

Chapter 1

Introduction

1.1 Introductory Remarks

Statistical physics embraces in particular statistical mechanics and statistical thermodynamics. The word statistical implies already that the subject deals with a large number of elements like the number of atoms or molecules in a macroscopic body. A theoretical treatment of statistical physics thus attempts to describe macroscopic phenomena in terms of microscopic processes. Elementary microscopic processes are obviously those of atoms and molecules. Statistical thermodynamics considers primarily microscopic processes in some enclosure like a box which imposes stringent boundary conditions on the dynamics of the particles. Consequently in a first approach to the subject one considers cases in which the interaction between individual atoms or molecules is of secondary importance, as in the case of a dilute gas in some container. The realization that the motion of atoms, *i.e.* their kinetic energy, is related to the macroscopically observed temperature was a considerable step forward in our understanding of the relationship between atomic physics and classical thermodynamics. Thus a perfect gas suggests itself naturally as a first object to consider, and then the question whether other cases, *e.g.* conduction electrons in a metal, can be considered similarly. And how are solids to be treated in this context? The naive picture of a solid as a lattice with atoms located at lattice sites suggests to consider these in analogy with harmonic oscillators, for instance, one oscillator at every lattice site. The simple one-dimensional harmonic oscillator serves in view of its mathematical simplicity in many areas of physics as a convenient first modelling example. Thus in a first attempt it is an obvious idea to abstract the atoms at lattice sites to such harmonic oscillators whose oscillations describe the vibrations of an atom or molecule. The harmonic oscillator

played a vital role in the development of quantized statistics as conceived by Planck: It was Planck's idea of considering the simple harmonic oscillator as statistically equivalent to a normal mode of vibration which led him to discretized energies. Thus both free particles and oscillators play a dominant role in our introduction to the subject here. However, the quantized simple one-dimensional harmonic oscillator has one limitation: Its eigenvalues are nondegenerate. Since degeneracy will be seen to be a characteristic of many particle states of statistical physics it is expedient to consider oscillators also in higher dimensions, for instance, in a model of solids. Our presentation here begins with elementary kinetic theory. We then introduce the concept of *a priori* probability and show that this can be identified with the degeneracy of states. In classical Maxwell–Boltzmann statistics we consider the number of arrangements W of particles among states of various degeneracies and then determine that particular arrangement which appears with maximum probability. We proceed similarly with quantum statistics, taking into account the indistinguishability of elements, the number of elements permissible per state, and whether the elements are conserved or nonconserved, and thus arrive at Bose–Einstein and Fermi–Dirac statistics. In the last chapter we consider the Darwin–Fowler method of mean values and observe that the more rigorously derived results of this method are the same as those obtained with maximization. However, before we consider quantum statistics we introduce the concept of entropy S as defined by Boltzmann by the relation $S = k \ln W$, k being Boltzmann's constant. Since our aim here is a presentation of the basic principles of statistical physics, including a clear distinction between classical and quantum statistics, we assume here a knowledge of basic quantum mechanics as well as elementary thermodynamics such as one acquires in introductory physics courses. Since we make here particular use of thermodynamics, we recapitulate below some of the basic equations of classical thermodynamics with particular reference to the various thermodynamic potentials. We emphasize: This is only a brief summary of selected equations without any attempt to enter into detailed explanations. For details we refer to the book of H.B. Callen [6].

1.2 Thermodynamic Potentials

We summarize here some very general relations of the thermostatics of homogeneous systems. These relations involve quantities known as *thermodynamic potentials*. We assume a constant number of particles N . The volume V is an external parameter. The *second law of thermodynamics* expressed in terms of entropy S , temperature T , heat Q , as well as (mean) internal energy E is

generally written in infinitesimal form as

$$TdS = dQ = dE + PdV \quad (1.1)$$

(the first law being the law of conservation of energy, $dQ = dE + PdV$). In this form the energy E is a function of S and V , *i.e.* $E = E(S, V)$. However, one can choose different combinations of independent macroscopic parameters like in mechanics one can derive Newton's equation from the Lagrangian $L(q, \dot{q})$ or from the Hamiltonian $H(q, p)$, the two quantities being related by a *Legendre transform*, *i.e.* the relation $H(q, p) = \dot{q}p - L(q, \dot{q})$, so that $p = \partial L / \partial \dot{q}$ and $\partial H / \partial \dot{q} = 0$. The various forms of thermodynamic potentials are related in a similar way. We can choose as independent macroscopic parameters the following sets:

- (a) N, S, V ,
- (b) N, S, P ,
- (c) N, T, V ,
- (d) N, T, P .

