# Introduction to Statistical Physics

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Statistical physics is a fundamental tool for understanding a wide range of physical phenomena. Without it, we would be unable to rigorously study phase transitions in nature, distinguish between a metal and an insulator, or explain remarkable phenomena such as gas condensation, superconductivity, and superfluidity.

This course is the result of thirteen years of teaching experience in this field. Its main objective is to help students understand how to derive the macroscopic properties of a system from the microscopic laws that govern the behavior of its constituents.

This document is an improved English version of my 2021 lecture note originally written in French. In this new edition, I have revised and clarified many explanations, added new ideas to enhance conceptual understanding, and included additional exercises to provide more practice and depth.

The lecture note is structured into four chapters. The first chapter provides a general introduction to statistical physics, presenting the key concepts and mathematical tools used in the study of complex physical systems. The subsequent chapters are dedicated to the detailed study of the various statistical ensembles: microcanonical, canonical, and grand canonical.

This course is complemented by a carefully selected and solved set of exercises, inspired by the textbook *Statistical Mechanics* by R.K. Pathria and Paul D. Beale. These problems are intended to reinforce conceptual understanding and provide practice in applying the formalism.

I hope this modest contribution will serve as a helpful resource for Master 1 students in Physics of Materials.

**Prerequisites:** Classical thermodynamics, analytical mechanics, and elementary quantum mechanics.

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# Chapter 1

# Introduction to Statistical Physics

## 1 Microstate, Macrostate, and Phase Space

In classical mechanics, a microstate of a system containing $N$ particles is characterized by the positions and velocities $(q_i, p_i)$ (for $i = 1, ..., N$), which are continuous variables. For a system state (or microstate) with $l$ degrees of freedom, it is defined by $(q_1, ..., q_l, p_1, ..., p_l)$. If the system consists of a single free particle, its state at any instant is defined in a 6-dimensional Euclidean space $(q_x, q_y, q_z, p_x, p_y, p_z)$: this is the phase space of a single free particle. In the general case, the dimension of this space (phase space) is given by $2lN$.

To enumerate microscopic states, we partition the phase space into elementary cells of volume $\Delta = h^{lN}$ ($h$ is a constant with the dimension of action, $\delta q \delta p$). Each elementary cell corresponds to a unique microscopic state.

For a macroscopic system, energy levels are often discrete. In the continuous limit (where states are very close), the number of microstates contained in the phase space volume $d\Gamma = d^{lN}q\, d^{lN}p$ at time $t$ around the point $(p, q)$, with energy between $E$ and $E + dE$, is given by:

$$d\Omega(N, V, E) = g(N, V, E)\, dE \tag{1.1.1}$$

where $g(N, V, E)$ is the density of states, given by:

$$g(E) = \frac{d\Gamma}{dE} = \int \frac{d^{lN}q\, d^{lN}p}{h^{lN}} \delta(E - E(q, p)) \tag{1.1.2}$$

The dimension of $g(E)$ is $[g(E)] = [1/E] = J^{-1}$. Note that in the purely quantum case, this number of states is interpreted as the degeneracy of the energy level $E$.

## 1.1 Phase Space and Liouville's Theorem

We already know that trajectories in phase space cannot cross, as this would imply two possible futures for the system. The question now is: How does the phase space volume change over time?

**The answer is that it does not change!** We will now prove this. Assume a point $(Q, P)$ evolves in time to $(Q', P')$ according to:

$$\begin{cases} q'_\alpha = q_\alpha + \dot{q_\alpha}\delta t = q'_\alpha(q_\alpha, \dot{q}_\alpha) \\ p'_\alpha = p_\alpha + \dot{p_\alpha}\delta t = p'_\alpha(p_\alpha, \dot{p}_\alpha) \end{cases}$$

Thus, we can write $(Q, P) \to (Q', P')$, i.e.:

$$\begin{cases} Q' \equiv Q'(Q, P) \\ P' \equiv P'(Q, P) \end{cases}$$

The volume $dQ'\, dP'$ at time $t > 0$ is equal to the trajectory multiplied by the volume at $t = 0$, i.e., $dQ'\, dP' = J\, dQ\, dP$, where:

$$J = \left| \frac{\partial(Q', P')}{\partial(Q, P)} \right| = \begin{vmatrix} \frac{\partial q'_1}{\partial q_1} & \cdots & \frac{\partial q'_1}{\partial p_{3N}} \\ \vdots & \ddots & \vdots \\ \frac{\partial p'_{3N}}{\partial q_1} & \cdots & \frac{\partial p'_{3N}}{\partial p_{3N}} \end{vmatrix}$$

Let us start with a simple case: a one-dimensional system with a single particle:

$$\begin{cases} q' = q + \dot{q}\delta t \\ p' = p + \dot{p}\delta t \end{cases}$$

The Jacobian is given by:

$$\begin{cases} \frac{\partial q'}{\partial q} = 1 + \frac{\partial \dot{q}}{\partial q}\delta t \\ \frac{\partial p'}{\partial p} = 1 + \frac{\partial \dot{p}}{\partial p}\delta t \end{cases}$$

and:

$$\begin{cases} \frac{\partial q'}{\partial p} = \frac{\partial \dot{q}}{\partial p}\delta t \\ \frac{\partial p'}{\partial q} = \frac{\partial \dot{p}}{\partial q}\delta t \end{cases}$$

This gives:

$$J = \begin{vmatrix} 1 + \frac{\partial \dot{q}}{\partial q}\delta t & \frac{\partial \dot{q}}{\partial p}\delta t \\ \frac{\partial \dot{p}}{\partial q}\delta t & 1 + \frac{\partial \dot{p}}{\partial p}\delta t \end{vmatrix}$$

Expanding:

$$\begin{aligned} J &= \left(1 + \frac{\partial \dot{q}}{\partial q}\delta t\right)\left(1 + \frac{\partial \dot{p}}{\partial p}\delta t\right) - \left(\frac{\partial \dot{q}}{\partial p}\delta t\right)\left(\frac{\partial \dot{p}}{\partial q}\delta t\right) \\ &= 1 + \left(\frac{\partial \dot{q}}{\partial q} + \frac{\partial \dot{p}}{\partial p}\right)\delta t + O(\delta t^2) \end{aligned} \tag{1.1.3}$$

We neglect $\delta t^2$ terms since our Taylor expansion is only to first order in $\delta t$. From Hamilton's equations:

$$\begin{cases} \dot{q} = \frac{\partial H}{\partial p} \\ \dot{p} = -\frac{\partial H}{\partial q} \end{cases}$$

we obtain:

$$\frac{\partial \dot{q}}{\partial q} + \frac{\partial \dot{p}}{\partial p} = \frac{\partial^2 H}{\partial p \partial q} - \frac{\partial^2 H}{\partial p \partial q} = 0 \tag{1.1.4}$$

Thus, $J = 1$! The same proof applies for more particles in higher dimensions, yielding:

$$J = 1 + \sum_{\alpha=1}^{3N}\left(\frac{\partial \dot{q}_\alpha}{\partial q_\alpha} + \frac{\partial \dot{p}_\alpha}{\partial p_\alpha}\right)\delta t + O(\delta t^2) \tag{1.1.5}$$

which gives $\frac{\partial \dot{q}_\alpha}{\partial q_\alpha} + \frac{\partial \dot{p}_\alpha}{\partial p_\alpha} = 0$.

This completes the proof. We can further observe that **since the volume does not change, it behaves like an incompressible fluid, where the shape changes but the occupied region is preserved.**

Let $\rho(Q, P)$ be the density of states in phase space containing $n$ points. The number of states $n_v$ in a volume $V$ is given by:

$$n_v = n \int_V dQ\, dP\, \rho(Q, P) \tag{1.1.6}$$

The increase in the number of points inside $V$ is then:

$$\frac{dn_v}{dt} = \frac{d}{dt}\left(n \int_V dQ\, dP\, \rho(Q, P)\right) = n \int_V dQ\, dP\, \frac{\partial \rho(Q, P)}{\partial t} \tag{1.1.7}$$

On the other hand, the increase in the number of points is accompanied by a flux of points

through the surface $\sigma$ of volume $V$:

$$\frac{dn_v}{dt} = -\oint_\sigma n\rho\vec{v}\cdot d\vec{\sigma} \tag{1.1.8}$$

where $d\vec{\sigma}$ is the infinitesimal surface element, $\vec{v}$ is the velocity (a $6N$-dimensional vector, $(Q,P)$), and $n\rho$ is the number of microstates at point $(Q,P)$. Using Gauss's theorem, we obtain:

$$\frac{dn_v}{dt} = -n\int_V \frac{\partial\rho}{\partial t}dQ\,dP = n\int_V dQ\,dP\,\nabla\cdot(\rho\vec{v}) \tag{1.1.9}$$

which finally gives:

$$\frac{\partial\rho}{\partial t} + \nabla\cdot(\rho\vec{v}) = 0 \tag{1.1.10}$$

Using:

$$\begin{aligned}\nabla\cdot(\rho\vec{v}) &= \sum_{i=1}^{3N}\left\{\frac{\partial}{\partial q_i}(\rho\dot{q}_i) + \frac{\partial}{\partial p_i}(\rho\dot{p}_i)\right\} \\ &= \sum_{i=1}^{3N}\left\{\frac{\partial\rho}{\partial q_i}\dot{q}_i + \frac{\partial\rho}{\partial p_i}\dot{p}_i\right\} + \rho\sum_{i=1}^{3N}\left\{\frac{\partial\dot{q}_i}{\partial q_i} + \frac{\partial\dot{p}_i}{\partial p_i}\right\} \\ &= \sum_{i=1}^{3N}\left\{\frac{\partial\rho}{\partial q_i}\dot{q}_i + \frac{\partial\rho}{\partial p_i}\dot{p}_i\right\}\end{aligned} \tag{1.1.11}$$

The last group of terms vanishes because, using the equations of motion:

$$\frac{\partial\dot{q}_i}{\partial q_i} = \frac{\partial^2 H(q_i,p_i)}{\partial q_i\partial p_i} = \frac{\partial^2 H(q_i,p_i)}{\partial p_i\partial q_i} = -\frac{\partial\dot{p}_i}{\partial p_i} \tag{1.1.12}$$

We recover Liouville's equation:

$$\frac{\partial\rho}{\partial t} + \sum_{i=1}^{3N}\left\{\frac{\partial\rho}{\partial q_i}\dot{q}_i + \frac{\partial\rho}{\partial p_i}\dot{p}_i\right\} = 0 \equiv \frac{d\rho}{dt} \tag{1.1.13}$$

We conclude:

- The local density of microstates, as seen by an observer moving with the flow of representative points, remains constant over time.
- If $\frac{\partial\rho}{\partial t} = 0$ and $\rho = \rho(E)$, the energy is conserved.

# 2 Average Values and the Ergodic Hypothesis

The measurement of a physical quantity $O(q,p)$ by a macroscopic observable is the time average:

$$\bar{O}^{(T)} = \lim_{T\to\infty} \frac{1}{T} \int_{t_0}^{t_0+T} O(q_{tr}(t), p_{tr}(t))\, dt \tag{1.2.1}$$

where $q_{tr}(t)$ is the value of $q$ along a specific trajectory in phase space.

