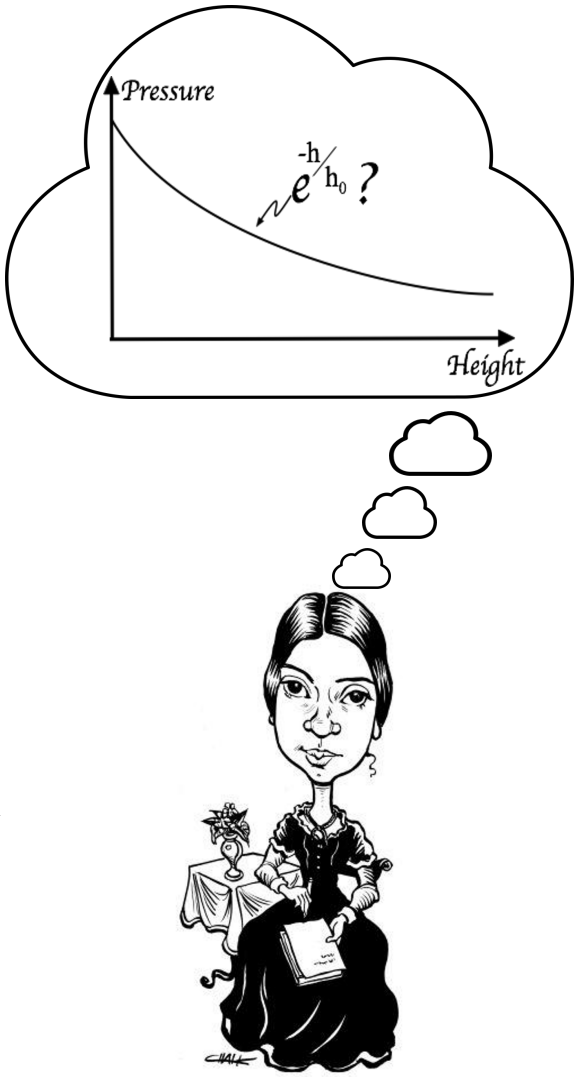
Chapter IX
Atoms, Caloric, and the Kinetic Theory of Heat

It troubled me as once I was,
For I was once a child,
Concluding how an Atom fell,
And yet the Heavens held.

The Heavens weighed the most by far,
Yet Blue and solid stood,
Without a bolt that I could prove.
Would Giants understand?

- Emily Dickinson



The idea that there is an indivisible unit of matter, an atom, dates back to the Greeks. It was advocated by Leucippus and Democritus, and ridiculed by Aristotle. The modern theory got going around 1785-1803 with the experiments and interpretations of Lavoisier, Dalton, and Proust (Joseph the chemist, not Marcel the writer). The most important result was that chemical reactions always involved different substances in definite proportions – which Dalton interpreted as arising from the pairing of elements to form molecules, in definite proportions (1:1, 1:2, etc.) This didn't persuade many physicists, however; it was one fairly complex hypothesis to explain one type of experimental result. In addition, the postulated atoms had a size and mass smaller than anything that can be directly observed. Not observable... this sounded suspicious.

Meanwhile, there was a fierce debate raging in physics about **the nature of heat**. Lying in a hot bath, or at the side of a hot fire, or under the hot Sun, one gets a strong impression that heat is a fluid. The fluid received an official name – ***caloric*** – and many books were written exploring the properties of caloric. For one thing, it's *self-repellent* – that's why heat always spreads to its

adjacent surroundings. Most scientists believed in caloric, certainly including Lavoisier and Carnot, perhaps the most famous chemist and physicist of their day.

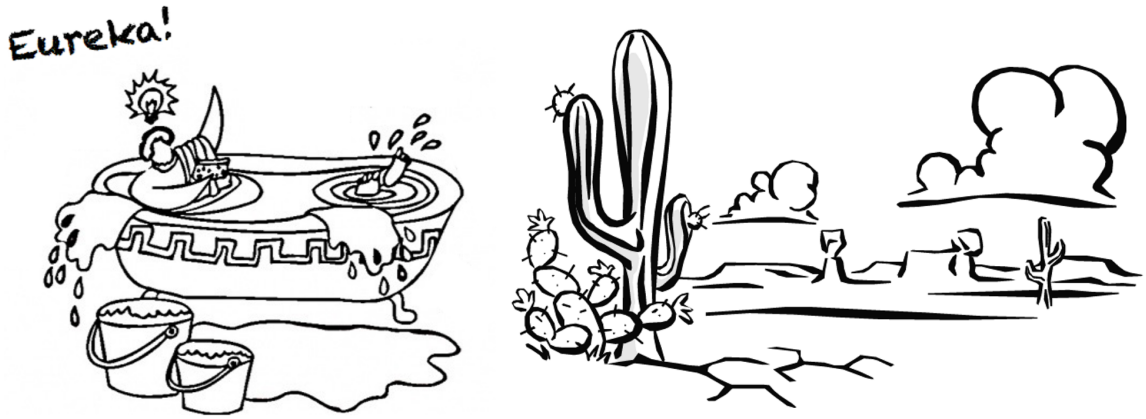


Figure 1: Heat doesn't always get you wet, but otherwise feels like a fluid.