In the case of (a) we have $E = E(S, V)$. In order to transform to set (b) we define (in analogy to mechanics above) the quantity $H(S, P)$ called *enthalpy* or *total heat* by the relation

$$H(S, P) := VP + E(S, V), \quad (1.2)$$

which is such that

$$\frac{\partial H}{\partial V} = 0 \quad \text{with} \quad P = -\frac{\partial E}{\partial V}. \quad (1.3)$$

In classical mechanics we have Hamilton's equations

$$\dot{q} = \frac{\partial H(q, p)}{\partial p}, \quad \dot{p} = -\frac{\partial H(q, p)}{\partial q}. \quad (1.4)$$

Correspondingly we have in the present case:

$$V = \left(\frac{\partial H}{\partial P} \right)_S, \quad T = \left(\frac{\partial H}{\partial S} \right)_V = \left(\frac{\partial H}{\partial S} \right)_P \quad (1.5)$$

(we shall see that these can also be read off the infinitesimal relations given below). Corresponding to each of the four transformations

$$(S, V) \rightarrow (S, P), \quad (S, V) \rightarrow (T, V), \quad (T, V) \rightarrow (T, P), \quad (S, P) \rightarrow (T, P),$$

we require one quantity corresponding to the Hamiltonian in mechanics, and hence four such quantities altogether if we include E . These four quantities, including E are referred to as *thermodynamic potentials*. These are:

$$\begin{array}{ll}
 E(S, V) & \text{called "internal energy",} \\
 H(S, P) = E(S, V) + PV & \text{called "enthalpy" or} \\
 \quad (= G(T, P) + TS) & \text{"total heat",} \\
 F(T, V) = E(S, V) - TS & \text{called "free energy",} \\
 G(T, P) = E(S, V) - TS + PV & \text{called "free enthalpy" or} \\
 \quad (= F(T, V) + PV) & \text{"Gibbs function".}
 \end{array}$$

We consider in each of these cases the relations corresponding to Hamilton's equations in mechanics.

(a) $E(S, V)$: We have from the second law of thermodynamics

$$dE = TdS - PdV$$

and

$$\therefore T = \left(\frac{\partial E}{\partial S} \right)_V, \quad -P = \left(\frac{\partial E}{\partial V} \right)_S, \quad (1.6)$$

and hence the *first Maxwell relation*:

$$\left(\frac{\partial T}{\partial V} \right)_S = - \left(\frac{\partial P}{\partial S} \right)_V. \quad (1.7)$$

(b) $H(S, P)$: We obtain from the definition of H :

$$dH(S, P) = dE + PdV + VdP = TdS + VdP, \quad (1.8)$$

and (recall also that $H(S, P) = E(S, V) + PV$)

$$\therefore \left(\frac{\partial H}{\partial P} \right)_S = V, \quad \left(\frac{\partial H}{\partial S} \right)_P = \left(\frac{\partial E}{\partial S} \right)_P = T, \quad (1.9)$$

and hence the *second Maxwell relation*:

$$\left(\frac{\partial V}{\partial S} \right)_P = \left(\frac{\partial T}{\partial P} \right)_S. \quad (1.10)$$

(c) $F(T, P)$: We obtain from the definition of F :

$$dF(T, V) = dE - TdS - SdT = -SdT - PdV, \quad (1.11)$$

and

$$\therefore \left(\frac{\partial F}{\partial T}\right)_V = -S, \quad \left(\frac{\partial F}{\partial V}\right)_T = \left(\frac{\partial E}{\partial V}\right)_T = -P, \quad (1.12)$$

and hence the *third Maxwell relation*:

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V. \quad (1.13)$$

(d) $G(T, P)$: We obtain from the definition of G :

$$dG(T, P) = dE - TdS - SdT + PdV + VdP = VdP - SdT, \quad (1.14)$$

and

$$\therefore \left(\frac{\partial G}{\partial T}\right)_P = -S = \left(\frac{\partial F}{\partial T}\right)_V, \quad \left(\frac{\partial G}{\partial P}\right)_T = V, \quad (1.15)$$

and hence the *fourth Maxwell relation*:

$$\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P. \quad (1.16)$$

These results can be read off the infinitesimal relations

$$\left. \begin{aligned} dH &= TdS + VdP, \\ dF &= -SdT - PdV, \\ dG &= S(-dT) + VdP. \end{aligned} \right\} \quad (1.17)$$

We shall see later in statistical thermodynamics that most of the thermodynamical relations required can be derived from the free energy F , which is therefore of particular importance. The natural question to follow is, of course: What is the use of the Maxwell relations? Since our main topic here is not classical thermodynamics, we only illustrate the use of a Maxwell relation below in the consideration of heat capacities. A few useful tricks in manipulating the relations in specific calculations are the following:

$$\left(\frac{\partial x}{\partial y}\right)_z = \left[\left(\frac{\partial y}{\partial x}\right)_z\right]^{-1}, \quad \left(\frac{\partial x}{\partial y}\right)_z = \left(\frac{\partial x}{\partial w}\right)_z \left[\left(\frac{\partial y}{\partial w}\right)_z\right]^{-1}. \quad (1.18)$$

Moreover, from $z = z(x, y)$ we obtain

$$dz = \left(\frac{\partial z}{\partial x}\right)_y dx + \left(\frac{\partial z}{\partial y}\right)_x dy, \quad (1.19)$$

so that for $z = \text{const.}$

$$0 = \left(\frac{\partial z}{\partial x}\right)_y \left(\frac{\partial x}{\partial y}\right)_z + \left(\frac{\partial z}{\partial y}\right)_x \quad \text{or} \quad \left(\frac{\partial x}{\partial y}\right)_z = -\frac{(\partial z/\partial y)_x}{(\partial z/\partial x)_y}. \quad (1.20)$$

1.3 Capacity of Heat

Throughout the text we shall frequently consider a quantity C known as the *capacity of heat* or *specific heat* (the latter frequently being defined as C per particle). This quantity is a measure of the capability of a substance to store heat; hence its name. One defines specifically and very generally the two quantities

$$\begin{aligned} C_V &= \left(\frac{dQ}{dT} \right)_V = T \left(\frac{\partial S}{\partial T} \right)_V, \\ C_P &= \left(\frac{dQ}{dT} \right)_P = T \left(\frac{\partial S}{\partial T} \right)_P. \end{aligned} \quad (1.21)$$

Temperature T and pressure P are easiest to measure. Thus consider for instance $S = S(T, P)$. Then

$$\begin{aligned} dQ &= T dS(T, P) \\ &= T \left[\left(\frac{\partial S}{\partial T} \right)_P dT + \left(\frac{\partial S}{\partial P} \right)_T dP \right] \\ &= C_P dT + T \left(\frac{\partial S}{\partial P} \right)_T dP. \end{aligned} \quad (1.22)$$

But $P = P(V, T)$, so that

$$dP(V, T) = \left(\frac{\partial P}{\partial T} \right)_V dT + \left(\frac{\partial P}{\partial V} \right)_T dV. \quad (1.23)$$

It follows that

$$\frac{dQ}{dT} = C_P + T \left(\frac{\partial S}{\partial P} \right)_T \left\{ \left(\frac{\partial P}{\partial T} \right)_V + \left(\frac{\partial P}{\partial V} \right)_T \frac{dV}{dT} \right\}, \quad (1.24)$$

and therefore

$$C_V = \left(\frac{dQ}{dT} \right)_V = C_P + T \left(\frac{\partial S}{\partial P} \right)_T \left(\frac{\partial P}{\partial T} \right)_V. \quad (1.25)$$

