

## CHAPTER 12

### “CLASSICAL” STATISTICAL PHYSICS AND THE PARTITION FUNCTION

#### Introduction

In the last chapter we developed the probability function for a microscopic subsystem in contact with a much larger reservoir. In this chapter, we will examine how to calculate from this probability function the average values for the various quantities of interest within a microscopic subsystem. We will show that all the pertinent parameters of the subsystem can be derived from a knowledge of the partition function.

#### The Average Energy and the Partition Function

Let us assume that the volume and the number of particles in the system of interest are held constant. The probability of finding the system with a particular energy  $E_r$  in this case is given simply by  $P_r = C e^{-\beta E_r}$ , and we can use this probability to determine the average values of various parameters of the system. For example, the average energy of the system is given by

$$\langle E \rangle = \frac{\sum_r E_r P_r}{\sum_r P_r} = \frac{\sum_r E_r e^{-\beta E_r}}{\sum_r e^{-\beta E_r}} \quad (12.1)$$

This same type of expression will obviously arise no matter what we are averaging. The denominator in this expression will be the same no matter what quantity is being averaged. As mentioned in the last chapter, the denominator, the “sum over all states” of the Boltzmann factor, designated by the symbol  $Z$

$$\boxed{Z \equiv \sum_r e^{-\beta E_r}} \quad (12.2)$$

is called the “partition function”. (The letter  $Z$  is from the German “*Zustandsumme*.”) In the case where we can consider the energy to be continuous, rather than discrete, this sum turns into an integral over all of phase space for energy ranging from the minimum energy (typically zero) to the maximum value of the energy. We will take up this in more detail later in the chapter.

Now, in terms of the partition function, the average energy can be written as

$$\langle E \rangle = \frac{1}{Z} \sum_r E_r e^{-\beta E_r} \quad (12.3)$$

Notice that the summation term in this last equation can be obtained by taking the partial derivative of the partition function with respect to  $\beta$ , except for a minus sign. That is,

$$\frac{\partial Z}{\partial \beta} = \sum_r -E_r e^{-\beta E_r} \quad (12.4)$$

Thus, we can write

$$\langle E \rangle = \frac{1}{Z} \sum_r E_r e^{-\beta E_r} = -\frac{1}{Z} \sum_r (-E_r) e^{-\beta E_r} = -\frac{1}{Z} \frac{\partial Z}{\partial \beta} \quad (12.5)$$

or

$$\boxed{\langle E \rangle = -\frac{\partial \ln Z}{\partial \beta}} \quad (12.6)$$

The average energy of a system can, therefore, be obtained from a knowledge of the partition function. In fact, we will show that we can determine *all* the macroscopic parameters of the system from a knowledge of the partition function.

As a further example, we will use the partition function to determine the standard deviation of the energy. Recall that the standard deviation is given by

$$\sigma_E^2 = \langle (E - \langle E \rangle)^2 \rangle = \langle E^2 + \langle E \rangle^2 - 2E\langle E \rangle \rangle = \langle E^2 \rangle - \langle E \rangle^2 \quad (12.7)$$

We have just shown how to determine the average energy from the partition function. Now look at the average of the square of the energy.

$$\langle E^2 \rangle = \frac{1}{Z} \sum_r E_r^2 e^{-\beta E_r} = \frac{1}{Z} \left\{ - \frac{\partial}{\partial \beta} \left( \sum_r E_r e^{-\beta E_r} \right) \right\} = \frac{1}{Z} \left( - \frac{\partial}{\partial \beta} \right)^2 \left( \sum_r e^{-\beta E_r} \right) \quad (12.8)$$

This can be written as

$$\langle E^2 \rangle = \frac{1}{Z} \frac{\partial^2 Z}{\partial \beta^2} = \frac{\partial}{\partial \beta} \left( \frac{1}{Z} \frac{\partial Z}{\partial \beta} \right) + \frac{1}{Z^2} \left( \frac{\partial Z}{\partial \beta} \right)^2 = \frac{\partial}{\partial \beta} \left( \frac{1}{Z} \frac{\partial Z}{\partial \beta} \right) + \langle E \rangle^2 \quad (12.9)$$

so that the standard deviation can also be written in terms of the partition function

$$\sigma_E^2 = \langle E^2 \rangle - \langle E \rangle^2 = \frac{\partial}{\partial \beta} \left( \frac{1}{Z} \frac{\partial Z}{\partial \beta} \right) = \frac{\partial^2 \ln Z}{\partial \beta^2} \quad (12.10)$$

One can show (Appendix 12.1) that the Helmholtz free energy is related to the partition function by the relation

$$F = -kT \ln Z \quad (12.11)$$

Since  $F = E - TS$ , the first law can be written as

$$dF = -S dT - p dV + \mu dN \quad (12.12)$$

from which we immediately obtain

$$\left( \frac{\partial F}{\partial T} \right)_{V,N} = -S \quad \left( \frac{\partial F}{\partial V} \right)_{T,N} = -p \quad \left( \frac{\partial F}{\partial N} \right)_{V,T} = \mu \quad (12.13)$$

Thus, a determination of the partition function enables one to determine the entropy, the energy, the pressure and the chemical potential for a system.

The same approach can be taken for a system where the volume and the number of particles can also vary. In this case the partition function is given by

$$Z = \sum_{E,V,N} e^{-\beta[E+PV-\mu N]} \quad (12.14)$$

where the sum is over all accessible energies, all possible volumes, and all possible numbers of particles. As mentioned earlier, any constant offset in energy, volume, or number of particles simply multiplies the partition function by a constant, and since all the parameters of interest are derived from partials of  $\ln(Z)$ , these constants will show up in both the numerator and denominator of the calculation, and, therefore, cancel. Likewise, if the volume and/or the number of particles is constant, this leads to constant multiplicative terms which also cancels in calculating any pertinent parameter.

