

Introduction

In this course we will cover selected topics in thermodynamics and statistical mechanics. Since we only have twelve weeks, the selection is necessarily limited. You will probably need to take a graduate course in thermal physics or do studying on your own in order to gain a thorough knowledge of the subject.

Classical (or maybe “conventional” is better) thermodynamics is an approach to thermal physics “from the large.” Statistical mechanics approaches the subject “from the small.” In thermodynamics, one is concerned with things like the pressure, temperature, volume, composition, etc., of various systems. These are macroscopic quantities and in many cases can be directly observed or felt by our senses. Relations between these quantities can be derived without knowing about the microscopic properties of the system.

Statistical mechanics takes explicit account of the fact that all systems are made of large numbers of atoms or molecules (or other particles). The macroscopic properties (pressure, volume, etc.) of the system are found as averages over the microscopic properties (positions, momenta, etc.) of the particles in the system.

In this course we will tend to focus more on the statistical mechanics rather than the thermodynamics approach. I believe this carries over better to modern subjects like condensed matter physics. In any case, it surely reflects my personal preference!

Some History (mostly taken from Reif)

As it turns out, thermodynamics developed some time before statistical mechanics. The fact that heat is a form of energy was becoming apparent in the late 1700’s and early 1800’s with Joule pretty much establishing the equivalence in the 1840’s. The second law of thermodynamics was recognized by Carnot in the 1820’s. Thermodynamics continued to be developed in the second half of the 19th century by, among others, Clausius, Kelvin and Gibbs.

Statistical mechanics was developed in the late 19th and early 20th centuries by Clausius, Maxwell, Boltzmann, and Gibbs.

I find all of this rather amazing because at the time of the initial development of thermodynamics, the principle of energy conservation hadn’t been firmly established. Statistical mechanics was developed when the existence of atoms and molecules was still being debated. The fact that macroscopic properties of systems can be understood in terms of the microscopic properties of atoms and molecules helped convince folks of the reality of atoms and molecules.

Still more amazing is the fact that the foundations of statistical mechanics were developed before quantum mechanics. Incorporating quantum mechanics did make some changes, especially in the counting of states, but the basic approach and ideas of statistical mechanics remained valid. I suspect that this is a reflection of both the strength and weakness of statistical methods. By averaging over many molecules you derive results that are independent of the detailed properties of individual molecules. The flip side is that you can't learn very much about these details with statistical methods.

Some Thermodynamic Concepts

From mechanics, we're familiar with concepts such as volume, energy, pressure (force per unit area), mass, etc. Two new quantities that appear in thermodynamics are *temperature* (T) and *entropy* (S).

We will find that temperature is related to the amount of energy in a system. Higher temperature means greater internal energy (usually). When two systems are placed in contact, energy in the form of heat flows from the higher temperature system to the lower temperature system. When the energy stops flowing the systems are in thermal equilibrium with each other and we say they are at the same temperature. It turns out if two systems are in thermal equilibrium with a third system, they are also in thermal equilibrium with each other. (This is sometimes called *the zeroth law of thermodynamics*.) So the concept of temperature is well defined. It's even more well defined than that as we will see later in the course.

Two systems can exchange energy by macroscopic processes, such as compression or expansion, or by microscopic processes. It is the microscopic process that is called heat transfer. Consider a collision among billiard balls. We think of this as a macroscopic process and we can determine the energy transfer involved by making measurements of a few macroscopic parameters such as the masses and velocity components. If we scale down by roughly 24 orders of magnitude, we consider a collision between molecules, a microscopic process. A very large number of collisions occur in any macroscopic time interval. A typical molecule in the atmosphere undergoes $\sim 10^{10}$ collisions per second. All these collisions result in the exchange of energy and it is the net macroscopic transfer of energy resulting from all the microscopic energy transfers that we call heat.

Recall that the *first law of thermodynamics* is

$$dU = dQ + dW ,$$

where dU is the change of (internal) energy of a system, dQ is energy added to the system via a heat transfer, and dW is energy added by doing work on the system.

