

# 20

## Classical Ensembles: Grand and Otherwise

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*Life is nature's solution to the problem of preserving information despite the second law of thermodynamics.*

Howard L. Resnikoff, *The Illusion of Reality*

Although the canonical ensemble is the work horse of classical statistical mechanics, several other ensembles often prove convenient. The most important of these is the ‘grand canonical ensemble’, which will be discussed in this chapter. This discussion will also serve as an introduction to the very important use of the quantum grand canonical ensemble, which will play a prominent role in the theories of boson and fermion fluids in Part IV.

### 20.1 Grand Canonical Ensemble

The physical situation described by the grand canonical ensemble is that of a system that can exchange both energy and particles with a reservoir. As usual, we assume that the reservoir is much larger than the system of interest, so that its properties are not significantly affected by relatively small changes in its energy or particle number. Note that the reservoir must have the same type (or types) of particle as the system of interest, which was not a requirement of the reservoir for the canonical ensemble.

Because the system of interest and the reservoir are in equilibrium with respect to both energy and particle number, they must have the same temperature  $T = T_R$  and chemical potential  $\mu = \mu_R$ . In thermodynamics, this situation would correspond to the thermodynamic potential given by the Legendre transform with respect to temperature and chemical potential,

$$U[T, \mu] = U - TS - \mu N. \quad (20.1)$$

The function  $U[T, \mu]$  is sometimes referred to as the ‘grand potential’. Since Legendre transforms conserve information, the grand potential is another representation of the fundamental relation and contains all thermodynamic information about the system.

For extensive systems, Euler’s equation, eq. (13.5), holds, and  $U[T, \mu]$  has a direct connection to the pressure

$$U[T, \mu] = U - TS - \mu N = -PV. \quad (20.2)$$

While the grand canonical ensemble is useful in classical statistical mechanics, it turns out to be essential in quantum statistical mechanics, as we will see in Chapters 27, 28, and 29. Since the basic idea is the same in both classical and quantum statistical mechanics, it is convenient to see how the grand canonical ensemble works in the classical case, without the added complexity of quantum mechanics.

## 20.2 Grand Canonical Probability Distribution

To describe a system that can exchange energy and particles with a reservoir, we must greatly expand our description of a microscopic state. Both the microcanonical and canonical ensembles for a system with  $N$  particles required only a  $6N$ -dimensional phase space to describe a microscopic state. When the particle number can vary, we need a different  $6N$ -dimensional phase space for each value of  $N$ . Since  $N$  can vary from zero to the total number of particles in the reservoir—which we can approximate by infinity—this is a significant change.

To find the probability of a state in this expanded ensemble of an infinite number of phase spaces, we return to the basic calculation of the probability distribution in a composite system. Assume that the reservoir and the system of interest can exchange both energy and particles with each other, but are completely isolated from the rest of the universe. The total number of particles is  $N_T = N + N_R$  and the total energy is  $E_T = E + E_R$ , where the subscripted  $R$  indicates properties of the reservoir.

The probability of the system of interest having  $N$  particles and energy  $E$  is given by a generalization of eq. (19.10)

$$P(E, N) = \frac{\Omega(E, V, N)\Omega_R(E_T - E, V_R, N_T - N)}{\Omega_T(E_T, V_T, N_T)}. \quad (20.3)$$

Following the same procedure as in Section 19.3, we take the logarithm of eq. (20.3) and expand  $\ln \Omega_R(E_T - E, V_R, N_T - N)$  in powers of  $E/E_T$  and  $N/N_T$ ,

$$\begin{aligned}
\ln P(E, N) &= \ln \Omega(E, V, N) + \ln \Omega_R(E_T - E, V_R, N_T - N) \\
&\quad - \ln \Omega_T(E_T, V_T, N_T) \\
&\approx \ln \Omega(E, V, N) + \ln \Omega_R(E_T, V_R, N_T) \\
&\quad - E \frac{\partial}{\partial E_T} \ln \Omega_R(E_T, V_R, N_T) \\
&\quad - N \frac{\partial}{\partial N_T} \ln \Omega_R(E_T, V_R, N_T) \\
&\quad - \ln \Omega_R(E_T, V_T, N_T).
\end{aligned} \tag{20.4}$$

In eq. (20.4) we have neglected terms of higher order in  $E/E_T$  and  $N/N_T$ , since the reservoir is assumed to be much bigger than the system of interest.

