Theoretical Statistical Physics (MKTP 1)
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Contents

Part I

Fundamental Physics

1 Introduction

a) From Microphysics to Macrophysics

Fundamental laws of interaction do not explain everything.

Examle: specifications of a makroscopic objects, consisting of many subparticles (ex.: solids, fluids, gases).

A typical number of particles is the Avogadro number : $N_{Av} \backsimeq 6 \cdot 10^{23}$. It denotes the number of molecules per mol, ex. number of water molecules in 18g water.

Typical questions:

- connections between pressure (p), volume (V), and temperature (T) of gases (constitutive equation)
- specific heat capacity of a material
- conductivity of a solid, colour of a fluid
- connection between magnetization and magnetic field
- melting of ice
- how does a refrigerator work?
- how does a supernova explode?
- energy budget of the Earth's atmosphere

Typical area of application:

- systems with many degrees of freedom $\Longleftrightarrow$macroscopic objects

Examples:

- we consider an isolated system - a gas with volume V and number of particles N. A classical mechanical description states $6N$ initial conditions $\Leftrightarrow$$6N$ degrees of freedom. If $6N > 2\times$ number of the motion constants, the system is not integratable.
- the distance between two trajectories, which initially did lay close to each other, grows exponentially with time.
- description of a water droplet for one second. One needs more information than it can be saved in the universe.

The goal of the statistical physics is to develop laws for the macro states by deriving them from the micro physics with the help of statistical methods.

b) New macroscopic laws

- qualitatively new laws
- new terms - e.g. entropy
- statistic laws are very exact, relative fluctuations $\backsim \frac{1}{\sqrt{N}}$
- predictive power only for systems with many degrees of freedom; uncertainty about the behaviour of the single atoms (quantum physics), but prediction about the whole system
- thermodynamics
- material properties
- non-equilibrium processes

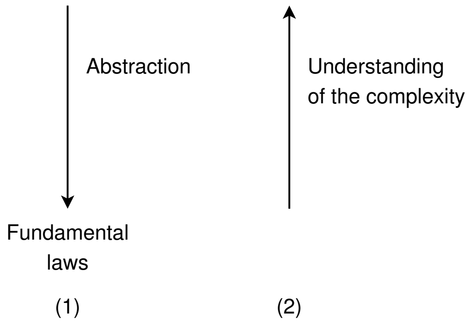
Scales for macroscopic systems:

- $L \gg$mean distance between particles in fluids and solids $\simeq 10^{-7}cm$, $N \gg 1$
- $t \gg$timescale of the microscopic motions:
  motion of an atom: $10^{-13}sec$
  motion of an electron (in solids): $10^{-15}sec$

c) Micro physical laws and their probabilistic nature

$\boxed{\text{Fundamental laws are of probabilistic nature}}$

The role of the statistical physics in the house of physics: foundation of the modern physics!
Two ways in physics:



(2) The role of statistics is obvious
(1) Fundamental theory: system with many (infinite) degrees of freedom; QFT, String theory (and for scattering of two particles) are formulated as statistical theories

- Calculating the predictions, which follow from the fundamental theory: methods of statistical physics just like in this lecture

  $\boxed{\text{Basic laws of physics are statistical in nature!}}$

  they make statements about:
  - probability, that when measuring an observable A once, one gets the value A_i
  - conditional probability for two measurements. If one measures a value A_i for an observable A, what is the probability that one measures value B_j for a second observable B.

1 Introduction

Remarks:

1. From micro-physics to micro-physics and from Planck's scale (10^{19} GeV) to energy scale of LHC (1000 GeV) - 16 orders of magnitude.
2. Universality: one does not consider all the details of the microscopic laws $\Rightarrow$ predictive power of the QFT!
3. Conceptional revolution due to the statistical physics. Modern physics : Plank, Boltzmann, Einstein
4. ~~Determinism~~ $\rightarrow$ probabilistic theory $\rightarrow$ predictive power

2 Basic concepts of statistical physics

a) Probability distribution and expectation values

i) States (Microstates)

We will denote states with τ and the number of states with Ω, whereas in the beginning we will examine only finite nubmer of states $\Omega < \infty$.

ii) Probability distribution

Every state τ is associated with a probability p_τ, which is the probability that this state is realized.

$$\tau \to p_\tau$$

For p_τ the following holds:

$$p_\tau \geqslant 0 \qquad \text{positivity} \tag{2.1}$$

$$\sum_\tau p_\tau = 1 \qquad \text{normalization} \tag{2.2}$$

$$\Rightarrow 0 \leq p_\tau \leq 1 \tag{2.3}$$

The probability distribution is $\{p_\tau\} = \{p_1, p_2, p_3, \dots\}$, which is an ordered sequence of Ω numbers. In the general case p_i and p_j are independant.

iii) Observables

Capital roman letters are used for observables, e.g. A.

classical observable: A has a fixed value A_τ in every state τ.

$$\tau \to A_\tau \in \operatorname{Spec} A \tag{2.4}$$

SpecA: The spectrum of an observable is the set of all possible measurement values $\{\lambda_A\}$, whereas $\lambda_A \in \mathbb{R}$. The probability to measure a certain value $\lambda_A$is given by:

$$p_{\lambda_A} = \sum_{\tau | A_\tau = \lambda_A} p_\tau \tag{2.5}$$

A linear combination of two classical observables A and B is again a classical observable.

$$C = f_A A + f_B B \qquad f_{A,B} \in \mathbb{R} \tag{2.6}$$

$$C_\tau = f_A A_\tau + f_B B_\tau \tag{2.7}$$

iv) Expectation value

$$\boxed{\langle A \rangle = \sum_\tau p_\tau A_\tau} \tag{2.8}$$

v) Dispersion

$$\begin{aligned} &= \sum_\tau p_\tau \left(A_\tau - \langle A\rangle\right)^2 = \sum_\tau \left(A_\tau^2 - 2A_\tau \langle A\rangle + \langle A\rangle^2\right) = \sum_\tau p_\tau A_\tau^2 - \langle A\rangle^2 \\ &= \left\langle A_\tau^2\right\rangle - \langle A_\tau\rangle^2 \end{aligned} \tag{2.9}$$

vi) Expectation values and probability distribution

The expectation values of a complete set of observables determine the probability distribution $\{p_\tau\}$ uniquely.

Examples:

- Consider Ω observables $A^{(\sigma)}$ with $A^{(\sigma)} = \delta_{\sigma\tau}$. Then:

  Table 2.1: A system with $A^{(\sigma)} = \delta_{\sigma\tau}$

τ	1	2	3	4
$A^{(\sigma)}$	0	1	0	0

  and therefore

  $$\left\langle A^{(\sigma)}\right\rangle = \sum_\tau p_\tau A_\tau^{(\sigma)} = p_\sigma \tag{2.10}$$

- Two-state system: A coin, spin, occupied and unoccupied States, computer bits.
  - τ: ↑, ↓ or $\langle 1\rangle$, $\langle 2\rangle$ or 1, 0
  - p: $p_\uparrow$, $p_\downarrow$ or p_1, p_2, $p_1 + p_2 = 1$
  - A : number up-down

  We define the observable A, for which holds that $A_1 = 1$ for state↑and $A_2 = -1$ for state ↓. Then, we can express the spin in z direction in terms of A: $S_z = \frac{\hbar}{2} \cdot A$. The number of particles is given by $N = \frac{1}{2}(A+1)$,which corresponds to $N_1 = 1$ and $N_2 = 0$. The expecation values of A and N are:

  $$\langle A\rangle = p_1 A_1 + p_2 A_2 = p_1 - (1 - p_1) = 2p_1 - 1 \tag{2.11}$$

  $$\langle N\rangle = \left\langle \frac{1}{2}(A+1)\right\rangle = p_1 \tag{2.12}$$

  Their dispersions could also be easily calculated. For A we need first:

  $$(A_1)^2 = 1 \tag{2.13}$$
  $$(A_2)^2 = 1 \tag{2.14}$$
  $$\left\langle A^2\right\rangle = p_1 A_1^2 + p_2 A_2^2 = p_1 + 1 - p_1 = 1 \tag{2.15}$$

  Then:

  $$\Delta A^2 = \left\langle A^2\right\rangle - \langle A\rangle^2 = 1 - (2p_1 - 1)^2 = 4p_1(1 - p_1) \tag{2.16}$$

And for N accordingly:

$$\begin{aligned}\left\langle N^2\right\rangle &= \left\langle \frac{1}{4}\left(A^2+2A+1\right)\right\rangle = \frac{1}{4}\left\langle A^2\right\rangle + \frac{1}{2}\left\langle A\right\rangle + \frac{1}{4} = p_1 && (2.17)\\ \Delta N^2 &= p_1\left(1-p_1\right) && (2.18)\end{aligned}$$

- Four-state system

Table 2.2: States τ in a four-state system

$\upuparrows$	$\upharpoonleft\downharpoonright$	$\upharpoonleft\downharpoonright$	$\downdownarrows$
11	10	01	00
$\vert 1\rangle$	$\vert 2\rangle$	$\vert 3\rangle$	$\vert 4\rangle$

Assume that all the states are equipotential, i. e. $p_1 = p_2 = p_3 = p_4 = \frac{1}{4}$. We can introduce a new variable called the total spin A (see table 2.3).

Table 2.3: Observables in a four-state system

	$\vert 1\rangle$	$\vert 2\rangle$	$\vert 3\rangle$	$\vert 4\rangle$	
A_τ	2	0	0	2	total spin
B_τ	1	1	-1	-1	spin 1
C_τ	1	-1	1	-1	spin 2

Then, we can compute the expectation values:

$$\langle A\rangle = \langle B\rangle = \langle C\rangle = 0 \qquad (2.19)$$

and the dispersion:

$$\begin{aligned}\left\langle B^2\right\rangle &= \left\langle C^2\right\rangle = 1 \\ \Delta B^2 &= 1 && (2.20)\\ \left\langle A^2\right\rangle &= 2 \\ \Delta A^2 &= 2 && (2.21)\end{aligned}$$

b) Reduced system

When only part of the information in $\{p_\tau\}$is needed or available, we can integrate out the redundant information, which results in a reduced probability distribution.

Examples:

- Suppose we have information only about spin 1 (from the previous example). Then, we can combine the probabilities for states with the same B_τ and arbitrary C_τ. As a consequence, the system turns into an effective two-state system.

Table 2.4: States of the reduced ensemble $\overline{\tau}$

$\uparrow$	$\downarrow$
$\vert 1\rangle$	$\vert 2\rangle$

Here $\overline{\tau} = |1\rangle$ groups the former states $\tau = |1\rangle$, $\tau = |2\rangle$ together, in which B_τ had the same values.

$\overline{p}_1 = p_1 + p_2$, $\overline{p}_2 = p_3 + p_4$

$\overline{B}_1 = 1$, $\overline{B}_2 = -1$

$\langle B\rangle = \overline{p}_1\overline{B}_1 + \overline{p}_2\overline{B}_2 = p_1 + p_2 - p_3 - p_4$

In this case B is a system observable, which means the information in the system is enough to compute the distribution of the measurement values. In contrast, A and C are environment observables.

- Now, consider the case when A is the system observable. Thus, the system becomes an effective three-state system with $\overline{A}_1 = 2$, $\overline{A}_2 = 0$, $\overline{A}_3 = -2$. The probability for each state is $\overline{p}_1 = p_1$, $\overline{p}_2 = p_2 + p_3$, $\overline{p}_3 = p_4$. We will continue examing the example in c).

c) Probabilistic observables

Can the mean value $\langle B\rangle$ in the reduced system be determined, i. e. by the formula $\langle B\rangle = \overline{p}_1\overline{B}_1 + \overline{p}_2\overline{B}_2 + \overline{p}_3\overline{B}_3$?

Table 2.5: Observables in the reduced system

	$\lvert\overline{1}\rangle$	$\lvert\overline{2}\rangle$	$\lvert\overline{3}\rangle$
$\overline{p}$	p_1	$p_2 + p_3$	p_4
A	2	0	-2
N	2	1	0
B	1	$\frac{p_2 - p_3}{p_2 + p_3}$	-1
B^2	1	1	1

$\overline{B}_2$ is the expectation value of B in the reduced state $|\overline{2}\rangle$and it is an average of the micro-states $|2\rangle$ and $|3\rangle$.

$$\begin{aligned}\overline{B}_2 &= \langle B\rangle_{2,3} = \frac{p_2}{p_2+p_3}\cdot 1 + \frac{p_3}{p_2+p_3}\cdot(-1)\\ &= \frac{p_2 - p_3}{p_2 + p_3}\end{aligned} \tag{2.22}$$

Here, $\frac{p_2}{p_2+p_3}$ gives the probability to measure 1 for the observable B and $\frac{p_3}{p_2+p_3}$ to measure -1.

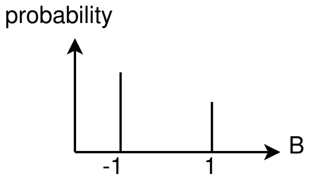


Figure 2.1: Probability distribution of a probabilistic variable

We should check and see that:

$$\langle B\rangle = 1\cdot\overline{p}_1 + \frac{p_2 - p_3}{p_2 + p_3}\overline{p}_2 - 1\cdot\overline{p}_3 = p_1 + p_2 - p_3 - p_4 \tag{2.23}$$

One should note that $\left(\overline{B}_2\right)^2 = \left(\frac{p_2 - p_3}{p_2 + p_3}\right)^2 \neq 1 = \left(B^2\right)_2$.

Consequently B has not a fixed value in state $\left|\overline{2}\right\rangle$ of the reduced ensemble. It rather has a probability distribution of values $B = \pm 1$ in the state $\left|\overline{2}\right\rangle$, with relative probabilities $\frac{p_2}{p_2+p_3}$ and $\frac{p_3}{p_2+p_3}$. B is a probabilistic observable, not a classical one. Probabilistic observables need additional information about probability distribution of measurement values in a given state.

$$B \text{ environment observable} \quad \underbrace{\rightarrow}_{\text{additional information}} \quad B \text{ system observable}$$

d) Quantum Statistics and density matrix

i) Expectation value

$$\langle A \rangle = \mathrm{tr}\,(\rho ?A) \tag{2.24}$$

where $?A$ is the operator associated with A and ρ is the density matrix

ii) Dispersion

$$\begin{aligned} \left\langle A^2 \right\rangle &= \mathrm{tr}\left(\rho ?A^2\right) && (2.25) \\ \Delta A^2 &= \left\langle A^2 \right\rangle - \langle A \rangle^2 && (2.26) \end{aligned}$$

iii) Diagonal operators

When A is diagonal:

$$\begin{aligned} ?A &= \begin{pmatrix} A_1 & & & 0 \\ & A_2 & & \\ & & \ddots & \\ 0 & & & A_\Omega \end{pmatrix} && (2.27) \\ ?A_{nm} &= A_n \delta_{nm} && (2.28) \end{aligned}$$

then expectation value is just:

$$\langle A \rangle = \mathrm{tr}\rho ?\mathrm{A} = \sum_{n,m} \rho_{nm} ?\mathrm{A}_{mn} = \sum_n \rho_{nn} \mathrm{A}_n \tag{2.29}$$

and we need only the diagonal elements of the density matrix. They can associated with probabilities $p_n = p_{nn}$.

Example: A two-state system

Let $?A = \begin{pmatrix} A_1 & 0 \\ 0 & A_2 \end{pmatrix}$ and $\rho = \begin{pmatrix} \rho_{11} & \rho_{12} \\ \rho_{12}^* & \rho_{22} \end{pmatrix}$, then:

$$\begin{aligned} \rho ?A &= \begin{pmatrix} \rho_{11} & \rho_{12} \\ \rho_{12}^* & \rho_{22} \end{pmatrix} \cdot \begin{pmatrix} A_1 & 0 \\ 0 & A_2 \end{pmatrix} = \begin{pmatrix} A_1\rho_{11} & A_2\rho_{12} \\ A_1\rho_{12}^* & A_2\rho_{22} \end{pmatrix} \\ \mathrm{tr}\rho ?A &= A_1\rho_{11} + A_2\rho_{22} \\ \langle A \rangle &= \sum_n \rho_{nn} A_n = \sum_\tau p_\tau A_\tau \end{aligned}$$

With $\{p_\tau\} = \{\rho_{nn}\}$ and $A_n = A_\tau$ one can see that classical statistics can be derived from quantum statistics.

iv) Properties of the density matrix

1. hermicity $\rho^\dagger = \rho \rightarrow$ all eigenvalues are real
2. positivity $\forall \lambda_n \geq 0$
3. normalization $\mathrm{tr}\rho = 1$, $\sum_n \lambda_n = 1$, $0 \leq \lambda_n \leq 1$

From 1, 2 and 3 follows that $\rho_{nn} \geq 0$ and $\sum_n \rho_{nn} = 1$. $\{\rho_{nn}\}$ has all the properties of a probability distribution.

Example: Two-state QM

Let ρ be a complex 2×2 matrix: $\rho = \begin{pmatrix} \rho_{11} & \rho_{12} \\ \rho_{12}^* & 1-\rho_{11} \end{pmatrix}$ with $\rho_{11} \in \mathbb{R}$, $0 \leq \rho_{11} \leq 1$ and $?A = \frac{\hbar}{2}\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$. We can find the expectation value:

$$\begin{aligned} \langle A \rangle &= \frac{\hbar}{2}\mathrm{tr}\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}\begin{pmatrix} \rho_{11} & \rho_{12} \\ \rho_{12}^* & 1-\rho_{11} \end{pmatrix} = \frac{\hbar}{2}\mathrm{tr}\begin{pmatrix} \rho_{11} & \rho_{12} \\ -\rho_{12}^* & -1+\rho_{11} \end{pmatrix} \\ &= \frac{\hbar}{2}\left(2\rho_{11} - 1\right) \end{aligned} \tag{2.30}$$

From the classical statistics we have $\langle A \rangle = p_1 A_1 + p_2 A_2$, if we set $p_1 = \rho_{11}$, $p_2 = 1-\rho_{11}$, $A_1 = \frac{\hbar}{2}$, $A_2 = -\frac{\hbar}{2}$, then we will become the same result if we put those values in.

The positivity condition for λ give us a condition for

$$\left(\rho_{11} - \lambda\right)\left(1 - \rho_{11} - \lambda\right) - f = 0 \tag{2.31}$$

$$f = \left|\rho_{12}\right|^2 \geq 0 \tag{2.32}$$

$$\lambda^2 - \lambda + \rho_{11}\left(1 - \rho_{11}\right) - f = 0 \tag{2.33}$$

$$\lambda_{1,2} = \frac{1}{2}\left(1 \pm \sqrt{1 - 4\left[\rho_{11}\left(1-\rho_{11}\right) - f\right]}\right) \tag{2.34}$$

$$\lambda_{1,2} \geq 0 \Rightarrow \rho_{11}\left(1-\rho_{11}\right) - f \geq 0 \tag{2.35}$$

$$\Rightarrow \rho_{11}\left(1-\rho_{11}\right) \geq 0 \tag{2.36}$$

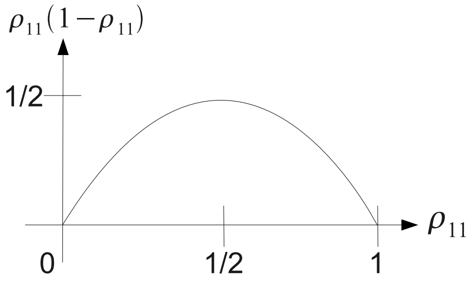


Figure 2.2: Positivity condition for two state density matrix

The positivity condition for two state density matrix is:

$$\boxed{f = \left|\rho_{12}\right|^2 \leq \rho_{11}\left(1-\rho_{11}\right)} \tag{2.37}$$

v) Non-diagonal operators

One may ask why do we need the information in ρ_{12}, since for the expectation value holds $\langle A\rangle = \sum_n \rho_{nn} ?A_n$, provided that $?A$ is diagonal. The answer is that ρ_{12} carries additional information for the probabilistic observables.