In the limit $T \to \infty$, the average $\bar{O}^{(T)}$ simplifies to the probabilistic average:

$$\langle O \rangle = \int d^l q\, d^l p\, p(q,p)\, O(q,p) \tag{1.2.2}$$

with:

$$\int p(q,p)\, d^l q\, d^l p = 1 \tag{1.2.3}$$

The two averages coincide in the limit $T \to \infty$:

$$\bar{O}^{(T)} = \langle O \rangle \tag{1.2.4}$$

This is the property of ergodicity. The ergodic hypothesis relies on the following assumptions:

- $p(q,p)$ takes the same value for all trajectories with the same energy (and does not depend on the initial conditions of a trajectory).
- $p(q,p)$ is uniform on the energy surface $H(q,p) = E$.

The justification for the equality (1.2.4) relies on the assumption that the process quickly loses memory of its past history, over a typical time scale $\tau_c$, which is the correlation time of the process.

# 3 Statistical Entropy

In thermodynamics, entropy is a state function that determines the macroscopic properties of a system at equilibrium. In other words, this function contains all thermodynamic properties (equations of state, calorimetric coefficients, etc.). The concept of entropy plays a crucial role in statistical physics, which is inherently probabilistic. Thus, there is a lack of information about the system's state, measured by entropy.

## 3.1 Boltzmann Entropy

The ergodic principle states that the equilibrium condition of a system is that all classical configurations permitted by conservation laws (the points $(p, q)$ in the accessible phase space) are equiprobable.

The number of accessible microstates for a macroscopic system is called the statistical weight. Intuitively, entropy is related to the number of accessible states: the more states, the higher the entropy. However, the number of states multiplies, whereas extensive entropy adds. A simple example is two particles that can be in $N_1$ and $N_2$ states, respectively; the system of two particles then has $N_1 \cdot N_2$ accessible states. To obtain an extensive quantity, we define:

$$S = k_B \ln(W)$$

where $W$ is the number of accessible microscopic states, and $k_B$ is Boltzmann's constant, which determines the temperature scale. If $k_B = 1$, $S$ is dimensionless, and temperature has the same dimension as energy. This is the same constant appearing in the ideal gas law $pV = Nk_BT$.

## 3.2 Entropy as a Measure of Missing Information

Consider a set of microstates $\{e_i\}$ where $i \in \{1, ..., W\}$. Each microstate has a probability $P_i$ with $0 \leq P_i \leq 1$ and $\sum_i P_i = 1$ for all $i$.

$W$ is the volume of the accessible phase space, as it represents the number of microstates (number of points). In quantum mechanics, $W$ is the degeneracy of the system's state. $S = \ln W$ measures our lack of knowledge about the system's microscopic state. At equilibrium, all possible configurations are equiprobable, with probability $P_i = \frac{1}{W}$.

We see that entropy $S = \ln W = \sum_i f_i$, where:

$$f_i = \begin{cases} -\frac{1}{W} \ln\left(\frac{1}{W}\right) & \text{for an allowed configuration } i \\ 0 & \text{for a configuration outside } W \end{cases}$$

We generalize the definition of $S$ as follows:

$$S = -\sum_i P_i \ln(P_i)$$

where $P_i$ is the probability of the system being in state $i$.

**Properties:**

1. It is easy to verify (exercise) that $S_{1+2} = S_1 + S_2$: $S$ defined this way is additive.
2. The maximum of $S$ (second law: $S \to S_{\max}$) is achieved when $P_i = \frac{1}{W}$: equiprobability of allowed configurations.
3. The minimum of $S$: $S$ vanishes when one of the probabilities $P_i = 1$, i.e., the event is certain. This value is a minimum, meaning the information is complete (no missing information).

## 3.3 Remarks on the Two Definitions of $S$

**Classical (Continuous) Version:**

$$S = \ln(W)$$

This entropy can be negative. It is also defined up to an additive constant (depending on the unit of volume in phase space).

**Quantum (Discrete) Version:**

$$S = -\sum_i p_i \ln p_i$$

$S$ is always non-negative (since $0 \leq p_i \leq 1$). It is uniquely defined.

**Relation Between the Two Definitions:**

Consider the probability density $P(p, q)$ of finding the system in state $(p, q)$. We discretize phase space:

The probability of being in a cell is $p_i = P(p, q) \cdot h^N$ (dimensionless), where $N$ is half the dimension of phase space. Thus:

$$-\sum_i p_i \ln p_i \to -\int d\Omega \cdot P(p, q) \cdot \ln\left(P(p, q) \cdot h^N\right) = -\langle \ln P(p, q) \rangle - N \ln h$$

If $P(p, q) =$ constant (within an energy window $\Delta E$), we recover the first definition $S = \ln W$. The replacement of the integral by the sum (or vice versa) is exact in the limit

$h \to 0$. Note that $S$ defined this way becomes positive in this limit because we add $-N \ln h \underset{h\to 0}{\to} +\infty$.

In quantum mechanics, there is a minimal scale for the variation of the probability distribution $P(p, q)$, related to the uncertainty principle:

$$\Delta p \Delta x \gtrsim h$$

The minimal volume cannot be smaller than $h$, implying that entropy is positive.

# 4 Application Exercises

## Exercise 1:

Assume that the entropy $S$ and the statistical weight $\Omega$ of a physical system are related by an arbitrary functional form:

$$S = f(\Omega) \tag{1.4.1}$$

Show that the additivity of $S$ and the multiplicativity of $\Omega$ necessarily imply that the functional $f(\Omega)$ is written as:

$$S = k \ln \Omega \tag{1.4.2}$$

**Solution:** We have:

$$S = S_1 + S_2 = f(\Omega_1, \Omega_2) = f(\Omega_1) + f(\Omega_2) \tag{1.4.3}$$

which gives:

$$\frac{dS}{d\Omega_1} = \Omega_2 f'(\Omega_1, \Omega_2) = f'(\Omega_1) + \frac{df(\Omega_2)}{d\Omega_1} = f'(\Omega_1) \tag{1.4.4}$$

since $\Omega_1$ and $\Omega_2$ are independent, and:

$$\frac{dS}{d\Omega_2} = \Omega_1 f'(\Omega_1, \Omega_2) = f'(\Omega_2) \tag{1.4.5}$$

Thus:

$$f'(\Omega_1, \Omega_2) = \frac{f'(\Omega_1)}{\Omega_2} = \frac{f'(\Omega_2)}{\Omega_1} \tag{1.4.6}$$

or equivalently:

$$\Omega_1 f'(\Omega_1) = \Omega_2 f'(\Omega_2) \tag{1.4.7}$$

This equality holds only if:

$$\Omega_1 f'(\Omega_1) = k \tag{1.4.8}$$

which gives:

$$f(\Omega_1) = k \ln \Omega_1 \tag{1.4.9}$$

# Exercise 2:

Derive the following thermodynamic formulas:

$$V\left(\frac{\partial P}{\partial T}\right)_{\mu} = S \tag{1.4.10}$$

$$V\left(\frac{\partial P}{\partial \mu}\right)_{T} = N \tag{1.4.11}$$

**Solution:** We have:

$$d\Omega = -SdT - PdV - Nd\mu \tag{1.4.12}$$

and:

$$d\Omega = -PdV - VdP \tag{1.4.13}$$

which gives:

$$SdT + Nd\mu = VdP \tag{1.4.14}$$

For constant $\mu$, we obtain:

$$S = V\left(\frac{\partial P}{\partial T}\right)_{\mu} \tag{1.4.15}$$

For constant $T$, we obtain:

$$N = V\left(\frac{\partial P}{\partial \mu}\right)_{T} \tag{1.4.16}$$

# Exercise 3:

A system consists of $N$ independent particles that can occupy one of two energy states: $\varepsilon_0$ or $-\varepsilon_0$. Calculate the thermodynamic weight of states with energy $E = M\varepsilon_0$ ($M = -N, N$) and discuss the statistical properties of the system for $E < 0$. Derive the relation between temperature and energy, as well as the specific heat.

**Solution:** Let $N_-$ be the number of particles in the state with energy $-\varepsilon_0$ and $N_+$ the number in the state with energy $\varepsilon_0$. The total energy is:

$$E = M\varepsilon_0 = -N_-\varepsilon_0 + N_+\varepsilon_0; \quad M = N_+ - N_- \tag{1.4.17}$$

Since $N = N_+ + N_-$, we obtain:

$$N_- = \frac{1}{2}(N - M); \quad N_+ = \frac{1}{2}(N + M) \tag{1.4.18}$$

There are $N!/(N_-!N_+!)$ ways to choose the $N_-$ particles occupying the state with energy $-\varepsilon_0$, each corresponding to a distinct microscopic state of energy $E$. The thermodynamic weight is thus:

$$W = \frac{N!}{\left(\frac{1}{2}(N-M)\right)!\left(\frac{1}{2}(N+M)\right)!} \tag{1.4.19}$$

The system's entropy is given by:

$$S(E) = k \log W \tag{1.4.20}$$

Using Stirling's approximation, we obtain:

$$S(E) \simeq -k\left(N_- \log(N_-/N) + N_+ \log(N_+/N)\right) \tag{1.4.21}$$

The temperature is given by:

$$\frac{1}{T} = \frac{\partial S}{\partial \varepsilon_0} = \frac{\partial S}{\partial M}\frac{\partial M}{\partial \varepsilon_0} = \frac{1}{\varepsilon_0}\frac{\partial S}{\partial M} = \frac{k}{2\varepsilon_0}\log\frac{N-M}{N+M} \tag{1.4.22}$$

For $M > 0$, the energy is positive ($E > 0$), but the temperature is negative ($T < 0$), which is unphysical. Thus, we require $M < 0$ (i.e., $E < 0$). From (1.4.22), we have:

$$\frac{N_-}{N_+} = \frac{N-M}{N+M} = e^{2\varepsilon_0/kT} \tag{1.4.23}$$

The probabilities of finding a particle in the $-\varepsilon_0$ and $\varepsilon_0$ states are:

$$\frac{N_-}{N} = \frac{e^{2\varepsilon_0/kT}}{e^{\varepsilon_0/kT} + e^{-\varepsilon_0/kT}} \tag{1.4.24}$$

# Exercise 4:

Consider a classical ideal gas of $N$ identical, indistinguishable particles of mass $m$ in a volume $V$. The gas is described by the Hamiltonian:

$$H = \sum_{i=1}^{3N} \frac{P_i^2}{2m} \tag{1.4.25}$$

where $P_i$ are the momenta conjugate to the Cartesian coordinates of atom $i$.

1. Calculate the number of accessible microstates $\Omega_0(E)$.
2. Using $\Omega_0(E)$, derive the equation of state. (Note: The volume of a unit sphere in $n$-dimensional space is $C_n = \pi^{n/2}/\Gamma(n/2+1)$.)
3. Prove the equipartition theorem.

