2.4 The Role of Distinguishability

The analysis in the previous section is based on the premise that the particles are distinguishable. This is appropriate for solid crystals where each atom is localized near a specific point in the crystal lattice. Unfortunately, it is not appropriate for fluids in which the particles (atoms, molecules, or fundamental particles) are free to move about within the system volume. In systems with freely moving particles, the particles of a given species are *indistinguishable*. Our task in this section is to examine how our analysis from the previous section must be changed to account for the indistiguishability of the particles in fluid systems.

In considering modifications to the analysis to account for indistinguishability, we will also account for restrictions on microstate occupancy. As discussed in Section 1.8, virtually all particles fall into two categories: bosons and fermions. There are no restrictions on the number of bosons that may occupy any given microstate. Most atoms and molecules behave as bosons. One exception is ^3He, which is a fermion. For a system of fermions, no more than one fermion may occupy a given microstate. Electrons and protons are perhaps the most important examples of particles that behave as fermions. The restriction on the occupancy of microstates for electrons is a consequence of the Pauli exclusion principle.

We first consider systems of bosons. As in the last section we are considering member systems in a microcanonical ensemble having specified N_a, N_b, V, and U. If we consider one energy level occupied by $N_{a,i}$ particles of species a, the number of ways of selecting the

$N_{a,i}$ particles from the total of N_a particles in the system is just 1, because the particles are indistinguishable. No matter which $N_{a,i}$ we choose, the particles occupying the energy level would "look" the same. However, we can permute the particles among the g_i microstates for the energy level in a number of ways. Because the particles are bosons, there are no restrictions on the way that the particles may occupy the microstates. From basic combinatorial analysis (see Appendix I) we can determine the number of these permutations as

$$\left\{\begin{array}{l}\textit{number of ways of arranging } N_{a,i} \\ \textit{indistinguishable particles among } g_i \textit{ microstates}\end{array}\right\} = \frac{(g_i + N_{a,i} - 1)!}{(g_i - 1)!N_{a,i}!}. \tag{2.53}$$

Because the arrangements within energy levels are independent of one another, the total number of ways of arranging the a species particles among the microstates is the product of such terms for all energy levels:

$$\left\{\begin{array}{l}\textit{number of ways of arranging} \\ \textit{species a particles among} \\ \textit{microstates dictated by } g_i \textit{ and } \{N_{a,i}\}\end{array}\right\} = \prod_{i=0}^{\infty} \frac{(g_i + N_{a,i} - 1)!}{(g_i - 1)!N_{a,i}!}. \tag{2.54}$$

A similar relation must apply for species b:

$$\left\{\begin{array}{l}\textit{number of ways of arranging} \\ \textit{species b particles among} \\ \textit{microstates dictated by } g_j \textit{ and } \{N_{b,j}\}\end{array}\right\} = \prod_{j=0}^{\infty} \frac{(g_j + N_{b,j} - 1)!}{(g_j - 1)!N_{b,j}!}. \tag{2.55}$$

For each arrangement of the a particles, the number of possible arrangements of b particles is given by Eq. (2.55). The total number of ways of combining the arrangements of the two species is therefore equal to the product of the right sides of Eqs. (2.54) and (2.55). We designate this total number of microstates for the specified pair of distributions $\{N_{a,i}\}$ and $\{N_{b,j}\}$, as

$$W_{\text{bos}} = \prod_{i=0}^{\infty} \frac{(g_i + N_{a,i} - 1)!}{(g_i - 1)!N_{a,i}!} \prod_{j=0}^{\infty} \frac{(g_j + N_{b,j} - 1)!}{(g_j - 1)!N_{b,j}!}. \tag{2.56}$$

Alternatively, the particles may be indistinguishable fermions. Again, because the particles are indistinguishable, selection of any $N_{a,i}$ particles of species a for energy level i amounts to the same occupancy. The fermions may be permuted among the g_i microstates, but no more than one may occupy a given microstate. Thus a microstate is either occupied by one particle or unoccupied. Combinatorial analysis again provides the means to calculate the number of such arrangements (see Appendix I):

$$\left\{\begin{array}{l}\textit{number of ways of selecting } N_{a,i} \textit{ microstates} \\ \textit{to be occupied from } g_i \textit{ total microstates}\end{array}\right\} = \frac{g_i!}{N_{a,i}!(g_i - N_{a,i})!}. \tag{2.57}$$

