Note 17   The Kinetic Theory of Gases

Sections Covered in the Text: Chapter 18

In Note 15 we reviewed macroscopic properties of matter, in particular, temperature and pressure. Here we see how the temperature and pressure of a gas arises from the average movement of its constituent atoms and molecules. This amounts to making a connection between the microscopic and macroscopic worlds. The theory that achieves this is a marvel of classical physics; it is called the *kinetic theory of gases*.

But we shall see that the kinetic theory, based as it is on classical Newtonian physics, is limited in what it can describe. We shall see the need of a new, modern, quantum, physics.

In addition, in this note we shall encounter an explanation for the fact that heat always flows spontaneously from a hot object to a cold object and never in the reverse. This fact is encapsulated in the *second law of thermodynamics*.

A Microscopic View of a Gas

The history of studies into the nature of gases is very long. We know from experiments too numerous to go into here (and the theory we shall present in this note) that an ordinary volume of gas is comprised of billions of molecules. At normal temperatures the molecules move in all directions at high speeds. We infer that the motion of any one molecule, if it could be followed, would be quite random. At any instant the molecules do not all move at the same speed, but with a range or distribution of speeds, some faster some slower. The speed distribution of a typical gas (N_2) at 20 °C has been studied in detail; it is drawn in Figure 17-1.

The figure indicates that although we cannot state what speed a particular molecule moves at (because, in fact, we cannot follow its movements), we can state what is its most likely or *probable* speed. You can see from the figure that 20% of the molecules have a speed in the range 500 – 600 m.s^{-1}. Some, of the order of 0.5%, are moving very slowly, in the range 0 – 100 m.s^{-1}. Others, of the order of 0.5%, are moving very quickly, in the range 1100-1200 m.s^{-1}. We shall see in this note that we can take the most probable speed as the average speed, to a good approximation. [1]
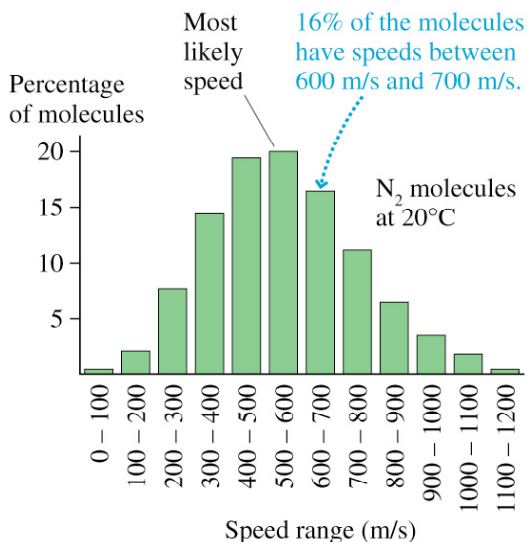

Figure 17-1. *The distribution of molecular speeds in a volume of nitrogen gas at a temperature of 20 °C as determined by experiment.*

Kinetic Theory of Ideal Gases

Assumptions

We saw in Note 15 that bulk properties of an ideal gas are described exactly by the *equation of state*:

$$pV = Nk_BT. \qquad …[17\text{-}1]$$

To simplify our task of describing a gas theoretically we shall make these additional assumptions about it:

1. It consists of many identical monatomic molecules of mass m.
2. Its molecules move randomly within the gas and collide elastically with the walls of the container.

With these assumptions we begin with the macroscopic property of pressure.

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[1]   Figure 17-1 bears a startling resemblance to the distribution of term test marks from a large class of PHYA10H3S students !

Kinetic Theory of Pressure

Consider a cubic container of side L and volume V of a monatomic gas. Suppose that at an instant of clock time a molecule is moving with instantaneous speed v_x in the positive x direction toward the right wall (Figure 17-2). The molecule collides with the wall and rebounds.
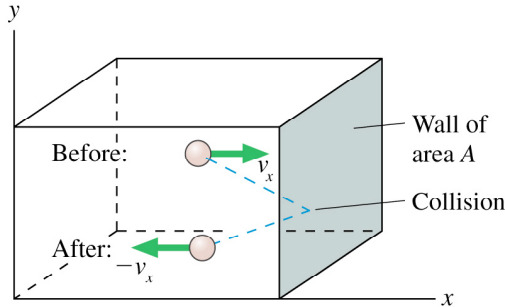

