1.1 INTRODUCTION TO HIGH-PRESSURE SCIENCE

High pressure research [1] is a field of enormous relevance both for its scientific interest and for its industrial and technological applications. Many
materials undergo fascinating changes in their physical and chemical characteristics when subjected to extreme pressure. This behavior is caused by the involvement in bonding of electrons that would otherwise not be chemically active under zero-pressure conditions (the difference between zero pressure and atmospheric pressure is negligible from the point of view of its effect on materials properties, and we will use both concepts interchangeably). By and large, current chemical knowledge and the traditional rules for valence electrons are at a loss to explain most of the changes induced when materials are compressed, which makes chemical bonding under pressure an exciting research topic that has received much attention in recent years [1] (see Chapter 5).

The study of pressure effects can be approached in two mostly complementary ways: experimentally and computationally. In both cases, the basic object under study is the change in crystal structure a material undergoes when a given pressure and temperature are applied as shown in its thermodynamic pressure-temperature phase diagram. Experimentally, the application of temperature is relatively straightforward, but imposing high pressure on a sample requires specialized techniques that have been under development for the past 80 years. The field of experimental high-pressure physics was pioneered by Percy Bridgman, who received the Nobel Prize for his efforts in 1946 [2].

There are two main experimental high-pressure techniques: dynamic compression methods based on shock waves, and static compression methods which make use of pressure cells. In a shock-wave compression experiment [3], a strong shock is applied to the sample and the propagation velocities of the shock wave inside the material are measured. Very high pressures (up to 500–1000 GPa) and temperatures (tens of thousands of K) can be attained with this technique. Static compression techniques are applied using pressure cells, notably diamond anvil cells [4]. These methods are more accurate than dynamic techniques, but they are also limited by the pressure scale, with the mechanical resistance of a diamond (slightly above 300 GPa) being the ultimate upper pressure limit for the technique. High temperatures, in the range of thousands of K, can be attained by laser heating, and diamond anvil cells can be coupled to other techniques: spectroscopic (infrared, Raman, x-ray) and optical. Experimental high-pressure techniques are explored in Part II of this book.

From the computational point of view, in the framework of density functional theory (DFT), the application of pressure is relatively straightforward: one simply compresses the unit cell and calculates the applied pressure either analytically from the self-consistent one-electron states or from the volume derivative of the calculated total energy. The latter requires fitting an equation of state. Conversely, temperature effects are difficult to model because they involve collective atomic vibrations—called phonons—propagating throughout
a crystal (see Chapter 3). The simplest computational approach to model the effects of temperature is to calculate the electronic energy, assuming the nuclear and electronic motions are decoupled (the adiabatic approximation), and then obtaining the phonon frequencies using the derivatives of said electronic energy with respect to the atomic movements. The phonon frequencies can be used in the harmonic approximation to calculate thermodynamic properties and phase stabilities at arbitrary pressure and temperature. Computational techniques for high-pressure studies are explored in this and the subsequent chapters in Part I.

Despite the difficulties in modeling temperature effects, theoretical approaches are necessary in cases for which experiments are either not feasible or difficult to interpret. An interesting example of synergy between computational and experimental approaches occurs in geophysics. Because the interior of the Earth is inaccessible, information about its composition and structure can only be inferred through indirect means [5, 6], primarily via seismic velocities measured during earthquakes. Calculated data (elastic moduli, longitudinal and shear velocities, thermal expansion and conduction, heat capacities, Grüneisen parameters, transition pressures, Clapeyron slopes, etc.) are very helpful in the interpretation of experimental data and in the construction of models of the Earth’s interior [7, 8]. The geophysical and astrophysical applications of high-pressure science are presented in Chapters 15 and 16, respectively.

High-pressure research also has very relevant technological applications (Chapter 14). Materials that are thermodynamically stable at high pressure and temperature are often metastable at zero pressure and room temperature, so it is possible to access new material phases with unique properties by the application of appropriate pressure and temperature conditions. The application of high pressure to biological samples is also of technological relevance because it is known that the microorganism activity is diminished or canceled by application of high pressures, a process called pascalization. In contrast to the preceding applications, the pressures exerted in this case are in the order of the tenths of a GPa, much smaller than in previous examples. Pascalization can be used to increase the shelf lives of perishable foodstuffs: juice, fish, meat, dairy products, etc. This has been one of the research lines of MALTA [9–12], and is explored in Chapters 12 and 13.

To summarize, high pressure is a very active field of research and one whose ramifications affect many scientific and technological fields, from astrophysics and geophysics to materials physics and the food industry. From the fundamental view, the behavior of materials at high pressure is still poorly understood, and the usual textbook chemistry rules that apply to zero-pressure chemistry are essentially useless when molecules and materials are subjected
to extreme compression. This makes high-pressure research an interesting and virtually unexplored field of study. In the remainder of the present chapter, we give an overview of the basic thermodynamic principles and mathematical tools that are needed to master the rest of the book. Namely, we review the thermodynamics fundamentals (Section 1.2), the equations of state used to describe the responses of materials to compression (Section 1.3), and the harmonic approximation, the basic theoretical framework in which temperature effects are modeled computationally (Section 1.4).