**Solution:** The number of states is given by:

$$\Omega_0(E,N,V) = \frac{1}{h^{3N}N!} \int_{\sum_{i=1}^{3N} P_i^2 \leq 2mE} dq_1 \dots dq_N \int dp_1 \dots dp_N \tag{1.4.26}$$

The position integral yields:

$$\int dq_1 \dots dq_N = V^N \tag{1.4.27}$$

The momentum integral equals the volume of a $3N$-dimensional sphere of radius $(2mE)^{1/2}$. Thus:

$$\Omega_0(E,N,V) = \frac{V^N}{h^{3N}N!} \frac{(2\pi mE)^{3N/2}}{\Gamma\left(\frac{3}{2}N+1\right)} \tag{1.4.28}$$

Using the entropy expression $S = k \log \Omega_0$ and Stirling's formula ($\log N! = N \log N - N$), we obtain:

$$S = Nk\left(\log\frac{V}{N} + \frac{3}{2}\log\frac{2E}{3N} + \log\frac{(2\pi m)^{3/2}}{h^3} + \frac{5}{2}\right) \tag{1.4.29}$$

From the relation:

$$P = T\left(\frac{\partial S}{\partial V}\right)_{E,N} = TNk/V \tag{1.4.30}$$

we obtain the ideal gas law:

$$PV = NkT \tag{1.4.31}$$

We also have:

$$\frac{1}{T} = \left(\frac{\partial S}{\partial E}\right)_{V,N} = \frac{3Nk}{E} \tag{1.4.32}$$

which gives:

$$E = \frac{3}{2}kT \tag{1.4.33}$$

## Exercise: Frenkel Defects

A perfect crystal consists of $N$ atoms regularly positioned on $N$ lattice sites. When an atom leaves its lattice site and occupies an interstitial position in the crystal, a **Frenkel defect** is formed: one vacancy and one interstitial atom.

The energy required to create a single Frenkel defect is $\varepsilon > 0$. Let $N_0$ denote the number of available interstitial sites in the crystal (assume $N$ and $N_0$ are of the same order of magnitude).

Consider a crystal with $n$ Frenkel defects, where $n \ll N$.

1. Compute the number of accessible microstates $\Omega(n)$ for the system assuming there are $n$ Frenkel defects.

2. Deduce the entropy $S(n)$ using Stirling's approximation.

3. Derive the microcanonical temperature $T^*$ of the system, defined by:

$$\frac{1}{T^*} = \left(\frac{\partial S}{\partial E}\right)_{E=n\varepsilon}$$

4. Show that the relation between $T^*$ and $n$ can be written as:

$$n \approx \sqrt{NN_0}\exp\left(-\frac{\varepsilon}{2kT^*}\right)$$

**Hint:** The number of accessible states can be computed as the number of ways of choosing $n$ vacancies among $N$ sites and $n$ occupied interstitial positions among $N_0$ sites:

$$\Omega(n) = \binom{N}{n}\binom{N_0}{n}$$

and the total energy is simply $E = n\varepsilon$.

# Solution: Frenkel Defects

**Problem Summary:** A crystal consists of $N$ atoms on lattice sites and $N_0$ interstitial sites. A Frenkel defect is created when an atom leaves its site and moves into an interstitial position, creating a vacancy and an interstitial atom. The energy to create one defect is $\varepsilon > 0$. The system has $n \ll N$ Frenkel defects. We are to:

- Calculate the number of accessible microstates $\Omega(n)$;
- Deduce the microcanonical temperature $T^*$;
- Show the relation:

$$n \approx \sqrt{N N_0} \exp\left(-\frac{\varepsilon}{2kT^*}\right).$$

## 1. Number of Microstates

To form $n$ Frenkel defects, we must:

- Choose $n$ atoms out of $N$ to leave their sites $\Rightarrow \binom{N}{n}$,
- Place those $n$ atoms into $n$ of the $N_0$ interstitial sites $\Rightarrow \binom{N_0}{n}$.

Thus, the number of accessible microstates is:

$$\Omega(n) = \binom{N}{n}\binom{N_0}{n}.$$

## 2. Entropy and Microcanonical Temperature

The entropy is:

$$S(n) = k \ln \Omega(n) = k\left[\ln\binom{N}{n} + \ln\binom{N_0}{n}\right].$$

Using Stirling's approximation ($\ln n! \approx n \ln n - n$), we write:

$$\ln\binom{N}{n} \approx N \ln N - n \ln n - (N-n)\ln(N-n),$$
$$\ln\binom{N_0}{n} \approx N_0 \ln N_0 - n \ln n - (N_0-n)\ln(N_0-n).$$

So the entropy becomes:

$$S(n) \approx k\left[-n \ln\left(\frac{n^2}{(N-n)(N_0-n)}\right) + N \ln N + N_0 \ln N_0 - (N-n)\ln(N-n) - (N_0-n)\ln(N_0-n)\right]$$

Now, using $n \ll N$, $n \ll N_0$:

$$(N-n) \approx N, \quad (N_0-n) \approx N_0 \Rightarrow \ln(N-n) \approx \ln N, \quad \ln(N_0-n) \approx \ln N_0.$$

So the leading-order expression simplifies:

$$S(n) \approx -2kn \ln\left(\frac{n}{\sqrt{NN_0}}\right).$$

## 3. Microcanonical Temperature

The total energy is:

$$E = n\varepsilon.$$

The microcanonical temperature $T^*$ is defined as:

$$\frac{1}{T^*} = \left(\frac{\partial S}{\partial E}\right) = \frac{1}{\varepsilon}\frac{dS}{dn}.$$

Using:

$$S(n) \approx -2kn \ln\left(\frac{n}{\sqrt{NN_0}}\right),$$

we differentiate:

$$\frac{dS}{dn} = -2k\left[\ln\left(\frac{n}{\sqrt{NN_0}}\right) + 1\right].$$

Thus:

$$\frac{1}{T^*} = \frac{1}{\varepsilon} \cdot \left(-2k\left[\ln\left(\frac{n}{\sqrt{NN_0}}\right) + 1\right]\right).$$

Invert to get:

$$T^* = -\frac{\varepsilon}{2k\left[\ln\left(\frac{n}{\sqrt{NN_0}}\right) + 1\right]}.$$

Now invert the expression to express $n$ in terms of $T^*$:

Let us ignore the additive $+1$ for an approximation (valid when $n$ is not too small). Then:

$$\ln\left(\frac{n}{\sqrt{NN_0}}\right) \approx -\frac{\varepsilon}{2kT^*} \Rightarrow \frac{n}{\sqrt{NN_0}} = \exp\left(-\frac{\varepsilon}{2kT^*}\right),$$

which gives the final result:

$$n \approx \sqrt{NN_0}\exp\left(-\frac{\varepsilon}{2kT^*}\right).$$

# Exercise: Electrons Trapped on Sites

## System Description

We consider a solid with $N$ distinguishable lattice sites and $N$ indistinguishable electrons. Each site can host:

- One electron with spin $\uparrow$, energy $\varepsilon_\uparrow = \varepsilon_0$
- One electron with spin $\downarrow$, energy $\varepsilon_\downarrow = \varepsilon_0$
- A pair of electrons ($\uparrow\downarrow$), energy $\varepsilon_{\uparrow\downarrow} = 2\varepsilon_0 + g$

$\varepsilon_0 < 0$ and $g > 0$. Sites can also be empty.

We denote:

$n_0 =$ number of empty sites, $\quad n_1 =$ number of singly-occupied sites, $\quad n_2 =$ number of doubly-occupied

By conservation:

$$n_0 + n_1 + n_2 = N \qquad (1)$$

$$n_1 + 2n_2 = N \qquad (2) \quad \text{(since there are } N \text{ electrons total)}$$

## Solving for $n_0$, $n_1$, and $n_2$

Subtracting (2) from (1):

$$(n_0 + n_1 + n_2) - (n_1 + 2n_2) = 0 \Rightarrow n_0 = n_2$$

From (1), using $n_0 = n_2$:

$$n_2 + n_1 + n_2 = N \Rightarrow n_1 = N - 2n_2$$

Hence:

$$n_0 = n_2, \quad n_1 = N - 2n_2$$

## Energy of the system

Each singly occupied site contributes $\varepsilon_0$, each doubly occupied site contributes $2\varepsilon_0 + g$:

$$E = n_1\varepsilon_0 + n_2(2\varepsilon_0 + g)$$

Using $n_1 = N - 2n_2$:

$$E = (N - 2n_2)\varepsilon_0 + n_2(2\varepsilon_0 + g) = N\varepsilon_0 + n_2 g$$

**Hence:**

$$E = N\varepsilon_0 + n_2 g \quad (3)$$

## Accessible energy range

**Minimum:** All electrons singly occupied $\Rightarrow n_2 = 0$:

$$E_{\min} = N\varepsilon_0$$

**Maximum:** All sites doubly or empty $\Rightarrow n_2 = \frac{N}{2}$:

$$E_{\max} = N\varepsilon_0 + \frac{N}{2}g$$

## Number of microstates $\Omega(E)$

Electrons are indistinguishable, sites are distinguishable.

- Choose $n_2$ sites to be doubly occupied: $\binom{N}{n_2}$ - From remaining $N - n_2$ sites, choose $n_1$ singly occupied: $\binom{N-n_2}{n_1}$ - For each singly occupied site, spin $\uparrow$ or $\downarrow$: $2^{n_1}$

Since $n_1 = N - 2n_2$:

$$\Omega(E) = \binom{N}{n_2}\binom{N - n_2}{N - 2n_2}2^{N-2n_2}$$

## Microcanonical Entropy and Temperature

Entropy:

$$S(E) = k \ln \Omega(E)$$

Temperature:

$$\frac{1}{T^*} = \left(\frac{\partial S}{\partial E}\right)_N = \frac{1}{g}\left(\frac{\partial S}{\partial n_2}\right) \quad (\text{since } E = N\varepsilon_0 + n_2 g)$$

Using Stirling's approximation:

$$\ln \binom{a}{b} \approx a\ln a - b\ln b - (a-b)\ln(a-b)$$

we find:

$$\frac{1}{T^*} = \frac{k}{g}\ln\left(\frac{(N-n_2)^2}{4n_2(N-2n_2)}\right) \Rightarrow n_2 = \frac{(N-n_2)^2}{4(N-2n_2)}e^{-g/kT^*}$$

## Plots and Physical Interpretation

Let $x = n_2/N$:

- $\Omega(E)$ has a maximum when $n_2$ is intermediate - $S^*(E)$ is concave as a function of $E$ - $\beta^*(E) = \frac{1}{T^*}$ decreases with $E$ since adding energy increases the number of doubly occupied sites - $T^*(E)$ increases with $E$

## Occupation numbers as functions of $T^*$

From $T^*(E)$ and $n_2(E)$, we deduce:

$$n_2(T^*), \quad n_1 = N - 2n_2, \quad n_0 = n_2$$

We can plot:

$$n_2(T^*) : \text{increasing with } T^*, \quad n_1(T^*) : \text{decreasing}$$

# Exercise 3, Problem 3

## Principal Elections on Sites

### States of a Site:

Each site can be in one of three states:

| State | Energy |
|---|---|
| (0) Unoccupied | 0 |
| (1) One actor | $\varepsilon_0$ |
| (2) Two actors | $2\varepsilon_0 + g$ |

### (1) Energy and Constraints:

Let: - $n_0$: number of sites in state (0), - $n_1$: number of sites in state (1), - $n_2$: number of sites in state (2), - $N$: total number of actors (not sites), - $\mathcal{N}$: total number of sites.

