8.333: Statistical Mechanics I

Lecturer: Professor Senthil Todadri

Notes by: Andrew Lin

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1 Introduction

Fact 1

To start off the class, all of the students introduced ourselves (whether we're an undergrad or grad student, what department we're in, and where we're located).

This is a graduate statistical mechanics class, so it will be taught at a level for first-year graduate students. Professor Todadri hopes to have a chance to see all of us on campus in the near future, but for now we're all learning virtually. His research is in quantum condensed matter physics, and he's been at MIT for 20 years. Recitations will be taught by Alex Siegenfeld – his research is about applying concepts from statistical physics to social and economic systems, particularly COVID-19.

Most of us should have seen the Canvas site by now – most of the course business will be conducted there. We'll find some information there about the syllabus, grading, and logistics, most of which will not be repeated. It's also good for us to sign up for the Piazza, so that we can ask questions and connect with each other in this virtual format. (Piazza will mostly be used for chatting, but the course staff may answer questions or refine answers occasionally.)

Homework will be assigned roughly once per week – since this is a graduate class, this will be weighted at 60 percent of the total grade. In other words, if we're doing a good job keeping up with the work, we have a good chance of receiving close to the full 60 percent. There will be three take-home, open book, open notes quizzes (designed to be more low-stakes) worth 8 percent each, and then there will be a synchronous final exam worth 16 percent. (Logistics for this will be announced later.)

There will be a variety of resources available to us for this class: many good books are listed on the Canvas site, but we'll cover topics from Professor Mehran Kardar's book. (The organization will be different, but we can find Professor Kardar's lectures on MIT OCW.) A particularly sophisticated book is the one by Landau and Lifshitz – we should consult it only if we have enough maturity to tackle it.

All lecture videos and handwritten class notes will be posted on Canvas, but (per department guidelines) recitations will not be recorded, so that students feel comfortable speaking up.

2 September 2, 2020

This class will be taught under the assumption that we have had some exposure to statistical mechanics and thermodynamics in the past. (For undergraduates, 8.044 is probably the relevant background.) The general question to answer for a class like this is **how to describe properties of macroscopic objects in terms of certain known laws describing the physics of atoms**. In other words, if we know (at least adequately) how physics describes small particles, can we describe how systems with many such particles behave?

Such a microscopic description depends on whether we're treating our particles classically or quantum mechanically – technically we should treat everything quantum mechanically, but the classical limit is sometimes adequate. In the **classical** case, a gas can be described by the coordinate and momentum of each particle, and we want to learn something based on the time-evolution of those coordinates. (We could theoretically use Newton's equations of motion and apply it to our large collection of atoms.) Alternatively, in the **quantum** case, we could specify the quantum many-body wavefunction. But in most macroscopic objects, there are $O(10^{23})$ atoms, and so trying to describe the system with either of the two treatments above is essentially impossible and also pretty useless.

So what's useful for physicists is not the exact mathematical description of each atom – instead, we want to extract information by developing **concepts and descriptions** which apply to the system as a whole, rather than any one of its constituents.

Example 2

From past physics experience, we may know that **temperature, heat, and pressure** are often useful for a macroscopic description of a system.

This means that we should understand what temperature, heat, and pressure mean at the microscopic level – how are they defined, and how do they arise? If we can take a small set of variables like these, and use that to capture the overall state of the system, then we've successfully completed a macroscopic description.

And the point is that the **difficulty** of describing our large systems at the microscopic level can be turned into an **advantage**:

Proposition 3

Statements of a statistical nature (about averages or fluctuations) become useful when systems have lots of degrees of freedom.

We will simplify our discussion throughout most of these lectures by focusing on **equilibrium** properties (rather than the approach to equilibrium) for our systems. To explain what "equilibrium" really means, remember that we're describing our large, macroscopic system in terms of a small number of variables.

Definition 4

If all macroscopic variables describing a system have assumed their average values in the absence of external forces, and those values do not change in time, then our system is at **equilibrium**.

The "not changing in time" statement will depend on the timescale over which we're considering or observing our system – as Feynman describes, this is the time when the "fast things" have happened already, but the "slow things" have not.

Example 5

A glass of water does not look like it is changing after it has been sitting on a table for a few minutes, but after a few days, the water will evaporate. So a meaningful notion of equilibrium does need to depend on our timescale.

It's important to note that our description of macroscopic systems, like the glass of water above, is often done while it is **constantly interacting** with the surrounding environment. This **environment** is often much larger than the system we care about – we usually can't do anything to get rid of it, but it still has some influence on our system. So this is an extra level of challenge: if we don't know the nature of the environment, or its explicit interaction with our system, it will be even more difficult to describe the properties that we care about.

So a tool we'll be using frequently throughout this class is **probability**: we want to be able to calculate how likely it is for our system to be in various possible states. After all, even if we have a completely specified microscopic description of our initial conditions, there is no way to solve the problem exactly without knowing how our environment behaves. And even a completely isolated system can be thought of as a large number of (smaller, but still macroscopic) systems that are interacting with each other: if the length scale for our whole big system is L, and we break it up into smaller systems of length ℓ, so that $L \gg \ell \gg a$ (where a is a microscopic length scale), it's believed that (after some evolution) each of our small subsystems should be "in equilibrium relative to the other subsystems," at least at short timescales.

Remark 6. *In the past few years, some exceptions to this "ability to internally equilibrate without an environment" have been found, but they are rare and have only been discovered recently. So it's interesting that the field is still evolving and that assumptions are still being challenged.*

Proposition 7 (A reasonable statement, not a theorem)
Consider a system in contact with its environment. If this system is sufficiently "generic" (we'll explain what this means later), then the probability of being in a certain state with energy E is the same as being in any other state with energy E.

To explain this, consider two such states a and b with respective energies E_a and E_b. If $E_a \approx E_b$, then weak interaction with the environment can cause transitions between these two states. (This is a general phenomenon – our environment will provide a perturbation to our system, which can cause this small energy difference $\Delta = E_b - E_a$.)

Thinking about this quantum mechanically, if we have some potential $V(t)$ applied to our system, that will cause us to have some rate of transition from the states a to b, and that rate is proportional to $|\left\langle b \middle| \int dt\, e^{i\Delta t/\hbar} V(t) \middle| a \right\rangle|^2$. This transition will therefore occur except when the above matrix element "prohibits" it (meaning the rate is 0), and in large systems in contact with some environment, such transitions will happen between states with the same energy without needing any energy transfer from the environment. (Since $\Delta = 0$, the rate is dependent on $\langle b|a\rangle$, which is basically never zero.) So the system will visit different states of the same energy, as long as some set of them isn't forbidden.

So when does this "forbidding accessing other states" happen? Certain conservation laws (e.g. conservation of spin) can come into play here – states of different total spin cannot be "kicked around" by the environment. But **generically, when we assume no other conservation laws are present** (here's our definition), nothing else about our system can prevent the environment from kicking us between possible states.

This means that the probability of being in a state should only depend on the energy E, and this is the framework with which we'll start to study many-body systems.

3 September 4, 2020 (Recitation)

We'll generally start recitations by discussing any questions from lecture that might come up, and then we'll discuss some topic – this week, we'll do a review of some probability theory.

Fact 8

During the proof of the "states with equal energy have equal probabilities" result, we used a formula for transition rates that is only valid when the two energies are different.

There was indeed a bit of handwaving that occurred during lecture. But the general idea is that quantum mechanically, probabilities of transforming from state a to b are the same as probabilities of transforming from state b back to state a under any given interaction. And if we have two states of unequal energy, the environment needs to input energy – the point is that "all transitions that can happen will happen" due to the large number of available microstates.

For a more rigorous proof of this kind of result, we should wait for the microcanonical ensemble to come up. This is because often in statistical mechanics, we start with closed systems with no attached environment. In such a setup, all states are equally likely (if the system is at a fixed energy), and then we try to argue from general principles that a subsystem of it (which we can think of as the actual "system" attached to an environment) behaves as we want.

Fact 9

Our main example of non-equilibrium systems in this class come from **hydrodynamics** – that is, how a gas or fluid tends towards equilibrium.

Fact 10

The "matrix element" or Fermi's golden rule argument has to do with time-dependent perturbation theory in quantum mechanics, but this is not super related to the material we'll be covering.

And finally, two answers to logistics questions: homework will be first assigned next week (and we'll always get a week to do it), and there will occasionally be extra credit problems on the homework to allow us to bump up our grade to the full 60 percent allotment. Also, even though +/- grade modifiers are not directly displayed on a transcript, a B+ specifically will be needed to place out of the physics qualifying exam.

There's a very formal way of thinking about probability, but mathematicians need to worry more about the details than physicists when working about infinite spaces. So this won't be "up to mathematical rigor," but it'll give the basic idea:

Definition 11

A **probability space** consists of a sample space Ω, such that for (some of the) events $E \subset \Omega$, we assign a probability $P(E) \in [0, 1]$ so that

- $P(\Omega) = 1$, and
- if $E_1 \cap E_2 = \varnothing$ are disjoint events, then $P(E_1 \cup E_2) = P(E_1) + P(E_2)$.

Here, the main idea is that "probabilities add to 1" if we cover the whole space with disjoint events.

Example 12

If we roll a die, the result of that die roll has $\Omega = \{1, 2, 3, 4, 5, 6\}$, and $\mathbb{P}(E) = \frac{|E|}{6}$.

Notice that there is no definition of "randomness" here: we've just assigned numbers to mathematical objects. So randomness is actually more subtle, and we're abstracting it away. The only case where probability does intersect with reality is that if we have N **independent trials** and we measure how many times N_E that event E occurs, we should have

$$\mathbb{P}(E) = \lim_{N \to \infty} \frac{N_E}{N};$$

that is, we expect that over time, we get the correct fraction of occurrences.

Definition 13

A **real random variable** is a map $X : \Omega \to \mathbb{R}$, which can also be defined by a **cumulative distribution function**

$$F(x) = \mathbb{P}(\{\omega \in \Omega : X(\omega) \le x\}) = \mathbb{P}(X \le x).$$

Here, the more formal notation is just used for reference: basically, $\{\omega \in \Omega : X(\omega) \le x\}$ refers to the "set" or "event" that X returns a value at most x.

Remark 14. *The reason we care about this abstract notion of a sample space (rather than thinking about drawing numbers from the real line directly) is that we might have different variables with weird correlations* (x, y, z).

We can equivalently also define a **probability distribution function**

$$p(x) = \frac{dF(x)}{dx},$$

which we can think of as the "relative probability of finding the value of X near x." Note that this derivative may not exist, which means we might have delta functions for discrete random variables, but we'll often be using continuous random variables in this class.

From here, we'll consider functions of random variables: suppose we have some new random variable

$$Y = g(X),$$

and we know the probability distribution function $p_X(x)$ of X. Our goal is to find the probability distribution function $p_Y(y)$, and we do this by noting that (in differential form)

$$p_Y(y)dy = \sum_{x : g(x) = y} p_X(x)dx,$$

and then solving for p_Y yields

$$\boxed{p_Y(y) = \sum_{x : g(x) = y} \frac{p_X(x)}{|g'(x)|}}.$$

The derivative term here basically accounts for the "slantedness" of g – that is, how wide of a range of x's maps onto a small interval around some y.

Definition 15

The **expectation value** of a function $g(X)$, denoted $\langle g(X)\rangle$, is

$$\langle g(X)\rangle = \int p(x)g(x)dx.$$

One specific example is the **moments** of a random variable X, which are

$$\langle X^m\rangle = \int p(x)x^m dx.$$

We'll assume in this class that moments are well-defined, but this is not always true for probability distributions especially with extreme values.

One way to get a handle on these moments is to combine the moments together:

Definition 16

The **characteristic function** of a random variable X is

$$\tilde{p}(k) \equiv \langle e^{-ikX}\rangle = \int p(x)e^{-ikx}dx.$$

Since this is the form of a Fourier transform, we can also invert this characteristic function to get the distribution function back:

$$p(x) = \int \frac{1}{2\pi}\tilde{p}(k)e^{ikx}dk.$$

If we assume that all moments are indeed well-defined, we can do a Taylor expansion here:

$$\tilde{p}(k) = \sum_{n=0}^{\infty} \frac{(-ik)^m}{m!}\langle X^m\rangle,$$

and therefore the mth derivative of the characteristic function

$$\left.\frac{d^m\tilde{p}}{dk^m}\right|_{k=0} = (-i)^m\langle X^m\rangle.$$

(In other words, the characteristic function "determines the moments.")

Remark 17. *The reason to use the characteristic function instead of the* **moment generating function** $\langle e^{tX}\rangle$ *is that the moment generating function is not always well-defined, because it can take on infinite values.*

We can start putting our random variables together now: suppose we have two **independent** random variables X and Y, which essentially means that "knowing X tells us nothing about Y, and vice versa." Now if we want to find the characteristic function of $X+Y$, then

$$\tilde{p}_{X+Y}(k) = \iint p(x)p(y)e^{-ikx}e^{-iky}dxdy$$

which then factors into two components,

$$= \tilde{p}_X(k)\tilde{p}_Y(k).$$

So this kind of "product structure" indicates that taking logarithms might be helpful, and what we can rewrite here is

$$\boxed{\ln\tilde{p}_{X+Y}(k) = \ln\tilde{p}_X(k) + \ln\tilde{p}_Y(k)}.$$

And the useful motivation here is that we might want to consider the natural log of the characteristic function, also called the **cumulant generating function**.

Definition 18

For all $m \geq 1$, the **cumulants** of a random variable X, denoted $\langle X^m \rangle_c$, are defined as the coefficients of the cumulant generating function:

$$\ln \tilde{p}(k) = \sum_{m=1}^{\infty} \frac{(-ik)^m}{m!} \langle X^m \rangle_c.$$

(This sum starts from 1 instead of 0, because the left-hand side takes in a value of 0 at 0 no matter what and there is no constant term in this Taylor series.)

By using the Taylor expansion of a logarithm $\ln(1+\varepsilon)$, we can work out a calculation, and this gives us the **mean**

$$\langle X \rangle_c = \langle X \rangle,$$

the **variance**

$$\langle X^2 \rangle_c = \langle X^2 \rangle - \langle X \rangle^2,$$

the **skewness**

$$\langle X^3 \rangle_C = \langle X^3 \rangle - 3\langle X^2 \rangle \langle X \rangle + 2\langle X \rangle^3,$$

and the **kurtosis**

$$\langle X^4 \rangle_c = \langle X^4 \rangle - 4\langle X^3 \rangle\langle X \rangle - 3\langle X^2 \rangle^2 + 12\langle X^2 \rangle\langle X \rangle^2 - 6\langle X \rangle^4$$

of a random variable. The cumulants might look somewhat arbitrarily defined, but they're important because **they add for two independent variables**. (For example, means and variances add, while the expectation values of the squares does not add in such a simple way.)

And now we can go over a nice trick for relating cumulants to moments: we can imagine the cumulants $\langle X^n \rangle_c$ as being a bag of n points, and $\langle X^n \rangle$ as referring to how to put n points into bags. (Points are distinguishable, but bags are not.) For example, $\langle X \rangle = \langle X \rangle_c$ because a single point goes in a bag,

$$\langle X^2 \rangle = \langle X \rangle_c^2 + \langle X \rangle_c,$$

because two points can be put into the same bag or two different bags, and

$$\langle X^3 \rangle = \langle X \rangle_c^3 + 3\langle X^2 \rangle_c \langle X \rangle_c + \langle X^3 \rangle_c,$$

since either the points go in the different bags, one of them is in its own bag in 3 different ways, or all three go in the same bag. A similar calculation can be done for $\langle X^4 \rangle$, and notice that we can recursively compute the cumulants in this way.

We'll now cover some common probability distributions:

Definition 19

The **Gaussian distribution** with mean λ and variance σ^2 has probability distribution function

$$p(x) = \frac{1}{\sqrt{2\pi\sigma^2}} e^{-\frac{(x-\lambda)^2}{2\sigma^2}}$$

We can compute the characteristic function of this Gaussian to be

$$\tilde{p}(k) = \int e^{-ikx} p(x) dx = e^{-ik\lambda} e^{-\sigma^2 k^2/2},$$

which means that the power series for the cumulant generating function is

$$\ln \tilde{p}(k) = -ik\lambda + \frac{(-ik)^2}{2!}\sigma^2,$$

indeed matching with the mean and variance that we described. (Notice that all higher cumulants $\langle X^m \rangle_c$ for $m > 2$ are 0.) What's interesting here, though, is that there is no skewness, kurtosis, or anything "higher" for a Gaussian, and that Gaussians are the only functions with this property! This means that we can write higher moments $\langle X^m \rangle$ in terms of just the mean and variance, which is a nice property.

Fact 20

We can also do calculations for discrete random variables, but we need to deal with delta functions. For example, the characteristic function of a random variable which is 1 with probability a and 0 with probability $1 - a$ is

$$\tilde{p}(k) = ae^{ik} + (1 - a).$$

And now we can talk about having multiple random variables that do have some dependence on each other. Suppose we have a vector of random variables $\vec{X} = (X_1, \cdots, X_N)$, which is a function $\Omega \to \mathbb{R}^N$. Then we can make some analogous definitions to the work above: we have a **joint probability distribution function**

$$p(\vec{x}) = \lim_{\forall i, dx_i \to 0} \frac{\mathbb{P}(\vec{X} \text{ is in the box around } \vec{x} \text{ of width } \prod_i dx_i)}{dx_1 dx_2 \cdots dx_N}.$$

In other words, we take a vanishing volume around $\vec{x}$ and find the "density" of likelihood around that region.

We can then compute the **unconditional probability distribution function** of the first s variables by integrating out the other variables:

$$p(x_1, \cdots, x_s) = \int \prod_{i=s+1}^{N} dx_i p(x_1, \cdots, x_N).$$

On the other hand, we can also compute a **conditional probability distribution function**, assuming that the other variables take on a specific value: this means we need to put in a **normalization factor**

$$p(x_1, \cdots, x_s | x_{s+1}, \cdots, x_N) = \frac{p(x_1, \cdots, x_N)}{A},$$

because we're modifying the sample space of allowed events. This A will depend on the values of $x_{s+1}, \cdots, x_N$, and it is such that

$$A = \int \prod_{i=1}^{s} dx_i p(x_1, \cdots, x_N)$$

(that is, we integrate out the unknown variables X_1 through X_s). And this is just the unconditional probability of the rest of the variables $p(x_{s+1}, \cdots, x_N)$, so we can put everything together now:

$$p(\vec{a}|\vec{b}) = \frac{p(\vec{a} \text{ and } \vec{b})}{p(\vec{b})},$$

and this is the well-known **Bayes' theorem**, leading us to a more formal definition:

Definition 21

Two random variables X and Y are **independent** if $p(x|y) = p(x)$ and $p(y|x) = p(y)$ (the unconditional and conditional probabilities are the same).

Bayes' rule also then tells us that the probability distribution functions factor as

$$p(x, y) = p(x)p(y).$$

And a final note, we should be careful to think about the differences between pairwise and mutual independence: just because any pair of variables in a set are independent does not mean that they are all mutually independent.

4 September 9, 2020

The first homework assignment has been posted – they will be posted weekly on Tuesdays. Office hours for Professor Todadri and the two TAs are also posted now; we can chat about homework problems or other questions for the course. (And we can always email if the times don't work for us.)

By the way, if any of us are taking this class without much physics background, we can ask Hamed (one of the TAs), who will conduct some informal physics review sessions.

Today's lecture will cover the **microcanonical ensemble**, as well as **classical Hamiltonian dynamics and Liouville's theorem**. We'll then begin to discuss **density of states** for many-body density.

Over the next few lectures, the goal we're working towards is to deal with a situation where a system is attached to a much larger environment, and the whole setup is in equilibrium. We want to get to a formula for the probability that our system is in some particular microscopic state a with energy E_a – namely, that the probability of occupation is

$$p(a) \propto e^{-\beta E_a},$$

where $\beta > 0$ is a constant which we can interpret as $\frac{1}{k_B T}$, where T is the absolute temperature of the system. (We'll call this the **central principle** – it's the crucial rule of calculation for equilibrium statistical mechanics, and sometimes textbooks actually start with a loose justification of this.) Then the constant of proportionality is just a normalization factor $\frac{1}{Z}$ such that

$$\sum_a p(a) = 1 \implies Z = \sum_a e^{-\beta E_a}.$$

Z here is known as the partition function, and it'll be important for us to study. But it'll take us some time to get to this result and give enough supporting evidence, and that's what we'll be developing now.

We're going to start with the "simplest" theoretical device, where we have a **system that is large and strictly isolated**. In such a system, the **total energy is strictly conserved**, and different parts of this isolated system are in equilibrium with each other. What we're interested in here is the values of various macroscopic properties, **averaged over some small (but nonzero) time interval and region of space**.

Example 22

If we want to extract a macroscopic quantity out of a gas in a room (such as the temperature), we'll measure on time scales longer than the time between collisions for atoms, and we'll measure on length scales larger than the distance between atoms. But for a system at equilibrium, we don't need to wait a year or measure the average temperature across the entire room to get a good measurement.

Fact 23

We'll assume (by tradition) that it's possible to calculate these averages correctly from a **uniform probability distribution** that assigns equal probabilities to all microscopic states with some fixed energy E.

This means that we're assuming the system is "generic enough" – we're basically assuming classical dynamics for generic initial conditions are chaotic. And also, we're basically **extending** the postulate we made earlier about an open system to a closed system (saying that particle trajectories will be fairly random, with the only restriction being that energy is totally conserved).

Definition 24

For a large, strictly isolated system, let $\Omega(E)$ be the total number of microscopic states (also referred to as **microstates**) with total energy E.

Then we can state our above assumptions as

$$p(a) = \begin{cases} \frac{1}{\Omega(E_a)} & E_a = E \\ 0 & \text{otherwise.} \end{cases}$$

We can dig into this assumption more clearly by using a concrete example:

Example 25

Consider a collection of N classical atoms, where N is very large (approaching infinity, and in practice close to Avogadro's number).

If we want to specify the state of a given particle, we specify its position and momentum, so when we have N atoms, we have $6N$ degrees of freedom (each atom has three real-number components for the position vector and three real-number components for the momentum vector). That means we can describe our microstate to be **a point in a** $6N$**-dimensional vector space** known as the **phase space**. We'll write this point as (q, p), where $q = (\vec{q}_1, \cdots, \vec{q}_N)$ encodes the coordinates of all N particles, and $p = (\vec{p}_1, \cdots, \vec{p}_N)$ encodes the momenta of those particles.

Remark 26. *If we stick entirely to classical mechanics, then every point in this phase space can count as a microstate, and then there are uncountably many microstates. But as we go along, we'll refine this by using quantum position-momentum uncertainty. This will then tell us that there's a "minimum volume" of phase space, set by Planck's constant.*

Assume now that we put our collection of N atoms into a rigid box. If we're given some initial condition (q, p), we can think about the dynamics of the atoms: they'll evolve according to the laws of classical dynamics, which are given by the **Hamiltonian equations of motion**

$$\frac{\partial \vec{q}_i}{\partial t} = \frac{\partial H}{\partial \vec{p}_i}, \quad \frac{\partial \vec{p}_i}{\partial t} = -\frac{\partial H}{\partial \vec{q}_i},$$

where $H = H(q, p)$ is the **Hamiltonian** of the system, which describes the total energy in terms of our current q, p. Notably, becomes our energy is conserved, our (q, p) phase space coordinates must move along a **surface of constant energy** $H(q, p) = c$. If we now assume that our system is generic – that is, there are no conservation laws (even momentum, because bouncing particles off the box will change the total momentum), and our initial conditions are generic – then **it is reasonable** for us to assume that the trajectory will uniformly cover that constant-energy surface. (In other words, if we take two equal volumes of phase space inside the surface, they will both be visited equally frequently on average by our trajectory.) **Then if we want to calculate physical quantities averaged over a long time, we can calculate averages over this probability distribution instead.**

Remark 27. *Mathematicians have tried to prove that this "mixing" occurs, but the regimes where the proofs are valid are only for impossibly long time scales that don't correspond to real-life time scales. But we'll still accept the assumption.*

Some related justification does come from the following result. Suppose we have a large number of copies of our system, distributed in phase space with some density $\rho(q, p, t)$, so that the number of systems in a volume $d\Gamma = \prod_i d^3\vec{q}_i d^3\vec{p}_i$ is $\rho(q, p, t)d\Gamma$. Then after an infinitesimal time δt, our variables evolve via

$$q_\alpha \to q'_\alpha = q_\alpha + \dot{q}_\alpha \delta t, \quad p_\alpha \to p'_\alpha = p_\alpha + \dot{p}_\alpha \delta t.$$

We can imagine a small box in phase space then moving to some other box in phase space. Then our volume $d\Gamma = \prod_i d^3\vec{q}_i d^3\vec{p}_i$ is distorted into

$$d\Gamma = \prod_i d^3\vec{q'}_i d^3\vec{p'}_i.$$

The question is how this changes under Hamiltonian dynamics. To first order, the changes that affect the volume of the box $dq_\alpha dp_\alpha$ are

$$dq_\alpha \to dq'_\alpha = dq_\alpha + \frac{\partial \dot{q}_\alpha}{\partial q_\alpha} dq_\alpha \delta t, \quad dp_\alpha \to dp'_\alpha = dp_\alpha + \frac{\partial \dot{p}_\alpha}{\partial p_\alpha} dp_\alpha \delta t$$

(the other terms in the chain rule are "rotations," so they don't contribute), and we can multiply the new infinitesimals together to find

$$dq'_\alpha dp'_\alpha = dq_\alpha dp_\alpha \left(1 + \left(\frac{\partial \dot{q}_\alpha}{\partial q_\alpha} + \frac{\partial \dot{p}_\alpha}{\partial p_\alpha}\right)\delta t + o((\delta t)^2)\right).$$

And now we can use the Hamilton equations of motion to write

$$\frac{\partial \dot{q}_\alpha}{\partial q_\alpha} = \frac{\partial}{\partial q_\alpha}\left(\frac{\partial H}{\partial p_\alpha}\right) = \frac{\partial^2 H}{\partial q_\alpha \partial p_\alpha},$$

and similarly (but just with a negative sign)

$$\frac{\partial \dot{p}_\alpha}{\partial p_\alpha} = -\frac{\partial}{\partial p_\alpha}\left(\frac{\partial H}{\partial q_\alpha}\right) = -\frac{\partial^2 H}{\partial q_\alpha \partial p_\alpha},$$

and we find that the order δt terms cancel out.

Remark 28. *We basically don't need to address second-order terms, because we're only looking at infinitesimal transformations, and the result we arrived at is essentially that the Jacobian is the identity matrix.*

And therefore $d\Gamma' = d\Gamma$, and this is the result we're looking for:

Theorem 29 (Liouville)

The phase space volume does not change under time evolution, so the density of the probability distribution in phase space has not changed as a function of time.

After all, if we have many copies of our system, we have some number of copies in any given phase space "volume containers", and then after an infinitesimal amount of time, we'll have that same number of copies in the updated phase space volume containers. (And because we can run this argument in reverse, it's not possible for two different volumes to end up in the same spot in phase space.) Importantly, though, **this doesn't mean the distribution is uniform, just constant under time-evolution**:

$$\frac{d\rho}{dt} = 0.$$

(We have a total time-derivative because the value of q and p depend on time "around any point" in phase space.) This can be written out as

$$\frac{\partial \rho}{\partial t} + \sum_{\alpha=1}^{3N} \left(\frac{\partial \rho}{\partial p_\alpha} \frac{\partial p_\alpha}{\partial t} + \frac{\partial \rho}{\partial q_\alpha} \frac{\partial q_\alpha}{\partial t} \right) = 0,$$

and therefore

$$\frac{\partial \rho}{\partial t} = -\sum_{\alpha} \left(\frac{\partial \rho}{\partial p_\alpha} \frac{\partial H}{\partial q_\alpha} - \frac{\partial \rho}{\partial q_\alpha} \frac{\partial H}{\partial p_\alpha} \right) \equiv \{\rho, H\}$$

is defined to be the **Poisson bracket** of the density ρ with the Hamiltonian H. Notice that when our system is **in equilibrium**, we should also have $\frac{\partial \rho_{\text{eq}}}{\partial t} = 0$, and that tells us that

$$\{\rho_{\text{eq}}, H\} = 0.$$

Such a result is always true if ρ_{eq}, the equilibrium density, only depends on the energy of our microstate:

$$\rho_{\text{eq}}(q, p) = \rho_{\text{eq}}(H(q, p)),$$

and that's a further point of support (though not a proof) for why the distribution is indeed uniform across all microstates with this fixed energy.

5 September 11, 2020 (Recitation)

We'll continue our discussion of probability theory today, looking at multiple random variables, and we'll also discuss Hamiltonian dynamics and chaos.

Like last time, suppose we have a set of random variables $(X_1, \cdots, X_n)$, with probability distribution function $p(x_1, \cdots, x_n)$. We know what it means for two variables to be independent already: two variables X and Y are independent if $p(x|y) = p(x)$, or equivalently $p(x, y) = p(x)p(y)$, but we need to be more specific when we have more than two variables at a time.

Remark 30. *Technically, there should be subscripts on the different p functions, so $p(x)$ should be $p_X(x)$.*

Definition 31

Random variables $(X_1, \cdots, X_n)$ are **pairwise independent** if X_i and X_j are independent for all $i \neq j$. In contrast, the variables are **mutually independent** if

$$p(x_1, \cdots, x_n) = p(x_1) \cdots p(x_n).$$

This last equation can be equivalently written as

$$p(x_{i_1}, \cdots, x_{i_n} | x_{j_1}, \cdots, x_{j_m}) = p(x_{i_1}, \cdots, x_{i_n})$$

for any two disjoint subsets of the random variables $\{X_{i_1}, \cdots, X_{i_n}\}$ and $\{X_{j_1}, \cdots, X_{j_m}\}$.

Example 32

Consider the three random variables X, Y, Z with the following distribution:

X	Y	Z	p
0	0	0	$\frac{1}{4}$
0	1	1	$\frac{1}{4}$
1	0	1	$\frac{1}{4}$
1	1	0	$\frac{1}{4}$

Basically, X, Y, Z are binary bits must sum to an even number, but all allowed states have equal probability. And now we can check that X and Y are independent, and so are X and Z, and so are Y and Z, but it's not true that X, Y, Z are mutually independent (knowing X and Y tells us information about Z).

Definition 33

Let $X_1, \cdots, X_n$ be random variables. The **joint characteristic function** is the function

$$\tilde{p}(\vec{k}) = \langle e^{-i\vec{k}\cdot\vec{X}} \rangle = \int \prod_j dx_j p(x_1, \cdots, x_n) e^{-i\sum_j k_j x_j},$$

where the argument $\vec{k}$ is an n-dimensional vector.

From this characteristic function, we can generate the moments of our random variable by taking derivatives, just like in the one-dimensional case:

$$\langle X_1^{m_1} X_2^{m_2} \cdots X_n^{m_n} \rangle = \left(\frac{\partial}{\partial(-ik_1)} \right)^{m_1} \cdots \left(\frac{\partial}{\partial(-ik_n)} \right)^{m_n} \tilde{p}(\vec{k}) \Big|_{\vec{k}=0}.$$

And similarly, we can compute the cumulants in the same way:

$$\langle X_1^{m_1} X_2^{m_2} \cdots X_n^{m_n} \rangle_c = \left(\frac{\partial}{\partial(-ik_1)} \right)^{m_1} \cdots \left(\frac{\partial}{\partial(-ik_n)} \right)^{m_n} (\ln \tilde{p}(\vec{k})) \Big|_{\vec{k}=0}.$$

The same "points in bags" argument for relating cumulants and moments works here: if we want to put two 1s and one 2 into bags, the different configurations are (112), two ways for (1)(12), one way for (2)(11), and one way for (1)(1)(2), so

$$\langle X_1^2 X_2 \rangle = \langle X_1^2 X_2 \rangle_c + 2\langle X_1 \rangle_c \langle X_1 X_2 \rangle_c + \langle X_2 \rangle_c \langle X_1^2 \rangle_c + \langle X_1 \rangle_c^2 \langle X_2 \rangle_c.$$

Definition 34

The **joint Gaussian** distribution in N dimensions is given by the probability distribution

$$p(\vec{x}) = \frac{1}{\sqrt{(2\pi)^N \det C}} \exp\left[-\frac{1}{2} (\vec{x} - \vec{\lambda})^T C^{-1} (\vec{x} - \vec{\lambda}) \right],$$

where $\vec{\lambda}$ is the "mean vector" and C is a symmetric **covariance matrix**.

Remark 35. *We can write the complicated vector expression as*

$$(\vec{x} - \vec{\lambda})^T C^{-1} (\vec{x} - \vec{\lambda}) = \sum_{i,j} C_{ij}^{-1} (x_i - \lambda_i)(x_j - \lambda_j).$$

Since the C_{ij} and C_{ji} terms contribute to the same coefficients, it makes sense by convention to make C symmetric.

We can write out the characteristic function of this multivariate Gaussian

$$\tilde{p}(\vec{k}) = e^{-ik_i\lambda_i - \frac{1}{2}C_{ij}k_ik_j},$$

where we **are** summing over i and j but just omitting the sums in notation (this is the Einstein convention). Therefore,

$$\ln \tilde{p}(\vec{k}) = -ik_i\lambda_i - \frac{1}{2}C_{ij}k_ik_j,$$

and this tells us (like in the one-variable case) that there are no higher-order cumulants beyond the mean and variance

$$\langle X_i \rangle_c = \lambda_i, \langle X_i, X_j \rangle_c = C_{ij}.$$

This leads us to a result that is important in field theories:

Theorem 36 (Wick's theorem)
Suppose we have a multivariate Gaussian with $\vec{\lambda} = 0$. Then

$$\langle X_1^{m_1} \cdots X_n^{m_n} \rangle = \begin{cases} 0 & \sum m_i \text{ is odd} \\ \text{sum over all } \textbf{pairwise contractions} & \text{otherwise.} \end{cases}$$

For example,

$$\langle X_1^2 X_2 X_3 \rangle = \langle X_1 X_1 X_2 X_3 \rangle = \langle X_1 X_1 \rangle \langle X_2 X_3 \rangle + 2\langle X_1 X_2 \rangle \langle X_1 X_3 \rangle,$$

because there are three ways to pair up the four indices into two pairs: the first 1 either pairs with the other 1, 2, or 3. This is particularly important (for example, for Feynman diagrams) because we often sample values from a Gaussian distribution.

We'll now consider **functions of random variables**, and we'll begin by reviewing the one-dimensional case. If we have a variable $Y = g(X)$, then the probability distribution of Y can be written as

$$p_Y(y) = \sum_{x: y(x) = y} p_X(x) \left| \frac{dx}{dy} \right|.$$

(This sum comes up if g is not a one-to-one function.) We're going to derive this equation in a way that generalizes well to the multi-dimensional case now. Notice that

$$\int_a^b p_Y(y) dy = \int_{-\infty}^{\infty} dx p_X(x) 1_{[a,b]}(g(x))$$

where $1_{[a,b]}$ is the **indicator function** that returns 1 if $g(x)$ is in the range $[a, b]$ and 0 otherwise. We can then rewrite this as

$$= \int_{-\infty}^{\infty} dx p_X(x) \int_a^b \delta(g(x) - y) dy$$

(since we're "picking out" values where $g(x)$ falls in the range from a to b). This means we can write the density function as

$$\boxed{p_Y(y) = \int_{-\infty}^{\infty} dx p_X(x) \delta(g(x) - y)}.$$

And now we'll generalize this to the multi-dimensional case: if we have a random variable $Y = g(X_1, \cdots, X_n)$, then

$$\boxed{p_Y(y) = \int \left(\prod_i dx_i\right) p(x_1, \cdots, x_n)\delta(g(x_1, \cdots, x_n) - y)}.$$

Remark 37. *As a reminder, delta functions are defined so that*

$$\int dx\, \delta(x - a) f(x) = f(a).$$

So we can compute something like

$$\int dx\, \delta(g(x) - a) f(x)$$

by doing a change of variables:

$$= \int dg(x) \frac{dx}{dg(x)} \delta(g(x) - a) f(x),$$

and now we need to be careful about the bounds and order of integration if g is not one-to-one, and also because of the positive or negative sign of the expression $\frac{dx}{dg(x)}$.

Example 38

Let $Y = X_1^2 + X_2^2$, where X_1, X_2 are independent random variables.

Then we can write the probability distribution function as

$$p_Y(y) = \int dx_1 dx_2 p_1(x_1) p_2(x_2) \delta(x_1^2 + x_2^2 - y),$$

and this can be simplified most easily by using a (polar) change of variables: set

$$r^2 = x_1^2 + x_2^2 \implies dx_1 dx_2 = r dr d\theta = \frac{1}{2} d\theta d(r^2),$$

so that $x_1 = r\cos\theta$ and $x_2 = r\sin\theta$. Then

$$p_Y(y) = \int \frac{1}{2} d\theta d(r^2) p_1(r\cos\theta) p_2(r\sin\theta) \delta(r^2 - y),$$

and now we can plug in $r^2 = y \implies r = \sqrt{y}$ (in polar coordinates, r is always nonnegative) wherever it appears to get

$$p_Y(y) = \int_0^{2\pi} \frac{d\theta}{2} p_1(\sqrt{y}\cos\theta) p_2(\sqrt{y}\sin\theta),$$

and we've removed the delta function from the expression.

Our last topic for the recitation is **Hamiltonian dynamics**. Suppose that we have N particles, and we can represent the positions and momenta in three dimensions with a $6N$-dimensional vector

$$(q_1, p_1, \cdots, q_{3N}, p_{3N}) \equiv (q, p).$$

Then a Hamiltonian H gives us the Hamilton's equations of motion

$$\frac{dp_i}{dt} \equiv \dot{p}_i = -\frac{\partial H}{\partial q_i}, \quad \frac{dq_i}{dt} \equiv \dot{q}_i = \frac{\partial H}{\partial p_i}.$$

Example 39

Consider the Hamiltonian

$$H = \sum_i \frac{p_i^2}{2m} + V(q),$$

where the first term is the kinetic energy and the second is the potential energy.

Then the Hamilton's equations tell us that

$$\dot{p}_i = -\frac{\partial V}{\partial q_i}$$

(this is Newton's second law), and

$$\dot{q}_i = \frac{p_i}{m}$$

(this connects with our classical definition of position and momentnum). In lecture, we defined the **Poisson bracket**

$$\{A, B\} = \sum_i \frac{\partial A}{\partial q_i}\frac{\partial B}{\partial p_i} - \frac{\partial A}{\partial p_i}\frac{\partial B}{\partial q_i}.$$

Notice that $\{A, B\} = -\{B, A\}$, and this is useful because it helps us work with the total derivative of a function like

$$\frac{d}{dt} f(p, q, t) = \frac{\partial f}{\partial t} + \sum_i \frac{\partial f}{\partial q_i}\dot{q}_i + \frac{\partial f}{\partial p_i}\dot{p}_i.$$

Substituting in with Hamilton's equations, we find that this becomes

$$= \frac{\partial f}{\partial t} + \sum_i \frac{\partial f}{\partial q_i}\frac{\partial H}{\partial p_i} - \frac{\partial f}{\partial p_i}\frac{\partial H}{\partial q_i} = \frac{\partial f}{\partial t} + \{f, H\}.$$

So if f has no explicit time-dependence (it just depends on our internal variables p and q), and it commutes with the Hamiltonian (so $\{f, H\} = 0$), then f will be a conserved quantity. And in particular,

$$\frac{dH}{dt} = \frac{\partial H}{\partial t} + \{H, H\} = \frac{\partial H}{\partial t}$$

(because $\{H, H\} = -\{H, H\}$ must be zero). So this tells us that **energy is conserved as long as H has no explicit time-dependence**.

Example 40

Consider an **ensemble**, meaning that we have a collection of separate systems, with a density $\rho(p, q, t)$.

It's important to note that this density tells us not about the properties of a particular system, but rather the "density in phase space" of the different possible configurations. Then we can consider the relationship between $\frac{d\rho}{dt}$ (what happens to a density that we follow around a point that we follow evolving according to Hamilton's equations?) and $\frac{\partial \rho}{\partial t}$ (how does probability density flow at a fixed point?). We proved during lecture that the former is zero, and we'll think about that some more here. We have the **conservation of number** equation

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

where the second (divergence) term tells us how much stuff is "flowing in or out" at the given point. (Here, $\vec{v}$ is the **phase space velocity**, defined as $(\dot{q}_1, \dot{p}_1, \cdots, \dot{q}_{3N}, \dot{p}_{3N})$.) That equation can be rewritten as

$$0 = \frac{\partial \rho}{\partial t} + \vec{v} \cdot \vec{\nabla}\rho + \rho \vec{\nabla} \cdot \vec{v},$$

and now the divergence of the velocity is

$$\vec{\nabla} \cdot \vec{v} = \sum_i \frac{\partial}{\partial q_i} \dot{q}_i + \frac{\partial}{\partial p_i} \dot{p}_i = \sum_i \frac{\partial^2 H}{\partial q_i \partial p_i} - \frac{\partial^2 H}{\partial p_i \partial q_i} = 0$$

by Hamilton's equations. (In other words, "phase space volume is conserved, because there is no divergence.) And this argument doesn't need to worry about "doing first-order calculations," like we needed in lecture with the chain rule, since we're computing a derivative more straightforwardly.

So knowing that phase space is conserved, and that the number of points is conserved, should tell us that the density is conserved. But we can find that explicitly: from the above equation,

$$\frac{d\rho}{dt} = \frac{\partial \rho}{\partial t} + \sum_i \dot{q}_i \frac{\partial \rho}{\partial q_i} + \dot{p}_i \frac{\partial \rho}{\partial p_i} = \frac{\partial \rho}{\partial t} + \vec{v} \cdot \vec{\nabla} \rho,$$

so we have that

$$0 = \frac{d\rho}{dt} + \rho(\vec{\nabla} \cdot \vec{v})$$

(note that this equation now has a **total** derivative). Since we just found that $\vec{\nabla} \cdot \vec{v} = 0$, $\frac{d\rho}{dt} = 0$, and therefore

$$\frac{\partial \rho}{\partial t} = -\{\rho, H\}.$$

And this is important to us because **at equilibrium**, we expect $\frac{\partial \rho}{\partial t} = 0$: there should be no average change in the density of states, and that means that $\{\rho, H\} = 0$ at equilibrium. It was mentioned in lecture that

$$\{f(H), H\} = f'(H)\{H, H\} = 0,$$

so it makes sense for ρ to be **just a function of the energy of the system**. (If there were other conserved quantities that had a Poisson bracket of zero with H, then ρ could also be a function of those other quantities, though.)

6 September 14, 2020

Our first homework assignment is due tomorrow evening – each of the course staff will have an office hour before we need to turn in the assignment. (And if time zones don't work out for any of us, we should send an email.)

We'll look more carefully at the **microcanonical distribution** today, which is a setup where calculating average macroscopic quantities over short space and time intervals can be done simply: recall that if our system is isolated with energy E, then we have the probability distribution

$$p(a) = \begin{cases} \frac{1}{\Omega(E)} & E_a = E \\ 0 & \text{otherwise.} \end{cases}$$

Last time, we showed Liouville's theorem (a classical dynamics result) as some justification for why this kind of result makes sense. Liouville's theorem says that if we have an **ensemble** (collection) of systems distributed in phase space with some density $\rho(\vec{q}, \vec{p}, t)$, then

$$\frac{d\rho}{dt} = 0 \implies \frac{\partial \rho}{\partial t} = -\{\rho, H\} = -\sum_\alpha \left(\frac{\partial \rho}{\partial q_\alpha} \frac{\partial H}{\partial p_\alpha} - \frac{\partial \rho}{\partial p_\alpha} \frac{\partial H}{\partial q_\alpha} \right).$$

And in particular, at equilibrium, since $\frac{\partial \rho_{\text{eq}}}{\partial t} = 0$, we must have $\{\rho_{\text{eq}}, H\} = 0$. Then as long as we have a generic system without any conservation laws, the equilibrium density can be just a function of the Hamiltonian H, and therefore the probability density basically "only depends on our energy."

Remark 41. *We're restricting ourselves to situations here where the Hamiltonian H is conserved, so it makes sense to define it as the energy of our system. (After all, systems with time-dependence in H are not at equilibrium.)*

We'll now make a few comments about why the microcanonical distribution "actually works:"

- The first thing we might notice is that **the microcanonical probability distribution is a δ-function**, which is only nonvanishing in phase space on a specific surface with some specified energy E. So the normalization factor $\Omega(E)$ is just the **area (or volume) of the surface** that we have. In practice, it's convenient to assume that this total energy E has some small uncertainty – maybe we don't know the exact energy of the state, so we'll often consider the distribution to be **uniform and nonzero in the shell**

  $$E \le E_a \le E + \Delta E.$$

  Our normalization factor then becomes the volume of this shell: $\Omega' = \Omega \Delta E$ (as long as the difference ΔE is small enough), but practically the answers won't change very much at the level of thermodynamic quantities.

- The claim that "time averages are ensemble averages" is basically a dynamical statement for the classical many-body statement: there are different explanations in the classical and quantum cases, so we'll need to discuss them separately. In the classical case, we're saying that dynamics are chaotic, so (except on a set of initial states with measure zero) we will evolve into a "seemingly-random" state, with that randomness following the microcanonical distribution. (The phrase "**ergodicity**" is the idea that phase space trajectories fill the constant-energy surface.) **So it's reasonable to assume that basically any initial system will reach equilibrium with enough time (meaning that the time it spends in various different states is roughly the same)**, and Liouville's theorem shapes what that equilibrium distribution looks like.

- For the quantum many-body system argument, consider such a system in a state with energy E_i, with $E < E_i < E + \Delta E$. Then there are $\Omega(E)\Delta E$ quantum eigenstates in this interval, and when in equilibrium, we know that averages of observables are given by averaging over a uniform distribution of states in energies $[E, E + \Delta E]$. So the probability of any eigenstate α is $\frac{1}{\Omega(E)\Delta E}$ if $E_\alpha \in [E, E + \Delta E]$ and 0 otherwise (much like what we've had so far), and we're saying that the average of any such observable is

  $$\langle O \rangle = \frac{1}{\Omega(E)\Delta E} \sum_{\alpha : E < E_\alpha < E + \Delta E} \langle \alpha | O | \alpha \rangle .$$

  We'll define this to be $\langle O \rangle_{\text{micro, E}}$. The reason for the above equality is a topic of current research: the main question is "what is the nature of quantum many-body chaos?". Here, we are analyzing **eigenstate thermalization hypothesis (ETH)** (Srednicki '94, Deutsch '91), which basically states that a state initially far away from equilibrium will evolve in time to be seemingly in equilibrium:

  Proposition 42

  If we consider a generic Hamiltonian, and we have some single eigenstate with a finite energy density (per unit volume), this eigenstate will behave "like a thermal ensemble."

  To be more precise, if $|\alpha\rangle$ is such an eigenstate, and we have some observables O which are sums of operators that can be localized in small regions of space (like the total magnetization or total energy), then

  $$\langle \alpha | O | \alpha \rangle = \langle O \rangle_{\text{micro, } E_\alpha} + o(e^{-\# N}),$$

with off-diagonal matrix elements $\alpha \neq \beta$ (where β is some other energy eigenstate) satisfying

$$\langle \alpha | O | \beta \rangle = o(e^{-\# N}).$$

Because N is being sent to infinity, the exponentially decaying terms go away, and our averages "look like what we expect" in the microcanonical distribution.

Example 43

If we have a spin 1/2 system with Hamiltonian

$$H = \sum_{i,j} \sigma_i^z \sigma_j^z + \sigma_i^x \sigma_i^y,$$

the kind of quantity we care about when we say we have a "localized" operator looks like $M = \sum_i \sigma_i^z$, rather than something like an infinite product of operators.

So now if we take some generic state, we can write it in terms of the energy eigenstates

$$|\psi\rangle = \sum_\alpha c_\alpha |\alpha\rangle .$$

Then the time-evolution of this state is

$$|\psi(t)\rangle = e^{-iHt/\hbar} |\psi\rangle = \sum_\alpha c_\alpha e^{-iE_\alpha t/\hbar} |\alpha\rangle ,$$

and then the expectation of our observable O is

$$\langle \psi(t) | O | \psi(t) \rangle = \sum_{\alpha,\beta} c_\alpha^* c_\beta e^{i(E_\alpha - E_\beta)t/\hbar} \langle \alpha | O | \beta \rangle .$$

And now we use the ETH hypothesis we've been mentioning above: due to exponential decay, we can write this as just

$$\approx \sum_\alpha |c_\alpha|^2 \langle \alpha | O | \alpha \rangle = \sum_\alpha |c_\alpha|^2 \langle O \rangle_{\text{micro, } E_\alpha}.$$

And if $|c_\alpha|$ is prepared so that it is initially sharply peaked with some energy E_0, we can use the fact that $\langle O \rangle_{\text{micro }, E}$ varies slowly with E (which we will explain later in this class), and this tells us that

$$\langle \psi(t) | O | \psi(t) \rangle \approx \langle O \rangle_{\text{micro, } E = E_\alpha} \sum_\alpha |c_\alpha|^2 = \langle O \rangle_{\text{micro, } E = E_\alpha}.$$

So this "thermalization" statement gives us some further foundation for the microcanonical distribution.

Remark 44. *Many of the arguments we've been presenting here have numerical and physical evidence, but there are some exceptions. We can search up the example of "many-body localization," which involves systems with a certain kind of strong disorder, as well as certain special kinds of cold atomic systems.*

From here on, we'll do "regular stat mech:" we'll assume the microcanonical distribution works, and we'll try doing some calculations with the density of states and systems in contact with each other.

7 September 16, 2020

Last class, we made some arguments about why the microcanonical distribution works (that is, why it's a legitimate way of thinking about the equilibrium state of our system). It's a complicated subject with lots of subtle aspects, and specifically, there's a lot of ongoing work looking into the **ETH (eigenstate thermal hypothesis)**. But we'll put that behind us for now, and we'll take the microcanonical distribution as a way of calculation for granted, looking at what consequences follow.

Recall that the probability distribution we've been talking about requires us to know the value of

$$\Omega(E)\Delta E = \{\text{total number of microstates with energy in } [E, E+\Delta E]\}.$$

This function $\Omega(E)$ actually grows very quickly: for a typical many-body system with N degrees of freedom, we'll typically have the order of growth

$$\Omega(E) \propto E^{cN}$$

for some constant $c > 0$. This function is known as the **density of states**, and we'll work out an example of this now:

Example 45

Consider N free (quantum mechanical) particles inside a rigid box of side length L.

(The motion of those particles is then described by the free-particle Schrodinger equation.) This system has total energy

$$E = \sum_{i=1}^{N} \frac{\vec{p}_i^2}{2m},$$

where $\vec{p}_i$ denotes the momentum of the Nth particle. We want to calculate the number of states within some specified energy level, and we'll make our life easier by assuming **periodic boundary conditions**. Then our particles in a box must satisfy

$$\vec{p}_i = \frac{2\pi\hbar}{L}\vec{n}_i, \qquad \vec{n}_i = (n_{ix}, n_{iy}, n_{iz}),$$

where n_{ix}, n_{iy}, n_{iz} are all integers, because we need $e^{i\vec{p}_i\cdot\vec{x}_i}$ to be periodic under $x_i \to x_i + L$ or similar translations in the y- and z-direction. So the number of states $\omega(E)$ with energy **at most** E is

$$\omega(E) = \sum_{\{\vec{p}_i\}} \left(\text{all possible } \vec{p}_i \text{ such that } \sum_i \frac{\vec{p}_i^2}{2m} \le E\right).$$

And now this sum can be approximated with an integral if we have a large enough box length L. For example, if we're summing up the x-components of one specific particle's momentum, we can replace with

$$\sum_{p_x} \Longrightarrow \int \frac{dp_x}{2\pi\hbar/L}$$

(because $\frac{2\pi\hbar}{L}$ is the spacing in phase space between our states, and we're using a Riemann sum). That means we can also write

$$\omega(E) = \left(\frac{L}{2\pi\hbar}\right)^{3N} \int \prod_i d^3p_i \; \theta\left(E - \sum_j \frac{\vec{p}_j^2}{2m}\right).$$

where θ is the Heaviside step function

$$\theta(x) = \begin{cases} 1 & x > 0, \\ 0 & x < 0. \end{cases}$$

This integral is also

$$\omega(E) = \left(\frac{L}{2\pi\hbar}\right)^{3N} \int_{\sum_j p_j^2 \le 2mE} \prod_i d^3 p_i$$

and now we want to understand the E-dependence of this quantity. To do this, we make a change of variables: if we let $\vec{p}_i = \sqrt{2mE}\vec{u}_i$, then

$$\omega(E) = \left(\frac{L}{2\pi\hbar}\right)^{3N} (2mE)^{3N/2} \int_{\sum_j p_j^2 \le 1} \prod_i d^3 p_i,$$

and now the integral is a unitless quantity: it's the volume of a unit sphere in $3N$ dimensions, so it's **some constant that's independent of the energy** E. Therefore, the **total** number of states

$$\omega(E) \propto \left(\frac{L}{2\pi\hbar}\right)^{3N} (2mE)^{3N/2} \propto E^{3N/2}.$$

Now, we want to count the number of states that are around some certain energy E – this is similar to finding the probability density function from the cumulative density function. Then the density of states is obtained by taking a derivative, since

$$\Omega(E)dE = \omega(E + dE) - \Omega(E)$$

(and then taking the limit as $dE \to 0$), and therefore we have

$$\Omega(E) = \frac{d\omega(E)}{dE} \propto E^{3N/2-1}.$$

The -1 in the exponent doesn't really play a role as N goes to infinity, and the point is that we've shown the **rapid growth** of Ω as a function of E for our special example. This enables us to make certain approximations that are exact in the limit $N \to \infty$, which will be useful for us.

