

An invitation to Quantum Statistical Mechanics

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Abstract

Quantum statistical mechanics deals with the study of quantum systems made up by a large number of particles. In particular it aims to understand the macroscopic behavior of these systems, starting from their microscopic fundamental description. While in the absence of interaction, the properties of many body systems can be deduced from the single particle Hamilton operator, in presence of interactions one needs to study the full N particle Schroedinger equation, with N very large and virtually infinite. This requires the development of new mathematical methods and tools.

These notes summarize the content of a course given at GSSI during March 2021, aiming to give an introduction to many particle problems in quantum mechanics, from a mathematical perspective, as a preparation to follow research seminars and advanced courses on this topic.

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1 Quantum Many particle systems

The mathematical description of many-particle quantum systems stems naturally from the one particle postulates we have discussed in the first part of the class. Systems of N (spinless) particles moving in $\Omega \subset \mathbb{R}^d$ are described by wave functions

$$\Psi_N \in L^2(\Omega^N, dx_1, \dots, dx_N) = L^2(\Omega)^{\otimes N} \quad (1.1)$$

with

$$\|\Psi_N\|_2^2 = \int_{\Omega^N} dx_1 \dots dx_N |\Psi_N(x_1, \dots, x_N)|^2 = 1, \quad (1.2)$$

where x_j denotes the position of the j -th particle. The probability to find the N particles in a region $X \subset \Omega^N$ when the system is described by the wave function $\Psi_N(x_1, \dots, x_N)$ is given by

$$\mathcal{P}(\{x_1, \dots, x_N\} \subset X; \psi_N(x_1, \dots, x_N)) = \int_X |\Psi_N(x_1, \dots, x_N)|^2 dx_1 \dots dx_N. \quad (1.3)$$

Many-body observables are described by self-adjoint operators on $L^2(\Omega^N)$. Let \mathcal{A} be an observable, represented by the self-adjoint operator A on $L^2(\Omega^N)$, then the probability to get a value of the observable \mathcal{A} in the interval $I \in \mathbb{R}$ is given by

$$\mathcal{P}(\mathcal{A} \in I; \psi_N(x_1, \dots, x_N)) = \langle \psi_N, E_A(I) \psi_N \rangle_{L^2(\Omega^N)} \quad (1.4)$$

where $\langle \cdot, \cdot \rangle_{L^2(\Omega^N)}$ is the scalar product in $L^2(\Omega^N)$ and $\{E_A(\lambda)\}$ denotes the spectral family associated to the self-adjoint operator A . Finally, the evolution of the N particle wave function is given by the solution of the Cauchy problem

$$\begin{cases} i\hbar \partial_t \psi_N(x_1, \dots, x_N; t) = H_N \psi_N(x_1, \dots, x_N; t) \\ \psi_N(x_1, \dots, x_N; 0) = \psi_{N,0}(x_1, \dots, x_N) \end{cases} \quad (1.5)$$

with H_N the Hamiltonian of the system which is a self-adjoint operator on $L^2(\Omega^N)$. Typically, one consider Hamiltonians with two body interactions having the form

$$H_N = \sum_{j=1}^N h_j + \sum_{1 \leq i < j \leq N} V_{ij}(x_i - x_j) \quad (1.6)$$

where h_j acts only on the degree of freedom of the j -th particle, and V_{ij} describes the interaction between particles i and j . More precisely, with a slight abuse of notation we are denoting with the same symbol h_j the operator on $L^2(\Omega^N)$ which acts as h_j on the j particle and as the identity on the remaining $N - 1$ particles and similarly V_{ij} is used to denote both the operator acting on the two-particle space and the operator on the whole N particle space which acts as the identity on the remaining $N - 2$ particles. The simplest non interacting Hamiltonian would be $H_N = \sum_j (-\frac{\hbar^2}{2m_j} \Delta_{x_j})$ with m_j the mass of the j -th particle. Note that restricting the attention to Hamiltonian of the form (1.6), one neglects the possibility of k -body interactions, for all $k \geq 3$. A three body interaction is a potential which depends at the same time on 3 particles $V(x_1, x_2, x_3)$. In physics fundamental interactions are two body interaction. However three body interaction or, more generally, k body interaction might also play a role. Note that existence and uniqueness of the solution of Eq. (1.5) is equivalent to self-adjointness of H_N .

Remark. Elementary particles have an internal degree of freedom called *spin*, which is characterized by a specific number which takes one of the values $S = 0, 1/2, 1, \dots$. In this class we will only consider the *spinless* case, corresponding to $S = 0$. More

generally, a quantum particle with spin S is described by a wave function in the Hilbert space $L^2(\Omega) \otimes \mathbb{C}^{(2S+1)} := L^2(\Omega; \mathbb{C}^{(2S+1)})$, hence a quantum system made up by N particles with spin S will be described by

$$\Psi_N(x_1, \delta_1; \dots; x_N, \delta_N) = \Psi_{\delta_1, \dots, \delta_N}(x_1, \dots, x_N) = \Psi_N(z_1, \dots, z_N) \quad (1.7)$$

with $z_j = (x_j, \delta_j)$, $x_j \in \Omega$ and $\delta_j \in \{1, 2, \dots, 2S + 1\}$. For example electrons are spin $1/2$ particles, hence their wave function is a pair of ordinary complex valued functions

$$\psi(x, \sigma) \in L^2(\Omega), \quad \sigma = 1, 2, \quad (1.8)$$

with normalization condition $\sum_{\sigma=1,2} \|\psi(x, \sigma)\|^2 = 1$.

1.A Bosons and Fermions

In the following we are going to consider systems of many identical particles. This has important consequences in quantum mechanics. Indeed, while in classical physics particles follow trajectories, and therefore it is always possible to follow a given target particle, in quantum mechanics there are no trajectories. So, identical particles are really indistinguishable.

Indistinguishability translates into the fact that we can only measure observables which are invariant with respect to any permutation of the N particles. For $\pi \in S_N$ an element of the group of permutations of N objects, let us consider the unitary operator U_π acting on $L^2(\Omega^N)$ s.t.

$$(U_\pi \Psi_N)(x_1, \dots, x_N) = \Psi_N(x_{\pi(1)}, \dots, x_{\pi(N)}) \quad (1.9)$$

We say that a N particle observable \mathcal{A} is permutation symmetric if and only if the corresponding self-adjoint operator A satisfies

$$U_\pi^* A U_\pi = A \quad \text{or equivalently} \quad [A, U_\pi] = 0 \quad \forall \pi \in S_N. \quad (1.10)$$

In particular if we are considering indistinguishable particles the Hamiltonian H_N defined in Eq. (1.6) has to be permutation symmetric, therefore the form of the one particle operators h_j has to be the same for any $j = i, \dots, N$, in the sense that for all $j = 1, \dots, N$

$$h_j = \mathbb{I} \otimes \dots \otimes \underset{j\text{-th position}}{h} \otimes \dots \otimes \mathbb{I}. \quad (1.11)$$

For example

$$h_j = -\Delta_{x_j} + V_{ext}(x_j) \quad (1.12)$$

for an external potential V_{ext} which acts in the same way on all particles. Similarly the two-body interaction V_{ij} can't depend on the pair ij . Summarizing, the typical Hamiltonian acting on N indistinguishable particles is

$$H_N = \sum_{j=1}^N (-\Delta_{x_j} + V_{ext}(x_j)) + \sum_{1 \leq i < j \leq N} V(x_i - x_j). \quad (1.13)$$

Note that from now on we are setting $\hbar = 1$ and we are considering particles of mass $1/2$.

Let $\psi \in L^2(\Omega^N)$ be the state of a quantum system made up by N identical particles. Then $\|U_\pi \psi\| = \|\psi\| = 1$ and clearly

$$\langle U_\pi \Psi_N, A U_\pi \Psi_N \rangle = \langle \Psi_N, U_\pi^* A U_\pi \Psi_N \rangle = \langle \Psi_N, A \Psi_N \rangle \quad (1.14)$$

for every permutation symmetric operator A . This means that the wave functions Ψ_N and $U_\pi \Psi_N$ for any $\pi \in S_N$ describe the same state. This would mean that there is not a one-to-one correspondence between physical states and wave functions. To

avoid this redundancy, one postulates that the only allowed wave functions are those for which $U_\pi \Psi_N = e^{i\alpha_\pi} \Psi_N$ for all $\pi \in S_N$.

It turns out that in three dimensions there are only two possible behaviors with respect to permutations satisfying the requirement that $U_\pi \Psi_N = e^{i\alpha_\pi} \Psi_N$ for all $\pi \in S_N$, namely

- completely symmetric wave functions

$$U_\pi \Psi_N(x_1, \dots, x_N) = \Psi_N(x_1, \dots, x_N) \quad \forall \pi \quad (1.15)$$

- completely antisymmetric wave functions

$$U_\pi \Psi_N(x_1, \dots, x_N) = \delta_\pi \Psi_N(x_1, \dots, x_N) \quad (1.16)$$

where δ_π is the sign of the permutation (*i.e.* $\delta_\pi = 1$ if π consists of an even number of transpositions, and $\delta_\pi = -1$ if π consists of an odd number of transpositions).

Particles described by symmetric wave functions are called bosons. Particles described by antisymmetric wave functions are called fermions. As it turns out the symmetry of a particle is directly related with its spin (this statement, known as the *spin statistics theorem* can be justified in relativistic quantum field theory). Particles with integer spin are bosons; particles with half integer spin are fermions (es electrons). Note: wave functions describing systems with distinguishable particles do not have symmetry restrictions; wave functions describing systems with different species of particles have symmetry conditions within particles of the same species.

We introduce the Hilbert space of symmetric and antisymmetric $L^2(\Omega^N)$ functions to be considered when dealing with N particle bosonic and fermionic systems respectively:

$$\begin{aligned} L_s^2(\Omega^N) &= \{\Psi_N \in L^2(\Omega^N) : U_\pi \Psi_N = \Psi_N \forall \pi \in S_N\} \\ L_a^2(\Omega^N) &= \{\Psi_N \in L^2(\Omega^N) : U_\pi \Psi_N = \delta_\pi \Psi_N \forall \pi \in S_N\}. \end{aligned} \quad (1.17)$$

Remark. It is common in the physics literature to refer to the choice of symmetry type as the *statistics* of the particles or of their wave function. More exactly the requirement of symmetry under exchange is referred to as *Bose-Einstein statistics*, the antisymmetry requirement is referred to as *Fermi-Dirac statistics*.

