



Heat—A Matter of Motion

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A. THE KINETIC THEORY

7.1 AN IDEAL GAS

During the 1840s, many scientists recognized that heat is not a substance but a form of energy that can be converted into other forms. James Prescott Joule and Rudolf Clausius went a step further. Heat can produce mechanical energy, and mechanical energy can produce heat; therefore, they reasoned, the “heat energy” of a substance is simply the kinetic energy of its atoms and molecules. This idea, which forms the basis of the *kinetic-molecular theory of heat*, is largely correct.

However, the idea of atoms and molecules was not completely accepted in the nineteenth century. (Molecules, as you know, are the smallest pieces of a substance. They may themselves be composed of atoms of simpler substances.) If such small bits of matter really existed, they would be too small to observe even under the most powerful microscopes. Since scientists could

not observe molecules, they could not confirm directly the hypothesis that heat is molecular kinetic energy. So they resorted to the *indirect* way of checking the plausibility of the hypothesis, which is always useful: They derived from this hypothesis predictions about the behavior of measurably large samples of matter, and then tested these predictions by experiment.

For reasons that will be explained, it is easiest to test such hypotheses by observing the properties of gases. The resulting development of the kinetic theory of gases in the nineteenth century led to one of the last major triumphs of Newtonian mechanics. This chapter deals mainly with the kinetic theory as applied to gases. We start with the observed properties of a simple gas; then, in the following sections, we will attempt to account for these properties and to understand origins of the laws of thermodynamics on the basis of the kinetic theory.

One of the most easily measured characteristics of a confined gas is its pressure. Experience with balloons and tires makes the idea of air pressure seem obvious. But there are important subtleties. One involves the pressure exerted by the air around us.

Galileo, in his book on mechanics, *Two New Sciences* (1638), noted that a lift-type pump cannot raise water more than the equivalent of 10 m. This fact was well known, and such pumps were widely used to obtain drinking water from wells and to remove water from mines. Already you have seen one important consequence of this limited ability of pumps to lift water out of deep mines: the initial stimulus for the development of steam engines. But why only 10 m? Why did the lift pumps work at all?

Air Pressure

These puzzles were solved as a result of experiments by Torricelli (a student of Galileo), as well as by Guericke, Pascal, and Boyle. By 1660, it was fairly clear that the operation of a “lift” pump depends on the pressure of the air. By removing some air above the water in the pump, it merely reduces the pressure at the top of the water in the pipe. It is the pressure exerted by the atmosphere on the pool of water below which forces water up the pipe. A good pump can reduce the pressure at the top of the pipe to nearly zero. Then the atmospheric pressure can force water up above the pool. But atmospheric pressure at sea level is not great enough to support a column of water any higher than 10 m. Mercury is almost 14 times as dense as water. Thus, ordinary pressure on a pool of mercury can support a column only one-fourteenth as high, or about 0.76 m (76 cm). This is a convenient height of an instrument for measuring atmospheric pressure. Therefore, much of the seventeenth-century research on air pressure was

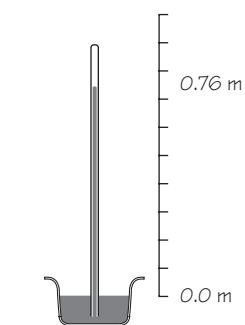


FIGURE 7.1 Torricelli's barometer is a glass tube standing in a pool of mercury. The topmost part of the tube is empty of air. The air pressure on the pool supports the weight of the column of mercury in the tube up to a height of about 0.76 m. The unit of pressure in the metric system is N/m^2 , which has been given the name "pascal" (symbol: Pa).

done with a column of mercury, a mercury *barometer*. Torricelli designed the first of these barometers.

The height of the mercury column that can be supported by air pressure does not depend on the diameter of the tube; that is, it depends not on the total amount of mercury, but only on its height. This may seem strange at first. To understand it, you must consider the difference between *pressure* and *force*. *Pressure is defined as the magnitude of the force acting perpendicularly on a surface divided by the area of that surface:*

$$P = \frac{F_{\perp}}{A} \quad (\text{in units of } \text{N/m}^2).$$

Thus, a large force may produce only a small pressure if it is spread over a large area. For example, you can walk on snow without sinking in it if you wear snowshoes. On the other hand, a small force can produce a very large pressure if it is concentrated on a small area. Women's spike-heel shoes have dented many a wooden floor or carpet. The pressure exerted by a spike heel can be greater than that under an elephant's foot!

In short, the pressure measurement is not affected by the cross-sectional area of the barometer tube or by the total weight of the column it supports, because pressure is the ratio of the two. Twice the weight owing to twice the size of the tube still provides the same value for the ratio that defines pressure.

The Relationship Between Pressure and Volume

In 1661, two English scientists, Richard Towneley and Henry Power, discovered an important basic relation. They found that—e.g., in a thin balloon—the *pressure exerted by a gas is inversely proportional to the volume occupied by that gas*. Doubling the pressure (by letting in more gas) will dou-



FIGURE 7.2 Because the force acts on a very small surface, the pressure under a thin, high heel is greater than under an elephant's foot (which acts on a larger surface).

ble the volume of the balloon. Using P for pressure and V for volume, this relationship is

$$P \propto \frac{1}{V}$$

or

$$P = \frac{a}{V}$$

or

$$PV = a,$$

where a is some constant. For example, if the volume of a given quantity of air in a balloon is halved (say, by compressing it), the pressure exerted by the gas inside doubles. On the other hand, if you double the volume of the

closed container with a certain amount of air inside, the pressure inside is halved. Robert Boyle confirmed this relation by extensive experiments. It is an empirical rule, now generally known as *Boyle's law*. However, the law holds true exactly only under special conditions, as given below.

