

Basic Principles Summarized

If, in some cataclysm, all of scientific knowledge were to be destroyed, and only one sentence passed on to the next generation of creatures, what a statement would contain the most information in the fewest words? I believe it is the atomic hypothesis that all things are made of atoms – little particles that move around in perpetual motion, attracting each other when they are a little distance apart, but repelling upon being squeezed into one another. In that one sentence, there is an enormous amount of information about the world, if just a little imagination and thinking are applied.

R.P. Feynman, *The Feynman Lectures on Physics*

Summary. The equilibrium state of matter in general (and condensed matter in particular) corresponds to the minimum value of its energy E (when $P_0 = T_0 = 0$), or of its Gibbs free energy, $G \equiv E + P_0V - TS$, (when $P_0 = \text{const.}$, $T_0 = \text{const.}$), where P_0 is the external pressure, T is the absolute temperature, V is the volume, and S is the entropy. This statement implies, among other things, that (when $P_0 = 0$) the internal squeezing pressure due to the attractive forces among the elementary particles making up the matter is counterbalanced by the internal expanding pressure due to the perpetual motion of these particles. This, crucial for equilibrium perpetual motion, stems mainly or exclusively from the wave nature of matter and is summarized in the three basic principles of Quantum Mechanics (QM). For condensed matter, the forces are mainly electric and are characterized by the charge e , while the perpetual motion depends mainly on Planck's constant, \hbar , and the electronic mass, m_e . Thus, properties of condensed matter depend on e , \hbar , m_e and possibly on other physical constants. This observation together with dimensional considerations leads to several semiquantitative results.

1.1 The Atomic Idea: From Elementary Particles to Solids

Matter is made up from microscopic elementary particles interacting with each other to form composite particles; the latter in turn combine with each other and/or with other elementary particles to create the next level in the hierarchy of the structures of matter, etc.

Thus: Two u quarks and one d quark make up the proton, while two d quarks and one u quark make up the neutron; protons and neutrons combine to create the various atomic nuclei; a nucleus attracts and traps electrons around it to form a neutral atom (when the number of trapped electrons equals the number Z of protons in the nucleus).¹ Atoms (and/or ions) come together to form molecules; atoms and/or ions² and/or molecules in huge numbers are more or less close-packed to form ordinary solids and liquids and other condensed macroscopic structures such as polymers. And the hierarchy continues to larger scales all the way to astronomical objects (planets, stars, galaxies, cluster of galaxies, etc.).

In this book we shall deal with the Physics of Solids such as metals, semi-conductors, alloys etc.; our aim is to *understand* their various properties. The key word in Solid State Physics (SSP) is *understanding*: It means that we do not restrict our search to find out what the magnitudes of the diverse quantities characterizing this or that type of solid are; we insist on finding out *why* these magnitudes are what they are. An answer to this “*why*” ought to stem from a few basic properties of the atoms making up the solid in order to be considered satisfactory. For example, one task of *SSP* is to *derive the observed value of the electrical resistivity of a copper wire at 300 K* ($\rho_e = 1.72 \mu\Omega \text{ cm}$) *starting from the information that the neutral atom of copper has 29 electrons* ($Z = 29$) *and a mass of 63.546 atomic units*.³

To go from the basic quantities characterizing the microscopic constituents of matter (essentially the atomic number Z of the participating atoms) to the various properties of a macroscopic system, such as a solid, it is a truly challenging task. It involves the employment of three essential ingredients (as shown in Fig. 1.1.):

1. *The forces* (or more generally the interactions), which are responsible for binding the constituents together. From the scale of atoms all the way up

¹ If the number of electrons is smaller than Z , a positively charged ion is formed called *cation*, while, if it is larger than Z , a negatively charged ion is formed called *anion*; Isolated ions are metastable structures, because they tend to combine with oppositely charged particles to form neutral structures.

² and possibly electrons (which are considered as point particles).

³ The atomic unit of mass, m_u , is equal to 1.660539×10^{-27} kg, i.e., 0.992776 times the proton mass, m_p , or 1822.89 times the electron mass, m_e . Note that the value of 63,546, as any other atomic mass, is derivable by employing some principles of Nuclear Physics and by using the value of the atomic number Z (which for copper is 29).

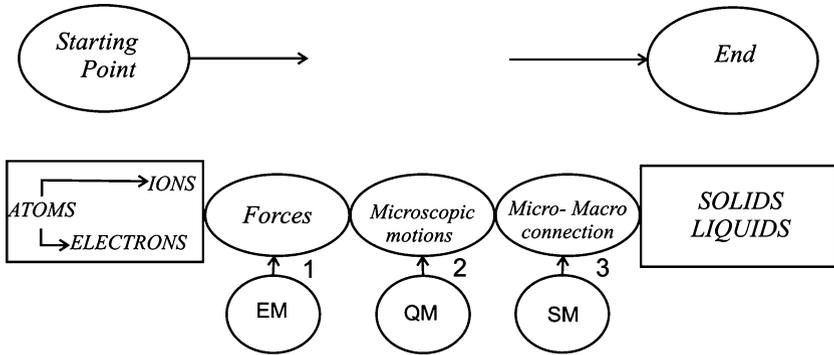


Fig. 1.1. To bridge the huge gap from atoms to solids (or liquids) three basic “foundations” are needed: Electromagnetism (EM), Quantum Mechanics (QM), and Statistical Mechanics (SM)

to that of an asteroid, the only force that plays a nonnegligible role is the *electromagnetic (EM)* one.⁴

2. *The microscopic motions* of the constituents under the action of the forces. The laws that govern these motions are those of *Quantum Mechanics (QM)* stemming from the fact that both interactions and particles have a dual wave–particle nature. We stress the fact that the World in all scales obeys quantum, not classical laws, although under some limited circumstances, it is possible that the conclusions of QM and Classical Mechanics practically coincide.
3. *The connection* between microscopic motions and macroscopic properties. This connection is provided by *Statistical Mechanics* and *Thermodynamics*.