The simplest example of a bosonic wave function is the product of N copies of an arbitrary wave function $\varphi \in L^2(\Omega)$:

$$\Psi_N(x_1, \dots, x_N) = \prod_{j=1}^N \varphi(x_j) \quad (1.18)$$

Clearly $\|\Psi_N\| = 1$ and Ψ_N is symmetric with respect to any permutation. More generally, starting from $\{\varphi_j\}_{j \geq 1}$ of $L^2(\Omega)$, we can consider products of the form

$$\varphi_{j_1} \otimes \dots \otimes \varphi_{j_N}. \quad (1.19)$$

Unless all the j_i 's are the same, this function is not symmetric w.r.t. permutations. However it can be made symmetric as follows:

$$P_N^S(\varphi_{j_1} \otimes \dots \otimes \varphi_{j_N})(x_1, \dots, x_N) := \sqrt{\frac{1}{\ell_1! \dots \ell_k! N!}} \sum_{\pi \in S_N} \varphi_{j_1}(x_{\pi(1)}) \dots \varphi_{j_N}(x_{\pi(N)}) \quad (1.20)$$

if $\{j_1, \dots, j_N\}$ contains k different indices appearing respectively $\ell_1, \ell_2, \dots, \ell_k$ times (where of course $\ell_1 + \dots + \ell_k = N$). Then $P_N^S(\varphi_{j_1} \otimes \dots \otimes \varphi_{j_N})(x_1, \dots, x_N)$ is a bosonic wave function.

What about fermionic wave functions? Given an arbitrary product

$$\varphi_{j_1} \otimes \cdots \otimes \varphi_{j_N} \quad (1.21)$$

one can try to antisymmetrize it, similarly as before

$$P_N^A(\varphi_{j_1} \otimes \cdots \otimes \varphi_{j_N})(x_1, \dots, x_N) := \sqrt{\frac{1}{N!}} \sum_{\pi \in S_N} \delta_{\pi} \varphi_{j_1}(x_{\pi(1)}) \cdots \varphi_{j_N}(x_{\pi(N)}) \quad (1.22)$$

Note however that the sum equal zero unless the $\{\varphi_j\}$ are linearly independent. In the latter case $P_N^A(\varphi_{j_1} \otimes \cdots \otimes \varphi_{j_N})$ is indeed a fermionic wave function. Note that $P_N^A(\varphi_{j_1} \otimes \cdots \otimes \varphi_{j_N})$ can be written as a determinant:

$$P_N^A(\varphi_{j_1} \otimes \cdots \otimes \varphi_{j_N})(x_1, \dots, x_N) = \frac{1}{\sqrt{N!}} \det \begin{vmatrix} \varphi_{i_1}(x_1) & \cdots & \varphi_{i_N}(x_1) \\ \varphi_{i_1}(x_2) & \cdots & \varphi_{i_N}(x_2) \\ \cdots & \cdots & \cdots \\ \varphi_{i_1}(x_N) & \cdots & \varphi_{i_N}(x_N) \end{vmatrix}. \quad (1.23)$$

Such a wave function is usually referred to as a *Slater determinant*. Note that since Slater determinant vanishes if the set is linearly dependent we get in particular that all φ_j s have to be different from each other. This fact is known as *Pauli exclusion principle*: in a N fermion system, two particles cannot be in the same state, two particle cannot be described by the same one particle wave function (this only applies to product wave functions).

Remark Starting from a basis $\{\varphi_j\}$ of the one-particle space $L^2(\Omega)$ we can obtain a basis of $L_s^2(\Omega^N)$ or $L_a^2(\Omega^N)$ by taking $\{P_N^S(\varphi_{j_1} \otimes \cdots \otimes \varphi_{j_N})\}$ or $\{P_N^A(\varphi_{j_1} \otimes \cdots \otimes \varphi_{j_N})\}$ respectively.

1.B Pure and mixed states

As we have seen N quantum particles in Ω can be described through a normalized wavefunction $\Psi_N \in L^2(\Omega^N)$ so that the expectation of an observable A in the state Ψ_N is given by $\langle \Psi_N, A\Psi_N \rangle$. Let us introduce now the projection $\gamma_N = |\Psi_N\rangle\langle\Psi_N|$, then the expectation of the observable A written in terms of γ_N takes the form

$$\langle \Psi_N, A\Psi_N \rangle = \text{Tr}(A\gamma_N). \quad (1.24)$$

where $\text{Tr}(S)$ denotes the trace of the operator S defined by $\text{Tr}(S) = \sum_k \langle \varphi_k, S\varphi_k \rangle$ for any $\{\varphi_k\}$ orthonormal basis. The reason why we introduced the equivalent description thorough γ_N of the system is that it be easily generalized to consider mixed states. More precisely, we can consider not only orthogonal projections but also operators of the form

$$\gamma_N = \sum_j \lambda_j |\Psi_{N,j}\rangle\langle\Psi_{N,j}| \quad (1.25)$$

where $0 \leq \lambda_j \leq 1$ such that $\sum_j \lambda_j = 1$ and $\Psi_{N,j} \in L^2(\Omega^N)$ such that $\|\Psi_{N,j}\|^2 = 1$. The interpretation is as follows: γ_N given by (1.25) described a system which is in the state $\Psi_{N,j}$ with probability λ_j .

Remark The introduction of states of the form given in Eq. (1.25) can be justified by saying that we want to include in our description of quantum systems, in addition to the *intrinsic probability* already encoded in the theory, the so called *epistemic probability*. Suppose for example that we only know that a certain N particle quantum system is in one of the orthonormal states $\{\psi_{N,1}, \psi_{N,2}, \dots, \psi_{N,n}\}$ with probabilities $\{p_1, p_2, \dots, p_n\}$ $p_i \geq 0$, $\sum_{i=1}^n p_i = 1$ respectively. If we now measure on the state the observable described by the operator A in $L^2(\Omega^N)$, it appears natural to require the expected outcome of the observation to be given by $\langle A \rangle = \sum_{n=1}^n p_i \langle \psi_i, A\psi_i \rangle$.

Recalling that by the spectral theorem for compact operators we know that every trace class operator γ_N can be rewritten in the form in Eq. (1.25) we can say that

a mixed N particle state is a non-negative trace class operator on $L^2(\Omega^N)$ such that $\text{Tr}(\gamma_N) = 1$ (Note that since $\gamma_N \geq 0$ and $\text{Tr}(\gamma_N) = 1$ we immediately get $0 \leq \lambda_j \leq 1/\forall j$ which also implies $\gamma_N \leq 1$). An operator γ_N satisfying the properties just mentioned is called a *density matrix*. A bosonic (fermionic) density matrix is defined analogously as a non-negative density matrix on $L_s^2(\Omega^N)$ ($L_a^2(\Omega^N)$) with unitary trace.

Remark A trace class operator is a compact operator A such that $\text{Tr}|A| = \sum_j |\lambda_j| < \infty$ where λ_j are its eigenvalues and $\Psi_{N,j}$ the corresponding eigenfunctions (A certainly has only discrete spectrum due to compactness).

The evolution equation of the state γ_N is given by the equation

$$i\hbar\partial_t\gamma_N(t) = [H, \gamma_N(t)], \quad \gamma_N(0) = \gamma_N \quad (1.26)$$

called *Von Neumann equation*. This evolution law can be easily checked for density matrices of the form $\gamma_N = \sum_j \lambda_j |\Psi_{N,j}\rangle\langle\Psi_{N,j}|$, with $\Psi_{N,j}$ satisfying the Schrodinger equation (1.5). Moreover the probabilistic prediction relative to an observable \mathcal{A} when the system is in the state $\gamma_N(t)$ is

$$\mathcal{P}(\mathcal{A} \in I; \gamma_N(t)) := \text{Tr}(\gamma_N(t)E_A(I)) \quad (1.27)$$

where $\{E_A(\lambda)\}$ denotes the spectral family associated to the self-adjoint operator A .

Remark Let us mention that von Neumann equation (1.26) differs from the Heisemberg equation which describes the evolution of the observables in the Heisemberg picture by a sign (see [4, Eq. (5.29)])

To conclude this section we would like to point out an important difference between pure (*i.e.* described by $\Psi_N \in L^2(\Omega^N)$ or, equivalently, by $\gamma_N = |\Psi_N\rangle\langle\Psi_N|$) and mixed states. Given two pure states Ψ_N and Φ_N we can consider the new pure state given by $\frac{\Psi_N + \Phi_N}{\sqrt{2}}$ corresponding to the density matrix

$$\gamma_{N,\text{pure}} = \frac{1}{2} \left[|\Psi_N\rangle\langle\Psi_N| + |\Psi_N\rangle\langle\Phi_N| + |\Phi_N\rangle\langle\Psi_N| + |\Phi_N\rangle\langle\Phi_N| \right]. \quad (1.28)$$

On the other hand, we can also consider the mixed state given by

$$\gamma_{N,\text{mixed}} = \frac{|\Psi_N\rangle\langle\Psi_N| + |\Phi_N\rangle\langle\Phi_N|}{2}. \quad (1.29)$$

Then, for any observables A we get

$$\begin{aligned} \text{Tr}(A\gamma_{N,\text{pure}}) &= \frac{1}{2} \left[\langle\Psi_N, A\Psi_N\rangle + \langle\Phi_N, A\Phi_N\rangle + \langle\Psi_N, A\Phi_N\rangle + \langle\Phi_N, A\Psi_N\rangle \right] \\ \text{Tr}(A\gamma_{N,\text{mixed}}) &= \frac{1}{2} \left[\langle\Psi_N, A\Psi_N\rangle + \langle\Phi_N, A\Phi_N\rangle \right] \end{aligned} \quad (1.30)$$

i.e. the expectation on the pure state contains additional off diagonal terms that can produce interference. One often distinguish between coherent (for pure states) and incoherent (for mixed states) superpositions. Note that, for a generic density matrix γ_N if $\text{Tr}\gamma_N^2 = 1$ then γ_N is a projector, and hence it is a pure state.

1.C Reduced density matrices

If γ_N is an N particle bosonic (fermionic) density matrix (in the case of indistinguishable particles the definition is slightly different), with kernel $\gamma_N(\vec{x}; \vec{y})$ we define the k -particle reduced density matrix to be the integral operator acting on the bosonic (fermionic) k particle space with kernel

$$\begin{aligned} \gamma_N^{(k)}(z_1, \dots, z_k; z'_1, \dots, z'_k) \\ := \frac{N!}{(N-k)!} \int_{\Omega^{N-k}} \gamma_N(z_1, \dots, z_k, z_{k+1} \dots z_N; z'_1, \dots, z'_k, z_{k+1} \dots z_N) dz_{k+1} \dots z_N \end{aligned} \quad (1.31)$$

where the presence of the factor $N!/(N-k)!$ comes from the symmetry assumptions. One says that $\gamma_N^{(k)}$ is obtained by taking the partial trace of γ_N over the last $(N-k)$ particles and writes

$$\gamma_N^{(k)} = \frac{N!}{(N-k)!} \text{Tr}_{k+1, \dots, N} \gamma_N \quad (1.32)$$

(the meaning of this operation is defined by (1.31)).

Exercise 1. Check that if γ_N is fermionic or bosonic density matrix then the k particle reduced density matrix $\gamma_N^{(k)}$ satisfies the following properties:

- i) $\gamma_N^{(k)}$ is non negative;
- ii) $\text{Tr} \gamma_N^{(k)} = \frac{N!}{(N-k)!}$.

