

## **PART II. Crystalline Structures & Lattice Waves**

### **References:**

- 1) “Principles of the Theory of Solids”, J. M. Ziman, Chapters 1 and 2.
- 2) “Solid State Physics”, N. W. Ashcroft and N. D. Mermin, Chapters 4, 5, 6, 7, 22, 23 and 24.

### **II.1. Translational Symmetry and Periodic Wave Functions**

**Topics:** translational symmetry, lattice vectors and lattice sites, Bravais lattices, Wigner-Seitz cells

#### **• Translational symmetry & lattice vectors**

For a  $D$ -dimensional crystal, there exists  $D$  basis vectors  $a_1, a_2, \dots, a_D$  such that the atomic structure of the crystal remains invariant under translation through any vector  $\mathbf{l}$  that is the sum of integral multiples of these basis vectors, which is defined as a *lattice vector*.

$$\mathbf{l} = \sum_{i=1}^D l_i \mathbf{a}_i, \quad (l_i: \text{integers}) \quad (\text{II.1})$$

The sites defined by the lattice vectors are known as the lattice sites.

In real crystals there are always defects present, and the translational symmetry also breaks down on the surfaces. Generally the surface effect is insignificant on the bulk properties of crystals. However, in reduced dimensions such as thin films (particularly for mono-atomic layer films like graphene), nano-ribbons and nano-wires, and quantum dots, the “edge effects” may become very important.

It should be noted that the symmetry of crystals is generally not restricted to translational symmetry. There are generally additional symmetries associated with rotation, reflection, etc. These symmetries can be classified by group theory, which we’ll visit later.

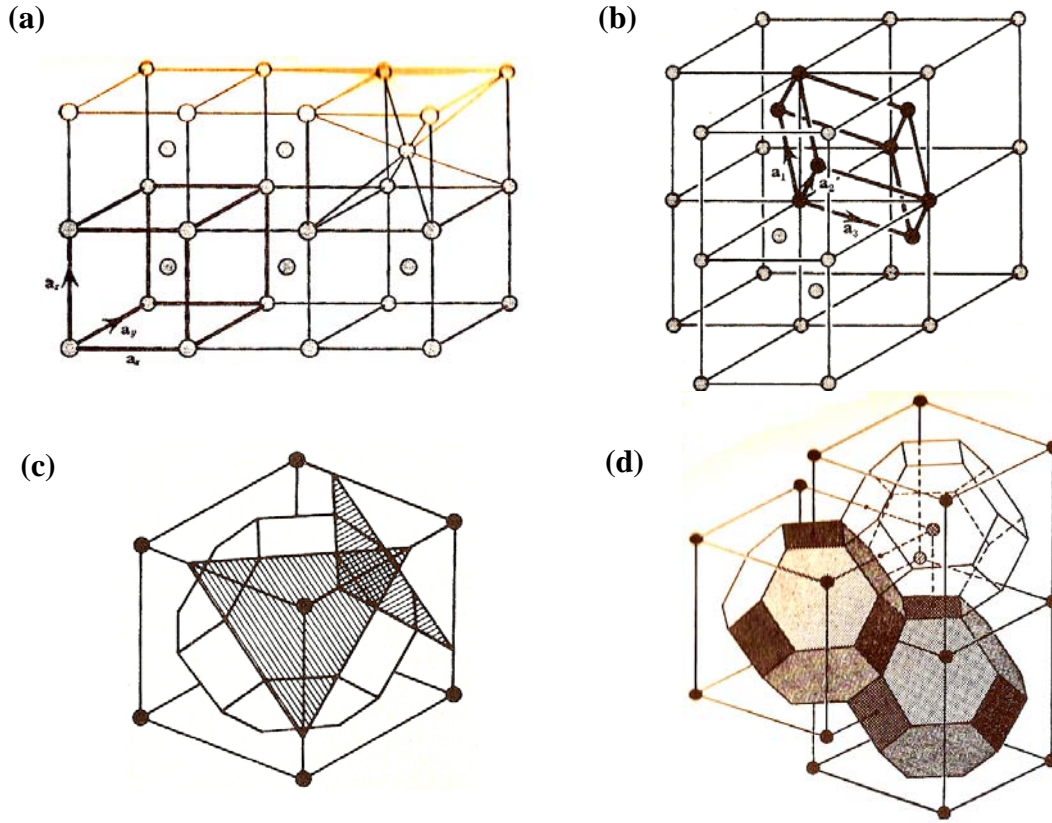
#### **[Example 1] Lattice vectors of a body-center-cubic (BCC) crystal**

Consider a cubic crystalline structure, the body-center-cubic (BCC) structure. Assuming that the lattice constant is  $a_0$ , we may naively construct the lattice vectors by taking the three unit vectors along the principal axes:  $\hat{a}_x \equiv a_0 \hat{x}$ ,  $\hat{a}_y \equiv a_0 \hat{y}$  and  $\hat{a}_z \equiv a_0 \hat{z}$ . However, in this case we would have two atoms per unit cell, and there would be two inequivalent atomic sites, one in the center and the other in the corner. Further, we would not be able to use EQ. (II.1) to translate a center atom to a corner atom, and vice versa. On the other hand, if we choose the following lattice vectors:

$$\hat{a}_1 \equiv \frac{1}{2} a_0 (-\hat{x} + \hat{y} + \hat{z}), \quad \hat{a}_2 \equiv \frac{1}{2} a_0 (\hat{x} - \hat{y} + \hat{z}), \quad \hat{a}_3 \equiv \frac{1}{2} a_0 (\hat{x} + \hat{y} - \hat{z}), \quad (\text{II.2})$$

we find that EQ. (II.2) can translate a corner atom to a center atom if  $\sum_i l_i = (\text{odd integer})$ , and to another corner atom if  $\sum_i l_i = (\text{even integer})$ .

We further note that the lattice vectors given in EQ. (II.2) also defines a unit cell that contains only one atom, which is known as a *Bravais lattice*.



**Fig. II.1:** Body-center-cubic lattice structure. (a) The cubic unit cell. (b) Generators ( $\mathbf{a}_1$ ,  $\mathbf{a}_2$ ,  $\mathbf{a}_3$ ) of the Bravais lattice. (c) The Wigner-Seitz cell. (d) Stacking of the Wigner-Seitz cells.

### • Bravais lattices

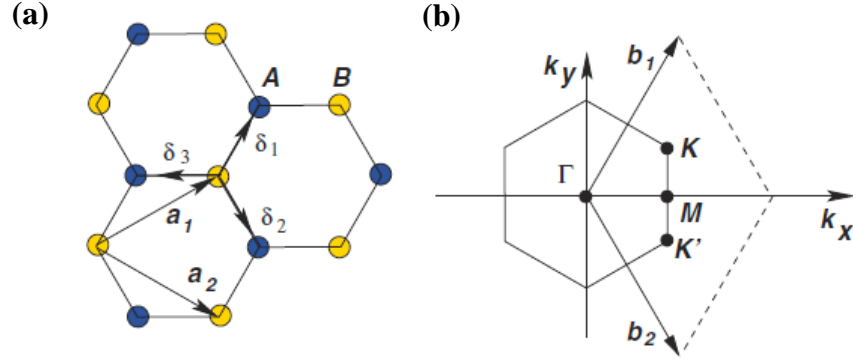
A *Bravais lattice* is a crystalline structure with only one atom per unit cell. There are 7 distinct groups of Bravais lattices, and the full symmetry group of a Bravais lattice is called the *point group* of the Bravais lattice. We'll consider the classification of Bravais lattices later in Part II. If a crystal contains more than one atom per unit cell, the crystalline structure should be described in terms of a lattice with a basis.

### • Wigner-Seitz cells

As we shall see later in the consideration of electronic bandstructures, it is often convenient to construct a unit cell of a crystal with high central symmetry. This construction may be accomplished by drawing the perpendicular bisector planes of the translation vectors from a chosen lattice site to its nearest neighboring equivalent sites. The connected bisector planes around the chosen lattice site constitute a *Wigner-Seitz cell*. An example of the Wigner-Seitz cell of a bcc structure is shown in Fig. II.1(c).

**[Example 2] Lattice vectors of graphene**

As a second example, we consider the honeycomb lattice structure of graphene, a monolayer of two-dimensional carbon. As illustrated in Fig. II.2(a), there are two atoms per unit cell and there are two inequivalent lattice sites A and B. Therefore, the honeycomb structure of graphene is not a Bravais lattice.



**Fig. II.2:** Honeycomb lattice of graphene and its Brillouin zone. **(a)** Lattice structure of graphene in real space, which consists of two interpenetrating triangular lattices. Here  $\mathbf{a}_1$  and  $\mathbf{a}_2$  denote the lattice unit vectors, and  $\delta_i$  ( $i = 1, 2, 3$ ) are the nearest-neighbor vectors. **(b)** The corresponding Brillouin zone in reciprocal space, with  $\mathbf{b}_1$  and  $\mathbf{b}_2$  representing the reciprocal lattice unit vectors. The Dirac cones are located at the  $K$  and  $K'$  points.