In Appendices A, B, and C we give an outline of electromagnetism, QM, and thermodynamics/statistical mechanics respectively. In the next Sects. 1.2–1.4 we summarize the most important relations and principles of these three fundamental branches of Physics.

We conclude this section with two remarks:

Taking into account: (a) the ambitious goals of SSP; (b) the huge number of types of solids including man-made structures; (c) the various and diverse properties of solids (thermal, mechanical, electrical, magnetic, etc.); and (d) the large number of parameters affecting these properties of solids (e.g., temperature, pressure, external fields, methods of preparation, etc.), it is clear that the subject matter of SSP is enormous and it is capable of practically unlimited expansion as scientific research is exploring new uncharted regimes (e.g., nanotechnology).

⁴ Living matter could be considered as an indirect exception in the sense that its survival seems to require a planetary system with its central star; for the latter, gravitational and nuclear forces (as well as electromagnetic) are essential.

Table 1.1. Connections between subareas of condensed-matter physics and applications of wider interest

Sub-area	Information Processing	Speech and data communications	Energy	Medical	Transportation	Space Technology	National Security
Electronic properties	●	◐	●	○	●	○	●
Phonons/ Electron-Phonon interaction	◐	○	◐	◐	○	○	○
Phase transitions	◐	○	◐	○	◐	○	●
Magnetism	●	●	●	◐	●	◐	◐
Semiconductor	●	●	●	◐	●	●	●
Defects/ diffusion	●	●	●		●	◐	●
Surfaces/interfaces	●	●	●	◐	●	◐	●
Low-temperature physics	◐	○	●	◐	○	○	○
Liquids	◐	○	◐	○	◐	◐	○
Polymers	●	◐	◐	●	●	◐	◐
Nonlinear dynamics, instabilities, chaos	◐	○		○	○	○	●

A solid circle indicates a critical connection between the subarea of condensed-matter physics and the area of application; a half-filled circle indicates an important or emerging connection; an open circle denotes the possibility of a connection; a blank implies connection is not known.

The achievement of a deeper understanding of why solids behave the way they do not only satisfied our intellectual desire to comprehend the World around us, but also allowed us to control the behavior of solids and to enrich them with new desirable features, leading thus to the development of new technology. As a matter of fact, solids have been historically proved to be of paramount importance for technological and economic development (starting from the Neolithic Age and the Age of metals (copper, iron) to the modern era of transistors, integrated circuits, chips, magnetic memories, computers, magnetic resonance imaging (MRI), solid state lasers, etc.).

Table 1.1 (taken from a 1986 publication of the National Academy Press⁵) shows the impact of *Condensed Matter Physics (CMP)* on various aspects of a modern society. CMP includes the study of Solids, Liquids, and states of matter intermediate between Solids and Liquids such as Polymers, Liquid Crystals, Glasses, Gels, etc. Special quantum states such as superfluids, Bose-Einstein condensates, etc. are also part of the content of CMP.

1.2 Permanent (i.e., Equilibrium) Structures of Matter Correspond to the Minimum of Their (Free) Energy

It is well known from Mechanics that *the stable equilibrium of a system corresponds to the absolute minimum of its total energy and vice versa*. What makes this principle very important for determining the properties and the

⁵ “Physics through the 1990s: Condensed-Matter Physics,” National Academy Press, 2101 Constitution Ave, NW Washington, DC 20418.

structure of matter is that physical systems do possess a finite minimum of their total energy; this minimum is realized because of the presence of both the potential energy (which, as we shall see, is negative and tends to squeeze the system) and the quantum kinetic energy (which is always positive and tends to blow the system apart). In other words, the total energy E of a system is the sum of two⁶ terms opposing each other: the total potential energy E_P and the total kinetic energy E_K :

$$E = E_K + E_P. \quad (1.1)$$

Both E_P and E_K depend on many parameters: For example, the volume V of the system, the electronic concentration $n_e(\mathbf{r})$, the placement \mathbf{R}_α of the atoms or ions of a solid in space, the orientation of the spins of the atoms or the ions, etc.

If one succeeds in minimizing the total energy E with respect to all of these free parameters, one has obtained a full determination of the *ground state* of the system (assuming that no external pressure is exercised on the system). As an example, let us minimize E with respect to the volume (assuming zero absolute temperature):

$$\frac{\partial E}{\partial V} = \frac{\partial E_K}{\partial V} + \frac{\partial E_P}{\partial V} = 0. \quad (1.2)$$

However, $-(\partial E/\partial V)_{T=0}$ is the total pressure,⁷ $-(\partial E_K/\partial V)_{T=0}$ is the positive pressure P_K due to the finite kinetic energy, and $-(\partial E_P/\partial V)_{T=0}$ is the negative pressure P_P due to the attractive potential energy. Thus, we conclude that the minimization of the total energy with respect to the volume implies that the total pressure must be equal to zero, or equivalently, that $P_K = |P_P|$; hence, it follows from (1.2) that the squeezing pressure of the potential energy is balanced exactly at equilibrium by the repulsive pressure of the kinetic energy. If there is a non-zero *external* squeezing pressure P_0 , equilibrium demands that the difference $P_K - |P_P|$ must be equal to P_0 :

$$P_0 = P_K - |P_P|, \quad (1.3)$$

This is equivalent to the minimization (with respect to the volume) of the quantity $E + P_0V$, which is called *enthalpy*.

Finally, if the system is placed in an environment of pressure P_0 and absolute temperature T_0 , the stable equilibrium corresponds to the minimization

⁶ A third term in the total energy is the so called rest energy, $\sum m_{io}c^2$, where m_{io} are the rest masses of the nuclei and the electrons making up the solid. However the formation, transformations and other changes in solids do not involve measurable changes in m_{io} ; thus, this third term is a constant which can be eliminated by a redefinition of the zero of the energy.

