

Ideal Quantum Gases

Out of perfection nothing can be made. Every process involves breaking something up.

Joseph Campbell

This chapter discusses the theory of ideal quantum gases. It develops general equations that will be valid for gases that consist of either bosons or fermions. Since the consequences of these equations are both non-trivial and very different for the two cases of bosons and fermions, the details of each of these cases will be dealt with in subsequent chapters.

This chapter will also discuss the interesting case of a quantum gas of distinguishable particles. Although all atoms are either bosons or fermions, and therefore indistinguishable, there are nevertheless real systems that are composed of distinguishable particles. In particular, colloidal particles can each be composed of about 10^9 molecules. The number of molecules in each particle will vary, as will the arrangement and number of each type of molecule. In short, while the particles in a colloid might be similar in size and composition, they do not have identical properties and they are not indistinguishable. While the properties of colloids can usually be obtained accurately using classical statistical mechanics, it is also of interest to see how quantum mechanics might affect the results.

We begin in the next section by discussing many-particle quantum states, which are needed to describe a macroscopic quantum system.

27.1 Single-Particle Quantum States

As is the case for most of statistical mechanics, we would like to put the theory of ideal quantum gases into a form that allows us to factorize the partition function. For ideal gases, that points to building up the macroscopic state in terms of single-particle states, which will then lead to such a factorization.

Consider a quantum ideal gas in a box of volume V . For simplicity, we will assume that the box is cubic, with length L , so that $V = L^3$. The sides of the box will be assumed to be impenetrable, also for simplicity.

For quantum ideal gases, we can write the Hamiltonian of a single particle of mass m as

$$H = \frac{|\vec{p}|^2}{2m} = -\frac{\hbar^2}{2m} \vec{\nabla}^2, \quad (27.1)$$

where

$$\vec{\nabla} = \left(\frac{\partial}{\partial x}, \frac{\partial}{\partial y}, \frac{\partial}{\partial z} \right). \quad (27.2)$$

The eigenfunctions of eq. (27.1) can be written in a form that is very similar to that of the electric field for the black-body problem in eq. (25.5), but is even simpler because the wave function ψ is a scalar, while the electric field is a vector

$$\psi_{\vec{k}}(\vec{r}) = \sqrt{\frac{8}{L^3}} \sin(k_x x) \sin(k_y y) \sin(k_z z). \quad (27.3)$$

(The derivation of the normalization constant is left to the reader.)

The wave numbers in eq. (27.3) are determined by the condition that the wave function vanishes at the boundaries

$$k_x = \frac{n_x \pi}{L} \quad (27.4)$$

$$k_y = \frac{n_y \pi}{L} \quad (27.5)$$

$$k_z = \frac{n_z \pi}{L}. \quad (27.6)$$

If the values of n_x , n_y , and n_z are integers, the boundary conditions are fulfilled. Since the overall sign of the wave function is unimportant, negative values of these integers do not represent distinct states; only non-zero, positive integers represent physically distinct states. The wave equation can also be written in terms of the values of $\vec{n} = \{n_x, n_y, n_z\}$,

$$\psi_{\vec{n}}(\vec{r}) = \sqrt{\frac{8}{L^3}} \sin\left(\frac{n_x \pi}{L} x\right) \sin\left(\frac{n_y \pi}{L} y\right) \sin\left(\frac{n_z \pi}{L} z\right). \quad (27.7)$$

The energy eigenvalues for a single-particle state are easily found,

$$H\psi_{\vec{k}}(\vec{r}) = -\frac{\hbar^2}{2m} \vec{\nabla}^2 \psi_{\vec{k}}(\vec{r}) = \frac{\hbar^2}{2m} (k_x^2 + k_y^2 + k_z^2) \psi_{\vec{k}}(\vec{r}) = \epsilon_{\vec{k}} \psi_{\vec{k}}(\vec{r}) \quad (27.8)$$

$$\epsilon_{\vec{k}} = \frac{\hbar^2}{2m} (k_x^2 + k_y^2 + k_z^2) = \frac{\hbar^2 \pi^2}{2mL^2} (n_x^2 + n_y^2 + n_z^2) = \epsilon_{\vec{n}}. \quad (27.9)$$

(The symbol ϵ will be reserved for the energies of single-particle states, or single-particle energy levels, while E will be used for the energy of an N -particle state.)

If we define

$$k^2 = k_x^2 + k_y^2 + k_z^2, \quad (27.10)$$

and

$$n^2 = n_x^2 + n_y^2 + n_z^2, \quad (27.11)$$

we can express eq. (27.9) more compactly,

$$\epsilon_{\vec{k}} = \frac{\hbar^2}{2m} k^2 = \frac{\hbar^2 \pi^2}{2mL^2} n^2 = \epsilon_{\vec{n}}. \quad (27.12)$$

Eq. (27.9) gives the single-particle energy eigenvalues for a particle in a three-dimensional, cubic box with sides of length L . This is the case on which we will concentrate. However, since we can preserve generality with little cost, I will replace the quantum number vector \vec{n} with a general quantum number α for most of the rest of this chapter. This means that the equations in this chapter will be valid for any system of non-interacting particles, even if those particles are moving in an external potential.

