THERMODYNAMICS AND INTRODUCTORY STATISTICAL MECHANICS

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CHAPTER 13

PRINCIPLES OF STATISTICAL MECHANICS

13.1 INTRODUCTION

Statistical Mechanics (or Statistical Thermodynamics, as it is often called) is concerned with predicting and as far as possible interpreting the macroscopic properties of a system in terms of the properties of its microscopic constituents (molecules, atoms, electrons, etc).

For example, thermodynamics can interrelate all kinds of macroscopic properties, such as energy, entropy, and so forth, and may ultimately express these quantities in terms of the heat capacity of the material. Thermodynamics, however, cannot predict the heat capacities: statistical mechanics can.

There is another difference. Thermodynamics (meaning macroscopic thermodynamics) is not applicable to small systems ($\sim 10^{12}$ molecules or less) or, as noted in Chapter 12, to large systems in the critical region. In both instances, failure is attributed to large fluctuations, which thermodynamics does not take into account, whereas statistical mechanics does.

How are the microscopic and macroscopic properties related? The former are described in terms of position, momentum, pressure, energy levels, wave functions, and other *mechanical* properties. The latter are described in terms of heat capacities, temperature, entropy, and others—that is, in terms of

thermodynamic properties. Until about the mid-nineteenth century, the two seemingly different disciplines were considered to be separate sciences, with no apparent connection between them. Mechanics was associated with names like Newton, LaGrange, and Hamilton and more recently with Schrodinger, Heisenberg, and Dirac. Thermodynamics was associated with names like Carnot, Clausius, Helmholtz, Gibbs, and more recently with Carathéodory, Born, and others. *Statistical mechanics is the branch of science that interconnects these two seemingly different subjects*. But statistical mechanics is not a mere extension of mechanics and thermodynamics. Statistical mechanics has its own laws (postulates) and a distinguished slate of scientists, such as Boltzmann, Gibbs, and Einstein, who are credited with founding the subject.

13.2 PRELIMINARY DISCUSSION—SIMPLE PROBLEM

The following simple (silly) problem is introduced to illustrate with a concrete example what statistical mechanics purports to do, how it does it, and the underlying assumptions on which it is based.

Consider a system composed of three particles (1, 2, and 3) having a fixed volume and a fixed energy, E. Each of the particles can be in any of the particle energy levels, ε_i, shown in Figure 13.1. We take the total energy, E, to be equal to 6 units.

Note: Historically, statistical mechanics was founded on classical mechanics. Particle properties were described in terms of momenta, positions, and similar characteristics and, although as a rule classical mechanics is simpler to use than quantum mechanics, in the case of statistical mechanics it is the other way around. It is much easier to picture a distribution of particles among discrete energy levels than to describe them in terms of velocities momenta, etc. Actually, our treatment will not be based on quantum mechanics. We will only use the language of quantum mechanics.

In the example discussed here, we have for simplicity taken the energy levels to be nondegenerate and equally spaced. Figure 13.2 illustrates how


$\varepsilon_4 = 4$
$\varepsilon_3 = 3$
$\varepsilon_2 = 2$
$\varepsilon_1 = 1$
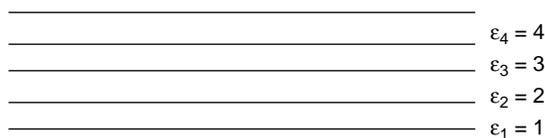
Figure 13.1   Representation of a set of equally spaced energy levels.
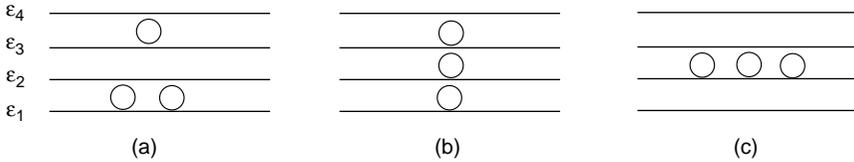
Figure 13.2   Distribution of three particles among the set of energy levels of Figure 13.1, having a total energy of 6 units.

the particles can be distributed among the energy levels under the constraint of total constant energy of 6 units. Although the total energy is the same regardless of how the particles are distributed, it is reasonable to assume that some properties of the system, other than the energy, E, will depend on the arrangement of the particles among the energy states. These arrangements are called *microstates* (or micromolecular states).

Note: It is wrong to picture the energy levels as shelves on which the particles sit. Rather, the particles are continuously colliding, and the microstates continuously change with time.