• **Periodic wave functions**

The translational invariance of a crystal may be represented by periodic wave functions  $f(\mathbf{r}) = f(\mathbf{r} + \mathbf{l})$ , where  $\mathbf{l}$  is a lattice vector. We may express  $f(\mathbf{r})$  in terms of a Fourier series:

$$f(\mathbf{r}) = \sum_{\mathbf{g}} A_{\mathbf{g}} e^{i\mathbf{g} \cdot \mathbf{r}}, \quad (\text{II.3})$$

where

$$A_{\mathbf{g}} = \frac{1}{v_c} \int_{\text{cell}} f(\mathbf{r}) e^{-i\mathbf{g} \cdot \mathbf{r}} d\mathbf{r}, \quad (\text{II.4})$$

$v_c = (V/N)$  denotes the volume of a unit cell,  $V$  is the total volume of the sample, and  $N$  is the total number of unit cells in the sample. From  $f(\mathbf{r}) = f(\mathbf{r} + \mathbf{l})$  and EQ. (II.3), we have  $e^{i\mathbf{g} \cdot \mathbf{l}} = 1$  so that

$$\mathbf{g} \cdot \mathbf{l} = 2\pi N = \sum_{i=1}^D g_i l_i a_i, \quad (\text{II.5})$$

and

$$\mathbf{g} \cdot \mathbf{l} = 2\pi N = \sum_{i=1}^D g_i l_i a_i \equiv 2\pi \sum_{i=1}^D n_i l_i, \quad (\text{II.6})$$

where  $n_i$  are integers. Hence, we find that the wave-vector  $\mathbf{g}$  is given by

$$\mathbf{g} \equiv (g_1, g_2, \dots, g_D) = \left( \frac{2\pi n_1}{a_1}, \frac{2\pi n_2}{a_2}, \dots, \frac{2\pi n_D}{a_D} \right) \equiv (2\pi n_1 b_1, 2\pi n_2 b_2, \dots, 2\pi n_D b_D) \equiv \sum_{i=1}^D 2\pi n_i \mathbf{b}_i. \quad (\text{II.7})$$

The wave-vector  $\mathbf{g}$  is a reciprocal lattice vector, and for  $D = 3$ , we find that

$$\mathbf{b}_1 = \frac{\mathbf{a}_2 \times \mathbf{a}_3}{\mathbf{a}_1 \cdot (\mathbf{a}_2 \times \mathbf{a}_3)}, \quad \mathbf{b}_2 = \frac{\mathbf{a}_3 \times \mathbf{a}_1}{\mathbf{a}_1 \cdot (\mathbf{a}_2 \times \mathbf{a}_3)}, \quad \mathbf{b}_3 = \frac{\mathbf{a}_1 \times \mathbf{a}_2}{\mathbf{a}_1 \cdot (\mathbf{a}_2 \times \mathbf{a}_3)}. \quad (\text{II.8})$$

Therefore, the basic cell spanned by the vectors  $2\pi\mathbf{b}_1$ ,  $2\pi\mathbf{b}_2$  and  $2\pi\mathbf{b}_3$  is the reciprocal lattice of the original direct lattice.

## II.2. The Reciprocal Lattice – Definitions & Properties

**Topics:** reciprocal lattices, Miller indices

Having defined the concepts of reciprocal lattices and reciprocal lattice vectors in Section II.1, the following geometric properties can be easily deduced from EQs. (II.7) and (II.8):

- [1] Each reciprocal lattice vector  $\mathbf{g}$  is normal to a set of lattice planes of the direct lattice.
- [2] If the components  $(n_1, n_2, n_3)$  of  $\mathbf{g}$  have no common factor, then  $|\mathbf{g}|$  is inversely proportional to the spacing of the lattice planes normal to  $\mathbf{g}$ .
- [3] The volume of the reciprocal unit cell is inversely proportional to the volume of the unit cell of the direct lattice.
- [4] The direct lattice is the reciprocal of its own reciprocal lattice.
- [5] The unit cell of the reciprocal lattice need not be a parallelepiped.

Additionally, from properties [1] and [2], it is convenient to characterize planes of the direct lattice by their normal vectors expressed in terms of the reciprocal lattice vectors. The integers  $(n_1, n_2, n_3)$  defined by EQ. (II.7), after removal of any common factors, are the *Miller indices* of a lattice plane. Further, the notation  $\{n_1, n_2, n_3\}$  refers to all different sets of planes that are equivalent in symmetry to the set indexed by  $(n_1, n_2, n_3)$ . For instance,  $\{1,1,0\}$  represents 12 sets of planes  $(1,1,0)$ ,  $(1,0,1)$ ,  $(0,1,1)$ ,  $(\bar{1},1,0)$ ,  $(1,\bar{1},0)$ ,  $(\bar{1},\bar{1},0)$ ,  $(1,0,\bar{1})$ ,  $(\bar{1},0,1)$ ,  $(\bar{1},0,\bar{1})$ ,  $(0,1,\bar{1})$ ,  $(0,\bar{1},1)$  and  $(0,\bar{1},\bar{1})$ , where we have used the notation  $\bar{n}$  for  $-n$ .

### II.3. Bloch Theorem & the Brillouin Zone

**Topics:** Bloch theorem, Brillouin zone, counting states

#### • Bloch theorem

The electronic wave-function  $\psi(\mathbf{r})$  under a crystalline potential  $\mathcal{V}(\mathbf{r})$  satisfies the Schrödinger equation:

$$\mathcal{H}\psi(\mathbf{r}) \equiv \left( -\frac{\hbar^2}{2m} \nabla^2 + \mathcal{V}(\mathbf{r}) \right) \psi(\mathbf{r}) = \varepsilon \psi(\mathbf{r}), \quad (\text{II.9})$$

where  $\mathcal{V}(\mathbf{r}) = \mathcal{V}(\mathbf{r} + \mathbf{l})$  for all  $\mathbf{l}$ , and  $\varepsilon$  represents the eigen-energy. From translational invariance and EQ. (II.9), we find  $\mathcal{H}\psi(\mathbf{r} + \mathbf{l}) = \mathcal{H}\psi(\mathbf{r}) = \varepsilon \psi(\mathbf{r}) = \varepsilon \psi(\mathbf{r} + \mathbf{l})$ . In other words, the wave functions  $\psi(\mathbf{r})$  and  $\psi(\mathbf{r} + \mathbf{l})$  are degenerate. Given that all translational symmetry operations are Abelian so that they can all be reduced to one-dimensional representations in the field of complex numbers, we may label every wave function by its wave vector  $\mathbf{k}$  and express it by the following relation

$$\psi_{\mathbf{k}}(\mathbf{r} + \mathbf{l}) = e^{i\mathbf{k} \cdot \mathbf{l}} \psi_{\mathbf{k}}(\mathbf{r}). \quad (\text{II.10})$$

Equation (II.10) is known as the Bloch theorem.

#### (Proof of the Bloch theorem)

For simplicity, let's consider a cubic volume of  $N^3$  lattice points with periodic boundary conditions in all three spatial dimensions. For primitive lattice vectors  $\hat{a}, \hat{b}, \hat{c}$ , the periodic boundary conditions yield the following relations:

$$\psi_{\mathbf{k}}(\mathbf{r}) = \psi_{\mathbf{k}}(\mathbf{r} + N\hat{a}) = \psi_{\mathbf{k}}(\mathbf{r} + N\hat{b}) = \psi_{\mathbf{k}}(\mathbf{r} + N\hat{c}). \quad (\text{II.11})$$

Next, we define the lattice translation operator  $\mathcal{T}$  operating on a position vector  $\mathbf{r}$  yields the following relation:

$$\mathcal{T}_{mnp} \mathbf{r} = \mathbf{r} + \mathbf{l}_{mnp} \equiv \mathbf{r} + m\hat{a} + n\hat{b} + p\hat{c}, \quad (\text{II.12})$$

where  $m, n, p$  are integers. Therefore, a lattice translation operator  $\mathcal{T}_{mnp}$  operating on a wave functions  $\psi_{\mathbf{k}}(\mathbf{r})$  gives

$$\mathcal{T}_{mnp} \psi_{\mathbf{k}}(\mathbf{r}) = \psi_{\mathbf{k}}(\mathbf{r} + m\hat{a} + n\hat{b} + p\hat{c}). \quad (\text{II.13})$$

Given that the operations of  $\mathcal{T}$  are abelian and form a cyclic group, the corresponding representations are one-dimensional. Hence,

$$\mathcal{T}_{mnp} \psi_{\mathbf{k}}(\mathbf{r}) = c_{mnp} \psi_{\mathbf{k}}(\mathbf{r}), \quad (\text{II.14})$$

where  $c_{mnp}$  are constants. Thus, from EQ. (II.14) we have

$$\mathcal{T}_{100}\psi_{\mathbf{k}}(\mathbf{r}) = \psi_{\mathbf{k}}(\mathbf{r} + \hat{a}) = c_{100}\psi_{\mathbf{k}}(\mathbf{r}). \quad (\text{II.15})$$

Similarly, we find that

$$\mathcal{T}_{N00}\psi_{\mathbf{k}}(\mathbf{r}) = \psi_{\mathbf{k}}(\mathbf{r} + N\hat{a}) = (c_{100})^N \psi_{\mathbf{k}}(\mathbf{r}). \quad (\text{II.16})$$

Combining EQs. (II.11) and (II.16), we find that

$$(c_{100})^N = 1, \quad \Rightarrow \quad c_{100} = e^{2\pi i \xi / N}, \quad \xi = 1, 2, 3, \dots, N.. \quad (\text{II.17})$$

