

Static and Transport Properties of Solids

CHAPTER OUTLINE

6.1 Band Picture	166
6.2 Bond Picture	167
6.3 Diamond Structure	168
6.4 Si and Ge	168
6.5 Zinc-Blende Semiconductors	170
6.6 Ionic Solids	172
6.7 Molecular Crystals	174
6.7.1 Molecular Solids.....	174
6.7.2 Hydrogen-Bonded Structures.....	174
6.8 Cohesion of Solids	174
6.8.1 Molecular Crystals: Noble Gases.....	174
6.8.2 Ionic Crystals.....	176
6.8.3 Covalent Crystals.....	177
6.8.4 Cohesion in Metals.....	178
6.9 The Semiclassical Model	179
6.10 Liouville's Theorem	182
6.11 Boltzmann Equation	183
6.12 Relaxation Time Approximation	184
6.13 Electrical Conductivity	186
6.14 Thermal Conductivity	187
6.15 Weak Scattering Theory of Conductivity	188
6.15.1 Relaxation Time and Scattering Probability.....	188
6.15.2 The Collision Term.....	188
6.15.3 Impurity Scattering.....	189
6.16 Resistivity Due to Scattering by Phonons	192
Problems	194
References	196

6.1 BAND PICTURE

In Chapter 4, we discussed how the different types of solids can be classified as metals, semimetals, insulators, and semiconductors according to the band picture. In Chapter 5, we considered some of the methods used for calculation of the energy bands of solids. To summarize the band picture of solids, one constructs Brillouin zones, which are the Wigner–Seitz cells of the reciprocal lattice. Each Brillouin zone can have N \mathbf{k} states (where N is the number of primitive cells in the crystal) and hence can accommodate $2N$ electrons (because each \mathbf{k} state can contain two electrons of opposite spin). The electrons in the lattice move in a periodic potential in a background of the positively charged ions (because the valence electrons have been stripped off from their parent atoms) that opens up an energy gap $2|V_{\mathbf{K}}|$ at each Brillouin zone boundary. In pure materials, there are no eigenstates for electrons with energies lying within these energy gaps. This can be restated as “the electron states are forbidden in this energy gap.” Normally, these energy gaps appear in the free electron parabola at the Brillouin zone boundaries because of the periodic potential. This is called the extended zone scheme because it is extended over the entire reciprocal space. However, any \mathbf{k} state in the extended zone scheme can be written as

$$\mathbf{k} = \mathbf{k}_1 \pm \mathbf{K}, \quad (6.1)$$

where \mathbf{K} is a reciprocal lattice vector, and \mathbf{k}_1 is a vector in the first Brillouin zone. Therefore, we can map the different segments of the extended zone into the first zone and use a band index n to identify them. These are called bands because each segment is an independent region of energy levels. For example, the state \mathbf{k}_i^n in the n th zone can be written as

$$\mathbf{k}_{in} = \mathbf{k}_i^n - \mathbf{K}, \quad (6.2)$$

where \mathbf{k}_{in} is the corresponding state in the reduced zone. In the reduced zone scheme, these electron energy bands are stacked above each other in the first Brillouin zone. The energy gap between the bands increases as one proceeds from the lowest zone to the higher zones. This is shown in Figure 6.1.

It is easy to classify the solids in the band picture (as we did in Chapter 4) by counting the number of electrons per unit cell. Thus, all monovalent and trivalent solids are good metals because they are either half-filled or one-and-a-half-filled bands. A divalent solid, which normally would be an insulator, is actually a poor conductor because of the overlap of the bands in three dimensions. Solids with five electrons per atom such as As, Sb, and Bi have two atoms per unit cell that would fill five bands, but due to a small overlap of the fifth and sixth band, there are a few electrons in both bands that can be excited to higher energy states, and hence these are poor conductors. These are known as semimetals. Solids with four electrons per atom range from insulators (diamond) to semiconductors (Ge, Si). Sn is either a metal or a semiconductor, depending on the phase in which it crystallizes, whereas Pb is a pure metal.

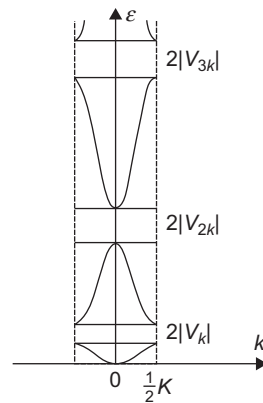


FIGURE 6.1

The bands stacked above each other in the reduced zone scheme.

6.2 BOND PICTURE

To be able to discuss the properties of diamond as well as that of semiconductors such as Ge and Si, which crystallize in the “diamond structure,” we need to discuss the bond picture of solids. The simplest bond picture is that of a covalent bond shown in Figure 6.2, which is formed by a hydrogen molecule.

There is a repulsive force between the two nuclei, but the attractive force between the two electrons and the nuclei lowers the energy of the system. This is the simplest example of a covalent bond. The simplest example of a tetrahedral bond is that of a methane molecule, shown in Figure 6.3.

Diamond, Si, and Ge crystallize in the diamond structure, which is essentially a fcc lattice with a basis of two atoms at $(0, 0, 0)$ and $(\frac{1}{4}, \frac{1}{4}, \frac{1}{4})$ per unit cell. It can be visualized as having an atom at each lattice point of a fcc lattice and another atom at each point of a second fcc lattice of which the corner is at one-fourth of the distance along the main diagonal of the cube. The valence electrons in the ground state of the free atoms have the configuration $2s^2 2p^2$, $3s^2 3p^2$, and $4s^2 4p^2$ for diamond, Si, and Ge, respectively. In the crystal, the ground state is formed from the configuration $nsnp^3$, where $n = 2, 3$, and 4 for diamond, Si, and Ge, respectively. The valence electrons form directed sp^3 tetrahedral bonding orbitals (from the orthonormal s and p orbitals) of the form (assuming no overlap)

$$\begin{aligned}\phi_1 &= \frac{1}{2}(s + p_x + p_y + p_z), \\ \phi_2 &= \frac{1}{2}(s - p_x + p_y + p_z), \\ \phi_3 &= \frac{1}{2}(s + p_x - p_y - p_z), \\ \phi_4 &= \frac{1}{2}(s - p_x - p_y - p_z).\end{aligned}\quad (6.3)$$

There is a tetrahedral bond between the atom that forms the center of the tetrahedron and the neighboring four atoms. In fact, there is only one way in which these tetrahedra can be arranged so that each atom forms bonds with four others. In the diamond structure, each atom is at the center of a tetrahedron with the nearest-neighbor atoms at the vertices. The diamond structure is shown in Figure 6.4.

The positions of the atoms in the unit cell of the diamond structure projected on a cube face are shown in Figure 6.5.

The points 0 and $\frac{1}{2}$ are on the fcc lattice, and those at $\frac{1}{4}$ and $\frac{3}{4}$ are on a similar lattice displaced among the body diagonal by one-fourth of its length.

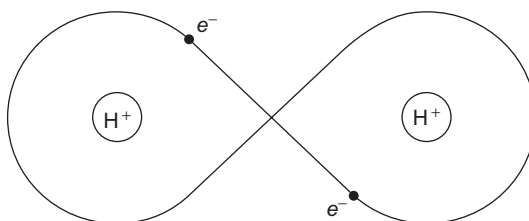


FIGURE 6.2
Covalent bond of a hydrogen molecule.

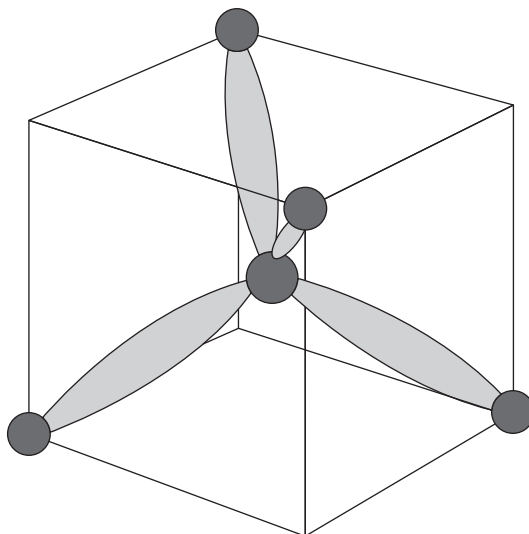
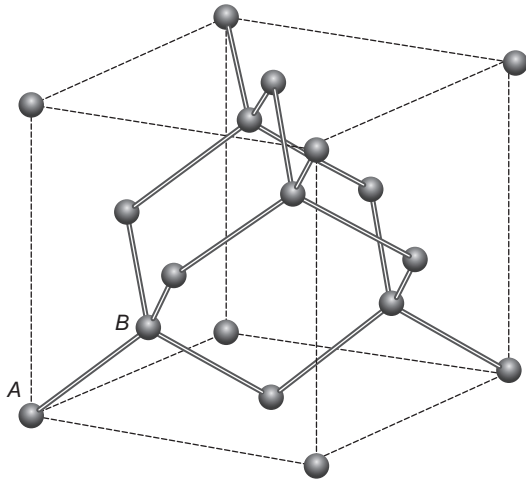
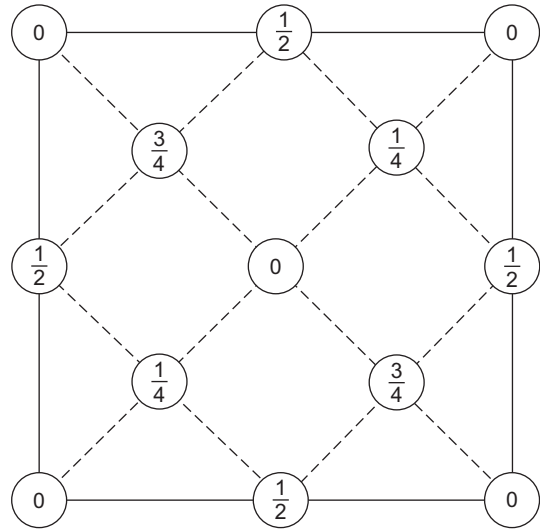


FIGURE 6.3
A simple example of tetrahedral bonding (methane molecule).

**FIGURE 6.4**

The diamond structure. Each atom forms the center of a tetrahedron.

**FIGURE 6.5**

Positions of the atoms in the unit cell of the diamond structure projected on a cube face.

6.3 DIAMOND STRUCTURE

Diamond obviously crystallizes in the diamond structure. The orbital electrons of carbon atom have the structure ($2s^2 2p^2$). When they form the diamond crystal, the valence electrons are in the state ($2s 2p^3$). They form the directional sp^3 orbitals as shown in Eq. (6.3). The tetrahedral bonding in diamond is due to the bonding between a carbon atom and its four nearest carbon atoms. However, diamond is an insulator because of the large energy gap between the filled valence band and the empty conduction band. At room temperature, the valence band is completely filled with electrons, whereas the conduction band is empty because the energy gap is too large for electrons to be excited to the conduction band. When an external electric field is applied, the electrons cannot be excited to the higher energy states that lie in the energy gap.

6.4 Si AND Ge

Si and Ge crystallize in the diamond structure. The Bravais lattice of the diamond structure has a basis of two atoms, each of which has eight sp electron states, but only four of them are occupied by electrons. Thus, the Brillouin zones have to accommodate 16 electron states, but only eight electrons (from the two atoms) fill them. Consequently, the band structure has eight sub-bands. Four of these are completely filled, and the other four are completely empty at 0°K .

Si and Ge are typical examples of semiconductors because the energy gap between the valence band and the conduction band is sufficiently small. At absolute zero, these are insulators, but at room temperature, a few electrons are excited from the valence band to the conduction band. The conductivity is small but increases with increase of temperature. The property of these intrinsic semiconductors can be easily understood from the bond picture that will help us understand the property of impurity or doped semiconductors as well as that of the p - n junctions and their importance in electronics.

A simple example can illustrate the formation of the energy gap in these solids by considering the fact that Si and Ge have covalent bonding. The sp states in a free atom form an eight-fold-degenerate level. In an Si dimer, the electron states would interact and form bonding and antibonding levels, as shown in Figure 6.6.

The tetrahedral bonding of Si is shown in Figure 6.7. An Si atom ($3s^2 3p^2$) has four valence electrons. In the crystalline form, a Silicon atom has the valence configuration ($3s 3p^3$), which forms four sp^3 hybrids and results in the tetrahedral bonding with the four nearest Si atoms. Therefore, each bond has two electrons shared by two Si atoms. In principle, the wave functions of these electrons would extend throughout the crystalline solid. However, the electron cloud, which is essentially a pair of electrons of opposite spin, is mostly located in the bond between the neighboring Si ions, as shown schematically in Figure 6.7. This is also confirmed by band calculations.

Ge also crystallizes in the diamond structure. In the Ge atom, the valence electrons have the ($4s^2 4p^2$) configuration, whereas in the crystalline form, the valence electrons have the ($4s 4p^3$) configuration. These form the sp^3 hybrids, as explained in Eq. (6.3). Each of these four orbital wave functions is directed toward the vertex of a tetrahedron, and hence, the electronic structure of Ge is almost identical to that of Si. The band structures of Si and Ge, calculated by Chelikowsky and Cohen³ using the empirical nonlocal pseudopotential method, are shown in Figures 6.8 and 6.9.

