

Summary of SK2758 Solid State Physics

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Abstract

This is a summary of SK2758 Solid State Physics. It contains the most essential formulae and discussions of the theory, I think.

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1 Crystals

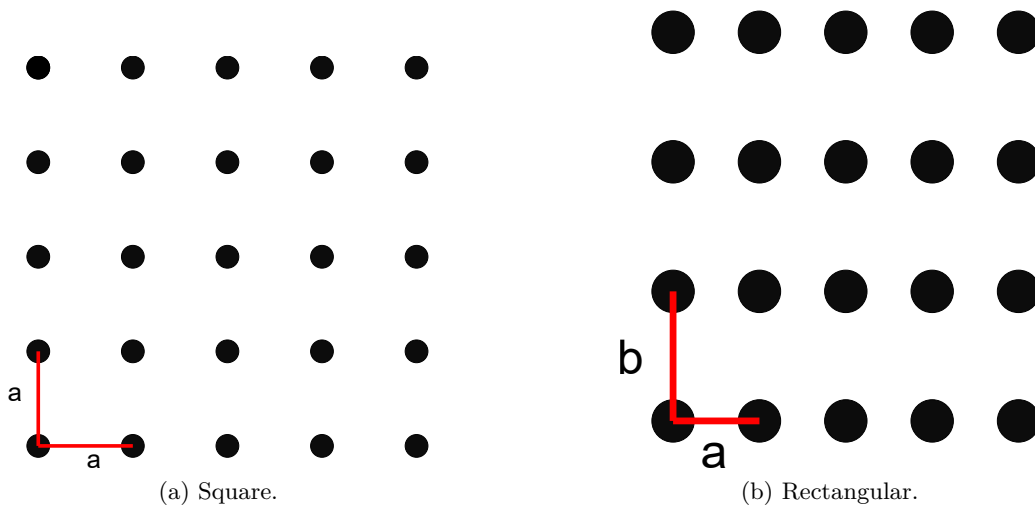
Crystals Solid state physics, as we will study it, is concerned with crystals. A crystal is an arrangement of atoms which is repeated periodically. When developing the physics of crystals, we will assume their repetition to be infinite.

Basis The arrangement of atoms which is repeated in a crystal is termed the basis.

Lattices The set of points to which the basis is attached is termed the lattice.

Bravais Lattices A Bravais lattice is a lattice such that the arrangement of lattice points looks exactly equal from any lattice point. This turns out to be equivalent to the lattice being infinite and symmetric under certain discrete translations. We will treat crystal lattices as Bravais lattices.

The two-dimensional Bravais lattices are the rectangular,



Lattice Vectors The set $\{\mathbf{a}_i\}$ of lattice vectors of a Bravais lattice is the smallest possible set of vectors such that translating the lattice by $u_i\mathbf{a}_i$, where the u_i are integers, leaves the lattice unchanged. There is an infinite number of ways to define the lattice vectors of a given lattice.

Primitive Lattice Vectors A set of lattice vectors is primitive if any two equivalent points are connected by integer combinations of the lattice vectors.

Crystal Axes The crystal axes are a set of directions that span space. These may be chosen according to, for instance, the primitive lattice vectors or other directions connected to the symmetry of the lattice.

Crystal Cell The crystal cell is the repeat unit of the crystal. It may be constructed in an infinite number of ways.

Lattice Constants Lattice constants are a set of parameters defining the dimensions of the cell.

Primitive Cell The primitive cell is a minimum-volume cell. It contains only one lattice point, and is thus termed a unit cell. Its infinite translation throughout space yields the lattice.

Primitive Basis The primitive basis is the basis associated with the primitive cell.

Wigner-Seitz Cell The Wigner-Seitz Cell is the cell constructed by for any lattice point dividing space into two at the middle of and normal to the line between the point in question and all other points, and choosing the smallest possible region of space containing the point from this.

Lattice Point Group The lattice point group is the group of operations which, applied about a lattice point (i.e. keeping this point fixed), leaves the lattice unchanged. Examples of possible fundamental operations include:

- rotations.
- reflections.

Lattice Space Group The space group of the Bravais lattices is the group of symmetries of all Bravais lattices of a given dimensionality. It contains both point groups and translations.

n -Fold Rotations An n -fold rotation is a rotation operation such that it reduces to the identity operation when applied n times. Lattices cannot be symmetric under 5-fold rotation.

Crystal Planes In a cell it is useful to define crystallographic planes. These are indicated by a set of indices (hkl), the computation of which we will return to. A bar above any element indicates that element to be negative.

A set of parallel planes such that all lattice points are contained in the set may be denoted $\{hkl\}$.

Crystallographic Directions Likewise we define crystallographic directions by the notation $[uvw]$. The indices are the set of the smallest integers such that they form a vector parallel to the one in question.

Random Stacking Randomly stacked crystals are formed by densely packed layers of atoms being stacked without long-range order in the stacking direction.