Remark 46. *Note that not all systems exhibit this rapid growth: in our homework assignment, we'll be able to look at a system of spins in a magnetic field, which behaves very differently.*

Because this quantity $\Omega(E)$ grows so quickly, it's easier and useful for us to extract a slower-growing quantity out of it, which is

$$S = k_B \ln \Omega(E).$$

Here, k_B is some constant which we identify with the Boltzmann constant, and S is now some function of the energy, the number of particles in our system, the volume, and so on. Later on in this class, we'll identify S with the entropy (from thermodynamics), but we'll work with its properties and understand why S plays this kind of descriptive role.

Our next goal of this class will be to establish what the term **thermal equilibrium** means when we have two (large) systems in contact with each other – we'll do that using the microcanonical distribution.

Example 47

Suppose two large systems A_1, A_2 are next to each other, each with N particles, so that energy can be exchanged between them but nothing else (not particles or volume).

In this setting, our combined system (A_1 and A_2) is still isolated from the outside environment, so the total energy

E will be fixed. We'll assume that any interaction between these systems is weak, so that we can make the assumption

$$E = E_1 + E_2,$$

where E_1 is the energy of system A_1 and E_2 is the energy of system A_2. (This basically means that we don't need to worry about particles in A_1 and A_2 having gravitational interactions and so on.) The strength of this interaction does influence how long it takes for the two systems A_1 and A_2 to equilibrate, but we'll just **assume we're in equilibrium** and try to calculate what's going on.

We know that $A_1 + A_2$ is an isolated system, so it follows the microcanonical distribution at equilibrium, meaning that a microstate (a_1, a_2) of the joint system occurs with probability $\frac{1}{\Omega(E)}$ if $E_1 + E_2 = E$ and 0 otherwise. And furthermore,

$$\Omega(E) = \int dE_1 \Omega_1(E_1)\Omega_2(E - E_1),$$

since we're only interested in states where the total energy sums to E. And now defining Ω_i to be the density of states of system A_i, and using that

$$\Omega_i = e^{S_i/k_B},$$

we can rewrite the above integral as

$$\Omega(E) = \int dE_1 e^{1/k_B(S_1(E_1)+S_2(E-E_1))}.$$

But remember that the entropy S is of order N if the density of states $\Omega_1(E)$ is of order E^{cN}. So we are really evaluating something that looks like

$$\int dx\, e^{N\phi(x)},$$

where N is very large and ϕ is some function of x, and such integrals can be evaluated with **saddle-point approximation**, which we'll describe now. Notice that $\Omega_1(E_1)$ is extremely rapidly increasing as a function of E_1, while $\Omega_2(E - E_1)$ is extremely rapidly decreasing (because $E - E_1$ rapidly decreases). Therefore, their product will be very sharply peaked at a specific value for E_1, and we will **equate the integral to the maximum value of the integrand**.

And the saddle point approximation is what helps us do this calculation: if we want to compute

$$I = \int dx\, e^{N\phi(x)}$$

for a real function ϕ and a very large value of N, notice that any differences in ϕ are amplified both by the multiplication by N and by the subsequent exponentiation. So if we let $x = x_{\text{max}}$ be the maximum value of ϕ, we can expand in a Taylor series

$$\phi(x) \approx \phi(x_{\text{max}}) - \frac{1}{2}|\phi''(x_{\text{max}})|(x - x_{\text{max}})^2 + \cdots,$$

and plugging this in yields

$$I = \int dx\, e^{N(\phi(x_{\text{max}}) - \frac{1}{2}|\phi''(x_{\text{max}})|(x-x_{\text{max}})^2+\cdots)}.$$

The first term in the exponent doesn't depend on x, so we can take it out of the integral, and that leaves us with

$$= e^{N\phi(x_{\text{max}})} \int dx\, e^{-\frac{N}{2}|\phi''(x_{\text{max}})|(x-x_{\text{max}})^2+\cdots}.$$

We can now **extend the limits of integration** to go from $-\infty$ to ∞, because the contributions on the tails basically don't matter – the largest contributions are coming near the middle. And we'll make the further approximation

$$\approx e^{N\phi(x_{\text{max}})} \int_{-\infty}^{\infty} dx\, e^{-\frac{N}{2}|\phi''(x_{\text{max}})|(x-x_{\text{max}})^2}.$$

by ignoring higher-order terms. (This is okay because $(x - x_{\text{max}})$ is of order $\frac{1}{\sqrt{N}}$, and thus the higher power terms have corrections in a power series in $\frac{1}{\sqrt{N}}$, which we can ignore in the limit.) This is now just a Gaussian integral, and we get the answer

$$\boxed{I \approx \sqrt{\frac{2\pi}{N|\phi''(x_{\text{max}})|}} e^{N\phi(x_{\text{max}})}}.$$

Note that if there are a few different local maxima for our function $\phi(x)$, we can (in principle) do the same approximation for each of them. But then we have

$$I = \sum_{x_{\text{max}}} \sqrt{\frac{2\pi}{N|\phi''(x_{\text{max}})|}} e^{N\phi(x_{\text{max}})},$$

but any unique global maximum will dominate the sum, so this is not necessary unless there are two different values of x which both reach the global maximum. And restricting **only to the global maxima** also helps us deal with the validity of our approximations – we won't get any weird tail behavior.

Fact 48

This kind of saddle-point integration can help us compute an asymptotic expression for the factorial $N!$, which we'll see during recitation.

So returning to the integrand we actually care about, we need to first find the maximum value of the integrand

$$e^{1/k_B(S_1(E_1)+S_2(E-E_1))}.$$

This occurs when the derivative of the exponent is zero, which happens at the value E_1^* where

$$\boxed{\left.\frac{\partial S_1}{\partial E_1}\right|_{E_1=E_1^*} = \left.\frac{\partial S_2}{\partial E_2}\right|_{E_2=E-E_1^*}},$$

and then replacing the integral with the integrand gives us the density of states

$$\Omega(E) = e^{\frac{1}{k_B}(S_1(E_1^*)+S_2(E-E_1^*))}.$$

So the boxed expression above is now the **condition for systems A_1 and A_2 to be in equilibrium with each other**. Since the left-hand side only depends on system A_1, and the right-hand side only depends on system A_2, we're dealing with a "matching of properties" between the two systems:

Definition 49

The **temperature** T of a system is defined via

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

In other words, two systems are at (thermal) equilibrium if $T_1 = T_2$, and this agrees with the usual description. (The reason for the reciprocal is a convention will make sense later.) Then the entropy of the full system satisfies

$$S(E) = k_B \ln \Omega(E) = k_B \left(\ln(\Omega_1(E_1^*)) + \ln(\Omega_2(E - E_1^*))\right) = S_1(E_1^*) + S_2(E_2^*),$$

and therefore **entropy is additive at equilibrium** for large systems. (This is already something we've been implicitly assuming when we say that the density of states increases as e^{cN}.)

Finally, we can now return to the gas of free particles from earlier again: since $\Omega(E) \propto E^{3N/2-1}$, the entropy of the system is

$$S(E, N) = \frac{3}{2} N k_B \ln E + C$$

for some constant C. (We're ignoring the -1 because it's negligible compared to the N term.) Therefore,

$$\frac{1}{T} = \frac{\partial S}{\partial E} = \frac{3}{2}\frac{N k_B}{E} \implies E = \frac{3}{2} N k_B T.$$

This is the familiar formula for the energy of an ideal gas in 3 space dimensions. This means that we've obtained a **macroscopic statement** just by knowing how to calculate the density of states of our system.

8 September 18, 2020 (Recitation)

Today, we'll talk about some mathematical details and examples related to the material from lecture.

The first topic of the recitation is the **saddle-point approximation**, which is one of the core reasons "all of statistical mechanics works." We'll start with the sum version: suppose we have an expression

$$\Omega = \sum_{i=1}^{n} e^{N\phi_i}.$$

Then the loose claim we're making is that $\Omega \sim e^{N\phi_{\max}}$ when N is large, where $\phi_{\max}$ was the largest value of ϕ over all indices. More rigorously, we're claiming that

$$\lim_{N\to\infty} \frac{\ln \Omega}{N} = \frac{\ln e^{N\phi_{\max}}}{N} = \phi_{\max}.$$

Proof of the asymptotic result. We know that the sum is at most equal to the quantity when all terms in the sum are equal to the maximum value, so

$$e^{N\phi_{\max}} \le \Omega \le n e^{N\phi_{\max}},$$

so taking the natural log and dividing by N gives us

$$\phi_{\max} \le \frac{\ln \Omega}{N} \le \phi_{\max} + \frac{\ln n}{N}.$$

So as long as the number of terms n is, for example, polynomial in N, the log term $\frac{\ln n}{N}$ will go to 0, and the sandwich theorem gives us the result. ☐

This sum version helps us out when we go to the integral version and have multiple global maxima, but we'll now look at the actual saddle-point approximation that we care about. If we start with an integral of the form

$$I = \int dx\, e^{N\phi(x)},$$

then we can rewrite this as a Taylor series around a (local or global) maximum $x = x_m$ as

$$= \int dx\, e^{N\left[\phi(x_m) + \frac{1}{2}\phi''(x_m)(x-x_m)^2 + \frac{1}{6}\phi'''(x_m)(x-x_m)^3 + \cdots\right]}.$$

(There's no first derivative because we're at a maximum.) The second derivative is negative, and we can pull out the constant and write this as

$$e^{N\phi(x_m)} \int dx\, e^{-\frac{N}{2}|\phi''(x_m)|(x-x_m)^2} \left(1 + \frac{N}{6}\phi'''(x_0)(x-x_m)^3 + \frac{N}{24}\phi''''(x_m)(x-x_m)^4 + \cdots\right),$$

where we've pulled the higher order $(x - x_m)$ terms out of the exponential and expanded the Taylor series. So now we can evaluate this integral – we take the limits of integration to $\pm\infty$, which is a small correction. Then the cubic term goes away in the integral because it is odd (and being integrated against the Gaussian from $-\infty$ to ∞). Furthermore, because the expected value of $(x - x_m)$ in the Gaussian is of order $\frac{1}{N}$ (since the width of the Gaussian is of order $\frac{1}{\sqrt{N}}$), the quartic term (that is, the term corresponding to $\frac{N}{24}\phi''''(x_m)(x - x_m)^4$) is again only a small correction of order $N \cdot \left(\frac{1}{\sqrt{N}}\right)^4 = \frac{1}{N}$:

$$= e^{N\phi(x_m)}\sqrt{\frac{2\pi}{N|\phi''(x_m)|}}\left(1 + O\left(\frac{1}{N}\right)\right).$$

And now if we do the same thing as before, where we take the log and then divide by N,

$$\frac{\ln I}{N} = \phi(x_m) + \frac{1}{2^N}\ln\left(\frac{2\pi}{N|\phi''(x_n)|}\right) + O\left(\frac{1}{N^2}\right)$$

(here we use the fact that $\ln(1+\varepsilon) \propto \varepsilon$), and so really we don't even care about the prefactor term: as $N \to \infty$, this quantity just approaches $\phi(x_m)$.

Remark 50. *This looks somewhat similar to the* **central limit theorem***: if we have a bunch of identically distributed random variables X_i with probability distribution*

$$p_X(x) \sim e^{\phi(x)},$$

we could consider N such random variables. Then we're drawing some connections to the fact that we get something close to a Gaussian when adding a bunch of these random variables together.

Our next topic is an application of the saddle-point approximation: our goal is to calculate an approximate value of the factorial $N!$, which we'll do with an auxiliary definition:

Definition 51

The **gamma function** is defined via the integral

$$\Gamma(N+1) = \int_0^\infty x^N e^{-x} dx$$

for all real numbers N.

We actually have that $\Gamma(N+1) = N!$ when N is an integer. To see that, we integrate by parts to see that

$$\int_0^\infty x^N d(-e^{-x}) = -x^N e^{-x}\big|_0^\infty + \int d(x^N)e^{-x} = N\int x^{N-1}e^{-x}dx.$$

Thus, $\Gamma(N+1) = N\Gamma(N)$, which gives us the familiar recursive formula $N! = N(N-1)!$. And now we can use this to show Stirling's approximation:

$$N! = \int_0^\infty e^{N\ln x - x}dx = \int_0^\infty e^{N\phi(x)}dx,$$

where $\phi(x) = \ln x - \frac{x}{N}$. And now we want to find the maximum value of ϕ: now the function ϕ does actually depend on N, but we can check that the predominant scaling of ϕ isn't changing, so this approximation is still fine. (The point is to not create any weird dependencies.) The maximum value of ϕ here occurs when

$$0 = \phi'(x) = \frac{1}{x} - \frac{1}{N} \implies x = N,$$

so the maximum value of ϕ here is

$$\phi(x_m) = \ln N - 1.$$

(Again, this does depend on N, but it's not as rapid as the growth of N, so it turns out this is fine. If we wanted to be rigorous, we'd have to check the above bounding a bit more carefully.) And now plugging this into our saddle point approximation, we find

$$\phi''(x_m) = -\frac{1}{x_m^2} \implies |\phi''(x_m)| = \frac{1}{N^2},$$

and therefore,

$$N! = \left(1 + O\left(\frac{1}{N}\right)\right) \cdot \sqrt{\frac{2\pi}{N|\phi''(x_m)|}} e^{N\phi(x_m)},$$

which evaluates to

$$\boxed{N! \sim \sqrt{2\pi N} e^{N \ln N - N} = \sqrt{2\pi N} \left(\frac{N}{e}\right)^N}.$$

Looking at the natural log instead, we find that

$$\ln N! = N \ln N - N + \frac{1}{2} \ln(2\pi N) + O\left(\frac{1}{N}\right),$$

and the first two terms here grow much faster than everything else, so we often don't even need more than that.

Remark 52. *For a more rigorous mathematical proof of Stirling's approximation, we can check Wikipedia or some other source. But we can check that the first three terms of this approximation (that we've displayed) do a pretty good job even for something like* $N = 10$.

We'll spend the rest of this class on some calculations, first in information theory:

Example 53

Consider a message of length $N \gg 1$, where each letter can be chosen from the m letters $\{x_1, \cdots, x_m\}$ with **frequency** $p_1, \cdots, p_m$, respectively.

In other words, we are given that exactly $p_i N$ of the total letters of the message must be x_i. Then the quantity

$$\Omega = \frac{N!}{\prod_{i=1}^n (p_i N)!}$$

tracks the number of total messages we can have (this is actually asymptotically the "same" number of messages we get if the p_i are probabilities instead of frequencies, at least in the limit $N \to \infty$ – we should see the **asymptotic equipartition theorem** if we're curious), and we can use Stirling's approximation to find that

$$\ln \Omega = \ln N! - \sum_{i=1}^m \ln((p_i N)!).$$

We'll drop everything except the first two terms, so that

$$\ln \Omega \sim N \ln N - N - \sum_i (N p_i \ln(N p_i) - N p_i).$$

The terms without logs cancel out, because $\sum p_i = 1$, and then we're left with

$$\ln \Omega \sim N \ln N - \sum_i (N p_i \ln N + N p_i \ln p_i).$$

And now the terms with $\ln N$s also cancel out, so this further simplifies to

$$\boxed{\ln \Omega \sim -N \sum_i p_i \ln p_i}.$$

This is really only rigorous at the level that

$$\lim_{N \to \infty} \frac{\ln \Omega}{N} = -\sum_i p_i \ln p_i,$$

but now the right hand is what is called the **information entropy** of the probability distribution.

For example, if we take $p_i = \frac{1}{m}$ for all m, then

$$\lim_{N \to \infty} \frac{\ln \Omega}{N} = -\sum_{i=1}^{m} \frac{1}{m} \ln \frac{1}{m} = \ln M,$$

which means that we get $\ln M$ "bits" of information per letter. But furthermore, $\ln M = \frac{\ln M^N}{N}$, so in the case where all p_is are equal, the number of states Ω is essentially M^N (the set of all possible messages)! So "**the total number of all messages is more-or-less the same as the number of messages where all letters occur with equal frequency**," and we can see that this is a kind of saddle-point approximation being made again: making the change from "all configurations" to "most likely configurations" in the form

$$\sum_{\{n_i\}} \frac{N!}{\prod_{i=1}^{m} n_i!} \to \frac{N!}{\prod_{i=1}^{m} (N/m)!},$$

is negligible as long as we're taking the log of both quantities and dividing by N.

Remark 54. *And this is a very rough justification of the microcanonical ensemble: "assuming everything is equally likely is the same as saying that anything goes." We still need assumptions like ergodicity, because we only have one system in real life, but we're saying that* **our ignorance** *almost allows us to sample from all equally likely states.*

And we'll finish with a discussion of equilibrium and temperature:

Example 55

Suppose we have two systems at energy E_1 and E_2. If the two systems are isolated from each other and everything else, then

$$\Omega = \Omega_1(E_1)\Omega_2(E_2),$$

so $S = S_1 + S_2$ and entropy is additive. But we want to look at how this works when our systems do interact and exchange energy.

In the case where the two systems are allowed to exchange energy, but we're still bound to a total energy of $E = E_1 + E_2$, then the total number of states becomes

$$\Omega = \sum_{E_1+E_2=E} \Omega_1(E_1)\Omega_2(E_2) = \sum_{E_1+E_2=E} \Omega_1(E_1)\Omega_2(E-E_1) = \sum_{E_1+E_2=E} \exp\left[N\left(\frac{N_1}{N}\frac{S_1(E_1)}{N_1} + \frac{N_2}{N}\frac{S_2(E_2)}{N_2}\right)\right],$$

where we've written this in a "saddle-point form" and taken $k_B = 1$. So now the saddle-point approximation lets us say that

$$\Omega(E) \sim \Omega_1(E_1^*)\Omega_2(E_2^*)$$

(as always, with $\sim$ valid after taking the ln and dividing by N, which goes to ∞ in the limit). This is again saying that "equilibrium means we just look at the most likely states:" we now actually have an expression

$$\lim_{N\to\infty} \frac{S(E)}{N} = \frac{N_1}{N}\frac{S_1(E_1^*)}{N_1} + \frac{N_2}{N}\frac{S_2(E_2^*)}{N_2},$$

but we really only care about the **extensive** parts of the system that scale with N, so physicists are okay with writing down an expression like

$$S(E) = S_1(E_1^*) + S_2(E_2^*).$$

From here, we define the **inverse temperature** β so that

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

(This is a more natural variable to use in statistical physics than T, for example if we need to work with negative temperatures.) And we say that **equilibrium** is reached when $T_1 = T_2$ (this is the point where the value of $\Omega_1(E_1)\Omega_2(E_2)$ is maximized) – unless there are multiple maxima or other quantities that are being exchanged, $T_1 = T_2$ is a sufficient condition for equilibrium.

9 September 21, 2020

Our final exam date has now been announced to be Thursday, December 17. The standard timeslot is 9am-noon, but our exam won't take that long since everyone is at home – it'll be designed to take about 1.5 hours instead, so that people in Pacific Time can still wake up earlier to take the exam. (We won't need to turn on our video or anything, but the course staff will be available during the exam time period to answer questions if they come up.) Our first quiz will be on September 30, and more details about that are to be posted later.

Remark 56. *We should expect a survey to be sent out about the class soon (as suggested by the department).*

Today, we're going to continue exploring the equilibrium state of two systems that are in contact with each other. As before, suppose we have these two systems A_1 and A_2, which can be in certain microstates (a_1, a_2) with energies (E_1, E_2). If these two systems are allowed to exchange energy, and we allow this system to evolve towards equilibrium, we will settle into a **microcanonical distribution** of the full systems. (We aren't thinking very much about the evolution towards equilibrium, which depends on the detailed dynamics of the two systems.)

And as we showed with the saddle-point approximation, this combined system at equilibrium will spend most of its time at a specific energy level – what we're basically saying is that we can pick some (E_1^*, E_2^*) energies for our systems so that for all $E_1 + E_2 = E$,

$$\Omega_1(E_1^*)\Omega_2(E_2^*) \geq \Omega_1(E_1)\Omega_2(E_2),$$

where (E_1^*, E_2^*) are the energies for (A_1, A_2) in the final equilibrium state. In other words, the entropy of the final system will satisfy

$$\boxed{S_{\text{final}} = k_B \ln(\Omega_1(E_1^*)\Omega_2(E_2^*)) \geq S_{\text{initial}} = k_B \ln(\Omega_1(E_1)\Omega_2(E_2))}.$$

This means that **entropy has increased** from the initial to final state: over the next few weeks, we'll formulate this into a more coherent law of thermodynamics. And we calculated this energy E_1^* by finding the maximum value of $S_1(E_1) + S_2(E - E_1)$. At such a point, the first derivative must vanish, and the second derivative must be negative, so

$$\left.\frac{\partial^2 S_1}{\partial E_1^2}\right|_{E_1=E_1^*} + \left.\frac{\partial^2 S_2}{\partial E_2^2}\right|_{E_2=E_2^*} < 0.$$

This is a “stability condition” for our equilibrium, and an analogous condition needs to be true if we have other conserved quantities in our system as well (such as spin).

Fact 57

We can relate this second derivative of S to a measurable quantity, but we'll postpone that discussion for now.

Example 58

For now, let's return to the (canonical) ideal gas system from last lecture. We're going to be **more careful** about the density of states calculation from last class this time, looking at prefactors and being more exact.

We showed that $\Omega(E) \sim E^{cN}$ for a gas with N particles, but we want an actual formula for the density of states of our non-relativistic gas here. Recall that we had the following integral expression for the number of states with energy at most E:

$$\omega(E) = \left(\frac{L}{2\pi\hbar}\right)^{3N} \int_{\vec{p}_1^2+\cdots+\vec{p}_N^2 \le 2mE} \prod_i d^3 p_i.$$

We then made the change of variables $\vec{p}_i = \sqrt{2mE}\,\vec{u}_i$, so that the integral became a dimensionless quantity in terms of N:

$$\omega(E) = \left(\frac{L}{2\pi\hbar}\right)^{3N} (2mE)^{3N/2} V,$$

where V is the volume of a unit sphere in $3N$ dimensions. To calculate this V, note that a sphere in d dimensions of radius R has volume

$$\int_0^R r^{d-1} dr s_d = \frac{R^d}{d} s_d$$

where s_d is the **solid angle**. We calculate this solid angle with a trick: if we consider the integral

$$I_d = \left(\int_{-\infty}^{\infty} e^{-x^2} dx\right)^d = (\sqrt{\pi})^d = \pi^{d/2},$$

we can also compute it in the alternative manner

$$= \int_{-\infty}^{\infty} dx_1 \cdots dx_d e^{-(x_1^2+\cdots+x_d^2)}.$$

But this integrand is also spherically symmetric in d dimensions, so we can evaluate it in radial coordinates: letting $r^2 = x_1^2 + \cdots + x_d^2$, we find that

$$I_d = \int_0^{\infty} dr r^{d-1} s_d e^{-r^2} = \frac{s_d}{2} \int_0^{\infty} dy y^{d/2-1} e^{-y}$$

where we've made the substitution $y = r^2$, and where s_d is the same solid angle in d dimensions as before. And now the integral is the Gamma function discussed in recitation, so it's exactly $\left(\frac{d}{2} - 1\right)!$ (If d is odd, we just use the Gamma function instead of the factorial.) And therefore

$$\pi^{d/2} = \frac{s_d}{2}\left(\frac{d}{2} - 1\right)! \implies \boxed{s_d = \frac{2\pi^{d/2}}{\left(\frac{d}{2}-1\right)!}}.$$

And now we can plug this into the volume V we're trying to find (setting $R = 1$ and plugging in $d = 3N$), and this gives us that

$$\omega(E) = \left(\frac{L}{2\pi\hbar}\right)^{3N} \frac{(2mE)^{3N/2}}{3N} \frac{2\pi^{3N/2}}{\left(\frac{3N}{2}-1\right)!}.$$

This time, we can obtain a formula for the density of states, which is

$$\Omega(E) = \frac{d\omega}{dE} = \frac{2m}{2}\left(\frac{L}{2\pi\hbar}\right)^{3N}(2mE)^{3N/2-1}\frac{2\pi^{3N/2}}{(\frac{3N}{2}-1)!}$$

Remark 59. *There's a slight notational difference here than in Kardar's book, in which $\Omega_{Kardar}(E)$ is defined to be the number of states in an energy window from $E-\Delta$ to $E+\Delta$. So there's an extra factor of 2Δ in $\Omega_{Kardar}(E)$ compared to our $\Omega(E)$. (But this is a factor of order 1 which doesn't plan into the final calculations.)*

Recall that our ideal gas system is inside a cubic box of length L, so we can define the volume $V = L^3$ to find the density of states in terms of the energy E, volume V, and number of particles N:

$$\Omega(E, V, N) = \frac{V^N}{(2\pi\hbar)^{3N}} m \frac{2\pi^{3N/2}}{(\frac{3N}{2}-1)!}(2mE)^{3N/2-1}.$$

We can then find the entropy by calculating

$$S(E, V, N) = k_B \ln \Omega(E, V, N).$$

If we take $N \to \infty, V \to \infty, E \to \infty$ **while keeping the ratios $\frac{E}{N}$ and $\frac{V}{N}$ finite** – this is called the **thermodynamic limit**, and we'll be taking this limit often – then we can use Stirling's approximation and only keep the terms of leading order in N. Then

$$S(E, V, N) = k_B\left[N \ln \frac{V}{(2\pi\hbar)^3} + \frac{3N}{2}\ln(2\pi mE) - \frac{3N}{2}\ln\frac{3N}{2} + \frac{3N}{2}\right],$$

which simplifies to

$$= Nk_B \ln\left[\frac{V}{(2\pi\hbar)^3}\left(\frac{4\pi emE}{3N}\right)^{3/2}\right].$$

(Here, e is Euler's constant, and it comes from the $\frac{3N}{2}$ in the entropy.) But **something isn't quite right here**: this answer is **not extensive**, because there's an weird dependence on the scale of our system inside the log term. We can be more formal about what we mean:

Definition 60

A quantity $f(E, V, N)$ is **extensive** if the transformation $(E, V, N) \to (\lambda E, \lambda V, \lambda N)$ takes f to λf.

(It makes sense for entropy to be extensive in the large N limit, based on the idea that "entropy basically adds when two systems combine.") We can check that doing this transformation to our above entropy expression sends S to $\lambda(S + Nk_B \ln \lambda)$, instead of λS, and this was an issue that Gibbs (one of the founders of statistical mechanics) noticed when thinking about thermodynamic considerations of two identical gases mixing with each other – this issue goes by the name of the **Gibbs paradox**.

The way Gibbs got around this issue was to propose that **gases are made out of indistinguishable particles**. In other words, we should count the number of states $\omega(E)$ (and subseqeuntly the density of states $\Omega(E)$) by allowing **permutations of the particles to be the same state**. Since a gas with N particles has $N!$ such permutations, the actual correct expression is

$$\boxed{\Omega(E, V, N) = \frac{1}{N!}\frac{V^N}{(2\pi\hbar)^{3N}} m \frac{2\pi^{3N/2}}{(\frac{3N}{2}-1)!}(2mE)^{3N/2-1}}.$$

The modified entropy then becomes (using Stirling's approximation on the $N!$ term)

$$\boxed{S(E, V, N) = Nk_B \ln\left[\frac{eV}{N(2\pi\hbar)^3}\left(\frac{4\pi emE}{3N}\right)^{3/2}\right]},$$

and this time the log argument only involves the finite constant ratios $\frac{V}{N}$ and $\frac{E}{N}$. So now **entropy is actually an extensive quantity**: S is now proportional to N, as expected.

Fact 61

This idea of treating different atoms as indistingiushable is really just a "hack" at first, and in classical statistical mechanics, it is just a postulate that we're asserting. But in quantum mechanics, we need this indistinguishability for determining which Hilbert space our particle wavefunctions live in (for instance, symmetric wavefunctions for bosons and antisymmetric ones for fermions), so we do (unavoidably) need the $\frac{1}{N!}$ factor for an accurate description of different states. (Basically, we can't "tag" individual particles and separate out which one is which in quantum mechanics.)

In other words, we get a sensible result in this case when we regard the classical gas as an approximation to the quantum gas.

Remark 62. *Note that if we were a physicist pre-quantum-mechanics, we would need some quantity that helped deal with the dimensionful volume in phase space. So the entropy depends on the units being used in classical mechanics, but in quantum statmech, we have a $2\pi\hbar$ to help balance out that volume factor. And this helps us remove ambiguity from the classical statmech description – we should think about it as the limit of the quantum description.*

10 September 23, 2020

Our next homework assignment has been posted – it's longer than previous homework assignments and carries twice the weight, because there is a quiz next week. So the pset will be due in two weeks, and we can pace ourselves accordingly.

Example 63

Today, we're going to consider a situation where our system is connected to a (much larger) **bath**. (The system and bath can still only interact by exchanging energy, though.)

Label the system of interest A_1 and the bath A_2 – we'll assume the number of degrees of freedom for the two systems satisfy $N_{A_2} \gg N_{A_1} \gg 1$. Much like before, we're taking the combined system $A_1 + A_2$ to be isolated from the rest of the world, so that it can be described by the usual microcanonical distribution when it's in equilibrium. Our goal is then to derive the probability distribution for the microstates of our system A_1.

To do this, suppose we have some **particular microstate** n of A_1 with energy E_n. If the total energy of the combined system $A_1 + A_2$ is E_0, then the probability of n is

$$p(n) = \mathbb{P}(A_1 \text{ is in state } n) \propto \Omega_2(E_0 - E_n),$$

because $\Omega_2(E_0 - E_n)$ tracks the density of states for our bath and therefore how many microstates can exist at this given (complementary) energy in the system.

Remark 64. *This is basically a conditional probability: we're taking the number of possible combined states* $\Omega_1(E_n)\Omega_2(E_0 - E_n)$*, and dividing through by* $\Omega_1(E_n)$ *because we're conditioning on an energy* E_n *for the first system.*

If we have a large bath, lots of the energy of the total system will be in the bath. This means that $E_0 \gg E_n$, and $\Omega_2(E_0 - E_n)$ is a rapidly decreasing function of E_n. From our above argument, we also know that

$$\ln p(n) = \ln(\Omega_2(E_0 - E_n)) + \text{constant},$$

and we can Taylor expand this to leading order as

$$\approx \text{const} - E_N \frac{\partial}{\partial E_0} \ln \Omega_2(E_0).$$

If our system A_1 is in equilibrium with the bath A_2, then we know that

$$\frac{\partial}{\partial E_0} \ln \Omega_2(E_0) = \frac{1}{k_B T},$$

where T is the common temperature of our system and bath. Therefore, we find that

$$\ln p(n) = c - \beta E_n,$$

where $\beta = \frac{1}{k_B T}$, which can be rewritten in the following statement:

Proposition 65 (Canonical ensemble)
The probability that a system is in a state n with energy E_n satisfies

$$p(n) \propto e^{-\beta E_n}.$$

In order to make this a valid probability distribution, our normalization constant, obtained via $\sum_n p(n) = 1$, must be the **partition function**

$$Z = \sum_n e^{-\beta E_n},$$

and therefore the probability of a state n is explicitly

$$p(n) = \frac{1}{Z} e^{-\beta E_n}.$$

We'll see that being able to calculate Z as a function of external variables, like T or V, will help us **extract information about equilibrium properties**.

Example 66
Let's calculate the average energy of our system A_1. (This is often called the **internal energy** and is denoted U.)

We know that E_1 is not fixed in this situation, because we can exchange energy between A_1 and A_2. But we can write out the average energy explicitly as

$$U = \langle E_1 \rangle = \sum_n p(n) E_n = \sum_n \frac{E_n e^{-\beta E_n}}{Z} = \frac{\sum_n E_n e^{-\beta E_n}}{\sum_n e^{-\beta E_n}},$$

and now a slight trick (taking advantage of the similarity of the numerator and denominator) yields

$$\boxed{U = -\frac{\partial}{\partial \beta} \ln\left(\sum_n e^{-\beta E_n}\right) = -\frac{\partial}{\partial \beta}(\ln Z)}.$$

So taking a single derivative gives us a useful macroscopic quantity!

Definition 67

Define the **(Helmholtz) free energy** via the equation

$$Z = e^{-\beta F}.$$

This turns out to be usefully related to the other quantities

$$F = -\frac{1}{\beta}\ln Z \implies U = \frac{\partial}{\partial \beta}(\beta F).$$

Knowing the free energy is equivalent to know the partition function, and the reason for introducing this expression is that derivatives of F are easy to measure (for example, as we've just shown, it's closely connected to U). We'll be able to extract macroscopic equilibrium behavior just from this quantity F, and we'll see many more applications and a sense of how it's an actual "energy" throughout the course.

One good step is to look at this internal or average energy U – basically, how close our measurements of the energy will be to the average value. For a large system, we claim that **the internal energy U is essentially given exactly by its average, with very small fluctuations**. This is something we'll develop a better understanding of as we discuss the central limit theorem, which we'll discuss at the end of this lecture.

For now, we can rewrite the partition function Z in terms of an integral, since a large system essentially has continuous possible values of energy:

$$Z = \sum_n e^{-\beta E_n} \to \int \Omega(E) e^{-\beta E} dE = \int e^{S/k_B - \beta E} dE.$$

Because we know that $\Omega(E)$ scales as E^{cN}, meaning that our entropy S is of order N (it is extensive), Ω is a rapidly increasing function of E, while $e^{-\beta E}$ is a rapidly decreasing function. So the saddle-point approximation works well here, and we expect that the integral is dominated by the maximum value of the integrand, meaning

$$Z \sim \Omega(\langle E \rangle) e^{-\beta \langle E \rangle}.$$

(We're saying that we expect to have a Gaussian-like shape after multiplying the rapidly increasing and rapidly decreasing functions, so the average is also the highest point.) Therefore, taking a log tells us that

$$F = U - \frac{1}{\beta}\ln \Omega + O\left(\frac{1}{N}\right) \implies \boxed{F = U - TS}.$$

Notice now that the internal energy is extensive ($U \sim N$), and we also know that $S \sim N$ from earlier lectures. So because T is just some constant, F itself must be extensive as well. This means that $Z = e^{-\beta F}$ exponentially decays in N – this makes sense because each term in the sum $\sum_n e^{-\beta E_n}$ is of order 1. (And we can often make sure F is indeed positive, by defining all energies relative to the ground state energy.)

Our next step is to take a closer look at the entropy and obtain it from the probability distribution directly. We know that

$$p(n) = \frac{e^{-\beta E_n}}{Z} \implies \ln p(n) = -\beta E_n - \ln Z.$$

Now taking averages, we find that (because $\ln Z$ is just a number)

$$\langle \ln p(n) \rangle = -\beta U = \beta F,$$

and plugging in our $F = U - TS$ tells us that

$$\langle \ln p(n) \rangle = -\frac{1}{k_B} S \implies \boxed{S = -k_B \sum_n p_n \ln p_n}.$$

Fact 68

This last equality is often the way that the **entropy of a probability distribution** is defined (for example, in information theory). Often, this is actually used as the starting principle of statistical mechanics, since the equilibrium state can be thought of as the state with the maximum entropy with certain constraints. Doing those calculations turns out to give us the same answers as our description here.

From here, we can be more careful about the energy distribution (beyond just looking at its average U) by considering the **width and fluctuations** of the probability distribution. (The goal is that this will allow us to show, by direct calculation instead of a qualititative argument, that the probability distribution is peaked at U.) Remember that this **canonical distribution**, while sharply peaked at its mean, has a nonzero probability of being at any energy, unlike the micocanonical distribution.

To do that, we'll calculate the **variance**

$$\langle E^2 \rangle - \langle E \rangle^2$$

of our energy distribution. The second term is already known to be U^2, because $U = \langle E \rangle = -\frac{\partial}{\partial \beta} \ln Z$. This motivates us to consider a further derivative

$$\frac{\partial^2}{\partial \beta^2}(\ln Z) = \frac{\partial}{\partial \beta}\left(\frac{1}{Z}\frac{\partial Z}{\partial \beta}\right),$$

which can be written out with the product rule as

$$\frac{1}{Z}\frac{\partial^2 Z}{\partial \beta^2} - \left(\frac{1}{Z}\frac{\partial Z}{\partial \beta}\right)^2.$$

But now this is just

$$= \frac{1}{Z}\sum_n E_n^2 e^{-\beta E_n} - \left(\frac{1}{Z}\sum_n E_n e^{-\beta E_n}\right)^2 = \langle E^2 \rangle - \langle E \rangle^2,$$

so we find that the **variance of our energy** is just

$$-\frac{\partial^2}{\partial \beta^2} \ln Z = -\frac{\partial}{\partial \beta}\langle E \rangle = -\frac{\partial U}{\partial \beta} = k_B T^2 \frac{\partial U}{\partial T}$$

(just making a change of variables in the last step). Here, $\frac{\partial U}{\partial T}$, denoted C_V, is called the **heat capacity** of our system, and the reason for the subscript V is that we've been considering systems at **fixed volume**. (We'll connect this to the thermodynamic definition of C_V when we start talking about heat later on.) In summary,

$$\langle E^2 \rangle - \langle E \rangle^2 = k_B T^2 C_V,$$

and because we can measure T and C_V in experiments (the latter is a measurement of how much energy we need to add to our system to raise its temperature), we can find out how the fluctuations behave explicitly. Since U is of order N, we find that C_V is also of order N, which means that the width of the distribution

$$\sigma = \sqrt{\langle E^2 \rangle - \langle E \rangle^2} \propto \sqrt{N}.$$

Even though $\sqrt{N}$ is a big number, we should be comparing this to the actual value of energies around the mean: as we take $N \to \infty$, we find that

$$\frac{\text{width energy}}{\text{mean energy}} \propto \frac{\sqrt{N}}{N} \to 0.$$

So fluctuations are extraordinarily small, and in the large N limit, the width is just a small perturbation. Since $\langle E^2 \rangle - \langle E \rangle^2$ is nonnegative – it can always be written as $\langle (E - \langle E \rangle)^2 \rangle$ – we find that the heat capacity C_V is **always positive**.

We'll finish this lecture with a (self-contained) discussion of the mathematical **central limit theorem**. Suppose we have N real-valued random variables $X_1, \cdots, X_N$, with joint probability distribution $p(x_1, \cdots, x_N)$ (meaning that the probability of being in a volume $\prod_i dx_i$ is $p(x_1, \cdots, x_N) dx_1 \cdots dx_N$, and $\int dx_1 \cdots dx_N p(x_1, \cdots, x_N) = 1$). We're going to assume that our N random variables are independent (this is a special case of the more general central limit theorem), so that

$$p(x_1, \cdots, x_N) = p_1(x_1) \cdots p_N(x_N).$$

We know that the average value of any function $f(x_1, \cdots, x_N)$ is

$$\langle f \rangle = \int dx_1 \cdots dx_N p(x_1, \cdots, x_N) f(x_1, \cdots, x_N),$$

and we're interested in looking at the distribution of $u = \frac{1}{N} \sum_{i=1}^N x_i$ for large N. This variable's probability distribution function can be written as

$$P(u) = \int dx_1 \cdots dx_N p(x_1, \cdots, x_N) \delta\left(u - \frac{1}{N} \sum_{i=1}^N x_i\right),$$

and we'll handle the delta function by writing it as an integral of its own:

$$= \frac{1}{2\pi} \int_{-\infty}^{\infty} d\lambda \int dx_1 \cdots dx_N) p(x_1, \cdots, x_N) e^{i\lambda(u - \frac{1}{N} \sum_i x_i)}.$$

Specializing to the case where our variables are independent, we find that

$$\boxed{P(u) = \frac{1}{2\pi} \int_{-\infty}^{\infty} d\lambda \left[\prod_{i=1}^N \left(\int dx_i p_i(x_i) e^{-i\lambda x_i / N} \right) \right] e^{i\lambda u}}.$$

But notice that we have characteristic functions in the inner integrals, which we can Taylor expand (right here, we're defining it with a negative sign, which is different from in the recitation):

$$\tilde{p}_i\left(\frac{\lambda}{N}\right) = \int dx_i p_i(x_i) e^{-i\lambda x_i / N} = \int dx_i p_i(x_i) \left(1 - \frac{i\lambda}{N} x_i - \frac{\lambda^2}{2N^2} x_i^2 + O\left(\frac{1}{N^3}\right)\right),$$

and the integrals turn the variables into moments:

$$= 1 - \frac{i\lambda}{N} \langle X_i \rangle - \frac{\lambda^2}{2N^2} \langle X_i^2 \rangle + O\left(\frac{1}{N^3}\right).$$

We can rewrite this expression as an exponential to the same order of approximation to find

$$\tilde{p}_i\left(\frac{\lambda}{N}\right) = \int dx_i p_i(x_i) e^{-i\lambda x_i / N} = e^{-\frac{i\lambda}{N} \langle X_i \rangle - \frac{\lambda^2}{2N^2} (\langle X_i^2 \rangle - \langle X_i \rangle^2) + O(\frac{1}{N^3})}.$$

Doing this makes it easier to multiply all of the individual integrals together when we plug back into the boxed expression above: we now have

$$P(u) = \frac{1}{2\pi} \int_{-\infty}^{\infty} d\lambda\, e^{i\lambda u} \prod_i \tilde{p}_i\left(\frac{\lambda}{N}\right) = \frac{1}{2\pi} \int_{-\infty}^{\infty} d\lambda e^{-\frac{i\lambda}{N} \sum_i \langle X_i \rangle - \frac{\lambda^2}{2N^2} \sum_i (\langle X_i^2 \rangle - \langle X_i \rangle^2) + O\left(\frac{1}{N^3}\right)} e^{i\lambda u}.$$

But also remember that some of these quantities are also in terms of u:

$$\langle u\rangle = \frac{1}{N}\sum_i \langle X_i\rangle, \quad \langle u^2\rangle = \frac{1}{N^2}\left[\sum_i (\langle X_i^2\rangle - \langle X_i\rangle^2) + \sum_{i,j}\langle X_i\rangle\langle X_j\rangle\right]$$

(since $\langle X_i X_j\rangle = \langle X_i\rangle\langle X_j\rangle$ whenever $i \neq j$ for our independent variables). Therefore, we can check that

$$\Delta \equiv \langle u^2\rangle - \langle u\rangle^2 = \frac{1}{N^2}\sum_i (\langle X_i^2\rangle - \langle X_i\rangle^2),$$

and we can plug everything back into the probability distribution function for u to find (in the limit $N \to \infty$)

$$P(u) = \frac{1}{2\pi}\int_{-\infty}^{\infty} d\lambda e^{i\lambda(u - \langle u\rangle - \frac{\lambda^2\Delta}{2} + O(\frac{1}{N^3}))}.$$

Now, evaluating the integral gives us a final answer in the limit $N \to \infty$ of

$$P(u) \approx \frac{1}{\sqrt{2\pi\Delta}} e^{-\frac{(u-\langle u\rangle)^2}{2\Delta}}.$$

And notice here that Δ is of order $\frac{1}{N}$, and what we've found is a **Gaussian distribution** with mean $\langle u\rangle$ of order 1 and width (standard deviation) $\sqrt{\Delta}$ of order $\frac{1}{\sqrt{N}}$. So just like before, we recover a sharply peaked distribution as long as N is large.

11 September 25, 2020 (Recitation)

We'll talk today about a variety of topics, possibly including Gibbs' paradox, free energy and fluctuations, the Central Limit Theorem, and Lagrange multipliers.

First of all, a clarification about Stirling's approximation: recall that we talked about how in the integral

$$N! = \int_0^{\infty} dx e^{N\ln x - x},$$

we can't exactly use the saddle-point approximation with a fixed function $\phi(x)$, because the integrand isn't perfectly a multiple of N. The way to get around this is to make the substitution $x = Ny$ to turn this into

$$= \int_0^{\infty} dy e^{N\ln(Ny) - Ny} = Ne^{N\ln N}\int_0^{\infty} dy e^{N(\ln y - y},$$

and now we can use the saddle-point approximation on the remaining function $\phi(y) = \ln y - y$: this will give us the answer $Ne^{N\ln N}\sqrt{\frac{2\pi}{N}}e^{-N}$ (since the integrand is maximized at $y = 1$), and this is indeed the same approximation we derived last time.

Also, there have been questions about the difference between $\Omega(E)$ and $\Omega(E)\Delta E$: as mentioned during lecture, we should technically use the latter because we want a unitless quantity, and $\Omega(E)$ has units of inverse energy. But

$$\frac{\ln \Omega(E)\Delta E}{N} = \frac{\ln \Omega(E)}{N} + \frac{\ln \Delta E}{N},$$

and the second term goes to 0 regardless of whatever units we're using, as long as ΔE is constant as N changes. And we're often taking derivatives of this natural log, which would make the second term go away anyway! So the whole point is that we can always ignore the arbitrary ΔE in our picture, as long as it's small enough to make sure the density of states is essentially constant within the interval $[E, E + \Delta E]$.

Example 69

Gibbs' paradox comes up when we mix two systems together. Suppose that we have two gases A and B (in the left and right side of a box, respectively) with a divider between them, such that the two gases are distinguishable – if we lift the divider, then entropy should increase.

But entropy increasing means we must be able to measure something about the change, and thus we must be able to distinguish between the two gases. Suppose, for example, that there exists some permeable boundary that allows B to pass through but not A. Then as the B particles move to the left, the pressure will move the divider all the way to the right, and the point is that **we can "take advantage of the entropy" to do some work by moving the divider**. (And this process is reversible – we could put in energy to move the divider back to its original position.)

On the other hand, if there is the same gas A in the two sides, there's a sense in which there is no way to "use" the extra entropy when we lift the divider. So even if we defined our entropy in a way where we're just count states, there isn't really any physical significance of the "extra entropy" obtained by lifting the divider – for instance, there's no way to create a reversible process which allows a noticeable heat transfer

$$dS = \frac{dQ_{\text{rev}}}{dT}.$$

So it makes sense to have this factor of indistinguishability of $\frac{1}{N!}$ when we define our entropy for the identical gases.

Remark 70. *Note that putting the barrier down in the gas with all A particles does force us to have some fixed number of particles on the left side (at equilibrium, basically an equal amount on each side), but the point of the saddle-point approximation here means we only need to consider the most probable configuration of the number of particles to leading order, instead of considering all possibilities.*

Our next topic centers around the **free energy**, which comes out of a closer look at the partition function

$$Z = \sum_\alpha e^{-\beta E_\alpha} \implies U = \langle E \rangle = -\frac{1}{Z}\frac{\partial Z}{\partial \beta}.$$

We can keep taking derivatives to find that the moments of the energy E satisfy

$$\langle E^n \rangle = \frac{1}{Z}\frac{\partial^n Z}{\partial(-\beta)^n}$$

for all $n \geq 1$, but we want to try writing this in another way that feels less like a trick. To do that, we'll look at the characteristic function

$$\langle e^{-ikE} \rangle = \frac{1}{Z}\sum_\alpha e^{-(\beta+ik)E_\alpha},$$

and now we can rewrite this by thinking of our partition function Z as a function of β:

$$= \frac{Z(\beta+ik)}{Z(\beta)}.$$

Then the moments are supposed to be related the nth derivatives of the characteristic function via

$$\langle E^n \rangle = \left.\frac{\partial^n \langle e^{-ikE} \rangle}{\partial(-ik)^n}\right|_{k=0} = \frac{1}{Z(\beta)} \left.\frac{\partial^n Z(\beta+ik)}{\partial(-ik)^n}\right|_{k=0},$$

and now taking the **partial** derivative with respect to $-ik$ is the same as taking it with respect to $-\beta$, because the arguments have the same dependence in Z:

$$= \frac{1}{Z(\beta)} \left.\frac{\partial^n Z(\beta + ik)}{\partial(-\beta)^n}\right|_{k=0} = \frac{1}{Z} \frac{\partial^n Z}{\partial(-\beta)^n}.$$

If we only cared about the moments, this wouldn't give us very much, but we also care about the cumulants. And now we access the cumulants easily, because

$$\langle E^n \rangle_c = \left.\frac{\partial^n \ln\langle e^{-ikE}\rangle}{\partial(-ik)^n}\right|_{k=0} = \frac{\partial^n}{\partial(-ik)^n}(\ln Z(\beta + ik) - \ln Z(\beta))|_{k=0} = \left.\frac{\partial^n}{\partial(-ik)^n} \ln Z(\beta + ik)\right|_{k=0} = \frac{\partial^n \ln Z}{\partial(-\beta)^n}.$$

This indeed shows us that the cumulants come from derivatives of $\ln Z$ – the cumulants turn out to be much more useful than the moments, because we care about the variance of energy rather than the second moment. We expect $\ln Z \sim N$ to be an extensive quantity if the different parts of the system are essentially independent of each other, because then the partition function will multiply across different subsystems (as long as energies add together): if our total system comes from two subsystems X and Y,

$$Z_{\text{total}} = \sum_{x,y} e^{-\beta(E_x + E_y)} = \sum_x e^{-\beta E_x} \sum_y e^{-\beta E_y} = Z_X Z_Y.$$

So that means that **the cumulants will all be proportional to N as well**, meaning that the energy, variance, and so on have this same N-independence. And we'll find something that our system scales higher cumulants like

$$\left\langle \left(\frac{E}{N}\right)^n \right\rangle_c \sim \frac{N}{N^n} = N^{1-n},$$

which is good – in fact, higher cumulants go to 0 fast, so we're really only left with the lowest order cumulants, and this gives us a Gaussian distribution with standard deviation proportional to $\frac{1}{\sqrt{N}}$.

And now this is where free energy comes into the picture! If we write our partition function as an integral

$$Z = \int dE\, \Omega(E) e^{-\beta E} = \int dE\, e^{S(E)/k_B - \beta E},$$

we can then make a change of coordinates to get

$$= \int d\left(\frac{E}{N}\right) N e^{-N\beta f\left(\frac{E}{N}\right)},$$

where $f = \frac{F}{N}$ is the "free energy per unit particle:

$$f\left(\frac{E}{N}\right) = \frac{E}{N} - \frac{S(E)}{\beta N k_B}.$$

This quantity can be thought of as an "effective energy:" even though different states get counted numbers of times, this value of f is the energy we should expect to have if each energy level only has one state, and we want our partition function to remain the same. Then the probability distribution of $\frac{E}{N}$ becomes

$$p\left(\frac{E}{N}\right) = \frac{N}{Z} e^{-\beta N f(E/N)};$$

since N is large, we can do a Taylor series expansion around the point which minimizes the free energy f (and therefore maximizes the integrand). Our function will look symmetric around the minimum, and it'll be approximately Gaussian, so the average is also the minimum:

$$\approx \frac{N}{Z} \exp\left(-\beta N f(\langle E/N \rangle)\right) \exp\left(-\frac{(E/N - \langle E/N \rangle)^2}{2\langle (E/N)^2 \rangle_c}\right).$$

Then we know that

$$1 = \int d\left(\frac{E}{N}\right) p\left(\frac{E}{N}\right) = \frac{N}{Z} e^{-\beta N f(\langle E/N \rangle)} \sqrt{2\pi \langle (E/N)^2 \rangle_c},$$

and now taking a logarithm gives us

$$\ln Z = -\beta F + \ln N + \ln \sqrt{\frac{2\pi \langle E^2 \rangle_c}{N^2}} = -\beta F + \ln \sqrt{2\pi k_B T^2 C_V}.$$

So the second term is a correction here – C_V is proportional to the size of the system, but it's not extensive, so the first term is the largest contribution. And in this argument, our key assumption was hidden: **we assumed that S was extensive, so that the total entropy is N times the entropy of an individual small component**. (In other words, in the second term of the definition of $f(E/N)$, we're assuming that as E and N scale at the same rate, $\frac{S(E)}{N}$ also stays constant.)

