

Spring term 2020

Statistical Physics (MATH327)

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LIVING LECTURE NOTES

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Module Information

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Contact hours:

Weeks 1–7:	We will have <i>three hours of lecture</i> and <i>one tutorial</i> . There will be question sheets for the tutorials. You will work through part of these questions in your time before the tutorial (non-assessed). Key elements will be discussed in the tutorial.
Week 8–10:	We will have <i>two hours of lecture</i> and <i>two hours Computer Lab</i> . In the Computer Lab sessions, we will study a statistical phenomenon (see page 110) with a computer experiment using MATLAB. A basic introduction to MATLAB will be provided, but familiarising yourself with MATLAB (if needed) could be beneficial. Support material to get started with MATLAB is provided at the VITAL page for MATH327.
Week 11–12:	We will have <i>three hours of lecture</i> and <i>one tutorial</i> . Both will include exam revision sessions.

Assessment:

12%	Two assessed homeworks assigned in week 3 and week 6 with equal weighting. A clear and neat presentation of all this contributes to your mark.
8%	A computer-based project due in week 11.
80%	Standard Examination.

Resources:

This portfolio covers the lecture material, the questions and tasks for the tutorial and the computer based project.

The MATH327 VITAL page has more support material. You might find the small podcasts on getting started with the software useful.

The list of further reading below provides some optional additional resources that may be helpful.

References

- [1] Charles Kittel and Herbert Kroemer, *Thermal Physics* (second edition, 1980)
- [2] David Tong, *Lectures on Statistical Physics* (2012), <https://www.damtp.cam.ac.uk/user/tong/statphys.html>
- [3] Daniel V. Schroeder, *An Introduction to Thermal Physics* (first edition, 2000)
- [4] F. Reif, *Fundamentals of Statistical and Thermal Physics* (first edition, 1965)
- [5] Ian Thompson, *Understanding Maple* (2016), <https://library.liv.ac.uk/record=b4395758> S8
- [6] Stormy Attaway, *MATLAB: A Practical Introduction to Programming and Problem Solving* (third edition, 2013)

Advanced Reading:

- [7] B. Barnes and G. R. Fulford, *Mathematical Modelling with Case Studies: Using Maple and MATLAB* (third edition, 2014).
- [8] R. K. Pathria, *Statistical Mechanics* (second edition, 1996)
- [9] Sidney Redner, *A Guide to First-Passage Processes* (first edition, 2007)
- [10] Pavel L. Krapivsky, Sidney Redner and Eli Ben-Naim, *A Kinetic View of Statistical Physics* (first edition, 2010)
- [11] Kerson Huang, *Statistical Mechanics* (second edition, 1987)
- [12] Michael Plischke and Birger Bergersen, *Equilibrium Statistical Physics* (third edition, 2005)
- [13] L. D. Landau and E. M. Lifshitz, *Statistical Physics, Part 1* (third edition, 1980)

Video Resources:

- [14] Ian Thompson, *Running Maple for the first time*
<https://stream.liv.ac.uk/4k67bdzt>
- [15] Ian Thompson, *Configuring Maple*,
<https://stream.liv.ac.uk/7pjge23a>

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What is Statistical Physics?

The physical sciences try to unlock the laws of nature and to understand the everyday-life or experimental observations. “Understand” frequently means to find the mathematical description that reproduces a cluster of physics observations and that allows to make predictions for other observables.

Physics over the last century has been a tremendous success story: in experiments, we can now create a vacuum that is better than in outer-space, and the coldest place in the universe is in our solid state physics labs. Amazingly, the mathematics to describe those realms of physics has been developed, in some cases, centuries before. Physicists now embark to find the mathematics of the theory of everything, which will combine the description of the subatomic with that of the grand scales—gravity.

The brand of “Statistical Physics” summarises those observations and laws of nature the successful mathematical description of which is *Probability Theory*. The quality of the mathematical description is usually outstanding to an extent that ‘randomness’ from the probabilistic description is hardly observed in the observables. In fact, **Ludwig Eduard Boltzmann** (1844–1906), the founder of statistical mechanics, had a hard time to defend his theories. His mental health deteriorated over the years, and he committed suicide on September 5, 1906, while on vacation with his wife and daughter in Duino, near Trieste.

While in Boltzmann’s times, phenomena such as temperature, pressure and diffusion were the objective, probability theory now is at the heart of modern physics. For instance, when in neutron stars gravity becomes so large that it crushes atoms by forcing electrons to combine with protons to form neutrons, it is probability theory that explains why the neutron matter does not collapse under the immense gravity. We will later understand the mathematics behind this (see quantum gases).

1 Central Limit Theorem

The high quality of probability theory descriptions can be traced to the involvement of some very large numbers. If we for instance go back to the stochastic description of properties of (classical) gases, 22.71 litres of gas under ‘normal conditions’ (a pressure of 100 kPa and a temperature of

0° Celsius) contain $6.02214076 \times 10^{23}$ gas particles (Avogadro's constant). If pressure arises from air particles colliding with the walls and pushing them 'out', why is the pressure not wildly fluctuating, but can be perfectly and reproducibly measured? The mathematical answer lies in the Law of Large Numbers and the Central Limit Theorem.

1.1 Probability Essentials

Experiment E and state ω : Each time an 'experiment' is performed, the world comes out in some state ω . The definition of the experiment includes the objects of interest.

Set of all states Ω : The set of all possible outcomes ω is denoted Ω and is called the universe of possible states. Note that it is obviously intricately tied to the experiment E.

Measurement $X(\omega)$: If we are interested in measuring some features of our states ω , we need to map each individual state ω to a one number X , in which we are interested. Hence, we can view X a function of ω and call it $X(\omega)$. In mathematics, $X(\omega)$ is called *random variable*. After having performed the experiment E once, it is the result of the measurement of X on the state ω that E produced.

Set of outcomes A : If we input all possible states $\omega \in \Omega$ to the function $X(\omega)$ and collate the outcome in a set, we generate the set A of a possible outcomes. Mathematically, we can write:

$$X : \Omega \rightarrow A .$$

The set A can be finite, infinite and countable, or infinite and continuous.

Set of events F: An *event* is any subset of the set of all outcomes A . According to our interest, we can group these subsets together to form the **set of events** F.

Examples:

- (A) Throwing a die:
- (B) Toss of a coin four times:
- (C) Argon (gas) atoms in a container:

In many cases, we want to characterise the states ω and introduce a unique number as a qualifier for the states. This means that we introduce a random variable $L(\omega)$ as a ‘label’. Since the label is unique, this function is *isomorphic*:

$$\omega \leftrightarrow L(\omega)$$

and we can synonymously use the set of outcomes A for Ω . We need to be careful since not all textbooks make the distinction between A and Ω , which can be a source of confusion.

Probability P : Every *event* has a probability P of occurring. Mathematically, we define the *probability measure* function P as

$$P : \mathcal{F} \rightarrow [0, 1] .$$

The probability measure function must satisfy two requirements:

- The probability of a countable union of mutually exclusive events must be equal to the countable sum of the probabilities of each of these events.
- The probability of the outcome set A must be equal to 1. This simply means that the experiment E must produce an outcome. This makes sense since we would simply say that the experiment did not take place if no output was produced.

The triple (A, \mathcal{F}, P) is called **probability space**.

Examples:

Assume that an experiment can only produce N possible states as outcomes. In this case, the state space is given by

$$\Omega = \{\omega_1, \omega_2, \dots, \omega_N\}.$$

Assume that we have a random variable $X(\omega)$ with the property

$$\text{if } X(\omega_i) \neq X(\omega_k) \implies \omega_i \neq \omega_k.$$

We do *not* exclude, that $X(\omega_i) = X(\omega_k)$ for some pair i, k $i \neq k$. We then define the set A of outcomes by all $X(\omega_i)$ that are different. The size of the set is $n \leq N$:

$$A = \{X_1 \dots X_n\}.$$

We could now choose as events the random variables X_i itself. The event space hence is given by

$$\mathcal{F} = \{X_1 \dots X_n\}.$$

We then can assign probabilities to each of these events:

$$P(X_i) =: p_i, \quad i = 1 \dots n.$$

Since these events are all mutually exclusive by construction, we find e.g. for $i \neq k$:

$$\begin{aligned} P(X_i \text{ or } X_k) &= P(X_i) + P(X_k) \\ P(X_1 \text{ or } X_2 \text{ or } \dots \text{ or } X_n) &= \sum_{i=1}^n P(X_i) = 1. \end{aligned}$$

Let us now consider some specific examples:

Throwing a die:

Roulette:

Toss a *fair* coin four times

Comments:

- Defining the probabilities is called *modelling*. Symmetries are a powerful way to inform this choice. E.g., for a so-called “fair” die, we expect that every side of the die shows up top with equal probability. This demand is actually enough to fix the probabilities $p_i, i = 1 \dots 6$.
- Rather than modelling, we could try to infer the probabilities from the abundance of certain events. To this end, we could repeat an experiment n times and the Law of Large Numbers can then help us to infer the probabilities.

1.2 The Law of Large Numbers

Suppose we carry out an experiment with a finite set of outcomes

$$A = \{X_1, X_2, \dots, X_{N_s}\}.$$

We consider each of the possible outcomes as events implying that the event space \mathcal{F} is equal to the set of outcomes, $\mathcal{F} = A$. As discussed before, we can

assign probabilities

$$p_i = P(X_i) \quad \text{with } p_i \in [0, 1], \quad \sum_{i=1}^{N_s} p_i = 1 .$$

We will use a slightly more elegant notation and write:

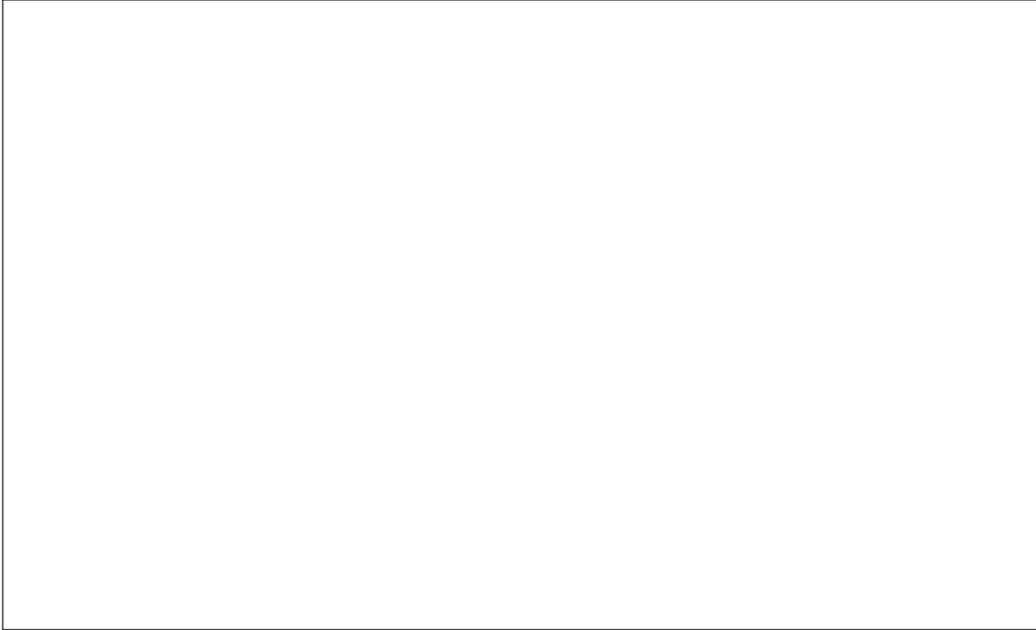
$$\sum_{X \in A} P(X) = 1 .$$

We then introduce the mean μ and the variance σ^2 in the usual way by

$$\mu = \langle X \rangle = \sum_{X \in A} X P(X) , \quad (1)$$

$$\sigma^2 = \langle (X - \mu)^2 \rangle = \sum_{X \in A} (X - \mu)^2 P(X) . \quad (2)$$

We now *repeat* the experiment n times, and call this a new experiment with outcome space B . For $n = 4$, this space looks like:



We call the outcome of the i th repetition $X^{(i)} \in A$, $1 \leq i \leq n$. The individual experiments are carried out *independently*. If one particular element of the outcome space B is given by

$$\omega = \{X_i^{(1)} X_k^{(2)} X_l^{(3)} X_m^{(4)}\} ,$$

the probability of this element is given by:

$$P(\omega) = P\left(X_i^{(1)}\right) P\left(X_k^{(2)}\right) P\left(X_l^{(3)}\right) P\left(X_m^{(4)}\right) .$$

Let us now return to the general case of n independent repetition of the same experiment. The *arithmetic mean*

$$\frac{1}{n} \sum_{i=1}^n X^{(i)}$$

is itself a random variable (it e.g. depends on the outcome of the first experiment $X_i^{(1)} \in A$), but we would expect that this has something to do with the mean μ . To reveal this connection, we calculate

$$\left\langle \left(\frac{1}{n} \sum_{i=1}^n X^{(i)} - \mu \right)^2 \right\rangle_B =$$

$$= \frac{\sigma^2}{n}.$$

This then implies:

$X^{(i)}$ is a sequence of random numbers with existing mean and standard deviation:

$$\langle X^{(i)} \rangle = \mu, \quad \langle (X^{(i)} - \mu)^2 \rangle = \sigma^2,$$

we then find:

$$\lim_{n \rightarrow \infty} \frac{1}{n} \sum_{i=1}^n X^{(i)} = \mu. \quad (\text{Law of Large Numbers}) .$$

1.3 Central Limit Theorem

A quick word in case we are dealing with a *continuous random variable* X . We specialise to the important case that X is a real number. Such a distribution has a probability density function $p(x)$, and therefore its probability of falling into a given interval, say $[a, b]$, is given by the integral

$$P(a \leq X \leq b) = \int_a^b p(x) dx .$$

We are now prepared to look at the Central Limit Theorem (CLT):

Let X_1, X_2, \dots, X_N be a sequence of N independent and identically distributed random variables. The probability distribution function $p(x)$ can be arbitrary, but we assume that mean and variance exist:

$$\langle x^\ell \rangle = \int x^\ell p(x) dx \quad \ell = \{1, 2\}, \quad \mu = \langle x \rangle, \quad \sigma^2 = \langle x^2 \rangle - \langle x \rangle^2 .$$

Define a new random variable S by

$$S = \sum_{i=1}^N X_i .$$

For sufficiently large N , the probability distribution of S is given by a normal distribution:

$$p(s) \rightarrow \frac{1}{\sqrt{2\pi N\sigma^2}} \exp \left\{ -\frac{(s - N\mu)^2}{2N\sigma^2} \right\} .$$

There are many versions of the CLT. This version is the one we are using throughout this lecture. Proofs can be found in many textbooks. Here, we focus on a first application: (normal) diffusion.

1.4 Diffusion on a line

Assume that we walk on a line with a given step length. At each step, we independently decide whether we step to the right (probability p) or to the left (probability $q = 1 - p$). Also assume that we perform N steps. We will vary N later. If each step takes time Δt , the time t after N steps is simply given by

$$t = \Delta t N . \quad (3)$$

If L/R denotes a step to the left / right, a typical event looks like:

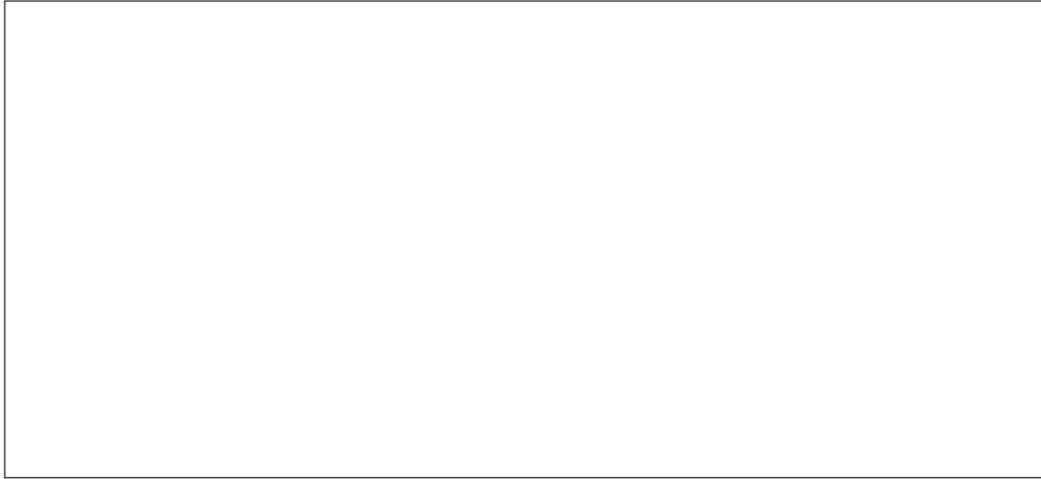
The probability that *exactly* this event occurs is given by:

The interesting question is: where are we after time t (or N steps)? Since stepping is a random process, we need to refine this question: Where are we most likely or, more precisely, if we do this experiment many times, what is the average position $\langle x \rangle$? We then would want to know: How precisely do we know this average or what is the variance $\langle x^2 \rangle - \langle x \rangle^2$?

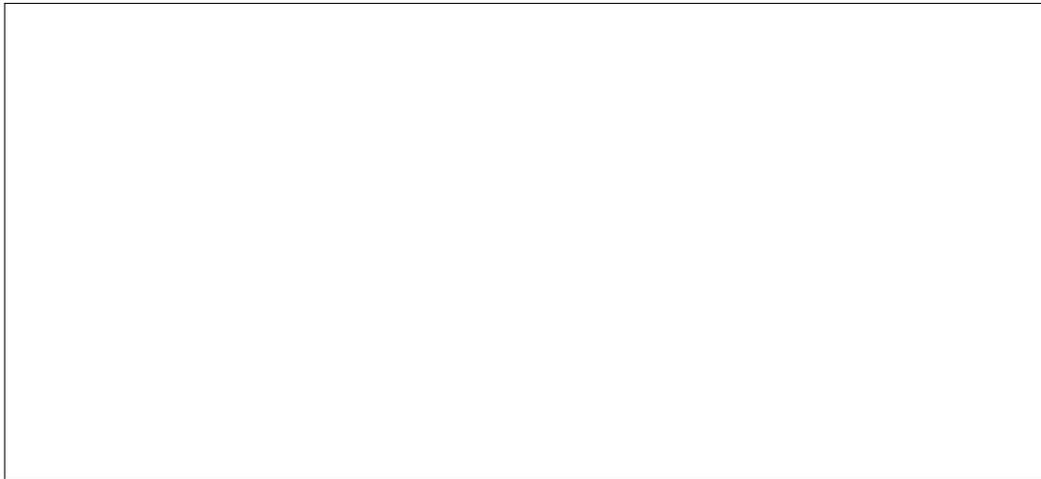
If k is the total number of steps to the right, we have $N - k$ steps to the left, and our position would be:

$$x = k - (N - k) = 2k - N .$$

The order with which we step to the left or right does not affect the position x where we end up. For example, take $N = 5$ and let us write down all events which end up at $x = 3$:



If $P(x)$ is the probability that we find ourselves at x , we here find:



For the general case of N steps and k steps to the right, we need to distribute k steps R to N slots (and fill the remaining places with L s). There are

$$\binom{N}{k} = \frac{N!}{k! (N-k)!}$$

possibilities to do so. Hence, the probability for k steps to the right (no matter in which order) is:

$$p_k = \binom{N}{k} p^k q^{N-k}.$$

We now can answer the above question for average position and variance:

$$\langle x \rangle = \sum_{k=0}^N (2k - N) p_k, \quad \langle x^2 \rangle = \sum_{k=0}^N (2k - N)^2 p_k. \quad (4)$$

Apparently, we need to calculate sums of the type:

$$\sum_{k=0}^N k^n p_k .$$

There is an excellent trick in stochastics to do this. We define the generating function

$$T(\theta) = \sum_{k=0}^N e^{\theta k} p_k. \quad (5)$$

We easily check (*do it!*) that

$$\lim_{\theta \rightarrow 0} \frac{d^n T(\theta)}{d\theta^n} = \sum_{k=0}^N k^n p_k . \quad (6)$$

Fortunately, we can calculate the closed form of $T(\theta)$ for our example here:

$T(\theta) =$

and finally obtain:

$$T(\theta) = (e^\theta p + q)^N .$$

We thus obtain:

$$\sum_{k=0}^N k p_k = \lim_{\theta \rightarrow 0} \frac{dT(\theta)}{d\theta} = N p \lim_{\theta \rightarrow 0} e^\theta (e^\theta p + q)^{N-1} = N p (p + q)^{N-1} = N p ,$$

$$\sum_{k=0}^N k^2 p_k = \lim_{\theta \rightarrow 0} \frac{d^2T(\theta)}{d\theta^2} = N^2 p^2 + N p q .$$

We hence obtain

$$\langle x \rangle =$$

$$\langle x^2 \rangle - \langle x \rangle^2 =$$

In summary, we find:

$$\langle x \rangle = N (2p - 1) , \quad \langle x^2 \rangle - \langle x \rangle^2 = 4 N p q . \quad (7)$$

We can interpret these finding by using time t (3) instead of time. We firstly find that the average changes linearly with time:

$$\langle x \rangle = v_{\text{dr}} t, \quad v_{\text{dr}} = (2p - 1)/\Delta t ,$$

where v_{dr} is called the drift velocity. If we quantify the uncertainty in the position Δx by the standard deviation, i.e.,

$$\Delta x = [\langle x^2 \rangle - \langle x \rangle^2]^{1/2} ,$$

and if we assume that the drift velocity is not vanishing, we find:

$$\Delta x / \langle x \rangle =$$

We observe that the uncertainty over the drift vanishes for large time.

Note that for $p = 1/2$, the drift vanishes. This is intuitively clear since we step left and right with the same probability $1/2$. It is then most likely to find the person (who steps) at the origin (the probability peaks there). However, in this case, the standard deviation Δx then quantifies the distance in which we can expect the person to find with some measure of probability. How does the standard deviation depend on time?

$$\Delta x =$$

In summary, we find the well know law of diffusion:

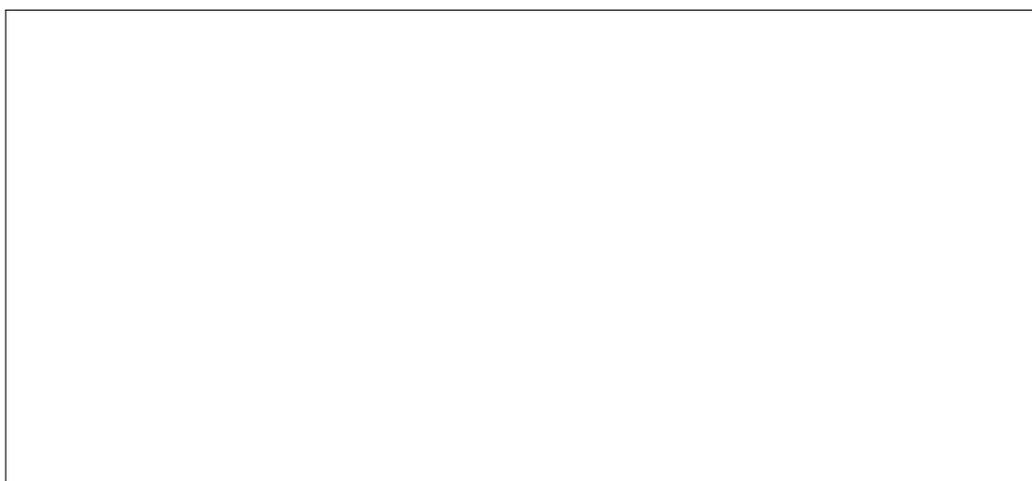
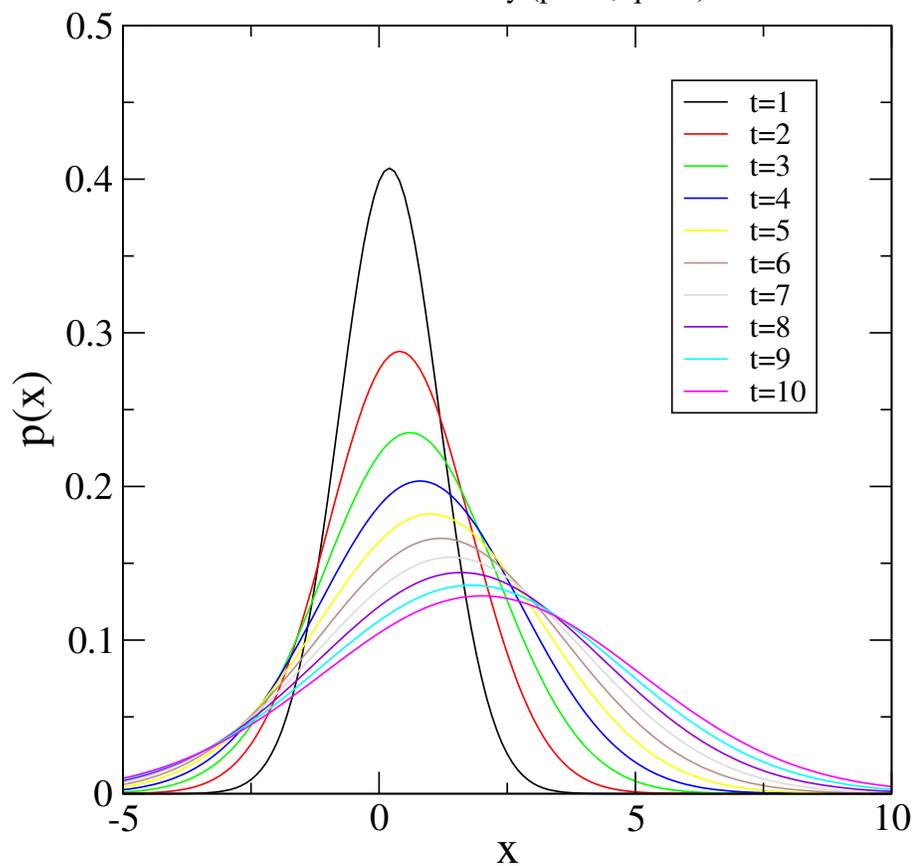
$$\Delta x = D \sqrt{t}, \quad D = \sqrt{4pq/\Delta t}, \quad (8)$$

where Δx is sometime called the diffusion length, and D is the so-called diffusion constant.

For a large number N of steps (or for large times t), we can invoke the Central limit theorem. The elementary process is a step to the right with probability p and to the left with q . Let us say we find ourselves at position X_1 . We repeat this experiment N times and get displacements $X_2 \dots X_N$. We are interested where we are after N steps. Hence, we are interested in

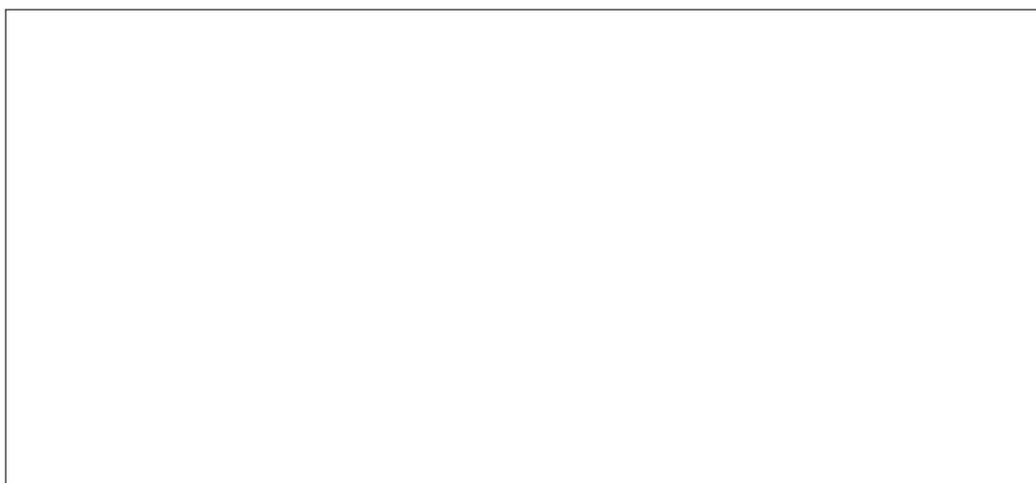
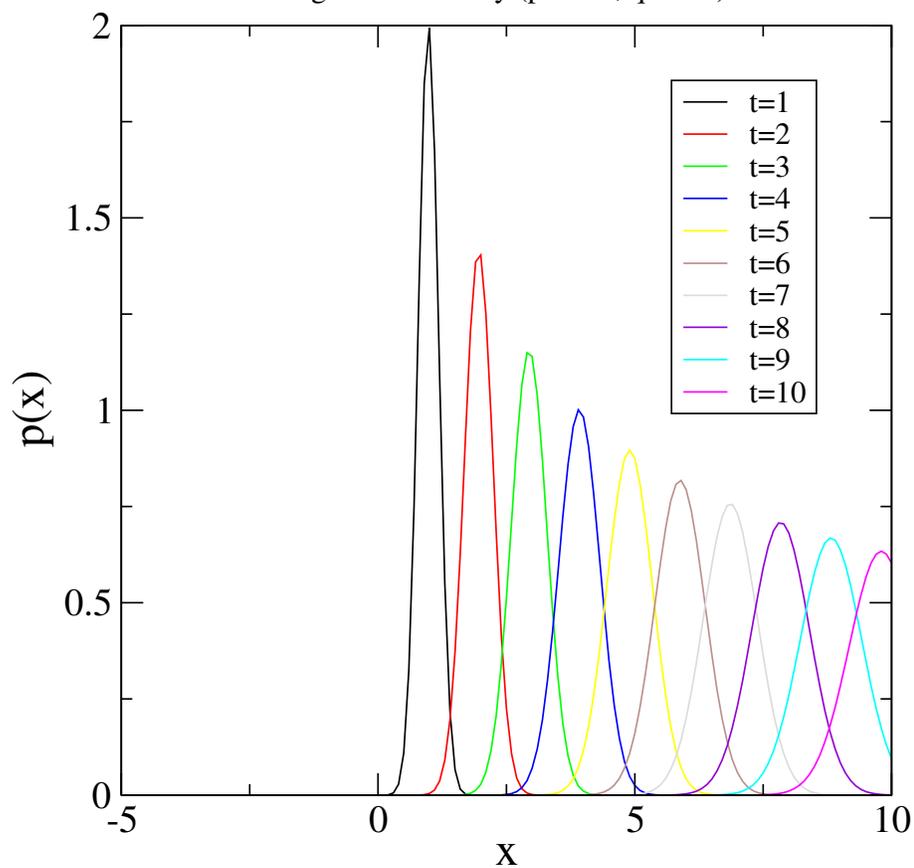
Discussions:

low drift velocity ($p=0.6, q=0.4$)



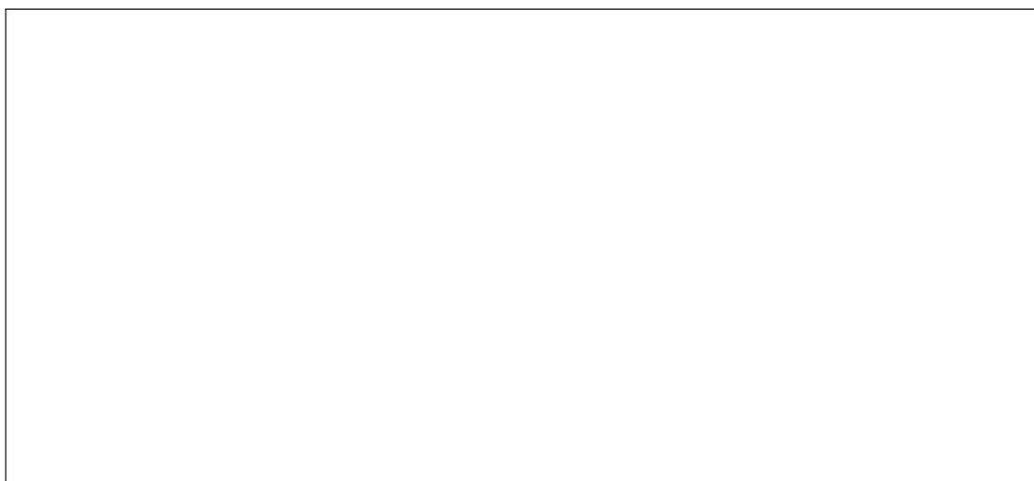
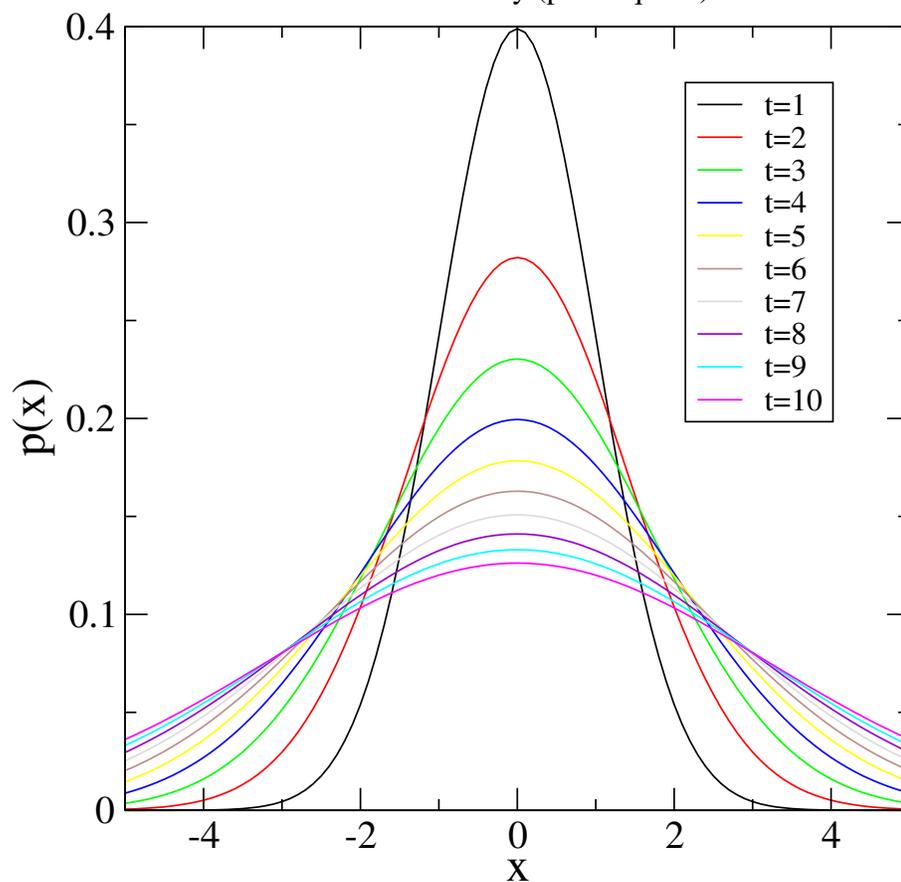
Discussions:

high drift velocity ($p=0.99, q=0.01$)



Discussions:

no drift velocity ($p=0.5$ $q=0.5$)



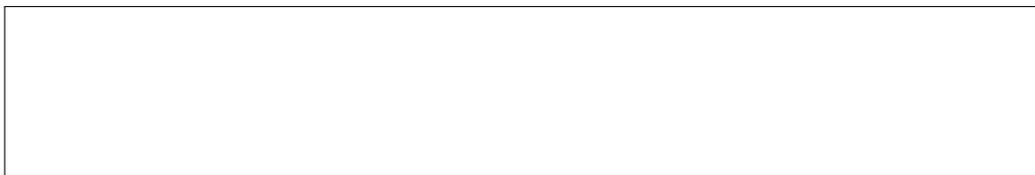
2 Micro-canonical ensemble and temperature

2.1 Entropy

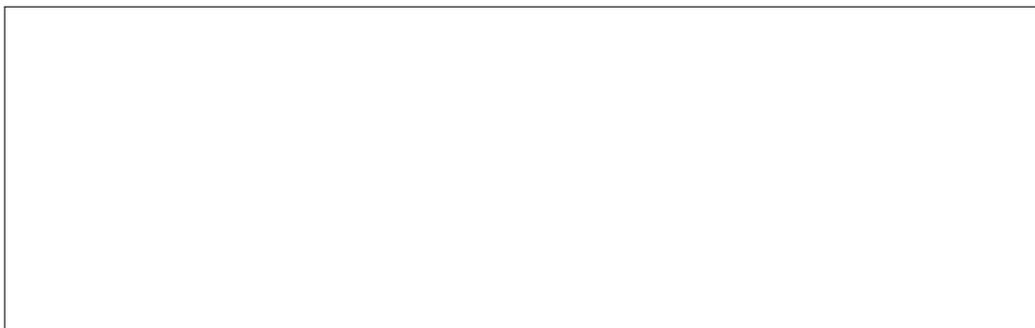
Consider a system of degrees of freedom coming out of a random process and call this state ω_1 .

