Statistical Physics

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Contents

0.1 Logistics

This document will be the companion document in your journey through introductory statistical mechanics.

We will be following

- Mehran Kardar's book "Statistical Physics of Particles".
- Much of the material in that book can be found in his course website: `https://web.mit.edu/8.333/www/`, under Lecture Notes, or in `https://ocw.mit.edu/courses/8-333-statistical-mechanics-i-statistical-mechanics-of-particles-fall-2013/pages/lecture-notes/`.
- The corresponding lecture videos by Mehran Kardar can be found in `https://www.youtube.com/playlist?list=PLUl4u3cNGP60gl3fdUTKRrt5t_GPx2sRg`.

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We will only focus on a **small** subset of the material covered in that course. Even though the lecture notes are sufficient, the book is more pleasant to read, because of nice illustrations and better typography. Reach out to me if you'd like an e-copy of the book.

Every week, I will post the link to the lecture note to read. Please also read the corresponding reading guide that will summarise the main points that I want you to absorb from the reading materials. To aid in our understanding, I will also post a set of discussion questions which I encourage you to solve / think about beforehand. I have listed the youtube videos just as an extra resource; you are not expected to have watched them before our meetings.

0.2 Why this topic?

Why study statistical physics? In physics, we are often taught the laws of motion: both from classical and quantum mechanics. These laws are almost always reversible (think about the differential equations governing Newton's laws and Schrodinger's equations). If we reverse the direction of time, the motion is backward. But if we see the world, when the number of constituent particles are large (any macroscopic object), and when we are not looking too closely at each particle (our observables are macroscopic), physical observables seem to irreversibly flow towards equilibrium. Once in equilibrium, they tend to stay there, and never go back to their initial conditions. Thermodynamics is a consistent theory that describes this behaviour. Statistical Mechanics is a theory that describes how this situation arises from the microscopic classical or quantum mechanics.

The plan for the bridge program is as follows:

1. Thermodynamics
2. Foundations of statistical mechanics
3. Ideal gas and equivalence of ensembles
4. Quantum Statistical Mechanics
5. Ideal Quantum Gases

0.3 Reading guide

While reading the weekly materials, remember that this is a graduate level text book; so don't feel disheartened if you don't fully understand the concepts. To help you grasp the logic (even if some of the details elude you at the beginning) I will provide some reading guide for each week.

In the reading guide, the whole material is divided into sections. For each section, I will provide a short **Context** that you should read *before* the material, along with a short **Learning goals** and , that you should read *after* going through that part of the material at least once.

It will be typically impossible to remember everything you read in these sections. So, at the end of the reading guide, I will add the **essential summary** for each section. This is what you should try to remember from each section. This will be followed by some **Problems** that you should attempt to solve before our online session.

0.4 Project

There are many many problems in many different areas of physics where ideas of statistical physics are useful. As a final exercise for this course, I want everyone to find one problem that they are interested in and try to solve it. You can look at the problems at the end of a chapter of your favorite books or online resources, and select one problem that appeals to you. I want you to understand the problem, try to solve it, and write up your attempts. At the end of the module, you will present the problem and your attempts to your colleagues. The idea is not to solve it correcly or even completely, but explain what the problem is, and how you think you may be able to tackle it using the tools developed in this course.

For example, if you are interested in astrophysics, you may be interested in a problem involving the thermodynamics of stars. If you are interested in statistics, you may be interested in the problem of random walks and how ideas of statistical mechanics can be applied to it. I also expect you to maintain an honor code and not look up solutions if they are available.

1 Thermodynamics

1.1 Reading Materials

The material can be found in Lecs 1-3 in `https://web.mit.edu/8.333/www/lectures/index.html`. Alternatively, you can read Pages 1-22 of the book ”Statistical Physics of Particles”.

1.2 Reading Guide

In the following, I will divide the reading material into the following sections.

1.2.1 Introduction and the zeroth law

Context:

Thermodynamics is an empirical theory: a self-consistent theory for many observed phenomena in real life, where simple observables of many particles tend to approach equilibrium under their own dynamics. This theory is not necessarily derivable from microscopic laws of physics; and more interestingly, can sometimes not apply to certain physical situations! While reading this section, think of examples such as,

1. If you add a drop of ink to a corner of a cup of water at room temperature, it mixes and swirls, and in sometime the entire liquid turns uniformly colored.
2. If you have an empty can at room temperature and introduce some gas through the nozzle, in some time the gas occupies the whole volume, and has a constant pressure after the gas has equilibriated.
3. If a Metallic conductor is connected to a battery across its ends, the current settles into a constant value after an initial transient behavior.
4. Many, many more instances ...