Example: Spin in arbitrary direction $?S_i = \frac{2}{\hbar} S_i$ (Table 2.6)

Table 2.6: Observables for a system with a spin in an arbitrary direction

	$\vert 1\rangle$	$\vert 2\rangle$
$?S_z$	1	-1
$?S_x$	$\rho_{12}+\rho_{12}^*$	$\rho_{12}+\rho_{12}^*$
$?S_x^2$, $?S_z^2$	1	1

We shall check if classical and quantum statistics produce discrepancies.

classical:

$$\begin{aligned} \langle ?S_x\rangle &= p_1\,(?S_x)_1 + p_2\,(?S_x)_2 = \rho_{11}\,(\rho_{12}+\rho_{12}^*) + (1-\rho_{11})\,(\rho_{12}+\rho_{12}^*) \\ &= \rho_{12}+\rho_{12}^* = 2\mathrm{Re}\,(\rho_{12}) \end{aligned} \tag{2.38}$$

quantum:

$$\begin{aligned} \langle ?S_x\rangle &= \mathrm{tr}\left\{\begin{pmatrix} \rho_{11} & \rho_{12} \\ \rho_{12}^* & \rho_{22}\end{pmatrix}\begin{pmatrix} 0 & 1 \\ 1 & 0\end{pmatrix}\right\} \\ &= \mathrm{tr}\begin{pmatrix} \rho_{12} & \rho_{11} \\ \rho_{22} & \rho_{12}^*\end{pmatrix} \\ &= \rho_{12}+\rho_{12}^* \end{aligned} \tag{2.39}$$

One can see that 2.38 and 2.39 give exactly the same result. Actually, this could be generalized for any quantum operator

$$?A = ?A^\dagger = \begin{pmatrix} A_{11} & A_{12} \\ A_{12}^* & A_{22}\end{pmatrix} \tag{2.40}$$

The probabilistic observable has mean values in the states $|1\rangle$ and $|2\rangle$ given by $\overline{A}_1$ and $\overline{A}_2$

$$\overline{A}_1 = A_{11} + \rho_{12}^* A_{12} + \rho_{12} A_{12}^* \tag{2.41}$$

$$\overline{A}_2 = A_{22} + \rho_{12}^* A_{12} + \rho_{12} A_{12}^* \tag{2.42}$$

It turns out quantum mechanics is the same as classical statistics, but with additional information for non-diagonal observables (probabilistic observables). As long as we are dealing with diagonal observables, there is no difference between the both approaches and this case non-diagonal elements of ρ are of no importance. Actually, the last statement is only true for a given point in time. Non-diagonal elements of ρ are important for the time evolution of the probability distribution $\{p_\tau\,(t)\} \triangleq \{\rho_{nn}(\tau)\}$.

vi) Pure quantum states

Consider a special form of the density matrix $\rho_{nm} = \psi_n \cdot \psi_m$, where ψ_n is a complex vector with Ω components and $\sum_n \psi_n^*\psi_n = 1$. In other words ψ_n is a wave function. Then:

$$\langle A\rangle = \rho_{nm} ?A_{mn} = \psi_m^* ?A_{mn}\psi_n = \langle \psi\,|\,A\,|\,\psi\rangle$$

$$p_n = \rho_{nn} = |\psi_n|^2 \geq 0$$

As already mentioned, only ρ_{nn} is needed for diagonal observables (pure states) in contradiction to probabilistic (mixed states). We can state the condition for pure states:

$$\rho^2 = \rho \tag{2.43}$$

because $\rho_{mn}\rho_{nk} = \psi_m\psi_n^*\psi_n\psi_k = \psi_m\psi_k = \rho_{nk}$.

vii) Change of the basis by unitary transformation

A unitary transformation is of the kind $\rho \to \rho' = U\rho U^\dagger$ where $U^\dagger U = 1$. ρ' has still all the properties of the density matrix: $(\rho')^\dagger = \rho'$, tr$\rho = 1$, positivity. Operators also can be transferred unitary $?A \to ?A' = U?AU^\dagger$. Nevertheless, the expectation values are invariant under this transformation:

$$\begin{aligned} \langle A \rangle &= \operatorname{tr}\left(\rho'?A'\right) = \operatorname{tr}\left(U\rho U^\dagger U?AU^\dagger\right) = \operatorname{tr}\left(U\rho?AU^\dagger\right) \\ &= \operatorname{tr}\left(U^\dagger U\rho?A^\dagger\right) = \operatorname{tr}\left(\rho?A^\dagger\right) \end{aligned} \tag{2.44}$$

Here are several important properties:

- Even if $?A$ is diagonal, $U?AU^\dagger$ can be non-diagonal in the general case.
- If ρ can be diagonalized, then $\rho' = \operatorname{diag}(\lambda_1, \lambda_2, \ldots, \lambda_\Omega)$
- Pure states are invariant:

$$\rho^2 = \rho \Leftrightarrow \rho'^2 = \rho' \tag{2.45}$$

One could see this $\rho'^2 = U\rho U^\dagger U\rho U^\dagger = U\rho^2U^\dagger = U\rho U^\dagger = \rho' \Rightarrow \rho'^2 = \rho' \Rightarrow \lambda_n^2 = \lambda_n \Rightarrow \lambda_n = 0, 1 \Rightarrow \rho'_{nm} = \delta_{mk}\delta_{nk} \Rightarrow \psi'_n = \delta_{nk}\mathrm{e}^{\imath\alpha}$, $\psi'^*_m = \delta_{mk}\mathrm{e}^{-\imath\alpha}$, which is a pure state.

viii) Pure and mixed states

Consider an observable $l = 1$, which could be associated with the angular momentum. Then, l_z could be -1, 0, 1. The system is described in table 2.3. Of course, $p_1 + p_2 + p_3 = 1$ must be satisfied. The density matrix of the system is:

Table 2.7: z-component of the angular momentum

l_z	1	0	-1
pure states	$\begin{pmatrix} 1 \\ 0 \\ 0 \end{pmatrix}$	$\begin{pmatrix} 0 \\ 1 \\ 0 \end{pmatrix}$	$\begin{pmatrix} 0 \\ 0 \\ 1 \end{pmatrix}$
density matrix	$\begin{pmatrix} 1 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}$	$\begin{pmatrix} 0 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 0 \end{pmatrix}$	$\begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 1 \end{pmatrix}$
probability	p_1	p_2	p_3

$$\rho = \begin{pmatrix} p_1 & 0 & 0 \\ 0 & p_2 & 0 \\ 0 & 0 & p_3 \end{pmatrix} \tag{2.46}$$

This is a mixed state as long as $\exists p_i \neq 0, 1$. One could check and see that in this case

$$\rho^2 = \begin{pmatrix} p_1^2 & 0 & 0 \\ 0 & p_2^2 & 0 \\ 0 & 0 & p_3^2 \end{pmatrix} \neq \rho \tag{2.47}$$

Example: Let us examine a system characterized by the following density matrix

$$\rho = \begin{pmatrix} \frac{1}{3} & 0 & 0 \\ 0 & \frac{1}{3} & 0 \\ 0 & 0 & \frac{1}{3} \end{pmatrix} \tag{2.48}$$

Here, all the states $l_z = -1, 0, 1$ have equal probability, so $\langle l_z \rangle = 0$. If we compare this with a pure state:

$$\psi = \frac{1}{\sqrt{3}} \begin{pmatrix} 1 \\ 1 \\ 1 \end{pmatrix} \tag{2.49}$$

$$\rho = \frac{1}{3} \begin{pmatrix} 1 & 1 & 1 \\ 1 & 1 & 1 \\ 1 & 1 & 1 \end{pmatrix} \tag{2.50}$$

we will see that both (2.48) and (2.50) have the same diagonal elements. Consequently, $\langle l_z \rangle$ is again zero. The difference though are the mean values of that probabilistic observables, because of the different off-diagonal elements.

e) Micro-states

Back to the quantum-mechanical point view; provided that $|\psi_n\rangle$ is a complete orthonormal basis, then ψ_n are micro-states.

Example: Hydrogen atom

$n = (?n, l, m, s)$, n is a multiple index. We assume that the micro-states are countable, although it is commonly otherwise. They are often also limited, e. g. only micro-states with $E < \frac{E_0}{5}$.

$$E = \frac{-E}{?n^2} \tag{2.51}$$

$$\psi_{1,2} \quad : \quad ?n = 1, l = 0, m = 0, s = \pm 1; E = -E_0 \tag{2.52}$$

$$\psi_{3,\ldots,10} \quad : \quad ?n = 2, l = 0, 1, m, s; E = -\frac{E_0}{4} \tag{2.53}$$

$$?n = 3 \quad : \quad E = -\frac{E_0}{9} \tag{2.54}$$

$$\Omega \quad = \quad 2 + 8 = 10 \tag{2.55}$$

The operator $?E = -E_0 \mathrm{diag}\left(1, 1, \frac{1}{4}, \cdots \frac{1}{4}\right)$. Let the distribution be equal $\rho = \mathrm{diag}\left(\frac{1}{10}, \ldots, \frac{1}{10}\right)$.

$$\langle E \rangle = \frac{1}{10}\left(2 + \frac{8}{4}\right)(-E_0) = -0.4 E_0 \tag{2.56}$$

Example: A particle in a box

$$-\frac{\hbar\Delta}{2M}\psi = E\psi \tag{2.57}$$

Consider a cubical box with an edge L.

$$\psi = \mathrm{e}^{\frac{\imath p_x x}{\hbar}}\mathrm{e}^{\frac{\imath p_y y}{\hbar}}\mathrm{e}^{\frac{\imath p_z z}{\hbar}}\psi_0 = \mathrm{e}^{\frac{\imath \vec{p}\vec{x}}{\hbar}}\psi_0 E = \frac{1}{2M}\vec{p}^2 \tag{2.58}$$

Periodical boundary conditions give $\psi\left(-\frac{L}{2}, y, z\right) = \psi\left(\frac{L}{2}, y, z\right)$ (and also for y and z). As $p_{x,y,z}$ have discrete values:

$$\begin{gathered}\vec{p} = \hbar\frac{2\pi}{L}\vec{m} \quad \vec{m} = (m_x, m_y, m_z)\\ m_{x,y,z} \in \mathbb{Z}\end{gathered} \tag{2.59}$$

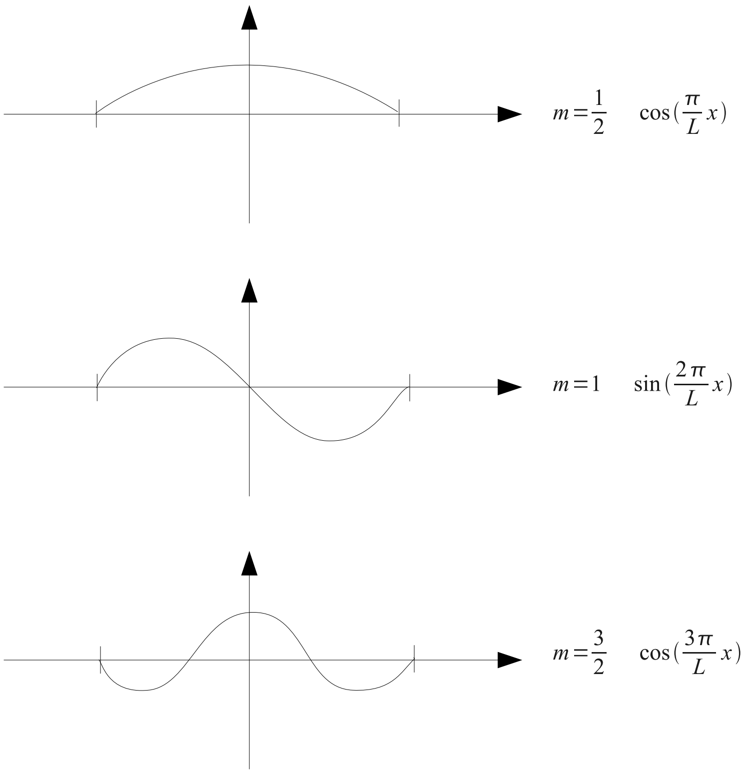


Figure 2.3: Wave functions of a particle in a box

f) Partition function

What is the number of states with given Energy, E, of a single particle, $N = 1$, in an one-dimensional, $d = 1$, box with volume L? We will denote the number of states in $[E, E + \delta E]$ with $\Omega(E, V)$. For our purposes, assume that $E \gg \frac{\hbar^2\pi^2}{2ML^2}$

$$\begin{gathered}\frac{\vec{p}^2}{2M} = \frac{\pi^2\hbar^2}{2M}\frac{n^2}{L^2}\\ E < \frac{\pi^2\hbar^2}{2M}\frac{n^2}{L^2} < E + \delta E\end{gathered} \tag{2.60}$$

If $\delta E \ll E$, we can approximate $\sqrt{E+\delta E} \approx \sqrt{E}\left(1+\frac{1}{2}\frac{\delta E}{E}\right) = \sqrt{E} + \frac{1}{2}\frac{\delta E}{\sqrt{E}}$.

$$\frac{\sqrt{2ME}}{\pi\hbar}L < n < \frac{\sqrt{2ME}}{\pi\hbar}L + \frac{1}{2\pi\hbar}\left(\frac{2M}{E}\right)^{1/2} L\delta E \tag{2.61}$$

$$\boxed{\Omega(E,V) = \frac{V}{2\pi\hbar}\left(\frac{2M}{E}\right)^{1/2}\delta E} \tag{2.62}$$

Which means that $\Omega \sim V$!

g) Continuous distribution and continuous variables

We will examine the continuous description of “closely situated” discrete States. We need to define the probability density $p(x)$ with:

$$\boxed{\begin{aligned}\int \mathrm{d}x\, p(x) &= 1\\ \int \mathrm{d}x\, p(x)A(x) &= \langle A\rangle\end{aligned}} \tag{2.63}$$

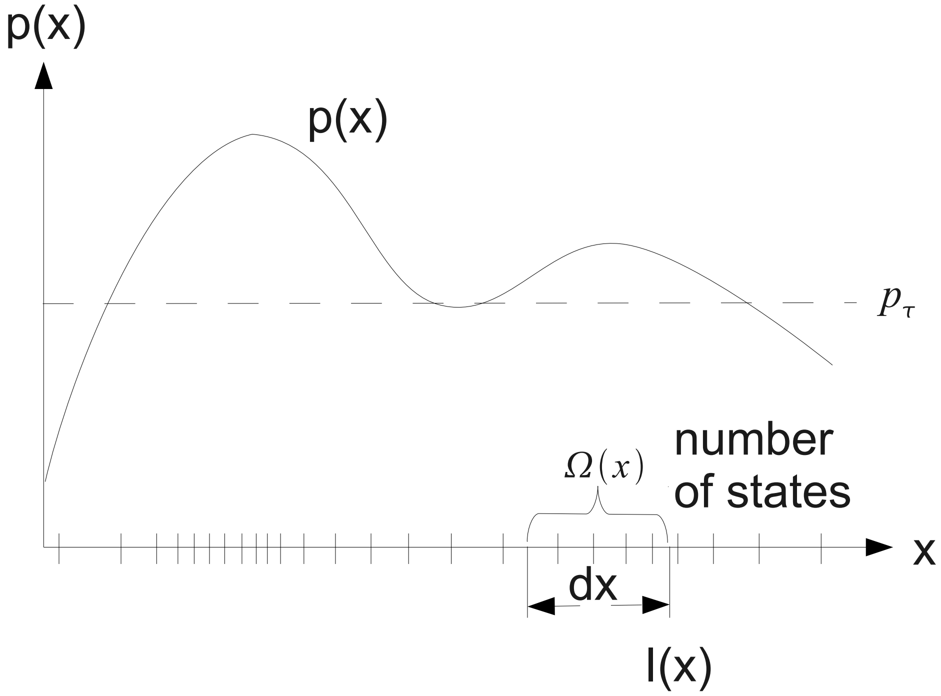


Figure 2.4: Probability distribution for a continuous variable

$I(x)$ Interval of states τ which belong to the interval $\left[x-\frac{\mathrm{d}x}{2}, x+\frac{\mathrm{d}x}{2}\right]$.

$\overline{p}(x)$ Mean probability in $I(x)$

$\Omega(x)$ Number of states belonging to $I(x)$

We can write that $p(x)\mathrm{d}x = \sum_{``\tau\in I(x)"} p_\tau = \overline{p}(x)\Omega(x)$.

$A(x) = \langle A\rangle_x$ mean value of A in interval $I(x)$.

$$\langle A\rangle_x = \frac{\sum_{\tau\in I(x)} p_\tau A_\tau}{\sum_{\tau\in I(x)} p_\tau} \tag{2.64}$$

Let us check if the continuous case is equivalent with the discrete:

$$\begin{aligned}\int \mathrm{d}x p(x)A(x) &= \sum_x \mathrm{d}x\, p(x)A(x) = \sum_x \underbrace{\left(\sum_{\tau\in I(x)} p_\tau\right)}_{\mathrm{d}x p(x)} \frac{\sum_{\tau\in I(x)} p_\tau A_\tau}{\sum_{\tau\in I(x)} p_\tau} \\ &= \sum_x \sum_{\tau\in I(x)} p_\tau A_\tau = \sum_\tau p_\tau A_\tau \end{aligned} \tag{2.65}$$

$p(x)\mathrm{d}x$ probability of reduced system with states x

$A(x)$ probabilistic observable

Note that $\langle A^2\rangle = \int \mathrm{d}x\, p(x)A^2(x) = \sum_\tau p_\tau A_\tau$ holds only if the dispersion of A vanishes in the continuum limit $\mathrm{d}x \to 0$

We shall see that $p(x)$ depends on the choice of the variables x. For that purpose, consider the explicit coordinate transformation

$$x = f(x') \tag{2.66}$$

$$\mathrm{d}x = \frac{\mathrm{d}f}{\mathrm{d}x'}\mathrm{d}x' \tag{2.67}$$

The expectation value of A in the new coordinates becomes:

$$\langle A\rangle = \int \mathrm{d}x\, p(x)A(x) = \int \mathrm{d}x'\, \underbrace{\frac{\mathrm{d}f}{\mathrm{d}x'} p\left(f\left(x'\right)\right)}_{p'(x')} \underbrace{A\left(f\left(x'\right)\right)}_{A'(x')} \tag{2.68}$$

This could be generalized for many variables:

$$\langle A\rangle = \int \mathrm{d}x_1 \ldots \mathrm{d}x_n\, p\left(x_1 \ldots x_n\right) A\left(x_1 \ldots x_n\right) \tag{2.69}$$

where $p(x)$ is transformed by the Jacobi determinant:

$$p'(x') = \det\left|\frac{\mathrm{d}f}{\mathrm{d}x'}\right| p\left(f\left(x'\right)\right) \tag{2.70}$$

$$x_i = f_i\left(x'_j\right) \tag{2.71}$$

$$\left|\frac{\mathrm{d}f}{\mathrm{d}x'}\right| = \det\begin{pmatrix} \frac{\mathrm{d}f_1}{\mathrm{d}x'_1} & \cdots & \frac{\mathrm{d}f_n}{\mathrm{d}x'_1} \\ \vdots & \ddots & \vdots \\ \frac{\mathrm{d}f_1}{\mathrm{d}x'_n} & \cdots & \frac{\mathrm{d}f_n}{\mathrm{d}x'_n} \end{pmatrix} \tag{2.72}$$

h) Probability density of energy

$$p\,(E)\,\mathrm{d}E \;=\; \overline{p}\,(E)\,\frac{\Omega\,(E)}{\delta E}\mathrm{d}E \tag{2.73}$$

$$\frac{\Omega(E)}{\delta E}\underset{\text{change of symbols}}{\rightarrow}\frac{\delta\Omega(E)}{\delta E}\underset{\text{continium limit}}{\rightarrow}\frac{\partial\Omega(E)}{\partial E} \tag{2.74}$$

$$\boxed{p(E)\mathrm{d}E = \overline{p}(E)\frac{\partial\Omega}{\partial E}\mathrm{d}E} \tag{2.75}$$

An example could be one particle in a linear box ($d = 1$, $N = 1$).

i) Equal probability for all values τ

We know that

$$\delta\Omega(E) \;\equiv\; \Omega(E) = \frac{V}{2\pi\hbar}\left(\frac{2M}{E}\right)^{1/2}\delta E \tag{2.76}$$

$$\Rightarrow \frac{\delta\Omega}{\delta E} \;\rightarrow\; \frac{V}{2\pi\hbar}\left(\frac{2M}{E}\right)^{1/2} \tag{2.77}$$

then:

$$p_j(E) = \begin{cases}\frac{V}{2\pi\hbar}\left(\frac{2M}{E}\right)^{1/2}Z^{-1} & \text{for } E < E_{\max}\\ 0 & \text{else}\end{cases} \tag{2.78}$$

Here, Z is a constant factor, which could be determined by the normalization condition $\int p(E)\mathrm{d}E = 1$

$$Z = \frac{V}{2\pi\hbar}\int_0^{E_{\max}}\mathrm{d}E\left(\frac{2M}{E}\right)^{1/2} \tag{2.79}$$

ii) Boltzmann distribution for micro-states τ

The Boltzmann distribution is given by the formula:

$$p_\tau = Z^{-1}\mathrm{e}^{-\frac{E_\tau}{k_\mathrm{B}T}} = Z^{-1}\mathrm{e}^{-\frac{E_\tau}{T}} \tag{2.80}$$

We have set $k_\mathrm{B} = 1$, which means we measure the temperature in energy units. E_τ is the energy of state τ.

$$p_\mathrm{B}(E) \;=\; \frac{V}{2\pi\hbar}\left(\frac{2M}{E}\right)^{1/2}\mathrm{e}^{-E/\mathrm{T}}Z^{-1} \tag{2.81}$$

$$\langle E\rangle \;=\; \int_0^{E_{\max}} p(E)E\,\mathrm{d}E \tag{2.82}$$

$$\left\langle E^2\right\rangle \;=\; \int_0^{E_{\max}} p(E)E^2\,\mathrm{d}E \tag{2.83}$$

It should be marked that $p(E)$ is the macroscopic probability distribution and p_τ is the microscopic.