### The Partition Function for a System Composed of Many Subsystems

Suppose the system of interest,  $A_0$ , can be subdivided into two similar systems,  $A_1$  and  $A_2$ , each of which can be in a certain energy state  $E_1$  or  $E_2$ . That is, the four possible states of the system can be specified by giving the total energy of the system in terms of that for each subsystem. These are:

- 1)  $E_1 = E_{11} + E_{21}$
- 2)  $E_2 = E_{11} + E_{22}$
- 3)  $E_3 = E_{12} + E_{21}$
- 4)  $E_4 = E_{12} + E_{22}$

The partition function is the sum over all energy states of the system, so that we have

$$Z = \sum_{\ell=1}^4 e^{-\beta E_{\ell}} = e^{-\beta(E_{11}+E_{21})} + e^{-\beta(E_{11}+E_{22})} + e^{-\beta(E_{22}+E_{21})} + e^{-\beta(E_{22}+E_{22})} \quad (12.15)$$

We can use the fact that the exponentials can be separated to give

$$Z = \sum_{\ell=1}^4 e^{-\beta E_{\ell}} = e^{-\beta E_{11}} e^{-\beta E_{21}} + e^{-\beta E_{11}} e^{-\beta E_{22}} + e^{-\beta E_{22}} e^{-\beta E_{21}} + e^{-\beta E_{12}} e^{-\beta E_{22}} \quad (12.16)$$

Now we can factor the terms to give

$$Z = \sum_{\ell=1}^4 e^{-\beta E_{\ell}} = e^{-\beta E_{11}} \{ e^{-\beta E_{21}} + e^{-\beta E_{22}} \} + e^{-\beta E_{12}} \{ e^{-\beta E_{21}} + e^{-\beta E_{22}} \} \quad (12.17)$$

or

$$Z = \sum_{\ell=1}^4 e^{-\beta E_{\ell}} = \{ e^{-\beta E_{11}} + e^{-\beta E_{12}} \} \{ e^{-\beta E_{21}} + e^{-\beta E_{22}} \} \quad (12.18)$$

$$Z = \sum_{\ell=1}^4 e^{-\beta E_{\ell}} = \sum_j e^{-\beta E_{1j}} \sum_j e^{-\beta E_{2j}} = Z_1 Z_2 \quad (12.19)$$

Thus, the partition function for a system composed of 2 subsystems is just the product of the partition function for the individual subsystems. *This result, however, is not correct if the subsystems are indistinguishable!* For example, if each of the subsystems of interest were atoms with various energy levels, this development would *only* be correct as long as the atoms were somehow *distinguishable* (perhaps by their location within a solid matrix). If the atoms are *not* distinguishable, this process is *incorrect*!

This is the same problem we encountered in flipping coins. We can count up the number of ways we can flip 10 different coins (labeled  $a, b, c, \dots$ ) and obtain the total number of different *states* of the system. However, if we are interested in how many ways we can obtain 3 heads and 7 tails, *with no regard for the order in which we obtain the 3 heads and 7 tails*, then we must divide the total number of possible states by  $3!$  and  $7!$  since there are  $3!$  different arrangements of the three heads and  $7!$  different arrangements of the 7 tails. Otherwise, we would overcount the number of ways of obtaining 3 heads and 7 tails.

Therefore, if we have  $N$  *identical* atoms, each with a given set of energy states, the partition function for the system of  $N$  identical atoms would be

$$Z = \begin{cases} \zeta^N & \text{for identical, distinguishable particles} \\ \frac{\zeta^N}{N!} & \text{for identical, indistinguishable particles} \end{cases} \quad (12.20)$$

where  $\zeta$  is the individual partition function for each atom given by

$$\zeta = \sum_s e^{-\beta E_s} \quad (12.21)$$

with  $E_s$  being the different possible energy states accessible to the individual atom. If the energy states are degenerate, we can write this last expression as

$$\zeta = \sum_s g(E_s) e^{-\beta E_s} \quad (12.22)$$

Notice that this equation assumes that the volume of an individual atom is constant. In some cases, where the volume of the atom is very small, the addition of this volume leads to an extremely small correction to the partition function we have given above, and is therefore ignored (see previous chapter). However, if the size of the atom were to grow very large this term might not be negligible.

### The Ideal Diatomic Gas

If we consider an ideal gas of diatomic molecules, the individual molecules will be indistinguishable, so that the partition function for an ideal gas of diatomic molecules will be

$$Z = \frac{\zeta^N}{N!} = \frac{1}{N!} \left\{ \sum_s e^{-\beta E_s} \right\}^N \quad (12.23)$$

where  $E_s = \epsilon_{\text{translation}} + \epsilon_{\text{rotation}} + \epsilon_{\text{vibration}} + \epsilon_{\text{electronic}} + \epsilon_{\text{nuclear}} + \dots$  and the sum is over all translational degrees of freedom, all rotational degrees of freedom, etc. Thus, the individual partition function can be further subdivided to give

$$\zeta = \sum_s e^{-\beta E_s} = \sum_t e^{-\beta \epsilon_t} \sum_r e^{-\beta \epsilon_r} \sum_v e^{-\beta \epsilon_v} \sum_e e^{-\beta \epsilon_e} \sum_n e^{-\beta \epsilon_n} \dots \quad (12.24)$$

where the sum over  $s$  is over *all* states. The individual molecular partition function is therefore made up of products of partition functions associated with each type of energy that the system can have, giving

$$\zeta = \zeta_t \zeta_r \zeta_v \zeta_e \zeta_n \dots \quad (12.25)$$

It is often convenient to write this last expression in the form

$$\zeta = \zeta_t \zeta_{\text{int}}$$

where

$$\zeta_{\text{int}} = \zeta_r \zeta_v \zeta_e \zeta_n \dots$$

In the following treatment of the ideal diatomic gas we will examine the translational partition function and each of the internal partition functions associated with rotation, vibration, electronic and nuclear excitation. Once we determine each of these, we can then evaluate the system partition function from which we can determine the Helmholtz free energy, and, from that, the other system parameters of interest.

### The Partition Function Associated with Translation

The translational part of the partition function *for a single particle* can be written

$$\zeta_t = \sum_t e^{-\beta \epsilon_t} \rightarrow \int e^{-\beta \epsilon_t} \frac{dp_x dq_x}{h_o} \frac{dp_y dq_y}{h_o} \frac{dp_z dq_z}{h_o} \quad (12.26)$$

where  $\epsilon_t = \frac{p_x^2 + p_y^2 + p_z^2}{2m}$ . This is the classical approximation introduced earlier where we integrate over the number of cells in phase space. Thus

$$\zeta_t = \frac{V}{h_o^3} \int e^{-\beta \epsilon_t} d\vec{p} \quad (12.27)$$

where  $d\vec{p} = dp_x dp_y dp_z$ . Evaluating this integral gives

$$\zeta_t = V \left( \frac{2\pi m k T}{h_o^2} \right)^{3/2} \quad (12.28)$$

However, notice that the partition function is a dimensionless quantity. This means that we can write the translational partition function in the form

$$\zeta_t = \frac{V}{v_Q} \quad (12.29)$$

where  $v_Q$  is the “quantum volume”, given by

$$v_Q = \left( \frac{2\pi m k T}{h_o^2} \right)^{-3/2} = \left( \frac{h_o}{\sqrt{2\pi m k T}} \right)^3 = \ell_Q^3 \quad (12.30)$$

and where  $\ell_Q$  is a characteristic quantum length. Although this last expression seems nice and compact, it is slightly dangerous, because you must remember that the quantum volume depends upon the temperature of the gas. For this reason it is not advisable to use this notation in calculations.

