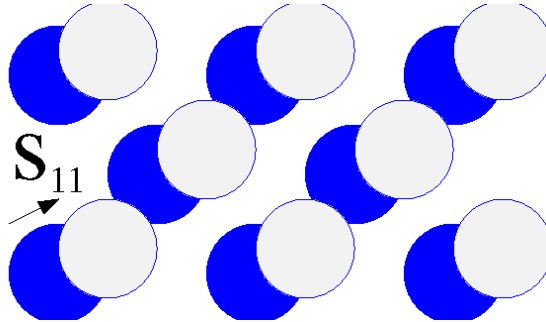


Figure 7: *If each ion is shifted by  $s_{1,1,i}$ , then the lattice energy is unchanged.*

tional invariance of  $\Phi$ . Suppose we make an overall shift of the lattice by an arbitrary displacement  $s_{n,\alpha,i}$  for all sites  $n$  and elements of the

basis  $\alpha$  (i.e.  $s_{n,\alpha,i} = s_{1,1,i}$ ). Then, since the interaction is only *between* ions, the energy of the system should remain unchanged.

$$\delta E = \frac{1}{2} \sum_{m,n,\alpha,\beta,i,j} \Phi_{0,\alpha,i}^{m-n,\beta,j} s_{n,\alpha,i} s_{m,\beta,j} = 0 \quad (45)$$

$$= \frac{1}{2} \sum_{mn\alpha,\beta,i,j} \Phi_{0,\alpha,i}^{m-n,\beta,j} s_{1,1,i} s_{1,1,j} \quad (46)$$

$$= \frac{1}{2} \sum_{i,j} s_{1,1,i} s_{1,1,j} \sum_{mn\alpha,\beta} \Phi_{0,\alpha,i}^{m-n,\beta,j} \quad (47)$$

Since we know that  $s_{1,1,i}$  is finite, it must be that

$$\sum_{m,n,\alpha,\beta} \Phi_{0,\alpha,i}^{m-n,\beta,j} = \sum_{p,\alpha,\beta} \Phi_{0,\alpha,i}^{p,\beta,j} = 0 \quad (48)$$

Now consider a strain on the system  $V_{m,\beta,j}$ , described by the strain matrix  $m_{\beta,j}^{\alpha,i}$

$$V_{m,\beta,j} = \sum_{\alpha,i} m_{\beta,j}^{\alpha,i} s_{m,\alpha,i} \quad (49)$$

After the stress has been applied, the atoms in the bulk of the sample

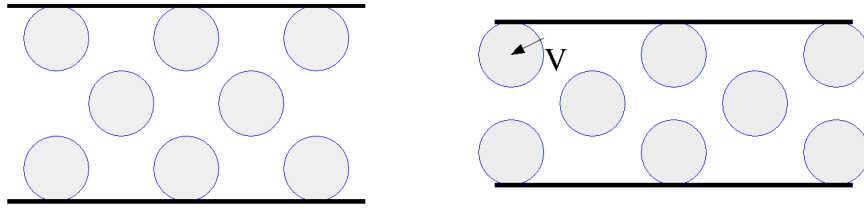


Figure 8: *After a stress is applied to a lattice, the movement of each ion (strain) is not only in the direction of the applied stress. The response of the lattice to an applied stress is described by the strain matrix.*

are again in equilibrium (those on the surface are maintained in equilibrium by the stress), and so the net force must be zero. Looking at



the central ( $n = 0$ ) atom this means that

$$0 = F_{0,\alpha,i} = - \sum_{m,\beta,j,\gamma,k} \Phi_{0,\alpha,i}^{m,\beta,j} m_{\beta,j}^{\gamma,k} s_{m,\gamma,k} \quad (50)$$

Since this applies for an arbitrary strain matrix  $m_{\beta,j}^{\gamma,k}$ , the coefficients for each  $m_{\beta,j}^{\gamma,k}$  must be zero

$$\sum_m \Phi_{0,\alpha,i}^{m,\beta,j} s_{m,\gamma,k} = 0 \quad (51)$$

An alternative way (cf. Callaway) to show this is to recall that the reflection symmetry of the lattice requires that  $\Phi_{0,\alpha,i}^{m,\beta,j}$  be even in  $m$ ; whereas,  $s_{m,\gamma,k}$  is odd in  $m$ . Thus the sum over all  $m$  yields zero.

Now let's apply these constraints to  $\mathbf{D}$  for an elemental lattice where  $r = 1$ , and we may suppress the basis indices  $\alpha$ .

$$D_i^j(\mathbf{q}) = \frac{1}{M} \sum_p \Phi_{0,i}^{p,j} e^{i\mathbf{q} \cdot (\mathbf{r}_p)} \quad (52)$$

For small  $q$  we may expand  $D$

$$D_i^j(\mathbf{q}) = \frac{1}{M} \sum_p \Phi_{0,i}^{p,j} \left( 1 + i\mathbf{q} \cdot (\mathbf{r}_p) - \frac{1}{2} (\mathbf{q} \cdot (\mathbf{r}_p))^2 + \dots \right) \quad (53)$$

We have shown above that the first two terms in this series are zero.

Thus,

$$D_i^j(\mathbf{q}) \approx -\frac{1}{2M} \sum_p \Phi_{0,i}^{p,j} (i\mathbf{q} \cdot (\mathbf{r}_p))^2 \quad (54)$$

Thus, the leading order (small  $\mathbf{q}$ ) eigenvalues  $\omega^2(\mathbf{q}) \sim q^2$ . I.e. they are acoustic modes. We have shown that all elemental lattices must have acoustic modes for small  $\mathbf{q}$ .

In fact, one may show that all harmonic lattices in which the energy is invariant under a rigid translation of the entire lattice must have at least one acoustic mode. We will not prove this, but rather make a simple argument. The rigid translation of the lattice corresponds to a  $\mathbf{q} = 0$  translational mode, since no energy is gained by this translation, it must be that  $\omega_s(\mathbf{q} = 0) = 0$  for the branch  $s$  which contains this mode. The acoustic mode may be obtained by perturbing (in  $\mathbf{q}$ ) around this point. Physically this mode corresponds to all of the elements of the basis moving together so as to emulate the motion in the elemental basis.

## 2 The Counting of Modes

In the sections to follow, we need to perform sums (integrals) of functions of the dispersion over the crystal momentum states  $\mathbf{k}$  within the reciprocal lattice. However, the translational and point group symmetries of the crystal, often greatly reduce the set of points we must sum. In addition, we often approximate very large systems with hypertoroidal models with periodic boundary conditions. This latter approximation becomes valid as the system size diverges so that the surface becomes of zero measure.

## 2.1 Periodicity and the Quantization of States

A consequence of approximating our system as a finite-sized periodic system is that we now have a discrete sum rather than an integral over  $\mathbf{k}$ . Consider a one-dimensional finite system with  $N$  atoms and periodic boundary conditions. We seek solutions to the phonon problem of the type

$$s_n = \epsilon(q)e^{i(qr_n - \omega t)} \quad \text{where } r_n = na \quad (55)$$

and we require that

$$s_{n+N} = s_n \quad (56)$$

or

$$q(n + N)a = qna + 2\pi m \quad \text{where } m \text{ is an integer} \quad (57)$$

Then, the allowed values of  $q = 2\pi m/Na$ . This will allow us to convert the integrals over the Brillouin zone to discrete sums, at least for cubic systems; however, the method is easily generalized for other Bravais lattices.