Fact 71

A case where the entropy S does not scale with the size of the system is where a bunch of electrons have interactions such that all are either spin up or spin down. In general, systems that can magnetize will not have entropies coming from the sum of the individual particles' entropies. So we should be careful not to describe such systems just with a few "average values!"

We'll conclude with a few mathematical tricks that are good to know. First of all, looking at the Central Limit Theorem, if we have a vector of random variables $\vec{X} = (X_1, \cdots, X_n)$, we want to consider the characteristic function

$$\ln\langle e^{-i\vec{k}\cdot\vec{X}} = -i \sum_i k_i \langle X_i \rangle_c + \frac{(-i)^2}{2} \sum_{i,j} k_i k_j \langle X_i X_j \rangle_c + \frac{(-i)^3}{3!} \sum_{i,j,\ell} k_i k_j k_\ell \langle X_i X_j X_\ell \rangle_c.$$

If the variables are independent, then we know that expectations are multiplicative, meaning that everything will just simplify to (after some calculation)

$$\ln\langle e^{i\vec{k}\cdot\vec{X}}\rangle = \ln \prod_{i=1}^{N} \langle e^{-ik_i X_i} = \sum_{i=1}^{N} \left(-ik_i \langle X_i \rangle_c + \frac{(-i)^2}{2!} k_i^2 \langle X_i^2 \rangle_c + \frac{(-i)^3}{3!} k_i^3 \langle X_i^3 \rangle_C + \cdots \right).$$

This doesn't help us deal with the sum of the random variables as we need in CLT, but it'll help get us started.

Finally, we'll do some intuition refreshers for Lagrange multipliers. Suppose that we're trying to maximize a scalar function $f(\vec{x})$ given some constraint $g(\vec{x}) = 0$: then we can consider the following Lagrangian

$$\mathcal{L}(\vec{x}, \lambda) = f(\vec{x}) - \lambda g(\vec{x}).$$

If we try to maximize this quantity instead, then we need $\frac{\partial \mathcal{L}}{\partial \lambda} = 0$, which enforces our constraint $g(\vec{x}) = 0$, as well as

$$\frac{\partial \mathcal{L}}{\partial \vec{x}} = 0 \implies \frac{\partial f(\vec{x})}{\partial \vec{x}} = \lambda \frac{\partial g(\vec{x})}{\partial \vec{x}}.$$

This means that our gradients must point in the same direction: using a physical analogy of energy, potential, and forces, we can think of $f(\vec{x})$ exerting a gradient force pulling us towards the maximum value, and at equilibrium, the force is balanced out by a "normal force" of some sort, which is always perpendicular to our constraint.

12 September 28, 2020

About half of us have completed the survey from last week, and the rest of us are urged to do so as well (so that we can give feedback on what's working for learning). And as a reminder, there will be a take-home exam posted on Wednesday, with two questions on the microcanonical ensemble and earlier topics. (We can consult class-related materials, but not each other, for the exam.)

We'll start today by talking a little about the central limit theorem, before looking at ideal gases and other thermodynamic concepts. Recall that the central limit theorem tell us that when we have N real-valued random variables X_i (for $1 \le i \le N$) with some probability distribution $p(x_1, \cdots, x_N)$, and when we make the simplifying assumption that the X_is are independent random variables, so that $p(X_1, \cdots, X_N) = p_1(x_1) \cdots p_N(x_N)$, then $u = \frac{1}{N} \sum_i x_i$ is distributed, in the limit $N \to \infty$, according to

$$P(u) \to \frac{1}{\sqrt{2\pi\Delta}} \exp\left(-\frac{(u - \langle u \rangle)^2}{2\Delta}\right),$$

where $\Delta = \langle u^2 \rangle - \langle u \rangle^2$ is the variance of the distribution and is order $\frac{1}{N}$. In other words, the average of the measurements u becomes (universally) Gaussian, with mean $\langle u \rangle \sim O(1)$ and width $\sqrt{\Delta} \sim O\left(\frac{1}{\sqrt{N}}\right)$.

Remark 72. *It's sufficient that the cumulants $\langle X_{i_1} \cdots X_{i_m} \rangle_c$ grow slower than $N^{m/2}$, instead of assuming that the X_is are independent. But we won't go through the proof of this more general case.*

We can notice that this theorem is related to how we discussed the internal energy in the canonical ensemble – the result there was that the mean value of E is very sharply peaked around the average U. And these two concepts can be connected as follows: suppose we break up a large system of length scale L into smaller subsystems of length scale ℓ, so that $L \gg \ell \gg a$ for a microscopic length scale a. If we're trying to find the total energy of our system, we have an integral over the energy density by essentially **summming over energies of subregions**. And if the cross-correlations of energies between different parts of the systems are small enough, we expect a "central limit theorem type result" to hold: as we saw, the energy will be of order N, while the width will be of order $\sqrt{N}$.

Fact 73

We should keep in mind that the Boltzmann distribution applies to a single microstate of the system or to the velocity of a single particle, not the total energy distribution.

Remark 74. *There are situations where the assumptions of the central limit theorem are violated – phenomena where "tail effects" dominate, which happens in some glassy dynamics. But there are ways to deal with those as well.*

For now, we'll move on to concepts of **heat and pressure**, two important thermodynamic quantities.

Example 75

Consider a system at equilibrium with a bath at some temperature T. If the temperature is changed to another temperature T' (for example, some energy gets injected into the bath), but external parameters like V and N for the system are fixed, the mean energy of the system must change.

Because the system and bath are isolated from the rest of the world, there must be some given energy transfer between the system and the bath, and this is called **heat** transferred to or from the system. In fact, we can relate the heat transfer to changes in the **entropy** of the system, which we'll derive now.

We start with an infinitesimal change in the state of our system, and we keep our external variables $V, \cdots$ fixed (so that no work is done on the system), so that the entropy $S = S(E, V, \cdots)$ satisfies

$$\Delta S = \frac{\Delta E}{T}$$

(because our temperature is defined as $\frac{1}{T} = \frac{\partial S}{\partial E}$). Thus, the heat transfer is $\Delta E = T\Delta S$, and we'll denote this quantity in general by ΔQ. In other words, we can write down the equation

$$\boxed{\Delta Q = T\Delta S},$$

where T is a function of S and E, to define the heat transfer – again, remember that this transfer happens when we change the temperature while keeping any specific external variables for the system fixed.

And now we'll try a contrasting calculation: instead of fixing V and modifying T, we can try changing the volume while keeping the temperature fixed. Intuitively, this should also lead to a change in mean energy of the system, because compression takes pressure and so on. (Microscopically, what's going on is that a particle in a box has different energy eigenvalues when the volume gets larger.)

Definition 76

The **pressure** of a system is negative of the average change in energy per unit volume change:

$$P = -\sum_n p_n \frac{\partial E_n}{\partial V},$$

where p_n is the probability of a microstate n, and E_n is its energy.

Usually, pressure is defined to be the force per unit area, but we can imagine a cubic box where we change the z-direction's length. Then the work done (which is the change in energy) is the force applied times the distance of particle movement, and now we can notice that the two definitions are equivalent.

From here, notice that we can calculate pressure from the free energy:

$$P = -\frac{1}{Z}\sum_n e^{-\beta E_n}\frac{\partial E_n}{\partial V} = \frac{k_B T}{Z}\frac{\partial}{\partial V}\left(\sum_n e^{-\beta E_n}\right) = k_B T \frac{1}{Z}\frac{\partial Z}{\partial V}$$

where the partial derivative is done at constant temperature. This then leads us to

$$P = k_B T \left(\frac{\partial}{\partial V}\ln Z\right)_T = -\left(\frac{\partial F}{\partial V}\right)_T.$$

Since we have a useful quantity out of one partial derivative of $F(T, V)$, it makes sense to consider the other quantity $\left(\frac{\partial F}{\partial T}\right)_V$. We can calculate this directly via

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

by the chain rule, and now we can convert this to a derivative with respect to β:

$$= -k_B \ln Z + k_B \beta \frac{\partial}{\partial \beta}\ln Z.$$

But both terms now look familiar, and we are left with

$$= \frac{F}{T} - \frac{U}{T} = -S,$$

which means we've arrived at the entropy! So putting this together,

$$\boxed{P = -\left(\frac{\partial F}{\partial V}\right)_T, \quad S = -\left(\frac{\partial F}{\partial T}\right)_V},$$

and now we can consider arbitrary infinitesimal changes in T and V:

$$dF = \left(\frac{\partial F}{\partial T}\right)_V dT + \left(\frac{\partial F}{\partial V}\right)_T dV = -SdT - PdV.$$

Therefore, if we have an internal energy $U = F + TS$, we have that

$$\boxed{dU} = -PdV - SdT + d(TS) = \boxed{-PdV + TdS}.$$

Therefore, we can write down partial derivative relations like

$$\boxed{P = -\left(\frac{\partial U}{\partial V}\right)_S, \quad T = \left(\frac{\partial U}{\partial S}\right)_V}.$$

We also know that $-PdV$ is the work done on our system, so we have

$$dU = dW \text{ when there is no change in entropy (and thus no heat flow).}$$

We should remember that these calculations have been done while ensuring that we are still in equilibrium, but they allow us to think about how certain thermodynamic quantities vary with others, as long as we specify what variables are fixed.

Before we continue down the path of thermodynamics, we'll illustrate the use of these ideas by revisiting an earlier example:

Example 77

Let's calculate the free energy F of a classical ideal gas explicitly in terms of V and T. Our Hamiltonian will again be $H = \sum_{i=1}^N \frac{\vec{p}_i^2}{2m}$.

We can first describe some statistical properties with the microcanonical distribution: recall that the density of states here is

$$\Omega(E, V, N) = A\left(\frac{eV}{N}\right)^N \left(\frac{E}{N}\right)^{3N/2},$$

where A is just some constant, and thus the entropy is

$$S = k_B \ln \Omega = k_B \ln\left(\left(\frac{V}{N}\right)^N \left(\frac{E}{N}\right)^{3N/2}\right) + c,$$

meaning that

$$\frac{1}{T} = \left(\frac{\partial S}{\partial E}\right)_V = \frac{3Nk_B}{2E} \implies E = \frac{3}{2}Nk_BT.$$

If we now want to calculate the pressure, we know that

$$dU = TdS - PdV \implies dS = \frac{1}{T}dU + \frac{P}{T}dV.$$

This means that

$$\frac{P}{T} = \left(\frac{\partial S}{\partial V}\right)_U,$$

but U is the symbol for the average energy of the system in the canonical distribution, so it really is equivalent to E. We can then find that

$$\frac{P}{T} = \frac{Nk_B}{V} \implies \boxed{PV = Nk_BT}.$$

This mostly illustrates that we've defined the pressure correctly, but what's more useful is to try arriving at these results using the canonical distribution. We care then about the partition function, which we'll now explicitly calculate:

$$Z = \frac{1}{N!}\sum_{\{\vec{p}_i\}} e^{-\beta\sum_i \vec{p}_i^2/2m},$$

where the $\frac{1}{N!}$ is the Gibbs factor and

$$\vec{p}_i = \frac{2\pi\hbar}{L}(n_{ix}, n_{iy}, n_{iz}),$$

for integers n_{ix}, n_{iy}, n_{iz} and a cubic box of length L (which we'll take to infinity eventually). We can convert this sum into an integral for large L to get

$$Z = \left(\frac{L}{2\pi\hbar}\right)^{3N}\frac{1}{N!}\int\prod_i d^3p_i e^{-\beta\sum_i \vec{p}_i^2/2m}.$$

If we do a similar change of variables $\vec{p}_i = \sqrt{2mk_BT}\vec{u}_i$, then

$$Z = \frac{V^N}{(2\pi\hbar)^{3N}N!}(2mk_BT)^{3N/2}\int\prod_i d^3u_i e^{-u_i^2}.$$

We can do the Gaussian integral, which is unitless, and we end up with a final answer of

$$Z = \frac{V^N}{(2\pi\hbar)^{3N}}\frac{1}{N!}(2\pi mk_BT)^{3N/2}.$$

From here, we can extract the free energy by using Stirling's approximation: we arrive at

$$F = -k_BT\ln Z = -Nk_BT\ln\left(\left(\frac{eV}{N}\right)\left(\frac{(2m\pi k_BT)^{3/2}}{(2\pi\hbar)^3}\right)\right).$$

We can now confirm that

$$P = -\left(\frac{\partial F}{\partial V}\right)_T = \frac{Nk_BT}{V},$$

which is the right answer, and the entropy S also works out to the correct value we calculated above. At the end of the day, this means that using the microcanonical and canonical ensembles give us the same values for these "average extensive quantities," which is what we expect.

13 September 30, 2020

First of all, those of us who haven't completed the course survey should do so as soon as possible so that "what is most helpful for the majority of the class" is most clear. And to make a quick note about last lecture: in the ideal gas, the canonical and microcanonical distributions giving us the same results wasn't a coincidence. We should expect this kind of behavior to work for statmech systems in general, because the energy is almost always peaked sharply around the mean value.

Today, we'll be talking about (classical) non-ideal gases at a very high level. The first step for doing this is writing the Hamiltonian for our gas of atoms via

$$H = \left(\sum_i \frac{\vec{p}_i^2}{2m} \right) + U(\{\vec{q}_i\}),$$

where the potential energy of interaction $U(\{\vec{q}_i\})$ could have one-body, two-body, or other interactions. To start, we'll assume the system can be treated classically – then our partition function will look like

$$Z = A \int \prod_{i=1}^{N} (d^3 p_i d^3 q_i) e^{-\beta H(p,q)},$$

where A is some undetermined constant when we're working within classical mechanics (because we don't have a well-defined "spacing" in phase space). But if we treat this classical system as an approximation to the underlying quantum system, then

$$A = \frac{1}{N!} \left(\frac{1}{2\pi\hbar} \right)^{3N},$$

where $\frac{1}{N!}$ comes from the Gibbs factor, and the other term comes from the uncertainty principle (atoms cannot be found infinitely close to each other).

Remark 78. *To explain the* $(2\pi\hbar)$ *factor in situations where we don't just have a fixed spacing between allowed eigenstates, the idea is that we are putting our system into a large box, and ultimately the system will not depend on boundary conditions very much for large volumes.*

If we know the form of U, for example if we know that atoms interact via the van der Waals interaction, then this partition function Z (and its derivatives and related quantities) can tell us lots of important information about the system, like its pressure or entropy. (However, in practice, having to do a large or infinite number of integrals for an integrand that can't be done exactly can be very difficult.)

We can solve half the problem completely generally for any system of this form, though, because given a Hamiltonian H of the form above where the potential energy U doesn't depend on the momentum, we can separate out the exponential $e^{-\beta H}$ into two terms. And we can do the momentum integral, which will always be the same as that for the ideal gas – **this term always factors out**. So we can deal with the kinetic energy component of the Hamiltonian for all classical systems at the same time, which we will do right now.

So now

$$Z = A \int \prod_i (d^3 p_i) e^{-\beta \vec{p}_i^2/2m} \int \prod_i (d^3 q_i) e^{-\beta U(\{\vec{q}_i\})},$$

and if we define Z_0 to be the partition function of the classical ideal gas (where $U = 0$), which is

$$Z_0 = A V^n \int \prod_i d^3 p_i e^{-\beta \sum_i \vec{p}_i^2/2m},$$

then the non-ideal gas must be written as

$$\boxed{Z = \frac{1}{V^N} Z_0 \int \prod_i d^3 q_i e^{-\beta U(\{q_i\})}}.$$

Rephrased, this means the kinetic and potential energy contributions to the free energy completely separately:

$$\boxed{F = -k_B T \ln Z = F_0 - k_B T \ln \left[\frac{1}{V^N} \int \prod_i d^3 q_i e^{-\beta U(\{q_i\})} \right]},$$

where $F_0 = -k_B T \ln Z_0$ is the free energy of the classical ideal gas.

Fact 79

This kind of calculation is only an **artifact of the classical treatment**, though – it's not true in quantum statistical mechanics! This is because the partition function there looks like

$$Z = \sum_n e^{-\beta E_n} = \mathrm{Tr}(e^{-\beta \hat{H}}),$$

where $\hat{H}$ is the Hamiltonian operator, and we can't separate the exponential in the same way because $\hat{p}$ and $\hat{q}$ **do not commute**.

This will come up again when we study quantum ideal gases, and then we'll be able to think about "when we can treat atomic motion as being classical." Essentially, classical statistical mechanics says that we can separate out thermodynamical properties from the dynamical ones, while quantum statistical mechanics says that they are "intimately linked."

So now if we look at the special case where U is a one-dimensional integral (for example, if the whole system is in some external potential), we can do the integrals separately and see how it gives us an explicit partition function. We'll do this calculation at some point later in the class, for instance for a harmonic oscillator potential. (It isn't too difficult, because the integrals end up being Gaussians.)

For now, we're going to use the formalism we've been building up to arrive at the laws of thermodynamics.

Proposition 80 (Zeroth law)

If two systems A_2, A_2 are in thermal equilibrium with a third system B, then they are in equilibrium with each other.

This is a statement that is "almost obvious," in the sense that we've been considering a lot of systems attached to external systems where only energy can be exchanged. Then the condition for equilibrium is that temperatures are equal between A_1 and B, and also between A_2 and B, so it seems like we then must have A_1 and A_2 at equilibrium because their temperatures are the same.

But we could ask what happens if other things are allowed to be exchanged as well (for example, some volume can be transferred into or out of A_1 from B, instead of just heat). To deal with this case, we can repeat the derivation by looking at the maximum density of states for the joint distribution for our system, and we find then that we must have an additional condition about the partial derivatives $\frac{\partial S}{\partial V}$, and that tells us then that the **pressures must match**. So this means we have an additional condition on top of temperature, and this should make sense to us: if two gases are in a box with a partition between them, the partition can only stay stationary if the pressures are equal on both sides. And then equality of pressure is transitive, so the zeroth law holds analogously.

Remark 81. *The laws of thermodynamics were established before statistical mechanics, so it was harder to find solid reasoning for a lot of them back then. But now hopefully those laws are easier to justify from our point of view.*

Proposition 82 (First law)

Energy is conserved; specifically, the change in the total energy of a system can be written as

$$dU = -PdV + TdS.$$

Here, $-PdV$ is known as the work done, and TdS is the increase in heat (corresponding to random internal **microscopic** motion).

Proposition 83 (Second law)

For a closed system, we have $\frac{dS}{dt} \geq 0$.

We'll reiterate the calculation we did a few lectures ago to justify this law. Again, consider two isolated systems A_1 and A_2 that are initially separated and in internal equilibrium, and then we bring them together and allow energy to flow. Initially, if the total energies of our systems are E_1^0 and E_2^0, then the densities of states are $\Omega_1(E_1^0)$ and $\Omega_2(E_2^0)$, respectively, and thus the total initial entropy is

$$S_i^0 = k_B \ln \Omega_i(E_i^0).$$

But now if we bring A_1 and A_2 in contact with each other, then the probability distribution of the joint system will evolve from the initial distribution to its final equilibrium distribution, and this process will occur so that **the sequence of states traversed runs through more and more probable distributions of the total energy** as it approaches equilibrium. (Here's where ergodicity is being used, but we're really assuming that when we ask for the microcanonical distribution to work in the first place.) Then the probability that A_1 has energy E_1 and A_2 has energy E_2, given a constraint on the total $E_1 + E_2 = E_1^0 + E_2^0$, is proportional to $\Omega_1(E_1)\Omega_2(E_2)$, so the value of

$$\Omega_1(E_1)\Omega_2(E_2) = e^{1/k_B(S_1(E_1)+S_2(E_2))}$$

must be maximized in the final equilibrium state, meaning that entropy indeed (almost) never decreases, especially in the thermodynamic limit.

We can consider this setup in another way as well: suppose we have two systems A_1 and A_2 in fixed volumes next to each other, and then the heat absorbed by system $\alpha \in \{1, 2\}$ is

$$\Delta Q_\alpha = E_{f\alpha} - E_{i\alpha}$$

(the final energy minus the initial energy when a system is at a fixed volume). We know we must have $\Delta Q_1 + \Delta Q_2 = 0$ by energy conservation, and let's consider the case if we only have an infinitesimal amount of heat transferred. Then the change in entropy of system A_α is

$$S_\alpha(E_f\alpha) - S_\alpha(E_i\alpha) = \left.\frac{\partial S_\alpha}{\partial E_\alpha}\right|_{E|lpha=E_i\alpha} dQ_\alpha = \boxed{\frac{dQ_\alpha}{T_\alpha}}.$$

This means that if the total change in entropy of the combined system is nonnegative as the second law suggests, then (using the fact that $dQ_1 = -dQ_2$)

$$\frac{dQ_1}{T_1} + \frac{dQ_2}{T_2} \geq 0 \iff dQ_1\left(\frac{1}{T_1} - \frac{1}{T_2}\right) \geq 0.$$

In other words, if $T_2 > T_1 > 0$, then $dQ_1 > 0$, meaning that heat flows from the hotter to the colder body, as we expect. (This has implications for systems like heat engines, but we won't cover those in this class.)

Proposition 84 (Third law)
For every macroscopic system, the entropy per particle $\lim_{N\to\infty} \frac{S}{N}$ goes to 0 as the temperature T goes to 0.

This statement cannot be true within classical statistical mechanics, since we only know the entropy up to an additive constant, so we cannot know its exact value at $T = 0$. So the justification needs to come from quantum statmech arguments. The idea (that we're not explicitly proving) is that **quantum systems with a large number of particles has a unique ground state, or at least one with a small degeneracy** g. As $T \to 0$, our system then settles into a ground state (because $e^{-\beta E_n}$ goes to 0 as $\beta \to \infty$), so

$$p_n = \begin{cases} 0 & n \text{ is an excited state} \\ \frac{1}{g} & n \text{ is one of the } g \text{ degenerate ground states.} \end{cases}$$

Then

$$S = k_B \sum_n p_n \ln p_n = k_B \ln g,$$

so the necessary condition is that $\lim N \to \infty \frac{\ln g}{N} = 0$ (meaning g just needs to grow slower than exponential in N). And this is a reasonable thing to believe generically (we won't have exponentially many ground states in typical systems).

Remark 85. *The third law is an empirically correct statement – when we have symmetries that create degeneracy in our systems, we will indeed see that g grows much more slowly than exponentially in N.*

14 September 2, 2020 (Recitation)

One topic of today's class is **heat engines and the second law**, but we'll start with a few clarifications of recent material first.

First of all, we know from classical mechanics that the pressure is defined as

$$P = \frac{\vec{F} \cdot \vec{n}}{A},$$

where $\vec{n}$ is the normal vector to our area A, and this can be rewritten as

$$= \frac{1}{A} \left(-\frac{\partial E}{\partial x} \right)_{dQ=0},$$

where we need to make sure the change in energy comes from changes in volume, not transfer of heat. And if we do this process slowly, we can rewrite this as a derivative at constant entropy $-\left(\frac{\partial E}{\partial V}\right)_S$, because the change in volume $dV = Adx$. Remembering that $dE = TdS - PdV$, we find that

$$dF = d(E - TS) = -SdT - PdV,$$

so we can also define pressure as

$$P = -\left(\frac{\partial F}{\partial V} \right)_T.$$

So we can measure pressure at constant temperature or entropy – it depends on whether we're looking at the free energy or the energy, but this explains to us why we often like working with F. (Keeping a system at constant temperature is much easier than doing so at constant entropy.)

Remark 86. *One way of thinking of the free energy is a way of quantifying how much energy we release (as heat) when we let our system settle into its ground state – it accounts for the fact that certain energy states might have more entropy than others.*

Specifically, if the change in entropy is

$$\Delta S_{\text{universe}} = \Delta S_{\text{env}} + \Delta S,$$

some of the change in entropy comes from heat transfer and others from the entropy of our excited states, so we can rewrite this as

$$= -\frac{\Delta E}{T} + \Delta S = \Delta(\ln Z),$$

which is a constant times the change in free energy $F = -k_B T \ln Z$. So **maximizing entropy is related to minimizing the free energy**.

So now let's look back at pressure and connect it to the derivation from class: we said that

$$P = \left\langle -\left(\frac{\partial E}{\partial V}\right)_S \right\rangle = -\sum_\alpha p_\alpha \frac{\partial E_\alpha}{\partial V},$$

where "constant entropy" essentially that "we keep the probability distribution the same." This can be rewritten as

$$-\frac{\partial}{\partial V}\left(\sum_\alpha p_\alpha E_\alpha\right)_{p_\alpha} = -\left(\frac{\partial \langle E \rangle}{\partial V}\right)_S,$$

since we're claiming that the p_αs are just constant here, meaning we can pull the derivative out of the sum.

Remark 87. *Quantum mechanically, justification for doing this comes from the adiabatic theorem in quantum mechanics, which says that slow enough evolution does not have us jump between eigenstates. And in the classical description, even if the Hamiltonian changes slowly with time, we can use Liouville's theorem to "trap" our states.*

Note that this is a different derivation from the one we did in class, in which we said that the canonical distribution allows us to do an explicit mathematical calculation:

$$P = -\sum_\alpha \frac{e^{-\beta E_\alpha}}{Z}\frac{\partial E_\alpha}{\partial V} = \frac{1}{\beta Z}\left(\frac{\partial Z}{\partial V}\right)_T = -\left(\frac{\partial F}{\partial V}\right)_T.$$

Fact 88

Let's clarify what the zeroth law means, and why it actually historically only refers to temperature (not other variables).

The idea is that **this is the only postulate we actually need to assume** – statements like "if two systems can exchange volume, then they must settle at the same pressure" is a basic property of Newtonian mechanics. The idea is that being at thermal equilibrium (that is, no longer exchanging heat) is a transitive property – we can think of this as saying that if a thermometer A is in equilibrium with a system B, and also with a system C, then B and C must actually be in thermal equilibrium if we put the two next to each other. This was something that we could observe but not prove (without understanding things at the microscopic level or knowing what heat is), and it's why the zeroth law exists as a postulate. Then we can define temperature by looking at the equivalence classes of thermal equilibrium.

On the other hand, pressure is already a well-defined quantity – there's no "mysterious process of heat," so there is no law to posit.

Fact 89

A final clarification before we talk about heat engines: the first law of thermodynamics is basically conservation of energy, and basically all energy we know of can be written as work.

This means our "mysterious heat" is written as

$$\Delta Q = \Delta E - \Delta W \implies dE = đW + đQ$$

The reason for the notation of $đ$ here is that work W and heat Q **are not state variables** – the amount of work a system does when it transfers between two states **depends on the path**. And if we have a **quasi-static process**, we can write

$$đW = \sum_i J_i dX_i,$$

where the X_i represent **extensive** properties of our system, like volume or length or area, and the J_i represent **intensive** properties, like pressure or force or surface tension. (So an example of a pair (J_i, X_i) is (F, L), or (σ, A), or $(-P, V)$.) And we need to keep in mind that some of these pairs have negative signs, like in the expression $-PdV$, and that can be thought of as "what happens when we put energy into a system." **Essentially, we can think of J_is as the derivatives of energy with respect to the X_is.**

And now we're ready to look at heat engines, and it'll make sense why we treat the TdS term in a special way when looking at changes in energy.

Example 90

Consider two heat reservoirs at temperature T_H and T_C: is it possible to use this temperature difference to do useful work?

During the Industrial Revolution, there were important practical considerations about how efficient systems could be. Any **heat engine** takes in some heat Q_H from the T_H reservoir and expels some heat Q_C from the T_C reservoir (we can assume the temperatures T_H and T_C stay constant because the environment is big), and in the process we do some work W. So then we know that

$$W + Q_C = Q_H,$$

and we want to maximize the **efficiency** of our energy

$$\eta = \frac{W}{Q_H} = 1 - \frac{Q_C}{Q_H}.$$

On a microscopic level, the second law of thermodynamics makes sense, but from a macroscopic perspective, we basically have to postulate the second law in some way. From here, Kelvin formulated (1) that $\eta < 1$, while Clausius claims (2) that if $W = 0$, then $Q_C \geq 0$ (we can't transfer energy from a cold place to a hot place). Both of these statements really tell us the same thing, which is that "heat flows from hot to cold."

Proposition 91

Kelvin's law and Clausius's law are equivalent.

Proof. To show that Clausius's law implies Kelvin's law, suppose that the latter is false. Then we can construct an engine that converts heat directly into work, and then we can use that work to move some heat from the cold system to the hot system, which means Clausius's law is not true.

On the other hand, suppose Clausius's law does not hold, and we can transfer some amount of heat Q from the cold reservoir to the hot reservoir. Then we can run another (possibly inefficient) heat engine so that the heat going in and coming out of the cold reservoir amounts to 0, and the net effect becomes that all of the net loss of energy from the high-temperature reservoir gets made into heat, which breaks Kelvin's law. ☐

Example 92

Consider a **Carnot engine**, which is a specific example of a reversible heat engine.

We perform the following steps, starting from some point in a diagram that tracks our pressure P versus our temperature T, and ending up back where we started:

- Isothermal expansion (by taking in some energy)
- Adiabatic expansion (no heat exchanged),
- Isothermal contraction (by expelling some energy),
- Adiabatic contraction (work is done on the gas, but no heat is exchanged.

If we do all of these steps very slowly, so that we're always in equilibrium and doing work in a reversible way, we would be able to reverse this whole process. This means that we have a reversible process here.

Proposition 93

No heat engine between temperatures T_C and T_H is more efficient than the Carnot engine.

Proof. Suppose we have a hypothetically more efficient engine than the Carnot engine. Then we can use the more efficient engine's outputted work to run the Carnot engine in reverse, and that means that we could use less heat Q_C than the Q'_C that is drawn by the Carnot engine. And this means that we're sending net heat from the cold temperature bath to the hot temperature bath, breaking Clausius' law. ☐

In other words, reversible heat engines must all be at max efficiency, and thus we can define the maximum efficiency for our engines as $\eta(T_H, T_C)$ just by looking at how the Carnot engine does.

And if we now consider a tiered heat engine system, so that one Carnot engine works between temperatures T_1 and T_2 and another works between temperatures T_2 and T_3, chosen to run at a rate so that the neat heat flowing into the T_2 bath is zero, we'll notice that

$$Q_2 = Q_1(1 - \eta(T_1, T_2)), \quad Q_3 = Q_2(1 - \eta(T_2, T_3)),$$

and substituting values in yields

$$= Q_1(1 - \eta(T_1, T_2))(1 - \eta(T_2, T_3)).$$

But the joint system is also a Carnot engine between T_1 and T_3, so this expression is also $Q_1(1 - \eta(T_1, T_3))$. Thus, defining $F(T_A, T_B) = 1 - \eta(T_A, T_B)$, we have

$$F(T_1, T_3) = F(T_1, T_2)F(T_2, T_3),$$

and this implies mathematically that

$$F(T_A, T_B) = \frac{f(T_B)}{f(T_A)}$$

for some function f. And now we've gotten back to the idea of defining temperature – we know that we have some freedom in our definition of temperature beyond just having equivalence classes, so we can choose $f(T) = T$. (We know $f(T)$ must be increasing as function of T, or else we end up with weird results if we are allowed to combine heat engines and get net effects of heat being transferred from lower to higher energies.) So this tells us what the efficiency of our heat engines looks like:

$$\frac{Q_C}{Q_H} = 1 - \eta(T_H, T_C) = \frac{T_C}{T_N}.$$

Remark 94. *We have a physical understanding of what "temperature" looks like, beyond the microscopic definition or this weird definition in terms of heat engines: another way to define temperature is to look at an ideal gas and consider (experimentally)*

$$T = \lim_{V \to \infty} \frac{PV}{Nk_B}.$$

It turns out this new definition is equivalent to our currently existing definitions, and we do this by running the Carnot cycle on an ideal gas and calculating the resulting efficiency. So this is indeed temperature as we know it.

In general, if we have a non-reversible engine, we know that we must have

$$\frac{Q_C}{Q_H} \geq \frac{T_C}{T_H}$$

(a general engine must have lower efficiency), meaning that

$$\frac{Q_C}{T_C} - \frac{Q_H}{T_H} \geq 0.$$

And now this is starting to look like the second law of thermodynamics: we know that we could associate these with entropy changes if we had a reversible process. (And we can think about the least efficient possible heat engine as well: if $Q_C = Q_H$, meaning that we do no work, we do indeed get a nonnegative quantity on the left side.) We can generalize this equation some more:

Theorem 95 (Clausius)

The heat inputted into a system over one cycle satisfies

$$\oint \frac{đQ}{T} \leq 0.$$

Proof. Consider a heat bath at a constant temperature T_0, and suppose our system is at some temperature T (which can change over the cycle). This heat bath will put some heat $đQ_R$ into a Carnot engine, which does some work $đW$ and puts some heat $đQ$ into our system. Over a cycle, we know that

$$\Delta Q_R = \oint đQ_R = \oint \frac{T_0}{T} đQ$$

because we are working with a (maximally-efficient) Carnot engine. Now Kelvin's law tells us that $\Delta Q_R \leq 0$, because we can't just convert heat to work (there's no bottom bath, so after the engine runs in a cycle, no heat can be expelled to a different bath. And therefore

$$\oint \frac{T_0}{T} đQ \leq 0 \implies \oint \frac{đQ}{T} \leq 0,$$

as desired. □

If every step here is reversible, we can run this argument in reverse as well, which proves that

$$\boxed{\oint \frac{đQ_{\text{rev}}}{T} = 0}.$$

15 October 5, 2020

Our quiz has been graded and returned to us. (Because of the shared Dropbox folder, it couldn't be returned by Canvas, so we should check our email.) The last part of the first problem was supposed to be the most challenging part of the quiz, but hopefully the rest of it was reasonably straightforward for us. (Looking at grading, most of us got those parts correct, and we did pretty well as a class.) A lot of students mentioned that the quiz took much longer than one hour, though.

One other logistical comment comes from the results of the survey sent out last week. Specifically, in response to "what comes in the way of doing well in this class," the majority of us said that it was difficult to find time to do justice to this class and also handling other expectations from other courses and responsibilities. For first-year graduate students, this may not be something specific to remote learning, but it is definitely a difficult transition. The main suggestion here from Professor Todadri is to "get the coursework out of the way" – since there are no qualifying exams being offered on entry, it makes sense to focus on coursework so that the second semester can focus on research. (And for the undergrads in the class, we're taking this voluntarily, so we should make the most of it.)

The other point that was getting in the way of the course for many people was finding it difficult to focus given what's going on in the world. And the main suggestion there is that structure is particularly important for our lives – forcing us to focus on work can help us avoid the news. (What this means is that our homework load will basically be the same as it would be in a non-virtual setting.)

We'll start the physics today with some comments on the third law of thermodynamics. Recall that the idea is that every quantum system with a large number of particles N has a unique ground state or a small degeneracy $g \ll N$, so that when $T \to 0$, our system will settle into (one of) the ground state(s) because of the canonical ensemble calculations (β goes to infinity). Then the probability of occupation at $T = 0$ is

$$p_n = \begin{cases} 0 & n \text{ is an excited state} \\ \frac{1}{g} & n \text{ is one of the ground states,} \end{cases}$$

and therefore the entropy is

$$S = -k_B \sum_n p_n \ln p_n = k_B \ln g.$$

Therefore **the entropy per particle $\frac{S}{N}$ of a quantum many-body system goes to zero as** $N \to \infty$, and this is the third law of thermodynamics we're working with.

Remark 96. *Remember that we can only make this statement in the quantum statmech situation, because* S *is only defined up to additive shifts in the classical case. And if we want to compare different systems, the arbitrary additive constant can be different in the classical case, but not in the quantum one.*

We're working with this third law at the level of "it's reasonable that this happens:" any special degeneracies of the ground state should be lifted if our Hamiltonian is generic enough, or if we perturb any "accidents" that come up from an accidentally degenerate Hamiltonian. And the third law holds empirically, so we want to understand how to use it.

Fact 97

We know that we can compare the entropy difference between two different temperatures by integrating a quantity related to the heat capacity (which we can measure). And the idea is that this allows us to **actually compute the entropy** T, because we know the entropy at temperature 0.

There's a small subtlety with this approach – in order to use this result, we need to make sure equilibrium as been reached. But as we go to lower temperatures, equilibration times can become very large (in the limit $T \to 0$). So the relevant question for us is **how small the temperature** T **needs to be before the entropy becomes sufficiently small**, and this depends on the system we're working with.

Example 98

Consider a solid with atomic nuclei having nonzero spin (say 1/2). This solid also has electronic degrees of freedom, either in moving around in a metal or from spin degrees of freedom. Then the nuclear spins are very weakly coupled to the electronic degrees of freedom, and also to each other.

For example, the strength of the hyperfine coupling in Hydrogen is related to the famous 21 cm line, and the differences are indeed very small in comparison. The point is that each nuclear spin talks to everything in its environment very weakly, so even down to very low temperatures the nuclear spins may remain disordered. At some temperature T_0, the entropy of the other degrees of freedom, like electronic excitations or translational degrees of freedom or lattice vibrations, have settled down and become negligible. And if the nuclear spins (which we're assuming to be 1/2) are completely disordered, and we have N nuclei, then the entropy in the spins is $S_0 = Nk_B \ln 2$.

So the entropy must go to S_0 as $T \to T_0$, and then once T drops below T_0, those weak interactions will eventually order themselves, leading to a final loss of entropy, so that $S \to 0$ as $T \to 0$ as we expect. So the idea is that we'll forget about nuclear spins (because they're weakly coupled compared to whatever we're actually trying to probe), and the "practical form" of the third law is that $S \to S_0$ as we decrease T but still keep it larger than T_0.

Proposition 99

The third law implies that heat capacity $C_V = \left(\frac{\partial U}{\partial T}\right)_V$ goes to 0 as $T \to 0$.

Proof. We know that changes in energy are related to changes in volume and entropy by the equation

$$dU = -PdV + TdS,$$

so

$$C_V = \left(\frac{\partial U}{\partial T}\right)_V = T\left(\frac{\partial S}{\partial T}\right)_V$$

(because $dV = 0$ when we take these derivatives). And now if we integrate $\frac{C_V}{T}$, we get the entropy difference between different temperatures, as mentioned, and if S goes to a constant (possibly zero, but it doesn't matter if we do something like in the above example), then $T\left(\frac{\partial S}{\partial T}\right)_V$ must go to 0 as long as our derivative is well-behaved. ☐

We can also write

$$T\left(\frac{\partial S}{\partial T}\right)_V = \left(\frac{\partial S}{\partial(\ln T)}\right)_V,$$

and then we're saying that S, if we treat it as a function of $\ln T$, goes to a constant as $-\ln T$ goes to infinity. We can similarly show that the specific heat $C_P = T\left(\frac{\partial S}{\partial T}\right)_P$ at constant pressure, as well as the the thermal expansion coefficient $\left(\frac{\partial V}{\partial T}\right)_P$, go to 0, but we won't show that here. We can try deriving this on our own.

Remark 100. *We can check that in a polymer (like on our quiz) or in other materials, it's possible for* $\left(\frac{\partial V}{\partial T}\right)_P$ *to be negative, because systems can have more entropy when coiled than when stretched out. (This is sometimes called an* **entropic force***, and this comes up in many situations.)*

We're going to shift gears now to a concrete example, so that we can illustrate the use of the canonical ensemble.

Example 101

In a "classical" ideal gas, the translational motion of atoms or particles is classical, but the internal motion within those particles may not be classical.

We'll start by proving an important result from classical statistical mechanics. To start, let x_i be any of the p_i or q_i degrees of freedom in a system, and consider

$$\left\langle x_i \frac{\partial H}{\partial x_j} \right\rangle = \frac{1}{N!}\frac{1}{Z}\int \prod_i \frac{d^3q_i d^3p_i}{(2\pi\hbar)^3} x_i \frac{\partial H}{\partial x_j} e^{-\beta H},$$

and now

$$\frac{\partial}{\partial x_j} e^{-\beta H} = -\beta \frac{\partial H}{\partial x_j} e^{-\beta H},$$

meaning that

$$\left\langle x_i \frac{\partial H}{\partial x_j} \right\rangle = -\frac{k_B T}{N! Z}\int \prod_i \frac{d^3q_i d^3p_i}{(2\pi\hbar)^3} x_i \frac{\partial}{\partial x_j}(e^{-\beta H}).$$

We can now integrate this by parts – we put the x_j-derivative on the x_i, and that gives us

$$= \frac{k_B T}{N! Z}\int \prod_i \frac{d^3q_i d^3p_i}{(2\pi\hbar)^3} \delta_{ij} e^{-\beta H}.$$

(The boundary term is gone, because $e^{-\beta H}$ makes those contributions negligible. We can object about the potential energy not being large at the boundary, but in any case these are boundary calculations which will not scale with N in the same way. We're going to apply this to Hamiltonians that are quadratic in the p and q, anyway.) So now the x_i is either p_i or q_i, so we'll specialize to two certain situations: if $x_i = x_j = p_i$, we find that

$$\left\langle p_i \frac{\partial H}{\partial p_i} \right\rangle = k_B T$$

(because this integral defines the partition function and we cancel out the Z in the denominator), meaning that

$$\left\langle \frac{p_i^2}{2m} \right\rangle = \frac{k_B T}{2}.$$

This means we can, for example, calculate the average kinetic energy in the x-direction for our system for a single particle. And now let's specialize to Hamiltonians of the form

$$H = \sum_i \frac{p_i^2}{2m} + \frac{1}{2}\sum_{i,j} u_{ij} q_i q_j,$$

which is a generalized simple harmonic oscillator. (This is a good approximation for systems that are near their **minimum potential energy**.) Then we find that

$$\langle H \rangle = \sum_i \left\langle \frac{p_i^2}{2m} \right\rangle + \frac{1}{2}\sum_{ij} u_{ij} \langle q_i q_j \rangle,$$

and now we can use the fact that

$$\left\langle q_i \frac{\partial H}{\partial q_j} \right\rangle = u_{ij}\langle q_i q_j \rangle = \delta_{ij} k_B T.$$

Therefore, we find that

$$\sum_{i,j} \frac{1}{2} u_{ij} \langle q_i q_j \rangle = \frac{3Nk_B T}{2},$$

and putting together all of our calculations leads us to the following result:

Theorem 102 (Equipartition theorem of classical stat mech)
Each quadratic degree of freedom contributes $\frac{k_B T}{2}$ to the total energy:

$$\langle H \rangle = 3Nk_B T.$$

In particular, this tells us that the heat capacity is $C_V = 3Nk_B$ for such a system C, at least within classical statistical mechanics. And this is important because we can calculate a measurable quantity – the specific heat – for a broad range of Hamiltonians. But perhaps we should be worried – this seems to mean that if we make a model for a single atom, where we just have an electron moving in a quadratic potential around the atomic nucleus, we might be able to keep adding more degrees of freedom and considering internal motion at various energy scales – when do they contribute to thermodynamics? And this concern was only resolved through quantum mechanics – this was one of the spots in pre-quantum physics where people realized the theory had serious structural issues.

Next class, we'll see how quantum mechanics helps us resolve this, and then we'll look at some more examples.

16 October 7, 2020

An extension has been granted for problem set 3 until Friday at noon, and the next problem set will be due on Wednesday instead of the usual Tuesday. Next Monday is a holiday (Indigenous People's Day), so we won't have class, but Tuesday will follow the Monday schedule. (So we'll have classes on Tuesday and Wednesday next week, and recitation on Friday as usual.) Office hours are adjusted accordingly – there was also a request for additional office hours, so there will be a new one added on Thursdays, either in the morning or evening.

We'll continue to examine the "classical" ideal gas today. Last time, we discussed the classical equipartition theorem for quadratic Hamiltonians, which holds when we have

$$H = \sum_i \frac{p_i^2}{2m} + \frac{1}{2}\sum_{ij} u_{ij} q_i q_j,$$

where we're summing over the degrees of freedom. What we found then was that $\langle H \rangle = U = 3Nk_B T$, meaning that the heat capacity is $C = 3Nk_B$: one way to state this equipartition theorem is that "each quadratic degree of freedom contributes $\frac{k_B T}{2}$ to the total energy."

This theorem doesn't hold in a quantum description of the same system, though – if we have a system like

$$H = \sum_i \frac{p_i^2}{2m} + \frac{1}{2} m\omega^2 \sum_i q_i^2,$$

meaning we have $3N$ identical simple harmonic oscillators, then each oscillator has a spectrum $E_{n_i} = \left(n_i + \frac{1}{2}\right)\hbar\omega$, and now we can calculate the thermodynamic properties by looking at these energy levels.

First of all, because the oscillators are decoupled, the total partition function is the partition function of a single simple harmonic oscillator, raised to the $3N$th power:

$$Z = \left(\sum_{n=0}^{\infty} e^{-\beta\left(n+\frac{1}{2}\right)\hbar\omega}\right)^{3N}.$$

Remark 103. We don't include the $\frac{1}{N!}$ Gibbs factor here, *because we're thinking about a situation where the $3N$ oscillators are all distinguishable (they sit in different orientations in phase space). This is different from having two electrons which can be swapped around because they are completely indistinguishable.*

This inner term is a geometric series:

$$Z_{\text{SHO}} = \sum_{n=0}^{\infty} e^{-\beta\left(n+\frac{1}{2}\right)} e^{-\beta\hbar\omega/2}(1 + e^{-\beta\hbar\omega} + e^{-2\beta\hbar\omega} + \cdots) = \frac{e^{-\beta\hbar\omega/2}}{1 - e^{-\beta\hbar\omega}}.$$

Therefore, the internal energy of a single simple harmonic oscillator is

$$U_{\text{SHO}} = -\frac{\partial}{\partial\beta}\ln Z_{\text{SHO}} = \frac{\hbar\omega}{2} + \frac{\hbar\omega e^{-\beta\hbar\omega}}{1 - e^{-\beta\hbar\omega}}.$$

The first term here is the ground state energy, and the second is the energy of our thermally excited states (since the harmonic oscillator can be in each of those higher-energy states with some probability). And the internal energy of the whole system of simple harmonic oscillators is the sum of the individual internal energies.

Next, we can also find that

$$C_{\text{SHO}} = \frac{dU_{\text{SHO}}}{dT} = k_B\left(\frac{\hbar\omega}{k_B T}\right)^2 \frac{e^{-\beta\hbar\omega}}{(1 - e^{-\beta\hbar\omega})^2}.$$

This is a complicated expression, but we can understand it by looking at the limits of high and low temperature. When we take $T \to \infty$, we have $T \gg \frac{\hbar\omega}{k_B}$, and $\beta \to 0$. So the numerator of the last term can be approximated to 1, and we keep the first two terms of the expansion of $e^{-\beta\hbar\omega} \approx 1 - \beta\hbar\omega$ in the denominator. This gives us

$$C_{\text{SHO}}(T \to \infty) \approx k_B\left(\frac{\hbar\omega}{k_B T}\right)^2 \frac{1}{(\beta\hbar\omega)^2} = k_B.$$

This is indeed in agreement with classical equipartition. But in the limit $T \to 0$, we have $T \ll \frac{\hbar\omega}{k_B}$, and we have $\beta \to \infty$. So then the denominator of the last term goes to 1, and what we end up with is

$$C_{\text{SHO}}(T \to 0) \approx k_B\left(\frac{\hbar\omega}{k_B T}\right)^2 e^{-\beta\hbar\omega}.$$

The blowing up of the $\frac{\hbar\omega}{k_B T}$ term is less significant than the exponential decay here at large β, so this expression **goes to 0 rapidly**. But now **this second result is in disagreement with classical equipartition**, and this is happening because we have discretized energy states. To understand that, notice that when $k_B T \gg \hbar\omega$, the differences of energy $\hbar\omega$ are negligible compared to our energy scale, so we get our classical result back again. On the other hand, when $k_B T \ll \hbar\omega$, levels are very pronounced, and we have very low population at **any** excited energy states. In fact, the probability of occupation satisfies

$$\frac{P(n=1)}{P(n=0)} = e^{-\hbar\omega/k_B T} \ll 1.$$

So it's only the ground state that is substantially occupied, and there is very little thermal energy in the system. We expect then that C_{SHO} should go to zero when $k_B T \ll \hbar\omega$, and this is the regime where classical equipartition fails. (In words, at low temperatures, we need very little heat to increase the temperature.)

Fact 104

If we graph C_{SHO} versus T, the value starts at 0 at $T = 0$ and approach k_B as T gets larger. And the other way to look at this is that below the scale $T = \frac{\hbar\omega}{k_B}$, our heat capacity starts to drop noticeably.

And this also helps us turn to the question of "why we don't care about internal degrees of freedom" (for example, if there are moving parts inside an atom or molecule). Classical equipartition would tell us that we should get an order-1 contribution from each of these, giving us an infinite heat capacity if we keep looking deeper, but quantum mechanics tells us that we **suppress contributions of modes with arbitrarily high energy scales** (we can assume those degrees of freedom have settled into their ground states, and we just focus on things active at the temperature we're working with). This resolved some of the 19th century issues with classical statistical mechanics.

Example 105

Let's consider the specific heat of a diatomic gas, which is something that could be measured in the 19th century but not properly explained by statistical mechanics. We'll assume the two atoms in the molecule are distinct (like carbon monoxide).

Such a diatomic molecule has various degrees of freedom: translations of the whole molecule, rotations of the molecule axis, vibrations of the two nuclei about their mean separation, and excitations of the internal electronic structure. But the electronic excitations tend to have a high energy – the energy scale in a small molecule is on the order of an electron-volt (eV), but we're considering the diatomic molecule at temperatures around room temperature. And an electron volt corresponds to 10^4 Kelvin (since $1\frac{\text{eV}}{k_B} \approx 10^4$ K), so experiments at order room temperature (give or take an order of magnitude) will treat 10^4 Kelvin as a huge number. **So we'll forget about electronic excitations completely** here, for the same qualitative description as we described in the SHO just now.

Our molecule is then essentially two balls connected with a spring, and what matters to us at our given temperatures is the nuclear motion. This means we can write the Hamiltonian of our diatomic gas as

$$H = H_t + H_r + H_v + H_e,$$

corresponding to translations, rotations, vibrations, and electronic excitations, respectively, and use that to get our partition function

$$Z = Z_t Z_r Z_v Z_e.$$

- By assumption that we're working at $k_B T \ll$ (electronic excitation energy), we can set Z_e to a constant 1.
- We can now look at the rotational Hamiltonian, which corresponds to the rotation of the vector connecting the center of the two atoms. Then

  $$H_r = \frac{\vec{L}^2}{2I},$$

  where $\vec{L}$ is the angular momentum of the rotations, and I is the moment of inertia. Then remember that $\vec{L}^2$ has eigenvalues $\ell(\ell+1)$, where each $\ell \in \{0, 1, 2, \cdots\}$ has degeneracy $2\ell+1$. Therefore, our rotational energies are

  $$E_r = \frac{\hbar^2 \ell(\ell+1)}{2I}$$

  with $(2\ell+1)$-fold degeneracy, and now we can calculate the partition function

  $$Z_r = \sum_{\ell=0}^{\infty} (2\ell+1) e^{\frac{-\beta\hbar^2\ell(\ell+1)}{2I}}.$$

Instead of calculating this explicitly, we'll look at the high and low temperature limits directly. If $k_B T \ll \frac{\hbar^2}{2I}$, then only the $\ell = 0$ state will be occupied, and our partition function will be approximately 1. (At small temperatures, the corrections are exponentially small, so the heat capacity contributions are exponentially small as well.) On the other hand, when $k_B T \gg \frac{\hbar^2}{2I}$, many levels are thermally excited, meaning we can approximate with the classical limit by converting the sum over ℓ into an integral. Then

$$Z_r(T) \approx \int_0^\infty d\ell(2\ell+1)e^{\frac{-\beta\hbar^2\ell(\ell+1)}{2I}},$$

and we'll change variables $x = \ell(\ell+1) \implies dx = (2\ell+1)d\ell$, meaning that at high temperaure,

$$Z_r(T) \approx \int_0^\infty dx e^{-\beta\hbar^2 x/2I} = \frac{2Ik_BT}{\hbar^2}.$$

We can also calculate the average rotational energy for high

$$U_r(T) = \langle E_r \rangle = k_B T.$$

This is again consistent with classical equipartition.

So what matters is the actual energy scale, and for a typical molecule, the spacing between energy levels is on the order of $\frac{\hbar^2}{I}$, which is on the order of 10^{-4} eV. And since this corresponds to a few degrees Kelvin, we are typically working in the limit where $k_B T \gg \frac{\hbar^2}{I}$ at room temperature, so we do want to factor in this factor of $k_B T$ into our heat capacity.

- Now we turn to the vibrational Hamiltonian H_v as a one-dimensional simple harmonic oscillator, in which

  $$H_v = \frac{p^2}{2\mu} + \frac{1}{2}\mu\omega^2 x^2,$$

  where x and p are the relative position and momenta of the vibration to center-of-mass equilibrium, and μ is the reduced mass. Then we have that

  $$E_n = \left(n + \frac{1}{2}\right)\hbar\omega,$$

  and what matters to us here is the typical frequency of the vibration. It turns out $\hbar\omega$ is on the order of 0.1 eV, corresponding to 10^3 K, which is still larger than room temperature. So whenever $T \ll 10^3 K$, we do not treat this vibration classically, and we have $Z \approx e^{-\beta\hbar\omega/2}$ – no contribution to the specific heat is made here.