To gain insight into this last relationship, let us consider the *quantum* partition function for translation in terms of a sum over the accessible energy states for a *one* dimensional system. This partition function would be written

$$\zeta_{1dt} = \sum_t e^{-\beta \epsilon_t}$$

where the energies are derived from the quantum mechanical particle in a box of length  $L$ . For a one-dimensional system, these energies are given by

$$E_n = \frac{n^2 h^2}{8mL^2} \quad (12.31)$$

and we would obtain

$$\zeta_{1dt} = \sum_t e^{-\beta \epsilon_t} = \zeta_{1dt} = \sum_n e^{-\beta \frac{n^2 h^2}{8mL^2}} \quad (12.32)$$

Unless  $L$  and/or  $T$  are extremely small, the energy levels are extremely close together, and this sum can be taken over to an integral, giving

$$\zeta_{1dt} = \int_0^\infty e^{-\beta \frac{n^2 h^2}{8mL^2}} dn = \sqrt{\frac{2\pi m k T}{h^2}} L = \frac{L}{\ell_Q} \quad (12.33)$$

For three dimensions, then, the partition function is given by

$$\zeta_t = \left( \frac{L}{\ell_Q} \right)^3 = \frac{V}{v_Q} \quad (12.34)$$

### The Partition Function Associated with Internal Degrees of Freedom

#### The Partition Function Associated with Electronic and Nuclear Excitation

First consider the electronic partition function

$$\zeta_e = \sum_e g(\epsilon_e) e^{-\beta \epsilon_e} \quad (12.35)$$

where the sum is over all electronic energy states. If we consider the ground state energy to be zero (a shift in the energy coordinate from the usual), then this can be written

$$\zeta_e = g(0)e^{-\beta 0} + g(\epsilon_1)e^{-\beta \epsilon_1} + g(\epsilon_2)e^{-\beta \epsilon_2} + g(\epsilon_3)e^{-\beta \epsilon_3} + \dots = g(0)1 + g(\epsilon_1)e^{-\beta \epsilon_1} + \dots \quad (12.36)$$

where  $\epsilon_i$  is the energy of the  $i^{th}$  excited state, and where  $g(\epsilon_i)$  is the degeneracy of each excited state. Now the first term in this series is one times the degeneracy of the ground state, but the second term (and all succeeding terms) is extremely small *for room temperature* ( $kT \simeq \frac{1}{40}$  eV ;  $k \simeq [12,000]^{-1}$  eV ). At room temperature, the first exponential term is

$$e^{-\beta \epsilon_1} \simeq e^{-(40\epsilon_1)} \quad (12.37)$$

For the first excited state of hydrogen ( $\simeq 10$  eV above the ground state), this term would be  $\simeq e^{-400}$ , or essentially zero. For energy spacings of the order of 1 eV this term is still of the order of  $1 \times 10^{-18}$  at room

temperature which is still negligibly small. Thus, *the electronic excitation partition function at room temperature is equal to the degeneracy of the ground state*. The electronic partition function will differ from this only when the temperature is several thousand degrees. The exact temperature would depend upon the degeneracy of the excited states. We say that the electron excitation degrees of freedom are “frozen out” or “turned off” at room temperature - i.e., the exponential factor  $\beta\epsilon_1$  is large, or  $\epsilon_1/kT \gg 1$ , which means that  $T \ll \Theta_e$ , where  $\Theta_e = \epsilon_1/k$  is the characteristic temperature for electronic excitation. This temperature for an excitation energy of 1 eV is approximately given by  $\Theta_e = 12,000$  K.

Since the separation between the energy levels inside the nucleus are much much greater than that for the electronic energy levels it should be obvious that we will obtain the same results for  $\zeta_n$ . That is  $\zeta_n$  is equal to the degeneracy of the ground state except in cases of *extremely* high temperatures. [For energy separations of the order of 1 keV the characteristic temperature is approximately given by  $\Theta_n = 12,000,000$  K.] Thus, under normal conditions (room temperature) we would expect the only contribution to the energy of the molecular system (except for ground-state degeneracy) to be from the translational, vibrational, and rotational motion of the molecule. In this case, the internal partition function simplifies to give

$$\zeta_{int} = g_e g_n \zeta_r \zeta_v \quad (12.38)$$

where  $g_e$  and  $g_n$  are the degeneracy of the electronic ground state and the nuclear ground state, respectively.

### The Partition Function Associated with Rotation

The rotational kinetic energy of a diatomic molecule can be expressed quantum mechanically as

$$\epsilon_r = \frac{\vec{L}^2}{2I} \quad (12.39)$$

where  $I$  is the moment of inertia about an axis perpendicular to the line joining the two atoms of the molecule, and where the angular momentum  $\vec{L}$  is given quantum mechanically by

$$\vec{L}^2 = \ell_x(\ell_x + 1)\hbar^2 \quad \ell_x = 0, 1, 2, \dots \quad (12.40)$$

The angular momentum vector  $\vec{L}$  can be oriented along an arbitrary axis (usually denoted by the z-axis) with components given by

$$L_z = m_\ell \hbar \quad m_\ell = 0, \pm 1, \pm 2, \dots, \pm \ell \quad (12.41)$$

There are  $2\ell + 1$  different values of  $L_z$  for each possible angular momentum quantum number. Since each of these  $2\ell + 1$  different states all have the same energy, the rotation partition function becomes

$$\zeta_r = \sum_{\ell} (2\ell + 1) e^{-\beta(\vec{L}^2/2I)} = \sum_{\ell} (2\ell + 1) e^{-\beta(\hbar^2/2I)[\ell(\ell+1)]} \quad (12.42)$$

