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On statistical mechanics:

what happens when there are too many particles?

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Introduction

In these notes, we will study the mathematical framework of statistical mechanics: the part of physics which focuses on systems composed by a large amount of microscopic constituents, like atoms or molecules. Statistical mechanics arises out from thermodynamics that deals with macroscopic physical quantities and it is able to explain them by means of the notions of ensemble and probability density distribution. In the first part, we will focus on classical systems, starting from some notions of thermodynamics in the language of differential geometry and classical Hamiltonian mechanics, passing through microcanonical, canonical and grand canonical ensembles, finishing with a superficially introduction of classical phase transitions. In the second part, we will focus on quantum systems: ensembles of identical particles in the language of second quantisation to describe Fermi-Dirac and Bose-Einstein gases.

Part I

Thermodynamics

Chapter 1

The 2 laws, which are 4

In this chapter, we will recall some notions of thermodynamics: states, equilibrium and the laws of thermodynamics.

1.1 Equilibrium

The topic of which thermodynamics studies is a class of systems composed by a large amount of particles, roughly speaking Avogadro number $N_A \simeq 6 \times 10^{23}$ constituents, once it reaches a macroscopic equilibrium configuration. To understand the notion of equilibrium, consider a system immersed in its surroundings. It can either interact with it by exchanging matter and/or energy (mechanical, electric, magnetic, chemical work) or be completely isolated. Once a sufficient amount of time has passed By, it reaches a stable configuration. Which particular configuration and its stability can be selected by different boundary conditions the system finds itself in, i.e. the specification on how the system is in contact and how it interacts with its surroundings. In other words, there is only one and only one final equilibrium configuration towards to the system evolves, once boundary conditions have been given. However, the way the system reaches the equilibrium configuration is irreversible. Equilibrium therefore means that once the system has reached its final configuration, it will stay there forever.

1.2 States

A state is a macroscopic configuration. Mathematically speaking, it is a point in the manifold $\mathcal{M}$ of thermodynamic states. To describe it, we need a chart given by macroscopic physical quantities, called thermodynamic variables. They can be divided into two groups, one conjugate to the other, according to their behaviour when the physical system is rescaled, i.e. when volume and number of particles change: extensive variables do scale with it whereas intensive ones do not. Some of them are written in Table 1.1. However, we have to be careful, since only volume is (by definition) extensive and all the others quantities can be considered extensive only if the surface terms are negligible when we take the thermodynamic limit, i.e. when we first describe the system with finite volume V and number of particles N and then we go to the limit in which $V \to \infty$ and $N \to \infty$ but keeping the density fixed $n = N/V$.

Each physical system has an equation of state, i.e. a functional relation among thermodynamic quantities which restrict the number of independent variables. Geometrically, it means that the only admissible states are a submanifold $\mathcal{A} \subset \mathcal{M}$ of the entire manifold of states, given by the constraint induced by the equation of state.

Example 1.1 (Perfect gas)**.** Consider a perfect gas. A chart on its 3-dimensional manifold can be (p, V, T) and its equation of state is $PV = Nk_BT$. This means that the allowed states are in a 2-dimensional manifold embedded in $\mathbb{R}^3$.

Extensive	Intensive
energy E	-
entropy S	temperature T
volume V	pressure p
number of particles N	chemical potential μ
polarization $\mathbf{P}$	electric field $\mathbf{E}$
magnetization $\mathbf{M}$	magnetic field $\mathbf{B}$

Table 1.1: Extensive and intensive thermodynamic variables.

1.3 The laws of thermodynamics

Thermodynamics is governed by a set of laws that every system must obey. They are a particular kind of laws, since they are limitation laws: they tell us only which processes cannot happen. Usually they are referred as the two laws of thermodynamics, but actually they are 4.

Law 1.1 (0th)
Let A and B be two thermodynamic systems in thermal contact. At equilibrium, only a subset of states $\mathcal{A} \subset \mathcal{M}_A \times \mathcal{M}_B$ is accessible and not the whole manifold. Mathematically, it means that there exists a functional relation of the kind

$$F_{AB}(a, b) = 0 \ , \tag{1.1}$$

with $a \in \mathcal{M}_A$ and $b \in \mathcal{M}_B$. Moreover, thermal equilibrium is an equivalence class, which can be proved that it means

$$F_{AB}(a, b) = f_A(a) - f_B(b) \ . \tag{1.2}$$

The combination of both (1.1) *and* (1.2) *allows us to define the empirical temperature*

$$t_A = f_A(a) = t_B = f_B(b) \ . \tag{1.3}$$

It is a limitation law because it limits the configuration that a system can reach in isolation when it is in thermal contact with a second one.

Law 1.2 (1st)
Let δQ be an infinitesimal heat and δL an infinitesimal work exchanged in a quasi-static process ($\delta Q > 0$ means absorbed by the system, $\delta L > 0$ means performed by the system). For any cyclic process, i.e. processes in which the initial and the final states coincide, we have

$$\oint (\delta Q - \delta L) = 0 \ .$$

This means that $\delta Q - \delta L$ is a 1-form that vanishes when line-integrated along a closed curve in $\mathcal{M}$ and, by the Poincaré lemma, it is also an exact differential, called the internal energy

$$dE = \delta Q - \delta L \ ,$$

However, heat and work are not exact differential, since $\oint \delta Q \neq 0$ and $\oint \delta H \neq 0$.
The generalisation for a system that can exchange matter is given by

$$\oint (\delta Q - \delta L + \mu dN) = \oint dE = 0 \ , \quad dE = \delta Q - \delta L + \mu dN \ , \tag{1.4}$$

where μ is the chemical potential, i.e. the necessary energy to add or remove a particle. Furthermore, we can express both δQ and δL as a linear combination of infinitesimal change of independent coordinates, e.g. $\delta L = pdV + BdM$. In the following, the only work considered will be the mechanical one $\delta L = pdV$. We assume that the internal energy is extensive and, therefore, the chemical potential is intensive.

It is a limitation law because it limits the configuration that a system can reach in isolation to those with $E = const$.

Law 1.3 (2nd)
For any cyclic process, we have

$$\oint \frac{\delta Q}{T} \begin{cases} = 0 & \text{reversible process} \\ < 0 & \text{irreversible process} \end{cases} .$$

For reversible processes, $\frac{\delta Q}{T} = 0$ is an exact differential. This implies that we can define a function, called entropy, which is always integrated along any reversible path

$$S(a) - S(b) = \int_a^b \frac{\delta Q}{T} \ , \tag{1.5}$$

Therefore, we have

$$dS \begin{cases} = 0 & \text{reversible process} \\ < 0 & \text{irreversible process} \end{cases} . \tag{1.6}$$

It is a limitation law because it limits the configuration that a system can reach in isolation to whose in which entropy cannot increase.

Law 1.4 (3rd)
Isothermal and adiabatic processes coincides when $T = 0$, or, equivalently, it is impossible to reach $T = 0$ with a finite number of processes. Mathematically,

$$\Delta S \to 0 \text{ as } T \to 0 . \tag{1.7}$$

Therefore, $T = 0$ is a singular point. Furthermore, if it were possible to reach $T = 0$, the second law $\delta Q \leq 0$ implies that it is impossible to raise the temperature. It is a thermodynamic feature, since it can be proved that it is impossible to realize an engine with efficiency $\eta = 1$.

It is a limitation law because it limits the configuration that a system can reach in isolation to whose in which $T \neq 0$.

Chapter 2

Thermodynamic potentials

In this chapter, we will study thermodynamic potentials: energy E, entropy S, Helmholtz free energy F, enthalpy, Gibbs free energy and grand potential. We will derive their definition, their differential and their equations of state.

Thermodynamic potentials are functions defined in the manifold, which are suited for a particular choice of the 3 coordinates (boundary conditions) and, therefore, they are useful if we find the system with all the other coordinates constant.

2.1 Internal energy

The first thermodynamic potential we are going to study is the internal energy E, which is defined by the first law of thermodynamic (1.4). Its differential is

$$dE \leq TdS - pdV + \mu dN \ . \tag{2.1}$$

This relation is called the fundamental equation of thermodynamics.

Proof. In fact, we invert (1.4)

$$\delta Q = dE + \delta L - \mu dN \ ,$$

we use $\delta L = pdV$ and we put it into (1.6)

$$dS \leq \frac{\delta Q}{T} = \frac{dE + pdV - \mu dN}{T} \ . \tag{2.2}$$

Finally, we isolate dE

$$dE \leq TdS - pdV + \mu dN \ . \tag{2.3}$$

q.e.d.

Notice that non-differential variables are intensive and differential one are extensive. This tells us that $E(S,V,N)$ is a function of the extensive variables S, V and N. The intensive variables T, p and μ can be derived from E by the following relations

$$T = \frac{\partial E}{\partial S}\Big|_{V,N} \; , \quad p = -\frac{\partial E}{\partial V}\Big|_{S,N} \; , \quad \mu = \frac{\partial E}{\partial N}\Big|_{S,V} \; . \tag{2.4}$$

These functional relations are called the equation of state of the system, since we can calculate one variable from it, e.g. $T = T(S,V,N)$, $p = p(S,V,N)$ or $\mu = \mu(S,V,N)$.

Proof. At constant V and N, (2.1) becomes

$$dE = TdS - p\underbrace{dV}_{0} + \mu\underbrace{dN}_{0} = TdS \; ,$$

hence

$$T = \frac{\partial E}{\partial S}\Big|_{V,N} \; .$$

At constant S and N, (2.1) becomes

$$dE = T\underbrace{dS}_{0} - pdV + \mu\underbrace{dN}_{0} = -pdV \; ,$$

hence

$$p = -\frac{\partial E}{\partial V}\Big|_{S,N} \; .$$

At constant S and V, (2.1) becomes

$$dE = T\underbrace{dS}_{0} - p\underbrace{dV}_{0} + \mu dN = \mu dN \; ,$$

hence

$$\mu = \frac{\partial E}{\partial S}\Big|_{S,V} \; .$$

q.e.d.

E is an extensive variable, i.e. it is an homogeneous function of degree one of the extensive variables

$$E(\lambda S, \lambda V, \lambda N) = \lambda E(S,V,N) \; , \quad \forall \lambda > 0 \; . \tag{2.5}$$

The physical meaning is that if we rescale the volume, the energy is rescaled by the same amount. Moreover, since energy is an homogeneous function of degree one of extensive variables and intensive variables are derivative of the energy with respect to extensive variables, we can conclude that intensive variable are homogeneous function of degree zero of the extensive variables

$$\begin{gathered} T(S,V,N) = T\left(\frac{S}{N},\frac{V}{N}\right) \ , \quad p(S,V,N) = p\left(\frac{S}{N},\frac{V}{N}\right) \ , \\ \mu(S,V,N) = \mu\left(\frac{S}{N},\frac{V}{N}\right) \ . \end{gathered} \tag{2.6}$$

By homogeneity properties (2.5), using $\lambda = N$, we can therefore write

$$\begin{aligned} E = E(S,V,N) = E\left(N\frac{S}{N},N\frac{V}{N},N\right) = NE\left(\frac{S}{N},\frac{V}{N},1\right) = Ne \ , \\ S = S(E,V,N) = S\left(N\frac{E}{N},N\frac{V}{N},N\right) = NS\left(\frac{E}{N},\frac{V}{N},1\right) = Ns \ , \end{aligned}$$

where we have defined specific energy e, specific entropy s and specific volume v as

$$e = \frac{E}{N} = e(s,v) \ , \quad s = \frac{S}{N} = s(e,v) \ , \quad v = \frac{V}{N} \ .$$

The Euler's theorem allows us to state that, if E is smooth, it can be written as

$$E = S\frac{\partial E}{\partial S} + V\frac{\partial E}{\partial V} + N\frac{\partial E}{\partial N} \ ,$$

or, equivalently,

$$E = TS - pV + \mu N \ . \tag{2.7}$$

Proof. In fact, using (2.4), we obtain

$$E = S\underbrace{\frac{\partial E}{\partial S}}_{T} + V\underbrace{\frac{\partial E}{\partial V}}_{-p} + N\underbrace{\frac{\partial E}{\partial N}}_{\mu} = TS - pV + \mu N \ .$$

q.e.d.

In order to be an exact differential, the exterior derivative of the right-handed side of (2.1) must have a null exterior derivative, which leads to the integrability conditions

$$-\frac{\partial T}{\partial V}\bigg|_{S,N} = \frac{\partial p}{\partial S}\bigg|_{V,N} \ , \quad \frac{\partial T}{\partial N}\bigg|_{S,V} = \frac{\partial \mu}{\partial S}\bigg|_{N,V} \ , \quad -\frac{\partial p}{\partial N}\bigg|_{V,S} = \frac{\partial \mu}{\partial V}\bigg|_{N,S} \ . \tag{2.8}$$

Proof. By means of the exterior derivative, we have

$$\begin{aligned}
d(dE) &= d(TdS) - d(pdV) + d(\mu dN) \\
&= \frac{\partial T}{\partial S}\underbrace{dS\wedge dS}_{0} + \frac{\partial T}{\partial V}dV\wedge dS + \frac{\partial T}{\partial N}dN\wedge dS - \frac{\partial p}{\partial S}dS\wedge dV - \frac{\partial p}{\partial V}\underbrace{dV\wedge dV}_{0} \\
&\quad - \frac{\partial p}{\partial N}dN\wedge dV + \frac{\partial \mu}{\partial S}dS\wedge dN + \frac{\partial \mu}{\partial V}dV\wedge dN + \frac{\partial \mu}{\partial N}\underbrace{dN\wedge dN}_{0} \\
&= \frac{\partial T}{\partial V}dV\wedge dS + \frac{\partial T}{\partial N}dN\wedge dS - \frac{\partial p}{\partial S}dS\wedge dV \\
&\quad - \frac{\partial p}{\partial N}dN\wedge dV + \frac{\partial \mu}{\partial S}dS\wedge dN + \frac{\partial \mu}{\partial V}dV\wedge dN \ .
\end{aligned}$$

At constant N, we obtain

$$\begin{aligned}
0 = d^2E &= \frac{\partial T}{\partial V}dV\wedge dS + \frac{\partial T}{\partial N}\underbrace{dN}_{0}\wedge dS - \frac{\partial p}{\partial S}dS\wedge dV \\
&\quad - \frac{\partial p}{\partial N}\underbrace{dN}_{0}\wedge dV + \frac{\partial \mu}{\partial S}dS\wedge\underbrace{dN}_{0} + \frac{\partial \mu}{\partial V}dV\wedge\underbrace{dN}_{0} \\
&= \frac{\partial T}{\partial V}dV\wedge dS - \frac{\partial p}{\partial S}dS\wedge dV = \frac{\partial T}{\partial V}dV\wedge dS + \frac{\partial p}{\partial S}dV\wedge dS \ ,
\end{aligned}$$

hence, by the linear independence of V and S, we find

$$-\frac{\partial T}{\partial V}\Big|_{S,N} = \frac{\partial p}{\partial S}\Big|_{V,N} \ .$$

At constant V, we obtain

$$\begin{aligned}
0 = d^2E &= \frac{\partial T}{\partial V}\underbrace{dV}_{0}\wedge dS + \frac{\partial T}{\partial N}dN\wedge dS - \frac{\partial p}{\partial S}dS\wedge\underbrace{dV}_{0} \\
&\quad - \frac{\partial p}{\partial N}dN\wedge\underbrace{dV}_{0} + \frac{\partial \mu}{\partial S}dS\wedge dN + \frac{\partial \mu}{\partial V}\underbrace{dV}_{0}\wedge dN \\
&= \frac{\partial T}{\partial N}dN\wedge dS + \frac{\partial \mu}{\partial S}dS\wedge dN = \frac{\partial T}{\partial N}dN\wedge dS - \frac{\partial \mu}{\partial S}dN\wedge dS \ ,
\end{aligned}$$

hence, by the linear independence of N and S, we find

$$\frac{\partial T}{\partial N}\Big|_{S,V} = \frac{\partial \mu}{\partial S}\Big|_{N,V} \ .$$

At constant S, we obtain

$$
\begin{aligned}
0 = d^2E &= \frac{\partial T}{\partial V} dV \wedge \underbrace{dS}_{0} + \frac{\partial T}{\partial N} dN \wedge \underbrace{dS}_{0} - \frac{\partial p}{\partial S} \underbrace{dS}_{0} \wedge dV \\
&\quad - \frac{\partial p}{\partial N} dN \wedge dV + \frac{\partial \mu}{\partial S} \underbrace{dS}_{0} \wedge dN + \frac{\partial \mu}{\partial V} dV \wedge dN \\
&= -\frac{\partial p}{\partial N} dN \wedge dV + \frac{\partial \mu}{\partial V} dV \wedge dN = -\frac{\partial p}{\partial N} dN \wedge dV - \frac{\partial \mu}{\partial V} dN \wedge dV \ ,
\end{aligned}
$$

hence, by the linear independence of N and V, we find

$$
-\frac{\partial p}{\partial N}\bigg|_{V,S} = \frac{\partial \mu}{\partial V}\bigg|_{N,S} \ .
$$

q.e.d.

2.2 Entropy

The second thermodynamic potential we are going to study is the entropy S. Inverting (2.1), we obtained its differential

$$
dS = \frac{1}{T} dE + \frac{p}{T} dV - \frac{\mu}{T} dN \ . \tag{2.9}
$$

Therefore, its equations of state are

$$
\frac{1}{T} = \frac{\partial S}{\partial E}\bigg|_{V,N} \ , \qquad \frac{p}{T} = \frac{\partial S}{\partial V}\bigg|_{E,N} \ , \qquad -\frac{\mu}{T} = \frac{\partial S}{\partial N}\bigg|_{E,V} \ . \tag{2.10}
$$

The Gibbs-Duhem relation expresses the chemical potential μ in terms of the pressure p and the temperature T

$$
SdT - Vdp + Nd\mu = 0 \ , \quad d\mu = vdp - sdT \ . \tag{2.11}
$$

Proof. Computing the differential of (2.7)

$$
dE = TdS + SdT - pdV + \mu dN + Nd\mu
$$

and comparing it with (2.1)

$$
dE = \cancel{TdS} + SdT - \cancel{pdV} + -Vdp + \cancel{\mu dN} + Nd\mu = \cancel{TdS} - \cancel{pdV} + \cancel{\mu dN} \ ,
$$

we obtain

$$
SdT - Vdp + Nd\mu = 0 \ ,
$$

which can be written as

$$
d\mu = \frac{V}{N} dp - \frac{S}{N} dT = vdp - sdT \ .
$$

q.e.d.

2.3 Thermodynamic states as a manifold

Since an equilibrium state is a point in the manifold $\mathcal{M}$, we need a chart to describe it, which in our case can be thought as an open subset of $\mathbb{R}^3$. An example of independent local coordinates are S, V and N and they can be used to solve thermodynamic, i.e. to find explicitly the fundamental equation

$$E = E(S, V, N)\ .$$

However, we could have chosen another thermodynamic potential, like the entropy

$$S = S(E, V, N) \tag{2.12}$$

and a chart would have had E, V and N as coordinates. Notice that at least one of the local coordinates in any chart for $\mathcal{M}$ must always be extensive.

Proof. By the $0th$ law and (2.6), there must exist a functional relation between intensive variables. This means that one of the three is already fixed once the other two are given and they cannot be used all three as independent coordinates. q.e.d.

Therefore, there are different thermodynamic potentials that we can use: all functions of 3 independent variables (of which one at least must be extensive) that can be used to define a different chart for $\mathcal{M}$. This implies that there are different approaches to thermodynamics. The standard method to find other potentials is to apply various kind of Legendre transform of (2.1), which exchanges the role of an extensive variable to its conjugate intensive variable as independent variable. The only requirement we need is that the hypothesis of the inverse function theorem are satisfied, e.g.

$$\frac{\partial^2 E}{\partial S^2}\Big|_{V,N} \neq 0\ , \quad \frac{\partial^2 E}{\partial V^2}\Big|_{S,N} \neq 0\ , \quad \frac{\partial^2 E}{\partial N^2}\Big|_{S,V} \neq 0\ .$$

In the next sections, we will study the most important in thermodynamics: Helmholtz free energy F, enthalpy H, Gibbs free energy G and grand potential Ω.

2.4 Helmholtz free energy

The Helmholtz free energy is defined as

$$F = E - TS\ . \tag{2.13}$$

Its differential is

$$dF \leq -SdT - pdV + \mu dN\ . \tag{2.14}$$

Its associated chart is

$$F = F(T, V, N)\ . \tag{2.15}$$

Proof. By a Legendre transform, which means to complete a differential, we obtain

$$dE \le TdS - pdV + \mu dN = d(TS) - SdT - pdV + \mu dN \ ,$$

hence,

$$dF = d(E - TS) \le -SdT - pdV + \mu dN \ .$$

q.e.d.

The equations of state are

$$S = -\frac{\partial F}{\partial T}\Big|_{V,N} \ , \quad p = -\frac{\partial F}{\partial V}\Big|_{T,N} \ , \quad \mu = \frac{\partial F}{\partial N}\Big|_{T,V} \ . \tag{2.16}$$

Proof. At constant V and N, we have

$$dF = -SdT - p\underbrace{dV}_{0} + \mu\underbrace{dN}_{0} = -SdT \ ,$$

hence,

$$S = -\frac{\partial F}{\partial T}\Big|_{V,N} \ .$$

At constant T and N, we have

$$dF = -S\underbrace{dT}_{0} - pdV + \mu\underbrace{dN}_{0} = -pdV \ ,$$

hence,

$$p = -\frac{\partial F}{\partial V}\Big|_{T,N} \ .$$

At constant T and V, we have

$$dF = -S\underbrace{dT}_{0} - p\underbrace{dV}_{0} + \mu dN = \mu dN \ ,$$

hence,

$$\mu = \frac{\partial F}{\partial N}\Big|_{T,V} \ .$$

q.e.d.

The integrability conditions are

$$\frac{\partial S}{\partial V}\Big|_{T,N} = \frac{\partial p}{\partial T}\Big|_{V,N} \ , \quad -\frac{\partial S}{\partial N}\Big|_{T,V} = \frac{\partial \mu}{\partial T}\Big|_{N,V} \ , \quad -\frac{\partial p}{\partial N}\Big|_{V,T} = \frac{\partial \mu}{\partial V}\Big|_{N,T} \ . \tag{2.17}$$

Proof. By means of the exterior derivative, we have

$$\begin{aligned}
d(dF) &= -d(SdT) - d(pdV) + d(\mu dN) \\
&= -\frac{\partial S}{\partial T}\underbrace{dT\wedge dT}_{0} - \frac{\partial S}{\partial V}dV\wedge dT - \frac{\partial S}{\partial N}dN\wedge dT - \frac{\partial p}{\partial T}dT\wedge dV - \frac{\partial p}{\partial V}\underbrace{dV\wedge dV}_{0} \\
&\quad - \frac{\partial p}{\partial N}dN\wedge dV + \frac{\partial \mu}{\partial T}dT\wedge dN + \frac{\partial \mu}{\partial V}dV\wedge dN + \frac{\partial \mu}{\partial N}\underbrace{dN\wedge dN}_{0} \\
&= -\frac{\partial S}{\partial V}dV\wedge dT - \frac{\partial S}{\partial N}dN\wedge dT - \frac{\partial p}{\partial T}dT\wedge dV \\
&\quad - \frac{\partial p}{\partial N}dN\wedge dV + \frac{\partial \mu}{\partial T}dT\wedge dN + \frac{\partial \mu}{\partial V}dV\wedge dN \ .
\end{aligned}$$

At constant N, we obtain

$$\begin{aligned}
0 = d^2F &= -\frac{\partial S}{\partial V}dV\wedge dT - \frac{\partial S}{\partial N}\underbrace{dN}_{0}\wedge dT - \frac{\partial p}{\partial T}dT\wedge dV \\
&\quad - \frac{\partial p}{\partial N}\underbrace{dN}_{0}\wedge dV + \frac{\partial \mu}{\partial T}dT\wedge \underbrace{dN}_{0} + \frac{\partial \mu}{\partial V}dV\wedge \underbrace{dN}_{0} \\
&= -\frac{\partial S}{\partial V}dV\wedge dT - \frac{\partial p}{\partial T}dT\wedge dV = -\frac{\partial S}{\partial V}dV\wedge dT + \frac{\partial p}{\partial T}dV\wedge dT \ ,
\end{aligned}$$

hence, by the linear independence of V and T, we find

$$\left.\frac{\partial S}{\partial V}\right|_{T,N} = \left.\frac{\partial p}{\partial T}\right|_{V,N} \ .$$

At constant V, we obtain

$$\begin{aligned}
0 = d^2F &= -\frac{\partial S}{\partial V}\underbrace{dV}_{0}\wedge dT - \frac{\partial S}{\partial N}dN\wedge dT - \frac{\partial p}{\partial T}dT\wedge \underbrace{dV}_{0} \\
&\quad - \frac{\partial p}{\partial N}dN\wedge \underbrace{dV}_{0} + \frac{\partial \mu}{\partial T}dT\wedge dN + \frac{\partial \mu}{\partial V}\underbrace{dV}_{0}\wedge dN \\
&= -\frac{\partial S}{\partial N}dN\wedge dT + \frac{\partial \mu}{\partial T}dT\wedge dN = -\frac{\partial S}{\partial N}dN\wedge dT - \frac{\partial \mu}{\partial T}dN\wedge dT \ ,
\end{aligned}$$

hence, by the linear independence of N and T, we find

$$-\left.\frac{\partial S}{\partial N}\right|_{T,V} = \left.\frac{\partial \mu}{\partial T}\right|_{N,V} \ .$$

At constant T, we obtain

$$\begin{aligned}
0 = d^2F &= -\frac{\partial S}{\partial V} dV \wedge \underbrace{dT}_{0} - \frac{\partial S}{\partial N} dN \wedge \underbrace{dT}_{0} - \frac{\partial p}{\partial T} \underbrace{dT}_{0} \wedge dV \\
&\quad - \frac{\partial p}{\partial N} dN \wedge dV + \frac{\partial \mu}{\partial T} \underbrace{dT}_{0} \wedge dN + \frac{\partial \mu}{\partial V} dV \wedge dN \\
&= -\frac{\partial p}{\partial N} dN \wedge dV + \frac{\partial \mu}{\partial V} dV \wedge dN = -\frac{\partial p}{\partial N} dN \wedge dV - \frac{\partial \mu}{\partial V} dN \wedge dV \ ,
\end{aligned}$$

hence, by the linear independence of N and V, we find

$$-\frac{\partial p}{\partial N}\bigg|_{V,T} = \frac{\partial \mu}{\partial V}\bigg|_{N,T} \ .$$

q.e.d.

2.5 Enthalpy

The enthalpy is defined as

$$H = E + pV \ .$$

Its differential is

$$dH \le TdS + Vdp + \mu dN \ . \tag{2.18}$$

Its associated chart is

$$H = H(p, S, N) \ .$$

Proof. By a Legendre transform, which means to complete a differential, we obtain

$$dE \le TdS - pdV + \mu dN = TdS - d(pV) + Vdp + \mu dN \ ,$$

hence,

$$dH = d(E + pV) \le TdS + Vdp + \mu dN \ .$$

q.e.d.

The equations of state are

$$T = \frac{\partial H}{\partial S}\bigg|_{p,N} \ , \quad V = -\frac{\partial H}{\partial p}\bigg|_{S,N} \ , \quad \mu = \frac{\partial H}{\partial N}\bigg|_{S,p} \ . \tag{2.19}$$

Proof. At constant p and N, we have

$$dH = TdS + V\underbrace{dp}_{0} + \mu\underbrace{dN}_{0} \ ,$$

hence,

$$T = \frac{\partial H}{\partial S}\Big|_{p,N} \ .$$

At constant S and N, we have

$$dH = T\underbrace{dS}_{0} + V dp + \mu\underbrace{dN}_{0} \ ,$$

hence,

$$V = -\frac{\partial H}{\partial p}\Big|_{S,N} \ .$$

At constant S and p, we have

$$dH = T\underbrace{dS}_{0} + V\underbrace{dp}_{0} + \mu dN \ ,$$

hence,

$$\mu = \frac{\partial H}{\partial N}\Big|_{S,p} \ .$$

q.e.d.

The integrability conditions are

$$\frac{\partial V}{\partial S}\Big|_{p,N} = \frac{\partial T}{\partial p}\Big|_{S,N} \ , \quad \frac{\partial V}{\partial N}\Big|_{p,S} = \frac{\partial \mu}{\partial p}\Big|_{N,S} \ , \quad \frac{\partial \mu}{\partial S}\Big|_{N,p} = \frac{\partial T}{\partial N}\Big|_{S,p} \ . \tag{2.20}$$

Proof. By means of the exterior derivative, we have

$$\begin{aligned}
d(dH) &= d(TdS) + d(Vdp) + d(\mu dN) \\
&= \frac{\partial T}{\partial S}\underbrace{dS \wedge dS}_{0} + \frac{\partial T}{\partial p} dp \wedge dS + \frac{\partial T}{\partial N} dN \wedge dS + \frac{\partial V}{\partial S} dS \wedge dp + \frac{\partial V}{\partial p}\underbrace{dp \wedge dp}_{0} \\
&\quad + \frac{\partial V}{\partial N} dN \wedge dp + \frac{\partial \mu}{\partial S} dS \wedge dN + \frac{\partial \mu}{\partial p} dp \wedge dN + \frac{\partial \mu}{\partial N}\underbrace{dN \wedge dN}_{0} \\
&= \frac{\partial T}{\partial p} dp \wedge dS + \frac{\partial T}{\partial N} dN \wedge dS + \frac{\partial V}{\partial S} dS \wedge dp \\
&\quad + \frac{\partial V}{\partial N} dN \wedge dp + \frac{\partial \mu}{\partial S} dS \wedge dN + \frac{\partial \mu}{\partial p} dp \wedge dN \ .
\end{aligned}$$

At constant N, we obtain

$$\begin{aligned}
0 = d^2H &= \frac{\partial T}{\partial p} dp \wedge dS + \frac{\partial T}{\partial N} \underbrace{dN}_{0} \wedge dS + \frac{\partial V}{\partial S} dS \wedge dp \\
&+ \frac{\partial V}{\partial N} \underbrace{dN}_{0} \wedge dp + \frac{\partial \mu}{\partial S} dS \wedge \underbrace{dN}_{0} + \frac{\partial \mu}{\partial p} dp \wedge \underbrace{dN}_{0} \\
&= \frac{\partial T}{\partial p} dp \wedge dS + \frac{\partial V}{\partial S} dS \wedge dp = \frac{\partial T}{\partial p} dp \wedge dS - \frac{\partial V}{\partial S} dS \wedge dp \ ,
\end{aligned}$$

hence, by the linear independence of S and p, we find

$$\left.\frac{\partial V}{\partial S}\right|_{p,N} = \left.\frac{\partial T}{\partial p}\right|_{S,N} .$$

At constant S, we obtain

$$\begin{aligned}
0 = d^2H &= \frac{\partial T}{\partial p} dp \wedge \underbrace{dS}_{0} + \frac{\partial T}{\partial N} dN \wedge \underbrace{dS}_{0} + \frac{\partial V}{\partial S} \underbrace{dS}_{0} \wedge dp \\
&+ \frac{\partial V}{\partial N} dN \wedge dp + \frac{\partial \mu}{\partial S} \underbrace{dS}_{0} \wedge dN + \frac{\partial \mu}{\partial p} dp \wedge dN \\
&= \frac{\partial V}{\partial N} dN \wedge dp + \frac{\partial \mu}{\partial p} dp \wedge dN = \frac{\partial V}{\partial N} dN \wedge dp - \frac{\partial \mu}{\partial p} dN \wedge dp \ ,
\end{aligned}$$

hence, by the linear independence of N and p, we find

$$\left.\frac{\partial V}{\partial N}\right|_{p,S} = \left.\frac{\partial \mu}{\partial p}\right|_{N,S} .$$

At constant p, we obtain

$$\begin{aligned}
0 = d^2H &= \frac{\partial T}{\partial p} \underbrace{dp}_{0} \wedge dS + \frac{\partial T}{\partial N} dN \wedge dS + \frac{\partial V}{\partial S} dS \wedge \underbrace{dp}_{0} \\
&+ \frac{\partial V}{\partial N} dN \wedge \underbrace{dp}_{0} + \frac{\partial \mu}{\partial S} dS \wedge dN + \frac{\partial \mu}{\partial p} \underbrace{dp}_{0} \wedge dN \\
&= \frac{\partial T}{\partial N} dN \wedge dS + \frac{\partial \mu}{\partial S} dS \wedge dN = \frac{\partial T}{\partial N} dN \wedge dS - \frac{\partial \mu}{\partial S} dS \wedge dN \ ,
\end{aligned}$$

hence, by the linear independence of S and N, we find

$$\left.\frac{\partial \mu}{\partial S}\right|_{N,p} = \left.\frac{\partial T}{\partial N}\right|_{S,p} .$$

q.e.d.

2.6 Gibbs free energy

The Gibbs free energy is defined as

$$G = E - TS + pV = F + pV = H - TS \ .$$

Its differential is

$$dG \leq -SdT + Vdp + \mu dN \ . \tag{2.21}$$

Its associated chart is

$$G = G(p, T, N) \ .$$

Proof. By a Legendre transform, which means to complete a differential, we obtain

$$dE \leq TdS - pdV + \mu dN = d(TS) - SdT - d(pV) + Vdp + \mu dN \ ,$$

hence

$$dG = d(E - TS + pV) \leq -SdT + Vdp + \mu dN \ .$$

q.e.d.

The equations of state are

$$S = -\left.\frac{\partial G}{\partial T}\right|_{p,N} \ , \quad V = \left.\frac{\partial G}{\partial p}\right|_{T,N} \ , \quad \mu = \left.\frac{\partial G}{\partial N}\right|_{p,T} \ . \tag{2.22}$$

Proof. At constant p and N, we have

$$dG = -SdT + V\underbrace{dp}_{0} + \mu\underbrace{dN}_{0} \ ,$$

hence,

$$S = -\left.\frac{\partial G}{\partial T}\right|_{p,N} \ .$$

At constant T and N, we have

$$dG = -S\underbrace{dT}_{0} + Vdp + \mu\underbrace{dN}_{0} \ ,$$

hence,

$$V = \left.\frac{\partial G}{\partial p}\right|_{T,N} \ .$$

At constant p and T, we have

$$dG = -S\underbrace{dT}_{0} + V\underbrace{dp}_{0} + \mu dN \ ,$$

hence,

$$\mu = \frac{\partial G}{\partial N}\Big|_{p,T} \ .$$

q.e.d.

The integrability conditions are

$$-\frac{\partial V}{\partial T}\Big|_{p,N} = \frac{\partial S}{\partial p}\Big|_{T,N} \ , \quad \frac{\partial V}{\partial N}\Big|_{p,T} = \frac{\partial \mu}{\partial p}\Big|_{N,T} \ , \quad -\frac{\partial S}{\partial N}\Big|_{T,p} = \frac{\partial \mu}{\partial T}\Big|_{N,p} \ . \tag{2.23}$$

Proof. By means of the exterior derivative, we have

$$\begin{aligned} d(dG) &= -d(SdT) + d(Vdp) + d(\mu dN) \\ &= -\frac{\partial S}{\partial T}\underbrace{dT\wedge dT}_{0} - \frac{\partial S}{\partial p}dp\wedge dT - \frac{\partial S}{\partial N}dN\wedge dT + \frac{\partial V}{\partial T}dT\wedge dp + \frac{\partial V}{\partial p}\underbrace{dp\wedge dp}_{0} \\ &\quad + \frac{\partial V}{\partial N}dN\wedge dp + \frac{\partial \mu}{\partial T}dT\wedge dN + \frac{\partial \mu}{\partial p}dp\wedge dN + \frac{\partial \mu}{\partial N}\underbrace{dN\wedge dN}_{0} \\ &= -\frac{\partial S}{\partial p}dp\wedge dT - \frac{\partial S}{\partial N}dN\wedge dT + \frac{\partial V}{\partial T}dT\wedge dp \\ &\quad + \frac{\partial V}{\partial N}dN\wedge dp + \frac{\partial \mu}{\partial T}dT\wedge dN + \frac{\partial \mu}{\partial p}dp\wedge dN \ . \end{aligned}$$

At constant N, we obtain

$$\begin{aligned} 0 = d^2G &= -\frac{\partial S}{\partial p}dp\wedge dT - \frac{\partial S}{\partial N}\underbrace{dN}_{0}\wedge dT + \frac{\partial V}{\partial T}dT\wedge dp \\ &\quad + \frac{\partial V}{\partial N}\underbrace{dN}_{0}\wedge dp + \frac{\partial \mu}{\partial T}dT\wedge\underbrace{dN}_{0} + \frac{\partial \mu}{\partial p}dp\wedge\underbrace{dN}_{0} \\ &= -\frac{\partial S}{\partial p}dp\wedge dT + \frac{\partial V}{\partial T}dT\wedge dp = -\frac{\partial S}{\partial p}dp\wedge dT - \frac{\partial V}{\partial T}dp\wedge dT \ , \end{aligned}$$

hence, by the linear independence of p and T, we find

$$-\frac{\partial V}{\partial T}\Big|_{p,N} = \frac{\partial S}{\partial p}\Big|_{T,N} \ .$$

At constant T, we obtain

$$\begin{aligned} 0 = d^2G &= -\frac{\partial S}{\partial p}dp\wedge\underbrace{dT}_{0} - \frac{\partial S}{\partial N}dN\wedge\underbrace{dT}_{0} + \frac{\partial V}{\partial T}\underbrace{dT}_{0}\wedge dp \\ &\quad + \frac{\partial V}{\partial N}dN\wedge dp + \frac{\partial \mu}{\partial T}\underbrace{dT}_{0}\wedge dN + \frac{\partial \mu}{\partial p}dp\wedge dN \\ &= \frac{\partial V}{\partial N}dN\wedge dp + \frac{\partial \mu}{\partial p}dp\wedge dN = \frac{\partial V}{\partial N}dN\wedge dp - \frac{\partial \mu}{\partial p}dp\wedge dN \ , \end{aligned}$$

hence, by the linear independence of p and N, we find

$$\left.\frac{\partial V}{\partial N}\right|_{p,T} = \left.\frac{\partial \mu}{\partial p}\right|_{N,T} .$$

At constant p, we obtain

$$\begin{aligned}
0 = d^2G &= -\frac{\partial S}{\partial p}\underbrace{dp}_{0}\wedge dT - \frac{\partial S}{\partial N}dN \wedge dT + \frac{\partial V}{\partial T}dT \wedge \underbrace{dp}_{0} \\
&+ \frac{\partial V}{\partial N}dN \wedge \underbrace{dp}_{0} + \frac{\partial \mu}{\partial T}dT \wedge dN + \frac{\partial \mu}{\partial p}\underbrace{dp}_{0}\wedge dN \\
&= -\frac{\partial S}{\partial N}dN \wedge dT + \frac{\partial \mu}{\partial T}dT \wedge dN = -\frac{\partial S}{\partial N}dN \wedge dT - \frac{\partial \mu}{\partial T}dN \wedge dT ,
\end{aligned}$$

hence, by the linear independence of N and T, we find

$$-\left.\frac{\partial S}{\partial N}\right|_{T,p} = \left.\frac{\partial \mu}{\partial T}\right|_{N,p} .$$

q.e.d.

2.7 Grand potential

The grand potential is defined as

$$\Omega = E - TS - \mu N = F - \mu N . \tag{2.24}$$

Its differential is

$$d\Omega \leq -SdT - pdV - Nd\mu . \tag{2.25}$$

Its associated chart is

$$\Omega = \Omega(T, V, \mu) . \tag{2.26}$$

Proof. By a Legendre transform, which means to complete a differential, we obtain

$$dE \leq TdS - pdV + \mu dN = d(TS) - SdT - pdV + (\mu N) - Nd\mu ,$$

hence,

$$d\Omega = d(E - TS - \mu N) \leq -SdT - pdV - Nd\mu .$$

q.e.d.

The equations of state are

$$S = -\frac{\partial\Omega}{\partial T}\Big|_{\mu,V} \ , \quad p = -\frac{\partial\Omega}{\partial V}\Big|_{T,\mu} \ , \quad \mu = -\frac{\partial\Omega}{\partial N}\Big|_{T,V} \ . \tag{2.27}$$

Proof. At constant μ and V, we have

$$d\Omega = -SdT - p\underbrace{dV}_{0} - N\underbrace{d\mu}_{0} = -SdT \ ,$$

hence,

$$S = -\frac{\partial\Omega}{\partial T}\Big|_{\mu,V} \ .$$

At constant T and μ, we have

$$d\Omega = -S\underbrace{dT}_{0} - pdV - N\underbrace{d\mu}_{0} = -pdV \ ,$$

hence,

$$p = -\frac{\partial\Omega}{\partial V}\Big|_{T,\mu} \ .$$

At constant T and V, we have

$$d\Omega = -S\underbrace{dT}_{0} - p\underbrace{dV}_{0} - Nd\mu = -Nd\mu \ ,$$

hence

$$\mu = -\frac{\partial\Omega}{\partial N}\Big|_{T,V} \ .$$

q.e.d.

The integrability conditions are

$$\frac{\partial S}{\partial\mu}\Big|_{T,V} = \frac{\partial N}{\partial T}\Big|_{\mu,V} \ , \quad \frac{\partial S}{\partial V}\Big|_{T,\mu} = \frac{\partial p}{\partial T}\Big|_{V,\mu} \ , \quad \frac{\partial p}{\partial\mu}\Big|_{V,T} = \frac{\partial N}{\partial V}\Big|_{\mu,T} \ . \tag{2.28}$$

Proof. By means of the exterior derivative, we have

$$\begin{aligned}
d(d\Omega) &= -d(SdT) - d(pdV) - d(Nd\mu) \\
&= -\frac{\partial S}{\partial T}\underbrace{dT\wedge dT}_{0} - \frac{\partial S}{\partial V}dV\wedge dT - \frac{\partial S}{\partial\mu}d\mu\wedge dT - \frac{\partial p}{\partial T}dT\wedge dV - \frac{\partial p}{\partial V}\underbrace{dV\wedge dV}_{0} \\
&\quad - \frac{\partial p}{\partial\mu}d\mu\wedge dV - \frac{\partial N}{\partial T}dT\wedge d\mu - \frac{\partial N}{\partial V}dV\wedge d\mu - \frac{\partial N}{\partial\mu}\underbrace{d\mu\wedge d\mu}_{0} \\
&= -\frac{\partial S}{\partial V}dV\wedge dT - \frac{\partial S}{\partial\mu}d\mu\wedge dT - \frac{\partial p}{\partial T}dT\wedge dV \\
&\quad - \frac{\partial p}{\partial\mu}d\mu\wedge dV - \frac{\partial N}{\partial T}dT\wedge d\mu - \frac{\partial N}{\partial V}dV\wedge d\mu \ .
\end{aligned}$$

At constant μ, we obtain

$$\begin{aligned}
0 = d^2\Omega &= -\frac{\partial S}{\partial V} dV \wedge dT - \frac{\partial S}{\partial \mu} \underbrace{d\mu}_{0} \wedge dT - \frac{\partial p}{\partial T} dT \wedge dV \\
&\quad - \frac{\partial p}{\partial \mu} \underbrace{d\mu}_{0} \wedge dV - \frac{\partial N}{\partial T} dT \wedge \underbrace{d\mu}_{0} - \frac{\partial N}{\partial V} dV \wedge \underbrace{d\mu}_{0} \\
&= -\frac{\partial S}{\partial V} dV \wedge dT - \frac{\partial p}{\partial T} dT \wedge dV = -\frac{\partial S}{\partial V} dV \wedge dT + \frac{\partial p}{\partial T} dV \wedge dT \ ,
\end{aligned}$$

hence, by the linear independence of V and T, we find

$$\left.\frac{\partial S}{\partial V}\right|_{T,\mu} = \left.\frac{\partial p}{\partial T}\right|_{V,\mu} .$$

At constant V, we obtain

$$\begin{aligned}
0 = d^2\Omega &= -\frac{\partial S}{\partial V} \underbrace{dV}_{0} \wedge dT - \frac{\partial S}{\partial \mu} d\mu \wedge dT - \frac{\partial p}{\partial T} dT \wedge \underbrace{dV}_{0} \\
&\quad - \frac{\partial p}{\partial \mu} d\mu \wedge \underbrace{dV}_{0} - \frac{\partial N}{\partial T} dT \wedge d\mu - \frac{\partial N}{\partial V} \underbrace{dV}_{0} \wedge d\mu \\
&= -\frac{\partial S}{\partial \mu} d\mu \wedge dT - \frac{\partial N}{\partial T} dT \wedge d\mu = -\frac{\partial S}{\partial \mu} d\mu \wedge dT + \frac{\partial N}{\partial T} d\mu \wedge dT \ ,
\end{aligned}$$

hence, by the linear independence of μ and T, we find

$$\left.\frac{\partial S}{\partial \mu}\right|_{T,V} = \left.\frac{\partial N}{\partial T}\right|_{\mu,V} .$$

At constant T, we obtain

$$\begin{aligned}
0 = d^2\Omega &= -\frac{\partial S}{\partial V} dV \wedge \underbrace{dT}_{0} - \frac{\partial S}{\partial \mu} d\mu \wedge \underbrace{dT}_{0} - \frac{\partial p}{\partial T} \underbrace{dT}_{0} \wedge dV \\
&\quad - \frac{\partial p}{\partial \mu} d\mu \wedge dV - \frac{\partial N}{\partial T} \underbrace{dT}_{0} \wedge d\mu - \frac{\partial N}{\partial V} dV \wedge d\mu \\
&= -\frac{\partial p}{\partial \mu} d\mu \wedge dV - \frac{\partial N}{\partial V} dV \wedge d\mu = -\frac{\partial p}{\partial \mu} d\mu \wedge dV + \frac{\partial N}{\partial V} d\mu \wedge dV \ ,
\end{aligned}$$

hence, by the linear independence of N and V, we find

$$\left.\frac{\partial p}{\partial \mu}\right|_{V,T} = \left.\frac{\partial N}{\partial V}\right|_{\mu,T} .$$

q.e.d.

A few comments can be made about these potentials. Notice that they are not homogeneous functions since they depend on mixed extensive and intensive variables. However, they are extensive, i.e.

$$F = Nf(T,v) \ , \quad H = Nh(p,s) \ , \quad G = Ng(T,p) \ , \quad \Omega = Nf\omega(T,\mu) \ , \tag{2.29}$$

where f is the specific Helmholtz free energy, h is the specific enthalpy, g is the specific Gibbs free energy and ω is the specific grand potential. Furthermore, observe that the chemical potential is also the Gibbs free energy per particle

$$g(T,p) = \mu(T,p) \ . \tag{2.30}$$

Proof. In fact, using (2.22) and (2.29)

$$\mu = \frac{\partial G}{\partial N} = \frac{\partial}{\partial N}(Ng) = g \ .$$

q.e.d.

Finally, notice that

$$\Omega = -pV \ . \tag{2.31}$$

Proof. Using (2.7) and (2.24)

$$\Omega = E - TS - \mu N = \cancel{TS} - pV + \cancel{\mu N} - \cancel{TS} - \cancel{\mu N} = -pV \ .$$

q.e.d.

2.8 Summary

A summary of all charts and differentials is given by

$$E(S,V,N) \ , \quad dE = TdS - pdV + \mu dN \ ,$$

$$\begin{aligned} S(E,V,N) \ , &\quad dS = dE/T + pdV/T - \mu dN/T \ , \\ F(T,V,N) \ , &\quad dF = -SdT - pdV + \mu dN \ , \\ H(S,p,N) \ , &\quad dH = TdS + Vdp + \mu dN \ , \\ G(T,p,N) \ , &\quad dG = -SdT + Vdp + \mu dN \ , \\ \Omega(T,V,\mu) \ , &\quad d\Omega = TdS - pdV + \mu dN \ . \end{aligned}$$

A summary of all the equations of state is given by

$$
\begin{aligned}
T = \frac{\partial E}{\partial S}\Big|_{V,N} , \quad & p = -\frac{\partial E}{\partial V}\Big|_{S,N} , \quad \mu = \frac{\partial E}{\partial N}\Big|_{S,V} , \\
\frac{1}{T} = \frac{\partial S}{\partial E}\Big|_{V,N} , \quad & \frac{p}{T} = \frac{\partial S}{\partial V}\Big|_{E,N} , \quad -\frac{\mu}{T} = \frac{\partial S}{\partial N}\Big|_{E,V} , \\
S = -\frac{\partial F}{\partial T}\Big|_{V,N} , \quad & p = -\frac{\partial F}{\partial V}\Big|_{T,N} , \quad \mu = \frac{\partial F}{\partial N}\Big|_{T,V} , \\
T = \frac{\partial H}{\partial S}\Big|_{p,N} , \quad & V = -\frac{\partial H}{\partial p}\Big|_{S,N} , \quad \mu = \frac{\partial H}{\partial N}\Big|_{S,p} , \\
S = -\frac{\partial G}{\partial T}\Big|_{p,N} , \quad & V = \frac{\partial G}{\partial p}\Big|_{T,N} , \quad \mu = \frac{\partial G}{\partial N}\Big|_{p,T} , \\
S = -\frac{\partial \Omega}{\partial T}\Big|_{\mu,V} , \quad & p = -\frac{\partial \Omega}{\partial V}\Big|_{T,\mu} , \quad \mu = -\frac{\partial \Omega}{\partial N}\Big|_{T,V} .
\end{aligned}
$$

A summary of all integrability conditions is given by

$$
\begin{aligned}
-\frac{\partial T}{\partial V}\Big|_{S,N} = \frac{\partial p}{\partial S}\Big|_{V,N} , \quad & \frac{\partial T}{\partial N}\Big|_{S,V} = \frac{\partial \mu}{\partial S}\Big|_{N,V} , \quad -\frac{\partial p}{\partial N}\Big|_{V,S} = \frac{\partial \mu}{\partial V}\Big|_{N,S} , \\
\frac{\partial S}{\partial V}\Big|_{T,N} = \frac{\partial p}{\partial T}\Big|_{V,N} , \quad & -\frac{\partial S}{\partial N}\Big|_{T,V} = \frac{\partial \mu}{\partial T}\Big|_{N,V} , \quad -\frac{\partial p}{\partial N}\Big|_{V,T} = \frac{\partial \mu}{\partial V}\Big|_{N,T} , \\
\frac{\partial V}{\partial S}\Big|_{p,N} = \frac{\partial T}{\partial p}\Big|_{S,N} , \quad & \frac{\partial V}{\partial N}\Big|_{p,S} = \frac{\partial \mu}{\partial p}\Big|_{N,S} , \quad \frac{\partial \mu}{\partial S}\Big|_{N,p} = \frac{\partial T}{\partial N}\Big|_{S,p} , \\
-\frac{\partial V}{\partial T}\Big|_{p,N} = \frac{\partial S}{\partial p}\Big|_{T,N} , \quad & \frac{\partial V}{\partial N}\Big|_{p,T} = \frac{\partial \mu}{\partial p}\Big|_{N,T} , \quad -\frac{\partial S}{\partial N}\Big|_{T,p} = \frac{\partial \mu}{\partial T}\Big|_{N,p} , \\
\frac{\partial S}{\partial \mu}\Big|_{T,V} = \frac{\partial N}{\partial T}\Big|_{\mu,V} , \quad & \frac{\partial S}{\partial V}\Big|_{T,\mu} = \frac{\partial p}{\partial T}\Big|_{V,\mu} , \quad \frac{\partial p}{\partial \mu}\Big|_{V,T} = \frac{\partial N}{\partial V}\Big|_{\mu,T} .
\end{aligned}
$$

Chapter 3

Stability conditions

In this chapter, we will rewrite integrability condition in terms of Jacobian determinant and we will study what are the stability conditions that a system must fulfill in order to be in equilibrium.

3.1 Maxwell's relations

Integrability condition can be written as Jacobian determinant in the following way

$$\frac{\partial a}{\partial b}\bigg|_{c,d} = \frac{\partial(a,c,d)}{\partial(b,c,d)} \ ,$$

such that it satisfies the property

$$\frac{\partial(a,c,d)}{\partial(b,c,d)} = -\frac{\partial(c,a,d)}{\partial(b,c,d)} = -\frac{\partial(a,c,d)}{\partial(c,b,d)} = \frac{\partial(a,d,c)}{\partial(b,c,d)} = \frac{\partial(a,c,d)}{\partial(b,d,c)} \ .$$

For the energy, they are

$$\frac{\partial(T,S,N)}{\partial(p,V,N)} = 1 \ , \quad \frac{\partial(T,S,V)}{\partial(\mu,N,V)} = -1 \ , \quad \frac{\partial(p,V,S)}{\partial(\mu,N,S)} = 1 \ .$$

Proof. Using the first of (2.8), we obtain

$$-\frac{\partial T}{\partial V}\bigg|_{S,N} = \frac{\partial p}{\partial S}\bigg|_{V,N} \to \frac{\partial(T,S,N)}{\partial(V,S,N)} = -\frac{\partial(p,V,N)}{\partial(S,V,N)} = \frac{\partial(p,V,N)}{\partial(V,S,N)} \ ,$$

hence, inverting the right-handed side, we find

$$1 = \frac{\partial(T,S,N)}{\partial(V,S,N)}\frac{\partial(p,V,N)}{\partial(V,S,N)}^{-1} = \frac{\partial(T,S,N)}{\partial(V,S,N)}\frac{\partial(V,S,N)}{\partial(p,V,N)} = \frac{\partial(T,S,N)}{\partial(p,V,N)} \ .$$

Using the second of (2.8), we obtain

$$\left.\frac{\partial T}{\partial N}\right|_{S,V} = \left.\frac{\partial \mu}{\partial S}\right|_{N,V} \to \frac{\partial(T,S,V)}{\partial(N,S,V)} = \frac{\partial(\mu,N,V)}{\partial(S,N,V)} = -\frac{\partial(\mu,N,V)}{\partial(N,S,V)} \ ,$$

hence, inverting the right-handed side, we find

$$-1 = \frac{\partial(T,S,V)}{\partial(N,S,V)}\frac{\partial(\mu,N,V)}{\partial(N,S,V)}^{-1} = \frac{\partial(T,S,V)}{\partial(N,S,V)}\frac{\partial(N,S,V)}{\partial(\mu,N,V)} = \frac{\partial(T,S,V)}{\partial(\mu,N,V)} \ .$$

Using the third of (2.8), we obtain

$$-\left.\frac{\partial p}{\partial N}\right|_{V,S} = \left.\frac{\partial \mu}{\partial V}\right|_{N,S} \to \frac{\partial(p,V,S)}{\partial(N,V,S)} = -\frac{\partial(\mu,N,S)}{\partial(V,N,S)} = \frac{\partial(\mu,N,S)}{\partial(N,V,S)} \ ,$$

hence, inverting the right-handed side, we find

$$1 = \frac{\partial(p,V,S)}{\partial(N,V,S)}\frac{\partial(\mu,N,S)}{\partial(N,V,S)}^{-1} = \frac{\partial(p,V,S)}{\partial(N,V,S)}\frac{\partial(N,V,S)}{\partial(\mu,N,S)} = \frac{\partial(p,V,S)}{\partial(\mu,N,S)} \ .$$

q.e.d.