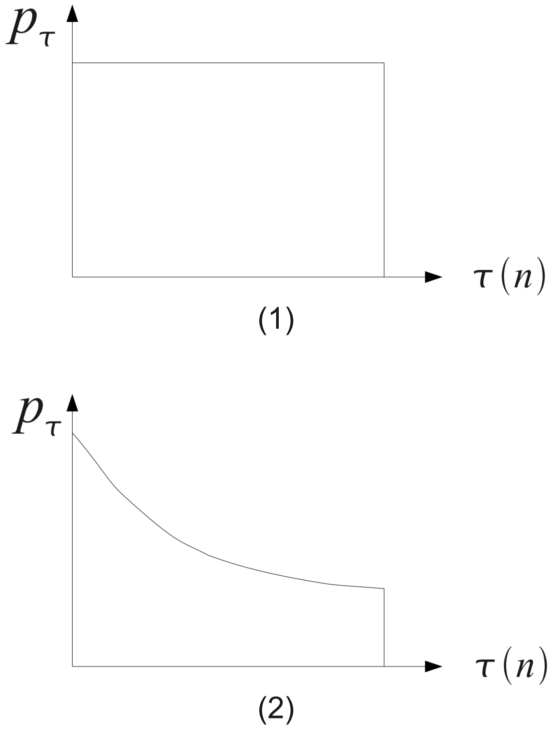


Figure 2.5: (1) is a equipotential distribution, (2) is the Boltzmann distribution

iii) Number of one particle states in a momentum interval

Number of one particle states in a momentum intervalΔp_x, Δp_y, Δp_z First, the one-dimensional case:

$$\Omega(p) = \frac{L}{2\pi\hbar}\Delta p_x \tag{2.84}$$

Periodical boundary conditions would give:

$$p_x < \frac{2\pi\hbar}{L}n < p_x + \Delta p_x \tag{2.85}$$

For an arbitrary we have $\Omega(\vec{p}) = \frac{V}{(2\pi\hbar)^d}\Delta p_1 \ldots \Delta p_d$, which in the most usual case of $d = 3$ is:

$$\boxed{\frac{\partial\Omega}{\partial p_x \partial p_y \partial p_z} = \frac{V}{(2\pi\hbar)^3}\Delta p_1 \Delta p_2 \Delta p_3} \tag{2.86}$$

Number of one particle states with energy E for arbitrary d

$$\frac{\partial\Omega}{\partial E} = \int \mathrm{d}^d\vec{p}\, \frac{\partial^d\Omega}{\partial p_1 \ldots \partial p_d}\delta\left(\frac{\vec{p}^2}{2M} - E\right) \tag{2.87}$$

$$\boxed{\frac{\partial\Omega}{\partial E} = \frac{V}{(2\pi\hbar)^d}\int \mathrm{d}^d\vec{p}\,\delta\left(\frac{\vec{p}^2}{2M} - E\right)} \tag{2.88}$$

For $d = 1$:

$$\begin{aligned}\int_{-\infty}^{\infty} \mathrm{d}p\,\delta\left(\frac{p^2}{2M} - E\right) &= \sqrt{2M}\int_0^{\infty} \mathrm{d}\varepsilon\,\varepsilon^{-1/2}\delta(\varepsilon - E) \\ &= \left(\frac{2M}{E}\right)^{1/2} \end{aligned} \tag{2.89}$$

with $\varepsilon = \frac{p^2}{2M}$. We have used that $|p| = \sqrt{2ME}$ and $\int_{-\infty}^{\infty} \mathrm{d}p = 2\int_0^{\infty} \mathrm{d}\,|p| = 2\int_0^{\infty} \mathrm{d}\varepsilon\,\sqrt{2M}\frac{1}{2}\varepsilon^{-1/2}$.

$$\frac{\partial \Omega}{\partial E} = \frac{L}{2\pi\hbar}\left(\frac{2M}{E}\right)^{1/2} \tag{2.90}$$

For $d = 3$:

$$\int \mathrm{d}^3\vec{p} = 4\pi\int_0^{\infty} \mathrm{d}\,|p|\;|p|^2 \tag{2.91}$$

with $\frac{|p|^2}{2M} = \varepsilon$

$$\begin{aligned}\int_{-\infty}^{\infty} \mathrm{d}p\,\delta\left(\frac{\vec{p}^2}{2M} - E\right) &= 4\pi\int_0^{\infty} \mathrm{d}\varepsilon\,\delta(\varepsilon - E)\underbrace{\sqrt{\frac{M}{2}}\varepsilon^{-1/2}}_{\frac{\partial|\vec{p}|}{\partial\varepsilon}}\underbrace{2M\varepsilon}_{|\vec{p}|^2} \\ &= 4\pi\sqrt{2}M^{3/2}E^{1/2}\end{aligned} \tag{2.92}$$

Number of states per energy is given by

$$\boxed{\frac{\partial \Omega}{\partial E} = \frac{V}{(2\pi\hbar)^3}4\sqrt{2}\pi M^{3/2}E^{1/2}} \tag{2.93}$$

Boltzmann probability distribution for one particle This Boltzmann probability distribution for one particle is given by

$$p(E) = \frac{\partial \Omega}{\partial E}\exp\left(-\frac{E}{T}Z^{-1}\right) \tag{2.94}$$

where Z is the normalization factor. To find it we use

$$\int \mathrm{d}E\,p(E) = 1 \tag{2.95}$$

so we get

$$Z = \int_0^{\infty} \mathrm{d}E\,\frac{\partial \Omega}{\partial E}\exp(-E/T) \tag{2.96}$$

where $\frac{\partial \Omega}{\partial E} = FE^{1/2}$, so

$$Z = F\int \mathrm{d}E\,E^{1/2}\exp(-E/T) = F?Z \tag{2.97}$$

and $p(E) = ?E^{-1}E^{1/2}\exp(-E/T)$. It is therefore possible to find this probability where $\hbar$ does not longer appear.

i) Correlation functions

If there are two observables A and B, what is the probability that measurement of A yields a specific values λ_A and λ_B? Imagine that B is measured after A, then the probability becomes $p\left(\lambda_B,\,\lambda_A\right)$.

i) Conditional Probability $p\left(\lambda_B|\lambda_A\right)$

The probability to find λ_B if λ_A is measured for A is called conditional probability and is written as $p(\lambda_B|\lambda_A)$.

$$p(\lambda_B, \lambda_A) = p(\lambda_B|\lambda_A)p(\lambda_A). \tag{2.98}$$

ii) Product Observable $B \circ A$

The product observable is defined as

$$\langle B \circ A\rangle = \sum_{(\lambda_B,\lambda_A)} p\left(\lambda_B, \lambda_A\right)\lambda_B\lambda_A = \sum_{\lambda_B}\sum_{\lambda_A} p\left(\lambda_B|\lambda_A\right)p\left(\lambda_A\right)\lambda_B\lambda_A \tag{2.99}$$

$$\text{Spec}\left(B \circ A\right) = \{\lambda_B\lambda_A\} \tag{2.100}$$

$\langle B \circ A\rangle$ depends on conditional probabilities, not only on $p\left(\lambda_B\right)$ and $p\left(\lambda_A\right)$.

iii) Correlation Function

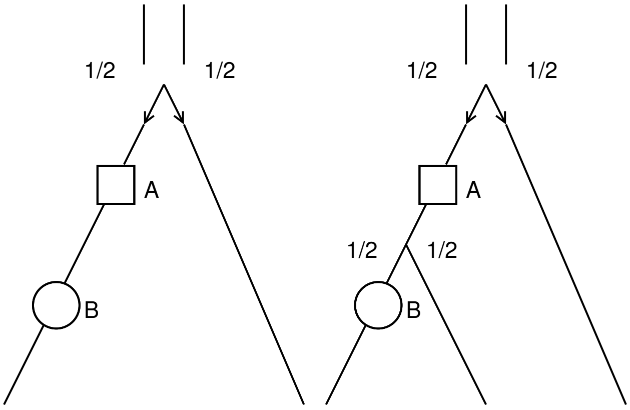
Correlation function is defined as

$$< B \circ A >_{\mathrm{c}} = < B \circ A > - < B >< A > \tag{2.101}$$

for $< B \circ A >_{\mathrm{c}} \neq 0$ then B and A are correlated.

Example: A falling marble

Imagine a marble that is falling out of pipe on a prism (Figure 2.6a). Moreover, it can to roll down any on the sides of the prism with equal probability. However, there are two detectors A and B on the left side. The corresponding measurement values are $\lambda_A = 1$ and $\lambda_B = 1$ if the marble goes through the detectors and 0 otherwise.



(a) Two possibilities (b) Three possibilities

Figure 2.6: A marble is falling down on a prism.

The probability to measure $\lambda_A = 1$ is $\frac{1}{2}$. It is easy to see that $p(\lambda_B|\lambda_A) = 1$. Therefore, $p(\lambda_B, \lambda_A) = \frac{1}{2}$. With this we calculate

$$\begin{aligned} \langle B \circ A \rangle &= \frac{1}{2} && (2.102) \\ \langle A \rangle &= \sum_{\lambda_A} p_A \lambda_A = \frac{1}{2} && (2.103) \\ \langle B \rangle &= \sum_{\lambda_B} \underbrace{p_B}_{=\frac{1}{2}} \lambda_B = \frac{1}{2} && (2.104) \\ \langle B \rangle \langle A \rangle &= \frac{1}{4} && (2.105) \\ \langle B \circ A \rangle_c &= \frac{1}{2} - \frac{1}{4} = \frac{1}{4} && (2.106) \end{aligned}$$

Is $\langle B \circ A \rangle = \langle A \circ B \rangle$ true? Although, it is true in this case, in general, it is not. A simple example is illustrated in figure 2.6b.

iv) Independent Observables

If the measurement of A does not influence B, then the probability

$$\boxed{p(\lambda_B|\lambda_A) = p(\lambda_B)} \tag{2.107}$$

is independent of λ_A. So only for independent observables

$$\boxed{p(\lambda_B, \lambda_A) = p(\lambda_B)p(\lambda_A)} \tag{2.108}$$

but we must keep in mind that this in general is not true. We can now also write the correlation function

$$\langle B \circ A \rangle = \sum_{\lambda_B} \sum_{\lambda_A} p(\lambda_B) p(\lambda_A) \lambda_B \lambda_A = \left[\sum_{\lambda_B} p(\lambda_B) \lambda_B \right] \left[\sum_{\lambda_A} p(\lambda_A) \lambda_A \right] \\ = \langle B \rangle \langle A \rangle \Rightarrow \langle B \circ A \rangle_c = 0 \tag{2.109}$$

An important note: the reverse statement ("$\Leftarrow$") is not true.

v) Classical Correlation Function

$$(B \circ A)_\tau = B_\tau A_\tau \tag{2.110}$$

The classical correlation function is

$$< BA >_c = \underbrace{\Sigma_\tau p_\tau B_\tau A_\tau}_{=\langle BA \rangle} - \underbrace{(\Sigma_\tau p_\tau B_\tau)}_{=<B>} (\Sigma_\tau p_\tau A_\tau) \tag{2.111}$$

In general $\langle BA \rangle_c \neq 0$. If $B = A$

$$< AA >_c = \Delta A^2 \tag{2.112}$$

There is an easy recipe for calculating conditional probabilities $p(\lambda_B|\lambda_A)$:

1. We eliminate all τ for which $A_\tau \neq \lambda_A$.

2. Now we have a new system with states τ' and

$$\overline{p}_{\tau'} = \frac{p_{\tau'}}{\Sigma_{\tau'} p_{\tau'}} \tag{2.113}$$

and now $A_{\tau'} = \lambda_A$ and $B_{\tau'} = B_{\tau}$

3. The result is:

$$p\left(\lambda_B, \lambda_A\right) = \sum_{\substack{\tau \\ A_\tau = \lambda_A, B_\tau = \lambda_B}} p_\tau \tag{2.114}$$

One should note that after the measurement of A the relative probabilities $\frac{p_{\tau'}}{p_{\rho'}}$ are the same as $\frac{p_\tau}{p_\rho}$ before the measurement of A.

$$\frac{p_{\tau'}}{p_{\rho'}} = \frac{p_\tau}{p_\rho} \tag{2.115}$$

In this lecture we will be mostly concerned with classical product of two observables $BA = AB$ and with classical correlation functions, which are special correlation functions. However, if the relative probabilities change after the measurement of A, then we have different conditional probabilities $B \circ A \neq BA$. Note that every consistent choice of conditional probabilities $p\left(\lambda_B|\lambda_A\right)$ leads to the definition of a product of two observables $B \circ A$. Many different products and correlation functions are possible; in general, the correct choice depends on the way how measurements are performed. This choice is important for statistical description of systems with few states like atoms (with bounded energy), where the measurements of a Fermi observable has a strong influence on the possible outcome of measurement of a second observable.

vi) Quantum correlations

We now have

$$\langle B \circ A \rangle = \mathrm{tr}\left(\rho \frac{?A?B + ?B?A}{2}\right) \tag{2.116}$$

for $?A, ?B$ diagonal, where $?A = \mathrm{diag}(A_n)$. Therefore

$$< B \circ A >= \sum_m \rho_m A_m B_m \tag{2.117}$$

The quantum product coincides with the classical in this case. However, if $?A$ and $?B$ do not commute, this is no longer correct, because in that case $?A$ and $?B$ cannot simultaneously be diagonal.

3 Systems with many states or particles

$\mathcal{N}$ is the particle number where $\mathcal{N} \approx N_{Avogadro} \approx 6 \cdot 10^{23}$.

a) Chain with $\mathcal{N}$ lattice sites

i) Probability distribution

First we treat fermions. A fermion is present on site j if $S_j =\uparrow$ and absent on site j if $S_j =\downarrow$. We have $\tau = \{s_j\}$ and $s_j = \pm 1$ for every j. Here $\Omega = 2^{\mathcal{N}}$. Let us define the number of fermions, N, which is the observable we want do discuss. For every collection of spins, what is the corresponding value of the observable

$$N = N(\{s_j\}) = \sum_j \frac{1}{2}(s_j + 1) \tag{3.1}$$

Lattice sites are independent and we say that the probability is q if the site is occupied, ↑, and $1-q$ if empty, ↓. So

$$p(\{s_j\}) = \prod_{j=1}^{\mathcal{N}} \left[\frac{1}{2} + \left(q - \frac{1}{2}\right) s_j\right] = q^N (1-q)^{\mathcal{N}-N} \tag{3.2}$$

ii) Macroscopic probability

We want to compute the macroscopic probability to find N fermions (particles), that is $p(N)$.

$$p(N) = q^N (1-q)^{(\mathcal{N}-N)} \Omega(N) \tag{3.3}$$

where

$$\Omega(N) = \frac{\mathcal{N}!}{N!(\mathcal{N}-N)!} \tag{3.4}$$

is the number of macroscopic states with N particles.

If we have 1 particle there are $\mathcal{N}$ possibilities. If we have 2 particles there are $\frac{\mathcal{N}(\mathcal{N}-1)}{2}$ possibilities and if we have 3 particles then there are $\frac{\mathcal{N}(\mathcal{N}-1)(\mathcal{N}-2)}{3!}$ possibilities.

We now introduce the binomial distribution

$$p(N) = q^N (1-q)^{\mathcal{N}-N} \frac{\mathcal{N}!}{N!(\mathcal{N}-N)!}$$

we get

$$(q+r)^{\mathcal{N}} = \sum_{N=0}^{\mathcal{N}} \frac{\mathcal{N}!}{N!(\mathcal{N}-N)!} q^N r^{\mathcal{N}-N} \tag{3.5}$$

since $\sum_N p(N) = 1$ we normalize

$$1 = \sum_N q^N (1-q)^{\mathcal{N}-N} \frac{\mathcal{N}!}{N!(\mathcal{N}-N)!} \tag{3.6}$$

The total number of micro-states is $\Omega = 2^{\mathcal{N}}$ but the total number for macro-states is $\mathcal{N}+1$. For the micro-states $\tau = \{s_j\}$ and for the macro states $\tau = N$. The marcostates are only characterized by the total fermion number N and are therefore simple.

iii) Expectation value

The expectation value is (with $r = 1 - q$)

$$\begin{aligned}\langle N\rangle &= \sum_N p(N)N\\ &= \sum_{N=0}^{\mathcal{N}} \frac{\mathcal{N}!}{N!(\mathcal{N}-N)!} N q^N (1-q)^{\mathcal{N}-N} = \sum_N \frac{\mathcal{N}!}{N!(\mathcal{N}-N)!} q\frac{\partial}{\partial q} q^N r^{\mathcal{N}-N}\\ &= q\frac{\partial}{\partial q}\sum_N \frac{\mathcal{N}!}{N!(\mathcal{N}-N)!} q^N r^{\mathcal{N}-N} = q\frac{\partial}{\partial q}(r+q)^{\mathcal{N}} = q\mathcal{N}(r+q)^{\mathcal{N}-1}\\ &= q\mathcal{N} \end{aligned} \tag{3.7}$$

iv) Dispersion

The dispersion is

$$\begin{aligned}< N^2 > &= \sum_N p(N)N^2\\ &= \left(q\frac{\partial}{\partial q}\right)^2 (q+r)^{\mathcal{N}} = q\frac{\partial}{\partial q}\left(\mathcal{N}q(q+r)^{\mathcal{N}-1}\right)\\ &= q\mathcal{N}\left[(q+r)^{\mathcal{N}-1} + (\mathcal{N}-1)q(q+r)^{\mathcal{N}-2}\right]\\ &= q\mathcal{N} + q^2\mathcal{N}(\mathcal{N}-1) = q^2\mathcal{N}^2 + \mathcal{N}(q-q^2)\end{aligned} \tag{3.8}$$

We also have

$$\triangle N^2 =< N^2 > - < N >^2 = \mathcal{N}q(1-q) \tag{3.9}$$

from where we get

$$\begin{aligned}\frac{\Delta N}{< N >} &= \frac{\sqrt{\mathcal{N}q(1-q)}}{\mathcal{N}q}\\ &= \frac{1}{\sqrt{\mathcal{N}}}\sqrt{\frac{1-q}{q}} =\end{aligned} \tag{3.10}$$

Relative fluctuations are $\sim \frac{1}{\sqrt{N}}$! The distribution get sharper, when N grows. An example: $N = 10^{20} \Longrightarrow \frac{\triangle N}{<N>} \sim 10^{-10}$.

This is the main reason why statistical physics has such a predictive power. The statistical uncertainty is so small, that one can practically calculate deterministically with mean values.

b) Uncorrelated probability distribution

Uncorrelated means that the observables relate to different lattice sites, that are uncorrelated. Does not mean that all correlations vanish.

i) Chain with $\mathcal{N}$ sites

Now we have one spin per lattice site, so we have $\mathcal{N}$ spins. Therefore the total spin, S, is given by

$$S = \sum_j s_j \tag{3.11}$$

In quantum mechanics the spin is $\frac{\hbar}{2}S$. We have our observable N,

$$N = \sum_j \frac{1}{2}(s_j + 1) = \frac{1}{2}S + \frac{1}{2}\mathcal{N} \tag{3.12}$$

and therefore

$$S = 2N - \mathcal{N} = \mathcal{N}(2q - 1) \tag{3.13}$$

and also

$$< S >= 2 < N > -\mathcal{N} = \mathcal{N}(2q - 1) \tag{3.14}$$

and

$$< S^2 >= 4 < N^2 > -4\mathcal{N} < N > +\mathcal{N}^2 \tag{3.15}$$

Similarly, we get

$$\Delta S^2 = 4\Delta N^2 = 4Nq(1 - q) \tag{3.16}$$

and also

$$\frac{\Delta S}{< S >} \sim \frac{1}{\sqrt{\mathcal{N}}} \tag{3.17}$$

Now, we have from equation (3.2)

$$p(S) = p(N = \frac{\mathcal{N} + S}{2}) = q^{\frac{\mathcal{N}+S}{2}}(1 - q)^{\frac{\mathcal{N}-S}{2}} \frac{\mathcal{N}!}{(\frac{\mathcal{N}+S}{2})!(\frac{\mathcal{N}-S}{2})!} \tag{3.18}$$

$$\begin{aligned} p(\{s_j\}) &= \prod_{j=1}^{\mathcal{N}} \left[\frac{1}{2} + (q - \frac{1}{2})s_j\right] \\ &= \prod_j p(s_j) \end{aligned} \tag{3.19}$$

We can now compute the correlation function.

ii) Correlation functions

Let us compute the correlation function for $l \neq k$ in a micro state τ

$$< s_l s_k >= \sum_{\{s_j\}} s_l s_k p(\{s_j\}) \tag{3.20}$$

First, so we have a look at the sum over all micro-states

$$\sum_{\{s_j\}} = \prod_j \sum_{s_j=\pm 1} \tag{3.21}$$

and use it because

$$\prod_j \sum_{s_j=\pm 1} p(s_j) = 1 \tag{3.22}$$

We can also compute the individual ones

$$< s_k >= \frac{\sum_{s_k=\pm 1} s_k p(s_k)}{\sum_{s_k} p(s_k)} \tag{3.23}$$

and we are almost done because we can write

$$< s_k s_l >= \frac{\sum_{s_k} s_k p(s_k) \sum_{s_l} s_l p(s_l)}{\sum_{s_k} p(s_k) \sum_{s_l} p(s_l)} =< s_k >< s_l > \tag{3.24}$$

and the definition of a correlation function was

$$< s_k s_l >_{\mathrm{c}} =< s_k s_l > - < s_k >< s_l > \tag{3.25}$$

which in our case is $< s_k s_l >_{\mathrm{c}} =< s_k s_l > - < s_k >< s_l >= 0$.

iii) Random walk in one dimension

Path has $\mathcal{N}$ steps. Assume a small example of a drunken professor in Sweden close to his house at the lake. We can let $\uparrow$ be a step to the house of the professor with $q = 0.6$ and $\downarrow$ be a step to the water with $1 - q = 0.4$. The position of the professor is therefore

$$N(s_j = 1) - N(s_j = -1) \tag{3.26}$$

iv) Measurement sequences

Now we have $\mathcal{N}$ independent measurements of the state system. Independent measurement $s_j = \pm 1$. The relative dispersion is $\sim \frac{1}{\sqrt{\mathcal{N}}}$. The first thing we want to compute is the average of the spins

$$< s_j >= \frac{< S >}{\mathcal{N}} \tag{3.27}$$

But what is the dispersion. It is not just $< s_j >^2$. It is

$$\Delta S^2 =< S^2 > - < S >^2 \tag{3.28}$$

$$\Delta S = 2\sqrt{\mathcal{N} q(1-q)}$$

We compute now

$$\Delta s = \frac{\Delta S}{\mathcal{N}} = \frac{2\sqrt{q(1-q)}}{\sqrt{\mathcal{N}}} \tag{3.29}$$

Attention $\Delta s \neq \Delta s_j$!

This brings us to the idea of statistical ensemble.

c) Statistical Ensemble

The statistical ensemble is always specified by the states τ and the probability distribution p_τ (or the density matrix for quantum statistics). Now we can imagine an ensemble as a repetition of systems number of times. We can for example have a statistical ensemble with only two states. In the real world, we can not have infinite number of repetitions, but a finite number.

d) Gauss distribution

Systems with many uncorrelated degrees of freedom can be described by a Gaussian distribution. It is an exact description in the limit when the number of particles $N \to \infty$.