Because the arrangements within the energy levels are independent, the total number of system microstates is the product of terms like the right side of Eq. (2.57) for all energy levels:

$$\left\{\begin{array}{l}\textit{number of ways of arranging} \\ \textit{species a particles among} \\ \textit{microstates dictated by } g_i \textit{ and } \{N_{a,i}\}\end{array}\right\} = \prod_{i=0}^{\infty} \frac{g_i!}{N_{a,i}!(g_i - N_{a,i})!}. \tag{2.58}$$

The corresponding equation for species b is

$$\left\{\begin{array}{l}\textit{number of ways of arranging} \\ \textit{species b particles among} \\ \textit{microstates dictated by } g_j \textit{ and } \{N_{b,j}\}\end{array}\right\} = \prod_{j=0}^{\infty} \frac{g_j!}{N_{b,j}!(g_j - N_{b,j})!}. \tag{2.59}$$

As in the case for bosons, the total number of microstates for the two-species system is the product of the terms on the right sides of Eqs. (2.58) and (2.59). To indicate that this result is for fermions, we denote the total number of microstates as

$$W_{\text{fer}} = \prod_{i=0}^{\infty} \frac{g_i!}{N_{a,i}!(g_i - N_{a,i})!} \prod_{j=0}^{\infty} \frac{g_j!}{N_{b,j}!(g_j - N_{b,j})!}. \tag{2.60}$$

The total number of microstates for either bosons or fermions can be represented by the relation

$$W_{\text{b/f}}(\{N_{a,i}\}, \{N_{b,j}\}) = \prod_{i=0}^{\infty} \frac{[g_i + \eta(N_{a,i} - 1)]!}{(g_i - \eta - \xi N_{a,i})!N_{a,i}!} \prod_{j=0}^{\infty} \frac{[g_j + \eta(N_{b,j} - 1)]!}{(g_j - \eta - \xi N_{b,j})!N_{b,j}!}, \tag{2.61}$$

where W for indistinguishable bosons corresponds to

$$\eta = 1, \quad \xi = 0 \quad \text{(indistinguishable bosons)}, \tag{2.62}$$

and for indistinguishable fermions we set

$$\eta = 0, \quad \xi = 1 \quad \text{(indistinguishable fermions)}. \tag{2.63}$$

For systems containing indistinguishable bosons or indistinguishable fermions, we again seek to find the occupation number sets $\{N_{a,i}\}, \{N_{b,j}\}$ that maximize $\ln W$ subject to the constraints (2.1)–(2.3). As before, we interpret the pair of occupation number sets that maximizes $\ln W$ as being the equilibrium distribution for the system. Taking the natural log of both sides of Eq. (2.61) and rearranging yields

$$\begin{aligned} \ln W_{\text{b/f}} = {} & \sum_{i=0}^{\infty} \ln\{[g_i + \eta(N_{a,i} - 1)]!\} - \sum_{i=0}^{\infty} \ln\{[g_i - \eta - \xi N_{a,i}]!\} \\ & - \sum_{i=0}^{\infty} \ln\{N_{a,i}!\} + \sum_{j=0}^{\infty} \ln\{[g_j + \eta(N_{b,j} - 1)]!\} \\ & - \sum_{j=0}^{\infty} \ln\{[g_j - \eta - \xi N_{b,j}]!\} - \sum_{j=0}^{\infty} \ln\{N_{b,j}!\}. \end{aligned} \tag{2.64}$$

Since all the factorials on the right side of Eq. (2.64) are expected to be large, we apply Stirling's approximation to each:

$$\begin{aligned}
\ln W_{b/f} = {} & \sum_{i=0}^{\infty}[[g_i+\eta(N_{a,i}-1)]\ln\{g_i+\eta(N_{a,i}-1)\}-[g_i+\eta(N_{a,i}-1)]] \\
& -\sum_{i=0}^{\infty}[[g_i-\eta-\xi N_{a,i}]\ln\{g_i-\eta-\xi N_{a,i}\}-[g_i-\eta-\xi N_{a,i}]] \\
& -\sum_{i=0}^{\infty}[N_{a,i}\ln N_{a,i}-N_{a,i}]+\sum_{j=0}^{\infty}[[g_j+\eta(N_{b,j}-1)] \\
& \times \ln\{g_j+\eta(N_{b,j}-1)\}-[g_j+\eta(N_{b,j}-1)]]-\sum_{j=0}^{\infty}[[g_j-\eta-\xi N_{b,j}] \\
& \times \ln\{g_j-\eta-\xi N_{b,j}\}-[g_j-\eta-\xi N_{b,j}]]-\sum_{j=0}^{\infty}[N_{b,j}\ln N_{b,j}-N_{b,j}].
\end{aligned} \tag{2.65}$$

Using the constraint relations (2.1) and (2.2), the above relation simplifies to

$$\begin{aligned}
\ln W_{b/f} = {} & \sum_{i=0}^{\infty}[[g_i+\eta(N_{a,i}-1)]\ln\{g_i+\eta(N_{a,i}-1)\}-[g_i-\eta-\xi N_{a,i}] \\
& \times \ln\{g_i-\eta-\xi N_{a,i}\}-N_{a,i}\ln N_{a,i}+(1-\eta-\xi)N_{a,i}] \\
& +\sum_{j=0}^{\infty}[[g_j+\eta(N_{b,j}-1)]\ln\{g_j+\eta(N_{b,j}-1)\}-[g_j-\eta-\xi N_{b,j}] \\
& \times \ln\{g_j-\eta-\xi N_{b,j}\}-N_{b,j}\ln N_{b,j}+(1-\eta-\xi)N_{b,j}]].
\end{aligned} \tag{2.66}$$

Differentiating, we obtain

$$\begin{aligned}
d(\ln W_{b/f}) = {} & \sum_{i=0}^{\infty}[\eta dN_{a,i}\ln\{g_i+\eta(N_{a,i}-1)\}+\eta dN_{a,i} \\
& +\xi dN_{a,i}\ln\{g_i-\eta-\xi N_{a,i}\}+\xi dN_{a,i}-dN_{a,i}\ln N_{a,i}-dN_{a,i} \\
& +(1-\eta-\xi)\,dN_{a,i}]+\sum_{j=0}^{\infty}[\eta dN_{b,j}\ln\{g_j+\eta(N_{b,j}-1)\} \\
& +\eta dN_{b,j}+\xi dN_{b,j}\ln\{g_j-\eta-\xi N_{b,j}\}+\xi dN_{b,j} \\
& -dN_{b,j}\ln N_{b,j}-dN_{b,j}+(1-\eta-\xi)\,dN_{b,j}].
\end{aligned} \tag{2.67}$$

Setting $d(\ln W_{b/f})=0$ and simplifying yields

$$\begin{aligned}
& \sum_{i=0}^{\infty}[\eta\ln\{g_i+\eta(N_{a,i}-1)\}+\xi\ln\{g_i-\eta-\xi N_{a,i}\}-\ln N_{a,i}]\,dN_{a,i} \\
& \quad +\sum_{j=0}^{\infty}[\eta\ln\{g_j+\eta(N_{b,j}-1)\}+\xi\ln\{g_j-\eta-\xi N_{b,j}\}-\ln N_{b,j}]\,dN_{b,j}=0.
\end{aligned} \tag{2.68}$$

Using the method of Lagrange multipliers, we multiply the differential constraint relations (2.16a), (2.16b), and (2.16c) by λ_1, λ_2, and λ_3, respectively, add the resulting equations, and subtract Eq. (2.68). The final result is

$$\begin{aligned}
& \sum_{i=0}^{\infty}[\lambda_1 dN_{a,i}+\lambda_3\varepsilon_i dN_{a,i}-[\eta\ln\{g_i+\eta(N_{a,i}-1)\} \\
& \quad +\xi\ln\{g_i-\eta-\xi N_{a,i}\}-\ln N_{a,i}]\,dN_{a,i}]+\sum_{j=0}^{\infty}[\lambda_2 dN_{b,j}+\lambda_3\varepsilon_j dN_{b,j} \\
& \quad -[\eta\ln\{g_j+\eta(N_{b,j}-1)\}+\xi\ln\{g_j-\eta-\xi N_{b,j}\}-\ln N_{b,j}]\,dN_{b,j}]=0,
\end{aligned} \tag{2.69}$$