The first experiment to raise trouble for the caloric theory was that of Count Rumford (whose real name was Benjamin Thompson; as an American Tory, he had to move to England and re-invent himself during the American Revolution). Observing the process of boring out a cannon, Rumford noted that as you continue to bore out a cannon with friction (motion), you continue to generate heat (caloric). Where does the caloric come from? You can bore out a cannon on the coldest of days, and you keep generating heat as long as you keep boring. You can measure the amount of caloric by measuring the quantity of hot water produced in cooling the cannon; and this proved, at the very least, that *caloric is not a conserved quantity*. Instead, it might be related to motion – the more motion, the more heat.

Most physicists were in the caloric camp, but not everybody. An alternative was the kinetic theory, which held that heat is just <u>microscopic kinetic energy</u>. This "kinetic theory" went all the way back to Robert Boyle, a contemporary of Newton. Experimenting with gases, Boyle learned that when you heat a gas, the pressure always increases . . . and when you compress a gas (e.g. by moving a piston in a cylinder, like in a bicycle pump or automobile engine), it always heats up. Mathematically, the pressure P, the temperature T, and the density ρ are related by

$$\boxed{P = \rho T} \qquad (1)$$

This is known as the *ideal-gas law*, and is often attributed to Boyle, although formulated more precisely later, by Daniel Bernoulli and Joseph-Louis Gay-Lussac. Boyle speculated that the source of the pressure exerted by a gas might be *the impact of small particules on the walls of the container,* and Bernoulli proved in 1738 that this hypothesis actually yields the correct experimental result, Equation (1).

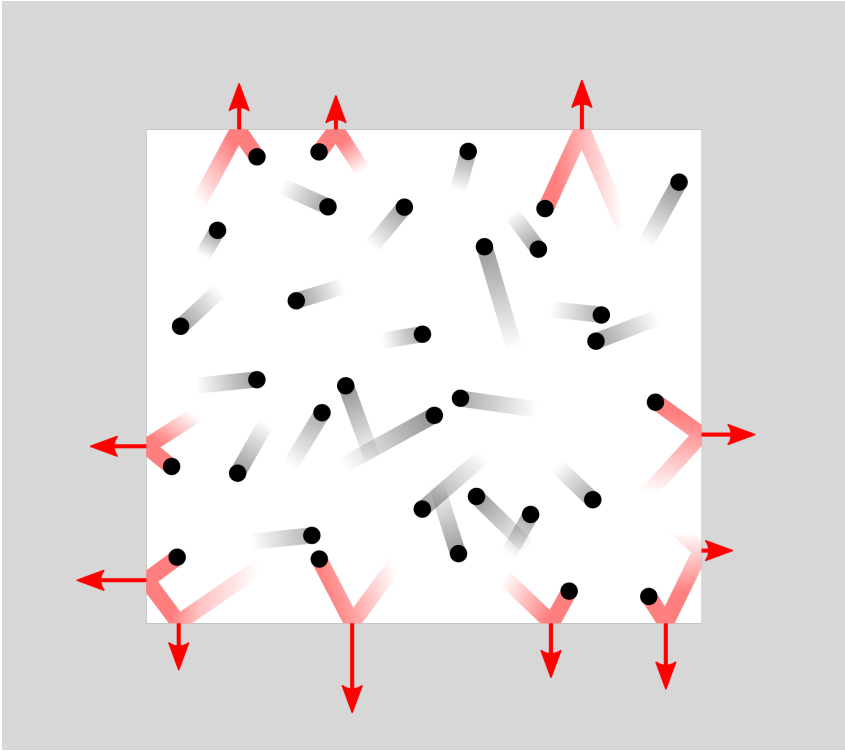


Figure 2: The Kinetic Theory. The gas particles move rapidly about, colliding with each others *and with the walls.* The latter constitutes the *pressure.*

That all sounds good, but was equally compatible with caloric, which was definitely the preferred theory. You could explain nearly everything with caloric. Pressure rises with temperature because gas acquires more of the self-repellent fluid. Temperature is just the density of caloric (amount per volume). Caloric is a macroscopic substance you can feel and measure.

