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Table of Contents

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Contents

Chapter 5. Thermodynamics

S=k log *W -- Inscription on the tomb of Ludwig Boltzmann, 1844-1906. Boltzmann, who originated the microscopic theory of thermodynamics, was driven to suicide by the criticism of his peers, who thought that physical theories shouldn't discuss purely hypothetical objects like atoms*.

In a developing country like China, a refrigerator is the mark of a family that has arrived in the middle class, and a car is the ultimate symbol of wealth. Both of these are *heat engines*: devices for converting between heat and other forms of energy. Unfortunately for the Chinese, neither is a very efficient device. Burning fossil fuels has made China's big cities the most polluted on the planet, and the country's total energy supply isn't sufficient to support American levels of energy consumption by more than a small fraction of China's population. Could we somehow manipulate energy in a more efficient way?

Conservation of energy is a statement that the total amount of energy

is constant at all times, which encourages us to believe that any energy transformation can be undone --- indeed, the laws of physics you've learned so far don't even distinguish the past from the future. If you get in a car and drive around the block, the net effect is to consume some of the energy you paid for at the gas station, using it to heat the neighborhood. There would not seem to be any fundamental physical principle to prevent you from recapturing all that heat and using it again the next time you want to go for a drive. More modestly, why don't engineers design a car engine so that it recaptures the heat energy that would otherwise be wasted via the radiator and the exhaust?

Hard experience, however, has shown that designers of more and more efficient engines run into a brick wall at a certain point. The generators that the electric company uses to produce energy at an oil-fueled plant are indeed much more efficient than a car engine, but even if one is willing to accept a device that is very large, expensive, and complex, it turns out to be impossible to make a perfectly efficient heat engine --- not just impossible with present-day technology, but impossible due to a set of fundamental physical principles known as the science of *thermodynamics*. And thermodynamics isn't just a pesky set of constraints on heat engines. Without thermodynamics, there is no way to explain the direction of time's arrow --- why we can remember the past but not the future, and why it's easier to break Humpty Dumpty than to put him back together again.

5.1 Pressure and Temperature

When we heat an object, we speed up the mind-bogglingly complex random motion of its molecules. One method for taming complexity is the conservation laws, since they tell us that certain things must remain constant regardless of what process is going on. Indeed, the law of conservation of energy is also known as the first law of thermodynamics.

But as alluded to in the introduction to this chapter, conservation of energy by itself is not powerful enough to explain certain empirical facts about heat. A second way to sidestep the complexity of heat is to ignore heat's atomic nature and concentrate on quantities like temperature and pressure that tell us about a system's properties as a whole. This approach is called macroscopic in contrast to the microscopic method of attack. Pressure and temperature were fairly well understood in the age of Newton and Galileo, hundreds of years before there was any firm evidence that atoms and

molecules even existed.

Unlike the conserved quantities such as mass, energy, momentum, and angular momentum, neither pressure nor temperature is additive. Two cups of coffee have twice the heat energy of a single cup, but they do not have twice the temperature. Likewise, the painful pressure on your eardrums at the bottom of a pool is not affected if you insert or remove a partition between the two halves of the pool.

We restrict ourselves to a discussion of pressure in fluids at rest and in equilibrium. In physics, the term "fluid" is used to mean either a gas or a liquid. The important feature of a fluid can be demonstrated by comparing with a cube of jello on a plate. The jello is a solid. If you shake the plate from side to side, the jello will respond by shearing, i.e., by slanting its sides, but it will tend to spring back into its original shape. A solid can sustain shear forces, but a fluid cannot. A fluid does not resist a change in shape unless it involves a change in volume.

5.1.1 Pressure

If you're at the bottom of a pool, you can't relieve the pain in your ears by turning your head. The water's force on your eardrum is always the same, and is always perpendicular to the surface where the eardrum contacts the water. If your ear is on the east side of your head, the water's force is to the west. If you keep your ear in the same spot while turning around so your ear is on the north, the force will still be the same in magnitude, and it will change its direction so that it is still perpendicular to the eardrum: south. This shows that pressure has no direction in space, i.e., it is a scalar. The direction of the force is determined by the orientation of the surface on which the pressure acts, not by the pressure itself. A fluid flowing over a surface can also exert frictional forces, which are parallel to the surface, but the present discussion is restricted to fluids at rest.

Experiments also show that a fluid's force on a surface is proportional to the surface area. The vast force of the water behind a dam, for example, in proportion to the dam's great surface area. (The bottom of the dam experiences a higher proportion of its force.)

Based on these experimental results, it appears that the useful way to define pressure is as follows. The pressure of a fluid at a given point is defined as $F_{\perp}/A$, where A is the area of a small surface inserted in the fluid at
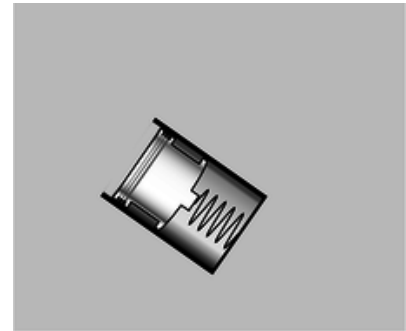
a / A simple pressure gauge consists of a cylinder open at one end, with a piston and a spring inside. The depth to which the spring is depressed is a measure of the pressure. To determine the absolute pressure, the air needs to be pumped out of the interior of the gauge, so that there is no air pressure acting outward on the piston. In many practical gauges, the back of the piston is open to the atmosphere, so the pressure the gauge registers equals the pressure of the fluid minus the pressure of the atmosphere.

that point, and $F_\perp$ is the component of the fluid's force on the surface which is perpendicular to the surface. (In the case of a moving fluid, fluid friction forces can act parallel to the surface, but we're only dealing with stationary fluids, so there is only an $F_\perp$.)

This is essentially how a pressure gauge works. The reason that the surface must be small is so that there will not be any significant difference in pressure between one part of it and another part. The SI units of pressure are evidently N/m^2, and this combination can be abbreviated as the pascal, 1 Pa=1 N/m^2. The pascal turns out to be an inconveniently small unit, so car tires, for example, normally have pressures imprinted on them in units of kilopascals.

Example 1: Pressure in U.S. units

In U.S. units, the unit of force is the pound, and the unit of distance is the inch. The unit of pressure is therefore pounds per square inch, or p.s.i. (Note that the pound is not a unit of mass.)

*Example 2: Atmospheric pressure in U.S. and metric units*

◊ A figure that many people in the U.S. remember is that atmospheric pressure is about 15 pounds per square inch. What is this in metric units?

◊

$$(15 \text{ lb})/(1 \text{ in}^2) = \frac{68 \text{ N}}{(0.0254 \text{ m})^2}$$

$$= 1.0 \times 10^5 \text{ N/m}^2$$

$$= 100 \text{ kPa}$$

**Only pressure differences are normally significant.**

If you spend enough time on an airplane, the pain in your ears subsides. This is because your body has gradually been able to admit more air into the cavity behind the eardrum. Once the pressure inside is equalized with the pressure outside, the inward and outward forces on your eardrums cancel out, and there is no physical sensation to tell you that anything unusual is going on. For this reason, it is normally only pressure differences that have any physical significance. Thus deep-sea fish are perfectly healthy in their habitat because their bodies have enough internal pressure to cancel the pressure from the water in which they live; if they are caught in a net and
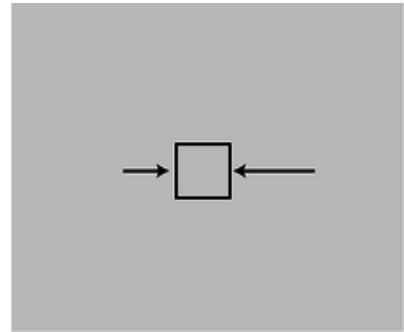
b / This doesn't happen. If pressure could vary horizontally in equilibrium, the cube of water would accelerate horizontally. This is a contradiction, since we assumed the fluid was in equilibrium.

c / The pressure is the same at all the points marked with dots.
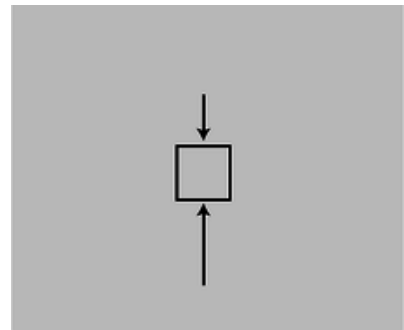
d / This does happen. The sum of the forces from the surrounding parts of the fluid is upward, canceling the downward force of gravity.

brought to the surface rapidly, they explode because their internal pressure is so much greater than the low pressure outside.

Example 3: Getting killed by a pool pump

◊ My house has a pool, which I maintain myself. A pool always needs to have its water circulated through a filter for several hours a day in order to keep it clean. The filter is a large barrel with a strong clamp that holds the top and bottom halves together. My filter has a prominent warning label that warns me not to try to open the clamps while the pump is on, and it shows a cartoon of a person being struck by the top half of the pump. The cross-sectional area of the filter barrel is 0.25 m^2. Like most pressure gauges, the one on my pool pump actually reads the difference in pressure between the pressure inside the pump and atmospheric pressure. The gauge reads 90 kPa. What is the force that is trying to pop open the filter?

◊ If the gauge told us the absolute pressure of the water inside, we'd have to find the force of the water pushing outward and the force of the air pushing inward, and subtract in order to find the total force. Since air surrounds us all the time, we would have to do such a subtraction every time we wanted to calculate anything useful based on the gauge's reading. The manufacturers of the gauge decided to save us from all this work by making it read the difference in pressure between inside and outside, so all we have to do is multiply the gauge reading by the cross-sectional area of the filter:

$$F = PA$$

$$= (90 \times 10^3 \text{ N/m}^2)(0.25 \text{ m}^2)$$

$$= 22000 \text{ N}$$

That's a lot of force!

The word "suction" and other related words contain a hidden misunderstanding related to this point about pressure differences. When you suck water up through a straw, there is nothing in your mouth that is attracting the water upward. The force that lifts the water is from the pressure of the water in the cup. By creating a partial vacuum in your mouth, you decreased the air's downward force on the water so that it no longer exactly canceled the upward force.

Variation of pressure with depth

The pressure within a fluid in equilibrium can only depend on depth, due to gravity. If the pressure could vary from side to side, then a piece of the fluid in between, b, would be subject to unequal forces from the parts of the

e / We have to wait for the thermometer to equilibrate its temperature with the temperature of Irene's armpit.

fluid on its two sides. Since fluids do not exhibit shear forces, there would be no other force that could keep this piece of fluid from accelerating. This contradicts the assumption that the fluid was in equilibrium.

self-check:

How does this proof fail for solids?

(answer in the back of the PDF version of the book)

To find the variation with depth, we consider the vertical forces acting on a tiny, imaginary cube of the fluid having infinitesimal height dy and areas dA on the top and bottom. Using positive numbers for upward forces, we have

$$P_{bottom}dA - P_{top}dA - F_g = 0 \; .$$

The weight of the fluid is $F_g = mg = \varrho \, Vg = \varrho \, dAdy \, g$, where ϱ is the density of the fluid, so the difference in pressure is

$$dP = -\rho g dy \qquad \qquad . \qquad\qquad \text{[variation in pressure with depth for}$$

a fluid of density ρ in equilibrium;

positive y is up.]

A more elegant way of writing this is in terms of a dot product, $dP = \rho \mathbf{g} \cdot d\mathbf{y}$, which automatically takes care of the plus or minus sign, depending on the relative directions of the $\mathbf{g}$ and $d\mathbf{y}$ vectors, and avoids any requirements about the coordinate system.

The factor of ϱ explains why we notice the difference in pressure when diving 3 m down in a pool, but not when going down 3 m of stairs. The equation only tells us the difference in pressure, not the absolute pressure. The pressure at the surface of a swimming pool equals the atmospheric pressure, not zero, even though the depth is zero at the surface. The blood in your body does not even have an upper surface.

In cases where g and ϱ are independent of depth, we can integrate both sides of the equation to get everything in terms of finite differences rather than differentials: $\Delta P = -\varrho \, g \, \Delta y$.

self-check:

In which of the following situations is the equation $\Delta P = -\rho \, g \, \Delta y$ valid? Why?\ (1) difference in pressure between a tabletop and the

feet (i.e., predicting the pressure of the feet on the floor)\ (2) difference in air pressure between the top and bottom of a tall building\ (3) difference in air pressure between the top and bottom of Mt. Everest\ (4) difference in pressure between the top of the earth's mantle and the center of the earth\ (5) difference in pressure between the top and bottom of an airplane's wing

(answer in the back of the PDF version of the book)

Example 4: Pressure of lava underneath a volcano

◊ A volcano has just finished erupting, and a pool of molten lava is lying at rest in the crater. The lava has come up through an opening inside the volcano that connects to the earth's molten mantle. The density of the lava is 4.1 g/cm^3. What is the pressure in the lava underneath the base of the volcano, 3000 m below the surface of the pool?