⁷ Remember the first law of Thermodynamics, $dE = -PdV + TdS$ and set $T = 0$.

of the quantity $E + P_0V - T_0S$, where S is the *entropy* of the system.⁸ Since at equilibrium $P = P_0$ and $T = T_0$, the quantity $E + P_0V - T_0S$ reduces to the so-called *Gibbs free energy*, $G \equiv E + PV - TS$. Hence,

Under conditions of constant pressure and temperature (and no exchange of matter), the stable equilibrium of a system corresponds to the minimization of its Gibbs free energy $G \equiv E + PV - TS$. (1.4)

Notice that when $P = T = 0$, the Gibbs free energy G reduces to the energy E , and thus, we recapture the initial statement of this section. The important message to be remembered is that we possess a recipe to predict (or to justify a posteriori) the equilibrium structures of matter and their properties. Here is the recipe:

For the system under study, obtain the Gibbs free energy G (under conditions of constant P and T), or the energy E (under conditions $P = T = 0$), as a function of various free parameters (such as the volume, the positions of the atoms or ions, the electronic concentration $n_e(\mathbf{r})$, etc.); minimize G or E with respect to all these free parameters; the resulting state is one of stable equilibrium to be observed in nature.

A word of caution is in order at this point: A system may stay for a very long time (even infinite for all practical purposes) in a state of metastable equilibrium corresponding to a local minimum of G (under conditions $T = \text{const}$, $P = \text{const}$). This may happen because the energy barrier separating this local minimum from the absolute minimum (corresponding to stable equilibrium) can be large enough to be practically impenetrable by quantum mechanical tunneling even in the presence of some external perturbations. It is even possible for a system to stay in an unstable state (corresponding to no minimum of E or G) for a very long time (practically infinite), if there is no mechanism for unloading its excess energy (e.g., a planet going around the Sun in the absence of gravitational waves), or, if the unloading of energy (or free energy) involves extremely slow motions of a huge number of microscopic particles (e.g., deformations of ordinary glasses under the influence of gravity take centuries); in the latter case, we are dealing with the so-called *kinetically arrested* unstable configurations.

⁸ This very important principle is an immediate consequence of the first ($dE = dQ - PdV$) and the second ($dQ \leq TdS$) law of thermodynamics. Indeed, by combining the two laws, we obtain $dE \leq TdS - PdV$, or $dE + PdV - TdS \leq 0$, or (taking into account that T and P are constant) $dG \leq 0$, where $G \equiv E + PV - TS$. The last inequality, under the said conditions, means that the Gibbs free energy G decreases with time (or, in extreme cases, remains constant), until its minimum value is reached, upon which no further spontaneous change can occur, and consequently, stable equilibrium is established.

1.3 Condensed Matter Tends to Collapse Under the Influence of Coulomb Potential Energy

The main contribution to the potential energy of ions and electrons making up molecules, solids, liquids, etc. is the Coulomb interaction among the electrical charges q_i of the constituent particles:

$$E_P = 1/2 \sum_{ij} \frac{q_i q_j}{r_{ij}}, \quad \text{G-CGS units.}^9 \quad (1.5)$$

The various terms contributing to the sum in (1.5) can be either positive (when $q_i q_j > 0$), meaning repulsion, or negative (when $q_i q_j < 0$), meaning attraction. For an electrically neutral system (where $\sum_i q_i = 0$), under the self-adjusting placement of the charges, E_P , as given by (1.5), becomes more and more negative meaning not only that attraction wins over repulsion, but also that the electrostatic forces tend to squeeze the system leading, if unopposed, to its eventual collapse.¹⁰

⁹ G in G-CGS stands for Gauss (see [E17], and App. A). In the SI system, (1.5) is written as $E_P = 1/2 \sum_{ij} \frac{q_i q_j}{4\pi\epsilon_0 r_{ij}}$.

¹⁰ It is worth to point out that the role of electromagnetism is *dual*: First, it provides the Coulomb forces that keep atoms or ions and electrons bound together to form larger structures such as molecules, solids, liquids, etc. Second, electromagnetic fields generated by external sources penetrate into the system under study, and drive it out of equilibrium or to a modified equilibrium state. This second role of electromagnetic forces is also extremely important both biologically and technologically (we see because, on the one hand, visible objects are secondary emitters of EM waves, and on the other hand, the receiving chain from the eye to the brain interacts strongly with EM fields; our telecommunications are based on the interaction of EM waves with matter, the latter being usually properly designed and fabricated solid state devices).

Several quantities characterize the response of materials to EM fields. Probably, the most important among them is the well-known *permittivity* (or *electrical permeability*, or *dielectric function*, if dimensionless), which connects the *electric induction* \mathbf{D} to the *electric field* \mathbf{E} (see Appendices A and D). The permittivity ϵ is simply connected to the conductivity σ through the relation $\epsilon(\mathbf{k}, \omega) = \epsilon_0 + (i\sigma(\mathbf{k}, \omega)/\omega)$ in SI [or $1 + (4\pi i\sigma(\mathbf{k}, \omega)/\omega)$ in G-CGS]. Knowing the permittivity of a material, we can determine the propagation, reflection, transmission, etc. of EM waves through this material (assuming that the magnetic permeability is equal to one); we can find how external charged particles interact with this material; we can find how the constituent particles interact among themselves and thus determine the average value of the potential energy of the material; finally we can determine the elementary collective excitations of the material such as longitudinal and transverse acoustic waves. In other words, the permittivity $\epsilon(\mathbf{k}, \omega)$ appears again and again in the course of studying condensed matter and constitutes a powerful tool for analyzing the behavior of solids.

1.4 Quantum Kinetic Energy Counterbalances Coulomb Potential Energy Leading to Stable Equilibrium Structures

Quantum Mechanics embodies the basic experimental fact that matter and interactions possess both particle and wave features. As a result, an angular frequency ω is associated with the energy ε of a particle¹¹ and a wavevector \mathbf{k} is associated with the momentum \mathbf{p} of a particle¹¹ (or of a quasi-particle such as a phonon or a magnon as we shall see later on in Chapters 6 and 21):

$$\varepsilon = \hbar\omega, \quad (1.6)$$

$$\mathbf{p} = \hbar\mathbf{k}, \quad (1.7)$$

where \hbar , Planck's constant (divided by 2π), is the “trade mark” of QM and probably the most important universal physical constant.