In this reading material, we first formalize this understanding into a law of thermodynamics, which describes the fundamental phenomenological property of equilibrium.

Section 1.1 and 1.2 of book / IA, IB, of lecture notes.

Learning goals:

- Understand how zeroth law of thermodynamics implies the definition of an empirical equation of state (1.6) and defines “temperature” Θ.
- Understand the meaning of ideal gas temperature scale, which provides a universal scale of temperature.

1.2.2 First law

Context:

Here you will learn about the first law of thermodynamics, which is a restatement of the conservation law of energy. Look out for the meaning of notions such as adiabatic, state functions, work, heat, and internal energy.

Note, you don't have to remember the meaning of the many terms introduced (especially the different response functions), but try to understand their meanings.

Section 1.3 of the book / IC of lecture notes.

Learning goals:

- Meaning of useful "work" versus useless "heat". Meaning of state function. Understand why the notation $đQ$ and $đW$ is different from dW.
- Understand the meaning of "generalized forces" and "generalized displacements". Understand the definition of extensive/ intensive quantities.
- Understand the concept of thermodynamic response functions (heat capacities, force constants, and thermal responses.

1.2.3 Second law

Context:

Here you will learn about the second law of thermodynamics, which codifies the meaning of irreversibility of thermodynamics, as well as defines the concept of entropy.

Section 1.4-1.6 of the book/ lecture notes.

Learning goals:

- Understand the diagrams for heat engines and refrigerators.
- How do the two second law statements follow from each other?
- How does one prove Carnot's theorem from the second law?
- Clausius's theorem and its proof using second law.
- Implications of Clausius's theorem and the definition of entropy.
- The fundamental identity of thermodynamics for reversible / quasi-static processes: $dE = TdS + \sum_i \mathbf{J}_i \mathbf{x}_i$. For example, for gas, $dE = TdS - PdV + \mu dN$.

1.2.4 Approach to equilibrium and thermodynamic potential

Context:

We postulated from zeroth. first, and second law that systems flow to equilibrium. Furthermore, we realized in the last section that in adiabatically isolated systems, the equilibrium state is the one that maximises entropy. But in real-life examples, our system is not often isolated, and exchanges heat and work with the environment. What is the equilibrium state then? In this section, we will define other thermodynamic potentials, that generalizes the maximization of entropy concept. Beware, this introduces a *lot* of new terminology, and is generally very difficult to remember. Your strategy, as ever, should be trying to understand the concept rather than remember the details.

Section 1.7 of the book/ I.G of lecture notes.

Learning goals:

- Understand the physical context where the different thermodynamic potentials arise. Understand Table 1.2.

1.3 Summary

1. 0th law leads to the definition of temperature
2. 1st law is conservation of energy, heat and work are not state functions; but the total heat input minus the total work output (or total heat input plus the total work input) is the total change in internal energy, which is a state function.
3. 2nd law leads to a definition of entropy, $S(B) - S(A) \equiv \int_A^B \frac{đQ_{\text{rev}}}{T}$, and the fact that entropy always increases in a system undergoing a thermodynamic process when there is no heat exchange with the environment. Equilibrium is reached in a closed system by maximizing entropy, $\delta S \geq 0$.
4. Fundamental equation of thermodynamics: for any reversible slow process close to equilibrium, the change in internal energy is:

   $$dE = TdS - PdV + \mu dN + ..., \tag{1.3.1}$$

   where all the quantities are state functions.
5. How does equilibrium change when there is a constant external force, or there is heat exchange with the environment? Under all these conditions, we can introduce new thermodynamic potentials (such as enthalpy, Gibbs free energy, Helmholtz free energy etc), which are to be minimized to reach the equilibrium. At equilibrium, if there is any further infinitesemal change in the state functions, there is a similar equation as above for its variation.

1.4 Problems

Problem 1.1: Irreversible processes

1. Consider two substances, initially at temperatures T_1^0 and T_2^0, coming to equilibrium at a final temperature T_f through heat exchange. By relating the direction of heat flow to the temperature difference, show that the change in the total entropy, which can be written as

   $$\Delta S = \Delta S_1 + \Delta S_2 \geq \int_{T_1^0}^{T_f} \frac{đQ_1}{T_1} + \int_{T_2^0}^{T_f} \frac{đQ_2}{T_2} = \int \frac{T_1 - T_2}{T_1 T_2} đQ,$$

   must be positive. First, prove the above equation, and then show that the integrand is positive; so $\Delta S \geq 0$.