And just like we've been doing in this class so far, translational motion is being treated classically. (As long as our temperature is above the "degeneracy tempreature" that we'll talk about for the quantum ideal gas later in this class, this is okay.) So we get a factor of $\frac{3N}{2}k_B$ from translation, and at room temperature, we ignore vibrational and electronic excitations, but we treat the rotations as significant, giving us an additional factor of Nk_B. This gives us a final answer of

$$C = \frac{3N}{2}k_B + Nk_B = \boxed{\frac{5N}{2}k_B}.$$

And if the temperature drops enough, C will drop to $\frac{3N}{2}k_B$ when the rotational degrees of freedom become insignificant, and then further to 0 after that. But that's something for us to study another time.

17 October 9, 2020 (Recitation)

Today, we'll start by finishing our discussion on heat engines and entropy, and then we'll talk about some ideas related to the third law and rotational degrees of freedom.

Last time, we discussed Clausius' theorem, which tells us that over a cycle, the total heat

$$\oint \frac{đQ}{T} \le 0.$$

Since reversible processes can be performed in the opposite direction, leading to the negative amount of heat being transferred, we must have

$$\oint \frac{đQ_{\text{rev}}}{T} = 0.$$

This allows us to make a **state variable** definition, independent of path taken:

Definition 106

The difference in entropy between two states is defined as

$$S(B) - S(A) = \int_A^B \frac{đQ_{\text{rev}}}{T}.$$

In particular, this tells us that $dS = \frac{đQ_{\text{rev}}}{T}$. We already know by the first law of thermodynamics that

$$dE = đW + đQ.$$

For reversible processes, we have $đQ = TdS$, and we can write $đW = \sum_i J_i dx_i$ (for example, $-PdV$ is one such possible term in this sum). So then

$$dE = TdS + \sum_i J_i dx_i,$$

where we can have terms corresponding to surface tension or magnetic fields or other state variables. The point is that this equation must be true **even if we don't take a reversible path** – it's possible that $đW$ and $đQ$ aren't equal to $\sum_i J_i dx_i$ and TdS, respectively, but their sum must still be the total energy change.

Example 107

Suppose we have a gas in a box, and a divider is lifted up so that the gas can do a (non-reversible) free expansion, where no heat is transferred

But we can also find another way to expand this gas slowly: if we want $dE = 0$ at all times,

$$dE = TdS - PdV \implies TdS = PdV.$$

The idea is that we use the gas to push our divider slowly so that heat is transferred, but work is also done. We'll end up in the same final state, and we can take the work that we've "saved" to push the divider back to the middle of the box.

And we can say that if we take a (possibly non-reversible) path from A to B, and then we take the reversible path back, Clausius' theorem tells us that

$$\int_A^B \frac{đQ}{T} + \int_B^A \frac{đQ_{\text{rev}}}{T} \le 0,$$

and then taking differentials simplifies this equation to

$$\frac{\text{đ}Q}{T} - dS \le 0 \implies dS \ge \frac{\text{đ}Q}{T} = 0.$$

So this gives us a minimum amount of entropy increase, and in particular if we have an **adiabatic** process where $\text{đ}Q = 0$, we must have $dS \ge 0$. (And we've arrived back at the second law of thermodynamics!)

We'll take this opportunity to make a few more connections between concepts of the class. We first defined entropy in terms of the number of microstates: $S = k_B \ln \Omega$, and now we can write out

$$dS = \left(\frac{\partial S}{\partial E}\right)_V dE + \left(\frac{\partial S}{\partial V}\right)_E dV = \frac{1}{T} dE + \frac{P}{T} dV.$$

Fact 108

The reason for the equality of the second terms is that $P = -\left(\frac{\partial E}{\partial V}\right)_S$, and at constant S, we can rearrange our partial derivatives as

$$0 = dS = \left(\frac{\partial S}{\partial E}\right)_V dE + \left(\frac{\partial S}{\partial V}\right)_E dV \implies \left(\frac{\partial E}{\partial V}\right)_S = -\frac{\left(\frac{\partial S}{\partial V}\right)_E}{\left(\frac{\partial S}{\partial E}\right)_V}.$$

Plugging in our definitions, this means

$$-P = -\frac{\left(\frac{\partial S}{\partial V}\right)_E}{1/T}.$$

(And this is the "**cyclical property**" of partial derivatives: $\left(\frac{\partial X}{\partial Y}\right)_Z \left(\frac{\partial Y}{\partial Z}\right)_X \left(\frac{\partial Z}{\partial X}\right)_Y = -1$.)

Rearranging, we find that

$$dS = \frac{1}{T}(dE + PdV) = \frac{1}{T}((\text{đ}Q + \text{đ}W) + PdV).$$

In a reversible process, we know that $\text{đ}W_{\text{rev}} = -PdV$, so as long as the work is being done reversibly, this equation above reduces to $dS = \frac{\text{đ}Q}{T}$. But in general, we have $\text{đ}W > -PdV$ for a not necessarily reversible process, and this gives us $dS > \frac{\text{đ}Q}{T}$. (We can think of the right-hand side of this inequality as "how much entropy the bath loses in heat transfer.")

Our next topic will be the **third law** of thermodynamics – remember that classically, we can't find the exact value of S, so the formulation of the law in a classical setting is

$$\lim_{T \to 0} S(T, x) = \text{constant}.$$

(In other words, if we cool down a system, the entropy goes to a constant which doesn't depend on the volume or pressure of our system.) In particular, this tells us that

$$\lim_{T \to 0} \left(\frac{\partial S}{\partial x}\right)_T = 0$$

for any other variable x. Then we can say that

$$S(T, x) - S(0, x) = \int_0^T \left(\frac{\partial S}{\partial T}\right)_x dT = \int_0^T \frac{C_x(T)}{T} dT,$$

where $C_x(T)$ is the heat capacity at constant x. And we know that integral is finite, so we must have $C_x(T) \to 0$ as $T \to 0$ so that the integral doesn't blow up.

And now with this behavior of heat capacity C_x in mind, we'll try to relate C_P and C_V to each other. First, if we use V as our variable x, we can take the equation

$$đQ_{\text{rev}} = TdS = dE + PdV,$$

and we can check that the heat capacity at constant volume is

$$\boxed{C_V} = \left(\frac{đQ_{\text{rev}}}{dT}\right)_V = T\left(\frac{\partial S}{\partial T}\right)_V = \boxed{\left(\frac{\partial E}{\partial T}\right)_V},$$

because at constant volume, we have no work and thus no PdV term. Similarly,

$$C_P = \left(\frac{đQ_{\text{rev}}}{dT}\right)_P = T\left(\frac{\partial S}{\partial T}\right)_P.$$

But $TdS = dE + PdV$, so we can rewrite this as

$$= \left(\frac{\partial E}{\partial T}\right)_P + P\left(\frac{\partial V}{\partial T}\right)_P,$$

and now we know that because E is a function of V and T, which we can vary independently,

$$dE = \left(\frac{\partial E}{\partial T}\right)_V dT + \left(\frac{\partial E}{\partial V}\right)_T dV \implies \left(\frac{\partial E}{\partial T}\right)_P = \left(\frac{\partial E}{\partial T}\right)_V + \left(\frac{\partial E}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P$$

(where we've essentially "divided by dT at constant pressure"). At this point, we can substitute the blue expressions to find that

$$\boxed{C_P = \left(\frac{\partial E}{\partial T}\right)_V + \left(\frac{\partial E}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P + P\left(\frac{\partial V}{\partial T}\right)_P}.$$

Substituting in our expression for C_V above gives us

$$\boxed{C_P = C_V + \left(\left(\frac{\partial E}{\partial V}\right)_T + P\right)\left(\frac{\partial V}{\partial T}\right)_P}.$$

For an ideal gas, we have $\left(\frac{\partial E}{\partial V}\right)_T = 0$, and $\left(\frac{\partial V}{\partial T}\right)_P = \frac{Nk_B}{P}$ because $PV = Nk_BT$. So **ideal gases** satisfy

$$\boxed{C_P = C_V + Nk_B}.$$

We expect both C_P and C_V go to zero as $T \to 0$, though, so that means that one of the two red terms should go to zero, and the **ideal gas approximation is not valid at zero temperature**. (We'll soon see that both of the red terms vanish, too.)

Remark 109. *What's breaking down in our classical formulation is that we can only derive something like* $PV = Nk_BT$ *from the classical Hamiltonian of an ideal gas, and the system is not described well at low temperature by this Hamiltonian. But the other arguments with derivatives are general and work for basically any system.*

To bring this back to the third law, we can write S as a function of V and T to find

$$dS = \left(\frac{\partial S}{\partial T}\right)_V dT + \left(\frac{\partial S}{\partial V}\right)_T dV \implies C_P = T\left(\frac{\partial S}{\partial T}\right)_P = T\left(\frac{\partial S}{\partial T}\right)_V + T\left(\frac{\partial S}{\partial V}\right)_T\left(\frac{\partial V}{\partial T}\right)_P$$

(where again we've "divided by dT at constant pressure"). Substituting in this time gives us

$$\boxed{C_P = C_V + T\left(\frac{\partial S}{\partial V}\right)_T\left(\frac{\partial V}{\partial T}\right)_P}.$$

So we have **two different ways** to relate C_P and C_V together, and in fact the "correction" error terms needs to line up. But in this latter case, it's more clear that the correction goes to 0 as $T \to 0$, because we have an explicit T term showing up.

We can notice that the **expansivity** term $\left(\frac{\partial V}{\partial T}\right)_P$ shows up in both red terms, and we're interested in how it behaves as $T \to 0$. Notice that

$$dE = TdS - PdV \implies dG = d(E - TS + PV) = -SdT + VdP,$$

where G is the **Gibbs free energy**. This is useful for us because it leads us to a **Maxwell relation**: taking the mixed partials of E in either order gives us

$$\left(\frac{\partial V}{\partial T}\right)_P = -\left(\frac{\partial S}{\partial P}\right)_T.$$

And since S goes to a constant as $T \to 0$, S cannot vary as a function of P in the limit, and therefore this is indeed $\boxed{0}$ (as long as we ignore smoothness concerns). Maxwell's relations (which we get by taking mixed partial derivatives) may not be super intuitive, but their point is to give us connections between different state variables changing in different ways.

Fact 110

The point is that we can describe a system like an ideal gas with any two variables, even though we have variables P, S, T, V, E, G and so on. So that gives us a lot of connected constraints, and that's why we work with so many partial derivatives. (And if we introduce new variables in pairs, like the number of particles and chemical potential, that will usually give us two more variables, but only one more degree of freedom. So we will always have added structure in that sense!)

We'll finish this recitation with some small comments. First of all, we'll talk about rotational degrees of freedom – suppose we have N atoms, meaning that we have $3N$ position degrees of freedom (along with their conjugate momenta). We can track the number of translational, rotational, and vibrational degrees of freedom in the following table:

# atoms	T	R	V
1	3	0	0
2	3	2	1
3 collinear	3	2	4
3 non-col.	3	3	3
$N \geq 3$ collinear	3	2	$3N - 5$
$N \geq 3$ non-col.	3	3	$3N - 6$

We can confirm that the sum always adds up to $3N$, but we can explicitly check in each of these cases where each of the translational and rotational degrees of freedom are coming from. If we're in the **classical limit**, we know that translational and rotational degrees of freedom each contribute $\frac{1}{2}k_BT$ to the total energy, while the vibrational degrees of freedom each contribute k_BT (because we also get energy from the momentum, since we have a harmonic oscillator). For example, when we write down the rotation Hamiltonian for the non-collinear case,

$$H_{\text{rot}} = \frac{1}{2}\left(\frac{L_x^2}{I_x} + \frac{L_y^2}{I_y} + \frac{L_z^2}{I_z}\right),$$

we're doing this in **body-fixed coordinates** (meaning that L_x is always referring to the same type of rotation with respect to the object I_x). On the other hand, we often write down the rotation Hamiltonian for the collinear case

$$H_{\text{rot}} = \frac{1}{2I} L^2$$

in **space-fixed coordinates**, because everything is in a line and the orientation doesn't matter. The point is that quantizing the collinear Hamiltonian is much easier than doing so for the body-fixed non-collinear Hamiltonian, so we need to be a lot more careful in the latter case.

Finally, let's consider an adiabatic expansion of an ideal gas to connect some of today's topics together: since energy can be written as $\alpha(PV)$ for some constant α,

$$0 = đQ = dE - đW = \alpha d(PV) + PdV.$$

This tells us that

$$\alpha V dP + (\alpha + 1) P dV = 0,$$

or

$$0 = \frac{dP}{P} + \frac{\alpha + 1}{\alpha} \frac{dV}{V},$$

and therefore PV^γ is a constant, where $\gamma = \frac{\alpha+1}{\alpha}$. And if f is the number of degrees of freedom that we have in our system, we have $\alpha = \frac{f}{2}$ by equipartition, so $\boxed{\gamma = \frac{\alpha+1}{\alpha} = \frac{f+2}{f} = \frac{C_P}{C_V}}$. This argument only works for an ideal gas, so it isn't a general statement, but it's commonly used. And this ratio $\frac{C_P}{C_V}$ can be defined for any gas, and we'll see its uses later on as well.

For example, when $N = 1$ (a single atom), we have $\gamma = \frac{5}{3}$, and when $N = 2$ (a diatomic gas), and we assume only rotational and translational degrees of freedom are engaged, $\gamma = \frac{7}{5}$. The idea is that the more degrees of freedom we have, the more it doesn't matter whether we heat at constant pressure or constant volume – the heat is just going towards internal degrees of freedom, and how the work is being done externally doesn't contribute very much.

18 October 13, 2020

We'll talk about equilibration of systems that can exchange particles, introducing the concepts of chemical potential and the grand canonical ensemble. From here, we'll discuss the kinetic theory of gases, but before that, we'll make a clean break and take some time to answer general questions about the material so far.

Example 111

Consider a cup of hot water sitting outside, which evaporates slowly into the atmosphere. Then the system (cup) is exchanging particles with its surrounding environment, and we want to be able to describe that.

Our first step is to determine what conditions must hold at equilibrium – for example, we've already seen constraints on temperature or pressure if we allow for energy or volume to be exchanged. The analysis will look similar in this case – we **start from the microcanonical ensemble**.

Call our large system A_1, and suppose it's in contact with a larger system A_2 (a bath) with which it can exchange **energy and particles**. As always, we say that A_2 typically has many more degrees of freedom than A_1. Then if we want to describe some given microstate r of A_1, we need to specify its energy E_r and particle number N_r. Letting E_0 and N_0 be the total energy and number of particles in the (isolated) composite system $A_1 + A_2$, just like before, we can write that

$$\mathbb{P}(A_1 \text{ in state } r) \propto \Omega_2(E_0 - E_r, N_0 - N_r),$$

and we can write this (as usual) in terms of the entropy as

$$= \exp\left(\frac{1}{k_B} S_2(E_0 - E_r, N_0 - N_r)\right).$$

We can Taylor expand this exponent, since $E_r \ll E_0$ and $N_r \ll N_0$ when A_1 is "small" compared to A_2. This yields

$$\frac{1}{k_B} S_2(E_0 - E_r, N_0 - N_r) \approx \frac{1}{k_B} S_2(E_0, N_0) - \beta E_r - \alpha N_r + \cdots,$$

where $\beta = \frac{1}{k_B}\frac{\partial S_2}{\partial E}$ is the usual inverse temperature, and we define $\alpha = \frac{1}{k_B}\frac{\partial S_2}{\partial N_0}$. So this tells us that

$$p(r) \propto e^{-\beta E_r - \alpha N_r},$$

and therefore we can write the probability distribution explicitly as

$$p(r) = \frac{1}{Z_G} e^{-\beta E_r - \alpha N_r},$$

where Z_G is the **grand partition function**

$$Z_G = \sum_r e^{-\beta E_r - \alpha N_r}.$$

(This is naturally called the **grand canonical distribution / ensemble**.) It turns out that using this probability distribution for calculations is just as valid as using either the microcanonical or canonical ensemble, and the justification for the switch will be similar as the passage from microcanonical to canonical ensemble. But certain calculations will be easier in certain frameworks than others, and we'll see it in great effect when we deal with quantum ideal gases.

We traditionally write the probability in a slightly different form

$$\boxed{p_r = \frac{1}{Z_G} e^{-\beta(E_r - \mu N_r)}},$$

where $\mu = -k_B T \alpha$ is the **chemical potential** of the system. So just like in the canonical ensemble, we can define equilibrium between our systems A_1 and A_2 to be where β, α (if they can exchange particles), P (if they can exchange volume), and other variables are all equal for the two systems, meaning that

$$T_1 = T_2, \quad P_1 = P_2, \quad \mu_1 = \mu_2.$$

Fact 112

We will soon see that the equations of state tell us more about how these different state variables are related – for example, P will be a function of T and μ in a gas, so whenever this condition can be satisfied, we must have the same equation of state everywhere to actually reach equilibrium.

We can do a similar calculation as with the canonical distribution to find that the grand canonical probability distribution is **sharply peaked** for both energy and particle number around the mean values $\langle E \rangle$ and $\langle N \rangle$. (In other words, we have that

$$\frac{\text{width of distribution}}{\text{mean of distribution}} \sim \frac{1}{\sqrt{N}} \to 0$$

in the limit $N \to \infty$.) This will show up on our homework, and the consequence is that we can work in either the microcanonical, canonical, or grand canonical ensembles **in the thermodynamic limit**.

We can write down the definition of the chemical potential as a partial derivative

$$\mu = -k_B T \alpha = -T \left(\frac{\partial S}{\partial N}\right)_{V,E}.$$

And we can write our grand partition function as an integral

$$Z_G = \int dE \sum_{N_r} \Omega(E_r, N_r) e^{-\beta(E_r - \mu N_r)} = \int dE \sum_{N_r} \exp\left(\frac{1}{k_B} S(E_r, N_r) - \beta(E_r, N_r)\right).$$

If we do the $\int dE \sum_{N_r}$ in a saddle-point approximation, we find that the integral is dominated by its maximum value, which occurs when E_r, N_r are at their mean $\langle E\rangle$ and $\langle N\rangle$. So in the thermodynamic limit,

$$Z_G = \exp\left(\frac{1}{k_B} S - \beta(\langle E\rangle - \mu\langle N\rangle)\right) = e^{-\beta(\langle E\rangle - TS - \mu\langle N\rangle)},$$

where we're defining S to take on its value at the equilibrium $E = \langle E\rangle$, $N = \langle N\rangle$. This leads us to define a new energy, much like the Helmholtz free energy, via

$$Z_G = e^{-\beta g} \implies \boxed{g = U - TS - \mu N}.$$

(Here, g is called the **grand potential**.) Because fluctuations are small, we'll use the same symbol for N and $\langle N\rangle$.

Now, we'll spend some time doing calculations in the grand canonical distribution, obtaining formulas in terms of the partition function. First of all, we know that

$$\langle N\rangle = \frac{1}{Z_G} \sum_r N_r e^{-\beta(E_r - \mu N_r)} = \frac{1}{Z_G} \frac{1}{\beta} \frac{\partial}{\partial \mu} \ln Z_G.$$

Plugging in a definition tells us that

$$\boxed{\langle N\rangle = -\frac{\partial g}{\partial \mu}}.$$

Similarly, we can try to calculate the average energy via

$$\langle E\rangle = \frac{1}{Z_G} \sum_r E_r e^{-\beta E_r - \mu N_r} = \frac{1}{Z_G} \sum_r (E_r - \mu N_r) e^{-\beta(E_r - \mu N_r)} + \mu N_r e^{-\beta E_r - \mu N_r}.$$

This reduces, using the previous result, to

$$= \frac{1}{Z_G}\left(-\frac{\partial}{\partial \beta} Z_G\right) + \mu\langle N\rangle,$$

so

$$\boxed{\langle E\rangle = \frac{\partial}{\partial \beta}(\beta g) + \mu\langle N\rangle = g - T\frac{\partial g}{\partial T} + \mu\langle N\rangle}.$$

And now we can look at the alternate definition of our entropy in terms of the probability distribution:

$$S = -k_B \sum_r p_r \ln p_r = -k_B \sum_r p_r \left(-\beta(E_r - \mu N_r) - \ln Z_G\right),$$

which can be written further as

$$= \beta k_B \langle E\rangle - \mu k_B \beta \langle N\rangle - \beta g k_B.$$

Putting this all together, we find that

$$S = \frac{U}{T} - \frac{\mu N}{T} - \frac{g}{T},$$

and indeed rearranging this recovers the same $g = U - TS - \mu N$ that we defined thermodynamically using the saddle-point approximation. Remembering our definition of the Helmholtz free energy $F = U - TS$ from the canonical partition function, we can also write down the equation $g = F - \mu N$. Since g is a function of variables T, V, μ, we can first understand how g varies as we vary each of those quantities. (This gave us relations between other thermodynamic quantities, like $dF = -SdT - PdV$, and we want to do the same thing here.) Notice that (we'll use E for energy instead of U)

$$\mu = -T\left(\frac{\partial S}{\partial N}\right)_{E,V}$$

and we also know that

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

Since S is generally a function of E, V, N, and we know that

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

from previous work, we know all three derivatives of entropy, and thus we can write

$$dS = \frac{1}{T}dE + \frac{P}{T}dV - \frac{\mu}{T}dN \implies \boxed{dE = TdS - PdV + \mu dN}.$$

So when we're allowed to vary the number of particles that we have, we get an extra term $+\mu dN$ which can also change the total energy of our system. (Even though N is always an integer, because it is very large, it's okay to take dN here.) Then

$$dF = d(E - TS) = -SdT - PdV + \mu dN,$$

again generalizing what we had earlier at fixed particle number, and finally

$$dG = d(F - \mu N) = -SdT - PdV - Nd\mu.$$

And now we have the equation for how G varies in terms of T, V, μ – all the derivatives are just thermodynamic quantities that we've already seen. In particular, this tells us that

$$N = -\left(\frac{\partial g}{\partial \mu}\right)_{T,V},$$

which is in agreement with earlier results, and similarly

$$S = -\left(\frac{\partial g}{\partial T}\right)_{\mu,V}, \quad P = -\left(\frac{\partial g}{\partial V}\right)_{T,\mu}.$$

But we know that $g = g(T, V, \mu)$ is an extensive quantity – it's proportional to V in the thermodynamic limit – and V is obviously extensive, while T and μ are not. So we must be able to write down

$$g = V\overline{g}(T, \mu)$$

for some function $\overline{g}$, and therefore

$$P = -\left(\frac{\partial g}{\partial V}\right)_{T,\mu} = -\overline{g}(T, \mu) = -\frac{g}{V}.$$

This means that $\boxed{PV = -g}$ – being able to calculate the grand potential g indeed gives us an explicit equation of state.

Example 113

Let's calculate the grand partition function for a classical ideal gas.

We have that

$$Z_G = \sum_{N=0}^{\infty} \frac{1}{N!} \int \prod_i \frac{d^3q_i d^3p_i}{(2\pi\hbar)^3} \exp\left(-\beta \frac{\vec{p}_i^2}{2m} + \beta\mu N\right)$$

(the Gibbs factor becomes even more important now). For any fixed N, this should be familiar to us, because it's the same answer as for our canonical ensemble. We end up with

$$Z_G = \sum_{N=0}^{\infty} \left(\frac{e^{\beta\mu N}}{N!}\right) \frac{V^N}{\lambda^{3N}},$$

where $\lambda = \frac{h}{\sqrt{2\pi m k_B T}}$ is the thermal de Broglie wavelength. And now this is really an exponential series when we sum over N: we end up with the answer

$$\boxed{Z_G = \sum_{N=0}^{\infty} \frac{1}{N!} \left(\frac{e^{\beta\mu}V}{\lambda^3}\right)^N = \exp\left(e^{\beta\mu}V/\lambda^3\right)}.$$

So the grand potential

$$g = -\frac{1}{\beta} \ln Z_G = -\frac{1}{\beta} e^{\beta\mu} \frac{V}{\lambda^3},$$

and now we notice that our volume only appears as a prefactor, exactly as we asserted earlier. And

$$N = -\left(\frac{\partial g}{\partial \mu}\right)_{V,T} = e^{\beta\mu} \frac{V}{\lambda^3},$$

which also tells us how to think about the chemical potential

$$\boxed{\mu = k_B T \ln \frac{N\lambda^3}{V} = k_B T \ln(n\lambda^3)},$$

where $n = \frac{N}{V}$ is the particle density.

Remark 114. *We'll see that this classical treatment is appropriate (at high temperature) as long as $n\lambda^3 \ll 1$, so that $\mu < 0$ in a classical ideal gas. But in a quantum ideal gas, at low temperature when $n\lambda^3$ becomes comparable to 1, we need to start thinking about quantum statistics. Then the chemical potential will sometimes evolve in such a way that μ can be positive (for example, for fermions).*

From here, we can calculate the pressure by taking a volume-derivative, and we find that for a classical ideal gas,

$$P = -\left(\frac{\partial g}{\partial V}\right)_{\mu,T} = \frac{k_B T e^{\beta\mu}}{V\lambda^3} = nk_B T = \frac{Nk_B T}{V},$$

again recovering the usual result.

19 October 14, 2020

Today's class is spending the first half an hour on questions from students.

- First, we should make sure to keep track of our fundamental assumptions – the laws of thermodynamics come from statistical mechanics, and they're statements about average quantities, so we don't need to assume them separately. And stat mech generally lets us calculate fluctuations, rather than just average values, which is much more powerful.

- We've seen a lot of state functions that are "functions of different things" – to get some intuition for why S is naturally a function of U, V, N, while g is naturally a function of other variables, we can think about what we've discussed so far in a general manner. Microscopically, we don't know anything about pressure or chemical potential, but we do know about the values of conserved quantities like energy or particle number if we're looking from a totally microscopic point of view (such as the microcanonical distribution). So defining $S = k_B \ln \Omega(E)$ means that it makes sense our **entropy is naturally a function of conserved quantities**.

  And from here, we do thermodynamics: putting systems in contact with heat baths, allowing us to exchange these conserved quantities, give us new state variables that can be written as partial derivatives. Defining partition functions based on our newly established probability distributions will naturally lead us to define Z in terms of new "free energies," which explains why we end up using the **thermodynamic conjguate variables** (for example, N versus μ in yesterday's class).

- The point of going to this generalized probabiltiy distribution is (1) that it represents a real physical system, or that (2) (even if our system is sort-of isolated, so it can't actually exchange quantities with a bath) it's **convenient to pretend** we can exchange particles and energy and use the grand canonical distribution to do calculations.

- Including the Gibbs factor or not in the calculation of the partition function depends on whether we have distinguishability – it's a question about the structure of the underlying Hilbert space. We'll discuss more details of this later in the course.

- If we have a mixture of two different atoms in a gas, the third law of thermodynamics doesn't actually tell us that the two types of atoms need to spatially separate – it just says that the system will evolve in some way that makes the entropy go to 0. (In this case, the two different types of atoms will form solids, which indeed have zero entropy at absolute zero.)

(Some discussion also occurred about exams and problem sets, which has been omitted here.)

For the next few weeks, we'll be talking about the kinetic theory of gases and the approach to equilibrium, and then we'll return to studying equilibrium of quantum gases, photons, phonons, Fermi and Bose gases, and so on. But the framework established in the past few lectures is the basic framework for statistical mechanics.

We're going to start looking at dynamics of our systems now, which we've been ignoring so far in our study.

Fact 115

The specific model that kinetic theory of gases is concerned with is a **dilute gas** of N atoms in a box of volume V which we can describe with classical mechanics, where two atoms **interact only at close range**.

If we consider the distribution of our particles in position-momentum phase space, and we look at a small volume $d^3q d^3p$ (note that "small" here means that the spacing is small compared to macroscopic dimensions, but still large compared to h^3). Then we'll define $f(\vec{q}, \vec{p}, t)$ to be the **distribution of atoms**, so that our small-volume box contains $f(\vec{q}, \vec{p}, t) d^3q d^3p$ total atoms.

So far, we've been assuming that in the absence of external time-dependent forces, we'll reach an equilibrium:

$$\lim_{t \to \infty} f(\vec{q}, \vec{p}, t) = f_{\text{eq}}(\vec{q}, \vec{p}).$$

Throughout this time-evolution, the total number of particles in our entire gas,

$$N = \int d^3q d^3p\, f(\vec{q}, \vec{p}, t)$$

must stay constant. But $f(\vec{q}, \vec{p}, t)$ may evolve because of changes in $(\vec{q}, \vec{p})$, either due to (1) collisions between particles or (2) external forces.

Fact 116

We'll ignore the first factor for now and try to write down an equation for $f(\vec{q}, \vec{p}, t)$, and then later we'll take into account interparticle collisions.

After a time δt passes, we know that $f(\vec{q}, \vec{p}, t) d^3q d^3p$ evolves into $f(\vec{q'}, \vec{p'}, t + \delta t) d^3q' d^3p'$, where

$$\vec{q'} = \vec{q} + \dot{\vec{q}}\delta t, \quad \vec{p'} = \vec{p} + \dot{\vec{p}}\delta t,$$

and $\dot{\vec{q}}, \dot{\vec{p}}$ are determined by the dynamics of the system. But we know from an earlier lecture that $d^3q' d^3p' = d^3q d^3p$ (phase space volume stays constant), so we must have

$$f(\vec{q'}, \vec{p'}, t + \delta t) = f(\vec{q}, \vec{p}, t).$$

(In other words, if we look at the value of our density f in our time-evolving coordinates, it will stay the same.) Taylor expanding, we find that to first order,

$$\delta t \left(\dot{\vec{q}} \cdot \frac{\partial f}{\partial \vec{q}} + \dot{\vec{p}} \cdot \frac{\partial f}{\partial \vec{p}} + \frac{\partial f}{\partial t} \right) = 0.$$

And now we have $\dot{\vec{q}} = \frac{\vec{p}}{m}$ by definition, and also the only way momentum can change is due to external forces (since we're ignoring collisions), meaning that $\dot{\vec{p}} = \vec{F}$. (Again, we're lumping in close-range interactions into "collisions," so for now we're assuming the particles move independently of each other.) So this tells us that (we're basically looking at the total time-derivative of f)

$$\frac{\partial f}{\partial t} + \frac{\vec{p}}{m} \frac{\partial f}{\partial \vec{q}} + \vec{F} \cdot \frac{\partial f}{\partial \vec{p}} = 0.$$

Our next step is to modify this equation in terms of collisions, which can "kick" particles in and out of our given volume element $d^3q d^3p$. Our equation then becomes

$$\frac{\partial f}{\partial t} + \frac{\vec{p}}{m} \frac{\partial f}{\partial \vec{q}} + \vec{F} \cdot \frac{\partial f}{\partial \vec{p}} = \left(\frac{\partial f}{\partial t} \right)_{\text{coll.}},$$

where $\left(\frac{\partial f}{\partial t}\right)_{\text{coll.}} d^3q d^3p$ is the net rate of flow of particles into our volume element $d^3q d^3p$. In order to calculate this, we'll need to make a few simplifying assumptions:

- We only have **binary collisions** (particles intersect pairwise), which is a reasonable assumption if our gas is dilute and the range of interaction is small enough.
- We ignore the effects of the wall of the container for our gas (these are just boundary condtiions).
- We'll also ignore the effects of external forces on the collision cross-section:

Definition 117

The **collision cross-section** $\sigma(\Omega)$ is define via

$$\sigma(\Omega)d\Omega = \frac{\text{number of atoms deflected with a solid angle between } \Omega \text{ and } \Omega + d\Omega \text{ per unit time}}{\text{incident flux}},$$

where the **incident flux** is the number of atoms that cross a unit area perpendicular to the incident beam per unit time.

In other words, we have an incoming flux of a beam of particles that scatter off of some object, and then we care about the density of appearance at each angle off of the object. (This is useful for calculating the strength of a scattering interaction.)

- The momentum of two atoms in the same volume element d^3q are uncorrelated with each other. More explicitly, if we condition two atoms' probability distributions such that they're near each other in position, then their momenta are independent.

This last assumption tells us that "collisions between particles generate enough randomness," and it's a bit harder to justify than the other ones. We may find more information about it under the name "molecular chaos." (We only need to make the assumption about momentum at short range to calculate f as a function of time, but we'll see soon why this is useful.)

20 October 16, 2020 (Recitation)

A poll for office hours was sent out, and the most popular time was Monday at 1pm, so that will be the new time.

Example 118

We'll start this recitation by discussing chemical reactions, seeing how high-school chemistry connects to the physics we've been doing.

First of all, consider the equation

$$dS = \frac{1}{T}dE + \frac{P}{T}dV - \sum_\alpha \frac{\mu_\alpha}{T}dN_\alpha,$$

where we're defining different kinds of particles α that can change into one another, but **no particles can be exchanged with the environment**. (Here, μ_α is the chemical potential for particle type α.) We reach equilibrium when $S_{\text{total}} = S + S_E$ is maximized, where S_E is the entropy of the environment, meaning that $dS + dS_E = 0$.

But notice that

$$dS_E = -\frac{1}{T}dE - \frac{P}{T}dV$$

(the negative signs because these are for the environment, not the system), so at constant energy E and volume V, equilibrium is equivalent to $dS = 0$, and that's the same as saying that

$$\sum_\alpha \mu_\alpha dN_\alpha = 0$$

if $dE, dV = 0$. And in fact, this condition is equivalent regardless of whether E and V are constant, because the entropy changes from the system and environment cancel out with each other.

And now remember that

$$\frac{\mu_\alpha}{T} = \left(\frac{\partial S}{\partial N_\alpha}\right)_{E,V},$$

but working with constant E and V is inconvenient, so we want to try to work with different state variables. First of all, because $TdS_{\text{total}} = TdS + TdS_E$, we have

$$TdS_{\text{total}} = TdS - dE - PdV = -dF - SdT - PdV$$

using the definition of free energy (because $d(TS) = TdS + SdT$), so at equilibrium, we can alternatively say that at constant T and V, $dF = 0$. And similarly, we can write things in terms of the Gibbs free energy: because $G = F + PV$, and $d(PV) = PdV + VdP$, we have

$$TdS_{\text{total}} = -dG - SdT + VdP.$$

So at constant temperature and pressure, equilibrium is equivalent to $dG = 0$. (And maximizing entropy is equivalent to dF or dG being minimized here.) Chemical experiments are easiest to do at constant temperature and pressure, because keeping volume constant requires a strong surrounding apparatus and so on. (And this helps us deal with **intensive** variables, which are potentially nicer than extensive ones – the only relevant extensive quantity is now the number of atoms for each of our different substances.)

Fact 119

Unless the entropy of a system is constant, we won't really be wanting to minimize energy E (we'd have the constraints that V, S are constant, which is a hard thing to do physically). And fundamentally, the point is that we're writing in terms of different variables.

So suppose that we have some chemical equation of the form

$$a_1 A_1 + a_2 A_2 + \cdots \rightleftharpoons b_1 B_1 + b_2 B_2 + \cdots .$$

(The $a_1, a_2, \cdots, b_1, b_2, \cdots$ are coefficients, and the $A_1, A_2, \cdots, B_1, B_2, \cdots$ are the different molecules in the balanced equation.) If this is the only way our particles can exchange with each other, then

$$dN_{A_j} = -a_j dx, \quad dN_{B_i} = b_i dx,$$

where x is the **reaction coordinate** tracking how far along our reaction has moved. On the other hand, we also know that (copying an equation from above)

$$0 = dG = -SdT + VdP + \sum_\alpha \mu_\alpha dN_\alpha,$$

and we're working at constant temperature and pressure, so

$$0 = \sum_\alpha \mu_\alpha dN_\alpha = \left(\sum_i \mu_{B_i} b_i - \sum_j \mu_{A_j} a_j\right) dx,$$

which means equilibrium is achieved at

$$\boxed{\sum_i \mu_{B_i} b_i = \sum_j \mu_{A_j} a_j}.$$

We know that μ_α is defined to be $\left(\frac{\partial G}{\partial N_\alpha}\right)_{T,P}$ For an ideal gas, **it turns out that**

$$\boxed{\mu_\alpha = \Delta G_\alpha^0 + k_B T \ln \frac{P}{P_0}},$$

where P_0 is standard pressure, T is measured in Kelvin, and $\Delta G_\alpha^0 = \mu_\alpha^0$ is the Gibbs free energy per atom at standard pressure. We'll prove this at the end of class (this turns out to also work for "ideal solutions" if we replace $\frac{P}{P_0}$ with the **concentration** $[\alpha]$).

Remark 120. *Everything here is being measured "per atom," which is why we have $k_B T$ instead of RT in the boxed equation.*

The reason these equations are useful is because values of ΔG^0 is usually listed in a table or on Wikipedia for various materials, and we can look them up when needed. But we can substitute these values into our equilibrium condition to find that

$$\sum_i b_i(\Delta G_{B_i}^0 + k_B T \ln[B_i]) = \sum_j a_j(\Delta G_{A_j}^0 + k_B T \ln[A_j]).$$

(The terms with natural logs of the concentrations can be thought of as "entropy factors" – remember that we're using units so that the concentrations are 1 at standard pressure.) And now the quantity

$$\Delta G_{\text{rxn}}^0 = -k_B T \ln\left(\frac{\prod_i [B_i]^{b_i}}{\prod_j [A_j]^{a_j}}\right) = -k_B T \ln K_{\text{eq}},$$

can be calculated by looking up the individual G^0s for our particles (and scaling by the coefficients). This K_{eq} is exactly the **equilibrium constant** we're used to from high school chemistry, and now we have a proof of this fact.

Note that we've used the ideal gas assumption here, and we always do this in high school chemistry – it allows us to calculate the exact chemical potential in terms of the concentration of our species. But that's an approximation, and if we're being more precise, we need to replace the concentration with an effective concentration called the **activity**.

Example 121

Let's now turn to the microcanonical, canonical, and grand canonical ensembles and compare how they behave.

In a microcanonical ensemble, we have a function $\Omega = \Omega(E, V, n)$, which is a function of all conserved (extensive) quantities, and we define $\boxed{S = k_B \ln \Omega}$. In the canonical ensemble, we consider a partition function instead, which can be written as

$$\int dE\,\Omega(E, V, N)e^{-\beta E} = \int dE\,e^{S/k_B - \beta E} \approx \int dE\,e^{-\beta F}$$

in the thermodynamic limit. Then F plays a similar role as entropy, because $\boxed{-\beta F = \ln Z}$.

The **Gibbs canonical ensemble** wasn't explicitly mentioned in lecture, but it's a system where we fix the pressure instead of the volume. We can write the partition function as (using the same notation as grand canonical ensemble from lecture, but they're different)

$$Z_G(T, P, N) = \int dV\,Z(T, V, N)e^{-\beta PV}.$$

(Notice that we're converting extensive quantities to intensive quantities one by one.) We're basically using $e^{-\beta PV}$ to penalize volumes based on their effect on the environmental entropy here, and now we can rewrite as

$$= dV e^{-\beta(F+PV)} \sim e^{-\beta G}.$$

So this means that $\boxed{-\beta G = \ln Z_G}$ for the Gibbs partition function Z_G. And more generally, we can write

$$Z_G(T, J, N) = \int dx Z(T, x, N)e^{\beta Jx},$$

where J and x form a conjugate pair of variables. This simplifies to

$$= \int dx e^{-\beta(F-Jx)},$$

and now remembering that like we found in the canonical ensemble,

$$\langle E^m \rangle_c = (-i)^m \frac{\partial^m \ln Z}{\partial \beta^m},$$

we can also find the cumulants of x via

$$\langle x^m \rangle_c = \frac{1}{\beta^m}\frac{\partial^m \ln Z_G}{\partial J^n}.$$

And finally, let's consider the grand partition function, which we'll denote

$$\mathbb{Q}(T, V, \mu) = \int dN Z(T, V, N)e^{\beta\mu N}.$$

(Here, the idea with the "penalty" factor is that exchanging particles changes the entropy of the environment as well.) Similarly, we write this as

$$= \int dN e^{-\beta(F-\mu N)} = e^{-\beta g},$$

where g is the Gibbs potential.

Example 122

By this point, we've made energy, volume, and number of particles all intensive, but not all at the same time – we may want to ask what happens if we did this process not to Z, but to Z_G.

Then we will find that we have a function R where all variables are intensive:

$$R(T, P, \mu) = \int dV \mathbb{Q}(T, V, \mu)e^{-\beta PV} = \int dV e^{-\beta(g+PV)}.$$

But this is **not an ensemble** – the issue is with this $g + PV$ term, and remember that we found $g = -PV$ from lecture! The argument here is that we must have

$$g(T, V, \mu) = \overline{g}(T, \mu)V = \left(\frac{\partial G}{\partial V}\right)_{T,\mu} = -\P(T, \mu)V,$$

and plugging this in either gives us an exponent of zero (if we chose the correct pressure P in terms of T, μ in our function R), or some constant $P - P(T, \mu)$ times V, meaning that the most likely volume is either 0 or infinite. So the issue is that **only one pressure is allowed for given** T, μ, and we can't really use three intensive quantities for that reason. (And this makes sense – we need to fix the system size in some way to describe it.)

This brings us to our final topic of today, **extensivity**. If we have an equation like

$$dE = TdS - PdV + \mu dN,$$

writing E as a function of S, V, N, our variables being extensive tells us that

$$E(\lambda S, \lambda V, \lambda N) = \lambda E(S, V, N).$$

(That is, if our system gets twice as large, we have twice as much entropy, volume, energy, and twice as many particles.) Taking the derivative with respect to λ at $\lambda = 1$, we find that

$$\frac{\partial}{\partial \lambda}\bigg|_{\lambda=1} = S\left(\frac{\partial E}{\partial S}\right)_{V,N} + V\left(\frac{\partial E}{\partial V}\right)_{S,N} + N\left(\frac{\partial E}{\partial N}\right)_{S,V} = E(S,V,N).$$

But this can be rewritten as

$$E = ST - VP + N\mu,$$

meaning that the energy has a very simple form because of extensivity. Then we can derive very simple expressions for our other state functions:

$$F = E - TS = -PV + \mu N,$$

$$G = F + PV = \mu N,$$

$$g = F - \mu N = -PV.$$

(Alternatively, we could have taken the λ-derivative directly from the definition of extensivity for F, G, or g.) Furthermore, we notice that the product rule gives us

$$dE = SdT + TdS - VdP - PdV + Nd\mu + \mu dN,$$

but we also know that $dE = TdS - PdV + \mu dN$ by definition, so

$$SdT - VdP + Nd\mu = 0.$$

And this is the **constraint of extensivity**: we can't vary T, P, μ independently of each other, because the contributions need to cancel out. And now we can write down relations like

$$\left(\frac{\partial \mu}{\partial P}\right)_T = \frac{V}{N}.$$

(There's a small technicality here. If we're only fixing T, we haven't actually fixed our system here – we can instead take $\left(\frac{\partial \mu}{\partial P}\right)_{T,V}$ or $\left(\frac{\partial \mu}{\partial P}\right)_{T,N}$, but neither of those matter because intensive relations are independent of the size of the system.) And we can use this to derive the chemical potential for an ideal gas, as promised: then

$$\left(\frac{\partial \mu}{\partial P}\right)_T = \frac{k_B T}{P} \implies \mu(P) = \mu(P_0) + k_B T \ln \frac{P}{P_0},$$

which is exactly what we wanted to show.

21 October 19, 2020

Our next quiz will be on Monday, October 26, with similar logistics as before (submit by 9am). The only difference from the previous quiz is that because of the upcoming election, the homework posted tomorrow will be a normal-length homework, due in two weeks (Monday, November 2). Topics included go up to the kinetic theory of gases.

First of all, answering a question from the class: if we take the energy eigenvalues for the hydrogen atom and calculate the partition function, we can calculate the partition function and find that the sum diverges. So this tells us that a single hydrogen atom in thermal equilibrium with a big bath at any nonzero temperature T will be ionized with probability one, and the bound state is not stable. But usually hydrogen atoms are not alone, and interactions with other particles will change this behavior in real life (except in outer space!).

In today's lecture, we'll discuss the kinetic theory of gases some more. Recall that we derived the following equation for the distribution $f(\vec{q}, \vec{p}, t)$ of particles:

$$\frac{\partial f}{\partial t} + \frac{\vec{p}}{m} \cdot \frac{\partial f}{\partial \vec{q}} + \vec{F} \cdot \frac{\partial f}{\partial \vec{p}} = \left(\frac{\partial f}{\partial t} \right)_{\text{coll}},$$

where $\vec{F}$ is the external force and the right-hand side of the equation describes changes due to particle collisions. We wish to write down an expression for the right-hand side using the particle distribution f itself, and recall that we do this with the following assumptions:

- Only binary collisions occur.
- We ignore the boundary-condition effects of the walls.
- We also ignore the effects of any external forces $\vec{F}$ on the collision cross-section.
- **The momenta of two atoms that are in the same spatial volume element are uncorrelated** (this is the assumption of **molecular chaos**).

In other words, the number of pairs of atoms in a spatial volume d^3q with momenta $(\vec{p}_1, \vec{p}_2)$ factorizes into a product of the form

$$\left(f(\vec{q}, \vec{p}_1, t) d^3q \, d^3p_1\right) \left(f(\vec{q}, \vec{p}_2, t) d^3q \, d^3p_2\right).$$

We're going to run with this as an assumption and try to extract information about the collision of particles in our system. We know that $\left(\frac{\partial f}{\partial t}\right)_{\text{coll}}$ depends both on particles leaving $(\vec{p}, \vec{q})$ because they collide (short-range) with another particle, and also on particles that enter a given $\vec{p}$ because of collisions at other positions or momenta into our given $(\vec{p}, \vec{q})$.

We'll consider the rate of leaving our given phase volume first. Suppose another particle with momentum $\vec{p}_1$ hits our particle with momentum $\vec{p}$, and after the collision the particles are scattered into momenta of $\vec{p}_2$ and $\vec{p}_3$, respectively. Conservation of momentum and energy tell us that

$$\vec{p}_1 + \vec{p} = \vec{p}_2 + \vec{p}_3, \quad \frac{\vec{p}_1^2}{2m} + \frac{\vec{p}^2}{2m} = \frac{\vec{p}_2^2}{2m} + \frac{\vec{p}_3^2}{2m},$$

because all of the interactions happen during a short time of collision, and external interactions don't affect this by assumption. So if we define the center-of-mass momentum

$$\vec{P} = \frac{\vec{p} + \vec{p}_1}{2} = \frac{\vec{p}_2 + \vec{p}_3}{2},$$

then the relative momenta are

$$\vec{p}_{\text{rel, i}} = \vec{p}_1 - \vec{p}, \quad \vec{p}_{\text{rel, f}} = \vec{p}_2 - \vec{p}_3.$$

Lemma 123

With the above definitions, the magnitude of the initial and final relative momenta are the same:

$$|\vec{p}_{\text{rel, i}}| = |\vec{p}_{\text{rel, f}}|.$$

Proof. We have that (in our usual frame)

$$\vec{p}^2 + \vec{p}_1^2 = \frac{1}{2}\left[(\vec{p} + \vec{p}_1)^2 + (\vec{p} - \vec{p}_1)^2\right].$$

The right simplifies to $2\vec{P}^2 + \frac{|\vec{p}_{\text{rel, i}}|^2}{2}$, but we also know that $\vec{p}^2 + \vec{p}_1^2 = \vec{p}_2^2 + \vec{p}_3^2$. So repeating the argument gives us

$$2\vec{P}^2 + \frac{|\vec{p}_{\text{rel, i}}|^2}{2} = 2\vec{P}^2 + \frac{|\vec{p}_{\text{rel, f}}|^2}{2},$$

and canceling gives the result. ☐

In other words, the direction of the initial and final momenta can be different, but the magnitude must stay the same in this center-of-mass frame. So now if we have an atom in a phase space volume $d^3q d^3p$ around $(\vec{q}, \vec{p})$, there are other atoms within the **same spatial volume** that can collide with it (we're using the short-range assumption here). So the incident flux of such atoms is proportional to the relative velocity:

$$f(\vec{q}, \vec{p}_1, t) d^3\vec{p}_1 \frac{|\vec{p} - \vec{p}_1|}{m}.$$

Therefore, the rate of collisions that deflect a single atom $(\vec{p}, \vec{p}_1)$ into $(\vec{p}_2, \vec{p}_3)$ is

$$\left(f(\vec{q}, \vec{p}_1, t) d^3 p_1 \frac{|\vec{p} - \vec{p}_1|}{m} \right) (\sigma(\Omega) d\Omega),$$

where Ω is the solid angle between $\vec{p}_{\text{rel, f}} = \vec{p}_2 - \vec{p}_3$ and $\vec{p}_{\text{rel, i}} = \vec{p}_1 - \vec{p}$. Multiplying by the number of atoms that exist at the $(\vec{q}, \vec{p})$ that we care about, we find that

$$\boxed{d^3q\, d^3p\, R_{\text{out}} = (d^3q\, d^3p\, f(\vec{q}, \vec{p}, t)) \int d^3p_1 d\Omega \sigma(\Omega) \frac{|\vec{p} - \vec{p}_1|}{m} f(\vec{q}, \vec{p}_1, t)},$$

where we can think of $\sigma(\Omega)$ as the cross-section corresponding to this particular collision from $(\vec{p}, \vec{p}_1)$ into $(\vec{p}_2, \vec{p}_3)$.

The next step is to calculate the rate of particles entering $d^3q d^3p$, and we do this by looking at the reverse process from $(\vec{p}_2, \vec{p}_3)$ into $(\vec{p}, \vec{p}_1)$. Then the incident flux into our volume element of an atom of momentum $\vec{p}_2$ at location $\vec{q}$ is

$$f(\vec{q}, \vec{p}_3, t) d^3 p_3 \frac{|\vec{p}_2 - \vec{p}_3|}{m},$$

so the total rate of such collisions into the correct momentum for a single atom is

$$f(\vec{q}, \vec{p}_3, t) d^3 p_3 \frac{|\vec{p}_2 - \vec{p}_3|}{m} \sigma(\vec{p}_2, \vec{p}_3 \to \vec{p}, \vec{p}_1) d\Omega.$$

Thus the total rate requires us to integrate over all possibilities and also account for the density of atoms: since we're counting particles scattered in from all initial states, we integrate over p_2 to find

$$\boxed{d^3q \int d^3p_2 R_{\text{in}} = d^3q \int d^3p_2\, d^3p_3\, f(\vec{q}, \vec{p}_2, t) f(\vec{q}, \vec{p}_3, t) \sigma(\vec{p}_2, \vec{p}_3 \to \vec{p}, \vec{p}_1) \frac{|\vec{p}_2 - \vec{p}_3|}{m} d\Omega}.$$

But we also know that $\vec{p} + \vec{p}_1 = \vec{p}_2 + \vec{p}_3 = \vec{P}$, and also that the final relative momentum $\vec{p}_{\text{rel, f}}$ only rotates from $\vec{p}_{\text{rel, i}}$. Therefore,

$$d^3\vec{p}\, d^3\vec{p}_{\text{rel, i}} = d^3\vec{p}\, d^3\vec{p}_{\text{rel, f}} \implies d^3p\, d^3p_1 = d^3p_2\, d^3p_3.$$

And because all of the dynamics work in reverse as well, we know that $\sigma(\vec{p}_2, \vec{p}_3 \to \vec{p}, \vec{p}_1) = \sigma(\vec{p}, \vec{p}_1 \to \vec{p}_2, \vec{p}_3)$. Therefore, we can also write the above expressions as

$$d^3q\, d^3p\, R_{\text{in}} = d^3q d^3p \int d^3p_1\, f(\vec{q}, \vec{p}_2, t) f(q, \vec{p}_3, t) \sigma(\Omega) d\Omega \frac{|\vec{p} - \vec{p}_1|}{m},$$

and

$$d^3q\, d^3p\, R_{\text{out}} = d^3q d^3p \int d^3p_1\, f(\vec{q}, \vec{p}, t) f(q, \vec{p}_1, t) \sigma(\Omega) d\Omega \frac{|\vec{p} - \vec{p}_1|}{m},$$

And putting this all together tells us that

$$\left(\frac{\partial f}{\partial t}\right)_{\text{coll}} = \int d^3p_1 d\Omega \sigma(\Omega)\frac{|\vec{p}-\vec{p}_1|}{m}(f_2f_3 - ff_1),$$

where $f = f(\vec{q}, \vec{p}, t)$ and $f_\alpha = f(\vec{q}, \vec{p}_\alpha, t)$. And now we have an equation that tells us how to calculate how a gas behaves not at equilibrium:

Proposition 124 (Boltzmann transport equation)

We have

$$\frac{\partial f}{\partial t} + \frac{\vec{p}}{m}\cdot\frac{\partial f}{\partial \vec{q}} + \vec{F}\cdot\frac{\partial f}{\partial \vec{p}} = \int d^3p_1 d\Omega \sigma(\Omega)\frac{|\vec{p}-\vec{p}_1|}{m}(f_2f_3 - ff_1).$$

Let's try to see what consequences this has for us by reconsidering our equilibrium state. If we assume our system has no external forces, meaning that $\vec{F} = 0$, then our equilibrium distribution f_{eq} should be independent of both $\vec{q}$ and also t (all positions are equivalent if there's no external potential), meaning the left side of this equation is 0 when $f = f_{\text{eq}}$. So

$$\int d^3p_1 d\Omega \sigma(\Omega)\frac{|\vec{p}-\vec{p}_1|}{m}(f_2^{\text{eq}}f_3^{\text{eq}} - f^{\text{eq}}f_1^{\text{eq}}) = 0,$$

and one sufficient condition for this to hold is if the integrand is always zero, and we can write this as

$$f_2^{\text{eq}}f_3^{\text{eq}} = f^{\text{eq}}f_1^{\text{eq}} \implies \ln f_2^{\text{eq}} + \ln f_3^{\text{eq}} = \ln f^{\text{eq}} + \ln f_1^{\text{eq}}.$$

So at equilibrium, we have a system where $\ln f_2^{\text{eq}} + \ln f_3^{\text{eq}}$ is collision invariant, but for our present model (a gas of particles at short-range interactions), the only additive collision invariants are $\vec{p}$ and energy E. So this forces us to write this additive invariant as a linear combination

$$\ln f^{\text{eq}} = A + \vec{B}\cdot\vec{v} + C\frac{p^2}{2m},$$

for some $A, \vec{B}, C$, and if the entire gas is collectively at rest, we can set $\vec{B} = 0$. And this leads us to (replacing e^A with A)

$$f^{\text{eq}} = Ae^{Cp^2/2m},$$

which looks a lot like the answer that we know as long as we set $\boxed{C = -\beta}$. The constant A is then determined by the density $n = \frac{N}{V}$ and the temperature T, since

$$n = \int d^3p f(\vec{q}, \vec{p}, t) = A\int d^3p e^{-\beta p^2/2m} = A(2\pi m k_B T)^{3/2}.$$

We end up with the answer

$$\boxed{f_{\text{eq}} = \frac{n}{(2\pi m k_B T)^{3/2}}e^{-\beta p^2/2m}}.$$

which is the **Boltzmann distribution** of an ideal gas.

