MATH327: More Is Different

Statistical Mechanics, Thermodynamics, and All That

David Schaich **Spring Term 2026**

LECTURE NOTES

Last modified 13 February 2026

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Module information and logistics

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Overview

"More Is Different" is the title of a famous 1972 essay by Philip Anderson, which established the concept of emergent phenomena — the idea that large, complex physical systems generally can't be understood by extrapolating the properties of small, simple systems. For example, consider the $\sim 10^{22}$ H_2O molecules in a cubic centimetre of water. While we can use Newton's laws (or the laws of quantum mechanics) to analyse a few of these molecules, this does not allow us to predict processes such as phase transitions of this water into steam or ice.

Instead, we have to apply the stochastic (i.e., probabilistic) techniques of *statistical mechanics* — one of the central pillars of modern physics, along with quantum mechanics and relativity. While statistical mechanics was originally developed in the context of thermodynamics in the nineteenth century, it is more generally applicable to any large-scale (macroscopic) behaviour that emerges from the microscopic dynamics of *many* underlying objects. It is intimately connected to quantum field theory, and has been applied to topics from nuclear physics and cosmology to climate science and biophysics, often with outstanding success (recently recognized by the 2021 and 2024 Nobel Prizes in Physics, to name just two).

The module outline on the previous page is organized around the concept of *statistical ensembles* introduced in the early 1900s. In essence, a statistical ensemble is a mathematical framework for concisely describing the properties of idealized physical systems subject to certain constraints. After studying the probability foundations underlying these frameworks, we meet the *micro-canonical ensemble* in unit 2 and the *canonical ensemble* in unit 3. The following two units 4–5 apply the canonical ensemble to investigate non-interacting ("ideal") gases and thermodynamic cycles. Unit 6 introduces a third statistical ensemble, the *grand-canonical ensemble*, which units 7–8 apply to several types of non-interacting quantum gases. (No prior exposure to quantum mechanics is required — see below for more information.) Finally, in unit 9 we begin to explore the effects of interactions, which open up a much broader landscape of applications that we will survey for the remainder of the term.

Schedule

Most weeks we will have the following schedule:

- Lecture at 10:00–10:50 on Tuesdays in Elec. Eng. Lecture Room E5 (205)
- Tutorial at 10:00–10:50 on Wednesdays in Room 106
- Lecture at 11:00–12:50 on Thursdays in Room 106

The tutorials in weeks 2, 3 and 4 (on 4, 11 and 18 February) will be computer lab sessions in Hub 502 PC Teaching Centre B, to provide opportunities for you to work on the computer assignment.

I will use Panopto to record lectures (and lecturey bits of tutorials and computer labs). These recordings will appear along with all other resources on our Canvas site,

canvas.liverpool.ac.uk/courses/84431

While these recordings will allow you to catch up if you must miss a lecture, you will gain the most benefit from attending in person so that you can ask questions and check your understanding.

Office hours will take place at 11:00 on Tuesdays and Wednesdays, following the class meeting. They will be hybrid, taking place in Room 123 of the Theoretical Physics Wing, with the option of joining via Zoom at this link (meeting ID 819 4732 3591, passcode Math327!). If these times do not work with your schedule, you can also make an appointment through calendly.com/daschaich, use the Canvas discussion board (where anonymous posting is enabled), or reach me by email at david.schaich@liverpool.ac.uk. I will aim to respond to emails and discussion board queries within 48 hours.

Assessment and academic integrity

There will be three in-term assignments. Each accounts for 15% of the module mark, with the remaining 55% coming from the final exam. The deadlines listed below have been centrally coordinated within the Department to minimize pile-up across different modules.

15% A computer assignment due **Wednesday, 18 February**

30% Two equally weighted homework assignments, the first due **Friday, 6 March** and the second due **Friday, 24 April**

55% A two-hour in-person final examination to be centrally scheduled within the May exam period

According to the University's new Additional Considerations Policy, late submissions completed within 7 days (168 hours) of the deadline will not be penalized. No submissions will be possible after that late submission window. Some disability support plans may provide an additional 7-day extension to each deadline, so I will aim to release model solutions 14 days after each deadline, with individual feedback returned soon after. I encourage you to meet the deadline if you can, so that your assessments in different modules don't start to pile up.

A second new feature of the Additional Considerations Policy is a "one and final submission" requirement that you can read more about here. The benefit of this new policy is faster feedback, since it allows me to begin marking without having to wait for possible resubmissions throughout the entire late submission window.

You already should have read and understood the Department's current academic integrity guidance as well as the University's Academic Integrity Policy. If you have any questions about what is or is not acceptable, please ask me or our Academic Integrity

Officer Alena Haddley. In all cases, the spirit of the Academic Integrity Policy should take precedence over legalistic convolutions of the text.

In particular, I encourage you to discuss the in-term assignments with each other, since discussing and debating your work is a very effective way to learn. Note that I say *your work* — your submissions for all assignments must be your own work representing your own understanding, and the examination must be done on your own. It is unacceptable to copy solutions in part or in whole from other students (current or prior) or from other sources (commercial or not). Should you make use of resources beyond the module materials — including generative AI tools such as ChatGPT, Copilot or Gemini — these must be explicitly referenced in your submissions. Clear and neat presentations of your workings and the logic behind them will contribute to your mark.

Main resources and materials

The main materials we will use are the lecture notes you are currently reading. As you read further, you will encounter gaps in the notes, which provide bite-sized opportunities for you to check your understanding. Past students have sometimes asked if there is a version of these lecture notes without gaps. There is not: I wrote these notes with the gaps in place by design. We will fill them during lectures, and you will benefit from considering whether you are satisfied with how each gap is filled.

The ten units into which the content is organized won't neatly match up with the twelve weeks of the term. Some units will require more time than others. Regular Canvas announcements will summarize what we cover each week.

We will use 'natural units' in which the Boltzmann constant $k = 1$, and logarithms have base e unless otherwise specified (i.e., $\log x = \ln x$). There is no need to memorize any equations. Many equations are numbered so that they can be referenced later on, not necessarily because they are important. Key results, definitions and concepts are highlighted by coloured boxes, and you should aim to be confident in your understanding of these.

Every year I take the opportunity to improve, extend, and sometimes correct these lecture notes. To ensure you have materials that are as stable as possible, each unit will be released on Canvas once we begin discussing the previous unit. (For example, lecture notes for unit 3 will appear when we begin unit 2.) Any significant corrections after that point will be flagged on the Canvas discussion board, and noted by the "Last modified" date at the bottom of each page.

Expected background

No prior exposure to quantum mechanics or computer programming is required — all necessary information on these topics will be provided. I do anticipate that you have previously seen the standard deviation, the binomial coefficient

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

that counts the number of possible ways to choose k objects out of a set of $N \geq k$ total objects, and gaussian integrals,

$$\int_{-\infty}^{\infty} e^{-a(x+b)^2}\, dx = \sqrt{\frac{\pi}{a}} \qquad\qquad a > 0.$$

Programming

You are welcome to complete the computer assignment using the programming language of your choice. I recommend Python, which is free, user-friendly, and very widely used around the world. During the computer labs we will review this demo that explains all the Python programming tools you'll need. Python is available on University computers and should work on personal computers. You can also write and run Python code using many cloud services, of which I have had the best experiences with Google's Colab and CoCalc.[1] You may need to create a free account, and you should make sure to save a local copy to reduce the risk of losing your work. Alternative languages could include C, Fortran, R, or even MATLAB (through the University's site license). I advise against using Maple, which may struggle to handle parts of the assignment.

How to get the most out of this module

At this point in your studies, this advice should be familiar, but it's worth repeating.

Come to class. This will ensure regular contact with the material, and help you check that you understand it. If the module is moving slower than you'd prefer, coming to class will give you opportunities to ask about more interesting extensions, applications or complications.

Before class, take a quick look at the upcoming pages in the lecture notes, and think about how any gaps could be filled. Look for the big ideas rather than digging in to every detail, and see if you have any questions (or objections) to raise in class. After class, take a closer look at the details, and make sure the gaps have been filled to your satisfaction. Even though the lecture notes reflect my plans for the module, they may not exactly match what happens in class, especially when questions arise. We may gloss over some topics that are explained clearly in the notes, and we may delve deeper into other topics that merit further consideration.

Work on the tutorial exercises and homework problems (including the computer assignment). The best way to learn mathematics is by doing mathematics. These exercises and assignments are designed to make you think and help develop your mathematical muscles. In particular, the tutorial exercises and homework problems will be harder than exam questions, since you'll have much more time to think about them — so take a look through them as soon as you have them, and don't leave them until the last minute. Afterwards, review the model solutions and feedback, to make sure any confusing points are resolved.

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[1] I have had worse experiences with replit.com, onlinegdb.com, mybinder.org and trinket.io — use these at your own risk.

Ask questions. Ask questions you think you're supposed to know the answer to. Ask questions you think everyone else knows the answer to. (They don't.) Ask questions about the big ideas, the specific details, and the connections between them. The opportunity to ask questions is the main benefit of taking a module. You can ask me; you can ask your classmates; you can ask the additional resources below.

Additional resources

The optional additional resources listed below may be helpful. You can use the module Reading List on Canvas to reach our library's records for the books.

Resources at roughly the level of this module:

1. David Tong, *Lectures on Statistical Physics* (2012), www.damtp.cam.ac.uk/user/tong/statphys.html
2. MIT OpenCourseWare for undergraduate Statistical Physics I (2013) and Statistical Physics II (2005), ocw.mit.edu/courses/8-044-statistical-physics-i-spring-2013/ ocw.mit.edu/courses/8-08-statistical-physics-ii-spring-2005/
3. Daniel V. Schroeder, *An Introduction to Thermal Physics* (2021)
4. Harvey Gould and Jan Tobochnik, *Statistical and Thermal Physics with Computer Applications* (2021)
5. J. Allday and S. Hands, *Introduction to Entropy: The Way of the World* (2024)
6. C. Kittel and H. Kroemer, *Thermal Physics* (1980)
7. F. Reif, *Fundamentals of Statistical and Thermal Physics* (1965)

More advanced and more specialized resources, which may be useful to consult concerning specific questions or topics:

8. MIT OpenCourseWare for postgraduate Statistical Mechanics I (2013) and Statistical Mechanics II (2014), ocw.mit.edu/courses/8-333-statistical-mechanics-i-statistical-mechanics-of-particles-fall-2013/ ocw.mit.edu/courses/8-334-statistical-mechanics-ii-statistical-physics-of-fields-spring-2014/
9. R. K. Pathria and P. D. Beale, *Statistical Mechanics* (2021)
10. Sidney Redner, *A Guide to First-Passage Processes* (2001)
11. Pavel L. Krapivsky, Sidney Redner and Eli Ben-Naim, *A Kinetic View of Statistical Physics* (2010)
12. Kerson Huang, *Statistical Mechanics* (1987)
13. Andreas Wipf, *Statistical Approach to Quantum Field Theory* (2013)

14. Weinan E, Tiejun Li and Eric Vanden-Eijnden, *Applied Stochastic Analysis* (2019)
15. Michael Plischke & Birger Bergersen, *Equilibrium Statistical Physics* (2006)
16. Sacha Friedli and Yvan Velenik, *Statistical Mechanics of Lattice Systems* (2018)
17. L. D. Landau and E. M. Lifshitz, *Statistical Physics, Part 1* (1969)

A general book about learning, emphasizing (among other things) the value of retrieval practice compared to re-reading lecture notes or re-watching videos:

18. Peter C. Brown, Henry L. Roediger III and Mark A. McDaniel, *Make it Stick: The Science of Successful Learning* (2014)
    A short summary video is also available

Programming resources:

19. MATH327 Python programming demo (2026)
20. Beginner's Guide to Python (2026)
21. W3Schools Python Tutorial (2026)
22. Software Carpentry tutorials:
    - Programming with Python (2025)
    - Plotting and Programming in Python (2025)
23. Stormy Attaway, *MATLAB: A Practical Introduction to Programming and Problem Solving* (2013)
24. B. Barnes and G. R. Fulford, *Mathematical Modelling with Case Studies: Using Maple and MATLAB* (2014)

In addition, there is a vast constellation of other online resources such as Stack Exchange and Wikipedia. These can be great places to *start* learning about a topic, but are often terrible places to *stop*.

Unit 1: Central limit theorem and diffusion

Introductory remarks: More Is Different

> *What is most exciting about our work is that it illuminates the chain of connections between, on the one hand, the simple underlying laws that govern the behavior of all matter in the universe and, on the other hand, the complex fabric that we see around us, exhibiting diversity, individuality, and evolution. The interplay between simplicity and complexity is the heart of our subject.* —Murray Gell-Mann (1969 Nobel laureate), 1996

Mathematical sciences such as physics aim to determine the laws of nature and understand how these govern experimental observations — both in everyday circumstances and under extreme conditions. This mathematical understanding is typically guided by reproducing a set of observations, with the resulting framework then used to make predictions for other "observables".

Over the past few centuries this process has been tremendously successful, with theoretical physics accurately predicting experimental and observational results from sub-atomic through to cosmological scales. Modern physics labs can create a vacuum better than in outer space and the coldest temperatures in the known universe, as well as going to the other extreme to reach temperatures of millions of degrees and pressures millions of times atmospheric pressure at sea level. Amazingly, many aspects of these realms of physics can be described by mathematics developed centuries ago.[2]

A crucial aspect of this success is the *emergence* of complicated physical phenomena from simple underlying mathematical laws. This module's name borrows from a famous 1972 essay by Philip Anderson (1977 Nobel laureate), "More Is Different", which helped to establish modern perspectives on emergent phenomena. We will focus on one particular domain in which simple mathematical principles enable amazing predictive capabilities: statistical mechanics (sometimes called probabilistic mechanics, statistical physics or statistical thermodynamics). Initially developed in the context of thermodynamics in the nineteenth century, statistical mechanics remains a central pillar of modern physics, and will retain this position in years to come. The foundations of statistical mechanics lie in the use of probability theory to mathematically describe experimental observations and corresponding laws of nature that involve stochastic randomness rather than being perfectly predictable.

The lack of perfect predictability in statistical mechanics is a matter of practicality rather than one of principle. It arises due to working with a large number of degrees of freedom — that is, a large number of independent objects such as atoms. For illustration, Avogadro's number $N_A \approx 6.022 \times 10^{23}$ is the large number of molecules in everyday amounts of familiar substances — about 18 grams of water or about 22 litres of air at sea-level atmospheric pressure. Specifying the positions and velocities of $\sim 10^{23}$ objects would require far more information than could be stored by even the biggest

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[2] A famous 1960 essay by Eugene Wigner (1963 Nobel laureate), "The Unreasonable Effectiveness of Mathematics in the Natural Sciences", and subsequent work in the philosophy of physics, elaborates on why this may be considered 'amazing'. This module will not comment extensively on philosophy.

existing supercomputers. Statistical mechanics instead produces simple mathematical descriptions of large-scale properties such as temperature, pressure and diffusion, which are generally of such outstanding quality that the underlying ‘randomness’ is effectively invisible.

Historically, the difficulty of detecting the stochastic processes underlying such *thermodynamic* properties made it challenging to convince skeptics that atoms and molecules really exist. Ludwig Boltzmann, a prominent early developer of statistical mechanics, endured a constant struggle to defend his ideas, which likely contributed to his deteriorating mental health and eventual suicide in 1906. A significant step to convincingly establish the existence of atoms was Albert Einstein’s use of statistical mechanics to explain the observed “Brownian motion” of particles suspended in fluids — this work was part of Einstein’s “miracle year” in 1905, along with special relativity and early contributions to quantum physics. Jean Perrin soon verified Einstein’s predictions and used them to determine Avogadro’s number; he was awarded the 1926 Nobel Prize in Physics for helping to demonstrate “the discontinuous structure of matter”.

Applications of statistical mechanics continue to advance “our understanding of complex physical systems” — quoting the 2021 Nobel Prize shared between Syukuro Manabe, Klaus Hasselmann and Giorgio Parisi. Even more recently, the 2024 Nobel Prize was awarded to John Hopfield and Geoffrey Hinton for “using ideas from statistical physics” to lay the foundations for machine learning and artificial neural networks. Other modern topics we will encounter in this module include explaining why stars don’t collapse under the ‘weight’ of their own gravity, and identifying effects of dark matter in temperature fluctuations observable in the cosmic microwave background lingering from the early years of the universe.

In this unit we focus on some of the foundational mathematics that will underlie our later development and application of statistical mechanics. Looking back to Boltzmann’s times, we can consider the following question some of his critics might have asked: *If the pressure of a gas in a container results from molecules stochastically colliding with the walls of that container, then how can the pressure be so stable, rather than itself fluctuating stochastically?* The mathematical answer lies in the **law of large numbers** and the **central limit theorem**, which we will review and apply to the physics of diffusion in one dimension.

1.1 Probability foundations

We begin by building a more formal mathematical framework around the concept of probability, through a sequence of definitions. First, a random **experiment** $\mathcal{E}$ involves setting up, manipulating and/or observing some (physical or hypothetical) system that involves some element of randomness. Flipping a coin is a simple random experiment. For the statistical ensembles we will focus on in later units, a typical experiment will be to allow a collection of particles to evolve in time, subject to certain constraints.

Each time an experiment is performed, the world is observed to be in some **state** ω. The specification of the experiment and the state must include all objects of interest, and may include more besides. When flipping a coin, for example, the full state could contain information not only about the final orientation of the coin, but also about its position — where exactly did it land?

The **set of all states** Ω collects all possible states ω that the given experiment $\mathcal{E}$ can produce, and is therefore intricately tied to $\mathcal{E}$ itself.

We are generally not interested in all aspects of the full state ω. For example, we won't care where a flipped coin lands. Instead we're typically only interested in whether it lands heads up or tails up — and we may want to set aside any state that doesn't cleanly reflect those options. The **measurement** $X(\omega)$ extracts and quantifies this information, acting as a function that maps the state ω to a number that we can mathematically manipulate. If we repeat the given experiment $\mathcal{E}$ many times and carry out the measurement X on each resulting state ω_i, we will obtain a sequence of numbers $X(\omega_i)$ that behave as a *random variable*.

Acting with the measurement X on all of the possible states in the set Ω defines the **set of all outcomes** (or **outcome space**) A:

$$X : \Omega \to A.$$

That is, A collects all possible measurement results that the given experiment $\mathcal{E}$ and measurement X can produce. A can be finite, countably infinite, or uncountably infinite (i.e., continuous).

