

Energy

(Schroeder Chapter One)

Physics A410*

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1 Temperature and Thermal Equilibrium

In conjunction with this topic, you should read Section 1.1 of Schroeder.

We start our consideration of thermal physics with a fundamental observational fact: If we put two things in contact with each other, one at a higher and one at a lower temperature, the hotter one will cool off and the colder one will warm up until eventually they have reached the same temperature. Some examples are a hot cup of coffee in a cool room and a cool thermometer in the mouth of a feverish child. When things have reached the same temperature, they've settled into a state called *thermal equilibrium*.

1.1 Defining Temperature

The problem with the previous statement is that we haven't defined what we mean by "temperature". As it turns out, the precise physical/mathematical definition of this seemingly intuitive concept depends on other concepts, so we'll have to wait a while (until we're covering chapter three) to define it.

For the time being, we'll work with a couple of ad hoc definitions:

1. Temperature is the thing that's the same when two objects are in thermal equilibrium
2. Temperature is what you measure with a thermometer

The first definition is not all that enlightening, but notice that it allows us to extend the second definition to things other than thermometers. If we want to know the temperature of a thermometer, we read it. If we want to know the temperature of something else, we put it in contact with a thermometer, wait for the object and the thermometer to reach thermal equilibrium, then read the thermometer.

So how does a thermometer work? Most thermometers operate on the principle that most things tend to expand when their temperatures increase. Some examples are:

1. A mercury thermometer. At higher temperatures, the same mass of mercury will take up more volume, causing it to creep farther down a glass tube.
2. A bimetal thermometer like you find in a thermostat; different metals expand by different amounts with temperature, so if you stick strips of two different metals together, the combination will have to curve to one side or another so that the more responsive metal can be shorter or longer as appropriate.
3. A gas thermometer, where a given mass of gas is forced to occupy a rubber bulb of fixed volume; if the temperature increases, the gas will exert a greater pressure on the walls of the bulb.

1.2 Temperature Scales

Historically, the two temperature scales in every day were developed in similar ways. The Fahrenheit scale used in the United States and the Celsius scale used in the rest of the world are both named after their creators, who each took a mercury thermometer, measured a “cold” and a “hot” temperature, called one 0° and the other 100° , then marked off equal intervals in between.

1.2.1 Fahrenheit

In the Fahrenheit scale, the cold temperature (0°F) was created by filling a bucket with salt and ice and making the lowest temperature Fahrenheit could manage, while the hot temperature (100°F) was measured on a very hot summer day.

1.2.2 Celsius

Unfortunately, those two reference temperatures are not reproducible, so they don't serve as good reference points which anyone else could use to make a Fahrenheit thermometer. Instead, you'd have to consider some reproducible temperature, like the temperature at which pure water freezes (32°F) or boils (212°F). Celsius decided to use these as his reference points in what was initially called the centigrade (100 degree) scale, in which water freezes at 0°C and boils at 100°C .

These two reference points, $0^\circ\text{C} = 32^\circ\text{F}$ and $100^\circ\text{C} = 212^\circ\text{F}$, along with the assumption that the degree marks are evenly spaced on both thermometers, are all that's needed to convert from one scale to the other.

1.2.3 Aside: Dimensional Analysis

This is a good time to mention a very useful technique in Physics, known as dimensional analysis. Basically, the idea is that the units of a quantity are part of the quantity, so instead of saying that a stick is d inches long, where $d = 10$ we say that it is d long, where $d = 10$ inches. The “inches” is a part of the quantity, and it's manipulated as if it were an algebraic variable. This makes it very easy to convert units, since you start with a relationship like

$$1 \text{ in} = 2.54 \text{ cm} \tag{1.1}$$

and divide both sides by “inches” to obtain the conversion factor

$$1 = 2.54 \frac{\text{cm}}{\text{in}} \tag{1.2}$$

Since you can multiply anything by 1 and not change its value, this allows you to write

$$d = 10 \text{ in} = 10 \text{ in} \times 2.54 \frac{\text{cm}}{\text{in}} = 25.4 \text{ cm} \tag{1.3}$$

where the inches have cancelled out. If you handle conversions of units this way, you're much less likely to divide when you should multiply, or vice versa, since if you do it the wrong way, the units won't cancel out correctly.

I mention this for two reasons: First, it will prove very useful when dealing with all of the thermodynamic constants which are defined in strange units. Second, it doesn't work with Fahrenheit and Celsius; if you try to consider the expression $0^\circ\text{C} = 32^\circ\text{F}$ as an algebraic equation, it makes no sense. This is because, while zero centimeters is the same as zero inches or zero miles or zero furlongs, zero degrees Celsius and zero degrees Fahrenheit are not the same temperature. The zeros of the scales are not the same.

