

Chapter 6

The Ensembles

In this chapter we discuss the three ensembles of statistical mechanics, the microcanonical ensemble, the canonical ensemble and the grand canonical ensemble. Here canonical means simply standard or acceptable and the canonical ensemble therefore holds the central place in statistical mechanics. Logically the canonical ensemble should be introduced first. The microcanonical and grand canonical ensembles then follow as a special case (all systems having identical energies) and an extension (to systems having variable number of particles) of the canonical ensemble, respectively. However to keep step with Chapter 2 and to emphasize the physics, we introduce the microcanonical ensemble first and the grand canonical ensemble last. An ensemble here means an assembly of systems.

In section 2.4 we described the thermodynamics of an isolated system in which U , V and the number of particles N had to be constant. The appropriate thermodynamic function to describe the isolated system was the entropy, $S = S(U, V, N)$. Since the independent variables of S are constant for an isolated system, S itself must take a single, constant value at equilibrium and is therefore an appropriate function to use. In section 2.5 we reviewed the thermodynamics of a system in contact with a heat bath in which energy could be exchanged between the heat bath and the system. In this case T , V and N of the system were constant and the appropriate thermodynamic function to describe the system was the Helmholtz free energy $F = F(T, V, N)$. Since at equilibrium the T , V , N are constant, F takes a single, non-fluctuating value at equilibrium. Finally, in section 2.6 we reviewed the thermodynamics of a system in contact with a heat and particle bath. In this case heat and particles can be exchanged between the system and the bath (its surroundings) at constant T and constant chemical potential μ . In this case the appropriate thermodynamic function is the thermodynamic potential, $\Omega = \Omega(T, V, \mu)$ which takes a single, minimum value at equilibrium.

In this chapter we will see that:

- (1) The Microcanonical ensemble describes an isolated system.
- (2) The Canonical ensemble describes a system in contact with a heat bath.

(3) The Grand Canonical ensemble describes a system in contact with a heat and particle bath.

Thus the appropriate ensemble to use depends upon the physical circumstances. Also, when there is particle exchange between the system and its surroundings but the fluctuations from some average value \bar{N} are vanishingly small, then there is little difference between the constant N and variable N cases. In this case the canonical ensemble and grand canonical ensembles would give the same result. Noticing this it is sometimes convenient, for calculation purposes, to use the grand canonical ensemble when N is constant and later impose the restriction that fluctuations from \bar{N} are insignificant. The appropriate ensemble to use is therefore also a question of convenience.

Finally, we have already introduced the canonical ensemble in detail in Chapter 5 in describing Gibbs' statistical mechanics. Gibbs' interpretation is the canonical ensemble method of statistical mechanics. Also, we introduced the grand canonical ensemble in sections 5.3 and 5.4 to calculate the partition function for the perfect quantum gases. We did that because it was easier to evaluate the grand canonical partition function in which N could vary than to calculate the canonical partition function for fixed N . Thus we have really already seen most of the physics and mathematics of the ensembles. The purpose of this chapter is to collect the results in a coherent form and to emphasize the formal connection between the ensembles themselves and between the ensembles and thermodynamics.

6.1 The Microcanonical Ensemble

A system (a solid, liquid or a gas) which is completely isolated from its surroundings has constant energy U and a constant number of particles N . We will suppose it is also contained at constant volume V . If the system has a number of different types of particles (a number of components), the number of each component, N_1, N_2, \dots is also constant. A micro-canonical ensemble is an assembly of mental copies of this isolated system. Since the energy of each copy is the same, $E = U$, the need to consider an ensemble is really superfluous. One system will do. The microcanonical ensemble is depicted in Fig. 2.1 as a single system.

Since all the copies have the same energy, U , the probability of observing the system with energy E_S is

$$P_S = \text{constant} \times \delta(E_S - U). \quad (6.1)$$

If the quantum energy state U of the system is degenerate with degeneracy W , then there are W states having energy U or equivalently W ways of forming the observed system. Using the equal a priori probability hypothesis and

$$\sum_{S=1}^W P_S = 1, \quad (6.2)$$

we must have

$$P_S = \frac{1}{W} . \quad (6.3)$$

This statistical probability and thermodynamics are related through the famous Boltzmann relation,

$$S = k \log W \quad (6.4)$$

This could be introduced as a hypothesis but it follows from the relation between S and P_S developed in the next section for the central canonical ensemble. This is eq. (6.11),

$$\begin{aligned} S &= -k \sum_S P_S \log P_S \\ &= -k W \left(\frac{1}{W} \log \frac{1}{W} \right) \\ &= k \log W (U, V, N) \end{aligned}$$

Thus, as expected, the appropriate thermodynamic function is $S(U, V, N)$ which is a maximum at equilibrium for an isolated system. This also demonstrates that Boltzmann's relation (eq. 6.4) applies to an isolated system.

