

CHAPTER 2

THE MICROSCOPIC PERSPECTIVE

Classical thermodynamics is self-contained and free-standing. It needs no assumptions regarding the ultimate nature of matter for its development or its application to practical problems. These are its cardinal virtues, and they provide the basis for the certitude its statements are accorded in science and engineering. However, the avoidance of theory which gives rise to this certitude produces what might be considered a shortcoming — an inability to provide insights into the ultimate nature of things. With thermodynamics we have learned to successfully correlate the variables of a system. We may be able to predict *what* will happen, but without theoretical insight we can not say *how* it happened.

In order to provide this insight, particularly in regard to the ultimate basis and interpretation of the laws and variables of classical thermodynamics, statistical mechanics came into being. At its inception in the mid-nineteenth century, statistical mechanics dealt with the application of statistical methods to systems containing an enormous number of particles in continuous motion. The motion and resulting collisions were assumed to conform to the laws of classical mechanics.

This approach yielded useful results, but it was found that quantum mechanics, developed in the early years of the twentieth century, was superior to classical mechanics in dealing with the behavior of these extremely small particles. While today the quantum mechanical view is universally accepted, there are some systems that can be adequately described by classical mechanics. These instances can be regarded as special limiting cases where the more-general quantum mechanics reduces to classical mechanics.

Quantum statistical mechanics has been successfully applied to a wide variety of systems, however, here we will be interested only in applications that bear upon the thermodynamic variables: energy, entropy, and temperature. Also, we will examine the simplest possible system — a monatomic ideal gas. The approach is intended to be heuristic rather than rigorous and the results will be gleaned for insight from the microscopic perspective.

2.1 FUNDAMENTAL CONCEPTS

Quantization of energy is the salient feature that distinguishes quantum mechanics from classical mechanics. The energy levels permissible to any molecule or atom are noncontinuous and are characterized by a set of discrete quantum numbers. These are the energy levels, or eigenvalues, for which it is possible to obtain solutions of the Schrödinger equation. For a particle in a box of dimensions L_x , L_y , and L_z , the permissible levels of translational energy are given by

$$e = \frac{h^2}{8m} \left(\frac{n_x^2}{L_x^2} + \frac{n_y^2}{L_y^2} + \frac{n_z^2}{L_z^2} \right) \quad (2-1)$$

where h is Planck's constant, m is the particle mass, and n_x , n_y , and n_z are the quantum numbers. These numbers are integers ranging from unity to extremely large values. Because extremely large values of the n 's are necessary in order to yield the energy levels accessible to a single particle, the energy difference between successive quantum states is extremely small. This means that an extremely large number of translational quantum states is available to a particle (atom or molecule). In addition, the particle's quantum state is continually changing as a result of collisions.

A system of thermodynamic interest will contain on the order of 10^{23} particles and, if frozen at a given instant, could be represented by a distribution of the many particles among the even more abundant permissible quantum states. Clearly, if thermodynamic properties are to be calculated, it will be necessary to resort to statistical methods based on probabilities.

In assigning probabilities to quantum states, the following rules are followed

- 1) quantum states of equal energy, e , have equal probabilities.
- 2) the statistical weight of a quantum state depends on its energy and is proportional to $\exp(-e/kT)$.

These statements are the basic postulates of quantum statistical mechanics.¹

¹ Actually, only statement 1 is a basic postulate. Statement 2 can be derived from it if one assumes that the weight of a state depends only on its energy. See, for example, K. Denbigh, *Principles of Chemical Equilibrium*, 3rd ed., Cambridge University Press, Cambridge, 1971, Chap. 11.

From these we determine the probability of finding a particle in its i th quantum state as

$$p_i = \frac{\exp(-e_i/kT)}{\sum \exp(-e_i/kT)} \quad (2-2)$$

The summation in the denominator is taken over all quantum states and is a normalizing factor needed to make the sum of the probabilities over all states equal to unity. This sum will be denoted by z and is called the particle partition function.

$$z = \sum \exp(-e_i/kT) \quad (2-3)$$

The assembly of particles may be described in a different manner using the concept of assembly quantum states. At any instant, the distribution of the N particles among their permissible quantum states can be considered to constitute a single quantum state of the assembly. The assembly quantum state is characterized by the total energy of the assembly. For an assembly of non-interacting particles, such as an ideal gas, the total energy is merely the sum of all the individual particle energies; for systems of interacting particles a potential energy term must be included. Due to the large number of particles and the large number of permissible particle quantum states, the number of assembly quantum states can be expected to be enormous. Because each collision changes the quantum states of two particles, the assembly quantum state is forever changing in an apparently chaotic manner.