◊

$$\Delta P = \rho g \Delta y$$

$$= (4.1 \text{ g/cm}^3)(9.8 \text{ m/s}^2)(3000 \text{ m})$$

$$= (4.1 \times 10^6 \text{ g/m}^3)(9.8 \text{ m/s}^2)(3000 \text{ m})$$

$$= (4.1 \times 10^3 \text{ kg/m}^3)(9.8 \text{ m/s}^2)(3000 \text{ m})$$

$$= 1.2 \times 10^8 \text{ N/m}^2$$

$$= 1.2 \times 10^8 \text{ Pa}$$

This is the difference between the pressure we want to find and atmospheric pressure at the surface. The latter, however, is tiny compared to the ΔP we just calculated, so what we've found is essentially the pressure, *P*.

Example 5: Atmospheric pressure

Gases, unlike liquids, are quite compressible, and at a given temperature, the density of a gas is approximately proportional to the pressure. The proportionality constant is discussed on page 304, but for now let's just call it *k*, ρ= *kP*. Using this fact, we can find the variation of atmospheric pressure with altitude, assuming constant temperature:

$$dP = -\rho g dy$$

$$dP = -kP g dy$$

$$\frac{dP}{P} = -kgdy$$

$$\ln P = -kgy + \text{constant} \qquad [\text{integrating both sides}]$$

$$P = (\text{constant})e^{-kgy} \qquad [\text{exponentiating both sides}]$$

Pressure falls off exponentially with height. There is no sharp cutoff to the atmosphere, but the exponential factor gets extremely small by the time you're ten or a hundred miles up.

5.1.2 Temperature

Thermal equilibrium

We use the term temperature casually, but what is it exactly? Roughly speaking, temperature is a measure of how concentrated the heat energy is in an object. A large, massive object with very little heat energy in it has a low temperature.

But physics deals with operational definitions, i.e., definitions of how to measure the thing in question. How do we measure temperature? One common feature of all temperature-measuring devices is that they must be left for a while in contact with the thing whose temperature is being measured. When you take your temperature with a fever thermometer, you are waiting for the mercury inside to come up to the same temperature as your body. The thermometer actually tells you the temperature of its own working fluid (in this case the mercury). In general, the idea of temperature depends on the concept of thermal equilibrium. When you mix cold eggs from the refrigerator with flour that has been at room temperature, they rapidly reach a compromise temperature. What determines this compromise temperature is conservation of energy, and the amount of energy required to heat or cool each substance by one degree. But without even having constructed a temperature scale, we can see that the important point is the phenomenon of thermal equilibrium itself: two objects left in contact will approach the same temperature. We also assume that if object A is at the same temperature as object B, and B is at the same temperature as C, then A is at the same temperature as C. This statement is sometimes known as the zeroth law of thermodynamics, so called because after the first, second, and third laws had been developed, it was realized that there was another law that was even more fundamental.

Thermal expansion

f / Thermal equilibrium can be prevented. Otters have a coat of fur that traps air bubbles for insulation. If a swimming otter was in thermal equilibrium with cold water, it would be dead. Heat is still conducted from the otter's body to the water, but much more slowly than it would be in a warm-blooded animal that didn't have this special adaptation.

g / A hot air balloon is inflated. Because of thermal expansion, the hot air is less dense than the surrounding cold air, and therefore floats as the cold air drops underneath it and pushes

The familiar mercury thermometer operates on the principle that the mercury, its working fluid, expands when heated and contracts when cooled. In general, all substances expand and contract with changes in temperature. The zeroth law of thermodynamics guarantees that we can construct a comparative scale of temperatures that is independent of what type of thermometer we use. If a thermometer gives a certain reading when it's in thermal equilibrium with object A, and also gives the same reading for object B, then A and B must be the same temperature, regardless of the details of how the thermometers works.

What about constructing a temperature scale in which every degree represents an equal step in temperature? The Celsius scale has 0 as the freezing point of water and 100 as its boiling point. The hidden assumption behind all this is that since two points define a line, any two thermometers that agree at two points must agree at all other points. In reality if we calibrate a mercury thermometer and an alcohol thermometer in this way, we will find that a graph of one thermometer's reading versus the other is not a perfectly straight $y=x$ line. The subtle inconsistency becomes a drastic one when we try to extend the temperature scale through the points where mercury and alcohol boil or freeze. Gases, however, are much more consistent among themselves in their thermal expansion than solids or liquids, and the noble gases like helium and neon are more consistent with each other than gases in general. Continuing to search for consistency, we find that noble gases are more consistent with each other when their pressure is very low.

As an idealization, we imagine a gas in which the atoms interact only with the sides of the container, not with each other. Such a gas is perfectly nonreactive (as the noble gases very nearly are), and never condenses to a liquid (as the noble gases do only at extremely low temperatures). Its atoms take up a negligible fraction of the available volume. Any gas can be made to behave very much like this if the pressure is extremely low, so that the atoms hardly ever encounter each other. Such a gas is called an ideal gas, and we define the Celsius scale in terms of the volume of the gas in a thermometer whose working substance is an ideal gas maintained at a fixed (very low) pressure, and which is calibrated at 0 and 100 degrees according to the melting and boiling points of water. The Celsius scale is not just a comparative scale but an additive one as well: every step in temperature is equal, and it makes sense to say that the difference in temperature between 18 and 28°C is the same as the difference between 48 and 58.

it up out of the way.
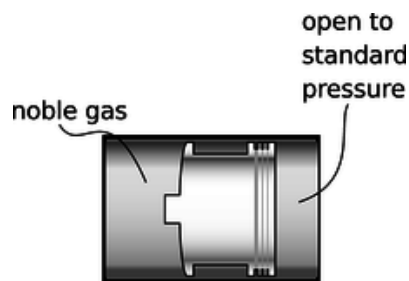
h / A simplified version of an ideal gas thermometer. The whole instrument is allowed to come into thermal equilibrium with the substance whose temperature is to be measured, and the mouth of the cylinder is left open to standard pressure. The volume of the noble gas gives an indication of temperature.
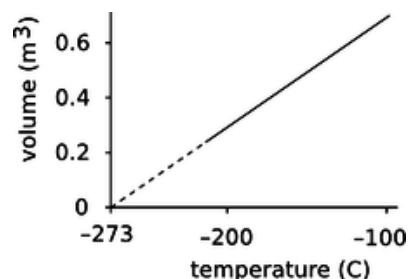
i / The volume of 1 kg of neon gas as a function of temperature (at standard pressure). Although neon would actually condense into a liquid at some point, extrapolating the graph gives to zero volume gives the same temperature as for any other gas: absolute zero.

Absolute zero and the kelvin scale

We find that if we extrapolate a graph of volume versus temperature, the volume becomes zero at nearly the same temperature for all gases: -273°\textup{C}. Real gases will all condense into liquids at some temperature above this, but an ideal gas would achieve zero volume at this temperature, known as absolute zero. The most useful temperature scale in scientific work is one whose zero is defined by absolute zero, rather than by some arbitrary standard like the melting point of water. The temperature scale used universally in scientific work, called the Kelvin scale, is the same as the Celsius scale, but shifted by 273 degrees to make its zero coincide with absolute zero. Scientists use the Celsius scale only for comparisons or when a change in temperature is all that is required for a calculation. Only on the Kelvin scale does it make sense to discuss ratios of temperatures, e.g., to say that one temperature is twice as hot as another.

Example 6: Which temperature scale to use

◊ You open an astronomy book and encounter the equation

$$(\text{light emitted}) = (\text{constant}) \times T^4$$

for the light emitted by a star as a function of its surface temperature. What temperature scale is implied?

◊ The equation tells us that doubling the temperature results in the emission of 16 times as much light. Such a ratio only makes sense if the Kelvin scale is used.

Although we can achieve as good an approximation to an ideal gas as we wish by making the pressure very low, it seems nevertheless that there should be some more fundamental way to define temperature. We will construct a more fundamental scale of temperature in section 5.4.

Discussion Questions

◊

Figure j/1 shows objects 1 and 2, each with a certain temperature T and a certain amount of thermal energy E. They are connected by a thin rod, so that eventually they will reach thermal equilibrium. We expect that the rate at which heat is transferred into object 1 will be given by some equation $dE_1/dt = k(\ldots)$, where k is a positive constant of proportionality and "…" is some expression that depends on the temperatures. Suppose that the following six forms are proposed for
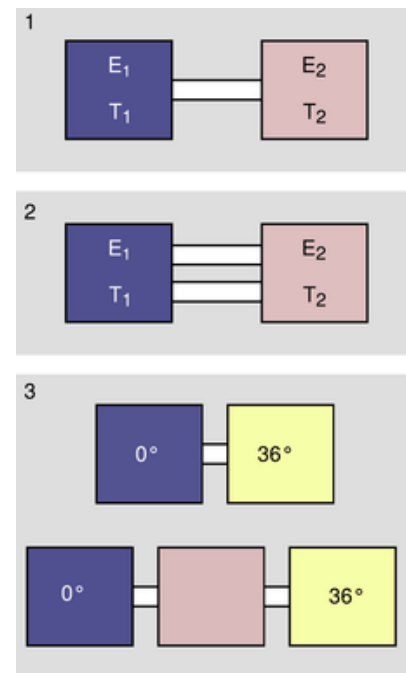
j / Discussion questions A-C.

"...."

1. T_1
2. T_2
3. $T_1\text{-}T_2$
4. $T_2\text{-}T_1$
5. T_1/T_2
6. T_2/T_1

Give physical reasons why five of these are not possible.

◊

How should the rate of heat conduction in j/2 compare with the rate in j/1?

◊

The example in j/3 is different from the preceding ones because when we add the third object in the middle, we don't necessarily know the intermediate temperature. We could in fact set up this third object with any desired initial temperature. Suppose, however, that the flow of heat is *steady*. For example, the 36° object could be a human body, the 0° object could be the air on a cold day, and the object in between could be a simplified physical model of the insulation provided by clothing or body fat. Under this assumption, what is the intermediate temperature? How does the rate of heat conduction compare in the two cases?

◊

Based on the conclusions of questions A-C, how should the rate of heat conduction through an object depend on its length and cross-sectional area? If all the linear dimensions of the object are doubled, what happens to the rate of heat conduction through it? How would this apply if we compare an elephant to a shrew?

5.2 Microscopic Description of An Ideal Gas

5.2.1 Evidence for the kinetic theory

Why does matter have the thermal properties it does? The basic answer must come from the fact that matter is made of atoms. How, then, do the atoms give rise to the bulk properties we observe? Gases, whose thermal

properties are so simple, offer the best chance for us to construct a simple connection between the microscopic and macroscopic worlds.

A crucial observation is that although solids and liquids are nearly incompressible, gases can be compressed, as when we increase the amount of air in a car's tire while hardly increasing its volume at all. This makes us suspect that the atoms in a solid are packed shoulder to shoulder, while a gas is mostly vacuum, with large spaces between molecules. Most liquids and solids have densities about 1000 times greater than most gases, so evidently each molecule in a gas is separated from its nearest neighbors by a space something like 10 times the size of the molecules themselves.

If gas molecules have nothing but empty space between them, why don't the molecules in the room around you just fall to the floor? The only possible answer is that they are in rapid motion, continually rebounding from the walls, floor and ceiling. In section 2.4 I have already given some of the evidence for the kinetic theory of heat, which states that heat is the kinetic energy of randomly moving molecules. This theory was proposed by Daniel Bernoulli in 1738, and met with considerable opposition because it seemed as though the molecules in a gas would eventually calm down and settle into a thin film on the floor. There was no precedent for this kind of perpetual motion. No rubber ball, however elastic, rebounds from a wall with exactly as much energy as it originally had, nor do we ever observe a collision between balls in which none of the kinetic energy at all is converted to heat and sound. The analogy is a false one, however. A rubber ball consists of atoms, and when it is heated in a collision, the heat is a form of motion of those atoms. An individual molecule, however, cannot possess heat. Likewise sound is a form of bulk motion of molecules, so colliding molecules in a gas cannot convert their kinetic energy to sound. Molecules can indeed induce vibrations such as sound waves when they strike the walls of a container, but the vibrations of the walls are just as likely to impart energy to a gas molecule as to take energy from it. Indeed, this kind of exchange of energy is the mechanism by which the temperatures of the gas and its container become equilibrated.

5.2.2 Pressure, volume, and temperature

A gas exerts pressure on the walls of its container, and in the kinetic theory we interpret this apparently constant pressure as the averaged-out result of vast numbers of collisions occurring every second between the gas molecules and the walls. The empirical facts about gases can be summarized

by the relation

$$PV \propto nT, \qquad \text{[ideal gas]}$$

which really only holds exactly for an ideal gas. Here n is the number of molecules in the sample of gas.

Example 7: Volume related to temperature

The proportionality of volume to temperature at fixed pressure was the basis for our definition of temperature.

Example 8: Pressure related to temperature

Pressure is proportional to temperature when volume is held constant. An example is the increase in pressure in a car's tires when the car has been driven on the freeway for a while and the tires and air have become hot.