Let's consider some examples to clarify these definitions. With an experiment of rolling a six-sided die and measuring the number (1–6) that comes out on top, what is the set of all outcomes A? What additional information could be included in a corresponding state ω?

What is the outcome space A if we toss a coin four times and measure whether it lands heads up (H) or tails up (T) each time?

What information could characterize a state ω for a gas of 10^{23} argon atoms in a container? What might be interesting to measure?

For convenience, we can introduce a unique number as a *label* to characterize each state ω in the set Ω. Generalizing the concept of measurement, this provides a label function $L(\omega)$ that also behaves as a random variable. Our condition of uniqueness makes $L(\omega)$ isomorphic, so that the label can be used interchangeably with the full state, $\omega \longleftrightarrow L(\omega)$.

While the measurements $X(\omega)$ we consider generally will not produce a unique number for each ω, we will design them precisely to remove irrelevant information that doesn't interest us. Ignoring that irrelevant information leaves us free to interchange the set of outcomes A for the set of states Ω. (Some textbooks may never distinguish between A vs Ω in the first place, though this can be a source of confusion.)

Only a couple of definitions remain. The next is to define an **event** to be any subset of the set of all outcomes A. For example, events resulting from rolling a die could include (i) rolling a 6, (ii) rolling anything but a 6, (iii) rolling any even number, and many more. Collecting all events of interest defines the **set of events** (or **event space**) $\mathcal{F}$.

We are now prepared for the final foundational definition in this section — the **probability** P of an event in the set $\mathcal{F}$. Mathematically, P is a *measure function*,

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

which must satisfy the following two requirements:

1. The probability of a countable union of mutually exclusive events must equal the sum of the probabilities of each of these events.
2. The probability of the outcome space ($\mathcal{F} = A$) must equal 1, even if A is uncountable. This simply means that the experiment $\mathcal{E}$ must produce a measurable outcome. We discard any experiment that doesn't produce such an outcome.

Combining the outcome space, event space and probability measure gives us a *probability space* $(A, \mathcal{F}, P)$.

For example, consider an experiment that can only produce N possible states, so that

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

As described above, the subscript is a label, and it is possible for two different states $\omega_i \neq \omega_j$ to produce the same measurement outcome $X(\omega_i) = X(\omega_j)$. This means that the size n of the outcome space A may be smaller than the size of Ω, $n \leq N$. We can write

$$A = \{X_1, X_2, \cdots, X_n\},$$

where each X_α is distinct and its label does not necessarily match the one on ω_i. We can take the individual X_α themselves to be the events we're interested in, choosing the event space

$$\mathcal{F} = \{X_1, X_2, \cdots, X_n\} = A. \tag{1}$$

These events are all mutually exclusive, so if we assign them probabilities

$$P(X_\alpha) \equiv p_\alpha \qquad \text{for } \alpha = 1, \cdots, n,$$

then the above requirements on probabilities demand that for any $\alpha \neq \beta$ we have

$$P(X_\alpha \text{ or } X_\beta) = p_\alpha + p_\beta$$

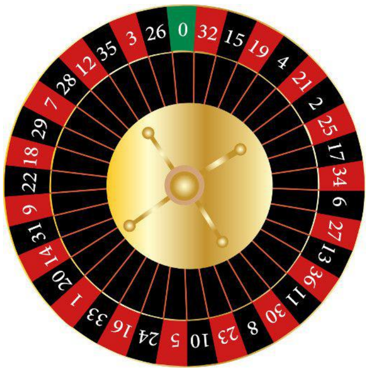
$$P(A) = P(X_1 \text{ or } X_2 \text{ or } \cdots \text{ or } X_n) = \sum_{\alpha=1}^{n} p_\alpha = 1.$$

Similarly choosing $\mathcal{F} = A$ for the six-sided die considered in an earlier gap, what are the probabilities p_1 through p_6 that result from assuming the die is fair?

Again taking $\mathcal{F} = A$ for the case of tossing a coin four times, what are the probabilities p_α that result from assuming the coin is fair? If we instead consider the event space

$$\mathcal{F} = \{\text{equal number of } H \text{ and } T,\ \text{different numbers of } H \text{ and } T\},$$

what are the probabilities p_{equal} and p_{diff} for the two events in this $\mathcal{F}$?



The standard European roulette wheel shown to the left (source) has 37 pockets labelled “0” through “36”. 18 of these pockets are coloured red, 18 are coloured black and 1 (pocket “0”) is coloured green. Let an experiment be a spin of the roulette wheel, measuring the label of the pocket where the ball comes to rest (which also provides the pocket’s colour).

What is the outcome space A for a spin of the roulette wheel? With $\mathcal{F} = A$, what are the probabilities p_α for a fair wheel? With

$$\mathcal{F} = \{\text{ball in a red pocket, ball in a black pocket, ball in the green pocket}\},$$

what are the corresponding probabilities p_{red}, p_{black} and p_{green}?

The process of assigning probabilities to events is called *modelling*. The gaps above demonstrate that *symmetries* are a powerful way to constrain probabilities. The symmetry between the six sides of a fair die, the two sides of a fair coin, and the 37 pockets of a fair roulette wheel each sufficed to completely determine the corresponding probabilities p_α.

Modelling can also be guided by empirical data obtained by repeating an experiment many times. For example, if we don’t know whether a set of dice are fair, we will be able to infer their probabilities p_α (with a certain confidence level) by rolling them enough times. The need to repeat the experiment many times comes from the law of large numbers, to which we now turn.

1.2 Law of large numbers

Let’s return to the setup leading to Eq. 1 above, with

$$\mathcal{F} = A = \{X_1, X_2, \cdots, X_n\}$$

for finite n, and probabilities $p_\alpha = P(X_\alpha)$ that obey

$$p_\alpha \in [0, 1] \qquad\qquad \sum_{\alpha=1}^{n} p_\alpha = 1.$$

We can generalize this notation by writing instead

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

and introducing similar expressions for the **mean** μ and **variance** σ^2 of the probability space,

$$\mu = \langle X \rangle = \sum_{X \in A} X\, P(X) \tag{2}$$

$$\sigma^2 = \left\langle (X - \mu)^2 \right\rangle = \sum_{X \in A} (X - \mu)^2\, P(X). \tag{3}$$

The angle bracket notation indicates the **expected** (or **expectation**) **value** with general definition

$$\langle f(X) \rangle = \sum_{X \in A} f(X)\, P(X), \tag{4}$$

which is a linear operation,

$$\langle c \cdot f(X) + g(X) \rangle = c \langle f(X) \rangle + \langle g(X) \rangle \, .$$

The square root of the variance, $\sqrt{\sigma^2} = \sigma$, is the **standard deviation**. What is σ expressed in terms of $\langle X^2 \rangle$ and $\langle X \rangle^2$?

We now define a new experiment that consists of *repeating* the original experiment R times, with each repetition independent of all the others. Using the same measurement as before for each repetition, we obtain a new outcome space that we can call B. For $R = 4$, what are some representative outcomes in the set B? What is the total size of B?

Each outcome in B contains R different $X^{(r)} \in A$, one for each repetition $r = 1, \cdots, R$, and each with mean $\langle X^{(r)} \rangle = \mu$ and variance $\langle (X^{(r)} - \mu)^2 \rangle = \sigma^2$. Considering the case $R = 4$ for simplicity, any element of B can be written as $X_i^{(1)} X_j^{(2)} X_k^{(3)} X_l^{(4)} \in B$ with corresponding probability

$$P_B\left(X_i^{(1)} X_j^{(2)} X_k^{(3)} X_l^{(4)}\right) = P_A\left(X_i^{(1)}\right) P_A\left(X_j^{(2)}\right) P_A\left(X_k^{(3)}\right) P_A\left(X_l^{(4)}\right),$$

using subscripts to distinguish between the probability spaces for the single experiment (A) and repeated experiment (B).

Averaging over all R repetitions defines the *arithmetic mean*

$$\overline{X}_R = \frac{1}{R} \sum_{r=1}^{R} X^{(r)}. \tag{5}$$

Unlike the true mean μ, the arithmetic mean $\overline{X}_R$ is a random variable — a number that may be different for each element of B. That said, $\overline{X}_R$ and μ are certainly related, and so long as the standard deviation exists — that is, so long as σ^2 is finite — this relation can be proved rigorously in the limit $R \to \infty$.[3]

Here we will not be fully rigorous, and take it as given that

$$\left\langle \left(X^{(i)} - \mu\right) \left(X^{(j)} - \mu\right) \right\rangle = \sigma^2 \delta_{ij} = \left\{ \begin{array}{ll} \sigma^2 & \text{for } i = j \\ 0 & \text{for } i \neq j \end{array} \right. ,$$

where the *Kronecker delta* $\delta_{ij} = 1$ for $i = j$ and vanishes for $i \neq j$. This is a consequence of our requirement that each repetition is independent of all the others. Using this result and the relation $\left(\sum_i a_i\right)\left(\sum_j b_j\right) = \sum_{i,j} (a_i b_j)$, express the following quantity in terms of σ and R:

$$\left\langle \left(\frac{1}{R} \sum_{r=1}^{R} X^{(r)} - \mu \right)^2 \right\rangle =$$

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[3] In the computer project we will numerically investigate a situation where σ^2 diverges.

You should find that your result vanishes in the limit $R \to \infty$, so long as σ^2 is finite. Since the square makes this expectation value a sum of non-negative terms, it can vanish only if every one of those terms is individually zero.

This establishes the **law of large numbers**:

$$\lim_{R\to\infty} \frac{1}{R} \sum_{r=1}^{R} X^{(r)} = \mu, \tag{6}$$

where we have assumed finite $\left\langle X^{(r)} \right\rangle = \mu$ and $\left\langle (X^{(r)} - \mu)^2 \right\rangle = \sigma^2$.

1.3 Probability distributions

It is not necessary to make the assumption (Eq. 1) that our outcome space contains only a countable number of possible outcomes. The considerations above continue to hold even if the random variable X is a continuous real number. In this case, however, the identification of probabilities with outcomes is slightly more complicated, which will be relevant when we consider the central limit theorem in the next section.

When the outcome can be any number on the real line, the fundamental object is a **probability distribution** (or **density function**) $p(x)$ defined for all $x \in \mathbb{R}$. Starting from this density, a probability is determined by integrating over a given interval. Calling this interval $[a, b]$, the integration produces the probability that the outcome X lies within the interval,

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

We similarly generalize the definition of an expectation value (Eq. 4) to an integral over the entire domain of the probability distribution,

$$\langle f(x) \rangle = \int f(x)\; p(x)\, dx\, .$$

In this module we will only consider definite integrals, and we may not explicitly write the limits of integrals over the entire domain. That is, for $x \in \mathbb{R}$ we have $\int dx = \int_{-\infty}^{\infty} dx$, with $\int p(x)\, dx = 1$. An important set of expectation values is

$$\left\langle x^{\ell} \right\rangle = \int x^{\ell}\; p(x)\, dx, \tag{7}$$

which provides the mean and variance of the probability distribution $p(x)$, through generalizations of Eqs. 2–3:

$$\mu = \langle x \rangle = \int x\; p(x)\, dx \qquad\qquad \sigma^2 = \left\langle x^2 \right\rangle - \langle x \rangle^2\, . \tag{8}$$

The expression for the variance should be familiar from your determination of the standard deviation in an earlier gap. Unless stated otherwise, we will assume the mean and variance are both finite for the probability distributions we consider.

1.4 Central limit theorem

The central limit theorem is a central result of probability theory (hence its name). Over the years it has been expressed in several equivalent ways, and there are also many distinct variants of the theorem accommodating different conditions and assumptions. Here we are interested in applying rather than proving the central limit theorem; you can find proofs in many textbooks.

The version of the theorem we use in this module assumes we have N independent random variables $x_1, \cdots, x_N$, each of which has the same (finite) mean μ and variance σ^2. Such random variables are said to be *identically distributed*, and a common way to obtain them is to repeat an experiment N times, as we considered in Section 1.2. Just as in Eq. 5, the sum

$$s = \sum_{i=1}^{N} x_i \tag{9}$$

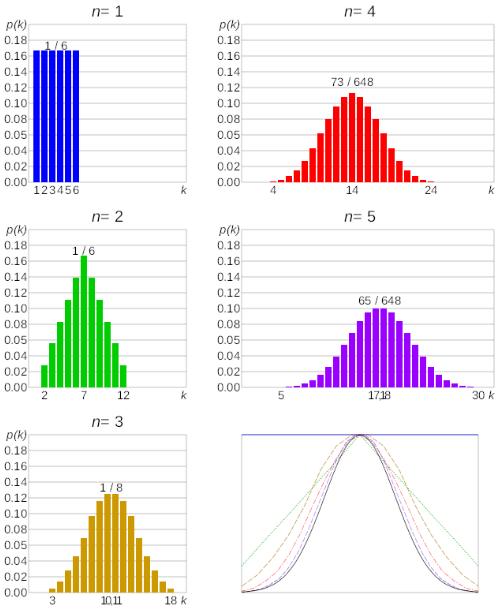
is itself a random variable.

The **central limit theorem** states that for large $N \gg 1$ the probability distribution for s is

$$p(s) \approx \frac{1}{\sqrt{2\pi N\sigma^2}} \exp\left[-\frac{(s-N\mu)^2}{2N\sigma^2}\right], \tag{10}$$

with the approximation becoming exact in the $N \to \infty$ limit.

In addition to asserting that the collective behaviour of many independent and identically distributed random variables x_i is governed by a **normal** (or **gaussian**) **distribution**, the central limit theorem further specifies the precise form of this distribution in terms of the mean and variance of *each individual* x_i.



commons.wikimedia.org/wiki/File:Dice_sum_central_limit_theorem.svg

In practice, N often doesn't need to be very large in order for the central limit theorem to provide a reasonable approximation. This is illustrated by the figure to the left, from Wikimedia Commons, which shows the probabilities for the sum of $n \leq 5$ rolls of a six-sided die rapidly approaching a gaussian distribution.

1.5 Diffusion and the central limit theorem

1.5.1 Random walk on a line

As a more powerful application and illustration of the central limit theorem, let's consider the behaviour of a randomly moving object. Such **random walks** appear frequently in mathematical modelling of stochastic phenomena (including Brownian motion), and can be applied to movement through either physical space or more abstract vector spaces. They are examples of Markov processes, in which the state of the system (in this case the position of the 'walker') at any time probabilistically depends only on the system's prior state at the previous point in time — there is no 'memory' of any earlier states. The resulting sequence of system states is known as a *Markov chain*, since each state is produced from the one before, like links in a chain.

Let's consider the simple example of a random walker that moves only in a single spatial dimension — to the left or to the right on a line — and can only take 'steps' of a fixed length, which we can set to $\ell = 1$ without loss of generality. At each point in time, the walker takes either a step to the right (R) with probability p or a step to the left (L) with probability $q = 1 - p$. We will further assume that each step takes a constant amount of time δt, so a walk of N steps will last for total time

$$t = N\delta t. \tag{11}$$

As an example, for $N = 6$ a representative walk can be written as $LRLRRR$, which leaves the walker $x = 2$ steps to the right of its starting point ($x = 0$). The opposite walk $RLRLLL$ would leave the walker at $x = -2$, with negative numbers indicating positions to the left of the starting point. How many possible walks are there for $N = 6$, and what is the probability (in terms of p and q) for the walks $LRLRRR$ and $RLRLLL$ to occur? How many possible walks are there for general N, and what is the probability for any particular walk involving r steps to the right to occur?

We are interested in the walker's final position x at time t after it has taken N steps. Just as for the sum of n rolls of a die considered in Section 1.4, there are a range of possible final positions x, each of which has some probability $P(x)$ of being realized. The key pieces of information we want to determine are the expectation value $\langle x \rangle$ and the standard deviation $\Delta x \equiv \sqrt{\langle x^2 \rangle - \langle x \rangle^2}$ that indicates the scale of fluctuations we can expect around $\langle x \rangle$ as the N-step walk is repeated many times from the same starting point. (We reserve the variables μ and σ^2 for the mean and variance *of the single-step process*, which will play an important role when we apply the central limit theorem in Section 1.5.3.)

Suppose the N total steps involve r steps to the right. What is the final position x of the walker in terms of N and r? Check your general answer for the cases $N = 6$ and $r = 4, 2$ considered above.

This relation makes it equivalent to consider either the probability P_r of taking r steps to the right, or the probability $P(x)$ of ending up at final position x. This equivalence **will not hold** for more general random walks in which the step length is no longer fixed and ℓ_i can vary from one step to the next.

Because the order in which steps are taken does not affect the final position x, to determine the probability $P(x)$ we have to count all possible ways of walking to x. For $N = 6$, what are all the possible walks that produce $x = 4$, and what is the corresponding probability $P(4)$?

Your answer should have a factor of 6 that corresponds to the binomial coefficient $\binom{N}{r} = \binom{6}{5} = 6$. In terms of this binomial coefficient, what is the general probability P_r that an N-step walk will include r steps to the right in any order?

Given this probability P_r, we can apply Eqs. 2–3 to find the expectation value $\langle x \rangle$ and the standard deviation Δx. As a first step, what are $\langle x \rangle$ and $\langle x^2 \rangle$ in terms of the expectation values $\langle r^n \rangle = \sum_{r=0}^{N} r^n \, P_r$?

$\langle x \rangle =$

$\langle x^2 \rangle =$

Now we need to calculate the necessary $\langle r^n \rangle$. A powerful way to do this is to define the **generating function**

$$G(\theta) = \sum_{r=0}^{N} e^{r\theta} \, P_r. \tag{12}$$

This approach introduces a parameter θ that we subsequently remove by setting $\theta = 0$. For example, $G(0) = \sum_{r=0}^{N} P_r = 1$. What do you obtain upon taking derivatives of the generating function and then setting $\theta = 0$?

$\left.\frac{d}{d\theta} G(\theta)\right|_{\theta=0} =$

$\left.\frac{d^n}{d\theta^n} G(\theta)\right|_{\theta=0} =$

For the current case of a fixed-step-length random walk in one dimension, the probabilities P_r produce a simple closed-form expression for the generating functional:

$$G(\theta) = \sum_{r=0}^{N} e^{r\theta} \, P_r = \sum_{r=0}^{N} e^{r\theta} \binom{N}{r} p^r q^{N-r} = \left(e^{\theta} p + q\right)^N, \tag{13}$$

making use of the binomial formula $(a+b)^N = \sum_{i=0}^{N} \binom{N}{i} a^i b^{N-i}$.