Examples of reduced densities

Consider the bosonic wave function $\Psi_N = \varphi^{\otimes N}$. The kernel of the k particle density matrix is given by

$$\begin{aligned} & \gamma_N^{(k)}(x_1, \dots, x_k; x'_1, \dots, x'_k) \\ &= \frac{N!}{(N-k)!} \int dx_{k+1} \dots dx_N \varphi(x_1) \dots \varphi(x_k) \overline{\varphi(x'_1)} \dots \overline{\varphi(x'_k)} |\varphi(x_{k+1})|^2 \dots |\varphi(x_N)|^2 \\ &= \frac{N!}{(N-k)!} \prod_{j=1}^k \varphi(x_j) \overline{\varphi(x'_j)}. \end{aligned} \quad (1.33)$$

Therefore

$$\gamma_N^{(k)} = \frac{N!}{(N-k)!} |\varphi\rangle \langle \varphi|^{\otimes k}. \quad (1.34)$$

Consider the fermionic state

$$\Psi_N(x_1, \dots, x_N) = \frac{1}{\sqrt{N!}} \det \begin{vmatrix} \varphi_{i_1}(x_1) & \dots & \varphi_{i_N}(x_1) \\ \dots & \dots & \dots \\ \varphi_{i_1}(x_N) & \dots & \varphi_{i_N}(x_N) \end{vmatrix} \quad (1.35)$$

where $\{\varphi_j\}$ define an orthonormal basis. The kernel of the one particle density matrix is given by

$$\begin{aligned} \gamma_N^{(1)}(x; x') &= N \int dx_2 \dots dx_N \left(\frac{1}{\sqrt{N!}} \sum_{\pi} \delta_{\pi} \varphi_{\pi_1}(x) \varphi_{\pi_2}(x_2) \dots \varphi_{\pi_N}(x_N) \right) \\ & \quad \times \left(\frac{1}{\sqrt{N!}} \sum_{\pi'} \delta_{\pi'} \overline{\varphi_{\pi'_1}(x')} \overline{\varphi_{\pi'_2}(x_2)} \dots \overline{\varphi_{\pi'_N}(x_N)} \right) \\ &= \frac{N}{N!} \sum_{\pi, \pi'} \varphi_{\pi_1}(x) \overline{\varphi_{\pi'_1}(x')} \prod_{j=2}^N \underbrace{\int dx_j \varphi_{\pi_j}(x_j) \overline{\varphi_{\pi'_j}(x_j)}}_{\delta_{\pi_j = \pi'_j} \|\varphi_{\pi_j}\|^2} \\ &= \frac{N}{N!} \sum_{\pi} \varphi_{\pi_1}(x) \overline{\varphi_{\pi_1}(x')} \\ &= \sum_{j=1}^N \varphi_j(x) \overline{\varphi_j(x')} \end{aligned} \quad (1.36)$$

Therefore

$$\gamma_N^{(1)} = \sum_{j=1}^N |\varphi_j\rangle \langle \varphi_j| \quad (1.37)$$

Note that $\frac{1}{N}\gamma_N^{(1)} = \frac{1}{N}\sum_{j=1}^N |\varphi_j\rangle\langle\varphi_j|$ is the density matrix of a one particle system in a mixed state being with equal probability in one of the N states $\varphi_1, \dots, \varphi_N$ (reducing to one particle, which means, as long as one consider one particle observables, the fermionic N -body system with wave function as above, behaves as a one particle system in a mixed state being with equal probability in one of the states φ_j).

Exercise 2. Compute $\gamma_N^{(2)}$ for the fermionic state defined in (1.35).

Reduced density matrices and observables

The reason why reduced density matrices are a convenient tool to deal with many particle problems becomes apparent if we focus on the goal of computing observables. If $k < N$, the k -th reduced density $\gamma_N^{(k)}$ does not contain the full information about the system under consideration. Integrating out the degrees of freedom of $(N-k)$ particles means that we lost a lot of information. However, the knowledge of $\gamma_N^{(k)}$ is enough, if we are only interested in computing the expectation of observables depending non trivially only on k particles.

In fact, given an operator $O^{(k)}$ on $L^2(\Omega^k)$ we can construct a permutation symmetric k -particle observable

$$O = \frac{1}{(N-k)!} \sum_{\pi \in S_N} O_{\pi(1), \dots, \pi(k)}^{(k)} \quad (1.38)$$

where $O_{\pi(1), \dots, \pi(k)}^{(k)}$ denotes the operator acting as $O^{(k)}$ on the particles $\pi(1), \dots, \pi(k)$ and as the identity on the remaining $N-k$ particles. The expectation of O on the state γ_N is then given by

$$\begin{aligned} \text{Tr}(O\gamma_N) &= \frac{1}{(N-k)!} \sum_{\pi \in S_N} \text{Tr}(O_{\pi(1), \dots, \pi(k)}^{(k)} \gamma_N) \\ &= \frac{1}{(N-k)!} \sum_{\pi \in S_N} \text{Tr}(O_{1, \dots, k}^{(k)} \gamma_N) \\ &= \frac{1}{(N-k)!} \sum_{\pi \in S_N} \text{Tr}_{1, \dots, k}(O_{\pi(1), \dots, \pi(k)}^{(k)}) \text{Tr}_{k+1, \dots, N} \gamma_N \\ &= \text{Tr}(O^{(k)} \gamma_N^{(k)}) \end{aligned} \quad (1.39)$$

where in the last line the trace is over the k particle space. For example, as we have seen the Hamiltonian acting on N indistinguishable particles has typically the form given in Eq. (1.13), therefore we can rewrite

$$H_N = H_1 + H_2 \quad (1.40)$$

where H_1 is the sum of one particle operators and H_2 is the sum of two particles operators. Thus, to compute H_1 and H_2 in the state described by the density matrix γ_N it is enough to know $\gamma_N^{(1)}$ and $\gamma_N^{(2)}$:

$$\text{Tr}H_N\gamma_N = \text{Tr}(-\Delta + V_{ext}(x))\gamma_N^{(1)} + \frac{1}{2}\text{Tr}V(x_1 - x_2)\gamma_N^{(2)} \quad (1.41)$$

If one focus on the problem of computing the minimum of the energy, $\gamma_N^{(1)}$ and $\gamma_N^{(2)}$ are the two most important reduced densities.

One may think that the problem of minimizing the energy

$$\inf_{\substack{\|\psi_N\|=1 \\ \psi_N \in L^2(\mathbb{R}^{dN})}} \langle \psi_N, H_N \psi_N \rangle = \inf_{0 \leq \gamma_N \leq 1} \text{Tr} \gamma_N H_N \quad (1.42)$$

is equivalent to minimize the quantity $\text{Tr}(-\Delta + V_{ext}(x))\gamma_N^{(1)} + \frac{1}{2}\text{Tr}V(x_1 - x_2)\gamma_N^{(2)}$ over all possible one and two particle density matrices. This problem looks much

simpler than the original one, because $\gamma_N^{(1)}$ and $\gamma_N^{(2)}$ are operators on $L^2(\Omega)$ and $L^2(\Omega^2)$ respectively, while γ_N is an operator over $L^2(\Omega^N)$ and N is going to be large. The reason why the second problem is not simpler is that it is very difficult to characterize the set of all those $\gamma^{(2)}$ for which there exists γ_N s.t. $\gamma^{(2)}$ is the two particle density matrix associated with γ_N (it is called the *N representability problem*). In fact there is no known set of conditions on $\gamma^{(2)}$ which guarantee the existence of γ_N . Some necessary conditions are known (it is certainly not enough that $\gamma^{(2)} \geq 0$ with $\text{Tr}\gamma^{(2)} = N(N-1)$), but sufficient conditions are not known.

What is known are necessary and sufficient conditions for a non negative trace class operator $\gamma^{(1)}$ with $\text{Tr}\gamma^{(1)} = N$ to be the one particle density matrix γ_N . We state the two theorems, one for bosons and one for fermions, referring to [1] for the proofs.

Theorem 1 (Admissibility of $\gamma^{(1)}$, bosons). *Let $\gamma^{(1)}$ be a s.a., non negative operator on $L^2(\mathbb{R}^3)$ with $\text{Tr}\gamma^{(1)} = N$, for some $N \in \mathbb{N}$. Then exists a bosonic density matrix γ_N (with $\gamma(x_{\pi_1}, \dots, x_{\pi_N}; x'_{\pi'_1}, \dots, x'_{\pi'_N}) = \gamma(x_1, \dots, x_N; x'_1, \dots, x'_N)$ for all $\pi, \pi' \in S_N$) such that $\gamma^{(1)} = N\text{Tr}_{2, \dots, N}\gamma_N$. If $N \geq 2$, γ can be chosen to be a pure state, that is there exists $\psi \in L^2(\mathbb{R}^{3N})$, symmetric, with $\gamma^{(1)} = N\text{Tr}_{2, \dots, N}|\psi\rangle\langle\psi|$.*

Theorem 2 (Admissibility of $\gamma^{(1)}$, fermions). *Let $\gamma^{(1)}$ satisfy the hypotheses of Theorem 1. Then there is a fermionic N-particle density matrix γ_N such that $\gamma^{(1)} = N\text{Tr}_{2, \dots, N}\gamma_N$ if and only if $\gamma^{(1)}$ satisfies the additional condition*

$$\gamma^{(1)} \leq 1. \tag{1.43}$$

It is not true, in general, that γ_N can be chosen to be a pure state. In particular, whenever $\gamma^{(1)}$ has $N-1$ eigenvalues equal to 1 and at least $N+1$ positive eigenvalues then cannot be pure.

2 Statistical Mechanics

In the previous section we introduced the mathematical formalism allowing us to describe many particle systems in quantum mechanics. Our next goal is to get information about the macroscopic observables characterizing quantum systems made up by a large number of particles (density of particles, energy, entropy, pressure...) in the very spirit of Statistical Mechanics. The core idea is that we are not interested in the microscopic details of the systems, but only in measuring macroscopic observables at equilibrium (and actually many different microscopic realizations of a given system may lead to the same set of macroscopic observables). This leads to the introduction of Statistical Ensembles, as in classical physics, namely to “rules” allowing to associate a probability measure to families of equilibrium quantum states, corresponding to a given set of macroscopic parameters. Before describing the set of statistical ensembles which are of relevance in quantum mechanics, we find useful to introduce the formalism of *second quantization*.

2.A Second Quantization

In this section we introduce the formalism of second quantization. As long as we work with states of exactly N particles, the formalism it is just a convenient language for calculations. It will become however essential to introduce the Grand Canonical Ensemble where the number of particle in the system is not fixed.

Let start introducing Fock space *i.e.* Hilbert space

$$\mathcal{F} = \bigoplus_{n \geq 0} \mathcal{H}_n \quad (2.1)$$

where $\mathcal{H}_n = L_s^2(\Omega^n)$ (respectively $L_a^2(\Omega^n)$) is the n -particle bosonic (fermionic) space and we set $\mathcal{H}_0 = \mathbb{C}$.

Given two vectors $\Phi = \{\Phi^{(n)}\}_{n \geq 0}$, $\Psi = \{\Psi^{(n)}\}_{n \geq 0} \in \mathcal{F}$ we define the inner product

$$\langle \Phi, \Psi \rangle_{\mathcal{F}} = \sum_{n \geq 0} \langle \Phi^{(n)}, \Psi^{(n)} \rangle_{\mathcal{H}_n} \quad (2.2)$$

and denote by $\|\cdot\|_{\mathcal{F}}$ the corresponding norm.