For the continuous distribution we have

$$p(x) = A \exp\left(\frac{-(x - \overline{x})^2}{2\sigma^2}\right) \tag{3.30}$$

where A is a normalization constant. The mean value of x is now defined as $\overline{x} =< x >$ and the variance is $\sigma = \Delta x = \sqrt{(\Delta x^2)}$. We can find the constant A by normalizing

$$\int\limits_{-\infty}^{\infty} \mathrm{d}x\, p(x) = 1 \tag{3.31}$$

so we have that

$$A = \frac{1}{\sqrt{2\pi}}\frac{1}{\sqrt{\sigma}} \tag{3.32}$$

We can also quantize to several variables x_i:

$$p = A\exp\left(-\frac{1}{2}A_{ij}\left(x_i - \overline{x}_i\right)^2\left(x_j - \overline{x}_j\right)^2\right) \tag{3.33}$$

As an example we can think about fermions on a one-dimensional lattice. We have the binomial distribution, for large N as

$$p(N) = \frac{\mathcal{N}!}{N!(\mathcal{N}-N)!}q^N r^{\mathcal{N}-N} \tag{3.34}$$

where $r = (1-q)$. We can now use the Stirling's formula

$$\lim_{N\to\infty}\ln(N!) = \left(N + \frac{1}{2}\right)\ln(N) - N + \frac{1}{2}\ln(2\pi) + O(\frac{1}{N}) \tag{3.35}$$

to get

$$\begin{aligned}
\alpha(N) &= \ln(p(N)) \\
&= \left(\mathcal{N} + \frac{1}{2}\right)\ln(\mathcal{N}) - \mathcal{N} + \frac{1}{2}\ln(2\pi) - \left(N + \frac{1}{2}\right)\ln(N) + \mathcal{N} - \frac{1}{2}\ln(2\pi) \\
&\quad - \left(\mathcal{N} - N + \frac{1}{2}\right)\ln(\mathcal{N}-N) + \mathcal{N} - N - \frac{1}{2}\ln(2\pi) + N\ln(q) + (\mathcal{N}-N)\ln(1-q) \\
&= \left(\mathcal{N} + \frac{1}{2}\right)\ln(\mathcal{N}) - \left(N + \frac{1}{2}\right)\ln(N) - \frac{1}{2}\ln(2\pi) \\
&\quad - \left(\mathcal{N} - N + \frac{1}{2}\right)\ln(\mathcal{N}-N) + \mathcal{N} - N + N\ln(q) + (\mathcal{N}-N)\ln(1-q)
\end{aligned} \tag{3.36}$$

It can be shown that

$$\alpha(N) = \frac{-(N-\overline{N})}{2\Delta N^2} \tag{3.37}$$

where $\overline{N} = \mathcal{N}q$ and $\Delta N^2 = \mathcal{N}q(1-q)$. The maximum is when the derivative is zero

$$0 = \left.\frac{\partial\alpha}{\partial N}\right|_{N=\overline{N}} \tag{3.38}$$

$$= \ln\left(\frac{\mathcal{N}-N}{N}\right) - \ln\left(\frac{1-q}{q}\right) - \frac{N}{2N(\mathcal{N}-N)} \tag{3.39}$$

we neglect the last term since N is large and get

$$0 \approx \ln\left(\frac{\mathcal{N}-N}{N}\right) - \ln\left(\frac{1-q}{q}\right) \tag{3.40}$$

$$\ln\left(\frac{\mathcal{N}-N}{N}\right) = \ln\left(\frac{1-q}{q}\right) \tag{3.41}$$

$$\overline{N} = \mathcal{N}q \tag{3.42}$$

We can also take the second derivative and get

$$\left.\frac{\partial^2 \alpha}{\partial N^2}\right|_{N=\overline{N}} \tag{3.43}$$

$$= - \frac{1}{\Delta N^2} \tag{3.44}$$

$$= - \frac{1}{\overline{N}(1-q)} \tag{3.45}$$

and the third one.

e) Thermodynamic limit

The thermodynamic limit is

$$\lim_{N\to\infty} \text{ and } \lim_{V\to\infty} \tag{3.46}$$

In this case the Gauss distribution becomes extremely sharp. For example, then for $\overline{N} = 10^{20}$ we have $\Delta N^2 = 2N = 2 \cdot 10^{20}$ when $q = 1/2$. If we have small deviations

$$N = \overline{N}(1 + 10^{-5}) \tag{3.47}$$

$$\frac{p(N)}{p(\overline{N})} = \exp\left(-\frac{1}{2\Delta N^2}\left(N - \overline{N}\right)^2\right) \tag{3.48}$$

$$= \exp\left(-\frac{\left(\overline{N}\left(1+10^{-5}\right) - \overline{N}\right)^2}{2\left(2\cdot 10^{20}\right)^2}\right) \tag{3.49}$$

$$= \exp\left(-\frac{1}{8\cdot 10^{10}}\right) \tag{3.50}$$

For even smaller $N = \overline{N}\left(1 + 10^{-10}\right)$ we have

$$\frac{p(N)}{p(\overline{N})} = e^{-\frac{1}{x}} \tag{3.51}$$

Therefore, we have only

$$\overline{N} - 5\Delta N \leq N \leq \overline{N} + 5\Delta N \tag{3.52}$$

4 Equilibrium ensembles

Equilibrium states are described by statistical ensembles with a static probability distribution.

If the probability distribution $\{p_\tau\}$ is time independent, then all expectation values of the observables are time independent, too. An example could be an isolated system after sufficiently long time, or just parts of the isolated system. Another possibility is an open system which is immersed in a heath bath.

Basic postulate for equilibrium states
An isolated system approaches an equilibrium state. After sufficiently long time an isolated system can be described by an equilibrium ensemble.

This conjecture was made by Boltzmann, but was never proven and most probably it is not true. There are two problems with the postulate. First, the time scale could be extremely large, compare systems like water, honey and glass. Second, one can work out time reversal microscopic equation, but the direction of time points toward equilibrium. Even though the basic postulate is not strictly true and important practical systems without equilibrium exist, the basic postulate is useful in many applications and it provides very good approximations.

a) Micro-canonical ensemble

We will be examining an isolated system in volume V with fixed energy E and fixed number of particles N.

i) Fundamental statistical postulate

Micro-states These are the states τ of a statistical ensemble, given by all possible quantum states with specified V, E, N. In quantum mechanics one has to choose a complete basis of eigenstates to E, N in a given V. Then

$$\psi_\tau \overset{\wedge}{=} \tau \tag{4.1}$$

Fundamental statistical postulate
In a equilibrium state of an isolated system all micro-states τ (with a given E, N) have the same probability p_τ.

An alternative way to say this is that an isolated system in equilibrium is with equal probability in each of the allowed states.

Micro-canonical ensemble
The number of micro-states with given E and N is $\Omega(E, N)$. Therefore

$$p_\tau = \Omega(E, N) \tag{4.2}$$

This raises several arguments in favour of the basic statistical postulate. To begin with, no state τ is preferred as compared to another one τ'. In addition to that, equipartition of states (equal p_τ) is constant in time. It is an important note that for a micro-canonical ensemble all expectation values and classical correlations for classical observables are uniquely fixed.

ii) Micro-canonical partition function

Micro-canonical partition function is denoted with Z_{mic} and

$$\begin{aligned} Z_{\text{mic}} &= \Omega(E) && (4.3)\\ p_{\tau} &= Z_{\text{mic}}^{-1} && (4.4) \end{aligned}$$

$Z_{\text{mic}}(E, N, V)$ depends on the thermodynamical variables V, E, N. Recall that $\Omega(E) \equiv \delta\Omega(E)$ is the number of states with energy between E and $E + \delta E$.

iii) Entropy S

For a micro-canonical ensemble:

$$\boxed{S = k_{\text{B}} \ln\Omega} \tag{4.5}$$

where k_{B} is the Boltzmann constant. If we set it to be equal to one, which simply means that we are measuring the temperature in energy units, e. g. eV, then we have:

$$\ln\Omega(E, N, V) = S(E, N, V) \tag{4.6}$$

This equation is valid for isolated systems in equilibrium. The entropy$S$ is an extensive thermodynamical potential, which means that $S \sim N$ for $N \to \infty$.

Examples:

1. Consider N uncorrelated particles. Each of them can be in F different states. Furthermore, let the energy be independent of the particles states $E = cN$. There are F^N possible micro-states.

$$\begin{aligned} \Omega &= F^N && (4.7)\\ \ln\Omega &= N \ln F && (4.8)\\ S &= k_{\text{B}} N \ln F && (4.9) \end{aligned}$$

2. Now, we will examine uncorrelated particles on $\mathcal{N}$ lattice sites with $E = cN, \mathcal{N} = bN$.

$$\begin{aligned} \Omega &= \frac{\mathcal{N}!}{N!(\mathcal{N} - N)!} && (4.10)\\ S &= ln\mathcal{N}! - lnN! - ln(\mathcal{N} - N)! && (4.11) \end{aligned}$$

Applying Stirling's formula on $\ln N!$ for large N gives:

$$\ln N! \approx N \ln N - N \tag{4.12}$$

$$\begin{aligned} S &= N - N \ln N + (\mathcal{N} - N) - (\mathcal{N} - N) \ln(\mathcal{N} - N) + \mathcal{N} \ln \mathcal{N} - \mathcal{N}\\ &= N \ln \frac{\mathcal{N} - N}{N} + \mathcal{N} \ln \frac{\mathcal{N}}{\mathcal{N} - N} = N \ln\left(\frac{\mathcal{N}}{N} - 1\right) - \mathcal{N} \ln\left(1 - \frac{N}{\mathcal{N}}\right)\\ &= N \ln\left(\frac{bV}{N} - 1\right) - b\frac{V}{N} \ln\left(1 - \frac{N}{bV}\right) && (4.13) \end{aligned}$$

$$S = Nf\left(\frac{N}{V}\right) \qquad \text{with} \frac{N}{V} = n \tag{4.14}$$

For small n we can approximate

$$S = N\left\{ln\left(\frac{b}{n} - 1\right) + 1\right\} \tag{4.15}$$

iv) Partition function for ideal classical gas

$$
\begin{aligned}
Z_{\text{mic}} &= \Omega &(4.16)\\
S &= lnZ_{\text{mic}} &(4.17)
\end{aligned}
$$

Our task is to count the number of quantum states in box with volume V (e.g. periodical boundary conditions) with given N, E.

Quantum states for one particle

$$
\begin{aligned}
\tau &\stackrel{\wedge}{=} \vec{p} = (p_1, p_2, p_3) &(4.18)\\
(p_1, p_2, p_3) &\Rightarrow n(p_1, p_2, p_3) &(4.19)\\
\sum_p n(p) &= 1 &(4.20)\\
E &= \sum_p E(p) n(p) &(4.21)\\
E &= \frac{\vec{p}^2}{2M} &(4.22)
\end{aligned}
$$

$$
\Omega = \sum_{\substack{p \\ \frac{\vec{p}^2}{2M} = E}} = \int \mathrm{d}^3 p \, \frac{\partial^3 \Omega}{\partial p^3} \delta\left(\frac{\vec{p}^2}{2M} - E\right) \delta E = \frac{V}{(2\pi\hbar)^3} \int \mathrm{d}^3 p \, \frac{\partial^3 \Omega}{\partial p^3} \delta\left(\frac{\vec{p}^2}{2M} - E\right) \delta E
$$

$$
= \frac{V}{(2\pi\hbar)^3} 4\sqrt{2}\pi M^{3/2} E^{1/2} \quad (4.23)
$$

Quantum states for two particles ($N = 2$)   The number of states for $N = 2$ are $n(p)$ with

$$
\begin{aligned}
\sum_p n(p) &= 2 &(4.24)\\
E &= \sum_p n(p) E(p) &(4.25)
\end{aligned}
$$

We should discriminate between fermions, for which $n(p) = 0, 1$, and bosons, for which $n(p)$ is arbitrary. Nevertheless, for both of them the equation

$$
\Omega = \Omega_1 + \Omega_2 \quad (4.26)
$$

should be satisfied. Here Ω_1 is the number of states with $n(\vec{p}_1) = 1, n(\vec{p}_2) = 1, \vec{p}_1 \neq \vec{p}_2$, and Ω_2

number of states with $n(\vec{p}) = 2 \begin{cases} 0 & \text{for fermions} \\ \Omega_2 = \sum\limits_{\substack{p \\ \frac{\vec{p}^2}{2M}}} \neq 0 & \text{for bosons} \end{cases}$

$$
\Omega_1 = \frac{1}{2} \sum_{\vec{p}_1} \sum_{\substack{\vec{p}_2 \\ E = \frac{\vec{p}_1^2}{2M} + \frac{\vec{p}_2^2}{2M}}} \quad (4.27)
$$

The factor $\frac{1}{2}$ in (4.27) is needed because state in which the first particle has momentum $\vec{p}_1$ and the second $\vec{p}_2$ is the same as the one in which the first has $\vec{p}_2$ and the second $\vec{p}_1$.

$$\Omega = \frac{1}{2} \sum_{\substack{\vec{p}_1 \\ E=\frac{\vec{p}_1^2}{2M}+\frac{\vec{p}_2^2}{2M}}} \sum_{\vec{p}_2} + \left(\Omega_2 - \frac{1}{2}\right) \tag{4.28}$$

We will the term $\left(\Omega_2 - \frac{1}{2}\right)$ in (4.28), which means that there would be no distinction between fermions and bosons anymore.

$$\Omega = \frac{1}{2} \int \mathrm{d}^3\vec{p}_1 \mathrm{d}^3\vec{p}_2 \left(\frac{V}{(2\pi\hbar)^3}\right)^2 \delta\left(\frac{\vec{p}_1^2}{2M} + \frac{\vec{p}_2^2}{2M} - E\right) \delta E \tag{4.29}$$

Quantum states for N particles

$$\sum_p n(p) = N \tag{4.30}$$

$$\sum_p n(p)E(p) = E \tag{4.31}$$

$$\boxed{\Omega = \frac{1}{N!} \int \mathrm{d}^3p_1 \ldots \mathrm{d}^3p_n \left(\frac{V}{(2\pi\hbar)^3}\right) \delta\left(\sum_j^N \frac{\vec{p}_j^{\,2}}{2M} - E\right) \delta E} \tag{4.32}$$

Equation (4.32) also neglects the particular behavior where two or more momenta commute. This is the classical approximation without any distinction between fermions and bosons.

Partition function We set

$$\omega = \frac{\Omega}{\delta E} (= \frac{\partial \Omega}{\partial E}) \tag{4.33}$$

To find ω, we have to evaluate a 3N-dimensional integral. For this purpose, we will use relations (4.34) and (4.35).

$$\int_{-\infty}^{\infty} \mathrm{d}^3\vec{p}_j = 2^3 \int_0^{\infty} \mathrm{d}^3|\vec{p}_j| \tag{4.34}$$

$$|\vec{p}_{j,k}| = \sqrt{2ME}x_{j,k} \qquad\qquad \frac{\vec{p}_j^2}{2M} = \vec{x}_j^2 E \tag{4.35}$$

such that $\sum_j \vec{x}_j^2 E = E$. Then

$$\int_{-\infty}^{\infty} \mathrm{d}^3\vec{p}_1 \ldots \mathrm{d}^3\vec{p}_N = (8ME)^{3N/2} \int_0^1 \mathrm{d}^3\vec{x}_j \ldots \mathrm{d}^3\vec{x}_N \tag{4.36}$$

$$\sum_j \frac{\vec{p}_j^2}{2M} = \sum_j \vec{x}_j^2 E \tag{4.37}$$

For our purposes, we also define $y_i = (x_{1,1}, x_{1,2}, x_{1,3}, x_{2,1}, \dots)$, which consists of N variables. So, finally, we can calculate ω:

$$\omega = \frac{1}{N!}\left(\frac{V}{(2\pi\hbar)^3}\right)^N (8ME)^{3N/2} \int_0^1 \mathrm{d}y_1 \dots \mathrm{d}y_{3N}\, \delta\left(\sum_i y_i^2 E - E\right)$$

$$= \frac{1}{N!} V^N \left(\frac{2ME}{\pi^2\hbar^2}\right)^{3N/2} \frac{1}{E} F \tag{4.38}$$

The term $\frac{1}{E}$ comes from the relation $\delta(Ex) = \frac{1}{E}\delta(x)$ and

$$F = \int_0^\infty \mathrm{d}y_1 \dots \mathrm{d}y_{3N}\, \delta\left(1 - \sum_{i=1}^{3N} y_i^2\right) \tag{4.39}$$

$$F = 2^{-3N} \int_{-\infty}^{\infty} \mathrm{d}y_1 \dots \mathrm{d}y_{3N}\, \delta\left(1 - \sum_{i=1}^{3N} y_i^2\right) \tag{4.40}$$

$2^{3N}F$ is the volume of a $3N-1$-dimensional unit sphere, which is equal to the surface of a $3N$-dimensional unit ball.

$$F = \underbrace{\frac{2}{\left(\dfrac{3N}{2} - 1\right)!}}_{\Gamma\left(\frac{3N}{2}\right)} \left(\frac{\pi}{4}\right)^{\frac{3N}{2}} \tag{4.41}$$

To check if (4.41) is true, we will develop the case for $N = 1$

$$F = \frac{1}{8} 4\pi = \frac{\pi}{2} = \frac{2}{\left(\frac{1}{2}\right)!}\left(\frac{\pi}{4}\right)^{\frac{3}{2}} = \frac{4}{\sqrt{\pi}} \pi^{\frac{3}{2}} \frac{1}{8} = \frac{\pi}{2} \tag{4.42}$$

We have use $\frac{1}{2}! = \Gamma\left(\frac{3}{2}\right) = \frac{1}{2}\sqrt{\pi}$

$$\boxed{\Omega = \frac{2}{N!\left(\frac{3N}{2} - 1\right)!}\left(\frac{M}{2\pi\hbar^2}\right)^{\frac{3N}{2}} E^{\frac{3N}{2}} V^N \frac{\delta E}{E}} \tag{4.43}$$

If $\frac{\delta E}{E} = \frac{1}{3N}$ is substituted, then

$$\boxed{\Omega = \frac{2}{N!\left(\frac{3N}{2}\right)!}\left(\frac{M}{2\pi\hbar^2}\right)^{\frac{3N}{2}} E^{\frac{3N}{2}} V^N} \tag{4.44}$$

N is typically around $6 \cdot 10^{23}$, therefore, Ω increases extremely rapidly with E and V.

v) Entropy of an ideal classical gas

With the help of our favorite approximated Stirling's formula (4.45) we can find the entropy of an ideal classical gas S.

$$\ln N! = N \ln N - N \tag{4.45}$$

$$S = k_{\mathrm{B}}\,(3N)\left\{\frac{1}{2}\ln\frac{M}{2\pi\hbar^2} + \frac{1}{3}\ln V + \frac{1}{2}\ln E - \frac{1}{3}\ln N + \frac{1}{3} - \frac{1}{2}\ln\frac{3N}{2} + \frac{1}{2}\right\} \tag{4.46}$$

$$\boxed{S = k_\mathrm{B}\,(3N)\left\{\frac{1}{2}\ln\frac{V}{N} + \frac{1}{2}\ln\frac{2}{3}\frac{E}{N} + \frac{1}{2}\ln\frac{M}{2\pi\hbar^2} + \frac{5}{6}\right\}} \tag{4.47}$$

$3N = f$ is the number of degrees of freedom. We can write:

$$S = c k_\mathrm{B} f \tag{4.48}$$

and, therefore, the number of states is

$$\Omega(E) \sim E^{cf} \tag{4.49}$$

vi) Thermodynamic limit

Thermodynamic limit is where the the quantities go to infinity, $V \to \infty$, $E \to \infty$, $N \to \infty$ but $\frac{N}{V} = n$ (particle density) and $\frac{E}{V} = \epsilon$ (energy density) are constants. We make the distinction between extensive quantities (A) where

$$\lim_{V\to\infty}\frac{<A>}{V} \tag{4.50}$$

is a constant and the intensive (A) where

$$\lim_{V\to\infty} <A> \tag{4.51}$$

is a constant. Some extensive and intensive quantities are listed in table 4.1. The ratio of two extensive is intensive.

Table 4.1: Examples for extensive and intensive quantities

extensive	intensive
V	p pressure
N	n
E	ϵ
S	$s = \frac{S}{V}$ entropy density

We now have

$$S = 3k_\mathrm{B} n \cdot V \cdot c(n,\epsilon) \tag{4.52}$$

where

$$c(n,\epsilon) = \frac{1}{2}\ln\frac{2\epsilon}{3n} - \frac{1}{3}\ln n + \frac{1}{2}\ln\frac{M}{2\pi\hbar^2} + \frac{5}{6} \tag{4.53}$$

We have to check the units, because we can only take the logarithm of a dimensionless number. We let $k_\mathrm{B} = 1$ and $\hbar = 1$. So

$$s = \frac{S}{V} = 3n\left(\ln n^{-\frac{1}{3}} + \ln\left(\frac{\epsilon}{n}\right)^{\frac{1}{2}} + \ln M^{\frac{1}{2}} + \text{ constant}\right) \tag{4.54}$$

$$\boxed{s = \frac{S}{V} = 3n\left(\ln\sqrt{\frac{M\epsilon}{n^{5/3}}} + \text{ constant}\right)} \tag{4.55}$$

We see that $M \sim M^1$, $\epsilon \sim M^4$, $n \sim M^3$. The units are therefore all right. The factor $\frac{1}{N!}$ in $\Omega\,(E)$ is very important, because it turns the entropy into an intensive quantity. The factor is absent in the classical description. It was first introduced by Max Planck in 1900, for which he was fervently criticized.

vii) The limit $E \to E_0$

We now have E_0 as the quantum mechanical energy of the ground state. We also have the difference $\delta E < E_1 - E_0$ with E_1 the the lowest excited state. So if the ground state is not degenerate

$$\lim_{E \to E_0} \Omega(E) = 1 \tag{4.56}$$

a simple consequence is that

$$\boxed{\lim_{E \to E_0} S = 0} \tag{4.57}$$

If we have q-fold degeneracy then

$$\lim_{E \to E_0} S = k_{\mathrm{B}} \ln q \ll k_{\mathrm{B}} f \tag{4.58}$$

So, often, the assumption is made that is is 0 because f is very very big and $\frac{S}{f}, \frac{S}{N} \to 0$.

viii) Derivatives of entropy

Temperature We take first the derivative with respect to E at fixed particle number and volume:

$$\boxed{\frac{1}{T} = \frac{\partial S}{\partial E}_{N,V}} \tag{4.59}$$

This defines the temperature T. We can now say that the temperature is a function of E, V and N. T is a new thermodynamic variable $T = T(E, V, N)$. So we can make a variable substitution in order to transform $E(T, V, N)$ into $S(T, V, N)$. We also see that the temperature is an intensive quantity because S and E are extensive and the ratio must therefore be intensive.