It's straightforward to take the necessary derivatives of Eq. 13, which simplify pleasantly since $\left(e^\theta p + q\right)\Big|_{\theta=0} = p + q = 1$:

$$\frac{d}{d\theta}\left(e^\theta p + q\right)^N\Bigg|_{\theta=0} =$$

$$\frac{d^2}{d\theta^2}\left(e^\theta p + q\right)^N\Bigg|_{\theta=0} =$$

Insert the resulting $\langle r \rangle$ and $\langle r^2 \rangle$ into the relations derived above:

$$\langle x \rangle =$$

$$(\Delta x)^2 = \langle x^2 \rangle - \langle x \rangle^2 =$$

In the end, you should obtain

$$\langle x \rangle = N(2p-1) \qquad\qquad \Delta x = 2\sqrt{Npq}. \tag{14}$$

We can check that this $\langle x \rangle$ produces the expected results in the special cases $p = 0$, $1/2$ and 1, while the standard deviation Δx also behaves appropriately by vanishing for both $p = 0$ and 1.

1.5.2 Law of diffusion

It's possible to interpret the results in Eq. 14 in a more intuitive way by expressing them in terms of the total time t taken by the random walk (Eq. 11). Inserting $N = t/\delta t$ into Eq. 14,

$$\langle x \rangle = \frac{t}{\delta t}(2p-1) = \frac{2p-1}{\delta t}t \equiv v_{\text{dr}}t,$$

we see that the *expected* final position of the walker depends linearly on time, with **drift velocity**

$$v_{\text{dr}} = \frac{2p-1}{\delta t} = \frac{N(2p-1)}{t} = \frac{\langle x \rangle}{t}. \tag{15}$$

The sign of v_{dr} indicates whether the walker is drifting to the right ($p > \frac{1}{2}$) or to the left ($p < \frac{1}{2}$). The typical scale of fluctuations (or the 'uncertainty') around the expected final position $\langle x \rangle$ is given by the standard deviation Δx, and also depends on time:

$$\Delta x = \sqrt{\langle x^2 \rangle - \langle x \rangle^2} = 2\sqrt{Npq} = 2\sqrt{\frac{pq}{\delta t}}\sqrt{t},$$

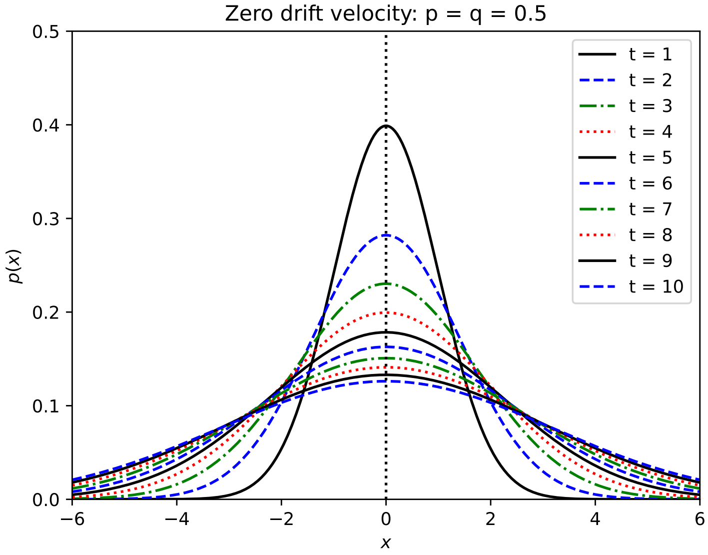
where the constant factor is non-negative. This $\sqrt{t}$ dependence is a very general result.

The **law of diffusion** states that

$$\Delta x = D\sqrt{t}, \tag{16}$$

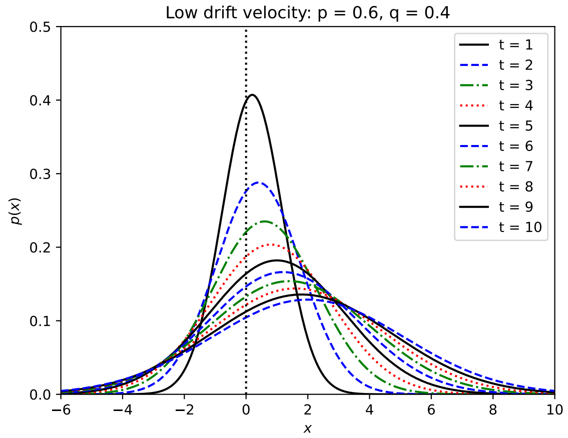
where $D > 0$ is the **diffusion constant**. The standard deviation Δx is sometimes also called the *diffusion length*.

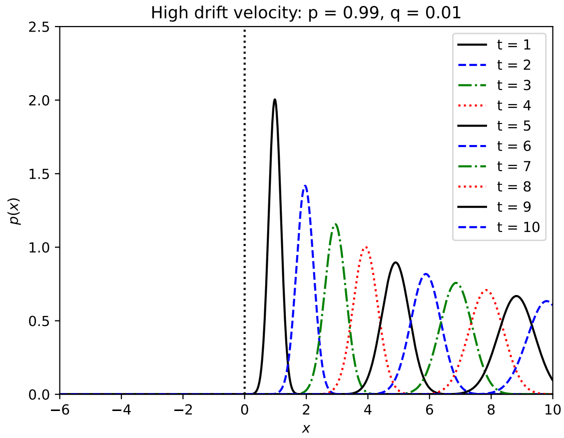
The result $D = 2\sqrt{\frac{pq}{\delta t}}$ that we computed above is specific to the simple example of a fixed-step-length random walk in one dimension and **will not hold** for more general random walks. The behaviour it describes is illustrated by the figure below, which plots the t-dependent probability distribution $p(x)$ that we'll soon derive using the central limit theorem (Eq. 17). What we can see already, even before completing that derivation, is that the probability distribution steadily spreads out — or *diffuses* — as time passes:



Here we are considering the special case $p = q = \frac{1}{2}$, for which the drift velocity $v_{\mathrm{dr}} = 0$ and the expectation value is always $\langle x \rangle = 0$ for any walk time t. However, as time goes on, there is a steady decrease in the probability that the walker will end up around its starting point $x \approx 0$. (As described in Section 1.3, we can determine this probability by integrating the distribution $p(x)$ over an appropriate interval.) Instead, the interval $-D\sqrt{t} \leq x \leq D\sqrt{t}$ within which we can expect to find the walker (with a constant 'one-sigma' or ~68% probability) steadily grows with characteristic dependence on the square root of the time the diffusive process lasts.

Except in the trivial cases $p = 0$ or $q = 0$, diffusion also occurs when the drift velocity is non-zero. This is shown in the two figures below, considering a low but non-zero drift velocity $v_{\text{dr}} = 0.2$ on the left, and a high $v_{\text{dr}} = 0.98$ on the right. All three figures were produced by this Python script.





In the figure on the left, the large diffusion constant $D \approx 0.980$ produces a plot that looks similar to the $v_{\text{dr}} = 0$ case on the previous page, but now the central peaks (and expectation values $\langle x \rangle$) for each t drift steadily to the right. The lower $D \approx 0.199$ for the figure on the right leads to less overlap among the distributions, but they still diffuse to exhibit lower and broader peaks as time passes.

When $p \neq \frac{1}{2}$ so that $\langle x \rangle \neq 0$, it is interesting to compare the drift in the expectation value against the growth in fluctuations around $\langle x \rangle$ due to diffusion. We can do this by considering the following *relative* uncertainty:

$$\frac{\Delta x}{\langle x \rangle} =$$

You should find that at large times this ratio vanishes proportionally to $1/\sqrt{t} \propto 1/\sqrt{N}$. Although the absolute uncertainty $\Delta x = D\sqrt{t}$ grows by diffusion, for $v_{\text{dr}} \neq 0$ the linear drift in the expectation value becomes increasingly dominant as time goes on.

1.5.3 Applying the central limit theorem

Based on our work in Section 1.4, we can see how to apply the central limit theorem to analyse this fixed-step-length random walk in one dimension, for large numbers of steps N or equivalently large times $t = N\delta t$. Each step in the random walk is an independent and identically distributed random variable x_i. The corresponding probability space involves only two possible outcomes: a step of length $\ell = 1$ to the right or to the left with probability p or q, respectively. From this we can easily compute the mean and variance *of the single-step process*:

$\mu = \langle x_i \rangle =$

$\langle x_i^2 \rangle =$

$\sigma^2 = \langle x_i^2 \rangle - \langle x_i \rangle^2 =$

The final position x of the walker after N steps is exactly the sum over these x_i given in Eq. 9. Its probability distribution $p(x)$ from the central limit theorem is therefore obtained directly from these single-step μ and σ^2, which we can also express in terms of the drift velocity and diffusion constant:

$$\begin{aligned} p(x) &= \frac{1}{\sqrt{2\pi(4Npq)}} \exp\left[-\frac{(x - N(2p-1))^2}{8Npq}\right] \\ &= \frac{1}{\sqrt{2\pi D^2 t}} \exp\left[-\frac{(x - v_{\text{dr}} t)^2}{2D^2 t}\right]. \end{aligned} \tag{17}$$

This expression was used to produce the three figures above. We could have jumped straight to the final line by considering Eq. 10 and noting

$$v_{\text{dr}} t = N(2p-1) = N\mu \qquad\qquad D^2 t = 4pq\frac{t}{\delta t} = N\sigma^2. \tag{18}$$

While this dependence on p and q is specific to the particular fixed-step-length random walk we're currently considering, the generic results $v_{\text{dr}} t = N\mu$ and $D^2 t = N\sigma^2$ in Eq. 18 **do hold** for any random walk with finite μ and σ^2 (so that the central limit theorem can be applied). This is remarkable, because it means that the diffusive process as a whole is determined entirely by the single-step mean and variance. So long as μ and σ^2 are finite, we end up with Eq. 17 as the large-t probability distribution for any markovian random walk in a single variable x.

This result is related to the generality of the law of diffusion (Eq. 16), which we can recognize in the structure of Eq. 17. Since $t > 0$, the exponential in the gaussian distribution $p(x)$ peaks at the drifting expectation value $x = v_{\text{dr}} t = \langle x \rangle$. The factor

$(x - v_{\mathrm{dr}}t)^2$ simply quantifies the distance from this peak. As t increases, so does the factor $2D^2t$ dividing this $(x - v_{\mathrm{dr}}t)^2$, meaning that a larger distance from the peak is needed for the overall argument of the exponential to reach a given value — in other words, the peak becomes broader. This in turn requires a lower peak, reflected in the $\frac{1}{\sqrt{t}}$ in the overall coefficient, which is set by requiring $\int p(x)\, dx = 1$. In other words, the law of diffusion holds whenever the central limit theorem is applicable. This requires that the mean and variance of the single-step process are finite, and in the computer project we will numerically investigate the *anomalous diffusion* that occurs when this condition is not satisfied.

Unit 2: Micro-canonical ensemble

2.1 Statistical ensembles and thermodynamic equilibrium

We begin this unit by establishing the concept of *statistical ensembles*, which was formalized by J. Willard Gibbs in 1902. (Gibbs also introduced the term 'statistical mechanics', in 1884.) Building on the probability foundations laid above, we will be interested in 'experiments' that simply allow a collection of degrees of freedom to evolve in time, subject to certain constraints. At a given time t_1, the arrangement of these degrees of freedom defines the state ω_1 of the system.

As a concrete example, consider a system of *spins* — arrows that can point either 'up' or 'down' — arranged in a line. Such spin systems will appear several times in the remainder of this module, since in addition to obeying simple mathematics analogous to flipping coins, spins also serve as good models of physical systems such as magnetic molecules. What would be a representative state (or *configuration*) for a system of $N = 8$ spins? How many distinct states are there for this system?

At a different time t_2, the system's state ω_2 is generally different from ω_1. However, there are some measurements we can perform that always produce the same outcome even as the system's state changes over time. These measurements define *conserved quantities*, such as the number of spins considered in the example above.

Another important conserved quantity is the *internal* energy E of an isolated (or 'closed') system,

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

The conservation of energy is presumably a familiar concept, and you may also know that it can be rigorously proven through Emmy Noether's first theorem.[4] Because conservation of energy was empirically observed long before Noether's theorem was proven, it also has a more grandiose name: the **first law of thermodynamics**. Another way of stating the first law is that any change in the internal energy of one particular system Ω must be matched by an equal and opposite change in the energy of some other system with which Ω is in contact. This will be important when we consider thermodynamic cycles later in the term.

For now, let's return to the example above, and endow the spin system with an internal energy by placing it in a 'magnetic field' of strength H. That is, if a spin is

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[4] There are complications when considering the dynamical space-time of general relativity, but that's beyond the scope of this module.

parallel to the field, it contributes energy $-H$ to the total energy E of the system. If a spin is anti-parallel to the field, it instead contributes energy H. For later convenience, we define a positive magnetic field $H > 0$ to point upward, and also define n_+ to be the number of spins pointing upward — parallel to the field and therefore contributing *negative* energy. Similarly, the remaining $n_- = N - n_+$ downward-pointing spins are anti-parallel to the field and contribute positive energy. What is the total energy E of the system in terms of n_+ and n_-? What is E for the representative 8-spin state you wrote down above? What fraction of the states of the spin system have this energy?

If instead we consider $N \sim 10^{23}$ hydrogen (H_2) molecules in a container, we can write a simple expression for the internal energy E by treating each molecule as a *point-like particle*, with no size or structure. In this case each molecule contributes only its kinetic energy, and

$$E = \frac{m}{2}\sum_{n=1}^{N} \vec{v}_n^{\,2} = \frac{1}{2m}\sum_{n=1}^{N} \vec{p}_n^{\,2},$$

where $\vec{v}_n$ is the velocity of the nth molecule, $\vec{p}_n = m\vec{v}_n$ is its momentum, and all molecules have the same mass m.

As forecast at the start of the module, we treat the time evolution of any given system as a stochastic process in which the system probabilistically adopts a sequence of states $\omega_i \in \Omega$:

$$\omega_1 \longrightarrow \omega_2 \longrightarrow \omega_3 \longrightarrow \omega_4 \longrightarrow \cdots$$

This approach is a matter of practicality rather than one of principle. In principle, Newton's laws would allow us to predict the exact time evolution of (say) 10^{23} hydrogen molecules, but only by specifying 10^{23} initial conditions and solving 10^{23} differential equations. Since we cannot hope to record so much information or carry out so many computations, we instead apply probability theory in order to analyse these systems.

This leads us to the following core definition: A **statistical ensemble** is the set of all states $\Omega = \{\omega_1, \omega_2, \cdots\}$ that a system can possibly adopt through its time evolution. Each state ω_i has some probability p_i of being adopted by the system, so we can recognize a statistical ensemble as a probability space.

Because these states ω_i depend on the 'microscopic' degrees of freedom that compose the overall system, we will refer to them as **micro-states** from now on. From the definition of probability in Section 1.1, we have the requirement $\sum_i p_i = 1$, which simply means that the system must be in *some* micro-state at any point in time. The fact that time evolution cannot change any conserved quantities, as discussed above, means that such conserved quantities characterize statistical ensembles. Throughout the next seven units we will consider different statistical ensembles with different sets of conserved quantities.

First we define the **micro-canonical ensemble** to be a statistical ensemble characterized by conserved internal energy E and conserved number of degrees of freedom N — which we will call **particle number** for short.

According to the discussion above, this means that a system governed by the micro-canonical ensemble is *isolated* in the sense that it cannot exchange energy or particles with any other system.

Now that the micro-canonical ensemble is defined, we can connect it to our intuition from everyday physical systems. Let's consider a collection of particles moving around and bouncing (or '*scattering*') off each other in a sealed container. To a first approximation, this should describe the behaviour of air in a room, which our lived experience indicates is spread quite uniformly throughout the room in a way that is stable as time passes. We do not expect all the air in a room to be concentrated in any one corner, nor do we expect strong collective gusts of wind without some clear external influence.

These qualitative expectations illustrate the idea of **thermodynamic equilibrium**, an axiomatic concept in statistical mechanics.[5] We can mathematically define thermodynamic equilibrium through the probabilities p_i that appear in the micro-canonical ensemble.

A micro-canonical system Ω with M micro-states ω_i is in thermodynamic equilibrium if and only if all probabilities p_i are equal. If M is finite, the requirement $\sum_i p_i = 1$ implies

$$p_i = \frac{1}{M}. \tag{19}$$

The full meaning and significance of this definition are not immediately obvious, and we will continue exploring them through consideration of derived quantities such as entropy and temperature. First, it's important to emphasize that this equilibrium is *dynamic*: There is not a single 'equilibrium micro-state' that the system sits in. Instead, the equilibrium system continues probabilistically adopting all possible micro-states as it evolves in time.

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[5] Our expectation that physical systems generically evolve towards thermodynamic equilibrium as time passes is more formally expressed as the ergodic hypothesis.

2.2 Entropy and its properties

2.2.1 Definition of entropy

We can gain further insight into thermodynamic equilibrium by considering a famous derived quantity.

The **entropy** of a statistical ensemble Ω with a countable number of micro-states M is defined to be

$$S = -\sum_{i=1}^{M} p_i \log p_i, \tag{20}$$

where p_i is the probability for micro-state ω_i to occur. Unless otherwise specified, "$\log$" indicates the natural logarithm with base e.

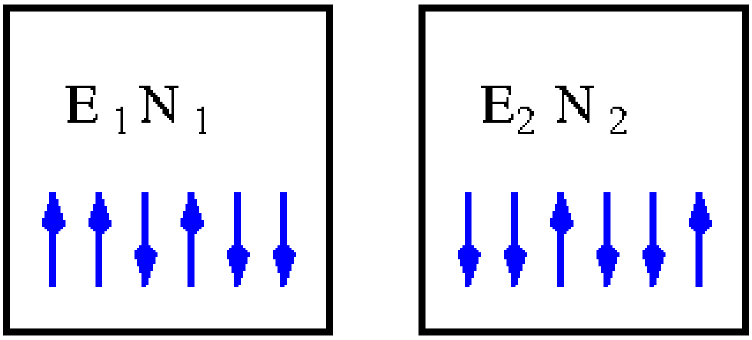
When the system under consideration is in thermodynamic equilibrium, we expect derived quantities such as the entropy to be stable over time, even as different micro-states are probabilistically adopted. This implies that such derived quantities are functions of the conserved quantities that are the same for all micro-states. Therefore, for the micro-canonical ensemble, the equilibrium entropy $S(E, N)$ is a function of the conserved energy and particle number.

