Soon after its appearance, the Fermi–Dirac statistics were applied by Fowler (1926) to discuss the equilibrium states of white dwarf stars and by Pauli (1927) to explain the weak, temperature-independent paramagnetism of alkali metals; in each case, one had to deal with a "highly degenerate" gas of electrons that obey Fermi–Dirac statistics. In the wake of this, Sommerfeld produced his monumental work of 1928 that not only put the electron theory of metals on a physically secure foundation but also gave it a fresh start in the right direction. Thus, Sommerfeld could explain practically all the major properties of metals that arose from conduction electrons and, in each case, obtained results that showed much better agreement with experiment than the ones following from the classical theories of Riecke (1898), Drude (1900), and Lorentz (1904–1905). Around the same time, Thomas (1927) and Fermi (1928) investigated the electron distribution in heavier atoms and obtained theoretical estimates for the relevant binding energies; these investigations led to the development of the so-called *Thomas–Fermi model* of the atom, which was later extended so that it could be applied to molecules, solids, and nuclei as well.[15]

Thus, the whole structure of statistical mechanics was overhauled by the introduction of the concept of indistinguishability of (identical) particles.[16] The statistical aspect of the problem, which was already there in view of the large number of particles present, was now augmented by another statistical aspect that arose from the probabilistic nature of the wave mechanical description. One had, therefore, to carry out a *two-fold* averaging of the dynamical variables over the states of the given system in order to obtain the relevant expectation values. That sort of a situation was bound to necessitate a reformulation of the ensemble theory itself, which was carried out step by step. First, Landau (1927) and von Neumann (1927) introduced the so-called *density matrix*, which was the quantum-mechanical analogue of the *density function* of the classical phase space; this was elaborated, both from statistical and quantum-mechanical points of view, by Dirac (1929–1931). Guided by the classical ensemble theory, these authors considered both *microcanonical* and *canonical* ensembles; the introduction of *grand canonical* ensembles in quantum statistics was made by Pauli (1927).[17]

The important question as to which particles would obey Bose–Einstein statistics and which Fermi–Dirac remained theoretically unsettled until Belinfante (1939) and Pauli (1940) discovered the vital connection between spin and statistics.[18] It turns out that those particles whose spin is an integral multiple of $\hbar$ obey Bose–Einstein statistics while those whose spin is a half-odd integral multiple of $\hbar$ obey Fermi–Dirac statistics. To date, no third category of particles has been discovered.

Apart from the foregoing milestones, several notable contributions toward the development of statistical mechanics have been made from time to time; however, most of those contributions were concerned with the development or perfection of mathematical techniques that make application of the basic formalism to actual physical problems more fruitful. A review of these developments is out of place here; they will be discussed at their appropriate place in the text.

[15]For an excellent review of this model, see March (1957).

[16]Of course, in many a situation where the wave nature of the particles is not so important, classical statistics continue to apply.

[17]A detailed treatment of this development has been given by Kramers (1938).

[18]See also Lüders and Zumino (1958).

1

The Statistical Basis of Thermodynamics

In the annals of thermal physics, the 1850s mark a very definite epoch. By that time the science of thermodynamics, which grew essentially out of an experimental study of the macroscopic behavior of physical systems, had become, through the work of Carnot, Joule, Clausius, and Kelvin, a secure and stable discipline of physics. The theoretical conclusions following from the first two laws of thermodynamics were found to be in very good agreement with the corresponding experimental results.[1] At the same time, the kinetic theory of gases, which aimed at explaining the macroscopic behavior of gaseous systems in terms of the motion of their molecules and had so far thrived more on speculation than calculation, began to emerge as a real, mathematical theory. Its initial successes were glaring; however, a real contact with thermodynamics could not be made until about 1872 when Boltzmann developed his H-theorem and thereby established a direct connection between entropy on one hand and molecular dynamics on the other. Almost simultaneously, the conventional (kinetic) theory began giving way to its more sophisticated successor — the ensemble theory. The power of the techniques that finally emerged reduced thermodynamics to the status of an "essential" consequence of the get-together of the *statistics* and the *mechanics* of the molecules constituting a given physical system. It was then natural to give the resulting formalism the name *Statistical Mechanics*.

As a preparation toward the development of the formal theory, we start with a few general considerations regarding the statistical nature of a macroscopic system. These considerations will provide ground for a statistical interpretation of thermodynamics. It may be mentioned here that, unless a statement is made to the contrary, the system under study is supposed to be in one of its equilibrium states.

1.1   The macroscopic and the microscopic states

We consider a physical system composed of N identical particles confined to a space of volume V. In a typical case, N would be an extremely large number — generally, of order 10^{23}. In view of this, it is customary to carry out analysis in the so-called *thermodynamic limit*, namely $N \to \infty$, $V \to \infty$ (such that the ratio N/V, which represents the *particle density n*, stays fixed at a preassigned value). In this limit, the *extensive* properties of the system

[1]The third law, which is also known as *Nernst's heat theorem*, did not arrive until about 1906. For a general discussion of this law, see Simon (1930) and Wilks (1961); these references also provide an extensive bibliography on this subject.

become directly proportional to the size of the system (i.e., proportional to N or to V), while the *intensive* properties become independent thereof; the particle density, of course, remains an important parameter for all physical properties of the system.

Next we consider the total energy E of the system. If the particles comprising the system could be regarded as noninteracting, the total energy E would be equal to the sum of the energies ε_i of the individual particles:

$$E = \sum_i n_i \varepsilon_i, \tag{1}$$

where n_i denotes the number of particles each with energy ε_i. Clearly,

$$N = \sum_i n_i. \tag{2}$$

According to quantum mechanics, the single-particle energies ε_i are discrete and their values depend crucially on the volume V to which the particles are confined. Accordingly, the possible values of the total energy E are also discrete. However, for large V, the spacing of the different energy values is so small in comparison with the total energy of the system that the parameter E might well be regarded as a *continuous* variable. This would be true even if the particles were mutually interacting; of course, in that case the total energy E cannot be written in the form (1).

The specification of the actual values of the parameters N, V, and E then defines a *macrostate* of the given system.

At the molecular level, however, a large number of possibilities still exist because at that level there will *in general* be a large number of different ways in which the macrostate (N,V,E) of the given system can be realized. In the case of a noninteracting system, since the total energy E consists of a simple sum of the N single-particle energies ε_i, there will obviously be a large number of different ways in which the individual ε_i can be chosen so as to make the total energy equal to E. In other words, there will be a large number of different ways in which the total energy E of the system can be distributed among the N particles constituting it. Each of these (different) ways specifies a *microstate*, or *complexion*, of the given system. In general, the various microstates, or complexions, of a given system can be identified with the independent solutions $\psi(\boldsymbol{r}_1, \ldots, \boldsymbol{r}_N)$ of the Schrödinger equation of the system, corresponding to the eigenvalue E of the relevant Hamiltonian. In any case, to a given macrostate of the system there does in general correspond a large number of microstates and it seems natural to assume, when there are no other constraints, that at any time t the system is *equally likely* to be in any one of these microstates. This assumption forms the backbone of our formalism and is generally referred to as the postulate of "equal *a priori* probabilities" for all microstates consistent with a given macrostate.

The actual number of all possible microstates will, of course, be a function of N, V, and E and may be denoted by the symbol $\Omega(N,V,E)$; the dependence on V comes in because the possible values ε_i of the single-particle energy ε are themselves a function

of this parameter.[2] Remarkably enough, it is from the magnitude of the number Ω, and from its dependence on the parameters N, V, and E, that complete thermodynamics of the given system can be derived!

We shall not stop here to discuss the ways in which the number $\Omega(N,V,E)$ can be computed; we shall do that only after we have developed our considerations sufficiently so that we can carry out further derivations from it. First we have to discover the manner in which this number is related to any of the leading thermodynamic quantities. To do this, we consider the problem of "thermal contact" between two given physical systems, in the hope that this consideration will bring out the true nature of the number Ω.

1.2 Contact between statistics and thermodynamics: physical significance of the number $\Omega(N,V,E)$

We consider two physical systems, A_1 and A_2, which are separately in equilibrium; see Figure 1.1. Let the macrostate of A_1 be represented by the parameters N_1, V_1, and E_1 so that it has $\Omega_1(N_1,V_1,E_1)$ possible microstates, and the macrostate of A_2 be represented by the parameters N_2, V_2, and E_2 so that it has $\Omega_2(N_2,V_2,E_2)$ possible microstates. The mathematical form of the function Ω_1 may not be the same as that of the function Ω_2, because that ultimately depends on the nature of the system. We do, of course, believe that all thermodynamic properties of the systems A_1 and A_2 can be derived from the functions $\Omega_1(N_1,V_1,E_1)$ and $\Omega_2(N_2,V_2,E_2)$, respectively.

We now bring the two systems into thermal contact with each other, thus allowing the possibility of exchange of energy between the two; this can be done by sliding in a conducting wall and removing the impervious one. For simplicity, the two systems are still separated by a rigid, impenetrable wall, so that the respective volumes V_1 and V_2 and the respective particle numbers N_1 and N_2 remain fixed. The energies E_1 and E_2, however, become variable and the only condition that restricts their variation is
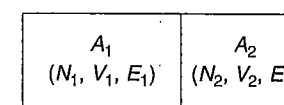
$$E^{(0)} = E_1 + E_2 = \text{const.} \tag{1}$$

A_1	A_2
(N_1, V_1, E_1)	(N_2, V_2, E_2)

FIGURE 1.1 Two physical systems being brought into thermal contact.

---

[2]It may be noted that the manner in which the ε_i depend on V is itself determined by the nature of the system. For instance, it is not the same for relativistic systems as it is for nonrelativistic ones; compare, for instance, the cases dealt with in Section 1.4 and in Problem 1.7. We should also note that, *in principle*, the dependence of Ω on V arises from the fact that it is the *physical dimensions* of the container that appear in the boundary conditions imposed on the wave functions of the system.

Here, $E^{(0)}$ denotes the energy of the composite system $A^{(0)} (\equiv A_1 + A_2)$; the energy of interaction between A_1 and A_2, if any, is being neglected. Now, at any time t, the subsystem A_1 is equally likely to be in any one of the $\Omega_1(E_1)$ microstates while the subsystem A_2 is equally likely to be in any one of the $\Omega_2(E_2)$ microstates; therefore, the composite system $A^{(0)}$ is equally likely to be in any one of the

$$\Omega_1(E_1)\Omega_2(E_2) = \Omega_1(E_1)\Omega_2(E^{(0)} - E_1) = \Omega^{(0)}(E^{(0)}, E_1) \tag{2}$$

microstates.[3] Clearly, the number $\Omega^{(0)}$ itself varies with E_1. The question now arises: at what value of E_1 will the composite system be in equilibrium? In other words, how far will the energy exchange go in order to bring the subsystems A_1 and A_2 into mutual equilibrium?

We assert that this will happen at that value of E_1 which *maximizes* the number $\Omega^{(0)}(E^{(0)}, E_1)$. The philosophy behind this assertion is that a physical system, left to itself, proceeds naturally in a direction that enables it to assume an ever-increasing number of microstates until it finally settles down in a macrostate that affords the *largest possible* number of microstates. Statistically speaking, we regard a macrostate with a larger number of microstates as a more probable state, and the one with the largest number of microstates as the most probable one. Detailed studies show that, for a typical system, the number of microstates pertaining to any macrostate that departs even slightly from the most probable one is "orders of magnitude" smaller than the number pertaining to the latter. Thus, the most probable state of a system is *the* macrostate in which the system spends an "overwhelmingly" large fraction of its time. It is then natural to identify this state with the *equilibrium* state of the system.

Denoting the equilibrium value of E_1 by $\overline{E}_1$ (and that of E_2 by $\overline{E}_2$), we obtain, on maximizing $\Omega^{(0)}$,

$$\left(\frac{\partial \Omega_1(E_1)}{\partial E_1}\right)_{E_1 = \overline{E}_1} \Omega_2(\overline{E}_2) + \Omega_1(\overline{E}_1)\left(\frac{\partial \Omega_2(E_2)}{\partial E_2}\right)_{E_2 = \overline{E}_2} \cdot \frac{\partial E_2}{\partial E_1} = 0.$$

Since $\partial E_2 / \partial E_1 = -1$, see equation (1), the foregoing condition can be written as

$$\left(\frac{\partial \ln \Omega_1(E_1)}{\partial E_1}\right)_{E_1 = \overline{E}_1} = \left(\frac{\partial \ln \Omega_2(E_2)}{\partial E_2}\right)_{E_2 = \overline{E}_2}.$$

Thus, our condition for equilibrium reduces to the equality of the parameters β_1 and β_2 of the subsystems A_1 and A_2, respectively, where β is defined by

$$\beta \equiv \left(\frac{\partial \ln \Omega(N, V, E)}{\partial E}\right)_{N, V, E = \overline{E}}. \tag{3}$$

[3]It is obvious that the macrostate of the composite system $A^{(0)}$ has to be defined by two energies, namely E_1 and E_2 (or else $E^{(0)}$ and E_1).

We thus find that when two physical systems are brought into thermal contact, which allows an exchange of energy between them, this exchange continues *until* the equilibrium values $\overline{E}_1$ and $\overline{E}_2$ of the variables E_1 and E_2 are reached. Once these values are reached, there is no more net exchange of energy between the two systems; the systems are then said to have attained a state of thermal equilibrium. According to our analysis, this happens only when the respective values of the parameter β, namely β_1 and β_2, become equal.[4] It is then natural to expect that the parameter β is somehow related to the *thermodynamic temperature* T of a given system. To determine this relationship, we recall the thermodynamic formula

$$\left(\frac{\partial S}{\partial E}\right)_{N, V} = \frac{1}{T}, \tag{4}$$

where S is the entropy of the system in question. Comparing equations (3) and (4), we conclude that an intimate relationship exists between the thermodynamic quantity S and the statistical quantity Ω; we may, in fact, write for any physical system

$$\frac{\Delta S}{\Delta(\ln \Omega)} = \frac{1}{\beta T} = \text{const.} \tag{5}$$

This correspondence was first established by Boltzmann who also believed that, since the relationship between the thermodynamic approach and the statistical approach seems to be of a fundamental character, the constant appearing in (5) must be a *universal constant*. It was Planck who first wrote the explicit formula

$$S = k \ln \Omega, \tag{6}$$

without any additive constant S_0. As it stands, formula (6) determines the *absolute* value of the entropy of a given physical system in terms of the total number of microstates accessible to it in conformity with the given macrostate. The zero of entropy then corresponds to the special state for which only one microstate is accessible ($\Omega = 1$) — the so-called "unique configuration"; the statistical approach thus provides a theoretical basis for the third law of thermodynamics as well. Formula (6) is of fundamental importance in physics; it provides a bridge between the microscopic and the macroscopic.

Now, in the study of the second law of thermodynamics we are told that the law of increase of entropy is related to the fact that the energy content of the universe, in its natural course, is becoming less and less available for conversion into work; accordingly, the entropy of a given system may be regarded as a measure of the so-called disorder or chaos prevailing in the system. Formula (6) tells us how disorder arises microscopically. Clearly, disorder is a manifestation of the largeness of the number of microstates the system can have. The larger the choice of microstates, the lesser the degree of predictability and hence the increased level of disorder in the system. Complete order prevails when and

[4]This result may be compared with the so-called "zeroth law of thermodynamics," which stipulates the existence of a *common* parameter T for two or more physical systems in thermal equilibrium.

only when the system has no other choice but to be in a unique state ($\Omega = 1$); this, in turn, corresponds to a state of vanishing entropy.