Examples:

(A) 8 arrows, say spins, with orientation either *up* or *down*



(B) A container with N moving H_2 molecules



The system evolves under the laws of physics into a new state ω_2 . We also introduce a *measurement* $E(\omega) \in \mathbb{R}$, which does not change under the evolution of the system. In particular, we have

$$E(\omega_1) = E(\omega_2) .$$

E is called a *conserved quantity*. An important example is the (*internal*) *Energy* of a closed system.

Definition: The fact that the total energy does not change during time evolution when the system adopts different elements of the output space is called the **First law of Thermodynamics**.

Examples:

(A) If a spin is parallel to an external magnetic field, it contributes the energy H to the internal Energy. If a spin is anti-parallel, its contribution is $-H$. If n_+ is the numbers of spins parallel and $n_- = N - n_+$ the number of anti-parallel spins, the internal energy is given by $E = H(n_+ - n_-)$.



(B) If the i th molecule has velocity \vec{v}_i and if all molecules have the same mass m , the internal energy is given by the sum of their so-called kinetic energies:

$$E = \sum_{i=1}^N \frac{m}{2} v_i^2 .$$

We treat the evolution from ω_1 to ω_2 as a random process.

Comment: This is a stark assumption since e.g. the laws of Newtonian mechanics would allow us to calculate the positions and the velocities of all the molecules from their initial values by solving an ODE. Note that the Newtonian laws are just an approximation, which works extremely well for macroscopic bodies, and the true underlying theory is Quantum Mechanics which adds an intrinsic random process to the time evolution. In case we do not invoke this theory, we could even turn Newtonian time evolution into a random process by just saying that we do not have any information on the positions of the molecules.

Example: This is best explained using hard-sphere collisions:



Time evolution is then a random process that sequentially generates a sequence of states

$$\omega_1 \longrightarrow \omega_2 \longrightarrow \omega_3 \longrightarrow \omega_4 \dots$$

Core definition: The set of all events $\Omega = \{\omega_1, \omega_2, \dots\}$ is called a *thermodynamical ensemble*. Each ensemble is characterised by the set of conserved quantities such as energy E or particle number N .

We then can assign probabilities p_i to each state ω_i , which characterise the physical system. A good deal of history and experimental evidence then went to finding those probabilities that reproduce observations. A derived quantity which will help to analyse physical systems is the *Entropy*.

Definition: If M is the number of states of Ω , the derived quantity

$$S = - \sum_{i=1}^M p_i \ln p_i$$

is called *Entropy*, where p_i is the probability for state i to occur. It is a function of the conserved quantities, e.g., of the internal energy E : $S = S(E)$.

In order to come up with a sensible definition for the p_i , let us consider a particular example, which will then lead us to a proper mathematical definition.

Example:

Let us assume we consider hard-sphere scattering and start with an improbable setting with small p_1 . Only the right half of a container is filled with moving hard spheres, which scatter.



It is probable that some of the spheres will be scattered to the left half of the container over time. It is also likely that we reach a sort of steady state after many collisions, which is “macroscopically” only characterised by the conserved quantities. We call this steady state the *thermodynamical equilibrium*. If we zoom in to a fraction of the volume, we could exchange those volumes and would still arrive at a state that is plausible.

Example:



This leads us to the mathematical definition:

Core definition: A physical system with state space Ω and set of probabilities $\{p_i, i = 1 \dots M\}$ is in *thermodynamical equilibrium*, if all probabilities are equal

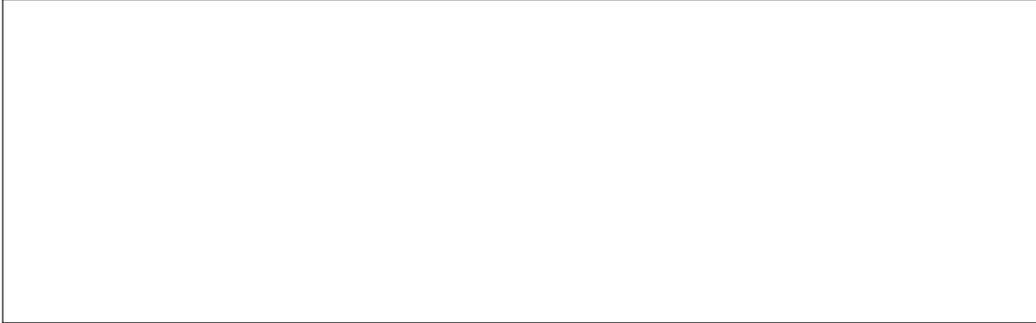
$$p_i = 1/M .$$

We draw a first conclusion: If a physical system $(\Omega, \{p_i, i = 1 \dots M\})$ is in thermodynamical equilibrium, the entropy is given by

$$S = - \sum_{i=1}^M \frac{1}{M} \ln \left(\frac{1}{M} \right) = \ln M . \quad (10)$$

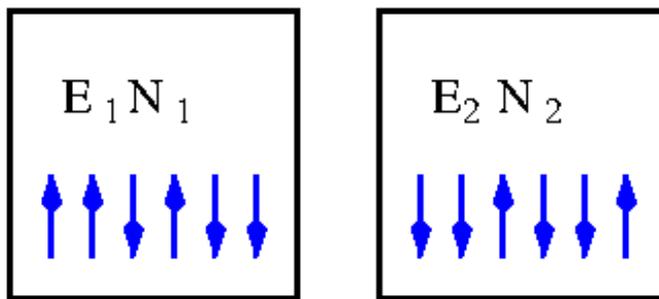
Example:

A chain of N spins (without constraints, i.e., $H = 0$) has the entropy in thermodynamical equilibrium:



2.2 Properties of Entropy

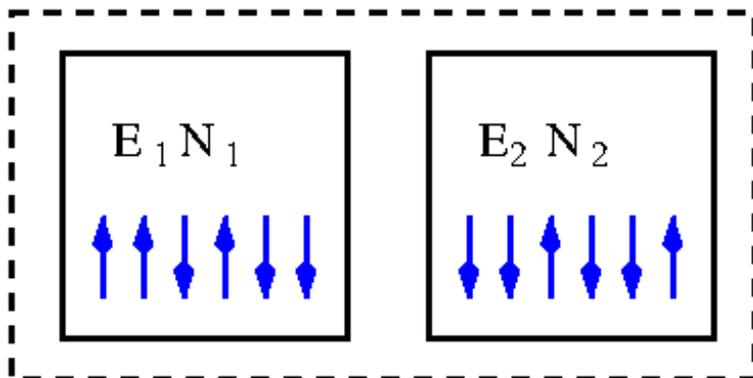
Let us consider two isolated statistical systems visualised as boxes below. We could think of our 1-dimension spin chain in an external field. Each of the systems is characterised by the internal Energy $E_{1/2}$ and the number $N_{1/2}$ of degrees of freedom, here spins. The state of the system in the left side is described by probabilities p_i , $i = 1 \dots M(E_1)$ where $M(E_1)$ is the total number of states. The probabilities q_k , $k = 1 \dots M(E_2)$ characterise the state of the system in the right box. Both systems are not necessarily in the thermodynamical equilibrium, where the set of states in either box would have the same probability.



By definition, both entropies are

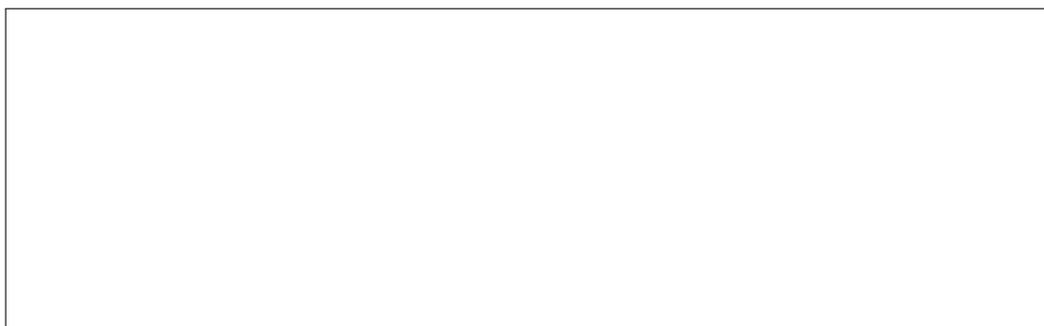
$$S_1 = - \sum_{i=1}^{M(E_1)} p_i \ln p_i, \quad S_2 = - \sum_{k=1}^{M(E_2)} q_k \ln q_k.$$

We now do not change the physics of the systems at all, but shift our point of view and consider the two boxes as *one* statistical system:



What is the Entropy of the in-thoughts combined system?

Now, we need to enumerate all possible states the combined system can attain.



Hence, there are $M(E_1)M(E_2)$ states in total. Since both systems are “isolated”, or in mathematical terms, “statistically independent”, the probability that system 1 is in state i and system 2 is in state k is given by $p_i q_k$. We then find for the Entropy of the combined system:

$$S = - \sum_{i=1}^{M(E_1)} \sum_{k=1}^{M(E_2)} p_i q_k \ln(p_i q_k)$$

Hence, we observe that the Entropy of two individual isolated systems adds up, i.e., $S = S_1 + S_2$, if both systems are *considered* as one statistical system. Of course, we can add now a third box with another statistical system and would find that its entropy adds to $S_1 + S_2$ and so on.

Key observation The Entropies of statistically independent (isolated) systems add up to form the Entropy of the combined system.

Definition: A measurement, which is additive for isolated subsystems, is called *extensive*.

Other examples for *extensive* measurements are the internal energy E and the number of degree of freedoms, N , since

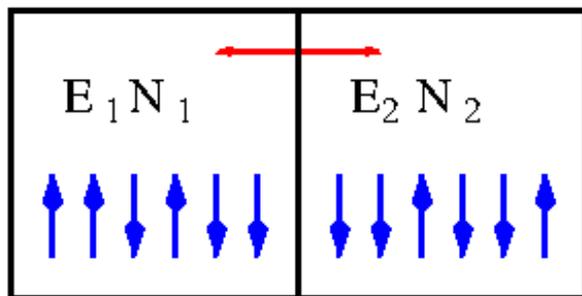
$$E = E_1 + E_2, \quad N = N_1 + N_2.$$

Let us now change the physical situation:

1. We will now assume that the system in either box is in thermodynamical equilibrium with all $p_i = p$ are the same as well as $q_k = q$. The corresponding entropies are hence given by

$$S_1 = \ln M(E_1), \quad S_2 = \ln M(E_2).$$

- Note that we naturally assume that $p \neq q$. Nevertheless, the *combined* system is *also* in thermodynamical equilibrium, since every state has the same probability $p_i q_k = pq$.
- Thermal contact:** The crucial change is now that we allow the two systems to exchange energy. Of course, the total energy $E = E_1 + E_2$ is conserved, but now the energy content of each box can change.



Before we allowed thermal contact, we found that the total entropy was $S(E) = S(E_1) + S(E_2)$, $E = E_1 + E_2$. We now allow a thermal contact and let the total system reach thermal equilibrium.

What is the entropy $S(E)$ of the thermalised system now?

Since the “big” system is in thermal equilibrium, we need to find the total number of states $M(E)$ since

$$S(E) = \ln M(E).$$

We consider the total energy E and the energy of system e_1 as variables: the energy in box 2 is then given by $e_2 = E - e_1$.¹ If it happens that system 1 has energy e_1 , the total number of states for this configuration is

$$M(e_1) M(E - e_1).$$

However, due to energy exchange, any value $0 \leq e_1 \leq E$ is also permissible. Hence, the total number of states is now:

$$M(E) = \sum_{e_1} M(e_1) M(E - e_1) > M(E_1) M(E - E_1) = M(E_1) M(E_2).$$

¹I use small letters since E_1 and E_2 are reserved for the energies in the initial state before we allowed thermal contact.

The inequality is true since all terms are positive and since $e_1 = E_1$ is one of them. We therefore derive the important result.

$$S(E) =$$

Key observation If two systems, which are in thermodynamic equilibrium with entropies $S(E_1)$ and $S(E_2)$, are allowed to exchange energy (i.e., are in “thermal contact”), the entropy $S(E_1 + E_2)$ of the combined system in equilibrium satisfies:

$$S(E_1 + E_2) > S(E_1) + S(E_2) .$$

The entropy always increases! This is called the **second law of thermodynamics**.

At least for the discrete systems, for which we can count states, the entropy is bounded from above. Hence, a thermalisation process increases the entropy until it is limited by the upper bound and reaches a maximum.

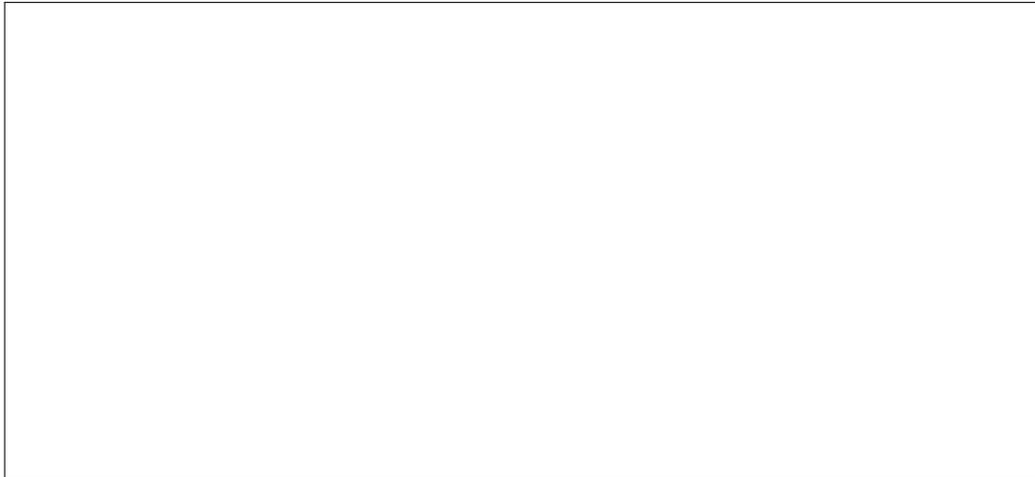
Key observation: A system in thermodynamical equilibrium has maximal entropy.

Let us check that this observation is consistent with our earlier definition of equilibrium, namely a situation in which all states of the system have the

same probability p . We are led to the task:

$$S = - \sum_i p_i \ln p_i \rightarrow \max , \quad \sum_i p_i = 1 .$$

To solve this problem, we use a Lagrange multiplier:



We indeed find that the entropy is maximal for $p_i = 1/M$, which was our definition of thermodynamical equilibrium before!

2.3 Temperature

As discussed in the previous subsections, in *thermodynamical equilibrium* (see above for the precise definition!), the entropy only depends on the conserved macroscopic parameters such as the number N of degrees of freedom or the internal energy E . In fact, we have

$$S(E) = \ln M(E) ,$$

where M is the total number of states of a given physical system. In everyday life, we are used to temperature rather than E to characterise a thermodynamical system. Here, I give a precise mathematical definition of temperature, and we will then check that this definition meets with our expectations.

Core definition: If a system is in thermodynamical equilibrium (and only then!) specified by the entropy $S(E)$ as a function of the internal energy E , the *temperature* T is defined by the derivative

$$\frac{1}{T(E)} = \left. \frac{\partial S}{\partial E} \right|_N \quad (11)$$

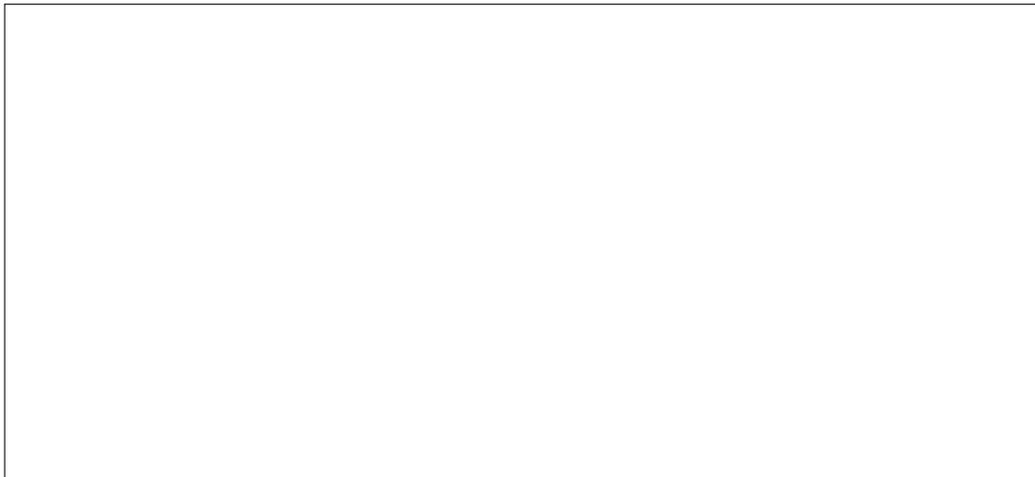
for a fixed number N of degrees of freedom.

Worked example: Consider a chain of N spins - with orientation up or down - in an external magnetic field H . If n_+ is the number of spins with orientation *up* and n_- the number of down-spins, the energy of the system is given by

$$E = H(n_+ - n_-). \quad (12)$$

The system of spins is exposed to a “heat bath” and undergoes random fluctuations in the spin orientation while the energy E is conserved. The system is in thermodynamical equilibrium.

Sketch the spin configuration with minimal energy E_{\min} and find E_{\min} .



Find the entropy S and the temperature T of the system as a function of E for the case $N \gg 1$.

For the entropy, we need to find the total number of states for a given energy

E . Note that n completely specifies E , and we only need to find the number of states for a given n :

$$M(E) = \binom{N}{n}, \quad n = (E/H + N)/2.$$

We define $\nu = E/H$ and note that $\nu + N$ is even because of (12). Thus, we find:

$$S(E) = \ln M(E) = \ln \binom{N}{(\nu + N)/2}.$$

For large N and with the help of a tutorial result, we find:

$$S(E) \approx \ln \left(\frac{2^N}{\sqrt{2\pi N}} \exp \left\{ -\frac{\nu^2}{2N} \right\} \right) = N \ln 2 - \frac{\nu^2}{2N} - \frac{1}{2} \ln(2\pi N).$$

We can now calculate the temperature:

$$\frac{1}{T(E)} = \left. \frac{\partial S}{\partial E} \right|_N = -\frac{1}{H^2} \frac{E}{N}.$$

Observations:

- The lowest temperature is reached for $E = E_{\min}$:

$$T_{\min} = H$$

and is *not* zero. This is specific to the spin system, and e.g. classical gases encapsulated in a box can reach zero temperature.

- If we raise the temperature from E_{\min} to $E \leq 0$, we find

$$\lim_{E \rightarrow 0^-} T(E) = \infty.$$

This is an ensemble where we have as many *up* as *down* spins.

- Can we have negative temperatures? Mathematically “Yes”, namely for $E > 0$. Note, however, that those systems do not naturally occur in nature: we would need to transfer energy in to the spin system by e.g. a Laser and then isolate the spins.

- For so-called “natural” systems, the relation (11) is invertible meaning that we can equally well characterise a system in thermodynamical equilibrium by temperature T rather than internal energy E .

COMMENTS

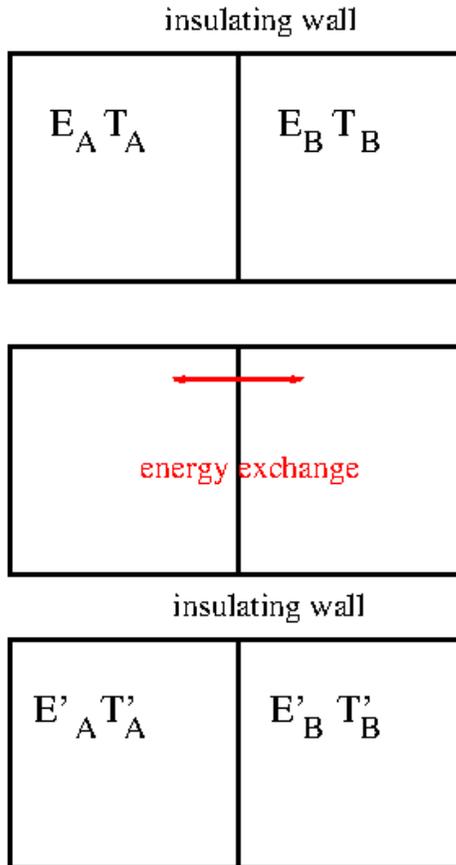
For “Natural systems”, the total number of states increases if the (conserved) internal energy is raised, i.e., $\partial M(E)/\partial E > 0$. Those systems have positive temperatures because:

2.4 Heat exchange

We still need to demonstrate that our definition of temperature is in line with everyday life experience. For example, if we bring together two containers with temperatures T_A and T_B and $T_A > T_B$, we would expect that energy flows from the hotter vessel into the colder vessel.

Mathematically this is a three stage process illustrated in the adjacent figure:

1. We prepare two systems in thermodynamical equilibrium with $E_A > E_B$. The wall between the containers is insulating.
2. We replace the insulating wall by a wall that allows energy exchange between the container. We wait until the combined system reaches the thermodynamical equilibrium.
3. We re-insert the insulating wall and now have two containers with energy E'_A and E'_B . The temperatures might change to T'_A and T'_B .



We will consider the case where E_A is not so much different from E_B so that we can expect

$$E'_{A/B} = E_{A/B} + \Delta E_{A/B}, \quad \frac{\Delta E_A}{E_A} \ll 1, \quad \frac{\Delta E_B}{E_B} \ll 1.$$

Let us briefly focus on system A: it evolves from the thermodynamical system at stage 1 into the thermodynamical system at stage 3. We know that the number of states (and hence the entropy) only depends on the energy. We

assume that we can expand the entropy in a Taylor series:²



The combined system at stage 3 is made of two isolated systems and therefore the combined entropy is the sum of the entropies of the individual systems (see subsection 2.2):

$$S_C = S_A(E'_A) + S_B(E'_B).$$

From the Second Law of Thermodynamics (see subsection 2.2), we know

$$S_C = S_A(E'_A) + S_B(E'_B) > S_A(E_A) + S_B(E_B).$$

Using the above result from the Taylor expansion, we observe:



We are now using energy conservation (or the First Law of Thermodynamics), and observe:

²This is true for most systems such as ideal gases. Near so-called 1st order phase transitions, we need to revise this assumption later.



Combining both results, we arrive at the important finding:

$$\left(\frac{1}{T_A} - \frac{1}{T_B} \right) \Delta E_A > 0 .$$

Without any loss of generality, we assumed that T_A is bigger than T_B , and, thus, the bracket in the above equation is negative. To satisfy the Second Law of Thermodynamics (i.e., the above inequality), we can conclude that (and since $\Delta E_A + \Delta E_B = 0$):

$$\Delta E_A < 0 , \quad \Delta E_B > 0 .$$

The important observation is that energy is flowing from the hot system into the cold system.

SUMMARY:

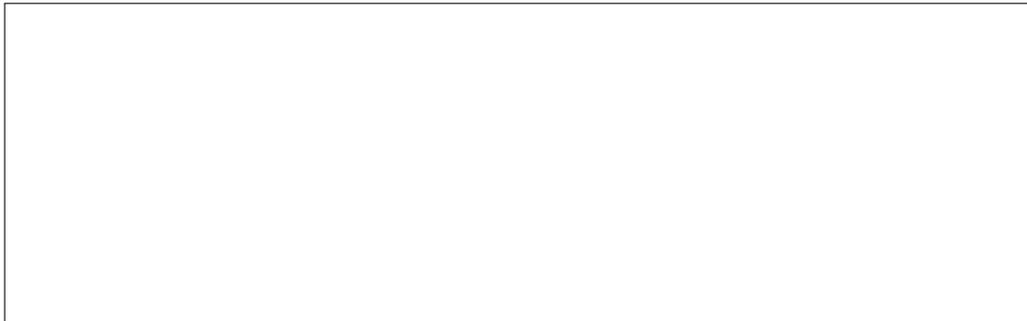
- Entropy is a mathematical tool and e.g. also used in information theory (where it is called Shannon Entropy).
- We defined a statistical system as the output space of a random process, where the events are generated by the law of physics during time evolution. Since the underlying physical processes obey energy conservation, the measurement of energy of an event is the same for all elements of the statistical ensemble (First Law of Thermodynamics).
- The statistical system is said to be in thermodynamical equilibrium when all the events (also called states) have equal probability.

- Physics input: The ergodicity conjecture is that almost any statistical system evolves towards the thermodynamical equilibrium.
- Mathematical consequence: in thermodynamical equilibrium, the entropy is only a function of the conserved quantities.
- Definition: Temperature quantifies the change in entropy when the total energy of the system changes (all in thermodynamical equilibrium).
- Mathematical consequence: the entropy increases over time (Second Law of Thermodynamics).
- Mathematical consequence: energy flows from a hot container into a cold container (and not vice versa!).

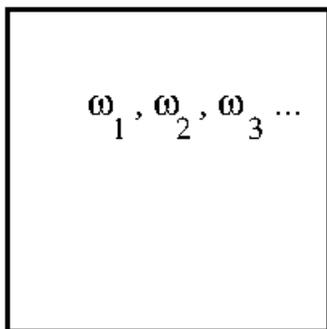
3 The canonical ensemble and Boltzmann's distribution

3.1 The heat-bath

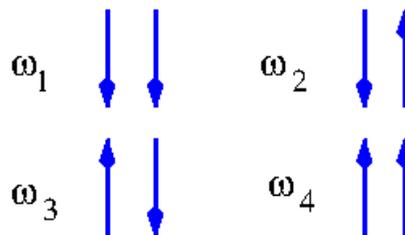
Explicit calculations with the micro-canonical ensemble are generically difficult. A practical way out is to consider the statistical system of interest immersed into a heat-bath of temperature T , say the surrounding. We view our system as small, with a number of degrees of freedom much smaller than that of the surrounding system. If we add our system to the heat-bath, its contribution to the total internal energy is small. When everything has equilibrated, our system will have to a good approximation the same temperature T as the initial heat-bath.



The “small” system has states $\omega_1, \omega_2, \dots, \omega_M$, which have energies $E_i, i = 1, 2, \dots, M$. For example, consider a system consisting of only two spins as shown below. In this case, our small system has only $M = 4$ states.

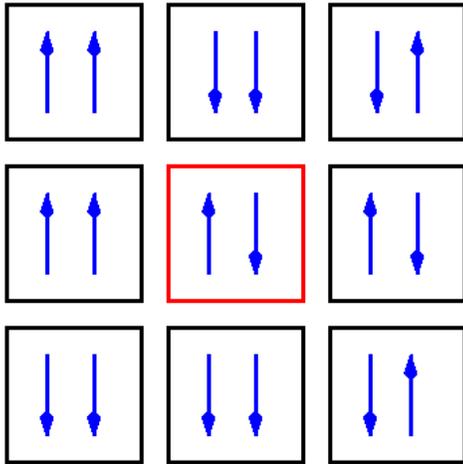


Example:



The heat-bath is made of the same material, in the above example “spins”. In order to get a technical grip on the heat-bath, we consider $N - 1 \gg 1$

replicas of our “small” system. All these systems are allowed to exchange energy and after a while are in thermodynamical equilibrium.



To describe the whole system, we introduce n_i as the number of times that we find ω_i in one of the N boxes.

For the above example, we find:

Definition: The n_i s are called **occupation numbers**.
Observation: If we pick a box at random, the probability to find a state ω_i in this box is given by $p_i = n_i/N$.

$n_k = 5$ means that 5 boxes out of the N boxes contain state ω_k . Thus, if we sum up all the occupation numbers, we recover the total number N of boxes:

$$\sum_{i=1}^M n_i = N. \tag{13}$$

What is the internal energy of the system?

We have n_k states ω_k in the system, each contributing energy E_k to the total internal energy E . Hence, we find:

$$\sum_{k=1}^M n_k E_k = E . \quad (14)$$

It turns out that E is specified by the occupation numbers, which makes them convenient parameters to describe the whole system.