1.2 THERMODYNAMICS OF SOLIDS UNDER PRESSURE

1.2.1 Basic Thermodynamics

Hydrostatic pressure, together with its extensive associated variable volume, is a fundamental quantity covered in most thermodynamics textbooks [13–17]. Pressure can be defined by considering the mechanical work exerted on a closed system (in which there is no matter exchange with the environment) through a change in its volume:

$$\delta W = -P_E dV.$$  \hspace{1cm} (1.1)

In this equation, $P_E$ is the pressure applied on the system or environmental pressure [18] (also, see the subsection on irreversible pressure-volume work and references therein in Chapter 2 of Reference 15). When both system and environment are in mechanical equilibrium with each other, $P_E = p$, with $p$ representing the system’s pressure (constant through the system). The definition of mechanical work is convenient to study, for instance, the behavior of gases and phase transitions in a closed system. Given that we are interested in the thermodynamic properties of solids under pressure, we start this chapter by presenting some fundamental quantities and the relations between them that will be used in the rest of the book.

Classical thermodynamics is a macroscopic theory based on a few axiomatic principles derived from empirical observations. These fundamental principles are called the laws of thermodynamics. The zeroth, first and second laws allow us to assert the existence of temperature $T$, internal energy $U$, and entropy $S$ as state functions of the system (see below). The first law states that for any infinitesimal process in a closed system (at rest and in absence of external fields):

$$dU = \delta Q + \delta W.$$  \hspace{1cm} (1.2)

In this equation, $dU$ is the infinitesimal internal energy change undergone by the system, $\delta Q$ is the infinitesimal heat flow into the system, and $\delta W$ is the infinitesimal work done on the system during the process. For a finite process, $Q$ and $W$ depend on the intermediate states through which the process evolves,
but $\Delta U$ depends only on the initial and the final states. This is symbolized in Equation (1.2) by using the exact differential notation ($dU$) for the internal energy but not for heat or work. Quantities like $U$ that depend only on the state of the system are called state variables or state functions, and it is possible to define a function (whose changes can be empirically measured) that depends only on the variables that determine the state of the system, $U(p, T, \ldots)$. As we show below, the same thermodynamic quantity can act as a variable (if it is independent) or as a function (if its value is given as a function of other independent variables).

The first law establishes the conservation of energy principle in an isolated system, in which there is no energy or matter exchange with the environment. That is, in an isolated system, the internal energy is a constant. When a closed system receives energy, either in the form of heat or work, its internal energy increases and the environment loses energy by the same amount. If one considers a cyclic process in a closed system, i.e., a process in which the initial and final states of the system are the same, the internal energy change of the system is zero:

$$\oint dU = 0,$$

which makes building a machine whose only effect is the constant generation of energy impossible.

The second law of thermodynamics deals with the difference between heat and work. It originates from the realization that it is impossible to build a cyclic machine that transforms heat into work with 100% efficiency. The second law, which was first proposed by Sadi Carnot through his analysis of steam engines, is therefore a principle of limited efficiency which, for a heat engine, is defined as the fraction of the heat input that is transformed into work. In the case in which heat is absorbed from a hot reservoir and released into a cold reservoir, the maximum efficiency of a heat engine depends only on the temperature of the two reservoirs, and can only be attained if the engine works reversibly (infinitely slowly and excluding dissipative effects) through an infinite series of equilibrium steps [15]. For any real (irreversible) process happening at a finite velocity and including dissipative effects, the efficiency is always less than the reversible upper bound.

The second law is formalized through the definition of entropy. Based on Carnot’s work, Clausius proved that for a reversible process in a closed system (whose temperature $T$ is constant throughout), the quantity $\delta Q_{\text{rev}}/T$ is an exact differential:

$$\oint \frac{\delta Q_{\text{rev}}}{T} = 0,$$
or, in other words, we can define a function \( S \) (the entropy) as:

\[
dS = \frac{\delta Q_{\text{rev}}}{T}, \tag{1.5}
\]

which depends only on the state of the system. The difference between the entropy in states \( A \) and \( B \), \( \Delta S = S_B - S_A \), can be calculated as the value obtained from Equation (1.5) in a hypothetical reversible process that goes from \( A \) to \( B \). A corollary of the definition in Equation (1.5) is that the change in entropy of a closed system during a reversible adiabatic process is zero.

The observation that it is not possible in practice to achieve the maximum thermal efficiency of an engine can be recast in terms of entropy. For an irreversible process in a closed system, Equation (1.5) becomes,

\[
dS > \frac{\delta Q}{T_E}, \tag{1.6}
\]

with \( T_E \) being the temperature of the environment. Therefore, the effect of any process on an adiabatically isolated system is to always increase its entropy. A corollary of this statement is that in an isolated system, thermodynamic equilibrium is attained once the entropy of the system is maximized, and no spontaneous processes within the system can occur henceforth. Note that \( T_E = T \), with \( T \) being the temperature of the system, only holds when both system and environment are in thermal equilibrium with each other. As we shall see below, the maximum entropy statement of the second law can be recast into minimum energy principles that affect certain functions when the state of the system is given by their associated variables.