The energy eigenstates in eq. (27.9) are often called ‘orbitals’ for historical reasons; the early work on fermions concentrated on electrons orbiting around a nucleus, which led to the use of the term. It might seem strange to see the term ‘orbitals’ when nothing is orbiting, but tradition is tradition. I will refer to them as single-particle states, which is less compact, but also (I believe) less confusing.

27.2 Density of Single-Particle States

Just as we needed the photon density of states to calculate the properties of black bodies, we will need the single-particle density of states to calculate the properties of a system of particles.

The density of states in \vec{n} -space is easy to find. Since there is one state at every point with integer components, the density of states is 1. To calculate the density of states as a function of energy, we make a transformation using a Dirac delta function, following the methods developed in Chapter 5:

$$D(\epsilon) = \int_0^\infty dn_x \int_0^\infty dn_y \int_0^\infty dn_z \delta(\epsilon - \epsilon_{\vec{n}}) \quad (27.13)$$

$$\begin{aligned}
&= \frac{1}{8} \int_0^\infty 4\pi n^2 dn \delta \left(\epsilon - \frac{\hbar^2 \pi^2}{2mL^2} n^2 \right) \\
&= \frac{\pi}{4} \left(\frac{2mL^2}{\hbar^2 \pi^2} \right)^{3/2} \int_0^\infty x^{1/2} dx \delta(\epsilon - x) \\
&= \frac{V}{4\pi^2} \left(\frac{2m}{\hbar^2} \right)^{3/2} \epsilon^{1/2}.
\end{aligned}$$

In the third line of eq. (27.13) we introduced a new variable of integration:

$$x = \left(\frac{\hbar^2 \pi^2}{2mL^2} \right) n^2. \quad (27.14)$$

In the fourth line of eq. (27.13) we replaced L^3 by the volume of the system, $V = L^3$.

Eq. (27.13) is valid for non-interacting fermions, bosons, or distinguishable particles (without spin). It will play a central role in Chapters 28, 29, and 30.

27.3 Many-Particle Quantum States

An N -particle wave function can be constructed from eq. (27.3) by multiplying single-particle wave functions,

$$\psi_N = \prod_{j=1}^N \psi_{\alpha_j}(\vec{r}_j). \quad (27.15)$$

In this equation, α_j represents the quantum number(s) that describe the wave function for the j -th particle.

Eq. (27.15) is a correct wave function for distinguishable particles, and we will return to it in Section 27.9. However, for indistinguishable particles, the wave function must be symmetrized for Bose–Einstein statistics¹ (bosons) or anti-symmetrized for Fermi–Dirac statistics² (fermions).

The wave function for bosons can be written as a sum over all permutations, P , of the assignments of particles to wave functions in the expression in eq. (27.15),

¹ Satyendranath Bose (1894–1974), Indian physicist, and Albert Einstein (1879–1956), German, Swiss, Austrian, and American physicist, Nobel Prize 1921.

² Enrico Fermi (1901–1954), Italian physicist, Nobel Prize 1938, and Paul Adrien Maurice Dirac (1902–1984), British physicist, Nobel Prize 1933.

$$\psi_N^{BE} = X_{BE} \sum_P \left[\prod_{j=1}^N \psi_{\alpha_j}(\vec{r}_j) \right]. \quad (27.16)$$

The normalization constant, X_{BE} , can be calculated, but does not play a significant role and will be left to the interested reader.

The wave function for fermions can be represented by a similar expression if we include a factor of $(-1)^P$, in which the exponent denotes the number of two-particle exchanges needed to construct the permutation P ,

$$\psi_N^{FD} = X_{FD} \sum_P (-1)^P P \left[\prod_{j=1}^N \psi_{\alpha_j}(\vec{r}_j) \right]. \quad (27.17)$$

X_{FD} is the normalization constant for Fermi-Dirac statistics, which will also be left to the reader.

Note that the many-particle wave function for fermions vanishes if two or more particles are in the same single-particle state ($\alpha_i = \alpha_j$ for $i \neq j$). Each single-particle state can either be empty or contain one particle. There is no such restriction for bosons, and any number of bosons can occupy a single-particle state.

The Hamiltonian of an N -particle system of independent particles is just

$$H_N = \sum_{j=1}^N H_j, \quad (27.18)$$

where H_j is the single-particle Hamiltonian for the j -th particle.

The N -particle eigenvalue equation is then

$$H_N \psi_N = E \psi_N = \sum_{j=1}^N \epsilon_{\alpha_j} \psi_N \quad (27.19)$$

for bosons, fermions, or distinguishable particles.