On \mathcal{F} we introduce the number of particle operator \mathcal{N} defined by

$$(\mathcal{N}\Psi)^{(n)} = n\Psi^{(n)} \quad (2.3)$$

for any $\Psi = \{\psi^{(n)}\}_{n \geq 0}$ such that

$$\sum_{n \geq 0} n^2 \|\psi^{(n)}\|_{\mathcal{H}_n}^2 < \infty. \quad (2.4)$$

Hence a vector $\Psi = \{\psi^{(n)}\}_{n \geq 0}$ describes a state which has n -particle with probability $\|\psi^{(n)}\|_{\mathcal{H}_n}^2$. Note that states with exactly N particles *i.e.* of the form $\Psi = \{0, \dots, 0, \psi_N, 0, \dots\}$ are eigenvectors of \mathcal{N} with eigenvalue N . The vacuum vector $\Omega = \{1, 0, \dots\}$ which describes a system with zero particles plays a special role.

On Fock space \mathcal{F} , a particularly useful concept are the creation and annihilation operators $a^*(f)$ and $a(f)$, with $f \in \mathcal{H}_1$, the one-particle Hilbert space. Their explicit definitions and properties depend on whether we are considering a system of bosons or fermions. In the bosonic space, given $\Psi = \{\Psi^{(n)}\}_{n \geq 0}$ such that $\Psi^{(n)} \in L_s^2(\Omega^n)$ an n -particle wave function, we set

$$\begin{aligned} (a^*(f)\Psi)^{(n)}(x_1, \dots, x_n) &= \frac{1}{\sqrt{n}} \sum_{i=1}^n f(x_i) \Psi^{(n-1)}(x_1, \dots, \cancel{x_i}, \dots, x_n), \\ (a(f)\Psi)^{(n)}(x_1, \dots, x_n) &= \sqrt{n+1} \int_{\Omega} dx f(x) \Psi^{(n+1)}(x_1, \dots, x_n, x). \end{aligned} \quad (2.5)$$

Thus, in the bosonic case $a^*(f), a(f)$ are densely defined unbounded operators whose domain is equal to the domain of $\mathcal{N}^{1/2}$. Moreover $a^*(f)$ is the adjoint of $a(f)$. Note that $a^*(f)$ is linear in f while $a(f)$ is antilinear and they satisfy the *canonical commutation relations (CCR)*:

$$[a(f), a^*(g)] = \langle f, g \rangle, \quad [a(f), a(g)] = [a^*(f), a^*(g)] = 0 \quad (2.6)$$

where given two operators A, B the commutator is defined by $[A, B] = AB - BA$.

Exercise 3. Check the validity of the CCR for bosonic creation and annihilation operators given in (2.6)

On the other hand for a fermionic wave function $\Psi = \{\Psi^{(n)}\}_{n \geq 0}$ such that $\Psi^{(n)} \in L_a^2(\Omega^n)$ we define

$$\begin{aligned} (a^*(f)\Psi)^{(n)}(x_1, \dots, x_n) &= \frac{1}{\sqrt{n}} \sum_{i=1}^n (-1)^{i-1} f(x_i) \Psi^{(n-1)}(x_1, \dots, \cancel{x_i}, \dots, x_n), \\ (a(f)\Psi)^{(n)}(x_1, \dots, x_n) &= \sqrt{n+1} \int_{\Omega} dx \overline{f(x)} \Psi^{(n+1)}(x_1, \dots, x_n, x). \end{aligned} \quad (2.7)$$

These operators satisfy the *canonical anticommutation relation (CAR)*, i.e.

$$\{a(f), a^*(g)\} = \langle f, g \rangle, \quad \{a(f), a(g)\} = \{a^*(f), a^*(g)\} = 0 \quad (2.8)$$

where we have introduced the anticommutator $\{A, B\} = AB + BA$.

Exercise 4. Check the validity of the CAR for fermionic creation and annihilation operators given in (2.8).

Note that by the CAR it follows in particular $a^*(f)^2 = 0$ for any $f \in \mathcal{H}_1$ implementing Pauli's exclusion principle. Moreover, unlike their bosonic counterpart in the fermionic case creation and annihilation operators are bounded. Indeed, using the CAR,

$$\begin{aligned} \|a(f)\Psi\|_{\mathcal{F}}^2 &= \langle a(f)\Psi, a(f)\Psi \rangle_{\mathcal{F}} = \langle \Psi, a^*(f)a(f)\Psi \rangle_{\mathcal{F}} \\ &= \|f\|^2 \|\Psi\|_{\mathcal{F}}^2 - \langle \Psi, a(f)a^*(f)\Psi \rangle_{\mathcal{F}} = \|f\|^2 \|\Psi\|_{\mathcal{F}}^2 - \|a^*(f)\Psi\|_{\mathcal{F}}^2 \\ &\leq \|f\|^2 \|\Psi\|_{\mathcal{F}}^2 \end{aligned} \quad (2.9)$$

which implies $\|a(f)\|, \|a^*(f)\| \leq \|f\|$.

Remark. A product of creation and annihilation operators is called *normal-ordered* if all creation operators are to the left of all annihilation operators.

Both in the fermionic and bosonic case, it is useful to introduce the operator-valued distributions a_x^* and a_x which formally creates and annihilates a particle in position x . More precisely we can define

$$(a_x \Psi)^{(n)}(x_1, \dots, x_n) = \sqrt{n+1} \Psi^{(n+1)}(x, x_1, \dots, x_n) \quad (2.10)$$

as a densely defined operator (since the expression makes sense on continuous functions). It is easy to check that

$$a(f) = \int dx \overline{f(x)} a_x. \quad (2.11)$$

On the other hand if we try to consider the adjoint of a_x it is not a densely defined operator; indeed it is formally given by

$$(a_x^* \Psi)^{(n)}(x_1, \dots, x_n) = \frac{1}{\sqrt{n}} \sum_{i \geq 1} \delta(x - x_i) \Psi^{(n-1)}(x_1, \dots, \cancel{x_i}, \dots, x_n). \quad (2.12)$$

Nevertheless we can make sense of it as a quadratic form through

$$\langle \Phi, a_x^* \Psi \rangle_{\mathcal{F}} = \langle a_x \Phi, \Psi \rangle_{\mathcal{F}} \quad (2.13)$$

or by considering it as a distribution, since by formally integrating against a test-function $f \in \mathcal{H}_1$ we can take a_x^* back to the well-defined operator

$$\int dx f(x) a_x^* = a^*(f). \quad (2.14)$$

In terms of these distributions the CCR on bosonic space reads

$$[a_x, a_y^*] = \delta(x - y), \quad [a_x, a_y] = [a_x^*, a_y^*] = 0 \quad (2.15)$$

where δ denotes the Dirac delta distribution. The CAR on fermionic Fock space read

$$\{a_x, a_y^*\} = \delta(x - y), \quad \{a_x, a_y\} = \{a_x^*, a_y^*\} = 0. \quad (2.16)$$

Note that

$$\langle \Psi, \int dx a_x^* a_x \Phi \rangle_{\mathcal{F}} = \int dx \langle \Psi, a_x^* a_x \Phi \rangle_{\mathcal{F}} = \int dx \langle a_x \Psi, a_x \Phi \rangle_{\mathcal{F}} = \langle \Psi, \mathcal{N} \Phi \rangle_{\mathcal{F}}. \quad (2.17)$$

Given a one-particle operator O we introduce its second quantization $d\Gamma(O)$ by

$$(d\Gamma(O)\Psi)^{(n)} = O^{(n)}\Psi^{(n)}, \quad (2.18)$$

where

$$O^{(n)} = \sum_{j=1}^n O_j^{(n)} = \sum_{j=1}^n \mathbb{I} \otimes \cdots \otimes_{j\text{-th position}} O \otimes \cdots \otimes \mathbb{I}. \quad (2.19)$$

The domain of $d\Gamma(O)$ is given by

$$D(d\Gamma(O)) = \{ \Psi \in \mathcal{F} : \Psi^{(n)} \in D(O^{(n)}) \forall n \in \mathbb{N} \text{ and } \sum_{n \geq 0} \|O^{(n)}\Psi^{(n)}\|_{\mathcal{H}_n}^2 < \infty \}. \quad (2.20)$$

In particular if O has operator kernel $O(x, y)$ then (again in the sense of quadratic forms)

$$\begin{aligned} \langle \Phi, d\Gamma(O)\Psi \rangle_{\mathcal{F}} &= \sum_{n \geq 1} \sum_{j=1}^n \langle \Phi^{(n)}, O_j^{(n)} \Psi^{(n)} \rangle \\ &= \sum_{n \geq 1} n \int_{\Omega^{n+2}} dx dy dx_2 \dots dx_n O(x, y) \overline{\Phi^{(n)}(x, x_2, \dots, x_n)} \Psi^{(n)}(y, x_2, \dots, x_n) \\ &= \sum_{n \geq 1} \int dx dy dx_2 \dots dx_n O(x, y) \overline{(a_x \Phi)^{(n-1)}(x_2, \dots, x_n)} (a_y \Psi)^{(n-1)}(x_2, \dots, x_n) \\ &= \int dx dy O(x, y) \langle a_x \Phi, a_y \Psi \rangle_{\mathcal{F}}. \end{aligned} \quad (2.21)$$

Thus (in the sense of quadratic forms)

$$d\Gamma(O) = \int dx dy O(x, y) a_x^* a_y. \quad (2.22)$$

Remark. Note that if we consider a one particle operator defined as $O\psi = O(x)\psi$, *i.e.* a multiplication operator then (2.22) is still formally correct setting $O(x; y) = O(x)\delta(x - y)$.

Note that even if O is bounded its second quantization $d\Gamma(O)$ doesn't have to be bounded. Nevertheless for bounded operators one can show

$$|\langle \Phi, d\Gamma(O)\Psi \rangle_{\mathcal{F}}| \leq \|O\| \langle \Phi, \mathcal{N} \Psi \rangle_{\mathcal{F}} \quad (2.23)$$

as can be easily checked by definition (2.22). We can extend (2.22) to operators involving more than one particle. Let O be a k -particle operator, we define its second quantization $d\Gamma(O)$ by

$$(d\Gamma(O)\Psi)^{(n)} = \sum_{\{i_1, \dots, i_k\}} O_{i_1, \dots, i_k}^{(n)} \Psi^{(n)} \quad (2.24)$$

where the sum runs over all sets $\{i_1, \dots, i_k\}$ of k different indices in $\{1, \dots, n\}$ and $O_{i_1, \dots, i_k}^{(n)}$ acts as O on the particles i_1, \dots, i_k and as the identity on the remaining $n - k$ particles. In particular if O has kernel $O(x_1, \dots, x_k, y_1, \dots, y_k)$ then one can show, proceeding similarly to the proof of (2.22),

$$d\Gamma(O) = \int dx_1 \dots dx_k dy_1 \dots dy_k O(x_1, \dots, x_k, y_1, \dots, y_k) a_{x_1}^* \dots a_{x_k}^* a_{y_1} \dots a_{y_k}. \quad (2.25)$$

Analogously to (2.23) we find for any bounded k -particle operator O that

$$|\langle \Phi, d\Gamma(O)\Psi \rangle_{\mathcal{F}}| \leq \|O\| \langle \Phi, \mathcal{N}(\mathcal{N} - 1) \dots (\mathcal{N} - k)\Psi \rangle_{\mathcal{F}}. \quad (2.26)$$

Let us now consider a many body Hamiltonian of the form

$$H_N = \sum_{i=1}^N h_i + \sum_{1 \leq i < j \leq N} V(x_i - x_j) \quad (2.27)$$

with h a one-particle operator and V is a potential. Using creation and annihilation operators, the Fock space Hamiltonian $d\Gamma(H) = \bigoplus_{n \geq 0} H_n$ can be rewritten as

$$\mathcal{H} := d\Gamma(H) = \int dx h(x, y) a_x^* a_y + \frac{1}{2} \int dx dy V(x - y) a_x^* a_y^* a_x a_y \quad (2.28)$$

where the equality has to be understood in the sense of quadratic forms.