For simplicity, let us now consider closed one-phase systems with pressure-volume work only undergoing a reversible process. Under these conditions, the mechanical work effected on the system is given by \( \delta W = -pdV \) and the heat absorbed by the system is given by \( \delta Q = TdS \). The change in internal energy is thus given by the fundamental equation:

\[
dU = TdS - pdV, \tag{1.7}
\]

which gives the expression of the exact differential \( dU \) in terms of two independent variables: entropy and volume. The internal energy \( U(S, V) \) as a function of these variables permits the calculation of all the other thermodynamic properties of the system through its derivatives. \( U \) is called a thermodynamic potential and \( S \) and \( V \) are its natural variables.

Entropy and volume are difficult variables to work with because, in general, isochoric and isoentropic conditions are not easy to achieve experimentally. Thermodynamic potentials that depend on other variables can be defined by
applying a Legendre transform to $U(S,V)$. In this way we define the enthalpy ($H(S,p)$), the Helmholtz free energy ($F(T,V)$), and the Gibbs free energy ($G(T,p)$) as:

$$H(S,p) = U + pV,$$
$$F(T,V) = U - TS,$$
$$G(p,T) = U + pV - TS = H - TS = F + pV.$$

$H$, $F$, and $G$ are the thermodynamic potentials for the indicated independent natural variables.

If a thermodynamic potential can be determined as a function of its natural variables, then all other thermodynamic properties for the system can be calculated by taking partial derivatives. For instance, if $G$ is known as a function of $T$ and $p$, the thermodynamic behavior of the system is completely determined. The $U$, $H$, $F$, and $G$ thermodynamic potentials can be used to express criteria for spontaneous change and equilibrium when the corresponding natural variables are held constant. For instance, $G$ can only decrease during the approach to reaction equilibrium at constant $T$ and $p$ in a closed system doing pressure-volume work only, reaching a minimum at equilibrium.

The fundamental relation for $U$, Equation (1.7), can be combined with the definitions for the enthalpy and the free energies (Equations (1.8) to (1.10)) to find analogous fundamental equations for the other thermodynamic potentials, valid for a reversible process:

$$dH = TdS + pdV,$$
$$dF = -SdT - pdV,$$
$$dG = -SdT + Vdp.$$

In addition, a number of useful relations can be derived from these equations. For instance, Equation (1.12) can be compared to the exact differential for $F(T,V)$:

$$dF = \left(\frac{\partial F}{\partial T}\right)_V dT + \left(\frac{\partial F}{\partial V}\right)_T dV.$$  

In this notation, the subscript in $\left(\frac{\partial F}{\partial T}\right)_V$ is used to express that the remaining independent variables other than $T$ for the $F$ function (in this case, only $V$) are held constant. Comparing Equation (1.14) and Equation (1.12), we arrive at:

$$S = -\left(\frac{\partial F}{\partial T}\right)_V, \quad p = -\left(\frac{\partial F}{\partial V}\right)_T.$$
Likewise, for the rest of the thermodynamic potentials,

\[
T = \left( \frac{\partial U}{\partial S} \right)_V, \hspace{1cm} p = -\left( \frac{\partial U}{\partial V} \right)_s, \hspace{1cm} (1.16)
\]

\[
T = \left( \frac{\partial H}{\partial S} \right)_p, \hspace{1cm} V = \left( \frac{\partial H}{\partial p} \right)_s, \hspace{1cm} (1.17)
\]

\[
S = -\left( \frac{\partial G}{\partial T} \right)_p, \hspace{1cm} V = \left( \frac{\partial G}{\partial p} \right)_T. \hspace{1cm} (1.18)
\]

The Maxwell relations can be obtained from the fundamental relations by calculating the mixed second derivatives of the thermodynamic potentials, which need to be the same regardless of the order in which they are taken. For instance,

\[
\left( \frac{\partial^2 F}{\partial T \partial V} \right) = \left( \frac{\partial^2 F}{\partial V \partial T} \right) \hspace{1cm} (1.19)
\]

leads, using Equation (1.15), to:

\[
\left( \frac{\partial p}{\partial T} \right)_V = \left( \frac{\partial S}{\partial V} \right)_T. \hspace{1cm} (1.20)
\]

Likewise, for the other state functions, one has:

\[
\left( \frac{\partial p}{\partial S} \right)_V = -\left( \frac{\partial T}{\partial V} \right)_s \hspace{1cm} \text{(from U),} \hspace{1cm} (1.21)
\]

\[
\left( \frac{\partial V}{\partial S} \right)_p = \left( \frac{\partial T}{\partial p} \right)_s \hspace{1cm} \text{(from H),} \hspace{1cm} (1.22)
\]

\[
\left( \frac{\partial V}{\partial T} \right)_p = -\left( \frac{\partial S}{\partial p} \right)_T \hspace{1cm} \text{(from G).} \hspace{1cm} (1.23)
\]

These relations between thermodynamic potential derivatives are useful because, even though the potentials can not be measured directly, some of their variations correlate with quantities that are experimentally accessible. For instance, the volume derivative of the Helmholtz function (Equation (1.15)) gives the pressure as a function of volume and temperature, an object that is called the “volumetric equation of state”, or simply the “equation of state”, and which plays a key role in theoretical and computational studies of materials under pressure, as we shall see in the next sections. Other material properties and their relation to the corresponding thermodynamic potentials include the...
isothermal ($\kappa_T$) and adiabatic ($\kappa_S$) compressibilities:

$$
\kappa_T = -\frac{1}{V} \left( \frac{\partial V}{\partial p} \right)_T = -\frac{1}{V} \left( \frac{\partial^2 G}{\partial p^2} \right)_T, \\
\kappa_S = -\frac{1}{V} \left( \frac{\partial V}{\partial p} \right)_S = -\frac{1}{V} \left( \frac{\partial^2 H}{\partial p^2} \right)_S,
$$