1.4.1 Heisenberg's Uncertainty Principle and the Minimum Kinetic Energy

From the wave-particle duality follows¹² Heisenberg's uncertainty principle, stating that

$$\Delta p_x \Delta x \geq \frac{\hbar}{2}, \quad (1.8)$$

where Δp_x is the standard deviation¹³ of the x -component of the particle's momentum vector and Δx is the standard deviation of the projection of the particle's position along the x -axis. The most important consequence of (1.8) is that it sets a lower non-zero limit to the average value ε_K of the kinetic energy of a particle confined in a volume V . Indeed, using the definition of standard deviation, we have

$$\langle \varepsilon_K \rangle = \frac{1}{2m} (\langle p_x^2 \rangle + \langle p_y^2 \rangle + \langle p_z^2 \rangle) \geq \frac{1}{2m} (\Delta p_x^2 + \Delta p_y^2 + \Delta p_z^2) \geq 4.87 \frac{\hbar^2}{mV^{2/3}}, \quad (1.9)$$

where V is the volume (assumed spherical) within which the particle is confined and m is the mass of a particle (for a proof of (1.9) see Problem 1.5s).¹⁴

¹¹ and vice versa, a quantum of energy ε is associated with a wave of frequency ω and a quantum of momentum \mathbf{p} is associated with a wave of wavevector \mathbf{k} .

¹² The spatial extent Δx of an one-dimensional wave packet involving plane waves of wavevectors covering a range Δk satisfies the relation $\Delta x \Delta k \gtrsim \frac{1}{2}$. Taking into account (1.7) we end up with (1.8).

¹³ The square of the standard deviation, ΔQ^2 , of a random quantity Q is defined as follows $\Delta Q^2 \equiv \langle Q^2 \rangle - \langle Q \rangle^2$, where the symbol $\langle \rangle$ denotes average value.

¹⁴ Notice that (1.9) is based on the nonrelativistic expression, $\mathbf{p}^2/2m$, for the kinetic energy. If the latter is equal to cp , as in the extreme relativistic case, or, as in the

Notice that in the classical limit ($\hbar = 0$) the lowest kinetic energy is zero, as it should be; notice also that the mass of the particle is in the denominator, which means that the smaller the mass, the larger the minimum kinetic energy; for this reason the latter is dominated by the electronic kinetic energy; finally, since the available volume to the $2/3$ power is in the denominator, more confinement increases the minimum kinetic energy.

The importance of a nonzero lower limit of the form of (1.9) for the kinetic energy can hardly be overestimated. A nonzero minimum kinetic energy implies a tendency for the constituent particles to fly apart; this tendency counterbalances the squeezing effect of the electrostatic Coulomb forces and the system ends up *in a unique equilibrium state of lowest total energy*. This unique equilibrium state is also *stable*, i.e., if the Coulomb forces momentarily squeeze the system further, the volume V would decrease, the kinetic energy, according to (1.9), would increase *more* than the potential energy, and it would drive the system back to equilibrium; similarly, if the kinetic energy inflates momentarily the volume away from its equilibrium value, the Coulomb forces would overcome the repulsive tendencies of the kinetic energy and they would drive the system back to equilibrium.

In conclusion, the permanent equilibrium structures of matter (for negligible external pressure P_0 and temperature T_0) is the outcome of two opposing factors: the potential energy, which tends to squeeze and eventually collapse the system, and the kinetic energy – of quantum origin stemming from Heisenberg’s uncertainty principle – which tends to blow the system apart to its constituent particles.

1.4.2 Pauli’s Exclusion Principle and the Enhancement of the Minimum Kinetic Energy

A second quantum principle of equal importance as the first one is *Pauli’s exclusion principle*; this principle stems also from the wave nature of particles, which makes identical particles *sharing the same space* indistinguishable;¹⁵ for half-integer spin particles ($s = 1/2, 3/2, \dots$), (called fermions), Pauli’s principle implies that:

classical wave case, then $\langle \varepsilon_\kappa \rangle \gtrsim 3\hbar c/V^{1/3}$. Note that V (assumed spherical) is proportional to $\Delta x^3 = \Delta y^3 = \Delta z^3$. Hence, Δx is proportional to $V^{1/3}$ and Δx^2 is proportional to $V^{2/3}$.

¹⁵ The connection between spin and the behavior of identical particles under interchanging any two of them is also playing an important role. The indistinguishability implies that the absolute square, $|\Psi(1, 2, 3, \dots)|^2$, of the wave function $\Psi(1, 2, 3, \dots)$ remains invariant under the interchange of any two particles (e.g. 1 and 2; 1 stands for \mathbf{r}_1, s_1 , etc.). Hence, the wave function itself either remains invariant under interchanging of any two particles, (e.g. $\Psi(1, 2, 3, \dots) = \Psi(2, 1, 3, \dots)$) for particles of integer spin, called bosons) or is multiplied by -1 (e.g. $\Psi(1, 2, 3, \dots) = -\Psi(2, 1, 3, \dots)$ for particles of half-integer spin, called fermions).

The probability of finding two or more identical fermions in the same orbital-spin state is zero. (1.10)

For spin one half particles, e.g., electrons, statement (1.10) means that at most two electrons (one with spin up and the other with spin down) can occupy the same *orbital* state. The role of Pauli's exclusion principle in explaining the structure of the Periodic Table of the Elements (Table H.5), and consequently, the basic principles of Chemistry is well-known. Perhaps not so well appreciated is its role in amplifying the kinetic energy of identical fermions sharing the same volume V . Indeed, as it is clear from Fig. 1.2, Pauli's exclusion principle forces fermions to occupy higher levels, while, if this principle were absent, the lowest total energy of N noninteracting identical particles would be obtained by placing all of them at the ground level ε_G .

Thus, *the minimum average energy per particle*, $\langle \varepsilon \rangle \equiv E_{\min}/N$ (where N is the total number of identical fermions), instead of being equal to the ground state energy ε_G , is raised to be somewhere between ε_G (chosen usually as zero), and the highest occupied level called the *Fermi energy*,^{16,17} E_F .