An important example of an isolated system that we have already considered was the perfect classical gas of Chapter 3. There we considered a gas at constant energy and sought the distribution of the individual particles over the single particle energy or velocity states (the Maxwell-Boltzmann distribution). We then evaluated the thermodynamic properties of the gas itself and obtained the Boltzmann relation (eq. 6.4) with

$$W = \frac{N!}{n_1! n_2! n_3! \dots}$$

Here n_i is the number of particles in the single particle energy state ϵ_i . The equilibrium or most probable state of the gas was that for which W was a maximum. Thus the whole gas can be regarded as an example of a microcanonical ensemble although in Chapter 3 we were more interested in the statistics of the individual particles.

Since isolated systems are difficult to realize in practice, the microcanonical ensemble is not often used.

6.2 The Canonical Ensemble

We consider now a system (a solid, liquid or a gas) in contact with a heat bath at constant temperature. A canonical ensemble is an assembly of mental copies of this system. Since energy can be transferred between the system and the heat bath, the energy of the systems in the assembly differ. To represent the possible energy states of the system adequately in the ensemble, we must

have enough copies that each state is represented at least once in the ensemble. All copies have the same temperature T , the temperature of the heat bath.

We could imagine constructing the canonical ensemble from the single system in the microcanonical ensemble of Fig. 2.1 in the following way. We divide the isolated system in Fig. 2.1 into many (say 10^9) parts. If the original system contained 10^{25} particles each part is still large enough to represent the macroscopic properties of the original system. We take one part as the system itself and regard the remaining parts as making up the mental copies in the canonical ensemble. We may also regard the one part as making up the system and the remaining parts as making up a heat bath. Since the new system is in good thermal contact with the remaining (surrounding) copies, there is exchange of heat between system and the heat bath. The exchange of heat serves to keep the system at constant T .

This canonical ensemble is the Gibbs canonical ensemble we considered in Chapter 5. Using the Boltzmann combinatorial method to find the probability of observing the system in energy state E_S in this ensemble we found

$$P_S = \frac{1}{Z} e^{-\beta E_S} \quad (6.5)$$

where

$$Z = \sum_S e^{-\beta E_S} \quad (6.6)$$

is the canonical partition function. This partition function is related to the Helmholtz free energy by

$$F(T, V, N) = -kT \log Z(T, V, N) \quad (6.7)$$

The relations forms the link between the microscopic states $E_S(V, N)$ of the system and its thermodynamic properties. It also allows us to write P_S in the compact form

$$P_S = e^{\beta(F - E_S)} \quad (6.8)$$

and clearly,

$$\sum_S P_S = 1. \quad (6.9)$$

The canonical ensemble is generally the most useful in practice since we most often deal with systems in thermal equilibrium (constant T) with their surroundings. The energy states fluctuate and the probability of observing the system in a given energy state at constant T is given by eq. (6.5). We also see that the microcanonical ensemble is a special case of the canonical ensemble in which all the systems have the same energy. Clearly if the energies of the systems in the canonical ensemble fluctuate little about some mean value, the canonical and microscopic ensembles will be identical. This is always the case if N is large enough since $\Delta E_{RMS}/E$ is proportional to $1/\sqrt{N}$. We saw an example of this in Chapter 5. There the classical gas properties were derived in the canonical ensemble and found identical to those obtained using the microcanonical ensemble.

We now develop some useful relations in the canonical ensemble. The internal energy is

$$U = \sum_S P_S E_S \quad (6.10)$$

and the entropy is,

$$S = -k \sum_S P_S \log P_S . \quad (6.11)$$

This follows from eq. (6.8) since

$$\log P_S = \beta (F - E_S)$$

and

$$\begin{aligned} \sum_S P_S \log P_S &= \frac{1}{kT} \left(\sum_S P_S F - \sum_S P_S E_S \right) \\ &= \frac{1}{kT} (F - U) = -S/k \end{aligned}$$

The free energy can be expressed as

$$F = U - TS = \sum_S P_S (E_S + kT \log P_S) \quad (6.12)$$

This expression for F is often useful if an approximate value for P_S being used.