Pressure Now we take the derivative with respect to V at fixed particle number and energy:

$$\boxed{\frac{p}{T} = \frac{\partial S}{\partial V}_{E,N}} \tag{4.60}$$

This defines the pressure p. We also see that the pressure is an intensive quantity.
Let us know compute this for out ideal gas of particles (note that the rest f is independent of volume):

$$\frac{\partial S}{\partial V} = k_{\mathrm{B}} \frac{\partial}{\partial V} \left(N \ln \frac{V}{N} + f(E, N) \right) = k_{\mathrm{B}} \frac{N}{V} = \frac{p}{T} \tag{4.61}$$

We get from this the ideal gas law

$$\boxed{pV = k_B N T} \tag{4.62}$$

This was actually a very easy derivation of the ideal gas law. T and p are determined by the change of the number of available states when E and V are changed.

Chemical potential Now we take the derivative with respect to N at fixed volume and energy:

$$\mu = -T \frac{\partial S}{\partial N}_{E,V} \tag{4.63}$$

This defines the chemical potential μ.

We can compute all these variables, if we have the entropy, which is the counting of states. This is the whole basically thermodynamics. We finish by making a little summary for entropy (we are looking at an micro-canonical ensemble for a system in equilibrium).

$$S = k_B \ln \Omega \tag{4.64}$$

and S is extensive. We also have seen that $\frac{S}{V} \to 0$ for $E \to E_0$. Also

$$\frac{1}{T} = \frac{\partial S}{\partial E}_{N,V} \tag{4.65}$$

This is no cheating, this is a very straightforward definition of these quantities. This is may not be intuitive, but it is a good definition. We continue with canonical ensembles.

b) Canonical ensemble

i) System in a heat bath

Canonical ensemble is a system in a heat bath intuitively speaking. Energy can be exchanged with the environment, but the particle number N remains constant. The heat bath is characterized by the temperature T. Now we will derive all properties of this system.

The system is connected to a big reservoir R with which it can exchange energy. An important thing is that the total system is isolated. We take the subsystem S and determine what is the probability distribution in this subsystem. We let the volume of the reservoir be much bigger $V_R \gg V_S$ and also the number of particles $N_R \gg N_S \gg 1$. The total system is a micro-canonical ensemble with total energy $E_G = E_S + E_R$ which is fixed. E_R and E_S are though not fixed separately. We now have an Hamiltonian which we can split (H_{int} is the Hamiltonian of the interaction).

$$?H = ?H_S + ?H_R + ?H_{\text{int}} \tag{4.66}$$

and the coupling is weak $|\langle ?H_{\text{int}}\rangle| \ll \langle ?H_S\rangle, \langle ?H_R\rangle$. Now $|\psi_n\rangle$ is the quantum state of S and $|\varphi_\nu\rangle$ is the quantum state of R. They make a complete basis, so

$$|\chi_\tau\rangle = |\psi_n\rangle |\phi_\nu\rangle \tag{4.67}$$

of $G = R + S$ where $\tau = (n, \nu)$. Now the energy is as follows

$$E_{S,n} = \langle \psi_n \,|\, H_S \,|\, \psi_n \rangle \tag{4.68}$$

$$E_{R,\nu} = \langle \varphi_\nu \,|\, H_R \,|\, \varphi_\nu \rangle \tag{4.69}$$

$$E_{G,\tau=(n,\nu)} = E_{S,n} + E_{R,\nu} = E_G \tag{4.70}$$

$$p_\tau = p_{n\nu} = \Omega_G^{-1}(E_G) \tag{4.71}$$

We now consider an observable that only “depends on S”, A_n, so

$$< A > = \sum_n \sum_\nu p_{n\nu} A_n = \sum_n p_n A_n \tag{4.72}$$

because

$$p_n = \sum_\nu p_{n\nu} \tag{4.73}$$

Our task is to compute this p_n and that is where the Boltzmann factor will come from, $p_n \sim \exp\left(\frac{E_n}{k_{\mathrm{B}}T}\right)$.

ii) Canonical partition function and Boltzmann factor

What are the p_n? It is simply

$$p_n = \sum_\nu \Omega_G^{-1}(E_G)\delta(E_{Sn} + E_{R\nu} - E_G)\delta E \tag{4.74}$$

where δ is the delta-function. So we have with the only constraint that $E_S + E_R = E_G$ that the sum is the number of states,

$$\boxed{p_n(E_S) = \frac{\Omega_R(E_R)}{\Omega_G(E_G)}} \tag{4.75}$$

What happens now if $E_S \ll E_G$? Then E_R is close to E_G and we can make a Taylor expansion of $\ln \Omega_R(E_R)$ around E_G (and note that $E_R - E_G = E_S$)

$$\ln \Omega_R(E_R) = \ln \Omega_R(E_G) + (E_R - E_G)\frac{\partial}{\partial E_G} \ln \Omega_R(E_G) + ... \tag{4.76}$$

We define now

$$\boxed{\beta = \frac{\partial}{\partial E_G} \ln \Omega_R(E)|_{E=E_G} = \frac{1}{k_B T}} \qquad \text{for } \beta \geq 0 \tag{4.77}$$

with T the temperature in the reservoir. We insert the Taylor expansion in the formula for p_n.

$$p_n(E_S) = \frac{\Omega_R(E_G)}{\Omega_G(E_G)} \exp(-\beta E_S) \tag{4.78}$$

We now introduce

$$Z_{\text{con}} = \Omega_G(E_G)/\Omega_R(E_G) \tag{4.79}$$

and get

$$\boxed{p_n(E_S) = Z_{\text{con}}^{-1} \exp(-\beta E_S)} \tag{4.80}$$

and this is the Boltzmann distribution.

In principle, we could also compute the partition function directly. We know that the sum of all p_n is 1. Therefore

$$\boxed{Z_{\text{con}} = \sum_n \mathrm{e}^{-\beta E_S}} \tag{4.81}$$

or

$$\sum_n p_n = \frac{\sum_n \mathrm{e}^{-\beta E_S}}{Z_{\text{con}}} = 1 \tag{4.82}$$

And in particular

$$Z_{\text{con}} = \sum_{E_S} \Omega(E_S)\mathrm{e}^{-\beta E} \tag{4.83}$$

$$= \int dE \omega(E) \mathrm{e}^{-\beta E_S}. \tag{4.84}$$

We see that $Z_{\text{con}} = Z_{\text{con}}(\beta, N, V)$.

iii) Connection between $< E >$ and β

Let us next compute the mean energy of our statistical ensemble. First the probability to find a given energy, $W(E)$:

$$W(E) = \Omega(E)\mathrm{e}^{-\beta E} Z_{\text{con}}^{-1} \tag{4.85}$$

$$W(E)dE = Z_{\text{con}}^{-1} w(E) \mathrm{e}^{-\beta E} dE \tag{4.86}$$

and therefore the mean energy

$$
\begin{aligned}
< E > &= \int dE W(E) E && (4.87)\\
&= \frac{\int dE w(E) E \mathrm{e}^{-\beta E}}{\int dE w(E) \mathrm{e}^{-\beta E}} && (4.88)
\end{aligned}
$$

So

$$< E >= -\frac{\partial}{\partial \beta} \ln Z_{\mathrm{con}}(\beta, N, V) \tag{4.89}$$

How is the probability distribution? We know that

$$W(E) \sim E^{c_s f_s} \, \mathrm{e}^{-\beta E} \tag{4.90}$$

where in the first exponential we have the degrees of freedom and therefore we have a very big number. This function first rises very fast and then decreases fast, so we actually have a very narrow peak.

5 Thermodynamics

a) Thermodynamical potentials

i) State variables, equations of state

The classical thermodynamics describes equilibrium states and transition from one equilibrium state to another. Without any doubt it has an imensive technological importance. It is mostly axiomatic, based on the law of thermodynamics and their consequences. Classical thermodynamics uses only a few macroscopical variables (both extensive and intensive) such as E, T, S, N, μ, V, P.

The thermodynamical limit gives a functional relationship between the state variables. Usually, no average values are used, because $\langle E\rangle \equiv E$, etc.

There are several practical question, which we will try to answer in this chapter:

- How much energy should be deposited in a system, so that its temperature rises by a certain amount, provided the volume stays constant?
- How much will the pressure increase during this process?
- How is heat transformed into mechanical energy? What is the efficiency factor of machines?
- When is a process reversable and when not?

Table 5.1: Different kinds of systems and their corresponding state and depedent variables

	State variables	Depedent variables
micro-cannonical ensemble; isolated system	$\ln Z_{\text{mic}}(E, N, V)$	S, T, μ, P
cannonical ensemble; closed system	$\ln Z_{\text{can}}(T, N, V)$	S, E, μ, P
grand cannonical ensemble; open system	$\ln Z_{\text{gc}}(T, \mu, V)$	S, E, N, P

The depedence of the depedent variables on the state variables is called equation of state.

Examples:

1. Equation of state fore an ideal gas
$$pV = n_M RT = k_{\text{B}} TN \tag{5.1}$$
Here, n_M is the number of moles and R is the gas constant, $R = 8.31\,{}^{\text{J}}/_{\text{mol}\cdot\text{K}}$
2. Van der Waals equation of state for a real gas
$$\left(p + \frac{n_M^2}{V^2} a\right)(V - n_M b) = n_M RT \tag{5.2}$$
with a and b specific constants of the gas. This equation could also be written in a more compact form:
$$\left(p + ?an^2\right) = \frac{nT}{1 - ?bn} \tag{5.3}$$

The goal of the statistical physics is to explain the equations of state and to derive them in their fundamental form. On the other hand, classical thermodynamics examines the consequesence of the existence of the equations of state. There are seven variables and only 4 equations, which automatically makes three of the variables indepedent (state), but, commonly, there are aslo other thermodynamical conditions. As already mentioned, variables split into two types: extensive (E, N, V, S) and intensive (T, μ, p). However, the choice of the state variables cannot be arbitrary - one of them should always be extensive.

Example: Grand cannonical ensemble with state variables T, μ, V.

$$\begin{aligned} S &= V f_S(T,\mu) && (5.4)\\ E &= V f_E(T,\mu) && (5.5)\\ N &= V f_N(T,\mu) && (5.6)\\ p &= f_p(T,\mu) && (5.7) \end{aligned}$$

Therefore, (p, T, μ) cannot be three indepedent variables at the same time.

ii) Thermodynamical potentials and partition function

$$S = S(E,N,V) = k_{\mathrm{B}} \ln Z_{\mathrm{mic}}(E,N,V) \qquad \text{entropy} \qquad (5.8)$$

$$F = F(T,N,V) = k_{\mathrm{B}} \ln Z_{\mathrm{can}}(T,N,V) \qquad \text{free energy} \qquad (5.9)$$

$$J = J(T,\mu,V) = k_{\mathrm{B}} \ln Z_{\mathrm{gc}}(T,\mu,V) \qquad \text{Gibbs potential} \qquad (5.10)$$

$$\begin{aligned} \left(\frac{\partial S}{\partial E}\right)_{N,V} &= \frac{1}{T} && (5.11)\\ \left(\frac{\partial S}{\partial N}\right)_{E,V} &= -\frac{\mu}{T} && (5.12)\\ \left(\frac{\partial S}{\partial V}\right)_{E,N} &= \frac{p}{T} && (5.13) \end{aligned}$$

Repetition from chapter 3:

$$\begin{aligned} S &= k_{\mathrm{B}} \ln Z_{\mathrm{mic}} = k_{\mathrm{B}} \ln \Omega && (5.14)\\ \frac{1}{T} &= \frac{\partial S}{\partial E}_{N,V} && (5.15)\\ -\frac{\mu}{T} &= \frac{\partial S}{\partial N}_{E,V} && (5.16) \end{aligned}$$

$$\begin{aligned} Z_{\mathrm{mic}} &= \sum_\tau ?\delta\left(E_\tau - E\right) ?\delta\left(N_\tau - N\right) && (5.17)\\ Z_{\mathrm{can}} &= \sum_\tau \exp\left(-\beta E_\tau\right) ?\delta\left(N_\tau - N\right) && (5.18)\\ Z_{\mathrm{gc}} &= \sum_\tau \exp\left\{-\beta\left(E_\tau - \mu N_\tau\right)\right\} && (5.19) \end{aligned}$$

Here, $\sum_\tau$ means a sum over all micro-states with arbitrary E_τ, N_τ.

$$E = -\frac{\partial}{\partial\beta}\ln Z_{\text{can}} \tag{5.20}$$

$$E-\mu N = -\frac{\partial}{\partial\beta}\ln Z_{\text{gc}} \tag{5.21}$$

$$N = \frac{1}{\beta}\frac{\partial}{\partial\mu}\ln Z_{\text{gc}} \tag{5.22}$$

Example: Photons

Photons have chemical potential of zero ($\mu = 0$), therefore, they have one variable less.

$$Z_{\text{can}} = \sum_\tau \exp\left(-\beta E_\tau\right) = Z_{\text{gc}} \tag{5.23}$$

The free energy for photons is:

$$F = k_{\text{B}}T\frac{\pi^2}{45}V\left(\hbar c\beta\right)^{-3} \tag{5.24}$$

from which one can derive the free energy per volume

$$\boxed{\frac{F}{V} = -\frac{\pi^2}{45}\left(\hbar c\right)^{-3}\beta^{-4} \overset{\hbar=c=k_{\text{B}}=1}{=} -\frac{\pi^2}{45}T^4} \tag{5.25}$$

iii) Entropy in canonical ensemble

The entropy is defined as

$$S = k_{\text{B}}\ln\Omega\left(\overline{E}\right) \tag{5.26}$$

In thermodynamical limit $\overline{E} = E$. It is important to note that the thermodynamic relations are invariant of the choice of the ensemble.

Relation between E, F, T, S

$$Z_{\text{can}} = \sum_\tau \mathrm{e}^{-\beta E_\tau} = \sum_E \Omega\left(E\right)\mathrm{e}^{-\beta E} \tag{5.27}$$

Since the function from (5.27) has a very narrow peak, it is more convenient to make an approximation

$$Z_{\text{can}} = \Omega\left(\overline{E}\right)\mathrm{e}^{-\beta\overline{E}} \tag{5.28}$$

$$\boxed{\ln Z_{\text{can}}\left(\beta\right) = \ln\Omega\left(\overline{E}\right) - \beta\overline{E}} \tag{5.29}$$

From (5.9) and (5.29) follows

$$F = -k_{\text{B}}T\ln Z_{\text{can}} = -k_{\text{B}}T\ln\Omega\left(\overline{E}\right) + \overline{E} = -TS + E \tag{5.30}$$

$$\boxed{F = E - TS} \tag{5.31}$$

Relation between S and Z_{can}

$$E=-\frac{\partial}{\partial\beta}\ln Z_{\mathrm{can}} \tag{5.32}$$

From (5.31) and (5.9) one can derive

$$S=\frac{E-F}{T}=k_{\mathrm{B}}\beta\left(-\frac{\partial}{\partial\beta}\ln Z_{\mathrm{can}}\right)+k_{\mathrm{B}}\ln Z_{\mathrm{can}} \tag{5.33}$$

$$\boxed{S=k_{\mathrm{B}}\left(1-\beta\frac{\partial}{\partial\beta}\right)\ln Z_{\mathrm{can}}} \qquad \text{for fixed } N,V \tag{5.34}$$

iv) Properties of the entropy

Energy distribution for subsystems Let R_1 and R_2 be two subsystems of a total system G with respective energies E_1 and E_2. Of course, the condition

$$E_1+E_2=E_G \tag{5.35}$$

should always be fullfilled. We would like to know what is the most probable value of E_1? Its probability distribution could be expressed as the ratio

$$w\left(E_1\right)=\frac{\Omega_1\left(E_1\right)\Omega_2\left(E_G-E_1\right)}{\Omega_G\left(E_G\right)} \tag{5.36}$$

So, the maximum of $w\left(E_1\right)$ coincides with the maximum of $\Omega_1\left(E_1\right)\Omega_2\left(E_G-E_1\right)$. But, we could also take the logarithm of tha last expression without changing the position of the maximum.

$$\max\left\{\ln\left[\Omega_1\left(E_1\right)\Omega_2\left(E_G-E_1\right)\right]\right\}=\max\left\{\ln\Omega_1\left(E_1\right)+\ln\Omega_2\left(E_G-E_1\right)\right\} \tag{5.37}$$

This is equivalent with maximising S_1+S_2 with the condition $E_1+E_2=E_G$. Now we can formulate the maximum principle for entropy.

In a equilibrium the entropy is maximised, but according to the constraints to the system.

The energies $E_1$and E_2 can be computed from the maximum of S_1+S_2 and (5.35).

Now, consider two isolated systems in equilibrium with arbitrary energies $E_1^{(0)}$ and $E_2^{(0)}$. Their entropies are $S_1^{(0)}$ and $S_2^{(0)}$. The total energy of the system is given by $E_G=E_1^{(0)}+E_2^{(0)}$. When the two systems are brought to contact, energy flows $E_1^{(0)}\to E_1, E_2^{(0)}\to E_2$ until S_1+S_2 is maximazed for given E_G. As a consequence,

$$\boxed{S_1+S_2\geq S_1^{(0)}+S_2^{(0)}} \tag{5.38}$$

Entropy can only increase.

The last statement is a key indregient of the second law of thermodynamics.

Additivity of entropy Assume that R_1 and R_2 are two isolated system, i. e. microcanonical ensembles. The number of states is:

$$\Omega_G\left(E_1+E_2\right) = \Omega_1\left(E_1\right)\cdot\Omega_2\left(E_2\right) \tag{5.39}$$

$$\Rightarrow S_G = S_1+S_2 \tag{5.40}$$

Relation 5.40 is true with accuracy $\frac{1}{\sqrt{N}}$. It is exactly true in the thermodynamical limes, where

$$w\left(E_1\right)=\frac{\Omega_1\left(E_1\right)\Omega_2\left(E_2\right)}{\Omega_G\left(E_G\right)}\approx 1 \tag{5.41}$$

b) Reversible and irreversible processes

i) / and constrains

We consider a isolated system in equilibrium with energy E (respectively $[E, E + \delta E]$.

Micro states:

Ω: number of states with energy E, which the system can occupy

$S = k \cdot ln\Omega$ $(\Omega = Z_{mic})$.

Generally the system is set by the constrains. They correspond to particular parameter. $\Omega = \Omega(E, y_1...y_k)$, respectively intervals

$[y_1, y_1 + \delta y_1], ...[y_k, y_k + \delta y_k]$.

Example 1 : fixed volume V_1

V_1: volume of the gas

Example 2: fixed energy of the particles E_1

E_1: energy of gas 1

V_1: volume of gas 1

N_1: number of particles of gas 1

One can consider this picture as two isolated systems, and can look at subsystems

$$\Omega_g(E, E_1, V, V_1, N, N_1) = \Omega(E_1, V_1, N_1)\Omega(E - E_1, V - V_1, N - N_1)$$

ii) Getting rid of the constraints

After long time the system gets in a new equilibrium $\Omega_i \to \Omega_p$. In this case it is always true that $\Omega_p \geq \Omega_i$. All the states compatible with the constrain conditions are still possible. But there appear new possible states with fixed energy E, which are otherwise banned from the constrains.

Getting rid of the constrains in an isolated system:

the entropy of the last state is larger or equal to the entropy of the first state $S_p \geq S_i$. Here the first and the last states are equilibrium states, it is not important what happens in between.

Example 1:

Getting rid of the barrier

$$\begin{aligned} \Omega_i &\sim V_1^N \\ \Omega_p &\sim V^N \\ \Omega_p &\gg \Omega_i \text{ for } V > V_1 \end{aligned}$$

Example 2:

The barrier is thermally made conductive; subsystem canonical ensemble.

$$\Omega_i = \Omega_{i1}\Omega_{i2}$$

$$\Omega_{1i} \approx \frac{1}{N_1!(\frac{2N_1}{3} - 1)!}(\frac{m}{2\pi\hbar^2})^{\frac{3N1}{2}} V_1^{N_1} E_1^{\frac{3N_1}{2}} \frac{\delta E_1}{E_1} \text{ diluted gas at high energy}$$

$$\Omega_p \approx \frac{1}{N_1!(\frac{2N_1}{3} - 1)!}(\frac{m}{2\pi\hbar^2})^{\frac{3N1}{2}} V_1^{N_1} E_1^{\frac{3N_1}{2}} \frac{\delta \overline{E}_1}{\overline{E}_1}$$

$$\begin{aligned}\Omega_i &\sim W(E_1)\\ \Omega_p &\sim W(\overline{E}_1)\end{aligned}$$

$$\Omega_p \gg \Omega_i \text{ for } E_1 \neq E_{1max} = \overline{E}_1$$

$$\Omega_p \approx \Omega_i \text{ for } T_1 = T_2$$

iii) Increase of entropy by removing of constrains.