Figure 17-2. *A molecule of gas collides with the right wall of the container and rebounds.*

In the collision the x-component of the molecule's velocity is changed from $+v_x$ to $-v_x$. This means that the molecule experiences an impulse of [2]

$$\left(J_x\right)_{molecule} = \Delta p = m\left(-v_x\right) - mv_x = -2mv_x.$$

According to Newton's third law the wall experiences the same magnitude of impulse but of opposite sign

$$\left(J_x\right)_{wall} = -\left(J_x\right)_{molecule} = +2mv_x. \quad \text{...[17-2]}$$

From the definition of impulse,

$$J_x = \int_0^{\Delta t_{coll}} F_x(t)dt,$$

where $F_x(t)$ is the x-component of the force the molecule exerts on the wall during the collision and Δt_{coll} is the elapsed time for the collision. The details of the function $F_x(t)$ are unknown to us. So to simplify matters (and to enable us to obtain a result at all), we replace the actual unknown collision force with an average force F_{avg}. Then

$$\left(J_x\right)_{wall} = \int_0^{\Delta t_{coll}} F_{avg}dt$$

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[2]   Recall that we defined impulse in Note 07. Impulse is the change in linear momentum.

$$= F_{avg}\Delta t_{coll} = 2mv_x$$

using eq[17-2]. Thus

$$F_{avg} = \frac{2mv_x}{\Delta t_{coll}}. \quad \text{...[17-3]}$$

If we multiply F_{avg} by the total number of collisions N_{coll} that occur during the time interval Δt_{coll} we get the net force exerted on the wall by all the molecules:

$$F_{net} = N_{coll}F_{avg} = 2mv_x\frac{N_{coll}}{\Delta t_{coll}}. \quad \text{...[17-4]}$$

At the moment we do not have an expression for N_{coll}. To find it we assume temporarily that all molecules have the same x-component of velocity v_x. These molecules all travel a distance $\Delta x = v_x\Delta t_{coll}$ along the x-axis during the elapsed time Δt_{coll}. They are all contained in the shaded region of the container redrawn in Figure 17-3.
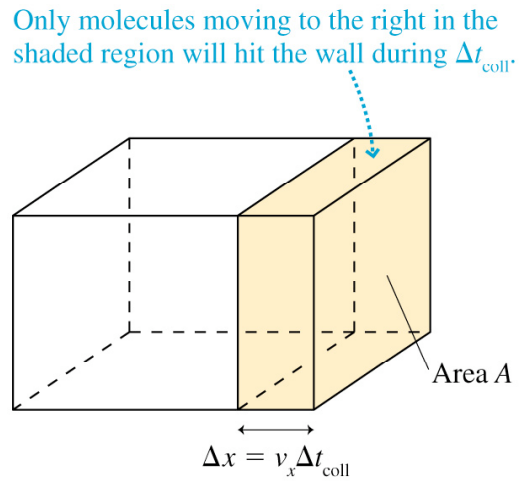

Figure 17-3. *Half of the molecules contained in the shaded region will collide with the wall in the time interval Δt_{coll}.*

On average half of the molecules are moving to the left in the container, half to the right. The shaded region has volume $A\Delta x$ where A is the surface area of the wall. Hence

$$N_{coll} = \frac{1}{2}\frac{N}{V}A\Delta x = \frac{1}{2}\frac{N}{V}Av_x\Delta t_{coll}. \quad \text{...[17-5]}$$

From eq[17-5] the rate of collisions with the wall is

$$rate \ of \ collisions = \frac{N_{coll}}{\Delta t_{coll}} = \frac{1}{2}\frac{N}{V}Av_x. \quad ...[17\text{-}6]$$

Substituting eq[17-6] into eq[17-4] the net force becomes

$$F_{net} = \left(2mv_x\right)\left(\frac{1}{2}\frac{N}{V}Av_x\right) = \frac{N}{V}mv_x^2 A. \quad ...[17\text{-}7]$$