The next step is to find the temperature T for a given total energy E . Since the system is in thermodynamical equilibrium, we just need to find the total number of states M_{all} . (' M ' is already reserved for the number of possible states in one box.) Assume that we have a given set of occupation numbers n_i . If, for example, $n_1 = 3$, we know that we have state ω_1 three times in the system but we have not specified *where* to find those three states. In fact, we have

$$\binom{N}{n_1} = \frac{N!}{n_1! (N - n_1)!}$$

possibilities to find a home for those n_1 states. We now need to distribute n_2 states to the remaining $N - n_1$ slots. For this we have

$$\binom{N - n_1}{n_2} = \frac{(N - n_1)!}{n_2! (N - n_1 - n_2)!}$$

possibilities. We then continue to distribute n_3 states and so on. The total number of states is therefore:

$$\begin{aligned} M_{\text{all}} &= \binom{N}{n_1} \binom{N - n_1}{n_2} \cdots = \frac{N!}{n_1! (N - n_1)!} \frac{(N - n_1)!}{n_2! (N - n_1 - n_2)!} \cdots \\ &= \frac{N!}{n_1! n_2! \dots n_M!} . \end{aligned}$$

The entropy is therefore given by:

$$S(E) = \ln(N!) - \sum_{i=1}^M \ln(n_i!) .$$

The E dependence enters via the constraint (14). In any macroscopic application the occupation numbers (and N) are fairly large numbers. For example, 22.71 litres of gas under normal conditions contains $N_A \approx 6.022 \times 10^{23}$ molecules, which is just the number of degrees of freedom. N_A is Avogadro's number. The number of potential states is usually much larger than the number of degrees of freedom. We therefore use the famous **Stirling** approximation (see tutorial):

$$\ln(n!) = n \ln n - n + \mathcal{O}(\ln n) .$$

We can neglect the $\mathcal{O}(\ln n)$ terms in comparison to n . For example, $\ln N_A \approx 54.8$ compared to the order 10^{23} . We find:



We finally find:

$$S(E) = N \ln N - \sum_{i=1}^M n_i \ln n_i + \mathcal{O}(\ln N) .$$

We can further simplify if we switch to occupation probabilities $p_i = n_i/N$ as alternative degrees of freedom. We find:



Altogether with the constraints (13) and (14), we find:

$$S(E) = -N \sum_{i=1}^M p_i \ln p_i , \quad (15)$$

$$\sum_{i=1}^M p_i = \frac{1}{N} \sum_{i=1}^M n_i = 1 , \quad (16)$$

$$\sum_{i=1}^M p_i E_i = \frac{1}{N} \sum_{i=1}^M n_i E_i = E/N . \quad (17)$$

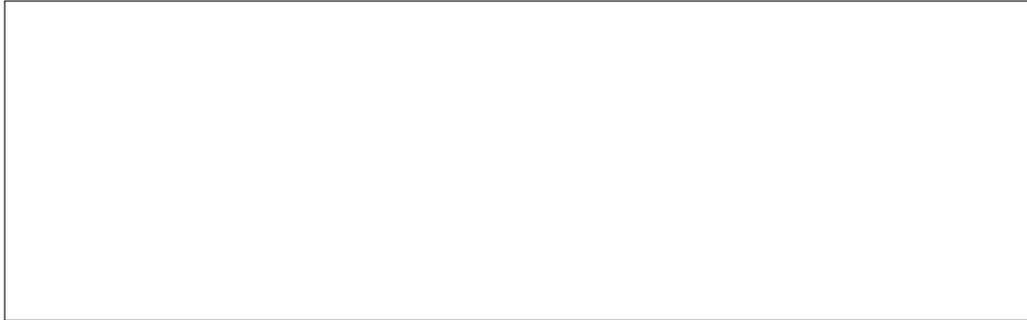
Remember that we are in thermodynamical equilibrium. The Second Law of Thermodynamics then suggests that the entropy is maximal. This is powerful, since it allows us to calculate the occupation probabilities p_i ! To do so, we need to maximise $S(E)$ in (15), taking into account the constraints (16) and (17). The way to do this is with the method of Lagrange:



The final solution is

$$p_i = \frac{1}{Z} \exp\{-\beta E_i\} , \quad (18)$$

where the free parameters Z and β must be chosen to satisfy the constraints. Indeed, (16) implies



and thus:

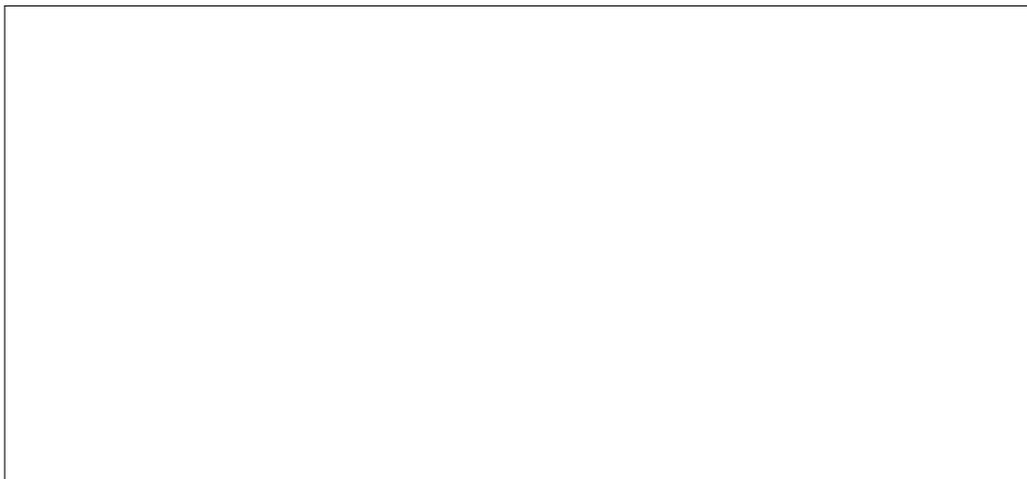
$$Z(\beta) = \sum_{i=1}^M \exp\{-\beta E_i\}. \quad (19)$$

Definition: $Z(\beta)$ in Eq. (19) is called the **partition function**. It is a primary quantity in statistical and condensed-matter physics, from which many thermodynamical observables can be derived.

Any dependence of $Z(\beta)$ on the heat-bath can only come through the other parameter $\beta(E)$, which is determined by the constraint (17):

$$\frac{1}{Z(\beta)} \sum_{i=1}^M E_i \exp\{-\beta E_i\} = \langle E \rangle(\beta) = E/N. \quad (20)$$

To extract $\beta(E)$ we insert (18) into (15) to derive the entropy as a function of E :



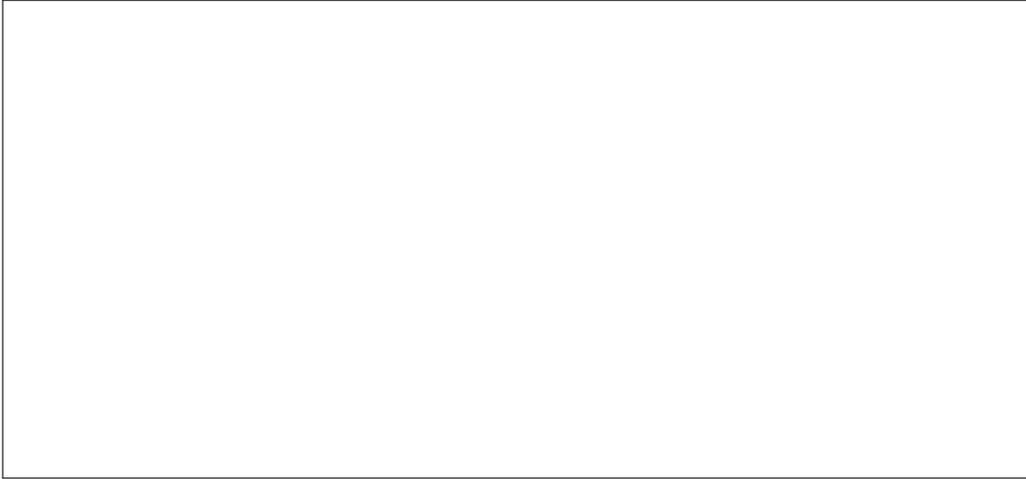
And thus, we find:

$$S(E) = \beta(E) E + N \ln Z(\beta(E)). \quad (21)$$

Rather than dealing with the total energy E , which is an extensive quantity and as such depends on the size of the heat-bath, it is much more intuitive to swap E for the intensive parameter T , i.e., temperature. As before, the connection is made via the relation:

$$\frac{1}{T(E)} = \frac{\partial S(E)}{\partial E}.$$

We can now insert (21) into the last equation and carry out a remarkable calculation:



In summary, we observe:

$$\frac{1}{T(E)} = \beta(E). \quad (22)$$

Let us scrutinise the mathematical steps to interpret the meaning of Eq. (22):

- We have calculated the entropy of the whole system as a function of the conserved total energy E . In this process, $\beta(E)$ must be chosen to satisfy a constraint.
- We then obtained the temperature $T(E)$ as a function of E . We already said that, for most systems, we can invert this relation providing $E = E(T)$ with, as usual for inverse functions, $T(E(T)) = T$.

- We can now define (with slight recycling of notation) $\beta(T) := \beta(E(T))$.
- Equation (22) then tells us:

$$\beta(T) = \frac{1}{T} .$$

This is a remarkable result: by switching from the overall conserved energy E to the temperature T , we have hidden the role of the heat-bath. Everything can now be calculated as a function of T using the states of one “small” system:

$$p_i = \frac{1}{Z(\beta)} \exp\{-\beta E_i\} , \quad (23)$$

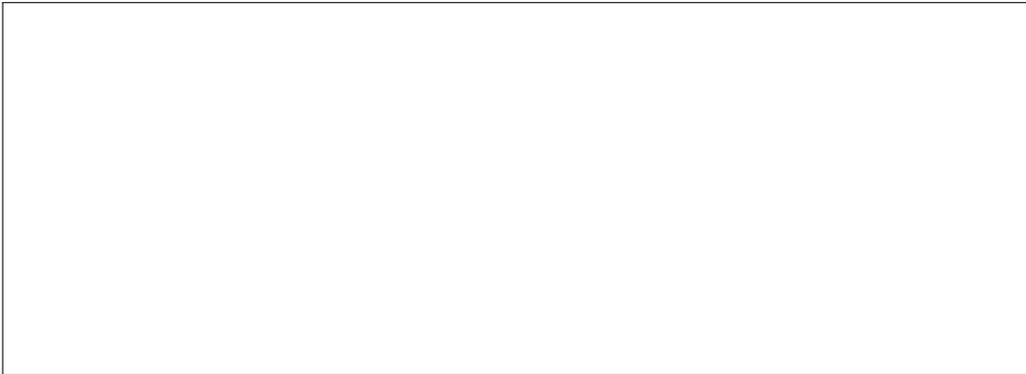
$$Z(\beta) = \sum_{i=1}^M \exp\{-\beta E_i\} , \quad \beta = 1/T . \quad (24)$$

DERIVED OBSERVABLES

We are now working with a fixed temperature T , dictated by the heat-bath, at the expense that the system’s energy is not conserved since it can exchange energy with the surrounding heat-bath. Hence, the *average internal energy* is a quantity of interest:

$$\langle E \rangle(T) = \frac{1}{Z(\beta)} \sum_{i=1}^M E_i \exp\{-\beta E_i\} = - \frac{d}{d\beta} \ln Z(\beta) . \quad (25)$$

We easily show the last equality by noting:



We can also consider the entropy $S(T)$ of our “small” system, as opposed to the $S(E) = NS(T)$ in Eq. (15) that also includes the heat-bath:

$$S(T) = - \sum_{i=1}^M p_i \ln p_i =$$

Altogether, we find:

$$S(T) = \beta \langle E \rangle(T) + \ln Z(\beta). \quad (26)$$

Another important quantity is the heat capacity c_v .³

Key definition: The heat capacity is defined by

$$c_v = \frac{d}{dT} \langle E \rangle.$$

Key observation: The heat capacity is always positive (and is only zero in exceptional cases):

$$c_v = \frac{1}{T^2} \langle (E - \langle E \rangle)^2 \rangle \geq 0.$$

(Fluctuation–Dissipation theorem)

The last expression is an example of a so-called **Fluctuation–Dissipation theorem**. The derivation is part of the homework problems. It is an important result since it reconciles our mathematical approach with everyday life experience: we would expect that, if we raise the temperature, the internal energy $\langle E \rangle$ increases. (Anything else would be very counter-intuitive!) Indeed, the theorem is telling us just this: the slope $\frac{d}{dT} \langle E \rangle$ is (generically) positive.

³The subscript V later will mean that we keep the volume constant; details have to wait until we introduce V properly below.

3.2 Helmholtz free energy

As we have seen, the partition function (24) plays a major role if our system is embedded in a large heat-bath at a given temperature. A quantity with the dimensions of energy related to the partition function is the following:

Key definition: If $Z(T)$ is the partition function of a canonical ensemble, the Helmholtz free energy is defined by

$$F(T) = -T \ln Z(T) . \quad (27)$$

KEY PROPERTIES:

We can express the average energy (25) of our system in terms of the temperature T and free energy $F(T)$:

$$\langle E \rangle(T) =$$

Likewise, we find from Eq. (26) a connection to the entropy:

$$S(T) =$$

In summary, we have the following results:

Key observations: If $F(T)$ is the Helmholtz free energy, we find

$$\langle E \rangle(T) = -T^2 \frac{d}{dT} \left(\frac{F(T)}{T} \right) , \quad (28)$$

$$S(T) = - \frac{d}{dT} F(T) , \quad (29)$$

$$\implies \langle E \rangle(T) = T S(T) + F(T) . \quad (30)$$

3.3 Spins in a magnetic fields revisited

Here, we work through a particular example in great detail. However, we will also make a very important observation: whether degrees of freedom are *distinguishable* or *identical* can make a huge difference for the thermal behaviour of the system. This feature is brought to you by quantum physics.

3.3.1 Spins in a solid

Let us consider N spins in a row, in a magnetic field H . The spins are *distinguishable* by their position in the solid.⁴ A configuration (or *event* in probability theory) is a set of N elements each of which is either $+1$ or -1 :



We have labelled the spins in a physical way, namely by their position in the solid. The spins do not interact with each other. The energy of a particular configuration is given by:

$$E(\{s_i\}) = H \sum_{i=1}^N s_i .$$

Each state is completely and uniquely specified by the spin values $\{s_i\}$.

Distinguishable: Thus, the sum over all states is given by the sum over all spin configurations.

⁴Properties of individual spins could be measured by a targeted experiment.

The partition function (24) is thus given by

$$\begin{aligned}
 Z_{\text{dist.}} &= \sum_{s_1=\pm 1} \cdots \sum_{s_N=\pm 1} \exp \left\{ -\beta E(\{s_i\}) \right\} = \sum_{\{s_i\}} \exp \left\{ -\beta E(\{s_i\}) \right\} \\
 &= \sum_{\{s_i\}} \exp \left\{ -\beta H \sum_{i=1}^N s_i \right\} \\
 &= \sum_{\{s_i\}} \exp \{-\beta H s_1\} \cdots \exp \{-\beta H s_N\}. \tag{31}
 \end{aligned}$$

We are now using

$$\sum_{i=1}^N \sum_{k=1}^N a_i b_k = \left(\sum_{i=1}^N a_i \right) \left(\sum_{k=1}^N b_k \right),$$

which also implies

$$\sum_{i,k,l} a_i b_k c_l = \left(\sum_{i=1}^N a_i \right) \left(\sum_{k=1}^N b_k \right) \left(\sum_{l=1}^N c_l \right), \quad \text{etc.}$$

Let us spend some time to enjoy a bit of our 5000-year mathematical legacy—the distributive rule:



We now can re-write Eq. (31):

$$\begin{aligned} Z_{\text{dist.}} &= \sum_{\{s_i\}} \exp\{-\beta H s_1\} \dots \exp\{-\beta H s_N\} = \\ &= \left(\sum_{s_1} e^{-\beta H s_1} \right) \dots \left(\sum_{s_N} e^{-\beta H s_N} \right) . \end{aligned}$$

If we rename the spin variable in each of the sums (to, say, s), we find

$$Z_{\text{dist.}} = \left(\sum_{s=\pm 1} e^{-\beta H s} \right)^N = (e^{-\beta H} + e^{\beta H})^N . \quad (32)$$

The Helmholtz free energy F in Eq. (27), for our case here

$$F(T) = -T N \ln (e^{-\beta H} + e^{\beta H}) , \quad (33)$$

is our starting point to calculate the internal energy $\langle E \rangle$ and entropy S :

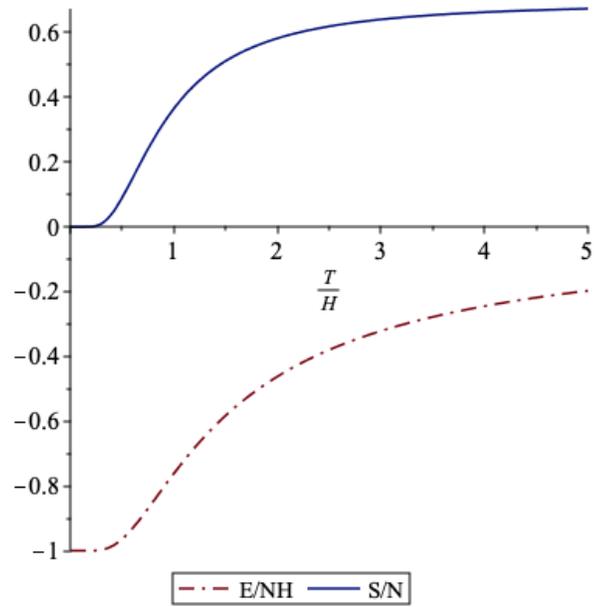


Hence, we have obtained:

$$\langle E \rangle(T) = -N H \tanh(\beta H) , \quad (34)$$

$$S(T) = -N H \beta \tanh(\beta H) + N \ln (e^{-\beta H} + e^{\beta H}) . \quad (35)$$

The figure below shows both in natural units as a function of the dimensionless ratio T/H :

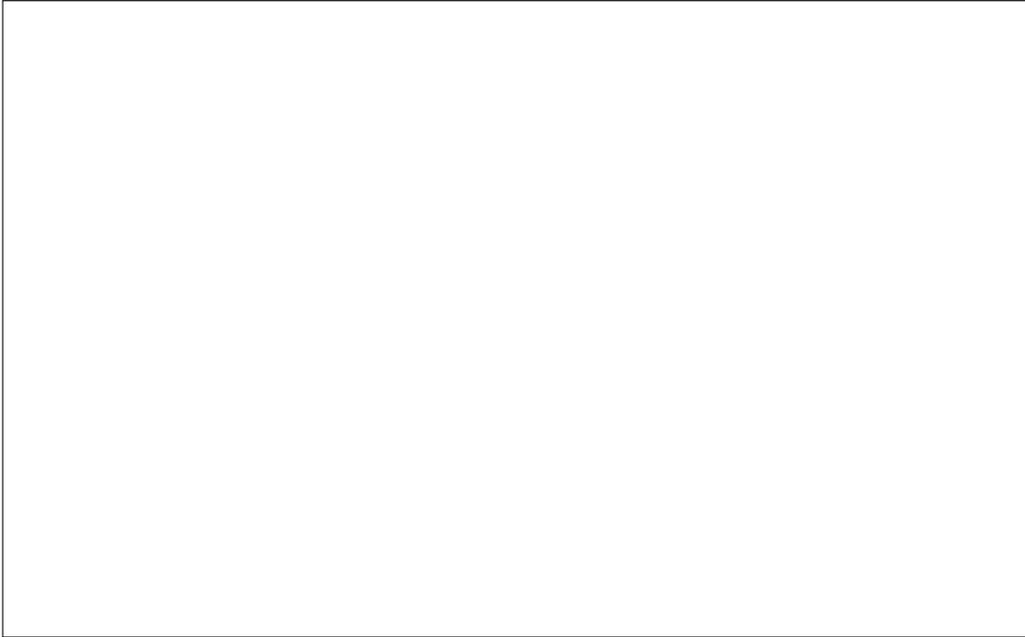


COMMENTS:

Let us study what happens at *low* temperatures as defined by

$$\beta H \gg 1 \quad \implies \quad e^{-\beta H} \ll 1 .$$

Expanding in powers of $\exp\{-\beta H\}$ we find:



With Maple we can get the next order in a convenient way:

$$\frac{E}{NH} = -1 + 2e^{-2\beta H} - 2e^{-4\beta H} + \mathcal{O}(e^{-6\beta H}) . \quad (36)$$

This has an interesting interpretation:

- At leading order, the energy is $E = -NH$. This energy is as low as it can get. We say the system is in the so-called *ground state*. In our case, *all* spins are pointing down.
- The next states with slightly higher energy are those where all spins except one are pointing down. The energy difference to the ground state is

$$\Delta E = -(N-1)H + H - [-NH] = 2H .$$

The probability that this so-called excited state is populated at small temperature is exponentially small, namely $\exp\{-\Delta E/T\}$. This is generically the case for systems with a gap between the ground state and excited states.

For the entropy, we find for low temperatures:

$$\frac{S}{N} = [1 + 2\beta H] e^{-2\beta H} + \mathcal{O}\left(e^{-4\beta H}\right). \quad (37)$$

COMMENT:

The entropy vanishes exponentially fast for low temperature (up to power-law corrections). This might be due to the discrete nature of our energy states. It is, however, generic that S vanishes for T approaching zero: in this limit systems are in their ground state, and generically (in quantum mechanics) there is only one ground state. In information theory, the system loses its capacity to store information at $T = 0$. The setting with $T = 0$ is also called *absolute zero*.

Let us also study the *high-temperature* limit: $\beta H \ll 1$. In this case, we can expand the exponentials in Eqs. (34) and (35) in a Taylor series of powers of βH . We find:

$$\frac{\langle E \rangle}{NH} = -\frac{1}{T/H} + \frac{1}{3(T/H)^3} + \mathcal{O}\left(\frac{1}{(T/H)^5}\right). \quad (38)$$

$$\frac{S}{N} = \ln 2 - \frac{1}{2(T/H)^2} + \mathcal{O}\left(\frac{1}{(T/H)^4}\right). \quad (39)$$

COMMENTS:

3.3.2 Gas of spins

We now consider N spins in a gas exposed to a magnetic field H . The spins are now indistinguishable. Note that the set-up is very similar to that of “spins in a solid” of the previous subsection: the only difference is now the elusive property of being *indistinguishable*. We will see that the mere ability to tell particles apart has some measurable impact on observables. This taps into the very modern field of quantum information: can information (knowledge) have an impact on the physical world?

The key input to answer this question comes from the decision that we sum over all *states* in the partition function (24), and this does not necessarily mean a sum over all spin orientations. This (physics) input from observed nature makes all the difference: observation tells us how we need to choose *states* to describe nature.

Let us consider the example of $N = 4$ spins. What are the states of this system?

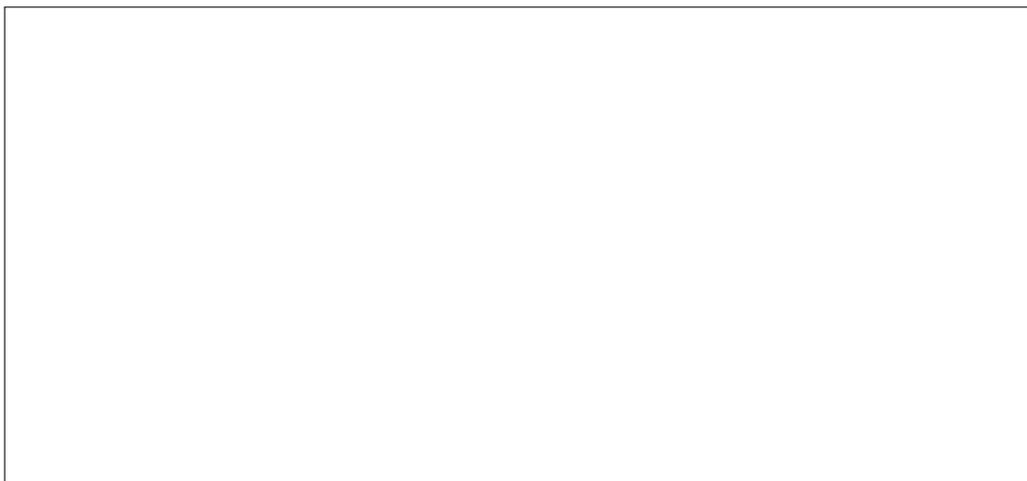


We see that due to the lack of any other distinctive feature, the states are uniquely characterised by the energy of the system.

Indistinguishable: Thus, the sum over all states will be a sum over all possible energy levels.

What are these possible energy levels?

The lowest feasible energy is $-N H$. If we change the orientation of *one* spin, say $s_i \rightarrow -s_i$, the energy changes by:



Hence, all possible energy levels are:

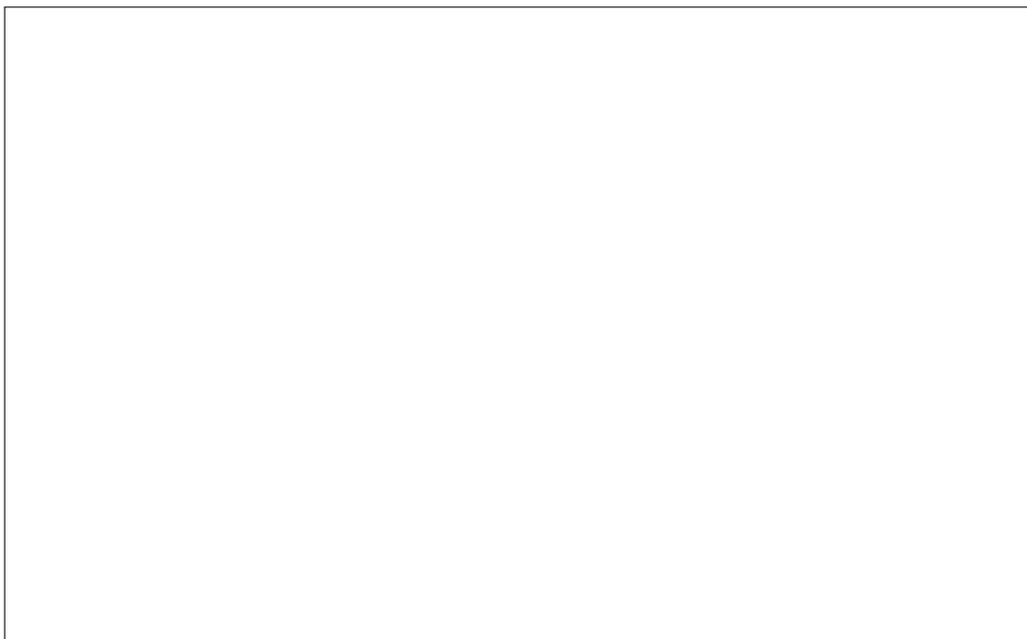
$$E_k = -N H + 2H k , \quad k = 0 \dots N .$$

This takes into account that the energy changes in units of $2H$ and that the upper limit for the energy is $N H$, corresponding to all spins pointing up.

We can now use the machinery of the previous subsection:

- Calculate the partition function Z from Eq. (24).
- Get the free energy F from Eq. (27), then derive the internal energy $\langle E \rangle$ and the entropy S as functions of the temperature using Eqs. (28) and (29).

For the partition function, we calculate:



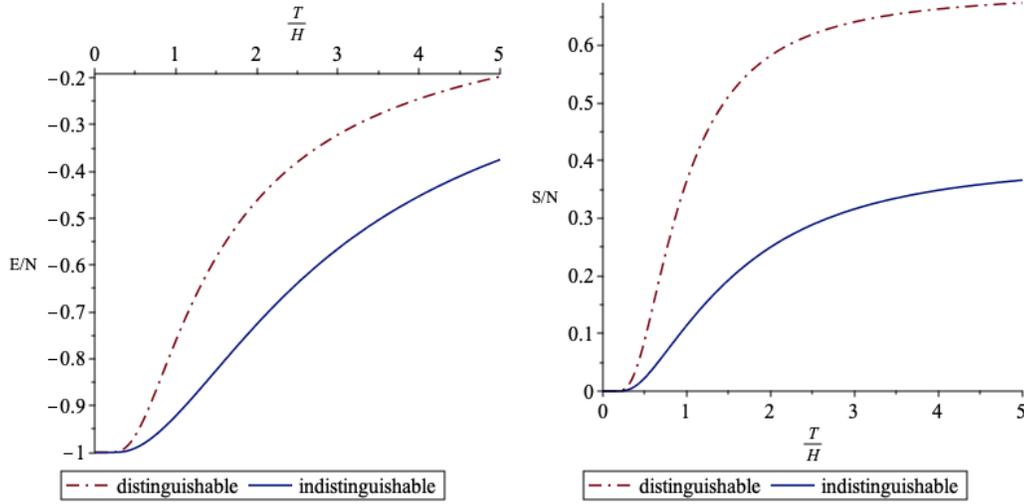
We finally obtain:

$$Z_{\text{indis.}} = e^{\beta H N} \frac{1 - e^{-2\beta H(N+1)}}{1 - e^{-2\beta H}}.$$

The free energy is therefore given by

$$F_{\text{indis.}}(T) = -N H - T \ln(1 - e^{-2\beta H(N+1)}) + T \ln(1 - e^{-2\beta H}) . \quad (40)$$

We will leave it to an exercise to derive explicit formulas for entropy and internal energy (e.g. using Maple). The results are shown below. Most striking is that the free energy in the indistinguishable case is *not* simply proportional to N . Equivalently, $F_{\text{indis.}}/N$ depends on N . This is a true quantum effect arising from the indistinguishable nature of the spins. Let us compare the results for spin systems with $N = 4$ in the cases that the spins can be distinguished (previous subsection) and cannot be distinguished.



COMMENTS:

Let us finally study the high-temperature limit $\beta H \ll 1$.

$$\frac{\langle E_{\text{indis.}} \rangle}{H} = -\frac{N(N+2)}{3(T/H)} + \mathcal{O}\left(\frac{1}{(T/H)^3}\right), \quad (41)$$

$$S_{\text{indis.}} = \ln(N+1) - \frac{N(N+2)}{6(T/H)^2} + \mathcal{O}\left(\frac{1}{(T/H)^3}\right). \quad (42)$$

The difference in the N dependence between these results compared to Eqs. (38) and (39) is striking. Most notably, the entropy only increases *logarithmically* with N in the indistinguishable case, while it is proportional to N in the distinguishable case.

4 Application: The classical ideal gas

4.1 The quantum salvation

What is a classical and ideal gas?

Classical: The gas consists of particles described by a momentum vector \vec{p} , perhaps a position vector \vec{x} and a mass m . Classical means that the speed of the particle is small compared to the vacuum speed of light. This means that the energy of the particle is given by

$$E = \frac{1}{2m} \vec{p}^2 ,$$

as dictated by *classical* (Newtonian) mechanics.

Ideal: The particles of the gas do not interact. The total energy of the gas is thus given by the sum of the energies of the individual particles:

$$E = \frac{1}{2m} \sum_{i=1}^N \vec{p}_i^2 . \quad (43)$$

We will consider the gas enclosed in a box with volume V . The box is placed into a heat-bath with which the gas can exchange energy. Box and heat-bath are in thermal equilibrium and the state of the gas is well described by the temperature T .



Conundrum: Recall that the partition function is calculated from the sum over all possible states. Here, however, lies a major obstacle: in the above setup we would describe the state by specifying the velocities of all the particles. Since the velocity components are real numbers, there would be non-countably infinitely many states, making the partition function as it stands ill-defined.

Quantum solution: Quantum physics turns the ill-defined problem into a well-defined one. Only the main line of reasoning is illustrated here, which cannot replace a course in quantum physics.⁵ In quantum mechanics, a particle moves according to a probability density function $|\psi(x)|^2$, where the so-called wave function $\psi(x)$ satisfies a wave-type equation, the Schrödinger equation, which replace the laws of classical mechanics. For a particle confined to a region between $-L/2$ and $L/2$ on the x -axis, the wave function is given by

$$\psi(x) = \cos(kx) \quad \text{or} \quad \psi(x) = \sin(kx) ,$$

where the momentum of the particle is related to k by:

$$p = \hbar k , \quad \hbar = \frac{h}{2\pi} , \quad h : \text{Planck's constant.}$$

The probability density must vanish at the boundaries at $x = \pm L/2$ leading to:

$$kL/2 = (n + 1/2)\pi , \quad \text{or} \quad kL/2 = m\pi .$$

This leads to the allowed (quantised) momenta:

$$p = \hbar \frac{\pi}{L} n , \quad n \in \mathbb{N}. \quad (44)$$

While there are still infinitely many states, they are now countable, so we can hope that the partition function is well defined.

4.2 Internal energy and entropy

Let us check how this pans out for just one particle in one dimension:

$$Z_1 = \sum_{n=1}^{\infty} \exp \left\{ -\frac{p_n^2}{2mT} \right\} = \sum_{n=1}^{\infty} \exp \left\{ -\frac{\hbar^2 \pi^2}{2mTL^2} n^2 \right\} .$$

On a macroscopic scale, \hbar is a very small number meaning that for such systems we can assume that:

$$\frac{\hbar^2 \pi^2}{2mTL^2} \ll 1 .$$

⁵If you have not yet visited such a course, please jump to the result in Eq. (44), which is all that we need to proceed.