(1.24)

with units of pressure$^{-1}$. The inverse of the compressibility, called bulk modulus, is often employed:

$$
B_T = \frac{1}{\kappa_T} = -V \left( \frac{\partial p}{\partial V} \right)_T = V \left( \frac{\partial^2 F}{\partial V^2} \right)_T, \\
B_S = \frac{1}{\kappa_S} = -V \left( \frac{\partial p}{\partial V} \right)_S = V \left( \frac{\partial^2 U}{\partial V^2} \right)_S.
$$

(1.25)

The bulk moduli have units of pressure. These intensive properties reflect the elastic response of a solid to hydrostatic compression. The bulk modulus is one of the basic quantities that determines the elasticity of a material (in the case of an isotropic material, together with the Poisson ratio, although one can use equivalently other measures such as the Young modulus or the shear modulus). Typical values for the bulk modulus at ambient conditions [19, 20] are: lithium (11 GPa), NaCl (24 GPa), aluminum (76 GPa), silicon (99 GPa), steel (160 GPa), and diamond (443 GPa). The difference between $B_T$ and $B_S$ is, in general, small compared to the value of the bulk modulus, so the terms are often used interchangeably.

The constant pressure ($C_p$) and constant volume ($C_v$) heat capacities are defined in terms of the heat necessary to raise reversibly the temperature of a closed system, and are defined as:

$$
C_p = \left( \frac{\delta Q}{\delta T} \right)_p = \left( \frac{\partial H}{\partial T} \right)_p = T \left( \frac{\partial S}{\partial T} \right)_p = -T \left( \frac{\partial^2 G}{\partial T^2} \right)_p, \\
C_v = \left( \frac{\delta Q}{\delta T} \right)_V = \left( \frac{\partial U}{\partial T} \right)_V = T \left( \frac{\partial S}{\partial T} \right)_V = -T \left( \frac{\partial^2 F}{\partial T^2} \right)_V,
$$

(1.28)

(1.29)

where we have used $\Delta H = Q_p$ and $\Delta U = Q_v$ in a closed system with pressure-volume work only undergoing constant pressure and constant volume processes, respectively. Heat capacities are extensive properties. Their equivalent intensive properties for pure substances, obtained by dividing the heat capacity by the amount of substance, are the constant pressure and constant volume molar heat capacities, usually represented in lower case ($c_p$ and $c_v$). $C_p$ and $C_v$ measure a system’s ability to store energy, and in consequence they are directly related to the available microscopic degrees of freedom. In a solid, their
temperature dependence is characteristic: \( C_p \) and \( C_v \) go to zero for \( T \to 0 \) and to the Dulong–Petit limit \((3R = 3N_Ak_B \text{ per mole of atoms, with } R \text{ the gas constant, } N_A \text{ the Avogadro’s constant, and } k_B \text{ the Boltzmann’s constant, } 1.3806488 \times 10^{-23} \text{ J/K}) or slightly above it in the high-temperature limit.

The (volumetric) coefficient of thermal expansion or thermal expansivity measures the response of volume to changes in temperature. It is defined as:

\[
\alpha = \alpha_V = \frac{1}{V} \left( \frac{\partial V}{\partial T} \right)_p = \frac{1}{V} \left( \frac{\partial^2 G}{\partial T \partial p} \right).
\]

(1.30)

The thermal expansion coefficient is a quantity with great relevance in engineering and architecture. The vast majority of materials have positive \( \alpha \), that is, they expand when heated at constant pressure, but some materials present extensive temperature ranges with negative thermal expansivity. A characteristic example of this behavior is the cubic zirconium tungstenate (ZrW\(_2\)O\(_8\)), which has a negative \( \alpha \) at all temperatures in its stability range [21]. Likewise, some composite materials like invar, a nickel-iron alloy, have very low thermal expansion coefficients and they are used in construction as well as in precision instruments.

The equations presented above can be used to derive thermodynamic relations between these material properties. For instance, the heat capacities are related by:

\[
C_p - C_v = \frac{\alpha^2VT}{\kappa_T}.
\]

(1.31)

Likewise, the difference between compressibilities is:

\[
\kappa_T - \kappa_S = \frac{\alpha^2TV}{C_p},
\]

(1.32)

and the ratio between heat capacities is the same as between bulk moduli and compressibilities:

\[
\frac{C_p}{C_v} = \frac{B_S}{B_T} = \frac{\kappa_T}{\kappa_S}.
\]

(1.33)

An important quantity that will appear later in this chapter is the thermal Grüneisen parameter:

\[
\gamma_{th} = \frac{V\alpha B_T}{C_v} = \frac{V\alpha B_S}{C_p},
\]

(1.34)

which represents the change in the vibrational characteristics caused by a change in volume. Because the product of the thermal coefficient with the bulk modulus is a simple derivative:

\[
\alpha B_T = \left( \frac{\partial S}{\partial V} \right)_T = \left( \frac{\partial p}{\partial T} \right)_V,
\]

(1.35)
the Grüneisen parameter can be rewritten as:

\[
\gamma_{th} = \frac{V}{C_v} \left( \frac{\partial S}{\partial V} \right)_T = \frac{V}{C_v} \left( \frac{\partial p}{\partial T} \right)_V.
\]

(1.36)

More relations, and the proofs for the ones given above can be found in Wallace’s book [16].

