A little book about matter

> "With this chapter we begin a new subject which will occupy us for some time. It is the first part of the analysis of the properties of matter from the physical point of view, in which, recognizing that matter is made out of a great many atoms, or elementary parts, which interact electrically and obey the laws of mechanics, we try to understand why various aggregates of atoms behave the way they do."
>
> — Feynman, *Lectures on Physics*, Vol. I, section 39–1

Lesson 2: Experiments with air

An important development that took place during the 1600s was about understanding the nature of air and what it meant to have no air at all.[1] One of Galileo's students, Torricelli, invented the **mercury barometer** in 1643, and with this new device in hand, a group of people set out to investigate the properties of air (here's how you make a mercury barometer.). The *experimentum crucis* (= "crucial experiment") was when a delegation led by Blaise Pascal's brother-in-law Florin Perier compared the level of a barometer at sea level to one at top of a local volcanic mountain called Puy de Dôme (in France). The conclusion was that air indeed exerted a pressure on its surroundings and there was less pressure at the top of the mountain than at the bottom. The experiment revealed that the atmosphere gets thinner as you go higher, and it even suggested that if you go high enough it will thin out entirely into a **vacuum** – just like the vacuum above the mercury in Torricelli's barometer tubes (in those days many people didn't believe that "nothing" could exist).

[1] In Wootton's book *The Invention Of Science*, he describes how the network of people performing experiments on air marked the beginning of the institutionalisation of science and it led to the founding of major scientific societies such as the Royal Society of London in 1660

Figure 1: Torricelli and his mercury barometer on the left (1643). On the right, Pascal's brother-in-law, Florin Perier, and his delegation on Puy de Dome performing some of the first experiments that were shared with a greater scientific community (1648).

The barometer is an interesting technological invention that led to a much better understanding of gases and paved the way to atomic theory[2]. The principle behind it is simple to illustrate: Fill a test tube (or a drinking glass with a flat, smooth rim) with some water all the way to the top, put a plastic cover (or piece of cardboard) on top, and gently invert the whole thing while holding the cover in place. Now slowly let go of the cover (do it over a sink

[2] Better scientific understanding very often follows from developments in technology.

just in case!) and notice that the water doesn't flow out! It's a great party trick to hold this over someone's head :) The explanation is as follows: The pressure from the atmosphere due to all the atoms bumping into the cover from below can easily hold the weight of the water. This also explains how straws work, see figure 2.

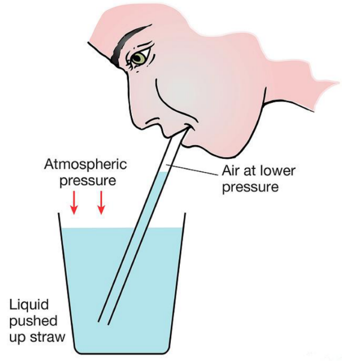

Figure 2: When you suck on one end of a straw, you are lowering the pressure of the air *inside the straw*, so that the outside atmosphere pushing down on your drink, can drive the liquid up the straw. In reality you are not the one sucking up the liquid, it's the atmosphere pushing it up the straw. If your straw is 10.3 m tall, you have to create a vacuum with your mouth in order to drink from it!

So how much water can the pressure of the atmosphere support in this way? Since ancient times it was known that you can't use a suction pump to lift up water from a depth of more than around 10.3 m (watch this video if you have time). Hence the average pressure of the atmosphere corresponds to the weight of a 10.3 m long column of water (this is quite a lot of pressure – I will use it to crush a soda can in class!). Torricelli realised that since mercury (Hg) is about 13.6 times more dense than water, he could make a smaller barometer, since the height of a mercury column would be 13.6 times smaller than 10.3 m which is about 760 mm (this is why pressure is sometimes given in units of mmHg = millimeters of mercury). As the density of air surrounding us changes with changing weather conditions, the overall pressure of the atmosphere changes and hence the level of mercury goes up and down over time. We can use these pressure changes to predict the weather: Lower than average pressure normally brings poor weather, higher than average normally brings nice, stable weather.