This implies that we can approximate the sum \sum_n by an integral $\int dn$:

$$Z_1 \approx \int_0^\infty dn \exp \left\{ -\frac{\hbar^2 \pi^2}{2mTL^2} n^2 \right\} = \frac{1}{2} \int_{-\infty}^\infty dn \exp \left\{ -\frac{\hbar^2 \pi^2}{2mTL^2} n^2 \right\} .$$

Using (44), we have

$$\frac{L}{\hbar\pi} dp = dn .$$

Reinstating the momentum variable, we find:

$$Z_1 \approx \frac{1}{2} \int \frac{L}{\hbar\pi} dp \exp \left\{ -\frac{p^2}{2mT} \right\} .$$

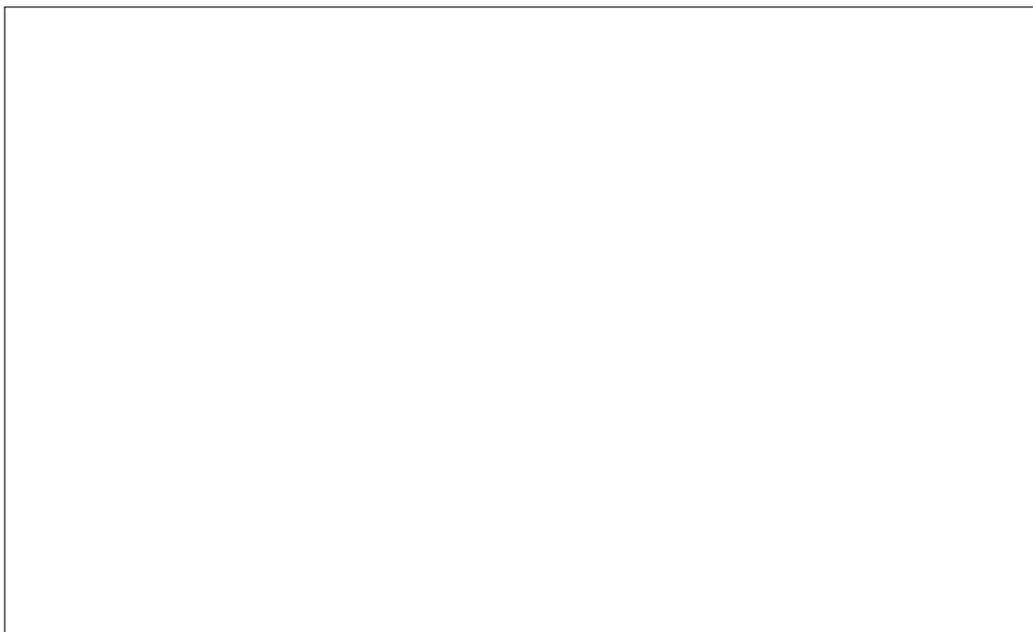
This integral is finite and indeed the partition function is well defined thanks to quantum physics. We are now in the position to generalise to three dimensions and N particles. For each dimension, we have an independent momentum variable and we generalise

$$p^2 \rightarrow p_x^2 + p_y^2 + p_z^2 .$$

We also have an independent momentum vector for each of the N particles. Altogether, the partition function is:

$$Z = \frac{1}{N!} \left(\frac{L}{2\pi\hbar} \right)^{3N} \int d^{3N}p \exp \left\{ -\sum_{k=1}^N \frac{\vec{p}_k^2}{2mT} \right\} . \quad (45)$$

We here assume that the particles are *indistinguishable*. In writing down the partition function, we have labeled the particles with numbers and have assigned the momenta $\vec{p}_1, \vec{p}_2, \vec{p}_3 \dots$ accordingly. If the particles are indistinguishable, this labeling is artificial, and the factor $1/N!$ corrects for the over-counting. Let us study this for just four particles in some detail:



The Gaussian integrals in (45) can be calculated in closed form:

$$Z = \frac{1}{N!} \left(\frac{L}{2\pi\hbar} \right)^{3N} (2\pi mT)^{3N/2}. \quad (46)$$

We will be working throughout with a large number of particles, i.e., $N \gg 1$. In this case, we can further simplify using Stirling's formula:

$$N! = \sqrt{2\pi N} N^N e^{-N}.$$

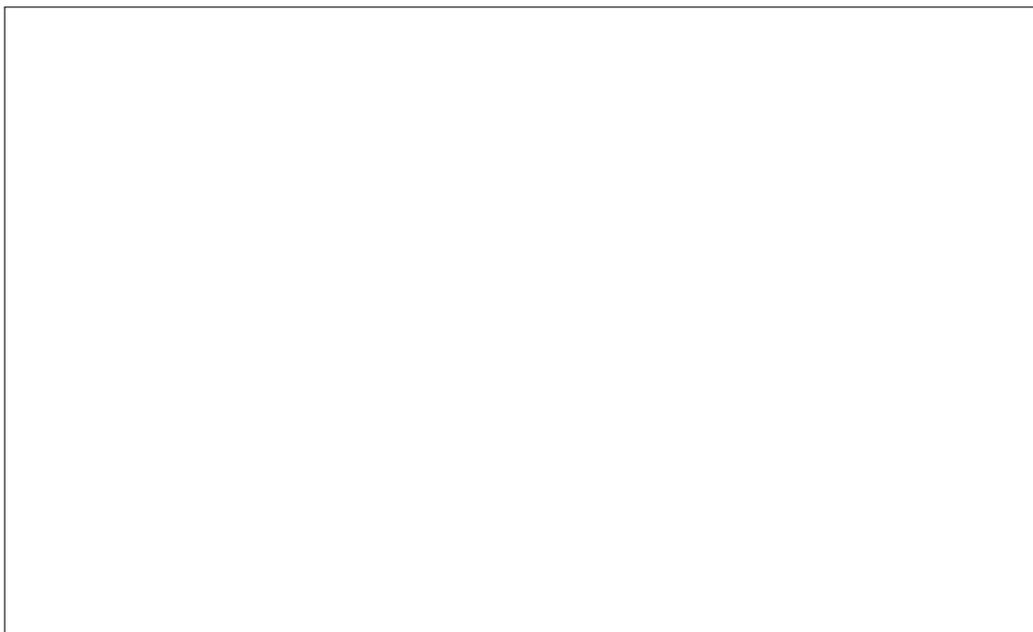
We find:

$$Z \approx \frac{1}{\sqrt{2\pi N}} \left[e \frac{V}{N} \left(\frac{2\pi Tm}{\hbar^2 4\pi^2} \right)^{3/2} \right]^N.$$

The free energy is hence given by:

$$F(T) = -NT \ln \left[e \frac{V}{N} \left(\frac{2\pi Tm}{\hbar^2 4\pi^2} \right)^{3/2} \right] + \mathcal{O}(\ln N). \quad (47)$$

It is now straightforward to calculate the internal energy and the entropy using Eqs. (28) and (29):



We finally obtain the result:

$$\langle E \rangle(T) = \frac{3}{2} N T, \quad (48)$$

$$S(T) = N \ln \left[e \frac{V}{N} \left(\frac{2\pi T m}{\hbar^2 4\pi^2} \right)^{3/2} \right] + \frac{3}{2} N. \quad (49)$$

For a compact notation, it is convenient to introduce the *thermal de Broglie*⁶ *wavelength*:

$$\lambda(T) = \left(\frac{\hbar^2 4\pi^2}{2\pi m T} \right)^{1/2} = \frac{h}{\sqrt{2\pi m T}}. \quad (50)$$

The entropy then takes the compact form:

$$S(T) = N \ln \left[e \frac{V}{N \lambda^3} \right] + \frac{3}{2} N. \quad (51)$$

⁶Louis Victor Pierre Raymond de Broglie, 7th duc de Broglie, 1882–1987, French physicist who made groundbreaking contributions to quantum theory.

COMMENTS:

4.3 The Gibbs paradox and the mixing entropy

Mathematics is based upon axioms, and theorems, which are proven starting from the axioms. Over the years, the knowledge of Mathematics grows. Assume that one day, a mathematician arrives at an inconsistency during proof (i.e., by using only what has been rigorously established), e.g. “ $2=3$ ”. The only⁷ conclusion left is that the axioms do not hold up and have to be changed. Luckily, this has not happened since more than 5000 years.

Something similar (and perhaps more likely to occur) can happen in Physics: assume that we have developed a theory (such as thermodynamics) that should describe one aspect of nature. This theory can be an approximation valid only for a certain parameter range. An example is classical mechanics, which is an excellent theory for phenomena at everyday life scales. This theory is superseded by Quantum Mechanics, which is also valid at particle length scales. Now and then it can happen that such a theory develops a contradiction within its own framework. This is called a *paradox*. If a mistake in the derivation of the paradox cannot be found, it would lead to the demise of the theory. Such a paradox was indeed found by Gibbs⁸ in the context of thermodynamics.

Consider a box of N *distinguishable* particles in a box. Other than being distinguishable, the particles have the same physical properties. Think of identical billiard balls, each with a different number on it. The box is in thermodynamical equilibrium and has two compartments separated by a wall:

⁷This might be an assumption: mathematicians also study what can be described by mathematics asking whether there can be something outside Mathematics and necessarily remains there.

⁸Josiah Willard Gibbs (February 11, 1839 – April 28, 1903) - E an American scientist



State (A): Let us call this state A. What is its entropy? We did such a calculation in Section 4.2: since the particles are now distinguishable, the factor $1/N!$ is missing from the partition function Z (46):

$$Z = \left(\frac{L}{\hbar 2\pi} \right)^{3N} (2\pi T m)^{3N/2} .$$

The Helmholtz free energy and the entropy is therefore given by

$$\begin{aligned} F(T) &= -N T \ln \left(V \left(\frac{2\pi T m}{\hbar^2 4\pi^2} \right)^{3/2} \right) . \\ S(T) &= -\frac{dF}{dT} = N \ln \left(\frac{V}{\lambda^3} \right) + \frac{3}{2} N , \end{aligned} \tag{52}$$

with λ in (50). We now can write down the entropy S_A of state (A). It is the sum of entropies for each compartment with volume $V/2$ and particle number $N/2$:



$$S_A = N \ln \left(\frac{V}{2} \frac{1}{\lambda^3} \right) + \frac{3}{2} N . \quad (53)$$

State (B): We arrive at state (B) by removing the separating wall.



Now, all N particles are distributed in volume V , and the entropy S_B of state (B) is given by the expression (52):

$$S_B = N \ln \left(V \frac{1}{\lambda^3} \right) + \frac{3}{2} N .$$

The entropy has increased as expected:

$$\Delta S = S_B - S_A = N \ln 2 .$$

State (C): We arrive at state (C) by reinserting the separating wall. During the process, we take care that $N/2$ particles are in each compartment when the process finished. Since both compartments as well as the whole volume

in state (B) was at the same temperature T throughout, nothing has changed and we are back at state (A). Hence:

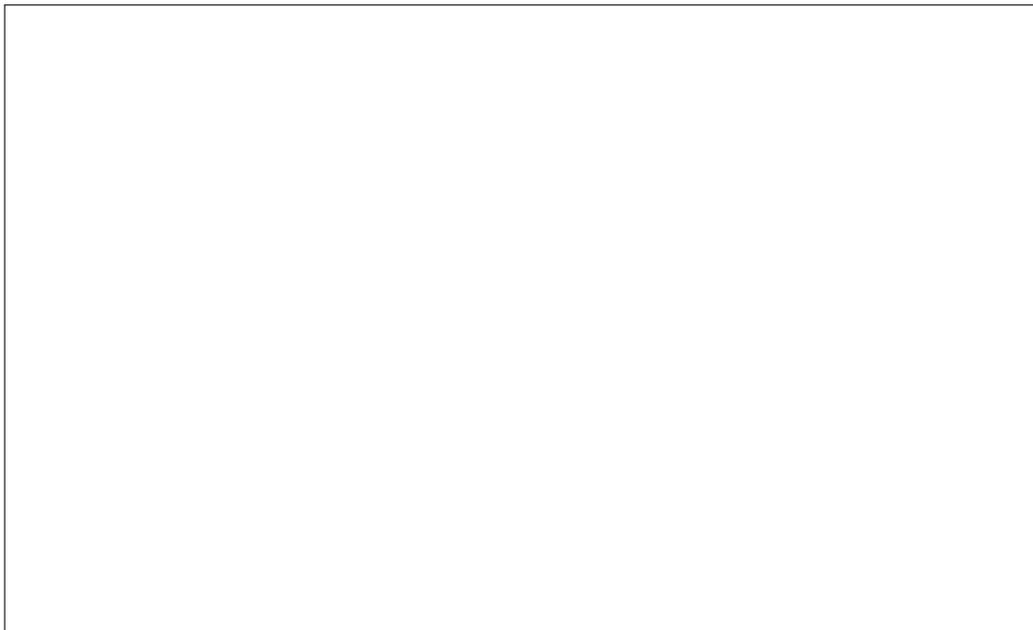
$$S_C = S_A.$$

This, however, is a serious problem for our framework:

$$B \longrightarrow C : \quad S_B > S_C .$$

In words: our system evolved from state (B) to state (C), but apparently the entropy has decreased. This violates the second law of thermodynamics (see subsection 2.2), namely that the entropy always increases or stays constant. This seems to be a inconsistency of our approach and is called the Gibbs paradox since it put forward by Gibbs in 1874–1875.

Luckily, something is wrong in the line of arguments in section “State (C)” above. After state (B), we do *NOT* arrive back at state (A). Remember that the particles are *distinguishable*: starting at state (A), we can number them. A natural choice (but any other would do as well) is to number the particles from 1 to $N/2$ in the left compartment and from $N/2$ to N in the right one. Once we are in state (C), we indeed have $N/2$ particles in each compartment at the same temperature, but the numbering is (most likely) all mixed up. State (C) is not State (A).



In fact, by redistributing numbers to $N/2$ particles on the left and right hand side produces many possible outcomes from state (C), and hence explains the increase in entropy.

However, we could still be in trouble: what happens if the particles are *indistinguishable*? In this case, we would indeed have that state (C) is the same as state (A). Let us check the entropies. We can use formula (51) for the case of an ideal gas with indistinguishable particles:

$$\begin{aligned}
 S_A &= \frac{N}{2} \ln \left[e \frac{V/2}{N/2} \frac{1}{\lambda^3} \right] + \frac{3}{2} \frac{N}{2} \\
 &+ \frac{N}{2} \ln \left[e \frac{V/2}{N/2} \frac{1}{\lambda^3} \right] + \frac{3}{2} \frac{N}{2} = N \ln \left[e \frac{V}{N} \frac{1}{\lambda^3} \right] + \frac{3}{2} N .
 \end{aligned}$$

For state (B), we have N particles in the volume V , and thus:

$$S_B = N \ln \left[e \frac{V}{N} \frac{1}{\lambda^3} \right] + \frac{3}{2} N .$$

We already said that for indistinguishable particles state (C) and state (A) are identical implying $S_C = S_A$. The crucial observation is that all these entropies are the same:

$$S_A = S_B = S_C .$$

This is what Gibbs had in mind: the wall is fictitious. Removing or reinserting it does not change anything.

Also note again that pure information can have a measurable physical effect. Mixing distinguishable particles, which otherwise have identical physical properties, leads to an increase in entropy. This increase is called *mixing entropy*.

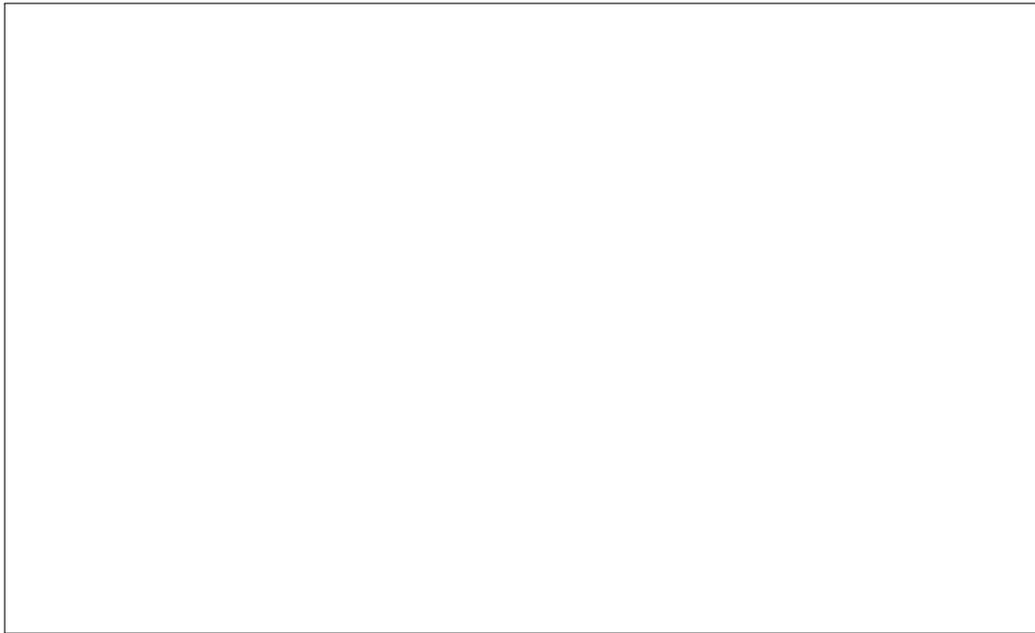
4.4 Pressure and the equation of state

It is remarkable that we needed quantum physics to properly define the partition function: the classical description of a gas with N particles specified by position and velocity, all real numbers, leads to a state space that is not *countable*. Quantum physics have provided a countable state space and, as a side-effect, introduced the volume V as a parameter in the partition function.

Definition: A parameter (other than temperature) in the canonical partition function, which might enter via the definition of the energy or the state space, is called *control parameter*.

4.4.1 Definition of pressure

As the name suggests, we can usually change the control parameter in an experimental setup. For example, we might change the volume V of a gas container in several ways:



The response of the thermodynamical system to a change in the control parameter then defines new thermodynamical quantities.

Key definition: Consider a thermodynamical system enclosed in a volume V and exposed to a heat-bath with temperature T .

(a) A change of the volume V without changing the entropy of the system is called *adiabatic*.

(b) The change of the internal energy under an adiabatic change of the volume is called **pressure**:

$$p = - \left. \frac{\partial \langle E \rangle}{\partial V} \right|_S . \quad (54)$$

COMMENT:

If the entropy of the container stays constant, it means that an energy exchange with the heat bath has *not* taken place. One way to realise is that the compression is very fast, so that there is no time for a heat exchange with the surrounding.

4.4.2 The equation of state

WORKED EXAMPLE - the Ideal Gas

We already worked out $\langle E \rangle$ and the entropy S for the ideal gas (see (48) and (51)). Since all N particles are enclosed in the volume V at all times, N does not change during an adiabatic change of volume. Constant entropy then implies

$$V T^{3/2} = \text{constant} , \quad (\text{adiabatic}) . \quad (55)$$

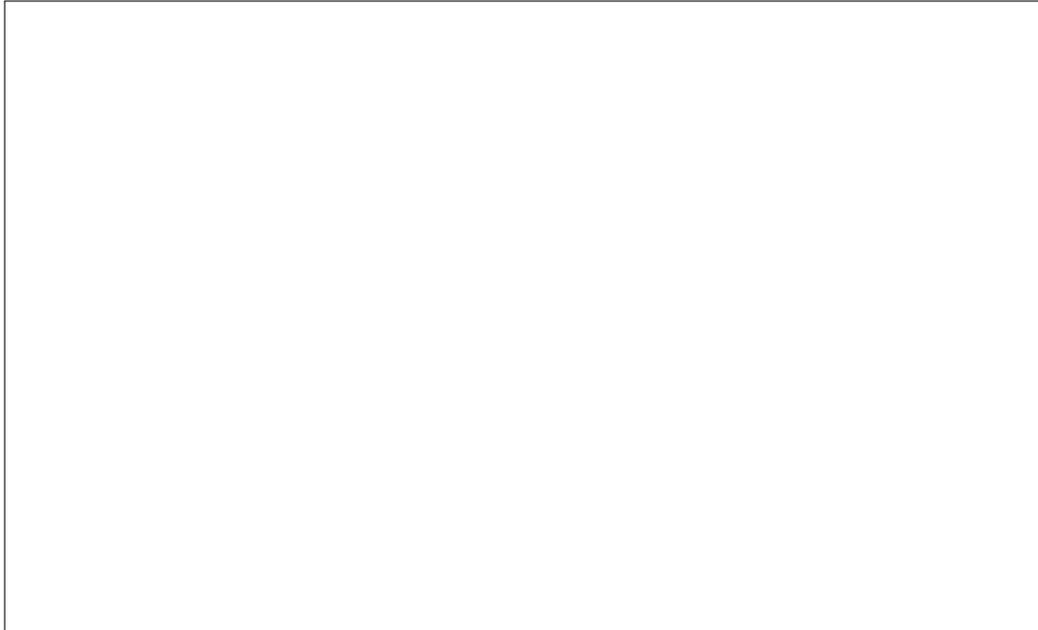
This equation already has some interesting experimental consequences: if we rapidly decrease the volume from V_H to $V_L < V_H$, the temperature in the container increases from T_0 to:

$$T = \left(\frac{V_H}{V_L} \right)^{2/3} T_0 > T_0 .$$

Using (55), i.e.,

$$T = c V^{-2/3} ,$$

for the internal energy (48), we find:



We finally arrive at a relation between thermodynamical quantities:

Key observation:

$$p V = N T \quad (\text{ideal gas law}) . \quad (56)$$

Definition: An thermodynamic equation, which relates state variables describing the state of matter under a given set of physical conditions, such as pressure, volume, temperature or internal energy, is called *equation-of-state*.

HISTORICAL REMARK: Elements of the Ideal Gas Law were discovered long before a stochastic description of gases were available. Accordingly, these laws were named after their discoverer:

Boyle's law (1662): Constant temperature, change pressure



Law of Charles and Gay-Lussac (1787): Constant pressure, change temperature



Dalton's law of partial pressures (1801): The pressure of a mixture of gases is equal to the sum of the pressures of all of the constituent gases alone (see exercises).



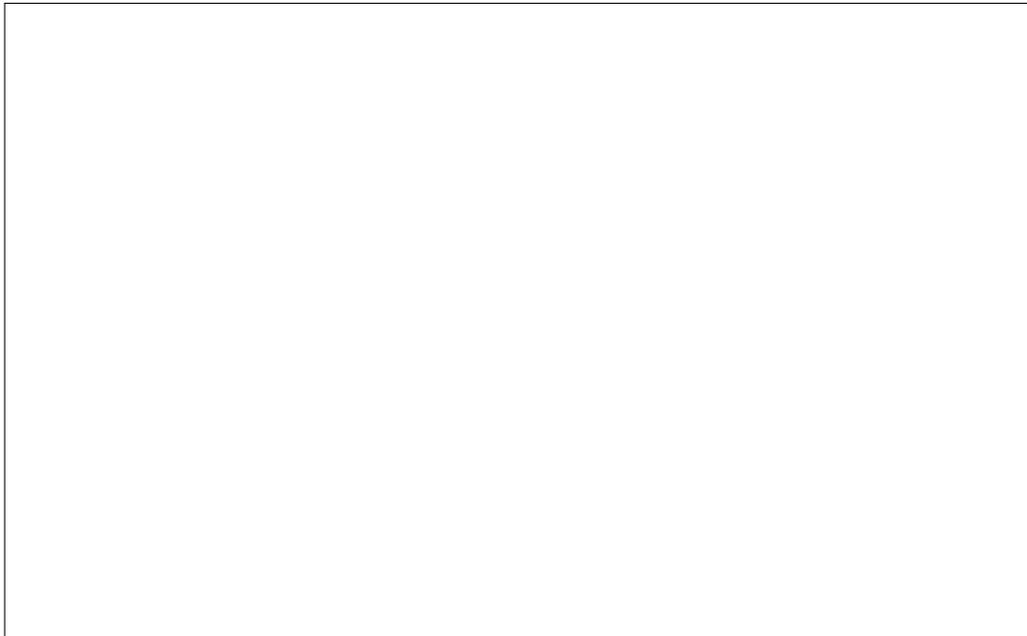
5 Thermodynamical cycles and engines

5.1 Work, pressure and force

In Section 4.4.1 we defined pressure in the canonical ensemble by considering various ways to change the volume of a container. Such changes in volume can result from a force on a movable piston. This suggests a connection between pressure and force, which we now formalize.

Definition: Consider an object described by its position \vec{x} in space, which is displaced by a vector $d\vec{x}$ due to a force $\vec{F}(\vec{x})$. The **work** done by this force is the resulting change in the energy of the object: $dW = dU = \vec{F} \cdot d\vec{x}$.

ILLUSTRATION:



EXAMPLE: Work done by gravity



Let us apply this to a container full of an ideal gas, exerting a force F on a movable piston with area A . If this force changes the position of the piston by $dx < 0$, the volume of the container decreases: $dV = A dx < 0$.



Since $dx < 0$, our definition of work states that the piston's energy has decreased,

$$dU = F dx < 0 .$$

The energy dE removed from the piston has been added to the internal energy $\langle E \rangle$ of the gas. Due to energy conservation,

$$d\langle E \rangle + dU = 0 .$$

Suppose this change in energy occurs without changing the entropy of the gas or its surroundings. (We will see below that this constant entropy means no **heat** has been exchanged in the process.) We can then invoke our definition of the pressure in Eq. (54) to find

$$p = - \left. \frac{d\langle E \rangle}{dV} \right|_S = - \frac{1}{A} \frac{d\langle E \rangle}{dx} = \frac{1}{A} \frac{dU}{dx} = \frac{1}{A} \frac{F dx}{dx} = \frac{F}{A} .$$

This identifies the pressure of a container of gas as the force per unit area that the gas exerts on the container wall, confirming that our mathematical definitions are consistent with everyday experiences.

Rearranging the expressions above, we can also relate the change in the internal energy $\langle E \rangle$ of the gas to the change of its volume *at constant entropy*:

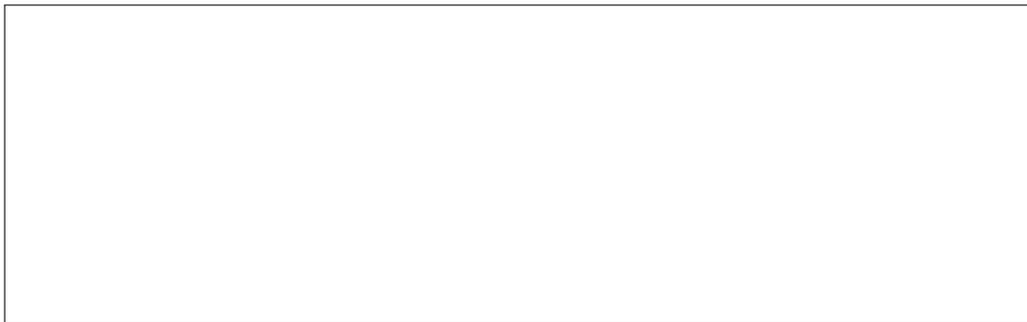
$$d\langle E \rangle = -dU = -F dx = -p A dx = -p dV = dW. \quad (57)$$

The negative sign in the last equality, $dW = -pdV$, identifies this as the work *delivered to* the system by its surroundings, increasing its internal energy $\langle E \rangle$. We could also talk about the work *done by* the system on its surroundings, which would have the opposite sign, $W_{\text{done}} = -W$.

5.2 Heat and entropy

Now let's switch things up by changing the temperature T of an ideal gas while keeping its volume constant. (As always for the canonical ensemble, the number of particles N is also constant.) How does this change the internal energy $\langle E \rangle$ and the entropy S ?

We can use our earlier expressions for $\langle E \rangle$ in Eq. (48) and S in Eq. (51), both of which now depend only on T :



Combining both equations, we find *at constant volume*

$$d\langle E \rangle = T dS \equiv dQ .$$

This defines the **heat** dQ added to or removed from the system in order to change its temperature while keeping the volume and particle number constant. Just as for the previous case of work, we take dQ to be positive if heat is added to the system to increase its internal energy $\langle E \rangle$.

5.3 Thermodynamical cycles

Since the particle number N does not change, the entropy S and internal energy $\langle E \rangle$ are functions only of the temperature T and the volume V . We can equivalently express T as a function of entropy and volume, $T(S, V)$. This allows us to make the internal energy another function of entropy and volume, $\langle E \rangle(T, V) \rightarrow \langle E \rangle(S, V)$. We can expand the internal energy to first order in a multi-variable Taylor expansion to find

$$\langle E \rangle(S, V) = \langle E \rangle(S_0, V_0) + \left. \frac{\partial \langle E \rangle}{\partial S} \right|_V (S - S_0) + \left. \frac{\partial \langle E \rangle}{\partial V} \right|_S (V - V_0) + \dots$$

Using Eqs. (11) and (57) while defining $d\langle E \rangle = \langle E \rangle(S, V) - \langle E \rangle(S_0, V_0)$, $dS = S - S_0$ and $dV = V - V_0$, this becomes

$$d\langle E \rangle = T dS - p dV = dQ + dW , \quad (58)$$

where we remove the higher-order terms by taking the differentials to be infinitesimally small.

Key equations for thermodynamical cycles:

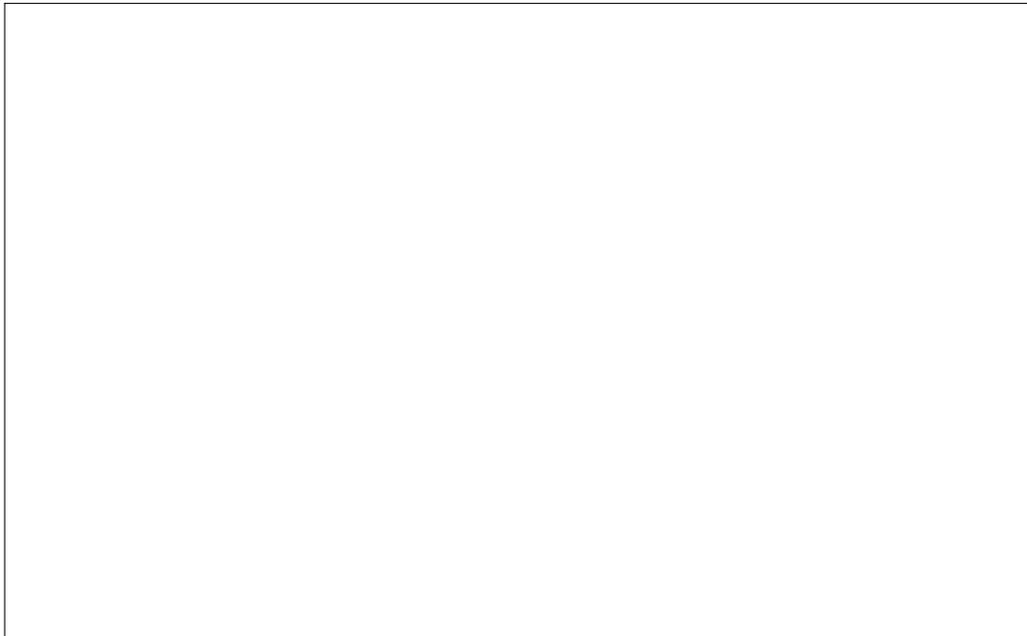
C1 The equation of state (ideal gas law): $pV = NT$

C2 The internal energy: $\langle E \rangle = \frac{3}{2} NT$

C3 The equation of constant entropy: $VT^{3/2} = \text{constant}$

C4 The change of internal energy: $d\langle E \rangle = TdS - pdV = dQ + dW$.

We can now expose the system to a variety of external changes: we can heat it at constant volume, we can heat it at constant pressure, we can compress it rapidly or slowly, or do a combination of these.

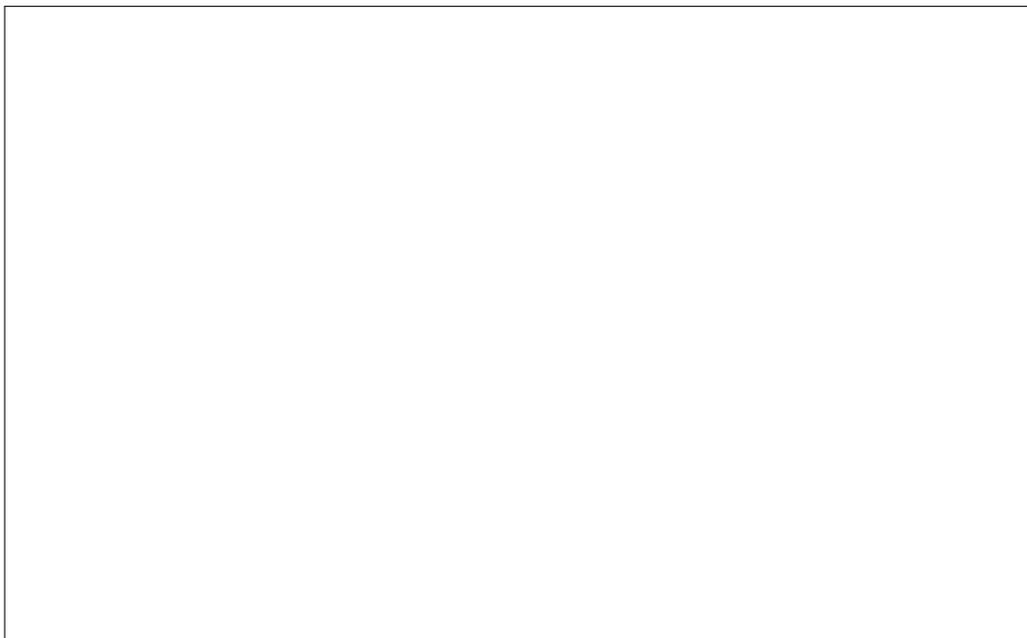


To keep track of such changes, it is convenient to visualise them through a “ pV diagram”. Each point in this diagram has a unique pair (p, V) . With the help of the equation of state (**C1**), $pV = NT$, we can also associate a temperature to each point, which tells us the internal energy from Eq. (**C2**). Each point thus uniquely describes the state of the gas in the container.