To construct the Boltzmann factor we need to apply the operator $\exp(-\beta H_N)$ to the wave function. Fortunately, this is easy. Simply expand the exponential in a series in powers of H_N , apply the eigenvalue equation, eq. (27.19), and sum the power series in E ,

$$\exp(-\beta H_N) \psi_N = \exp(-\beta E) \psi_N = \exp \left(-\beta \sum_{j=1}^N \epsilon_{\alpha_j} \right) \psi_N. \quad (27.20)$$

27.4 Quantum Canonical Ensemble

In principle, we could go to the canonical ensemble and sum the Boltzmann factor in eq. (27.20) over all N -particle states, just as we did for black bodies in Chapter 25 and harmonic solids in Chapter 26. Unfortunately, if we try to do this the canonical partition function does not factor. The difficulty has to do with enumerating the states. If the total number of particles is fixed, we can only put a particle in one state if we simultaneously take it out of some other state. We did not run into this problem for either black bodies or harmonic solids because neither photons nor phonons are conserved.

To be able to sum freely over the number of particles in each single-particle state—and thereby factorize the partition function—we need to introduce a reservoir that can exchange particles with the system of interest. This brings us to the grand canonical ensemble, which is the subject of the next section.

27.5 Grand Canonical Ensemble

The grand canonical partition function was introduced for classical statistical mechanics in Sections 20.1 and 20.2. The equations describing the quantum grand canonical ensemble are the same as those for the classical case, as long as we now interpret $\Omega(E, V, N)$ to mean the degeneracy of an N -particle quantum state with energy E .

Eq. (20.9) gives the quantum mechanical grand canonical probability distribution for E and N ,

$$P(E, N) = \frac{1}{\mathcal{Z}} \Omega(E, V, N) \exp[-\beta E + \beta \mu N], \quad (27.21)$$

and eq. (20.10) gives us the quantum grand canonical partition function,

$$\mathcal{Z} = \sum_{N=0}^{\infty} \sum_E \Omega(E, V, N) \exp[-\beta E + \beta \mu N]. \quad (27.22)$$

The sum over E in eq. (27.22) denotes the sum over all energy levels of the N -particle system, with $\Omega(E, V, N)$ representing the degeneracy. It replaces the integral over the continuum of energies in the classical case that was used in eq. (20.10).

For a quantum system of non-interacting particles, the N -particle energies are given by

$$E = \sum_{j=1}^N \epsilon_{\alpha_j}, \quad (27.23)$$

so that

$$\exp[-\beta E + \mu N] = \exp[-\beta \sum_{j=1}^N (\epsilon_{\alpha_j} - \mu)] = \prod_{j=1}^N \exp[-\beta (\epsilon_{\alpha_j} - \mu)]. \quad (27.24)$$

We can also rewrite eq. (27.22) in terms of sums over the eigenstates, thereby eliminating the degeneracy factor $\Omega(E, V, N)$

$$\mathcal{Z} = \sum_{N=0}^{\infty} \sum_{\{\alpha_j\}} \prod_{j=1}^N \exp[-\beta (\epsilon_{\alpha_j} - \mu)]. \quad (27.25)$$

27.6 A New Notation for Energy Levels

To simplify the expression for the grand canonical partition function, it is useful to change the notation. So far, we have been describing an N -particle state by listing the set of single-particle quantum numbers that specify that state. If more than one particle were in a particular single-particle state, the corresponding quantum number would occur more than once in the list.

An alternative representation would be to specify for each state the number of times it appears in the list, which we will call the occupation number.

Perhaps an example would help illustrate the two representations. In the following table I have indicated each state by a line and indicated the each time it occurs by an ‘ \times ’.

To represent the data in Table 27.1, we could have a list of quantum numbers,

$$\{\alpha_j\} = \{\alpha_1, \alpha_2, \alpha_2, \alpha_4, \alpha_4, \alpha_4, \alpha_5\}, \quad (27.26)$$

Table 27.1 *Representations of energy levels.*

quantum number α	Energy levels	Occupation number, n_α
6	—	0
5	\times	1
4	$\times \times \times$	3
3	—	0
2	$\times \times$	2
1	\times	1

or, equivalently, a list of occupation numbers for the energy levels,

$$\{n_\alpha\} = \{1, 2, 0, 3, 1, 0\}. \quad (27.27)$$

Both representations contain exactly the same information. However, the representation in terms of occupation numbers turns out to be more useful for the evaluation of the grand canonical partition function.

With this change in notation, the expression for the grand canonical partition function becomes

$$\mathcal{Z} = \sum_{N=0}^{\infty} \sum_{\{n_\alpha\}}^{\sum n_\alpha = N} \prod_{\epsilon} \exp[-\beta(\epsilon_\alpha - \mu)n_\alpha], \quad (27.28)$$

where the sum over n_α is understood to include only allowed values of n_α .

