Appendix B

Elements of statistical physics

Thermodynamics is the privileged approach to describe the quantum state of atomic gases, once they are cooled down to ultra-low temperatures. It permits to account for a huge amount of physical properties of ultracold quantum gases, provided they are at thermal equilibrium. More precisely, we shall make intensive use of statistical physics all along this work. The latter establishes the relationship between microscopic dynamics and macroscopic thermodynamics. The purpose of this section is to provide the reader with a brief reminder of its basic principles. Our aim is not to describe it in its full generality but, rather, to recall the main results that will be directly useful for our discussions. It also serves to define the main notations used all along the work. For more exhaustive introductions to statistical physics, the interested reader is invited to refer to more complete books, for instance Refs. [207–211].

B.1 The statistical approach

In this section, we review basic aspects of general statistical physics. We first introduce the notion of microscopic versus macroscopic descriptions of a given physical system, whose relationship is at the very heart of statistical physics. We then discuss the basic principle of statistical physics, known as the Boltzmann principle, as well as the notion of ergodicity. We finally review the basics of the Gibbs ensembles and recall how to compute relevant quantities from the partition function.

B.1.1 From microscopics to macroscopics

To start with, consider a physical system defined in some phase space. For the sake of concreteness, we may think of a gas of particles, confined in some finite region of space, interacting with external fields and, possibly, with each other. Such a simple system can be described at different levels, either microscopically or macroscopically. While the two descriptions are perfectly legitimate, they provide orthogonal descriptions of the same systems in many respects.

Microscopic description

The microscopic description assumes that the constituents of the system, say the particles of the gas, are sufficiently well known to establish a basis for the description of the full system. In
practice, it is useful to distinguish classical and quantum systems although, as we shall see, their microscopic descriptions share their most fundamental features.

Classical gases – For a classical gas of $N$ particles, the various constituents may be distinguished by a label $j \in [1..N]$, where $N$ is the total number of particles. The so-called microstate of each particle can be well identified by its coordinates in the phase space, i.e. its real-space position $r_j$ and its momentum $p_j$. The corresponding one-body microstate is written $\lambda_j \equiv (r_j, p_j)$. Then, the microscopic state of the full system is completely described by the set of the $N$ phase-space positions of the $N$ particles. In the following, the many-body microstate will be written $\Lambda \equiv \{\lambda_1, \ldots, \lambda_N\}$, see Fig. B.1(a).

Having formulated the possible microstates of the system, we can turn to their dynamics. For a classical system, it is governed by the Newton equations of motion,

$$\frac{dr_j}{dt} = \frac{p_j(t)}{m} \quad \text{and} \quad \frac{dp_j}{dt} = F_j \left( \{r_j(t), p_j(t)\}, t \right), \quad (B.1)$$

where $F_j$ is the force applied to the particle $j$ owing to external fields, on the one hand, and to interactions with the other particles, on the other hand. Equivalently, the equations of motion can be formulated in the Hamilton picture, namely

$$\frac{dr_j}{dt} = +\frac{\partial H}{\partial p_j} \quad \text{and} \quad \frac{dp_j}{dt} = -\frac{\partial H}{\partial r_j}, \quad (B.2)$$

where $H(\{r_j, p_j\}, t)$ is the Hamiltonian of the system. One of the most fundamental aspects of such a description is that it is deterministic. Assuming that the microstate of the system is known at some initial time $t_0$, one can, in principle, determine exactly its microstate at any time, not only in the future ($t > t_0$) but also in the past ($t < t_0$). Note that this holds also in principle for chaotic systems. However, for the latter the dynamics is exponentially sensitive to the initial conditions,
so that, in practice, one can hardly determine the microstate of the system at time $t$ from the necessarily approximate knowledge of its microstate at time $t_0$.

**Quantum gases** – A quite similar approach applies to quantum systems, at least to some extent. Consider a single particle $j$ and a basis $\{|\alpha\rangle, \alpha \in \mathbb{N}\}$ of the one-body Hilbert space $\mathcal{H}^{(j)}$. The one-body microstate of the system can be described by its coordinates in the Hilbert space, i.e. the coefficients $c_\alpha(\lambda_j) \in \mathbb{C}$, where $|\lambda_j\rangle \equiv \sum_\alpha c_\alpha(\lambda_j)|\alpha\rangle$, see Fig. B.1(b).

Similarly as for the classical case, the dynamics is purely deterministic as long as the system is isolated. It is governed by the Schrödinger equation,

$$i\hbar \frac{d|\Lambda(t)\rangle}{dt} = \hat{H}(t)|\Lambda(t)\rangle,$$

where $|\Lambda(t)\rangle$ is the many-body state of the full system and $\hat{H}(t)$ is the, possibly time-dependent, quantum many-body Hamiltonian. Again, one can determine exactly the many-body microstate of the system at any time $t$ from its knowledge at any reference time $t_0$. The above description is very similar to that of classical systems. There are, however, two main differences.

First, the above description holds only as long as no measurement is performed onto the system. In the opposite case, the system cannot be considered isolated any longer for it is coupled to the measurement apparatus. In order to apply Eq. (B.3), one must consider the dynamics of the larger system composed of the system of interest plus the measurement apparatus. As regards the system of interest itself, the dynamics is made of Hamiltonian evolutions interrupted at each measurement process by quantum jumps. Each quantum jump corresponds to the projection of the quantum microstate onto the Hilbert sub-space associated to the actual result of the measurement. Except whenever explicitly mentioned, we shall disregard this case in the following and assume that the measurements are performed at the very end of the dynamical, Hamiltonian, evolution of the system.

Second, in general, the many-body quantum state $|\Lambda\rangle$ cannot be written as the set of the $N$ one-body microstates of its $N$ constituents. This is actually possible only if the $N$ constituents are distinguishable, that is when one can ascribe a different label to each constituent. It is possible for lattice-spin systems where each spin is attached to a well-defined localized and immobile lattice atom. In the case of mono-species gases, however, the different particles cannot be distinguished from each other. The principles of quantum mechanics then tell us that it is fundamentally impossible to label the particles, see Sec. B.3 below.

**Macroscopic description**

While in principle complete, the microscopic description is too much detailed to yield useful information. Clearly, it is unreasonable to handle the complete set of positions and momenta of all the particles. For a mole of a classical, mono-atomic gas for instance, it represents about $6N_A$ degrees of freedom, where $N_A \approx 6.02214040 \times 10^{23}$ is the Avogadro number. From a practical point of view, storing and making calculations on such a huge amount of data is intractable even for the most powerful existing large-scale computing clusters. Consider for instance a large-scale computer made of about $6 \times 10^5$ computing cores for a peak power of 10.51 petaFLOPS\(^1\). It

\(^1\)The features considered here are from the K-computer, which was one of the largest clusters in the world in the mid 2010’s. It was constructed by Fujitsu and operated at the Riken institute in Kobe, Japan.
represents about $10^{16}$ elementary operations per second. Then, computing one single time step for the $6N_A$ variables represents about 10 years of calculation, assuming only a single operation per variable. Moreover, for a RAM of 2Go per core, given that storing a real number needs at least 4o, the total memory allows to store the phase-space positions of about $10^{13}$ particles at most, that is 10 orders of magnitude smaller than the Avogadro number. It is thus hopeless to simulate a realistic number of particles on classical computers. In addition, the microscopic dynamics of a gas is usually extremely rapid. For instance, the typical time scale of collisions is of the order of the nano-second ($i.e. 10^{-9}$s). It is orders of magnitude smaller that the typical time scales we are interested in when studying macroscopic effects, such as heat transfers or hydrodynamic flows for instance.

Our practical incapacity of describing the full microscopic dynamics of most systems is thus not a shame. In general the useful part of the information is restricted to a very limited number of variables. The latter depend on the system and on the physical quantities we are interested in. For instance, the homogeneous classical gas of $N$ particles is usually described by only three variables, namely the pressure $P$, the temperature $T$, and the density $n$ for instance. If, in addition, the particles of the gas carry a magnetic moment and are subjected to a magnetic field, we may add the magnetization to the list of useful variables. These “useful variables” are called the \textit{macroscopic variables} and their complete set forms the \textit{macrostate of the system}. The macroscopic variables of a given system are generally related by some equation, called the \textit{equation of state of the system}. A celebrated example is the ideal gas law for classical mono-atomic gas,

\[ P = nk_B T, \]  

where

\[ k_B = 1.38064852(79) \times 10^{23} \text{ J.K}^{-1} \]  

is the Boltzmann constant.

The macroscopic variables of a given system are not unique. In some cases, it may be fruitful to use a given set of macroscopic variables rather than another. In the case of the classical mono-atomic gas for instance, one may use the energy $E$ and the number of particles $N$ to characterize the macrostate of the system, rather than the pressure and the temperature. The equivalence of these two macroscopic descriptions is in this case ensured by the well-known relations \cite{210,211}

\[ P = \frac{2E}{3\Omega} \quad \text{and} \quad T = \frac{2E}{3Nk_B}. \]  

. In the following, we shall refer to such the macroscopic description using the energy and the number of particles for both classical and quantum gases.

