

CHAPTER 4

BOLTZMAN STATISTICS, FERMI-DIRAC STATISTICS, AND BOSE-EINSTEIN STATISTICS

1 Statement of the problem

- The results that we have derived up to now are valid for macroscopic systems.
- In order to apply these equations, it is necessary to have the set of eigenvalues $\{E_j(N, V)\}$ of the N -body Schrodinger equation.
- In general, this is an impossible task!

Simplification (exploiting independence)

- There are many important systems, however, in which the N -body Hamiltonian operator can be written as a sum of independent individual Hamiltonians.
- If the Hamiltonian of a many-body system can be written as a sum of one-body Hamiltonians, then the energy of the system is the sum of individual energies, and the wave function is a product of the single-particle wave functions.
- This leads to a great simplification of the partition function, and allows us to apply the results with relative ease.

Complications (due to indistinguishability)

- The wave functions of a system of identical particles must satisfy certain symmetry requirements with respect to the interchange of the particles.
- **Bosons** : symmetric & no restriction of the distribution over their available energy states,
- **Fermions** : no two identical fermions can occupy the same single particle energy state. This restriction follows immediately from the requirement that wave function be antisymmetric (see Problem 1-26).

- These considerations become important in enumerating the many-body energy states available to the system.

Examples of simplified Hamiltonian

1. A dilute gas, where intermolecular interactions can be neglected.
2. Decomposition of the Hamiltonian of a polyatomic molecule into its various degrees of freedom:

$$H \approx H_{\text{translational}} + H_{\text{rotational}} + H_{\text{vibrational}} + H_{\text{electronic}} + \dots \quad (4-1)$$

(can be corrected by the introduction of small interaction terms)

3. quasi-particles, which mathematically behave like independent real particles, e.g., photons, phonons, plasmons, magnons, rotons, and other “ons.”

2 Issues

1) Reduction of N-body Problem to one-body problem

Consider a system of distinguishable particles.

$\{\varepsilon_j^a\}$ → the individual (molecular) energy states
 where $a \rightarrow$ the particle (distinguishable),
 $j \rightarrow$ the state.

In this case, the canonical partition function becomes

$$\begin{aligned} Q(N, V, T) &= \sum_j e^{-E_j/kT} = \sum_{i,j,k,\dots} e^{-(\varepsilon_i^a + \varepsilon_j^b + \varepsilon_k^c + \dots)/kT} \\ &= \sum_i e^{-\varepsilon_i^a/kT} \sum_j e^{-\varepsilon_j^b/kT} \sum_k e^{-\varepsilon_k^c/kT} \dots = q_a q_b q_c \dots \end{aligned} \quad (4-2)$$

where $q(V, T) = \sum_i e^{-\varepsilon_i/kT}$, a molecular partition function (4-3)

If the energy states of all the particles $\{\varepsilon_i\}$ are the same, then

$$Q(N, V, T) = [q(V, T)]^N \quad (\text{distinguishable particles}) \quad (4-4)$$

2) Further reduction into the individual degrees of freedom of the single particles is desirable

The molecular Hamiltonian can be approximated by a sum of Hamiltonians for the various degrees of freedom of the molecule.

$$q_{\text{molecule}} = q_{\text{translational}} q_{\text{rotational}} q_{\text{vibrational}} q_{\text{electronic}} \cdots \quad (4-5)$$

where, for example,

$$q_{\text{translational}} = \sum_j e^{-\varepsilon_j^{\text{trans}} / kT} \quad (4-6)$$

3) Indistinguishability of atoms and molecules

But, atoms and molecules are, in general, not distinguishable; thus the utility of Eq. (4-4) is severely limited. In this case, the N -body energy is

$$E_{ijkl\dots} = \varepsilon_i + \varepsilon_j + \varepsilon_k + \varepsilon_l + \cdots \quad (4-7)$$

and the partition function is

$$Q(N, V, T) = \sum_{i,j,k,l,\dots} e^{-(\varepsilon_i + \varepsilon_j + \varepsilon_k + \varepsilon_l + \dots) / kT} \quad (4-8)$$

Because the molecules are indistinguishable, one cannot sum over i, j, k, l, \dots separately as we did to get Eq. (4-2).