Recall that eq[17-7] is based on our earlier assumption that the molecules have the same speed. To make the equation more accurate we now replace v_x^2 with its average value and obtain:

$$F_{net} = \frac{N}{V}m\left(v_x^2\right)_{avg}A. \quad\quad ...[17\text{-}8]$$

Now, in general, a molecule can be moving in any direction. Its speed is the magnitude of the velocity vector in 3D space:

$$v = \sqrt{v_x^2 + v_y^2 + v_z^2}. \quad\quad ...[17\text{-}9]$$

Squaring eq[17-9] and averaging we have

$$\left(v^2\right)_{avg} = \left(v_x^2 + v_y^2 + v_z^2\right)_{avg},$$

$$= \left(v_x^2\right)_{avg} + \left(v_y^2\right)_{avg} + \left(v_z^2\right)_{avg}. \quad ...[17\text{-}10]$$

Taking the square root of $(v^2)_{avg}$ we obtain what is called the *root-mean-square speed* v_{rms}:

$$v_{rms} = \sqrt{\left(v^2\right)_{avg}}. \quad\quad ...[17\text{-}11]$$

Now the averages of each component squared are equal, i.e.,

$$\left(v_x^2\right)_{avg} = \left(v_y^2\right)_{avg} = \left(v_z^2\right)_{avg}. \quad ...[17\text{-}12]$$

Hence $\quad v_{rms}^2 = \left(v^2\right)_{avg}$

$$= \left(v_x^2\right)_{avg} + \left(v_y^2\right)_{avg} + \left(v_z^2\right)_{avg}$$

$$= 3\left(v_x^2\right)_{avg}, \quad\quad ...[17\text{-}13]$$

using eqs[17-10] and [17-12]. It follows therefore from eq[17-13] that

$$\left(v_x^2\right)_{avg} = \frac{1}{3}v_{rms}^2. \quad\quad ...[17\text{-}14]$$

Using eq[17-14] in eq[17-8] the net force becomes

$$F_{net} = \frac{1}{3}\frac{N}{V}mv_{rms}^2 A.$$

This means that the pressure on the wall is

$$p = \frac{F_{net}}{A} = \frac{1}{3}\frac{N}{V}mv_{rms}^2. \quad\quad ...[17\text{-}15]$$

Thus the theory predicts that the pressure p (a macroscopic quantity) is proportional to the square of the average speed of the molecules (a microscopic quantity). Now let us turn to its counterpart expression for temperature.

Kinetic Theory of Temperature

A molecule of mass m and velocity v has translational kinetic energy

$$\varepsilon = \frac{1}{2}mv^2.$$

Thus the average translational kinetic energy is

$$\varepsilon_{avg} = \frac{1}{2}m\left(v^2\right)_{avg} = \frac{1}{2}mv_{rms}^2, \quad ...[17\text{-}16]$$

using eq[17-11]. From eq[17-15] we can write

$$p = \frac{2}{3}\frac{N}{V}\left(\frac{1}{2}mv_{rms}^2\right) = \frac{2}{3}\frac{N}{V}\varepsilon_{avg}, \quad\quad ...[17\text{-}17]$$

using eq[17-16]. We can rearrange eq[17-17] to get

$$pV = \frac{2}{3}N\varepsilon_{avg}. \quad\quad ...[17\text{-}18]$$

From eqs[17-1] and [17-18] we can write

$$pV = Nk_BT = \frac{2}{3}N\varepsilon_{avg},$$

from which it follows that

$$\varepsilon_{avg} = \frac{3}{2}k_BT. \quad\quad ...[17\text{-}19]$$

Turning eq[17-19] around we get an expression for temperature:

$$T = \frac{2}{3k_B} \varepsilon_{avg}. \qquad \ldots[17\text{-}20]$$

Thus the temperature T (a macroscopic quantity) is proportional to ε_{avg}, the average translational kinetic energy of the molecules (a microscopic quantity). From eqs[17-16] and [17-19] we have

$$\varepsilon_{avg} = \frac{1}{2} m v_{rms}^2 = \frac{3}{2} k_B T, \qquad \ldots[17\text{-}21]$$

from which it follows that the rms speed of a molecule is

$$v_{rms} = \sqrt{\frac{3k_B T}{m}}. \qquad \ldots[17\text{-}22]$$

Let us consider a numerical example of molecular speeds predicted by the kinetic theory.

Example Problem 17-1
Calculating the RMS Speed of a Molecule From the Kinetic Theory of Gases

What is the rms speed of a nitrogen molecule at room temperature predicted by the kinetic theory of gases?