An easy, *approximate*, but physically transparent way to obtain the minimum total kinetic energy per particle of N identical spin 1/2 fermions is the following: The N particles divide the available common (homogeneous) space of volume V into $N/2$ equal subvolumes; in order to satisfy Pauli's principle, only two fermions are placed in each subvolume (one with spin up and the other with spin down). However, now the available volume for each fermion is $V/(N/2) = 2V/N$. Substituting $2V/N$ instead of V in (1.9), we obtain¹⁸

$$\langle \varepsilon_K \rangle = 3.07 \frac{\hbar^2 N^{2/3}}{mV^{2/3}}, \quad (3.07 \rightarrow 2.87), \quad (1.11)$$

while an accurate calculation by summing up the kinetic energies of all N fermions and dividing by N gives a similar expression with the only

¹⁶ More accurately the Fermi level lies in the middle between the highest occupied and the lowest empty state (under conditions of minimum total energy). See footnote in next page.

¹⁷ As we shall see, for a three-dimensional, spin 1/2, nonrelativistic, free fermion system $\langle \varepsilon_K \rangle = 0.6E_F$ and $E_F = \hbar^2 (3\pi^2 N/V)^{2/3} / 2m$. (If ε_G is chosen as the zero of energy).

¹⁸ From the definition of $\langle \varepsilon_K \rangle \equiv E_{K,\min}/N$ and (1.11), it follows that $E_{K,\min} \sim N^{5/3}$. A more general definition of E_F , applicable to interacting systems as well, is the following: $E_F(N) \equiv U(N+1) - U(N) \xrightarrow{N \rightarrow \infty} \partial U / \partial N$ (where U is the total energy (written usually either as U or E ; see also (C.8) and (C.49)). This more general definition reduces to the one given in Fig. 1.2, if the particles do not interact with the following clarification: $E_F(N)$ coincides with the lowest unoccupied level, if N is even, and with the highest occupied level, if N is odd. Thus, E_F , on average, is exactly at the middle of these two levels. Hence, in the present case, where $U = E_K$, $E_F = \partial E_{K,\min} / \partial N = \frac{5}{3} \frac{1}{N} E_{K,\min} = \frac{5}{3} \langle \varepsilon_K \rangle$ or $\langle \varepsilon_K \rangle = 0.6E_F$.

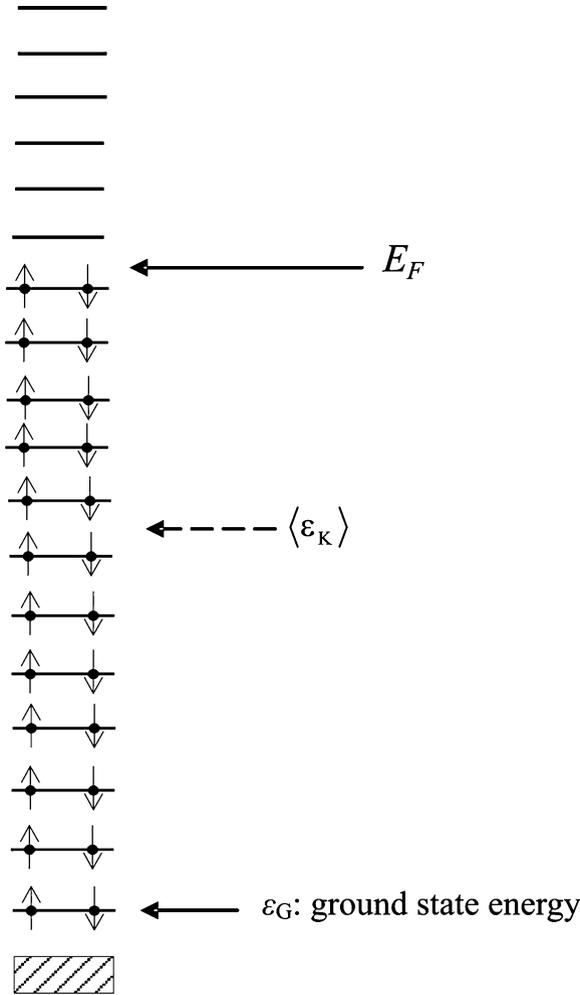


Fig. 1.2. The energy levels associated with each spatial single-electron state are given in order of increasing energy starting from the ground state. The lowest total kinetic energy of N (e.g., $N = 20$) electrons, consistent with Pauli's principle, is obtained by occupying the lowest ten spatial states by two electrons each (one with spin up and one with spin down). The highest occupied state is called the *Fermi level*¹⁶ and is denoted by E_F

difference in the numerical prefactor, which is smaller¹⁹ than 3.07 and equal to $0.3 (3\pi^2)^{2/3} = 2.87$ (see footnote 18).

¹⁹ It is expected to be smaller, since any approximate solution raises the total energy.

Thus, the presence of N identical fermions in the *same volume* amplifies the Heisenberg based average kinetic energy per particle by a factor proportional to $N^{2/3}$ as a result of Pauli's exclusion principle. This kinetic energy of quantum origin is essential in establishing and stabilizing the structure of solids. So, do not ever forget it!

1.4.3 Schrödinger's Spectral Discreteness and the Rigidity of the Ground State

The third principle, which could be called *Schrödinger's principle*, states that the energy spectrum of a particle confined in a finite volume V is discrete; the energy separation $\delta\varepsilon$ between two consecutive low-lying energy levels is given by a similar expression as in (1.9):

$$\delta\varepsilon = \eta \frac{\hbar^2}{mV^{2/3}}, \quad (1.12)$$

where η is a numerical factor typically of the order of unity; its value depends on the form of the confining potential. This discreteness stems again from the wave nature of the particles. (It is well known that EM waves confined to a finite volume, e.g., in a cavity, acquire a discrete frequency spectrum; for a more familiar case, think of a guitar string, which produces only the fundamental note and its harmonics and nothing in between; this discreteness in frequency is transferred to the energy spectrum because of (1.6). The explicit form of (1.12) can be obtained by the following arguments: The quantity $\delta\varepsilon$ ought to depend on \hbar (as a quantum effect), on m (since m is a characteristic of the particle), and on V (as a measure of the confinement); the only combination of these three quantities with dimensions of energy is the one shown in (1.12)).

