Lecture Notes on Statistical Mechanics & Thermodynamics

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Abstract

Various lecture notes to be supplemented by other course materials.

Contents

Basic Info

This is an advanced undergraduate course on thermodynamics and statistical physics. Topics include basics of temperature, heat, and work; state-counting, probability, entropy, and the second law; partition functions and the Boltzmann distribution; applications to engines, refrigerators, and computation; phase transitions; basic quantum statistical mechanics and some advanced topics.

    The course will use Schroeder's An Introduction to Thermal Physics as a textbook. We will follow the book fairly closely, though there will also be some extra supplemental material on information theory, theoretical limits of computation, and other more advanced topics. If you're not planning to go on to graduate school and become a physicist, my best guess is that the subject matter and style of thinking in this course may be the most important/useful in the physics major, as it has significant applications in other fields, such as economics and computer science.

1   What Are We Studying?

This won't all make sense yet, but it gives you an outline of central ideas in this course.

We're interested in the *approximate* or *coarse-grained* properties of *very large* systems. You may have heard that chemists define $N_A = 6.02 \times 10^{23}$ as a mole, which is the number of atoms in a small amount of stuff (ie 12 grams of Carbon-12). Compare this to all the grains of sand on all of the world's beaches $\sim 10^{18}$, the number of stars in our galaxy $\sim 10^{11}$, or the number of stars in the visible universe $\sim 10^{22}$. Atoms are small and numerous, and we'll be taking advantage of that fact!

Here are some examples of systems we'll study:

- We'll talk a lot about gases. Why? Because gases have a large number of degrees of freedom, so statistics applies to them, but they're simple enough that we can deduce their properties by looking at one particle at a time. They also have some historical importance. But that's it.

- Magnetization – are magnetic dipoles in a substance aligned, anti-aligned, random? Once again, if they don't interact, its easy, and that's part of why we study them!

- Metals. Why and how are metals all roughly the same (answer: they're basically just gases of electrons, but note that quantum mechanics matters a lot for their behavior).

- Phase Transitions, eg gas/liquid/solid. This is obviously a coarse-grained concept that requires many constituents to even make sense (how could you have a liquid consisting of only one molecule?). More interesting examples include metal/superconductor, fluid/superfluid, gas/plasma, aligned/random magnetization, confined quarks/free quarks, Higgs/UnHiggsed, and a huge number of other examples studied by physicists.

- Chemical reactions – when, how, how fast do they occur, and why?

Another important idea is *universality* – in many cases, systems with very different underlying physics behave the same way, because statistically, ie on average, they end up being very similar. For example, magnetization and the critical point of water both have the same physical description! Related ideas have been incredibly important in contemporary physics, as the same tools are used by condensed matter and high-energy theorists; eg superconductivity and the Higgs mechanism are essentially the same thing.

Historically physicists figured out a lot about *thermodynamics* without understanding *statistical mechanics*. Note that

- Thermodynamics deals with Temperature, Heat, Work, Entropy, Energy, etc as rather abstract macroscopic concepts obeying certain rules or 'laws'. It works, but it's hard to explain why without appealing to...

- Statistical Mechanics gets into the details of the physics of specific systems and makes statistical predictions about what will happen. If the system isn't too complicated, you can directly **derive thermo from stat mech**. So statistical mechanics provides a much more complete picture, and is easier to understand, but at the same time the analysis involved in stat mech is more complicated. It was discovered by Maxwell, Boltzmann, Gibbs, and many others, who provided a great deal of evidence for the existence of atoms themselves along the way.

A Very Brief Introduction

So what principles do we use to develop stat mech?

- Systems tend to be in typical states, ie they tend to be in and evolve towards **the most likely states**. This is the second law of thermodynamics (from a stat mech viewpoint). Note

$$S \equiv k_B \log N \tag{1.0.1}$$

  is the definition of entropy, where N is the number of accessible states, and k_B is a pointless constant included for historical reasons. (You should really think of entropy as a pure number, simply the log of the number of accessible states.)

For example, say I'm a bank robber, and I'm looking for a challenge, so instead of stealing \$100 bills I hijack a huge truck full of quarters. But I end up crashing it on the freeway, and 10^6 quarters fly everywhere, and come to rest on the pavement. How many do you expect will be heads vs tails? The kind of reasoning you just (intuitively) employed is exactly the sort of thinking we use in stat mech. You should learn basic statistical intuition well, as its very useful both in physics, and in the rest of science, engineering, and economics. It's very likely the most universally important thing you can learn well as a physics undergraduate.

Is there any more to stat mech than entropy? Not much! Only that

- The laws of physics have to be maintained. Mostly this means that **energy is conserved**.

This course will largely be an exploration of the consequences of basic statistics + physics, which will largely mean counting + energy conservation.

Say I have 200 coins, and I restrict myself to coin configurations with the same number of heads and tails. Now I start with the heads in one pile and the tails in the other (100 each). I play a game where I start randomly flipping a head and a tail over simultaneously. After a while, will the two 100-coin piles still be mostly heads and mostly tails? Or will each pile have roughly half heads and half tails? This is a pretty good toy model for heat transfer and entropy growth.

Connections with Other Fields

The methods of this course are useful in a broad range of fields in and outside of physics:

- In stat mech we learn how to sum or average over distributions of states. We do something quite similar in Quantum Mechanics. In fact, there are deep and precise connections between the *partition function* in stat mech and the *path integral* in quantum mechanics.

- Information Theory concerns how much information we can store, encode, and transmit, and is also built on the idea of entropy (often called Shannon Entropy in that context).

- Because gases are easy, engines use them, and they were important to the development of thermo and stat mech, we'll talk somewhat about how thermodynamics places fundamental limitations on the efficiency of engines. There are similar constraints on the efficiency of computation, which are just as easy to understand (though a bit less pessimistic).

- Machine Learning systems are largely built on the same conceptual foundations. In particular, 'learning' in ML is essentially just statistical regression, and differences between ML models are often measured with a version of entropy. More importantly, even when ML systems are deterministic algorithms, they are so complicated and have so many parameters that we use statistical reasoning to understand them – this is identical to the situation in stat mech, where we describe deterministic underlying processes using probability and statistics. (It's also what we do when we talk about probability in forecasting, eg when we say there's a 30% probability someone will win an election.)

2 Energy in Thermal Physics

2.1 Temperature and Energy

Temperature

Temperature is an intrinsic property of both of two systems that are in equilibrium, ie that are in contact much longer than a relaxation time.

- Contact can be physical, or it can be established through radiation, or via mutual conduct with some other substance/fluid. But **heat** must be exchanged for temperature...

- Other kinds of equilibrium might be **energy = thermal**, **volume = mechanical**, **particles = diffusive**.

- Objects that give up energy are at a higher temperature.

So more specifically, objects at higher temperature *s*pontaneously give up heat energy to objects at lower temperature. From the point of view of Mechanics or E&M, this is **weird**! Nothing like this is true of momentum, charge, force, ie they aren't spontaneously emitted and absorbed!?

- Operationally, use a thermometer. These are usually made of substances that *expand when hotter*.

- Scale is basically arbitrary for now. Just mark some points and see how much expansion happens for a single material! Celsius from boiling water vs freezing.

- Different materials (eg mercury vs metal) expand a bit differently, so precise measurements require care and more thought. But in many cases expansion is linear in temperature, so we get same approximate results.

Hmm, are any materials more interesting than others for this purpose?
    What if we use **a gas** to measure temperature?

- Operationally, a gas can keep on shrinking. In fact, at some temperature its volume or pressure will go to zero!

- This temperature is called **absolute zero**, and defines the zero point of the absolute temperature scale.

Ideal Gas and the Energy-Temperature Relation

Gases are the harmonic oscillator of thermodynamics – the reason is that we want to study a large number of very simple (approximately independent!) degrees of freedom in a fairly intuitive context. Everyone breathes and has played with a balloon.

Low-density gases are nearly ideal, and turn out to satisfy (eg experiments demonstrate this)

$$PV = NkT \tag{2.1.1}$$

where k is Boltzmann's constant (which is sort of arbitrary and meaningless, as we'll see, but we have to keep it around for historical reasons).

- Note that Chemists use Avogadro's number $N_A = 6.02 \times 10^{23}$ and $nR = Nk$ where n is molar density. This is also totally arbitrary, but it hints at something very important – there are **very big** numbers floating around!

- Of course the ideal gas law is an approximation, but it's a good approximation that's important to understand.

Why are we talking about this? Because the **relationship between temperature and energy is simple for an ideal gas**. Given

- the ideal gas law

- the relationship between pressure and energy

we can derive the relationship between temperature and energy.

Consider a molecule of gas and piston with area A controlling a volume $V = LA$. Let's imagine its only a single molecule, as that's equivalent to many totally non-interacting molecules. The average pressure is

$$\bar{P} = \frac{\bar{F}_{x,onpiston}}{A} = -\frac{\bar{F}_{x,onmolecule}}{A} = -\frac{m\left(\frac{\Delta v_x}{\Delta t}\right)}{A}\left(\tag{2.1.2}\right.$$

Its natural to use the double-round-trip time

$$\delta t = 2\frac{L}{v_x} \tag{2.1.3}$$

Note that

$$\Delta v_x = -2v_x \tag{2.1.4}$$

So we find that

$$\bar{P} = -\frac{m}{A}\frac{(-2v_x)}{2L/v_x} = \frac{mv_x^2}{V} \tag{2.1.5}$$

The two factors of v_x come from the momentum transfer and from the time between collisions.

If we have N molecules, the total pressure is the sum, so we can write

$$\bar{P}V = Nm\bar{v_x^2} \tag{2.1.6}$$

So far we haven't made any assumptions. But if we assume the ideal gas law, we learn that

$$\frac{1}{2}kT = \frac{1}{2}m\bar{v_x^2} \tag{2.1.7}$$

or the average total kinetic energy is

$$\frac{3}{2}kT = \frac{1}{2}m\left(\bar{v_x^2} + \bar{v_y}2 + \bar{v_z^2}\right) \Big(\tag{2.1.8}$$

Cool! We have related energy to temperature, by assuming the (empirical for now) ideal gas law.

We can also get the RMS speed of the molecules as

$$\bar{v}^2 = \frac{3kT}{m} \tag{2.1.9}$$

Is the sum or average of the squares of numbers equal to the sum squared? So this isn't the average speed, but it's pretty close. (What does it being close tell us about the shape of the distribution of speeds?)

Our result is true for ideal gases. The derivation breaks down at very low temperatures, when the molecules get very close together, though actually the result is still true (just not our argument). We'll discuss this later in the course.

Equipartition of Energy

The equipartition theorem, which we'll prove later in the course, says that all 'quadratic' degrees of freedom have average energy $= \frac{1}{2}kT$. This means kinetic energies and harmonic oscillator potential energies:

- Atoms in molecules can rotate, and their bonds can vibrate.

- Solids have 3 DoF per molecular motion and 3 DoF for the potential energy in bonds.

- Due to QM, some motions can be frozen out, so that they don't contribute.

This is all useful for understanding how much heat energy various substances can absorb.

2.2 Heat and Work

Book says that we can't define energy... actually, we can define it as the conserved quantity associated with time translation symmetry, for those who know about Noether's theorem.

Recall that **temperature** is a measure of an object's tendency to spontaneously give up energy... temperature often increases with energy, but not always, and it's important not to confuse temperature with energy or heat.

In thermodynamics we usually discuss energy in the form of **heat** or **work**.

- Heat is the spontaneous flow of energy due to temperature differences.

- Work is any other transfer of energy... you do work by pushing a piston, stirring a cup, running current through a resistor or electric motor. In these cases the internal energy of these systems will increase, and they will usually 'get hotter', but we don't call this heat.

- Note that these are both descriptions of energy transfers, not total energies *in* a system.

These aren't the everyday usages of these terms.

If I consider shining a flashlight with an incandescent bulb on something, I'm honestly not clear if that's heat or work – it's work since it's intentional (and the electrical 'heating' of the filament is definitely work), but when the flashlight emits light, it's actually 'spontaneous' thermal radiations, so the classification is unclear.

The change in the internal energy of a system is

$$\Delta U = Q + W \tag{2.2.1}$$

and this is just energy conservation, sometimes called the first law of thermodynamics.

- Note these are the amounts of heat and work *entering* the system.

- Note that we often want to talk about infinitessimals, but note that 'dQ' and 'dW' aren't the change in anything, since heat and work flow in or out, they aren't properties of the system itself.

Processes of heat transfer are often categorized as

- Conduction is by molecular contact

- Radiation is by emission of electromagnetic waves

- Convection is the bulk motion of a gas or liquid

Compression Work

For compression work we have

$$W = \vec{F} \cdot \vec{dx} \rightarrow F\Delta x \tag{2.2.2}$$

for a simple piston. If compression happens *slowly*, so the gas stays in equilibrium, then I can replace

$$W = PA\Delta x = -P\Delta V \tag{2.2.3}$$

This is called **quasistatic** compression. To leave this regime you need to move the piston at a speed of order the speed of sound or more (than you can make shock waves).

That was for infinitesimal changes, but for larger changes we have

$$W = -\int_{V_i}^{V_f} P(V)dV \tag{2.2.4}$$

as long as the entire process is quasistatic.

Now let's consider two types of compressions/expansions of an ideal gas, where we hold different quantities constant. These are

- **isothermal** – holds temperature constant

- **adiabatic** – no heat flow

- Which do you think is slower??

For an isotherm of an ideal gas we have

$$P = \frac{NkT}{V} \tag{2.2.5}$$

with T fixed, and so it's easy to compute

$$W = -\int_{V_i}^{V_f} \frac{NkT}{V}dV = NkT \log \frac{V_i}{V_f} \tag{2.2.6}$$

as the work done *on the gas*. If it contracts the work done on the gas is positive, if it expands the work done on the gas is negative, or in other words it does work on the environment (ie on the piston). How much heat flows? We just have

$$Q = \Delta U - W = -W \tag{2.2.7}$$

so heat is equal to work.

What if no heat is exchanged? By equipartition we have

$$U = \frac{f}{2}NkT \tag{2.2.8}$$

where f is the number of degrees of freedom per molecule. If f is constant then

$$dU = \frac{f}{2}NkdT \tag{2.2.9}$$

so that we have

$$\frac{f}{2}NkdT = -PdV \tag{2.2.10}$$

which along with ideal gas gives

$$\frac{f}{2}\frac{dT}{T} = -\frac{dV}{V} \tag{2.2.11}$$

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so that

$$VT^{f/2} = constant \tag{2.2.12}$$

or

$$V^{\gamma}P = constant \tag{2.2.13}$$

where $\gamma = 1 + \frac{2}{f}$ is the adiabatic exponent.

Heat Capacities

Heat capacity is the amount of heat needed to raise its temperature. The **specific heat capacity** is the heat capacity per unit mass.

As stated, specific heat capacity is ambiguous because Q isn't a state function. That is

$$C = \frac{Q}{\Delta T} = \frac{\Delta U - W}{\Delta T} \tag{2.2.14}$$

It's possible that U only depends on T (but likely not!), but W definitely depends on the process.

- Most obvious choice is $W = 0$, which usually means heat capacity at constant volume

$$C_V = \left(\frac{\partial U}{\partial T}\right)_V \tag{2.2.15}$$

  This could also be called the 'energy capacity'.

- Objects tend to expand when heated, and so its easier to use constant pressure

$$C_P = \left(\frac{\Delta U + P\Delta V}{\Delta T}\right)_P = \left(\frac{\partial U}{\partial T}\right)_P + P\left(\frac{\partial V}{\partial T}\right)_P \tag{2.2.16}$$

  For gases this distinction is important.

Interesting and fun to try to compute C_V and C_P theoretically.

When the equipartition theorem applies and f is constant, we find

$$C_V = \frac{\partial U}{\partial T} = \frac{\partial}{\partial T}\left(\frac{f}{2}NkT\right) = \frac{f}{2}Nk \tag{2.2.17}$$

For a monatomic gas have $f = 3$, while gases with rotational and vibrational DoF have (strictly) larger f. So C_V allows us to measure f.

Constant pressure? For an ideal gas the only difference is the addition of

$$\left(\frac{\partial V}{\partial T}\right)_P = \frac{\partial}{\partial T}\frac{NkT}{P} = \frac{Nk}{P} \tag{2.2.18}$$

so that

$$C_P = C_V + Nk \tag{2.2.19}$$

Interestingly C_P is independent of P, because for larger P the gas just expands less.

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Phase Transitions and Latent Heat

Sometimes you can put heat in without increasing the temperature at all! This is the situation where there's **Latent Heat**, and usually occurs near a first order phase transition. We say that the

$$L \equiv \frac{Q}{m} \tag{2.2.20}$$

is the latent heat per mass needed to accomplish the transformation. Conventionally this is at constant pressure, as its otherwise ambiguous. Note it takes 80 cal/g to melt water and 540 cal/g to boil it (note it takes 100 cal/g to heat water from freezing to boiling).

Enthalpy

Since we often work at constant pressure, it'd be convenient if we could avoid constantly having to include compression-expansion work. We can do this be defining the enthalpy

$$H = U + PV \tag{2.2.21}$$

This is the **total energy we'd need to create the system out of nothing at constant pressure**. Or if you annihilate the system, you could get H back having the atmosphere contract! It's useful because

$$\begin{aligned} \Delta H &= \Delta U + P\Delta V \\ &= Q + W_{other} \end{aligned} \tag{2.2.22}$$

where W_{other} is non-compression work. If no other form of work, $\Delta H = Q$. Means

$$C_P = \left(\frac{\partial H}{\partial T}\right)_P \tag{2.2.23}$$

Could all C_P the "enthalpy capacity" while C_V is "energy capacity". No need for any heat at all, since could just be 'other' work (eg a microwave oven).

For example, boiling a mole of water at 1 atmosphere takes $40,660$ J, but via ideal gas

$$PV = RT \approx 3100 \text{ J} \tag{2.2.24}$$

at room temperature, so this means 8% of the energy put in went into pushing the atmosphere away.

3 Entropy and the 2nd Law

3.1 State Counting and Probability

Why do irreversible processes seem to occur, given that the laws of physics are reversible? The answer is that irreversible processes are overwhelmingly probable.

Two-State Systems, Microstates, and Macrostates

Let's go back to our bank robber scenario, taking it slow.

If I have a penny, a nickel, and a dime and a flip them, there are 8 possible outcomes. If the coins are fair, each has 1/8 probability. Note that there are 3 ways of getting 2 heads and a tail, so the probability of that outcome (2 heads and a tail) is 3/8. But if I care about whether the tail comes from the penny, nickel, or dime, then I might want to discriminate among those three outcomes. This sort of choice of what to discriminate, what to care about, or *what I can actually distinguish* plays an important role in stat mech. Note that

- A **microstate** is one of these 8 different outcomes.

- A **macrostate** ignores or 'coarse-grains' some of the information. So for example just giving information about how many heads there were, and ignoring which coin gave which H/T outcome, defines a macrostate.

- The number of microstates in a macrostate is called the **multiplicity** of the macrostate. We often use the symbol Ω for the multiplicity.

If we label macrostates by the number of heads n, then for $n = 0, 1, 2, 3$ we find

$$p(n) = \frac{\Omega(n)}{\Omega(all)} = \frac{1}{8}, \frac{3}{8}, \frac{3}{8}, \frac{1}{8} \tag{3.1.1}$$

How many total microstates are there if we have N coins? It's 2^N, as each can be H or T. What are the multiplicities of the macrostates with n heads with $N = 100$? Well note that

$$\Omega(0) = 1, \quad \Omega(1) = 100, \quad \Omega(2) = \frac{100 \times 99}{2}, \quad \Omega(3) = \frac{100 \times 99 \times 98}{3 \times 2} \tag{3.1.2}$$

In general we have

$$\Omega(n) = \frac{N!}{n!(N-n)!} \tag{3.1.3}$$

which is N choose n. So this gives us a direct way to compute the probability of finding a given number of heads, even in our bank robbery scenario where $N = 10^6$.

We can immediately make this relevant to physics by studying the simplest conceivable magnetic system, a **two-state paramagnet**. Here each individual magnetic dipole has only two states (because of QM), so it can only point up or down, and furthermore each dipole behaves as though its magnetic moment is independent of the others (they interact very weakly... in fact, in our approximation, they don't interact at all). Now H/T just becomes $\uparrow / \downarrow$, so a microstate is

$$\cdots \uparrow\uparrow\uparrow\downarrow\uparrow\downarrow\downarrow\uparrow\downarrow\downarrow\uparrow \cdots \tag{3.1.4}$$

while a macrostate is specified by the **total magnetization**, which is just $N_\uparrow - N_\downarrow = 2N_\uparrow - N$, and multiplicity

$$\Omega(N_\uparrow) = \frac{N!}{N_\uparrow! N_\downarrow!} \tag{3.1.5}$$

This really becomes physics if we apply an **external magnetic field**, so that the system has an energy corresponding with how many little dipoles are aligned or anti-aligned with the external field.

Silly Comments on Large Numbers

We saw that $N_A = 6.02 \times 10^{23}$. But if we have that many spins, and each can be up or down, then... we get really large numbers! Let's note what's worth keeping track of here, eg consider

$$10^{23} + 50 \tag{3.1.6}$$

or

$$8973497 \times 10^{10^{23}} \tag{3.1.7}$$

With very very large numbers, units don't even matter! Be very careful though, because in many calculations the very very large, or just very large numbers cancel out, and so you really do have to carefully keep track of pre-factors.

Important Math

Now we will derive the special case of a very universal result, which provides information about the aggregate distribution of many independent random events.

Since N is large, $N!$ is really large. How big? One way to approximate it is to note that

$$N! = e^{\log N!} = e^{\sum_{n=1}^{N} \log n} \tag{3.1.8}$$

Now we can approximate

$$\sum_{n=1}^{N} \log n \approx \int_0^N dx \log x = N(\log N - 1) \tag{3.1.9}$$

which says that

$$N! \sim N^N e^{-N} \tag{3.1.10}$$

This is the most basic part of *Stirling's Approximation* to the factorial. The full result is

$$N! \approx N^N e^{-N} \sqrt{2\pi N} \tag{3.1.11}$$

You can derive this more precise result by taking the large N limit of the exact formula

$$N! = \int_0^\infty x^N e^{-x} dx \tag{3.1.12}$$

That was a warm-up to considering the distribution of H/T, or spins in a paramagnet.

$$\begin{aligned}
\Omega(n) &= \frac{N!}{n!(N-n)!} \\
&\approx \frac{N^N e^{-N}}{n^n e^{-n}(N-n)^{N-n}e^{n-N}}
\end{aligned} \tag{3.1.13}$$

Now if we write $n = xN$ then this becomes

$$\begin{aligned}
\Omega(n) &\approx \frac{N^N}{x^{xN}N^{xN}(1-x)^{N(1-x)}N^{N(1-x)}} \\
&\approx \left(\frac{1}{x^x(1-x)^{(1-x)}}\right)^N \\
&\approx e^{N(-x\log x - (1-x)\log(1-x))}
\end{aligned} \tag{3.1.14}$$

The prefactor of N in the exponent means that this is very, very sharply peaked at its maximum, which is at $x = \frac{1}{2}$. Writing $x = \frac{1}{2} + y$ we have

$$-x\log x - (1-x)\log(1-x) = \log 2 - 2y^2 - \frac{4}{3}y^4 + \cdots \tag{3.1.15}$$

so that

$$\begin{aligned}
\Omega\left(n = \frac{1+y}{2}N\right) &\approx 2^N e^{-2Ny^2} \\
&\approx 2^N e^{-2\frac{(2n-N)^2}{N}}
\end{aligned} \tag{3.1.16}$$

This is a special case of the **central limit theorem**, which is arguably the most important result in probability and statistics. The distribution we have found is the **Gaussian Distribution**, or the 'bell curve'. Its key feature is its variance, which says intuitively that

$$n - \frac{N}{2} \lesssim \text{few} \times \sqrt{N} \tag{3.1.17}$$

where here $\sqrt{N}$ is the standard deviation. Thus we expect that $\frac{2n-N}{N} \lesssim \frac{1}{\sqrt{N}} \ll 1$.

This means that if we flip a million fair coins, we expect the difference between the number of heads and the number of tails to be of order 1000, and *not* of order $10,000$. And if the difference was only, say, 3, then we might be suspicious that the numbers are being faked.

Paramagnets and Random Walks

More relevantly for physics, this tells us that if we have $\sim 10^{23}$ dipoles in a paramagnet (recall Avogadro's number), with their dipole moments randomly arranged, then the total contribution to the magnetic moment we should expect is of order $\sim \sqrt{10^{23}} \approx 3 \times 10^{11}$. That seems like a big

number, but it's a *very small* fraction of the total, namely $\sim 10^{-11}$ fraction. Thus the difference between up and down spins is minute.

We have also largely solved the problem of a (1-dimensional) random walk. Note that 'heads' and 'tails' can be viewed as steps to the right or left. Then the total $n_H - n_T$ is just the number of steps taken to the right. This means that if we take N random steps, we should expect to be a distance of order $\sqrt{N}$ from our starting point. This is also an important, classic result.

3.2   Two Coupled Paramagnets

With two coupled paramagnets, we can study **heat flow** and irreversible processes.