Solution:
Room temperature is 20 °C or 293 K. The mass of a single molecule of N_2 is 4.68 x 10^{-26} kg. Thus from eq[17-22],

$$v_{rms} = \sqrt{\frac{3\left(1.38 \times 10^{-23} J.K^{-1}\right)(293\ K)}{4.68 \times 10^{-26} kg}} = 509 \text{ m.s}^{-1}.$$

Remarkably, this speed is within the most likely, or average, speed bar of Figure 17-1.

We now apply the kinetic theory to calculate the thermal energy and specific heats of various systems. We shall compare the results we get with the experimental measurements listed in Note 16. We shall see that the comparison is a good one in some cases and bad in others. Even when the results are bad they will yield useful insights into the theory.

Calculations of Thermal Energy and Specific Heat

Monatomic Ideal Gas (3 DFs)

Recall that the thermal energy of a system is the sum of the kinetic and potential energies of its constituent particles: $E_{th} = K_{micro} + U_{micro}$. In a monatomic gas such as helium or neon $U_{micro} = 0$ and the kinetic energy is entirely translational. This means that the thermal energy of a monatomic gas of N atoms is

$$E_{th} = K_{micro} = \varepsilon_1 + \varepsilon_2 + \ldots \varepsilon_N = N\varepsilon_{avg} \qquad \ldots[17\text{-}23]$$

Substituting ε_{avg} from eq[17-21] we have

$$E_{th} = \frac{3}{2} N k_B T = \frac{3}{2} n R T \text{ (monatomic)} \qquad \ldots[17\text{-}24]$$

Thus the kinetic theory predicts that the thermal energy of a monatomic gas is directly proportional to temperature. E_{th} is independent of atomic mass, which means that any two monatomic gases with the same number of moles at the same temperature should have the same thermal energy.

If the temperature of a monatomic gas changes by ΔT, its thermal energy changes by

$$\Delta E_{th} = \frac{3}{2} n R \Delta T. \qquad \ldots[17\text{-}25]$$

We have already seen in Note 16 that

$$\Delta E_{th} = n C_V \Delta T. \qquad \ldots[17\text{-}26]$$

Equating eqs[17-25] and [17-26] and simplifying,

$$C_V = \frac{3}{2} R = 12.5 \text{ J.mol}^{-1} \text{ K}^{-1} \text{ (monatomic)} \qquad \ldots[17\text{-}27]$$

You can see that the value predicted agrees very well with the experimental values of C_V for monatomic gases listed in Table 16-2. For reference Table 16-2 is reproduced below.

Also part of the kinetic theory is the so-called *equipartition theorem*. This theorem will assist us in our analysis of systems of greater complexity than a monatomic gas.

Table 16-2. *Experimental measurements of molar specific heats (J.mol^{-1} K^{-1}) of a selection of gases.*

Gas	Cp	Cv	Cp – Cv
Monatomic			
He	20.8	12.5	8.3
Ne	20.8	12.5	8.3
Ar	20.8	12.5	8.3
Diatomic			
H$_2$	28.7	20.4	8.3
N$_2$	29.1	20.8	8.3
O$_2$	29.2	20.9	8.3

Each atom has microscopic translational kinetic energy *and* microscopic potential energy along all three axes.
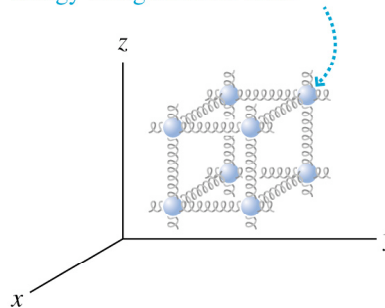

Figure 17-4. *Representation of a solid.*

Equipartition Theorem

The translational kinetic energy of a single particle (atom) in a monatomic gas can be written

$$\varepsilon = \frac{1}{2}mv^2 = \frac{1}{2}mv_x^2 + \frac{1}{2}mv_y^2 + \frac{1}{2}mv_z^2$$

$$= \varepsilon_x + \varepsilon_y + \varepsilon_z. \qquad \text{…[17-28]}$$

where ε_x, ε_y and ε_z are the energies associated with translational motion along the three axes. We can think of ε_x, ε_y and ε_z as independent *modes* of energy storage in the system. We define the number of *degrees of freedom* (abbreviated DF) as the number of distinct and independent modes of energy storage. Thus a monatomic gas has three degrees of freedom. In due course we shall see that other types of matter (solids, diatomic molecules) have more than three degrees of freedom.