1.2.4 Kelvin

There is, however, a temperature which does make a sensible zero; the easiest way to define it now is in connection with the gas thermometer. Recall that this thermometer measures the pressure of gas constrained to occupy a fixed volume, and thus deduces the temperature, since the same amount of gas in the same volume exerts a greater pressure at higher temperatures. The pressure is not directly proportional to the Celsius or Fahrenheit temperature (it would be pretty strange if it were, since it would become negative at temperatures that actually exist on the Earth), but it is *indirectly* proportional:

$$(\text{Pressure}) = (\text{Constant \#1}) + (\text{Constant \#2}) \times (\text{Celsius Temperature}) \quad (1.4)$$

For gases at low density, when you extrapolate this relation down, you always find that the pressure should go to zero at the same temperature, -273.15°C . (This temperature is called *Absolute Zero*, and in fact temperatures lower than this are not only impossible, but undefined according to the technical definition of temperature.) This is the basis for the definition of the *Kelvin* temperature scale, defined by

$$(\text{Kelvin Temperature}) = (\text{Celsius Temperature}) + 273.15 \quad (1.5)$$

When the temperature is expressed in Kelvin, the pressure of a low-density gas really is *directly* proportional to its temperature, expressed in Kelvin. In fact, whenever the temperature appears as T in any equation, we'll always be talking about the temperature measured on a scale where Absolute Zero is 0. Among other things, this allows dimensional analysis to work sensibly.

Note that when we're talking about *changes* in temperature, that things work the same in Celsius and Kelvin, since the scales are only offset, and the degrees are the same size. So the change in temperature between water's freezing (0°C or 273.15 K) and boiling points (100°C or 373.15 K) is 100 Celsius degrees, which is the same as 100 Kelvin.

2 The Ideal Gas Law

In conjunction with this topic, you should read Section 1.2 of Schroeder.

The discussion of gas thermometers also ties nicely into the next topic to be introduced, the *ideal gas law*. We said that the pressure of an ideal gas at constant volume was directly proportional to its temperature (measured on the Kelvin scale, whose zero is Absolute Zero):

$$P \propto T \quad (2.1)$$

It is also sensible, thinking qualitatively, that if we did not constrain the gas to occupy the same volume, but merely maintained the same pressure on it, it would expand as its temperature rose. One possible quantitative expression of this, which turns out to hold for low-density gases, is

$$PV \propto T \tag{2.2}$$

Now, the one other thing we'd expect to find in this expression is the number of gas molecules contained in the given volume. It's fairly sensible to assume that, all else being equal, this will be proportional to the volume, leaving us

$$PV \propto NT \tag{2.3}$$

All that's missing is the proportionality constant, which is called Boltzmann's constant; the full expression is

$$PV = NkT \tag{2.4}$$

where Boltzmann's constant is experimentally determined to be

$$k = 1.381 \times 10^{-23} \text{ J/K} \tag{2.5}$$

The units on this are Joules per Kelvin. This is a good time to check that the units of everything make sense. The units of the left-hand side are

$$(\text{Pressure}) \times (\text{Volume}) = \frac{(\text{Force})}{(\text{Length})^2} \times (\text{Length})^3 = (\text{Force}) \times (\text{Length}) \tag{2.6}$$

while the units of the right-hand side are

$$\frac{(\text{Energy})}{(\text{Temperature})} \times (\text{Temperature}) = (\text{Energy}) \tag{2.7}$$

And sure enough, energy has units of force times distance.

A few words about the ideal gas law (2.3): first, it only applies approximately, to some gases, basically in circumstances where you can ignore the interactions of gas molecules with each other. But it is the case for all substances that *some* relationship holds among the temperature, pressure, and volume (or density). This is called an *equation of state*, and basically reflects the fact that only two of those three quantities are independent. This is something which will come up over and over again in mathematical forms.

Finally, you may be more familiar with the ideal gas law as stated by Chemists:

$$PV = nRT \tag{2.8}$$

(pronounced "piv-nert"). In (2.8), n is not the number of gas molecules but the number of "moles", where a mole is about 6×10^{23} particles, and the constant is

$$R = 8.31 \frac{\text{J}}{\text{mol K}} \tag{2.9}$$

Basically the reason for this is that Chemists don't like to deal with very large or small numbers like the number of molecules in a reasonable amount of gas or Boltzmann's constant

in everyday units, respectively. I leave you to read more about this in Section 1.2 of the textbook, but simply note that you can nearly convert between the two forms by dimensional analysis alone, if you consider Avogadro's number to be a conversion factor between particles and moles:

$$N_A = 6.02 \times 10^{23} \frac{\text{particles}}{\text{mol}} \quad (2.10)$$

2.1 Microscopic Picture of an Ideal Gas

Our first theoretical handle on what temperature means comes by applying the ideal gas equation of state to a simple microscopic model of a gas.

Consider the gas to be made up of N molecules, each of mass m , flying around the inside of a box, not interacting with each other, and bouncing elastically off the walls. In this model, we can understand the left-hand side of the ideal gas equation of state; the volume of the box is self-explanatory, but what is the pressure? Recall that pressure is force per unit area, and in this case it's the magnitude of the force per unit area which the gas exerts on the walls of its box. Focus on the one of the six walls of the box, perpendicular to what we'll call the x -direction. If the length of the box in the x direction is L and the area of the walls perpendicular to this direction is A , the volume of the box will be $V = AL$.