Now note that the sum over $\{n_\alpha\}$ is limited to those cases in which $\sum n_\alpha = N$, but the result is then summed over all values of N . We can simplify this double sum by removing the sum over N and removing the limit on the sum over $\{n_\alpha\}$,

$$\mathcal{Z} = \sum_{\{n_\alpha\}} \prod_{\alpha} \exp[-\beta(\epsilon_\alpha - \mu)n_\alpha]. \quad (27.29)$$

The limitation to allowed values of n_α is, of course, still in effect.

Eq. (27.29) can be greatly simplified by exchanging sums and products in much the same way as we exchanged integrals and products for classical statistical mechanics in Section 19.12. Exchanging the sum and product is the key step that leads to the factorization of the grand canonical partition function. This trick is just as important in quantum statistical mechanics as it is in classical statistical mechanics, and so deserves its own section.

27.7 Exchanging Sums and Products

In eq. (27.29) we found a sum of products of the form $\sum_{\{n_\alpha\}} \prod_{\alpha} \exp[-\beta(\epsilon_\alpha - \mu)n_\alpha]$, which can be transformed into a product of sums. This is another application of what we have called the best trick in statistical mechanics,

$$\begin{aligned} \sum_{\{n_\alpha\}} \prod_{\alpha} \exp[-\beta(\epsilon_\alpha - \mu)n_\alpha] &= \sum_{n_{\alpha_1}} \sum_{n_{\alpha_2}} \dots e^{-\beta(\alpha_1 - \mu)n_{\alpha_1}} e^{-\beta(\alpha_2 - \mu)n_{\alpha_2}} \dots \\ &= \sum_{n_{\alpha_1}} e^{-\beta(\alpha_1 - \mu)n_{\alpha_1}} \sum_{n_{\alpha_2}} e^{-\beta(\alpha_2 - \mu)n_{\alpha_2}} \dots \\ &= \prod_{\alpha} \sum_{n_\alpha} \exp[-\beta(\epsilon_\alpha - \mu)n_\alpha]. \end{aligned} \quad (27.30)$$

As in Section 19.12, where we discussed the classical version of this trick, care must be taken with the indices of the sums on each side of the equality. The sum on the left side of eq. (27.30) is over the entire set $\{n_\alpha\}$ for the N -particle system, while the sum in the last line on the right is only over the values taken on by the single-particle quantum number n_α .

27.8 Grand Canonical Partition Function for Independent Particles

Inserting the equality in eq. (27.30) into eq. (27.29), we find the following expression for the grand canonical partition function

$$\mathcal{Z} = \prod_{\alpha} \sum_{n_{\alpha}} \exp[-\beta(\epsilon_{\alpha} - \mu)n_{\alpha}]. \quad (27.31)$$

The evaluation of the grand canonical partition function has been reduced to the product of sums over the number of particles occupying each of the states. Each of these sums will turn out to be quite easy to evaluate for ideal gases, making the transition to the grand canonical ensemble definitely worth the effort.

The logarithm of the grand canonical partition function gives us the Legendre transform of the energy with respect to temperature and chemical potential, just as it did in the case of classical statistical mechanics

$$\ln \mathcal{Z} = -\beta U[T, \mu] = \tilde{S}[\beta, (\beta\mu)] \quad (27.32)$$

$$U[T, \mu] = U - TS - \mu N. \quad (27.33)$$

Once the grand canonical potential has been calculated, all thermodynamic information can be obtained by the methods discussed in Part 2.

In particular, if the system is extensive, which is the case in most problems of interest, Euler's equation tells us that

$$\ln \mathcal{Z} = -\beta U[T, \mu] = \tilde{S}[\beta, (\beta\mu)] = \beta PV. \quad (27.34)$$

This provides a good method of calculating the pressure in a quantum gas.

Before we continue with the derivation of the basic equations for bosons and fermions, we will make a slight detour in the next two sections to discuss the properties of distinguishable quantum particles. We will return to identical particles in Section 27.11.

27.9 Distinguishable Quantum Particles

The most common systems of distinguishable particles are colloids, in which the particles are usually composed of many atoms. Because of the large mass of colloidal particles, it is rarely necessary to treat them quantum mechanically. On the other hand, it is instructive to see how the quantum grand canonical partition function for distinguishable particles differs from that of fermions or bosons.

The distinguishing feature of a many-particle wave function for distinguishable particles is that it is not generally symmetric or antisymmetric. This means that any wave function of the form given in eq. (27.15) is valid. This equation is repeated here for convenience, with the notation modified to denote the product over single-particle states as a product over values of α_j ,

$$\psi_N = \prod_{j=1}^N \psi_{\alpha_j}(\vec{r}_j). \quad (27.35)$$

Since the particles are distinguishable and can move between the system and the reservoir, we must include a factor giving the number of ways we can have N particles in the system and the remaining N_R particles in the reservoir. Letting the total number of particles be $N_T = N + N_R$, the factor is

$$\frac{N_T!}{N!N_R!}. \quad (27.36)$$

This is exactly the same factor that we introduced in Chapter 4 for a classical ideal gas of distinguishable particles; the combinatorics are identical in the two cases.