By inserting Eq. 19 into Eq. 20 you can quickly compute a simple expression for the entropy of a micro-canonical ensemble in thermodynamic equilibrium:

Your result should depend only on the number of micro-states M, diverging as $M \to \infty$. While the energy E and particle number N are not explicit in this expression, $\{E, N, M\}$ are inter-related and can be expressed in terms of each other given the details of any specific situation under consideration. For example, what is the equilibrium entropy of the system of N spins considered above, if the magnetic field is turned off, $H = 0$? What is the entropy if $E = 0$ with $H > 0$ (which requires $n_+ = n_-$)?

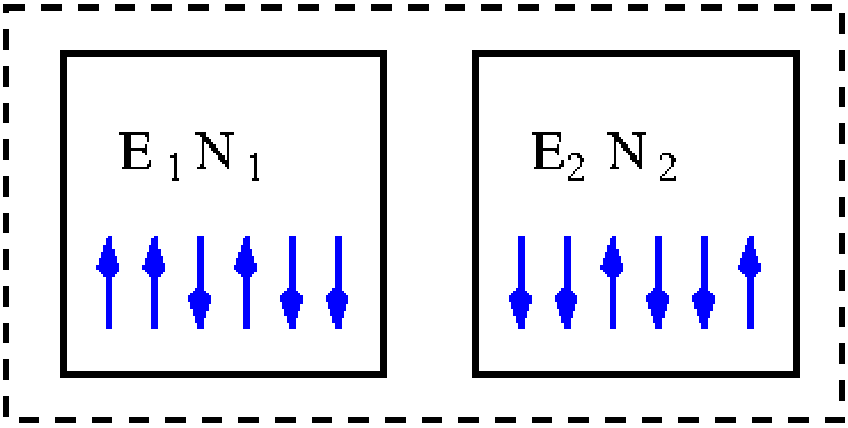
2.2.2 Extensivity

The increase in entropy for an increasing number of micro-states M is a reflection of entropy being an *extensive* quantity. Extensive quantities are formally defined by considering how they behave if two isolated subsystems are *analysed* as a single system — while still remaining isolated from each other, exchanging neither energy nor particles. This is clearest to consider through the specific example shown below of two isolated spin subsystems, Ω_1 & Ω_2, characterized by the energies E_1 & E_2 and particle numbers N_1 & N_2, respectively. To simplify the subsequent analysis, we can assume that both subsystems are placed in magnetic fields with the same H, so that $E_S = -H\left(n_+^{(S)} - n_-^{(S)}\right)$ for $S \in \{1, 2\}$.



We can take system Ω_1 to have M_1 micro-states with probabilities p_i while system Ω_2 has M_2 micro-states with probabilities q_k. As discussed above, each M_S is determined by E_S and N_S. The entropies of the two systems are

$$S_1 = -\sum_{i=1}^{M_1} p_i \log p_i \qquad\qquad S_2 = -\sum_{k=1}^{M_2} q_k \log q_k.$$



Now we keep these two subsystems isolated from each other, but consider them as a combined system Ω_{1+2}, as illustrated above. In order to compute the entropy S_{1+2}, we need to figure out the number of micro-states M_{1+2} the combined system could possibly adopt, and then determine the corresponding probability for each micro-state. Both steps are simplified by the subsystems being isolated from each other, so that they are statistically independent. Specifically, with subsystem Ω_1 in any one of its M_1 micro-states $\omega_i^{(1)}$, subsystem Ω_2 could independently adopt any of its M_2 micro-states, implying $M_{1+2} = M_1 M_2$.

Similarly, statistical independence means that the combined probability of subsystem Ω_1 adopting micro-state $\omega_i^{(1)}$ while subsystem Ω_2 adopts $\omega_k^{(2)}$ is the product of the individual probabilities, $p_i q_k$. We can check this is a well-defined probability, with

$$\sum_{M_{1+2}} p_i q_k = \sum_{i=1}^{M_1} \sum_{k=1}^{M_2} p_i q_k = \left[\sum_{i=1}^{M_1} p_i\right] \cdot \left[\sum_{k=1}^{M_2} q_k\right] = 1 \cdot 1 = 1.$$

Inserting the probability $p_i q_k$ into Eq. 20, and recalling $\log(a \cdot b) = \log a + \log b$, what is the combined entropy S_{1+2} of these two independent subsystems?

$S_{1+2} =$

You should find that the total entropy is the sum of the entropies of the two isolated subsystems, which is also how the energies and particle numbers behave,

$$E_{1+2} = E_1 + E_2 \qquad\qquad N_{1+2} = N_1 + N_2.$$

This behaviour identifies the energy, particle number and entropy as **extensive** quantities, which are defined to be those that add up across independent subsystems. This can be contrasted with **intensive** quantities, which are defined to be independent of the extent of the system, and hence the same (on average) for subsystems as for the combined system. Temperature and density are everyday examples of intensive quantities, though we will see below that the micro-canonical approach introduces some subtleties. It is possible for quantities to be neither extensive nor intensive, for example the number of micro-states $M_{1+2} = M_1 M_2$.

Finally, suppose that each subsystem is independently in thermodynamic equilibrium, with finite M_1 and M_2, implying

$$p_i = \frac{1}{M_1} \qquad\qquad q_k = \frac{1}{M_2}$$
$$S_1 = \log M_1 \qquad\qquad S_2 = \log M_2.$$

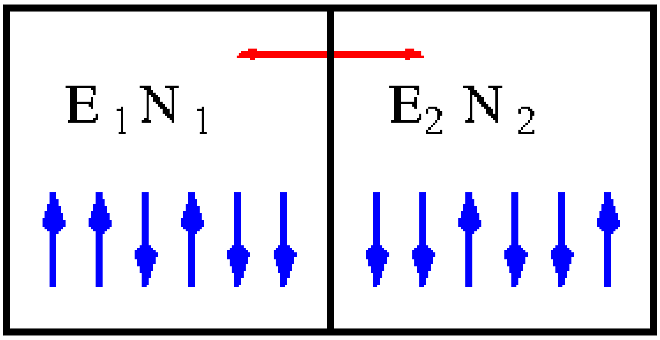
As a consequence we can establish that Ω_{1+2} is also in thermodynamic equilibrium, since the probabilities

$$p_i q_k = \frac{1}{M_1 M_2} = \frac{1}{M_{1+2}}$$

are identical all of its micro-states. In this situation it's even easier to see $S_{1+2} = \log{(M_1 M_2)} = \log M_1 + \log M_2 = S_1 + S_2$.

2.2.3 Second law of thermodynamics

Let's continue considering two subsystems, with one significant change: Suppose the subsystems are now able to exchange energy (but not particles) with each other. We'll say they are in *thermal contact* with each other, rather than being fully isolated. We'll also wait long enough after establishing thermal contact for the combined system Ω to reach equilibrium. This is illustrated below:



The total energy $E = E_1 + E_2$ remains conserved, so the overall system Ω is still governed by the micro-canonical ensemble. However, the individual energies E_1 and E_2 can now change over time, meaning that *each subsystem is no longer micro-canonical*.

The overall system Ω is *not* the same as the combined Ω_{1+2} considered above. We need to reconsider the total number of micro-states M that Ω could adopt, which is much more difficult than before because we can no longer apply statistical independence. Our key remaining tool is the conservation of the total energy E.

Considering a micro-state in which the N_1 spins contribute energy e_1 to the total, we know that the N_2 spins must contribute the remaining $E - e_1$. Our work above implies there are $M_{e_1} = M_{e_1}^{(1)} M_{E-e_1}^{(2)}$ micro-states providing this particular distribution of energies, where $M_{e_1}^{(1)}$ is the number of micro-states of the formerly isolated subsystem Ω_1 with energy e_1, and $M_{E-e_1}^{(2)}$ similarly corresponds to Ω_2 with energy $E - e_1$. We also know that it's possible to have $e_1 = E_1$, since that's the initial energy of Ω_1 before it was brought into thermal contact with Ω_2. When $e_1 = E_1$, we have $M_{E_1} = M_1 M_2$, covering all the micro-states of the combined Ω_{1+2} when the two subsystems were isolated. *In addition*, we also have to count any other micro-states for which $e_1 \neq E_1$:

$$M = \sum_{e_1} M_{e_1}^{(1)} M_{E-e_1}^{(2)} = M_1 M_2 + \sum_{e_1 \neq E_1} M_{e_1}^{(1)} M_{E-e_1}^{(2)} \geq M_1 M_2. \tag{21}$$

Equality holds when $e_1 = E_1$ is the only possibility — this is an extremely special case, in which the two subsystems remain individually micro-canonical, with fixed E_1 and E_2. This is all we can say in full generality, without specifying more details of a particular example, but it allows us to obtain a famous result for the total entropy S of Ω *in thermodynamic equilibrium*:

$$S = \log M \geq \log\left(M_1 M_2\right) = S_{1+2}.$$

This is a form of the **second law of thermodynamics**,

$$S \geq S_{1+2} = S_1 + S_2.$$

In words, whenever initially isolated (sub)systems in thermodynamic equilibrium are brought into thermal contact with each other and allowed to exchange energy, the total entropy of the overall system can never decrease. Indeed, it generically increases except in extremely special cases.

Though we won't go through a more general derivation here, it turns out that the total entropy never decreases (and generically increases) as time passes, under *any* circumstances. This has many far-reaching consequences, the first of which is a more general definition of thermodynamic equilibrium that (unlike Eq. 19) will also apply when we consider statistical ensembles other than the micro-canonical ensemble. For simplicity we assume that any system under consideration has a finite number of micro-states, which means that its entropy is bounded from above. To motivate the definition below, note that the overall system Ω may have undergone an equilibration process to reach its thermodynamic equilibrium after any independently equilibrated subsystems were brought into thermal contact — and in this process the entropy was non-decreasing.

A system is defined to be in **thermodynamic equilibrium** if its entropy is maximal.

We can *derive* Eq. 19 from this definition. All we need to do is maximize the entropy $S = -\sum_i p_i \log p_i$ subject to the three micro-canonical constraints of conserved energy, conserved particle number, and well-defined probabilities $\sum_i p_i = 1$. It turns out that only the final constraint needs to be incorporated into the maximization, through the method of **Lagrange multipliers**. As a reminder, this method involves maximizing the modified entropy

$$\overline{S}(\lambda) = S + \lambda\left(\sum_{i=1}^{M} p_i - 1\right) = -\sum_{i=1}^{M} p_i \log p_i + \lambda\left(\sum_{i=1}^{M} p_i - 1\right),$$

and subsequently imposing $\sum_i p_i = 1$. Here λ is a parameter called the 'multiplier'. In short, this procedure is valid because $\dfrac{\partial \overline{S}}{\partial \lambda} = 0$ once we impose $\sum_i p_i = 1$, so that any extremum of $\overline{S}$ corresponds to an extremum of $S = \overline{S}(\lambda = 0)$.

Recalling $\frac{\partial}{\partial x_k}\sum_i f(x_i) = \frac{\partial f(x_k)}{\partial x_k}$, what is the probability p_k that maximizes the modified entropy $\overline{S}$?

$$0 = \frac{\partial \overline{S}}{\partial p_k} =$$

You should find that p_k is some constant that depends on λ. We don't care about λ; so long as we know p_k is constant, then we must have $p_k = \frac{1}{M}$ in order to satisfy $\sum_k p_k = 1$. As advertised, we recover Eq. 19 from our new definition of thermodynamic equilibrium based on the second law.

2.3 Temperature

In the micro-canonical ensemble, the conserved internal energy and particle number are fundamental, while the temperature (like the entropy) is a derived quantity. As discussed below Eq. 20, in thermodynamic equilibrium such derived quantities are functions of the conserved $\{E, N\}$. In this section we will state the definition of temperature for the micro-canonical ensemble and apply this to a spin system. In the next section we will check that this definition reproduces our expectations from everyday experiences.

In thermodynamic equilibrium, the **temperature** $T(E, N)$ in the micro-canonical ensemble is defined by

$$\frac{1}{T} = \left.\frac{\partial S}{\partial E}\right|_N . \tag{22}$$

In words, the (inverse) temperature is set by the dependence of the entropy on the internal energy for a fixed number of degrees of freedom.

Since this definition is not terribly intuitive, we will again gain insight by considering N spins in a line, in a magnetic field of strength H. We saw above that $E = -H(n_+ - n_-)$ for n_+ and $n_- = N - n_+$ spins respectively pointing up and down. With N fixed, each (conserved) value of E defines a *different* micro-canonical system, which we can expect to have a different number of micro-states $M(E)$, different entropy $S(E)$ and different temperature $T(E)$. We will compute the functional forms of each of these three quantities, starting with $M(E)$.

Even though the total energy E remains fixed as time passes, individual spins can 'flip' between pointing up or down. Such spin flips simply have to come in pairs so that the overall $n_\pm$ both remain the same. As illustration, what are representative spin configurations that produce the minimal energy $E_{\text{min}} \equiv E_0$ and the next-to-minimal E_1? What are E_0 and E_1 in terms of $\{N, H\}$, and how many distinct micro-states are there for each of E_0 and E_1?

Your results should generalize to

$$M(E_{n_-}) = \binom{N}{n_-} = \frac{N!}{n_-!\,(N - n_-)!} = \binom{N}{n_+}. \tag{23}$$

To take the derivative in Eq. 22, we need to express n_- in terms of $\{E, N\}$. It will also be useful to avoid the factorial operation, which is inconvenient to differentiate. For $N \gg 1$, we can accomplish both these goals by treating the spin system as a random walk in the space of its possible energies E and applying the central limit theorem:[6]

- Each spin adds to $x \equiv \frac{E}{-H} = 2n_+ - N$ a 'step' of fixed 'length' ± 1. Our task therefore coincides with the special case we considered in Section 1.5.
- We don't impose any preference for positive vs. negative energies, meaning $p = q = \frac{1}{2}$ in the terminology of Section 1.5.
- With $p = q = \frac{1}{2}$, every one of the 2^N possible configurations of N spins is equally probable. Therefore the probability P_{n_+} that our overall 'walk' ends up producing a configuration with $n_+ = \frac{1}{2}(x + N)$ is simply the fraction of those 2^N states with this n_+, in which we can recognize Eq. 23:

$$P_{n_+} = \frac{1}{2^N}\binom{N}{n_+} = \frac{M(E_{n_-})}{2^N} \qquad \Longrightarrow \qquad M(E_{n_-}) = 2^N P_{n_+}.$$

- To estimate P_{n_+} for $N \gg 1$, we apply the central limit theorem just as in Section 1.5.3. In particular, we can re-use our computation that $\mu = 2p - 1 = 0$ and $\sigma^2 = 4pq = 1$, to find

$$p(x) \approx \frac{1}{\sqrt{2\pi N}} \exp\left[-\frac{x^2}{2N}\right].$$

  This is the probability *distribution* from which we want to extract P_{n_+}.

---

[6] Applying Stirling's formula, $\log(N!) \approx N \log N - N$, is another possible approach.

- From a tutorial problem we know that $P_{\text{const}}(n_+) = p(2n_+ - N)\Delta n_+$ is a good approximation. With $\Delta n_+ = 1$ and $2n_+ - N = \frac{E}{-H}$, we therefore find

$$M(E) \approx 2^N p(2n_+ - N) = \frac{2^N}{\sqrt{2\pi N}} \exp\left[-\frac{E^2}{2NH^2}\right]. \tag{24}$$

What is the derivative of the log of Eq. 24 with N fixed?

$$\left.\frac{\partial}{\partial E}\log M\right|_N =$$

You should find the temperature

$$T \approx -\frac{NH^2}{E} \qquad\qquad N \gg 1, \tag{25}$$

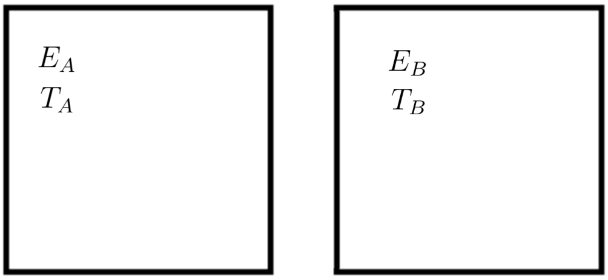
which in several ways does *not* seem to match our expectations from everyday experiences: This T diverges as $E \to 0$ for $n_+ \approx n_-$, and it is negative whenever $n_+ < n_-$ to produce $E > 0$. You can check that this $T < 0$ corresponds to the number of micro-states decreasing for larger internal energies, $\frac{\partial M}{\partial E} < 0$. In **natural** systems, larger energies make more micro-states accessible, producing $\frac{\partial M}{\partial E} > 0$ and a positive temperature. If $H = 0$, we also have $E = 0$ and T is ill-defined.

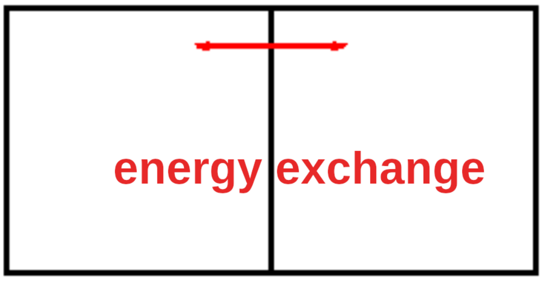
Restricting our attention to $H > 0$ and $n_+ > n_-$, we also see that the resulting non-negative temperature cannot vanish. It is minimized by the most-negative energy you found above, $T_{\text{min}} = H > 0$ for $E_{\text{min}} = -NH$. The non-zero minimum temperature is specific to spin systems, while some of the other oddities result from the micro-canonical approach more generally. This will motivate turning to the canonical ensemble in Unit 3, but first we can check that some aspects of the micro-canonical temperature defined in Eq. 22 do match our everyday expectations, at least in the 'natural' positive-temperature regime.

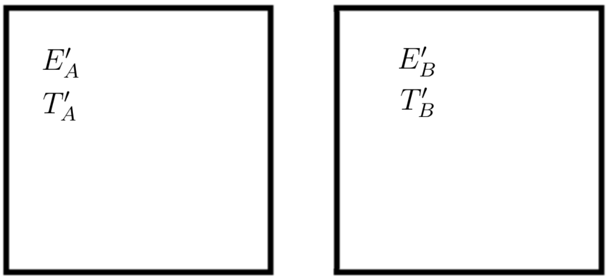
2.4 Heat exchange

From Eq. 25 for the temperature of a micro-canonical spin system, we can see that 'natural' positive temperatures correspond to negative energies, and therefore increase as the energy increases by becoming less negative (with a smaller magnitude). Such a direct relation between energy and temperature is very generic, and we will study it in more detail when considering thermodynamic cycles in a few weeks. For now, considering unspecified systems that exhibit this natural behaviour, let's ask what would happen if we take two initially isolated micro-canonical systems — Ω_A and Ω_B with temperatures T_A and T_B in thermodynamic equilibrium — and bring them into thermal contact.