The equipartition theorem can be stated in these words:

The thermal energy of a system of particles is equally divided among all the possible energy modes. For a system of N particles at temperature T, the energy stored in each mode (each degree of freedom) is (1/2)Nk$_B$T or, in terms of moles, (1/2)nRT.

Thus according to the equipartition theorem the thermal energy of a monatomic gas is *3 x (1/2)nRT = (3/2)nRT*, in agreement with eq[17-24]. Let us now see how well the kinetic theory describes the thermal properties of a solid.

A Solid (6 DFs)

Though not an ideal gas, a solid can be analyzed with the kinetic theory of gases with partial success. A solid may be represented as is shown in Figure 17-4.

We can think of a solid as a collection of atoms held in a lattice-like structure by molecular bonds (represented by springs in the figure). Each atom is able to vibrate with kinetic energy in the x-, y- and z-directions and has, therefore, three degrees of vibrational energy. Each degree of vibrational energy has associated with it a degree of potential energy (potential energy stored in the springs). Thus a solid has a total of six degrees of freedom.

According to the equipartition theorem, the energy stored in each of these six degrees of freedom is $(1/2)Nk_BT$. Thus the total thermal energy of a solid is

$$E_{th} = 3Nk_BT = 3nRT \text{ (solid)} \qquad \text{…[17-29]}$$

If the temperature changes by ΔT then the thermal energy changes by

$$\Delta E_{th} = 3nR\Delta T. \qquad \text{…[17-30]}$$

Recall (Note 16) that the molar specific heat C of a solid is defined by

$$\Delta E_{th} = nC\Delta T. \qquad \text{…[17-31]}$$

Equating eqs[17-30] and [17-31] and cancelling common factors we have

$$C = 3R = 25.0 \text{ J.mol}^{-1}\text{ K}^{-1} \text{ (solids) …[17-32]}$$

You can see that the value 25.0 J.mol^{-1} K^{-1} agrees within a few percent with the few values of C for solids listed in Table 16-1. So we can claim with some satisfaction that the kinetic theory describes a solid pretty well. Let us now look at a system with more than six degrees of freedom.

A Diatomic Molecule (8 DF)

A diatomic molecule, like a monatomic molecule, has three modes of translational motion. In addition, a diatomic molecule such as N_2 has the vibrational and rotational modes illustrated in Figure 17-5. Since the vibrational mode has both kinetic and potential energy the total number of modes comes to eight.

Thus the kinetic theory of gases predicts a C_V for a gas consisting of diatomic molecules of

$$C_V = 8 \times \left(\frac{1}{2}\right)R = 33.2 \text{ J.mol}^{-1}\text{ K}^{-1}.$$

You can see that this value differs substantially from the measured value of $C_V = 20.8$ J.mol⁻¹ K⁻¹ listed in Table 16-2. Why is this? In fact, it appears as if a diatomic molecule should actually have five degrees of freedom not eight (making for $C_V = (5/2)R = 20.8$ J.mol⁻¹ K⁻¹, a better agreement with what is observed).

Rotation end-over-end
about the z-axis

Rotation end-over-end
about the y-axis

Rotation about its own axis

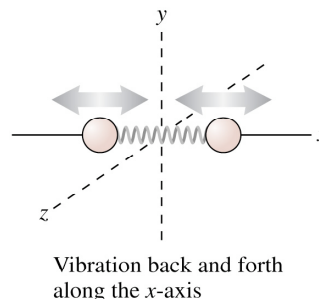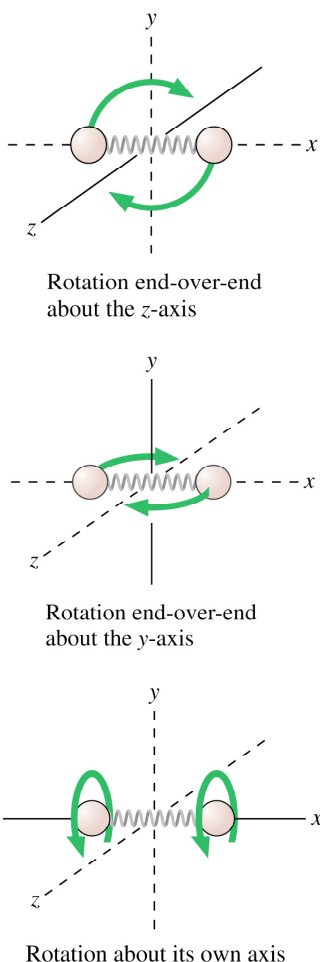Vibration back and forth
along the x-axis