Equation (1.12) implies in particular that the first excited state is separated from the ground state by a nonzero energy difference $\delta\varepsilon_0 \sim \hbar^2/mV^{2/3}$. Now, if an external perturbation (e.g., a quantum, $\varepsilon = \hbar\omega$, of an EM wave of frequency ω) is applied to our particle (or, more generally, to our system), the latter may attempt to absorb this quantum of energy; however, if $\hbar\omega < \delta\varepsilon_0$, this absorption cannot take place, since $\hbar\omega$ is not enough to kick up the system to the next level; thus, the system will remain in its ground state. In other words, the discreteness of the energy spectrum bestows *stability* on the physical systems (against external temporary perturbations unable to transfer energy higher than $\delta\varepsilon_0$), while, nevertheless, it allows *changes* (if the available energy exceeds $\delta\varepsilon_0$). Because of (1.12), the smaller the volume, the larger the excitation energy $\delta\varepsilon_0$; hence, the tinier the system the more stable it is. This is why atomic nuclei are absolutely unchanged under ordinary perturbations.²⁰ This extended stability to external perturbations explains why atoms

²⁰ For example, the first excited energy level of the nucleus of C^{12} is according to (1.12) equal to $1,41\eta$ MeV (the experimental value is $4,43$ MeV) to be compared

and small molecules exhibit the same features and possess the same properties in very diverse environments leading thus to their admirably predictable and repeatable physicochemical behavior.

Notice also that (1.12) in combination with Pauli principle implies that each discrete level can accept a finite number of spin $1/2$ particles, i.e., twice the degeneracy²¹ of the level. This observation explains the shell atomic structure of the electrons trapped around the nucleus. (See Figs. 2.1 and 2.2 in the next chapter).

1.5 Dimensional Analysis

The dimensional analysis may allow us, under certain circumstances, to find out how a quantity of interest depends on other known quantities and/or on some parameters assumed known; in other words it may allow us to produce (instead of memorize) physics formulae. To apply this analysis, a physical insight is required as to identify all possible known quantities or parameters on which the quantity of interest may depend.

To clarify this matter, let us examine the specific example of the phase velocity v of sea waves: v must depend on the acceleration of gravity g , since the gravitational forces are the ones that tend to restore a flat equilibrium surface of the sea water and thus drive the oscillatory motion of the water near the surface; the wavelength λ may play a role, since it is the most important parameter characterizing a wave; the physical properties of the sea water such as its density ρ_m is another candidate quantity for entering the formula for v . Let us assume at this point that we have exhausted²² the list of quantities influencing v . The three quantities g , λ , ρ_m can define a system of units; this means that a combination of the form $g^\mu \lambda^\nu \rho_m^\xi$ can produce the dimensions of length, time, and mass and hence, the dimensions of any physical quantity²³ with a proper choice of the exponents μ , ν , ξ . To produce dimensions of velocity, we have to choose $\mu = 1/2$, $\nu = 1/2$ and $\xi = 0$ (any other choice for ξ will retain a power of mass besides powers of length and time, the latter coming from λ and g). Hence,

with the thermal energy $k_B T = 26$ meV for $T = 300$ K, i.e., $k_B T / \delta \varepsilon_0 = 5.8 \times 10^{-9}$ for C^{12} at $T = 300$ K.

²¹ The degeneracy of a discrete level is the maximum number of different spatial eigenstates belonging to this level.

²² Actually, the depth of the sea d may play a role, if $d \lesssim \lambda$. The surface tension coefficient, a_s , may also enter since the surface tension tends to minimize the surface, and consequently, tends to restore a flat surface; however, this restoring force is insignificant in comparison with the gravitational force unless the wavelength is of the order of centimeters or less.

²³ The unit of absolute temperature can be produced from the unit of energy by dividing by k_B , the Boltzmann's constant. Length is produced by choosing $\nu = 1$, $\mu = \xi = 0$; time is produced by choosing $\mu = -1/2$, $\nu = 1/2$, and $\xi = 0$; finally mass is produced by choosing $\mu = 0$, $\nu = 3$, and $\xi = 1$.

$$v = \eta\sqrt{g\lambda}, \quad (1.13)$$

where the numerical constant η cannot be determined from dimensional analysis (it is actually equal²⁴ to $1/\sqrt{2\pi}$). Formula (1.13) is correct as long as the depth d of the sea is much larger than the wavelength λ ; otherwise v would depend also on the dimensionless ratio $x \equiv 2\pi d/\lambda = kd$

$$v = \sqrt{\frac{g\lambda}{2\pi}} f(x), \quad (1.14)$$

where the function $f(x)$, $x = 2\pi d/\lambda$, cannot be determined from dimensional analysis; actually $f(x) = \tanh x$. Can you employ dimensional analysis to answer the following questions: *What is the velocity of propagation of a tsunami (for which $d \ll \lambda$)? What is the value of v if $d = 1$ km and $\lambda \simeq 60$ km?*

Another example worth presenting is the EM energy per unit time and unit surface, J , emitted by a black body of temperature T (in K). The quantities that we expect to enter in the formula for J are: (1) Obviously, the absolute temperature, T ; remember, however, that *the quantity of physical meaning is not T itself but the combination $k_{\text{B}}T$ (always) where k_{B} is Boltzmann's constant*, see [ST35, §9]; (2) the velocity of light c (since we are dealing with EM radiation); (3) the Planck constant \hbar (since black body radiation is a quantum effect; actually this is the phenomenon that led to the introduction of \hbar for the first time). In the absence of any other obvious additional quantity let us be optimistic and assume that $k_{\text{B}}T$ (with dimensions of energy), c , and \hbar (with dimensions of energy time) are the only ones determining J . The latter has dimensions of energy over time and over length square. Now $\hbar/k_{\text{B}}T$ has dimensions of time, and $c\hbar/k_{\text{B}}T$ has dimensions of length. Hence, the only combination of $k_{\text{B}}T$, c , \hbar that has the same dimensions as J is $k_{\text{B}}T/(\hbar/k_{\text{B}}T) \cdot (c\hbar/k_{\text{B}}T)^2$. Thus,

$$J = \eta \frac{(k_{\text{B}}T)^4}{c^2\hbar^3}, \quad (1.15)$$

where η is a numerical factor (actually it turns out that $\eta = \pi^2/60$).