A few experiments didn't fit quite so well. Count Rumford's experiment on the boring of cannon. James Joule's experiments, which showed that in general, 4.18 J of mechanical energy always produced one calorie of heat. The simplest interpretation of that is that heat ***is*** mechanical energy. Joule's free-expansion experiment: when a hot gas pushes against a piston with a vacuum behind it, it does so with no cooling of the gas. That was strange: it makes the density of caloric less, so why doesn't the temperature fall? But kinetic theory had some powerful objections too. Perhaps the most serious was simply this: it requires believing in the existence of entities (atoms) too small to detect! Could that be considered a "scientific" theory? And it couldn't answer a pretty simple question: if mechanical energy produces heat at a known rate (4.18 J => 1 calorie), then why can't heat produce mechanical energy at that rate?[1]

In the 1840s, James Joule and Herman Helmholtz made frequent and strong defenses of the kinetic theory. Joule was a brilliant experimenter who had

1. We now know the answer to that: the second law of thermodynamics!

been a student of Dalton, and thus firmly believed in atoms. Helmholtz was just brilliant, period. He was perhaps the greatest German physicist of his time, and also made many important discoveries in physiology and medicine (he was an MD). His 1847 book "On the Conservation of Vis Viva" asserted the conservation of energy and identified heat as merely microscopic kinetic energy – as Bernoulli had stated, with considerable scientific evidence, a century earlier. By about 1850, the kinetic theory had many adherents, though still commonly opposed by the more philosophically-minded physicists, who were troubled by the appeal to unobservable particles.

By the way, why did the debate about atoms so closely involve the properties of gases? Solids and liquids allegedly consist of atoms, too. But in solids and liquids, the separation between atoms is similar to their sizes, and there are significant forces between neighboring atoms. That really complicates things. On Earth, gases present a far simpler laboratory. If this debate had taken place on Jupiter, where the density of gases is similar to the density of water, we might still be arguing about it.

The Macro- and the Micro-World

Still, no one could see atoms. Tests of the theory had to rely on the scaling between macroscopic physical quantities, which you can measure, and the underlying microscopic quantities, which you can't. One useful key to connecting them is "Avogadro's number", customarily written as 6×10^{23}. It's the number of molecules in one gram of hydrogen, the simplest gas. That tells you the mass of one hydrogren atom, namely 1.7×10^{-24} grams. Pretty tiny![2]

You can more easily calculate these masses if you use the modern system of ***atomic mass unit*** (***amu***). Basically, every atom has a mass of *A* amus, where A is the atomic weight and 1 amu = 1.7×10^{-24} g. So look up *A* on your periodic table, and account for the molecular complexity if you're dealing with molecules rather than atoms. For example O_2 is 32 amu, H_2O is 18 amu, CO_2 is 44, DNA is... (just kidding).

The other key is energy. Atoms and molecules in a gas have kinetic energy, while the macroscopic quantity is heat. Joule gave the equivalent: 4.18 J = 1 calorie. That's nice. But it's just a conversion factor between two things in the macro-world: the KE of a spinning paddle-wheel, and the temperature rise of water (1 calorie is defined as the heat to raise 1 g of water by 1 degree centigrade). What about the KE of an actual atom?

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2. By the way, electrons don't matter here. They amount to less than 0.1% of the mass of atoms, and are therefore negligible. Also, they're an anachronism – not discovered until 1897, whereas atomic masses were known with decent accuracy much earlier.

Ludwig Boltzmann put the (almost-) finishing touches on the kinetic theory. He derived

$$\langle KE \rangle = (1/2)\, m \langle v^2 \rangle = kT, \qquad (2)$$

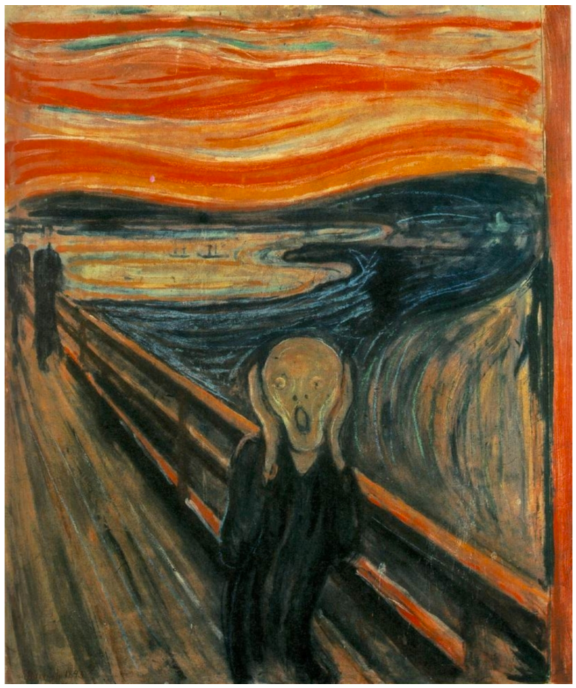
where k = Boltzmann's constant = 1.38×10^{-23} J/K deg. This is solved by $\langle v \rangle = \sqrt{(2kT/m)}$. Remembering that 1 amu = 1.7×10^{-27} kg, this implies that the average speed at room temperature (T=300 K) for the majority species in our atmosphere (N_2) is about 400 m/s.