The above step can be generalized to all three dimensions so that the wavefunction in a crystal can be expressed in the following form:

$$\psi_{\mathbf{k}}(\mathbf{r}) = e^{i\mathbf{k} \cdot \mathbf{r}} u_{\mathbf{k}}(\mathbf{r}), \quad (\text{II.18})$$

provided that  $u_{\mathbf{k}}(\mathbf{r})$  has the periodicity of the lattice and that  $N\mathbf{k}$  is a reciprocal lattice vector given by

$$N\mathbf{k} \equiv \xi \hat{a}^* + \eta \hat{b}^* + \zeta \hat{c}^*, \quad (\text{II.19})$$

with  $\xi, \eta, \zeta$  being integers. For a translation  $\mathbf{l}_{mnp}$  and using EQ. (II.18), we have

$$\begin{aligned} \psi_{\mathbf{k}}(\mathbf{r} + \mathbf{l}_{mnp}) &= e^{i\mathbf{k} \cdot (\mathbf{r} + \mathbf{l}_{mnp})} u_{\mathbf{k}}(\mathbf{r} + \mathbf{l}_{mnp}) = e^{i\mathbf{k} \cdot (\mathbf{r} + \mathbf{l}_{mnp})} u_{\mathbf{k}}(\mathbf{r}) = e^{i\mathbf{k} \cdot \mathbf{l}_{mnp}} e^{i\mathbf{k} \cdot \mathbf{r}} u_{\mathbf{k}}(\mathbf{r}), \\ &= e^{i\mathbf{k} \cdot \mathbf{l}_{mnp}} \psi_{\mathbf{k}}(\mathbf{r}) = e^{i2\pi(m\xi + n\eta + p\zeta)/N} \psi_{\mathbf{k}}(\mathbf{r}) = c_{mnp} \psi_{\mathbf{k}}(\mathbf{r}), \end{aligned} \quad (\text{II.20})$$

which is consistent with the requirement in EQ. (II.14) and also satisfies EQ. (II.10).

In a special “empty lattice” case with  $\mathcal{V}(\mathbf{r}) = 0$ , the solutions to EQ. (II.9) are plane-waves given by

$$\psi_{\mathbf{k}}(\mathbf{r}) = e^{i\mathbf{k} \cdot \mathbf{r}}. \quad (\text{II.21})$$

It is often convenient to express the wave function for  $\mathcal{V}(\mathbf{r}) \neq 0$  by the following:

$$\psi_{\mathbf{k}}(\mathbf{r}) = e^{i\mathbf{k} \cdot \mathbf{r}} u_{\mathbf{k}}(\mathbf{r}). \quad (\text{II.22})$$

From EQs. (II.10) and (II.22), it is obvious that

$$u_{\mathbf{k}}(\mathbf{r}) = u_{\mathbf{k}}(\mathbf{r} + \mathbf{l}). \quad (\text{II.23})$$

### • Brillouin zone

The expression in EQ. (II.10) is in fact not unique, because for any wave vector  $\mathbf{k}'$  differs from  $\mathbf{k}$  by a reciprocal lattice vector  $\mathbf{g}$ , we have

$$\psi_{\mathbf{k}}(\mathbf{r} + \mathbf{l}) = e^{i\mathbf{k} \cdot \mathbf{l}} \psi_{\mathbf{k}}(\mathbf{r}) = e^{i(\mathbf{k}' + \mathbf{g}) \cdot \mathbf{l}} \psi_{\mathbf{k}}(\mathbf{r}) = e^{i\mathbf{k}' \cdot \mathbf{l}} \psi_{\mathbf{k}}(\mathbf{r}). \quad (\text{II.24})$$

Therefore, a proper choice of wave vectors  $\mathbf{k}$  is to restrict them within the unit cell of the reciprocal lattice, known as *the first Brillouin zone*, so that the wave vectors  $\mathbf{k}$  are kept as close to the center of the reciprocal lattice as possible. Any wave vector can thus be represented by a point in the first Brillouin zone in *the reduced zone scheme*.

### • Counting states

To count the number of states for a finite-size sample with dimensions given by  $(L_1\mathbf{a}_1 \times L_2\mathbf{a}_2 \times L_3\mathbf{a}_3)$ , we employ the *cyclic*, or *Born-von Karman boundary conditions*:

$$\psi_{\mathbf{k}}(\mathbf{r} + L_1\mathbf{a}_1) = \psi_{\mathbf{k}}(\mathbf{r}), \quad \psi_{\mathbf{k}}(\mathbf{r} + L_2\mathbf{a}_2) = \psi_{\mathbf{k}}(\mathbf{r}), \quad \psi_{\mathbf{k}}(\mathbf{r} + L_3\mathbf{a}_3) = \psi_{\mathbf{k}}(\mathbf{r}). \quad (\text{II.25})$$

From EQs. (II.10) and (II.25), we find that

$$e^{i\mathbf{k} \cdot (L_1\mathbf{a}_1)} = e^{i\mathbf{k} \cdot (L_2\mathbf{a}_2)} = e^{i\mathbf{k} \cdot (L_3\mathbf{a}_3)} = 1, \quad (\text{II.26})$$

which implies that

$$\mathbf{k} = k_1\mathbf{b}_1 + k_2\mathbf{b}_2 + k_3\mathbf{b}_3 = \frac{2\pi n_1}{L_1}\mathbf{b}_1 + \frac{2\pi n_2}{L_2}\mathbf{b}_2 + \frac{2\pi n_3}{L_3}\mathbf{b}_3, \quad (\text{II.27})$$

where  $n_i$  ( $i = 1, 2, 3$ ) are integers. Comparing EQ. (II.27) with EQ. (II.7), we find that the allowed values of  $\mathbf{k}$  are obtained by dividing the generators of the reciprocal lattice into  $L_1$  parts in  $\mathbf{a}_1$  direction,  $L_2$  parts in  $\mathbf{a}_2$  direction, and  $L_3$  parts in  $\mathbf{a}_3$  direction. Therefore, there are  $N = (L_1 \times L_2 \times L_3)$  allowed values of  $\mathbf{k}$  because

$$-\frac{1}{2}L_1 < n_1 < \frac{1}{2}L_1, \quad -\frac{1}{2}L_2 < n_2 < \frac{1}{2}L_2, \quad -\frac{1}{2}L_3 < n_3 < \frac{1}{2}L_3, \quad (\text{II.28})$$

which is exactly equal to the total number of cells. In other words, there are exactly as many allowed wave vectors in the first Brillouin zone as there are unit cells in a crystal.

From EQs. (II.7) and (II.8) we note that the volume of the first Brillouin zone is given by  $(8\pi^3/v_c)$ . Hence, the volume of per allowed  $\mathbf{k}$ -vector in reciprocal space is

$$\frac{1}{N} \frac{8\pi^3}{v_c} = \frac{1}{N} \frac{8\pi^3}{(V/N)} = \frac{8\pi^3}{V}. \quad (\text{II.29})$$

Therefore, there are  $(V/8\pi^3)$  allowed  $\mathbf{k}$  vectors per unit volume of the reciprocal space. This result is independent of any assumed zone structure.

In general  $N$  is a very large number. Hence, the distributions of  $\mathbf{k}$  vectors are nearly continuous, and the sum over  $\mathbf{k}$  vectors may be replaced by an integral:

$$\sum_{\mathbf{k}} \rightarrow \int d\mathbf{k} \equiv \frac{V}{8\pi^3} \iiint d^3k. \quad (\text{II.30})$$

We remark that the Born-von Karman boundary conditions in EQ. (II.25) in fact cannot be achieved physically in three dimensions, although in two dimensions we may draw a network of cells on a torus to

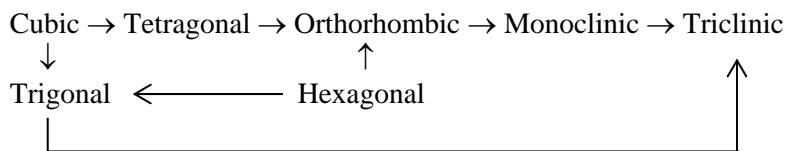
achieve cyclic conditions in both directions. However, we may consider the Born-von Karman boundary conditions a useful mathematical tool, which may be further justified by the fact that the density of states in the limit of large quantum numbers is insensitive to the precise form of the boundary conditions.

## II.4. Classifications of the Bravais Lattice & Crystalline Structures

There are 7 distinct groups of Bravais lattices, and the full symmetry group of a Bravais lattice is called the *point group* of the Bravais lattice. If we relax the restriction to point group operations and consider the full symmetry group of the Bravais lattice, there are a total of 14 distinct *space groups* of Bravais lattices.

1. **Cubic (3)** – simple cubic (*sc*), body-centered-cubic (*bcc*), and face-centered-cubic (*fcc*).
2. **Tetragonal (2)** – simple tetragonal and centered-tetragonal.
3. **Orthorhombic (4)** – simple orthorhombic, base-centered orthorhombic, body-centered orthorhombic, and face-centered orthorhombic.
4. **Monoclinic (2)** – simple monoclinic (reduced from either simple orthorhombic or base-centered orthorhombic) and centered monoclinic (reduced from body-centered orthorhombic or face-centered orthorhombic).
5. **Triclinic (1)** – accomplished by tilting the c-axis of a monoclinic Bravais lattice.
6. **Trigonal (1)** – a crystalline structure generated by three primitive vectors of equal length that make equal angle with one another; also known as the rhombohedral Bravais lattice.
7. **Hexagonal (1)** – simple monoclinic and centered monoclinic.