How can dimensional analysis²⁵ be applied to the determination of the properties of solids? Since the kinetic energy of the electrons (which involves

²⁴ To make the numerical constant closer, or even equal, to one it is better to use $\lambda/2\pi$ instead of λ , since the phase of the wave involves the combination x ($2\pi/\lambda$) and not x/λ .

²⁵ In the general case, the dimensional analysis works as follows:

1. We identify all possible quantities A_1, \dots, A_n on which the quantity of interest, X , may depend. (This is a crucial and far from trivial step.)
2. If $n \leq 3$, there is usually a unique combination of the form $A_1^{\mu_1} \dots A_n^{\mu_n}$ which has the same dimensions as X . Then the desired formula for X has been found: $X = \eta A_1^{\mu_1} \dots A_n^{\mu_n}$ where η is an undetermined numerical constant

Planck's constant \hbar and the electronic mass, m_e) and the Coulomb forces (which involve the proton and electron charge $\pm e$) are the main actors in determining the state of solids, we conclude that solid-state properties would depend in general on \hbar , e , and m_e . These three quantities define a system of units (with the help of k_B and ε_0, μ_0 (in SI), see Table H.2) that is called atomic²⁶ system of units; in particular the unit of length in this system is the well-known **Bohr radius**, $a_B = \hbar^2/e^2 m_e$ ($= 4\pi\varepsilon_0 \hbar^2/e^2 m_e$ in SI), $a_B = 0.529 \text{ \AA}$, and the unit of time, $t_0 = m_e a_B^2/\hbar = \hbar^3/e^4 m_e$ ($= (4\pi\varepsilon_0)^2 \hbar^3/e^4 m_e$ in SI), $t_0 = 2.419 \times 10^{-17} \text{ s}$. Usually, it is more convenient to use the triad \hbar , m_e , a_B , instead of the triad \hbar , m_e , e .

Besides the fundamental physical constants \hbar , m_e , a_B (and k_B if temperature is needed) the properties of solids are expected to depend on the type of atoms involved, i.e., on their atomic numbers Z_i ; other properties of atoms such as their mass $m_{\alpha i}$ may also be involved.²⁷ External conditions such as the temperature T and to a lesser degree the pressure P may influence the properties of solids²⁸ as well. Other hidden quantities may also enter. Thus, any quantity X pertaining to the solid state can be expressed in terms of known quantities and parameters as follows:

$$\frac{X}{X_0} \equiv \bar{X} = f_x \left(Z_i, \frac{m_{\alpha i}}{m_e}(Z_i), \frac{T}{T_0}, \frac{P}{P_0}, \frac{c}{v_0}, \dots \right), \quad (1.16)$$

-
3. If $n > 3$, we choose three quantities A_1, A_2, A_3 , which define a system of units (in the sense that three different combinations of the form $A_1^{\mu_1} A_2^{\mu_2} A_3^{\mu_3}$ can be found which have the dimension of length, time, and mass respectively)
 4. By a proper choice of ν_1, ν_2, ν_3 , we form the combination $A_1^{\nu_1} A_2^{\nu_2} A_3^{\nu_3} \equiv X_0$, where X_0 has the same dimensions as the quantity of interest X
 5. We create also combinations $A_1^{\xi_{1n}} A_2^{\xi_{2n}} A_3^{\xi_{3n}} \equiv A_{n0}$ which have the same dimensions as A_n , ($n = 4, 5, \dots$) and we define the dimensionless quantities A_n/A_{n0} ($n = 4, 5, \dots$)
 6. Having determined the quantities $X_0, A_{40}, A_{50}, \dots$ in terms of the chosen quantities A_1, A_2, A_3 , we are ready to express X in terms of A_1, \dots, A_n as follows

$$X = X_0 f \left(\frac{A_4}{A_{40}}, \frac{A_5}{A_{50}}, \dots \right),$$

where the unknown function f cannot be determined from dimensional analysis; additional information(s) or even a complete physical theory is needed to find out what f is.

- ²⁶ The unit of mass in this system is m_e ; however, notice that the mass $m_u \equiv \frac{1}{12} m_C$, where m_C is the mass of carbon-12, is also defined as the atomic unit of mass; $m_u = 1822.89 m_e$.
- ²⁷ We remind the readers that the properties of an atom can be derived in terms of Z by employing methods of nuclear and atomic physics.
- ²⁸ The velocity of light, c , may also appear especially for heavy atoms where relativistic effects are not negligible; some nuclear properties may also play a role.

where \bar{X} is the value²⁹ of X in atomic units, X_0 is the combination $X_0 = \hbar^{v_1} m_e^{v_2} a_B^{v_3}$, which has the same dimensions as X (see Table H.2) and f_x is a function of the *dimensionless* quantities $Z_i, m_{\alpha i}/m_e, \dots$; T_0 is the atomic unit of temperature, $T_0 = \hbar^2/m_e a_B^2 k_B = 315,775 \text{ K}$, P_0 is the atomic unit of pressure, $P_0 = \hbar^2/m_e a_B^5 = 2.9421 \times 10^{13} \text{ N/m}^2 = 2.9421 \times 10^8 \text{ bar}$, and $v_0 = \hbar/m_e a_B = c/137 = 2187.69 \text{ km/s}$ is the atomic unit of velocity. The success or not of (1.16) in providing quick and reliable estimates for the magnitude of physical quantities depends on whether or not f_x is a smooth function of Z_i and of other hidden dimensionless variables (which are implicit functions of Z_i). In the next chapter we shall present applications of (1.16) in estimating several quantities of physical interest. As we shall see, there are impressively accurate estimates (given the generality and simplicity of (1.16)) as well as some “first attempt” failures which are, however, very instructive.