Exercise 5. Check that the second quantization of the N particles free Hamiltonian $H_N = \sum_{i=1}^N -\Delta_{x_j}$ is given by $\mathcal{H} = \int dx \nabla a_x^* \nabla a_x$ in the sense of quadratic forms. (You can proceed similarly to Eq. (2.17))

Let us conclude this section by noting that if $\{u_k\}_{k \geq 0}$ are an ONB of \mathcal{H}_1 then the second quantization of any one-particle operator O can be conveniently rewritten in the sense of quadratic forms as

$$d\Gamma(O) = \sum_{i, j \geq 0} \langle u_i, O u_j \rangle a_i^* a_j \quad (2.29)$$

where we introduced the notations $a_k = a(u_k)$, $a_k^* = a^*(u_k)$. Analogously for a two particle operator O we find

$$d\Gamma(O) = \sum_{i, j, k, l \geq 0} \langle u_i \otimes u_j, O u_k \otimes u_l \rangle a_i^* a_j^* a_k a_l. \quad (2.30)$$

Hence for the many body Hamiltonian in Fock space we have

$$\sum_{i, j \geq 0} \langle u_i, h u_j \rangle a_i^* a_j + \frac{1}{2} \sum_{i, j, k, l \geq 0} \langle u_i \otimes u_j, V u_k \otimes u_l \rangle a_i^* a_j^* a_k a_l. \quad (2.31)$$

Moreover a basis of \mathcal{F} can be obtained from $\{u_i\}_{i \geq 0}$ taking

$$\{P_S^N(u_{i_1} \otimes \dots \otimes u_{i_n})\}_{\substack{n \geq 0 \\ i_1, \dots, i_n \geq 0}} \quad (2.32)$$

for bosons and

$$\{P_A^N(u_{i_1} \otimes \cdots \otimes u_{i_n})\}_{\substack{n \geq 0 \\ i_1, \dots, i_n \geq 0}} \quad (2.33)$$

for fermions where P_S^N and P_A^N denote the projection on the N -particle symmetric/antisymmetric subspace defined in Eq. (1.20) and Eq. (1.22) respectively. Equivalently the generic element in the basis can be rewritten as

$$\frac{1}{\sqrt{n_{i_1}! \dots n_{i_M}!}} a^*(u_{i_M})^{n_{i_M}} \dots a^*(u_{i_1})^{n_{i_1}} \Omega \quad (2.34)$$

where $M = 1, 2, \dots$, and $1 \leq i_1 < i_2 < \dots < i_M$. Note that n_{i_1}, \dots, n_{i_M} run over positive integers for bosons and are just 1 for fermions. The basis element defined in (2.34) is often denoted by $|n_{i_1}, \dots, n_{i_M}\rangle$. The basis we just constructed is usually referred to as *occupation number basis*.

2.B Statistical Ensembles

Aim of this section is to provide a brief description of statistical ensembles in quantum mechanics. For a more detailed discussion we refer the reader to [3]. Throughout the whole section we restrict ourselves to the three dimensional box $\Lambda = [0, L]^3$. We consider the Hamiltonian H_N acting on $L^2(\Lambda^N)$ and such that it has purely discrete spectrum.

As we have discussed in Sec.1 epistemic probability enters in quantum mechanics through the concept of density matrix (see Sect. 1.B). Hence, quantum statistical mechanics postulates the form of the density matrix at equilibrium, when a given set of macroscopic parameters has been fixed.

Microcanonical Ensemble

The microcanonical ensemble describes an isolated quantum system with volume Λ , energy E and a fixed number of particle N , and is characterized by a uniform probability distribution (analogously to the classical case). Namely the equilibrium state of a quantum system whose energy lies in the interval $[E, E + \Delta]$ for $0 < \Delta \ll E$ is given by

$$\rho_{MC} = \frac{\sum_{j: \lambda_j \in [E, E + \Delta]} |\Psi_{N,j}\rangle \langle \Psi_{N,j}|}{\text{Tr}(\sum_{j: \lambda_j \in [E, E + \Delta]} |\Psi_{N,j}\rangle \langle \Psi_{N,j}|)} = \frac{\sum_{j: \lambda_j \in [E, E + \Delta]} |\Psi_{N,j}\rangle \langle \Psi_{N,j}|}{\#\{\lambda_j \in [E, E + \Delta]\}}. \quad (2.35)$$

known as microcanonical density matrix. Indeed ρ_{MC} describes a situation where all the energy eigenstates whose energy lies in $[E, E + \Delta]$ contribute with equal weights. The entropy is defined in analogy to the classical case to be

$$\begin{aligned} S(\rho_{MC}) &= -\text{Tr}(\rho_{MC} \log \rho_{MC}) \\ &= \sum_{j: \lambda_j \in [E, E + \Delta]} \frac{1}{\#\{\lambda_j \in [E, E + \Delta]\}} \log(\#\{\lambda_j \in [E, E + \Delta]\} |\Psi_{N,j}\rangle \langle \Psi_{N,j}|) \\ &= \log(\#\{\lambda_j \in [E, E + \Delta]\}) \end{aligned} \quad (2.36)$$

where in the second line we used functional calculus to write the operator $\rho_{MC} \log \rho_{MC}$.

Remark. Note that for a pure state $\rho = |\Psi\rangle \langle \Psi|$ we get $S(\rho) = \text{Tr}(\rho \log \rho) = 0$. Moreover, of all the ensembles whose energy lies in the interval $[E, E + \Delta]$, the entropy of the microcanonical ensemble is the greatest.

The temperature T in the microcanonical ensemble is defined by the thermodynamic relation $T^{-1} = \frac{\partial S}{\partial E}$.

Canonical Ensemble

The canonical ensemble describes the set of equilibrium states corresponding to the physical situation where the macroscopic quantities which are fixed are the volume, the number of particles and the temperature of the system. In this situation one postulates that the equilibrium state is given by the so called *canonical density matrix* defined by

$$\rho_N^\beta = \frac{e^{-\beta H_N}}{Z_C(\beta)}, \quad Z_C(\beta) = \text{Tr}(e^{-\beta H_N}) \quad (2.37)$$

where $\beta = T^{-1}$ denotes the inverse temperature and the normalization factor $Z_C(\beta)$ is called canonical partition function. The state ρ_N^β is known as the N particle *Gibbs state* at inverse temperature β .

Remark. Ideally, one expects the canonical density matrix to be obtainable from a micro-canonical density matrix describing a system composed by a subsystem in contact with a heat bath, by taking the trace over the degrees of freedom of the bath (see [3, Sec. 2.6.1] for details).

The entropy of the canonical ensemble is

$$\begin{aligned} S(\rho_N^\beta) &= -\text{Tr}(\rho_N^\beta \log \rho_N^\beta) \\ &= \beta \text{Tr}(\rho_N^\beta H_N) + \log(Z_C(\beta)) \end{aligned} \quad (2.38)$$

One can check that the canonical ensemble has the greatest entropy of all ensembles with the same average energy (see [3, Sect. 2.6.3] for a proof).

Let the free energy at temperature T in the N particle state ρ_N be defined by

$$F(T; \rho_N) = \text{Tr}(H_N \rho_N) - TS(\rho_N) \quad (2.39)$$

We notice that at zero temperature minimizing the free energy is equivalent to minimize the energy, and indeed in this case a minimizer of $F(T; \rho_N)$ is the pure state corresponding to the ground state vector of H_N . On the other hand, as more the temperature increases, as the entropy plays a more important role, and minimizing the free energy requires a balance among minimization of the energy and maximization of the entropy. One can check that the minimizer of $F(T; \rho_N)$ is the canonical density matrix ρ_N^β and

$$F_N^\beta := F(T; \rho_N^\beta) = -T \log(Z_C(\beta)). \quad (2.40)$$

Grand Canonical Ensemble

We now wish to allow in addition the exchange of matter between the subsystem on the one hand and the heat bath on the other; this will be a consistent generalization of the canonical ensemble.

This idea leads to consider the situation where the number of particles in the system is not fixed, but one rather fixes the chemical potential (or equivalently the expectation of the number of particles). Rigorously this reflects in the fact that the proper Hilbert space for our equilibrium states is the Fock space

$$\mathcal{F}(\Lambda) = \bigoplus_{n=0}^{+\infty} \mathcal{H}_n \quad (2.41)$$

where $\mathcal{H}_n = L_s^2(\Lambda^n)$ (bosonic case) or $\mathcal{H}_n = L_a^2(\Lambda^n)$ (fermionic case) and the Hamiltonian acting on $\mathcal{F}(\Lambda)$ is

$$\mathcal{H} := \bigoplus_{n=0}^{+\infty} H_n. \quad (2.42)$$

Let \mathcal{N} be the particle number operator defined in (2.3). Then the equilibrium state in the grand canonical ensemble is postulated to be the density matrix in Fock space

$$\rho_{\mu}^{\beta} = \frac{e^{-\beta(\mathcal{H}-\mu\mathcal{N})}}{Z_{\text{GC}}(\beta, \mu)}, \quad Z_{\text{GC}}(\beta, \mu) = \text{Tr}(e^{-\beta(\mathcal{H}-\mu\mathcal{N})}) \quad (2.43)$$

known as *grand canonical density matrix*. The entropy in the grand canonical ensemble is equal to

$$S(\rho_{\mu}^{\beta}) = -\text{Tr}(\rho_{\mu}^{\beta} \log \rho_{\mu}^{\beta}) = \beta \text{Tr}(\rho_{\mu}^{\beta} (\mathcal{H} - \mu\mathcal{N})) + \log(Z_{\text{GC}}(\beta, \mu)). \quad (2.44)$$

The grand potential is given by

$$\Omega(\beta, \mu) = -\frac{1}{\beta} \log(Z_{\text{GC}}(\beta, \mu)). \quad (2.45)$$

Using the Baker-Hausdorff-Campbell formula (\mathcal{N} commutes with \mathcal{H}) we find

$$N = \langle \mathcal{N} \rangle = \frac{\text{Tr}(\mathcal{N} e^{-\beta(\mathcal{H}-\mu\mathcal{N})})}{Z_{\text{GC}}(\beta, \mu)} = \frac{\text{Tr}(\mathcal{N} e^{-\beta\mathcal{H}} e^{\beta\mu\mathcal{N}})}{\text{Tr}(e^{-\beta(\mathcal{H}-\mu\mathcal{N})})} = -\left(\frac{\partial \Omega(\beta, \mu)}{\partial \mu}\right). \quad (2.46)$$

Analogously, the expectation value of the energy can be found to be

$$E = \frac{\text{Tr}(\mathcal{H} e^{-\beta(\mathcal{H}-\mu\mathcal{N})})}{\Omega(\beta, \mu)} = \left(\frac{\partial(\beta\Omega)}{\partial \beta}\right)_{\beta\mu}. \quad (2.47)$$

where, in taking the derivative, the product $\beta\mu$ is held constant.

