12. Quantum gases

In the previous chapter we derived the grand canonical distribution. It applies to a system in equilibrium with a reservoir of energy and particles. This kind of system is referred to as an open system. The grand canonical distribution is given by:

$$P_r = \frac{1}{Z}\exp(-\beta E_r + \beta\mu N_r)$$

where

$$Z = \sum_r \exp(-\beta E_r + \beta\mu N_r)$$

Here, we use r to label the microstates to avoid a later clash of notation. Microstate r contains N_r particles and has energy E_r.

12.1. N as a function of μ

In the grand canonical distribution, microstates of the system with all numbers of particles are possible. However, we expect that for large N , the distribution of the particle number will become sharp.

The mean number of particles is calculated as follows:

$$\overline{N} = \sum_r N_r P_r = \frac{1}{Z}\sum_r N_r \exp\left(\beta\left[N_r\mu - E_r\right]\right)$$

$$\overline{N} = \frac{1}{\beta}\frac{\partial \ln Z}{\partial \mu}$$

where a similar idea to chapter 6 — where the mean energy was written as a derivative with respect to β — has been used.

By a similar argument for the energy fluctuations in chapter 5, we find

$$\frac{\left(\Delta\overline{N^2}\right)^{1/2}}{\overline{N}} \sim \frac{1}{N^{1/2}}$$

Therefore, we see that N is sharp about $\overline{N}$ (i.e., fluctuations are small on the scale of the mean).

Thus, we

Key Point 16:

choose μ to fix $\overline{N} = N(\mu)$

in the same way that in the canonical distribution for a large system choosing T fixes $\overline{E} = E(T)$
.

Remember also that μ depends on temperature.

12.2. Indistinguishable particles

Quantum particles have access to a set of states (we will call them 'single-particle- states') defined by the solutions to the Schrödinger equation for one particle in a box. We will use $i = 1, 2, \ldots \infty$ as a label of these states, and will denote the associated energies by $\epsilon_1, \epsilon_2, \ldots \epsilon_\infty$. Note: In the following, the term 'quantum state' will be used interchangeably with 'single-particle state.'

Recall the definition of a microstate (chapter 2) for

- **Distinguishable particles**: A microstate is specified by $i_1, i_2, \ldots, i_N$, i.e., the state of each particle.

Now for

- **Indistinguishable particles**: A microstate is specified by $n_1, n_2, \ldots$, where n_i is the occupation number, i.e., the number of particles in single-particle state i.

Thus, for indistinguishable particles in microstate r specified by the set $\{n_i\}$:

$$N_r = \sum_i n_i \quad \text{and} \quad E_r = \sum_i n_i \epsilon_i$$

where ϵ_i is the energy of single-particle state i.

We can write:

$$\beta(N_r \mu - E_r) = \beta \sum_i n_i(\mu - \epsilon_i)$$

and the sum over all possible microstates r becomes:

$$\sum_r \to \sum_{n_1} \sum_{n_2} \cdots$$

i.e., a sum over all possible occupation numbers n_i of all quantum states.

It should be noted that in the canonical distribution, where N is fixed, a sum over all n_i is non-trivial because, for example, the value of occupation number n_1 affects what values the other occupation numbers are allowed to take. However, in the grand canonical distribution, the sums 'decouple,' and the problem of the constraint on N is replaced by the problem of choosing μ to give the desired $N(\mu)$.

Now consider the grand canonical partition function:

$$Z = \sum_r \exp\left(\beta\left[N_r\mu - E_r\right]\right)$$

$$= \left[\sum_{n_1}\sum_{n_2}\cdots\right] \exp\left(\beta\sum_i n_i(\mu - \epsilon_i)\right)$$

$$= \left[\sum_{n_1}\exp\left(\beta n_1(\mu - \epsilon_1)\right)\right] \times \left[\sum_{n_2}\exp\left(\beta n_2(\mu - \epsilon_2)\right)\right] \times \cdots$$

$$= Z_1 \times Z_2 \times \cdots = \prod_i Z_i$$

where $Z_i = \sum_{n_i} e^{\beta n_i(\mu - \epsilon_i)}$ is the partition function for *quantum state* i.

Thus, a factorization into single-state partition functions occurs. This should be contrasted with the factorization into single-particle partition functions that occurred in the canonical (Boltzmann) distribution.