The hierarchy of symmetries among the 7 crystal systems of may be summarized in the “flow diagram” below where each Bravais lattice point group contains all those point groups that can be reached from it by following the direction of the arrows:



In crystallography, there are 32 point groups and 230 space groups, which will be discussed further in Part V when we consider symmetries and group theory.

To determine the microscopic structures of a crystal, we need to employ an electromagnetic probe with a wavelength comparable to the inter-atomic distances, which are typically on the order of a few  $10^{-10}$  m, which correspond to energies on the order of several kilovolts (keV), which are characteristic of x-ray energies. Using x-ray diffraction techniques, we may deduce the crystalline structures of solids by analyzing the distribution of x-rays scattered by a rigid, periodic arrays of ions. There are generally two ways of viewing the scattering of x-rays by a perfect periodic structure. One is due to Bragg and the other to von Laue. The former is widely used by crystallographers, and the latter exploits the reciprocal lattice. Both can



be proven to be equivalent. We will only consider the Bragg diffraction in this course. You may consult Ashcroft and Mermin for the von Laue approach and the equivalence of the two approaches.

### • Bragg reflection

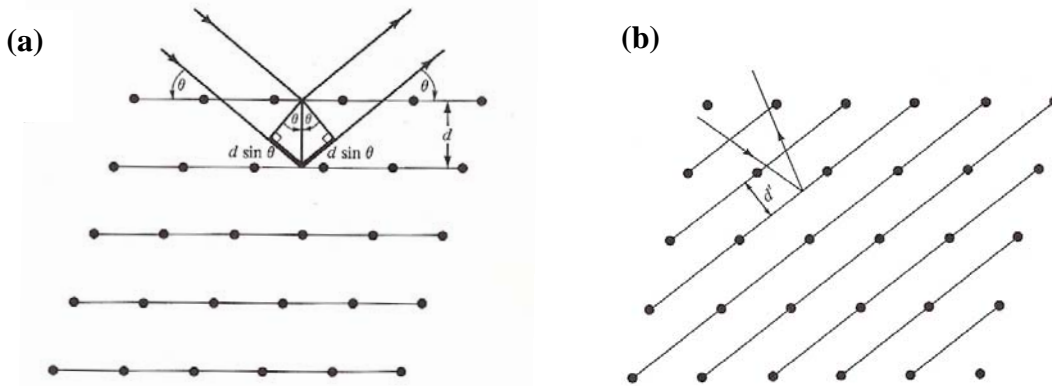
In crystalline materials, for certain sharply defined wavelengths and incident x-ray directions, intense peaks of scattered radiation can be observed. These sharp peaks are known as the *Bragg peaks*, and the conditions for their appearance involve the following:

- (1) The x-rays should be specularly reflected by the ions in any one plane;
- (2) The reflected x-rays from successive planes interfere constructively.

The above two conditions lead to the celebrated Bragg diffraction condition:

$$n\lambda = 2d \sin \theta, \quad (\text{II.31})$$

where  $\lambda$  denotes the wavelength of the x-ray,  $d$  is the distance between a set of parallel planes of ions,  $\theta$  is the incident angle of the x-ray relative to the set of planes, and the integer  $n$  represents the order of the corresponding reflection, as schematically shown in Fig. II.3(a). Similarly, the same incident beam can result in a different Bragg peak for a different set of planes that are separated at a distance  $d'$  and an incident angle  $\theta'$ , as illustrated in Fig. II.3(b).



**Fig. II.3:** Bragg reflection from lattice planes. **(a)** Reflection from a specific set of lattice planes that are separated by a distance  $d$  and are forming an angle  $\theta$  with the incident x-ray beam. **(b)** Reflection of the same incident beam from a different set of lattice planes that are separated by a distance  $d'$  and are forming an angle  $\theta'$  relative to the incident x-ray.

In addition to the condition given in EQ. (II.31), we note that high-density planes generally have more intense Bragg peaks. Additionally, for crystals with a nontrivial basis, we must consider the structural factor, as explained below.

### • Geometrical structure factor

The above description of Bragg reflection has assumed constructive scattering of x-rays from a Bravais lattice. The concept can be generalized to crystals with a  $\nu$ -atom basis per unit cell. For simplicity, let's

consider the situation of a monatomic lattice, and define the positions of the atoms in a basis as  $d_1, \dots, d_\nu$  within a primitive cell. In this case, if a Bragg peak is associated with a change in the wave vector  $\mathbf{K} \equiv \mathbf{k}' - \mathbf{k}$ , then the phase difference between the x-rays scattered at sites  $\mathbf{d}_i$  and  $\mathbf{d}_j$  is  $[\mathbf{K} \cdot (\mathbf{d}_i - \mathbf{d}_j)]$  so that the amplitude of the two rays becomes different by a factor  $e^{i\mathbf{K} \cdot (\mathbf{d}_i - \mathbf{d}_j)}$ . Thus, the total contribution from all atoms in the basis is given by the geometrical structure factor  $S_{\mathbf{K}}$ :

$$S_{\mathbf{K}} \equiv \sum_{j=1}^{\nu} e^{i\mathbf{K} \cdot \mathbf{d}_j}, \quad (\text{II.32})$$

EQ. (II.32) suggests that interferences of the waves scattered by identical ions within a basis can diminish the intensity of the Bragg peak ( $\propto |S_{\mathbf{K}}|^2$ ) associated with a given reciprocal lattice vector  $\mathbf{K}$ .

### • Atomic form factor

More generally, in the event that the ions in the basis of a crystal are not identical, the structural factor in EQ. (II.32) has to be rewritten into the following form:

$$S_{\mathbf{K}} \equiv \sum_{j=1}^{\nu} f_j(\mathbf{K}) e^{i\mathbf{K} \cdot \mathbf{d}_j}, \quad (\text{II.33})$$

where  $f_j(\mathbf{K})$  is known as the *atomic form factor*, which is determined by the internal structure of the ion at position  $\mathbf{d}_j$  in the basis. Specifically, the atomic form factor may be related to the charge distribution  $\rho_j(\mathbf{r})$  of the ion under consideration:

$$f_j(\mathbf{K}) \equiv -\frac{1}{e} \int d\mathbf{r} e^{i\mathbf{K} \cdot \mathbf{r}} \rho_j(\mathbf{r}), \quad (\text{II.34})$$

For identical ions, the atomic form factors are identical, and so EQ. (II.33) reduces back to EQ. (II.32).

## II.5. Lattice Dynamics

In real crystals the constituent atoms do not stay rigidly at their equilibrium positions. Rather, thermal fluctuations will result in oscillations of the atoms about their equilibrium positions. In the limit of small oscillations, we may approximate the motion of atoms in a crystal by simple harmonic oscillators. In the following we shall consider two approximations for the lattice dynamics of such “harmonic crystals”. One is the Debye approximation with a dispersions relation  $\omega \propto q$ , and the other is the Einstein model  $\omega \sim \text{constant}$ .

### • Lattice displacements; normal modes of lattice vibrations

For a lattice displacement field  $\mathbf{u}_s$  of an atom  $s$  (with a mass  $M_s$ ) in a basis at site  $\mathbf{l}$ , the kinetic energy ( $K.E.$ ) of the system is given by

$$K.E. = \sum_{l,s} \frac{1}{2} M_s |\dot{\mathbf{u}}_{sl}|^2. \quad (\text{II.35})$$

Assume small vibrations so that the potential energy  $\mathcal{V}(\mathbf{r})$  of the lattice may be expanded around the equilibrium positions where all displacement fields are zero, we have, for  $\mathbf{u}_{sl} \equiv \sum_{\mu} u_{sl}^{\mu} \hat{\mathbf{e}}_{\mu}$  :

$$\mathcal{V} = \mathcal{V}_0 + \sum_{l,s,\mu} u_{sl}^{\mu} \left[ \frac{\partial \mathcal{V}}{\partial u_{sl}^{\mu}} \right]_0 + \frac{1}{2} \sum_{l',s',\mu'} \sum_{l,s,\mu} u_{s'l'}^{\mu'} u_{sl}^{\mu} \left[ \frac{\partial^2 \mathcal{V}}{\partial u_{sl}^{\mu} \partial u_{s'l'}^{\mu'}} \right]_0 + \dots \quad (\text{II.36})$$

The constant term in EQ. (II.36) is unimportant and the first-order term must vanish near equilibrium. Hence, the second-order harmonic potential term together with the kinetic energy in EQ. (II.34) leads to the equation of motion:

$$M_s \ddot{u}_{sl}^{\mu} = - \sum_{l',s',\mu'} \left[ \frac{\partial^2 \mathcal{V}}{\partial u_{sl}^{\mu} \partial u_{s'l'}^{\mu'}} \right]_0 u_{s'l'}^{\mu'} \equiv - \sum_{l',s',\mu'} G_{sl;s'l'}^{\mu\mu'} u_{s'l'}^{\mu'}. \quad (\text{II.37})$$

Equivalently, we may rewrite EQ. (II.37) into

$$M_s \ddot{\mathbf{u}}_{sl} = - \sum_{l',s'} \mathbf{G}_{sl;s'l'} \cdot \mathbf{u}_{s'l'}. \quad (\text{II.38})$$