   This is an example of the more general condition that "in a closed system, equilibrium is characterized by the maximum value of entropy S."

   Hint: Heat will flow from the hotter object to the colder object. Assume one object is hotter than the other. Next, try to use Clausius's theorem. Recall, that theorem applies to cyclic processes and the definition of entropy requires $đQ_{rev}$ for reversible processes.

2. Now consider a gas with adjustable volume V, and diathermal walls, embedded in a heat bath of constant temperature T, and fixed pressure P. The change in the entropy of the bath is given by

   $$\Delta S_{\text{bath}} = \frac{\Delta Q_{\text{bath}}}{T} = -\frac{\Delta Q_{\text{gas}}}{T} = -\frac{1}{T}(\Delta E_{\text{gas}} + P\Delta V_{\text{gas}}).$$

   By considering the change in entropy of the combined system establish that "the equilibrium of a gas at fixed T and P is characterized by the minimum of the Gibbs free energy $G = E + PV - TS$."

   Hint: The system and bath together can be considered as a closed system. So, $\Delta S_{gas} + \Delta S_{bath} \geq 0$ from previous part.

Problem 1.2: Chemical equilibrium and law of mass action

Suppose two chemical species, A and B, undergo the reaction $2A \leftrightarrow B$. Assume the equation of state of A and B is that of an ideal gas. For an ideal gas, the chemical potential μ is given in terms of number of molecules N, volume V and temperature T, as,

$$\mu = -k_B T \log \frac{T^{3/2} V}{\alpha N} + \frac{5 k_B T}{2},$$

where k_B is the Boltzmann constant, and α is gas dependent constant.

The two species are placed in a container held at fixed temperature and pressure and allowed to come to equilibrium. We will compute the equilibrium ratio of densities of the two species. Species i has N_i molecules and density $\rho_i = N_i/V$.

1. What should be the relation between μ_A and μ_B for the chemical equilibrium between the two species?

   Hint: $N_A + 2N_B$ *is conserved by the dynamics. Minimize the Gibbs free energy with respect to variations in* N_A *and* N_B*.*

2. Determine the relationship between the equilibrium densities ρ_A and ρ_B.

   Hint: Use the expression for the chemical potential for ideal gas. Your formula will involve α_A *and* α_B*.*

2 Foundations of statistical mechanics

2.1 Reading Materials

The material will be parts of Lecs 7 and 12 in `https://web.mit.edu/8.333/www/lectures/index.html`. Alternatively, you can read Pages 57-62 and 98-102 of the book ”Statistical Physics of Particles”.

2.2 Reading Guide

In the following, I will divide the reading material into the following sections.

2.2.1 General definitions

Context:

We want to justify the empirical observations of thermodynamics, that macroscopic quantities equilibriate (i.e. they reach a steady value), by starting from equations of motion for a *large* number of particles. However, before that we first need to define what equilibrium is! At first glance, it is surprising that things equilibriate in the absence of an external force: isn't that exactly what Newton's laws forbid? The resolution is that when we think of equilibriation, we are considering only the equilibriation of very coarse-grained observables, such as pressure and volume and temperature, and not properties of individual atoms or molecules.

This naturally leads to the idea of ensembles of macrostates, which will be very useful for statistical mechanics. This also explains why we use the word‘statistical’: we are considering averages of *many* variables. In this section you will encounter the ideas of phase space, microstates, macrostates, and ensemble averages.

Try to understand the questions posed at the beginning of the section. In this module we will only focus on the first question. The rest of the chapter (which we will not cover here) addresses the (possibly more interesting) last two questions.

Section 3.1 of book / III A of Lecture Notes.

2.2.2 Liouville's theorem

Context:

We will answer the first question by understanding the Liouville's theorem. Even if the proof is a bit confusing (and you can skip it at first), try to understand the meaning of Eq 14 (the basic assumption of statistical mechanics).

Also when you are reading the proof the theorem (which leads up to equations 9, 10), note the difference between the total derivative $\frac{d\rho}{dt}$ and partial derivative $\frac{\partial\rho}{\partial t}$. If $\rho(t,x)$ is function of (t,x), the first quantity refers to the time derivative of ρ as we move along the trajectory $x(t)$. The second quantity refers to the time derivative at a fixed position x.

More important than the proof of Liouville's theorem, are its consequences: especially the points 3 and 4 mentioned after the proof. Even if you skip the proof, read on for the consequences!

Section 3.2 of book / III B of Lecture Notes.