We note that the energy gaps in both Ge and Si are indirect. The highest occupied state lies at Γ . However, the lowest lying unoccupied state is near the X point, and thus the gap is “indirect.”

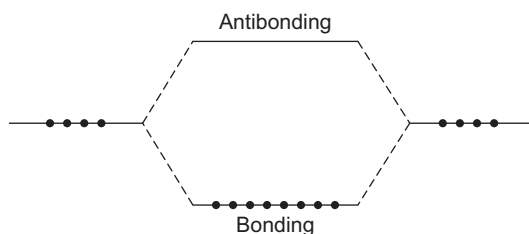


FIGURE 6.6

Bonding and antibonding levels in a silicon dimer.

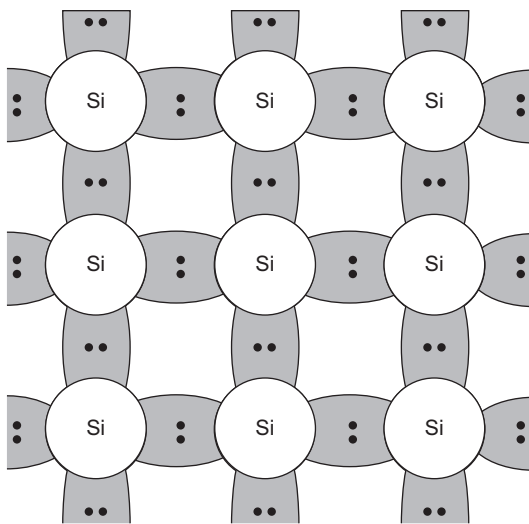
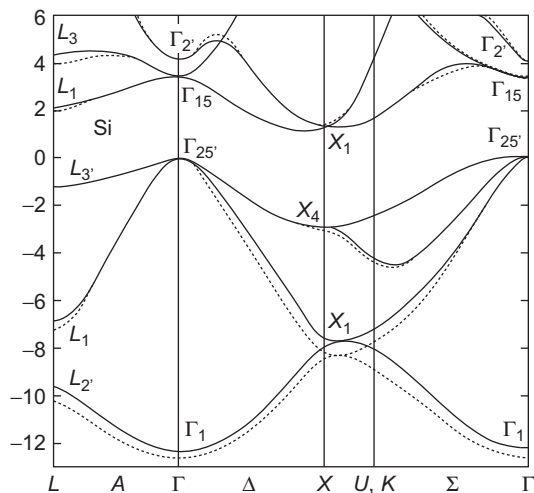


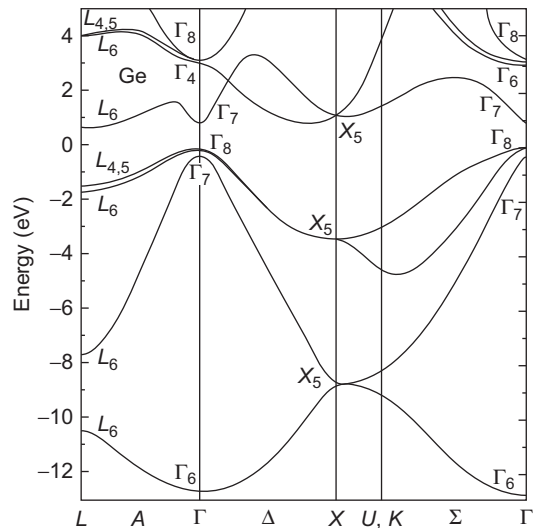
FIGURE 6.7

Electronic structure (schematic) of Si.

**FIGURE 6.8**

Band structure of Si calculated by Chelikowsky and Cohen by using nonlocal pseudopotential. The dashed lines are results obtained by using local pseudopotential.

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**FIGURE 6.9**

Band structure of Ge calculated by Chelikowsky and Cohen by using nonlocal pseudopotential.

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6.5 ZINC-BLENDE SEMICONDUCTORS

The III–V zinc-blende semiconductors such as GaAs and InSb have the same basis core of closed shells as Si and Ge. However, Ga and In have three outer electrons, whereas As and Sb have five outer electrons. In addition, Ga or In occupies all the A sites in the diamond structure, whereas As or Sb occupies all the B sites (see Figure 6.4). The bond picture of GaAs is shown in Figure 6.10.

The bond structure of InSb is similar to that of GaAs. We note that the bond structures of GaAs and InSb are different from that of Si or Ge in the sense that because Ga (or In) has three outer electrons and As (or Sb) has five outer electrons, there is a shrinking of the charge clouds toward As (or Sb), and away from Ga (or In). These compounds are also semiconductors like Si and Ge, but with a smaller energy gap. Their band structures, as calculated by Chelikowsky and Cohen using a nonlocal pseudopotential method, are shown in Figures 6.11 and 6.12.

ZnS, which is a II–VI compound, has the zinc-blende structure (in fact, the name is derived from it). It is also a semiconductor like the III–V compounds. In ZnS, Zn has two electrons, and S has six electrons in the outermost shells. However, the S^{6+} ions attract the eight electrons surrounding it and try to pull them further in through a process known as electron affinity. The S^{6+} ions try to form a closed shell, and the Zn^{2+} ions barely hold on to the two outermost electrons. In the process, the two electrons in each bond are much closer to S than to Zn because the bond electrons are greatly polarized by the residual charge on the ions. The zinc sulphide bond is shown schematically in Figure 6.13.

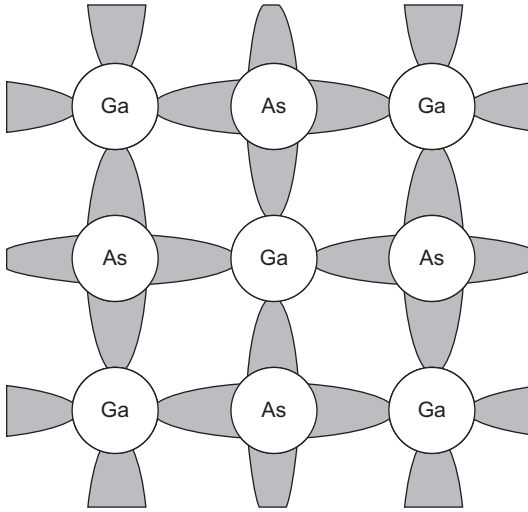


FIGURE 6.10

Bond structure of GaAs.

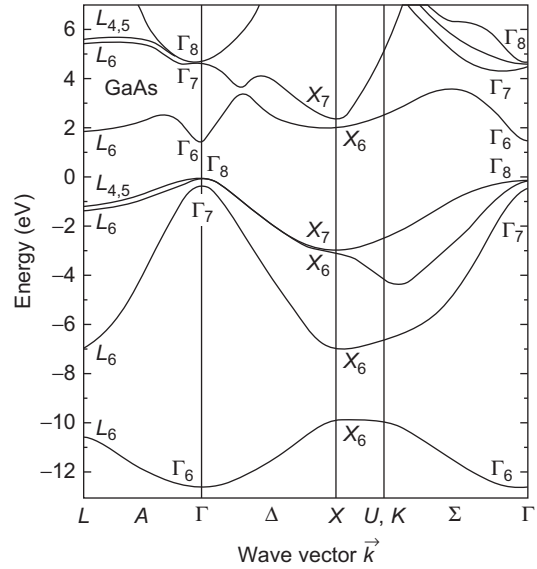


FIGURE 6.11

Band structure of GaAs calculated by Chelikowsky and Cohen.

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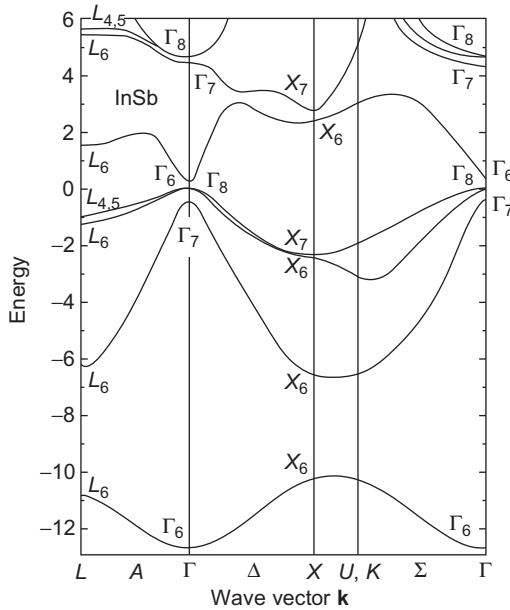


FIGURE 6.12

Band structure of InSb calculated by Chelikowsky and Cohen.

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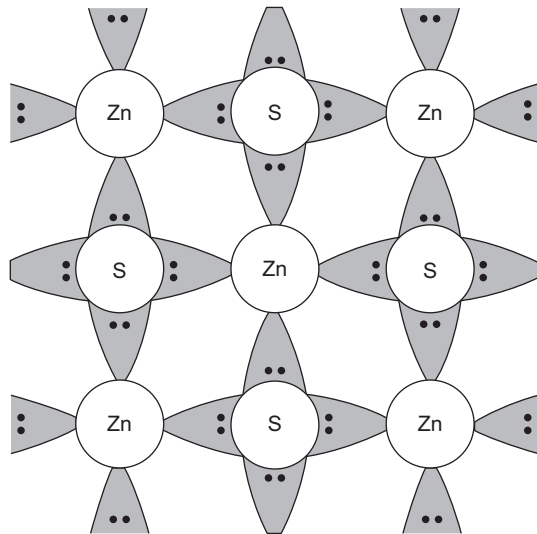


FIGURE 6.13

Schematic picture of zinc sulphide bond.

6.6 IONIC SOLIDS

In CuCl, the copper atom has one electron in its outermost shell, whereas the chlorine atom has seven electrons. In the crystalline form, the Cu atom loses its electron, which is captured by the chlorine atom. CuCl crystallizes in an alternating lattice. The attraction is between the Cu^+ and Cl^- ions. In fact, there are two alternate crystal structures in which the ionic crystals crystallize: the NaCl structure and the CsCl structure. The important factor in the crystal structure in an ionic crystal is to have as many negative ions as possible around a positive ion. A schematic diagram of sodium chloride is shown in Figure 6.14.

The sodium chloride crystal structures are shown in Figure 6.15. In the sodium chloride structure, the space lattice is *fcc*, and the basis has one Na^+ ion at (000) and one Cl^- ion at $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$.

The cesium chloride crystal structure is shown in Figure 6.16. The space lattice is simple cubic, and the basis has one Cs^+ ion at (000) and one Cl^- ion at $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$.

We have discussed the progression of the band structure from perfectly covalent silicon in which the four electrons are distributed around the Si^{4+} ion cores in tetrahedral bonding, to covalent gallium arsenide, where there is more charge of the electron cloud surrounding the As^{5+} core than Ga^{3+} . Consequently, GaAs has a small ionic character. The zinc sulphide crystal is weakly covalent because Zn^{2+} has very few valence electrons while S^{6+} is almost full; therefore, the electron cloud is mostly around S^{6+} . ZnS is also partly ionic in character. Sodium chloride is perfectly ionic because the Na^+ ion has lost its valence electron to the chlorine atom that becomes the Cl^- ion. The attraction between the ions of opposite sign results in the ionic bond.

A schematic diagram of the progression from perfectly covalent to perfectly ionic crystals is shown in Figure 6.17.

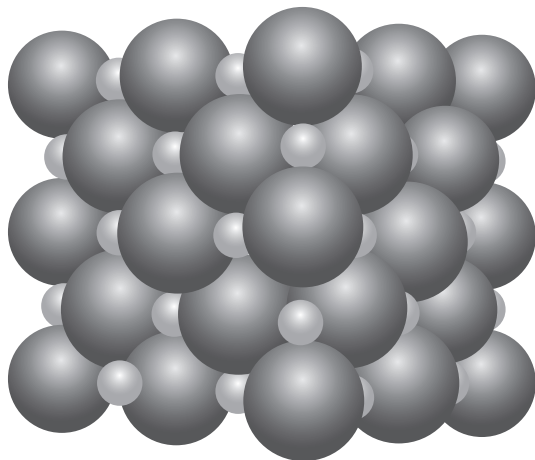


FIGURE 6.14

A schematic diagram of sodium chloride.

