

14 Mar.

Plan:

Grand-canonical ensemble } Quantum ideal ~~gases~~
Quantum statistics

→ Energy & particle # fluctuate

Temperature & chemical potential

Grand-canonical partition function Z_g

Potential $\Phi = -T \log Z_g$

energy, entropy, particle number

Unit 7: Quantum statistics

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7.1 Quantized energy levels and their micro-states

Now that we have defined the grand-canonical ensemble, we will apply it to investigate quantum statistical systems. The first step is to introduce quantum statistics itself, building on the initial glimpse that we got in Section 4.1. It is worth reiterating that no prior knowledge of quantum physics is assumed, nor will this module attempt to teach quantum mechanics. We will simply consider quantum behaviour as an ansatz (that turns out to be realized in nature), and analyze the resulting systems by making use of the statistical physics tools we have developed.

Looking back to our derivation of the canonical partition function for a classical (that is, non-quantum) ideal gas in Section 4.1, we can recall that we engaged in slightly circular argumentation. First, because the partition function is defined as a sum over micro-states ω_i ,

$$Z = \sum_i e^{-E(\vec{p}_i)/T},$$

we had to conjecture that the gas particles' momenta \vec{p}_i are quantized and can take only particular discrete values, rather than varying continuously. These quantized momenta produce a countable number of discrete energy levels, leading to a countable number of micro-states and hence a well-defined partition function that takes the form of a sum over all possible discrete momenta for each particle. Second, we then argued that when $L\sqrt{mT} \gg \hbar$, any energy levels with non-negligible Boltzmann factors are spaced very close to each other. Therefore the function being summed varies very smoothly, allowing us to approximate that sum as a multi-dimensional integral. That is, we went right back to working with continuously varying momenta, despite the formal need to regulate the system by quantization.

$$E \propto \frac{\hbar^2}{mTL^2}$$

Two changes are required to define quantum statistics. First, not surprisingly, we need to retain discrete energy levels rather than approximating these as continuous. This will allow our calculations to remain valid even in the quantum regime where $L\sqrt{mT} \sim \hbar$. The second change is more subtle, and is connected to the fundamental indistinguishability of identical particles governed by quantum mechanics — a fact about nature that we will take as given. The issue is how to handle micro-states in which multiple indistinguishable particles occupy the same energy level.

To build up to this issue, we will first see what happens when we ignore it and apply our usual classical approach to compute the grand-canonical partition function for a system with discrete energy levels. Despite the quantized energy levels, this calculation will still produce a non-quantum result known as **Maxwell-Boltzmann (MB) statistics**, named after **James Clerk Maxwell** and Ludwig Boltzmann. We will then consider how this approach can break down, and use this insight to develop true quantum statistics in the following sections. Finally, we

will wrap up this unit by confirming that Maxwell–Boltzmann statistics remains an excellent approximation to quantum statistics in the classical limit.

7.1.1 Maxwell–Boltzmann statistics

Let's begin our classical derivation of the grand-canonical partition function for a system with discrete energy levels by defining some necessary notation. We label the discrete energy levels \mathcal{E}_ℓ for $\ell = 0, 1, \dots, L$, where L can be taken to infinity while retaining a countable number of micro-states and hence well-defined partition functions. The energy level \mathcal{E}_ℓ may be characterized by extra information in addition to the actual value of its energy, E_ℓ . As we saw in Section 4.1, it is therefore possible for distinct energy levels $\{\mathcal{E}_m, \mathcal{E}_n\}$ to have the same energy $E_m = E_n$ for $m \neq n$. Such energy levels with the same value of the energy are said to be *degenerate*. We will label energy levels so that $E_m \leq E_n$ for $m < n$. Without loss of generality, we can take $E_\ell \geq E_0 \geq 0$.

Now starting from the general expression for the grand-canonical partition function, Eq. 74,

$$Z_g(\beta, \mu) = \sum_i e^{-\beta(E_i - \mu N_i)},$$

we just need to define the micro-states ω_i with energy E_i and particle number N_i . In the classical Maxwell–Boltzmann approach, we first sum over all possible particle numbers,

$$Z_g^{\text{MB}}(\beta, \mu) = \sum_{i, N_i=0} e^{-\beta E_i} + \sum_{j, N_j=1} e^{-\beta(E_j - \mu)} + \sum_{k, N_k=2} e^{-\beta(E_k - 2\mu)} + \dots,$$

where the micro-states labelled $\{\omega_i, \omega_j, \omega_k, \dots\}$ are those that have $N = 0, 1, 2, \dots$ particles, respectively. We can recognize N -particle canonical partition functions $Z_N(\beta)$ in the expression above:

$$Z_g^{\text{MB}}(\beta, \mu) = Z_0(\beta) + e^{\beta\mu} Z_1(\beta) + e^{2\beta\mu} Z_2(\beta) + \dots = \sum_{N=0}^{\infty} [e^{\beta\mu}]^N Z_N(\beta). \quad (82)$$