Polytypism Polytypism is a milder variation of random stacking, where the order of the stacked layers is extremely long-range.

X-Ray Diffraction X-ray diffraction is the process of shining X-rays onto a material in order to characterize it. Before atomic physics, it was discovered that solids scattered X-rays intensely in specific directions, as opposed to light, which was reflected by the solid. In the context of solid-state physics, we can interpret this as crystal planes acting as diffraction grids that scatter the X-rays. This interpretation makes sense because the wavelength of X-rays is comparable to interatomic distances in a solid, consistent with the regime in which classical wave physics predicts that diffraction phenomena are significant, and the scattered light being localized is consistent with diffraction of other waves.

Bragg's Law Bragg's law was a first attempt at explaining X-ray diffraction patterns. To derive it, consider a solid composed of aligned and stacked atomic planes separated by a distance d on which electromagnetic radiation of wavelength λ is incident at angle θ to the planes, and suppose each plane reflects the radiation specularly (following the law of reflection) and elastically (preserving the wavelength). Comparing radiation reflected from two adjacent layers, the light in the lower layer travels a distance $2d \sin \theta$ longer. In order for the radiation from these layers to interfere constructively, we must have

$$2d \sin \theta = n\lambda, \quad n = 1, 2, \dots$$

This is Bragg's law. It is a very rough description of X-ray diffraction, but predicts the phenomenology correctly. It also predicts that diffraction occurs for $\lambda < 2d$, which is why light, for instance, is not diffracted by solids.

Fourier Analysis and Reciprocal Space The translational symmetry of the lattice implies that the tools of Fourier analysis are applicable when studying solid-state physics. Any observable A defined on the crystal lattice may be written as

$$A = \sum_{\mathbf{G}} A_{\mathbf{G}} e^{i\mathbf{G} \cdot \mathbf{r}}.$$

The coefficients in the series expansion are given by

$$A_{\mathbf{G}} = \frac{1}{V_{\text{cell}}} \int_{\text{cell}} d^d \mathbf{r} A(\mathbf{r}) e^{-i\mathbf{G} \cdot \mathbf{r}}.$$

In order for A to be an observable, we must have $A_{-\mathbf{G}} = A_{\mathbf{G}}^*$. The fact that A is an observable on the crystal lattice implies that it must have the same symmetries - in particular translational symmetry. This implies

$$A(\mathbf{r} + u_i \mathbf{a}_i) = A(\mathbf{r}) \implies u_i \mathbf{G} \cdot \mathbf{a}_i = 2\pi n$$

where n is an integer. The vectors \mathbf{G} must have reciprocal length as their dimension, and are thus vectors in what is termed reciprocal space.

The Reciprocal Lattice The simplest choice of vectors satisfying

$$u_i \mathbf{G} \cdot \mathbf{a}_i = 2\pi n$$

is integer combinations of a set of vectors $\{\mathbf{b}_i\}$ such that $\mathbf{a}_i \cdot \mathbf{b}_j = 2\pi \delta_{ij}$. The set of vectors $\{\mathbf{b}_i\}$ thus defines a Bravais lattice in reciprocal space, termed the reciprocal lattice. In three dimensions, the explicit formula for the reciprocal lattice vectors is

$$\mathbf{b}_1 = \frac{2\pi}{V_{\text{cell}}} \mathbf{a}_2 \times \mathbf{a}_3, \quad V_{\text{cell}} = \mathbf{a}_1 \cdot (\mathbf{a}_2 \times \mathbf{a}_3)$$

with cyclic permutation of the indices yielding the other two.

Crystal Planes and the Reciprocal Lattice Assume that there is a lattice point in the origin and that the closest crystal plane with orientation specified by the normal vector \mathbf{n} is a distance d from the origin. Any plane parallel to the plane in question is described by

$$\mathbf{r} \cdot \mathbf{n} = md, \quad m = 0, \pm 1, \dots$$

Consider now a translation by \mathbf{T} such that the lattice is left invariant. Assuming the translation to be between lattice points, the translation must satisfy the equation of some crystal plane, implying

$$\mathbf{T} \cdot \mathbf{n} = md.$$

In particular, if the translation is to a point in a plane adjacent to the origin, we have

$$\mathbf{T} \cdot \frac{2\pi}{d} \mathbf{n} = 2\pi.$$

Comparing this to the definition of the reciprocal lattice implies that the plane is normal to a reciprocal lattice vector

$$\mathbf{G} = \frac{2\pi}{d} \mathbf{n}.$$

This is the shortest reciprocal lattice vector describing the plane. The expression above implies

$$d = \frac{2\pi}{|\mathbf{G}|}.$$

Miller Indices Returning to the indexing system for crystal planes, we may decompose the normal vector as

$$\mathbf{G} = h\mathbf{b}_1 + k\mathbf{b}_2 + l\mathbf{b}_3.$$

These indices are exactly the indices used to describe a crystal plane, and are termed Miller indices. As \mathbf{G} is the shortest vector describing the plane, the indices cannot contain any common factors.