The equation of motion in EQ. (II.38) may be further simplified by considering the translational symmetry so that the tensor  $\mathbf{G}$  is a function of their relative positions  $\mathbf{h} = \mathbf{l}' - \mathbf{l}$ . Thus, we have

$$M_s \ddot{\mathbf{u}}_{sl} = - \sum_{\mathbf{h},s'} \mathbf{G}_{ss'}(\mathbf{h}) \cdot \mathbf{u}_{s',l+\mathbf{h}}. \quad (\text{II.39})$$

Given that the displacement field must satisfy the Bloch form, there exists a wave-vector  $\mathbf{q}$  such that

$$\mathbf{u}_{sl}(t) = e^{i\mathbf{q} \cdot \mathbf{l}} \mathbf{u}_{s0}(t). \quad (\text{II.40})$$

Therefore, EQ. (II.39) becomes

$$M_s \ddot{\mathbf{u}}_{s,0} e^{i\mathbf{q} \cdot \mathbf{l}} = - \sum_{\mathbf{h},s'} \mathbf{G}_{ss'}(\mathbf{h}) \cdot \mathbf{u}_{s',0} e^{i\mathbf{q} \cdot (\mathbf{l} + \mathbf{h})}. \quad (\text{II.41})$$

We may write  $\mathbf{u}_{s,0} = \mathbf{U}_{s,\mathbf{q}}$  so that EQ. (II.41) can be expressed by the following formula

$$M_s \ddot{\mathbf{U}}_{s,\mathbf{q}} = - \sum_{s'} \left\{ \sum_{\mathbf{h}} \mathbf{G}_{ss'}(\mathbf{h}) e^{i\mathbf{q} \cdot \mathbf{h}} \right\} \cdot \mathbf{U}_{s',\mathbf{q}} \equiv - \sum_{s'} \mathbf{G}_{ss'}(\mathbf{q}) \cdot \mathbf{U}_{s',\mathbf{q}}, \quad (\text{II.42})$$

where

$$\mathbf{G}_{ss'}(\mathbf{q}) \equiv \sum_{\mathbf{h}} \mathbf{G}_{ss'}(\mathbf{h}) e^{i\mathbf{q} \cdot \mathbf{h}}. \quad (\text{II.43})$$

For a three-dimensional crystal with  $N$  unit cells and  $n$  atoms per unit cell, we note that EQ. (II.41) involves  $3nN$  equations whereas EQ. (II.42) reduces to  $3n$  equations. Therefore, the eigenvalue equation becomes

$$\sum_{s', \mu'} \left\{ \mathbf{G}_{ss'}^{\mu\mu'}(\mathbf{q}) - \omega^2 M_s \delta_{ss'} \delta_{\mu\mu'} \right\} U_{s', \mathbf{q}}^{\mu'} = 0, \quad (\text{II.44})$$

leading to  $3n$  normal modes. These normal modes of lattice vibrations are known as the *phonons*, and there energy spectra  $\omega(\mathbf{q})$  are given by solving the secular equations in EQ. (II.44).

In general, for a  $d$ -dimensional crystal with  $n$  atoms per unit cell, there are  $(nd)$  phonons in total, among which we have  $d$  acoustic phonons and  $(n-1)d$  optical phonons. As we shall see from the following examples of one-dimensional crystals, the dispersion relation of acoustic phonons near the zone center is linear. In contrast, the optical phonons are significantly higher in energy than acoustic phonons and are generally weakly dispersive.

### • Acoustic and optical phonons

Consider the simplest example of a one-dimensional crystal of one atom per unit cell, with a lattice constant  $a$  and an atomic mass  $M$ . If we assume that only the nearest neighbor interaction is relevant and that the corresponding force constant is  $\alpha$ , the equation of motion becomes

$$M \ddot{\mathbf{u}}_l = -\alpha (2\mathbf{u}_l - \mathbf{u}_{l+a} - \mathbf{u}_{l-a}), \quad (\text{II.45})$$

which leads to an equation of a simple harmonic oscillator so that the resulting eigen-frequency is

$$\omega_q = 2\sqrt{\frac{\alpha}{M}} \sin\left(\frac{qa}{2}\right). \quad (\text{II.46})$$

In the long wavelength limit  $q \rightarrow 0$ , the dispersion relation becomes

$$\omega_q \rightarrow \sqrt{\frac{\alpha}{M}} (qa), \quad (\text{II.47})$$

which corresponds to an acoustic mode.

Next, we consider a slightly more complicated case of a linear chain of atoms with the same spacing  $a$  and two alternating atoms of different masses  $M_1$  and  $M_2$ . If we further assume that only the nearest neighbor interaction is relevant and that the corresponding force constant is  $\alpha$ , the equations of motion become

$$\begin{aligned} M_1 \ddot{U}_1 &= -2\alpha U_1 + 2\alpha \cos(qa) U_2, \\ M_2 \ddot{U}_2 &= -2\alpha U_2 + 2\alpha \cos(qa) U_1. \end{aligned} \quad (\text{II.48})$$

Solving the secular equation for EQ. (II.48), we find two normal modes with the following dispersion relations:

$$\omega_{\pm}^2(\mathbf{q}) = \alpha \left( \frac{1}{M_1} + \frac{1}{M_2} \right) \pm \alpha \sqrt{\left( \frac{1}{M_1} + \frac{1}{M_2} \right)^2 - \frac{4 \sin^2(qa)}{M_1 M_2}}, \quad (\text{II.49})$$

which correspond to an acoustic mode  $\omega_-(\mathbf{q})$  and an optical mode  $\omega_+(\mathbf{q})$ . In the long wavelength limit  $q \rightarrow 0$ , we find that

$$|\omega_+(\mathbf{q})| \sim \sqrt{2\alpha \left( \frac{1}{M_1} + \frac{1}{M_2} \right)} \sim \text{constant} \quad (\text{II.50})$$

and

$$|\omega_-(\mathbf{q})| \sim \sqrt{\frac{2\alpha}{M_1 + M_2}} (qa) \rightarrow 0. \quad (\text{II.51})$$

## II.6. Lattice Specific Heat & Debye Frequency

To evaluate the specific heat of a crystal, we must make approximations to the phonon dispersion relation. There are generally two models for such approximations: the Debye and the Einstein models.

### • The Debye model

The Debye formula for lattice specific heat  $C_V$  (assuming a three-dimensional crystal)

$$C_V \equiv \frac{1}{V} \frac{\partial \bar{\mathcal{E}}}{\partial T} = \frac{1}{k_B T^2} \frac{1}{8\pi^3} \sum_{\text{polarizations}} \iiint \frac{(\hbar \omega_q)^2 e^{\hbar \omega_q / k_B T}}{(e^{\hbar \omega_q / k_B T} - 1)^2} d^3 q, \quad (\text{II.52})$$

where the average total energy  $\bar{\mathcal{E}}$  of all branches of phonons is given by

$$\bar{\mathcal{E}} \equiv \sum_{\mathbf{q}} \left( \bar{n}_{\mathbf{q}} + \frac{1}{2} \right) \hbar \omega_{\mathbf{q}} = \sum_{\mathbf{q}} \left[ \frac{1}{(e^{\hbar \omega_{\mathbf{q}} / k_B T} - 1)} + \frac{1}{2} \right] \hbar \omega_{\mathbf{q}} \sim \sum_{\mathbf{q}} \frac{\hbar \omega_{\mathbf{q}}}{(e^{\hbar \omega_{\mathbf{q}} / k_B T} - 1)}, \quad (\text{II.53})$$

and we have neglected the quantum oscillations in the last step of EQ. (II.53).

For  $n$  atoms per unit cell and  $N$  cells in the crystal, if we define  $D(\omega) d\omega$  as the fraction of modes in the frequency range  $\omega \rightarrow \omega + d\omega$ , EQ. (II.52) becomes:

$$C_V = 3nNk_B \int \frac{(\hbar \omega / k_B T)^2 e^{\hbar \omega / k_B T}}{(e^{\hbar \omega / k_B T} - 1)^2} D(\omega) d\omega. \quad (\text{II.54})$$

To evaluate EQ. (II.54), we use the Debye approximation in which all phonon dispersion relations are assumed to be acoustic like so that  $\omega_{\mathbf{q}} = sq$ . In particular, for a crystal with a polyatomic basis, the optical

branches of the phonon spectrum are approximated by the high  $q$  values of the linear dispersion relation. Further, the Debye wave-vector  $q_D$  is related to the volume of a unit cell via the following expression:

$$N = \frac{V}{(2\pi)^3} \frac{4}{3} \pi q_D^3 \rightarrow q_D = \left( \frac{6N\pi^2}{V} \right)^{1/3} = \left( \frac{6\pi^2}{v_c} \right)^{1/3}. \quad (\text{II.55})$$

Hence, the fraction of modes  $D(\omega)d\omega$  in the frequency range  $\omega \rightarrow \omega + d\omega$  for the Debye model becomes

$$D(\omega)d\omega = 4\pi q^2 dq / \left( \frac{4\pi}{3} q_D^3 \right) = \frac{3\omega^2}{\omega_D^3} d\omega, \quad (\text{II.56})$$

so that EQ. (II.52) can be evaluated explicitly by the following expression

$$C_V = 3Nk_B \int_0^{\omega_D} \frac{(\hbar\omega/k_B T)^2 e^{\hbar\omega/k_B T}}{(e^{\hbar\omega/k_B T} - 1)^2} \frac{3\omega^2}{\omega_D^3} d\omega = 3Nk_B \left( \frac{T}{\Theta_D} \right)^3 3 \int_0^{\Theta_D/T} \frac{z^4 e^z}{(e^z - 1)^2} dz. \quad (\text{II.57})$$

In EQ. (II.57) we have defined the Debye temperature  $\Theta_D \equiv (\hbar\omega_D/k_B)$ . Given the explicit expression in EQ. (II.57), we proceed to consider two extreme conditions, in the high-temperature ( $T \gg \Theta_D$ ) and low-temperature ( $T \ll \Theta_D$ ) limits.