We must also avoid double counting when two or more particles are in the same single-particle state. This leads to a factor of

$$\frac{N!}{\prod_{\alpha} n_{\alpha}!}. \quad (27.37)$$

If we include both of these factors, and note that the factor of $N_T!$ and $N_R!$ are not included in the entropy—or the grand canonical partition function—we find an expression for \mathcal{Z} of the following form:

$$\mathcal{Z} = \prod_{\alpha} \sum_{n_{\alpha}=0}^{\infty} \frac{1}{n_{\alpha}!} \exp[-\beta(\epsilon_{\alpha} - \mu)n_{\alpha}] = \prod_{\alpha} \exp(\exp[-\beta(\epsilon_{\alpha} - \mu)]). \quad (27.38)$$

If we take the logarithm of the partition function, this expression simplifies,

$$\ln \mathcal{Z} = \sum_{\alpha} \exp[-\beta(\epsilon_{\alpha} - \mu)] = \beta PV. \quad (27.39)$$

The last equality is, of course, valid only in the case that the system is extensive.

27.10 Sneaky Derivation of $PV = Nk_B T$

The form of eq. (27.39) has a curious consequence. If we calculate the predicted value of N from the grand canonical partition function (see eq. (27.42)), we find

$$\begin{aligned} \langle N \rangle &= k_B T \frac{\partial}{\partial \mu} \ln \mathcal{Z} \\ &= k_B T \frac{\partial}{\partial \mu} \sum_{\alpha} \exp[-\beta(\epsilon_{\alpha} - \mu)] \\ &= \sum_{\alpha} \exp[-\beta(\epsilon_{\alpha} - \mu)] = \ln \mathcal{Z} = \beta PV. \end{aligned} \quad (27.40)$$

where the last equality comes from eq. (27.39), and is valid for extensive systems. Eq. (27.40) is, of course, equivalent to

$$PV = Nk_B T, \quad (27.41)$$

if the fluctuations of N are neglected.

This derivation of the ideal gas law depends only on distinguishability, extensivity, and the total wave function's being a product of the single-particle eigenstates. Extensivity is necessary to eliminate, for example, a system in a gravitational field.

The most interesting feature about this derivation is that it is fully quantum mechanical. The ideal gas law does *not* depend on taking the classical limit!

27.11 Equations for $U = \langle E \rangle$ and $\langle N \rangle$

In this section we return to calculations of the properties of bosons and fermions. Eq. (27.31) for the grand canonical partition function is, in principle, sufficient to perform such calculations. However, it turns out not to be the most efficient method for obtaining the properties of fermions and bosons. In this section we will derive the equations for the energy and number of particles, which will be the basis for the methods discussed in the rest of the chapter, as well as Chapters 28 and 29.

Beginning with the formal expression for the grand canonical partition function in eq. (27.31),

$$\mathcal{Z} = \prod_{\alpha} \sum_{n_{\alpha}} \exp[-\beta(\epsilon_{\alpha} - \mu)n_{\alpha}], \quad (27.42)$$

we can easily find an expression for the average number of particles by taking a logarithmic derivative with respect to μ ,

$$\begin{aligned} \frac{\partial}{\partial \mu} \ln \mathcal{Z} &= \sum_{\alpha} \frac{\partial}{\partial \mu} \ln \sum_{n_{\alpha}} \exp[-\beta(\epsilon_{\alpha} - \mu)n_{\alpha}] \\ &= \sum_{\alpha} \left[\frac{\sum_{n_{\alpha}} \beta n_{\alpha} \exp[-\beta(\epsilon_{\alpha} - \mu)n_{\alpha}]}{\sum_{n_{\alpha}} \exp[-\beta(\epsilon_{\alpha} - \mu)n_{\alpha}]} \right] \\ &= \beta \sum_{\alpha} \langle n_{\alpha} \rangle \\ &= \beta \langle N \rangle. \end{aligned} \quad (27.43)$$

The quantity $\langle n_{\alpha} \rangle$ clearly represents the average number of particles in the state α ,

$$\langle n_{\alpha} \rangle = \frac{\sum_{n_{\alpha}} n_{\alpha} \exp[-\beta(\epsilon_{\alpha} - \mu)n_{\alpha}]}{\sum_{n_{\alpha}} \exp[-\beta(\epsilon_{\alpha} - \mu)n_{\alpha}]}. \quad (27.44)$$

The equation for the average number of particles as a derivative of the grand canonical partition function is, of course, related to the corresponding thermodynamic identity in terms of the Legendre transform of the energy with respect to T and μ ,

$$\langle N \rangle = \frac{1}{\beta} \frac{\partial}{\partial \mu} \ln \mathcal{Z} = \frac{1}{\beta} \frac{\partial}{\partial \mu} (-\beta U[T, \mu]) = \frac{\partial(PV)}{\partial \mu}. \quad (27.45)$$

The average number of particles is then

$$\langle N \rangle = \sum_{\alpha} \langle n_{\alpha} \rangle. \quad (27.46)$$

We will leave the proof of the corresponding equation for the energy to the reader.

$$U = \langle E \rangle = \sum_{\alpha} \epsilon_{\alpha} \langle n_{\alpha} \rangle. \quad (27.47)$$

Eqs. (27.46) and (27.47) turn out to be key to a relatively easy calculation of the properties of fermions and bosons. Since we are going to use them frequently in the next two chapters, we will need to evaluate $\langle n_{\alpha} \rangle$ for both fermions and bosons, which will be done in the next two sections.