Comment:

Now, we will bypass the rest of the discussions on kinetic theory that attempts to answer the 2nd and 3rd questions posed in the beginning: how and when equilibrium is reached. This discussion gets fairly technical; but the underlying mechanism is the emergence of irreversibility due to 'the assumption of molecular chaos'. This is a fascinating topic, which I encourage you to explore after the course.

2.2.3 General definitions and the microcanonical ensemble

Context:

The Liouville's theorem and the description of equilibrium of ensembles lead to the central postulate of statistical mechanics (eq 1 in this section): at equilibrium, all microstates that are consistent with a particular constraint are equally likely. The constraint may just be energy, for example, if the total energy is conserved.

Note, try to understand the meaning of the normalization factor $\Omega(E, \mathbf{x})$ as the number of accessible microstates. Also, Eq 2 defines the entropy of a probability distribution (which turns out to be related to the thermodynamic entropy we studied earlier). Read more about entropy of probability distributions in Wikipedia.

Kardar goes on to show how all the laws of thermodynamics follow from eq 1 and 2. It is fascinating, but don't get too disheartened if you don't understand all of it. We will study this with examples in the rest of the course.

Section 4.1 and 4.2 of book / IV A and IV B of Lecture Notes.

2.3 Summary

1. Ensembles of microstates
2. Liouville's theorem and equilibrium
3. Microcanonical ensemble

2.4 Problems

Problem 2.1: Statistical mechanics from coin flips: Consider a biased coin, which flips to Heads (H) with probability p and Tails (T) with probability $1-p$. We will consider the statistics of the outcome of $N \gg 1$ flips of this coin. There are two situations: (1) I can flip a single coin N times and gather its statistic, or (2) I can flip

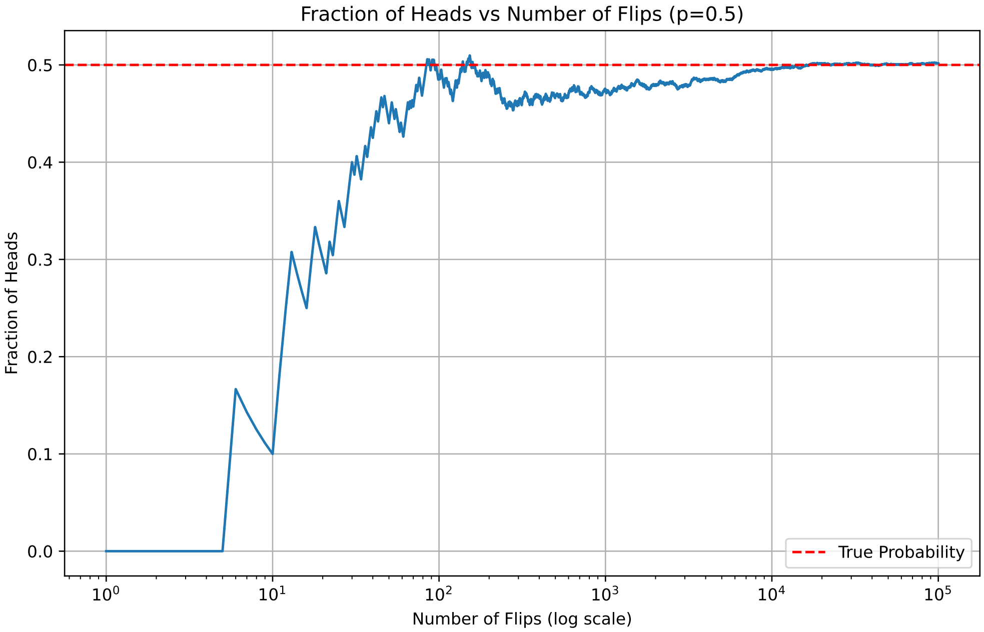

Figure 2.4.1: Statistical Mechanics from coin flips: a single experiment of N coin flips. The fraction of H is plotted.

an *ensemble* of N coins and flip them and gather its statistic. Ergodic hypothesis says that as $N \gg 1$, (certain) time averaged quantities from will converge to the ensemble averaged quantities from (2). The quantity we consider is the fraction of H obtained in N flips, as I increase N.

The ergodic hypothesis can be viewed in this numerical plot of a particular experiment in Fig. 2.4.1. We find that the fraction equilibriates to a steady state value. Here we will show that the steady state value is actually the ensemble average.

1. Suppose we have N coin flips, and have found there are m heads and $N - m$ tails. What is the probability of *any a specific sequence of H and T* has this property? How many such sequences are there with this property? What is the probability that in an experiment we obtain m heads, $P(m)$?