To calculate thermodynamic properties using the concept of assembly quantum states, probabilities are determined according to the following rules which closely resemble those applied to a single particle

- 1) assembly quantum states of equal energy E have equal probabilities.
- 2) the statistical weight of an assembly quantum state depends on its energy E and is proportional to $\exp(-E/kT)$.

Again, these statements are simply basic postulates that can not be proven but are justified by the success of the relations deriving from them. The overwhelming success of quantum statistical mechanics gives us no cause for doubt. With these rules, we write for the probability of an assembly quantum state

$$P_i = \frac{\exp(-E_i/kT)}{\sum \exp(-E_i/kT)} \quad (2-4)$$

As before, the denominator normalizes the probabilities and is the assembly partition function denoted by Z

$$Z = \sum \exp(-E_i / kT) \quad (2-5)$$

The derivation of thermodynamic properties can be based on either the particle or the assembly view; here we find it more convenient to use the latter. The total energy of the assembly can be identified with the internal energy of thermodynamics and written in terms of the probabilities and energies of the assembly quantum states as

$$U = \sum P_i E_i \quad (2-6)$$

Alternatively, it can be expressed in terms of the partition function as²

$$U = kT^2 \left(\frac{\partial \ln Z}{\partial T} \right)_v \quad (2-7)$$

Inspection of Eqs. (2-6) and (2-7) suggests that it is possible through quantum statistical mechanics to determine absolute values of the internal energy while classical thermodynamics is capable of dealing only with its changes. This is not the case! Even though one consistently finds U instead of ΔU in the literature of quantum statistical mechanics, it must be understood that E_i is the energy of an assembly quantum state relative to an unknown zero-level value. If the E_i in Eqs. (2-4)—(2-6) were replaced with $E'_i - E_0$, where E'_i is the absolute value and E_0 the zero level value, it is easy to show³ that the left-hand side of Eq. (2-6) becomes the internal energy change between the zero level and the state under consideration.

Equation (2-7) shows that the partition function links the microscopic and macroscopic realms and from this equation we can obtain other thermodynamic properties using the thermodynamic network. For the entropy, we obtain⁴

$$S = S_0 + k \ln Z + kT \left[\frac{\partial \ln Z}{\partial T} \right]_v \quad (2-8)$$

² For details see Appendix 2A.

³ See Appendix 2B.

⁴ For the derivation of Eq. (2-8) see Appendix 2C.

The integration constant S_0 must now be determined. For all systems amenable to treatment by quantum statistical mechanics, it has been found that a single quantum state exists at the lowest energy level ($Z = 1$) and thus $S = S_0$ at zero absolute temperature. Although there is no general proof of this nondegeneracy, Schrödinger has shown⁵ that if the first n quantum states are of equal energy (where n is a number comparable to Avogadro's number) the last two right-hand terms of Eq. (2-8) are very close to zero. Setting $S = S_0$ seems reasonable and if we invoke the third law of thermodynamics by setting S equal to zero at zero T , S_0 becomes zero and Eq. (2-8) simplifies to

$$S = k \ln Z + kT \left[\frac{\partial \ln Z}{\partial T} \right]_v \quad (2-9)$$

Equations relating other thermodynamic properties to the partition function can be derived, however, here our interest is only in the energy and the entropy. The more familiar expression

$$S = -k \sum P_i \ln P_i \quad (2-10)$$

can be obtained by manipulating Eq. (2-9)⁶.

For an isolated system, the energy remains constant and hence, according to our first postulate, all quantum states are equally likely. If there is a total of Ω permissible assembly quantum states, the probability of any one of these states will be $1/\Omega$ and Eq. (2-10) becomes

$$S = k \ln \Omega \quad (2-11)$$

This is the equation upon which almost all attempts to obtain a physical picture of entropy are based.