Then the total energy is:

$$E = n_1\varepsilon_0 + n_2(2\varepsilon_0 + g)$$

Total number of actors:

$$N = n_1 + 2n_2$$

Total number of sites:

$$\mathcal{N} = n_0 + n_1 + n_2$$

Energy relative to ground level:

$$E - N\varepsilon_0 = n_2 g$$

We can express:

$$n_1 = N - 2n_2, \quad n_0 = \mathcal{N} - n_1 - n_2$$

Boundaries:

$$\text{If } n_2 = 0 \Rightarrow E_{\min} = N\varepsilon_0$$

$$\text{If } n_1 = 0 \Rightarrow n_2 = N/2 \Rightarrow E_{\max} = N\varepsilon_0 + \frac{N}{2}g$$

**(2) Microstate Counting:**

Each site in state (1) has two configurations (e.g., spin), hence a factor $2^{n_1}$. The number of ways to distribute $n_0$, $n_1$, and $n_2$ among $\mathcal{N}$ sites is:

$$\Omega(E) = 2^{n_1} \cdot \frac{\mathcal{N}!}{n_0!\, n_1!\, n_2!}$$

Using the constraint $n_0 = \mathcal{N} - n_1 - n_2$, we can write:

$$\Omega(E) = 2^{n_1} \cdot \frac{\mathcal{N}!}{(\mathcal{N} - n_1 - n_2)!\, n_1!\, n_2!}$$

Or alternatively, in terms of $N$, replacing $n_1 = N - 2n_2$, we get:

$$\Omega(E) = 2^{N-2n_2} \cdot \frac{\mathcal{N}!}{(\mathcal{N} - N + n_2)!\, (N - 2n_2)!\, n_2!}$$

**(3) Thermodynamic Quantities:**

Entropy (Boltzmann's definition):

$$S^* = k \log \Omega(E)$$

Inverse temperature:

$$\beta^* = \frac{1}{kT} = \frac{1}{k} \frac{\partial S^*}{\partial E}$$

Using Stirling's approximation:

$$\log \Omega(E) \approx n_1 \log 2 + \log(\mathcal{N}!) - \log(n_0!) - \log(n_1!) - \log(n_2!)$$

But since $\mathcal{N}$ is fixed and we are differentiating with respect to $E$, only the terms depending on $n_1$ and $n_2$ vary:

$$\frac{\partial \log \Omega}{\partial E} \approx (\log 2 - \log n_1) \frac{dn_1}{dE} - \log n_2 \cdot \frac{dn_2}{dE}$$

From:

$$n_1 = N - 2n_2, \quad E = N\varepsilon_0 + n_2 g \Rightarrow \frac{dn_2}{dE} = \frac{1}{g}, \quad \frac{dn_1}{dE} = -\frac{2}{g}$$

Then:

$$\beta^* = \frac{1}{k}\left[(\log 2 - \log n_1)\left(-\frac{2}{g}\right) - \log n_2 \cdot \frac{1}{g}\right]$$

$$= \frac{1}{gk}\left[2\log n_1 - 2\log 2 - \log n_2\right] = \frac{1}{gk}\left[\log\left(\frac{n_1^2}{4n_2}\right)\right]$$

So:

$$\beta^* = \frac{1}{gk}\log\left(\frac{n_1^2}{4n_2}\right) \Rightarrow T = \frac{gk}{\log\left(\frac{n_1^2}{4n_2}\right)}$$

Alternative expression:

$$\beta^* = \frac{2}{gk}\log\left(\frac{n_1}{2n_2}\right), \quad T = \frac{gk}{2\log\left(\frac{n_1}{2n_2}\right)}$$

**(4) Occupation Numbers as Functions of Energy:**

From:

$$E = N\varepsilon_0 + n_2 g \Rightarrow n_2 = \frac{E - N\varepsilon_0}{g}$$

$$n_1 = N - 2n_2 = N - 2\cdot\frac{E - N\varepsilon_0}{g} = N\left(1 + 2\frac{\varepsilon_0}{g}\right) - 2\cdot\frac{E}{g}$$

# Chapter 2

# Isolated Systems at Equilibrium

The fundamental idea of statistical physics is that during a measurement, each microscopic state or fluctuation that can occur is actually an average over all possible microscopic states. To understand this concept, we need to define what we mean by the probability or distribution of microscopic states. We make the following hypothesis about many-body systems: For an isolated system with fixed total energy and size (volume $V$ and particle number $N$), all microscopic states are equally probable at thermodynamic equilibrium. We postulate that the phase space density is uniform in the accessible region of phase space.

## 1 Statistical Ensemble

Consider a collection of N replicas of the same system prepared under identical initial conditions. The limit $N \to \infty$ constitutes a statistical ensemble. If the system is completely isolated, it is characterized by the microcanonical ensemble.

## 2 Microcanonical Distribution and Partition Function

In the microcanonical ensemble, it is more practical to consider that $E$ lies in the interval between $E$ and $E + \delta E$. At equilibrium, all microstates are equally probable with probability $Pd\Gamma = \rho_m(q,p)d\Gamma/Z_m$, where $Z_m$ is a constant representing the number of accessible microstates where $p$ and $q$ satisfy $E \leq H(p,q) \leq E + \delta E$. These states have

equal statistical weight:

$$\rho_m(\Gamma) = \begin{cases} C & \text{if } E < H(\Gamma) < E + \delta E \\ 0 & \text{otherwise.} \end{cases}$$

The triplet (N, E, V) represents the fixed parameters or independent variables of the microcanonical ensemble.

The dimension of the constant $C$ is determined by: $\rho_m(\Gamma)$ is a density in phase space, and $\int \rho_m(\Gamma) d\Gamma$ is dimensionless. Therefore: $[C] = (Js)^{-3N}$ since $[d\Gamma] = (Js)^{3N}$. It represents the number of microstates per unit volume in phase space. A quantum microstate with $N$ particles occupies a phase space volume of $N!h^{3N}$, where the $N!$ factor accounts for particle indistinguishability. Thus:

$$C = \frac{1}{N!h^{3N}}$$

The partition function $Z_m$ becomes:

$$Z_m = \int_{E<H(\Gamma)<E+\delta E} \rho_m(\Gamma) d\Gamma = \frac{1}{N!h^{3N}} \int_{E<H(\Gamma)<E+\delta E} d\Gamma$$

## 2.1 Application Examples

**Example 1:** For a 1D harmonic oscillator with Hamiltonian:

$$H(x,p) = \frac{p^2}{2m} + \frac{1}{2}m\omega^2 x^2$$

the microcanonical partition function is:

$$Z_m = \frac{2\pi\delta E}{h\omega}$$

**Example 2:** For an ideal classical gas of $N$ identical particles with Hamiltonian:

$$H = \sum_{i=1}^{3N} \frac{p_i^2}{2m}$$

the microcanonical partition function is:

$$Z_m(N,V,E) = \frac{V^N}{N!h^{3N}} \left(\frac{2\pi mE}{h^2}\right)^{(3N/2)} \frac{1}{(3N/2)!} \frac{3N}{2} \frac{\delta E}{E}$$

# 3 Supplementary Exercises

## Exercise 4: Quantum Microcanonical Ensemble (Intermediate)

**Problem:** Consider a quantum system with discrete energy levels $E_n = n\hbar\omega$ ($n = 0, 1, 2, ...$).

1. Calculate the number of microstates $\Omega(E)$ for energy $E = M\hbar\omega$.
2. Derive the entropy $S(E)$ and temperature $T$.
3. Compare with the classical harmonic oscillator result.

**Solution:**

1. $\Omega(E)$ equals the number of ways to distribute $M$ quanta:

$$\Omega(E) = \binom{M+N-1}{M} \approx \frac{(M+N)^M}{M!} \quad (\text{for } N \gg 1)$$

2. Entropy and temperature:

$$S(E) = k_B \ln \Omega \approx k_B \left[M \ln\left(1+\frac{N}{M}\right) + N \ln\left(1+\frac{M}{N}\right)\right]$$

$$\frac{1}{T} = \frac{\partial S}{\partial E} = \frac{k_B}{\hbar\omega} \ln\left(1+\frac{N}{M}\right)$$

3. Classical limit ($M \gg N$): Recovers $E = Nk_BT$.

## Exercise 5: Relativistic Ideal Gas (Advanced)

**Problem:** For a relativistic gas with $\epsilon = cp$:

1. Show that the microcanonical partition function scales as $Z_m \propto V^N E^{3N}$.
2. Derive the equation of state $PV = \frac{1}{3}U$.

3. Compute the heat capacity at constant volume.

**Solution:**

1. Phase space volume scales as $p^{3N} \Rightarrow Z_m \propto V^N \int_0^{\sqrt{E^2/c^2}} p^{3N-1} dp$.

2. Pressure:
$$P = \frac{U}{3V} \quad (\text{from } dS = \frac{1}{T}dE + \frac{P}{T}dV)$$

3. $C_V = 3Nk_B$ (ultra-relativistic case).

## Exercise 6: Interacting Spins (Expert)

**Problem:** For the Ising model with Hamiltonian $H = -J\sum_{\langle ij \rangle} \sigma_i \sigma_j$ ($\sigma_i = \pm 1$):

1. Calculate $\Omega(E)$ for a 1D chain of $N$ spins.

2. Show that entropy $S(E)$ is non-analytic at $E = -NJ$.

3. Interpret this result in terms of phase transitions.

**Solution:**

1. $\Omega(E) = 2\binom{N}{k}$ where $k = (NJ - E)/2J$.

2. Entropy has a kink at ground state ($E = -NJ$).

3. Indicates a zero-temperature phase transition.

## Exercise 7: Gravitational System (Challenging)

**Problem:** For $N$ particles interacting via $V(r) = -GM^2/r$:

1. Show that the microcanonical partition function diverges.

2. Propose a regularization method using a cutoff $\Lambda$.

3. Discuss the thermodynamic limit $N \to \infty$.

**Solution:**

1. Divergence arises from $r \to 0$ in $\int d^{3N}r$.

2. Regularized version:
$$Z_m \propto \int_{\Lambda}^{R} \frac{r^{3N-1}dr}{r^{N(N-1)/2}}$$

3. Thermodynamic limit requires careful scaling of $G$.

# Chapter 3

# Statistical Ensembles at Equilibrium

## 1 Introduction

In the *microcanonical ensemble*, each system has $N$ molecules, a volume $V$, and energy between $E$ and $E + \delta E$. For a non-isolated system in contact with a thermal reservoir at temperature $T$ and in thermal equilibrium, which ensemble is appropriate?

The answer is the *canonical ensemble*, where the temperature is fixed by the reservoir, while the system's energy fluctuates.