   Hint: Note the subtle differences in the first and third sub-questions. The answers should remind you of the fundamental assumption of statistical mechanics: all accessible microstates are equally likely for a given macrostate. Here, a microstate is any sequence of coin flip outcomes, while a macrostate is a collection of sequences which all have m Heads.

2. At what value of m is the probability $P(m)$ maximized?

   Hint: Consider $\log P(m)$*, and use Stirling's approximation,*

$$\log Q! \approx Q \log \frac{Q}{e}$$

for $Q \gg 1$. This approximation will be our friend for the rest of our course!

3. What is the expected value ('mean') of the number of heads, i.e. $\overline{m} = \sum_{m=0}^{N} mP(m)$? What is the variance of the expected number of heads, defined as $\mathrm{var}_m = \sum_{m=0}^{N}(m-\overline{m})^2 P(m)$? How does the standard deviation (square root of the variance) compare to the mean, $\overline{m}$, at large N?

   Comment: You may have seen this in statistics as 'central limit theorem'. These two problems require some mathematical trickery to solve, so don't spend too much time on this if you don't know already. But the answer is physically important. You will find that $\overline{m}$ is proportional to N, but the standard deviation is proportional to $\sqrt{N}$, so much smaller than the mean, when $N \gg 1$

Problem 2.2: Quantum harmonic oscillators: Consider N independent quantum oscillators subject to a Hamiltonian

$$\mathcal{H}(\{n_i\}) = \sum_{i=1}^{N} \hbar\omega \left(n_i + \frac{1}{2}\right),$$

where $n_i = 0, 1, 2, \cdots$ is the quantum occupation number for the ith oscillator.

1. Calculate the entropy S, as a function of the total energy E.

   Hint: You have to count $\Omega(E)$, the number of microstates with energy E. Assume $N \gg 1$. This combinatorial problem can also be regarded as the number of ways of rearranging $M = \sum_i n_i$ balls, and $N-1$ partitions along a line. Then use $S = k_B \log \Omega$.

2. Calculate the temperature using thermodynamics relation between entropy and energy.

   Hint: Use Stirling's approximation,

   $$\log Q! \approx Q \log \frac{Q}{e}$$

   for $Q \gg 1$, to find a simple expression using

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

3. Calculate the energy E, and heat capacity C, as functions of temperature T, and N.

   Hint: Heat capacity is defined as $C = \frac{\partial E}{\partial T}$. Invert the previous result (after Stirling's approximation) to obtain this result.

4. Plot $\frac{C}{Nk_B}$ for a fixed value of ω (choosing $\hbar/k_B$, as a function of T. What is it's behavior at high T? This is exactly the behavior expected for classical harmonic oscillators.

   Hint: Heat capacity is defined as $C = \frac{\partial E}{\partial T}$. *Invert the previous result to obtain this result.*

3 Classical statistical mechanics

3.1 Reading Materials

The material will be parts of Lecs 13 and 14 (only example 2 in Section IV G) in `https://web.mit.edu/8.333/www/lectures/index.html`. Alternatively, you can read Pages 105-115 of the book ”Statistical Physics of Particles”.

3.2 Reading Guide

In the following, I will divide the reading material into the following sections. This week, we will learn about how to use the microcanonical ensemble to derive the ideal gas law (which turns out to require lots of computations). Then we introduce a different ensemble, namely the canonical ensemble, using which we can derive the results very easily. Incredibly, the answers from both approaches give the same answer!

3.2.1 The ideal gas

Context:

Recall the microcanonical ensemble that we studied last time. We will use that for ideal classical gas (point particles buzzing around without any inter-particle interactions). Note, this section requires you to perform lots of integrals, which may look nasty at first, but are actually some of the few integrals we can perform exactly. It will be useful to keep the Wikipedia page on Gaussian integrals open. The strategy we will follow is as follows: we use the microcanonical ensemble to count the number of microstates $\Omega(E, V, N)$ (using multi-dimensional integral), then use the entropy relation $S = k_B \log \Omega$ to find entropy $S(E, V, N)$. Next, we use thermodynamics to derive the gas laws. Pause to appreciate the derivation of a *macroscopic* law of physics from microscopic physics and statistical methods, even though the calculation may seem messy.

To derive the expression for pressure P, temperature T. recall the basic thermodynamics equation, $dE = TdS - PdV + \mu dN$; from which it follows that, $T^{-1} = \frac{\partial S}{\partial E}$ and $P/T = \frac{\partial S}{\partial V}$.

Section 4.4 in the book / IV D of Notes.