2.2 THE MICROSCOPIC VIEW

2.2.1 Energy. We define energy as a measure of the capacity of a system for change. The system can be of any size ranging from the Universe down to a single subatomic particle. We also know that energy exists in different forms which are interconvertable although we are unable to explicate the mechanism for its conversion. The reason for this lack of detailed understanding is that

⁵ E. Schrödinger, *Statistical Thermodynamics*, Cambridge University Press, Cambridge, 1960, Chap. 3.

⁶ See Appendix 2D for details of this transformation.

energy is one of our fundamental physical concepts; we may explain phenomena in terms of energy but can not explain energy. If we were able to explain it, our explanation would have to be in terms of something more fundamental, but there is nothing more fundamental. In spite of our inability to explain it, we have a reasonably good sense of what it is and have learned to use it as a useful concept in dealing with physical systems. The microscopic view has contributed very little to our understanding of energy.

2.2.2 Temperature. In our development of quantum statistical mechanics, it was simply stated that the weighing factor for different energy states contained the absolute temperature. In a more rigorous development, this weighting factor can be derived using only the postulate of equal probabilities for states of equal energy. In this derivation, the absolute temperature is identified when the final results are compared with various thermodynamic functions. Thus, there is no special microscopic vantage point from which we can obtain a more enlightened view of temperature.

2.2.3 Entropy. When written for a change of state within an isolated system, Eq. (2-11) becomes

$$S_2 - S_1 = k \ln \frac{\Omega_2}{\Omega_1} \quad \text{(2-11a)}$$

and because we must have $S_2 > S_1$, we conclude that $\Omega_2 > \Omega_1$. Thus, an increase in entropy is interpreted microscopically as an increase in Ω , the total number of permissible quantum states. The system moves in the direction of more possibilities, or it can be said that there is a spreading of the system among quantum states.

Entropy is often identified with disorder even though the terms order and disorder are neither precise nor objective. From a microscopic viewpoint the association of a positive entropy change with an increase in disorder seems quite reasonable for a phase change or mixing process. For other processes, the association is less obvious and for at least one process (the adiabatic crystallization of a subcooled liquid) it fails completely.⁷ Another complication arises with the disorder interpretation of entropy when we recall that entropy is defined only for an equilibrium state and therefore Ω_1 and Ω_2 refer to equilibrium states. The accepted microscopic view of an equilibrium state entails complete

⁷ See Ex. 4-1 of this textbook.

randomness with regard to particle motion — chaos or maximum disorder. It therefore seems inappropriate to regard $\Omega_2 > \Omega_1$ as representing an increase in disorder when each state would represent maximum disorder. It is clear that the entropy-as-disorder view is flawed and can lead to ambiguous or erroneous interpretations.

There is another difficulty associated with using Ω to obtain a physical microscopic interpretation of entropy; it is not based on virtual observables such as positions and velocities. The significance of Ω is not found on a purely physical level but rather in terms of something which can exist only in the mind — the permissible number of quantum states. This concept comes into being only when we move further into the mental realm and begin to translate the physical into the mathematical description — Ω is a parameter in our model of the system. Rudolf Carnap⁸ seems to have had this in mind when he stated that the statistical concept of entropy is a logical instead of a physical concept.

2.3 THE IDEAL MONATOMIC GAS

2.3.1 A Naive Approach. An ideal gas has no interaction energy and therefore the energy of any assembly quantum state, E_i , is simply the sum of the energies of the particle quantum states at that instant

$$E_i = \sum_{j=1}^N e_j \quad (2-12)$$

where e_j is the energy of the quantum state in which we find the j^{th} particle and the summation is taken over all particles. When Eq. (2-12) is substituted into Eq. (2-5), the assembly partition function is

$$Z = \sum \exp \left(- \sum_{j=1}^N e_j / kT \right) \quad (2-13)$$

which can be shown⁹ to be

$$Z = z^N \quad (2-14)$$

⁸ P.A. Schilpp, ed., *The Philosophy of Rudolf Carnap*, The Open Court Publishing Co., La Salle, IL, 1963, p. 37.

⁹ See Appendix 2E for details.