27.12 $\langle n_\alpha \rangle$ for Bosons

For bosons, there are an infinite number of possibilities for the occupation of a single-particle state. This makes the evaluation of eq. (27.44) only slightly more difficult than the corresponding sum for fermions, since we can carry out the sum over all positive integers,

$$\sum_{n_\alpha=0}^{\infty} \exp[-\beta(\epsilon_\alpha - \mu)n_\alpha] = (1 - \exp[-\beta(\epsilon_\alpha - \mu)])^{-1} \quad (27.48)$$

The numerator of eq. (27.44) for bosons can be obtained by differentiating eq. (27.48) with respect to β and cancelling a factor of $(\epsilon_\alpha - \mu)$ on both sides,

$$\sum_{n_\alpha=0}^{\infty} n_\alpha \exp[-\beta(\epsilon_\alpha - \mu)n_\alpha] = \exp[-\beta(\epsilon_\alpha - \mu)] (1 - \exp[-\beta(\epsilon_\alpha - \mu)])^{-2} \quad (27.49)$$

The average occupation number is then given by the ratio of these quantities, according to eq. (27.44),

$$\begin{aligned} \langle n_\alpha \rangle &= \frac{\exp[-\beta(\epsilon_\alpha - \mu)] (1 - \exp[-\beta(\epsilon_\alpha - \mu)])^{-2}}{(1 - \exp[-\beta(\epsilon_\alpha - \mu)])^{-1}} \\ &= (\exp[\beta(\epsilon_\alpha - \mu)] - 1)^{-1}. \end{aligned} \quad (27.50)$$

Note the strong similarity between the expression for the occupation number for bosons and the average number of excited particles in a simple harmonic oscillator, which we derived in eq. (24.76) in Section 24.10. They are both manifestations of the same mathematical structure, which we first encountered in the solution to the quantum simple harmonic oscillator in Section 24.10.

There is also an important property of eq. (27.50), which will play an essential role in determining the properties of a Bose gas in Chapter 28. The average number of particles, $\langle n_\alpha \rangle$, must be a positive number, but the last line of eq. (27.50) is negative unless $\epsilon_\alpha - \mu > 0$ for all energy levels ϵ_α . Therefore, the chemical potential of a Bose gas must have a value below the lowest energy level.

27.13 $\langle n_\alpha \rangle$ for Fermions

Since there are only two possibilities for the occupation of a single-particle state by fermions, the evaluation of eq. (27.44) is quite easy. The denominator and the numerator are calculated first,

$$\sum_{n_\alpha=0}^1 \exp[-\beta(\epsilon_\alpha - \mu)n_\alpha] = 1 + \exp[-\beta(\epsilon_\alpha - \mu)] \quad (27.51)$$

$$\sum_{n_\epsilon=0}^1 n_\alpha \exp[-\beta(\epsilon_\alpha - \mu)n_\alpha] = 0 + \exp[-\beta(\epsilon_\alpha - \mu)] \quad (27.52)$$

The average occupation number is then given by the ratio of these quantities, according to eq. (27.44),

$$\langle n_\alpha \rangle = \frac{\exp[-\beta(\epsilon_\alpha - \mu)]}{1 + \exp[-\beta(\epsilon_\alpha - \mu)]} = (\exp[\beta(\epsilon_\alpha - \mu)] + 1)^{-1}. \quad (27.53)$$

Note the strong similarity between the expression for the occupation number for fermions and the average number of excited particles in a two-level system, which we derived in eq. (24.57) in Section 24.9.

27.14 Summary of Equations for Fermions and Bosons

We can summarize the equations for $\langle n_\alpha \rangle$ by writing

$$\langle n_\alpha \rangle = (\exp[\beta(\epsilon_\alpha - \mu)] \pm 1)^{-1}, \quad (27.54)$$

where the upper (plus) sign refers to fermions and the lower (minus) sign refers to bosons.

Eqs. (27.46) and (27.47) can then be written compactly:

$$\langle N \rangle = \sum_\alpha (\exp[\beta(\epsilon_\alpha - \mu)] \pm 1)^{-1} \quad (27.55)$$

$$U = \sum_\alpha \epsilon_\alpha (\exp[\beta(\epsilon_\alpha - \mu)] \pm 1)^{-1} \quad (27.56)$$

For the rest of the discussion in this chapter, as well as the following chapters on fermions and bosons, we will write N for $\langle N \rangle$. While this is not really correct, and we should keep the distinction between N and $\langle N \rangle$ in mind, it is tiresome to constantly write the brackets.