Aside: you will often see the heat and work written as $\bar{d}Q$ and $\bar{d}W$. This is a reminder that these quantities are not perfect differentials, just small changes. A system (in equi-

librium) has a well defined internal energy $U(P, V, \dots)$ which can be differentiated with respect to P , V , \dots , but there is no such thing as the heat or work content of a system. The heat and work refer to energy transfers during a change to the system.

So the first law really boils down to a statement of energy conservation. You can change the energy of a system by adding energy microscopically (dQ) or macroscopically (dW).

While we're at it, the *second law of thermodynamics* can be stated in many ways, but one way (without worrying too much about rigor) is: it's impossible to turn heat completely into work with no other change. So for example, if you build a heat engine (like a power plant) you can't turn all the heat you get (from burning coal) completely into electrical energy. You must dump some waste heat. From this law, one can derive the existence of entropy and the fact that it must always increase. (Or you can define entropy, and state the second law in terms of the increase in entropy).

Entropy

Earlier, we mentioned that temperature is related to internal energy. So, a picture we might carry around is that as the temperature goes up, the velocities of the random motions of the molecules increase, they tumble faster, they vibrate with greater amplitude, etc. What kind of picture can we carry around for entropy? Well that's harder, but as the course goes along we should develop such a picture.

To start, we might recall that the change in entropy of a system is the heat added to the system divided by the temperature of the system (all this is for a reversible process, etc.):

$$dS = dQ/T .$$

If a $dQ > 0$ is added to one system, $-dQ$ must be added to a second system. To ensure that entropy increases, $T_1 < T_2$; the first system is cooler than the second system. The molecules in the first system speed up and the molecules in the second system slow down. After the heat is transferred (in a direction which makes entropy increase) the distribution of molecular speeds in the two systems is more nearly the same. The *probability* that a fast molecule is from system 1 has increased while the probability that a fast molecule is from system 2 has decreased. Similarly, the probability that a slow molecule is from system 2 has increased and the probability a slow molecule is from system 1 has decreased. In other words, as a result of the increase of entropy, the odds have become more even. So increasing entropy corresponds to a leveling of the probabilities.

Higher entropy means more uniform probability for the possible states of the system consistent with whatever constraints might exist (such as a fixed total energy of the system). So entropy is related to the number of accessible states of the system and we will

find that maximizing the entropy is equivalent to assuming that each accessible state is equally likely.

The first law of thermodynamics can be written as

$$dU = dQ + dW = T dS - p dV \quad \text{or} \quad dS = dU/T + p dV/T ,$$

where we've assumed that the number of particles in the system is constant and the work done on the system results from pressure acting while the volume changes. Suppose the system is an ideal gas. Then the energy depends only on temperature

$$dU = nC_V dT ,$$

where n is the number of moles and C_V is the molar specific heat at constant volume which we take to be constant. The equation of state is

$$pV = nRT \quad \text{or} \quad p/T = nR/V ,$$

where R is the gas constant. We plug these into the first law and obtain

$$dS = nC_V \frac{dT}{T} + nR \frac{dV}{V} ,$$

which can be integrated to give

$$S_f - S_i = nC_V \log \frac{T_f}{T_i} + nR \log \frac{V_f}{V_i} .$$

So, we have an expression for the entropy difference between any two states of an ideal gas. But how can we relate this to what's going on at the microscopic level? (Note, unless otherwise stated, by log, I mean a natural logarithm, \log_e .)

First, let's make a distinction between the *macroscopic state* and the *microscopic state*. The macroscopic state is completely specified (at equilibrium!) by a small number of parameters such as p , V , n , etc. Classically, the microscopic state requires the specification of the position and velocity of each particle

$$\mathbf{r}_1, \mathbf{v}_1, \mathbf{r}_2, \mathbf{v}_2, \dots, \mathbf{r}_N, \mathbf{v}_N ,$$

where N is the number of particles. N is usually a huge number, comparable to Avogadro's number, the number of particles in a mole, $N_0 = 6.02 \times 10^{23}$. Since there is such a large ratio of microscopic to macroscopic parameters, it must be that many microscopic states may produce a given macroscopic state.

How many microscopic states are there? Why do we want to know? The idea is that the macroscopic state which is generated by the most microscopic states is the most likely. Suppose we say that

$$S \propto \log g ,$$

where g is the number of microstates corresponding to the macrostate.