Remark 125. *Angular momentum is also conserved, but for a free collection of particles, conservation of momentum implies conservation of angular momentum – we can't have a rotating gas without external forces.*

This calculation tells us that the Boltzmann distribution is consistent with the Boltzmann transport equation, but in fact there is a stronger result:

Theorem 126 (Boltzmann H-theorem)
From a function $f(\vec{q}, \vec{p}, t)$, construct a function $H(t) = \int d^3pd^3qf \ln f$. If f satisfies the Boltzmann equation, then $\frac{dH}{dt} \le 0$.

This should look like a second law of thermodynamics type result, because H is essentially an entropy.

Proof of a simple case. We'll assume that there is no external force, and that f is independent of $\vec{q}$. Then

$$\frac{dH}{dt} = V\int d^3p\frac{\partial f}{\partial t}(1 + \ln f),$$

and now if $\frac{\partial f}{\partial t} = 0$, that implies that $\frac{dH}{dt} = 0$, and this is precisely the equilibrium condition. But in general, we use the Boltzmann equation to find

$$\frac{\partial f}{\partial t} = \int d^3p_1 d\Omega\sigma(\Omega)\frac{|\vec{p} - \vec{p}_1|}{m}(f_2f_3 - ff_1),$$

and we get that

$$\frac{1}{V}\frac{dH}{dt} = \int d^3pd^3p_1d\Omega d\sigma(\Omega)(f_2f_3 - ff_1)(1 + \ln f)\frac{|\vec{p} - \vec{p}_1|}{m}.$$

$\square$

Interchanging the two dummy variables p, p_1, we also have

$$\frac{1}{V}\frac{dH}{dt} = \int d^3pd^3p_1d\Omega d\sigma(\Omega)(f_2f_3 - ff_1)(1 + \ln f_1)\frac{|\vec{p} - \vec{p}_1|}{m}.$$

So we can average the two equations together and find

$$= \frac{1}{2}\int d^3pd^3p_1d\Omega d\sigma(\Omega)(f_2f_3 - ff_1)(2 + \ln f + \ln f_1)\frac{|\vec{p} - \vec{p}_1|}{m}.$$

Now changing our coordinates to p_2 and p_3 instead of p and p_1, using that $d^3pd^3p_1 = d^3p_2d_3^p$ and that the magnitudes of the relative momenta are the same, we end up with

$$= \frac{1}{4}\int d^3pd^3p_1d\Omega\sigma(\Omega)(f_2f_3 - ff_1)(\ln f + \ln f_1 - \ln f_2 - \ln f_3)\frac{|\vec{p} - \vec{p}_1|}{m},$$

simplifying to

$$= \frac{1}{4}\int d^3pd^3p_1d\Omega\sigma(\Omega)(f_2f_3 - ff_1)(\ln(ff_1) - \ln(f_2f_3))\frac{|\vec{p} - \vec{p}_1|}{m}.$$

But the point here is that

$$(f_2f_3 - ff_1)(\ln(ff_1) - \ln(f_2f_3)) \le 0$$

always (consider the cases where $f_2f_3 > ff_1$ and vice versa), and the other parts of the integrand are all positive. So this quantity is always nonnegative, as desired, with equality only when $f_2f_3 - ff_1 = 0$, which is again our usual equilibrium condition.

22 October 21, 2020

Last class, we derived the Boltzmann transport equation, and we checked that we get the correct Maxwell-Boltzmann distribution if we additionally impose equilibrium. From there, we looked at Boltzmann's H-theorem, which stated that

$$\frac{dH}{dt} = \frac{d}{dt}\left(\int d^3pd^3q\, f(q, p, t)\ln f(q, p, t)\right) \le 0,$$

with equality if and only if f is the equilibrium distribution f_{eq}.

Fact 127

The form of this expression H looks a lot like the entropy of a probability distribution, and we can in fact show that H and S look very similar at equilibrium.

If we assume that there are no external forces, we must have

$$f_{\text{eq}} = Ae^{-\beta p^2/2m}$$

for some A (which we computed last time), and then integrating q out gives us

$$H = V \int d^3p\, f_{\text{eq}}(p) \ln f_{\text{eq}}(p) \implies \frac{H}{V} = \int d^3p\, Ae^{-\beta p^2/2m} \left[\ln A - \frac{\beta p^2}{2m} \right].$$

Now a direct integration gives us

$$= n \ln A - \beta A \int d^3p \frac{p^2}{2m} e^{-\beta p^2/2m},$$

where n is the density of the gas, and now we can evaluate this last integral with

$$\int d^3p \frac{p^2}{2m} e^{-\beta p^2/2m} = -\frac{\partial}{\partial \beta} \left(\int d^3p\, e^{-\beta p^2/2m} \right) = -\frac{\partial}{\partial \beta} \left(\frac{n}{A} \right).$$

Since n is a constant independent of temperature (and thus independent of β), we find that

$$H = n \ln A - \beta n A \frac{\partial}{\partial \beta} \left(\frac{1}{A} \right) = n \ln A + n\beta \frac{\partial(\ln(1/A))}{\partial \beta}.$$

And now because we calculated last class that $A = \frac{n}{(2\pi m k_B T)^{3/2}}$, our final answer ends up being

$$H = n \ln \left[\frac{n}{(2\pi m k_B T)^{3/2}} \right] - \frac{3}{2} n,$$

which is in agreement with ideal gas entropy up to scaling:

$$S = -k_B V H + (\text{constant}).$$

So this H is basically the same as our entropy, modulo an additive constant which is undetermined in classical mechanics.

But now $\frac{dH}{dt} \le 0$ means that there is an arrow of time – the time-evolution of our system is irreversible! Our next point of interest is then **where this comes from**. Our proof of the H-theorem follows rigorously from the Boltzmann equation, so there must be some irreversibility inherent in the Boltzmann equation too. (We used time-reversibility at the microscopic scale during our argument, so it's not about the equations of motion themselves.)

So to place what's going on here, we need to examine the assumptions that we established at the beginning of this derivation, namely the one about **molecular chaos**. Molecular chaos tells us that the distribution of pairs of atoms at some spatial point is given by the product of the single-particle distributions. But let's try something else: let's denote the number of pairs of atoms at $(\vec{q}_1, \vec{p}_1)$ and $(\vec{q}_2, \vec{p}_2)$ within a region $d^3q_1 d^3p_1 d^3q_2 d^3p_2$, by $f_2(\vec{q}_1, \vec{p}_1, \vec{q}_2, \vec{p}_2, t) d^3q_1 d^3p_1 d^3q_2 d^3p_2$. A reasonable assumption to make is the "opposite" to the one we actually made, which is that f_2 factors in terms of the single-particle f:

$$f_2(\vec{q}_1, \vec{p}_1, \vec{q}_2, \vec{p}_2, t) = f(\vec{q}_1, \vec{p}_1, t) f(\vec{q}_2, \vec{p}_2, t)$$

when $\vec{q}_1, \vec{q}_2$ are very far away (rather than when they are very close to each other). And it makes sense to say that there is some distance or range of interaction d such that when $|\vec{q}_1 - \vec{q}_2| \ll d$, the two particles strongly interact and we shouldn't expect a factorization. So our **best hope** is to be in a situation where most collisions do actually satisfy $|\vec{q}_1 - \vec{q}_2| \gg d$ (meaning the factorization holds and our derivation is valid), but that our collisions between particles also occur at the "same" $\vec{q}_1$ and $\vec{q}_2$, meaning that $|\vec{q}_1 - \vec{q}_2|$ is smaller than the length scale L at which our system is being probed. In other words, our particles must be close enough to look like they coincide at the L scale, but not too close to cause interactions at the d scale!

Fact 128

In summary, the Boltzmann equation is a coarse-grained description of the dynamics which are valid at length scales $\gg d$ and time scale $\gg \tau_c$ (the collision time). Because our resolution length scale L is much larger than d, even when our particles have $\vec{q}_1 \approx \vec{q}_2$, most of the time the distance between the two particles will still be at least d.

This isn't exactly where irreversibility has been explicitly introduced, though – the point where this happens comes from another aspect of the molecular chaos assumption. If we look more carefully at our derivation, what we actually assumed was that **incoming particles** (just before colliding) satisfy

$$f_2(\vec{q}, \vec{p}, \vec{q}, \vec{p}_1, t)|_{\text{before}} = f(\vec{q}, \vec{p}, t) f(\vec{q}, \vec{p}_1, t),$$

which allows us to calculate the rates of leaving and entering the momentum $\vec{p}$ (by looking at the collision forward and backward). But we know that when our particles evolve in the collision via

$$(\vec{q}, \vec{p}, \vec{q}, \vec{p}_1, t) \to (\vec{q}, \vec{p}_2, \vec{q}, \vec{p}_3, t)$$

(we assume the collision is instantaneous at our time scale), we must have

$$f_2(\vec{q}, \vec{p}, \vec{q}, \vec{p}_1, t)|_{\text{before}} = f_2(\vec{q}, \vec{p}_2, \vec{q}, \vec{p}_3, t)|_{\text{after}}$$

because of the Hamiltonian equations of motion that govern our underlying system. The point is that we can write collision terms either in terms of $f_2|_{\text{before}}$ and $f_2|_{\text{after}}$, so if we make the molecular chaos assumption for $f_2|_{\text{after}}$, that means we replace $ff_1 - f_2f_3$ from the collision term with $f_2f_3 - ff_1$ (since the rate of leaving is governed by either the "before" or "after" pair of particles). Then we'd end up getting the opposite sign in our H-theorem, which is physically incorrect – thus, it makes sense to make this molecular chaos assumption only for the before-collision situation. This can all be summed up in the following statement:

Proposition 129

Colliding introduces correlations between particles, and thus the joint distribution $f_2|_{\text{after}}$ does not satisfy the molecular chaos assumption.

What's interesting about this is that if we reverse the exact microscopic equations that govern our system, and we think about the above proposition, there must be some subtle correlations between the incoming particles. And the details of this are hidden and still pretty unknown – it has to do with the coarse-graining inherent in the Boltzmann equation. When we don't examine the system at our very short length scales (like d) or short time scales (like τ_c), we throw out those subtle correlations, and that gives us irreversibility.

Remark 130. *We can read Kerson Huang's Statistical Mechanics book for more details on this point.*

To finish today's lecture, we'll start discussing the **approach to equilibrium** for a gas, now that we have the Boltzmann equation to work with. It's worth first thinking about what time and length scales play a role in the physics of our system:

- The shortest relevant time scale is τ_c, the (typical) duration of a collision. The Boltzmann equation is only valid at time scales much larger than τ_c and length scales larger than d.
- The next shortest time scale is the **mean free time** τ, which is the typical time an atom spends between collisions with other atoms. This can be closely associated to the **mean free path** ℓ, which is the distance between successive collisions.
- We can assume that our gas is at **local equilibrium** after a few collisions, so it's reasonable to assume **local** equilibrium at time scales larger than τ and length scales greater than ℓ, but still smaller than macroscopic time and length scales. If we're at this third time scale (which is what we care about for macroscopic probes and measurements), that means we have local but not necessarily global equilibrium. Thus, the one-particle distribution f relaxes to its equilibrium form with possible slow $\vec{q}, t$ dependence (due to lack of global equilibrium).

Fact 131

Such states are specified by the local values of the **quantities conserved during collisions**, as well as local values of entropy.

- The final time and length scale is the time required for relaxation to **global equilibrium**.

In order to analyze this last situation, we'll need to make some more simplifications beyond the Boltzmann equation, and we'll discuss this next time.

23 October 23, 2020 (Recitation)

Today, we'll give an example calculation for the grand canonical ensemble, and then we'll focus on coarse-graining and the arrow of time in the Boltzmann equation and physics in general.

First of all, a question about combining partition functions: when can we multiply or add partition functions of subsystems together to figure out the partition function for the whole system? Remember that the definition of the **canonical** partition function starts off as

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

where we sum over all possible distinguishable states i (at some fixed volume V and number of particles N). Thermodynamics tells us that we have a set of extensive variables like E, V, N, M, along with their intensive conjugate variables $T, -P, \mu, B$ – what we're saying in the canonical ensemble is that all of the extensive variables (conserved quantities) get fixed except for energy E. In order to account for the varying energy, we need its intensive counterpart T to come into the picture (and we can always think of these counterparts as derivatives with respect to their corresponding extensive variable).

For example, if we have an ideal gas, computing this partition function is equivalent to

$$\frac{1}{N!} \int \prod_{i=1}^{N} \frac{d^3 p_i d^3 q_i}{h^3} e^{-\beta E(\{p,q\})},$$

where the $\frac{1}{N!}$ comes from us not being able to distinguish between particles being permuted. But what we can notice is that the **energy can be written as a sum of the individual particles**:

$$-\beta E(\{p, q\}) = -\beta(E_1 + \cdots + E_N),$$

where E_1 only depends on particle 1's coordinates, E_2 only depends on particle 2's coordinates, and so on. So then we can factor the integral by writing the exponent as a product, turning this into

$$\frac{1}{N!}\prod_{i=1}^{N}\int \frac{d^3p\,d^3q}{h}e^{-\beta E(p_i,q_i)}.$$

And now each term of the product is the partition function for a single particle, and therefore this is a case where we can multiply partition functions together. (On the other hand, we add partition functions together if we know the system is one of two possible disjoint sets of states, but this doesn't happen when combining particles' partition functions together.)

Example 132

Suppose we have N_0 particles in a d-dimensional space of volume V, so that if n particles bind together, we have an additional energy term $-\varepsilon_n$. (We'll ignore rotational and vibrational energy here.) Our goal is to figure out the behavior of this system (the pressure, the distribution of the clusters, and so on).

We'll start with the canonical partition function to do a calculation, but we'll soon see that the grand canonical ensemble works better for this problem. Our first attempt will give us

$$Z = \sum_{\substack{(N_1, N_2, \cdots, N_N) \\ \sum_{n=1}^{N} nN_n = N_0}} \prod_{n=1}^{N_0} \frac{1}{N_n!}\left(\frac{Ve^{\beta\varepsilon_n}}{\lambda_n^d}\right)^{N_n}$$

where we're summing over how many clusters we have of size $1, 2, \cdots, N$ respectively, and the fraction $\left(\frac{Ve^{\beta\varepsilon_n}}{\lambda_n^d}\right)$ is the partition function for a single ideal-gas cluster, meaning that

$$\lambda_n = \frac{h}{\sqrt{2\pi nmk_BT}}$$

(since this cluster has n times the mass of a typical particle). Note that we have a product $\prod_{i=1}^{N}$ in the expression for Z, because the contributions to the partition function for each cluster size are independent of each other. But this is a very annoying sum to calculate because of the weird constraint, so we'll use the grand canonical ensemble instead.

It might seem like going to the grand canonical ensemble and computing $\mathbb{Q}$, especially because we're now allowing N to vary a little bit. But what we'll do is pick our chemical potential μ so that $\langle N\rangle = \sum_n n\langle N_n\rangle = N_0$, and the sharply peaked nature of N means this is good enough – we're describing basically the same system as if we had exactly N_0 particles. (This is a matter of mathematical convenience!) So the partition function is now calculated by letting N_n vary over all nonnegative integers for each n:

$$\mathbb{Q} = \sum_{N=0}^{\infty} e^{\beta\mu N}Z(T, V, N) = \prod_{n=1}^{\infty}\sum_{N_n=0}^{\infty}\frac{1}{N_n!}\left(\frac{V}{\lambda_n^d}e^{\beta\mu n+\beta\varepsilon_n}\right)^{N_n}.$$

What we've really done is **eliminated the constraint** $\sum_n nN_n = N_0$, as long as we include a factor of $e^{\beta\mu N}$ in our partition function! And this basically lets us "switch the sum and product" in our earlier expression for Z, and now computing this expression is a lot more reasonable to deal with than the previous one.

Fact 133

Notice a trick that we used in the equality above: inside of the sum we have an $e^{\beta\mu n N_n}$ term, and taking the product of those over all n gives us $e^{\beta\mu\sum_n N_n}$. So we've factored the $e^{\beta\mu N}$ term in $\mathbb{Q}$ into its individual n-components when going from the left to the right side above.

To simplify the expression now, each term of the product looks like $\sum_{N_n=0}^{\infty}\frac{1}{N_n!}x^{N_n}$ for some complicated expression x, but that's exactly the formula for an exponential. So this simplifies to

$$\mathbb{Q} = \prod_{n=1}^{\infty}\exp\left[\frac{V}{\lambda_n^d}e^{\beta\mu n+\beta\varepsilon_n}\right],$$

and now we have a grand partition function that factors in n, the cluster size! This tells us that the grand potential is

$$g = -k_BT\ln\mathbb{Q} = -k_BT\sum_{n=1}^{\infty}\frac{V}{\lambda_n^d}e^{\beta\mu n+\beta\varepsilon_n} = \sum_{n=1}^{\infty}g_n,$$

where g_n is the grand potential for the n-cluster particles! This will make it easier for us to compare the distributions of different types. So now using that

$$dg = -SdT - PdV - Nd\mu = -SdT - PdV - \sum_{n=1}^{\infty}nN_nd\mu,$$

we find that the expected number of particles of cluster size n is (we take a derivative with respect to μn, because there's the extra n in the equation above – alternatively because the chemical potential μ_n has n times as much influence on n particles, or because the reaction between nA_1 and A_n is reversible)

$$\langle N_n\rangle = -\left(\frac{\partial g_n}{\partial(\mu n)}\right)_{T,V} = \frac{V}{\lambda_n^d}e^{\beta\mu n+\beta\varepsilon_n},$$

and the expected number of total particles is

$$\langle N\rangle = -\left(\frac{\partial g}{\partial\mu}\right)_{T,V} = \sum_{n=1}^{\infty}n\frac{V}{\lambda_n^d}e^{\beta\mu n+\beta\varepsilon_n}.$$

Numerically, we can use this last equation to find a μ that gives us our desired average N_0, which we then plug in to the rest of our calculations.

Remark 134. *For an analogy of this approximation of N_0 particles, we can think of how we might budget our time between different activities in real life. Instead of rearranging every hour of our time each time, we can use μ as a measurement of how busy we are, and we can assign a priority (energy) to each task that we want to do. And this is an easier way to adjust our schedule (by giving ourselves some slack rather than fixing every hour).*

Let's now look at some special cases of our setup:

Example 135

If $\varepsilon_n = 0$ for all n, then

$$\langle N_1\rangle = -\left(\frac{\partial g_1}{\partial\mu}\right)_{T,V} = \frac{V}{\lambda_1^d}e^{\beta\mu}.$$

The $\frac{V}{\lambda_1^d}$ is the number of independent quantum states our system can be in, so we expect $N_1 \ll \frac{V}{\lambda_1^d}$ in the classical limit. So $e^{\beta\mu}$ needs to be very small, meaning that our chemical potential μ must be negative. And the same calculation yields

$$\langle N_n \rangle = \frac{V}{\lambda_n^d} e^{\beta\mu n},$$

so we'll have very few particles for large n because μ is negative. And this means that in the classical limit, we'll only have single particles – indeed, if there's no binding energy, we don't expect particles to stick together.

Notice that this behavior **also occurs if** $\varepsilon_n = n\varepsilon$ for any energy ε, because that means that

$$\langle N_n \rangle = \frac{V}{\lambda_n^d} e^{\beta(\mu+\varepsilon)n}.$$

So we're just making a substitution in our system of $\mu \to \mu + \varepsilon$ (saying that all particles have an inherent energy of $-\varepsilon$), without changing the physics of what's going on.

Example 136

Now let's consider the case where $\varepsilon_n = \varepsilon(n-1)$, which means that any two clusters that come together reduce the energy by ε.

The formula now gives us

$$\langle N_n \rangle = \frac{V}{\lambda_n^d} e^{\beta(\mu+\varepsilon)n-\beta\varepsilon}.$$

To understand the distribution of particles, we can calculate that

$$\langle N_1 \rangle = \frac{V}{\lambda_1^d} e^{\beta\mu}, \quad N_n = n^{d/2} \langle N_1 \rangle e^{\beta(n-1)(\mu+\varepsilon)}.$$

where $n^{d/2}$ comes from the λs being differently for the different masses of clusters. So the exponential decay term means that we will still expect many more small clusters than large clusters.

Example 137

Now suppose that $\varepsilon_2 = \varepsilon$ but $\varepsilon_n = 0$ for all other n (so only clusters of two particles are energetically favorable).

Then we find that the dimensionless quantities are

$$\langle N_2 \rangle = 2^{d/2} \langle N_1 \rangle e^{\beta\mu+\beta\varepsilon} \implies \frac{\langle N_2 \rangle}{V/\lambda_2^d} = \left(\frac{\langle N_1 \rangle}{V/\lambda_1^d} \right)^2 e^{\beta\varepsilon}.$$

And now notice that for something like hydrogen gas, ε is between 4 and 5 eV, which is on the order of 10^4 Kelvin. That means that at room temperature, the $e^{\beta\varepsilon}$ term is incredibly large, so even though the $\left(\frac{\langle N_1 \rangle}{V/\lambda_1^d} \right)^2$ term is very small in the classical limit, we still expect to only ever see diatomic hydrogen gas (rather than monatomic hydrogen) at room temperature.

Finally, if we want to calculate the equation of state for this grand canonical ensemble, we have

$$P = -\left(\frac{\partial g}{\partial V} \right)_{\mu,T},$$

which we can compute and then substitute in our value of μ. And we can also calculate the pressure due to a particle type of cluster by setting

$$P_n = -\left(\frac{\partial g_n}{\partial V} \right)_{\mu,T}.$$

The whole point is that the different cluster types are interacting independently, and that's what makes lots of our calculations much easier throughout this problem.

In the last part of this recitation, we'll consider the **arrow of time**.

Example 138

At the beginning of a game of pool, we have a single (cue) ball moving at a momentum $\vec{p}_0$ toward a group of N balls at rest. (We assume elastic collisions, and also assume that N is larger than it actually is.)

We can think of the interactions as a sequence of 2-particle collisions – as soon as the first collision occurs, we have lots and lots of these happening in a short amount of time. Remember that in the Boltzmann equation derivation, we assumed **molecular chaos**, which gives us uncorrelated momenta before each collision. Then the starting distribution is

$$f_1(\vec{p}) = \frac{N-1}{N}\delta(0) + \frac{1}{N\sqrt{2\pi\sigma^2}} \exp\left(-\frac{(\vec{p}-\vec{p}_0)^2}{2\sigma^2}\right),$$

since the starting momentum has some uncertainty. At the beginning, because (for large N) basically all of the particles have zero momentum. So we actually start off satisfying the molecular chaos assumption because only one particle has nonzero momentum. But what we're further assuming is that after each collision but before the next, things are more or less random. (We also need to make the assumption of **random scattering cross-section**.)

But now if we reverse time, we'll apparently have N particles that come together elastically, correlated exactly so that $N-1$ of them end up at rest. So there must have been subtle correlations at the beginning – smudging any momentum a little would have significantly changed the configuration – but remember that there's still some randomness from the initial condition we wrote down above. So even if we did the particle evolution exactly, we'd have a weird randomness where all of the deviations correlate in a way that all of the variance goes into the one particle not at rest. The fundamental thing happening differently backwards from forwards is that **smudging makes a much larger impact** on the backward dynamics than the forward dynamics, because our initial condition is far from equilibrium.

24 October 26, 2020

Our (take-home) quiz is happening right now – if we have any questions, we should email all of the 8.333 staff (and whoever sees it first can respond).

Last week, we started looking at the kinetic theory of gases and comparing different timescales of behavior. Today, we'll continue exploring the approach to equilibrium, looking at conservation laws.

Recall that the shortest timescale is τ_c, the duration of a collision. (At timescales shorter than τ_c, we need to use the exact microscopic dynamics.) The next shortest timescale is the mean free time between collisions τ, followed by the timescales for local and global equilibrium (which we'll just denote τ_{eq}).

As a summary of the properties of these different quantities, the Boltzmann equation is valid at timescales $t \gg \tau_c$, and we can assume that local equilibrium is established if $t \gg \tau$. The point is that we don't need the full power of the Boltzmann equation once local equilibrium is reached, because the degrees of freedom are just (entropy and) the conserved quantities that we use on the macroscopic scale, except that they're allowed to vary. (And then when $t \gg \tau_{\text{eq}}$, global equilibrium is reached.) For example, local equilibrium means pressure is defined everywhere, meaning we don't need to look so fully at the dynamics. So we'll focus on time scales $t \gg \tau$ and try to analyze **what happens to our conserved quantities**.

Definition 139

The (local time-dependent) density is given by integrating out the momentum:

$$n(\vec{q}, t) = \int d^3\vec{p}\, f(\vec{q}, \vec{p}, t).$$

This function n tells us the density at a particular point in space and in time, and now we can define the **local expectation value** for a physical quantity $O(\vec{q}, \vec{p}, t)$ via

$$\langle O(\vec{q}, t)\rangle = \frac{1}{n(\vec{q}, t)} \int d^3p\, f(\vec{q}, \vec{p}, t) O(\vec{q}, \vec{p}, t).$$

As we just stated, the dynamics of our system for $t \gg \tau$ are determined by the evolution of our conserved quantities and by the local value of the entropy. If we consider a quantity $\chi(\vec{q}, \vec{p})$ (associated with an atom at $(\vec{q}, \vec{p})$ in phase space), which is **conserved by collisions** (so examples would be momentum or energy), we're stating that

$$\chi(\vec{q}, \vec{p}) + \chi(\vec{q}_1, \vec{p}_1) = \chi(\vec{q}_2, \vec{p}_2) + \chi(\vec{q}_3, \vec{p}_3).$$

Proposition 140

Suppose $\chi(\vec{q}, \vec{p})$ is conserved by collisions. Then

$$J = \int d^3p\, \chi(\vec{q}, \vec{p}) \left(\frac{\partial f}{\partial t}\right)_{\text{coll.}} = 0.$$

Proof. Substituting in the expression for the collision term, we have that

$$J = \int d^3p d^3p_1 d\Omega\, \sigma(\Omega) \frac{|\vec{p} - \vec{p}_1|}{m} (f(p_2)f(p_3) - f(p)f(p_1))\chi(\vec{q}, \vec{p}).$$

The manipulations from here will look similar to the H-theorem. Changing $\vec{p}$ and $\vec{p}_1$ with each other only changes $\chi(\vec{q}, \vec{p})$ and keeps everything else the same, so we also have (averaging the two such equations that we get)

$$J = \frac{1}{2} \int d^3p d^3p_1 d\Omega\, \sigma(\Omega) \frac{|\vec{p} - \vec{p}_1|}{m} (f(p_2)f(p_3) - f(p)f(p_1))(\chi(\vec{q}, \vec{p}) + \chi(\vec{q}_1, \vec{p}_1)).$$

And now if we exchange $\vec{p}, \vec{p}_1$ with $\vec{p}_2, \vec{p}_3$, this further simplifies to

$$= \frac{1}{4} \int d^3p d^3p_1 d\Omega\, \sigma(\Omega) \frac{|\vec{p} - \vec{p}_1|}{m} (f(p_2)f(p_3) - f(p)f(p_1))(\chi(\vec{q}, \vec{p}) + \chi(\vec{q}_1, \vec{p}_1) - \chi(\vec{q}_2, \vec{p}_2) - \chi(\vec{q}_3, \vec{p}_3)),$$

and this is 0 by conservation of χ. □

Substituting this back into the Boltmann equation gives us

$$\int d^3p\, \chi(\vec{q}\vec{p}) \left(\frac{\partial}{\partial t} + \frac{\vec{p}}{m} \cdot \frac{\partial}{\partial \vec{q}} + \vec{F} \cdot \frac{\partial}{\partial \vec{p}}\right) f = 0.$$

We can rearrange this a little, taking integrals out and making appropriate corrections, to find that

$$\frac{\partial}{\partial t}\left(\int d^3p\, \chi(\vec{q}, \vec{p}) f\right) + \frac{\partial}{\partial \vec{q}}\left(\int d^3p\, \chi(\vec{q}, \vec{p}) \frac{\vec{p}}{m} f\right) - \int d^3p \frac{\partial \chi}{\partial \vec{q}} \cdot \frac{\vec{p}}{m} f - \vec{F} \cdot \int d^3p \frac{\partial \vec{\chi}}{\partial \vec{p}} f = 0,$$

where the first term comes from the $\frac{\partial}{\partial t}$, the second and third term come from the $\frac{\vec{p}}{m} \cdot \frac{\partial}{\partial \vec{q}}$ and the product rule, and the last term comes from **integration by parts**, assuming that $\vec{F}$ is some external force and is therefore momentum-independent. (The boundary term involves the value of $\chi \cdot f$ at infinite momentum, and we require that f goes away rapidly enough because we have a well-defined finite distribution.) And now we can rewrite this a little in terms of averages:

$$\boxed{\frac{\partial}{\partial t}(n\langle\chi\rangle)+\frac{\partial}{\partial q_\alpha}\left(n\left\langle\frac{p_\alpha}{m}\chi\right\rangle\right)-n\left\langle\frac{p_\alpha}{m}\frac{\partial\chi}{\partial q_\alpha}\right\rangle-n\vec{F}\cdot\left\langle\frac{\partial\chi}{\partial\vec{p}}\right\rangle=0}.$$

where we're using repeated index notation (summing over all α). This is the equation that relates the dynamics of our conserved quantities, and again, it's most powerful when $t \gg \tau$ (since this is the timescale where evolution is governed by conserved quantities)!

Example 141

If we're looking at a monatomic gas, there are five conserved quantities: the particle number, the three components of momentum, and the kinetic energy.

We'll apply the formula we just derived for our conserved quantities

- Let's first try setting $\chi = 1$ (which is clearly conserved), corresponding to the particle number N. Then the last two terms disappear, and we're left with

  $$\frac{\partial n}{\partial t}+\frac{\partial}{\partial q_\alpha}\left(n\left\langle\frac{p_\alpha}{m}\right\rangle\right)=0.$$

  This should make a lot of physical sense if we consider the **local velocity** of the fluid (that is, the gas)

  $$u_\alpha=\frac{\langle p_\alpha\rangle}{m}.$$

  Then the equation above becomes

  $$\frac{\partial n}{\partial t}+\frac{\partial}{\partial q_\alpha}J_{n_\alpha}=0,$$

  where $\vec{J}_n = n\vec{u}$ is the particle current. And this is the familiar **continuity equation** – we could have written it down from undergraduate physics, because density can only change locally if particles flow to or away from a point.

- Next, we set $\chi = \frac{p_\alpha}{m}$, which we define to be v_α (for a given component α). This time, the third term disappears, and let's change the dummy index to β:

  $$\frac{\partial}{\partial t}(n\langle v_\alpha\rangle)+\frac{\partial}{\partial q_\beta}(n\langle v_\beta v_\alpha\rangle)-\frac{nF_\alpha}{m}=0.$$

  We'll now relate the second term to the **covariance** between v_α, v_β:

  $$\langle v_\alpha v_\beta\rangle=\langle(v_\alpha-u_\alpha)(v_\beta-u_\beta)\rangle+\langle v_\alpha\rangle u_\beta+\langle v_\beta\rangle u_\alpha-u_\alpha u_\beta,$$

  where u_α, u_β are **defined to be the average values** of v_α, v_β, and thus this simplifies to

  $$=\langle(v_\alpha-u_\alpha)(v_\beta-u_\beta)\rangle+u_\alpha u_\beta+u_\beta u_\alpha-u_\alpha u_\beta=\langle(v_\alpha-u_\alpha)(v_\beta-u_\beta)\rangle+u_\alpha u_\beta.$$

  Plugging this back in (and also making a few other substitutions) gives us

  $$\frac{\partial}{\partial t}(nu_\alpha)+\frac{\partial}{\partial q_\beta}(nu_\alpha u_\beta+n\langle(v_\alpha-u_\alpha)(v_\beta-u_\beta)\rangle)-\frac{nF_\alpha}{m}=0.$$

  This motivates us to make the following definition:

Definition 142

The **pressure tensor** is defined as

$$P_{\alpha\beta} = mn\langle (v_\alpha - u_\alpha)(v_\beta - u_\beta)\rangle.$$

At this stage, this is still a symbol, but we'll see it relates to the actual pressure soon. This allows us to write down

$$\frac{\partial}{\partial t}(nu_\alpha) + \frac{\partial}{\partial q_\beta}(nu_\alpha u_\beta) = \frac{nF_\alpha}{m} = -\frac{1}{m}\partial_\beta P_{\alpha\beta}.$$

Expanding out the derivatives gives us

$$n\frac{\partial u_\alpha}{\partial t} + u_\alpha \frac{\partial n}{\partial t} + u_\alpha \frac{\partial}{\partial q_\beta}(nu_\beta) + nu_\beta \frac{\partial}{\partial q_\beta} u_\alpha = \frac{nF_\alpha}{m} - \frac{1}{m}\partial_\beta P_{\alpha\beta},$$

but the second and third terms on the left-hand side cancel out by the continuity equation, so we end up with

$$\left(\frac{\partial}{\partial t} + \vec{u}\cdot\frac{\partial}{\partial \vec{q}}\right)\vec{u} = \frac{\vec{F}}{m} - \frac{1}{mn}\frac{\partial}{\partial \vec{q}}P.$$

Since the operator on the left-hand side will appear frequently, we'll define the **material derivative** (or Lagrangian derivative)

$$D_t = \frac{\partial}{\partial t} + \vec{u}\cdot\frac{\partial}{\partial \vec{q}},$$

so that our equation looks like

$$\boxed{D_t\vec{u} = \frac{\vec{F}}{m} - \frac{1}{mn}\frac{\partial}{\partial \vec{q}}P}.$$

The idea is that a pressure gradient leads to a force, so indeed $P_{\alpha\beta}$ has to do with the ordinary pressure here.

- Finally, let's try setting $\chi = E = \frac{\vec{p}^2}{2m} = \frac{1}{2}m\vec{v}^2$ – it's best to state the result in terms of the kinetic energy with local flow subtracted:

$$\varepsilon = \frac{1}{2}m(\vec{v} - \vec{u})^2.$$

Again, the third term disappears again when we substitute E into the original boxed equation:

$$\frac{\partial}{\partial t}(n\langle E\rangle) + \frac{\partial}{\partial q_\alpha}\left(n\left\langle \frac{p_\alpha}{m}E\right\rangle\right) - n\vec{F}\cdot\left\langle\frac{\partial E}{\partial \vec{p}}\right\rangle = 0,$$

which simplifies to

$$\frac{\partial}{\partial t}(n\langle E\rangle) + \frac{\partial}{\partial q_\alpha}(n\langle v_\alpha E\rangle) - n\vec{F}\cdot\vec{u} = 0.$$

A quick notation rewrite turns this into

$$\partial_t(n\langle E\rangle) + \partial_\alpha(n\langle v_\alpha\langle E\rangle) = n\vec{F}\cdot\vec{u},$$

and then we can rewrite $\langle v_\alpha E\rangle = \langle (v_\alpha - u_\alpha)E\rangle + u_\alpha\langle E\rangle$, so that

$$n\partial_t(\langle E\rangle) + \partial_\alpha(n\langle u_\alpha\langle E\rangle + n\langle (v_\alpha - u_\alpha)E\rangle) = n\vec{F}\cdot\vec{u}.$$

Using the definition of the material derivative D_t above, we end up with

$$nD_t\langle E\rangle + \partial_\alpha(n\langle (v_\alpha - u_\alpha)E\rangle) = n\vec{F}\cdot\vec{u}.$$

To make this cleaner, it's time to put things in terms of ε: we can now write

$$E = \varepsilon + m\vec{v} \cdot \vec{u} - \frac{1}{2}m\vec{u}^2,$$

meaning that

$$E = \varepsilon + m(\vec{v} - \vec{u}) \cdot \vec{u} + \frac{1}{2}m\vec{u}^2.$$

Thus $\langle E \rangle = \langle \varepsilon \rangle + \frac{1}{2}m\vec{u}^2$, and we can also multiply through by $(v_\alpha - u_\alpha)$ before taking an average to find

$$\langle (v_\alpha - u_\alpha)E \rangle = \langle (v_\alpha - u_\alpha)\varepsilon \rangle + \frac{1}{2}mu_\beta \langle (v_\alpha - u_\alpha)(v_\beta - u_\beta) \rangle.$$

If we now define the **local heat flux**

$$h_\alpha = n\langle (v_\alpha - u_\alpha)\varepsilon \rangle$$

and the **rate of strain tensor** (for clarification, notice that the tensor has two indices, while the average velocity u has one)

$$u_{\alpha\beta} = \frac{1}{2}(\partial_\alpha u_\beta + \partial_\beta u_\alpha),$$

then our definitions plug back in to yield

$$\langle (v_\alpha - u_\alpha)E \rangle = \frac{h_\alpha}{m} + \frac{u_\beta P_{\alpha\beta}}{n}.$$

Plugging this back into our original equation, the left hand side becomes

$$= n(D_t \varepsilon + m\vec{u} \cdot D_t \vec{u}) + \partial_\alpha (h_\alpha + u_\beta P_{\alpha\beta}),$$

so that the left-hand side of the energy equation gives us (after some tedious algebra)

$$= nD_t \varepsilon + n\vec{F} \cdot \vec{u} - u_\beta \partial_\alpha P_{\alpha\beta} + \partial_\alpha h_\alpha + u_{\alpha\beta} P_{\alpha\beta} + u_\beta \partial_\alpha P_{\alpha\beta}.$$

Meanwhile, the right-hand side is $n\vec{F} \cdot \vec{u}$, so cancelling finally gives us

$$D_t \varepsilon = -\frac{1}{n}\partial_\alpha h_\alpha - \frac{1}{n}P_{\alpha\beta} u_{\alpha\beta}.$$

Putting all of this together and making some more small manipulations, we have the equations

$$D_t n = -n\partial_\alpha u_\alpha,$$

$$mD_t u_\alpha = F_\alpha - \frac{1}{n}\partial_\beta P_{\alpha\beta},$$

$$D_t \varepsilon = -\frac{1}{n}\left(\partial_\alpha h_\alpha + P_{\alpha\beta} u_{\alpha\beta}\right).$$

Each of these describes the evolution of one of local flow velocity, energy density, and particle number. We still need to know more about the right-hand sides of these equations, because we have these new objects $P_{\alpha\beta}$, $u_{\alpha\beta}$, and h_α. Next time, we'll discuss how to relate these quantities to properties of the flow, so that we can extract the dynamics!

25 October 28, 2020

Fact 143

Because of the upcoming election, Alex will spend some time on Friday in recitation talking about applications of statistical mechanics to polarization (of voting).

In today's lecture, we'll continue the study of the approach to equilibrium, looking at "0th order hydrodynamics." For reference, we'll copy down all of the relevant equations from our derivation last class again: letting $n(\vec{q}, t)$ be the local particle density and $\varepsilon = \frac{1}{2}m(\vec{v} - \vec{u})^2$ be the energy independent of local flow, we have that

$$D_t n = -n\partial_\alpha u_\alpha,$$

$$mD_t u_\alpha = F_\alpha - \frac{1}{n}\partial_\beta P_{\alpha\beta},$$

$$D_t\varepsilon = -\frac{1}{n}(\partial_\alpha h_\alpha + P_{\alpha\beta}u_{\alpha\beta}),$$

where $u_\alpha = \left\langle \frac{p_\alpha}{m} \right\rangle$ is the local flow velocity, $D_t = \frac{\partial}{\partial t} + \vec{u} \cdot \frac{\partial}{\partial \vec{q}}$, $P_{\alpha\beta} = mn\langle (v_\alpha - u_\alpha)(v_\beta - u_\beta)\rangle$ is the pressure tensor, $u_{\alpha\beta} = \frac{1}{2}(\partial_\alpha u_\beta + \partial_\beta u_\alpha)$ is the rate of strain tensor, and $h_\alpha = n\langle (v_\alpha - u_\alpha)\varepsilon\rangle$ is the local heat flux. The first equation above is the continuity equation rewritten in terms of the material derivative D_t (measuring change when we move along with the fluid), the second tells us about evolution of local flow velocity through a "force equation," and the third tells us about evolution of energy. And remember that **all of these equations come from the Boltzmann equation**, but the point is that looking at times $t \gg \tau$ allows us to characterize our fluid with local equilibrium values of conserved quantities and how the entropy depends on them.

To actually make use of the above equations, we need more information about $P_{\alpha\beta}$ and h_α, and these are determined by the full particle distribution function $f(\vec{q}, \vec{p}, t)$. At equilibrium, we know the form of f, so at local equilibrium we can make a zeroth order approximation

$$f^{(0)}(\vec{q}, \vec{p}, t) \approx \frac{n(\vec{q}, t)}{2\pi mk_B T(\vec{q}, t)^{3/2}} \exp\left(-\frac{(\vec{p} - m\vec{u}(\vec{q}, t))^2}{2mk_B T(\vec{q}, t)}\right),$$

where we're accounting for the fact that $n, T, \vec{u}$ can change over space and time (because we're not at global equilibrium yet), and also that the gas may be flowing (not just at rest). And now that we have the distribution, we can calculate all of the average values that we need, because we have the Gaussian weight. For example,

$$\langle (v_\alpha - u_\alpha)(v_\beta - u_\beta)\rangle = \frac{k_B T}{m}\delta_{\alpha\beta},$$

which is the usual result of velocity fluctuations from the Maxwell-Boltzmann distribution, so the pressure tensor is

$$P^{(0)}_{\alpha\beta} = nk_B T\delta_{\alpha\beta}.$$

And we know that for an ideal gas in complete equilibrium, this is indeed the pressure from the diagonal terms of the tensor (we have the usual $P = \frac{Nk_B T}{V}$). We can also find that

$$\varepsilon = \frac{1}{2}m\langle (\vec{v} - \vec{u})^2\rangle = \frac{3}{2}k_B T,$$

which also looks like our usual result. Next, for the heat flux h_α, we notice that $f^{(0)}$ is even in $v_\alpha - u_\alpha$, so all odd expectation values of $v_\alpha - u_\alpha$ will vanish. So $\vec{h}^{(0)} = 0$ – there is no heat flux at this zeroth order. (In other words, this approximation gives us **adiabatic** behavior.) So putting everything back together, we have

$$\begin{aligned} D_t n &= -n\partial_\alpha u_\alpha, \\ mD_t u_\alpha &= F_\alpha - \frac{1}{n}\partial_\alpha(nk_B T), \\ D_t T &= -\frac{2}{3}T(\partial_\alpha u_\alpha), \end{aligned}$$

and combining the first and third equations gives us

$$\frac{1}{n}D_t n = -\partial_\alpha u_\alpha = \frac{3}{2T}D_t T.$$

Therefore,

$$D_t(\ln nT^{-3/2}) = 0,$$

and thus this flow leaves $nT^{-3/2}$ invariant. In fact, $\ln(nT^{-3/2})$ is (up to an additive constant) the negative **entropy per particle** of our gas, so the **local entropy does not change** through evolution of our system to equilibrium, which leads us to this adiabatic flow.

Fact 144

In other words, what we've learned is that global equilibrium **will not be reached** in this zeroth order approximation (because entropy needs to be increased for us to get there)!

To understand the dynamics more clearly, we'll consider a special case where $\vec{F} = 0$ (there are no external forces), and we have a small disturbance from equilibrium. Specifically, let $(\overline{n}, \overline{T})$ be the density and temperature of an equilibrium state when the gas is at rest – the density is uniform if there are no external forces – and consider a small perturbation

$$n(\vec{q}, t) = \overline{n} + \nu(\vec{q}, t), \quad T(\vec{q}, t) = \overline{T} + \theta(\vec{q}, t),$$

where $\nu, \theta, \vec{u}$ are all small (so the gas moves slowly, and also we only change the temperature and particle density by a little bit). If we linearize our above equations and expand the conservation laws to first order, we can replace D_t with ∂_t (because we have a $\frac{\partial}{\partial t}$ term that dominates the $\vec{u} \cdot \frac{\partial}{\partial \vec{q}}$ term, and whatever we're taking a derivative of is already small, so we get "second-order smallness" there). So now our equations look like

$$\begin{aligned} \partial_t \nu &= -\overline{n}\partial_\alpha u_\alpha, \\ m\partial_t u_\alpha &= -k_B\partial_\alpha\theta - \frac{k_B\overline{T}}{\overline{n}}\partial_\alpha\nu, \\ \partial_t\theta &= -\frac{2}{3}\overline{T}\partial_\alpha u_\alpha. \end{aligned}$$

And these are **(coupled) linear differential equations with constant coefficients**, which are exactly solvable by writing down the matrix eigenvalue problem (we have a 5 by 5 matrix, because u has three components, and we also have ν and θ). We find that (using block matrices, so that the γ indices form row vectors and the α indices form column vectors):

$$\omega \begin{bmatrix} \nu(\vec{k}, \omega) \\ u_\alpha(\vec{k}, \omega) \\ \theta(\vec{k}, \omega) \end{bmatrix} = \begin{bmatrix} 0 & \overline{n}k_\gamma & 0 \\ \frac{k_B\overline{T}}{\overline{n}m}k_\alpha & 0 & \frac{k_B}{m}k_\alpha \\ 0 & \frac{2}{3}\overline{T}k_\gamma & 0 \end{bmatrix} \begin{bmatrix} \nu(\vec{k}, \omega) \\ u_\gamma(\vec{k}, \omega) \\ \theta(\vec{k}, \omega) \end{bmatrix},$$

and now we want to diagonalize the matrix. But there are **two zero-frequency modes** that correspond to transverse velocities where $\vec{k} \cdot \vec{u} = 0$ (we can do the multiplication on the right side to find that the first and last rows of the matrix go away), so that gives us two eigenvalues of 0, called **shear modes**. And related to our earlier discussion, these **do not relax to equilibrium in our zeroth order approximation**, because there is no amplitude decay for this eigenvalue 0.

The third zero-frequency mode that we can observe comes from the "decayless" flow of entropy that we were studying earlier. This mode satisfies

$$\frac{\nu}{\overline{n}} = \frac{\theta}{\overline{T}}, \quad \text{eigenvector} \begin{bmatrix} \overline{n} \\ 0 \\ -\overline{T} \end{bmatrix},$$

and we can indeed plug this eigenvector in and directly check that there is zero frequency. And now we only have two eigenvalues left, and these actually correspond to modes that we physically understand well (longitudinal sound modes). The dispersion relation is

$$\omega(\vec{k}) = \pm v_\ell |\vec{k}|, \quad v_\ell = \sqrt{\frac{5}{2}\frac{k_B \overline{T}}{m}}.$$

Putting all of this together, what the zeroth order approximation tells us is that we have no relaxation to equilibrium, but we have shear and entropy modes which stay there forever (disturbance doesn't evolve, because the frequency is zero). Other than those, we also have two sound modes that are undamped in this approximation.

We can correct the issues with this result by using a better solution of the Boltzmann equation, specifically picking a better distribution f than $f^{(0)}$ so that relaxation to equilibrium is actually captured. Notice that $\left(\frac{\partial f^{(0)}}{\partial t}\right)_{\text{coll.}} = 0$, but in general

$$\left(\partial_t + \frac{\vec{p}}{m} \cdot \partial_{\vec{q}} + \vec{F} \cdot \partial_{\vec{p}}\right) f^{(0)} \neq 0,$$

so we **do not actually have a solution to the Boltzmann equation** here. What we'll do, then, is write

$$f(\vec{q}, \vec{p}, t) = f^{(0)}(\vec{q}, \vec{p}, t) + g(\vec{q}, \vec{p}, t)$$

and linearize the Boltzmann transport equation in g. The collision term

$$\left(\frac{\partial f}{\partial t}\right)_{\text{coll.}} = \int d^3 p_1 d\Omega\, \sigma(\Omega) \frac{|\vec{p} - \vec{p}_1|}{m} (f_2 f_3 - f f_1)$$

then linearizes to

$$\approx \int d^3 p_1 d\Omega\, \sigma(\Omega) \frac{|\vec{p} - \vec{p}_1|}{m} (g_2 f_3 + f_2 g_3 - f g_1 - g f_1)$$

at order g, and a typical term on the right hand side now kind of looks like (we can take g out of the integral because we're not integrating over p_1)

$$-g \int d^3 p_1\, d\Omega\, \sigma(\Omega) \frac{|\vec{p} - \vec{p}_1|}{m} f_1 \approx -\frac{g}{\tau},$$

where τ is the mean free time between collisions. Trying to actually work with the actual collision terms coming from g can be very hard, so what we're going to do is cheat and just use

$$\left(\frac{\partial f}{\partial t}\right)_{\text{coll.}} = -\frac{g}{\tau} = -\frac{(f - f^{(0)})}{\tau},$$

which is called the **relaxation-time approximation**. This allows us to solve for g, and what we'll find next time is that all of our modes that we computed above will acquire a damping factor depending on τ. So then we'll finally have a way to characterize the behavior of this system towards equilibrium!

26 October 30, 2020 (Recitation)

We'll spend this class on a high-level review of kinetic theory (the Boltzmann equation, hydrodynamics), and then we'll see how statistical physics can be applied to elections, particularly instability and negative political representation.

In the textbook, Kardar defines the operator $\mathcal{L}$ via

$$\mathcal{L}f = \frac{df}{dt} = \left(\frac{\partial}{\partial t} + \frac{\vec{p}}{m}\frac{\partial}{\partial \vec{q}} + \vec{F} \cdot \frac{\partial}{\partial \vec{p}}\right) f(p, q, t),$$

which is 0 if we have no collisions by Liouville's theorem. (Liouville's theorem tells us that $\frac{d\rho}{dt}$, where ρ is a distribution of all particles in $6N$-dimensional space, while f is a distribution in 6-dimensional space for particle density.) But otherwise, we need to account for an extra collision time, and then we derived that

$$\boxed{\mathcal{L}f = \left(\frac{\partial f}{\partial t}\right)_{\text{coll.}} = \int d^3p_1 d\Omega\, \sigma(\Omega) \frac{|\vec{p}_1 - \vec{p}|}{m}(f_2(p_2, p_3, \cdots) - f_2(p, p_1, \cdots))}.$$

where $f_2(p_2, p_3, \cdots)$ tells us about the density of finding a pair of particles at momenta p_2, p_3, respectively. We'll define this as the collision expression $\mathcal{L}f = C[f_2]$.