Using the Factorization of Z consider the probability of a microstate $r = \{n_1, n_2, n_3, ...\}$:

$$P_r = P(n_1, n_2, ...) = \frac{\exp\left(\beta n_1(\mu - \epsilon_1)\right)}{Z_1} \times \frac{\exp\left(\beta n_2(\mu - \epsilon_2)\right)}{Z_2} \times \cdots$$

$$= P(n_1)P(n_2)\cdots$$

where the single state distribution is:

$$P(n_i) = \frac{\exp\left(\beta n_i(\mu - \epsilon_i)\right)}{Z_i}$$

To understand this result, one can think of the quantum state i as being free to exchange particles with the rest of the quantum states, which therefore act as a reservoir of particles and energy. Thus, the quantum state i is itself an open system.

12.3. Fermions and Bosons

In first year quantum mechanics, you have met the concepts of:

- **Spin**
- **Fermions and bosons**

Fermions have spin equal to a half-integral multiple of $\hbar$, e.g., the magnetic dipoles we considered in the model magnet have spin $s = 1/2$, and therefore, there are $2s + 1 = 2$ spin states (up or down for the dipole).

Examples of fermions are electrons, neutrons, protons, and composite particles made of an odd number of fermions, e.g., ^{3}He, whose nucleus contains two protons and a neutron and is therefore a fermion; also, the whole atom is a fermion.

Bosons have spin equal to an integral multiple of $\hbar$ (note that they can have spin zero). Examples are photons and composite particles made up of an even number of fermions, e.g., ^{4}He.

The most important thing for our purposes is the **Pauli exclusion principle**:

> **There can be at most one fermion in any quantum state.**

In quantum mechanics, you will see how this comes from the antisymmetry of the many-particle wavefunction for fermions, but the boxed fact is all you need to know here.

Now, consider the single state partition function. Due to the exclusion principle for fermions, an occupation number n_i can only take the values 0 or 1. Therefore, for fermions:

$$Z_i = \sum_{n_i=0,1} \exp\left(\beta n_i(\mu - \epsilon_i)\right) = 1 + \exp\left(\beta(\mu - \epsilon_i)\right)$$

On the other hand, there is no such restriction for bosons, for which n_i can take all values from 0 to ∞.

For bosons:

$$Z_i = \sum_{n_i=0}^{\infty} \exp\left(\beta n_i(\mu - \epsilon_i)\right) = \frac{1}{1 - \exp\left(\beta(\mu - \epsilon_i)\right)}$$

for $\exp\left(\beta(\mu - \epsilon_i)\right) < 1$.

To understand this result for bosons, recall from chapter 8 that:

$$\sum_{n=0}^{\infty} x^n = \frac{1}{1-x} \quad \text{for } |x| < 1 \, .$$

We can now calculate $\overline{n}_i$, the average number of particles in quantum state i. To do the calculation at the same time for fermions and bosons, write:

$$Z_i = \left[1 \pm \exp\left(\beta(\mu - \epsilon_i)\right)\right]^{\pm 1}$$

where $-$ refers to bosons, and $+$ refers to fermions.

Now:

$$\overline{n}_i = \sum_{n_i} n_i P(n_i) = \frac{1}{\beta}\frac{\partial \ln Z_i}{\partial \mu}.$$

Thus:

$$\overline{n}_i = \pm \frac{1}{\beta}\frac{\partial}{\partial \mu} \ln\left[1 \pm \exp\left(\beta(\mu - \epsilon_i)\right)\right]$$

$$= \pm \frac{1}{\beta}(\pm\beta)\frac{\exp\left(\beta(\mu - \epsilon_i)\right)}{1 \pm \exp\left(\beta(\mu - \epsilon_i)\right)}$$

$$= \frac{\exp\left(\beta(\mu - \epsilon_i)\right)}{1 \pm \exp\left(\beta(\mu - \epsilon_i)\right)}$$

$$= \frac{1}{\exp\left(\beta(\epsilon_i - \mu)\right) \pm 1}$$

The final results for the mean number of particles in quantum state i (that has energy ϵ_i) are known as the **Fermi-Dirac** and **Bose-Einstein** distributions:

Key Point 17:

$$\overline{n}_i = f_{\pm}(\epsilon_i) = \frac{1}{\exp\left(\beta(\epsilon_i - \mu)\right) \pm 1}$$

where $+$ refers to fermions, and $-$ refers to bosons.

$N(\mu)$ (or $\mu(N)$) is determined by the equation:

$$N = \sum_i \overline{n}_i = \sum_i f_\pm(\epsilon_i)$$