Figure 17-5. *The various modes of a diatomic molecule in addition to the three translational modes.*

The answer has to do with quantum effects making their appearance with the diatomic molecule. Classical Newtonian physics via the equipartition theorem has a natural limitation in that it treats all of the degrees of freedom equally, meaning that at any given temperature all of them will be equally active and equally able to store energy. However, it can be shown that quantum effects predict that three of the modes—the two vibrational modes and the single rotational mode—will not be active at ordinary temperatures. This is reflected in the experimental data of C_V for hydrogen gas (Figure 17-6).
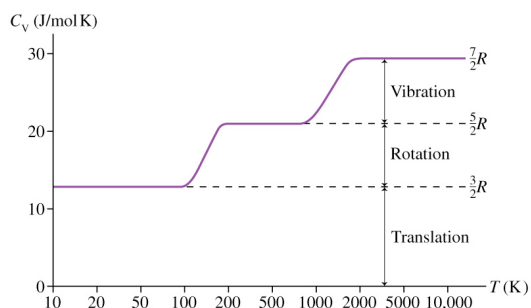

Figure 17-6. *Hydrogen molar specific heat at constant volume as a function of temperature. At ordinary temperatures (200 – 800)K only five degrees of freedom are active.*

Only quantum (statistical) physics can explain why certain modes become active only at certain temperatures. We must leave the details to a higher-level course in physics.

Irreversible Processes and the Second Law of Thermodynamics

We have seen that in a thermal interaction—such as warming your cold hands over a hot object—heat flows from the hot object to the cold. We know from experience that the reverse never happens, that is, that your hands never become colder and the hot object hotter. It is natural to ask why this should be so. Why isn't heat transferred spontaneously from a cold object to a hot object? In fact, none of the physics we have studied thus far would prevent this from happening. We shall see that the search for the answer to this question will lead us to the second law of thermodynamics.

First we need a few more definitions. Any process can be classified as being *reversible* or *irreversible*. A reversible process is a process that can run equally well forward or backward in time. An example is an interaction or collision between two microscopic particles (Figure 17-7). If a movie were taken of that interaction, it would look the same (except for a reversal in sign) if run backward as forward. There would be no way to distinguish the backward running movie from the forward. In fact, all interactions at the microscopic level are reversible.
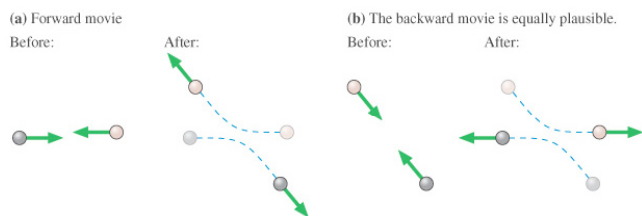

Figure 17-7. *All interactions at the microscopic level are reversible processes.*

On the other hand there are interactions that are very definitely irreversible. A case in point is the collision between a speeding car and a brick wall (Figure 17-8). If a movie were made of this interaction and then run backwards we would see the damaged car miraculously repair itself and then speed off in reverse! It would be obvious the movie is running backwards. The backward-running movie would show a process that is physically impossible. The process of the car hitting a wall is a macroscopic process. It only makes sense run in one direction in time.
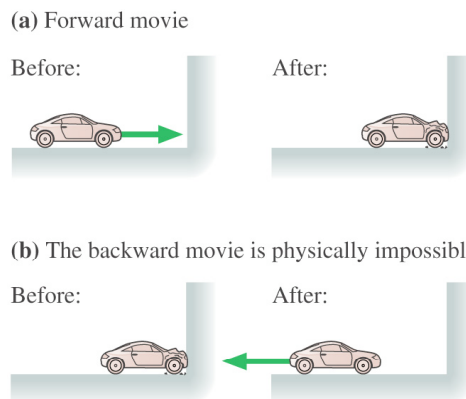
(a) Forward movie

(b) The backward movie is physically impossible.