For the energy, they are

$$\frac{\partial(p,S,V)}{\partial(N,S,V)} = -\frac{\partial(\mu,S,N)}{\partial(V,S,N)} = \frac{\partial(\mu,S,N)}{\partial(N,S,V)} \ .$$

Proof. Using the first of (2.8)

$$-\left.\frac{\partial T}{\partial V}\right|_{S,N} = -\left.\frac{\partial p}{\partial S}\right|_{V,N} \to \frac{\partial(T,N,S)}{\partial(V,N,S)} = -\frac{\partial(p,N,V)}{\partial(S,N,V)} = \frac{\partial(p,N,V)}{\partial(V,N,S)} \ ,$$

hence, inverting the right-handed side

$$1 = \frac{\partial(T,N,S)}{\partial(V,N,S)}\frac{\partial(p,N,V)}{\partial(V,N,S)}^{-1} = \frac{\partial(T,N,S)}{\partial(V,N,S)}\frac{\partial(V,N,S)}{\partial(p,N,V)} = \frac{\partial(T,N,S)}{\partial(p,N,V)} \ .$$

Using the second of (2.8)

$$\left.\frac{\partial T}{\partial N}\right|_{S,V} = -\left.\frac{\partial \mu}{\partial S}\right|_{N,V} \to \frac{\partial(T,V,S)}{\partial(N,V,S)} = -\frac{\partial(\mu,V,N)}{\partial(S,V,N)} = \frac{\partial(\mu,V,N)}{\partial(N,V,S)} \ ,$$

hence, inverting the right-handed side

$$1 = \frac{\partial(T,V,S)}{\partial(N,V,S)}\frac{\partial(\mu,V,N)}{\partial(N,V,S)}^{-1} = \frac{\partial(T,V,S)}{\partial(N,V,S)}\frac{\partial(N,V,S)}{\partial(\mu,V,N)} = \frac{\partial(T,V,S)}{\partial(\mu,V,N)} \ .$$

Using the third of (2.8)

$$\frac{\partial p}{\partial N}\bigg|_{V,S} = -\frac{\partial \mu}{\partial V}\bigg|_{N,S} \to \frac{\partial(p,S,V)}{\partial(N,S,V)} = -\frac{\partial(\mu,S,N)}{\partial(V,S,N)} = \frac{\partial(\mu,S,N)}{\partial(N,S,V)} \ ,$$

hence, inverting the right-handed side

$$1 = \frac{\partial(p,S,V)}{\partial(N,S,V)}\frac{\partial(\mu,S,N)}{\partial(N,S,V)}^{-1} = \frac{\partial(p,S,V)}{\partial(N,S,V)}\frac{\partial(N,S,V)}{\partial(\mu,S,N)} = \frac{\partial(p,S,V)}{\partial(\mu,S,N)} \ .$$

q.e.d.

TO BE CONTINUED.
Not all the Maxwell's relations are independent, but only 6 of them

$$\frac{\partial(p,V,S)}{\partial(\mu,N,S)} = 1 \ , \quad \frac{\partial(p,V,T)}{\partial(\mu,N,T)} = 1 \ , \quad \frac{\partial(p,V,N)}{\partial(T,S,N)} = 1 \ ,$$

$$\frac{\partial(T,S,\mu)}{\partial(p,V,\mu)} = 1 \ , \quad \frac{\partial(T,S,p)}{\partial(N,\mu,p)} = 1 \ , \quad \frac{\partial(T,S,V)}{\partial(N,\mu,V)} = 1 \ .$$

The geometrical interpretation is that coordinate transformations, which mean that we changed into a different chart of independent variables, preserve volumes.

3.2 Stability conditions

Every thermodynamic potential has a natural chart. In fact, the configuration of stable equilbrium can be obtained by a set of variational principle, which can be derived by fixing to constants the natural independent variables. This variations principle derive from the second law of thermodynamics, since all systems evolve spontaneously to maximise the entropy. Therefore, minima of the thermodynamic potentials correspond to stable equilibrium under boundary condition which keep constant the natural variables

$$(T,V,N) = const \to \delta F = 0 \ , \delta^2 F > 0 \ ,$$

$$(S,p,N) = const \to \delta H = 0 \ , \delta^2 H > 0 \ ,$$

$$(T,p,N) = const \to \delta G = 0 \ , \delta^2 G > 0 \ ,$$

$$(T,V,\mu) = const \to \delta \Omega = 0 \ , \delta^2 \Omega > 0 \ .$$

Equilibrium of two subsystems requires that T, p and μ are equal.

Proof. Consider two subsystems A and B with extensive variables (E_A, V_A, N_A) and (E_B, V_B, N_B). Therefore $E = E_A + E_B$, $V = V_A + V_B$ and $N = N_A + N_B$. The whole system is at fixed boundary conditions $E, V, S = const$. The entropy is additive

$$S = S_A + S_B = S_A(E_A, V_A, N_A) - S_B(E - E_A, V - V_A, N - N_A) \ .$$

Computing its derivative and imposing it to zero, using (2.10)

$$\begin{aligned}
0 = \delta S &= \frac{\partial S_A}{\partial E_A}\delta E_A + \frac{\partial S_A}{\partial E_A}\delta E_A + \frac{\partial S_A}{\partial V_A}\delta V_A + \frac{\partial S_A}{\partial N_A}\delta N_A \\
&\quad + \frac{\partial S_B}{\partial E_B}\underbrace{\delta(E - E_A)}_{-\delta E_A} + \frac{\partial S_B}{\partial V_B}\underbrace{\delta(V - V_A)}_{-\delta V_A} + \frac{\partial S_B}{\partial N_B}\underbrace{\delta(N - N_A)}_{-\delta N_A} \\
&= \frac{\partial S_A}{\partial E_A}\delta E_A + \frac{\partial S_A}{\partial V_A}\delta V_A + \frac{\partial S_A}{\partial N_A}\delta N_A - \frac{\partial S_B}{\partial E_B}\delta E_A - \frac{\partial S_B}{\partial V_B}\delta V_A - \frac{\partial S_B}{\partial N_B}\delta N_A \\
&= \delta E_A\Big(\underbrace{\frac{\partial S_A}{\partial E_A}}_{\frac{1}{T_A}} - \underbrace{\frac{\partial S_B}{\partial E_B}}_{\frac{1}{T_B}}\Big) + \delta V_A\Big(\underbrace{\frac{\partial S_A}{\partial V_A}}_{\frac{p_A}{T_A}} - \underbrace{\frac{\partial S_B}{\partial E_B}}_{\frac{p_B}{T_B}}\Big) + \delta N_A\Big(\underbrace{\frac{\partial S_A}{\partial N_A}}_{-\frac{\mu_A}{T_A}} - \underbrace{\frac{\partial S_B}{\partial N_B}}_{-\frac{\mu_B}{T_B}}\Big) \\
&= \delta E_A\Big(\frac{1}{T_A} - \frac{1}{T_B}\Big) + \delta V_A\Big(\frac{p_A}{T_A} - \frac{p_B}{T_B}\Big) + \delta N_A\Big(-\frac{\mu_A}{T_A} + \frac{\mu_B}{T_B}\Big) \ ,
\end{aligned}$$

hence, by the arbitrarity of δE_A, δV_A and δN_A,

$$T_A = T_B \ , \quad p_A = p_B \ , \quad \mu_A = \mu_B \ .$$

q.e.d.

At $T, p, N = const$, the stability condition is

$$\begin{aligned}
&E_{SS} = \frac{\partial T}{\partial S}\Big|_V > 0 \ , \quad E_{VV} = -\frac{\partial p}{\partial V}\Big|_S > 0 \ , \\
&E_{SS}E_{VV} - E_{SV}^2 = -\frac{\partial T}{\partial S}\Big|_V \frac{\partial p}{\partial V}\Big|_S - \Big(\frac{\partial p}{\partial S}\Big|_V\Big)^2 = -\frac{\partial T}{\partial S}\Big|_V \frac{\partial p}{\partial V}\Big|_S - \Big(\frac{\partial T}{\partial V}\Big|_S\Big)^2 > 0 \ ,
\end{aligned} \tag{3.1}$$

Proof. We know that $E = E(S, V, N)$. AT constant N, its variation is

$$\begin{aligned}
\delta E &= \underbrace{\frac{\partial E}{\partial S}\Big|_V}_{T}\delta S + \underbrace{\frac{\partial E}{\partial V}\Big|_S}_{-p}\delta V \\
&\quad + \frac{1}{2}\Big(\underbrace{\frac{\partial^2 E}{\partial S^2}\Big|_V}_{E_{SS}}\delta S^2 + 2\underbrace{\frac{\partial^2 E}{\partial S \partial V}}_{E_{SV}}\delta S\delta V + \underbrace{\frac{\partial^2 E}{\partial V^2}\Big|_S}_{E_{VV}}\delta V^2\Big) \\
&= T\delta S - p\delta V + \frac{1}{2}\Big(E_{SS}\delta S^2 + 2E_{SV}\delta S\delta V + E_{VV}\delta V^2\Big) \ .
\end{aligned}$$

The first derivative terms vanishes, since

$$\begin{aligned}\delta G &= \delta E - T\delta S + p\delta V \\ &= \cancel{T\delta S} - \cancel{p\delta V} + \frac{1}{2}\Big(E_{SS}\delta S^2 + 2E_{SV}\delta S\delta V + E_{VV}\delta V^2\Big) - \cancel{T\delta S} + \cancel{p\delta V} \\ &= \frac{1}{2}\Big(E_{SS}\delta S^2 + 2E_{SV}\delta S\delta V + E_{VV}\delta V^2\Big)\ .\end{aligned}$$

The condition to be a minimum is that

$$E_{SS} > 0\ , \quad E_{VV} > 0\ , \quad E_{SS}E_{VV} - E_{SV}^2 > 0\ .$$

Respectively, they become

$$E_{SS} = \frac{\partial}{\partial S}\underbrace{\frac{\partial E}{\partial S}}_{T} = \frac{\partial T}{\partial S} > 0\ ,$$

$$E_{VV} = \frac{\partial}{\partial V}\underbrace{\frac{\partial E}{\partial V}}_{-p} = -\frac{\partial p}{\partial V} > 0\ ,$$

$$E_{SS}E_{VV} - E_{SV}^2 = -\frac{\partial T}{\partial S}\Big|_V\frac{\partial p}{\partial V}\Big|_S - \left(\frac{\partial p}{\partial S}\Big|_V\right)^2 = -\frac{\partial T}{\partial S}\Big|_V\frac{\partial p}{\partial V}\Big|_S - \left(\frac{\partial T}{\partial V}\Big|_S\right)^2 > 0\ .$$

q.e.d.

We define the stability conditions in terms of the specific heat

$$C_V = T\frac{\partial S}{\partial T}\Big|_V > 0\ ,$$

the adiabatic compressibility

$$\chi_S = -\frac{1}{V}\frac{\partial V}{\partial p}\Big|_S > 0$$

and the isothermal compressibility

$$\chi_T = -\frac{1}{V}\frac{\partial V}{\partial p}\Big|_T > 0\ .$$

Proof. For the first, using (3.1) and $T > 0$

$$C_V = T\frac{\partial S}{\partial T}\Big|_V > 0\ .$$

For the second, using (3.1) and $V > 0$

$$\chi_S = -\frac{1}{V}\frac{\partial V}{\partial p}\Big|_S > 0 \ .$$

For the third, using (3.1) and (**??**)

$$\begin{aligned}
0 &< \frac{\partial T}{\partial V}\Big|_S \frac{\partial T}{\partial V}\Big|_S + \frac{\partial T}{\partial S}\Big|_V \frac{\partial p}{\partial V}\Big|_S \\
&- \frac{\partial T}{\partial V}\Big|_S \frac{\partial p}{\partial S}\Big|_V + \frac{\partial T}{\partial S}\Big|_V \frac{\partial p}{\partial V}\Big|_S \\
&= \frac{\partial(T,p)}{\partial(S,V)} \\
&= \frac{\partial(T,p)}{\partial(S,V)} = \frac{\partial(T,p)}{\partial(T,V)}\frac{\partial(T,V)}{\partial(S,V)} \\
&= \frac{\partial p}{\partial V}\Big|_T \frac{\partial T}{\partial S}\Big|_V \\
&= \frac{T}{C_V}\frac{\partial p}{\partial V}\Big|_T \ ,
\end{aligned}$$

hence, by $T > 0$, $C_V > 0$ and $V > 0$,

$$\chi_T = -\frac{1}{V}\frac{\partial V}{\partial p}\Big|_T > 0 \ .$$

q.e.d.

Consequently to stability, F is a concave of T and covex of V, whereas G is concave of both T and p.

Proof. For the concavity of F of T

$$C_V = T\frac{\partial S}{\partial T}\Big|_V = -T\frac{\partial^2 F}{\partial T^2}\Big|_V > 0 \ ,$$

hence

$$\frac{\partial^2 F}{\partial T^2}\Big|_V < 0 \ .$$

For the convexity of F of V

$$\chi_T = -\frac{1}{V}\frac{\partial V}{\partial p}\Big|_T = \left(V\frac{\partial^2 F}{\partial V^2}\Big|_T\right)^{-1} > 0 \ ,$$

hence

$$\frac{\partial^2 F}{\partial V^2}\Big|_T > 0 \ .$$

For the concavity of G of T

$$C_P = T\frac{\partial S}{\partial T}\Big|_P = -T\frac{\partial^2 G}{\partial T^2}\Big|_p > 0 \ ,$$

hence

$$\frac{\partial^2 G}{\partial T^2}\Big|_p < 0 \ .$$

For the concavity of G of p

$$\chi_T = -\frac{1}{V}\frac{\partial V}{\partial p}\Big|_T = -\frac{1}{V}\frac{\partial^2 G}{\partial p^2}\Big|_T > 0 \ ,$$

hence

$$\frac{\partial^2 G}{\partial p^2}\Big|_T < 0 \ .$$

q.e.d.

Furthermore, the second law of thermodynamics can be expressed, in order to maximise the entropy, by imposing that first derivatives vanish and the hessian, i.e. the matrix with its second derivatives, must be negative defined. Therefore, it must be (locally) concave in E, V and N.

When cease to work at constant N, the stability condition is

$$\frac{\partial N}{\partial \mu}\Big|_{V,T} = \frac{N^2}{V}\chi_T > 0 \ .$$

Proof. In fact

$$\begin{aligned}
\frac{\partial N}{\partial \mu}\Big|_{V,T} &= \frac{\partial(N,V,T)}{\partial(\mu,V,T)} \\
&= \frac{\partial(N,V,T)}{\partial(N,p,T)}\frac{\partial(N,p,T)}{\partial(p,V,T)}1\frac{\partial(p,V,T)}{\partial(\mu,V,T)} \\
&= \frac{\partial(N,V,T)}{\partial(N,p,T)}\frac{\partial(N,p,T)}{\partial(p,V,T)}\frac{\partial(p,V,T)}{\partial(\mu,N,T)}\frac{\partial(p,V,T)}{\partial(\mu,V,T)} \\
&= \frac{\partial(N,V,T)}{\partial(N,p,T)}\frac{\partial(N,p,T)}{\partial(\mu,N,T)}\frac{\partial(p,V,T)}{\partial(\mu,V,T)} \\
&= -\frac{\partial V}{\partial p}\Big|_{N,T}\frac{\partial p}{\partial \mu}\Big|_{V,T}\frac{\partial p}{\partial \mu}\Big|_{N,T}
\end{aligned}$$

Now we use (2.11)

$$\frac{\partial p}{\partial \mu}\Big|_{V,T} = \frac{\partial p}{\partial \mu}\Big|_{N,T} = \left(\frac{\partial \mu}{\partial p}\Big|_T\right) = \frac{N}{V} \ ,$$

hence

$$\frac{\partial N}{\partial \mu}\Big|_{V,T} = -\frac{N^2}{V^2}\frac{\partial V}{\partial p}\Big|_{N,T} = \frac{N^2}{V}\chi_T > 0 \ .$$

q.e.d.

Moreover, we have the relation

$$\chi_T(C_P - C_V) = TV\alpha_p^2 \ ,$$

which implies that

$$C_P > C_V \iff \chi_T > \chi_S \ .$$

Proof. We start from

$$C_V = T\frac{\partial S}{\partial T}\Big|_V = \frac{\partial E}{\partial T}\Big|_V \ ,$$
$$C_p = T\frac{\partial S}{\partial T}\Big|_p = \frac{\partial E}{\partial T}\Big|_p + p\frac{\partial V}{\partial T}\Big|_p \ ,$$

which imply that

$$TdS = C_V dT + (\frac{\partial E}{\partial V}\Big|_T + p)dV = C_V dT + T\frac{\partial p}{\partial T}\Big|_V dV \ ,$$
$$TdS = C_p dT + (\frac{\partial E}{\partial p}\Big|_T + \frac{\partial V}{\partial p}\Big|_T)dp = C_p dT - T\frac{\partial V}{\partial T}\Big|_p dp \ .$$

Comparing them

$$(C_p - C_V)dT = T(\frac{\partial V}{\partial T}\Big|_p dp + \frac{\partial p}{\partial T}\Big|_V dV) \ ,$$
$$(C_p - C_V) = T\frac{\partial V}{\partial T}\Big|_p \frac{\partial p}{\partial T}\Big|_V \ .$$

We use

$$\frac{\partial p}{\partial T}\Big|_V = \frac{\partial(p,V)}{\partial T, V} = \frac{\partial(p,V)}{\partial(p,T)}\frac{\partial(p,T)}{\partial(T,V)} = -\frac{\partial V}{\partial T}\Big|_p \frac{\partial p}{\partial V}\Big|_T \ ,$$

hence

$$C_p - C_V = \frac{T}{V\chi_T}\Big(\frac{\partial V}{\partial T}\Big|_p\Big)^2 \ ,$$

or, defining the thermal expansion coefficient

$$\alpha_p = \frac{1}{V}\frac{\partial V}{\partial T}\Big|_p \ , \tag{3.2}$$

we have

$$\chi_T(C_P - C_V) = TV\alpha_p^2 \ ,$$

Finally, we obtain

$$\frac{C_p}{C_V} = \frac{\chi_T}{\chi_S} \ .$$

q.e.d.

3.3 Statistical mechanics

It is important to say that this is all thermodynamics can tell us, thus in order to find the explicit expression of E, we must go into statistical mechanics.

Part II

Classical statistical mechanics

Chapter 4

Classical mechanics

In this chapter, we will recall some basic notion of Classical (Hamiltonian) Mechanics.

4.1 States, observables, time evolution

Consider a dynamical system composed by N degrees of freedom in a d-dimensional space. A physical state is defined as a point P in a $2dN$-dimensional manifold $\mathcal{M}^{dN}$, called the phase space, which is the Cartesian product of N single-particle manifolds $\mathcal{M}^d$. More formally, the phase space is the cotangent bundle $T^*\mathcal{C}$ of the configuration space $\mathcal{C}$. In this (smooth) manifold, we locally introduce a chart, which looks like $\mathbb{R}^{2dN}$, labelled by generalised coordinates q^i and generalised momenta p_i, where $i = 1, \dots dN$. Therefore, a state can be individuated once has been given

$$\{(q^i,\ p_i)\}_{i=1}^{dN} \in \mathcal{M}^{dN} \ .$$

However, we can combine this 2 different set of coordinates q^i and p_i into a more convenient single one ξ_i in the following way:

$$\xi^j = \begin{cases} q^i & j = 1, \dots dN \\ p_i & j = dN+1, \dots 2dN \end{cases} \ . \tag{4.1}$$

Moreover, we introduce the standard (Lebesgue) measure

$$d\Gamma = \prod_{i=1}^{N} d^d q^i \ d^d p_i = \prod_{j=1}^{2N} d^d \xi_j \ . \tag{4.2}$$

In the phase space, an observable is a smooth real function

$$f \colon \mathcal{M}^{dN} \to \mathbb{R}$$

and a measurement of this observable at a given time t_0 in a fixed point $(q^i(t_0),\ \tilde{p}_i(t_0))$ is the evaluation of the corresponding function in that point

$$f = f(q^i(t_0), p_i(t_0)) \ .$$

In order to describe time evolution of the system, we need to introduce a special real function $H(q^i,\ p_i,\ t)$, called the Hamiltonian of the system. Through it, we can find how the systems evolve in time by solving the equations of motion, called the Hamilton's equations

$$\dot{q}^i = \frac{\partial H}{\partial p_i} \ , \quad \dot{p}_i = -\frac{\partial H}{\partial q^i} \ , \quad \text{or} \quad \dot{\xi}^j = J^{jk}\frac{\partial H}{\partial \xi^k} \ , \tag{4.3}$$

where J^{jk} is the symplectic matrix, a $2N \times 2N$ constant-valued matrix given by

$$J^{jk} = \begin{bmatrix} 0 & \mathbb{I}_N \\ -\mathbb{I}_N & 0 \end{bmatrix} \ .$$

Example 4.1. Consider a 1-dimensional harmonic oscillator of mass m and frequency ω, vibrating around an equilibrium position q_0. Its Hamiltonian is given by

$$H(q,p) = \frac{p^2}{2m} + \frac{m\omega^2}{2}(q-q_0)^2 \ ,$$

while the Hamilton's equations are

$$\dot{q} = \frac{\partial H}{\partial p} = \frac{p}{m} \ , \quad \dot{p} = -\frac{\partial H}{\partial q} = -m\omega^2(q-q_0) \ .$$

It is important to highlight that the Hamilton's equations are deterministic: once initial conditions $(q^i(t_0), p_i(t_0)) \in \mathcal{M}^{dN}$ are given, the trajectory in phase space of the system is uniquely and completely determined. This means that there is one and only one trajectory passing through each point of the phase space and two trajectories can never intersect. It is a consequence of the existence and uniqueness theorem of differential equations.

Theorem 4.1 (Conservation of energy)
If the Hamiltonian does not depend explicitly on time, it can be interpreted physically as the energy of the system, which is constants

$$H(q^i(t), p_i(t)) = H(q^i(t_0), p_i(t_0)) = E = const \ .$$

4.2 Probability density distribution

Now, we give a few definitions. A macrostate is defined by the knowledge of macroscopic thermodynamic quantities (boundary conditions, like $p, V, N, T, \ldots$); whereas a microstate is defined by the knowledge of the microscopic behaviour of the system in the phase space (q^i, p_i), which is fixed by the initial conditions. However, in general, there are more microstates associated to the same macrostates, since the information carried by a microstate is much more than the one carried by a macrostate. Intuitively, we can say that a system in a defined macrostate can be represented not by only one but by several microstates. This gives rise to the concept of ensemble. We fixed a macrostate set-up, we created a large amount of copies of the same physical system and we look at the different microstate that can represent this macrostate. Mathematically, it can be studied with the introduction of a probability density distribution

$$\rho(q_i(t), p_i(t), t) \colon \mathcal{M}^{dN} \to \mathbb{R}^+ \ ,$$

such that it satisfies the following properties

1. positivity, i.e.

$$\rho(q_i,\ p_i,\ t) \geq 0 \ ,$$

2. normalisation, i.e.

$$\int_{\mathcal{M}^n} \prod_{i=1}^{N} d^d q_i d^d p_i \ \rho(q_i, p_i, t) = \int_{\mathcal{M}^n} d\Gamma \ \rho(q_i, p_i, t) = 1 \ . \tag{4.4}$$

The probability to find the system in a finite portion of the phase space $\mathcal{U} \subset \mathcal{M}^{dN}$ is

$$\int_{\mathcal{U}} d\Gamma \ \rho(q_i,\ p_i,\ t) \ .$$

Notice that there is a dimensional problem: a measure must be dimensionless but the measure we have introduced into the phase space $d\Gamma$ has the dimension of an action at the power of dN, i.e. $[d\Gamma] = [E]^{dN}[t]^{dN}$. To solve this problem, we introduce an ad hoc constant h, called the scale factor, which leads is to a dimensionless volume element

$$d\Omega = \frac{d\Gamma}{h^{dN}} = \frac{\prod_{i=1}^{N} d^d q^i d^d p^i}{h^{dN}} \ .$$

4.3 Liouville's theorem

Given 2 functions of the phase space $f(q^i, p_i)$ and $g(q^i, p_i)$, we can define a bilinear mapping, called the Poisson's brackets, defined by as

$$\{f, g\} = \frac{\partial f}{\partial q^i}\frac{\partial g}{\partial p_i} - \frac{\partial f}{\partial p_i}\frac{\partial g}{\partial q^i} = \frac{\partial f}{\partial \xi^j} J^{jk} \frac{\partial g}{\partial \xi^k} \ , \tag{4.5}$$

such that it satisfies the following properties, $\forall h(q^i, p_i)$

1. antisymmetry, i.e.
$$\{f, g\} = -\{g, f\} ,$$

2. Leibniz rule, i.e.
$$\{f, gh\} = g\{f, h\} + \{f, g\}h ,$$

3. Jacobi identity, i.e.
$$\{f, \{g, h\}\} + \{g, \{h, f\}\} + \{h, \{f, g\}\} = 0 .$$

Notice that the symplectic matrix can be defined by the Poisson brackets

$$\{\xi^j, \xi^k\} = J^{jk} .$$

A canonical transformation $\xi \to \eta$ is a transformation of the phase space coordinates that preserve the structure of the Poisson's brackets

$$\{\xi^j, \xi^k\} = \{\eta^j, \eta^k\} = J^{jk} .$$

To a system of first-order differential equations, like the Hamilton's ones, we can associate an Hamiltonian flow generated by the Hamiltonian vector field

$$\mathbf{H} = J^{jk} \frac{\partial H}{\partial \xi^k} \frac{\partial}{\partial \xi^j} .$$

Physically, with a fluid analogy, it keeps track of the motion of all particles.

Theorem 4.2
Time evolution governed by the Hamilton's equations is a canonical transformation.

Theorem 4.3
Canonical transformations preserve volumes in phase space.

Proof. A canonical transformation can be written as

$$J^{ab} = \{\eta^a, \eta^b\} = \frac{\partial \eta^a}{\partial \xi^j} J^{jk} \frac{\partial \eta^b}{\partial \xi^k} .$$

Now, we compute the determinant of this expression, observing that $M = \partial\eta/\partial\xi$ is the Jacobian matrix of this transformation, and we obtain, using the properties of the determinant

$$\det J = \det(MJM^T) = \overset{2}{\det} M \det J ,$$

hence

$$|\det J| = 1 .$$

q.e.d.

Combining the last 2 theorems, we can state an important theorem, named after Liouville.

Theorem 4.4 (Liouville)
The volume through the (Hamiltonian) flow generated by the Hamilton's equations is constant

$$\mathrm{vol}\,\Omega(t_0) = \mathrm{vol}\,\Omega(t) \ .$$

See Figure *4.3**.*

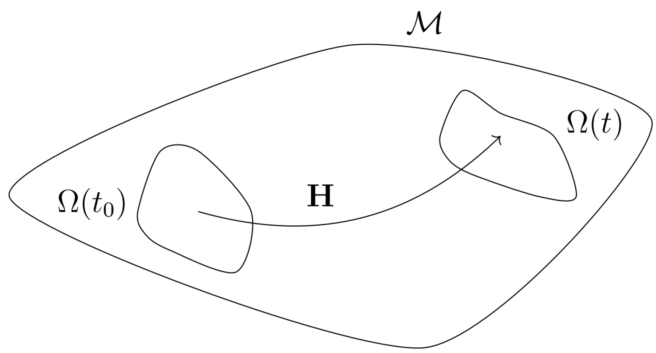

Figure 4.1: The (Hamiltonian) flow of the system in which $\mathrm{vol}\,\Omega(t_0) = \mathrm{vol}\,\Omega(t)$.

An important corollary of the Liouville's theorem can be state about the property of the probability density distribution.

Corollary 4.1
The probability density distribution is constant in time. Mathematically

$$\frac{d\rho}{dt} = \frac{\partial\rho}{\partial t} + \{\rho, H\} = 0 \ . \tag{4.6}$$

The physical interpretation of this corollary is that particles do not appear nor disappear due to conservation of charge, mass, etc.

Proof. Consider the flow of a portion of phase space as it was a fluid with associated density ρ and current $\mathbf{J} = \rho\mathbf{v}$. By the Liouville's theorem, it must satisfy a continuity equation

$$\frac{\partial\rho}{\partial t} + \boldsymbol{\nabla}\cdot\mathbf{J} = 0 \ .$$

We introduce a local chart (q^i, p_i) for the manifold and for the tangent space, in order to have $\mathbf{v} = (\dot{q}^i, \dot{p}_i)$ and $\boldsymbol{\nabla} = (\partial/\partial q^i, \partial/\partial p_i)$. Therefore, the continuity equation becomes

$$\begin{aligned}
0 &= \frac{\partial\rho}{\partial t} + \boldsymbol{\nabla}\cdot\mathbf{J} \\
&= \frac{\partial\rho}{\partial t} + \sum_i (\partial/\partial q^i, \partial/\partial p_i)\cdot(\dot q^i, \dot p_i) \\
&= \frac{\partial\rho}{\partial t} + \sum_i (\frac{\partial}{\partial q^i}(\rho\dot q^i) + \frac{\partial}{\partial p_i}(\rho\dot p_i)) \\
&= \frac{\partial\rho}{\partial t} + \sum_i (\frac{\partial\rho}{\partial q^i}\underbrace{\dot q^i}_{\frac{\partial H}{\partial p_i}} + \rho\frac{\partial}{\partial q^i}\underbrace{\dot q^i}_{\frac{\partial H}{\partial p_i}} + \frac{\partial\rho}{\partial p_i}\underbrace{\dot p_i}_{-\frac{\partial H}{\partial q^i}} + \rho\frac{\partial}{\partial p_i}\underbrace{\dot p_i}_{-\frac{\partial H}{\partial q^i}}) \\
&= \frac{\partial\rho}{\partial t} + \sum_i (\frac{\partial\rho}{\partial q^i}\frac{\partial H}{\partial p_i} + \rho\cancel{\frac{\partial^2 H}{\partial p_i\partial q^i}} - \frac{\partial\rho}{\partial p_i}\frac{\partial H}{\partial q^i} - \rho\cancel{\frac{\partial^2 H}{\partial q^i\partial p_i}}) \\
&= \frac{\partial\rho}{\partial t} + \sum_i (\frac{\partial\rho}{\partial q^i}\frac{\partial H}{\partial p_i} - \frac{\partial\rho}{\partial p_i}\frac{\partial H}{\partial q^i}) \\
&= \frac{\partial\rho}{\partial t} + \{\rho, H\}\ ,
\end{aligned}$$

where we have used the Hamilton's equations (4.3), the fact that partial derivatives commute and the definition of Poisson's brackets (4.5). q.e.d.

For stationary systems, i.e. when $\frac{\partial\rho}{\partial t} = 0$, the necessary condition for equilibrium is $\{\rho, H\} = 0$, which is satisfied only if

$$\rho(q^i, p_i) = const\ ,$$

like in the microcanonical ensemble, or

$$\rho(q^i, p_i) = \rho(H(q^i, p_i))\ , \tag{4.7}$$

like in the canonical or in the grand canonical ensemble.

Proof. For the first, we have

$$\{\rho, H\} = \underbrace{\frac{\partial\rho}{\partial q^i}}_{0}\frac{\partial H}{\partial p_i} - \underbrace{\frac{\partial\rho}{\partial p_i}}_{0}\frac{\partial H}{\partial q^i} = 0\ .$$

For the second, we have

$$\{\rho, H\} = \frac{\partial\rho}{\partial q^i}\frac{\partial H}{\partial p_i} - \frac{\partial\rho}{\partial p_i}\frac{\partial H}{\partial q^i} = \frac{\partial\rho}{\cancel{\partial H}}\cancel{\frac{\partial H}{\partial q^i}}\frac{\partial H}{\partial p_i} - \frac{\partial\rho}{\cancel{\partial H}}\cancel{\frac{\partial H}{\partial p_i}}\frac{\partial H}{\partial q^i} = 0$$

where we have developed the dependence of ρ on H by the chain rule and the fact that partial derivatives commute. q.e.d.

The average value of an observable f is given by the volume of the function in phase space, weighted by the probability density distribution

$$\langle f \rangle = \int_{\mathcal{M}^{dN}} d\Gamma \ \rho(q^i, \ p_i) f(q^i, \ p_i) \ , \tag{4.8}$$

while the standard deviation is defined by

$$(\Delta f)^2 = \langle f^2 \rangle - \langle f \rangle^2 \ .$$

4.4 Energy foliation

Consider a time-independent Hamiltonian $H = H(q^i, p_i)$, which implies by the theorem (4.1) that energy is conserved $E = \text{const}$. In this case, there exists $2dN - 1$ independent (local) constants of motion. However, we are interested in global integrals, which are isolating, i.e. they admit hypersurfaces in phase space, and foliating, i.e. they admit a foliation of phase space via surfaces of constant value, called level surfaces. The most important global foliating isolating integral is the energy, sometimes it is even the only one. Therefore, we foliate the whole phase space into $2dN - 1$-dimensional hypersurfaces S_E of constant energy. See Figure 4.4. Notice that the structure of the manifold does not depend on the dynamics, but hypersurfaces do, because they depend on the different Hamiltonian H chosen by the dynamics. In fact, different Hamiltonian will have different foliations. Furthermore, a different choice of the initial conditions means a different hypersurface.

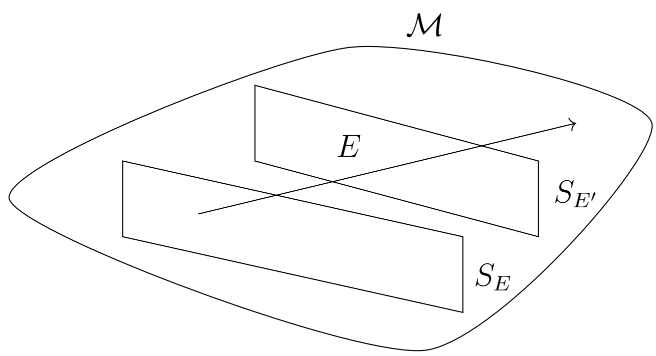

Figure 4.2: Foliation of the phase space $\mathcal{M}$ by hypersurfaces S_E if constant energy. In this case $E' > E$.

Taking advantage of this foliation structure, it is easier to compute integral in phase space. In fact, if we define the gradient of the Hamiltonian,

$$\boldsymbol{\nabla} H = \frac{\partial H}{\partial \boldsymbol{\xi}} \ ,$$

which is by definition orthogonal to the energy hypersurfaces and has norm equals to

$$||\boldsymbol{\nabla} H|| = \sqrt{\sum_i (\frac{\partial H}{\partial \xi_i})^2} \ ,$$

then we can decompose the phase space measure (4.2) into

$$d\Gamma = dAdl = \underbrace{\frac{dA}{||\boldsymbol{\nabla} H||}}_{dS_E} \underbrace{||\boldsymbol{\nabla} H||dl}_{dE} = dS_E dE \ , \tag{4.9}$$

where dA is the area element of the energy hypersurfaces and dl is the line element orthogonal to this surface. Intuitively, we have passed from an integration of a volume of phase space $d\Gamma$ into an integration over hypersurfaces depending on the energy dS_E along with an integration over energy dE. dE is invariant, therefore dS_E is an invariant area element. The volume of phase space enclosed by the energy hypersurface S_E

$$\Sigma(E) = \{\boldsymbol{\xi} \in \mathcal{M} \colon 0 \leq H(\xi) \leq E\}$$

is given by

$$\Sigma(E) = \int_{0 \leq H \leq E} d\Gamma = \int_0^E dH \int_{S_E} dS_H = \int_0^E dH \ \omega(H) \tag{4.10}$$

where we have defined the density of states ω as

$$\omega(E) = \int_{\mathcal{M}^{dN}} d\Gamma \ \delta(H - E) = \int_{S_E} dS_H = \frac{\partial \Sigma}{\partial E} \ , \tag{4.11}$$

where the Dirac delta $\delta(H-E)$ constrains ourselves into the hypersurface of energy $H = E$.

4.5 Ergodicity

An important and fundamental concept in statistical mechanics is ergodicity. A physical system is said to be ergodic on an energy hypersurface of constant energy S_E if and only if, in time evolution, almost[1] every point $\xi^j \in S_E$ passes through every neighbourhood $U \subset S_E$. In other word, in a finite time interval $t \in (-\infty, \infty)$, the system samples every small neighbourhood of the surface and the set of trajectories is dense. Ergodicity implies that the only isolating integral is energy and there are no other conservation laws.

Given an observable f, we can associate 2 different in principle average values (4.8)

[1] Up to a null measure set

1. phase-space average over the energy hypersurface S_E, since the motion is confined inside S_E

$$\langle f\rangle_E = \frac{1}{\omega(E)}\int_{S_E} dS_H\; f = \frac{1}{\omega(E)}\int_{\mathcal{M}} d\Gamma\;\delta(H-E)f = \frac{1}{\omega(E)}\frac{\partial}{\partial E}\int_{\Sigma(E)} d\Gamma\; f\;,$$

2. (infinite) time average, that can be experimentally obtained by observing the system over a long amount of time

$$\langle f\rangle_\infty = \lim_{t\to\infty}\int_{t_0}^{t_0+\infty} dt\; f(q^i(t),p_i(t))\;,$$

which is valid for almost every initial condition and it is independent of the initial time t_0.

Ergodicity and average values are connected by a theorem.

Theorem 4.5
A system is ergodic if and only if

$$\langle f\rangle_E = \langle f\rangle_\infty\;. \tag{4.12}$$

In these notes, we will consider only ergodic systems.

4.6 Ensembles

Thermodynamics provides the completely macroscopic description of a physical system (equations of state, relations between thermodynamic quantities) once a single thermodynamic potential has been given. See Table 4.1.

Ensemble	Thermodynamic potential
microcanonical	entropy S
canonical	Helmoltz free energy F
grand canonical	grand potential Ω

Table 4.1: Ensembles with associated thermodynamic potential.

Chapter 5

Microcanonical ensemble

5.1 Microcanonical probability density distribution

Consider a physical system which is isolated from the environment, i.e. it cannot exchange neither energy nor matter so that the boundary conditions are fixed E, N and V. Of course, isolated systems are a bit nonphysical. Since energy is conserved and the Hamiltonian is time-independent, the trajectory of motion is restricted on the surface S_E and not on all the phase space. This kind of set-up is called microcanonical ensemble and it has associated a probability density distribution, which a priori is uniform

$$\rho_{mc}(q^i,\ p_i) = C\delta(H(q^i, p_i) - E) \ ,$$

where C is a normalisation constant, which can be evaluated by (4.4)

$$1 = \int_{\mathcal{M}^N} d\Omega\ \rho_{mc} = \int_{\mathcal{M}^N} d\Omega\ C\delta(H - E) = C \underbrace{\int_{\mathcal{M}^N} d\Omega\ \delta(H - E)}_{\omega(E)} = C\omega(E) \ .$$

Hence, the microcanonical probability density distribution is

$$\rho_{mc}(q^i,\ p_i) = \frac{1}{\omega(E)}\delta(H(q^i, p_i) - E) \ . \tag{5.1}$$

This distribution can be evaluated by the following argument: suppose that the system has not exactly energy equals to E, but the latter is in a range $H \in [E, E + \Delta E]$, where ΔE is an infinitesimal displacement of energy, i.e. $\Delta E \ll 1$. The volume in phase space (4.10) becomes

$$\Gamma(E) = \int_E^{E+\Delta E} dE'\ \omega(E') \simeq \omega(E)\Delta E = \frac{\partial \Sigma(E)}{\partial E}\Delta E \ .$$

Consequently, the distribution becomes

$$\rho_{mc}(q^i, p_i) = \begin{cases} \frac{1}{\Gamma(E)} & H \in [E, E + \Delta E] \\ 0 & otherwise \end{cases}$$

Therefore, in the limit for which $\Delta E \to 0$, we can find exactly (5.1), up to the normalisation constant.

Let $f(q^i, p_i)$ be an observable, then its microcanonical average (or equivalenty is energy hypersurface average) is

$$\langle f(q^i, p_i) \rangle_{mc} = \int_{\mathcal{M}} d\Omega \; \rho_{mc} f = \int_{\mathcal{M}} d\Omega \; \frac{1}{\omega(E)} \delta(H - E) f = \frac{1}{\omega(E)} \int_{S_E} dS_E \; f = \langle f \rangle_E \; . \tag{5.2}$$

5.2 Entropy as microcanonical potential

A local chart with coordinates (E, V, N) is suitable for entropy (2.12). Hence, we need to find an expression for entropy. The first guess is to define the microcanonical entropy S_{mc} as

$$S_{mc}(E, V, N) = k_B \ln \Gamma(E) \; , \tag{5.3}$$

which, in the thermodynamic limit, it is equivalent to

$$s_{mc} = \lim_{td} \frac{S_{mc}}{N} = k_B \lim_{td} \frac{\log \omega(E)}{N} = \underbrace{k_B \lim_{td} \frac{\log \Sigma(E)}{N}}_{H \in [0,E]} = \underbrace{k_B \lim_{td} \frac{\log \Gamma(E)}{N}}_{H \in [E, E+\Delta E]} \; .$$

The logarithm is justified by the fact that the volume of a N-particle phase space is $(W_1)^N$, where W_1 is the volume of a single particle phase space. According to the properties of the logarithm, in this way, entropy becomes extensive.

Now, we need to prove that (5.3) is indeed the thermodynamic entropy. The first property that it must fulfill is additivity: given 2 subsystems A and B, the total entropy is the sum of the 2 separately subsystems entropy

$$s_{mc}^{tot} = s_{mc}^{(1)} + s_{mc}^{(2)} \; .$$

Proof. Consider two isolated subsystems A and B in contact at thermal equilibrium with the same temperature $T = T_1 = T_2$ but whatsoever volume V_1 and V_2 and energies E_1 and E_2. The total system is isolated and it can be treated as a microcanonical ensemble. The entropy of the subsystems will be respectively

$$S_1 = k_B \ln \Gamma_1(E_1) \; , \quad S_2 = k_B \ln \Gamma_2(E_2) \; .$$

where $\Gamma_1(E_1) \simeq \omega_1(E_1)\Delta E_1$ and $\Gamma_2(E_2) \simeq \omega_2(E_2)\Delta E_2$. The total energy is $E = E_1 + E_2 + E_{surface}$ but, in the thermodynamic limit, the energy exchanged by the surface is a subleading term (E_1 and E_2 go as L^3 whereas $E_{surface}$ goes as L^2) and then it can be neglected. Therefore, the total energy becomes $E = E_1 + E_2$. The joint density of states is

$$\begin{aligned}\omega(E) &= \int_{\mathcal{M}^N} \underbrace{d\Gamma_1}_{dE_1 dS_{E_1}} \underbrace{d\Gamma_2}_{dE_2 dS_{E_2}} \delta(H-E)\\ &= \int dE_1 \int dS_{E_1} \int dE_2 \int dS_{E_2}\ \delta(E-E_1-E_2)\\ &= \int dE_1 \int dE_2\ \omega_1(E_1)\omega_2(E_2)\delta(E-E_1-E_2)\\ &= \int_0^E dE_1\ \omega_1(E_1)\omega_2(E_2=E-E_1)\ .\end{aligned}$$

Notice that the integrand is a positive function and it has a maximum in $E_1^* \in [0, E]$. Hence, we can find an upper bound for the integral, which is

$$\begin{aligned}\int_0^E dE_1\ \omega_1(E_1)\omega_2(E_2=E-E_1) &\leq \omega_1(E_1^*)\omega_2(E_2^*=E-E_1^*) \underbrace{\int_0^E dE_1}_{E}\\ &= \omega_1(E_1^*)\omega_2(E_2^*=E-E_1^*)E\ .\end{aligned} \tag{5.4}$$

On the other hand, it is always possible to find a value for a small enough ΔE in order to have

$$\omega_1(E_1^*)\omega_2(E_2^*=E-E_1^*)\Delta E \leq \omega(E)\ . \tag{5.5}$$

Putting together (5.4) and (5.5), we obtain, after a series of manipulations

$$\Delta E\omega_1(E_1^*)\omega_2(E_2^*) \leq \omega(E) \leq \omega_1(E_1^*)\omega_2(E_2^*)E\ ,$$

$$\underbrace{\omega_1(E_1^*)\Delta E}_{\Gamma_1(E_1^*)}\underbrace{\omega_2(E_2^*)\Delta E}_{\Gamma_2(E_2^*)} \leq \underbrace{\omega(E)\Delta E}_{\Gamma(E)} \leq \frac{E}{\Delta E}\underbrace{\omega_1(E_1^*)\Delta E}_{\Gamma_1(E_1^*)}\underbrace{\omega_2(E_2^*)\Delta E}_{\Gamma_2(E_2^*)}\ ,$$

$$\Gamma_1(E_1^*)\Gamma(E_2^*) \leq \Gamma(E) \leq \frac{E}{\Delta E}\Gamma(E_1^*)\Gamma(E_2^*)\ .$$

Now, we can take the logarithm, since it is a monotonic function, after another series of manipulations, we obtain

$$\log(\Gamma_1(E_1^*)\Gamma(E_2^*)) \leq \log\Gamma(E) \leq \log(\frac{E}{\Delta E}\Gamma(E_1^*)\Gamma(E_2^*))\ ,$$

$$k_B \log\Big(\Gamma_1(E_1^*)\Gamma(E_2^*)\Big) \leq k_B\log\Gamma(E) \leq k_B\log\Big(\frac{E}{\Delta E}\Gamma(E_1^*)\Gamma(E_2^*)\Big)\ ,$$

$$
\begin{aligned}
k_B \log \Gamma_1(E_1^*) + k_B \log \Gamma(E_2^*) &\leq k_B \log \Gamma(E) \\
&\leq k_B \log \frac{E}{\Delta E} + k_B \log \Gamma(E_1^*) + k_B \log \Gamma(E_2^*) \ , \\
\frac{k_B \log \Gamma_1(E_1^*) + k_B \log \Gamma(E_2^*)}{N} &\leq \frac{k_B \log \Gamma(E)}{N} \\
&\leq \frac{k_B \log \Gamma(E_1^*) + k_B \log \Gamma(E_2^*)}{N} + \frac{k_B \log \frac{E}{\Delta E}}{N} \ .
\end{aligned}
$$

Finally, we take the thermodynamic limit, noticing that the last term vanishes, since E goes like N and $\lim_{N\to\infty} \frac{1}{N} \log N = 0$

$$
\begin{aligned}
\underbrace{\lim_{TD} \frac{k_B \log \Gamma_1(E_1^*)}{N}}_{s_{mc}^{(1)}} + \underbrace{\lim_{TD} \frac{k_B \log \Gamma(E_2^*)}{N}}_{s_{mc}^{(2)}} &\leq \underbrace{\lim_{TD} \frac{k_B \log \Gamma(E)}{N}}_{s_{mc}} \\
&\leq \underbrace{\lim_{TD} \frac{k_B \log \Gamma_1(E_1^*)}{N}}_{s_{mc}^{(1)}} + \underbrace{\lim_{TD} \frac{k_B \log \Gamma(E_2^*)}{N}}_{s_{mc}^{(2)}} \ ,
\end{aligned}
$$

hence

$$
s_{mc}(E) = s_{mc}^{(1)}(E_1^*) + s_{mc}^{(2)}(E_2^*) \ . \tag{5.6}
$$

q.e.d.

From (5.6), we can also deduce 2 properties that entropy fulfills: for isolated system, spontaneous processes leads to an increase in entropy, which is verified because spontaneous processes leads also to an increase in phase space volume; at equilibrium, entropy is maximum, which is verified by the asterisks. Furthermore, in the thermodynamic limit, microcanonical entropy coincides with thermodynamic entropy

$$
s_{mc} = s_{td} \ .
$$

Proof. Since entropy is maximum at equilibrium, also $\Gamma_1(E_1)\Gamma_2(E_2)$ is so and it has null variation

$$
\begin{aligned}
0 &= \delta(\Gamma_1(E_1^*)\Gamma_2(E_2^* = E - E_1^*)) \\
&= \delta\Gamma_1(E_1^*)\Gamma_2(E_2^*) + \Gamma_1(E_1^*)\delta\Gamma_2(E_2^*) \\
&= \frac{\partial \Gamma_1}{\partial E_1}\bigg|_{E_1^*} \delta E_1 \Gamma_2(E_2^*) + \Gamma_1(E_1^*) \frac{\partial \Gamma_2}{\partial E_2}\bigg|_{E_2^*} \delta E_2 \ ,
\end{aligned}
$$

where we have used Leibniz rule and we have exploited the dependence on energy.

Since $E = \text{const}$, it has a null variation $0 = \delta E = \delta E_1 + \delta E_2$ and

$$
\delta E_2 = -\delta E_1 \ . \tag{5.7}
$$

Hence, with a series of manipulations, we obtain

$$\begin{aligned}
0 &= \frac{\partial \Gamma_1}{\partial E_1}\Big|_{E_1^*} \delta E_1 \Gamma_2(E_2^*) - \Gamma_1(E_1^*) \frac{\partial \Gamma_2}{\partial E_2}\Big|_{E_2^*} \delta E_1 \ , \\
0 &= \frac{\partial \Gamma_1}{\partial E_1}\Big|_{E_1^*} \Gamma_2(E_2^*) - \Gamma_1(E_1^*) \frac{\partial \Gamma_2}{\partial E_2}\Big|_{E_2^*} \ , \\
\frac{\partial \Gamma_1}{\partial E_1}\Big|_{E_1^*} \Gamma_2(E_2^*) &= \Gamma_1(E_1^*) \frac{\partial \Gamma_2}{\partial E_2}\Big|_{E_2^*} \ , \\
\frac{1}{\Gamma_1(E_1^*)} \frac{\partial \Gamma_1}{\partial E_1}\Big|_{E_1^*} &= \frac{1}{\Gamma_2(E_2^*)} \frac{\partial \Gamma_2}{\partial E_2}\Big|_{E_2^*} \ , \\
\frac{\partial \log \Gamma_1}{\partial E_1}\Big|_{E_1^*} &= \frac{\partial \log \Gamma_2}{\partial E_2}\Big|_{E_2^*} \ .
\end{aligned}$$

This is a relation valid for all systems at equilibrium, which is the 0th law of thermodynamic. Finally, we use the first thermodynamic relation in (2.10) to have

$$S_{mc}(E) = S_{td}(E) \times const$$

where the constant can be chosen the Boltzmann constant, in order to have k_B in the same unit of energy over temperature. q.e.d.

The universal Boltzmann's formula is

$$s_{mc} = s_{td} = k_B \log \omega(E) = -k_B \langle \log \rho_{mc} \rangle_{mc} \ . \tag{5.8}$$

Proof. In fact, using (5.2) and the properties of logarithms,

$$\begin{aligned}
\langle \log \rho_{mc} \rangle_{mc} &= \int d\Gamma \ \rho_{mc} \log \rho_{mc} \\
&= \int d\Gamma \ \frac{1}{\omega(E)} \delta(H-E) \log \Big(\frac{1}{\omega(E)} \delta(H-E) \Big) \\
&= \int dS_E \ \frac{1}{\omega(E)} \log \frac{1}{\omega(E)} \\
&= -\frac{1}{\omega(E)} \log \omega(E) \underbrace{\int dS_E}_{\omega(E)} \\
&= -\log \omega(E) \ .
\end{aligned}$$

q.e.d.

Chapter 6

Canonical ensemble

6.1 Canonical probability density distribution

Consider a physical system which can exchange energy with the environment but matter, so that the boundary conditions are fixed T, N and V. Notice that temperature has substituted energy. Physically, it can be thought as the system is immersed in a bigger reservoir with $N_S \ll N_E$ and $V_S \ll V_E$ but at equilibrium with the same temperature $T_S = T_E = T$. See Figure 6.1.

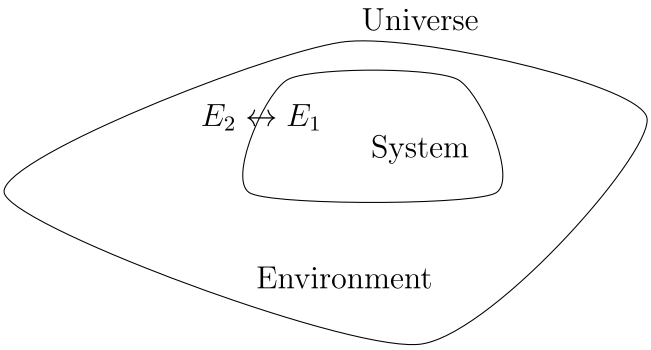

Figure 6.1: Pictorial representation of canonical ensemble.

Globally, energy is conserved and the universe, composed by the union of the system and the environment, can be considered isolated and, therefore, a microcanonical ensemble. This kind of set-up is called canonical ensemble and it has associated a probability density distribution

$$\rho_c(q^i, p_i) = \frac{1}{Z_N} \exp(-\beta H(q^i, p_i)) \ , \tag{6.1}$$

where β is

$$\beta = \frac{1}{k_B T}$$

and Z_N is the partition function

$$Z_N[V,T] = \int_{\mathcal{M}^N} d\Omega \ \exp(-\beta H(q^i, p_i)) \ , \tag{6.2}$$

which depends on the temperature through β and volume and temperature due to the integration domain $\mathcal{M}^N = V \otimes \mathbb{R}^d$. Notice that the probability is a function of the Hamiltonian, like Liouville's theorem said (4.7).