3 Non-Interacting Particles

In this section we apply the formalism developed in the previous sections to analyze the simplest possible case of a many body quantum system, corresponding to N non interacting identical particles. In particular we are going to see how the bosonic and fermionic nature of quantum particles lead to very different physical behaviors, still in this very simple situation. We will start our analysis with a discussion about the unitary evolution and the spectral properties of non interacting quantum systems at zero temperature, and then analyze the role of the temperature in determining the equilibrium properties of the same systems.

3.A Unitary evolution and spectral properties

The simplest case where we can study the time evolution and spectral properties of a many body system is the case of N non interacting identical particles:

$$H_N = \sum_{j=1}^N h_j \quad (3.1)$$

with h_j defined as in (1.11) for some one-particle operator h . Since for any $i \neq j$ the one particle hamiltonians h_i, h_j act on different coordinates we immediately get $[h_i, h_j] = 0$. Hence, using the Baker-Campbell- Hausdorff formula we find

$$e^{-itH_N} = \prod_{j=1}^N e^{-ith_j} = e^{-ith} \otimes \dots \otimes e^{-ith}. \quad (3.2)$$

This in particular implies that, if $\psi_0 = \varphi_{i_1} \otimes \dots \otimes \varphi_{i_N}$ then

$$e^{-iH_N t} \psi_0 = e^{-ith} \varphi_{i_1} \otimes \dots \otimes e^{-ith} \varphi_{i_N} \quad (3.3)$$

(if ψ_0 is the symmetrization or antisymmetrization of $\varphi_{i_1} \otimes \dots \otimes \varphi_{i_N}$, then $e^{-iH_N t} \psi_0$ is the symmetrization or antisymmetrization of $e^{-ith} \varphi_{i_1} \otimes \dots \otimes e^{-ith} \varphi_{i_N}$). Computing the evolution generated by H_N reduces therefore to solve the one particle problem described by h .

Also the spectrum of the many body Hamiltonian can be easily characterized starting from the spectrum of the one particle operator h . Let us consider the case where h has purely discrete spectrum, namely h has eigenvalues e_1, e_2, e_3, \dots with a complete set of eigenvectors $\varphi_1, \varphi_2, \varphi_3, \dots$. Then, it's easy to check that every product vector $\varphi_{i_1} \otimes \dots \otimes \varphi_{i_N}$ is an eigenvector of H_N with eigenvalue $(e_{i_1} + \dots + e_{i_N})$.

This in particular implies that $P_N^S(\varphi_{i_1} \otimes \dots \otimes \varphi_{i_N})$ and $P_N^A(\varphi_{i_1} \otimes \dots \otimes \varphi_{i_N})$ are eigenvectors respectively in $L_s^2(\Omega^N)$ and $L_a^2(\Omega^N)$. Let us stress that since, as we already discussed, $P_N^A(\varphi_{i_1} \otimes \dots \otimes \varphi_{i_N}) = 0$ if there are two indices $j \neq k$ such that $\varphi_{i_j} = \varphi_{i_k}$ we conclude that $P_N^A(\varphi_{i_1} \otimes \dots \otimes \varphi_{i_N}) = 0$ gives a fermionic eigenvector only if $\varphi_{i_j} \neq \varphi_{i_k}$ for all $j \neq k$ due to the Pauli Exclusion Principle.

To compute the ground state of H_N we use the fact that by assumption if $\{\varphi_i\}$ are an ONB of $L^2(\Omega^N)$ then the symmetrization of $\{P_N^s(\varphi_{i_1} \otimes \varphi_{i_N})\}$ constitute an OBN of $L_s^2(\Omega^N)$. Hence we deduce that the ground state of the many-body bosonic Hamiltonian is given by

$$\Psi_N = \varphi_1 \otimes \dots \otimes \varphi_1 \quad (3.4)$$

with φ_1 the ground state of h . Indeed

$$H_N \Psi_N = N e_1 \Psi_N \quad (3.5)$$

and Ψ_N has the right symmetry.

On the contrary, as an effect of the Pauli Principle the ground state of the fermionic system is given by the Slater determinant

$$\Psi_N = \det \begin{vmatrix} \varphi_1(x_1) & \dots & \varphi_N(x_1) \\ \dots & \dots & \dots \\ \varphi_1(x_N) & \dots & \varphi_N(x_N) \end{vmatrix}. \quad (3.6)$$

Then the ground state energy of a fermionic system is much larger than the ground state energy of bosonic systems. This difference among the bosonic and fermionic case has an important effect: the Stability of Matter (see [1]).

Remak. In general the spectrum of $H = \sum h_j$ as an operator on the full space is the set sum of the N copies of the spectrum of h . These eigenvalues are also eigenvalues of H in the symmetric subspace. However, not all eigenvalues are eigenvalues of H on the fermionic sector.

Free particles

We now consider as an example of special interest for us, that is the case in which the Hamiltonian of the system is

$$H_N = \sum_{i=1}^N h_i, \quad h = -\Delta \quad (3.7)$$

acting on $L_s^2(\Lambda^N)$ or $L_a^2(\Lambda^N)$ depending on whether we are considering bosons or fermions. Here $\Lambda = [0, L]^3$ denotes the three dimensional rectangular box and we are putting periodic boundary conditions. Recall that in this case the single particle eigenvalues are given by

$$e_p = p^2, \quad p \in \Lambda^* = \frac{2\pi}{L} \mathbb{Z}^3 \quad (3.8)$$

and the associated eigenfunctions are

$$u_p(x) = \frac{1}{L^{3/2}} e^{ipx}. \quad (3.9)$$

Applying what we discussed above we immediately get that in the bosonic case the ground state of the system is the constant function

$$u_0^{\otimes N}(x_1, \dots, x_N) = \frac{1}{\sqrt{L^{3N}}} \quad (3.10)$$

and the ground state energy is zero.

On the other hand, in the fermionic case the ground state energy is obtained filling the first N energy levels of the one-particle Hamiltonian, namely one can introduce *Fermi energy* ε_F which is the energy below which there are exactly N eigenstates, *i.e.* ε_F is defined by the equation

$$N = \sum_{\substack{p \in \Lambda^* \\ p^2 \leq \varepsilon_F}} 1 = \sum_{p \in \Lambda^*} n(e_p) \quad (3.11)$$

where

$$n(e_p) = \begin{cases} 1 & e_p \leq \varepsilon_F \\ 0 & e_p > \varepsilon_F. \end{cases} \quad (3.12)$$

Then the ground state energy of the fermionic system is

$$E_0 = \sum_{p \in \Lambda^*} e_p n(e_p) \quad (3.13)$$

3 Non-Interacting Particles

Note that in the *thermodynamic limit* $L \rightarrow +\infty$ we get that the particle density satisfies

$$n := \lim_{L \rightarrow +\infty} \frac{N}{L^3} = \frac{1}{(2\pi)^3} \int_{\mathbb{R}^3} n(\varepsilon_p) dp = \frac{1}{(2\pi)^3} \frac{4}{3} \pi \varepsilon_F^{3/2} \quad (3.14)$$

where we noted that $\frac{1}{L^3} \sum_{p \in \Lambda^*} \rightarrow \frac{1}{(2\pi)^3} \int_{\mathbb{R}^3}$ for $L \rightarrow \infty$. Thus we get

$$\varepsilon_F = (6\pi^2 n)^{2/3}. \quad (3.15)$$

Electrons in atoms.

A classical example of a fermionic non interacting system is an atom with N electrons and Z protons (typically atoms are neutral, that is $Z = N$), when we neglect the interaction among the electrons. In such a case the N -electron Hamiltonian (in the reference frame centered in the nucleus) is given by

$$H_N = \sum_{j=1}^N h_j := \sum_{j=1}^N \left(-\Delta_{x_j} - \frac{Z_\alpha}{|x_j|} \right) \quad (3.16)$$

where we set $\hbar = 2\mu_j = 1$ (here μ_j is the reduced mass of the electron and the nucleus). We know that h_j has eigenvalues

$$E_n = -C/n^2 \quad (3.17)$$

with $2n^2$ eigenvectors ψ_{n,ℓ,m,m_s} characterized by the following quantum numbers

$$\begin{aligned} \ell &= 0, 1, \dots, n-1 && \text{(total angular momentum)} \\ m &= -\ell, \dots, \ell && \text{(z-component of the angular momentum)} \\ m_s &= \pm 1 && \text{(spin)} \end{aligned}$$

Note that h has continuous spectrum $[0, +\infty)$. On the other hand, since we are interested in the bottom of the spectrum we will focus only on its (negative) eigenvalues. (see [4] for a detailed study of the spectrum of h).

According to what we discussed above in the general case the ground state of H_N is given by a Slater determinant built starting from $\varphi_1, \dots, \varphi_N$, being the first N non degenerate eigenvectors of h_j corresponding to the lowest energies. Hence for $N > 2$ we have

$$\varphi_1 := \psi_{0,0,0,1} \quad \varphi_2 := \psi_{0,0,0,-1} \quad (3.18)$$

which are the two fermionic wave functions corresponding to $n = 0$, which are identified by the quantum numbers $\ell = m = 0$ and $m_s = \pm 1$. Then $\varphi_3, \dots, \varphi_{10}$ are identified by the eight eigenvectors corresponding to $n = 1$, two of them having $\ell = 0$ (with $m = 0$ and $m_s = \pm 1$) and the remaining with $\ell = 1$ (with corresponding values of $m = -1, 0, 1$ and $m_s = \pm 1$). And so on. For example the electron configuration of an atom with 14 electrons is given by

$$C^{14} \quad 1s^2 \ 2s^2 \ 2p^6 \ 3s^2 \ 3p^2 \quad (3.19)$$

where the first number correspond to the value of n , the notation s and p is used to denote the orbitals with $\ell = 0$ and $\ell = 1$ respectively and the number in the apex is the number of electron which are placed in each orbital.

3.B Ideal Quantum Gases

In this section, we want to derive the thermodynamic properties of ideal quantum gases, i.e. non-interacting particles, on the basis of quantum statistics. The calculation of the grand potential is found to be the most expedient way to proceed.