4) The symmetry requirement of fermions/bosons complicates the summation

Fermions: No two identical fermions can occupy the same single-particle energy state. Thus in Eq. (4-8), terms in which two or more indices are the same cannot be included in the summation. The indices i, j, k, l , and so on, are not independent of one another, and a direct evaluation of $Q(N, V, T)$ for fermions by means of Eq. (4-8) is very difficult.

Bosons Because the particles are indistinguishable, the state of $\varepsilon_j + \varepsilon_i + \varepsilon_j + \varepsilon_j + \dots$ is identical with $\varepsilon_j + \varepsilon_j + \varepsilon_i + \varepsilon_j + \dots$, and so on. Such a state should be included only once. Consequently, a direct evaluation of Q for bosons by means of Eq. (4-8) also is difficult.

3 BOLTZMANN STATISTICS

Complications arise when two or more indices are the same. If it were not for this kind of term, one could carry out the summation in (4-8) in an unrestricted manner, and then correct the sum by dividing by $N!$ It turns out that this procedure yields an excellent approximation in many (most) cases for the following reason.

Condition for Boltzman

We showed in Section 1-3 that for a particle in a box, the number of molecular quantum states with energy $\leq \varepsilon$ is

$$\Phi(\varepsilon) = \frac{\pi}{6} \left(\frac{8ma^2\varepsilon}{h^2} \right)^{3/2}$$

for $m=10^{-22}g$, $a = 10\text{cm}$, $T=300\text{K}$, $\Phi(\varepsilon) = O(10^{30})$. Although this calculation is done for one particle in a cube (i.e., one molecule of an ideal gas), the order of magnitude of the result is general. Thus we see that the number of molecular quantum states available to a molecule at room temperature, say, is much greater than the number of molecules in the system for all but the most extreme densities. Since each particle has many individual states to choose from, it will be a rare event for two particles to be in the same molecular state. Therefore the vast majority of terms in Eq. (4-8) will have all different indices.

This allows us to sum over all the indices unrestrictedly and divide by $N!$ to get

$$Q(N, V, T) = \frac{q^N}{N!} \quad (\text{indistinguishable particles}) \quad (4-10)$$

with

$$q(V, T) = \sum_j e^{-\varepsilon_j/kT}$$

for a system of identical, indistinguishable particles satisfying the condition that the number of available molecular states is much greater than the number of particles.

Equation (4-10) is an extremely important result, since it reduces a many-body problem to a one-body problem. The indistinguishability of the particles has been included by dividing by $N!$, a valid procedure for most systems under most conditions.

The condition $\Phi(\varepsilon) \gg N$ is (using (4-9) and $\varepsilon = \frac{3}{2}kT$)

$$\frac{\pi}{6} \left(\frac{12mkT}{h^2} \right)^{3/2} \gg \frac{N}{V} \quad (4-11)$$

- favored by large mass, high temperature, and low density.
- satisfied for all but the very lightest molecules at very low T .

Table 4-1. The quantity $(6N/\pi V)(h^2/12mkT)^{3/2}$ for a number of simple systems*

	T (°K)	$\frac{6N}{\pi V} \left(\frac{h^2}{12mkT} \right)^{3/2}$
liquid helium	4	1.6
gaseous helium	4	0.11
gaseous helium	20	2.0×10^{-3}
gaseous helium	100	3.5×10^{-5}
liquid neon	27	1.1×10^{-2}
gaseous neon	27	8.2×10^{-5}
gaseous neon	100	3.1×10^{-6}
liquid argon	86	5.1×10^{-4}
gaseous argon	86	1.6×10^{-6}
liquid krypton	127	5.4×10^{-5}
gaseous krypton	127	2.0×10^{-7}
electrons in metals (sodium)	300	1465

* This quantity must be much less than unity for Eq. (4-10) to be valid. The temperatures associated with the liquid states are the normal boiling points [cf. Eq. (4-11)].

- When Eq. (4-10) is valid, that is, when the number of available molecular states is much greater than the number of particles in the system, we say that the particles obey Boltzmann statistics.
- Boltzmann statistics is an approximation that becomes increasingly better at higher temperatures.
- We shall show in Chapter 7 that at high enough temperatures, one can describe the energy of a system by classical mechanics.
- Since the limiting case of Boltzmann statistics and the use of classical mechanics both require a high-temperature limit, Boltzmann statistics is also called the classical limit.