Following the experiments of Torricelli, Pascal, and Perier, the study of empty space became one of the hottest topics in science. In order to investigate this phenomenon, scientists needed very efficient pumps that could suck air out of glass bottles and other vessels. These pumps were hi-tech by the standards of the day – the seventeenth-century equivalent of modern particle accelerators[3]. The best air pumps available in the 1600s were made by Robert Hooke (of Hooke's law fame), who was working at the time as an assistant to Robert Boyle. Boyle was a pioneering scientist who helped found the Royal Society of London and he gave Hooke the task of investigating the pressure of air in greater detail.

[3] Modern particle accelerators rely on an almost perfect vacuum being created inside of them, hence there is a direct line from these early experiments to cutting edge modern physics!

Hooke took a glass tube shaped like the letter J, with the top open and the short end closed, see figure 3. He poured mercury into the tube to fill the U-bend at the bottom, sealing off the air trapped in the short arm of the J. When the mercury was at the same level on both sides of the U-bend, it meant that the trapped air was at atmospheric pressure. But when more mercury was poured into the tube, because of its extra weight the pressure increased and forced the air in the closed end into a smaller space. Hooke's careful measurements showed that the volume of the trapped air was inversely proportional to the pressure. This result was first explicitly stated in Boyle's book from 1662 and as a result it has become known as **Boyle's law** even though Hooke actually deserves the credit!

The realisation that air exerts a pressure, has weight, and can be extracted to leave a vacuum, led directly to the steam engine and the industrial revolution. These experiments also supported the

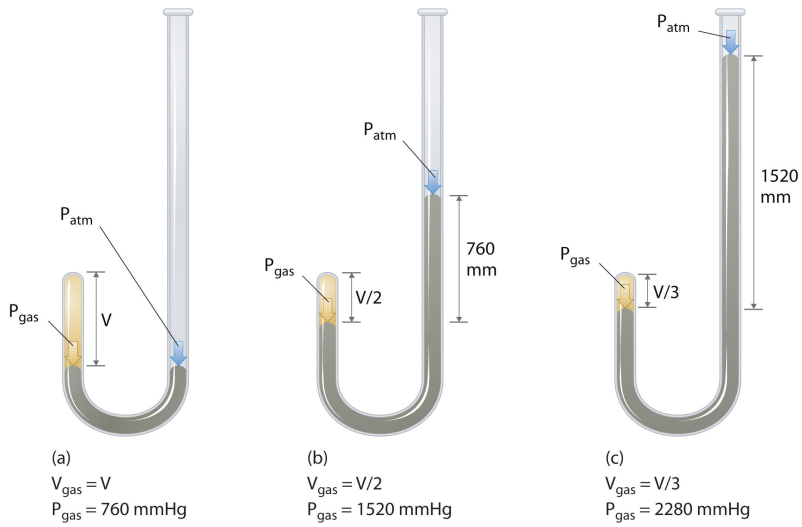

Figure 3: Hooke first trapped some normal air in the closed end of the tube. In this case the trapped air is exerting as large a pressure on the mercury (Hg) as the air in the open end is, which we know to be 760 mmHg. He then added another 760 mm of mercury to the open end, thereby doubling the pressure on the trapped gas, and noticed that the volume halved. Adding another 760 mm of mercury and tripling the pressure, decreased the volume by a factor 3. An inversely proportional relationship!

idea that air is made of moving particles (atoms and molecules) colliding with one another, although these ideas were first properly introduced in the early 1800s. It's not a coincidence that John Dalton, one of the first atomic theorists loved walking through the countryside of England taking atmospheric measurements (see figure 4). In 1787 at age 21 Dalton began his meteorological diary in which, during the succeeding 57 years, he entered more than 200,000 observations. Truly understanding reality requires persistence and careful attention to detail!

Figure 4: The road to reality. John Dalton spent many years walking the hills of the Lake District collecting data on atmospheric variations. Before the invention of aeroplanes and weather balloons, the only way to take measurements of temperature and humidity at an altitude was to climb a mountain. His experiments with air and other gases paved the way for the atomic theory. In place of the unified atomic mass unit (u) one can instead use the unit dalton (Da) in memory of John Dalton.