This is a general result known as the fugacity expansion, where $e^{\beta\mu}$ is called the fugacity. Organizing the calculation in this way allows us to take advantage of our experience with the canonical ensemble.

In particular, because we continue to consider only 'ideal' systems in which the particles don't interact with each other, each $Z_N(\beta)$ is simply the product of the single-particle partition functions $Z_1(\beta)$ for all N independent particles,

$$Z_N(\beta) = \frac{1}{N!} [Z_1(\beta)]^N,$$

with the factor of $N!$ included to correct for over-counting indistinguishable particles. This is exactly the derivation we performed in Section 4.1, to obtain Eq. 51 for the classical ideal gas. Inserting this Z_N into Eq. 82, we have

$$Z_g^{\text{MB}}(\beta, \mu) = \sum_{N=0}^{\infty} [e^{\beta\mu}]^N \frac{1}{N!} [Z_1(\beta)]^N = \sum_{N=0}^{\infty} \frac{1}{N!} [e^{\beta\mu} Z_1(\beta)]^N = \exp [e^{\beta\mu} Z_1(\beta)].$$

In the case of a system with discrete energy levels E_ℓ , the single-particle partition function is simply

$$Z_1(\beta) = \sum_{\ell=0}^L e^{-\beta E_\ell}$$

where each micro-state corresponds to the particle being in a different energy level. This gives us the Maxwell-Boltzmann grand-canonical partition function

classical $Z_g^{\text{MB}}(\beta, \mu) = \exp \left[e^{\beta\mu} \sum_{\ell=0}^L e^{-\beta E_\ell} \right] = \exp \left[\sum_{\ell=0}^L e^{-\beta(E_\ell - \mu)} \right]. \quad (83)$

7.1.2 Over-counting and quantum statistics

The problem with the derivation above was already mentioned in the footnote accompanying Eq. 51. In short, the factor of $\frac{1}{N!}$ that we included to fix the over-counting of micro-states for N indistinguishable particles is only correct when each of these particles is in a different energy level. When the particles' energies can vary continuously it is effectively impossible for two of them to have exactly the same energy, making it safe to assume a different energy level for each particle. More generally, this assumption can remain an excellent approximation whenever there are many more energy levels than there are particles to occupy them. However, the assumption breaks down when there is a non-negligible chance of two particles occupying the same energy level, which is what happens in the quantum regime.

$\hbar \ll L\sqrt{mT}$

We can illustrate the problem by considering a simple system with $N = 2$ particles that can occupy any of five energy levels, \mathcal{E}_0 through \mathcal{E}_4 . For a further simplification, let's suppose that all five energy levels are degenerate, with $E_\ell = 0$ for $\ell = 0, \dots, 4$. This means the canonical partition function simply counts the (positive integer) number of micro-states. For example, the single-particle partition function is

$$Z_1 = \sum_{\ell=0}^4 e^{-\beta E_\ell} = \sum_{\ell=0}^4 1 = 5$$

for all $\beta = 1/T$.

Computing the canonical partition function for this system is therefore equivalent to counting the number of ways $N = 2$ balls can be placed in $L+1 = 5$ boxes. We can represent possible micro-states by drawing these balls and boxes, for example $\square \bullet \square \square \square$ and $\square \square \bullet \bullet \square$. What is the two-particle partition function if the balls are distinguishable?

$$Z_D = 2^5 = Z_1^N$$

$\frac{1}{N!}$

For indistinguishable particles, our derivation above would predict the partition function $Z_I = \frac{1}{2} Z_D$, which is not an integer and therefore cannot be correct.