Boltzman Distribution for molecular energy

Let us examine Eq. (4-10). The total energy of the N -body system is

$$E = N\bar{\varepsilon} = kT^2 \left(\frac{\partial \ln Q}{\partial T} \right)_{N,V} = N \sum_j \varepsilon_j \frac{e^{-\varepsilon_j/kT}}{q} \quad (4-12)$$

The first equality is valid, because the molecules are assumed to be independent, and hence their energies are additive. We see from Eq. (4-12) that the average energy of a particle is

$$\bar{\varepsilon} = \sum_j \varepsilon_j \frac{e^{-\varepsilon_j/kT}}{q} \quad (4-13)$$

We can conclude from this equation that the probability that a molecule is in the j -th energy state is

$$\pi_j = \frac{e^{-\varepsilon_j/kT}}{\sum_j e^{-\varepsilon_j/kT}} = \frac{e^{-\varepsilon_j/kT}}{q} \quad (4-14)$$

It is interesting to note that the fluctuations in ε are of the same order as ε itself (see Problems 4-18 and 4-19), that is, the probability distribution for single molecules is not sharp. A sharp probability distribution is a many-body effect.

The similarity between molecular states and states of the N-body system

The similarity between Eq. (4-14) for molecular states and Eq. (2-12) for states of the entire N -body system is not fortuitous. Equation (4-14) can be derived by the same mathematical formalism of Chapter 2.

The ensemble is considered to be the N actual molecules in thermal contact with each other. The number of molecules n_j in the state with energy ε_j is found by maximizing a combinatorial factor similar to Eq. (1-77).

This point of view was the one originally proposed by Boltzmann. It is valid only for systems in which the total energy is a sum of individual molecular energies, that is, only for dilute gases. The conceptual generalization of these ideas by Gibbs was a magnificent achievement, which allowed statistical thermodynamics to be applicable to all physical systems.

Furthermore, the derivation given in Chapter 2 is rigorous, since macroscopic systems can be labeled, and the size of the ensemble can be increased arbitrarily. This is not so for the Boltzmann approach, since the molecules cannot be labeled, and the system is finite.

Equation (4-14) can be reduced further if we assume that the energy of the molecule can be written in the form [cf. Eq. (4-1)]

$$\varepsilon = \varepsilon_i^{\text{trans}} + \varepsilon_j^{\text{rot}} + \varepsilon_k^{\text{vib}} + \varepsilon_l^{\text{elec}} + \dots$$

Then Eq. (4-14) and Eq. (4-5) can be combined to give, for example,

$$\pi_j^{\text{vib}} = \frac{e^{-\varepsilon_j^{\text{vib}}}}{q^{\text{vib}}} \quad (4-15)$$

for the probability that a molecule is in the j -th vibrational state irrespective of the other degrees of freedom.

Although (4-10) is applicable to most systems, (4-8) is the general case. To exactly evaluate (4-8), we must consider the effect of the **symmetry requirements** of N -body wave functions on the sum over states.

4 F-D & B-E Statistics

General partition function applicable for both fermions and bosons

General approach to evaluate (4-8):

Let $E_j(N, V)$ the energy states available to a system containing N molecules,

ε_k the molecular quantum states,

$n_k = n_k(E_j)$ the number of molecules in the k -th molecular state

when the system itself is in the quantum state with energy E_j .

$\{n_k\}$ specifies a quantum state of the entire system.

The energy of the system is
$$E_j = \sum_k \varepsilon_k n_k \quad (4-16)$$

and, of course,

$$N = \sum_k n_k \quad (4-17)$$

where

We can write
$$Q(N, V, T) = \sum_j e^{-\beta E_j} = \sum_{\{n_k\}} * e^{-\beta \sum_i \varepsilon_i n_i} \quad (4-18)$$

where the asterisk in the summation signifies the restriction $N = \sum_k n_k$.