Writing out the first few terms of this last sum gives

$$\zeta_r = 1 + 3e^{-\beta(\hbar^2/2I)2} + \dots \quad (12.43)$$

Now, if  $\beta(\hbar^2/2I) \gg 1$ , or  $T \ll \frac{\hbar^2}{2Ik} = \Theta_r$ , where  $\Theta_r$  is the excitation temperature for rotation, then the partition function will simply be equal to unity, i.e., the rotational motion “freezes out”. Thus, if the system temperature is much less than the excitation temperature for rotation, then the system will act as though there is no energy in rotation and

$$\zeta_r = 1 \quad T \ll \Theta_r \quad (12.44)$$

Let's calculate  $\Theta_r$  for a typical gas, say  $N_2$ , where the rotational moment of inertia is  $\simeq 1.4 \times 10^{-46}$  kg-m<sup>2</sup>/s<sup>2</sup>, and where  $\hbar^2 = (1.06 \times 10^{-34} \text{ J} \cdot \text{s})^2$  and  $k = 1.381 \times 10^{-23}$  J/K. This gives

$$\Theta_r = \frac{1}{k} \left( \frac{\hbar^2}{2I} \right) = 2.9 \text{ K} \quad (12.45)$$

So we see that at room temperature,  $T \approx 100 \times \Theta_r$ . This means that at room temperature we are *sure* to see the effects of rotation.

Writing the partition function in terms of the excitation temperature  $\Theta_r$ , we have

$$\zeta_r = \sum_{\ell} (2\ell + 1) e^{-\beta(\hbar^2/2I)[\ell(\ell+1)]} = \sum_{\ell} (2\ell + 1) e^{-(\Theta_r/T)[\ell(\ell+1)]} \quad (12.46)$$

Now since  $\Theta_r/T \simeq 1/100$  at room temperature, we obtain

$$\zeta_r = 1 + 3e^{-(1/100)} + 5e^{-(3/100)} + \dots = 1 + 3(0.99) + 5(0.97) + \dots \quad (12.47)$$

This sum can be converted to an integral (since the step sizes are so small) to give

$$\zeta_r = \int (2\ell + 1) e^{-\beta(\hbar^2/2I)[\ell(\ell+1)]} d\ell \quad (12.48)$$

But  $(2\ell + 1)d\ell = d(\ell^2 + \ell)$ , so that we can write

$$\zeta_r = \int_0^{\infty} e^{-\beta(\hbar^2/2I)(\ell^2+\ell)} d(\ell^2 + \ell) = \int_0^{\infty} e^{-\beta(\hbar^2/2I)x} dx = -\frac{e^{-\beta(\hbar^2/2I)x}}{\beta(\hbar^2/2I)} \Big|_0^{\infty} \quad (12.49)$$

or

$$\zeta_r = \frac{kT}{\hbar^2/2I} = \frac{T}{\Theta_r} \quad T \gg \Theta_r \quad (12.50)$$

where

$$\Theta_r = \frac{1}{k} \left( \frac{\hbar^2}{2I} \right) \quad (12.51)$$

[Note: One can also consider the possible rotation of the molecule about the internuclear axis. In this case, the moment of inertia is very small  $\simeq 2000$  times less than the moment of inertia of the axis we have chosen above. In this case, the excitation temperature for rotation is 2000 times greater than the excitation temperature which we calculated. Thus, at room temperature, rotation about the internuclear axis is very unlikely. Furthermore, the temperature at which this would begin to make a difference is far above the temperature which would first cause the molecule to become dissociated!]

### The Partition Function Associated with Vibration

For a diatomic molecule there is only one possible type of vibration - that caused by a change in the internuclear separation. Quantum mechanically, the energy of a simple harmonic oscillator is given by

$$\epsilon_v = \left( n + \frac{1}{2} \right) \hbar\omega \quad n = 0, 1, 2, \dots \quad (12.52)$$

If we again measure energies relative to the ground state ( $\epsilon_0 = \hbar\omega/2$ ), then we can express this energy as

$$\epsilon_v = n\hbar\omega \quad (12.53)$$

and the vibrational partition function will become

$$\zeta_v = \sum_v e^{-\beta\epsilon_v} = \sum_n e^{-n\beta\hbar\omega} \quad (12.54)$$

This last sum can be cast in the form of a geometric series

$$\zeta_v = \sum_n e^{-n\beta\hbar\omega} = \sum_n (\zeta')^n \quad (12.55)$$

where

$$\zeta' = e^{-\beta\hbar\omega} \quad (12.56)$$

Using that fact that

$$\sum_{n=0}^{\infty} a^n = \frac{1}{1-a} \quad \text{for } |a| < 1 \quad (12.57)$$

we obtain

$$\zeta_v = \frac{1}{1 - e^{-\beta\hbar\omega}} \quad (12.58)$$

Defining the excitation temperature for vibration as  $\Theta_v = \hbar\omega/k$ , this can be written

$$\zeta_v = \frac{1}{1 - e^{-\Theta_v/T}} \quad (12.59)$$

When  $T \ll \Theta_v$ , the vibrational partition function becomes unity, and vibrational motion “freezes out”. When  $T \gg \Theta_v$  we can expand the exponential to obtain

$$\zeta_v = \frac{1}{1 - [1 - \frac{\Theta_v}{T} + \dots]} = \frac{T}{\Theta_v} = \frac{kT}{\hbar\omega} \quad (12.60)$$

The characteristic angular frequency of vibration for  $N_2$  is  $2 \times 10^{14} \text{ s}^{-1}$ , giving a value of about 1500K for  $\Theta_v$ . Thus, at room temperature, vibrational motion is frozen out.

### Summary

We have shown that the partition function can be written as

$$Z = \frac{\zeta^N}{N!} = \frac{1}{N!} \{\zeta_t \zeta_r \zeta_v \zeta_e \zeta_n \dots\}^N = \frac{1}{N!} \{\zeta_t \zeta_{int}\}^N \quad (12.61)$$

where  $\zeta$  is the individual partition function for each identical diatomic molecule, and where this partition function can be further broken down into the product of partition functions for the various type of energy stored in the system (both internal and external). We have also shown that the electronic and nuclear partition functions are equal to  $g_e$  and  $g_n$ , respectively, at temperatures below about 1000K. Thus, for room temperature, we can express the partition function in terms of the product of single-particle partition functions according to

$$Z = \frac{\zeta^N}{N!} = \frac{1}{N!} \{g_e g_n \zeta_t \zeta_r \zeta_v\}^N \quad (12.62)$$

where our results for the individual partition functions are summarized below.

