

Thermal Properties of Matter

Up to this point we have largely examined thermal properties of matter on the “macroscopic” (large, lab-sized) scale. We will continue that examination today, but also begin to consider the behavior of matter on a “microscopic” (molecular) level.

Ideal Gas Law

One of the simplest and most useful macroscopic models for matter is the ideal gas. This is a particularly good model because while no gas obeys the ideal gas law to arbitrarily high precision, all gases at low pressure obey the law to a quite good approximation.

To understand the ideal gas law, recall the concept of pressure. When a gas is contained in a fixed volume, the gas will exert a force outward on all walls of the container. The average force on a wall, divided by its area, gives the pressure of the gas. The pressure of the gas (P) may depend on a number of properties, including the container volume (V), the gas temperature (T , in absolute units!), the number of molecules (N), and possibly the composition of the gas.

The ideal gas law is based on the following observations:

- When a fixed amount of gas is held at a fixed volume (constant N and V), the pressure of the gas is proportional to the temperature: $P \propto T$.
- When a fixed amount of gas is held at a fixed temperature (constant N and T), the pressure of the gas is *inversely* proportional to the volume: $P \propto 1/V$.

- When fixed volume of gas is held at a fixed temperature (constant V and T), the pressure is proportional to the amount of gas in the container: $P \propto N$.

The above observations suggest that the quantity $(PV)/(NT)$ should be constant for a given kind of gas, but may depend on the *type* of gas. If you compute the quantity for different kinds of gas, you find that $(PV)/(NT) = k_B$, a constant that is the same for pretty much any gas you consider. Therefore, we have the **ideal gas law**:

$$PV = Nk_B T ,$$

where k_B is a universal constant of nature known as “Boltzmann’s constant” in honor of one of the most important contributors to statistical thermodynamics.

(Wait, the book called that k , not k_B . What gives? Well, we already had k meaning spring constant and wave number, and that was pretty darn confusing, wasn’t it? Let’s keep the “B” for Boltzmann and help ourselves out a little.)

You may have seen the ideal gas law written before as $PV = nRT$, where n is the number of “moles” of gas, and R is the “ideal gas constant.” This is exactly the same law. Recall that one mole is equivalent to $N_A = 6.02 \times 10^{23}$ molecules (Avogadro’s number). Then

$$nR = Nk_B \implies R = N_A k_B .$$

Kinetic Theory of Gases

If we imagine a gas as a collection of microscopic balls that bounce elastically off the walls of a container, we begin to understand the energy and temperature of the gas at the microscopic level. Every time a molecule bounces off a wall, its momentum changes by a factor of twice the incoming component of momentum. This means that the molecule will exert an *impulse* on the wall.¹ The force exerted by this collision will exert a large, sharp force on one small spot on the wall. However, in a gas we have many (10^{24} or so) molecules hitting points all over the wall, and frequently enough that if we were to measure the force on the wall it would appear constant and uniform over the surface. Your textbook

¹Recall the ConcepTest from last term in which a person threw balls against a rigid sail in order to propel the cart it was attached to.

derives a relationship between the pressure and volume of a large number of molecules bouncing around in a container. You should pay careful attention to this derivation, which involves computing averages over the surface of the wall, the short time between successive collisions of a single molecule, and the large number of molecules in the gas.

The result of the derivation in your book is that the pressure and volume of a gas are related to the average kinetic energy of the molecules in the gas:

$$PV = \frac{1}{3}Nm(v^2)_{\text{av}} = \frac{2}{3}NK_{\text{av}} = \frac{2}{3}K_{\text{tr}} ,$$

where $(v^2)_{\text{av}}$ and K_{av} are, respectively, the average “squared speed” and average kinetic energy of a single molecule in the gas, and K_{tr} is the *total* translational kinetic energy of *all* molecules in the gas.