We now connect these empirical facts to the kinetic theory of a classical ideal gas. For simplicity, we assume that the gas is monoatomic (i.e., each molecule has only one atom), and that it is confined to a cubical box of volume V, with L being the length of each edge and A the area of any wall. An atom whose velocity has an x component v_x will collide regularly with the left-hand wall, traveling a distance $2L$ parallel to the x axis between collisions with that wall. The time between collisions is $\Delta t = 2L/v_x$, and in each collision the x component of the atom's momentum is reversed from $-mv_x$ to mv_x. The total force on the wall is

$$F = \sum \frac{\Delta p_{x,i}}{\Delta t_i} \qquad \text{[monoatomic ideal gas]} \qquad ,$$

where the index i refers to the individual atoms. Substituting $\Delta p_{x,i} = 2mv_{x,i}$ and $\Delta t_i = 2L/v_{x,i}$, we have

$$F = \sum \frac{mv_{x,i}^2}{L} \qquad \text{[monoatomic ideal gas]} \qquad .$$

The quantity $mv_{x,i}^2$ is twice the contribution to the kinetic energy from the part of the atoms' center of mass motion that is parallel to the x axis. Since we're assuming a monoatomic gas, center of mass motion is the only type of motion that gives rise to kinetic energy. (A more complex molecule could rotate and vibrate as well.) If the quantity inside the sum included the y and z components, it would be twice the total kinetic energy of all the molecules. Since we expect the energy to be equally shared among x, y, and z motion,[1]

the quantity inside the sum must therefore equal 2/3 of the total kinetic energy, so

$$F = \frac{2K_{total}}{3L} \qquad \text{[monoatomic ideal gas]} \qquad .$$

Dividing by A and using $AL=V$, we have

$$P = \frac{2K_{total}}{3V} \qquad \text{[monoatomic ideal gas]} \qquad .$$

This can be connected to the empirical relation $PV \propto nT$ if we multiply by V on both sides and rewrite K_{total} as $n\bar{K}$, where $\bar{K}$ is the average kinetic energy per molecule:

$$PV = \frac{2}{3}n\bar{K} \qquad \text{[monoatomic ideal gas]} \qquad .$$

For the first time we have an interpretation of temperature based on a microscopic description of matter: in a monoatomic ideal gas, the temperature is a measure of the average kinetic energy per molecule. The proportionality between the two is $\bar{K} = (3/2)kT$, where the constant of proportionality k, known as Boltzmann's constant, has a numerical value of 1.38×10^{-23} J/K. In terms of Boltzmann's constant, the relationship among the bulk quantities for an ideal gas becomes

$$PV = nkT \qquad , \qquad \text{[ideal gas]}$$

which is known as the ideal gas law. Although I won't prove it here, this equation applies to all ideal gases, even though the derivation assumed a monoatomic ideal gas in a cubical box. (You may have seen it written elsewhere as $PV=NRT$, where $N=n/N_A$ is the number of moles of atoms, $R=kN_A$, and $N_A=6.0\times10^{23}$, called Avogadro's number, is essentially the number of hydrogen atoms in 1 g of hydrogen.)

Example 9: Pressure in a car tire

◊ After driving on the freeway for a while, the air in your car's tires heats up from 10°C to 35°C. How much does the pressure increase?

◊ The tires may expand a little, but we assume this effect is small, so the volume is nearly constant. From the ideal gas law, the ratio of the pressures is the same as the ratio of the absolute temperatures,

$$P_2/P_1 = T_2/T_1$$

$$= (308 \text{ K})/(283 \text{ K})$$

$$= 1.09 \qquad ,$$

or a 9% increase.

Discussion Questions

◊

Compare the amount of energy needed to heat 1 liter of helium by 1 degree with the energy needed to heat 1 liter of xenon. In both cases, the heating is carried out in a sealed vessel that doesn't allow the gas to expand. (The vessel is also well insulated.)

◊

Repeat discussion question A if the comparison is 1 kg of helium versus 1 kg of xenon (equal masses, rather than equal volumes).

◊

Repeat discussion question A, but now compare 1 liter of helium in a vessel of constant volume with the same amount of helium in a vessel that allows expansion beyond the initial volume of 1 liter. (This could be a piston, or a balloon.)

5.3 Entropy As a Macroscopic Quantity

5.3.1 Efficiency and grades of energy

Some forms of energy are more convenient than others in certain situations. You can't run a spring-powered mechanical clock on a battery, and you can't run a battery-powered clock with mechanical energy. However, there is no fundamental physical principle that prevents you from converting 100% of the electrical energy in a battery into mechanical energy or vice-versa. More efficient motors and generators are being designed every year. In general, the laws of physics permit perfectly efficient conversion within a broad class of forms of energy.

Heat is different. Friction tends to convert other forms of energy into heat even in the best lubricated machines. When we slide a book on a table, friction brings it to a stop and converts all its kinetic energy into heat, but we never observe the opposite process, in which a book spontaneously converts heat energy into mechanical energy and starts moving! Roughly speaking,

heat is different because it is disorganized. Scrambling an egg is easy. Unscrambling it is harder.

We summarize these observations by saying that heat is a lower grade of energy than other forms such as mechanical energy.

Of course it is possible to convert heat into other forms of energy such as mechanical energy, and that is what a car engine does with the heat created by exploding the air-gasoline mixture. But a car engine is a tremendously inefficient device, and a great deal of the heat is simply wasted through the radiator and the exhaust. Engineers have never succeeded in creating a perfectly efficient device for converting heat energy into mechanical energy, and we now know that this is because of a deeper physical principle that is far more basic than the design of an engine.
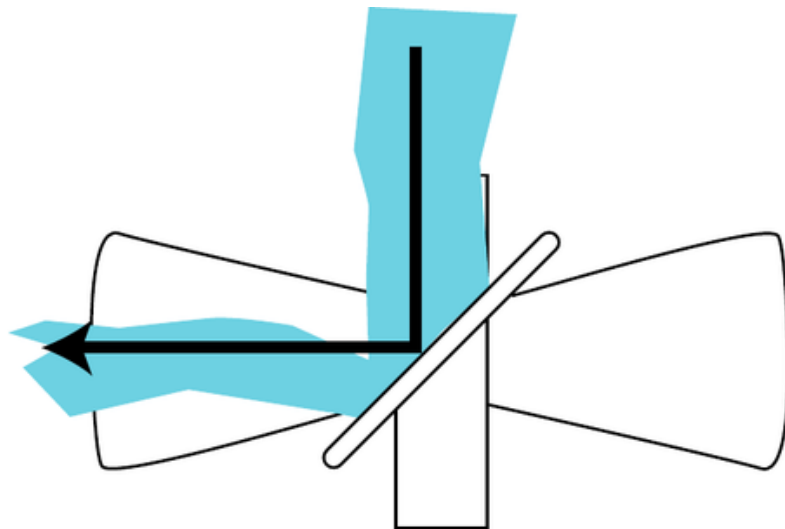
a / 1. The temperature difference between the hot and cold parts of the air can be used to extract mechanical energy, for example with a fan blade that spins because of the rising hot air currents. 2. If the temperature of the air is first allowed to become uniform, then no mechanical energy can be extracted. The same amount of heat energy is present, but it is no longer accessible for doing mechanical work.

5.3.2 Heat engines

Heat may be more useful in some forms than in others, i.e., there are different grades of heat energy. In figure a/1, the difference in temperature can be used to extract mechanical work with a fan blade. This principle is used in power plants, where steam is heated by burning oil or by nuclear reactions, and then allowed to expand through a turbine which has cooler steam on the

other side. On a smaller scale, there is a Christmas toy, b, that consists of a small propeller spun by the hot air rising from a set of candles, very much like the setup shown in figure a.

In figure a/2, however, no mechanical work can be extracted because there is no difference in temperature. Although the air in a/2 has the same total amount of energy as the air in a/1, the heat in a/2 is a lower grade of energy, since none of it is accessible for doing mechanical work.

In general, we define a heat engine as any device that takes heat from a reservoir of hot matter, extracts some of the heat energy to do mechanical work, and expels a lesser amount of heat into a reservoir of cold matter. The efficiency of a heat engine equals the amount of useful work extracted, W, divided by the amount of energy we had to pay for in order to heat the hot reservoir. This latter amount of heat is the same as the amount of heat the engine extracts from the high-temperature reservoir, Q_H. (The letter Q is the standard notation for a transfer of heat.) By conservation of energy, we have $Q_H = W + Q_L$, where Q_L is the amount of heat expelled into the low-temperature reservoir, so the efficiency of a heat engine, W/Q_H, can be rewritten as

$$\text{efficiency} = 1 - \frac{Q_L}{Q_H} \qquad . \qquad \text{[efficiency of any heat engine]}$$

It turns out that there is a particular type of heat engine, the Carnot engine, which, although not 100% efficient, is more efficient than any other. The grade of heat energy in a system can thus be unambiguously defined in terms of the amount of heat energy in it that cannot be extracted even by a Carnot engine.

How can we build the most efficient possible engine? Let's start with an unnecessarily inefficient engine like a car engine and see how it could be improved. The radiator and exhaust expel hot gases, which is a waste of heat energy. These gases are cooler than the exploded air-gas mixture inside the cylinder, but hotter than the air that surrounds the car. We could thus improve the engine's efficiency by adding an auxiliary heat engine to it, which would operate with the first engine's exhaust as its hot reservoir and the air as its cold reservoir. In general, any heat engine that expels heat at an intermediate temperature can be made more efficient by changing it so that it expels heat only at the temperature of the cold reservoir.
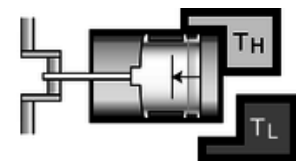
Similarly, any heat engine that absorbs some energy at an intermediate temperature can be made more efficient by adding an auxiliary heat engine to

b / A heat engine. Hot air from the candles rises through the fan blades, and makes the angels spin.

c / Sadi Carnot (1796-1832)

d / The beginning of the first expansion stroke, in which the working gas is kept in thermal equilibrium with the hot reservoir.

it which will operate between the hot reservoir and this intermediate temperature.

Based on these arguments, we define a Carnot engine as a heat engine that absorbs heat only from the hot reservoir and expels it only into the cold reservoir. Figures d-g show a realization of a Carnot engine using a piston in a cylinder filled with a monoatomic ideal gas. This gas, known as the working fluid, is separate from, but exchanges energy with, the hot and cold reservoirs. As proved on page 323, this particular Carnot engine has an efficiency given by

$$\text{efficiency} = 1 - \frac{T_L}{T_H} \qquad , \qquad \text{[efficiency of a Carnot engine]}$$

where T_L is the temperature of the cold reservoir and T_H is the temperature of the hot reservoir.

Even if you do not wish to dig into the details of the proof, the basic reason for the temperature dependence is not so hard to understand. Useful mechanical work is done on strokes d and e, in which the gas expands. The motion of the piston is in the same direction as the gas's force on the piston, so positive work is done on the piston. In strokes f and g, however, the gas does negative work on the piston. We would like to avoid this negative work, but we must design the engine to perform a complete cycle. Luckily the pressures during the compression strokes are lower than the ones during the expansion strokes, so the engine doesn't undo all its work with every cycle. The ratios of the pressures are in proportion to the ratios of the temperatures, so if T_L is 20% of T_H, the engine is 80% efficient.

We have already proved that any engine that is not a Carnot engine is less than optimally efficient, and it is also true that all Carnot engines operating between a given pair of temperatures T_H and T_L have the same efficiency. (This can be proved by the methods of section 5.4.) Thus a Carnot engine is the most efficient possible heat engine.

5.3.3 Entropy

We would like to have some numerical way of measuring the grade of energy in a system. We want this quantity, called entropy, to have the following two properties:

(1) Entropy is additive. When we combine two systems and consider
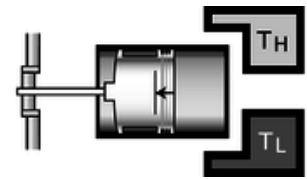
e / The beginning of the second expansion stroke, in which the working gas is thermally insulated. The working gas cools because it is doing work on the piston and thus losing energy.
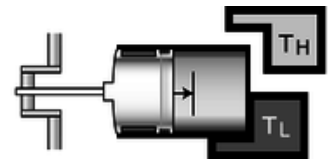
f / The beginning of the first compression stroke. The working gas begins the stroke at the same temperature as the cold reservoir, and remains in thermal contact with it the whole time. The engine does negative work.
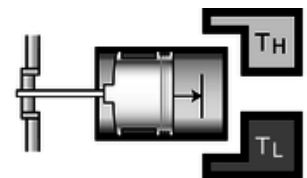
g / The beginning of the second compression stroke, in which mechanical work is absorbed, heating the working gas back up to T_H.

them as one, the entropy of the combined system equals the sum of the entropies of the two original systems. (Quantities like mass and energy also have this property.)

(2) The entropy of a system is not changed by operating a Carnot engine within it.

It turns out to be simpler and more useful to define changes in entropy than absolute entropies. Suppose as an example that a system contains some hot matter and some cold matter. It has a relatively high grade of energy because a heat engine could be used to extract mechanical work from it. But if we allow the hot and cold parts to equilibrate at some lukewarm temperature, the grade of energy has gotten worse. Thus putting heat into a hotter area is more useful than putting it into a cold area. Motivated by these considerations, we define a change in entropy as follows:

$$\Delta S = \frac{Q}{T} \qquad \text{[change in entropy when adding}$$

heat Q to matter at temperature T;

ΔS is negative if heat is taken out]

A system with a higher grade of energy has a lower entropy.

Example 10: Entropy is additive.