The probability that without constraints the system, after sufficiently long time, goes back in the initial states:

$$W_i = \frac{\Omega_i}{\Omega_p}$$

$\frac{1}{\Omega_p}$ is the probability that the system is in one particular macro-state (system without constrains).
Ω_i are the number of micro-states sufficing the initial conditions.

$$W_i \ll 1 \text{ if } \Omega_i \ll \Omega_p$$

Example 1:

$$V = 2V_1$$

$$W_i = (\frac{1}{2})^N \text{ (factor } \frac{1}{2} \text{for each molecule)}$$

Example 2:

$$W_i = W(E_1)\delta E \text{ for an intervall } [E_1 - \frac{1}{2}\delta E; E_1 + \frac{1}{2}\delta E]$$

$$\frac{\delta E}{E} \geq \frac{1}{\sqrt{N}}$$

$\Rightarrow W(E_{max})\delta E = W(E)\delta E \approx 1$
$W(E_1)$ is exponentially inhibited for $E_1 \neq \overline{E}$.

Removing of constrains

Before: fixed initial value y_i.
After: Probability distribution $W(y)\delta y \sim \Omega(y)$.
Generally $\overline{y} \neq y_i$, $\overline{y}$is the maximum of $W(y)$, $\frac{\partial W}{\partial y}(\overline{y}) = 0$.
Generalization on multiple variables $y_1...y_k$:

$$N \to \infty$$

Sharp value $y_f = \overline{y} = y_{max}$, (generally $y_l \neq y_i$). y_f is defined by the maximal entropy ($\Omega(y_{max})$).

$$\boxed{S(y_f)\text{maximal}}$$

When there are no constrains the parameters get such that the entropy becomes maximal (at given limiting conditions as V, N, E of the system).

Example:

y : the energy in a partial volume of the system
$S(E,N,V;y)$: calculated with given constrains
$\frac{\partial S}{\partial y}|_{E,N,V} = 0 \Rightarrow y$

$$\boxed{\text{When getting near to the equilibrium state, the entropy of a system grows.}}$$

Consequences from the postulates:

Initial conditions are very improbable for large N_λ, if the corresponding probability distributions aren't uniform distributions over all micro-states.

$$\begin{aligned} W_i &= \frac{\Omega_i}{\Omega_p} \ll 1 \\ S_i &< S_p \end{aligned}$$

From the equilibrium-state point of view:
states similar to the equilibrium $\triangleq$transition from improbable to probable state.

iv) The second law of thermodynamics (introducing constrains).

How can the initial conditions be restored?
i) in an isolated system
The restoration of the barriers in general doesn't restore the initial conditions.
New parameter $\overline{y}$ instead of y_i. (Examples 1,2). We remove more constrains, at most the entropy rises.

$$\boxed{\text{An isolated system cannot spontanously go from a probable in an unprobable state!}}$$

Precisions:

- "will not switch" - it is extremely improbable that this transition happens.
- "states" - here macro-states described by a probability distribution p_f ; equilibrium state described by micro-canonical ensemble, $p_f = \frac{1}{\Omega}$.

Another states: no uniform distribution of the micro-states ($p_f \neq \frac{1}{\Omega}$).

Second law of thermodynamics

$$\boxed{\text{The entropy of a closed system cannot decrease!}}$$

Historical formulations:

$$\boxed{\text{Heat cannot flow from a body with lower to one with higher temperature!}}$$

Clausius

$$\boxed{\text{It is impossible to produce work continuously by lowering the temperature of a system, without other changes i}}$$

$$Kelvin$$

$\Longleftrightarrow$ impossibility of perpetuum mobile.

0. Law

$$T,\ T_1, = T_2$$

1. Law

$$E,\ \text{conservation of } E$$

2. Law

$$S,\ S\text{cannot decrease}$$

3. Law

$$S_{min} = 0$$

v) Reversible processes

$$\boxed{\text{A process (i)}\rightarrow\text{(f) in a closed system is reversible, if (f)}\rightarrow\text{(i) is also possible.}}$$

in other cases the process is called irreversible.

In a closed system:

increase of entropy ⇔ irreversible process

A reversible process is one occupying the hole system , for example adiabatic (the entropy stays constant).

vi) Reversible processes for open systems

Definition :

It must be possible, that an inverse of this process can be made, so that the system gets back in the initial state, without changing the environment. Carnot-process is an example of a reversible process.

The temperature difference between the reservoirs is lowered and work is done. Inverse process - fridge - work is done in order to make the temperature difference between the reservoirs larger.

Irreversible processes:

dissipative processes

Typically energy is being divided between many degrees of freedom, example: mechanical energy transformed in heat (pendulum in air).

Examples: mechanical friction, eddy currents, viscose friction, balance of the temperature of two heat reservoirs.

vii) Thermodynamics and non-equilibrium states

The course of an irreversible process cannot be described by thermodynamical potentials.

Part II

Statistical systems

6 Ideal quantum gas

An ideal gas is such that the interaction between its point-like particles is negligible. An ideal gas can consist of molecules, photons, electrons, excited states in solids (quasiparticles). It is usually a good approximation for low pressure or other conditions.

a) Occupation number basis

One particle Let the Hamiltonian be H_1. Then for one particle

$$H_1 \psi_\nu = E_\nu \psi_\nu \qquad \psi_\nu = \psi_\nu (Q) \tag{6.1}$$

Example: A particle in a box ($L_x = L_y = L_z = L$)

$$H = -\frac{\hbar^2}{2m} \left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right) \tag{6.2}$$

$$\nu = (m_x, m_y, m_z) \qquad \text{with } m_{x,y,z} \in \mathbb{N} \tag{6.3}$$

Therefore, the energy levels are

$$E_\nu = \frac{\pi^2 \hbar^2}{2mL^2} \left(m_x^2 + m_y^2 + m_z^2 \right) \tag{6.4}$$

The wave function $\psi_\nu (Q)$ can be expressed in position coordinates $Q = (x, y, z)$ or impulse $Q = (k_x, k_y, k_z)$.

N identical particles The Hamiltonian is just

$$H = \sum_{i=1}^{N} H_i \tag{6.5}$$

$$\psi_{\{\nu_i\}}^{(N)} (Q) = P \left[\psi_{\nu_1} (Q_1) \psi_{\nu_2} (Q_2) \ldots \psi_{\nu_N} (Q_N) \right] = \psi_\alpha (Q_1 \ldots Q_N) \tag{6.6}$$

i) Bosons

P is completely symmetric in Q_i

$$P \equiv \frac{1}{N!} \sum_{\text{Perm}\{Q_i\}} \tag{6.7}$$

$$\begin{aligned} \Rightarrow \psi_\alpha (Q_1 \ldots Q_i \ldots Q_k \ldots Q_N) &= \psi_\alpha (Q_1 \ldots Q_k \ldots Q_i \ldots Q_N) & (6.8) \\ \Rightarrow \psi_{\nu_1 \ldots \nu_i \ldots \nu_k \ldots \nu_N} (Q) &= \psi_{\nu_1 \ldots \nu_k \ldots \nu_i \ldots \nu_N} (Q) & (6.9) \end{aligned}$$

Exchange of two identical particles does not change the wave function, e.g. $\mathrm{e}^{\imath \vec{k}_1 \vec{x}} \mathrm{e}^{\imath \vec{k}_2 \vec{y}} + \mathrm{e}^{\imath \vec{k}_1 \vec{y}} \mathrm{e}^{\imath \vec{k}_2 \vec{x}}$. In quantum mechanics they also have to be indistinguishable.

$$\alpha : (\nu_1, \nu_2, \ldots, \nu_N) \tag{6.10}$$

It is not important which particle is in state ν, but how many are in state ν.

Occupation number basis $\psi_{n'}$

$$\tau \equiv \{n_1, n_2, \dots, n_k \dots\} = \{n_\nu\} \qquad n_\nu \in \mathbb{N} \qquad \begin{array}{ll} n_1 & \#\text{ Particles in } \nu = 1 \\ n_k & \#\text{ Particles in } \nu = k \end{array} \tag{6.11}$$

There can be infinitely many particles in every state ν.

$$N = \sum n_\nu \tag{6.12}$$

$\psi_{\{\nu_i\}} \equiv \psi_\alpha$ and $\psi_{\{n_\nu\}} \equiv \psi_\tau$ are different choices of bosons, which directly correspond to each other.

Example: One dimensional harmonic Oscillator

$N=1$	ψ_1	$n_1 = 1$	$\psi_{10000...}$	E_1
	ψ_2	$n_2 = 1$	$\psi_{01000...}$	E_2
$N=2$	$\psi_{13} \equiv \psi_{31}$	$n_1 = 1, n_3 = 1$	$\psi_{10100...}$	$E_1 + E_3$
	ψ_{22}	$n_2 = 2$	$\psi_{02000...}$	$2E_2$
$N=5$	ψ_{13345}		$\psi_{10211...}$	$E_1 + 2E_3 + E_4 + E_5$
$N=0$			$\psi_{00000...}$	$E = 0$

$\psi_{\{\nu_i\}}$ is the basis in Hilbert space with fixed number of particles N: $\mathscr{H}_N$. $\psi_{\{n_\nu\}}$ is the basis the Fock space.

$$\mathscr{F} = \mathscr{H}_0 \oplus \mathscr{H}_1 \oplus \mathscr{H}_2 \oplus \dots \mathscr{H}_N \oplus \dots \mathscr{H} \tag{6.13}$$

It describes states without fixed number of particles. $\mathscr{F}$ is the discrete sum over all Hilbert spaces $\mathscr{H}_N$. Therefore, $\psi_{\{n_\nu\}}$ is very suitable for systems with arbitrary number of particles, because then there is no limit for $n_\nu : n_\nu \in \mathbb{N}$. This is fulfilled for the grand canonical ensemble (otherwise $\sum n_\nu = N$).

$$H\psi_{\{n_v\}} = \sum_\nu E_\nu n_\nu \psi_{\{n_\nu\}} \tag{6.14}$$

$$\boxed{E = \sum_\nu E_\nu n_\nu} \tag{6.15}$$

It should be noted that occupation number basis for systems with particle interaction also exists.

ii) Fermions

P is completely antisymmetric in Q_i for fermions.

$$\Rightarrow \psi_{\{\nu_i\}}\left(Q_1 \dots Q_i \dots Q_k \dots Q_N\right) = -\psi_{\{\nu_i\}}\left(Q_1 \dots Q_k \dots Q_i \dots Q_N\right) \tag{6.16}$$

For $N = 2$

$$\psi_{34}\left(Q_1, Q_2\right) \sim \left(\psi_3\left(Q_1\right)\psi_4\left(Q_2\right) - \psi_3\left(Q_2\right)\psi_4\left(Q_1\right)\right) \sim \psi_{43}\left(Q_1, Q_2\right) \tag{6.17}$$

$$\Rightarrow \psi_{33}\left(Q_1, Q_2\right) \equiv 0 \Rightarrow \nu_1 \neq \nu_2 \tag{6.18}$$

This is a consequence from Pauli's Principle.

For an arbitrary N:

$$\psi_{\nu_1 \dots \nu_i \dots \nu_k \dots \nu_N} = -\psi_{\nu_1 \dots \nu_k \dots \nu_i \dots \nu_N} \tag{6.19}$$

$$\nu_i = \nu_k \Rightarrow \psi = 0 \tag{6.20}$$

Two fermions cannot be in the same state simultaneously. Therefore, n_ν in $\psi_{\{n_\nu\}}$ could be either 0 or 1.

$$N = \sum_\nu n_\nu \tag{6.21}$$

$$E = \sum_\nu E_\nu n_\nu \tag{6.22}$$

b) Partition function for grand canonical ensemble

$$Z_{\text{gc}} = \sum_n \exp(-\beta \left\{ \sum_\nu E_\nu n_\nu - \mu \sum_\nu n_\nu \right\} \tag{6.23}$$

where

$$\sum_\nu E_\nu n_\nu = E \tag{6.24}$$

,and

$$\sum_\nu = N \tag{6.25}$$

$$Z_{\text{gc}} = \sum_E \sum_N \Omega(E, N, V) \exp(-\beta(E - \mu N) \tag{6.26}$$

-we compete Ω indirectly by computing Z_{gc}

$$Z_{\text{gc}} = \sum_{\{n_\nu\}} \exp\{-\beta n_\nu(E_\nu - \mu\} = \sum_{\{n_1\}} \prod_\nu \exp\{-\beta n_\nu(E_\nu - \mu\} \doteq \prod_\nu (\sum_{n_\nu} \exp\{-\beta n_\nu(E_\nu - \mu)\} \tag{6.27}$$

Every term in this sum .....

$$\ln Z_{\text{gc}} = \sum_\nu \ln \sum_{n_\nu} \exp\{-\beta n_\nu(E_\nu - \mu)\} \tag{6.28}$$

! for every ν :

$$\sum_{n_\nu} = \begin{cases} \sum_{n_\nu=1}^{\infty} & bosons \\ \sum_{n_\nu=0}^{\infty} & fermions \end{cases} \tag{6.29}$$

One particle state ν
(p_1, p_2, p_3), $\overrightarrow{p}$, (m_1, m_2, m_3)
$E_\nu = E(\overrightarrow{p})$
sequence of occupation states $\{n_\nu\}$ — $\{n(\overrightarrow{p})\}$, $\overrightarrow{p} \to n(\overrightarrow{p})$, for each $\overrightarrow{p}$ indicate $n(\overrightarrow{p})$; given sequence $\triangleq$given function $n(\overrightarrow{p})$
fermions

$$n_\nu = 0, 1 \tag{6.30}$$

bosons

$$n_\nu = 0, 1, 2...\infty \tag{6.31}$$

$$\tau \triangleq \{n_\nu\} \tag{6.32}$$

$$\sum_{\tau} \triangleq \sum_{\{n_\nu\}} = \sum_{n_1}\sum_{n_2}...\sum_{n_k}... = \prod_{\nu}(\sum_{n_\nu}) \tag{6.33}$$

bosons

$$\sum_{\{n_\nu\}} = \prod_{\nu}(\sum_{n_\nu=0}^{\infty}) \tag{6.34}$$

fermions

$$\sum_{\{n_\nu\}} = \prod_{\nu}(\sum_{n_\nu=0}^{1}) \tag{6.35}$$

$\sum_{n_\nu} \triangleq$sum over all possible functions $n(\overrightarrow{p})$(functional integral !)
Free fermions

$$\ln Z_{\text{gc}}^{(B)} = \sum_{\nu} \ln[1 + \exp\{-\beta(E_\nu - \mu)\}] \tag{6.36}$$

Bosons

$$\ln Z_{\text{gc}}^{(B)} = \sum_{\nu} \ln[\sum_{j=0}^{\infty}(\exp\{-\beta(E_\nu - \mu)\}^j] \tag{6.37}$$

$j = n_\nu$

$$1 + x + x^2 + x^3 + ... = \frac{1}{1-x} \tag{6.38}$$

$$\ln Z_{\text{gc}}^{(B)} = \sum_{\nu} \ln \frac{1}{1 - \exp\{-\beta(E_\nu - \mu)\}} \tag{6.39}$$

All that has to be done now is a sum over all one-particle-states!

c) Occupation Numbers

i) Mean occupation number for bosons.

$$\overline{N} = \frac{1}{\beta}\frac{\partial}{\partial\mu} \ln Z_{\text{gc}} = \sum_{\tau} \frac{N_\tau \exp(-\beta(E_\tau - \mu N_\tau)}{Z_{\text{gc}}} = \sum_{\tau} N_\tau p_\tau \tag{6.40}$$

Bosons

$$\begin{aligned}
\overline{N} &= \sum_{\nu}\{-\frac{1}{\beta}\frac{\partial}{\partial\mu}\ln\{1 - \exp[-\beta(E_\nu - \mu)]\}\} && (6.41)\\
&= \sum_{\nu} \frac{1}{\beta}\frac{\frac{\partial}{\partial\mu}\exp[-\beta(E_\nu - \mu)]}{1 - \exp[-\beta(E_\nu - \mu)]} && (6.42)\\
&= \sum_{\nu} \frac{\exp[-\beta(E_\nu - \mu)]}{1 - \exp[-\beta(E_\nu - \mu)]} && (6.43)\\
&= \sum_{\nu} \overline{n}_\nu && (6.44)
\end{aligned}$$

$\overline{n}_\nu$: mean occupation number for state ν

$$\overline{n}_\nu^{(B)} = \frac{1}{\exp[\beta(E_\nu - \mu) - 1} \tag{6.45}$$

This is the Bose-Einstein-statistics.
Proof :

$$Z(\beta;\mu_1...\mu_\nu)=\sum_{n_1}...\sum_{n_\nu}\exp[-\beta\sum_\nu(E_\nu n_\nu-\mu_\nu n_\nu)] \tag{6.46}$$

$$\overline{n}_\nu=\frac{1}{\beta}\frac{\partial}{\partial\mu}\ln Z_{|\mu_\nu=\mu} \tag{6.47}$$

Bosons

$$\ln Z(\beta;\mu_\nu)=\sum_\nu\ln\frac{1}{1-\exp[-\beta(E_\nu-\mu)]} \tag{6.48}$$

ii) Fermions

$$\overline{N}=\sum_\nu\overline{n}_\nu \tag{6.49}$$

$$\overline{n}_\nu=\frac{\exp[-\beta(E_\nu-\mu)}{1+\exp[-\beta(E_\nu-\mu)]} \tag{6.50}$$

Fermi-Dirac-Statistics

$$\overline{n}_\nu^{(F)}=\frac{1}{\exp[\beta(E_\nu-\mu)]+1} \tag{6.51}$$

$$0\leq\overline{n}_\nu^{(F)}\leq 1 \tag{6.52}$$

$$\overline{n}_\nu^{(F)}\to 0 \text{ for } E_\nu-\mu\gg kT \tag{6.53}$$

$$\overline{n}_\nu^{(F)}\to \text{ for } E_\nu-\mu<0 \text{ and } kT\ll|E_\nu-\mu| \tag{6.54}$$

iii) Mean Energy

$$\overline{E}=\left(-\frac{\partial}{\partial\mu}+\frac{\mu}{\beta}\frac{\partial}{\partial\mu}\right)\ln Z_{\text{gc}}=-\frac{\partial}{\delta\beta}\ln Z_{\text{gc}}+\mu\overline{N} \tag{6.55}$$

Bosons

$$\overline{E}=\sum_\nu\frac{(E_\nu-\mu)\exp[-\beta(E_\nu-\mu)}{1-\exp[-\beta(E_\nu-\mu)}+\mu\overline{N}=\sum_\nu(E_\nu-\mu)\overline{n}_\nu^{(B)}+\mu\sum_\nu\overline{n}_\nu^{(B)} \tag{6.56}$$

$$\overline{E}=\sum_\nu E_\nu\overline{n}_\nu \tag{6.57}$$

The same is true for fermions!
The formula for other macroscopical values look the same.
$\overline{n}_\nu$:... macroscopical value

iv) Chemical Potential

Which value should be chosen for μ?

iv).1 Conserved number of particles.

Example:
N_e : electrical charge and lepton number
N_i : for the number of molecules of the same sort, if one can neglect the chemical transitions
N_B: number of baryons

$$\overline{N} = \frac{1}{\beta}\frac{\partial}{\partial\mu}\ln Z_{\text{gc}}(\beta,\mu) = \overline{N}(\beta,\mu) \tag{6.58}$$

$$\Rightarrow \mu(\overline{N},T) \quad \text{termodynamical marginal case} \tag{6.59}$$

Grand canonical and canonical ens amble equivalent

$$\mu = \mu(N,T) \tag{6.60}$$

Multiple conserved quantum numbers N_i, multiple variables μ_i

iv).2 No conserved number of particles

Example: photons, pions.
The canonical ensemble does not depend on N. $\mu \equiv 0$. No limitation of the number of sumands $\sum_{\{n_\nu\}}$, because$N$ is not a conserved quantum number. The middle occupation numbers characterize the canonical ensemble.

iv).3 Approximately conserved quantum numbers

$$\mu \neq 0$$

When we also consider time scales smaller than the time for decay.

v) Boltzmann statistics

Energies large in comparison with kT.

$$E_\nu - \mu \gg kT$$

$$n_\nu \approx \exp\{-\beta(E_\nu - \mu)\}$$

for fermions and bosons
Maxwell-Boltzmann statistics for classical particles

$$n_\nu = c \cdot \exp(-\frac{E_\nu - \mu}{kT}) = ?c \cdot \exp(-\frac{E\nu}{kT}) \tag{6.61}$$

$$\exp(-\frac{E\nu}{kT}) \quad \text{is the} \quad \text{Boltzmann factor} \tag{6.62}$$

$E_\nu$is the energy of the one-particle-state ν.
Recall earlier lecture: $\Omega(E,N)$ with approximation that Ω is dominated by microstates ν is occupied at most once

$$\triangleq \overline{n_\nu} \ll 1$$

Check:

$$\ln Z_{\mathrm{gc}} = \sum_{\nu} \exp\{-\beta(E_\nu - \mu\} \tag{6.63}$$

$$\Rightarrow \quad J(T,\mu) \tag{6.64}$$

use thermodynamics for $S(E,N) \to \Omega(E,N)$.

d) Photon gas

We will examine the electromagnetical radiation in equilibrium. The temperature T is defined as the temperature of the walls of the cube. This example prooved to be decisive in the development of modern Physics. The classical field theory could not give a correct answer, because there was a huge deviation in the observed frequency distibution of the radiation.

i) Black body radiation

Consider photons in equilibrium at temperature T. The mean occupation number is

$$\overline{n}_0 = \frac{1}{\exp(\beta E_\nu) - 1} \tag{6.65}$$

We need one photon state ν and their energy E_ν. From Maxwell equations follows

$$\frac{1}{c^2}\frac{\partial^2 \vec{E}}{\partial t^2} = \nabla^2 \vec{E} \tag{6.66}$$

We can set $\vec{E} = \vec{E}(r)\exp(-\imath wt)$

$$\nabla^2 \vec{E}(r) + \frac{\omega^2}{c^2}\vec{E} = 0 \tag{6.67}$$

$\vec{E}(r)$ can be expressed as

$$\vec{E}(r) = \vec{A}\exp \imath\vec{k}\vec{r} \tag{6.68}$$

The exact boundary conditions are not important, but we can take a cube with length L and assume periodical boundary conditions:

$$\vec{k} = \frac{2\pi}{L}\vec{n} \quad n_{x,y,z} \in \mathbb{Z} \tag{6.69}$$

$$\vec{k}^2 = \frac{\omega^2}{c^2} \quad \omega = c\left|\vec{k}\right| \quad c = 1 \tag{6.70}$$

$$\vec{\nabla}\vec{E}(r) = 0 \Rightarrow \vec{k}\vec{A} = 0 \tag{6.71}$$

The electromagnetic wave is transversal, so there are 2 degrees of freedom for every $\vec{k}$. Photons are massless particles with spin 1 and helicity $H = \pm 1$.