13.3   TIME AND ENSEMBLE AVERAGES

During the time of measurement on a single system, the system undergoes a large number of changes from one microstate to another. The observed macroscopic properties of the system are *time averages* of the properties of the instantaneous microstates—that is, of the mechanical properties. Time-average calculations are virtually impossible to carry out. A way to get around this difficulty is to replace the time average of a *single* system by an *ensemble* average of a very large collection of systems. That is, instead of looking at one system over a period of time, one looks at a (mental) collection of a large number of systems (all of which are replicas of the system under consideration) at a *given instance of time*. Thus, in an ensemble of systems, all systems have certain properties in common (such as same N, V, E) but differ in their microscopic specifications; that is, they have different microstates. The assumption that the time average may be replaced by an ensemble average is stated as postulate:

- *Postulate I: the observed property of a single system over a period of time is the same as the average over all microstates (taken at an instant of time).*
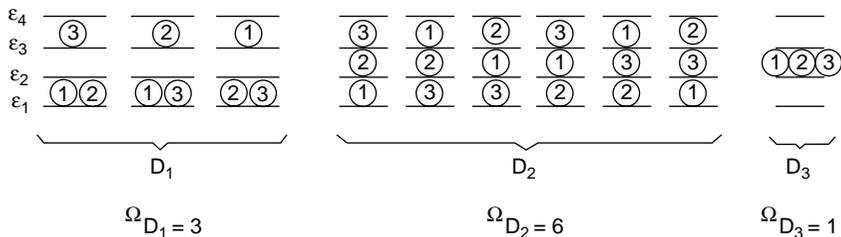
Figure 13.3   Identity of the particles corresponding to the arrangements in Figure 13.2. The symbol Ω_{Di} represents the number of quantum states associated with distribution Di.

13.4   NUMBER OF MICROSTATES, Ω_D, DISTRIBUTIONS D_i

For the system under consideration, we can construct 10 microstates (Figure 13.3). We might characterize these microstates by the symbols Ψ_1, Ψ_2, and so forth. (In quantum mechanics, the Ψ symbols could represent wave functions.) The microstates can be grouped into three different classes, characterized by the particle distributions D_1, D_2, D_3. Let Ω_D, denote the number of microstates belonging to distribution D_1, etc. Thus, $\Omega_{D_1} = 3$, $\Omega_{D_2} = 6$, and $\Omega_{D_3} = 1$.

Each of the systems constituting the ensemble made up of these microstates has the same N, V, and E, as noted before, but other properties may be different, depending on the distribution. Specifically, let χ_1 be a property of the systems when the system is in the distribution D_1, χ_2 when the distribution is D_2, and χ_3 when the distribution is D_3. The ensemble average, which we say is equal to the time average (and thus to the observed property) is

$$\langle \chi \rangle_{ensemble} = \chi_{obs} = (3\chi_1 + 6\chi_2 + \chi_3)/10 \qquad (13\text{-}1)$$

This result is based on a number of assumptions, in addition to the time-average postulate, assumptions that are implied but not stated. In particular

1) *Equation 13-1* assumes that all microstates are equally probable. (Attempts to prove this have been only partially successful.) This assumption is so important that it is adopted as a fundamental postulate of statistical mechanics.
   • *Postulate II: all microstates have equal a priori probability.*
2) Although we refer to the microscopic entities as "particles," we are noncommittal as to the nature of the particles. They can mean elementary particles (electrons, protons, etc.), composites of elementary particles, aggregates of molecules, or even large systems.

3) In this example, the assumption was made that each particle retains its own set of *private* energy level. This is generally not true—interaction between the particles causes changes in the energy levels. Neglecting the interactions holds for ideal gases and ideal solids but not for real systems. In this course, we will only treat ideal systems, and the assumption of private energy levels will be adequate. This assumption is not a necessary requirement of statistical mechanics, and the rigorous treatment of realistic systems is not based on it.

4) In drawing pictures of the 10 microstates, it was assumed that all particles are distinguishable, that is, that they can be labeled. This is true classically, but not quantum mechanically. In quantum mechanics, identical particles (and in our example, the particles are identical) are *indistinguishable*. Thus, instead of there being three different micro-states in distribution D_1, there is only one, i.e., $\Omega_{D_1} = 1$. Similarly, $\Omega_{D_2} = 1$ and $\Omega_{D_3} = 1$. Moreover, quantum mechanics may prohibit certain particles (fermions) from occupying the same energy state (think of Pauli's Exclusion Principle), and in such cases distributions D_1 and D_3 are not allowed.

In summary, attention must be paid to the nature of the particles in deciding what statistical count is appropriate.

1) If the particles are classical, i.e., *distinguishable*, we must use a certain type of statistical count, namely the *Maxwell-Boltzmann* statistical count.

2) If the particles are quantal, that is, *indistinguishable* and there are *no restrictions as to the number of particles per energy state*, we have to use the *Bose-Einstein* statistical count.

3) If the particles are quantal, that is, *indistinguishable and restricted to no more than one particle per state*, then we must use the *Fermi-Dirac* statistical count.

4) Although in this book we deal with particles, which for most part are quantal (atoms, molecules, etc), our treatment will not be based on explicit quantum mechanical techniques. Rather, the effects of quantum theory will be taken into account by using the so-called *corrected* classical Maxwell-Boltzmann statistics. This is a simple modification of the Maxwell-Boltzmann statistics but, as will be shown, can be applied to most molecular gases at ordinary temperatures.