- 1) The partition function for electronic excitation is just equal to the degeneracy of the electronic ground state,  $g_e$ , for temperatures less than several thousand Kelvin - in many cases this is just unity.
- 2) The partition function for nuclear excitation is just equal to the degeneracy of the nuclear ground state,  $g_n$ , for temperatures less than several million Kelvin - in many cases this is just unity.
- 3) The partition function for translation (valid for all temperatures) is given by

$$\zeta_t = V \left( \frac{2\pi mkT}{h_o^2} \right)^{3/2} \quad (12.63)$$

- 4) The partition function for rotation (valid for all temperatures) is given by

$$\zeta_r = \sum_{\ell} (2\ell + 1) e^{-\beta(\hbar^2/2I)[\ell(\ell+1)]} \quad (12.64)$$

which reduces to

$$\zeta_r = 1 \quad \text{when } T \ll \Theta_r \quad (12.65)$$



or

$$\zeta_r = \frac{kT}{h^2/2I} = \frac{T}{\Theta_r} \quad \text{when } T \gg \Theta_r \quad (12.66)$$

And, since

$$\Theta_r = \frac{1}{k} \left( \frac{h^2}{2I} \right) \simeq 3\text{K} \quad (12.67)$$

the correct form for the partition function at room temperature is given by equation 12.0.

- 5) For vibration the partition function has the form (valid for all temperature)

$$\zeta_v = \frac{1}{1 - e^{-\beta h \omega}} \quad (12.68)$$

which reduces to

$$\zeta_v = 1 \quad \text{when } T \ll \Theta_v \quad (12.69)$$

or

$$\zeta_v = \frac{kT}{h \omega} \quad \text{when } T \gg \Theta_v \quad (12.70)$$

Here, the “turn-on” temperature is given by

$$\Theta_v = \frac{h \omega}{k} \simeq 1500\text{K} \quad (12.71)$$

so that the correct form for the partition function at room temperature is given by equation 12.0.

You will notice that each of the internal degrees of freedom for the diatomic molecule have a “turn-on” temperature, or a temperature below which the motion is “frozen out”. One might ask if this is possible for translational motion as well. To investigate this let's consider the way we determined the “turn-on” temperature for electron excitation. When the exponential factor  $e^{-\beta \epsilon}$  is large, all the terms of the partition function other than that for  $\epsilon = 0$  are essentially zero, and are “frozen out”. In the case of a free particle moving in *one* dimension in a square well of length  $L$ , the energy is given by  $E_n = n^2 h^2 / 8mL^2 = n^2 (h^2 / 8mL^2)$ . Taking the term  $h^2 / 8mL^2$  as the energy  $\epsilon$ , we find that the “turn-on” temperature for translation is given by

$$\Theta_{tr} = \epsilon_{tr} / k = h^2 / 8mkL^2 = \frac{(6.626 \times 10^{-34} \text{ J} \cdot \text{s})^2}{8m(1.66 \times 10^{-27} \text{ kg})(1.381 \times 10^{-23} \text{ J/K})} \frac{1}{L^2} \quad (12.72)$$

where  $m$  is the mass in atomic mass units and  $L$  is the length in meters. Thus, the “turn-on” temperature for translation is

$$\Theta_{tr} = \frac{2.394 \times 10^{-18} \text{ K}}{m[\text{amu}] \times L[\text{m}]^2} \quad (12.73)$$

Notice that only when the size of the container approaches that of a atom ( $10^{-10}$ ) does the characteristic temperature for translation even begin to approach room temperature.

### Application to the Ideal Diatomic Gas

The natural log of the partition function for an ideal diatomic gas at room temperature, then can be expressed as

$$\ln Z = \ln \left[ \frac{1}{N!} \{g_e g_n \zeta_t \zeta_r \zeta_v\}^N \right] = N [\ln g_e + \ln g_n + \ln \zeta_t + \ln \zeta_r + \ln \zeta_v] - \ln N!$$

which, using Sterling's approximation, can be written

$$\ln Z = \ln \left[ \frac{1}{N!} \{g_e g_n \zeta_t \zeta_r \zeta_v\}^N \right] = N [\ln g_e + \ln g_n + \ln \zeta_t + \ln \zeta_r + \ln \zeta_v] - [N \ln N - N]$$

or

$$\ln Z = \ln \left[ \frac{1}{N!} \{g_e g_n \zeta_t \zeta_r \zeta_v\}^N \right] = N [\ln g_e + \ln g_n + \ln \zeta_t + \ln \zeta_r + \ln \zeta_v - \ln N + 1] \quad (12.74)$$

Now the log of each term dealing with the internal partition function is given by

$$\ln \zeta_t = \ln V + \frac{3}{2} \ln \left( \frac{2\pi m k T}{h_o^2} \right) = \ln V + \frac{3}{2} \ln k T + \frac{3}{2} \ln \left( \frac{2\pi m}{h_o^2} \right) \quad (12.75)$$

$$\ln \zeta_r = \ln k T + \ln \frac{2I}{\hbar^2}$$

$$\ln \zeta_v = \ln 1 = 0$$

Combining terms we can write

$$\ln Z = N \left[ \ln g_e + \ln g_n + \ln V + \frac{5}{2} \ln k T + \frac{3}{2} \ln \left( \frac{2\pi m}{h_o^2} \right) + \ln \left( \frac{2I}{\hbar^2} \right) - \ln N + 1 \right] \quad (12.76)$$

which can be further simplifies to give

$$\ln Z = -N \left[ \ln N - \ln V - \frac{5}{2} \ln k T - \sigma \right] \quad (12.77)$$

where  $\sigma$  is simply a constant depending upon the parameters of a single molecule, given by

$$\sigma = 1 + \frac{3}{2} \ln \left( \frac{2m\pi}{h_o^2} \right) + \ln \left( \frac{2I}{\hbar^2} \right) + \ln g_e + \ln g_n \quad (12.78)$$

Now that we know the expression for  $\ln Z$ , the *energy* of the system can be found using

$$\langle E \rangle = - \frac{\partial}{\partial \beta} \ln Z \quad (12.79)$$

Writing  $\ln Z$  in terms of  $\beta$ , we have

$$\ln Z = -N \left[ \ln N - \ln V - \frac{5}{2} \ln \left( \frac{1}{\beta} \right) - \sigma \right] \quad (12.80)$$

from which we obtain

$$\langle E \rangle = - \frac{\partial}{\partial \beta} \left[ \frac{5}{2} N \ln \left( \frac{1}{\beta} \right) \right] \quad (12.81)$$

or

$$\langle E \rangle = - \frac{5}{2} N \beta \frac{\partial(1/\beta)}{\partial \beta} = - \frac{5}{2} N \beta \left( - \frac{1}{\beta^2} \right) = \frac{5}{2} N k T \quad (12.82)$$