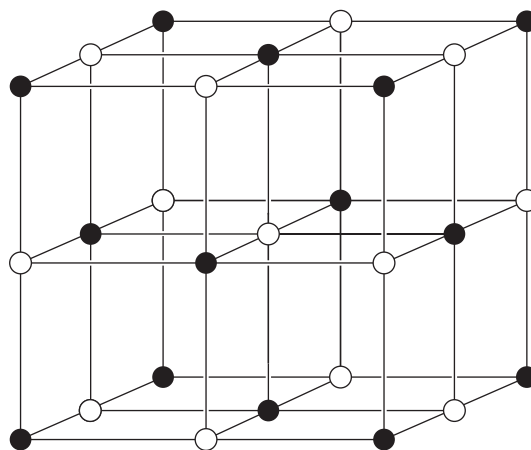
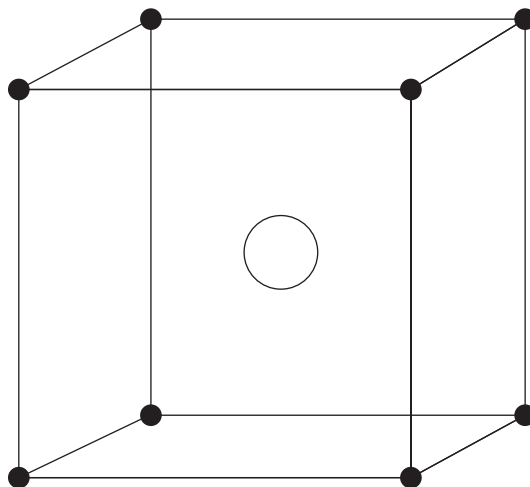
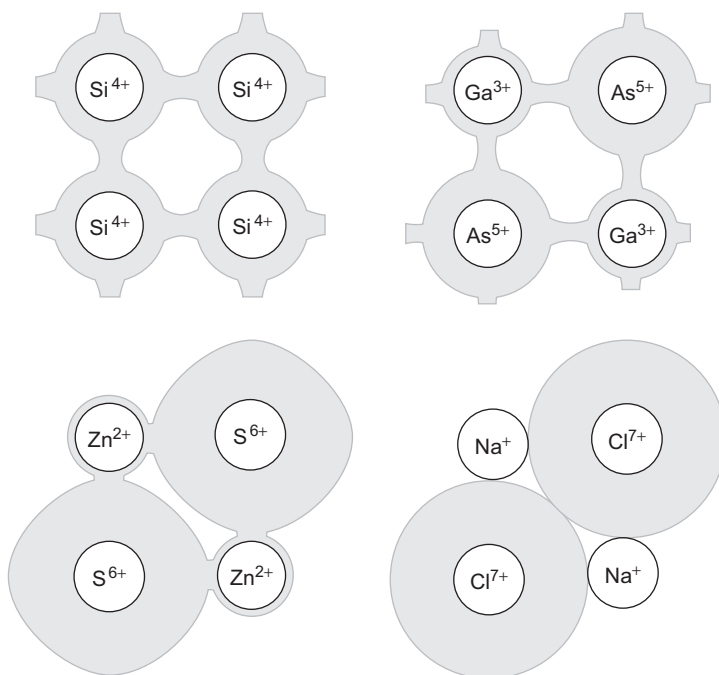


FIGURE 6.15

Sodium chloride crystal structure.

**FIGURE 6.16**

Cesium chloride structure.

**FIGURE 6.17**

A schematic diagram of progression from perfectly covalent to perfectly ionic crystals.

6.7 MOLECULAR CRYSTALS

6.7.1 Molecular Solids

The column VIII elements are good examples of molecular solids. The solid noble gases (except helium) crystallize in monatomic fcc Bravais lattices. Each atom has a stable closed-shell type, which gets deformed in the solid. However, the solid is held together by the van der Waals or fluctuating dipole forces. These forces are very weak and can be qualitatively calculated by considering two atoms (A and B) at a distance r . At any instant, if atom A has an instantaneous dipole moment \mathbf{p}_A (of which the time-averaged value vanishes), then the electric field at atom B due to atom A is proportional to p_A/r^3 . The dipole moment at atom B due to this electric field is given by

$$p_B \sim \frac{\alpha p_A}{r^3}, \quad (6.4)$$

where α is the polarizability of the atom. The interaction energy between two dipoles of moment p_A and p_B is given by

$$V_i = -\beta \frac{p_A p_B}{r^3} \approx -\alpha \beta \frac{p_A^2}{r^6} = -\frac{A}{r^6}, \quad (6.5)$$

where β is the polarizability of atom B and $A = \alpha \beta p_A^2$. Thus, the lowering of energy between two atoms due to the van der Waals force is very small.

6.7.2 Hydrogen-Bonded Structures

In the hydrogen-bonded structures, the forces between the molecular groups are through a shared proton. The chemical properties of the molecules dominate the properties of these structures.

6.8 COHESION OF SOLIDS

The cohesive energy is the difference between the energy of a solid and the energy of a gas of widely separated atoms from which the solid is eventually constituted. Essentially, the determination of the cohesive energy answers two separate questions. First, it explains how a large group of atoms form a crystalline solid when they come together. Second, it explains which crystal structure leads to the lowest energy.

As we have seen, crystals can be divided into five categories: *molecular*, *ionic*, *covalent*, *metallic*, and *hydrogen bonded*. We will discuss the cohesive energy of each type of solids.

6.8.1 Molecular Crystals: Noble Gases

The van der Waals interaction between two molecules, which are well separated at a distance \mathbf{r} , is derived (using a classical theory) in Eq. (6.5). However, the term that is proportional to r^{-6} (Eq. 6.5) represents the interaction energy between the molecules at large distances that do not have a permanent dipole moment. We note that the induced dipole moment in van der Waals interaction is such that it is always attractive and hence lowers the energy of the system. It may be noted that quantum or thermal fluctuations always induce small dipole moments in atoms that normally do not have any dipole moments. However, when the atoms come close together such that their separation

is of the same order as that of the atomic radii, there is an additional repulsive force between them. This additional force is proportional to r^{-12} . The resulting potential, which is the sum of the attractive force arising out of the van der Waals term (Eq. 6.5) and the repulsive force, can be written as

$$\phi(r) = -\frac{A}{r^6} + \frac{B}{r^{12}}, \quad (6.6)$$

where A and B are positive constants. For convenience, we introduce the parameters $\sigma = \left(\frac{B}{A}\right)^{1/6}$ and $\epsilon = \frac{A^2}{4B}$, so that Eq. (6.6) can be written as

$$\phi(r) = 4\epsilon \left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^6 \right]. \quad (6.7)$$

This is known as the Lennard–Jones 6-12 potential. The Lennard–Jones parameters ϵ and σ are appropriately chosen to reproduce the thermodynamic properties of gaseous neon, argon, krypton, and xenon at low temperatures. The Leonard–Jones potential $\phi/4\epsilon$ has been plotted against r/a in Figure 6.18.

The total potential energy U of a crystal of N atoms separated by \mathbf{R} (using periodic boundary conditions so that each atom has identical surroundings) is given by (from Eq. 6.7)

$$U = \frac{1}{2}N \sum_{\mathbf{R} \neq 0} \phi(\mathbf{R}) = 2N\epsilon \sum_{\mathbf{R} \neq 0} \left[\left(\frac{\sigma}{R}\right)^{12} - \left(\frac{\sigma}{R}\right)^6 \right], \quad (6.8)$$

where the sum is over all nonzero vectors for the bcc lattice (He) or the fcc lattice (all other noble gases). Here, the factor $\frac{1}{2}$ is multiplied because the interaction energy of each atom has been counted twice. The potential energy per atom is given by

$$u = U/N = 2\epsilon \sum_{\mathbf{R} \neq 0} \left[\left(\frac{\sigma}{R}\right)^{12} - \left(\frac{\sigma}{R}\right)^6 \right]. \quad (6.9)$$

If the nearest-neighbor distance is r , we can rewrite Eq. (6.9) as

$$u = 2\epsilon \left[A_{12} \left(\frac{\sigma}{r}\right)^{12} - A_6 \left(\frac{\sigma}{r}\right)^6 \right], \quad (6.10)$$

where

$$A_n = \sum_{\mathbf{R} \neq 0} \left(\frac{r}{R}\right)^n. \quad (6.11)$$

It can be shown that $A_6 = 14.45$ for a fcc structure and 12.25 for a bcc structure while $A_{12} = 12.13$ for a fcc structure and 9.11 for a bcc structure.

The nearest-neighbor equilibrium spacing r_0 is easily obtained from Eq. (6.10) from the expression,

$$\frac{\partial u}{\partial r} = 0 \Big|_{r=r_0}. \quad (6.12)$$

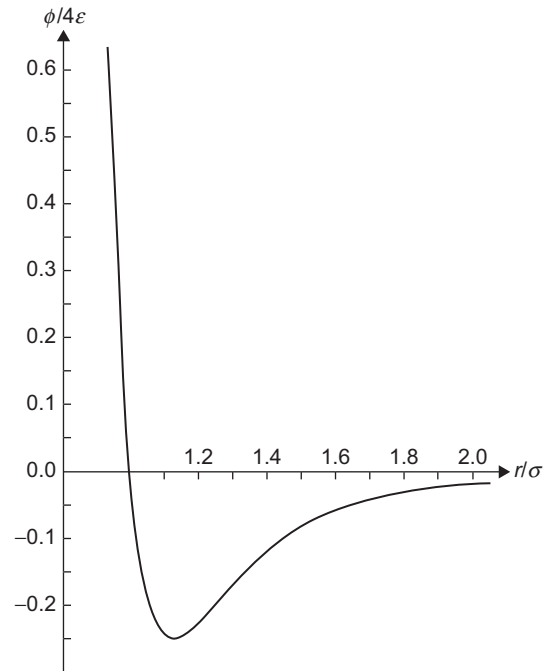


FIGURE 6.18

The Leonard–Jones 6-12 potential.

From Eqs. (6.10) and (6.12), we obtain,

$$r_0 = \sigma \left(\frac{2A_{12}}{A_6} \right)^{1/6}. \quad (6.13)$$

The cohesive energy per ion pair at equilibrium, $u_0 \equiv \varepsilon/N$, is obtained from Eqs. (6.10) and (6.13),

$$u_0 = -\epsilon \frac{A_6^2}{2A_{12}} \approx -8.6 \epsilon, \quad (6.14)$$

for a fcc lattice. The Bulk modulus B is given by

$$B = V \frac{\partial^2 \varepsilon}{\partial V^2}. \quad (6.15)$$

For a fcc lattice,

$$\frac{V}{N} = \frac{r^3}{\sqrt{2}} = v, \quad \frac{\partial}{\partial v} = \frac{\sqrt{2}}{3r^3} \frac{\partial}{\partial r}. \quad (6.16)$$

Therefore, at equilibrium,

$$B_0 = \frac{\sqrt{2}}{9r_0} \frac{\partial^2 u}{\partial r^2} \Big|_{r=r_0} = \frac{4\epsilon}{\sigma^3} A_{12} \left(\frac{A_6}{A_{12}} \right)^{5/2}. \quad (6.17)$$

6.8.2 Ionic Crystals

The ionic crystals crystallize in four common lattice structures: the sodium chloride, the cesium chloride, the zinc-blende, and the wurtzite structures. The largest term in the interaction energy is the Coulomb interaction because the particles in the ionic crystals are electrically charged ions. The dipole interaction, considered for molecular crystals, which is inversely proportional to the sixth power of the interionic distance, is easily neglected. However, the short-range core-core repulsion due to the Pauli principle prevents the crystal from collapsing. We assume that in the first unit cell, the negative ion is at the origin, and the positive ion is at a distance \mathbf{d} (\mathbf{d} is a translation vector through $a/2$ of a cubic side). The total cohesive energy per ion pair is

$$u(d) = u^{\text{coulomb}}(d) + u^{\text{core}}(d). \quad (6.18)$$

As an example, we consider the sodium chloride structure that is a fcc Bravais of negative ions at site \mathbf{R}_i and a second Bravais lattice of positive cations displaced by \mathbf{d} from the first lattice. The total potential energy of a single anion or cation is given by

$$u = -\frac{e^2}{d} \left\{ 1 + \sum_{i \neq 0} \left(\frac{d}{|\mathbf{R}_i + \mathbf{d}|} - \frac{d}{R_i} \right) \right\}. \quad (6.19)$$

The total potential energy for $N/2$ ions pair (or N ions) is given by

$$U = -\frac{Ne^2}{2d} \left\{ 1 + \sum_{i \neq 0} \left(\frac{d}{|\mathbf{R}_i + \mathbf{d}|} - \frac{d}{R_i} \right) \right\}. \quad (6.20)$$

The energy per ion pair is obtained by dividing Eq. (6.20) by $N/2$ ions, and we obtain

$$u^{coul}(d) = -\frac{e^2}{d} \left\{ 1 + \sum_{i \neq 0} \left(\frac{d}{|\mathbf{R}_i + \mathbf{d}|} - \frac{d}{R_i} \right) \right\}. \quad (6.21)$$

The evaluation of the summation is complicated and depends on the lattice structure in addition to containing diverging terms. It can be shown, by performing an Ewald summation (Problem 6.4), that

$$u^{coul}(d) = -\frac{\alpha e^2}{d}, \quad (6.22)$$

where α is known as the Madelung constant, which depends on the crystal structure.

The repulsive term $u_{core}(d)$, which is essential in preventing a collapse, can only be estimated approximately by a phenomenological term,

$$u_{core}(d) = \frac{A}{12d}. \quad (6.23)$$

The total energy per pair of ions is obtained from Eqs. (6.22) and (6.23),

$$u(d) = -\alpha \frac{e^2}{d} + \frac{A}{12d}. \quad (6.24)$$

The equilibrium distance d_0 is obtained from the relation

$$\frac{\partial u(d)}{\partial d} = 0. \quad (6.25)$$

From Eqs. (6.24) and (6.25), we obtain

$$\alpha \frac{e^2}{d_0^2} = 12 \frac{A}{d_0^3}, \quad (6.26)$$

which leads to

$$d_0 = \left(\frac{12A}{\alpha e^2} \right)^{1/11}. \quad (6.27)$$

The phenomenological constant A is obtained by matching the minimum of the potential to the experimental results.