Proof. Consider the universe as a microcanonical ensemble, with associated probability density distribution as

$$\rho_{mc}(q_i^{(1)}, p_i^{(1)}, q_i^{(2)}, p_i^{(2)}) = \frac{1}{\omega(E)}\delta(H(q_i^{(1)}, p_i^{(1)}, q_i^{(2)}, p_i^{(2)}) - E) \ ,$$

where 1 is the system, 2 is the environment and the total Hamiltonian is

$$H(q_i^{(1)}, p_i^{(1)}, q_i^{(2)}, p_i^{(2)}) = H_1(q_i^{(1)}, p_i^{(1)}) + H_2(q_i^{(2)}, p_i^{(2)}) \ .$$

To find the probability density distribution for only the degrees of freedom associated to the system, we have to integrate over the degrees of freedom of the environment to wash them out

$$\rho^{(1)} = \int d\Omega_2 \ \rho_{mc} = \int d\Omega_2 \ \frac{1}{\omega(E)}\delta(H-E) = \frac{1}{\omega(E)} \underbrace{\int dS_{E_2}}_{\omega(E_2)} = \frac{1}{\omega(E)}\omega(E_2 = E-E_1) \ .$$

Notice that this distribution is normalised, since

$$\begin{aligned}
\int d\Omega_1 \ \rho^{(1)} &= \frac{1}{\omega(E)} \int d\Omega_1 \omega(E_2 = E - E_1) \\
&= \frac{1}{\omega(E)} \int_0^E dE_1 \ \underbrace{\int_{S_{E_1}} dS_{H_1}}_{\omega(E-1)} \omega(E_2 = E - E_1) \\
&= \frac{1}{\omega(E)} \underbrace{\int_0^E dE_1 \omega(E_1)\omega(E_2 = E - E_1)}_{\omega(E)} = 1 \ ,
\end{aligned}$$

where the last expression follows from $E = E_1 + E_2$, $d\Omega = d\Omega_1 d\Omega_2$ and

$$\begin{aligned}
\omega(E) &= \int d\Omega\delta(H-E) \\
&= \int d\Omega_1 d\Omega_2 \delta(E-E_1-E_2) \\
&= \int dE_1 \int dE_2 \underbrace{\int_{S_{E_1}} dS_{H_1}}_{\omega(E_1)} \underbrace{\int_{S_{E_2}} dS_{H_2}}_{\omega(E_2)} \delta(E-E_1-E_2) \\
&= \int dE_1 \int dE_2 \omega(E_1)\omega(E_2)\delta(E-E_1-E_2) \\
&= \int dE_1 \omega(E_1)\omega(E_2 = E-E_1) \ .
\end{aligned}$$

In order to compute $\omega(E_2)$, we introduce the entropy

$$S_2(E_2) = k_B \ln \omega_2(E_2) \ .$$

For the considerations made in the microcanonical, at equilibrium entropy is at maximum but if we make small variation δE_1 to E_1, in order to preserve equilibrium, the entropy get Taylor expanded around E as

$$k_B \ln \omega_2(E_2) = S_2(E_2) \simeq S_2(E) + \underbrace{\delta E_2}_{-\delta E_1 \simeq -E_1} \underbrace{\frac{\partial S_2}{\partial E_2}\Big|_{E=E_2}}_{\frac{1}{T}} = S_2(E) - E_1 \frac{1}{T} \ ,$$

where we have used (5.7) and the first thermodynamic relation in (2.10). Hence, the density of states of the system is

$$\omega_2(E_2) = \exp(\frac{S_2(E)}{k_B} - E_1 \frac{1}{k_B T}) = \exp(\frac{S_2(E)}{k_B}) \exp(-\frac{E_1}{k_B T}) \ .$$

Finally, putting together and dropping the indices, we obtain

$$\rho_c = \frac{\omega_2(E_2)}{\omega(E)} = \underbrace{\frac{1}{\omega(E)} \exp(\frac{S_{mc}(E)}{k_B})}_{C} \exp(-\frac{E_1}{k_B T}) = C \exp(-\frac{E_1}{k_B T}) \ , \tag{6.3}$$

where C is a normalisation constant, which can be evaluated by (4.4)

$$1 = \int_{\mathcal{M}^N} d\Omega \rho = \int_{\mathcal{M}^N} d\Omega \ C \exp(-\frac{E_1}{k_B T}) = C \int_{\mathcal{M}^N} d\Omega \ \exp(-\frac{E_1}{k_B T}) \ .$$

q.e.d.

The partition function can also be written as

$$Z_N[T,V] = \int_0^\infty dE\ \omega(E)\exp(-\beta E)\ .$$

Proof. In fact, using (4.9) we have

$$Z_N = \int_{\mathcal{M}^N} d\Omega\exp(-\beta H) = \int_0^\infty dE\ \underbrace{\int dS_E}_{\omega(E)}\ \exp(-\beta H) = \int_0^\infty dE\,\omega(E)\exp(-\beta E)\,.$$

q.e.d.

Now, it is important to distinguish 2 different type of particles: indistinguishable and distinguishable particles. Particles are called indistinguishable if they cannot be distinguished if compared with others and they are distinguishable otherwise. In principle, in classical physics, there are no indistinguishable particles, because even if they all have the same mass, charge, spin, etc, we could always follow their trajectory. Therefore, indistinguishable particles arise only in quantum mechanics, when the uncertainty principle is introduce and the trajectory distinction cannot be made anymore. To take into account this property, we introduce a new term ζ_N, defined as

$$\zeta_N = \begin{cases} 1 & \text{distinguishable} \\ N! & \text{indistinguishable} \end{cases}\ .$$

Hence, the partition function becomes

$$Z_N = \int \frac{\prod_{i=1}^N d^dq^id^dp^i}{h^{dN}\zeta_N}\ \exp(-\beta H) = \int \frac{d\Omega_N}{\zeta_N}\ \exp(-\beta H)\ ,$$

where we have redefined the phase space measure

$$d\Omega_N = \frac{\prod_{i=1}^N d^dq^id^dp_i}{h^{dN}}\ .$$

For distinguishable particles, e.g. particles of n different species with energy $H = \sum_{i=1}^n H_i$ and numbers $N = \sum_{i=1}^n N_i$, the total partition function is the multiplication of single species partition functions

$$Z_N = \prod_{i=1}^n Z_{N_i}\ .$$

Proof. In fact,

$$\begin{aligned} Z_N &= \int_{\mathcal{M}=\mathcal{M}^{(1)}\times\ldots\times\mathcal{M}^{(n)}} d\Omega \ \exp(-\beta H) \\ &= \int_{\mathcal{M}=\mathcal{M}^{(1)}\times\ldots\times\mathcal{M}^{(n)}} \prod_{i=1}^{n} d\Omega_i \ldots d\Omega_n \ \exp(-\beta \sum_{i=1}^{N} H_i) \\ &= \prod_{i=1}^{n} \int_{\mathcal{M}^{(i)}} d\Omega_i \ \exp(-\beta H_i) = \prod_{i=1}^{n} Z_{N_i} \ . \end{aligned}$$

q.e.d.

Example 6.1. If we have only 2 types of particles, the total partition function is

$$Z_N = Z_{N_1} Z_{N_2} \ .$$

Consequently, if all particles are of the same species, and therefore identical, the total partition function is

$$Z_N = (Z_1)^N \ ,$$

where Z_1 the single-particle partition function. If we take into consideration also indistinguishability, for different species, the canonical partition function becomes

$$Z_N = \frac{1}{\zeta_N} \prod_{i=1}^{n} Z_{N_i} \ ,$$

whereas for same species particles, it becomes

$$Z_N = \frac{(Z_1)^N}{\zeta_N} \ .$$

Let $f(q^i, p_i)$ be an observable, then its canonical average is

$$\langle f(q^i, p_i) \rangle_c = \int_{\mathcal{M}} d\Omega \ \rho_c f = \int_{\mathcal{M}} d\Omega \ \frac{\exp(-\beta H)}{Z_N} f \ .$$

6.2 Helmoltz free energy as canonical potential

A local chart with coordinates (T, V, N) is suitable for Helmoltz free energy (2.15). Hence, we need to find an expression for this thermodynamic potential. The first guess is to define the canonical Helmoltz free energy as

$$Z_N[V, T] = \exp(-\beta F[T, V, N]) \ , \tag{6.4}$$

or, equivalently,

$$F[T,V,N] = -\frac{1}{\beta}\ln Z_N \ . \tag{6.5}$$

Furthermore, the canonical internal energy is

$$E = \langle H\rangle_c = \int d\Omega \frac{\exp(-\beta(H))}{Z_N} H \ . \tag{6.6}$$

Proof. By normalisation condition, we have

$$1 = \int d\Omega \frac{\exp(-\beta H)}{Z_N} = \int d\Omega \frac{\exp(-\beta H)}{\exp(-\beta F)} = \int d\Omega \exp(-\beta(H-F)) \ .$$

Now, since F depends on the temperature $F(T)$ or $F(\beta)$, it is possible to derive it with respect to β, where the left handed side is null because it is the derivative of a constant 1, and we obtain

$$\begin{aligned}
0 &= \frac{\partial}{\partial\beta}\Big(\int d\Omega \exp(-\beta(H-F))\Big) \\
&= \int d\Omega \exp(-\beta(H-F))\Big(-(H-F) + \beta\frac{\partial F}{\partial\beta}\Big) \\
&= -\underbrace{\int d\Omega \frac{\exp(-\beta H)}{Z_N} H}_{E} + F\underbrace{\int d\Omega \frac{\exp(-\beta H)}{Z_N}}_{1} + \beta\frac{\partial F}{\partial\beta}\underbrace{\int d\Omega \frac{\exp(-\beta H)}{Z_N}}_{1} \\
&= -E + F + \beta\frac{\partial F}{\partial\beta} \ .
\end{aligned}$$

Hence, using the first expression of (2.16), we find

$$F = E - \beta\frac{\partial F}{\partial\beta} = E + T\frac{\partial F}{\partial T} = E - TS \ ,$$

where in the first step we have used

$$\beta\frac{\partial}{\partial\beta} = \frac{1}{k_B}T\frac{\partial T}{\partial\beta}\frac{\partial}{\partial T} = \frac{1}{k_B T}\Big(\frac{\partial}{\partial T}\frac{1}{k_B T}\Big)^{-1}\frac{\partial}{\partial T} = -\frac{1}{T}T^2\frac{\partial}{\partial T} = -T\frac{\partial}{\partial T} \ .$$

This result shows explicitly that F is indeed the Helmotz free energy (2.13). q.e.d.

Notice that canonical entropy can be written as

$$S_c = \frac{E-F}{T} \ . \tag{6.7}$$

An useful expression for the internal energy is

$$E = -\frac{\partial}{\partial\beta}\ln Z_N \ , \tag{6.8}$$

Proof. Using (6.6),

$$E = \int d\Omega \frac{\exp(-\beta H)}{Z_N} H = -\frac{1}{Z_N}\frac{\partial}{\partial\beta}\int d\Omega \exp(-\beta H)$$
$$= -\frac{1}{Z_N}\frac{\partial Z_N}{\partial\beta} = -\frac{\partial}{\partial\beta}\ln Z_N \ ,$$

where we have used the trick to extract the derivative with respect to β. q.e.d.

The universal Boltzmann's formula is valid also in this ensemble

$$S_c = -k_B\langle\ln\rho_c\rangle_c \ .$$

Proof. In fact, using (6.6), (6.7) and (6.5)

$$\begin{aligned}
-k_B\langle\ln\rho_c\rangle_c &= -k_B\int d\Omega\rho_c\ln\rho_c \\
&= -k_B\int d\Omega\rho_c\ln\frac{\exp(-\beta H)}{Z_N} \\
&= -k_B\int d\Omega\rho_c\ln\exp(-\beta H) - k_B\int d\Omega\rho_c\ln Z_N \\
&= k_B\beta\underbrace{\int d\Omega\rho_c H}_{E} - k_B\underbrace{\ln Z_N}_{\beta F}\underbrace{\int d\Omega\rho_c}_{1} \\
&= \frac{E-F}{T} = S_c \ .
\end{aligned}$$

q.e.d.

6.3 Equipartition theorem

An important theorem, that can be proved in the canonical ensemble, is the famous equipartition theorem. In this section, we will proved a generalised version of it.

Theorem 6.1 (Generalised equipartition theorem)
Let $\xi \in [a,b]$ be a sympletic coordinate. Let ξ_j with $j \neq 1$ be all the other ones. Suppose also

$$\int\prod_{j\neq 1} d\xi_j[\xi_1\exp(-\beta H)]_a^b = 0 \ . \tag{6.9}$$

Then

$$\langle\xi_1\frac{\partial H}{\partial\xi_1}\rangle_c = k_B T \ . \tag{6.10}$$

Proof. By normalisation condition, we have

$$1 = \int d\Omega \, \frac{\exp(-\beta H)}{Z_N} = \frac{1}{Z_N} \int d\xi_1 \prod_{j\neq 1} d\xi_j \, \exp(-\beta H) \ ,$$

where we have omitted dimensional and indistinguishability factors for convenience. Now, using a differential relation, which is equivalent to an intergation by parts,

$$d(\xi_1 \exp(-\beta H)) = d\xi_1 \exp(-\beta H) + \xi \exp(-\beta H)(-\beta)\frac{\partial H}{\partial \xi_1} d\xi_1 \ ,$$

we invert it

$$d\xi_1 \exp(-\beta H) = d(\xi_1 \exp(-\beta H)) + \beta \xi \exp(-\beta H)\frac{\partial H}{\partial \xi_1} d\xi_1$$

and we insert it to find

$$\begin{aligned}
1 &= \frac{1}{Z_N} \int (\prod_{j\neq 1} d\xi_j)(d(\xi_1 \exp(-\beta H)) + \beta \xi \exp(-\beta H)\frac{\partial H}{\partial \xi_1} d\xi_1) \\
&= \underbrace{\frac{1}{Z_N} \prod_{j\neq 1} d\xi_j [\xi_1 \exp(-\beta H)]_a^b}_{0} + \frac{\beta}{Z_N} \int \underbrace{\prod_{j\neq 1} d\xi_j d\xi_1}_{d\Omega} \ \xi_1 \frac{\partial H}{\partial \xi_1} \exp(-\beta H) \\
&= \beta \int d\Omega \ \xi_1 \frac{\partial H}{\partial \xi_1} \frac{\exp(-\beta H)}{Z_N} \\
&= \beta \langle \xi_1 \frac{\partial H}{\partial \xi_1} \rangle_c
\end{aligned}$$

where we have used the hypothesis (6.9). Hence

$$\langle \xi_1 \frac{\partial H}{\partial \xi_1} \rangle_c = \frac{1}{\beta} = k_B T \ .$$

q.e.d.

One may wonder which are the physical systems that satisfy the strange condition (6.9). Examples are systems with Hamiltonian composed by a quadratic momentum (with $a = -\infty$ and $b = \infty$) or a confining potential which go to infinity on the extremes a and b. For the first case, we have $p \in (-\infty, \infty)$, $H = H(p^2)$ and

$$p \exp(-\beta p^2)\Big|_{-\infty}^{\infty} = 0 \ ,$$

whereas for the second case, we have $q \in [a, b]$, $V = V(q)$ such that $V(a) = V(b) = \infty$ and

$$q \exp(-\beta V(q))\Big|_a^b = 0 \ .$$

Corollary 6.1 (Equipartition theorem)
If ξ_1 appears quadratically in H, then its contribution to E is $\frac{1}{2}k_BT$.

Proof. Consider $H = A\xi_1^2 + B\xi_j^2$ with $j \neq 1$, then by the means of the previous theorem, we obtain

$$\langle \xi_1 \frac{\partial H}{\partial \xi_1} \rangle_c = \langle \xi 2A\xi_1 \rangle_c = k_BT \ ,$$

hence

$$\langle A\xi_1^2 \rangle_c = \frac{1}{2}k_BT \ .$$

q.e.d.

Example 6.2. Consider a perfect gas, composed by N particles in 3 dimension, with Hamiltonian $H = \sum_{i=1}^{3N} \frac{p_i^2}{2m}$. Applying the equipartition theorem, since there are $3N$ quadratic momenta terms, the energy is $E = \frac{3}{2}Nk_BT$.

Example 6.3. Consider a system composed by N uncoupled harmonic oscillators of masses m_i and frequencies ω_i in 3 dimension with Hamiltonian $H = \sum_{i=1}^{3N} \frac{p_i^2}{2m_i} + \frac{m_i\omega_i q_i^2}{2}$. Applying the equipartition theorem, since there are $3N$ quadratic momenta terms and $3N$ quadratic coordinates terms, the energy is $E = 3Nk_BT$, known as the Dulong-Petit laws for the specific heat at constant volume $C_V = 3Nk_B$.

Chapter 7

Grand canonical ensemble

7.1 Grand canonical probability density distribution

Consider a physical system which can exchange both energy and matter with the environment, so that the boundary conditions are fixed T, V and μ. Notice that chemical potential has substituted number of particle. Physically, it can be thought as the system is immersed in a bigger reservoir with $N_S \ll N_E$ and $V_S \ll V_E$ but at equilibrium with the same temperature $T_S = T_E = T$. See Figure 7.1.

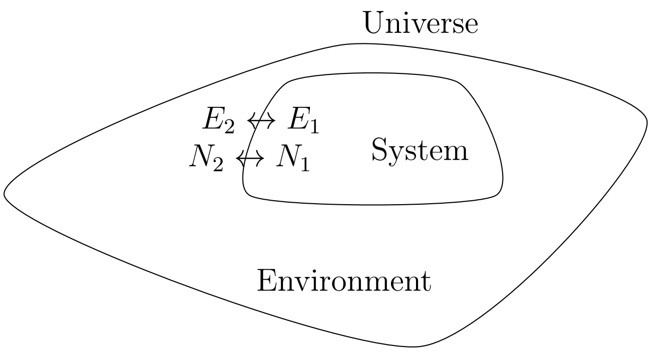

Figure 7.1: Pictorial representation of grand canonical ensemble.

Globally, number of particles is conserved and the universe, composed by the union of the system and the environment, can be considered a canonical ensemble. In fact we suppose that first we have gone from microcanonical to canonical. This kind of set-up is called grand canonical ensemble and it has associated a probability density distribution

$$\rho_c(q^i, p_i) = \frac{z^N}{\mathcal{Z}} \exp(-\beta H(q^i, p_i, N)) \ , \tag{7.1}$$

where z is the fugacity

$$z = \exp(\beta\mu)$$

and $\mathcal{Z}$ is the grand canonical partition function

$$\mathcal{Z}(z, V, T) = \sum_{N=0}^{\infty} z^N Z_N = \sum_{N=0}^{\infty} z^N \int_{\mathcal{M}^N} d\Omega \exp(-\beta H) \ , \tag{7.2}$$

which depends on fugacity z explicitly, the temperature through β and volume and temperature due to the integration domain $\mathcal{M}^N = V \otimes \mathbb{R}^d$. Notice that the probability is a function of the Hamiltonian, like Liouville's theorem said (4.7).

Proof. Consider the universe as a canonical ensemble, with associated probability density distribution is

$$\rho_c(q_i^{(1)}, p_i^{(1)}, q_i^{(2)}, p_i^{(2)}) = \frac{\exp(-\beta H(q_i^{(1)}, p_i^{(1)}, q_i^{(2)}, p_i^{(2)}))}{Z_N[T, V]} \ ,$$

where 1 is the system, 2 is the environment and the total Hamiltonian is

$$H(q_i^{(1)}, p_i^{(1)}, q_i^{(2)}, p_i^{(2)}) = H_1(q_i^{(1)}, p_i^{(1)}) + H_2(q_i^{(2)}, p_i^{(2)}) \ .$$

Following the same procedure used in the canonical ensemble, we integrate over the degrees of freedom of the environment

$$\begin{aligned}
\rho^{(1)} &= \int d\Omega_2 \ \rho_c \\
&= \int d\Omega_2 \frac{\exp(-\beta(H_1 + H_2))}{Z_N} \\
&= \exp(-\beta H_1) \frac{1}{Z_N} \underbrace{\int d\Omega_2 \exp(-\beta H_2)}_{Z_{N_2}} \\
&= \exp(-\beta H_1) \frac{Z_{N_2}[T, V_2]}{Z_N[T, V]} \ ,
\end{aligned}$$

where we have written explicitly the factor $N!$. Now, we have to find the normalisation factor for the distribution. We start from the normalisation condition

$$\begin{aligned}
1 &= \sum_{N_1=0}^{N} \int_{\mathcal{M}^{N_1}} d\Omega_1 \ \rho_{gc} \\
&= \sum_{N_1=0}^{N} \int_{\mathcal{M}^{N_1}} d\Omega_1 \ \exp(-\beta H_1) \frac{Z_{N_2}[T, V_2]}{Z_N[T, V]} \ .
\end{aligned}$$

Now, since the normalisation changes with the number of particles, we explicitate this dependence in the phase space measure by writing the factor $1/N!$. Hence, recalling that the canonical partition function is an integral, we obtain

$$
\begin{aligned}
&\sum_{N_1=0}^{N} \frac{N!}{N_1!N_2!} \int_{\mathcal{M}^{N_1}} d\Omega_1 \ \exp(-\beta H_1) \frac{Z_{N_2}[T,V_2]}{Z_N[T,V]} \\
&= \sum_{N_1=0}^{N} \frac{N!}{N_1!N_2} \frac{\int_{\mathcal{M}^{N_1}} d\Omega_1 \ \exp(-\beta H_1) \int_{\mathcal{M}^{N_2}} d\Omega_2 \ \exp(-\beta H_2)}{\int_{\mathcal{M}^N} d\Omega \ \exp(-\beta H)} \\
&= \sum_{N_1=0}^{N} \frac{N!}{N_1!N_2} \frac{(V_1)^{N_1}(V_2)^{N_2}}{V^N} \frac{\frac{\int_{\mathcal{M}^{N_1}} d\Omega_1 \ \exp(-\beta H_1)}{(V_1)^{N_1}} \frac{\int_{\mathcal{M}^{N_2}} d\Omega_2 \ \exp(-\beta H_2)}{(V_2)^{N_2}}}{\frac{\int_{\mathcal{M}^N} d\Omega \ \exp(-\beta H)}{V^N}} \ .
\end{aligned}
$$

Going into the thermodynamic limit, we at once recognise that the last term is equal to 1

$$
\lim_{td} \frac{\frac{\int_{\mathcal{M}^{N_1}} d\Omega_1 \ \exp(-\beta H_1)}{(V_1)^{N_1}} \frac{\int_{\mathcal{M}^{N_2}} d\Omega_2 \ \exp(-\beta H_2)}{(V_2)^{N_2}}}{\frac{\int_{\mathcal{M}^N} d\Omega \ \exp(-\beta H)}{V^N}} = 1 \ ,
$$

On the other hand, using $N = N_1 + N_2$, the remaining term can be rewritten as

$$
\sum_{N_1=0}^{N} \frac{N!}{N_1!N_2!} \frac{(V_1)^{N_1}(V_2)^{N_2}}{V^N} = \sum_{N_1=0}^{N} \binom{N}{N_1} \left(\frac{V}{V}\right)^{N_1} \left(\frac{V_2}{V}\right)^{N-N_1} = \left(\frac{V_1+V_2}{V}\right)^{N} \ ,
$$

where we have used

$$
(a+b)^n = \sum_{i=1}^{n} \binom{n}{i} a^i b^{n-i} \ ,
$$

which in the thermodynamic limit goes as well to 1

$$
\lim_{td} \left(\frac{V_1+V_2}{V}\right)^{N} = 1 \ .
$$

Hence

$$
\lim_{td} \sum_{N_1=0}^{N} \frac{N!}{N_1!N_2!} \int_{\mathcal{M}^{N_1}} d\Omega_1 \ \exp(-\beta H_1) \frac{Z_{N_2}[T,V_2]}{Z_N[T,V]} = 1 \ .
$$

Now, using (6.4) and (2.16), we Taylor expand at the first order in $N_1 \ll N = N_2$ and $V_1 \ll V_2 = V$ and we obtain

$$
\begin{aligned}
\frac{Z_{N_2}[T,V]}{Z_N[T,V]} &= \frac{\exp(-\beta F(T,N_2,V_2))}{\exp(-\beta F(T,N,V))} \\
&= \exp(-\beta(F(T,N-N_1,V-V_1) - F(T,N,V))) \\
&\simeq \exp(-\beta(\underbrace{\frac{\partial F}{\partial N}\bigg|_{T,V}}_{\mu}(-N_1) + \underbrace{\frac{\partial F}{\partial V}\bigg|_{T,N}}_{-p}(-V_1))) \\
&= \exp(-\beta(-\mu N_1 + pV_1)) \ .
\end{aligned}
$$

Hence, we drop the indices and we find

$$\begin{aligned}
\rho_{gc} &= \frac{\exp(-\beta H)}{N!}\exp(-\beta(-\mu N + pV)) \\
&= \frac{\exp(-\beta H)}{N!}\underbrace{\exp(\beta\mu)^N}_{z^N}\exp(-\beta pV) \\
&= \frac{z^N\exp(-\beta H)}{N!}\exp(-\beta pV)\ ,
\end{aligned}$$

where we have introduced the fugacity $z = \exp(\beta\mu)$. Finally, using the normalisation condition, we obtain

$$\begin{aligned}
1 &= \sum_{N=0}^{\infty}\int_{\mathcal{M}^N} d\Omega\rho_{gc} \\
&= \sum_{N=0}^{\infty}\int_{\mathcal{M}^N} d\Omega\frac{z^N\exp(-\beta H)}{N!}\exp(-\beta pV) \\
&= \exp(-\beta pV)\sum_{N=0}^{\infty} z^N \underbrace{\int_{\mathcal{M}^N} d\Omega N!\exp(-\beta H)}_{Z_N} \\
&= \exp(-\beta pV)\underbrace{\sum_{N=0}^{\infty} z^N Z_N}_{\mathcal{Z}} \\
&= \exp(-\beta pV)\mathcal{Z}\ .
\end{aligned}$$

Therefore

$$\mathcal{Z} = \sum_{N=0}^{\infty} z^N Z_N = \exp(\beta pV) \tag{7.3}$$

and

$$\rho_{gc}(q_i,p_i) = \frac{\exp(-\beta(H(q_i,p_i)-\mu N))}{\mathcal{Z}} = \frac{\exp(-\beta\mathfrak{H}(q_i,p_i))}{\mathcal{Z}}\ ,$$

where $\mathfrak{H} = H - \mu N$ is the grand canonical hamiltonian. q.e.d.

Let $f(q^i, p_i)$ be an observable, then its grancanonical average is

$$\begin{aligned}
\langle f(q^i, p_i)\rangle_{gc} &= \sum_{N=0}^{\infty} \int_{\mathcal{M}} d\Omega\ \rho_{gc} f_N \\
&= \sum_{N=0}^{\infty} \int_{\mathcal{M}} d\Omega\ \frac{\exp(-\beta(H-\mu N))}{\mathcal{Z}} f_N \\
&= \frac{1}{\mathcal{Z}} \sum_{N=0}^{\infty} z^N Z_N \int_{\mathcal{M}} d\Omega \frac{\exp(-\beta H)}{Z_N} f_N \\
&= \frac{1}{\mathcal{Z}} \sum_{N=0}^{\infty} z^N Z_N \langle f_N\rangle_c\ ,
\end{aligned}$$

which shows that we can compute it from the canonical average.

7.2 Grand potential as grand canonical potential

A local chart with coordinates (T, V, μ) is suitable for grand potential (2.26). Hence, we need to find an expression for this thermodynamic potential. The first guess is to define the grand canonical grand potential as

$$\mathcal{Z} = \exp(-\beta\Omega[T, V, \mu])\ , \tag{7.4}$$

or, equivalently,

$$\Omega = -\frac{1}{\beta} \ln \mathcal{Z}\ . \tag{7.5}$$

Proof. It is indeed the grand potential, using (2.31) and (7.3)

$$\mathcal{Z} = \exp(-\beta\Omega) = \exp(\beta p V)\ .$$

q.e.d.

The grand canonical internal energy is defined as

$$E = \langle H\rangle_{gc} = \sum_{N=0}^{\infty} \int_{\mathcal{M}} d\Omega\ \frac{\exp(-\beta(H-\mu N))}{\mathcal{Z}} H\ , \tag{7.6}$$

but we can be also compute it with

$$E = -\frac{\partial}{\partial\beta} \ln \mathcal{Z}\Big|_z\ . \tag{7.7}$$

Proof. In fact, using (7.1)

$$
\begin{aligned}
E &= \sum_{N=0}^{\infty} \int d\Omega \, \frac{\exp(-\beta(H+\mu N))}{\mathcal{Z}} H \\
&= -\sum_{N=0}^{\infty} \frac{z^N}{\mathcal{Z}} \frac{\partial}{\partial \beta} \underbrace{\int d\Omega \exp(-\beta H)}_{Z_N} \\
&= -\frac{1}{\mathcal{Z}} \frac{\partial}{\partial \beta} \underbrace{\sum_{N=0}^{\infty} z^N Z_N}_{\mathcal{Z}} \Big|_z \\
&= -\frac{1}{\mathcal{Z}} \frac{\partial}{\partial \beta} \mathcal{Z} \Big|_z \, ,
\end{aligned}
$$

where we have used the trick to extract the derivative with respect to β, keeping z constant. q.e.d.

The grand canonical number of particles is defined as

$$
N = \langle N \rangle_{gc} = \sum_{N=0}^{\infty} \int_{\mathcal{M}} d\Omega \, \frac{\exp(-\beta(H-\mu N))}{\mathcal{Z}} N \, , \tag{7.8}
$$

but we can be also compute it with

$$
N = z \frac{\partial}{\partial z} \ln \mathcal{Z} \Big|_T \, . \tag{7.9}
$$

Proof. In fact, using (7.1)

$$
\begin{aligned}
N &= \sum_{N=0}^{\infty} z^N Z_N N = \frac{z}{\mathcal{Z}} \sum_{N=0}^{\infty} N z^{N-1} Z_N = \frac{z}{\mathcal{Z}} \frac{\partial}{\partial z} \sum_{N=0}^{\infty} z^N Z_N \Big|_T \\
&= \frac{z}{\mathcal{Z}} \frac{\partial}{\partial z} \mathcal{Z} \Big|_T = z \frac{\partial}{\partial z} \ln \mathcal{Z} \Big|_T \, ,
\end{aligned}
$$

where we have used the trick to extract the derivative with respect to z, keeping T constant. q.e.d.

The universal Boltzmann's formula is still valid in this ensemble

$$
S_{gc} = -k_B \langle \ln \rho_{gc} \rangle_{gc} \, .
$$

Proof. Using (7.5), (7.6), (7.8) and the inverse of (2.24)

$$
\begin{aligned}
-k_B\langle \ln \rho_{gc}\rangle_{gc} &= -k_B \int d\Omega\ \rho_{gc} \ln \rho_{gc} \\
&= -k_B \sum_{N=0}^{\infty} \frac{z^N}{\mathcal{Z}} \int d\Omega\ \exp(-\beta H) \ln \rho_{gc} \\
&= -k_B \sum_{N=0}^{\infty} \frac{z^N}{\mathcal{Z}} \int d\Omega\ \exp(-\beta H)(-\beta H + \beta\mu N + \ln \mathcal{Z}) \\
&= k_B\beta \underbrace{\sum_{N=0}^{\infty} \frac{z^N}{\mathcal{Z}} \int d\Omega\ \exp(-\beta H) H}_{E} - k_B\beta\mu \underbrace{\sum_{N=0}^{\infty} \frac{z^N}{\mathcal{Z}} \int d\Omega\ \exp(-\beta H) N}_{N} \\
&\quad + k_B \ln \mathcal{Z} \underbrace{\sum_{N=0}^{\infty} \frac{z^N}{\mathcal{Z}} \int d\Omega\ \exp(-\beta H)}_{1} \\
&= \frac{E - \mu N - \Omega}{T} = S\ .
\end{aligned}
$$

q.e.d.

Chapter 8

Entropy and counting of states

In this chapter, we will introduce entropy using a different approach. Standardly, enetropy is defined by the 2nd law of thermodynamic (1.6), which tells us also that an equilibrium system is characterised to be the configuration with maximum entropy. However, in the microcanonical ensembl, entropy is defined in terms of the number of states (5.3) or by the Boltzmann's universal law (5.8)

$$S = -k_B \langle \ln \rho \rangle = k_B \ln \Sigma = \lim_{td} S_{td} \ .$$

Now, consider a system in the canonical ensemble with a discrete set of energy values (but it can be generalise for the grancanonical one and for continuous energy levels) and with associated probability density distribution (6.1)

$$\rho_c(E_r) = \frac{\exp(-\beta E_r)}{Z_N} \ ,$$

where the canonical partition function (6.2)is

$$Z_N = \int_{\mathcal{M}^N} d\Omega \ \exp(-\beta H(q^i, p_i)) = \int_0^\infty dE \int_{S_E} dS_E \ \exp(-\beta E) \simeq \sum_{r=1}^{p} g_r \exp(-\beta E_r)$$

and g_r is the multiplicity or degeneracy, i.e. how many levels have the same energy. Notice that it known only the energy levels, the the completely description of the microscopic degrees of freedom.

So far, we have started from an a-priori probability density distribution, based on the knowledge of phase space (microstates, equations of motion, ergodicity, etc), and at the end we have derived the entropy. However, we will change the picture and do the converse: the probability distibution is the one corresponding to maximum entropy, given the macroscopic constains. Entropy becomes the starting concept and the distribution the inference. Quantitavitely, we introduce the Shannon's information entropy

$$H = -\sum_{i=1}^{N} p_i \ln p_i \ . \tag{8.1}$$

It is the only function, up to constants, that, given a random variable x such that it has N possible outcomes x_i with probability p_i, has the following properties

1. it is continuous with p_i,
2. is monotonically increasing with N,
3. it is invariant under compositions of subsystems, i.e. independent on the choice of how we collect in group, e.g. a dice can be collected in even and odd numbers or in greater and less than a fixed number.

8.1 Inference problem

To study this problem, we need to investigate the concept of probability. In ensemble theory, the probability is interpreted to be objective, since it can be obtained by studying the infinite-limit of frequency and occurencies. On the other hand, probability can be associated to the human ignorance and expectation values are given by available information. Now, we have to solve the inference problem: given certain constraints for a function $\langle f \rangle$, what is the expectation value for another function g? The answer can be found with the principle of maximum entropy, subjected to Lagrange multipliers given by the constraints

$$\sum_{i=1}^{N} p_i = 1 \ , \quad \sum_{i=1}^{N} p_i f(x_i) = \langle f(x) \rangle \ .$$

Hence, the problem reduces to maximise the constrained entropy

$$H = -\sum_{i=1}^{N} p_i \ln p_i + \alpha\Big(\sum_{i=1}^{N} p_i - 1\Big) + \beta\Big(\sum_{i=1}^{N} p_i f(x_i) - \langle f \rangle\Big) + \text{other constraints} \dots \ . \tag{8.2}$$

In particular, we can manipulate the first term and express the result in terms of how many states are occupied. In fact, if we introduce the number of ways $W_{\{n_r\}}$ we can find n_r systems with energy E_r, given a set of discrete energy levels E_r, each of degeneracy g_r on which we distribute n_r particles, the inference problem transforms into finding the density distribution n_r^*, i.e. the one which maximises (8.2), with entropy

$$S = \ln W_{\{n_r\}}$$

and constraint on energy and number of particles

$$N = \sum_r n_r \ , \quad E = \sum_r n_r E_r \ .$$

Finally, in order to count $W_{\{n_r\}}$, we need to take into account distinguishablility of particles. Therefore, we decomposed it into two terms

$$W_{\{n_r\}} = W^{(1)}_{\{n_r\}} W^{(2)}_{\{n_r\}} \ , \tag{8.3}$$

where $W^{(1)}_{\{n_r\}}$ counts in how many we can put n_r particles in the energy level E_r and $W^{(2)}_{\{n_r\}}$ takes into account the degeneracy of these levels. In this way, under the assumption of validity of Stirling's approximation (large number of particles) and of smoothness of n_r, Boltzmann's classical, Fermi-Dirac's and Bose-Einstein's quantum distributions can be all derived.

Part III

Applications of classical statistical mechanics

Chapter 9

Microcanonical ensemble

9.1 Non-relativistic ideal gas in d-dimensions

Consider a non-relativistic ideal (non-interacting) gas of N particles in an d-dimensional manifold with a finite volume V^N: $\mathcal{M}_N = V^N \times \mathbb{R}^{dN}$. Its hamiltonian is

$$H = \sum_i \frac{p_i^2}{2m} \ .$$

The number of states $\Sigma(E)$ is

$$\Sigma(E) = \frac{2V^N}{\xi_N dN\Gamma(dN/2)} \left(\frac{2\pi m E}{h^2}\right)^{dN/2} \ .$$

Proof. By definition,

$$\Sigma(E) = \int_{H(q_i,p_i)\leq E} d\Omega = \int_{H(q_i,p_i)\leq E} \frac{\prod_i d^d q_i d^d p_i}{h^{dN}\xi_N} = \frac{1}{h^{dN}\xi_N} \int_{H(q_i,p_i)\leq E} \prod_i d^d q_i d^d p_i \ .$$

From the energy,

$$H = \sum_i \frac{p_i^2}{2m} \leq E \ ,$$

$$\sum_i p_i^2 \leq 2mE \ .$$

Hence, by the volume of a dN-sphere of radius $\sqrt{2mE}$ (A.1),

$$\begin{aligned}\Sigma(E) &= \frac{1}{h^{dN}\xi_N}\int_{\sum_i p_i^2\le 2mE}\prod_i d^dq_i d^dp_i \\ &= \frac{1}{h^{dN}\xi_N}\underbrace{\int_{V^N}\prod_i d^dq_i}_{V^N}\underbrace{\int_{\sum_i p_i^2\le 2mE}\prod_i d^dp_i}_{\frac{\pi^{dN/2}(2mE)^{dN/2}}{\Gamma(dN/2+1)}} \\ &= \frac{V^N}{h^{dN}\xi_N}\frac{\pi^{dN/2}(2mE)^{dN/2}}{\Gamma(dN/2+1)} \\ &= \left(\frac{2\pi mE}{h^2}\right)^{dN/2}\frac{2V^N}{\Gamma(dN/2)\xi_N dN}\ .\end{aligned}$$

q.e.d.

The density state $\omega(E)$ is

$$\omega(E) = \frac{V^N}{\xi_N\Gamma(dN/2)}\left(\frac{2\pi m}{h^2}\right)^{\frac{dN}{2}}E^{dN/2-1}\ .$$

Proof. By definition,

$$\begin{aligned}\omega(E) &= \frac{\partial\Sigma(E)}{\partial E} \\ &= \frac{\partial}{\partial E}\left(\frac{2\pi mE}{h^2}\right)^{dN/2}\frac{2V^N}{\Gamma(dN/2)\xi_N dN} \\ &= \left(\frac{2\pi m}{h^2}\right)^{dN/2}\frac{2V^N}{\Gamma(dN/2)\xi_N dN}\frac{\partial E^{dN/2}}{\partial E} \\ &= \left(\frac{2\pi m}{h^2}\right)^{dN/2}\frac{2V^N}{\Gamma(dN/2)\xi_N dN}\frac{dN}{2}E^{dN/2-1} \\ &= \frac{V^N}{\xi_N\Gamma(dN/2)}\left(\frac{2\pi m}{h^2}\right)^{\frac{dN}{2}}E^{dN/2-1}\ .\end{aligned}$$

q.e.d.

Notice that

$$\omega(E) = \frac{dN}{2E}\Sigma(E)\ , \quad \Gamma(E) = \omega(E)\Delta E = \frac{dN}{2E}\Sigma(E)\Delta E\ . \tag{9.1}$$

As a consequence, in the thermodynamic limit, we have the following equivalent relations

$$\lim_{TD}\frac{\ln\Gamma(E)}{N} = \lim_{TD}\frac{\ln\omega(E)}{N} = \lim_{TD}\frac{\ln\Sigma(E)}{N}\ .$$

Proof. Observing (9.1), we find that the logarithmic expression differs only for factors $\ln \Delta E$ and $\ln \frac{dN}{2E}$, which are neglectible in the thermodynamic limit since they do not scale as N. q.e.d.

The entropy is

$$\frac{S}{k_B} = \ln \Gamma(E) = \ln \omega(E) + \ln \Delta E = \ln \Sigma(E) = \ln \Sigma(E) + \ln \frac{dN}{2E} + \ln \Delta E \ ,$$

In the thermodynamic limit, it becomes

$$S = k_B \begin{cases} \frac{d}{2}N + N\ln\left(V(\frac{4\pi mE}{dNh^2})^{d/2}\right) & \text{for distinguishable particles} \\ \frac{d+2}{2}N + N\ln\left(\frac{V}{N}(\frac{4\pi mE}{dNh^2})^{d/2}\right) & \text{for indistinguishable particles} \end{cases} .$$

Proof. By definition, using the Stirling approximation (B.1),

$$\begin{aligned}
\frac{S}{k_B} &= \ln \Sigma(E) \\
&= \ln\left(\frac{2V^N}{\xi_N dN\Gamma(dN/2)}\left(\frac{2\pi mE}{h^2}\right)^{dN/2}\right) \\
&= \cancel{\ln 2} + N\ln V - \ln \xi_N - \cancel{\ln d} - \cancel{\ln N} - \ln\Gamma(dN/2) + N\ln\left(\frac{2\pi mE}{h^2}\right)^{d/2} \\
&= N\ln V - \ln\xi_N - \underbrace{\ln\Gamma(dN/2)}_{\frac{dN}{2}\ln\frac{dN}{2}-\frac{dN}{2}} + N\ln\left(\frac{2\pi mE}{h^2}\right)^{d/2} \\
&= N\ln V - \ln\xi_N - \frac{dN}{2}\ln\frac{dN}{2} + \frac{dN}{2} + N\ln\left(\frac{2\pi mE}{h^2}\right)^{d/2} \\
&= N\ln V - \ln\xi_N - N\ln\left(\frac{dN}{2}\right)^{d/2} + \frac{dN}{2} + N\ln\left(\frac{2\pi mE}{h^2}\right)^{d/2} \\
&= -\ln\xi_N + \frac{dN}{2} + N\ln\left(V(\frac{4\pi mE}{dNh^2})^{d/2}\right) .
\end{aligned}$$

Now, we treat the distinguishable and indistinguishable case separately. For distinguishable particles $\xi_N = 1$, we find

$$\frac{S}{k_B} = -\ln 1 + \frac{dN}{2} + N\ln\left(V\frac{4\pi mE}{dNh^2}\right)^{d/2} = \frac{d}{2}N + N\ln\left(V(\frac{4\pi mE}{dNh^2})^{d/2}\right) .$$

For indistinguishable particles $\xi_N = N!$, we find

$$\begin{aligned}
\frac{S}{k_B} &= -\underbrace{\ln N!}_{N\ln N - N} + \frac{dN}{2} + N\ln\left(V(\frac{4\pi mE}{dNh^2})^{d/2}\right) \\
&= -N\ln N + N + \frac{dN}{2} + N\ln\left(V(\frac{4\pi mE}{dNh^2})^{d/2}\right) \\
&= \frac{d+2}{2}N + N\ln\left(\frac{V}{N}(\frac{4\pi mE}{dNh^2})^{d/2}\right) .
\end{aligned}$$

q.e.d.

The internal energy is

$$E = \frac{dNk_BT}{2} \ .$$

Proof. By (??)

$$\frac{1}{T} = \frac{\partial S}{\partial E} = k_B \frac{dN}{2}\frac{\partial}{\partial E}\ln E = k_B \frac{dN}{2E} \ ,$$

hence

$$E = \frac{dNk_BT}{2} \ .$$

q.e.d.

The equation of state is

$$pV = Nk_BT \ .$$

Proof. By (??)

$$\frac{p}{T} = \frac{\partial S}{\partial V} = k_B N \frac{\partial}{\partial V}\ln V = k_B \frac{N}{V} \ ,$$

hence

$$pV = Nk_BT \ .$$

q.e.d.

9.2 Non-relativistic ideal gas in 3-dimensions

Now, consider the case in which $d = 3$. The number of states $\Sigma(E)$ is

$$\Sigma(E) = \frac{2V^N}{\xi_N dN \Gamma(3N/2)}\left(\frac{2\pi m E}{h^2}\right)^{3N/2} \ .$$

The density state $\omega(E)$ is

$$\omega(E) = \frac{V^N}{\xi_N \Gamma(3N/2)}\left(\frac{2\pi m}{h^2}\right)^{\frac{3N}{2}} E^{3N/2-1} \ .$$

Notice that

$$\omega(E) = \frac{3N}{2E}\Sigma(E) \ , \quad \Gamma(E) = \omega(E)\Delta E = \frac{3N}{2E}\Sigma(E)\Delta E \ .$$

The entropy is

$$\frac{S}{k_B} = \ln \Gamma(E) = \ln \omega(E) + \ln \Delta E = \ln \Sigma(E) = \ln \Sigma(E) + \ln \frac{3N}{2E} + \ln \Delta E \ ,$$

In the thermodynamic limit, it becomes

$$S = k_B \begin{cases} \frac{3}{2}N + N \ln \left(V (\frac{4\pi m E}{3Nh^2})^{3/2} \right) & \text{for distinguishable particles} \\ \frac{5}{2}N + N \ln \left(\frac{V}{N} (\frac{4\pi m E}{3Nh^2})^{3/2} \right) & \text{for indistinguishable particles} \end{cases} .$$

The internal energy is

$$E = \frac{3}{2} N k_B T \ .$$

The equation of state is

$$pV = N k_B T \ .$$

9.3 Gas of harmonic oscillators in 3-dimensions

Consider a non-relativistic (non-interacting) gas of N particles in an d-dimensional manifold confined by an harmonic potential of frequency ω. Its hamiltonian is

$$H = \sum_i \left(\frac{p_i^2}{2m} + \frac{m\omega^2}{2} q_i^2 \right) .$$

The number of states $\Sigma(E)$ is

$$\Sigma(E) = \frac{1}{\xi_N \Gamma(dN/2) dN} \left(\frac{2\pi E}{h\omega} \right)^{dN} .$$

Proof. By definition,

$$\Sigma(E) = \int_{H(q_i,p_i) \le E} d\Omega = \int_{H(q_i,p_i) \le E} \frac{\prod_i d^d q_i d^d p_i}{h^{dN} \xi_N} = \frac{1}{h^{dN} \xi_N} \int_{H(q_i,p_i) \le E} \prod_i d^d q_i d^d p_i \ .$$

We make a change of variable into x_j, with $j = 1, \ldots 2dN$,

$$p_i = \sqrt{2mE} x_j \ , \quad q_i = \sqrt{\frac{2E}{m\omega^2}} x_{dN+j} \ .$$

The differentials become

$$dp_i = \sqrt{2mE} dx_j \ , \quad dq_i = \sqrt{\frac{2E}{m\omega^2}} dx_{dN+j} \ .$$

From the energy,

$$H = \sum_i \left(\frac{p_i^2}{2m} + \frac{m\omega^2}{2} q_i^2 \right) \le E \ ,$$

$$\sum_j x_j^2 \le 1 \ .$$

Hence, by the volume of a $2dN$-sphere of radius 1 (A.1),

$$\begin{aligned}
\Sigma(E) &= \frac{1}{h^{dN}\xi_N} \int_{\sum_i \left(\frac{p_i^2}{2m} + \frac{m\omega^2}{2} q_i^2 \right) \le E} \prod_i d^d q_i d^d p_i \\
&= \frac{1}{h^{dN}\xi_N} (2mE)^{dN/2} \left(\frac{2E}{m\omega^2} \right)^{dN/2} \underbrace{\int_{\sum_j x_j^2 \le 1} \prod_j dx_j}_{\frac{\pi^{dN}}{\Gamma(dN+1)}} \\
&= \frac{1}{\xi_N \Gamma(dN+1)} \left(\frac{2\pi E}{h\omega} \right)^{dN} \\
&= \frac{1}{\xi_N \Gamma(dN) dN} \left(\frac{2\pi E}{h\omega} \right)^{dN} \ .
\end{aligned}$$

q.e.d.

The density state $\omega(E)$ is

$$\omega(E) = \frac{1}{\xi_N \Gamma(dN)} \left(\frac{2\pi}{h\omega} \right)^{dN} E^{dN-1} \ .$$

Proof. By definition,

$$\begin{aligned}
\omega(E) &= \frac{\partial \Sigma(E)}{\partial E} \\
&= \frac{\partial}{\partial E} \frac{1}{\xi_N \Gamma(dN) dN} \left(\frac{2\pi E}{h\omega} \right)^{dN} \\
&= \frac{1}{\xi_N \Gamma(dN) dN} \left(\frac{2\pi}{h\omega} \right)^{dN} \frac{\partial}{\partial E} E^{dN} \\
&= \frac{1}{\xi_N \Gamma(dN) dN} \left(\frac{2\pi}{h\omega} \right)^{dN} dN E^{dN-1} \\
&= \frac{1}{\xi_N \Gamma(dN)} \left(\frac{2\pi}{h\omega} \right)^{dN} E^{dN-1} \ .
\end{aligned}$$

q.e.d.

In the thermodynamic limit, the entropy becomes

$$S = k_B \begin{cases} dN + N\ln\left(\frac{2\pi E}{h\omega dN}\right)^d & \text{for distinguishable particles} \\ (d+1)N + N\ln\left(\frac{1}{N}(\frac{2\pi E}{h\omega dN})^d\right) & \text{for indistinguishable particles} \end{cases} .$$

Proof. By definition, using the Stirling approximation (B.1),

$$\begin{aligned}
\frac{S}{k_B} &= \ln \Sigma(E) \\
&= \ln \frac{1}{\xi_N \Gamma(dN/2) dN}\left(\frac{2\pi E}{h\omega}\right)^{dN} \\
&= -\ln \xi_N - \ln\Gamma(dN) - \cancel{\ln d} - \cancel{\ln N} + N\ln\left(\frac{2\pi E}{h\omega}\right)^d \\
& - \ln \xi_N - \underbrace{\ln\Gamma(dN)}_{dN\ln(dN)-dN} + N\ln\left(\frac{2\pi E}{h\omega}\right)^d \\
&= -\ln \xi_N - dN\ln(dN) + dN + N\ln\left(\frac{2\pi E}{h\omega}\right)^d \\
&= -\ln \xi_N + dN + N\ln\left(\frac{2\pi E}{h\omega dN}\right)^d .
\end{aligned}$$

Now, we treat the distinguishable and indistinguishable case separately. For distinguishable particles $\xi_N = 1$, we find

$$\frac{S}{k_B} = -\ln 1 + dN + N\ln\left(\frac{2\pi E}{h\omega dN}\right)^d = dN + N\ln\left(\frac{2\pi E}{h\omega dN}\right)^d .$$

For indistinguishable particles $\xi_N = N!$, we find

$$\begin{aligned}
\frac{S}{k_B} &= -\underbrace{\ln N!}_{N\ln N - N} + dN + N\ln\left(\frac{2\pi E}{h\omega dN}\right)^d \\
&= -N\ln N + N + dN + N\ln\left(\frac{2\pi E}{h\omega dN}\right)^d \\
&= (d+1)N + N\ln\left(\frac{1}{N}\frac{2\pi E}{h\omega dN}\right)^d .
\end{aligned}$$

q.e.d.

The internal energy is

$$E = dNk_BT .$$

Proof. By (**??**)

$$\frac{1}{T} = \frac{\partial S}{\partial E} = k_B dN \frac{\partial}{\partial E} \ln E = k_B \frac{dN}{E} \ ,$$

hence

$$E = dNk_BT \ .$$

q.e.d.

Chapter 10

Canonical ensemble

10.1 Non-relativistic ideal gas in d-dimensions

Consider an indistinguishable non-relativistic ideal (non-interacting) gas of N particles in an d-dimensional manifold with a finite volume V^N: $\mathcal{M}_N = V^N \times \mathbb{R}^{dN}$. If we did not confined the particles is a finite volume, we would have found undesidered divergences. Its hamiltonian is

$$H = \sum_i \frac{p_i^2}{2m} \ .$$

The canonical partition function Z is

$$Z = \frac{V^N}{\xi_N \lambda_T^{dN}} = \frac{V^N}{\xi_N} (\frac{2m\pi}{\beta h^2})^{dN/2} \ .$$

Proof. By definition, using the gaussian integral (C.1),

$$
\begin{aligned}
Z &= \int_{\mathcal{M}^N} d\Omega \exp(-\beta H(q_i,p_i)) \\
&= \int_{\mathcal{M}^N} \frac{\prod_i d^d q_i d^d p_i}{h^{dN}\xi_N} \exp(-\beta H(q_i,p_i)) \\
&= \frac{1}{h^{dN}\xi_N} \int_{\mathcal{M}^N} \prod_i d^d q_i d^d p_i \exp(-\beta H(q_i,p_i)) \\
&= \frac{1}{h^{dN}\xi_N} \underbrace{\int_{V^N} \prod_i d^d q_i}_{V^N} \underbrace{\prod_i \int_{\mathcal{M}^N} d^d p_i \exp(-\beta \frac{p_i^2}{2m})}_{(\frac{2m\pi}{\beta})^{dN/2}} \\
&= \frac{V^N}{h^{dN}\xi_N} (\frac{2m\pi}{\beta})^{dN/2} \\
&= \frac{V^N}{\xi_N} (\frac{2m\pi}{\beta h^2})^{dN/2} \\
&= \frac{V^N}{\xi_N \lambda_T^{dN}}
\end{aligned}
$$

where we have defined the thermal wavelength

$$
\lambda_T = \sqrt{\frac{\beta h^2}{2m\pi}} \ .
$$

q.e.d.

For indistinguishable particles, the canonical partition function Z is

$$
Z = \frac{V^N}{N!\lambda_T^{dN}} = \frac{V^N}{N!}(\frac{2m\pi}{\beta h^2})^{dN/2} \ .
$$

An useful intermediary formula is

$$
\ln Z = N(1 - \ln(\frac{N}{V}\lambda_T^d)) = N(1 - \ln(n\lambda_T^d)) \ .
$$

Proof. In fact, using the Stirling approximation (B.1),

$$\begin{aligned}
\ln Z &= \ln \frac{V^N}{N!\lambda_T^{dN}} \\
&= N\ln(V\lambda_T^d) - \underbrace{\ln N!}_{N\ln N - N} \\
&= N - N\frac{V\lambda_T^d}{N} \\
&= N(1-\ln(\frac{N}{V}\lambda_T^d)) \\
&= N(1-\ln(n\lambda_T^d)) \ ,
\end{aligned}$$

where we have defined the density

$$n = \frac{N}{V} \ .$$

q.e.d.

The internal energy E is

$$E = \frac{d}{2}Nk_BT \ .$$

Proof. By (??)

$$\begin{aligned}
E &= -\frac{\partial \ln Z}{\partial \beta} \\
&= -\frac{\partial}{\partial\beta}N(1-\ln(n\lambda_T^d)) \\
&= -Nd\frac{\partial}{\partial\beta}\ln(\lambda_T) \\
&= -Nd\frac{\partial}{\partial\beta}\ln(\beta^{1/2}) \\
&= \frac{Nd}{2}\frac{1}{\beta} \\
&= \frac{d}{2}Nk_BT \ .
\end{aligned}$$

q.e.d.

The Helmoltz free energy F is

$$F = \frac{N}{\beta}(\ln(n\lambda_T^d) - 1) \ .$$

Proof. By (**??**)

$$F = -\frac{\ln Z}{\beta} = \frac{N}{\beta}(\ln(n\lambda_T^d) - 1) \ .$$

q.e.d.