The Effect of Temperature on Gas Pressure and Volume

Boyle recognized that if the temperature of a gas changes during an experiment, the relation $P = a/V$ no longer applies. For example, the pressure exerted by a gas in a closed container of fixed size increases if the gas is heated, even though its volume remains constant. However, if the temperature of a gas is held constant, then Boyle's law does apply. Thus we modify the rule as follows:

$$P = \frac{a}{V} \quad \text{if } T \text{ is constant.} \quad (\text{a})$$

Many scientists throughout the eighteenth century also investigated how, say in a thin balloon, gases expand when heat is supplied, even though the pressure remains the same. Eventually, evidence for a surprisingly simple general law appeared. The French chemist Joseph-Louis Gay-Lussac (1778–1850) found that all the gases he studied (air, oxygen, hydrogen, carbon dioxide, etc.) changed their volume in the same way. *If the pressure remained constant, then the change in volume was proportional to the change in temperature.* This may be expressed in symbols:

$$\Delta V \propto \Delta T, \quad \text{if } P \text{ is constant.} \quad (\text{b})$$

On the other hand, *if the volume was kept constant (say, in using a rigid container), the change in pressure of the gas inside was proportional to the change in temperature:*

$$\Delta P \propto \Delta T \quad \text{if } V \text{ is constant.} \quad (\text{c})$$

The experimental data obtained by Boyle, Gay-Lussac, and many other scientists are expressed in the three proportionalities, (a), (b), and (c). These relate the three main characteristics of a fixed amount of a gas—the pressure, volume, and temperature, each measured from zero—when any one variable is held constant. Introducing a new constant, k , these three pro-

portionalities may be joined together into a single, general equation known as the *ideal gas law*.

$$PV = kT$$

This equation is one of the most important discoveries about gases, but in use one must be careful about the units! The proportionality constant k depends on the kind of gas; T , the temperature of the gas, has to be given on the absolute, or Kelvin, scale, where, as defined earlier,

$$T \text{ (K)} = t \text{ (}^\circ\text{C)} + 273.15.$$

(T is temperature in the same units as used for the definition of entropy given earlier in Chapter 6: $S = \Delta Q/T$.) The pressure P is always the *total* pressure (in units of N/m^2 , which is given the name Pascal, abbreviation Pa), *including* the so-called ambient pressure of the atmosphere. Thus a car tire blown up to 32 lb/in^2 above atmospheric pressure has an actual gas pressure inside of $32 \text{ lb/in}^2 + 15 \text{ lb/in}^2 = 47 \text{ lb/in}^2$, or in mks units $2.2 \times 10^5 \text{ Pa} + 1.0 \times 10^5 \text{ Pa} = 3.2 \times 10^5 \text{ Pa}$.

The equation relating P , V , and T is called the *ideal gas law* because it is not completely accurate for real gases at very low pressures. It also does not apply when pressure is so high, or temperature so low, that the gas

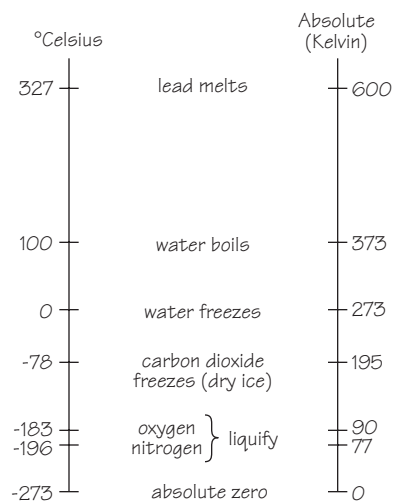


FIGURE 7.3 Comparison of the Celsius and Absolute temperature scales.

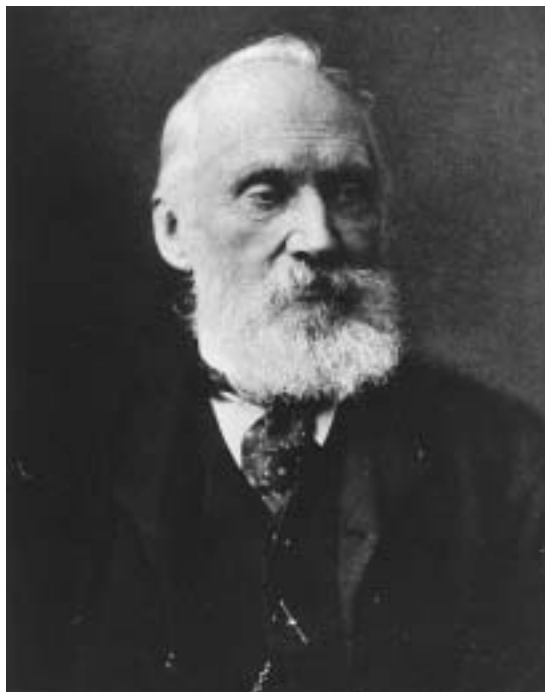


FIGURE 7.4 Lord Kelvin (William Thomson) (1824–1907).

nearly changes to a liquid. Thus, it is not a law of physics in the same sense as the majestic law of conservation of energy, which is valid under all circumstances. Rather, it simply gives an experimentally based and useful but approximate summary of the observed properties of real gases.

Consider what would happen if we tried to lower the temperature of the gas to absolute zero; that is, $T = 0$ K (or, in Celsius, $t = -273.15^\circ\text{C}$). In this extreme case, the entire factor involving temperature would be zero. According to the ideal gas law, the PV term must also fall to zero at this temperature. At constant pressure, the volume would shrink to zero. In fact, all real gases become liquid before that temperature is reached. Both experiment and thermodynamic theory indicate that it is impossible actually to cool anything—gas, liquid, or solid—down to exactly this temperature. However, a series of cooling operations can produce temperatures closely approaching this limit.

In view of the unique meaning of the lowest temperature for a gas obeying the ideal gas law, Lord Kelvin (William Thomson) proposed the *absolute temperature scale* and put its zero at -273.15°C . This is why the absolute scale is sometimes called the Kelvin scale, and why temperatures on this scale are measured in kelvins.

The ideal gas law, $PV = kT$, summarizes *experimental facts* about gases. The kinetic theory of gases offers a *theoretical* explanation for these facts. To prepare for that, we need to develop a kinetic model of a gas.

7.2 A MODEL FOR THE GASEOUS STATE

What are the differences between a gas and a liquid or solid? You know by observation that, if not compressed, liquids and solids have definite volume. Even if their shapes change, they still take up the same amount of

Gases can be confined without a container. A star, for example, is a mass of gas confined by gravitational force. Another example is the Earth's atmosphere.

space. A gas, on the other hand, will spontaneously expand to fill any container (such as a room). If not confined, it will leak out and spread in all directions. Gases have low densities compared to those of liquids and solids, typically about 1000 times smaller. Therefore gas molecules are usually relatively far apart from one another. In the model of a gas we

are constructing here, we can reasonably assume that the forces between molecules act only over very short distances. In other words, gas molecules are considered to be moving freely most of the time. In liquids, the molecules are closer together; forces act among them continually, and keep them from flying apart. In solids, the molecules are usually even closer together, and the forces between them keep them in a definite orderly arrangement.