## 2 Canonical Distribution and Partition Function

Consider a system $\Sigma$ immersed in a large reservoir $R$. At equilibrium, both share a fixed temperature $T$, but their energies vary between 0 and $E^{(0)}$, where $E^{(0)}$ is the total energy of the combined system $A^0 = R + \Sigma$. If $E_\Sigma$ and $E_r$ are the instantaneous energies of $\Sigma$ and $R$, respectively:

$$E_\Sigma + E_r = E^{(0)} = \text{constant}.$$

Since $R \gg \Sigma$, we have:

$$\frac{E_\Sigma}{E^{(0)}} = 1 - \frac{E_r}{E^{(0)}} \ll 1.$$

The probability $P_i$ of finding $\Sigma$ in a state with energy $E_i$ is:

$$P_i \propto \Omega(E_r) = \Omega(E^{(0)} - E_i),$$

where $\Omega(E_r)$ is the number of reservoir states with energy $E_r$. Expanding $\ln \Omega(E_r)$ around $E_r = E^{(0)}$ (i.e., $E_i = 0$):

$$\ln \Omega(E_r) = \text{const} - \beta E_i + \cdots ,$$

with $\beta = \frac{1}{k_B T}$. Normalizing $\sum_i P_i = 1$, we obtain the canonical distribution:

$$P_i = \frac{e^{-\beta E_i}}{\sum_i e^{-\beta E_i}}.$$

The normalization factor is the **canonical partition function**:

$$Z = \sum_i e^{-\beta E_i}.$$

For continuous systems, the probability density of a microstate $\{p, q\}$ is:

$$\rho(p, q)\, dp\, dq = \frac{1}{Z} \frac{1}{h^{3N} N!} e^{-\beta H(p,q)}\, dp\, dq,$$

leading to the continuous partition function:

$$Z = \frac{1}{h^{3N} N!} \int e^{-\beta H(p,q)}\, dp\, dq.$$

# 3 Thermodynamic Quantities in the Canonical Ensemble

The partition function $Z$ encodes all thermodynamic information. Key quantities include:

- **Average energy**:
$$\langle E \rangle = -\frac{\partial}{\partial \beta} \ln Z.$$
- **Entropy**:
$$S = k_B \left( \ln Z + \beta \langle E \rangle \right).$$
- **Helmholtz free energy** $F = -k_B T \ln Z$, from which we derive:
$$S = -\left( \frac{\partial F}{\partial T} \right)_{N,V}, \quad P = -\left( \frac{\partial F}{\partial V} \right)_{N,T}, \quad \mu = \left( \frac{\partial F}{\partial N} \right)_{V,T}.$$

### Example: Classical Ideal Gas

For $N$ non-interacting particles with Hamiltonian $H = \sum_i \frac{p_i^2}{2m}$, the partition function is:

$$Z(\beta, N) = \frac{V^N}{N!\Lambda^{3N}}, \quad \text{where} \quad \Lambda = \frac{h}{\sqrt{2\pi m k_B T}}.$$

# 4 Application Exercises

### Exercise 1: Entropy in the Canonical Ensemble

Show that the entropy $S$ can be expressed as:

$$S = -k_B \sum_s \rho_s \ln \rho_s, \quad \rho_s = \frac{e^{-\beta E_s}}{Z}.$$

**Solution** : Using $F = -k_B T \ln Z$ and $S = -\left(\frac{\partial F}{\partial T}\right)_{N,V}$, we derive:

$$\begin{aligned}
S = \left(\frac{\partial F}{\partial T}\right)_{N,V} &= k_B \frac{\partial}{\partial T}(T \ln Z) \\
&= k_B \ln Z + \frac{k_B T}{Z}\frac{\partial Z}{\partial T} \\
&= k_B \ln Z + \frac{k_B T}{Z}\left(\frac{1}{k_B T^2}\sum_s E_s e^{-E_s/k_B T}\right) \\
&= \frac{k_B}{Z}\left(Z \ln Z + \frac{1}{k_B T}\sum_s E_s e^{-E_s/k_B T}\right) \\
&= -\frac{k_B}{Z}\sum_s e^{-E_s/k_B T}\left(\ln \frac{1}{Z} - \frac{E_s}{k_B T}\right) \\
&= -k_B \sum_s \rho_s \ln\left(\frac{e^{-E_s/k_B T}}{Z}\right) \\
&= -k_B \sum_s \rho_s \ln \rho_s
\end{aligned}$$

## Exercise [2]: (Exam from October 25, 2011, Physics Degree L3 PAPP, University of Paris-Sud 11)

In an orthonormal frame $(\vec{i}, \vec{j}, \vec{k})$, we study an ideal gas subjected to gravity $\vec{g} = -g\vec{k}$. The gas is composed of $N$ point-like, identical, indistinguishable molecules of mass $m$. It

is confined in a cylindrical box of cross-section $S$ and height $L$, hence volume $V = S \times L$, in contact with a thermostat at temperature $T$. The Hamiltonian of a single molecule is:

$$H_1 = \frac{P^2}{2m} + mgz$$

1- What is the dimension of the phase space for $N = 1$?

2- What is the volume of an elementary phase space cell?

3- What are the macroscopic quantities defining a macroscopic state for this one-molecule system?

4- Deduce the canonical state density $\rho$ in terms of the macroscopic quantities.

5- Compute the partition function of the system $z(1, V, T)$. Show that it can be written as:

$$z(1, V, T) = \frac{V}{\Lambda^3} \left( \frac{1 - e^{-\beta mgL}}{\beta mgL} \right)$$

where $\beta = 1/(k_B T)$ and $\Lambda$ is the thermal wavelength defined by

$$\Lambda = \frac{h}{\sqrt{2\pi m k_B T}}$$

6- Give a simple expression to compute $E(1, V, T)$, the mean internal energy of the one-particle system, from $z(1, V, T)$, and then calculate it.

Now consider an ideal gas composed of $N$ molecules in volume $V = S \times L$, at temperature $T$.

2.1- What is the dimension of the phase space for $N$ particles?

2.2- Justify that the partition function $Z(N, V, T)$ can be written in terms of the single-particle partition function as:

$$Z(N, V, T) = \frac{1}{N!} z(1, V, T)^N$$

2.3- Compute the energy of the system and show that it is written as:

$$E(N, V, T) = \frac{3}{2} N k_B T + N k_B T \left( 1 - \frac{\beta mgL}{e^{\beta mgL} - 1} \right)$$

2.4- Decompose this energy into kinetic and potential parts using the equipartition theorem, then comment on the result.

2.5- Explain, without calculation, when the gravitational effect can be neglected.

**Solution:**

1- The phase space has dimension 6.

2- The volume of an elementary phase space cell is $h^3$.

3- The macroscopic quantities are $N$, $V$, and $T$.

4- The canonical state density is:

$$\rho = \frac{1}{h^3} e^{-\beta p^2/2m} e^{-\beta mgz}$$

5- The partition function is:

$$\begin{aligned} z(1,V,T) &= \frac{1}{h^3}\int_C \rho(\tau)d\tau \\ &= \frac{1}{h^3}\int_S dxdy \int_0^L dz e^{-\beta mgz} \int d^3p\, e^{-\beta p^2/2m} \\ &= \frac{S}{\Lambda^3}\cdot\frac{1-e^{-\beta mgL}}{\beta mg} \\ &= \frac{V}{\Lambda^3}\left(\frac{1-e^{-\beta mgL}}{\beta mgL}\right) \end{aligned}$$

6- The internal energy is:

$$\begin{aligned} E(1,V,T) &= -\frac{\partial}{\partial\beta}\ln z(1,V,T) \\ &= \frac{3}{2}k_BT + k_BT\left(1-\frac{\beta mgL}{e^{\beta mgL}-1}\right) \end{aligned}$$

2.1- The dimension of the phase space is $6N$.

2.2- The full partition function is:

$$Z(N,V,T) = \frac{1}{N!}z(1,V,T)^N$$

2.3- The energy is:

$$E(N,V,T) = \frac{3}{2}Nk_BT + Nk_BT\left(1 - \frac{\beta mgL}{e^{\beta mgL}-1}\right)$$

2.4- Using equipartition:

$$E(N,V,T) = E_c + E_p = \left\langle \sum_i \frac{p_i^2}{2m} \right\rangle + \left\langle \sum_i mgz_i \right\rangle$$

We find:

$$E_c = \frac{3}{2}Nk_BT \quad \text{and} \quad E_p = Nk_BT\left(1 - \frac{\beta mgL}{e^{\beta mgL}-1}\right)$$

The kinetic part agrees with the equipartition theorem.

2.5- The gravitational effect is negligible when $\beta mgL \ll 1$, i.e., $mgL \ll k_BT$. Thus, gravity can be neglected at high temperatures.

## Exercise 3: Two-Level System with Translational Degrees (Advanced)

For $N$ particles with internal states (ground state $E = 0$, degeneracy $g_1$; excited state $E$, degeneracy $g_2$), show that:

$$Z(N,V,T) = \frac{V^N}{N!\Lambda^{3N}}\left(g_1 + g_2e^{-\beta E}\right)^N.$$

Compute the heat capacity $C_V$ and analyze its low-temperature behavior.

**Solution** : At low $T$, $C_V \approx \frac{3}{2}Nk_B$, as only the ground state is populated.

## Exercise 4: Quantum Particles in a 1D Box (Research-Level)

For $N$ indistinguishable particles in a box of length $a$:

1. Derive the quantum partition function $Z(T,N,a)$ using single-particle levels $\varepsilon_n = \frac{\pi^2\hbar^2n^2}{2ma^2}$.

2. Show that at low $T$, $F \approx Nk_BT\ln N + \frac{N\pi^2\hbar^2}{2ma^2}$.

3. For quasi-continuous levels, approximate $Z$ via Gaussian integrals.

**Key Insight** : The discrete-to-continuum transition highlights the role of quantum statistics in small systems.

## Exercise 5: Non-Ideal Gas with Pair Interactions (Bonus)

For particles interacting via $U(r^N) = \sum_{i<j} u(r_{ij})$, show that the partition function generalizes to:

$$Z(N, V, T) = \frac{1}{N!\Lambda^{3N}} \int e^{-\beta U(r^N)} \, d^N r.$$

Discuss the challenges in evaluating this for realistic potentials (e.g., Lennard-Jones).

# Chapter 4

# Systems of Independent and Indistinguishable Particles

## 0.1 Bosons and Fermions

In nature, particles are classified based on their spin angular momentum projection $S_z$ along the $OZ$ axis:

- **Bosons**: Integer spin $S = n\hbar$ ($n \in \mathbb{N}$). Their wavefunctions are symmetric under particle exchange (symmetrization postulate). Examples: photons, Helium-4 atoms.
- **Fermions**: Half-integer spin $S = (n+1/2)\hbar$. Their wavefunctions are antisymmetric (antisymmetrization postulate), leading to the Pauli exclusion principle: no two fermions can occupy the same quantum state simultaneously. Examples: electrons, protons.

## 0.2 Canonical Ensemble Challenges

For indistinguishable particles, microstates are uniquely described by occupation numbers $n_\lambda$ of single-particle states $\lambda$, constrained by $\sum_\lambda n_\lambda = N$. The canonical partition function becomes:

$$Z_c = \sum_{\{\lambda_j\}} g(\{n_\lambda\}, N) e^{-\beta \sum_{j=1}^{N} \varepsilon_{\lambda_j}}, \tag{4.0.1}$$

where $g(\{n_\lambda\}, N)$ accounts for indistinguishability. Unlike distinguishable particles, $Z_c$ cannot be factorized due to $g(\{n_\lambda\}, N)$'s dependence on occupation numbers. This motivates the grand canonical ensemble.