In micro-canonical terms, the temperatures T_A and T_B are derived from the corresponding energies E_A and E_B, while thermal contact allows the two systems to exchange energy (but not particles) as non-isolated subsystems of a combined micro-canonical system Ω_C. Once the two subsystems have been in thermal contact long enough for the combined system to have reached thermodynamic equilibrium, it will have temperature T_C. We can then re-isolate the two subsystems, which will remain in thermodynamic equilibrium with energies $\{E'_A, E'_B\}$ and temperatures $\{T'_A, T'_B\}$. This three-step procedure is illustrated below.







From everyday experience, we expect that this energy exchange will result in a net flow of energy from the hotter system to the colder system, cooling the former by heating the latter. We will now check that the micro-canonical definition of temperature in Eq. 22 predicts this expected behaviour. With $S \in \{A, B\}$, we can write

$$E'_S = E_S + \Delta E_S$$

and consider for simplicity the case where the change in energy is relatively small,

$$\left|\frac{\Delta E_S}{E_S}\right| \ll 1.$$

Since we can build up large changes in energy through a series of smaller changes, this assumption doesn't lead to any loss of generality. We also know $\Delta E_B = -\Delta E_A$ thanks to conservation of energy.

Equation 22 tells us that we need to consider the entropies as functions of E_S and E_S' in order to connect the temperatures to any flow of energy. Because we don't change the number of particles in each system, we only need to consider the energy dependence of the entropy. We assume $S(E)$ is continuous and infinitely differentiable,[7] which allows us to expand each of the final entropies $S(E_S')$ in a Taylor series,

$$S(E_S') = S(E_S + \Delta E_S) \approx S(E_S) + \left.\frac{\partial S}{\partial E}\right|_{E_S} \Delta E_S,$$

neglecting all $\mathcal{O}(\Delta E_S^2)$ terms because we consider relatively small changes in energy. What is the expression above in terms of the initial temperatures T_S?

From the second law of thermodynamics, we know that the total entropy of these systems can never decrease as time passes:

$$S(E_A) + S(E_B) \le S(E_A + E_B) = S(E_A') + S(E_B'). \tag{26}$$

The final equality means that re-isolating the two subsystems doesn't change the entropy. This is because E_A' is not fixed and could take any value from zero to $E_A + E_B$ at the moment when the subsystems are re-isolated. Computing the final entropy $S(E_A') + S(E_B')$ therefore requires summing over all possible values of E_A', producing exactly the sum in Eq. 21 for the overall system. We will see something similar when we consider the 'Gibbs paradox' in Unit 4.

What do you find when you insert your linearized Taylor series into Eq. 26?

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[7] This assumption breaks down at a *phase transition*, where we would need to be more careful. We will learn about phase transitions towards the end of the term.

Applying conservation of energy should produce

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

Recalling from Section 2.2.3 that equality holds only in extremely special cases, we can identify three possibilities consistent with this result. If $T_A > T_B$, then $\left(\frac{1}{T_A} - \frac{1}{T_B}\right)$ is negative and we will generically have $\Delta E_A < 0$, so that energy flows out of the hotter system Ω_A and into the colder one. Our restriction to natural systems means this flow of energy reduces the higher temperature, and increases the lower temperature, bringing the temperatures of the two subsystems closer to each other. Similarly, if $T_A < T_B$, we will generically have $\Delta E_A > 0$, meaning that energy still flows from the hotter system Ω_B into the colder one, again reducing the difference in their temperatures. We can finally conclude that $T_A = T_B$ is the very special case where there is no energy flow, $\Delta E_S = 0$, keeping the temperatures the same. All of this is exactly what we would expect based on our everyday experience of temperature as an intensive quantity.

Unit 3: Canonical ensemble

3.1 The thermal reservoir

3.1.1 Replicas and occupation numbers

While it is reasonable to forbid particle exchange, for example by sealing gases inside airtight containers, it is not practical to prevent energy exchange as would be needed to fully isolate statistical systems. Any thermal insulator is imperfect, and any observation of the system would require exchanging energy with the external observer. In practice it is more convenient to work with physical systems that are characterized by their (intensive) temperatures rather than their (extensive) internal energies.

This leads us to define the **canonical ensemble** to be a statistical ensemble characterized by its fixed temperature T and conserved particle number N, with the temperature held fixed through contact with a **thermal reservoir**.

The second part of this definition connects the fixed temperature to the fundamental fact of energy conservation (the first law of thermodynamics). This is done by proposing that our system of interest Ω is in thermal contact with a much larger external system Ω_{res} — the thermal reservoir, sometimes called a "heat bath". The overall combined system $\Omega_{\text{tot}} = \Omega_{\text{res}} \otimes \Omega$ is governed by the micro-canonical ensemble, with conserved total energy $E_{\text{tot}} = E_{\text{res}} + E \approx E_{\text{res}}$, while the energy E of Ω is allowed to fluctuate. The key qualitative idea is that, in thermodynamic equilibrium, Ω has a negligible effect on the overall system. In particular, the temperature of that overall system — and therefore the temperature of Ω, by intensivity — is set by the reservoir and remains fixed even as E fluctuates. This effectively generalizes the setup we used to analyse heat exchange in the previous section, where we saw that thermal contact causes a net flow of energy from hotter systems to colder systems. When these systems are 'natural', this cools the hotter one by heating the colder one.

The mathematical implementation of this argument, as developed by Gibbs, proceeds by considering a well-motivated ansatz for the form of the thermal reservoir Ω_{res}. The goal, which will be useful to keep in mind as we go through the lengthy analysis, is to show that the specific form of Ω_{res} is ultimately irrelevant. This will allow us to work directly with the system of interest, Ω, independent of the details of the thermal reservoir that fixes its temperature.

Without further ado, we take Ω_{tot} to consist of many ($R \gg 1$) identical **replicas** of the system Ω that we're interested in. All of these replicas are in thermal contact with each other, and in thermodynamic equilibrium.[8] Choosing any one of the replicas to be the system of interest, Ω, the other $R - 1 \approx R$ replicas collectively form the thermal

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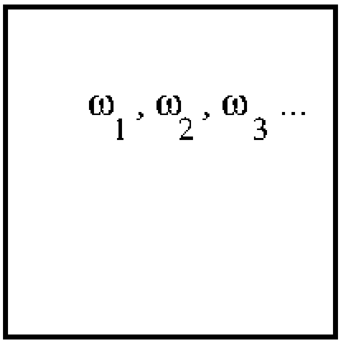
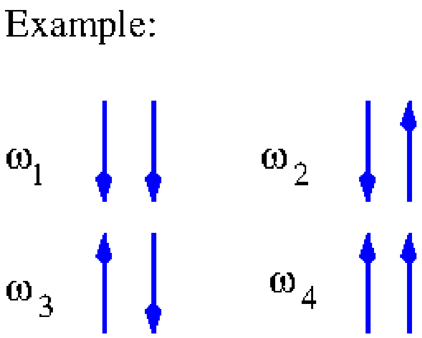
[8] The thermal contact between any two replicas can be indirect, mediated by a sequence of intermediate replicas. This transitivity of thermodynamic equilibrium is sometimes called the zeroth law of thermodynamics. It declares that if systems Ω_A & Ω_B are in thermodynamic equilibrium while systems Ω_B & Ω_C are in thermodynamic equilibrium, then Ω_A & Ω_C must also be in thermodynamic equilibrium.

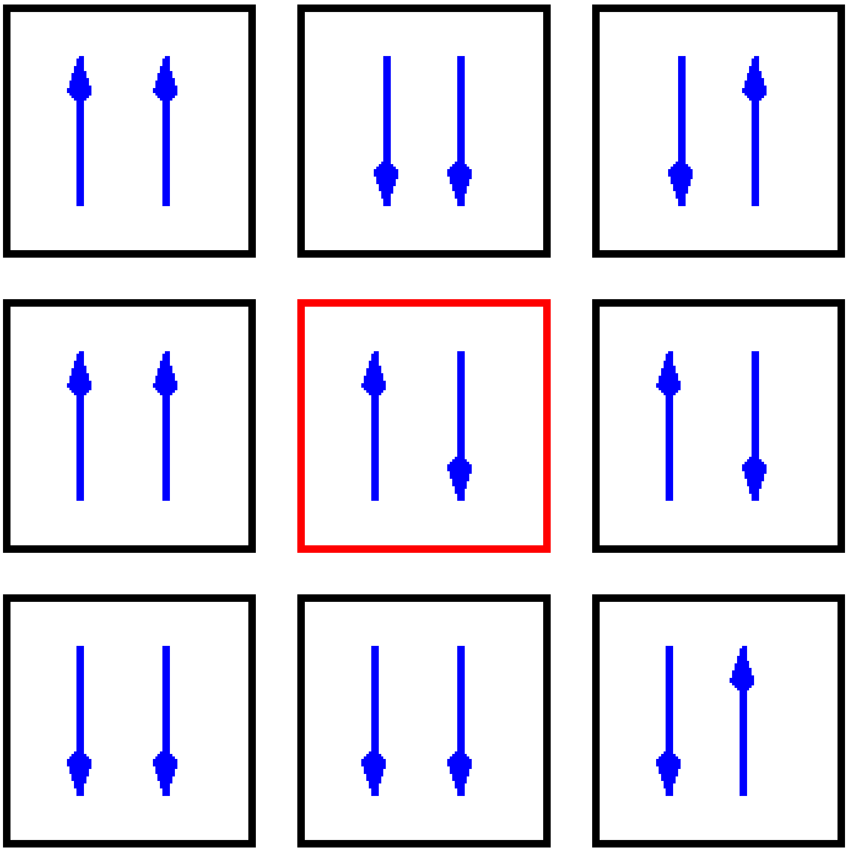
reservoir Ω_{res}. Assuming we want to study reasonable systems Ω, this ansatz ensures that Ω_{res} is also reasonable, simply much larger.

An extremely small example of this setup is illustrated by the figures below, where the system of interest is just $N = 2$ spins. For now we assume the spins are *distinguishable*, so that ↓↑ and ↑↓ are both distinct micro-states. This means that each individual replica has the $M = 4$ micro-states ω_i defined below.





To form the overall system Ω_{tot} we now bring together the $R = 9$ replicas shown below. We draw boxes around each replica to remind us that they are allowed to exchange only energy with each other, while the $N = 2$ spins per replica are fixed in place. We pick out one of these replicas (in the red box) to serve as the system Ω we will consider. The other 8 are the thermal reservoir Ω_{res} that fixes the temperature of Ω.



A convenient way to analyse the overall system of R replicas, Ω_{tot}, is to define the **occupation number** n_i to be the number of replicas that adopt the micro-state $\omega_i \in \Omega$ in any given micro-state of Ω_{tot}. The index $i \in \{1, 2, \cdots, M\}$ runs over all M micro-states of Ω. In the example above, three of the replicas have the micro-state $\omega_1 = \downarrow\downarrow$, meaning $n_1 = 3$. What are the occupation numbers $\{n_2, n_3, n_4\}$ for the other three ω_i in the figures above? Are all replicas are accounted for, $\sum_i n_i = R$?

Normalizing the occupation number by R gives us a well-defined *occupation probability*, $p_i = n_i/R$ with $\sum_i p_i = 1$. At the moment, this p_i is the probability that if we choose a replica at random it will be in micro-state ω_i.

Now let us consider conservation of energy, which continues to apply to the total energy E_{tot} of the overall system Ω_{tot}. We assume that each replica's energy E_r is independent of all the other replicas. This is guaranteed for the non-interacting systems we will focus on until Unit 9, and also holds when interactions are allowed within each replica but not between different replicas. The thermal contact between replicas allows E_r to fluctuate subject to conservation of E_{tot}, but there are at most M possible values E_i it can have, corresponding to the M micro-states $\omega_i \in \Omega$. Some distinct micro-states $\omega_i \neq \omega_j$ may have the same energy $E_i = E_j$, which doesn't affect the analysis. This allows us to rearrange a sum over replicas into a sum over the micro-states of Ω:

$$E_{\text{tot}} = \sum_{r=1}^{R} E_r = \sum_{i=1}^{M} n_i E_i, \tag{27}$$

with the occupation number n_i counting how many times micro-state ω_i appears among the R replicas. We can assume that R and M are both finite, so we don't need to worry about rearranging the sums.

3.1.2 Partition function

Following Gibbs, we've taken the thermal reservoir Ω_{res} to consist of $R - 1$ replicas of the system of interest, Ω. The next step is to further simplify the mathematics by assuming that the overall R-replica system Ω_{tot} is fully specified by a fixed set of M occupation numbers $\{n_i\}$. This is equivalent to assuming that the occupation probabilities $\{p_i\}$ are constant in time, as a reflection of thermodynamic equilibrium. From Eq. 27, we see that this ensures conservation of the total energy E_{tot}, and we can apply the micro-canonical tools we developed in the previous unit. Recall our ultimate goal of showing that such details of the thermal reservoir are irrelevant to the system Ω.

Based on the conservation of E_{tot}, we want to determine the (intensive) temperature of Ω_{tot}, which fixes the temperature of the system of interest, Ω. According to our previous work, to do this we first need to compute the overall number of micro-states

M_{tot} as a function of E_{tot}, from which we can derive the micro-canonical entropy and temperature since the system is in thermodynamic equilibrium. From the fixed occupation numbers n_i, we already know how many times each micro-state ω_i appears among the R replicas. To determine M_{tot} we just need to count how many possible ways there are of distributing the $\{n_i\}$ micro-states among the R replicas.

If we consider first the micro-state ω_1, the number of possible ways of distributing n_1 copies of this micro-states among the R replicas is just the binomial coefficient

$$\binom{R}{n_1} = \frac{R!}{n_1!\;(R-n_1)!}.$$

Moving on to ω_2, we need to keep in mind that n_1 replicas have already been assigned micro-state ω_1, so there are only $R - n_1$ replicas left to choose from. What is the resulting number of possible ways of distributing these n_2 micro-states?

Repeating this process for all micro-states $\{\omega_1, \omega_2, \cdots, \omega_M\}$, recalling $(R - \sum_i n_i)! = 0! = 1$, you should obtain a product that 'telescopes' to

$$M_{\text{tot}} = \frac{R!}{n_1!\;n_2!\;\cdots\;n_M!}. \tag{28}$$

This confirms that the order in which we assign micro-states to replicas is irrelevant, since integer multiplication is commutative.

Thanks to thermodynamic equilibrium, the entropy of the micro-canonical Ω_{tot} is

$$S(E_{\text{tot}}) = \log M_{\text{tot}} = \log(R!) - \sum_{i=1}^{M} \log(n_i!),$$

where the dependence on E_{tot} enters through the occupation numbers via Eq. 27. With $R \gg 1$ and $n_i \gg 1$ for all $i = 1, \cdots, M$, we can approximate each of these logarithms using the first two terms in Stirling's formula,

$$\log(N!) = N \log N - N + \mathcal{O}(\log N) \approx N \log N - N \qquad \text{for } N \gg 1.$$

In order for *every* occupation number to be large, $n_i \gg 1$, the number of replicas must be much larger than the number of micro-states of Ω. As we have discussed before, the number of micro-states M is typically a very large number, so with $R \gg M$ we are formally considering truly enormous thermal reservoirs! This enormity helps ensure that the detailed form of the reservoir will be irrelevant.

Using the approximation above, what do you find for $S(E_{\text{tot}})$ in terms of R and n_i? What is the entropy in terms of the occupation probabilities $p_i = n_i/R$?

$$S(E_{\text{tot}}) = \log(R!) - \sum_{i=1}^{M} \log(n_i!) \approx$$

In your result, the dependence on E_{tot} now enters through the occupation probabilities p_i. In order to determine the temperature, we have to express the entropy explicitly in terms of E_{tot}. We do this by applying our knowledge that thermodynamic equilibrium implies maximal entropy.

Following the same steps as in Section 2.2.3, we maximize the entropy, now with two Lagrange multipliers to account for two constraints on the occupation probabilities:

$$\sum_{i=1}^{M} p_i = 1 \qquad\qquad \sum_{i=1}^{M} n_i E_i = R \sum_{i=1}^{M} p_i E_i = E_{\text{tot}}.$$

Writing everything in terms of occupation probabilities, we therefore need to maximize the modified entropy

$$\overline{S} = -R \sum_{i=1}^{M} p_i \log p_i + \alpha \left(\sum_{i=1}^{M} p_i - 1 \right) - \beta \left(R \sum_{i=1}^{M} p_i E_i - E_{\text{tot}} \right).$$

Here we've chosen the sign of β for later convenience. What is the occupation probability p_k that maximizes $\overline{S}$?

$$0 = \frac{\partial \overline{S}}{\partial p_k} =$$

By defining a new parameter Z in terms of α, you should find

$$p_k = \frac{1}{Z} e^{-\beta E_k}. \tag{29}$$

As before, we need to fix the parameters $\{Z, \beta\}$ by demanding that the two constraints above are satisfied. The first of these constraints is straightforward and produces an important result:

$$1 = \sum_{i=1}^{M} p_i = \frac{1}{Z} \sum_{i=1}^{M} e^{-\beta E_i} \qquad \Longrightarrow \qquad Z(\beta) = \sum_{i=1}^{M} e^{-\beta E_i}. \tag{30}$$

Eq. 30 defines the canonical **partition function** $Z(\beta)$, a fundamental quantity in the canonical ensemble, from which many other derived quantities can be obtained.