Crucial step

This restriction turns out to be mathematically awkward. We then use the grand canonical partition function instead

$$Z(V, T, \mu) = \sum_{N=0}^{\infty} Q(N, V, T) e^{\mu\beta N}$$

Use Eq. (4-18) for $Q(N, V, T)$ and $\lambda = e^{\beta\mu}$ to get

$$Z(V, T, \mu) = \sum_{N=0}^{\infty} \lambda^N \sum_{\{n_k\}}^* e^{-\beta \sum_i \varepsilon_i n_i} = \sum_{N=0}^{\infty} \sum_{\{n_k\}}^* \lambda^{\sum n_i} e^{-\beta \sum_i \varepsilon_i n_i} = \sum_{N=0}^{\infty} \sum_{\{n_k\}}^* \prod_k (\lambda e^{-\beta \varepsilon_k})^{n_k} \quad (4-19)$$

Since we are summing over all values of N , each n_k ranges over all possible values, and (4-19) can be written as (see Problem 4-6)

$$Z(V, T, \mu) = \sum_{n_1=0}^{n_1^{\max}} \sum_{n_2=0}^{n_2^{\max}} \cdots \prod_k (\lambda e^{-\beta \varepsilon_k})^{n_k} \quad (4-20)$$

Or in a more lucid form:

$$Z(V, T, \mu) = \sum_{n_1=0}^{n_1^{\max}} (\lambda e^{-\beta \varepsilon_1})^{n_1} \sum_{n_2=0}^{n_2^{\max}} (\lambda e^{-\beta \varepsilon_2})^{n_2} \cdots = \prod_k \sum_{n_k=0}^{n_k^{\max}} (\lambda e^{-\beta \varepsilon_k})^{n_k} \quad (4-21)$$

The crucial step from (4-19) to (4-20) is possible only because we are summing over all values of N , or, in other words, since we are using the grand canonical partition function. Now apply Eq. (4-21) to fermions and bosons.

FERMI-DIRAC STATISTICS

In *Fermi-Dirac* statistics, each of the $n_k = 0$ or 1, since no two particles can be in the same quantum state. $n_1^{\max} = 1$. (4-21) is simply

$$Z_{\text{FD}} = \prod_k (1 + \lambda e^{-\beta \varepsilon_k}) \quad (4-22)$$

BOSE-EINSTEIN STATISTICS

In *Bose-Einstein* statistics, $n_k = 0, 1, 2, \dots$, since there is no restriction on the occupancy of each state. Therefore, $n_k^{\max} = \infty$, and (4-21) becomes

$$Z_{\text{BE}} = \prod_k \sum_{n_k=0}^{\infty} (\lambda e^{-\beta \varepsilon_k})^{n_k} = \prod_k \sum_{n_k=0}^{\infty} (1 - \lambda e^{-\beta \varepsilon_k})^{-1} \quad \lambda e^{-\beta \varepsilon_k} < 1 \quad (4-23)$$

Hint. $\sum_{j=0}^{\infty} x^j = (1-x)^{-1}$ for $x < 1$.

Unified formula

Equations (4-22) and (4-23) are the two fundamental distributions of the statistical thermodynamics of systems of independent particles. We can combine these two equations into

$$Z_{\text{FD, BE}} = \prod_k (1 \pm \lambda e^{-\beta \varepsilon_k})^{\pm 1} \quad (4-24)$$

+ sign: Fermi-Dirac statistics, – sign: Bose-Einstein statistics.

Using (3-33), we see that [note: $d\lambda = d[e^{\mu N}] = e^{\mu N} d\mu = \lambda d\mu$]

$$\bar{N} = N = \sum_k \bar{n}_k = kT \left(\frac{\partial \ln Z}{\partial \mu} \right)_{V, T} = \lambda \left(\frac{\partial \ln Z}{\partial \lambda} \right)_{V, T} = \sum_k \frac{\lambda e^{-\beta \varepsilon_k}}{1 \pm \lambda e^{-\beta \varepsilon_k}} \quad (4-25)$$

The average number of particles in the k -th quantum state is

$$\bar{n}_k = \frac{\lambda e^{-\beta \varepsilon_k}}{1 \pm \lambda e^{-\beta \varepsilon_k}} \quad (4-26)$$

(4-26) is the quantum statistical counterpart of (4-14). Multiply (4-26) by ε_k and sum over k to get the quantum statistical version of (4-13).

$$\bar{E} = N\bar{\varepsilon} = \sum_k \bar{n}_k \varepsilon_k = \sum_k \frac{\lambda \varepsilon_k e^{-\beta \varepsilon_k}}{1 \pm \lambda e^{-\beta \varepsilon_k}} \quad (4-27)$$

Lastly, (3-16) gives

$$pV = kT \ln Z = \pm kT \sum_k \ln [1 \pm \lambda e^{-\beta \epsilon_k}] \quad (4-28)$$

Equations (4-25) through (4-28) are the fundamental formulas of Fermi-Dirac (+) and Bose-Einstein (-) statistics.