3.2.2 Gibbs paradox

Context:

We just learnt that the ideal gas laws can be derived using the microcanonical ensemble. But, if we look carefully, we will find that the entropy derived in Eq 33 is not ‘extensive’! This means, that suppose I scale $E, V, N \to \lambda E, \lambda V, \lambda N$, entropy S should have scaled as $S \to \lambda S$, but, the expression has some extra factors.

This is one of the first ‘puzzles’ that is eventually solved by using quantum mechanics rather than classical mechanics. But amazingly, Gibbs, pre-empted Quantum mechanics by many decades, by putting a ‘fudge’ factor in the number of microstates $\Omega \to \Omega/N!$. This is resolved in what is called the ‘Gibbs paradox’. This following reading material tries to justify this, but honestly, it is only satisfactorily justified when we use quantum mechanics and combine that with stat mech later.

Quantum mechanics enters another way in the expression! Notice that we are presenting the ’number’ of microstates as an integral over the position and momentum of each particle, $\prod_{i=1}^{N} \int d^3q_i d^3p_i$. But, a number has no dimension, while the integrand has the dimension of Momentum times position (also called ‘action’), raised to $3N$, 3 coming from the number of dimensions, and N coming from the number of particles. So, this dimension has to be normalized, and at this stage we have to introduce an ad-hoc constant of dimension of action, h to normalize the integral, as shown in eq 51. This is ad-hoc in classical physics, but turns out to be nothing but the Planck’s constant in quantum physics! So statistical mechanics pre-empted quantum mechanics in many ways (we will see more examples later in the course).

So, you may skip some of the details justifying this expression using classical mechanics in this section (since the true justification is quantum!). But make sure you understand why the modified expression for the entropy is extensive! Also check, that the ideal gas laws we derived are not modified.

Sec 4.5 of book / IV E of Notes.

3.2.3 Canonical ensemble

Context:

Microcanonical ensemble is nice, but cumbersome to work with. Now we introduce another ensemble (recall ensmeble is a collection of microstates with some probability distribution). The canonical ensemble arises naturally when the system exchanges energy with a reservoir fixed at temperature T.

This part of the reading is conceptually dense, but quite important. Focus on understanding the definition of partition function (Eq 57), the canonical probability distribution (Eq 56), relation between partition function and free energy (Eqs. 60-63). The discussion after Eq 63 is important but a bit technical: the upshot is that the probability is highly peaked, so many computations can be done using its most likely argument.

Sec 4.6 of book / IV F of Notes.

3.2.4 Ideal gas in canonical ensemble

Context:

Next we will learn about how to use the canonical ensemble to derive the ideal gas laws. Its important to follow this computation fully, and will also be added as an exercise. Note how $Z[T, V, N]$ is computed in Eq 79 and 80. Then as before, we use thermodynamics to derive the macroscopic quantities. Since the partition function is related to the Helmoholtz Free energy, we recall the thermodynamic relation, $dF = -SdT - PdV + \mu dN$.

3.3 Problems

Problem 3.1:

Microcanonical and canonical ensemble from information entropy: In this problem we will connect the idea of entropy from information theory with the thermodynamic entropy. For a probability distribution $\{p_i\}$ with $i = 1, 2, \cdots, N$ outcomes, the Shannon entropy is defined as $H(\{p_i\}) = -\sum_i p_i \log p_i$ (with the identification $0 \log 0 = 0$). This captures the amount of uncertainty in the probability distribution: if probability is 1 for a particular outcome (totally certain), the entropy is 0; while if the probability of all outcomes are the same i.e. $p_i = 1/N$(totally uncertain), the entropy is its maximum $\log N$ (you will show this in the problem). This concept was discovered by Gibbs in the context of thermodynamics, reinterpreted in quantum mechanics by von Neumann, and rediscovered by Shannon in information theory.

1. We want to derive the microcanonical ensemble as the probability distribution that maximizes entropy. Maximize $H(\{p_i\})$ with the constraint that the probabilities must sum to 1, i.e. $\sum_i p_i = 1$. What is the entropy of this probability distribution? Compare this with the microcanonical entropy $S = k_B \log \Omega$, where Ω (number of microstates) and N (number of outcomes) should be analogous.

   Hint: Use Lagrange multipliers to extremize the functional $H(\{p_i\}) - A(\sum_i p_i - 1)$ *with respect to* p_i*, where the Lagrange multiplier* A *can be set to impose the constraint.*

2. Next, we maximize the entropy with the constraint that the average energy of the distribution is fixed. Assign some energy E_i to every outcome i, and demand that $\sum_i p_i E_i = E$ is fixed, while the entropy is to be maximized. What is the probability distribution $\{p_i\}$ that satisfies this?

