Figure 1: When the atom hits the wall of the box and bounces back with the same speed, its change in velocity is $-2v_x$

5   Kinetic theory of the ideal gas

- The ideal gas is one of the few cases where the connection between microstates and macrostates can be made explicitly.

- The pressure is connected to the average velocity of the gas molecules.

- The equipartition assumption and independence of molecules leads to the ideal gas law.

- More generically, the definition of temperature in terms of entropy can be used to derive other non-ideal gas laws.

- The ideal gas law is a relation that is true for a gas in internal equilibrium and only if the molecules are sufficiently diffuse so that they don't interact with each other too much.

5.1   Pressure from microscopic physics

Consider a single atom with mass m and velocity v_x in the x-direction. It is trapped in a box with reflecting walls a distance d apart, which means that when the atom hits the side of the box, it reverses its direction and heads the other way. If you recall from classical mechanics, the force imparted by such a collision is the change in the momentum *per time*.[1] So the average force imparted by a collision is

$$F_x = \frac{2mv_x}{t_0}, \tag{1}$$

where t_0 is how often the collision happens. t_0 is the time the atom takes to do one round trip in the box, which is $2d/v_x$. Therefore, the pressure on the sides of the box is

$$p = \frac{F_x}{A} = \frac{2mv_x^2}{2d \cdot d^2} = \frac{mv_x^2}{d^3} = \frac{mv_x^2}{V}, \tag{2}$$

because the area of the side of the box is d^2 and the volume of the box is $V = d^3$.

The kinetic energy is given by $\frac{1}{2}m|v|^2$, so we really want the total velocity of the atom $|v|^2 = v_x^2 + v_y^2 + v_z^2$. On average, the velocity is the same in every direction, so

$$\langle |v|^2 \rangle = 3\langle v_x^2 \rangle, \tag{3}$$

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[1]You can see this by rewriting $F = ma$ as $F = \frac{dp}{dt}$, where p is the momentum

where $\langle\rangle$ means to take the average of whatever's inside. That means that the average velocity squared is three times the average velocity squared in any given direction.

Combining Eqns 3 and 2, we get

$$p = \frac{m\langle|v|^2\rangle}{3V} \tag{4}$$

for a single atom in a box. Now comes the **ideal gas approximation**–we assume that for N atoms,

$$pV = \frac{Nm\langle|v|^2\rangle}{3}; \tag{5}$$

that is, the atoms don't interfere with each other. This equation relates a microscopic quantity on the right (v) with two macroscopic quantities on the left (pV).

5.2 Using equipartition to find the ideal gas law

For an ideal gas, the average kinetic energy is the internal energy. The ideal gas approximation says that the atoms don't interact with each other, so there is no potential energy in the system. We can use equipartion to say for a gas made of single atoms (monatomic gas):

$$U = \frac{3}{2}NkT = \frac{N}{2}m\langle|v|^2\rangle. \tag{6}$$

It turns out that the constant normally in equipartition is actually zero in this case.

Combining Eqns 5 and 6, you can confirm that

$$pV = NkT, \tag{7}$$

the famous ideal gas law.

5.3 Using entropy to find the ideal gas law

We can also use the principle of maximum entropy to derive the ideal gas law. Given the macrostates of U, V, and N, we need to compute the entropy of the system. We use the previous result that $\Omega(U, V, N) = (g(U)V)^N$, where g is an unknown function of U and N.

For more N, we use the ideal gas approximation to determine that $\Omega(U, V, N) = \Omega(U, V, 1)^N$. Using the definition of entropy and that $\ln AB = \ln A + \ln B$, we get:

$$S(U, V, N) = Nk\ln(V) + f(U, N), \tag{8}$$

where f is an unknown function of U and N equal to $Nk\ln g(U)$. The important thing to know about f is that it doesn't depend on V.

Going back to Unit 4, we can use the definition of pressure in terms of entropy:

$$\frac{\partial S}{\partial V} = \frac{p}{T} = \frac{Nk}{V}, \tag{9}$$

which easily gives us the ideal gas law.

This derivation is particularly useful because it applies to any system in which we can compute the entropy! Other systems than ideal gases have different relationships between pressure, volume, and temperature.

5.4 Limitations of the ideal gas law

As you might imagine from the name, the ideal gas law is an idealization; the approximation that the atoms don't interact with each other is not precisely correct. Usually the approximation gets better as the density (number of atoms per volume) gets smaller, so on average each atom is very far from the others. Using the techniques in this chapter, it is possible to derive alternative gas laws that are somewhat more realistic, if a little bit more unwieldy.
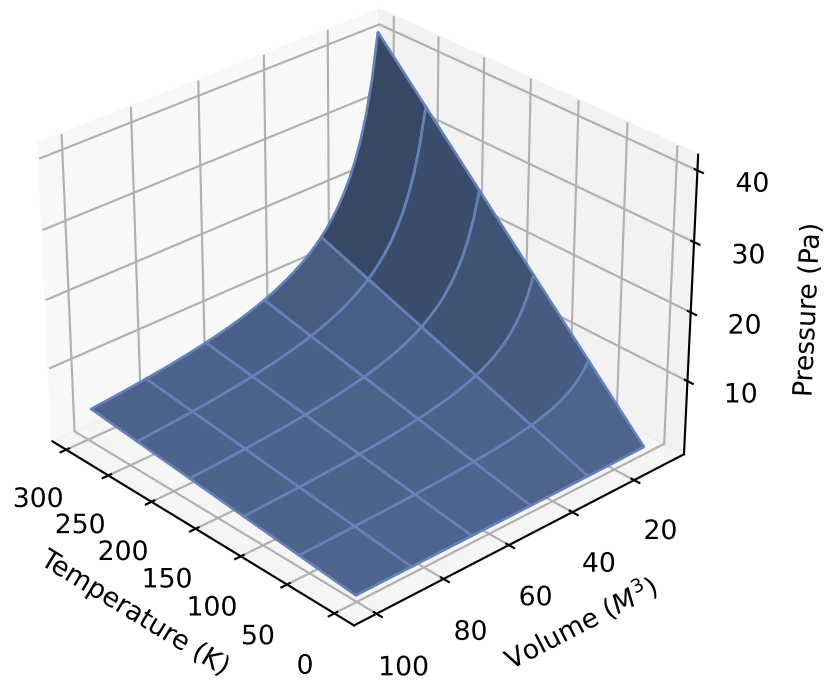
Figure 2: $pV = NkT$ means that when the gas is in internal equilibrium, the relation holds. This is a relationship between the macrostate variables, called an equation of state. If the system is in internal equilibrium then the state exists somewhere on this surface. Each light blue line on the surface represents a process where one variable is held constant. For example, the line at T=50 K shows the relationship between volume and pressure at 50 K.