5 Connection with Boltzmann statistics

We noted above that both kinds of statistics should go over into Boltzmann or classical statistics **in the limit of high temperature or low density**, where the number of available molecular quantum states is much greater than the number of particles.

Average number of molecules

The condition implies $\bar{n}_k \rightarrow 0$ (**the average number of molecules in any state is very small**), since most states will be unoccupied and those few states that are occupied will most likely contain only one molecule. **This is achieved by letting $\lambda \rightarrow 0$.**

Thermodynamically, this means the limit of $N/V \rightarrow 0$ for fixed T , or $T \rightarrow \infty$ for fixed N/V (See Problem 4-3.)

For small λ , (4-26) becomes

$$\bar{n}_k = \lambda e^{-\beta \epsilon_k} \quad (\lambda \text{ small})$$

If we sum both sides of this equation over k to eliminate λ , we have

$$\frac{\bar{n}_k}{N} = \frac{e^{-\beta \epsilon_k}}{q} \quad \text{where} \quad q = \sum_j e^{-\beta \epsilon_j} \quad (4-29, 4-30)$$

the Boltzmann or classical limit for both F-D and B-E statistics.

Mean molecular energy

Equations (4-27) and (4-28) also reduce to the formulas of Section 4-1 as $\lambda \rightarrow 0$.

Equation (4-27) becomes $E \rightarrow \sum_j \lambda \epsilon_j e^{-\beta \epsilon_j}$.

Since $n_j \rightarrow \lambda e^{-\beta \epsilon_j}$, we have

$$\bar{\varepsilon} = \frac{\bar{E}}{N} \rightarrow \frac{\sum_j \varepsilon_j e^{-\beta \varepsilon_j}}{\sum_j e^{-\beta \varepsilon_j}} \quad (4-31)$$

This is the same as (4-13).

PV=kT(λq)=NkT

Similarly, for small λ we can expand the logarithm in (4-28) to get

$$pV \rightarrow (\pm kT) \left(\pm \lambda \sum_j e^{-\beta \varepsilon_j} \right) \quad (4-32)$$

We have used $\ln(1+x) \approx x$ for small x . Using (4-30), this becomes

$$pV = \lambda kT \sum_j e^{-\beta \varepsilon_j} \quad (4-33)$$

or

$$\beta pV = \ln Z = \lambda q \quad (4-34)$$

Equation (3-33) can be used to show that $\lambda q = N$, and so Eq. (4-34) is the perfect gas law as expected.

[Note $N = kT (\partial \ln Z / \partial \mu) = kT (\partial Z / \partial \mu) / Z = (kT) (\beta e^{\mu N}) / q = \lambda / q$]

λq vs. Z

We can also derive Eq. (4-10) directly from Eq. (4-34) for Z:

$$Z = e^{\lambda q} = \sum_{N=0}^{\infty} \frac{(\lambda q)^N}{N!}$$

If we compare this to Eq. (3-15), see that

$$Q(N, V, T) = \frac{q^N}{N!}$$

Final notes

- The formulas of F-D and B-E statistics reduce to those of Boltzmann statistics in the classical limits.
- Note, however, that the molecular partition function q is not a relevant quantity when we are dealing with quantum statistics, that is, F-D or B-E statistics. In spite of the fact that we have neglected inter-molecular forces, the individual particles of the system are not independent because of the symmetry requirements of the wave functions.
- There are a few systems such as electrons in metals, liquid helium, electromagnetic radiation, for which one **must** use quantum statistics (Chapter 10).
- For most systems that we shall study in this book, however, we shall be able to use Boltzmann or classical statistics (Chapters 5-8).