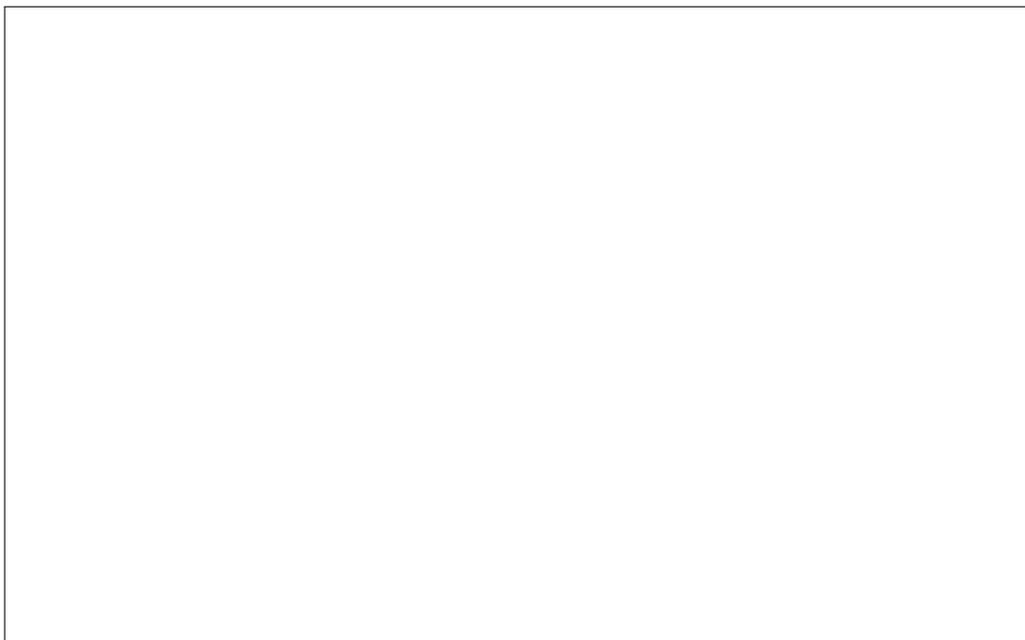
A change in the state of the gas caused by a change in its external parameters hence can be described by a line in the pV diagram.

WORKED EXAMPLES

Draw the pV diagram for an isothermal (constant- T) expansion and calculate the change in pressure.



Draw the pV diagram for an adiabatic (constant- S) compression and calculate the changes in pressure and temperature.



After a sequence of these changes, we could find ourselves *back at the starting point* in the pV diagram. In this case we could repeat the process over and over again, so we call it a thermodynamical cycle. As we will see below, such thermodynamical cycles can do work on their surroundings by transferring heat from a hot reservoir to a cold reservoir. This is used in car engines, refrigerators and heat pumps, among other applications.

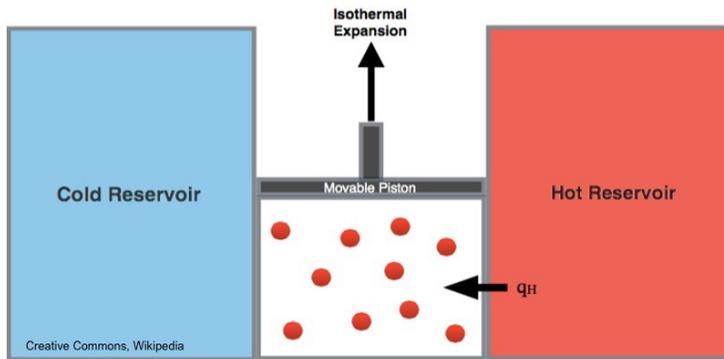
5.4 The Carnot cycle

The archetype of a thermodynamic cycle was proposed by the French physicist Sadi Carnot in 1824, and is nowadays known as the Carnot cycle. In this case our system of interest is a container filled with an ideal gas that has access to two different heat reservoirs, one ‘hot’ reservoir with temperature T_H and one ‘cold’ reservoir with temperature T_L .

Stage One:

● - Heated ideal gas particle
 q_H - heat from hot reservoir

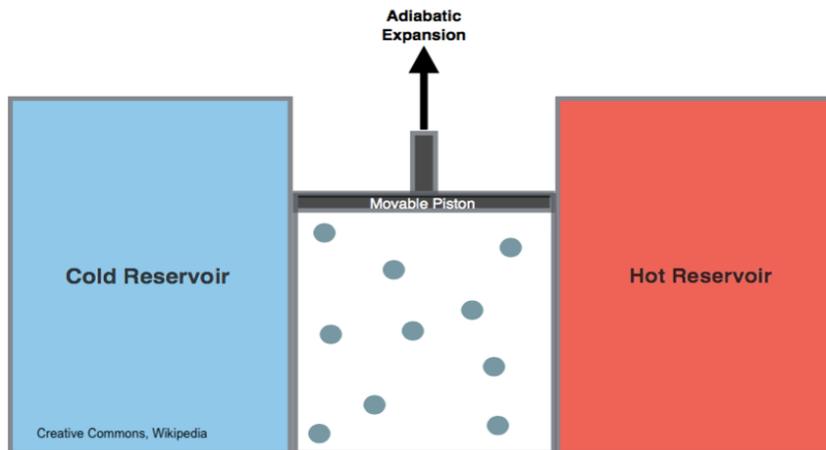
At this stage heat is released from the hot reservoir and is absorbed by the ideal gas particles within the system. Thus, the temperature of the system rises. The high temperature causes the gas particles to expand; pushing the piston upwards and doing work on the surroundings.



Stage Two:

● - Ideal gas particle that is cooled.

At this stage expansion continues, however there is no heat exchange between system and surroundings. Thus, the system is undergoing adiabatic expansion. The expansion allows the ideal gas particles to cool, decreasing the temperature of the system.

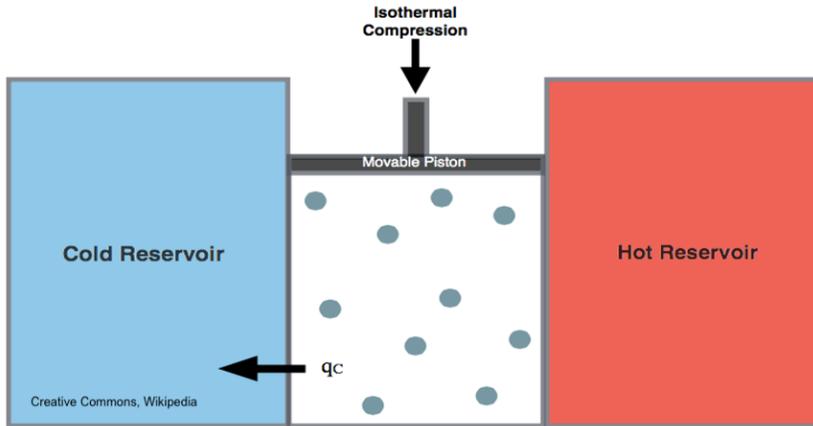


Stage Three:

At this stage the surroundings do work on the system which causes heat to be released (q_c). The temperature within the system remains the same. Thus, isothermal compression occurs.

q_c - heat released from system to cold reservoir

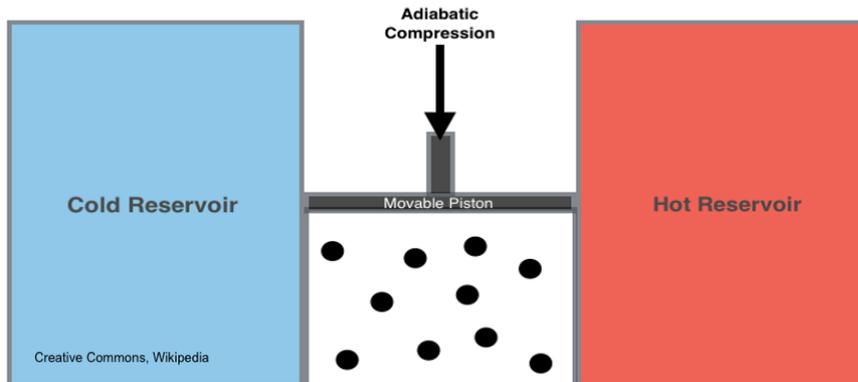
● - Ideal gas particle that is cooled.



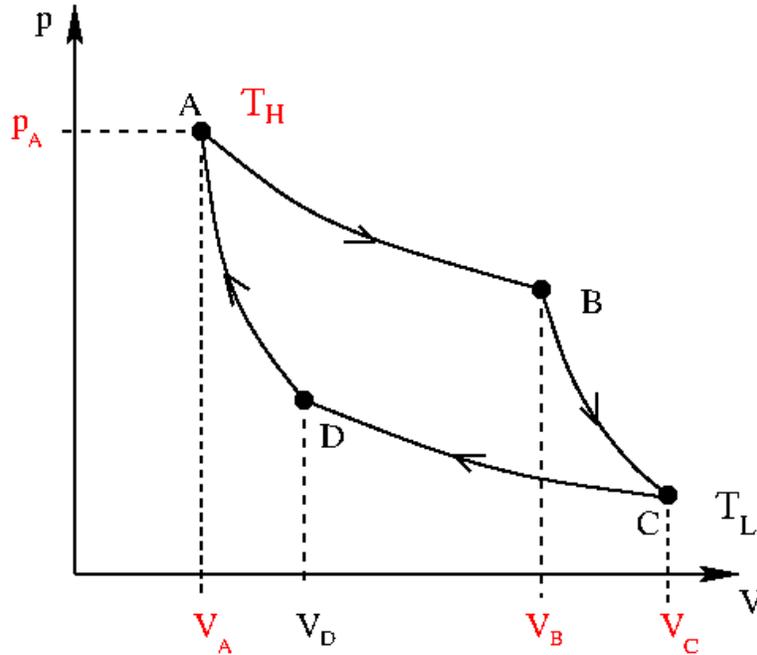
Stage Four:

No heat exchange occurs at this stage, however, the surroundings continue to do work on the system. Adiabatic compression occurs which raises the temperature of the system as well as the location of the piston back to its original state (prior to stage one).

● - Ideal gas particle at normal temperature prior to Carnot Cycle commencement.



The figure below shows the pV diagram for the Carnot cycle.



WORKED DETAILS:

Consider p_A , T_H and the volumes V_A , V_B and V_C as given. Assigning input to variables is quite tedious, since picking the wrong combination of variables could easily lead to inconsistencies. The above choice is inspired by a real experiment: we start at state A at normal condition with p_A the atmospheric pressure, T_H the temperature of the surrounding and V_A our volume initially. We then slowly expand (isothermal) until we reach V_B . We then rapidly expand (adiabatic) until we reach V_C . The temperature and pressure at B and C is what we could measure, and, hence, we should be able to calculate those. We then slowly compress (isothermal) until we reach V_D and then rapidly back to V_A . We cannot just give a value for V_D , since if we pick this value wrong, we would not get back to V_A with the final compression. This is telling us that we need to calculate V_D in order to complete the cycle.

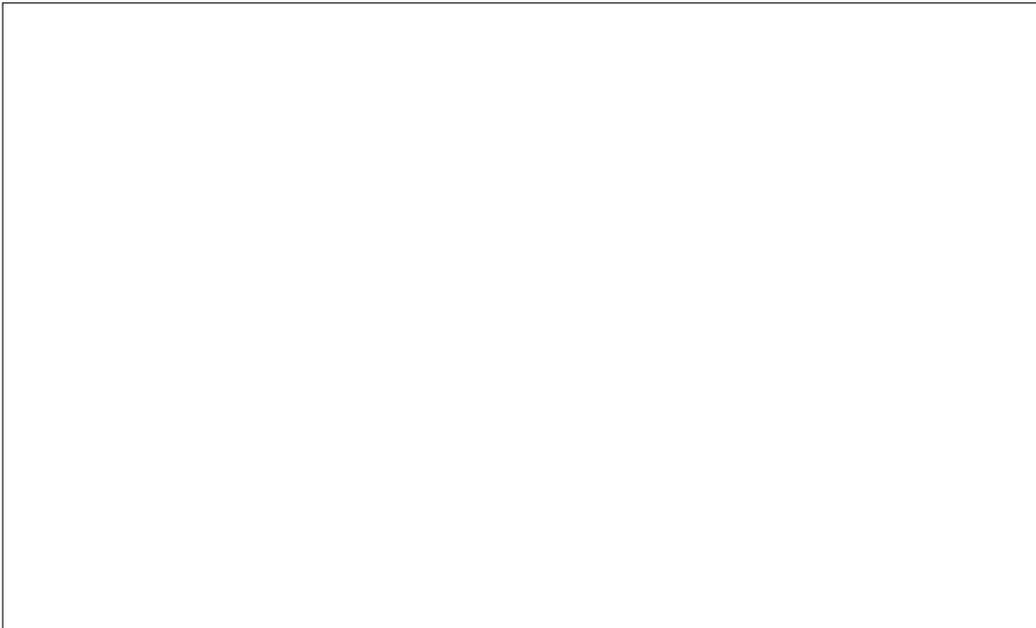
- Calculate at each of the points A, B, C, D any unknown volume, pressure, or temperature.

- For each of the stages, calculate the heat transfer Q into or out of the system.
- For each of the stages, calculate the work W done by the gas in the container. Recall that (if work is gained, W is negative).

Stage 1: from $A \rightarrow B$



Stage 2: from $B \rightarrow C$

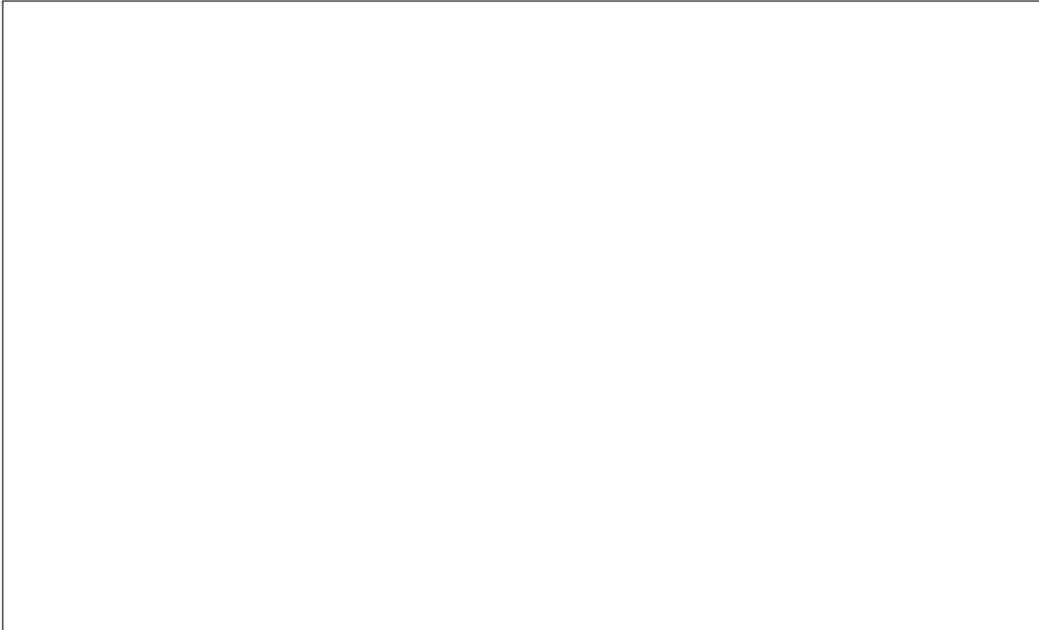


Stage 3+4: from $C \rightarrow D \rightarrow A$

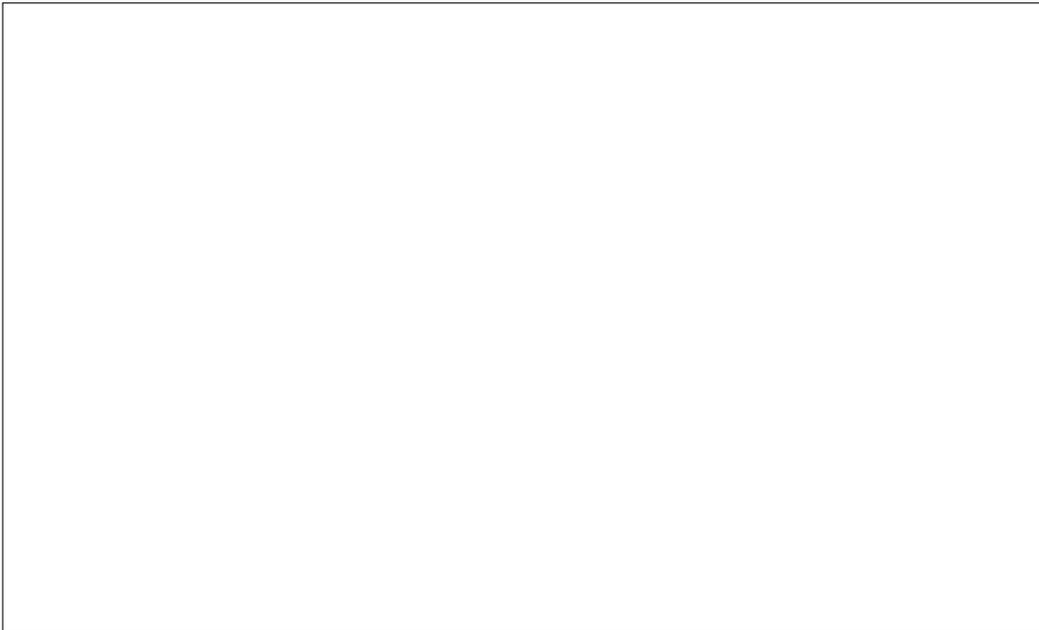


Let us now calculate the work delivered to the internal energy of the gas:

Stage 1: from $A \rightarrow B$



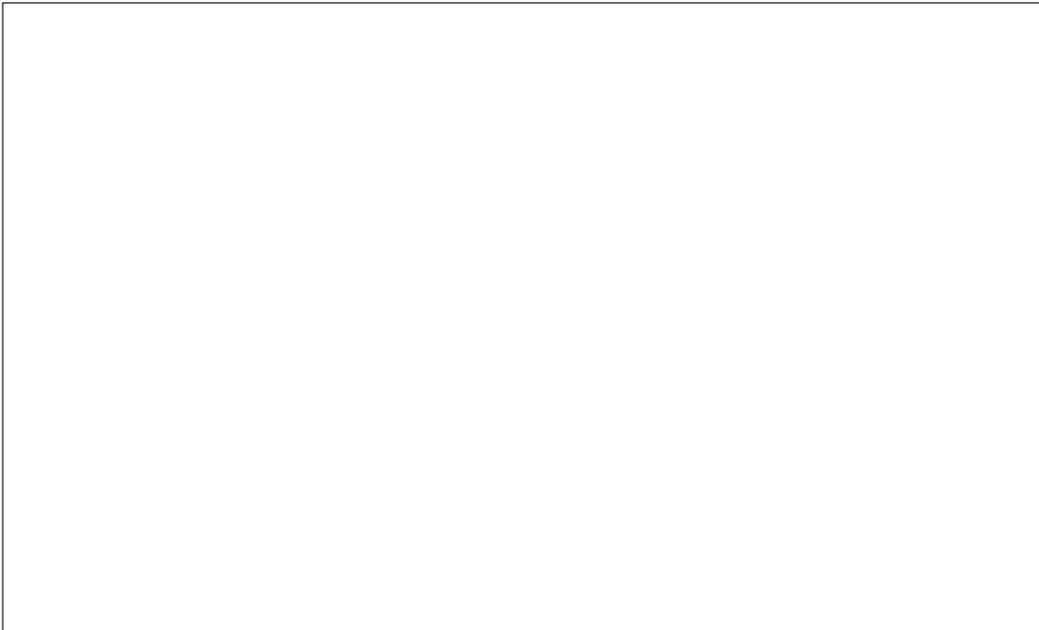
Stage 2: from $B \rightarrow C$



Stage 3: from $C \rightarrow D$



Stage 4: from $D \rightarrow A$



The total amount of work delivered to the gas throughout one Carnot cycle is hence given by:

$$W = W_1 + W_2 + W_3 + W_4 .$$

Using $W_2 + W_4 = 0$ and the explicit expressions for W_1 and W_3 , we find:

$$\begin{aligned} W &= -N (T_H - T_L) \ln \left(\frac{V_B}{V_A} \right) = -p_A V_A \left(1 - \frac{T_L}{T_H} \right) \ln \left(\frac{V_B}{V_A} \right) \quad (59) \\ &= -p_A V_A \left(1 - \left(\frac{V_B}{V_C} \right)^{2/3} \right) \ln \left(\frac{V_B}{V_A} \right) . \end{aligned}$$

Let us now study the heat flow in each stage. The key equation is C4:

$$dE_i = dQ + dW , \quad dW = -p dV .$$

Stage 1: The internal energy is a function of the temperature only, i.e., $E_i = 3/2 N T$. This means that during an isothermal process - expansion or compression - the internal energy does *not change*: $dE_i = 0$. We therefore find:

$$0 = dQ + dW , \quad \Rightarrow \quad Q_1 = -W_1 .$$

Remember, $W_1 < 0$, i.e., the gas is doing work, and therefore $Q_1 > 0$, i.e., heat is flowing into the gas.

Stage 2/4: Those are adiabatic processes: the entropy is constant:

$$dS = 0 \quad \Rightarrow \quad dQ = T dS = 0 .$$

No heat exchange takes place: $Q_2 = Q_4 = 0$.

Stage 3: It is an isothermal again:

$$Q_3 = -W_3 .$$

This time, $W_3 > 0$ and the gas was receiving work. As a consequence, $Q_3 < 0$ and heat is flowing out of the gas container.

Definition: The efficiency η of a thermodynamical engine is defined by

$$\eta = W_{done}/Q_{in} ,$$

where W_{done} is the work delivered by the cycle and Q_{in} is the amount of heat flowing into the gas.

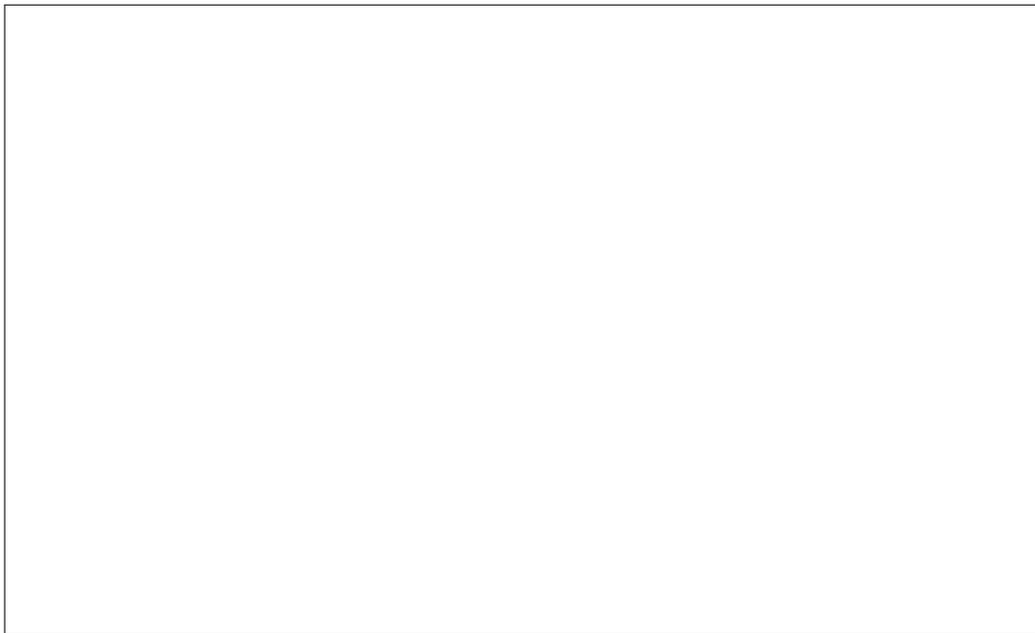
For the Carnot cycle, the container was receiving heat only during stage 1:

$$Q_{in} = Q_1 = -W_1 .$$

Remember that W was the work *delivered* to the gas. Hence, we have:

$$W_{done} = -W .$$

We therefore find:



Altogether, we find the important result

$$\eta = 1 - \frac{T_L}{T_H} \quad (\text{Carnot cycle}).$$

COMMENTS

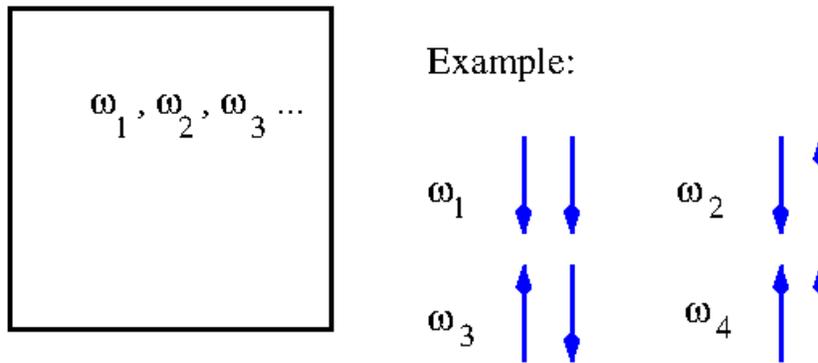
- The higher the temperature difference, the more efficient is the thermodynamical engine.
- If we reverse the order of the stages of the Carnot cycle (all calculations remain the same), the gas receives work and transports heat from the cold to the hot reservoir. This is what a **refrigerator** does!
- In winter, a refrigerator works better in the kitchen than in the garage since the temperature difference between inside and the surrounding is bigger.
- From all thermodynamical cycles, the Carnot cycle has the best efficiency.⁹ If for some reason, T_H and T_L approach each other, *all* thermodynamical engines stop working.

⁹We have not discussed this here. A derivation can be found e.g. in the textbook [1].

6 The grand-canonical ensemble

6.1 Review: Micro-canonical and canonical ensembles

Let us review the statistical ensembles we have considered so far. The starting point for an ensemble is always a set of M states $\omega_1, \omega_2, \dots, \omega_M$, like those illustrated below. We then impose constraints to incorporate information about the physics-based systems we wish to model mathematically. As our first example, in the *micro-canonical* ensemble we required that the total energy E and particle number N of the system both be conserved, with conservation of energy known as the first law of thermodynamics.

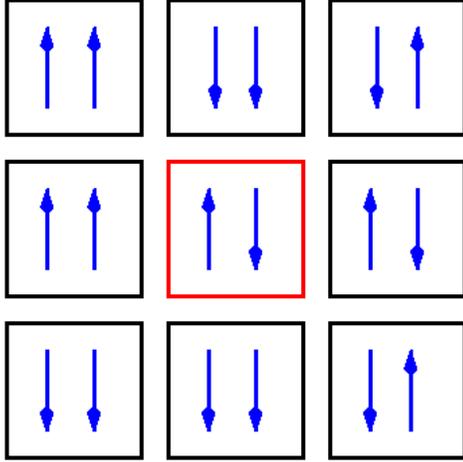


We then introduced the concept of *thermodynamical equilibrium*, the situation in which each of the M micro-states ω_i occurs with the same probability $p_i = 1/M$. We also derived an extremely useful quantity known as *entropy*,

$$S(E, N) = - \sum_{i=1}^M p_i \ln p_i = \ln M ,$$

which provides important characterizations of statistical systems. In particular, the second law of thermodynamics states that the total entropy of an isolated system can never decrease over time, implying that thermodynamical equilibrium corresponds to maximal entropy. We will generally express the entropy as a function of the quantities characterizing the ensemble under consideration; for the micro-canonical ensemble these are E and N .

We then changed perspective to consider the above prototype of a system surrounded by many identical system.



We then allowed an *energy exchange* between those systems. We say that our “small” system is immersed in the big system, which is the so-called heat-bath.

We still are interested in the properties of our “small” system: now, the energy of our small system is not conserved anymore, but we can define the average of the energy as internal energy of our small system, i.e., $\langle E \rangle$, with is a function of temperature T and particle number N of boxes.

In subsection 3.1, we found a clever way to describe a clever mathematical way to describe the whole of the system - occupation numbers: n_i is the number of the state ω_i realised in any of the boxes. This also tells us something about our small system. n_i divided by N , the number of boxes, is an estimate for the p_i of finding state ω_i realised in our “small” box.

We then were able to work out the entropy of the whole system as a function of the total energy (which we repeat here for later use):

$$S(E) = -N \sum_{i=1}^M p_i \ln p_i , \quad (60)$$

$$\sum_{i=1}^M p_i = \frac{1}{N} \sum_{i=1}^M n_i = 1 , \quad (61)$$

$$\sum_{i=1}^M p_i E_i = \frac{1}{N} \sum_{i=1}^M n_i E_i = E/N . \quad (62)$$

Eq. (61) just tells us that the number of boxes is N , and Eq. (62) is saying that the energy of the whole system is E .

We then considered the system to be in thermodynamical equilibrium, implying maximal entropy. This entirely fixes the probabilities p_i from Eqs. (60, 61, 62):

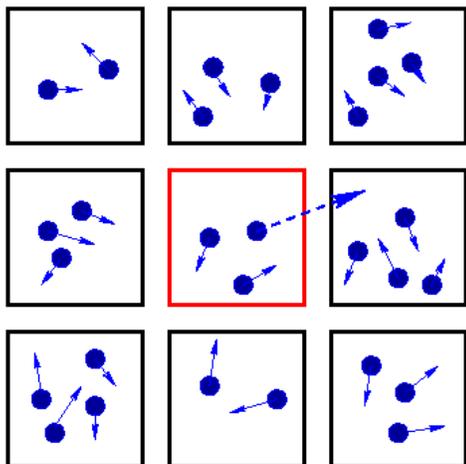
$$p_i = \frac{1}{Z} \exp\{-\beta E_i\}, \quad Z = \sum_{i=1}^M \exp\{-\beta E_i\} \quad \beta = 1/T.$$

COMMENTS:

- It is remarkable that the only input left from the heat-bath is the temperature T .
- The micro-canonical and canonical ensembles are equally valid statistical ensembles, which model different experimental settings. The micro-canonical description refers to an isolated system characterized by the (conserved) energy and particle number. The canonical description refers to a “small” system that can exchange energy (but not particles) with a much larger heat-bath, and is therefore characterized by the temperature and particle number.

6.2 The particle reservoir

After this review, we are now ready to embark yet to another perspective. While the description of a fixed particle number in each of the boxes is quite natural for the spin system, but less so for the ideal gas:



If we do not think of the boxes as bounded by real walls, we need to allow that our “small” system loses and gains particles from its surroundings. We say that our “small” system is embedded in a *particle reservoir*. In addition to the *energy exchange* between the boxes, we now also allow *particle exchange*.

6.3 The grand-canonical partition function

Luckily, we have now all the mathematics in place to describe the new scenario. We still consider M micro-states in each box, $\omega_1 \dots \omega_M$, but each definition of a micro-state now includes the number N_i of particles in the box for state ω_i . We still work with occupation numbers n_i and corresponding probabilities p_i of finding a state ω_i in a box. We now have a new constraint: namely, that the total number of particles in all boxes is fixed, call it $N N_p$. Remember, N is the number of boxes and, hence, N_p could be interpreted as a reference for the particle number per box. We have now the constraint:

$$\sum_{i=1}^N n_i N_i = N N_p \quad \Rightarrow \quad \sum_{i=1}^N p_i N_i = N_p .$$

If we recall the calculation of the entropy in subsection 3.1, it does not refer to the definition of the micro-state ω_i at all. Hence, the equations (60, 61, 62) are unchanged. We just have a further constraining equation:

$$S(E) = -N \sum_{i=1}^M p_i \ln p_i , \quad (63)$$

$$\sum_{i=1}^M p_i = 1 , \quad \sum_{i=1}^M p_i E_i = E/N , \quad (64)$$

$$\sum_{i=1}^N p_i N_i = N_p . \quad (65)$$

The next step is to recall that we are in a thermodynamical equilibrium, which maximises the entropy:



We finally obtain:

$$p_i = \frac{1}{Z_g} \exp\{-\beta E_i + \beta \mu N_i\}. \quad (66)$$

With the first equation in (64), we fix the first Lagrange multiplier:

$$Z_g = \sum_{i=1}^M \exp\{-\beta E_i + \beta \mu N_i\}. \quad (67)$$

The other constraint equations become:

$$\sum_{i=1}^M E_i \exp\{-\beta E_i + \beta \mu N_i\} = \frac{E}{N} Z_g, \quad (68)$$

$$\sum_{i=1}^M N_i \exp\{-\beta E_i + \beta \mu N_i\} = N_p Z_g. \quad (69)$$

These are two equations for the unknown Lagrange multipliers β and μ , which determines those in terms of the only parameter in the system: E and N_p .