Our initial model of a gas is thus very simple, following Newton's advice to start with the simplest hypotheses. We will assume that the molecules behave like extremely small balls or marbles; they are tiny spheres or clumps of spheres that exert no force at all on each other except when they happen to make contact. Moreover, all the collisions of these spheres are assumed to be perfectly elastic. Thus, the total kinetic energy of two spheres is the same before and after they collide.

Note that the word "model" is used in two different senses in science. Earlier we mentioned the model of Newcomen's engine which James Watt was given to repair. That was a *working model*. It actually did function, although it was much smaller than the original engine, and contained some parts made of different materials. Now we are discussing a *theoretical model* of a gas. This model exists only in the imagination. Like the points, lines, triangles, and spheres studied in geometry, this theoretical model can be discussed mathematically. The results of such a discussion is intended to understand the real world although, of course, the model will eventually have to be tested to see if it approximates reality.

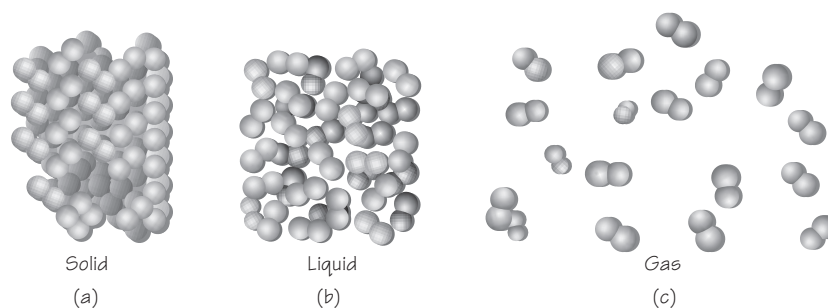


FIGURE 7.5 A very simplified “model” of the three states of matter: (a) solid, (b) liquid, and (c) gas.

Our theoretical model represents the gas as consisting of *a large number of very small particles in rapid, disordered motion*. “A large number” means something like a billion billion (10^{18}) or more particles in a sample as small as a bubble in a soft drink. “Very small” means a diameter about a hundred-millionth of a centimeter (10^{-8} cm). “Rapid motion” means an average speed at normal temperatures of a few hundred meters per second.

What is meant by “disordered” motion? Nineteenth-century kinetic theorists assumed that each individual molecule moved in a definite way, determined by Newton’s laws of motion. Of course, in practice it is impossible to follow billions upon billions of particles at the same time. They move in all directions, and each particle changes its direction and speed during collisions with other particles or with the wall of the container. Therefore, we cannot make a definite prediction of the motion of any one *individual* particle. Instead, we must be content with describing the *average* behavior of large collections of particles. From moment to moment, each individual molecule behaves according to the laws of motion. But it is easier to describe the *average* behavior, and to assume complete ignorance about any *individual* motions.

The word “gas” was originally derived from the Greek word *chaos*; it was first used by the Belgian chemist Jan Baptista van Helmont (1580–1644).

To see why this is so, consider the results of flipping a large number of coins all at once. If you assume the coins behave randomly, you can confidently predict that flipping a million coins will give approximately 50% heads and 50% tails. The same principle applies to gas molecules bouncing around in a container. You can safely assume, for example, that about as many are moving in one direction as in another. Furthermore, at a given moment the same number of molecules is equally likely to be found in any

one cubic centimeter of space inside the container as in any other. “Disordered,” then, means that velocities and positions are distributed *randomly*. Each molecule is just as likely to be moving to the right as to the left (or in any other direction). It is just as likely to be near the center as near the edge (or any other position).

7.3 THE SPEEDS OF MOLECULES

The basic idea of the kinetic theory of matter is that heat energy is related to the kinetic energy of moving molecules. As we shall see, this is right. This idea had been frequently suggested in the past. However, many difficulties stood in the way of its general acceptance. Some of these difficulties are well worth mentioning. They show that not all good ideas in science (any more than outside science) are immediately successful.

In 1738, the Swiss mathematician Daniel Bernoulli showed how a kinetic model could explain a well-known property of gases. This property is described by a variant of Boyle’s law: As long as the temperature does not change, the pressure of a gas is proportional to its density.

$$P \propto D \quad \text{if } T \text{ is constant.}$$

Here density D is defined as the amount of mass (m) per unit volume (V) of the gas, $D = m/V$.



FIGURE 7.6 Daniel Bernoulli (1700–1782).

Bernoulli assumed that the pressure of a gas is simply a result of the impacts of individual molecules striking the wall of the container. If the density of the gas were twice as great, there would be twice as many molecules per cubic centimeter. Thus, Bernoulli said, there would be twice as many molecules striking the wall per second and hence twice the pressure. Bernoulli's proposal seems to have been the first step toward the modern kinetic theory of gases. Yet it was generally ignored by other scientists in the eighteenth century. One reason for this was that Newton had proposed a different theory in his *Principia* (1687). Newton showed that Boyle's law *could* be explained by a model in which particles *at rest* exert forces that repel neighboring particles. Newton did not claim that he had proved that gases *really are* composed of such fixed, mutually repelling particles. But most scientists, impressed by Newton's discoveries, simply assumed that his treatment of gas pressure was also right. (It was not.)

The kinetic theory of gases was proposed again in 1820 by English physicist John Herapath. Herapath, on his own, rediscovered Bernoulli's findings on the relations between pressure and density, or volume, of a gas and the speeds of the particles. Herapath's work was also ignored by most other scientists.