The relevant framework to describe the dynamics of macroscopic variables is thermodynamics, as worked out in 19-th century. It is based on three basic principles, which drastically differ from the microscopic laws of mechanics. \textit{The first law of thermodynamics} states that, during a transformation, the total energy of the system varies according to the formula

\[ dE = \delta W + \delta Q. \]  

It means that the transfer of energy $dE$ between the system and its environment results from the work $\delta W$ of all the external macroscopic forces, on the one hand, and from the transfer of heat
\(\delta Q\), on the other hand. The work constitutes the noble form of energy transfers and can usually be determined as done in microscopic mechanics. The heat constitutes a degenerate form of energy and encapsulates the action of all the microscopic forces that are not accounted for in the macroscopic description. It includes for instance, the effect of the collisions between the particles of the system and those of its environment at their interface.

The most fundamental aspect of thermodynamics is irreversibility. From a heuristic point of view, we know by experience that large systems do not behave deterministically as regards macroscopic quantities. Consider for instance a gas confined in a bottle and placed in an empty room. When the bottle is broken, the gas expands and occupies the whole available space of the room. A deterministic behavior would allow the gas to come back after some time to its initial state, that is with all the molecules located near by the broken bottle. It is in principle possible. In practice, however, it has never been observed. This fundamental behavior is called irreversibility. Irreversibility is accounted for in the second law of thermodynamics,

\[
dS = \frac{\delta Q}{T} + \delta S_{\text{crea}}, \quad \delta S_{\text{crea}} \geq 0, \quad (B.8)
\]

which describes the variation of the entropy \(S\) during a transformation. The latter is a quantity that measures the degree of disorder in the system, that is the fact that the macroscopic description misses a significant part of the full information on the actual microstate of the system. The second law of thermodynamics first states that this disorder increases due to the heat transfer \(\delta Q\). A simple interpretation is that when the system gains energy in a degenerate form, the thermal agitation of its molecules increases, hence increasing the disorder of the system. Moreover the second law states that there is a second contribution, \(\delta S_{\text{crea}}\), to the increase of the entropy. The latter is always positive and therefore does not allow any way back. More precisely, reversible transformations correspond to \(\delta S_{\text{crea}} = 0\) and irreversible transformations to \(\delta S_{\text{crea}} > 0\).

One sometimes adds a third principle to thermodynamics, known as the Nernst principle. It states that the entropy of any system vanishes in the limit of zero temperature. It is satisfied in classical physics where the entropy is defined up to an arbitrary constant, which can be chosen appropriately. In quantum physics, however, the entropy is defined without a constant. Nevertheless, the principle is satisfied, provided the ground state is non-degenerate. Then there is a single occupied state at zero temperature and the entropy is null. Conversely, if the ground state is \(g\) times degenerated, it follows from the Boltzmann definition of the entropy [see Eq. (B.13) below] that the entropy, \(S = k_B \ln(g)\), is non-zero.

**About the relationship between microscopics and macroscopics**

The very distinction between the microscopic and macroscopic descriptions of a given system is of utmost importance to understand the basic concepts of statistical physics. As discussed above, macrostates contain much less information than microstates and, obviously, there are much less accessible macrostates than microstates. As a simple illustration, consider a system made of \(N = 3\) particles. For simplicity, we assume that the single-particle spectrum is a non-degenerate ladder of energy spacing \(\varepsilon_1\) and the particles are indistinguishable, see Fig. B.2. On the one hand, the macrostate \(\Lambda\) is represented by the arrangement of the 3 particles on the ladder. On the other hand, we choose to represent the macrostate by its total energy \(E\). Consider now the macrostate
of energy $E = 5\varepsilon_1$. This unique macrostate is realized by several microstates. More precisely, in the example considered here, it is realized by the 5 microstates $\Lambda_j$ shown on Fig. B.2. They correspond to all the possibilities to spread the 3 particles on the scales of the ladder for the fixed total energy $E = 5\varepsilon_1$. It is then obvious that several microstates correspond to the same macrostate.

More generally, it is easy to realize that the number of microstates corresponding to a given macrostate grows exponentially with the number of constituents. Indeed, the total number of $N$-body microstates is related to the size of the phase space. Up to subtleties associated to the possible indistinguishability of the bodies, the latter is the tensor product of the one-body phase spaces. It thus grows exponentially with $N$. In contrast, the total energy of the system is the sum of the energies of its constituents, up to the interaction energy. It thus typically scales at most algebraic with $N$. The number of energy levels grows similarly. Hence, the ratio of the number of microstates to the number of macrostates scales essentially exponentially with the number of particles.

It follows that for a macroscopic system made of a huge number of constituents a macrostate is realized by a plethora of microstates. In contrast, a given microstate is the realization of a well defined macrostate. Therefore, the probability $P(E)$ that the system is in given a macrostate is the sum of the probabilities $P_\Lambda$ of all its microstate realizations,

$$P(E) = \sum_{\Lambda, E_\Lambda = E} P_\Lambda . \tag{B.9}$$

The distinction between these two probabilities and their relation will be pivotal in the following.

**B.1.2 Basic principle of statistical physics and the Gibbs ensembles**

We now turn to the central point of statistical physics, namely the determination of the probability distribution of the microstates.

The main idea of the Boltzmann approach is that the dynamics of typical many-body systems is dominated by fast and numerous interactions between the constituents and, possibly with those
of its environment. As a result the system continuously jumps from one accessible microstate to another and it is hopeless to determine its value or its exact dynamics. Hence, if we are not interested in the dynamics that takes place at the very short time scale of the microscopic interactions between the constituents, the only relevant quantity is the fraction of time it spends in each microstate. If we now think in terms of erratic jumps between the accessible microstates, the only relevant information we need is the probability \( P_\Lambda \) that the system is in each microstate \( \Lambda \). The edifice of statistical physics then follows from the natural principle put forward by Boltzmann:

Boltzmann’s principle : The best statistical description of a complex system is the one that attributes the same probability to all the accessible microstates if no particular constraint favors some microstates with respect to other ones.

This principle is revolutionary in the sense that it proposed to overcome the extreme difficulty of solving exactly the many-body problem by simply assuming that the dynamics is probabilistic. Note that this idea is just a heuristic approach, which has no microscopic justification. The microscopic dynamics, and hence in principle the exact macroscopic dynamics, remain purely deterministic. However, it is too complicated for us to fully appreciate it. It thus seems erratic to us and we can describe what we observe by a probabilistic approach. The operative validity of the Boltzmann principle is that it works remarkably well in practice. Hence, although it is unjustified at the microscopic level, it is an empirical fact that it is efficient at the macroscopic level for a huge amount of systems. For instance, it is able to describe remarkably well the main properties of systems as different as gases, liquids, metals, superconductors, black-body radiation, astrophysical objects, and ultracold atoms to name just a few. While it is not our purpose to discuss it in full details, let us stress that a fundamental outcome of the Boltzmann approach is that it accounts for thermodynamic irreversibility. It turns out that there are exponentially more microscopic realizations of the typical macrostates we observe than the particular macrostates we never observe, such as in the example of the gas escaping from the broken bottle. Hence, while possible in principle such macrostates are never observed in practice. For more details, see for instance Refs. [210,211].

Another practical issue is related to physical measurements. When we measure some physical quantity on a given physical system, the result of the measurement fluctuates and we usually make averages. The latter can be performed in two ways if the measurement is non-destructive. On the one hand, we may measure the same quantity at different times on the same system and make a time average. On the other hand, we may measure the same quantity at the same evolution time on different realizations of the same system, and then make an average of the result, hence realizing a statistical average. The relevance of the statistical approach is based on the assumption that the two ways of performing measurements yield the same result. This is called the ergodicity principle.

Ergodicity principle : For a sufficiently complex many-body system, the fast microscopic dynamics ensures that the time average, \( \langle O \rangle_t \equiv \lim_{t_{\text{meas}} \to \infty} \frac{1}{t_{\text{meas}}} \int_0^{t_{\text{meas}}} dt \, O(t) \), and the statistical average, \( \langle O \rangle_{\text{stat}} \equiv \sum_{\Lambda} P_\Lambda O_\Lambda \), of any physical quantity \( O \) are equal,

\[
\langle O \rangle_t = \langle O \rangle_{\text{stat}}. \tag{B.10}
\]
Figure B.3 | Schematic representation of a system coupled to a bath. A system $S$ is made of a number of constituents. The constituents interact with each other, as well as with those of the bath $B$ in contact with the system. The coupling between the system and the bath may lead to complex transfers of heat (exchange of energy) or matter (exchange of particles). The composite system $B \otimes S$ is assumed to be isolated from the rest of the Universe $U$.

