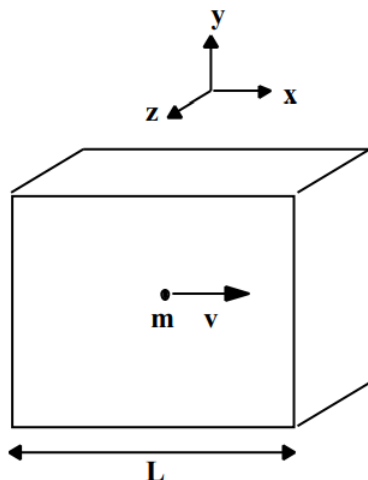


1.0: Concepts and Principles

Applying Newton's Second Law

Although the ultimate goal is to study a collection of a large number of particles, we'll start out by looking at just a single particle. Imagine a particle of mass m and speed v confined inside an elastic cube of edge length L .



Since we're imagining, imagine the particle to be moving in the $+x$ -direction, perpendicular to a face of the cube. The particle will strike the wall and bounce off. Let's apply Newton's second law to the particle during the time interval in which it is in contact with the wall, $\Delta t_{\text{collision}}$:

$$\Sigma F = ma$$

$$F_{\text{average}} = m \left(\frac{\Delta v}{\Delta t_{\text{collision}}} \right)$$

Notice that we have replaced the instantaneous force acting on the particle with the average force over the time interval of interest. Since the wall is perfectly elastic, the collision should just reverse the direction of the particle's speed.

$$F_{\text{average}} = m \left(\frac{v_f - v_i}{\Delta t_{\text{collision}}} \right)$$

$$F_{\text{average}} = m \left(\frac{(-v) - (v)}{\Delta t_{\text{collision}}} \right)$$

$$F_{\text{average}} = \frac{-2mv}{\Delta t_{\text{collision}}}$$

This is the average force on the particle. The average force on the wall is equal in magnitude but opposite in direction.

$$F_{\text{averageonwall}} = \frac{2mv}{\Delta t_{\text{collision}}}$$

This is the average force on the wall during the relatively small time interval of the collision. There are long lulls (when the particle is moving toward the other wall and then returning) that the average force on the wall is zero. If we want the average force on the wall during the entire motion of the particle (and we do) we have to divide not by $\Delta t_{\text{collision}}$ but by $\Delta t_{\text{round-trip}}$, the time to make a complete round-trip journey. Thus, the average force on the wall during the entire journey of the particle is:

$$F_{\text{averageonwall}} = \frac{2mv}{\Delta t_{\text{round-trip}}}$$

Since we know the speed of the particle, we know $F_{\text{averageonwall}} = \frac{2mv}{\Delta t_{\text{round-trip}}}$. A total distance traveled of $2L$, at a speed of v , takes a time of:

$$\Delta t_{\text{round-trip}} = \frac{2L}{v}$$

so

$$F_{\text{averageonwall}} = \frac{2mv}{\left(\frac{2L}{v}\right)}$$

$$F_{\text{averageonwall}} = \frac{mv^2}{L}$$

Thus, we have determined the average force a *single* particle of mass m and speed v would exert on the wall of a cube of edge length L . The question remains, however, what would this average force be if we had N particles?

To generalize our relation we must make two adjustments. First, if we had N identical particles, all moving in an identical manner, it would seem obvious that the average force on the wall would be N times greater,

$$F_{\text{averageonwall}} = \frac{Nmv^2}{L}$$

This would be true, however, only if all N particles were moving with the same speed in the same direction, in this case the x direction.

$$F_{\text{averageonwall}} = \frac{Nmv_x^2}{L}$$

What if the particles were moving in all directions at many possible speeds? *On average*, there is no reason why the particles should be going faster in the x than the y or the z direction. Thus,

$$(v_x^2)_{\text{average}} = (v_y^2)_{\text{average}} = (v_z^2)_{\text{average}}$$

Since

$$v^2 = v_x^2 + v_y^2 + v_z^2$$

we will assume that

$$(v^2)_{\text{average}} = (v_x^2)_{\text{average}} + (v_y^2)_{\text{average}} + (v_z^2)_{\text{average}}$$

$$(v^2)_{\text{average}} = (v_x^2)_{\text{average}} + (v_x^2)_{\text{average}} + (v_x^2)_{\text{average}}$$

$$(v^2)_{\text{average}} = 3(v_x^2)_{\text{average}}$$

$$(v_x^2)_{\text{average}} = \frac{1}{3}(v^2)_{\text{average}}$$

So, averaging over all the various velocities leads to:

$$F_{\text{averageonwall}} = \frac{Nm(v^2)_{\text{average}}}{3L}$$

Let's try to remember that the force and the squared speed are averages, yet state the relation as:

$$F = \frac{Nm\overline{v^2}}{3L}$$

It would be nice to have a relationship that does not explicitly depend on the length of the container. We can accomplish this by defining the *pressure* (p) of the gas as the average force exerted by the gas on one square meter of its container. Thus, pressure is measured in Newtons per square meter, which is given the formal SI name of *pascal*, abbreviated Pa.