By equations (5) and (6), we also have

$$\beta = \frac{1}{kT}. \tag{7}$$

The universal constant k is generally referred to as the *Boltzmann constant*. In Section 1.4 we shall discover how k is related to the gas constant R and the Avogadro number N_A; see equation (1.4.3).[5]

1.3 Further contact between statistics and thermodynamics

In continuation of the preceding considerations, we now examine a more elaborate exchange between the subsystems A_1 and A_2. If we assume that the wall separating the two subsystems is movable as well as conducting, then the respective volumes V_1 and V_2 (of subsystems A_1 and A_2) also become variable; indeed, the total volume $V^{(0)}(= V_1 + V_2)$ remains constant, so that effectively we have only one more independent variable. Of course, the wall is still assumed to be impenetrable to particles, so the numbers N_1 and N_2 remain fixed. Arguing as before, the state of equilibrium for the composite system $A^{(0)}$ will obtain when the number $\Omega^{(0)}(V^{(0)}, E^{(0)}; V_1, E_1)$ attains its largest value; that is, when not only

$$\left(\frac{\partial \ln \Omega_1}{\partial E_1}\right)_{N_1, V_1; \, E_1 = \overline{E}_1} = \left(\frac{\partial \ln \Omega_2}{\partial E_2}\right)_{N_2, V_2; \, E_2 = \overline{E}_2}, \tag{1a}$$

but also

$$\left(\frac{\partial \ln \Omega_1}{\partial V_1}\right)_{N_1, E_1; \, V_1 = \overline{V}_1} = \left(\frac{\partial \ln \Omega_2}{\partial V_2}\right)_{N_2, E_2; \, V_2 = \overline{V}_2}. \tag{1b}$$

Our conditions for equilibrium now take the form of an equality between the pair of parameters (β_1, η_1) of the subsystem A_1 and the parameters (β_2, η_2) of the subsystem A_2 where, by definition,

$$\eta \equiv \left(\frac{\partial \ln \Omega(N, V, E)}{\partial V}\right)_{N, E, V = \overline{V}}. \tag{2}$$

Similarly, if A_1 and A_2 came into contact through a wall that allowed an exchange of particles as well, the conditions for equilibrium would be further augmented by the equality

[5]We follow the notation whereby equation (1.4.3) means equation (3) of Section 1.4. However, while referring to an equation in the same section, we will omit the mention of the section number.

---

of the parameter ζ_1 of subsystem A_1 and the parameter ζ_2 of subsystem A_2 where, by definition,

$$\zeta \equiv \left(\frac{\partial \ln \Omega(N, V, E)}{\partial N}\right)_{V, E, N = \overline{N}}. \tag{3}$$

To determine the physical meaning of the parameters η and ζ, we make use of equation (1.2.6) and the basic formula of thermodynamics, namely

$$dE = T \, dS - P \, dV + \mu \, dN, \tag{4}$$

where P is the thermodynamic pressure and μ the chemical potential of the given system. It follows that

$$\eta = \frac{P}{kT} \quad \text{and} \quad \zeta = -\frac{\mu}{kT}. \tag{5}$$

From a physical point of view, these results are completely satisfactory because, thermodynamically as well, the conditions of equilibrium between two systems A_1 and A_2, if the wall separating them is both conducting and movable (thus making their respective energies and volumes variable), are indeed the same as the ones contained in equations (1a) and (1b), namely

$$T_1 = T_2 \quad \text{and} \quad P_1 = P_2. \tag{6}$$

On the other hand, if the two systems can exchange particles as well as energy but have their volumes fixed, the conditions of equilibrium, obtained thermodynamically, are indeed

$$T_1 = T_2 \quad \text{and} \quad \mu_1 = \mu_2. \tag{7}$$

And finally, if the exchange is such that all three (macroscopic) parameters become variable, then the conditions of equilibrium become

$$T_1 = T_2, \quad P_1 = P_2, \quad \text{and} \quad \mu_1 = \mu_2. \tag{8}[6]$$

It is gratifying that these conclusions are identical to the ones following from statistical considerations.

Combining the results of the foregoing discussion, we arrive at the following recipe for deriving thermodynamics from a statistical beginning: determine, for the macrostate (N, V, E) of the given system, the number of all possible microstates accessible to the system; call this number $\Omega(N, V, E)$. Then, the entropy of the system in that state follows from

[6]It may be noted that the same would be true for any two parts of a single thermodynamic system; consequently, in equilibrium, the parameters T, P, and μ would be constant *throughout* the system.

the fundamental formula

$$S(N,V,E) = k \ln \Omega(N,V,E), \tag{9}$$

while the leading *intensive fields*, namely temperature, pressure, and chemical potential, are given by

$$\left(\frac{\partial S}{\partial E}\right)_{N,V} = \frac{1}{T}; \quad \left(\frac{\partial S}{\partial V}\right)_{N,E} = \frac{P}{T}; \quad \left(\frac{\partial S}{\partial N}\right)_{V,E} = -\frac{\mu}{T}. \tag{10}$$

Alternatively, we can write[7]

$$P = \left(\frac{\partial S}{\partial V}\right)_{N,E} \Big/ \left(\frac{\partial S}{\partial E}\right)_{N,V} = -\left(\frac{\partial E}{\partial V}\right)_{N,S} \tag{11}$$

and

$$\mu = -\left(\frac{\partial S}{\partial N}\right)_{V,E} \Big/ \left(\frac{\partial S}{\partial E}\right)_{N,V} = \left(\frac{\partial E}{\partial N}\right)_{V,S}, \tag{12}$$

while

$$T = \left(\frac{\partial E}{\partial S}\right)_{N,V}. \tag{13}$$

Formulae (11) through (13) follow equally well from equation (4). The evaluation of $P, \mu,$ and T from these formulae indeed requires that the energy E be expressed as a function of the quantities $N, V,$ and S; this should, in principle, be possible once S is known as a function of $N, V,$ and E.

The rest of the thermodynamics follows straightforwardly; see Appendix H. For instance, the Helmholtz free energy A, the Gibbs free energy G, and the enthalpy H are given by

$$A = E - TS, \tag{14}$$

$$G = A + PV = E - TS + PV$$

$$= \mu N \tag{15}[8]$$

---

[7]In writing these formulae, we have made use of the well-known relationship in partial differential calculus, namely that "if three variables x, y, and z are mutually related, then (see Appendix H)

$$\left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial z}\right)_x \left(\frac{\partial z}{\partial x}\right)_y = -1."$$

[8]The relation $E - TS + PV = \mu N$ follows directly from (4). For this, all we have to do is to regard the given system as having grown to its present size in a gradual manner, such that the intensive parameters, $T, P,$ and μ stayed constant throughout the process while the extensive parameters N, V, and E (and hence S) grew *proportionately* with one another.

---

and

$$H = E + PV = G + TS. \tag{16}$$

The specific heat at constant volume, C_V, and the one at constant pressure, C_P, would be given by

$$C_V \equiv T\left(\frac{\partial S}{\partial T}\right)_{N,V} = \left(\frac{\partial E}{\partial T}\right)_{N,V} \tag{17}$$

and

$$C_P \equiv T\left(\frac{\partial S}{\partial T}\right)_{N,P} = \left(\frac{\partial(E+PV)}{\partial T}\right)_{N,P} = \left(\frac{\partial H}{\partial T}\right)_{N,P}. \tag{18}$$

1.4   The classical ideal gas

To illustrate the approach developed in the preceding sections, we shall now derive the various thermodynamic properties of a classical ideal gas composed of monatomic molecules. The main reason why we choose this highly specialized system for consideration is that it affords an explicit, though asymptotic, evaluation of the number $\Omega(N,V,E)$. This example becomes all the more instructive when we find that its study enables us, in a most straightforward manner, to identify the Boltzmann constant k in terms of other physical constants; see equation (3). Moreover, the behavior of this system serves as a useful reference with which the behavior of other physical systems, especially real gases (with or without quantum effects), can be compared. And, indeed, in the limit of high temperatures and low densities the ideal-gas behavior becomes typical of most real systems.

Before undertaking a detailed study of this case it appears worthwhile to make a remark that applies to all *classical* systems composed of *noninteracting* particles, irrespective of the internal structure of the particles. This remark is related to the explicit dependence of the number $\Omega(N,V,E)$ on V and hence to the *equation of state* of these systems. Now, if there do not exist any spatial correlations among the particles, that is, if the probability of any one of them being found in a particular region of the available space is completely independent of the location of the other particles,[9] then the total number of ways in which the N particles can be spatially distributed in the system will be simply equal to the product of the numbers of ways in which the individual particles can be accommodated in the same space independently of one another. With N and E fixed, each of these numbers will be directly proportional to V, the volume of the container; accordingly, the total number of ways will be directly proportional to the Nth power of V:

$$\Omega(N,E,V) \propto V^N. \tag{1}$$

---

[9]This will be true if (i) the mutual interactions among particles are negligible, and (ii) the wave packets of individual particles do not significantly overlap (or, in other words, the quantum effects are also negligible).

so that, for the ratio of the two specific heats, we have

$$\gamma = C_P/C_V = \frac{5}{3}. \tag{28}$$

Now, suppose that the gas undergoes an *isothermal* change of state ($T = \text{const.}$ and $N = \text{const.}$); then, according to (23), the total energy of the gas would remain constant while, according to (26), its pressure would vary inversely with volume (Boyle's law). The change in the entropy of the gas, between the initial state i and the final state f, would then be, see equation (21),

$$S_f - S_i = Nk\ln(V_f/V_i). \tag{29}$$

On the other hand, if the gas undergoes a *reversible adiabatic* change of state ($S = \text{const.}$ and $N = \text{const.}$), then, according to (22) and (23), both E and T would vary as $V^{-2/3}$; so, according to (25) or (26), P would vary as $V^{-5/3}$. These results agree with the conventional thermodynamic ones, namely

$$PV^{\gamma} = \text{const.} \quad \text{and} \quad TV^{\gamma-1} = \text{const.}, \tag{30}$$

with $\gamma = \frac{5}{3}$. It may be noted that, thermodynamically, the change in E during an adiabatic process arises solely from the external work done by the gas on the surroundings or vice versa:

$$(dE)_{\text{adiab}} = -PdV = -\frac{2E}{3V}dV; \tag{31}$$

see equations (1.3.4) and (25). The dependence of E on V follows readily from this relationship.

The considerations of this section have clearly demonstrated the manner in which the thermodynamics of a macroscopic system can be derived from the multiplicity of its microstates (as represented by the number Ω or Γ or Σ). The whole problem then hinges on an asymptotic enumeration of these numbers, which unfortunately is tractable only in a few idealized cases, such as the one considered in this section; see also Problems 1.7 and 1.8. Even in an idealized case like this, there remains an inadequacy that could not be detected in the derivations made so far; this relates to the *explicit* dependence of S on N. The discussion of the next section is intended not only to bring out this inadequacy but also to provide the necessary remedy for it.

1.5 The entropy of mixing and the Gibbs paradox

One thing we readily observe from expression (1.4.21) is that, contrary to what is logically desired, the entropy of an ideal gas, as given by this expression, is *not* an extensive
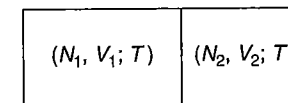
| $(N_1, V_1; T)$ | $(N_2, V_2; T)$ |

FIGURE 1.3 The mixing together of two ideal gases 1 and 2.

property of the system! That is, if we increase the size of the system by a factor α, keeping the intensive variables unchanged,[15] then the entropy of the system, which should also increase by the same factor α, does not do so; the presence of the $\ln V$ term in the expression affects the result adversely. This in a way means that the entropy of this system is different from the sum of the entropies of its parts, which is quite unphysical. A more common way of looking at this problem is to consider the so-called *Gibbs paradox*.

Gibbs visualized the mixing of two ideal gases 1 and 2, both being initially at the same temperature T; see Figure 1.3. Clearly, the temperature of the mixture would also be the same. Now, before the mixing took place, the respective entropies of the two gases were, see equations (1.4.21) and (1.4.23),

$$S_i = N_i k \ln V_i + \frac{3}{2} N_i k \left\{ 1 + \ln\left(\frac{2\pi m_i kT}{h^2}\right) \right\}; \quad i = 1, 2. \tag{1}$$

After the mixing has taken place, the total entropy would be

$$S_T = \sum_{i=1}^{2} \left[N_i k \ln V + \frac{3}{2} N_i k \left\{ 1 + \ln\left(\frac{2\pi m_i kT}{h^2}\right) \right\} \right], \tag{2}$$

where $V = V_1 + V_2$. Thus, the net increase in the value of S, which may be called the *entropy of mixing*, is given by

$$(\Delta S) = S_T - \sum_{i=1}^{2} S_i = k \left[N_1 \ln \frac{V_1 + V_2}{V_1} + N_2 \ln \frac{V_1 + V_2}{V_2} \right]; \tag{3}$$

the quantity ΔS is indeed positive, as it must be for an *irreversible* process like mixing. Now, in the special case when the initial particle densities of the two gases (and, hence, the particle density of the mixture) are also the same, equation (3) becomes

$$(\Delta S)^* = k \left[N_1 \ln \frac{N_1 + N_2}{N_1} + N_2 \ln \frac{N_1 + N_2}{N_2} \right], \tag{4}$$

which is again positive.

[15]This means an increase of the parameters N, V, and E to αN, αV, and αE, so that the energy per particle and the volume per particle remain unchanged.

So far, it seems all right. However, a paradoxical situation arises if we consider the mixing of two samples of the *same* gas. Once again, the entropies of the individual samples will be given by (1); of course, now $m_1 = m_2 = m$, say. And the entropy after mixing will be given by

$$S_T = Nk\ln V + \frac{3}{2}Nk\left\{1 + \ln\left(\frac{2\pi mkT}{h^2}\right)\right\}, \tag{2a}$$

where $N = N_1 + N_2$; note that this expression is numerically the same as (2), with $m_i = m$. Therefore, the entropy of mixing in this case will also be given by expression (3) and, if $N_1/V_1 = N_2/V_2 = (N_1 + N_2)/(V_1 + V_2)$, by expression (4). The last conclusion, however, is unacceptable because the mixing of two samples of the same gas, with a common initial temperature T and a common initial particle density n, is clearly a *reversible* process, for we can simply reinsert the partitioning wall into the system and obtain a situation that is in no way different from the one we had before mixing. Of course, we tacitly imply that in dealing with a system of identical particles we cannot track them down individually; all we can reckon with is their numbers. When two dissimilar gases, even with a common initial temperature T, and a common initial particle density n, mixed together the process was irreversible, for by reinserting the partitioning wall one would obtain two samples of the mixture and not the two gases that were originally present; to that case, expression (4) would indeed apply. However, in the present case, the corresponding result should be

$$(\Delta S)^*_{1\equiv 2} = 0. \tag{4a}[16]$$

The foregoing result would also be consistent with the requirement that the entropy of a given system is equal to the sum of the entropies of its parts. Of course, we had already noticed that this is not ensured by expression (1.4.21). Thus, once again we are led to believe that there is something basically wrong with that expression.

To see how the above paradoxical situation can be avoided, we recall that, for the entropy of mixing of two samples of the same gas, with a common T and a common n, we were led to result (4), which can also be written as

$$(\Delta S)^* = S_T - (S_1 + S_2) \approx k[\ln\{(N_1 + N_2)!\} - \ln(N_1!) - \ln(N_2!)], \tag{4}$$

instead of the logical result (4a). A closer look at this expression shows that we would indeed obtain the correct result if our original expression for S were diminished by an *ad hoc* term, $k\ln(N!)$, for that would diminish S_1 by $k\ln(N_1!)$, S_2 by $k\ln(N_2!)$ and S_T by $k\ln\{(N_1 + N_2)!\}$, with the result that $(\Delta S)^*$ would turn out to be zero instead of the expression appearing in (4). Clearly, this would amount to an *ad hoc* reduction of the statistical numbers Γ and Σ by a factor $N!$. This is precisely the remedy proposed by Gibbs to avoid the paradox in question.