Likewise, the Helmholtz free energy is given by

$$F = -k T \ln Z = N k T \left[ \ln N - \ln V - \frac{5}{2} \ln (k T) - \sigma \right] \quad (12.83)$$

from which we can determine the entropy, pressure, and chemical potential according to

$$\left(\frac{\partial F}{\partial T}\right)_{V,N} = -S \quad \left(\frac{\partial F}{\partial V}\right)_{T,N} = -p \quad \left(\frac{\partial F}{\partial N}\right)_{V,T} = \mu \quad (12.84)$$

For the pressure of the system we obtain

$$p = -\left(\frac{\partial F}{\partial V}\right)_{T,N} = -\frac{\partial}{\partial V}[-NkT \ln V] = \frac{NkT}{V} \quad (12.85)$$

which is just the equation for an ideal gas

$$pV = NkT \quad (12.86)$$

The chemical potential,  $\mu$  is given by

$$\begin{aligned} \mu &= \left(\frac{\partial F}{\partial N}\right)_{V,T} = \frac{\partial}{\partial N} \left\{ NkT \left[ \ln N - \ln V - \frac{5}{2} \ln \left( \frac{1}{\beta} \right) - \sigma \right] \right\} \\ &= kT \left[ \ln N - \ln V - \frac{5}{2} \ln \left( \frac{1}{\beta} \right) - \sigma \right] + NkT \left[ \frac{1}{N} \right] \\ &= kT \left[ \ln N - \ln V - \frac{5}{2} \ln \left( \frac{1}{\beta} \right) - \sigma + 1 \right] \end{aligned} \quad (12.87)$$

Likewise, the entropy is given by

$$\begin{aligned} S &= \left(\frac{\partial F}{\partial T}\right)_{V,N} = -\frac{\partial}{\partial T} \left\{ NkT \left[ \ln N - \ln V - \frac{5}{2} \ln (kT) - \sigma \right] \right\} \\ &= -Nk \left[ \ln N - \ln V - \frac{5}{2} \ln (kT) - \sigma - \frac{5}{2} \right] \\ &= -Nk \left[ \ln N - \ln V - \frac{5}{2} [1 + \ln (kT)] - \sigma \right] \end{aligned} \quad (12.88)$$

### Insights Regarding Internal Degrees of Freedom

The partition function for any gas can be expressed by the relation

$$Z = \frac{\zeta^N}{N!} = \frac{1}{N!} \{ \zeta_t \zeta_r \zeta_v \zeta_e \zeta_n \dots \}^N = \frac{1}{N!} \{ \zeta_t \zeta_{int} \}^N \quad (12.89)$$

All pertinent parameters can be calculated from the natural log of the partition function,

$$\ln Z = \ln \left[ \frac{1}{N!} \{ \zeta_t \zeta_{int} \}^N \right] = N [\ln \zeta_t + \ln \zeta_{int}] - \ln N! \quad (12.90)$$

and since

$$\ln \zeta_t = \ln V + \frac{3}{2} \ln \left( \frac{2\pi mkT}{h_o^2} \right) = \ln V + \frac{3}{2} \ln kT + \frac{3}{2} \ln \left( \frac{2\pi m}{h_o^2} \right) \quad (12.91)$$

this becomes

$$\ln Z = N \left[ \ln V + \frac{3}{2} \ln kT + \frac{3}{2} \ln \left( \frac{2\pi m}{h_o^2} \right) + \ln \zeta_{int} \right] - [N \ln(N) - N] \quad (12.92)$$

or

$$\ln Z = N \left[ \ln V + \frac{3}{2} \ln kT - \ln N + \ln \zeta_{int} + \frac{3}{2} \ln \left( \frac{2\pi m}{h_o^2} \right) + 1 \right] \quad (12.93)$$

Now, from this last equation, we can determine the average energy of the system, the pressure, the heat capacity, the entropy, and the chemical potential.

The average energy of the system is just

$$E = - \frac{\partial}{\partial \beta} \ln Z = - N \frac{\partial}{\partial \beta} \left[ \frac{3}{2} \ln kT + \ln \zeta_{int} \right] = \frac{3}{2} NkT + N\epsilon_{int} = \frac{3}{2} NkT + E_{int} \quad (12.94)$$

where  $\epsilon_{int}$  is the average internal energy per particle, and  $E_{int}$  is the average internal energy of the system. The heat capacity is obviously given by

$$C_V = \frac{3}{2} Nk + \frac{\partial E_{int}}{\partial T} \quad (12.95)$$

Now the internal energy is only a function of the rotational energy part, given by

$$E_{int} = N \left[ - \frac{\partial \ln \zeta_{int}}{\partial \beta} \right] = N \left[ - \frac{\partial \ln \zeta_r}{\partial \beta} \right] = N \left[ - \frac{\partial \ln kT}{\partial \beta} \right] = NkT$$

so that we obtain an additional factor of  $Nk$  for the heat capacity.

The Helmholtz free energy is given by

$$F = - kT \ln Z = - NkT \left[ \ln V + \frac{3}{2} \ln kT - \ln N + \ln \zeta_{int} + \frac{3}{2} \ln \left( \frac{2\pi m}{h_o^2} \right) + 1 \right]$$

which can be expressed as

$$F = - kT \ln Z = - NkT \left[ \ln V + \frac{3}{2} \ln kT - \ln N + \frac{3}{2} \ln \left( \frac{2\pi m}{h_o^2} \right) + 1 \right] - NkT \ln \zeta_{int}$$

or

$$F = - NkT \left[ \ln V + \frac{3}{2} \ln kT - \ln N + \frac{3}{2} \ln \left( \frac{2\pi m}{h_o^2} \right) + 1 \right] + F_{int} \quad (12.96)$$

from which we can determine the pressure, the entropy, and the chemical potential. The pressure is given by

$$P = - \left( \frac{\partial F}{\partial V} \right)_{T,N} = \frac{NkT}{V} \quad (12.97)$$

since  $F_{int}$  does not depend upon the pressure. Thus, the pressure of a gas does not depend upon the internal energy of the individual particles. The entropy of the system is given by

$$S = - \left( \frac{\partial F}{\partial T} \right)_{V,N} = Nk \left[ \ln V + \frac{3}{2} \ln kT - \ln N + \ln \zeta_{int} + \frac{3}{2} \ln \left( \frac{2\pi m}{h_o^2} \right) + 1 \right] + NkT \left[ \frac{3}{2} \frac{1}{T} + \frac{\partial \ln \zeta_{int}}{\partial T} \right]$$

which can be written

$$S = Nk \left[ \ln V + \frac{3}{2} \ln kT - \ln N + \ln \zeta_{int} + \frac{3}{2} \ln \left( \frac{2\pi m}{h_o^2} \right) + \frac{5}{2} \right] - \left( \frac{\partial F_{int}}{\partial T} \right)_{V,N} \quad (12.98)$$