# 1 Grand Canonical Ensemble

The grand canonical ensemble describes systems exchanging energy and particles with a reservoir at fixed temperature $T$ and chemical potential $\mu$. Key relations:

- **Grand partition function**:

$$Z_{gc}(T, \mu, V) = \sum_{N=0}^{\infty} e^{\beta\mu N} Z_c(T, N, V). \tag{4.1.1}$$

- **Grand potential**:

$$\Phi(T, \mu, V) = -k_B T \ln Z_{gc}. \tag{4.1.2}$$

## 1.1 Derivation

For a system $\Sigma$ coupled to a reservoir $R$:

$$E_{\text{tot}} = E_\Sigma + E_R = \text{constant}, \tag{4.1.3}$$

$$N_{\text{tot}} = N_\Sigma + N_R = \text{constant}. \tag{4.1.4}$$

The probability $P_{\Sigma,i}$ of finding $\Sigma$ in state $i$ with energy $E_i$ and particle number $N_i$ is:

$$P_{\Sigma,i} \propto \Omega(N^{(0)} - N_i, E^{(0)} - E_i), \tag{4.1.5}$$

Expanding $\ln \Omega$ around $(N^{(0)}, E^{(0)})$:

$$\ln \Omega \approx \text{const} + \beta\mu N_i - \beta E_i, \tag{4.1.6}$$

yielding the grand canonical distribution:

$$P_{\Sigma,i} = \frac{e^{-\beta(E_i - \mu N_i)}}{Z_{gc}}. \tag{4.1.7}$$

# 2 Quantum Statistics

## 2.1 Fermi-Dirac Statistics

For fermions ($n_\lambda \in \{0, 1\}$):

$$Z_\lambda = 1 + e^{-\beta(\varepsilon_\lambda - \mu)}, \tag{4.2.1}$$

$$\langle n_\lambda \rangle = \frac{1}{e^{\beta(\varepsilon_\lambda - \mu)} + 1}. \tag{4.2.2}$$

## 2.2 Bose-Einstein Statistics

For bosons ($n_\lambda \in \mathbb{N}$):

$$Z_\lambda = \frac{1}{1 - e^{-\beta(\varepsilon_\lambda - \mu)}} \quad (\varepsilon_\lambda > \mu), \tag{4.2.3}$$

$$\langle n_\lambda \rangle = \frac{1}{e^{\beta(\varepsilon_\lambda - \mu)} - 1}. \tag{4.2.4}$$

## 2.3 Classical Limit

At high $T$ or low density ($\langle n_\lambda \rangle \ll 1$), both statistics reduce to Maxwell-Boltzmann:

$$\langle n_\lambda \rangle \approx e^{-\beta(\varepsilon_\lambda - \mu)}. \tag{4.2.5}$$

# 3 Applications

## 3.1 Ideal Quantum Gases

- **Fermions**: Electron gas in metals (Fermi energy).
- **Bosons**: Bose-Einstein condensation (BEC).

## 3.2 Example: Photon Gas

For photons ($\mu = 0$):

$$\langle n_\lambda \rangle = \frac{1}{e^{\beta\varepsilon_\lambda} - 1} \quad \text{(Planck distribution)}. \tag{4.3.1}$$

# 4 Application Exercises

# 5 Application Exercises

## Exercise No°1:

A gas is in contact with a surface. On the surface, there are $N_0$ localized sites capable of adsorbing gas molecules (each site can adsorb either zero or one gas molecule). Find the grand canonical partition function and determine the chemical potential as a function of the average number of particles $N$ adsorbed on the surface. It is assumed that the canonical partition function of a single adsorbed molecule depends only on temperature, and that all adsorbed molecules do not interact.

**Solution** :

The molecules are independent, implying that the canonical partition function of the $N$ adsorbed molecules is the product of the partition functions of each individual molecule. Moreover, since the sites are localized (distinguishable), we must determine all the ways to select $N$ sites from the $N_0$ available. The partition function of the $N$ adsorbed molecules is

$$Z_c(T,N) = \frac{N_0!}{N!(N_0-N)!} Z_c^N(T,1)$$

We now determine the grand canonical partition function by summing over all possible values of $N$, i.e., $N = 0, 1, 2, \ldots, N_0$, yielding

$$\begin{aligned} Z(T,z) &= \sum_{N=0}^{N_0} z^N Z_c(T,N) \\ &= \sum_{N=0}^{N_0} \frac{N_0!}{N!(N_0-N)!} z^N Z_c^N(T,1) \end{aligned}$$

where $z$ is the fugacity. Using the binomial theorem, the partition function becomes

$$\begin{aligned} Z(T,z) &= \sum_{N=0}^{N_0} \frac{N_0!}{N!(N_0-N)!} (zZ_c(T,1))^N 1^{N_0-N} \\ &= (zZ_c(T,1)+1)^{N_0} \end{aligned}$$

The average number of adsorbed molecules is

$$\begin{aligned}\langle N\rangle &= z\left(\frac{\partial Z(T,z)}{\partial z}\right)_T \\ &= N_0\frac{zZ_c(T,1)}{zZ_c(T,1)+1} \\ &= \frac{N_0}{z^{-1}Z_c(T,1)^{-1}+1}\end{aligned}$$

which leads to

$$1+\frac{1}{zZ_c(T,1)} = \frac{N_0}{\langle N\rangle}$$

or equivalently,

$$zZ_c(T,1) = e^{\beta\mu}Z_c(T,1) = \frac{\langle N\rangle}{N_0-\langle N\rangle}$$

the chemical potential is

$$\mu = k_BT\ln\left(\frac{\langle N\rangle}{Z_c(T,1)(N_0-\langle N\rangle)}\right)$$

# Exercise No°2:

An ideal gas of $N$ non-interacting molecules with a magnetic moment $\mu$ and mass $m$ is immersed in a magnetic field $\vec{B}=(0,0,B)$. The Hamiltonian of the system is

$$H = \tfrac{P^2}{2m} - S\mu B$$

where $m$ is the mass of the molecule and $P$ its momentum. $S=\pm1$, meaning the magnetic moment is either parallel or antiparallel to $\vec{B}$. These two types of molecules have densities $n_+$ and $n_-$ respectively. Compute the ratio $n_-/n_+$ as a function of $B$ at equilibrium.

**Solution** :

Starting from the single-particle Hamiltonian, we can write the chemical potentials of the

molecules with magnetic moment parallel and antiparallel to the field:

$$\mu_+ = \mu_+^0 - \mu B$$
$$\mu_- = \mu_-^0 + \mu B$$

where $\mu_\pm$ is the chemical potential of an ideal gas with density $n_\pm$ and Hamiltonian $H = p^2/2m$, given by

$$\mu_\pm^0 = k_B T \ln(n_\pm \Lambda^3)$$

where $\Lambda = h/\sqrt{2\pi m k_B T}$ is the thermal wavelength. This leads to

$$k_B T \ln(n_- \Lambda^3) + \mu B = k_B T \ln(n_+ \Lambda^3) - \mu B$$

from which we directly extract the ratio $n_-/n_+$:

$$n_-/n_+ = e^{-2\mu B/k_B T}$$

# Exercise No°3:

Show that the entropy of a system in the grand canonical ensemble

$$S = k_B T \left(\tfrac{\partial q}{\partial T}\right)_{z,V} - N k_B \ln z + k_B q$$

can be written as

$$S = k_B \left(\tfrac{\partial}{\partial T}(Tq)\right)_{\mu,V}$$

where $q$ is a function of $z$, $T$, and $V$. $z$ is the fugacity, which depends on $T$ and $\mu$, and $-k_B T q = \phi$ is the grand potential.

**Solution** :

We have

$$S = k_B T \left(\frac{\partial q}{\partial T}\right)_{z,V} - N k_B \ln z + k_B q$$

and

$$dq = \left(\frac{\partial q}{\partial z}\right)_{V,T} dz + \left(\frac{\partial q}{\partial V}\right)_{z,T} dV + \left(\frac{\partial q}{\partial T}\right)_{z,V} dT$$

But $z$ is a function of $\mu$ and $T$, so

$$dz = \left(\frac{\partial z}{\partial \mu}\right)_T d\mu + \left(\frac{\partial z}{\partial T}\right)_\mu dT$$

Injecting $dz$ into $dq$, we get

$$dq = \left(\frac{\partial q}{\partial z}\right)_{V,T}\left(\frac{\partial z}{\partial \mu}\right)_T d\mu + \left[\left(\frac{\partial q}{\partial z}\right)_{V,T}\left(\frac{\partial z}{\partial T}\right)_\mu + \left(\frac{\partial q}{\partial T}\right)_{z,V}\right] dT + \left(\frac{\partial q}{\partial V}\right)_{z,T} dV$$

Thus we find

$$\left(\frac{\partial q}{\partial T}\right)_{\mu,V} = \left(\frac{\partial q}{\partial z}\right)_{V,T}\left(\frac{\partial z}{\partial T}\right)_\mu + \left(\frac{\partial q}{\partial T}\right)_{z,V}$$

and since $N = z\left(\frac{\partial q}{\partial z}\right)_{V,T}$, it follows that

$$\left(\frac{\partial q}{\partial T}\right)_{\mu,V} = \frac{N}{z}\left(\frac{\partial z}{\partial T}\right)_\mu + \left(\frac{\partial q}{\partial T}\right)_{z,V}$$

Using the definition of fugacity:

$$\begin{aligned}\left(\frac{\partial z}{\partial T}\right)_\mu &= \frac{\partial}{\partial T} e^{\mu/k_B T} \\ &= -\frac{\mu}{k_B T^2} z\end{aligned}$$

we obtain

$$\left(\frac{\partial q}{\partial T}\right)_{\mu,V} = -\frac{N\mu}{k_B T^2} + \left(\frac{\partial q}{\partial T}\right)_{z,V}$$

Substituting into the expression for $S$ yields

$$\begin{aligned}S &= k_B T\left\{\frac{N\mu}{k_B T^2} + \left(\frac{\partial q}{\partial T}\right)_{\mu,V}\right\} - N k_B \ln z + k_B q \\ &= k_B\left\{T\left(\frac{\partial q}{\partial T}\right)_{\mu,V} + q\right\} \\ &= k_B\left(\frac{\partial (Tq)}{\partial T}\right)_{\mu,V}\end{aligned}$$

# Exercise No°4:

We consider a system of $N$ non-interacting quantum harmonic oscillators. We assume that the frequency $\omega$ of these oscillators is temperature-dependent: $\omega = \omega(T)$. Show that in the canonical ensemble, the entropy is not given by

$$S = k_B \left( \ln Z_c + \beta \langle E \rangle \right)$$

where $\langle E \rangle$ is the average energy and $Z_c$ is the canonical partition function. Propose a correct expression for the entropy.

**Solution:** The energy levels of a quantum harmonic oscillator are

$$\epsilon_n = \hbar\omega \left( n + \tfrac{1}{2} \right), \quad n \in \mathbb{N}$$

The partition function of a single oscillator is

$$\begin{aligned} Z_1(T) = \sum_{n=0}^{\infty} e^{-\beta\hbar\omega(n+\frac{1}{2})} &= e^{-\beta\hbar\omega/2} \sum_{n=0}^{\infty} e^{-n\beta\hbar\omega} \\ &= \frac{e^{-\beta\hbar\omega/2}}{1 - e^{-\beta\hbar\omega}} \end{aligned}$$

Therefore, the canonical partition function of the system is

$$Z_c(T) = Z_1(T)^N = \left[ \frac{e^{-\beta\hbar\omega/2}}{1 - e^{-\beta\hbar\omega}} \right]^N$$

The average energy is

$$\langle E \rangle = -\frac{\partial}{\partial\beta} \ln Z_c(T) = -\frac{\partial}{\partial\beta} \left[ N \ln Z_1(T) \right]$$

We now test the formula

$$S = k_B \left( \ln Z_c + \beta \langle E \rangle \right)$$

We compute this explicitly:

$$S = k_B \left( \ln Z_c - \beta \frac{\partial}{\partial\beta} \ln Z_c \right)$$

This formula comes from the relation

$$S = -\left(\frac{\partial F}{\partial T}\right)_V$$

where the Helmholtz free energy $F = -k_B T \ln Z_c$, and assuming that $Z_c$ depends only on $T$ through $\beta = 1/k_B T$.