Temperature and Kinetic Energy

Stop for a second to appreciate this. The quantity PV , which has units of energy, is actually related to the total translational kinetic energy of all molecules in a gas! *The pressure and volume of a macroscopic quantity of gas tells you something about how much energy it has.*

If we apply the ideal gas law, we find that

$$Nk_{\text{B}}T = \frac{2}{3}NK_{\text{av}} \implies K_{\text{av}} = \frac{3}{2}k_{\text{B}}T .$$

In other words, the average translational kinetic energy of a single molecule of the gas is closely related to the temperature of the gas.

What may be more surprising is that this result is independent of the gas. You can have low molecular weight gases like hydrogen or helium, or high molecular weight gases like uranium hexafluoride. You can have monatomic, diatomic, or polyatomic gases. The result is the same. Each molecule of the gas will have, on average, a translational kinetic energy $K_{\text{av}} = (3/2)k_{\text{B}}T$.

However, while all gases at the same temperature have the same average kinetic energy per molecule, they will *not* all have the same average *speed* per molecule. Unfortunately, the average speed of a molecule is not an easy quantity to calculate. Instead, we seek a different kind of average: square the speeds of all molecules, compute the average of these

squared speeds, then take the square root. This is the so-called “root mean square” (rms) speed, $v_{\text{rms}} \equiv \sqrt{(v^2)_{\text{av}}}$.

According to our analysis,

$$\frac{1}{2}m(v^2)_{\text{av}} = \frac{3}{2}k_{\text{B}}T \quad \Rightarrow \quad v_{\text{rms}} = \sqrt{\frac{3k_{\text{B}}T}{m}}.$$

This property leads to some interesting results. First, consider our atmosphere. Hydrogen and helium molecules are much lighter than oxygen and nitrogen molecules. The rms speed of hydrogen and helium are high enough that these molecules tend to escape from Earth’s gravitational pull. The rms speeds of oxygen and nitrogen are much smaller, and most are gravitationally bound to Earth, providing our atmosphere. That’s why you won’t find much hydrogen or helium gas in our atmosphere, and it won’t stay a long time if you put some in the atmosphere.

Second, consider this result from nuclear physics. The two most important isotopes of uranium are ^{238}U , which is by far the most common and not particularly useful for nuclear reactions, and the slightly less massive ^{235}U , which is very useful for nuclear reactions (both for power and for weapons). Unfortunately, ^{235}U is less than 1% of all naturally occurring uranium, and you can’t chemically separate the isotopes to get the ^{235}U you need. Instead, you need to *physically* separate the isotopes, collecting the desired ^{235}U .

One way to separate the isotopes called **gaseous diffusion**. First, create a gas of uranium hexafluoride (UF_6). The molecules containing ^{235}U isotope are slightly less massive than the molecules containing ^{238}U , and therefore will move slightly faster in the gas on average. The molecules with ^{235}U will pass through a membrane slightly more quickly, so first gas that you collect on the other side of the membrane will have an increased concentration of ^{235}U . If you continue this process of **uranium enrichment**, repeatedly passing increasingly enriched gas through filter membranes, you can build up a high enough ^{235}U concentration for nuclear power (3–5 percent ^{235}U), or even nuclear weapons (> 85 percent ^{235}U). The city of Oak Ridge, TN was created during WWII to produce weapons-grade uranium using the gaseous diffusion process.

Equipartition

Let's go back to the result that the average kinetic energy per molecule is equal to $(3/2)k_B T$. If you carefully look at the derivation of the kinetic energy per molecule, you will find that the factor of 3 in this equation comes from the fact that the molecule is allowed to move in three dimensions. While one specific molecule may move more in one dimension and less in others, we know that on average, $(v_x^2)_{av} = (v_y^2)_{av} = (v_z^2)_{av}$. That means, on average, a molecule will have equal amounts of energy for motion in each dimension. The total average kinetic energy of a molecule is

$$K_{av} = \frac{1}{2}m(v^2)_{av} = \frac{1}{2}m(v_x^2)_{av} + \frac{1}{2}m(v_y^2)_{av} + \frac{1}{2}m(v_z^2)_{av} .$$

We say that the translational motion in each dimension represents a **degree of freedom** for the molecule. For translational motion, the kinetic energy is, on average, equivalent to $(1/2)k_B T$ for each dimension it moves in.