[16]In view of this, we fear that expression (3) may also be inapplicable to this case.

If we agree with the foregoing suggestion, then the modified expression for the entropy of a classical ideal gas would be

$$S(N, V, E) = Nk\ln\left[\frac{V}{Nh^3}\left(\frac{4\pi mE}{3N}\right)^{3/2}\right] + \frac{5}{2}Nk \tag{1.4.21a}$$

$$= Nk\ln\left(\frac{V}{N}\right) + \frac{3}{2}Nk\left\{\frac{5}{3} + \ln\left(\frac{2\pi mkT}{h^2}\right)\right\}, \tag{1a}$$

which indeed is truly extensive! If we now mix two samples of the same gas at a common initial temperature T, the entropy of mixing would be

$$(\Delta S)_{1\equiv 2} = k\left[(N_1 + N_2)\ln\left(\frac{V_1 + V_2}{N_1 + N_2}\right) - N_1\ln\left(\frac{V_1}{N_1}\right) - N_2\ln\left(\frac{V_2}{N_2}\right)\right] \tag{3a}$$

and, if the initial particle densities of the samples were also equal, the result would be

$$(\Delta S)^*_{1\equiv 2} = 0. \tag{4a}$$

It may be noted that for the mixing of two dissimilar gases, the original expressions (3) and (4) would continue to hold even when (1.4.21) is replaced by (1.4.21a).[17] The paradox of Gibbs is thereby resolved.

Equation (1a) is generally referred to as the *Sackur–Tetrode* equation. We reiterate the fact that, by this equation, the entropy of the system does indeed become a truly extensive quantity. Thus, the very root of the trouble has been eliminated by the recipe of Gibbs. We shall discuss the physical implications of this recipe in Section 1.6; here, let us jot down some of its immediate consequences.

First of all, we note that the expression for the energy E of the gas, written as a function of N, V, and S, is also modified. We now have

$$E(N, V, S) = \frac{3h^2 N^{5/3}}{4\pi mV^{2/3}}\exp\left(\frac{2S}{3Nk} - \frac{5}{3}\right), \tag{1.4.22a}$$

which, unlike its predecessor (1.4.22), makes energy too a truly extensive quantity. Of course, the thermodynamic results (1.4.23) through (1.4.31), derived in the previous section, remain unchanged. However, there are some that were intentionally left out, for they would come out correct only from the modified expression for $S(N, V, E)$ or $E(S, V, N)$. The most important of these is the chemical potential of the gas, for which we obtain

$$\mu \equiv \left(\frac{\partial E}{\partial N}\right)_{V,S} = E\left[\frac{5}{3N} - \frac{2S}{3N^2 k}\right]. \tag{5}$$

[17]Because, in this case, the entropy S_T of the mixture would be diminished by $k\ln(N_1! N_2!)$, rather than by $k\ln\{(N_1 + N_2)!\}$.

In view of equations (1.4.23) and (1.4.25), this becomes

$$\mu = \frac{1}{N}[E + PV - TS] \equiv \frac{G}{N}, \tag{6}$$

where G is the Gibbs free energy of the system. In terms of the variables N, V, and T, expression (5) takes the form

$$\mu(N, V, T) = kT \ln \left\{ \frac{N}{V} \left(\frac{h^2}{2\pi mkT} \right)^{3/2} \right\}. \tag{7}$$

Another quantity of importance is the Helmholtz free energy:

$$A = E - TS = G - PV = NkT \left[\ln \left\{ \frac{N}{V} \left(\frac{h^2}{2\pi mkT} \right)^{3/2} \right\} - 1 \right]. \tag{8}$$

It will be noted that, while A is an extensive property of the system, μ is intensive.

1.6   The "correct" enumeration of the microstates

In the preceding section we saw that an *ad hoc* diminution in the entropy of an N-particle system by an amount $k\ln(N!)$, which implies an *ad hoc* reduction in the number of microstates accessible to the system by a factor ($N!$), was able to correct the unphysical features of some of our former expressions. It is now natural to ask: why, *in principle*, should the number of microstates, computed in Section 1.4, be reduced in this manner? The physical reason for doing so is that the particles constituting the given system are not only identical but also *indistinguishable*; accordingly, it is unphysical to label them as No. 1, No. 2, No. 3, and so on and to speak of their being *individually* in the various single-particle states ε_i. All we can sensibly speak of is their distribution over the states ε_i by *numbers*, that is, n_1 particles being in the state ε_1, n_2 in the state ε_2, and so on. Thus, the correct way of specifying a microstate of the system is through the distribution numbers $\{n_j\}$, and not through the statement as to "which particle is in which state." To elaborate the point, we may say that if we consider two microstates that differ from one another merely in an interchange of two particles in different energy states, then according to our original mode of counting we would regard these microstates as distinct; in view of the indistinguishability of the particles, however, these microstates are not distinct (for, physically, there exists no way whatsoever of distinguishing between them).[18]

---

[18]Of course, if an interchange took place among particles in the same energy state, then even our original mode of counting did not regard the two microstates as distinct.

Now, the total number of permutations that can be effected among N particles, distributed according to the set $\{n_i\}$, is

$$\frac{N!}{n_1! \, n_2! \dots}, \tag{1}$$

where the n_i must be consistent with the basic constraints (1.1.1) and (1.1.2).[19] If our particles were distinguishable, then all these permutations would lead to "distinct" microstates. However, in view of the indistinguishability of the particles, these permutations must be regarded as leading to one and the same thing; consequently, for *any* distribution set $\{n_i\}$, we have one, and only one, distinct microstate. As a result, the total number of distinct microstates accessible to the system, consistent with a given macrostate (N, V, E), would be severely cut down. However, since factor (1) itself depends on the numbers n_i constituting a particular distribution set and for a given macrostate there will be many such sets, there is no straightforward way to "correct down" the number of microstates computed on the basis of the classical concept of "distinguishability" of the particles.

The recipe of Gibbs clearly amounts to disregarding the details of the numbers n_i and slashing the whole sequence of microstates by a *common* factor $N!$; this is correct for situations in which all N particles happen to be in different energy states but is certainly wrong for other situations. We must keep in mind that by adopting this recipe we are still using a spurious *weight factor*,

$$w\{n_i\} = \frac{1}{n_1! \, n_2! \dots}, \tag{2}$$

for the distribution set $\{n_i\}$ whereas in principle we should use a factor of *unity*, irrespective of the values of the numbers n_i.[20] Nonetheless, the recipe of Gibbs does correct the situation in a gross manner, though in matters of detail it is still inadequate. In fact, it is only by taking $w\{n_i\}$ to be equal to unity (or zero) that we obtain true *quantum statistics*!

We thus see that the recipe of Gibbs corrects the enumeration of the microstates, as necessitated by the indistinguishability of the particles, only in a gross manner. Numerically, this would approach closer and closer to reality as the probability of the n_i being greater than 1 becomes less and less. This in turn happens when the given system is at a sufficiently high temperature (so that many more energy states become accessible) and has a sufficiently low density (so that there are not as many particles to accommodate). It follows that the "corrected" classical statistics represents truth more closely if the expectation values of the *occupation numbers* n_i are much less than unity:

$$\langle n_i \rangle \ll 1, \tag{3}$$

---

[19]The presence of the factors $(n_i!)$ in the denominator is related to the comment made in the preceding note.
[20]Or a factor of *zero* if the distribution set $\{n_i\}$ is disallowed on certain physical grounds, such as the Pauli exclusion principle.

that is, if the numbers n_i are generally 0, occasionally 1, and rarely greater than 1. Condition (3) in a way defines the *classical limit*. We must, however, remember that it is because of the application of the correction factor $1/N!$, which replaces (1) by (2), that our results agree with reality *at least* in the classical limit.

In Section 5.5 we shall demonstrate, in an independent manner, that the factor by which the number of microstates, as computed for the "labeled" molecules, be reduced so that the formalism of classical statistical mechanics becomes a true limit of the formalism of quantum statistical mechanics is indeed $N!$.

Problems

1.1. **(a)** Show that, for two *large* systems in thermal contact, the number $\Omega^{(0)}(E^{(0)}, E_1)$ of Section 1.2 can be expressed as a Gaussian in the variable E_1. Determine the root-mean-square deviation of E_1 from the mean value $\overline{E}_1$ in terms of other quantities pertaining to the problem.

   (b) Make an explicit evaluation of the root-mean-square deviation of E_1 in the special case when the systems A_1 and A_2 are ideal classical gases.

1.2. Assuming that the entropy S and the statistical number Ω of a physical system are related through an arbitrary functional form

$$S = f(\Omega),$$

show that the additive character of S and the multiplicative character of Ω *necessarily* require that the function $f(\Omega)$ be of the form (1.2.6).

1.3. Two systems A and B, of identical composition, are brought together and allowed to exchange both energy and particles, keeping volumes V_A and V_B constant. Show that the minimum value of the quantity (dE_A/dN_A) is given by

$$\frac{\mu_A T_B - \mu_B T_A}{T_B - T_A},$$

where the μ's and the T's are the respective chemical potentials and temperatures.

1.4. In a classical gas of hard spheres (of diameter D), the spatial distribution of the particles is no longer uncorrelated. Roughly speaking, the presence of n particles in the system leaves only a volume $(V - nv_0)$ available for the $(n+1)$th particle; clearly, v_0 would be proportional to D^3. Assuming that $Nv_0 \ll V$, determine the dependence of $\Omega(N, V, E)$ on V (compare to equation (1.4.1)) and show that, as a result of this, V in the ideal-gas law (1.4.3) gets replaced by $(V - b)$, where b is four times the actual volume occupied by the particles.

1.5. Read Appendix A and establish formulae (1.4.15) and (1.4.16). Estimate the importance of the linear term in these formulae, relative to the main term $(\pi/6)\varepsilon^{*3/2}$, for an oxygen molecule confined to a cube of side 10 cm; take $\varepsilon = 0.05$ eV.

1.6. A cylindrical vessel 1 m long and 0.1 m in diameter is filled with a monatomic gas at $P = 1$ atm and $T = 300$ K. The gas is heated by an electrical discharge, along the axis of the vessel, which releases an energy of 10^4 joules. What will the temperature of the gas be immediately after the discharge?

1.7. Study the statistical mechanics of an extreme relativisitic gas characterized by the single-particle energy states

$$\varepsilon(n_x, n_y, n_z) = \frac{hc}{2L}\left(n_x^2 + n_y^2 + n_z^2\right)^{1/2},$$

instead of (1.4.5), along the lines followed in Section 1.4. Show that the ratio C_P/C_V in this case is 4/3, instead of 5/3.

1.8. Consider a system of quasiparticles whose energy eigenvalues are given by

$$\varepsilon(n) = nh\nu; \quad n = 0, 1, 2, \ldots.$$

Obtain an asymptotic expression for the number Ω of this system for a given number N of the quasiparticles and a given total energy E. Determine the temperature T of the system as a function of E/N and $h\nu$, and examine the situation for which $E/(Nh\nu) \gg 1$.

1.9. Making use of the fact that the entropy $S(N, V, E)$ of a thermodynamic system is an extensive quantity, show that

$$N\left(\frac{\partial S}{\partial N}\right)_{V,E} + V\left(\frac{\partial S}{\partial V}\right)_{N,E} + E\left(\frac{\partial S}{\partial E}\right)_{N,V} = S.$$

Note that this result implies that $(-N\mu + PV + E)/T = S$, that is, $N\mu = E + PV - TS$.

1.10. A mole of argon and a mole of helium are contained in vessels of equal volume. If argon is at 300 K, what should the temperature of helium be so that the two have the same entropy?

1.11. Four moles of nitrogen and one mole of oxygen at $P = 1$ atm and $T = 300$ K are mixed together to form air at the same pressure and temperature. Calculate the entropy of mixing per mole of the air formed.

1.12. Show that the various expressions for the entropy of mixing, derived in Section 1.5, satisfy the following relations:

   (a) For all $N_1, V_1, N_2,$ and V_2,

$$(\Delta S)_{1\equiv 2} = \{(\Delta S) - (\Delta S)^*\} \geq 0,$$

   the equality holding when and only when $N_1/V_1 = N_2/V_2$.

   (b) For a given value of $(N_1 + N_2)$,

$$(\Delta S)^* \leq (N_1 + N_2)k\ln 2,$$

   the equality holding when and only when $N_1 = N_2$.

1.13. If the two gases considered in the mixing process of Section 1.5 were initially at different temperatures, say T_1 and T_2, what would the entropy of mixing be in that case? Would the contribution arising from this cause depend on whether the two gases were different or identical?

1.14. Show that for an ideal gas composed of monatomic molecules the entropy change, between any two temperatures, when the pressure is kept constant is 5/3 times the corresponding entropy change when the volume is kept constant. Verify this result *numerically* by calculating the actual values of $(\Delta S)_P$ and $(\Delta S)_V$ per mole of an ideal gas whose temperature is raised from 300 K to 400 K.

1.15. We have seen that the (P, V)-relationship during a reversible adiabatic process in an ideal gas is governed by the exponent γ, such that

$$PV^\gamma = \text{const.}$$

Consider a mixture of two ideal gases, with mole fractions f_1 and f_2 and respective exponents γ_1 and γ_2. Show that the *effective* exponent γ for the mixture is given by

$$\frac{1}{\gamma - 1} = \frac{f_1}{\gamma_1 - 1} + \frac{f_2}{\gamma_2 - 1}.$$

1.16. Establish thermodynamically the formulae

$$V\left(\frac{\partial P}{\partial T}\right)_\mu = S \quad \text{and} \quad V\left(\frac{\partial P}{\partial \mu}\right)_T = N.$$

Express the pressure P of an ideal classical gas in terms of the variables μ and T, and verify the above formulae.

2

Elements of Ensemble Theory

In the preceding chapter we noted that, for a given *macrostate* (N, V, E), a statistical system, at any time t, is equally likely to be in any one of an extremely large number of distinct *microstates*. As time passes, the system continually switches from one microstate to another, with the result that, over a reasonable span of time, all one observes is a behavior "averaged" over the variety of microstates through which the system passes. It may, therefore, make sense if we consider, at a *single* instant of time, a rather large number of systems — all being some sort of "mental copies" of the given system — which are characterized by the same macrostate as the original system but are, naturally enough, in all sorts of possible microstates. Then, under ordinary circumstances, we may expect that the average behavior of any system in this collection, which we call an *ensemble*, would be identical to the time-averaged behavior of the given system. It is on the basis of this expectation that we proceed to develop the so-called *ensemble theory*.

For classical systems, the most appropriate framework for developing the desired formalism is provided by the *phase space*. Accordingly, we begin our study of the various ensembles with an analysis of the basic features of this space.

2.1 Phase space of a classical system

The microstate of a given classical system, at any time t, may be defined by specifying the *instantaneous* positions and momenta of all the particles constituting the system. Thus, if N is the number of particles in the system, the definition of a microstate requires the specification of $3N$ position coordinates $q_1, q_2, \ldots, q_{3N}$ and $3N$ momentum coordinates $p_1, p_2, \ldots, p_{3N}$. Geometrically, the set of coordinates (q_i, p_i), where $i = 1, 2, \ldots, 3N$, may be regarded as a point in a space of $6N$ dimensions. We refer to this space as the *phase space*, and the phase point (q_i, p_i) as a *representative point*, of the given system.