Except whenever mentioned, we shall only focus on statistical averages and forget about time averages in the following. We shall thus omit the index ”stat” and refer to the quantity $\langle O \rangle$. Yet, it is important at this stage to distinguish again two very different notions of averages that may be hidden in the quantity $\langle O \rangle$. The statistical average we have discussed above is related to the fact that the microstate $\Lambda$ of the system is not determined but occurs with some probability $P_\Lambda$. For a classical system, the value of the observable $O$ is well defined by the microstate $\Lambda$ and has thus some determined value $O_\Lambda$. In constrast, for a quantum system, the quantity $O_\Lambda$ is itself an average value, which in this case is of a quantum nature. In general, $|\Lambda\rangle$ is not an eigenvalue of the observable $\hat{O}$ and the result of the measurement of the quantity $\hat{O}$ fluctuates from one measurement to another. For a given microstate $\Lambda$, assumed to be known here, the quantity $O_\Lambda$ is the quantum average of the measurements, i.e. $O_\Lambda = \langle \Lambda | \hat{O} | \Lambda \rangle$.

### B.1.3 Canonical Gibbs ensembles

Proceeding with the application of the Boltzmann principle now depends on the concrete situation in hand. In general, the accessible microstates of the system cannot be completely random because of conservation laws, implying constraints. Generally speaking, we consider some finite system $S$ made of a huge number of particles that may interact, with each other and with external fields, see Fig. B.3. The system is generally connected to its direct environment. The latter is referred to as the bath, $B$. It is assumed to be much bigger than the system of interest. The rest of the Universe, $U$, is irrelevant here.
Microcanonical ensemble

Let us start with the simplest case, known as the microcanonical ensemble, where the system of interest $S$ is isolated. It means that it does not exchange energy nor matter with any bath. Then the number of particles $N$ and the energy $E$ are conserved quantities. Hence, if we prepare the system with a given number of particles and a given energy, the only accessible microstates should have this number of particles and this energy. In practice, the energy cannot be known exactly, so one generally assumes it is comprised in between $E - \Delta E/2$ and $E + \Delta E/2$, see Fig. B.4. According to the Boltzmann principle, since nothing privileged any microstate $\Lambda$ with an energy $E_\Lambda$ such that $E - \Delta E/2 < E_\Lambda < E + \Delta E/2$ from another, we should attribute the same probability to all the accessible microstates. It immediately yields the probability distribution

$$P_\Lambda = \frac{1}{W(E, \Delta E)} , \quad \text{for} \quad E - \Delta E/2 < E_\Lambda < E + \Delta E/2,$$

(B.11)

where $W(E, \Delta E)$ is the number of microstates $\Lambda$ with an energy $E_\Lambda$ in the interval $[E - \Delta E/2, E + \Delta E/2]$, and $P_\Lambda = 0$ otherwise. Note that in principle the number of particles cannot be known exactly either. Hence, we should extend the probability distribution to all the microstates with a number of particles $N_\Lambda$ such that $N - \Delta N/2 < N_\Lambda < N + \Delta N/2$, where $\Delta N$ is the uncertainty on the number of particles. It yields the more general probability distribution

$$P_\Lambda = \frac{1}{W(E, N; \Delta E, \Delta N)} , \quad \text{for} \quad \begin{cases} E - \Delta E/2 < E_\Lambda < E + \Delta E/2 \\ N - \Delta N/2 < N_\Lambda < N + \Delta N/2 \end{cases},$$

(B.12)

where $W(E, N; \Delta E, \Delta N)$ is the number of microstates $\Lambda$ with an energy $E_\Lambda$ in the interval $[E - \Delta E/2, E + \Delta E/2]$ and a number of particles $N_\Lambda$ in the interval $[N - \Delta N/2, N + \Delta N/2]$, and $P_\Lambda = 0$ otherwise.

One of the most genius ideas put forward by Boltzmann was to associate the number of accessible microstates $W(E, N; \Delta E, \Delta N)$ to the entropy. In thermodynamics, the entropy is associated to the notion of disorder, that is nothing but a measure of our ignorance of the actual microstate of the system. It is exactly provided by the number of microstates associated to the macrostate of the system. However, while the entropy $S$ is an extensive quantity, i.e. it grows linearly with the system size, the number of microstates $W(E, N; \Delta E, \Delta N)$ grows exponentially
with the system size, as discussed above. Boltzmann hence proposed the relation

\[ S(E, N) = k_B \ln [\mathcal{W}(E, N; \Delta E, \Delta N)] , \]  

where \( k_B \) is some constant. Its value, \( k_B = 1.38064852(79) \times 10^{-23} \text{J.K}^{-1} \), is determined to match the ideal gas law as found experimentally. Equation (B.13) is known as the Boltzmann law.

Canonical ensemble

Let us now turn to a more complicated case and assume that the system of interest \( S \) exchanges energy, but not matter with some bath \( B \). This case is known as the canonical ensemble. Clearly, we can no longer apply the same procedure as above. The continuous exchange of energy between the system and the bath establishes some mutual equilibrium where energy losses will be dynamically compensated by energy gains by the system in very short times. If the bath is much larger than the system, the energy fluctuations will be small as regards the bath but may be significant as regards the system. Hence, the energy of the system cannot be assumed to be close to its average value with negligible fluctuations. It is also clear that the same probability cannot be ascribed to all the microstates of the system. Otherwise, the average energy of the system would diverge since the spectrum may have no upper bound, as in a gas for instance.

Although we cannot apply the result of the microcanonical ensemble to the system \( S \), we may do it to the larger system \( B \otimes S \) composed of the bath and the system of interest, which is isolated from the rest of the Universe. To proceed, we need make two fundamental hypotheses:

(i) The bath is assumed to be much larger than the system of interest.

(ii) The system of interest and the bath are almost independent and their mutual interaction is assumed to be weak.

Hypothesis (i) has been briefly mentioned above. In practice, it means that the energy fluctuations of the bath are much smaller than its average energy, i.e. \( \Delta E_B \ll \langle E_B \rangle \). Hypothesis (ii) means that the intrinsic energies of the bath and the system of interest are both much larger than their mutual interaction energy. This is in general well verified if the system is large enough and the interactions inside the system and with the bath are of similar nature and short ranged. In this case, the intrinsic interaction energy of the system of interest \( S \) is dominated by the bulk, of typical size \( L^d \), where \( L \) is the typical diameter of the system \( S \) and \( d \) its spatial dimension. In contrast, the interaction with the bath is located at the interface, of typical size \( L^{d-1} \), i.e. much smaller than the bulk. Note that this hypothesis may be wrong for systems strongly confined in one dimension or in the presence of long-range interactions. We, however, disregard these cases, except possibly whenever mentioned explicitly.

Since the numbers of particles of the bath and the system are fixed, they can be disregarded. The macrostates are thus determined by the sole energies of the two. More precisely, the total energy of the composite system, \( E_{B \otimes S} = E_{\text{tot}} \), being conserved, it is not a variable. The macrostate of the composite system can thus be characterized by the sole energy \( E \) of the system of interest \( S \). The energy of the bath would then be determined using the simple relation

\[ E_B = E_{\text{tot}} - E. \]
It is then fruitful to group the latter in ensembles of microstates for which the energy of the system of interest, $E_S$, has a given value, see Fig. B.5. Since all the microstates of each ensemble have the same energy, these ensembles define the macrostate of the composite system $B \otimes S$. Each ensemble contains $W_{B \otimes S}(E)$ microstate elements. Besides, since the energy $E$ also defines the macrostate of the system $S$, the probability that the latter has energy $E$ is the same as the probability that the composite system is characterized by this energy for $S$, i.e.

$$P_S(E) = P_{B \otimes S}(E).$$

The latter is then found by applying the microcanonical ensemble to the composite system $B \otimes S$, for is isolated. It follows that the same probability must be ascribed to all the microstates of $B \otimes S$ with energy $E_{\text{tot}}$. Hence, the probability of the macrostate of the composite system $B \otimes S$ of energy $E$ for the system $S$ is proportional to this number, i.e.

$$P_{B \otimes S}(E) \propto W_{B \otimes S}(E, E_B).$$

Now, since the system of interest and the bath are almost independent, any microstate of the composite system is approximately determined by a microstate of the system of interest on the one hand and by a microstate of the bath on the other hand. Hence, the number of microstates of the composite system is approximately the product of the numbers of microstates of the system of interest and of the bath,

$$W_{B \otimes S}(E, E_B) \simeq W_S(E) \times W_B(E_B).$$

Moreover, according to the Boltzmann principle, all the microstates corresponding to a given macrostate of the system of interest should have the same probability since nothing should privilege one with respect to another. Hence the probability of a given microstate $\Lambda$ of the system $S$, of energy $E_\Lambda$, is

$$P_\Lambda = \frac{P_S(E_\Lambda)}{W_S(E_\Lambda)}.$$

Then, combining the four formulas above, we find

$$P_\Lambda \propto W_B(E_{\text{tot}} - E_\Lambda).$$
Note that, since $\Lambda$ is an element of the ensemble of microstates of the system $S$ with an energy $E$, we have $E_{\Lambda} = E$. We thus end up with the remarkable conclusion that the probability of a microstate $\Lambda$ of the system $S$ is proportional to the number of microstates of the bath $B$ at the total energy minus the energy $E_{\Lambda}$ of the microstate of the system $S$. To conclude, note that the energies of the microstates of $S$ define the order of magnitude of the fluctuations of the energy of the bath, $E_{\Lambda} \sim \Delta E$. Since $\Delta E \ll E_{\text{tot}}$ for a sufficiently large bath, the above formula can be Taylor expanded. In practice, it is fruitful to actually work on it logarithm, which yields

$$\ln (P_{\Lambda}) \simeq \text{cst} - \frac{d \ln (W_{B})}{dE_{B}} (E_{\text{tot}}) \times E_{\Lambda}.$$ 