Since changes in entropy are defined by an additive quantity (heat) divided by a non-additive one (temperature), entropy is additive.

Example 11: Entropy isn't changed by a Carnot engine.

The efficiency of a heat engine is defined by
    efficiency = 1 - Q_L / Q_H ,
and the efficiency of a Carnot engine is
    efficiency = 1 - T_L / T_H ,
so for a Carnot engine we have $Q_L / Q_H = T_L / T_H$, which can be rewritten as $Q_L / T_L = Q_H / T_H$. The entropy lost by the hot reservoir is therefore the same as the entropy gained by the cold one.

Example 12: Entropy increases in heat conduction.

When a hot object gives up energy to a cold one, conservation of energy tells us that the amount of heat lost by the hot object is the same as the amount of heat gained by the cold one. The change in entropy is - Q / T_H + Q / T_L, which is positive because $T_L < T_H$.

h / Entropy can be understood using the metaphor of a water wheel. Letting the water levels equalize is like letting the entropy maximize. Taking water from the high side and putting it into the low side increases the entropy. Water levels in this metaphor correspond to temperatures in the actual definition of entropy.

Example 13: Entropy is increased by a non-Carnot engine.

The efficiency of a non-Carnot engine is less than 1 - T_L/T_H, so $Q_L/Q_H > T_L/T_H$ and $Q_L/T_L > Q_H/T_H$. This means that the entropy increase in the cold reservoir is greater than the entropy decrease in the hot reservoir.

Example 14: A book sliding to a stop

A book slides across a table and comes to a stop. Once it stops, all its kinetic energy has been transformed into heat. As the book and table heat up, their entropies both increase, so the total entropy increases as well.

All of these examples involved closed systems, and in all of them the total entropy either increased or stayed the same. It never decreased. Here are two examples of schemes for decreasing the entropy of a closed system, with explanations of why they don't work.

Example 15: Using a refrigerator to decrease entropy?

◊ A refrigerator takes heat from a cold area and dumps it into a hot area. (1) Does this lead to a net decrease in the entropy of a closed system? (2) Could you make a Carnot engine more efficient by running a refrigerator to cool its low-temperature reservoir and eject heat into its high-temperature reservoir?

◊ (1) No. The heat that comes off of the radiator coils is a great deal more than the heat the fridge removes from inside; the difference is what it costs to run your fridge. The heat radiated from the coils is so much more than the heat removed from the inside that the increase in the entropy of the air in the room is greater than the decrease of the entropy inside the fridge. The most efficient refrigerator is actually a Carnot engine running in reverse, which leads to neither an increase nor a decrease in entropy.

(2) No. The most efficient refrigerator is a reversed Carnot engine. You will not achieve anything by running one Carnot engine in reverse and another forward. They will just cancel each other out.

Example 16: Maxwell's demon

◊ Maxwell imagined a pair of rooms, their air being initially in thermal equilibrium, having a partition across the middle with a tiny door. A miniscule demon is posted at the door with a little ping-pong paddle, and his duty is to try to build up faster-moving air molecules in room B and slower moving ones in room A. For instance, when a fast molecule is headed through the door, going from A to B, he lets it by, but when a slower than average molecule tries the same thing, he hits it back into room A. Would this decrease the total entropy of

the pair of rooms?

◊ No. The demon needs to eat, and we can think of his body as a little heat engine, and his metabolism is less efficient than a Carnot engine, so he ends up increasing the entropy rather than decreasing it.

Observations such as these lead to the following hypothesis, known as the second law of thermodynamics:

The entropy of a closed system always increases, or at best stays the same: $\Delta S \geq 0$.

At present our arguments to support this statement may seem less than convincing, since they have so much to do with obscure facts about heat engines. In the following section we will find a more satisfying and fundamental explanation for the continual increase in entropy. To emphasize the fundamental and universal nature of the second law, here are a few exotic examples.

Example 17: Entropy and evolution

A favorite argument of many creationists who don't believe in evolution is that evolution would violate the second law of thermodynamics: the death and decay of a living thing releases heat (as when a compost heap gets hot) and lessens the amount of energy available for doing useful work, while the reverse process, the emergence of life from nonliving matter, would require a decrease in entropy. Their argument is faulty, since the second law only applies to closed systems, and the earth is not a closed system. The earth is continuously receiving energy from the sun.

Example 18: The heat death of the universe

Living things have low entropy: to demonstrate this fact, observe how a compost pile releases heat, which then equilibrates with the cooler environment. We never observe dead things to leap back to life after sucking some heat energy out of their environments! The only reason life was able to evolve on earth was that the earth was not a closed system: it got energy from the sun, which presumably gained more entropy than the earth lost.

Victorian philosophers spent a lot of time worrying about the heat death of the universe: eventually the universe would have to become a high-entropy, lukewarm soup, with no life or organized motion of any kind. Fortunately (?), we now know a great many other things that will make the universe inhospitable to life long before its entropy is maximized. Life on earth, for instance, will end when the sun evolves into a giant star and vaporizes our planet.

Example 19: Hawking radiation

Any process that could destroy heat (or convert it into nothing but mechanical work) would lead to a reduction in entropy. Black holes are supermassive stars whose gravity is so strong that nothing, not even light, can escape from them once it gets within a boundary known as the event horizon. Black holes are commonly observed to suck hot gas into them. Does this lead to a reduction in the entropy of the universe? Of course one could argue that the entropy is still there inside the black hole, but being able to "hide" entropy there amounts to the same thing as being able to destroy entropy.

The physicist Steven Hawking was bothered by this question, and finally realized that although the actual stuff that enters a black hole is lost forever, the black hole will gradually lose energy in the form of light emitted from just outside the event horizon. This light ends up reintroducing the original entropy back into the universe at large.

Discussion Questions

◊

In this discussion question, you'll think about a car engine in terms of thermodynamics. Note that an internal combustion engine doesn't fit very well into the theoretical straightjacket of a heat engine. For instance, a heat engine has a high-temperature heat reservoir at a single well-defined temperature, T_H. In a typical car engine, however, there are several very different temperatures you could imagine using for T_H: the temperature of the engine block (~100°C), the walls of the cylinder (~250°C), or the temperature of the exploding air-gas mixture (~1000°C, with significant changes over a four-stroke cycle). Let's use T_H~1000°C.

Burning gas supplies heat energy Q_H to your car's engine. The engine does mechanical work W, but also expels heat Q_L into the environment through the radiator and the exhaust. Conservation of energy gives

$$Q_H = Q_L + W ,$$

and the relative proportions of Q_L and W are usually about 90% to 10%. (Actually it depends quite a bit on the type of car, the driving conditions, etc.)

(1) Q_L is obviously undesirable: you pay for it, but all it does is heat the neighborhood. Suppose that engineers do a really good job of getting

rid of the effects that create Q_L, such as friction. Could Q_L ever be reduced to zero, at least theoretically?

(2) A gallon of gas releases about 140 MJ of heat Q_H when burned. Estimate the change in entropy of the universe due to running a typical car engine and burning one gallon of gas. (You'll have to estimate how hot the environment is. For the sake of argument, assume that the work done by the engine, W, remains in the form of mechanical energy, although in reality it probably ends up being changed into heat when you step on the brakes.) Is your result consistent with the second law of thermodynamics?

(3) What would happen if you redid the calculation in #2, but assumed Q_L=0? Is this consistent with your answer to #1?

◊

Example 11 on page 310 showed that entropy isn't changed by a Carnot engine, by using the expression for the efficiency of a Carnot engine. Prove the same thing by applying the definition of entropy to each of the four strokes of the Carnot engine.

5.4 Entropy As a Microscopic Quantity

5.4.1 A microscopic view of entropy

To understand why the second law of thermodynamics is always true, we need to see what entropy really means at the microscopic level. An example that is easy to visualize is the free expansion of a monoatomic gas. Figure a/1 shows a box in which all the atoms of the gas are confined on one side. We very quickly remove the barrier between the two sides, a/2, and some time later, the system has reached an equilibrium, a/3. Each snapshot shows both the positions and the momenta of the atoms, which is enough information to allow us in theory to extrapolate the behavior of the system into the future, or the past. However, with a realistic number of atoms, rather than just six, this would be beyond the computational power of any computer.[2]
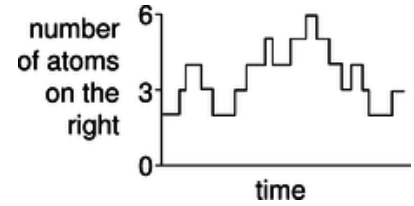
But suppose we show figure a/2 to a friend without any further information, and ask her what she can say about the system's behavior in the future. She doesn't know how the system was prepared. Perhaps, she thinks, it was just a strange coincidence that all the atoms happened to be in the right
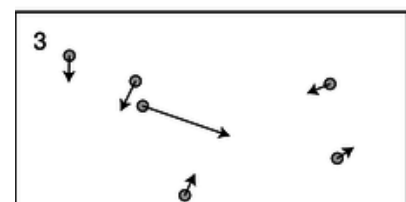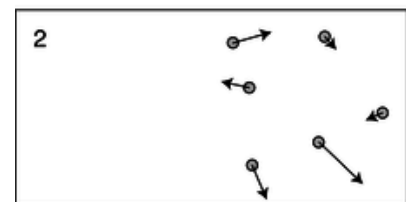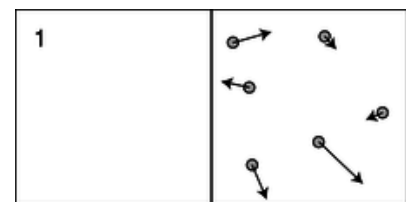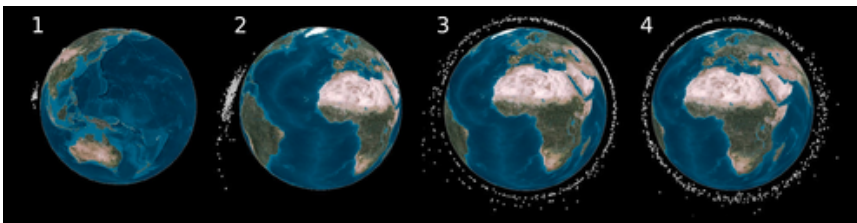
half of the box at this particular moment. In any case, she knows that this unusual situation won't last for long. She can predict that after the passage of any significant amount of time, a surprise inspection is likely to show roughly half the atoms on each side. The same is true if you ask her to say what happened in the past. She doesn't know about the barrier, so as far as she's concerned, extrapolation into the past is exactly the same kind of problem as extrapolation into the future. We just have to imagine reversing all the momentum vectors, and then all our reasoning works equally well for backwards extrapolation. She would conclude, then, that the gas in the box underwent an unusual fluctuation, b, and she knows that the fluctuation is very unlikely to exist very far into the future, or to have existed very far into the past.

What does this have to do with entropy? Well, state a/3 has a greater entropy than state a/2. It would be easy to extract mechanical work from a/2, for instance by letting the gas expand while pressing on a piston rather than simply releasing it suddenly into the void. There is no way to extract mechanical work from state a/3. Roughly speaking, our microscopic description of entropy relates to the *number of possible states*. There are a lot more states like a/3 than there are states like a/2. Over long enough periods of time --- long enough for equilibration to occur --- the system gets mixed up, and is about equally likely to be in any of its possible states, regardless of what state it was initially in. We define some number that describes an interesting property of the whole system, say the number of atoms in the right half of the box, R. A high-entropy value of R is one like $R=3$, which allows many possible states. We are far more likely to encounter $R=3$ than a low-entropy value like $R=0$ or $R=6$.

c / Earth orbit is becoming cluttered with space junk, and the pieces can be thought of as the "molecules" comprising an exotic kind of gas. These image shows the evolution of a cloud of debris arising from a 2007 Chinese test of an anti-satellite rocket. Panels 1-4 show the cloud five minutes, one hour, one day, and one month after the impact. The entropy seems to have maximized by panel 4.

5.4.2 Phase space

a / A gas expands freely, doubling its volume.

b / An unusual fluctuation in the distribution of the atoms between the two sides of the box. There has been no external manipulation as in figure a/1.

There is a problem with making this description of entropy into a mathematical definition. The problem is that it refers to the number of possible states, but that number is theoretically infinite. To get around the problem, we coarsen our description of the system. For the atoms in figure a, we don't really care exactly where each atom is. We only care whether it is in the right side or the left side. If a particular atom's left-right position is described by a coordinate x, then the set of all possible values of x is a line segment along the x axis, containing an infinite number of points. We break this line segment down into two halves, each of width Δx, and we consider two different values of x to be variations on the same state if they both lie in the same half. For our present purposes, we can also ignore completely the y and z coordinates, and all three momentum components, p_x, p_y, and p_z.

Now let's do a real calculation. Suppose there are only two atoms in the box, with coordinates x_1 and x_2. We can give all the relevant information about the state of the system by specifying one of the cells in the grid shown in figure d. This grid is known as the *phase space* of the system. The lower right cell, for instance, describes a state in which atom number 1 is in the right side of the box and atom number 2 in the left. Since there are two possible states with $R=1$ and only one state with $R=2$, we are twice as likely to observe $R=1$, and $R=1$ has higher entropy than $R=2$.