But to have a notion of energy, we need to introduce a background magnetic field, so that $\uparrow$ has energy μ and $\downarrow$ has energy $-\mu$. Then if we have 100 magnetic moments in a Paramagnet, the energy of the system can range from

$$-100\mu, -98\mu, -96\mu, \cdots, 0, \cdots 98\mu, 100\mu \tag{3.2.1}$$

Note that there's a unique configuration with minimum and maximum energy, whereas there are $\frac{100!}{50!50!}$ configurations with energy 0.

So let's assume that we have two paramagnets, which can exchange energy between them by flipping some of the dipoles.

- We will treat the two paramagnets as **weakly coupled**, so that energy flows between them slowly and smoothly, ie energy exchange within each paramagnet is much faster than between the two. We'll call these energies U_A and U_B.

- $U_{total} = U_A + U_B$ is fixed, and we refer to the macrostate just via U_A and U_B. Note that the number of spins in each paramagnet N_A and N_B are fixed.

The total number of states is just

$$\Omega_{tot} = \Omega_A \Omega_B = \Omega(N_A, U_A)\Omega(N_B, U_B) \tag{3.2.2}$$

Now we will introduce the key **assumption of statistical mechanics**:

- In an isolated system in thermal equilibrium, all accessible (ie possible) microstates are equally probable.

A microstate might be inaccessible because it has the wrong energy, or the wrong values of conserved charges. Otherwise it's accessible.

Microscopically, if we can go from $X \to Y$, we expect we can also transition from $Y \to X$ (this is the principle of detailed balance). Really there are so many microstates that we can't possible 'visit' all of them, so the real assumption is that the microstates we do see are a **representative sample** of all the microstates. Sometimes this is called the 'ergodic hypothesis' – averaging over time is the same as averaging over all accessible states. This isn't obvious, but should seem plausible – we're assuming the transitions are 'sufficiently random'.

For simplicity, let's imagine that the total energy is $U_A + U_B = 0$, and the two paramagnets have $N_A = N_B = N$ dipoles each. How many configurations are there with all spins up in one paramagnet, and all spins down in the other? Just one! But with n up spins in the first paramagnet and $N - n$ up spins in the second, there are

$$
\begin{aligned}
\Omega_{tot} &= \Omega(N, (N-n)\mu)\Omega(N, (n-N)\mu) = \frac{(2N)!}{n!(N-n)!} \times \frac{(N)!}{n!(N-n)!} \\
&= \left(\frac{(N)!}{n!(N-n)!}\right)^2
\end{aligned}
\tag{3.2.3}
$$

Thus the number of states is vastly larger when $n = N$. In fact, we can directly apply our analysis of combinatorics to conclude that the number of states has an approximately Gaussian distribution with width $\sqrt{N}$.

Note that this is mathematically identical to the coin flipping example from the first lecture.

3.3   Another Example: 'Einstein Solid'

The book likes to use a simple toy model where a 'solid' is represented as a system of N identical but separate harmonic oscillators. They are treated as quantum oscillators, which means that they have energy

$$
E = \left(\frac{1}{2} + n\right)\hbar\omega
\tag{3.3.1}
$$

for some non-negative integer n. And actually we'll drop the $1/2$, as only energy differences are relevant. Also, since all energies are multiples of $\hbar\omega$, we'll just refer to this as an 'energy unit' and not keep track of it.

This wasn't Einstein's greatest achievement by any means, and it does not describe real solids. But it's an easy toy example to play with, as we'll see. More realistic models would require fancier combinatorics.

If the total ES has E units of energy and N oscillators, then the number of states is

$$
\Omega(N, E) = \frac{(E + N - 1)!}{E!(N-1)!}
\tag{3.3.2}
$$

Let's briefly check this for $N = 3$, then we have

$$
\Omega(3, 0) = 1, \quad \Omega(3, 1) = 3, \quad \Omega(3, 2) = 6, \quad \Omega(3, 3) = 10, \quad \cdots
\tag{3.3.3}
$$

We can prove our general formula by writing a configuration as

$$
\bullet|\bullet\bullet||\bullet\bullet\bullet\bullet|\bullet|\bullet\bullet|||\bullet\bullet
\tag{3.3.4}
$$

where $\bullet$ denote units of energy and $|$ denote transitions between oscillators. So this expression has $E = 12$ and $N = 9$. Thus we just have a string with $N - 1$ of the $|$ and E of the $\bullet$, we can put the $|$ and $\bullet$ anywhere, and they're indistinguishable.

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If this reasoning isn't obvious, first consider how to count a string of N digits, say $N = 7$. A configuration might be

$$4561327 \qquad (3.3.5)$$

and so it's clear that there are

$$7 \times 6 \times 5 \times 4 \times 3 \times 2 \times 1 = 7! \qquad (3.3.6)$$

configurations. But in the case of the $\bullet$ and $|$, there are only two symbols, so we divide to avoid over-counting identical configurations.

Two Coupled Einstein Solids

The formula for counting configurations for an Einstein solid is very (mathematically) similar to that for counting states of a paramagnet. But it's slightly different in its dependence on energy and number of oscillators.

If we fix $E = E_A + E_B$ for the two ESs, then the number of configurations is

$$
\begin{aligned}
\Omega_{tot} &= \frac{(E_A + N_A - 1)!}{E_A!(N_A - 1)!} \times \frac{(E_B + N_B - 1)!}{E_B!(N_B - 1)!} \\
&= \left(\frac{1}{(N_A - 1)!(N_B - 1)!} \right) \frac{(E_A + N_A - 1)!(E - E_A + N_B - 1)!}{E_A!(E - E_A)!}
\end{aligned}
\qquad (3.3.7)
$$

so we can study how many configurations there are as a function of E_A, where we fix the total energy E and the number of oscillators in each ES.

It's not so easy to get intuition about this formula directly, so let's approximate it. First we will just study $\Omega(E, N)$ itself. An interesting approximation is the high-temperature and (mostly) classical limit, where $E \gg N$, so that each oscillator will tend to have a lot of energy (that is E/N is large).

(If we view the 'pool' of total energy as very large, then we could assign each oscillator to have energy randomly chosen between 0 and $2E/N$, so that overall the total energy works out. This would give us $(2E/N)^N$ configurations, which is very close to the right answer.)

We already did the relevant math. But once again, using Stirling's formula

$$
\begin{aligned}
\log \frac{(E + N)!}{E!N!} &\approx (E + N)\log(E + N) - E - N - E\log E + E - N\log N + N \\
&\approx (E + N)\log(E + N) - E\log E - N\log N
\end{aligned}
\qquad (3.3.8)
$$

In the large E/N limit, we have

$$
\begin{aligned}
\log(E + N) &= \log E + \log\left(1 + \frac{N}{E}\right)(\\
&\approx \log E + \frac{N}{E}
\end{aligned}
\qquad (3.3.9)
$$

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This then gives that

$$\log \Omega \approx N \log \frac{E}{N} + N \tag{3.3.10}$$

which means that

$$\Omega(N, E) \approx e^N \left(\frac{E}{N} \right)^N \tag{3.3.11}$$

We can make sense of this by noting that this is roughly equal to the number of excited energy levels per oscillator, E/N, raised to a power equal to the number of oscillators.

Thus using this approximation, we see that

$$\Omega_{tot} \approx \left(\frac{E_A}{N_A} \right)^{N_A} \left(\frac{E - E_A}{N_B} \right)^{N_B} \tag{3.3.12}$$

This is maximized as a function of E_A when

$$E_A = \frac{N_A}{N_A + N_B} E \tag{3.3.13}$$

which is when the two ESs have energies proportional to the number of oscillators in each.

Repeating the math we used previously, we can parameterize

$$E_A = \frac{N_A}{N_A + N_B} E + x \tag{3.3.14}$$

and we find that

$$
\begin{aligned}
\Omega_{tot} &\approx \left(\frac{E}{N} + \frac{x}{N_A} \right)^{N_A} \left(\frac{E}{N} - \frac{x}{N_B} \right)^{N_B} \\
&\approx \exp \left[N_A \log \left(\frac{E}{N} + \frac{x}{N_A} \right) + N_B \log \left(\frac{E}{N} - \frac{x}{N_B} \right) \right] \left(\right. \\
&\approx \left(\frac{E}{N} \right)^N \exp \left[-\frac{N}{2 N_A N_B} \left(\frac{N x}{E} \right)^2 \right]
\end{aligned} \tag{3.3.15}
$$

Thus we see that we have another Gaussian distribution in x/ρ, where $\rho = E/N$ is the energy density. The exponent becomes large whenever $\frac{x}{\rho} > \sqrt{\frac{N_A N_B}{N}}$. This means that (assuming $N_A \sim N_B$) x/ρ is much much larger than 1, but much much smaller than N.

The punchline is that configurations that maximize Ω are **vastly more numerous** than those that do not, and that macroscopic fluctuations in the energy are therefore (beyond) astronomically unlikely. Specifically, since $N \gtrsim 10^{23}$ in macroscopic systems, we would need to measure energies to 11 sig figs to see these effects.

The limit where systems grow to infinite size and these approximations become arbitrarily good is called the **thermodynamic limit**.

3.4   Ideal Gases

All large systems – ie systems with many accessible states or degrees of freedom – have the property that only a tiny fraction of macrostates have reasonably large probabilities. Let us now apply this reasoning to the ideal gas. What is the multiplicity of states for an ideal gas?

In fact, in the ideal limit the atoms don't interact, so... what is the multiplicity of states for a single atom in a box with volume V?

If you know QM then you can compute this exactly. Without QM it would seem that there are an infinite number of possible states, since the atom could be anywhere (it's location isn't quantized!).

But we can get the right answer without almost any QM.

- First note that the number of states must be proportional to the volume V.

- But we can't specify a particle's state without also specifying its momentum. Thus the number of states must be proportional to the volume in momentum space, V_p.

Note that the momentum space volume is constrained by the total energy $\vec{p}^2 = 2mU$.

We also need a constant of proportionality, but in fact that's (essentially) why Planck's constant $\hbar$ exists! You may have heard that $\delta x \delta p > h/2$, ie this is the uncertainty principle. So we can write

$$\Omega_1 = \frac{V V_p}{h^3} \tag{3.4.1}$$

by dimensional analysis. You can confirm this more precisely if you're familiar with QM for a free particle in a box.

If we have two particles, then there are two added complications

- We must decide if the particles are distinguishable or not. For distinguishable particles we'd have Ω_1^2, while for indistinguishable particles we'd have $\frac{1}{2}\Omega_1^2$.

- We need to account for momentum conservation as $\vec{p}_1^2 + \vec{p}_2^2 = 2mU$. With more particles we have a sum over all of their momenta.

For N indistinguishable particles we have

$$\Omega_N = \frac{1}{N!} \frac{V^N}{h^{3N}} \times (\text{momentum hypersphere area}) \tag{3.4.2}$$

where the momentum hypersphere is the volume in momentum space, constrained by momentum conservation.

The surface area of a D-dimensional sphere is

$$A = \frac{2\pi^{D/2}}{(\frac{D}{2} - 1)!} R^{D-1} \tag{3.4.3}$$

We know that $R = \sqrt{2mU}$, where U is the total energy of the gas, and that $D = 3N$. Plugging this in gives

$$
\begin{aligned}
\Omega_N &= \frac{1}{N!} \frac{V^N}{h^{3N}} \frac{2\pi^{3N/2}}{\left(\frac{3N}{2} - 1\right)!} (2mU)^{\frac{3N-1}{2}} \\
&\approx \frac{1}{N!} \frac{\pi^{3N/2}}{\left(\frac{3N}{2}\right)!} \frac{V^N}{h^{3N}} (2mU)^{\frac{3N}{2}}
\end{aligned}
\tag{3.4.4}
$$

where we threw away some 2s and -1s because they are totally insignificant. This eliminates the distinction between 'area' and 'volume' in momentum space, because momentum space has the enormous dimension $3N$. With numbers this big, units don't really matter!

Note that we can write this formula as

$$
\Omega_N = f(N) V^N U^{3N/2}
\tag{3.4.5}
$$

so the dependence on Volume and Energy are quite simple.

Interacting Ideal Gases

Let's imagine that we have two ideal gases in a single box with a partition. Then we just multiply multiplicities:

$$
\Omega_{tot} = f(N)^2 (V_A V_B)^N (U_A U_B)^{3N/2}
\tag{3.4.6}
$$

Since $U_A + U_B = U_{tot}$, we see that multiplicity is maximized very sharply by $U_A = U_B = U_{tot}/2$. And the peaks are very, very sharp as a functions of U_A – we once again have a Gaussian distribution for fluctuations about this equilibrium. Though the exact result is the simpler function

$$
(x(1 - x))^P
\tag{3.4.7}
$$

for very, very large $P = 3N/2$. It should be fairly intuitive that this function is very sharply maximized at $x = 1/2$.

If the partition can move, then it will shift around so that

$$
V_A = V_B = V_{tot}/2
\tag{3.4.8}
$$

as well. This will happen 'automatically', ie the pressures on both sides will adjust to push the partition into this configuration. Once again, the peak is extremely sharp.

Finally, we could imagine $N_A \neq N_B$ to start, but we could poke a hole in the partition to see how the molecules move. Here the analysis is a bit more complicated – it requires using Stirling's formula again – but once again there's a very, very sharply peaked distribution.

Note that as a special case, putting all the molecules on one side is 2^{-N} less likely than having them roughly equally distributed. This case exactly like flipping N coins!

3.5   Entropy

We have now seen in many cases that the highest multiplicities macrostates are vastly, vastly more numerous than low-multiplicity microstates, and that as a result systems tend to evolve towards these most likely states. **Multiplicity tends to increase.**

For a variety of reasons, it's useful to replace the multiplicity with a smaller number, its logarithm, which is the **entropy**

$$S \equiv \log \Omega \tag{3.5.1}$$

For historical reasons, *in physics* we actually define

$$S \equiv k \log \Omega \tag{3.5.2}$$

where k is the largely meaningless but historically necessary Boltzmann constant.

Notice that because logarithms turn multiplication into addition, we have

$$S_{tot} = S_A + S_B \tag{3.5.3}$$

when $\Omega_{tot} = \Omega_A \times \Omega_B$. This is quite convenient for a variety of reasons. For one thing, the entropy is a much smoother function of other thermodynamic variables (ie it doesn't have an extremely sharp peak).

Since the logarithm is a monotonic function, the tendency of multiplicity to increase is the same thing as saying that **entropy tends to increase**:

$$\delta S \geq 0 \tag{3.5.4}$$

That's the 2nd law of thermodynamics!

Note that the 2nd law picks an arrow of time. That's a big deal. This arrow of time *really* comes from the fact that *initial conditions in the universe had low entropy.* (If you start with a low entropy final condition and run physics backwards, entropy would increase as time went backward, not forward.)

Can you oppose the 2nd law and decrease entropy through intelligence and will? No. You can work hard to decrease the entropy in one system, but always at the cost of far more entropy creation elsewhere. Maxwell discussed this idea as 'Maxwell's Demon'.

Entropy of an Ideal Gas

We can compute the entropy of an ideal gas from the multiplicity formula

$$
\begin{aligned}
S &= \log\left[\frac{1}{N!}\frac{\pi^{3N/2}}{(\frac{3N}{2})!}\frac{V^N}{h^{3N}}(2mU)^{\frac{3N}{2}}\right] \\
&= Nk\left[(1-\log N)+\frac{3}{2}\pi+\frac{3}{2}\left(1-\log\frac{3N}{2}\right)+\log\frac{V}{h^3}+\log 2mU\right] \\
&= Nk\left[\frac{5}{2}+\log\ \frac{V}{N}\left(\frac{4\pi mU}{3Nh^2}\right)^{3/2}\right] \\
&= Nk\left[\frac{5}{2}+\log\ \frac{1}{n}\left(\frac{4\pi mu}{3h^2}\right)^{3/2}\right]
\end{aligned}
\tag{3.5.5}
$$

where $u = U/N$ and $n = N/V$ are the energy density and number density, respectively. Apparently this is called the Sackur-Tetrode equation, but I didn't remember that.

What would this result have looked like if we had used distinguishable particles??? The problem associated with this is called the Gibbs paradox. We'll talk about **extensive** vs **intensive** quantities more thoroughly later.

Entropy dependence on volume (with fixed U and N) is simplest, ie just

$$
\Delta S = Nk\log\frac{V_f}{V_i}
\tag{3.5.6}
$$

Note that this makes sense in terms of doubling the volume and gas particles being in either the left or right half of the new container.

This formula applies both to **expansion that does work**, eg against a piston (where the gas does work, and heat flows in to replace the lost internal energy) and to **free expansion** of a gas. These are quite different scenarios, but result in the same change in entropy.

What about increasing the energy U while fixing V and N? Where did the exponent of $3/2$ come from, and why does it take that value?

Entropy of Mixing

Another way to create entropy is to mix two different substances together. There are many more states where they're all mixed up than when they are separated, so mixing creates entropy.

One way to think about it is if we have gas A in one side of a partition, and gas B on the other side, then when they mix they each double in volume, so we end up with

$$
\Delta S = (N_A+N_B)k\log 2
\tag{3.5.7}
$$

in extra entropy. It's important to note that this only occurs if the two gases are different (distinguishable).

Note that doubling the number of molecules of the same type of gas in a fixed volume does not double the entropy. This is because while out front $N \to 2N$, we also have the $\log \frac{1}{n} \to \log \frac{1}{2n}$, and so the change in the entropy is strictly less than a factor of 2.

(Now you may wonder if the entropy ever goes down; it doesn't, because for $N(X - \log N)$ to be a decreasing function of N, we must have $S < 0$, which means a multiplicity less than 1!)

In fact, the very definition of entropy strongly suggests that $S \geq 0$ always.

A Simple Criterion for Reversible Processes

Reversible processes must have

$$\Delta S = 0 \tag{3.5.8}$$

because otherwise they'd violate the second law of thermodynamics! Conversely, processes that create entropy $\Delta S > 0$ must be irreversible.

- Free expansion, or processes requiring heat exchange will increase entropy. We'll see soon that reversible changes in volume must be quasistatic with $W = -P\Delta V$, and no heat flow.

- From a quantum point of view, these quasistatic processes slowly change the energy levels of atoms in a gas, but they do not change the occupancy of any energy levels. This is what keeps multiplicity constant.

- We saw earlier that heat 'wants' to flow precisely because heat flow increases entropy (multiplicity). The only way for heat to flow without a change in entropy is if it flows extremely slowly, so that we can take a limit where multiplicity almost isn't changing.

To see what we mean by the last point, consider the entropy of two gases separated by a partition. As a function of the internal energies, the total entropy is

$$S_{tot} = \frac{3}{2}Nk \log \left((U_{tot} - \delta U)(U_{tot} + \delta U) \right) \tag{3.5.9}$$

So we see that as a function of δU, the multiplicity *does not change* when $\delta U \ll U_{tot}$. More precisely

$$\frac{\partial S_{tot}}{\partial \delta U} = 0 \tag{3.5.10}$$

at $\delta U = 0$. So if we keep δU infinitesimal, we can cause heat to move energy across the partition without any change in entropy or multiplicity. In fact, this idea will turn out to be important...

4 Interactions and Temperature

4.1 What is Temperature?

Early in the course we tentatively defined temperature as a quantity that's equal when two substances are in thermal equilibrium. And we know it has something to do with energy. But what is it really?

The only important ideas here are **entropy/multiplicity tend to increase** until we reach equilibrium, so they stop increasing when we're in equilibrium, and **energy can be shared, but total energy is conserved**.

If we divide our total system into sub-systems A and B, then we have $U_A + U_B = U_{tot}$ is fixed, and total entropy $S_{tot} = S_A + S_B$ is maximized. This means that

$$\frac{\partial S_{tot}}{\partial U_A}\bigg|_{equilibrium} = 0 \tag{4.1.1}$$

But

$$\begin{aligned}\frac{\partial S_{tot}}{\partial U_A} &= \frac{\partial S_A}{\partial U_A} + \frac{\partial S_B}{\partial U_A} \\ &= \frac{\partial S_A}{\partial U_A} - \frac{\partial S_B}{\partial U_B}\end{aligned} \tag{4.1.2}$$

where to get the second line we used energy conservation, $dU_A = -dU_B$. Thus we see that at equilibrium

$$\frac{\partial S_A}{\partial U_A} = \frac{\partial S_B}{\partial U_B} \tag{4.1.3}$$

So the **derivative of the entropy with respect to energy** is the thing that's the same between substances in thermal equilibrium.

If we look at units, we note that the energy is in the denominator, so it turns out that temperature is really defined to be

$$\frac{1}{T} \equiv \left(\frac{\partial S}{\partial U}\right)_{N,V} \tag{4.1.4}$$

where the subscript means that we're holding other quantities like the number of particles and the volume fixed.

Let's check something basic – does heat flow from larger temperatures to smaller temperatures? The infinitessimal change in the entropy is

$$\delta S = \frac{1}{T_A}\delta U_A + \frac{1}{T_B}\delta U_B = \left(\frac{1}{T_A} - \frac{1}{T_B}\right)\delta U_A \tag{4.1.5}$$

So we see that to increase the total entropy (as required by the 2nd law of thermodynamics), if $T_A < T_B$ then we need to have $\delta U_A > 0$ – that is, the energy of the low-temperature sub-system increases, as expected.

What if we hadn't known about entropy, but were just using multiplicity? Then we would have found that

$$\begin{aligned}\frac{\partial \Omega_{tot}}{\partial U_A} &= \frac{\partial \Omega_A}{\partial U_A}\Omega_B + \Omega_A\frac{\partial \Omega_B}{\partial U_A} \\ &= \Omega_A\Omega_B\left(\frac{1}{\Omega_A}\frac{\partial \Omega_A}{\partial U_A} - \frac{1}{\Omega_B}\frac{\partial \Omega_B}{\partial U_B}\right)\bigg(\end{aligned} \tag{4.1.6}$$

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and we would have *learned through this computation* that entropy was the more natural quantity, rather than multiplicity. I emphasize this to make it clear that **entropy isn't arbitrary**, but is actually a natural quantity in this context.

Note that we now have a **crank to turn** – whenever there's a quantity X that's **conserved**, we can consider what happens when two systems are brought into contact, and find the equilibrium configuration where $S(X_A, X_B)$ is maximized subject to the constraint that $X_A + X_B$ is constant. We can do this for X = Volume, Number of Particles, and other quantities.

Examples

For an Einstein Solid, we computed $S(U)$ a while ago and found

$$S = Nk \log \frac{u}{\epsilon} = Nk \log \frac{U}{N\epsilon} + Nk \tag{4.1.7}$$

where ϵ is some energy unit in the oscillators. So the temperature is

$$T = \frac{U}{Nk} \tag{4.1.8}$$

This is what the equipartition theorem would predict, since a harmonic oscillator has a kinetic energy and a potential.

More interestingly, for an monatomic ideal gas we found

$$S = Nk \log V + \frac{3}{2} Nk \log U + \log f(N) \tag{4.1.9}$$

Thus we find that

$$U = \frac{3}{2} NkT \tag{4.1.10}$$

which once again agrees with equipartition.

4.2 Entropy and Heat Capacity

We can use our newfound knowledge of temperature to define and understand the heat capacity. It's important to know what we're holding constant; at constant volume we define

$$C_V \equiv \left(\frac{\partial U}{\partial T} \right)_{N,V} \tag{4.2.1}$$

which you might also think of as the **energy capacity**.

For a monatomic ideal gas this is

$$C_V = \frac{\partial}{\partial T} \frac{3}{2} NkT = \frac{3}{2} Nk \tag{4.2.2}$$

which can be experimentally verified, though many systems have more exotic C_V.

In general, if you want to compute C_V you need to

1. Compute S in terms of U and other quantities.

2. Compute T from the derivative of S

3. Solve for $U(T)$, and then differentiate it.

We'll learn a quite different and often more efficient route in a few lectures.

Measuring Entropy via C_V

We can measure entropy, or at least entropy differences, using heat. As long as work $W = 0$, we have that

$$dS = \frac{dU}{T} = \frac{Q}{T} \tag{4.2.3}$$

So if we can measure T and Q then we know how much the entropy changed!

- If T stays constant than this works even for finite changes in S.

- If the volume is changing, but the process is quasistatic, then this rule also applies.

A related statement is that

$$dS = \frac{C_V dT}{T} \tag{4.2.4}$$

If the temperature does change, then we can just use $C_V(T)$, by thinking of the changes as tiny steps. So

$$\Delta S = \int_{T_i}^{T_f} \frac{C_V}{T} dT \tag{4.2.5}$$

In some examples C_V is approximately constant. For instance if we heat a cup of water from room temperature to boiling, we have

$$\Delta S \approx (840 \ J/K) \int_{293}^{373} \frac{1}{T} dT = (840 \ J/K) \log \frac{373}{293} \approx 200 J/K \approx 1.5 \times 10^{25} \tag{4.2.6}$$

In fundamental units this is an increase of 1.5×10^{25}, so that the multiplicity increases by a factor of $e^{\Delta S}$, which is a truly large number. This is about 2 per molecule.

If we knew C_V all the way down to zero, then we could compute

$$S_f - S(0) = \int_0^{T_f} \frac{C_V}{T} dT \tag{4.2.7}$$

So what is $S(0)$? Intuitively, it should be $S(0) = 0$, so that $\Omega = 1$, the unique lowest energy state. Unless there isn't a unique ground state.