The following calculation should be familiar from a analogous one in subsection 3.1. Inserting (66) into the entropy equation (63) yields:

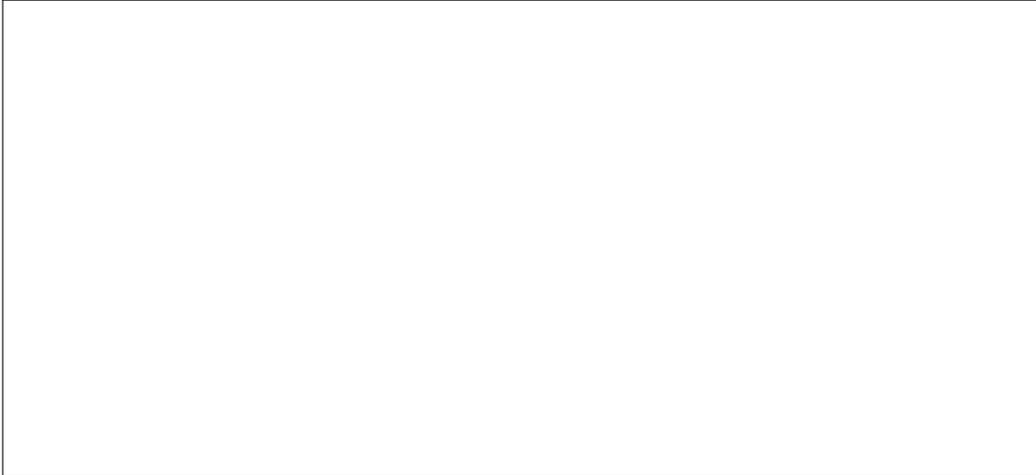


$$S(E, N_p) = \beta(E, N_p) E - N [\beta \mu](E, N_p) N_p + N \ln Z_g .$$

We defined the temperature in (11), which we recall here:

$$\frac{1}{T(E, N_p)} = \left. \frac{\partial S(E, N_p)}{\partial E} \right|_{N_p} .$$

After a short calculation:



we find that for the Lagrange multiplier β the same expression as before (see (22)):

$$\frac{1}{T(E, N_p)} = \beta(E, N_p) . \tag{70}$$

We still have to find a meaning for the last remaining Lagrange multiplier μ . We calculate:

$$\left. \frac{\partial S}{\partial N_p} \right|_E =$$

Key Definition: The derived quantity

$$\mu = -T \left. \frac{1}{N} \frac{\partial S}{\partial N_p} \right|_E. \quad (71)$$

is called *chemical potential*. It is related to the change of the entropy of a statistical system by adding a particle to the system while keeping its energy constant.

This is a definition that hinges on the “big” system, which is specified by the overall energy E and the total number of particles N_p . It also contains a reference to the number of boxes N . It would be convenient to have an expression for the chemical potential μ that only depends on “small” box properties. This can be indeed achieved.

Assume that we have calculated the entropy, which is consequently a function of E and N_p :

$$S = S(E, N_p). \quad (72)$$

If we solve this equation for E , i.e.,

$$E = E(S, N_p),$$

we can use the latter to replace E as variable in all sort of equations. Hence, S and N_p are becoming our new *independent* variables. The constraint (68)

then becomes:

$$\langle E \rangle = \frac{1}{Z_g} \sum_{i=1}^M E_i \exp\{-\beta E_i + \beta \mu N_i\} = \frac{1}{N} E(S, N_p).$$

We then find:

$$\left. \frac{\partial \langle E \rangle}{\partial N_p} \right|_S = \frac{1}{N} \frac{dE(S, N_p)}{dN_p} \quad S : \text{constant.} \quad (73)$$

We then differentiate (72) by N_p and keep in mind that S is constant:

$$0 = \left. \frac{\partial S}{\partial E} \right|_{N_p} \frac{dE}{dN_p} + \left. \frac{\partial S}{\partial N_p} \right|_E$$

Using the definition of temperature and chemical potential, this becomes:

$$0 = \frac{1}{T} \frac{dE}{dN_p} - N \frac{\mu}{T}.$$

Using this in (73), we finally obtain:

$$\left. \frac{\partial \langle E \rangle}{\partial N_p} \right|_S = \mu. \quad (74)$$

Interpretations:

- The chemical potential is the change in internal energy when we add a particle to the system adiabatically (without changing its entropy).
- Above, we still have S and N_p as independent variables. We can, however, now use some constraint equations to express S and N_p as functions of T and μ . In this case, T and μ become the two independent variables.

6.4 The grand-canonical potential

We now have the grand-canonical partition function $Z_g(T, \mu)$ defined with no explicit reference to the heat-bath or particle reservoir. Their role is simply to set the temperature T and chemical potential μ that characterize the “small” system in the grand-canonical ensemble. Similarly to the Helmholtz free energy considered for the canonical ensemble in Section 3.2, it is convenient to define a quantity related to the logarithm of the grand-canonical partition function.¹⁰

Key definition: With $Z_g(T, \mu)$ the grand-canonical partition function, the **grand-canonical potential** is

$$\Omega(T, \mu) \equiv -T \ln Z_g(T, \mu). \quad (75)$$

Analogously to the Helmholtz free energy, derivatives of the grand-canonical potential are related to the internal energy $\langle E \rangle$, the average particle number $\langle N \rangle$ and the entropy S . Let’s first consider the derivative with respect to the chemical potential:



We find

$$\langle N \rangle(T, \mu) = -\frac{\partial \Omega(T, \mu)}{\partial \mu}.$$

¹⁰The grand-canonical potential is sometimes called the “Landau free energy” to highlight its similarity with the Helmholtz free energy.

The derivative with respect to the temperature is a little more complicated:



To interpret this, let us recall the fundamental definition of the entropy (now also a function of T and μ):

$$S(T, \mu) = - \sum_{i=1}^M p_i \ln p_i \qquad p_i = \frac{1}{Z_g} \exp \left\{ - \frac{E_i - \mu N_i}{T} \right\}$$



This tells us two things:

$$S(T, \mu) = - \frac{\partial \Omega(T, \mu)}{\partial T}$$
$$\Omega(T, \mu) = -T \cdot S(T, \mu) + \langle E \rangle(T, \mu) - \mu \langle N \rangle(T, \mu).$$

Finally, to extract the internal energy $\langle E \rangle(T, \mu)$, we need to consider

$$-\frac{\partial \ln Z_g(T, \mu)}{\partial T} = \frac{\partial}{\partial T} \left[\frac{\Omega(T, \mu)}{T} \right] =$$

In summary, we find the following:

Key observations: With $\Omega(T, \mu)$ the grand-canonical potential,

$$\langle N \rangle(T, \mu) = -\frac{\partial \Omega(T, \mu)}{\partial \mu} \quad (76)$$

$$S(T, \mu) = -\frac{\partial \Omega(T, \mu)}{\partial T} \quad (77)$$

$$\langle E \rangle(T, \mu) = -T^2 \frac{\partial}{\partial T} \left[\frac{\Omega(T, \mu)}{T} \right] + \mu \langle N \rangle \quad (78)$$

$$\Omega(T, \mu) = -T \cdot S(T, \mu) + \langle E \rangle(T, \mu) - \mu \langle N \rangle(T, \mu) \quad (79)$$

7 Anomalous Diffusion

COMPUTER PROJECT

7.1 Recap

We already encountered *diffusion* in section 1.4. It is widespread phenomenon and describes chemical spill as well as the tracking of a pedestrian. Its underlying assumptions are:

General conditions for diffusion:

- If x_n is the position of the walker at time t_n , the position x_{n+1} only depends on x_n .
- The displacement $x := x_{n+1} - x_n$ is described by a stochastic process with probability distribution $p(x)$.

We usually work with equally distributed time steps $t_n = \Delta t n$.

Key observations for (normal) diffusion:

- The standard deviation for the 1-step process

$$\sigma = \sqrt{\langle x^2 \rangle - \langle x \rangle^2}$$

exists and is finite.

- For a large number of steps N , the probability distribution $P(x_N)$ is Gaussian:

$$P(x_N) = \frac{1}{\sqrt{2\pi t D^2}} \exp \left\{ -\frac{(x_N - v_{\text{dr}} t)^2}{2t D^2} \right\},$$

where the drift velocity v_{dr} and the diffusion constant D are given by:

$$v_{\text{dr}} = \langle x \rangle / \Delta t, \quad D = \sigma / \sqrt{\Delta t}.$$

- The diffusion length is

$$\ell = \sqrt{\langle x_N^2 \rangle - \langle x_N \rangle^2} = D \sqrt{t}. \quad (80)$$

This is the famous law of diffusion.

COMPUTER PROJECT PART A

Student ID:

Marks: _____ (of 50)

Instructions: Complete the three exercises below. Scan this sheet and your workings, and submit along with your code on VITAL. While the guidance below specifies some relevant MATLAB commands, you may use a different programming option if you prefer. This sheet contributes 4% to your overall mark for this module.

Due date: 3 April 2020, 17:00.

Exercise 1: (Pseudo-)Random numbers

Initialise the random number generator. In MATLAB, this can be done using the command `rng(314156)`. Generate a sequence of n uniformly distributed random numbers $u_i \in [0, 1]$ with $i = 1, \dots, n$ using the MATLAB command `rand`.

Complete the table below by estimating the average and the standard deviation σ as

$$\langle u \rangle \approx \frac{1}{n} \sum_{i=1}^n u_i,$$

$$\sigma \approx \sqrt{\frac{1}{n} \left(\sum_{i=1}^n u_i^2 \right) - \langle u \rangle^2}.$$

n	10	20	100	200	1000	100,000
$\langle u \rangle$						
σ						

Calculate the exact average and standard deviation:

$$\langle u \rangle = \text{_____}, \quad \sigma = \text{_____}.$$

Exercise 2: Histogram

Initialise the random number generator, in MATLAB using `rng(314156)`. If $u \in [0, 1]$ is a uniformly distributed random number (see Exercise 1), define the random number x by

$$x = \text{asin}(2u - 1), \quad x \in [-\pi/2, \pi/2],$$

where `asin` is MATLAB's arcsine command.

Generate an array X of 100,000 random numbers x . Plot the histogram of these random numbers using the MATLAB command `histogram`.

Starting with the relation $p(u) du = p(x) dx$, calculate the probability distribution $p(x)$ of the random number x .

$$p(x) = \text{_____}.$$

Use this to calculate the exact average and standard deviation:

$$\langle x \rangle = \text{_____}, \quad \sigma = \text{_____}.$$

Does your histogram match these results?

Exercise 3: Random walk

Initialise the random number generator, in MATLAB using `rng(314156)`.

CORE PROCESS: Start with $x_0 = 0$. For a given N , perform the iteration

$$x_k = x_{k-1} + x, \quad k = 1, \dots, N,$$

where x in each step is a random number with (see Exercise 2)

$$p(x) = \frac{1}{2} \cos(x), \quad x \in [-\pi/2, \pi/2].$$

(a) Using the Core Process, generate a sequence of n random numbers $(x_N)_i$ with $i = 1, \dots, n$. If we consider each $(x_N)_i$ to be the result of random walk i , this will give us n N -step random walks to analyse.

Estimate the standard deviation $\ell_2(N)$ of this N -step process as

$$\ell_2(N) \approx \left[\frac{1}{n} \sum_{i=1}^n (x_N)_i^2 \right]^{1/2}.$$

Complete the table for $N = 100$:

n	10	20	100	200	1000	100,000
$\ell_2(100)$						

Calculate $\ell_2(N)$ as a function of N using the central limit theorem. What do you get for $N = 100$?

$$\ell_2(N) = \text{_____}, \quad \ell_2(100) = \text{_____}.$$

(b) Now choose $n = 100,000$. Estimate $\ell_2(N)$ for $N = 1, \dots, 500$. Plot $\ell_2(N)$ as a function of N . Fit the result to

$$\ell_2(N) = D \sqrt{N}.$$

What is your estimate for the diffusion constant D ? Calculate the exact diffusion constant D_{exact} and compare:

$$D = \text{_____}, \quad D_{\text{exact}} = \text{_____}.$$

7.2 Anomalous diffusion

The general setting for diffusion as outlined in the conditions on page 111 still apply.

Key observations for anomalous diffusion:

- The standard deviation for the 1-step process does not exist.
- The Central Limit Theorem *does not* apply, and the probability distribution for a large number of steps is not necessarily a normal distribution, and must be calculated in each case.

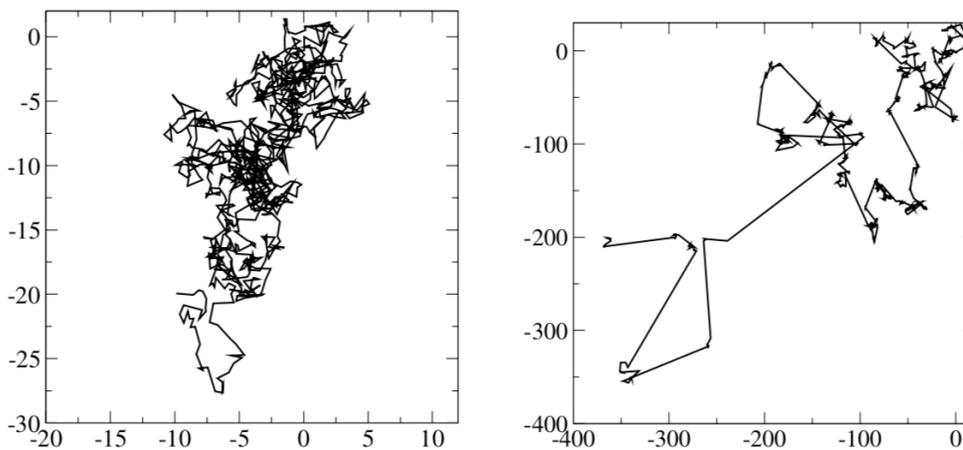
Let us consider a particular case of a Cauchy–Lorentz distribution:

$$p_L(x) = \frac{1}{\pi b} \frac{1}{1 + (x/b)^2}. \quad (81)$$

The free parameter b plays the role of a width. The corresponding moments are

$$\langle x^\theta \rangle = \int_{-\infty}^{\infty} dx x^\theta \frac{1}{\pi b} \frac{1}{1 + (x/b)^2},$$

and we indeed observe that the second moment $\theta = 2$ does not exist. The distribution is “bell shaped” as the normal distribution, but the corresponding random walks have quite different features as it is illustrated below:



The figures each show 1000 steps, using a normally distributed 1-step process on the left but the Cauchy–Lorentz distribution $p_L(x)$ on the right.

COMMENTS:

Also the random walk based upon $p_L(x)$ has an intrinsic length scale. This, however, cannot be defined anymore by the standard deviation. Hence, we define a whole new class of diffusion lengths (depending on the parameter θ):

Definition: The generalised diffusion length is given by

$$\ell_\theta = \langle |x|^\theta \rangle^{1/\theta} . \quad (82)$$

We recover the definition of the standard deviation for $\theta = 2$. We now can choose θ small enough so that the definition works for $p_L(x)$ as well. In fact, we can choose anything $0 < \theta < 1$.

Definition: That a probability distribution has a second moment, is not a big constraint. All these systems have a standard diffusive law (80). The surprise was big when systems were discovered with a diffusive law $\ell \propto t^\alpha$ that either exhibits *super-diffusion* with $\alpha > 1/2$ or *sub-diffusion* with $\alpha < 1/2$.

An example for super-diffusion are active cellular transport processes such as telomeres in the nucleus of cells.¹¹

The objective is to describe super-diffusion as a diffusive process with a 1-step probability distribution that evades the CLT.

¹¹I. Bronshtein et al., “Transient anomalous diffusion of telomeres in the nucleus of mammalian cells”, *Physical Review Letters* **103**:018102 (2009), doi:10.1103/PhysRevLett.103.018102.

COMPUTER PROJECT PART B

Student ID:

Marks: _____ (of 50)

Instructions: Complete the two exercises below. Scan this sheet and your workings, and submit along with your code on VITAL. While the guidance below specifies some relevant MATLAB commands, you may use a different programming option if you prefer. This sheet contributes 4% to your overall mark for this module.

Due date: 1 May 2020, 17:00.

Exercise 4: Distribution

Initialise the random number generator, in MATLAB using `rng(314156)`. If $u \in [0, 1]$ is a uniformly distributed random number, define the random number x by

$$x = \tan\left(\frac{2u - 1}{2}\pi\right), \quad x \in \mathbb{R}.$$

Generate an array X of 1,000,000 random numbers x . Plot the histogram of these random numbers using the MATLAB command `histogram`. An x -axis domain from -4 to 4 with 201 bins should suffice to see all interesting features—the online MATLAB documentation indicates the syntax `histogram(data, 201, 'BinLimits', [-4, 4])`.

Calculate the probability distribution $p(x)$ of the random number x .

$$p(x) = \underline{\hspace{2cm}}.$$

Does this result look consistent with your histogram?

Exercise 5: Anomalous diffusion

Initialise the random number generator, in MATLAB using `rng(314156)`.

CORE PROCESS: Start with $x_0 = 0$. For a given N , perform the iteration

$$x_k = x_{k-1} + x, \quad k = 1, \dots, N,$$

where x in each step is a random number with (see Exercise 4)

$$p(x) = \frac{1}{\pi} \frac{1}{1+x^2}, \quad x \in \mathbb{R}.$$

(a) Using the Core Process, generate a sequence of n random numbers $(x_N)_i$ with $i = 1, \dots, n$. If we consider each $(x_N)_i$ to be the result of random walk i , this will give us n N -step random walks to analyse.

Estimate the diffusion length $\ell_\theta(N)$ of this N -step process as

$$\ell_\theta(N) \approx \left[\frac{1}{n} \sum_{i=1}^n |(x_N)_i|^\theta \right]^{1/\theta}.$$

We will consider two different values $\theta = 0.4$ and $\theta = 0.8$, for which the absolute value (MATLAB command `abs`) is needed to ensure $\ell_\theta(N) \in \mathbb{R}$.

Complete the table for $N = 100$:

n	10	20	100	200	1000	100,000
$\ell_{0.4}(100)$						
$\ell_{0.8}(100)$						

(b) Now choose $n = 100,000$. For each of $\theta = 0.4$ and $\theta = 0.8$, estimate $\ell_\theta(N)$ for $N = 1, \dots, 500$. Plot the two $\ell_\theta(N)$ as functions of N . Fit each of these two $\ell_\theta(N)$ to

$$\ell_\theta(N) = D N^\alpha.$$

What is your estimate for the exponent α and the diffusion constant D ?

$$\begin{aligned} \theta = 0.4 : \quad \alpha &= \text{_____}, & D &= \text{_____}, \\ \theta = 0.8 : \quad \alpha &= \text{_____}, & D &= \text{_____}. \end{aligned}$$

How does your result depend on the value of θ ? (Checking different values of n may help to distinguish real effects from statistical fluctuations.)

8 Application: Quantum gases

We already said in section 4.1 the sum over all states is not the same as the sum over all particles. In classical Newtonian mechanics (see the “ideal gas”), the only characteristic was the energy: the sum over all micro-states then became a sum over all energies.

We then noticed (see section 4.1) that the sum over all micro-states is actually badly defined for continuous degrees of freedom: the energy of a gas in a box of volume V can be any real number, the sum would involve to count all real numbers, which is mathematical impossible. At this point, we encounter quantum physics: a particle in a box still has an infinite amount of states, but those *can* be counted.

COMMENTS:

- Although quantum mechanics came to the rescue, the sum over all energies is still considered classical physics. It makes the assumption that micro-states are labelled by the energy, and quantum statistical physics is more subtle than this.
- We have developed the mathematical apparatus of statistical physics in chapters 3, 4 and 6. The only new element here will be the definition of micro-states for the quantum case.

In the following, we will study the quantum statistics of non-interacting particles. Particles could be traditional matter particles such as electrons or photons - the particles of light.

Our starting point is an energy spectrum consisting of discrete (countable) energies E_i ; some of the energies can be the same: we say that this energy level is degenerate, but we still account for them here with different labels i .

In classical physics, micro-states are characterised by these energies and, e.g., the grand-canonical partition function is given by

$$Z_{\text{classical}} = \sum_{i=1}^M \exp \left\{ -\beta \sum_{p=1}^{N_i} E_p + \beta \mu N_i \right\}, \quad (83)$$

where the internal energy $E_i = \sum_{p=1}^{N_i} E_p$ of micro-state i is given by the sum over the energy levels of the N_i particles in the micro-state.

While classical physics can be an extremely good approximation (as we will find below), the underlying definition of micro-states in nature is different. Here, we map, say N , particles, to the energies:



Physics background: If particles are indistinguishable, they can be exchanged without changing physics observables. We say that ‘swapping’ two particles is a symmetry. The quantum physics framework implies that particles can then be labeled by ‘quantum numbers’, arising from the representations from the corresponding symmetry group. The case of the “swapping symmetry” leads to a binary characterisation of particles: we say particles are either *fermions* or *bosons*. Well known examples are electrons, which are fermions, and photons (particles of light), which are bosons. Another particle, which recently came to fame, is the Higgs boson, who is the only ‘matter’ particle (so far) that is a boson.

Physics input: (non-degenerate) energy states can be populated by any number of bosons, but only by at most one fermion.

Definition of the quantum statistical ensemble:

- The quantum statistical ensemble of non-interacting particles is defined by an energy spectrum E_i , $i = 1 \dots M$ (M can go to infinity) and by occupation numbers n_i for each energy.
- $n_i \in \mathbb{N}_0$ for bosons and $N_i = \{0, 1\}$ for fermions.
- The total energy E of the (non-interacting) system is given by:

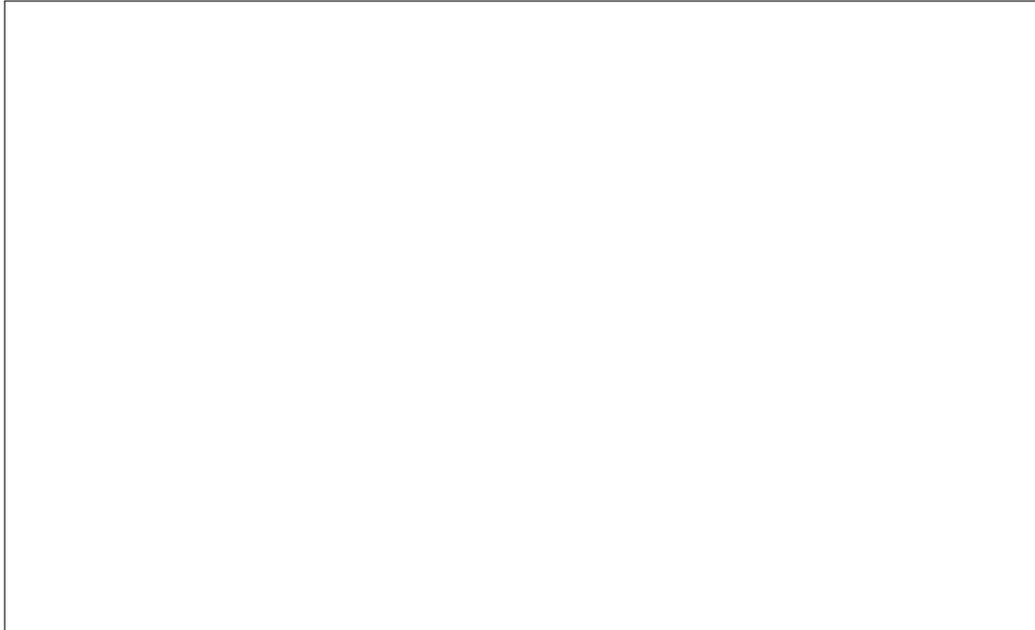
$$E = \sum_i E_i n_i .$$

BOSE GAS

Let us consider now a gas of bosons in a volume V . We consider the situation that this volume is immersed in a bigger system and that we allow energy exchange (heat-bath characterised with temperature T) and particle exchange (particle reservoir characterised by the chemical potential μ). We have studied the mathematics of the grand-canonical ensemble in detail in section 6. The partition function is given, as usual, by the sum over all micro-states, which is now a sum over all mappings of particles to energies:

$$Z_{bose} = \sum_{n_1=0}^{\infty} \dots \sum_{n_M=0}^{\infty} \exp \left\{ -\beta \sum_{i=1}^M E_i n_i + \beta \mu \sum_{i=1}^M n_i \right\} .$$

We can carry out one sum after the other:



We finally obtain the sometimes called *Bose Statistics*;

$$\ln Z_{bose} = - \sum_{i=1}^M \ln \left[1 - \exp \left(- \frac{E_i - \mu}{T} \right) \right]. \quad (84)$$

As in the classical physics case, we arrive at a sum over all energy levels, but now with different terms (compare with (83)).

Let us consider the case of high temperatures $T \gg E_i$, for which we can assume

$$\exp \left(- \frac{E_i - \mu}{T} \right) \ll 1.$$

We then can use the leading-order expansion

$$- \ln(1 - x) = x + \mathcal{O}(x^2),$$

and find:

$$\ln Z_{bose} = \sum_{i=1}^M \exp \left(- \frac{E_i - \mu}{T} \right).$$

We make the important observation that we recover the classical physics result at high temperatures. It depends, of course, on the energy spectrum but room temperatures are usually considered to be very high. This explains the tremendous success of the classical statistics for everyday life settings.

Addendum: The high-temperature limit of the Bose gas

The high-temperature limit of the Bose gas is a bit subtle. To reveal this, let's compute the average particle number from the corresponding grand-canonical potential

$$\Omega_{\text{bose}} = -T \ln Z_{\text{bose}} = T \sum_{\ell=1}^L \ln [1 - \exp(-\beta E_{\ell} + \beta \mu)],$$

labelling the energy levels E_{ℓ} with $\ell = 1, \dots, L$ to reduce possible confusion with the micro-states $i = 1, \dots, M$. We have

$$\langle N \rangle = -\frac{\partial \Omega}{\partial \mu} =$$

We can organize this as $\langle N \rangle = \sum_{\ell=1}^L \langle n_{\ell} \rangle$, defining the average occupation number for each energy level as

$$\langle n_{\ell} \rangle = \frac{1}{\exp(\beta E_{\ell} - \beta \mu) - 1}$$

When considering the high-temperature limit $\beta \rightarrow 0$ (so that $T \rightarrow \infty$), we need to keep in mind the grand-canonical constraint on the total number of particles in the system and its surroundings, from Eq. (65):

$$N_{\text{tot}} = N_r \langle N \rangle = N_r N_p \quad \text{is conserved,}$$

where $\langle N \rangle = N_p$ is the average number of particles in the “small” system, and the surroundings are made up of a fixed number $(N_r - 1)$ of replicas of that small system.

If we naively take $\beta \rightarrow 0$, we have

$$\exp(\beta E_\ell - \beta\mu) \rightarrow 1 \quad \text{and} \quad \langle n_\ell \rangle = \frac{1}{\exp(\beta E_\ell - \beta\mu) - 1} \rightarrow \infty$$

for all ℓ ! The number of particles in every energy level $\langle n_\ell \rangle$ is diverging, and so therefore is the total $\langle N \rangle = \sum_{\ell=1}^L \langle n_\ell \rangle$.

The cure **required** in order for the Bose gas to satisfy the grand-canonical constraint is to send $\mu \rightarrow -\infty$ as $T \rightarrow \infty$. While a constant ratio μ/T would suffice to keep each individual $\langle n_\ell \rangle$ from diverging at high temperatures, because the constraint is on the sum $\langle N \rangle$ it turns out that we really need $-\mu \gg T \gg E_i$ to satisfy the constraint. (We will not prove this here.) In this limit, $(E_\ell - \mu)/T \gg 1$ and

$$\exp\left(-\frac{E_\ell - \mu}{T}\right) \ll 1,$$

as stated above.

Addendum: The classical grand-canonical $Z_{\text{classical}}$

In Eq. (78), we had the generic grand-canonical partition function

$$Z_g = \sum_{i=1}^M \exp \{-\beta E_i + \beta \mu N_i\},$$

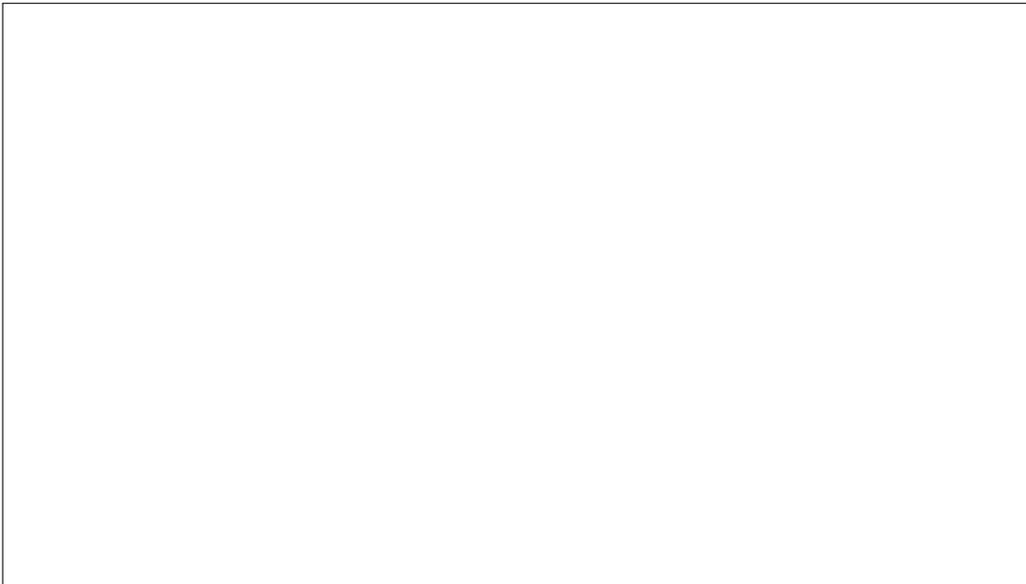
where the sum is over **micro-states** i with energy E_i and particle number N_i .

As we did for the quantum Bose gas, let's rearrange this expression in terms of the occupation numbers n_ℓ for the energy levels E_ℓ with $\ell = 1, \dots, L$. With these definitions, $E_i = \sum_{\ell=1}^L E_\ell n_\ell$ and $N_i = \sum_{\ell=1}^L n_\ell$.

The expression for Z_g above implicitly makes the assumption that the particles are distinguishable. While we are interested in the case of indistinguishable particles, in classical physics it is possible to distinguish particles with different energies. Only the n_ℓ particles with the same energy level are indistinguishable among themselves, which brings in factors of $n_\ell!$ to produce

$$Z_{\text{classical}} = \sum_{n_1=0}^{\infty} \cdots \sum_{n_L=0}^{\infty} \frac{1}{n_1!} \cdots \frac{1}{n_L!} \exp \left\{ -\beta \sum_{\ell=1}^L E_\ell n_\ell + \beta \mu \sum_{\ell=1}^L n_\ell \right\}.$$

We can evaluate this much like we did for the quantum Bose gas:



We obtain the result

$$-\frac{\Omega_{\text{classical}}}{T} = \ln Z_{\text{classical}} = \sum_{\ell=1}^L \exp\left(-\frac{E_{\ell} - \mu}{T}\right),$$

matching the high-temperature limit of the Bose gas above.

We can again compute the average particle number

$$\langle N \rangle = -\frac{\partial \Omega}{\partial \mu} =$$

We again obtain $\langle N \rangle = \sum_{\ell=1}^L \langle n_{\ell} \rangle$, but now with the classical average occupation number

$$\langle n_{\ell}^{(\text{cl})} \rangle = \exp(-\beta E_{\ell} + \beta \mu).$$

Recalling the expression for the quantum Bose gas,

$$\langle n_{\ell}^{(\text{bose})} \rangle = \frac{1}{\exp(\beta E_{\ell} - \beta \mu) - 1},$$

we see that classical physics is recovered in the high-temperature limit where $\beta(E_{\ell} - \mu) \gg 1$ makes the exponential factor much greater than 1.

FERMI GAS

We are now going to study a gas of fermions in a volume V . We again consider the setting of a grand-canonical ensemble. If we now sum over the micro-states, we need to take into account that there is at most one fermion per energy:

$$Z_{fermi} = \sum_{n_1=0,1} \cdots \sum_{n_M=0,1} \exp \left\{ -\beta \sum_{i=1}^M E_i n_i + \beta \mu \sum_{i=1}^M n_i \right\} .$$

Following the lines above, we carry out each sum and arrive at: the so-called *Fermi statistics*.¹²

$$\ln Z_{fermi} = \sum_{i=1}^M \ln \left[1 + \exp \left(-\frac{E_i - \mu}{T} \right) \right] . \quad (85)$$

As in the classical physics case, we arrive at a sum over all energy levels, but now with different terms (compare with (83)).

If we again consider the case of high temperatures $T \gg E_i$, we find:

$$\ln Z_{fermi} = \sum_{i=1}^M \exp \left(-\frac{E_i - \mu}{T} \right) = \ln Z_{classical} .$$

It is quite remarkable that in the classical high temperature limit the difference between fermions and bosons disappear, which is probably one explanation why it took some time to discover this quantum feature.