[1] The Dulong and Petit law at high temperatures ( $T \gg \Theta_D$ ):

$$C_V \sim 3Nk_B \left( \frac{T}{\Theta_D} \right)^3 3 \int_0^{\Theta_D/T} \frac{z^4}{z^2} dz = 3Nk_B. \quad (\text{II.58})$$

[2] The  $T^3$ -law of specific heat at low temperatures ( $T \ll \Theta_D$ ):

$$C_V \sim 3Nk_B \left( \frac{T}{\Theta_D} \right)^3 3 \int_0^\infty z^4 e^{-z} dz = \frac{12\pi^4}{5} Nk_B \left( \frac{T}{\Theta_D} \right)^3. \quad (\text{II.59})$$

Next, we consider the Einstein model, which is a better approximation to the dispersion relations of the optical phonons.

### • The Einstein Model:

In contrast to the Debye model, the Einstein approximation replaces the frequency of each optical branch by a frequency  $\omega_E$  that does not depend on the phonon momentum  $\mathbf{q}$ . For  $n$  primitive cells per unit volume, each optical branch contributes

$$\frac{n\hbar\omega_E}{e^{\hbar\omega_E/k_B T} - 1} \quad (\text{II.60})$$

to the thermal energy density in the Einstein model. Therefore, if there are  $\nu_0$  optical branches, the specific heat due to optical phonons in the Einstein approximation becomes:

$$C_V^{Optical} = n\nu_0 k_B \frac{(\hbar\omega_E/k_B T)^2 e^{\hbar\omega_E/k_B T}}{(e^{\hbar\omega_E/k_B T} - 1)^2}. \quad (\text{II.61})$$

If we define the Einstein temperature  $\Theta_E \equiv (\hbar\omega_E/k_B)$ , the specific heat given in EQ. (II.51) implies that for  $T \gg \Theta_E$ , each optical phonon mode contributes a constant  $(k_B/V)$  to the specific heat, as required by the Dulong and Petit law. On the other hand, for  $T \ll \Theta_E$ , the specific heat contributions from optical modes decrease exponentially, suggesting the difficulty in thermally exciting the optical modes at low temperatures.

## II.7. Lattice Spectrum

The Debye model is clearly a rough approximation, which does not capture important spectral features near *critical points*. In the following we consider spectral characteristics near critical points at various dimensions, and describe *van Hove's theorem* and *van Hove singularities* for 3D, 2D and 1D systems.

More specifically, critical points may appear when we consider the phonon density of states  $D(\omega)$  at certain momenta where the group velocity of phonons vanish. Recall that the density of states for one branch of phonons in three dimensions may be expressed in terms of the following momentum integration:

$$D(\omega)d\omega = \frac{v_c}{(2\pi)^3} \iiint d^3q = \frac{1}{8\pi^3 N} \iint dS_\omega dq_\perp \equiv \frac{1}{8\pi^3 N} \iint \frac{dS_\omega}{|\mathbf{v}_q|}, \quad (\text{II.54})$$

where  $\mathbf{v}_q \equiv \nabla_q \omega(\mathbf{q})$  is the group velocity of a wave packet of a wave-vector  $\mathbf{q}$  in the dispersive medium of the lattice.

Note that: (1)  $\mathbf{v}_q = 0$  is possible at  $q = q_c$ ,  $q_c$  is a critical point where  $\omega_c = \omega(q_c)$ .

(2)  $D(\omega)$  is for one branch of phonons.

(3) There are different types of critical points, depending on the dimensionality and the sign of  $\alpha_i$ .

### • For a 3D system:

Expand the energy near a critical point  $q_c$ :  $\omega = \omega_c + \alpha_1 \xi_1^2 + \alpha_2 \xi_2^2 + \alpha_3 \xi_3^2$ , where  $\xi_i \equiv q_i - q_{ci}$ ,  $i = 1, 2, 3$ . In this case, there are four types of critical points, depending on sign of  $\alpha_i$ .

$M_0$ : a minimum,  $\alpha_1, \alpha_2, \alpha_3 > 0$

$M_1$ : a saddle point with one  $\alpha_i < 0$  and two  $\alpha_i > 0$

$M_2$ : a saddle point with one  $\alpha_i > 0$  and two  $\alpha_i < 0$

$M_3$ : a maximum,  $\alpha_1, \alpha_2, \alpha_3 < 0$

Near the critical points, the density of states  $D(\omega)$  deviates completely from the simple assumption given by the Debye model. For instance, we consider  $D(\omega)$  near  $M_0$ :

$$\begin{aligned} D(\omega)d\omega &\sim \int_0^{q_R} \frac{2\pi q_{\perp} dq_{\perp}}{\sqrt{(\omega - \omega_c) - q_{\perp}^2}} && \text{if } (\omega - \omega_c) - q_{\perp}^2 > 0, \\ &= 0 && \text{if } (\omega - \omega_c) - q_{\perp}^2 < 0. \end{aligned} \quad (\text{II.55})$$

We summarize in the following the phonon density of states near critical points in a 3D system:

Minimum  $M_0$ :

$$\begin{aligned} D(\omega) &= c_1 + c_2 \sqrt{\omega - \omega_c}, && \omega > \omega_c, \\ &= c_3 + \dots, && \omega < \omega_c; \end{aligned} \quad (\text{II.56})$$

Saddle point  $M_1$ :

$$\begin{aligned} D(\omega) &= c_1 - c_2 \sqrt{\omega_c - \omega}, && \omega < \omega_c, \\ &= c_3 + \dots, && \omega > \omega_c; \end{aligned} \quad (\text{II.57})$$

Saddle point  $M_2$ :

$$\begin{aligned} D(\omega) &= c_1 - c_2 \sqrt{\omega - \omega_c}, && \omega > \omega_c, \\ &= c_3 + \dots, && \omega < \omega_c. \end{aligned} \quad (\text{II.58})$$

Maximum  $M_3$ :

$$\begin{aligned} D(\omega) &= c_1 + c_2 \sqrt{\omega_c - \omega}, && \omega < \omega_c, \\ &= c_3 + \dots, && \omega > \omega_c; \end{aligned} \quad (\text{II.59})$$

where  $c_1$ ,  $c_2$ , and  $c_3$  are constants.

• **For a 2D-system:**

$$\omega = \omega_c + \alpha_1 \xi_1^2 + \alpha_2 \xi_2^2.$$

There are three types of singularities:

Minimum  $P_0$  ( $\alpha_1, \alpha_2 > 0$ ):

$$\begin{aligned} D(\omega) &= c_1 + \dots && \omega > \omega_c, \\ &= c_2 + c_1 && \omega < \omega_c; \end{aligned} \quad (\text{II.60})$$

Saddle point  $P_1$  ( $\alpha_1 > 0, \alpha_2 < 0$  or  $\alpha_2 > 0, \alpha_1 < 0$ ):



$$D(\omega) = c_1 - \frac{c_2}{\pi} \ln \left| 1 - \frac{\omega}{\omega_c} \right| + \dots \quad (\text{II.61})$$

Maximum  $P_2$  ( $\alpha_1, \alpha_2 < 0$ ):

$$\begin{aligned} D(\omega) &= c_1 + c_2 & \omega > \omega_c, \\ &= c_1 + \dots & \omega < \omega_c. \end{aligned} \quad (\text{II.62})$$

• **For a 1D system:**

$$\omega = \omega_c + \alpha_1 \xi_1^2.$$

There are two types of singularities:

Minimum  $Q_0$  ( $\alpha_1 > 0$ ):

$$\begin{aligned} D(\omega) &= c_1 + \dots & \omega < \omega_c, \\ &= c_1 + c_2 / \sqrt{\omega - \omega_c} & \omega > \omega_c; \end{aligned} \quad (\text{II.63})$$

Maximum  $Q_1$  ( $\alpha_1 < 0$ ):

$$\begin{aligned} D(\omega) &= c_1 + c_2 / \sqrt{\omega_c - \omega} & \omega < \omega_c, \\ &= c_1 + \dots & \omega > \omega_c. \end{aligned} \quad (\text{II.64})$$

• **van Hove theorem:**

Given that the phonon spectrum  $\omega(q)$  is a continuous periodic function of  $q$  throughout the Brillouin zone, the spectrum for 3D and 2D crystals must contain at least one saddle point for each branch of the phonon modes. Additionally, the slope of  $D(\omega)$  must be approaching  $-\infty$  at the upper bound of the spectrum.

## II.8. Diffraction by Crystals with Lattice Vibrations

Our earlier discussion of the Bragg reflection in Part II.4 has assumed rigid atoms in the solids. In reality, lattice vibrations will broaden the Bragg peaks, and the degree of broadening is temperature dependent, which may be expressed in terms of the *Debye-Waller factor*.