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In practice many systems have **residual entropy** at (effective) $T \approx 0$, due to eg re-arrangements of molecules in a crystal that cost very, very little energy. There can also be residual entropy from **isotope mixing**. (Interestingly Helium actually re-arranges its isotopes at $T = 0$, as it remains a liquid.)

Note that to avoid a divergence in our definitions, it would seem that

$$C_V \to 0 \quad \text{as} \quad T \to 0 \tag{4.2.8}$$

This, and the statement that $S(0) = 0$, are both sometimes called the third law of thermodynamics. Apparently ideal gas formulas for heat capacities must be wrong as $T \to 0$, as we have already observed.

Historic View of Entropy

Historically $dS = Q/T$ was the definition of entropy used in thermodynamics. It was an important and useful quantity, even though no one knew what it was! Nevertheless, they got quite far using $\Delta S \geq 0$ as the 2nd law of thermodynamics.

4.3 Paramagnets – Everything You Know Is Wrong

Now we will solve the two-state paramagnet model. This is almost identical to the toy model with coin flipping from the very first day of class! However, we'll see some features that you may find very surprising.

The paramagnet is **ideal** in that it just consists of non-interacting dipoles. Also, we will invoke quantum mechanics to study **quantized** dipoles that can only point up or down:

$$\cdots \uparrow\uparrow\downarrow\uparrow\downarrow\downarrow\uparrow\downarrow\downarrow\uparrow \cdots \tag{4.3.1}$$

We've already counted the states in this system. So what we need to do is add energy (and energy conservation). The dipoles don't interact, so the only energy comes from assuming there's an external magnetic field, so that

$$U = \mu B(N_\downarrow - N_\uparrow) = \mu B(N - 2N_\uparrow) \tag{4.3.2}$$

The magnetization is just

$$M = -\frac{U}{B} \tag{4.3.3}$$

so it's proportional to the energy. Recall the multiplicity of states is

$$\Omega(N_\uparrow) = \frac{N!}{N_\uparrow! N_\downarrow!} \tag{4.3.4}$$

Note that we can solve for $N_\uparrow$ in terms of U via

$$N_\uparrow = \frac{N}{2} - \frac{U}{2\mu B} \tag{4.3.5}$$

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which means that $N_\uparrow = N/2$ for $U = 0$. Where is multiplicity maximized?

We see that as a function of energy U, multiplicity is maximized at $U = 0$, and it *goes down* when we increase or decrease U! This is very different from most other systems, as **typically multiplicity increases with energy**, but not here.

Let's draw the plot of $S(U)$. In the minimum energy state the graph is very steep, so the system wants to absorb energy, as is typical for systems at very low energy. But at $U = 0$ the slope goes to *zero*, so in fact that system stops wanting to absorb more energy. And then for $U > 0$ the slope becomes *negative*, so the paramagnet **wants to spontaneously give up energy**!

But remember that

$$T \equiv \left(\frac{\partial S}{\partial U}\right)^{-1} \tag{4.3.6}$$

Thus when $S'(U) = 0$, we have $T = \infty$. And when $S'(U) < 0$, we have that T **is negative**.

Note that *negative temperatures are* **larger** *than positive temperature*, insofar as systems at negative temperature give up energy more freely that systems at any positive temperature. When $|T|$ small and $T < 0$, temperature is at its effective maximum.

It's possible to actually do experiments on systems at negative temperature using nuclear paramagnets by simply flipping the external magnetic field. Nuclear dipoles are useful because they don't equilibrate with the rest of the system, so they can be studied in isolation.

Negative temperature can only occur in equilibrium for systems with bounded total energy and finite number of degrees of freedom.

Aside from simply demonstrating a new phenomenon, this example is useful for emphasizing that **entropy is more fundamental than temperature**.

Explicit Formulae

It's straightforward to apply Stirling's approximation to get an analytic solution for large N.

The entropy is

$$S \approx N \log N - N_\uparrow \log N_\uparrow - (N - N_\uparrow) \log(N - N_\uparrow) \tag{4.3.7}$$

To get the temperature we just have

$$\frac{1}{T} = \left(\frac{\partial S}{\partial U}\right)_{N,B} = \frac{\partial N_\uparrow}{\partial U} \frac{\partial S}{\partial N_\uparrow} = -\frac{1}{2\mu B} \frac{\partial S}{\partial N_\uparrow} \tag{4.3.8}$$

Then the last derivative can be evaluated giving

$$\frac{1}{T} = \frac{k}{2\mu B} \log \frac{N - U/\mu B}{N + U/\mu B} \tag{4.3.9}$$

where T and U have opposite signs, as expected. Solving for U gives

$$U = -N\mu B \tanh \frac{\mu B}{kT}, \quad M = N\mu \tanh \frac{\mu B}{kT} \tag{4.3.10}$$

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Then the heat capacity at constant magnetic field is

$$C_B = \left(\frac{\partial U}{\partial T}\right)_{N,B} = Nk\left(\frac{\mu B}{kT}\right)^2 \frac{1}{\cosh^2\left(\frac{\mu B}{kT}\right)} \tag{4.3.11}$$

This goes to zero very fast at both low and high temperature, and is maximized at $T \to \infty$ (with either sign).

All this work wasn't for nothing. For physical magnets at room temperature, $kT \approx 0.025eV$, while if $\mu = \mu_B \approx 5.8 \times 10^{-5}eV/T$ is the Bohr magneton (the value for an electron), then $\mu B \sim 10^{-5}eV$ even for strong magnets. Thus $\mu B/(kT) \ll 1$. In that limit

$$\tanh x \approx x \tag{4.3.12}$$

and so we see that the magnetization is

$$M \approx N\mu\left(\frac{\mu B}{kT}\right) \tag{4.3.13}$$

which is called Curie's law, as it was discovered experimentally by Pierre Curie. At high temperature this works for all paramagnets, even those with a fundamenatlly more complicated description (eg with more than two states, and some interactions).

4.4   Mechanical Equilibrium and Pressure

Next we would like to consider systems whose volumes can change through interaction. The idea is that **exchange of volumes should be related to pressure through the entropy**. We're turning the crank!

So let's imagine two gases separated by a movable partition. The gases can exchange both energy and volume, but total energy and volume are fixed.

Total entropy should be maximized, so we expect that

$$\frac{\partial S_{total}}{\partial V_A} = 0 \tag{4.4.1}$$

By the same analysis that led to temperature, we can re-write this as

$$\frac{\partial S_A}{\partial V_A} - \frac{\partial S_B}{\partial V_B} = 0 \tag{4.4.2}$$

since $V_A + V_B = V_{total}$ is fixed, and the entropy of the full system is the sum of the individual entropies. Thus we conclude that

$$\frac{\partial S_A}{\partial V_A} = \frac{\partial S_B}{\partial V_B} \tag{4.4.3}$$

at equilibrium, and so we should expect this to have a simple relationship with the pressure! Note this is at *fixed energy and fixed number of particles*, and we are assuming that we are also in thermal

equilibrium. If the partition were to move without this assumption, energies would not be fixed, and things would be more complicated.

Since $T_A = T_B$ and $T \times S$ has units of energy, we can identify the pressure by

$$P = T \left(\frac{\partial S}{\partial V} \right)_{U,N} \tag{4.4.4}$$

where we are free to multiply by T since we are in thermal equilibrium.

Let's check this in an example. For an ideal gas we have that

$$S = Nk \log V + \cdots \tag{4.4.5}$$

where the ellipsis denotes functions of U and N that are independent of V. So we find that

$$P = T \frac{\partial}{\partial V} (Nk \log V) = \frac{NkT}{V} \tag{4.4.6}$$

So we have derived the ideal gas law! Or alternatively, we have verified our expression for the pressure in a familiar example.

Thermodynamic Identity

We can summarize the relation between entropy, energy, and volume by a thermodynamic identity. Let's consider how S changes if we change U and V a little. This will be

$$dS = \left(\frac{\partial S}{\partial U} \right)_V dU + \left(\frac{\partial S}{\partial V} \right)_U dV \tag{4.4.7}$$

where we fix volume when we vary U, and fix U when we vary the volume. We can recognize these quantities and write

$$dS = \frac{1}{T} dU + \frac{P}{T} dV \tag{4.4.8}$$

This is most often written as

$$dU = TdS - PdV \tag{4.4.9}$$

This is true for any system where T and P make sense, and nothing else is changing (eg number of particles). This formula reminds us how to compute everything via partial derivatives.

Heat and Entropy

The thermodynamic identity looks a lot like energy conservation, ie

$$dU = Q + W \tag{4.4.10}$$

where we interpret $Q \sim TdS$ and $W \sim -PdV$. Can we make this precise?

Not always. This is true if the volume changes *quasistatically*, if there's no other work done, and if no other relevant variables are changing. Then we know that $W = -PdV$, so that

$$Q = TdS \quad \text{(quasistatic)} \tag{4.4.11}$$

This means that $\Delta S = Q/T$, even if there's work being done. If the temperature changes, we can still compute

$$(\Delta S)_P = \int\!\!\!\int \left(\frac{C_P}{T} dT\right) \tag{4.4.12}$$

if the process is quasistatic.

Also, if $Q = 0$, then the entropy doesn't change. In other words

$$\text{quasistatic} + \text{adiabatic} = \text{isentropic} \tag{4.4.13}$$

We'll note later that isentropic processes are interesting.

What about exceptions, which abound? Say we hit a piston really hard. Then the work done on the gas is

$$W > -PdV \tag{4.4.14}$$

because we hit the molecules harder than in a quasistatic process. However, we can choose to only move the piston infinitesimally, so that the

$$dS = \frac{dU}{T} + \frac{P}{T} dV > \frac{Q}{T} \tag{4.4.15}$$

This is really just a way of saying that we're doing work on the gas while keeping V constant, and so U, T, and S will increase. It looks like compression work but it's 'other' work.

A more interesting example is **free expansion** of the gas into a vacuum. No work is done and no heat flows, but S increases.

It's easy to create more entropy, with or without work and heat. But we can't ever decrease it.

4.5 Diffusive Equilibrium and Chemical Potential

We're turning the crank again, this time using conservation of particle number!

Let's consider two systems that can share particle number. The usual logic tells us that

$$\frac{\partial S_A}{\partial N_A} = \frac{\partial S_B}{\partial N_B} \tag{4.5.1}$$

in equilibrium, where the partial derivatives are at fixed energy and volume.

We can multiply by $-T$ to get the conventional object **chemical potential**

$$\mu \equiv -T \left(\frac{\partial S}{\partial N}\right)_{U,V} \tag{4.5.2}$$

This is the quantity that's the same for two systems in equilibrium. It's the potential for sharing particles.

Since we added a minus sign, if two systems aren't in equilibrium the one with **smaller** μ **gains particles**. This is like temperature. Particles flow towards low chemical potential.

We can generalize the thermodynamic identity as

$$dS = \frac{1}{T}dU + \frac{P}{V}dV - \frac{\mu}{T}dN \tag{4.5.3}$$

where the minus sign comes from the definition. Thus

$$dU = TdS - PdV + \mu dN \tag{4.5.4}$$

Sometimes we refer to μdN as the 'chemical work'.

The general thermodynamic identity is useful for remembering the relations between various thermodynamic quantities. For example note that

$$dU = \mu dN \tag{4.5.5}$$

which provides another way to think about μ as

$$\mu = \left(\frac{\partial U}{\partial N}\right)_{S,V} \tag{4.5.6}$$

This is how much energy changes when we add a particle and keep S, V fixed.

Usually to add particles without changing S, you need to remove energy. But if you need to give the particle potential energy to add it, this contributes to μ.

Let's compute μ for an ideal gas. We take

$$S = Nk\left[\log\ V\left(\frac{4\pi mU}{3h^2}\right)^{3/2}\right) - \log N^{5/2}\right] \tag{4.5.7}$$

Thus we have

$$\begin{aligned} \mu &= -Tk\left[\log\ V\left(\frac{4\pi mU}{3h^2}\right)^{3/2}\right) - \log N^{5/2}\right] + TNk\frac{5}{2N} \\ &= -kT\log\left[\frac{V}{N}\left(\frac{4\pi mU}{3Nh^2}\right)^{3/2}\right] \\ &= -kT\log\left[\frac{V}{N}\left(\frac{2\pi mkT}{h^2}\right)^{3/2}\right] \end{aligned} \tag{4.5.8}$$

where at the end we used $U = \frac{3}{2}NkT$.

For gas at room temperature and atmospheric pressure, $V/N \approx 4 \times 10^{-26} m^3$, whereas the other factor is, for helium, about $10^{-31} m^3$ and so the logarithm is 12.7, and $\mu = -0.32$ eV for helium at 300 K, 10^5 N/m.

Increasing the density of particles increases the chemical potential, as particles don't 'want' to be there.

So far we used only one particle type, but with many types we have a chemical potential for each. If two systems are in diffusive equilibrium all the chemical potentials must be the same.

So we see that through the idea of maximizing entropy/multiplicity, we have been led to define T, P, and μ, and the relation

$$dU = TdS - PdV + \mu dN \tag{4.5.9}$$

for classical thermodynamics.

4.6 Extensive and Intensive Quantities

There's an important distinction that we've alluded to but haven't discussed directly, between **extensive** and **intensive** quantities. The distinction is whether the quantity doubles when we double the amount of stuff, or if it stays the same. So extensive quantities are

$$V, N, S, U, H, \text{mass} \tag{4.6.1}$$

while intensive quantities are

$$T, P, \mu, \text{density} \tag{4.6.2}$$

If you multiply note that

$$\text{extensive} \times \text{intensive} = \text{extensive} \tag{4.6.3}$$

for example volume $\times$ density $=$ mass. Conversely, if the ratios of extensive quantities will be intensive.

Note that *you should never add an intensive and an extensive quantity* – this is often wrong by dimensional analysis, but in cases where it's not, it also doesn't make sense conceptually.

So intensive/extensive is like a new kind of dimensional analysis that you can use to check what you're calculating.

5 Engines and Refrigerators

A **heat engine** absorbs heat energy and turns it into work. Note that this doesn't include electric motors, which turn electricity and mechanical work. **Internal combustion engines** in cars officially don't absorb heat, rather they produce it from combustion, but we can treat them as though the heat was coming from outside.

Engines can't convert heat into work perfectly. As we'll see, the reason is that absorbing heat increases the entropy of the engine, and if its operating on a **cycle**, then it must somehow get rid of that entropy before it can cycle again. This leads to inefficiency. Specifically, the engine must dump **waste heat** into the environment, and so only some of the heat it initially absorbed can be converted into work.

We can actually say a lot about this without knowing anything specific about how the engine works. We can just represent it with a **hot reservoir**, the engine itself, and a **cold reservoir**.

Energy conservation says that

$$Q_h = W + Q_c \tag{5.0.1}$$

and that the efficiency is

$$e = \frac{W}{Q_h} = 1 - \frac{Q_c}{Q_h} \tag{5.0.2}$$

This already says that efficiency is at most 1. We can get a stronger bound using the 2nd law of thermodynamics.

Note that the entropy extracted from the hot reservoir is

$$S_h = \frac{Q_h}{T_h} \tag{5.0.3}$$

while the entropy absorbed by the cold reservoir is

$$S_c = \frac{Q_c}{T_c} \tag{5.0.4}$$

Thus we must have $S_c - S_h \geq 0$ or

$$\frac{Q_c}{T_c} \geq \frac{Q_h}{T_h} \tag{5.0.5}$$

but this implies

$$\frac{Q_c}{Q_h} \geq \frac{T_c}{T_h} \tag{5.0.6}$$

This then tells us that

$$e = 1 - \frac{Q_c}{Q_h} \leq 1 - \frac{T_c}{T_h} \tag{5.0.7}$$

This is the famous Carnot bound on the efficiency of heat engines.

Most engines are significantly less efficient than this, because they produce excess entropy, often through the heat transfer processes themselves. Note that to be maximally efficient, the engine has to be at T_h and T_c during each transfer!

Carnot Cycle

The arguments above also suggest how to build a maximally efficient engine – at least in theory. Let's see how it would work.

The basic point is that **we don't want to produce excess entropy**. This means that

- heat transfers must happen exactly at T_h and T_c

- there shouldn't be any other heat transfers

This basically fixes the behavior the engine, as pointed out by Sadi Carnot in 1824.

To have heat transfers exactly at T_h and T_c, we must expand or contract the gas **isothermally**. To otherwise not produce any entropy, we should have **adiabatic** expansion and contraction for the other parts of the cycle, ie with $Q = 0$. That's how we get the gas from T_h to T_c and back.

You should do problem 4.5 to check that this all works out, but based on our understanding of energy conservation and the 2nd law of thermodynamics, it should actually be 'obvious' that this is a maximally efficient engine.

Note that Carnot engines are extremely impractical, because they must operate extremely slowly to avoid producing excess entropy.

It's easier to draw the Carnot cycle in T and S space rather than P and V space.

5.1   Refrigerators

Theoretically, a refrigerator is just a heat engine run in reverse.

We define the coefficient of performance of a refrigerator as

$$COP = \frac{Q_c}{W} = \frac{Q_c}{Q_h - Q_c} = \frac{1}{\frac{Q_h}{Q_c} - 1} \tag{5.1.1}$$

We *cannot* just use the inequality from our discussion of engines, because heat flows in the opposite direction.

Instead, the entropy dumped into the hot reservoir must be at least as large as that drawn from the cold reservoir, which means that

$$\frac{Q_h}{T_h} \geq \frac{Q_c}{T_c} \tag{5.1.2}$$

so that

$$\frac{Q_h}{Q_c} \geq \frac{T_h}{T_c} \tag{5.1.3}$$

This then tells us that

$$COP \leq \frac{1}{\frac{T_h}{T_c} - 1} = \frac{T_c}{T_h - T_c} \tag{5.1.4}$$

So in theory we can refrigerate very, very well when $T_c \approx T_c$. This should be intuitive, because in this limit we need not transfer almost any entropy while transferring heat.

Conversely, if $T_c \ll T_h$ then the performance is very poor. It takes an immense amount of work to cool something towards absolute zero.

It should also be clear from the way we derived it that the maximally efficient refrigerator would be a Carnot cycle run in reverse.

Brief Timeline

Carnot came up with ingenius arguments that engines couldn't be more efficient than the Carnot cycle, and that they must always produce waste heat. But he didn't distinguish very clearly between entropy and heat. Clausius defined entropy (and coined the term) clearly as Q/T, but he didn't know what it really was. Boltzmann mostly figured this out by 1877.

5.2   Real Heat Engines

Let's discuss some real heat engines.

Internal combustion engines fill a chamber with fuel and air, then combust it, expanding the gas and pushing the piston; then the material vents and is replaced with lower temperature/pressure gas, the piston compresses, and the cycle starts again. This is called the **Otto cycle**. Notice there's no hot reservoir, but combustion behaves the same way.

We can idealize this with **fixed volume** changes in pressure and **adiabatic** compression and expansion operations.

Let's compute the efficiency, recalling that $V^\gamma P = $ constant where γ is the adiabatic exponent, where $\gamma = 1 + \frac{2}{f}$. On the adiabats, no heat is exchanged, so *all heat exchanges occur at constant volume*. This means that when the heat is exchanged, no work is done, and so *the heat is equal to the change in internal energy of the gas*. Thus we have that

$$Q_h = \frac{f}{2} Nk(T_3 - T_2) \tag{5.2.1}$$

and

$$Q_c = \frac{f}{2} Nk(T_4 - T_1) \tag{5.2.2}$$

so that the efficiency is

$$e = \frac{T_3 - T_4 - T_2 + T_1}{T_3 - T_2} = 1 - \frac{T_4 - T_1}{T_3 - T_2} \tag{5.2.3}$$

It turns out that this simplifies nicely, using the fact that on adiabats

$$T_3 V_2^{\gamma-1} = T_4 V_1^{\gamma-1} \tag{5.2.4}$$

and

$$T_1 V_1^{\gamma-1} = T_2 V_2^{\gamma-1} \tag{5.2.5}$$

This leads to

$$e = 1 - \frac{rT_3 - rT_2}{T_3 - T_2} = 1 - r \tag{5.2.6}$$

where $r = \left(\frac{V_2}{V_1}\right)^{\gamma-1}$. So in other words, the overall efficiency is

$$e = 1 - \left(\frac{V_2}{V_1}\right)^{\gamma-1} \tag{5.2.7}$$

For air $\gamma = 7/5$ and we might have $V_2/V_1 = 8$, so that the efficiency is around 56%.

Recall that $TV^{\gamma-1}$ is fixed on an adiabat, so to compare this efficiency with Carnot we can solve for V ratios in terms of T ratios, and we find

$$e = 1 - \frac{T_1}{T_2} = 1 - \frac{T_4}{T_3} \tag{5.2.8}$$

which doesn't involve the extreme temperatures, so it less efficient than Carnot. In practice real gasoline engines are 20-30% efficient.

You can get greater efficiency with higher compression ratio, but the fuel will pre-ignite once it gets too hot. We can take advantage of this using **diesel engines**, which simply use heat from compression to ignite the mixture. They spray the fuel/air mixture as the piston starts to move outward, meaning that (to some approximation) they have a constant volume and a constant pressure piece in their cycles, which means computing their efficiency is more complicated. They ultimately have higher efficiency (around 40%) using very high compression ratios, which are limited by not melting the engine.

Steam Engines

See the tables and diagrams in the book.

These use a **Rankine** cycle, and go outside the ideal gas regime, as the steam condenses!

Here water gets pumped in, heats into steam and pushes a turbine (as it cools and decreases in pressure), then is condensed back into water.

We can't compute the efficiency from first principles. But under constant pressure conditions, the heat absorbed is equal to the change in enthalpy H. So t we can write the efficiency as

$$e = 1 - \frac{Q_c}{Q_h} = 1 - \frac{H_4 - H_1}{H_3 - H_2} \approx 1 - \frac{H_4 - H_1}{H_3 - H_1} \tag{5.2.9}$$

where the last approximation is good because the pump adds very little energy to the water, and the PV term is small for liquids.

There are tables called 'steam tables' that simply list the enthalpies and entropies of steam, water, and water-steam mixtures in various conditions. We need the entropies because for the steam+water mixture, we only get H by using the fact that $3 \to 4$ is an adiabat, so $S_3 = S_4$, allowing us to use the S values of the tables to get H.

5.3 Real Refrigerators

Real refrigerators follow a cycle much like the inverse of the Rankine cycle. The working substance changes back and forth between a liquid and a gas. That liquid-gas transition (boiling point) must be much lower in a refrigerator though, because we want to get to lower temperatures.

A variety of fluids have been used, including carbon dioxide, ammonia (dangerous), Freon, and now HFC-134a.

The PV diagram involves first from 1 the gas is compressed adiabatically, raising P and T. Then from 2 to 3 it gives up heat and liquefies in the condenser. Then from 3 to 4 it passes through a throttling valve – a narrow opening – emerging on the other side at much lower pressure and temperature. Finally it absorbs heat and turns back into a gas in the evaporator.

We can write the COP using enthalpies

$$COP = \frac{Q_c}{Q_h - Q_c} = \frac{H_1 - H_4}{H_2 - H_3 - H_1 + H_4} \tag{5.3.1}$$

Enthalpies at $1, 2, 3$ can be looked up, with point 2 we can assume S is constant during compression. We can understand point 4 by thinking more about throttling.

Throttling

Throttling, or the Joule-Thomson process involves pushing a fluid through a tiny hole or plug from a region with pressure P_i to one with pressure P_f. Initial and final volumes are V_i and V_f. There is no heat flow, so

$$U_f - U_i = Q + W = 0 + W_{left} + W_{right} \tag{5.3.2}$$

which gives

$$U_f - U_i = P_i V_i - P_f V_f \tag{5.3.3}$$

or

$$U_f + P_f V_f = U_i + P_i V_i \tag{5.3.4}$$

or just conservation of enthalpy.

The purpose is to cool the fluid below the cold reservoir temperature, so it can absorb heat. This wouldn't work if the fluid were an ideal gas, since $H = \frac{f+2}{2} NkT$.

But in a dense gas or liquid, the energy contains a potential term which decreases (due to attractive forces) when the molecules get close together. So

$$H = U_{pot} + U_{kin} + PV \tag{5.3.5}$$

and so as the gas molecules get further apart, U_{pot} increases, and the kinetic energy and temperature tend to decrease.

If we use $H_3 = H_4$ in refrigeration, then we have

$$COP = \frac{H_1 - H_3}{H_2 - H_1} \tag{5.3.6}$$

and so we just need to look up the enthalpies.

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Cooling MORE

See the book for some fun reading.

- You can make dry ice by liquifying CO_2 at higher pressure, then when you throttle you get dry ice frost residue.

- Making liquid Nitrogen is more difficult. You can just throttle for a while, but you need to start at higher pressure.

- Then you need to do it more efficiently, so you can use a heat exchanger to cool one gas as another is throttled.

However, throttling isn't good enough for hydrogen or helium, as these gases become hotter when throttled. This is because attractive interactions between gas molecules are very weak, so interactions are dominated by positive potential energies (repulsion). Hydrogen and Helium were first liquified in 1898 and 1908 respectively.

One can use further evaporative cooling to get from 4.2 K (boiling point of helium at 1 atm) to about 1 K. To go even further need

- A helium dilution refrigerator, where ^{3}He evaporates into a liquid bath with ^{4}He. We use the ^{3}He to take heat from the ^{4}He. This can get us from 1K to a few milliK.