This definition has the desirable property that if we have two non-interacting systems with states g_1 and g_2 , and we bring them together, the entropy is additive.

$$S = S_1 + S_2 .$$

Since the systems are non-interacting, bringing the systems together does not change the states available to either system, and any microstate of system 1 may be combined with any microstate of system 2 to yield a microstate of the combined system. This means that there are a total of $g_1 \cdot g_2$ states altogether. By defining the entropy with a logarithm, we ensure that it's additive (at least in this case!).

So let's count states. At first sight, you might think there are an infinite number of states because \mathbf{r} and \mathbf{v} are continuous variables. Well, perhaps if you change them only slightly, you don't really get a new state.

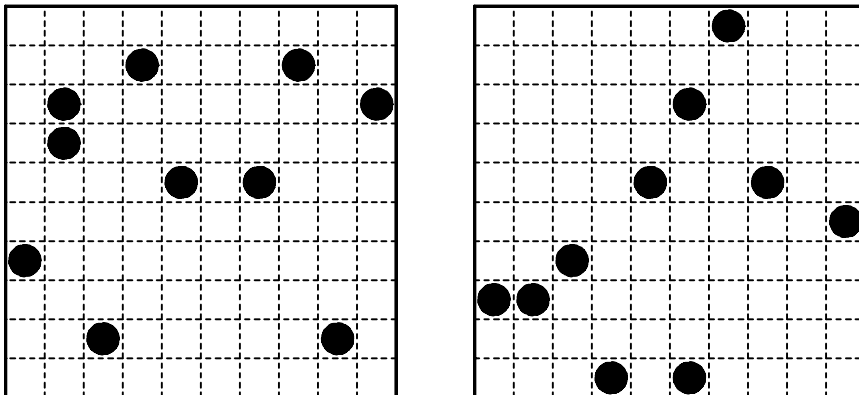
Example: Ideal Gas Entropy

Consider one mole of ideal gas at STP. Its volume is $V = 22.4 \text{ L} = 2 \times 10^4 \text{ cm}^3$ and it contains $N_0 = 6 \times 10^{23}$ molecules. How big is a molecule? Answer: about $1 \text{ \AA} = 10^{-8} \text{ cm}$. A molecular volume is $V_m \approx 10^{-24} \text{ cm}^3$. Imagine dividing our total volume V into cells the size of a molecule. There are $M = V/V_m = 2 \times 10^{28}$ cells. Let's specify the micro-position state by stating which cells have molecules in them. That is, we are going to specify the positions of the molecules to a molecular diameter. How many states are there? Pick a cell for the first molecule. This can be done in M ways. Pick a cell for the second molecule. This can be done in $M - 1 \approx M$ ways. For the third molecule, there are $M - 2 \approx M$ ways. Continue to the N^{th} molecule for which there are $M - N \approx M$ ways to pick a cell. Altogether there are about

$$g \approx M^N \approx (10^{28})^{10^{24}} ,$$

ways to distribute the molecules in the cells. The fact that we get M^N rather than a binomial coefficient depends on the fact that $M \approx 10^{28} \gg N \approx 10^{24}$. Also, we should probably divide by $N!$ to account for permutations of the molecules in the cells (since we can't distinguish one molecule from another), but leaving this out won't hurt anything at this point.

As an example, consider a two dimensional gas containing $N = 10$ molecules and $M = 100$ cells. The figure shows a couple of the possible position microstates of this gas.



There are

$$M!/N!(M - N)! = 1.7 \times 10^{13}$$

distinct states. Our approximation gives 10^{20} states; the difference is mostly due to ignoring the $10!$ in the denominator.

Knowing the number of states, we have

$$\begin{aligned} S &\propto N \log M , \\ &= N \log \frac{V}{V_m} , \\ &\quad \text{constant for given amount of gas} \\ &= \underbrace{N \log V}_{\text{volume term in entropy}} - \overbrace{N \log V_m} . \end{aligned}$$

The $N \log V_m$ term is a constant for a given amount of gas and disappears in any calculation of the change in entropy, $S_f - S_i$. Similarly, the $N!$ correction would also disappear. So a lot of the (really awful?) approximations we made just don't matter because things like the size of a molecule drop out as long as we only consider entropy differences.

