# 6.4: Statistical Mechanics of Independent Identical Particles

## 6.4.1 Partition function

Now that we have an energy eigenbasis, the obvious thing to do is to calculate the canonical partition function

$$Z(\beta)=\sum_{\text{states}} e^{-\beta E}, \tag{6.4.1}$$

where for fermions and bosons, respectively, the term “state” implies the occupation number lists:

| | |
|---|---|
| fermions | $(n_1, n_2, \cdots, n_M)$, $n_r = 0, 1$, subject to $\sum_r n_r = N$ |
| bosons | $(n_1, n_2, \cdots, n_M)$, subject to $\sum_r n_r = N$ |

As we have seen, it is difficult to even count these lists, much less enumerate them and perform the relevant sum! It can be done, but there is a trick that renders it unnecessary. (Don’t be ashamed if you don’t see the trick. . . neither did Einstein or Fermi. They both did it the hard, canonical way.)

The trick here, as in so many places in statistical mechanics, is to use the grand canonical ensemble. In this ensemble, the partition function is

$$\Xi(\beta, \mu)=\sum_{\text{states}} e^{-\beta E+\beta \mu N}=\sum_{\text{states}} e^{-\beta \sum_r\left(n_r \epsilon_r-\mu n_r\right)}=\sum_{\text{states}} \prod_{r=1}^M e^{-\beta n_r\left(\epsilon_r-\mu\right)} \tag{6.4.2}$$

where the term “state” now implies the occupation number lists without any restriction on total particle *number*:

| | |
|---|---|
| fermions | $(n_1, n_2, \cdots, n_M)$, $n_r = 0, 1$ |
| bosons | $(n_1, n_2, \cdots, n_M)$ |

Writing out the sum over states explicitly, we have for fermions

$$\begin{aligned}\Xi(\beta, \mu) &=\sum_{n_1=0}^1 \sum_{n_2=0}^1 \ldots \sum_{n_M=0}^1 \prod_{r=1}^M e^{-\beta n_r\left(\epsilon_r-\mu\right)} \\ &=\left[\sum_{n_1=0}^1 e^{-\beta n_1\left(\epsilon_1-\mu\right)}\right]\left[\sum_{n_2=0}^1 e^{-\beta n_2\left(\epsilon_1-\mu\right)}\right] \cdots\left[\sum_{n=0}^1 e^{-\beta n_M\left(\epsilon_1-\mu\right)}\right]\end{aligned}.$$

A typical factor in the product is

$$\left[\sum_{n_r=0}^1 e^{-\beta n_r\left(\epsilon_r-\mu\right)}\right]=1+e^{-\beta\left(\epsilon_r-\mu\right)}, \tag{6.4.3}$$

so for fermions

$$\Xi(\beta, \mu)=\prod_{r=1}^M 1+e^{-\beta\left(\epsilon_r-\mu\right)}. \tag{6.4.4}$$

Meanwhile, for bosons, the explicit state sum is

$$\begin{aligned}\Xi(\beta, \mu) &=\sum_{n_1=0}^{\infty} \sum_{n_2=0}^{\infty} \ldots \sum_{n_{M=0}}^{\infty} \prod_{r=1}^M e^{-\beta n_r\left(\epsilon_r-\mu\right)} \\ &=\left[\sum_{n_1=0}^{\infty} e^{-\beta n_1\left(\epsilon_1-\mu\right)}\right]\left[\sum_{n_2=0}^{\infty} e^{-\beta n_2\left(\epsilon_1-\mu\right)}\right] \cdots\left[\sum_{n_M=0}^{\infty} e^{-\beta n_M\left(\epsilon_1-\mu\right)}\right]\end{aligned}.$$

and a typical factor in the product is

$$\begin{aligned}\left[\sum_{n_r=0}^{\infty} e^{-\beta n_r(\epsilon_r-\mu)}\right] &= 1+\left[e^{-\beta(\epsilon_r-\mu)}\right]+\left[e^{-\beta(\epsilon_r-\mu)}\right]^2+\left[e^{-\beta(\epsilon_r-\mu)}\right]^3+\cdots \\ &= \frac{1}{1-e^{-\beta(\epsilon_r-\mu)}}\end{aligned},$$

where in the last line we have summed the geometric series under the assumption that $\epsilon_r > \mu$. Thus for bosons

$$\Xi(\beta,\mu)=\prod_{r=1}^{M} \frac{1}{1-e^{-\beta(\epsilon_r-\mu)}}. \tag{6.4.5}$$

The two results are compactly written together as

$$\Xi(\beta,\mu)=\prod_{r=1}^{M}\left[1 \pm e^{-\beta(\epsilon_r-\mu)}\right]^{\pm 1}, \tag{6.4.6}$$

where the + sign refers to fermions and the − sign to bosons.