5) Although pictures may be drawn to illustrate how the particles are distributed among the energy levels and how the number of micro-states can be counted in a given distribution, this can only be

accomplished when the number of particles is small. If the number is large (approaching Avogadro's number), this would be an impossible task. Fortunately, it need not be done. What is important, as will be shown, is knowing the *number of microstates*, Ω_{D^*}, *belonging to the most probable distribution*. There are mathematical techniques for obtaining such information, called *Combinatory Analysis*, to be taken up in Section 13.5.

6) In our illustrative example, the distribution, D_2, is more probable than either D_1 or D_3. Had we used a large number of particles (instead of 3) and a more complex manifold of energy levels, the distribution D_2 would be so much more probable so that, for all practical purposes, the other distributions may be ignored. In terms of the most probable distribution as D^*, we can write

$$\langle \chi \rangle = \chi_{obs} = (\Omega_D \chi_1 + \cdots + \Omega_{D^*} \chi^* + \cdots)/\Sigma_D \Omega_{D_i} \approx \chi^* \quad (13\text{-}2)$$

7) The ensemble constructed in our example—in which all systems have the same N, V, and E—is not unique. It is a particular ensemble, called the *microcanonical* ensemble. There are other ensembles: the *canonical* ensemble, in which all systems have the same N and V but different Es; the *grand canonical ensemble*, in which the systems have the same V but different Es and Ns; and still other kinds of ensembles. Different ensembles allow different kinds of fluctuations. (For example, in the canonical ensemble, there can be no fluctuations in N because N is fixed, but in the grand canonical ensemble, there are fluctuations in N.) Ensemble differences are significant when the systems are small; in large systems, however, the fluctuations become insignificant with the possible exception of the critical region, and all ensembles give essentially the same results. In this course, we use only the microcanonical ensemble.

13.5 MATHEMATICAL INTERLUDE VI: COMBINATORY ANALYSIS

1. In how many ways can N distinguishable objects be placed in N positions? Or in how many ways can N objects be permuted, N at a time?
   - *Result*: the first position can be filled by any of the N objects, the second by $N - 1$, and so forth; thus

$$\mathcal{U} = P_N^N = (N - 1)(N - 2)\ldots 1 = N! \quad (13\text{-}3)$$

2. In how many ways can m objects be drawn out of N? Or in how many ways can N objects be permuted m at a time?
   - *Result*: the first object can be drawn in N different ways, the second in $N - 1$ ways, and the m*th* in $(N - m + 1)$ ways:

$$И = P_N^m = N(N - 1)\ldots(N - m + 1) \qquad (13\text{-}4a)$$

   - Multiplying numerator and denominator by $(N - m)! = (N - m)$ $(N - m - 1)\ldots 1$ yields

$$И = P_N^m = N!/(N - m)! \qquad (13\text{-}4b)$$

3. In how many ways can m objects be drawn out of N? The identity of the m objects is immaterial. This is the same as asking, In how many ways can N objects, taken m at a time, be *combined?*

   Note: there is a difference between a *permutation* and a *combination*. In a permutation, the identity and order of the objects are important; in a combination, only the identity is important. For example, there are six permutations of the letters A, B, and C but only one combination.

$$И = C_N^m = N!/[(N - m)!m!] \qquad (13\text{-}5)$$

4. In how many ways can N objects be divided into two piles, one containing $N - m$ objects and the other m objects? The order of the objects in each pile is unimportant.
   - *Result*: we need to divide the result given by *Eq. 13-4b* by m! to correct for the ordering of the m objects:

$$И = P_N^m = N!/[(N - m)!m!] \qquad (13\text{-}6)$$

   (This is the same as *Eq. 13-5*.)

5. In how many ways can N (distinguishable) objects be partitions into c classes, such that there be N_1 objects in class 1, N_2 objects in class 2, and so on, with the stipulation that the order within each class is unimportant?
   - *Result*: obviously

$$И = N!\left(\frac{N!}{N_1!N_2!\cdots N_i!}\right) \qquad (13\text{-}7)$$

This expression is the same as the coefficient of multinomial expansion:

$$(f_1 + f_2 + \cdots f_c)^N = \sum \left\{[N!/(N_1!N_2!\cdots N_C!)]f_1^{N_1}f_2^{N_2}\cdots f_C^{N_i}\right\} \qquad (13\text{-}8)$$

6. In how many ways can one arrange N distinguishable objects among g boxes. There are no restrictions as to the number of objects per box.
   - *Result*: the first object can go into any of the g boxes, so can the second, and so forth:

$$И = g^N \qquad\qquad (13\text{-}9)$$

7. In how many ways can N *distinguishable* objects be distributed into g boxes $(g \geq N)$ with the stipulation that no box may contain more than one object?
   - *Result*:

$$И = g!/(g - N)! \qquad\qquad (13\text{-}10)$$

8. In how many ways can N *indistinguishable* objects be put in g boxes such that there would be no more than one object per box?
   - *Result*:

$$И = g!/[(g - N)!N!] \qquad\qquad (13\text{-}11)$$

9. In how many ways can N *indistinguishable* objects be distributed among g boxes? There are no restrictions as to the number of objects per box. Partition the space into g compartments. If there are g compartments, there are $g - 1$ partitions. To start, treat the objects and partitions on the same footing. In other words, permute $N + g - 1$ entities. Now correct for the fact that permuting objects among themselves gives nothing new, and permuting partitions among themselves does not give anything different.
   - *Result*:

$$И = (g + N - 1)!/[(g - 1)!N!] \qquad\qquad (13\text{-}12)$$

This formula was first derived by Einstein.