We consider a crystalline potential  $\mathcal{V}(\mathbf{r})$  which is no longer perfectly periodic due to the presence of lattice vibrations. Denoting the equilibrium positions of atoms in the periodic lattice structure by  $\mathbf{l}$  and the actual positions of the atoms by  $\mathbf{R}_l$ , we have

$$\mathcal{V}(\mathbf{r}) = \sum_l \mathcal{V}_a(\mathbf{r} - \mathbf{R}_l), \quad (\text{II.65})$$

where  $\mathcal{V}_a(\mathbf{r})$  is the potential of an individual atom, and we have assumed a Bravais lattice for simplicity. Now consider the diffraction of a beam of photons or neutrons by the lattice potential  $\mathcal{V}(\mathbf{r})$  from an initial momentum  $\mathbf{k}$  to a final momentum  $\mathbf{k}'$ . For  $\mathbf{K} \equiv \mathbf{k}' - \mathbf{k}$ , the scattering matrix is given by

$$\begin{aligned}\mathcal{M}_{\mathbf{k},\mathbf{k}'} &= \int d\mathbf{r} e^{-i\mathbf{k}' \cdot \mathbf{r}} \sum_l \mathcal{V}_a(\mathbf{r} - \mathbf{R}_l) e^{i\mathbf{k} \cdot \mathbf{r}}, \\ &= \sum_l e^{i(\mathbf{k} - \mathbf{k}') \cdot \mathbf{R}_l} \int d\mathbf{r} e^{i(\mathbf{k} - \mathbf{k}') \cdot (\mathbf{r} - \mathbf{R}_l)} \mathcal{V}_a(\mathbf{r} - \mathbf{R}_l) \\ &\equiv \mathcal{V}_a(\mathbf{K}) \left[ \frac{1}{N} \sum_l e^{-i\mathbf{K} \cdot \mathbf{R}_l} \right],\end{aligned}\tag{II.66}$$

where we have defined the Fourier transform of the atomic potential by the following:

$$\mathcal{V}_a(\mathbf{K}) \equiv \frac{1}{V_c} \int d\mathbf{r} e^{-i\mathbf{K} \cdot \mathbf{r}} \mathcal{V}_a(\mathbf{r}).\tag{II.67}$$

For perfect crystals in the absence of lattice vibrations,  $\mathbf{R}_l$  is given by a lattice vector:

$$\mathbf{R}_l = \mathbf{l} = l_1 \mathbf{a}_1 + l_2 \mathbf{a}_2 + l_3 \mathbf{a}_3,\tag{II.68}$$

where  $l_i$  ( $i = 1, 2, 3$ ) are integers. We may also express the scattering wave vector  $\mathbf{K}$  in terms of the primitive reciprocal lattice vectors:

$$\mathbf{K} = K_1 \mathbf{b}_1 + K_2 \mathbf{b}_2 + K_3 \mathbf{b}_3.\tag{II.69}$$

Hence, the structure factor becomes:

$$\begin{aligned}\frac{1}{N} \sum_l e^{-i\mathbf{K} \cdot \mathbf{l}} &= \left( \sum_{0 \leq l_1 < L_1} e^{-iK_1 l_1} \right) \left( \sum_{0 \leq l_2 < L_2} e^{-iK_2 l_2} \right) \left( \sum_{0 \leq l_3 < L_3} e^{-iK_3 l_3} \right) \\ &= \left( \frac{1 - e^{-iK_1 L_1}}{1 - e^{-iK_1}} \right) \left( \frac{1 - e^{-iK_2 L_2}}{1 - e^{-iK_2}} \right) \left( \frac{1 - e^{-iK_3 L_3}}{1 - e^{-iK_3}} \right).\end{aligned}\tag{II.70}$$

Here  $L_1$ ,  $L_2$  and  $L_3$  represent the numbers of primitive cells per unit length along the three principal axes of the crystal. The quantity given in EQ. (II.70) fluctuate rapidly as  $\mathbf{K}$  varies, and the average over a finite range of  $K$  values gives zero unless the denominators vanish under the condition:

$$e^{-iK_1} = e^{-iK_2} = e^{-iK_3} = 1.\tag{II.71}$$

In other words, the structure factor is only non-trivial if  $\mathbf{K}$  coincides with one of the reciprocal lattice vector  $\mathbf{g}$ . Therefore, EQ. (II.70) may be rewritten into the following relation

$$\frac{1}{N} \sum_l e^{-i\mathbf{K} \cdot \mathbf{l}} = \delta_{\mathbf{K}, \mathbf{g}},\tag{II.72}$$

and the scattering matrix in EQ. (II.66) becomes:

$$\mathcal{M}_{\mathbf{k},\mathbf{k}'} \equiv \mathcal{V}_a(\mathbf{g}) \delta_{\mathbf{k}'-\mathbf{k},\mathbf{g}}, \quad (\text{II.73})$$

which is consistent with the Bragg reflection condition.

Next, we relax the condition in EQ. (II.68) to include the lattice displacement vector  $\mathbf{u}_l$ :

$$\mathbf{R}_l = \mathbf{l} + \mathbf{u}_l = \mathbf{l} + \sum_{q>0} \left( \mathbf{u}_q e^{i\mathbf{q}\cdot\mathbf{l}} + \mathbf{u}_q^* e^{-i\mathbf{q}\cdot\mathbf{l}} \right), \quad (\text{II.74})$$

where we have assumed that the displacement field is real so that  $\mathbf{u}_q^* = \mathbf{u}_{-q}$ . Inserting EQ. (II.74) into the structure factor in EQ. (II.66), we obtain

$$\begin{aligned} \frac{1}{N} \sum_l e^{-i\mathbf{K}\cdot\mathbf{R}_l} &= \frac{1}{N} \sum_l \exp \left[ -i\mathbf{K}\cdot \left\{ \mathbf{l} + \sum_{q>0} \left( \mathbf{u}_q e^{i\mathbf{q}\cdot\mathbf{l}} + \mathbf{u}_q^* e^{-i\mathbf{q}\cdot\mathbf{l}} \right) \right\} \right] \\ &= \frac{1}{N} \sum_l \left[ e^{-i\mathbf{K}\cdot\mathbf{l}} \prod_{q>0} \exp \left\{ -i\mathbf{K}\cdot \left( \mathbf{u}_q e^{i\mathbf{q}\cdot\mathbf{l}} + \mathbf{u}_q^* e^{-i\mathbf{q}\cdot\mathbf{l}} \right) \right\} \right] \\ &= \frac{1}{N} \sum_l \left[ e^{-i\mathbf{K}\cdot\mathbf{l}} \prod_{q>0} \left\{ 1 - i\mathbf{K}\cdot \left( \mathbf{u}_q e^{i\mathbf{q}\cdot\mathbf{l}} + \mathbf{u}_q^* e^{-i\mathbf{q}\cdot\mathbf{l}} \right) - \left| \mathbf{K}\cdot\mathbf{u}_q \right|^2 + \dots \right\} \right]. \end{aligned} \quad (\text{II.75})$$

Clearly the lowest order term in EQ. (II.75) is simply identical to EQ. (II.72), which gives the diffraction pattern of an ideal crystal. The first correction term in EQ. (II.75) is a sum of all the terms linear in  $\mathbf{K}\cdot\mathbf{u}_q$ :

$$\begin{aligned} \frac{1}{N} \sum_l e^{-i\mathbf{K}\cdot\mathbf{l}} \sum_q \left( 1 - i\mathbf{K}\cdot\mathbf{u}_q \right) e^{i\mathbf{q}\cdot\mathbf{l}} &= \sum_q \left( 1 - i\mathbf{K}\cdot\mathbf{u}_q \right) \left\{ \frac{1}{N} \sum_l e^{i(\mathbf{q}-\mathbf{K})\cdot\mathbf{l}} \right\} \\ &= \sum_q \left( 1 - i\mathbf{K}\cdot\mathbf{u}_q \right) \delta_{\mathbf{K}-\mathbf{q},\mathbf{g}}. \end{aligned} \quad (\text{II.76})$$

Therefore, the scattering matrix to the first order in  $\mathbf{K}\cdot\mathbf{u}_q$  is given by:

$$\mathcal{M}_{\mathbf{k},\mathbf{k}'} \equiv \mathcal{V}_a(\mathbf{g}) \delta_{\mathbf{k}'-\mathbf{k},\mathbf{g}} + \mathcal{V}_a(\mathbf{K}) \sum_q \left( 1 - i\mathbf{K}\cdot\mathbf{u}_q \right) \delta_{\mathbf{K}-\mathbf{q},\mathbf{g}}. \quad (\text{II.77})$$

For  $\mathbf{K}$  within the first Brillouin zone and considering both terms associated with  $\mathbf{u}_q$  and  $\mathbf{u}_q^*$ , we have  $\mathbf{g} = 0$ ,  $\pm\mathbf{q} = \mathbf{K} = (\mathbf{k}' - \mathbf{k})$ , and

$$\mathcal{M}_{\mathbf{k},\mathbf{k}'} = \left[ -i(\mathbf{k}' - \mathbf{k}) \cdot \mathbf{u}_q \right] \mathcal{V}_a(\mathbf{k}' - \mathbf{k}). \quad (\text{II.78})$$

In this case, the scattering process for momentum from  $\mathbf{k}$  to  $\mathbf{k}'$  that involves either emitting or absorbing a phonon  $\mathbf{q}$  within the first Brillouin zone is known as the *normal process*, or the *N-process*. On the other hand, if  $\mathbf{g} \neq 0$  and  $\pm\mathbf{q} = \mathbf{K} - \mathbf{g}$ , we have  $\mathbf{k}' = \mathbf{k} + \mathbf{g} \pm \mathbf{q}$ . This process that involves phonons outside of the first Brillouin zone is known as the *Umklapp process*, or the *U-process*.