What is the force exerted on this face by all of the collisions of molecules off of it? Let's focus on one molecule. For most of its flight, it's exerting no force on the wall, except when it collides with it. Recalling that one of the ways to describe force is as the time rate of change of momentum,

$$\vec{F} = \frac{d\vec{p}}{dt} \quad (2.11)$$

we see that the important thing to consider about an impulsive force (one which operates only for a very short time) is the change of momentum associated with it. In this case, it's a lot easier to think about the change in the gas molecule's momentum and then infer the momentum transferred to the wall by Newton's third law.

Since the collision is elastic, we know that the magnitude of the velocity vector is unchanged, and all the collision does is reverse the x component of the velocity:

$$(v_x)_{\text{after}} = -(v_x)_{\text{before}} \quad (2.12a)$$

$$(v_y)_{\text{after}} = (v_y)_{\text{before}} \quad (2.12b)$$

$$(v_z)_{\text{after}} = (v_z)_{\text{before}} \quad (2.12c)$$

The change in the momentum of the molecule is thus

$$(\Delta p_x)_{\text{molecule}} = -2m |v_x| \quad (2.13a)$$

$$(\Delta p_y)_{\text{molecule}} = 0 \quad (2.13b)$$

$$(\Delta p_z)_{\text{molecule}} = 0 \quad (2.13c)$$

where we find it convenient to talk about $|v_x|$, which is the same before and after the collision. (Note that it's also unchanged in collisions off the other walls, since they only affect v_y and

v_z .) By Newton's third law, or equivalently by conservation of momentum, the impulse imparted to the wall is

$$(\Delta p_x)_{\text{wall}} = 2m |v_x| \quad (2.14a)$$

$$(\Delta p_y)_{\text{wall}} = 0 \quad (2.14b)$$

$$(\Delta p_z)_{\text{wall}} = 0 \quad (2.14c)$$

Now, what we're actually interested in is the time-averaged force exerted by the molecule on this wall of the box; this may not seem very useful when we're only dealing with one molecule, since at any moment there's either no force or rather a lot, but when we consider all the molecules in the box, at any time, some fraction of them will be colliding with the wall, and the force as a function of time will be smoothed out and nearly constant. So, to get the average force, we need to divide the impulse by the time between collisions:

$$\vec{F}_{\text{avg}} = \frac{\Delta \vec{p}}{\Delta t} \quad (2.15)$$

What is Δt ? Well, it's the time the molecule takes to travel to the other side of the box and back, so $\Delta t/2$ is the time to travel the length L of the box in the x direction. This means

$$|v_x| = \frac{L}{\Delta t/2} \quad (2.16)$$

or

$$\Delta t = \frac{2L}{|v_x|} \quad (2.17)$$

putting it together, the average force on the wall due to collisions with this molecule is entirely in the x direction, and its only non-zero component is given by

$$F_{x \text{ avg}} = \frac{2m |v_x|}{2L/|v_x|} = \frac{mv_x^2}{L} \quad (2.18)$$

The average pressure is the magnitude of this force divided by the area A of the wall:

$$P_{\text{avg, one molecule}} = \frac{mv_x^2}{AL} = \frac{mv_x^2}{V} \quad (2.19)$$

Now let's think about all of the molecules, remembering that the large number of randomly moving molecules will mean the time-average takes care of itself. Give each molecule a label $\alpha = 1, 2, \dots, N$; then the average pressure due to the α th molecule is

$$P_\alpha = \frac{mv_{x\alpha}^2}{V} \quad (2.20)$$

Since the total force on the wall is given by adding up the force due to each molecule, the total pressure must be the sum of the pressures associated with the individual molecules:

$$P = \sum_{\alpha=1}^N P_\alpha = \sum_{\alpha=1}^N \frac{mv_{x\alpha}^2}{V} \quad (2.21)$$

Now it's time to apply the ideal gas equation of state and relate the motions of the individual particles to the temperature of the gas. Multiplying through by V , we get

$$NkT = PV = \sum_{\alpha=1}^N mv_{x\alpha}^2 \quad (2.22)$$

or (pulling m out of the sum because it's the same for all the molecules)

$$kT = m \frac{1}{N} \sum_{\alpha=1}^N v_{x\alpha}^2 \quad (2.23)$$

But the expression multiplied by on the right-hand side is just the average¹ v_x^2 of all the particles:

$$\overline{v_x^2} \equiv \frac{1}{N} \sum_{\alpha=1}^N v_{x\alpha}^2 \quad (2.24)$$

which gives us

$$kT = m\overline{v_x^2} \quad (2.25)$$

This is still a little awkward because it makes reference to a particular direction, but if we consider that there was nothing particularly special about that wall of the box, we realize the same holds for the y and z components:

$$\overline{v_y^2} = \overline{v_z^2} = \overline{v_x^2} = \frac{kT}{m} \quad (2.26)$$

This then lets us talk about the average squared speed of the molecules

$$\overline{v^2} = \overline{\vec{v} \cdot \vec{v}} = \overline{v_x^2} + \overline{v_y^2} + \overline{v_z^2} = \frac{3kT}{m} \quad (2.27)$$

Note that the average of the squares of a set of numbers is not the same as the square of their average², so we can't actually say anything about the average speed without knowing how the speeds are distributed; what we can talk about is the "root mean square" speed

$$v_{\text{rms}} = \sqrt{\overline{v^2}} = \frac{\sqrt{3kT}}{m} \quad (2.28)$$

3 Equipartition Theorem

In conjunction with this topic, you should read Section 1.3 of Schroeder.