The Miller indices may also be computed from the real lattice according to the following rules:

1. For each axis, defined by the lattice vectors, identify the intercepts of the plane with the axis as units of the lattice parameters.
2. Compute the reciprocals of each intercept.
3. Reduce to three integers with the same ratio.

Interplanar Distances Consider the set of $\{hkl\}$ planes. We are interested in computing the distance between two adjacent such planes. To do this, we will first need a unit normal to any such plane. According to the construction of the Miller indices, the vectors

$$\mathbf{v}_1 = \frac{1}{h}\mathbf{a}_1 - \frac{1}{k}\mathbf{a}_2, \quad \mathbf{v}_2 = \frac{1}{h}\mathbf{a}_1 - \frac{1}{l}\mathbf{a}_3$$

span the plane, apart from some constant spatial shift. Hence we are interested in a vector that is simultaneously normal to both of these. One possible choice is

$$\mathbf{G}_{hkl} = h\mathbf{b}_1 + k\mathbf{b}_2 + l\mathbf{b}_3.$$

From this, obtaining a unit normal is trivial. Next we need a vector from one plane to the other. One possible choice is

$$\mathbf{T} = \frac{1}{h}\mathbf{a}_1,$$

as one cell has space for h planes of this type when counted along the \mathbf{a}_1 direction. From this, the distance is given by

$$d = \frac{1}{|\mathbf{G}_{hkl}|} \mathbf{G}_{hkl} \cdot \mathbf{T} = \frac{2\pi}{|\mathbf{G}_{hkl}|},$$

which is true for any Bravais lattice.

Diffraction by Solids Using the language of Fourier analysis and reciprocal space, we will try to derive a more sophisticated diffraction condition.

To do this, consider a crystal exposed to far-field radiation described by a wave vector \mathbf{k} which is scattered elastically by the crystal in an arbitrary direction and observed in the far-field region in some direction, in which the wave vector is \mathbf{k}' . Considering the interference between two points displaced by \mathbf{r} , the phase difference between the radiation from the two points is $(\mathbf{k} - \mathbf{k}') \cdot \mathbf{r}$. Supposing that the amplitude of the scattered wave is proportional to the electron density (or, really, any property defined on the lattice), the total scattered amplitude is proportional to the (confusingly termed) scattering amplitude

$$F = \int d^d\mathbf{r} n(\mathbf{r}) e^{i(\mathbf{k}-\mathbf{k}') \cdot \mathbf{r}}.$$

Adding the series expansion of the electron density yields

$$F = \int d^d\mathbf{r} \sum_{\mathbf{G}} n_{\mathbf{G}} e^{i\mathbf{G} \cdot \mathbf{r}} e^{-i\Delta\mathbf{k} \cdot \mathbf{r}} = \int d^d\mathbf{r} \sum_{\mathbf{G}} n_{\mathbf{G}} e^{i(\mathbf{G}-\Delta\mathbf{k}) \cdot \mathbf{r}} = \sum_{\mathbf{G}} \int d^d\mathbf{r} n_{\mathbf{G}} e^{i(\mathbf{G}-\Delta\mathbf{k}) \cdot \mathbf{r}}.$$

For the case $\Delta\mathbf{k} = \mathbf{G}$ for any one particular reciprocal lattice vector, the exponential in this term vanishes, leaving a term $V n_{\mathbf{G}}$. It can be shown that all other terms in the scattering amplitude vanish, yielding $F = V n_{\mathbf{G}}$ for this case and $F = 0$ otherwise. The most fundamental diffraction condition is thus

$$\Delta\mathbf{k} = \mathbf{G}.$$

While we have in principle obtained a diffraction condition now, we can simplify it by using the fact that the scattering is elastic. We obtain

$$2\mathbf{k} \cdot \mathbf{G} + G^2 = 0.$$

It may be rewritten by swapping \mathbf{G} for $-\mathbf{G}$, which is also a reciprocal lattice vector, to yield

$$2\mathbf{k} \cdot \mathbf{G} = G^2.$$

Note that this implies that information about the reciprocal lattice, and therefore the lattice itself, may be obtained from diffraction experiments.

Laue's Equations The fundamental diffraction criterion implies

$$\Delta \mathbf{k} \cdot \mathbf{a}_i = 2\pi v_i$$

for some integer v_i , simultaneously for all lattice vectors. This implies that reflections are only found at the intersection of three cones in reciprocal space. This is very strict, and such reflections must be found by sweeping in crystal orientation and/or wavelength or by chance.

The Ewald Sphere The Ewald sphere is a tool for visualizing the necessary conditions for diffractions. To construct it, draw the incident wave vector starting in a point such that it terminates in a reciprocal lattice point. From the starting point, draw a sphere of radius k . All reciprocal lattice points corresponding to a diffraction peak are found on this sphere.