Figure e shows a corresponding calculation for three atoms, which makes the phase space three-dimensional. Here, the $R=1$ and 2 states are three times more likely than $R=0$ and 3. Four atoms would require a four-dimensional phase space, which exceeds our ability to visualize. Although our present example doesn't require it, a phase space can describe momentum as well as position, as shown in figure f. In general, a phase space for a monoatomic gas has six dimensions per atom (one for each coordinate and one for each momentum component).

5.4.3 Microscopic definitions of entropy and temperature

Two more issues need to be resolved in order to make a microscopic definition of entropy.

First, if we defined entropy as the number of possible states, it would be a multiplicative quantity, not an additive one: if an ice cube in a glass of water has M_1 states available to it, and the number of states available to the water is M_2, then the number of possible states of the whole system is the
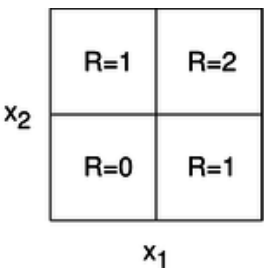
d / The phase space for two atoms in a box.
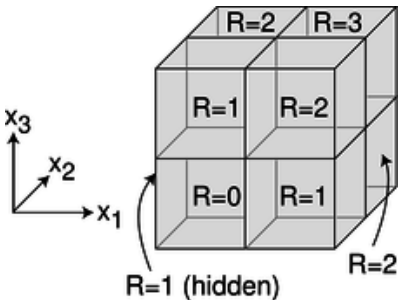
e / The phase space for three atoms in a box.
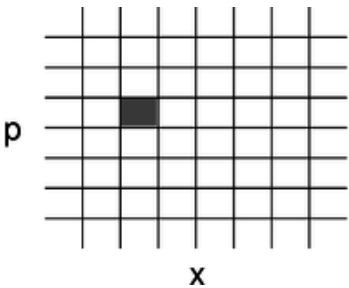
f / A phase space for a single atom in one dimension, taking

product $M_1 M_2$. To get around this problem, we take the natural logarithm of the number of states, which makes the entropy additive because of the property of the logarithm $\ln (M_1 M_2) = \ln M_1 + \ln M_2$.

The second issue is a more trivial one. The concept of entropy was originally invented as a purely macroscopic quantity, and the macroscopic definition $\Delta S = Q/T$, which has units of J/K, has a different calibration than would result from defining $S = \ln M$. The calibration constant we need turns out to be simply the Boltzmann constant, k.

\mythmhdr{Microscopic definition of entropy} The entropy of a system is $S = k \ln M$, where M is the number of available states.[3]

This also leads to a more fundamental definition of temperature. Two systems are in thermal equilibrium when they have maximized their combined entropy through the exchange of energy. Here the energy possessed by one part of the system, E_1 or E_2, plays the same role as the variable R in the examples of free expansion above. A maximum of a function occurs when the derivative is zero, so the maximum entropy occurs when

$$\frac{d (S_1 + S_2)}{dE_1} = 0 \qquad .$$

We assume the systems are only able to exchange heat energy with each other, $dE_1 = -dE_2$, so

$$\frac{dS_1}{dE_1} = \frac{dS_2}{dE_2} \qquad ,$$

and since the energy is being exchanged in the form of heat we can make the equations look more familiar if we write dQ for an amount of heat to be transferred into either system:

$$\frac{dS_1}{dQ_1} = \frac{dS_2}{dQ_2} \qquad .$$

In terms of our previous definition of entropy, this is equivalent to $1/T_1 = 1/T_2$, which makes perfect sense since the systems are in thermal equilibrium. According to our new approach, entropy has already been defined in a fundamental manner, so we can take this as a definition of temperature:

$$\frac{1}{T} = \frac{dS}{dQ} \qquad ,$$

momentum into account.

g / Ludwig Boltzmann's tomb, inscribed with his equation for entropy.
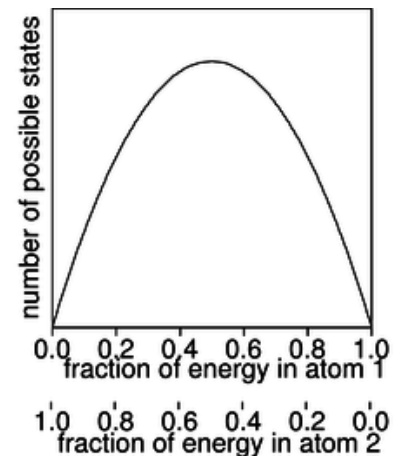
h / A two-atom system has the highest number of available states when the energy is equally divided. Equal energy division is therefore the most likely possibility at any given moment in time.

where *dS* represents the increase in the system's entropy from adding heat *dQ* to it.
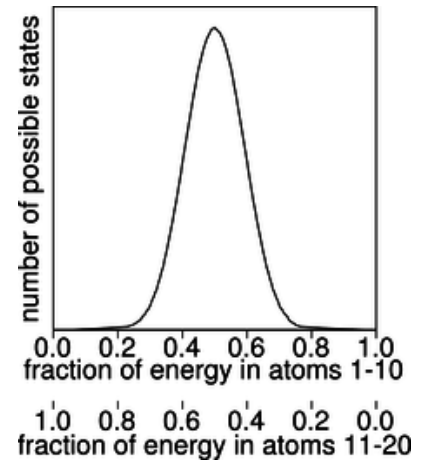
Examples with small numbers of atoms

Let's see how this applies to an ideal, monoatomic gas with a small number of atoms. To start with, consider the phase space available to one atom. Since we assume the atoms in an ideal gas are noninteracting, their positions relative to each other are really irrelevant. We can therefore enumerate the number of states available to each atom just by considering the number of momentum vectors it can have, without considering its possible locations. The relationship between momentum and kinetic energy is $E=(p_x^2+p_y^2+p_z^2)/2m$, so if for a fixed value of its energy, we arrange all of an atom's possible momentum vectors with their tails at the origin, their tips all lie on the surface of a sphere in phase space with radius $|\mathbf{p}| = \sqrt{2mE}$. The number of possible states for that atom is proportional to the sphere's surface area, which in turn is proportional to the square of the sphere's radius, $|\mathbf{p}|^2 = 2mE$.

Now consider two atoms. For any given way of sharing the energy between the atoms, $E=E_1+E_2$, the number of possible combinations of states is proportional to E_1E_2. The result is shown in figure h. The greatest number of combinations occurs when we divide the energy equally, so an equal division gives maximum entropy.

By increasing the number of atoms, we get a graph whose peak is narrower, i. With more than one atom in each system, the total energy is $E=(p_{x,1}^2+p_{y,1}^2+p_{z,1}^2+p_{x,2}^2+p_{y,2}^2+p_{z,2}^2+...)/2m$. With *n* atoms, a total of $3n$ momentum coordinates are needed in order to specify their state, and such a set of numbers is like a single point in a $3n$-dimensional space (which is impossible to visualize). For a given total energy *E*, the possible states are like the surface of a $3n$-dimensional sphere, with a surface area proportional to p^{3n-1}, or $E^{(3n-1)/2}$. The graph in figure i, for example, was calculated according to the formula $E_1^{29/2}E_2^{29/2}=E_1^{29/2}(E-E_1)^{29/2}$.

Since graph i is narrower than graph h, the fluctuations in energy sharing are smaller. If we inspect the system at a random moment in time, the energy sharing is very unlikely to be more lopsided than a 40-60 split. Now suppose that, instead of 10 atoms interacting with 10 atoms, we had a 10^{23} atoms interacting with 10^{23} atoms. The graph would be extremely narrow,

0.0 0.2 0.4 0.6 0.8 1.0
fraction of energy in atoms 1-10

1.0 0.8 0.6 0.4 0.2 0.0
fraction of energy in atoms 11-20

i / When two systems of 10 atoms each interact, the graph of the number of possible states is narrower than with only one atom in each system.
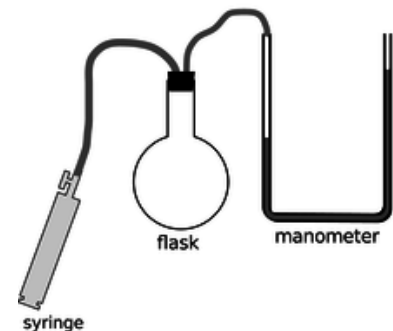
j / An experiment for determining the shapes of molecules.

and it would be a statistical certainty that the energy sharing would be nearly perfectly equal. This is why we never observe a cold glass of water to change itself into an ice cube sitting in some warm water!

By the way, note that although we've redefined temperature, these examples show that things are coming out consistent with the old definition, since we saw that the old definition of temperature could be described in terms of the average energy per atom, and here we're finding that equilibration results in each subset of the atoms having an equal share of the energy.

Entropy of a monoatomic ideal gas

Let's calculate the entropy of a monoatomic ideal gas of n atoms. This is an important example because it allows us to show that our present microscopic treatment of thermodynamics is consistent with our previous macroscopic approach, in which temperature was defined in terms of an ideal gas thermometer.

The number of possible locations for each atom is $V/\Delta x^3$, where Δx is the size of the space cells in phase space. The number of possible combinations of locations for the atoms is therefore $(V/\Delta x^3)^n$.

The possible momenta cover the surface of a $3n$-dimensional sphere, whose radius is $\sqrt{2mE}$, and whose surface area is therefore proportional to $E^{(3n-1)/2}$. In terms of phase-space cells, this area corresponds to $E^{(3n-1)/2} / \Delta p^{3n}$ possible combinations of momenta, multiplied by some constant of proportionality which depends on m, the atomic mass, and n, the number of atoms. To avoid having to calculate this constant of proportionality, we limit ourselves to calculating the part of the entropy that does not depend on n, so the resulting formula will not be useful for comparing entropies of ideal gas samples with different numbers of atoms.

The final result for the number of available states is

$$M = \left(\frac{V}{\Delta x^3}\right)^n \frac{E^{(3n-1)/2}}{\Delta p^{3n-1}} \qquad , \qquad [\text{function of } n]$$

so the entropy is

$$S = nk \ln V + \frac{3}{2} nk \ln E + (\text{function of } \Delta x, \Delta p, \text{ and } n) \qquad ,$$

where the distinction between n and n-1 has been ignored. Using $PV=nkT$ and

$E=(3/2)nkT$, we can also rewrite this as

$$S = \frac{5}{2}nk \ln T - nk \ln P + \dots, \qquad \text{[entropy of a monoatomic ideal gas]}$$

where "..." indicates terms that may depend on Δx, Δp, m, and n, but that have no effect on comparisons of gas samples with the same number of atoms.

self-check:

Why does it make sense that the temperature term has a positive sign in the above example, while the pressure term is negative? Why does it make sense that the whole thing is proportional to n?

(answer in the back of the PDF version of the book)

To show consistency with the macroscopic approach to thermodynamics, we need to show that these results are consistent with the behavior of an ideal-gas thermometer. Using the new definition $1/T=dS/dQ$, we have $1/T=dS/dE$, since transferring an amount of heat dQ into the gas increases its energy by a corresponding amount. Evaluating the derivative, we find $1/T=(3/2)nk/E$, or $E=(3/2)nkT$, which is the correct relation for a monoatomic ideal gas.

Example 20: A mixture of molecules

◊ Suppose we have a mixture of two different monoatomic gases, say helium and argon. How would we find the entropy of such a mixture (say, in terms of V and E)? How would the energy be shared between the two types of molecules, i.e., would a more massive argon atom have more energy on the average than a less massive helium atom, the same, or less?

◊ Since entropy is additive, we simply need to add the entropies of the two types of atom. However, the expression derived above for the entropy omitted the dependence on the mass m of the atom, which is different for the two constituents of the gas, so we need to go back and figure out how to put that m-dependence back in. The only place where we threw away m's was when we identified the radius of the sphere in momentum space with $\sqrt{2mE}$, but then threw away the constant factor of m. In other words, the final result can be generalized merely by replacing E everywhere with the product mE. Since the log of a product is the sum of the logs, the dependence of the final result on m and E can be broken apart into two different terms, and we find

$$S = nk \ln V + \frac{3}{2}nk \ln m + \frac{3}{2}nk \ln E + \dots$$

The total entropy of the mixture can then be written as

$$S \quad = \quad n_1 k \ln V \quad + \quad n_2 k \ln V \quad + \quad \frac{3}{2} n_1 k \ln m_1 \quad + \quad \frac{3}{2} n_2 k \ln m_2$$

$$+ \quad \frac{3}{2} n_1 k \ln E_1 \quad + \quad \frac{3}{2} n_2 k \ln E_2 \quad + \quad \ldots$$

Now what about the energy sharing? If the total energy is $E=E_1+E_2$, then the most ovewhelmingly probable sharing of energy will the the one that maximizes the entropy. Notice that the dependence of the entropy on the masses m_1 and m_2 occurs in terms that are entirely separate from the energy terms. If we want to maximize S with respect to E_1 (with $E_2=E-E_1$ by conservation of energy), then we differentiate S with respect to E_1 and set it equal to zero. The terms that contain the masses don't have any dependence on E_1, so their derivatives are zero, and we find that the molecular masses can have no effect on the energy sharing. Setting the derivative equal to zero, we have

$$0 = \frac{\partial}{\partial E_1} \left(n_1 k \ln V + n_2 k \ln V + \frac{3}{2} n_1 k \ln m_1 + \frac{3}{2} n_2 k \ln m_2 \right.$$

$$\left. + \frac{3}{2} n_1 k \ln E_1 + \frac{3}{2} n_2 k \ln(E - E_1) + \ldots \right)$$

$$= \frac{3}{2} k \left(\frac{n_1}{E_1} - \frac{n_2}{E - E_1} \right)$$

$$0 = \frac{n_1}{E_1} - \frac{n_2}{E - E_1}$$

$$\frac{n_1}{E_1} = \frac{n_2}{E_2} \quad .$$

In other words, each gas gets a share of the energy in proportion to the number of its atoms, and therefore every atom gets, on average, the same amount of energy, regardless of its mass. The result for the average energy per atom is exactly the same as for an unmixed gas, $\bar{K} = (3/2)kT$.