$Z(\beta)$ still depends on the other as-yet-unknown parameter $\beta(E_{\text{tot}})$. By applying our second constraint, Eq. 27, we can relate β to E_{tot}:

$$E_{\text{tot}} = R \sum_{i=1}^{M} p_i E_i = \frac{R}{Z(\beta)} \sum_{i=1}^{M} E_i \, e^{-\beta E_i} = R \frac{\sum_{i=1}^{M} E_i \, e^{-\beta E_i}}{\sum_{j=1}^{M} e^{-\beta E_j}}. \tag{31}$$

This relation is a bit complicated, but will suffice for our goal of expressing the entropy in terms of E_{tot}. Inserting Eq. 29 for p_i into your earlier result for the entropy, what do you obtain upon applying Eqs. 30 and 31?

$$S(E_{\text{tot}}) = -R \sum_{i=1}^{M} p_i \log p_i =$$

There is a pleasant simplification when we take the derivative to determine the temperature. Defining $\beta' \equiv \frac{\partial}{\partial E_{\text{tot}}} \beta(E_{\text{tot}})$, we have

$$\frac{1}{T} = \frac{\partial}{\partial E_{\text{tot}}} S(E_{\text{tot}}) = \frac{\partial}{\partial E_{\text{tot}}} \left[E_{\text{tot}} \beta + R \log Z(\beta) \right] = \beta + E_{\text{tot}} \beta' + R \frac{1}{Z} \frac{\partial Z(\beta)}{\partial \beta} \beta'.$$

Using Eq. 31 we can compute

$$\frac{1}{Z} \frac{\partial Z(\beta)}{\partial \beta} = \frac{1}{Z} \frac{\partial}{\partial \beta} \sum_{i=1}^{M} e^{-\beta E_i} = -\frac{1}{Z} \sum_{i=1}^{M} E_i \, e^{-\beta E_i} = -\sum_{i=1}^{M} p_i E_i = -\frac{E_{\text{tot}}}{R},$$

so that we don't need to figure out the explicit form of β':

$$\frac{1}{T} = \beta + E_{\text{tot}}\beta' - E_{\text{tot}}\beta' = \beta. \tag{32}$$

What's truly remarkable about Eqs. 29, 30 and 32 is that they make no reference to the R replicas or any extensive quantity of the overall system, such as E_{tot} — all information about the thermal reservoir has vanished. This is the goal we have been pursuing since the start of this unit! The large thermal reservoir is still present to fix the temperature T characterizing the canonical system Ω, but beyond that nothing about it is relevant (or even knowable) in the canonical approach. Every aspect of Ω can now be specified in terms of its fixed temperature T and conserved particle number N, starting with the parameter $\beta = 1/T$.

In particular, the partition function from Eq. 30 is simply

$$Z(T) = \sum_{i=1}^{M} e^{-E_i/T}. \tag{33}$$

and together with β specifies the probabilities

$$p_i = \frac{1}{Z} e^{-E_i/T} \tag{34}$$

from Eq. 29. This p_i is now the thermodynamic equilibrium probability that Ω adopts micro-state ω_i with (non-conserved) internal energy E_i. This probability distribution is called either the **Boltzmann distribution** or the **Gibbs distribution**, while $e^{-E_i/T}$ itself is known as a **Boltzmann factor**. All micro-states with the same energy have the same probability in thermodynamic equilibrium, which is consistent with the micro-canonical behaviour we saw in Unit 2.

3.2 Internal energy, heat capacity, and entropy

In addition to fixing the temperature of the system Ω, the thermal reservoir also allows the internal energy of Ω to fluctuate. The system simply exchanges energy with the reservoir, satisfying the first law of thermodynamics. Although the internal energy fluctuates, its expectation value $\langle E\rangle$ is an important derived quantity in thermodynamic equilibrium. Applying the general definition from Eq. 4 to the probability space of the canonical ensemble,

$$\langle E\rangle(T) = \sum_{i=1}^{M} E_i\, p_i = \frac{1}{Z}\sum_{i=1}^{M} E_i\, e^{-\beta E_i}.$$

Here we highlight the dependence of $\langle E\rangle$ on the temperature, and also freely interchange $\beta = 1/T$.

The expression above may look familiar from our work in the previous section:

$$\frac{\partial}{\partial \beta} \log Z =$$

In this case it is easier to take the derivative with respect to β as opposed to

$$\frac{\partial}{\partial \beta} = \frac{\partial T}{\partial \beta}\frac{\partial}{\partial T} = -\frac{1}{\beta^2}\frac{\partial}{\partial T} = -T^2\frac{\partial}{\partial T}. \tag{35}$$

In Section 2.3, we saw that 'natural' micro-canonical systems exhibit higher (derived) temperatures for larger (conserved) internal energies. Here, in the canonical approach, the average internal energy $\langle E \rangle$ is the derived quantity while the temperature is fixed. From our everyday experience, we expect a similar direct relation between temperature and energy, which the following result confirms.

The **heat capacity** is defined to be

$$c_v = \frac{\partial}{\partial T}\langle E \rangle, \tag{36}$$

and is always non-negative, $c_v \geq 0$.

The subscript indicates that the volume of the system is kept fixed; we'll consider the role of the volume more carefully starting in Unit 4. In a homework assignment you will confirm $c_v \geq 0$ by deriving a **fluctuation–dissipation** (or **fluctuation–response**) **relation**. That relation will be a special case of a more general theorem, and will connect the fluctuations of the internal energy around its expectation value, $(E_i - \langle E \rangle)^2$, to the energy's *response* to a change in temperature, $\frac{\partial}{\partial T}\langle E \rangle$. Only extremely special cases will produce $c_v = 0$, meaning that the heat capacity is generically positive, in agreement with our intuition that higher temperatures produce larger internal energies.

Finally, we can compute the entropy of Ω with no reference to the thermal reservoir, apart from its role fixing the temperature in thermodynamic equilibrium. Since the general definition of the entropy in Eq. 20 continues to hold for the canonical ensemble, we just need to insert the probabilities p_i from Eq. 34:

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

You should find that the entropy depends on $\log Z$.

3.3 Helmholtz free energy

This dependence of the entropy on $\log Z$ is in accordance with our earlier claim that the partition function is a fundamental quantity in the canonical ensemble. Recalling from Eq. 33 that Z is a sum over all micro-states, we can view this result as the canonical counterpart to the micro-canonical entropy being the logarithm of the number of micro-states. (Thermodynamic equilibrium is required in both cases.) This motivates the following definition of a quantity with the dimensions of energy that is related to $\log Z$, which provides simpler and more elegant expressions for the derived quantities we considered above.

The **Helmholtz free energy** of a system in the canonical ensemble is

$$F(T) = -T \log Z(T) \qquad\qquad F(\beta) = -\frac{\log Z(\beta)}{\beta}, \tag{37}$$

where Z is the partition function of the system. In terms of this free energy, Eqs. 33 and 34 are

$$Z = e^{-F/T} \qquad\qquad p_i = e^{(F-E_i)/T}.$$

The Helmholtz free energy is named after Hermann von Helmholtz and reveals its usefulness when we take its derivative. The derivative involves $\frac{\partial}{\partial T}\log Z$, which is worth collecting in advance based on Eq. 35:

$$-\frac{\partial}{\partial T}\left(\frac{F(T)}{T}\right) = \frac{\partial}{\partial T}\log Z(T) =$$

$$\frac{\partial}{\partial T}F(T) =$$

From these results we can read off the more elegant expressions promised above:

$$S(T) = -\frac{\partial}{\partial T}F(T) \tag{38}$$

$$\langle E\rangle(T) = -T^2\frac{\partial}{\partial T}\left(\frac{F(T)}{T}\right) = \frac{\partial}{\partial \beta}\left[\beta F(\beta)\right] = TS(T) + F(T). \tag{39}$$

3.4 The physics of information

As a first application of the canonical ensemble, we will explore physically observable effects that depend on the information content of a statistical system. A famous scientific question illustrating the importance of information, which you may have heard of, is the black hole information paradox. However, that topic is well beyond the scope of this module since it depends on quantum mechanics and general relativity in addition to statistical mechanics. Here we will consider simple spin systems as introduced in Section 2.1, contrasting the behaviour of their average internal energy $\langle E\rangle$ and entropy S depending on whether or not the spins can (in principle) be distinguished from each other. It's important to appreciate that the "information" discussed here is an intrinsic property of the system — what is *knowable* about it in principle. It does not matter whether or not any observer actually knows this information; so long as it can possibly be known it will have an effect.

3.4.1 Distinguishable spins in a solid

We begin with the setup from Section 2.1: A system of N spins arranged in a line, placed in an external magnetic field of strength H, and in thermodynamic equilibrium. We further specify that the spins are embedded in a solid material that fixes their positions and prevents them from moving. This allows them to be distinguished from one another: An observer can target an appropriate position in the solid to measure the corresponding spin. Each spin measured in this way will be either parallel or anti-parallel to the magnetic field. The canonical system therefore has $M = 2^N$ distinct micro-states ω_i with energies E_i and probabilities $p_i = \frac{1}{Z}e^{-E_i/T}$, each defined by the orientations of all N spins.

To streamline our notation, we can represent the orientation of the nth spin as $s_n \in \{1, -1\}$, where $s_n = 1$ indicates alignment parallel to the field and $s_n = -1$ indicates alignment anti-parallel to the field. With this notation, the internal energy of the system in micro-state ω_i specified by the N spins $\{s\}$ is simply

$$E_i = -H \sum_{n=1}^{N} s_n. \tag{40}$$

To compute the canonical partition function Z_D, where the subscript reminds us of the spins' distinguishability, we have to sum over all 2^N possible spin configurations $\{s\}$. In this process we can save some space by defining the dimensionless variable $x = \beta H = \frac{H}{T}$:

$$\begin{aligned}
Z_D &= \sum_{s_1=\pm1} \cdots \sum_{s_N=\pm1} e^{-\beta E_i} = \sum_{s_1=\pm1} \cdots \sum_{s_N=\pm1} \exp\left[x \sum_{n=1}^{N} s_n\right] \\
&= \sum_{s_1=\pm1} \cdots \sum_{s_N=\pm1} e^{xs_1} \cdots e^{xs_N} = \left(\sum_{s_1=\pm1} e^{xs_1}\right) \cdots \left(\sum_{s_N=\pm1} e^{xs_N}\right) \\
&= \left(\sum_{s=\pm1} e^{xs}\right)^N = \left(e^x + e^{-x}\right)^N = \left[2\cosh\left(\beta H\right)\right]^N,
\end{aligned} \tag{41}$$

distributing the summations since all the spins are independent of each other.

The corresponding Helmholtz free energy

$$F_D(\beta) = -\frac{\log Z(\beta)}{\beta} = -\frac{N \log\left[2\cosh\left(\beta H\right)\right]}{\beta} \tag{42}$$

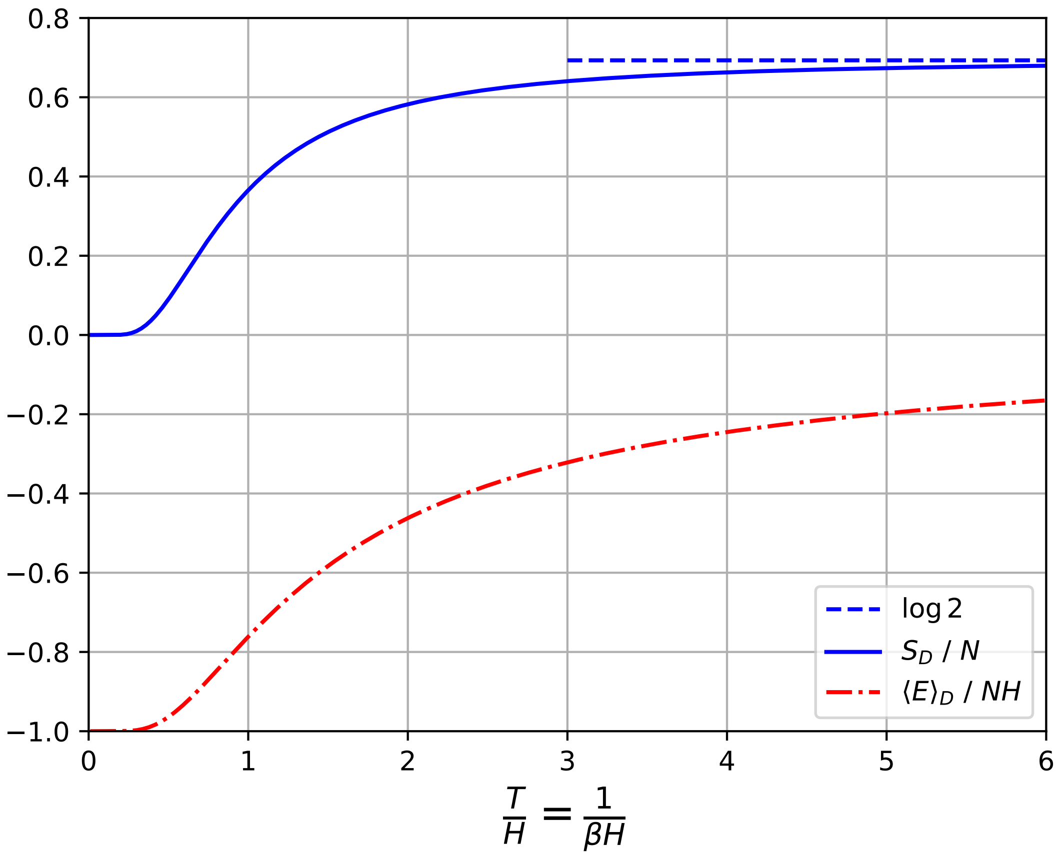
is all we need to compute the average internal energy:

$$\left\langle E \right\rangle_D = \frac{\partial}{\partial \beta}\left[\beta F_D(\beta)\right] =$$

From this we immediately obtain the entropy

$$S_D = \beta\left(\left\langle E \right\rangle_D - F_D\right) = -N\beta H \tanh\left(\beta H\right) + N \log\left[2\cosh\left(\beta H\right)\right]. \tag{43}$$

These results for $\left\langle E \right\rangle_D$ and S_D are plotted on the next page as functions of $\frac{T}{H} = \frac{1}{\beta H}$, using this Python code. Since both these quantities are extensive, we normalize them by showing $\frac{\left\langle E \right\rangle_D}{NH}$ and $\frac{S_D}{N}$.



Let's analyse the asymptotic behaviour of these functions, starting with **low temperatures**. In contrast to the micro-canonical Eq. 25, in the canonical ensemble there is no issue with taking the independent variable $T \to 0$. This corresponds to $\beta H \to \infty$ and $\tanh(\beta H) \to 1$, approaching the "ground-state" energy $E_{\text{min}} = E_0 = -NH$ you computed in Section 2.3. This energy is only produced by the single micro-state in which all the spins are aligned with the magnetic field, $s_n = 1$ for all n (or $n_+ = N$ and $n_- = 0$ in the notation from Section 2.3). Correspondingly, $\log\left[2\cosh(\beta H)\right] \to \log e^{\beta H} = \beta H$ and the two terms in Eq. 43 cancel out, so that $S_D \to 0$. This vanishing entropy is a generic consequence of temperatures approaching *absolute zero*.

For low but non-zero temperatures, $\langle E\rangle_D$ and S_D will be affected by the non-zero probability for the system to adopt micro-states ω_i with higher energies $E_i > E_0$. These higher-energy configurations are often referred to as "excited states". Note that each energy $E_i > E_0$ may correspond to many different micro-states. For example, in Section 2.3 you also computed the energy $E_1 = -(N-2)H$ of the first excited state, which is realized by the N distinct micro-states with $n_- = 1$. In the case of spin systems, we can instead refer to *energy levels* that are all separated by a constant *energy gap* $\Delta E \equiv E_{n_-+1} - E_{n_-} = 2H$.

We can compute the effects of the higher energy levels at low temperatures $\beta H \gg 1$ by expanding $\langle E \rangle_D$ in powers of $e^{-\beta H} \ll 1$. What is the first temperature-dependent term in this expansion?

$$\frac{\langle E \rangle_D}{NH} =$$

You should find that the excited-state effects are *exponentially* suppressed by the energy gap ΔE at low temperatures,

$$\frac{\langle E \rangle_D}{NH} = -1 + 2e^{-\beta \Delta E} + \mathcal{O}\left(e^{-2\beta \Delta E}\right).$$

This is a generic feature of canonical systems with a non-zero energy gap, and is due to the exponentially suppressed probability for the system to adopt any of the microstates with the higher energy,

$$\frac{\frac{1}{Z} e^{-\beta E_{n_-+1}}}{\frac{1}{Z} e^{-\beta E_{n_-}}} = e^{-\beta \Delta E}.$$

The low-temperature expansion of Eq. 43 for the entropy in powers of $e^{-\beta H} \ll 1$ is similar:

$$\frac{S_D}{N} =$$

Here the leading term includes a linear factor of $\beta \Delta E \gg 1$, but this can't overcome the now-expected exponential suppression:

$$\frac{S_D}{N} = \beta \Delta E e^{-\beta \Delta E} + e^{-\beta \Delta E} + \mathcal{O}\left(\beta \Delta E e^{-2\beta \Delta E}\right).$$

In the limit of **high temperatures** we should instead expand in powers of the small factor $\beta H \ll 1$. This is straightforward for $\langle E \rangle_D$:

$$\frac{\langle E \rangle_D}{NH} = -\tanh(\beta H) = -\beta H + \frac{(\beta H)^3}{3} + \mathcal{O}\left([\beta H]^5\right),$$

which vanishes $\sim \frac{1}{T}$ as $T \to \infty$. This matches the micro-canonical behaviour we saw for this system from Eq. 25, where the derived temperature diverged as the conserved energy approached zero.

For the entropy, there is a similar connection to micro-canonical behaviour at high temperatures:

$$\frac{S_D}{N} =$$

As $\frac{T}{H} \to \infty$, the result

$$\frac{S_D}{N} = \log 2 - \frac{(\beta H)^2}{2} + \mathcal{O}\left([\beta H]^4\right)$$

approaches the asymptotic value $S_D \to N \log 2 = \log M$ for the $M = 2^N$ micro-states (with different energies). Conceptually, in this limit the energy of each spin is negligible compared to the temperature, and the system approximately behaves as though the energy were zero for all micro-states (and hence conserved).

3.4.2 Indistinguishable spins in a gas

Next, let's consider nearly the same setup, with N spins in thermodynamic equilibrium, in an external magnetic field of strength H. The only difference is that now the spins are allowed to move, like particles in a one-dimensional gas. We demand that they move slowly, so that we can ignore their kinetic energy and the total energy of the system continues to be given by Eq. 40. Since the spins don't interact with each other, they can freely move past each other, and even occupy the same space, making it impossible for them to be distinguished from one another.

To compute the fundamental canonical partition function (Eq. 33), we have to sum over the micro-states of the system. These micro-states are no longer in one-to-one correspondence with the full configurations $\{s\}$ of the N spins. Because the spins are now indistinguishable, certain spin configurations also cannot be distinguished from each other. The simplest example comes from the two-spin system considered in Section 3.1.1, where the configurations ↓↑ and ↑↓ now both correspond to a single micro-state. In this micro-state, we know only that one spin is $s_i = 1$ while the other is $s_k = -1$; it's not possible to distinguish which is which.