13.6 FUNDAMENTAL PROBLEM IN STATISTICAL MECHANICS

We present a set of energy levels $\varepsilon_1, \varepsilon_2, \ldots \varepsilon_i \ldots$; with degeneracies $g_1, g_2, \ldots g_i \ldots$; and occupation numbers $N_1, N_2, \ldots N_i \ldots$. In how many ways can those N particles be distributed among the set of energy levels, with the stipulation that there be N_1 particles in level 1, N_2 particles in level 2, and so forth?

Obviously, the answer will depend on whether the particles are distinguishable or indistinguishable, whether there are restrictions as to how may particles may occupy a given energy state, etc. In this book, we will treat, in some detail, the statistical mechanics of *distinguishable* particles, as noted before, and correct for the indistinguishability by a simple device. The justification for this procedure is given below.

13.7   MAXWELL-BOLTZMANN, FERMI-DIRAC, BOSE-EINSTEIN STATISTICS. "CORRECTED" MAXWELL-BOLTZMANN STATISTICS

13.7.1   Maxwell-Boltzmann Statistics

Particles are distinguishable, and there are no restrictions as to the number of particles in any given state.
   Using Combinatory Analysis *Eqs. 13-7, 13-8, 13-9* gives the number of microstates in the distribution, D.

$$\Omega_D^{MB} = [N!/(N_1!N_2! \cdots N_i! \cdots)]g_1^N g_2^N \cdots g_i^N \cdots \qquad (13\text{-}13)$$

13.7.2   Fermi-Dirac Statistics

Particles are indistinguishable and restricted to no more than one particle per state.
   Using *Eq. 13.11* of the Combinatory Analysis gives

$$\Omega_D^{FD} = \{g_1!/[(g_1 - N_1)!N_1!]\}\{g_2!/[g_2 - N_2)!N_2!]\} \cdots$$
$$= \Pi_i\{g_i!/(g_i - N_i)!N_i!\} \qquad (13\text{-}14)$$

13.7.3   Bose-Einstein Statistics

Particles are indistinguishable, and there are no restrictions.
   Using *Eq. 13-12*, gives

$$\Omega_D^{BE} = [(g_1 + N_1 - 1)!/(g_1 - 1)!N_1!][(g_2 + N_2 - 1)!/(g_2 - 1)!N_2!] \cdots$$
$$= \Pi_i[(g_i + N_i - 1)!/(g_i - 1)!N_i!] \qquad (13\text{-}15)$$

The different statistical counts produce thermodynamic values, which are vastly different. Strictly speaking, all identical quantum-mechanical particles are indistinguishable, and we ought to use only Fermi-Dirac or Bose-Einstein statistics. For electrons, Fermi-Dirac statistics must be used; for liquid Helium II (consisting of He^4) at very low temperature, Bose-Einstein Statistics has to be used. Fortunately, for most molecular systems (except systems at very low temperatures), the number of degeneracies of a quantum state far exceeds the number of particles of that state. For most excited levels $g_i \gg N_i$ and as a result, the Bose-Einstein and Fermi-Dirac Ω values approach a common value, the common value being The Maxwell-Boltzmann Ω_D divided by N!

Proof of the above statement is based on three approximations, all reasonable, when $g_i \gg N_i$. They are

1) Stirling's Approximation

$$\ln N! \approx N \ln N - N \qquad (\text{N large}) \qquad (13\text{-}16)$$

2) Logarithmic expansion, $\ln(1 \pm x) \approx \pm x$ (x small) $\qquad (13\text{-}17a)$
3) Neglect of 1 compared with g_i/N_i $\qquad (13\text{-}17b)$

EXERCISE

1. Using these approximations show that

$$\ln \Omega_D^{FD} = \ln \Omega_D^{BE} = \Sigma_i N_i [\ln(g_i/N_i) + 1] \qquad (13\text{-}18)$$

2. Also, show that

$$\ln \Omega_D^{MB} = \ln N! + \Sigma_i N_i [1 + \ln(g_i/N_i)] \qquad (13\text{-}19a)$$

$$= N \ln N + \Sigma_i N_i \ln(g_i/N_i) \qquad (13\text{-}19b)$$

which is the same as *Equation 13-18* except for the addition of $\ln N!$.