¹²Enrico Fermi (1901–1954) was an Italian–American physicist and the creator of the world’s first nuclear reactor. He was awarded the 1938 Nobel Prize in Physics.

Addendum: High-temperature limit of the Fermi gas

As before, let's compute the average particle number from the grand-canonical potential to explore the high-temperature limit of the Fermi gas. Labelling the energy levels E_ℓ with $\ell = 1, \dots, L$, we have

$$\Omega_{\text{fermi}} = -T \ln Z_{\text{fermi}} = -T \sum_{\ell=1}^L \ln [1 + \exp(-\beta E_\ell + \beta \mu)],$$

$$\langle N \rangle = -\frac{\partial \Omega}{\partial \mu} =$$

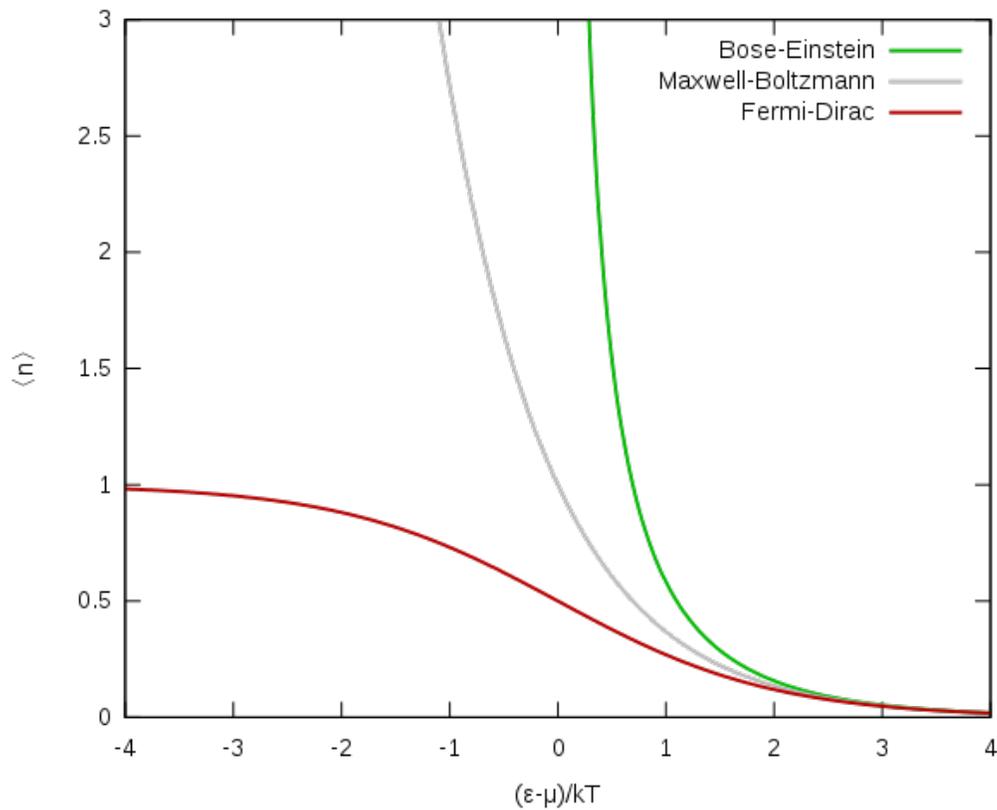
The behaviour of the resulting average occupation numbers is very different than for the Bose gas:

$$\langle n_\ell \rangle = \frac{1}{\exp(\beta E_\ell - \beta \mu) + 1}.$$

This ranges between 0 (when the exponential factor is very large) and 1 (when the exponential factor is very small), consistent with our quantum physics input that there can be at most one fermion per energy state.

Even though there is no longer any possibility of a divergent $\langle n_\ell \rangle$, we still need $-\mu \gg T \gg E_i$ in order for the sum total $\langle N \rangle = \sum_{\ell=1}^L \langle n_\ell \rangle$ to satisfy the grand-canonical constraint on total particle number. In this limit we again recover the classical $\langle n_\ell^{(\text{cl})} \rangle = \exp(-\beta E_\ell + \beta \mu)$, because the $\beta(E_\ell - \mu) \gg 1$ makes the exponential factor much greater than 1.

The figure below¹³ shows an average occupation number for the Bose, Fermi and classical (Maxwell–Boltzmann) gases, demonstrating how all three distributions approximately agree even when $-\mu/T$ is not all that large. (The constant k converts between units and can be set to $k = 1$.)



¹³Source:
commons.wikimedia.org/wiki/File:Fermi-Dirac_Bose-Einstein_Maxwell-Boltzmann_statistics.svg

8.1 Gas of photons and the Maxwell distribution

The energy of a photon is determined by its wavelength λ or by its (angular) frequency $\omega = 2\pi c/\lambda$. (This c is the vacuum speed of light, which is sometimes set to $c = 1$ by a redefinition of units.) Its energy is

$$E_{\text{ph}} = \hbar\omega = \hbar c \sqrt{\vec{k}^2}, \quad (86)$$

where \vec{k} is the wave vector. If the photons are confined to a volume V , the allowed wave vectors are

$$(k_x, k_y, k_z) = \left(\frac{2\pi}{L} m_1, \frac{2\pi}{L} m_2, \frac{2\pi}{L} m_3 \right), \quad i = 1, 2, 3, \quad V = L^3.$$

We have now arrived at our energy spectrum:

$$E_{\text{ph},i} = \hbar\omega = \hbar c \sqrt{\vec{k}^2(m_1, m_2, m_3)}, \quad i = (m_1, m_2, m_3).$$

Photons have an additional quantum number, polarisation, implying that each energy level is twice degenerated.

We have already done a good deal of the calculation and can now just use the Bose statistics from Eq. (84) to get the partition function:

$$\ln Z_{\text{ph}} = -2 \sum_i \ln \left[1 - \exp \left(- \frac{E_{\text{ph},i} - \mu}{T} \right) \right].$$

The factor of 2 counts the twofold degeneracy due to the polarisation mentioned above. We consider large volumes so that we can approximate the sum by an integral using the leading order of a Poisson re-summation (we have studied this in detail with the exercise sheet on page 157):

$$\ln Z_{\text{ph}} = -2 \int dm_1 dm_2 dm_3 \ln \left[1 - \exp \left(- \frac{E_{\text{ph},i} - \mu}{T} \right) \right].$$

With a simple substitution:



we find:

$$\ln Z_{\text{ph}} = -2 V \int \frac{d^3 k}{(2\pi)^3} \ln \left[1 - \exp \left(- \frac{\hbar c k - \mu}{T} \right) \right] .$$

The integral only depends on $k = \sqrt{k^2}$, which suggests to use the frequency as integration variable:

$$\omega = c k , \quad d^3 k \rightarrow 4\pi dk k^2 = \frac{4\pi}{c^3} d\omega \omega^2 .$$

Altogether, we arrive at:

$$\ln Z_{\text{ph}} = - \frac{V}{c^3 \pi^2} \int_0^\infty d\omega \omega^2 \ln \left[1 - \exp \left(- \frac{\hbar\omega - \mu}{T} \right) \right] . \quad (87)$$

Physics input: Photons can be easily created, for example by charged particles collisions. Hence, adding a photon to a box of photon a gas is generically adding a negligible amount of energy to the systems. That is, a gas of photon is well described by a vanishing chemical potential, $\mu = \left. \frac{\partial \langle E \rangle}{\partial N_p} \right|_S = 0$.

We are now in the position to calculate thermodynamical observables. We consider the case $\mu = 0$. We leave detailed calculations to an exercise sheet.

Internal energy of a photon gas:

$$\begin{aligned} \langle E \rangle &= \frac{V}{c^3 \pi^2} \int_0^\infty d\omega \omega^2 \frac{\hbar\omega}{\exp\left(\frac{\hbar\omega}{T}\right) - 1} = \frac{V T^4}{\hbar^3 c^3 \pi^2} \int_0^\infty dx \frac{x^3}{\exp\{x\} - 1} \\ &= \frac{\pi^2 V T^4}{15 \hbar^3 c^3} . \end{aligned} \quad (88)$$

We observe that the energy density increases like T^4 with temperature, i.e., $\langle E \rangle / V \propto T^4$.

Which (small) frequency interval contributes the most to the internal energy of a photon gas?

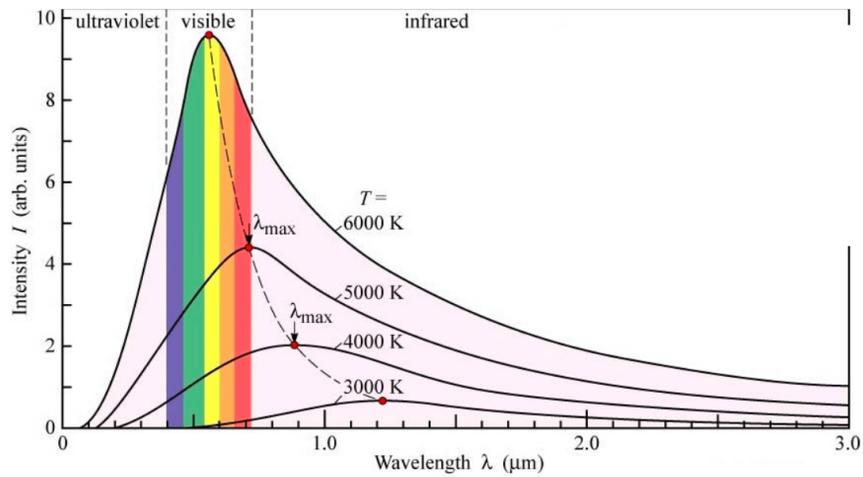
To answer this question, we introduce the spectral density $P(\omega)$ by

$$\langle E \rangle = \int d\omega P(\omega), \quad P(\omega) = \frac{\hbar V}{c^3 \pi^2} \frac{\omega^3}{\exp\left(\frac{\hbar\omega}{T}\right) - 1}. \quad (89)$$

$P(\omega)$ is called the Planck spectrum.

DISCUSSIONS:

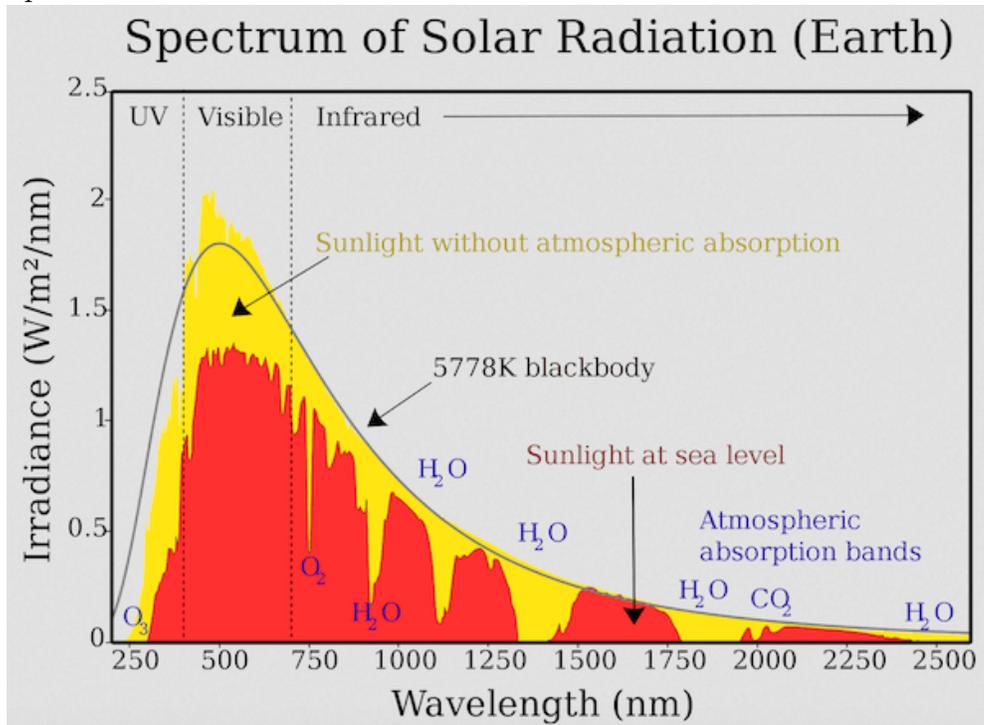
The Planck spectrum as function of the wave length $\lambda = 2\pi c/\omega$:



The Planck Distribution function (Source: E. Schubert, *Light Emitting Diodes*).

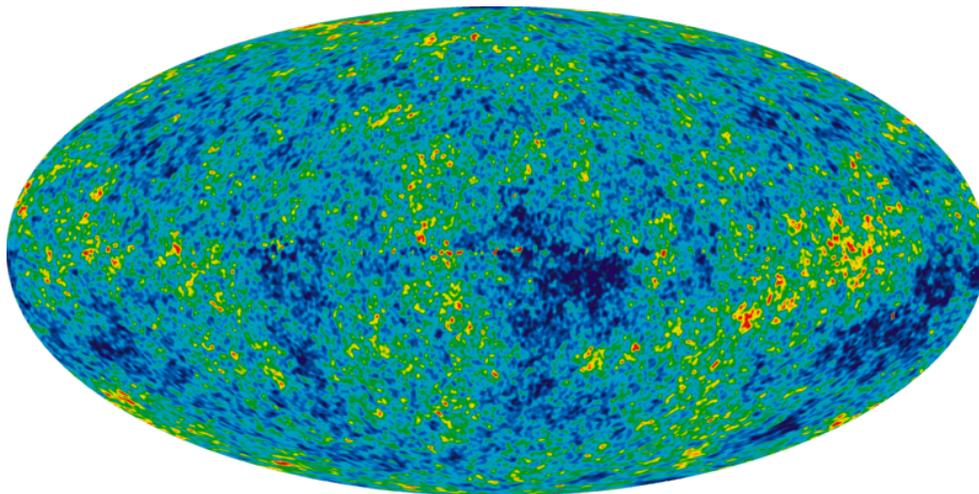
COMMENTS:

Spectrum of our sun:

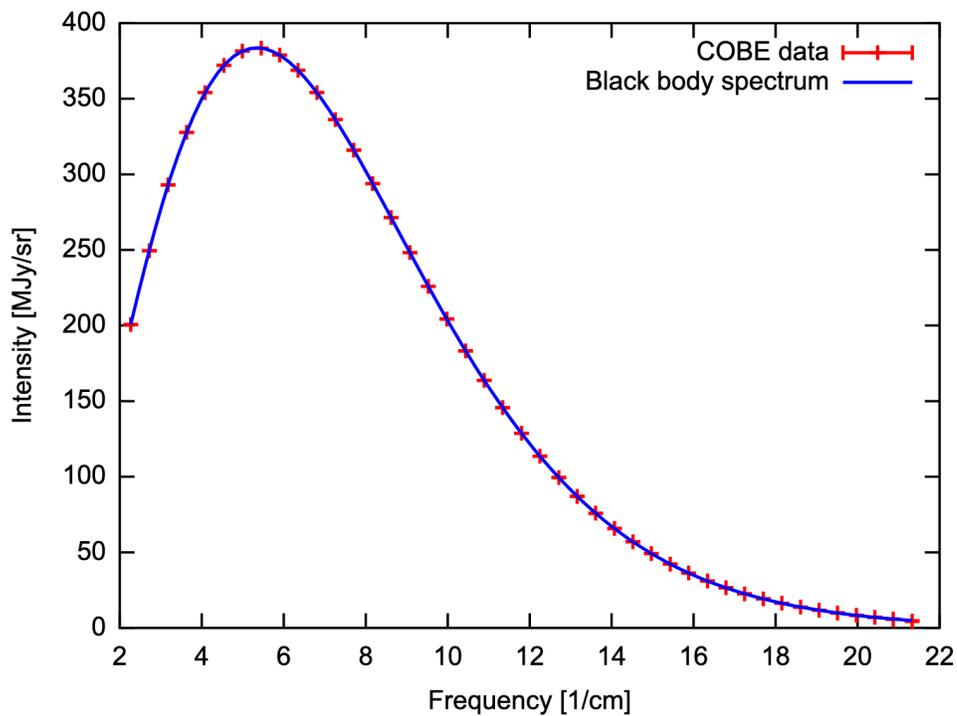


COMMENTS:

Spectrum of the night sky (not from the stars): The Cosmic Microwave Background temperature fluctuations from the 7-year Wilkinson Microwave Anisotropy Probe data seen over the full sky.



Cosmic microwave background spectrum (from COBE)



8.2 Quantum gas of fermions

Let us consider a non-relativistic gas of fermions. We again adopt the experimental setup of a heat-bath (temperature T) and particle reservoir (chemical potential μ).

We already worked out the energy spectrum in section 4.1:

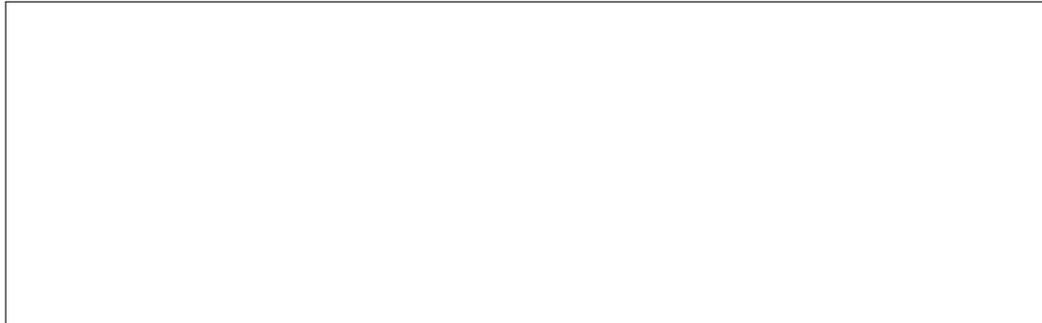
$$E(p) = \frac{p^2}{2m}, \quad p = |\vec{p}|, \quad \vec{p} = \hbar \frac{\pi}{L} \vec{m}, \quad \vec{m} \in \mathbb{N}^3.$$

We already calculated the statistics for systems of fermions in Eq. (85), and were able to reduce it to sum over the energy spectrum. We thus obtain:

$$\ln Z_{fermi} = \sum_{\vec{m}} \ln \left[1 + \exp \left(-\frac{\vec{p}^2}{2mT} + \frac{\mu}{T} \right) \right].$$

We assume sufficiently large volumes so that we can replace:

$$\sum_{m=0}^{\infty} \rightarrow \frac{1}{2} \sum_{m=-\infty}^{\infty} \rightarrow \frac{1}{2} \int_{-\infty}^{\infty} dm.$$



We finally observe:

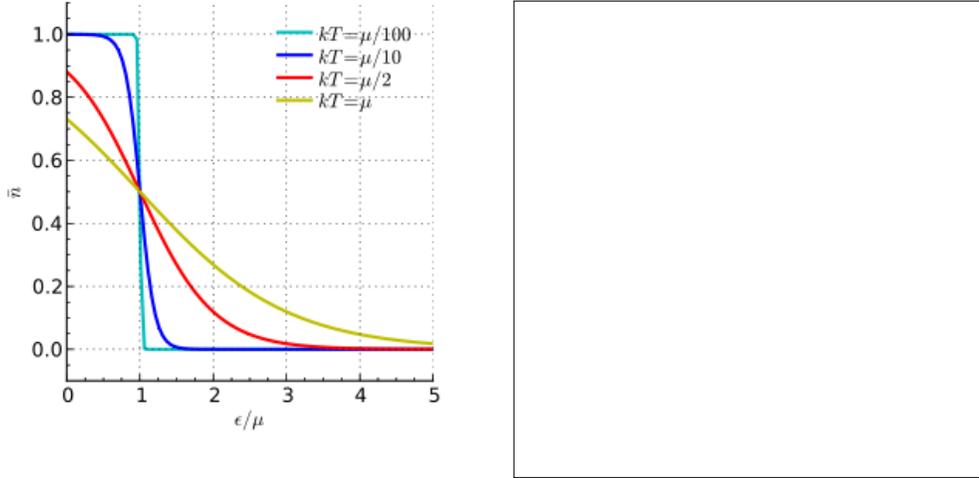
$$\ln Z_{fermi} = \frac{V}{2\pi^2 \hbar^3} \int_0^{\infty} dp p^2 \ln \left[1 + \exp \left(-\frac{E(p) - \mu}{T} \right) \right]. \quad (90)$$

A new quantum phenomenon comes to light if we study the particle number:

$$\langle N \rangle = T \frac{\partial \ln Z_{fermi}}{\partial \mu} = \frac{V}{2\pi^2 \hbar^3} \int_0^{\infty} dp p^2 \frac{1}{\exp \left(\frac{E(p) - \mu}{T} \right) + 1}. \quad (91)$$

Let us study the so-called Fermi function

$$n(E) = \frac{1}{\exp\left\{\frac{E-\mu}{T}\right\} + 1} .$$



For large temperatures, we enter the classical regime, and we have done the calculation in section 4.1. Let us focus on the cold regime, where we can approximate the Fermi function by a step function:

$$n(E) \approx \begin{cases} 1 & \text{for } E < \mu \\ 0 & \text{else} \end{cases} .$$

It means that we can cut integrals such as (91) when $E(p)$ reaches μ . It is therefore convenient to switch from the momentum variable p to the energy variable E by substitution:

$$E = \frac{p^2}{2m}, \quad p = \sqrt{2mE}, \quad dp = \sqrt{\frac{m}{2E}} dE .$$

Thus, we find from (91):

$$\langle N \rangle \approx \frac{V m^{3/2}}{\sqrt{2\pi^2 \hbar^3}} \int_0^\mu dE \sqrt{E} = \frac{\sqrt{2} V m^{3/2}}{3 \pi^2 \hbar^3} \mu^{3/2} . \quad (92)$$

This is the desired relation between particle number and chemical potential. This relation does not depend on the temperature T because we are basically looking at the leading order of the low temperature expansion. Higher orders

in the temperature can be systematically taken into account. This can be found in the literature under the name *Sommerfeld expansion*.¹⁴

Along the same lines, we can calculate the internal energy:

$$\begin{aligned}\langle E \rangle &= \frac{V}{2\pi^2\hbar^3} \int_0^\infty dp p^2 \frac{E(p)}{\exp\left(\frac{E(p)-\mu}{T}\right) + 1} = \frac{V m^{3/2}}{\sqrt{2}\pi^2\hbar^3} \int_0^\infty dE \sqrt{E} n(E) \\ &\approx \frac{V m^{3/2}}{\sqrt{2}\pi^2\hbar^3} \int_0^\mu dE \sqrt{E} E = \frac{\sqrt{2} V m^{3/2}}{5 \pi^2\hbar^3} \mu^{5/2} = \frac{3}{5} \mu \langle N \rangle.\end{aligned}\quad (93)$$

We make a very important observation:

Key observation: Although the temperature vanishes, the internal energy $\langle E \rangle$ is positive.

INTERPRETATION:

A surprise is waiting for us if we look at the pressure (54):

$$p = - \left. \frac{\partial \langle E \rangle}{\partial V} \right|_{S,N}. \quad (94)$$

¹⁴Arnold Johannes Wilhelm Sommerfeld, 1868–1951, was a German theoretical physicist who pioneered developments in atomic and quantum physics.

The derivative has to be taken at constant entropy S , and we need to handle S first:

$$S = -\frac{\partial \Omega}{\partial T} = \frac{\partial}{\partial T} \left(T \ln Z_{\text{fermi}} \right).$$

Let us consider the function

$$\ln \left[1 + \exp \left(-\frac{E - \mu}{T} \right) \right]$$

for small temperatures T :

INTERPRETATION:

Hence, we find for (90):

$$\ln Z_{\text{fermi}} = \frac{V m^{3/2}}{\sqrt{2\pi^2 \hbar^3}} \int_0^\mu dE \sqrt{E} \frac{\mu - E}{T}$$

This means that for any $E(p)$ we have $\Omega = T \ln Z_{\text{fermi}}$ independent of T at low temperatures, implying the entropy vanishes.

INTERPRETATION:

We can make μ the subject of the equation (92) and insert this into the equation (93) for the thermal energy.

$$\langle E \rangle = \frac{2}{5} \langle N \rangle^{5/3} \frac{\hbar^2}{m} V^{-2/3} .$$

We now can use Eq. (94) to calculate the pressure, treating $\langle N \rangle$ as a constant, with the entropy S also constant, namely zero:

$$p = \frac{4}{15} \frac{\hbar^2}{m} \rho^{5/3} , \quad \rho := \frac{\langle N \rangle}{V} \quad (\text{density}) .$$

The interesting observation is that the pressure *does not vanish* at zero temperature. It is a pure quantum effect that keeps up the pressure.

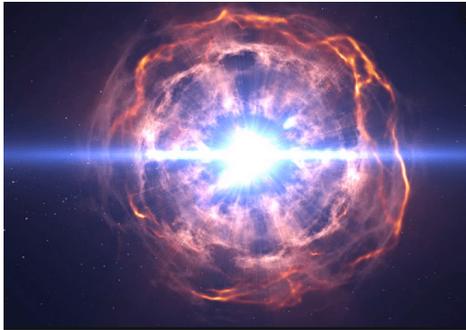
At high temperature, we recover the ideal (classical) gas with the equation of state:

$$pV = \langle N \rangle T , \quad p = \rho T .$$

We thus have qualitatively the following function $p(T)$:

INTERPRETATION:

This explains a cosmic phenomenon—the supernova explosion of stars:



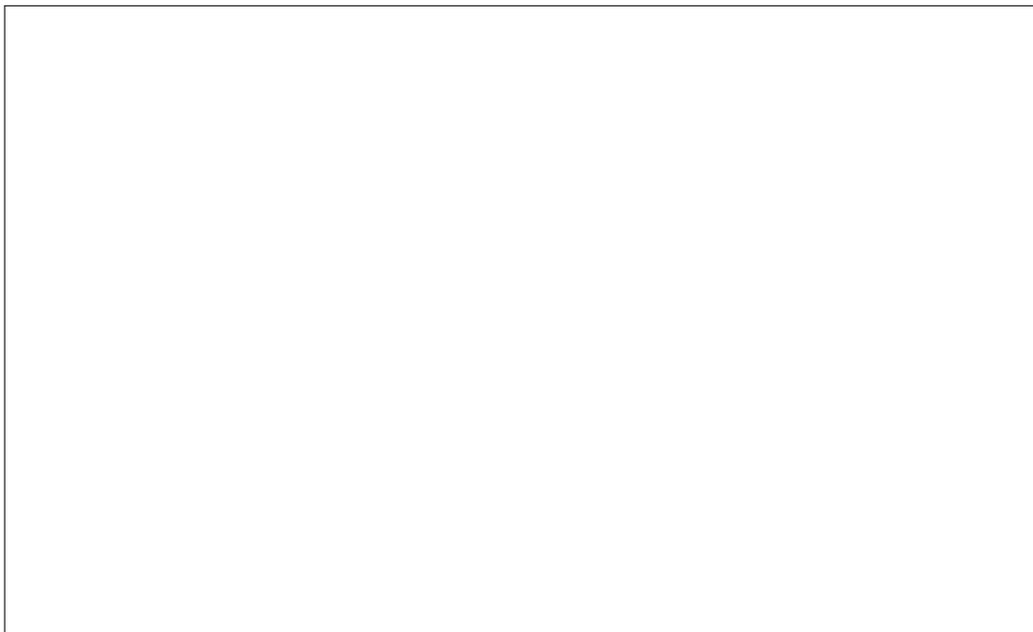
9 Phase transitions

Phase transitions are spectacular phenomena in statistical physics. They describe everyday occurrences like liquid turning into solids at their freezing points, as well as more exotic behaviour such as quarks and gluons (elementary particles out of which we are made) changing from a plasma into composite protons and neutrons early in the history of the universe (roughly one millionth of a second after the Big Bang). What does it take to describe such a drastic change in the properties of matter?

A second question, which we going to study, is: what is actually the fundamental difference between matter in either phase? For example, what is the difference between ice and water? After all, both substances are made out of the same constituents namely H_2O molecules.

9.1 Interacting theories

Key ingredient, and in many cases a sufficient ingredient, is some (e.g. short range) interaction between the degrees of freedom of our statistical ensemble. We will address both questions above by means of the now familiar spin model: degrees of freedom are the spins $s_i \in \{-1, +1\}$, where i labels the position of the spin in e.g. a spin chain or a lattice:



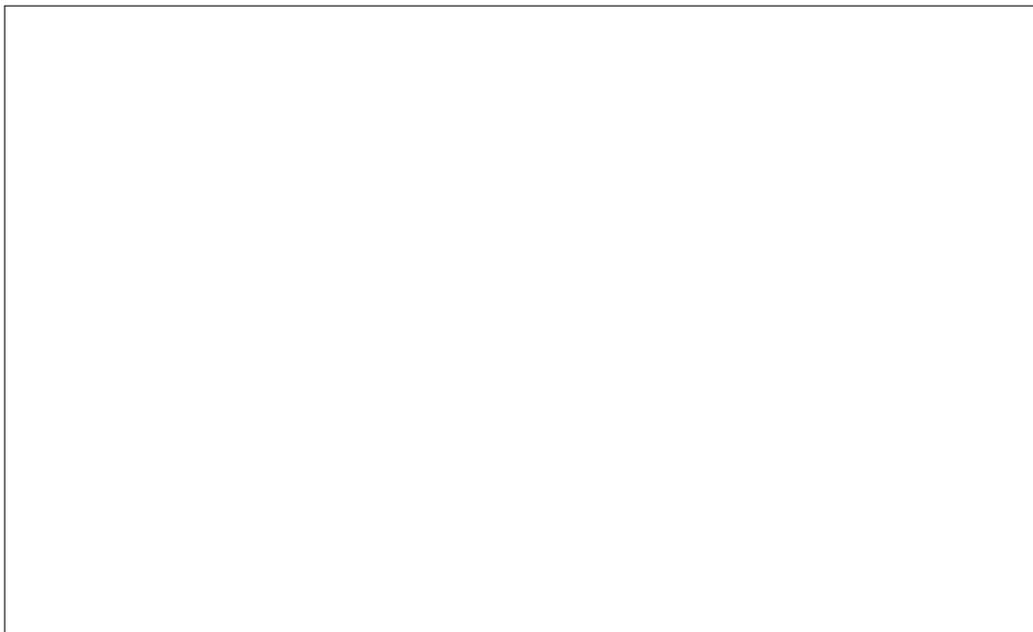
Once we know the energy E of the spin system, we can start to do statistics and (e.g.) expose the system of spins to a heatbath with temperature T . We have previously studied spins interacting with an external magnetic field H :

$$E = -H \sum_i s_i \quad (\text{non-interacting}) .$$

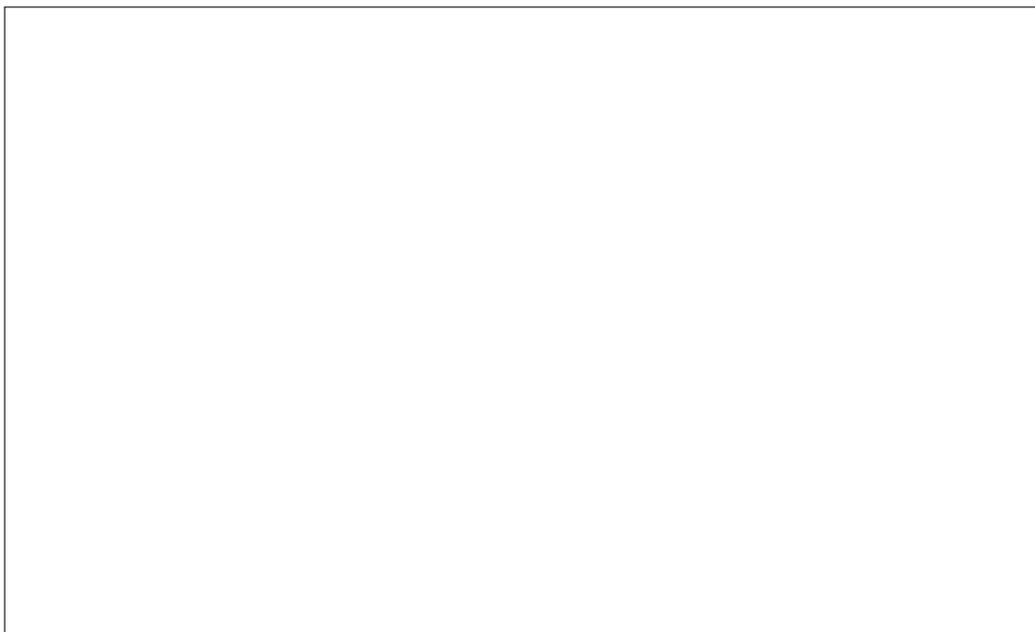
What qualifies this spin system as *non-interacting*?

Defnition: ΔE_i is the change of the total energy E of a statistical system if *only* the state of the i th degree of freedom is changed. If ΔE_i is independent of all degrees of freedom $k \neq i$, the statistical system is called *non-interacting*.