Generalizing, we can conclude that a single distinct micro-state corresponds to all possible permutations of spins with fixed $\{n_+, n_-\}$. This means that each micro-state is now in one-to-one correspondence with the energy $E = -H(n_+ - n_-)$, which we can continue to organize as energy levels separated by a constant energy gap $\Delta E = 2H$. As a quick example, enumerate the energy levels when $N = 4$ and list the spin configurations associated with the corresponding micro-states. How many micro-states are there for N spins?

A convenient way to label these micro-states and energy levels is to define

$$E_k = -NH + 2Hk = -H(N - 2k)$$

for micro-state ω_k with $k = n_- = 0, \cdots N$. To compute the partition function Z_I, with the subscript reminding us about the spins' indistinguishability, we now have

$$Z_I = \sum_{k=0}^{N} e^{-\beta E_k} = \sum_{k=0}^{N} e^{\beta H(N-2k)} = e^{N\beta H} \sum_{k=0}^{N} \left(e^{-2\beta H}\right)^k = e^{N\beta H} \frac{1 - e^{-2(N+1)\beta H}}{1 - e^{-2\beta H}}. \tag{44}$$

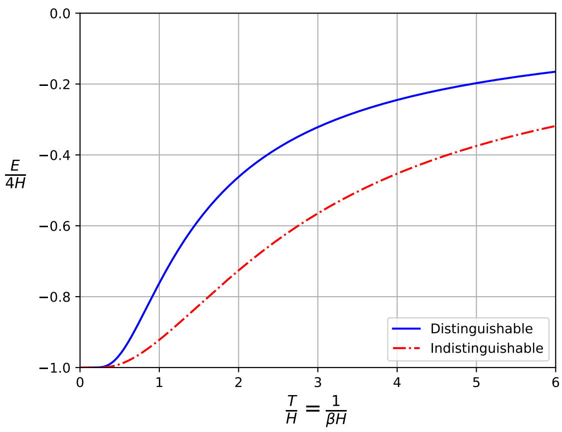
The geometric series in the last step can be reconstructed by considering

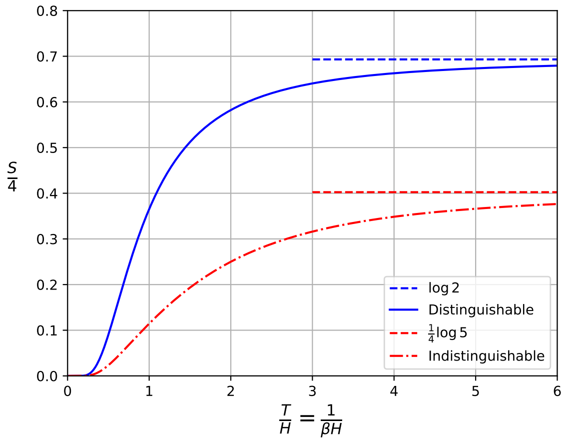
$$\sum_{k=0}^{N} x^k = \sum_{k=0}^{\infty} x^k - \sum_{k=N+1}^{\infty} x^k = \frac{1}{1-x} - x^{N+1} \sum_{\ell=0}^{\infty} x^\ell = \frac{1}{1-x} - \frac{x^{N+1}}{1-x}.$$

The corresponding Helmholtz free energy is

$$F_I(\beta) = -\frac{\log Z_I(\beta)}{\beta} = -NH - \frac{\log\left[1 - e^{-2(N+1)\beta H}\right]}{\beta} + \frac{\log\left[1 - e^{-2\beta H}\right]}{\beta}. \tag{45}$$

In contrast to Eq. 42, $F_I(\beta)$ is no longer proportional to N. In a homework assignment you will use F_I to determine the average internal energy $\left\langle E \right\rangle_I$ and entropy S_I shown in the figures on the next page, and also analyse the low- and high-temperature expansions like we did for the distinguishable case above. Unlike our results for the distinguishable case, you will find that $\frac{\langle E \rangle_I}{NH}$ and $\frac{S_I}{N}$ depend on N, which requires us to fix $N = 4$ in the plots on the next page.





The solid blue lines in these figures are exactly the distinguishable-spin results we previously discussed. The red dash-dotted lines are the new results for indistinguishable spins. We see that the same $T \to 0$ limits are approached in both cases: $E \to -NH$ and $S \to 0$. At low temperatures, the indistinguishable results approach these limits more quickly — they still feature exponential suppression of excited-state effects by the energy gap, $\propto e^{-\beta\Delta E}$, but this now comes with additional factors of N.

At high temperatures there is an even more striking difference. While the average internal energy $\langle E\rangle_I$ continues to vanish $\sim\frac{1}{T}$ as $T \to \infty$ (with different N dependence), the entropy approaches the asymptotic value $S_I \to \log{(N+1)} = \log M$ for the $M = N+1$ micro-states. This logarithmic dependence on N is very different from the $S_D \to N\log 2$ limit we found for distinguishable spins, and reflects the exponentially smaller number of micro-states that exist for indistinguishable spins, $N+1$ vs. 2^N.

Finally, away from those low- and high-temperature limits, the left figure above shows a significant difference in the internal energies of the spin systems, depending only on whether or not the spins can be distinguished from each other in principle. This is a physically measurable effect caused by the intrinsic information content of a statistical system, and a simple illustration of phenomena that remain at the leading edge of ongoing research. As Rolf Landauer put it in a famous 1991 essay: Information is physical.

Unit 4: Ideal gases

4.1 Volume, energy levels, and partition function

We now apply the canonical ensemble to investigate non-relativistic, classical, ideal gases. Using statistical mechanics we will explore how the large-scale behaviours of such gases emerge from the properties of the particles that compose them. The key particle properties are specified by the adjectives used above:

- **Classical** systems are those for which we can ignore the effects of quantum mechanics. Among other things, this allows us to simultaneously define both the position (x, y, z) and the momentum $\vec{p} = (p_x, p_y, p_z)$ of each particle with arbitrary precision.
- **Non-relativistic** particles move with speeds small compared to the speed of light, which allows us to ignore small effects due to special relativity. The particles are therefore governed by the laws Isaac Newton published all the way back in 1687. In particular, the energy of each particle of mass m is
  $$E_n = \frac{1}{2m} p_n^2,$$
  where $p_n^2 = \vec{p}_n \cdot \vec{p}_n = (p_x)_n^2 + (p_y)_n^2 + (p_z)_n^2$ is the inner (or 'dot') product of the momentum vector for the nth particle in the micro-state of interest.
- **Ideal** gases are those whose constituent particles don't interact with each other. As a result, the total energy of the gas is simply the sum of the energies of the N individual particles,
  $$E = \frac{1}{2m} \sum_{n=1}^{N} p_n^2. \tag{46}$$

As is now familiar for the canonical ensemble, we consider the gas to be in thermodynamic equilibrium, and in thermal contact with a large external thermal reservoir with which it can exchange energy but not particles. To prevent particle exchange, we can specify that the gas is enclosed in a cubic box with volume $V = L^3$. The thermal reservoir fixes the temperature T of the gas.

The starting point for our analysis is to compute the partition function

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

Unfortunately there is a challenge confronting this sum over all possible micro-states ω_i of the N-particle system. These micro-states depend on the momenta $\vec{p}_n$ for all N particles, and it's intuitive to suppose that each component of $(p_x, p_y, p_z)_n$ is a continuously varying real number that can (in principle) be distinguished with arbitrary precision. This implies an uncountably infinite set of distinct momenta and hence an uncountably infinite set of micro-states, making the summation above ill-defined.

To proceed, we *regularize* the system so that there are a countable number of micro-states we can sum over to define the partition function. We do this by positing that the particles' momentum components can take only discrete (or 'quantized') values that depend on the volume of the box. Specifically, we declare that the possible momenta are

$$\vec{p} = (p_x, p_y, p_z) = \hbar\frac{\pi}{L}(k_x, k_y, k_z) \qquad\qquad k_{x,y,z} \in \mathbb{Z}. \tag{47}$$

The constant factor $\hbar$ ("h-bar") is known as the (reduced) Planck constant, named after Max Planck). Like the Boltzmann constant k, the Planck constant is another unit conversion factor (relating inverse length $\frac{1}{L}$ and momentum p), which is just $\hbar = 1$ in natural units. Despite this, we will retain explicit factors of $\hbar$ in these lecture notes.

What are the energies that correspond to these discretized momenta?

You should find energies that fall into discrete *energy levels*, somewhat similar to the spin system considered in Section 3.4. Unlike the spin system, in this case the energy gaps between subsequent energy levels are not constant.

Similar discrete energy levels turn out to be realized in nature, thanks to quantum mechanics — if you have previously studied quantum physics, you may spot a resemblance with a particle in a box. For the purposes of this module we can just adopt Eq. 47 as an ansatz. Even with this perspective, it will be useful to maximize the similarity with quantum physics. We can do this by observing that negating any component of the momentum has no effect on the energy $E \propto p^2 \propto k^2$, and hence all non-zero $\pm k_i$ pairs make equal contributions to the partition function. Therefore, restricting the discrete momenta to non-negative $k_{x,y,z} = 0, 1, 2, \cdots$ only changes Z by a constant factor C, which cancels out in the expectation value of any observable that depends only on the inner product p^2:

$$\left\langle f(p^2) \right\rangle = \frac{\sum_{k_{x,y,z} \in \mathbb{Z}} f(p^2) e^{-E_i/T}}{Z} \qquad \longrightarrow \qquad \frac{C \sum_{k_{x,y,z} \in \mathbb{N}} f(p^2) e^{-E_i/T}}{CZ}.$$

For example, the constant factor does not contribute to $\langle E \rangle = \frac{\partial}{\partial \beta} \log Z$.

Although there are still an infinite number of possible momenta and energy levels for each particle in the gas, these are now countable, making our partition function well-defined. Let's start by considering the partition function Z_1 for a single particle. The micro-states for this single-particle system are completely specified by the particle's p^2,

$$Z_1 = \sum_i \exp\left[-\frac{E_i}{T}\right] = \sum_{\vec{p}} \exp\left[-\frac{p^2}{2mT}\right] = \sum_{k_{x,y,z}=0}^{\infty} \exp\left[-\frac{\hbar^2\pi^2}{2mTL^2}\left(k_x^2 + k_y^2 + k_z^2\right)\right].$$

We can separately sum over each of the independent (k_x, k_y, k_z), and recognize that all three summations are identical:

$$\begin{aligned}
Z_1 &= \sum_{k_x=0}^{\infty} \exp\left[-\frac{\hbar^2\pi^2}{2mTL^2}k_x^2\right] \sum_{k_y=0}^{\infty} \exp\left[-\frac{\hbar^2\pi^2}{2mTL^2}k_y^2\right] \sum_{k_z=0}^{\infty} \exp\left[-\frac{\hbar^2\pi^2}{2mTL^2}k_z^2\right] \\
&= \left(\sum_{k_i=0}^{\infty} \exp\left[-\frac{\hbar^2\pi^2}{2mTL^2}k_i^2\right]\right)^3 .
\end{aligned}$$

Now that the sum over micro-states has been turned into a sum over momenta, our system has been regularized and we are free to switch back from discrete to continuous momenta.[9] We can start by converting from integer k_i to continuous real $\widehat{k}_i$:

$$\sum_{k_i=0}^{\infty} \exp\left[-\frac{\hbar^2\pi^2 k_i^2}{2mTL^2}\right] \to \int_0^{\infty} \exp\left[-\frac{\hbar^2\pi^2\widehat{k}_i^2}{2mTL^2}\right] d\widehat{k}_i = \frac{1}{2}\int_{-\infty}^{\infty} \exp\left[-\frac{\hbar^2\pi^2\widehat{k}_i^2}{2mTL^2}\right] d\widehat{k}_i \, .$$

The final equality simply notes that the integrand is an even function of $\widehat{k}_i$, as it depends only on $\widehat{k}_i^2$. Next we use Eq. 47 to return to the original momenta $p_i = \hbar\frac{\pi}{L}\widehat{k}_i$,

$$\sum_{k_i=0}^{\infty} \exp\left[-\frac{\hbar^2\pi^2}{2mTL^2}k_i^2\right] \to \frac{1}{2}\int \exp\left[-\frac{p_i^2}{2mT}\right]\left(\frac{L}{\pi\hbar}\,dp_i\right).$$

We end up with the single-particle partition function

$$Z_1 = \left(\frac{L}{2\pi\hbar}\right)^3 \int \exp\left[-\frac{p^2}{2mT}\right] d^3p,$$

where $p^2 = p_x^2 + p_y^2 + p_z^2$ and $d^3p = dp_x\,dp_y\,dp_z$. (Some textbooks may skip the formal regularization and simply introduce this expression as a definition, using dimensional analysis to justify the factors of L and $\hbar$.) We can now account for all N particles in the ideal gas, which are completely independent and don't interact with each other. Assuming we can distinguish these particles from each other, then each of them simply contributes an independent factor of Z_1 to the overall partition function

$$Z_D = \left(\frac{L}{2\pi\hbar}\right)^{3N} \int \exp\left[-\sum_{n=1}^{N}\frac{p_n^2}{2mT}\right] d^{3N}p, \tag{48}$$

where the subscript reminds us of the particles' distinguishability. We will consider the indistinguishable case below.

We can recognize that each of the $3N$ independent integrations in Eq. 48 is a gaussian integral,

$$\frac{L}{2\pi\hbar}\int \exp\left[-\frac{p_i^2}{2mT}\right] dp_i = \frac{L}{2\pi\hbar}\sqrt{2\pi mT} = \sqrt{\frac{mTL^2}{2\pi\hbar^2}} \equiv \frac{L}{\lambda_{\text{th}}(T)}.$$

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[9] If we were truly doing quantum physics, this switch would be an approximation that is valid when $\hbar^2\pi^2 \ll 2mTL^2$, which holds unless T or L is *extremely* small. In this regime, the function being summed above varies very smoothly as the integer k_i increases, for any k_i small enough to leave the exponential factor non-negligible. You can find further discussion of this in Section 6.7 of Dan Schroeder's *Introduction to Thermal Physics*.

In the last step we have made the notation more compact by defining the *thermal de Broglie wavelength* (named after Louis de Broglie),

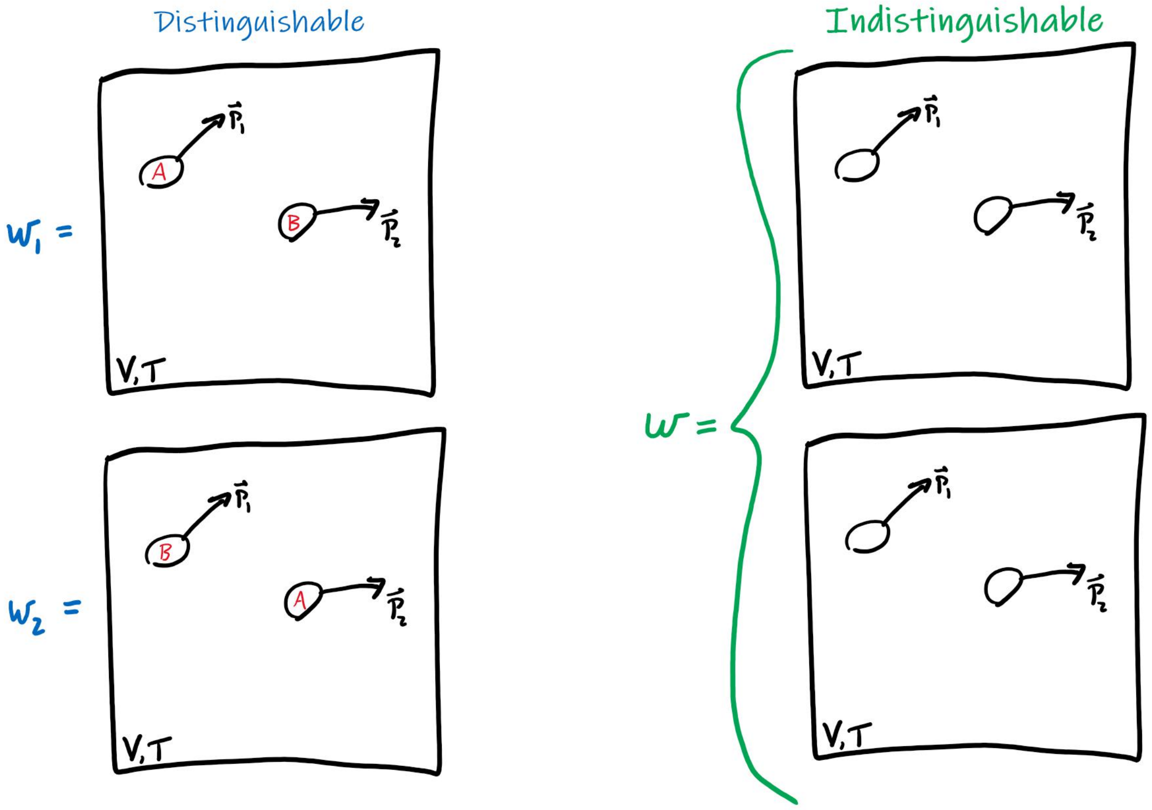
$$\lambda_{\text{th}}(T) = \sqrt{\frac{2\pi\hbar^2}{mT}}. \tag{49}$$

Performing all $3N$ gaussian integrals,

$$Z_D = \left(\frac{mTL^2}{2\pi\hbar^2}\right)^{3N/2} = \left(\frac{L}{\lambda_{\text{th}}}\right)^{3N} = \left(\frac{V}{\lambda_{\text{th}}^3}\right)^N, \tag{50}$$

since the volume of the box is $V = L^3$. It is worth emphasizing here that the partition function *depends on the volume of the gas*, in addition to the fixed temperature T and conserved particle number N. This dependence may persist in other quantities derived from the partition function, which we will consider in the next section.

First, let's determine what we would have with indistinguishable particles. For a classical gas, distinguishability means that we can label the particles and use those labels to tell them apart. In the simple two-particle example illustrated below, these labels mean we have a different micro-state ω_1 when particle A has momentum $\vec{p}_1$ while particle B has momentum $\vec{p}_2$, compared to micro-state ω_2 in which particle A has momentum $\vec{p}_2$ while particle B has momentum $\vec{p}_1$.