which simplifies to

$$\begin{aligned}
& \sum_{i=0}^{\infty}[\lambda_1+\lambda_3\varepsilon_i-\eta\ln\{g_i+\eta(N_{a,i}-1)\}-\xi\ln\{g_i-\eta-\xi N_{a,i}\}+\ln N_{a,i}]\,dN_{a,i} \\
& \quad +\sum_{j=0}^{\infty}[\lambda_2+\lambda_3\varepsilon_j-\eta\ln\{g_j+\eta(N_{b,j}-1)\}-\xi\ln\{g_j-\eta-\xi N_{b,j}\} \\
& \quad +\ln N_{b,j}]\,dN_{b,j}=0.
\end{aligned} \tag{2.70}$$

At the maximum, the coefficients of the $dN_{a,i}$ and $dN_{b,j}$ terms must all be zero, which implies that

$$\lambda_1+\lambda_3\varepsilon_i-\eta\ln\{g_i+\eta(N_{a,i}-1)\}-\xi\ln\{g_i-\eta-\xi N_{a,i}\}+\ln N_{a,i}=0, \tag{2.71a}$$

$$\lambda_2+\lambda_3\varepsilon_j-\eta\ln\{g_j+\eta(N_{b,j}-1)\}-\xi\ln\{g_j-\eta-\xi N_{b,j}\}+\ln N_{b,j}=0. \tag{2.71b}$$

For bosons, we set $\eta=1$ and $\xi=0$ in Eqs. (2.71a,b) and rearrange to obtain

$$N_{a,i}=g_i e^{-\lambda_1}e^{-\lambda_3\varepsilon_i}\left(1+\frac{N_{a,i}}{g_i}-\frac{1}{g_i}\right), \tag{2.72a}$$

$$N_{b,j}=g_j e^{-\lambda_2}e^{-\lambda_3\varepsilon_j}\left(1+\frac{N_{b,j}}{g_j}-\frac{1}{g_j}\right)\quad \text{(for bosons)}. \tag{2.72b}$$

For fermions, we set $\eta = 0$ and $\xi = 1$ in Eqs. (2.71a,b) and obtain

$$N_{a,i} = g_i e^{-\lambda_1} e^{-\lambda_3 \varepsilon_i} \left(1 - \frac{N_{a,i}}{g_i}\right), \tag{2.73a}$$

$$N_{b,j} = g_j e^{-\lambda_2} e^{-\lambda_3 \varepsilon_j} \left(1 - \frac{N_{b,j}}{g_j}\right) \quad \text{(for fermions).} \tag{2.73b}$$

Equations (2.72a,b) and (2.73a,b) can be solved explicitly for $N_{a,i}$ and $N_{b,j}$, but the resulting relations are complicated and it is difficult to carry the analysis further. Instead, we note that for systems of particles with moderate to high energies, the degeneracy of the most populated energy levels is enormous (see Example 1.4). For such circumstances, the number of microstates for each energy level is much larger than the number of particles in the system occupying that level and very few of the available microstates are occupied. Systems in which this is true are said to exhibit *dilute occupancy*. For conditions that result in dilute occupancy, $N_{a,i}/g_i$, $N_{b,j}/g_j$, $1/g_i$, and $1/g_j$ are negligible compared to one. If we neglect these ratios compared to one in Eqs. (2.72a,b) and (2.73a,b), we find that both sets of equations reduce to

$$N_{a,i} = g_i e^{-\lambda_1} e^{-\lambda_3 \varepsilon_i}, \tag{2.74a}$$

$$N_{b,j} = g_j e^{-\lambda_2} e^{-\lambda_3 \varepsilon_j}. \tag{2.74b}$$

Using the constraints (2.1) and (2.2) on $N_{a,i}$ and $N_{b,j}$, we can eliminate the multipliers λ_1 and λ_2 and obtain

$$\frac{N_{a,i}}{N_a} = \frac{g_i e^{-\lambda_3 \varepsilon_i}}{\sum_{i=0}^{\infty} g_i e^{-\lambda_3 \varepsilon_i}}, \tag{2.75a}$$

$$\left(\textit{for indistinguishable bosons or fermions in the limit of dilute occupancy}\right)$$

$$\frac{N_{b,j}}{N_b} = \frac{g_j e^{-\lambda_3 \varepsilon_j}}{\sum_{j=0}^{\infty} g_j e^{-\lambda_3 \varepsilon_j}}, \tag{2.75b}$$

which is identical to the Boltzmann statistics result obtained for distinguishable particles with no restrictions on microstate occupancy.