Brillouin Zones To introduce the concept of Brillouin zones, rewrite the diffraction condition as

$$\mathbf{k} \cdot \frac{1}{2} \mathbf{G} = \left(\frac{1}{2} G \right)^2.$$

For a fixed \mathbf{G} , this equation defines the set of wave vectors terminating on the bisector of \mathbf{G} . This is similar to the construction of the Wigner-Seitz cell in real space, but now extended to construct zones using all points in the reciprocal lattice. Constructing these bisectors divides the reciprocal space into Brillouin zones (a single Brillouin zone is the combinations of all zones a fixed number of zones from the central zone). The central zone, which is the Wigner-Seitz cell in reciprocal space, is the first Brillouin zone.

Volume of the Brillouin Zone We would like to compute the volume of the Brillouin zone in terms of the volume of the unit cell. To do this, we note that the unit cell volume is given by

$$V_c = \mathbf{a}_1 \cdot (\mathbf{a}_2 \times \mathbf{a}_3).$$

Using this, the volume of the Brillouin zone is given by

$$V_r = \mathbf{b}_1 \cdot (\mathbf{b}_2 \times \mathbf{b}_3).$$

The vector in the parenthesis is given by

$$\begin{aligned} \mathbf{b}_2 \times \mathbf{b}_3 &= \frac{(2\pi)^2}{V_c^2} (\mathbf{a}_3 \times \mathbf{a}_1) \times (\mathbf{a}_1 \times \mathbf{a}_2) \\ &= \frac{(2\pi)^2}{V_c^2} ((\mathbf{a}_3 \cdot (\mathbf{a}_1 \times \mathbf{a}_2)) \mathbf{a}_1 - (\mathbf{a}_3 \cdot (\mathbf{a}_1 \times \mathbf{a}_1)) \mathbf{a}_2) \\ &= \frac{(2\pi)^2}{V_c} \mathbf{a}_1, \end{aligned}$$

and thus the volume of the Brillouin zone is given by

$$V_r = \frac{(2\pi)^3}{V_c}.$$

The Structure Factor and Atomic Form Factor The diffraction condition is stated in terms of reciprocal lattice vectors obtained from the primitive lattice vectors. However, especially in experimental contexts, the primitive unit cell is not the geometry of choice for studying materials. Instead, one can use inherent ambiguities in choices of repeat units of the crystal to study geometries with, for instance, more or simpler symmetries. When considering such geometries, the diffraction conditions is only necessary, not sufficient. We will now study diffraction for such cases.

Consider a crystal built up of some kind of cell, not necessarily a primitive one. When the diffraction condition is satisfied, i.e. $\Delta \mathbf{k} = \mathbf{G}$ for some reciprocal lattice vector corresponding to the chosen cell, the scattering amplitude for a crystal of N cells becomes

$$F = \int d^d \mathbf{r} n(\mathbf{r}) e^{-i \mathbf{G} \cdot \mathbf{r}} = N \int_{\text{cell}} d^d \mathbf{r} n(\mathbf{r}) e^{-i \mathbf{G} \cdot \mathbf{r}} = N S_{\mathbf{G}},$$

where we have introduced the structure factor $S_{\mathbf{G}}$, which describes the effect of the electron distribution in the cell on the scattering amplitude for a given diffraction peak.

Writing the electron density as a superposition of contributions from each atom in the basis (this decomposition is not unique, but somehow this is not a problem), we obtain

$$S_{\mathbf{G}} = \int_{\text{cell}} d^d \mathbf{r} \sum n_j(\mathbf{r} - \mathbf{r}_j) e^{-i\mathbf{G} \cdot \mathbf{r}}$$

where the \mathbf{r}_j are the positions of the atoms in the basis. We rewrite this as

$$S_{\mathbf{G}} = \sum \int_{\text{cell}} d^d \mathbf{r} n_j(\mathbf{r} - \mathbf{r}_j) e^{-i\mathbf{G} \cdot \mathbf{r}} = \sum e^{-i\mathbf{G} \cdot \mathbf{r}_j} \int_{\text{cell}} d^d \mathbf{r} n_j(\mathbf{r}) e^{-i\mathbf{G} \cdot \mathbf{r}}.$$

Defining the atomic form factor

$$f_{j,\mathbf{G}} = \int_{\text{cell}} d^d \mathbf{r} n_j(\mathbf{r}) e^{-i\mathbf{G} \cdot \mathbf{r}}$$

we have

$$S_{\mathbf{G}} = \sum f_{j,\mathbf{G}} e^{-i\mathbf{G} \cdot \mathbf{r}_j}.$$

The requirement for diffraction is thus that $\Delta \mathbf{k} = \mathbf{G}$ and the structure factor being non-zero.