Of course, the coordinates q_i and p_i are functions of the time t; the precise manner in which they vary with t is determined by the canonical equations of motion,

$$
\left.
\begin{aligned}
\dot{q}_i &= \frac{\partial H(q_i, p_i)}{\partial p_i} \\
\dot{p}_i &= -\frac{\partial H(q_i, p_i)}{\partial q_i}
\end{aligned}
\right\} \quad i = 1, 2, \ldots, 3N,
\tag{1}
$$

where $H(q_i, p_i)$ is the *Hamiltonian* of the system. Now, as time passes, the set of coordinates (q_i, p_i), which also defines the microstate of the system, undergoes a continual change. Correspondingly, our representative point in the phase space carves out a

trajectory whose direction, at any time t, is determined by the *velocity vector* $\boldsymbol{v} \equiv (\dot{q}_i, \dot{p}_i)$, which in turn is given by the equations of motion (1). It is not difficult to see that the trajectory of the representative point must remain within a limited region of the phase space; this is so because a finite volume V directly limits the values of the coordinates q_i, while a finite energy E limits the values of both the q_i and the p_i [through the Hamiltonian $H(q_i, p_i)$]. In particular, if the total energy of the system is known to have a *precise* value, say E, the corresponding trajectory will be restricted to the "hypersurface"

$$H(q_i, p_i) = E \tag{2}$$

of the phase space; on the other hand, if the total energy may lie anywhere in the range $\left(E - \frac{1}{2}\Delta, E + \frac{1}{2}\Delta\right)$, the corresponding trajectory will be restricted to the "hypershell" defined by these limits.

Now, if we consider an ensemble of systems (i.e., the given system, along with a large number of mental copies of it) then, at any time t, the various members of the ensemble will be in all sorts of possible microstates; indeed, each one of these microstates must be consistent with the given macrostate that is supposed to be common to all members of the ensemble. In the phase space, the corresponding picture will consist of a swarm of representative points, one for each member of the ensemble, all lying within the "allowed" region of this space. As time passes, every member of the ensemble undergoes a continual change of microstates; correspondingly, the representative points constituting the swarm continually move along their respective trajectories. The overall picture of this movement possesses some important features that are best illustrated in terms of what we call a *density function* $\rho(q, p; t)$.[1] This function is such that, at any time t, the number of representative points in the "volume element" $(d^{3N}q\, d^{3N}p)$ around the point (q, p) of the phase space is given by the product $\rho(q, p; t) d^{3N}q\, d^{3N}p$. Clearly, the density function $\rho(q, p; t)$ symbolizes the manner in which the members of the ensemble are distributed over all possible microstates at different instants of time. Accordingly, the *ensemble average* $\langle f \rangle$ of a given physical quantity $f(q, p)$, which may be different for systems in different microstates, would be given by

$$\langle f \rangle = \frac{\int f(q, p) \rho(q, p; t) d^{3N}q\, d^{3N}p}{\int \rho(q, p; t) d^{3N}q\, d^{3N}p}. \tag{3}$$

The integrations in (3) extend over the whole of the phase space; however, it is only the populated regions of the phase space ($\rho \neq 0$) that really contribute. We note that, in general, the ensemble average $\langle f \rangle$ may itself be a function of time.

An ensemble is said to be *stationary* if ρ does not depend explicitly on time, that is, at all times

$$\frac{\partial \rho}{\partial t} = 0. \tag{4}$$

---

[1] Note that (q, p) is an abbreviation of $(q_i, p_i) \equiv (q_1, \ldots, q_{3N}, p_1, \ldots, p_{3N})$.

Clearly, for such an ensemble the average value $\langle f \rangle$ of *any* physical quantity $f(q, p)$ will be independent of time. Naturally, a stationary ensemble qualifies to represent a system in *equilibrium*. To determine the circumstances under which equation (4) may hold, we have to make a rather detailed study of the movement of the representative points in the phase space.

2.2   Liouville's theorem and its consequences

Consider an arbitrary "volume" ω in the relevant region of the phase space and let the "surface" enclosing this volume be denoted by σ; see Figure 2.1. Then, the rate at which the number of representative points in this volume increases with time is written as

$$\frac{\partial}{\partial t} \int_\omega \rho\, d\omega, \tag{1}$$

where $d\omega \equiv (d^{3N}q\, d^{3N}p)$. On the other hand, the *net* rate at which the representative points "flow" out of ω (across the bounding surface σ) is given by

$$\int_\sigma \rho\, \boldsymbol{v} \cdot \hat{\boldsymbol{n}}\, d\sigma; \tag{2}$$

here, $\boldsymbol{v}$ is the velocity vector of the representative points in the region of the surface element $d\sigma$ while $\hat{\boldsymbol{n}}$ is the (outward) unit vector normal to this element. By the divergence theorem, (2) can be written as

$$\int_\omega \mathrm{div}(\rho \boldsymbol{v}) d\omega; \tag{3}$$

of course, the operation of divergence here means

$$\mathrm{div}(\rho \boldsymbol{v}) \equiv \sum_{i=1}^{3N} \left\{ \frac{\partial}{\partial q_i}(\rho \dot{q}_i) + \frac{\partial}{\partial p_i}(\rho \dot{p}_i) \right\}. \tag{4}$$
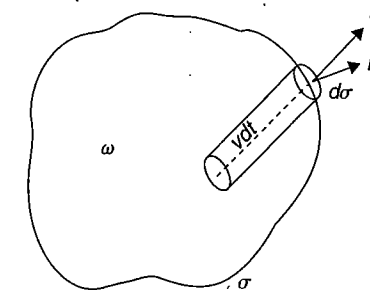

FIGURE 2.1 The "hydrodynamics" of the representative points in the phase space.

In view of the fact that there are no "sources" or "sinks" in the phase space and hence the total number of representative points remains conserved,[2] we have, by (1) and (3),

$$\frac{\partial}{\partial t}\int_{\omega}\rho\, d\omega = -\int_{\omega}\mathrm{div}(\rho\boldsymbol{v})d\omega, \tag{5}$$

that is,

$$\int_{\omega}\left\{\frac{\partial\rho}{\partial t} + \mathrm{div}(\rho\boldsymbol{v})\right\}d\omega = 0. \tag{6}$$

Now, the necessary and sufficient condition that integral (6) vanish for all arbitrary volumes ω is that the integrand itself vanish *everywhere* in the relevant region of the phase space. Thus, we must have

$$\frac{\partial\rho}{\partial t} + \mathrm{div}(\rho\boldsymbol{v}) = 0, \tag{7}$$

which is the *equation of continuity* for the swarm of the representative points.

Combining (4) and (7), we obtain

$$\frac{\partial\rho}{\partial t} + \sum_{i=1}^{3N}\left(\frac{\partial\rho}{\partial q_i}\dot{q}_i + \frac{\partial\rho}{\partial p_i}\dot{p}_i\right) + \rho\sum_{i=1}^{3N}\left(\frac{\partial\dot{q}_i}{\partial q_i} + \frac{\partial\dot{p}_i}{\partial p_i}\right) = 0. \tag{8}$$

The last group of terms vanishes identically because, by the equations of motion, we have, for all i,

$$\frac{\partial\dot{q}_i}{\partial q_i} = \frac{\partial^2 H(q_i,p_i)}{\partial q_i\partial p_i} \equiv \frac{\partial^2 H(q_i,p_i)}{\partial p_i\partial q_i} = -\frac{\partial\dot{p}_i}{\partial p_i}. \tag{9}$$

Further, since $\rho \equiv \rho\,(q,p;t)$, the remaining terms in (8) may be combined to form the "total" time derivative of ρ, with the result that

$$\frac{d\rho}{dt} = \frac{\partial\rho}{\partial t} + [\rho,H] = 0. \tag{10}[3]$$

Equation (10) embodies *Liouville's theorem* (1838). According to this theorem, the "local" density of the representative points, *as viewed by an observer moving with a representative point,* stays constant in time. Thus, the swarm of the representative points moves in

---

[2]This means that in the ensemble under consideration neither are any new members being added nor are any old ones being removed.

[3]We recall that the *Poisson bracket* $[\rho,H]$ stands for the sum

$$\sum_{i=1}^{3N}\left(\frac{\partial\rho}{\partial q_i}\frac{\partial H}{\partial p_i} - \frac{\partial\rho}{\partial p_i}\frac{\partial H}{\partial q_i}\right),$$

which is identical to the group of terms in the middle of (8).

the phase space in essentially the same manner as an incompressible fluid moves in the physical space!

A distinction must be made, however, between equation (10) on one hand and equation (2.1.4) on the other. While the former derives from the basic mechanics of the particles and is therefore *quite generally* true, the latter is only a requirement for equilibrium which, in a given case, may or may not be satisfied. The condition that ensures simultaneous validity of the two equations is clearly

$$[\rho,H] = \sum_{i=1}^{3N}\left(\frac{\partial\rho}{\partial q_i}\dot{q}_i + \frac{\partial\rho}{\partial p_i}\dot{p}_i\right) = 0. \tag{11}$$

Now, one possible way of satisfying (11) is to assume that ρ, which is already assumed to have no explicit dependence on time, is *independent* of the coordinates (q,p) as well, that is,

$$\rho(q,p) = \mathrm{const.} \tag{12}$$

over the relevant region of the phase space (and, of course, is zero everywhere else). Physically, this choice corresponds to an ensemble of systems that at *all* times are *uniformly* distributed over all possible microstates. The ensemble average (2.1.3) then reduces to

$$\langle f\rangle = \frac{1}{\omega}\int_{\omega} f(q,p)d\omega; \tag{13}$$

here, ω denotes the total "volume" of the relevant region of the phase space. Clearly, in this case, *any* member of the ensemble is equally likely to be in *any* one of the various possible microstates, inasmuch as *any* representative point in the swarm is equally likely to be in the neighborhood of *any* phase point in the allowed region of the phase space. This statement is usually referred to as the postulate of "equal *a priori* probabilities" for the various possible microstates (or for the various volume elements in the allowed region of the phase space); the resulting ensemble is referred to as the *microcanonical ensemble*.

A more general way of satisfying (11) is to assume that the dependence of ρ on (q,p) comes only through an explicit dependence on the Hamiltonian $H(q,p)$, that is,

$$\rho(q,p) = \rho[H(q,p)]; \tag{14}$$

condition (11) is then identically satisfied. Equation (14) provides a class of density functions for which the corresponding ensemble is stationary. In Chapter 3 we shall see that the most natural choice in this class of ensembles is the one for which

$$\rho(q,p) \propto \exp[-H(q;p)/kT]. \tag{15}$$

The ensemble so defined is referred to as the *canonical ensemble*.

2.3 The microcanonical ensemble

In this ensemble the macrostate of a system is defined by the number of molecules N, the volume V, and the energy E. However, in view of the considerations expressed in Section 1.4, we may prefer to specify a range of energy values, say from $\left(E - \frac{1}{2}\Delta\right)$ to $\left(E + \frac{1}{2}\Delta\right)$, rather than a sharply defined value E. With the macrostate specified, a choice still remains for the systems of the ensemble to be in *any one* of a large number of possible microstates. In the phase space, correspondingly, the representative points of the ensemble have a choice to lie *anywhere* within a "hypershell" defined by the condition

$$\left(E - \frac{1}{2}\Delta\right) \le H(q,p) \le \left(E + \frac{1}{2}\Delta\right). \tag{1}$$

The volume of the phase space enclosed within this shell is given by

$$\omega = \int' d\omega \equiv \int' \left(d^{3N}q\, d^{3N}p\right), \tag{2}$$

where the primed integration extends only over that part of the phase space which conforms to condition (1). It is clear that ω will be a function of the parameters N, V, E, and Δ.

Now, the microcanonical ensemble is a collection of systems for which the density function ρ is, at all times, given by

$$\rho(q,p) = \text{const.} \quad \begin{array}{ll} \text{if } \left(E - \frac{1}{2}\Delta\right) \le H(q,p) \le \left(E + \frac{1}{2}\Delta\right) \\ 0 \qquad \text{otherwise} \end{array} \Bigg\}. \tag{3}$$

Accordingly, the expectation value of the number of representative points lying in a volume element $d\omega$ of the relevant hypershell is simply proportional to $d\omega$. In other words, the *a priori* probability of finding a representative point in a given volume element $d\omega$ is the same as that of finding a representative point in an equivalent volume element $d\omega$ located *anywhere* in the hypershell. In our original parlance, this means an equal *a priori* probability for a given member of the ensemble to be in *any one* of the various possible microstates. In view of these considerations, the ensemble average $\langle f \rangle$, as given by equation (2.2.13), acquires a simple physical meaning. To see this, we proceed as follows.

Since the ensemble under study is a stationary one, the ensemble average of any physical quantity f will be independent of time; accordingly, taking a time average thereof will not produce any new result. Thus

$$\langle f \rangle \equiv \text{the ensemble average of } f$$

$$= \text{the time average of (the ensemble average of } f).$$

Now, the processes of time averaging and ensemble averaging are completely independent, so the order in which they are performed may be reversed without causing any change in the value of $\langle f \rangle$. Thus

$$\langle f \rangle = \text{the ensemble average of (the time average of } f).$$

Now, the time average of any physical quantity, taken over a sufficiently long interval of time, must be the same for *every* member of the ensemble, for after all we are dealing with only *mental copies* of a given system.[4] Therefore, taking an ensemble average thereof should be inconsequential, and we may write

$$\langle f \rangle = \text{the long-time average of } f,$$

where the latter may be taken over *any* member of the ensemble. Furthermore, the long-time average of a physical quantity is all one obtains by making a measurement of that quantity on the given system; therefore, it may be identified with the value one expects to obtain through experiment. Thus, we finally have

$$\langle f \rangle = f_{\exp}. \tag{4}$$

This brings us to the most important result: *the ensemble average of any physical quantity f is identical to the value one expects to obtain on making an appropriate measurement on the given system.*

The next thing we look for is the establishment of a connection between the mechanics of the microcanonical ensemble and the thermodynamics of the member systems. To do this, we observe that there exists a direct correspondence between the various microstates of the given system and the various locations in the phase space. The volume ω (of the allowed region of the phase space) is, therefore, a direct measure of the multiplicity Γ of the microstates accessible to the system. To establish a numerical correspondence between ω

[4]To provide a *rigorous* justification for this assertion is not trivial. One can readily see that if, for any particular member of the ensemble, the quantity f is averaged only over a *short* span of time, the result is bound to depend on the relevant "subset of microstates" through which the system passes during that time. In the phase space, this will mean an averaging over only a "part of the allowed region." However, if we employ instead a sufficiently long interval of time, the system may be expected to pass through *almost* all possible microstates "without fear or favor"; consequently, the result of the averaging process would depend only on the macrostate of the system, and not on a subset of microstates. Correspondingly, the averaging in the phase space would go over *practically* all parts of the allowed region, again "without fear or favor." In other words, the representative point of our system will have traversed each and every part of the allowed region *almost* uniformly. This statement embodies the so-called *ergodic theorem* or *ergodic hypothesis*, which was first introduced by Boltzmann (1871). According to this hypothesis, the trajectory of a representative point passes, in the course of time, through *each and every* point of the relevant region of the phase space. A little reflection, however, shows that the statement as such requires a qualification; we better replace it by the so-called *quasiergodic hypothesis*, according to which the trajectory of a representative point traverses, in the course of time, *any neighborhood of any point* of the relevant region. For further details, see ter Haar (1954, 1955), Farquhar (1964).