- Magnetic cooling using

$$M = N\mu \tanh \frac{\mu B}{kT} \tag{5.3.7}$$

where we start with mostly up spins, and then smoothly decrease B, so that T also decreases as the population of up and down spins stays the same. This is analogous to cooling of an ideal gas by adiabatic expansion, following isothermal compression. We can't get to 0K this way due to dipole-dipole interactions, ie an imperfect paramagnet.

- There's also laser cooling.

6 Thermodynamic Potentials

Forces push us towards minima of energies. Probability pushes us towards maximization of entropy. Are there **thermodynamic potentials** mixing U and S that combine to tell us how a system will tend to change?

And a related question – we have seen that enthalpy H is useful when we are in an environment with constant pressure. What if instead we're connected to a **reservoir at constant** T? Perhaps there's a natural way to account for heat transfer to and from this reservoir, just as H automatically accounts for work due to the ambient pressure?

Let's assume the environment acts as a reservoir of energy, so that it can absorb or release unlimited energy without any change in its temperature. If S_R is the reservoir entropy, then

$$dS_{total} = dS + dS_R \geq 0 \tag{6.0.1}$$

by the 2nd law.

We would like to *eliminate the reservoir*. For this, let's use the thermodynamic identity for the reservoir

$$dS_R = \frac{1}{T}dU_R + \frac{P}{T}dV_R - \frac{\mu}{T}dN_R \tag{6.0.2}$$

and let's hold V_R and N_R fixed, so only energy can be exchanged. Then we can write

$$dS_{total} = dS + \frac{1}{T}dU_R \tag{6.0.3}$$

since $T_R = T$. But energy is conserved, so we have that

$$dS_{total} = dS - \frac{1}{T}dU = -\frac{1}{T}(dU - TdS) = -\frac{1}{T}dF \tag{6.0.4}$$

where we define the **Helmholtz free energy** as

$$F = U - TS \tag{6.0.5}$$

We have defined it with a minus sign because now we have that

$$dF \leq 0 \tag{6.0.6}$$

which means that F can only **decrease**. So it's a kind of 'potential' such that we can only move to lower and lower values of F at fixed T, V, N.

And now we can just ignore the reservoir and account for the 2nd law using F. The system will just try to minimize F.

We can play the same game letting the volume of the system change, and working at constant pressure, so that

$$dS_{total} = dS - \frac{1}{T}dU - \frac{P}{T}dV = -\frac{1}{T}(dU - TdS + PdV) = -\frac{1}{T}dG \tag{6.0.7}$$

where

$$G = U - TS + PV \tag{6.0.8}$$

and we work at constant T and constant P. Thus in this case its the **Gibbs free energy** that must decrease.

We can summarize this as

- At constant U and V, S increases.

- At constant T and V, F tends to decrease.

- At constant T and P, G tends to decrease.

All three assume no particles enter or leave, though one can also make even more potentials if we consider diffusion of particles.

We can think about this directly by just noting that in

$$F \equiv U - TS \tag{6.0.9}$$

S 'wants' to increase, and (one may think that) U 'wants' to decrease. The latter is only because it can give energy to the environment, and thereby increase the total entropy of the universe.

Wait what? Here what's happening is that if U decreases without S increasing, then this means that the entropy of the system isn't changing – but the entropy of the environment will definitely change by $\frac{dU}{T}$. So the fact that objects 'want' to roll down hills (and then not roll back up again!) ultimately comes from the 2nd law of thermodynamics.

Note also that the desire to give away energy isn't very great if T is large, since then the system may not want to do this and risk 'losing valuable entropy'. This is one way of seeing that at high temperature, our system will have a lot of energy.

Reasoning for the Gibbs free energy

$$G \equiv U + PV - TS \tag{6.0.10}$$

is similar, except that the environment can also 'take' volume from the system.

Why Free Energy?

We can also interpret F and G as analogues to H – these are the amount of energy needed to create a system, minus the heat-energy that we can get for free from the environment. So for example in

$$F = U - TS \tag{6.0.11}$$

we see that we can get heat $Q = T\Delta S = TS$ from the environment for free when we make the system.

Conversely, F is the amount of energy that comes out as work if we annihilate the system, because we have to dump some heat $Q = TS$ into the environment just to get rid of the systems entropy. So the available or 'free' energy is F.

Above we meant all work, but if we're in a constant pressure environment then we get some work for free, and so in that context we can (combining H and F, in some sense) define

$$G = U - TS + PV \tag{6.0.12}$$

which is the systems energy, minus the heat term, plus the work the constant P atmosphere will automatically do.

We call U, H, F, G thermodynamic potentials, which differ by adding PV or $-TS$. They are all useful for considering changes in the system, and changes in the relevant potential. Note that

$$\Delta F = \Delta U - T\Delta S = Q + W - T\Delta S \tag{6.0.13}$$

If no new entropy is created then $Q = T\Delta S$, otherwise $Q < T\Delta S$, and so we have

$$\Delta F \leq W \tag{6.0.14}$$

at constant T. This includes all work done on the system. Similarly, we find that

$$\Delta G \leq W_{other} \tag{6.0.15}$$

at constant T, P, where W_{other} includes work done other than by pressure.

Changes in H, F, G are very useful to know, and so are tabulated by chemists and engineers. We rarely talk about their absolute values, since that would include all of the energy (even $E = mc^2$ energy), so instead these quantities are usually viewed as changes from a convenient reference point.

More Thermodynamic Identities and Legendre Transforms

We learned the identity

$$dU = TdS - PdV + \mu dN \tag{6.0.16}$$

In this sense we are automatically thinking about U as a function of S, V, N, since its these quantities that we're directly varying.

We can use this plus the definitions of H, F, G to write down *a ton* of other thermodynamic identities. The math that we use is the 'Legendre transform'. Given a convex function $f(y)$, it makes it possible to effectively 'switch variables' and treat $f'(y) = x$ as the independent variable. See 0806.1147 for a nice discussion.

Say we have a function so that its differential is

$$df = xdy \tag{6.0.17}$$

Then if we consider a new function

$$g = xy - f \tag{6.0.18}$$

then we have

$$dg = ydx + xdy - df = ydx \tag{6.0.19}$$

So now we can instead use our new function $g(x)$ in place of $f(y)$.

For example, perhaps instead of using the entropy $S(E)$ as a function of E, we would instead like to make $\frac{\partial S}{\partial E} = \frac{1}{T}$, ie the temperature, the independent variable. That way we can use T as our 'knob' instead of E, perhaps because we can control T but not E.

Although it may seem a bit mysterious – and the number of possibilities is rather mystifying – we can apply these ideas very directly. For example since

$$H = U + PV \tag{6.0.20}$$

we have

$$dH = dU + PdV + VdP \tag{6.0.21}$$

and so we can write

$$\begin{aligned} dH &= TdS - PdV + \mu dN + PdV + VdP \\ &= TdS + \mu dN + VdP \end{aligned} \tag{6.0.22}$$

so we can think of the enthalpy as a function of S, N, P. We traded V for P and switched from energy U to enthalpy H.

We can really go to town and do this for all the thermodynamic potentials. For example, for F we find

$$dF = -SdT - PdV + \mu dN \tag{6.0.23}$$

and this tells us how F changes as we change T, V, N, and also that F is naturally dependent on those variables. We also have

$$dG = -SdT + VdP + \mu dN \tag{6.0.24}$$

and we get other identities from it.

Gibbs Free Energy and Chemical Potential

Combining the previous results with the idea of intensive/extensive variables, we can derive a cute fact about G.

Recall that

$$\mu = \left(\frac{\partial G}{\partial N}\right)_{T,P} \tag{6.0.25}$$

This says that adding particles at fixed T, P simply increases G by μ.

You might think that μ changes as you change N, but this can't happen with T, P fixed, because G is an extensive quantity that must grow proportionally to μ. Thus we see that

$$G = N\mu \tag{6.0.26}$$

an amazingly simple relation, which provides a new interpretation for G and μ.

Our argument was subtle – why doesn't it apply to

$$\mu = \left(\frac{\partial F}{\partial N}\right)_{T,V} \tag{6.0.27}$$

The reason is that with fixed V, as you change N the system becomes more and more dense. So an intensive quantity is changing as you change N, namely the density N/V. It was crucial in the case of G that all fixed quantities were intensive.

With more types of particles, we just have $G = \sum_i N_i \mu_i$. Note though that μ_i for a mixture are *not* equal to μ_i for a pure substance.

We can use this to get a formula for μ for an ideal gas. Using the fact that

$$V = \left(\frac{\partial G}{\partial P}\right)_{T,N} \tag{6.0.28}$$

we see that

$$\frac{\partial \mu}{\partial P} = \frac{1}{N}\frac{\partial G}{\partial P} = \frac{V}{N} \tag{6.0.29}$$

But by the ideal gas law this is kT/P. So we can integrate to get

$$\mu(T, P) - \mu(T, P_0) = kT \log\left(\frac{P}{P_0}\right) \tag{6.0.30}$$

for any reference P_0, usually atmospheric pressure.

This formula also applies to each species independently in a mixture, if P is the partial pressure of that species. This works because ideal gases are non-interacting – that's essentially what makes them ideal.

Example Application of G – Electrolysis & Batteries

Let's consider the electrolysis process

$$H_2O \rightarrow H_2 + \frac{1}{2}O_2 \tag{6.0.31}$$

We'll assume we start with a mole of water.

Reference tables say that $\Delta H = 286$ kJ for this reaction. It turns out $P\Delta V = 4$ kJ to push the atmosphere away, the remaining 282 kJ remains in the system. But do we have to supply all of the 286 kJ as work, or can some enter as heat?

For this we need to look at the entropies for a mole of each species

$$S_{H_2O} = 70\,J/K, \quad S_{H_2} = 131\,J/K, \quad S_{O_2} = 205\,J/K \tag{6.0.32}$$

So during the reaction we have an entropy change of

$$S_{H_2} + \frac{1}{2}S_{O_2} - S_{H_2O} \tag{6.0.33}$$

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and so the maximum amount of heat that can enter the system is

$$T\Delta S = (298K)(163 J/k) = 49 kJ \tag{6.0.34}$$

So the electrical work we need to do is 237 kJ. Thi sis the ΔG of the Gibbs free energy:

$$\Delta G = \Delta H - T\Delta S \tag{6.0.35}$$

Standard tables include this information. If you perform the reaction in reverse, you can get ΔG of energy out.

The same reasoning applies to batteries. For example lead-acid cells in car batteries run the reaction

$$Pb + PbO_2 + 4H^+ + 2SO_4^{2-} \rightarrow 2PbSO_4 + 2H_2O \tag{6.0.36}$$

Tables say $\Delta G = -390$ kJ/mol in standard conditions, so per mole of metallic lead we get 390 kJ from the battery.

Note that $\Delta H = -312$ kJ/mol for this reaction, so we actually get extra energy from heat absorbed from the environment! When we charge the battery and run the reaction in reverse, we have to put the extra 78 kJ of heat back into the environment.

You can also compute the battery voltage if you know how many electrons get pushed around per reaction. For this reaction 2 electrons get pushed through the circuit, so the electrical work per electron is

$$\frac{390 kJ}{2 \times N_A} = 3.24 \times 10^{-19} J = 2.02 eV \tag{6.0.37}$$

A volt is the voltage needed to give an electron 1 eV, so the voltage is 2.02 V. Car batteries have six cells to get to 12 V.

7 Partition Functions and Boltzmann Statistics

Now we will develop some more powerful tools for studying general systems.

Specifically, we will obtain a formula for the **probability** of a finding any system in a given microstate, assuming that the system is in equilibrium with a reservoir of temperature T.

7.1 Boltzmann Factors

We'll consider an analysis that applies to any system. But since Hydrogen atoms tend to be familiar, we can phrase the analysis in terms of a single electron in some hydrogen atom orbital.

A central point is that we are not considering a truly isolated system, but one that it's contact with a 'thermal bath', ie some other system with a great deal of energy and entropy, and fixed temperature T.

Let's simplify by considering the ratio of probabilities to be in two specific microstates of interest, s_1 and s_2, with energies $E(s_1), E(s_2)$ and probabilities $P(s_1), P(s_2)$. How can we find the ratio?

We know that for an *isolated* system, all accessible microstates are equally probable. Our atom isn't isolated, but the atom + reservoir system is isolated. We expect that we're equally likely to find this combined system in any microstate.

The reservoir will have $\Omega_R(s_1)$ available microstates when the atom is in s_1, and $\Omega_R(s_2)$ microstates when the atom is in s_2. These will be different because the reservoir has more or less energy, and thus it has access to more or less states. Since all states in total are equally likely, the ratio of probabilities must be

$$\frac{P(s_2)}{P(s_1)} = \frac{\Omega_R(s_2)}{\Omega_R(s_1)} \tag{7.1.1}$$

So we just need to write the right-side in a more convenient form that doesn't make reference to the reservoir.

Note that something a bit surprising happened – because multiplicity depends so strongly on states and energies, changing our single atom's state just a bit actually had a significant effect on the multiplicity of a giant reservoir of energy. This contrasts with most questions in physics, where the state of a single atom has almost no relevance to the behavior of a large reservoir.

But that's easy by noting that

$$\frac{P(s_2)}{P(s_1)} = \frac{e^{S_R(s_2)}}{e^{S_R(s_1)}} = e^{S_R(s_2)-S_R(s_1)} \tag{7.1.2}$$

Now we can use the thermodynamic identity

$$dS_R = \frac{1}{T}(dU_R + PdV_R - \mu dN_R) \tag{7.1.3}$$

We can write all of these changes in terms of properties of the atom!

We know dN_R really is zero here, because reservoir particle number isn't changing. We will set $dV_R = 0$, even though in principle it may change, because the change in it is very tiny (eg a million times smaller than the term we'll keep).

This then leads to

$$S_R(s_2) - S_R(s_1) = \frac{1}{T}[U_R(s_2) - U_R(s_1)] = -\frac{1}{T}[E(s_2) - E(s_1)] \tag{7.1.4}$$

Notice this is another situation where defining the natural quantity as $\beta = 1/T$ might have been more convenient. Anyway, we find that

$$\frac{P(s_2)}{P(s_1)} = \frac{e^{-\frac{E(s_2)}{kT}}}{e^{-\frac{E(s_1)}{kT}}} \tag{7.1.5}$$

So the ratio strongly suggests that we can simply define a universal **Boltzmann factor** of

$$e^{-E(s)/kT} \tag{7.1.6}$$

as the proportionality factor for any given state s with energy $E(s)$.

Note that probabilities aren't equal to this factor because they also have to add up to 1! And so we need to divide by the sum of all Boltzmann factors, including all states. We call that sum over these factors

$$Z = \sum_s e^{-\frac{E(s)}{kT}} \tag{7.1.7}$$

the **partition function**. The true probabilities are

$$P(s) = \frac{1}{Z} e^{-\frac{E(s)}{kT}} \tag{7.1.8}$$

This is perhaps the most important fact or formula in statistical mechanics.

The partition function Z itself is extremely useful. Notice that while it doesn't depend on any one state (since it depends on all states and energies), it does depend on the temperature. It essentially **counts** the effective number of states that are accessible; for that interpretation we just set $E = 0$ for the ground state.

Notice that when we think about statistical mechanics using Boltzmann factors, Temperature plays a more fundamental role.

Example - Hydrogen in the Sun

The sun's atmosphere has a temperature around 5800 K. The relative probability of finding an atom in a its first excited state as compared to the ground state is

$$e^{-(E_2 - E_1)/kT} \tag{7.1.9}$$

with $\delta E = 10.2$ eV, and we have $kT = 0.5$ eV (note that an eV is about $10,000$ K). So the ratio of probabilities is about $e^{-20.4} \approx 1.4 \times 10^{-9}$. Since there are four excited states, the portion in the first excited state is about about 5×10^{-9}.

Atoms in the atmosphere of the sun can be absorbed if they can induce a transition between states. A hydrogen atom in the first excited state can transition *up in energy* to give the Balmer series, which give missing wavelengths in sunlight. Some other lines are also missing due to other kinds of atoms, but these transition from their ground state. So there must be way more hydrogen than other atoms in the sun's atmosphere!

7.2 Average or Expectation Values

We saw that the probability to be in a given state is

$$P(s) = \frac{e^{-\beta E(s)}}{Z} \tag{7.2.1}$$

Given the probability to be in any given state, we can easily (in principle) compute the average or **expectation value** for any quantity $f(s)$. Formally this means that

$$
\begin{aligned}
\bar{f} &= \sum_s P(s) f(s) \\
&= \frac{1}{Z} \sum_s e^{-\beta E(s)} f(s) \\
&= \frac{\sum_s e^{-\beta E(s)} f(s)}{\sum_s e^{-\beta E(s)}}
\end{aligned}
\tag{7.2.2}
$$

For example, the simplest thing we might want to know about is the average energy itself, ie $f(s) = E(s)$. Thus we have that

$$
\bar{E} = \frac{\sum_s e^{-\beta E(s)} E(s)}{\sum_s e^{-\beta E(s)}}
\tag{7.2.3}
$$

for the average energy.

The average energy is actually easier to compute because

$$
\bar{E} = -\frac{1}{Z} \frac{\partial Z}{\partial \beta}
\tag{7.2.4}
$$

as we can easily check by explicit computation. That's why I wrote the partition function in the way I did.

Note that **expectation values are additive**, so the average total energy of two objects is the sum of their individual average energies. So if you have a collection of identical particles

$$
U = N\bar{E}
\tag{7.2.5}
$$

This means that in many cases, working atom-by-atom is no different than studying the whole system (if we only care about averages).

7.2.1 Paramagnets

For paramagnets, there's just up and down dipole moment, so

$$
\begin{aligned}
Z &= e^{-\beta(-\mu B)} + e^{-\beta(+\mu B)} = e^{\beta(\mu B)} + e^{-\beta(\mu B)} \\
&= 2\cosh(\beta \mu B)
\end{aligned}
\tag{7.2.6}
$$

and so we can easily compute the up and down probabilities. The average energy is

$$
\bar{E} = -\frac{1}{Z} \frac{\partial Z}{\partial \beta} = -\mu B \tanh(\beta \mu B)
\tag{7.2.7}
$$

which is what we found before. We also get the Magnetization right.

7.2.2 Rotation

A more interesting example is the rotational motion of a diatomic molecule.

In QM, rotations are quantized with total angular momentum $j\hbar$. The energy levels are

$$E(j) = j(j+1)\epsilon \tag{7.2.8}$$

for some fixed energy ϵ inversely proportional to the molecules moment of inertia. The number of energy levels at angular momentum j is $2j+1$. (Here we are assuming the two ends of the molecule are non-identical.)

Given this structure, we can immediately write the partition function

$$\begin{aligned} Z &= \sum_{j=0}^{\infty}(2j+1)e^{-E(j)/kT} \\ &= \sum_{j=0}^{\infty}(2j+1)e^{-j(j+1)\frac{\epsilon}{kT}} \end{aligned} \tag{7.2.9}$$

Unfortunately we can't do the sum in closed form, but we can approximate it.

Note that for a CO molecule, $\epsilon = 0.00024$ eV, so that $\epsilon/k = 2.8$ K. Usually we're interested in much larger temperatures, so that $\epsilon/kT \ll 1$. This is the classical limit, where the quantum spacing doesn't matter much. Then we have

$$Z \approx \int_0^{\infty}(2j+1)e^{-j(j+1)\frac{\epsilon}{kT}}\,dj = \frac{kT}{\epsilon} \tag{7.2.10}$$

when $kT \gg \epsilon$. As one might expect, the partition function increases with temperature. Now we find

$$\bar{E} = -\frac{\partial \log Z}{\partial \beta} = kT \tag{7.2.11}$$

Differentiating with respect to T gives the contribution to the heat capacity per molecule

$$C_V \supset \frac{\partial \bar{E}}{\partial T} = k \tag{7.2.12}$$

as expected for 2 rotational DoF. Note that this only holds for $kT \gg \epsilon$; actually the heat capacity goes to zero at small T.

If the molecules are made of indistinguishable atoms like H_2 or O_2, then turning it around gives back the same molecule, and there are half as many rotatational degrees of freedom. Thus we have

$$Z = \frac{kT}{2\epsilon} \tag{7.2.13}$$

The extra $1/2$ cancels out when we compute the average energy, so it has no effect on heat capacity. At low temperatures we need to more carefully consider QM to get the right answer.

7.2.3 Very Quantum System

What if we have a very quantum system, so that energy level splittings are much larger than kT? Then we have

$$Z \approx 1 + e^{-\beta E_1} \tag{7.2.14}$$

where E_1 is the lowest excited state, and we are assuming $E_n > E_1 \gg kT$. Note that the expectation of the energy is

$$\bar{E} = 0 + E_1 e^{-\beta E_1} = E_1 e^{-\beta E_1} \tag{7.2.15}$$

where we have set the energy of the ground state to 0 as our normalization.

We also have that

$$\frac{\partial \bar{E}}{\partial T} = \frac{E_1 e^{-\frac{E_1}{kT}}}{kT^2} \tag{7.2.16}$$

It may appear that as $T \to 0$ this blows up, but actually it goes to zero very rapidly, because exponentials dominate power-laws. For comparison note that $x^n e^{-x} \to 0$ as $x \to \infty$, this is just the $x \to 1/x$ version of that statement.

7.2.4 This is Powerful

Anytime we know the energy levels of a system, we can do statistical mechanics. This is usually much more efficient than using combinatorics to count states, then determine $S(E)$, and then figure out T-dependence from there.

7.3 Equipartition

We have discussed the equipartition theorem... now let's derive it.

Recall that it doesn't apply to all systems, but just to quadratic degrees of freedom with energies like

$$E = kq^2 \tag{7.3.1}$$

where $q = x$ as in a harmonic oscillator, or $q = p$ as in the kinetic energy term. We'll just treat q as the thing that parameterizes states, so that different q corresponds to a different independent state.

This leads to

$$\begin{aligned} Z &= \sum_q e^{-\beta E(q)} = \sum_q e^{-\beta k q^2} \\ &\approx \int_{-\infty}^{\infty} e^{-\beta k q^2} dq \end{aligned} \tag{7.3.2}$$

Really the *latter* should be the definition in the classical limit, but we might also imagine starting with a QM description with discrete q and smearing it out. Anyway, we can evaluate the integral by a change of variables to $x = \sqrt{\beta k}q$ so that

$$Z \approx \frac{1}{\sqrt{\beta k}} \int_{-\infty}^{\infty} e^{-x^2} dx \tag{7.3.3}$$

The integral is just some number, so we're free to write

$$Z = \frac{C}{\sqrt{\beta}} \tag{7.3.4}$$

for some new number C. Note that $C = \sqrt{\frac{\pi}{k}} \frac{1}{\Delta q}$ where Δq indicates the possible QM discreteness of q.

Now the average energy is

$$\bar{E} = -\frac{\partial \log Z}{\partial \beta} = \frac{1}{2} kT \tag{7.3.5}$$

which is the equipartition theorem. Notice that k and Δq drop out. But that only works because we assumed Δq was very small, in particular so that

$$kq\Delta q, \ k\Delta q^2 \ll kT \tag{7.3.6}$$

This is just the statement that we can take the classical limit, because energy level spacings are small.

7.4   Maxwell Speed Distribution

As another application of Boltzmann factors, we can determine the distributions of speeds in a gas. From equipartition we already know that

$$v_{rms} = \sqrt{\frac{3kT}{m}} \tag{7.4.1}$$

but that's only an average (or more precisely, a **moment** of the distribution). With Boltzmann factors we can just write down the distribution itself.

Here we are really computing a probability density, which gives a probability $P(\vec{v})d^3\vec{v}$ or $P(s)ds$ for speed. So the integral gives the probability that v lies in some interval. Here $P(\vec{v})$ or $P(s)$ is a probability **distribution function**. Note that its only $P(s)ds$ that has the right units for probability.

By the way, the moments of the distribution would be

$$\int_0^{\infty} ds \, s^n P(s) \tag{7.4.2}$$

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where this is the nth moment. The v_{rms} is the square root of the 2nd moment.

The Boltzmann factor for a gas molecule is the simple

$$e^{-\frac{m\vec{v}^2}{2kT}} \tag{7.4.3}$$

using the usual formula for kinetic energy. But if we want to compute the probability distribution for speed $P(s)$, we need to account for the dimensionality of space. This means that we have

$$P(s) \propto \iint_{|\vec{v}|=s} d^2\vec{v}\, e^{-\frac{m\vec{v}^2}{2kT}} = 4\pi s^2 e^{-\frac{m\vec{v}^2}{2kT}} \tag{7.4.4}$$

We used proportional to because we need to normalize. For that we need to compute the constant N such that

$$
\begin{aligned}
N &= \int_0^\infty ds\, 4\pi s^2 e^{-\frac{m\vec{v}^2}{2kT}} \\
&= 4\pi \left(\frac{2kT}{m}\right)^{3/2} \int_0^\infty x^2 e^{-x^2} dx
\end{aligned} \tag{7.4.5}
$$

Thus we have that

$$
\begin{aligned}
P(v) &= \frac{1}{N} 4\pi s^2 e^{-\frac{m\vec{v}^2}{2kT}} \\
&= \left(\frac{m}{2\pi kT}\right)^{3/2} 4\pi s^2 e^{-\frac{m\vec{v}^2}{2kT}}
\end{aligned} \tag{7.4.6}
$$

This is the Maxwell distribution for the speeds of molecules. It may look complicated, but its just a Boltzmann factor times a geometric factor.