6.8.3 Covalent Crystals

The theory of cohesion in the covalent crystals involves much more complex calculation than that of ionic or molecular crystals. The main reason is that in the crystalline form, the valence electrons in covalent crystals are distributed in a very different way than they are in a group of isolated atoms or ions. Previously, for noble gases and ionic crystals, we obtained reasonable results by calculating the potential energy of a large number of deformed ions or atoms that were arranged in the relevant crystal structure. To calculate the cohesive energy of covalent crystals, we have to calculate their band structure by following techniques discussed in Chapter 5. In fact, the theory of chemical bonding in molecules is used to describe the cohesion in covalent insulators.

We can make a qualitative discussion by considering a specific case. For example, we place a set of carbon atoms in the sites of a diamond structure, where the lattice constant is large enough so that there is no interaction between the ions, and consequently, the cohesive energy is zero. As the lattice constant is gradually reduced, the atomic orbitals would start overlapping, and the interaction energy between the atoms placed at the designated lattice sites would correspondingly decrease. If the outermost shell of the isolated atom were filled, this overlap would lead to core–core repulsion due to the Pauli exclusion principle, and the energy would increase. However, because the outermost shells of the carbon atoms are partially filled, the electrons are flexible enough to rearrange themselves whenever there is overlap between neighboring wave functions. The primary reason for this flexibility is due to the fact that in the same atomic shell, there are empty energy levels. Thus, when the lattice constant of the (hypothetical) diamond structure is reduced to an appropriate value (the actual lattice constant of diamond), the cohesion energy will be sufficient to form the crystal. The overlap of the outermost shells leads to lowering of the energy. The new levels formed by the electrons are no longer localized around a single atom or ion. The bond picture of covalent solids in general, and the tetrahedral bonding in diamond structure in particular, partially explains the cohesion in such crystals. However, as noted earlier, the theory of cohesion in covalent crystals requires more complex calculations.

6.8.4 Cohesion in Metals

In general, the theory of the cohesion of metals also requires band theory calculations. However, the explanation of cohesion for the alkali metals is comparatively easier because one can consider an alkali metal to consist of a sea of electrons moving around in a background of localized positively charged atomic cores that are located at the lattice sites. There are three types of contributions to the cohesive energy of alkali metals: the interaction between the sea of electrons and the background of positive ions, the average kinetic energy of the electrons, and the exchange energy.

The interaction between the ion cores and the sea of electrons can be expressed as

$$\varepsilon_{el} = - \int d\mathbf{r} n(\mathbf{r}) \sum_i \frac{e^2}{|\mathbf{r} - \mathbf{R}_i|} + \frac{e^2}{2} \sum_{i \neq j} \frac{1}{|\mathbf{R}_i - \mathbf{R}_j|} + \frac{1}{2} \int d\mathbf{r}_1 d\mathbf{r}_2 \frac{e^2 n(\mathbf{r}_1) n(\mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|}, \quad (6.28)$$

where $n(\mathbf{r})$ is the electron density. We note that the first term in Eq. (6.28) is the sum of the attractive Coulomb interaction between the electrons and the ions; the second term is the sum of the repulsive interaction between the positively charged ions of charge e at the lattice sites \mathbf{R}_i and \mathbf{R}_j (the factor 1/2 prevents double counting); and the third term is the direct electron–electron interaction term that is a function of the electron densities $n(\mathbf{r}_1)$ and $n(\mathbf{r}_2)$. If $n(\mathbf{r})$ is taken as a constant, $n = N/V$. It can be easily shown by adapting a technique used similar to that for ionic crystals in Problem 6.4,

$$\frac{\varepsilon_{el}}{N} = -\frac{1}{2} \alpha \frac{e^2}{r_s}, \quad (6.29)$$

where α is the Madelung constant and r_s (defined in Chapter 3) is the free space around each electron in an electron gas,

$$r_s = \left(\frac{3V}{4\pi N} \right)^{1/3}. \quad (6.30)$$

We also showed in Chapter 3 that the average kinetic energy of the electrons is given by

$$\frac{\epsilon_k}{N} = \frac{3}{5} \epsilon_F = \frac{3\hbar^2 k_F^2}{10m} = \frac{3\hbar^2}{10m} \left(\frac{9\pi}{4}\right)^{2/3} \frac{1}{r_s^2}. \quad (6.31)$$

The exchange term arises due to the fact that electrons at \mathbf{r}_1 and \mathbf{r}_2 flip places while interacting with each other. Because the wave function is antisymmetric, a negative sign is introduced due to this interaction. The exchange integral can be written as

$$\epsilon_{ex} = - \int \frac{e^2 d\mathbf{r}_1 d\mathbf{r}_2}{|\mathbf{r}_1 - \mathbf{r}_2|} \sum_{n < m} [\phi_n^*(\mathbf{r}_1) \phi_m^*(\mathbf{r}_2) \phi_n(\mathbf{r}_2) \phi_m(\mathbf{r}_1) \delta_{\chi_i \chi_j}], \quad (6.32)$$

where ϕ 's are the one-particle wave functions and χ 's are the spin index. In the jellium model, the exchange energy can be shown to be

$$\frac{\epsilon_{ex}}{N} = - \frac{3e^2}{4\pi} \left(\frac{9\pi}{4}\right)^{1/3} \frac{1}{r_s}. \quad (6.33)$$

Adding Eqs. (6.29), (6.31), and (6.33); using the value $\alpha = 1.792$ for fcc, bcc, and hcp lattices; expressing the results in terms of Bohr radius $a_0 = 0.529 \text{ \AA}$; and measuring the energy in units of electron volts per atom, we obtain

$$\frac{\epsilon}{N} = \left[\frac{-24.35}{(r_s/a_0)} + \frac{30.1}{(r_s/a_0)^2} - \frac{12.5}{(r_s/a_0)} \right] eV/atom. \quad (6.34)$$

The minimum of $\frac{\epsilon}{N}$ occurs when $\frac{r_s}{a_0} \approx 1.6$. However, for alkali metals, the observed values of $\frac{r_s}{a_0}$ are between 2 and 6. The significant difference between the theoretical value and the experimental results is due to the neglect of correlation energy in this derivation. The treatment of correlation energy is beyond the scope of the present discussions because they are treated by using quantum field theory. Qualitatively, one can summarize the effect of correlation by stating that the correlations tend to keep the electrons apart, thereby further decreasing the energy of the system derived in Eq. (6.34).

We will now formulate the semiclassical model of electron dynamics and then derive the Boltzmann equations, which are essential for understanding the study of solids.

6.9 THE SEMICLASSICAL MODEL

The semiclassical model predicts the position \mathbf{r} and the wave vector \mathbf{k} of each electron evolved in the presence of external electric field \mathbf{E} and magnetic field \mathbf{B} in the absence of collisions. The basic assumptions of the semiclassical model are as follows:

1. The band index n is a constant of motion, and there are no “interband transitions.”
2. The position of an electron in a crystal with inversion symmetry evolves according to

$$\dot{\mathbf{r}} = \mathbf{v}_n(\mathbf{k}) = \frac{1}{\hbar} \frac{\partial \epsilon_{n\mathbf{k}}}{\partial \mathbf{k}}. \quad (6.35)$$

3. The electron wave vector obeys the equation of motion

$$\hbar \dot{\mathbf{k}} = -e\mathbf{E}(\mathbf{r}, t) - \frac{e}{c} \dot{\mathbf{r}} \times \mathbf{B}(\mathbf{r}, t), \quad (6.36)$$

where $\mathbf{E}(\mathbf{r}, t)$ and $\mathbf{B}(\mathbf{r}, t)$ are electric and magnetic fields that may vary spatially. Eqs. (6.35) and (6.36) can be derived from the Lagrangian formulation in classical mechanics as follows (see Symon¹⁰).

If the forces acting on a dynamical system depend on the velocities, we can define a function $U(q_1, q_2, \dots, q_f; \dot{q}_1, \dot{q}_2, \dots, \dot{q}_f, t)$, called the velocity-dependent potential (which includes the ordinary potential energy V), such that the generalized force Q_k associated with the coordinate q_k is given by

$$Q_k = \frac{d}{dt} \frac{\partial U}{\partial \dot{q}_k} - \frac{\partial U}{\partial q_k}, \quad k = 1, \dots, f. \quad (6.37)$$

The Lagrangian function is defined as

$$L = T - U, \quad (6.38)$$

and the equations of motion can be written as

$$\frac{d}{dt} \frac{\partial L}{\partial \dot{q}_k} - \frac{\partial L}{\partial q_k} = 0. \quad (6.39)$$

If we consider a system described in terms of a fixed system of coordinates, the kinetic energy T is a homogeneous quadratic function of the generalized velocities $\dot{q}_1, \dot{q}_2, \dots, \dot{q}_n$, we obtain from Euler's theorem,

$$\sum_{k=1}^f \dot{q}_k \frac{\partial T}{\partial \dot{q}_k} = 2T. \quad (6.40)$$

If V , the potential energy, is a function of the coordinates q_1, q_2, \dots, q_f , the total energy from Eqs. (6.40) and (6.41) is

$$E = T + V. \quad (6.41)$$

The Hamiltonian function is defined as

$$H = \sum_{k=1}^f p_k \dot{q}_k - L. \quad (6.42)$$

We can also write

$$\begin{aligned} dL &= \sum_{k=1}^f \left(\frac{\partial L}{\partial \dot{q}_k} d\dot{q}_k + \frac{\partial L}{\partial q_k} dq_k \right) + \frac{\partial L}{\partial t} dt \\ &= \sum_{k=1}^f (p_k d\dot{q}_k + \dot{p}_k dq_k) + \frac{\partial L}{\partial t} dt. \end{aligned} \quad (6.43)$$

From Eqs. (6.42) and (6.43), we obtain

$$dH = \sum_{k=1}^f (\dot{q}_k dp_k - \dot{p}_k dq_k) - \frac{\partial L}{\partial t} dt. \quad (6.44)$$

Thus, we obtain

$$\dot{q}_k = \frac{\partial H}{\partial p_k} \text{ and } \dot{p}_k = -\frac{\partial H}{\partial q_k}, \quad k = 1, \dots, f, \quad (6.45)$$

Eq. (6.42) can be written in the generalized form that whenever there is a Lagrangian $L(\mathbf{Q}, \dot{\mathbf{Q}})$, it is also possible to derive a Hamiltonian, using the formulae

$$H = \sum_l \dot{Q}_l P_l - L \quad (6.46)$$

and

$$P_l = \frac{\partial L}{\partial \dot{Q}_l}. \quad (6.47)$$

Here, the Q 's are the three components of \mathbf{r}_c and the three components of \mathbf{k}_c (the subscript c is for classical values that we will drop in the future).

In an electromagnetic field, the electromagnetic force on an electron of charge $-e$ can be written as

$$\mathbf{F} = -e\mathbf{E} - \frac{e}{c}\mathbf{V} \times \mathbf{B}. \quad (6.48)$$

The Hamiltonian can also be written by replacing the Hamiltonian in a pure perfect crystal lattice by an equivalent Hamiltonian operator $\varepsilon_n(-i\nabla)$, where n is the band index. Thus, the electron is treated as free because the effect of the lattice potential is included in $\varepsilon_n(-i\nabla)$, the modified kinetic energy. If the potential of the external field is $U(\mathbf{r})$, the equivalent Hamiltonian operator can be written in the alternate form,

$$H(\mathbf{r}, \mathbf{p}) = \varepsilon_n(-i\nabla) + U(\mathbf{r}). \quad (6.49)$$

According to the quantum mechanical formulation, the Hamiltonian operator is obtained by replacing the classical momentum variable \mathbf{p} by $-i\hbar\nabla$ in the classical Hamiltonian function. Thus, by reversing the steps, we obtain the equivalent classical Hamiltonian from Eq. (6.49) by replacing $-i\nabla$ by \mathbf{p}/\hbar ,

$$H(\mathbf{r}, \mathbf{p}) = \varepsilon_n(\mathbf{p}/\hbar) + U(\mathbf{r}). \quad (6.50)$$

Here, the basic assumption is that the energy functions $\varepsilon_n(\mathbf{k})$ are known from band structure calculations, and thus, there is no need to include the explicit form of the periodic potential of the ions.