Using Eq. (2-1) for the particle quantum numbers one obtains, after some mathematical manipulation, the assembly partition function in terms of the system variables¹⁰

$$Z = z^N = V^N \left(\frac{2\pi mkT}{h^2} \right)^{3N/2} \quad (2-15)$$

and through the application of Eqs. (2-7) and (2-9) one also obtains the internal energy

$$U = \frac{3}{2} NkT \quad (2-16)$$

and entropy

$$S = Nk \left[\ln V + \frac{3}{2} \ln \left(\frac{2\pi kmT}{h^2} \right) + \frac{3}{2} \right] \quad (2-17)$$

From U and S we may determine the Helmholtz Free Energy.

$$A = U - TS = -NkT \left[\ln V + \frac{3}{2} \ln \left(\frac{2\pi kmT}{h^2} \right) \right] \quad (2-18)$$

and use the relation $(\partial A / \partial V)_T = -P$ to obtain the equation of state

$$\left(\frac{\partial A}{\partial V} \right)_T = -P = -\frac{NkT}{V} \quad (2-19)$$

The number of particles N can be expressed as the product of the number of mols n and Avogadro's number \mathbf{N} . Using the relation $\mathbf{N}k = R$, these results can be restated

$$U = \frac{3}{2} nRT \quad (2-16a)$$

$$S = nR \ln V + \frac{3}{2} nR \ln T + S_0 \quad (2-17a)$$

$$PV = nRT \quad (2-19a)$$

Equation (2-16) was derived on the basis that only translational energy need be considered. While this is believed to be the only type of energy subject to change in a physical process, the monatomic gas atoms may possess other types of energy (e.g., energy associated with internal states of the atom) whose unknown

¹⁰ See Appendix 2F for details.

values do not allow us to assign an absolute value to the internal energy. As previously shown, it is therefore more appropriate to write Eq. (2-16a) for a change in state

$$U_2 - U_1 = \frac{3}{2} nR(T_2 - T_1) \quad (2-16b)$$

For a gram atom of gas ($n = 1$) we have

$$u_2 - u_1 = \frac{3}{2} R(T_2 - T_1) \quad (2-16c)$$

Because the constant volume heat capacity of a monatomic gas has been found to be constant and equal to $3/2 R$, perfect agreement exists here between thermodynamic results and the results of quantum statistical mechanics as is also the case for the equation of state.

If we use Eq. (2-17a) to represent the entropy change of a gram atom of gas undergoing a change in volume and temperature, we obtain

$$S_2 - S_1 = R \ln \frac{V_2}{V_1} + C_V \ln \frac{T_2}{T_1} \quad (2-17b)$$

which is exactly the thermodynamic expression for an ideal gas with constant heat capacity.

Thus, it would appear that what we have called the naive approach to the application of quantum statistical mechanics to a monatomic ideal gas has been outstandingly successful. Actually, this success is only partial because there are two applications of Eq. (2-17) that do not fit the facts: absolute entropies are in error and the equation yields a nonzero entropy change when two portions of the same gas are mixed. The key to the difficulty lies in the second problem.

For the isothermal mixing of two quantities of the same gas, we write

$$\begin{aligned} V_{12} &= V_1 + V_2 \\ N_{12} &= N_1 + N_2 \\ \Delta S &= S_{12} - S_1 - S_2 \end{aligned}$$

and use Eq. (2-17) for the entropies

$$\Delta S = k \left[(N_1 + N_2) \ln (V_1 + V_2) - N_1 \ln V_1 - N_2 \ln V_2 \right]$$

If two 1/2-mol quantities are combined, we have

$$N_1 = N_2 = \frac{N}{2}; \quad N_{12} = N$$

and can simplify the expression for ΔS to

$$\Delta S = k [N] = R \ln 2$$

This is the entropy change on mixing as given by Eq. (14-22) of this textbook, however, we do not expect an entropy change on mixing the same gas. This problem is sometimes identified as the Gibb's paradox¹¹ although it can be considered a special case of the mixing paradox which will be dealt with in chapter 7 of this essay.