When observing electron distributions in solids, these appear close to those of free atoms. This does not mean that electrons are not distributed in a solid versus for free atoms, but that these corrections do not have a major effect on the atomic form factors. Thus it may be relevant to write these as

$$f_{j,\mathbf{G}} = \int d^d \mathbf{r} n_j(\mathbf{r}) e^{-i\mathbf{G} \cdot \mathbf{r}}$$

where the electron distribution is that of a free atom and the integration is performed over all of space.

The astute reader might have noticed that when considering the primitive unit cell of a crystal with one atom in the basis, the structure factor is trivial. One could thus ask whether this was really necessary. The answer to the latter question is left to experimentalists, but I can confirm that this derivation neither adds nor subtracts to our knowledge. If you have chosen the primitive cell, the structure factor is trivial and diffraction occurs for every observation such that the diffraction criterion is satisfied. For other choices of cells, certain reciprocal lattice vectors will produce a structure factor equal to zero. This is because these do not correspond to reciprocal lattice vectors of the primitive cell. Someone should prove this more rigorously. Can we be sure that other choices of cells cover all possible reciprocal lattice vectors of the primitive cell? Yes, as non-primitive cells must have longer lattice vectors, corresponding to shorter reciprocal lattice vectors, implying that the reciprocal lattice vectors of the primitive cell should be possible to express as combinations of the reciprocal lattice vectors of the non-primitive cell.

Cohesive Energy The cohesive energy of a crystal is the energy required to separate the crystal into neutral free atoms at rest at infinite separation.

Types of Crystal Binding The different types of crystal binding and their origins are

- van der Waals binding, which occurs due to fluctuating electric dipoles in atoms and molecules.
- ionic binding, which occurs due to Coulomb forces between ions.
- covalent binding, which occurs due to the filling of electron states localized between atoms.
- metal binding, where valence electrons form a gas throughout the crystal and balance repulsion between the metal atoms in the lattice.

van der Waals Energy The van der Waals interaction between two atoms in a crystal or molecule is modelled as a potential of the form

$$V = 4\varepsilon \left(\left(\frac{\sigma}{R} \right)^{12} - \left(\frac{\sigma}{R} \right)^6 \right)$$

with a positive term from Pauli repulsion and a negative term from attraction between fluctuating dipoles.

For a crystal of N atoms the cohesive energy due to van der Waals interaction becomes

$$U = 2N\varepsilon \left(\sum_j \left(\frac{\sigma}{R_j} \right)^{12} - \left(\frac{\sigma}{R_j} \right)^6 \right).$$

Re-expressing this in terms of nearest-neighbour distances R in the lattice, we can write $R_j = p_j R$ to obtain

$$U = 2N\varepsilon \left(\left(\frac{\sigma}{R} \right)^{12} \sum_j \frac{1}{p_j^{12}} - \left(\frac{\sigma}{R} \right)^6 \sum_j \frac{1}{p_j^6} \right)$$

where we have divided by two in order to distribute the interaction energy evenly between the atoms. The two summations are determined solely by the crystal structure.

Ionic Binding Ionic interactions between two atoms in a crystal is modelled as a potential of the form

$$V = \lambda e^{-\frac{R_{ij}}{\rho}} \pm \frac{q^2}{4\pi\varepsilon_0 R_{ij}}$$

with a positive term from Pauli repulsion and a negative term from attraction between charged particles. The Pauli term is typically only included for nearest neighbours.

For a crystal of N atoms the cohesive energy due to ionic interaction becomes

$$U = N \left(Z\lambda e^{-\frac{R}{\rho}} + \sum_j (-1)^{g(j)} \frac{q^2}{4\pi\varepsilon_0 R_j} \right)$$

where we have introduced the nearest-neighbour distance R and the function g describing whether atom j has an equal or opposite charge to that of the atom in the origin. Re-expressing the Coulomb term in terms of nearest-neighbour distances we obtain

$$U = N \left(Z\lambda e^{-\frac{R}{\rho}} - \alpha \frac{q^2}{4\pi\varepsilon_0 R_{ij}} \right)$$

where Z is the coordination number of a given ion and

$$\alpha = \sum \frac{(-1)^{g(j)}}{p_j}$$

is termed the Madelung constant and depends only on the crystal structure.

Covalently Bound Solids Solids bound by covalent force have localized electrons due to the nature of the bonds in the solid, meaning that such bonds are typically found in insulators and semiconductors.

Metals Electrons in metals move around in a gas, hence metals are generally good conductors.

Atomic Radii The introduced parameters in the interaction potentials described above that have dimensions of length are essentially dependent on atomic radii. It turns out that atomic radii are largely independent of the composition of the material in which any given atom is found. However, they are significantly affected by coordination number.

2 Phonons and Crystal Vibration

The Monoatomic Chain Vibrations in a crystal lattice along a certain crystal direction are vibrations along a chain of atoms lying in that direction. Hence we will need to understand the (classical) physics of particles on chains.