The $N \log V$ term is the volume term in the ideal gas entropy. By considering the microstates in velocity, we would obtain the temperature term (and we will later in the term!).

What Those Large Numbers Mean

The key aspect of all this is the large number of states! Suppose we have a gas in equilibrium in a container of volume $2V$. Why doesn't the gas, by chance, wind up in one-half the container with volume V ? How many states are there in each case?

$$g_1 = \left(\frac{V}{V_m} \right)^N, \quad g_2 = \left(\frac{2V}{V_m} \right)^N.$$

And,

$$\begin{aligned} \frac{g_2}{g_1} &= 2^N, \\ &= 2^{\text{Avogadro's Number}}, \\ &= 2^{6 \times 10^{23}}, \\ &= 10^{2 \times 10^{23}}, \\ &= 1 \underbrace{000 \dots 000}_{2 \times 10^{23} \text{ zeros}}. \end{aligned}$$

Such a state might be legal, but it's **extremely!!!** unlikely. The fact that a system in equilibrium has the maximum possible entropy is nothing more than the fact that the normal equilibrium state has so many more ways to occur than an obviously weird state, that the weird state just never occurs.

Quantum Mechanics and Counting States

You might be thinking that's it pretty flaky to assert that we need only specify a molecular position to a molecular diameter. We've shown that as long as it's small, the resolution has no effect on our calculation of changes in the entropy, so this is OK for classical mechanics.

If we consider quantum mechanics, then we find that systems are in definite states. There are many ways to see this. An example is to consider a particle in a box and fit the wave functions in.

Another way is to consider the uncertainty principle,

$$\Delta p_x \Delta x \geq \hbar/2.$$

If the state of the system is specified by a point in the $x p_x$ diagram (phase space), then one can't tell the difference between states which are as close or closer than the above. So we can divide up this phase space into cells of $\hbar/2$ and we can specify a state by saying which cells are occupied and which are not.

As a numerical example, consider air (N_2) at room temperature. $m_{\text{N}_2} = 28m_p = 28 \times 1.7 \times 10^{-24} \text{ g} = 4.8 \times 10^{-23} \text{ g}$. A typical kinetic energy is $mv^2/2 = 3kT/2$ with $T = 300 \text{ K}$ and $k = 1.38 \times 10^{-16} \text{ erg/K}$, then $E \sim 6 \times 10^{-14} \text{ erg}$, $v \sim 5.1 \times 10^4 \text{ cm/s}$, $p \sim 2.4 \times 10^{-18} \text{ g cm/s}$. The molecular size is about $r \sim 1 \text{ \AA} = 10^{-8} \text{ cm}$, so

$$pr = 2.4 \times 10^{-26} \text{ g cm}^2/\text{s} > \hbar = 1 \times 10^{-27} \text{ erg s}.$$

Thus, at room temperature, one can specify the momentum of a molecule to a reasonable fraction of a typical momentum and the position to about the molecular size and still be consistent with quantum mechanics and the uncertainty principle. That is, room temperature air is classical, but not wildly separated from the quantum domain. If we consider lower temperatures or higher densities, electrons in metals, etc. quantum effects will be more important.

The ideal gas at STP is a “low occupancy” system. That is, the probability that any particular state is occupied is extremely small. This means that the most likely number of occupants of a particular state is zero, one occurs very rarely, and we just don’t need to worry about two at all. This is the classical limit and corresponds to the *Boltzmann distribution*.

If we have higher occupancy systems (denser and/or colder), then states occupied by two or more particles can become likely. At this point quantum mechanics enters. There are two kinds of particles: integer spin particles called *bosons* (such as photons or other particles that we associate with waves) and half-integer spin particles called *fermions* (protons, electrons, particles that we associate with matter). An arbitrary number of bosons can be placed in a single quantum state. This leads to *Bose-Einstein statistics* and the *Bose distribution*. At most one fermion can be placed in a quantum state. This leads to *Fermi-Dirac statistics* and the *Fermi distribution*.

A lot of what we do this term will be learning about and applying the Boltzmann, Bose, and Fermi distributions!