2.3.2 A Forced Fit. The unfortunate result of a nonzero entropy change for mixing the same gas can be remedied by writing the assembly partition function as

$$Z = \frac{V^N}{N!} \left(\frac{2\pi mkT}{h^2} \right)^{3N/2} \quad \text{(2-20)}$$

where it is seen that this is merely the previous (or naive) partition function, Eq. (2-15), divided by N factorial. This adjustment can be justified by considering the particles of the gas to be indistinguishable instead of distinguishable as we tacitly assumed in evaluating the partition function as expressed by Eq. (2-15). When we evaluated Eq. (2-13), we considered all possible assembly quantum states defined by Eq. (2-12). Thus, if two particles switched quantum states, we would have identified two different assembly quantum states. But if we could not distinguish the particles, we wouldn't have noticed the switch and therefore would have seen only a single quantum state. We have therefore used too many assembly quantum states in evaluating the partition function. We have used permutations to determine the number of assembly quantum states when we should have used combinations and therefore we correct the situation by dividing by N factorial.

Using Eq. (2-20) in Eqs. (2-7) and (2-9) we obtain, as before, Eq. (2-16) for the internal energy and Eq. (2-19) for the equation of state but for the entropy obtain¹²

¹¹ E. Schrödinger, *Statistical Thermodynamics*, Cambridge University Press, Cambridge, 1960, Chap. 8.

¹² Use is made of Stirling's approximation $\ln N! = N \ln N - N$

$$S = Nk \left[\ln \frac{V}{N} + \frac{3}{2} \ln \left(\frac{2\pi mkT}{h^2} \right) + \frac{5}{2} \right] \quad (2-21)$$

For changes involving constant N , this equation reduces to Eq. (2-17b); further, it yields the correct absolute entropies and yields zero entropy change on mixing the same gas.

The classical statistical mechanical treatment of the monatomic ideal gas yielded an entropy expression equivalent to Eq. (2-17). Gibbs¹³ recognized the need for the inclusion of $N!$ into the assembly partition function and justified it on the basis that the interchange of like particles should be of no statistical consequence. Yet, Gibbs still held the classical notion that the particles were distinguishable. He believed that the particles obeyed the laws of classical mechanics and, despite the impossible computational difficulties, were in principle traceable and hence identifiable. Today, in the age of quantum physics, it is essential to specify whether or not the constituent particles of a system are distinguishable. For a single-component system, only those particles which can be tied to a spatial location, such as a crystal lattice, can be considered distinguishable.

We have noted that the naive approach gives the correct results for internal energy and the equation of state as well as entropy changes in a system of constant N . However, in order to bring the statistical entropy into complete agreement with known thermodynamic results, it was necessary to introduce the concept of particle indistinguishability. Again, it appears that in order to deal successfully with entropy it is necessary to go a step beyond a description of the system in terms of virtual observables. Instead of a model involving only physical quantities, we have considered factors such as distinguishability which arise from our mathematical treatment and exist only in the mind of the model maker. The focus has been shifted from the system to our representation of the system¹⁴ — again a move from the physical to the logical realm.

¹³J.W. Gibbs, *Elementary Principles of Statistical Mechanics*, Yale University Press, Dover ed., 1960, p. 187.

¹⁴This has been the direction taken by modern physics. Heisenberg has stated that quantum mechanics does not deal with systems but with our description of systems.

2.4 A CAVEAT

In this chapter, our interest has been directed toward applications of quantum statistical mechanics that would provide us with a microscopic interpretation of entropy and we have seen that the results leave something to be desired. Thus, it is quite possible that the reader will obtain a negative impression and form the opinion that quantum statistical mechanics is of little value. This is most definitely not the case! The onus for this incongruity should not be placed on quantum statistical mechanics but rather on the manner in which entropy is defined (more about this later). Moreover, quantum statistical mechanics has yielded many fruitful results covering a wide variety of systems and often its results and calculation methods are preferred to those of classical thermodynamics.¹⁵

¹⁵ An example is the calculation of absolute entropies and other thermodynamic properties of ideal gases.