Finally, the Nernst–Simon statement of the third law of thermodynamics says that for any isothermal process that involves only substances in internal equilibrium, the entropy change \(\Delta S\) goes to zero as \(T\) goes to zero. This statement emerged from the works by Richards, Nernst and Simon in the first decade of the past century. Based on the arbitrary choice that the entropy of each element is zero at 0 K, the Nernst–Simon statement of the third law is used to find conventional entropies of compounds: \(S_0 = 0\) for each element or compound in internal equilibrium, where the zero subscript represents 0 K conditions [15].

Microscopically, the entropy is related to the number of microscopic states available to an isolated system for a given volume, internal energy, and number of particles. The relation between entropy and the available number of states compatible with the volume, energy, and number of particles of an isolated system \(\Omega\) is given by Boltzmann’s postulate:

\[
S = k_B \ln \Omega(U,V,N).
\]

(1.37)

At 0 K, only the system’s lowest available energy level is populated and \(\Omega\) becomes the degeneracy of this energy level. For this statistical-mechanical result to be consistent to the thermodynamic result \(S_0 = 0\) for a substance, the degeneracy of the ground level of the one-component system would have to be 1. To make the statistical-mechanical and thermodynamic entropies agree, the convention of ignoring contributions to \(S\) coming from nuclear spins and isotopic mixing is adopted (see more details in Section 21.9 of Reference 15).

The Helmholtz free energy and the Gibbs free energy are related to different statistical ensembles whose macroscopic states are fixed by the values of their natural variables [17]. These are the canonical and the isothermal-isobaric ensembles, respectively. \(F\) and \(G\) are related to the partition functions of the corresponding ensemble by a simple relation:

\[
F(N,V,T) = -k_B T \ln Z(N,V,T),
\]

(1.38)

\[
G(N,p,T) = -k_B T \ln \Delta(N,p,T).
\]

(1.39)

The partition functions are calculated using the available energy levels of the system. For instance, the canonical partition function is:

\[
Z(N,V,T) = \sum_i \exp \left( -\frac{E_i(N,V)}{k_BT} \right),
\]

(1.40)
where the $i$ sums over all states available to the system for the given volume and number of particles, $E_i$ is the energy of that state, and $T$ is the thermodynamic temperature. For a given temperature, if the energy levels are separated by differences much larger than $k_B T$, only the ground energy level ($E_0$) contributes to the sum, and $F(N,V,T) = E_0$ for a non-degenerate ground energy level. Conversely, if the separation of all available energy levels is very small compared to $k_B T$, the partition function reduces to the number of available states and $F$ is a constant times $k_B T$, a result known as the equipartition theorem in classical statistical mechanics.

1.2.2 Principle of Minimum Energy

The second law of thermodynamics—that thermodynamic equilibrium in an isolated system is achieved when the entropy of the system is maximized—can be recast in several ways, depending on the independent variables we use. For every one of the thermodynamic potentials defined above ($U$, $H$, $F$, and $G$), and for a closed system (with pressure-volume work only) in which their corresponding independent variables are fixed, thermodynamic equilibrium is reached when the value of the corresponding potential is minimized.

A useful generalization of the Gibbs free energy is the availability or non-equilibrium Gibbs energy of the system, $G^*$, a function that gives the Gibbs energy of the system away from equilibrium, either material—phase and chemical—or thermal and mechanical equilibrium [22, 23]. It can be shown from the second law that at a fixed environmental temperature $T_E$ and pressure $P_E$, the most stable state of the system is that at which the function $G^* = U + P_E V - T_E S$ has its lowest possible value. This function is only equal to the Gibbs free energy $G$ when the system is at thermal and mechanical equilibrium with the environment ($T_E = T$, $P_E = p$). In the remaining chapters of this book, for simplicity, no distinction will be made between $p$ and $P_E$ or between $G$ and $G^*$, even for systems out of mechanical equilibrium. Which of those quantities is used will be clear from the context.

Let us consider now the particular case of a one-component crystal phase. For a solid, the more convenient variables, in the sense that they can be easily controlled experimentally, are pressure and temperature. In an infinite periodic solid, there are only two sources of energy levels that enter the isothermal-isobaric partition function: electronic and vibrational. For the majority of solids at the usual temperatures, the excited electronic levels are inaccessible, so the thermal contributions to $G^*$ are mostly determined by the vibrational levels.