Note that this distribution is very asymmetric, insofar as it's parabolic at small v, where its geometry-dominated, but exponential (Gaussian) at large v, where it falls off exponentially fast.

Note that the most common, mean, and average speeds are all different. We have

$$v_{max} = \sqrt{\frac{2kT}{m}} \tag{7.4.7}$$

The mean speed (1st moment) is

$$\bar{v} = \int_0^\infty ds\, sP(s) = \sqrt{\frac{8kT}{\pi m}} \tag{7.4.8}$$

So we have $v_{max} < \bar{v} < v_{rms}$.

7.5   Partition Function and Free Energy

We began the course focused on the multiplicity Ω and $S = \log \Omega$, which tends to increase. These are the fundamental quantities for an isolated system.

For a system at temperature T (in contact with a reservoir), the partition function $Z(T)$ is the fundamental quantity. We know that $Z(T)$ is proportional to the number of accessible states. Since $Z(T)$ should (thus) tend to increase, its logarithm will tend to increase too. This suggests a relationship with $-F$, where F is the Helmholtz free energy. In fact

$$F = -kT \log Z, \quad Z = e^{-F/kT} \tag{7.5.1}$$

One could even take this as the definition of F. Instead, we'll derive it from our other definition

$$F = U - TS \tag{7.5.2}$$

To derive the relationship with Z, note that

$$\left(\frac{\partial F}{\partial T}\right)_{V,N} = -S = \frac{F - U}{T} \tag{7.5.3}$$

This is a differential equation for F. Let's show that $-kT \log Z$ satisfies this differential equation, and with the same initial condition.

Letting $\tilde{F} = -kT \log Z$, we have that

$$\frac{\partial \tilde{F}}{\partial T} = -k \log Z - kT \frac{\partial}{\partial T} \log Z \tag{7.5.4}$$

but

$$\frac{\partial}{\partial T} \log Z = \frac{U}{kT^2} \tag{7.5.5}$$

This then tells us that $\tilde{F}$ obeys the correct differential equation.

They also agree at $T = 0$, since both F and $\tilde{F}$ will be 1, as the system will just be in its ground state. So they are the same thing.

One reason why this formula is so useful is that

$$S = -\frac{\partial F}{\partial T}, \quad P = -\frac{\partial F}{\partial V}, \quad \mu = \frac{\partial F}{\partial N} \tag{7.5.6}$$

where we fix the T, V, N we aren't differentiating with respect to. So from Z we can get all of these quantities.

7.6 From Laplace Transforms to Legendre Transforms

Let's consider another derivation/explanation of the relationship between F and Z.

Note that $e^{S(E)}$ is the multiplicity of states at energy E. Thus

$$\begin{aligned} Z &= \sum_s e^{-E(s)/kT} \\ &= \int_0^\infty dE \, e^{S(E) - \frac{E}{kT}} \end{aligned} \tag{7.6.1}$$

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From this perspective, the statement that

$$F = -kT \log Z \tag{7.6.2}$$

is equivalent to the statement that we can just view

$$
\begin{aligned}
Z &= \int_0^\infty dE \, e^{S(E) - \frac{E}{kT}} \\
&\approx e^{S(U) - \frac{U}{kT}}
\end{aligned}
\tag{7.6.3}
$$

That is, somehow we have simply forgotten about the integral! What's going on? Have we made a mistake?

The reason why this is alright is that the function

$$e^{S(E) - \frac{E}{kT}} \tag{7.6.4}$$

will be very, very sharply peaked at the energy $U = \bar{E}$. Its so sharply peaked that its integral is simply **dominated by the value at the peak**. This 'sharply peaked' behavior is *exactly* what we spent the first couple of weeks of class going on and on about. So

$$F = -kT \log Z = U - TS \tag{7.6.5}$$

is actually true because we are taking averages in the thermodynamic limit.

This provides a new perspective on thermodynamic potentials. That is, if we work in the **microcanonical ensemble**, that is the ensemble of states with fixed energy U, then its natural to study the multiplicity

$$\Omega(U) = e^{S(U)} \tag{7.6.6}$$

and expect that systems in equilibrium will maximize this quantity. But we can introduce a temperature by 'averaging over states' weighted by a Boltzmann factor. This puts us in the **canonical ensemble**, the ensemble of states of all energies with fixed average energy. And it's simply given by taking the **Laplace transform** with respect to energy

$$Z(\beta) = \int_0^\infty dE \, e^{-\beta E} e^{S(E)} \tag{7.6.7}$$

where $\beta = 1/kT$ as usual. Notice that we have traded a function of energy U for a function of temperature T, just as in the Legendre transform discussion. This isn't a coincidence!

The statement that this is dominated by its maximum also implies that the **canonical and microcanonical ensembles** are the same thing in the thermodynamic limit. Further, it tells us that since

$$-kT \log Z = U - TS(U) \tag{7.6.8}$$

we learn that the **Legendre transform is just the thermodynamic limit of the Laplace transform**. This is a useful way to think about Legendre transforms in thermodynamics.

We can obtain all the other thermodynamic potentials, and all of the other Legendre transforms, in exactly this way.

8 Entropy and Information

8.1 Entropy in Information Theory

We have been thinking of entropy as simply

$$S = \log \Omega \tag{8.1.1}$$

But for a variety of reasons, it's more useful to think of entropy as a **function of the probability distribution** rather than as depending on a number of states.

If we have Ω states available, and we believe the probability of being in any of those states is **uniform**, then this probability will be

$$p_i = \frac{1}{\Omega} \tag{8.1.2}$$

for any of the states $i = 1, \cdots, \Omega$. So we see that

$$S = -\log p \tag{8.1.3}$$

for a uniform distribution with all $p_i = p = 1/\Omega$. But notice that this can also be viewed as

$$S \equiv -\sum_i p_i \log p_i \tag{8.1.4}$$

since all p_i are equal, and their sum is 1 (since probabilities are normalized). We have not yet demonstrated it for distributions that are not uniform, but this will turn out to be the most useful general notion of entropy. It can also be applied for continuous probability distributions, where

$$S \equiv -\int dx\, p(x) \log p(x) \tag{8.1.5}$$

Note that $0 \log 0 = 0$ (this is what we find from a limit).

This arises in information theory as follows. Say we have a long sequence of 0s and 1s, ie

$$\cdots 011100101000011 \cdots \tag{8.1.6}$$

If this is truly a fully random sequence, then the number of possibilities is 2^N if it has length N, and the entropy is just the log of this quantity. This also means that the entropy per bit is

$$S_{bit} = \frac{1}{N} \log 2^N = \log 2 \tag{8.1.7}$$

But what if we know that in fact 0s occur with probability p, and 1s with probability $1 - p$? For a long sequence, we'll have roughly pN of the 0s, so this means that the number of such messages will be

$$\frac{N!}{(pN)!((1-p)N)!} \approx \frac{N^N}{(pN)^{pN}(N-pN)^{N-pN}}$$

$$= \left(\frac{1}{p^p(1-p)^{1-p}}\right)^N = e^{NS_{bit}} \tag{8.1.8}$$

where we see that

$$S_{bit} = -p \log p - (1-p) \log(1-p) \tag{8.1.9}$$

So the entropy S that we've studied in statistical mechanics, ie the log of the number of possible sequences, naturally turns into the definition in terms of probability distributions discussed above.

This has to do with information theory because NS quantifies *the amount of information we actually gain by observing the sequence.* Notice that as Warren Weaver wrote in an initial popularization of Shannon's ideas:

- "The word information in communication theory is not related to what you do say, but to what you could say. That is, information is a measure of one's freedom of choice when one selects a message."

8.2 Choice, Uncertainty, and Entropy

Shannon showed in his original paper that entropy has a certain nice property. It characterizes how much 'choice' or 'uncertainty' or 'possibility' there is in a certain random process. This should seem sensible given that we just showed that entropy counts the amount of information that a sequence can carry.

Let's imagine that there are a set of possible events that can occur with probabilities $p_1, \cdots, p_n$. We want a quantity that measures how much 'possibility' there is in these events. For example, if $p_1 = 1$ and the others are 0, then we'd expect there's no 'possibility'. While if $n \gg 1$ and the p_i are uniform, then 'almost anything can happen'. We want a quantitate measure of this idea.

We will show that entropy is the unique quantity $H(p_i)$ with the following natural properties:

1. H is continuous in the p_i.

2. If all p_i are equal, so that all $p_i = 1/n$, then H should increase with n. That is, having more equally likely options increases the amount of 'possibility' or 'choice'.

3. If the probabilities can be broken down into a series of events, then H must be a weighted sum of the individual values of H. For example, the probabilities for events A, B, C

$$\{A, B, C\} = \left\{ \frac{1}{2}, \frac{1}{3}, \frac{1}{6} \right\} (\tag{8.2.1}$$

can be rewritten as the process

$$\{A, B \text{ or } C\} = \left\{ \frac{1}{2}, \frac{1}{2} \right\} \left(\text{then} \quad \{B, C\} = \left\{ \frac{2}{3}, \frac{1}{3} \right\} (\tag{8.2.2}$$

We are requiring that such a situation follows the rule

$$H\left(\frac{1}{2}, \frac{1}{3}, \frac{1}{6} \right) = H\left(\frac{1}{2}, \frac{1}{2} \right) (+ \frac{1}{2} H\left(\frac{2}{3}, \frac{1}{3} \right) (\tag{8.2.3}$$

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We will show that up to a positive constant factor, the entropy S is the only quantity with these properties.

Before we try to give a formal argument, let's see why the logarithm shows up. Consider

$$H\left(\frac{1}{4},\frac{1}{4},\frac{1}{4},\frac{1}{4}\right) = H\left(\frac{1}{2},\frac{1}{2}\right) + 2\frac{1}{2}H\left(\frac{1}{2},\frac{1}{2}\right)$$
$$= 2H\left(\frac{1}{2},\frac{1}{2}\right) \tag{8.2.4}$$

Similarly

$$H\left(\frac{1}{8},\cdots,\frac{1}{8}\right) = 3H\left(\frac{1}{2},\frac{1}{2}\right) \tag{8.2.5}$$

and so this is the origin of the logarithm. To really prove it, we will take two fractions, and note that $\frac{1}{s^n} \approx \frac{1}{t^m}$ for sufficiently large n and m. The only other point we then need is that we can approximate any other numbers using long, large trees.

Here is the formal proof. Let

$$A(n) \equiv H\left(\frac{1}{n},\cdots,\frac{1}{n}\right) \tag{8.2.6}$$

for n equally likely possibilities. By using an exponential tree we can decompose a choice of s^m equally likely possibilities into a series of m choices among s possibilities. So

$$A(s^m) = mA(s) \tag{8.2.7}$$

We have the same relation for some t and n, ie

$$A(t^n) = nA(t) \tag{8.2.8}$$

By taking arbitrarily large n we can find an n, m with $s^m \le t^n < s^{m+1}$, and so by taking the logarithm and re-arranging we can write

$$\frac{m}{n} \le \frac{\log t}{\log s} \le \frac{m}{n} + \frac{1}{n} \tag{8.2.9}$$

which means that we can make

$$\left|\frac{m}{n} - \frac{\log t}{\log s}\right| < \epsilon \tag{8.2.10}$$

Using monotonicity we have that

$$mA(s) \le nA(t) < (m+1)A(s) \tag{8.2.11}$$

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So we also find that

$$\left| \frac{m}{n} - \frac{A(t)}{A(s)} \right| < \epsilon \tag{8.2.12}$$

and so we conclude via these relations that

$$A(t) = K \log t \tag{8.2.13}$$

for some positive constant K, since we can make ϵ arbitrarily small.

But now by continuity we are essentially done, because we can approximate any set of probabilities p_i arbitrarily well by using a very fine tree of equal probabilities.

Notice that the logarithm was picked out by our assumption 3 about the way that H applies to the tree decomposition of a sequence of events.

8.3   Other Properties of Entropy

These properties all make sense in the context of information theory, where S counts the uncertainty or possibility.

1. S = 0 only if there's a single outcome.

2. S is maximized by the uniform distribution.

3. Suppose there are two events, x and y, where at each event n and m possibilities can occur, respectively. The full joint entropy is

$$S(x, y) = \sum_{i,j} p(i, j) \log p(i, j) \tag{8.3.1}$$

whereas there are partial entropies

$$S(x) = \sum_{i,j} p(i,j) \log \sum_{j} p(i,j)$$

$$S(y) = \sum_{i,j} p(i,j) \log \sum_{i} p(i,j) \tag{8.3.2}$$

Then we have the inequality

$$S(x, y) \leq S(x) + S(y) \tag{8.3.3}$$

with equality only if the two events are independent, so that $p(i, j) = p(i)p(j)$.

4. Any change in the probabilities that makes them more uniform increases the entropy. More quantitatively, if we perform an operation

$$p_i' = a_{ij} p_j \tag{8.3.4}$$

where $\sum_i a_{ij} = \sum_j a_{ij} = 1$ and $a_{ij} > 0$, then S increases. This means that if x and y are correlated, the total entropy is always less than or equal to the sum of the entropies from x and y individually.

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8.4 A More Sophisticated Derivation of Boltzmann Factors

Boltzmann factors can be derived in another simple and principled way – they are the probabilities that **maximize the entropy given the constraint that the *average* energy is held fixed**. We can formalize this with some Lagrange multipliers, as follows.

We want to fix the expectation value of the energy and the total probability while maximizing the entropy. We can write this maximization problem using a function (Lagrangian)

$$L = -\sum_i p_i \log p_i + \beta \left(\langle E \rangle - \sum_i p_i E_i \right) + \nu \left(\sum_i p_i - 1 \right) \tag{8.4.1}$$

where we are maximizing/extremizing L with respect to the p_i and β, ν; the latter are Lagrange multipliers.

Varying gives the two constraints along with

$$-\log p_i - 1 - \beta E_i + \nu = 0 \tag{8.4.2}$$

which implies that

$$p_i = e^{\nu - 1 - \beta E_i} \tag{8.4.3}$$

Now ν just sets the total sum of the p_i while β is determined by the average energy itself. So we have re-derived Boltzmann factors in a different way. This derivation also makes it clear what abstract assumptions are important in arriving at $e^{-\beta E}$.

8.5 Limits on Computation

In practice, computation has a number of inefficiencies. Despite decades of progress, my impression is that most of the waste is still due to electrical resistance and heat dissipation. We'll perform a relevant estimate in a moment. But what are the ultimate limits on computation?

We have seen several times that irreversible processes are those that create entropy. Conversely, for a process to be reversible, it must not create any entropy.

However, computers tend to create entropy, and thus waste, for what may be a surprising reason – they *erase* information. For example, say we add two numbers, eg

$$58 + 23 = 81 \tag{8.5.1}$$

We started out with information representing both 58 and 23. Typically this would be stored as an integer, and for example a 16 bit integer has information, or entropy, $16 \log 2$. But at the end of the computation, we don't remember what we started with, rather we just know the answer. Thus we have created an entropy

$$S = 2 \times (16 \log 2) - (16 \log 2) = 16 \log 2 \tag{8.5.2}$$

through the process of erasure!

Since our computer will certainly be working at finite temperature, eg room temperature, we will be forced by the laws of thermodynamics to create heat

$$Q = k_B T (16 \log 2) \approx 5 \times 10^{-20} \text{ Joules} \tag{8.5.3}$$

Clearly this isn't very significant for one addition, but it's interesting as its the fundamental limit.

Furthermore, computers today are very powerful. For example, it has been estimated that while training AlphaGo Zero, roughly

$$10^{23} \text{ float point operations} \tag{8.5.4}$$

were performed. Depending on whether they were using 8, 16, or 32 bit floating point numbers (let's assume the last), this meant that erasure accounted for

$$Q = k_B T (32 \log 2) \times 10^{23} \sim 8000 \text{ Joules} \tag{8.5.5}$$

of heat. That's actually a macroscopic quantity, and the laws of thermodynamics say that it's impossible to do better with irreversible computation!

But note that this isn't most of the heat. For example, a currently state of the art GPU like the Nvidia Tesla V100 draw about 250 Watts of power and perform at max about 10^{14} flop/s. This means their theoretical minimum power draw is

$$Q = k_B T (16 \log 2) \times 10^{14} flop/s \sim 10^{-5} \text{ Watts} \tag{8.5.6}$$

Thus state of the art GPUs are still tens of millions of times less efficient than the theoretical minimum. We're much, much further from the theoretical limits of computation than we are from the theoretical limits of heat engine efficiency.

In principle we can do even better through *reversible computation.* After all, there's no reason to make erasures. For example, when adding we could perform an operation mapping

$$(x, y) \rightarrow (x, x + y) \tag{8.5.7}$$

for example

$$(58, 23) \rightarrow (58, 81) \tag{8.5.8}$$

so that no information is erased. In this case, we could in principle perform any computation we like without producing any waste heat at all. But we need to keep all of the input information around to avoid creating entropy and using up energy.

9   Transport, In Brief

Let's get back to real physics and discuss transport. This is a fun exercise. We'll study the transport of heat (energy), of momentum, and of particles.

9.1 Heat Conduction

We'll talk about radiation later, in the quantum stat mech section. And discussing convection is basically hopeless, as fluid motions and mixings can be very complicated. But we can try to discuss **conduction** using some simple models and physical intuition.

The idea is roughly that molecules are directly bumping into each other and transferring energy. But this can also mean that energy is carried by lattice vibrations in a solid, or by the motion of free electrons (good electrical conductors tend to have good heat conductivity too).

We can start by just making a simple guess that

$$Q \propto \frac{\Delta T \delta t A}{\delta x} \tag{9.1.1}$$

or

$$\frac{dQ}{dt} \propto A \frac{dT}{dx} \tag{9.1.2}$$

The overall constant is called the thermal conductivity of a given fixed material. So

$$\frac{dQ}{dt} = -k_t A \frac{dT}{dx} \tag{9.1.3}$$

which is called the Fourier heat conduction law.

Thermal conductivities of common materials vary by four orders of magnitude, in $W/(mK)$: air 0.026, wood 0.08, water 0.6, glass 0.8, iron 80, copper 400. In common household situations thin layers of air are very important as insulation, and can be more important than glass itself.

Heat Conductivity of an Ideal Gas

Let's derive the simplest example of this, the conductivity for an ideal.

An important relevant parameter is the **mean free path**, which is the distance a molecule can go before interacting with another molecule. It's typically much larger than the distance between molecules in a dilute gas. Let's estimate it.

Collisions happen when molecules get within $2r$ of each other, where r is some rough estimate of the 'size' the molecule. Really this is related to the **cross section** for interaction. Anyway, molecules collide when the volume swept out

$$\pi(2r)^2 \ell \tag{9.1.4}$$

is of order the volume per molecule, ie

$$\pi(2r)^2 \ell \approx \frac{V}{N} \tag{9.1.5}$$

or

$$\ell \approx \frac{V}{4\pi r^2 N} \tag{9.1.6}$$

for the mean free path ℓ. This is an approximation in all sorts of ways, but it's roughly correct.

In air the volume per particle is, using the ideal gas approximation, about

$$\frac{V}{N} \approx \frac{kT}{P} \approx 4 \times 10^{-26} m^3 \tag{9.1.7}$$

at room temperature. If the radius of nitrogen or oxygen molecules is about 1.5 angstroms, then the mean free path is about 150 nm, which is about 40 times greater than the average separation between air molecules. The average collision time is

$$\bar{\Delta t} = \frac{\ell}{\bar{v}} \approx 3 \times 10^{-10} s \tag{9.1.8}$$

so this gives another relevant quantity. Apparently they're colliding very frequently!

Now let's study heat conduction. Imagine a surface across which we are studying heat flow. The energy crossing this surface will be about $U_L/2$ from the left and $U_R/2$ from the right, if we study a time Δt and a thickness away from the surface of order ℓ. This leads to a net heat flow

$$Q = \frac{1}{2}(U_1 - U_2) = -\frac{1}{2}C_V(T_2 - T_1) = -\frac{1}{2}C_V \ell \frac{dT}{dx} \tag{9.1.9}$$

This leads to a prediction for the thermal conductivity as

$$k_t = \frac{C_V \ell}{2A\Delta t} = \frac{C_V}{2V}\ell\bar{v} \tag{9.1.10}$$

in terms of the MFP and average velocity. For an ideal gas

$$\frac{C_V}{V} = \frac{fP}{2T} \tag{9.1.11}$$

where f is the number of active DoF per molecule.

This suggests a general scaling law that since $\bar{v} \approx \sqrt{T}$ and ℓ is independent of temperature, we expect $k_T \propto \sqrt{T}$. This has been confirmed for a wide variety of gases.

9.2   Viscosity

Another quantity that you may have heard of is viscosity. It concerns the spread of *momentum* through a fluid.

To understand this, we want to think of a picture of a fluid flowing in the $\hat{x}$ direction, but where the velocity of the fluid changes in the z direction. This could lead to chaotic turbulence, but let's assume that's not the case, so that we have **laminar** flow.

In almost all cases, as one might guess intuitively, fluids tend to resist this **shearing**, differential flow. This resistance is called **viscosity**. More viscosity means more resistance to this differential.

It's not hard to guess what the viscous force is proportional to. We'd expect that

$$\frac{F_x}{A} \propto \frac{du_x}{dz} \tag{9.2.1}$$

and the proportionality constant is the viscosity, ie

$$\frac{F_x}{A} \propto \eta \frac{du_x}{dz} \tag{9.2.2}$$

for coefficient of viscosity η. Although F_x/A has units of pressure, it isn't a pressure, rather its **shear stress**.

Viscosities vary a great deal with both material and temperature. Gases have lower viscosities than fluids. And ideal gases have viscosity independent of pressure but increasing with temperature.

This can be explained because viscosity depends on *momentum density* in the gas, the *mean free path*, and the *average thermal speed*. The first two depend on the density, but this cancels between them – a denser gas carries more momentum, but it carries it less far! But since molecules move faster at higher temperature, more momentum gets transported, and so in a gas $\eta \propto \sqrt{T}$ just as for heat conductivity.

In a liquid, viscosity actually decreases with temperature because the molecules don't stick to each other as much or as well at higher temperature, and this 'sticking' is the primary cause of liquid viscosity. Note that in effect $\eta = \infty$ for a solid, where 'sticking' dominates.

9.3   Diffusion

Now let's talk about the spread of particles from high concentration to low concentration.

Let's imagine the density n of particles increases uniformly in the $\hat{x}$ direction. The **flux** is the net number of particles crossing a surface, we'll write it as $\vec{J}$. Once again we'd guess that

$$J_x = -D \frac{dn}{dx} \tag{9.3.1}$$

where D is the **diffusion coefficient**, which depends on both what's diffusing and what it's diffusing through. Diffusion for large molecules is slower than for small molecules, and diffusion is much faster through gases than through liquids. Values ranging from 10^{-11} to 10^{-5} m^2/s can be found. Diffusion coefficients increase with temperature, because molecules move faster.

Diffusion is a very inefficient way for particles to travel. If I make a rough estimate for dye in water that I want roughly all the dye to move through a glass of water then

$$\frac{N}{A\Delta t} = D \frac{N/V}{\delta x} \tag{9.3.2}$$

and $V = A\delta x$, then i have that

$$\Delta t \approx \frac{V \delta x}{AD} \approx \frac{\delta x^2}{D} \tag{9.3.3}$$

for a glass of water with $\delta x \approx 0.1$ m and a $D \approx 10^{-9} m^2/s$, it would take 10^7 seconds, or about 4 months!

Real mixing happens through convection and turbulence, which is much, much faster, but also more complicated.

10 Quantum Statistical Mechanics

Let's get back to our main topic and (officially) begin to discuss quantum statistical mechanics.

10.1 Partition Functions for Composite Systems

We'd like to understand what happens if we combine several different systems together – what is the partition function for the total system, in terms of the partition functions for the constituents?

The simplest and most obvious case is when we have two non-interacting distinguishable systems. Then we have

$$Z_{total} = \sum_{s_1, s_2} e^{-\beta E_1(s_1)} e^{-\beta E_2(s_2)} = Z_1 Z_2 \tag{10.1.1}$$

This follows because every state of the total systems is (s_1, s_2), the Cartesian product. And furthermore, there is no relation or indistinguishability issue between states in the first and second system.

I put this discussion under the Quantum Stat Mech heading because, in many cases, the systems are **indistinguishable**. In that case the state $s_{total} = (s_1, s_2) = (s_2, s_1)$, ie these are the same state. We can approximate the partition function for that case by

$$Z_{total} \approx \frac{1}{2} Z_1 Z_2 \tag{10.1.2}$$

but this is only approximate, because we have failed to account correctly for $s_1 = s_2$, in which case we don't need the 1/2. In the limit that most energy levels are unoccupied, this isn't a big problem. We'll fix it soon.

These expressions have the obvious generalizations

$$Z_{total} = \prod_{i=1}^{N} Z_i \tag{10.1.3}$$

for distinguishable and

$$Z_{total} = \frac{1}{N!} \prod_{i=1}^{N} Z_i \tag{10.1.4}$$

for indistinguishable particles or sub-systems.

Ideal Gas from Boltzmann Statistics

The natural application of our approximations above is to ideal gases. We still haven't computed Z for an ideal gas!

The total partition function is

$$Z_{total} = \frac{1}{N!} Z_1^N \tag{10.1.5}$$

in terms of the partition function for a single gas molecule, Z_1. So we just have to compute that.