   Hint: Use Lagrange multipliers to extremize the functional $H(\{p_i\}) - A(\sum_i p_i - 1) - B(\sum_i p_i E_i)$ *with respect to* p_i *, and Lagrange multipliers* A *(that sets the normalization) and* B *(that sets the energy constraint). You will find that* $p_i = \frac{e^{-BE_i}}{\sum_i e^{-BE_i}}$*, where* B *is fixed by the equation* $\sum_i \frac{E_i e^{-BE_i}}{\sum_j e^{-BE_j}} = E$*. Identify* B *with the inverse temperature* $\beta = (k_B T)^{-1}$*, and out pops the canonical ensemble!*

Problem 3.2: Ideal Gas in canonical ensemble: Here you will rederive the ideal gas laws using canonical ensemble. Much of this is already in the notes. But, at the end you will also derive the heat capacity of ideal gas in this formalism.

1. Derive Eq. 4.79 and 4.81 in the book / notes. Pay attention to the factors of $N!$

(Gibbs paradox) and h^3 (for dimension matching) in 4.79.

2. From the free energy in 4.81, derive the ideal gas law, by deriving equations 4.82-84. How do we get the expression of the internal energy E?

   Comment: You have to use the thermodynamic relation $F = E + TS$*. Note,* S *is also derivable from* $F(T, V, N)$ *using the equation* $S = -\frac{\partial F}{\partial T}$*. See that by combining these expressions, you find the equation* $E = \frac{\partial \beta F}{\partial \beta}$*, where* $\beta = \frac{1}{k_B T}$*. This is another way of extracting the interal energy from the free energy.*

3. What is the heat capacity (at constant volume) $C_V = \frac{\partial E}{\partial T}$ of the ideal gas?

4 Classical to quantum statistical mechanics

4.1 Reading Materials

In this week the reading includes the grand canonical ensemble. Then we venture out of the classical realm and enter the quantum world. I find the discussion of quantum statistical mechanics in Kardar a little terse. So for this part I recommend a different reference, `https://scholar.harvard.edu/schwartz/teaching`.

1. Kardar 4.9 / Lecture 14, Section IV I: Grand canonical ensemble.
2. Notes by Matthew Schwartz: Introduction to Quantum Statistical Mechanics.

4.2 Reading Guide

1. Grand canonical ensemble: Recall that the central quantity in microcanonical ensemble is $\Omega(E, V, N)$, the number of microstates at constant E, V, N. In the canonical ensemble, we compute the partition function, $Z(T, V, N)$, at constant T, V, N. But often we are dealing with very large N, which may even naturally change in our system (the number of particles may be exchanged with the environment, or may not be conserved, like photons). In such cases, it is generally very difficult to perform computations in the previous two ensembles. As we did for the canonical ensemble where we moved from E to T, by choosing the inverse temperature β to be the Lagrange multiplier that sets the average energy, we will introduce the so-called grand canonical ensemble, where the chemical potential μ fixes the average (not exact) number of partcles. It turns out that computations in this ensemble are often very simple.
2. Quantum statistical mechanics: We introduced two ad-hoc descriptions in our setup of classical stat mech: we had to regulate our integrals like $\int dqdp$ with h, and also introduce a $N!$ factor to the canonical ensemble to resolve the Gibbs paradox. Both are resolved by considering quantum mechanics, and we will see in this lecture notes how. Note, in the lecture notes by Schwartz, there are a few callbacks to earlier lectures in the course, which you may need to ignore. The notes also have a great summary.

4.3 Problems

Problem 4.1: Curie susceptibility:

In this problem we will derive Curie's law for the magnetic susceptibility. For many paramagnetic materials, the magnetization of the material is directly proportional to an applied magnetic field, for sufficiently high temperatures and small fields. However, if the material is heated, this proportionality is reduced.

Consider N non-interacting quantized spins in a magnetic field $\vec{B} = B\hat{z}$, and at a temperature T. The work done by the field is given by BM_z, with a magnetization $M_z = \mu \sum_{i=1}^{N} m_i$. For each spin, m_i takes only the $2s+1$ values $-s, -s+1, \cdots, s-1, s$. Note, here μ is the magnetic moment of each spin, and not the chemical potential.

1. Calculate the Gibbs partition function $\mathcal{Z}(T,B)$ and show that,

$$\mathcal{Z}(T,B) = e^{\beta\mu Bs}\frac{1-e^{-\beta(2s+1)\mu B}}{1-e^{-\beta\mu B}}.$$

   (Note that the ensemble corresponding to the macrostate (T,B) includes magnetic work.)