In order to have a concrete system in mind, we consider N non-interacting, nonrelativistic particles in the three dimensional box $\Lambda^{3N} = [0, L]^{3N}$, with periodic boundary conditions. The Hamiltonian is simply

$$H_N = \sum_{i=1}^N h_i, \quad h = -\Delta. \quad (3.20)$$

The Hamiltonian in Fock space is given by

$$\mathcal{H} = \sum_{p \in \Lambda^*} e_p a_p^* a_p \quad (3.21)$$

where we are using the notation $a_p = a(u_p)$, $a_p^* = a^*(u_p)$ with u_p the one-particle eigenfunctions defined in (3.9). Analogously

$$\exp(-\beta(\mathcal{H} - \mu\mathcal{N})) = e^{\sum_{p \in \Lambda^*} \varepsilon_p a_p^* a_p} \quad (3.22)$$

where $\varepsilon_p = -\beta(e_p - \mu)$ with $e_p = p^2$ the eigenvalues of the one-particle operator. One can easily check that the eigenvalues of the operator defined in (3.22) are $\sum_{n_p, p \in \Lambda^*} \prod_{p \in \Lambda^*} e^{\varepsilon_p n_p}$ where $n_p \in \{0, 1\}$ for fermions and $n_p \in \{0, 1, 2, \dots\}$ for bosons.

Exercise 6. Using CCR or CAR in the bosonic and fermionic case respectively, check that the eigenvectors of the operator defined in Eq. (3.22) are given by the occupation number basis defined at the end of Sec. 2.A associated to the one particle basis $\{u_p\}_{p \in \Lambda^*}$.

We are ready to compute the grand partition function Z_{GC} defined in Eq. (2.43). We find

$$Z_{GC}(\beta, \mu) = \text{Tr}(e^{-\beta(H - \mu\mathcal{N})}) = \prod_{p \in \Lambda^*} \sum_{n_p} e^{\varepsilon_p n_p} \quad (3.23)$$

where n_p , $p \in \Lambda^*$ takes on the allowed value depending on the symmetry. In particular in (3.23) we recognize in the bosonic case a product of geometric series (note that we have to ask $\varepsilon_p > 0 \forall p$, i.e. $\mu < e_p \forall p$ to have convergence) while in the fermionic case the sum over n_p simply reduces to $1 + e^{\varepsilon_p}$. Summarizing we found

$$Z_{GC}(\beta, \mu) = \text{Tr}(e^{-\beta(H - \mu\mathcal{N})}) = \prod_{p \in \Lambda^*} \begin{cases} \frac{1}{1 - e^{\varepsilon_p}} & \text{for bosons} \\ 1 + e^{\varepsilon_p} & \text{for fermions.} \end{cases} \quad (3.24)$$

Thus, the grand canonical potential is

$$\Omega(\beta, \mu) = -\frac{1}{\beta} \log Z_{GC}(\beta, \mu) = \begin{cases} \frac{1}{\beta} \sum_{p \in \Lambda^*} \log(1 - e^{\varepsilon_p}) & \text{for bosons} \\ -\frac{1}{\beta} \sum_{p \in \Lambda^*} \log(1 + e^{\varepsilon_p}) & \text{for fermions} \end{cases} \quad (3.25)$$

and from it we can derive all the thermodynamic quantities of interest. In particular, by (2.46), the expected number of particle is

$$N = \langle \mathcal{N} \rangle = -\frac{\partial \Omega(\beta, \mu)}{\partial \mu} = \sum_{p \in \Lambda^*} n(\varepsilon_p) \quad (3.26)$$

where

$$n(\varepsilon_p) = \begin{cases} \frac{1}{e^{-\varepsilon_p} - 1} & \text{for bosons} \\ \frac{1}{e^{-\varepsilon_p} + 1} & \text{for fermions.} \end{cases} \quad (3.27)$$

Note that $n(\varepsilon_p)$ is the expected value of the operator $\mathcal{N}_p = a_p^* a_p$. Indeed,

$$\begin{aligned} \langle \mathcal{N}_p \rangle &= \frac{\sum_{n_p} n_p e^{\varepsilon_p n_p} \prod_{\substack{q \in \Lambda^* \\ q \neq p}} \sum_{n_q} e^{\varepsilon_q n_q}}{\prod_{q \in \Lambda^*} \sum_{n_q} e^{\varepsilon_q n_q}} \\ &= \frac{\sum_{n_p} n_p e^{\varepsilon_p n_p}}{\sum_{n_p} e^{\varepsilon_p n_p}} = - \frac{\partial}{\partial x} \log \sum_n e^{-nx} \Big|_{x=\beta(\varepsilon_p - \mu)} = n(\varepsilon_p) \end{aligned} \quad (3.28)$$

Note that to have $n(\varepsilon_p) > 0$ we have to assume $\mu < \varepsilon_p$ for any $p \in \Lambda^*$ which implies $\mu < 0$. This is not really a restriction, however, since as μ varies within $(-\infty, 0)$ for bosons, and $(-\infty, \infty)$ for fermions, clearly N varies between 0 and $+\infty$.

As for the energy, from (2.47) we find

$$E = \left(\frac{\partial(\beta \Omega(\beta, \mu))}{\partial \beta} \right)_{\beta \mu} = \sum_{p \in \Lambda^*} \varepsilon_p n(\varepsilon_p). \quad (3.29)$$

We consider the particle density in the thermodynamic limit $L \rightarrow \infty$. Using (3.26) and (3.27) we get

$$n = \lim_{L \rightarrow +\infty} \frac{\langle \mathcal{N} \rangle}{L^3} = \begin{cases} \frac{1}{(2\pi)^3} \int_{\mathbb{R}^3} \frac{1}{e^{\beta(p^2 - \mu)} - 1} dp & \text{for bosons} \\ \frac{1}{(2\pi)^3} \int_{\mathbb{R}^3} \frac{1}{e^{\beta(p^2 - \mu)} + 1} dp & \text{for fermions} \end{cases} \quad (3.30)$$

Setting $x = \beta p^2$ we can rewrite

$$n = \begin{cases} \frac{1}{\lambda^3} \frac{2}{\sqrt{\pi}} \int_0^{+\infty} \frac{\sqrt{x}}{z^{-1} e^x - 1} dx & \text{for bosons} \\ \frac{1}{\lambda^3} \frac{2}{\sqrt{\pi}} \int_0^{+\infty} \frac{\sqrt{x}}{z^{-1} e^x + 1} dx & \text{for fermions} \end{cases} \quad (3.31)$$

where $z = e^{\beta \mu}$ and we introduced the *Thermal wavelength*

$$\lambda = \sqrt{\frac{4\pi}{T}}. \quad (3.32)$$

Note that n is increasing in z . Thus, in the fermionic case all densities are allowed since $z \in (0, +\infty)$. On the contrary, in the bosonic case where $z < 1$, *i.e.* $\mu < 0$ the achievable densities are $n \in (0, n_c(\beta))$ where

$$n_c(\beta) = \lim_{\mu \rightarrow 0} n = \frac{1}{(2\pi)^3} \int_{\mathbb{R}^3} \frac{1}{e^{\beta p^2} - 1} dp < \infty \quad (3.33)$$

since the integrand behaves like $|p|^{-2}$ for small p , which is integrable in 3 dimensions. Thus, it seems that densities $n > n_c(\beta)$ are not admissible. Note in particular that $\lim_{\beta \rightarrow \infty} n_c(\beta) = 0$, hence the admissible densities, according to (3.33), would be extremely small at low temperature. The point is that if we go back to the original sum we had in (3.26) we see that the term corresponding to $p = 0$ diverges when $\mu \rightarrow 0$. Hence, we have to be more careful and the limit $L \rightarrow +\infty$ and $\mu \rightarrow 0$ has to be taken simultaneously. More precisely, we set

$$\mu = - \frac{1}{\beta L^3 (n - n_c(\beta))} \quad \text{as } L \rightarrow +\infty. \quad (3.34)$$

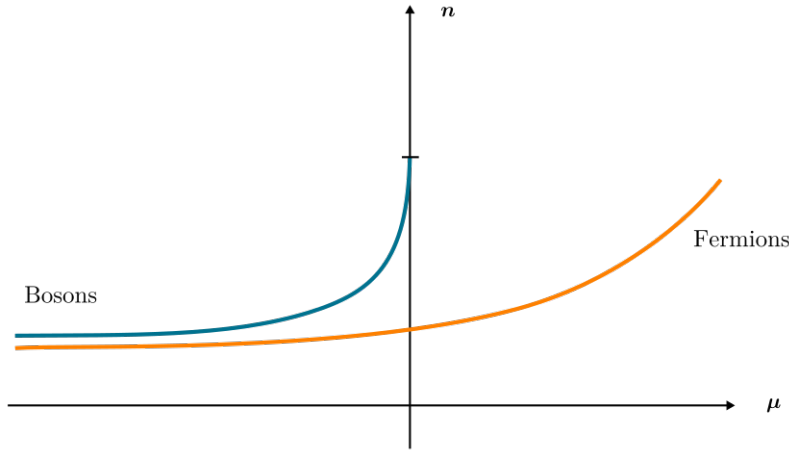


Figure 1: Particle density of an ideal quantum gas at infinite volume, as a function of the chemical potential μ .

With this choice of μ we get

$$\lim_{L \rightarrow +\infty} \frac{\langle a_0^* a_0 \rangle}{L^3} = \lim_{L \rightarrow +\infty} \frac{1}{L^3} \frac{1}{e^{L^{-3}(n-n_c(\beta))^{-1}} - 1} = n - n_c(\beta) \quad (3.35)$$

that is, the zero momentum state is occupied by a macroscopic fraction of all the particles¹. This phenomenon is called *Bose-Einstein Condensation* (often denoted BEC). As we discussed in the previous section at $T = 0$ the N -particle state has all particles placed in single-particle groundstate $u_0(x) = L^{-3/2}$ for all $x \in \Lambda$, hence the zero particle state is macroscopically occupied. Condensation is about that property being stable at $T > 0$. Note that the only momentum which might be macroscopically occupied is $p = 0$. Indeed, the smallest positive eigenvalue of the Laplacian equals $(\frac{2\pi}{L})^2$, thus the corresponding averaged occupation number per unit volume in the limit $L \rightarrow +\infty$ behaves as

$$\frac{1}{L^3} \frac{1}{e^{L^{-3}(\rho-\rho_c(\beta))^{-1}} e^{\beta(2\pi)^2 L^{-2}} - 1} \sim \frac{C}{L} \rightarrow 0 \quad \text{as } L \rightarrow +\infty. \quad (3.36)$$

Summarizing we proved the occurrence of BEC at inverse temperature β^{-1} above the critical density $n_c(\beta)$ given by

$$\begin{aligned} n_c(\beta) &= \frac{1}{(2\pi)^3} 4\pi \int_0^\infty dp \frac{p^2}{e^{\beta p^2} - 1} \\ &= \frac{1}{\lambda^3} \frac{1}{\Gamma(3/2)} \int_0^\infty dt \frac{\sqrt{t}}{e^t - 1} = \frac{1}{\lambda^3 \zeta(3/2)} \end{aligned} \quad (3.37)$$

where Γ denotes the gamma function, ζ the Riemann zeta function and we used the relation

$$\zeta(s) = \frac{1}{\Gamma(s)} \int_0^\infty \frac{x^{s-1}}{e^x - 1} dx. \quad (3.38)$$

Equivalently, recalling the definition of λ given in Eq. (3.32) we have that for a system at density n we have condensation in the zero momentum mode for $T < T_c(n)$ defined by

$$T_c(n) = \frac{4\pi}{\zeta(3/2)^{2/3}} n^{2/3}. \quad (3.39)$$

¹One says that there is a *macroscopic occupation* of a single one particle state, if the ratio among the expected number of particles in that state and the total expectation of the number of particles N goes to a constant in the limit $N \rightarrow \infty$.