13.7.4 "Corrected" Maxwell-Boltzmann Statistics

It is seen that Ω_D^{FD} and Ω_D^{BE} reach a common value, namely, $\Omega_D^{MB}/N!$, which will be referred to as *Corrected Maxwell-Boltzmann.* Thus

$$\Omega_D^{CMB} = \Omega_D^{MB}/N! \qquad (13\text{-}20a)$$

or, using Eq. 13-16

$$\ln \Omega_D^{CMB} = \Sigma_i N_i \ln(g_i/N_i) + N \qquad (13\text{-}20b)$$

13.8 SYSTEMS OF DISTINGUISHABLE (LOCALIZED) AND INDISTINGUISHABLE (NONLOCALIZED) PARTICLES

We mentioned in the preceding paragraph that in this course we would be dealing exclusively with molecular systems that are quantum mechanical in nature and therefore will use CMB statistics. Is there ever any justification for using MB statistics? Yes—when dealing with crystalline solids. Although the particles (atoms) in a crystalline sold are strictly indistinguishable, they are in fact localized at lattice points. Thus, by labeling the lattice points, we label the particles, making them effectively *distinguishable*. In summary, both the Maxwell-Boltzmann and the Corrected Maxwell-Boltzmann Statistics will be used in this course, the former in applications to *crystalline solids* and the latter in applications to *gases.*

13.9 MAXIMIZING Ω_D

Let D^* be the distribution for which Ω_{D^*} or rather $\ln \Omega_{D^*}$ is a maximum, characterized by the set of occupation numbers $N_1^*, N_2^*, \ldots N_i^* \ldots$ etc. Although the N_i values are strictly speaking discrete, they are so large that we may treat them as continuous variables and apply ordinary mathematical techniques to obtain their maximum values. Furthermore, because we will be concerned here with the most probable values, we will drop the * designation, from here on, keeping in mind that in the future Ω_D will describe the most probable value. To find the maximum values of N_i, we must have

$$\Sigma_i(\partial \ln \Omega_D/\partial N_i)\delta N_i = 0 \qquad (13\text{-}21)$$

subject to the constraints

$$N \text{ is constant or } \Sigma_i \, \delta N_i = 0 \qquad (13\text{-}22)$$
$$E \text{ is constant or } \Sigma_i \, \varepsilon_i\delta N_i = 0 \qquad (13\text{-}23)$$

If there were no constraints, the solution to this problem would be trivial. With the constraints, not all of the variables are independent. An easy way to get around this difficulty is to use the Method of Lagrangian (or Undetermined) Multipliers. Multiplying *Eq. 13-22* by α and *Equation 13-23* by β and subtracting them from *Equation 13-21* gives

$$\Sigma_i(\partial \ln \Omega_D/\partial N_i - \alpha - \beta\varepsilon_i)\delta N_i = 0 \qquad (13\text{-}24)$$

The Lagrange multipliers make all variables $N_1, N_2, \ldots N_i, \ldots$ effectively independent. To see this, let us regard N_1 and N_2 as the dependent variables and all the other N values as independent variables. Independent means that we can vary them any way we want to or not vary them at all. We choose not to vary $N_4, N_5 \ldots$, etc., that is, we set $\delta N_4, \delta N_5, \ldots$ equal to zero. *Equation 13-24* then becomes,

$$(\partial \ln \Omega_D / \partial N_1 - \alpha - \beta \varepsilon_1) \delta N_1 + (\partial \ln \Omega_D / \partial N_2 - \alpha - \beta \varepsilon_2) \delta N_2$$
$$+ (\partial \ln \Omega_D / \partial N_3) - \alpha - \beta \varepsilon_3) \delta N_3 = 0 \qquad (13\text{-}25)$$

We can choose α and β so as to make two terms zero, then the third term will be zero also. Repeating this process with δN_4, δN_5, etc. shows that for every arbitrary i (including subscripts $i = 1$, $i = 2$)

$$\partial \ln \Omega_D / \partial N_i - \alpha - \beta \varepsilon_i = 0 \text{ all } i \qquad (13\text{-}26)$$

13.10   PROBABILITY OF A QUANTUM STATE: THE PARTITION FUNCTION

13.10.1   Maxwell-Boltzmann Statistics

Using *Eq. 13-19b* we first write

$$\ln \Omega_D = (N_1 + N_2 + \cdots N_i \ldots) \ln(N_1 + N_2 + \cdots N_i + \cdots)$$
$$+ (N_1 \ln g_1 + N_2 \ln g_2 + \cdots N_i \ln g_i + \cdots)$$
$$- (N_1 \ln N_1 + N_2 \ln N_2 + \cdots N_i \ln N_i + \cdots) \qquad (13\text{-}27)$$

We differentiate with respect to N_i, which we regard here as particular variable, holding constant all other variables. This gives

$$\partial \ln \Omega_D^{MB} / \partial N_i = \ln N + N/N + \ln g_i - \ln N_i - N_i/N_i$$
$$= \ln(Ng_i/N_i) = \alpha + \beta \varepsilon_i \qquad (13\text{-}28)$$

or the probability, $\mathcal{P}_i$, that the particle is in state i

$$\mathcal{P}_i = N_i/N = g_i e^{-\alpha} e^{-\beta \varepsilon_i} \qquad (13\text{-}29)$$