However, in this case, $\omega = \omega(T)$, so $Z_c$ depends on $T$ both explicitly through $\beta$ and implicitly through $\omega(T)$. Hence, we must write the entropy as:

$$S = -\left(\frac{\partial F}{\partial T}\right)_V = -\left(\frac{\partial}{\partial T}\left[-k_B T \ln Z_c(T, \omega(T))\right]\right)$$

$$\Rightarrow S = k_B \ln Z_c + k_B T \left(\frac{\partial \ln Z_c}{\partial T}\right)$$

This result differs from

$$S = k_B \left(\ln Z_c + \beta \langle E \rangle\right)$$

because in the latter, one only accounts for the explicit dependence of $Z_c$ on $T$ via $\beta$, but not through the implicit dependence via $\omega(T)$.

**Correct expression for entropy:**

$$S = k_B \ln Z_c + k_B T \left(\frac{\partial \ln Z_c}{\partial T}\right) = -\left(\frac{\partial F}{\partial T}\right)_V$$

# Exercise No°5:

We consider a system composed of $N$ distinguishable particles that can occupy three energy levels:

$$\varepsilon_0 = 0, \quad \varepsilon_1 = \varepsilon, \quad \varepsilon_2 = 2\varepsilon$$

1. Compute the canonical partition function of the system.
2. Determine the average energy of the system.
3. Determine the specific heat at constant volume.
4. Plot the entropy as a function of temperature.

**Solution: 1. Partition function:**

The single-particle partition function is given by:

$$Z_1 = \sum_{i=0}^{2} e^{-\beta\varepsilon_i} = e^{-\beta\cdot 0} + e^{-\beta\varepsilon} + e^{-2\beta\varepsilon} = 1 + e^{-\beta\varepsilon} + e^{-2\beta\varepsilon}$$

Since the particles are distinguishable and non-interacting, the total partition function is:

$$Z_c = Z_1^N = \left(1 + e^{-\beta\varepsilon} + e^{-2\beta\varepsilon}\right)^N$$

**2. Average energy:**

The average energy is given by:

$$\langle E\rangle = -\frac{\partial}{\partial\beta}\ln Z_c = -\frac{\partial}{\partial\beta}\left[N\ln Z_1\right] = -N\frac{1}{Z_1}\frac{dZ_1}{d\beta}$$

Compute the derivative:

$$\frac{dZ_1}{d\beta} = \frac{d}{d\beta}\left(1 + e^{-\beta\varepsilon} + e^{-2\beta\varepsilon}\right) = -\varepsilon e^{-\beta\varepsilon} - 2\varepsilon e^{-2\beta\varepsilon}$$

Then:

$$\langle E\rangle = N\cdot\frac{\varepsilon e^{-\beta\varepsilon} + 2\varepsilon e^{-2\beta\varepsilon}}{1 + e^{-\beta\varepsilon} + e^{-2\beta\varepsilon}}$$

**3. Specific heat at constant volume:**

The specific heat per particle is given by:

$$C_V = \frac{1}{N}\frac{d\langle E\rangle}{dT} = \frac{1}{N}\cdot\frac{d\langle E\rangle}{d\beta}\cdot\frac{d\beta}{dT} = -k_B\beta^2\cdot\frac{d\langle E\rangle}{d\beta}$$

Let us denote $x = \beta\varepsilon$, then:

$$\langle E\rangle = N\varepsilon\cdot\frac{e^{-x} + 2e^{-2x}}{1 + e^{-x} + e^{-2x}}$$

Then:

$$C_V = Nk_Bx^2\left[\frac{e^{-x} + 4e^{-2x} + 4e^{-3x}}{(1 + e^{-x} + e^{-2x})^2} - \left(\frac{e^{-x} + 2e^{-2x}}{1 + e^{-x} + e^{-2x}}\right)^2\right]$$

**4. Entropy as a function of temperature:**

The entropy is given by:

$$S = k_B \left(\ln Z_c + \beta \langle E \rangle\right) = N k_B \left(\ln Z_1 + \beta \cdot \frac{\varepsilon(e^{-\beta\varepsilon} + 2e^{-2\beta\varepsilon})}{Z_1}\right)$$

This can be plotted as a function of $T$ numerically using software like Python/Matplotlib or Mathematica by evaluating $S(T)$ for fixed values of $N$ and $\varepsilon$.

## Exercise No°6: System of Distinguishable Particles with Four Energy Levels

Consider a system of $N$ **distinguishable particles** with four discrete energy levels given by:

$$\varepsilon_0 = 0, \quad \varepsilon_1 = \varepsilon, \quad \varepsilon_2 = 2\varepsilon, \quad \varepsilon_3 = 3\varepsilon.$$

1. **Partition function:**
   (a) Write the **single-particle partition function** $Z_1(T)$.
   (b) Deduce the **total partition function** $Z_N(T)$ for the entire system.
2. **Thermodynamic quantities:**
   (a) Compute the average energy $\langle E \rangle$.
   (b) Compute the entropy $S(T)$.
   (c) Compute the heat capacity $C(T)$.
3. **Numerical study:** For $N = 100$, $\varepsilon = 1$, and $T \in [0.1, 10]$, plot:
   (a) $\langle E(T) \rangle$
   (b) $S(T)$
   (c) $C(T)$
4. **Asymptotic behavior:**
   (a) Analyze the limits as $T \to 0$ and $T \to \infty$ for $\langle E \rangle$, $S$, and $C$.

**Solution:**

## 1. Partition Function

(a) The single-particle partition function is:

$$Z_1(T) = \sum_{n=0}^{3} e^{-\beta\varepsilon_n} = 1 + e^{-\beta\varepsilon} + e^{-2\beta\varepsilon} + e^{-3\beta\varepsilon}$$

(b) Since particles are distinguishable and non-interacting:

$$Z_N(T) = (Z_1(T))^N$$

## 2. Thermodynamic Quantities

(a) The average energy is given by:

$$\langle E\rangle = -\frac{\partial \ln Z_N}{\partial\beta} = -\frac{\partial}{\partial\beta}\left(N \ln Z_1\right) = -N\frac{\partial \ln Z_1}{\partial\beta}$$

$$\Rightarrow \langle E\rangle = N\frac{1}{Z_1}\sum_{n=0}^{3}\varepsilon_n e^{-\beta\varepsilon_n} = N\frac{\varepsilon e^{-\beta\varepsilon} + 2\varepsilon e^{-2\beta\varepsilon} + 3\varepsilon e^{-3\beta\varepsilon}}{Z_1}$$

(b) Entropy from:

$$S = \frac{\langle E\rangle}{T} + k_B \ln Z_N = \frac{\langle E\rangle}{T} + Nk_B \ln Z_1$$

(c) Heat capacity:

$$C = \langle E\rangle T = T\left(N\frac{1}{Z_1}\sum_{n=0}^{3}\varepsilon_n e^{-\varepsilon_n/T}\right)$$

which can be computed numerically.

## 3. Numerical Study

Use Python to plot $\langle E\rangle(T)$, $S(T)$, and $C(T)$ for $N = 100$, $\varepsilon = 1$, and $T \in [0.1, 10]$.

## 4. Limits

(a) As $T \to 0$: all particles occupy the ground state, so:

$$\langle E \rangle \to 0, \quad S \to 0, \quad C \to 0$$

(b) As $T \to \infty$: all states are equally populated:

$$\langle E \rangle \to N \cdot \frac{0 + \varepsilon + 2\varepsilon + 3\varepsilon}{4} = \frac{3}{2} N\varepsilon$$

$$S \to N k_B \ln 4, \quad C \to 0$$

# Chapter 5

# Introduction to Phase Transitions

## 1 Introduction

In the previous chapters, we focused on a class of models where particles do not interact with each other. Specifically, we studied ideal gas systems as simple examples. In this chapter, we will consider the effects of particle interactions, which induce correlations among the constituents of the system. We introduce the theory of phase transitions to study the manifestations of these interactions. Our focus will be on the study of a simple, yet widely used, model known as the 1D Ising model, which serves as a simplified representation of the temperature and magnetic field behavior of certain magnetic materials.

## 2 The 1D Ising Model

The model we discuss here is the Ising model, a simple yet powerful tool in statistical physics. This model is defined as follows: consider a regular lattice where each site is labeled in a certain way, and on each site, we define a scalar variable with two possible states, $\sigma = \pm 1$. These variables can represent quantum spins $s = \frac{1}{2}$, or a classical system with two microscopic states, such as a magnetic moment with anisotropy aligned along an axis, where the possible values are $\pm\mu$.

A state of the system is characterized by the N-tuple $(\sigma_1, \sigma_2, \ldots, \sigma_N)$. Thus, the space of configurations is $\Omega = \{1, -1\}^N$, with $2^N$ possible states.

These variables are coupled to an external field $h$ and interact with each other via pairwise interactions. The Hamiltonian (energy) of the system in the state $\{\sigma_i\} =$

$(\sigma_1, \sigma_2, \ldots, \sigma_N)$ is given by:

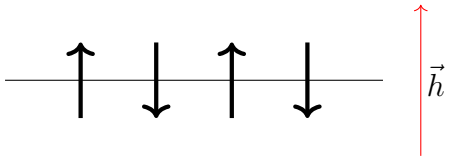
$$H\left(\{\sigma_i\}\right) = -\sum_{\langle i,j \rangle} J_{ij}\sigma_i\sigma_j - \sum_i h\sigma_i \tag{5.2.1}$$

The first term in the Hamiltonian represents the interaction between nearest neighbors, denoted $\langle i, j \rangle$, while the second term is the energy of each spin in the external field $\vec{h}$.

It is important to note that the sign of $J_{ij}$ dictates the nature of the interaction between sites $i$ and $j$:

- $J_{ij} > 0$: The energy is minimized when the spins are parallel. We refer to this as a ferromagnetic interaction.
- $J_{ij} < 0$: The spins tend to be antiparallel to minimize the energy. This is an antiferromagnetic interaction.

We begin our study with the one-dimensional case, where the lattice forms a linear chain. We apply an external magnetic field $\vec{h}$ and calculate the partition function without approximations.




The appropriate ensemble for studying this system is the canonical ensemble, since the number of particles in the system is fixed. The partition function is given by:

$$Z_c(T) = \sum_{\{\sigma_i\} \in \Omega} e^{-\frac{H(\{\sigma_i\})}{T}} \tag{5.2.2}$$

In the following, we assume that interactions are non-zero only between nearest neighbors. This restriction simplifies the calculations but does not qualitatively alter the essential physical properties of the model compared to a less simplified case. The range of interactions is finite.