Remark 145. *In class, we then used the shorthand*

$$f_2 = f(p_2), f_3 = f(p_3),$$

because we treated the momenta as uncorrelated, but we'll ignore this notation for now – f_2 is the two-particle density throughout this recitation.

In order to derive the boxed expression above, we only had to make a few assumptions: we assumed there were no 3-particle collisions, and we ignored the effect of the external force $\vec{F}$ on collisions too (because we derived the expressions using Newtonian physics). Since we can treat walls as external forces, we're also ignoring those boundary conditions. (Basically, the timescale of a particle is very fast, so any external force mainly acts between collisions rather than between collisions.) So no inaccuracies or "coarse-graining" has been done yet.

But then the next approximation is that we can **factor f_2 into one-particle densities**, and we evaluate all f's in the collision term at a single point $\vec{q}$. Then we find that

$$\mathcal{L}f = C[f_2] = C[f, f] = \int d^3p_1 d\Omega\, \sigma(\Omega) \frac{|\vec{p}_1 - \vec{p}|}{m}(f(p_2)f(p_3) - f(p)f(p_1))$$

(the Cs are just extra notation – something like $C[f_1, f_2]$ doesn't really make sense). Then we looked at the expression

$$H(t) = \int d^3q\, d^3p\, f \ln f,$$

which looks reasonably similar to a (negative) entropy (since f is a probability distribution), even though f doesn't actually describe microstates. (And remember that we could derive the canonical ensemble by maximizing the real entropy – we'll see something similar on our problem set this week.) And now if we use the Boltzmann equation, which is exactly the statement $\mathcal{L}(f) = C[f, f]$, then the H-**theorem** tells us that $\frac{dH}{dt} \le 0$. If we write out this statement in more detail, we write that

$$\frac{dH}{dt} = \int d^3p\, d^3q\, \frac{\partial f}{\partial t}(\ln f + 1) = \int d^3p\, d^3q\, \frac{df}{dt}(\ln f + 1)$$

(in this case, it doesn't matter whether we take a total or partial derivative, because **phase space volume is conserved** under the evolution of the single-particle Hamiltonian). And then the $+1$ doesn't contribute to total integral, because total particle density is conserved, and thus we end up with

$$= \int d^3p\, d^3q\, (\mathcal{L}f) \ln f = \int d^3p\, d^3q\, C[f, f] \ln f.$$

And now we "symmetrize" over $f(p), f(p_1), f(p_2)$, and $f(p_3)$ as we did in class: since the expression looks the same with certain swaps of dummy variables, this is also just

$$\frac{1}{4} \int d^3q\, d^3p\, d^3p_1 d\Omega\, \sigma(\Omega) \frac{|\vec{p}_1 - \vec{p}|}{m} (f(p_2)f(p_3) - f(p)f(p_1))(\ln(f(p_3)f(p_2)) - \ln(f(p)f(p_1)))$$

(the idea is that by integrating over both p and p_1, we're considering all pairs of particles coming at each other, rather than just fixing one of the momenta). But now this integrand must always be nonpositive, because we have an expression of the form $(A - B)(\ln B - \ln A)$, and ln preserves ordering, and thus we've derived $\frac{dH}{dt} \le 0$.

The next thing we considered from there was that for a collision-conserved quantity χ, we have

$$\int d^3p\, C[f, f] \chi(p, q, t) = 0.$$

(This was basically a symmetrization argument similar to the H-theorem from class.) We can then use the fact that $C[f, f] = \mathcal{L}f$ again to find that

$$0 = \int d^3p\, (\mathcal{L}f)\chi = \int d^3p\, \mathcal{L}(f\chi) - f\mathcal{L}(\chi),$$

since $\mathcal{L}$ is a differential operator. We then derived the hydrodynamic equations by plugging in various conserved quantities $\chi = 1, \chi = \vec{p}$, and $\chi = \frac{\vec{p}^2}{2m}$ (we assume monatomic gas because there can't really be other degrees of freedom in our derivation, though a slight modification works for polyatomic gases too). The results involve the **material derivative** D_t, which is the **total derivative with respect to flow lines for the average velocity, instead of the flow lines along the velocity of a single particle**:

$$\begin{aligned} D_t n &= -n\partial_\alpha u_\alpha, \\ mD_t u_\alpha &= F_\alpha - \frac{1}{n}\partial_\beta P_{\alpha\beta}, \\ D_t \varepsilon &= -\frac{1}{n}(\partial_\alpha h_\alpha + P_{\alpha\beta} u_{\alpha\beta}), \end{aligned}$$

We've explained these equations in lecture already, but if we define

$$c_\alpha = \frac{p_\alpha}{m} - u_\alpha,$$

that makes it easier to define the pressure tensor (created from deviations of velocity from the average)

$$P_{\alpha\beta} = mn\langle c_\alpha c_\beta \rangle,$$

the local reference-frame energy

$$\varepsilon = \frac{1}{2}m\langle c^2 \rangle,$$

the heat transfer term coming from asymmetric distributions in energy along different axes

$$h_\alpha = nm\left\langle \frac{c^2}{2} c_\alpha \right\rangle,$$

and the symmetrized derivative (all derivatives ∂_α are in terms of the position coordinates)

$$u_{\alpha\beta} = \frac{1}{2}(\partial_\alpha u_\beta + \partial_\beta u_\alpha).$$

(There might have been a bit of abuse of notation during class between the energy and average value of energy.) So now we look at **zeroth-order hydrodynamics**: since $\mathcal{L}$ has units of inverse time, we should think of a certain timescale $\mathcal{L} \sim \frac{1}{\tau}$ as the time to global equilibrium. On the other hand, we have $C[f, f] \sim \frac{1}{\tau_x}$, and the collision time τ_x is much smaller than τ. So we can think of this as having an equation like

$$3x = 10^4(x^2 - 4),$$

and since the right side is much larger than the left, we can basically set the left side to 0 at zeroth order in x. So what we say is that we are ignoring collisions' role as we approach equilibrium: our equation is

$$0 = C[f, f].$$

So our hydrodynamics don't account for collisions between flows, but we can still try to get some physics out of it. To solve for the kinds of functions f that work for us here, note that

$$\frac{dH}{dt} = \int d^3q \, d^3p \, C[f, f] \ln f,$$

so our approximation implies that $\frac{dH}{dt} = 0$. One possible solution for H is

$$\ln f(p, q) + \ln f(p_1, q) - \ln f(p_2, q) - \ln f(p_3, q) = 0,$$

and because $\frac{dH}{dt}$ is integrating over a nonpositive thing everywhere, we indeed need this equality to be true at all points! Thus, we know that

$$\ln f(p, q) = \alpha(q) + \vec{\gamma}(q) \cdot \vec{p} - \beta(q)\frac{\vec{p}^2}{2m} :$$

in other words, $\ln f$ should be a combination of the conserved quantities if it needs to be conserved by collisions. This tells us that

$$f \propto n(q, t) e^{-\beta(q,t)\frac{1}{2m}(\vec{p} - m\vec{u}(q,t))^2}$$

(so f looks like the global equilibrium distribution $ne^{-\beta E}$, except that n, β, E can all change as a function of time and also position). The key, though, is that

$$P_{\alpha\beta} \propto \delta_{\alpha\beta}, \quad h_\alpha = 0$$

(pressure points outward instead of having weird shear, and the above distribution is symmetric around deviations of velocity), and what we found next was that local values of entropy don't change, so we don't actually do any relaxation to global equilibrium for this approximation.

So if we look at the first-order picture (which we'll discuss more in the future), what we should assume is $\mathcal{L}f \sim O(\varepsilon)$ (for some small ε) and write $f = f^{(0)} + \varepsilon(\delta f)$, where δf is of the same order as the zeroth order $f^{(0)}$. Then we know that

$$C[f^{(0)}, f^{(0)}] = 0 \implies C[f, f] = A\varepsilon(\delta f) + O(\varepsilon^2)$$

for some linear operator A that can depend on $f^{(0)}$, and also that

$$\mathcal{L}f = \mathcal{L}f^{(0)} + \varepsilon\mathcal{L}(\delta f) = \mathcal{L}f^{(0)} + O(\varepsilon^2).$$

So the new equation is (to first order)

$$\mathcal{L}f^{(0)} = \mathcal{L}f = A\varepsilon(\delta f),$$

and now we make the huge approximation: because A has units of inverse time, we're replacing A with $\frac{1}{\tau}$. (In other words, we diagonalize and assume all of the eigenvalues are the same.) We'll see how this plays out in more detail on Monday.

The last 10 minutes of this class will be dedicated to elections:

Example 146

Suppose we have some political opinions $x \in \mathbb{R}^d$ (a vector representing a single person's opinions), and we have some distribution of opinions $f(x)$. An election takes in a function f and outputs the opinions of a single candidate $y[f] \in \mathbb{R}^d$. We'll write everything in terms of 1-dimensional functions $f(x)$.

Political **representation** can then be described by "how the outcome changes if the xs change by an infinitesimal amount" using a functional derivative:

$$r(f, x) = \frac{d}{dx}\frac{\delta y}{\delta f(x)},$$

(The reason for the $\frac{d}{dx}$ term is that we "move" an opinion from one spot x to a different spot $x + \delta x$.) Then we define an **unstable election** if $y[f]$ is discontinuous, and we can have **negative representation** $r(f, x) < 0$: – perhaps opinions x moving in one direction cause the outcome to move in the other direction. It turns out that if we assume overall translational invariance, meaning that

$$y[f] + c = y[f(x + c)]$$

(shifting everyone's opinion by the same amount also shifts the election result by that amount), then necessarily **instability leads to negative representation**. But unfortunately, elections in the US, especially in the past few decades, have become increasingly unstable, so people aren't being politically represented properly.

To tie this back to the statistical physics, we want to think about phase transitions between stable and unstable configurations.

Example 147

Let's use a toy model where the choice of winning candidate follows

$$y^* = \text{argmax}_{y \in \mathbb{R}} \int dx\, f(x) u(y - x)$$

for some utility function u.

We often assume that the utility functions u are concave, but it makes sense that preferences become weaker as people become farther from both election candidates, so the utility function could be Gaussian as a function of $y - x$. And then we can calculate representation

$$r(f, x) \propto -u''(y - x).$$

So for the Gaussian, people who are sufficiently far away from the candidates (that is, $|y^* - x|$ is sufficiently large) are negatively represented!

And this maximization problem can be replaced as choosing a function $F(y)$ that minimize the free energy. As we create a more polarized distribution, we should expect that $F(y)$ follows a double-well potential: the minima occur according to party preference, and with enough energy we can move between the two wells (which is what happens from election to election).

27 November 2, 2020

The election is coming up tomorrow, and it's a stressful and uncertain time for everyone – we'll hope that it isn't too chaotic and that things proceed like they do in previous elections. We should make sure to stay safe!

Our first quiz has been graded, and our score and comments have been released to us. One comment about one of the problems: in problem 2, most of the class found that if we start with the high-pressure metal phase and heat it at constant pressure, it will eventually transition into the insulating phase. This is the opposite of the usual behavior we expect, since adding thermal energy usually causes electrons to move around! In this case, it is the **entropy** that drives the transition to insulation, and this does happen in certain organic materials, as well as certain low-temperature behavior of Helium. For example, heating a solid is usually supposed to give us a liquid, but sometimes we get lots of degrees of freedom from the (barely interacting) spins in atoms' nuclei, and that gives us a big boost in entropy that is not present in the liquid. (We can search up the Pomeranchuk effect for other examples.)

We'll continue thinking about the approach to equilibrium today, looking at first order hydrodynamics in the kinetic theory of gases. Recall that we started with conditions of local equilibrium, using the zeroth order approximation (or guess)

$$f^{(0)} = f^{(0)}_{\text{eq.}}(n(\vec{q},t), T(\vec{q},t), u(\vec{q},t)).$$

Working with this a bit, we then found shear modes and sound waves that propagate without any damping, and in particular we found that we don't actually approach equilibrium at all. This is because

$$\left(\partial_t + \frac{\vec{p}}{m}\cdot\partial_{\vec{q}} + \vec{F}\cdot\partial_{\vec{p}}\right) f^{(0)} \neq 0,$$

even though the collision term on the right-hand side was assumed to be 0, so $f^{(0)}$ isn't actually a solution of the Boltzmann equation. So our next step was to linearize a deviation around this: we wrote $f = f^{(0)} + g$, where all functions here are of $\vec{q}, \vec{p}, t$. Then, we linearize as a function of g and make a **relaxation-time approximation** where the collision term is replaced with

$$-\frac{g}{\tau} = -\frac{f - f^{(0)}}{\tau}.$$

(A more precise argument would have given different timescales τ for each of the different modes we found in the zeroth-order approximation, but we'll work with this for now.) So now we have

$$\left(\partial_t + \frac{\vec{p}}{m}\cdot\partial_{\vec{q}} + \vec{F}\cdot\partial_{\vec{p}}\right)(f^{(0)} + g) = -\frac{g}{\tau}.$$

Remark 148. *If we look at a case where there is no $\vec{q}$ or $\vec{p}$-dependence, and the fluid isn't moving (for example, because we've reached global equilibrium), we end up with an equation like $\partial_t g = -\frac{g}{\tau}$, which is an exponential decay of the deviation term g. So indeed we expect some type of approach to equilibrium with this model now, and it's why the negative sign is important.*

To arrive at a leading-order solution, we actually ignore the g on the left-hand side of this equation. This is because the dominant term is the derivative of $f^{(0)}$: more precisely, if $f^{(0)}$ varies significantly on a length scale L, then $\frac{vf^{(0)}}{L}$ is on the order of $\frac{g}{\tau}$, so

$$\left|\frac{g}{f^{(0)}}\right| \approx \frac{v\tau}{L} \approx \frac{\ell}{L},$$

where ℓ is the mean free path. So we're making the assumption that **deviations from equilibrium occur on length scales longer than the mean free path**.

With this new approximation, it is much easier to solve

$$g = -\tau\left(\partial_t + \frac{\vec{p}}{m}\dot{\partial}_{\vec{q}} + \vec{f}\cdot\partial_{\vec{p}}\right) f^{(0)}.$$

Since we already have our previous guess for $f^{(0)}$ from last lecture, we can calculate the derivatives directly to find the expression for g. But instead of calculating the derivatives of $f^{(0)}$, it turns out to be more convenient to calculate the derivatives of $\ln f^{(0)}$, since

$$\frac{g}{f^{(0)}} = -\tau\left(\partial_t + \frac{\vec{p}}{m}\cdot\partial_{\vec{q}} + \vec{F}\cdot\partial_{\vec{p}}\right)(\ln f^{(0)}).$$

Here, we recall that

$$\ln f^{(0)} = \ln(nT^{-3/2}) - \frac{m\vec{c}^2}{2k_BT} - \frac{3}{2}\ln(2\pi m k_B),$$

where $\vec{c} = \vec{v} - \vec{u}$ is the velocity in the co-moving frame with the fluid. We will denote the operator $\left(\partial_t + \frac{\vec{p}}{m}\cdot\partial_{\vec{q}} + \vec{F}\cdot\partial_{\vec{p}}\right)$ by $\mathcal{L}$ from here on, so that

$$\boxed{\mathcal{L}} = \partial_t + \vec{u}\cdot\partial_{\vec{q}} + \vec{c}\cdot\partial_{\vec{q}} + \vec{F}\cdot\partial_{\vec{p}} = D_t + \vec{c}\cdot\partial_{\vec{q}} + \vec{F}\cdot\partial_{\vec{p}} = \boxed{D_t + \vec{c}\cdot\partial_{\vec{q}} + \frac{\vec{F}}{m}\cdot\partial_{\vec{c}}}.$$

Now we've replaced references to $\vec{p}$ with references to $\vec{c}$, and now the expression expands out to

$$\mathcal{L}(\ln f^{(0)}) = D_t(\ln(nT^{-3/2})) + \frac{mc^2}{2k_BT^2}D_tT - \frac{m}{k_BT}c_\alpha D_t c_\alpha + c_\alpha\left(\frac{\partial_\alpha n}{n} - \frac{3}{2}\frac{\partial_\alpha T}{T}\right) + \frac{m\vec{c}^2}{2k_BT^2}c_\alpha\partial_\alpha T - \frac{m}{k_BT}c_\alpha c_\beta\partial_\alpha c_\beta - \frac{F_\alpha c_\alpha}{k_BT}.$$

Using the fact that $D_t c_\alpha = -D_t u_\alpha$, $\partial_\alpha c_\beta = -\partial_\alpha u_\beta$, and applying the zeroth order hydrodynamic equations (that $f^{(0)}$ satisfies), we have

$$\mathcal{L}(\ln f^{(0)}) = -\frac{m\vec{c}^2}{3k_BT}\partial_\alpha u_\alpha + \frac{c_\alpha}{k_BT}\left(F_\alpha - \frac{1}{n}\partial_\alpha(nk_BT)\right) + c_\alpha\left(\frac{\partial_\alpha n}{n} - \frac{3}{2}\frac{\partial_\alpha T}{T}\right) + \frac{m\vec{c}^2}{2k_BT^2}c_\alpha\partial_\alpha T + \frac{m}{k_BT}c_\alpha c_\beta\partial_\alpha u_\beta - \frac{F_\alpha c_\alpha}{k_BT}.$$

And now we do some more simplification (algebra omitted, but worth going through ourselves) to find that

$$\boxed{g = -\tau f^{(0)}\left(\frac{m}{k_BT}\left(c_\alpha c_\beta - \frac{c^2}{3}\delta_{\alpha\beta}\right)u_{\alpha\beta} + \left(\frac{mc^2}{2k_BT} - \frac{5}{2}\right)\frac{c_\alpha}{T}\partial_\alpha T\right)}.$$

To check if this is legitimate, we can do a quick check:

$$\int d^3p\, g = -\tau n\left(\frac{m}{k_BT}\left\langle c_\alpha c_\beta - \frac{c^2}{3}\delta_{\alpha\beta}\right\rangle_0 u_{\alpha\beta} + \left\langle\left(\frac{mc^2}{2k_BT} - \frac{5}{2}\right)c_\alpha\right\rangle_0\frac{\partial_\alpha T}{T}\right)$$

where the 0 subscript refers to averages with respect to the Gaussian distribution $f^{(0)}$ for velocity. And we can easily show that

$$\langle c_\alpha c_\beta\rangle_0 = \left\langle\frac{c^2}{3}\right\rangle_0\delta_{\alpha\beta},$$

and also that

$$\left\langle\left(\frac{mc^2}{2k_BT} - \frac{5}{2}\right)c_\alpha\right\rangle_0 = 0$$

because everything is odd in c, which is symmetric. So indeed $\int d^3p\, g = 0$, and this implies that $\int d^3p\, f = \int d^3p\, f^{(0)} = n$, so adding our deviation **rearranges but does not add particles** – in fact, it preserves the density of particles at each $\vec{q}$ and t, and we only redistribute how the particles behave in momentum space.

And now calculating averages of various observables to first order in τ can be done as

$$\langle O\rangle^{(1)} = \frac{1}{n}\int d^3p\, O(f^{(0)} + g) = \langle O\rangle^{(0)} + \left\langle\frac{g}{f^{(0)}}O\right\rangle_0.$$

If O is a polynomial in the c_αs, for example, the last term here requires calculations over averages of c_αs with respect to the Gaussian distribution $f^{(0)}$, but now we can make use of **Wick's theorem** from recitation 1:

$$\langle c_{\alpha_1} c_{\alpha_2} \cdots c_{\alpha_{2n}} \rangle = \left(\frac{k_B T}{m} \right)^n \cdot (\text{sum over all possible products of paired averages}).$$

This lets us calculate all of the quantities: for example,

$$\left\langle \frac{p_\alpha}{m} \right\rangle = u_\alpha - \tau \left\langle \left(\frac{mc^2}{2k_B T} - \frac{5}{2} \right) c_\beta c_\alpha \right\rangle \frac{\partial_\beta T}{T},$$

and then

$$P_{\alpha\beta}^{(1)} = nm\langle c_\alpha c_\beta \rangle^{(1)} = nm \left[\langle c_\alpha c_\beta \rangle^{(0)} - \frac{\tau m}{k_B T} \left\langle \left(c_\mu c_\nu - \frac{c^2}{3} \delta_{\mu\nu} \right) c_\alpha c_\beta \right\rangle u_{\mu\nu} \right]$$

simplifies to

$$= nk_B T \delta_{\alpha\beta} - 2nk_B T \tau \left(u_{\alpha\beta} - \frac{\delta_{\alpha\beta} u_{\gamma\gamma}}{3} \right).$$

(Recall that we're still summing over repeated indices.) And now we can define the **viscocity**

$$\mu = nk_B T \tau,$$

meaning that we're claiming that

$$P_{\alpha\beta}^{(1)} = nk_B T \delta_{\alpha\beta} - 2\mu \left(u_{\alpha\beta} - \frac{\delta_{\alpha\beta} u_{\gamma\gamma}}{3} \right),$$

Example 149

Let's think about the meaning of $P_{\alpha\beta}$ and μ now, because we have some extra terms compared to the "usual" pressure.

We know that if we have a conserved quantity χ that is associated with a single atom, then χn is the total value of χ in a given region of space, divided by its volume. Since J_χ, the current density, is given by the rate at which χ flows past a point, we know that

$$J_{\chi\alpha} = n\chi v_\alpha,$$

and if we switch to the co-moving frame, we have

$$\tilde{J}_{\chi,\alpha} = n\chi(v_\alpha - u_\alpha).$$

Since the momentum is conserved, we can choose χ to be the βth component of the momentum in the co-moving frame. Now we have

$$\tilde{J}_{p_\beta,\alpha} = mn(v_\beta - u_\beta)(v_\alpha - u_\alpha),$$

so the average "current density of momentum" (transmitted by flow of the gas itself) is $mn\langle (v_\beta - u_\beta)(v_\alpha - u_\alpha) \rangle$. But this quantity is also measuring force per unit area, since the rate of change of momentum is force! So this indeed makes sense as a "pressure" object, and this also explains why we should think about it as a tensor rather than a single number.

So now let's look at the off-diagonal elements of the pressure tensor: for example,

$$P_{xy} = \text{current of } p_x \text{ along the } y\text{-direction},$$

and those off-diagonal terms are just (in these first-order hydrodynamics)

$$P_{xy} = -2\mu(u_{xy}) = -\mu(\partial_x u_y + \partial_y u_x).$$

So if we have a fluid flowing in the $\vec{x}$-direction, we can write the velocity as $\vec{u} = (u_x, 0, 0)$, where u_x can be a function of y. Then we can write down the relation

$$P_{xy} = -\mu \frac{du_x}{dy},$$

telling us about the force per unit area in the xz-plane, and the role that μ plays here is exactly the standard definition of viscocity!

Returning to our earlier work, we now need to calculate the heat flux, which was zero in zeroth-order hydrodynamics. It turns out to be

$$h_\alpha^{(1)} = n\left\langle c_\alpha \frac{mc^2}{2}\right\rangle^{(1)},$$

which requires us to calculate the average in

$$= -\frac{n\tau}{T}\partial_\beta T\left\langle \frac{mc^2}{2} c_\alpha \left(\frac{mc^2}{2k_B T} - \frac{5}{2}\right) c_\beta\right\rangle.$$

Using Wick's theorem yields

$$h_\alpha^{(1))} = \left(-\frac{5n\tau k_B^2 T}{2m}\right)\partial_\alpha T = -k\partial_\alpha T,$$

where $k = \frac{5n\tau k_B^2 T}{2m}$ is the **heat conductivity**. So at first order, a non-uniform temperature does produce a heat flow that smooths it out, which is what we want. Similarly, if we have a shear flow, we'll oppose that flow with a non-zero viscosity, further getting us towards global equilibrium.

Fact 150

Notice that k is proportional to the mean free time τ, and similarly the viscosity also has a factor of τ. So if we take the ratio $\frac{k}{\mu}$, those two factors will cancel out, and we can indeed measure $\frac{k}{\mu}$ in a variety of gases to test the relaxation approximation. It turns out that it is pretty well-satisfied in the dilute gas limit with weak interactions!

Next time, we'll plug everything back into the conservation equations, and we'll show that in linearized hydrodynamics, we have finite damping rates for our different normal modes.

28 November 4, 2020

Fact 151

Class began with a discussion about everyone's thoughts on the election and election process.

We'll finish the discussion of first order hydrodynamics today, showing that the long-wavelength modes relax (damp) to equilibrium, which will conclude our discussion of kinetic theory. Then we'll move on to a completely different topic – quantum ideal gases – but before that, we'll take some time to ask questions about the course material in general.

Remark 152. *These past few lectures have had a lot of algebra, and it's easy for us to get lost in the calculations. But if we look back at the notes after this section of the class, hopefully we can see the bigger picture and the strategies we've been using. Our homework, due next Tuesday, should help us develop some more intuition too.*

We've been working to characterize the deviation g from equilibrium $f^{(0)}$ at linear order, and we can do this by plugging in the heat flux and pressure tensor we derived last time into our conservation equations. (The goal is to show that these will indeed lead to relaxation to global equilibrium). Recall that two of our linearized hydrodynamic equations are

$$\text{(for density:) } \boxed{\partial_t \nu = -\overline{n}\partial_\alpha u_\alpha},$$

where $\nu = n - \overline{n}$ is the deviation of density, and

$$\text{(for momentum:) } m\partial_t u_\alpha = -\frac{1}{\overline{n}}\partial_\beta P_{\alpha\beta},$$

where we found last time that

$$P_{\alpha\beta} = nk_B T\delta_{\alpha\beta} - 2\mu\left(u_{\alpha\beta} - \delta_{\alpha\beta}\frac{u_{\gamma\gamma}}{3}\right),$$

with $\mu = nk_B\overline{T}\tau$ the viscosity coefficient in the relaxation-time approximation. So if we plug in this pressure tensor into the momentum equation, what we end up with is

$$\boxed{m\partial_t u_\alpha = -k_B\partial_\alpha\theta - \frac{k_B\overline{T}}{\overline{n}}\partial_\alpha\nu + \frac{\mu}{\overline{n}}\left(\frac{\partial_\alpha\partial_\beta}{3} + \delta_{\alpha\beta}\partial_\gamma\partial_\gamma\right)u_\beta},$$

where $\theta = T - \overline{T}$. (Remember that we're specializing to a case where we're perturbing about a state where the fluid is at rest in global equilibrium, meaning there is a fixed density $\overline{n}$ and temperature $\overline{T}$.)

Remark 153. *If we instead plug in the pressure tensor into the non-linearized momentum equation, we end up with the* **Navier-Stokes equation** *(the basic equation of fluid dynamics).*

What we've written down is a linearized version of Navier-Stokes, and the first two terms on the right-hand side already existed in the zeroth order hydrodynamic equation. If we do a similar substitution into the energy equation, we find that

$$\boxed{\partial_t\theta = -\frac{2}{3}\left(\overline{T}\partial_\alpha u_\alpha - \frac{K}{nk_B}\partial_\alpha\partial_\alpha\theta\right)},$$

where $K = \frac{5}{2}\frac{\overline{n}k_B^2\overline{T}\tau}{m}$ is the thermal conductivity. As a sanity check, if $u_\alpha = 0$ (so the fluid is at rest), we have

$$\partial_t\theta \propto \partial_\alpha\partial_\alpha\theta,$$

which is the **heat (or diffusion) equation**! Since θ is the deviation in temperature, what we're saying is that **heat is transported through diffusion** in our gas. And the heat diffusion constant is the thermal conductivity, divided by the heat capacity $\frac{3}{2}nk_B$ of the gas, which is indeed what we expect.

So we want to take these three boxed equations, which are linear coupled differential equations with constant coefficients, and we can solve them with a Fourier transform like we did before. For clarification, this means that we want to look for solutions of the form

$$\nu(\vec{q}, t) = e^{i(\vec{k}\cdot\vec{q}-\omega t)}\tilde{\nu}(\vec{k}, \omega),$$
$$u_\alpha(\vec{q}, t) = e^{i(\vec{k}\cdot\vec{q}-\omega t)}\tilde{u}_\alpha(\vec{k}, \omega),$$
$$\theta(\vec{q}, t) = e^{i(\vec{k}\cdot\vec{q}-\omega t)}\tilde{\theta}(\vec{k}, \omega),$$

and the $\tilde{\theta}$s are the Fourier coefficients. Plugging these in, each time-derivative multiplies the function by $-i\omega$, and each space-derivative along α brings a factor of ik_α. So derivatives just give us multiplication, and the original differential equations will reduce to a set of coupled ordinary linear equations for the quantities $\tilde{\nu}, \tilde{u}_\alpha$, and $\tilde{\theta}$, which is a linear algebra eigenvalue problem. What we end up with is (remembering that the parts of the matrix with indices are in block form)

$$\omega \begin{bmatrix} \tilde{\nu} \\ \tilde{u}_\alpha \\ \tilde{\theta} \end{bmatrix} = \begin{bmatrix} 0 & \overline{n} k_\beta & 0 \\ \frac{k_B \overline{T}}{m\overline{n}} \delta_{\alpha\beta} k_\beta & \frac{-i\mu}{m\overline{n}} \left(k^2 \delta_{\alpha\beta} + \frac{k_\alpha k_\beta}{3} \right) & \frac{k_B}{m} \delta_{\alpha\beta} k_\beta \\ 0 & \frac{2}{3} \overline{T} k_\beta & \frac{-2iKk^2}{3k_B \overline{n}} \end{bmatrix} \begin{bmatrix} \tilde{\nu} \\ \tilde{u}_\alpha \\ \tilde{\theta} \end{bmatrix},$$

and now we look for the eigenvalues of this 5×5 matrix, which tell us how the mode frequencies have been modified now that we have a better solution to the Boltzmann equation. Recall that in our first attempt, the terms proportional to K and μ did not exist, and we had three zero-frequency modes. But the viscosity should take away the two shear modes that we found, and the last zero-frequency mode, the "entropy mode," originally had density and temperature vary in a way so that there was no pressure anywhere – that won't happen anymore, either.

We could find values of ω by brute force, but let's make our lives a bit easier: if we consider a transverse mode with $\vec{k} \cdot \vec{u}_T = 0$, which were initially the shear modes with zero frequency, the middle part of the matrix is no longer zero, and what we end up with is a frequency

$$\omega_T = -\frac{i\mu}{m\overline{n}} k^2.$$

This is a pure imaginary eigenvalue, and if we plug that in to the $e^{-i\omega t}$ component of our solutions, we find that

$$u_T(\vec{q}, t) \propto e^{i(\vec{k} \cdot \vec{q})} e^{-\mu k^2 t/(m\overline{n})}.$$

So we end up with an **exponential decay of this mode**, meaning that its amplitude decays to zero: this mode is damped over a characteristic time

$$\tau_{\text{transverse}}(k) \sim \frac{m\overline{n}}{\mu k^2} \sim \frac{m\overline{n}}{\mu} \lambda^2,$$

where λ is the wavelength of the mode. So any flow pattern with velocity modulated in a transverse direction must decay to zero, and that's indeed what we want if the system should relax back to equilibrium.

For the remaining modes, we have $\vec{u}$ parallel to $\vec{k}$ (since we've dealt with the transverse modes already), meaning we can write $\vec{u} = \hat{k} u_\ell$. We can now simplify our equation to (now we have a 3×3 matrix, because we only consider a single scalar $\tilde{u}_\ell$)

$$\omega \begin{bmatrix} \tilde{\nu} \\ \tilde{u}_\ell \\ \tilde{\theta} \end{bmatrix} = \begin{bmatrix} 0 & \overline{n} k & 0 \\ \frac{k_B \overline{T} k}{m\overline{n}} & \frac{-4i\mu k^2}{3m\overline{n}} & \frac{k_B k}{m} \\ 0 & \frac{2}{3} \overline{T} k & \frac{-2iKk^2}{3k_B \overline{n}} \end{bmatrix} \begin{bmatrix} \tilde{\nu} \\ \tilde{u}_\ell \\ \tilde{\theta} \end{bmatrix},$$

and because we're working only to linear order in τ, we can simplify our life some more – we have three remaining modes which had frequencies $(0, v_\ell k, -v_\ell k)$ in the zeroth order equation, and we expect that they will all pick up a negative imaginary component: $(\omega_e^{(1)}(k), v_\ell k - i\gamma, -v_\ell k - i\gamma)$. Note that the determinant of the matrix above is easy to calculate – it's $\frac{2i}{3} \frac{K \overline{T} k^4}{m\overline{n}}$ – and that also needs to be the product of the three eigenvalues. So

$$(\omega_e^{(1)}(k))(-v_\ell^2 k^2 - \gamma^2) \approx (\omega_e^{(1)}(k))(-v_\ell^2 k^2)$$

to linear order in τ, because each of the modifications γ and $\omega_e^{(1)}$ are small. Therefore, we can solve to find

$$\omega_e^{(1)}(k) = -i \left(\frac{2Kk^2}{5k_B \overline{n}} \right),$$

and thus the (originally zero-frequency) entropy mode is getting damped as well. We can finish by noting that the trace is the sum of the eigenvalues: thus

$$\omega_e^{(1)}(k) + v_\ell k - i\gamma - v_\ell k - i\gamma = -i \left(\frac{4\mu k^2}{3m\overline{n}} + \frac{2Kk^2}{3k_B \overline{n}} \right),$$

and the $v_\ell k$ terms cancel on the left and we can plug in the $\omega_e^{(1)}(k)$ value. This finally gives us

$$\gamma = k^2\left(\frac{2\mu}{3m\overline{n}} + \frac{2K}{15k_B\overline{n}}\right).$$

At the end of the day, what matters is that all of our modes get damped, and in fact the damping rate is proportional to k^2. Thus, long-wavelength disturbances of the medium take a long time to relax, but they will still eventually do so. Indeed, τ_{eq}, the equilibration time, is then much larger than τ (as we mentioned several lectures ago)! So we've described the approach to equilibrium in some detail, using these linearized hydrodynamic equations.

Fact 154

Effects like turbulence (in fluid dynamics) are not coming up in our analysis here, because everything's being done to first order. If we want to apply this to a liquid, we have to show that these equations are more general than their original context, and that depends on the microscopic behavior.

And in general, there are different adequate approximations that come up for different timescales – the full microscopic picture, the Boltzmann transport equation, hydrodynamics, and so on. It's impossible to try to solve everything exactly, but we can make appropriate assumptions to make the calculations feasible for us.

29 November 6, 2020 (Recitation)

We'll have a general discussion of length and time scales in the context of first order hydrodynamics today, and then we'll think about Wick's theorem some more if we have time.

As always, we're starting with the Boltzmann equation

$$\mathcal{L}[f] = \left(\partial_t + \frac{p_\alpha}{m}\partial_\alpha + F_\alpha\frac{\partial}{\partial p_\alpha}\right) f = C[f,f],$$

where we calculated the collision term using the molecular chaos assumption. A quick recap of what we did with this: this equation is still too hard to solve in its current state, so we wrote $f = f^{(0)} + g = f^{(0)}(1+\tilde{g})$, where $C[f^{(0)}, f^{(0)}] = 0$ (basically $f^{(0)}$ is equilibrium) and $\tilde{g} = \frac{g}{f^{(0)}}$. Then we find that

$$\mathcal{L}[f^{(0)}]+\mathcal{L}[g] = \int d^3p_1 d\Omega\, \sigma(\Omega)\frac{|p-p_1|}{m}\left(f^{(0)}(p_2)f^{(0)}(p_3)(1+\tilde{g}(p_2))(1+\tilde{g}(p_3)) - f^{(0)}(p)f^{(0)}(p_1)(1+\tilde{g}(p))(1+\tilde{g}(p_1))\right)$$

(writing in terms of $\tilde{g}$ is nice because that makes things factor out), and now we also know that $f^{(0)}(p_2)f^{(0)}(p_3) = f^{(0)}(p)f^{(0)}(p_1)$, because $C[f^{(0)}, f^{(0)}] = 0$ tells us that $\frac{dH}{dt} = 0$, and that forced us to have $\ln f^{(0)}(p_0) + \ln f^{(0)}(p_1) = \ln f^{(0)}(p_2) + \ln f^{(0)}(p_3)$. This enables us to rewrite

$$\mathcal{L}[f^{(0)}] + \mathcal{L}[g] = \int d^3p_1 d\Omega\, \sigma(\Omega)\frac{|p-p_1|}{m} f^{(0)}(p)f^{(0)}(p_1)\left((1+\tilde{g}(p_2))(1+\tilde{g}(p_3)) - (1+\tilde{g}(p))(1+\tilde{g}(p_1))\right),$$

and then expanding and writing this to first order in $\tilde{g}$ gives us

$$= \int d^3p_1 d\Omega\, \sigma(\Omega)\frac{|p-p_1|}{m} f^{(0)}(p)f^{(0)}(p_1)\left(\tilde{g}(p_2)+\tilde{g}(p_3)-\tilde{g}(p)-\tilde{g}(p_1)\right) + O(\tilde{g}^2),$$

which we define in terms of a new operator C_L as

$$= f^{(0)}(p)C_L[\tilde{g}] + O(\tilde{g}^2).$$

Example 155

Let's quickly shift gears and develop a helpful mathematical principle: if we have an equation like $ax = B(x^2-4)$, we can think of our solution as a perturbation $x = x_0 + \varepsilon$, where $B(x_0^2-4) = 0$ is the solution if we ignore the left side of the equation.

Plugging this in gives us

$$\frac{a}{B}x_0 + \frac{a}{B}\varepsilon = 2x_0\varepsilon + \varepsilon^2 \implies \varepsilon\left(2x_0 - \frac{a}{B} + \varepsilon\right) = \frac{a}{B}x_0.$$

But if $\frac{a}{B}$ is small, then ε should be small along with it, and it's consistent for us to say that $\varepsilon = \frac{1}{2}\frac{a}{B} + O\left(\frac{a}{B}\right)^2$.

So returning to our original question, we have a linear operator on the left side, $\mathcal{L}[f] + \mathcal{L}[g]$, which is "pretty small." So we want to know when it's self-consistent to make the linear approximation

$$\boxed{\mathcal{L}[f^{(0)}] = f^{(0)}C_L[\tilde{g}]},$$

and this is true (the equivalent of checking whether $\frac{a}{B}$ is small) if the following conditions hold:

- The magnitude of our external force must be much less than $\frac{p}{\tau_x}$, where τ_x is the characteristic time of our operator. ($\frac{p}{\tau_x}$ is the typical amount of force that our particles are experiencing, because every mean collision time, we'll get our momentum changed on the order of p.)
- We need $\frac{\partial_\alpha f}{f} \ll \frac{1}{v\tau_x} \sim \frac{1}{\ell_x}$, where ℓ_x is the mean free path for the particles. (In other words, the differences in f at different regions must be not noticeable by a traveling particle, compared to the influences of collisions it experiences as it travels between those two regions.)
- Finally, we need $\frac{\partial_t f}{f} \ll \frac{1}{\tau_x}$, which is a similar idea as the one above.

The first and second conditions are true if we set up our initial conditions properly, and the variations in f can be caused either by initial conditions or external forces. But if everything is small (and we have long-wavelength fluctuations), waiting a bit will make the collision terms get rid of fast fluctuations. Combined with the fact that g is small, and that means that $C[f, f]$ is small, we find that the solution form we've presented is self-consistent! Here's one way to think about this: a perturbation to our system that is very large or rapidly varying might cause the different terms here to have large influences. But if our initial conditions aren't large and our force does not have a huge impact, our deviations will behave properly.

Example 156

For illustration, let's think about our previous problem set and consider a force $\vec{F} = \vec{E}_0 e^{i\omega t + i\vec{k}\cdot\vec{q}}$. Recall that we approximate our collision term as $-\frac{f - f_{\text{eq}}}{\tau}$ (this is the time for electrons bouncing off impurities, rather than scattering off each other).

Now we have

$$\mathcal{L}[f_{\text{eq}}] + \mathcal{L}[g] = -\frac{g}{\tau},$$

because the equilibrium f_{eq} has collision term zero under our relaxation-time approximation. But notice that the approximation

$$f^{(0)}C_L(\tilde{g}) = -f^{(0)}\frac{\tilde{g}}{\tau} = -\frac{g}{\tau}$$

is essentially approximating the parenthetical $(\tilde{g}(p_2) + \tilde{g}(p_3) - \tilde{g}(p) - \tilde{g}(p_1))$ term from earlier in our calculation as **only having** the $-\tilde{g}(p)$ term, and also making other assumptions about how the rest of the integrand's p-dependence looks. There are plenty of corrections that are actually added for what's going on at other momenta, and we're essentially treating the other terms on average as "not doing anything" because we integrate over them. (Basically, "scattering is a pretty random process," so effects from other p_is don't do anything to p.) And we're also assuming that all τs that show up in this equation are the same, which is physically unlikely when looking over different values of $\vec{p}$.

So returning to our example, it's not important that $\mathcal{L}[g]$ itself is small relative to $\mathcal{L}[f]$ – we just need to be able to do a **self-consistent order-by-order expansion** with it, and that requires $\tilde{g}$ to be small relative to f and also $\mathcal{L}[f_{\text{eq}}] \ll \frac{1}{\tau}$ (meaning the electric field is much smaller than $\frac{p}{\tau}$, which will typically hold). Expanding gives us (to first order, noting that g is the same order as E_α)

$$\partial_t g + \frac{p_\alpha}{m}\partial_\alpha g + E_\alpha \frac{\partial}{\partial p_\alpha} f_{\text{eq}} = -\frac{g}{\tau}.$$

And now if $\omega\tau \ll 1$, and $|k|v\tau \sim |k|\ell \ll 1$ (meaning that the electron has gone through many collisions before the electron reaches an electric field with a different spatial or temporal dependence), the **first two terms here on the left side will be negligible**. (For something like a metal at room temperature, we have $\tau \approx 10^{-14}$ s and $\ell \approx 10$ nm.) And then we get a direct proportion relating g to the electric field, and the problem can be solved from there.

Looking further down the derivation, if we write down the hydrodynamic equations

$$\begin{aligned} D_t n &= -n\partial_\alpha u_\alpha, \\ mD_t u_\alpha &= F_\alpha - \frac{1}{n}\partial_\beta P_{\alpha\beta} \\ D_t \varepsilon &= \frac{1}{n}P_{\alpha\beta}u_{\alpha\beta} - \frac{1}{n}\partial_\alpha h_\alpha, \end{aligned}$$

we're taking the equation $\mathcal{L}[f] = C[f, f]$ and integrating (averaging) over the local momenta. We then need to learn what $P_{\alpha\beta}$ and h_α values are – as written, they can depend on a complicated distribution, but this is where we "coarse-grain" over the small τ_x: we do an expansion so that we can write $P_{\alpha\beta}$ and h_α in terms of conserved-quantities. And we do this with another order-by-order expansion: we can write $P_{\alpha\beta}, h_\alpha, \varepsilon$ as functions of $\vec{u}$, n, and T, which give us five differential equations for five variables. And for the first order case, we use $\mathcal{L}[f^{(0)}] = -\frac{g}{\tau_x}$, and note that there is no correction to $\vec{u}, n, \varepsilon$ in this first-order approximation, because we derived these equations from the equation $0 = \int d^3p\mathcal{L}[f]\chi(p)$ (the collision-conserved quantities can't change along the flow lines). So we must have

$$\int d^3p g(p)\chi(p) = -\tau \int d^3p \mathcal{L}[f^{(0)}]\chi(p) = 0,$$

with the last equality true because we're writing $\mathcal{L}[f^{(0)}] = C[f^{(0)} + g, f^{(0)} + g]$ and evaluating that to first order. There's a lot to keep track of, but what's important to take away is the overall logic!

Finally, we'll talk a bit about Wick's theorem: suppose we need to compute an average value

$$\langle c_{\alpha_1} \cdots c_{\alpha_{2n}} \rangle_0,$$

where each c_α is an iid centered Gaussian drawn from a fixed distribution, and the O indicates average over that Gaussian. Then the only nonzero cumulants are the first and second order cumulants (the mean and variance), so if the means are zero, we only care about **contributions from the variance**. Thus, we want to do a cumulant expansion, which is the set of different ways to pair up the c_is:

$$= \langle c_{\alpha_1} c_{\alpha_2} \rangle \langle c_{\alpha_3} c_{\alpha_4} \rangle \cdots + \text{(other permutations)},$$

noting that $\langle c_\alpha c_\beta \rangle$ is isotropic (meaning it'll be $A\delta_{\alpha\beta}$ for some A, depending on the variance).

For example, calculating

$$\langle c_\alpha c_\beta c_\gamma c_\delta \rangle_0$$

will have two factors of A because we have two pairs, and then we just do all of the pairings:

$$= A^2(\delta_{\alpha\beta}\delta_{\gamma\delta} + \delta_{\alpha\gamma}\delta_{\beta\gamma} + \delta_{\alpha\delta}\delta_{\beta\gamma}).$$

In our derivation of first-order hydrodynamics, this comes up because we often integrate an observable $\mathcal{O}$ and get an equation the form

$$\int dx \frac{e^{-x^2/2}}{\sqrt{2\pi}}(1 + \tilde{g}(x))\tilde{O},$$

and we can integrate $\tilde{O}$ (which can usually be written in terms of the c_αs) **with respect to the Gaussian**:

$$= \langle \tilde{O} \rangle_0 + \langle \tilde{O}\tilde{g} \rangle_0.$$

And since $\tilde{O}$ often looks like $c^2 c_\alpha$ or $c_\alpha c_\beta$, we can use Wick's theorem directly in this way.

30 November 9, 2020

Because of Veterans Day, we won't have class on Wednesday. And by popular demand, the due date for our problem set this week is extended to Thursday at noon. (There are some special rules this year for Thanksgiving week, which will affect future problem set logistics too – we'll hear more information about that and our upcoming quiz soon.)

Today, we'll start a new topic. Now that we've finished with kinetic theory (which essentially served to provide a more useful description by approximating statistical mechanics at longer timescales), we'll begin discussing **quantum ideal gases**, starting with the ideal Bose gas.

Fact 157

Some of us may not have taken quantum mechanics before, and the most important thing is that (especially since we've come this far in a graduate physics class) **quantum physics is important for us to learn if we haven't done so already**. The rest of the class can probably be followed without knowing quantum mechanics, but it'll be a lot easier to appreciate conclusions with the relevant background.

One of the fundamental reasons for this topic is that as the temperature of a gas decreases, Boltzmann statistics becomes increasingly inapplicable, and we need to be more careful about **indistinguishability of particles** and its effect on the structure of our Hilbert space. When we're working in three dimensions, there are two general types of behavior for identical particles under exchange:

- **Bosons**, for which the quantum wavefunction is **symmetric** under exchange, so for particles at positions x_1, x_2,

$$\psi(x_1, x_2) = \psi(x_2, x_1),$$

- **Fermions**, for which the quantum wavefunction is **antisymmetric** under exchange, meaning

$$\psi(x_1, x_2) = -\psi(x_2, x_1).$$

We're always going to be interested in a large system of identical particles, and throughout this course, we'll only deal with systems where those particles are noninteracting. (Interactions between qantum mechanical particles are discussed in 8.513 and 8.514, which are the quantum many-body physics classes.) If we have such a set of non-interacting identical quantum particles, we can let the single-particle eigenstates be denoted $|r\rangle$, and a many-body eigenstate written as $|r_1, r_2, \cdots, r_N\rangle$. Naively, the wavefunction looks like a superposition of states of the form $\psi_{r_1}\psi_{r_2}\cdots\psi_{r_N}$ (which are products of the single-particle wavefunctions), but we can specialize in the case of bosons and fermions. For bosons, we're only able to consider the subspace of states which are symmetric under permutations, and for fermions, we only consider the subspace which is antisymmetric under those permutations. And we can state that in another way as follows:

Proposition 158

If we have a system of bosons, then any number of particles can occupy any given single-particle state. But if we have a system of fermions, any single-particle state can only be occupied at most once.

Basically, if we antisymmetrize a wavefunction where two particles have the same single-particle wavefunction, then the subsequent exchange will make everything cancel out, and we won't have a valid wavefunction at all. And this is exactly what we might hear in atomic physics as the **Pauli exclusion principle**.

Now, if we want to specify the eigenstates for our many-body system, we can index them as $(n_1, n_2, \cdots)$, where n_r is the occupation number for the single-particle state $|r\rangle$. (For example, if there are 100 single-particle states, and there are 10 particles, we can ask how many particles are in the state $|1\rangle$ and $|2\rangle$ and so on, up to $|100\rangle$.) This is equivalent to providing the eigenstate of every individual particle, but it is easier to use the n_i notation for thermodynamic description later on. So we have the constraint

$$\sum_r n_r = N = \text{total number of particles.}$$

For bosons, the only additional constraint is that $n_r \geq 0$ for each r, but for fermions, we also need that $n_r \leq 1$ (each state $|r\rangle$ can only have 0 or 1 particles). If we let ε_r be the energy of the single-particle state $|r\rangle$, then we can also write down the canonical partition function

$$Z = \sum_{\{n_1, n_2, \cdots\}} e^{-\beta \sum_r n_r \varepsilon_r},$$

with the constraint $\sum_r n_r = N$ over the big sum. It turns out that it's often easier to calculate with the grand partition function, fixing the chemical potential instead and then working with the grand free energy to get what we want. Specifically, we just need to be able to handle the sum

$$\boxed{Z_G = \sum_{\{n_1, n_2, \cdots\}} e^{-\beta \sum_r n_r(\varepsilon_r - \mu)}},$$

this time with no additional constraint on the big sum (except the $n_r \leq 1$ constraint in the fermion case), and now our problem is completely well-defined – the difficulty now comes in the mathematics.

In the **ideal Bose gas** (meaning we have bosons), since each n_i can be any nonnegative integer, we can do the sums independently over each n_r, so we can factor this sum as

$$Z_G = \prod_r \left(\sum_{n_r=0}^{\infty} e^{-\beta n_r(\varepsilon_r - \mu)} \right).$$

Each term here is an infinite geometric series

$$1 + e^{-\beta(\varepsilon_r - \mu)} + e^{-2\beta(\varepsilon_r - \mu)} + \cdots = \frac{1}{1 - e^{-\beta(\varepsilon_r - \mu)}},$$

and thus we have our answer in the Bose gas case:

$$Z_G = \prod_r \frac{1}{1 - e^{-\beta(\varepsilon_r - \mu)}} = e^{-\beta g},$$

where g is the grand free energy. Taking the log tells us that

$$\boxed{g = k_B T \sum_r \ln(1 - e^{-\beta(\varepsilon_r - \mu)}}\,,$$

so if we can evaluate this sum over single-particle states, we'll have our final answer for the grand free energy.

Example 159

Consider a gas of such bosons confined to a large box of volume V (and no external potential acting on the system).

We know that each single-particle state here can be labeled by the momentum $\vec{p}$, so

$$g = k_B T \sum_{\vec{p}} \ln(1 - e^{-\beta(\vec{p}^2/(2m) - \mu)}).$$

More specifically, if the box is $L \times L \times L$, we know that

$$\vec{p} = \frac{2\pi\hbar}{L}(m_x, m_y, m_z),$$

with m_x, m_y, m_z all integers. Since we'll end up taking the thermodynamic limit $L \to \infty$, keeping the ratio $\frac{N}{L^3}$ fixed as always, this is the real sum that we want to evaluate, and because the spacing $\frac{2\pi\hbar}{L}$ goes to 0 in this limit, we can proceed by turning this into an integral (this should sound familiar to us!). Then we find that

$$g = k_B T V \int \frac{d^3 p}{(2\pi\hbar)^3} \ln\left(1 - e^{-\beta(\vec{p}^2/(2m) - \mu)}\right),$$

and now thermodynamic quantities can come out of derivatives of this free energy.

Definition 160

From here on, $\bar{d}^3 p$ will denote $\frac{d^3 p}{(2\pi\hbar)^3}$.

We can find the density of the gas

$$\rho = \frac{\langle N \rangle}{V} = -\frac{1}{V}\frac{\partial g}{\partial \mu},$$

which we can do by bringing the derivative into the integral, yielding

$$\rho = \int \bar{d}^3 p \frac{e^{-\beta p^2/2m} e^{\beta\mu}}{1 - e^{-\beta p^2/2m} e^{\beta\mu}}.$$

This is some function of T and μ, as we expect, and in order to evaluate this integral, we'll set $z = e^{\beta\mu}$ and perform the change of variables $x^2 = \frac{\beta p^2}{2m}$, leaving us with

$$\rho = \frac{4\pi}{(2\pi\hbar)^3}(2mk_B T)^{3/2} \int_0^\infty dx \frac{x^2 z e^{-x^2}}{1 - z e^{-x^2}},$$

where the 4π comes from the angular integrals when we switch to spherical coordinates (and now we're left with the radial integral, which is why the bounds have changed).