James Prescott Joule, however, did see the value of Herapath's work. In 1848, he read a paper to the Manchester Literary and Philosophical Society in which he tried to revive the kinetic theory. This paper, too, was ignored by other scientists. For one thing, physicists do not generally look in the publications of a "literary and philosophical society" for scientifically important papers. However, evidence for the equivalence of heat and mechanical energy continued to mount. Several other physicists independently worked out the consequences of the hypothesis that the heat energy in a gas is explained and given by the kinetic energy of its molecules. Rudolf Clausius in Germany published a paper in 1856 on "The Nature of the Motion We Call Heat." This paper established the basic principles of kinetic theory essentially in the form accepted today. Soon afterward, James Clerk Maxwell in Britain and Ludwig Boltzmann in Austria set forth the full mathematical details of the theory.

Maxwell's Velocity Distribution

It did not seem likely that at a given moment all molecules in a gas would have the same speed. In 1859, Maxwell applied the mathematics of probability to this problem. He suggested that the speeds of molecules in a gas are distributed over all possible values. Most molecules have speeds not very far from the average speed. Some have much lower speeds and some much higher speeds.

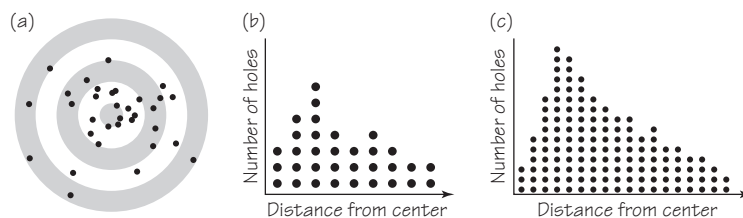


FIGURE 7.7 Target practice experiment: (a) scatter of holes in target; (b) graph showing number of holes in each ring from the bull's-eye; (c) graph showing that the distribution becomes smooth for a very large number of shots and for very narrow rings.

A simple example helps to understand Maxwell's distribution of molecular speeds. Suppose a person shoots arrows at a practice target. Some arrows will probably hit the bull's-eye. Others will miss by smaller or larger amounts, as shown in (a) in the sketch above. The number of arrows scattered at various distances from the center are counted. A graph of the results is shown in (b). This graph shows the distribution of the holes made by arrow hits for one set of shots. If you plot the distribution of hits for a very large number of shots, you will get a distribution like the one in (c). For still larger numbers of arrow shots the *spread* between the holes you see in (c) will become smaller, ultimately too small to be noticed. By analogy, the number of molecules in a gas being very large indeed, a graph showing the distribution of molecular *speeds* is smooth at any scale that can be drawn.

The actual shape of the curve shown in (c) was determined by many things about the bow, the arrows, the person, and so on. Other processes give rise to other shapes of curves. The speeds of the molecules in a gas are determined by the collisions they have with each other. Maxwell used

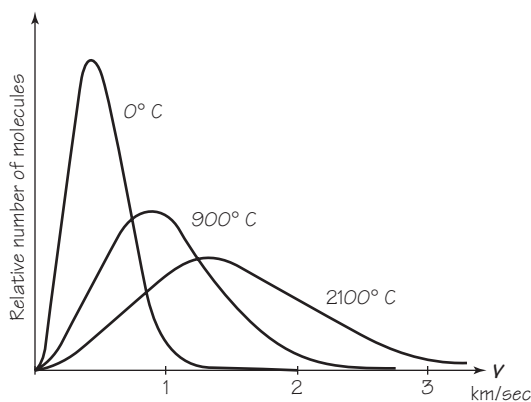


FIGURE 7.8 Maxwell's distribution of speeds in gases at different temperatures.

a clever mathematical argument to deduce what the distribution of molecular speeds should be.

Maxwell's proposed distribution for molecular speeds in a gas is shown in the diagram in graphical form for three different temperatures. For a gas at any given temperature, the "tail" of each curve is much longer on the right (high speeds) than on the left (low speeds). As the temperature increases, the peak of the curve shifts to higher speeds, and the speed distribution becomes more broadly spread out.

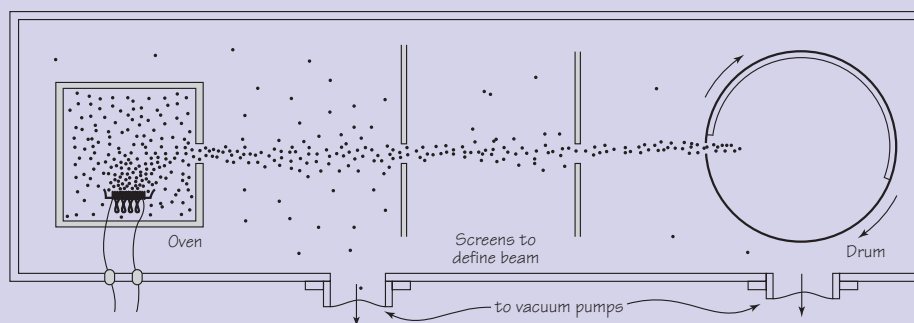
All this had to be tested, to see if the theoretical model is of real use, or not. The best test was a direct one, by experiments in the 1920s. Otto Stern in Germany devised an ingenious method for measuring the speeds in a beam of molecules. Stern and others found that molecular speeds are indeed distributed according to Maxwell's theory. This gave a most direct proof of the kinetic-molecular model of a gas. (See next page.)

7.4 THE SIZES OF MOLECULES

On the way to that proof, there were reasonably skeptical questions to wrestle with. Was it reasonable to suppose that gases consist of molecules moving at speeds up to several hundred meters per second at room temperature? If that model were correct, gases should mix with each other very rapidly. But anyone who has studied chemistry knows that they do not. Suppose someone opens a bottle of perfume or a container containing ammonia gas in a corner of the classroom. Several minutes may pass before the odor is noticed at the other end. But according to Maxwell's speed distribution, each of the gas molecules should have crossed the room hundreds of times by then. Therefore, something must be wrong with the kinetic-theory model.

Rudolf Clausius recognized this as a valid objection to his own version of the kinetic theory. His 1856 paper had assumed that the particles are so small that they can be treated like mathematical points. If this were true, particles would almost never collide with one another. However, the observed *slowness* of diffusion and mixing convinced Clausius to change his model. He thought it likely that the molecules of a gas are not vanishingly small, but of a finite size. Particles of finite size moving very rapidly would often collide with one another. An individual molecule might have an instantaneous speed of several hundred meters per second, but it changes its direction of motion every time it collides with another molecule. The more often it collides with other molecules, the less likely it is to move very far in any one direction. How often collisions occur depends on their size and

DIRECT MEASUREMENT OF MOLECULAR SPEEDS



A narrow beam of molecules is formed by letting molecules of a hot gas pass through a series of slits. In order to keep the beam from spreading out, collisions with randomly moving molecules must be avoided. Therefore, the source of gas and the slits are housed in a highly evacuated chamber. The molecules are then allowed to pass through a slit in the side of a cylindrical drum that can be spun very rapidly. The general scheme is shown in the drawing above.