We can express the grand canonical partition function for bosons by inserting eq. (27.48) in eq. (27.42),

$$\mathcal{Z} = \prod_\alpha (1 - \exp[-\beta(\epsilon_\alpha - \mu)])^{-1}. \quad (27.57)$$

We can express the grand canonical partition function for fermions by inserting eq. (27.51) in eq. (27.42),

$$\mathcal{Z} = \prod_{\alpha} (1 + \exp[-\beta(\epsilon_{\alpha} - \mu)]). \quad (27.58)$$

Finally, we can express the logarithm of the grand canonical partition function in a compact form for both cases,

$$\ln \mathcal{Z} = \pm \sum_{\alpha} \ln (1 \pm \exp[-\beta(\epsilon_{\alpha} - \mu)]) = \beta PV. \quad (27.59)$$

The upper signs refer to fermions, and the lower signs to bosons. The last equality is valid only when the system is extensive, but that will be true of most of the cases we will consider.

If we use the density of states that we calculated in Section 27.2, we can write the logarithm of the grand canonical partition function in terms of an integral.

$$\ln \mathcal{Z} = \pm \int_0^{\infty} D(\epsilon) \ln (1 \pm \exp[-\beta(\epsilon - \mu)]) d\epsilon = \beta PV. \quad (27.60)$$

27.15 Integral Form of Equations for N and U

In Section 27.2 we calculated the density of single-particle states, $D(\epsilon)$, for non-interacting particles in a box, with the result given in eq. (27.13),

$$N = \int_0^{\infty} D(\epsilon) (\exp[\beta(\epsilon - \mu)] \pm 1)^{-1} d\epsilon \quad (27.61)$$

$$U = \int_0^{\infty} D(\epsilon) (\exp[\beta(\epsilon - \mu)] \pm 1)^{-1} \epsilon d\epsilon. \quad (27.62)$$

For more general systems, which we will discuss later in this chapter, the density of states, $D(\epsilon)$, will have a different structure, which might be considerably more complex. However, we will still be able to express eqs. (27.55) and (27.56) in integral form.

The integral form of the equations can even be used if the energy spectrum is partially discrete, if we represent the discrete part of the spectrum with a delta function of the form $X\delta(\epsilon - \epsilon_1)$, where the constant X represents the degeneracy of the energy level at ϵ_1 .

One of the most interesting aspects of eqs. (27.61) and (27.62) is that they completely separate the quantum statistics (which enter as the factor $(\exp[\beta(\epsilon - \mu)] \pm 1)^{-1}$) and the effects of the Hamiltonian (which are reflected in the density of states, $D(\epsilon)$). We will spend considerable effort in understanding the properties of systems of non-interacting particles, which might seem to be very special cases. Nevertheless, the methods we

develop will apply directly to much more general cases, as long as we are able to calculate the density of states, $D(\epsilon)$. We will even be able to obtain very general results in the following chapters for the consequences of the various kinds of structure in $D(\epsilon)$ that can arise.

27.16 Basic Strategy for Fermions and Bosons

The basic strategy for dealing with problems of fermions and bosons differs from that usually employed for other problems in quantum statistical mechanics, where the first task is almost always to evaluate the canonical partition function. Although it is possible to solve problems with fermions and bosons by evaluating the grand canonical partition function, it is almost always better to use eqs. (27.55) and (27.56) (or eqs. (27.61) and (27.62)) for the average number of particles and the average energy.

The first step in solving problems involving fermions and bosons is to use eq. (27.55) (or eq. (27.61) to obtain N as a function of T and μ , that is $N = N(T, \mu)$.

Next, note that we rarely know the value of the chemical potential, while we almost always do know the number of particles in the system. Furthermore, the number of particles is generally fixed during experiments, while the chemical potential is not. This suggests inverting the function $N = N(T, \mu)$ that we found from eq. (27.55) or eq. (27.61) to give us $\mu = \mu(T, N)$.

Finally, we use eq. (27.56) or eq. (27.62) to find the energy as a function of T and N (the latter through the function $\mu = \mu(T, N)$). This gives us two equations of state that will probably answer any questions in which we are interested. If we need a complete fundamental relation, we can—at least in principle—find it by integrating the equations of state, as discussed in Chapter 13. A fundamental relation can be found from eq. (27.59), which also provides a quick way of calculating the pressure for extensive systems.

The details of how these calculations can be carried out in practice will be discussed in Chapters 28 and 29.

27.17 $P = 2U/3V$

The equation in the title of this section is easy to derive for a three-dimensional, monatomic, classical, ideal gas or a quantum gas of distinguishable particles. We need only combine the ideal gas law,

$$PV = Nk_B T, \quad (27.63)$$

with the equation for the energy,

$$U = \frac{3}{2} Nk_B T, \quad (27.64)$$

to get

$$P = \frac{2}{3} \frac{U}{V}. \quad (27.65)$$

The surprising thing about eq. (27.65) is that it is also true for ideal Fermi and Bose gases, even though eqs. (27.63) and (27.64) are not.