Figure 17-8. *An example of an irreversible interaction.*

For the most part, macroscopic processes are irreversible and microscopic processes are reversible. The flow of heat from a hot object to a cold object, though dependent on reversible microscopic collisions between particles, is itself an irreversible process.

To get an idea of a process that can run in one direction only in time consider the two "systems" shown in Figure 17-9. Each "system" consists of a box with a number of identical balls inside. These systems undergo an "interaction" resulting in balls being moved from one box to the other. To simulate this interaction we adopt the following algorithm. In any elapsed time, say 1 second, we select a ball (or no ball) at random from both boxes. If indeed we pick a ball we move it to the other box. Whether we select a ball or no ball at all is entirely a matter of chance.

This means that, with the number of balls illustrated in the figure, there is a 1 in 11 chance that any particular ball, or no ball, will be selected from Box 1. If, in fact, we do pick a ball as our random choice, we move it to Box 2. Similarly, in the same second, there is a 1 in 6 chance that any particular ball, or no ball, will be selected from Box 2. If a ball is, in fact, chosen it is moved to Box 1.
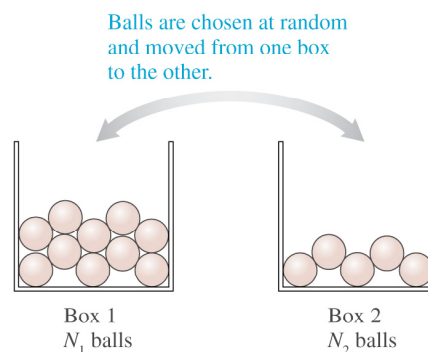

Balls are chosen at random and moved from one box to the other.

Box 1
N_1 balls

Box 2
N_2 balls

Figure 17-9. *Two systems interacting. This interaction can only go one way in time.*

This algorithm means that there is a greater chance that a ball—any ball—will be moved from Box 1 (10/11 = 0.9) to Box 2 than the reverse (5/6 = 0.8) to Box 1. This means that over time the number of balls in Box 2 will increase, the number of balls in Box 1 will decrease. Over time the number of balls in both boxes will approach the same number. This is a state of equilibrium. This interaction simulates the flow of heat from a hot object to a cold object.

The state of the systems before the interaction is in fact more ordered than is the state of the systems after the interaction (when the systems are in equilibrium). A state variable called *entropy* is defined to measure the disorder in a system (the probability that a macroscopic state will occur).

The Second Law of Thermodynamics

The second law of thermodynamics is a new law for us. It states, in effect, that macroscopic systems evolve irreversibly towards equilibrium, or towards a state of the same or greater disorder. The law can be put in these words:

The entropy of an isolated system never decreases. The entropy either increases, until the system reaches equilibrium, or, if the system began in equilibrium, stays the same.

This concludes our study of the basic physics of heat. In Note 18 we shall see how the physics of heat will enable us to explain the working of practical devices, such as the heat engine and the refrigerator.

To Be Mastered

- Assumptions: *kinetic theory of gases*

- Derivations: *kinetic theory of pressure:* $p = \dfrac{1}{3}\dfrac{N}{V}mv_{rms}^2$

  kinetic theory of temperature: $T = \dfrac{2}{3k_B}\varepsilon_{avg}$

- Derivations: *thermal energy of a monatomic gas:* $E_{th} = \frac{3}{2}nRT$

  specific heat of a monatomic gas: $C_V = \frac{3}{2}R$

- Definitions: *Equipartition Theorem*
- Application of kinetic theory to: *a monatomic gas (3 DFs)*
  a solid (6 DFs)
  a diatomic molecule (8 DFs)
- Definition: *Second Law of Thermodynamics*

Typical Quiz/Test/Exam Questions

1. Use kinetic theory to explain the origin of the pressure of a gas.

2. State the classical equipartition theorem, defining any symbols you use.

3. In outer space there is one hydrogen atom per cubic centimeter, and the temperature is 3.5 K. Calculate the rms speed of hydrogen atoms in outer space and the pressure they exert.