The entropy S is

$$S = Nk_B\Big(\frac{d+2}{2} - \ln(n\lambda_T^d)\Big) \ .$$

Proof. By (**??**)

$$\begin{aligned} S &= \frac{E-F}{T} \\ &= \frac{1}{T}\Big(\frac{d}{2}Nk_BT - \frac{N}{\beta}(\ln(n\lambda_T^d) - 1)\Big) \\ &= \frac{N}{\beta T}\Big(\frac{d+2}{2} - \ln(n\lambda_T^d)\Big) \\ &= Nk_B\Big(\frac{d+2}{2} - \ln(n\lambda_T^d)\Big) \end{aligned}$$

q.e.d.

Entropy becomes negative at a certain critical temperature

$$T_c = \frac{2m\pi k_B}{h^2}e^{(d+2)/2}n^{-2/d} \ .$$

Proof. In fact, $S < 0$ for

$$Nk_B\Big(\frac{d+2}{2} - \ln(n\lambda_T^d)\Big) < 0 \ ,$$

$$\frac{d+2}{2} - \ln(n\lambda_T^d) < 0 \ ,$$

$$\frac{d+2}{2} < \ln(n\lambda_T^d) \ ,$$

$$e^{(d+2)/2} < n\lambda_T^d \ ,$$

$$e^{(d+2)/2} < n\Big(\frac{h^2\beta}{2m\pi}\Big)^{d/2} \ ,$$

$$e^{(d+2)/d}n^{2/d} < \frac{h^2\beta}{2m\pi} \ ,$$

$$\frac{2m\pi}{h^2}e^{(d+2)/2}n^{-2/d} < \beta \ ,$$

hence

$$T < \frac{2m\pi k_B}{h^2} e^{(d+2)/2} n^{-2/d} = T_c \ .$$

q.e.d.

The equation of state is

$$pV = Nk_BT \ . \tag{10.1}$$

Proof. By(**??**)

$$p = -\frac{\partial F}{\partial V} = -\frac{\partial}{\partial V}\frac{N}{\beta}(\ln(n\lambda_T^d) - 1) = \frac{N}{\beta}\frac{\partial}{\partial V}\ln V = \frac{N}{V\beta} \ ,$$

hence

$$pV = Nk_BT \ .$$

q.e.d.

The chemical potential μ is

$$\mu = frac1\beta \ln(n\lambda_T^d) \ .$$

Proof. By (**??**)

$$\mu = \frac{\partial F}{\partial N} = \frac{\partial}{\partial N}\frac{N}{\beta}(\ln(n\lambda_T^d) - 1) = \frac{1}{\beta}(\ln(n\lambda_T^d) - \cancel{1}) + \cancel{\frac{1}{\beta}} = frac1\beta \ln(n\lambda_T^d) \ .$$

q.e.d.

The specific heats C_V and C_p are

$$C_V = N\frac{d}{2}k_B \ , \quad C_p = N\frac{d+2}{2}k_B \ .$$

Proof. At V constant

$$C_V = \frac{\partial E}{\partial T} = \frac{\partial}{\partial T}\frac{d}{2}Nk_BT = N\frac{d}{2}k_B \ .$$

At p constant, using (10.1)

$$C_p = C_V + p\frac{\partial V}{\partial T} == C_V + p\frac{\partial}{\partial T}\frac{Nk_BT}{p} = N\frac{d}{2}k_B + Nk_B = \frac{d+2}{2}k_B \ .$$

q.e.d.

10.2 Non-relativistic ideal gas in 3-dimensions

Now, consider the case in which $d = 3$. For indistinguishable particles, the canonical partition function Z is

$$Z = \frac{V^N}{N!\lambda_T^{3N}} = \frac{V^N}{N!}(\frac{2m\pi}{\beta h^2})^{3N/2} \ .$$

The internal energy E is

$$E = \frac{3}{2}Nk_BT \ .$$

The Helmoltz free energy F is

$$F = \frac{N}{\beta}(\ln(n\lambda_T^3) - 1) \ .$$

The entropy S is

$$S = Nk_B\Big(\frac{5}{2} - \ln(n\lambda_T^3)\Big) \ .$$

Entropy becomes negative at a certain critical temperature

$$T_c = \frac{2m\pi k_B}{h^2}e^{3/2}n^{-2/3} \ .$$

A plot of this is in Figure 10.1.

The equation of state is

$$pV = Nk_BT \ .$$

The chemical potential μ is

$$\mu = \frac{1}{\beta}\ln(n\lambda_T^3) \ .$$

A plot of this is in Figure 10.2.

The specific heats C_V and C_p are

$$C_V = N\frac{3}{2}k_B \ , \quad C_p = N\frac{5}{2}k_B \ .$$

Notice that there are two problems: entropy cannot be negative and the specific heat $C_V \to 0$ for $T \to 0$, by thermodynamics. This means that this model is not correct and we must go quantum.

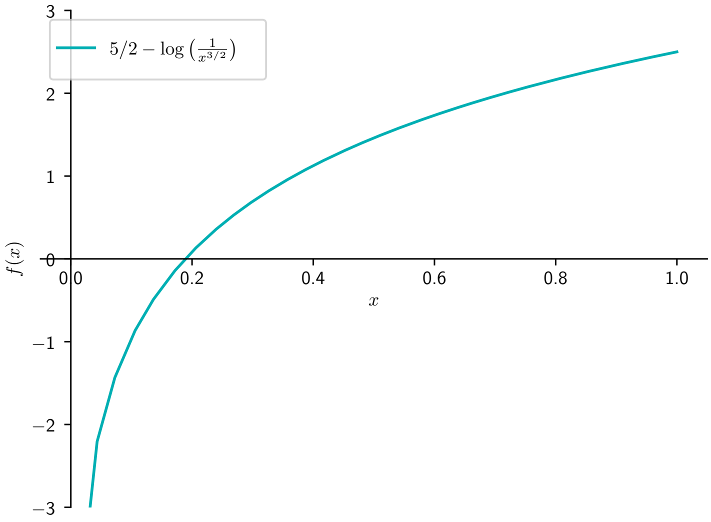

Figure 10.1: A plot of the entropy S as a function of T. We have used $x = \frac{2\pi m k_B T n^{2/3}}{h^2}$ and $f(x) = \frac{S}{N k_B}$.

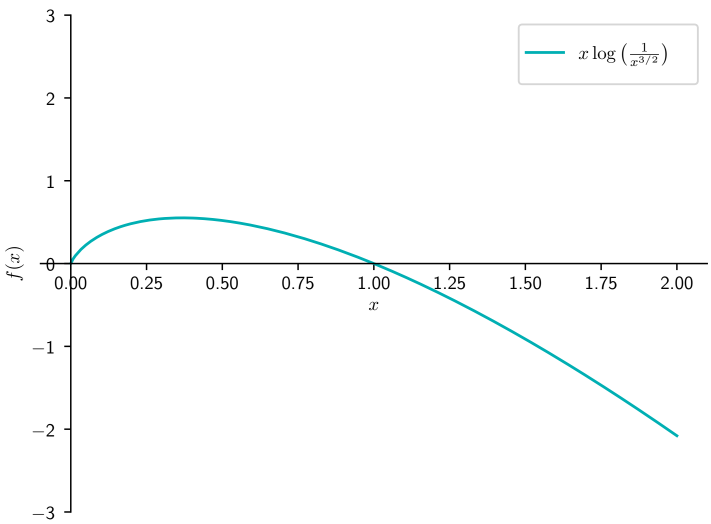

Figure 10.2: A plot of the chemical potential μ as a function of T. We have used $x = \frac{2\pi m k_B T n^{2/3}}{h^2}$ and $f(x) = \frac{2\pi m \mu}{h^2 n^{3/2}}$.

10.3 Gas of harmonic oscillators in d-dimensions

Consider a distinguishable non-relativistic (non-interacting) gas of N particles in an d-dimensional manifold confined by an harmonic potential of frequency ω. Its hamiltonian is

$$H = \sum_i \left(\frac{p_i^2}{2m} + \frac{m\omega^2}{2} q_i^2\right) .$$

The canonical partition function Z is

$$Z = \frac{1}{\xi_N} \left(\frac{2\pi k_B T}{h\omega}\right)^{dN} .$$

Proof. By definition, using the gaussian integral (C.1),

$$\begin{aligned}
Z &= \int_{\mathcal{M}^N} d\Omega \exp(-\beta H(q_i, p_i)) \\
&= \int_{\mathcal{M}^N} \frac{\prod_i d^d q_i d^d p_i}{h^{dN} \xi_N} \exp(-\beta H(q_i, p_i)) \\
&= \frac{1}{h^{dN} \xi_N} \int_{\mathcal{M}^N} \prod_i d^d q_i d^d p_i \exp(-\beta H(q_i, p_i)) \\
&= \frac{1}{h^{dN} \xi_N} \underbrace{\int_{V^N} \prod_i d^d q_i \exp(-\beta \frac{m\omega^2}{2} q_i^2)}_{(\frac{2\pi}{m\omega\beta})^{dN/2}} \underbrace{\prod_i \int_{\mathcal{M}^N} d^d p_i \exp(-\beta \frac{p_i^2}{2m})}_{(\frac{2m\pi}{\beta})^{dN/2}} \\
&= \frac{1}{h^{dN} \xi_N} (\frac{2\pi}{m\omega\beta})^{dN/2} (\frac{2m\pi}{\beta})^{dN/2} \\
&= \frac{1}{\xi_N} \left(\frac{2\pi}{h\omega\beta}\right)^{dN} \\
&= \frac{1}{\xi_N} \left(\frac{2\pi k_B T}{h\omega}\right)^{dN} .
\end{aligned}$$

q.e.d.

For distinguishable particles, the canonical partition function Z is

$$Z = \left(\frac{2\pi k_B T}{h\omega}\right)^{dN} = (Z_1)^N .$$

An useful intermediary formula is

$$\ln Z = dN \ln \frac{2\pi k_B T}{h\omega} .$$

Proof. In fact, using the Stirling approximation (B.1),

$$\ln Z = \ln \left(\frac{2\pi k_B T}{h\omega}\right)^{dN} = dN \ln \frac{2\pi k_B T}{h\omega} \ .$$

q.e.d.

The internal energy E is

$$E = dNk_BT \ .$$

Proof. By (**??**)

$$E = -\frac{\partial \ln Z}{\partial \beta} = -\frac{\partial}{\partial \beta} dN \ln \frac{2\pi}{h\omega\beta} = dN\frac{1}{\beta} = dNk_BT \ .$$

q.e.d.

The Helmoltz free energy F is

$$F = \frac{dN}{\beta} \ln \frac{h\omega}{2\pi k_B T} \ .$$

Proof. By (**??**)

$$F = -\frac{\ln Z}{\beta} = -\frac{dN}{\beta} \ln \frac{2\pi k_B T}{h\omega} = \frac{dN}{\beta} \ln \frac{h\omega}{2\pi k_B T} \ .$$

q.e.d.

The entropy S is

$$S = dNk_B(1 - \ln \frac{h\omega}{2\pi k_B T}) \ .$$

Proof. By (**??**)

$$S = \frac{E-F}{T} = \frac{1}{T}\left(dNk_BT - \frac{dN}{\beta} \ln \frac{h\omega}{2\pi k_B T}\right) = dNk_B(1 - \ln \frac{h\omega}{2\pi k_B T}) \ .$$

q.e.d.

Entropy becomes negative at a certain critical temperature

$$T_c = \frac{h\omega}{2\pi k_B e} \ .$$

Proof. In fact, $S < 0$ for

$$dNk_B(1 - \ln\frac{h\omega}{2\pi k_B T}) < 0 \ ,$$

$$1 - \ln\frac{h\omega}{2\pi k_B T} < 0 \ ,$$

$$1 < \ln\frac{h\omega}{2\pi k_B T} \ ,$$

$$e < \frac{h\omega}{2\pi k_B T} \ ,$$

hence

$$T < \frac{h\omega}{2\pi k_B e} = T_c \ .$$

q.e.d.

The equation of state is

$$p = 0 \ . \tag{10.2}$$

Proof. By(**??**)

$$p = -\frac{\partial F}{\partial V} = 0 \ .$$

q.e.d.

The chemical potential μ is

$$\mu = \frac{d}{\beta}\ln\frac{h\omega}{2\pi k_B T} \ .$$

Proof. By (**??**)

$$\mu = \frac{\partial F}{\partial N} = \frac{\partial}{\partial N}\frac{dN}{\beta}\ln\frac{h\omega}{2\pi k_B T} = \frac{d}{\beta}\ln\frac{h\omega}{2\pi k_B T} \ .$$

q.e.d.

The specific heats C_V and C_p are

$$C_V = dNk_B \ , \quad C_p = dNk_B \ .$$

Proof. At V constant

$$C_V = \frac{\partial E}{\partial T} = \frac{\partial}{\partial T} dNk_BT = dNk_B \ .$$

At p constant, using (10.2)

$$C_p = C_V + p\frac{\partial V}{\partial T} == C_V + p\frac{\partial}{\partial T}\frac{Nk_BT}{p} = C_V = dNk_B \ .$$

q.e.d.

10.4 Gas of harmonic oscillators in 1-dimension

Now, consider the case in which $d = 1$. For distinguishable particles, the canonical partition function Z is

$$Z = \left(\frac{2\pi k_BT}{h\omega}\right)^N = (Z_1)^N \ .$$

The internal energy E is

$$E = Nk_BT \ .$$

The Helmoltz free energy F is

$$F = \frac{N}{\beta}\ln\frac{h\omega}{2\pi k_BT} \ .$$

The entropy S is

$$S = Nk_B(1 - \ln\frac{h\omega}{2\pi k_BT}) \ .$$

Entropy becomes negative at a certain critical temperature

$$T_c = \frac{h\omega}{2\pi k_Be} \ .$$

A plot of this is in Figure 10.3.

The equation of state is

$$p = 0 \ .$$

The chemical potential μ is

$$\mu = \frac{1}{\beta}\ln\frac{h\omega}{2\pi k_BT} \ .$$

A plot of this is in Figure 10.4.

The specific heats C_V and C_p are

$$C_V = Nk_B \ , \quad C_p = Nk_B \ .$$

Notice that also here there are two problems: entropy cannot be negative and the specific heat $C_V \to 0$ for $T \to 0$, by thermodynamics. This means that this model is not correct and we must go quantum.

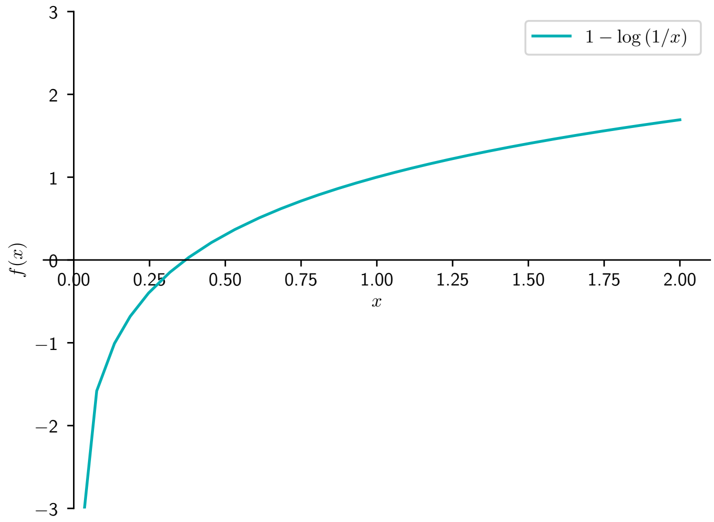

Figure 10.3: A plot of the entropy S as a function of T. We have used $x = \frac{2\pi k_B T}{h\omega}$ and $f(x) = \frac{S}{Nk_B}$.

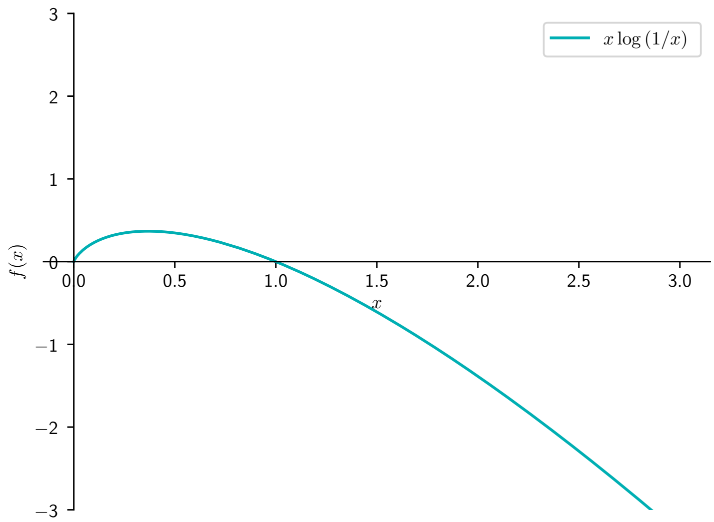

Figure 10.4: A plot of the chemical potential μ as a function of T. We have used $x = \frac{2\pi k_B T}{h\omega}$ and $f(x) = \frac{2\pi\mu}{h\omega}$.

10.5 Ultra-relativistic ideal gas

Consider an indistinguishable ultra-relativistic ideal (non-interacting) gas of N particles in an d-dimensional manifold with a finite volume V^N: $\mathcal{M}_N = V^N \times \mathbb{R}^{dN}$. Its hamiltonian is

$$H = \sum_i c|p_i| \ .$$

The canonical partition function Z is

$$Z = \frac{1}{\xi_N}\left(\frac{8\pi V}{(\beta hc)^3}\right)^N \ .$$

Proof. By definition, using the gaussian integral (C.1),

$$\begin{aligned}
Z &= \int_{\mathcal{M}^N} d\Omega \exp(-\beta H(q_i,p_i)) \\
&= \int_{\mathcal{M}^N} \frac{\prod_i d^3q_i d^3p_i}{h^{3N}\xi_N} \exp(-\beta H(q_i,p_i)) \\
&= \frac{1}{h^{3N}\xi_N} \int_{\mathcal{M}^N} \prod_i d^3q_i d^3p_i \exp(-\beta H(q_i,p_i)) \\
&= \frac{1}{h^{3N}\xi_N} \underbrace{\int_{V^N} \prod_i d^d q_i}_{V^N} \prod_i \int_{\mathcal{M}^N} d^d p_i \exp(-\beta c p_i) \\
&= \frac{V^N}{h^{3N}\xi_N} \prod_i \int_{\mathcal{M}^N} d^d p_i \exp(-\beta c p_i) \ .
\end{aligned}$$

Now, in order to evaluate the integral, we use the polar coordinates in the momentum space (p,θ,ϕ)

$$\prod_i \int_{\mathcal{M}^N} d^3 p_i \exp(-\beta c p_i) = \prod_i 4\pi \int_0^\infty dp\ p^2 \exp(-\beta c p_i)$$

We change variable

$$z = \beta c p \ , \quad dz = -\beta c dp \ ,$$

and we find

$$\prod_i \frac{4\pi}{(\beta c)^3} \underbrace{\int_0^\infty dz\ z^2 \exp(-z)}_{\Gamma(3)} = \prod_i \frac{4\pi}{(\beta c)^3} \underbrace{\Gamma(3)}_{2} = \prod_i \frac{8\pi}{(\beta c)^3} = \left(\frac{8\pi}{(\beta c)^3}\right)^N \ .$$

Therefore

$$Z = \frac{V^N}{h^{3N}\xi_N}\left(\frac{8\pi}{(\beta c)^3}\right)^N = \frac{1}{\xi_N}\left(\frac{8\pi V}{(\beta hc)^3}\right)^N \ .$$

q.e.d.

For indistinguishable particles, the canonical partition function Z is

$$Z = \frac{1}{N!}\Big(\frac{8\pi V}{(\beta hc)^3}\Big)^N \ .$$

An useful intermediary formula is

$$\ln Z = N(1 - \ln\frac{n(\beta hc)^3}{8\pi}) \ .$$

Proof. In fact, using the Stirling approximation (B.1),

$$\begin{aligned}
\ln Z &= \ln\frac{1}{N!}\Big(\frac{8\pi V}{(\beta hc)^3}\Big)^N \\
&= -\underbrace{\ln N!}_{N\ln N - N} + N\ln\frac{8\pi V}{(\beta hc)^3} \\
&= N(1 - \ln\frac{N(\beta hc)^3}{8\pi V}) \\
&= N(1 - \ln\frac{n(\beta hc)^3}{8\pi}) \ ,
\end{aligned}$$

where we have defined the density

$$n = \frac{N}{V} \ .$$

q.e.d.

The internal energy E is

$$E = 3Nk_BT \ .$$

Proof. By (**??**)

$$E = -\frac{\partial \ln Z}{\partial\beta} = -\frac{\partial}{\partial\beta}N(1-\ln\frac{n(\beta hc)^3}{8\pi}) = N\frac{\partial}{\partial\beta}\ln(\beta^3) = 3N\frac{\beta^2}{\beta^3} = 3N\frac{1}{\beta} = 3Nk_BT \ .$$

As an aside, it can be also derived from the generalised equipartion theorem (**??**). In fact

$$k_BT = \langle p_i\frac{\partial H}{\partial p_i}\rangle = \langle p_i\frac{\partial}{\partial p_i}c\sqrt{p_1^2+p_2^2+p_3^2}\rangle = \langle c\frac{p_i^2}{\sqrt{p_1^2+p_2^2+p_3^2}}\rangle \ ,$$

hence

$$\langle H\rangle = \langle c\frac{p_1^2+p_2^2+p_3^2}{\sqrt{p_1^2+p_2^2+p_3^2}}\rangle = \sum_{i=1}^{3}\underbrace{\langle c\frac{p_i^2}{\sqrt{p_1^2+p_2^2+p_3^2}}\rangle}_{k_BT} = 3k_BT \ .$$

q.e.d.

The Helmoltz free energy F is

$$F = \frac{N}{\beta}(\ln \frac{n(\beta hc)^3}{8\pi} - 1) \ .$$

Proof. By (??)

$$F = -\frac{\ln Z}{\beta} = \frac{N}{\beta}(\ln \frac{n(\beta hc)^3}{8\pi} - 1) \ .$$

q.e.d.

The entropy S is

$$S = Nk_B(4 - \ln \frac{n(\beta hc)^3}{8\pi}) \ .$$

Proof. By (??)

$$\begin{aligned} S &= \frac{E - F}{T} \\ &= \frac{1}{T}\Big(3Nk_BT - \frac{N}{\beta}(\ln \frac{n(\beta hc)^3}{8\pi} - 1)\Big) \\ &= 3Nk_B - Nk_B(\ln \frac{n(\beta hc)^3}{8\pi} - 1) \\ &= Nk_B(4 - \ln \frac{n(\beta hc)^3}{8\pi}) \ . \end{aligned}$$

q.e.d.

Entropy becomes negative at a certain critical temperature

$$T_c = \frac{hc}{k_B}\Big(\frac{n}{8\pi e^4}\Big)^{1/3} \ .$$

Proof. In fact, $S < 0$ for

$$Nk_B(4 - \ln \frac{n(\beta hc)^3}{8\pi}) < 0 \ ,$$

$$4 - \ln \frac{n(\beta hc)^3}{8\pi} < 0 \ ,$$

$$4 < \ln \frac{n(\beta hc)^3}{8\pi} \ ,$$

$$e^4 < \frac{n(\beta hc)^3}{8\pi} \ ,$$

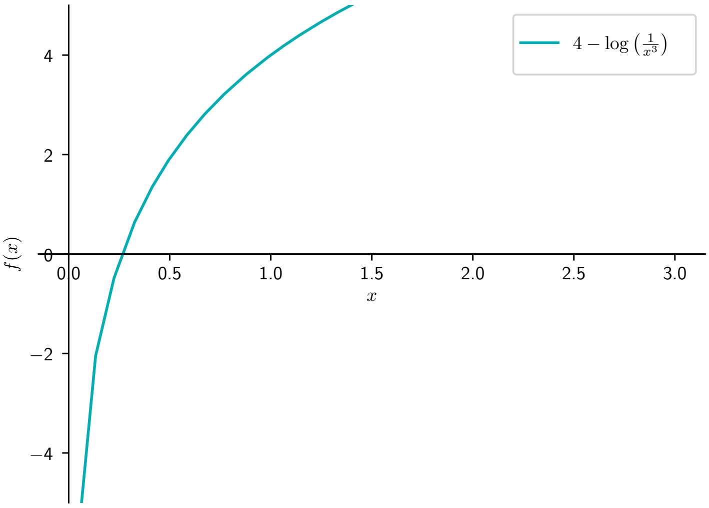

Figure 10.5: A plot of the entropy S as a function of T. We have used $x = \frac{(8\pi)^{1/3} k_B T}{hcn^{1/3}}$ and $f(x) = \frac{S}{Nk_B}$.

$$e^4 < \frac{n(hc)^3}{8\pi k_B^3 T^3} \ ,$$

$$T^3 < \frac{n(hc)^3}{8\pi k_B^3 e^4} \ ,$$

hence

$$T < \frac{hc}{k_B} \left(\frac{n}{8\pi e^4} \right)^{1/3} = T_c \ .$$

q.e.d.

A plot of this is in Figure 10.5.

The equation of state is

$$pV = Nk_B T \ . \tag{10.3}$$

Proof. By(**??**)

$$p = -\frac{\partial F}{\partial V} = -\frac{\partial}{\partial V} \frac{N}{\beta} (\ln \frac{n(\beta hc)^3}{8\pi} - 1) = \frac{N}{\beta} \frac{\partial}{\partial V} \ln V = \frac{N}{V\beta} \ ,$$

hence

$$pV = Nk_B T \ .$$

q.e.d.

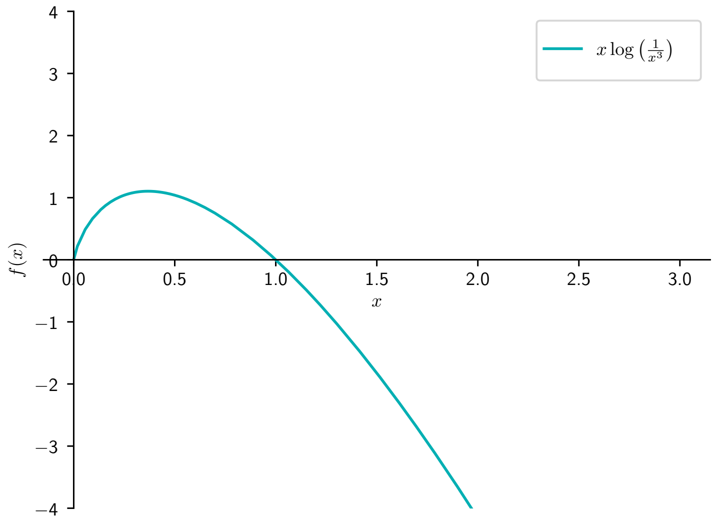

Figure 10.6: A plot of the chemical potential μ as a function of T. We have used $x = \frac{(8\pi)^{1/3}k_B T}{hcn^{1/3}}$ and $f(x) = \frac{(8\pi)^{1/3}\mu}{hcn^{1/3}}$.

The chemical potential μ is

$$\mu = \frac{1}{\beta}\ln\frac{n(\beta hc)^3}{8\pi}\ .$$

Proof. By (??)

$$\mu = \frac{\partial F}{\partial N} = \frac{\partial}{\partial N}\frac{N}{\beta}(\ln\frac{n(\beta hc)^3}{8\pi} - 1) = \frac{1}{\beta}(\ln\frac{n(\beta hc)^3}{8\pi} - 1 + 1) = \frac{1}{\beta}\ln\frac{n(\beta hc)^3}{8\pi}\ .$$

q.e.d.

A plot of this is in Figure 10.6.
The specific heats C_V and C_p are

$$C_V = 3Nk_B\ , \quad C_p = 4Nk_B T\ .$$

Proof. At V constant

$$C_V = \frac{\partial E}{\partial T} = \frac{\partial}{\partial T}3Nk_B T = 3Nk_B\ .$$

At p constant, using (10.3)

$$C_p = C_V + p\frac{\partial V}{\partial T} = C_V + p\frac{\partial}{\partial T}\frac{Nk_BT}{p} = 3Nk_B + Nk_B = 4Nk_BT \ .$$

q.e.d.

10.6 Maxwell-Boltzmann velocity distribution

Consider a non-relativistic ideal (non-interacting) gas of N particles in an 3-dimensional manifold $\mathcal{M}^N = \mathbb{R}^6$, confined into a potential $V(q_i)$. In this discussion we put $h = 1$. Its hamiltonian is

$$H = \sum_i \left(\frac{p_i^2}{2m} + V(q_i)\right) \ .$$

The probability distribution density ρ_c for each particle is

$$\rho_c(q_i, p_i) = \frac{\exp(-\beta(\frac{p_i^2}{2m} + V(q_i)))}{(\frac{2\pi m}{\beta})^{3/2}\int_{\mathbb{R}^3} d^3q \exp(-\beta V(q))} \ .$$

Proof. By definition,

$$\rho_c(q_i, p_i) = \mathcal{N}\exp(-\beta(\frac{p_i^2}{2m} + V(q_i))) \ ,$$

where the normalisation constant is, using the gaussian integral (C.1)

$$\begin{aligned} 1 &= \int_{\mathbb{R}^6}\prod_i d^3q\ d^3p \mathcal{N}\exp(-\beta(\frac{p^2}{2m} + V(q))) \\ &= \mathcal{N}\int_{\mathbb{R}^3} d^3q\ \exp(-\beta V(q)) \underbrace{\int_{\mathbb{R}^3} d^3p\ \exp(-\beta\frac{p^2}{2m})}_{\left(\frac{2\pi m}{\beta}\right)^{3/2}} \\ &= \mathcal{N}\left(\frac{2\pi m}{\beta}\right)^{3/2}\int_{\mathbb{R}^3} d^3q\ \exp(-\beta V(q)) \ , \end{aligned}$$

hence

$$\mathcal{N} = \left(\left(\frac{2\pi m}{\beta}\right)^{3/2}\int_{\mathbb{R}^3} d^3q\ \exp(-\beta V(q))\right)^{-1} \ .$$

q.e.d.

The marginal probability density distribution is

$$\rho(q_i) = \frac{\exp(-\beta V(q_i))}{\int_{\mathbb{R}^3} d^3q \exp(-\beta V(q))} \ .$$

Proof. By definition,

$$\begin{aligned}
\rho(q_i) &= \int_{\mathbb{R}^3} d^3p \ \rho_c(q_i, p) \\
&= \int_{\mathbb{R}^3} d^3p \ \frac{\exp(-\beta(\frac{p^2}{2m} + V(q_i)))}{(\frac{2\pi m}{\beta})^{3/2} \int_{\mathbb{R}^3} d^3q \exp(-\beta V(q))} \\
&= \frac{\exp(-\beta V(q_i))}{\int_{\mathbb{R}^3} d^3q \exp(-\beta V(q))} \cancel{\frac{\int_{\mathbb{R}^3} d^3p \ \exp(-\beta \frac{p^2}{2m})}{(\frac{2\pi m}{\beta})^{3/2}}} \\
&= \frac{\exp(-\beta V(q_i))}{\int_{\mathbb{R}^3} d^3q \exp(-\beta V(q))} \ .
\end{aligned}$$

q.e.d.

If we have a potential defined as

$$V(q) = \begin{cases} 0 & \text{inside a region } \mathcal{A} \\ \infty & \text{outside a region } \mathcal{A} \end{cases} \ ,$$

the probability is null outside this region and uniform inside it.

Proof. In fact

$$\rho(q_i) = \frac{1}{\int_{\mathcal{A}} d^3q} = \frac{1}{\mathcal{A}} \ .$$

q.e.d.

The momentum probability density distribution is

$$\rho(p) = (2\pi m k_B T)^{-3/2} \exp(-\beta \frac{p^2}{2m}) = \prod_i (2\pi m k_B T)^{-1/2} \exp(-\beta \frac{p_i^2}{2m}) \ .$$

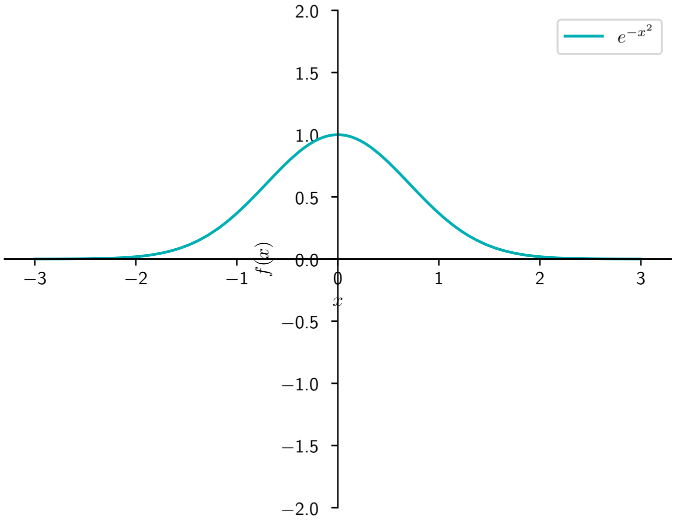

Figure 10.7: A plot of the momentum probability density distribution. We have used $x = \sqrt{\frac{\beta}{2m}}p$ and $f(x) = (2\pi m k_B T)^{3/2}\rho$.

Proof. By definition,

$$\begin{aligned}
\rho(p) &= \int_{\mathbb{R}^3} d^3q \ \rho_c(q,p) \\
&= \int_{\mathbb{R}^3} d^3q \ \frac{\exp(-\beta(\frac{p^2}{2m} + V(q)))}{(\frac{2\pi m}{\beta})^{3/2}\int_{\mathbb{R}^3} d^3q' \exp(-\beta V(q'))} \\
&= \frac{\exp(-\beta\frac{p^2}{2m})}{(\frac{2\pi m}{\beta})^{3/2}} \cancel{\frac{\int_{\mathbb{R}^3} d^3q \ \exp(-\beta V(q))}{\int_{\mathbb{R}^3} d^3q' \exp(-\beta V(q'))}} \\
&= \frac{\exp(-\beta\frac{p^2}{2m})}{(\frac{2\pi m}{\beta})^{3/2}} \\
&= (2\pi m k_B T)^{-3/2} \exp(-\beta\frac{p^2}{2m}) \\
&= \prod_i (2\pi m k_B T)^{-1/2} \exp(-\beta\frac{p_i^2}{2m}) \ .
\end{aligned}$$

q.e.d.

A plot of this is in Figure 10.7.

The velocity probability density distribution is

$$\rho(p) = (\frac{m}{2\pi k_B T})^{1/2} \exp(-\beta \frac{m v_i^2}{2}) \ .$$

Proof. With a change of variable

$$p_i = m v_i \ , \quad \rho(v_i) dv_i = \rho(p_i) dp_i = \rho(p_i) m dv_i \ ,$$

we find

$$\rho(v_i) = m\rho(p_i) = (\frac{2\pi k_B T}{m})^{-1/2} \exp(-\beta \frac{m^2 v_i^2}{2m}) = (\frac{m}{2\pi k_B T})^{1/2} \exp(-\beta \frac{m v_i^2}{2}) \ .$$

q.e.d.

The velocity modulus probability density distribution is

$$\rho(v) = (\frac{m}{2\pi k_B T})^{3/2} 4\pi v^2 \exp(-\beta \frac{m v^2}{2}) \ .$$

Proof. With a change of variable into the polar coordinates (v, θ, ϕ)

$$\rho(v_1, v_2, v_3) dv_1 dv_2 dv_3 = \rho(v_1, v_2, v_3) v^2 \sin\theta d\theta d\phi dv = \rho(\theta, \phi, v) d\theta d\phi dv \ ,$$

we find

$$\rho(v) = 4\pi v^2 \prod_i \rho(v_i) = (\frac{m}{2\pi k_B T})^{3/2} 4\pi v^2 \exp(-\beta \frac{m v^2}{2}) \ .$$

q.e.d.

A plot of this is in Figure 10.8.
The most probable velocity value is

$$v_p = \sqrt{\frac{2 k_B T}{m}} \ .$$

Proof. By definition,

$$0 = \frac{d\rho(v)}{dv} = 2v \exp(-\beta \frac{m v^2}{2}) - \beta m v^3 \exp(-\beta \frac{m v^2}{2}) \ ,$$

hence

$$v_p = \sqrt{\frac{2 k_B T}{m}} \ .$$

q.e.d.

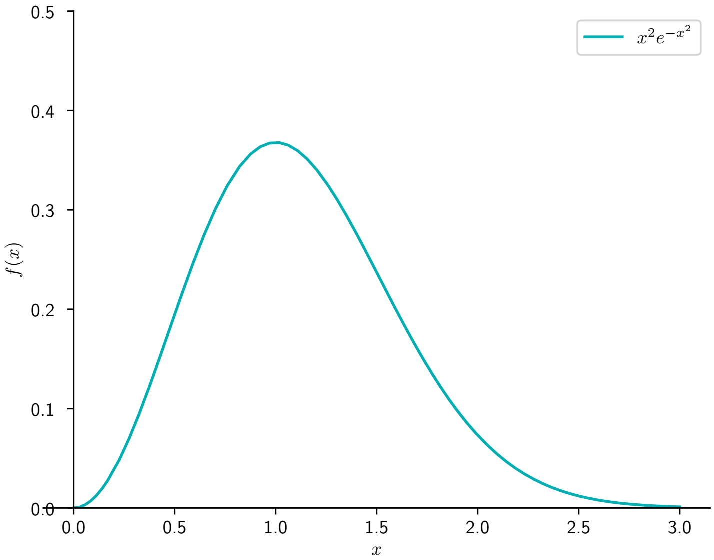

Figure 10.8: A plot of the velocity modulus probability density distribution. We have used $x = \sqrt{\frac{\beta m}{2}}v$ and $f(x) = \rho$.

The mean velocity value is

$$\langle v \rangle = \sqrt{\frac{8k_BT}{\pi m}} \ .$$

Proof. By definition,

$$\langle v \rangle = \int_{\mathbb{R}^3} dv\ \rho(v)v = (\frac{m}{2\pi k_BT})^{3/2} 4\pi \int_{\mathbb{R}^3} dv\ v^3 \exp(-\beta\frac{mv^2}{2}) \ .$$

We make a change of variables

$$t = \frac{m\beta v^2}{2} \ , \quad dt = m\beta v dv \ ,$$

hence

$$\begin{aligned}
\langle v \rangle &= (\frac{m}{2\pi k_BT})^{3/2} 4\pi \left(\frac{2}{m\beta}\right)\frac{1}{m\beta} \underbrace{\int_0^\infty dt\ t\exp(-t)}_{\Gamma(2)} \\
&= \sqrt{\frac{8}{m\pi\beta}} \underbrace{\Gamma(2)}_{1} = \sqrt{\frac{8}{m\pi\beta}} \\
&= \sqrt{\frac{8k_BT}{\pi m}} \ .
\end{aligned}$$

q.e.d.

The mean square velocity value is

$$\langle v^2\rangle = \frac{3k_BT}{m} \ .$$

Proof. By definition,

$$\langle v^2\rangle = \int_{\mathbb{R}^3} dv\ \rho(v)v^2 = (\frac{m}{2\pi k_B T})^{3/2}4\pi \int_{\mathbb{R}^3} dv\ v^4 \exp(-\beta\frac{mv^2}{2}) \ .$$

We make a change of variables

$$t = \frac{m\beta v^2}{2} \ , \quad dt = m\beta v dv \ ,$$

hence

$$\begin{aligned}
\langle v^2\rangle &= (\frac{m}{2\pi k_B T})^{3/2}4\pi\left(\frac{2}{m\beta}\right)\frac{1}{m\beta}\left(\frac{2}{m\beta}\right)^{1/2}\underbrace{\int_0^\infty dt\ t^{3/2}\exp(-t)}_{\Gamma(5/2)} \\
&= \frac{4}{\sqrt{\pi}m\beta}\underbrace{\Gamma(5/2)}_{\frac{3\sqrt{\pi}}{4}} \\
&= \frac{3}{\beta m} \\
&= \frac{3k_BT}{m} \ .
\end{aligned}$$

q.e.d.

10.7 Magnetic solid

A solid, composed by N atoms/molecules with an intrinsic magnetic moment $\boldsymbol{\mu}$ in an external magnetic field $\mathbf{B}$, can be modelled by an hamiltonian

$$H = -\sum_i \boldsymbol{\mu}\cdot\mathbf{B} = -\mu B\sum_i \cos\theta_i \ .$$

where the phase space coordinates are ϕ_i and θ_i.

The canonical partition function Z is

$$Z = \left(\frac{4\pi\sinh(\beta\mu B)}{\beta\mu B}\right)^N \ .$$

Proof. By definition

$$
\begin{aligned}
Z &= \int_{\mathcal{M}} d\Omega \exp(-\beta H(\theta_i)) \\
&= \underbrace{\prod_i \int_0^{2\pi} d\phi_i}_{(2\pi)^N} \prod_i \int_0^{\pi} d\theta_i \ \sin\theta_i \exp(-\beta\mu B\cos\theta_i) \\
&= (2\pi)^N \prod_i \int_0^{\pi} d\theta_i \ \sin\theta_i \exp(-\beta\mu B\cos\theta_i) \ .
\end{aligned}
$$

We make a change of variable

$$
x_i = \cos\theta_i \ , \quad dx_i = -\sin\theta_i d\theta_i \ ,
$$

with extremis

$$
\theta_i = 0 \to x_i = 1 \ , \quad \theta_i = \pi \to x_i = 0 \ ,
$$

hence

$$
\begin{aligned}
Z &= (2\pi)^N \prod_i \int_{-1}^{1} dx_i \ \exp(-\beta\mu B x) \\
&= (2\pi)^N \Big(\frac{\exp(-\beta\mu B x)}{-\beta\mu B}\Big|_{-1}^{1} \Big)^N \\
&= (2\pi)^N \Big(\frac{1}{-\beta\mu B} \underbrace{(\exp(-\beta\mu B) - \exp(\beta\mu B))}_{-2\sinh\beta\mu B} \Big)^N \\
&= (2\pi)^N \Big(\frac{1}{\beta\mu B} (2\sinh(\beta\mu B)) \Big)^N \\
&= \Big(\frac{4\pi\sinh(\beta\mu B)}{\beta\mu B} \Big)^N \ .
\end{aligned}
$$

q.e.d.

An useful intermediary formula is

$$
\ln Z = N \ln \frac{4\pi\sinh(\beta\mu B)}{\beta\mu B} \ .
$$

Proof. In fact,

$$
\ln Z = \ln \Big(\frac{4\pi\sinh(\beta\mu B)}{\beta\mu B} \Big)^N = N \ln \frac{4\pi\sinh(\beta\mu B)}{\beta\mu B} \ .
$$

q.e.d.

The internal energy E is

$$E = -N\mu B(\coth(\beta\mu B) + \frac{1}{\beta\mu B}) \ .$$

Proof. By (??)

$$\begin{aligned}
E &= -\frac{\partial \ln Z}{\partial \beta} \\
&= -\frac{\partial}{\partial \beta} N \ln \frac{4\pi \sinh(\beta\mu B)}{\beta\mu B} \\
&= -N\frac{\partial}{\partial \beta} \ln \sinh(\beta\mu B) + N\frac{\partial}{\partial \beta} \ln \beta \\
&= -N\mu B \coth(\beta\mu B) + \frac{N}{\beta} \\
&= -N\mu B(\coth(\beta\mu B) + \frac{1}{\beta\mu B}) \ .
\end{aligned}$$

To study the limit for $\beta \to 0$ or $T \to \infty$, we Taylor expand for the variable $x = \beta\mu B$

$$\lim_{x\to 0} \frac{E}{N\mu B}(x) \simeq 0 \ ,$$

hence

$$E \xrightarrow{T\to\infty} 0 \ .$$

To study the limit for $\beta \to \infty$ or $T \to 0$, we Taylor expand for the variable $x = \beta\mu B$

$$\lim_{x\to \infty} \frac{E}{N\mu B}(x) \simeq -1 \ ,$$

hence

$$E \xrightarrow{T\to 0} -N\mu B \ .$$

q.e.d.

A plot of this is in Figure 10.9.

The Helmoltz free energy F is

$$F = -\frac{N}{\beta} \ln \frac{4\pi \sinh(\beta\mu B)}{\beta\mu B} \ .$$

Proof. By (??)

$$F = -\frac{\ln Z}{\beta} = -\frac{N}{\beta} \ln \frac{4\pi \sinh(\beta\mu B)}{\beta\mu B} \ .$$

q.e.d.

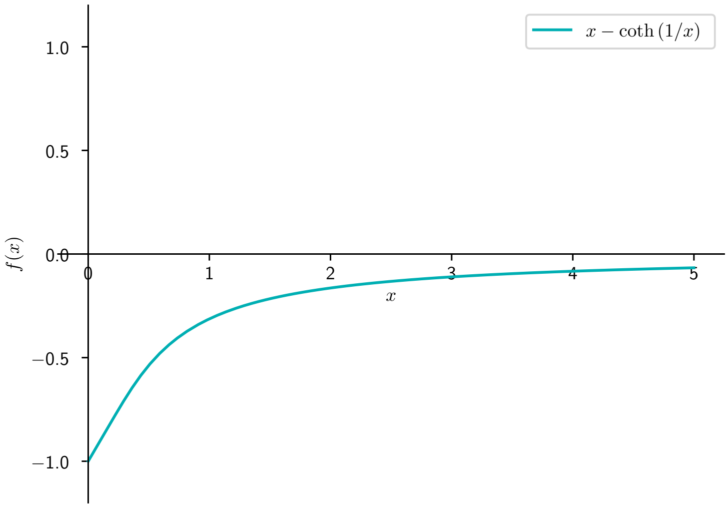

Figure 10.9: A plot of the internal energy E as a function of T. We have used $x = \frac{1}{\beta\mu B}$ and $f(x) = \frac{E}{N\mu B}$.

The entropy S is

$$S = Nk_B\Big(\ln\frac{4\pi\sinh(\beta\mu B)}{\beta\mu B} - \beta\mu B(\coth(\beta\mu B) - \frac{1}{\beta\mu B})\Big) \ .$$

Proof. By (**??**)

$$\begin{aligned} S = \frac{E-F}{T} &= \frac{1}{T}\Big(- N\mu B(\coth(\beta\mu B) + \frac{1}{\beta\mu B}) + \frac{N}{\beta}\ln\frac{4\pi\sinh(\beta\mu B)}{\beta\mu B}\Big) \\ &= Nk_B\Big(\ln\frac{4\pi\sinh(\beta\mu B)}{\beta\mu B} - \beta\mu B(\coth(\beta\mu B) - \frac{1}{\beta\mu B})\Big) \ . \end{aligned}$$

q.e.d.

The intrinsic magnetic moment $\mathbf{M}$ is

$$\mathbf{M} = (0, 0, N\mu(\coth(\beta\mu B) - \frac{1}{\beta\mu B})) \ .$$

Proof. By definition, since we have oriented $\mathbf{B} = (0, 0, B)$,

$$M_x = -\frac{\partial F}{\partial B_x} = M_y = -\frac{\partial F}{\partial B_y} = 0 \ ,$$

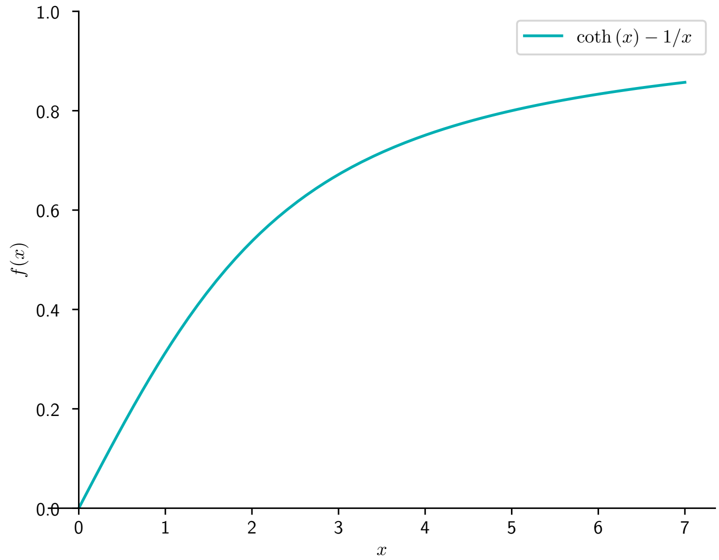

Figure 10.10: A plot of the intrinsic magnetic moment **M** as a function of β. We have used $x = \beta\mu B$ and $f(x) = \frac{M_z}{N\mu}$.

but

$$
\begin{aligned}
M_z &= -\frac{\partial F}{\partial B} \\
&= \frac{\partial}{\partial B}\frac{N}{\beta}\ln\frac{4\pi\sinh(\beta\mu B)}{\beta\mu B} \\
&= \frac{N}{\beta}\frac{\partial}{\partial \beta}\ln\sinh(\beta\mu B) - \frac{N}{\beta}\frac{\partial}{\partial B}\ln B \\
&= N\mu\coth(\beta\mu B) - \frac{N}{\beta B} \\
&= N\mu\Big(\coth(\beta\mu B) - \frac{1}{\beta\mu B}\Big) \ .
\end{aligned}
$$

q.e.d.

A plot of this is in Figure 10.10.
The isothermal susceptibility χ_β is

$$
\chi_\beta = N\mu^2\beta(\frac{1}{(\beta\mu B)^2} - \frac{1}{\sinh^2(\beta\mu H)}) \ .
$$

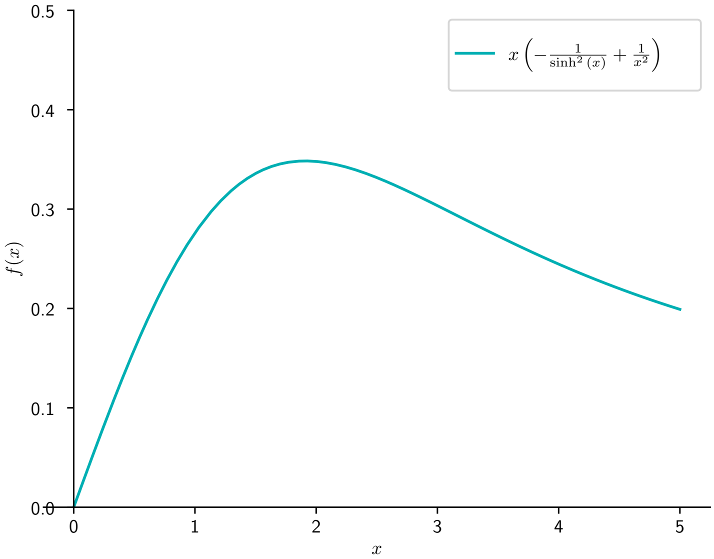

Figure 10.11: A plot of the intrinsic magnetic moment **M** as a function of β. We have used $x = \beta\mu B$ and $f(x) = \frac{B\chi_\beta}{N\mu}$.

Proof. By definition

$$\begin{aligned}
\chi_\beta &= \frac{\partial M}{\partial B} \\
&= \frac{\partial}{\partial B} N\mu(\coth(\beta\mu B) - \frac{1}{\beta\mu B}) \\
&= N\mu(-\frac{\beta\mu}{\sinh^2(\beta\mu B)} + \frac{\beta\mu}{(\beta\mu B)^2}) \\
&= N\mu^2\beta(\frac{1}{(\beta\mu B)^2} - \frac{1}{\sinh^2(\beta\mu H)}) \ .
\end{aligned}$$

q.e.d.

A plot of this is in Figure 10.11.

For $T \to \infty$, the Curie law is

$$\chi_\beta = \frac{C}{T} \ ,$$

where the Curie constant is

$$C = \frac{N\mu^2}{3k_B} \ .$$

Proof. To study the limit for $\beta \to 0$ or $T \to \infty$, we Taylor expand for the variable $x = \beta\mu B$

$$\frac{B\chi_\beta}{N\mu}(x) \simeq \frac{x}{3} + O\left(x^2\right) \ ,$$

hence

$$\frac{B\chi_\beta}{N\mu} = \frac{\beta\mu B}{3} \ ,$$

which means

$$\chi_\beta = \frac{N\mu^2}{3k_B}\frac{1}{T} = \frac{C}{T} \ .$$

q.e.d.

Chapter 11

Grand canonical ensemble

11.1 Non-relativistic ideal gas in d-dimensions

Consider an indistinguishable non-relativistic ideal (non-interacting) gas of N particles in an d-dimensional manifold with a finite volume V^N: $\mathcal{M}_N = V^N \times \mathbb{R}^{dN}$.

Recall that the canonical partition function is

$$Z = \frac{V^N}{N!\lambda_T^{dN}} = \frac{V^N}{N!}(\frac{2m\pi}{\beta h^2})^{dN/2} \ .$$

The grancanonical partition function is

$$\mathcal{Z} = \exp(\frac{zV}{\lambda_T^d}) \ .$$

Proof. By definition, using the Taylor expansion of the exponential,

$$\mathcal{Z} = \sum_{N=0}^{\infty} z^N Z_N = \sum_{N=0}^{\infty} \frac{1}{N!}\left(\frac{zV}{\lambda_T^d}\right)^N = \exp(\frac{zV}{\lambda_T^d}) \ .$$

q.e.d.

The internal energy E is

$$E = \frac{zV}{\lambda_T^d}\frac{d}{2\beta} \ .$$

Proof. By (**??**)

$$
\begin{aligned}
E &= -\frac{\partial \ln \mathcal{Z}}{\partial \beta}\Big|_z \\
&= -\frac{\partial}{\partial \beta} \ln \exp(\frac{zV}{\lambda_T^d}) \\
&= -\frac{\partial}{\partial \beta} \frac{zV}{\lambda_T^d} \\
&= -\frac{1}{zV} \frac{\partial}{\partial \beta} \left(\frac{2m\pi}{\beta h^2}\right)^{d/2} \\
&= -\frac{1}{zV} \left(\frac{2m\pi}{h^2}\right)^{d/2} \frac{\partial}{\partial \beta} \beta^{-d/2} \\
&= \frac{1}{zV} \left(\frac{h^2}{2m\pi}\right)^{d/2} \frac{d}{2} \beta^{-d/2-1} \\
&= \frac{zV}{\lambda_T^d} \frac{d}{2\beta} \ .
\end{aligned}
$$

q.e.d.

The number of particle N is

$$N = \frac{V}{\lambda_T^d} \ .$$

Proof. By (**??**)

$$N = z \frac{\partial}{\partial z} \ln \mathcal{Z} = z \frac{\partial}{\partial z} \frac{zV}{\lambda_T^d} = \frac{V}{\lambda_T^d} \ .$$

q.e.d.

The equation of state is

$$p = \frac{z}{\beta \lambda_T^d} \ .$$

Proof. By definition

$$p = \frac{1}{\beta V} \ln \mathcal{Z} = \frac{1}{\beta V} \frac{zV}{\lambda_T^d} = \frac{z}{\beta \lambda_T^d} \ .$$

q.e.d.