Now, using the Boltzmann formula (B.13) for the bath, we find

$$\frac{d \ln (W_{B})}{dE_{B}} (E_{\text{tot}}) = \frac{1}{k_{\text{B}}} \frac{dS_{B}}{dE_{B}} (E_{\text{tot}}).$$

We then recognize in the last term of the right-hand side of this equation the thermodynamic definition of the temperature, $T \equiv \frac{dE_{B}}{dS_{B}} (E_{\text{tot}})$. In principle, it is the temperature of the bath but it is also that of the system $S$ since the two are assumed to be in equilibrium. The second last formula thus reads

$$\ln (P_{\Lambda}) \simeq \text{cst} - \frac{E_{\Lambda}}{k_{\text{B}} T}.$$ 

Integrating this formula, we thus end up with the explicit form of the probability distribution of the microstates $\Lambda$ of the system $S$ in the canonical ensemble,

$$P_{\Lambda} = \frac{\exp (-\beta E_{\Lambda})}{Z_{c}} \quad \text{with} \quad Z_{c} = \sum_{\Lambda} \exp (-\beta E_{\Lambda}) \quad \text{(B.14)}$$

and $\beta = \frac{1}{k_{\text{B}} T}$. The quantity $Z_{c}$, known as the canonical partition function, is just introduced as the normalization factor of the probability distribution. As will be recalled in Sec. B.1.4, it, however, plays a pivotal role in statistical physics.

**Grand-canonical ensemble**

Let us finally turn to the case where the system of interest exchanges both energy and particles with the bath. This case is known as the grand-canonical ensemble. It can be treated similarly as the canonical ensemble by applying the micro-canonical ensemble to the composite system $B \otimes S$ and we just outline the procedure. The unique difference with the canonical ensemble is that the macro-states of the system $S$, of the bath $B$, and of the composite system $B \otimes S$ are now defined by both the energy $E$ and the number of particles $N$ of the system $S$. Proceeding similarly as for the canonical ensemble, we find

$$P_{\Lambda} \propto W_{B} (E_{\text{tot}} - E_{\Lambda}, N_{\text{tot}} - N_{\Lambda}),$$

for each microstate $\Lambda$ of the system $S$. Assuming that the exchange of the energy and number of particles are much smaller those of the bath, i.e. $E \ll E_{\text{tot}}$ and $N \ll N_{\text{tot}}$, the logarithm of the above expression is Taylor expanded as

$$\ln (P_{\Lambda}) \simeq \text{cst} - \left. \frac{\partial \ln (W_{B})}{\partial E_{B}} \right|_{N_{B}} (E_{\text{tot}}, N_{\text{tot}}) \times E_{\Lambda} - \left. \frac{\partial \ln (W_{B})}{\partial N_{B}} \right|_{E_{B}} (E_{\text{tot}}, N_{\text{tot}}) \times N_{\Lambda}.$$
Using the Boltzmann relation (B.13) and the thermodynamic quantities
\[
\beta \equiv \frac{1}{k_B T} = \frac{1}{k_B} \frac{\partial S_B}{\partial E_B} \bigg|_{N_B} \quad \text{and} \quad \alpha \equiv \beta \mu = -\frac{1}{k_B} \frac{\partial S_B}{\partial N_B} \bigg|_{E_B},
\]  
where \(\mu\) is the chemical potential, and normalizing the probability distribution of the microstates of the system \(S\) yields the formula
\[
P_\Lambda = \frac{\exp(-\beta E_\Lambda + \alpha N_\Lambda)}{Z_{GC}} \quad \text{with} \quad Z_{GC} = \sum_\Lambda \exp(-\beta E_\Lambda + \alpha N_\Lambda). \tag{B.16}
\]
It is just the generalization of its canonical counterpart, including fluctuations of the number of particles in addition to the fluctuations of the energy. The quantity \(Z_{GC}\) is the so-called grand-canonical partition function. Note that the same expressions can alternatively be written
\[
P_\Lambda = \frac{\exp[-\beta(E_\Lambda - \mu N_\Lambda)]}{Z_{GC}} \quad \text{with} \quad Z_{GC} = \sum_\Lambda \exp[-\beta(E_\Lambda - \mu N_\Lambda)]. \tag{B.17}
\]
The two expressions above are obviously equivalent. They only differ by the use of the thermodynamic quantities \(\alpha\) in the former and \(\mu\) in the latter. While the expressions with the chemical potential \(\mu\) are often used, the ones with the quantity \(\alpha\) are more appropriate in some cases, see for instance Sec. B.1.4.

### B.1.4 The partition function: A useful tool

The practical importance of the partition function cannot be overestimated. It can be used to determine the average value of almost any physical quantity at thermodynamic equilibrium. For instance, the average energy can be found as follows. Using Eq. (B.17), one first writes
\[
\langle E \rangle = \sum_\Lambda E_\Lambda P_\Lambda = \sum_\Lambda E_\Lambda \frac{\exp(-\beta E_\Lambda + \alpha N_\Lambda)}{Z_{GC}} = \frac{1}{Z_{GC}} \sum_\Lambda E_\Lambda \exp(-\beta E_\Lambda + \alpha N_\Lambda).
\]
The trick is then to notice that the coefficient \(E_\Lambda\) right after the sum sign can be inserted into the exponential, provided we differentiate it. We then find
\[
\langle E \rangle = \frac{1}{Z_{GC}} \sum_\Lambda - \frac{\partial \exp(-\beta E_\Lambda + \alpha N_\Lambda)}{\partial \beta} \bigg|_\alpha,
\]
or, equivalently,
\[
\langle E \rangle = -\left. \frac{\partial \ln Z_{GC}}{\partial \beta} \right|_\alpha. \tag{B.18}
\]
Note that this example is a case where it is better to use Eq. (B.17) rather than Eq. (B.16). This is because the quantity to fix in the derivative is \(\alpha\) and not \(\mu\). The fluctuations of the energy, \(\Delta E \equiv \sqrt{\langle E^2 \rangle - \langle E \rangle^2}\), can be calculated using the same kind of tricks. One first writes
\[
\langle E^2 \rangle = \sum_\Lambda E_\Lambda^2 P_\Lambda = \sum_\Lambda E_\Lambda^2 \frac{\exp(-\beta E_\Lambda + \alpha N_\Lambda)}{Z_{GC}} = \frac{1}{Z_{GC}} \sum_\Lambda \frac{\partial^2 \exp(-\beta E_\Lambda + \alpha N_\Lambda)}{\partial \beta^2} \bigg|_\alpha = \frac{1}{Z_{GC}} \frac{\partial^2 Z_{GC}}{\partial \beta^2} \bigg|_\alpha.
\]
Then, using this result and Eq. (B.18), one finds
\[
\Delta E^2 = \frac{1}{Z_{GC}} \frac{\partial^2 Z_{GC}}{\partial \beta^2} \bigg|_{\alpha} - \frac{1}{Z^2_{GC}} \left( \frac{\partial Z_{GC}}{\partial \beta} \right)^2 = \frac{\partial}{\partial \beta} \left( \frac{1}{Z_{GC}} \frac{\partial Z_{GC}}{\partial \beta} \right) \bigg|_{\alpha},
\]
and finally
\[
\Delta E^2 = + \frac{\partial^2 \ln Z_{GC}}{\partial \beta^2} \bigg|_{\alpha}. \tag{B.19}
\]

While we have worked within the grand-canonical ensemble, the same formulas apply to the canonical ensemble.

Yet, within the grand-canonical ensemble, one can proceed similarly with derivatives with respect to \(\alpha\) rather than \(\beta\). One then finds the general formulas for the average number of particles,
\[
\langle N \rangle = + \frac{\partial \ln Z_{GC}}{\partial \alpha} \bigg|_{\beta} = + \frac{1}{\beta} \frac{\partial \ln Z_{GC}}{\partial \mu} \bigg|_{\beta}, \tag{B.20}
\]
and for its fluctuations, \(\Delta N \equiv \sqrt{\langle N^2 \rangle - \langle N \rangle^2}\),
\[
\Delta N^2 = + \frac{\partial^2 \ln Z_{GC}}{\partial \alpha^2} \bigg|_{\beta} = + \frac{1}{\beta^2} \frac{\partial^2 \ln Z_{GC}}{\partial \mu^2} \bigg|_{\beta}. \tag{B.21}
\]

Note that in the latter derivatives, the quantity \(\beta\) is fixed. It is thus equivalent to differentiate with respect to \(\alpha\) or with respect to \(\mu\) and divide by \(\beta\). In contrast, for the corresponding formulas for energy, the variable to fix in the partial derivatives is \(\alpha\), an not \(\mu\).