Recalling that

$$S_R = k_B \ln \Omega_R(E_T, V_R, N_T), \tag{20.5}$$

we see that we have already found the derivatives of  $\ln \Omega$  in eq. (8.12). Therefore,  $\beta_R = 1/k_B T_R$  is given by

$$\beta_R \equiv \frac{\partial}{\partial E_T} \ln \Omega_R(E_T, V_R, N_T). \tag{20.6}$$

Similarly, by comparison with eq. (8.34), we see that the chemical potential of the reservoir is given by the other partial derivative in eq. (20.4),

$$-\mu_R \beta_R \equiv \frac{\partial}{\partial N_T} \ln \Omega_R(E_T, V_R, N_T). \tag{20.7}$$

Since  $\beta = \beta_R$  and  $\mu = \mu_R$ , and the quantities  $E_T, N_T, V_R$  do not depend on either  $E$  or  $N$ , we can combine  $\ln \Omega_R(E_T, V_R, N_T)$  and  $\ln \Omega_R(E_T, V_T, N_T)$  into a single value denoted by  $-\ln \mathcal{Z}$ ,

$$\ln P(E, N) \approx \ln \Omega(E, V, N) - \beta E + \beta \mu N - \ln \mathcal{Z}. \tag{20.8}$$

Exponentiating this equation gives us the grand canonical probability distribution for  $E$  and  $N$ ,

$$P(E, N) = \frac{1}{\mathcal{Z}} \Omega(E, V, N) \exp [-\beta E + \beta \mu N]. \tag{20.9}$$

The normalization condition determines  $\mathcal{Z}$ , which depends on both  $T = 1/k_B \beta$  and  $\mu$  (and, of course,  $V$ ),

$$\mathcal{Z} = \sum_{N=0}^{\infty} \int_0^{\infty} dE \Omega(E, V, N) \exp [-\beta E + \beta \mu N]. \quad (20.10)$$

The lower limit in the integral over the energy in eq. (20.10) has been taken to be zero, which is the most common value. More generally it should be the lowest allowed energy.

The normalization ‘constant’  $\mathcal{Z}$  is called the grand canonical partition function. It is constant in the sense that it does not depend on  $E$  or  $N$ , although it does depend on  $\beta$  and  $\mu$ .

The grand canonical partition function can also be expressed as a Laplace transform of the canonical partition function. Since eq. (19.18) gave the canonical partition function as,

$$Z(T, V, N) = \int_0^{\infty} dE \Omega(E, V, N) \exp(-\beta E) dE, \quad (20.11)$$

we can rewrite eq. (20.10) as,

$$\mathcal{Z}(T, V, \mu) = \sum_{N=0}^{\infty} Z(T, V, N) \exp [\beta \mu N]. \quad (20.12)$$

## 20.3 Importance of the Grand Canonical Partition Function

The grand canonical partition function plays much the same role as the canonical partition function. It is directly related to the grand canonical thermodynamic potential  $U[T, \mu]$ . To see this, consider the value of  $\ln P(E, N)$  at its maximum. The location of the maximum, as before, gives the equilibrium values of  $E = E_{eq} = U$  and  $N = N_{eq}$ . We can rewrite eq. (20.8) to solve for  $\ln \mathcal{Z}$ ,

$$\ln \mathcal{Z} = \ln \Omega(E_{eq}, V, N_{eq}) - \beta E_{eq} + \beta \mu N_{eq} - \ln P(E_{eq}, N_{eq}). \quad (20.13)$$

We already know that the first three terms on the right of eq. (20.13) are proportional to the size of the system. However,  $P(E_{eq}, N_{eq})$  will be proportional to  $\sqrt{\langle E_{eq} \rangle}$  and  $\sqrt{\langle N_{eq} \rangle}$ , so that  $\ln P(E_{eq}, N_{eq})$  will only be of order  $\ln E_{eq}$  and  $\ln N_{eq}$ . For  $N_{eq} \approx 10^{20}$ ,  $\ln P(E_{eq}, N_{eq})$  is completely negligible, and we can discard it in eq. (20.13),

$$\ln \mathcal{Z} = \ln \Omega(E, V, N) - \beta E + \beta \mu N. \quad (20.14)$$

Since we know that the microcanonical entropy is given by

$$S = k_B \ln \Omega, \quad (20.15)$$

we can rewrite eq. (20.14) as

$$\ln \mathcal{Z} = S/k_B - \beta E + \beta \mu N, \quad (20.16)$$

or,

$$\ln \mathcal{Z} = -\beta (E - TS - \mu N) = -\beta U[T, \mu]. \quad (20.17)$$

If the system is extensive, Euler's equation, eq. (13.5), holds, and,

$$\ln \mathcal{Z} = -\beta U[T, \mu] = \beta PV. \quad (20.18)$$

This equation gives us a convenient way to calculate the pressure as a function of  $T$  and  $\mu$ , as illustrated next for the classical ideal gas in eq. (20.21).

Eq. (20.18) is directly analogous to eq. (19.48). It provides a way to calculate the fundamental relation, and we can immediately invoke everything we learned in Part II about how to use thermodynamic potentials to calculate thermodynamic properties.