The ideal gas law

As scientists performed further experiments with air, they discovered a few laws that they combined into one law called the **ideal gas law**. This law first appeared as an **empirical law** (a law based purely on experimental results). It was only after Clausius, Maxwell, and Boltzmann from 1857–1871 made theoretical progress using **statistical methods**[4] that it became possible to rigorously derive the ideal gas law theoretically from Newton's laws of mo-

[4] *Statistical mechanics* is a mathematical framework that applies statistical methods and probability theory to large assemblies of microscopic entities. It does not assume or postulate any natural laws, but explains the macroscopic behavior of nature from the behavior of such ensembles. Statistical mechanics arose out of the development of classical thermodynamics, a field for which it was successful in explaining macroscopic physical properties – such as temperature, pressure, and heat capacity.

tion. This was a result that reinforced how powerful Newtonian mechanics was. The theory describing a gas in this way is often referred to as the **kinetic theory of gases**. Let's first explore the experiments that led to the ideal gas equation being formulated. (If you haven't got any equipment available, then you can simulate the experiments using this PhET simulation.)

Boyle's law (1662)

Boyle's law states that for a given amount of gas at a particular constant temperature T, the pressure p of a gas is inversely proportional to its volume V (see figure 3 again):

$$p \propto \frac{1}{V} \iff pV = \text{constant} \quad (\text{given a constant } T)$$

Charle's law (1780)

For a given amount of gas at a particular constant pressure p, the volume V of a gas depends on its temperature T (in degrees celsius) as shown in figure 5 (notice you get different slopes for different constant pressures). As you can see gases tend to expand as the temperature rises.

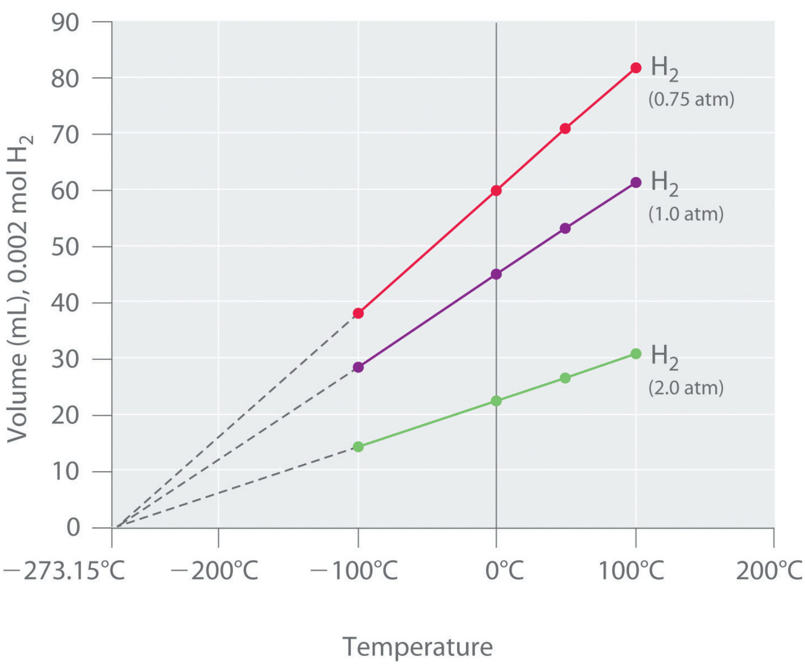

Figure 5: Data plots showing how the volume of a gas depends on it temperature (in degrees celsius).

Is volume directly proportional to temperature? No, because the straight lines don't go through the origin. However, the graphs suggest that if we shifted the origin of the temperature scale −273.15 units to the left, then the relationship would indeed be directly proportional. Hence let's define a new temperature scale, measured in **kelvin**, K, as follows

$$T(\text{measured in K}) \equiv T(\text{measured in °C}) + 273.15$$

Note that a one kelvin increase in temperature is equal to a one degree celsius increase, the only difference is that the zero has been shifted. Using this unit, we can now state that volume indeed is directly proportional to temperature given a constant pressure and this is referred to as Charle's law:

$$V \propto T \iff \frac{V}{T} = \text{constant} \quad (\text{given a constant } p)$$

Temperature measured in kelvin is referred to as an **absolute temperature** (although we often omit the term absolute when it's clear from the context). 0 K is defined as the **absolute zero** and scientists routinely achieve temperatures that come very close to this (nano- and picokelvin, i.e. 10^{-9} K and 10^{-12} K). At these temperatures matter exhibits quantum effects such as Bose-Einstein condensation, superconductivity and superfluidity (see this timeline of low temperature achievements - a lot of Nobel Prizes have been given out in this area of physics). The ideal gas model that we will derive later is not valid at such low temperatures (among other things, a gas will start to condense into a liquid long before reaching those low temperatures).