### B.2 Statistical physics of the ideal classical gas

We now apply the principles of statistical physics to one of the simplest many-body systems, namely an ideal classical gas. It can be described as an assembly of mono-atomic particles that do not interact with each other, in the classical regime. The quantum counterpart of the ideal gas is discussed in Sec. B.3. The ideal gas we consider is at thermodynamic equilibrium and can be coupled to a bath or not. In both cases, thermodynamic equilibrium is realized by thermalization effects induced by interactions. Hence, the interactions between the particles of the gas with each other and/or with the particles of the bath cannot be strictly ignored. Here, we assume, more precisely, that they are much weaker than the other energy terms, for instance kinetic and potential energies.

For the sake of simplicity, we shall work with discrete one-body states \(\lambda\). The main quantity of interest will be the average number of particles that populate the one-body state \(\lambda\), represented by the quantity \(\langle N_\lambda \rangle\), also called the occupation number. It can used to compute the average value of any physical quantity \(O\) that depends on the state \(\lambda\), which reads
\[
\langle O \rangle = \sum_\lambda \langle N_\lambda \rangle O_\lambda. \tag{B.22}
\]
In a classical gas, however, the one-body state $\lambda = (r, p)$ is a continuous quantity. In $d$ space dimensions, it spans $\mathbb{R}^{2d}$, or a sub-ensemble of the latter. The quantity $\langle N_\lambda \rangle$ is then a function of the position and momentum variables, $\langle N_\lambda \rangle = f(r, p)$, and the discrete sum $\sum_\Lambda$ in Eq. (B.22) should be substituted to the continuous sum $\int d\mathbf{r} d\mathbf{p}$. However, while the former is dimensionless, the latter has the dimension of a position times a momentum to the power of the dimension of the system. Determining the normalization factor is more subtle than what may be anticipated. In fact, it can be shown that each one-body state $(r, p)$ occupies the phase-space volume $(2\pi \hbar)^d$. Remarkably, this normalization factor includes the quantum of action $\hbar = \frac{2\pi \hbar}{d}$. It is thus reminiscent of the quantum nature of the gas. Hence, Eq. (B.22) should be substituted to the formula

$$
\langle O \rangle = \int \frac{d\mathbf{r} d\mathbf{p}}{(2\pi \hbar)^d} f(r, p) O(r, p).
$$

(B.23)

for any physical observable $O$ that depends on the phase-space coordinates $(r, p)$. For instance, it may apply to the kinetic energy $E_k(p) = \frac{p^2}{2m}$, where $m$ is the particle mass, and to the potential energy $E_p(r) = V(r)$ if the gas is subjected to the external potential $V(r)$. In the following, we shall use both the discrete and continuous formulations depending on the situation in hand.

### B.2.1 One particle

Let us start with just one particle. Since the particle is unique, the one-body state $\lambda$ and the "many-body" state $\Lambda$ are obviously the same and the results of the Sec. B.1.3 can be directly applied. Moreover, the average number of particles in each state $\lambda$ is nothing but the probability that the system is in the state $\lambda$. In the canonical ensemble where the temperature $T$ is fixed by an external bath, we thus find

$$
\langle N_\lambda \rangle = \exp\left(\frac{-\beta \varepsilon_\lambda}{Z_1}\right) \text{ with } Z_1 = \sum_\lambda \exp\left(\frac{-\beta \varepsilon_\lambda}{Z_1}\right).
$$

(B.24)

The quantity $Z_1$ is the one-body partition function, $\beta = 1/k_B T$ is the inverse temperature, and $\varepsilon_\lambda$ is the energy of the one-body state $\lambda$.

It is worth noting that the average number of particles in the one-body state $\lambda$ and its fluctuations can be found using formal derivatives of the one-body partition function,

$$
\langle N_\lambda \rangle = -\frac{1}{\beta} \frac{\partial \ln Z}{\partial \varepsilon_\lambda} \quad \text{and} \quad \Delta N^2_\lambda = +\frac{1}{\beta^2} \frac{\partial^2 \ln Z}{\partial \varepsilon^2_\lambda}.
$$

(B.25)

Note that we omitted the index 1 in the partition function for the same formula applies to any ideal gas, be it classical or quantum. This remark will be useful in the following. The demonstration of these formulas are similar to that used for Eqs. (B.20) and (B.21).

### B.2.2 Many particles in the canonical ensemble

Let us now turn to $N$ particles, still in the canonical ensemble. One may first note that, since the particles are independent, we expect that the average number of particles in the one-body state $\lambda$...
is that of for one particle, Eq. (B.24), multiplied by the number of particles $N$,

$$
\langle N_\lambda \rangle = N \frac{\exp (-\beta \varepsilon_\lambda)}{Z_1}.
$$

This quantity is known as the \textit{Boltzmann distribution}. Let us recover this result for both discernable and indiscernable particles.

**Discernable particles**

For the classical gas, we may a priori label the particles by an index $j \in [1..N]$. As discussed above, the $N$-body state reads

$$
\Lambda \equiv (\lambda_1, \ldots, \lambda_N),
$$

where each $\lambda_j$ spans the ensemble of one-body microstates, and its energy is $E_\Lambda = \sum_j \varepsilon_{\lambda_j}$ since the particles are independent. The $N$-body canonical partition function can now be computed from Eqs. (B.14) and (B.27). It yields

$$
Z_c = \sum_\Lambda \exp (-\beta E_\Lambda) = \sum_{\lambda_1 \ldots \lambda_N} \exp \left( -\beta \sum_{1 \leq j \leq N} \varepsilon_{\lambda_j} \right) = \prod_{1 \leq j \leq N} \sum_{\lambda_j} \exp \left( -\beta \varepsilon_{\lambda_j} \right).
$$

Since all the particles are identical, the index $j$ is mute in the term inside the product and we recognize the one-body partition function (B.24). Hence, in the discernable case, we find

$$
(Z_c)_{\text{dis}} = (Z_1)^N.
$$

Using the avatar of Eq. (B.25) for the canonical partition function $Z = (Z_c)_{\text{dis}}$, Eq. (B.28), we find Eq. (B.26), as expected.

**Indiscernable particles**

In fact, identical particles in a gas should be treated as being indiscernable. Consider first just two particles. In the discernable case as treated above, we have assumed that the two-body microstate $\Lambda$ where, say, particle 1 is in the one-body state $\lambda$ and particle 2 in the one-body state $\lambda'$ is different from the 2-body microstate $\Lambda'$ where particle 1 is in the one-body state $\lambda'$ and particle 2 in the one-body state $\lambda$, see for instance Figs. B.6(a1) and (a2). In constrast, since the particles 1 and 2 are identical in the indiscernable case, the two two-body microstates $\Lambda$ and $\Lambda'$ are physically the same. Hence, when listing the $N$-body microstates to compute the partition function as done in the discernable case, we count twice the same state, if $\lambda \neq \lambda'$.

More generally, in a classical gas, the phase-space density is small and it is very unlikely that two particles occupy the same one-body state $\lambda$. Hence, when listing the $N$-body microstates as in the discernable way, we actually count $N!$ times the same indiscernable $N$-body microstate. It corresponds to all the permutations of the $N$ particles between the $N$ populated microstates, see Figs. B.6(a) and (b). It follows that the (correct) discernable partition function should be divided by $N!$ compared to the discernable case, and we find

$$
(Z_c)_{\text{inds}} = \frac{(Z_1)^N}{N!}.
$$
Figure B.6 | Examples of microstates in a 5-particle classical gas. The lines (a) and (b) correspond to situations where the particles occupy different sets of one-body microstates. In the discernable case, each can be realized by $5!$ possible permutations of the particles occupying the same set of one-body microstates. Three examples are shown in panels (a1), (a2) and (a3) on the one hand and in panels (b1), (b2) and (b3) on the other hand. In the indiscernable case, such permutations are irrelevant and all realizations (aj) on the one hand and (bj) on the other hand correspond to the same 5-body microstate, (a) and (b) respectively.

Since the average number of particles in the one-body state $\lambda$ is found from the derivative of the logarithm of the partition function, see the avatar of Eq. (B.25) for the partition function $Z = (Z_c)_{ind}$, Eq. (B.29), it is not affected by the term $N!$ and we recover Eq. (B.26) also in the indiscernable case.