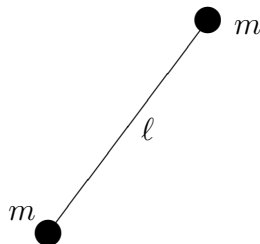
In the previous section, we showed that for any gas obeying the ideal gas law, the average translational kinetic energy $\frac{1}{2}mv_x^2 + \frac{1}{2}mv_y^2 + \frac{1}{2}mv_z^2$ is given by

$$\frac{3}{2}kT \quad (3.1)$$

¹An alternate notation for this is to use angle brackets: $\langle v_x^2 \rangle$

²Exercise: demonstrate this with the three numbers 1, 2, and 3. Take the square of each number and average those, then average the three original numbers and square that, and you'll see the two are not equal.

But this is not the only sort of energy that can be associated with the motion of gas molecules. For example, Nitrogen (N_2) is a diatomic molecule made up of two Nitrogen atoms. A crude model of this would be a dumbbell:



This shape can also *rotate*, a motion which carries with it *rotational kinetic energy* equal to

$$\frac{1}{2}I\omega^2 \quad (3.2)$$

where I is the moment of inertia

$$I = \sum mr^2 = m\left(\frac{\ell}{2}\right)^2 + m\left(\frac{\ell}{2}\right)^2 \quad (3.3)$$

and ω is the angular frequency ($=2\pi$ divided by the period of rotation)

In fact, this shape can rotate about two different axes; if the dumbbell is instantaneously parallel to the z axis, the rotational kinetic energy is

$$\frac{1}{2}I_x\omega_x^2 + \frac{1}{2}I_y\omega_y^2 \quad (3.4)$$

The moment of inertia about the z axis is negligible ($I_z \approx 0$), so we don't worry about rotations about the z axis.

The total internal energy of translation and rotation for a diatomic molecule is thus

$$\frac{1}{2}mv_x^2 + \frac{1}{2}mv_y^2 + \frac{1}{2}mv_z^2 + \frac{1}{2}I_x\omega_x^2 + \frac{1}{2}I_y\omega_y^2 \quad (3.5)$$

and the quantities ω_x , ω_y , v_x , v_y , and v_z are called the *degrees of freedom* for this molecule. Because the kinetic energy associated with each of these DOFs is proportional to the measure of it, we call these *quadratic degrees of freedom*.

There is a conjecture, which we will not prove, but which is usually true:

Equipartition Theorem: Each quadratic degree of freedom has associated with it an average energy of $\frac{1}{2}kT$ *per particle*.

This means that, for example, a diatomic gas (which has three translational and two rotational degrees of freedom associated with it) made up of N particles will, at a temperature of T , have an internal energy of $\frac{5}{2}NkT$.

Of course, this is not the only way a diatomic molecule can move. It's also possible for it to vibrate, with the two atoms oscillating towards and away from each other, and the bond between them getting shorter and longer. However, under ordinary conditions, the collisions that a typical diatomic gas undergoes are just not violent enough to excite its vibrational

degrees of freedom. We say that they are *frozen out*. At sufficiently low temperatures, even rotational degrees of freedom can be frozen out. Which degrees of freedom are excited and which are frozen out depends on the type of molecule and the temperature.

Molecules of a more complicated shape are called *polyatomic*, and in general don't have all their atoms lying on a single axis. They will have three non-zero moments of inertia and a rotational kinetic energy of

$$\frac{1}{2}I_x\omega_x^2 + \frac{1}{2}I_y\omega_y^2 + \frac{1}{2}I_z\omega_z^2 \quad (3.6)$$

which gives them three rotational degrees of freedom, which are all quadratic.

Vibration, when not frozen out, gives two quadratic DOFs per bond. The apparent double-counting can be understood if we realize that a harmonic oscillator has both potential and kinetic energy, which are quadratic in the displacement and velocity, respectively. I.e., if the length of the "spring" is ℓ and its unstretched length is ℓ_0 , the total energy stored in a one-dimensional oscillator is

$$E = \frac{1}{2}m\dot{\ell}^2 + \frac{1}{2}k(\ell - \ell_0)^2 \quad (3.7)$$

The number of degrees of freedom per particle which are not frozen out is referred to as f , and it consists of

- Three translational degrees of freedom (v_x , v_y , and v_z)
- Zero, two, or three rotational degrees of freedom, depending on whether the molecule is monatomic, diatomic, or polyatomic, assuming rotation is not frozen out
- Two vibrational degrees of freedom per bond, assuming vibration is not frozen out.

More complicated molecules have even more exotic DOFs which can be excited, corresponding to assorted twisting and flexing of the molecule.