## 2.2 Translational Invariance: First Brillouin Zone

We can use the translational invariance of the crystal to reduce the complexity of sums or integrals of functions of the dispersion over the crystal momentum states. As shown above, translationally invariant systems have states which are not independent. It is useful then to define a region of  $\mathbf{k}$ -space which contains only independent states. Sums

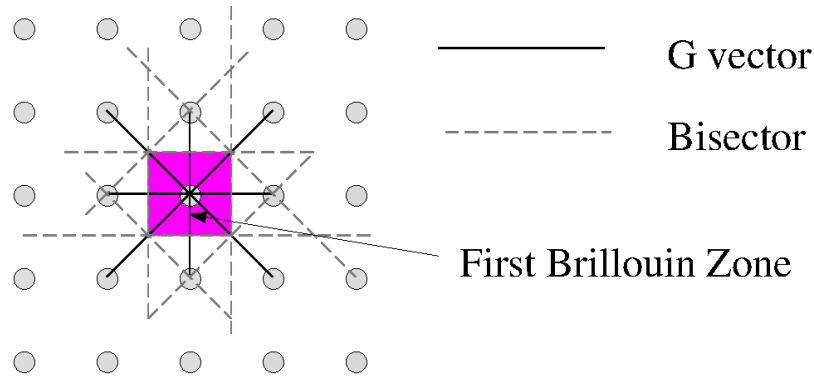


Figure 9: *The First Brillouin Zone.* The end points of all vector pairs that satisfy the Bragg condition  $\mathbf{k} - \mathbf{k}_0 = \mathbf{G}_{hkl}$  lie on the perpendicular bisector of  $\mathbf{G}_{hkl}$ . The smallest polyhedron centered at the origin of the reciprocal lattice and enclosed by perpendicular bisectors of the  $G$ 's is called the first Brillouin zone.

over  $\mathbf{k}$  may then be confined to this region. This region is defined as the smallest polyhedron centered at the origin of the reciprocal lattice and enclosed by perpendicular bisectors of the  $G$ 's is called the Brillouin zone (cf. Fig. 9). Typically, we choose to include only half of the bounding surface within the first Brillouin zone, so that it can also be defined as the set of points which contains only independent states.

From the discussion in chapter 3 and in this chapter, it is also clear that the reciprocal lattice vectors have some interpretation as momentum. For example, the Laue condition requires that the change in momentum of the scatterer be equal to a reciprocal lattice translation vector. The end points of all vector pairs that satisfy the Bragg condition  $\mathbf{k} - \mathbf{k}_0 = \mathbf{G}_{hkl}$  lie on the perpendicular bisector of  $\mathbf{G}_{hkl}$ . Thus, the FBZ is also the set of points which cannot satisfy the Bragg condition.

### 2.3 Point Group Symmetry and Density of States

Two other tricks to reduce the complexity of these sums are worth mentioning here although they are discussed in detail elsewhere.

The first is the use of the point group symmetry of the system. It is clear from their definition in chapter 3, the reciprocal lattice vectors have the same point group symmetry as the lattice. As we discussed in chapter 2, the knowledge of the group elements and corresponding degeneracies may be used to reduce the sums over  $\mathbf{k}$  to the irreducible wedge within the the First Brillouin zone. For example, for a cubic system, this wedge is only  $1/2^3 3!$  or  $1/48$ th of the the FBZ!

The second is to introduce a phonon density of states to reduce the multidimensional sum over  $k$  to a one-dimensional integral over energy. This will be discussed in chapter 5.

## 3 Normal Modes and Quantization

In this section we will derive the equations of motion for the lattice, determine the canonically conjugate variables (the the sense of Lagrangian mechanics), and use this information to both first and second quantize the system.

Any lattice displacement may be expressed as a sum over the eigenvectors of the dynamical matrix  $\mathbf{D}$ .

$$s_{n,\alpha,i} = \frac{1}{\sqrt{M_\alpha N}} \sum_{\mathbf{q},s} Q_s(\mathbf{q}, t) \epsilon_{\alpha,i}^s(\mathbf{q}) e^{i\mathbf{q}\cdot\mathbf{r}_n} \quad (58)$$

Recall that  $\epsilon_{\alpha,i}^s(\mathbf{q})$  are distinguished from  $\mathbf{u}_{\alpha,i}^s(\mathbf{q})$  only in that they are normalized. Also since  $\mathbf{q} + \mathbf{G}$  is equivalent to  $\mathbf{q}$ , we need sum only over the first Brillouin zone. Finally we will assume that  $Q_s(\mathbf{q}, t)$  contains the harmonic time dependence and since  $s_{n,\alpha,i}$  is real  $Q_s^*(\mathbf{q}) = Q_s(-\mathbf{q})$ .

We may rewrite both the kinetic and potential energy of the system as sums over  $Q$ . For example, the kinetic energy of the lattice

$$T = \frac{1}{2} \sum_{n,\alpha,i} M_\alpha (\dot{s}_{n\alpha,i})^2 \quad (59)$$

$$= \frac{1}{2N} \sum_{n,\alpha,i} \sum_{\mathbf{q},\mathbf{k},r,s} \dot{Q}_r(\mathbf{q}) \epsilon_{\alpha,i}^r(\mathbf{q}) e^{i\mathbf{q}\cdot\mathbf{r}_n} \dot{Q}_s(\mathbf{k}) \epsilon_{\alpha,i}^s(\mathbf{k}) e^{i\mathbf{k}\cdot\mathbf{r}_n} \quad (60)$$

Then as

$$\frac{1}{N} \sum_n e^{i(\mathbf{k}+\mathbf{q})\cdot\mathbf{r}_n} = \delta_{\mathbf{k},-\mathbf{q}} \quad \text{and} \quad \sum_{\alpha,i} \epsilon_{\alpha,i}^r \epsilon_{\alpha,i}^{*s} = \delta_{rs} \quad (61)$$

the kinetic energy may be reduced to

$$T = \frac{1}{2} \sum_{\mathbf{q},r} \left| \dot{Q}_r(\mathbf{q}) \right|^2 \quad (62)$$

The potential energy may be rewritten in a similar fashion

$$\begin{aligned} V &= \frac{1}{2} \sum_{n,m,\alpha,\beta,i,j} \Phi_{n,\alpha,i}^{m,\beta,j} s_{n,\alpha,i} s_{m,\beta,j} \\ &= \frac{1}{2} \sum_{n,m,\alpha,\beta,i,j} \frac{\Phi_{0,\alpha,i}^{m-n,\beta,j}}{N \sqrt{M_\alpha M_\beta}} \\ &\quad \sum_{\mathbf{q},\mathbf{k},s,r} Q_s(\mathbf{q}, t) \epsilon_{\alpha,i}^s(\mathbf{q}) e^{i\mathbf{q}\cdot\mathbf{r}_n} Q_r(\mathbf{k}, t) \epsilon_{\beta,j}^r(\mathbf{k}) e^{i\mathbf{k}\cdot\mathbf{r}_m} \end{aligned} \quad (63)$$