Note that determining whether identical classical particles should be considered discernable or indiscernable is a priori not a simple question. On the one hand, we can label the particles and define the $N$-body microstate by the ordered list of microstates of each particle (discernable approach). On the other hand, one can list all possible microstates and count the number of particles that populate it (indiscernable approach). Both ways of listing the $N$-body microstates is a priori legitimate in the classical world. There are actually two rather subtle reasons why the discernable approach is the correct one. From a purely classical point of view, it turns out that, in the discernable case, the entropy is not an extensive quantity (Gibbs paradox). In contrast, the factor $N!$ that appear in the indiscernable case, see Eq. (B.29), restores the extensive character property of the entropy. The indiscernable counting thus appears more appropriate. However, making a choice between the two approaches on this basis rests on the hypothesis that the entropy should extensive, which may be debated. More profoundly, the fact that identical classical particles should be considered indiscernable is reminiscent of their quantum nature. It is indeed now known that identical quantum particles are fundamentally indiscernable, see Sec. B.3. Hence, one should keep this property in the classical regime, at least as long as predictions from the discernable and indiscernable approaches differ.
In the remainder of this work, we only consider indiscernable particles, except whenever mentioned explicitly.

### B.2.3 Many particles in the grand-canonical ensemble

To conclude the discussion of the ideal classical gas, let us turn to the grand-canonical ensemble. In this case, the total number of particles, $N$, fluctuates. Hence the definition of a many-body microstate of the system should thus be extended and include the variable $N$ in addition to the list of the one-body states $\lambda_j$. We thus represent it by

$$\Lambda \equiv (N; \lambda_1, ..., \lambda_N), \quad \text{up to permutations.}$$

Let us then compute the grand-canonical partition function from Eq. (B.17). It yields

$$Z_{\text{gc}} = \sum_{\Lambda} \exp(-\beta E_\Lambda + \alpha N_\Lambda) = \sum_N \left[ \sum_{\Lambda, N_\Lambda = N} \exp(-\beta E_\Lambda) \right] \exp(\alpha N).$$

Now, the sum term inside the square brackets is nothing but the $N$-body partition function computed above in the canonical ensemble, $Z_c$. Using Eq. (B.29), valid for indiscernable particles, we thus find

$$Z_{\text{gc}} = \sum_N \frac{Z_1^N}{N!} \exp(\alpha N) = \sum_N \frac{[Z_1 \exp(\alpha)]^N}{N!}.$$

Recognizing the Taylor expansion of the exponential function, we then find

$$Z_{\text{gc}} = \exp(e^{\alpha Z_1}). \quad \text{(B.30)}$$

The grand-canonical partition function is thus a simple function of the one-body partition function, as for the canonical case, and here of the parameter $\alpha$.

This partition function can now be used to compute statistical averages of various quantities associated to numbers of particles. On the one hand, using Eq. (B.20) and noting that the quantity $Z_1$ does not depend on $\alpha$, which was introduced only for controlling the number of particles in the grand-canonical ensemble, we find

$$\langle N \rangle = e^{\alpha Z_1}. \quad \text{(B.31)}$$

On the other hand, using Eqs. (B.25) and (B.31), and noting that the quantity $\alpha$ does not depend on $\varepsilon_\lambda$, we find

$$\langle N_\lambda \rangle = -\frac{1}{\beta} e^{\alpha} \frac{\partial Z_1}{\partial \varepsilon_\lambda}.$$

Then, using Eq. (B.24), we find

$$\langle N_\lambda \rangle = e^\alpha e^{-\beta \varepsilon_\lambda}. \quad \text{(B.32)}$$

Finally, combining Eqs. (B.31) and (B.32), one can eliminate $e^\alpha$, which yields

$$\langle N_\lambda \rangle = \langle N \rangle \frac{e^{-\beta \varepsilon_\lambda}}{Z_1}. \quad \text{(B.33)}$$
As expected, it is the same formula as in the canonical ensemble, Eq. (B.26), changing the number of particles $N$, relevant to the canonical ensemble, into its average value, $\langle N \rangle$, relevant to the grand-canonical ensemble.

One may also compute the fluctuations $\Delta N_\lambda$ of the number of particles in the one-body state $\lambda$. Using again Eqs. (B.24), (B.25), and (B.30), we find

$$\Delta N_\lambda^2 = \frac{e^{\alpha} \partial^2 Z_1}{\beta^2 \partial \varepsilon^2_\lambda} = e^{\alpha} e^{-\beta \varepsilon_\lambda}.$$

Comparing to Eq. (B.32), one then finds

$$\Delta N_\lambda^2 = \langle N_\lambda \rangle.$$

Hence, the fluctuations of the number of particles in a one-body state equals the square root of its population. In particular, one finds $\Delta N_\lambda / \langle N_\lambda \rangle = 1 / \sqrt{\langle N_\lambda \rangle}$. We shall see in Sec. B.3.4 that, in the classical regime the population of each one-body state is small, $\langle N_\lambda \rangle \ll 1$. It follows that the relative fluctuations of the population is each one-body state are always large. In contrast, for the total number of particles, one similarly finds

$$\Delta N / \langle N \rangle = 1 / \sqrt{\langle N \rangle},$$

which is small in large systems, $\langle N \rangle \gg 1$.

### B.3 Ideal quantum gas

As discussed above, the indiscernability of identical particles plays a non-negligible role in the determination of the grand-canonical partition function of the ideal gas. In the classical regime, however, it remains rather marginal. In particular, the indiscernable approach ensures the extensive character of the entropy but it does not affect the Boltzmann distribution. In contrast, indiscernability plays a major role in the quantum regime. In the following, we only outline the main ideas underlying the adapted description of the ideal quantum gas and focus more precisely on the derivation of the Bose-Einstein and Fermi-Dirac distributions, which are the quantum counterparts of the Boltzmann distribution. A more complete presentation, including a detailed introduction to the adapted formalism can be found in Chap. C.

#### B.3.1 Indiscernability of quantum particles

Be they classical or quantum, identical particles cannot be distinguished from a single-shot image since no observable provides a distinctive feature to one particle compared another particle. In a classical gas, however, one can ascribe an arbitrary label to each particle at the initial time and follow its trajectory to identify it at a latter time. This is not possible in a quantum gas because the very notion of real-space trajectory does not exist. Hence, for almost any initial particle wavefunction, there is a finite probability that the particle is at any position in space at any latter time. Moreover, any measurement of the position of the particle would project the
particle wavefunction to a Dirac peak at the position where the particle would have been found with probability one. For this reason, one cannot label identical particles in quantum physics. Note, however, that one can distinguish particles of different natures or in different internal states. For instance, one can distinguish a rubidium (Rb) atom from a lithium (Li) atom, or two rubidium atoms of different isotopes, e.g. $^{85}$Rb and $^{87}$Rb. Similarly, one can distinguish two atoms of the same isotope in different internal states, e.g. two $^6$Li atom in the hyperfine states $|F = 9/2, m_F = 9/2\rangle$ and $|F = 9/2, m_F = 7/2\rangle$, respectively, as long as the latter are stable, i.e. as long as they are not coupled to other internal states. In the following, except whenever mentioned explicitly, we restrict ourselves to gases of strictly identical particles.

**Fock basis**

It follows from the discussion above that the many-body microstate $|\Lambda\rangle$ of a quantum gas cannot be determined by listing its particles and attributing a one-body state $|\lambda\rangle$ to each one, as done for the classical gas. In turn, one can list all the possible one-body states $\lambda$ and determine the number of particles, $N_\lambda$, that populate it. We can thus write

$$|\Lambda\rangle \equiv |N_0, N_1, N_2, ...\rangle,$$

or $|\Lambda\rangle \equiv \{|N_\lambda\rangle\}$ in a more compact form. Note that in this form, we make no distinction between the identical particles, as required. The ensemble of such states forms a basis of the indiscernable many-body microstates, known as the **Fock basis**.

The number identical particles in a given one-body state $|\lambda\rangle$ is not arbitrary. The quantum theory actually shows that there are two kinds of particles, called **bosons** and **fermions**, see Chap. C. For bosons, one can put any number of particles in the same one-body microstate. For fermions, one cannot put more than one particle in the same one-body microstate. Hence, the possible numbers of particles in the same one-body microstate span different ensembles in the two cases,

$$\begin{aligned}
\text{bosons:} & \quad N_\lambda \in \mathbb{N}, \\
\text{fermions:} & \quad N_\lambda \in \{0, 1\}.
\end{aligned}$$

As can be easily anticipated, this difference is fundamental, see also below. Before proceeding, note that the complete Fock basis is adapted to the grand-canonical ensemble since it can accommodate an arbitrary total number of particles. This is the case we shall consider in the following. The canonical ensemble is more difficult to treat because one should add the additional constraint that the sum of populations in the various one-body microstates equals the total number of particles, $\sum_\lambda N_\lambda = N$.

**Bose enhancement and Fermi exclusion**

To illustrate the major difference in particle counting for classical particles, bosons, and fermions, consider a system of two identical particles in three possible one-body states and in the micro-canonical ensemble, see Fig. B.7. We assume no interactions between the particles.

