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 $\mathcal{E}_\ell$.

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 $n_\ell = 0, 1, 2, \cdots$. 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 simultaneously symmetric and antisymmetric, which is only possible if it is exactly zero. In other words no systems with multiple identical fermions in the same energy level can possibly exist.

Looking back at the example system of $N = 2$ particles with five energy levels in the previous section, all 15 micro-states we wrote down are possible if the particles are bosons. How many micro-states are allowed if the particles are fermions?

The ten with $n_\ell \in \{0,1\}$: 11000 10100 10010 10001 01010 01100 01001 00110 00101 00011

This difference in the possible micro-states ensures that bosons and fermions exhibit different quantum statistics. We will now consider each case in turn.

7.3 Bose–Einstein statistics

The quantum statistics of bosons is known as **Bose–Einstein** (BE) statistics, named after Satyendra Nath Bose and Albert Einstein. As described above, to carry out the sum over all micro-states in the grand-canonical partition function

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

we first sum over all energy levels $\mathcal{E}_\ell$, and then over all possible occupation numbers $n_\ell \in \mathbb{N}_0$ for each energy level.

Consider first the simple case of a system that only has a single energy level $\mathcal{E}_0$, with energy E_0. In this case, each micro-state ω_i is uniquely described by its particle number N_i, which is just the occupation number of $\mathcal{E}_0$. What is the energy E_i of micro-state ω_i with occupation number $n_0 = N_i$?

$E_i = N_i E_0 = n_0 E_0$

Sorry!

Summing over all possible occupation numbers for this single energy level, the Bose–Einstein grand-canonical partition function for this system is

$$Z_g^{\text{BE}}(\beta, \mu) = \sum_{n_0=0}^{\infty} e^{-\beta(E_0-\mu)n_0} = \sum_{n_0=0}^{\infty} \left[e^{-\beta(E_0-\mu)}\right]^{n_0} = \frac{1}{1 - e^{-\beta(E_0-\mu)}}. \tag{84}$$

In the last step we recognized the geometric series

$$\frac{1}{1-x} = 1 + x + x^2 + \cdots ,$$

$-\beta(\varepsilon_0 - \mu) < 0$

which only converges for $x = e^{-\beta(E_0-\mu)} < 1$. For natural systems with $\beta = 1/T > 0$, this condition requires $E_0 - \mu > 0$ or equivalently $\mu < E_0$. Since we can take all $E_\ell \geq 0$ without loss of generality, this constraint is consistent with the negative chemical potential $\mu < 0$ that we discussed in Unit 6.

At this point, it is straightforward to generalize to multiple energy levels $\mathcal{E}_\ell$ with $\ell = 0, 1, \cdots, L$. Because we consider only ideal systems with non-interacting particles, the micro-state ω_i defined by the set of occupation numbers $\{n_\ell\}$ has total energy and particle number

$$E_i = \sum_{\ell=0}^{L} E_\ell n_\ell \qquad\qquad N_i = \sum_{\ell=0}^{L} n_\ell. \tag{85}$$

The general Bose–Einstein grand-canonical partition function is therefore

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

$$Z_g^{\text{BE}}(\beta,\mu) = \sum_{n_0=0}^{\infty}\sum_{n_1=0}^{\infty}\cdots\sum_{n_L=0}^{\infty} \exp\left[-\beta\sum_{\ell=0}^{L}(E_\ell-\mu)\,n_\ell\right].$$

We can apply the identity $e^{\sum_i x_i} = \prod_i e^{x_i}$ to rewrite

$$\exp\left[-\beta\sum_{\ell=0}^{L}(E_\ell-\mu)\,n_\ell\right] = \left(e^{-\beta(E_0-\mu)n_0}\right)\left(e^{-\beta(E_1-\mu)n_1}\right)\cdots\left(e^{-\beta(E_L-\mu)n_L}\right).$$

Recalling $\mu < E_\ell$ for all ℓ, by rearranging the terms we find

$$\begin{aligned} Z_g^{\text{BE}}(\beta,\mu) &= \left(\sum_{n_0=0}^{\infty} e^{-\beta(E_0-\mu)n_0}\right)\left(\sum_{n_1=0}^{\infty} e^{-\beta(E_1-\mu)n_1}\right)\cdots\left(\sum_{n_L=0}^{\infty} e^{-\beta(E_L-\mu)n_L}\right) \\ &= \prod_{\ell=0}^{L}\frac{1}{1-e^{-\beta(E_\ell-\mu)}}. \end{aligned} \tag{86}$$

This grand-canonical partition function defines the quantum Bose–Einstein statistics of bosons. Its structure as the product of an independent contribution for each energy level is reminiscent of the result $Z_N \propto Z_1^N$ for the classical N-particle canonical partition function discussed in Section 7.1. In such situations we say that the calculation *factorizes* into a product of many simpler terms, allowing us to build up the full result on the basis of much easier computations. Looking back to Eq. 83, we can also observe factorization in the classical Maxwell–Boltzmann grand-canonical partition function,

$$Z_g^{\text{MB}}(\beta,\mu) = \exp\left[\sum_{\ell=0}^{L} e^{-\beta(E_\ell-\mu)}\right] = \prod_{\ell=0}^{L}\exp\left[e^{-\beta(E_\ell-\mu)}\right]. \tag{87}$$

In all of these cases, factorization is possible because the particles are non-interacting. Starting in Unit 9 we will consider non-ideal systems in which the particles can interact with each other, where the absence of factorization will make analyses much more difficult.