Let  $\mathbf{r}_l = \mathbf{r}_m - \mathbf{r}_n$

$$V = \frac{1}{2} \sum_{n,l,\alpha,\beta,i,j} \frac{\Phi_{0,\alpha,i}^{l,\beta,j}}{N \sqrt{M_\alpha M_\beta}} \sum_{\mathbf{q}, \mathbf{k}, s, r} Q_s(\mathbf{q}, t) \epsilon_{\alpha,i}^s(\mathbf{q}) e^{i\mathbf{q} \cdot \mathbf{r}_n} Q_r(\mathbf{k}, t) \epsilon_{\beta,j}^r(\mathbf{k}) e^{i\mathbf{k} \cdot (\mathbf{r}_l + \mathbf{r}_n)} \quad (64)$$

and sum over  $n$  to obtain the delta function  $\delta_{\mathbf{k}, -\mathbf{q}}$  so that

$$V = \frac{1}{2} \sum_{l,\alpha,\beta,i,j,s,r} Q_s(-\mathbf{k}) \epsilon_{\alpha,i}^s(-\mathbf{k}) Q_r(\mathbf{k}) \epsilon_{\beta,j}^r(\mathbf{k}) \frac{1}{\sqrt{M_\alpha M_\beta}} \Phi_{0,\alpha,i}^{l,\beta,j} e^{i\mathbf{k} \cdot \mathbf{r}_l}. \quad (65)$$

Note that the sum over  $l$  on the last three terms yields  $\mathbf{D}$ , so that

$$V = \frac{1}{2} \sum_{l,\alpha,\beta,i,j,s,r} D_{\alpha,i}^{\beta,j}(\mathbf{k}) Q_s(-\mathbf{k}) \epsilon_{\alpha,i}^s(-\mathbf{k}) Q_r(\mathbf{k}) \epsilon_{\beta,j}^r(\mathbf{k}). \quad (66)$$

Then, since  $\sum_{\beta,j} D_{\alpha,i}^{\beta,j}(\mathbf{k}) \epsilon_{\beta,j}^r(\mathbf{k}) = \omega_r^2(\mathbf{k}) \epsilon_{\alpha,i}^r(\mathbf{k})$  and  $\epsilon_{\alpha,i}^s(-\mathbf{k}) = \epsilon_{\alpha,i}^{*s}(\mathbf{k})$ ,

$$V = \frac{1}{2} \sum_{\alpha,i,\mathbf{k},r,s} \epsilon_{\alpha,i}^r(\mathbf{k}) \epsilon_{\alpha,i}^{*s}(\mathbf{k}) \omega_r^2(\mathbf{k}) Q_s^*(\mathbf{k}) Q_r(\mathbf{k}) \quad (67)$$

Finally, since  $\sum_{\alpha,i} \epsilon_{\alpha,i}^r(\mathbf{k}) \epsilon_{\alpha,i}^{*s}(\mathbf{k}) = \delta_{r,s}$

$$V = \frac{1}{2} \sum_{\mathbf{k},s} \omega_s^2(\mathbf{k}) |Q_s(\mathbf{k})|^2 \quad (68)$$

Thus we may write the Lagrangian of the ionic system as

$$L = T - V = \frac{1}{2} \sum_{\mathbf{k},s} \left( \left| \dot{Q}_s(\mathbf{k}) \right|^2 - \omega_s^2(\mathbf{k}) |Q_s(\mathbf{k})|^2 \right), \quad (69)$$

where the  $Q_s(\mathbf{k})$  may be regarded as canonical coordinates, and

$$P_r^*(\mathbf{k}) = \frac{\partial L}{\partial Q_r(\mathbf{k})} = \dot{Q}_s^*(\mathbf{k}) \quad (70)$$

(no factor of 1/2 since  $Q_s^*(\mathbf{k}) = Q_s(-\mathbf{k})$ ) are the canonically conjugate momenta.

The equations of motion are

$$\frac{d}{dt} \left( \frac{\partial L}{\partial \dot{Q}_s^*(\mathbf{k})} \right) - \frac{\partial L}{\partial Q_s^*(\mathbf{k})} \quad \text{or} \quad \ddot{Q}_s(\mathbf{k}) + \omega_s^2(\mathbf{k})Q_s(\mathbf{k}) = 0 \quad (71)$$

for each  $\mathbf{k}, s$ . These are the equations of motion for  $3rN$  independent harmonic oscillators. Since going to the Q-coordinates accomplishes the decoupling of these equations, the  $\{Q_s(\mathbf{k})\}$  are referred to as normal coordinates.

### 3.1 Quantization and Second Quantization

P.A.M. Dirac laid down the rules of quantization, from Classical Hamilton-Jacobi classical mechanics to Hamiltonian-based quantum mechanics following the path (Dirac p.84-89):

1. First, identify the classical canonically conjugate set of variables  $\{q_i, p_i\}$
2. These have Poisson Brackets

$$\{\{u, v\}\} = \sum_i \left( \frac{\partial u}{\partial q_i} \frac{\partial v}{\partial p_i} - \frac{\partial u}{\partial p_i} \frac{\partial v}{\partial q_i} \right) \quad (72)$$

$$\{\{q_i, p_j\}\} = \delta_{i,j} \quad \{\{p_i, p_j\}\} = \{\{q_i, q_j\}\} = 0 \quad (73)$$

3. Then define the quantum Poisson Bracket (the commutator)

$$[u, v] = uv - vu = i\hbar\{\{u, v\}\} \quad (74)$$



4. In particular,  $[q_i, p_j] = i\hbar\delta_{i,j}$ , and  $[q_i, q_j] = [p_i, p_j] = 0$ .

Thus, following Dirac, we may now quantize the normal coordinates

$$[Q_r^*(\mathbf{k}), P_s(\mathbf{q})] = i\hbar\delta_{\mathbf{k},\mathbf{q}}\delta_{r,s} \quad \text{where the other commutators vanish.} \quad (75)$$

Furthermore, since we have a system of  $3rN$  uncoupled harmonic oscillators we may immediately second quantize by introducing

$$a_s(\mathbf{k}) = \frac{1}{\sqrt{2\hbar}} \left( \sqrt{\omega_s(\mathbf{k})} Q_s(\mathbf{k}) + \frac{i}{\sqrt{\omega_s(\mathbf{k})}} P_s(\mathbf{k}) \right) \quad (76)$$

$$a_s^\dagger(\mathbf{k}) = \frac{1}{\sqrt{2\hbar}} \left( \sqrt{\omega_s(\mathbf{k})} Q_s^*(\mathbf{k}) - \frac{i}{\sqrt{\omega_s(\mathbf{k})}} P_s^*(\mathbf{k}) \right), \quad (77)$$

or

$$Q_s(\mathbf{k}) = \sqrt{\frac{\hbar}{2\omega_s(\mathbf{k})}} (a_s(\mathbf{k}) + a_s^\dagger(-\mathbf{k})) \quad (78)$$

$$P_s(\mathbf{k}) = -i\sqrt{\frac{\hbar\omega_s(\mathbf{k})}{2}} (a_s(\mathbf{k}) - a_s^\dagger(-\mathbf{k})) \quad (79)$$

Where

$$[a_s(\mathbf{k}), a_r^\dagger(\mathbf{q})] = \delta_{r,s}\delta_{\mathbf{q},\mathbf{k}} \quad [a_s(\mathbf{k}), a_r(\mathbf{q})] = [a_s^\dagger(\mathbf{k}), a_r^\dagger(\mathbf{q})] = 0 \quad (80)$$

This transformation  $\{Q, P\} \rightarrow \{a, a^\dagger\}$  is canonical, since it preserves the commutator algebra Eq. 75, and the Hamiltonian becomes

$$H = \sum_{k,s} \hbar\omega_s(\mathbf{k}) \left( a_s^\dagger(\mathbf{k})a_s(\mathbf{k}) + \frac{1}{2} \right) \quad (81)$$

which is a sum over  $3rN$  independent quantum oscillators, each one referred to as a phonon mode!