For discernable, classical, particles (left column in Fig. B.7), the two-body microstates are constructed by putting particle 1 (blue) in any of the three one-body states and then particle 2
Figure B.7 | Simple illustration of the Bose enhancement and Pauli blocking effects. Consider two particles (blue and red in the discernable case; orange in the indiscernable case) and three possible one-body states (columns). In the indiscernable case (left panel), there are nine possible two-body microstates (lines). The probability that the two particles are in the same one-body state is 1/3 and the probability that they are in different one-body states is 2/3. In the case of identical bosons (central panel), there are six possible two-body microstates. The probability that the two particles are in the same or different one-body states is now both 1/2. In the case of identical fermions (right panel), there are only three possible two-body microstates. Since two fermions cannot be in the same one-body state, the probability that the two particles are in different one-body states is 1.

For identical quantum particles, one should proceed differently. For identical bosons (central column in Fig. B.7), one can put the two particles in the same one-body microstate (3 possibilities, upper lines in Fig. B.7) or into different ones \((C_3^2 = 3\) possibilities, lower lines in Fig. B.7). Then the probability that two bosons are in the same one-body state is 1/2, \(i.e.\) larger than the value 1/3 found in the case of discernable, classical particles. Hence, identical bosons tend to group together even though there is no physical attraction between the particles. This phenomenon is called Bose enhancement.

For identical fermions (right column in Fig. B.7), since two particles cannot populate the same one-body state, one must remove all the two-body microstates where the particles are in the same one-body state. The probability that the two particles are in different one-body states is thus 1 and the probability that they are in the same one-body state is thus exactly 0, \(i.e.\) lower than the value 1/3 found in the case of discernable, classical particles. Hence, identical fermions behave as if they would infinitely repel each other. This phenomenon is called Fermi exclusion.

The problem of spreading two identical, non-interacting particles in three different states is just a simple example to illustrate the major difference between classical particles, bosons, and fermions. We shall discuss later that more striking manifestations of the same phenomena. In the following, we rest on deriving the quantum distributions for bosons and fermions. More profound
B.3.2 Bose-Einstein distribution

Let us start with a gas of identical bosons and compute the grand-canonical partition function. For a many-body Fock state $| \Lambda \rangle$ associates to the one-body state basis $\{ | \lambda \rangle \}$, we have $N_\Lambda = \sum_\lambda N_\lambda$ and, since the particles do not interact with each other, $E_\Lambda = \sum_\lambda N_\lambda \epsilon_\lambda$, where $\epsilon_\lambda$ is the energy of the one-body state $| \lambda \rangle$. Then, using the definition of the grand-canonical partition function, Eq. (B.17), one finds

$$Z_{GC} = \sum_\Lambda \exp \left[ -\beta (E_\Lambda - \mu N_\Lambda) \right] = \sum_{\{N_\lambda, \lambda\}} \exp \left[ -\sum_\lambda \beta (\epsilon_\lambda - \mu) N_\lambda \right] = \prod_\lambda \sum_{N_\lambda} \exp \left[ -\beta (\epsilon_\lambda - \mu) N_\lambda \right],$$

where $\{N_\lambda, \lambda\}$ represents the ensemble of ensembles of numbers of particles $N_\lambda$ for each one-body state $| \lambda \rangle$. The contributions of the different one-body states can thus be factorized, which yields,

$$Z_{GC} = \prod_\lambda Z_\lambda, \quad \text{with} \quad Z_\lambda = \sum_{N_\lambda} \left( \exp \left[ -\beta (\epsilon_\lambda - \mu) \right] \right)^{N_\lambda}. \quad (B.37)$$

Note that in $N_{\lambda}$ we have written ”$\lambda$” in between brackets because it is mute and can thus be omitted. For bosons, $N_{\lambda}$ spans the full ensemble $\mathbb{N}$ and we recognize, in the formula for $Z_\lambda$, the sum of a geometrical series, $Z_\lambda = 1 / \left\{ 1 - \exp \left[ -\beta (\epsilon_\lambda - \mu) \right] \right\}$. We finally end up with

$$Z_{GC} = \prod_\lambda Z_\lambda, \quad \text{where} \quad Z_\lambda = \frac{1}{1 - \exp \left[ -\beta (\epsilon_\lambda - \mu) \right]}. \quad (B.38)$$

As usual, this partition function allows us to compute the average value of a variety of physical quantities. Let us focus on those related to the numbers of particles.

Let us start with the average number of particles in a given one-body microstate $\lambda$. Using Eqs. (B.25) and (B.38), we find

$$\langle N_\lambda \rangle = -\frac{1}{\beta} \frac{\partial \ln Z_{GC}}{\partial \epsilon_\lambda} = \frac{1}{\beta} \frac{\partial \ln Z_\lambda}{\partial \epsilon_\lambda} = \frac{\exp \left[ -\beta (\epsilon_\lambda - \mu) \right]}{1 - \exp \left[ -\beta (\epsilon_\lambda - \mu) \right]}. \quad (B.39)$$

Then, multiplying above and below the division bar by $\exp \left[ \beta (\epsilon_\lambda - \mu) \right]$, we find

$$\langle N_\lambda \rangle = \frac{1}{\exp \left[ \beta (\epsilon_\lambda - \mu) \right] - 1}. \quad (B.39)$$

This formula is called the Bose-Einstein distribution, see Fig. B.8(a). Together with the Fermi-Dirac distribution, see below, it is one of the most important formulas of this course. It represents the population of bosons in a each one-body microstate of the ideal Bose gas, i.e. the counterpart of the Boltzmann distribution for bosons. Note that the Bose-Einstein distribution gives the average number of particles in the one-body state $\lambda$, not a probability, although the total number of particles does not appear explicitly. Actually, the latter is hidden in the factor $\exp (\beta \mu) = \exp (\alpha), \quad (B.39)$
pretty much as for the classical gas in the grand-canonical ensemble, see Eq. (B.32). It should be noted that the geometric sum above converges only for $\beta (\varepsilon_\lambda - \mu) > 0$. For positive temperature, $\beta > 0$, the condition is thus $\mu < \varepsilon_\lambda$ for all one-body microstates $\lambda$. It is equivalent to the condition

$$\mu < \varepsilon_0,$$

where $\varepsilon_0$ is the ground-state energy of the single-particle problem. We shall come back later to this inequality.

One can compute its fluctuations similarly as done for the average number of particles in the one-body state $\lambda$. Using Eqs. (B.25) and (B.39), it yields

$$\Delta N^2_\lambda = \frac{1}{\beta^2} \frac{\partial^2 \ln Z_{GC}}{\partial \varepsilon_\lambda^2} = \frac{1}{\beta} \frac{\partial \langle N_\lambda \rangle}{\partial \varepsilon_\lambda} = \frac{\exp[-\beta(\varepsilon_\lambda - \mu)]}{1 - \exp[-\beta(\varepsilon_\lambda - \mu)]} + \frac{(\exp[-\beta(\varepsilon_\lambda - \mu)])^2}{(1 - \exp[-\beta(\varepsilon_\lambda - \mu)])^2},$$

and finally

$$\Delta N^2_\lambda = \langle N_\lambda \rangle + \langle N_\lambda \rangle^2.$$

Examination of Eqs. (B.39) and (B.41) and comparison to Eqs. (B.33) and (B.34) show that both the average value and the fluctuations of the population of any one-body state is enhanced compared to the classical case, see Fig. B.8(b). This is consistent with the Bose enhancement phenomenon, introduced in a simple case in Sec. B.3.1.

### B.3.3 Fermi-Dirac distribution

Let us now turn to fermions. The computation of the grand-canonical partition function and its derivatives are found in the same way as for bosons. In particular, Eq. (B.37) is unchanged. However, for fermions, $N_\lambda$ only assumes the two values 0 and 1 and the sum in the formula for $Z_\lambda$ comprises only the corresponding two terms. It yields

$$Z_{GC} = \prod_\lambda Z_\lambda, \quad \text{with} \quad Z_\lambda = 1 + \exp[-\beta(\varepsilon_\lambda - \mu)].$$

Remarkably the fermionic formula for $Z_\lambda$ is the inverse of its bosonic counterpart with the minus sign changed into a plus sign.

Computing the average number of particles in the one-body state $\lambda$ from Eqs. (B.25) and (B.38) then yields

$$\langle N_\lambda \rangle = \frac{1}{\beta} \frac{\partial \ln Z_{GC}}{\partial \varepsilon_\lambda} = \frac{1}{\beta} \frac{\partial \ln Z_\lambda}{\partial \varepsilon_\lambda} = \frac{\exp[-\beta(\varepsilon_\lambda - \mu)]}{1 + \exp[-\beta(\varepsilon_\lambda - \mu)]},$$

and, finally,

$$\langle N_\lambda \rangle = \frac{1}{\exp[\beta(\varepsilon_\lambda - \mu)] + 1}.$$

This formula is called the Fermi-Dirac distribution, see Fig. B.8(a). Together with its bosonic counterpart, the Bose-Einstein distribution, it is one of the most important formulas of this course.
The Fermi-Dirac and Bose-Einstein distributions only differ by the $\pm$ sign in the denominator. We shall, however, see that this sign as crucial impacts on many physical properties of degenerate quantum gases. In contrast to the case of bosons, the chemical potential $\mu$ can span the entire $\mathbb{R}$, without restrictions. Note also that for any parameters, we find $\langle N_{\lambda} \rangle \leq 1$, which is compatible to the Fermi exclusion principle.