It turns out that only translational motion contributes to the pressure of the gas (molecules collide with container walls), so the kinetic model above only tells us how translational kinetic energy contributes to the total thermal energy of the gas. Are there other ways for the gas to store thermal energy?

It turns out that there are other degrees of freedom for a gas. For a monatomic gas, like helium, where each molecule is essentially a point mass bouncing around the container, there are only the three *translational* degrees of freedom. However, for diatomic gases like hydrogen (H_2) or polyatomic gases like steam (H_2O), there are other degrees of freedom because these molecules have extended masses and are held together by molecular bonds. For example, a diatomic molecule can be pictured like a dumbbell with all of the mass concentrated at the ends. Not only will such a molecule have translational kinetic energy, but it also can have *rotational* kinetic energy. For reasons I will show in class, it turns out that diatomic gases and linear polyatomic gases (like CO_2) have *two* rotational degrees of freedom (there will be rotational kinetic energy for rotation around two axes, but not the third) in addition to three translational degrees of freedom. Other polyatomic gases that are not linear will have *three* rotational degrees of freedom.

Energy can also be stored in molecular vibrations. The molecular bond between two atoms behaves somewhat like a spring.² It turns out that there are *two degrees of freedom for each vibrational dimension* because vibrations are associated with both kinetic and potential energy. For a diatomic molecule like H₂, there could be as many as seven degrees of freedom: three translational, two rotational, and two vibrational (for vibrations along the molecular length).

On the other hand, consider a solid instead of a gas. The crystal structures of solids involve interesting patterns, but for our purpose let's just consider a solid as a collection of molecules "locked in place" in a regular pattern. The bonds between the molecules act as tiny springs. The molecules are not allowed to move through space or to rotate, so there are no translational or rotational degrees of freedom. However, the molecules will vibrate back and forth in three dimensions. With two vibrational degrees of freedom per dimension, that means that the molecules in all solids will have *six* degrees of freedom.

An interesting result from more fundamental physics, the **equipartition theorem**, states that for a large collection of molecules, each degree of freedom will contribute an energy $(1/2)k_B T$ to the total thermal energy of a molecule. For helium, the average energy per molecule will be $(3/2)k_B T$. For hydrogen, the average energy per molecule can be as high as $(7/2)k_B T$. For a molecule in a solid, the average kinetic energy per molecule will be $(6/2)k_B T = 3k_B T$.

The equipartition theorem can be seen as an example of molecules "sharing" energy as they interact with each other and their surroundings. A diatomic molecule that is not rotating may start to rotate when it collides with a wall. A molecule that is rotating may have that rotation slow when it collides with the wall. Try to imagine a molecule *not* vibrating after it hits another molecule or a wall.

Molar Heat Capacities

So far we have been talking about average energies per molecule, but now let's go back and talk about the total energy of a gas. The total translational kinetic energy of all of the molecules in a gas is $K_{tr} = (3/2)Nk_B T = (3/2)nRT$. If the molecules in the gas have f

²Remember last term when I told you that nothing in nature obeys simple harmonic motion exactly, but a surprising number of things obey it approximately? This is an example.

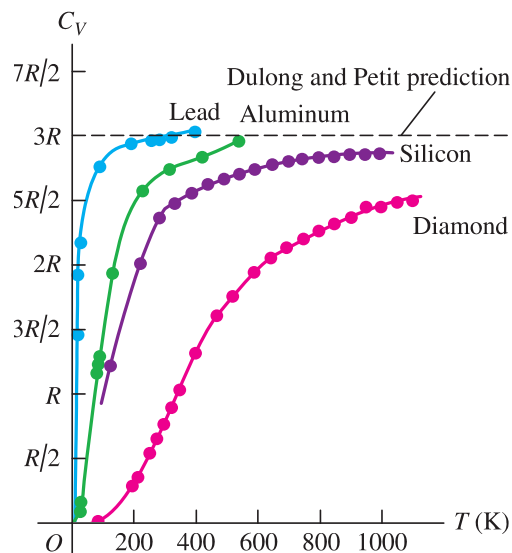
degrees of freedom, the total **thermal energy** of the molecules in the gas is

$$E_{\text{tot}} = \left(\frac{f}{2}\right) N k_B T = \left(\frac{f}{2}\right) n R T$$