It is easy to eliminate $e^{-\alpha}$, since

$$\Sigma_i N_i/N = 1 = e^{-\alpha} \Sigma_i g_i e^{-\beta \varepsilon_i} \qquad (13\text{-}30)$$

or,

$$e^{-\alpha} = 1/(\Sigma_i g_i \varepsilon^{-\beta \varepsilon_i}) \qquad (13\text{-}31)$$

and so,

$$\mathcal{P}_i = N_i/N = g_i e^{-\beta \varepsilon_i}/\Sigma_i g_i e^{-\beta \varepsilon_i} \qquad (13\text{-}32)$$

The quantity in the denominator, denoted as q,

$$q = \Sigma_i g_i e^{-\beta \varepsilon_i} \qquad (13\text{-}33)$$

is called the *partition function*. The partition function plays an important role in statistical mechanics (as we shall see): all thermodynamic properties can be derived from it.

13.10.2 Corrected Maxwell-Boltzmann Statistics

$$\ln \Omega_D^{CMB} = \Sigma_i N_i (\ln g_i - \ln N_i + 1) \qquad (13\text{-}34)$$

$$\partial \ln \Omega_D^{CMB}/\partial N_i = \ln g_i - \ln N_i - N_i/N_i + 1 = \alpha + \beta \varepsilon_i \qquad (13\text{-}35)$$

$$\ln(g_i/N_i) = \alpha + \beta \varepsilon_i \qquad (13\text{-}36)$$

and the probability, $\mathcal{P}_i$, is

$$\mathcal{P}_i = N_i/N = (g_i e^{-\alpha} e^{-\beta \varepsilon_i})/N \qquad (13\text{-}37)$$

Using $\Sigma_i \mathcal{P}_i = 1$, gives

$$e^{-\alpha} = N/(\Sigma_i g_i e^{-\beta \varepsilon_i}) \qquad (13\text{-}38)$$

Finally,

$$\mathcal{P}_i = N_i/N = g_i e^{-\beta \varepsilon_i}/\left(\Sigma_i g_i e^{-\beta \varepsilon_i}\right) \qquad (13\text{-}39)$$

It is curious that the probability of a state, $\mathcal{P}_i$, is the same for the Maxwell-Boltzmann as for the Corrected Maxwell-Boltzmann expression. This is also true for some other properties, such as the energy (as will be shown shortly), but not all properties. The entropies, for example, differ.

The average value of a given property, χ (including the average energy, ε), is for both types of statistics.

$$\langle \chi \rangle = \Sigma_i \chi_i \mathcal{P}_i = \Sigma_i \chi_i g_i e^{-\beta \varepsilon_i} / \Sigma_i g_i e^{-\beta \varepsilon_i} \qquad (13\text{-}40)$$

Also, the ratio of the population in state j to state i, is, regardless of statistics

$$N_j/N_i = (g_j/g_i)e^{-\beta(\varepsilon_1 - \varepsilon_i)} \qquad (13\text{-}41)$$

CHAPTER 14

THERMODYNAMIC CONNECTION

14.1 ENERGY, HEAT, AND WORK

The total energy for either localized and delocalized particles (solids, and gases) is, using *Eq. 13-32* or *Eq. 13-39*,

$$E = \Sigma_i N_i \varepsilon_i = N(\Sigma_i \varepsilon_i \, e^{-\beta \varepsilon_i} / \Sigma_i g_i \, e^{-\beta \varepsilon_i}) \qquad (14\text{-}1)$$

$$= N(\Sigma_i \varepsilon_i g_i e^{-\beta \varepsilon_i} / q) \qquad (14\text{-}2)$$

It follows immediately, that *Eq. 14-2* can be written

$$E = -N(\partial \ln q / \partial \beta)_V \qquad (14\text{-}3)$$

The subscript, V, is introduced because the differentiation of lnq is under conditions of constant ε_i. Constant volume (particle-in-a box!) ensures that the energy levels will remain constant.

Note: The quantity within parentheses in *Eqs. 14-2* and *14-3* represent also the average particle energy, and the equations may also be written as

$$E = N\langle \varepsilon \rangle \qquad (14\text{-}4)$$

Let us now consider heat and work. Let us change the system from a state whose energy is E to a neighboring state whose energy is E'. If E and E' differ infinitesimally, we may write for a closed system (N fixed)

$$dE = \Sigma_i \varepsilon_i \, dN_i + \Sigma_i N_i \, d\varepsilon_i \qquad (14\text{-}5)$$

