Statistical Mechanics

Statistical mechanics provides the theoretical link between the microscopic laws of physics and the macroscopic laws of thermodynamics. Rather than attempt to solve the microscopic laws in their entirety (which is presumably very difficult), one abstracts some key concepts, such as conservation laws, and augments them with certain statistical assumptions about the behavior of systems with large numbers of particles in order to make the problem tractable.

The first goal will be to make contact with the first law of thermodynamics, $T\,dS = dU + P\,dV$, as given in Eq. (WA.1) (for constant N). Consider a system of N particles whose possible energy is E_i. One way to obtain statistical information is to create an ensemble (i.e., one replicates this system a large number of times, M, and imagines that the various systems can exchange energy with each other). Let M_i denote the number of systems with energy E_i. The total number of systems must be M, so

$$\sum_i M_i = M. \tag{WB.1}$$

Conservation of energy requires that

$$\sum_i M_i E_i = E, \tag{WB.2}$$

where E is the total energy of the ensemble.

The total number of ways in which M systems can be distributed into groups with $(M_1, M_2, \ldots)$ members in each group, respectively, is

$$W = \frac{M!}{M_1!\,M_2!\ldots}. \tag{WB.3}$$

One wishes to find the most-probable set of values for the M_i. Therefore, one looks for the set that maximizes W [or equivalently $\ln(W)$] subject to the constraints imposed by Eqs. (WB.1) and (WB.2). Thus, introducing Lagrange multipliers α and β to enforce the constraints, one has

$$\delta\left[\ln W - \alpha\left(\sum_i M_i - N\right) - \beta\left(\sum_i M_i E_i - E\right)\right] = 0. \tag{WB.4}$$

Use is made of Stirling's approximation, $\ln M! \approx M \ln M - M$ for $M \gg 1$, to write this as

$$\delta \left[M \ln M - M - \sum_i (M_i \ln M_i - M_i) - \alpha \left(\sum_i M_i - M \right) - \beta \left(\sum_i M_i E_i - E \right) \right] = 0.$$
(WB.5)

One may now differentiate with respect to the individual M_i and set the derivatives equal to zero. This leads to

$$M_i = e^{-\alpha - \beta E_i}.$$
(WB.6)

The probability of finding a particular state i in the most-likely probability distribution is given by the formula

$$p_i = \frac{M_i}{M} = \frac{e^{-\beta E_i}}{\sum_i e^{-\beta E_i}},$$
(WB.7)

where, clearly, $\sum p_i = 1$. Equation (WB.7) indicates that it less probable to find high-energy states than low-energy states.

Introduce the canonical partition function for the N-particle system

$$Z_N = \sum_i e^{-\beta E_i}.$$
(WB.8)

The function Z_N is given by a sum of terms, each term representing the relative probability for finding the system in the state i with energy E_i. The mean entropy of a system is defined as

$$S = \frac{k_B}{M} \ln W = -k_B \sum_i p_i \ln p_i,$$
(WB.9)

where use has been made of Eq. (WB.7). The mean energy of the system, interpreted as the internal energy, U, is given by

$$U = \sum_i p_i E_i.$$
(WB.10)

Note that if a small change were made in the $\{p_i\}$, the corresponding changes in the entropy and internal energy would give rise to

$$\delta \left(U - \frac{S}{k_B \beta} \right) = \left(\sum_i E_i \delta p_i + \frac{1}{\beta} \sum_i \ln p_i \delta p_i + \frac{1}{\beta} \sum_i \delta p_i \right)$$
(WB.11)

since $\sum_i \delta p_i = 0$. This is consistent with the first law of thermodynamics $dU - T\, dS = -P\, dV$, when T and V (and N) are held constant. Thus one may interpret the parameter $\beta = 1/k_B T$ as being proportional to the inverse absolute temperature. The Helmholtz free energy is $F = U - TS$ and, from Eqs. (WB.7), (WB.8), and (WB.9), is simply related to the partition function

$$Z_N = e^{-\beta F}.$$
(WB.12)

Now consider an N-particle system of noninteracting identical particles. The individual energies for a given particle will be denoted by ϵ_i. A state of the system is defined by specifying the number of particles in each state (i.e., by a set of integers $\{n_i\}$). Thus

$$N = \sum_i n_i, \tag{WB.13}$$

$$E(n_1, n_2, \ldots) = \sum_i n_i \epsilon_i. \tag{WB.14}$$

From Eq. (WA.1) recall that the first law of thermodynamics for a system with a variable number of particles may be written as $T\,dS = dU - \mu\,dN + P\,dV$, where μ is the chemical potential. The analysis proceeds much as before, with the exception that one now will be measuring the energies of the particles relative to the chemical potential. The average number of particles in a given state is given by

$$\langle n_j \rangle = \frac{\sum_{n_1} \sum_{n_2} \cdots n_j e^{-\beta \Sigma_i (\epsilon_i - \mu) n_i}}{\sum_{n_1} \sum_{n_2} \cdots e^{-\beta \Sigma_i (\epsilon_i - \mu) n_i}} = \frac{\sum_{n_j} n_j e^{-\beta(\epsilon_j - \mu) n_j}}{\sum_{n_j} e^{-\beta(\epsilon_j - \mu) n_j}}. \tag{WB.15}$$

For particles with spin $\frac{1}{2}$, $\frac{3}{2}$, ... obeying Fermi–Dirac statistics, such as electrons (spin $\frac{1}{2}$), the only possible values for n_j are 0 or 1. This leads to the mean number of particles in a given state:

$$f(\epsilon_j, T) = \langle n_j \rangle = \frac{1}{e^{\beta(\epsilon_j - \mu)} + 1}. \tag{WB.16}$$

This is known as the *Fermi–Dirac distribution function*. For particles with spin 0, 1, 2,... obeying Bose–Einstein statistics, such as photons or phonons, any nonnegative integer is acceptable for n_j. Performing the sums in Eq. (WB.15) leads to the *Bose–Einstein distribution function*:

$$\langle n_j \rangle = \frac{1}{e^{\beta(\epsilon_j - \mu)} - 1}. \tag{WB.17}$$

In the high-temperature limit, Eqs. (WB.16) and (WB.17) both reduce to the Maxwell–Boltzmann distribution when $\epsilon_j - \mu \gg k_B T$:

$$\langle n_j \rangle \longrightarrow e^{-\beta(\epsilon_j - \mu)}. \tag{WB.18}$$