   Hint: The variation of the internal energy is $dU = TdS + BdM$. Think of which among B, M is the 'generalized force' and which, the 'generalized displacement'. The Gibbs energy is $G = U - TS - BM$, leading to $dG = -SdT - MdB$.

2. Calculate the Gibbs free energy $G(T,B)$, and show that for small B,

$$G(B) = G(0) - \frac{N\mu^2 s(s+1)B^2}{6k_BT} + \mathcal{O}(B^4).$$

   Hint: Trick is to use Taylor series; but you can use Mathematica! You can also use this expression for the next steps without proof.

3. Calculate the zero field susceptibility $\chi = \partial M_z/\partial B|_{B=0}$, and show that it satisfies Curie's law

$$\chi = c/T.$$

   Hint: The average magnetization M_z is related to the Gibbs free energy as $G = -M_zB$.

4. Show that $C_B - C_M = cB^2/T^2$, where C_B and C_M are heat capacities at constant B

Problem 4.2: Occupation numbers for non-interacting quantum gas

Consider a non-interacting quantum gas, where the single particle energy levels are discrete, labeled by i, with energy ϵ_i, which can all be chosen to be non-negative, with the ground state being at energy 0. We want to derive the average number of particles in any given state, at a particular temperature.

1. Show that the grand partition function with inverse temperature β and chemical potential μ is given by,

$$Z = \prod_i \sum_{n_i} e^{-\beta n_i(\epsilon_i - \mu)}$$

   See that one can rewrite this as a product of grand partition functions of each level i, Z_i.

2. Find the occupation numbers of the level i for bosons (where n_i can be $0, 1, \cdots, \infty$) and fermions (where n_i can be $0, 1$). You can use the fact that the grand potential

is related to the grand partition function as $\Phi_i = -k_B T \log Z_i$. Are there any restrictions on μ for bosons or fermions?

3. For $T \to 0$, how do n_i for fermions look like, as a function of $\epsilon - \mu_0$, where μ_0 to represent the chemical potential of the system at $T = 0$. Make a plot of this mean occupation number as a function of ϵ (drawing it is fine).

5 Bosons and fermions

5.1 Reading Materials

In this week the reading includes the quantum statistical mechanics with bosons and fermions.

1. Notes by Matthew Schwartz: Bose Einstein condensate; Skip section 3.2.
2. Notes by Matthew Schwartz: Metals (Read only sections 1 and 2, and the summary if you are curious!)

5.2 Problems

Problem 5.1: Bose Einstein condensate:

How was the BEC discovered in the laboratory? What property of the BEC was probed in the experiments that discovered BEC in the lab? Why was it challenging?

Problem 5.2: Fermi gas:

Consider the free fermi gas, which are non-interacting, non-relativistic fermions, with mean number of particles in each single-particle energy state is given by

$$\langle n_\epsilon \rangle = \frac{1}{e^{\beta(\epsilon-\mu)}+1}. \tag{5.2.1}$$

Assume the fermions are kept in a $L \times L \times L$ three dimensional box, and the energy is related to the wavenumber of the fermion as $E = \frac{\hbar^2 k^2}{2m}$. Assume that the fermions are electrons with two internal spin states.

1. What is the density of states for this system? You can compute this by counting the number of states at a given energy level, via the correspondence, $2\sum_n \to \int g(\epsilon) d\epsilon$.

   Hint: This is shown in Matthew Schwartz's notes.

2. The chemical potential μ_0 is generally referred to as the *Fermi energy* of the system and is denoted by ϵ_F. Using the density of states to perform an integration, the defining equation for the Fermi energy is given by

$$\int_0^{\epsilon_F} g(\epsilon) d\epsilon = N. \tag{5.2.2}$$

   Show that the corresponding *Fermi momentum* is given by

$$p_F = \left(\frac{3N}{4\pi V}\right)^{1/3} h, \tag{5.2.3}$$

and the Fermi energy is given by

$$\epsilon_F = \left(\frac{3N}{4\pi V}\right)^{2/3} \frac{h^2}{2m}. \tag{5.2.4}$$

3. Show that the ground-state energy is given by

$$\frac{E_0}{N} = \frac{3}{5}\epsilon_F. \tag{5.2.5}$$

4. What is the degeneracy pressure for the free fermi gas at zero temperature?

   The degeneracy pressure just completely arises from the fermionic statistics and no thermal motion ($T = 0$). The degeneracy pressure for ultrarelativistic fermions can prevent stellar collapse for old white dwarfs, which leads to the famous Chandrasekhar limit (you can read more about it in these Notes.