The equations of motion can be written in the canonical Hamiltonian form (Eq. 6.45),

$$\dot{\mathbf{r}} = \frac{\partial H}{\partial \mathbf{p}}, \quad (6.51)$$

and

$$\dot{\mathbf{p}} = -\frac{\partial H}{\partial \mathbf{r}}. \quad (6.52)$$

From Eqs. (6.50) and (6.51), we obtain

$$\dot{\mathbf{r}} \equiv \mathbf{v}_n(\mathbf{k}) = \frac{\partial H}{\partial \mathbf{p}} = \frac{\partial}{\partial \mathbf{p}} \{ \varepsilon_n(\mathbf{p}/\hbar) + U(\mathbf{r}) \} = \frac{\partial \varepsilon_n(\mathbf{p}/\hbar)}{\partial \mathbf{p}} = \frac{1}{\hbar} \frac{\partial \varepsilon_n(\mathbf{k})}{\partial \mathbf{k}}. \quad (6.53)$$

From Eqs. (6.48), (6.50), and (6.52), we obtain

$$\dot{\mathbf{p}} = -\frac{\partial H}{\partial \mathbf{r}} = -\frac{\partial U}{\partial \mathbf{r}} = \mathbf{F} = -e \left[\mathbf{E}(\mathbf{r}, t) + \frac{1}{c} \mathbf{v}_n(\mathbf{k}) \times \mathbf{B}(\mathbf{r}, t) \right]. \quad (6.54)$$

An alternate way to approach the problem is by defining the vector and scalar potentials \mathbf{A} and ϕ as

$$\mathbf{B} = \nabla \times \mathbf{A} \quad (6.55)$$

and

$$\mathbf{E} = -\nabla \phi - \frac{1}{c} \frac{\partial \mathbf{A}}{\partial t}. \quad (6.56)$$

From Eqs. (6.48), (6.55), and (6.56), we can write \mathbf{F} as

$$\mathbf{F} = e \nabla \phi + \frac{e}{c} \frac{\partial \mathbf{A}}{\partial t} - \frac{e}{c} \nabla (\mathbf{v} \cdot \mathbf{A}). \quad (6.57)$$

One can show from Eqs. (6.41) and (6.42) that the Hamiltonian for the electrons in the n th band can be written as

$$H(\mathbf{r}, \mathbf{p}) = \varepsilon_n \left(\frac{1}{\hbar} \left[\mathbf{p} + \frac{e}{c} \mathbf{A}(\mathbf{r}, t) \right] \right) - e \phi(\mathbf{r}, t) \quad (6.58)$$

and

$$\hbar \dot{\mathbf{k}} = -e \mathbf{E} - \frac{e \mathbf{v}}{c} \times \mathbf{B}, \quad (6.59)$$

where the variables $\hbar \mathbf{k}$ are defined as

$$\hbar \mathbf{k} = \mathbf{p} + \frac{e}{c} \mathbf{A}(\mathbf{r}, t). \quad (6.60)$$

The canonical crystal momentum \mathbf{p} (which is the canonical momentum in the Hamiltonian formulation) can be written as

$$\mathbf{p} = \hbar \mathbf{k} - \frac{e}{c} \mathbf{A}(\mathbf{r}, t). \quad (6.61)$$

6.10 LIOUVILLE'S THEOREM

We will now briefly discuss Liouville's theorem before proceeding further. The configuration and the motion of a system is specified by the coordinates and momenta, $q_1, q_2, \dots, q_f; p_1, p_2, \dots, p_f$. The $2f$ -dimensional space is called the phase space of the mechanical system. The velocity of the phase points is given by the Hamilton equations in Eq. (6.45). The possible state of the mechanical system is represented by each phase point that is occupied by a "particle" that moves according to the equation of motion (Eq. 6.45). These particles trace out paths that represent the history of the mechanical system. The solutions of the equations of motion are uniquely determined because the positions and momenta are given, and hence, there is only one possible path through each phase point. Liouville's theorem states that the phase "particles" move as an incompressible fluid. The phase volume occupied by a set of "particles" is a constant. The proof of Liouville's theorem can be found in any standard book of classical mechanics (see Symon¹⁰).

6.11 BOLTZMANN EQUATION

The Boltzmann equation can be obtained by first considering the continuity equation. Here, we consider the motion of particles illustrated in Figure 6.19. We consider a large number of a conserved collection of identical particles at position x , moving with a velocity $v(x)$ and density $g(x)$. In a time Δt , the total number of particles moving into a small region dx minus the number of particles that are moving out is equal to

$$\Delta g(x) = v(x)g(x)\Delta t - v(x+dx)g(x+dx)\Delta t. \quad (6.62)$$

In the limit $\Delta t \rightarrow 0$,

$$\frac{\partial g}{\partial t} = -\frac{\partial}{\partial x}v(x)g(x, t). \quad (6.63)$$

Eq. (6.63) can be generalized for many variables as

$$\frac{\partial g}{\partial t} = -\sum_i \frac{\partial}{\partial x_i} v_i(\vec{x})g(\vec{x}, t). \quad (6.64)$$

We define $g_{\mathbf{rk}}(t)$ as the occupation number of electrons at time t with position \mathbf{r} and wave vector \mathbf{k} . Thus, $g_{\mathbf{rk}}(t)$ is the probability that a state is occupied at time t . From Eq. (6.64), we obtain

$$\frac{\partial g_{\mathbf{rk}}}{\partial t} = -\frac{\partial}{\partial \mathbf{r}} \cdot \dot{\mathbf{r}} g_{\mathbf{rk}} - \frac{\partial}{\partial \mathbf{k}} \cdot \dot{\mathbf{k}} g_{\mathbf{rk}}. \quad (6.65)$$

In an electromagnetic field, we have derived

$$\begin{aligned} \dot{\mathbf{r}} &= \frac{1}{\hbar} \frac{\partial \mathcal{E}}{\partial \mathbf{k}} = \mathbf{v}, \\ \hbar \dot{\mathbf{k}} &= -e\mathbf{E} - \frac{e}{c} \mathbf{v} \times \mathbf{B} = \mathbf{F}(\mathbf{r}, \mathbf{k}). \end{aligned} \quad (6.66)$$

\mathbf{E} does not depend on \mathbf{k} , and \mathbf{v} does not depend on \mathbf{r} . Further,

$$\frac{\partial}{\partial \mathbf{k}} \cdot \mathbf{v} \times \mathbf{B} = \mathbf{B} \cdot \frac{\partial}{\partial \mathbf{k}} \times \mathbf{v} = 0 \text{ because } \mathbf{v} = \frac{1}{\hbar} \frac{\partial \mathcal{E}}{\partial \mathbf{k}}. \quad (6.67)$$

From Eqs. (6.65) through (6.67), we obtain

$$\frac{\partial g}{\partial t} = -\dot{\mathbf{r}} \cdot \frac{\partial}{\partial \mathbf{r}} g - \dot{\mathbf{k}} \cdot \frac{\partial}{\partial \mathbf{k}} g. \quad (6.68)$$

From Eqs. (6.66) and (6.68), we obtain

$$\frac{\partial g}{\partial t} + \mathbf{v} \cdot \frac{\partial}{\partial \mathbf{r}} g + \frac{1}{\hbar} \mathbf{F} \cdot \frac{\partial}{\partial \mathbf{k}} g = 0. \quad (6.69)$$

However, there are momentum transfers caused by thermal fluctuations and impurities, which are not included in Eq. (6.69). To include these,

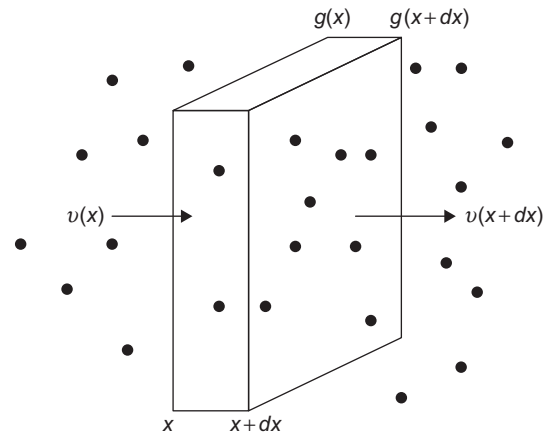


FIGURE 6.19

Density of particles at x and $x + dx$.

Boltzmann added a collision term to Eq. (6.69), and the resulting equation, known as the Boltzmann equation, can be written as

$$\frac{\partial g}{\partial t} + \mathbf{v} \cdot \frac{\partial}{\partial \mathbf{r}} g + \frac{1}{\hbar} \mathbf{F} \cdot \frac{\partial}{\partial \mathbf{k}} g = \left(\frac{\partial g}{\partial t} \right)_{coll}. \quad (6.70)$$

The terms on the left side of the equation are known as the drift terms, and the term on the right side is known as the collision term.

6.12 RELAXATION TIME APPROXIMATION

In thermal equilibrium, the distribution function reduces to the Fermi function

$$f_{\mathbf{r}\mathbf{k}} = \frac{1}{e^{\beta_{\mathbf{r}}(\epsilon_{\mathbf{k}} - \mu_{\mathbf{r}})} + 1}, \quad (6.71)$$

where $T(\mathbf{r})$ is the temperature at \mathbf{r} and $\mu_{\mathbf{r}}$ is the constant that produces the correct density $n(\mathbf{r})$. The collision term $\left(\frac{\partial g}{\partial t} \right)_{coll}$ in Eq. (6.70) must be such that the distribution g must relax toward thermal equilibrium. The simplest approximation for this to happen is the relaxation time approximation,

$$\left(\frac{\partial g}{\partial t} \right)_{coll} = -\frac{1}{\tau_e} (g_{\mathbf{r}\mathbf{k}} - f_{\mathbf{r}\mathbf{k}}), \quad (6.72)$$

where τ_e is defined as the relaxation time. In the simplest solutions, τ_e is considered as a constant τ .

If we approach the same problem in an alternate method, we can argue that because $g = g(\mathbf{r}, \mathbf{k}, t)$, we can write

$$\frac{dg}{dt} = \frac{\partial g}{\partial t} + \dot{\mathbf{r}} \cdot \frac{\partial g}{\partial \mathbf{r}} + \dot{\mathbf{k}} \cdot \frac{\partial g}{\partial \mathbf{k}}. \quad (6.73)$$

From Eqs. (6.70), (6.72), and (6.73), we obtain

$$\frac{dg}{dt} = -\frac{g - f}{\tau_e}. \quad (6.74)$$

Integrating Eq. (6.74), we obtain

$$g(\mathbf{r}, \mathbf{k}, t) = \int_{-\infty}^t dt' f(\mathbf{r}(t'), \mathbf{k}(t')) \frac{e^{-(t-t')/\tau_e}}{\tau_e}. \quad (6.75)$$

Here, $\mathbf{r}(t')$ and $\mathbf{k}(t')$, which are solutions of the semiclassical equations, evolve in time such that $\mathbf{r}(t) = \mathbf{r}$ and $\mathbf{k}(t) = \mathbf{k}$. Integrating Eq. (6.75) by parts, we obtain

$$g(\mathbf{r}, \mathbf{k}, t) = f(\mathbf{r}, \mathbf{k}) - \int_{-\infty}^t dt' e^{-(t-t')/\tau_e} \frac{d}{dt'} f(\mathbf{r}(t'), \mathbf{k}(t')). \quad (6.76)$$

Because f is the Fermi function, which is evaluated at local temperature and chemical potential,

$$\frac{d}{dt'} f(\mathbf{r}(t'), \mathbf{k}(t')) = \left(\dot{\mathbf{r}}(t') \cdot \frac{\partial}{\partial \mathbf{r}} + \dot{\mathbf{k}}(t') \cdot \frac{\partial}{\partial \mathbf{k}} \right) f(\mathbf{r}(t'), \mathbf{k}(t')). \quad (6.77)$$

From Eq. (6.71), we obtain

$$\frac{\partial f}{\partial \mathbf{r}} = \frac{\partial f}{\partial \varepsilon} \left[-\frac{\partial \mu}{\partial \mathbf{r}} - \frac{(\varepsilon - \mu)}{T} \frac{\partial T}{\partial \mathbf{r}} \right], \quad (6.78)$$

$$\frac{\partial f}{\partial \mathbf{k}} = \frac{\partial f}{\partial \varepsilon} \frac{\partial \varepsilon}{\partial \mathbf{k}} = \hbar \mathbf{v}_{\mathbf{k}} \frac{\partial f}{\partial \varepsilon}, \quad (6.79)$$

and

$$\frac{\partial f}{\partial \varepsilon} = -\frac{\partial f}{\partial \mu}. \quad (6.80)$$

In addition, from Eq. (6.66), we have

$$\dot{\mathbf{k}} \cdot \frac{\partial f}{\partial \mathbf{k}} = -e \mathbf{v}_{\mathbf{k}} \cdot \mathbf{E}. \quad (6.81)$$

Substituting Eqs. (6.77) through (6.81) in Eq. (6.76), we obtain

$$g(\mathbf{r}, \mathbf{k}, t) = f(\mathbf{r}, \mathbf{k}) - \int_{-\infty}^t dt' e^{-(t-t')/\tau_e} \mathbf{v}_{\mathbf{k}} \cdot \left[e \mathbf{E} + \frac{\partial \mu}{\partial \mathbf{r}} + \frac{\varepsilon_{\mathbf{k}} - \mu}{T} \frac{\partial T}{\partial \mathbf{r}} \right] \frac{\partial f(t')}{\partial \mu}. \quad (6.82)$$