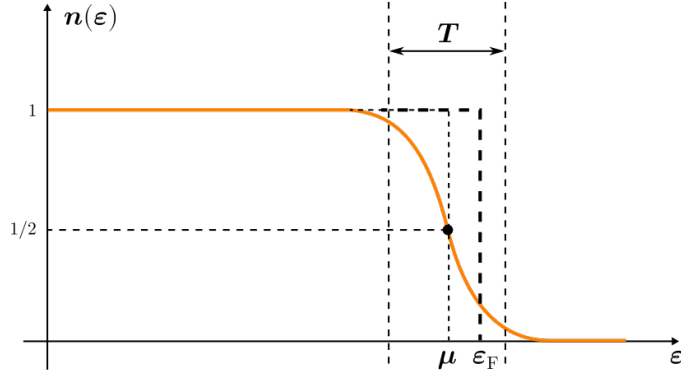


Figure 2: Fermi distribution function $n(\varepsilon)$ for low temperatures compared with the step function corresponding to $T = 0$.

Remark. BEC represents a phase transition in the usual sense, namely that the thermodynamic functions exhibit a non-analytic behavior (see [2] for details).

We have shown that bosons undergo Bose Einstein Condensation. Now, we want to consider fermions and discuss the form of $n(\varepsilon_p)$ in the limit $z = e^{\beta\mu} \rightarrow +\infty$. To better understand the interest in considering this limit let us note that it corresponds to a situation in which $n\lambda^3 \gg 1$ (cf. Eq.(3.31)). Equivalently introducing the $v = 1/n$ the average volume per particle we have for $z \rightarrow +\infty$ that $\frac{\lambda^3}{v} \gg 1$ hence the quantum length scale λ is much larger than the mean inter-particle distance $v^{1/3}$ (classical length scale) and we expect quantum effects to be predominant. Note that, recalling the definition of λ this regime can be obtained by sending $T \rightarrow +\infty$. We rewrite

$$\begin{aligned} n &= \frac{1}{\lambda^3} \frac{2}{\sqrt{\pi}} \int_{-\log z}^{+\infty} \frac{(y + \log z)^{3/2}}{e^y + 1} dy \\ &= \frac{1}{\lambda^3} \frac{4}{3\sqrt{\pi}} \int_{-\log z}^{+\infty} (y + \log z)^{3/2} \frac{d}{dy} \left(\frac{-1}{e^y + 1} \right) dy \end{aligned} \quad (3.40)$$

where in the first line we changed variable introducing $y = x - \log z$ and in the second line we integrated by parts. Thus for large z we get

$$n \sim \frac{1}{\lambda^3} \frac{4}{3\sqrt{\pi}} (\log z)^{3/2} \int_{-\infty}^{+\infty} \frac{d}{dy} \left(\frac{-1}{e^y + 1} \right) dy = \frac{1}{\lambda^3} \frac{4}{3\sqrt{\pi}} (\log z)^{3/2}. \quad (3.41)$$

We conclude therefore

$$(\log z)^{3/2} \sim \frac{3\sqrt{\pi}}{4} \frac{\lambda^3}{v} = 6\pi^2 \frac{\beta^{3/2}}{v} \quad (3.42)$$

which using Eq. (3.15) gives

$$\log z = \beta\mu = \beta\varepsilon_F \implies \mu = \varepsilon_F. \quad (3.43)$$

Thus, we have shown that in the limit of small temperatures $T \rightarrow 0$ the chemical potential converges to ε_F and then $n(\varepsilon) = \frac{1}{e^{\beta(\varepsilon - \mu)} + 1}$ approaches the shape of the step function we found in the zero temperature case (see (3.12)). The situation is shown in Fig. 2.

Remark. We discussed the regimes in which quantum effects are most apparent for bosons and fermions corresponding respectively to $z = e^{\beta\mu} \rightarrow 1$ and $z = e^{\beta\mu} \rightarrow +\infty$. Let us now comment what happens in the opposite regime $z \rightarrow 0$ which corresponds to the *classical limit* $\lambda^3/v \ll 1$. In that case one finds (see [3, sec. 4.2] for details):

$$pv \sim \begin{cases} T \left(1 - \frac{1}{2^{5/2}} \frac{\lambda^3}{v} \right) & \text{for bosons} \\ T \left(1 + \frac{1}{2^{5/2}} \frac{\lambda^3}{v} \right) & \text{for fermions} \end{cases} \quad (3.44)$$

where p denotes the pressure in the thermodynamic limit obtained as

$$p = \lim_{L \rightarrow +\infty} -\frac{\Omega(\beta, \mu)}{L^3}. \quad (3.45)$$

Hence, at the first order Eq. (3.44) reduces to the equation of states of the classical ideal gas. Moreover the first correction is positive for fermions (recall Pauli principle!) and negative for bosons.

3.C Black body radiation

What we discussed so far also allows us to discuss the thermal properties of the radiation field, described as a collection of bosonic particles (known as *photons*) and to obtain the Planck law for the blackbody radiation within the statistical mechanics approach just introduced. In the following we will consider photons in a cavity $\Lambda = [0, L]^3$ with Neumann boundary conditions and we will use that

- i) Photons obey the dispersion relation $e_p = c|p| = h\nu$, with $p \in 2\pi/L\mathbb{Z}^3 \setminus \{0\}$ and ν the frequency. Moreover they are bosons with a spin $s = 1$. Since they are completely relativistic particles (*i.e.* their mass is zero and their velocity is c), their spins have only two possible orientations, *i.e.* parallel or antiparallel to p , corresponding to right-hand or left-hand circularly polarized light. The degeneracy factor for photons is therefore equal to 2. Note that the relation among p and ν above corresponds to De-Broglie hypothesis, namely to associate to a particle of momentum p a wavelength $\lambda = h/|p|$; with $\lambda\nu = c$ we conclude $\nu = c|p|/h$.
- ii) Since photons are emitted and absorbed by the material of the cavity walls, the number of photons is not conserved. Hence we need to work in the grand canonical ensemble with $\mu = 0$ (indeed the role of the chemical potential is to fix the average particle density in the system).

Remark. Note that differently from previous sections here we are writing explicitly the dependence on the Plank constant h to make apparent that what we find is exactly Plank formula for radiant energy.

If we assume the mutual interactions of photons to be zero, we find that the photonic grand canonical Hamiltonian has the form

$$\mathcal{H}_{\text{ph}} = \sum_{\lambda=\pm 1} \sum_{p \neq 0} e_p a_{p,\lambda}^* a_{p,\lambda} \quad (3.46)$$

where $a_{p,\lambda} := a(u_{p,\lambda})$, $a_{p,\lambda}^* := a^*(u_{p,\lambda})$ and $u_{p,\lambda}$ are the eigenfunctions associated to momentum p and polarization $\lambda = \pm 1$.

Our aim is to compute the energy density of the black body radiation, in order to compare it with the formula obtained by Planck at the dawn of the quantum theory. Hence the photonic grand canonical partition function is given by an expression similar to (3.23), with $e_p = c|p|$, $\mu = 0$ and a power 2 taking into account for the two possible polarizations λ .

$$Z_{\text{ph}}(\beta, \mu = 0) = \prod_{p \neq 0} \sum_{n_{p,\lambda}} e^{-\beta e_p n_{p,\lambda}} = \left[\prod_{p \neq 0} \frac{1}{1 - e^{-\beta e_p}} \right]^2 \quad (3.47)$$

Proceeding as in the derivation of (3.27) and (3.29) and rewriting the energy e_p in terms of the light frequency $\nu = cp/h$, thus getting $e_p = h\nu$, we obtain that the average energy per mode ν of the system described by \mathcal{H}_{ph} is given by

$$\langle E_\nu \rangle = \frac{h\nu}{e^{\beta h\nu} - 1} \quad (3.48)$$

which was indeed Planck assumption. Note that the number of ways of choosing $\nu \in 2\pi(hL/c)^{-1}\mathbb{Z}^3$ (recalling $\nu = cp/h$ and $p \in 2\pi/L\mathbb{Z}^3$) in the thin spherical shell

$|\nu| \in [\nu, \nu + \delta]$ is twice $4\pi(hL/c)^3\nu^2\delta(1 + o(\delta/\nu))$ with the factor two coming from the fact that the light has two different polarizations. Thus, we get that the expected energy density of the black body at inverse temperature β is given by

$$e_\beta = \lim_{L \rightarrow +\infty} \frac{\text{Tr}(\rho_{\mu=0}^\beta \mathcal{H}_{\text{ph}})}{L^3} = \frac{8\pi}{c^3} \int_0^{+\infty} \nu^2 \langle E_\nu \rangle d\nu = \frac{8\pi}{c^3} \int_0^{+\infty} \frac{h\nu^3}{e^{\beta h\nu} - 1} d\nu \quad (3.49)$$

that is we recover Planck formula for radiant energy.

Notice that if $\beta h\nu \ll 1$ we have

$$\langle E_\nu \rangle = \frac{1}{\beta} (1 + \mathcal{O}(\beta h\nu)) \quad (3.50)$$

which is indeed the classical prediction (note that at the classical level the energy is independent on the frequency), while for $\beta h\nu \gg 1$ we find $\langle E_\nu \rangle = h\nu e^{-\beta\nu} (1 + \mathcal{O}(e^{-\beta h\nu}))$ which is going to zero as $\nu \rightarrow \infty$, as observed in experiments.

4 Conclusions

So far, we just considered examples of non interacting many-body Hamiltonians. Still, the very simple models we considered have given us the opportunity to discuss several intriguing aspects entering in the description of many-particles quantum systems, as the very different physical behaviors induced by the statistics, and identify the conditions where the quantum effects are predominant with respect to the classical ones or viceversa.

If we now aim to describe real physical systems we need to take into account for the interactions among the particles, and to consider systems made up by a large number of microscopic particles. From our previous discussions it should be clear that in presence of interactions the analysis of the unitary evolution and of the thermodynamic properties of the N - particle Hamiltonian is far more involved and this is indeed the source of several research lines. Let us emphasize that, in typical situations it would be fair enough to obtain an effective description of the many-body system, providing an approximation to the evolution of the system or to its equilibrium properties in certain regimes, and/or up to certain time scales. The research line focusing on the derivation of the macroscopic properties of many body systems include the derivation of *effective equations* for the dynamics of many body systems, and the emergence of *collective phenomena* in those systems (the phenomenon of BEC discussed above is a typical example of collective phenomena arising in a many body quantum systems). In particular, the role of mathematics appears to be crucial to establish the range of validities of effective theories which are often introduced on the basis of heuristic approaches, or to provide precise error bounds on macroscopic approximations, in terms of number of particles, temperature and so on. But this indeed, would be another (very challenging) story largely still to be written.

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