With the help of the fourth Maxwell relation (1.16) this equation becomes

$$C_V = C_P - T \left(\frac{\partial V}{\partial T} \right)_P \left(\frac{\partial P}{\partial T} \right)_V. \quad (1.26)$$

One now defines as *expansion coefficient* α the expression

$$\alpha := \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_P. \quad (1.27)$$

One also defines as *isothermal compressibility* κ the expression

$$\kappa := -\frac{1}{V} \left(\frac{\partial V}{\partial P} \right)_T, \quad (1.28)$$

and as *stress coefficient* β :

$$\beta := \frac{1}{P} \left(\frac{\partial P}{\partial T} \right)_V. \quad (1.29)$$

These parameters are introduced because they are relatively easy to determine experimentally. We can now express the difference $C_V - C_P$ in terms of these parameters. Thus, using Eq. (1.20), we have

$$\left(\frac{\partial P}{\partial T} \right)_V = -\frac{(\partial V / \partial T)_P}{(\partial V / \partial P)_T} = \frac{\alpha V}{\kappa V} = \frac{\alpha}{\kappa}. \quad (1.30)$$

It follows that

$$C_V = C_P - \frac{\alpha^2 V T}{\kappa}. \quad (1.31)$$

Concerning further properties of heat capacities, in particular their behaviour in approaching the absolute zero of temperature (and the third law of thermodynamics according to which $S(T, V)$ and $S(T, P)$ approach a constant independent of external parameters) we refer to the book of Callen [6]. The same applies to the question of which experimental data are required in order to determine S, E, F .

1.4 Frequently Used Terms

In closing this recapitulation of some aspects of classical thermodynamics we summarize some frequently used terms. We mentioned already W , the number of arrangements of (say N) elements (atoms, molecules). It is this quantity which Boltzmann related to entropy in his famous formula $S = k \ln W$ (the subject of Chapter 5). Considering dS , we have in general (for external parameters X_i like V or a magnetic field H)

$$dS = k d \ln W(E, X_i, t) \quad (1.32)$$

together with the relations

$$dQ = dE + dW \quad \text{and} \quad dW = \sum_i \phi_i dX_i \stackrel{(1.1)}{=} PdV + MdH. \quad (1.33)$$

Note that t is here a macroscopic time. Then:

A process is *quasistatic* if

$$\frac{\partial W}{\partial t} \sim 0. \quad (1.34)$$

A process is *reversible* if

$$dS = 0 \quad (W_{\text{initial}} = W_{\text{final}}). \quad (1.35)$$

A process is said to be *isothermal* if

$$dT = 0 \quad (T_{\text{initial}} = T_{\text{final}}). \quad (1.36)$$

A process is said to be *adiabatic* if

$$dQ = 0. \quad (1.37)$$

1.5 Applications and Examples

Example 1.1: Equivalence of E and entropy S equilibrium principles

Assuming E is the total energy of a system A in contact with a heat bath R , and S the entropy, show that the equilibrium values of the internal parameters (*e.g.* temperature T) can be determined from either the *minimum energy principle* or the *maximum entropy principle*, *i.e.*

$$\delta E = 0 \quad \text{with} \quad \delta^2 E > 0, \quad \text{or} \quad \delta S = 0 \quad \text{with} \quad \delta^2 S < 0. \quad (1.38)$$

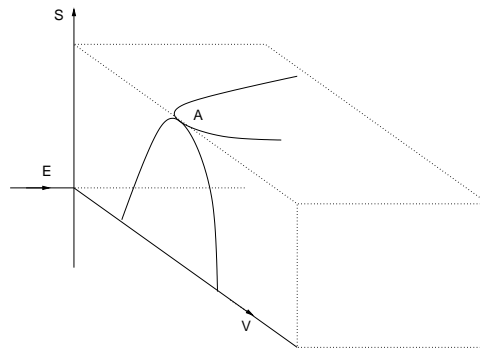


Fig. 1.1 Maximum S , minimum E of equilibrium state A .