Consider a chain of atoms at positions $x_n = na + u_n$, the first term of which is the equilibrium position and the second is the fluctuations from equilibrium. Assuming a harmonic potential with intensity C between nearest neighbours in the chain, your favorite choice of equations of motion will yield

$$m \frac{d^2 x_n}{dt^2} = m \frac{d^2 u_n}{dt^2} = C(x_{n+1} - x_n) - C(x_n - x_{n-1}) = C(x_{n+1} + x_{n-1} - 2x_n) = C(u_{n+1} + u_{n-1} - 2u_n).$$

When studying lattice vibrations, we are interested in solutions to the equations of motion which are travelling waves, of the form

$$u_n = u_0 e^{i(Kna - \omega t)}.$$

Inserting this into the equations of motion yields

$$-m\omega^2 u_0 e^{i(Kna - \omega t)} = C u_0 e^{i(Kna - \omega t)} (e^{iKa} + e^{-iKa} - 2) = 2C u_0 e^{i(Kna - \omega t)} (\cos Ka - 1) = -4C u_0 e^{i(Kna - \omega t)} \sin^2\left(\frac{Ka}{2}\right)$$

This implies the dispersion relation

$$\omega = \sqrt{\frac{4C}{m}} \left| \sin\left(\frac{Ka}{2}\right) \right|.$$

To continue our study, we introduce

$$\xi = \frac{Ka}{2\pi}, \quad \omega_0 = \sqrt{\frac{4C}{m}},$$

allowing us to write the dispersion relation as

$$\omega = \omega_0 |\sin(\pi\xi)|.$$

Firstly we note that the dispersion relation has a period of π in the new coordinates. In addition, we note that ξ for this chain is a measure of progression in the reciprocal lattice - each integer value of ξ corresponds to a reciprocal lattice point. This means that all of the physics of the chain are contained within the interval $-\frac{1}{2} < \xi < \frac{1}{2}$, which is the first Brillouin zone of the lattice.

The periodicity of the dispersion relation has an interpretation. Suppose that $K = k + \frac{2\pi}{a}$ where k is within the first Brillouin zone. The motion of any particle in the chain when exposed to such a wave is given by

$$u_n = u_0 e^{i(Kna - \omega t)} = u_0 e^{2\pi n i} e^{i(kna - \omega t)} = u_0 e^{i(kna - \omega t)}.$$

Hence the periodicity of the dispersion relation is due to the fact that the travelling wave is only defined at discrete points.

The group velocity of such lattice vibrations is given by

$$v_g = \frac{d\omega}{dK} = \frac{1}{2\omega} \frac{d\omega^2}{dK} = \frac{1}{2\omega_0 |\sin(\pi\xi)|} \cdot \frac{2a\omega_0^2}{2} \sin\left(\frac{Ka}{2}\right) \cos\left(\frac{Ka}{2}\right) = \frac{1}{2} a\omega_0 \cos(\pi\xi) \operatorname{sgn}(\sin(\pi\xi)),$$

where the last factor merely describes the direction of propagation. In the long-wavelength limit, close to the origin in reciprocal space, we obtain

$$\omega \approx \omega_0 \pi \xi = \frac{1}{2} Ka\omega_0, \quad v_g \approx \frac{1}{2} a\omega_0,$$

implying the linear dispersion relation $\omega = v_g K$. Identifying Ca as a measure of the tension and $\frac{m}{a}$ as the density, we also have

$$v_g = \sqrt{\frac{T}{\rho}},$$

as expected for acoustic waves in a solid. When approaching the Brillouin zone boundary, we obtain

$$v_g = 0,$$

representing a standing wave solution. The wavelength corresponding to the zone boundary is the shortest wavelength that can propagate in the material.

The Diatomic Chain To study the effect of the basis, consider a chain of atoms with two atoms in the basis and lattice parameter a . Denoting the fluctuations of each type of atom by u and v respectively and only considering nearest-neighbour interactions, the equations of motion are

$$m_1 \frac{d^2 u_n}{dt^2} = C(v_n + v_{n-1} - 2u_n), \quad m_2 \frac{d^2 v_n}{dt^2} = C(u_{n+1} + u_n - 2v_n).$$

We again look for plane wave solutions of the form

$$u_n = u_0 e^{i(Kna - \omega t)}, \quad v_n = v_0 e^{i(Kna - \omega t)}.$$

Inserting this into the equations of motion yields

$$\begin{aligned} -m_1 \omega^2 u_0 e^{i(Kna - \omega t)} &= C \left(v_0 e^{i(Kna - \omega t)} + v_0 e^{i(K(n-1)a - \omega t)} - 2u_0 e^{i(Kna - \omega t)} \right) \\ &= C e^{-i(Kna - \omega t)} (v_0 (1 + e^{-iKa}) - 2u_0), \\ -m_2 \omega^2 v_0 e^{i(Kna - \omega t)} &= C \left(u_0 e^{i(K(n+1)a - \omega t)} + u_0 e^{i(Kna - \omega t)} - 2v_0 e^{i(Kna - \omega t)} \right) \\ &= C e^{i(Kna - \omega t)} (u_0 (e^{iKa} + 1) - 2v_0). \end{aligned}$$