The equipartition theorem says that each non-frozen-out DOF gets an average energy of $\frac{1}{2}kT$ per particle, so the total energy is

$$U = \frac{f}{2}NkT \quad (3.8)$$

Another thing to note about the equipartition theorem is that although we justified it for a monatomic gas using a simplified model (with no interactions between molecules) and the ideal gas equation of state, it turns out to hold even when the ideal gas law doesn't. The approximations underlying the calculation that $PV = Nm\overline{v_x^2}$ turn out to be the same ones needed for the ideal gas law $PV = NkT$ to be valid, and even when neither of them is a very good approximation, the equipartition theorem can be. Note, however, that not all systems satisfy the equipartition theorem, only those whose forms of internal energy are all quadratic.

4 Heat and Work

In conjunction with this topic, you should read Sections 1.4 and 1.5 of Schroeder.

With the equipartition theorem and the microscopic model of the ideal gas, we got a physical handle on the internal energy U stored in the molecular motions of a typical substance. Now we think about how energy can enter or leave a thermodynamic system. From mechanics we know that energy can be added to a system via *work*, the macroscopic motion of some outside agent exerting a force on part of the system. (Examples include a piston pushing into a cylinder of gas and a spoon vigorously stirring a drink.) However, in thermodynamics, we also need to consider the spontaneous transfer of energy from an object at a higher temperature to one at a lower temperature. The energy thus transferred is referred to as *heat*. The transfer of heat adds energy to the lower-temperature object and takes it away from the higher-temperature one. This will usually (but not always; there are a few pathological counterexamples) increase the temperature of the former and decrease the temperature of the latter, bringing them closer to thermal equilibrium.

Note the different physical meanings of heat, energy, and temperature:

- *Energy* is a property of a system, which can be stored in various forms (e.g., kinetic, potential).
- *Temperature* is another property of a system, which describes its tendency to spontaneously exchange energy with its surroundings.
- *Heat* is energy which flows spontaneously into or out of a system due to differences in temperature. It is meaningless to say that a system contains a given amount of heat, since heat is just what flows from one object or system to another.

4.1 Conservation of Energy

Physically, we know that energy can never be created or destroyed, only moved from one part of the universe to another or converted from one form to another. This means that when one system does work on another, or when heat flows from one system to another, the energy lost by one system is gained by the other.

We often talk about a *system* in contact with an *environment*, in which case we refer to the system's energy as U . If a process changes the energy of the system, this change has to be due to a certain amount of energy entering the system in the form of heat Q or as a result of work W done on the system. (If the system loses energy in the form of heat $Q < 0$, and if the system does net work *on* the environment, $W < 0$.) Work is defined as all the changes in internal energy of the system which are not due to heat flow, so almost by definition the total change in the internal energy U is

$$\Delta U = Q + W \tag{4.1}$$

(We follow Schroeder's convention of defining W as the work done *on* the system *by* the environment, rather than vice versa. See the footnote on page 18.) Note that there's no such thing as a "change in heat" or "change in work" because they're not properties of the system, only of the process which changes the energy.

Often, we'll want to consider an arbitrarily small, or infinitesimal, change in energy, associated with infinitesimal amounts of work. We'll write this as

$$dU = \bar{d}Q + \bar{d}W \quad (4.2)$$

note the slash through the \bar{d} , which emphasizes that $\bar{d}Q$ and $\bar{d}W$ are *not* infinitesimal changes in anything (the way that dU is), but rather infinitesimal amounts of heat and work. Schroeder chooses to leave off the \bar{d} altogether, but I think it's important to keep track of which quantities are infinitesimal.

4.2 Units of Energy and Heat

Recall from mechanics that energy has units of force times distance. In the MKS (SI) system, the standard unit is the Joule

$$1 \text{ J} = 1 \text{ kg m}^2/\text{s}^2 \quad (4.3)$$

We won't really use it in this course, but the corresponding cgs (gaussian) unit is the erg:

$$1 \text{ erg} = 1 \text{ g cm}^2/\text{s}^2 \quad (4.4)$$

Historically, before heat was understood as the transfer of thermal energy, it was measured in units of calories, where a calorie is the amount of heat needed to increase the temperature of one gram of water by one degree Celsius (equivalently, by one Kelvin). It turns out that $1 \text{ cal} = 4.186 \text{ J}$, but in some problems (mostly those involving heating water) it is still useful to work in terms of calories. Note that the Calories in your food are actually kilocalories (and European food labels actually call them this, as well as also giving the chemical energy contained in food in Joules), which is why drinking cold beer is not significantly less fattening than drinking it merely cool. (Raising the temperature of a half-liter ($500 \text{ ml} \approx 500 \text{ g}$) of beer by 5°C consumes $5 \times 500 = 2500$ calories, which is only 2.5 kcal.)

4.3 Compression Work

“Work” is basically any way of transferring energy into or out of a system, other than spontaneous heat flow. So for example, stirring, shaking, and cooking something in a microwave are all forms of work. But one of the most important ways to do work on a system is to compress it, i.e., to squeeze it and reduce its volume. (Conversely, if we let a system expand, it does work on its surroundings, so the work we do on it is negative.) In particular, we're interested in the compression of a gas which proceeds slowly enough that the gas has time to respond to the changes in its volume and is approximately in equilibrium. This is known as a *quasistatic* compression.