To summarize: Equation (1.16) is extremely important because it allows us to obtain “an enormous amount of information” regarding the qualitative and quantitative behavior of condensed matter “if just a little imagination and thinking is applied.”

1.6 Key Points

Three ideas are “sine qua non” for understanding the properties of solids:

- The *atomic idea*, according to which solids are made of atoms (or ions and electrons), which are brought together mainly by the action of electrostatic forces; the latter if unopposed, would squeeze the solid to its collapse.
- What counterbalances the squeezing electrostatic pressure is the pressure of the *kinetic energy*, which is of quantum nature; the latter embodies three basic principles:
 - *Heisenberg’s* uncertainly principle, which leads to the existence of a minimum kinetic energy inversely proportional to the mass of the particle and to the $2/3$ power of the volume within which the particle is confined (nonrelativistic behavior is assumed).
 - *Pauli’s* exclusion principle, which enhances the average kinetic energy per particle of a system (consisting of N identical fermions sharing the same volume V) by a factor proportional to $N^{2/3}$.
 - *Schrödinger’s* discreteness principle, which makes the ground state rigid to some extent by inhibiting excitation of the system by external perturbations, if the energy of the latter is lower than the energy of the first excited state above the ground state.
- Stable equilibrium states of matter (such as solids) correspond to the minimum value of the total energy, which consists of the potential part and the kinetic part (if $P = T = 0$); or the total Gibbs free energy,

²⁹ Throughout this book a bar over any physical quantity X denotes its value at the atomic system of units: $\bar{X} \equiv X/X_0$.

$G \equiv E + PV - TS$, (if $P = \text{const}$, $T = \text{const}$). The minimization is with respect to various adjustable quantities such as the volume, the position of atoms in space, the concentration of electrons, etc. The potential energy is characterized mainly by the electron or proton charge, $\mp e$, and the kinetic energy by Planck's constant, \hbar , and the mass of the electron m_e . Thus, all properties of solids would depend at least on e , \hbar , m_e , or equivalently on a_B , \hbar , m_e . This observation coupled with dimensional considerations and "a little thinking" produces a wealth of information regarding macroscopic properties of solids (see (1.16)).

1.7 Questions and Problems

1.1 Why is the quantum kinetic energy characterized mainly by the electronic mass m_e and not by the ionic mass, m_a ?

1.2 Why was the thermal kinetic energy of electrons and ions in a solid ignored in comparison with the quantum kinetic energy?

Hint: Consider the case of aluminum (for which $V/N_e = 5.5 \text{ \AA}^3$) at $T \simeq 300 \text{ K}$ (see Tables H.2 and H.4).

1.3 Can you show that the equilibrium established between the quantum kinetic energy and the electrostatic energy is stable?

Hint: From (1.5) it follows that E_P/N is proportional to $e^2 N^{1/3}/V^{1/3}$.

1.4 Consider two identical particles confined within the same volume V . Since the two particles do not follow some orbit, they are indistinguishable; their indistinguishability implies that all observable properties, such as the absolute value of the square of their total wavefunction, $|\Psi(1, 2)|^2$, remain invariant under the interchange of the particles, $1 \rightarrow 2$ and $2 \rightarrow 1$: $|\Psi(1, 2)|^2 = |\Psi(2, 1)|^2$. Using the last relation, show that $\Psi(1, 2) = \pm \Psi(2, 1)$.

For half-integer spin particles the minus sign holds, while for integer spin particle the plus sign applies. How Pauli's principle, as stated in (1.10), follows from this?

1.5s Prove (1.9) by employing Heisenberg's uncertainty principle and the relation $\varepsilon_k = p^2/2m$.³⁰

1.6 Show that in the extreme relativistic limit, $mc^2 \ll cp$, Heisenberg's principle leads to the relation $\varepsilon_k \gtrsim 3\hbar c/V^{1/3}$, where V is the spherical volume within which the particle is confined.

1.7 Combining the result of Problem 1.5s with Pauli's exclusion principle prove (1.11). How will (1.11) be modified if $\langle \varepsilon_k \rangle$ is much larger than the rest energy mc^2 ?

³⁰ The letter s after the number of the problem means that the corresponding problem is solved; the solution can be found in the part "solution of selected problems" p. 779

Answer:

$$\langle \varepsilon_K \rangle = E_{K,\min}/N = \eta \hbar c (N/V)^{1/3}, \quad E_F = \frac{4}{3} \langle \varepsilon_K \rangle, \quad \eta = 2.32.$$

- 1.8 For the hydrogenic s states calculate the energy difference $\delta\varepsilon$ between two consecutive levels and check whether (1.12) is satisfied. What is the value of η ?
- Hint:* Identify the $V^{-2/3}$ appearing in (1.12) with $(4\pi/3)^{-2/3} \langle r^{-2} \rangle$.
- 1.9s By employing dimensional analysis, find the wavelength λ_m at which the spectral distribution $dJ_\lambda/d\lambda$ of black body's radiation exhibits a maximum.
- 1.10s By employing dimensional analysis, find the scattering cross-section for a photon by an isolated electron.
- 1.11s By dimensional analysis, find the natural linewidth and the corresponding life-time of an excited atomic level which decays by dipole type emission.
- 1.12s A black hole of mass M , as a result of its strong gravitational field, emits black body radiation through a quantum fluctuation mechanism proposed by Hawking. By dimensional analysis find the effective temperature of this radiation.
- 1.13s High-frequency electric currents in a good conductor of conductivity σ are confined in a region of width δ near the surface. How does δ , the so-called *skin depth*, depend on the relevant parameters?

Further Reading

- Landau & Lifshitz, *Stat. Phys.* [ST35], Chap. 20, pp. 59–63.
- Eisberg & Resnick, *Quantum Physics of Atoms, Molecules, Solids, Nuclei and Particles* [Q23], pp. 6–21.



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