## 20.4 $\mathcal{Z}(T, V, \mu)$ for the Ideal Gas

In Section 19.10.1 we derived the partition function for the classical ideal gas, with the result given in eq. (19.62),

$$Z = \frac{1}{h^{3N} N!} (2\pi m k_B T)^{3N/2} V^N.$$

Inserting this equation into eq. (20.12) for the grand canonical partition function, we find

$$\begin{aligned} \mathcal{Z}(T, V, \mu) &= \sum_{N=0}^{\infty} \frac{1}{h^{3N} N!} (2\pi m k_B T)^{3N/2} V^N \exp [\beta \mu N] \\ &= \sum_{N=0}^{\infty} \frac{1}{N!} \left( \frac{(2\pi m k_B T)^{3/2}}{h^3} V e^{\beta \mu} \right)^N \\ &= \exp \left( (2\pi m k_B T)^{3/2} h^{-3} V e^{\beta \mu} \right). \end{aligned} \quad (20.19)$$

Taking the logarithm of eq. (20.19) gives us the grand canonical thermodynamic potential for the classical ideal gas,

$$-\beta U[T, \mu] = (2\pi m k_B T)^{3/2} h^{-3} V e^{\beta \mu} = \beta PV. \quad (20.20)$$

The last equality is, of course, true only because the ideal gas is extensive. Note that the pressure depends only on  $\beta$  and  $\mu$ , and can be obtained by dividing out the product  $\beta V$  in eq. (20.20),

$$P = k_B T (2\pi m k_B T)^{3/2} h^{-3} e^{\beta \mu}. \quad (20.21)$$

## 20.5 Summary of the Most Important Ensembles

The three ensembles that we have discussed so far are the most important.

**The microcanonical ensemble** fixes the energy, volume, and number of particles. The formula for the entropy of an isolated system is,

$$S = k_B \ln \Omega(E, V, N), \quad (20.22)$$

where

$$\Omega(E, V, N) = \frac{1}{h^{3N} N!} \int dq \int dp \delta(E - H(p, q)). \quad (20.23)$$

The origin of these equations is Boltzmann's definition of the entropy of a composite system in terms of the logarithm of the probability distribution. Eq. (20.22) can also be written in the form

$$\Omega(E, V, N) = \exp(S(E, V, N)/k_B). \quad (20.24)$$

The width of both the energy distribution and the particle-number distribution is zero in the microcanonical ensemble. This is clearly an approximation.

**The canonical ensemble** describes a system in equilibrium with a thermal reservoir at temperature  $T$ . The canonical partition function is given by

$$Z = \int dE \Omega(E, V, N) \exp(-\beta E), \quad (20.25)$$

and is related to the Helmholtz free energy  $F$  by

$$Z = \exp(-\beta F) = \exp(S[\beta]/k_B). \quad (20.26)$$

The width of the particle-number distribution is zero in the canonical ensemble. The energy distribution has a relative width of the order of  $1/\sqrt{N}$ , which is not exactly correct, but is a much better approximation than zero. We will return to this point in Chapter 21.

**The grand canonical ensemble** describes a system that can exchange both energy and particles with a reservoir, which is assumed to be characterized by temperature  $T$  and chemical potential  $\mu$ . The grand canonical partition function is given by

$$\mathcal{Z} = \sum_{N=0}^{\infty} \int_0^{\infty} dE \Omega(E, V, N) \exp(-\beta E + \beta \mu N), \quad (20.27)$$

and its relationship to  $U[T, \mu]$  is

$$\mathcal{Z} = \exp(-\beta U[T, \mu]) = \exp(S[\beta, (\beta \mu)]/k_B) = \exp(\beta PV), \quad (20.28)$$

where the last equality is valid only for extensive systems.

Both the energy distribution and the particle-number distribution have non-zero widths in the grand canonical ensemble.

## 20.6 Other Classical Ensembles

For every thermodynamic potential there is a corresponding ensemble in statistical mechanics. Every Legendre transform in thermodynamics corresponds to a Laplace transform in statistical mechanics. In each case, the logarithm of a partition function produces a thermodynamic potential. The only feature that is slightly different is found in the grand canonical partition function, for which the Laplace transform takes the form of a sum instead of an integral. None of these transforms should present any difficulties, since they are all derived using the same principles.

## 20.7 Problems

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### PROBLEM 20.1

#### A non-extensive thermodynamic system

Consider a classical gas of  $N$  weakly interacting atoms of mass  $m$ , enclosed in a container of volume  $V$  and surface area  $A$ .

The interactions between the atoms are so weak that they may be neglected (ideal gas approximation). However, the interaction of the atoms with the walls of the container may NOT be neglected. Some fraction of the atoms are adsorbed onto the walls of the container in equilibrium. Your job will be to calculate the average number  $N'$  of adsorbed atoms on the walls.

A simple model for the atoms adsorbed onto the walls is to treat them as a two-dimensional ideal gas. The energy of an adsorbed atom is taken to be

$$\epsilon(\vec{p}) = \frac{|\vec{p}|^2}{2m} - \epsilon_o$$

where  $\vec{p}$  is the two-dimensional momentum and  $\epsilon_o$  is a known parameter that describes the energy of adsorption.

The entire system is in equilibrium and in thermal contact with a heat reservoir at temperature  $T$ .

1. What is the classical partition function of the adsorbed atoms if  $N'$  of them are adsorbed onto the walls of the container?
  2. What is the chemical potential  $\mu_S$  of the atoms adsorbed on the surface?
  3. What is the chemical potential  $\mu_V$  of the  $N - N'$  atoms in the volume of the container?
  4. When the atoms in the volume and those adsorbed on the walls are in equilibrium, what is the average number of atoms adsorbed as a function of the temperature?
  5. What are the high- and low-temperature limits of the ratio of the number of adsorbed atoms to the total number of atoms?
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