Solution: We establish the equivalence of the two principles by showing that if the energy is not minimal, then at equilibrium the entropy can not be maximal. Thus we begin by assuming that at a given maximal entropy the energy E is not minimal. We consider the *second law of thermodynamics*,

$$TdS = dQ = dE + dW. \quad (1.39)$$

We keep the entropy constant, so that $dQ = 0$. Since the energy is not that of a minimum, we can lower the energy by an amount dE by allowing the system to perform the amount of work dW (with no change in the entropy — for instance by allowing a piston to slowly push the gas outside,

quasistatically and adiabatically). Thereafter we re-establish the original energy of the system by adding the amount of heat dQ . Then the energy of the system is the same as before. However, we have increased the entropy by the amount dQ/T . Also we assumed that the system occupied a state of maximal entropy in its state of equilibrium. Hence our assumption must be wrong, *i.e.* the energy of the system in equilibrium at maximum entropy must be minimal. Hence the equilibrium state follows from both principles. This is what one would expect, as a state of equilibrium is usually connected with a minimum of energy. This equivalence is illustrated in Fig. 1.1 in which the point A represents a state of equilibrium with in one case S maximal at $E = \text{const.}$, and in the other case E minimal at $S = \text{const.}$

Example 1.2: Heat capacity from equation of state

Show that $C_V(T, V)$ can be derived from the equation of state.

Solution: We choose T and V as independent parameters of S , *i.e.* we start from $S = S(T, V)$. Then

$$dS = \left(\frac{\partial S}{\partial T}\right)_V dT + \left(\frac{\partial S}{\partial V}\right)_T dV \stackrel{(1.21), (1.13)}{=} \frac{1}{T} C_V dT + \left(\frac{\partial P}{\partial T}\right)_V dV. \quad (1.40)$$

Thus

$$C_V = T \left(\frac{\partial S}{\partial T}\right)_V, \quad (1.41)$$

and

$$\left(\frac{\partial}{\partial V} C_V\right)_T = \left(\frac{\partial}{\partial V}\right)_T \left[T \left(\frac{\partial S}{\partial T}\right)_V \right] = T \left(\frac{\partial}{\partial T}\right)_V \left(\frac{\partial S}{\partial V}\right)_T \stackrel{(1.13)}{=} T \left(\frac{\partial}{\partial T}\right)_V \left(\frac{\partial P}{\partial T}\right)_V, \quad (1.42)$$

i.e.

$$\left(\frac{\partial C_V}{\partial V}\right)_T = T \left(\frac{\partial^2 P}{\partial T^2}\right)_V. \quad (1.43)$$

We can obtain the right hand side from the equation of state ($P = \dots$). Hence C_V follows from the equation

$$C_V(T, V) = C_V(T, V_1) + \int_{V_1}^V \left(\frac{\partial C_V(T, V')}{\partial V'}\right)_T dV'. \quad (1.44)$$

1.6 Problems without Worked Solutions

Example 1.3: Van-der-Waals gas

The equation of state of a van-der-Waals gas is*

$$\left(P + \frac{a^2}{V^2}\right)(V - b) = NkT, \quad a, b > 0. \quad (1.45)$$

Derive for this gas an expression for the difference $C_P - C_V$, and from this its value in the limit $V \rightarrow \infty$. (Answer for $V \rightarrow \infty$: $C_P - C_V = Nk$).

Example 1.4: Velocity of sound in a gas

The velocity of sound in a gas is given by the relation

$$v_s = \sqrt{-\frac{V}{\rho} \left(\frac{\partial P}{\partial V}\right)_S}, \quad (1.46)$$

*Note that for a perfect gas $PV = (N/N_0)RT = NkT$. Here k is Boltzmann's constant given by $k = R/N_0$, where N_0 is Avogadro's number (the number of particles of mass m of an element of atomic weight N_0m), and R is the gas constant, and N the number of particles.

where ρ is the density of the gas. The capacity of heat at constant pressure can be expressed as

$$C_P(T) = A + BT + CT^2, \quad (1.47)$$

and A, B, C can be looked up in Tables. Express v_s in terms of P, T and C_P for a perfect gas with equation of state $PV = RT$. (Answer: $v_s = \sqrt{PC_P(T)/\rho\{C_P(T) - R\}}$).