To get Z_1 we need to add up the Boltzmann factors for all of the microstates of a single molecule of gas. This combines into

$$Z_1 = Z_{tr} Z_{int} \tag{10.1.6}$$

where the first is the kinetic energy from translational DoF, and the latter are internal states such as vibrations and rotations. There can also be *electronic* internal states due to degeneracies in the ground states of the electrons in a molecule. For example, oxygen molecules have 3-fold degenerate ground states.

Let's just focus on Z_{tr}. To do this correctly we need quantum mechanics.

This isn't a QM course, so I'm mostly just going to tell you the result. A particle in a 1-d box must have momentum

$$p_n = \frac{h}{2L} n \tag{10.1.7}$$

as it must be a standing wave (with Dirichlet boundary conditions). So the energy levels are

$$E_n = \frac{p_n^2}{2m} = \frac{h^2 n^2}{8mL^2} \tag{10.1.8}$$

From the energies, we can write down the partition function

$$Z_{1d} = \sum_n e^{-\beta \frac{h^2 n^2}{8mL^2}} \tag{10.1.9}$$

Unless the box is extremely small, or T is extremely small we can approximate this by the integral

$$Z_{1d} \approx \int_0^\infty dn\, e^{-\beta \frac{h^2 n^2}{8mL^2}} = \frac{L}{\frac{h}{\sqrt{2\pi mk_B T}}} \tag{10.1.10}$$

where we can define a quantum length scale

$$\ell_Q = \frac{h}{\sqrt{2\pi mk_B T}} \tag{10.1.11}$$

It's roughly the de Broglie wavelength of a particle of mass m with kinetic energy kT. At room temperature for nitrogen, this length is $\sim 10^{-11}$ meters.

The partition function in 3d is just

$$Z_{3d} = Z_{1d}^3 \tag{10.1.12}$$

because the x, y, z motions are all independent. This gives

$$Z_{3d} = \frac{V}{\ell_Q^3} \tag{10.1.13}$$

So the total partition function for an ideal gas is

$$Z \approx \frac{1}{N!} \left(\frac{V}{\ell_Q^3} Z_{int} \right)^N \tag{10.1.14}$$

where we don't know Z_{int} and it depends on the kind of molecule.

We can now compute the expected energy. Note that

$$\log Z = N \left(\log V + \log Z_{int} - \log N - 3 \log \ell_Q + 1 \right) \tag{10.1.15}$$

and we can find

$$U = -\frac{\partial}{\partial \beta} \log Z \tag{10.1.16}$$

This gives

$$U = \frac{3}{2} N k T + U_{int} \tag{10.1.17}$$

which confirms equipartition once again, plus the interaction term. The heat capacity is

$$C_V = \frac{3}{2} N k + \frac{\partial U_{int}}{\partial T} \tag{10.1.18}$$

We can compute the other properties of our gas using

$$F = -kT \log Z = F_{int} - NkT(\log V - \log N - 3 \log \ell_Q + 1) \tag{10.1.19}$$

For example we can find the pressure, entropy, and chemical potential this way. We will once again recover expressions we've seen earlier in the semester.

10.2 Gibbs Factors

We can modify our original derivation of Boltzmann factors to account for the possibility that particles are exchanged between the reservoir and the system. The result are **Gibbs** factors and the **Grand Canonical Ensemble**. The latter means that we fix **Temperature and Chemical Potential**. Whereas in the microcanonical ensemble we fixed energy and particle number, and in the canonical ensemble we fixed temperature and particle number.

Gibbs factors will be useful soon for quantum statistical physics because they allow us to re-organize our thinking in terms of the number of particles in each state, rather than in terms of states as given by a configuration of a fixed number of particles.

Recall that

$$\frac{P(s_2)}{P(s_1)} = e^{S_R(s_2) - S_R(s_1)} \tag{10.2.1}$$

Now we need to use

$$dS_R = \frac{1}{T}(dU_R + P dV_R - \mu dN_R) \tag{10.2.2}$$

to find that

$$S_R(s_2) - S_R(s_1) = -\frac{1}{T}\left(E(s_2) - E(s_1) - \mu N(s_2) + \mu N(s_1)\right) \tag{10.2.3}$$

where E and N refer to the system. Thus we find that the Gibbs factor is

$$e^{-(E-\mu N)/(k_B T)} \tag{10.2.4}$$

and so the probabilities are

$$P(s) = \frac{1}{\mathcal{Z}} e^{-(E-\mu N)/(k_B T)} \tag{10.2.5}$$

where

$$\mathcal{Z} = \sum_s e^{-(E(s)-\mu N(s))/(k_B T)} \tag{10.2.6}$$

where the sum includes all states, ranging over all values of E and all N. This is the promised **grand partition function** or **grand canonical distribution**. In the presence of more types of particles, we have chemical potentials and numbers for each.

Carbon Monoxide Poisoning

Carbon monoxide poisoning illustrates the use of the grand canonical ensemble.

We can idealize hemoglobin as having two states, occupied and unoccupied (by oxygen). So

$$\mathcal{Z} = 1 + e^{-(\epsilon - \mu)/kT} \tag{10.2.7}$$

where $\epsilon = -0.7$ eV. The chemical potential μ is high in the lungs, where oxygen is abundant, but lower in cells where oxygen is needed. Near the lungs the partial pressure of oxygen is about 0.2 atm, and so the chemical potential is

$$\mu = -kT \log\left(\frac{V Z_{int}}{N \ell_Q^3}\right) \approx -0.6 eV \tag{10.2.8}$$

So at body temperature 310 K we find that the Gibbs factor is

$$e^{-(\epsilon - \mu)/kT} \approx 40 \tag{10.2.9}$$

and so the probability of occupation by oxygen is 98%.

But things change in the presence of carbon monoxide, CO. Then there are three possible states

$$\mathcal{Z} = 1 + e^{-(\epsilon-\mu)/kT} + e^{-(\epsilon'-\mu')/kT} \tag{10.2.10}$$

The CO molecule will be less abundant. If it's 100 times less abundant, then

$$\delta\mu = kT\log 100 \approx 0.12 \ eV \tag{10.2.11}$$

But CO binds more tightly to hemoglobin, so that $\epsilon' \approx -0.85$ eV. In total this means

$$e^{-(\epsilon'-\mu')/kT} \approx 120 \tag{10.2.12}$$

which means that the oxygen occupation probability sinks to 25%. This is why CO is poisonous.

10.3 Bosons and Fermions

Now let's correct our mistake, where we took

$$Z \approx \frac{1}{N!}Z_1^N \tag{10.3.1}$$

This was approximate because it ignores what happens when two particles are in the same state.

In fact, there are two types of particles, **fermions** and **bosons**. We can put as many identical bosons as we like in the same state, but due to the **Pauli exclusion principle**, identical fermions cannot be in the same state. This has extremely important implications for statistical physics. Note that bosons always have integer spin, and fermions always have half-integer spin.

Note that this idea is irrelevant in the classical limit, when $Z_1 \gg N$, or when

$$V/N \gg \ell_Q^3 \tag{10.3.2}$$

When this is violated, the wavefunctions of the particles start to overlap, and quantum effects become important. Systems that are quantum are either very dense or very cold, since we recall that

$$\ell_Q = \frac{h}{\sqrt{2\pi m k_B T}} \tag{10.3.3}$$

We can picture this as a situation where the particle's individual wavefunctions start to overlap. We can't separate them (make the wavefunctions more narrow) without giving them a lot of momentum, increasing the energy and temperature of the gas.

Distribution Functions

We introduced the Gibbs ensemble to make computing the distribution functions easier. The idea is to *focus on individual, specific states that (some number of) particles can be.*

If we have a given single-particle state, then the probability of it being occupied by n particles is

$$P(n) = \frac{1}{\mathcal{Z}} e^{-\frac{n}{kT}(\epsilon - \mu)} \tag{10.3.4}$$

So we can use this to determine the $\mathcal{Z}$ for fermions and bosons.

In the case of fermions, the only occupancy allowed is $n = 0, 1$. That means that for any given state, we simply have

$$\mathcal{Z} = 1 + e^{-\frac{1}{kT}(\epsilon - \mu)} \tag{10.3.5}$$

This allows us to compute the occupancy

$$\bar{n} = 0P(0) + P(1) = \frac{1}{e^{+\frac{1}{kT}(\epsilon - \mu)} + 1} \tag{10.3.6}$$

Note the *crucial* sign flip in the denominator! This is the **Fermi-Dirac distribution**. The F-D distribution vanishes when $\epsilon \gg \mu$ and goes to 1 when $\epsilon \ll \mu$. **Draw it!**

In the case of **bosons** all values of n are allowed. That means that

$$
\begin{aligned}
\mathcal{Z} &= \sum_{n=0}^{\infty} \left(e^{-\frac{n}{kT}(\epsilon - \mu)} \right. \\
&= \frac{1}{1 - e^{-\frac{1}{kT}(\epsilon - \mu)}}
\end{aligned} \tag{10.3.7}
$$

by summing the geometric series. Notice that crucially the signs in the denominator here are different.

Let's look at the expected occupancy. This is

$$
\begin{aligned}
\bar{n} &= \sum_{n=0}^{\infty} n P(n) \\
&= -\frac{\partial}{\partial x} \log \mathcal{Z}
\end{aligned} \tag{10.3.8}
$$

where $x = \frac{1}{kT}(\epsilon - \mu)$. By computing directly with this formula we find

$$\bar{n} = \frac{1}{e^{+\frac{1}{kT}(\epsilon - \mu)} - 1} \tag{10.3.9}$$

where once again we emphasize that the signs here are crucial! This is the **Bose-Einstein distribution**.

Notice that the B-E distribution goes to infinity as $\epsilon \to \mu$. This means that in that limit, the state achieves infinite occupancy! In the case of fermions this was impossible because occupancy can only be 0 or 1. This divergence is Bose condensation. **Draw it!**

Let's compare these results to the classical limit, where we'd have a **Boltzmann distribution**. In the Boltzmann distribution

$$\bar{n} = e^{-(\epsilon - \mu)/kT} \ll 1 \tag{10.3.10}$$

Draw it! I wrote the last inequality because the classical limit obtains when we don't have many particles in the same state. In this limit, it's fine to simply ignore large occupancies. Note that this is equal to both the F-D and B-E distributions in the desired limit. The **classical limit is low occupancy**.

In the rest of this section we will apply these ideas to simple systems, treating 'quantum gases'. That means that we can pretend that the systems are governed by single-particle physics. This applies to electrons in metals, neutrons in neutron stars, atoms in a fluid at low temperature, photons in a hot oven, and even 'phonons', the quantized sound (vibrations) in a solid. We'll determine μ in most cases indirectly, using the total number of particles.

10.4 Degenerate Fermi Gases

An extremely important application of quantum stat mech is to gases of fermions, or fermions at low temperature. Most importantly, this theory describes most of the properties of metals, which are just 'gases' of free electrons. This also applies to nuclei, white dwarves, and neutron stars.

Here low temperature means 'quantum', not 'low compared to room temperature'. That is we mean

$$\frac{V}{N} \lesssim \ell_Q^3 = \left(\left(\frac{h}{\sqrt{2\pi m k T}} \right) \right)^3 \approx (4\ nm)^3 \tag{10.4.1}$$

where the last is for an electron at room temperature. The reason metals are at 'low temperatures' is because there is roughly one conduction electron per atom, and the atomic spacing are roughly 0.2 nm. So we're **far** outside the limit of Boltzmann statistics, and in fact closer to the limit $T = 0$. So let's start with that.

Zero Temperature

Recall the F-D distribution

$$\bar{n}_{FD} = \frac{1}{e^{\frac{1}{kT}(\epsilon - \mu)} + 1} \tag{10.4.2}$$

In the limit that $T = 0$ this is a step function. *All states with $\epsilon < \mu$ are occupied, and all others are unoccupied.*

We call

$$\epsilon_F \equiv \mu(T = 0) \tag{10.4.3}$$

the **Fermi Energy**. In this low-temperature state of affairs the fermion gas is said to be 'degenerate'.

How can we determine ϵ_F? It can be fixed if we know how many electrons are actually present. If we imagine adding electrons to an empty box, then they simply fill the states from lowest energy up. To add one more electron you need $\epsilon_F = \mu$ of energy, and our understanding that

$$\mu = \left(\frac{\partial U}{\partial N}\right)_{S,V} \tag{10.4.4}$$

makes perfect sense. Note that adding an electron doesn't change S, since we're at zero temperature and the state is unique!

To compute ϵ_F we'll assume that the electrons are free particles in a box of volume $V = L^3$. This isn't a great approximation because of interactions with ions in the lattice, but we'll neglect them anyway.

As previously seen, the allowed wavefunctions are just sines and cosines, with momenta

$$\vec{p} = \frac{h}{2L}\vec{n} \tag{10.4.5}$$

where $\vec{n} = (n_x, n_y, n_z)$. Energies are therefore

$$\epsilon = \frac{h^2}{8mL^2}\vec{n}^2 \tag{10.4.6}$$

To visualize the allowed states, its easiest to draw them in $\vec{n}$-space, where only *positive integer coordinates* are allowed. Each point describes two states after accounting for electron spins. Energies are proportional to $\vec{n}^2$, so states start at the origin and expand outward to fill availabilities.

The Fermi energy is just

$$\epsilon_F = \frac{h^2 n_{max}^2}{8mL^2} \tag{10.4.7}$$

We can compute this by computing the total volume of the interior region in the space, which is

$$N = 2 \times \frac{1}{8} \times \frac{4}{3}\pi n_{max}^3 = \frac{\pi n_{max}^3}{3} \tag{10.4.8}$$

Thus we find that

$$\epsilon_F = \frac{h^2}{8m}\left(\frac{3N}{\pi V}\right)^{2/3} \tag{10.4.9}$$

Is this intensive of extensive? What does that mean? (Shape of 'box' is irrelevant.)

We can compute the average energy per electron by computing the total energy and dividing. That is

$$\begin{aligned} U &= 2\frac{1}{8}\iiint\left(d^3n\frac{h^2}{8mL^2}\vec{n}^2\right) \\ &= \int_0^{n_{max}}dn(\pi n^2)\frac{h^2}{8mL^2}\vec{n}^2 \\ &= \frac{\pi h^2 n_{max}^5}{40mL^2} \\ &= \frac{3}{5}N\epsilon_F \end{aligned} \tag{10.4.10}$$

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where the 3/5 is a geometrical factor that would be different in more or fewer spatial dimensions.

Note that $\epsilon_F \sim$ few eV, which is much much larger than $kT \approx \frac{1}{40}$ eV. This is the same as the comparison between the quantum volume and the average volume per particle. The Fermi temperature is

$$T_F \equiv \frac{\epsilon_F}{k_B} \gtrsim 10^4 \ K \qquad (10.4.11)$$

which is hypothetical insofar as metals would liquefy before reaching this temperature.

Using the standard or thermodynamic definition of the pressure we can find

$$
\begin{aligned}
P &= -\frac{\partial U}{\partial V} \\
&= -\frac{\partial}{\partial V} \left(\frac{3}{5} N \frac{h^2}{8m} \left(\frac{3N}{\pi V} \right)^{2/3} \right) \\
&= \frac{2N\epsilon_F}{5V} = \frac{2U}{3V}
\end{aligned}
\qquad (10.4.12)
$$

which is the **degeneracy pressure**. Electrons don't want to be compressed, as they want space! (Remember this has nothing to do with electrostatic repulsion.)

The degeneracy pressure is enormous, of order $10^9 \ N/m^2$, but it isn't measurable, as it is canceled by the electrostatic forces that pulled the electrons into the metal in the first place. The bulk modulus is measureable, and its just

$$B = -V \left(\frac{\partial P}{\partial V} \right)_T = \frac{10}{9} \frac{U}{V} \qquad (10.4.13)$$

This quantity is also large, but its not completely canceled by electrostatic forces, and (very roughly) accords with experiment.

Small Temperatures

The distribution of electrons barely changes when $T_F \gg T > 0$, but we need to study finite temperature to see how metals change with temperature – for example, to compute the heat capacity!

Usually particles want to acquire a thermal energy kT, but in a degenerate Fermi gas they can't, because most states are occupied. So it's only the state near the **Fermi surface** that can become excited. Furthermore, it's only states within kT of the Fermi surface that can be excited. So the number of excitable electrons is proportional to T.

This suggests that

$$\delta U \propto (NkT)(kT) \sim N(kT)^2 \qquad (10.4.14)$$

By dimensional analysis then, since the only energy scale around is ϵ_F, we should have

$$\delta U \approx N \frac{(kT)^2}{\epsilon_F} \qquad (10.4.15)$$

This implies that

$$C_V \propto N \frac{kT}{\epsilon_F} \tag{10.4.16}$$

This agrees with experiments. Note that it also matches what we expect from the 3rd law of thermodynamics, namely that $C_V \to 0$ as $T \to 0$.

Density of States

A natural object of study is the density of states, which is the **number of single-particle states per unit of energy**. For a Fermi gas note that

$$\epsilon = \frac{h^2}{8mL^2}\vec{n}^2, \quad |\vec{n}| = \frac{L}{h}\sqrt{8m\epsilon} \tag{10.4.17}$$

so that

$$dn = \frac{L}{h}\sqrt{\frac{2m}{\epsilon}}d\epsilon \tag{10.4.18}$$

This means that we can write integrals like

$$\begin{aligned}
U &= \int_0^{n_{max}} dn(\pi n^2)\frac{h^2}{8mL^2}n^2 \\
&= \int_0^{\epsilon_F} d\epsilon\, \epsilon \left[\frac{\pi}{2}\left(\frac{8mL^2}{h^2}\right)^{3/2}\sqrt{\epsilon}\right]\left(
\end{aligned} \tag{10.4.19}$$

where the quantity in square brackets is the **density of states**

$$g(\epsilon) = \frac{\pi}{2}(8m)^{3/2}\frac{V}{h^3}\sqrt{\epsilon} = \frac{3N}{2\epsilon_F^{3/2}}\sqrt{\epsilon} \tag{10.4.20}$$

The total energy is the integral of the number of states at a given energy times that energy $\epsilon g(\epsilon)$. Note that this expression does not depend on N except through V; in the last formula N cancels.

The density of states is a useful concept in a variety of systems. It doesn't depend on statistical mechanics, rather determining it is just a quantum mechanics problem.

At zero temperature we have

$$N = \int_0^{\epsilon_F} g(\epsilon)d\epsilon \tag{10.4.21}$$

but at higher temperature we have to multiply by the non-trivial occupancy, which is really the right way to think about zero temperature as well

$$N = \int_0^\infty g(\epsilon)\bar{n}_{FD}(\epsilon)d\epsilon = \int_0^\infty \frac{g(\epsilon)}{e^{\frac{1}{kT}(\epsilon-\mu)} + 1}d\epsilon \tag{10.4.22}$$

similarly for the energy

$$U = \int_0^\infty \epsilon g(\epsilon)\bar{n}_{FD}(\epsilon)d\epsilon = \int_0^\infty \frac{\epsilon g(\epsilon)}{e^{\frac{1}{kT}(\epsilon-\mu)}+1}d\epsilon \tag{10.4.23}$$

The zero temperature limit is just a special case.

Note that at $T > 0$ the chemical potential changes. Its determined by the fact that the integral expression for N must remain fixed, and since $g(\epsilon)$ is larger for larger ϵ, the chemical potential must change to compensate. In fact it must decrease slightly. We can compute it by doing the integrals and determining $\mu(T)$. Then we can determine $U(T)$ as well.

Sommerfeld Expansion – Evaluating Integrals at Low Temperature

Unfortunately, we can't do the integrals for N or U explicitly and analytically. But we can approximate them in the limit

$$k_B T \ll \epsilon_F \tag{10.4.24}$$

which we have seen is a very good approximation.

To get started, we can write

$$N = g_0 \int_0^\infty \frac{\sqrt{\epsilon}}{e^{\frac{1}{kT}(\epsilon-\mu)}+1}d\epsilon \tag{10.4.25}$$

The only interesting region in the integral is when $\epsilon \approx \mu$, as otherwise the $\bar{n}_{FD}$ factor is simply 1 or 0. So to isolate this region, we can integrate by parts, writing

$$N = \frac{2}{3}g_0\epsilon^{3/2}\bar{n}_{FD}(\epsilon)\Big|_0^\infty + \frac{2}{3}g_0 \int_0^\infty \epsilon^{3/2}\left(-\frac{d\bar{n}_{FD}}{d\epsilon}\right)d\epsilon \tag{10.4.26}$$

The boundary term vanishes, and so what we're left with is nicer, because $\frac{d\bar{n}_{FD}}{d\epsilon}$ is basically zero except near $\epsilon \approx \mu$.

We will now start writing

$$x = \frac{\epsilon - \mu}{kT} \tag{10.4.27}$$

to simplify the algebra. In these terms we see that

$$\frac{d\bar{n}_{FD}}{d\epsilon} = \frac{1}{kT}\frac{e^x}{(e^x+1)^2} \tag{10.4.28}$$

So we need to evaluate the integral

$$\begin{aligned} N &= \frac{2}{3}g_0 \int_0^\infty \frac{1}{kT}\frac{e^x}{(e^x+1)^2}\epsilon^{3/2}d\epsilon \\ &= \frac{2}{3}g_0 \int_{-\mu/kT}^\infty \frac{e^x}{(e^x+1)^2}\epsilon^{3/2}dx \end{aligned} \tag{10.4.29}$$

So far this was exact, but now we will start making approximations.

First of all, note that $\mu/kT \gg 1$ and that the integrand falls off exponentially when $-x \gg 1$. This means that we can approximate

$$N \approx \frac{2}{3}g_0 \int_{-\infty}^{\infty} \frac{e^x}{(e^x+1)^2}\epsilon^{3/2}dx \tag{10.4.30}$$

up to exponentially small corrections. Then we can expand

$$\epsilon^{3/2} = \mu^{3/2} + (\epsilon - \mu)\frac{3}{2}\mu^{1/2} + \frac{3}{8}(\epsilon - \mu)^2\mu^{-1/2} + \cdots \tag{10.4.31}$$

So we're left with

$$N \approx \frac{2}{3}g_0 \int_{-\infty}^{\infty} \frac{e^x}{(e^x+1)^2}\left[\mu^{3/2} + \frac{3}{2}kT\mu^{1/2}x + \frac{3}{8}\frac{(kT)^2}{\mu^{1/2}}x^2 + \cdots\right]dx \tag{10.4.32}$$

Now the integral can be performed term-by-term. This provides a series expansion of the result, while neglecting some exponentially small corrections.

The first term is

$$\int_{-\infty}^{\infty} \frac{e^x}{(e^x+1)^2}dx = \int_{-\infty}^{\infty} -\partial_x\left(\frac{1}{e^x+1}\right)dx = 1 \tag{10.4.33}$$

The second term vanishes because

$$\int_{-\infty}^{\infty} \frac{xe^x}{(e^x+1)^2}dx = \int_{-\infty}^{\infty} \frac{x}{(e^x+1)(e^{-x}+1)}dx = 0 \tag{10.4.34}$$

since the integrand is odd. Finally, the integral

$$\int_{-\infty}^{\infty} \frac{x^2 e^x}{(e^x+1)^2}dx = \frac{\pi^2}{3} \tag{10.4.35}$$

though it's harder to evaluate.

Assembling the pieces, we find that

$$\begin{aligned} N &= \frac{2}{3}g_0\mu^{3/2}\left(1 + \frac{\pi^2}{8}\frac{(kT)^2}{\mu^2} + \cdots\right) \\ &= N\left(\frac{\mu}{\epsilon_F}\right)^{3/2}\left(1 + \frac{\pi^2}{8}\frac{(kT)^2}{\mu^2} + \cdots\right) \end{aligned} \tag{10.4.36}$$

This shows that $\mu/\epsilon_F \approx 1$, and so we can use that in the second term to solve and find

$$\frac{\mu}{\epsilon_F} \approx 1 - \frac{\pi^2}{12}\frac{(kT)^2}{\epsilon_F^2} + \cdots \tag{10.4.37}$$

so the chemical potential decreases a bit as T increases.

We can evaluate the energy integrals using the same tricks, with the result that

$$U = \frac{3}{5} N \frac{\mu^{5/2}}{\epsilon_F^{3/2}} + \frac{3\pi^2}{8} N \frac{(kT)^2}{\epsilon_F} + \cdots \tag{10.4.38}$$

We can plug in for μ to find that

$$U = \frac{3}{5} N \epsilon_F + \frac{\pi^2}{4} N \frac{(kT)^2}{\epsilon_F} + \cdots \tag{10.4.39}$$

so that we have the energy in terms of T. As expected, it increases with temperature with the anticipated parametric dependence.

10.5   Bosons and Blackbody Radiation

Now we will consider what we expect to find for electromagnetic radiation inside a box.

Classically, this radiation takes the form of excitations of the electromagnetic field. Without quantum mechanics, there is no notion of occupancy, and instead each degree of freedom is approximately quadratic. This means that we have $\frac{1}{2}kT$ of energy per DoF. But there are infinitely many modes at short distances, leading to an infinite energy! This is called the *ultraviolet catastrophe.*

Quantum Mechanics was invented, in part, to solve this problem.