Now, when we consider an ensemble of systems, the foregoing statement should hold for every member of the ensemble; thus, *irrespective of the initial (and final) states* of the various systems, the long-time average of any physical quantity f should be the same for every member system.

and Γ, we need to discover a *fundamental volume* ω_0 that could be regarded as "equivalent to one microstate." Once this is done, we may say that, asymptotically,

$$\Gamma = \omega/\omega_0. \tag{5}$$

The thermodynamics of the system would then follow in the same way as in Sections 1.2–1.4, namely through the relationship

$$S = k\ln\Gamma = k\ln(\omega/\omega_0), \quad \text{etc.} \tag{6}$$

The basic problem then consists in determining ω_0. From dimensional considerations, see (2), ω_0 must be in the nature of an "angular momentum raised to the power $3N$." To determine it exactly, we consider certain simplified systems, both from the point of view of the phase space and from the point of view of the distribution of quantum states.

2.4   Examples

We consider, first of all, the problem of a classical ideal gas composed of monatomic particles; see Section 1.4. In the microcanonical ensemble, the volume ω of the phase space accessible to the representative points of the (member) systems is given by

$$\omega = \int' \ldots \int' \left(d^{3N}q \, d^{3N}p \right), \tag{1}$$

where the integrations are restricted by the conditions that (i) the particles of the system are confined in physical space to volume V, and (ii) the total energy of the system lies between the limits $\left(E - \frac{1}{2}\Delta \right)$ and $\left(E + \frac{1}{2}\Delta \right)$. Since the Hamiltonian in this case is a function of the p_i alone, integrations over the q_i can be carried out straightforwardly; these give a factor of V^N. The remaining integral is

$$\int \ldots \int_{\left(E - \frac{1}{2}\Delta \right) \le \sum_{i=1}^{3N} \left(p_i^2/2m \right) \le \left(E + \frac{1}{2}\Delta \right)} d^{3N}p = \int \ldots \int_{2m\left(E - \frac{1}{2}\Delta \right) \le \sum_{i=1}^{3N} y_i^2 \le 2m\left(E + \frac{1}{2}\Delta \right)} d^{3N}y,$$

which is equal to the volume of a $3N$-dimensional hypershell, bounded by hyperspheres of radii

$$\sqrt{\left[2m\left(E + \frac{1}{2}\Delta \right) \right]} \quad \text{and} \quad \sqrt{\left[2m\left(E - \frac{1}{2}\Delta \right) \right]}.$$

For $\Delta \ll E$, this is given by the thickness of the shell, which is almost equal to $\Delta (m/2E)^{1/2}$, multiplied by the surface area of a $3N$-dimensional hypersphere of radius $\sqrt{(2mE)}$. By

equation (7) of Appendix C, we obtain for this integral

$$\Delta \left(\frac{m}{2E} \right)^{1/2} \left\{ \frac{2\pi^{3N/2}}{[(3N/2) - 1]!} (2mE)^{(3N-1)/2} \right\},$$

which gives

$$\omega \simeq \frac{\Delta}{E} V^N \frac{(2\pi mE)^{3N/2}}{[(3N/2) - 1]!}. \tag{2}$$

Comparing (2) with (1.4.17 and 1.4.17a), we obtain the desired correspondence, namely

$$(\omega/\Gamma)_{\text{asymp}} \equiv \omega_0 = h^{3N};$$

see also Problem 2.9. Quite generally, if the system under study has $\mathcal{N}$ degrees of freedom, the desired conversion factor is

$$\omega_0 = h^{\mathcal{N}}. \tag{3}$$

In the case of a single particle, $\mathcal{N} = 3$; accordingly, the number of microstates available would asymptotically be equal to the volume of the allowed region of the phase space divided by h^3. Let $\Sigma(P)$ denote the number of microstates available to a free particle confined to volume V of the physical space, its momentum p being less than or equal to a specified value P. Then

$$\Sigma(P) \approx \frac{1}{h^3} \int \ldots \int_{p \le P} \left(d^3q \, d^3p \right) = \frac{V}{h^3} \frac{4\pi}{3} P^3, \tag{4}$$

from which we obtain for the number of microstates with momentum lying between p and $p + dp$

$$g(p) dp = \frac{d\Sigma(p)}{dp} dp \approx \frac{V}{h^3} 4\pi p^2 dp. \tag{5}$$

Expressed in terms of the particle energy, these expressions assume the form

$$\Sigma(E) \approx \frac{V}{h^3} \frac{4\pi}{3} (2mE)^{3/2} \tag{6}$$

and

$$a(\varepsilon) d\varepsilon = \frac{d\Sigma(\varepsilon)}{d\varepsilon} d\varepsilon \approx \frac{V}{h^3} 2\pi (2m)^{3/2} \varepsilon^{1/2} d\varepsilon. \tag{7}$$

The next case we consider here is that of a one-dimensional *simple harmonic oscillator*. The classical expression for the Hamiltonian of this system is

$$H(q,p) = \frac{1}{2}kq^2 + \frac{1}{2m}p^2, \tag{8}$$

where k is the spring constant and m the mass of the oscillating particle. The space coordinate q and the momentum coordinate p of the system are given by

$$q = A\cos(\omega t + \phi), \quad p = m\dot{q} = -m\omega A\sin(\omega t + \phi), \tag{9}$$

A being the amplitude and ω the (angular) frequency of vibration:

$$\omega = \sqrt{(k/m)}. \tag{10}$$

The energy of the oscillator is a constant of the motion, and is given by

$$E = \frac{1}{2}m\omega^2 A^2. \tag{11}$$

The phase-space trajectory of the representative point (q, p) of this system is determined by eliminating t between expressions (9) for $q(t)$ and $p(t)$; we obtain

$$\frac{q^2}{(2E/m\omega^2)} + \frac{p^2}{(2mE)} = 1, \tag{12}$$

which is an ellipse, with axes proportional to $\sqrt{E}$ and hence area proportional to E; to be precise, the area of this ellipse is $2\pi E/\omega$. Now, if we restrict the oscillator energy to the interval $\left(E - \frac{1}{2}\Delta, E + \frac{1}{2}\Delta\right)$, its representative point in the phase space will be confined to the region bounded by elliptical trajectories corresponding to the energy values $\left(E + \frac{1}{2}\Delta\right)$ and $\left(E - \frac{1}{2}\Delta\right)$. The "volume" (in this case, the area) of this region will be

$$\int \cdots \int_{\left(E - \frac{1}{2}\Delta\right) \le H(q,p) \le \left(E + \frac{1}{2}\Delta\right)} (dq\,dp) = \frac{2\pi\left(E + \frac{1}{2}\Delta\right)}{\omega} - \frac{2\pi\left(E - \frac{1}{2}\Delta\right)}{\omega} = \frac{2\pi\Delta}{\omega}. \tag{13}$$

According to quantum mechanics, the energy eigenvalues of the harmonic oscillator are given by

$$E_n = \left(n + \frac{1}{2}\right)\hbar\omega; \quad n = 0, 1, 2, \dots \tag{14}$$

In terms of phase space, one could say that the representative point of the system must move along one of the "chosen" trajectories, as shown in Figure 2.2; the area of the phase space between two consecutive trajectories, for which $\Delta = \hbar\omega$, is simply $2\pi\hbar$.[5] For arbitrary values of E and Δ, such that $E \gg \Delta \gg \hbar\omega$, the number of eigenstates within the allowed

---

[5]Strictly speaking, the very concept of phase space is invalid in quantum mechanics because there, in principle, it is wrong to assign to a particle the coordinates q and p *simultaneously*. Nevertheless, the ideas discussed here are tenable in the correspondence limit.
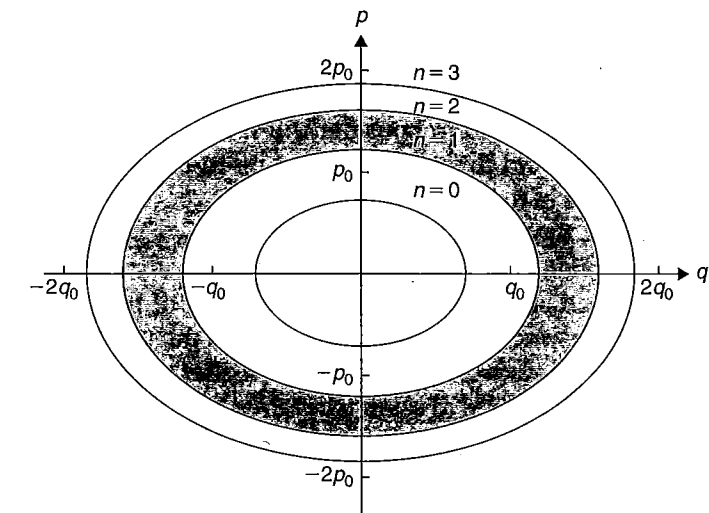
FIGURE 2.2 Eigenstates of a linear harmonic oscillator, in relation to its phase space.

energy interval is very nearly equal to $\Delta/\hbar\omega$. Hence, the area of the phase space equivalent to one eigenstate is, asymptotically, given by

$$\omega_0 = (2\pi\Delta/\omega)/(\Delta/\hbar\omega) = 2\pi\hbar = h. \tag{15}$$

If, on the other hand, we consider a system of N harmonic oscillators along the same lines as above, we arrive at the result: $\omega_0 = h^N$ (see Problem 2.7). Thus, our findings in these cases are consistent with our earlier result (3).

2.5 Quantum states and the phase space

At this stage we would like to say a few words on the central role played here by the Planck constant h. The best way to appreciate this role is to recall the implications of the Heisenberg uncertainty principle, according to which we cannot specify *simultaneously* both the position and the momentum of a particle exactly. An element of uncertainty is inherently present and can be expressed as follows: assuming that all conceivable uncertainties of measurement are eliminated, even then, by the very nature of things, the product of the uncertainties Δq and Δp in the *simultaneous* measurement of the canonically conjugate coordinates q and p would be of order $\hbar$:

$$(\Delta q \Delta p)_{\min} \sim \hbar. \tag{1}$$

Thus, it is impossible to define the position of a representative point in the phase space of the given system more accurately than is allowed by condition (1). In other words, around any point (q, p) in the (two-dimensional) phase space, there exists an area of order $\hbar$ within

which the position of the representative point cannot be pinpointed. In a phase space of $2\mathcal{N}$ dimensions, the corresponding "volume of uncertainty" around any point would be of order $\hbar^{\mathcal{N}}$. Therefore, it seems reasonable to regard the phase space as made up of elementary cells, of volume $\sim \hbar^{\mathcal{N}}$, and to consider the various positions within such a cell as *nondistinct*. These cells could then be put into one-to-one correspondence with the quantum-mechanical states of the system.

It is, however, obvious that considerations of uncertainty alone cannot give us the *exact* value of the conversion factor ω_0. This could only be done by an *actual* counting of microstates on one hand and a computation of volume of the relevant region of the phase space on the other, as was done in the examples of the previous section. Clearly, a procedure along these lines could not be possible until after the work of Schrödinger and others. Historically, however, the first to establish the result (2.4.3) was Tetrode (1912) who, in his well-known work on the chemical constant and the entropy of a monatomic gas, assumed that

$$\omega_0 = (zh)^{\mathcal{N}}, \tag{2}$$

where z was supposed to be an unknown numerical factor. Comparing theoretical results with the experimental data on mercury, Tetrode found that z was very nearly equal to unity; from this he concluded that "it seems rather plausible that z is *exactly* equal to unity, as has already been taken by O. Sackur (1911)."[6]

In the extreme relativistic limit, the same result was established by Bose (1924). In his famous treatment of the photon gas, Bose made use of Einstein's relationship between the momentum of a photon and the frequency of the associated radiation, namely

$$p = \frac{h\nu}{c}, \tag{3}$$

and observed that, for a photon confined to a three-dimensional cavity of volume V, the relevant "volume" of the phase space,

$$\int' (d^3q\, d^3p) = V4\pi p^2 dp = V(4\pi h^3 \nu^2 / c^3) d\nu, \tag{4}$$

would correspond exactly to the Rayleigh expression,

$$V(4\pi \nu^2 / c^3) d\nu, \tag{5}$$

for the number of normal modes of a radiation oscillator, *provided that* we divide phase space into elementary cells of volume h^3 and put these cells into one-to-one correspondence with the vibrational modes of Rayleigh. It may, however, be added that a two-fold multiplicity of these states ($g = 2$) arises from the spin orientations of the photon

[6]For a more satisfactory proof of this result, see Section 5.5, especially equation (5.5.22).

(or from the states of polarization of the vibrational modes); this requires a multiplication of both expressions (4) and (5) by a factor of 2, leaving the conversion factor h^3 unchanged.

Problems

2.1. Show that the volume element

$$d\omega = \prod_{i=1}^{3N} (dq_i\, dp_i)$$

of the phase space remains *invariant* under a canonical transformation of the (generalized) coordinates (q, p) to any other set of (generalized) coordinates (Q, P).

[*Hint*: Before considering the most general transformation of this kind, which is referred to as a *contact* transformation, it may be helpful to consider a *point* transformation — one in which the new coordinates Q_i and the old coordinates q_i transform only among themselves.]

2.2. **(a)** Verify *explicitly* the invariance of the volume element $d\omega$ of the phase space of a single particle under transformation from the Cartesian coordinates (x, y, z, p_x, p_y, p_z) to the spherical polar coordinates $(r, \theta, \phi, p_r, p_\theta, p_\phi)$.

(b) The foregoing result seems to contradict the intuitive notion of "equal weights for equal solid angles," because the factor $\sin\theta$ is invisible in the expression for $d\omega$. Show that if we average out any physical quantity, whose dependence on p_θ and p_ϕ comes only through the kinetic energy of the particle, then as a result of integration over these variables we do indeed recover the factor $\sin\theta$ to appear with the subelement $(d\theta\, d\phi)$.

2.3. Starting with the line of zero energy and working in the (two-dimensional) phase space of a classical rotator, draw lines of constant energy that divide phase space into cells of "volume" h. Calculate the energies of these states and compare them with the energy eigenvalues of the corresponding quantum-mechanical rotator.

2.4. By evaluating the "volume" of the relevant region of its phase space, show that the number of microstates available to a rigid rotator with angular momentum $\leq M$ is $(M/\hbar)^2$. Hence determine the number of microstates that may be associated with the quantized angular momentum $M_j = \sqrt{\{j(j+1)\}}\hbar$, where $j = 0, 1, 2, \ldots$ or $\frac{1}{2}, \frac{3}{2}, \frac{5}{2}, \ldots$. Interpret the result physically.

[*Hint*: It simplifies to consider motion in the variables θ and φ, with $M^2 = p_\theta^2 + (p_\phi / \sin\theta)^2$.]

2.5. Consider a particle of energy E moving in a one-dimensional potential well $V(q)$, such that

$$m\hbar \left| \frac{dV}{dq} \right| \ll \{m(E - V)\}^{3/2}.$$

Show that the allowed values of the momentum p of the particle are such that

$$\oint p\, dq = \left(n + \frac{1}{2}\right) h,$$

where n is an integer.

2.6. The generalized coordinates of a simple pendulum are the angular displacement θ and the angular momentum $ml^2\dot{\theta}$. Study, both mathematically and graphically, the nature of the corresponding trajectories in the phase space of the system, and show that the area A enclosed by a trajectory is equal to the product of the total energy E and the time period τ of the pendulum.

2.7. Derive (i) an *asymptotic* expression for the number of ways in which a given energy E can be distributed among a set of N one-dimensional harmonic oscillators, the energy eigenvalues of the oscillators being $\left(n + \frac{1}{2}\right)\hbar\omega$; $n = 0, 1, 2, \ldots$, and (ii) the corresponding expression for the "volume" of the relevant region of the phase space of this system. Establish the correspondence between the two results, showing that the conversion factor ω_0 is precisely h^N.