Thus, there are two ways to change the energy: (1) by changing the energy levels and (2) by reshuffling the particles among the energy levels. Changing the energy levels requires changing the volume, and it makes sense to associate this process with *work*. The particle reshuffling term must then be associated with *heat*. In *short*, we define the elements of heat and of work as

$$dq = \Sigma_i \varepsilon_i \, dN_i \qquad (14\text{-}6)$$

$$dw = \Sigma_i N_i \, d\varepsilon_i \qquad (14\text{-}7)$$

14.2 ENTROPY

In our discussion of thermodynamics, we frequently made use of the notion that, if a system is isolated, its entropy is a maximum. An isolated system does not exchange energy or matter with the surroundings; therefore, if a system has constant energy, constant volume, and constant N, it is an isolated system. In statistical mechanics, we noticed that under such constraints the number of microstates tends to a maximum. This strongly suggests that there ought to be a connection between the entropy and the number of microstates, Ω or *thermodynamic probability*, as it is sometimes referred to. But there is a problem! Entropy is additive: the entropy of two systems 1 and 2 is $S = S_1 + S_2$, but the number of microstates of two combined systems is multiplicative, that is, $\Omega = \Omega_1 \times \Omega_2$. On the other hand, the log of $\Omega_1 \times \Omega_2$ is additive. This led Boltzmann to suggest the following (which we will take as a postulate):

- *Postulate III: the entropy of a system is $S = k \, ln \, \Omega$.*

Here, k represents the "Boltzmann constant" (i.e., $k = 1.38066 \times 10^{-23}$ J/K) and Ω refers to the number of microstates, consistent with the macroscopic constraints of constant E, N, and V.

Note: Strictly speaking, the above postulate should include all microstates, that is, $\Sigma_D \, \Omega_D$, but, as noted before, in the thermodynamic limit, only the most probable distribution will effectively count, and thus we will have the basic definition, $S = k \, ln \, \Omega_{D^*}$.

14.2.1 Entropy of Nonlocalized Systems (Gases)

Using *Eq. 13-34*, we obtain

$$S = k \ln \Omega_D^{CMB} = k \ln \Sigma_i N_i [\ln(g_i/N_i) + 1] \qquad (14\text{-}8)$$

Replacing g_i/N_i by $e^{\beta \varepsilon_i} q/N$ (which follows from *Eq. 13-39*, we get

$$S = k \Sigma_i N_i [\ln(q/N) + \beta \varepsilon_i + 1] \qquad (14\text{-}9)$$

$$= k[N \ln(q/N) + \beta \Sigma_i N_i \varepsilon_i + N] \qquad (14\text{-}10)$$

or

$$S = k(N \ln q + \beta E - N \ln N + N) \qquad (14\text{-}11)$$

14.2.2 Entropy of Localized Systems (Crystalline Solids)

Using *Eq. 13-19b* gives for localized systems

$$S = k \ln \Omega_D^{MB} = k \, N \ln N + k \Sigma_i N_i \ln(g_i/N_i) \qquad (14\text{-}12)$$

Using again *Eq. 13-39* or *Eq. 13-33* to replace g_i/N_i yields

$$S = k[N \ln N + \Sigma_i N_i (\ln(q/N) + \beta \varepsilon)] \qquad (14\text{-}13)$$

$$= k(N \ln N + N \ln q - N \ln N + \beta \Sigma_i N_i \varepsilon_i) \qquad (14\text{-}14)$$

$$= k(N \ln q + \beta E) \qquad (14\text{-}15)$$

14.3 IDENTIFICATION OF β WITH 1/KT

In thermodynamics, heat and entropy are connected by the relation, $dS = (1/T) \, dq_{rev}$. We have already identified the statistical-mechanical element of heat, namely, $dq = \Sigma_i \varepsilon_i \, dN_i$. Let us now seek to identify dS. Although the entropies for localized and delocalized systems differ, the difference is in N, which for a closed system is constant. Thus, we can treat both entropy forms simultaneously by defining

$$S = k(N \ln q + \beta E + \text{constant})$$

$$= k(N \ln \Sigma_i g_i e^{-\beta \varepsilon_i} + \beta E + \text{constant}) \qquad (14\text{-}16)$$

For fixed N, S is a function of β, V and thus $\varepsilon_1, \varepsilon_2, \ldots, \varepsilon_i, \ldots$. Let us differentiate S with respect to β and ε_i:

$$dS = (\partial S/\partial \beta)_{\varepsilon_i} \, d\beta + \Sigma_i (\partial S/\partial \varepsilon_i)_{\beta,\varepsilon,j\neq i} \, d\varepsilon_i$$
$$= k[(-N\Sigma_i\varepsilon_ig_ie^{-\beta\varepsilon_i}/\Sigma_i \, g_ie^{-\beta\varepsilon_i})d\beta - N\beta(\Sigma_ig_ie^{-\beta\varepsilon_i}/\Sigma_ig_ie^{-\beta\varepsilon_i})d\varepsilon_i$$
$$+ Ed\beta + \beta dE] \tag{14-17}$$