As the drum rotates, the slit moves out of the beam of molecules. No more molecules can enter until the drum has rotated through a whole revolution. Meanwhile, the molecules in the drum continue moving to the right, some moving quickly and some moving slowly.

Fastened to the inside of the drum is a sensitive film that acts as a detector. Any molecule striking the film leaves a mark. The faster molecules strike the film first, before the drum

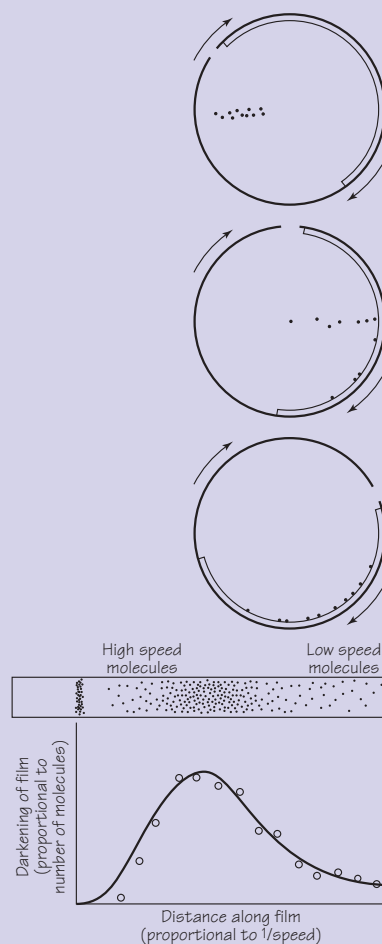


FIGURE 7.9 Schematic presentation of Otto Stern's experiment on the distribution of the speeds of gas molecules.

has rotated very far. The slower molecules hit the film later, after the drum has rotated farther. In general, molecules of different speeds strike different parts of the film.

The darkness of the film at any point is proportional to the number of molecules that hit it there. Measurement of the darkening of the film shows the relative distribution of molecular speeds. The speckled strip represents the unrolled film, showing the impact position of molecules

over many revolutions of the drum. The heavy band indicates where the beam struck the film before the drum started rotating. (It also marks the place to which infinitely fast molecules would get once the drum was rotating.)

A comparison of some experimental results with those predicted from theory is shown in the graph. The dots show the experimental results, and the solid line represents the predictions from the kinetic theory.

on how crowded the molecules are. For most purposes, you can think of molecules as being relatively far apart and of very small size. But they are just large enough and crowded enough to get in one another's way. Realizing this, Clausius was able to modify his model to explain why gases mix so slowly, a process known as *diffusion*.

Clausius now was faced with a problem that plagues every theoretical physicist. If a simple model is modified to explain better the observed properties, it becomes more complicated. Some plausible adjustment or approximation may be necessary in order to make any predictions from the model. If the predictions disagree with experimental data, is this because of a flaw in the model or a calculation error introduced by the approxima-

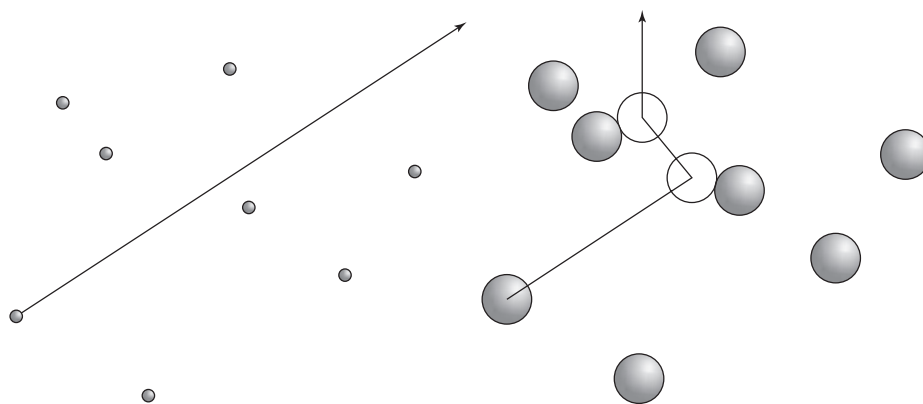


FIGURE 7.10 The larger the molecules, the more likely they are to collide with each other, thus delaying the progress of a molecule through the gas.

tions? The development of a theory often involves a compromise between adequate explanation of the data and mathematical convenience.

Nonetheless, it soon became clear that the new model was a great improvement over the old one. It turned out that certain other properties of gases also depend on the size of the molecules. By combining data on several such properties, it was possible to work backward and find fairly reliable values for molecular sizes. Here, only the result of these calculations is reported. Typically, the diameter of gas molecules came out to be of the order of 10^{-10} to 10^{-9} m. This is not far from the modern values—an amazingly good result. After all, no one previously had known whether a molecule was many times smaller or bigger than that. In fact, as Lord Kelvin remarked:

The idea of an atom has been so constantly associated with incredible assumptions of infinite strength, absolute rigidity, mystical actions at a distance and indivisibility, that chemists and many other reasonable naturalists of modern times, losing all patience with it, have dismissed it to the realms of metaphysics, and made it smaller than “anything we can conceive.”

Kelvin showed that other methods could also be used to estimate the size of atoms and molecules. None of these methods gave results as reliable as did the kinetic theory. But it was encouraging that they all led to the same order of magnitude (power of ten).

One early attempt to obtain the order of magnitude of the size of a molecule was made by Benjamin Franklin. Dropping a spoonful of oil on a pond, he was able to estimate the width of a single molecule by assuming that the oil formed a slick one molecule thick, then comparing the original volume of the oil to the area covered by the oil on the pond. A similar experiment is provided in the *Student Guide*, “Avogadro’s Number and the Size and Mass of a Molecule.”