If a system is held at a fixed temperature $T_E = T$ and a constant hydrostatic pressure $P_E$ (or simply $P$), the equilibrium state minimizes the
non-equilibrium Gibbs energy of the crystal phase,

\[ G^*(x, V; P, T) = F^*(x, V; T) + PV = E_{\text{sta}}(x, V) + F_{\text{vib}}^*(x, V; T) + PV, \]  

with respect to all internal configuration parameters. In this equation, \( E_{\text{sta}} \) is the electronic (static) energy of the solid that is obtainable, for instance, through computational techniques. \( F_{\text{vib}}^* \) is the non-equilibrium vibrational Helmholtz free energy. The structure of a periodic infinite crystal is determined by its volume \( V \) and a number of coordinates, which include the variables that determine the geometry of the unit cell (angles and lattice parameters) as well as the crystallographic coordinates of the atoms whose values are not fixed by symmetry. All these variables are gathered in the \( x \) vector. Additional free energy terms can be used for other degrees of freedom that may represent accessible energy levels at the given temperature and that may contribute to the free energy of the solid, for instance, electronic contributions (in a metal), configurational entropy (in a disordered crystal), etc.

The principle of minimum energy for \( G^* \) says that thermodynamic equilibrium is reached at the \( x \) and \( V \) values for which \( G^* \) is a minimum at given \( T \) and \( P \). That is:

\[ G(p = P, T) = \min_{x, V} G^*(x, V; P, T). \]  

At the \( x \) and \( V \) for which \( G^* \) is a minimum, the value of the system pressure \( p \) is equal to the environmental pressure \( P \).

1.2.3 Hydrostatic Pressure and Thermal Pressure

The minimum energy principle represented by Equation (1.42) can be used to predict \( x(p, T) \), the volume, \( V(p, T) \), and the equilibrium Gibbs function \( G(p, T) \) of a crystal at any given pressure and temperature. In the context of the computational determination of these quantities, however, finding the global minimum of \( G^*(x, V; P, T) \), which involves finding all terms in Equation (1.41) for a large number of \( x \) and \( V \) values, is prohibitive.

A common approach to simplify this problem is to restrict the variables \( x \) to those resulting from a minimization of the electronic (static) energy at any given volume:

\[ x_{\text{opt}}(V) \text{ from } E_{\text{sta}}(V) = \min_x E_{\text{sta}}(x, V). \]  

If no crystal vibrations were present, then \( F_{\text{vib}}^* \) would disappear, and this approach would be strictly correct. Note, however, that \( E(x, V) \) is still a huge
potential energy surface where all crystal phases compatible with that volume are represented. Despite this, crystal structure prediction or a judicious selection of candidate phases can render this problem tractable (see Chapter 4). In the presence of crystal vibrations, Equation (1.43) embodies the approximation that the variation of $F^\ast_{\text{vib}}$ with $\mathbf{x}$ is negligible compared to that of $E_{\text{sta}}$. This “statically constrained” approximation [24–27] transforms Equation (1.41) into:

$$G^*(V; P, T) = E_{\text{sta}}(\mathbf{x}_{\text{opt}}(V), V) + F^\ast_{\text{vib}}(\mathbf{x}_{\text{opt}}(V), V; T) + PV,$$

(1.44)

where all degrees of freedom except for the volume have been eliminated (c.f. Equation (1.41)).

The minimum energy principle can now be applied to Equation (1.44). The equilibrium volume at $P$ and $T$ is found by making the volume derivative of $G^*$ zero, which leads to the mechanical equilibrium condition:

$$\left(\frac{\partial G^*}{\partial V}\right)_{P,T} = 0 = -p_{\text{sta}} - p_{\text{th}} + P.$$

(1.45)

In this equation, $p_{\text{sta}} = -dE_{\text{sta}}/dV$ is the static pressure, $p_{\text{th}} = -(\partial F^\ast_{\text{vib}}/\partial V)_T$ is the thermal pressure, and $P$ is the applied external pressure. At mechanical equilibrium, the sum of static and thermal pressure balances the external pressure applied on the solid:

$$P = p_{\text{sta}} + p_{\text{th}}.$$  

(1.46)

The thermal pressure, which is usually negative, represents the expansion effect caused by the atomic vibrations in the crystal. It can be used, for instance, to estimate the thermal expansion of molecular crystals in order to compare static DFT with experimental x-ray crystal structures in molecular solids [28]. If the equilibrium is stable (or metastable) then $G^*$ must be a minimum with respect to variations (or small variations) in the volume at constant $P$ and $T$. In other words, the second derivative of $G^*$ with respect to volume (at constant $T$ and $P$) must be positive. This second derivative is equal to $B_T V$, thus obtaining the usual criterion for mechanical stability ($B_T > 0$).

In the statically constrained approximation, the thermal pressure depends only on volume and temperature. In reality, $p_{\text{th}}$ depends on all variables $\mathbf{x}$ and particularly on the shape of the unit cell for a particular volume. The statically constrained approximation can be partially relaxed [26, 27, 29] by considering both volume and strain in Equation (1.43). The thermal pressure is then generalized to a thermal stress:

$$\sigma_{\text{th},ij}(\varepsilon_{ij}, V; T) = \frac{1}{V} \frac{\partial F^\ast_{\text{vib}}(\mathbf{x}_{\text{opt}}(\varepsilon_{ij}, V), \varepsilon_{ij}, V; T)}{\partial \varepsilon_{ij}},$$

(1.47)
where $\varepsilon$ is the strain tensor—a measure of the deformation of the solid with respect to the equilibrium geometry at volume $V$ (also see Chapter 2). In the statically constrained approximation, the thermal stress tensor $\sigma$ would be diagonal and its elements equal to minus the thermal pressure. However, even this generalization leads to a computationally prohibitive iterative process involving an “excessive number of calculations” [26].