Quantifying

$$E = \hbar\omega \quad \vec{p} = \hbar\vec{k} \tag{6.72}$$

$$E_\nu = \hbar c\left|\vec{k}\right| = 2\pi\hbar c\,|\vec{n}| \quad \nu = (n_x, n_y, n_z, H) \tag{6.73}$$

$$E_\nu = \frac{2\pi\hbar c}{L}\,|\vec{n}| \quad V = L^3 \tag{6.74}$$

We split ν in two

$$\nu = (\nu_T, \nu_I) \tag{6.75}$$

$$\begin{aligned} \nu_T &\equiv (n_x, n_y, n_z) && \text{translational degrees of freedom} \\ \nu_I &\equiv H && \text{inner degree of freedom} \end{aligned} \tag{6.76}$$

Density of the translational states The translational state lay very densely for a very large volume ($E_\nu \sim \frac{1}{L}$). Therefore, we can exchange the sum with an integral

$$\sum_{\nu_T} \rightarrow V \int \frac{\mathrm{d}^3 p}{(2\pi\hbar)^3} \tag{6.77}$$

ii) Spectrum of black body radiation

We want to compute the mean number of photons per volume in a momentum interval $\left[\vec{k}, \vec{k} + \mathrm{d}\vec{k}\right], \vec{p} = \hbar\vec{k}$

$$\frac{1}{V} \underbrace{2}_{H=\pm 1} \overline{n}(k) \frac{V}{(2\pi\hbar)^3} \mathrm{d}^3 p = \frac{1}{(2\pi)^3} 2\overline{n}(k) \mathrm{d}^3 k = \frac{2}{\exp(\beta\hbar\omega) - 1} \frac{\mathrm{d}^3 k}{(2\pi)^3} \tag{6.78}$$

We can use $\omega = \omega(\vec{k}) = c\left|\vec{k}\right|, E = \hbar\omega$

$$\mathrm{d}^3 k = 4\pi \left|k\right|^2 \mathrm{d}\left|k\right| = \frac{4\pi}{c^3}\omega^2 \mathrm{d}\omega \tag{6.79}$$

The mean number of photons pro volume in frequency interval $[\omega, \omega + \mathrm{d}\omega]$ is

$$?n\left(\omega\right)\mathrm{d}\omega = \frac{8\pi}{(2\pi c)^3} \frac{\omega^2}{\exp(\beta\hbar\omega) - 1} \mathrm{d}\omega \tag{6.80}$$

(6.80) does not diverge for $\omega \rightarrow 0$. The mean photon energy pro volume in the frequency interval $[\omega, \omega + \mathrm{d}\omega]$ is

$$\boxed{\overline{u}(\omega, T)\mathrm{d}\omega = \frac{\hbar}{\pi^2 c} \frac{\omega^3}{\exp(\beta\hbar\omega) - 1} \mathrm{d}\omega} \tag{6.81}$$

(6.81) could be transformed with $\eta = \beta\hbar\omega = \frac{\hbar\omega}{k_\mathrm{B}T}$ to the original form, postulated by Planck in 1900

$$\overline{u}(\eta, T)\mathrm{d}\eta = \frac{(k_\mathrm{B}T)^4}{\pi^2(\hbar c)^3} \frac{\eta^3 \mathrm{d}\eta}{\exp\eta - 1} \tag{6.82}$$

Of course, (6.81) can be expressed as a function of the wavelength $\omega = \frac{2\pi c}{\lambda}$

$$\overline{u}(\lambda, T)\mathrm{d}\lambda = 16\pi^2\hbar c \frac{1}{\exp\left(\frac{2\pi\hbar c}{k_\mathrm{B}T\lambda}\right) - 1} \frac{\mathrm{d}\lambda}{\lambda^5} \tag{6.83}$$

The maximum in the spectrum of the sun, which has surface temperature $T \approx 5800\,\mathrm{K}$, is $\lambda_\mathrm{max} = 500\,\mathrm{nm}$. This green light, to which the human eye is to most sensistive.

When $\hbar\omega \ll k_\mathrm{B}T$

$$\overline{u}(\omega, T)\mathrm{d}\omega = \frac{\hbar}{\pi^2 c^3} \frac{\omega^3}{\beta\hbar\omega} \mathrm{d}\omega = \frac{k_\mathrm{B}T}{\pi^2 c^3} \omega^2 \mathrm{d}\omega \tag{6.84}$$

(6.84) coincides with the result derived from the classical electrodynamics. Noteworthy is that there is no $\hbar$ in (6.84). However, a problem arises, when one integrates over the frequency

$$\int_0^\infty \mathrm{d}\omega \overline{u}(T, \omega) \rightarrow \infty \tag{6.85}$$

A solution is offered by quantum statistics of photons.

iii) Energy density

$$\epsilon = \frac{E}{V} = \int_0^\infty \mathrm{d}\omega\, \overline{u}(\omega, T) = \int_0^\infty \mathrm{d}\eta\, \overline{u}(\eta, T) = \tag{6.86}$$

$$\epsilon = \frac{(k_\mathrm{B}T)^4}{\pi^2 c^3 \hbar^3} \underbrace{\int_0^\infty \mathrm{d}\eta\, \frac{\eta^3}{\mathrm{e}^\eta - 1}}_{\frac{\pi^4}{15}} \tag{6.87}$$

$$\epsilon = \frac{\pi^2}{15} \frac{(k_\mathrm{B}T)^4}{(c\hbar)^3} \tag{6.88}$$

(6.88) is called Stefan-Boltzmann law.

Natural units

$$\hbar = c = k_\mathrm{B} = 1 \tag{6.89}$$

$k_\mathrm{B} = 1$ Temperature is measured in energy units, e.g. eV. $1\,\mathrm{K} = 8.617 \cdot 10^{-5}\,\mathrm{eV}$

$c = 1$ Mass is also measured in energy units, e.g. $m_\mathrm{e} = 511\,\mathrm{keV}$ $1\,\mathrm{eV} = 1.783 \cdot 10^{-33}\,\mathrm{g}$

$\hbar = 1$ Time and length are measured in inverse energy units $1\,\mathrm{fm} = 10^{-15}\,\mathrm{m} = \frac{1}{197}\,\mathrm{MeV}$ $1\,\mathrm{m} = 5.068 \cdot 10^6\,(\mathrm{eV})^{-1}$

iv) Canonical partition function

$$\ln Z_\mathrm{can}(\beta, V) = \sum_\nu \ln \frac{1}{1 - \exp\{-\beta E_\nu\}} \tag{6.90}$$

$$\sum_\nu = V \int \frac{\mathrm{d}^3 k}{(2\pi)^3} \qquad E_\nu = \hbar c \left|\vec{k}\right| = \hbar\omega = \frac{\eta}{\beta} \tag{6.91}$$

$$\ln Z_\mathrm{can} = \frac{V}{\pi^2} \left(\frac{k_\mathrm{B}T}{\hbar c}\right)^3 \int_0^\infty \mathrm{d}\eta\, \eta^2 \ln \frac{1}{1 - \mathrm{e}^{-\eta}} \tag{6.92}$$

$$\ln Z_\mathrm{can} = \frac{\pi^2}{45} V (\beta c \hbar)^{-3} \tag{6.93}$$

We can make a small check.

$$E = -\frac{\partial}{\partial \beta} \ln Z_\mathrm{can} = \frac{\pi^2}{15} V (\hbar c)^{-3} \beta^{-4} \tag{6.94}$$

$$\epsilon = \frac{E}{V} = \frac{\pi^2}{15} (\hbar c)^{-3} \beta^{-4} \tag{6.95}$$

One can easily see that (6.88) and (6.95) are identical.

Notes

1. Macroscopic observables is not only the energy E, but also the energy distribution as a function of the frequency
2. From Z_can other observables could be derived, e.g. the pressure of the photon gas. ⇒Thermodynamic potentials →classical thermodynamics.

v) Free energy and equation of state

$$\ln Z_{\text{can}} = \frac{\pi^2}{45} V \left(\frac{k_{\mathrm{B}} T}{\hbar c}\right)^3 \tag{6.96}$$

$$\Rightarrow F = -\frac{\tau}{3} V T^4 \tag{6.97}$$

For (6.97) we have used natural units and $F = -k_{\mathrm{B}} T \ln Z_{\text{can}}$ and have set

$$\tau = \frac{k_{\mathrm{B}}^4 \pi^2}{15 c^3 \hbar^3} \tag{6.98}$$

$$S = \left(-\frac{\partial F}{\partial T}\right)_V = \frac{4}{3}\tau V T^3 \tag{6.99}$$

$$E = F + TS = \tau V T^4 \tag{6.100}$$

$$p = -\left(\frac{\partial F}{\partial V}\right)_T = \frac{\tau}{3} T^4 = \frac{1}{3}\frac{E}{V} = \frac{1}{3}\epsilon \tag{6.101}$$

$$\boxed{\epsilon = \frac{\pi^2}{15} T^4} \tag{6.102}$$

$$\boxed{p = \frac{1}{3}\epsilon} \tag{6.103}$$

e) Fermi gas

i) Quasi-particles

We consider low temperatures. What does that mean? We have to compare it with something. Is is slow compared to the Fermi temperature, so $T \ll T_F$. Of course there is a transition between the low an high temperature regime but we will not deal with that. Low temperature is important when considering particles and hole, for example in solid state physics. We are not only interested in the free Fermi gas, but when interactions happen. Free Fermi gas is when the interaction between the quasi-particles can be neglected.

ii) $T \to 0$

Our starting poing is the formula

$$\overline{n}_\nu^{(F)} = \frac{1}{\exp(\beta(E_\nu - \mu)) + 1} \tag{6.104}$$

which we will evaluate in the limit then $T \to 0$ or when $\beta T << |E_\nu - \mu|$. When $kT \to 0$, we have $\beta \to \infty$. We have

$$\overline{n}_\nu^{(F)} = 0 \tag{6.105}$$

when $E_\nu > \mu$ and

$$\overline{n}_\nu^{(F)} = 1 \tag{6.106}$$

for the case when $E_\nu < \mu$. This gives us the famous Fermi surface. The Fermi energy is defined as

$$\epsilon_F = \lim_{T \to 0} \mu \tag{6.107}$$

As we have nonrelativistic fermions, we can also define the Fermi momentum

$$\frac{p_F^2}{2M} = \epsilon_F = \frac{\hbar k_F^2}{2M} \tag{6.108}$$

which can also be written in terms of the Fermi wave number k_F.

iii) Computation ϵ_F

We now have

$$N = 2\frac{V}{(2\pi)^3}\int\limits_{k^2<k_F^2} d^3k = \frac{V}{\pi^2}\int_0^{k_F} d|k||k|^2 = \frac{V}{3\pi^2}k_F^3 \tag{6.109}$$

and therefore we have

$$k_F = \left(3\pi^2\frac{N}{V}\right)^{1/3} \tag{6.110}$$

and an expression for ϵ_F which is valid for free non-relativistic fermions

$$\epsilon_F = \frac{\hbar^2}{2M}\left(3\pi^2\frac{N}{V}\right)^{2/3} \tag{6.111}$$

with $kT_F = \epsilon_F$.

iv) Thermodynamics

We know that the energy is a function of T, V and N, so $E(T,V,N)$. The lowest state of the system is $E(T=0) = E_0$ which is gotten by counting the states multiplying by the energy of the states

$$E_0 = 2\frac{V}{(2\pi)^3}\int\limits_{k^2<k_F^2} d^3k\frac{\hbar^2k^2}{2M} \tag{6.112}$$

$$= \frac{V}{(\pi)^3}\frac{\hbar^2}{2M}\int\limits_0^{k_F} k^4 d^3k \tag{6.113}$$

$$= \frac{V\hbar^2}{10\pi^2M}k_F^5 \tag{6.114}$$

$$= \frac{3}{10}\frac{\hbar^2k_F^2}{M}N \tag{6.115}$$

$$= \frac{3}{5}N\epsilon_F \tag{6.116}$$

$$\boxed{E_0 = \frac{3}{5}N\epsilon_F} \tag{6.117}$$

if we remember that $N = \frac{V}{3\pi^2}k_F^3$ and $\epsilon_F = \frac{\hbar^2k_F^2}{2M}$.
Now we have a good starting point, the equation of state

$$E(T=0,N,V) = \frac{3\hbar^2}{10M}(3\pi^2n)^{2/3}N \tag{6.118}$$

v) Number of states per particle for given one particle energy

We want to go beyond the standard dispersion relation and have some general relation

$$E_\nu = \epsilon(|\vec{k}|) \tag{6.119}$$

In the non-relativistic case we would have $\epsilon = \vec{k}^2/2M$ and in the relativistic case $\epsilon = \hbar c|k|$. The k_F is same as before. The computation of the Fermi energy does though change, $\epsilon_F = \epsilon(k_F)$.
We start by computing the ground state energy. We have

$$\boxed{N = g_I \frac{V}{6\pi^2} k_F^3} \tag{6.120}$$

and the energy is

$$E_0 = g_I \frac{V}{(2\pi)^3} \int\limits_{k^2<k_F^2} \mathrm{d}^3k\, \epsilon(|k|) \tag{6.121}$$

$$E_0 = g_I \frac{V}{(2\pi)^3} \int \mathrm{d}^3k \int_0^{\epsilon_F} \mathrm{d}\epsilon\, \epsilon \tag{6.122}$$

We can now invert the integration and define the quantity which gives us the number of states per particle,

$$E_0 = N \int\limits_0^{\epsilon_F} \mathrm{d}\epsilon\, \Omega_1(\epsilon)\epsilon \tag{6.123}$$

with

$$\boxed{\Omega_1(\epsilon) = g_I \frac{V}{N} \int \frac{\mathrm{d}^3k}{(2\pi)^3} \delta\left(\epsilon - \epsilon(|k|)\right) \Omega_1(\epsilon) = g_I \frac{V}{N} \int \frac{\mathrm{d}^3k}{(2\pi)^3} \delta\left(\epsilon - \frac{\hbar^2 k^2}{2M}\right)} \tag{6.124}$$

which is the number of states per energy per mass.

vi) Ω_1 for $\epsilon(k) = \frac{k^2}{2M}$

We integrate the equation above by changing into polar coordinates and the result is (only true for $\epsilon > 0$)

$$\Omega_1(\epsilon) = \frac{3}{2} \epsilon_F^{-3/2} \epsilon^{1/2} \tag{6.125}$$

but we will not derive it in class.
The energy per particle is then

$$\frac{E_0}{N} = \frac{3}{2} \epsilon_F^{-3/2} \frac{2}{5} \epsilon_F^{5/2} = \frac{3}{5} \epsilon_F \tag{6.126}$$

We use thermodynamic observation for determination of microscopical properties. We compute observables with free $\Omega_1(\epsilon)$.

vii) $E(T)$

We have

$$E(T, \nu, N) = N \int\limits_{-\infty}^{\infty} d\epsilon \Omega_1(\epsilon) \frac{\epsilon}{e^{\beta(\epsilon-\mu)} + 1} \tag{6.127}$$

We can compute the particle number as a function of the chemical potential

$$N = N \int_{-\infty}^{\infty} d\epsilon \Omega_1(\epsilon) \frac{1}{e^{\beta(\epsilon-\mu)} + 1} \tag{6.128}$$

and we get a type of normalization condition, where this is valid for arbitrary temperatures

$$1 = \int_{-\infty}^{\infty} d\epsilon \Omega_1(\epsilon) \frac{1}{e^{\beta(\epsilon-\mu)} + 1} \tag{6.129}$$

So if we know Ω_1 we get a function of β and ν by using this normalization condition. Therefore we get the chemical potential as a function of temperature.

Now we look at small temperatures. If $T > 0$ the fermi surface is not a step function but a smooth one. We want to compute the edges, which are the difference between the step function and the smooth one. If electrons have energy bigger than the energy μ, which is higher than the Fermi surface, we call that particles. If they have less energy, we can call them missing electrons or holes.
Our approximations are that $kT << |\epsilon_F - \epsilon|$ and we consider the difference between two cases, when $T \neq 0$ and when $T = 0$ for fixed N and V.

$$E - E_0 = N \int d\epsilon \Omega_1(\epsilon)\epsilon \left(\frac{1}{e^{\beta(\epsilon-\mu)} + 1} - \Theta(\epsilon_F - \epsilon) \right) \tag{6.130}$$

viii) Compute $\mu(t)$ from normalization

We have

$$0 = \int_{-\infty}^{\infty} d\epsilon \Omega_1(\epsilon) \left(\frac{1}{e^{\beta(\epsilon-\mu)} + 1} - \Theta(\epsilon_F - \epsilon) \right) \tag{6.131}$$

Now we have

$$\Omega_1(\epsilon) = \Omega_1(\epsilon_F) + \Omega_1'(\epsilon_F)(\epsilon - \epsilon_F) \tag{6.132}$$

and the Sommerfeld approximation

$$\mu = \epsilon_F + \Delta\mu \tag{6.133}$$

and let $x = \beta(\epsilon - \epsilon_F)$ so we therefore get

$$0 = \int_{-\infty}^{\infty} dx \left(\Omega_1(\epsilon_F) + \Omega_1'(\epsilon_F) \frac{x}{\beta} \right) \left(\frac{1}{e^x e^{-\beta\Delta\mu} + 1} - \Theta(-x) \right) \tag{6.134}$$

Now we to Taylor expansion around $\beta\Delta\mu$ and get

$$\frac{1}{e^x e^{-\beta\Delta\mu} + 1} = \frac{1}{e^x(1 - \beta\Delta\mu) + 1} \tag{6.135}$$

$$= \frac{1}{(e^x + 1)(1 - \beta\Delta\mu \frac{e^x}{e^x+1})} \tag{6.136}$$

$$= \frac{1}{e^x + 1} + \beta\Delta\mu \frac{e^x}{(e^x + 1)^2} \tag{6.137}$$

We now use this into the expression above and get

$$0 = \int_{-\infty}^{\infty} dx \left(\Omega_1(\epsilon_F) + \Omega_1'(\epsilon_F)\frac{x}{\beta}\right)\left(f(x) + \beta\Delta\mu\frac{e^x}{(e^x+1)^2}\right) \tag{6.138}$$

where

$$f(x) = \frac{1}{e^x+1} - \Theta(-x) \tag{6.139}$$

which has the property that $f(-x) = -f(x)$ so it is antisymmetric. $f(x)$ has a jump in $x = 0$. This function has two useful properties. First that

$$\int_{-\infty}^{\infty} dx f(x) = 0 \tag{6.140}$$

and also that

$$\int_{-\infty}^{\infty} dx f(x) x = \frac{\pi^2}{6} \tag{6.141}$$

We now have from the normalization equation

$$\beta\Delta\mu\Omega_1(\epsilon_F)\int_{-\infty}^{\infty} dx \frac{e^x}{(e^x+1)^2} = -\frac{\Omega_1'(\epsilon_F)}{\beta}\frac{\pi^2}{6} \tag{6.142}$$

and now finally $\Delta\mu \sim \frac{\Omega_1'}{\beta^2}$ and since $\mu = \epsilon_F + \Delta\mu$ we get

$$\mu = \epsilon_F - \frac{\pi^2}{6}\frac{\Omega_1'(\epsilon_F)}{\Omega_1(\epsilon_F)}(kT)^2 \tag{6.143}$$

f) Non-relativistic bosons

i) Chemical Potential

We will take a look at one-atom gases, without excited internal degrees of freedom and $g_I = 1$, such as hydrogen.

$$?n_\nu = \frac{1}{\exp\left[\beta\left(E_\nu - \mu\right)\right] - 1} \tag{6.144}$$

The lowest energy ist $E_0 \Rightarrow \mu < E_0$. We will take $E_0 = 0$ without loss of generality, $\mu < 0$. Otherwise rescale E_ν, μ by some additive shift, which is allowed because only $E_\nu - \mu$ matters and it is indepedent on the shift. Example for bosons are atoms with the appropriate spins with $E_\nu = \frac{p^2}{2M}$

ii) Number of bosons in ground state

$$?n_0 = \frac{1}{\mathrm{e}^{-\beta\mu} - 1} \tag{6.145}$$

This could be approximated for small $|\beta\mu|$:

$$?n_0 = \frac{1}{1 - \beta\mu - 1} = -\frac{1}{\beta\mu} = -\frac{k_\mathrm{B}T}{\mu} \tag{6.146}$$