B. APPLYING THE KINETIC THEORY

7.5 KINETIC-THEORY EXPLANATION OF THE IDEAL GAS LAW

As we now know, according to the kinetic theory, the pressure of a gas results from the continual impacts of gas particles against the container wall. This explains why pressure is inversely proportional to the volume and di-

If the pressure were kept constant, then according to the ideal gas law, the *volume* of a sample of gas would shrink to zero at -273°C .

rectly proportional to density: the smaller the volume or the greater the density, the greater the number of particles colliding with the wall.

But pressure also depends on the *speed* of the individual particles (hence, on the kinetic energy, $\frac{1}{2}mv^2$ of them). This speed determines the force exerted on the wall during each impact and the frequency of the impacts. If the collisions with the wall are perfectly elastic, the law of conservation of momentum will describe the results of the impact. (The detailed reasoning for this procedure is worked out in the *Student Guide*.) An atom bouncing off a wall undergoes a change of momentum. As you know from Section 5.4, whenever there is a change of momentum, there must be a force exerted on the object, an atom in this case. At the same time, there must be a reaction force on the wall that repelled the atom, which contributes to what we observe as pressure. This is a beautifully simple application of Newtonian mechanics.

Applying Newtonian mechanics to the kinetic-molecular model of gases, the result of the actual calculation (in three dimensions of motion) leads to the conclusion that pressure P is related to the average of the squared speed of the atoms $(v^2)_{\text{av}}$ by the expression

$$P = \frac{\frac{1}{3}m(v^2)_{\text{av}}}{V},$$

where V is the volume of the gas, and m is the mass of an individual gas atom. The steps in the derivation are quite straightforward (see the derivation in the *Student Guide*) and a beautiful case of applying Newton's laws in a region Newton himself never did.

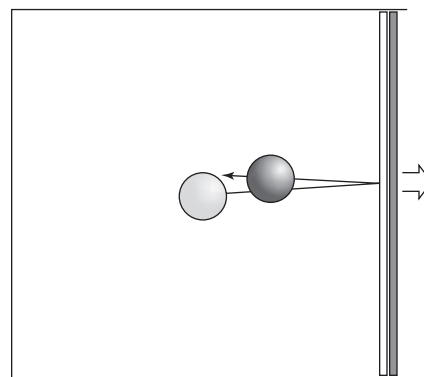


FIGURE 7.11 Model of gas particle in a container with a moveable wall.

We now have two expressions for the pressure of a gas. One summarizes the experimental facts, $PV = kT$. The other is derived by Newton's laws from a theoretical model, $PV = \frac{1}{3}m(v^2)_{av}$. The *theoretical* expression will agree with the *experimental* expression only if $kT = \frac{1}{3}m(v^2)_{av}$. This would mean that the temperature of a gas is proportional to $(v^2)_{av}$. The mass m of each molecule is a constant, so the temperature T is also proportional to $m(v^2)_{av}$. But this allows us also to write $T \propto \frac{1}{2}m(v^2)_{av}$, which immediately tells us that according to *the kinetic theory the temperature of a gas is proportional to the average kinetic energy of its molecules!* We already had some idea that raising the temperature of a material somehow affected the motion of its "small parts." We were aware that the higher the temperature of a gas, the more rapidly its molecules are moving. But the conclusion $T \propto \frac{1}{2}m(v^2)_{av}$ is a precise quantitative relationship derived from the kinetic model and empirical laws. At last we know for certain, for a gas, that heat is not some fluid (caloric) or other substance. It is just the kinetic energy of the particles (atoms) making up the material (or, as we shall see later, radiant energy).



FIGURE 7.12 Balloon for carrying weather forecasting apparatus.

Kinetic-Theory Explanation of the Temperature–Volume Relationship

The kinetic theory makes possible other quantitative predictions. We know by experience (e.g., by inflating a bicycle tire quickly) that when a gas is compressed or condensed rapidly, its temperature changes. The general gas law ($PV = kT$) applies. Can our model explain this result?

In the model used in the previous subsection, atoms or molecules were bouncing back and forth between the walls of a box. Every collision with the wall was perfectly elastic, so the particles rebounded with no loss in speed (or kinetic energy). Suppose the outside force that holds one wall in place is suddenly increased. What will happen to the wall? The wall moves inward, compressing the gas. As it compresses the gas, it does work on the particles, increasing their kinetic energy. As kinetic energy goes up, the temperature of the gas should rise—which is just what happens when a gas is compressed quickly.

If the outside force on the wall is decreased instead of increased, just the opposite happens. Again, what we learned earlier in mechanics comes in handy. As long as the wall was stationary, the particles did no work on it, and the wall did no work on the particles. Now if the wall is free to move outward, in the same direction as the force exerted on it by the particles as they smash into the wall, the picture changes. Since the particles, by their collisions, exert a force on the wall and the wall moves in the direction of

the force, the particles must be doing work on the wall. The energy needed to do this work must come from somewhere. The only available source of energy here is part or all of the kinetic energy ($\frac{1}{2}mv^2$) of the particles. In fact, it can be shown that molecules colliding perfectly elastically with a receding wall rebound with slightly less speed. Therefore, the kinetic energy of the particles must decrease. The

This phenomenon can be demonstrated by means of the expansion cloud chamber, or cooling of CO_2 fire extinguisher while in use. In the last case, the “wall” is the air mass being pushed away.

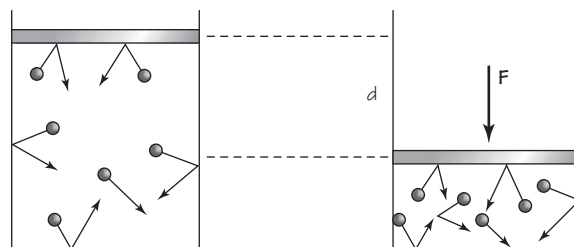


FIGURE 7.13 Particles in a cylinder being compressed.

relationship $T \propto \frac{1}{2}m(v^2)_{\text{av}}$ implies that the temperature of the gas will drop. This is exactly what happens when a container holding a gas expands!