Definition 161

The **thermal de Broglie wavelength** is defined through the equation

$$\frac{\hbar^2}{2m\lambda_T^2} = k_B T \implies \lambda_T^2 = \frac{\hbar^2}{2mk_B T}.$$

Physically, the motivation for this is that particles with a thermal energy $k_B T = \frac{p_{\text{typical}}^2}{2m}$ gives an uncertainty in position given by $\frac{\hbar}{p_{\text{typical}}}$. (Our definition might be off by a factor of π from other ones.) Then we find that

$$\rho\lambda_T^3 = \frac{1}{2\pi^2}\int_0^\infty dx \frac{x^2 z e^{-x^2}}{1 - ze^{-x^2}},$$

and now we can't evaluate this integral in terms of elementary functions, but we can do so with some special ones. Expanding the denominator gives us

$$= \frac{1}{2\pi^2}\int_0^\infty dx\, x^2 z e^{-x^2}(1 + ze^{-x^2} + z^2 e^{-2x^2} + \cdots),$$

which rewrites to

$$= \frac{1}{2\pi^2}\int_0^\infty dx\, x^2 \sum_{n=1}^\infty z^n e^{-x^2 n}.$$

We now just have Gaussian integrals weighted by an x^2 factor, and evaluating those one at a time gives us

$$= \frac{1}{8\pi^{3/2}}\sum_{n=1}^\infty \frac{z^n}{n^{3/2}}.$$

This can be written in terms of the function

$$\zeta_{3/2}(z) = \sum_{n=1}^\infty \frac{z^n}{n^{3/2}},$$

and we get our answer for the particle density (remembering that $z = e^{\beta\mu}$)

$$\boxed{\rho\lambda_T^3 = \frac{1}{8\pi^{3/2}}\zeta_{3/2}(z)}.$$

Next time, we'll use another series expansion to calculate the average energy, which will be a different zeta function. We'll then be able to take the resulting expressions to get some interesting physics!

31 November 13, 2020 (Recitation)

We'll start by finishing the story of kinetic theory and hydrodynamics from last time, and then we'll discuss separation of scales and begin a review of density matrices.

Recall that for any collision-conserved quantity χ, we have

$$\int d^3p C[f,f]\chi(p) = 0.$$

Furthermore, if f satisfies the Boltzmann equation $\mathcal{L}[f] = C[f,f]$, then we also have $\int d^3p\mathcal{L}[f]\chi(p) = 0$, and this is what gives us the hydrodynamic equations. For example, setting $\chi = 1$ gives us

$$D_t u_\alpha = -n\partial_t u_\alpha,$$

setting $\chi = p$ gives us

$$mD_t u_\alpha = F_\alpha - \frac{1}{n}\partial_\beta P_{\alpha\beta},$$

and setting $\chi = \frac{p^2}{2m}$ gives us

$$D_t \varepsilon = -\frac{1}{n}P_{\alpha\beta}u_{\alpha\beta} - \frac{1}{n}\partial_\alpha h_\alpha.$$

These are exact equations, but we can make a first-order approximation and assuming $\mathcal{L}[f^{(0)}] = C[f^{(1)}, f^{(1)}]$ (which is only true to first order). Then we have $\int d^3p\mathcal{L}[f^{(0)}]\chi(p) = 0$, and this gives us **zeroth order hydrodynamics** (because all of the equations are in terms of $f^{(0)}$).

Next, we can say that $\mathcal{L}[f^{(1)}] = C[f^{(2)}, f^{(2)}]$ to second order, and thus $\int d^3p\mathcal{L}f^{(1)}]\chi(p) = 0$. This then gives us first order hydrodynamics, and our perturbation from $f^{(0)}$) will be of order $\frac{\tau_x}{\tau_u^2}$, where τ_u is the timescale of $\mathcal{L}$ (the rate of relaxation to global equilibrium), and τ_x is the mean collision time. (Alternatively, $\frac{g}{f^{(0)}}$ is of order $\frac{\tau_x}{\tau_u}$.)

Remark 162. *Here, $f^{(0)}$ satisfies the hydrodynamic equations to zeroth order, so $C[f^{(0)}, f^{(0)}] = 0$. Then we define $f^{(1)} = f^{(0)} + g$ (when solved to first order), to get the next-order solution, through the equation $\mathcal{L}[f^{(0)}] = C[f^{(1)}, f^{(1)}]$ (which holds to first order). The next-order correction is then defined through $\mathcal{L}[f^{(1)}] = C[f^{(2)}, f^{(2)}]$ (which holds to second order), and so on – this iterative order-by-order calculation is basically how perturbation theory works.*

Let's now look at the Navier-Stokes equation, which comes from the first-order hydrodynamic equation with relaxation time approximation: because $f^{(1)}) = f^{(0)} - \tau\mathcal{L}[f^{(0)}]$, we basically take

$$\int d^3p\mathcal{L}[f^{(0)} - \tau\mathcal{L}[f^{(0)}]]\chi(p) = 0,$$

and we replace τ with certain effective parameters μ, K. (We don't actually need the assumptions of the Boltzmann equation – we can derive this with conservation laws directly, too.) And we might ask why the Navier-Stokes equation is always considered close to exact – why do we never ask for the second-order expansion? It turns out $\frac{\tau_x}{\tau_u}$ is really small – the order of the mean free path, versus the order of probing the system, gives us a huge gap, and we're not interested in the small-scale details.

Then the natural followup is why first order matters to us – why not stay at zeroth order? The answer here is that we need to compare timescales to each other, and we know that all of our frequencies have zero imaginary part in the zeroth order hydrodynamic equations. So our timescales for oscillation don't have any decay timescales – no modes decay to equilibrium – so even though $\frac{\tau_x}{\tau_u^2}$ is small compared to other timescales, it's still large compared to 0, and it still qualitatively changes the system. Remember that the damping rate is on the order of $\mathcal{L}[f^{(0)}]$, which is proportional to $\tau_x v^2 k^2$, where k is the wave number for our modes. This can then be rewritten as $\rho\mu k^2$, where μ is the viscosity, and thus if our variations are long wavelength enough, our damping rate is very small.

And this kind of logic means, for example, that studies of material properties versus atomic physics versus quantum field theory don't need to be considered with each other, because they're dealing with different time scales. This separation of scales is part of what makes physics work!

Fact 163

In the kinetic theory of gases, if there's no scale between τ_x and τ_u, we shouldn't expect any behavior to happen between those two scales, unless it happens at all scales. But this idea comes up in other situations too.

Similarly, if we look at the distribution of the sizes of cities, there is no particular scale – it follows a power law, and no particular population is picked out. (The only scales here are the smallest number of people needed to fill a settlement, and the maximum number of people on Earth.) This gives rise to a "fractal" behavior, which we can also see in the shape of coastlines.

The idea of **turbulence** in fluid physics also comes up in wealth distribution and education, because lots of inefficiencies from the large to small scale gives us a dissipative system. (If financial flows came in at a small scale at the service level, there would be less chance for turbulence to occur.) Returning back to kinetic theory, a large μ gives us less turbulence, but $\mu = 0$ also gives us no turbulence! So perturbations will break down completely – small nonzero values of μ give us turbulent behavior, but $\mu = 0$ gives us zeroth order hydrodynamics. Usually, averages in thermodynamics will work, but turbulence will not give us a normal distribution where we can average out small-scale behavior.

In the remaining time, we'll start a discussion of density matrices:

Definition 164

A **density matrix** is given by a sum over quantum states

$$\rho(t) = \sum_\alpha p_\alpha \left|\psi_\alpha\right\rangle \left\langle\psi_\alpha\right|,$$

where p_α is the probability of being in the state α and the ψ_α states are normalized.

These objects come up if we have, for example, an entangled set of particles and we only look at part of that system. (So for example, a particle might be in a spin-up state with probability $\frac{1}{2}$, or a spin-down state with probability $\frac{1}{2}$, and density matrices can encode this information.) We can think about how this changes over time, and we can do this by first applying a product rule to

$$\boxed{i\hbar\partial_t\rho} = \sum_\alpha p_\alpha(i\hbar\partial_t \left|\psi_\alpha\right\rangle \left\langle\psi_\alpha\right| + \left|\psi_\alpha\right\rangle i\hbar\partial_t \left\langle\psi_\alpha\right|,$$

and then this can be written as

$$= \sum_\alpha p_\alpha(H\left|\psi_\alpha\right\rangle \left\langle\psi_\alpha\right| - \left|\psi_\alpha\right\rangle \left\langle\psi_\alpha\right| H) = H\rho - \rho H = \boxed{[H, \rho]}$$

because H is Hermitian on kets, so it is anti-Hermitian on bras. This might look similar to the classical $\partial_t\rho = \{H, \rho\}$, and it's sometimes thought of as an analog of "Liouville's theorem," but **there is no conservation of phase space in quantum mechanics** – in quantum mechanics, we just have a set of states, and momentum and position are useful ways to describe a state, but they're not the only way to do so.

We can then think about the expectation value of an operator relative to this density matrix, and this is just the linear combination

$$\langle\hat{O}\rangle = \sum_\alpha p_\alpha \left\langle\psi_\alpha\middle|\hat{O}\middle|\psi_\alpha\right\rangle = \operatorname{tr}\left[\hat{O}\sum_\alpha p_\alpha \left|\psi_\alpha\right\rangle\left\langle\psi_\alpha\right|\right],$$

which can also be written as

$$= \operatorname{tr}[\hat{O}\rho] = \operatorname{tr}[\rho\hat{O}],$$

which is a sum over a complete orthonormal set of states

$$= \sum_n \left\langle n\middle|\rho\hat{O}\middle|n\right\rangle.$$

(In contrast, the classical version would be

$$\langle\hat{O}\rangle = \int \frac{d^{3N}p\, d^{3N}q}{h^{3N}}\rho\hat{O},$$

where ρ was the classical density of states in $6N$-dimensional phase space.) If we think about the trace of just the density matrix, we find that

$$\operatorname{tr}(\rho) = \sum_{n,\alpha} p_\alpha \langle n|\psi_\alpha\rangle \langle \psi_\alpha|n\rangle = \sum_\alpha p_\alpha \sum_n |\langle n|\psi_\alpha\rangle|^2 = \sum_\alpha p_\alpha = 1.$$

This density matrix is also Hermitian (just by plugging into the definition) and positive semidefinite (no negative eigenvalues). We'll explore some more properties next time.

32 November 16, 2020

Our third quiz will be on Wednesday, with the same procedures (take-home, 24 hours to submit) as the first two, covering the kinetic theory of gases. Also, our next problem set will be due the Wednesday after Thanksgiving, since there are no classes during the break. Because no homework can be due beyond December 4 (since this class has a final exam), this will likely be the last assignment that is officially due. A ninth problem set will be posted, covering subject matter for the final exam, and it is recommended but not counted in our grade. (And our final exam isn't allowed to be take-home by MIT laws, meaning that it will be timed over a 3-hour period. For those of us in different time zones, there will be an alternate accommodation.)

We'll continue discussing the ideal Bose gas today, looking at Bose-Einstein condensation. Recall from last class that we have the equation

$$\rho\lambda_T^3 = \frac{1}{8\pi^{3/2}}\zeta_{3/2}(z),$$

where ρ is the density of the gas, $\lambda_T = \sqrt{\frac{\hbar}{2mk_BT}}$ is a characteristic length, $z = e^{\beta\mu}$ (where μ is the chemical potential), and the $\zeta_{3/2}$ function is defined through the power series

$$\zeta_{3/2}(z) = \sum_{n=1}^{\infty} \frac{z^n}{n^{3/2}}.$$

Definition 165

The functions $\zeta_m(z)$ are defined via

$$\zeta_m(z) = \sum_{n=1}^{\infty} \frac{z^n}{n^m}.$$

(These are also known in mathematics as the **polylogarithm functions**, denoted $\mathrm{Li}_m(z)$.)

Our next step is to calculate the average energy of the system, which is given by

$$\langle E\rangle = \frac{1}{Z_G}\sum_{\{n_i\}}\left(\sum_r n_r\varepsilon_r\right)e^{-\beta\sum_i n_i(\varepsilon_i-\mu)} = \frac{\partial}{\partial\beta}(\beta g) + \mu\langle N\rangle.$$

Doing some calculations simplifies this to

$$= V\int \bar{d}^3p\,\frac{p^2}{2m}\,\frac{1}{e^{\beta(p^2/2m-\mu)}-1},$$

where $\bar{d}^3p = \frac{d^3p}{(2\pi\hbar)^3}$, and this should make physical sense because this fraction, known as the **Bose factor**, is the energy associated with a particular momentum. We can further write this as

$$= V\int \bar{d}^3p\,\frac{p^2}{2m}\,\frac{1}{z^{-1}e^{\beta p^2/2m}-1} = \frac{4\pi}{(2\pi\hbar)^3}V\int_0^\infty dp\,\frac{p^4}{2m}\,\frac{1}{z^{-1}e^{\beta p^2/2m}-1},$$

where we've switched to spherical coordinates and done the angular integrals. Now if we make a change of variables and let $x^2 = \frac{\beta p^2}{2m}$, we find that (this way we can factor out the temperature dependence as much as possible)

$$\langle E \rangle = \frac{(k_B T)(4\pi V)(2mk_B T)^{3/2}}{(2\pi\hbar)^3} \int_0^\infty dx \frac{x^4 ze^{-x^2}}{1 - ze^{-x^2}}.$$

(So now the only dependence of this integral on the temperature is in the z.) At this point, we can do the integral by a power series:

$$= \frac{Vk_B T}{4\pi^2 \lambda_T^3} \int_0^\infty dx x^4 \sum_{n=1}^\infty z^n e^{-nx^2},$$

and now we can do each Gaussian integral weighted by an x^4 to find

$$\boxed{\langle E \rangle = \frac{V}{8\pi^2 \lambda_T^3} \left(\frac{3}{2} k_B T \right) \sqrt{\pi} \zeta_{5/2}(z)}.$$

Dividing this expression by the one for density ρ that we derived earlier, we find that

$$\frac{E}{V} = \frac{3}{2} k_B T \rho \frac{\zeta_{5/2}(z)}{\zeta_{3/2}(z)}.$$

We can analyze this in some limiting cases:

- If $\rho\lambda_T^3 \ll 1$, and λ_T is inversely proportional to $\sqrt{T}$, this means we're looking at the high-temperature or low-density limit. We expect that the statistics of the particles should not matter in this limit (we should get a classical result). Notice that $\zeta_{3/2}(z) \ll 1$ in this limit, because we found earlier that $\rho \propto \zeta_{3/2}(z)$, and that means that $z \ll 1$. Given this, we also learn that $\zeta_{3/2}(z) \approx \zeta_{5/2}(z)$ (the higher-order terms don't contribute much to either expression). Therefore we have

  $$\frac{E}{V} = \frac{3}{2} k_B T \rho,$$

  which is the usual classical ideal gas result. (And notice also that this means $e^{\beta\mu} \ll 1$, so μ must be large and negative. But that's something we already knew this from studying the classical ideal gas.)

- Because $\rho\lambda_T^3 \propto \zeta_{3/2}(z)$, which is a monotonically increasing function of z, we must have z increase as $\rho\lambda_T^3$ increases. So the value of $z = e^{\beta\mu}$ is determined by solving the equation

  $$\rho\lambda_T^3 = \frac{1}{8\pi^{3/2}} \zeta_{3/2}(z),$$

  and in order to do that more explicitly (which we avoided having to do in the high-temperature limit), let's understand the structure of this $\zeta_{3/2}$ function. The function starts off linear for small z, but when we hit $z > 1$, the series starts to diverge (and for $z \gg 1$ this series will diverge), and thus it is finite and increasing for $0 < z \le 1$ but divergent for $z > 1$ (for example, by the ratio test on successive terms of the infinite series). Thus, we can find a solution for z as long as

  $$8\pi^{3/2} \rho\lambda_T^3 \le \zeta_{3/2}(1) \approx 2.612.$$

  In other words, there's a critical temperature T_c, obtained by solving the equation above:

  $$k_B T_c \ge \left(\frac{8\pi^{3/2}}{\zeta_{3/2}(1)} \left(\frac{\hbar^2}{2m} \right)^{3/2} \rho \right)^{2/3} = \frac{2\pi\hbar^2}{m} \left(\frac{\rho}{\zeta_{3/2}(1)} \right)^{2/3},$$

  and everything we're saying here only makes sense above this temperature $T = T_c$. But it's natural to think about what happens to the physics of the Bose gas as our temperature falls below this critical value – if we have this phase transition, where in our calculations did we go wrong?

- To get more insight into that, we can consider the other extreme temperature of $T = 0$. Then all of the bosons occupy the single ground state with zero momentum, and we have macroscopic occupation of a single quantum state. So if we raise the temperature by only a little bit, it makes sense that we'll have a macroscopically large occupation (that is, a **finite fraction** of our total N particles) in the ground state. Recall that in our derivation of the grand free energy g, we replaced our sum over states in Z_G with an integral, and the only place we could have gone wrong is in converting that sum to an integral. Indeed, if there is this macroscopically large occupation of the zero-momentum state, our sum-to-integral approximation cannot be valid.

So we're going to go back to our discrete sum for the grand free energy

$$g = \frac{1}{\beta} \sum_{\vec{p}} \ln\left(1 - e^{-\beta p^2/2m} e^{\beta\mu}\right) = \frac{1}{\beta} \sum_{r} \ln\left(1 - e^{-\beta(\varepsilon_r - \mu)}\right),$$

where our labeling over r is a sum over particular single-particle quantum states (that is, particular momenta $\vec{p}$). We know that the average occupation of a quantum state r is

$$\langle n_r \rangle = \frac{1}{Z_G} \sum_{\{n_i\}} n_r e^{-\beta \sum_i (\varepsilon_i - \mu) n_i},$$

which we obtain by differentiating with respect to ε_r:

$$= -\frac{1}{\beta Z_G} \frac{\partial Z_G}{\partial \varepsilon_r} = -\frac{1}{\beta} \frac{\partial}{\partial \varepsilon_r} \ln Z_G = \frac{\partial g}{\partial \varepsilon_r}.$$

So if we use the above discrete sum expression for g, we find that

$$\boxed{\langle n_r \rangle = \frac{1}{e^{\beta(\varepsilon_r - \mu)} - 1}}.$$

Since the left hand side is some nonnegative value, we must have $\varepsilon_r - \mu \geq 0$ for all r, but if we apply this on the ground state, we find that

$$\mu \leq \varepsilon_0 = 0$$

when our energy is $\varepsilon = \frac{p^2}{2m}$ – thus, **the chemical potential of the ideal Bose gas is negative for free particles with this dispersion**. Notice, though, that if μ is very close to 0, we can expand in a power series to find that

$$\langle n_0 \rangle = \frac{1}{e^{-\beta\mu - 1}} \approx \frac{1}{1 - \beta\mu - 1} = -\frac{k_B T}{\mu}.$$

This tells us that

$$\mu = -\frac{k_B T}{\langle n_0 \rangle},$$

and if $\langle n_0 \rangle$ is macroscopic – proportional to V – we have $\mu \propto \frac{1}{V}$, which goes to 0 as the system size grows. So the situation where macroscopic occupation occurs is one where our chemical potential is sufficiently small (relative to the system size).

We can now look at behavior for excited states, and to find the energy of the first excited state, we know that energy is proportional to p^2, and the momentum spacing is proportional to $\frac{1}{L}$. So the energy spacing is of order $\frac{1}{L^2} = \frac{1}{V^{2/3}}$ – more specifically,

$$\varepsilon_1 \sim \frac{\hbar^2}{2mL^2}.$$

Therefore,

$$\frac{\varepsilon_1}{|\mu|} \propto \frac{1/V^{2/3}}{1/V} = V^{1/3},$$

which goes to infinity as our system size increases. That means that we can ignore the μ contribution in our occupation number in the following expression:

$$\langle n_1 \rangle = \frac{1}{e^{\beta(\varepsilon_1 - \mu)} - 1} \approx \frac{1}{e^{\beta\varepsilon_1} - 1},$$

and similarly for all other excited states n_r. In other words, if we ask about the mean number of particles at any particular non-ground state, it's going to be a finite number – not on the order of the total particle number N, and thus **only the ground state is macroscopically occupied**. A way to explain this is that our "excess density is dumped into the ground state:" if we have any extra density beyond $8\pi^{3/2}\rho\lambda_T^3 = \zeta_{3/2}(1)$, then it all goes into the ground state, and this is exactly the behavior of **Bose-Einstein condensation** occurring for temperatures $T < T_c$.

Fact 166

Even if this huge jump in occupation number from n_1 to n_0 seems surprising mathematically, Bose-Einstein condensation does happen physically – for example, there are labs in Building 26 at MIT that create this environment on a daily basis!

With our new understanding, we can now understand how to calculate the number of particles N: since only the ground state has a huge occupation,

$$\langle N \rangle = \sum_r \langle n_r \rangle = \langle n_0 \rangle + V \int \bar{d}^3 p \frac{1}{e^{\beta \vec{p}^2/2m} - 1},$$

where we've also incorporated the fact that we must have $\mu = 0$ to see this condensation behavior. And we've already calculated this integral, and evaluation gives us

$$\boxed{\rho = \frac{\langle n_0 \rangle}{V} + \frac{1}{8\pi^{3/2}\lambda_T^3}\zeta_{3/2}(1)},$$

and this ground-state density term "soaks up" all of the extra particles we have beyond the critical temperature T_c.

Remark 167. *If we replace our box with a harmonic potential and cool down the gas until it Bose condenses, releasing the gas will give us a Gaussian wavefunction in momentum space from the macroscopic occupation of the ground state. So the velocity distribution should be Gaussian, and releasing the potential means that we'll see the particles spread out in a velocity distribution like we expect! But the technological feats required to make this happen in a real lab are incredible.*

33 November 18, 2020

We talked about the low-temperature phase of the Bose gas last time, and we saw that there is a macroscopic occupation of a single quantum state (the one at zero momentum). We then derived an expression for the density **at low temperature**, which can be rearranged for writing things in terms of the occupation number:

$$\rho = \frac{\langle n_0 \rangle}{V} + \frac{1}{8\pi^{3/2}\lambda_T^3}\zeta_{3/2}(1) \implies \langle n_0 \rangle = (8\pi^{3/2}\rho\lambda_T^3 - \zeta_{3/2}(1))\frac{V}{8\pi^{3/2}}(\lambda_T^3).$$

Remembering that we defined the critical temperature T_c last time, and plugging in its value tells us that

$$\langle n_0 \rangle = V\left(\rho - \rho\left(\frac{T}{T_c}\right)^{3/2}\right) \implies \frac{\langle n_0 \rangle}{V} = \rho\left(1 - \left(\frac{T}{T_c}\right)^{3/2}\right).$$

So $\langle n_0 \rangle$ is indeed proportional to V as promised, and furthermore, once the temperature goes below the critical temperature T_c, we start getting a nonnegative fraction of occupation of the ground state. And as $T \to 0$ and $T \to T_c$, we do indeed get $\langle n_0 \rangle \to \rho V = N$ and $\langle n_0 \rangle \to 0$ respectively, which is also the behavior that we expect from yesterday's discussion. (Our Bose gas is not classical immediately once we cross $T = T_c$, though: as we discussed last time, the condition is $\rho\lambda_T^3 \ll 1$.)

Remember that the macroscopic occupation of the single-particle ground state here is called **Bose-Einstein condensation**, and we'll do another calculation related to this phenomenon, calculating the total energy at $T < T_c$. Because particles in the ground state all have zero energy, the only energy contribution comes from the occupation of the excited states, and we already saw that the contribution from all nonzero momenta can be safely approximated as an integral (we don't have macroscopic occupation at any energy other than the ground state energy). The chemical potential μ is 0 in a Bose-Einstein condensate, so $z = 1$ in our previous result tells us that

$$\frac{E\lambda_T^3}{V} = \frac{1}{8\pi^{3/2}}\left(\frac{3}{2}k_B T\right)\zeta_{5/2}(1).$$

Therefore, the energy per particle is (again plugging in results from the previous lecture)

$$\frac{E}{V} = \frac{3}{2}k_B T\left(\frac{N - N_0}{V}\right)\frac{\zeta_{5/2}(1)}{\zeta_{3/2}(1)}.$$

(This is in contrast to the $\frac{E}{V} = \left(\frac{3}{2}k_B T\rho\right)\frac{\zeta_{5/2}(z)}{\zeta_{3/2}(z)}$ that we previously had for $T > T_c$: the changes are that we now set $z = 1$, and the density ρ is replaced with the density of the **uncondensed** particles. Using the value of $\langle n_0 \rangle$ we derived earlier on in class, which tells us that a fraction $\left(\frac{T}{T_c}\right)^{3/2}$ of the particles are uncondensed, we have

$$\boxed{\frac{E}{V} = \frac{3}{2}k_B T\frac{N}{V}\left(\frac{T}{T_c}\right)^{3/2}\frac{\zeta_{5/2}(1)}{\zeta_{3/2}(1)}}.$$

This lets us compute the heat capacity, which scales as

$$C_V = \frac{\partial E}{\partial T} \sim T^{3/2}$$

in the regime $T < T_c$, while for $T \gg T_c$, the heat capacity should be $\frac{3}{2}Nk_B$, matching the classical case. So plotting $\frac{C_v}{N}$ will give us $T^{3/2}$ growth at first, but then we actually have a kink in the derivative at $T = T_c$. It turns out the heat capacity actually increases above $\frac{3}{2}k_B$ at low temperatures (for non-interacting particles), and then at the phase transition $T = T_c$, C_V is continuous but not differentiable, and then the value relaxes back down towards $\frac{3}{2}k_B$.

Fact 168

Phase transitions are often hard to understand, and 8.334 discusses a lot of the theoretical technology needed for understanding them. In most settings where we have to worry about interactions between the different degrees of freedom, we usually require sophisticated analysis to understand what happens.

So the ideal gas is amazing in that we can actually analyze the phase transition in an elementary way, and somehow the identity of particles enforces long-range knowledge of particles on other particles because of the symmetry! We'll see how the Fermi gas exhibits even more spectacular behavior than the Bose gas after Thanksgiving break.

Example 169

Variants of this phenomenon have been observed in a lab – for example, a weakly interacting Bose gas, for instance Helium-4, does undergo a condensation.

Helium becomes a liquid when we cool it under constant pressure at 4 Kelvin, and at around 2 Kelvin, we get a phase transition that is closely related to the Bose condensation. We find that as $T \to 0$, we do have a macroscopic occupation, but there is a depletion of the condensate due to repulsive interactions. (And at ambient pressure for Helium-4, the fraction of particles that are condensed is only about 10 percent.)

On the other hand, when we cool Helium-3 below 2 Kelvin, it just stays a liquid. Helium-3 does undergo a transition into a low-temperature phase when we cool it further, but it only happens at milliKelvin temperatures. And the fact that Helium-3 and Helium-4 are fermions and bosons, respectively, means that the statistics of fermions and bosons do lead to completely different physics! We're encouraged to look up the physics of **superfluids** to learn more as well.

That's all we'll say about Bose-Einstein condensation for now, and now let's talk about **blackbody radiation** (which was one of the reasons statistical mechanics came up in the first place), which is the electromagnetic radiation occurring in thermal equilibrium (that is, the equilibrium of a gas of photons).

Photons are essentially non-interacting, so a photon gas can be treated as an ideal gas. (If we include quantum electrodynamics corrections, there are weak interactions between photons, but unless the electric fields are very high, these nonlinear modifications can be ignored.) In addition, they are bosons, so a lot of the calculations we've been doing will still apply.

Example 170

Consider electromagnetic radiation in a large cavity, where the radiation reaches equilibrium through absorption and emission of photons by the atoms in the walls of the cavity.

A key point about this photon gas is that the number of total photons is not conserved because of this absorption and emission – instead, N is determined by conditions of thermal equilibrium. Most textbooks make the following statement:

Fact 171

If we have a fixed temperature T and volume V for the cavity, the thermal equilibrium state is the one with the minimum free energy F. And we know that $\left(\frac{\partial F}{\partial N}\right)_{T,V} = 0$ at equilibrium, so $\mu = 0$ for the photon gas.

What this means is that we can take our generic formulas for a Bose gas and just set $\mu = 0$, but the main point is really that N is not a fixed constant independent of the other thermodynamic quantities. Regardless, we know that the occupation of a particular single-particle state with energy $\varepsilon_k = \hbar c|\vec{k}|$ is

$$\langle n_k \rangle = \frac{1}{e^{\beta\varepsilon_k - 1}} = \frac{1}{e^{\beta\hbar c k} - 1}.$$

(Remember that we label states of a photon by their momentum – the wavenumber of the photon – and the polarization of the photon. But for any fixed polarization and k vector, we get a single state, and the occupation is then given by this standard formula.) We're often instead interested in the **total number** of photons within some momentum region, though, and then we need to include the polarization factor of 2, too.

So the number of photons in a range $d^3p = \hbar^3 d^3k$ around some momentum $\vec{p}$ is

$$dN_k = 2V \frac{d^3p}{(2\pi\hbar)^3} n_k,$$

where the $V\frac{d^3p}{(2\pi\hbar)^3}$ is the standard phase space factor. Since n_k only depends on the modulus of $\vec{k}$, we can then switch to spherical coordinates and do the angular integrals to find that

$$\int d\Omega dN_k = 2V\frac{4\pi}{(2\pi)^3}|\vec{k}|^2 d|\vec{k}|\frac{1}{e^{\beta\hbar c|\vec{k}|}-1},$$

This can then be converted to a frequency distribution: in the frequency range $[\omega, \omega + d\omega]$, the number of photons satisfies

$$dN_\omega = V\frac{8\pi}{8\pi^3}\frac{d\omega}{c^3}\frac{\omega^2}{e^{\beta\hbar\omega}-1} = \frac{V}{\pi^2 c^3}d\omega\frac{\omega^2}{e^{\beta\hbar\omega}-1},$$

and the energy stored in this frequency range is

$$\boxed{dE_\omega = \hbar\omega dN_\omega = \frac{V\hbar}{\pi^2 c^3}\frac{\omega^3 d\omega}{e^{\beta\hbar\omega}-1}}.$$

This is the **Planck blackbody law**, and we've derived it from the ideal Bose gas! Plotting $\frac{1}{V}\frac{dE_\omega}{d\omega}$ as a function of ω, we find that at low frequencies (meaning $\hbar\omega \ll k_B T$), we can expand $e^{\beta\hbar\omega} \approx 1 + \beta\hbar\omega$ and find that

$$dE_\omega \approx \frac{V}{\pi^2 c^3}k_B T\omega^2 d\omega,$$

and this answer is actually known in **classical** electrodynamics – it's known as the **Rayleigh-Jeans formula**, and notice that the $\hbar$ doesn't even appear here – the derivation of this result can be obtained from equipartition. But the other limit is the interesting one: when $\hbar\omega \gg k_B T$, we find that the exponential in the denominator dominates the -1, and thus

$$dE_\omega \approx \left(\frac{V\hbar\omega^3}{\pi^2 c^3}d\omega\right)e^{-\beta\hbar\omega},$$

which means emission is strongly suppressed at high frequencies due to the exponential decay! The maximum of the distribution can therefore found in the regime $\hbar\omega \sim k_B T$, and this should sound similar to previous discussions we've had with low and high-temperature limits and how quantum mechanics plays a role.

Finally, we can calculate the total energy

$$E = \int d\omega\frac{dE_\omega}{d\omega} = \frac{V\hbar}{\pi^2 c^3}\int_0^\infty d\omega\frac{\omega^3}{e^{\beta\hbar\omega}-1}.$$

We can obtain the temperature-dependence by scaling it out of this integral: if we set $z = \frac{\hbar\omega}{k_B T}$, then we find that

$$E = \left(\frac{V\hbar}{\pi^2 c^3}\right)\left(\frac{k_B T}{\hbar}\right)^4\int_0^\infty dx\frac{x^3}{e^x - 1}.$$

The integral turns out to have the value $\frac{\pi^4}{15}$, so we end up with

$$\boxed{E = \frac{V\pi^2}{15}\frac{(k_B T)^4}{(\hbar c)^3}},$$

and this T^4-dependence is characteristic of many three-dimensional systems. (Intuitively, the phase space volume has three powers of the momentum, and momentum is proportional to energy for a massless particle. And then we get another factor of $k_B T$ from the energy of the particles.)

34 November 20, 2020 (Recitation)

We'll continue our discussion of density matrices today, looking at entanglement. Recall that a density matrix is defined as a sum over a set of quantum states

$$\rho = \sum_\alpha p_\alpha \left|\psi_\alpha\right\rangle \left\langle\psi_\alpha\right|$$

(which is an operator), and we can define the expectation values of some other operator relative to the density matrix via

$$\langle \tilde{O} | = \rangle \sum_\alpha p_\alpha \left\langle \psi_\alpha \middle| \hat{O} \middle| \psi_\alpha \right\rangle ,$$

and if we insert a complete set of states, this can be written as

$$= \sum_{\alpha,n} p_\alpha \left\langle \psi_\alpha \middle| \hat{O} \middle| n \right\rangle \left\langle n | \psi_\alpha \right\rangle = \sum_n \left\langle n \middle| \rho\tilde{O} \middle| n \right\rangle = \text{tr}[\rho\tilde{O}].$$

We found also that

$$i\hbar\partial_t \rho = [H, \rho],$$

meaning that equilibrium occurs if and only if $[H, \rho] = 0$, and then the equilibrium density matrix can only be written in terms of things that commute with H (including H itself).

- If we look at the microcanonical ensemble, our density matrix looks like

  $$\rho(E) = \frac{1}{\Omega(E)} \delta(\hat{H} - E).$$

  To figure out what this means, it's helpful to go to a specific basis, and we can do that by using an orthonormal energy eigenbasis. (We can define the delta function of a Hermitian operator by defining it on energy eigenstates

  $$\delta(\hat{H}) \left|m\right\rangle = \delta(Em) \left|m\right\rangle ,$$

  and then extending to the rest of the space from there.) So now we have

  $$\langle n|\rho|m\rangle = \frac{1}{\Omega} \left\langle n \middle| \delta(\hat{H} - E) \middle| m \right\rangle = \frac{1}{\Omega} \left\langle n \middle| \delta(\hat{H} - E) \middle| m \right\rangle ,$$

  and now we can evaluate the operator on the ket to write this as

  $$= \frac{1}{\Omega} \langle n|\delta(E_m - E)|m\rangle = \frac{1}{\Omega} \delta(E_m - E)\delta_{mn}.$$

  Because $\text{tr}\rho = 1$, we must have

  $$1 = \sum_n \langle n|\rho|n\rangle = \sum_n \frac{1}{\Omega} \delta(E_n - E),$$

  which means that

  $$\Omega = \sum_n \delta(E_n - E),$$

  and we've found our definition for the normalization factor.

- In the canonical ensemble, we now know that the overall system (our system plus the bath) is defined by the microcanonical ensemble $\rho = \frac{1}{\Omega}\delta(\hat{H} - E_T)$ for the total energy E_T. To get a description of just the system, we'll want to look at operators of the (tensor product) form $\hat{O} = 1_B \otimes \hat{O}_S$ which do nothing to the bath, and then

$$\text{tr}[\rho\tilde{O}] = \sum_{n_S, n_B} \left\langle n_S, n_B \middle| \rho 1_B \otimes \hat{O}_S \middle| n_S, n_B \right\rangle,$$

where we have to label over both the system and the bath. But now we can separate out this sum because the bath states have no interaction with the $\hat{O}_S$, and then do a sum (partial trace) over all bath states using the function $\text{tr}_B[A] = \sum_{n_B} \langle n_B | A | n_B \rangle$:

$$= \sum_{n_S} \left\langle n_S \middle| \text{tr}_B[\rho]\tilde{O}_S \middle| n_S \right\rangle = \text{tr}_S[\text{tr}_B[\rho]\tilde{O}_S].$$

Thus, it makes sense to define the density matrix of the system via

$$\boxed{\rho_S = \text{tr}_B[\rho]}$$

so that expectations of operators behave as we want: $\text{tr}[\rho\hat{O}] = \text{tr}[\rho_S \hat{O}_S]$ for operators $\hat{O}$ of the separable form, meaning that we can indeed disregard the bath's effects. So now

$$\rho_S = \sum_{n_B} \left\langle n_B \middle| \frac{1}{\Omega} \delta(\hat{H} - E_T) \middle| n_B \right\rangle,$$

which in the thermodynamic limit becomes

$$\approx \sum_{n_B} \left\langle n_B \middle| \frac{1}{\Omega} \delta(\hat{H}_S + \hat{H}_B - E_T) \middle| n_B \right\rangle.$$

(We know that it is not exactly true that $\hat{H}_S + \hat{H}_B = \hat{H}$ because there are interactions between the system and the bath, but we assume those are weak.) So now we can write this as

$$\frac{1}{\Omega} \sum_{n_B} \delta(\hat{E}_B - (E_T - \hat{H}_S)),$$

using that $\hat{H}_B$ can be replaced with an energy eigenvalue because it's acting on the energy eigenstate n_B. And notice that this is

$$= \frac{1}{\Omega} \Omega_B(E_T - \hat{H}_S),$$

and now by the same arguments that we made about sharply-peaked energy near the beginning of class, this can be written as

$$= \frac{1}{\Omega} e^{S_B(E_T - \hat{H}_S} = \frac{1}{Z} e^{-\beta \hat{H}_S}$$

by linearly expanding the entropy term and putting the constant term in the normalization constant Z. And again, if we take a trace over the system states, we should get 1 for this density matrix ρ_S, so

$$1 = \text{tr}_S \left[\frac{1}{Z} e^{-\beta \hat{H}_S} \right] \implies Z = \text{tr}_S e^{-\beta \hat{H}_S} = \sum_{n_S} e^{-\beta E_S},$$

which is what we expect. Notice that we ended up with a probability distribution which helps us write down the density matrix:

$$\langle n_S | \rho_S | m_S \rangle = \frac{1}{Z} e^{-\beta E_{n_S}} \delta_{m_S n_S} \implies \rho_S = \sum_{n_S} p_{n_S} |n_S\rangle \langle n_S|$$

And even if there's only a particular state overall with a given energy, the derivation here still goes through! Even if the combined system is in a precise (pure) state, the tracing can still give us a probabilistic density matrix.

Example 172

Suppose that our Hamiltonian is $H_1 = \frac{\vec{p}^2}{2m}$, and our system is constrained to a box of volume V. Use eigenstates

$$H_1 \left|\vec{k}\right\rangle = \frac{\hbar^2 k^2}{2m} \left|\vec{k}\right\rangle.$$

We have

$$\left\langle \vec{x} \middle| \vec{k} \right\rangle = \frac{e^{-\vec{k}\cdot\vec{x}}}{\sqrt{V}},$$

so that the plane wave is equally likely to be at any point, and then the partition function is

$$Z_1 = \mathrm{tr}\rho = \sum_{\vec{k}} e^{-\beta\hbar^2 k^2/(2m)} = V \int \text{đ}^3 k\, e^{-\beta\hbar^2 k^2/(2m)} = \frac{V}{\lambda^3},$$

where λ is the de Broglie wavelength. To get a sense now of what the density matrix means, we can look at the matrix units in the position basis by expanding the expression for ρ over $\vec{k}$-states, and we find that because we have an energy eigenbasis,

$$\rho = \frac{1}{Z_1} \sum_{\vec{k}} \left|\vec{k}\right\rangle \left\langle \vec{k}\right| e^{-\beta\hbar^2 k^2/(2m)},$$

which means

$$\langle \vec{x}' | \rho | \vec{x} \rangle = \sum_{\vec{k}} \left\langle \vec{x}' \middle| \vec{k} \right\rangle \left\langle \vec{k} \middle| \vec{x} \right\rangle \frac{1}{Z_1} e^{-\beta\hbar^2 k^2/(2m)}.$$

We can then write this as an integral:

$$= \frac{\lambda^3}{V} V \int \text{đ}^3 k\, \frac{e^{i\vec{k}\cdot(\vec{x}'-\vec{x})}}{V} e^{-\beta\hbar^2 k^2/(2m)},$$

which is a Gaussian integral in $\vec{k}$, giving us a final answer of

$$= \frac{1}{V} \exp\left[-\frac{\pi(\vec{x}-\vec{x}')^2}{\lambda^2}\right]$$

In other words, if we look at the density matrix and the off-diagonal terms in position space, a small λ (which occurs at high temperature) gives us a Gaussian width that is also localized as long as we don't probe the system beyond that length scale. So when we look at the quantum mechanical statistics, thermal noise actually makes the system classical – the position basis almost diagonalizes the density matrix.

Remark 173. *We could also similarly calculate the grand canonical ensemble, and that also gives us the same types of expressions as classical statistical mechanics. But everything basically looks like what we might expect.*

Example 174

We can now move on to density matrices' role in entanglement: we know the corresponding density matrices for spins in the $+z, -z$ directions are $\begin{bmatrix} 1 & 0 \\ 0 & 0 \end{bmatrix}$ and $\begin{bmatrix} 0 & 0 \\ 0 & 1 \end{bmatrix}$, which tells us that (for example)

$$\rho_{\pm x} = \frac{1}{2}\begin{bmatrix} 1 & \pm 1 \\ \pm 1 & 1 \end{bmatrix}.$$

We can write down something like

$$\rho_{\text{mixed}} = \frac{1}{2}(\rho_z + \rho_{-z}) = \frac{1}{2}(\rho_{+x} + \rho_{-x}) = \begin{bmatrix} 1/2 & 0 \\ 0 & 1/2 \end{bmatrix}.$$

This is called a "fully mixed state." Now if we have two entangled spins in a particular pure state, we should note that

$$\frac{1}{\sqrt{2}}(|\uparrow\uparrow\rangle \pm |\downarrow\downarrow\rangle) \neq \frac{1}{2}(|\uparrow\rangle + |\downarrow\rangle) \otimes (|\uparrow\rangle + |\downarrow\rangle)$$

cannot be factored into two single-particle states. In fact, what we end up with is

$$\rho_\pm = \frac{1}{2}\begin{bmatrix} 1 & 0 & 0 & \pm 1 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ \pm 1 & 0 & 0 & 1 \end{bmatrix},$$

which can also be written as

$$= \boxed{\frac{1}{2}(|\uparrow\uparrow\rangle\langle\uparrow\uparrow| \pm |\uparrow\uparrow\rangle\langle\downarrow\downarrow| \pm |\downarrow\downarrow\rangle\langle\uparrow\uparrow| + |\downarrow\downarrow\rangle\langle\downarrow\downarrow|)}.$$

And now if we trace over the second particle's states (in other words, we only observe the first particle and try to describe it as a state), we can divide our 4 × 4 matrices into four 2 × 2 submatrices, and we trace over the sum of the diagonals of each of those. So

$$\text{tr}_2[\rho_2] = \frac{1}{2}\begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix}$$

(the second and third term in the boxed expression above don't contribute to our tracing because they're off-diagonal terms). So as soon as we've cut off part of our system, we go from a pure state to something that looks random!

So now if we consider a third spin, suppose that we started off with one of the two states

$$|\psi_\pm\rangle = \frac{1}{\sqrt{2}}(|\uparrow\uparrow\uparrow\rangle \pm |\downarrow\downarrow\downarrow\rangle.$$

Then if we do some calculations, we'll find that

$$\text{tr}_3[\rho_\pm] = \frac{1}{2}(|\uparrow\uparrow\rangle\langle\uparrow\uparrow|) + |\downarrow\downarrow\rangle\langle\downarrow\downarrow|)$$

So what's interesting is that complex phases go away when we add this third spin from our environment: the ± doesn't change the value of $\text{tr}_3[\rho_\pm]$. And very roughly, if the third spin is "us" looking at the particle, and the second spin is the measurement device, our consciousness not being able to observe all of the quantum details means that we have to "trace over" our observer's uncertainty, and that creates the randomness.

35 November 30, 2020

We've now gotten our quizzes back – many of us did well overall, though there were many comments about the quiz being too long. So we'll make a few remarks here – the first problem was relatively basic material, but the second problem was designed to have the basic physics and the main equations to write down given to us. So the idea was to analyze the consequences of the equations using the methods we've learned in the past few weeks of the course – many of us were able to make substantial progress, but what was required was an ability to put together different aspects of physics, which comes from experience and "physics maturity."

Our final is a 3-hour (**cumulative, open book**) timed exam, and the questions will be a lot shorter than the ones on the quizzes, but they will cover a broader range of topics. The format of a take-home exam makes it so that many people keep working on the quiz until everything is solved, within the allotted 24 hours, and a timed exam will be different in that regard. (An announcement will be posted on Canvas, and policies for makeup exams because of time zones will also be posted.) There will be a Zoom room open during the exam where we can ask questions as well.

As a final note, there will likely be a slight extension for this week's problem set (announcement to be posted).

Today's class will focus on an application of the statistical mechanics of bosons to the **specific heat of solids**.

Fact 175

The calculation that we're doing today was first done in 1905 by Einstein (who did a lot of things in that year, including the photoelectric effect, special relativity, and Brownian motion), and this particular idea was important because it showed that quantum mechanics needed to be applied to the physics of a solid. Since then, this idea has developed into a field of the quantum mechanical theory of solids!

Example 176

Suppose we have a crystalline solid, where the atoms are arranged into a lattice. We want to calculate the contribution to the solid's specific heat from **small vibrational motion** about the atom's equilibrium position.

At any nonzero temperature, we know that atoms will vibrate about their mean positions, and that thermal motion gives rise to some entropy and thus an associated heat capacity. Here, we'll consider a simple treatment of the dynamics, where we begin with the Hamiltonian

$$H = \sum_{i=1}^{N} \frac{\vec{p}_i^2}{2m} + V(\{\vec{q}_i\}),$$

where V is an inter-atomic interaction potential. We'll assume that the equilibrium crystalline structure is found by minimizing the potential energy term $V(\{\vec{q}_i\})$, and the resulting periodic (**three-dimensional**) lattice points can be labeled with three basis vectors $\hat{a}, \hat{b}, \hat{c}$, so that any point of the (equilibrium) lattice is an integer combination

$$\vec{r} = \ell\hat{a} + m\hat{b} + n\hat{c},$$

with $\ell, m, n \in \mathbb{Z}$. Then the position of the atom at the site $\vec{r}$ will be given by

$$\vec{q}(\vec{r}) = \vec{r} + \vec{u}(\vec{r}),$$

where $\vec{u}(\vec{r})$ is the oscillation of this particular atom. If V^* is the minimum potential energy (at the equilibrium lattice state), a Taylor expansion tells us that our new potential energy due to this oscillation is (summing over all indices α, β)

$$V = V^* + \frac{1}{2} \sum_{\vec{r},\vec{r}',\alpha,\beta} \frac{\partial^2 V}{\partial q_{\vec{r}_\alpha} \partial q_{\vec{r}'_\beta}} u_\alpha(\vec{r}) u_\beta(\vec{r}') + O(u^3).$$

Here, each u represents a displacement from a given site $\vec{r}$ or $\vec{r}'$ – this approximation is good in the low-temperature limit – and we'll drop the V^* from here on because it is just a constant. We can ask for a more specific criterion for when this approximation is valid, and the point is that we just want to ensure that the u's are small (one way to say this is that **we need to be able to identify each particle with its corresponding lattice site**). But it turns out that the conclusions that we'll end up reaching are still valid about the equilibrium state, though not necessarily the ground state, as long as our temperature is below the melting point of the solid.

Fact 177

We're also assuming that the temperature is low enough for electronic degrees of freedom to be ignored, and this is true if we have an insulator.

So now we have our Hamiltonian

$$H = \sum_{\vec r} \frac{\vec p_{r}^{\,2}}{2m} + \frac{1}{2} \sum_{\vec r, \vec r', \alpha, \beta} \frac{\partial^2 V}{\partial q_{\vec r_\alpha} \partial q_{\vec r'_\beta}} u_\alpha(\vec r) u_\beta(\vec r'),$$

which describes the oscillations around the sites (that's why we sum over the sites r here). From here on, we'll denote $K_{\alpha\beta}(\vec r, \vec r') = \frac{\partial^2 V}{\partial q_{\vec r_\alpha} \partial q_{\vec r'_\beta}}$. Note that translational symmetry tells us that the interaction between atoms

$$K_{\alpha\beta}(\vec r, \vec r') = K_{\alpha\beta}(\vec r - \vec r')$$

only depends on the relative displacement vector between the atoms, not where in the crystal we're looking. And this is a **system of coupled harmonic oscillators**, which we typically solve using **normal modes**. But this problem can first be simplified because we have a translational symmetry in our system, which will help us decouple the differential equations and go to Fourier transformed variables. The idea is to have our Fourier transform over a discrete set: we write

$$u_\alpha(\vec r) = \frac{1}{\sqrt{N}} \sum_{\vec k} e^{i \vec k \cdot \vec r} \tilde u_\alpha(\vec k),$$

where N is the total number of lattice points in our lattice.

Proposition 178

Here, the $\vec k$ vectors can only live in a finite range, called the **Brillouin zone**.

To explain what's going on here, if we consider a cubic lattice with spacing a, meaning

$$\vec r a(\ell \hat x + m \hat y + n \hat z).$$

Notice that if we take $k_\alpha \to k_\alpha + \frac{2\pi}{a}$, then $e^{i\vec k \cdot \vec r}$ is unchanged (we add 2π to the exponent). So no new normal modes are created outside of this $\frac{2\pi}{a}$ range in each component, and thus we restrict the k_α values to the interval $\left[-\frac{\pi}{a}, \frac{\pi}{a}\right]$. (And something similar happens in a general lattice, too – the Brillouin zone is a unit cell of the reciprocal lattice, up to constant factors.)

Returning now to the potential energy, we will see the different Fourier modes decouple explicitly:

$$V = \frac{1}{2n} \sum_{\vec r, \vec r', \alpha, \beta, \vec k, \vec k'} K_{\alpha\beta}(\vec r - \vec r') e^{i(\vec k \cdot \vec r + \vec k' \cdot \vec r')} \tilde u_\alpha(\vec k) \tilde u_\beta(\vec k').$$

If we change coordinates so we use relative and center-of-mass coordinates, meaning $\vec \rho = \vec r - \vec r'$ and $\vec R = \frac{\vec r + \vec r'}{2}$, then our potential energy becomes

$$V = \frac{1}{2N} \sum_{\alpha, \beta, \vec k, \vec k'} \left(\sum_{\vec R} e^{i(\vec k + \vec k') \cdot \vec R} \right) \left(\sum_{\vec \rho} K_{\alpha\beta}(\vec \rho) e^{i(\vec k - \vec k') \cdot \vec \rho / 2} \right) \tilde u_\alpha(\vec k) \tilde u_\beta(\vec k').$$

So we've separated the sum over $\vec R$ and $\vec \rho$, and this is good because $\vec k$ doesn't depend on $\vec R$ by lattice translational symmetry! If we now sum over $\vec{R}$, we find that

$$\sum_{\vec{R}} e^{i(\vec{k}+\vec{k}')\cdot\vec{R}} = N\delta_{\vec{k}+\vec{k}',0}$$

by symmetry (these terms wind around the unit circle unless $\vec{k}+\vec{k}'$ is just 0). So now our potential energy will simplify to

$$V = \frac{1}{2}\sum_{\alpha,\beta,\vec{k}} \left[\sum_{\vec{\rho}} K_{\alpha\beta}(\vec{\rho})e^{i\vec{k}\cdot\vec{\rho}}\right] \tilde{u}_\alpha(\vec{k})\tilde{u}_\beta(-\vec{k}).$$

If we now define

$$\tilde{K}_{\alpha\beta}(\vec{k}) = \sum_{\vec{\rho}} K_{\alpha\beta}(\vec{\rho})e^{i\vec{k}\cdot\vec{\rho}}$$

to be the Fourier transform of K, then

$$V = \frac{1}{2}\sum_{\alpha,\beta,\vec{k}} \tilde{K}_{\alpha\beta}(\vec{k})\tilde{u}_\alpha(\vec{k})\tilde{u}_\beta(-\vec{k})$$

and indeed the different Fourier modes have now almost decoupled. The only remaining simplification is that because $u_\alpha(\vec{r})$ is real, we have the simple relation

$$\tilde{u}_\alpha(-\vec{k}) = \tilde{u}_\alpha(\vec{k})^*$$

between the Fourier coefficients. So the essential idea that made this all possible was the sum over $\vec{R}$ giving us a delta function condition, and this was only possible because $K_{\alpha\beta}$ only depends on the relative position between the sites.

So now the structure of the 3 by 3 matrix $\tilde{K}_{\alpha\beta}$ at each point in the Brillouin zone determines our dynamics. If there are symmetries (for example, rotational) in our crystal, that also gives us further restrictions on the matrix elements.

Example 179

For simplicity, we'll assume here that

$$\tilde{K}_{\alpha\beta}(\vec{k}) = \delta_{\alpha\beta}\tilde{K}(\vec{k})$$

is a multiple of the identity matrix. This is not completely correct, but it's good enough that we can illustrate the main points.