If we take the above expression and divide it by the surface area of the wall, L^2 , the resulting ratio will be the pressure of the gas on the wall of the container.

$$F = \frac{Nmv^2}{3L}$$

$$\frac{F}{L^2} = \frac{Nmv^2}{3L^3}$$

$$p = \frac{Nmv^2}{3L^3}$$

$$p = \frac{Nmv^2}{3V}$$

with L^3 replaced by V , the volume of the container.

We now have a relationship that combines macroscopic quantities, such as the pressure and volume of the gas, and microscopic quantities, such as the mass and average squared velocity of individual particles.

To complete the macroscopic description, I will make a radical definition: I hereby define the average kinetic energy of an individual particle to be proportional to a quantity I will call *temperature* (T).¹

$$\frac{1}{2}mv^2 \propto T$$

Thus, temperature is a macroscopic measurement of a microscopic quantity; an individual particle's average kinetic energy. Selecting a proportionality constant so that the resulting relationship is as simple as possible leads me to select " $\frac{3}{2} k$ " as the constant. The " $\frac{3}{2}$ " makes the resulting relation simple and the " k " is in honor of Ludwig Boltzmann and is called the Boltzmann constant.²

$$\frac{1}{2}mv^2 = \frac{3}{2}kT$$

$$mv^2 = 3kT$$

Note

¹ We will measure temperature in kelvin, abbreviated K.

² The Boltzmann constant is experimentally determined to be 1.38×10^{-23} joules/kelvin.

Therefore our relationship between macroscopic variables becomes

$$p = \frac{Nmv^2}{3V}$$

$$p = \frac{N(3kT)}{3V}$$

$$p = \frac{NkT}{V}$$

$$pV = NkT$$

This relation is termed the *equation of state* for an ideal gas because it forms a relationship between the parameters that define the state the gas is in; its pressure, volume and temperature.

An alternative form of the same relation, written in terms of the number of moles of particles³ (n) rather than number of particles (N) is

$$pV = nRT$$

By comparing the two relations you should notice that R , the *universal gas constant*, is equal to the product of the Boltzmann constant and the number of particles in a mole. Thus, $R = 8.31$ joules/kelvin.

Note

³ 6.02×10^{23} particles comprise one mole of particles.

Applying the Work-Energy Relation

The equation of state relates the *state variables* of a gas: pressure, volume and temperature. If you know the value of two of these variables, you can always determine the third. However, the relation says nothing about the *process* by which the gas arrived at that state. The easiest way to investigate processes is through the application of the work-energy relation.

In general terms, the work-energy relation states that the energy of a particle is changed through the application of work. Schematically,

$$\text{initial energy} + \text{work} = \text{final energy}$$

Thus, in general terms, work is the transfer of energy to a particle. We could state the work-energy relation in these more general terms.

$$\text{initial energy} + \text{energy transfer} = \text{final energy}$$

Since our collection of particles is non-interacting, there is no gravitational or elastic potential energy present. The only form of energy present is kinetic.

$$\text{initial kinetic energy} + \text{energy transfer} = \text{final kinetic energy}$$

This form of the work-energy relation must hold for each and every particle. If we apply this result to all of the particles in the gas, and sum the results, we arrive at

$$\text{total initial KE of all particles} + \text{total energy transfer to gas} = \text{total final KE of all particles}$$

The total kinetic energy of all of the particles in a gas is termed the *internal energy* (U_{internal}) of the gas. Thus,

$$U_{\text{internal}, i} + \text{total energy transfer to gas} = U_{\text{internal}, f}$$

with

$$U_{\text{internal}} = N \left(\frac{1}{2} m v^2 \right)$$

$$U_{\text{internal}} = N \left(\frac{3}{2} k T \right)$$

$$U_{\text{internal}} = \frac{3}{2} N k T$$

or

$$U_{\text{internal}} = \frac{3}{2} n R T$$

Now comes the tricky part. What is the total energy transfer to the gas? Remember that the energy transfer to each particle is due to the application of forces external to that particle. Since the particles do not interact with each other, except through elastic collisions, all the energy transfer must be done through collisions of the particles with the walls of the container. This transfer of energy to the gas is via two, distinct methods.