In Quantum Statistical Mechanics the Boltzmann factor P_S is often written as an operator,

$$\hat{\rho}_C = e^{\beta(F - \hat{H})} \quad (6.13)$$

where H is the Hamiltonian. This follows from the Schrödinger equation,

$$\hat{H} |E_S\rangle = E_S |E_S\rangle , \quad (6.14)$$

so that when the exponential in ρ is expanded as a power series

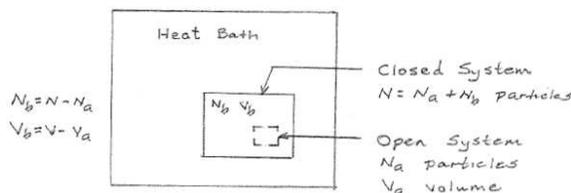
$$\hat{\rho}_C |E_S\rangle = e^{\beta(F - E_S)} |E_S\rangle . \quad (6.15)$$

We may calculate the average value of a property A in the following way. If A takes on the value A_S when the system is in state S , then

$$\hat{A} |E_S\rangle = A_S |E_S\rangle \quad (6.16)$$

The statistical average of A is

$$\begin{aligned} \langle A \rangle &= \sum_S P_S A_S \\ &= \sum_S \langle E_S | P_S A_S | E_S \rangle \end{aligned} \quad (6.17)$$

Figure 6.1: Open Sub-system of N_a particles in a volume V_a .

assuming the eigenstates E_S are normalized. Using the operator equations (6.15) and (6.16) we may write

$$\begin{aligned} \langle A \rangle &= \sum_S \langle E_S | \hat{\rho}_C \hat{A} | E_S \rangle \\ &\equiv \text{Tr} \left\{ \hat{\rho}_C \hat{A} \right\} \end{aligned} \quad (6.18)$$

Here the trace, Tr , is defined as the sum over the states $\langle E_S | E_S \rangle$. The compact form (eq. 6.18) is often used to represent averages in the canonical ensemble and $\hat{\rho}_C$ in eq. (6.13) is called the canonical density operator.

6.3 The Grand Canonical Ensemble

Here we consider an open system in contact with a heat and particle bath. The system is open meaning that particles as well as heat can be exchanged between the bath and the system. An example is a solid or liquid (the system) in contact with its vapor (the bath) in equilibrium so that particles are freely exchanged between the liquid and the vapor. Since the vapor and liquid are in equilibrium, the chemical potential, μ , is the same in each (and particles are exchanged to maintain μ the same in each phase) The grand canonical ensemble is an assembly of mental copies of this open system. In the ensemble all possible states of the system are represented; that is, all possible values of N and all possible energy states $E_S(N)$ for a given N .

We can construct a grand canonical ensemble from the canonical ensemble depicted in Fig. 6.1. We sub-divide the closed system having N particles in Fig. 6.1 into two parts; one small part having N_a particles in volume V_a and the second having N_b particles in the remaining volume, V_b . We choose $N_a \ll N_b = N - N_a$. This division is depicted in Fig. 6.1. The small sub-system is our open system and particles can be freely exchanged between it and the remaining $N - N_a$ particles. The ensemble is then an assembly of mental copies of this open sub-system.

To develop the statistics for the open system we recall that the probability of observing the closed system of N particles in energy state E_S is from eq. (6.5),

$$P_S = Z^{-1} e^{-\beta E_S} = e^{\beta(F - E_S)}$$

Assuming weak mechanical contact between the sub-system (N_a particles) and the remainder of the system (N_b particles) we can write

$$E_S = E_{S_a}(N_a) + E_{S_b}(N_b)$$

and

$$F(T, V, N) = F_a(T, V_a, N_a) + F_b(T, V_b, N_b)$$

so that

$$P_S = e^{-\beta E_{S_a}(N_a)} \times e^{-\beta E_{S_b}(N_b)} \times e^{\beta F(T, V, N)}$$

The probability $P_{S_a}(N_a)$ of observing the sub-system in energy state $E_{S_a}(N_a)$ for any given state of the system b is

$$P_{S_a}(N_a) = \sum_{S_b} P_S(N) = e^{-\beta E_{S_a}(N_a)} e^{\beta(F - F_b)}$$

where as usual

$$F_b = -kT \log \sum_{S_b} e^{-\beta E_{S_b}(N_b)}$$

Since $N_a \ll N - N_b$ we may write

$$\begin{aligned} F_a &= F - F_b = \left(\frac{\partial F}{\partial N} \right) N_a + \left(\frac{\partial F}{\partial V} \right) V_a \\ &= \mu N_a - p_a V_a \end{aligned}$$

Thus

$$P_{S_a}(N_a) = e^{-\beta p_a V_a} e^{-\beta(E_{S_a}(N_a) - \mu N_a)} \quad (6.19)$$