The number of phonons in state  $(\mathbf{k}, s)$  is given by the operator

$$n_s(\mathbf{k}) = a_s^\dagger(\mathbf{k})a_s(\mathbf{k}) \quad (82)$$

and  $a_s^\dagger(\mathbf{k})$  and  $a_s(\mathbf{k})$  create and destroy phonons respectively, in the state  $(\mathbf{k}, s)$

$$a_s^\dagger(\mathbf{k}) |n_s(\mathbf{k})\rangle = \sqrt{n_s(\mathbf{k}) + 1} |n_s(\mathbf{k}) + 1\rangle \quad (83)$$

$$a_s(\mathbf{k}) |n_s(\mathbf{k})\rangle = \sqrt{n_s(\mathbf{k})} |n_s(\mathbf{k}) - 1\rangle \quad (84)$$

If  $|0\rangle$  is the normalized state with no phonons present, then the state with  $\{n_s(\mathbf{k})\}$  phonons in each state  $(\mathbf{k}, s)$  is

$$|\{n_s(\mathbf{k})\}\rangle = \left[ \left( \prod_{\mathbf{k},s} \frac{1}{n_s(\mathbf{k})!} \right)^{\frac{1}{2}} \right] \prod_{\mathbf{k},s} (a_s^\dagger(\mathbf{k}))^{n_s(\mathbf{k})} |0\rangle \quad (85)$$

Finally the lattice point displacement

$$s_{n,\alpha,i} = \frac{1}{\sqrt{M_\alpha N}} \sum_{\mathbf{q},s} \sqrt{\frac{\hbar}{2\omega_s(\mathbf{q})}} (a_s(\mathbf{q}) + a_s^\dagger(-\mathbf{q})) \epsilon_{\alpha,i}^s(\mathbf{q}) e^{i\mathbf{q}\cdot\mathbf{r}_n} \quad (86)$$

will be important in the next section, especially with respect to zero-point motion (i.e.  $\langle s^2 \rangle_{T=0} \neq 0$ ).

## 4 Theory of Neutron Scattering

To “see” the lattice with neutrons, we want their De Broglie wavelength  $\lambda = h/p$

$$\lambda_{\text{neutron}} = \frac{0.29\text{\AA}}{\sqrt{E}} \quad \text{E measured in eV} \quad (87)$$

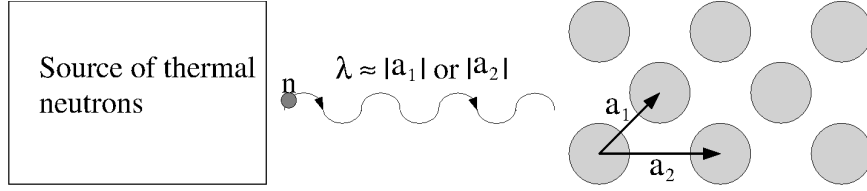


Figure 10: *Neutron Scattering.* The De Broglie wavelength of the neutrons must be roughly the same size as the lattice constants in order to learn about the lattice structure and its vibrational modes from the experiment. This dictates the use of thermal neutrons.

to be of the same length as the intersite distance on the lattice. This means that their kinetic energy  $E \approx \frac{1}{2}Mv^2 \approx 0.1\text{eV}$ , or  $E/k_b \approx 1000\text{K}$ ; i.e. thermal neutrons.

Since the neutron is chargeless, it only interacts with the atomic nucleus through a short-ranged nuclear interaction (ignoring any spin-spin interaction). The range of this interaction is 1 Fermi ( $10^{-13}\text{cm}$ .) or about the radius of the atomic nucleus. Thus

$$\lambda \sim \mathbf{A} \gg \text{range of the interaction} \sim 10^{-13}\text{cm}. \quad (88)$$

Thus the neutron cannot "see" the detailed structure of the nucleus, and so we may approximate the neutron-ion interaction potential as a contact interaction

$$V(\mathbf{r}) = \sum_{\mathbf{r}_n} V_n \delta(\mathbf{r} - \mathbf{r}_n) \quad (89)$$

i.e., we may ignore the angular dependence of the scattering factor  $f$ .

## 4.1 Classical Theory of Neutron Scattering

Due to the importance of lattice vibrations, which are inherently quantum in nature, there is a limit to what we can learn from a classical theory of diffraction. Nevertheless it is useful to compare the classical result to what we will develop for the quantum problems.

For the classical problem we will assume that the lattice is elemental ( $r = 1$ ) and start with a generalization of the formalism developed in the last chapter

$$I \propto |\rho(\mathbf{K}, \Omega)|^2 \quad (90)$$

where  $\mathbf{K} = \mathbf{k}_0 - \mathbf{k}$  and  $\Omega = \omega_0 - \omega$ . Furthermore, we take

$$\rho(\mathbf{r}(t)) \propto \sum_n \delta(\mathbf{r} - \mathbf{r}_n(t)) \quad (91)$$

where

$$\mathbf{r}_n(t) = \mathbf{r}_n + \mathbf{s}_n(t) \quad \text{and} \quad \mathbf{s}_n(t) = \frac{1}{\sqrt{M}} \mathbf{u}(\mathbf{q}) e^{i(\mathbf{q} \cdot \mathbf{r}_n - \omega(\mathbf{q})t)} \quad (92)$$

describes the harmonic motion of the s-mode with wave-vector  $\mathbf{q}$ .

$$\rho(\mathbf{K}, \Omega) \propto \sum_n \int dt e^{i[\mathbf{K} \cdot (\mathbf{r}_n + \mathbf{s}_n(t)) - \Omega t]}. \quad (93)$$

For  $|\mathbf{K}| \sim 2\pi/\mathbf{A}$  and  $\mathbf{s}_n(t) \ll \mathbf{A}$  we may expand

$$\rho(\mathbf{K}, \Omega) \propto \sum_n \int dt e^{i[\mathbf{K} \cdot (\mathbf{r}_n) - \Omega t]} (1 + i\mathbf{K} \cdot \mathbf{s}_n(t) + \dots) \quad (94)$$

The first term yields a finite contribution only when

$$\mathbf{K} = \mathbf{k}_0 - \mathbf{k} = \mathbf{G} \quad \text{and} \quad \Omega = \omega_0 - \omega = 0 \quad (95)$$

which are the familiar Bragg conditions for elastic scattering.

The second term, however, yields something new. It only yields a finite result when

$$\mathbf{K} \pm \mathbf{q} = \mathbf{k}_0 - \mathbf{k} \pm \mathbf{q} = \mathbf{G} \quad \text{and} \quad \Omega \pm \omega_s(\mathbf{q}) = \omega_0 - \omega \pm \omega_s(\mathbf{q}) = 0 \quad (96)$$

When multiplied by  $\hbar$ , these can be interpreted as conditions for the conservation of (crystal) momentum and energy when the scattering event involves the creation (destruction) of a lattice excitation (phonon). These processes are called Stokes and antistokes processes, respectively, and are illustrated in Fig. 11.