We model a quasistatic compression using a cylinder with a sliding piston. We call the area of the end of the piston A and the height of the cylinder L . If the gas has a pressure P , it will take a force of magnitude PA to hold the piston in place. To start the piston moving into the cylinder will require a little additional force, and stopping it will require we reduce the force with which we push it into the cylinder. But the quasistatic nature of the process means that the additional force is negligible, and we assume there's a force of PA being

applied on the gas by the moving piston during the compression. We recall from mechanics that the work done by a constant force is the dot product of the force with the displacement

$$W = \vec{F} \cdot \vec{\Delta r} \quad (4.5)$$

In this case, the force applied on the gas and the movement of the piston are the same for a compression (in which $\Delta L < 0$) so the work done is

$$W = (PA)(-\Delta L) \quad (4.6)$$

But what's more generally useful is the change in volume; since the area is constant in our piston model, this is

$$\Delta V = A(\Delta L) \quad (4.7)$$

which makes the work done *on* the gas

$$W = -P\Delta V \quad (4.8)$$

Note that for an expansion $\Delta V > 0$ and $W < 0$ because the gas is doing work on the outside world.

The problem with this derivation is that we assumed the pressure (and thus the force on the piston) was a constant throughout the process. But since pressure and volume are related (e.g., by the ideal gas law or another equation of state), a finite change in volume in general corresponds to a pressure which varies throughout the process. We can get around that by talking about an infinitesimal compression with volume change dV , during which an infinitesimal amount of work

$$dW = -P dV \quad (4.9)$$

is done on the gas. The work for finite compressions or expansions can be built up from these infinitesimal pieces:

$$W = - \int_{V_i}^{V_f} P(V) dV \quad (4.10)$$

Here the limits of integration are the initial and final volumes of the gas, so a compression has $V_i < V_f$ and an expansion has $V_i > V_f$.

The dependence $P(V)$ depends in general on how the compression or expansion is performed. For example, for an ideal gas, $P = NkT/V$, and we need to consider how the temperature changes during the process. There are two important types of quasistatic expansions which we will now consider:

- In an *adiabatic* compression or expansion, no heat flows into or out of the gas, so that the (compression) work is responsible for all the change in internal energy:

$$dQ = 0 \quad \implies \quad dU = dW = -P dV \quad (4.11)$$

Physically, an adiabatic process can occur when the system is insulated and unable to exchange heat with its environment, or when the process occurs too quickly for the heat exchange to take place (but still slowly enough to be quasistatic)

- In an *isothermal* compression or expansion, the temperature of the system doesn't change. (In general, heat must flow into or out of the system to accomplish this.) Physically an isothermal process can occur when the system is in contact with an environmental "heat reservoir" which allows it to remain in thermal equilibrium with the environment. Typically, this also requires that the process proceed slowly enough for the necessary heat exchange to take place.

4.3.1 Isothermal Compression of an Ideal Gas

We consider the isothermal compression of an ideal gas first, since the math is a bit easier. In an isothermal process, the temperature is a constant, so we can use the ideal gas law to show that the pressure is inversely proportional to the volume (with the proportionality constant remaining constant through the process):

$$P(V) = \frac{NkT}{V} \quad (4.12)$$

plugging this into (4.10) gives us

$$W = -NkT \int_{V_i}^{V_f} \frac{dV}{V} = -NkT \ln V \Big|_{V_i}^{V_f} = -NkT(\ln V_f - \ln V_i) = NkT \ln \frac{V_i}{V_f} \quad (4.13)$$

For an ideal gas, we know the internal energy is just proportional to the temperature by the equipartition theorem, so $\Delta T = 0$ means $\Delta U = 0$ and thus

$$0 = \Delta U = Q + W \quad (4.14)$$

and

$$Q = -W = -NkT \ln \frac{V_i}{V_f} \quad (4.15)$$

4.3.2 Adiabatic Compression of an Ideal Gas

To calculate the work done in an adiabatic expansion or compression, we need to work out the relationship between P and V so that we can correctly perform the integral

$$W = - \int_{V_i}^{V_f} P(V) dV \quad (4.16)$$

What we know for an adiabatic process, from (4.11) is that

$$dU = -P dV \quad (4.17)$$

We can turn this into a relationship between volume and temperature using the Equipartition theorem. If f is the number of non-frozen-out degrees of freedom (assumed to be all quadratic), the equipartition theorem tells us

$$U = \frac{f}{2} NkT \quad (4.18)$$

and thus, for an infinitesimal step of a process in which the temperature changes by dT , the corresponding change in the internal energy is

$$dU = \frac{f}{2} Nk dT \quad (4.19)$$

which makes the key relationship for an adiabatic compression

$$\frac{f}{2} Nk dT = -P dV \quad (4.20)$$

This relationship connects P , V , and T , but for an ideal gas, those are also related by the equation of state