The fluctuations of the average number of particles in the one-body state $\lambda$ are also computed as before. One easily finds

$$
\Delta N^2_{\lambda} = \frac{1}{\beta^2} \frac{\partial^2 \ln Z_{\text{GC}}}{\partial \epsilon_{\lambda}^2} = -\frac{1}{\beta} \frac{\partial \langle N_{\lambda} \rangle}{\partial \epsilon_{\lambda}} = \exp\left[-\beta(\epsilon_{\lambda} - \mu)\right] \frac{\exp\left[-\beta(\epsilon_{\lambda} - \mu)\right]}{1 + \exp\left[-\beta(\epsilon_{\lambda} - \mu)\right]} - \exp\left[-\beta(\epsilon_{\lambda} - \mu)\right],
$$

and finally

$$
\Delta N^2_{\lambda} = \langle N_{\lambda} \rangle - \langle N_{\lambda} \rangle^2
$$

(B.44)

Examination of Eqs. (B.43) and (B.44) and comparison to Eqs. (B.33) and (B.34) show that both the average value and the fluctuations of the population of any one-body state are now suppressed compared to the classical case, see Fig. B.8(b). This is the opposite of bosons and consistent with Fermi exclusion, as introduced in Sec. B.3.1.

**B.3.4 Classical limit**

To conclude this section, let us discuss the classical limit, that is the conditions under which the quantum Bose-Einstein and Fermi-Dirac distributions can be substituted to the classical Boltzmann distribution. We present several criteria and introduce the pivotal notion of de Broglie wavelength.

**Criteria**

Let us first discuss the various criteria.

*Condition for a given one-body microstate* – The most general criterion consists in noting that the classical limit should occur when Bose and Fermi gases lose their distinction. It requires that
the bosonic and fermionic occupation numbers \( \langle N_{\lambda} \rangle = 1 / \{ \exp[\beta(\epsilon_\lambda - \mu)] \pm 1 \} \) are almost equal. This occurs when the \( \pm 1 \) term in the Bose-Einstein and Fermi-Dirac distribution is negligible compared to the exponential term, \( \exp[\beta(\epsilon_\lambda - \mu)] \gg 1 \). It yields the criterion

\[
\epsilon_\lambda - \mu \gg k_B T .
\]

Under this condition, we indeed recover the Boltzmann formula \( \langle N_{\lambda} \rangle = \exp[-\beta(\epsilon_\lambda - \mu)] \) for a given one-body microstate \( \lambda \). This criterion states that the occupation number follows the Boltzmann distribution for any one-body state with an energy \( \epsilon_\lambda \) larger than the chemical potential \( \mu \) at the level of the thermal energy \( k_B T \).

Note that the condition \( \exp[\beta(\epsilon_\lambda - \mu)] \gg 1 \) used above is equivalent to the condition \( \langle N_{\lambda} \rangle \ll 1 \).

The interpretation of this criterion is simple. If the average number of particles in a given one-body state \( \lambda \) is much smaller than one, then it is very unlikely that two or more particles populate the same one-body state. It means that two identical particles essentially never meet in the same one-body state and quantum effects, such as Bose enhancement or Fermi exclusion, are irrelevant. The classical description is thus expected to be accurate.

**Condition for the full one-body spectrum** — The above criterion is fulfilled for all one-body states \( \lambda \) if and only if the condition (B.45) is fulfilled for the ground state \( \lambda = 0 \). It yields the stronger condition \( \exp[\beta(\epsilon_0 - \mu)] \gg 1 \). At this stage, it is convenient to introduce a quantity that will be useful in the following, called the *fugacity*,

\[
z \equiv \exp[\beta(\mu - \epsilon_0)] .
\]

Then the condition for the full spectrum to be in the classical limit reads

\[
\epsilon_\lambda - \mu \gg k_B T , \quad \forall \lambda \quad \text{or, equivalently,} \quad z \ll 1 .
\]

Under this condition, all the one-body states, and hence the system, behave classically.

**Condition for a gas of particles** — Any of the conditions above is valid for any system. Let us now consider a gas of particles. For the sake of simplicity, we assume without loss of generality that the ground state energy is zero, \( \epsilon_0 = 0 \). Using Eq. (B.31), the condition (B.48) may be written \( \langle N \rangle / Z_1 \ll \exp(\beta\mu) \). Since for a classical gas, the typical energy per particle is \( \epsilon_{typ} \sim k_B T \), we have \( \mu \sim k_B T \), and the last criterion reads

\[
\langle N \rangle \ll Z_1 .
\]

This criterion can be interpreted as follows. By analogy with the microcanonical ensemble, the one-body partition function \( Z_1 \) may be interpreted as the typical number of significantly populated many-body microstates. Hence, the criterion (B.49) states that the classical limit requires the total number of particles be much smaller than the total number of available one-body states. In other words, the typical occupation number of each one-body state is much smaller than unity. As also discussed for one of the criteria above, it means that quantum effects are irrelevant.
Thermal de Broglie wavelength

For a gas of particles, it is worth going further and develop the last argument above. For the homogeneous ideal classical gas, the one-body partition function can be evaluated easily. Here we only stand on order of magnitude. Alternatively, an exact, explicit calculation can be done. Using the continuous formulation, we find

$$ Z_1 = \int \frac{drdp}{(2\pi \hbar)^d} \exp(-\beta p^2/2m) \sim \frac{\Omega}{\hbar^d} (mk_BT)^{d/2} \sim \frac{\Omega}{\lambda^d_T}, \quad (B.50) $$

where $\Omega$ is the volume of the gas in dimension $d$ and

$$ \lambda_T = \sqrt{\frac{2\pi \hbar^2}{mk_BT}} \quad (B.51) $$

is the so-called thermal de Broglie wavelength. The latter is the typical wavelength of the particles in a gas at temperature $T$. Indeed, the typical momentum of which is $p_{typ} \sim \sqrt{mk_BT}$ close to the classical limit and $\lambda_T \propto \hbar/p_{typ}$. By analogy with the diffraction limit in optics, the thermal de Broglie wavelength can also be seen as the typical size of a quantum wavepacket at temperature $T$. More precisely, it can be shown that the thermal de Broglie wavelength is the minimal order of magnitude of the size of a typical particle wavepacket at temperature $T$.

Then, using the expression for $Z_1$, the condition (B.49) may be written

$$ n\lambda^d_T \ll 1 \quad \text{or, equivalently,} \quad \lambda_T \ll a, \quad (B.52) $$

where $n$ is the density of the gas and $a = n^{-1/d}$ is the typical distance between the particles.

This remark offers a clear interpretation to the validity condition (B.52). Assume that the typical size of the particle wavepackets is much smaller that the typical distance between particles, i.e. $a \gg \lambda_T$. Then the wavepackets do not overlap and interference effects are vanishingly small, see Fig. B.9(a). Hence, the particles essentially never meet and the difference between bosons and fermions is irrelevant. Conversely, when the particle wavepackets overlap significantly, i.e. if $\lambda_T \gg a$, quantum effects play a role, see Fig. B.9(b). In this case, the physics of the gas should be treated in the quantum framework. Importantly, Eq. (B.52) thus shows that the quantum effects appear in systems of low temperature and/or high density. In condensed matter systems, such as solids, the density of electrons is high and quantum effects play a major role in electronic conduction, even at temperatures well above ambient temperature. Conversely, in atomic gases, the density is low and it is necessary to cool them down to extremely low temperature to reach quantum degeneracy.

The criterion (B.52) is universal and applies equally to Bose and Fermi gases. However, we shall see that quantum effects manifest in radically different ways in Bose and Fermi systems. In Bose gases, they induce a phase transition, known as Bose-Einstein condensation, see Chap. 2. In Fermi gases, they induce a crossover from the classical gas to the degenerate Fermi gas, see Chap. 4.
Figure B.9 | Classical versus quantum regimes in an ideal gas. In a gas at the interface between the classical and quantum regimes, the typical de Broglie wavelength is $\lambda_T = \sqrt{\frac{2\pi\hbar^2}{mk_B T}}$ and the inter-particle distance is $a \sim n^{-1/d}$ for an homogeneous gas of density $n$ in dimension $d$. (a) For $\lambda_T \ll a$, the particle wavepackets do not overlap and the gas behaves classically. (b) For $\lambda_T \gg a$, the particle wavepackets overlap significantly and the quantum effects show up.