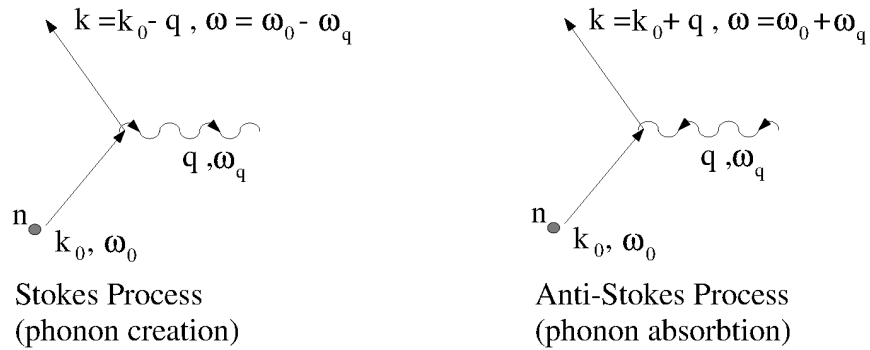


Figure 11: *Stokes and antistokes processes in inelastic neutron scattering involving the creation or absorption of a lattice phonon.*

Clearly, the anti-Stokes process can only happen at finite temperatures where real (as opposed to virtual) phonons are excited. Thus, our classical formalism does not correctly describe the temperature dependence of the scattering. Several other things are missing in the classical theory, including:

- Security in the validity of the result.

- The effects of zero-point motion.
- Correct temperature dependence.

## 4.2 Quantum Theory of Neutron Scattering

To address these concerns, we will do a fully quantum calculation. Several useful references for this calculation include

- Ashcroft and Mermin, Appendix N, p. 790)
- Callaway, p. 36–.
- Hook and Hall (for experiment) Ch. 12 p.342–

We will imagine that the scattering shown in Fig. 12 occurs in a box of volume  $V$ . The momentum transfer, from the neutron to the lattice

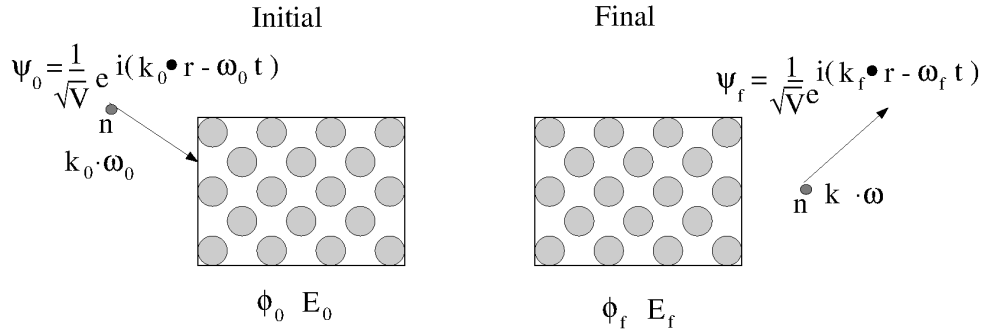


Figure 12: *The initial (left) and final (right) states of the neutron and lattice during a scattering event. The initial system state is given by  $\Psi_0 = \phi_0 \psi_0$ , with energy  $\epsilon_0 = E_0 + \hbar \omega_0$  where  $\omega_0 = k_0^2/2M$ . The final system state is given by  $\Psi_f = \phi_f \psi_f$ , with energy  $\epsilon_f = E_f + \hbar \omega_f$  where  $\omega_f = k_f^2/2M$ .*

is  $\mathbf{K} = \mathbf{k}_0 - \mathbf{k}_f$  and the energy transfer which is finite for inelastic

scattering is  $\hbar\Omega = \hbar(\omega_0 - \omega_f)$ . Again we will take the neutron-lattice interaction to be local

$$V(\mathbf{r}) = \sum_{r_n} V(\mathbf{r} - \mathbf{r}_n) = \frac{1}{N} \sum_{\mathbf{q}, n} V(\mathbf{q}) e^{i\mathbf{q} \cdot (\mathbf{r} - \mathbf{r}_n)} = \int \frac{d^3q}{V} V_0 \sum_n e^{i\mathbf{q} \cdot (\mathbf{r} - \mathbf{r}_n)} \quad (97)$$

where the locality of the interaction ( $V(\mathbf{r} - \mathbf{r}_n) \propto \delta(\mathbf{r} - \mathbf{r}_n)$ ) indicates that  $V(\mathbf{q}) = V(0) = V_0$ . Consistent with Aschcroft and Mermin, we will take

$$V(\mathbf{r}) = \frac{2\pi\hbar^2 a}{M} \frac{1}{V} \sum_{\mathbf{r}_n} \int d^3q e^{i\mathbf{q} \cdot (\mathbf{r} - \mathbf{r}_n)} \quad (98)$$

where  $a$  is the scattering length, and  $V_0 = \frac{2\pi\hbar^2 a}{M}$  is chosen such that the total cross section  $\sigma = 4\pi a^2$ .

To formulate our quantum theory, we will use Fermi's golden rule for time dependent perturbation theory. (This is fully equivalent to the lowest-order Born approximation). The probability per unit time for a neutron to scatter from state  $\mathbf{k}_0$  to  $\mathbf{k}_f$  is given by

$$P = \frac{2\pi}{\hbar} \sum_f \delta(\epsilon_0 - \epsilon_f) |\langle \Psi_0 | V | \Psi_f \rangle|^2 \quad (99)$$

$$= \frac{2\pi}{\hbar} \sum_f \delta(E_0 + \hbar\omega_0 - E_f - \hbar\omega_f) \left| \frac{1}{V} \int d^3r e^{i(\mathbf{k} - \mathbf{k}_0) \cdot \mathbf{r}} \langle \phi_0 | V(\mathbf{r}) | \phi_f \rangle \right|^2 \quad (100)$$

If we now substitute in the ion-neutron potential Eq. 98, then the integral over  $\mathbf{r}$  will yield a delta function  $V\delta(\mathbf{q} + \mathbf{k} - \mathbf{k}_0)$  which allows the

$\mathbf{q}$  integral to be evaluated

$$P = a^2 \frac{(2\pi\hbar)^3}{(MV)^2} \sum_f \delta(E_0 - E_f + \hbar\Omega) \left| \sum_{\mathbf{r}_n} \langle \phi_0 | e^{-i\mathbf{K}\cdot\mathbf{r}_n} | \phi_f \rangle \right|^2 \quad (101)$$

Now, before proceeding to a calculation of the differential cross section  $\frac{d\sigma}{d\Omega d\mathbf{E}}$  we must be able to convert this probability (rate) for eigenstates into a flux of neutrons of energy  $E$  and momentum  $\mathbf{p}$ . A differential volume element of momentum space  $d^3p$  contains  $V d^3p / (2\pi\hbar)^3$  neutron states. While this is a natural consequence of the uncertainty principle, it is useful to show this in a more quantitative sense: Imagine a cubic volume  $V = L^3$  with periodic boundary conditions so that for any state  $\Psi$  in  $V$ ,

$$\Psi(x + L, y, z) = \Psi(x, y, z) \quad (102)$$

If we write  $\Psi(\mathbf{r}) = \frac{1}{N} \sum_{\mathbf{q}} e^{i\mathbf{q}\cdot\mathbf{r}} \Psi(\mathbf{q})$ , then it must be that

$$q_x L = 2\pi m \quad \text{where } m \text{ is an integer} \quad (103)$$

with similar relations for the  $y$  and  $z$  components. So for each volume element of  $\mathbf{q}$ -space  $\left(\frac{2\pi}{L}\right)^3$  there is one such state. In terms of states  $\mathbf{p} = \hbar\mathbf{q}$ , the volume of a state is  $(2\pi\hbar/L)^3$ . Thus  $d^3p$  contains  $V d^3p / (2\pi\hbar)^3$  states.