The proof begins with the integral form of the equations for the grand canonical partition function from eq. (27.60),

$$\ln \mathcal{Z} = \pm \int_0^\infty D(\epsilon) \ln(1 \pm \exp[-\beta(\epsilon - \mu)]) d\epsilon = \beta PV, \quad (27.66)$$

and the average energy from eq. (27.62)

$$U = \int_0^\infty D(\epsilon) (\exp[\beta(\epsilon - \mu)] \pm 1)^{-1} \epsilon d\epsilon. \quad (27.67)$$

In both of these equations, the density of states is given by eq. (27.13),

$$D(\epsilon) = \frac{V}{4\pi^2} \left(\frac{2m}{\hbar^2} \right)^{3/2} \epsilon^{1/2} = X \epsilon^{1/2}, \quad (27.68)$$

where we have introduced a constant X to simplify the algebra.

To derive eq. (27.65) we integrate the expression for $\ln \mathcal{Z}$ by parts, so that

$$\ln \mathcal{Z} = \pm X \int_0^\infty \epsilon^{1/2} \ln(1 \pm \exp[-\beta(\epsilon - \mu)]) d\epsilon, \quad (27.69)$$

becomes

$$\begin{aligned} \ln \mathcal{Z} = \pm X & \left[\frac{2}{3} \epsilon^{3/2} \ln(1 \pm \exp[-\beta(\epsilon - \mu)]) \right]_0^\infty \\ & \mp X \int_0^\infty \frac{2}{3} \epsilon^{3/2} (1 \pm \exp[-\beta(\epsilon - \mu)])^{-1} (\mp \beta \exp[-\beta(\epsilon - \mu)]) d\epsilon. \end{aligned} \quad (27.70)$$

The first term on the right in eq. (27.70) vanishes exactly. Comparing eq. (27.70) with eq. (27.67) leaves us with

$$\ln \mathcal{Z} = \frac{2X\beta}{3} \int_0^\infty \epsilon^{3/2} (\exp[\beta(\epsilon - \mu)] \pm 1)^{-1} d\epsilon = \frac{2\beta}{3} U. \quad (27.71)$$

Since $\ln \mathcal{Z} = \beta PV$ for an extensive system, this gives us eq. (27.65).

It is rather remarkable that eq. (27.65) holds for any form of statistics in either classical or quantum mechanics. The factor $2/3$ does depend on the system being three-dimensional, but that proof will be left to the reader.

27.18 Problems

PROBLEM 27.1

Identities in the grand canonical ensemble

We have seen that derivatives of partition functions can be used to express various quantities of interest. Derive identities for the following in terms of derivatives of the quantum-mechanical, grand canonical partition function.

1. The average number of particles in the system, $\langle N \rangle$, in terms of a derivative with respect to μ .
2. The average number of particles in the system, $\langle N \rangle$, in terms of a derivative with respect to the fugacity, $\lambda = \exp(\beta\mu)$.
3. The average energy as a function of β and μ in terms of derivatives.

PROBLEM 27.2

More on the grand canonical ensemble

We have previously derived a general expression for the grand canonical partition function for a system of independent identical particles

$$\mathcal{Z} = \prod_{\epsilon} \sum_{n_{\epsilon}} \exp[-\beta(\epsilon - \mu)n_{\epsilon}]$$

where the product over ϵ is actually the product over the single-particle eigenstates. Each eigenstate must be counted separately, even when several eigenstates have the same energy (also denoted by ϵ).

The sum over n_{ϵ} is only over *allowed* values of n_{ϵ} .

For bosons, an arbitrary number of particles can be in the same state, so n_{ϵ} can take on any non-negative integer value, $n_{\epsilon} = \{0, 1, 2, \dots\}$.

For fermions, no more than one particle can be in a given state, so n_{ϵ} can only take on the values 0 and 1, $n_{\epsilon} = \{0, 1\}$.

Do each of the following for both fermions and bosons:

1. Carry out the sum in the grand canonical partition function explicitly.
2. Using the result from the previous question, calculate the average number of particles $\langle N \rangle$ in terms of β and μ .
3. Calculate the average number of particles in an eigenstate with energy ϵ , denoted by $\langle n_{\epsilon} \rangle$.

4. Express the average number of particles $\langle N \rangle$ in terms of a sum over $\langle n_{\epsilon} \rangle$.
5. Calculate the average energy in terms of a sum over $\langle n_{\epsilon} \rangle$.

PROBLEM 27.3

Fermion and boson fluctuations

Prove that the fluctuations about the average number of particles in an eigenstate, $\langle n \rangle$, is given by

$$\delta^2 \langle n \rangle = \langle n \rangle (1 \pm \langle n \rangle)$$

where one of the signs is for fermions and the other is for bosons.

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