Now 400 m/s is about 850 mph. Does that seem right? Do the molecules in your room really move that fast?

Yes, they do. The speed of sound is 770 mph, and since sound is a longitudinal wave, the speed of the particles carrying the sound should equal the speed of sound. Very, very nice – the speed of sound just naturally falls out of the kinetic theory of gases!

And so do the laws of pressure, too. The kinetic theory says that **gas exerts pressure by virtue of the force of colliding particles** – as Boyle had speculated in the 1700s, and as shown in Figure 2.

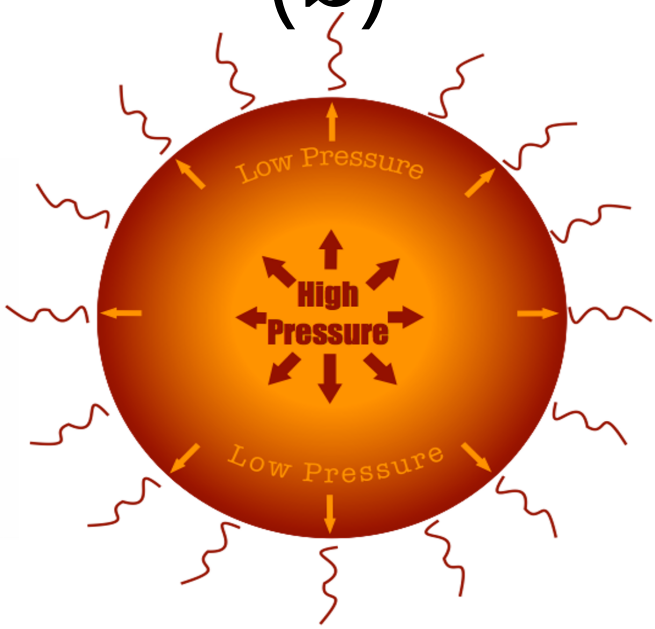
Here are some everyday pressure situations:



(a)

(b)

(c)



(d)

(a) is certainly common enough. Edward Munch's life had more than its fair share of the slings and arrows of outrageous fortune... but maybe none that relate to the kinetic theory. So we'll pass on to (b).

(b) Why do helium balloons rise in air? We say "because they're lighter than air". But what that means is: "because the force below the balloon exceeds the force above the balloon by more than the weight of the balloon". Normal atmospheric pressure at sea level is 15 pounds per square inch (15 psi), because

at sea level, 14 pounds of atmosphere overlies each square inch. 5 miles up, you're above half the atmosphere, so the pressure is just 7.5 psi. That difference in pressure – the ***pressure gradient*** – is what propels the balloon upward. It's extremely small – just 0.001 psi per meter – but that's what does the job. And it's amazingly reliable; if it ever varies appreciably, balloons will fall, and airplanes will fly into the sides of mountains on foggy days (because their barometers will tell lies). Or, if there are no balloons or planes around to illustrate the point, at least there will be severe updrafts or downdrafts in the air.

In fairness, this picture is of the hot-air balloon in *Around the World in 80 Days.* Here the principle is slightly different. Heated air produces a greater pressure (Equation 1), which presses upward and thus provides lift.

(c) A football, or anything sealed with air inside, deflates in cold weather, because the air particles sealed inside hit the walls with less force. (The outside atmospheric pressure is always guaranteed to be 15 psi; otherwise there would be gigantic winds, as nearby high-pressure regions invade low-pressure regions.) Try this yourself with an empty and tightly-capped plastic bottle in your freezer!

(c) Aside from gigantic differences in mass and temperature, stars are just like the Earth's atmosphere. The pressure is enormous at the center – enough to hold up the entire star. Near the edge of the star, the pressure is low. *The pressure gradient is what holds up the star.*

And the atmosphere... and the ocean... and anything floating on the ocean, from a rubber ducky to an aircraft carrier. **It's the answer to Emily Dickinson's question.**