## 6.4.2 Mean occupation numbers

In our previous work, we have always found the partition function and worked from there. Surprisingly, however, for the situation of quantal ideal gases it is more useful to find the mean occupation numbers, such as

$$\langle n_5\rangle = \frac{\sum_{\text{states}} n_5 e^{-\beta(E-\mu N)}}{\sum_{\text{states}} e^{-\beta(E-\mu N)}} = \frac{\sum_{\text{states}} n_5 e^{-\beta\sum_r(n_r\epsilon_r-n_r\mu)}}{\Xi(\beta,\mu)}. \tag{6.4.7}$$

Note that the averages $\langle n_r\rangle$ are functions of $\beta$ and $\mu$ (as well as of $r$) but it is notationally clumsy to show that dependence.

How can such averages be evaluated? A slick trick would be helpful here! Consider the derivative

$$\frac{\partial \ln\Xi}{\partial \epsilon_5} = \frac{1}{\Xi}\frac{\partial \Xi}{\partial \epsilon_5} = \frac{1}{\Xi}\sum_{\text{states}}(-\beta n_5)\, e^{-\beta\sum_r(n_r\epsilon_r-n_r\mu)} = -\beta\langle n_5\rangle . \tag{6.4.8}$$

Using the explicit expression (6.37) for $\Xi$ (where the + sign refers to fermions and the − sign to bosons), this gives

$$\langle n_5\rangle = -\frac{1}{\beta}\frac{\partial \ln\Xi}{\partial \epsilon_5} \tag{6.4.9}$$

$$= -\frac{1}{\beta}\left\{\frac{\partial}{\partial \epsilon_5}\sum_{r=1}^{M}\ln\left[1 \pm e^{-\beta(\epsilon_r-\mu)}\right]^{\pm 1}\right\} \tag{6.4.10}$$

$$= -\frac{1}{\beta}\left\{\frac{\partial}{\partial \epsilon_5}\ln\left[1 \pm e^{-\beta(\epsilon_5-\mu)}\right]^{\pm 1}\right\} \tag{6.4.11}$$

$$= -\frac{1}{\beta}\left\{\pm\frac{\pm(-\beta)e^{-\beta(\epsilon_5-\mu)}}{\left[1 \pm e^{-\beta(e_5-\mu)}\right]}\right\} \tag{6.4.12}$$

$$= \frac{1}{e^{\beta(\epsilon_S-\mu)} \pm 1}, \tag{6.4.13}$$

leaving us with the final result.

$$\langle n_r\rangle = \frac{1}{e^{\beta(\epsilon_r-\mu)} \pm 1}. \tag{6.4.14}$$

As before, the + sign refers to fermions and the − sign to bosons.

The mean occupation numbers play such an important role that it is easy to forget that they are only averages, that there will be fluctuations, that for a given $T$ and $\mu$ not all states will have exactly $\langle n_5\rangle$ building blocks of level 5 (see problem 6.13). Keep this in mind if you ever find yourself saying “occupation number” rather than “mean occupation number”.

In practice, these results from the grand canonical ensemble are used as follows: One uses these results to find quantities of interest as functions of temperature, volume, and chemical potential, such as the pressure $p(T, V, \mu)$. But most experiments are done with a fixed number of particles $N$, so at the very end of your calculation you will want to find $\mu(T, V, N)$ in order to express your final answer as $p(T, V, N)$. You can find $\mu(T, V, N)$ by demanding that

$$N=\sum_{r=1}^{M}\langle n_r\rangle=\sum_{r=1}^{M}\frac{1}{e^{\beta(e_r-\mu)}\pm 1}. \tag{6.4.15}$$