Planck Distribution

Instead of equipartition, each mode of the electromagnetic field, which is its own harmonic oscillator, can only have energy

$$E_n = n\hbar\omega \tag{10.5.1}$$

where the values of ω are fixed by the boundary conditions of the box. This n is the number of **photons**!

The partition function is

$$Z = \frac{1}{1 - e^{-\beta\hbar\omega}} \tag{10.5.2}$$

for the Bose-Einstein distribution. So the average energy in an oscillator is

$$\bar{E} = -\frac{d}{d\beta} \log Z = \frac{\hbar\omega}{e^{\beta\hbar\omega} - 1} \tag{10.5.3}$$

The number of photons is just given by $\bar{n}_{BE}$. But in the context of photons, its often called the Planck distribution.

This solves the ultraviolet catastrophe, by suppressing the high energy contributions exponentially. This really required quantization, so that high energy modes are 'turned off'.

Note that for photons $\mu = 0$. At equilibrium this is required by the fact that photons can be freely created or destroyed, ie

$$\left(\frac{\partial F}{\partial N}\right)_{T,V} = 0 = \mu_\gamma \tag{10.5.4}$$

This explains why μ didn't appear in the Planck distribution.

Photons in a Box

We would like to know the total number and energy of photons inside a box.

As usual, the momentum of these photons is

$$p_m = \frac{hm}{2L} \tag{10.5.5}$$

but since they are relativistic, the energy formula is now

$$\epsilon = pc = \frac{hcm}{2L} \tag{10.5.6}$$

This is also just what we get from their frequencies.

The energy in a mode is just the occupancy times the energy. This is

$$U = 2 \sum_{m_x,m_y,m_z} \left(\frac{hc|m|}{2L} \frac{1}{e^{\frac{hc|m|}{2LkT}} - 1} \right) \tag{10.5.7}$$

Converting to an integral, we have

$$\begin{aligned}
U &= \iint_0^\infty dm \frac{\pi}{2} m^2 \frac{hcm}{L} \frac{1}{e^{\frac{hcm}{2LkT}} - 1} \\
&= \iint_0^\infty dm \frac{\pi hcm^3}{2L} \frac{1}{e^{\frac{hcm}{2LkT}} - 1}
\end{aligned} \tag{10.5.8}$$

We can then change variables to $\epsilon = \frac{hcm}{2L}$ and use $L^3 = V$ to find

$$\frac{U}{V} = \iint_0^\infty d\epsilon \frac{8\pi\epsilon^3}{(hc)^3} \frac{1}{e^{\epsilon/kT} - 1} \tag{10.5.9}$$

the integrand is the **spectrum**, or energy density per unit photon energy

$$u(\epsilon) = \frac{8\pi\epsilon^3}{(hc)^3} \frac{1}{e^{\epsilon/kT} - 1} \tag{10.5.10}$$

The number density is just u/ϵ. The spectrum peaks at $\epsilon \approx 2.8kT$; the ϵ^3 comes from living in 3-dimensions.

To evaluate the integral, its useful to change variables to $x = \epsilon/kT$, so that all of the physical quantities come out of the integral, giving

$$\frac{U}{V} = \frac{8\pi(kT)^4}{(hc)^3} \int_0^\infty \frac{x^3}{e^x - 1} dx \tag{10.5.11}$$

This means that one can determine the temperature of an oven by letting a bit of radiation leak out and looking at its color.

Total Energy

Doing the last integral gives

$$\frac{U}{V} = \frac{8\pi^5(kT)^4}{15(hc)^3} \tag{10.5.12}$$

Note that this *only depend on kT, as the other constants are just there to make up units.* Since its an energy density, pure dimensional analysis could have told us that it had to scale as $(kT)^4$.

Numerically, the result is small. At a typical oven temperature of 460 K, the energy per unit volume is $3.5 \times 10^{-5} J/m^3$. This is much smaller than the thermal energy of the air inside the oven... because there are more air molecules than photons. And that's because the photon wavelengths are smaller than the typical separations between air molecules at this temperature.

Entropy

We can determine the entropy by computing C_V and then integrating $\frac{C_V}{T} dT$. We have that

$$C_V = \frac{\partial U}{\partial T}\bigg|_V = 4aT^3 \tag{10.5.13}$$

where $a = \frac{8\pi^5 k^4}{15(hc)^3}$. Since our determinations were fully quantum, this works down to $T = 0$, which means that

$$S(T) = \int_0^T \frac{C_V}{t} dt = \frac{4}{3} aT^3 \tag{10.5.14}$$

The total number of photons scales the same way, but with a different coefficient.

CMB

The Cosmic Microwave Background is the most interesting photon gas; it's at about 2.73 K. So its spectrum peaks at 6.6×10^{-4} eV, with wavelength around in a millimeter, in the far infrared.

The CMB has far less energy than ordinary matter in the universe, but it has far more entropy – about 10^9 units of S per cubic meter.

Photons Emission Power

Now that we have understood 'photons in a box', we would like to see how radiation will be emitted from a hot body. A natural and classical starting point is to ask what happens if you poke a hole in the box of photons.

Since all light travels at the same speed, the spectrum of emitted radiation will be the same as the spectrum in the box. To compute the amount of radiation that escapes, we just need to do some geometry.

To get out through the hole, radiation needs to have once been in a hemisphere of radius R from the hole. The only tricky question is how much of the radiation at a given point on this hemisphere goes out through a hole with area A. At an angle θ from the perpendicular the area A looks like it has area

$$A_{eff} = A \cos \theta \tag{10.5.15}$$

So the fraction of radiation that's pointed in the correct direction, and thus gets out is

$$\int_0^{\pi/2} d\theta 2\pi R^2 \sin \theta \frac{A_{eff}}{4\pi R^2}$$
$$= \int_0^{\pi/2} d\theta \sin \theta \cos \theta \frac{A}{2} = \frac{A}{4} \tag{10.5.16}$$

Other than that, the rate is just given by the speed of light times the energy density, so we find

$$c \frac{A}{4} \frac{U}{V} = \frac{2\pi^5 A (kT)^4}{15 h^3 c^2} \tag{10.5.17}$$

In fact, this is the famous power per unit area blackbody emission formula

$$P = A \frac{2\pi^5 k^4}{15 h^3 c^2} T^4 = A\sigma T^4 \tag{10.5.18}$$

where σ is known as the Stefan-Boltzmann constant, with value $\sigma = 5.67 \times 10^{-8} \frac{W}{m^2 K^4}$. The dependence on the fourth power of the temperature was discovered by Stefan empirically in 1879.

Universality of Black Body Spectrum

This rule actually applies to emission from any non-reflecting surface, and is referred to as **blackbody radiation**. The argument that the hole and blackbody are the same is simply to put them in contact with each other via radiation, and demand that since they're in equilibrium, to avoid violating the 2nd law of thermodynamics, they must emit in the same way. Note that by adding filters, this implies the full spectra must be the same.

The same argument implies that the **emissivity** e of the material at any given wavelength must be such that $1 - e$ is its reflection coefficient. So good reflectors must be poor emitters, and vice versa. In this case the spectrum will be modified, since e generally depends on wavelength.

Sun and Earth

We can use basic properties of the Earth and Sun to make some interesting deductions.

The Earth receives 1370 W/m^2 from the sun (known as the solar constant). The earth's 150 million km from the sun. This tells us the sun's total luminosity is 4×10^{26} Watts.

The sun's radius is a little over 100 times earth's, or 7×10^8 m. So its surface area is 6×10^{18} m^2. From this information, if we assume an emissivity of 1, we can find that

$$T = \left(\frac{luminosity}{\sigma A} \right)^{1/4} = 5800 \ K \tag{10.5.19}$$

This means that the sun's spectrum should peak at

$$\epsilon = 2.82kT = 1.41 \ eV \tag{10.5.20}$$

which is in the near infrared. This is testable and agrees with experiment. This is close to visible red light, so we get a lot of the sun's energy in the visible spectrum. Note that 'peak' and 'average' aren't quite the same here. (Perhaps in some rough sense evolution predicts that we should be able to see light near the sun's peak?)

We can also easily estimate the Earth's equilibrium temperature, assuming its emission and absorption are balanced. If the power emitted is equal to the power absorbed and emissivity is 1 then

$$(solar \ constant)\pi R^2 = 4\pi R^2 \sigma T^4 \tag{10.5.21}$$

which gives

$$T \approx 280 \ K \tag{10.5.22}$$

This is extremely close to the measured average temperature of 288 K.

Earth isn't a perfect blackbody, as clouds (and other stuff) reflect about 30% of the light, so that the earth's predicted temperature is 255 K. Emissivity and absorption don't balance because Earth emits in Infrared and mostly absorbs in near IR and visible.

However, the earth's surface is warmer than the upper atmosphere, so while 255 K applies to the atmosphere, the surface is warmer due to the greenhouse effect. If we treat the atmosphere as a thin layer intermediate between the earth's surface, we get an extra factor of 2 in power on the surface, which brings the temperature back up by $2^{1/4}$ to 303 K. This is a bit high, but roughly right again.

10.6 Debye Theory of Solids

Now we get to see why I was complaining about the Einstein model early in the course.

The point is that the vibrations in a solid are sound waves, and so they have a range of wavelengths and corresponding frequencies, with $\lambda f = c_s$. So it doesn't make sense to treat them as copies of the same harmonic oscillator.

In fact, the 'phonons' of sound are extremely similar to the photons of light, except that phonons travel at c_s, have 3 polarizations, can have different speeds for different polarizations (and even directions!), and cannot have wavelength smaller than (twice) the atomic spacing.

All this means that we have a simple relation

$$\epsilon = hf = \frac{hc_s}{2L}|\vec{n}| \tag{10.6.1}$$

and these modes have a Bose-Einstein distribution

$$\bar{n}_{BE} = \frac{1}{e^{\epsilon/(kT)} - 1} \tag{10.6.2}$$

with vanishing chemical potential, as phonons can be created and destroyed.

The energy is also the usual formula

$$U = 3 \sum_{n_x, n_y, n_z} \left(\epsilon \bar{n}_{BE}(\epsilon) \right) \tag{10.6.3}$$

The only complication is that we need to decide what range of sum or integration to do for the $\vec{n}$.

Formally we should sum n_i from 1 to $\sqrt[3]{N}$. But that would be annoying, so let's pretend that instead we have a sephere in n-space with

$$n_{max} = \left(\frac{6N}{\pi} \right)^{1/3} \tag{10.6.4}$$

so that the total volume in n-space is the same. This approximation is exact at both low and high temperatures! Why?

Given this approximation, we can easily convert our sum into spherical coordinates and compute the total average energy. This is

$$\begin{aligned} U &= 3 \int_0^{n_{max}} dn \frac{4\pi n^2}{8} \frac{\epsilon}{e^{\frac{\epsilon}{kT}} - 1} \\ &= \frac{3\pi}{2} \int_0^{n_{max}} dn \frac{hc_s}{2L} \frac{n^3}{e^{\frac{hc_s n}{2LkT}} - 1} \end{aligned} \tag{10.6.5}$$

Don't be fooled – this is almost exactly the same as our treatment of photons.

We can change variables to

$$x = \frac{hc_s}{2LkT} n \tag{10.6.6}$$

This means that we are integrating up to

$$x_{max} = \frac{hc_s}{2LkT} n_{max} = \frac{hc_s}{2kT} \left(\frac{6N}{\pi V} \right)^{1/3} = \frac{T_D}{T} \tag{10.6.7}$$

where

$$T_D = \frac{hc_s}{2k} \left(\frac{6N}{\pi V}\right)^{1/3} \tag{10.6.8}$$

is the **Debye Temperature**.

The integral for energy becomes

$$U = \frac{9NkT^4}{T_D^3} \int_0^{T_D/T} \frac{x^3}{e^x - 1} dx \tag{10.6.9}$$

We can just integrate numerically, but what about physics?

In the limit that $T \gg T_D$, the upper limit of the integral is very small, so

$$\int_0^{T_D/T} \frac{x^3}{e^x - 1} dx \approx \int_0^{T_D/T} x^2 dx \approx \frac{1}{3}\left(\frac{T_D}{T}\right)^3 \tag{10.6.10}$$

so that we find

$$U = 3NkT \tag{10.6.11}$$

in agreement with equipartition and also the Einstein model.

In the opposite limit of $T \ll T_D$ the upper limit doesn't matter, as its almost infinity, and we find

$$U = \frac{3\pi^4 Nk}{5T_D^3} T^4 \tag{10.6.12}$$

which means that phonons are behaving exactly like photons, and physics is dominated by the number of excited modes.

This means that at low temperature

$$C_V = \frac{12\pi^4 Nk}{5T_D^3} T^3 \tag{10.6.13}$$

and this T^3 rule beautifully agrees with experimental data. Though for metals, to really match, we need to also include the electron contribution.

Some Comments on Debye

Let's compare this to the Fermi energy

$$\epsilon_F = \frac{h^2}{8m_e} \left(\frac{3N}{\pi V}\right)^{2/3} \tag{10.6.14}$$

for electrons. Notice that the power-law dependence on the density is different because electrons are non-relativistic. In particular, we have

$$\frac{\epsilon_D}{\epsilon_F} \propto \frac{c_s m_e}{h}\left(\frac{V}{N}\right)^{1/3} \tag{10.6.15}$$

This shows that if V/N doesn't vary all that much, the main thing determining ϵ_D is the speed of sound c_s. If we had time to cultivate a deeper understanding of materials, we could try to estimate if we should expect this quantity to be order one.

You should also note that for $T \gg T_D$ we might expect that solids will melt. Why? If not, it means that the harmonic oscillator potentials have significant depth, so we can excite many, many modes without the molecules escaping.

10.7   Bose-Einstein Condensation

So far we have only treated bosons where $\mu = 0$, so that particles can be created and destroyed. But what about bosonic atoms, where N is fixed? In that case we'll have to follow the same procedure as for Fermions. But we get to learn about B-E condensation, another rather shocking consequence of quantum mechanics.

Note that in the limit $T \to 0$ this is obvious – the bosons will all be in their ground state, which is the same state for all N atoms. That this state has energy

$$\epsilon_0 = \frac{h^2}{8mL^2}(1 + 1 + 1) = \frac{3h^2}{8mL^2} \tag{10.7.1}$$

which is a *very small energy* if L is macroscopic.

Let's determine μ in this limit. We see that

$$N_0 = \frac{1}{e^{\frac{\epsilon_0 - \mu}{kT}} - 1} \approx \frac{kT}{\epsilon_0 - \mu} \tag{10.7.2}$$

This means that $\mu = \epsilon_0$ at $T = 0$, and just a bit larger for small, positive T. But the question is, how low must T be for N_0 to be large?

We determine μ by fixing N, and it's usually easiest to think of this as

$$N = \int_0^\infty d\epsilon \, g(\epsilon) \frac{1}{e^{\frac{\epsilon - \mu}{kT}} - 1} \tag{10.7.3}$$

Here $g(\epsilon)$ is the usual density of states. For spin-zero bosons in a box, this is identical to the case of electrons (ignoring a 2 for spin) so that

$$g(\epsilon) = \frac{2}{\sqrt{\pi}}\left(\frac{2\pi m}{h^2}\right)^{3/2} V\sqrt{\epsilon} \tag{10.7.4}$$

Note that this is an approximation assuming a discretum of states, which isn't a good approximation, really, for very small energies.

As we've seen before, we cannot do the integral analytically.

Let's see what happens if we just choose $\mu = 0$. In that case, using our usual $x = \epsilon/kT$ type change of variables we have

$$N = \frac{2}{\sqrt{\pi}} \left(\frac{2\pi mkT}{h^2} \right)^{3/2} V \int_0^\infty \frac{\sqrt{x}\,dx}{e^x - 1} \tag{10.7.5}$$

Numerically this gives

$$N = 2.612 \left(\frac{2\pi mkT}{h^2} \right)^{3/2} V \tag{10.7.6}$$

This really just means that there's a particular T_c for which it's true that $\mu = 0$, so that

$$kT_c = 0.527 \frac{h^2}{2\pi m} \left(\frac{N}{V} \right)^{2/3} \tag{10.7.7}$$

At $T > T_c$ we know that $\mu < 0$ so that the total N is fixed. But what about at $T < T_c$?

Actually, our integral representation breaks down at $T < T_c$ as the discreteness of the states becomes important. The integral does correctly represent the contribution of high energy states, but fails to account for the few states near the bottom of the spectrum.

This suggests that

$$N_{excited} \approx 2.612 \left(\frac{2\pi mkT}{h^2} \right)^{3/2} V \tag{10.7.8}$$

for $T < T_c$. (This doesn't really account for low-lying states very close to the ground state.)

Thus we have learned that at temperature $T > T_c$, the chemical potential is negative and all atoms are in excited states. But at $T < T_c$, the chemical potential $\mu \approx 0$ and so

$$N_{excited} \approx N \left(\frac{T}{T_c} \right)^{3/2} \tag{10.7.9}$$

and so the rest of the atoms are in the ground state with

$$N_0 = N - N_{excited} \approx N \left[\left(- \left(\frac{T}{T_c} \right)^{3/2} \right] \right(\tag{10.7.10}$$

The accumulation of atoms in the ground state is **Bose-Einstein condensation**, and T_c is called the condensation temperature.

Notice that as one would expect, this occurs when quantum mechanics becomes important, so that the quantum length

$$\frac{V}{N} \approx \ell_Q^3 = \left(\frac{h}{\sqrt{2\pi mkT}} \right)^3 \tag{10.7.11}$$

So condensation occurs when the wavefunctions begin to overlap quite a bit.

Notice that *having many bosons helps* – that is for fixed volume

$$kT_c = 0.527 \frac{h^2}{2\pi m}\left(\frac{N}{V}\right)^{2/3} \propto N^{2/3}\epsilon_0 \tag{10.7.12}$$

We do not need a kT of order the ground state energy to get all of the bosons into the ground state!

Achieving BEC

BEC with cold atoms was first achieved in 1995, using a condensate of about 1000 rubidium-87 atoms. This involved laser cooling and trapping. By 1999 BEC was also achieved with sodium, lithium, hydrogen.

Superfluids are also BECs, but in that case interactions among the atoms are important for the interesting superfluidic properties. The famous example is helium-4, which has a superfluid component below 2.17 K.

Note that superconductivity is a kind of BEC condensation of pairs of electrons, called Cooper pairs. Helium-3 has a similar pairing-based superfluidic behavior at extremely low temperatures.

Why? Entropy

With distinguishable particles, the ground state's not particularly favored until $kT \sim \epsilon_0$. But with indistinguishable particles, the counting changes dramatically.

The number of ways of arranging N indistinguishable particles in Z_1 1-particle states is

$$\frac{(N + Z_1)!}{N!Z_1!} \sim e^{Z_1}\left(\frac{N}{Z_1}\right)^{Z_1} \tag{10.7.13}$$

for $Z_1 \ll N$. Whereas in the distinguishable case we just have Z_1^N states, which is far, far larger. So in the QM case with Bosons, at low temperatures we have **very small relative multiplicity or entropy**, as these states will be suppressed by $e^{-U/kT} \sim e^{-N}$. So we quickly transition to a BEC.

10.8   Density Matrices and Classical/Quantum Probability

As a last comment on quantum statistical mechanics, I want to mention how we actually combine quantum mechanics with statistics, and to emphasize that statistical probabilities and quantum probabilities are totally different.

11   Phase Transitions

A **phase transition** is a discontinuous change in the properties of a substance as its environment (pressure, temperature, chemical potential, magnetic field, composition or 'doping') only change

infinitesimally. The different forms of a substance are called phases. A diagram showing the equilibrium phases as a function of environmental variables is called a phase diagram.

On your problem set you'll show (if you do all the problems) that BEC is a phase transition.

Phase structure of water has a **triple point** where all meet, and a **critical point** where water and steam become indistinguishable (374 C and 221 bars for water). No ice/liquid critical point, though long molecules can form **liquid crystal** phase where molecules move but stay oriented. There are many phases of ice at high pressure. Metastable phases are possible via super-cooling/heating etc.

The pressure at which a gas can coexist with its solid or liquid phase is called the **vapor pressure**. At $T = 0.01$ Celsius and $P = 0.006$ bar all three phases can coexist at the **triple point**. At low pressure ice sublimates directly into vapor.

We've seen sublimation of CO_2, this is because the triple point is above atmospheric pressure, at 5.2 bars. Note pressure lowers the melting temperature of ice, which is unusual (because ice is less dense than water).

There are also phase transitions between fluid/superfluid and to superconductivity (eg in the temperature and magnetic field plane). Ferromagnets can have domains of up or down magnetization, and there's a critical point at $B = 0$ and $T = T_c$ called the Curie point.

Phase transitions have been traditionally classified as 'first order' or 'second order' depending on whether the Gibbs energy or its various derivatives are discontinuous; we usually just say first order or 'continuous'.

Diamond and Graphite

Graphite is more stable than Diamond in the atmosphere, as the Gibbs free energy of a mole of diamond is 2900 J higher than that of graphite. Recall

$$G = U - TS + PV \tag{11.0.1}$$

To analyze what happens under other conditions, we can usefully note that

$$\left(\frac{\partial G}{\partial P}\right)_{T,N} = V, \quad \left(\frac{\partial G}{\partial T}\right)_{P,N} = -S \tag{11.0.2}$$

Since diamond has a smaller volume than graphite, as pressure increases its G doesn't increase as fast as that of graphite, so at 15k atmospheres of pressure diamond becomes more stable. Thus diamonds must form deep in the earth – deeper than about 50 km.

Graphite has more entropy, so at high temperatures graphite is even more stable compared to Diamond, and so at higher temperatures Diamonds are more likely to convert to graphite.

In general, many properties of phase transitions follow from thinking carefully about the behavior of the free energy.

11.1 Clausius-Clapeyron

Given the relations for derivatives of G, it's easy to see how phase boundaries must depend on P and T.

At the boundary we must have that the two phases have $G_1 = G_2$. But this also means that

$$dG_1 = dG_2 \tag{11.1.1}$$

along the phase boundary, which means that

$$-S_1 dT + V_1 dP = -S_2 dT + V_2 dP \tag{11.1.2}$$

so that

$$\frac{dP}{dT} = \frac{S_1 - S_2}{V_1 - V_2} \tag{11.1.3}$$

and this determines the slope of the phase boundary (eg between a liquid and gas transition).

We can re-write this in terms of the latent heat L via

$$L = T(S_1 - S_2) \tag{11.1.4}$$

and use the change in volume $\Delta V = V_1 - V_2$ so that

$$\frac{dP}{dT} = \frac{L}{T\Delta V} \tag{11.1.5}$$

This is the **Clausius-Clapeyron relation**. We can use it to trace out phase boundaries.

11.2   Non-Ideal Gases

Gases become ideal in the limit of very low density, so that $N/V \to 0$. Thus it's natural to treat this as a small parameter and expand in it. For this purpose, motivated by the ideal gas law, it's natural to write

$$\frac{P}{kT} = \frac{N}{V} + B_2(T) \left(\frac{N}{V}\right)^2 + B_3(T) \left(\frac{N}{V}\right)^3 + \cdots \tag{11.2.1}$$

We can actually try to compute the functions $B_n(T)$ by doing what's called a 'cluster expansion' in the interactions of the gas molecules.

But for now, let's just see what we get if we include the first correction. A particular equation of state that's of this form, and which keeps only the first two terms, is the famous va der Waals equation of state

$$\left(P + a\frac{N^2}{V^2}\right)(V - Nb) = NkT \tag{11.2.2}$$

or

$$P = \frac{NkT}{V - Nb} - a\frac{N^2}{V^2} \tag{11.2.3}$$

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for constants a and b. This formula is just an approximation! Note that the absence of higher order terms means that we are neglecting effects from interactions among many molecules at once, which are certainly important at high density.

We can also write the vdW equation more elegantly in terms of purely intensive quantities as

$$P = \frac{kT}{v - b} - a\frac{1}{v^2} \tag{11.2.4}$$

where $v = V/N$. This makes it clear that the total amount of stuff doesn't matter!

The modification by b is easy to understand, as it means that the fluid cannot be compressed down to zero volume. Thus b is a kind of minimum volume occupied by a molecule. It's actually well approximated by the cube of the average width of a molecule, eg 4 angstroms cubed for water.

The a term accounts for short-range attractive forces between molecules. Note that it scales like N^2/V^2, so it corresponds to forces on all the molecules from the molecules, and it effectively decreases the pressure (for $a > 0$), so it's attractive. The constant a varies a lot between substances, in fact by more than two orders of magnitude, depending on how much molecules interact.

Now let's investigate the implications of the van der Waals equation. We'll actually be focused on the qualitative implications. Let's plot pressure as a function of volume at fixed T. At large T curves are smooth, but at small T they're more complicated, and have a local minimum! How can a gas's pressure decrease when its volume decreases!?

To see what really happens, let's compute G. We have

$$dG = -SdT + VdP + \mu dN \tag{11.2.5}$$

At fixed T and N this is just $dG = VdP$ so

$$\left(\frac{\partial G}{\partial V}\right)_{T,N} = V\left(\frac{\partial P}{\partial V}\right)_{T,N} \tag{11.2.6}$$

From the van der Waals equation we can compute derivatives of P, giving

$$\left(\frac{\partial G}{\partial V}\right)_{T,N} = \frac{2aN^2}{V^2} - \frac{NkTV}{(V - Nb)^2} \tag{11.2.7}$$

Integrating then gives

$$G = -NkT\log(V - Nb) + \frac{N^2bkT}{V - Nb} - \frac{2aN^2}{V} + c(T) \tag{11.2.8}$$

where $c(T)$ is some constant that can depend on T but not V.