11.2 Virial expansion and Van der Waals gases

Consider the basic equations (of state) of the grand canonical ensemble (7.5) and (7.9)

$$\Omega = -pV = -\frac{1}{\beta}\ln \mathcal{Z} \ , \quad N = z\frac{\partial}{\partial z}\ln \mathcal{Z} \ . \tag{11.1}$$

The goal of the virial expansion is to expand the equations of state in powers of the density $n = N/V$ or in the inverse of the specific volume $v = V/N$. The system we are treating is a gas of particles with the same mass m and with an interacting potential depending only on the reciprocate distance

$$H = \sum_{i=1}^{N}\frac{p_i^2}{2m} + \sum_{i<j} U_{ij} = \sum_{i=1}^{N}\frac{p_i^2}{2m} + \sum_{i<j} U(|q_i - q_j|) \ .$$

The grand canonical partition function (7.2) can be considered a series expansion in terms of $z \ll 1$

$$\mathcal{Z} = \sum_{N=0}^{\infty} z^N Z_N \simeq 1 + zZ_1 + z^2 Z_2 + \dots \ .$$

Notice that an expansion is $z \ll 1$ means indeed an expansion in density $n \ll 1$, which physically is a diluite gas.

At first order, we have

$$\mathcal{Z} \simeq 1 + zZ_1 + O(z^2) \ ,$$

where the partition function for 1 particle is

$$Z_1 = \frac{V}{\lambda_T^3}$$

and λ_T^3 is the thermal wavelength

$$\lambda_T = \sqrt{\frac{\beta h^2}{2\pi m}} \ .$$

Proof. In fact, using (6.2), the gaussian integral (C.1) and not considering the potential, since 1 particle does not interact with itself,

$$Z_1 = \int_{\mathcal{M}^1} d\Omega \exp(-\beta H) = \int_V \int_{\mathbb{R}^3} \frac{d^3q\, d^3p}{h^3} \exp(-\beta\frac{p^2}{2m}) = \underbrace{\int_V d^3q}_{V} \underbrace{\int_{\mathbb{R}^3} \frac{d^3p}{h^3} \exp(-\beta\frac{p^2}{2m})}_{\frac{1}{\lambda_T^3}} = \frac{V}{\lambda_T^3} \ .$$

q.e.d.

Hence, the equation of state can be written as

$$PV = nk_BT \ ,$$

which means that at first order, we have recovered a perfect gas.

Proof. For the first of (11.1), we obtain

$$pV = \frac{1}{\beta}\ln \mathcal{Z} \simeq \frac{1}{\beta}\ln(1+\frac{zV}{\lambda_T^3}) + O(z^2) \simeq \frac{zV}{\beta\lambda_T^3} + O(z^2) \ ,$$

where we have used $\ln(1+x) \simeq x$ for $x \ll 1$. For the second of (11.1), we obtain

$$N = z\frac{\partial}{\partial z}\ln \mathcal{Z} \simeq z\frac{\partial}{\partial z}\ln(1+\frac{zV}{\lambda_T^3}) + O(z^2) \simeq z\frac{\partial}{\partial z}\frac{zV}{\lambda_T^3} = \frac{zV}{\lambda_T^3} + O(z^2) \ ,$$

hence

$$z = \frac{N\lambda_T^3}{V} \ .$$

Finally, combining the two by substituing z, we have

$$pV \simeq \frac{N\lambda_T^3}{V}\frac{V}{\beta\lambda_T^3} = \frac{N}{\beta} = Nk_BT \ .$$

q.e.d.

At second order, we have

$$\mathcal{Z} \simeq 1 + zZ_1 + \frac{z^2Z_2}{2!} + O(z^3) \ ,$$

where the partition function for 2 particles is

$$Z_2 = \frac{V}{2\lambda_T^6}J_2(\beta)$$

and, using center of mass coordinates $r = q_1 - q_2$,

$$J_2(\beta) = \int d^3r \ \exp(-\beta U(r)) \ .$$

Proof. In fact, using (6.2) and the gaussian integral (C.1)

$$\begin{aligned}
Z_2 &= \int_{\mathcal{M}^2} d\Omega \exp(-\beta H) \\
&= \int_V\int_{\mathbb{R}^3}\frac{d^3q_1\ d^3p_1}{h^3}\int_V\int_{\mathbb{R}^3}\frac{d^3q_1\ d^3p_1}{h^3}\exp(-\beta(\frac{p^2}{2m}+\frac{p^2}{2m}+U(|q_1-q_2|))) \\
&= \underbrace{\int_{\mathbb{R}^3}\frac{d^3p_1}{h^3}\exp(-\beta\frac{p_1^2}{2m})}_{\frac{1}{\lambda_T^3}}\underbrace{\int_{\mathbb{R}^3}\frac{d^3p_2}{h^3}\exp(-\beta\frac{p_2^2}{2m})}_{\frac{1}{\lambda_T^3}}\int_V d^3q_1\int_V d^3q_2\exp(-\beta U(|q_i-q_j|)) \\
&= \frac{1}{\lambda_T^6}\int_V d^3q_1\int_V d^3q_2\exp(-\beta U(|q_i-q_j|)) \ .
\end{aligned}$$

Now, we make a change into the center of mass coordinates $R = (q_1 + q_2)/2$ and $r = |q_1 - q_2|$, and we find

$$Z_2 = \frac{1}{\lambda_T^6} \underbrace{\int_V d^3R}_{V} \underbrace{\int_V d^3r \exp(-\beta U(r))}_{J_2(\beta)} = \frac{V}{\lambda_T^6} J_2(\beta) \ .$$

q.e.d.

Hence, the two equations of state can be written as

$$\beta p = \frac{z}{\lambda_T^3} + \frac{z^2}{2\lambda_T^6} \tilde{J}_2(\beta) \ , \quad N = \frac{zV}{\lambda_T^3} + \frac{z^2 V}{\lambda_T^6} \tilde{J}_2(\beta) \ ,$$

where we have defined

$$\tilde{J}_2(\beta) = J_2(\beta) - V = \int_V d^3r (\exp(-\beta U(r)) - 1) \ .$$

Proof. For the first of (11.1), we obtain

$$\begin{aligned} pV &= \frac{1}{\beta} \ln \mathcal{Z} \\ &\simeq \frac{1}{\beta} \ln(1 + \frac{zV}{\lambda_T^3} + \frac{z^2 V}{2\lambda_T^6} J_2(\beta)) + O(3) \\ &\simeq \frac{1}{\beta} \Big((\frac{zV}{\lambda_T^3} + \frac{z^2 V}{2\lambda_T^6} J_2(\beta)) - \frac{1}{2} (\frac{zV}{\lambda_T^3} + \frac{z^2 V}{2\lambda_T^6} J_2(\beta))^2 \Big) + O(z^3) \\ &= \frac{1}{\beta} (\frac{zV}{\lambda_T^3} + \frac{z^2 V}{2\lambda_T^6} J_2(\beta) - \frac{z^2 V^2}{2\lambda_T^6}) + O(z^3) \\ &= \frac{1}{\beta} (\frac{zV}{\lambda_T^3} + \frac{z^2 V}{2\lambda_T^6} \underbrace{(J_2(\beta) - V)}_{\tilde{J}_2(\beta)}) + O(z^3) \\ &= \frac{1}{\beta} (\frac{zV}{\lambda_T^3} + \frac{z^2 V}{2\lambda_T^6} \tilde{J}_2(\beta)) + O(z^3) \ , \end{aligned}$$

where we have used $\ln(1 + x) \simeq x - x^2/2$ for $x \ll 1$. For the second of (11.1), we obtain

$$\begin{aligned}
N &= z\frac{\partial}{\partial z}\ln\mathcal{Z} \\
&\simeq z\frac{\partial}{\partial z}\ln(1+\frac{zV}{\lambda_T^3}+\frac{z^2V}{2\lambda_T^6}J_2(\beta)) \\
&\simeq z\frac{\partial}{\partial z}\Big((\frac{zV}{\lambda_T^3}+\frac{z^2V}{2\lambda_T^6}J_2(\beta))-\frac{1}{2}(\frac{zV}{\lambda_T^3}+\frac{z^2V}{2\lambda_T^6}J_2(\beta))^2\Big)+O(z^3) \\
&= z\frac{\partial}{\partial z}(\frac{zV}{\lambda_T^3}+\frac{z^2V}{2\lambda_T^6}J_2(\beta)-\frac{z^2V^2}{2\lambda_T^6})+O(z^3) \\
&= z\frac{\partial}{\partial z}(\frac{zV}{\lambda_T^3}+\frac{z^2V}{2\lambda_T^6}\underbrace{(J_2(\beta)-V)}_{\tilde{J}_2(\beta)})+O(z^3) \\
&= z\frac{\partial}{\partial z}(\frac{zV}{\lambda_T^3}+\frac{z^2V}{2\lambda_T^6}\tilde{J}_2(\beta))+O(z^3) \\
&= \frac{zV}{\lambda_T^3}+\frac{z^2V}{\lambda_T^6}\tilde{J}_2(\beta)\ .
\end{aligned}$$

q.e.d.

Now, we have to solve this system of second degree by imposing an ansatz for $z(n)$

$$z(n) = An + Bn^2 + O(n^3)\ ,$$

which gives rise to the equation of state of an interacting gas in the approximation of a diluite gas

$$p\beta = n - n^2\frac{\tilde{J}(2)}{2} + O(n^3)\ .$$

Notice that the first order is the same as the perfect gas, whereas the second order is a correction due to the interactions.

Proof. In fact, using

$$n = \frac{N}{V} = \frac{z}{\lambda_T^3} + \frac{z^2}{\lambda_T^6}\tilde{J}_2(\beta)\ ,$$

we find

$$\begin{aligned}
z &= An + Bn^2 + O(n^3) \\
&= A(\frac{z}{\lambda_T^3}+\frac{z^2}{\lambda_T^6}\tilde{J}_2(\beta)) + B(\frac{z}{\lambda_T^3}+\frac{z^2}{\lambda_T^6}\tilde{J}_2(\beta))^2 + O(z^3) \\
&= A(\frac{z}{\lambda_T^3}+\frac{z^2}{\lambda_T^6}\tilde{J}_2(\beta)) + B\frac{z^2}{\lambda_T^6} + O(z^3) \\
&= z\frac{A}{\lambda_T^3} + z^2(\frac{\tilde{J}_2(\beta)}{\lambda_T^6}+1\lambda_T^6) + O(z^3)\ ,
\end{aligned}$$

which implies that, since the coefficient in z must be 1 and in z^2 must be 0,

$$\frac{A}{\lambda_T^3} = 1 \ , \quad \frac{\tilde{J}_2(\beta)}{\lambda_T^6} + 1\lambda_T^6 = 0 \ ,$$

$$A = \lambda_T^3 \ , \quad B = -\lambda_T^3 \tilde{J}_2(\beta) \ ,$$

hence

$$z = \lambda_T^3 n - \lambda_T^3 \tilde{J}_2(\beta) n^2 \ ,$$

which they are called respectively the first virial and the second virial coefficients. Finally, combining all two, we obtain

$$\begin{aligned}
p\beta &= \frac{z}{\lambda_T^3} + \frac{z^2}{2\lambda_T^6}\tilde{J}_2(\beta) + O(n^3) \\
&= \frac{1}{\lambda_T^3}(\lambda_T^3 n - \lambda_T^3 \tilde{J}_2(\beta) n^2) + \frac{\tilde{J}_2(\beta)}{2\lambda_T^6}(\lambda_T^3 n - \lambda_T^3 \tilde{J}_2(\beta) n^2)^2 + O(n^3) \\
&= n - n^2 \tilde{J}_2(\beta) + \frac{1}{2} n^2 \tilde{J}_2(\beta) + O(n^3) \\
&= n - n^2 \frac{\tilde{J}_2(\beta)}{2} + O(n^3) \ .
\end{aligned}$$

q.e.d.

Notice that $z \propto \lambda_T^3 \ll 1$ physically means that $T \gg 1$. Therefore, this approximation is valid for hot diluite gas.

Now, we build a physical model to calculate explicitly this expansion. Particles are considered as hard rigid spheres of radius r_0 that do not overlap. Instead, the potential is repulsive for small distances, attractive for large distances and it behaves at 0 and at ∞ as

$$U(r \to 0) \to \infty \ , \quad U(r \to \infty) \to 0 \ .$$

One of the most famous potential that behaves so is the Lennard-Jones one. A plot of this is in Figure 11.1.

The equation of state becomes

$$(p + \frac{a}{v^2})(v - b) = k_B T \ ,$$

where a is the average attractive potential and b is the finite volume.

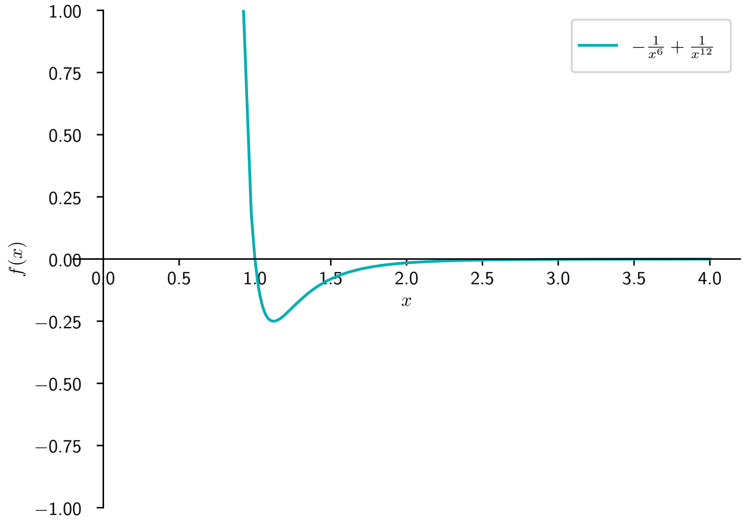

Figure 11.1: A plot of a Lennard-Jones-like potential. We have used $x = r$ and $f(x) = r^{-12} - r^{-6}$.

Proof. First, we need to evaluate $\tilde{J}_2(\beta)$

$$
\begin{aligned}
\tilde{J}_2(\beta) &= \int d^3r(\exp(-\beta U(r)) - 1) \\
&= 4\pi \int_0^{2r_0} dr\ r^2 \underbrace{(\exp(-\beta U(r)) - 1)}_{-1} + 4\pi \int_{2r_0}^{\infty} dr\ r^2 \underbrace{(\exp(-\beta U(r)) - 1)}_{\beta U(r)} \\
&\simeq \underbrace{-\,4\pi \int_0^{2r_0} dr\ r^2}_{2b} + \beta \underbrace{4\pi \int_{2r_0}^{\infty} dr\ r^2 U(r)}_{2a} \\
&= -2b + 2\beta a\ ,
\end{aligned}
$$

where for the first integral we have used

$$\exp(-\beta U(r)) - 1 \rightarrow r \rightarrow 0(-1)$$

and for the second integral we have used

$$\exp(-\beta U(r)) - 1 \rightarrow r \rightarrow \infty 1 - \beta U(r) - 1 = -\beta U(r)\ .$$

Hence

$$\frac{\tilde{J}_2(\beta)}{2} = b - \beta a$$

and

$$p\beta = n - n^2 \frac{\tilde{J}(2)}{2} = n - n^2(b - \beta a) = n(1 + n(b - \beta a)) \ .$$

Finally, after some manipulations, using $v = 1/n$,

$$\beta(p + an^2) = n(1 + nb) \ ,$$

$$k_B T = \frac{p + an^2}{n(1 + nb)} \simeq \frac{1}{n}(p + an^2)(1 - nb) = v(p + \frac{a}{v^2})(1 - \frac{b}{v}) = (p + \frac{a}{v^2})(v - b) \ ,$$

where we have used $(1 + x)^{-1} \simeq 1 - x$ for $x \ll 1$. q.e.d.

Chapter 12

Entropy

12.1 Maxwell-Boltzmann distribution

We can distribute N particle in p boxes in ways

$$W_{n_r}^{(1)} = \frac{N!}{n_1! \dots n_p!} \ ,$$

whereas there is no restriction for the states

$$W_{n_r}^{(2)} = \prod_r g_r^{n_r} \ ,$$

hence

$$W_{n_r} = \frac{N!}{n_1! \dots n_p!} \prod_{r=1}^{p} g_r^{n_r} = N! \prod_{r=1}^{p} \frac{g_r^{n_r}}{n_r!} \ .$$

Maximising the constrained entropy, we find the Boltzmann canonical distribution

$$p_r^* = \frac{n_r^*}{N} = \frac{g_r \exp(-\beta E_r)}{\sum_r g_r \exp(-\beta E_r)} \ .$$

Proof. The entropy is, using the Stirling approximation (B.1),

$$\begin{aligned}
S &= \ln W_{n_r} \\
&= \ln\left(N! \prod_{r=1}^{p} \frac{g_r^{n_r}}{n_r!}\right) \\
&= \ln N! + \sum_{r=1}^{p} \ln \frac{g_r^{n_r}}{n_r!} \\
&= \underbrace{\ln N!}_{N\ln N - N} + \sum_{r=1}^{p} (\ln g_r^{n_r} - \underbrace{\ln n_r!}_{n_r \ln n_r - n_r}\ ) \\
&= N \ln N - \cancel{N} + \sum_{r=1}^{p} n_r \ln g_r - \sum_{r=1}^{p} n_r \ln n_r - \cancel{\sum_{r=1}^{p} n_r} \\
&= N \ln N + \sum_{r=1}^{p} n_r \ln g_r + \sum_{r=1}^{p} n_r \ln n_r \ .
\end{aligned}$$

The constrained entropy is

$$S = N \ln N + \sum_{r=1}^{p} n_r \ln g_r - \sum_{r=1}^{p} n_r \ln n_r + \alpha\Big(N - \sum_{r=1}^{p} n_r\Big) + \beta\Big(E - \sum_{r=1}^{p} n_r E_r\Big) \ .$$

The maximum is

$$0 = \frac{\partial S}{\partial n_r} = \ln g_r - \ln n_r - 1 - \alpha - \beta E_r \ ,$$

hence

$$n_r^* = \frac{g_r \exp(-\beta E_r)}{\exp(1+\alpha)} \ .$$

We find α by the normalisation condition

$$N = \sum_r n_r^* = \sum_r \frac{g_r \exp(-\beta E_r)}{\exp(1+\alpha)} \ ,$$

hence

$$\exp(1+\alpha) = \frac{\sum_r g_r \exp(-\beta E_r)}{N} \ .$$

Finally, if we identify $\beta = 1/k_B T$ the probability distribution density is

$$p_r^* = \frac{n_r^*}{N} = \frac{g_r \exp(-\beta E_r)}{\sum_r g_r \exp(-\beta E_r)} \ .$$

q.e.d.

A plot of this is in Figure 12.1.

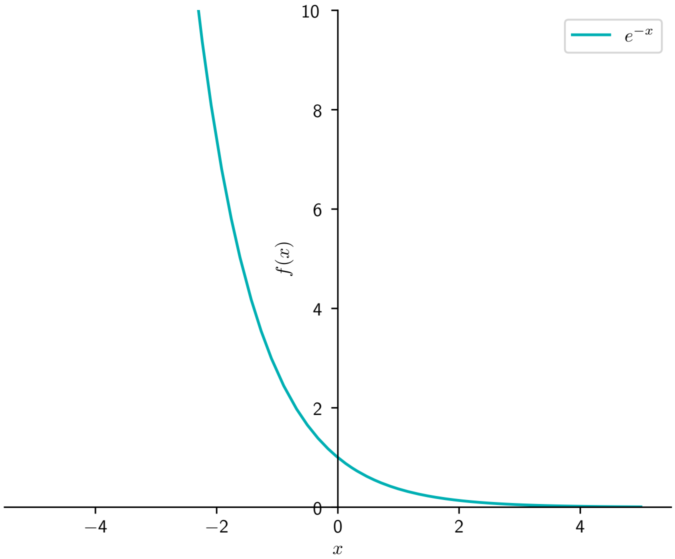

Figure 12.1: A plot of the probability density distribution p_r^* as a function of βE_r. We have used $x = \beta E_r$ and $f(x) = p_r^* \frac{\sum_r g_r \exp(-\beta E_r)}{g_r}$.

12.2 Fermi-Dirac distribution

For fermions, there is no restriction on how we can distribute N particle in p boxes in ways, since they are indistinguishable

$$W_{n_r}^{(1)} = 1 \ ,$$

whereas we can distribute n_r objects in g_r boxes

$$W_{n_r}^{(2)} = \prod_r \binom{g_r}{n_r} = \prod_r \frac{g_r!}{n_r!(g_r - n_r)!} \ ,$$

hence

$$W_{n_r} = \prod_r \binom{g_r}{n_r} = \prod_r \frac{g_r!}{n_r!(g_r - n_r)!} \ .$$

Maximising the constrained entropy, we find the Bose-Einstein distribution

$$n_r^* = \frac{g_r}{\exp(\alpha + \beta E_r) + 1} \ .$$

Proof. The entropy is, using the Stirling approximation (B.1),

$$
\begin{aligned}
S &= \ln W_{n_r} \\
&= \ln\Big(\prod_r \frac{g_r!}{n_r!(g_r-n_r)!}\Big) \\
&= \sum_r \Big(\underbrace{\ln g_r!}_{g_r \ln g_r - g_r} - \underbrace{\ln n_r!}_{n_r \ln n_r - n_r} - \underbrace{\ln(g_r-n_r)!}_{(g_r-n_r)\ln(g_r-n_r)-g_r+n_r} \Big) \\
&= \sum_r \Big(g_r \ln g_r - \cancel{g_r} - n_r \ln n_r + \cancel{n_r} - (g_r-n_r)\ln(g_r-n_r) + \cancel{g_r} - \cancel{n_r} \Big) \\
&= \sum_r \Big(g_r \ln g_r - n_r \ln n_r - (g_r-n_r)\ln(g_r-n_r) \Big) \ .
\end{aligned}
$$

The constrained entropy is

$$
S = \sum_r \Big(g_r \ln g_r - n_r \ln n_r - (g_r-n_r)\ln(g_r-n_r) \Big) + \alpha\Big(N - \sum_{r=1}^{p} n_r\Big) + \beta\Big(E - \sum_{r=1}^{p} n_r E_r\Big) \ .
$$

The maximum is

$$
\begin{aligned}
0 &= \frac{\partial S}{\partial n_r} \\
&= -\ln n_r - \cancel{1} + \ln(g_r-n_r) + \cancel{1} - \alpha - \beta E_r \\
&= -\ln n_r + \ln(g_r-n_r) - \alpha - \beta E_r \\
&= \ln\big(\frac{g_r}{n_r} - 1\big) - \alpha - \beta E_r \ ,
\end{aligned}
$$

hence

$$
\begin{aligned}
\frac{g_r}{n_r} - 1 &= \exp(\alpha + \beta E_r) \ , \\
n_r^* &= \frac{g_r}{\exp(\alpha + \beta E_r) + 1} \ .
\end{aligned}
$$

q.e.d.

A plot of this is in Figure 12.2.

12.3 Bose-Einstein distribution

For bosons, there is no restriction on how we can distribute N particle in p boxes in ways, since they are indistinguishable

$$
W_{n_r}^{(1)} = 1 \ ,
$$

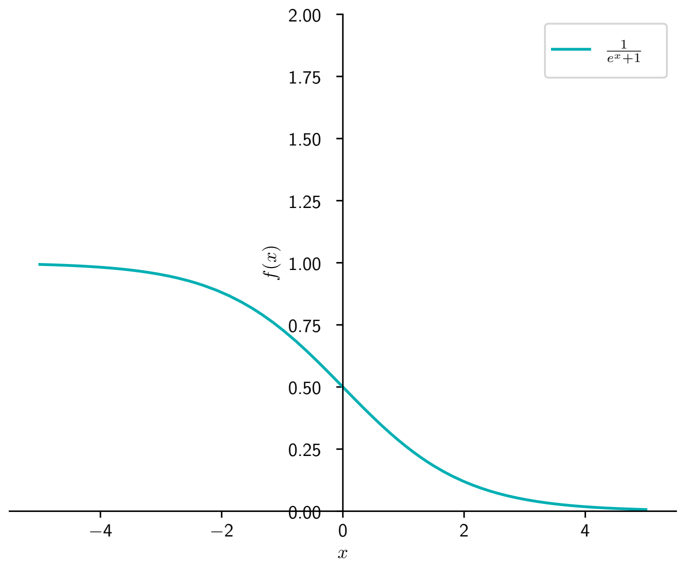

Figure 12.2: A plot of the Fermi-Dirac distribution n_r^* as a function of $\alpha + \beta E_r$. We have used $x = \alpha + \beta E_r$ and $f(x) = \frac{n_r^*}{g_r}$.

whereas we can distribute n_r objects in g_r boxes

$$W_{n_r}^{(2)} = \prod_r \binom{n_r + g_r - 1}{n_r} = \prod_r \frac{(n_r + g_r - 1)!}{n_r!(g_r - 1)!} ,$$

hence

$$W_{n_r} = \prod_r \frac{(n_r + g_r - 1)!}{n_r!(g_r - 1)!} .$$

Maximising the constrained entropy, we find the Bose-Einstein distribution

$$n_r^* = \frac{g_r}{\exp(\alpha + \beta E_r) - 1} .$$

Proof. The entropy is, using the Stirling approximation (B.1),

$$
\begin{aligned}
S &= \ln W_{n_r} \\
&= \ln \prod_r \frac{(n_r + g_r - 1)!}{n_r!(g_r - 1)!} \\
&= \sum_r \Big(\underbrace{\ln(n_r + g_r - 1)!}_{(n_r+g_r-1)\ln(n_r+g_r-1)-n_r-g_r+1} - \underbrace{\ln n_r!}_{n_r \ln n_r - n_r} - \underbrace{\ln(g_r - 1)!}_{(g_r-1)\ln(g_r-1)-g_r+1} \Big) \\
&= \sum_r \Big((n_r + g_r - 1)\ln(n_r + g_r - 1) - \cancel{n_r} - \cancel{g_r} + \cancel{1} \\
&\quad - n_r \ln n_r + \cancel{n_r} - (g_r - 1)\ln(g_r - 1) + \cancel{g_r} - \cancel{1} \Big) \\
&= \sum_r \Big((n_r + g_r - 1)\ln(n_r + g_r - 1)\ln n_r - n_r \ln n_r - (g_r - 1)\ln(g_r - 1) \Big)
\end{aligned}
$$

The constrained entropy is

$$
\begin{aligned}
S = &\sum_r \Big((n_r + g_r - 1)\ln(n_r + g_r - 1)\ln n_r - n_r \ln n_r - (g_r - 1)\ln(g_r - 1) \Big) \\
&+ \alpha \Big(N - \sum_{r=1}^{p} n_r \Big) + \beta \Big(E - \sum_{r=1}^{p} n_r E_r \Big) .
\end{aligned}
$$

The maximum is

$$
\begin{aligned}
0 &= \frac{\partial S}{\partial n_r} \\
&= \ln(n_r + g_r - 1) + \cancel{1} - \ln n_r - \cancel{1} - \alpha - \beta E_r \\
&= \ln(n_r + g_r - 1) - \ln n_r - \alpha - \beta E_r \\
&= \ln(\frac{g_r - 1}{n_r} + 1) - \alpha - \beta E_r ,
\end{aligned}
$$

hence, for $g_r \gg 1$,

$$
\frac{g_r - 1}{n_r} + 1 = \exp(\alpha + \beta E_r) ,
$$

$$
n_r^* = \frac{g_r - 1}{\exp(\alpha + \beta E_r) - 1} \simeq \frac{g_r}{\exp(\alpha + \beta E_r) - 1} .
$$

q.e.d.

A plot of this is in Figure 12.3.

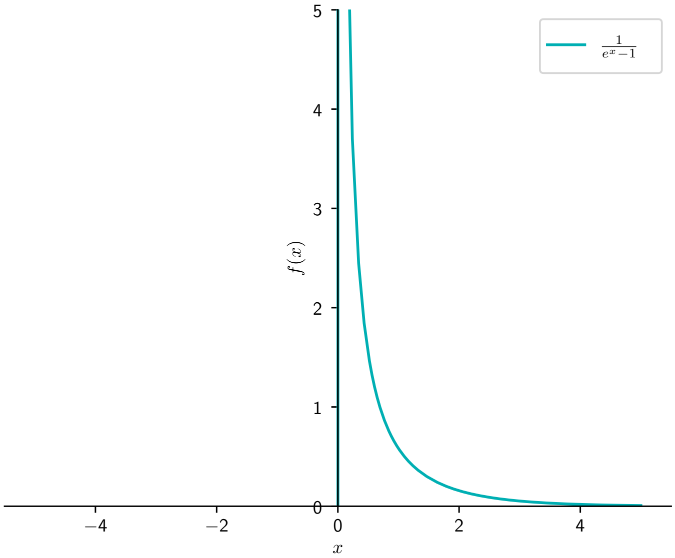

Figure 12.3: A plot of the Bose-Einstein distribution n_r^* as a function of $\alpha + \beta E_r$. We have used $x = \alpha + \beta E_r$ and $f(x) = \frac{n_r^*}{g_r}$.

12.4 Two-levels system

Consider a system composed by 2 levels of energies $\epsilon_+ = +\epsilon$ and $\epsilon_- = -\epsilon$. The constrains are

$$E = \epsilon(n_+ - n_-) \ , \quad N = n_+ + n_- \ .$$

They can be inverted as

$$n_+ = \frac{N}{2} + \frac{E}{2\epsilon} \ , \quad n_+ = \frac{N}{2} - \frac{E}{2\epsilon} \ . \tag{12.1}$$

We can distribute N objects in n_+ boxes

$$\Omega(E) = \binom{N}{n_+} = \frac{N!}{n_+!(N-n_+)!} = \frac{N!}{n_+!n_-!} \ .$$

The entropy is

$$S = -Nk_B\Big((\frac{1}{2} + \frac{E}{2\epsilon N})\ln(\frac{1}{2} + \frac{E}{2\epsilon N}) + (\frac{1}{2} - \frac{E}{2\epsilon N})\ln(\frac{1}{2} - \frac{E}{2\epsilon N})\Big) \ .$$

Proof. By definition, using the Stirling approximation (B.1),

$$\begin{aligned}
\frac{S}{k_B} &= \ln \Omega(E) \\
&= \ln \frac{N!}{n_+!n_-!} \\
&= \underbrace{\ln N!}_{N\ln N - N} - \underbrace{\ln n_+!}_{n_+\ln n_+ - n_+} - \underbrace{\ln n_-!}_{n_-\ln n_- - n_-} \\
&= N\ln N - \cancel{N} - n_+\ln n_+ + \cancel{n_+} - n_-\ln n_- + \cancel{n_-} \\
&= N\ln N - n_+\ln n_+ - n_-\ln n_- \\
&= (n_+ + n_-)\ln N - n_+\ln n_+ - n_-\ln n_- \\
&= n_+\ln\frac{N}{n_+} + n_-\ln\frac{N}{n_-} \\
&= (\frac{N}{2} + \frac{E}{2\epsilon})\ln\frac{N}{\frac{N}{2}+\frac{E}{2\epsilon}} + (\frac{N}{2} - \frac{E}{2\epsilon})\ln\frac{N}{\frac{N}{2}-\frac{E}{2\epsilon}} \\
&= N\Big((\frac{1}{2} + \frac{E}{2\epsilon N})\ln\frac{1}{\frac{1}{2}+\frac{E}{2\epsilon N}} + (\frac{1}{2} - \frac{E}{2\epsilon N})\ln\frac{1}{\frac{1}{2}-\frac{E}{2\epsilon N}}\Big) \\
&= -N\Big((\frac{1}{2} + \frac{E}{2\epsilon N})\ln(\frac{1}{2} + \frac{E}{2\epsilon N}) + (\frac{1}{2} - \frac{E}{2\epsilon N})\ln(\frac{1}{2} - \frac{E}{2\epsilon N})\Big) \; .
\end{aligned}$$

q.e.d.

A plot of this is in Figure 12.4.

The temperature is

$$T = \frac{2\epsilon}{k_B}\frac{1}{\ln\frac{\frac{1}{2}-\frac{E}{2\epsilon N}}{\frac{1}{2}+\frac{E}{2\epsilon N}}} \; .$$

Proof. Using (**??**)

$$\begin{aligned}
T &= (\frac{\partial S}{\partial E})^{-1} \\
&= -(\frac{k_B}{2\epsilon}\ln(\frac{1}{2}+\frac{E}{2\epsilon N}) + \cancel{\frac{k_B}{2\epsilon}} - \frac{k_B}{2\epsilon}\ln(\frac{1}{2}-\frac{E}{2\epsilon N}) - \cancel{\frac{k_B}{2\epsilon}})^{-1} \\
&= -(\frac{k_B}{2\epsilon}\ln\frac{\frac{1}{2}+\frac{E}{2\epsilon N}}{\frac{1}{2}-\frac{E}{2\epsilon N}})^{-1} \\
&= -\frac{2\epsilon}{k_B}\frac{1}{\ln\frac{\frac{1}{2}+\frac{E}{2\epsilon N}}{\frac{1}{2}-\frac{E}{2\epsilon N}}} \\
&= \frac{2\epsilon}{k_B}\frac{1}{\ln\frac{\frac{1}{2}-\frac{E}{2\epsilon N}}{\frac{1}{2}+\frac{E}{2\epsilon N}}} \; .
\end{aligned}$$

q.e.d.

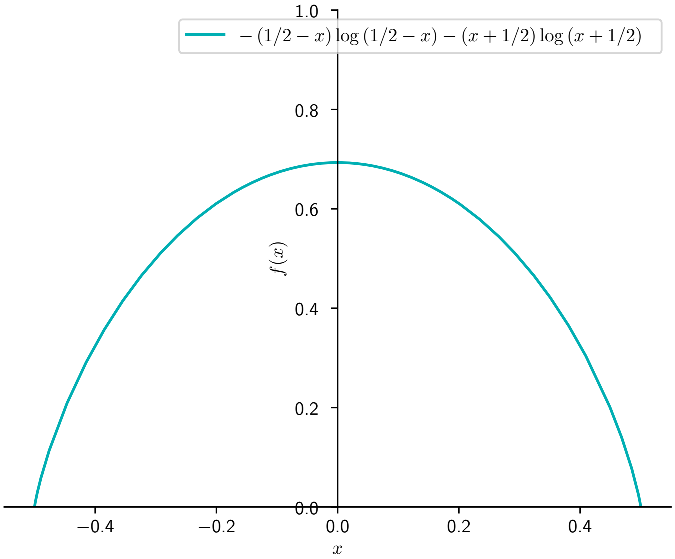

Figure 12.4: A plot of the entropy S as a function of E. We have used $x = \frac{E}{2\epsilon N}$ and $f(x) = \frac{S}{Nk_B}$.

A plot of this is in Figure 12.5.

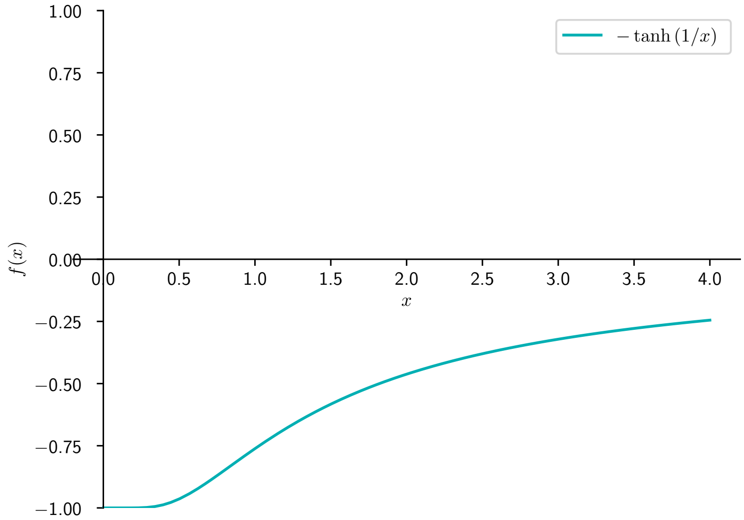

Figure 12.5: A plot of the temperature T as a function of E. We have used $x = \frac{E}{2\epsilon N}$ and $f(x) = \frac{k_B T}{2\epsilon}$.

Part IV

Phase transition

Chapter 13

Classical phase transitions

In the last part of these notes, we will study phase transitions and critical phenomena of classical physical systems. In particular, we will deal with fluids and magnetic (spin) systems.

13.1 Classical fluids

Consider a classical fluid, e.g. water, composed by atoms or molecules interacting via a 2-body potential, i.e. a potential that depends only on the reciprocate distance between 2 constituents. It can present itself in 3 different phases, which microscopically have the same Hamiltonian, but the macroscopic variables change:

1. solid, i.e. it has its own shape and volume;
2. liquid, i.e. it has its own volume, but it has the shape of the container;
3. gas, i.e. it has the shape and volume of the container.

They can be represented in a phase diagram (T, p). See Figure (13.1) for the water and Figure (13.2) for the Helium. Notice that Helium has 2 liquid different phases, normal liquid and superfluid, i.e. zero viscosity and dissipationless flow. The phase diagram can be divided into region containing a single phase. At the boundary of these regions, we can have 2 different kind of coexistence phases in equilibrium: coexistence lines and triple points.

A coexistence line is a line along which 2 phases are in equilibrium. A coexistence point or triple point is a point in which 3 phases are in equilibrium. Examples in the water phase diagram of coexistence lines are $S-L$, $L-V$ and $S-V$ separation lines, whereas there is only a single triple point. To study when coexistence phases system are in equilibrium, we exploit the grand canonical ensemble. For coexistence lines, in order to have equilibrium, we have

$$T_1 = T_2 \ , \quad T_1 = T_2 \ , \quad p_1 = p_2 \ , \quad \mu_1 = \mu_2 \ ,$$

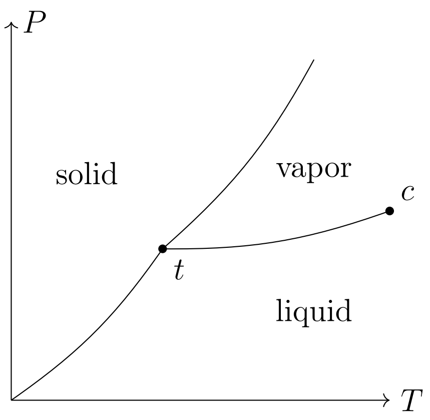

Figure 13.1: Qualitative phase diagram of the water. t is a triple point and c is a critical point.

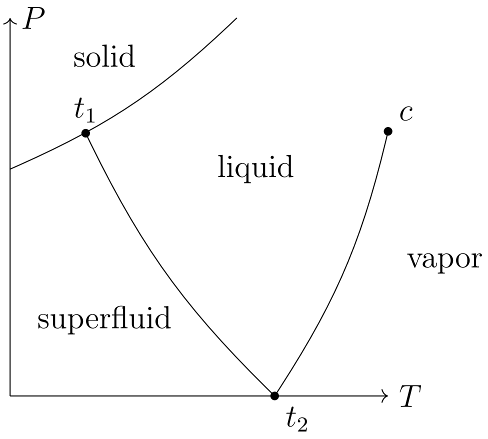

Figure 13.2: Qualitative phase diagram of the Helium. t_1 and t_2 are triple points and c is a critical point.

which provide respectively thermal, mechanical and chemical equilibrium. Writing μ in terms of the other thermodynamic functions, we obtain a constraint

$$\mu_1(T, p) = \mu_2(T, p) \ ,$$

which individuates a line in the (T, p) plane. Similarly, for triple points, in order to have equilibrium, we have

$$T_1 = T_2 = T_3 \ , \quad p_1 = p_2 = p_3 \ , \quad \mu_1 = \mu_2 = \mu_3 \ ,$$

where we have denoted with $1, 2, 3$ different phases. Writing μ in terms of the other thermodynamic functions, we obtain 2 constraint s

$$\mu_1(T, p) = \mu_2(T, p) = \mu_3(T, p) \ ,$$

which individuates a point in the (T, p) plane.

We can generalise this result with the Gibbs' phase rule, which states that, in a system with l distinct species, the number of coexistence phases in equilibrium r is bounded above by

$$r \leq l + 2 \ .$$

In the water case, $l = 1$ and $r = 3$, so that at most we have indeed 3 coexisting phases.

Notice that the coexistence curve $L - V$ terminates at a critical point, in which there is no more distinction between liquid and vapor, because we can circumnavigate from right to go from one phase to the other.

13.2 Classification of phase transitions

Away from a critical point, a phase transition involves latent heat Δq, since T is constant, but thermal energy is used or released to change the phase. It can be estimated via the Clausius-Clapeyron equation

$$\frac{dp}{dT} = \frac{s_2 - s_1}{v_1 - v_2} = \frac{\Delta q}{T \Delta v} \ . \tag{13.1}$$

Proof. In order to remain along the coexistence line, the constraint holds

$$\mu_1(p, T) = \mu_2(p, T) \ .$$

We differentiate it using the chain rule, keeping in mind that $p = p(T)$,

$$\left.\frac{\partial \mu_1}{\partial T}\right|_p + \left.\frac{d\mu_1}{dp}\right|_T \frac{dp}{dT} = \left.\frac{\partial \mu_2}{\partial T}\right|_p + \left.\frac{d\mu_2}{dp}\right|_T \frac{dp}{dT} \ .$$

Hence, we isolate dp/dT and we find

$$\frac{dp}{dT} = \frac{\frac{\partial \mu_1}{\partial T}|_p - \frac{\partial \mu_2}{\partial T}|_p}{\frac{\partial \mu_2}{\partial p}|_T - \frac{\partial \mu_2}{\partial p}|_T} \ .$$

Since a change in phase does not mean a change in total number of particles, we can work with a fixed amount of them. The thermodynamic potential to use is therefore the Gibbs free energy $G(p, T, N) = \mu(p, T)N$ or the Gibbs free energy per particle

$$g = \frac{G}{N} = \mu(p, T) \ .$$

Using the last relation of (2.22)

$$\left.\frac{\partial \mu}{\partial p}\right|_T = \left.\frac{\partial g}{\partial p}\right|_T = \frac{1}{N} \left.\frac{\partial G}{\partial p}\right|_T = \frac{V}{N} = v \ ,$$

whereas, using the first relation of (2.22)

$$\left.\frac{\partial \mu}{\partial T}\right|_p = \left.\frac{\partial g}{\partial T}\right|_p = \frac{1}{N}\left.\frac{\partial G}{\partial T}\right|_p = -\frac{S}{N} = -s \ .$$

Combining the *two*, we obtain

$$\frac{dp}{dT} = \frac{\frac{\partial \mu_1}{\partial T}|_p - \frac{\partial \mu_2}{\partial T}|_p}{\frac{\partial \mu_2}{\partial p}|_T - \frac{\partial \mu_2}{\partial p}|_T} = -\frac{s_1 - s_2}{v_2 - v_1} = \frac{s_2 - s_1}{v_2 - v_1} \ .$$

Finally, using the second law of thermodynamics (1.5), we find

$$\Delta s = \frac{\Delta q}{T} \ ,$$

which implies that

$$\frac{dp}{dT} = \frac{\Delta q}{T \Delta v} \ .$$

q.e.d.

Suppose that in a system there is latent heat. Observing (13.1), we can state that the latent heat Δq is different from zero, only when $s_1 \neq s_2$, which corresponds to a change in order of the system. Recalling the first of (2.22), we can say that the phase 1 must be more stable at low temperatures while phase 1 must be more stable at high temperatures. This implies that there is a cusp-like behaviour of G, or equivalently on μ,

$$\frac{\partial \mu_1}{\partial T} > \frac{\partial \mu_2}{\partial T} \ .$$

Therefore, at the phase transition temperature, the Gibbs free energy is continuous ($\mu_1 = \mu_2$) but its first derivative in T is not, resulting in a cusp-like behaviour. Moreover, if it does change volume as well $v_2 \neq v_1$, its first derivative in p has a similar behaviour. However, at $T = T_c$, discontinuity of first derivatives disappears, since we cannot distinguish anymore the 2 phases. However, there could be other discontinuities in higher derivatives, e.g. specific heat or compressibility are defined as second derivatives of thermodynamic potentials. Hence, we classify phase transitions in 2 different kind

1. 1st order phase transitions, i.e. those in which the 1st derivatives of thermodynamic potentials are discontinuous;

2. continuous phase transitions, i.e. those in which the higher derivatives of thermodynamic potentials are discontinuous.

In our case, the former are those in which there is a jump $v_2 \neq v_1$ and $s_2 \neq s_1$ and the latter are those in which $v_2 = v_1$ and $s_2 = s_1$. To summarise, a phase transition happens when there is a singular point for a thermodynamic potential. In the next section, we will develop the mathematical framework of a phase transition in terms of this quantity in the thermodynamic limit.

13.3 Theorems of Lee and Young

Consider a classical fluid in a volume $V \subset \mathbb{R}^3$. As mentioned before, we will analyse it in the grand canonical ensemble. The Hamiltonian of the system is

$$H = \sum_{i=1}^{N} (\frac{p_i^2}{2m} + U_N(q_i))$$

and the grand canonical partition function is

$$\mathcal{Z}(z, T, V) = \sum_{N=0}^{\infty} z^N \frac{Q_N(T, V)}{N! \lambda_T^3} ,$$

where we have defined a positive quantity

$$Q_N(T, V) = \int_{V^N} \prod_{i=1}^{N} d^3 q^i \exp(-\beta U_N(q^i)) .$$

Proof. The canonical partition function (6.2) is

$$\begin{aligned} Z_N &= \int_{\mathcal{M}^N} \prod_{i=1}^{N} \frac{d^3 q^i \; d^3 p^i}{N! h^{3N}} \exp(-\beta \sum_j \frac{p_j}{2m} + U_N(q^i)) \\ &= \frac{1}{N!} \underbrace{\int_{\mathbb{R}^{3N}} \prod_{i=1}^{N} \frac{d^3 p^i}{h^{3N}} \; \exp(-\beta \frac{p_i}{2m})}_{\frac{1}{\lambda_T^{3N}}} \underbrace{\int_{V^N} \prod_{i=1}^{N} d^3 q^i \; \exp(-\beta U_N(q_i))}_{Q_N} = \frac{Q_N(T, V)}{N! \lambda_T^{3N}} . \end{aligned}$$

Finally, using (7.2), we find

$$\mathcal{Z} = \sum_{N=0}^{\infty} z^N Z_N = \sum_{N=0}^{\infty} z^n \frac{Q_N}{N! \lambda_T^{3N}} .$$

q.e.d.

Now, we need to study when this power series in z converges. The first step is to promote z into a complex variable, but always keeping in mind that the physical states are only the ones for which $z \in \mathbb{R}^+$. A reasonable assumption for the behaviour of the potential is that U_N is bounded from below by a constant that does not grow faster than N, i.e. $U_N \geq -BN$ with $B > 0$. This implies that

$$|\mathcal{Z}| \leq \exp(\frac{V \exp(\beta B) |z|}{\lambda_T^3}) .$$

Proof. In fact, using the assumption, we have

$$\exp(-\beta U_N) \leq \exp(\beta BN) \ ,$$

hence, Q_N becomes

$$Q_N = \int_{V^N} \prod_{i=1}^{N} d^3q^i \exp(-\beta U_N(q^i)) \leq \exp(\beta BN) \underbrace{\int_{V^N} \prod_{i=1}^{N} d^3q^i}_{V^N} = \exp(\beta BN) V^N$$

and the canonical partition function becomes

$$Z_N = \frac{Q_N}{N!\lambda_T^{3N}} \leq \frac{V^N}{N!\lambda_T^{3N}} \exp(\beta BN) \ .$$

Finally, we find that the grand canonical partition function becomes

$$|\mathcal{Z}| \leq \sum_{N=0}^{\infty} \frac{|z|^N}{N!\lambda_T^{3N}} V^N \exp(\beta BN) = \exp(\frac{V \exp(\beta B)|z|}{\lambda_T^3}) \ .$$

q.e.d.

Notice that there is a problem. An exponential has an infinite convergence radius and, therefore, $\mathcal{Z}$ is analytical $\forall z \in \mathbb{C}$, in particular for $z \in \mathbb{R}^+$. Furthermore, $\mathcal{Z}$ cannot vanish $\forall N$ since it is convergent and it is a sum of positive terms.

Since we are working in the grand canonical ensemble, we can introduce a redefined grand potential

$$\psi = \frac{\beta\Omega}{V} = \lim_{td} \frac{\ln \mathcal{Z}}{V} \ ,$$

for which it is valid

$$p\beta = \psi \ , \quad n = z\frac{\partial}{\partial z}\psi \ .$$

Proof. For the first, using the first of (11.1)

$$\Omega = -pV = -\frac{1}{\beta} \ln \mathcal{Z} \ ,$$

hence

$$p\beta = \frac{\ln \mathcal{Z}}{V} = \psi \ .$$

For the second, using the second of (11.1)

$$N = z\frac{\partial}{\partial z} \ln \mathcal{Z} = -\frac{z}{\beta}\frac{\partial}{\partial z} \ln \Omega \ ,$$

hence

$$n = \frac{N}{V} = -\frac{z}{\beta}\frac{\partial}{\partial z}\frac{\ln \Omega}{V} = -\frac{z}{\beta}\frac{\partial}{\partial z}\psi \ .$$

q.e.d.

These results can be formally stated by 2 theorems, proved by Lee and Young, in terms of ψ.

Theorem 13.1 (Lee, Young I)
Let U_N be the potential such that $U_N \geq -BN$ with $B > 0$. Let also that boundaries of the volume do not increase faster than $V^{2/3}$, in order to neglect surface terms. Then ψ exists, it is a continuous and monotonically increasing function of $z \in \mathbb{R}^+$.

Theorem 13.2 (Lee, Young II)
Given an open subset of the complex plane containing an interval of $\mathbb{R}^+$ such that it does not contain zeroes of $\mathcal{Z}$, then $V^{-1} \ln \mathcal{Z}$ converges uniformly for $V \to \infty$ in any closed set of this region, ψ exists and it is analytic.

This means that there are no phase transitions and there is a single stable phase, since there cannot happen singularities for zero-free regions. How is it possible? We have not yet computed the thermodynamic limit. In fact, consider a system composed by hard spheres occupying a finite volume v. Since particles cannot overlap, the maximum number of particles is $M = V/v$. Therefore, $\mathcal{Z}$ is a polynomial function in z of degree M and, by the fundamental theorem of algebra, it has exactly M zeroes but, by the theorems of Lee and Young, no zeros are in $\mathbb{R}^+$. However, if we go into the thermodynamic limit ($V \to \infty$ implies that $M \to \infty$), the number of zeroes increases. It may happen that, at a certain temperature, zeroes accumulate towards an isolated point $z = z_c$, which divides $\mathbb{R}^+$ into 2 regions corresponding 2 different phases. $\mathcal{Z}(V \to \infty, T, \mu)$ has a zero in $z = z_c$. Furthermore, ψ is continuous but it is not analytic anymore: 1*st* order phase transitions or continuous phase transitions may occur. See Figure 13.3.

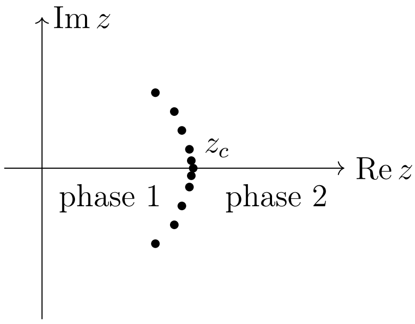

Figure 13.3: Accumulation of zeros in $z = z_c$ in the complex plane of z that divides the real axis into two different phases 1 and 2.

In the next chapter, we will study the paradigmatic example for phase transitions: the Ising model.

Chapter 14

Ising model

The Ising model deals with spin. However, spin is a quantum physical quantity that does not have a classical counterpart, so when we talk about classical spin, we mean localised magnetic moments that couple with an external magnetic field.

14.1 Simple Ising model

Consider a system composed by a discrete lattice, e.g. an hypercubic lattice in Figure (14.1), of dimension d. Lattice sites are labelled by $i \in \mathbb{Z}_d$. For each vertex, there is a degree of freedom (classical spin) attached to a vector $\mathbf{S}_i \in \mathbf{R}^n$ with fixed magnitude $|\mathbf{S}_i| = \text{const}$. Therefore, $\mathbf{S}_i \in \mathbb{S}^{n-1}$, where $\mathbb{S}^{n-1}$ is the $(n-1)$-dimensional sphere of radius $|\mathbf{S}_i|$. Two adjacent vertices are called neighborhoods. Each site has therefore z neighborhood, called the coordination number. For a d-dimensional hybercubic lattice, $z = 2d$.

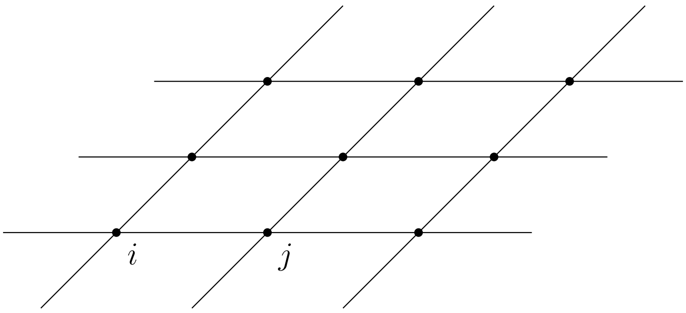

Figure 14.1: An hybercubic lattice of dimension 2. i and j are neighbourhood sites

We will not study the more general model, but we will restrict ourselves to the simple model in which $n = 1$ and the spin $\mathbf{S}_i$ can have only two values $\mathbf{S}_i = \sigma_i = \pm 1$. We will denote a possible configuration state as $\{\sigma_i\}_{i\in\mathcal{L}}$ and the phase space will be a discrete space composed by 2^N states $\{\{\sigma_i\}_{i\in\mathcal{L}} \colon \sigma_i = \pm 1\}$. The Hamiltonian of the system can be decomposed into two parts: a term that describes the interaction between neighborhood sites H_{int} and a term that describes the coupling with an external field H_{field}

$$H(\sigma_i) = H_{int} + H_{field} \ , \quad H_{int} = -J \sum_{i \text{ near } j} \sigma_i \sigma_j \ , \quad H_{field} = -B \sum_{i=1}^{N} \sigma_i \ ,$$

where B is an external magnetic field and J is the interaction constant, which is invariant under translations and rotations. We allow sites to interact with each other because otherwise there would not have a phase transition. We can study what is the minimum energy configuration state according to the sign of B and J:

1. for $J > 0$, all the spins are aligned $\sigma_i = \sigma_j$ for i near j, called ferromagnetic model;
2. for $J < 0$, all the spins are antialigned $\sigma_i = -\sigma_j$ for i near j, called antiferromagnetic model;
3. for $B > 0$, all the spins are aligned upwards $\sigma_i = +1$;
4. for $B < 0$, all the spins are aligned upwards $\sigma_i = -1$.