• **Debye-Waller factor**

Next, we consider the second order contribution (*i.e.* terms associated with  $|\mathbf{K} \cdot \mathbf{u}_q|^2$ ) to the scattering matrix in addition to the aforementioned single-phonon scattering process. By inspecting EQ. (II.75), we find that explicit inclusion of the second order contribution entails multiplying both the elastic and the one-phonon inelastic processes by a factor

$$e^{-2W} \equiv \prod_q \left\{ 1 - |\mathbf{K} \cdot \mathbf{u}_q|^2 \right\}, \quad (\text{II.79})$$

where  $q$  runs the values of the entire Brillouin zone. The factor expressed in EQ. (II.79) is known as the *Debye-Waller factor*.

We may rewrite the Debye Waller factor in EQ. (II.79) by using the following identity:

$$\lim_{N \rightarrow \infty} \prod_{n=1}^N \left( 1 - \frac{1}{N} a_n \right) = \exp \left\{ 1 - \frac{1}{N} \sum_{n=1}^N a_n \right\}. \quad (\text{II.80})$$

Hence, we obtain

$$e^{-2W} = \exp \left\{ 1 - 2 \sum_q \frac{1}{2} |\mathbf{K} \cdot \mathbf{u}_q|^2 \right\}, \quad (\text{II.81})$$

$$\Rightarrow W = \frac{1}{2} \sum_q |\mathbf{K} \cdot \mathbf{u}_q|^2. \quad (\text{II.82})$$

To evaluate EQ. (II.82) explicitly, we need to find the amplitude  $\mathbf{u}_q$  of the  $q$ -th phonon mode, which may be approximated by considering the phonon mode as a simple harmonic oscillator with a mean energy given by the Bose-Einstein formula:

$$\bar{\epsilon}_q = \left( \bar{n}_q + \frac{1}{2} \right) \hbar \omega_q = NM (\dot{u}_q)^2 = NM \omega_q^2 u_q^2, \quad (\text{II.83})$$

where we have assumed a Bravais lattice for simplicity,  $M$  denotes the mass of each atom, and  $N$  is the total number of primitive cells. Inserting the expression of  $\mathbf{u}_q$  from EQ. (II.83) into EQ. (II.82), we have:

$$\begin{aligned} W &= \frac{1}{2} \sum_q |\mathbf{K} \cdot \mathbf{u}_q|^2 = \frac{1}{2} \frac{\hbar K^2}{NM} \sum_q \frac{1}{\omega_q} \left( n_q + \frac{1}{2} \right) \\ &= \frac{1}{2} \frac{\hbar K^2}{NM} \frac{1}{8\pi^3} \iiint d^3q \frac{1}{\omega_q} \left( \bar{n}_q + \frac{1}{2} \right) = \frac{1}{2} \frac{\hbar K^2}{M} \int_0^{\omega_D} d\omega \left( \frac{1}{e^{\hbar\omega/k_B T} - 1} + \frac{1}{2} \right) \frac{3\omega}{\omega_D^3} \\ &= \frac{3}{2} \frac{\hbar^2 K^2 T^2}{M k_B \Theta_D^3} \int_0^{\Theta_D/T} dz \left( \frac{1}{e^z - 1} + \frac{1}{2} \right). \end{aligned} \quad (\text{II.84})$$

In the high temperature limit,  $T \gg \Theta_D$ , EQ. (II.84) takes the form

$$W \rightarrow \frac{3}{2} \frac{\hbar^2 K^2 T}{M k_B \Theta_D^2}, \quad (\text{II.85})$$

and the Debye-Waller factor becomes

$$e^{-2W} \sim \exp\left(-\frac{3\hbar^2 K^2 T}{M k_B \Theta_D^2}\right). \quad (\text{II.86})$$

Hence, the Debye-Waller factor depends sensitively on temperature and the scattering wave vector in the high-temperature limit. On the other hand, for  $T \rightarrow 0$ , EQ. (II.84) approaches a constant:

$$W \rightarrow \frac{3}{8} \frac{\hbar^2 K^2}{M k_B \Theta_D}. \quad (\text{II.87})$$

The finding in EQ. (II.87) suggests that the effect of zero-point motion is not negligible and may be observed directly from experiments.

#### • Lindemann criterion for melting

The mean square amplitude of lattice vibrations in the high-temperature limit may also be used for estimating the melting temperature. Similar to the results derived in EQs. (II.84) and (II.85), for  $T \gg \Theta_D$  we find that the mean square amplitude of each atom about its equilibrium lattice site is given by

$$\frac{1}{N} \sum_l |u_l|^2 = \sum_q |u_q|^2 = \frac{3\hbar}{NM} \frac{1}{8\pi^3} \iiint d^3q \frac{1}{\omega_q} \left( \bar{n}_q + \frac{1}{2} \right) \rightarrow \frac{9\hbar^2 T}{M k_B \Theta_D^2}, \quad (T \gg \Theta_D). \quad (\text{II.88})$$

Therefore, for a crystal with a mean radius  $r_s$  of the primitive cell, we expect melting to occur when the root-mean-square displacement attains some standard value ( $x_m r_s$ ) at the melting temperature  $T_m$ :

$$T_m = \frac{x_m^2}{9\hbar^2} r_s^2 M k_B \Theta_D^2. \quad (\text{II.89})$$

Typically  $x_m$  is in the range of 0.2 ~ 0.25 in most solids. The condition given in EQ. (II.89) is known as the *Lindemann criterion for melting*, and the formula may be used for estimating the Debye temperature of solids from the empirical knowledge of  $T_m$ . Additionally, from EQs. (II.85) and (II.89) the value of the Debye-Waller factor  $W$  can be estimated by the following expression:

$$W = \frac{x_m^2 r_s^2}{6} \frac{T}{T_m} K^2 \sim \frac{x_m^2}{q_D^2} \frac{T}{T_m} K^2, \quad \text{where } q_D = \left( \frac{9\pi}{2} \right)^{1/3} \left( \frac{1}{r_s} \right). \quad (\text{II.90})$$

## II.9. Anharmonicity & thermal expansion

Up to this point we have only considered harmonic lattice vibrations by assuming an energy minimum around the equilibrium position. In reality, several important physical phenomena, such as thermal

expansion, are associated with the anharmonic terms. These terms contribute to the free energy so that the resulting energy minimum is not necessarily associated with the "equilibrium configuration" where the displacement field vanishes. The entire crystal may either expand or contract until it finds a volume where the free energy reaches a new minimum. In this final section of Part II, we consider the phenomenology of anharmonic effects on the thermal expansion coefficient of a crystal.

In general the frequency  $\omega$  of the lattice modes is a function of volume  $V$ , so that the frequency change  $\Delta\omega$  is proportional to the volume change  $\Delta V$  by the following relation:

$$\frac{\Delta\omega}{\omega} = -\gamma \frac{\Delta V}{V}, \quad (\text{II.91})$$

where  $\gamma$  is known as the *Grüneisen constant*, and the thermal expansion coefficient is given by the temperature derivative of the dilation ( $\Delta V/V$ ).

In the presence of anharmonicity, the total free energy  $F$  of the crystal as a function of volume may be given by the following expression:

$$F = U - TS = \frac{1}{2} \frac{1}{\kappa} \left( \frac{\Delta V}{V} \right)^2 + k_B T \sum_q \ln \left( 2 \sinh \frac{\hbar \omega_q}{2k_B T} \right), \quad (\text{II.92})$$

where the first term is the potential energy associated with the compressibility  $\kappa$  of the crystal as an elastic medium, and the second term is the sum of the free energies of the phonon modes. We may minimize the free energy in EQ. (II.92) relative to volume and use the expression in EQ. (II.91), which yields:

$$\frac{1}{\kappa} \left( \frac{\Delta V}{V} \right) = \sum_q \frac{1}{2} \gamma \hbar \omega_q \left( \coth \frac{\hbar \omega_q}{2k_B T} \right) = \gamma \bar{\varepsilon}(T). \quad (\text{II.93})$$

Therefore, the dilation is related to the temperature dependent energy  $\bar{\varepsilon}(T)$  of the phonon modes via the *Grüneisen formula*:

$$\left( \frac{\Delta V}{V} \right) = \kappa \gamma \bar{\varepsilon}(T), \quad (\text{II.94})$$

and the thermal expansion coefficient is given by

$$\frac{\partial}{\partial T} \left( \frac{\Delta V}{V} \right) = \kappa \gamma \frac{\partial}{\partial T} \bar{\varepsilon}(T) \equiv \kappa \gamma c_v(T), \quad (\text{II.95})$$

where  $c_v(T)$  is the specific heat.

The above description based on the expression in EQ. (II.91) has implicitly assumed that all phonon modes have the same *Grüneisen constant*. This assumption is clearly oversimplified because dilation affects different lattice modes differently. For instance, the  $\gamma$  value for longitudinal phonons is generally much larger than those for the transverse modes. Therefore, the result given in EQ. (II.93) needs to be modified to account for different  $\gamma$  values associated with different phonon modes.