2.8. Following the method of Appendix C, replacing equation (C.4) by the integral

$$\int\limits_0^\infty e^{-r} r^2 dr = 2,$$

show that

$$V_{3N} = \int \cdots \int\limits_{0 \le \sum\limits_{i=1}^N r_l \le R} \prod_{i=1}^N \left(4\pi r_i^2 dr_i \right) = (8\pi R^3)^N / (3N)!.$$

Using this result, compute the "volume" of the relevant region of the phase space of an extreme relativistic gas ($\varepsilon = pc$) of N particles moving in three dimensions. Hence, derive expressions for the various thermodynamic properties of this system and compare your results with those of Problem 1.7.

2.9. (a) Solve the integral

$$\int \cdots \int\limits_{0 \le \sum\limits_{i=1}^{3N} |x_i| \le R} (dx_1 \ldots dx_{3N})$$

and use it to determine the "volume" of the relevant region of the phase space of an extreme relativistic gas ($\varepsilon = pc$) of $3N$ particles moving in one dimension. Determine, as well, the number of ways of distributing a given energy E among this system of particles and show that, asymptotically, $\omega_0 = h^{3N}$.

(b) Compare the thermodynamics of this system with that of the system considered in Problem 2.8.

The Canonical Ensemble

In the preceding chapter we established the basis of ensemble theory and made a somewhat detailed study of the microcanonical ensemble. In that ensemble the macrostate of the systems was defined through a fixed number of particles N, a fixed volume V, and a fixed energy E [or, preferably, a fixed energy range $(E - \frac{1}{2}\Delta, E + \frac{1}{2}\Delta)$]. The basic problem then consisted in determining the number $\Omega(N, V, E)$, or $\Gamma(N, V, E; \Delta)$, of *distinct* microstates accessible to the system. From the asymptotic expressions of these numbers, complete thermodynamics of the system could be derived in a straightforward manner. However, for most physical systems, the mathematical problem of determining these numbers is quite formidable. For this reason alone, a search for an alternative approach within the framework of the ensemble theory seems necessary.

Practically, too, the concept of a fixed energy (or even an energy range) for a system belonging to the real world does not appear satisfactory. For one thing, the total energy E of a system is hardly ever measured; for another, it is hardly possible to keep its value under strict physical control. A far better alternative appears to be to speak of a fixed temperature T of the system — a parameter that is not only directly observable (by placing a "thermometer" in contact with the system) but also controllable (by keeping the system in contact with an appropriate "heat reservoir"). For most purposes, the precise nature of the reservoir is not very relevant; all one needs is that it should have an infinitely large heat capacity, so that, irrespective of energy exchange between the system and the reservoir, an overall constant temperature can be maintained. Now, if the reservoir consists of an infinitely large number of mental copies of the given system we have once again an ensemble of systems — this time, however, it is an ensemble in which the macrostate of the systems is defined through the parameters N, V, and T. Such an ensemble is referred to as a *canonical* ensemble.

In the canonical ensemble, the energy E of a system is variable; in principle, it can take values anywhere between zero and infinity. The question then arises: what is the probability that, at any time t, a system in the ensemble is found to be in one of the states characterized by the energy value E_r?[1] We denote this probability by the symbol P_r. Clearly, there are two ways in which the dependence of P_r on E_r can be determined. One consists of regarding the system as in equilibrium with a heat reservoir at a *common* temperature T and studying the statistics of the energy exchange between the two. The other consists of regarding the system as a member of a canonical ensemble (N, V, T), in which an energy $\mathcal{E}$ is being shared by $\mathcal{N}$ identical systems constituting the ensemble, and studying the

---

[1]In what follows, the energy levels E_r appear as purely *mechanical* quantities — independent of the temperature of the system. For a treatment involving "temperature-dependent energy levels," see Elcock and Landsberg (1957).

statistics of this sharing process. We expect that in the thermodynamic limit the final result in either case would be the same. Once P_r is determined, the rest follows without difficulty.

3.1   Equilibrium between a system and a heat reservoir

We consider the given system A, immersed in a very large heat reservoir A'; see Figure 3.1. On attaining a state of mutual equilibrium, the system and the reservoir would have a *common* temperature, *say* T. Their energies, however, would be variable and, in principle, could have, at any time t, values lying anywhere between 0 and $E^{(0)}$, where $E^{(0)}$ denotes the energy of the composite system $A^{(0)}(\equiv A + A')$. If, at any particular instant of time, the system A happens to be in a state characterized by the energy value E_r, then the reservoir would have an energy E'_r, such that

$$E_r + E'_r = E^{(0)} = \text{const.} \tag{1}$$

Of course, since the reservoir is supposed to be much larger than the given system, any *practical* value of E_r would be a very small fraction of $E^{(0)}$; therefore, for all practical purposes,

$$\frac{E_r}{E^{(0)}} = \left(1 - \frac{E'_r}{E^{(0)}}\right) \ll 1. \tag{2}$$

With the state of the system A having been specified, the reservoir A' can still be in *any one* of a large number of states compatible with the energy value E'_r. Let the number of these states be denoted by $\Omega'(E'_r)$. The prime on the symbol Ω emphasizes the fact that its functional form will depend on the nature of the reservoir; of course, the details of this dependence are not going to be of any particular relevance to our final results. Now, the larger the number of states available to the reservoir, the larger the probability of the reservoir assuming that particular energy value E'_r (and, hence, of the system A assuming the corresponding energy value E_r). Moreover, since the various possible states (with a given energy value) are *equally likely* to occur, the relevant probability would be directly proportional to this number; thus,

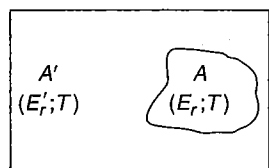$$P_r \propto \Omega'(E'_r) \equiv \Omega'(E^{(0)} - E_r). \tag{3}$$

FIGURE 3.1 A given system A immersed in a heat reservoir A'; in equilibrium, the two have a common temperature T.

In view of (2), we may carry out an expansion of (3) around the value $E'_r = E^{(0)}$, that is, around $E_r = 0$. However, for reasons of convergence, it is essential to effect the expansion of its logarithm instead:

$$\ln \Omega'(E'_r) = \ln \Omega'(E^{(0)}) + \left(\frac{\partial \ln \Omega'}{\partial E'}\right)_{E' = E^{(0)}} (E'_r - E^{(0)}) + \cdots$$

$$\simeq \text{const} - \beta' E_r, \tag{4}$$

where use has been made of formula (1.2.3), whereby

$$\left(\frac{\partial \ln \Omega}{\partial E}\right)_{N,V} \equiv \beta; \tag{5}$$

note that, in equilibrium, $\beta' = \beta = 1/kT$. From (3) and (4), we obtain the desired result:

$$P_r \propto \exp(-\beta E_r). \tag{6}$$

Normalizing (6), we get

$$P_r = \frac{\exp(-\beta E_r)}{\sum_r \exp(-\beta E_r)}, \tag{7}$$

where the summation in the denominator goes over *all* states accessible to the system A. We note that our final result (7) bears no relation whatsoever to the physical nature of the reservoir A'.

We now examine the same problem from the ensemble point of view.

3.2   A system in the canonical ensemble

We consider an ensemble of $\mathcal{N}$ identical systems (which may be labelled as $1, 2, \ldots, \mathcal{N}$), sharing a total energy $\mathcal{E}$; let $E_r(r = 0, 1, 2, \ldots)$ denote the energy eigenvalues of the systems. If n_r denotes the number of systems which, at any time t, have the energy value E_r, then the set of numbers $\{n_r\}$ must satisfy the obvious conditions

$$\left.\begin{array}{l} \sum_r n_r = \mathcal{N} \\ \sum_r n_r E_r = \mathcal{E} = \mathcal{N} U, \end{array}\right\} \tag{1}$$

where $U(= \mathcal{E}/\mathcal{N})$ denotes the average energy per system in the ensemble. Any set $\{n_r\}$ that satisfies the restrictive conditions (1) represents a possible mode of distribution of the total energy $\mathcal{E}$ among the $\mathcal{N}$ members of the ensemble. Furthermore, any such mode can be realized in a number of ways, for we may effect a reshuffle among those members of the ensemble for which the energy values are different and thereby obtain a state of the

ensemble that is distinct from the original one. Denoting the number of different ways of doing so by the symbol $W\{n_r\}$, we have

$$W\{n_r\} = \frac{\mathcal{N}!}{n_0! \, n_1! \, n_2! \ldots}. \tag{2}$$

In view of the fact that all possible states of the ensemble, which are compatible with conditions (1), are *equally likely* to occur, the frequency with which the distribution set $\{n_r\}$ may appear will be directly proportional to the number $W\{n_r\}$. Accordingly, the "most probable" mode of distribution will be the one for which the number W is a maximum. We denote the corresponding distribution set by $\{n_r^*\}$; clearly, the set $\{n_r^*\}$ must also satisfy conditions (1). As will be seen in the sequel, the probability of appearance of other modes of distribution, however little they may differ from the most probable mode, is extremely low! Therefore, for all practical purposes, the *most probable distribution set* $\{n_r^*\}$ is the only one we have to contend with.

However, unless this has been mathematically demonstrated, one must take into account *all* possible modes of distribution, as characterized by the various distribution sets $\{n_r\}$, along with their respective weight factors $W\{n_r\}$. Accordingly, the *expectation values*, or *mean values*, $\langle n_r \rangle$ of the numbers n_r would be given by

$$\langle n_r \rangle = \frac{\sum_{\{n_r\}}' n_r W\{n_r\}}{\sum_{\{n_r\}}' W\{n_r\}}, \tag{3}$$

where the primed summations go over all distribution sets that conform to conditions (1). In principle, the mean value $\langle n_r \rangle$, as a fraction of the total number $\mathcal{N}$, should be a natural analog of the probability P_r evaluated in the preceding section. In practice, however, the fraction $n_r^*/\mathcal{N}$ also turns out to be the same.

We now proceed to derive expressions for the numbers n_r^* and $\langle n_r \rangle$, and to show that, in the limit $\mathcal{N} \to \infty$, they are identical.

The method of most probable values
Our aim here is to determine that distribution set which, while satisfying conditions (1), maximizes the weight factor (2). For simplicity, we work with $\ln W$ instead:

$$\ln W = \ln(\mathcal{N}!) - \sum_r \ln(n_r!). \tag{4}$$

Since, in the end, we propose to resort to the limit $\mathcal{N} \to \infty$, the values of n_r (which are going to be of any practical significance) would also, in that limit, tend to infinity. It is, therefore, justified to apply the Stirling formula, $\ln(n!) \approx n \ln n - n$, to (4) and write

$$\ln W = \mathcal{N} \ln \mathcal{N} - \sum_r n_r \ln n_r. \tag{5}$$

If we shift from the set $\{n_r\}$ to a slightly different set $\{n_r + \delta n_r\}$, then expression (5) would change by an amount

$$\delta(\ln W) = -\sum_r (\ln n_r + 1)\delta n_r. \tag{6}$$

Now, if the set $\{n_r\}$ is maximal, the variation $\delta(\ln W)$ should vanish. At the same time, in view of the restrictive conditions (1), the variations δn_r themselves must satisfy the conditions

$$\left. \begin{array}{l} \sum_r \delta n_r = 0 \\ \sum_r E_r \delta n_r = 0. \end{array} \right\} \tag{7}$$

The desired set $\{n_r^*\}$ is then determined by the method of *Lagrange multipliers*,[2] by which the condition determining this set becomes

$$\sum_r \{-(\ln n_r^* + 1) - \alpha - \beta E_r\}\delta n_r = 0, \tag{8}$$

where α and β are the Lagrangian undetermined multipliers that take care of the restrictive conditions (7). In (8), the variations δn_r become completely arbitrary; accordingly, the only way to satisfy this condition is that all its coefficients must vanish identically, that is, for *all r*,

$$\ln n_r^* = -(\alpha + 1) - \beta E_r,$$

which gives

$$n_r^* = C \exp(-\beta E_r), \tag{9}$$

where C is again an undetermined parameter.

To determine C and β, we subject (9) to conditions (1), with the result that

$$\frac{n_r^*}{\mathcal{N}} = \frac{\exp(-\beta E_r)}{\sum_r \exp(-\beta E_r)}, \tag{10}$$

the parameter β being a solution of the equation

$$\frac{\mathcal{E}}{\mathcal{N}} = U = \frac{\sum_r E_r \exp(-\beta E_r)}{\sum_r \exp(-\beta E_r)}. \tag{11}$$

[2] For the method of Lagrange multipliers, see ter Haar and Wergeland (1966, Appendix C.1).

3.43. Consider a system of charged particles (not dipoles), obeying classical mechanics and classical statistics. Show that the magnetic susceptibility of this system is identically zero (Bohr–van Leeuwen theorem).
[Note that the Hamiltonian of this system in the presence of a magnetic field $H (= \nabla \times A)$ will be a function of the quantities $p_j + (e_j/c)A(r_j)$, and not of the p_j as such. One has now to show that the partition function of the system is independent of the applied field.]

3.44. The expression (3.3.13) for the entropy S is equivalent to Shannon's (1949) definition of the information contained in a message $I = -\sum_r P_r \ln(P_r)$, where P_r represents the probability of message r.

    (a) Show that information is maximized if the probabilities of all messages are the same. Any other distribution of probabilities reduces the information. In English, "e" is more common than "z", so $P_e > P_z$, so the information per character in an English message is less than the optimal amount possible based on the number of different characters used in an English text.

    (b) The information in a text is also affected by correlations between characters in the text. For example, in English, "q" is always followed by "u", so this pair of characters contains the same information as "q" alone. The probability of a character indexed by r followed immediately by character indexed by r' is $P_{r,r'} = P_r P_{r'} G_{r,r'}$, where $G_{r,r'}$ is the character-pair correlation function. If pairs of characters are uncorrelated, then $G_{r,r'} = 1$. Show that if characters are uncorrelated then the information in a two-character message is twice the information of a single-character message and that correlations ($G_{r,r'} \neq 1$) reduce the information content.
[*Hint:* Use the inequality $\ln x \leq x - 1$.]

    (c) Write a computer program to determine the information per character in a text file by determining the single-character probabilities P_r and character-pair correlations $G_{r,r'}$. Computers usually use one full byte per character to store information. Since one byte can store 256 different messages, the potential information per byte is $\ln 256 = 8 \ln 2 \equiv 8$ bits. Show that the information per character in your text file is considerably less than 8 bits and explain why it is possible for file-compression algorithms to reduce the size of a computer file without sacrificing any of the information contained in the file.

4

The Grand Canonical Ensemble

In the preceding chapter we developed the formalism of the canonical ensemble and established a scheme of operations for deriving the various thermodynamic properties of a given physical system. The effectiveness of that approach became clear from the examples discussed there; it will become even more vivid in the subsequent studies carried out in this text. However, for a number of problems, both physical and chemical, the usefulness of the canonical ensemble formalism turns out to be rather limited and it appears that a further generalization of this formalism is called for. The motivation that brings about this generalization is physically of the same nature as the one that led us from the microcanonical to the canonical ensemble — it is just the next natural step from there. It comes from the realization that not only the energy of a system but the number of particles as well is hardly ever measured in a "direct" manner; we only estimate it through an indirect probing into the system. Conceptually, therefore, we may regard both N and E as *variables* and identify their expectation values, $\langle N \rangle$ and $\langle E \rangle$, with the corresponding thermodynamic quantities.

The procedure for studying the statistics of the variables N and E is self-evident. We may *either* (i) consider the given system A as immersed in a large reservoir A' with which it can exchange both energy and particles *or* (ii) regard it as a member of what we may call a *grand canonical ensemble*, which consists of the given system A and a large number of (mental) copies thereof, the members of the ensemble carrying out a mutual exchange of both energy and particles. The end results, in either case, are asymptotically the same.