The chemical potential is given by

$$\mu = \left( \frac{\partial F}{\partial N} \right)_{V,T} = - kT \left[ \ln V + \frac{3}{2} \ln kT - \ln N + \frac{3}{2} \ln \left( \frac{2\pi m}{h_o^2} \right) + 1 \right] - NkT \left[ - \frac{1}{N} \right] - kT \ln \zeta_{int}$$

which simplifies to

$$\mu = -kT \left[ \ln V + \frac{3}{2} \ln kT - \ln N + \frac{3}{2} \ln \left( \frac{2\pi m}{h_o^2} \right) \right] - kT \ln \zeta_{int} \quad (12.99)$$

or

$$\mu = -kT \ln \left[ \frac{V \zeta_{int}}{N} \left( \frac{2m\pi kT}{h^2} \right)^{3/2} \right] \quad (12.100)$$

which can be written as

$$\mu = -kT \ln \left[ \frac{V \zeta_{int}}{N v_Q} \right] \quad (12.101)$$

Notice that for a fixed temperature and volume, as the number of particles is increased, the chemical potential becomes less negative. Particles in a system always flow from higher chemical potential to lower chemical potential (from higher concentration to lower concentration).

## Appendix 12.1

### The Relationship between the Helmholtz Free Energy and the Partition Function

[Also do a proof based upon Schroeder, chapter 6, pages 247, 248]

In this appendix, we want to prove that the Helmholtz free energy  $F$  can be expressed by the equation

$$F = -kT \ln Z \quad (12.1)$$

where  $Z$  is the partition function. For this proof, we will use the integral representation of the partition function

$$Z = \int \frac{dp^{3N} dq^{3N}}{N! h_o^{3N}} e^{-\beta E(p,q)} \quad (12.2)$$

It is important to realize that the expression for the energy in this equation is a function *only* of the position and/or velocity of the particles making up the system. The expression for the energy is *not* explicitly a function of the temperature of the reservoir.

Our proof is equivalent to showing that the expression for  $Z$  in equation 1 is the same as that in equation 2, or

$$Z = e^{-\beta F(\beta,V,N)} = \int \frac{dp^{3N} dq^{3N}}{N! h_o^{3N}} e^{-\beta E(p,q)} \quad (12.3)$$

This latter equation can be written as

$$e^{+\beta F(\beta,V,N)} \int \frac{dp^{3N} dq^{3N}}{N! h_o^{3N}} e^{-\beta E(p,q)} = 1 \quad (12.4)$$

but, since the Helmholtz free energy is not explicitly a function of  $p$  and  $q$ , this last equation can be written as

$$\int \frac{dp^{3N} dq^{3N}}{N! h_o^{3N}} e^{-\beta[E(p,q)-F(\beta,V,N)]} = 1 \quad (12.5)$$

Taking the partial derivative of both sides of this last equation with respect to  $\beta$ , we obtain

$$\frac{\partial}{\partial \beta} \left\{ \int \frac{dp^{3N} dq^{3N}}{N! h_o^{3N}} e^{-\beta[E(p,q)-F(\beta,V,N)]} \right\} = 0 \quad (12.6)$$

$$\int \frac{dp^{3N} dq^{3N}}{N! h_o^{3N}} e^{-\beta[E(p,q)-F(\beta,V,N)]} \left[ -(F-E) - \beta \left( \frac{\partial F}{\partial \beta} - \frac{\partial E}{\partial \beta} \right) \right] = 0 \quad (12.7)$$

Since the energy is not explicitly a function of  $\beta$ , this last equation reduces to

$$-(F-E) - \beta \left( \frac{\partial F}{\partial \beta} \right)_{V,N} = 0 \quad (12.8)$$

We can write this in a little different fashion by noticing that

$$\left( \frac{\partial F}{\partial \beta} \right)_{V,N} = \left( \frac{\partial F}{\partial T} \right)_{V,N} \left( \frac{\partial T}{\partial \beta} \right)_{V,N} = \left( \frac{\partial F}{\partial T} \right)_{V,N} \left( -\frac{T}{\beta} \right) \quad (12.9)$$

from which we obtain

$$-(F-E) - \beta \left[ \left( \frac{\partial F}{\partial T} \right)_{V,N} \left( -\frac{T}{\beta} \right) \right] = -(F-E) + TS = 0 \quad (12.10)$$

or

$$F = E - TS \quad (12.11)$$

which is the Helmholtz free energy as we defined it previously.

### Appendix 12.2

If we use the probability of finding a subsystem  $A$  with energy  $E_r$ , volume  $V_r$ , and number of particles  $N_r$ , as

$$P_r = C e^{-\beta'[E_r + P'V_r - \mu'N_r]} \quad (12.12)$$

we can express the partition function

$$Z = \sum_r e^{-\beta'[E_r + P'V_r - \mu'N_r]} \quad (12.13)$$

as we pointed out earlier. However, we must remember that *the pressure in this expression is the pressure in the reservoir*, and  $P' dV$  of the reservoir is  $-P' dV$  for the small subsystem! An ill advised procedure of finding the average pressure of the subsystem is the following:

$$\frac{\partial Z}{\partial V} = \sum_r (-\beta P') e^{-\beta'[E_r + P'V_r - \mu'N_r]}$$

$$\frac{\partial Z}{\partial V} = -\beta Z \left\{ \frac{1}{Z} \sum_r P' e^{-\beta[E_r + P'V_r - \mu'N_r]} \right\} = -\beta Z \langle P' \rangle$$

so,

$$\langle P' \rangle = -\frac{1}{\beta Z} \frac{\partial Z}{\partial V} = -\frac{1}{\beta} \frac{\partial \ln Z}{\partial V} \quad (12.14)$$

This procedure would give the opposite sign we obtained in the development above, because we have erroneously worked with the pressure of the *reservoir*!