Although the form of the distributions (2.75a,b) is the same as Boltzmann statistics for distinguishable particles, the relations for W for indistinguishable bosons and fermions are different from the relation for W that applied to distinguishable bosons. We must therefore reexamine how the change in the relation for W affects the thermodynamic properties for the system. Since by definition $S = k_B \ln W$, we set S/k_B equal to the right side of Eq. (2.66), and use the distributions (2.75a,b) to evaluate $N_{a,i}$ and $N_{b,j}$. In addition, because we have dilute occupancy, we neglect $N_{a,i}/g_i$, $N_{b,j}/g_j$, $1/g_i$, and $1/g_j$ compared to one, where appropriate. For both the boson and fermion particle types, the resulting equation for S/k_B reduces to

$$\frac{S}{k_B} = \lambda_3 U + N_a \ln Z_a - N_a \ln N_a + N_b \ln Z_b - N_b \ln N_b + N_a + N_b. \tag{2.76}$$

To evaluate λ_3 we use the same approach as was used in Section 2.3 for distinguishable particles. We differentiate with respect to λ_3, evaluate the derivatives and solve for λ_3. The result of this manipulation is

$$\lambda_3 = \frac{1}{k_B (\partial U/\partial S)_{N_a, N_b, V}} = \frac{1}{k_B T}. \tag{2.77}$$

It follows directly that for a system that exhibits dilute occupancy, the distributions and the partition function definitions for indistinguishable bosons or fermions are identical to the Boltzmann statistics case:

$$\frac{N_{a,i}}{N_a} = \frac{g_i e^{-\varepsilon_i/k_B T}}{Z_a}, \tag{2.49a}$$

$$\frac{N_{b,j}}{N_b} = \frac{g_j e^{-\varepsilon_j/k_B T}}{Z_b}, \tag{2.49b}$$

where

$$Z_a = \sum_{i=0}^{\infty} g_i e^{-\varepsilon_i/k_B T}, \tag{2.50a}$$

$$Z_b = \sum_{j=0}^{\infty} g_j e^{-\varepsilon_j/k_B T}. \tag{2.50b}$$

It follows from these relations and the energy constraint (2.3) that the relation for U is identical to that for Boltzmann statistics of distinguishable particles:

$$U = \frac{N_a k_B T^2}{Z_a}\left(\frac{\partial Z_a}{\partial T}\right)_{N_a, N_b, V} + \frac{N_b k_B T^2}{Z_b}\left(\frac{\partial Z_b}{\partial T}\right)_{N_a, N_b, V}. \tag{2.52}$$

Substituting $\lambda_3 = 1/k_B T$ into Eq. (2.76) yields the following relation for the entropy:

$$\frac{S}{k_B} = \frac{U}{k_B T} + N_a \ln\left\{\frac{Z_a}{N_a}\right\} + N_b \ln\left\{\frac{Z_b}{N_b}\right\} + N_a + N_b. \tag{2.78}$$

Note that this relation differs from the entropy relation obtained for distinguishable bosons. The net effect of particle indistinguishability is to reduce the entropy of the system. Equations (2.49), (2.50), (2.52), and (2.78) thus provide the linkage between microscale energy storage and the macroscopic thermodynamic properties for a system of indistinguishable bosons or fermions in the moderate to high energy limit where dilute occupancy occurs.

What about low-energy systems? It turns out that in very cold systems we cannot invoke the dilute occupancy approximation and we must allow for low degeneracy and quantum effects in the analysis of the statistical behavior of such systems. We will return to examine such systems in more detail in Section 6.4. Fortunately, in engineering applications the overwhelming majority of system types and particle energy levels encountered do lie in ranges where dilute occupancy occurs. The results summarized above therefore provide a useful foundation for thermodynamic analysis of this broad range of system types.