This is a homogenous system of equations in the amplitudes. A non-trivial solution (corresponding to there being motion in the system) corresponds to the determinant of the coefficient matrix being zero. This implies

$$\begin{aligned} \begin{bmatrix} 2C - m_1 \omega^2 & -C(1 + e^{-iKa}) \\ -C(e^{iKa} + 1) & 2C - m_2 \omega^2 \end{bmatrix} &= 0, \\ (2C - m_1 \omega^2)(2C - m_2 \omega^2) - C^2(1 + e^{-iKa})(e^{iKa} + 1) &= 0, \\ m_1 m_2 \omega^4 - 2C(m_1 + m_2)\omega^2 + 2C^2(1 - \cos(Ka)) &= 0, \end{aligned}$$

with solution

$$\omega^2 = \frac{2C(m_1 + m_2) \pm \sqrt{4C^2(m_1 + m_2)^2 - 8m_1 m_2 C^2(1 - \cos(Ka))}}{2m_1 m_2}.$$

Defining

$$\omega_0 = \sqrt{\frac{C(m_1 + m_2)}{m_1 m_2}}$$

we obtain

$$\omega^2 = \omega_0^2 \left(1 \pm \sqrt{1 - 4 \frac{m_1 m_2}{(m_1 + m_2)^2} \sin^2\left(\frac{1}{2}Ka\right)} \right).$$

The two choices of sign here represent two so-called branches of the dispersion relation, one termed the optical branch and the other the acoustic branch. The terminology will be clarified later.

We proceed by studying the limiting cases. In the low-wavelength limit we have

$$\begin{aligned} \omega^2 &\approx \omega_0^2 \left(1 \pm \sqrt{1 - \frac{m_1 m_2}{(m_1 + m_2)^2} (Ka)^2} \right) \\ &\approx \omega_0^2 \left(1 \pm 1 \mp \frac{m_1 m_2}{2(m_1 + m_2)^2} (Ka)^2 \right), \end{aligned}$$

yielding

$$\omega_{\text{op}} \approx \sqrt{2}\omega_0, \quad \omega_{\text{ac}} \approx \frac{\sqrt{C}}{\sqrt{2(m_1 + m_2)}} |Ka|.$$

For the optical branch, we thus obtain

$$\frac{u_0}{v_0} = \frac{2C}{2C - 2m_1 \omega_0^2} = \frac{2m_2}{2m_2 - 2(m_1 + m_2)} = -\frac{m_2}{m_1},$$

and for the acoustic branch we obtain

$$\frac{u_0}{v_0} = \frac{2C}{2C - 2m_1 \frac{C}{2(m_1+m_2)} (Ka)^2} \approx 1,$$

This reveals the nature of the nomenclature, as acoustic modes correspond to atoms oscillating in phase and propagating acoustic waves, whereas optical modes correspond to atoms being in anti-phase and can thus be excited by electromagnetic waves in ionic crystals.

Simultaneously plotting the dispersion relations of the two branches in the first Brillouin zone yields two different curves. As the anti-phase solution in the low-wavelength limit for the optical branch corresponds to a periodicity of $\lambda = a$ for the motion, we can interpret excitations of oscillations in the chain as starting in the acoustic branch for small K and following this dispersion relation before moving into the optical branch when crossing the Brillouin zone boundary. This transition is not smooth, as at the Brillouin zone boundary we have

$$\begin{aligned} \omega^2 &= \omega_0^2 \left(1 \pm \sqrt{1 - 4 \frac{m_1 m_2}{(m_1 + m_2)^2}} \right) \\ &= \frac{\omega_0^2}{m_1 + m_2} \left(m_1 + m_2 \pm \sqrt{(m_1 + m_2)^2 - 4m_1 m_2} \right) \\ &= \frac{C}{m_1 m_2} (m_1 + m_2 \pm (m_1 - m_2)), \end{aligned}$$

assuming $m_1 > m_2$, with permuting the indices yielding the other result. Specifically, for the two branches we obtain

$$\omega_{\text{op}} = \sqrt{\frac{2C}{m_2}}, \quad \omega_{\text{ac}} = \sqrt{\frac{2C}{m_1}},$$

and frequencies between these two cannot be excited in the chain. This gap must thus be crossed in order for the described excitation to occur. Furthermore, as each of these frequencies correspond (I think) to the harmonic oscillation frequencies of only one sort of atom in the harmonic potential created by the static nearest neighbours, we can interpret it as each branch approaching a state where only one kind of atom is excited, and the frequency gap is due to the different masses of the atoms.

Crystal Vibrations in Three Dimensions In three dimensions there are certain effects which are not considered in our previous description, but which can be explained using similar reasoning.

In general, moving to three dimensions produces both longitudinal and transverse vibration modes. This will be true for all branches.