4.1 Equilibrium between a system and a particle-energy reservoir

We consider the given system A as immersed in a large reservoir A', with which it can exchange both energy and particles; see Figure 4.1. After some time has elapsed, the system and the reservoir are supposed to attain a state of mutual equilibrium. Then, according to Section 1.3, the system and the reservoir will have a common temperature T and a common chemical potential μ. The fraction of the total number of particles $N^{(0)}$ and the fraction of the total energy $E^{(0)}$ that the system A can have at any time t are, however, variables (whose values, in principle, can lie anywhere between zero and unity). If, at a particular instant of time, the system A happens to be in *one* of its states characterized by the number N_r of particles and the amount E_s of energy, then the number of particles in the reservoir would be N'_r and its energy E'_s, such that

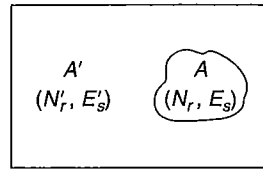$$N_r + N'_r = N^{(0)} = \text{const.} \tag{1}$$

FIGURE 4.1 A statistical system immersed in a particle–energy reservoir.

and

$$E_s + E_s' = E^{(0)} = \text{const.} \tag{2}$$

Again, since the reservoir is supposed to be much larger than the given system, the values of N_r and E_s that are going to be of practical importance will be very small fractions of the total magnitudes $N^{(0)}$ and $E^{(0)}$, respectively; therefore, for all practical purposes,[1]

$$\frac{N_r}{N^{(0)}} = \left(1 - \frac{N_r'}{N^{(0)}}\right) \ll 1 \tag{3}$$

and

$$\frac{E_s}{E^{(0)}} = \left(1 - \frac{E_s'}{E^{(0)}}\right) \ll 1. \tag{4}$$

Now, in the manner of Section 3.1, the probability $P_{r,s}$ that, at any time t, the system A is found to be in an (N_r, E_s)-state would be directly proportional to the number of microstates $\Omega'(N_r', E_s')$ that the reservoir can have for the corresponding macrostate (N_r', E_s'). Thus,

$$P_{r,s} \propto \Omega'(N^{(0)} - N_r, E^{(0)} - E_s). \tag{5}$$

Again, in view of (3) and (4), we can write

$$\ln \Omega'(N^{(0)} - N_r, E^{(0)} - E_s) = \ln \Omega'(N^{(0)}, E^{(0)})$$
$$+ \left(\frac{\partial \ln \Omega'}{\partial N'}\right)_{N'=N^{(0)}} (-N_r) + \left(\frac{\partial \ln \Omega'}{\partial E'}\right)_{E'=E^{(0)}} (-E_s) + \cdots$$
$$\simeq \ln \Omega'(N^{(0)}, E^{(0)}) + \frac{\mu'}{kT'} N_r - \frac{1}{kT'} E_s; \tag{6}$$

see equations (1.2.3), (1.2.7), (1.3.3), and (1.3.5). Here, μ' and T' are, respectively, the chemical potential and the temperature of the reservoir (and hence of the given system

---

[1]Note that A here could well be a relatively small "part" of a given system $A^{(0)}$, while A' represents the "rest" of $A^{(0)}$. That would give a truly practical perspective to the grand canonical formalism.

---

as well). From (5) and (6), we obtain the desired result:

$$P_{r,s} \propto \exp(-\alpha N_r - \beta E_s), \tag{7}$$

where

$$\alpha = -\mu/kT, \quad \beta = 1/kT. \tag{8}$$

On normalization, it becomes

$$P_{r,s} = \frac{\exp(-\alpha N_r - \beta E_s)}{\sum\limits_{r,s} \exp(-\alpha N_r - \beta E_s)}; \tag{9}$$

the summation in the denominator goes over *all* the (N_r, E_s)-states accessible to the system A. Note that our final expression for $P_{r,s}$ is independent of the choice of the reservoir.

We shall now examine the same problem from the ensemble point of view.

4.2 A system in the grand canonical ensemble

We now visualize an ensemble of $\mathcal{N}$ identical systems (which, of course, can be labeled as $1, 2, \ldots, \mathcal{N}$) mutually sharing a total number of particles[2] $\mathcal{N}\overline{N}$ and a total energy $\mathcal{N}\overline{E}$. Let $n_{r,s}$ denote the number of systems that have, at any time t, the number N_r of particles and the amount E_s of energy ($r, s = 0, 1, 2, \ldots$); then, obviously,

$$\sum_{r,s} n_{r,s} = \mathcal{N}, \tag{1a}$$

$$\sum_{r,s} n_{r,s} N_r = \mathcal{N}\overline{N}, \tag{1b}$$

and

$$\sum_{r,s} n_{r,s} E_s = \mathcal{N}\overline{E}. \tag{1c}$$

Any set $\{n_{r,s}\}$, of the numbers $n_{r,s}$, which satisfies the restrictive conditions (1), represents one of the possible modes of distribution of particles and energy among the members of our ensemble. Furthermore, any such mode of distribution can be realized in $W\{n_{r,s}\}$ different ways, where

$$W\{n_{r,s}\} = \frac{\mathcal{N}!}{\prod\limits_{r,s}(n_{r,s}!)}. \tag{2}$$

---

[2]For simplicity, we shall henceforth use the symbols $\overline{N}$ and $\overline{E}$ instead of $\langle N \rangle$ and $\langle E \rangle$.

We may now define the *most probable* mode of distribution, $\{n_{r,s}^*\}$, as the one that maximizes expression (2), satisfying at the same time the restrictive conditions (1). Going through the conventional derivation, see Section 3.2, we obtain for a large ensemble

$$\frac{n_{r,s}^*}{\mathcal{N}} = \frac{\exp(-\alpha N_r - \beta E_s)}{\sum_{r,s} \exp(-\alpha N_r - \beta E_s)};\tag{3}$$

compare to the corresponding equation (3.2.10) for the canonical ensemble. Alternatively, we may define the *expectation* (or *mean*) values of the numbers $n_{r,s}$, namely

$$\langle n_{r,s} \rangle = \frac{\sum_{\{n_{r,s}\}}' n_{r,s} W\{n_{r,s}\}}{\sum_{\{n_{r,s}\}}' W\{n_{r,s}\}},\tag{4}$$

where the primed summations go over all distribution sets that conform to conditions (1). An asymptotic expression for $\langle n_{r,s} \rangle$ can be derived by using the method of Darwin and Fowler — the only difference from the corresponding derivation in Section 3.2 being that, in the present case, we will have to work with functions of more than one (complex) variable. The derivation, however, runs along similar lines, with the result

$$\lim_{\mathcal{N} \to \infty} \frac{\langle n_{r,s} \rangle}{\mathcal{N}} \simeq \frac{n_{r,s}^*}{\mathcal{N}} = \frac{\exp(-\alpha N_r - \beta E_s)}{\sum_{r,s} \exp(-\alpha N_r - \beta E_s)},\tag{5}$$

in agreement with equation (4.1.9). The parameters α and β, so far undetermined, are eventually determined by the equations

$$\overline{N} = \frac{\sum_{r,s} N_r \exp(-\alpha N_r - \beta E_s)}{\sum_{r,s} \exp(-\alpha N_r - \beta E_s)} \equiv -\frac{\partial}{\partial \alpha} \left\{ \ln \sum_{r,s} \exp(-\alpha N_r - \beta E_s) \right\}\tag{6}$$

and

$$\overline{E} = \frac{\sum_{r,s} E_s \exp(-\alpha N_r - \beta E_s)}{\sum_{r,s} \exp(-\alpha N_r - \beta E_s)} \equiv -\frac{\partial}{\partial \beta} \left\{ \ln \sum_{r,s} \exp(-\alpha N_r - \beta E_s) \right\},\tag{7}$$

where the quantities $\overline{N}$ and $\overline{E}$ here are supposed to be preassigned.

4.3 Physical significance of the various statistical quantities

To establish a connection between the statistics of the grand canonical ensemble and the thermodynamics of the system under study, we introduce a quantity q, defined by

$$q \equiv \ln \left\{ \sum_{r,s} \exp(-\alpha N_r - \beta E_s) \right\};\tag{1}$$

the quantity q is a function of the parameters α and β, and also of all the E_s.[3] Taking the differential of q and making use of equations (4.2.5), (4.2.6), and (4.2.7), we get

$$dq = -\overline{N} d\alpha - \overline{E} d\beta - \frac{\beta}{\mathcal{N}} \sum_{r,s} \langle n_{r,s} \rangle dE_s,\tag{2}$$

so that

$$d(q + \alpha \overline{N} + \beta \overline{E}) = \beta \left(\frac{\alpha}{\beta} d\overline{N} + d\overline{E} - \frac{1}{\mathcal{N}} \sum_{r,s} \langle n_{r,s} \rangle dE_s \right).\tag{3}$$

To interpret the terms appearing on the right side of this equation, we compare the expression enclosed within the parentheses with the statement of the first law of thermodynamics, that is,

$$\delta Q = d\overline{E} + \delta W - \mu d\overline{N},\tag{4}$$

where the various symbols have their usual meanings. The following correspondence now seems inevitable:

$$\delta W = -\frac{1}{\mathcal{N}} \sum_{r,s} \langle n_{r,s} \rangle dE_s, \quad \mu = -\alpha/\beta,\tag{5}$$

with the result that

$$d(q + \alpha \overline{N} + \beta \overline{E}) = \beta \delta Q.\tag{6}$$

The parameter β, being the integrating factor for the heat δQ, must be equivalent to the reciprocal of the absolute temperature T, so we may write

$$\beta = 1/kT\tag{7}$$

and, hence,

$$\alpha = -\mu/kT.\tag{8}$$

[3]This quantity was first introduced by Kramers, who called it the *q-potential*.

The quantity $(q + \alpha\overline{N} + \beta\overline{E})$ would then be identified with the thermodynamic variable S/k; accordingly,

$$q = \frac{S}{k} - \alpha\overline{N} - \beta\overline{E} = \frac{TS + \mu\overline{N} - \overline{E}}{kT}. \tag{9}$$

However, $\mu\overline{N}$ is identically equal to G, the Gibbs free energy of the system, and hence to $(\overline{E} - TS + PV)$. So, finally,

$$q \equiv \ln\left\{\sum_{r,s}\exp(-\alpha N_r - \beta E_s)\right\} = \frac{PV}{kT}. \tag{10}$$

Equation (10) provides the essential link between the thermodynamics of the given system and the statistics of the corresponding grand canonical ensemble. It is, therefore, a relationship of central importance in the formalism developed in this chapter.

To derive further results, we prefer to introduce a parameter z, defined by the relation

$$z \equiv e^{-\alpha} = e^{\mu/kT}; \tag{11}$$

the parameter z is generally referred to as the *fugacity* of the system. In terms of z, the q-potential takes the form

$$q \equiv \ln\left\{\sum_{r,s}z^{N_r}e^{-\beta E_s}\right\} \tag{12}$$

$$= \ln\left\{\sum_{N_r=0}^{\infty}z^{N_r}Q_{N_r}(V,T)\right\} \quad \text{(with } Q_0 \equiv 1\text{)}, \tag{13}$$

so we may write

$$q(z,V,T) \equiv \ln \mathcal{Q}(z,V,T), \tag{14}$$

where

$$\mathcal{Q}(z,V,T) \equiv \sum_{N_r=0}^{\infty}z^{N_r}Q_{N_r}(V,T) \quad \text{(with } Q_0 \equiv 1\text{)}. \tag{15}$$

Note that, in going from expression (12) to (13), we have (mentally) carried out a summation over the energy values E_s, with N_r fixed, thus giving rise to the partition function $Q_{N_r}(V,T)$; of course, the dependence of Q_{N_r} on V comes from the dependence of the E_s on V. In going from (13) to (14), we have (again mentally) carried out a summation over all the numbers $N_r = 0,1,2,\cdots,\infty$, thus giving rise to the *grand partition function* $\mathcal{Q}(z,V,T)$ of the system. The q-potential, which we have already identified with PV/kT, is, therefore, the logarithm of the grand partition function.

It appears that in order to evaluate the grand partition function $\mathcal{Q}(z,V,T)$ we have to go through the routine of evaluating the partition function $Q(N,V,T)$. In principle, this is indeed true. In practice, however, we find that on many occasions an explicit evaluation of the partition function is extremely hard while considerable progress can be made in the evaluation of the grand partition function. This is particularly true when we deal with systems in which the influence of quantum statistics and/or interparticle interactions is important; see Sections 6.2 and 10.1. The formalism of the grand canonical ensemble then proves to be of considerable value.

We are now in a position to write down the full recipe for deriving the leading thermodynamic quantities of a given system from its q-potential. We have, first of all, for the pressure of the system

$$P(z,V,T) = \frac{kT}{V}q(z,V,T) \equiv \frac{kT}{V}\ln\mathcal{Q}(z,V,T). \tag{16}$$

Next, writing N for $\overline{N}$ and U for $\overline{E}$, we obtain with the help of equations (4.2.6), (4.2.7), and (11)

$$N(z,V,T) = z\left[\frac{\partial}{\partial z}q(z,V,T)\right]_{V,T} = kT\left[\frac{\partial}{\partial\mu}q(\mu,V,T)\right]_{V,T} \tag{17}$$

and

$$U(z,V,T) = -\left[\frac{\partial}{\partial\beta}q(z,V,T)\right]_{z,V} = kT^2\left[\frac{\partial}{\partial T}q(z,V,T)\right]_{z,V}. \tag{18}$$

Eliminating z between equations (16) and (17), one obtains the equation of state, that is, the (P,V,T)-relationship, of the system. On the other hand, eliminating z between equations (17) and (18), one obtains U as a function of N, V, and T, which readily leads to the specific heat at constant volume as $(\partial U/\partial T)_{N,V}$. The Helmholtz free energy is given by the formula

$$A = N\mu - PV = NkT\ln z - kT\ln\mathcal{Q}(z,V,T)$$

$$= -kT\ln\frac{\mathcal{Q}(z,V,T)}{z^N}, \tag{19}$$

which may be compared with the canonical ensemble formula $A = -kT\ln Q(N,V,T)$; see also Problem 4.2. Finally, we have for the entropy of the system

$$S = \frac{U - A}{T} = kT\left(\frac{\partial q}{\partial T}\right)_{z,V} - Nk\ln z + kq. \tag{20}$$

4.4 Examples

We shall now study a couple of simple problems, with the explicit purpose of demonstrating how the method of the q-potential works. This is not intended to be a demonstration of the power of this method, for we shall consider here only those problems that can be solved equally well by the methods of the preceding chapters. The real power of the new method will become apparent only when we study problems involving quantum-statistical effects and effects arising from interparticle interactions; many such problems will appear in the remainder of the text.