In other words, the quantity $\mu$ serves as a parameter to insure normalization, very much as the quantity $Z$ serves to insure normalization in the canonical ensemble through

$$1=\sum_n\frac{e^{-\beta E_n}}{Z}. \tag{6.4.16}$$

You might wonder, in fact, about the relation between the canonical probability

$$\frac{e^{-\beta E_n}}{Z}, \tag{6.4.17}$$

which we have seen many times before, and the recently derived occupancy probability

$$\frac{1}{N}\frac{1}{e^{\beta(\epsilon_r-\mu)}\pm 1}. \tag{6.4.18}$$

The first result applies to both interacting and non-interacting systems, both classical and quantal. The second applies only to non-interacting quantal systems. Why do we need a new probability? What was wrong with our derivation (in section 4.1) of the canonical probability that requires us to replace it with an occupancy probability? The answer is that nothing was wrong and that the occupancy probability doesn't replace the canonical probability. The canonical probability and the occupancy probability answer different questions. The first finds the probability that the entire system is in the many-body state $n$. The second finds the probability that the one-body level $r$ is used as a building block in constructing the many-body state. Indeed, although we derived the occupancy probability result through a grand canonical argument, it is also possible to derive the occupancy probabilities from strict canonically arguments, proof that these two probabilities can coexist peacefully.

## 6.4.3 The Boltzmann limit

This is the limit where particles are far enough apart that overlap of wavefunction is minimal, so we needn't worry about symmetrization or antisymmetrization. Equivalently, it is the limit where $\langle n_r\rangle \ll$ for all $r$.

## 6.4.4 Problems

*6.10 Evaluation of the grand canonical partition function*

Can you find a simple expression for $\Xi(\beta, \mu)$ for non-interacting particles in a one-dimensional harmonic well? For non-interacting particles in a one-dimensional infinite square well? For any other potential? Can you do anything valuable with such an expression once you've found it?

*6.11 Entropy of quantal ideal gases*

This problem derives an expression for the entropy of a quantal ideal gas in terms of the mean occupation numbers hnri. (Compare problem 4.3.) Throughout the problem, in the symbols $\pm$ and $\mp$, the top sign refers to fermions and the bottom sign refers to bosons.

a. Use the connection between thermodynamics and statistical mechanics to show that, for any system,

$$\frac{S(T,V,\mu)}{k_B}=\ln\Xi-\beta\frac{\partial\ln\Xi}{\partial\beta}. \tag{6.4.19}$$

b. Show that for the quantal ideal gas,

$$\ln\Xi(T,V,\mu)=\mp\sum_r\ln(1\mp\langle n_r\rangle). \tag{6.4.20}$$

c. The mean occupation numbers $\langle n_r\rangle$ are functions of $T$, $V$, and $\mu$ (although it is notationally clumsy to show this dependence). Show that

$$\begin{aligned}\beta \frac{\partial\langle n_r\rangle}{\partial\beta})_{V,\mu} &= -\beta\left(\epsilon_r-\mu\right)\langle n_r\rangle\left(1\mp\langle n_r\rangle\right) \\ &= -\left[\ln(1\mp\langle n_r\rangle)-\ln\langle n_r\rangle\right|\langle n_r\rangle\left(1\mp\langle n_r\rangle\right)\end{aligned}.$$

d. Finally, show that

$$S(T,V,\mu)=-k_B\sum_r\left[\langle n_r\rangle\ln\langle n_r\rangle\pm(1\mp\langle n_r\rangle)\ln(1\mp\langle n_r\rangle)\right]. \tag{6.4.21}$$

e. Find a good approximation for this expression in the Boltzmann limit, $\langle n_r\rangle\ll 1$.

f. (Optional.) Find an expression for $C_V$ in terms of the quantities $\langle n_r\rangle$.

*6.12 Isothermal compressibility of quantal ideal gases*

a. Show that in a quantal ideal gas, the isothermal compressibility is

$$\kappa_T=\frac{1}{\rho k_BT}\left[1\mp\frac{\sum_r\left(n_r\right)^2}{\sum_r\langle n_r\rangle}\right], \tag{6.4.22}$$

where as usual the top sign refers to fermions and the bottom sign to bosons. (Clue: Choose the most appropriate expression for $\kappa_T$ from those uncovered in problem 3.33.)

b. Compare this expression to that for a classical ("Maxwell-Boltzmann") ideal gas.

c. The negative sign in the expression for fermions opens the possibility that κT could be negative. Prove that this potential horror never happens. d. Do the relative sizes of the three compressibilites (fermion, classical, boson) adhere to your qualitative expectations? (Compare problem 6.29.)

*6.13 Dispersion in occupation number*

Find an expression analogous to (6.45) giving the dispersion in the occupation numbers. (Clue: A slick trick would be helpful here.) Answer:

$$\Delta n_r=\frac{1}{e^{\beta(\epsilon_r-\mu)/2}\pm e^{-\beta(\epsilon_r-\mu)/2}}=\sqrt{\langle n_r\rangle\left(1\mp\langle n_r\rangle\right)} \tag{6.4.23}$$