(6.146) can become very large for $\mu \to 0^-$. Macroscopic $?n_0$ is equivalent with Bose-Einstein condensate. $\frac{?n_0}{N}$ gives the fraction of condensed atoms or the superfluid density. In the thermodynamical limit $V \to \infty$:

$$\frac{?n_0}{N} \to 0 \qquad\qquad \text{no condensation}$$

$$\frac{?n_0}{N} \to n_s > 0 \qquad\qquad \text{Bose-Einstein cond.}$$

iii) Qualitive behaviour of $\overline{n}_0\left(E_\nu\right)$ for $T \to 0$

The smaller temperature means that there less particles with higer energies due to the stronger Boltzmann supression. $\overline{n}_0$ increases for small $E_\nu \Rightarrow \mu\left(T \to 0, N\right) \to 0$

iv) Gibbs potential

$$J = -k_\mathrm{B}T \ln Z_\mathrm{gc} = -pV \tag{6.147}$$

$$\begin{aligned} J &= -k_\mathrm{B}T \sum_\nu \ln\left(\frac{1}{1-\exp\left\{-\beta\left(E_\nu-\mu\right)\right\}}\right) \\ &= k_\mathrm{B}Tg_IV \int \frac{\mathrm{d}^3k}{\left(2\pi\right)^3} \ln\left(1-\exp\left\{-\frac{1}{k_\mathrm{B}T}\left[\underbrace{\frac{\hbar^2\vec{k}^2}{2M}}_{\epsilon(\vec{k})}-\mu\right]\right\}\right) \end{aligned}$$

g) Classical ideal gas

i) Classical approxiamtion

The classical approximation is for the case

$$E_\nu - \mu \gg k_\mathrm{B}T, \qquad\qquad \frac{\hbar^2\vec{k}^2}{2M} - \mu \gg k_\mathrm{B}T \tag{6.148}$$

The occupation number becomes

$$\overline{n}_\nu = \frac{1}{\mathrm{e}^{\beta(E_\nu-\mu)} \mp 1} \to \mathrm{e}^{-\beta(E_\nu-\mu)} \qquad\qquad \text{for bosons and fermions} \tag{6.149}$$

This means the classical approximation is valid for $\overline{n}_\nu \ll 1$

ii) Gibbs potential

$$\begin{aligned} J &= k_\mathrm{B}Tg_IV \int \frac{\mathrm{d}^3k}{\left(2\pi\right)^3} \ln\left(1-\exp\left\{-\frac{1}{k_\mathrm{B}T}\left[\frac{\hbar^2\vec{k}^2}{2M}-\mu\right]\right\}\right) \\ &= -\frac{k_\mathrm{B}Tg_IV}{w\pi^2} \int\limits_0^\infty \mathrm{d}\left|\vec{k}\right| \left|\vec{k}\right|^2 \exp\left\{-\frac{1}{k_\mathrm{B}T}\left[\frac{\hbar^2\vec{k}^2}{2M}-\mu\right]\right\} \end{aligned}$$

It is the same for bosons and fermions.

$$J = -k_{\mathrm{B}} T g_I \frac{V}{2\pi^2} \exp\left(\frac{\mu}{k_{\mathrm{B}}T}\right) I_J \tag{6.150}$$

$$I_J = \int_0^\infty \mathrm{d}x\, x^2 \exp\left(-bx^2\right) = -\frac{\partial}{\partial b} \int_0^\infty \mathrm{d}x\, \exp\left(-bx^2\right) = \frac{\partial}{\partial b}\left(\frac{1}{2}\sqrt{\frac{\pi}{b}}\right) = \frac{1}{4}\pi^{1/2} b^{-3/2} \tag{6.151}$$

with $b = \frac{\hbar^2}{2Mk_{\mathrm{B}}T}$

iii) Thermal de Broglie wavelength

We define

$$\lambda(T) = \left(\frac{2\pi\hbar^2}{Mk_{\mathrm{B}}T}\right)^{1/2} \tag{6.152}$$

$$\lambda^2 = 4\pi b \Rightarrow b = \frac{\lambda^2}{4\pi} \Rightarrow b^{-3/2} = \lambda^{-3}\left(4\pi\right)^{3/2} \tag{6.153}$$

$$\Rightarrow I_J = 2\pi^2\lambda^{-3} \tag{6.154}$$

iv) Thermodynamics

$$\boxed{J = -k_{\mathrm{B}} T g_I V \lambda^{-3}(T) \exp\frac{\mu}{k_{\mathrm{B}}T}} \tag{6.155}$$

$$J = -pV \tag{6.156}$$

$$N = -\left(\frac{\partial J}{\partial \mu}\right)_{T,V} = -\frac{1}{k_{\mathrm{B}}T} J = \frac{pV}{k_{\mathrm{B}}T} \tag{6.157}$$

From (6.157) one can derive the equation of state for the ideal gas

$$pV = k_{\mathrm{B}} N T \tag{6.158}$$

Now, let us make a comparission with the thermodynamical derivation.

$$\begin{aligned} J &= -k_{\mathrm{B}} T V \exp\frac{\mu}{k_{\mathrm{B}}T} ?a(T) && (6.159) \\ \Rightarrow ?a(T) &= g_I \lambda^{-3}(T) \sim T^{3/2} && (6.160) \\ E &= k_{\mathrm{B}} T N \frac{\partial \ln ?a}{\partial \ln T} = \frac{3}{2} k_{\mathrm{B}} N T && (6.161) \end{aligned}$$

6.161 does not involve the degeneracy g_I. The function $?a(T)$ is uniquely defined.

$$c_V = \frac{3}{2} k_{\mathrm{B}} N \Rightarrow \frac{c_V}{N} = \frac{3}{2} k_{\mathrm{B}} \tag{6.162}$$

h) Bose-Einstein Condensation

We will discuss the case when we keep n fixed and lower T.

i) $n(\mu)$

$$\frac{N}{V} = \int \frac{\mathrm{d}^3 k}{(2\pi)^3} \frac{1}{\exp \beta \left(\frac{\hbar^2 k^2}{2M} - \mu \right) - 1} \tag{6.163}$$

For the calculation of the integral we transform to spherical coordinates.

$$\Rightarrow \int \frac{\mathrm{d}^3 k}{(2\pi)^3} = \frac{1}{2\pi^2} \int \mathrm{d}\,|k|\ |k|^2 = \frac{1}{4\pi^2} \int \mathrm{d}k^2 \sqrt{k^2} \tag{6.164}$$

We also use the following variable z

$$z = \frac{\hbar^2 k^2}{2M k_\mathrm{B} T} = \frac{\lambda(T)^2 k^2}{4\pi} \tag{6.165}$$

$$k^2 = \frac{4\pi z}{\lambda^2} \tag{6.166}$$

$$\Rightarrow n = \frac{1}{4\pi^2} \left(\frac{4\pi}{\lambda^2} \right)^{3/2} \int\limits_0^\infty \mathrm{d}z \sqrt{z} \frac{1}{\mathrm{e}^{z - \beta\mu} - 1} \tag{6.167}$$

$$\boxed{n\lambda^3 = \frac{2}{\sqrt{\pi}} \int \mathrm{d}z \sqrt{z} \frac{1}{\mathrm{e}^{z - \beta\mu} - 1}} = f(\beta\mu) \tag{6.168}$$

μ is negative, if we increase towards 0_-, then $-\beta\mu \to 0_+ \Rightarrow f(\beta\mu)$ increases.

ii) Critical temperature

We want to compute $n\lambda^3$ for $\mu = 0$ (the maximal value of μ)

$$n\lambda^3 = \frac{2}{\sqrt{\pi}} \underbrace{\int \mathrm{d}z \sqrt{z} \frac{1}{e^z - 1}}_{\Gamma\left(\frac{3}{2}\right)\phi\left(\frac{3}{2}\right)} \tag{6.169}$$

$\Gamma\left(\frac{3}{2}\right) = \frac{1}{2}\sqrt{\pi}$ and $\phi\left(\frac{3}{2}\right) = 2.612$

$$\boxed{\left(n\lambda^3\right)_\mathrm{c} = \phi\left(\frac{3}{2}\right)} \tag{6.170}$$

$$\lambda_\mathrm{c} = \left(\phi\left(\frac{3}{2}\right)\right)^{1/3} n_\mathrm{c}^{-1/3} \tag{6.171}$$

$$\lambda_\mathrm{c}^2 = \frac{2\pi\hbar^2}{M k_\mathrm{B} T_\mathrm{c}} = \left(\phi\left(\frac{3}{2}\right)\right)^{2/3} n_\mathrm{c}^{-2/3} \tag{6.172}$$

$$k_\mathrm{B} T_\mathrm{c} = \frac{2\pi\hbar^2}{M} \left(\phi\left(\frac{3}{2}\right)\right)^{-2/3} n_\mathrm{c}^{2/3} = 3.31 \frac{\hbar^2}{M} n_\mathrm{c}^{2/3} \tag{6.173}$$

If T reaches T_c for a given n, then μ reaches 0. So, what happens for $T < T_\mathrm{c}$?

iii) Ground state of bosonic gas

The ground state is at $T = 0$, which corresponds to the minimum of the energy. All bosons are in the state with the lowest energy E_0. In a box with periodic boundary conditions the energy is $E_0 = \frac{\hbar^2 k_0^2}{2M}$, where $\hbar k_0$ is the lowest possible discrete momentum; or in a cavity the lowest resonance frequency w_0 is excited with $E_0 = \hbar w_0$. $\Rightarrow \overline{n}_{\nu=0}(T = 0) = N$, which diverges in the thermodynamic limit. The macroscopic number of particles in the ground state $\nu = 0$ are:

$$\frac{\overline{n}_{\nu=0}}{V} = \frac{N}{V} = n_0 \tag{6.174}$$

Therefore, a problem arise in the transition from discrete sum $\sum_\nu$ to an integral $\int \frac{\mathrm{d}^3 k}{(2\pi)^3}$, because the atoms in the ground state are not properly counted. That is why

$$n = n_0 + ?n(T) \tag{6.175}$$

$n_0 \neq 0$ in the case of BEC, $?n(T)$ is the number of non-condensed thermal atoms.

iv) Bose-Einstein Condensation

As already mentioned the condensation occurs for $T < T_\mathrm{c}$. The chemical potential μ becomes 0.

$$?n(T) = \phi\left(\frac{3}{2}\right)\lambda(T)^{-3} < n \tag{6.176}$$

$$\Rightarrow n_0(T) = n - ?n(T) > 0 \tag{6.177}$$

$$\frac{?n(T)}{?n(T_\mathrm{c})} = \frac{\lambda^3(T_\mathrm{c})}{\lambda^3(T)} = \left(\frac{T}{T_\mathrm{c}}\right)^{3/2} \tag{6.178}$$

$$?n(T_\mathrm{c}) = n \Rightarrow ?n(T) = \left(\frac{T}{T_\mathrm{c}}\right)^{3/2} n \tag{6.179}$$

$$n_0(T) = \left\{1 - \left(\frac{T}{T_\mathrm{c}}\right)^{3/2}\right\} n \tag{6.180}$$

For $T < T_\mathrm{c}$

$$E = \frac{g_I M^{3/2} T^{5/2} V}{\sqrt{2}\pi^2\hbar^3} \underbrace{\int_0^\infty \mathrm{d}z \, \frac{z^{3/2}}{\mathrm{e}^z - 1}}_{\Gamma(\frac{5}{2})\phi(\frac{5}{2})} \quad (k_\mathrm{B} = 1) \tag{6.181}$$

$$\frac{E}{NT} = 0.77 \left(\frac{T}{T_\mathrm{c}}\right)^{3/2} \tag{6.182}$$

Compare (6.182) with the result for the classical gas $\frac{E}{NT} = \frac{3}{2}$

7 Gas of interacting particles

a) Interactions and complexity

- So far we had only free particles. From now on we will consider interactions, which is a major change and introduced complexity.
- Phase transitions
- long range correlations

We will examine two regions

- low temperature: few states are excited → collective modes → quasi-particles. For example
  - solids: acoustic waves, phonons
  - magnetic systems: magnons, spin waves
- high temperature

At high temperatures interaction could be treated as pertubation: for small T there is order, for large T disorder.

The aim of statistical physics is to described all these phenoma, starting from known microphysics - atomic physics - and bridge it to macrophysics. A key for that are statistical fluctuations and correlations

b) Real gases

Interactions between atoms or molecules cannot be neglected in real gases. Let us denote the distance between two particles with R. Then the acting potential is $V(R)$ (usually due to van der Waals forces). Typically this is the Lennard-Jones potential:

$$V(R) = V_0 \left[\left(\frac{R_0}{R} \right)^{12} - 2 \left(\frac{R_0}{R} \right)^6 \right] \tag{7.1}$$

We will approximate the particles as hard spheres and will take into account only the attractive interaction. The approximated potential is

$$V(R) = \begin{cases} \infty & \text{for } R < R_0 \\ -V_0 \left(\frac{R_0}{R} \right)^6 & \text{for } R > R_0 \end{cases} \tag{7.2}$$

c) Mean field approxiamtion

We will consider a single molecule which is in an effective potential, created by the other molecules. This reduced the problem to a single with an effective Hamiltonian.

i) Classical statistics in phase space

The Hamiltonian is

$$H = \sum_i \frac{\vec{p}_i^2}{2M} + \sum_{ij} V(\vec{r}_i - \vec{r}_j) \tag{7.3}$$

The problem is that in quantum mechanics $\vec{p}_i$ and $\vec{r}_i$ do not commute and it is not easy to diagonalize H.

Take a look at the classical limit for fixed N

$$\sum_\tau \to \frac{1}{N!} \prod_{i=1}^{N} \int \mathrm{d}^3 r_i \frac{\mathrm{d}^3 p_i}{(2\pi\hbar)^3} \tag{7.4}$$

For free particles it is exact

$$\sum_\tau = \frac{1}{N!} V^N \prod_{i=1}^{N} \int \frac{\mathrm{d}^3 p_i}{(2\pi\hbar)^3} \tag{7.5}$$

ii) Average potential

We replace the potential with an average one

$$\sum_{ij} V(\vec{r}_i - \vec{r}_j) \to \sum_i U_{\text{eff}}(\vec{r}_i) \tag{7.6}$$

This is the average potential “seen” by one particle, created by interaction with all other particles.

$$\begin{aligned}
Z_{\text{can}} &= \frac{1}{N!} \prod_i \int \frac{\mathrm{d}^3 r_i\, \mathrm{d}^3 p_i}{(2\pi\hbar)^3} \exp\left\{-\beta \left[\sum_f \frac{p_f^2}{2M} + \sum_{jk} V(\vec{r}_j - \vec{r}_k)\right]\right\} && (7.7)\\
&= \frac{1}{N!} \prod_i \int \frac{\mathrm{d}^3 r_i\, \mathrm{d}^3 p_i}{(2\pi\hbar)^3} \exp\left\{-\beta \left[\frac{p_i^2}{2M} + U_{\text{eff}}(\vec{r}_i)\right]\right\} && (7.8)
\end{aligned}$$

iii) Approximation of the canonnical partition function

$$\begin{aligned}
Z_{\text{can}} &\approx \frac{1}{N!} \left\{\int \frac{\mathrm{d}^3 r_i\, \mathrm{d}^3 p_i}{(2\pi\hbar)^3} \exp\left[-\beta\left(\frac{p_i^2}{2M} + U_{\text{eff}}(\vec{r}_i)\right)\right]\right\}^N && (7.9)\\
&= Z_{\text{ideal}} V^{-N} \left[\int \mathrm{d}^3 r\, \exp\left(-\beta U_{\text{eff}}(r)\right)\right]^N && (7.10)\\
&= Z_{\text{ideal}} \left(Z_{WW}^{(1)}\right)^N && (7.11)
\end{aligned}$$

$$\begin{aligned}
F &= -k_{\mathrm{B}} T \ln Z_{\text{can}} && (7.12)\\
&= -k_{\mathrm{B}} T \ln Z_{\text{ideal}} - N k_{\mathrm{B}} T \ln Z_{WW}^{(1)} && (7.13)\\
&= F_{\text{ideal}} - N k_{\mathrm{B}} T \ln Z_{WW}^{(1)} && (7.14)
\end{aligned}$$

$$\begin{aligned}
F_{\text{ideal}} &= k_{\mathrm{B}} T N \left\{1 - \ln\left[\frac{N}{V}\left(\frac{2\pi\hbar^2}{m k_{\mathrm{B}} T}\right)^{3/2}\right]\right\} && (7.15)\\
&= -k_{\mathrm{B}} T N + k_{\mathrm{B}} T N \ln \frac{N}{V} - \frac{3}{2} k_{\mathrm{B}} N T \ln \frac{m k_{\mathrm{B}} T}{2\pi\hbar^2} && (7.16)
\end{aligned}$$

iv) Calculation of $Z_{WW}^{(1)}$

We will consider two effects

- excluded Volume
- attractive interaction

$$Z_{WW}^{(1)} = \frac{1}{V} \int \mathrm{d}^3 r \, \exp\left(-\beta U_{\mathrm{eff}}(r)\right) \tag{7.17}$$

As seen from (7.2), there are two regions: V_{ex} with $U_{\mathrm{eff}} \to \infty$; and the rest with $U_{\mathrm{eff}} \to -\overline{W}$

$$\Rightarrow Z_{WW}^{(1)} = \frac{V - V_{\mathrm{ex}}}{V} \exp -\beta \overline{W} \tag{7.18}$$

v) Excluded volume V_{ex}

V_{ex} is the mead excluded volume for one atom. The total excluded volume is

$$N V_{\mathrm{ex}} = \frac{1}{2} \underbrace{N(N-1)}_{\text{number of pairs}} \underbrace{\frac{4\pi}{3} a^3}_{\text{excluded volume pro pair}} \tag{7.19}$$

$$V_{\mathrm{ex}} \approx \frac{1}{2} N \frac{4\pi}{3} a^3 = \frac{2\pi}{3} a^3 N = b_0 N \tag{7.20}$$

vi) Mean potential $\overline{W}$

$\overline{W}$ is the mean potential "seen" by a single atom. The potential energy of all atoms is $N\overline{W}$

$$N\overline{W} = \frac{1}{2} \underbrace{N(N-1)}_{\text{number of pairs}} \overline{\underbrace{u}_{\text{mean potential en. pro pair}}} \tag{7.21}$$

$$\overline{u} = 4\pi \int \mathrm{d}R \, R^2 W(R) V^{-1} \tag{7.22}$$

$$\overline{W} = \frac{1}{2} N \overline{u} = \frac{2\pi N}{V} \int \mathrm{d}R \, R^2 W(R) \tag{7.23}$$

$$\boxed{\overline{W} = -\frac{N}{V} b_1} \tag{7.24}$$

$$Z_{WW}^{(1)} = \frac{V - V_{\mathrm{ex}}}{V} \exp - \frac{\overline{W}}{k_{\mathrm{B}} T} \tag{7.25}$$

$$\ln Z_{WW}^{(1)} = \ln \left(\frac{V - b_0 N}{V} \right) - \frac{\overline{W}}{k_{\mathrm{B}} T} \tag{7.26}$$

$$= \ln \left(\frac{V - b_0 N}{V} \right) + \frac{N}{V k_{\mathrm{B}} T} b_1 \tag{7.27}$$

vii) Free energy

$$F = F_{\text{ideal}} - Nk_{\text{B}}T\ln Z_{WW}^{(1)} \tag{7.28}$$

$$F = \underbrace{-k_{\text{B}}TN + k_{\text{B}}NT\ln\frac{N}{V}}_{F_{\text{ideal}}} \underbrace{- k_{\text{B}}NT\ln\frac{V-b_0N}{V}}_{Z_{WW}^{(1)}} \underbrace{- \frac{3}{2}k_{\text{B}}NT\ln\frac{mk_{\text{B}}T}{2\pi\hbar^2}}_{F_{\text{ideal}}} \underbrace{- k_{\text{B}}NT\frac{N}{Vk_{\text{B}}T}b_1}_{Z_{WW}^{(1)}} \tag{7.29}$$

$$\boxed{F = -k_{\text{B}}NT + k_{\text{B}}NT\ln\frac{N}{V-b_0N} - \frac{3}{2}k_{\text{B}}NT\ln\frac{mk_{\text{B}}T}{2\pi\hbar^2} - b_1\frac{N^2}{V}} \tag{7.30}$$

d) Equation of state

$$p = -V\frac{\partial F}{\partial V}_{N,T} = \frac{k_{\text{B}}NT}{V-b_0N} - b_1\left(\frac{N}{V}\right)^2 \tag{7.31}$$

This is the van der Waals equation of state.

$$\boxed{p = \frac{k_{\text{B}}nT}{1-b_0n} - b_1n^2} \tag{7.32}$$

Van der Waals equation of state describes qualitively correctly the phase transition from gas to liquid.

e) Heat capacity of real gases

$$C_V = T\frac{\partial S}{\partial T}_{V,N} = -T\frac{\partial^2 F}{\partial T^2}_{V,N} \tag{7.33}$$

Entropy density

$$\frac{S}{V} = -\frac{\partial}{\partial T}\left(\frac{F}{V}\right)_n = -\left(k_{\text{B}}n + k_{\text{B}}n\ln\frac{n}{1-b_0n} - \frac{3}{2}k_{\text{B}}n\ln\frac{mk_{\text{B}}T}{2\pi\hbar^2} - \frac{3}{2}k_{\text{B}}n\right) \tag{7.34}$$

$$\boxed{\frac{S}{V} = k_{\text{B}}n\left(\frac{5}{2} - \ln\frac{n}{1-b_0n} + \frac{3}{2}\ln\frac{mk_{\text{B}}T}{2\pi\hbar^2}\right)} \tag{7.35}$$

From (7.35) follows that the entropy density does not depend on b_1

$$\frac{C_v}{V} = \frac{\partial}{\partial\ln T}\left(\frac{S}{V}\right)_n = \frac{3}{2}k_{\text{B}}n \tag{7.36}$$

$$\boxed{c_V = \frac{3}{2}k_{\text{B}}n} \tag{7.37}$$

There is no difference in the specific heat capacity of real gas and van der Waals gas.

f) Equipartition