Equipartition

Example [20] is a special case of a more general statement called the equipartition theorem. Suppose we have only one argon atom, named Alice, and one helium atom, named Harry. Their total kinetic energy is $E = p_x^2/2m + p_y^2/2m + p_z^2/2m + \{p'\}_x^2/2m' + \{p'\}_y^2/2m' + \{p'\}_z^2/2m'$, where the primes indicate Harry. We have six terms that all look alike. The only difference among them is that the constant factors attached to the squares of the momenta have different values, but we've just proved that those

differences don't matter. In other words, if we have any system at all whose energy is of the form $E=(\ldots)p_1{}^2+(\ldots)p_2{}^2+\ldots$, with any number of terms, then each term holds, on average, the same amount of energy, $\frac{1}{2}kT$. We say that the system consisting of Alice and Harry has six degrees of freedom. It doesn't even matter whether the things being squared are momenta: if you look back over the logical steps that went into the argument, you'll see that none of them depended on that. In a solid, for example, the atoms aren't free to wander around, but they can vibrate from side to side. If an atom moves away from its equilibrium position at $x=0$ to some other value of x, then its electrical energy is $(1/2)\varkappa\, x^2$, where $\varkappa$ is the spring constant (written as the Greek letter kappa to distinguish it from the Boltzmann constant k). We can conclude that each atom in the solid, on average, has $\frac{1}{2}kT$ of energy in the electrical energy due to its x displacement along the x axis, and equal amounts for y and z. This is known as equipartition, meaning equal partitioning, or equal sharing. The equipartition theorem says that if the expression for the energy looks like a sum of squared variables, then each degree of freedom has an average energy of $\frac{1}{2}kT$. Thus, very generally, we can interpret temperature as the average energy per degree of freedom (times $k/2$).

An unexpected glimpse of the microcosm

You may have the feeling at this point that of course Boltzmann was right about the literal existence of atoms, but only very sophisticated experiments could vindicate him definitively. After all, the microscopic and macroscopic definitions of entropy are equivalent, so it might seem as though there was no real advantage to the microscopic approach. Surprisingly, very simple experiments are capable of revealing a picture of the microscopic world, and there is no possible macroscopic explanation for their results.

In 1819, before Boltzmann was born, Clément and Desormes did an experiment like the one shown in figure j. The gas in the flask is pressurized using the syringe. This heats it slightly, so it is then allowed to cool back down to room temperature. Its pressure is measured using the manometer. The stopper on the flask is popped and then immediately reinserted. Its pressure is now equalized with that in the room, and the gas's expansion has cooled it a little, because it did mechanical work on its way out of the flask, causing it to lose some of its internal energy E. The expansion is carried out quickly enough so that there is not enough time for any significant amount of

heat to flow in through the walls of the flask before the stopper is reinserted. The gas is now allowed to come back up to room temperature (which takes a much longer time), and as a result regains a fraction b of its original overpressure. During this constant-volume reheating, we have $PV=nkT$, so the amount of pressure regained is a direct indication of how much the gas cooled down when it lost an amount of energy ΔE.
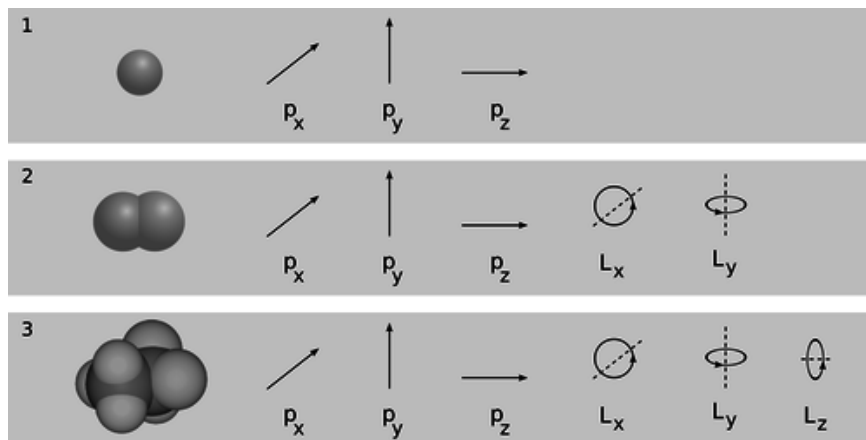
k / The differing shapes of a helium atom (1), a nitrogen molecule (2), and a difluoroethane molecule (3) have surprising macroscopic effects.

If the gas is monoatomic, then we know what to expect for this relationship between energy and temperature: $\Delta E=(3/2)nk\Delta T$, where the factor of 3 came ultimately from the fact that the gas was in a three-dimensional space, k/1. Moving in this space, each molecule can have momentum in the x, y, and z directions. It has three degrees of freedom. What if the gas is not monoatomic? Air, for example, is made of diatomic molecules, k/2. There is a subtle difference between the two cases. An individual atom of a monoatomic gas is a perfect sphere, so it is exactly the same no matter how it is oriented. Because of this perfect symmetry, there is thus no way to tell whether it is spinning or not, and in fact we find that it can't rotate. The diatomic gas, on the other hand, can rotate end over end about the x or y axis, but cannot rotate about the z axis, which is its axis of symmetry. It has a total of five degrees of freedom. A polyatomic molecule with a more complicated, asymmetric shape, k/3, can rotate about all three axis, so it has a total of six degrees of freedom.

Because a polyatomic molecule has more degrees of freedom than a monoatomic one, it has more possible states for a given amount of energy. That is, its entropy is higher for the same energy. From the definition of

temperature, $1/T=dS/dE$, we conclude that it has a lower temperature for the same energy. In other words, it is more difficult to heat n molecules of difluoroethane than it is to heat n atoms of helium. When the Clément-Desormes experiment is carried out, the result b therefore depends on the shape of the molecule! Who would have dreamed that such simple observations, correctly interpreted, could give us this kind of glimpse of the microcosm?

Lets go ahead and calculate how this works. Suppose a gas is allowed to expand without being able to exchange heat with the rest of the universe. The loss of thermal energy from the gas equals the work it does as it expands, and using the result of homework problem 2 on page 333, the work done in an infinitesimal expansion equals PdV, so

$$dE + P\,dV = 0 \ .$$

(If the gas had not been insulated, then there would have been a third term for the heat gained or lost by heat conduction.)

From section 5.2 we have $E=(3/2)PV$ for a monoatomic ideal gas. More generally, the equipartition theorem tells us that the 3 simply needs to be replaced with the number of degrees of freedom α, so $dE=(\alpha/2)PdV+(\alpha/2)VdP$, and the equation above becomes

$$0 = \frac{\alpha + 2}{2}PdV + \frac{\alpha}{2}VdP \qquad .$$

Rearranging, we have

$$(\alpha + 2)\frac{dV}{V} = -\alpha\frac{dP}{P} \qquad .$$

Integrating both sides gives

$$(\alpha+2) \ln V = -\alpha \ln P + \text{constant} \ ,$$

and taking exponentials on both sides yields

$$V^{\alpha+2} \propto P^{-\alpha} \ .$$

We now wish to reexpress this in terms of pressure and temperature. Eliminating $V \propto (T/P)$ gives

$$T \propto P^{b} \ ,$$

where $b=2/(\alpha+2)$ is equal to 2/5, 2/7, or 1/4, respectively, for a monoatomic,

diatomic, or polyatomic gas.

Example 21: Efficiency of the Carnot engine

As an application, we now prove the result claimed earlier for the efficiency of a Carnot engine. First consider the work done during the constant-temperature strokes. Integrating the equation *dW=PdV*, we have $W = \int P dV$. Since the thermal energy of an ideal gas depends only on its temperature, there is no change in the thermal energy of the gas during this constant-temperature process. Conservation of energy therefore tells us that work done by the gas must be exactly balanced by the amount of heat transferred in from the reservoir.

$$Q = W$$
$$= \int P dV$$

For our proof of the efficiency of the Carnot engine, we need only the ratio of Q_H to Q_L, so we neglect constants of proportionality, and simply subsitutde $P \propto T/V$, giving

$$Q \propto \int \frac{T}{V} dV \propto T \ln \frac{V_2}{V_1} \propto T \ln \frac{P_1}{P_2} \quad .$$

The efficiency of a heat engine is

$$\text{efficiency} = 1 - \frac{Q_L}{Q_H} \quad .$$

Making use of the result from the previous proof for a Carnot engine with a monoatomic ideal gas as its working gas, we have

$$\text{efficiency} = 1 - \frac{T_L \ln(P_4/P_3)}{T_H \ln(P_1/P_2)},$$

where the subscripts 1, 2, 3, and 4 refer to figures [d](#)--[g](#) on page 309. We have shown above that the temperature is proportional to P^b on the insulated strokes 2-3 and 4-1, the pressures must be related by $P_2/P_3=P_1/P_4$, which can be rearranged as $P_4/P_3=P_1/P_2$, and we therefore have

$$\text{efficiency} = 1 - \frac{T_L}{T_H} \quad .$$

5.4.4 The arrow of time, or "this way to the Big Bang"

Now that we have a microscopic understanding of entropy, what does that tell us about the second law of thermodynamics? The second law defines a forward direction to time, "time's arrow." The microscopic treatment of entropy, however, seems to have mysteriously sidestepped that whole issue. A graph like figure [b](#) on page 314, showing a fluctuation away from

equilibrium, would look just as natural if we flipped it over to reverse the direction of time. After all, the basic laws of physics are conservation laws, which don't distinguish between past and future. Our present picture of entropy suggests that we restate the second law of thermodynamics as follows: low-entropy states are short-lived. An ice cube can't exist forever in warm water. We no longer have to distinguish past from future.

But how do we reconcile this with our strong psychological sense of the direction of time, including our ability to remember the past but not the future? Why do we observe ice cubes melting in water, but not the time-reversed version of the same process?

The answer is that there is no past-future asymmetry in the laws of physics, but there is a past-future asymmetry in the universe. The universe started out with the Big Bang. (Some of the evidence for the Big Bang theory is given on page 354.) The early universe had a very low entropy, and low-entropy states are short-lived. What does "short-lived" mean here, however? Hot coffee left in a paper cup will equilibrate with the air within ten minutes or so. Hot coffee in a thermos bottle maintains its low-entropy state for much longer, because the coffee is insulated by a vacuum between the inner and outer walls of the thermos. The universe has been mostly vacuum for a long time, so it's well insulated. Also, it takes billions of years for a low-entropy normal star like our sun to evolve into the high-entropy cinder known as a white dwarf.

The universe, then, is still in the process of equilibrating, and all the ways we have of telling the past from the future are really just ways of determining which direction in time points toward the Big Bang, i.e., which direction points to lower entropy. The psychological arrow of time, for instance, is ultimately based on the thermodynamic arrow. In some general sense, your brain is like a computer, and computation has thermodynamic effects. In even the most efficient possible computer, for example, erasing one bit of memory decreases its entropy from $k \ln 2$ (two possible states) to $k \ln 1$ (one state), for a drop of about 10^{-23} J/K. One way of determining the direction of the psychological arrow of time is that forward in psychological time is the direction in which, billions of years from now, all consciousness will have ceased; if consciousness was to exist forever in the universe, then there would have to be a never-ending decrease in the universe's entropy. This can't happen, because low-entropy states are short-lived.

Relating the direction of the thermodynamic arrow of time to the

existence of the Big Bang is a satisfying way to avoid the paradox of how the second law can come from basic laws of physics that don't distinguish past from future. There is a remaining mystery, however: why did our universe have a Big Bang that was low in entropy? It could just as easily have been a maximum-entropy state, and in fact the number of possible high-entropy Big Bangs is vastly greater than the number of possible low-entropy ones. The question, however, is probably not one that can be answered using the methods of science. All we can say is that if the universe had started with a maximum-entropy Big Bang, then we wouldn't be here to wonder about it. A longer, less mathematical discussion of these concepts, along with some speculative ideas, is given in "The Cosmic Origins of Time's Arrow," Sean M. Carroll, Scientific American, June 2008, p. 48.