Note that the thermodynamically stable state has *minimum* G. This is important because at a given value of pressure P, there can be more than one value of G. We see this by plotting G and P parametrically as functions of V. This shows the volume changes abruptly at a gas-liquid transition!

We can determine P at the phase transition directly, but there's another cute, famous method. Since the total change in G is zero across the transition, we have

$$0 = \oint dG = \oint \left(\frac{\partial G}{\partial P}\right)_{T,N} dP = \oint VdP \tag{11.2.9}$$

We can compute this last quantity from the PV diagram. This is called the **Maxwell construction**. This is a bit non-rigorous, since we're using unstable states/phases to get the result, but it works.

Repeating the analysis shows where the liquid gas transition occurs for a variety different temperatures. The corresponding pressure is the **vapor pressure** where the transition occurs. At the vapor pressure at a fixed volume, liquid and gas can coexist.

At high temperature, there is no phase boundary! Thus there's a **critical temperature** T_c and a corresponding P_c and $V_c(N)$ at which the phase transition disappears. At the critical point, liquids and gases become identical! The use of the volume in all of this is rather incidental. Recall that $G = N\mu$, and so we can rephrase everything purely in terms of intensive quantities.

Note though that while van der Waals works qualitatively, it fails quantitatively. This isn't surprising, since it ignores multi-molecule interactions.

11.3   Phase Transitions of Mixtures

Phase transitions become more complicated when we consider mixtures of different kinds of particles. Essentially, this is due to the **entropy of mixing**. As usual, we should study the Gibbs free energy

$$G = U + PV - TS \tag{11.3.1}$$

In the unmixed case, with substances A and B, we would expect

$$G = (1 - x)G_A + xG_B \tag{11.3.2}$$

where x is the fraction and $G_{A/B}$ are the Gibbs free energies of unmixed substances.

But if we account for entropy of mixing, then instead of a straight line, S_{mix} will be largest when $x \approx 1/2$, so that G will be smaller than this straight line suggests. Instead G will be concave up as a function of x.

We can roughly approximate

$$S_{mixing} \approx -N \left(x \log x + (1 - x) \log(1 - x) \right) \tag{11.3.3}$$

where N is the total number of molecules. This is correct for ideal gases, and for liquids or solids where the molecules of each substance are roughly the same. This leads to

$$G = (1 - x)G_A + xG_B - Nk_BT \left(x \log x + (1 - x) \log(1 - x) \right) \tag{11.3.4}$$

This is the result for an **ideal mixture**. Liquid and solid mixtures are usually far from ideal, but this is a good starting point.

Since the derivative of G wrt x at $x = 0$ and $x = 1$ is actually infinite, equilibrium phases almost always contain impurities.

Even non-ideal mixtures tend to behave this way, unless there's some non-trivial energy or U dependence in mixing, eg with oil and water, where the molecules are only attracted to their own kind. In that case the G of mixing can actually be concave down – that's why oil and water don't mix, at least at low T. Note that at higher T there's a competition between the energy effect and

the entropy effect. Even at very low T, the entropy dominates near $x = 0$ or $x = 1$, so oil and water will have some 'impurities'.

Note that concave-down $G(x)$ simply indicates an instability where the mixture will split up into two unmixed substances. In this region we say that the two phases are **immiscible** or have a solubility gap.

So we end up with two stable mixtures at small $x > 0$ and large $x < 1$, and unmixed substances between. Solids can have solubility gaps too.

You can read about a variety of more complicated applications of these ideas in the text.

11.4 Chemical Equilibrium

Chemical reactions almost never go to completion. For example consider

$$H_2O \leftrightarrow H^+ + OH^- \tag{11.4.1}$$

Even if one configuration of chemicals is more stable (water), every once in a while there's enough energy to cause the reaction to go the other way.

As usual, the way to think about this quantitatively is in terms of the Gibbs free energy

$$G = U - TS + PV \tag{11.4.2}$$

and to consider the chemical reaction as a system of particles that will react until they reach an equilibrium. We end up breaking up a few H_2O molecuels because although it costs energy, the entropy increase makes up for that. Of course this depends on temperature though!

We can plot G as a function of x, where $1 - x$ is the fraction of H_2O. Without any mixing we would expect $G(x)$ to be a straight line, and since U is lower for water, we'd expect $x = 0$. However, due to the entropy of mixing, equilibrium will have $x > 0$ – recall that $G'(x)$ is infinite at $x = 0$! **Plot this.**

We can characterize the equilibrium condition by the fact that the slope of $G(x)$ is zero. This means that

$$0 = dG = \sum_i \left(\mu_i dN_i \right. \tag{11.4.3}$$

where we assumed T, P are fixed. The sum on the right runs over all species. But we know that

$$dN_{H_2O} = -1, \quad dN_{H^+} = -1, \quad dN_{OH^-} = 1 \tag{11.4.4}$$

because atoms are conserved. So this implies that

$$\mu_{H_2O} = \mu_{H^+} + \mu_{OH^-} \tag{11.4.5}$$

at equilibrium. Since the chemical potentials are a function of species concentration, this determines the equilibrium concentrations!

The equilibrium condition is always the same as the reaction itself, with names of chemicals replaced by their chemical potentials. For instance with

$$N_2 + 3H_2 \leftrightarrow 2NH_3 \tag{11.4.6}$$

we would have

$$\mu_{N_2} + 3\mu_{H_2} \leftrightarrow 2\mu_{NH_3} \tag{11.4.7}$$

simply by noting how the various dN_i must change.

Note that these results apply beyond 'Chemistry', for instance they also apply to the reactions about nuclei in the early universe!

If the substances involved in reaction are all ideal gases, then recall that we can write their chemical potentials as

$$\mu^i = \mu_0^i + kT \log \frac{P_i}{P_0} \tag{11.4.8}$$

where μ_0^i is the chemical potential in a fixed 'standard' state when its partial pressure is P_0. So for example, for the last chemical reaction we can write

$$kT \log \left(\frac{P_{N_2} P_{H_2}^3}{P_{NH_3}^2 P_0^2} \right) = 2\mu_0^{NH_3} - \mu_0^{N_2} - 3\mu_0^{H_2} = \frac{\Delta G_0}{N} \tag{11.4.9}$$

which means that

$$\frac{P_{N_2} P_{H_2}^3}{P_{NH_3}^2 P_0^2} = e^{-\frac{\Delta G_0}{NkT}} = K \tag{11.4.10}$$

where K is the **equilibrium constant**. This equation is called the **law of mass action** by chemists. Even if you don't know K a priori, you can use this equation to determine what happens if you add reactants to a reaction.

For this particular reaction – Nitrogen fixing – we have to use high temperatures and very high pressures – this was invented by Fritz Haber, and it revolutionized the production of fertilizers and explosives.

Ionization of Hydrogen

For the simple reaction

$$H \leftrightarrow p + e \tag{11.4.11}$$

we can compute everything from first principles. We have the equilibrium condition

$$kT \log \left(\frac{P_H P_0}{P_p P_e} \right) = \mu_0^p + \mu_0^e - \mu_0^H \tag{11.4.12}$$

We can treat all of these species as structureless monatomic gases, so that we can use

$$\mu = -kT \log \left[\frac{kT}{P} \left(\frac{2\pi mkT}{h^2} \right)^{3/2} \right] ($$

(11.4.13)

The only additional issues is that we need to subtract the ionization energy of $I = 13.6$ eV from μ_0^H. Since $m_p \approx m_H$ we have

$$- \log \left(\frac{P_H P_0}{P_p P_e} \right) = kT \log \left[\frac{kT}{P_0} \left(\frac{2\pi mkT}{h^2} \right)^{3/2} \right] (- \frac{I}{kT}$$

(11.4.14)

Then with a bit of algebra we learn that

$$\frac{P_p}{P_H} = \frac{kT}{P_e} \left(\frac{2\pi mkT}{h^2} \right)^{3/2} e^{-I/kT}$$

(11.4.15)

which is called the **Saha equation**. Note that $P_e/kT = N_e/V$. If we plug in numbers for the surface of the sun this gives

$$\frac{P_p}{P_H} \lesssim 10^{-4}$$

(11.4.16)

so less than one atom in ten thousand are ionized. Note though that this is much, much larger than the Boltzmann factor by itself!

11.5 Dilute Solutions

When studying mixtures, there's a natural, 'simplest possible' limit that we can take, where one substance dominates. In this case, molecules of the other substances are always isolated from each other, as their immediate neighbors are molecules of the dominant substance. This is the limit of dilute solutions, and the dominant substance is called the **solvent**, while the other components are **solutes**.

In this case we can think of the solutes as almost like an 'ideal gas', since they are approximately non-interacting. It's the kind of problem we know how to solve!

So we need to compute the Gibbs free energy and chemical potentials. If the solvent is A, then to start with, with no solute, we have

$$G = N_A \mu_0(T, P)$$

(11.5.1)

Now we imagine adding B molecules, and G changes by

$$dG = dU + PdV - TdS$$

(11.5.2)

The dU and PdV terms don't depend on N_A, rather they only depend on how B molecules interact with their A-molecule neighbors. But TdS depends on N_B due to the freedom we have in placing the B molecules. The number of choices is proportional to N_A, so we get one term

$$dS \supset k \log N_A$$

(11.5.3)

But we also need to account for the redundancy because B molecules are identical. The result is

$$
\begin{aligned}
G &= N_A\mu_0(T,P) + N_B f(T,P) - N_B kT \log N_A + kT \log N_B! \\
&= N_A\mu_0(T,P) + N_B f(T,P) - N_B kT \log N_A + N_B kT \left(\log N_B - 1\right)
\end{aligned}
\tag{11.5.4}
$$

where $f(T,P)$ doesn't depend on N_A. It is what accounts for the interaction of B molecules with the A molecules that surround them. This expression is valid as long as $N_B \ll N_A$.

The chemical potentials follow from

$$
\mu_A = \left(\frac{\partial G}{\partial N_A}\right)_{T,P,N_B} = \mu_0(T,P) - \frac{N_B}{N_A}kT
\tag{11.5.5}
$$

and

$$
\mu_B = \left(\frac{\partial G}{\partial N_B}\right)_{T,P,N_A} = f(T,P) + kT \log \frac{N_B}{N_A}
\tag{11.5.6}
$$

Adding solute reduces μ_A and increases μ_B. Also, these chemical potentials depend only on the intensive ration N_B/N_A.

Osmotic Pressure

If we have pure solvent on one side of a barrier permeable only by solvent, and solute-solvent solution on the other side, then solvent will want to move across the barrier to further dilute the solution. This is called **osmosis**.

To prevent osmosis, we could add additional pressure to the solution side. This is the **osmotic pressure**. It's determined by equality of solvent chemical potential. So we need

$$
\mu_0 - \frac{N_B}{N_A}kT = \mu_0 + \delta P \frac{\partial \mu_0}{\partial P}
\tag{11.5.7}
$$

Note that

$$
\frac{\partial \mu_0}{\partial P} = \frac{V}{N}
\tag{11.5.8}
$$

at fixed T, N because $G = N\mu$, and so

$$
\delta P \frac{V}{N_A} = \frac{N_B}{N_A}kT
\tag{11.5.9}
$$

or

$$
\delta P = \frac{N_B kT}{V}
\tag{11.5.10}
$$

is the osmotic pressure.

Boiling and Freezing Points

The boiling and freezing points of a solution are altered by the presence of the solute. Often we can assume the solute never evaporates, eg if we consider salt in water. Intuitively, the boiling point may increase (and the freezing point decrease) because the effective liquid surface area is decreased due to the solute 'taking up space' near the surface and preventing liquid molecules from moving. In the case of freezing, the solute takes up space for building solid bonds.

Our theorizing above provides a quantitative treatment of these effects. For boiling we have

$$\mu_0(T, P) - \frac{N_B}{N_A} kT = \mu_{gas}(T, P) \tag{11.5.11}$$

and so the N_B/N_A fraction of solute makes the liquid chemical potential smaller, so that higher temperatures are needed for boiling.

If we hold the pressure fixed and vary the temperature from the pure boiling point T_0 we find

$$\mu_0(T_0, P) + (T - T_0)\frac{\partial \mu_0}{\partial T} - \frac{N_B}{N_A} kT = \mu_{gas}(T, P) + (T - T_0)\frac{\partial \mu_{gas}}{\partial T} \tag{11.5.12}$$

and we have that

$$\frac{\partial \mu}{\partial T} = -\frac{S}{N} \tag{11.5.13}$$

so that

$$-(T - T_0)\left(\frac{S_{liquid} - S_{gas}}{N_A}\right) = \frac{N_B}{N_A} kT \tag{11.5.14}$$

The difference in entropies between gas and liquid is L/T_0, where L is the latent heat of vaporization, so we see that

$$T - T_0 = \frac{NkT_0^2}{L} \tag{11.5.15}$$

where we treat $T \approx T_0$ on the RHS.

A similar treatment of pressure shows that

$$\frac{P}{P_0} = 1 - \frac{N_B}{N_A} \tag{11.5.16}$$

for the boiling transition – we need to be at lower pressure for boiling to occur.

11.6   Critical Points

Now let us further discuss the critical point. We will see that critical points are *universal*.

Note that both

$$\frac{dP}{dV} = 0, \quad \frac{d^2P}{dV^2} = 0 \tag{11.6.1}$$

at the critical point, which helps us to easily identify it (eg using the van der Waals equation). A cute way to say this is to write the vdW equation using intensive variables as

$$Pv^3 - (Pb + kT)v^2 + av - ab = 0 \tag{11.6.2}$$

The critical point occurs when all three roots of the cubic coincide, so that

$$p_c(v - v_c)^3 = 0 \tag{11.6.3}$$

and if we expand this out we can identify that

$$kT = \frac{8a}{27b}, \quad v_c = 3b, \quad P_c = \frac{a}{27b^2} \tag{11.6.4}$$

Law of Corresponding States

We can eliminate a, b completely if we re-write the vdW equation in terms of T_c, v_c, and P_c. Furthermore, we can then write the equation in dimensionless variables

$$\bar{T} = \frac{T}{T_c}, \quad \bar{v} = \frac{v}{v_c}, \quad \bar{P} = \frac{P}{P_c} \tag{11.6.5}$$

so that the vdW equation becomes

$$\bar{P} = \frac{8}{3} \frac{\bar{T}}{\bar{v} - 1/3} - \frac{3}{\bar{v}^2} \tag{11.6.6}$$

This is often called the law of corresponding states. The idea being that all gases/liquids *correspond* with each other once expressed in these variables. This extends the extreme equivalence among gases implied by the ideal gas law to the vdW equation.

Furthermore, since T_c, v_c, p_c only depend on a, b, there must be a relation among them, it is that

$$\frac{p_c v_c}{kT} = \frac{3}{8} \tag{11.6.7}$$

Thus all gases described by the vdW equation must obey this relation! Of course general gases depend on more than the two parameters a, b, since vdW required truncating the expansion in the density.

This universality has been confirmed in experiments, which show that all gases, no matter their molecular makeup, behave very similarly in the vicinity of the critical point. Let's explore that.

Approaching the Critical Point

It turns out that the most interesting question is to ask how various quantities such as v, T, P behave as we approach the critical point. We're now going to do a naive analysis that will turn out to be wrong for interesting reasons.

For $T < T_c$ so that $\bar{T} < 1$, the vdW equation has two solutions to

$$\bar{P} = \frac{8}{3}\frac{\bar{T}}{\bar{v} - 1/3} - \frac{3}{\bar{v}^2} \tag{11.6.8}$$

corresponding to a v_{gas} and v_{liquid}. This means that we can write

$$\bar{T} = \frac{(3\bar{v}_l - 1)(3\bar{v}_g - 1)(\bar{v}_l + \bar{v}_g)}{8\bar{v}_g^2\bar{v}_l^2} \tag{11.6.9}$$

We can expand near the critical point by expanding in $v_g - v_l$, whcih gives

$$\bar{T} \approx 1 - \frac{1}{16}(\bar{v}_g - \bar{v}_l)^2 \tag{11.6.10}$$

or

$$\bar{v}_g - \bar{v}_l \propto \sqrt{T_c - T} \tag{11.6.11}$$

so this tells us how the difference in molecular volumes varies near the critical temperature.

We can answer a similar question about pressure with no work, giving

$$P - P_c \propto (v - v_c)^3 \tag{11.6.12}$$

since the first and second derivatives of P wrt volume at P_c vanish.

As a third example, let's consider the compressibility

$$\kappa = -\frac{1}{v}\frac{\partial v}{\partial P}\bigg|_T \tag{11.6.13}$$

We know that at T_c the derivative of pressure wrt volume vanishes, so we must have that

$$\frac{\partial v}{\partial P}\bigg|_{T,v_c} = -a(T - T_c) \tag{11.6.14}$$

which we can invert to learn that

$$\kappa \propto \frac{1}{T - T_c} \tag{11.6.15}$$

Note that to discover these last two facts, we didn't even need the vdW equation. Rather, we assumed that the scaling behavior near the critical point was **analytic**, ie it has a nice Taylor series expansion.

Actually, our results are quite wrong, even the ones that didn't rely on vdW!

In fact, all gas-liquid transitions seem to universally behave as

$$\begin{aligned}
v_g - v_l &\propto (T_c - T)^{0.32} \\
p - p_c &\propto (v - v_c)^{4.8} \\
\kappa &\propto \frac{1}{(T - T_c)^{1.2}}
\end{aligned} \tag{11.6.16}$$

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which differ significantly from our predictions. In particular, these are *non-analytic*, ie they don't have a nice Taylor series expansion about the critical point.

We already saw a hint of why life's more complicated at the critical point – there are **large fluctuations**, for example in the density. The fact that the compressibility

$$-\frac{1}{v}\frac{\partial v}{\partial P}\bigg|_T \propto \frac{1}{(T-T_c)^\gamma} \tag{11.6.17}$$

(where we though $\gamma = 1$, and in fact $\gamma = 1.2$) means that the gas/liquid is becoming arbitrarily compressible at the critical point. But this means that there will be huge, local fluctuations in the density. In fact one can show that locally

$$\frac{\Delta n^2}{n} = -kT\frac{\partial \langle n \rangle}{\partial v}\bigg|_{P,T}\frac{1}{v}\frac{\partial v}{\partial P}\bigg|_{N,T} \tag{11.6.18}$$

so that fluctuations in density are in fact diverging. This also means that we *can't use an equation of state that only accounts for average pressure, volume, and density.*

Understanding how to account for this is the subject of 'Critical Phenomena', with close links to Quantum Field Theory, Conformal Field Theory, and the 'Renormalization Group'. Perhaps they'll be treated by a future year-long version of this course. But for now we'll move on to study a specific model that shows some interesting related features.

12   Interactions

Let's study a few cases where we can include the effects of interactions.

12.1   Ising Model

The Ising Model is one of the most important non-trivial models in physics. It can be interpreted as either a system of interacting spins or as a lattice gas.

As a Magnetic System

The kind of model that we've already studied has energy or Hamiltonian

$$E_B = -B\sum_{i=1}^{N} s_i \tag{12.1.1}$$

where s_i are the spins, an d we can only have

$$s_i = \pm 1 \tag{12.1.2}$$

This is our familiar paramagnet.

The Ising model adds an additional complication, a coupling between nearest neighbor spins, so that

$$E = -J \sum_{\langle ij \rangle} s_i s_j - B \sum_{i=1}^{N} s_i \tag{12.1.3}$$

where the notation $\langle ij \rangle$ implies that we only sum over the nearest neighbors. How this actually works depends on the dimension – one can study the Ising model in 1, 2, or more dimensions. We can also consider different lattice shapes. We often use q to denote the number of nearest neighbors.

If $J > 0$ then neighboring spins prefer to be aligned, and the model acts as a ferromagnet; when $J < 0$ the spins prefer to be anti-aligned and we have an anti-ferromagnet.

We can thus describe the Ising model via a partition function

$$Z = \sum_{s_i} e^{-\beta E[s_i]} \tag{12.1.4}$$

The B and $J > 0$ will make the spins want to align, but temperature causes them to want to fluctuate. The natural observable to study is the magnetization

$$m = \frac{1}{N\beta} \frac{\partial}{\partial B} \log Z \tag{12.1.5}$$

As a Lattice Gas

With the same math we can say different words and view the model as a lattice gas. Since the particles have hard cores, only one can sit at each site, so the sites are either full, $n_i = 1$, or empty, $n_i = 0$. Then we can further add a reward in energy for them to sit on neighboring sites, so that

$$E = -4J \sum_{\langle ij \rangle} n_i n_j - \mu \sum_i n_i \tag{12.1.6}$$

where μ is the chemical potential, which determines overall particle number. This Hamiltonian is the same as above with $s_i = 2n_i - 1$.

Mean Field Theory

The Ising model can be solved in $d = 1$ and, when $B = 0$, in $d = 2$; the latter is either very complicated or requires very fancy techniques. But we can try to say something about its behavior by approximating the effect of the interactions by an averaging procedure.

The idea is to write each spin as

$$s_i = (s_i - m) + m \tag{12.1.7}$$

where m is the average spin throughout the lattice. Then the neighboring interactions are

$$s_i s_j = (s_i - m)(s_j - m) + m(s_j - m) + m(s_i - m) + m^2 \tag{12.1.8}$$

The approximation comes in when we assume that the fluctuations of spins away from the average are small. This means we treat

$$(s_i - m)(s_j - m) \to 0 \qquad (12.1.9)$$

but note that this does't mean that

$$(s_i - m)^2 = 0 \qquad (12.1.10)$$

as this latter statement is never true, since we will sum over $s_i = \pm 1$. The former statement is possibly true because $s_i \neq s_j$. In this approximation the energy simplifies greatly to

$$
\begin{aligned}
E_{mft} &= -J \sum_{\langle ij \rangle} \left[m(s_i + s_j) - more^2 \right] - B \sum_i s_i \\
&= \frac{1}{2} JNqm^2 - (Jqm + B) \sum_i s_i \qquad (12.1.11)
\end{aligned}
$$

where $Nq/2$ is the number of nearest neighbor pairs. So the mean field approximation has removed the interactions. Instead we have

$$B_{eff} = B + Jqm \qquad (12.1.12)$$

so that the spins see an extra contribution to the magnetic field set by the mean field of their neighbors.

Now we are back in paramagnet territory, and so we can work out that the partition function is

$$
\begin{aligned}
Z &= e^{-\beta \frac{JNqm^2}{2}} (e^{-\beta B_{eff}} + e^{\beta B_{eff}})^N \\
&= e^{-\beta \frac{JNqm^2}{2}} 2^N \cosh^N(\beta B_{eff}) \qquad (12.1.13)
\end{aligned}
$$

However, this is a function of m... yet m is the average spin, so this can't be correct unless it predicts the correct value of m. We resolve this issue by computing the magnetization using m and solving for it, giving

$$m = \tanh(\beta B + \beta Jqm) \qquad (12.1.14)$$

We can understand the behavior by making plots of these functions.

Vanishing B

Perhaps the most interesting case is $B = 0$. The behavior depends on the value of βJq, as can be noted from the expansion of tanh.

If $\beta Jq < 1$, then the only solution is $m = 0$. So for $T > Jq$, ie at high temperatures, the average magnetization vanishes. Thermal fluctuations dominate and the spins do not align.

However if $T < Jq$, ie at low temperatures, we have a solution $m = 0$ as well as magnetized solutions with $m = \pm m_0$. The latter correspond to phases where the spins are aligning. It turns out that $m = 0$ is unstable, in a way analogous to the unstable solutions of the van der Waals equation.

The critical temperature separating the phases is

$$kT_c = Jq \tag{12.1.15}$$

and at this temperature, the magnetization abruptly turns off.

At finite B, the magnetization is never zero, but instead always aligns with B; it smoothly shuts off as $T \to \infty$, but is finite for any finite T. Though in fact at small T there are other solutions that are unstable or meta-stable.

But wait... are these results even correct??? Mean Field Theory was an uncontrolled approximation. It turns out that MFT is qualitatively correct for $d \geq 2$ (in terms of the phase structure), but is totally wrong for an Ising chain, in $d = 1$ – in that case there is no phase transition at finite temperature. It's amusing to note that MFT is exact for $d \to \infty$.

Free Energy

We can understand the phase structure of the Ising model by computing the free energy. In the MFT approximation it is

$$F = -\frac{1}{\beta} \log Z = \frac{1}{2} JNqm^2 - \frac{N}{\beta} \log(2 \cosh(\beta B_{eff})) \tag{12.1.16}$$

Demanding that F be in a local minimum requires $dF/dm = 0$, which requires that

$$m = \tanh(\beta B_{eff}) \tag{12.1.17}$$

To determine which solutions dominate, we just calculate $F(m)$. For example when $B = 0$ and $T < T_c$ we have the possibilities $m = 0, \pm m_0$, and we see that $F(m = 0) = 0$ while $F(\pm m_0) < 0$, so that the aligned phases dominate.

Usually *we can only define F in equilibrium*. But we can take a maverick approach and pretend that $F(T, B, m)$ actually makes sense away from equilibrium, and see what it says about various phases with different values of m. This is the Landau theory of phases. It is the beginning of a rich subject...

12.2   Interacting Gases

Maybe someday.