If the particles are indistinguishable, no such labeling is possible, and there is only one micro-state for these $\{\vec{p}_1, \vec{p}_2\}$, rather than two. This factor of 2 is not accidental, as you can explore by counting how many micro-states there are for three distinguishable particles with momenta $\{\vec{p}_1, \vec{p}_2, \vec{p}_3\}$, compared to the single micro-state for the indistinguishable case:

Generalizing to N particles, we find that ideal gases with distinguishable particles have $N!$ times more micro-states compared to otherwise-identical ideal gases with indistinguishable particles: There are N possible ways to label the particle with momentum $\vec{p}_1$, then $N-1$ possible labels for $\vec{p}_2$, and so on.[10] The partition function sums over these micro-states, but depends only on their energies, which are independent of any labeling. Therefore this factor of $N!$ is the only difference between Eq. 50 and the partition function for indistinguishable particles,

$$Z_I = \frac{1}{N!}\left(\frac{mTL^2}{2\pi\hbar^2}\right)^{3N/2} = \frac{1}{N!}\left(\frac{L}{\lambda_{\text{th}}}\right)^{3N} = \frac{1}{N!}\left(\frac{V}{\lambda_{\text{th}}^3}\right)^{N}. \tag{51}$$

4.2 Internal energy, and entropy

Now that we have the canonical partition function, let's apply our work from Unit 3 to predict the large-scale behaviour of the ideal gas it describes. Our first targets are the average internal energy $\langle E\rangle$ and entropy S for the gas, as functions of its fixed temperature T, conserved particle number N, and the volume $V = L^3$ of the box in which it is contained. Let's begin with the slightly more complicated case of indistinguishable particles, Eq. 51. Recalling the derivatives in Eqs. 38–39, we should keep the temperature dependence explicit in our workings, rather than hidden inside the thermal de Broglie wavelength $\lambda_{\text{th}}(T)$.

By writing down the Helmholtz free energy,

$$F_I = -T\log Z_I = -\frac{3NT}{2}\log\left(\frac{mTL^2}{2\pi\hbar^2}\right) + T\log\left(N!\right),$$

we can quickly extract the internal energy,

$$\langle E\rangle_I = -T^2\frac{\partial}{\partial T}\left(\frac{F_I}{T}\right) = -T^2\frac{\partial}{\partial T}\left(-\frac{3N}{2}\log T + T\text{-independent}\right) = \frac{3}{2}NT.$$

---

[10] This argument assumes the momenta themselves are distinguishable, $\vec{p}_i \neq \vec{p}_k$ for any $i \neq k$. This is a reliable assumption for classical gases with $L\sqrt{mT} \gg \hbar$, but will need to be revisited when we consider quantum statistics.

This in turn provides the entropy

$$S_I = \frac{\langle E \rangle_I - F_I}{T} = \frac{3}{2}N + \frac{3N}{2} \log\left(\frac{mTL^2}{2\pi\hbar^2}\right) - \log\left(N!\right).$$

We can clean this up by reintroducing the thermal de Broglie wavelength,

$$\frac{3N}{2} \log\left(\frac{mTL^2}{2\pi\hbar^2}\right) = \frac{3N}{2} \log\left(\frac{L^2}{\lambda_{\text{th}}^2}\right) = N \log\left(\frac{V}{\lambda_{\text{th}}^3}\right),$$

and by applying Stirling's formula to find

$$S_I = \frac{3}{2}N + N \log\left(\frac{V}{\lambda_{\text{th}}^3}\right) - N \log N + N = \frac{5}{2}N + N \log\left(\frac{V}{N\lambda_{\text{th}}^3}\right).$$

We can interpret $N\lambda_{\text{th}}^3$ as the volume 'occupied' by the N particles.

What are the corresponding results for the case of distinguishable particles, starting from Eq. 50 for the partition function Z_D?

$F_D =$

$\langle E \rangle_D =$

$S_D =$

You should find that the energy is the same whether or not we can label the particles:

$$\langle E \rangle_D = \langle E \rangle_I = \frac{3}{2}NT. \tag{52}$$

This agrees with the argument in the previous section that multiplying Z by a constant factor (here $N!$) does not change the internal energy expectation value.[11]

However, the entropy reflects the extra information that distinguishability provides:

$$S_D = \frac{3}{2}N + N \log\left(\frac{V}{\lambda_{\text{th}}^3}\right) \qquad\qquad S_I = \frac{5}{2}N + N \log\left(\frac{V}{N\lambda_{\text{th}}^3}\right). \tag{53}$$

---

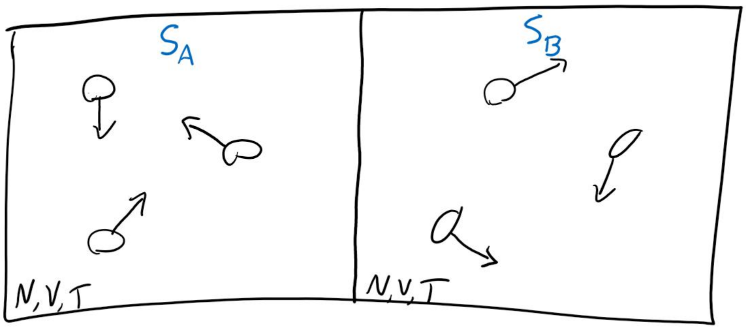
[11] The spin system we considered in Section 3.4 behaved differently because its number of distinguishable micro-states per indistinguishable micro-state was the energy-dependent binomial coefficient $\binom{N}{n_+}$. The energy dependence caused Z_D vs. Z_I to differ by more than a simple constant factor.

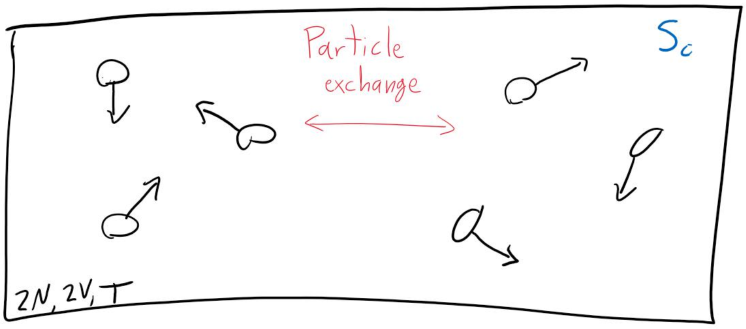
The difference $S_I - S_D = N - N\log N \to -\log(N!) < 0$, meaning $S_I < S_D$, as expected. We can also note that $\lambda_{\text{th}} \to \infty$ as the temperature approaches absolute zero, $T \to 0$, apparently producing negative entropies for fixed V. This is a warning sign that our classical assumptions are breaking down in this regime, and quantum effects would need to be taken into account.

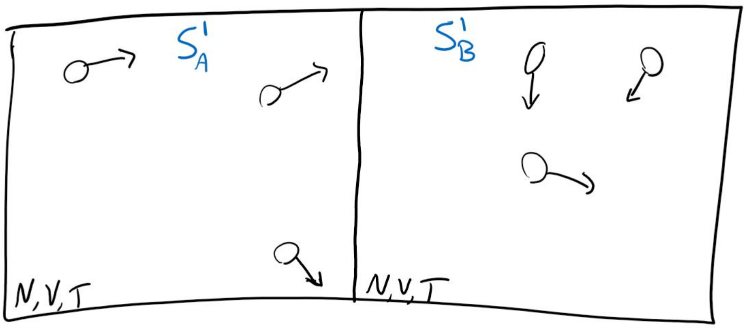
4.3 The mixing entropy and the 'Gibbs paradox'

In Section 2.4 we analysed what would happen if we allowed two micro-canonical systems to exchange energy, and then re-isolated them. We saw that this procedure obeys the second law of thermodynamics — the entropy never decreases, though we have to be careful to account for all of the entropy after re-isolating the two systems.

We can now carry out a similar thought experiment of allowing two *canonical* systems to exchange *particles*, and then re-separating them. We demand that both canonical ensembles are in thermodynamic equilibrium with each other, for instance by sharing the same thermal reservoir with temperature T. This procedure is illustrated below, where we simplify the setup by taking the two initial systems to have equal volumes, $V_A = V_B = V$, and numbers of particles, $N_A = N_B = N$.







We can represent the process of combining and re-separating these systems as

$$\Omega_A + \Omega_B \longrightarrow \Omega_C \longrightarrow \Omega_A' + \Omega_B'.$$

What is the entropy for each of these three stages? Since the entropies depend on whether or not the particles in the gas are distinguishable from each other, let's first consider the case of *indistinguishable* particles.

The initial entropy is the sum of the contributions from the two canonical systems, $S_A + S_B$, both of which are the same thanks to our simplification above:

$S_A + S_B =$

To find the entropy S_C of the combined system, we just need to consider what happens when we double the volume and also double the number of particles:

$S_C =$

You should find $S_C = S_A + S_B$, which is consistent with the second law.

Things are more complicated when we re-separate the systems. Analogously to our considerations in Section 2.4, we need to sum over all the possible ways of dividing the $2N$ indistinguishable particles between the two re-separated boxes. In particular, we need to perform this sum at the stage of computing the partition function Z' for $\Omega_A' + \Omega_B'$, since this is the fundamental quantity from which the entropy is then derived as $S' = \frac{\partial}{\partial T}\left(T \log Z'\right)$. In other words, we have to consider a logarithm of a sum rather than a sum of logarithms.

If ν particles end up in system Ω_A', then the other system Ω_B' must contain the remaining $2N - \nu$ particles, giving us

$$Z_\nu = \frac{1}{\nu!}\left(\frac{V}{\lambda_{\text{th}}^3}\right)^{\nu} \times \frac{1}{(2N-\nu)!}\left(\frac{V}{\lambda_{\text{th}}^3}\right)^{2N-\nu} = \frac{1}{\nu!\,(2N-\nu)!}\left(\frac{V}{\lambda_{\text{th}}^3}\right)^{2N}.$$

Summing over all possible values of $0 \leq \nu \leq 2N$,

$$Z' = \sum_{\nu=0}^{2N} Z_\nu = \left(\frac{V}{\lambda_{\text{th}}^3}\right)^{2N} \sum_{\nu=0}^{2N} \frac{1}{\nu!\,(2N-\nu)!} = \left(\frac{V}{\lambda_{\text{th}}^3}\right)^{2N} \frac{1}{(2N)!} \sum_{\nu=0}^{2N} \binom{2N}{\nu}$$

$$\Longrightarrow S_A' + S_B' = 2N \frac{\partial}{\partial T}\left(T \log\left[\frac{V}{\lambda_{\text{th}}^3}\right]\right) - \log[(2N)!] + \log\left[\sum_{\nu=0}^{2N} \binom{2N}{\nu}\right].$$

This is a complicated expression. In the 1870s, Gibbs introduced the following argument that helps to simplify it, which we will explore further in tutorials: For large $N \gg 1$, the entropy of the two subsystems is nearly saturated by the case in which the particles are divided roughly evenly between them, rather than being mostly in one of them. Equivalently, there are far more micro-states with $N'_A \approx N'_B \approx N$, compared to all other terms in the sum above.

Therefore we can safely set $N'_A = N'_B = N$, which was already incorporated into the illustration above.[12] This means $\Omega'_A = \Omega_A$ and $\Omega'_B = \Omega_B$, producing a final entropy of $S'_A + S'_B = S_A + S_B$ that satisfies the second law:

$$S'_A + S'_B = S_C = S_A + S_B.$$

This is just what we would expect from everyday experience: Opening a door between two identical rooms doesn't produce any observable effects, nor does reversing that process by closing the door.

Something interesting happens when we repeat this analysis for the case of *distinguishable* particles, using our result for $S_D(N, V)$ in Eq. 53. If we consider the difference between the combined entropy S_C and the initial entropy $S_A + S_B$,

$$\begin{aligned}\Delta S_{\text{mix}} &= S_C - (S_A + S_B) = S_D(2N, 2V) - 2S_D(N, V) \\ &= 3N + 2N \log\left(\frac{2V}{\lambda_{\text{th}}^3}\right) - \left[3N + 2N \log\left(\frac{V}{\lambda_{\text{th}}^3}\right)\right] = 2N \log 2 > 0, \end{aligned} \qquad (54)$$

we find the entropy increases upon combining the two initial systems. This $\Delta S_{\text{mix}} > 0$ is known as the **mixing entropy**.

This result $S_C > S_A + S_B$ is to be expected from the second law of thermodynamics. However, repeating the argument above — that we should have $N'_A \approx N'_B \approx N$ leading to $S'_A + S'_B = S_A + S_B$ after re-separating the systems — would produce the prediction $S'_A + S'_B < S_C$, indicating a *decrease* in the entropy by ΔS_{mix} and an apparent violation of the second law. This is known as the 'Gibbs paradox', though Gibbs himself explained how a paradox is avoided.

The explanation is that because the particles are now distinguishable, $N'_A = N_A$ no longer suffices to establish $\Omega'_A = \Omega_A$ and $S'_A = S_A$. Recovering Ω_A would additionally require that the N'_A particles in the re-separated system are the *same* distinguishable particles that were initially in Ω_A. While we can still expect $N'_A \approx N'_B \approx N$, the vast majority of the resulting micro-states will not correspond to micro-states of Ω_A and Ω_B. Summing over these additional possibilities ensures $S'_A + S'_B > S_A + S_B$, and it turns out $S'_A + S'_B \geq S_C$ as well, obeying the second law of thermodynamics.

These thought experiments provide another example of behaviour that depends on the intrinsic information content of the system — whether or not the particles in an ideal gas can be distinguished from each other in principle. Mixing gases of distinguishable particles introduces a positive mixing entropy, Eq. 54, but for gases of indistinguishable particles there is no change in entropy when we let two subsystems mix, or when we reverse that process and re-separate them. Due to the second law, processes that produce an increase in entropy are irreversible.

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[12] Formally this is only exact in the *thermodynamic limit* $N \to \infty$, a concept we will discuss in Unit 9.

4.4 Pressure, ideal gas law, and equations of state

Below Eq. 50 we emphasized that the ideal gas partition function depends on the volume of the gas, V, in addition to the fixed temperature T and conserved particle number N that always characterize systems governed by the canonical ensemble. Parameters like V that appear in the partition function are called **control parameters**, with the idea that they can (in principle) be controlled in experiments. Control parameters generally enter the partition function through the definition of the energies E_i for the micro-states ω_i. Another example is the magnetic field strength H for the spin systems we considered earlier.

Focusing on ideal gases for now, we see that all dependence on V drops out in our results for the average internal energy, Eq. 52. On the other hand, the entropies in Eq. 53 do depend on the volume. For both cases of distinguishable and indistinguishable particles, the entropy S depends on the same combination of volume and temperature: $V\lambda_{\text{th}}^{-3} \propto VT^{3/2}$. If we keep N fixed and consider using our experimental control to change the volume and the temperature of the system, the entropy will typically change as a consequence, unless the following relation is satisfied:

$$VT^{3/2} = \text{constant} \qquad \Longrightarrow \qquad S = \text{constant}.$$

Such **constant-entropy (or isentropic) processes** will be important in our upcoming analyses of thermodynamic cycles.[13] These cycles will involve making changes to control parameters, which is a topic we have already started to consider through the micro-canonical temperature (Eq. 22) and the canonical heat capacity (Eq. 36). The pressure of an ideal gas is similarly connected to a change in its volume, which we can motivate by thinking about squeezing an inflated balloon into a small box.

The **pressure** is defined to be

$$P = -\frac{\partial}{\partial V}\left\langle E \right\rangle\Big|_S, \tag{55}$$

with constant entropy S. In words, the pressure is the isentropic response of the system's internal energy to a change in its volume.

In Unit 5 we will look in detail at processes that change some or all of the pressure, volume, temperature, or internal energy of an ideal gas, with N fixed. Although changing the temperature departs from the assumptions of the canonical ensemble, we will be able to analyse such a process as a change from one canonical system (in thermodynamic equilibrium with a thermal reservoir that fixes the initial temperature T_0) to another (in thermodynamic equilibrium with a different thermal reservoir that fixes the final temperature T_f).

If we consider an isentropic process with N fixed, then the temperature and volume are related,

$$VT^{3/2} = c^{3/2} \qquad \longrightarrow \qquad T = cV^{-2/3},$$

---

[13] The term *isentropic* is based on the Greek word $\iota\sigma o\varsigma$ ("isos"), meaning "equal".

with c a constant. By inserting this into Eq. 52, we can relate the average internal energy to the volume,

$$\langle E\rangle = \frac{3}{2}NT = \frac{3c}{2}NV^{-2/3} \qquad \text{for constant entropy.}$$

Using this constant-entropy expression, what is the pressure for the ideal gas?

$$P = -\left.\frac{\partial}{\partial V}\langle E\rangle\right|_S =$$

You should find the **ideal gas law**,

$$PV = NT, \tag{56}$$

which is an example of an **equation of state**.

The "state" referred to by this terminology is different from the micro-states that we have mostly discussed up until now. Whereas each micro-state is defined by detailed information about the microscopic degrees of freedom that constitute the system, this **macro-state** concerns only the large-scale (*macroscopic*) properties of the system, such as its pressure, volume, temperature, entropy, or internal energy. (Macro-states are sometimes called "system states" or "thermodynamic states".) Equations of state are relations between these large-scale properties.

Historically, equations of state were observed empirically and studied experimentally well before the mathematical development of statistical mechanics. In the 1660s, for instance, Robert Boyle experimented with changing the pressure of a gas while holding its temperature fixed, finding a special case of the ideal gas law,

$$PV = \text{constant} \qquad \text{for constant } N \text{ and } T,$$

which became known as "Boyle's law". (I include the quotation marks to emphasize the limitations of assigning an individual sole credit for advances arising from the work of broad scientific communities.)

Other equations of state reflecting different aspects of the ideal gas law were uncovered during the Industrial Revolution:

- $\frac{V}{T} = \text{constant}$ for constant N and P (1787, "Charles's law")

- $\dfrac{P}{T} = $ constant for constant N and V (1802, "Gay-Lussac's law")
- $\dfrac{V}{N} = $ constant for constant P and T (1812, "Avogadro's law")

In the 1830s Émile Clapeyron combined these empirical results into the ideal gas law itself, which August Krönig and Rudolf Clausius independently derived on the basis of statistical mechanics in the 1850s. These historical considerations are useful to illustrate how progress in scientific and mathematical understanding went hand-in-hand with industrial developments, including the design of engines and related machines, which are connected to our next topic of thermodynamic cycles.