Now, we will analyse the system in the canonical ensemble. Since we are in a discrete space, the canonical partition function is made over a sum of all the 2^N states, instead of an integral,

$$Z_N = \sum_{\sigma_i = \pm 1} \exp(-\beta H(\sigma_i)) \ .$$

The thermodynamic equilibrium corresponds to the configuration of minimum (Helmoltz) free energy.

Suppose the external magnetic field is shut down, i.e. $B = 0$. What is the equilibrium configuration? At low temperature (and low energies), Helmoltz free energy is at minimum when entropy is small and all spins are aligned, because there are only 2 possible states (all upwards or all downwards). At high temperature (and high energies), Helmoltz free energy is at minimum when entropy is large and all spins are random-aligned, because all spins point in all directions.

By means of the magnetisation

$$M = \langle \sum_{i=1}^{N} \sigma_i \rangle_c = \sum_{i=1}^{N} \langle \sigma_i \rangle_c \ , \tag{14.1}$$

where the second expression follows from translation invariance, we can quantitatively study the phase transition.

14.2 Mean-field approximation

In general, it is difficult to compute the total canonical partition function because it cannot be reduced to the computation of the 1-particle canonical partition function Z_1 since there is an interacting term

$$Z_N = \sum_{\{\sigma_i=\pm 1\}} \exp(-\beta H) \neq (Z_1)^N \ .$$

However, we can make an useful approximation by neglecting the quadratic fluctuation term in the expansion of the interacting term in the Hamiltonian

$$\begin{aligned}
\sigma_i\sigma_j &= ((\sigma_i - m) + m)((\sigma_j - m) + m) \\
&= m^2 + m(\sigma_i - m) + m(\sigma_j - m) + (\sigma_i - m)(\sigma_j - m) \\
&\simeq m^2 + m(\sigma_i - m) + m(\sigma_j - m) \\
&= m^2 + m\sigma_i - m^2 + m\sigma_j - m^2 \\
&= -m^2 + m(\sigma_i + \sigma_j) \ ,
\end{aligned}$$

where $m = M/N$. The physical interpretation of the mean-field approximation is the following: when fluctuations with respect to the mean field m are negligible, we do not have to compute every link with respect to each others but only with respect to the mean field m. In the mean-field approximation, the magnetisation is given by the equation

$$m = \tanh(\beta(Jzm + B)) \ .$$

Proof. In fact, the Hamiltonian is

$$\begin{aligned}
H_{mf} &= -J \sum_{i \text{ near } j} (-m^2 + m(\sigma_i + \sigma_j)) - B\sum_i \sigma_i \\
&= m^2 J \underbrace{\sum_{i \text{ near } j} 1}_{\frac{Nz}{2}} - Jm \sum_{i \text{ near } j} (\sigma_i + \sigma_j) - B\sum_i \sigma_i \\
&= \frac{m^2 zNJ}{2} - Jmz\sum_i \sigma_i - B\sum_i \sigma_i \\
&= \frac{m^2 zNJ}{2} - (Jmz + B)\sum_i \sigma_i \ ,
\end{aligned}$$

where we have estimates that the number of links, given the coordination number z which tells how many neighboring sites, is $Nz/2$. The canonical partition function becomes

$$\begin{aligned}
Z_N^{mf} &= \sum_{\{\sigma_i=\pm 1\}} \exp(-\beta H_{mf}) \\
&= \exp(-\beta \frac{Jznm^2}{2}) \sum_{\{\sigma_i=\pm 1\}} \exp(\beta(B+Jmz)\sum_i \sigma_i) \\
&= \exp(-\beta \frac{Jznm^2}{2}) (\sum_{\{\sigma_i=\pm 1\}} \exp(\beta(B+Jmx)\sigma_i))^N \\
&= \exp(-\beta \frac{Jznm^2}{2}) (\exp(\beta(B+Jmz)) + \exp(-\beta(B+Jmz)))^N \\
&= \exp(-\beta \frac{Jznm^2}{2}) (2\cosh(\beta(B+Jmz)))^N \ .
\end{aligned}$$

The Helmoltz free energy is

$$\begin{aligned}
F &= -\frac{1}{\beta} \ln Z_N^{mf} \\
&= -\frac{1}{\beta}(-\beta \frac{JzNm^2}{2}) N \ln(2\cosh(\beta(B+Jmz))) \\
&= \frac{JzNm^2}{2} N \ln(2\cosh(\beta(B+Jmz))) \ .
\end{aligned}$$

The magnetisation is

$$\begin{aligned}
m &= \frac{1}{N} \langle \sum_i \sigma_i \rangle_c \\
&= \frac{1}{N} \sum_{\{\sigma_i=\pm 1\}} \sum_i \sigma_i \exp(-\beta H) \\
&= -\frac{1}{\beta N} \sum_{\{\sigma_i=\pm 1\}} \frac{1}{Z_N} \frac{\partial}{\partial \beta} \exp(-\beta H) \\
&= -\frac{1}{\beta N} \frac{\partial \ln Z_N}{\partial \beta} \ .
\end{aligned}$$

Hence

$$m = \tanh(\beta(B+Jmz)) \ .$$

q.e.d.

Now, we have a self-consistent equation for m to solve. The condition for having a solution is

$$m \begin{cases} > 0 & B > 0 \\ < 0 & B < 0 \end{cases} \ . \tag{14.2}$$

Particular attention is the study of the solution for $B = 0$. The magnetisation becomes

$$m = \tanh \frac{Jmz}{k_B T} = \tanh(\frac{T_c}{T} m) \ ,$$

where $T_c = Jz/k_B$ is the critical temperature, that depends on z. Calling $\tilde{m} = T_c m/T$, we have

$$\frac{T\tilde{m}}{T_c} = \tanh \tilde{m} \ ,$$

which can be solved graphically by finding the intersection between the plots of the right-handed side (a straight line) and of the left-handed side (an hyperbolic tangent).See Figure 14.2. Therefore, by looking at the plot, we can conclude that

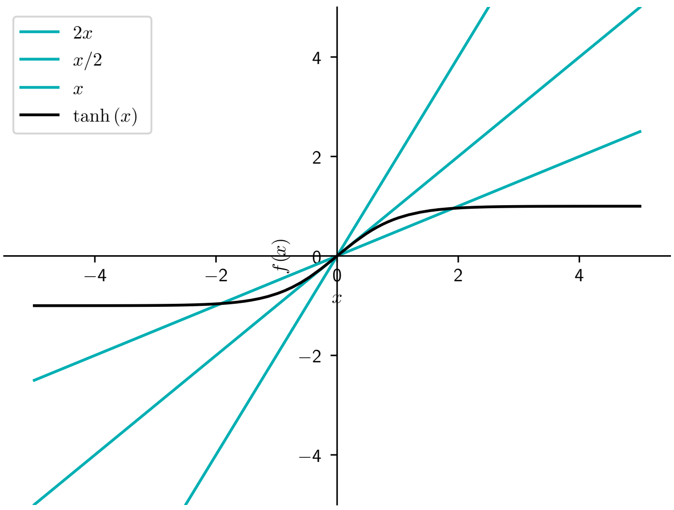

Figure 14.2: A plot of the graphical solution of $T\tilde{m}/T_c = \tanh \tilde{m}$ for different value of $T/T_c = 1/2, 1, 2$.

1. for $T \geq T_c$, there is only one solution $m = 0$;
2. for $T < T_c$, there are two non-trivial solutions $m(T) = \pm m_0(T)$, one positive and one negative.

To summarise

$$m = \begin{cases} 0 & T > T_c \\ \pm m_0(T) & T < T_c \end{cases} \ . \tag{14.3}$$

Now, we are able to compute the phase diagram (T, B). In fact, for $B \neq 0$, we recover (14.2), whereas for $B = 0$, $m \neq 0$ for $T < T_c$ (ferromagnetic phase) and $m = 0$ for $T \geq T_c$ (paramagnetic phase). See Figure (14.3). By looking at it, we can observe that m is an order parameter, since when it is zero there is disorder and when it is different from zero, there is order. It signals as well when there is a phase transition, since by its value we can say if we are in a ferromagnetic or in a paramagnetic phase. See Figure (14.4).

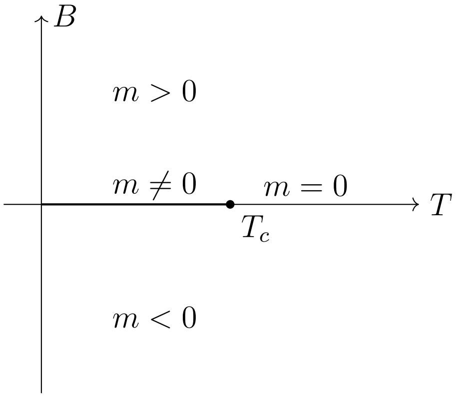

Figure 14.3: Phase diagram of the Ising model.

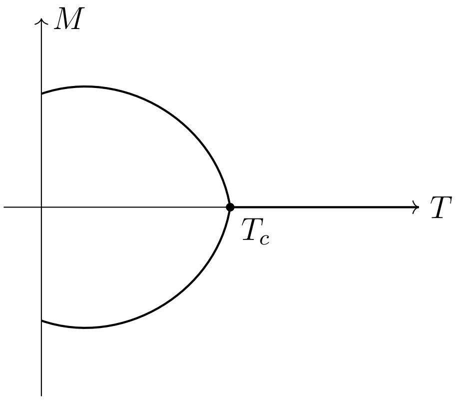

Figure 14.4: Qualitative plot of M in function of T.

In particular, in a neighborhood of T_c, we can estimate that the behaviour is

$$M \sim (T - T_c)^{\beta} \ , \tag{14.4}$$

where $\beta \in \mathbb{R}$ is a parameter and $T < T_C$. *beta* characterises the phase transition, since it tells at which speed $M \to 0$ when approaching $T \to T_c$. It is one of the 6 so-called critical exponents.

Other information can be found in the 2-point correlation function between 2 different sites

$$G_{ij} = \langle \sigma_i \sigma_j \rangle - \langle \sigma_i \rangle \langle \sigma_j \rangle = \langle \sigma_i \sigma_j \rangle - m^2 \ ,$$

which in the limit for which $r = |i - j|$ is large, it can be estimated to be

$$G(r) \propto \begin{cases} \exp(-\frac{r}{\xi}) & T \neq T_c \\ r^{-d+2-\eta} & T = T_c \end{cases} , \tag{14.5}$$

where ξ is the correlation length

$$\xi(T) = |1 - \frac{T}{T_c}|^{-\nu} \xrightarrow{T \to T_c} \infty \ . \tag{14.6}$$

where η and ν are critical exponents. Physically, ξ tells us what is the radius inside which all the spins are strongly correlated. For $T = T_c$, all spins are correlated since they are all aligned. See Figure (14.5).

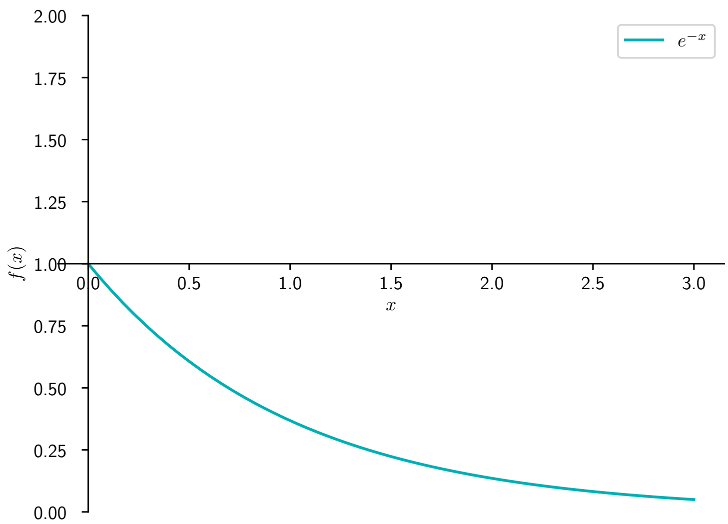

Figure 14.5: A plot of the correlation function for $\xi = 1$ at $T \neq T_c$.

14.3 Spontaneous symmetry breaking

In the classical fluid system, we can find phase transition by studying symmetries of the system. In fact, we can distinguish solid from fluid by the translation or rotations invariance, since solid has only discrete invariance, whereas fluid has continuous invariance. However, we cannot distinguish with symmetries between gas and liquid. This means that the phase transition $V-L$ is not breaking any symmetry, but the phase transition $L-S$ does. Also in the Ising model, we can similarly notice that a phase transition can arise from a spontaneous symmetry breaking. In fact, the interacting term in the Hamiltonian H_{int} is invariant under the global symmetry group $\mathbb{Z}_2$

$$\sigma_i \to -\sigma_i \ , \quad \sigma_i \to \sigma_i \ .$$

However, the second term breaks explicitly the symmetry, since under this transformation it transforms as $H_{field} \to -H_{field}$. Moreover, notice that, by definition (14.1), under this symmetry we have

$$m = \frac{M}{N} = \frac{1}{N}\sum_{i=1}^{N}\langle\sigma_i\rangle_c \to -\frac{1}{N}\sum_{i=1}^{N}\langle\sigma_i\rangle_c = -\frac{M}{N} = -m \ , \tag{14.7}$$

which implies that the only possible value of m is zero. In fact, for $T > T_c$ there is indeed $m = 0$, but for $T < T_c$, the equilibrium state is no longer invariant under this symmetry. The Hamiltonian remains the same, but equilibrium states are not invariant anymore. This is the definition of a spontaneous symmetry breaking.

Formally, we can state that, at high temperature, we have a disordered phase, which is highly symmetric that correspond to a symmetry group G, whereas, at low temperature, we have an ordered phase, which is lowly symmetric that correspond to a symmetry subgroup $G_0 \subset G$. Let O be an observable (not-invariant under G) such that

$$\phi = \langle O\rangle = \begin{cases} 0 & T > T_c \\ \phi_0(T) \neq 0 & T < T_c \end{cases} .$$

Then we say that a symmetry is spontaneously broken and ϕ is an ordered parameter. In the Ising model, we can identify $\phi = m$, since it is not invariant under $\mathbb{Z}_2$ by (14.7) and it is indeed a step function in $T = T_c$ by (14.3). As phase transitions, also symmetry breaking needs the thermodynamic limit. In fact, we can arrive to a spontaneous symmetry breaking only in a way that are not equivalent. The first one is to shut down the external field and then compute the thermodynamic limit

$$\langle O\rangle_{N,V,B\neq 0} \xrightarrow{B\to 0} 0 \xrightarrow{td} 0 \ .$$

The second one is to first compute the thermodynamic limit and then to shut down the external field

$$\langle O\rangle_{N,V,B\neq 0} \xrightarrow{td} \langle O\rangle_{n,B\neq 0} \xrightarrow{B\to 0} \begin{cases} 0 & T > T_c \\ O_0 \neq 0 & T < T_c \end{cases} .$$

Therefore, we can individuate ϕ as

$$\phi = \lim_{B\to 0}\lim_{td}\langle O\rangle_{N,V,B} \ ,$$

where the two limits do not commute.

14.4 Critical exponents and universality classes

During the study of phase transitions, we some parameters like (14.4), (**??**) and (14.6). These are the critical exponents and they describe the behavior of physical quantities near the critical temperature of a phase transitions. We define the reduced temperature

$$\epsilon = \frac{T_c - T}{T_c} \ ,$$

which tells us how much we are far away from the phase transition in terms of temperature. The critical exponent associated to an observable f is

$$\lambda_f = \lim_{\epsilon \to 0} \frac{\ln f(\epsilon)}{\ln \epsilon} \ ,$$

so that

$$f(\epsilon) \simeq g(\epsilon)|\epsilon|^{\lambda_f} \ .$$

Proof. In fact, for $\epsilon \ll 1$,

$$\frac{\ln f(\epsilon)}{\ln \epsilon} = \frac{\ln g(\epsilon)|\epsilon|^{\lambda_f}}{\ln \epsilon} = \underbrace{\frac{\ln g(\epsilon)}{\ln \epsilon}}_{0} + \frac{\lambda_f \ln \epsilon}{\ln epsilon} \simeq \lambda_f \ .$$

q.e.d.

The 6 critical exponents are

1. α in the specific heat $C_{B=0} \simeq |\epsilon|^{-\alpha}$,
2. β in the specific heat $\phi \simeq |\epsilon|^{\beta}$,
3. γ in the specific heat $\chi_{B=0} \simeq |\epsilon|^{-\gamma}$,
4. δ in the specific heat $B \simeq \text{sgn}(\phi)|\phi|^{\delta}$,
5. ν in the specific heat $\xi \simeq |\epsilon|^{-\nu}$,
6. η in the specific heat $G(r) \simeq r^{-d+2-\eta}$.

$alpha$, γ and ν have a minus sign to prevent divergences. They are calculated with the scaling hypothesis which states that Helmoltz free energy is an homogeneous function of ϵ and B

$$f(\lambda\epsilon, \lambda B) = \lambda f(\epsilon, B) \ .$$

Therefore, phase transitions can be classified into classes that are independent of the microscopic Hamiltonian. Due to the scale invariance, different systems may have the same behaviour of phase transition. The parameter of classification are

1. dimension of the space d,
2. symmetry group of the Hamiltonian H,
3. residual symmetry subgroup G_0.

Recall that the mean field approximation is exact for $d \geq 4$ while it works poorly for decreasing d. However, for $d = 2$, we have the exact solution.

Part V

Identical particles and second quantisation

Chapter 15

Quantum Mechanics

In this chapter, we will study the mathematical framework of quantum mechanics necessary to study quantum statistical mechanics.

15.1 States and projectors

In quantum mechanics, a pure state of a quantum particle is represented by a normalised vector in a (separable) Hilbert space $|\psi\rangle \in \mathcal{H}$. This is the best knowledge we can have. An Hilbert space $\mathcal{H}$ is a vector space on $\mathbb{C}$, i.e. in which a linear superposition of vectors is still in the space

$$\lambda|\psi\rangle + \mu|\phi\rangle \in \mathcal{H} \ , \quad \forall|\psi\rangle, |\phi\rangle \in \mathcal{H} \ , \forall\lambda, \mu \in \mathbb{C} \ ,$$

endowed with a scalar product $\langle\psi|\phi\rangle$. In particular, via the scalar product, it is possible to associate a norm to the state, which is set to 1 by the probability intepretation $||\psi||^2 = \langle\psi|\psi\rangle = 1$. In the Schroedinger representation, this means that the wave function is a square-integrable function $\psi(t, \mathbf{x}) \in L^2(\mathbb{R}^d)$. The probability intepretation tells us that $|\psi(t, \mathbf{x})|$ is the probability density to find the particle in a volume element $d^d x$ at time t and the normalisation condition that the total probability to find the particle in the whole $\mathbb{R}^d$ is 1

$$\int_{\mathbb{R}^d} d^d x \ |\psi(t, x)|^2 = 1 \ .$$

However, by the normalisation condition, a state is not associated to a single vector, but a class of equivalence of them, called a ray in the Hilbert space, since two states are physically equivalent if $|\psi'\rangle = \exp(i\varphi)|\psi\rangle$, because their norms are the same. This is the best knlowledge we can have.

To remove this ambiguity, we introduce the notion of projection operators or projectors, which uniquely determine a state

$$P_\psi = \frac{|\psi\rangle\langle\psi|}{\langle\psi|\psi\rangle} \ ,$$

which for normalisation states becomes

$$P_\psi = |\psi\rangle\langle\psi| \ . \tag{15.1}$$

Proof. If $|\psi'\rangle = \exp(i\varphi)|\psi\rangle$ and $\langle\psi'| = \exp(-i\varphi)\langle\psi|$, we have

$$P_{\psi'} = |\psi'\rangle\langle\psi'| = \cancel{\exp(i\varphi)}|\psi\rangle\cancel{\exp(-i\varphi)}\langle\psi| = |\psi\rangle\langle\psi| = P_\psi \ .$$

q.e.d.

It projects onto the 1-dimensional subspace $\mathcal{H}_\psi = \{\lambda|\psi\rangle \colon \lambda \in \mathbb{C}\}$ generated by the state $|\psi\rangle$

$$P_\psi \colon \mathcal{H} \to \mathcal{H}_\psi \ .$$

Proof. In fact, $\forall|\phi\rangle \in \mathcal{H}$, we decomposed the Hilbert space into the direct orthogonal sum of the subspace spanned by $\mathcal{H}_\psi$ and its orthogonal complement $\mathcal{H}^\perp$:

$$|\phi\rangle = \alpha|\psi\rangle + \beta|\psi^\perp\rangle \ ,$$

where $|\psi\rangle \in \mathcal{H}_\psi$, $|\psi^\perp\rangle \in \mathcal{H}^\perp$ and $\langle\psi|\psi^\perp\rangle = 0$. Therefore, the action of the projector is

$$P_\psi|\phi\rangle = \alpha P_\psi|\psi\rangle + \beta P_\psi|\psi^\perp\rangle = \alpha|\psi\rangle \underbrace{\langle\psi|\psi\rangle}_{1} + \beta|\psi\rangle \underbrace{\langle\psi|\psi^\perp\rangle}_{0} = \alpha|\psi\rangle \in \mathcal{H}_\psi \ .$$

q.e.d.

Moreover, since the projectors is orthogonal, we can define the projector onto the orthogonal subspace as $P_\psi^\perp = \mathbb{I} - P_\psi$ such that it satisfies $P_\psi P_\psi^\perp = P_\psi^\perp P_\psi = 0$. This can be generalised for a generic set of orthogonal subspaces. In fact, given an orthonormal basis $\{|e_n\rangle\}$, a projector onto an element of this basis is $P_n = |e_n\rangle\langle e_n|$ and the orthonormality condition reads as $P_n P_m = P_m P_n = 0$ for $n \neq m$.

It satisfies the following properties

1. boundness, i.e.
$$||P_\psi|| < \infty \ ,$$
2. hermiticity, i.e.
$$P_\psi^\dagger = P_\psi \ ,$$
3. idempotence, i.e.
$$P_\psi^2 = P_\psi \ , \tag{15.2}$$
4. positive defined, i.e. $\forall|\phi\rangle \in \mathcal{H}$
$$\langle\phi|P_\psi|\phi\rangle \geq 0 \ ,$$

5. trace equals to 1, i.e.
$$\operatorname{tr} P_\psi = 1 \ .$$

Actually, there is a theorem that ensures that an operators such that it satifies these 5 conditions is indeed a projector.

Proof. For the boundness, $\forall |\phi\rangle \in \mathcal{H}$

$$||P_\psi|\phi\rangle||^2 = \langle\phi|P_\psi^\dagger P_\psi|\phi\rangle = \langle\phi|\psi\rangle \underbrace{\langle\psi|\psi\rangle}_{1}\langle\psi|\phi\rangle = |\langle\psi|\phi\rangle|^2 \leq ||\phi||^1 \ ,$$

hence
$$||P_\psi|| = \frac{||P_\psi|\phi\rangle||}{||\phi||} \leq 1 \ .$$

For the hermiticity

$$P_\psi^\dagger = (|\psi\rangle\langle\psi|)^\dagger = \langle\psi|^\dagger|\psi\rangle^\dagger = |\psi\rangle\langle\psi| = P_\psi \ .$$

For the idempotence

$$P_\psi^2 = (|\psi\rangle\langle\psi|)^2 = |\psi\rangle \underbrace{\langle\psi|\psi\rangle}_{1}\langle\psi| = |\psi\rangle\langle\psi| = P_\psi \ .$$

For the positive definedness

$$\langle\phi|P_\psi|\phi\rangle = \langle\phi|\psi\rangle\langle\psi|\phi\rangle = |\langle\psi|\phi\rangle|^2 \geq 0 \ .$$

For the trace, since it is independent from the choice of the basis, we choose $|\psi\rangle = |\psi_1\rangle$ such that $\langle\psi|\psi_n\rangle = \delta_{n,1}$ and

$$\operatorname{tr} P_\psi = \sum_{n=0}^{\infty}\langle\psi_n|P_\psi|\psi_n\rangle = \sum_{n=0}^{\infty}\underbrace{\langle\psi_n|\psi\rangle}_{\delta_{n,1}}\langle\psi|\psi_n\rangle = \sum_{n=0}^{\infty}\underbrace{\delta_{n,1}}_{n=1}\langle\psi|\psi_n\rangle = \langle\psi|\psi_1\rangle = \langle\psi_1|\psi_1\rangle = 1 \ .$$

q.e.d.

Given an orthonormal basis $\{|e_n\rangle\}_{n=1}^{\infty}$ of a separable Hilbert space, the trace is defined as
$$\operatorname{tr} A = \sum_{n=1}^{\infty} A_{nn} = \sum_{n=1}^{\infty}\langle e_n|A|e_n\rangle \ .$$
It may happen that this series is not convergent. If it is convergent, the operator A is called a trace-class operator. Furthermore, if it is absolute convergent, the trace is independent on the choice of the basis. Recall that in the finite-dimensional case, the trace of a matrix is always convergent and independent on the choice of the basis.

15.2 Observables and time evolution

An observable is a linear hermitian operator $\hat{A}$ acting on the Hilbert space. We require the self-adjointness because, by the spectral theorem, they are always diagonalisable with a positive spectrum. This means that its eigenvalues are real and it always admit an orthonormal eigenbasis $\{|\psi_n\rangle\}$

$$A|\psi_n\rangle = \lambda_n|\psi_n\rangle \ , \tag{15.3}$$

where $\lambda_n \in \mathbb{R}$. In this way, $\forall|\phi\rangle \in \mathcal{H}$, we can expand it into the eigenbasis

$$|\phi\rangle = \sum_{n=1}^{\infty} c_n|\psi_n\rangle \ , \tag{15.4}$$

where $c_n \in \mathbb{C}$.

The eigenprojectors, defined as

$$P_n = |\psi_n\rangle\langle\psi_n| \ ,$$

satisfy the following properties

1. self-adjointness, i.e.
$$P_n^\dagger = P_n \ ,$$
2. orthonormality, i.e.
$$P_n P_m = \delta_{nm} P_n \ ,$$
3. completeness relation, i.e.
$$\sum_{n=0}^{\infty} P_n = \mathbb{I} \ , \tag{15.5}$$
4. spectral decomposition, i.e.
$$\hat{A} = \sum_{n=0}^{\infty} \lambda_n P_n \ . \tag{15.6}$$

Prepare a quantum system in a state $|\psi\rangle$. A measurement of an observable $\hat{A}$ has outcomes corresponding to its eigenvalues λ_n with probability $p_n = |c_n|^2$. Recall that λ_n are the coefficients in (15.3) and c_n in (15.4). Its average value is

$$\langle A\rangle = \langle\psi|\hat{A}|\psi\rangle = \sum_n \lambda_n |c_n|^2 = \sum_n \lambda_n p_n \ , \tag{15.7}$$

whereas its standard deviation is

$$(\Delta A)^2 = \langle A^2\rangle - \langle A\rangle^2 \ .$$

Proof. In fact, using (15.3) and (15.4)

$$
\begin{aligned}
\langle A\rangle &= \langle\psi|\hat{A}|\psi\rangle \\
&= \sum_{m=0}^{\infty} c_m^* \langle\psi_m| \sum_{n=0}^{\infty} c_n \underbrace{\hat{A}|\psi_n\rangle}_{\lambda_n|\psi_n\rangle} \\
&= \sum_{n=0}^{\infty}\sum_{m=0}^{\infty} \lambda_n c_m^* c^n \underbrace{\langle\psi_m|\psi_n\rangle}_{\delta_{nm}} \\
&= \sum_{n=0}^{\infty}\sum_{m=0}^{\infty} \lambda_n c_m^* c^n \underbrace{\delta_{nm}}_{n=m} \\
&= \sum_{n=0}^{\infty} \lambda_n \underbrace{c_n^* c_n}_{|c_n|^2} \\
&= \sum_n \lambda_n |c_n|^2 \ .
\end{aligned}
$$

q.e.d.

Notice that measurement in quantum mechanics is a destructive process, since the wave function collapses into one of the eigenstates.

Time evolution of a quantum system is governed by a special observable, the hamiltonian $\hat{H}$, through the Schroedinger equation

$$i\hbar\frac{\partial}{\partial t}|\psi(t)\rangle = \hat{H}|\psi(t)\rangle \ .$$

Notice that this equation is linear, consistent with the superposition principle. It is also at first-order in time, meaning that once the initial condition is fixed, $|\psi(t)\rangle$ is completely determined.

Moreover, for a time-independent hamiltonian, time evolution can be equivalently expressed by a unitary operator $\hat{U}(t)$

$$|\psi(t)\rangle = \hat{U}(t)|\psi(0)\rangle \ , \tag{15.8}$$

where $\hat{U}(t) = \exp(\frac{i}{\hbar}\hat{H}t)$. Since it is unitary

$$\hat{U}^\dagger(t) = \exp(-\frac{i}{\hbar}\hat{H}t) = \hat{U}(-t) = U^{-1}(t) \ ,$$

it preserves the probability.

15.3 Density matrices and mixed states

The projector (15.1) is also called a density matrix ρ_ψ. In terms of the density matrix, the average value (15.7) of an operator $\hat{A}$ is

$$\langle A\rangle = \langle\psi|\hat{A}|\psi\rangle = \mathrm{tr}(\hat{A}\rho_\psi)\ .$$

Proof. In fact, using (15.5)

$$\begin{aligned}
\langle A\rangle &= \langle\psi|\hat{A}|\psi\rangle \\
&= \langle\psi|\mathbb{I}\hat{A}|\psi\rangle \\
&= \sum_{n=0}^{\infty}\langle\psi|P_n\hat{A}|\psi\rangle \\
&= \sum_{n=0}^{\infty}\langle\psi|\psi_n\rangle\langle\psi_n|\hat{A}|\psi\rangle \\
&= \sum_{n=0}^{\infty}\langle\psi_n|\hat{A}\underbrace{|\psi\rangle\langle\psi|}_{\rho_\psi}|\psi_n\rangle \\
&= \sum_{n=0}^{\infty}\langle\psi_n|\hat{A}\rho_\psi|\psi_n\rangle \\
&= \mathrm{tr}(\hat{A}\rho_\psi)\ ,
\end{aligned}$$

where we have exchanged brakets because they are only numbers. q.e.d.

The time evolution of the density matrix is

$$\rho_\psi(t) = \exp(-\frac{i}{\hbar}\hat{H}t)\rho_\psi(0)\exp(\frac{i}{\hbar}\hat{H}t)\ .$$

Proof. In fact, using (15.8)

$$\rho_\psi(t) = |\psi(t)\rangle\langle\psi(t)| = \exp(-\frac{i}{\hbar}\hat{H}t)\underbrace{|\psi(0)\rangle\langle\psi(0)|}_{\rho_\psi(0)}\exp(\frac{i}{\hbar}\hat{H}t) = \exp(-\frac{i}{\hbar}\hat{H}t)\rho_\psi(0)\exp(\frac{i}{\hbar}\hat{H}t)\ .$$

q.e.d.

Mixed states

A mixed state belonging to a classical mixture is a system which can be found in a state $|\psi_n\rangle$ with a probability p_n

$$\{|\psi_n\rangle, p_n\} \ ,$$

where $p_n \geq 0$ and $\sum_{n=0}^{\infty} p_n = 1$. The difference from a pure state is that, in a mixed state, the system is in a classical fixed state before the measurement whereas in a pure state, the state is in a quantum superposition. The density matrix of a mixed state is

$$\rho = \sum_n p_k |\psi_n\rangle\langle\psi_n| = \sum_n p_n \rho_n \ , \tag{15.9}$$

It defines a statistical ensemble.

Similarly to the pure state case, it satisfies the following properties

1. boundness, i.e.
$$||\rho|| < \infty \ ,$$
2. hermiticity, i.e.
$$\rho^\dagger = \rho \ ,$$
3. positive defined, i.e. $\forall |\phi\rangle \in \mathcal{H}$
$$\langle\phi|\rho|\phi\rangle \geq 0 \ ,$$
4. trace equals to 1, i.e.
$$\operatorname{tr} \rho = 1 \ .$$

However, the idempotence property (15.2) is a particular property of only pure states. There is a theorem that states that a state is pure if and only if $\rho^2 = \rho$.

Proof. In the simple case of orthogonal states $|\psi_n\rangle$, i.e. $\langle\psi_n|\psi_m\rangle = \delta_{nm}$, we have

$$\begin{aligned}
\rho^2 &= \sum_n p_n |\psi_n\rangle\langle\psi_n| \sum_m p_m |\psi_m\rangle\langle\psi_m| \\
&= \sum_n \sum_m p_n p_m |\psi_n\rangle \underbrace{\langle\psi_n|\psi_m\rangle}_{\delta_{nm}} \langle\psi_m| \\
&= \sum_n \sum_m p_n p_m |\psi_n\rangle \underbrace{\delta_{nm}}_{n=m} \langle\psi_m| \\
&= \sum_n p_n^2 |\psi_n\rangle\langle\psi_n| \\
&= \sum_n p_n^n \rho_n \ .
\end{aligned}$$

This means that if $\rho^2 = \rho$, we obtain

$$p_n^2 = p_n \ ,$$

which means that $p_{\overline{n}} = 1$ for a single $\overline{n}$ and for all the others $p_n = 0$ for $n \neq \overline{n}$, but this is indeed a pure state $\rho = |\psi_{\overline{n}}\rangle\langle\psi_{\overline{n}}|$. q.e.d.

However, the average value of an observable is the same as the pure states

$$\langle \hat{A} \rangle = \langle \psi | \hat{A} | \psi \rangle = \mathrm{tr}(\rho \hat{A}) \ . \tag{15.10}$$

Proof. In fact,

$$\langle \hat{A} \rangle = \sum_n p_n \langle \hat{A} \rangle_n = \sum_n p_n \, \mathrm{tr}(\hat{A}\rho_n) = \mathrm{tr}(\hat{A} \underbrace{\sum_n p_n \rho_n}_{\rho}) = \mathrm{tr}(\hat{\rho}) \ ,$$

where we have used the linearity of the trace. q.e.d.

Notice that in the classical case, the average value of an observable is (**??**)

$$\langle f \rangle = \int_{\mathcal{M}} d^d x \ f(x)\rho(x) \ ,$$

which shows that, in the quantum case, we have substituted the integral with the trace, the function with the observable operator and the density distribution with the density matrix.

15.4 Composite systems

Consider a quantum system composed by 2 particles. The total Hilbert space is the tensor product between the 2 single particle Hilbert spaces

$$\mathcal{H}_{tot} = \mathcal{H}_1 \otimes \mathcal{H}_2 \ .$$

Given an orthonormal basis for each Hilbert space $\{|\psi_n\rangle\} \in \mathcal{H}_1$ and $\{|\phi_m\rangle\} \in \mathcal{H}_2$, the orthonormal basis for the total Hilbert space is

$$\{|\psi_n\rangle_1 |\phi_m\rangle_2 = |\psi_n \phi_m\rangle\} \ ,$$

such that a generic state can be expanded into this basis, $\forall |\phi\rangle \in \mathcal{H}_{tot}$

$$|\phi\rangle = \sum_n \sum_m \alpha_{nm} |\psi_n \phi_m\rangle \ ,$$

where $\alpha_{nm} \in \mathbb{C}$ and the normalisation condition reads $\sum_{nm} |\alpha_{nm}|^2 = 1$.

If the 2 particle are identical, we have $\mathcal{H}_1 = \mathcal{H}_2 = \mathcal{H}$. Therefore $\mathcal{H}_{tot} = \mathcal{H}^{\otimes 2}$.

The scalar product between two sparable is

$$\langle \psi_n \phi_m | \psi_{n'} \phi_{m'} \rangle = \langle \psi_n | \psi_{n'} \rangle_1 \langle \phi_m | \phi_{m'} \rangle_2 \ ,$$

such that if the two states are orthonormal we have

$$\langle \psi_n \phi_m | \psi_{n'} \phi_{m'} \rangle = \langle \psi_n | \psi_{n'} \rangle_1 \langle \phi_m | \phi_{m'} \rangle_2 = \delta_{nn'} \delta_{mm'} \ .$$

By linerity, we can generalised this construction for N particles. However, for infinite dimensional Hilbert spaces, we need the convergence of $\sum_{nm} |\alpha_{nm}|^2$ in order to remain in a Hilbert space. The total Hilbert space is

$$\mathcal{H}_{tot} = \mathcal{H}_1 \otimes \ldots \otimes \mathcal{H}_N \ ,$$

its orthonormal basis is

$$|e_{n_1}\rangle \ldots |e_{n_N}\rangle$$

and its scalar product is

$$\langle \cdot | \cdot \rangle = \prod_k \langle \cdot | \cdot \rangle_k \ .$$

A generic state can be expanded into the orthonormal basis, $\forall |\phi\rangle \in \mathcal{H}_{tot}$

$$|\phi\rangle = \sum_{n_1, \ldots n_N} \alpha_{n_1, \ldots n_N} |e_{n_1}\rangle \ldots |e_{n_N}\rangle \ .$$

If all the particles are identical, we have $\mathcal{H}_1 = \ldots = \mathcal{H}_N = \mathcal{H}$. Therefore $\mathcal{H}_{tot} = \mathcal{H}^{\otimes N}$.

N particles

Explicitly, a single particle lives in $\mathbb{R}^3$ and its Hilbert space is $\mathcal{H} = L^2(\mathbb{R}^3) \ni \psi(x)$. The scalar product is

$$\langle \psi | \phi \rangle = \int d^3x \ \psi^*(x) \phi(x) \ ,$$

where the normalisation condition is

$$||\psi||^2 = \langle \psi | \psi \rangle = \int_{\mathbb{R}^3} d^3x \ |\psi(x)|^2 < \infty \ .$$

For N distinguishable particles, the total Hilbert space is $\mathcal{H}_{tot} = \mathcal{H} \otimes \ldots \otimes \mathcal{H}$ and a generic state is $|\psi_{n_1} \ldots \psi_{n_N}\rangle$ where $|\psi_{n_j}\rangle$ is a single particle state. Explicitly, N distinguishable particle live in $\mathbb{R}^{3N}$ and their Hilbert space is $\mathcal{H}_N = L^2(\mathbb{R}^3) \otimes \ldots \otimes L^2(\mathbb{R}^3) = L^2(\mathbb{R}^{3N}) \ni \psi(x_1, \ldots x_N)$. Therefore, an orthonormal basis is $\{u_{\alpha_1(x_1)} \ldots u_{\alpha_N(x_N)} = u_{\alpha_1 \ldots \alpha_N}(x_1, \ldots x_N)\}$ where $\{u_\alpha(x)\}$ is the single particle orthonormal basis. A generic state can be expanded in this basis as

$$\psi(x_1, \ldots x_N) = \sum_{\alpha_1 \ldots \alpha_N} c_{\alpha_1 \ldots \alpha_N} u_{\alpha_1 \ldots \alpha_N}(x_1, \ldots x_N) \ .$$

Distinguishable and indistinguishable particles

Choosing $\alpha_1 = a$ and $\alpha_2 = b$ or viceversa, we obtain

$$u_{\alpha_1=a}(x_1)u_{\alpha_2=b}(x_2) \neq u_{\alpha_1=b}(x_1)u_{\alpha_2=a}(x_2) \ ,$$

but if the particle are indistinguishable, we have

$$u_{\alpha_1=a}(x_1)u_{\alpha_2=b}(x_2) \propto u_{\alpha_1=b}(x_1)u_{\alpha_2=a}(x_2) \ ,$$

where the proportionality factor is due to the fact that states are the same up to a global phase factor. This means that they are invariant under permutations

$$\psi(P(x_1,\dots x_N)) = \exp(i\alpha_P)\psi(x_1,\dots x_N) \ ,$$

since in this way

$$|\psi(P(x_1,\dots x_N))|^2 = |\psi(x_1,\dots x_N)|^2 \ ,$$

where P belongs to the permutation group. In the next chapter, we will evaluate the phase factor α_P.

Chapter 16

Identical particles

In Quantum Mechanics, particles are said to be identical if they have all the same quantum numbers, like charge, mass, spin, etc. It follows from the uncertainty principle that identical particles are also indistinguishable, because it prevent the only way to completely distinguish each others: tracking their trajectories. This leads to properties that arise only in the quantum world, like Fermi-Dirac or Bose-Einstein statistics.

To understand how we can implement indistinguishability into our framework, consider a system composed by N identical particles that can live in $\mathbb{R}^d$. The wave-function describing them will be a square-intergable complex function $\psi(\mathbf{x}_1, \ldots, \mathbf{x}_N) \in L_2(\mathbb{R}^{Nd})$. Indistinguishability implies that all observables must be invariant under permutation of particles and 2 states that differ only for a permutation must have the same probability. Combining together this two requests means that the physical quantity to be invariant is $|\psi|^2$ and not ψ, so that

$$|\psi(P(x_1, \ldots, x_N))|^2 = |\psi(x_1, \ldots, x_N)|^2 \ ,$$

where P is a permutation such that $P(\mathbf{x}_1, \ldots, \mathbf{x}_N) = (\mathbf{x}_{i_1}, \ldots, \mathbf{x}_{i_N})$. Therefore, the two wave function are the same up to a globally $U(1)$ phase factor α_P, depending on the permutation

$$\psi(P(x_1, \ldots x_N)) = \exp(i\alpha_P)\psi(x_1, \ldots x_N) \ . \qquad (16.1)$$

16.1 Permutation group

The permutation of N elements form a group P_N. In fact, the composition of 2 permutations PQ is defined as the permutation obtained by applying first P and then Q, the identity permutation $\mathbb{I}$ does not change anything and the inverse is the permutation such that $PP^{-1} = \mathbb{I}$. This group is generated by transposition, i.e. a swap of two consecutive elements, since any permutation $P \in P_N$ can be decomposed, into a sequences of

$$\sigma_i \colon (1, 2, \ldots, i, i+1, \ldots N) \mapsto (1, 2, \ldots, i+1, i, \ldots N) \ ,$$

in the following way

$$P = \sigma_{\alpha_1} \sigma_{\alpha_2} \ldots \ . \tag{16.2}$$

However, this decomposition is not unique but there is a quantity that conserve in each possible decomposition: the number of transpositions is always even or odd. Therefore, we can define the sign of a permutation $\forall P \in P_N$

$$\mathrm{sgn}(P) = \begin{cases} +1 & \text{even number of transposition in its decomposition} \\ -1 & \text{odd number of transposition in its decomposition} \end{cases} \ .$$

Example 16.1. Given 4 numbers $(1, 2, 3, 4)$,

1. the identity is
$$(1, 2, 3, 4) \overset{\mathbb{I}}{\mapsto} (1, 2, 3, 4) \ ,$$
2. the inverse of
$$(1, 2, 3, 4) \overset{P}{\mapsto} (2, 3, 1, 4)$$
is
$$(1, 2, 3, 4) \xmapsto{P^{-1}} (3, 1, 2, 4) \ ,$$
so that
$$(1, 2, 3, 4) \overset{P}{\mapsto} (2, 3, 1, 4) \xmapsto{P^{-1}} (1, 2, 3, 4) \ .$$

Furthermore, P can be decomposed into

$$(1, 2, 3, 4) \overset{\sigma_1}{\mapsto} (2, 1, 3, 4) \overset{\sigma_2}{\mapsto} (2, 3, 1, 4) \ ,$$

so that $P = \sigma_1 \sigma_2$ and its sign is $\mathrm{sgn}(P) = +1$. To see that it is not unique, we can find another more complicated decomposition

$$\begin{aligned} (1, 2, 3, 4) &\overset{\sigma_3}{\mapsto} (1, 2, 4, 3) \overset{\sigma_1}{\mapsto} (2, 1, 4, 3) \overset{\sigma_2}{\mapsto} (2, 4, 1, 3) \\ &\overset{\sigma_3}{\mapsto} (2, 4, 3, 1) \overset{\sigma_2}{\mapsto} (2, 3, 4, 1) \overset{\sigma_3}{\mapsto} (2, 3, 1, 4) \ , \end{aligned}$$

so that $P = \sigma_3 \sigma_1 \sigma_2 \sigma_3 \sigma_2 \sigma_3$.

Useful properties of transpositions are

1. if $|i - j| > 2$, which means that they are not next to each other,
$$\sigma_i \sigma_j = \sigma_j \sigma_i \ , \tag{16.3}$$

2.
$$\sigma_i\sigma_{i+1}\sigma_i = \sigma_{i+1}\sigma_i\sigma_{i+1} \ , \tag{16.4}$$

3.
$$(\sigma_i)^2 = \mathbb{I} \ . \tag{16.5}$$

Proof. A transposition can be pictorially seen in Figure 16.1. Proofs can be seen in Figure 16.2, Figure 16.3 and Figure 16.4. q.e.d.

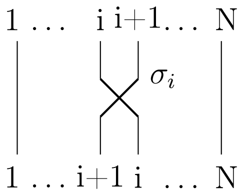

Figure 16.1: A pictorial diagram of a transposition σ_i.

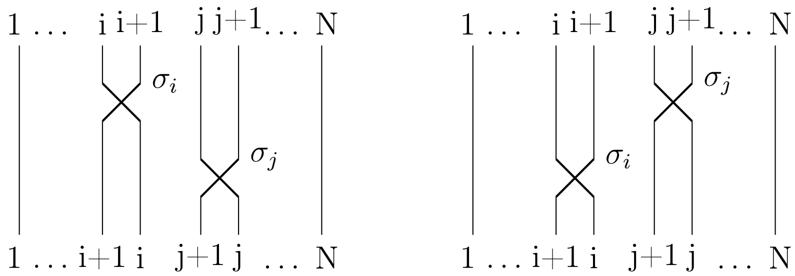

Figure 16.2: A pictorial diagram of a transposition $\sigma_i\sigma_j$ on the left and $\sigma_j\sigma_i$ on the right, where $|i-j|>2$.

16.2 Bosons and fermions

Now, we are able to calculate explicitly (16.1), which is

$$\alpha_P = \alpha_1 + \dots \alpha_N \ , \tag{16.6}$$

where α_i is the phase factor that label the transposition σ_{α_i}, i.e.

$$\psi(\sigma_{\alpha_i}(x_1, \dots x_N)) = \exp(i\alpha_i)\psi(x_1, \dots x_N) \ .$$

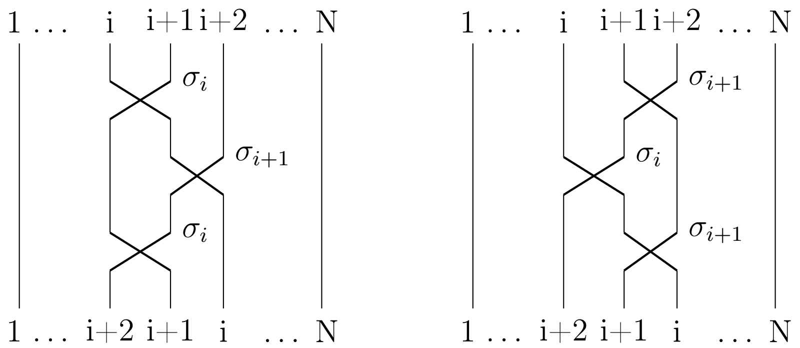

Figure 16.3: A pictorial diagram of a transposition $\sigma_i \sigma_{i+1} \sigma_i$ on the left and $\sigma_{i+1} \sigma_i \sigma_{i+1}$ on the right.

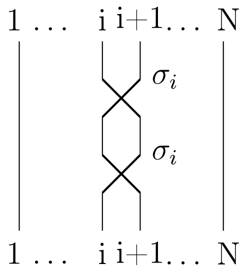

Figure 16.4: A pictorial diagram of a transposition $(\sigma_i)^2$.

Proof. In fact, using (**??**) and properties of exponentials, we obtain

$$\begin{aligned}
\psi(P(x_1, \dots, x_N)) &= \psi((\sigma_{\alpha_1} \dots \sigma_{\alpha_N})(x_1, \dots, x_N)) \\
&= \exp(i\alpha_1)\psi((\sigma_{\alpha_2} \dots \sigma_{\alpha_N})(x_1, \dots, x_N)) \\
&\vdots \\
&= \exp(i\alpha_1) \dots \exp(i\alpha_N)\psi(x_1, \dots, x_N) \\
&= \exp(i \underbrace{(\alpha_1 + \dots \alpha_N)}_{\alpha_P})\psi(x_1, \dots x_N) \\
&= \exp(i\alpha_P)\psi(x_1, \dots, x_N) \ .
\end{aligned}$$

q.e.d.

Furthermore, we can also find which are the possible values of α_P:

1. $\alpha_P = 0$ and $\exp(i\alpha_P) = 1$, which correspond respectively to a bosonic totally symmetric wavefunction, i.e. under P

$$\psi(x_1, \dots x_N) \stackrel{P}{\mapsto} (+1)\psi(x_1, \dots x_N) \ ,$$

2. $\alpha_P = \pi$ and $\exp(i\alpha_P) = \mathrm{sgn}(P)$, which correspond respectively to a fermionic totally antysymmetric wavefunction, i.e. under P

$$\psi(x_1, \dots x_N) \overset{P}{\mapsto} \mathrm{sgn}(P)\psi(x_1, \dots x_N) = \begin{cases} +\psi(x_1, \dots x_N) & \mathrm{sgn}(P) = +1 \\ -\psi(x_1, \dots x_N) & \mathrm{sgn}(P) = -1 \end{cases} .$$

Coming to hand a theorem that can be proved only in the realm of quantum field theory, the spin-statistic theorem, we can associate a particular value of the spin to this two statistics: bosons, which have symmetric wavefunctions, are associated to integer spin particles, whereas fermions, which have antisymmetric wavefunctions, are associated to half-integer spin particles.

Proof. Using (16.3)

$$\psi(x_1, \dots x_N) \overset{\sigma_i}{\longmapsto} \exp(i\alpha_i)\psi(x_1, \dots x_N) \overset{\sigma_i\sigma_j}{\longmapsto} \exp(i\alpha_i)\exp(i\alpha_j)\psi(x_1, \dots x_N) \ ,$$

$$\psi(x_1, \dots x_N) \overset{\sigma_j}{\longmapsto} \exp(i\alpha_j)\psi(x_1, \dots x_N) \overset{\sigma_j\sigma_i}{\longmapsto} \exp(i\alpha_j)\exp(i\alpha_i)\psi(x_1, \dots x_N) \ ,$$

hence

$$\exp(i\alpha_i)\exp(i\alpha_j) = \exp(i\alpha_j)\exp(i\alpha_i) \ ,$$

which means that they commute

$$\alpha_i + \alpha_j = \alpha_j + \alpha_i \ . \tag{16.7}$$

Using (16.4)

$$\begin{aligned} \psi(x_1, \dots x_N) &\overset{\sigma_i}{\longmapsto} \exp(i\alpha_i)\psi(x_1, \dots x_N) \\ &\overset{\sigma_i\sigma_{i+1}}{\longmapsto} \exp(i\alpha_i)\exp(i\alpha_{i+1})\psi(x_1, \dots x_N) \\ &\overset{\sigma_i\sigma_{i+1}\sigma_i}{\longmapsto} \exp(i\alpha_i)\exp(i\alpha_{i+1})\exp(i\alpha_i)\psi(x_1, \dots x_N) \ , \end{aligned}$$

$$\begin{aligned} \psi(x_1, \dots x_N) &\overset{\sigma_{i+1}}{\longmapsto} \exp(i\alpha_{i+1})\psi(x_1, \dots x_N) \\ &\overset{\sigma_{i+1}\sigma_i}{\longmapsto} \exp(i\alpha_{i+1})\exp(i\alpha_i)\psi(x_1, \dots x_N) \\ &\overset{\sigma_{i+1}\sigma_i\sigma_{i+1}}{\longmapsto} \exp(i\alpha_{i+1})\exp(i\alpha_i)\exp(i\alpha_{i+1})\psi(x_1, \dots x_N) \ , \end{aligned}$$

hence

$$\exp(i\alpha_i)\exp(i\alpha_{i+1})\exp(i\alpha_i) = \exp(i\alpha_{i+1})\exp(i\alpha_i)\exp(i\alpha_{i+1}) \ ,$$

which means that

$$\alpha_i + \alpha_{i+1} + \alpha_i = \alpha_{i+1} + \alpha_i + \alpha_{i+1} \ . \tag{16.8}$$

Putting together this two properties (16.7) and (16.8), we have

$$\alpha_i + \alpha_{i+1} + \alpha_i = \alpha_{i+1} + \alpha_i + \alpha_{i+1} \ ,$$

$$\cancel{\alpha_{i+1}} + \cancel{\alpha_i} + \alpha_i = \cancel{\alpha_{i+1}} + \cancel{\alpha_i} + \alpha_{i+1} \ ,$$
$$\alpha_i = \alpha_{i+1} \ .$$

Therefore, $\forall i = 1, \dots N-1$ and $\alpha_i \in [0, 2\pi[$ we have $\alpha_i = \alpha_{i+1} = \alpha$. Using (**??**)

$$\exp(i\alpha)^2 = \exp(2i\alpha) = \mathbb{I} = \exp(0) \ ,$$

which means that

$$\alpha = 0, \pi \ .$$

Finally, there are only two possibilities

$$\psi(x_1, \dots x_N) \overset{\sigma_i}{\longmapsto} \underbrace{\exp(i0)}_{+1} \psi(x_1, \dots x_N) = \psi(x_1, \dots x_N)$$

and

$$\psi(x_1, \dots x_N) \overset{\sigma_i}{\longmapsto} \underbrace{\exp(i\pi)}_{-1} \psi(x_1, \dots x_N) = -\psi(x_1, \dots x_N) \ .$$

q.e.d.

The Hilbert space of indistinguishable particle is smaller than the distinguishable one, because we have seen that the phase factor can only have two possible values. In the next chapters, we will see how we can describe such spaces, in terms of the symmetrised or antisymmetrised Hilbert space $\mathcal{H}_{S/A}$ in the language of first quantisation and in terms of the Fock space $\mathcal{F}_{B/F}$ in the language of second quantisation.