The first problem we propose to consider here is that of the classical ideal gas. In Section 3.5 we showed that the partition function $Q_N(V, T)$ of this system could be written as

$$Q_N(V, T) = \frac{[Q_1(V, T)]^N}{N!}, \tag{1}$$

where $Q_1(V, T)$ may be regarded as the partition function of a single particle in the system. First of all, we should note that equation (1) does not imply any restrictions on the particles having *internal* degrees of motion; those degrees of motion, if present, would affect the results only through Q_1. Second, we should recall that the factor $N!$ in the denominator arises from the fact that the particles constituting the gas are, in fact, *indistinguishable*. Closely related to the indistinguishability of the particles is the fact that they are *nonlocalized*, for otherwise we could distinguish them through their very sites; compare, for instance, the system of harmonic oscillators, which was studied in Section 3.8. Now, since our particles are nonlocalized they can be *anywhere* in the space available to them; consequently, the function Q_1 will be directly proportional to V:

$$Q_1(V, T) = Vf(T), \tag{2}$$

where $f(T)$ is a function of temperature alone. We thus obtain for the grand partition function of the gas

$$\mathcal{Q}(z, V, T) = \sum_{N_r=0}^{\infty} z^{N_r} Q_{N_r}(V, T) = \sum_{N_r=0}^{\infty} \frac{\{zVf(T)\}^{N_r}}{N_r!}$$

$$= \exp\{zVf(T)\}, \tag{3}$$

which gives

$$q(z, V, T) = zVf(T). \tag{4}$$

Formula (4.3.16) through (4.3.20) then lead to the following results:

$$P = zkTf(T), \tag{5}$$

$$N = zVf(T), \tag{6}$$

$$U = zVkT^2 f'(T), \tag{7}$$

$$A = NkT\ln z - zVkTf(T), \tag{8}$$

and

$$S = -Nk\ln z + zVk\{Tf'(T) + f(T)\}. \tag{9}$$

Eliminating z between (5) and (6), we obtain the equation of state of the system:

$$PV = NkT. \tag{10}$$

We note that equation (10) holds irrespective of the form of the function $f(T)$. Next, eliminating z between (6) and (7), we obtain

$$U = NkT^2 f'(T)/f(T), \tag{11}$$

which gives

$$C_V = Nk \frac{2Tf(T)f'(T) + T^2\{f(T)f''(T) - [f'(T)]^2\}}{[f(T)]^2}. \tag{12}$$

In simple cases, the function $f(T)$ turns out to be directly proportional to a certain power of T. Supposing that $f(T) \propto T^n$, equations (11) and (12) become

$$U = n(NkT) \tag{11a}$$

and

$$C_V = n(Nk). \tag{12a}$$

Accordingly, the pressure in such cases is directly proportional to the energy density of the gas, the constant of proportionality being $1/n$. The reader will recall that the case $n = 3/2$ corresponds to a nonrelativistic gas while $n = 3$ corresponds to an extreme relativistic one.

Finally, eliminating z between equation (6) and equations (8) and (9), we obtain A and S as functions of N, V, and T. This essentially completes our study of the classical ideal gas.

The next problem to be considered here is that of a system of independent, *localized* particles — a model which, in some respects, approximates a solid. Mathematically, the

problem is similar to that of a system of harmonic oscillators. In either case, the microscopic entities constituting the system are mutually *distinguishable*. The partition function $Q_N(V, T)$ of such a system can be written as

$$Q_N(V, T) = [Q_1(V, T)]^N. \tag{13}$$

At the same time, in view of the localized nature of the particles, the single-particle partition function $Q_1(V, T)$ is essentially independent of the volume occupied by the system. Consequently, we may write

$$Q_1(V, T) = \phi(T), \tag{14}$$

where $\phi(T)$ is a function of temperature alone. We then obtain for the grand partition function of the system

$$\mathcal{Q}(z, V, T) = \sum_{N_r=0}^{\infty} [z\phi(T)]^{N_r} = [1 - z\phi(T)]^{-1}; \tag{15}$$

clearly, the quantity $z\phi(T)$ must stay below unity, so that the summation over N_r is convergent.

The thermodynamics of the system follows straightforwardly from equation (15). We have, to begin with,

$$P \equiv \frac{kT}{V} q(z, T) = -\frac{kT}{V} \ln\{1 - z\phi(T)\}. \tag{16}$$

Since both z and T are intensive variables, the right side of (16) vanishes as $V \to \infty$. Hence, in the thermodynamic limit, $P = 0$.[4] For other quantities of interest, we obtain, with the help of equations (4.3.17) through (4.3.20),

$$N = \frac{z\phi(T)}{1 - z\phi(T)}, \tag{17}$$

$$U = \frac{zkT^2\phi'(T)}{1 - z\phi(T)}, \tag{18}$$

$$A = NkT\ln z + kT\ln\{1 - z\phi(T)\}, \tag{19}$$

and

$$S = -Nk\ln z - k\ln\{1 - z\phi(T)\} + \frac{zkT\phi'(T)}{1 - z\phi(T)}. \tag{20}$$

From (17), we get

$$z\phi(T) = \frac{N}{N+1} \simeq 1 - \frac{1}{N} \quad (N \gg 1). \tag{21}$$

[4]It will be seen in the sequel that P actually vanishes like $(\ln N)/N$.

It follows that

$$1 - z\phi(T) = \frac{1}{N+1} \simeq \frac{1}{N}. \tag{22}$$

Equations (17) through (20) now give

$$U/N = kT^2\phi'(T)/\phi(T), \tag{18a}$$

$$A/N = -kT\ln\phi(T) + O\left(\frac{\ln N}{N}\right), \tag{19a}$$

and

$$S/Nk = \ln\phi(T) + T\phi'(T)/\phi(T) + O\left(\frac{\ln N}{N}\right). \tag{20a}$$

Substituting

$$\phi(T) = [2\sinh(\hbar\omega/2kT)]^{-1} \tag{23}$$

into these formulae, we obtain results pertaining to a system of *quantum-mechanical*, one-dimensional harmonic oscillators. The substitution

$$\phi(T) = kT/\hbar\omega, \tag{24}$$

on the other hand, leads to results pertaining to a system of *classical*, one-dimensional harmonic oscillators.

As a corollary, we examine here the problem of *solid–vapor equilibrium*. Consider a single-component system, having two phases — solid and vapor — in equilibrium, contained in a closed vessel of volume V at temperature T. Since the phases are free to exchange particles, a state of mutual equilibrium would imply that their chemical potentials are equal; this, in turn, means that they have a common fugacity as well. Now, the fugacity z_g of the gaseous phase is given by, see equation (6),

$$z_g = \frac{N_g}{V_g f(T)}, \tag{25}$$

where N_g is the number of particles in the gaseous phase and V_g the volume occupied by them; in a typical case, $V_g \simeq V$. The fugacity z_s of the solid phase, on the other hand, is given by equation (21):

$$z_s \simeq \frac{1}{\phi(T)}. \tag{26}$$

Equating (25) and (26), we obtain for the *equilibrium particle density* in the vapor phase

$$N_g/V_g = f(T)/\phi(T). \tag{27}$$

Now, if the density in the vapor phase is sufficiently low and the temperature of the system sufficiently high, the vapor pressure P would be given by

$$P_{\text{vapor}} = \frac{N_g}{V_g} kT = kT \frac{f(T)}{\phi(T)}. \tag{28}$$

To be specific, we may assume the vapor to be monatomic; the function $f(T)$ is then of the form

$$f(T) = (2\pi mkT)^{3/2}/h^3. \tag{29}$$

On the other hand, if the solid phase can be approximated by a set of three-dimensional harmonic oscillators characterized by a single frequency ω (the *Einstein* model), the function $\phi(T)$ would be

$$\phi(T) = [2\sinh(\hbar\omega/2kT)]^{-3}. \tag{30}$$

However, there is one important difference here. An atom in a solid is energetically more stabilized than an atom that is free — that is why a certain threshold energy is required to transform a solid into separate atoms. Let ε denote the value of this energy per atom, which in a way implies that the zeros of the energy spectra ε_g and ε_s, which led to the functions (29) and (30), respectively, are displaced with respect to one another by an amount ε. A *true* comparison between the functions $f(T)$ and $\phi(T)$ must take this into account. As a result, we obtain for the vapor pressure

$$P_{\text{vapor}} = kT \left(\frac{2\pi mkT}{h^2}\right)^{3/2} [2\sinh(\hbar\omega/2kT)]^3 e^{-\varepsilon/kT}. \tag{31}$$

In passing, we note that equation (27) also gives us the necessary condition for the formation of the solid phase. The condition clearly is:

$$N > V \frac{f(T)}{\phi(T)}, \tag{32}$$

where N is the total number of particles in the system. Alternatively, this means that

$$T < T_c, \tag{33}$$

where T_c is a *characteristic* temperature determined by the implicit relationship

$$\frac{f(T_c)}{\phi(T_c)} = \frac{N}{V}. \tag{34}$$

Once the two phases appear, the number $N_g(T)$ will have a value determined by equation (27) while the remainder, $N - N_g$, will constitute the solid phase.

4.5 Density and energy fluctuations in the grand canonical ensemble: correspondence with other ensembles

In a grand canonical ensemble, the variables N and E, for any member of the ensemble, can lie anywhere between zero and infinity. Therefore, on the face of it, the grand canonical ensemble appears to be very different from its predecessors — the canonical and the microcanonical ensembles. However, as far as thermodynamics is concerned, the results obtained from this ensemble turn out to be identical to the ones obtained from the other two. Thus, in spite of strong facial differences, the overall behavior of a given physical system is practically the same whether it belongs to one kind of ensemble or another. The basic reason for this is that the "relative fluctuations" in the values of the quantities that vary from member to member in an ensemble are practically negligible. Therefore, in spite of the different surroundings that different ensembles provide to a given physical system, the overall behavior of the system is not significantly affected.

To appreciate this point, we shall evaluate the relative fluctuations in the particle density n and the energy E of a given physical system in the grand canonical ensemble. Recalling that

$$\overline{N} = \frac{\sum_{r,s} N_r e^{-\alpha N_r - \beta E_s}}{\sum_{r,s} e^{-\alpha N_r - \beta E_s}}, \tag{1}$$

it readily follows that

$$\left(\frac{\partial \overline{N}}{\partial \alpha}\right)_{\beta, E_s} = -\overline{N^2} + \overline{N}^2. \tag{2}$$

Thus

$$\overline{(\Delta N)^2} \equiv \overline{N^2} - \overline{N}^2 = -\left(\frac{\partial \overline{N}}{\partial \alpha}\right)_{T,V} = kT \left(\frac{\partial \overline{N}}{\partial \mu}\right)_{T,V}. \tag{3}$$

From (3), we obtain for the relative mean-square fluctuation in the particle density $n \, (= N/V)$

$$\frac{\overline{(\Delta n)^2}}{\overline{n}^2} = \frac{\overline{(\Delta N)^2}}{\overline{N}^2} = \frac{kT}{\overline{N}^2} \left(\frac{\partial \overline{N}}{\partial \mu}\right)_{T,V}. \tag{4}$$

In terms of the variable $v \, (= V/\overline{N})$, we may write

$$\frac{\overline{(\Delta n)^2}}{\overline{n}^2} = \frac{kTv^2}{V^2} \left(\frac{\partial (V/v)}{\partial \mu}\right)_{T,V} = -\frac{kT}{V} \left(\frac{\partial v}{\partial \mu}\right)_T. \tag{5}$$

To put this result into a more practical form, we recall the thermodynamic relation

$$d\mu = v\,dP - s\,dT, \tag{6}$$

according to which $d\mu$ (at constant T) $= v\,dP$. Equation (5) then takes the form

$$\frac{\overline{(\Delta n)^2}}{\overline{n}^2} = -\frac{kT}{V}\frac{1}{v}\left(\frac{\partial v}{\partial P}\right)_T = \frac{kT}{V}\kappa_T, \tag{7}$$

where κ_T is the isothermal compressibility of the system.

Thus, the relative root-mean-square fluctuation in the particle density of the given system is *ordinarily* $O(N^{-1/2})$ and, hence, negligible. However, there are exceptions, like the ones met with in situations accompanying *phase transitions*. In those situations, the compressibility of a given system can become excessively large, as is evidenced by an almost "flattening" of the isotherms. For instance, at a critical point the compressibility diverges, so it is no longer intensive. Finite-size scaling theory described in Chapters 12 and 14 indicates that at the critical point the isothermal compressibility scales with system size as $\kappa_T(T_c) \sim N^{\gamma/d\nu}$ where γ and ν are certain critical exponents and d is the dimension. For the case of experimental liquid–vapor critical points, $\kappa_T(T_c) \sim N^{0.63}$. Accordingly, the root-mean-square density fluctuations grow faster than $N^{1/2}$ — in this case, like $N^{0.82}$. Thus, in the region of phase transitions, especially at the critical points, we encounter unusually large fluctuations in the particle density of the system. Such fluctuations indeed exist and account for phenomena like *critical opalescence*. It is clear that under these circumstances the formalism of the grand canonical ensemble could, in principle, lead to results that are not necessarily identical to the ones following from the corresponding canonical ensemble. In such cases, it is the formalism of the grand canonical ensemble that will have to be preferred because only this one will provide a correct picture of the actual physical situation.

We shall now examine fluctuations in the energy of the system. Following the usual procedure, we obtain

$$\overline{(\Delta E)^2} \equiv \overline{E^2} - \overline{E}^2 = -\left(\frac{\partial \overline{E}}{\partial \beta}\right)_{z,V} = kT^2\left(\frac{\partial U}{\partial T}\right)_{z,V}. \tag{8}$$

To put expression (8) into a more comprehensible form, we write

$$\left(\frac{\partial U}{\partial T}\right)_{z,V} = \left(\frac{\partial U}{\partial T}\right)_{N,V} + \left(\frac{\partial U}{\partial N}\right)_{T,V}\left(\frac{\partial N}{\partial T}\right)_{z,V}, \tag{9}$$

where the symbol N is being used interchangeably for $\overline{N}$. Now, in view of the fact that

$$N = -\left(\frac{\partial}{\partial\alpha}\ln\mathcal{Q}\right)_{\beta,V}, \quad U = -\left(\frac{\partial}{\partial\beta}\ln\mathcal{Q}\right)_{\alpha,V}, \tag{10}$$

we have

$$\left(\frac{\partial N}{\partial\beta}\right)_{\alpha,V} = \left(\frac{\partial U}{\partial\alpha}\right)_{\beta,V} \tag{11}$$

and, hence,

$$\left(\frac{\partial N}{\partial T}\right)_{z,V} = \frac{1}{T}\left(\frac{\partial U}{\partial\mu}\right)_{T,V}. \tag{12}$$

Substituting expressions (9) and (12) into equation (8) and remembering that the quantity $(\partial U/\partial T)_{N,V}$ is the familiar C_V, we get

$$\overline{(\Delta E)^2} = kT^2 C_V + kT\left(\frac{\partial U}{\partial N}\right)_{T,V}\left(\frac{\partial U}{\partial\mu}\right)_{T,V}. \tag{13}$$

Invoking equations (3.6.3) and (3), we finally obtain

$$\overline{(\Delta E)^2} = \langle(\Delta E)^2\rangle_{\text{can}} + \left\{\left(\frac{\partial U}{\partial N}\right)_{T,V}\right\}^2\overline{(\Delta N)^2}. \tag{14}$$

Formula (14) is highly instructive; it tells us that the mean-square fluctuation in the energy E of a system in the grand canonical ensemble is equal to the value it would have in the canonical ensemble *plus* a contribution arising from the fact that now the particle number N is also fluctuating. Again, under ordinary circumstances, the relative root-mean-square fluctuation in the energy density of the system would be practically negligible. However, in the region of phase transitions, unusually large fluctuations in the value of this variable can arise by virtue of the second term in the formula.

4.6   Thermodynamic phase diagrams

One of the great successes of thermodynamics and statistical mechanics over the last 150 years has been in the study of phase transitions. Statistical mechanics provides the basis for accurate models for a wide variety of thermodynamic phases of materials and has led to a detailed understanding of phase transitions and critical phenomena.

Condensed materials exist in a variety of phases that depend on thermodynamic parameters such as temperature, pressure, magnetic field, and so on. Thermodynamics and statistical mechanics can be used to determine the properties of individual phases, and the locations and characteristics of the phase transitions that occur between those phases. Thermodynamic phases are regions in the phase diagram where the thermodynamics properties are analytic functions of the thermodynamic parameters, while phase transitions are points, lines, or surfaces in the phase diagram where the thermodynamic properties are nonanalytic. Much of the remainder of this text is devoted to using statistical mechanics to explain the properties of material phases and phase transitions.