We have the central result that the probability of observing the open sub-system having N_a particles and in energy state $E_{S_a}(N_a)$ is proportional to $\exp(-\beta(E_S(N_a) - \mu N_a))$. We now focus our attention entirely on the sub-system and drop the subscript a and write this probability as

$$P_S(N) \propto e^{-\beta(E_S(N) - \mu N)}$$

We also define the grand canonical partition function as in section 5.3 by

$$\mathcal{Z} = \sum_{S, N} e^{-\beta(E_S(N) - \mu N)} \quad (6.20)$$

Since we want the probability to be normalized so that

$$\sum_{S, N} P_S(N) = 1 \quad (6.21)$$

we have, from (6.19) and (6.20),

$$\sum_{S, N} P_S(N) = 1 = e^{-\beta P V} \mathcal{Z} \quad (6.22)$$

This gives

$$P_S(N) = \mathcal{Z}^{-1} e^{-\beta(E_S(N) - \mu N)} \quad (6.23)$$

and our relation between thermodynamics and statistics for open systems as

$$pV = kT \log \mathcal{Z}(T, V, \mu). \quad (6.24)$$

In the thermodynamic summary in Chapter 2 we saw that the thermodynamic potential

$$\Omega(T, V, \mu) = F(T, V, N) - \mu \bar{N} \quad (6.25)$$

was a constant (a minimum) for an open system in equilibrium with a heat and particle bath. In this relation μ is

$$\mu = \left(\frac{\partial F}{\partial N} \right)_{T, V} = \left(\frac{\partial G}{\partial N} \right)_{T, P}$$

Also μ is the Gibbs Free energy per particle, $G = \mu \bar{N}$. The thermodynamic potential is the appropriate function to describe an open system since T , V and μ are constant so that Ω will be constant while F , for example, can fluctuate as N fluctuates. The Ω can be directly related to \mathcal{Z} using the thermodynamic relation, $G = F + pV$ so that

$$\Omega = G - pV - \mu \bar{N} = -pV$$

and

$$\Omega = -kT \log \mathcal{Z}(T, V, \mu) \quad (6.26a)$$

This can be used as the fundamental relation between statistics and thermodynamics for open systems. It is interesting to note that in going from a closed to an open system (at constant μ) we transferred from F to Ω using eq. (6.25) in our thermodynamic summary in Chapter 2. This gave us a function $\Omega(T, V, \mu)$ of variables T , V , and μ rather than a function $F(T, V, N)$ of variables T , V , and N . In introducing the grand canonical ensemble we have effectively made the same transformation of variables by summing over N . That is

$$\begin{aligned} \mathcal{Z}(T, V, \mu) &= \sum_N \sum_S e^{-\beta(E_S(N) - \mu N)} \\ &= \sum_N e^{-\beta \mu N} Z(T, V, N) \end{aligned} \quad (6.26b)$$

This serves to eliminate the dependence on N and introduce μ .

Using the thermodynamic potential we can obtain some useful relations for $P_S(N)$, \bar{N} , U and S . From eq. (6.25)

$$\Omega = U - TS - \mu \bar{N} = \sum_{S, N} P_S(N) E_S(N) - TS - \mu \bar{N}$$

Hence

$$P_S(N) = \frac{\partial \Omega}{\partial E_S(N)} = -\beta^{-1} \frac{\partial}{\partial E_S(N)} \log \mathcal{Z} \quad (6.27)$$

and

$$\bar{N} = - \left(\frac{\partial \Omega}{\partial \mu} \right)_{T,V} = \beta^{-1} \frac{\partial}{\partial \mu} (\log \mathcal{Z})_{T,V} \quad (6.28)$$

Also,

$$\begin{aligned} \frac{\partial}{\partial \beta} \log \mathcal{Z} &= -\mathcal{Z}^{-1} \sum_{S,N} (E_S(N) - \mu N) e^{-\beta(E_S(N) - \mu N)} \\ &= - \sum_{S,N} P_S(N) E_S(N) + \mu \bar{N} \end{aligned}$$

so that

$$U = - \frac{\partial}{\partial \beta} (\log \mathcal{Z})_{V,\mu} + \mu \bar{N} \quad (6.29)$$

The entropy is related to the grand canonical probability function $P_S(N)$ in the same form as eq. (6.11). That is

$$S = -kT \sum_{S,N} P_S(N) \log P_S(N) = -k \langle \log P_S(N) \rangle \quad (6.30)$$