The incident neutron flux of states (velocity times density) is

$$\mathbf{j} = \frac{\hbar\mathbf{k}_0}{M} |\Psi_0|^2 = \frac{\hbar\mathbf{k}_0}{M} \left| \frac{1}{\sqrt{V}} e^{i\mathbf{k}_0\cdot\mathbf{r}} \right|^2 = \frac{\hbar\mathbf{k}_0}{MV} \quad (104)$$



Then since the number of neutrons is conserved

$$j \frac{d\sigma}{dEd\Omega} dEd\Omega = \frac{\hbar k_0}{MV} \frac{d\sigma}{dEd\Omega} dEd\Omega = PV \frac{d^3p}{(2\pi\hbar)^3} = PV \frac{p^2 dp d\Omega}{(2\pi\hbar)^3} \quad (105)$$

And for thermal (non-relativistic) neutrons  $E = p^2/2M$ , so  $dE = pdp/M$ , and

$$\frac{\hbar k_0}{MV} \frac{d\sigma}{dEd\Omega} dEd\Omega = PV \frac{\hbar k M dEd\Omega}{(2\pi\hbar)^3} \quad (106)$$

or

$$\frac{d\sigma}{dEd\Omega} = P \frac{k (MV)^2}{k_0 (2\pi\hbar)^3}. \quad (107)$$

Substituting in the previous result for  $P$

$$\frac{d\sigma}{dEd\Omega} = \frac{k (MV)^2}{k_0 (2\pi\hbar)^3} a^2 \frac{(2\pi\hbar)^3}{(MV)^2} \sum_f \delta(E_0 - E_f + \hbar\Omega) \left| \sum_{\mathbf{r}_n} \langle \phi_0 | e^{-i\mathbf{K}\cdot\mathbf{r}_n} | \phi_f \rangle \right|^2 \quad (108)$$

or

$$\frac{d\sigma}{dEd\Omega} = \frac{k N a^2}{k_0 \hbar} S(\mathbf{K}, \Omega) \quad (109)$$

where

$$S(\mathbf{K}, \Omega) = \frac{1}{N} \sum_f \delta(E_0 - E_f + \hbar\Omega) \left| \sum_{\mathbf{r}_n} \langle \phi_0 | e^{-i\mathbf{K}\cdot\mathbf{r}_n} | \phi_f \rangle \right|^2. \quad (110)$$

We may deal with the Dirac delta function by substituting

$$\delta(\Omega) = \int_{-\infty}^{\infty} \frac{dt}{2\pi} e^{i\Omega t}. \quad (111)$$

so that

$$S(\mathbf{K}, \Omega) = \frac{1}{N} \sum_f \int_{-\infty}^{\infty} \frac{dt}{2\pi} e^{i((E_0 - E_f)/\hbar + \Omega)t} \sum_{\mathbf{r}_n, \mathbf{r}_m} |\langle \phi_0 | e^{i\mathbf{K}\cdot\mathbf{r}_n} | \phi_f \rangle| |\langle \phi_f | e^{-i\mathbf{K}\cdot\mathbf{r}_m} | \phi_0 \rangle|. \quad (112)$$

then as

$$e^{-iHt/\hbar} |\phi_l\rangle = e^{-iE_l t/\hbar} |\phi_l\rangle \quad (113)$$

where  $H$  is the lattice Hamiltonian, we can write this as

$$S(\mathbf{K}, \Omega) = \frac{1}{N} \sum_f \int_{-\infty}^{\infty} \frac{dt}{2\pi} e^{i\Omega t} \sum_{\mathbf{r}_n, \mathbf{r}_m} \left\langle \phi_0 \left| e^{iHt/\hbar} e^{i\mathbf{K}\cdot\mathbf{r}_n} e^{-iHt/\hbar} \right| \phi_f \right\rangle \left\langle \phi_f \left| e^{-i\mathbf{K}\cdot\mathbf{r}_m} \right| \phi_0 \right\rangle, \quad (114)$$

and the argument in the first expectation value is the time-dependent operator  $e^{i\mathbf{K}\cdot\mathbf{r}_n}$  in the Heisenberg representation

$$e^{i\mathbf{K}\cdot\mathbf{r}_n(t)} = e^{iHt/\hbar} e^{i\mathbf{K}\cdot\mathbf{r}_n} e^{-iHt/\hbar}. \quad (115)$$

Thus,

$$\begin{aligned} S(\mathbf{K}, \Omega) &= \frac{1}{N} \sum_f \int_{-\infty}^{\infty} \frac{dt}{2\pi} e^{i\Omega t} \sum_{\mathbf{r}_n, \mathbf{r}_m} \left\langle \phi_0 \left| e^{i\mathbf{K}\cdot\mathbf{r}_n(t)} \right| \phi_f \right\rangle \left\langle \phi_f \left| e^{-i\mathbf{K}\cdot\mathbf{r}_m} \right| \phi_0 \right\rangle \\ &= \frac{1}{N} \int_{-\infty}^{\infty} \frac{dt}{2\pi} e^{i\Omega t} \sum_{\mathbf{r}_n, \mathbf{r}_m} \left\langle \phi_0 \left| e^{i\mathbf{K}\cdot\mathbf{r}_n(t)} e^{-i\mathbf{K}\cdot\mathbf{r}_m} \right| \phi_0 \right\rangle. \end{aligned} \quad (116)$$

Now since  $\mathbf{r}_n(t) = \mathbf{r}_n + \mathbf{s}_n(t)$  (with  $\mathbf{r}_n$  time independent),

$$S(\mathbf{K}, \Omega) = \frac{1}{N} \sum_{n,m} \int_{-\infty}^{\infty} \frac{dt}{2\pi} e^{i(\mathbf{K}\cdot(\mathbf{r}_n - \mathbf{r}_m) + \Omega t)} \left\langle \phi_0 \left| e^{i\mathbf{K}\cdot\mathbf{s}_n(t)} e^{-i\mathbf{K}\cdot\mathbf{s}_m} \right| \phi_0 \right\rangle. \quad (117)$$

This formula is correct at zero temperature. In order to describe finite  $T$  effects (ie., anti-stokes processes involving phonon absorption) we must introduce a thermal average over all states

$$\langle \phi_0 | A | \phi_0 \rangle \rightarrow \langle A \rangle = \sum_l e^{-\beta E_l} \langle \phi_l | A | \phi_l \rangle / \sum_l e^{-\beta E_l}. \quad (118)$$

With this substitution,

$$S(\mathbf{K}, \Omega) = \frac{1}{N} \sum_{n,m} \int_{-\infty}^{\infty} \frac{dt}{2\pi} e^{i(\mathbf{K} \cdot (\mathbf{r}_n - \mathbf{r}_m) + \Omega t)} \left\langle e^{i\mathbf{K} \cdot \mathbf{s}_n(t)} e^{-i\mathbf{K} \cdot \mathbf{s}_m} \right\rangle. \quad (119)$$

and  $S(\mathbf{K}, \Omega)$  is called the dynamical structure factor.