1.2.4 Phase Equilibria

At a given temperature $T$ and pressure $P$, there are many different atomic arrangements of a crystal (corresponding to different values of $V$ and $x$ in Equation (1.41)) that are local minima of the non-equilibrium Gibbs function $G^\star$. A corollary of the minimum energy principle is that of all these minima, only the one with the lowest $G^\star$ (the global minimum) represents the thermodynamically stable phase, and the rest are metastable phases. The two-dimensional plot that represents the stable crystal phase as a function of temperature $T$ and pressure $p$ is called a (pressure-temperature) phase diagram. An example is shown in Figure 1.1.

The phase diagram of a solid determines the behavior of the material at arbitrary temperature and pressure conditions, and is therefore of great technological relevance. Even though only one of the phases is thermodynamically stable at a given pressure and temperature, metastable phases of pure crystalline solids, which are not usually represented in a phase diagram, are the rule rather than the exception. Carbon is the traditional example: graphite is the stable polymorph at zero pressure and room temperature, but diamonds are observed (metastable) because the transition from diamond to graphite...
is kinetically very unfavorable under room conditions (the energy barrier the material needs to overcome to go from one phase to the other is too high, see Chapter 2). As a matter of fact, the artificial generation of diamonds requires pressures and temperatures well beyond the thermodynamic limits of the graphite phase.

The boundaries between regions associated to different phases represent particular states of a system in which two phases may coexist. For a given temperature, the pressure at which one phase transforms reversibly into another is called the transition pressure, \( p_{tr}(T) \). Along the two-phase equilibrium curves, the value of \( G(p, T) \) per mole is the same for both phases. By using this result, one can calculate properties of the curve such as its slope at a given point, which is given by the Clapeyron equation:

\[
\frac{dp_{tr}}{dT} = \frac{\Delta S_{tr}}{\Delta V_{tr}} = \frac{\Delta H_{tr}}{T \Delta V_{tr}},
\]

where \( \Delta S_{tr} \) and \( \Delta V_{tr} \) are the differences in entropy and volume between both phases at that point. During most phase transitions, energy is absorbed or released by the system and the volume increases or decreases without change in temperature and pressure. This "latent heat" (or the volume change) is used to drive the transition from one phase to the other. The latent heat is given by \( \Delta H_{tr} \).

From a thermodynamic point of view, phase transitions can be classified according to the derivatives of \( G \) that are discontinuous across the transformation [30]. First order phase transitions involve latent heat and are characterized by an infinite heat capacity at the transition temperature and pressure as well as by discontinuities in the properties that are derivatives of the Gibbs function: \( V \) and \( -S \). Most phase transitions belong in this category; boiling water is an example of a first order phase transition.

In contrast, high order or continuous phase transitions do not involve latent heat. In second-order phase transitions, there is a discontinuity in the heat capacity, but it does not diverge. The isothermal compressibility and the thermal expansion coefficient, which contain also second derivatives of \( G \) with respect to \( T \) and/or \( p \), are discontinuous too. The first derivatives of \( G \), volume and minus entropy, show changes in their slopes, but they are continuous across the transition. In consequence, the Clapeyron equation cannot be applied. An example of a second-order phase transition is the onset of a superconducing regime in a material. See more details in Chapter 3 and also in References 15 and 30. Other phase transition classifications using different criteria are presented in Chapter 2.
1.3 EQUATIONS OF STATE

An equation of state (EOS) is a relationship between the thermodynamic variables relevant for a given mass of a solid phase under study at equilibrium. For a solid phase under pressure, the volumetric EOS is written in terms of pressure $p$, volume $V$, and temperature $T$:

$$F(p, V, T) = 0.$$ (1.49)

A simple equation of state, presented in Murnaghan’s historical paper [31], is based on the principle of conservation of mass combined with Hooke’s law for an infinitesimal variation of stress in a solid. The Murnaghan EOS can also be obtained by assuming a linear variation of the isothermal bulk modulus with pressure, $B_T(p) = B_0 + B_0' p$, and integrating $B_T = -V(\partial p/\partial V)_T$:

$$V(p) = V_0 \left(1 + \frac{B_0'}{B_0} p \right)^{-1/B_0'},$$ (1.50)

which can be inverted to:

$$p(V) = \frac{B_0}{B_0'} \left[ \left( \frac{V_0}{V} \right)^{B_0'} - 1 \right].$$ (1.51)

The hydrostatic work equation, $\delta W = -pdV$, can then be used to integrate this equation of state to give:

$$E(V) = E_0 + \frac{B_0 V}{B_0'} \left[ \frac{(V_0/V)^{B_0'}}{B_0' - 1} + 1 \right] \frac{B_0 V_0}{B_0' - 1},$$ (1.52)

for the volume-dependent energy at zero temperature. In these and the subsequent equations in this section, the subscript “0” represents zero-pressure conditions. That is, $V_0$ is the (zero-pressure) equilibrium volume, $E_0$ is the energy at that volume, etc. In the rest of this section, we consider only static energies, although the same equations of state (or rather, their derivatives) can be used to fit experimental pressure-volume isotherms, which contain zero-point and temperature effects.