Macroscopic Energy Transfer

First imagine a collision of a particle with a stationary wall. An analogy to this situation would be a tennis ball bouncing off of a stationary tennis racket. The tennis ball rebounds off of the racket with approximately the same speed, and hence the same energy, as it had when it struck the racket. Thus, there is no energy transfer to the ball during this type of collision.

Now imagine a tennis ball striking a moving racket. If the racket is moving toward the ball, the ball will rebound off the racket with a greatly increased speed. Hence, there is energy transfer *to* the ball during this collision. If the racket is moving away *from* the ball, the ball will rebound with a decreased speed. Hence, there is energy transfer *from* the ball during this collision.

From this analogy, we can see that energy can be transferred to or from the gas of particles if the walls of the container are in motion. If the walls of the container are in motion, then the volume of the container must be changing. Thus, if the volume of the container is changing, an energy transfer is taking place. This energy transfer is termed *macroscopic* because the mechanism causing it is the motion of a macroscopic object, a container wall.

Since the container walls are moved by the application of forces acting over distances, this energy transfer is the familiar energy transfer termed *work*. In fact, from the definition of work,

$$W = \int (F \cos \phi) dr$$

with F the average force acting on the container wall and dr the distance the container wall moves.

The force acting on the container wall can be written in terms of the pressure on the wall and the area of the wall, and let dr be the distance the container wall moves in the direction of the force:

$$W = \int (pA) dr$$

A change in wall position, dr , leads to a change in container volume, dV , given by

$$dV = A(dr)$$

Thus,

$$W = \int p(dV)$$

This is the work done *on* the container by the gas. Since we are interested in the energy transfer to the gas, we need the work done *on* the gas *by* the container, which is

$$W = - \int p(dV)$$

Work is the macroscopic transfer of energy to the gas by means of changes in gas volume.

Microscopic Energy Transfer

Now let's look more closely at the collision of a gas particle with the container wall. Realistically, the container wall is composed of a huge number of particles. The container wall also has a definite temperature, implying that the particles comprising the wall have average kinetic energies proportional to this temperature. Thus, *even if the wall is macroscopically stationary, the individual particles comprising the wall are in motion*. Therefore, the collision of a gas particle is not really with a stationary wall but rather with a microscopically moving wall particle! In addition, since we already know that energy can be transferred during an elastic collision between two moving objects, we should realize that energy can be transferred even when the walls are macroscopically stationary. This *microscopic* transfer of energy is termed *heat*.

However, let's not get carried away. Granted, the wall particles are in motion, but aren't the collisions between gas particles and wall particles equally likely to occur when the wall particles are moving toward the gas particles (transfer of energy to the gas) as when the wall particles are moving away from the gas particles (transfer of energy from the gas)? If this is true, the net energy flow should be zero!

The above argument *is* true, assuming the colliding particles have the same kinetic energy as the wall particles. The argument is simply a complicated way of saying that if the wall and the gas particles have the same kinetic energy, and are therefore at the same temperature, no net energy will be transferred from the wall to the gas. There will be no transfer of energy via heat if both objects are at the same temperature.

But what if the temperature of the wall is higher than that of the gas? This means that the wall particles have more kinetic energy than the gas particles. Although you will still have some collisions in which energy is transferred from the gas (when the wall particles are moving away from the gas particles), the amount of energy transferred to the gas (when the wall particles are moving toward the gas particles) will be greater. Overall, the particles with more kinetic energy will transfer energy to the particles with less kinetic energy. Hence, energy will flow from high kinetic energy particles to low kinetic energy particles, or, put more simply,

from high temperature to low temperature. Again, this microscopic flow of energy from high temperature to low temperature particles is called heat. Physicists use the symbol Q to represent the amount of energy transferred via heat.

Thus, our application of the work-energy relation to an ideal gas leaves us with

$$U_{\text{internal}, i} + \text{total energy transfer to gas} = U_{\text{internal}, f}$$

$$U_{\text{internal}, i} + W + Q = U_{\text{internal}, f}$$

This relationship, often referred to as the First Law of Thermodynamics, states that the internal energy of a gas can be changed through energy transfer to the gas via work or heat.

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