$$PV = NkT \quad (4.21)$$

so for example, the differential equation relating V and T is

$$\frac{f}{2} Nk dT = -\frac{NkT dV}{V} \quad (4.22)$$

i.e.,

$$\frac{f dT}{2 T} = -\frac{dV}{V} \quad (4.23)$$

Which we can solve by integrating from initial to final values

$$\frac{f}{2} \ln \frac{T_f}{T_i} = \frac{f}{2} \int_{T_i}^{T_f} \frac{dT}{T} = - \int_{V_i}^{V_f} \frac{dV}{V} = - \ln \frac{V_f}{V_i} \quad (4.24)$$

or, exponentiating both sides,

$$\left(\frac{T_f}{T_i} \right)^{f/2} = \frac{V_i}{V_f} \quad (4.25)$$

i.e.,

$$V_i T_i^{f/2} = V_f T_f^{f/2} \quad (4.26)$$

which means that $VT^{f/2}$ is a constant in the process.

To get the shape in the P - V plane, we can implicitly differentiate the ideal gas law to get

$$P dV + V dP = Nk dT \quad (4.27)$$

then divide the left side by PV and the right by NkT (which are equal, so the result is still a valid equation) to get

$$\frac{dV}{V} + \frac{dP}{P} = \frac{dT}{T} = -\frac{2 dV}{f V} \quad (4.28)$$

which can be solved for

$$\frac{dP}{P} = -\underbrace{\frac{f+2}{f}}_{:=\gamma} \frac{dV}{V} \quad (4.29)$$

which, by the same sort of integration as before, tells us that

$$PV^\gamma = \text{constant} \quad (4.30)$$

γ is called the *adiabatic exponent*.

5 Heat Capacity

We've noted that heat tends to flow into objects of lower temperature and out of objects of higher temperature, and that this heat exchange tends to bring the objects towards equilibrium. So in general, putting heat into an object, which usually (depending on what work is being done) adds to its internal energy, also usually increases its temperature. (We've shown that for a system with f quadratic degrees of freedom per particle, $U = NkTf/2$, but we'd like to define heat capacity to apply even to systems with non-quadratic degrees of freedom, like water.) The heat capacity of an object is a measure of how much heat it can absorb for a given increase in temperature:

$$C = \frac{Q}{\Delta T} \quad (5.1)$$

Of course, a finite input of heat can change the properties (including the heat capacity) of a system, so we really should talk about differential changes, and write

$$dQ = C dT \quad (5.2)$$

But there's another problem. The state of a system is specified by any two out of the three variables P , T , V (if we know two of them, the equation of state allows us to write the third in terms of those two). But specifying the change in temperature doesn't specify how the other independent variable (either pressure or volume) is varying. In particular, the amount of heat flow associated with a given temperature change is different if the process occurs at constant pressure than it is at constant volume.

5.1 Constant Volume

The only type of work we consider when defining the heat capacity is compression work, which means the heat associated with an infinitesimal process is

$$dQ = dU - dW = dU + PdV \quad (5.3)$$

To find the heat capacity at constant volume, we consider the state variables U and P as functions of T and V . In general, the infinitesimal change in a function $X(T, V)$ of two variables, in terms of the changes made in those variables, is

$$dX = \left(\frac{\partial X}{\partial T}\right)_V dT + \left(\frac{\partial X}{\partial V}\right)_T dV \quad (5.4)$$

where the subscripts on the partial derivatives specify what quantity is being held constant. The heat capacity at constant volume is the infinitesimal heat dQ entering the system when the volume is held constant and the temperature changes by an infinitesimal amount dT . This is

$$C_V = \left(\frac{\delta Q}{\delta T}\right)_V = \left(\frac{\partial U}{\partial T}\right)_V + P \left(\frac{\partial V}{\partial T}\right)_V = \left(\frac{\partial U}{\partial T}\right)_V \quad (5.5)$$

where the fact that the second term is zero is related to the fact that at constant V no work is done.

5.2 Constant Pressure

For a process at constant pressure, we need to treat the internal energy U and the volume V as functions of T and P . Again, we start with

$$dQ = dU + PdV \quad (5.6)$$

and consider the infinitesimal heat flowing for an infinitesimal change dT , this time at constant *pressure*. This gives us

$$C_P = \left(\frac{\delta Q}{\delta T} \right)_P = \left(\frac{\partial U}{\partial T} \right)_P + P \left(\frac{\partial V}{\partial T} \right)_P \quad (5.7)$$

Now the second term does not vanish. (Also, if the internal energy is not a function of T alone, the partial derivative $\left(\frac{\partial U}{\partial T} \right)_P$ will be different from $\left(\frac{\partial U}{\partial T} \right)_V$.)

5.3 Examples

We can actually either recognize or calculate the heat capacity for several of the systems we've studied.