For crystals with a monoatomic basis, different crystal directions will produce different dispersion relations due to variations in the geometry of the bonds along different directions.

For crystals with more atoms in the basis, each atom in the basis beyond the first will add a new optical branch.

Phonons While our discussion up to now have been classical nature, one could instead have constructed the Hamiltonian of the chain and studied it using quantum mechanics. Through a somewhat lengthy process, you would then arrive at the result that the chain can be described as a set of quantum harmonic oscillators. The energies of such a systems are quanta of $\hbar\omega$. Each such energy quantum is termed a phonon.

Phonons are quasi-particles, meaning that they behave as particles but are nothing but many-body effects in reality. More specifically, they interact as though they had energy $\hbar\omega$ and momentum $\hbar\mathbf{K}$, the latter being termed crystal momentum. This allows us to measure their dispersion.

Inelastic Neutron Scattering Inelastic neutron scattering is a powerful method for measuring phonon dispersion, as it is only by this method that the entire dispersion relation can be measured. As we are studying inelastic scattering, we are concerned with cases where the neutrons either create or absorb phonons. The conservation laws for a single neutron before and after scattering are

$$\frac{\hbar^2 k^2}{2m} = \frac{\hbar^2 (k')^2}{2m} \pm \hbar\omega, \quad \hbar\mathbf{k} = \hbar\mathbf{k}' \pm \hbar\mathbf{K} + \hbar\mathbf{G},$$

where the last term in the momentum conservation is due to the periodicity of the phonon dispersion relation with respect to the different Brillouin zones forcing us to move \mathbf{K} to the first Brillouin zone.

In an experiment, a neutron with energy $E = \frac{\hbar^2 k^2}{2m}$ is sent into a sample, scattered and detected by a detector that measures both its direction of motion and its energy $E' = \frac{\hbar^2 (k')^2}{2m}$. From this, the frequency of the phonon with which the neutron interacted and the full scattered wave vector can be obtained. As the crystal structure contains all information about the reciprocal lattice, the phonon wave vector can also be calculated. Plotting the phonon frequency against the wave number finally yields the dispersion relation.

Phonon Contributions to Heat Capacity As phonons have energy, they contribute to the heat capacity of a crystal. Using statistical mechanics, we can determine how large this contribution is by treating the phonon gas as a collection of non-interacting harmonic oscillators.

The following paragraphs will mostly summarize essential results. For details, please see my summary of SI1162 Statistical Physics.

Heat Capacity from Classical Statistics In classical mechanics, the equipartition theorem yields

$$U = 3Nk_B T, \quad C_V = 3Nk_B,$$

known as the Dulong-Petit rule. The molar heat capacity is thus

$$c_V = 3sN_A k_B = 3R$$

where N_A is the Avogadro number and s the number of atoms in the basis.

This result agrees with experiments at high temperatures, but does not agree with the result that the heat capacity vanishes at low temperatures.

Heat Capacity from Quantum Statistics In order to use quantum statistics, we use the results that the energies of a harmonic oscillator are $E_n = (n + \frac{1}{2}) \hbar \omega$. In order to do statistics, however, we need a density of states which ideally should take polarization into account as well. The models described below are all attempts at appropriate choices of the density of states.

The Einstein Model The Einstein model proposes the density of states

$$\rho(\omega) = 3N \delta(\omega - \omega_E)$$

where ω_E is termed the Einstein frequency. When taking polarization into account, the density of states may be split up into terms containing different Einstein frequencies for different polarizations. One obtains

$$c_V = 3sR (\beta \hbar \omega_E)^2 \frac{e^{\beta \hbar \omega_E}}{(e^{\beta \hbar \omega_E} - 1)^2}.$$

where $\beta = \frac{1}{k_B T}$. This prediction both vanishes at low temperatures and approaches the Dulong-Petit rule at high temperatures. However, its low-temperature behaviour does not match with experiments.

The Einstein model describes optical phonons well due to their narrower frequency distribution. However, the low-temperature limitations of the model is due to it not describing acoustic phonons well.

The Debye Model The Debye model, working from a linear dispersion relation and the standard k-space density of states, proposes the density of states

$$\rho(\omega) = \frac{2}{2\pi^2} \frac{V}{v^3} \omega^2$$

up to some maximal frequency ω_D , termed the Debye frequency. The requirement that the number of phonons be equal to $3N$ yields

$$\omega_D = \left(\frac{6\pi^2 N}{V} \right)^{\frac{1}{3}} v.$$

In order to proceed with the calculations, one often uses the average

$$\frac{3}{v^3} = \sum \frac{1}{v_p^3}$$

to obtain

$$c_V = 9sR \left(\frac{T}{T_D} \right)^3 \int_0^{\beta \hbar \omega_D} dx \frac{x^4 e^x}{(e^x - 1)^2}$$

where $T_D = \frac{\hbar \omega_D}{k_B}$.

This model both yields the correct low-temperature and high-temperature behaviour.