6.2: 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

$$PV \propto nT, \text{[ideal gas]} \tag{6.2.1}$$

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

Example $6.2.1$: 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

$$F = \sum \frac{\Delta p_{x,i}}{\Delta t_i} \text{[monoatomic ideal gas]}, \tag{6.2.2}$$

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

$$F=\sum \frac{m v_{x, i}^2}{L}[\text{monoatomic ideal gas}]. \tag{6.2.3}$$

The quantity $m v_{x, i}^2$ 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

$$F=\frac{2 K_{total}}{3 L}[\text{monoatomic ideal gas}]. \tag{6.2.4}$$

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

$$P=\frac{2 K_{total}}{3 V}[\text{monoatomic ideal gas}]. \tag{6.2.5}$$

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:

$$PV=\frac{2}{3} n \bar{K}[\text{monoatomic ideal gas}]. \tag{6.2.6}$$

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

$$PV=nkT, [\text{ideal gas}] \tag{6.2.7}$$

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 $N_A=6.0 \times 10^{23}$, called Avogadro's number, is essentially the number of hydrogen atoms in 1 g of hydrogen.)

Example 6.2.2: Pressure in a car tire

▷ After driving on the freeway for a while, the air in your car's tires heats up from $10^{\circ}\mathrm{C}$ to $35^{\circ}\mathrm{C}$. 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,

$$\begin{aligned} P_2/P_1 &= T_2/T_1 \\ &= (308\ \mathrm{K})/(283\ \mathrm{K}) \\ &= 1.09, \end{aligned}$$

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.)

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