APPENDIX 2A
The relationship between U and Z

Combining Eqs. (2-4) and (2-6) yields

$$U = \frac{\sum E_i \exp(-E_i/kT)}{\sum \exp(-E_i/kT)} \quad (2-22)$$

Recognizing that

$$kT^2 \frac{d}{dT} \exp(-E_i/kT) = E_i \exp(-E_i/kT)$$

we can write Eq. (2-22) as

$$U = \frac{kT^2 \frac{d}{dT} \sum \exp(-E_i/kT)}{\sum \exp(-E_i/kT)}$$

or

$$U = \frac{kT^2}{Z} \left(\frac{dZ}{dT} \right) = kT^2 \left(\frac{\partial \ln Z}{\partial T} \right)_V \quad (2-23)$$

The condition of constant volume has been specified for the derivative in Eq. (2-23) because, in general, E may depend upon the volume¹⁶ and the differentiation step leading to Eq. (2-23) is valid only for constant E , hence constant V .

¹⁶ For example, Eq. (2-1) shows the particle quantum states to depend on the volume $L_x L_y L_z$.

APPENDIX 2B

No absolute value for internal energy

The E_i previously used is actually $E_i' - E_o$, where E_i' is the absolute, but unknown, value and E_o , is what was taken as the zero-level value. The energy of a quantum state is actually $E_i' = E_i + E_o$ and the partition function is

$$Z' = \sum e^{-(E_i + E_o)/kT}$$

or

$$Z' = e^{-E_o/kT} \sum e^{-E_i/kT}$$

which can be written as

$$Z' = (e^{-E_o/kT}) Z$$

or as

$$\ln Z' = \frac{-E_o}{kT} + \ln Z$$

where Z and Z' are based on E_i and E_i' respectively. If we now differentiate with respect to T and multiply the result by kT^2 , we obtain

$$kT^2 \left(\frac{\partial \ln Z'}{\partial T} \right)_V = E_o + kT^2 \left(\frac{\partial \ln Z}{\partial T} \right)_V$$

Identifying the left-hand term with U' , the absolute value of U , we obtain

$$U = U' - U_o = kT^2 \left(\frac{\partial \ln Z}{\partial T} \right)_V$$

and see that U is relative and not absolute.

APPENDIX 2C

Derivation of Eq. (2-8) from Eq. (2-7)

The heat capacity C_v can be obtained from the internal energy U as expressed by Eq. (2-7)

$$C_v = \left(\frac{\partial U}{\partial T} \right)_v = k \frac{\partial}{\partial T} \left[T^2 \left(\frac{\partial \ln Z}{\partial T} \right)_v \right]_v$$

which yields

$$C_v = 2kT \left(\frac{\partial \ln Z}{\partial T} \right)_v + kT^2 \left(\frac{\partial^2 \ln Z}{\partial T^2} \right)_v$$

For a constant-volume process, we may write

$$dS = \frac{C_v dT}{T} = 2k \left(\frac{\partial \ln Z}{\partial T} \right)_v dT + kT \left(\frac{\partial^2 \ln Z}{\partial T^2} \right)_v dT$$

and integrate to obtain

$$S = S_o + 2k \int \frac{d \ln Z}{dT} dT + k \int T \frac{d}{dT} \left(\frac{d \ln Z}{dT} \right) dT$$

or

$$S = S_o + 2k \int d \ln Z + k \int T d \left(\frac{d \ln Z}{dT} \right)$$

Integrating the second integral by parts gives

$$S = S_o + 2k \ln Z + kT \frac{d \ln Z}{dT} - k \ln Z$$

which reduces to the final result

$$S = S_o + k \ln Z + kT \left(\frac{\partial \ln Z}{\partial T} \right)_v$$

APPENDIX 2D

Derivation of Eq. (2-10) from Eq. (2-9)

In establishing the equivalence of Eqs. (2-9) and (2-10), it is convenient to begin with Eq. (2-10) and use Eqs. (2-4) and (2-5) for P_i and Z respectively.

$$\begin{aligned}\Sigma P_i \ln P_i &= \Sigma \frac{\exp(-E_i/kT)}{Z} \left[-\frac{E_i}{kT} - \ln Z \right] \\ \Sigma P_i \ln P_i &= -\Sigma \frac{E_i \exp(-E_i/kT)}{kTZ} - \frac{\ln Z}{Z} \Sigma \exp(-E_i/kT)\end{aligned}$$

From Eq. (2-22) the first right-hand summation is seen to be U/kT . The second summation is Z , therefore

$$\Sigma P_i \ln P_i = -\frac{U}{kT} - \ln Z = -\frac{1}{k} \left[\frac{U}{T} + k \ln Z \right]$$