5.3.1 Water

Recall that we said a calorie was defined as the amount of heat added to one gram of water under certain conditions to raise the temperature by 1°C . Well, that tells us that the heat capacity of one gram of water under those conditions is

$$C = 1 \text{ cal}/^\circ\text{C} \quad (5.8)$$

Note a couple of things:

- We could just as correctly have said $C = 1 \text{ cal}/\text{K}$, since we're talking about changes, i.e., differences, in temperature.
- The volume of liquid water is not strongly dependent on temperature, so it doesn't matter much whether we're talking about constant pressure or volume. $P \left(\frac{\partial V}{\partial T} \right)_P$ is a small correction.
- This is the heat capacity of 1 gram of water. To raise the temperature of 10 grams of water by one degree, we'd need 10 calories of heat. To describe this as a property of water, we need to define the *specific heat capacity* or just *specific heat*

$$c = \frac{C}{M} \quad (5.9)$$

where M is the total mass of the system. (I think this is better than the m that Schroeder uses in his equation (1.42), since it could be confused with the mass per particle M/N from the exponential atmosphere problem.)

5.3.2 Systems With Only Quadratic Degrees of Freedom

If all of the relevant degrees of freedom are quadratic, we know the explicit form of the internal energy U from the equipartition theorem, $U = \frac{f}{2}NkT$. This means we can calculate

$$C_V = \left(\frac{\partial U}{\partial T} \right)_V = \frac{Nfk}{2} \quad (5.10)$$

Although we also know the partial derivative

$$\left(\frac{\partial U}{\partial T} \right)_P = \frac{Nfk}{2} \quad (5.11)$$

we can't calculate the heat capacity C_P at constant pressure without knowing the equation of state, which gives V as a function of T and P .

5.3.3 Ideal Gas

One simple equation of state is the ideal gas law, which can be solved for

$$V = \frac{NkT}{P} \quad (5.12)$$

so the correction term is

$$P \left(\frac{\partial V}{\partial T} \right)_P = P \frac{Nk}{P} = Nk \quad (5.13)$$

Which means that for an ideal gas with f quadratic degrees of freedom,

$$C_V = \frac{Nfk}{2} \quad (5.14a)$$

$$C_P = \frac{Nfk}{2} + Nk = C_V + Nk = \frac{N(f+2)k}{2} \quad (5.14b)$$

so the heat capacity at constant pressure is higher than at constant volume. This is typical, since at constant pressure, some of the heat input into the system is expended as work done by the system on the environment ($W < 0$) rather than all being stored as internal energy.

5.4 Latent Heat

Heat capacity describes the heat input associated with a temperature change, but what happens when we melt ice. We are adding heat and converting ice at 0°C to water at 0°C . The temperature doesn't change ($\Delta T = 0$) but we have to add a finite amount of heat ($Q > 0$). (As an aside, this is why ice is better than cold water at cooling drinks.) This is an example of a *phase transition*. If we tried to define a heat capacity associated with the transition, it would be infinite:

$$"C" = \frac{Q}{\Delta T} = \frac{Q}{0} = \infty \quad (5.15)$$

On the other hand, it takes a quantifiable amount of heat to melt one gram of ice or boil one gram of water. The property of a substance which defines this is called the *latent heat* and is defined as

$$L = \frac{Q}{M} \quad (5.16)$$

(so to be consistent, we might want to call it ℓ , since it's analogous to the specific heat c).

Some examples are

$$L_{\text{melting ice}} = 333 \text{ J/g} = 80 \text{ cal/g} \quad (5.17)$$

and

$$L_{\text{boiling water}} = 2260 \text{ J/g} = 540 \text{ cal/g} \quad (5.18)$$

So if you started with a gram of ice at 0°C , and wanted to convert it to a water vapor at 100°C , you'd need to add 80 calories of heat to melt it, 100 more calories to increase the temperature from 0°C to 100°C , and 540 calories to boil it,

Again, to be careful we need to specify whether latent heats are specified at constant pressure or volume. By convention (and because this is easiest to control in a lab situation), they are defined at constant pressure.

5.5 Enthalpy

Constant-pressure processes are so common, we'd get tired of always accounting for the compression work to relate heat to change in internal energy:

$$dU = dQ + dW = dQ + dW_{\text{other}} - P dV \quad (5.19)$$

We'd like to define a property of the state of the system whose change is equal to the heat flow (plus any non-compression work) in a constant pressure process. That quantity is called the *Enthalpy* and defined by

$$H = U + PV \quad (5.20)$$

If we perform implicit differentiation to think about an infinitesimal change in H , the sum and product rules tell us

$$dH = dU + d(PV) = (dQ + dW_{\text{other}} - P dV) + (P dV + V dP) = dQ + dW_{\text{other}} + V dP \quad (5.21)$$

For a constant-pressure process ($\Delta P = 0$), the change in enthalpy is just the heat flowing into the system plus the non-compression work done on it:

$$\Delta H = Q + W_{\text{other}} \quad (5.22)$$

So for example, the heat capacity at constant pressure is

$$C_P = \left(\frac{\partial H}{\partial T} \right)_P \quad (5.23)$$

The letter H is chosen to stand for enthalpy because of its close connection to heat for a constant-pressure process.

There is a nice physical interpretation of the enthalpy as the amount of energy you'd need to create a system at constant pressure. In addition to the internal energy, you'd also need to do an amount of work PV to move a volume V of air out of the way (at constant pressure) to make room for the system.

A Appendix: Correspondence to Class Lectures

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