#### 4.2.1 The Debye-Waller Factor

To simplify this relation further, recall that the exponentiated operators within the brackets are linear functions of the creation and annihilation operators  $a^\dagger$  and  $a$ .

$$\mathbf{s}_{n,\alpha}(t) = \frac{1}{\sqrt{M_\alpha N}} \sum_{\mathbf{q},s} \sqrt{\frac{\hbar}{2\omega_s(\mathbf{q})}} \epsilon_\alpha^s(\mathbf{q}) (a_s(\mathbf{q})(t) + a_s^\dagger(-\mathbf{q})(t)) e^{i\mathbf{q} \cdot \mathbf{r}_n} \quad (120)$$

So that, in particular  $\langle \mathbf{s}_{n,\alpha,i}(t) \rangle = \langle \mathbf{s}_{n,\alpha,i}(0) \rangle = 0$ . Then let  $A = i\mathbf{K} \cdot \mathbf{s}_{n,\alpha,i}(t)$  and  $B = i\mathbf{K} \cdot \mathbf{s}_{m,\alpha,i}(0)$  and suppose that the expectation values of  $A$  and  $B$  are small. Then

$$\begin{aligned} \langle e^A e^B \rangle &= \left\langle \left(1 + A + \frac{1}{2}A^2 + \dots\right) \left(1 + B + \frac{1}{2}B^2 + \dots\right) \right\rangle \\ &\approx \left\langle 1 + A + B + AB + \frac{1}{2}A^2 + \frac{1}{2}B^2 + \dots \right\rangle \\ &\approx 1 + \frac{1}{2} \langle 2AB + A^2 + B^2 \rangle + \dots \\ &\approx e^{\frac{1}{2} \langle 2AB + A^2 + B^2 \rangle} \end{aligned} \quad (121)$$

This relation is in fact true to all orders, as long as  $A$  and  $B$  are linear functions of  $a^\dagger$  and  $a$ . (c.f. Ashcroft and Mermin, p. 792, Callaway pp.

41-48). Thus

$$\left\langle e^{i\mathbf{K}\cdot\mathbf{s}_n(t)} e^{-i\mathbf{K}\cdot\mathbf{s}_m} \right\rangle = e^{-\frac{1}{2}\langle(\mathbf{K}\cdot\mathbf{s}_n(t))^2\rangle} e^{-\frac{1}{2}\langle(\mathbf{K}\cdot\mathbf{s}_m)^2\rangle} e^{\langle\mathbf{K}\cdot\mathbf{s}_n(t)\mathbf{K}\cdot\mathbf{s}_m\rangle}. \quad (122)$$

Since the Hamiltonian has no time dependence, and the lattice is invariant under translations  $r_n$

$$\left\langle e^{i\mathbf{K}\cdot\mathbf{s}_n(t)} e^{-i\mathbf{K}\cdot\mathbf{s}_m} \right\rangle = e^{-\langle(\mathbf{K}\cdot\mathbf{s}_n)^2\rangle} e^{\langle\mathbf{K}\cdot\mathbf{s}_{n-m}(t)\mathbf{K}\cdot\mathbf{s}_0\rangle}, \quad (123)$$

where the first term is called the Debye-Waller factor  $e^{-2W}$ .

$$e^{-2W} = e^{-\langle(\mathbf{K}\cdot\mathbf{s}_n)^2\rangle}. \quad (124)$$

Thus letting  $l = n - m$

$$S(\mathbf{K}, \Omega) = e^{-2W} \sum_l \int_{-\infty}^{\infty} \frac{dt}{2\pi} e^{i(\mathbf{K}\cdot\mathbf{r}_l + \Omega t)} e^{\langle\mathbf{K}\cdot\mathbf{s}_l(t)\mathbf{K}\cdot\mathbf{s}_0\rangle}. \quad (125)$$

Here the Debye-Waller factor contains much of the crucial quantum physics. It is finite, even at  $T = 0$  due to zero-point fluctuations, and since  $\langle\mathbf{K}\cdot\mathbf{s}_n\rangle^2$  will increase with temperature, the total strength of the Bragg peaks will diminish with increasing  $T$ . However, as long as a crystal has long-ranged order, it will remain finite.

#### 4.2.2 Zero-phonon Elastic Scattering

One may disentangle the elastic and inelastic processes by expanding the exponential in the equation above.

$$e^{\langle\mathbf{K}\cdot\mathbf{s}_l(t)\mathbf{K}\cdot\mathbf{s}_0\rangle} = \sum_m \frac{1}{m!} (\langle\mathbf{K}\cdot\mathbf{s}_l(t)\mathbf{K}\cdot\mathbf{s}_0\rangle)^m \quad (126)$$

If we approximate the exponential by 1, ie. take only the first,  $m = 0$  term, then

$$S_0(\mathbf{K}, \Omega) = e^{-2W} \sum_l \int_{-\infty}^{\infty} \frac{dt}{2\pi} e^{i(\mathbf{K} \cdot \mathbf{r}_l - \Omega t)}. \quad (127)$$

And we recover the lowest order classical result (modified by the Debye-Waller factor) which gives us the Bragg conditions that  $S_0(\mathbf{K}, \Omega)$  is only finite when  $\mathbf{K} = \mathbf{G}$  and  $\Omega = \omega_0 - \omega_f = 0$ .

$$S_0(\mathbf{K}, \Omega) = e^{-2W} \delta(\Omega) N \sum_{\mathbf{G}} \delta_{\mathbf{K}, \mathbf{G}}, \quad (128)$$

$$\frac{d\sigma_0}{dE d\Omega} = \frac{k}{k_0} \frac{Na^2}{\hbar} e^{-2W} \delta(\Omega) N \sum_{\mathbf{G}} \delta_{\mathbf{K}, \mathbf{G}} \quad (129)$$

However, now the scattering intensity is reduced by the Debye-Waller factor  $e^{-2W}$ , which accounts for zero-point motion and thermal fluctuations.

### 4.2.3 One-Phonon Inelastic Scattering

When  $m = 1$ , then the scattering involves either the absorption or creation of a phonon. To evaluate

$$S_1(\mathbf{K}, \Omega) = e^{-2W} \sum_l \int_{-\infty}^{\infty} \frac{dt}{2\pi} e^{i(\mathbf{K} \cdot \mathbf{r}_l + \Omega t)} \langle \mathbf{K} \cdot \mathbf{s}_l(t) \mathbf{K} \cdot \mathbf{s}_0(0) \rangle. \quad (130)$$

we need

$$\mathbf{s}_{n,\alpha}(t) = \frac{1}{\sqrt{M_\alpha N}} \sum_{\mathbf{q}, s} \sqrt{\frac{\hbar}{2\omega_s(\mathbf{q})}} \epsilon_\alpha^s(\mathbf{q}) (a_s(\mathbf{q}, t) + a_s^\dagger(-\mathbf{q}, t)) e^{i\mathbf{q} \cdot \mathbf{r}_n} \quad (131)$$

in the Heisenberg representation, and therefore we need,

$$\begin{aligned}
a(\mathbf{q}, t) &= e^{iHt/\hbar} a(\mathbf{q}) e^{-iHt/\hbar} \\
&= e^{i(\omega(\mathbf{q})ta^\dagger(\mathbf{q})a(\mathbf{q}))} a(\mathbf{q}) e^{-i(\omega(\mathbf{q})ta^\dagger(\mathbf{q})a(\mathbf{q}))} \\
&= a(\mathbf{q}) e^{i(\omega(\mathbf{q})t(a^\dagger(\mathbf{q})a(\mathbf{q})-1))} e^{-i(\omega(\mathbf{q})ta^\dagger(\mathbf{q})a(\mathbf{q}))} \\
&= a(\mathbf{q}) e^{-i\omega(\mathbf{q})t}
\end{aligned} \tag{132}$$

where we have used the fact that  $(a^\dagger a)^n a = (a^\dagger a)^{n-1} a^\dagger a a = (a^\dagger a)^{n-1} (a a^\dagger - 1) a = (a^\dagger a)^{n-1} a (a^\dagger a - 1) = a (a^\dagger a - 1)^n$ . Similarly  $a^\dagger(\mathbf{q}, t) = a^\dagger(\mathbf{q}) e^{i\omega(\mathbf{q})t}$ .