## 2.1 Exact Solution of the 1D Ising Model in Zero External Field

We first consider the case where the external field is zero, i.e., $\|\vec{h}\| = 0$. The Hamiltonian of the system then becomes:

$$H = -\sum_{\langle i,j \rangle} J\sigma_i\sigma_j \tag{5.2.3}$$

where we have assumed that $J_{ij} = J$, a constant, and $\langle i, j \rangle$ denotes nearest-neighbor pairs. The partition function in the canonical ensemble is given by:

$$Z_c(T) = \sum_{\sigma_1=\pm 1} \cdots \sum_{\sigma_N=\pm 1} e^{\beta \sum_{i=1}^{N} J\sigma_i\sigma_{i+1}} \tag{5.2.4}$$

where we have numbered the spins as $1, 2, \ldots, N$. We consider open boundary conditions, i.e., $\sigma_{N+1} = 0$ (a chain with $N$ spins and $N - 1$ nearest-neighbor links). By separating the even and odd parts of the exponential, we obtain:

$$e^{\beta J\sigma_i\sigma_{i+1}} = \cosh(\beta J) + \sigma_i\sigma_{i+1}\sinh(\beta J) \tag{5.2.5}$$

The partition function becomes:

$$Z_c(T) = \sum_{\sigma_1=\pm 1} \cdots \sum_{\sigma_N=\pm 1} \prod_{i=1}^{N} (\cosh(\beta J) + \sigma_i\sigma_{i+1}\sinh(\beta J)) \tag{5.2.6}$$

Expanding this product, we have:

$$Z_c(T) = (\cosh(\beta J))^{N-1} \sum_{\sigma_1=\pm 1} \cdots \sum_{\sigma_N=\pm 1} \prod_{i=1}^{N} (1 + \sigma_i\sigma_{i+1}\tanh(\beta J)) \tag{5.2.7}$$

At high temperatures, $\tanh(\beta J) \to 0$, so we expand in powers of $\tanh(\beta J)$. The leading term in this expansion will give:

$$Z_c = 2^N(\cosh(\beta J))^{N-1} \tag{5.2.8}$$

If we instead impose periodic boundary conditions, i.e., $\sigma_{N+1} = \sigma_1$, we get an additional non-zero contribution from the cyclic boundary terms:

$$Z_c = 2^N(\cosh(\beta J))^N \tag{5.2.9}$$

This additional term arises due to the periodicity, and it plays a crucial role in the behavior of the system in the thermodynamic limit.

## 2.2 Solution in Non-zero External Field, Transfer Matrix Method

Now, we consider the case where $h \neq 0$. In this case, the system becomes more complex, and we will use a powerful method called the transfer matrix approach, which is particularly useful in one or two dimensions but difficult to apply in higher dimensions.

Assuming periodic boundary conditions:

$$\sigma_{N+1} = \sigma_1 \tag{5.2.10}$$

The Hamiltonian becomes:

$$H = -\sum_{i=1}^{N} J\sigma_i\sigma_{i+1} - \sum_{i=1}^{N} h\sigma_i \tag{5.2.11}$$

The term $e^{-\beta H}$ in the expression for the partition function can be written as:

$$e^{-\beta H} = \prod_{i=1}^{N} e^{\beta J\sigma_i\sigma_{i+1} + \beta h\sigma_i} \tag{5.2.12}$$

This can be rewritten using transfer matrices $T_{\sigma_i\sigma_{i+1}}$ as:

$$Z_c = \sum_{\sigma_1}\sum_{\sigma_2}\cdots\sum_{\sigma_N} T_{\sigma_1\sigma_2}T_{\sigma_2\sigma_3}\ldots T_{\sigma_N\sigma_1} \tag{5.2.13}$$

The transfer matrix $T_{\sigma_i\sigma_{i+1}}$ is a $2 \times 2$ matrix, which can be written as:

$$T = \begin{pmatrix} e^{\beta J+\beta h} & e^{-\beta J+\beta h} \\ e^{-\beta J-\beta h} & e^{\beta J-\beta h} \end{pmatrix} \tag{5.2.14}$$

The partition function is then given by the trace of the transfer matrix raised to the power $N$:

$$Z_c = \mathrm{Tr}(T^N) \tag{5.2.15}$$

The eigenvalues of the transfer matrix can be found, and from this, we can obtain information about the thermodynamic properties of the system.

# 3 Phase Transitions in the Ising Model

The Ising model exhibits a phase transition in dimensions greater than one. For 1D systems, however, it does not undergo a phase transition at any finite temperature. This is due to the lack of long-range interactions that would lead to spontaneous symmetry breaking. The 1D model remains disordered for all temperatures, but in higher dimensions, a critical temperature $T_c$ exists at which a phase transition occurs.

This transition is characterized by a change in the nature of the system's symmetry. Below $T_c$, the system undergoes spontaneous magnetization, whereas above $T_c$, the system exhibits no long-range order.

# 4 Summary and Outlook

In this chapter, we have introduced the basic concept of phase transitions, with a particular focus on the 1D Ising model. We discussed its exact solution and the importance of interaction terms in shaping the thermodynamic behavior of the system. The absence of a phase transition in 1D highlights the role of dimensionality in determining the existence of critical phenomena.

In the following chapters, we will generalize our study to higher-dimensional systems and explore more complex models exhibiting nontrivial phase transitions. "'latex

# 5 Application Exercises

The canonical partition function of a one-dimensional Ising model subjected to an external magnetic field is

$$Z_c = \sum_{S_1,\dots S_N=\pm 1} e^{-\sum_{i=1}^{N}(hS_i + KS_iS_{i+1})}$$

where $h = \beta\mu B$ and $K = \beta J$. The system is under periodic boundary conditions ($S_{N+1} = S_1$).

1- Show that $Z_c = \mathrm{Tr}(Z_1^N)$ where

$$Z_1 = \begin{pmatrix} e^{-h+K} & e^{-K} \\ e^{-K} & e^{h+K} \end{pmatrix}$$

2- Using the fact that the trace is representation-independent, show that

$$Z_c = \lambda_+^N + \lambda_-^N$$

where $\lambda_+$ and $\lambda_-$ are the eigenvalues of the matrix $Z_1$.

3- Determine these eigenvalues and show that in the thermodynamic limit ($N \to \infty$)

$$\begin{aligned} \frac{\ln Z_c}{N} &= \ln \lambda_+ \\ &= K + \ln \left[ \cosh(h) + \left( \sinh^2(h) + e^{-4K} \right)^{1/2} \right] \end{aligned}$$

4- Evaluate the average magnetization and show that it vanishes when $h \to 0^+$

**Solution:**

1-

$$\begin{aligned} \mathrm{Tr}(Z_1^N) &= \sum_{S_1,\ldots S_N=\pm 1} \prod_{J=1}^{N} e^{\left((S_J+S_{J+1})\frac{h}{2}+KS_JS_{J+1}\right)} \\ &= \sum_{S_1,\ldots S_N=\pm 1} e^{-\sum_{J=1}^{N}(hS_J+KS_JS_{J+1})} \\ &= Z_c \end{aligned}$$

2-

$$\begin{aligned} \mathrm{Tr}(Z_1^N) &= \left[ \begin{pmatrix} \lambda_+ & 0 \\ 0 & \lambda_- \end{pmatrix} \right]^N \\ &= \left[ \begin{pmatrix} \lambda_+^N & 0 \\ 0 & \lambda_-^N \end{pmatrix} \right] \\ &= \lambda_+^N + \lambda_-^N \end{aligned}$$

3- Let us consider a matrix $M = \begin{pmatrix} a & b \\ c & d \end{pmatrix}$ and diagonalize it using

$$\begin{aligned} |\lambda I - M| &= (\lambda - a)(\lambda - d) - bc = 0 \\ &= \lambda^2 - (a+d)\lambda + ad - bc = 0 \end{aligned}$$

The solution of this equation is

$$\lambda_\pm = \frac{a+d}{2} \pm \sqrt{\left(\frac{a-d}{2}\right)^2 + bc}$$

Applying this method, we obtain

$$\lambda_\pm = e^K \left[\cosh h \pm \sqrt{\sinh^2 h + e^{-4K}}\right]$$

which gives

$$\begin{aligned} Z_c &= \lambda_+^N + \lambda_-^N \\ &= \lambda_+^N \left(1 + \left(\frac{\lambda_-}{\lambda_+}\right)^N\right) \end{aligned}$$

In the thermodynamic limit $N \to \infty$

$$\begin{aligned} \frac{\ln Z_c}{N} &\simeq \ln \lambda_+ \\ &\simeq K + \ln\left[\cosh h + \sqrt{\sinh^2 h + e^{-4K}}\right] \end{aligned}$$

4-

$$\begin{aligned} \langle S_i \rangle &= \frac{\partial}{\partial h}\left(\frac{\ln Z_c}{N}\right) \\ &= \frac{\sinh h + \frac{\sinh h \cosh h}{\sqrt{\sinh^2 h + e^{-4K}}}}{\cosh h + \sqrt{\sinh^2 h + e^{-4K}}} \end{aligned}$$

In the case where $h \to 0$

$$\begin{aligned}\lim_{h\to 0}\langle S_i\rangle &= \lim_{h\to 0}\sinh h\left(\frac{1+\cosh h/\sqrt{\sinh^2 h+e^{-4K}}}{\cosh h+\sqrt{\sinh^2 h+e^{-4K}}}\right)\\ &= 0\end{aligned}$$

In the absence of an external magnetic field, the magnetization per site vanishes and the system does not undergo a phase transition in one dimension.

# Exercise No.$^2$:

Let $\langle S\rangle$ be the average spin value and $\vec{B}$ the magnetic field applied to a system of $N$ interacting spins 1/2. The Hamiltonian of the system is written as

$$H = (J\langle S\rangle + g\mu_B)\sum_i S_i^z$$

where $J$ is the coupling constant, $g$ is the Landé factor and $\mu_B$ is the Bohr magneton.

1 Find the equation satisfied by $\langle S\rangle$. Provide a method of resolution.

2 Show that there exists a critical temperature $T_c$ below which there is a non-trivial solution $\langle S\rangle \neq 0$

3 Calculate $\langle S\rangle$ near $T_c$ for $T < T_c$ and show that

$$\langle S\rangle = \left(1-\frac{T}{T_c}\right)^{1/2}$$

4 Show that the magnetic susceptibility satisfies the Curie–Weiss law.

**Solution:**

1 The Hamiltonian of the system is $H = \sum_i H_i$ where

$$H_i = (2J\langle S\rangle + g\mu_B)\, S_i^z$$

Thus

$$\begin{aligned} Z &= \sum_{\{i\}} e^{-\beta H} \\ &= \prod_i \sum_{\{S_i\}} e^{-\beta H_i} \\ &= \prod_i Z_i \end{aligned}$$

where

$$\begin{aligned} Z_i &= \sum_{S_i=\pm 1/2} e^{-\beta H_i} \\ &= e^{-\beta(2J\langle S\rangle + g\mu_B)(\frac{1}{2})} + e^{-\beta(2J\langle S\rangle + g\mu_B)(-\frac{1}{2})} \\ &= 2\cosh\left[\beta\left(J\langle S\rangle + \frac{1}{2}g\mu_B\right)\right] \end{aligned}$$

We see that $Z_i$ does not depend on $i$, so $Z = Z_i^N$.

2-

$$\begin{aligned} \langle S\rangle &= \sum_{S_i} S_i \frac{e^{-\beta H_i}}{Z_i} \\ &= \frac{1}{Z_i}\sum_{S_i} S_i e^{-\beta H_i} \\ &= \frac{1}{2}\tanh\left[\beta\left(J\langle S\rangle + \frac{1}{2}g\mu_B\right)\right] \end{aligned}$$

The self-consistency comes from the fact that $\langle S\rangle$ is defined implicitly by this equation.

3- For $B = 0$, this equation can admit a non-trivial solution if $\beta$ and $J$ satisfy certain conditions. If $\langle S\rangle$ is very small, we can expand the hyperbolic tangent:

$$2\langle S\rangle = \beta J\langle S\rangle - \frac{1}{3}\left(\beta J\langle S\rangle\right)^3$$

which gives

$$\langle S\rangle^2 = \frac{3\left(\beta J - 2\right)}{\left(\beta J\right)^2}$$

Since $\beta_c = 1/k_B T_c = 2/J$, this solution becomes

$$\langle S \rangle = \left(1 - \frac{T}{T_c}\right)^{1/2}$$

4 To be completed...

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