Neglecting the time dependence of all terms except the exponential factor, the integral can be easily done, and we obtain

$$g(\mathbf{r}, \mathbf{k}) = f(\mathbf{r}, \mathbf{k}) - \tau_e \mathbf{v}_{\mathbf{k}} \cdot \left[e \mathbf{E} + \frac{\partial \mu}{\partial \mathbf{r}} + \frac{\varepsilon_{\mathbf{k}} - \mu}{T} \frac{\partial T}{\partial \mathbf{r}} \right] \frac{\partial f}{\partial \mu}. \quad (6.83)$$

The current density can be written as

$$\mathbf{J} = -2e \int e \mathbf{v}_{\mathbf{k}} g(\mathbf{k}) d\mathbf{k}, \quad (6.84)$$

which can be rewritten in the alternate form

$$\mathbf{J} = -2 \int e \mathbf{V}_{\mathbf{k}} f(\mathbf{k}) d\mathbf{k} - 2 \int e^2 \tau_e \mathbf{V}_{\mathbf{k}} (\mathbf{V}_{\mathbf{k}} \cdot \mathbf{E}) \frac{\partial f}{\partial \varepsilon} - \frac{e}{T} (\mathbf{K}_1 \cdot (-\nabla T)), \quad (6.85)$$

where

$$\mathbf{K}_n = \frac{1}{4\pi^2} \frac{\tau_e}{\hbar} \iint \mathbf{V}_{\mathbf{k}} \mathbf{V}_{\mathbf{k}} (\varepsilon - \mu)^n \left(-\frac{\partial f}{\partial \varepsilon_n} \right) \frac{dS}{v_{\mathbf{k}}} d\varepsilon \cdot (-\nabla T), \quad (6.86)$$

and we have used $\iint d\mathbf{k} = \frac{1}{8\pi^2} \iint \frac{dS}{\hbar v_{\mathbf{k}}} d\varepsilon$ for integration over a constant energy surface (Problem 6.7). Eq. (6.86) indicates that even if there were no electric field, the thermal gradient, ∇T , would give rise to an electric current. This is known as the thermo-electric effect, which we will discuss later. We note that Eq. (6.85) can be rewritten in the alternate form

$$\mathbf{J} = -2 \int e \mathbf{V}_{\mathbf{k}} f(\mathbf{k}) d\mathbf{k} + e^2 \mathbf{K}_0 \cdot \mathbf{E} - \frac{e}{T} \mathbf{K}_1 \cdot (-\nabla T). \quad (6.87)$$

6.13 ELECTRICAL CONDUCTIVITY

In an electric field \mathbf{E} , which is independent of time, there is no variation of g , f , μ , and T with position. We can rewrite Eq. (6.83) in the simpler form

$$g(\mathbf{k}) = f(\mathbf{k}) - \tau_e \mathbf{v}_k \cdot [e\mathbf{E}] \frac{\partial f}{\partial \mu}. \quad (6.88)$$

To calculate the electrical conductivity, we need to first calculate the current density,

$$\mathbf{J} = -2e \int e \mathbf{v}_k g(\mathbf{k}) d\mathbf{k}. \quad (6.89)$$

From Eqs. (6.88) and (6.89), we obtain

$$\mathbf{J} = -2 \int e \mathbf{v}_k f(\mathbf{k}) d\mathbf{k} - 2 \int e^2 \tau_e \mathbf{v}_k \cdot (\mathbf{v}_k \cdot \mathbf{E}) \frac{\partial f}{\partial \epsilon}, \quad (6.90)$$

where we have used the identity,

$$\frac{\partial f}{\partial \mu} = -\frac{\partial f}{\partial \epsilon}. \quad (6.91)$$

In Eq. (6.90), because f_k is the equilibrium Fermi distribution function,

$$-\int e \mathbf{v}_k f_k d\mathbf{k} \equiv 0. \quad (6.92)$$

From Eqs. (6.90) and (6.92), we obtain

$$\mathbf{J} = \frac{1}{4\pi^3} \iint e^2 \tau_e \mathbf{v}_k (\mathbf{v}_k \cdot \mathbf{E}) \left(-\frac{\partial f}{\partial \epsilon} \right) \frac{dS}{\hbar v_k} d\epsilon, \quad (6.93)$$

where we have changed an integral over a volume of \mathbf{k} space into integrations over surfaces of constant energy (Problem 6.7).

In a metal,

$$-\left(\frac{\partial f}{\partial \epsilon} \right) = \delta(\epsilon - \epsilon_F). \quad (6.94)$$

We obtain from Eqs. (6.93) and (6.94),

$$\mathbf{J} = \frac{1}{4\pi^3} \frac{e^2 \tau_e}{\hbar} \int \frac{\mathbf{v}_k \mathbf{v}_k dS_F}{v_k} \cdot \mathbf{E}. \quad (6.95)$$

The equation for electric conductivity tensor can be expressed as

$$\mathbf{J} = \sigma \cdot \mathbf{E}. \quad (6.96)$$

From Eqs. (6.95) and (6.96), we obtain

$$\sigma = \frac{1}{4\pi^3} \frac{e^2 \tau_e}{\hbar} \int \frac{\mathbf{v}_k \mathbf{v}_k dS_F}{v_k}. \quad (6.97)$$

In crystals with cubic symmetry, the conductivity tensor is a scalar and if \mathbf{E} and \mathbf{J} are both in the same x direction,

$$(\mathbf{v}_k \mathbf{v}_k \cdot \mathbf{E})_x = E v_x^2 = \frac{1}{3} v^2 E. \quad (6.98)$$

From Eqs. (6.97) and (6.98), we obtain

$$\sigma = \frac{e^2}{12\hbar\pi^3} \int \Lambda dS_F, \quad (6.99)$$

where Λ is the mean free path

$$\Lambda = \tau v. \quad (6.100)$$

6.14 THERMAL CONDUCTIVITY

The thermal conductivity experiment is usually done by keeping the specimen in an open circuit. This implies that the specimen has an electric field \mathbf{E} , but there is no electric current; i.e., $\mathbf{J} = 0$. From Eqs. (6.87) and (6.92), we have an electric field in the wire

$$\mathbf{E} = -\frac{1}{e} \mathbf{K}_0^{-1} \mathbf{K}_1 \frac{1}{T} \cdot \nabla T. \quad (6.101)$$

The thermal conductivity can be calculated from the total flux of heat (per unit volume)

$$\mathbf{U} = 2 \int f_k \{ \varepsilon(\mathbf{k}) - \mu \} \mathbf{v}_k d\mathbf{k}. \quad (6.102)$$

From Eqs. (6.83), (6.86), and (6.102), we obtain

$$\mathbf{U} = -e \mathbf{K}_1 \cdot \mathbf{E} + \frac{1}{T} \mathbf{K}_2 \cdot (-\nabla T). \quad (6.103)$$

From Eqs. (6.101) and (6.103), we obtain

$$\mathbf{U} = \frac{1}{T} (\mathbf{K}_1 \mathbf{K}_0^{-1} \mathbf{K}_1 \cdot \nabla T - \mathbf{K}_2 \cdot \nabla T), \quad (6.104)$$

which can be rewritten in the alternate form

$$\mathbf{U} = \frac{1}{T} (\mathbf{K}_2 - \mathbf{K}_1 \mathbf{K}_0^{-1} \mathbf{K}_1) \cdot (-\nabla T). \quad (6.105)$$

The thermal conductivity κ is defined as

$$\mathbf{U} = \kappa \cdot (-\nabla T). \quad (6.106)$$

If we neglect the second term of Eq. (6.105) for metals, we obtain from Eqs. (6.105) and (6.106)

$$\kappa \approx \frac{1}{T} \mathbf{K}_2. \quad (6.107)$$

Using the expansion (Problem 6.8)

$$\int F(\varepsilon) d\varepsilon \left(\frac{-\partial f_0}{\partial \varepsilon} \right) d\varepsilon = F(\mu) + \frac{1}{6} \pi^2 (k_B T)^2 \left[\frac{\partial^2 F(\varepsilon)}{\partial \varepsilon^2} \right]_{\varepsilon=\mu} + \dots, \quad (6.108)$$

and $\sigma = e^2 K_0$ [from Eq. (6.87) under isothermal conditions], we can write

$$\kappa = \frac{\pi^2}{3} \frac{k^2}{e^2} T \sigma. \quad (6.109)$$

This is also known as the Wiedemann–Franz law.

6.15 WEAK SCATTERING THEORY OF CONDUCTIVITY

6.15.1 Relaxation Time and Scattering Probability

We will now consider a more realistic description of the collisions by assuming that there is a scattering probability

$$\frac{W_{\mathbf{k},\mathbf{k}'} d\mathbf{k}' dt}{(2\pi)^3}, \quad (6.110)$$

which is the probability in an infinitesimal time interval dt that an electron with wave vector \mathbf{k} is scattered into any one of the group of levels with the same spin in an infinitesimal k -space volume element $d\mathbf{k}'$ about \mathbf{k}' . These levels are not forbidden by the exclusion principle in the sense that they are not occupied. Because, by definition, $g(\mathbf{k}')$ is the fraction of levels in the volume element $d\mathbf{k}'$ about \mathbf{k}' that are occupied, the fraction that is unoccupied is $1-g(\mathbf{k}')$, and hence, the total probability per unit time for a collision (which is precisely the definition of $\frac{1}{\tau(\mathbf{k})}$), is given by (from Eq. 6.110)

$$\frac{1}{\tau(\mathbf{k})} = \int \frac{d\mathbf{k}'}{(2\pi)^3} W_{\mathbf{k},\mathbf{k}'} [1-g(\mathbf{k}')]. \quad (6.111)$$

We note that $\tau(\mathbf{k})$ is not the usual relaxation time defined in Eq. (6.72) but explicitly depends on the distribution function $g(\mathbf{k})$.

6.15.2 The Collision Term

The number of electrons scattered out of the volume element $d\mathbf{k}$ about \mathbf{k} in time interval dt is given by

$$dn_{out} = - \left(\frac{dg(\mathbf{k})}{dt} \right)_{out} \frac{d\mathbf{k}}{(2\pi)^3} dt. \quad (6.112)$$

The total number of electrons per unit volume in $d\mathbf{k}$ about \mathbf{k} that suffer a collision in time interval dt is also obtained from Eq. (6.111) as

$$dn_{out} = \frac{dt}{\tau(\mathbf{k})} g(\mathbf{k}) \frac{d\mathbf{k}}{(2\pi)^3}. \quad (6.113)$$

From Eqs. (6.111) through (6.113), we obtain

$$\left(\frac{dg(\mathbf{k})}{dt} \right)_{out} = - \frac{g(\mathbf{k})}{\tau(\mathbf{k})} = -g(\mathbf{k}) \int \frac{d\mathbf{k}'}{(2\pi)^3} W_{\mathbf{k},\mathbf{k}'} [1-g(\mathbf{k}')]. \quad (6.114)$$

The electrons not only scatter out of the level \mathbf{k} , but are also scattered into it from other levels. By making a similar argument as before (see Problem 6.8), we obtain

$$\left(\frac{dg(\mathbf{k})}{dt}\right)_{in} = \frac{g^0(\mathbf{k})}{\tau(\mathbf{k})} = (1 - g(\mathbf{k})) \int \frac{d\mathbf{k}'}{(2\pi)^3} W_{\mathbf{k}',\mathbf{k}} g(\mathbf{k}'). \quad (6.115)$$

If we define

$$\left(\frac{dg(\mathbf{k})}{dt}\right)_{coll} = \left(\frac{dg(\mathbf{k})}{dt}\right)_{in} + \left(\frac{dg(\mathbf{k})}{dt}\right)_{out}, \quad (6.116)$$

we obtain from Eqs. (6.114) through (6.116)

$$\left(\frac{dg(\mathbf{k})}{dt}\right)_{coll} = \int \frac{d\mathbf{k}'}{(2\pi)^3} \{g(\mathbf{k}')[1 - g(\mathbf{k})]W_{\mathbf{k}',\mathbf{k}} - g(\mathbf{k})[1 - g(\mathbf{k}')]W_{\mathbf{k},\mathbf{k}'}\}. \quad (6.117)$$

In the relaxation-time approximation, Eq. (6.104) can be rewritten as

$$\left(\frac{dg(\mathbf{k})}{dt}\right)_{coll} = \left[\frac{g^0(\mathbf{k}) - g(\mathbf{k})}{\tau(\mathbf{k})}\right]. \quad (6.118)$$

6.15.3 Impurity Scattering

In any real specimen, at very low temperatures, the main source of collisions would be impurities because the scattering of electrons by the thermal vibrations of the ions and the electron–electron scattering become increasingly weak as the temperature is lowered. This impurity–electron scattering will be elastic as long as the energy gap between the impurity ground state and the excited state is large compared to $k_B T$. We consider the case of elastic scattering by fixed substitutional impurities that are located at random lattice sites \mathbf{R} in the crystal. The basic assumptions made in this calculation are as follows:

1. There is a relatively small number of impurities in the crystal, such that one can consider the electrons to be interacting with one impurity at a time.
2. There are very few excited impurity ions that lose energy to electrons in collisions.
3. There are very few empty electronic levels that are low enough in energy to receive an electron after it has lost enough energy to excite an impurity ion.
4. The scattering potential U , which describes the interaction between an electron and a single impurity, is spherically symmetrical and weak.
5. The energies of the occupied electronic states $\varepsilon_{\mathbf{k}}$ are isotropic and depend only on the magnitude of \mathbf{k} .
6. The probability of scattering between two levels \mathbf{k} and \mathbf{k}' vanishes unless $k = k'$ and depends on the common value of their energies and on the angle between \mathbf{k} and \mathbf{k}' .