Thus,

$$\mathbf{s}_{n,\alpha}(t) = \frac{1}{\sqrt{M_\alpha N}} \sum_{\mathbf{q},s} \frac{\sqrt{\hbar} e^{i\mathbf{q}\cdot\mathbf{r}_n}}{\sqrt{2\omega_s(\mathbf{q})}} \epsilon_\alpha^s(\mathbf{q}) \left( a_s(\mathbf{q}) e^{-i\omega_s(\mathbf{q})t} + a_s^\dagger(-\mathbf{q}) e^{i\omega_s(\mathbf{q})t} \right) \tag{133}$$

and

$$\mathbf{s}_{0,\alpha}(0) = \frac{1}{\sqrt{M_\alpha N}} \sum_{\mathbf{p},r} \sqrt{\frac{\hbar}{2\omega_r(\mathbf{p})}} \epsilon_\alpha^r(\mathbf{p}) (a_r(\mathbf{p}) + a_r^\dagger(-\mathbf{p})) \tag{134}$$

Recall, we want to evaluate

$$S_1(\mathbf{K}, \Omega) = e^{-2W} \sum_l \int_{-\infty}^{\infty} \frac{dt}{2\pi} e^{i(\mathbf{K}\cdot\mathbf{r}_l + \Omega t)} \langle \mathbf{K} \cdot \mathbf{s}_l(t) \mathbf{K} \cdot \mathbf{s}_0(0) \rangle. \tag{135}$$

Clearly, the only terms which survive in  $\langle \mathbf{K} \cdot \mathbf{s}_l(t) \mathbf{K} \cdot \mathbf{s}_0(0) \rangle$  are those with  $r = s$  and  $\mathbf{p} = -\mathbf{q}$ . Furthermore, the sum over  $l$  yields a delta function  $N \sum_{\mathbf{G}} \delta_{\mathbf{K}+\mathbf{q},\mathbf{G}}$ . Then as  $\epsilon(\mathbf{G} - \mathbf{k}) = \epsilon(-\mathbf{k}) = \epsilon^*(\mathbf{k})$ , and  $\omega(\mathbf{G} - \mathbf{k}) = \omega(\mathbf{k})$ ,

$$\begin{aligned}
S_1(\mathbf{K}, \Omega) &= e^{-2W} \int_{-\infty}^{\infty} \frac{dt}{2\pi} e^{i\Omega t} \sum_{\mathbf{q},\mathbf{G},s} \frac{\hbar |\mathbf{K} \cdot \epsilon(\mathbf{K})|^2}{2\omega_s(\mathbf{q}) M} \delta_{\mathbf{K}+\mathbf{q},\mathbf{G}} \\
&\quad \left[ e^{-i\omega_s(\mathbf{q})t} \langle a_s(-\mathbf{K}) a_s^\dagger(-\mathbf{K}) \rangle + e^{i\omega_s(\mathbf{q})t} \langle a_s^\dagger(-\mathbf{K}) a_s(-\mathbf{K}) \rangle \right]
\end{aligned} \tag{136}$$

The occupancy of each mode  $n(\mathbf{q})$  is given by the Bose factor

$$\langle n(\mathbf{q}) \rangle = \frac{1}{e^{\beta\omega(\mathbf{q})} - 1} \quad (137)$$

So, finally

$$S_1(\mathbf{K}, \Omega) = e^{-2W} \sum_s \frac{\hbar}{2M\omega_s(\mathbf{K})} |\mathbf{K} \cdot \boldsymbol{\epsilon}^s(\mathbf{K})|^2 \quad (138)$$

$$[(1 + n_s(\mathbf{K}))\delta(-\Omega + \omega_s(\mathbf{K})) + n_s(\mathbf{K})\delta(\Omega + \omega_s(\mathbf{K}))] .$$

For the first term, we get a contribution only when  $\Omega - \omega_s(\mathbf{K}) = \omega_0 - \omega_f - \omega_s(\mathbf{K}) = 0$ ; ie., the final energy of the neutron is smaller than the initial energy. The energy is lost in the creation of a phonon. Note that this can happen at any temperature, since  $(1 + n_s(\mathbf{K})) \neq 0$  at any  $T$ . The second term is only finite when  $\Omega + \omega_s(\mathbf{K}) = \omega_0 - \omega_f + \omega_s(\mathbf{K}) = 0$ ; ie., the final energy of the neutron is larger than the initial energy. The additional energy comes from the absorption of a phonon. Thus phonon absorption is only allowed at finite temperatures, and in fact, the factor  $n_s(\mathbf{K}) = 0$  at zero temperature. These terms correspond to the Stokes and anti-Stokes processes, respectively, illustrated in Fig. 13.

If we were to continue our expansion of the exponential to larger values of  $m$ , we would find multiple-phonon scattering processes. However, these terms are usually of minimal contribution to the total cross section, due to the fact that the average ionic excursion  $s$  is small, and are usually neglected.

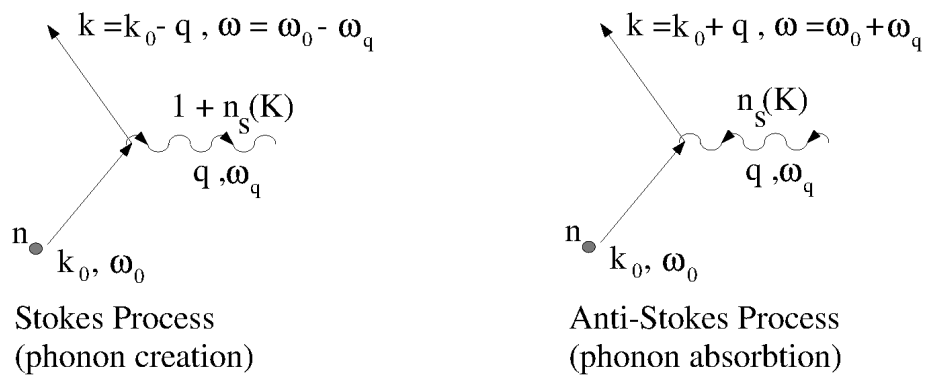


Figure 13: *Stokes and anti-Stokes processes in inelastic neutron scattering involving the creation or absorption of a lattice phonon. The anti-Stokes process can only occur at finite- $T$ , when  $n_s(\mathbf{K}) \neq 0$ .*