7.4 Fermi–Dirac statistics

The quantum statistics of fermions is known as **Fermi–Dirac** (FD) statistics, named after Enrico Fermi and Paul Dirac. The derivation of the Fermi–Dirac grand-canonical partition function is very similar to the Bose–Einstein case considered in the previous section. We again proceed by summing over all energy levels $\mathcal{E}_\ell$, and just have to account for the more limited possible occupation numbers $n_\ell \in \{0, 1\}$ for each energy level.

Taking the same approach of first considering a simple system with only a single energy level, Eq. 84 would just change to

$$Z_g^{\mathsf{FD}}(\beta, \mu) = \sum_{n_0=0}^{1} e^{-\beta(E_0-\mu)n_0} = 1 + e^{-\beta(E_0-\mu)}.$$

Generalizing to multiple energy levels $\mathcal{E}_\ell$ with $\ell = 0, 1, \cdots, L$, the micro-state energies $E_i = \sum_\ell E_\ell n_\ell$ and particle numbers $N_i = \sum_\ell n_\ell$ remain the same as in Eq. 85, and the computation again factorizes,

$$\begin{aligned}
Z_g^{\mathsf{FD}}(\beta, \mu) &= \sum_{n_0=0}^{1} \sum_{n_1=0}^{1} \cdots \sum_{n_L=0}^{1} \exp\left[-\beta \sum_{\ell=0}^{L} (E_\ell - \mu)\, n_\ell\right] \\
&= \left(\sum_{n_0=0}^{1} e^{-\beta(E_0-\mu)n_0}\right)\left(\sum_{n_1=0}^{1} e^{-\beta(E_1-\mu)n_1}\right)\cdots\left(\sum_{n_L=0}^{1} e^{-\beta(E_L-\mu)n_L}\right) \\
&= \prod_{\ell=0}^{L} \left[1 + e^{-\beta(E_\ell-\mu)}\right]. \qquad (88)
\end{aligned}$$

This grand-canonical partition function defines the quantum Fermi–Dirac statistics of fermions. In both this case and the case of classical Maxwell–Boltzmann statistics there is no constraint on $\beta(E_\ell - \mu)$.

In Unit 8 we will take Z_g^{BE} and Z_g^{FD} as starting points to analyze quantum gases of bosons and fermions, respectively. Before beginning those more detailed analyses, let's quickly compare the three types of statistics that we have derived in this unit, while they are all close to hand.

7.5 The classical limit

In Section 7.1 we claimed that if the probability of multiple particles occupying the same energy level is negligible, then the classical Maxwell–Boltzmann statistics can be an excellent approximation to quantum statistics — both bosonic and fermionic. We will wrap up this unit by demonstrating this result and clarifying the conditions that correspond to this 'classical limit' of quantum statistics.

It is useful to start by asking when we should expect classical statistics to predict a non-negligible probability for multiple particles to occupy the same energy level, leading to the over-counting problems that are solved by quantum statistics. This is actually a question we have already considered, back in Section 3.4 (and the first homework assignment). There we used the canonical ensemble to analyze classical spin systems with discrete energy levels, finding that at low temperatures the systems are dominated by their lowest-energy micro-states, with only exponentially suppressed corrections coming from any higher-energy micro-states. In the present context, this corresponds to a classical prediction of exponentially small probabilities for particles to occupy any energy levels with $E_\ell > E_0$ — effectively guaranteeing that the lowest energy level $\mathcal{E}_0$ will be occupied by multiple particles and classical statistics will break down.

In short, the low-temperature regime is where quantum and classical statistics disagree, while **high temperatures correspond to the classical limit** of quantum statistics. If you are not convinced by the argument leading to this conclusion, you can find a more detailed derivation based on the equation of state and thermal de Broglie wavelength in Section 3.5 of David Tong's *Lectures on Statistical Physics* (the first item in the list of further reading on page 5). 15 Mar.

For now, we want to consider the grand-canonical ensemble at high temperatures, to see whether the quantum and classical statistics we derived in the previous sections become equivalent in this regime. However, it can be subtle to work with the grand-canonical ensemble at high temperatures, due to the dependence of the average number of particles on the temperature. To demonstrate this subtlety, let's compute the average particle number $\langle N\rangle(T,\mu)$ starting from the grand-canonical partition function, for both classical and quantum statistics.

For convenience, let's collect our earlier results for the grand-canonical partition functions corresponding to classical Maxwell–Boltzmann statistics (Eq. 87), the quantum Bose–Einstein statistics of bosons (Eq. 86) and the quantum Fermi–Dirac statistics of fermions (Eq. 88):

$$Z_g^{\text{MB}} = \prod_{\ell=0}^{L} \exp\left[e^{-\beta(E_\ell-\mu)}\right]$$

$$Z_g^{\text{BE}} = \prod_{\ell=0}^{L} \frac{1}{1-e^{-\beta(E_\ell-\mu)}} \qquad\qquad Z_g^{\text{FD}} = \prod_{\ell=0}^{L}\left[1+e^{-\beta(E_\ell-\mu)}\right].$$

Recalling $\log\left[\prod_i x_i\right] = \sum_i \log x_i$, the corresponding grand-canonical potentials $\Phi = -T\log Z_g$ for these three cases are

$$\Phi_{\text{MB}} = -T\sum_{\ell=0}^{L} e^{-\beta(E_\ell-\mu)}$$

$$\Phi_{\text{BE}} = T\sum_{\ell=0}^{L}\log\left[1-e^{-\beta(E_\ell-\mu)}\right] \qquad\qquad \Phi_{\text{FD}} = -T\sum_{\ell=0}^{L}\log\left[1+e^{-\beta(E_\ell-\mu)}\right].$$