5.4.5 Quantum mechanics and zero entropy

The previous discussion would seem to imply that absolute entropies are never well defined, since any calculation of entropy will always end up having terms that depend on Δp and Δx. For instance, we might think that cooling an ideal gas to absolute zero would give zero entropy, since there is then only one available momentum state, but there would still be many possible position states. We'll see later in this book, however, that the quantum mechanical uncertainty principle makes it impossible to know the location and position of a particle simultaneously with perfect accuracy. The best we can do is to determine them with an accuracy such that the product $\Delta p \Delta x$ is equal to a constant called Planck's constant. According to quantum physics, then, there is a natural minimum size for rectangles in phase space, and entropy can be defined in absolute terms. Another way of looking at it is that according to quantum physics, the gas as a whole has some well-defined ground state, which is its state of minimum energy. When the gas is cooled to absolute zero, the scene is not at all like what we would picture in classical physics, with a lot of atoms lying around motionless. It might, for instance, be a strange quantum-mechanical state called the Bose-Einstein condensate, which was achieved for the first time recently with macroscopic amounts of atoms. Classically, the gas has many possible states available to it at zero temperature, since the positions of the atoms can be chosen in a variety of ways. The classical picture is a bad approximation under these circumstances, however. Quantum mechanically there is only one ground state, in which each atom is spread out over the available volume in a cloud of probability. The entropy is therefore zero at zero temperature. This fact, which cannot be understood in terms of classical physics, is known as the third law of

thermodynamics.

5.4.6 Summary of the laws of thermodynamics

Here is a summary of the laws of thermodynamics:

- **The zeroth law of thermodynamics (page 301)** If object A is at the same temperature as object B, and B is at the same temperature as C, then A is at the same temperature as C.
- **The first law of thermodynamics (page 296)** Energy is [4] conserved.
- **The second law of thermodynamics (page 312)** The entropy of a closed system always increases, or at best stays the same: $\Delta S \geq 0$.
- **The third law of thermodynamics (page 325)** The entropy of a system approaches zero as its temperature approaches absolute zero.

From a modern point of view, only the first law deserves to be called a fundamental law of physics. Once Boltmann discovered the microscopic nature of entropy, the zeroth and second laws could be understood as statements about probability: a system containing a large number of particles is overwhelmingly likely to do a certain thing, simply because the number of possible ways to do it is extremely large compared to the other possibilities. The third law is also now understood to be a consequence of more basic physical principles, but to explain the third law, it's not sufficient simply to know that matter is made of atoms: we also need to understand the quantum-mechanical nature of those atoms, discussed in chapter 13. Historically, however, the laws of thermodynamics were discovered in the eighteenth century, when the atomic theory of matter was generally considered to be a hypothesis that couldn't be tested experimentally. Ideally, with the publication of Boltzmann's work on entropy in 1877, the zeroth and second laws would have been immediately demoted from the status of physical laws, and likewise the development of quantum mechanics in the 1920's would have done the same for the third law.
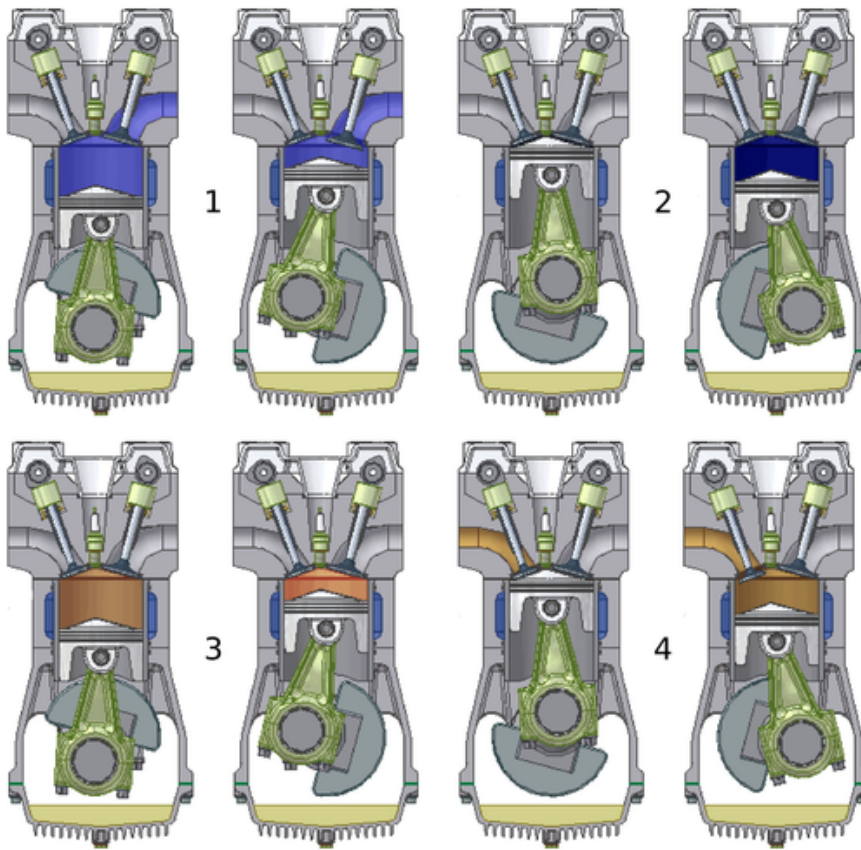
l / The Otto cycle. 1. In the exhaust stroke, the piston expels the burned air-gas mixture left over from the preceding cycle. 2. In the intake stroke, the piston sucks in fresh air-gas mixture. 3. In the compression stroke, the piston compresses the mixture, and heats it. 4. At the beginning of the power stroke, the spark plug fires, causing the air-gas mixture to burn explosively and heat up much more. The heated mixture expands, and does a large amount of positive mechanical work on the piston. An animated version can be viewed in the Wikipedia article "Four-stroke engine."

5.5 More About Heat Engines

So far, the only heat engine we've discussed in any detail has been a fictitious Carnot engine, with a monoatomic ideal gas as its working gas. As a more realistic example, figure l shows one full cycle of a cylinder in a standard gas-burning automobile engine. This four-stroke cycle is called the Otto cycle, after its inventor, German engineer Nikolaus Otto. The Otto cycle is more complicated than a Carnot cycle, in a number of ways:

- The working gas is physically pumped in and out of the cylinder through valves, rather than being sealed and reused indefinitely as in the Carnot engine.
- The cylinders are not perfectly insulated from the engine block, so heat energy is lost from each cylinder by conduction. This makes the engine

less efficient that a Carnot engine, because heat is being discharged at a temperature that is not as cool as the environment.

- Rather than being heated by contact with an external heat reservoir, the air-gas mixture inside each cylinder is heated by internal combusion: a spark from a spark plug burns the gasoline, releasing heat.
- The working gas is not monoatomic. Air consists of diatomic molecules (N_2 and O_2), and gasoline of polyatomic molecules such as octane (C_8H_{18}).
- The working gas is not ideal. An ideal gas is one in which the molecules never interact with one another, but only with the walls of the vessel, when they collide with it. In a car engine, the molecules are interacting very dramatically with one another when the air-gas mixture explodes (and less dramatically at other times as well, since, for example, the gasoline may be in the form of microscopic droplets rather than individual molecules).

This is all extremely complicated, and it would be nice to have some way of understanding and visualizing the important properties of such a heat engine without trying to handle every detail at once. A good method of doing this is a type of graph known as a P-V diagram. As proved in homework problem 2, the equation $dW=Fdx$ for mechanical work can be rewritten as $dW=PdV$ in the case of work done by a piston. Here P represents the pressure of the working gas, and V its volume. Thus, on a graph of P versus V, the area under the curve represents the work done. When the gas expands, dx is positive, and the gas does positive work. When the gas is being compressed, dx is negative, and the gas does negative work, i.e., it absorbs energy. Notice how, in the diagram of the Carnot engine in the top panel of figure a, the cycle goes clockwise around the curve, and therefore the part of the curve in which negative work is being done (arrowheads pointing to the left) are below the ones in which positive work is being done. This means that over all, the engine does a positive amount of work. This net work equals the area under the top part of the curve, minus the area under the bottom part of the curve, which is simply the area enclosed by the curve. Although the diagram for the Otto engine is more complicated, we can at least compare it on the same footing with the Carnot engine. The curve forms a figure-eight, because it cuts across itself. The top loop goes clockwise, so as in the case of the Carnot engine, it represents positive work. The bottom loop goes counterclockwise, so it represents a net negative contribution to the work. This is because more work is expended in forcing out the exhaust than is generated in the intake stroke.

To make an engine as efficient as possible, we would like to make the loop have as much area as possible. What is it that determines the actual
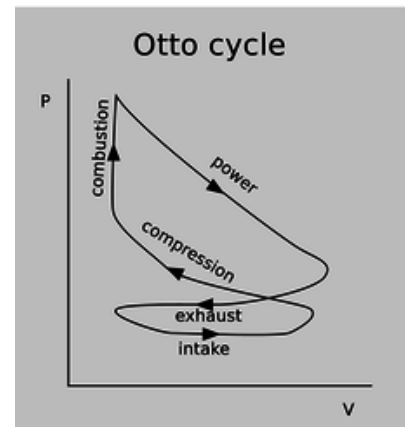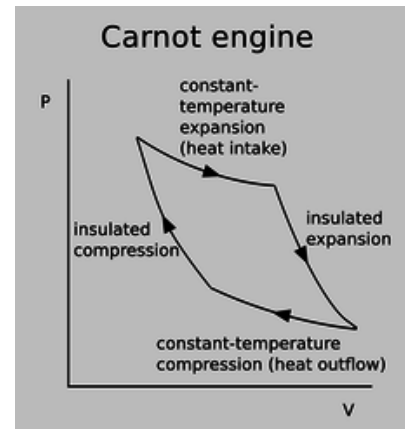
a / P-V diagrams for a Carnot engine and an Otto engine.
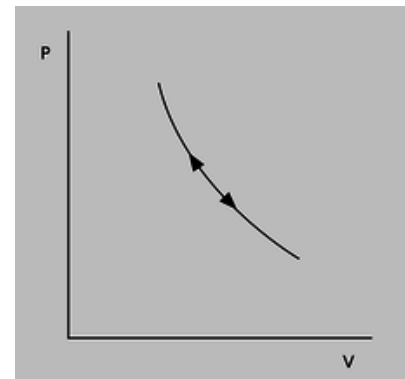
b / Example 23,

shape of the curve? First let's consider the constant-temperature expansion stroke that forms the top of the Carnot engine's P-V plot. This is analogous to the power stroke of an Otto engine. Heat is being sucked in from the hot reservoir, and since the working gas is always in thermal equilibrium with the hot reservoir, its temperature is constant. Regardless of the type of gas, we therefore have $PV=nkT$ with T held constant, and thus $P \propto V^{-1}$ is the mathematical shape of this curve --- a $y=1/x$ graph, which is a hyperbola. This is all true regardless of whether the working gas is monoatomic, diatomic, or polyatomic. (The bottom of the loop is likewise of the form $P \propto V^{1}$, but with a smaller constant of proportionality due to the lower temperature.)
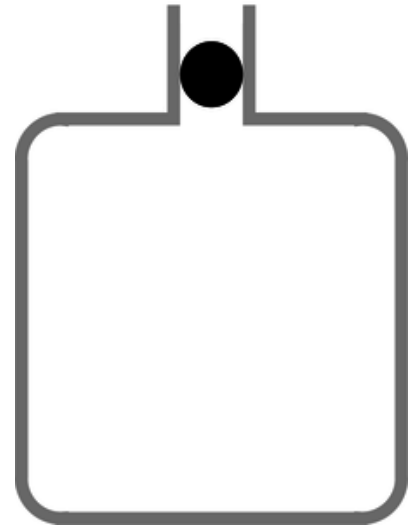
Now consider the insulated expansion stroke that forms the right side of the curve for the Carnot engine. As shown on page 322, the relationship between pressure and temperature in an insulated compression or expansion is $T \propto P^{b}$, with $b=2/5$, $2/7$, or $1/4$, respectively, for a monoatomic, diatomic, or polyatomic gas. For P as a function of V at constant T, the ideal gas law gives $P \propto T/V$, so $P \propto V^{-\gamma}$, where $\gamma=1/(1-b)$ takes on the values 5/3, 7/5, and 4/3. The number γ can be interpreted as the ratio C_P/C_V, where C_P, the heat capacity at constant pressure, is the amount of heat required to raise the temperature of the gas by one degree while keeping its pressure constant, and C_V is the corresponding quantity under conditions of constant volume.

c / Example 24.

e / A T-S diagram for a Carnot engine.

Example 22: The compression ratio
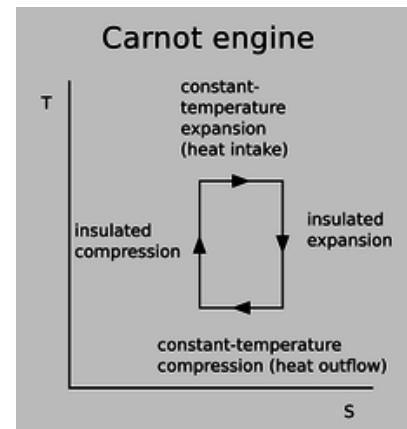
Operating along a constant-temperature stroke, the amount of mechanical work done by a heat engine can be calculated as follows:

$$PV = nkT$$

Setting $c = nkT$ to simplify the writing, $P = cV^{-1}$

$$W = \int_{V_i}^{V_f} PdV$$
$$= c \int_{V_i}^{V_f} V^{-1}dV$$
$$= c \ln V_f - c \ln V_i$$
$$= c \ln(V_f/V_i)$$

The ratio V_f/V_i is called the *compression ratio* of the engine, and higher values result in more power along this stroke. Along an insulated stroke, we have $P \propto V^{\gamma}$, with $\gamma \neq 1$, so the result for the work no longer has this perfect mathematical property of depending only on the ratio V_f/V_i. Nevertheless, the compression ratio is still a good figure of merit for predicting the performance of any heat engine, including an internal combustion engine. High compression ratios tend to make the working gas of an internal combustion engine heat up so much that it spontaneously explodes. When this

happens in an Otto-cycle engine, it can cause ignition before the sparkplug fires, an undesirable effect known as pinging. For this reason, the compression ratio of an Otto-cycle automobile engine cannot normally exceed about 10. In a diesel engine, however, this effect is used intentionally, as an alternative to sparkplugs, and compression ratios can be 20 or more.