Substituting for U as given by Eq. (2-7) yields

$$\Sigma P_i \ln P_i = -\frac{1}{k} \left[kT \left(\frac{\partial \ln Z}{\partial T} \right)_V + k \ln Z \right]$$

From Eq. (2-8) the bracketed term is seen to be S and we write

$$S = -k \Sigma P_i \ln P_i$$

APPENDIX 2E

Relating the assembly and particle partition functions

Consider the simplest case of only two particles identified with subscripts i and j . The assembly partition function can be written

$$Z = \sum \exp \left[- \frac{(e_i + e_j)}{kT} \right]$$

For simplicity let

$$\frac{e_i}{kT} = x_i \text{ 56 and } \frac{e_j}{kT} = y_j \text{ 57}$$

and note that

$$Z = \sum e^{-x_i - y_j} = \sum e^{-x_i} e^{-y_j}$$

We will write out a few terms in the summation which is taken over all possible combinations of i and j

$$\begin{aligned} Z = & e^{-x_1} e^{-y_1} + e^{-x_1} e^{-y_2} \dots + e^{-x_1} e^{-y_j} + \dots \\ & e^{-x_2} e^{-y_1} + e^{-x_2} e^{-y_2} \dots + e^{-x_2} e^{-y_j} + \dots \\ & \dots + e^{-x_i} e^{-y_1} + e^{-x_i} e^{-y_2} \dots + e^{-x_i} e^{-y_j} + \dots \end{aligned}$$

The summation can be rearranged to

$$\begin{aligned} Z = & e^{-x_1} (e^{-y_1} + e^{-y_2} \dots + e^{-y_j} + \dots) + \\ & e^{-x_2} (e^{-y_1} + e^{-y_2} \dots + e^{-y_j} + \dots) \dots + \\ & e^{-x_i} (e^{-y_1} + e^{-y_2} \dots + e^{-y_j} + \dots) + \dots \end{aligned}$$

which becomes

$$Z = (e^{-x_1} + e^{-x_2} \dots + e^{-x_i} + \dots) (e^{-y_1} + e^{-y_2} \dots + e^{-y_j} + \dots)$$

or

$$Z = \sum_i e^{-x_i} \left(\sum_j e^{-y_j} \right)$$

Because the two particles are identical, we can write

$$Z = \left[\sum \exp \left(- \frac{e_i}{kT} \right) \right]^2 = z^2$$

which on generalizing becomes

$$Z = z^N$$

APPENDIX 2F

In evaluating the particle partition function z , we note that a monatomic gas can possess only translational energy and observe from Eq. (2-1) that the components of translational energy are independent (i.e., the quantum numbers n_x , n_y , and n_z are independent). This allows us to write

$$z = \Sigma \exp \left[- \frac{(e_x + e_y + e_z)}{kT} \right]$$

and by analogy with the mathematics that led from Eq. (2-13) to Eq. (2-14) we may write

$$z = z_x z_y z_z$$

Using Eq. (2-1) the particle partition function for x-translational energy is

$$z_x = \Sigma \exp \left(- \frac{h^2 n_x^2}{8 m L_x^2 kT} \right)$$

The summation is taken over all values of n_x and, as we have previously noted, quite large values of n_x are involved with extremely small spacing between energy levels. Thus, the summation may be closely approximated by the integral

$$z_x = \int_0^{\infty} \exp \left(- \frac{n_x^2 h^2}{8 m L_x^2 kT} \right) dn_x$$

which has the value¹⁷

$$z_x = \left(\frac{2\pi m k T L_x^2}{h^2} \right)^{1/2}$$

The particle partition function now becomes

$$z = z_x z_y z_z = V \left(\frac{2\pi m k T}{h^2} \right)^{3/2}$$

where the product $L_x L_y L_z$ has been replaced with V , the volume of the box. The assembly partition function is now

¹⁷ Details of this integration are provided by G.S. Rushbrooke, *Introduction to Statistical Mechanics*, Oxford University Press, London, 1949, Chap. 3.

$$Z = z^N = V^N \left(\frac{2\pi mkT}{h^2} \right)^{3N/2}$$