Gay-Lussac's law (1808)

Gay-Lussac's law states that for a given amount of gas with a constant volume V, the pressure p of a gas is directly proportional to its absolute temperature T:

$$p \propto T \iff \frac{p}{T} = \text{constant} \quad (\text{given a constant } V)$$

Think of heating up a gas enclosed in a metal container.

Avogadro's law (1811)

Avogadro discovered that the volume V of a gas is directly proportional to the quantity n of a gas, given a constant pressure and temperature. This is now called Avogadro's law:

$$V \propto n \iff \frac{V}{n} = \text{constant} \quad (\text{given a constant } p, T)$$

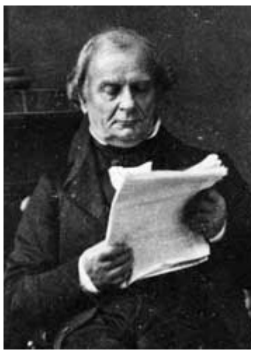

Figure 6: Benoît Paul Émile Clapeyron (1799–1864) was a French engineer and physicist, one of the founders of thermodynamics.

The ideal gas law (1834)

In 1834, Clapyron (the gentleman on the right), combined all the above empirical gas laws into one expression:

$$\frac{pV}{nT} = \text{constant} \equiv R$$

where R is called the **gas constant** (we'll find its value in a minute) and we often write this **ideal gas law/equation** as follows:

$$pV = nRT$$

Convince yourself that whenever two of the four variables (p, V, n, T) in the above equation are held constant, you get one of the above four gas laws. There are two more laws 'hidden' in the ideal gas law, because you can pick 2 out of 4 items in 6 ways - what are they? In our next lesson we will derive the ideal gas law using Newtonian mechanics.

Lesson 2: Exercises

1. What is 0 °C in kelvin? What is 100 °C in kelvin? These two temperatures are respectively the freezing point and boiling point of water and they are the defining points of the **Celsius** temperature scale.

2. What is a healthy body temperature in kelvin?

3. (Boyle's law) For a given temperature sketch how p depends on V. What do we call such a curve in mathematics? In thermodynamics we call them **isothermals**.

4. (Boyle's law) 1 L of air at 1 atmospheric pressure is slowly compressed to a volume of 0.2 L at constant temperature.

   (a) What is the pressure of the air (measured relative to 1 atmospheric pressure)?

   (b) Your answer to (a) is only correct provided the compression happens slowly which enables the temperature to remain constant (heat has time to be exchanged with the surroundings). Graph the process in a pV-diagram.

   (c) If the volume decreases rapidly, what will happen? A process in which heat cannot be exchanged with its surroundings is called an **adiabatic** process. Convince yourself that adiabatic curves are steeper than isothermals going through the same point in a pV-diagram.

5. (Charles' law) A balloon takes up a certain volume at 28 °C. The balloon is now put into a freezer that is −18 °C and after a while the volume shrinks a bit.

   (a) What fraction of the original volume is the new volume?

   (b) I tried this experiment at home and I measured the circumference of the balloon reduce from 49.4 cm to 47.0 cm. Check that this is in agreement with your calculation in (a). (Is the difference within the expected uncertainty if the radius has an absolute uncertainty of 0.1 cm?)

   (c) Draw this **isobaric** process (= constant pressure) in a pV diagram.

6. (Gay-Lussac's law) An amount of gas is enclosed in a fixed metal container at one atmospheric pressure at temperature 0 °C. What does the pressure increase to when it is heated up to 100 °C? Draw this isovolumetric (or isochoric) process in a pV diagram.

7. If the atmospheric pressure at ground level corresponds to roughly 10 meters of water and can easily crush an empty can, why don't we experience this pressure all the time?

8. There are different types of barometers, see here. You can easily make your own water barometer that is not 10.3 meters tall as explained here (10.3 m requires a vacuum at the top).

9. In the inverted drinking glass experiment, you will notice that it even works if you don't fill up the glass. Try it out. How is that possible if the air trapped on top of the water is atmospheric air at the same pressure as outside? Shouldn't the extra weight of the water easily push away the cover? Related questions to think about: How do suction cups work? Has capillary action got anything to do with this? If trees are sucking up water, how can they be taller than 10.3 meters?

Answers to all the exercises.