Let us check whether the above spin model satisfies this condition:



The above property has far reaching mathematical consequences, namely the possibility to calculate the partition function in closed form (see also (32)):



How strenuous would be the calculation if we would *not* have the factorisation property? In the case of N spins, we would need to do the sum

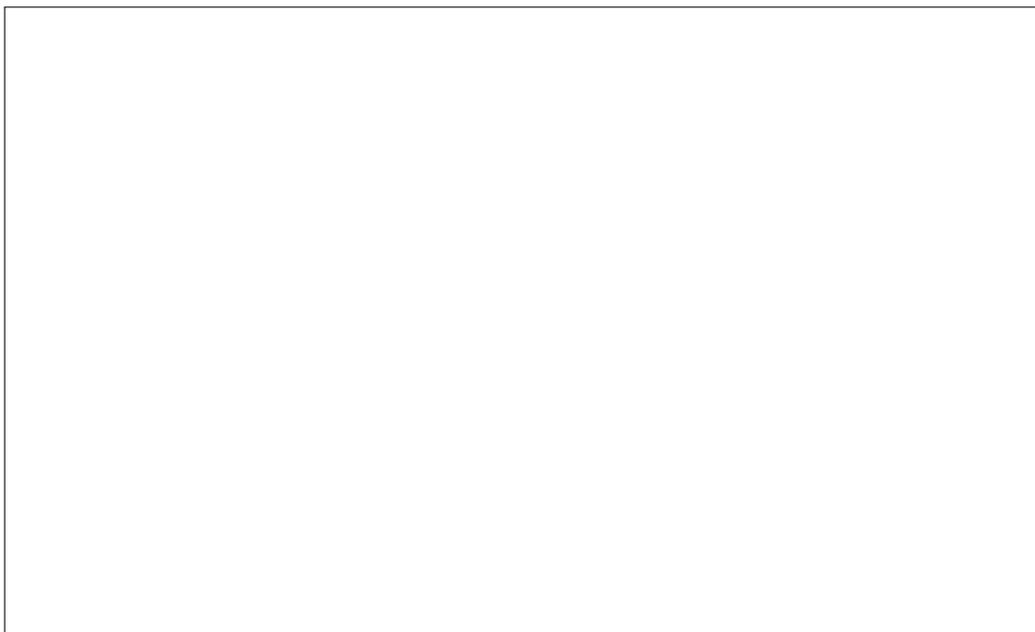
$$\sum_{\{s_i\}} = \sum_{s_1=\pm 1} \dots \sum_{s_N=\pm 1} .$$

This sum has 2^N terms. This calculation gets becomes intractable:

$$2^{100} \approx 1.26 \times 10^{30} , \quad 2^{10,000} \approx 2.00 \times 10^{3010} .$$

The latter sum is even out of reach of modern supercomputers.

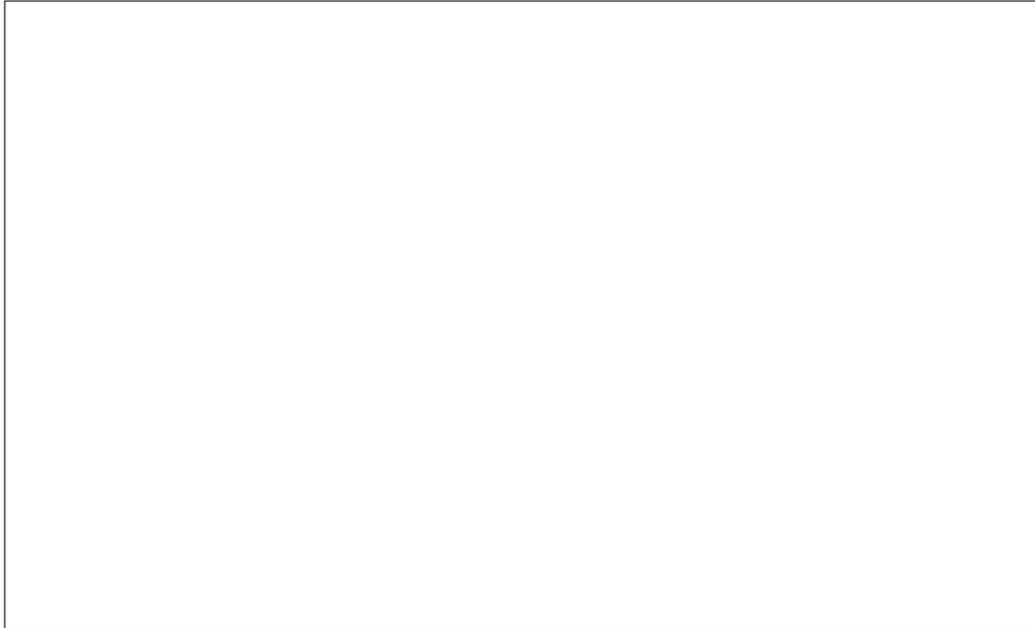
Before we make the above spin system *interacting*, we introduce the lattice and related objects: *site*, *link*, *plaquette*, and *cube*.



Let us now consider the following generalisation:

$$E = - \sum_{\{l=(xy)\}} s_x s_y - H \sum_x s_x . \quad (95)$$

The first sum extends over *all links* of the lattice. Let us now calculate the change in energy if we change the spin at site x :



Hence, we find:

$$s_x \rightarrow (-1) s_x : \quad \Delta E_x = 2(h_x + H) s_x, \quad h_x = \sum_{y \in l=(xy)} s_y .$$

This formula has an intuitive interpretation: The surrounding spins at positions $y \in l = (xy)$ generate a local magnetic field h_x , which adds to the external field H . Note that ΔE_x now depends on spins other than s_x , confirming that the system is interacting. We will see that this simple system is already able to describe the phenomenon of a phase transition.

Expose this spin system to a heat-bath with temperature $T = 1/\beta$, the task is to calculate the canonical partition function:

$$Z(T, N, H) = \sum_{\{s_x\}} \exp \left\{ \beta \sum_{l=(xy)} s_x s_y + \beta H \sum_x s_x \right\} . \quad (96)$$

This model is the famous Ising¹⁵ model, which was developed as a mathematical model for ferromagnetism. It reached fame as it was one of the first models that gave a mathematical rigorous derivation of phase transitions.

¹⁵Ernst Ising (1900–1998) was a German physicist, who is best remembered for the development of the Ising model. He was a professor of physics at Bradley University, Illinois, USA.

9.2 The Ising model

Let us qualitatively understand what is going on in the Ising model.

High temperature limit: $T \rightarrow \infty$, $\beta \rightarrow 0$: In this case, the partition function is H independent:

$$Z(\beta \rightarrow 0) = \sum_{\{s_x\}} = 2^N .$$

The system become non-interacting and the spins can fluctuate freely. The magnetisation of a spin ensemble is

$$M = n_+ - n_- ,$$

where n_{\pm} is the number of spins with ± 1 . The number of possibilities to realise a certain n_+ (and hence $n_- = N - n_+$) is

$$\binom{N}{n_+} = \binom{N}{n_-} .$$

For large N , this overwhelmingly peaks at $n_+ = n_- = \frac{1}{2}N$, implying we most likely find a spin configuration with M close to zero. We say that the spin system is in a *disordered* state.

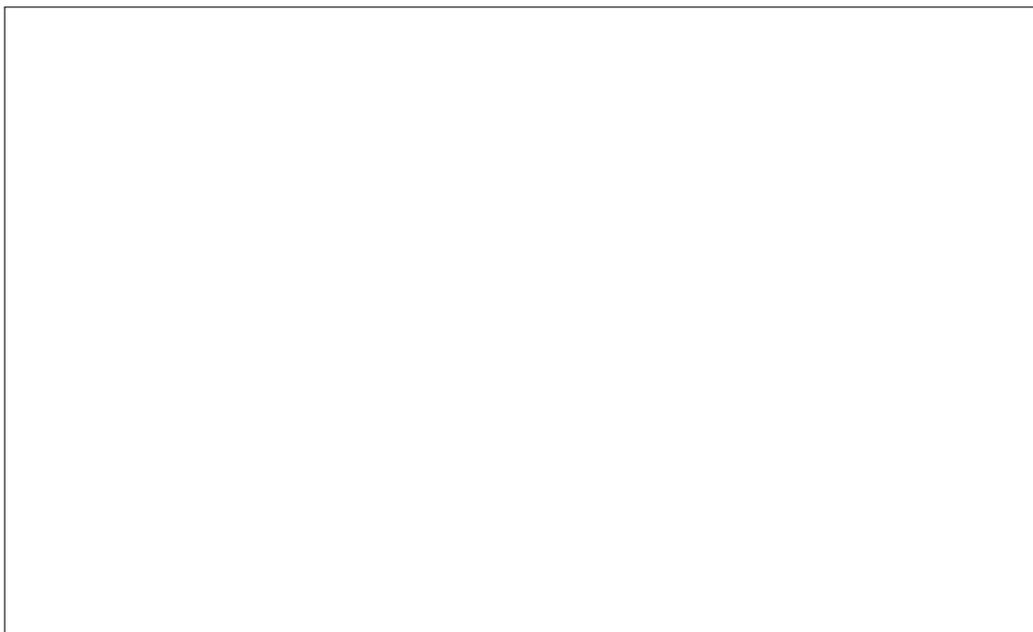
Low temperature limit: $T \rightarrow 0$, $\beta \rightarrow \infty$: It is enough to study $H = 0$ for now. What is the probability $p(E)$ to find a spin system with certain energy E ? This is marginal and we can write:

$$p(E) = \rho(E) \exp\{\beta E\} / Z , \quad E = \sum_{l=(xy)} s_x s_y ,$$

where $\rho(E)$ is the called *density of states*, which quantifies the number of spin configurations compatible with an overall energy E . An ensemble of independent spins corresponds to a small value of E and to a large $\rho(E)$ since there are many possibilities to arrange spins to $E = 0$. The maximal energy is reached E if all spins are parallel:

$$s_x = \pm 1 \forall x : E_{max} = \sum_{l=(xy)} (\pm 1)^2 = dN$$

where N is the number of spins, and d is the dimension of the lattice. This is illustrated below:



For large energies $\rho(E)$ becomes small, in fact, $\rho(E_{max}) = 2$. We have two competing factors: $\rho(E)$ decreases with E while the Gibbs factor increases. The most likely energy is hence somewhere between $E = 0$ and $E = dN$ depending on β .

Note that $\rho(E)$ is independent of β . What happens if we can make β as large as we want? We said that the probability for having $E = E_{max}$ is

$$P(E_{max}) = 2 \exp\{\beta E_{max}\} / Z(\beta) .$$

All spins are parallel. The micro-state with energy closest to E_{max} is obtained when we flip exactly one spin. The energy E_- of this state is

$$E_- = E_{max} - 4 ,$$

since



We have N possibilities to choose the site and then again this spin could be up or down. The number of micro-states with this energy is thus $\rho(E_-) = 2N$. Hence, the probability to find E_- in the thermodynamical ensemble is given by

$$P(E_-) = 2N \exp\{\beta(E_{max} - 4)\}/Z(\beta).$$

Let us compare these probabilities:

$$P(E_{max})/P(E_-) = \frac{\exp\{4\beta\}}{N}.$$

This means that for a given N , we always have

$$P(E_{max}) \gg P(E_-) \quad \text{for } \beta \text{ sufficiently large.}$$

Observation (Ising model): For any given number of spins, the thermodynamical ensemble is always described by an *ordered state* of all spins parallel at sufficiently low temperatures.

COMMENTS:

- A thermodynamical system is generically in an ordered state at low temperatures and in a disordered state at high temperatures.

- How both regimes connect when the temperature varies depends on the details of the model and its dimension d . Everything is possible: a gradual ‘smooth’ change from the ordered to the disordered state (**crossover**), a rapid, but smooth transition (**high-order phase transition**), a rapid, discontinuous transition (**first-order phase transition**).
- For a finite number N of degrees of freedom, the transition is always smooth. You have to consider the limit $N \rightarrow \infty$ to observe a true discontinuity in thermodynamical observables.
- Peierls¹⁶ has presented a proof that in $D \geq 2$ the magnetisation turns off abruptly at some finite value of the temperature, called the *critical temperature* T_c with no magnetisation at all for higher temperatures $T > T_c$.

9.3 The Mean-Field approximation

To study a potentially rapid transition between an ordered phase and a disordered phase, we need a quantitative approach to the partition function (96). An intuitive approximation, which usually gives good *qualitative* insights is the so-called **mean-field approximation**. Let us single out a particular site $x = x_0$ and write the partition function as:

$$Z(T, N, H) = \sum_{s_{x_0}} \sum_{\{s_x, x \neq x_0\}} F(s_x, x \neq x_0) \exp\{\beta(h_{x_0} + H) s_{x_0}\},$$

$$h_{x_0} = \sum_{y \in l=(x_0y)} s_y.$$

We already said that h_{x_0} has the interpretation of a magnetic field produced by the surrounding spins. The central assumption is that this field does not fluctuate much so that we can replace:

$$h_{x_0} \rightarrow \langle h_{x_0} \rangle = \sum_{y \in l=(x_0y)} \langle s_y \rangle = 2d \langle s \rangle.$$

¹⁶Sir Rudolf Ernst Peierls, CBE FRS, 1907 – 1995 was a Jewish German-born British physicist who played a major role in the Manhattan Project and Tube Alloys, Britain’s nuclear programme.

With this approximation, we get:

$$Z(T, N, H) \approx Z_{\text{MF}}(T, N, H) = c \sum_{s_{x_0}} \exp\{\beta(2d \langle s \rangle + H) s_{x_0}\},$$
$$c = \sum_{\{s_x, x \neq x_0\}} F(s_x, x \neq x_0) .$$

This partition function can now be calculated:

$$Z_{\text{MF}}(T, N, H) = 2c \cosh\left(\beta(2d \langle s \rangle + H)\right) .$$

What would we then estimate for the magnetisation M ?

Remember:

$$M = \left\langle \sum_x s_x \right\rangle = N \langle s \rangle .$$

It is important to note that no site is singled out implying

$$\langle s_x \rangle = \langle s_y \rangle = \langle s \rangle \quad \forall x, y .$$

Let us now estimate M by calculating $\langle s_{x_0} \rangle$:



Hence, in mean-field approximation, we find:

$$\langle s_{x_0} \rangle = \frac{c}{Z_{\text{MF}}} \sum_{s_{x_0}} s_{x_0} \exp\{\beta(2d \langle s \rangle + H) s_{x_0}\} = \frac{c}{2Z_{\text{MF}}} \sinh(\beta(2d \langle s \rangle + H)),$$

which leads to the so-called *self-consistent* equation:

$$\langle s \rangle = \tanh(\beta(2d \langle s \rangle + H)). \quad (97)$$

Let us discuss the solutions of this equation graphically. We introduce two functions ($x = \langle s \rangle$):

$$f(x) = x, \quad g(x) = \tanh(2d\beta x + \beta H).$$

We are looking for solutions x of $f = g$. Let us study first $H \neq 0$:



We see that there is always a unique solution x . For large β (i.e., at low temperatures $T = 1/\beta$), we find:

$$\langle s \rangle \approx 1 \quad \text{for } H > 0, \quad \langle s \rangle \approx -1 \quad \text{for } H < 0.$$

Let us now switch to the interesting case $H = 0$.



We see that there is always the solution $x = \langle s \rangle = 0$. If, however, β is large enough, we find two more solutions $x = \pm x_m$. For small enough temperatures, $\beta > \beta_{crit}$, we find ordered states with magnetisations:

$$M = N \langle s \rangle = \pm N x_m .$$

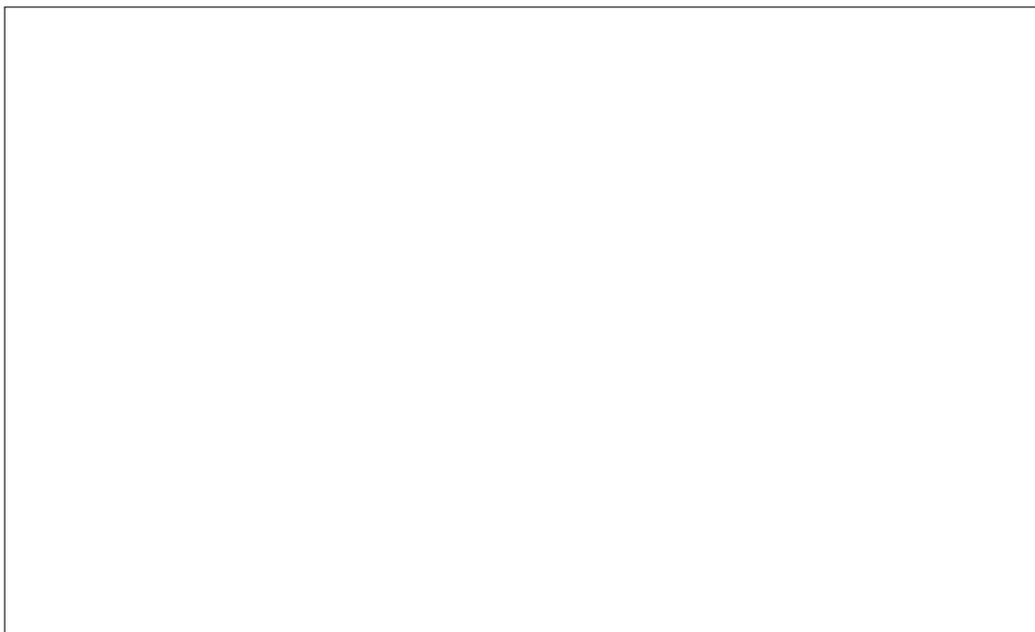
For this to happen, the slope of the tanh at $x = 0$ must be bigger than 1 or:

$$\beta > \beta_{crit} = \frac{1}{T_c} = \frac{1}{2d} = \frac{1}{4} \quad \text{2-dim Ising.} \quad (98)$$

Let us study the solution x_m for β close to but above β_{crit} . In this regime, x_m is still small so that we can approximate:

$$\tanh(u) = u - \frac{1}{3} u^3 \dots .$$

We find:



$$\langle s \rangle \propto (T_c - T)^{1/2}, \quad T < T_c.$$

COMMENTS:

- The mean-field approximation provides good first insights into interacting statistical systems, but can fail at the *quantitative level*.
- The exact solution for the two-dimensional Ising model was found by Lars Onsager in 1944,¹⁷ and predicts

$$\beta_{\text{crit}} = \frac{1}{2} \ln(1 + \sqrt{2}) = 0.4406867935\dots, \\ \langle s \rangle(T) \propto (T_c - T)^{1/8}. \quad (99)$$

¹⁷Lars Onsager (1903–1976) was a Norwegian–American physical chemist who was awarded the 1968 Nobel Prize in Chemistry.

10 Exercises for tutorials and self-study

TP1: The probability distribution $p(x_{(1)})$ for the step length of a promenader is given by

$$p(x_{(1)}) = 6x_{(1)}(1-x_{(1)}) \quad \text{for} \quad 0 \leq x_{(1)} \leq 1, \quad p(x_{(1)}) = 0 \quad \text{else.}$$

- What is the most likely step length? Calculate the mean μ for the step length and its standard deviation σ .
- The promenader now makes $N \gg 1$ steps. Find the probability distribution $p(x)$ for the position of the promenader as a function of N .
- Calculate the intervals in which the promenader can be found after $N = 100$ steps with 80%, 90% and 99% probabilities.

Hint: you might want to use:

$$\begin{aligned} 2 \int_0^u dx \frac{1}{\sqrt{2\pi}} \exp\{-x^2/2\} &= 0.8 & \text{for} & \quad u = 1.281551566\dots, \\ 2 \int_0^u dx \frac{1}{\sqrt{2\pi}} \exp\{-x^2/2\} &= 0.9 & \text{for} & \quad u = 1.644853627\dots, \\ 2 \int_0^u dx \frac{1}{\sqrt{2\pi}} \exp\{-x^2/2\} &= 0.99 & \text{for} & \quad u = 2.575829304\dots, \end{aligned}$$

TP2: Show that for large N , we can approximate:

$$\binom{N}{n} \approx \frac{2^N}{\sqrt{2\pi N}} \exp\left\{-\frac{x^2}{2N}\right\}, \quad x = 2n - N.$$

Carry out the following steps:

- Consider the experiment of tossing a coin where Heads is assigned $X = 1$ and Tails $X = -1$. Repeat this experiment N times and find the probability $p(x)$, $x = (x + N)/2$ that you got n times Heads.
- Find $p(x)$ using the Central Limit Theorem and the assumption $N \gg 1$.

Compare the result from part (a) and part (b).

TP3: Stirling's formula provides an excellent approximation to $n!$ for large n , which is part of the Mathematics legacy and which will be very useful in the lecture:

$$n! = \sqrt{2\pi n} n^n e^{-n} \left(1 + \mathcal{O}\left(\frac{1}{n}\right) \right).$$

Carry out the following steps:

a. Show that

$$n! = \int_0^\infty dx x^n e^{-x} \quad \text{and} \quad n! = e^{n \ln n} n e^{-1} \int_{-1}^\infty e^{n(\ln(y+1)-y)} dy.$$

b. Use the substitution $u = \sqrt{ny}$ and show (with $\epsilon = 1/\sqrt{n}$)

$$\int_{-1}^\infty e^{n(\ln(y+1)-y)} dy = \frac{1}{\sqrt{n}} \int_{-\sqrt{n}}^\infty du \left[1 + a u^3 \epsilon + (bu^4 + cu^6) \epsilon^2 + \mathcal{O}(\epsilon^3) \right] e^{-u^2/2}$$

and find the numbers a , b and c .

c. Discuss the error if you replace the lower bound $-\sqrt{n}$ by $-\infty$, and do so. Perform the integration and show:

$$n! = \sqrt{2\pi n} n^n e^{-n} \left(1 + \frac{12}{n} + \mathcal{O}\left(\frac{1}{n^{3/2}}\right) \right).$$

d. Compare $n!$ with the result from the above formula for $n = 1, 2, 3, 4, 5$ and for $n = 100$.

TP4: Duplicated **HW7** below.

TP5: Poisson resummation provides a means to approximate a discrete sum by a continuous integral. If $f(n)$ is a function for which the Fourier transform

$$g(k) \equiv \int_{-\infty}^{\infty} dn f(n) \exp [2\pi i k \cdot n]$$

exists, the Poisson summation formula is

$$\sum_{n=-\infty}^{\infty} f(n) = \sum_{k=-\infty}^{\infty} g(k). \quad (100)$$

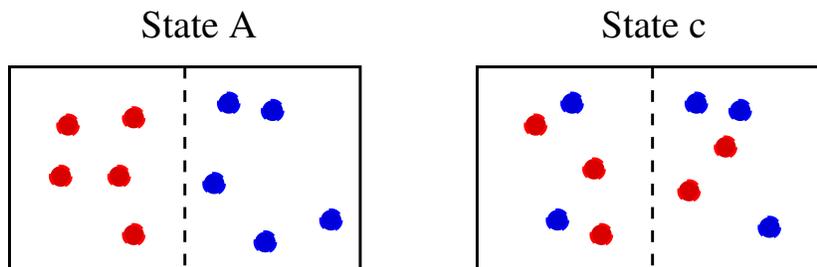
a. Using the Poisson summation formula, show that, for $a > 0$,

$$\sum_{n=-\infty}^{\infty} \frac{1}{a^2 + n^2} = \frac{\pi}{a} \coth(\pi a).$$

b. For $0 < a \ll 1$, show that

$$\sum_{n=-\infty}^{\infty} \exp [-an^2] = \int_{-\infty}^{\infty} dn \exp [-an^2] + \mathcal{O}(\exp [-\pi^2/a]).$$

TP6: Consider a container of volume V with two identically sized compartments. Each compartment contains $N/2$ identical particles. **All** N particles have identical physical properties, *except* that those initially in the left compartment (the “reds”) are distinguishable from those in right compartment (the “blues”) by their colour. The container is exposed to a heat-bath of temperature T . This is called system A , and its entropy is S_A .



We remove the wall separating the two compartments. After a while, we reinsert the wall, making sure that each compartment contains $N/2$ particles but allowing the colours to mix. This is called system C with entropy S_C . Calculate the mixing entropy

$$\Delta S = S_C - S_A .$$

The following special case of the Chu–Vandermonde identity may be useful:

$$\sum_{k=0}^N \binom{N}{k}^2 = \binom{2N}{N} .$$

TP7: A statistical system is immersed in a heat-bath and particle reservoir. It is in thermodynamical equilibrium and characterised by temperature T and chemical potential μ .

The grand-canonical potential is defined by

$$\Omega(T, \mu) = -T \ln Z_g(T, \mu) \qquad Z_g(T, \mu) = \sum_{i=1}^M \exp\{-\beta E_i + \beta \mu N_i\},$$

where $\beta = 1/T$.

a. Show that

$$\langle N \rangle = - \frac{\partial \Omega(T, \mu)}{\partial \mu} .$$

b. Start from

$$S(T, \mu) = - \sum_{i=1}^M p_i \ln p_i \qquad p_i = \frac{1}{Z_g} \exp\{-\beta E_i + \beta \mu N_i\}$$

and show that

$$\Omega(T, \mu) = -T S(T, \mu) + \langle E \rangle - \mu \langle N \rangle .$$

c. Show that

$$S(T, \mu) = - \frac{\partial \Omega(T, \mu)}{\partial T} .$$

d. Show that

$$\langle E \rangle = -T^2 \frac{\partial}{\partial T} \left[\frac{\Omega(T, \mu)}{T} \right] + \mu \langle N \rangle .$$

TP8: Duplicated **HW8** below.

TP9: A statistical system with M micro-states is characterised by the energy E_i for $i = 1, \dots, M$. Show that the grand-canonical partition function $Z_g(T, \mu)$ for chemical potential μ is

$$Z_g(T, \mu) = \sum_{N=0}^{\infty} Z(T, N) e^{\beta \mu N},$$

where $Z(T, N)$ is the corresponding canonical partition function for N particles with the same energy E_i .

11 Exercises for assignments and self-study

HW1: A ‘Random Walker’ takes a step to the right with probability $p = 0.7$ and to the left with probability $q = 0.3$. It does $N = 10$ steps in total.

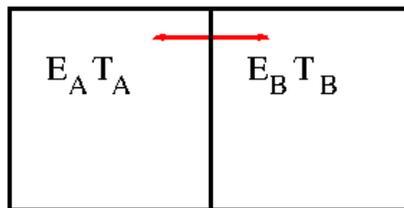
- Calculate the probabilities p_k for all k , where k is the walker’s position after the 10 steps.
- Calculate the mean μ and the standard deviation σ for the 1-step process. Write down the probability distribution $p(x)$ of the walker after 10 steps using the CLT approximation.
- Using the relation $P(a \leq x \leq b) = \int_a^b p(u) du$, plot the p_k and $P(x_k)$ in one graph (e.g. using Maple).

Hint: For plotting, see the help Maple code `maple_help_sh1.mw` under ‘support’ on Vital.

HW2: An oil spill 500m away from a marine protected area (MPA) is described by a one-dimensional diffusion process with a diffusion constant of $10 \text{ cm}/\sqrt{\text{min}}$ and a drift velocity of $60 \text{ cm}/\text{min}$ towards the MPA.

How long does it take until more than 2% of the oil is inside the MPA?

HW3: Two boxes contain an equal number $N \gg 1$ of spins in an external magnetic field H but with different internal energies $E_A < 0$ and $E_B < E_A$.



Initially both boxes are isolated and in thermodynamical equilibrium.

- Write down the total number of states for both boxes $M(E_A)$ and $M(E_B)$. Using the large number approximation (CLT), calculate the entropy for each of the boxes and the corresponding temperatures, T_A and T_B , as a function of E_A and E_B , respectively.
- Show that $T_A > T_B$.
- Both boxes are now allowed to exchange energy and reach thermodynamical equilibrium. Using the CLT approximation, calculate the total number of states of the combined system C with energy $E = E_A + E_B$:

$$M_C(E) = \int \frac{dE_A}{H} M(E_A) M(E - E_A).$$

- Calculate the temperature T_C of the combined system.
- Show that your result for T_C in part (d) satisfies $T_B < T_C < T_A$.

HW4: Revisit the tutorial problem (and most importantly the Maple script) and find the number A in:

$$n! = \sqrt{2\pi n} n^n e^{-n} \left(1 + \frac{12}{n} + \frac{A}{n^{3/2}} + \mathcal{O}\left(\frac{1}{n^{5/2}}\right) \right).$$

Compare your formula for $n = 1, 2, 3, 4, 5$ and $n = 100$ with $n!$ in a table.

HW5: Start with the definition of $\langle E \rangle$ for the canonical ensemble from Eq. (25) in the lecture notes, and show that the heat capacity can be expressed as

$$c_v = \frac{1}{T^2} \langle (E - \langle E \rangle)^2 \rangle .$$

HW6: Show that the entropy S is related to the Helmholtz free energy F according to Eq. (29), which we copy below:

$$S(T) = -\frac{d}{dT} F(T),$$

where T is the temperature.

HW7: Consider a gas of $N \gg 1$ indistinguishable spins. In lecture we derived Eq. (40) for the Helmholtz free energy F , which we copy below:

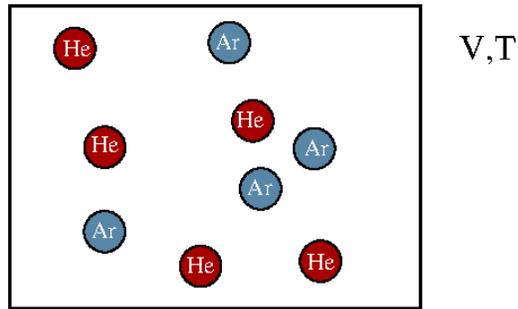
$$F_{\text{indis.}}(T) = -N H - T \ln(1 - e^{-2H(N+1)/T}) + T \ln(1 - e^{-2H/T}) .$$

Calculate the internal energy $\langle E \rangle$ as a function of T . Derive the leading-order behaviour of $\langle E \rangle$ in each of the low-temperature ($T/H \ll 1$) and high-temperature ($T/H \gg 1$) limits. In the low-temperature case, include the leading T -dependent correction to the constant $\lim_{T \rightarrow 0} \langle E \rangle = -NH$.

Hint: Maple (or the like) may help with some of the menial labour.

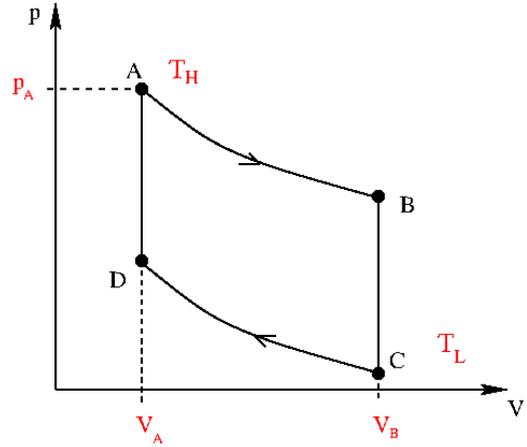
HW8:

A container of volume V contains a mixture of two gases with particle numbers N_1 and N_2 . The particles in each gas are indistinguishable. The container is in thermal equilibrium with a heat-bath of temperature T .



- Calculate the partition function and write down the Helmholtz free energy $F(T)$.
- Calculate the internal energy $\langle E \rangle$ and the entropy S .
- Derive the pressure p and demonstrate Dalton's law. Derive the equation of state in the form $f(p, V, T) = 0$.

HW9: A container with an ideal gas has access to two different heat reservoirs, one ‘hot’ reservoir with temperature T_H and one ‘cold’ with T_L . The container performs a thermodynamic cycle according to the adjacent pV -diagram. The starting point $\{p_A, T_H, V_A\}$ is given, as are V_B and $T_L < T_H$. The processes A to B and C to D take place at constant temperature (isothermal).



- Describe an experimental apparatus that realises the above cycle.
- Calculate whatever variables (p, V, T) are unknown at the points B, C and D .
- Calculate the net work W_{done} delivered by the cycle.
- Calculate the heat Q_{in} that enters the gas. Ignore waste heat expelled during the cycle.
- Calculate the efficiency $\eta = W_{\text{done}}/Q_{\text{in}}$. How does the efficiency of this cycle compare with that of a Carnot cycle operating with the same temperatures T_H and T_L ?

HW10: An ideal gas of indistinguishable particles is immersed in a heat-bath with temperature T and a particle reservoir with chemical potential μ .

- Show that the grand-canonical partition function Z_g is

$$Z_g(T, \mu) = \exp \left[\frac{V}{\lambda^3} e^{\beta \mu} \right],$$

where the so-called thermal de Broglie wavelength is

$$\lambda = \frac{h}{\sqrt{2\pi mT}}.$$

- b. Calculate the internal energy $\langle E \rangle$ and the average particle number $\langle N \rangle$ to show

$$\langle E \rangle = \frac{3}{2} T \langle N \rangle. \quad (101)$$