Now think about what happens if you add energy to a system as heat. We want to keep the volume of the system constant so no work will be done by or on the system (that's for next class!) Recall that $Q = mc\Delta T$, where the quantity mc is the heat capacity of the object. Instead of mass (m) representing the amount of substance, let's use the number of moles (n). Then we can write $Q = nC_V\Delta T$, where $C_V = mc/n$ is the **molar heat capacity at constant volume** for the substance. (The heat capacity of one mole of the substance when the volume is held fixed.)

If heat is the only way that energy is transferred to the substance, we have $\Delta E_{\text{tot}} = Q$, so $\Delta E_{\text{tot}} = nC_V\Delta T$. Using the equation above, we find that $C_V = (f/2)R$. It turns out that the ideal gas constant is much more than a proportionality constant in nature—it's a heat capacity that is relevant for all substances, not just gases! Among other things, this means that for all solids at sufficiently high temperature, $C_V = 3R$. This is known as the **law of Dulong and Petit**.

The picture below shows the actual measured C_V as a function of temperature for different solids:



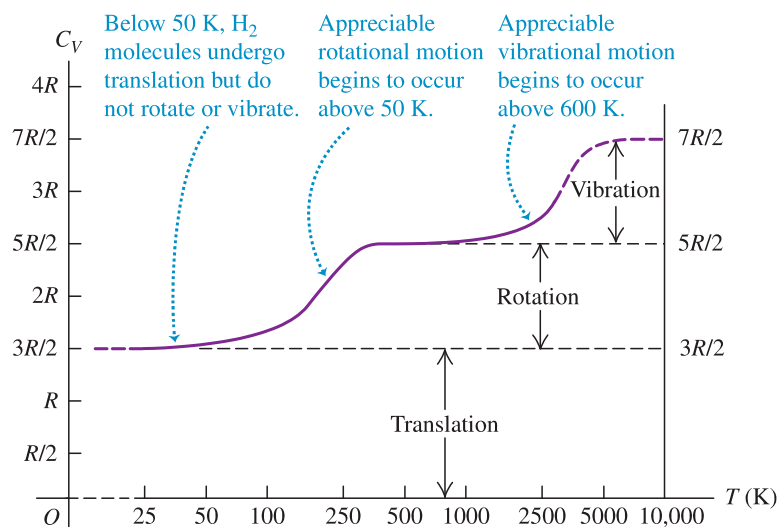
What's going on here? The law works in the limit of high temperatures, but fails for low temperatures. Furthermore, different solids approach the limit at different speeds. It turns out that it's hard to excite vibrational modes at low temperature. At low temperatures for a solid, some vibrations will be excited, but many will not. We say that some of the vibrational degrees of freedom are "frozen out" and do not contribute to the heat capacity. How quickly the vibrational degrees of freedom are activated is related to the nature of the bonds in the crystal structure.

You can also see this when you examine the molar heat capacity of hydrogen (H_2). There should be seven degrees of freedom, so you would expect $C_V = (7/2)R$.

However, what you actually see is that $C_V = (3/2)R$ for low temperatures. This means at those low temperatures, only the translational degrees of freedom are active. The rotational and vibrational degrees of freedom are frozen out.

When you get to around room temperature and higher, $C_V = (5/2)R$. Two more degrees of freedom have been activated. It turns out that these are the rotational degrees of freedom, because rotations require less energy than vibrations. In the temperature range below room temperature, the rotational degrees of freedom are only partially activated. For diatomic gases at standard temperature, you will find that $C_V = (5/2)R$.

Finally, at very high temperatures, the vibrational modes are activated and we see that $C_V \rightarrow (7/2)R$, as expected.



You will notice that we have discussed the thermal properties of gases and solids in some detail. What about liquids? It turns out that they are *orders-of-magnitude* more complicated than solids or gases. Perhaps we should accept our limitations and end our investigation here.