The rate at which an electron at \mathbf{k} makes a transition to \mathbf{k}' is given by Fermi's golden rule (see, for example, Goswami⁴),

$$W_{\mathbf{k},\mathbf{k}'} = \frac{2\pi}{\hbar} \delta(\varepsilon(\mathbf{k}) - \varepsilon(\mathbf{k}')) |\langle \mathbf{k} | U_{\mathbf{r}}(\mathbf{r}) | \mathbf{k}' \rangle|^2, \quad (6.119)$$

where

$$U_t(\mathbf{r}) = \sum_{\mathbf{R}} U(\mathbf{r} - \mathbf{R}). \quad (6.120)$$

Here, $U(\mathbf{r} - \mathbf{R})$ are spherically symmetric potentials centered at sites \mathbf{R} . In simple cases, one can write

$$U_t(\mathbf{r}) = n_i U(\mathbf{r}), \quad (6.121)$$

where n_i is the number of impurities per unit volume. In more rigorous derivations, one can consider $U_t(\mathbf{r})$ as the sum of pseudopotentials of impurity atoms added to a perfect crystal or of atoms dislocated from their regular positions in the crystal. Here,

$$\langle \mathbf{k} | U | \mathbf{k}' \rangle = \int d\mathbf{r} \psi_{n\mathbf{k}}^*(\mathbf{r}) U(\mathbf{r}) \psi_{n\mathbf{k}}(\mathbf{r}), \quad (6.122)$$

and the Bloch functions $\psi_{n\mathbf{k}}(\mathbf{r})$ are normalized,

$$\int_{cell} d\mathbf{r} |\psi_{n\mathbf{k}}(\mathbf{r})|^2 = v_{cell}. \quad (6.123)$$

We note from Eq. (6.119) that $W_{\mathbf{k},\mathbf{k}'} = 0$ unless $\varepsilon(\mathbf{k}) = \varepsilon(\mathbf{k}')$. In addition, $W_{\mathbf{k},\mathbf{k}'}$ is independent of the electron distribution function in the independent electron approximation. Further, because $U(\mathbf{r})$ is spherically symmetric, $W_{\mathbf{k},\mathbf{k}'}$ depends only on the angle between \mathbf{k} and \mathbf{k}' , and therefore, we obtain

$$W_{\mathbf{k},\mathbf{k}'} = W_{\mathbf{k}',\mathbf{k}}. \quad (6.124)$$

This symmetry is also known as “detailed balancing.” From Eqs. (6.117) and (6.124), we obtain

$$\left(\frac{\partial g(\mathbf{k})}{\partial t} \right)_{coll} = - \int \frac{d\mathbf{k}'}{(2\pi)^3} W_{\mathbf{k},\mathbf{k}'} [g(\mathbf{k}) - g(\mathbf{k}')]. \quad (6.125)$$

We further assume that the solution of the Boltzmann equation g has the form

$$g_{\mathbf{k}} = f_{\mathbf{k}} + \mathbf{a}(\varepsilon) \cdot \mathbf{k}, \quad (6.126)$$

where \mathbf{a} is a vector that depends on \mathbf{k} only through its magnitude $\varepsilon(\mathbf{k})$ and $f_{\mathbf{k}}$ is the local equilibrium distribution function (Fermi function). We define the relaxation time through

$$\frac{1}{\tau_{\varepsilon}} [g(\mathbf{k}) - f(\mathbf{k})] = \int \frac{d\mathbf{k}'}{(2\pi)^3} W_{\mathbf{k},\mathbf{k}'} [g(\mathbf{k}) - g(\mathbf{k}')]. \quad (6.127)$$

Because $W_{\mathbf{k},\mathbf{k}'}$ vanishes unless $\varepsilon(\mathbf{k}) = \varepsilon(\mathbf{k}')$, $\mathbf{a}(\varepsilon) = \mathbf{a}(\varepsilon')$ and we obtain from Eqs. (6.126) and (6.127),

$$\frac{1}{\tau_{\varepsilon}} \mathbf{a}(\varepsilon) \cdot \mathbf{k} = \mathbf{a}(\varepsilon) \cdot \int \frac{d\mathbf{k}'}{(2\pi)^3} W_{\mathbf{k},\mathbf{k}'} (\mathbf{k} - \mathbf{k}'). \quad (6.128)$$

From Eq. (6.128) and Eq. (3) of Problem 6.8, we obtain

$$\frac{1}{\tau_{\varepsilon}} = \int \frac{d\mathbf{k}'}{(2\pi)^3} W_{\mathbf{k},\mathbf{k}'} (1 - \hat{\mathbf{k}} \cdot \hat{\mathbf{k}}'). \quad (6.129)$$

When \mathbf{k} and \mathbf{k}' are on the Fermi surface, $k = k' = k_F$. If we define

$$\mathbf{q} = \mathbf{k} - \mathbf{k}', \quad (6.130)$$

we obtain

$$q^2 = 2k_F^2(1 - \hat{\mathbf{k}} \cdot \hat{\mathbf{k}}') \quad (6.131)$$

or

$$(1 - \hat{\mathbf{k}} \cdot \hat{\mathbf{k}}') = 2 \left(\frac{q}{2k_F} \right)^2. \quad (6.132)$$

We can now write from Eqs. (6.119) and (6.130),

$$W_{\mathbf{k}, \mathbf{k}'} = \frac{2\pi}{\hbar} \left| \int \frac{d\mathbf{r}}{V} e^{i\mathbf{q} \cdot \mathbf{r}} \sum_{\mathbf{R}} U(\mathbf{r} - \mathbf{R}) \right|^2 \delta(\varepsilon_F - \varepsilon(\mathbf{k}')). \quad (6.133)$$

Eq. (6.133) can be rewritten in the alternate form

$$W_{\mathbf{k}, \mathbf{k}'} = \frac{2\pi}{\hbar} \frac{1}{V^2} \left| \sum_{\mathbf{R}} e^{i\mathbf{q} \cdot \mathbf{R}} \int d\mathbf{r} e^{i\mathbf{q} \cdot \mathbf{r}} U(\mathbf{r}) \right|^2 \delta(\varepsilon_F - \varepsilon(\mathbf{k}')). \quad (6.134)$$

We define the static structure factor

$$S(\mathbf{q}) = \frac{1}{N_s} \left| \sum_{\mathbf{R}} e^{i\mathbf{q} \cdot \mathbf{R}} \right|^2, \quad (6.135)$$

and the Fourier transform of the scattering potential $U(\mathbf{r})$

$$U(\mathbf{q}) = \int d\mathbf{r} e^{i\mathbf{q} \cdot \mathbf{r}} U(\mathbf{r}), \quad (6.136)$$

where N_s is the number of scatterers. From Eqs. (6.130) and (6.134) through (6.136), we obtain

$$W_{\mathbf{k}, \mathbf{k}'} = \frac{2\pi N_s}{\hbar V^2} S(\mathbf{q}) |U(\mathbf{q})|^2 \delta(\varepsilon_F - \varepsilon(|\mathbf{k} - \mathbf{q}|)). \quad (6.137)$$

Substituting Eqs. (6.132) and (6.137) in Eq. (6.129), we obtain

$$\frac{1}{\tau_e} = \frac{2\pi N_s}{\hbar V} \int \frac{d\mathbf{k}'}{(2\pi)^3} S(\mathbf{q}) |U(\mathbf{q})|^2 \delta(\varepsilon_F - \varepsilon(|\mathbf{k} - \mathbf{q}|)) 2 \left(\frac{q}{2k_F} \right)^2. \quad (6.138)$$

Eq. (6.138) can be rewritten in the alternate form,

$$\frac{1}{\tau_e} = \frac{N_s}{\hbar V} \frac{1}{4\pi} \int \frac{q^4}{k_F^2} dq S(\mathbf{q}) |U(\mathbf{q})|^2 \int_{-1}^1 d(\cos \theta) \delta\left(\varepsilon_F - \varepsilon\left(\sqrt{k_F^2 + q^2 - 2k_F q \cos \theta}\right)\right). \quad (6.139)$$

We also use the results of the angular integration,

$$\int_{-1}^1 d(\cos \theta) \delta\left(\varepsilon_F - \varepsilon\left(\sqrt{k_F^2 + q^2 - 2k_F q \cos \theta}\right)\right) = \frac{\theta(2k_F - q)}{q(\partial\varepsilon/\partial k_F)}, \quad (6.140)$$

where $\theta(x-a)$ is the step function,

$$\begin{aligned}\theta(x-a) &= 1, & \text{for } x > a \\ &= 0, & \text{for } x < a.\end{aligned}\quad (6.141)$$

The step function is related to the Dirac delta function,

$$\delta(x-a) = d\theta(x-a)/dx. \quad (6.142)$$

From Eqs. (6.139) through (6.142), we obtain (Problem 6.10)

$$\frac{1}{\tau_e} = \frac{1}{4\pi\hbar^2 k_F^2 v_F} \frac{N_s}{V} \int_0^{2k_F} dq q^3 S(\mathbf{q}) |U(\mathbf{q})|^2. \quad (6.143)$$

The resistivity (in the relaxation time approximation) is given by

$$\rho = \frac{m}{ne^2\tau_e} = \frac{3\pi N_s}{4e^2\hbar v_F^2 k_F^4 V} \int_0^{2k_F} dq q^3 S(\mathbf{q}) |U(\mathbf{q})|^2. \quad (6.144)$$

6.16 RESISTIVITY DUE TO SCATTERING BY PHONONS

We consider only one atom per unit cell that is located at the lattice site (its equilibrium position) at zero temperature. At a finite temperature, the deviation of the atom or ion from equilibrium position is (from Chapter 2)

$$\mathbf{u}_l = \mathbf{r} - \mathbf{R}_l - \mathbf{d}. \quad (6.145)$$

The static structure factor is defined in Eq. (1.64). We obtain

$$\sum_l e^{i\mathbf{q}\cdot(\mathbf{R}_l+\mathbf{u}_l)} = \sum_l e^{i\mathbf{q}\cdot\mathbf{R}_l} [1 + i\mathbf{q}\cdot\mathbf{u}_l + \dots]. \quad (6.146)$$

The structure factor of the unperturbed lattice, $\sum_l e^{i\mathbf{q}\cdot\mathbf{R}_l}$, has no contribution to the resistivity. From Eqs. (2.158) and (2.182), we have the Fourier transform of

$$\hat{\mathbf{u}}_l = \frac{1}{\sqrt{MN}} \sum_{\mathbf{k}} \hat{\mathbf{e}}_{\rightarrow} \hat{Q}_{\rightarrow} e^{i\mathbf{k}\cdot\mathbf{R}_l}, \quad (6.147)$$

where

$$\hat{Q}_{\rightarrow} = \left[\frac{\hbar}{2\omega_{\rightarrow}} \right]^{\frac{1}{2}} \left(\hat{a}_{\rightarrow} + \hat{a}_{\rightarrow}^{\dagger} \right). \quad (6.148)$$

We can rewrite from Eqs. (6.147) and (6.148),

$$\mathbf{u}_l = \frac{1}{\sqrt{N}} \sum_{\mathbf{k}\lambda} [\hat{u}_{\mathbf{k}\lambda} e^{i\mathbf{k}\cdot\mathbf{R}_l} + \hat{u}_{\mathbf{k}\lambda}^{\dagger} e^{-i\mathbf{k}\cdot\mathbf{R}_l}], \quad (6.149)$$

where

$$\hat{u}_{\mathbf{k}\lambda} = \sqrt{\frac{\hbar}{2M\omega_{\vec{k}\lambda}}} \vec{\epsilon}_{\mathbf{k}\lambda} \hat{a}_{\mathbf{k}\lambda}. \quad (6.150)$$

From Eqs. (6.146) and (6.149), we obtain

$$\sum_l e^{i\mathbf{q} \cdot (\mathbf{R}_l + \mathbf{u}_l)} = \frac{1}{\sqrt{N}} \sum_{\mathbf{k}} i [\hat{u}_{\mathbf{k}} \cdot \mathbf{q} e^{i(\mathbf{k}+\mathbf{q}) \cdot \mathbf{R}_l} + \hat{u}_{\mathbf{k}}^\dagger \cdot \mathbf{q} e^{i(\mathbf{q}-\mathbf{k}) \cdot \mathbf{R}_l}], \quad (6.151)$$

where only the longitudinal mode ($\mathbf{q} \parallel \mathbf{k}$) is retained. Because

$$\sum_l e^{i(\mathbf{q}+\mathbf{k}) \cdot \mathbf{R}_l} = N \delta_{\mathbf{K}, \mathbf{q}+\mathbf{k}}, \quad (6.152)$$

Eq. (6.151) can be rewritten in the alternate form

$$\sum_l e^{i\mathbf{q} \cdot (\mathbf{R}_l + \mathbf{u}_l)} = \sqrt{N} \sum_{\mathbf{k}} i [\hat{u}_{\mathbf{k}} \cdot \mathbf{q} \delta_{\mathbf{K}, \mathbf{q}+\mathbf{k}} + \hat{u}_{\mathbf{k}}^\dagger \cdot \mathbf{q} \delta_{\mathbf{K}, \mathbf{q}-\mathbf{k}}]. \quad (6.153)$$

In the N-process (normal scattering), $\mathbf{K} = 0$ and $\mathbf{q} = \mathbf{k}$; i.e., the wave vectors of electrons and phonons are equal. In the Umklapp process (U-process), $\mathbf{K} \neq 0$. In the following discussion, we will consider the N-process.