The first term within brackets of *Eq. 14-17* is $-N\langle\varepsilon\rangle d\beta = -E\,d\beta$ and cancels the third term. The second term of *Eq. 14-17* is (using Eq. 13-39) $-\beta\Sigma_iN_id\varepsilon_i = -\beta dw$. Therefore,

$$dS = k\beta(dE - dw) = k\beta dq_{rev} \tag{14-18}$$

Here dq refers to an element of heat and not to the partition function. The differential dS is an exact differential, since it was obtained by differentiating $S(\beta, \varepsilon_i)$ with respect β and ε_i, and so dq must be reversible, as indicated. Obviously, $k\beta$ must be the inverse temperature, i.e., $k\beta = 1/T$ or

$$\beta = 1/kT \tag{14-19}$$

14.4 PRESSURE

From $dw = \Sigma_i \, N_i \, d\varepsilon_i$, we obtain on replacing N_i (Eq. 13-39)

$$P = -\partial w/\partial V = -\Sigma_iN_i\partial\varepsilon_i/\partial V \tag{14-20}$$
$$= -N\Sigma_i(\partial\varepsilon_i/\partial V) \, g_i \, e^{-\beta\varepsilon_i}/\Sigma_ig_ie^{-\beta\varepsilon_i} \tag{14-21}$$

Note that the derivative of the logarithm of the partition function, q, is

$$\partial \ln q/\partial V = \Sigma_i[-\beta(\partial\varepsilon_i/\partial V)g_i(e^{-\beta\varepsilon_i}/\Sigma_ig_ie^{-\beta\varepsilon_i})] \tag{14-22}$$

Consequently,

$$P = (N/\beta)(\partial \ln q/\partial V) = NkT(\partial \ln q/\partial V)_T \tag{14-23}$$

APPLICATION

It will be shown later that the translational partition function of system of independent particles (ideal gases), is

$$q_{tr} = (2\pi mkT/h^2)^{3/2}V \qquad (14\text{-}24)$$

Applying *Eq. 14-23* shows that

$$P = NkT \, \partial/\partial V \left[\ln(2\pi mkT/h^2)^{3/2} + \ln V\right]$$
$$= NkT/V \qquad (14\text{-}25)$$

14.5 THE FUNCTIONS E, H, S, A, G, AND μ

From the expressions of E and S in terms of the partition functions and the standard thermodynamic relations, we can construct all thermodynamic potentials.

1. Energy

$$E = kNT^2(\partial \ln q/\partial T)_V \qquad (14\text{-}26)$$

This expression is valid for both the localized and delocalized systems.
2. Enthalpy

$$H = E + PV$$
$$= kNT^2(\partial \ln q/\partial T)_V + kNT(\partial \ln q/\partial V)_T V \qquad (14\text{-}27)$$

For an ideal gas, the second term is kNT. For an ideal solid (a solid composed of localized but non-interacting particles), the partition function is independent of volume, and the second term is zero.
3. Entropy
   — *for nonlocalized systems*

$$S = kN[\ln(q/N) + 1] + kNT(\partial \ln q/\partial T)_V \qquad (14\text{-}28)$$

   — *for localized systems*

$$S = kN \ln q + kNT(\partial q/\partial T)_V \qquad (14\text{-}29)$$

4. Helmholtz Free Energy, $A = E - TS$
   — *for nonlocalized systems*

$$A = kNT^2(\partial \ln q/\partial T)_V - kNT^2(\partial \ln q/\partial T)_V$$

$$- kNT[\ln(q/N) + 1] \tag{14-30}$$

$$= -kNT \ln(q/N) - kNT \text{ (for ideal gas)} \tag{14-31}$$

   — *for localized sytems*

$$A = kNT^2(\partial \ln q/\partial T)_V - kNT \ln q - kNT^2(\partial \ln q/\partial T)_V \tag{14-32}$$

$$= -kNT \ln q \text{(for ideal solid)} \tag{14-33}$$

5. Gibbs Free Energy, $G = A + PV$
   — *for nonlocalized systems*

$$G = -kNT \ln(q/N) - kNT + kNT(\partial \ln q/\partial V)_T V \tag{14-34}$$

$$= -kNT \ln(q/N) \text{ (for an ideal gas)} \tag{14-35}$$

   — *for localized systems*

$$G = -kTN \ln q + kNT(\partial \ln q/\partial V)_T V \tag{14-36}$$

$$= -kTN \ln q \text{ (for ideal solid)} \tag{14-37}$$

6. Chemical Potential, $\mu = G/N$

In statistical mechanics, unlike thermodynamics, it is customary to define the chemical potential as the free energy per molecule, not per mole. Thus, the symbol μ, used in this part of the course outlined in this book, represent the free energy per molecule.
   — *for nonlocalized systems,*

$$\mu = -kT \ln(q/N) - kT + (kT(\partial \ln q/\partial V)_T)V \tag{14-38}$$

$$= -kT \ln(q/N) \text{ (for ideal gas)} \tag{14-39}$$

   — *for localized systems*

$$\mu = -kT \ln q + [kT(\partial \ln q/\partial V)_T]V \tag{14-40}$$

$$= -kT \ln q \text{ (for an ideal solid)} \tag{14-41}$$

Note: Solids, and not only ideal solids, are by and large incompressible. The variation of ln q with V can be expected to be very small (i.e., PV is very small), and no significant errors are made when terms in $(\partial \ln q/\partial V)_T$ are ignored. Accordingly, there is then no essential difference between E and H and between A and G in solids.

We now have formal expressions for determining all the thermodynamic functions of gases and solids. What needs to be done next is to derive expressions for the various kinds of partition functions that are likely to be needed.