We can do a similar idea for the kinetic energy, writing

$$p_\alpha(\vec{r}) = \frac{1}{\sqrt{N}}\sum_{\vec{k}} e^{i\vec{k}\cdot\vec{r}}\tilde{p}_\alpha(\vec{k}).$$

Since this energy is defined on each site, we find a simpler answer for this term, and plugging in everything we have so far gives us

$$H = \sum_{\vec{k},\alpha}\left[\frac{1}{2m}|\tilde{p}_\alpha(\vec{k})|^2 + \frac{\tilde{K}(\vec{k})}{2}|\tilde{u}_\alpha(\vec{k})|^2\right].$$

This Hamiltonian then has $3N$ independent simple harmonic oscillators, indexed by wave number and component, with frequencies

$$\omega_\alpha(\vec{k}) = \sqrt{\frac{\tilde{K}(\vec{k})}{m}}.$$

Here, the $\tilde{K}(\vec{k}$ term tells us the energy term for deforming the lattice, so it's a type of **stiffness** (expected to be positive for all but 3 of the $3N$ modes, and we'll see what's going on there later). Because of these harmonic oscillators, we expect classically (from equipartition) for there to be a heat capacity of $3Nk_B$ from the lattice vibrations.

But if we plot $\frac{C}{N}$ as a function of T, we know from experiments that the actual measured value of $\frac{C}{N}$ decreases at low T to 0. So we need to treat the lattice vibrations quantum mechanically instead, just like with polyatomic molecules – modes with an energy much larger than $k_B T$ are not excited, so they can be ignored at certain temperatures. We'll see the details of that next time!

36 December 2, 2020

As mentioned in the class announcement, we should let the course staff know if the 9am Eastern final exam time is inconvenient.

We'll continue with the discussion of the specific heat of solids today. Last time, we found that we could determine the normal modes for vibrational motion of a crystalline solid in Fourier space, and we wrote down the Hamiltonian accordingly:

$$H = \sum_{\vec{k},\alpha} \left[\frac{1}{2m} |\vec{p}_\alpha(\vec{k})|^2 + \frac{\tilde{K}(\vec{k})}{2} |\tilde{u}_\alpha(\vec{k})|^2 \right],$$

where we've assumed the stiffness $\tilde{K}(\vec{k})$ comes from a diagonal matrix $\tilde{K}_{\alpha\beta}$. So then we have $3N$ independent simple harmonic oscillators with frequency $\omega_\alpha(\vec{k}) = \sqrt{\frac{\tilde{K}(\vec{k})}{m}}$, and classical statmech tells us then that the specific heat must be $3Nk_B$. But this answer is experimentally wrong, so we're looking into the details more carefully today.

In quantum statmech, we expect that the contribution to heat capacity drops once $T \lesssim \frac{\hbar\omega}{k_B}$, where ω is the oscillation frequency. We know that the quantum eigenvalues for the harmonic oscillators are labeled by integers $\{n_{\vec{k},\alpha}\}$, and

$$E(\{n_{\vec{k},\alpha}\}) = \sum_{\vec{k},\alpha} \hbar\omega_\alpha(\vec{k}) \left(n_{\vec{k},\alpha} + \frac{1}{2} \right),$$

with each $n_{\vec{k},\alpha}$ a nonnegative integer. And now the quantum statmech of a single oscillator can be repeated for any number of decoupled oscillators – the partition function is

$$Z = \sum_{\{n_k\}} e^{-\beta E(\{n_{\vec{k},\alpha}\})},$$

which can be factored in terms of the individual oscillators as

$$= \prod_{\vec{k},\alpha} \sum_{n_{\vec{k},\alpha}} e^{-\beta\hbar\omega_\alpha(\vec{k})\left(n_{\vec{k},\alpha} + \frac{1}{2}\right)}.$$

(Remember that the oscillators are distinguishable because they're corresponding to different wavenumbers, so there's no Gibbs factor here.) This can further be simplified as

$$e^{-\beta E_0} \prod_{n_{\vec{k},\alpha}} \sum_{\vec{k},\alpha} e^{-\beta\hbar\omega_\alpha(\vec{k})\left(n_{\vec{k},\alpha}\right)},$$

where $E_0 = \sum_{\vec{k},\alpha} = \frac{\hbar\omega_{\vec{k},\alpha}}{2}$ is the ground state energy (that ends up being an overall constant for the purposes that we care about right now). And now evaluating each geometric series gives us

$$Z = e^{-\beta E_0} \prod_{\vec{k},\alpha} \left[\frac{1}{1 - e^{-\beta\hbar\omega_\alpha(\vec{k})}} \right].$$

If we define $n_{k,\alpha}$ to be the occupation number of the mode $\vec{k}, \alpha$, we can find that

$$\langle n_{\vec{k},\alpha} \rangle = \frac{\sum_{n=0}^{\infty} n e^{-\beta n \hbar \omega_\alpha(\vec{k})}}{\sum_{n=0}^{\infty} e^{-\beta n \hbar \omega_\alpha(\vec{k})}} = \frac{1}{e^{\beta \hbar \omega_\alpha(\vec{k}) - 1}}.$$

This expression looks very similar to the photon occupation formula for blackbody radiation, so we can consider the quantized lattice vibrations to be particles, specifically bosons with dispersion $\omega_\alpha(\vec{k})$ (So we have quanta of the sound wave modes!) These particles are known as **phonons**, and what we're obtaining is a description of the phonons and their spectrum inside the solid.

Remark 180. *Also, the chemical potential μ for this system of phonons is 0, because the particle number is not conserved (due to defects or boundary conditions) and the energy $-\hbar\omega_\alpha(\vec{k})$ is not part of the chemical potential term.*

So now our average energy for the whole system is

$$\langle E \rangle = E_0 + \sum_{\vec{k},\alpha} \hbar \omega_\alpha(\vec{k}) \langle n_{\vec{k},\alpha} \rangle = E_0 + \sum_{\vec{k},\alpha} \frac{\hbar \omega_\alpha(\vec{k})}{e^{\beta \hbar \omega_\alpha(\vec{k}) - 1}},$$

but we need to turn this into something that's more useful or explicit. So we'll describe specific models for the dispersion $\omega_{\vec{k},\alpha}$ (this is just a different notation for $\omega_\alpha(\vec{k})$) from here to get some sense of what's really going on.

Example 181

Suppose we have the **Einstein model**, where $\omega_{\vec{k},\alpha} = \omega_E \neq 0$ for all $(\vec{k}, \alpha)$.

Then directly plugging in gives us

$$E = E_0 + \frac{3N\hbar\omega_E}{e^{\beta\hbar\omega_E} - 1},$$

and the heat capacity can then be calculated as

$$C = \frac{dE}{dT} = (3Nk_B) \left(\frac{\hbar\omega_E}{k_B T} \right)^2 \frac{e^{-\beta\hbar\omega_E}}{(1 - e^{-\beta\hbar\omega_E})^2}.$$

In the high-temperature limit $\hbar\omega_E \ll k_B T$, we indeed have $C \to Nk_B$, because we can approximate $\frac{e^{-\beta\hbar\omega_E}}{(1-e^{-\beta\hbar\omega_E})^2} \approx \frac{1}{(\beta\hbar\omega_E)^2}$ and most terms cancel out. But in the low-temperature limit, we have $k_B T \ll \hbar\omega_E$ and thus $C \to 0$, and both of these correctly reproduce experimental results. (So Einstein was willing to take quantum mechanics seriously as early as 1905!)

But notice that in the low-temperature limit, we have $C \propto e^{-\beta\hbar\omega_E}$, but in experiments we see that $C \sim T^3$ in basically every crystalline material! To resolve this discrepancy, note that the **translation symmetry** of the microscopic Hamiltonian mean that some modes will have very low energy, so the Einstein model is overdoing the decay near $T = 0$. So it must mean that the modes are not all the same frequency, and some modes have much lower ω (and thus contribute a bigger heat capacity).

wW'll therefore need to understand the translations a little bit better. It costs no energy to do a uniform translation of the whole crystal – the potential energy term $V(\{\vec{q}_i\})$ only cares about the separation between various $\vec{q}_i$s – therefore, a uniform displacement of the atoms $u_\alpha(\vec{r}) = u_\alpha^{(0)}$ of all atoms also costs no energy. A natural next conclusion is to say that if $u_\alpha(\vec{r})$ varies very slowly on the scale of lattice spacing (more precisely, we want it to vary slowly across the range of interaction), then the energy cost is also small. (In other words, if we plot the displacement u versus r, and it varies as a long-wavelength sine wave, then on the scale of the lattice spacing, u will look constant and the energy cost is low.)

With the previous discussion in mind, consider $\tilde{K}(\vec{k})$ at small $|\vec{k}|$. We know that the $\vec{k} = 0$ mode corresponds to a uniform displacement, so $\tilde{K}(0) = 0$, and this was a detail that was missed in the Einstein model! We also know that $\tilde{K}(\vec{k}) = \tilde{K}(-\vec{k})$ for our simple enough models, so we can Taylor expand

$$\tilde{K}(\vec{k}) = \tilde{K}(0) + \lambda_{\alpha\beta} k_\alpha k_\beta + O(k^4).$$

Example 182

Suppose we're looking at a simple case with a cubic symmetry, meaning that

$$\lambda_{\alpha\beta} = \lambda\delta_{\alpha\beta} \implies \tilde{K}(\vec{k}) \sim \lambda\vec{k}^2 + (\text{higher order}).$$

Then the corresponding normal mode frequencies are

$$\omega(\vec{k}) = \sqrt{\frac{\tilde{K}(\vec{k})}{m}} = v|\vec{k}|$$

for small $\vec{k}$, where $v = \sqrt{\frac{\lambda}{m}}$, and thus we have a **linear dispersion at low wavenumber!** So these are ordinary sound waves that can be described by elasticity theory. (Note that there are three polarizations for the sound wave, all with the same velocity, because the displacement can be along the x-, y-, or z-direction of our cubic crystal.

Remark 183. *It's not realistic for this to be true in a real crystal – in particular, because sound waves have two transverse and one longitudinal mode, But the transverse vibrations should be less stiff than the longitudinal ones, and because the stiffness determines sound velocity, these modes will have a lower velocity than the longitudinal ones, and that is indeed the generic situation.*

So now the average occupation of a sound mode at $(\vec{k}, \alpha)$ can be approximated as

$$\langle n_{\vec{k},\alpha} \rangle = \frac{1}{e^{\beta\hbar\omega_\alpha(\vec{k}) - 1}} \approx \frac{1}{e^{\beta\hbar v|\vec{k}| - 1}}$$

for small $|\vec{k}|$. And if we want to find the average energy at low temperature, we can just keep the contribution from sound modes with low $|\vec{k}|$, where the $\sum'$ means that we only sum over some values of $|\vec{k}|$:

$$\langle E \rangle|_{\text{low T}} \approx \text{const} + \sum_{\vec{k},\alpha}{}' \frac{\hbar v|\vec{k}|}{e^{\beta\hbar v|\vec{k}| - 1}},$$

and if we then convert the sum to an integral and switch to spherical coordinates, we find (because we pull out three factors of $\frac{L}{2\pi}$)

$$\langle E \rangle|_{\text{low T}} \approx \text{const} + \frac{(3V)(4\pi)}{8\pi^3} \int_0^{k_0} dk \frac{k^2 \hbar v k}{e^{\beta\hbar v k - 1}}.$$

This expression now depends on k_0, but the integrand dies off rapidly for $\beta\hbar v k \gg 1$ (because of the denominator). So we're actually just going to replace the upper limit by ∞, and we find that

$$\langle E \rangle|_{\text{low T}} \approx \text{const} + \frac{(3V)(4\pi)}{8\pi^3} \int_0^{\infty} dk \frac{k^2 \hbar v k}{e^{\beta\hbar v k - 1}} = \text{const} \frac{3\hbar v V}{2\pi^2} \left(\frac{k_B T}{\hbar v} \right)^4 \int_0^\infty \frac{dx\, x^3}{e^x - 1},$$

which simplifies to

$$\langle E \rangle|_{\text{low T}} \approx \text{const} + \frac{\pi^2 V}{10(\hbar v)^3} (k_B T)^4 \implies \lim_{t \to 0} C(T) = \frac{2\pi^2 V}{5(\hbar v)^3} k_B (k_B T)^3.$$

This is known as the **Debye model**, and it's a good approximation to use below the critical **Debye temperature** where

$$(\hbar v)\frac{\pi}{a} = k_B T_D$$

and a is the lattice spacing. (And when we're much larger than that temperature, we should use the classical equipartition result.)

Remark 184. *We can say more about the modes of oscillation when the ground state doesn't have the symmetry of the microscopic Hamiltonian, too (this has to do with Goldstone's theorem). Then we'll find again that there will be modes of low frequency at low wavelength.*

In the last five minutes, we'll get started on our final topic of the course, which is the **ideal Fermi gas**. In most circumstances, we deal with bosons and fermions as the two types of particle statistics, and the idea with fermions is that the many-particle wavefunction is antisymmetric under particle exchange. And there's a deep result that relates the statistics of a particle to its spin (half-integer spin versus integer spin), and nuclear matter is determined by the behavior of the protons and neutrons (so Fermi statistics does play a role there because neutrons are fermions). Since electrons are fermions as well, anything electronic also has to do with Fermi statistics. Overall, the key thing that we should remember is that **each single-particle state can be occupied by at most one particle**, which is the Pauli exclusion principle.

So each single-particle state r will have some energy ε_r, and if we consider particles with spin-1/2 but also assume single-particle energies do not depend on spin (so we'll just get lots of factors of 2), we'll want to calculate the partition function of our system. And the grand partition function

$$Z_G = \sum_{\{n_{r,\alpha}\}} e^{-\beta \sum_{r,\alpha} n_{r,\alpha}(\varepsilon_r - \mu)},$$

where α is either ↑ or ↓, and $n_{r,\alpha}$ is always either 0 or 1 by the Pauli exclusion principle. So this actually means we have (factoring through states)

$$Z_G = \prod_{r,\alpha}\left(1 + e^{-\beta(\varepsilon_r - \mu)}\right) = \prod_r \left(1 + e^{-\beta(\varepsilon_r-\mu)}\right)^2 = e^{-\beta g}.$$

And thus we've found our grand free energy already:

$$\boxed{g = -2k_B T \sum_r \ln(1 + e^{-\beta(\varepsilon_r - \mu)})}.$$

We'll continue to explore the implications of this in the next lecture!

37 December 4, 2020 (Recitation)

We'll talk today about phase transitions, which will help us discuss the Bose-Einstein condensation more clearly.

Definition 185

A **phase transition** is a discontinuity in some derivative of a thermodynamic variable.

A derivative of a thermodynamic variable is technically itself a thermodynamic variable, but most of the thermodynamic variables we've considered so far (and have explicitly named) are continuous. So the phase transitions often come up in other derivatives (for example, a discontinuity in the second derivative of energy) – what's interesting here is that thermodynamics itself looks very continuous, so it's interesting when we get sharp behavior.

Example 186

Consider a system of n classical spins $\sigma_1, \cdots, \sigma_N$, where each spin is ± 1 (but we cannot have superpositions). Then the Hamiltonian is

$$H = -\frac{J}{N}\sum_{i<j}\sigma_i\sigma_j - h\sum_i \sigma_i.$$

In other words, spins are favored to be aligned with each other, and we also have a magnetic field. We then have

$$-\beta F_n = \ln Z_n,$$

where the partition function

$$Z_N = \sum_{\{\sigma_i\}} e^{-\beta H}.$$

This is a finite sum, so it's an analytic function and thus the log of the partition function should also not have any discontinuities (meaning F_N is analytic). But if we take the limit as $N \to \infty$, we claim that the resulting function $\lim_{N\to\infty} F_N$ is not analytic, so we can't vary the parameters β, h, J in the limit.

Remark 187. *This issue with convergence in the limit can be seen if we look at the functions x^n on $[0,1]$: pointwise, these functions converge to a discontinuous function as $n \to \infty$ (it's 0 everywhere except 1 and 1 at 1), even though each x^n is analytic. And another example of this kind of behavior is $\lim_{N\to\infty} \tanh(Nx) = sgn(x)$.*

So we'll solve this model – first of all, every spin interacts with every other spin in the system, so the Hamiltonian can be written in terms of quantities that are symmetric under permutations. And what really matters in this example is how many spins are up and how many are down, so the Hamiltonian can be written in terms of the extensive quantity $M = \sum_i \sigma_i$, and we'll define $m = \frac{M}{N}$ to be an intensive version of that. Then $n_+ = \frac{1+m}{2}$ and $n_- = \frac{1-m}{2}$ are the fraction of spins that are up and down, respectively, and our Hamiltonian becomes

$$H = -\frac{J}{N} frac12 \left(\sum_{i,j}\sigma_i\sigma_j - n\right) - h\sum_i \sigma_i = -\frac{JM^2}{2N} - \frac{J}{2} - hM,$$

where the $-n$ comes from the n copies of σ_i^2 that we introduce when we changed the sum indices. We don't care about constants in the Hamiltonian, so we can write

$$H = -M\left(\frac{J}{2}m + h\right) = -Nm\left(\frac{J}{2}m + h\right).$$

The partition function can now be written as

$$\frac{\ln Z_N}{N} = \frac{1}{N}\ln\sum_{M=-N}^{N}\binom{N}{Nn_+}e^{\beta N m\left(\frac{J}{2}m+h\right)} = \frac{1}{2}\ln\sum_{M=-N}^{N}\exp\left[N\left(\beta m\left(\frac{J}{2}m+h\right) - n_+\ln n_+ - n_-\ln n_- + \cdots\right)\right]$$

by using Stirling's formula and putting everything into a common exponent. So this partition function has a term that encourages m to be large ($N\left(\beta m\left(\frac{J}{2}m+h\right)\right)$), while the entropy (combinatorial) term wants to push us back towards the middle, where $n_+ = n_-$. And this is still analytic for any finite N, but we want to see what happens in the appropriate limit. If we consider large βJ, we expect the first term to dominate, which means we have

$$\lim_{N\to\infty}\lim_{h\to 0} m(h) = 0$$

for the magnetization, because for any finite N, the system is completely symmetric as $h \to 0$. But this is not always equal to the swapped order of limits

$$\lim_{h\to 0}\lim_{N\to\infty} m(h),$$

and the key point is that **phase transitions take $N \to \infty$ first!** For small β (large temperature), this double limit is indeed 0, but once we get past $\frac{1}{\beta} = J$, we get a bifurcation – the system will be in one state with positive magnetization or another with negative magnetization $m(h)$. So as $h \to 0$, the answer depends on which of these two "branches" we took. And physically, this is **spontaneous magnetization**: cooling a magnetic material down causes it to go from being paramagnetic to ferromagnetic.

Fact 188

If we plot m as a function of h for various values of βJ, we find that for $\beta J < 1$, we have a continuous function, for $\beta J > 1$, there is a jump in the value at $h = 0$, and for $\beta J = 1$, it has infinite derivative (so is "barely" continuous).

We'll now do a bit more math to justify this result. Defining a new intensive quantity f_n, we find that

$$-\beta f_n = -\frac{\beta F_N}{N} = \frac{1}{N}\sum_{M=-N}^{N} e^{-N\beta f(m)},$$

where

$$\beta f(m) = -\beta h m - \frac{\beta J}{2}m^2 - \ln 2 + \frac{m^2}{2} + \frac{m^4}{12} + \frac{m^6}{30} + \cdots,$$

and this infinite Taylor series coming from the entropy terms is convergent for any $m < 1$. Plotting $\beta f(m)$ against m at $h = 0$ then tells us that whenever $\beta J < 1$, we have a positive m^2-coefficient, but whenever $\beta J > 1$, the quadratic term is negative while all other terms are positive. So that means we have two minima not at the origin whenever $\beta J > 1$, a stable minimum whenever $\beta J < 1$, and a very "flat" shape at exactly $\beta J = 1$. And the issue is that we do the saddle-point approximation where we only consider the minimum value of $\beta f(m)$ as $N \to \infty$, so we indeed get the desired bifurcation once the temperature gets small enough.

To find the exact points for the minima, we set $f'(m) = 0$, which means we want

$$0 = -\beta h - \beta J m + \tanh^{-1}(m).$$

So the equilibrium value of m is given by

$$m^* = \tanh(\beta J m^* + h),$$

and indeed if $h = 0$ and $\beta J < 1$, there is only the solution $m^* = 0$, but otherwise we have multiple possible solutions.

And now let's consider another solution: if we consider the Hamiltonian H_i for a single spin (here H is not the sum $\sum_i H_i$ because of double counting), we have

$$H_i = (-Jm - h)\sigma_i$$

(technically there's a small factor which is not super important because of σ_i^2). We can define $h' = Jm + h$ here to be the effective magnetic field from both the external field and the other spins, and this actually helps us find out m: the magnetization should be equal to the average spin

$$m = \langle \sigma_i \rangle = \frac{e^{\beta h'} - e^{-\beta h'}}{e^{\beta h'} + e^{-\beta h'}}$$

(because of the Boltzmann probabilities of being in states with energy 1 or -1), and this is exactly $\tanh(\beta h') = \tanh(\beta J m + \beta h)$. So we've found the above equation in another way, but we've made the same kind of saddle-point approximation that the empirical average is exactly the statistical expectation. So it's important to track our limits, but this is a well-justified calculation.

Fact 189

If we're in a lattice, people make this kind of approximation as well even if there aren't interactions between all pairs of spins, and that is well-justified in 4 or more dimensions (there are enough interactions) but not in 2 or 3. But this is something that's explored more in 8.334!

If we look at the case where $N \gg 1, \beta J > 1$, and $h \ll J$, we'll have $m \approx \pm m^*$, where m_* is given by the positive solution to $m^* = \tanh(\beta J m^*)$. Then the expectation value is

$$\langle m \rangle = m^* \frac{e^{N\beta h m^*} - e^{-N\beta h m^*}}{e^{N\beta h m^*} + e^{-N\beta h m^*}} = m^* \tanh(N\beta h m^*),$$

and thus we see that $\lim_{N\to\infty} \langle m \rangle = m^* \text{sgn}(h)$. So this is where the discontinuity comes in, and we've finally found a rigorous justification. But if we take any finite N and consider the $h \to 0$ limit, we still find the solution $\langle m \rangle = 0$, so that helps us describe the phase transition in the limit.

And there aren't macroscopic materials that actually float between two states – once we choose one of them, it's "stuck" because the spins won't all flip at once. In reality, we also need to consider kinetics beyond true equilibrium too. But still, N is very large, so we do observe abrupt transitions.

So now we'll turn to Bose-Einstein condensates: if we have a system of **distinguishable** particles, for example because they're pinned to a lattice, then the partition function is

$$Z_n = (Z_1)^N \implies f = \frac{F_N}{N} = f_1 = -k_B T \ln Z_1.$$

There aren't any discontinuities here for any finite N. Similarly, remember that in a classical gas of **indistinguishable particles**, we wrote down the function

$$\mathbb{Q} = \sum_{N=0}^{\infty} \frac{1}{N!} (Z_1)^N e^{\beta \mu N} = \exp\left[Z_1 e^{\beta\mu}\right],$$

and thus we find that

$$N = \frac{\partial \ln \mathbb{Q}}{\partial(\beta\mu)} = Z_1 e^{\beta\mu}.$$

But this calculation is actually wrong, because we're taking into account that the particles are indistinguishable. So it doesn't account for the possibility of two particles being exactly in the same state, and thus we're not quite counting correctly. (In other words, if N particles are in all different states, there are $N!$ ways to permute that, but if the particles are in the same state we shouldn't still divide by $N!$.)

So if we use bosons, we should look at the set of states α that the particles can be in, and we write

$$\mathbb{Q} = \prod_{\alpha} \sum_{n_\alpha = 0}^{\infty} e^{\beta(\mu - E_\alpha) n_\alpha} = \prod_{\alpha} \frac{1}{1 - e^{\beta(\mu - E_n)}}.$$

In both of the cases, if $\mu \ll E_0$, both expressions here are approximately $\prod_\alpha (1 + e^{\beta(\mu - E_\alpha)})$. So the probability of being in any state more than once is very unlikely, which means our distinguishability concerns become less important.

And when we have fermions, every state is either occupied or not, and so we just directly have this answer

$$\mathbb{Q} = \prod_{\alpha} (1 + e^{\beta(\mu - E_\alpha)}),$$

which is the same as the approximate values for the classical gas and bosons at low μ. But we'll see more examples of this on Monday.

So now if we go back to bosons, we find that

$$\beta g = \sum_\alpha \ln(1 - e^{-\beta(E_\alpha - \mu)}.$$

But if $\mu = E_\alpha$ for some α, we get a divergent term, and we can imagine something weird happening as μ gets very close to E. If our system is finite, the density is

$$n = \frac{N}{V} = \frac{1}{V}\sum_\alpha \frac{1}{e^{\beta(E_\alpha - \mu)} - 1} = \int_{\varepsilon_0}^\infty dE \frac{g(E)}{V}\frac{1}{e^{\beta(E-\mu)} - 1},$$

where $g(E)$ is the density of states (possibly allowing for delta functions because of condensation). In lecture, when calculating density for a gas, we approximated the density of states $\overline{g}$ by transferring from a sum to an integral, and it turns out that if we do this calculation in d dimensions, we have a density near the ground state of

$$\frac{\overline{g}(E_0)}{V} \sim \frac{2mL^2}{\hbar^2 L^d}.$$

To interpret this, note that when $d \geq 3$, $\overline{g}$ goes to 0 even though we have delta-function occupations, since the spacing between the allowed energy states is too large. And that's why we have Bose-Einstein condensation in three dimensions but not two – the approximation with the integral is insufficient!

Again, this returns to the issue of the "order of taking limits." For any finite V, our chemical potential μ will get arbitrarily close to 0 (but not hit it exactly), but when we take $V \to \infty$, we get a sharp approach to 0, rather than a smooth approach, for small T. So in the limit we do get a kink in the derivative of μ at T_c, and that's where the phase transition for BEC is coming from.

In the previous phase transition with the spins, the cause was the interaction (the desire for spins to be independent was overwhelmed by the energy of interactions). But in this case, we're getting a much bigger probability of everything being in the same state, but relative to the independent case, there's an "entropic force" pushing them together with larger probability.

38 December 7, 2020

An announcement has been sent out about how the class will wrap up – our exam is next week, and Alex is offering to teach an extra review session this Friday. Practice exams from two previous years (from Professor Kardar's version of the course) have also been posted, and their solutions will be posted tonight or tomorrow. But we should note that topics like density matrices will not be included, and also the problems are fairly elaborate. So the intention for the exam we'll have is to be simpler than those.

We'll continue the discussion of the ideal Fermi gas today: recall that if we have single-particle energy levels r with energy ε_r, and we assume ε_r is independent of the spin α being ↑ or ↓, we have

$$Z_G = \sum_{n_{r,\alpha}} e^{-\beta \sum_{r,\alpha} n_{r,\alpha}(\varepsilon_r - \mu)},$$

and $n_{r,\alpha}$ is either 0 or 1 for each r, α because we're working with fermions. That means that

$$Z_G = \prod_{r,\alpha}(1 + e^{-\beta(\varepsilon_r - \mu)}) = \prod_r (1 + e^{-\beta(\varepsilon_r - \mu)})^2 = e^{-\beta g}$$

for the grand free energy g, which gets us to the final equation from last time,

$$g = -2k_BT\sum_r \ln(1+e^{-\beta(\varepsilon_r-\mu)}.$$

Example 190

Suppose we work with standard nonrelativistic particles in a large cubic box with dispersion $\frac{p^2}{2m}$.

As we've seen many times, the momentum spacing becomes small between allowed energy levels, and thus we should try to replace the sum over momentum by an integral. We might worry now that we missed the Bose-Einstein condensation phenomenon in the boson case, but that's not an issue here because we can't have macroscopic occupation of any state – the occupation is always 0 or 1! So we'll go ahead and approximate

$$g = -2k_BTV\int d\!\!{}^-{}^3p\ln(1+e^{-\beta(p^2/2m-\mu)}),$$

and we can find the density using the grand free energy's derivative, as usual:

$$\rho = \frac{N}{V} = -\frac{1}{V}\frac{\partial g}{\partial\mu} = 2\int d\!\!{}^-{}^3p\frac{1}{e^{\beta(p^2/2m-\mu)}+1}.$$

Notice that this looks very similar in form to the Bose case, but we have a $+1$ instead of a -1 in the denominator, and this will completely change the physics. And the average occupation number of any single-particle state (r,α) is

$$\langle n_{r,\alpha}\rangle = \frac{1}{2}\frac{\partial g}{\partial\varepsilon_r} = \frac{1}{e^{\beta(\varepsilon_r-\mu)}+1}$$

(dividing by 2 because we only want the occupation of one of the two allowed αs). Introducing the usual fugacity $z = e^{\beta\mu}$, we change variables with $x^2 = \frac{\beta p^2}{2m}$ to find

$$\rho = \frac{8\pi}{(2\pi\hbar)^3}(2mk_BT)^{3/2}\int dx\,\frac{x^2ze^{-x^2}}{1+ze^{-x^2}}.$$

So we now have an extra factor of 2 from the spin degeneracy, and the sign in the denominator has changed. In terms of the usual thermal de Broglie wavelength and then expanding as a power series,

$$\rho\lambda_T^3 = \frac{1}{\pi^2}\int_0^\infty dx\,\frac{x^2ze^{-x^2}}{1+ze^{-x^2}} = \frac{1}{\pi^2}\int_0^\infty dx\,x^2\sum_{n=1}^\infty(-1)^{n+1}z^ne^{-nx^2},$$

and doing the Gaussian x^2-weighted integrals gives us

$$= \frac{1}{4\pi^{3/2}}\sum_{n=1}^\infty(-1)^{n+1}\frac{z^n}{n^{3/2}}.$$

We'll now define a function similar to the zeta function:

Definition 191

Define the functions $f_m(z)$ via

$$f_m(z) = \sum_{n=1}^\infty(-1)^{n+1}\frac{z^n}{n^m}.$$

(The integral form of this function, from before we evaluated the integral, is an alternate definition of the function f, and that is defined outside the radius of convergence for this series.)

Issues of convergence will be analyzed soon, but we'll see that there aren't going to be any problems. We have our equation

$$\boxed{4\pi^{3/2}\rho\lambda_T^3 = f_{3/2}(z)}.$$

So now the average energy can be calculated in the same way as for the Bose case, and we find that

$$\langle E\rangle = 2V\int đ^3p\frac{p^2}{2m}\cdot\frac{1}{e^{\beta(p^2/2m-\mu)}+1}$$

(we weight occupation numbers of states with their corresponding energies), which evaluates to

$$= (k_BT)\frac{8\pi V}{(2\pi\hbar)^3}(2mk_BT)^{5/2}\int_0^\infty dx\frac{x^4ze^{-x^2}}{1+ze^{-x^2}}$$

and then doing the same series expansion gives us

$$= \frac{Vk_BT}{2\pi^2\lambda_T^3}\int_0^\infty x^4\sum_{n=1}^\infty(-1)^{n+1}e^{-nx^2}z^n = \frac{V}{4\pi^{3/2}\lambda_T^3}\left(\frac{3}{2}k_BT\right)f_{5/2}(z).$$

These expansions are really most useful in the high-temperature, low-density limit, meaning that our gas is almost classical. So now $\rho\lambda_T^3 \ll 1$, meaning that we expect z to be small, and thus

$$4\pi^{3/2}\rho\lambda_T^3 = f_{3/2}(z) \approx z - \frac{z^2}{2^{3/2}} + \frac{z^3}{3^{3/2}} \approx z.$$

Similarly,

$$\frac{\langle E\rangle}{V} = \frac{3}{2}k_BT\rho\frac{f_{5/2}(z)}{f_{3/2}(z)} \approx \frac{3}{2}k_BT\rho,$$

which is what we expect for a classical Boltzmann gas.

But in the regime when $\rho\lambda_T^3 \gg 1$, we'll need to try something different, because **quantum effects become important**. If we first study the $T = 0$ behavior, we know that every particle occupies the lowest energy level possible, subject to the condition that no level is occupied by more than one particle. If we're working in the grand canonical ensemble, we see that as $\beta \to \infty$ (meaning $T \to 0$),

$$\langle n_{r,\alpha}\rangle = \frac{1}{e^{\beta(\varepsilon_r-\mu)}+1}$$

goes to 0 for $\varepsilon_r > \mu$ and 1 $\varepsilon_r < \mu$, meaning that our chemical potential μ is the "cutoff" point for which energy levels are allowed! And thus the grand canonical distribution is able to reach the conclusion that all energy levels with $\varepsilon_r \le \mu$ are fully occupied, and the maximum energy of the occupied levels is called the **Fermi energy** E_F – it's an important energy scale that characterizes a system of fermions. (And $\mu = E_F$ at zero temperature, but we'll ask about how μ behaves for nonzero temperatures later on.)

To relate this back to the density, note that at temperature $T = 0$,

$$N = \sum_{r,\alpha}\langle n_{r,\alpha}\rangle = 2V\int đ^3p\theta\left(\mu - \frac{p^2}{2m}\right)$$

(the step function θ tells us we only keep energies that are low enough), and this evaluates to

$$= \frac{2V}{(2\pi\hbar)^3}\cdot(\text{volume of a 3D sphere with radius } p_F = \sqrt{2m\mu} = \frac{2V}{(2\pi\hbar)^3}\frac{4}{3}\pi p_F^3.$$

(Here, p_F is called the **Fermi momentum**, and the spherical surface defined by $\frac{p_F^2}{2m} = \mu$ is the **Fermi surface**.)

Therefore, the density is

$$\rho = \frac{1}{3\pi^2}\left(\frac{p_F}{\hbar}\right)^3 = \frac{k_F^3}{3\pi^2},$$

meaning the Fermi wavenumber is $(3\pi^2\rho)^{1/3}$ and the Fermi energy is $\frac{p_F^2}{2m} = \frac{\hbar^2}{2m}(3\pi^2\rho)^{2/3}$. So a higher density for our gas gives us a higher Fermi energy – indeed, having more particles means we need to occupy more and more levels to accommodate all of them, and it goes up with an exponent of $2/3$ with the given dispersion in three dimensions.

Our Fermi surface is therefore a separation in momentum space which distinguishes occupied and unoccupied states, and we want to calculate the total ground state energy now by adding up the states of the occupied particles. This is

$$E = 2V\int_{|\vec{p}|<p_F} \bar{d}^3p\,\frac{p^2}{2m} = \frac{2V(4\pi)}{(2\pi\hbar)^3}\int_0^{p_F} dp\,\frac{p^4}{2m},$$

so we have

$$E = \frac{V}{\pi^2}\frac{\hbar^2}{10m}k_F^5 = \frac{V}{\pi^2}\frac{\hbar^2}{10m}(3\pi^2\rho)^{5/3}.$$

Therefore, the energy also increases as the density increases (again making sense), and thus the average energy per particle also increases:

$$\frac{E}{N} = \frac{1}{\rho}\frac{E}{V} = \left(\frac{1}{\pi^2}\frac{\hbar^2}{10m}k_F^5\right)\left(\frac{3\pi^2}{k_F^3}\right) = \frac{3}{10m}\hbar^2k_F^2 = \frac{3}{5}E_F.$$

This is the kind of expression we expect: the Fermi energy is the main energy scale in this problem, and all the particles have some energy between zero and E_F, so the average should be somewhere in between. Then the total ground state energy can also be rewritten to see the N and V dependence

$$E = \frac{3}{5}(3\pi^2)^{2/3}\left(\frac{\hbar^2}{2m}\right)N^{5/3}V^{-2/3},$$

and we know that the pressure can be written as (because the free energy and internal energy are the same at $T = 0$ – we should usually take a derivative of F)

$$P = -\left(\frac{\partial E}{\partial V}\right)_{N,T} = \frac{2}{5}(3\pi^2)^{2/3}\left(\frac{\hbar^2}{2m}\right)\left(\frac{N}{V}\right)^{5/3} = \frac{2}{5}\frac{NE_f}{V} = \frac{2}{3}\frac{E}{V}.$$

Notice that this pressure is nonzero even at zero temperature – it's known sometimes as a **degeneracy pressure**. (This occurs because the Pauli exclusion principle pushes particles away from each other, and it's a quantum mechanical effect.) And this basic idea gives rise to many phenomena: for example, it's why two atoms have a strong repulsion when we try to push them together, and in fact in the absence of the Pauli exclusion principle, macroscopic matter would not be stable at all!

Example 192

Electrons are fermions, and let's try doing these calculations for electrons moving freely inside of a metal.

If we approximate the electrons as an ideal Fermi gas, the typical spacing between ions is on the order of an angstrom (10^{-10} m), and thus that's also the order of separation between electrons – ρ is of order 10^{30} per meter, and thus k_F is of order the interparticle spacing, 10^{10} per meter. Since the electron mass is half an MeV, we can then estimate the Fermi energy E_F, and it turns out to correspond to about 10^4 or 10^5 Kelvin. We know that such metals usually melt long before we get to that temperature, so in most regimes that metals exist as solids, the temperature we're dealing with is much smaller than the Fermi temperature of the electrons. So we almost never get the behavior where $\rho\lambda_T^3 \ll 1$ – even at room temperature, quantum effects are extremely important, and electronic properties of a metal can be studied only by accounting for Fermi statistics.

We can then estimate the typical magnitude of the velocity of an electron by taking an electron sitting at the Fermi surface: then

$$\frac{1}{2}mv_F^2 = E_F \implies v_F \sim 10^6 \text{m/s},$$

which is about two orders of magnitude away from the speed of light. So it's not high enough that we need to worry about relativity, but it's not as small as we might expect in a classical gas (in which the typical velocity $\sqrt{\frac{k_B T}{m}}$ is much smaller than v_F at ordinary temperatures T). So the **Fermi velocity** v_F is something we should keep an eye on when we study these kinds of systems!

So we know that the chemical potential is large in the $T = 0$ limit (it's a positive number equal to the energy scale E_F). But in the high-temperature limit, we know that μ must be large and negative. So things need to evolve between these two limits in some way, and we'll start looking at the nonzero temperature limits now. (Remember that μ starts off small and negative but then sticks at 0 below $T = T_c$ in the Bose gas, which is a different behavior.)

We now take $T \neq 0$ but still small, meaning that $T \ll \frac{E_F}{k_B}$. (The temperature $T_F = \frac{E_F}{k_B}$ is called the **Fermi temperature**.) If we try to think about the plot of occupation number versus energy, we no longer have a step function from 1 to 0 at E_F: we know that

$$\langle n_{r,\alpha}\rangle = \frac{1}{e^{\beta(\varepsilon_r - \mu)} + 1}$$

will be a smooth function that approximates the step function (in fact, only in a window around E_F of order $k_B T$ will we be able to notice the transition from occupation 1 to occupation 0, and this is the only regime where there's a deviation from the ground state value). Then we can ask about the average energy, which will let us calculate the heat capacity of the gas, and let's do that calculation now. Our strategy in the grand canonical ensemble is always the same: we have our two governing equations

$$\rho = 2\int d\!\!\bar{}^3 p \frac{1}{e^{\beta(p^2/2m - \mu)} + 1},$$

$$\langle E\rangle = 2\int d\!\!\bar{}^3 p \frac{p^2/2m}{e^{\beta(p^2/2m - \mu)} + 1}.$$

Changing the variable of integration by converting to spherical coordinates, doing the angular integrals, and letting $\varepsilon = \frac{p^2}{2m} \implies d\varepsilon = \frac{p\,dp}{m}, dp = \sqrt{\frac{m}{2\varepsilon}}d\varepsilon$ gives us the conversion of measure

$$2\int \frac{d\!\!\bar{}^3 p}{(2\pi\hbar)^3} = \frac{8\pi}{8\pi^3\hbar^3}\int dp\, p^2 = \frac{\sqrt{2}}{\pi^2\hbar^3}m^{3/2}\int d\varepsilon\, \frac{\varepsilon^{1/2}}{e^{\beta(\varepsilon-\mu)} + 1},$$

so that

$$\boxed{\rho = \frac{(8m)^{3/2}}{\pi^2\hbar^3}\int_0^\infty d\varepsilon \frac{\varepsilon^{1/2}}{e^{\beta(\varepsilon-\mu)} + 1}}, \quad \boxed{E = \frac{(8m)^{3/2}}{\pi^2\hbar^3}\int_0^\infty \frac{\varepsilon^{3/2}}{e^{\beta(\varepsilon-\mu)} + 1}}.$$

We can now do these two integrals in the appropriate limit, where we extract the leading-order dependence by doing a series of elementary steps and putting them together. If we set $a = \frac{(8m)^{3/2}}{\pi^2\hbar^3}$, we need to calculate integrals of the form $\int_0^\infty d\varepsilon \frac{g(\varepsilon)}{e^{\beta(\varepsilon-\mu)}+1}$, where $g = a\varepsilon^{1/2}$ or $a\varepsilon^{3/2}$, respectively. So the quantity we're interested in evaluating is

$$I = \int_0^\infty d\varepsilon \frac{g(\varepsilon)}{e^{\beta(\varepsilon-\mu)} + 1},$$

and if we change variables with $x = \beta(\varepsilon - \mu)$, meaning $d\varepsilon = k_B T dx$, then

$$I = k_B T\int_{-\beta\mu}^\infty dx\, \frac{g(\mu + k_B T x)}{e^x + 1}$$

which we can split up into

$$= k_B T \left(\int_{-\beta\mu}^{0} dx \frac{g(\mu + k_B T x)}{e^x + 1} + \int_0^\infty dx \frac{g(\mu + k_B T x)}{e^x + 1} \right),$$

and changing variables again on the first term gives us

$$= k_B T \left(\int_0^{\beta\mu} dx \frac{g(\mu - k_B T x)}{e^{-x} + 1} + \int_0^\infty dx \frac{g(\mu + k_B T x)}{e^x + 1} \right).$$

This can then be rewritten as

$$= k_B T \left(\int_0^{\beta\mu} dx g(\mu - k_B T x) \left(1 - \frac{1}{e^x + 1} \right) + \int_0^\infty dx \frac{g(\mu + k_B T x)}{e^x + 1} \right).$$

And now when we expand out the integral into its two parts, the first term here is $k_B T \int_0^{\beta\mu} dx g(\mu - k_B T x) = \int_0^\mu d\varepsilon g(\varepsilon)$ (the zero-temperature value of the quantity that we're trying to calculate), and the other term is $-k_B T \int_0^{\beta\mu} dx \frac{g(\mu - k_B T x)}{e^x + 1}$. Thus, we can rearrange to

$$I = \int_0^\mu d\varepsilon g(\varepsilon) - k_B T \left(\int_0^{\beta\mu} dx \frac{g(\mu - k_B T x)}{e^x + 1} - \int_0^\infty dx \frac{g(\mu + k_B T x)}{e^x + 1} \right).$$

The point of all of this calculation has let us isolate the zero-temperature value of our quantities ρ and E, and next time we'll see how to use the low-temperature approximation to complete the desired calculation for extracting out physically relevant answers.

39 December 9, 2020

Today, we'll understand the low-temperature thermodynamics of the ideal Fermi gas – we understood the zero-temperature situation last class, and we're going to evaluate the integrals from last class in this low-temperature approximation. Recall that we tried to evaluate expressions like

$$I = \int_0^\infty d\varepsilon \frac{g(\varepsilon)}{e^{\beta(\varepsilon - \mu)} + 1},$$

where $g(\varepsilon) = a\varepsilon^{1/2}$ for the density ρ, $a\varepsilon^{3/2}$ for the energy E, and $a = \frac{(8m)^{3/2}}{\pi^2 h^3}$ is a constant. We did this by massaging the integral into another form

$$I = \int_0^\mu d\varepsilon g(\varepsilon) - k_B T \left[\int_0^{\beta\mu} dx \frac{g(\mu - k_B T x)}{e^x + 1} - \int_0^\infty dx \frac{g(\mu + k_B T x)}{e^x + 1} \right],$$

and now the first term is the value of the integral I at zero temperature, while the remaining terms can be thought of as a correction. We'll see how this form lends itself to making a good approximation in the limit as $\beta \to \infty$ now. First of all, notice that the integrand dies off rapidly whenever $x \gtrsim 1$, because g is some power function but the denominator is exponentially decaying. And also, $\beta\mu \sim \frac{E_F}{k_B T} = \frac{T_F}{T} \gg 1$ is large in the low-temperature limit, so x is much smaller than $\beta\mu$ in the important contributions to the integral. And thus we'll Taylor expand these functions as

$$g(\mu + k_B T x) \approx g(\mu) + k_B T x g'(\mu) + \cdots$$

so that the bracketed term can be written as

$$= \int_0^{\beta\mu} dx \frac{g(\mu) - k_B T x g'(\mu) + \cdots}{e^x + 1} - \int_0^\infty dx \frac{g(\mu) + k_B T x g'(\mu) + \cdots}{e^x = 1}.$$

And because the weight of the integrand for $x \geq \beta\mu$ is almost zero, it's acceptable to replace the upper limit of the first integral here with ∞ (and the error is of error $e^{\beta\mu}$, which is small) to get cancellations

$$= -2k_B T g'(\mu) \int_0^\infty dx \, \frac{x}{e^x + 1} + \text{(higher-order corrections)}.$$

We can calculate the value of the integral directly, and the bracketed term turns out to be $-\frac{\pi^2}{6} k_B T g'(\mu)$. This gives us the following result when we plug things back in:

Proposition 193

At low temperature,

$$I \approx \int_0^\mu d\varepsilon \, g(\varepsilon) + \frac{\pi^2}{6}(k_B T)^2 g'(\mu).$$

We can now specialize to the two functions for $g(\varepsilon)$ that help us write down the density and energy of our ideal Fermi gas. For ρ, we set $g(\varepsilon) = a\varepsilon^{1/2}$, and then we have that

$$\boxed{\rho = \frac{2a}{3}\mu^{3/2} + \frac{\pi^2}{6}(k_B T)^2 \frac{a}{2\sqrt{\mu}} + \cdots}.$$

So if we're working in a **Fermi gas at fixed density**, this gives us μ as a function of T: it's equal to the Fermi energy at zero temperature, but now we can calculate it for low nonzero temperature as well. Plugging in $T = 0$, we find that $\rho = \frac{2a}{3} E_F^{3/2}$, and thus if we plug that in and write $\mu = E_F + \delta\mu$, we find that

$$\frac{2a}{3}(E_F + \delta\mu)^{3/2} + \frac{\pi^2}{6}(k_B T)^2 \frac{a}{2\sqrt{E_F + \delta\mu}} = \frac{2a}{3} E_F^{3/2}.$$

Since the equation is valid for small T, $\delta\mu$ will be small (meaning that $\frac{|\delta\mu|}{E_F} \ll 1$), and thus we can Taylor expand to linear order. This yields, after some algebra, that

$$\delta\mu = -\frac{\pi^2}{12}\frac{(k_B T)^2}{E_F}.$$

And we could have guessed most this by dimensional analysis: everything changes at order T^2, so the change in $\delta\mu$ must be of order $\frac{(k_B T)^2}{E_F}$. And the sign of this change could maybe have been guessed as well, because in the high-temperature limit of the classical gas, the chemical potential is negative. And thus we find that at low temperature,

$$\boxed{\mu \approx E_F \left(1 - \frac{\pi^2}{12}\left(\frac{k_B T}{E_F}\right)^2\right)}.$$

We can also calculate the energy by setting $g(\varepsilon) = a\varepsilon^{3/2}$, which yields

$$\frac{E}{V} = \frac{2a}{5}\mu^{5/2} + \frac{\pi^2}{6}(k_B T)^2 \frac{3a\sqrt{\mu}}{2},$$

and we're looking for answers that are accurate to this order (T^2) of the low-temperature system. So we can rewrite this as

$$\approx \frac{2a}{5}(E_F + \delta\mu)^{5/2} = \frac{\pi^2}{6}(k_B T)^2 \frac{3a}{2}\sqrt{E_F}$$

(we don't need to turn the $\sqrt{E_F}$ into a $\sqrt{E_F + \delta\mu}$, because we already have a $(k_B T)^2$ in front of it). Thus,

$$\frac{E}{V} = \frac{E_{\text{ground}}}{V} + aE_F^{3/2}\delta\mu + \frac{\pi^2}{6}(k_B T)^2 \frac{3a}{2}\sqrt{E_F}$$

to order T^2, and plugging in the $\delta\mu$ we found above gives us

$$\frac{E}{V} = \frac{E_{\text{ground}}}{V} - a\sqrt{E_F}\frac{\pi^2}{12}(k_BT)^2 + \pi^2(k_BT)^2\frac{a}{4}\sqrt{E_F} = \frac{E_{\text{ground}}}{V} + \frac{a\pi^2}{6}\sqrt{E_F}(k_BT)^2,$$

and therefore

$$\boxed{\frac{E}{V} = \frac{E_{\text{ground}}}{V} + \frac{(8m)^{3/2}}{6\hbar^3}\sqrt{E_F}(k_BT)^2}.$$

What's important is that the energy has changed by an amount proportional to T^2, and if we set $\gamma = \frac{(8m)^{3/2}}{6\hbar^3}\sqrt{E_F}k_B^2$, we can calculate the heat capacity per unit volume

$$\frac{C_V}{V} = \frac{1}{V}\frac{dE}{dT} = \gamma T.$$

Notice that this heat capacity does go to 0 as T goes to 0, consistent with the third law of thermodynamics, but it's still linear in T (which is larger than the heat capacity of the Bose gas, which goes as $T^{3/2}$). To get some intuition for this result, we can rewrite the correction term for the energy more transparently as

$$\frac{E}{V} = \frac{E_{\text{ground}}}{V} + \frac{a\pi^2}{6}\sqrt{E_F}(k_BT)^2 + \cdots = \frac{2a}{5}E_F^{5/2} + \frac{a\pi^2}{6}\sqrt{E_F}(k_B)T^2 + \cdots,$$

which we can then write as

$$= \frac{2a}{5}E_F^{5/2}\left(1 + \frac{5}{12}\pi^2\left(\frac{k_BT}{E_F}\right)^2 + \cdots\right).$$

Since we know that the mean energy per particle is $\frac{3}{5}\frac{N}{V}E_F$ (from last class), we find that

$$E = \frac{3}{5}NE_F\left(1 + \frac{5}{12}\pi^2\left(\frac{k_BT}{E_F}\right)^2 + \cdots\right) = \boxed{\frac{3}{5}NE_F + N\frac{\pi^2}{4}\left(\frac{k_BT}{E_F}\right)^2 + \cdots}.$$

Thus, the correction term can be thought of as the thermal energy k_BT for a **fraction of the** N particles in the system, proportional to $\frac{k_BT}{E_F}$. (Basically, most of the N particles are not thermally excited, but a small fraction are, and they gain energy proportional to k_BT each.) And if we remember that the graph of occupation $\langle n_{r,\alpha}\rangle$ deviates slightly from the zero-temperature step function, indeed the window of deviation is proportional to k_BT (around the Fermi energy E_F). If we look at the **Fermi sea** (the set of all energy levels below E_F), then the average occupation is not changed for most of the states. (Exciting the particles deep into the Fermi sea is often not possible because of Pauli exclusion, and doing so for particles near the Fermi surface happens much more frequently.) So the low-temperature Fermi gas will generally gain these extra factors of $\frac{k_BT}{E_F}$, compared to any classical results.

And we'll finish this class with a few applications of the theory of the ideal Fermi gas:

1. Much like a crystalline solid is explained by boson gas calculations, the ideal Fermi gas model provides a basis for the theory of metals.
2. We also get a starting point for the theory of the liquid phase of Helium-3 (a fermion): it becomes a liquid at low temperature and ambient pressure, as discussed a few lectures ago, with lots of weird properties.
3. Because nucleons are fermions, we are also able to study the structure of atomic nuclei and include an important contribution to the energetics of the nucleus. If we take a heavy atomic nucleus, the protons repel electrostatically, and the strong nuclear force binds them together, but there's also a degeneracy pressure that keeps the nucleons apart. So this is a sensible starting point for a full calculation of the binding energy!
4. Some stars (in particular white dwarfs) are composed of highly ionized Helium, instead of Hydrogen. And we can model this star as a gas of ions and electrons, and the densities are high enough that the electron gas is

highly degenerate. So the main physical effects that determine stability come from the competition between the gravitational attraction and degeneracy pressure. And it turns out the Fermi momentum in this system is very large, so we need to treat this as a relativistic Fermi gas. And as the mass increases, the degeneracy pressure must increase, and thus the density increases as well. People recognized that beyond a certain critical mass (about 1.4 times the solar mass), this is no longer possible, and that's known as the **Chandrasekhar limit**. And thus only small stars can form white dwarfs!