Chapter 17

Second quantisation

17.1 Symmetric/antisymmetric Hilbert space

2 particles

Consider 2 particles. If they are distinguishable, the total Hilbert space is

$$\mathcal{H}_{tot} = \mathcal{H} \otimes \mathcal{H} \ ,$$

whereas if the particles are indistinguishable, we can decomposed the Hilbert space into

$$\mathcal{H}_{tot} = \mathcal{H}_S \oplus_\perp \mathcal{H}_A \ .$$

Proof. In fact, given two states $|a\rangle_1 \in \mathcal{H}_1$ and $|b\rangle_2 \in \mathcal{H}_2$, we have

$$\begin{aligned}
|a\rangle_1|b\rangle_2 &= \frac{2}{2}|a\rangle_1|b\rangle_2 + \frac{1}{2}|b\rangle_1|a\rangle_2 - \frac{1}{2}|b\rangle_1|a\rangle_2 \\
&= \underbrace{\frac{|a\rangle_1|b\rangle_2 + |b\rangle_1|a\rangle_2}{2}}_{|\psi_S\rangle} + \underbrace{\frac{|a\rangle_1|b\rangle_2 - |b\rangle_1|a\rangle_2}{2}}_{|\psi_A\rangle} \\
&= |\psi_S\rangle + |\psi_A\rangle \ .
\end{aligned}$$

Furthermore, the permutation group for 2 particles is $P_2 = \{\mathbb{I}, \sigma\}$. The symmetric part $|\psi_S\rangle \in \mathcal{H}_S$, since

$$\sigma|\psi_S\rangle = \sigma\frac{|a\rangle_1|b\rangle_2 + |b\rangle_1|a\rangle_2}{2} = \frac{|b\rangle_1|a\rangle_2 + |a\rangle_1|b\rangle_2}{2} = \frac{|a\rangle_1|b\rangle_2 + |b\rangle_1|a\rangle_2}{2} = |\psi_S\rangle \ ,$$

where we used the commutativity property. The antysymmetric part is $|\psi_A\rangle \in \mathcal{H}_A$, since

$$\sigma|\psi_A\rangle = \sigma\frac{|a\rangle_1|b\rangle_2 - |b\rangle_1|a\rangle_2}{2} = \frac{|b\rangle_1|a\rangle_2 - |a\rangle_1|b\rangle_2}{2} = -\frac{|a\rangle_1|b\rangle_2 - |b\rangle_1|a\rangle_2}{2} = -|\psi_A\rangle \ ,$$

where we used the commutativity property. Finally, the decomposition is orthogonal, since

$$
\begin{aligned}
\langle\psi_S|\psi_A\rangle &= \frac{\langle a|_1\langle b|_2 + \langle b|_1\langle a|_2}{2}\,\frac{|a\rangle_1|b\rangle_2 - |b\rangle_1|a\rangle_2}{2}\\
&= \frac{1}{4}(\underbrace{\langle a|a\rangle_1}_{1}\underbrace{\langle b|b\rangle_2}_{1} - \langle a|b\rangle_1\langle b|a\rangle_2 + \langle b|a\rangle_1\langle a|b\rangle_2 - \underbrace{\langle b|b\rangle_1}_{1}\underbrace{\langle a|a\rangle_2}_{1})\\
&= \frac{1}{4}(-\langle a|b\rangle_1\langle b|a\rangle_2 + \langle b|a\rangle_1\langle a|b\rangle_2)
\end{aligned}
$$

and

$$
\begin{aligned}
-\langle\psi_S|\psi_A\rangle &= -\frac{\langle a|_1\langle b|_2 + \langle b|_1\langle a|_2}{2}\,\frac{|a\rangle_1|b\rangle_2 - |b\rangle_1|a\rangle_2}{2}\\
&= -\frac{1}{4}(\underbrace{\langle a|a\rangle_1}_{1}\underbrace{\langle b|b\rangle_2}_{1} - \langle a|b\rangle_1\langle b|a\rangle_2 + \langle b|a\rangle_1\langle a|b\rangle_2 - \underbrace{\langle b|b\rangle_1}_{1}\underbrace{\langle a|a\rangle_2}_{1})\\
&= -\frac{1}{4}(-\langle a|b\rangle_1\langle b|a\rangle_2 + \langle b|a\rangle_1\langle a|b\rangle_2)\\
&= \frac{1}{4}(-\langle a|b\rangle_2\langle b|a\rangle_1 + \langle b|a\rangle_2\langle a|b\rangle_1)\ ,
\end{aligned}
$$

which means that $\langle\psi_S|\psi_A\rangle = -\langle\psi_S|\psi_A\rangle$. Therefore, the only solution is $\langle\psi_S|\psi_A\rangle = 0$. q.e.d.

Notice that Pauli's exclusion principle is encoded into the antysymmetric part, because if $a = b$ we have $|\psi_A\rangle = 0$.

The decomposition is equivalent to define two orthogonal projectors: the symmetriser

$$\hat{S}\colon \mathcal{H} \to \mathcal{H}_S$$

and the antisymmetriser

$$\hat{A}\colon \mathcal{H} \to \mathcal{H}_A\ ,$$

such that they satisfy the properties

$$\hat{S}^\dagger = \hat{S}\ , \quad \hat{A}^\dagger = \hat{A}\ , \quad \hat{S}^2 = \hat{S}\ , \quad \hat{A}^2 = \hat{A}\ , \quad \hat{S}\hat{A} = \hat{A}\hat{S} = 0\ . \tag{17.1}$$

N particles

Generalising for N particles, if they are distinguishable, the total Hilbert space is

$$\mathcal{H}_{tot} = \mathcal{H} \otimes \ldots \mathcal{H}$$

and a state is $|\psi\rangle = |a_1\rangle_1 \ldots |a_N\rangle_N = |1, \ldots N\rangle$ where $|a_j\rangle \in \mathcal{H}$.

However, if the particle are indistinguishable, similarly to the 2 particles case, we can define the symmetriser

$$\hat{S} \colon |\psi\rangle \mapsto \frac{1}{N!} \sum_{P \in P_N} |P(1), \dots P(N)\rangle$$

and the antisymmetriser

$$\hat{A} \colon |\psi\rangle \mapsto \frac{1}{N!} \sum_{P \in P_N} sgn(P) |P(1), \dots P(N)\rangle \ ,$$

where $P(1, \dots N) \mapsto (P(1), \dots P(N))$. They satisfy the orthogonal projector properties (17.1). Notice that for $N > 2$ particles, the total Hilbert space is $\mathcal{H}_{tot} = \mathcal{H}_S \otimes \mathcal{H}_A \otimes \mathcal{H}'$, where bosons work only in $\mathcal{H}_S$, fermions work only in $\mathcal{H}_A$ and $\mathcal{H}'$ is not physical.

Example 17.1. For $N = 3$, we can have $\psi_S \in mathcal H_S$

$$\psi_S = \hat{S}\psi = \psi(1,2,3) + \psi(1,3,2) + \psi(2,1,3) + \psi(2,3,1) + \psi(3,1,2) + \psi(3,2,1)$$

and $\psi_A \in mathcal H_A$

$$\psi_A = \hat{A}\psi = \psi(1,2,3) - \psi(1,3,2) - \psi(2,1,3) + \psi(2,3,1) + \psi(3,1,2) - \psi(3,2,1) \ .$$

However, we can also have $\psi' \in \mathcal{H}'$ such that

$$\psi' = \psi(1,2,3) + \psi(1,3,2) - \psi(2,1,3) - \psi(2,3,1) + \psi(3,1,2) + \psi(3,2,1) \ .$$

For N distinguishable particle, consider an orthonormal basis for the total Hilbert space

$$\{u_{\alpha_1}(x_1) \dots u_{\alpha_N}(x_N)\}_{\alpha_1, \dots \alpha_N = 0}^{\infty} \ ,$$

where $\{u_{\alpha_K}(x_k)\}_{\alpha_k=1}^{\infty}$ is an orthonormal basis for a single Hilbert space $\mathcal{H}_1$. Notice that they are labelled by the ordered set $(\alpha_1, \dots \alpha_N)$ and we are specifying which particle is in which states.

In order to construct an orthonormal basis for $\mathcal{H}_A$ and $\mathcal{H}_S$ for N indistinguishable particles, we project the distinguishable orthonormal basis respectively with the antisymmetriser and the symmetriser

$$|n_1, \dots n_j, \dots\rangle = C \begin{cases} \hat{S} \\ \hat{A} \end{cases} u_{\alpha_1}(x_1) \dots u_{\alpha_N}(x_N) \ .$$

By the properties of the projectors, they are orthonormal but they are not normalised. Therefore, we need to choose a normalisation constant

$$C = \begin{cases} \sqrt{\frac{N!}{n_1! \dots n_k! \dots}} & \mathcal{H}_S \\ \sqrt{N!} & \mathcal{H}_A \end{cases} \ .$$

On the contrary for the distinguishable case, now we lose information, because we know only how many particle are in each state and not anymore which is in which state. We label the states with $n_1, \dots n_k, \dots$ with $j = 1, \dots \infty$, which are the occupation number. For bosons, we have $n_k = 0, 1, \dots, \infty$, whereas for fermions, we have $n_k = 0, 1$. For both cases, there is the constrain $N = \sum_k n_k$, which is an infinite sum but mostly are zero occupied. Moreover, given the set α_k, we uniquely determine the occupation number n_k, but given the occupation number n_k, we use the symmetric or antisymmetric property to uniquely determine the state, because it is in $1-1$ correspondence to the set n_k.

Nonetheless, there is another way to describe fermionic or bosonic quantum space in a intrinsic way, called the second quantisation because we make a further quantisation, promoting fields to operators.

17.2 Bosonic case

We define bosonic creation and annihilation operators such that they satisfies the properties

$$[\hat{a}, \hat{a}^\dagger]_- = \hat{a}\hat{a}^\dagger - \hat{a}^\dagger\hat{a} = \mathbb{I} \ . \tag{17.2}$$

Furthermore, the number operator $\hat{N} = \hat{a}^\dagger\hat{a}$ such that

$$[\hat{N}, \hat{a}] = -\hat{a} \ , \quad [\hat{N}, \hat{a}^\dagger] = \hat{a}^\dagger \ .$$

By analogy with the harmonic oscillator, the ground state is the vacuum

$$\hat{a}|0\rangle = 0 \ ,$$

and a generic state is defined by the ladder operators

$$|\psi\rangle = \frac{1}{\sqrt{n!}}(\hat{a}^\dagger)^N|0\rangle \ .$$

17.3 Fermionic case

We define fermionic creation and annihilation operators such that they satisfies the properties

$$[\hat{a}, \hat{a}^\dagger]_+ = \hat{a}\hat{a}^\dagger + \hat{a}^\dagger\hat{a} = \mathbb{I} \ . \tag{17.3}$$

Furthermore, the number operator $\hat{N} = \hat{a}^\dagger\hat{a}$ such that

$$[\hat{N}, \hat{a}] = -\hat{a} \ , \quad [\hat{N}, \hat{a}^\dagger] = \hat{a}^\dagger \ .$$

The properties can be obtained from the Pauli matrices

$$\sigma_\pm = \sigma_1 \pm i\sigma_2 \ ,$$

such that

$$(\sigma_+)^\dagger = \sigma_- \ , \quad (\sigma_-)^\dagger = \sigma_+ \ , \quad (\sigma_+)^2 = (\sigma_-)^2 = 0 \ , \quad [\sigma_-, \sigma_+]_+ = \mathbb{I} \ .$$

By analogy with the harmonic oscillator, the ground state is the vacuum

$$\hat{a}|0\rangle = 0 \ ,$$

and a generic state is defined by the ladder operators

$$|\psi\rangle = \frac{1}{\sqrt{n!}}(\hat{a}^\dagger)^N|0\rangle \ .$$

However, the anticommutator relation ensures the validity of the Pauli's exclusion principle. In fact, we have

$$a^2 = (\hat{a}^\dagger)^2 = 0 \ .$$

17.4 Fock space

Consider a single particle Hilbert space $\mathcal{H}$ with an orthonormal basis $\{|e_n\rangle\}_{n=1}^\infty$. To each $|e_n\rangle$, we associate an annihilation and a creation operators

$$|e_n\rangle \mapsto \{\hat{a}_n, \hat{a}_n^\dagger\}_{n=1}^\infty \ ,$$

such that they satisfy

$$[\hat{a}_n, \hat{a}_m]_\pm = [\hat{a}_n^\dagger, \hat{a}_m^\dagger]_\pm = 0 \ , \quad [\hat{a}_n, \hat{a}_m^\dagger]_\pm = \delta_{nm} \ ,$$

where the minus sign correponds to the commutator (bosons) (17.2) and the plus sign to the anticommutator (fermions) (17.3).

The normalised vacuum state, which describes a no particle state, is defined by the annihilation of every annihilation operator

$$\hat{a}_n|0\rangle = 0 \quad \forall n \ .$$

It generates a subspace of dimension 1

$$\mathcal{H}_{S/A}^{(0)} = \{\lambda|0\rangle \colon \lambda \in \mathbb{C}\} \ . \tag{17.4}$$

Now, we define the one-particle state. For each $|e_n\rangle$, we associate a number operator $\hat{n}_k = \hat{a}_k^\dagger \hat{a}_k$ such that

$$\hat{n}_k \hat{a}_k^\dagger|0\rangle = 1\hat{a}_k^\dagger|0\rangle \ , \quad \hat{n}_{k'}\hat{a}_k^\dagger|0\rangle = 0 \quad k' \neq k \ .$$

For a n particle state, we have

$$\hat{a}_k^\dagger|0\rangle = |n_1 = 0, \dots n_k = 1, \dots n_N = 0\rangle = |e_k\rangle \ .$$

However, for

$$\hat{a}_{k_1}^\dagger \hat{a}_{k_2}^\dagger|0\rangle = |e_{k_1}\rangle|e_{k_2}\rangle$$

we have for fermions, if $k_1 = k_2 = k$

$$(\hat{a}_k^\dagger)^2|0\rangle = 0 \ ,$$

whereas for bosons

$$(\hat{a}_k^\dagger)^2|0\rangle \neq 0 \ .$$

Furthermore, if $k_1 \neq k_2$, we have for fermions

$$\hat{a}_{k_1}^\dagger \hat{a}_{k_2}^\dagger|0\rangle = -\hat{a}_{k_2}^\dagger \hat{a}_{k_1}^\dagger|0\rangle \ ,$$

whereas for bosons

$$\hat{a}_{k_1}^\dagger \hat{a}_{k_2}^\dagger|0\rangle = \hat{a}_{k_2}^\dagger \hat{a}_{k_1}^\dagger|0\rangle \ .$$

There is a $1-1$ correspondence between the orthonormal basis $\{|e_n\rangle\}_{n=1}^\infty$ of $\mathcal{H}$ and the orthonormal basis $\{\hat{a}_k|0\rangle\}_{k=1}^\infty$ of $\mathcal{H}_{S/A}$. Hence for N particles, we have

$$\mathcal{H}_{S/A}^{(N)} = \{|n_1, \dots n_k, \dots\rangle = \frac{1}{\sqrt{\prod_j n_j}}(\hat{a}_1^\dagger)^{n_1} \dots (\hat{a}_k^\dagger)^{n_k} \dots |0\rangle\} \ .$$

If N is not fixed, like the passage from canonical to grancanonicl ensemble, the total Fock space is

$$\mathcal{F} = \bigoplus_{N=0}^{\infty} \mathcal{H}_{S/A}^{(N)} \ .$$

It satisfies the following properties

1. orthonormality, i.e.

$$\langle n'_1, \dots n'_k, \dots | n_1, \dots n_k, \dots\rangle = \delta_{n'_1, n_1} \dots \delta_{n'_k, n_k} \dots \ ,$$

2. annihilation $\hat{a}_k \colon \mathcal{H}_{S/A}^{(N)} \to \mathcal{H}_{S/A}^{(N-1)}$, i.e.

$$\hat{a}_k|n_1, \dots n_k, \dots\rangle = \eta_k \sqrt{n_k}|n_1, \dots (n_k - 1), \dots\rangle \ ,$$

   where for bosons $\eta_k = 1$ and for fermions $\eta_k = (-1)^{\sum_{j<k} n_j}$,

3. creation $\hat{a}_k^\dagger \colon \mathcal{H}_{S/A}^{(N)} \to \mathcal{H}_{S/A}^{(N+1)}$, i.e. for bosons

$$\hat{a}_k^\dagger|n_1, \dots n_k, \dots\rangle = \sqrt{n_k + 1}|n_1, \dots (n_k + 1), \dots\rangle \ ,$$

   and for fermions

$$\hat{a}_k^\dagger|n_1, \dots n_k, \dots\rangle = \eta_k \sqrt{1 - n_k}|n_1, \dots (n_k + 1), \dots\rangle \ ,$$

4. number operator $\hat{n}_k = \hat{a}_k^\dagger \hat{a}_k$ such that

$$\hat{n}_k|n_1,\dots n_k,\dots\rangle = n_k|n_1,\dots n_k,\dots\rangle$$

and the total number operator $\hat{N} = \sum_k \hat{n}_k \sum_k \hat{a}_k^\dagger \hat{a}_k$ such that

$$\hat{N}|n_1,\dots n_k,\dots\rangle = \Big(\sum_k n_k\Big)|n_1,\dots n_k,\dots\rangle \ .$$

17.5 Field operators

In the first quantisation, we quantise observables to operators, while, in the second quantisation, we quantise fields to operators. Now, a generic particle state is represented by $|f\rangle = \sum_k f_k|e_k\rangle \in \mathcal{H}$, which is equivalent to $sum_k f_k \hat{a}_k^\dagger|0\rangle$. Hence, we define the field operators

$$\hat{\psi}^\dagger(f) = \sum_k f_k \hat{a}_k^\dagger \ , \quad \hat{\psi}(f) = \sum_k f_k^* \hat{a}_k \ ,$$

in order to get a state $\hat{\psi}(f)|0\rangle$. The related commutator relations become

$$[\hat{\psi}(f), \hat{\psi}^\dagger(g)]_\pm = \langle f|g\rangle \mathbb{I} \ .$$

Proof. In fact,

$$\begin{aligned}
[\hat{\psi}(f), \hat{\psi}^\dagger(g)]_\pm &= [\sum_k f_k^* \hat{a}_k, \sum_m g_m \hat{a}^\dagger]_\pm \\
&= \sum_k \sum_m f_k^* g_m \underbrace{[\hat{a}_k, \hat{a}_m^\dagger]}_{\delta_{km}\mathbb{I}} \\
&= \sum_k \sum_m f_k^* g_m \underbrace{\delta_{km}}_{k=m} \mathbb{I} \\
&= \sum_k f_k^* g_k \mathbb{I} \\
&= \langle f|g\rangle \mathbb{I} \ .
\end{aligned}$$

where we have used

$$|f\rangle = \sum_k f_k|e_k\rangle \ , \quad |g\rangle = \sum_m g_m|e_m\rangle \ , \quad \langle f|g\rangle = \sum_k \sum_m f_k^* g_m \underbrace{\langle e_k|e_m\rangle}_{\delta_{km}} = \sum_k f_k^* g_k \ .$$

q.e.d.

Consider a single particle state in $\mathcal{H} = L^2(\mathbb{R}^d) \ni \psi(x)$ with an orthonormal basis $u_k(x)$ such that to each ket there are ladder operators $\hat{a}_k$ and $\hat{a}_k^\dagger$. Hence $L^2(\mathbb{R}^d) \ni f(x) = \sum_k f_k u_k(x)$ and we define field operators

$$\hat{\psi}(x) = \sum_k u_k^*(x)\hat{a}_k \ , \quad \hat{\psi}^\dagger(x) = \sum_k u_k(x)\hat{a}_k^\dagger \ ,$$

which is alinear superposition of annihilation and creation operators. Actually, it is called an operator-valued function because its output is an operator. In fact

$$\int_{\mathbb{R}^d} d^d x \ \psi^\dagger(x) \sum_k u_k^*(x)\hat{a}_k^\dagger = \sum_k \hat{a}_k^\dagger \int_{\mathbb{R}^d} d^d x \ u_k^*(x) f(x) = \sum_k \hat{a}_k^\dagger f_k \ ,$$

where we have exchanged sum and integral because they are convergent.

The commutation relations are

$$[\psi(x), \psi^\dagger(y)] = \mathbb{I}\delta(x-y) \ .$$

Proof. In fact,

$$\begin{aligned}[\hat{\psi}(f), \hat{\psi}^\dagger(g)]_\pm &= [\int d^d x \ f^*(x)\hat{\psi}(x), \int d^d y \ g(y)\hat{\psi}^\dagger(y)]_\pm \\ &= \int d^d x \int d^d y \ f^*(x) g(y) [\psi(x), \psi^\dagger(y)] \ ,\end{aligned}$$

which must be equal to

$$\langle f|g\rangle = \int d^d x \ f^*(x) g(x) \ .$$

Hence

$$[\psi(x), \psi^\dagger(y)] = \mathbb{I}\delta(x-y) \ .$$

q.e.d.

For instance, a plane wave $u(x) = \exp(i\mathbf{k}\cdot\mathbf{x})$ and $\hat{\psi}(x) = \sum_k \hat{a}_k^\dagger \exp(i\mathbf{k}\cdot\mathbf{x})$. Notice that field operators are basis independent

17.6 Operators

Consider a Fock space $\mathcal{F} = \bigoplus_{N=0}^\infty \mathcal{H}_{B/F}^{(N)}$ with orthonormal basis $|n_1, \dots n_k, \dots\rangle = \frac{1}{\sqrt{\prod_j n_j!}} (\hat{a}_1^\dagger)^{n_1} \dots (\hat{a}_k^\dagger)^{n_k} \dots |0\rangle$, which is in $1-1$ correspondence to the orthonormal basis $\psi_{n_1 \dots n_k \dots}(x_1, \dots x_k, \dots) = c_N \begin{bmatrix} \hat{S} \\ \hat{A} \end{bmatrix} u_{\alpha_1}(x_1) \dots u_{\alpha_k}(x_k) \dots$, where $hatS$ is the symmetriser and $\hat{A}$ is the antisymmetriser.

We define a one-body operator, associated to a system in which all the particles are the same, as

$$\hat{O}^{(1)} = \sum_{j=1}^{N} \hat{O}(\hat{p}_j, \hat{x}_j) \ .$$

Since it is self-adjoint, it exists an orthonormal basis of eigenvalues $\{u_\alpha(x)\}$, such that

$$\hat{O}(\hat{p}, \hat{x}) u_\alpha(x) = \epsilon_\alpha u_\alpha(x) \ .$$

Since

$$\begin{aligned}
\hat{O}^{(1)} \psi_{n_1 \ldots n_k \ldots}(x_1, \ldots x_k, \ldots) &= \Big(\sum_{j=1}^{\infty} \hat{O}(\hat{p}_j, \hat{x}_j) \Big) \psi_{n_1 \ldots n_k \ldots}(x_1, \ldots x_k, \ldots) \\
&= \Big(\sum_{j=1}^{\infty} \hat{O}(\hat{p}_j, \hat{x}_j) \Big) c_N \begin{bmatrix} \hat{S} \\ \hat{A} \end{bmatrix} u_{\alpha_1}(x_1) \ldots u_{\alpha_k}(x_k) \ldots \\
&= c_N \begin{bmatrix} \hat{S} \\ \hat{A} \end{bmatrix} \Big(\sum_{j=1}^{\infty} \hat{O}(\hat{p}_j, \hat{x}_j) u_{\alpha_1}(x_1) \ldots u_{\alpha_k}(x_k) \ldots \Big) \\
&= c_N \begin{bmatrix} \hat{S} \\ \hat{A} \end{bmatrix} \Big(\sum_{j=1}^{\infty} u_{\alpha_1}(x_1) \ldots \underbrace{\hat{O}(\hat{p}_j, \hat{x}_j) u_{\alpha_j}(x_j)}_{\epsilon_{\alpha_j} u_{\alpha_j}(x_j)} \ldots \Big) \\
&= \Big(\sum_{j=1}^{\infty} \epsilon_j n_j \Big) \psi_{n_1 \ldots n_k \ldots}(x_1, \ldots x_k, \ldots) \ .
\end{aligned}$$

For the Fock space, we have

$$\hat{O}_F^{(1)} = \sum_{j=1}^{\infty} \epsilon_j \hat{n}_j = \sum_{j=1}^{\infty} \epsilon_j \hat{a}_j^\dagger \hat{a}_j \ ,$$

where

$$\epsilon_j = \langle u_j(x) | \hat{O}(\hat{p}_j, \hat{x}_j) | u_j(x) \rangle \ .$$

Hence

$$\hat{O}_F^{(1)} = \sum_{j=1}^{\infty} \langle u_j(x) | \hat{O}(\hat{p}_j, \hat{x}_j) | u_j(x) \rangle \hat{a}_j^\dagger \hat{a}_j \ .$$

Since it is dependent of the basis, because we choose the eigenbasis, we choose a different arbitrary basis

$$\psi^\dagger(x) = \sum_k u_k(x) \hat{a}_k^\dagger = \sum_m v_m(x) b_m^\dagger \ ,$$

and we define the one-body operator

$$\hat{O}_F^{(1)} = \int d^d x \ \hat{\varphi}^\dagger(x) \hat{O}(\hat{p}, \hat{x}) \hat{\varphi}(x) \ , \tag{17.5}$$

which this time is basis independent.

Proof. In fact

$$
\begin{aligned}
\int d^dx\ \hat{\varphi}^\dagger(x)\hat{O}(\hat{p},\hat{x})\hat{\varphi}(x) &= \int d^dx\ \Big(\sum_k u_k(x)\hat{a}^\dagger(x)\Big)\hat{O}(\hat{p},\hat{x})\Big(\sum_m u^*_m(x)\hat{a}_m(x)\Big) \\
&= \sum_k\sum_m \hat{a}^\dagger_k\hat{a}_m \int d^dx\ u_k(x)\,\underbrace{\hat{O}(\hat{p},\hat{x})u^*_m(x)}_{\epsilon_m u^*_m(x)} \\
&= \sum_k\sum_m \hat{a}^\dagger_k\hat{a}_m\epsilon_m \underbrace{\int d^dx\ u_k(x)u^*_m(x)}_{\delta_{km}} \\
&= \sum_k\sum_m \hat{a}^\dagger_k\hat{a}_m\epsilon_m \underbrace{\delta_{km}}_{k=m} \\
&= \sum_k \hat{a}^\dagger_k\hat{a}_k\epsilon_k = \hat{O}^{(1)}_F\ .
\end{aligned}
$$

q.e.d.

It can be written as

$$\hat{O}^{(1)}_F = \sum_k\sum_m t_{km}\hat{b}^\dagger_k\hat{h}_m\ ,$$

where the transition amplitude is

$$t_{km} = \langle v_k|\hat{O}(\hat{p},\hat{x})|v_m\rangle\ .$$

To summarise, the onebody operator is

$$\hat{O}^{(1)}_F = \begin{cases} \sum_{mm'} t_{mm'}\hat{b}^\dagger_m\hat{b}_m & \text{arbitrary basis} \\ \sum_k \epsilon_k\hat{a}^\dagger_k\hat{a}_k & \text{eigenbasis} \end{cases}\ .$$

17.7 Examples

The density operator of a single particle j is

$$\hat{\rho}_j = \delta(x - x_j)$$

and the corresponding field operator is

$$\hat{\varphi}(x_j) = \int d^dx\psi(x)\delta(x - x_j)\ .$$

The onebody operator is

$$\hat{\rho}^{(1)} = \sum_{j=1}^N \delta(x - x_j)\ ,$$

which in the basis independent definition (17.5) on the Fock space

$$\hat{\rho}_F = \int d^d y \hat{\psi}^\dagger(y)\delta(x-y)\hat{\psi}(y) = \hat{\psi}^\dagger\hat{\psi} = \sum_{kk'} u_k^*(x)u_{k'}(x)\hat{a}_k^\dagger\hat{a}_{k'} \ .$$

The number of particle operator is

$$\begin{aligned}
\hat{N} &= \int d^d x \hat{\rho}_F^{(1)}(x) \\
&= \int d^d x \sum_{kk'} u_k^*(x)u_{k'}(x)\hat{a}_k^\dagger\hat{a}_{k'} \\
&= \sum_{kk'} \hat{a}_k^\dagger\hat{a}_{k'} \underbrace{\int d^d x u_k^*(x)u_{k'}(x)}_{\delta_{kk'}} \\
&= \sum_{kk'} \hat{a}_k^\dagger\hat{a}_{k'} \underbrace{\delta_{kk'}}_{k=k'} \\
&= \sum_k \hat{a}_k^\dagger\hat{a}_k = \sum_k \hat{n}_k \ ,
\end{aligned}$$

which is consistent with the definition of ρ since it can be seen as a density of particle whose intergral is indeed the number of particles.

Free non-relativistic 3-dimensional particles

Consider the hamiltonian of a single particle described by the wave function $\psi(x) \in L^2(\mathbb{R}^d)$

$$\hat{H}_1 = \frac{\hbar^2\hat{p}^2}{2m} = -\frac{\hbar^2}{2m}\nabla_x^2 \ .$$

The onebody operator for N particles is

$$\hat{H} = \sum_{j=1}^N \frac{\hbar^2 hatp_j^2}{2m} = -\sum_{j=1}^N \frac{\hbar^2}{2m}\nabla_{x_j}^2 \ .$$

On the Fock space, it becomes

$$H = \sum_k \epsilon_k \hat{a}_k^\dagger \hat{a}_k \ ,$$

where

$$\hat{H}_1 u_k(x) = -\frac{\hbar^2}{2m}u_k(x) = \epsilon_k u_k(x) \ .$$

However, wave plane solutions do not belong in $u_k(x) \sim \exp(i\mathbf{k}\cdot\mathbf{x}) \notin L^2(\mathbb{R}^d)$, because they are not normalisable. The trick is to go into a finite volume V and consider the space $L^2(V)$. The simple example is the particle in a cube of length L describer by the coordinates $(x, y, z) \in [0, L]$. The Schoredinger's equation becomes

$$-\frac{\hbar^2}{2m}\nabla_x^2 u_k(x,y,z) = \epsilon_k u_k(x,y,z) \ .$$

Now, we do not choose the Dirichlet or the Neumann boundary condition, but we choose the periodic boundary conditions

$$\begin{cases} u(x=0,y,z) = u(x=L,y,z) \\ u(x,y=0,z) = u(x,y=L,z) \\ u(x,y,z=0) = u(x,y,z=L) \end{cases} \ ,$$

which trasforms the cube into a 3-torus.

The ansatz solution is

$$u_\alpha(\mathbf{x}) = c\exp(i\mathbf{k}\cdot\mathbf{x}) \ ,$$

where c is a normalisation constant and

$$\nabla_2 u_\alpha(\mathbf{x}) = -(k_x^2 + k_y^2 + k_z^2)u_\alpha(\mathbf{x}) = \epsilon_{\mathbf{k}} = -k^2 \ .$$

Imposing the periodic boundary conditions, we obtain

$$u_{\mathbf{k}}(0,y,z) = \cancel{c}\exp(i\cancel{(k_y y + k_z z)}) = u_{\mathbf{k}}(L,y,z) = \cancel{c}\exp(i(k_x L + \cancel{k_y y + k_z z})) \ ,$$

hence

$$\exp(ik_x L) = 0$$

and

$$k_x = \frac{2\pi}{L}n_x \ ,$$

where $n \in \mathbb{Z}$ is an integer number. Simiarly for y and z, we have

$$\mathbf{k} = (k_x, k_y, k_z) = \frac{2\pi}{L}\mathbf{n} = \frac{2\pi}{L}(n_x, n_y, n_z)$$

where $n_x, n_y, n_z \in \mathbb{Z}$. Finally, the energy eigenvalues are

$$\epsilon_{n_x,n_y,n_z} = -\frac{4\pi^2}{L^2}(n_x^2 + n_y^2 + n_z^2)$$

and the eigenstates are

$$u_{n_x,n_y,n_z} = c\exp(i\frac{2\pi}{L}(n_x x + n_y y + n_z z)) \in L^2(V) \ .$$

The normalisation constant is

$$C = \frac{1}{\sqrt{V}} \ .$$

In fact

$$1 = ||u_{n_x,n_y,n_z}||^2 = \int_V dx\ dy\ dz\ |c|^2 |\exp(i\mathbf{k}\cdot\mathbf{x})|^2 = |c|^2 V\ .$$

Hence, the onebody operator is

$$\hat{O}^{(1)} = \sum_{j=1}^{N} \frac{\hat{p}_j^2}{2m} = -\sum_{j=1}^{N} \frac{\hbar^2}{2m} \nabla^2_{\mathbf{x}_j}\ ,$$

and choosing the orthonormal basis of wavefunctions, we have in the Fock space

$$\hat{O}_F = \sum_{\mathbf{k}} \epsilon_{\mathbf{k}} \hat{a}^\dagger_{\mathbf{k}} \hat{a}_{\mathbf{k}}\ ,$$

where $\mathbf{k} = \frac{2\pi}{L}(n_x, n_y, n_z)$ and $\epsilon_{\mathbf{k}} = \frac{\hbar^2}{2m} k^2$.

Interaction potential

Now, consider a different operator than the onebody one: the two particles operatior, used to describe interaction potential

$$\hat{O}^{(2)} = \sum_{i<j} V(x_i, x_j) = \frac{1}{2} \int dx \int dy V(x,y) \hat{\psi}^\dagger(x) \hat{\psi}^\dagger(y) \psi(y) \psi(x)\ ,$$

or

$$\hat{O}^{(2)} = \frac{1}{2} \sum_{ijkl} V_{ijkl} \hat{a}^\dagger_i \hat{a}^\dagger_j \hat{a}_k \hat{a}_l\ ,$$

where the first expression is basis-independent, while in the last one it is in the eigenbasis.

Proof. Maybe in the future. q.e.d.

Part VI

Quantum statistical mechanics

Chapter 18

Microcanonical ensemble

The microcanonical ensemble is characterised by constant volume, energy and number of particle. Since N is fixed, we can work in the Hilbert space $\mathcal{H}_{tot}$. Given a time-independent hamiltonian operator $\hat{H}$, we find the energy eigenbasis $|\psi_j\rangle \in \mathcal{H}_{tot}$

$$\hat{H}|\psi_j\rangle = E_j|\psi_j\rangle \ .$$

However, there could be some degeneracy we want to consider, i.e. $E_{j,\alpha} = E_{j,\beta}$ for $|\psi_{j,\alpha}\rangle \neq |\psi_{j,\beta}\rangle$. Therefore, we have

$$\hat{H}|\psi_{j,\alpha}\rangle = E_j|\psi_{j,\alpha}\rangle \ , \tag{18.1}$$

where $\alpha = 1, \dots n_j$.

The density operator for mixed states is (15.9)

$$\rho_{mc} = \sum_{\alpha=1}^{n_j} p_\alpha |\psi_{j,\beta}\rangle\langle\psi_{j,\beta}| \ ,$$

where p_α is the probability for the eigenstate $|\psi_{j,\beta}\rangle$. Since $E = E_j$ is fixed, all the eigenstates have the same probability to occur. Therefore $p_\alpha = \frac{1}{n_j}$ and

$$\rho_{mc} = \frac{1}{n_j}\sum_{\alpha=1}^{n_j} |\psi_{j,\alpha}\rangle\langle\psi_{j,\alpha}| = \frac{1}{n_j}\hat{P}_j \ ,$$

where

$$P_j = \sum_{\alpha=1}^{n_j} |\psi_{j,\alpha}\rangle\langle\psi_{j,\alpha}|$$

is the projector onto the energy eigenspace. Notice that we can expand the hamiltonian using (15.6)

$$\hat{H} = \sum_j E_j \hat{P}_j \tag{18.2}$$

or the total number operator

$$\hat{N} = \sum_j n_j \hat{P}_j \ . \tag{18.3}$$

The average of an observable $\hat{A}$ in the microcanonical ensemble is

$$\langle A \rangle_{mc} = \frac{1}{n_j} \sum_{\alpha=1}^{n_j} \langle \psi_{n,\alpha} | \hat{A} | \psi_{n,\alpha} \rangle \ .$$

Proof. In fact, choosing an orthonormal basis $|e_j\rangle$, the trace is

$$\mathrm{tr}_{\mathcal{H}_{tot}} \hat{A} = \sum_j \langle e_j | \hat{A} | e_j \rangle \ .$$

Therefore, using (15.10)

$$\begin{aligned}
\langle A \rangle_{mc} &= \mathrm{tr}_{\mathcal{H}_{tot}} (\hat{A} \rho_{mc}) \\
&= \mathrm{tr}_{\mathcal{H}_{tot}} \left(\hat{A} \frac{1}{n_j} \sum_{\alpha=1}^{n_j} |\psi_{j,\alpha}\rangle\langle\psi_{j,\alpha}| \right) \\
&= \frac{1}{n_j} \sum_{\alpha=1}^{n_j} \mathrm{tr}_{\mathcal{H}_{tot}} \left(\hat{A} |\psi_{j,\alpha}\rangle\langle\psi_{j,\alpha}| \right) \\
&= \frac{1}{n_j} \sum_{\alpha=1}^{n_j} \langle \psi_{j,\alpha} | \hat{A} | \psi_{j,\alpha} \rangle \ .
\end{aligned}$$

q.e.d.

The entropy in the microcanonical ensemble is

$$S_{mc} = k_B \log n_j \ ,$$

where n_j is the number of states with $E = E_j$. Notice that it is similar to the classical case (**??**).

Proof. In fact, using (**??**)

$$S_{mc} = -k_B \langle \log \rho_{mc} \rangle_{mc} = -k_B \, \mathrm{tr}_{\mathcal{H}_{tot}} (\rho_{mc} \log \rho_{mc}) \ .$$

In matrix notation, the density operator is

$$\rho_{mc} = \begin{bmatrix} \begin{bmatrix} \frac{1}{n_1} & 0 & \dots & 0 \\ 0 & \frac{1}{n_1} & \dots & 0 \\ \dots & \dots & \dots & \dots \\ 0 & 0 & \dots & \frac{1}{n_1} \end{bmatrix} & 0 & \dots & 0 & \dots & \dots \\ 0 & \begin{bmatrix} \frac{1}{n_2} & 0 & \dots & 0 \\ 0 & \frac{1}{n_2} & \dots & 0 \\ \dots & \dots & \dots & \dots \\ 0 & 0 & \dots & \frac{1}{n_2} \end{bmatrix} & \dots & 0 & \dots & \dots \\ \dots & \dots & \dots & \dots & \dots & \dots \\ 0 & 0 & \dots & \begin{bmatrix} \frac{1}{n_j} & 0 & \dots & 0 \\ 0 & \frac{1}{n_j} & \dots & 0 \\ \dots & \dots & \dots & \dots \\ 0 & 0 & \dots & \frac{1}{n_j} \end{bmatrix} & \dots & \dots \\ \dots & \dots & \dots & \dots & \dots & \dots \\ \dots & \dots & \dots & \dots & \dots & \dots \end{bmatrix} .$$

$$= \sum_j \begin{bmatrix} 0 & 0 & \dots & 0 & \dots & \dots \\ 0 & 0 & \dots & 0 & \dots & \dots \\ \dots & \dots & \dots & \dots & \dots & \dots \\ 0 & 0 & \dots & \begin{bmatrix} \frac{1}{n_j} & 0 & \dots & 0 \\ 0 & \frac{1}{n_j} & \dots & 0 \\ \dots & \dots & \dots & \dots \\ 0 & 0 & \dots & \frac{1}{n_j} \end{bmatrix} & \dots & \dots \\ \dots & \dots & \dots & \dots & \dots & \dots \end{bmatrix}$$

In order to compute the logarithm of 0, we use a trick: we define a small parameter ϵ and we make it go to zero. In this way, the limit becomes $\epsilon \log \epsilon \xrightarrow{\epsilon \to 0} = 0$. Finally, we compute the trace

$$\mathrm{tr}_{\mathcal{H}_{tot}}(\rho_{mc} \log \rho_{mc}) = \mathrm{tr} \begin{bmatrix} 0 & 0 & \dots & 0 & \dots & \dots \\ 0 & 0 & \dots & 0 & \dots & \dots \\ \dots & \dots & \dots & \dots & \dots & \dots \\ 0 & 0 & \dots & \begin{bmatrix} \frac{1}{n_j} \log \frac{1}{n_j} & 0 & \dots & 0 \\ 0 & \frac{1}{n_j} \log \frac{1}{n_j} & \dots & 0 \\ \dots & \dots & \dots & \dots \\ 0 & 0 & \dots & \frac{1}{n_j} \log \frac{1}{n_j} \end{bmatrix} & \dots & \dots \\ \dots & \dots & \dots & \dots & \dots & \dots \end{bmatrix}$$

$$= \sum_j \frac{1}{n_j} \log \frac{1}{n_j} = n_j \frac{1}{n_j} \log \frac{1}{n_j} = -\log n_j \ .$$

Hence,

$$S_{mc} = -k_B \operatorname{tr}_{\mathcal{H}_{tot}}(\rho_{mc} \log \rho_{mc}) = k_B \log n_j \ .$$

q.e.d.

Notice that entropy is always a positive function, since there is at least one state occupied $n_j \geq 1$, which implies $S \geq 0$.

Chapter 19

Canonical ensemble

The canonical ensemble is characterised by constant volume, temperature and number of particle. Energy, which can be exchange in an external reservoir, can be in one of the eigenstates (18.1) with probability

$$p_j \propto \exp(-\beta E_j) \ . \tag{19.1}$$

Consider a family of projectors $\{\hat{P}_j\}$, the density matrix of a mixed states is

$$\rho_c = \frac{1}{Z_N} \sum_j \exp(-\beta E_j) \hat{P}_j = \frac{\exp(-\beta \hat{H})}{Z_N} \ ,$$

where the quantum canonical partition function is

$$Z_N(T, V) = \mathrm{tr}_{\mathcal{H}_{tot}} \left(\frac{\exp(-\beta \hat{H})}{Z_N} \right) \ .$$

Proof. For a mixed state, the density matrix is (15.9)

$$\rho_c = \sum_j p_j \hat{P}_j = C \sum_j \exp(-\beta E_j) \hat{P}_J \ ,$$

where the probability is given by (19.1) and C is a normalisation function.

Moreover, using (18.2)

$$
\begin{aligned}
\rho_c &= C \sum_j \exp(-\beta E_j) \hat{P}_J \\
&= C \sum_j \sum_k \frac{1}{k!} (-\beta E_j)^k \underbrace{\hat{P}_j}_{(P_j)^k} \\
&= C \sum_j \sum_k \frac{1}{k!} (-\beta E_j \hat{P}_j)^k \\
&= C \sum_k \frac{1}{k!} (-\beta \sum_j E_j \hat{P}_j)^k \\
&= C \exp(-\beta \underbrace{\sum_j E_j \hat{P}_j}_{\hat{H}}) \\
&= C \exp(-\beta \hat{H}) \ ,
\end{aligned}
$$

where we have used the Taylor expansion of the exponential, one of the properties of the projectors (15.2) and we have exchanged the two series.

Finally, We set $C = \frac{1}{Z_N}$, where Z_N is the quantum canonical partition function, and by the normalisation condition

$$
1 = \mathrm{tr}_{\mathcal{H}_{tot}} \, \rho_c = \frac{1}{Z_N} \mathrm{tr}_{\mathcal{H}_{tot}} \exp(-\beta \hat{H}) \ ,
$$

hence

$$
Z_N = \mathrm{tr}_{\mathcal{H}_{tot}} \exp(-\beta \hat{H}) \ .
$$

q.e.d.

We define the Helmoltz free energy

$$
Z_N = \exp(-\beta F) \ ,
$$

or equivalently

$$
F = -\frac{1}{\beta} \log Z_N \ .
$$

The average energy is

$$
E = \langle \hat{H} \rangle_c = -\frac{\partial}{\partial \beta} \log Z_N \ .
$$

Proof. In fact,

$$\begin{aligned}
E &= \langle \hat{H} \rangle_c \\
&= \mathrm{tr}_{\mathcal{H}_{tot}}(\hat{H}\rho_c) \\
&= \mathrm{tr}_{\mathcal{H}_{tot}}\Big(\hat{H}\frac{\exp(-\beta\hat{H})}{Z_N}\Big) \\
&= \frac{1}{Z_N}\,\mathrm{tr}_{\mathcal{H}_{tot}}\Big(-\frac{\partial}{\partial\beta}\exp(-\beta\hat{H})\Big) \\
&= -\frac{1}{Z_N}\frac{\partial}{\partial\beta}\underbrace{\mathrm{tr}_{\mathcal{H}_{tot}}\exp(-\beta\hat{H})}_{Z_N} \\
&= -\frac{1}{Z_N}\frac{\partial}{\partial\beta}Z_N \\
&= -\frac{\partial}{\partial\beta}\log Z_N \ .
\end{aligned}$$

q.e.d.

The entropy is

$$S = \frac{E-F}{T} = \frac{\partial F}{\partial T} \ .$$

Proof. In fact, using (**??**)

$$\begin{aligned}
S_c &= -k_B\langle \log\rho_c\rangle_c \\
&= -k_B\,\mathrm{tr}_{\mathcal{H}_{tot}}(\rho_c\log\rho_c) \\
&= -k_B\,\mathrm{tr}_{\mathcal{H}_{tot}}(\frac{\exp(-\beta\hat{H})}{Z_N}\log\frac{\exp(-\beta\hat{H})}{Z_N}) \\
&= -k_B\,\mathrm{tr}_{\mathcal{H}_{tot}}\Big(\frac{\exp(-\beta\hat{H})}{Z_N}(\log\exp(-\beta\hat{H}) - \log Z_N)\Big) \\
&= -k_B\,\mathrm{tr}_{\mathcal{H}_{tot}}(\frac{\exp(-\beta\hat{H})}{Z_N}(-\beta\hat{H} - \log Z_N)) \\
&= k_B\beta\ \underbrace{\mathrm{tr}_{\mathcal{H}_{tot}}(\frac{\exp(-\beta\hat{H})}{Z_N}\hat{H})}_{E} + k_B\,\mathrm{tr}_{\mathcal{H}_{tot}}(\frac{\exp(-\beta\hat{H})}{Z_N}\underbrace{\log Z_N}_{-\beta F}) \\
&= \frac{E}{T} - k_B\beta F\ \frac{1}{Z_N}\underbrace{\mathrm{tr}_{\mathcal{H}_{tot}}(\exp(-\beta\hat{H}))}_{Z_N} \\
&= \frac{E-F}{T} \ .
\end{aligned}$$

q.e.d.

Notice that the entropy is well defined because the trace of the exponential of the energy eigenvalues diverges only if they are negative. Thus, we assume that $E_j \geq \min E_j = 0$.

Chapter 20

Grancanonical ensemble

The grancanonical ensemble is characterised by constant volume, temperature and chemical potential. Since N is not fixed, we work in the full Fock space $\mathcal{F}_N$. However, we restrict the hamiltonian operator in the Fock space to the condition that it conserves the number of particles, i.e. $[\hat{H}, \hat{N}] = 0$

$$\hat{H}\Big|_{\mathcal{F}_N} = \hat{H}_N \ .$$

An example of physical system which does not satisfy this condition is a photons absorbed by an electron. Energy can be in one of the eigenstates, each for a fixed N

$$\hat{H}^{(N)}|\psi_{j,\alpha}^{(N)}\rangle = E_j^{(N)}|\psi_{j,\alpha}^{(N)}\rangle \ ,$$

with probability

$$p_j^{(N)} \propto \exp(-\beta(E_j - \mu N)) \ . \tag{20.1}$$

Consider a family of projectors $\{\hat{P}_j^{(N)}\}$

$$\hat{P}_j^N = \sum_\alpha |\psi_{j,\alpha}^{(N)}\rangle\langle\psi_{j,\alpha}^{(N)}| \ ,$$

the density matrix of a mixed states is

$$\rho_{gc} = \frac{1}{\mathcal{Z}}\sum_N \sum_j \exp(-\beta(E_j - \mu N))\hat{P}_j^{(N)} = \frac{\exp(-\beta(\hat{H} - \mu\hat{N}))}{\mathcal{Z}} \ ,$$

where $z = \exp(\beta\mu)$ is the fugacity and the quantum grancanonical partition function is

$$\mathcal{Z} = \sum_{N=0}^{\infty} \mathrm{tr}_{\mathcal{H}_{tot}}\left(\exp(-\beta(\hat{H} - \mu\hat{N}))\right) = \sum_{N=0}^{\infty} z^N Z_N \ .$$

Proof. For a mixed state, the density matrix is (15.9)

$$\rho_{gc} = \sum_N \sum_j p_j \hat{P}_j^{(N)} = C \sum_N \sum_j \exp(-\beta(E_j^{(N)} - \mu N)) \hat{P}_j^{(N)} ,$$

where the probability is given by (20.1) and C is a normalisation function.

Moreover, using (18.2) and (18.3)

$$\begin{aligned}
\rho_{gc} &= C \sum_N \sum_j \exp(-\beta(E_j - \mu N)) \hat{P}_j^{(N)} \\
&= C \sum_N \sum_j \sum_k \frac{1}{k!} (-\beta(E_j^{(N)} - \mu N))^k \underbrace{\hat{P}_j^{(N)}}_{(P_j^{(N)})^k} \\
&= C \sum_j \sum_k \frac{1}{k!} (-\beta(E_j^{(N)} \hat{P}_j^{(N)} - \mu N P_j^{(N)}))^k \\
&= C \sum_k \frac{1}{k!} (-\beta \sum_N \sum_j (E_j^{(N)} \hat{P}_j^{(N)} - \mu N P_j^{(N)}))^k \\
&= C \exp(-\beta(\underbrace{\sum_j \sum_N E_j^{(N)} \hat{P}_j^{(N)})}_{\hat{H}} - \mu \underbrace{\sum_j \sum_N N \hat{P}_j^{(N)})}_{\hat{N}} \\
&= C \exp(-\beta(\hat{H} - \mu \hat{N})) ,
\end{aligned}$$

where we have used the Taylor expansion of the exponential, one of the properties of the projectors (15.2) and we have exchanged the two series.

Finally, We set $C = \frac{1}{\mathcal{Z}}$, where $\mathcal{Z}$ is the quantum canonical partition function, and by the normalisation condition

$$1 = \mathrm{tr}_{\mathcal{F}}\, \rho_{gc} = \sum_N \frac{1}{\mathcal{H}_{tot}} \mathrm{tr}_{\mathcal{F}} \exp(-\beta(\hat{H} - \mu \hat{N})) ,$$

hence

$$\begin{aligned}
\mathcal{Z} &= \mathrm{tr}_{\mathcal{F}} \exp(-\beta(\hat{H} - \mu \hat{N})) \\
&= \sum_{N=0}^{\infty} \mathrm{tr}_{\mathcal{H}_{tot}} \exp(-\beta(\hat{H} - \mu \hat{N})) \\
&= \sum_{N=0}^{\infty} z^N \underbrace{\mathrm{tr}_{\mathcal{H}_{tot}} \exp(-\beta \hat{H})}_{Z_N} \\
&= \sum_N z^N Z_N .
\end{aligned}$$

q.e.d.

Consider an observable $\hat{A}$ such that it conserves the number of particles, i.e. $[\hat{A}, \hat{N}]$, the average value is

$$\langle \hat{A} \rangle_{gc} = \mathrm{tr}_{\mathcal{F}}(\hat{A}\rho_{gc}) = \frac{1}{\mathcal{Z}} \sum_{N=0}^{\infty} z^N Z_N \langle \hat{A} \rangle_c \ .$$

Proof. In fact,

$$\begin{aligned}
\langle \hat{A} \rangle_{gc} &= \mathrm{tr}_{\mathcal{F}}(\hat{A}\rho_{gc}) \\
&= \sum_{N=0}^{\infty} \mathrm{tr}_{\mathcal{H}_{tot}} \Big(\hat{A} \frac{z^N \exp(-\beta \hat{H})}{\mathcal{Z}}) = \frac{1}{\mathcal{Z}} \sum_{N=0}^{\infty} z^N \, \mathrm{tr}_{\mathcal{H}_{tot}} (\hat{A} \exp(-\beta \hat{H})) \\
&= \frac{1}{\mathcal{Z}} \sum_{N=0}^{\infty} z^N Z_N \underbrace{\frac{\mathrm{tr}_{\mathcal{H}_{tot}} (\hat{A} \exp(-\beta \hat{H}))}{Z_N}}_{\langle \hat{A} \rangle_c} \\
&= \frac{1}{\mathcal{Z}} \sum_{N=0}^{\infty} z^N Z_N \langle \hat{A} \rangle_c \ .
\end{aligned}$$

q.e.d.

We define the granpotential

$$\Omega = -\frac{1}{\beta} \log \mathcal{Z} \ ,$$

the energy in the grancanonical is

$$E - \mu N = \langle \hat{H} - \mu \hat{N} \rangle = -\frac{\partial}{\partial \beta} \log \mathcal{Z} \ .$$

Proof. In fact

$$\begin{aligned}
E - \mu N &= \langle \hat{H} - \mu \hat{N} \rangle \\
&= \mathrm{tr}_{\mathcal{F}} \left((\hat{H} - \mu \hat{N}) \frac{\exp(-\beta(\hat{H} - \mu \hat{N}))}{\mathcal{Z}} \right) \\
&= -\frac{1}{\mathcal{Z}} \frac{\partial}{\partial \beta} \underbrace{\mathrm{tr}_{\mathcal{F}} (\exp(-\beta(\hat{H} - \mu \hat{N})))}_{\mathcal{Z}} \\
&= -\frac{1}{\mathcal{Z}} \frac{\partial}{\partial \beta} \mathcal{Z} \\
&= -\frac{\partial}{\partial \beta} \log \mathcal{Z} \ .
\end{aligned}$$

q.e.d.

The entropy in the grancanonical ensemble is

$$S = \frac{E - \mu N - \Omega}{T} \ .$$

Proof. In fact

$$\begin{aligned}
S &= -k_B \langle \log \rho_{gc} \rangle_{gc} \\
&= -k_B \operatorname{tr}_{\mathcal{F}} (\rho_{gc} \log \rho_{gc}) \\
&= -k_B \operatorname{tr}_{\mathcal{F}} \left(\frac{\exp(-\beta(\hat{H} - \mu \hat{N}))}{\mathcal{Z}} \log \frac{\exp(-\beta(\hat{H} - \mu \hat{N}))}{\mathcal{Z}} \right) \\
&= -k_B \operatorname{tr}_{\mathcal{F}} \left(\frac{\exp(-\beta(\hat{H} - \mu \hat{N}))}{\mathcal{Z}} (\log \exp(-\beta(\hat{H} - \mu \hat{N})) - \log \mathcal{Z}) \right) \\
&= k_B \beta \underbrace{\operatorname{tr}_{\mathcal{F}} \frac{\exp(-\beta(\hat{H} - \mu \hat{N}))}{\mathcal{Z}} (\hat{H} - \mu \hat{N})}_{E - \mu N} + k_B \underbrace{\operatorname{tr}_{\mathcal{F}} \log \mathcal{Z}}_{-\beta \Omega} \\
&= \frac{E - \mu N - \Omega}{T} \ .
\end{aligned}$$

q.e.d.