Example 23: Sound

Figure b shows a P-V plot for a sound wave. As the pressure oscillates up and down, the air is heated and cooled by its compression and expansion. Heat conduction is a relatively slow process, so typically there is not enough time over each cycle for any significant amount of heat to flow from the hot areas to the cold areas. (This is analogous to insulated compression or expansion of a heat engine; in general, a compression or expansion of this type, with no transfer of heat, is called *adiabatic*.) The pressure and volume of a particular little piece of the air are therefore related according to $P \propto V^{\gamma}$. The cycle of oscillation consists of motion back and forth along a single curve in the P-V plane, and since this curve encloses zero volume, no mechanical work is being done: the wave (under the assumed ideal conditions) propagates without any loss of energy due to friction.

The speed of sound is also related to γ. See example 13 on p. 373.

Example 24: Measuring γ using the "spring of air"

Figure c shows an experiment that can be used to measure the γ of a gas. When the mass m is inserted into bottle's neck, which has cross-sectional area A, the mass drops until it compresses the air enough so that the pressure is enough to support its weight. The observed frequency ω of oscillations about this equilibrium position y_o can be used to extract the γ of the gas.

$$\omega^2 = \frac{k}{m}$$
$$= -\frac{1}{m}\frac{dF}{dy}\bigg|_{y_o}$$
$$= -\frac{A}{m}\frac{dP}{dy}\bigg|_{y_o}$$
$$= -\frac{A^2}{m}\frac{dP}{dV}\bigg|_{V_o}$$

We make the bottle big enough so that its large surface-to-volume ratio prevents the conduction of any significant amount of heat through its walls during one cycle, so $P \propto V^{\gamma}$, and $dP/dV = -\gamma P/V$. Thus,

$$\omega^2 = \gamma \frac{A^2}{m}\frac{P_o}{V_o}$$

Example 25: The Helmholtz resonator

When you blow over the top of a beer bottle, you produce a pure tone. As you drink more of the beer, the pitch goes down. This is similar to example 24, except that instead of a solid mass m sitting inside the neck of the bottle, the moving mass is the air itself. As air rushes in and out of the bottle, its velocity is highest at the bottleneck, and since kinetic energy is proportional to the square of the velocity, essentially all of the kinetic energy is that of the air that's in the neck. In other words, we can replace m with $AL\rho$, where L is the length of the neck, and ρ is the density of the air. Substituting into the earlier result, we find that the resonant frequency is

$$\omega^2 = \gamma \frac{P_o}{\rho} \frac{A}{LV_o} \qquad .$$

This is known as a Helmholtz resonator. As shown in figure d, a violin or an acoustic guitar has a Helmholtz resonance, since air can move in and out through the f-holes. Problem 10 is a more quantitative exploration of this.
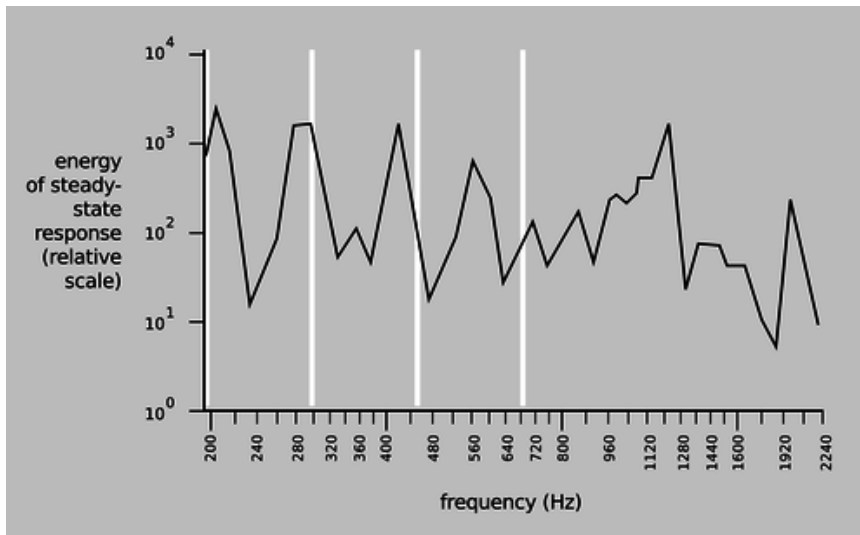
d / The resonance curve of a 1713 Stradivarius violin, measured by Carleen Hutchins. There are a number of different resonance peaks, some strong and some weak; the ones near 200 and 400 Hz are vibrations of the wood, but the one near 300 Hz is a resonance of the air moving in and out through those holes shaped like the letter F. The white lines show the frequencies of the four strings.

We have already seen, based on the microscopic nature of entropy, that any Carnot engine has the same efficiency, and the argument only employed the assumption that the engine met the definition of a Carnot cycle: two insulated strokes, and two constant-temperature strokes. Since we didn't have to make any assumptions about the nature of the working gas being used, the result is evidently true for diatomic or polyatomic molecules, or for

a gas that is not ideal. This result is surprisingly simple and general, and a little mysterious --- it even applies to possibilities that we have not even considered, such as a Carnot engine designed so that the working "gas" actually consists of a mixture of liquid droplets and vapor, as in a steam engine. How can it always turn out so simple, given the kind of mathematical complications that were swept under the rug in example 22? A better way to understand this result is by switching from P-V diagrams to a diagram of temperature versus entropy, as shown in figure e. An infinitesimal transfer of heat dQ gives rise to a change in entropy $dS=dQ/T$, so the area under the curve on a T-S plot gives the amount of heat transferred. The area under the top edge of the box in figure e, extending all the way down to the axis, represents the amount of heat absorbed from the hot reservoir, while the smaller area under the bottom edge represents the heat wasted into the cold reservoir. By conservation of energy, the area enclosed by the box therefore represents the amount of mechanical work being done, as for a P-V diagram. We can now see why the efficiency of a Carnot engine is independent of any of the physical details: the definition of a Carnot engine guarantees that the T-S diagram will be a rectangular box, and the efficiency depends only on the relative heights of the top and bottom of the box.

\backofchapterboilerplate{thermo}

Homework Problems

1. (a) Show that under conditions of standard pressure and temperature, the volume of a sample of an ideal gas depends only on the number of molecules in it.
(b) One mole is defined as 6.0×10^{23} atoms. Find the volume of one mole of an ideal gas, in units of liters, at standard temperature and pressure ($0°C$ and 101 kPa). (answer check available at lightandmatter.com)

2. A gas in a cylinder expands its volume by an amount dV, pushing out a piston. Show that the work done by the gas on the piston is given by $dW = PdV$.

3. (a) A helium atom contains 2 protons, 2 electrons, and 2 neutrons. Find the mass of a helium atom. (answer check available at lightandmatter.com)
(b) Find the number of atoms in 1.0 kg of helium. (answer check available at lightandmatter.com)
(c) Helium gas is monoatomic. Find the amount of heat needed to raise the

temperature of 1.0 kg of helium by 1.0 degree C. (This is known as helium's heat capacity at constant volume.) (answer check available at lightandmatter.com)

4. A sample of gas is enclosed in a sealed chamber. The gas consists of molecules, which are then split in half through some process such as exposure to ultraviolet light, or passing an electric spark through the gas. The gas returns to thermal equilibrium with the surrounding room. How does its pressure now compare with its pressure before the molecules were split?

5. Most of the atoms in the universe are in the form of gas that is not part of any star or galaxy: the intergalactic medium (IGM). The IGM consists of about 10^{-5} atoms per cubic centimeter, with a typical temperature of about 10^3 K. These are, in some sense, the density and temperature of the universe (not counting light, or the exotic particles known as "dark matter"). Calculate the pressure of the universe (or, speaking more carefully, the typical pressure due to the IGM).(answer check available at lightandmatter.com)

6. Estimate the pressure at the center of the Earth, assuming it is of constant density throughout. Note that g is not constant with respect to depth --- as shown in example <u>19</u> on page 105, g equals Gmr/b^3 for r, the distance from the center, less than b, the earth's radius.
(a) State your result in terms of G, m, and b.(answer check available at lightandmatter.com)
(b) Show that your answer from part a has the right units for pressure.
(c) Evaluate the result numerically. (answer check available at lightandmatter.com)
(d) Given that the earth's atmosphere is on the order of one thousandth the earth's radius, and that the density of the earth is several thousand times greater than the density of the lower atmosphere, check that your result is of a reasonable order of magnitude.

7. (a) Determine the ratio between the escape velocities from the surfaces of the earth and the moon. (answer check available at lightandmatter.com)
(b) The temperature during the lunar daytime gets up to about 130°\textup{C}. In the extremely thin (almost nonexistent) lunar atmosphere, estimate how the typical velocity of a molecule would compare with that of the same type of molecule in the earth's atmosphere. Assume that the earth's atmosphere has a temperature of 0°\textup{C}. (answer check available at lightandmatter.com)

(c) Suppose you were to go to the moon and release some fluorocarbon gas, with molecular formula C_nF_{2n+2}. Estimate what is the smallest fluorocarbon molecule (lowest n) whose typical velocity would be lower than that of an N_2 molecule on earth in proportion to the moon's lower escape velocity. The moon would be able to retain an atmosphere made of these molecules. (answer check available at lightandmatter.com)

8. Refrigerators, air conditioners, and heat pumps are heat engines that work in reverse. You put in mechanical work, and the effect is to take heat out of a cooler reservoir and deposit heat in a warmer one: $Q_L+W=Q_H$. As with the heat engines discussed previously, the efficiency is defined as the energy transfer you want (Q_L for a refrigerator or air conditioner, Q_H for a heat pump) divided by the energy transfer you pay for (W).

Efficiencies are supposed to be unitless, but the efficiency of an air conditioner is normally given in terms of an EER rating (or a more complex version called an SEER). The EER is defined as Q_L/W, but expressed in the barbaric units of of Btu/watt-hour. A typical EER rating for a residential air conditioner is about 10 Btu/watt-hour, corresponding to an efficiency of about 3. The standard temperatures used for testing an air conditioner's efficiency are 80° F (27°C) inside and 95° F (35°C) outside.

(a) What would be the EER rating of a reversed Carnot engine used as an air conditioner? (answer check available at lightandmatter.com)
(b) If you ran a 3-kW residential air conditioner, with an efficiency of 3, for one hour, what would be the effect on the total entropy of the universe? Is your answer consistent with the second law of thermodynamics? (answer check available at lightandmatter.com)

9. Even when resting, the human body needs to do a certain amount of mechanical work to keep the heart beating. This quantity is difficult to define and measure with high precision, and also depends on the individual and her level of activity, but it's estimated to be about 1 to 5 watts. Suppose we consider the human body as nothing more than a pump. A person who is just lying in bed all day needs about 1000 kcal/day worth of food to stay alive. (a) Estimate the person's thermodynamic efficiency as a pump, and (b) compare with the maximum possible efficiency imposed by the laws of thermodynamics for a heat engine operating across the difference between a body temperature of 37°C and an ambient temperature of 22°C. (c) Interpret your answer.\hwans{hwans:heart-efficiency}

10. Example 25 on page 330 suggests analyzing the resonance of a violin at 300 Hz as a Helmholtz resonance. However, we might expect the equation for the frequency of a Helmholtz resonator to be a rather crude approximation here, since the f-holes are not long tubes, but slits cut through the face of the instrument, which is only about 2.5 mm thick. (a) Estimate the frequency that way anyway, for a violin with a volume of about 1.6 liters, and f-holes with a total area of 10 cm^2. (b) A common rule of thumb is that at an open end of an air column, such as the neck of a real Helmholtz resonator, some air beyond the mouth also vibrates as if it was inside the tube, and that this effect can be taken into account by adding 0.4 times the diameter of the tube for each open end (i.e., 0.8 times the diameter when both ends are open). Applying this to the violin's f-holes results in a huge change in L, since the ~ 7 mm width of the f-hole is considerably greater than the thickness of the wood. Try it, and see if the result is a better approximation to the observed frequency of the resonance.\hwans{hwans:violin-helmholtz}

Footnotes

[1] This equal sharing will be justified more rigorously on page 320.
[2] Even with smaller numbers of atoms, there is a problem with this kind of brute-force computation, because the tiniest measurement errors in the initial state would end up having large effects later on.
[3] This is the same relation as the one on Boltzmann's tomb, just in a slightly different notation.