Brownian Motion

Many different kinds of experimental evidence support these conclusions and therefore support the kinetic-theory model of a gas. Perhaps the most sophisticated evidence is the motion of very small particles seen through a microscope, when they are suspended in a gas or liquid. The gas or liquid molecules themselves are too small to be seen directly, but their effects on a larger particle (e.g., a particle of smoke) can be observed through the microscope. At any instant, swarms of molecules moving at very different speeds are striking the larger particle from all sides. So many molecules are taking part that their total effect *nearly* cancels. Any remaining effect changes in magnitude and direction from moment to moment. Therefore, the impact of the *invisible* molecules makes the visible *particles* appear to “dance” or jitter randomly in the view field of the microscope. The hotter the gas or liquid, the more lively the motion, as the relationship $T \propto \frac{1}{2}m(v^2)_{\text{av}}$ predicts.

This observation is known as *Brownian motion*. It was named after the English botanist, Robert Brown, who in 1827 observed the phenomenon

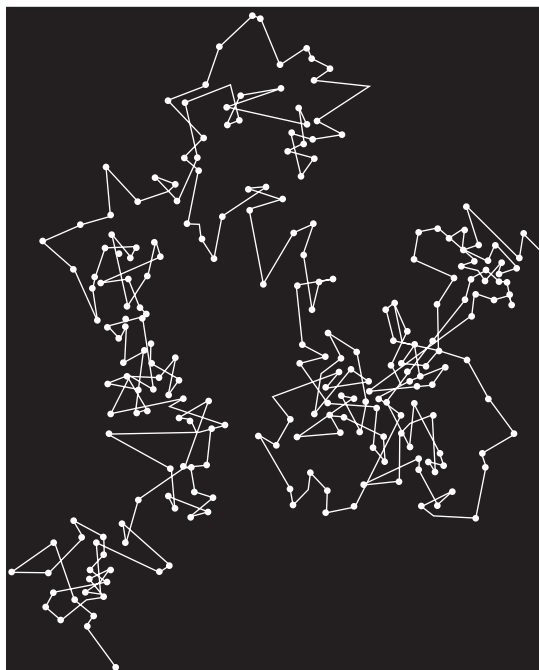


FIGURE 7.14 Track of a particle in Brownian motion. Successive positions, recorded every 20 seconds, are connected by straight lines. The actual paths between recorded positions would be as erratic as the overall path.

while looking at a suspension of the microscopic grains of plant pollen. The same kind of motion of suspended particles (“thermal motion”) also exists in liquids and solids, although there the particles are far more constrained than in gases.

The origin of Brownian motion remained a mystery for many years, until in 1905 Albert Einstein, using the kinetic theory, predicted that such motion should occur. Comparison between his detailed predictions and the observations of Brownian motion helped to convince most of the remaining sceptics at the time about the reality of atoms. This phenomenon, which is simple to set up and fascinating to watch, gives striking evidence that the smallest parts of all matter in the Universe are indeed in a perpetual state of lively, random motion.

7.6 KINETIC-THEORY EXPLANATION OF THE SECOND LAW

The kinetic-theory model can explain the behavior of a gas when it is compressed or expanded, warmed or cooled. In the late nineteenth century, the model was refined to take into account many effects we have not discussed. There proved to be limits beyond which the model breaks down. For example, radiated heat comes from the Sun through the vacuum of space, or from an electric grill. This is not explainable in terms of the thermal motion of particles; rather, that thermal radiation is a form of electromagnetic waves. But in most cases the model worked splendidly, explaining the phenomenon of heat in terms of the ordinary motions of submicroscopic particles. It fulfilled much of the hope Newton had expressed in the *Principia* and in the *Opticks* that all phenomena of nature could be explained in terms of the motion of the small parts of matter (atoms).

As we noted earlier, a basic philosophical theme of the Newtonian cosmology is the idea that the world is like a machine whose parts never wear out and which never runs down. This idea inspired the search for conservation laws applying to matter and motion. So far in this text, you have seen that this search has been successful. We can measure “matter” by mass, and “motion” by momentum or by kinetic energy. By 1850, the law of conservation of mass had been firmly established in chemistry. In physics, the laws of conservation of momentum and of energy had been equally well established.

Yet these successful conservation laws could not banish the suspicion that somehow the world *is* running down, the parts of the machine *are* wearing out. Energy may be conserved in burning fuel, but it loses its *usefulness* as

Our life runs down in sending
up the clock.
The brook runs down in sending
up our life.
The sun runs down in sending
up the brook.
And there is something sending
up the sun.
It is this backward motion toward
the source,
Against the stream, that most we
see ourselves in
The tribute of the current to the
source.
It is from this in nature we are
from.
It is most us.

Excerpt from
“West-Running Brook,”
(by Robert Frost).

the heat goes off into the atmosphere. The coal burned in a steam engine can never be recovered once it is burned. Mass may be conserved in scrambling an egg, but the organized *structure* of the egg is lost forever. In these transformations, something is conserved, but something is also lost. Some processes are irreversible; that is, they will not run backward. There is no way to unscramble an egg, although such a change would not violate mass conservation. There is no way to draw smoke and hot fumes back into a blackened stick, forming a new, unburned match. There is no way to run a steam engine backward and obtain all of the heat originally obtained from the burning of the fuel.

Section 6.4 discussed one type of irreversible process, that involving heat engines, which is governed by *the second law of thermodynamics*. As we saw, that law can be stated in several equivalent ways:

- Heat will not by itself flow from a cold body to a hot one.
- It is impossible to convert fully a given amount of heat into work.
- The entropy of an isolated system, and therefore of the Universe, tends to increase.

The processes of scrambling an egg, of mixing smoke and air, or of wearing down a piece of machinery do not, at first sight, seem to obey the same laws as do heat engines. However, these processes are also governed by the second law. Heat, as you have seen, is represented by the *disordered* motions



FIGURE 7.15 Waterfall.



FIGURE 7.16 Stroboscopic photograph of a bouncing ball.

of atoms and molecules. Converting ordered mechanical work into heat—say, the push of a piston straight into a cylinder full of gas—thus leads to an increase in disordered motion in the heated material. In fact, entropy can be defined mathematically as a measure of the disorder of a system (though it is not necessary to go into the mathematics here). In sum, irreversible processes are processes for which entropy increases, and the increase in entropy is a measure of the increase in the disorder of the atoms, molecules, and any other components making up the system.