This follows from eqs. (6.23) and (6.26) since

$$\log P_S(N) = - (E_S(N) - \mu N) - \log \mathcal{Z}$$

and

$$\begin{aligned} -\beta^{-1} \sum_{S,N} P_S(N) \log P_S(N) &= \sum_{S,N} P_S(N) [E_S(N) - \mu N] - \Omega \\ &= U - \mu \bar{N} - \Omega = TS. \end{aligned}$$

We could also introduce a density operator $\hat{\rho}_{GC}$ for the grand canonical ensemble in analogy with $\hat{\rho}_C$ in eq. (6.13) the canonical ensemble. This is

$$\hat{\rho}_{GC} = e^{\beta \Omega} e^{-\beta(\hat{H} - \mu \hat{N})} \quad (6.31)$$

Average values in the grand canonical ensemble are,

$$\begin{aligned} \langle A \rangle &= \text{Tr} \left\{ \hat{\rho}_{GC} \hat{A} \right\} \\ &\equiv \sum_{S,N} \left\langle E_S(N) \left| \hat{\rho}_{GC} \hat{A} \right| E_S(N) \right\rangle \end{aligned} \quad (6.32)$$

The relation eq. (6.11) and eq. (6.30) can be expressed in terms of ρ_C and ρ_{GC} as

$$S = -k \operatorname{Tr} \{ \rho_C \log \rho_C \} = -k \operatorname{Tr} \{ \rho_{GC} \log \rho_{GC} \} \quad (6.33)$$

Finally, when do we use the grand canonical ensemble? Clearly we use it to describe open systems where the number of particles is variable. If we have more than one kind of particle, a multicomponent system, then

$$P_S(N_1, N_2, \dots) = \mathcal{Z}^{-1} e^{-\beta(E_S - \mu_1 N_1 - \mu_2 N_2 - \dots)}$$

and

$$\mathcal{Z} = \sum_{N_1, N_2, \dots} \sum_S e^{-\beta(E_S - \mu_1 N_1 - \mu_2 N_2 - \dots)}$$

where N_1 and μ_1 are the number and chemical potential of type 1 particles and so on.

We can also use the grand canonical ensemble to describe a closed system if this is convenient. In section 5.4 we saw that the RMS fluctuation in the number of particles N about the average value \bar{N} in an open system is

$$(\Delta N)_{\text{RMS}} \equiv \left[\overline{N^2} - (\bar{N})^2 \right]^{\frac{1}{2}} \propto \sqrt{\bar{N}}$$

Thus the fluctuation in the number of particles is

$$\frac{(\Delta N)_{\text{RMS}}}{\bar{N}} \propto \frac{1}{\sqrt{\bar{N}}},$$

which is vanishingly small for a large system of particles ($N \sim 10^{23}$). This is generally true for open systems except near a phase transition or a critical point. With these exceptions there is essentially no difference between an open and a closed system containing a macroscopically large number of particles. Thus we could use a grand ensemble to describe a closed system since we can ignore all the states having N particles different from the average \bar{N} . This means we could calculate \mathcal{Z} for a closed system pretending N was variable, if that were convenient, and ignore all the states $N \neq \bar{N}$ at the end of the calculation. After \mathcal{Z} is obtained, we approximate (6.26b) by

$$\mathcal{Z}(T, V, \mu) = e^{-\beta\mu\bar{N}} \mathcal{Z}(T, V, \bar{N}) \quad (6.34)$$

to obtain

$$F = -kT \log Z = -kT \log \mathcal{Z} - \mu\bar{N}$$

and

$$P_S = P_S(\bar{N}) = - \frac{\partial}{\partial E_S(\bar{N})} \log \mathcal{Z}(T, V, \bar{N})$$

for the closed system. This is what we did in section 5.3 for the quantum gases. Thus the choice of the ensemble is also a matter of convenience.

We can also use the grand ensemble to describe a closed system in which all the energy states are fixed at $E_S = U$ as well as all $N = \bar{N}$ in this case \mathcal{Z} in eq. (6.34) reduces to

$$\begin{aligned}\mathcal{Z} &= e^{\beta\mu\bar{N}} \sum_S e^{-\beta E_S(\bar{N})} \\ &= e^{\beta\mu\bar{N}} e^{-\beta U} W\end{aligned}$$

where W is the degeneracy of the single energy state. Using eq. (6.26a)

$$\Omega = U - TS - \mu\bar{N} = -\mu\bar{N} + U - kT \log W$$

and

$$S = k \log W(U, V, N)$$

Thus we can use the grand ensemble in any case should it be convenient provided N is large.