$= 12.5$

We can see where the over-counting correction goes wrong by explicitly writing down all micro-states in both cases of distinguishable and indistinguishable particles. In the distinguishable case, we can suppose that the balls are red (\bullet) and blue (\circ), and compactly label micro-states by recording whether each box is empty ("0"), contains the red ball ("R"), the blue ball ("B") or both balls ("2"):

$$\boxed{}\boxed{}\boxed{\bullet}\boxed{\circ} = \underline{00R0B} \qquad \boxed{}\boxed{}\boxed{\bullet\circ}\boxed{} = \underline{00200}.$$

The full set of micro-states is then

<u>RB000</u>	0R0B0	<u>BR000</u>	0B0R0	20000	
R0B00	0R00B	B0R00	0B00R	02000	
R00B0	00RB0	B00R0	00BR0	00200	= 25
R000B	00R0B	B000R	00B0R	00020	
0RB00	000RB	0BR00	000BR	00002	

If we now consider indistinguishable particles where we can only know the number $R = B = 1$, we see that the third and fourth columns above duplicate the first two columns. This is exactly the over-counting that the usual factor of $\frac{1}{N!} = \frac{1}{2}$ corrects. On the other hand, the micro-states in the final column, with both particles in the same energy level, were not over-counted, and must not be divided by $N!$. This leaves us with 15 micro-states, rather than $25/2$:

11000	01010	20000
10100	01001	02000
10010	00110	00200
10001	00101	00020
01100	00011	<u>00002</u>

We can generalize this simple exercise by systematically labeling the micro-states for indistinguishable particles by occupation numbers n_ℓ , similar to those that we encountered when using replicas to set up the canonical ensemble in Section 3.1 and the grand-canonical ensemble in Section 6.2. In this case the occupation number n_ℓ is simply the number of particles in energy level \mathcal{E}_ℓ . This change of perspective is the final ingredient we need to define quantum statistics as opposed to classical statistics.

In **quantum statistics**, the micro-states are defined by considering each energy level \mathcal{E}_ℓ in turn, and summing over the possible occupation numbers n_ℓ that it could have. This differs from the classical approach in which we define the micro-states by considering each particle in turn, and summing over the possible energies that it could have.

Because quantum mechanics requires all particles of the same type to be indistinguishable, the classical approach requires that we correct for over-counting,

and we have now seen how this becomes non-trivial whenever multiple particles can occupy the same energy level. The quantum approach of summing over the occupation numbers of the quantized energy levels avoids this issue, and requires no additional factors to correct over-counting.

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7.2 Bosons and fermions

In Sections 7.3 and 7.4 we will carry out explicit computations to show how the quantum statistics defined above work in practice. First, there is one more fact about nature that we need to take into account. This concerns the occupation numbers n_ℓ that are possible for each energy level \mathcal{E}_ℓ .

Using quantum mechanics and special relativity, it is possible to prove that all particles in three spatial dimensions fall into two distinct classes. (More exotic behaviour is possible for particles confined to two-dimensional surfaces.) This result is known as the spin–statistics theorem, while the two types of particles it describes are called **bosons** (named after Satyendra Nath Bose) and **fermions** (named after Enrico Fermi). These two classes of particles obey different rules for their possible occupation numbers, and therefore give rise to distinct quantum statistics.

Any non-negative number of identical bosons can simultaneously occupy the same energy level, corresponding to occupation numbers $n_\ell = 0, 1, 2, \dots$. Physical examples of bosons include photons (particles of light), pions, helium-4 atoms and the famous Higgs particle.

On the other hand, it is impossible for multiple identical fermions to occupy the same energy level, meaning that their only possible occupation numbers are $n_\ell = 0$ and 1. This behaviour is known as the *Pauli exclusion principle* (named after Wolfgang Pauli) and has extremely important consequences, including the existence of chemistry and life. Physical examples of fermions include electrons, protons, neutrons, neutrinos and helium-3 atoms.

The reason multiple identical fermions cannot occupy the same energy level is due to a feature of quantum mechanics, and not because they physically repel each other. This paragraph will imprecisely describe that aspect of quantum physics for the curious, and can be skipped without any problem. Consider a system of identical quantum particles occupying various energy levels. Loosely speaking, all observable properties of this system depend on the *square* of the quantum function that defines it. Interchanging any pair of indistinguishable particles must leave all these observable properties unchanged. Just as $\sqrt{1} = \pm 1$, there are two ways the underlying quantum function can behave to leave its square unchanged: it can be completely symmetric or completely antisymmetric under all possible interchanges. Bosons correspond to the symmetric case, while fermions correspond to the antisymmetric case. At the same time, if two identical particles are occupying the same energy level, then the quantum function itself must remain unchanged (i.e., symmetric) when they are interchanged. In the fermionic case, the resulting quantum function must therefore be simulta-