From Eqs. (6.135) and (6.153), we obtain

$$\begin{aligned} S(\mathbf{q}) &= \frac{1}{N} \sum_l \langle |e^{i\mathbf{q} \cdot (\mathbf{R}_l + \mathbf{u}_l)}|^2 \rangle \\ &\approx \langle |\hat{u}_{\mathbf{q}}^\dagger \cdot \mathbf{q}|^2 \rangle, \end{aligned} \quad (6.154)$$

because $\delta_{0, \mathbf{q}-\mathbf{k}} \neq 0$ can be nonzero only when both \mathbf{k} and \mathbf{q} are in the first Brillouin zone.

From Eqs. (6.137) and (6.141), we obtain

$$S(\mathbf{q}) = \frac{\hbar}{2M\omega_{\mathbf{q}}} |\vec{\epsilon} \cdot \vec{q}|^2 \langle \hat{a}_{\mathbf{q}} \hat{a}_{\mathbf{q}}^\dagger + \hat{a}_{\mathbf{q}}^\dagger \hat{a}_{\mathbf{q}} \rangle, \quad (6.155)$$

where $\vec{\epsilon}$ is the polarization vector of the longitudinal mode. $S(\mathbf{q})$ can be rewritten in the alternate form,

$$S(\mathbf{q}) = \frac{\hbar q^2}{2M\omega_{\mathbf{q}}} (2n_{\mathbf{q}} + 1). \quad (6.156)$$

From Eq. (6.144) and (6.156), we obtain

$$\rho = \frac{3\pi}{e^2 \hbar v_F^2} \left(\frac{N_s}{V} \right) \frac{1}{4k_F^4} \int_0^{2k_F} dq q^3 \frac{\hbar q^2}{2M\omega_{\mathbf{q}}} (2n_{\mathbf{q}} + 1) |U(q)|^2. \quad (6.157)$$

It can be shown after some algebra that ρ can be written as

$$\rho = \frac{3\pi}{e^2 \hbar v_F^2} \left(\frac{N_s}{V} \right) \frac{1}{4k_F^4} \frac{\hbar}{2Mc} \left(\frac{k_B T}{\hbar c} \right)^5 \int_0^{2\Theta/T} dz z^4 \frac{e^z + 1}{e^z - 1} \left| U \left(\frac{zk_F T}{\Theta} \right) \right|^2. \quad (6.158)$$

In Eq. (6.158), $\Theta = \frac{\hbar k_F c}{k_B}$; $z = \frac{q\Theta}{k_F T}$, Θ is the Debye temperature, c is the velocity of the longitudinal wave, and M is the mass of the ion. At large temperatures, ρ is linear in T , while at very low temperatures, $\rho \sim T^5$.

PROBLEMS

6.1. Derive Eq. (6.10) from Eq. (6.9).

6.2. Two noble gas atoms of charge Ze , each surrounded by Z electrons, are at $\mathbf{0}$ and \mathbf{R} , where \mathbf{R} is so large that there is no interaction between the electronic charges around the two nuclei. The Hamiltonian of the system can be written as

$$H = H_1 + H_2 + H_I, \quad (1)$$

where the interaction Hamiltonian H_I is given by

$$H_I = e^2 \left[\frac{Z^2}{R} - \sum_{j=1}^Z \left(\frac{Z}{|\mathbf{r}_j^{(1)} - \mathbf{R}|} + \frac{Z}{r_j^{(2)}} \right) + \sum_{i,j=1}^Z \frac{1}{|\mathbf{r}_i^{(1)} - \mathbf{r}_j^{(2)}|} \right]. \quad (2)$$

- a. Show that the effect of the first-order perturbation is exponentially small because the ground state of the two atoms is spherically symmetric and the charge distributions hardly overlap because they are far apart.
- b. Show that in the second-order perturbation theory, all contributions to the relevant integrals are small unless $|\mathbf{r}_j^{(1)}| \ll R$ and $|\mathbf{r}_j^{(2)} - \mathbf{R}| \ll R$. Thus, one can expand Eq. (2) as

$$H_I \approx -\frac{e^2}{R^3} \sum_{i,j} \left[\frac{3(\mathbf{r}_j^{(1)} \cdot \mathbf{R})(\mathbf{r}_i^{(2)} - \mathbf{R})}{R^2} - \mathbf{r}_j^{(1)} \cdot (\mathbf{r}_i^{(2)} - \mathbf{R}) \right]. \quad (3)$$

- c. Hence, show that the leading term in the second-order perturbation theory, $\Delta E = \langle 0 | H_I | 0 \rangle + \sum_k \frac{|\langle 0 | H_I | k \rangle|^2}{E_0 - E_k}$, varies as $-\frac{1}{R^6}$.

This is essentially the quantum theory of the van der Waals force.

6.3. Derive Eq. (6.17) for the Bulk modulus at equilibrium.

6.4. We have derived in Eq. (6.21)

$$u^{coul}(d) = -\frac{e^2}{d} \left\{ 1 + \sum_{i \neq 0} \left(\frac{d}{|\mathbf{R}_i + \mathbf{d}|} - \frac{d}{R_i} \right) \right\}, \quad (1)$$

Rewrite the expression as

$$u^{coul}(d) = \frac{e^2}{d} \{ dS(0) - dS(\mathbf{d}) - 1 \}. \quad (2)$$

$S(\mathbf{d})$ can be written as (because \mathbf{R}_i is a vector)

$$S(\mathbf{d}) = \sum_{i \neq 0} \frac{1}{|\mathbf{d} - \mathbf{R}_i|}, \quad (3)$$

which can be expressed in the integral form

$$S(\mathbf{d}) = \int_0^\infty \frac{2dr}{\sqrt{\pi}} \sum_{i \neq 0} e^{-r^2 |\mathbf{d} - \mathbf{R}_i|^2}. \quad (4)$$

Eq. (4) can also be rewritten as

$$S(\mathbf{d}) = \int_0^\infty \frac{2dr}{\sqrt{\pi}} \int \frac{d\mathbf{k}}{r^3 \sqrt{\pi^3}} \sum_{\mathbf{R}_i \neq 0} e^{-k^2/r^2 + 2i\mathbf{k} \cdot (\mathbf{d} - \mathbf{R}_i)}. \quad (5)$$

Using the relation,

$$\sum_i e^{i\mathbf{q} \cdot \mathbf{R}_i} = (2\pi)^3 \frac{1}{\Omega} \sum_{\mathbf{K}} \delta(\mathbf{q} - \mathbf{K}), \quad (6)$$

where $\delta(\mathbf{q} - \mathbf{K})$ is the Dirac delta function and Ω is the volume of the unit cell, show that Eq. (5) can be rewritten as

$$S(\mathbf{d}) = \int_0^\infty \frac{2dr}{\sqrt{\pi}} \int \frac{d\mathbf{k}}{r^3 \sqrt{\pi^3}} \left[\left\{ \sum_{\mathbf{K}} \frac{(2\pi)^3}{\Omega} \delta(2\mathbf{k} - \mathbf{K}) \right\} - 1 \right] e^{-k^2/r^2 + 2i\mathbf{k} \cdot \mathbf{d}}. \quad (7)$$

Show that Eq. (7) can be simplified as

$$S(\mathbf{d}) = \int_0^\infty \frac{2dr}{\sqrt{\pi}} \left[\frac{\pi^3}{r^3 \sqrt{\pi^3}} \sum_{\mathbf{K}} \frac{1}{\Omega} e^{-K^2/4r^2 + i\mathbf{K} \cdot \mathbf{d}} - e^{d^2 r^2} \right], \quad (8)$$

$$= \sum_{\mathbf{K}} \frac{4\pi}{\Omega K^2} e^{i\mathbf{K} \cdot \mathbf{d}} - \frac{1}{d}. \quad (9)$$

In deriving Eqs. (4) and (9), we have used the identity

$$\frac{1}{d} = \int_0^\infty \frac{2dr}{\sqrt{\pi}} e^{-d^2 r^2}. \quad (10)$$

Eq. (9) diverges for the $\mathbf{K} = 0$ term. $S(0)$ also diverges. However, $S(\mathbf{d}) - S(0)$ does not diverge, which can be shown by rewriting $S(\mathbf{d})$ from Eqs. (4) and (8) as

$$S(\mathbf{d}) = \int_0^G \frac{2dr}{\sqrt{\pi}} \left[\frac{\pi^3}{r^3 \sqrt{\pi^3}} \sum_{\mathbf{K} \neq 0} \frac{1}{\Omega} e^{-K^2/4r^2 + i\mathbf{K} \cdot \mathbf{d}} - e^{d^2 r^2} \right] + \int_G^\infty \frac{2dr}{\sqrt{\pi}} \sum_{\mathbf{R}_i \neq 0} e^{-r^2 (\mathbf{d} - \mathbf{R}_i)^2}, \quad (11)$$

where G is of the order of a reciprocal lattice vector. Eq. (11) can be rewritten by using the procedure followed earlier as

$$S(\mathbf{d}) = \sum_{\mathbf{K} \neq 0} \frac{4\pi}{\Omega K^2} e^{-K^2/4G^2 + i\mathbf{K} \cdot \mathbf{d}} - \int_0^G \frac{2dr}{\sqrt{\pi}} e^{-d^2 r^2} + \int_G^\infty \frac{2dr}{\sqrt{\pi}} \sum_{\mathbf{R}_i \neq 0} e^{-r^2 (\mathbf{d} - \mathbf{R}_i)^2}. \quad (12)$$

Each of the terms in Eq. (12) converges. Similarly, one can show that $S(0)$ also converges. Thus, $dS(\mathbf{d}) - dS(0)$ converges, although the individual summations in Eq. (9) do not

converge. Hence, we define

$$dS(\mathbf{d}) - dS(0) + 1 = \alpha, \quad (13)$$

where α is the Madelung constant.

6.5. Derive Eq. (6.35) from Eq. (6.34).

6.6. Derive Eq. (6.82) from Eqs. (6.72) through (6.81).

6.7. Derive Eq. (6.93) from Eq. (6.92).

6.8. According to the Sommerfeld expansion rule,

$$\int_{-\infty}^{\infty} d\varepsilon H(\varepsilon) f(\varepsilon) = \int_{-\infty}^{\mu} H(\varepsilon) d\varepsilon + \sum_{n=1}^{\infty} a_n (k_B T)^{2n} \frac{d^{2n-1}}{d\xi^{2n-1}} H(\varepsilon) \Big|_{\varepsilon=\mu}. \quad (1)$$

Here, $\xi(2n) = 2^{2n-1} \frac{\pi^{2n}}{(2n)!} B_n$, $f(\varepsilon)$ is the Fermi distribution function, ξ is the Riemann zeta function, and B_n are the Bernoulli numbers. If

$$H(\varepsilon) = \frac{dF(\varepsilon)}{d\varepsilon}, \quad (2)$$

show (by using the values $\xi(2) = \frac{\pi^2}{6}$ and $B_1 = \frac{1}{6}$) that

$$\int_{-\infty}^{\infty} d\varepsilon F(\varepsilon) \left(\frac{-\partial f}{\partial \varepsilon} \right) = F(\mu) + \frac{\pi^2}{6} (k_B T)^2 \left[\frac{\partial^2 F(\varepsilon)}{\partial \varepsilon^2} \right]_{\varepsilon=\mu}. \quad (3)$$

6.9. Derive Eq. (6.115) by making the same arguments made for Eq. (6.114).

6.10. Write the vector \mathbf{k}' in terms of its components

$$\mathbf{k}' = \mathbf{k}'_{\parallel} + \mathbf{k}'_{\perp} = (\hat{\mathbf{k}} \cdot \mathbf{k}') \hat{\mathbf{k}} + \mathbf{k}'_{\perp}. \quad (1)$$

Show that because the collision probability $W_{\mathbf{k},\mathbf{k}'}$ depends only on the angle between \mathbf{k} and \mathbf{k}' (for elastic scattering),

$$\int d\mathbf{k}' W_{\mathbf{k},\mathbf{k}'} \mathbf{k}'_{\perp} = 0. \quad (2)$$

Hence, show that because for $k \neq k'$, $W_{\mathbf{k},\mathbf{k}'} = 0$,

$$\int d\mathbf{k}' W_{\mathbf{k},\mathbf{k}'} = \mathbf{k} \int d\mathbf{k}' W_{\mathbf{k},\mathbf{k}'} (\hat{\mathbf{k}} \cdot \hat{\mathbf{k}}'). \quad (3)$$

6.11. Derive Eq. (6.143) from (6.139) through (6.142).

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