The probability of finding the subsystem with an energy value given by  $E_r$  is given by

$$P_r = C e^{-\beta E_r}$$

but  $E_r$  is a function of the number of particles  $N_r$  in the subsystem, the volume  $V_r$  of the subsystem, the entropy  $S_r$  of the subsystem, etc., Thus, we can write

$$P_r = C e^{-E_r(V_r, N_r, S_r)}$$

where

$$dE_r = \delta Q_r - \delta W_r + \mu dN_r = T_r dS_r - P_r dV_r + \mu dN_r$$

Notice that this is the first law equation which we derived at the very beginning when we assured that the system of interest is in contact with its surrounding (which could easily be the reservoir of the universe). This equation is valid. However, just as in the case at the beginning of the semester, the number of particles added to the system of interest are removed from the surroundings, so  $dN_r = -dN_{\text{surroundings}}$ ,  $dV_r = -dV_{\text{surroundings}}$ , etc.

**The following procedure is incorrect!**

### Work and the Average Pressure

If the system  $A$  can be characterized by some external parameter (the volume, an external electric or magnetic field, etc.), we can write the change in energy of the system in terms of this external parameter,

$$dE = \frac{\partial E}{\partial x} dx = -F_x dx \quad (12.15)$$

In general, this can be written

$$dE = \sum_i \frac{\partial E}{\partial x_i} dx_i \quad (12.16)$$

where the sum is over all the possible external parameters of interest. In the case where the external parameter is the position of the wall of the subsystem, or the volume, we have

$$dE = -P dV$$

Using the partition function

$$Z = \sum_r e^{-\beta E_r(V,N)} \quad (12.17)$$

we can determine the average pressure using the relationship  $P = -(\partial E/\partial V)_{S,N}$  and obtain

$$\langle P \rangle = \frac{1}{Z} \sum_r \left[ - \left( \frac{\partial E_r}{\partial V} \right)_{N,S} \right] e^{-\beta E_r} = \frac{1}{\beta Z} \left( \frac{\partial Z}{\partial V} \right)_{N,S}$$

or

$$\boxed{\langle P \rangle = \frac{1}{\beta} \frac{\partial \ln Z}{\partial V}} \quad (12.18)$$

**[NOTE: This last procedure is not correct! The temperature and volume are not independent, so that the partial of  $\beta$  with respect to volume is not, in general, zero! This process is designated as a constant entropy process, not a constant temperature process!]**

Notice that the average pressure which we have derived here is *not* the pressure of the reservoir used to derive the Boltzmann function. The average pressure calculated in *this* way is the actual pressure of the system of interest (see Appendix 12.1).

### The Average Chemical Potential

The average chemical potential can be found in a manner similar to the average pressure. Since

$$\mu = \left( \frac{\partial E}{\partial N} \right)_{S,V} \quad (12.19)$$

we can write

$$\langle \mu \rangle = \frac{1}{Z} \sum_r \left( \frac{\partial E_r}{\partial N} \right) e^{-\beta E_r} = - \frac{1}{\beta Z} \frac{\partial}{\partial N} Z \quad (12.20)$$

or

$$\boxed{\langle \mu \rangle = - \frac{1}{\beta} \frac{\partial \ln Z}{\partial N}} \quad (12.21)$$



**[Note: Again this is incorrect, because a change in the number of particles effects the change in the entropy of the system - these are *not* independent!]**

### The Partition Function and Classical Thermodynamics

**[Note: This would seem to be a nice way to derive things, but it is based upon the eroneous equations developed above, and is, therefore, invalid!]**

We have demonstrated that  $Z$  is a function of the temperature  $T$  (through  $\beta$ ) and any external system parameters (through the dependence of the energy of the system on these parameters), as well as the number of particles in the system, so that

$$Z = Z(\beta, V, N) \quad (12.22)$$

Taking the differential of the natural log of  $Z$ , then, we obtain

$$d(\ln Z) = \frac{\partial \ln Z}{\partial V} dV + \frac{\partial \ln Z}{\partial \beta} d\beta + \frac{\partial \ln Z}{\partial N} dN \quad (12.23)$$

or

$$d(\ln Z) = \beta \langle P \rangle dV - \langle E \rangle d\beta - \beta \langle \mu \rangle dN \quad (12.24)$$

This can be rewritten in terms of the change in the average internal energy by using the relation

$$d[\beta \langle E \rangle] = \beta [d\langle E \rangle] + \langle E \rangle d\beta \quad (12.25)$$

which gives

$$d(\ln Z) = \beta \langle \delta W \rangle - d[\beta \langle E \rangle] + \beta [d\langle E \rangle] - \beta \langle \mu \rangle dN \quad (12.26)$$

or, making use of the first law,

$$d(\ln Z + \beta \langle E \rangle) = \beta [\langle \delta W \rangle + \langle dE \rangle - \langle \mu \rangle dN] = \beta \langle \delta Q \rangle$$

This reduces to

$$d(\ln Z + \beta \langle E \rangle) = \frac{\langle \delta Q \rangle}{kT} = \frac{\langle dS \rangle}{k} \quad (12.27)$$

from which we obtain

$$\boxed{\langle S \rangle \equiv k(\ln Z + \beta \langle E \rangle)}$$

If we multiply this last equation by the temperature  $T$ , we obtain

$$T \langle S \rangle = kT \ln Z + \langle E \rangle \quad (12.28)$$

from which we obtain

$$\boxed{F \equiv \langle E \rangle - T \langle S \rangle = -kT \ln Z} \quad (12.29)$$

where we have used our previous definition of the Helmholtz free energy  $F$ .

From our earlier development, we found:

$$\left( \frac{\partial F}{\partial T} \right)_{V,N} = -S \quad \left( \frac{\partial F}{\partial V} \right)_{T,N} = -P \quad \left( \frac{\partial F}{\partial N} \right)_{V,T} = \mu \quad (12.30)$$

This means that by using the relationship  $F = -kT \ln Z$ , we can easily determine the pressure, the entropy, and the chemical potential of a system from a knowledge of the partition function. In addition, we can determine the

average energy from the equation

$$\langle E \rangle = - \frac{\partial}{\partial \beta} \ln Z \quad (12.31)$$