A collection of equations of state for solids can be obtained from the strain-stress (StSs) family of relations. We describe the energy of a crystal as a Taylor expansion in the strain $f$:

$$E = \sum_{k=0}^{n} c_k f^k.$$ (1.53)

Some of the equations of state arising from different strain definitions follow.
1.3.1 Birch–Murnaghan Family

The Birch–Murnaghan (BM) EOS family is based on the Eulerian strain, which is defined as:

\[ f = \frac{1}{2} \left[ \left( \frac{V_r}{V} \right)^{2/3} - 1 \right], \quad (1.54) \]

where \( V_r \), the reference volume, is usually the zero-pressure equilibrium volume of the phase under study \( (V_0) \).

The StSs series can be expanded to any order \( n > 1 \) (Equation (1.53)). The resulting \( n \)-degree polynomial EOS has coefficients that can be found by imposing the limiting conditions for the derivatives at the reference point \( (V_r) \):

\[
\lim_{f \to 0} \left\{ V; E; p = \frac{dE}{dV}; B = -V \frac{dp}{dV}; B' = \frac{dB}{dp}; \ldots \right\} = \left\{ V_0; E_0; 0; B_0; B'_0; \ldots \right\}. \quad (1.55)
\]

For instance, solving these equations for the fourth-order \( (n = 4) \) Birch–Murnaghan EOS gives:

\[
\begin{align*}
V_r &= V_0; \quad (1.56) \\
c_0 &= E_0; \quad (1.57) \\
c_1 &= 0; \quad (1.58) \\
c_2 &= \frac{9}{2} V_0 B_0; \quad (1.59) \\
c_3 &= \frac{9}{2} V_0 B_0 (B'_0 - 4); \quad (1.60) \\
c_4 &= \frac{3}{8} V_0 B_0 \{ 9[B_0 B''_0 + (B'_0)^2] - 63 B'_0 + 143 \}. \quad (1.61)
\end{align*}
\]

The polynomial strain EOS can be rearranged to produce the second-order Birch–Murnaghan equations, which are non-linear in the volume, and are typically used in solid-state simulations [32]:

\[
\begin{align*}
E &= E_0 + \frac{9}{2} B_0 V_0 f^2 = E_0 + \frac{9}{8} B_0 V_0 (x^{-2/3} - 1)^2, \quad (1.62) \\
p &= 3B_0 f (1 + 2f)^{5/2} = \frac{3}{2} B_0 \left( x^{-7/3} - x^{-5/3} \right), \quad (1.63) \\
B &= B_0 (7f + 1)(2f + 1)^{5/2}, \quad (1.64)
\end{align*}
\]

with \( x = (V/V_0) \).

Higher order BM EOS result in even more cumbersome non-linear expressions that are not always easy to converge. Furthermore, the Eulerian strain is just one of an infinite number of possible definitions [33]. Other options are
1.1 INTRODUCTION TO HIGH-PRESSURE SCIENCE

HIGH pressure research [1] is a field of enormous relevance both for its scientific interest and for its industrial and technological applications. Many
materials undergo fascinating changes in their physical and chemical characteristics when subjected to extreme pressure. This behavior is caused by the involvement in bonding of electrons that would otherwise not be chemically active under zero-pressure conditions (the difference between zero pressure and atmospheric pressure is negligible from the point of view of its effect on materials properties, and we will use both concepts interchangeably). By and large, current chemical knowledge and the traditional rules for valence electrons are at a loss to explain most of the changes induced when materials are compressed, which makes chemical bonding under pressure an exciting research topic that has received much attention in recent years [1] (see Chapter 5).

The study of pressure effects can be approached in two mostly complementary ways: experimentally and computationally. In both cases, the basic object under study is the change in crystal structure a material undergoes when a given pressure and temperature are applied as shown in its thermodynamic pressure-temperature phase diagram. Experimentally, the application of temperature is relatively straightforward, but imposing high pressure on a sample requires specialized techniques that have been under development for the past 80 years. The field of experimental high-pressure physics was pioneered by Percy Bridgman, who received the Nobel Prize for his efforts in 1946 [2].

There are two main experimental high-pressure techniques: dynamic compression methods based on shock waves, and static compression methods which make use of pressure cells. In a shock-wave compression experiment [3], a strong shock is applied to the sample and the propagation velocities of the shock wave inside the material are measured. Very high pressures (up to 500–1000 GPa) and temperatures (tens of thousands of K) can be attained with this technique. Static compression techniques are applied using pressure cells, notably diamond anvil cells [4]. These methods are more accurate than dynamic techniques, but they are also limited by the pressure scale, with the mechanical resistance of a diamond (slightly above 300 GPa) being the ultimate upper pressure limit for the technique. High temperatures, in the range of thousands of K, can be attained by laser heating, and diamond anvil cells can be coupled to other techniques: spectroscopic (infrared, Raman, x-ray) and optical. Experimental high-pressure techniques are explored in Part II of this book.

From the computational point of view, in the framework of density functional theory (DFT), the application of pressure is relatively straightforward: one simply compresses the unit cell and calculates the applied pressure either analytically from the self-consistent one-electron states or from the volume derivative of the calculated total energy. The latter requires fitting an equation of state. Conversely, temperature effects are difficult to model because they involve collective atomic vibrations—called phonons—propagating throughout