Chapter 21

Quantum gas

21.1 Generic quantum gas

Consider a quantum gas. The hamiltonian operator of one particle, labelled by k is

$$\hat{H}_k = \epsilon_k \hat{n}_k = \epsilon_k \hat{a}_k^\dagger \hat{a}_k \ ,$$

where $\hat{n}_k = \hat{a}_k^\dagger \hat{a}_k$ is the number operator and ϵ_k is the energy eigenvalue associated to the eigenbasis $|u_k(x)\rangle$ by the eigenvalue relation

$$\hat{H}_k |u_k(x)\rangle = \epsilon_k |u_k(x)\rangle \ .$$

Therefore, the hamiltonian one-body operator in the Fock space $\mathcal{F}$, created by the ladder operators $\hat{a}_k^\dagger$ each associated to the element of the eigenbasis $|u_k(x)\rangle$, is

$$\hat{H} = \sum_k \hat{H}_k = \sum_k \epsilon_k \hat{n}_k = \sum_k \epsilon_k \hat{a}_k^\dagger \hat{a}_k \ .$$

In $\mathcal{F}$, the total number onebody operator is

$$\hat{N} = \sum_k \hat{n}_k \ ,$$

where their eignevalues are given with respect to an orthonormal basis $|n_1, \dots n_k, \dots\rangle$ by the eigenvalue relation

$$\hat{n}_k |n_1, \dots n_k, \dots\rangle = n_k |n_1, \dots n_k, \dots\rangle \ .$$

In particular, we distinguish the bosonic and the fermionic case

$$n_k = \begin{cases} 0, 1, 2, \dots & \text{bosons} \\ 0, 1 & \text{fermions} \end{cases} \ .$$

We exploit the grancanonical ensemble. The grancanonical partition function is

$$\mathcal{Z} = \mathrm{tr}_{\mathcal{F}} \exp(-\beta(\hat{H} - \mu\hat{N})) = \prod_k \sum_{n_1,\dots n_k,\dots} \exp(-\beta(\epsilon_k - \mu)n_k) \ .$$

Proof. In fact,

$$\begin{aligned}
\mathcal{Z} &= \mathrm{tr}_{\mathcal{F}} \exp(-\beta(\hat{H} - \mu\hat{N})) \\
&= \sum_{n_1,\dots n_k,\dots} \langle n_1,\dots n_k,\dots | \exp(-\beta \sum_k (\epsilon-\mu) \underbrace{\hat{n}_k)|n_1,\dots n_k,\dots\rangle}_{n_k|n_1,\dots n_k,\dots\rangle} \\
&= \sum_{n_1,\dots n_k,\dots} \langle n_1,\dots n_k,\dots | \underbrace{\exp(-\beta \sum_k}_{\prod_k \exp} (\epsilon-\mu) n_k)|n_1,\dots n_k,\dots\rangle \\
&= \sum_{n_1,\dots n_k,\dots} \prod_k \exp(\beta(\epsilon-\mu)n_k)\langle n_1,\dots n_k,\dots | n_1,\dots n_k,\dots\rangle \\
&= \prod_k \sum_{n_1,\dots n_k,\dots} \exp(-\beta(\epsilon_k - \mu)n_k) \ ,
\end{aligned}$$

where in the last passage, we have switched the product with the sum because $n_1,\dots,n_k,\dots$ are independent. q.e.d.

Furthermore, for bosons and fermions, it becomes

$$\mathcal{Z} = \begin{cases} \prod_k \frac{1}{1-\exp(-\beta(\epsilon_k-\mu))} & \text{bosons} \\ \prod_k \Big(1 + \exp(-\beta(\epsilon_k - \mu))\Big) & \text{fermions} \end{cases} ,$$

or, in compact notation,

$$\mathcal{Z}_{\mp} = \prod_k \Big(1 \mp \exp(-\beta(\epsilon_k - \mu))\Big)^{\mp} ,$$

where the minus is associated to bosons and the plus to fermions.

Proof. For fermions, $n_k = 0, 1$

$$\mathcal{Z}_+ = \prod_k \sum_{n_1,\dots n_k,\dots=0}^{1} \exp(-\beta(\epsilon_k - \mu)n_k) = \prod_k \Big(1 + \exp(-\beta(\epsilon_k - \mu))\Big) \ .$$

For bosons, $n_k = 0, 1, 2, \ldots$

$$
\begin{aligned}
\mathcal{Z}_- &= \prod_k \sum_{n_1,\ldots n_k,\ldots=0}^{\infty} \exp(-\beta(\epsilon_k - \mu) n_k) \\
&= \prod_k \underbrace{\sum_{n_1,\ldots n_k,\ldots=0}^{\infty} \exp(-\beta(\epsilon_k - \mu))^{n_k}}_{\text{geometrical series}} \\
&= \prod_k \frac{1}{1 - \exp(-\beta(\epsilon_k - \mu))} \ .
\end{aligned}
$$

Notice that the condition of convergence of the geometrical series is $\mu < \min \epsilon_k = 0$, which we have set to zero for convenience. q.e.d.

The grancanonical potential is

$$
\Omega_\mp = -\frac{1}{\beta} \log \mathcal{Z}_\mp = \pm \frac{1}{\beta} \sum_{\boldsymbol{k}} \log\Big(1 \mp \exp(-\beta(\epsilon_{\boldsymbol{k}} - \mu))\Big) \ .
$$

Proof. In fact

$$
\begin{aligned}
\Omega_\mp &= -\frac{1}{\beta} \log \mathcal{Z}_\mp \\
&= -\frac{1}{\beta} \underbrace{\log \Big(\prod_k}_{\sum_k \log} (1 \mp \exp(-\beta(\epsilon_k - \mu)))^{\mp} \Big) \\
&= -(\mp) \sum_k \log \Big(1 \mp \exp(-\beta(\epsilon_k - \mu))\Big) \\
&= \pm \frac{1}{\beta} \sum_k \log \Big(1 \mp \exp(-\beta(\epsilon_k - \mu))\Big) \ .
\end{aligned}
$$

q.e.d.

The grancanonical average number of particle in an energy level state $\overline{k}$ is

$$
\langle \hat{n}_{\overline{k}} \rangle_{gc} = \mathrm{tr}_{\mathcal{F}} \left(\hat{n}_{\overline{k}} \frac{\exp(-\beta \sum_k (\epsilon_k - \mu) \hat{n}_k)}{\mathcal{Z}} \right) = \frac{\partial \Omega}{\partial \epsilon_{\overline{k}}} = \frac{1}{\exp(\beta(\epsilon_{\overline{k}} \mp 1))} \ .
$$

Proof. In fact

$$
\begin{aligned}
\langle \hat{n}_{\overline{k}} \rangle_{gc} &= \mathrm{tr}_{\mathcal{F}} \left(\hat{n}_{\overline{k}} \frac{\exp(-\beta \sum_k (\epsilon_k - \mu)\hat{n}_k)}{\mathcal{Z}} \right) \\
&= \frac{1}{\mathcal{Z}} \mathrm{tr}_{\mathcal{F}} \Big(-\frac{1}{\beta} \frac{\partial}{\partial \epsilon_{\overline{k}}} \exp(-\beta \sum_k (\epsilon_k - \mu)\hat{n}_k) \Big) \\
&= -\frac{1}{\beta \mathcal{Z}} \frac{\partial}{\partial \epsilon_{\overline{k}}} \underbrace{\mathrm{tr}_{\mathcal{F}} \Big(\exp(-\beta \sum_k (\epsilon_k - \mu)\hat{n}_k) \Big)}_{\mathcal{Z}} \\
&= -\frac{1}{\beta \mathcal{Z}} \frac{\partial}{\partial \epsilon_{\overline{k}}} \mathcal{Z} = \\
&= \frac{\partial}{\partial \epsilon_{\overline{k}}} \underbrace{\Big(-\frac{\log \mathcal{Z}}{\beta} \Big)}_{\Omega} \\
&= \frac{\partial}{\partial \epsilon_{\overline{k}}} \Omega \ .
\end{aligned}
$$

Therefore,

$$
\begin{aligned}
\frac{\partial}{\partial \epsilon_{\overline{k}}} \Omega &= \frac{\partial}{\partial \epsilon_{\overline{k}}} \Big(\pm \frac{1}{\beta} \sum_k \log(1 \mp \exp(-\beta(\epsilon_k - \mu))) \Big) \\
&= \pm \frac{1}{\beta} (-\beta) \frac{\exp(-\beta(\epsilon_k - \mu))}{1 \mp \exp(-\beta(\epsilon_k - \mu))} \\
&= \mp \frac{1}{1 \mp \exp(\beta(\epsilon_k - \mu))} \\
&= \frac{1}{\exp(\beta(\epsilon_k - \mu)) \mp 1} \ .
\end{aligned}
$$

q.e.d.

The average total number of particle is

$$
N = \langle \hat{N} \rangle_{gc} = \langle \sum_k \hat{n}_k \rangle_{gc} = \sum_k \frac{1}{\exp(\beta(\epsilon_k - \mu)) \mp 1} \ .
$$

The average energy is

$$
E = \langle \hat{H} \rangle_{gc} = \mathrm{tr}_{\mathcal{F}} \left(\hat{H} \frac{\exp(-\beta(\hat{H} - \mu \hat{N}))}{\mathcal{Z}} \right) = \sum_k \epsilon_k \langle \hat{n}_k \rangle
$$

Proof. In fact

$$
\begin{aligned}
E &= \langle \hat{H} \rangle_{gc} \\
&= \mathrm{tr}_{\mathcal{F}} \left(\hat{H} \frac{\exp(-\beta(\hat{H} - \mu\hat{N}))}{\mathcal{Z}} \right) \\
&= \frac{1}{\mathcal{Z}} \mathrm{tr}_{\mathcal{F}} \left(-\frac{\partial}{\partial \beta} \exp(-\beta(\hat{H} - \mu\hat{N})) \right) \\
&= -\frac{1}{\mathcal{Z}} \frac{\partial}{\partial \beta} \underbrace{\mathrm{tr}_{\mathcal{F}} \left(\exp(-\beta(\hat{H} - \mu\hat{N})) \right)}_{\mathcal{Z}} \\
&= -\frac{\partial}{\partial \beta}\Big|_z \log \mathcal{Z} \\
&= -\frac{\partial}{\partial \beta}\Big|_z (\mp \sum_k \log \left(1 \mp \exp(-\beta(\epsilon_k - \mu)) \right)) \\
&= \mp \sum_k \frac{\epsilon_k \exp(-\beta(\epsilon_k - \mu))}{1 \mp \exp(-\beta(\epsilon_k - \mu))} \\
&= \sum_k \frac{\epsilon_k}{\exp(\beta(\epsilon_k - \mu)) \mp 1} \\
&= \sum_k \epsilon_l \langle \hat{n}_k \rangle
\end{aligned}
$$

where we have kept the fugacity z constant. q.e.d.

21.2 Non-relativistic non-interacting quantum gas

So far, we have made computations for a generic quantum gas. From now on, we will deal with non-relativistic non-interacting quantum gas. The finite-volume energy eigenvalues are

$$
\epsilon_k = \frac{\hbar^2 k^2}{2m} \qquad \mathbf{k} = \frac{2\pi}{L}\mathbf{n} \ ,
$$

where $\mathbf{n} = (n_1, n_2, n_3) \in \mathbb{Z}^3$. In the thermodynamic limit, the spectrum $\mathbf{k}$ becomes continuous, but $\mathbf{n}$ not, because

$$
\Delta K_i = \frac{2\pi}{L}(n_i + 1 - n_i) = \frac{2\pi}{L} \ .
$$

Therefore, sums in k becomes integrals in dk

$$
\sum_k = \sum_{n_1, n_2, n_2 = -\infty}^{\infty} \to \frac{V}{2\pi^2} \int dk \ k^2 \ .
$$

Proof. In fact, in 1-dimensional

$$\sum_{n_1} \underbrace{\Delta n_1}_{1} = \sum_{k_1} \frac{L}{2\pi} \Delta k_1 \to \frac{L}{2\pi} \int dk_1 \ .$$

Similarly, in the 3-dimensional case

$$\begin{aligned}
\sum_{n_1,n_2,n_3=-\infty}^{\infty} \underbrace{\Delta n_1 \Delta n_2 \Delta n_3}_{1} &\to \left(\frac{L}{2\pi}\right)^3 \int dk_1 dk_2 dk_3 \\
&= \left(\frac{L}{2\pi}\right)^3 \int dk_1 dk_2 dk_3 \\
&= \left(\frac{L}{2\pi}\right)^3 \int dk^3 \\
&= \left(\frac{L}{2\pi}\right)^3 4\pi \int dk \ k^2 \\
&= \frac{V}{2\pi^2} \int dk \ k^2 \ .
\end{aligned}$$

q.e.d.

The grandcanonical potential is

$$\Omega_{\mp} = \mp \frac{2}{3} AV \int_0^{\infty} d\epsilon^{\frac{3}{2}} \frac{1}{\exp(\beta(\epsilon - \mu)) \mp 1} \ .$$

Proof. In fact

$$\begin{aligned}
\Omega_{\mp} &= \pm \frac{1}{\beta} \sum_k \log \Big(1 \mp \exp(-\beta(\epsilon_k - \mu)) \Big) \\
&\to \pm \frac{1}{\beta} \frac{V}{2\pi^2} \int_{-\infty}^{\infty} dk \ k^2 \log \Big(1 \mp \exp(-\beta(\epsilon_k - \mu)) \Big) \ .
\end{aligned}$$

Under a change of variable

$$\epsilon = \frac{\hbar^2 k^2}{2m} \ , \quad k^2 dk = \frac{1}{2} \left(\frac{2m}{\hbar^2}\right)^{\frac{3}{2}} \sqrt{\epsilon} d\epsilon \ ,$$

we obtain

$$\begin{aligned}
\Omega_{\mp} &= \pm\frac{AV}{\beta}\int_0^\infty \underbrace{d\epsilon\sqrt{\epsilon}}_{\frac{2}{3}d\epsilon^{\frac{3}{2}}}\log(1\mp\exp(-\beta(\epsilon_k-\mu))) \\
&= \pm\frac{2}{3}\frac{AV}{\beta}\int_0^\infty d\epsilon^{\frac{3}{2}}\log(1\mp\exp(-\beta(\epsilon_k-\mu))) \\
&= \pm\frac{2}{3}\frac{AV}{\beta}\underbrace{\epsilon^{\frac{3}{2}}}_{0\text{ for }\epsilon=0}\underbrace{\log(1\mp\exp(-\beta(\epsilon_k-\mu)))}_{0\text{ for }\epsilon=\infty}\Big|_0^\infty \\
&\mp\frac{2}{3}\frac{AV}{\beta}\beta\int_0^\infty d\epsilon^{\frac{3}{2}}\frac{1}{\exp(\beta(\epsilon-\mu))\mp 1} \\
&= \mp\frac{2}{3}AV\int_0^\infty d\epsilon^{\frac{3}{2}}\frac{1}{\exp(\beta(\epsilon-\mu))\mp 1} \\
&= \mp\frac{2}{3}AV\int_0^\infty d\epsilon^{\frac{3}{2}}\frac{1}{\exp(\beta(\epsilon-\mu))\mp 1}\ .
\end{aligned}$$

where we have integrated by parts and, introducing the degeneracy ($g = 2s+1$ for spin particles), we have called

$$A = \frac{g}{4\pi^2}\left(\frac{2m}{\hbar^2}\right)^{\frac{3}{2}}\ .$$

q.e.d.

The equation of state reads as

$$\Omega = -pV = -\frac{2}{3}E\ .$$

Furthermore, we have the formulas

$$N = AV\int_0^\infty d\epsilon\epsilon^{\frac{1}{2}}n(\epsilon)\ ,$$

$$P = \frac{2}{3}\frac{E}{V} = \frac{2}{3}A\int_0^\infty d\epsilon\epsilon^{\frac{3}{2}}n(\epsilon)\ .$$

21.3 Expanding with respect to fugacity z

We can expand the density with respect to the fugacity $z = \exp(\beta\mu) \geq 0$

$$n = \frac{g}{\lambda_T^3}f^{\mp}_{\frac{3}{2}}\ ,$$

where

$$f_l^{\mp} = \begin{cases}\sum_{n=0}^\infty \frac{2^{n+1}}{(n+1)^l} & f^-\text{ for bosons}\\ \sum_{n=0}^\infty \frac{(-1)^n 2^{n+1}}{(n+1)^l} & f^+\text{ for fermions}\end{cases}\ .$$

Proof. Under a change of variable

$$x^2 = \beta\epsilon \ , \quad \beta d\epsilon = 2x dx \ ,$$

we obtain

$$\begin{aligned}
n &= A \int_0^\infty dx \ \frac{2x}{\beta} \frac{x}{\sqrt(\beta)(\exp(x^2)z^{-1}) \mp 1} \\
&= \frac{4g}{\sqrt{\pi}\lambda_T^3} \int_0^\infty dx \ \frac{x^2 z}{\exp(x^2) \mp 2} \\
&= \frac{4g}{\sqrt{\pi}\lambda_T^3} \int_0^\infty dx \ x^2 z \exp(-x^2) \sum_{n=0}^\infty (\pm 1) z^n \exp(-nx^2) \\
&= \frac{4g}{\sqrt{\pi}\lambda_T^3} \sum_{n=0}^\infty (\pm 1)^n z^{n+1} \underbrace{\int_0^\infty dx \ x^2 \exp(-x^2(n+1))}_{\frac{\sqrt{\pi}}{4(n+1)^{\frac{3}{2}}}} \\
&= \frac{g}{\lambda_T^3} \sum_{n=0}^\infty (\pm 1)^n \frac{z^{n+1}}{(n+1)^{\frac{3}{2}}} \\
&= \frac{g}{\lambda_T^3} f_{\frac{3}{2}}^{\mp} \ .
\end{aligned}$$

q.e.d.

Notice that for bosons, the convergence of the series implies $z < 1$, which means $\mu > 0$.

21.4 Classical limit

21.5 Semiclassical limit

Chapter 22

Fermions

In this chapter, we restrict ourselves with the fermionic case. The equations of state are

$$n = \frac{g}{\lambda_T^3} f^+_{\frac{3}{2}}(z) \ , \quad \beta p = \frac{g}{\lambda_T^3} f^+_{\frac{5}{2}}(z) \ ,$$

where

$$f_l^+(z) = \sum_{n=0}^{\infty} \frac{(-1)^n z^{n+1}}{(n+1)^l}$$

which is an alternate-sign power series in $z = \exp(\beta\mu) > 0$, always positive. It absolutely converges for $z < 1$ and pointwisely converges for $z > 1$. Moreover, it is a monotonic function in z.

It is interesting to study its behaviour for $z \ll 1$. In fact, in the classical limit

$$f_{\frac{3}{2}}(z) \sim f_{\frac{5}{2}}(z) \sim z \ ,$$

and in the semiclassical limit

$$f_{\frac{3}{2}}(z) \sim z - \frac{z^2}{2^{\frac{3}{2}}} \ , \quad f_{\frac{5}{2}}(z) \sim z - \frac{z^2}{2^{\frac{5}{2}}} \ .$$

22.1 Low temperature limit

For the zero temperature limit $T = 0$, the Fermi-Dirac distribution becomes

$$n(\epsilon) = \frac{1}{\exp(\beta(\epsilon - \mu)) + 1} \xrightarrow{T \to 0} \begin{cases} 0 & \epsilon > \mu \\ \frac{1}{2} & \epsilon = \mu \\ 1 & \epsilon < \mu \end{cases} \ .$$

It is a step function in $\epsilon = \mu$. This energy value is called Fermi energy ϵ_F. Physically, it means that all the states below this energy level are occupied. Hence, for $\epsilon < \epsilon_F$, we have as many states as particles. If we add a particle, we increase ϵ_F, whereas if we remove a particle, we decrease ϵ_F. This is the procedure to dope a material.

For small T, it is no longer a step function, but it can be accurately approximate to it for a certain range $\Delta\epsilon$. Physically, more energetic particle are transfered over ϵ_F. We define Fermi temperature T_F

$$\epsilon_F = \lim_{T\to 0} \mu(T) = k_B T_F \ .$$

In fact, if $\Delta\epsilon \ll \epsilon_F$, which means $T \ll T_F$, we can approximate $n(\epsilon)$ with a step function without making a big error.

22.2 Fermi Energy for a non-relativistic non-interacting quantum gas

In the 3-dimensional case, the density is

$$n = A\frac{2}{3}\epsilon_F^{\frac{3}{2}} \ .$$

Proof. In fact, using $n(\epsilon) = \theta(-\epsilon_F)$

$$\begin{aligned} n &= A\int_0^\infty d\epsilon \epsilon^{\frac{1}{2}} n(\epsilon) \\ &= A\int_0^{\epsilon_F} d\epsilon \epsilon^{\frac{1}{2}} \\ &= A\frac{2}{3}\epsilon_F^{\frac{3}{2}} \ . \end{aligned}$$

q.e.d.

The energy is

$$E = AV\frac{2}{5}\epsilon_F^{\frac{5}{2}} \ .$$

Proof. In fact, using $n(\epsilon) = \theta(-\epsilon_F)$

$$\begin{aligned} n &= A\int_0^\infty d\epsilon \epsilon^{\frac{3}{2}} n(\epsilon) \\ &= A\int_0^{\epsilon_F} d\epsilon \epsilon^{\frac{3}{2}} \\ &= A\frac{2}{5}\epsilon_F^{\frac{5}{2}} \ . \end{aligned}$$

q.e.d.

Notice that at $T = 0$, there is a positive pressure

$$p = \frac{2}{5} n \epsilon_F > 0 \ .$$

This can be seen visually, because at $T = 0$, there are particle with energy $\epsilon \neq 0$, unlikely the classical case, in which $p = 0$.

Proof. In fact

$$p = \frac{2}{3}\frac{E}{V} = \frac{2}{3}\frac{E}{N}\frac{N}{V} = \frac{2}{5} n \epsilon_F \ .$$

q.e.d.

Chapter 23

Bosons

In this chapter, we restrict ourselves with the bosonic case. The equations of state are

$$n = \frac{g}{\lambda_T^3} f^-_{\frac{3}{2}}(z) \ , \quad \beta p = \frac{g}{\lambda_T^3} f^-_{\frac{5}{2}}(z)$$

where

$$f_l^-(z) = \sum_{n=0}^{\infty} \frac{z^{n+1}}{(n+1)^l}$$

which is a positive-terms power series in $z = \exp(\beta\mu) > 0$, always positive. It absolutely converges for $z < 1$ and converges for $z > 1$ only if $l < 2$. Moreover, it is a monotonic function in z. At $z = 1$, it becomes the Riemann zeta

$$g_{\frac{3}{2}}(z = 1) = \sum_{n=0}^{\infty} \frac{1}{n+1}^{\frac{3}{2}} = \zeta(\frac{3}{2}) \ .$$

Notice that in $z = 1$, it has a vertical derivative, and for $z > 1$, it is not defined according to the physical $\mu > 0$ in the grandcanonical ensemble.

We can study the behaviour of the chemical potential μ. It goes to $-\infty$ for $T \to \infty$ but the equilibrium condition implies that $\frac{\partial \mu}{\partial T} < 0$, therefore, it cannot increase.

23.1 Low temperature limit

23.2 Bose-Einstein condensate

Part VII

Application of quantum statistical mechanics

Chapter 24

Quantum ensemble

24.1 Magnetic 1/2-spin

Consider a system composed by N distinguishable magnetic dipoles in an external magnetic field along the z-axis, with spin $S = 1/2$. Its hamiltonian is

$$\hat{H} = \sum_i S_i^{(z)} B \ ,$$

where

$$S_i^{(z)} = \frac{1}{2} \begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix} \ .$$

The canonical partition function is

$$Z = \left(2 \cosh \frac{\beta B}{2}\right)^N \ .$$

Proof. By definition, for distinguishable particles,

$$\begin{aligned} Z &= (Z_1)^N \\ &= \left(\mathrm{tr}_{\mathcal{H}} \exp(-\beta \hat{H}_1)\right)^N \\ &= \left(\mathrm{tr}_{\mathcal{H}} \exp(-\beta B \begin{bmatrix} \frac{1}{2} & 0 \\ 0 & -\frac{1}{2} \end{bmatrix})\right)^N \\ &= \left(\mathrm{tr}_{\mathcal{H}} \begin{bmatrix} \exp(-\frac{\beta B}{2}) & 0 \\ 0 & \exp(\frac{\beta B}{2}) \end{bmatrix}\right)^N \\ &= \left(\exp(-\frac{\beta B}{2}) + \exp(\frac{\beta B}{2})\right)^N \\ &= \left(2 \cosh \frac{\beta B}{2}\right)^N \ . \end{aligned}$$

q.e.d.

The Helmoltz free energy F is

$$F = -Nk_BT\ln\left(2\cosh\frac{\beta B}{2}\right) .$$

Proof. By definition,

$$F = -\frac{\ln Z}{\beta} = -Nk_BT\ln\left(2\cosh\frac{\beta B}{2}\right) .$$

q.e.d.

The internal energy E is

$$E = -N\frac{B}{2}\tanh\frac{\beta B}{2} .$$

Proof. By definition,

$$E = -\frac{\partial\ln Z}{\partial\beta} = -N\frac{\partial\beta}{\partial\ln}\left(2\cosh\frac{\beta B}{2}\right) = -N\frac{B}{2}\tanh\frac{\beta B}{2} .$$

q.e.d.

A plot of this is in Figure 24.1.
The magnetisation M is

$$M = -\frac{N}{2}\tanh\frac{\beta B}{2} .$$

Proof. By definition,

$$M = \frac{\partial F}{\partial B} = -Nk_BT\frac{\partial}{\partial B}\ln\left(2\cosh\frac{\beta B}{2}\right) = -\frac{N}{2}\tanh\frac{\beta B}{2} .$$

q.e.d.

A plot of this is in Figure 24.2.

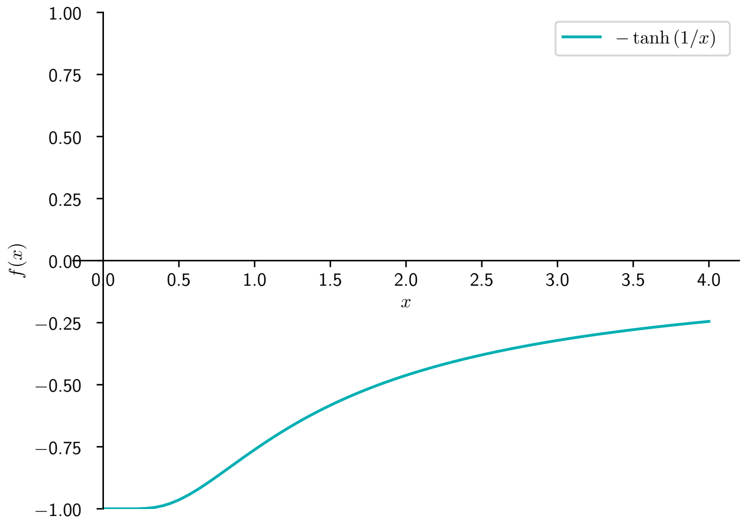

Figure 24.1: A plot of the energy E as a function of T. We have used $x = \frac{2k_BT}{B}$ and $f(x) = \frac{2E}{BN}$.

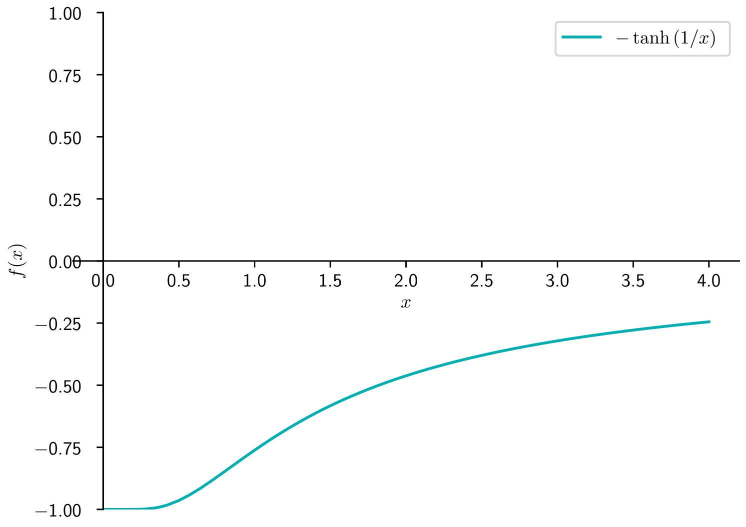

Figure 24.2: A plot of the magnetisation M as a function of T. We have used $x = \frac{2k_BT}{B}$ and $f(x) = \frac{2M}{N}$.

24.2 Magnetic 1-spin

Consider a system composed by N distinguishable magnetic dipoles in an external magnetic field along the z-axis, with spin $S = 1$. Its hamiltonian is

$$\hat{H} = \sum_i S_i^{(z)} B \ ,$$

where

$$S_i^{(z)} = \begin{bmatrix} 1 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & -1 \end{bmatrix} \ .$$

The canonical partition function is

$$Z = \Big(2\cosh(\beta B) + 1\Big)^N \ .$$

Proof. By definition, for distinguishable particles,

$$\begin{aligned} Z &= (Z_1)^N \\ &= \Big(\mathrm{tr}_{\mathcal{H}} \exp(-\beta \hat{H}_1)\Big)^N \\ &= \Bigg(\mathrm{tr}_{\mathcal{H}} \exp(-\beta B \begin{bmatrix} 1 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & -1 \end{bmatrix}))\Bigg)^N \\ &= \Bigg(\mathrm{tr}_{\mathcal{H}} \begin{bmatrix} \exp(-\beta B) & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & \exp(\beta B) \end{bmatrix}\Bigg)^N \\ &= \Big(\exp(-\beta B) + 1 + \exp(\beta B)\Big)^N \\ &= \Big(2\cosh(\beta B) + 1\Big)^N \ . \end{aligned}$$

q.e.d.

The Helmoltz free energy F is

$$F = -N k_B T \ln\Big(2\cosh(\beta B) + 1\Big) \ .$$

Proof. By definition,

$$F = -\frac{\ln Z}{\beta} = -N k_B T \ln\Big(2\cosh(\beta B) + 1\Big) \ .$$

q.e.d.

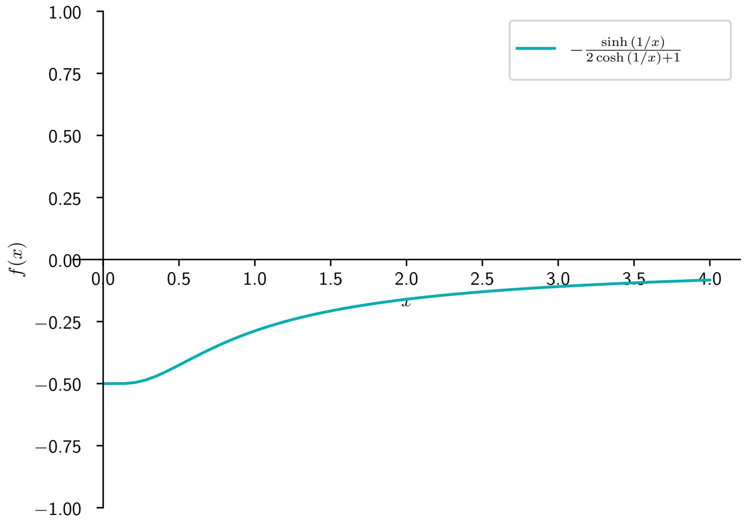

Figure 24.3: A plot of the energy E as a function of T. We have used $x = \frac{k_B T}{B}$ and $f(x) = \frac{2E}{BN}$.

The internal energy E is

$$E = -2NB \frac{\sinh(\beta B)}{2\cosh(\beta B) + 1} \,.$$

Proof. By definition,

$$E = -\frac{\partial \ln Z}{\partial \beta} = -N \frac{\partial}{\partial \beta} \ln \Big(2\cosh(\beta B) + 1 \Big) = -2NB \frac{\sinh(\beta B)}{2\cosh(\beta B) + 1} \,.$$

q.e.d.

A plot of this is in Figure 24.3.
The magnetisation M is

$$M = -\frac{N}{2} \frac{\sinh(\beta B)}{2\cosh(\beta B) + 1} \,.$$

Proof. By definition,

$$M = \frac{\partial F}{\partial B} = -N k_B T \frac{\partial}{\partial B} \ln \Big(2\cosh(\beta B) + 1 \Big) = -2N \frac{\sinh(\beta B)}{2\cosh(\beta B) + 1} \,.$$

q.e.d.

A plot of this is in Figure 24.4.

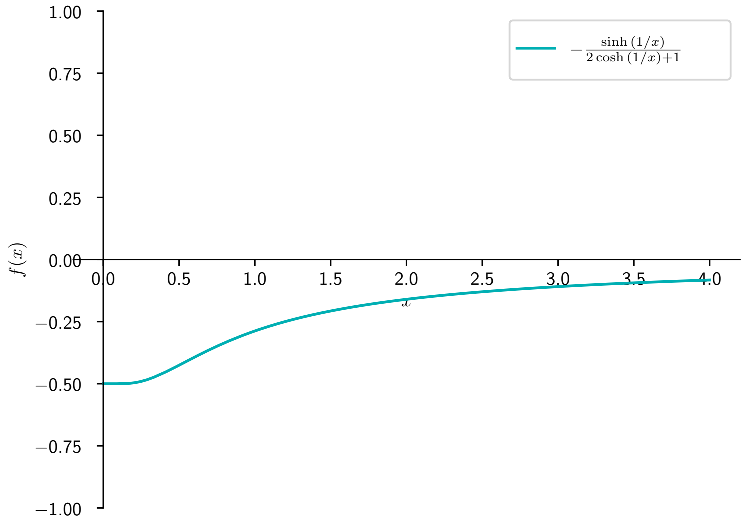

Figure 24.4: A plot of the magnetisation M as a function of T. We have used $x = \frac{2k_B T}{B}$ and $f(x) = \frac{M}{2N}$.

24.3 Quantum harmonic oscillators

Consider a system composed by N distinguishable quantum harmonic oscillators. Its hamiltonian is

$$\hat{H} = \sum_i \hbar\omega(\hat{a}_i \hat{a}_i^\dagger + \frac{1}{2}) \ .$$

The canonical partition function is

$$Z = \left(\frac{\exp(-\frac{\beta\hbar\omega}{2})}{1 - \exp(-\beta\hbar\omega)} \right)^N \ .$$

Proof. By definition, for distinguishable particles,

$$\begin{aligned}
Z &= (Z_1)^N \\
&= \Big(\mathrm{tr}_{\mathcal{H}} \exp(-\beta \hat{H}_1) \Big)^N \\
&= \Big(\mathrm{tr}_{\mathcal{H}_i} \exp(-\beta \hbar\omega (\hat{a}_i \hat{a}_i^\dagger + \frac{1}{2})) \Big)^N \\
&= \Big(\sum_i \langle n_i | \exp(-\beta \hbar\omega (\hat{a}_i \hat{a}_i^\dagger + \frac{1}{2})) | n_i \rangle \Big)^N \\
&= \Big(\sum_i \exp(-\beta \hbar\omega (n_i + \frac{1}{2})) \Big)^N \\
&= \Big(\exp(-\frac{\beta\hbar\omega}{2}) \sum_i \exp(-\beta\hbar\omega)^{n_i} \Big)^N \\
&= \Big(\exp(-\frac{\beta\hbar\omega}{2}) \frac{1}{1 - \exp(-\beta\hbar\omega)} \Big)^N \\
&= \Big(\frac{\exp(-\frac{\beta\hbar\omega}{2})}{1 - \exp(-\beta\hbar\omega)} \Big)^N \ .
\end{aligned}$$

q.e.d.

The Helmoltz free energy F is

$$F = N k_B T (\frac{\beta\hbar\omega}{2} + \ln(1 - \exp(-\beta\hbar\omega))) \ .$$

Proof. By definition,

$$\begin{aligned}
F &= -\frac{\ln Z}{\beta} \\
&= -N k_B T \ln \Big(\frac{\exp(-\frac{\beta\hbar\omega}{2})}{1 - \exp(-\beta\hbar\omega)} \Big) \\
&= -N k_B T (\ln \exp(-\frac{\beta\hbar\omega}{2}) - \ln(1 - \exp(-\beta\hbar\omega))) \\
&= -N k_B T (-\frac{\beta\hbar\omega}{2} - \ln(1 - \exp(-\beta\hbar\omega))) \\
&= N k_B T (\frac{\beta\hbar\omega}{2} + \ln(1 - \exp(-\beta\hbar\omega))) \ .
\end{aligned}$$

q.e.d.

The internal energy E is

$$E = N(\frac{\hbar\omega}{2} + \frac{\hbar\omega}{\exp(-\beta\hbar\omega) - 1}) \ .$$

Proof. By definition,

$$
\begin{aligned}
F &= -\frac{\partial \ln Z}{\partial \beta} \\
&= -N\frac{\partial}{\partial \beta}\ln\left(\frac{\exp(-\frac{\beta\hbar\omega}{2})}{1-\exp(-\beta\hbar\omega)}\right) \\
&= -N\frac{\partial}{\partial \beta}(\ln\exp(-\frac{\beta\hbar\omega}{2}) - \ln(1-\exp(-\beta\hbar\omega))) \\
&= -N\frac{\partial}{\partial \beta}(-\frac{\beta\hbar\omega}{2} - \ln(1-\exp(-\beta\hbar\omega))) \\
&= N\frac{\partial}{\partial \beta}(\frac{\beta\hbar\omega}{2} + \ln(1-\exp(-\beta\hbar\omega))) \\
&= N(\frac{\hbar\omega}{2} - \frac{\hbar\omega}{1-\exp(-\beta\hbar\omega)}) \\
&= N(\frac{\hbar\omega}{2} + \frac{\hbar\omega}{\exp(-\beta\hbar\omega)-1}) \ .
\end{aligned}
$$

q.e.d.

The specific heat is

$$C_V = N\frac{\hbar^2\omega^2}{k_B T^2}\frac{\exp(\beta\hbar\omega)}{(\exp(\beta\hbar\omega)-1)^2} \ .$$

Proof. In fact

$$C_V = \frac{\partial E}{\partial T} = N\frac{\partial}{\partial T}(\frac{\hbar\omega}{2} + \frac{\hbar\omega}{\exp(-\beta\hbar\omega)-1}) = N\frac{\hbar^2\omega^2}{k_B T^2}\frac{\exp(\beta\hbar\omega)}{(\exp(\beta\hbar\omega)-1)^2} \ .$$

q.e.d.

Chapter 25

Fermions

25.1 White dwarf

A white dwarf is an helium star woth mass $M \sim 10^{30} kg$ and a density of $\rho = 10^{10} kg/m^3$ at a temperature of $10^7 K$. Our approxiated model is composed by N electrons and $N/2$ helium nuclei.

Assuming $M = N(m_e + 2m_p) \sim 2Nm_p$, the electronic dentity is

$$n = 3 \times 10^{36} m^{-3} \ .$$

Proof. In fact

$$n = \frac{N}{V} = \frac{N\rho}{M} = \frac{N\rho}{2Nm_p} = \frac{\rho}{2m_p} = \frac{10^{10}}{2 \times 1.6 \times 10^{-27}} = 3 \times 10^{36} m^{-3} \ .$$

q.e.d.

The Fermi momentum p_F is

$$p_F = h\left(\frac{3n}{4\pi g}\right)^{1/3} = 6.63 \times 10^{-34} \times \left(\frac{3 \times 10^{10}}{4 \times 3.14 \times 2}\right)^{1/3} = 0.88 Mev/c \ .$$

Proof. In fact, using $p = \hbar k$

$$N = g \sum_n \to g \frac{V}{(2\pi)^3} \int d^3k = g \frac{V}{(2\pi\hbar)^3} \int d^3p = g \frac{4\pi V}{(2\pi\hbar)^3} \int_0^{p_F} dp p^2 = g \frac{4\pi V}{(2\pi\hbar)^3} \frac{p_F^3}{3} \ ,$$

hence

$$p_F = h\left(\frac{3n}{4\pi g}\right)^{1/3} = 6.63 \times 10^{-34} \times \left(\frac{3 \times 10^{10}}{4 \times 3.14 \times 2}\right)^{1/3} = 0.88 Mev/c \ .$$

q.e.d.

The Fermi energy ϵ_F is

$$\epsilon_F = \sqrt{(p_F c)^2 + (mc^2)^2} - mc^2 = 0.5 Mev \ .$$

The Fermi temperature T_F is

$$T_F = \frac{\epsilon_F}{k_B} = 10^{10} K \ ,$$

which means that we are in the regime $T \ll T_F$ and we can use $T = 0$.

The internal energy E is

$$E = \frac{\pi V m^4 c^5}{\pi^2 \hbar^3} f(x_F) \ .$$

Proof. In fact,

$$\begin{aligned}
E &= g \sum_n \epsilon \to g \frac{V}{(2\pi)^3} \int d^3 k \epsilon \\
&= g \frac{V}{(2\pi\hbar)^3} \int d^3 p \epsilon \\
&= g \frac{4\pi V}{(2\pi\hbar)^3} \int_0^{p_F} dp p^2 \epsilon \\
&= g \frac{4\pi V}{(2\pi\hbar)^3} \int_0^{p_F} dp p^2 c \sqrt{p^2 + (mc)^2} \ .
\end{aligned}$$

Now we make a change of variable

$$x = \frac{p}{mc} \ , \quad dp = mc dx \ ,$$

hence

$$\begin{aligned}
E &= g \frac{4\pi V}{(2\pi\hbar)^3} c (mc)^3 \int_0^{x_F} dx \ x^2 (mc) \sqrt{x^2 + 1} \\
&= \frac{4 g \pi V m^4 c^5}{h^3} \int_0^{x_F} dx \ x^2 \sqrt{x^2 + 1} \\
&= \frac{4 g \pi V m^4 c^5}{h^3} f(x_F) \\
&= \frac{V m^4 c^5}{\pi^2 \hbar^3} f(x_F) \ ,
\end{aligned}$$

where

$$f(x_F) = \int_0^{x_F} dx \ x^2 \sqrt{x^2 + 1} \ .$$

q.e.d.

The pressure P is

$$P = \frac{m^4c^5}{\pi^2\hbar^3}\Big(\frac{x_F^3}{3}\sqrt{1+x_F^2} - f(x_F)\Big) \ .$$

Proof. In fact,

$$\begin{aligned}
P &= -\frac{\partial E}{\partial V} \\
&= -\frac{\partial}{\partial V}\frac{Vm^4c^5}{\pi^2\hbar^3}f(x_F) \\
&= -\frac{\pi m^4c^5}{\pi^2\hbar^3}f(x_F) - \frac{Vm^4c^5}{\pi^2\hbar^3}\frac{\partial x_F}{\partial V}\frac{\partial f(x_F)}{\partial x_F} \\
&= -\frac{m^4c^5}{\pi^2\hbar^3}f(x_F) - \frac{Vm^4c^5}{\pi^2\hbar^3}\frac{\partial}{\partial V}\Big(\frac{h}{mc}\Big(\frac{3N}{4\pi gV}\Big)^{1/3}\Big)\frac{\partial f(x_F)}{\partial x_F} \\
&= -\frac{m^4c^5}{\pi^2\hbar^3}f(x_F) - \frac{Vm^4c^5}{\pi^2\hbar^3}\Big(\frac{h}{mc}\Big(\frac{3N}{4\pi gV}\Big)^{1/3}\Big)\frac{\partial}{\partial V}V^{-1/3}\frac{\partial f(x_F)}{\partial x_F} \\
&= -\frac{m^4c^5}{\pi^2\hbar^3}f(x_F) + \frac{1}{3}\frac{Vm^4c^5}{\pi^2\hbar^3}\Big(\frac{h}{mc}\Big(\frac{3N}{4\pi gV}\Big)^{1/3}\Big)V^{-4/3}\frac{\partial f(x_F)}{\partial x_F} \\
&= \frac{m^4c^5}{\pi^2\hbar^3}\Big(\frac{x_F^3}{3}\sqrt{1+x_F^2} - f(x_F)\Big) \ .
\end{aligned}$$

q.e.d.

Now, we solve the integral

$$f(x) = \frac{x^5}{4\sqrt{x^2+1}} + \frac{3x^3}{8\sqrt{x^2+1}} + \frac{x}{8\sqrt{x^2+1}} - \frac{\operatorname{asinh}(x)}{8} \ .$$

In the non-relativistic limit, $x_F \ll 1$, we can make the approximations

$$g(x) = \frac{x^3}{3}\sqrt{1+x^2} = \frac{x^3}{3} + \frac{x^5}{6} + O\left(x^6\right)$$

and

$$f(x_F) = \frac{x^3}{3} + \frac{x^5}{10} + O\left(x^6\right) \ .$$

In the ultra-relativistic limit, $x_F \gg 1$ or equivalemty $y_F = 1/x_F \ll 1$, we can make the approximations

$$g(1/x) = \frac{1}{3x^4} + \frac{1}{6x^2} + O\left(\frac{1}{x}\right)$$

and

$$f(1/x) = \frac{1}{4x^4} + \frac{1}{4x^2} + O\left(\frac{1}{x}\right) \ .$$

Imposing the equilibrium condition $dE = 0$, between the gravitational and the pressure forces, and the structure of a sphere, the pressure must be

$$P = \frac{\alpha G M^2}{4\pi R^4}$$

and the Fermi momentum is

$$p_F = \frac{\hbar}{R}\left(\frac{9\pi M}{8 m_p}\right)^{1/3} .$$

Proof. For the gravitational force

$$E_g = -\alpha\frac{GM^2}{R} , \quad dE_g = \alpha\frac{GM^2}{R^2}dR .$$

For the pressure force

$$E_p = -pV = -p\frac{4}{3}\pi R^3 , \quad dE_p = -4\pi p R^2 dR .$$

Imposing the equilibrium condition,

$$0 = dE = dE_g + dE_p = alpha\frac{GM^2}{R^2}dR - 4\pi p R^2 dR ,$$

hence

$$p = \frac{\alpha G M^2}{4\pi R^4} .$$

The Fermi momentum is

$$p_F = h\left(\frac{3n}{4\pi g}\right)^{1/3} = h\left(\frac{3}{8\pi}\frac{M}{2m_p\frac{4}{3}\pi R^3}\right)^{1/3} = \frac{\hbar}{R}\left(\frac{9\pi M}{8m_p}\right)^{1/3} .$$

q.e.d.

In the ultra-relativistic limit

$$P = \frac{m^4c^5}{12\pi\hbar^3}(x_F^4 - x_F^2) = \frac{\alpha G M^2}{4\pi R^4} .$$

Chapter 26

Bosons

26.1 Blackbody radiation

Part VIII

Appendix

Chapter A

Volume of an N-dimensional sphere

In this appendix chapter, we will prove that the volume of an N-dimensional sphere of radius R is

$$V_n(R) = \frac{\pi^{n/2} R^n}{\Gamma(n/2+1)} \ . \tag{A.1}$$

Proof. Consider the rotationally invariant function f

$$f(x_1, \dots x_n) = \exp(-\frac{1}{2}\sum_{i=1}^{n} x_i^2) = \prod_{i=1}^{n} \exp(-\frac{1}{2}x_i^2) = \ .$$

Using the Gaussian integral, this function can be integrated over all $\mathbb{R}^n$, with volume element $dV = dx_1 \dots dx_n$, and it gives

$$\begin{aligned}\int_{\mathbb{R}^n} dV\ f &= \int_{\mathbb{R}^n} \prod_{i=1}^{n} dx_i\ f = \int_{\mathbb{R}^n} \prod_{i=1}^{n} dx_i\ \ \exp(-\frac{1}{2}\sum_{i=1}^{n} x_i^2) \\ &= \prod_{i=1}^{n} \underbrace{(\int_{\mathbb{R}} dx_i\ \ \exp(-\frac{1}{2}x_i^2))}_{(2\pi)^{1/2}} = \prod_{i=1}^{n} (2\pi)^{1/2} = (2\pi)^{n/2} \ .\end{aligned}$$

Exploiting the rotational invariant property, we can decomposed the volume element into a surface element dA, which integrated gives an $(n-1)$-dimensional sphere $S^{n-1}(r)$ of radius r, multiplied by a length element dr, i.e.

$$\int_{\mathbb{R}^n} dV\ f = \int_0^\infty dr \int_{S^{n-1}(r)} dA\ f \ .$$

Since the area is proportial to the radius, e.g. for $n = 3$ the area is $A \propto r^2$, the radius-dependence of the area is given by $A_{n-1}(r) = r^{n-1} A_{n-1}(1)$. Therefore, putting it inside the integral, we obtain

$$A_{n-1}(1) \int_0^\infty dr r^{n-1} \exp(-\frac{1}{2}r^2) \ .$$

Now, we make a change of variables into

$$t = \frac{r^2}{2} \ , \quad r = (2t)^{1/2} \ , \quad dr = 2^{-1/2} t^{-1/2} dt$$

to have the integral of the gamma function

$$\begin{aligned}\int_0^\infty dr\ r^{n-1} \exp(-\frac{1}{2} r^2) &= 2^{(n-1)/2} 2^{-1/2} \int_0^\infty dt\ t^{(n-1)/2} t^{-1/2} \exp(-t) \\ &= 2^{n/2-1} \underbrace{\int_0^\infty dt\ t^{n/2-1} \exp(-t)}_{\Gamma(n/2)} = 2^{n/2-1} \Gamma(n/2) \ .\end{aligned}$$

Now, we combine the two results together to obtain the surface

$$(2\pi)^{n/2} = A_{n-1}(1) 2^{n/2-1} \Gamma(n/2) \ ,$$

hence

$$A_{n-1}(1) = \frac{2\pi^{n/2}}{\Gamma(n/2)} \ .$$

Finally, in order to find the volume we need to integrate from 0 to R

$$\begin{aligned}V_n(R) &= \int_0^R dr A_{n-1}(r) = \int_0^R dr\ A_{n-1}(1) r^{n-1} = \frac{2\pi^{n/2}}{\Gamma(n/2)} \int_0^R dr\ r^{n-1} \\ &= \frac{2\pi^{n/2}}{\Gamma(n/2)} \frac{r^n}{n}\Big|_0^R = \frac{2\pi^{n/2}}{n\Gamma(n/2)} R^n = \frac{\pi^{n/2} R^n}{\Gamma(n/2+1)} \ .\end{aligned}$$

q.e.d.

Chapter B

Stirling approximation

In this appendix chapter, we will prove the Stirling approximation

$$\ln n! \simeq n \ln n - n \ . \tag{B.1}$$

Proof. The factorial can be expressed in integral form via the gamma function

$$\Gamma(n+1) = n! = \int_0^\infty dt\ t^n \exp(-t)\ .$$

Now, we make a change of variables into

$$t = nx\ , \quad x = \frac{t}{n}\ , \quad dx = \frac{dt}{n}\ ,$$

to have

$$\begin{aligned}
\int_0^\infty dt\ t^n \exp(-t) &= int_0^\infty dt\ \exp(\ln t^n)\exp(-t) \\
&= \int_0^\infty dt\ \exp(n\ln t - t) \\
&= n\int_0^\infty dx\ \exp(n\ln(nx) - nx) \\
&= n\int_0^\infty dx\ \exp(n\ln x + n\ln n - nx) \\
&= n\exp(n\ln n)\int_0^\infty dx\ \exp(n(\ln x - x))\ .
\end{aligned}$$

In the limit for which n is large, we can use the Laplace approximation method

$$\int_a^b dx\ \exp(nf(x)) \simeq \exp(nf(x_0))\sqrt{\frac{2\pi}{n|f''(x_0)|}}\ .$$

where $x_0 \in [a,b]$ is a stationary point of $f(x)$. A simple sketch of the proof is given by means of the Taylor expansion around x_0

$$f(x) \simeq f(x_0) - \frac{1}{2}|f''(x_0)|(x-x_0)^2 \ ,$$

hence, integrating the Gaussian integral,

$$\begin{aligned}\int_a^b dx \ \exp(nf(x)) &\simeq \exp(nf(x_0)) \int_a^b dx \ \exp(-\frac{n}{2}|f''(x_0)|(x-x_0)^2) \\ &= \sqrt{\frac{2\pi}{n|f''(x_0)|}} \ .\end{aligned}$$

In our case, $a = 0$, $b = \infty$ and $f(x) = \ln x - x$, which has a maximum in $x_0 = 1$ and second derivatives equals to $|f''(x)| = 1/x^2$. Therefore

$$\int_0^\infty dx \ \exp(n(\ln x - x)) \simeq \exp(n(\ln x_0 - x_0))\sqrt{\frac{2\pi x_0^2}{n}}\Big|_{x_0=1} = \exp(-n)\sqrt{\frac{2\pi}{n}} \ .$$

Now, we combine the two results together

$$n! \simeq n\exp(n\ln n)\exp(-n)\sqrt{\frac{2\pi}{n}} = \exp(n\ln n - n)\sqrt{2\pi n} = n^n\exp(-n)\sqrt{\frac{2\pi}{n}} \ ,$$

which can be rewritten in terms of logarithms rather than exponentials

$$\ln n! \simeq \ln(n^n\exp(-n)\sqrt{\frac{2\pi}{n}}) = n\ln n - n + O(\ln n) \ .$$

q.e.d.

Chapter C

Gaussian integral

In this appendix chapter, we will prove that the Gaussian integral is

$$\int_{-\infty}^{\infty} dx \;\exp(-x^2) = \sqrt{\pi}\ . \tag{C.1}$$

Proof. We start from the square Gaussian integral, which it is the square same integral for the mute properties of the integration variables

$$\begin{aligned}\left(\int_{-\infty}^{\infty} dx \;\exp(-x^2)\right)^2 &= \int_{-\infty}^{\infty} dx \;\exp(-x^2) \int_{-\infty}^{\infty} dy \;\exp(-y^2)\\ &= \int_{-\infty}^{\infty} dx \int_{-\infty}^{\infty} dy \;\exp(-(x^2+y^2))\ .\end{aligned}$$

Now, we make a change of variables and we use polar coordinates (r,θ)

$$r^2 = x^2 + y^2\ , \quad \theta = \arctan\frac{y}{x}\ , \quad dx\ dy = r\ dr\ d\theta\ , \quad (r,\theta) \in [0,\infty) \times [0, 2\pi]\ ,$$

to obtain

$$\begin{aligned}\int_{-\infty}^{\infty} dx \int_{-\infty}^{\infty} dy \;\exp(-(x^2+y^2)) &= \underbrace{\int_0^{2\pi} d\theta}_{2\pi} \int_0^{\infty} dr\ r\exp(-r^2)\\ &= 2\pi \int_0^{\infty} dr\ r\exp(-r^2)\\ &= \pi \int_0^{\infty} dr\ 2r\exp(-r^2)\\ &= \pi\exp(-r^2)\Big|_0^{\cancel{\infty}} = \pi\ .\end{aligned}$$

Now, we combine the two results together

$$\left(\int_{-\infty}^{\infty} dx \;\; \exp(-x^2)\right)^2 = \pi \ ,$$

hence

$$\int_{-\infty}^{\infty} dx \;\; \exp(-x^2) = \sqrt{\pi} \ .$$

q.e.d.

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