7.7 MAXWELL'S DEMON AND THE STATISTICAL VIEW OF THE SECOND LAW

The Austrian physicist Ludwig Boltzmann, thinking about “irreversible” phenomena, detected a loophole in the rather pessimistic picture of a Universe running down as entropy increased. He concluded that the tendency toward dissipation of energy is not an *absolute* law of physics that holds in every situation. Rather, when it concerns the behavior of many particles, it is only a *statistical* law.

Think of a balloon filled with air containing billions upon billions of molecules. Boltzmann agreed that, of all conceivable arrangements of the gas molecules at a given instant, their motion would nearly always be completely “disordered,” as we have noted (see the meaning of “disorder” in Section 7.2). Yet, it is conceivable that at some moment most of the molecules happen, by chance, to be moving in the same direction. In any ran-

FIGURE 7.17 Ludwig Boltzmann (1844–1906).



Consider also a pool table. The ordered motion of a cue ball moving into a stack of resting ones soon gets “randomized.”

dom arrangement fluctuations from complete disorder are bound to occur. But the greater the fluctuation toward order, the less likely it is to occur. For collections of particles as large as 10^{23} , the chance of a fluctuation large enough to be measurable is vanishingly small, but not zero. By the same argument, it is *conceivable* that a cold kettle of water will heat up on its own after being struck by only the most energetic molecules that happen to be in the surrounding air. It is also *conceivable* that for a brief moment air molecules will “gang up” and strike only one side of a rock, pushing it uphill. Such events, while conceivable, are *utterly improbable*.

For *small* collections of particles, however, it is a different story. Just as it is quite probable that the average height of the people on a particular bus will be considerably greater or less than the national average, it is probable in the same way that more molecules will hit one side of a microscopic particle than the other side. That is just what causes the observable, Brownian motion of microscopic particles in a gas or liquid. Fluctuations, virtually undetectable for any large collection of molecules familiar in the everyday world, are an important aspect of the world of very small particles.

One outcome of these considerations is that the second law of thermo-

To illustrate Boltzmann's argument, consider a pack of cards when it is shuffled. Most possible arrangements of the cards after shuffling are fairly disordered. If you start with an ordered arrangement, for example, the cards sorted by suit and rank, then shuffling would almost certainly lead to a more disordered arrangement. (Nevertheless, it does occasionally happen that a player is dealt 13 spades, even if no one has stacked the deck.)

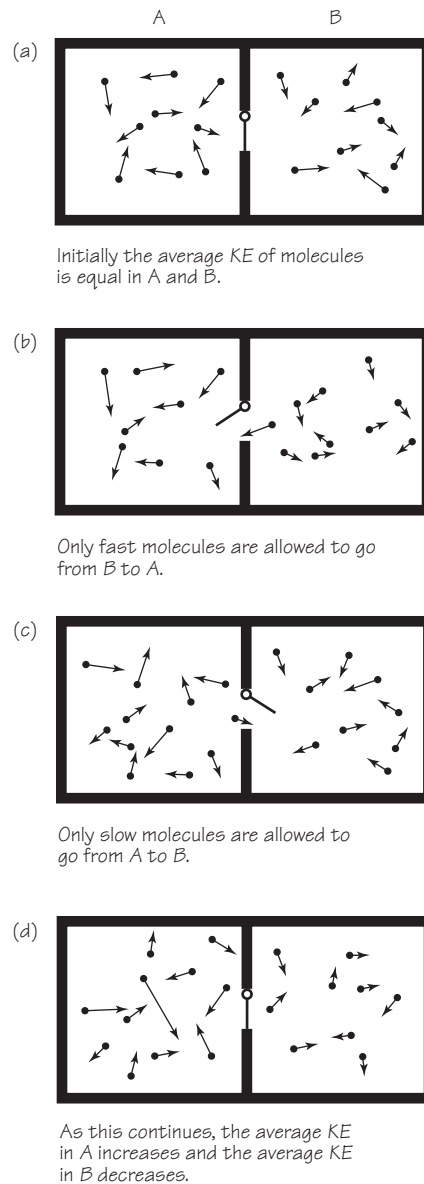
dynamics is different in character from all the other fundamental laws of physics presented so far. The difference is that it deals with probabilities, not certainties. For example, it says it is highly probable that when ice is dropped into hot water, the ordered structure of the cube will break apart and the cube will melt, forming water. But this law does not rule out the extremely unlikely possibility that the slowest molecules of hot water will join together for an instant to form an ice cube. Such an event has never been observed, and probably never will be, but it is possible in principle. The second law is thus a statistical law, giving the statistical outcome of a huge number of individual events (collisions of molecules).

Testing the limits of conceivable consequences of the second law, Maxwell proposed an interesting "thought experiment." Suppose a container of gas is divided by a thin membrane into two parts, the gas in one part being hotter than in the other. "Now conceive of a finite being," Maxwell suggested, "who knows the paths and velocities of all the molecules but who can do no work except open and close a hole in the diaphragm." This "finite being," now referred to as "Maxwell's demon," can make the hot gas hotter and the cold gas cooler, just by letting fast molecules move in only one direction through the hole (and slow molecules in the other), as is shown in the diagram.

Of course, there exists no such fanciful demon (even in machine form) that can observe and keep track of all the molecules in a gas—hence no such procedure for violating the second law can be realized in practice. If somehow such a "demon" could be made to exist, one might find that the demon's own entropy is affected by its actions. For example, its entropy might increase enough to compensate for the decrease in entropy of the gas. This is what happens in other systems where local order is created, such as in a tray of water freezing into ice cubes in a freezer; the entropy must increase somewhere else in the universe, such as in the room outside the freezer, where waste heat from the freezer engine is exhausted.

Some biologists have suggested that certain large molecules, such as enzymes, may function as "Maxwell's demons." Large molecules may influence the motions of smaller molecules to build up the ordered structures of living systems. This result is different from that of lifeless objects and is in apparent violation of the second law of thermodynamics. This suggestion, however, shows a misunderstanding of the law. The second law does not say that the order can *never* increase in any system. It makes that claim *only for closed or isolated systems*. Any "open" system, one that can exchange

FIGURE 7.18 How Maxwell’s “demon” could use a small, massless door to increase the order of a system and make heat flow from a cold gas to a hot gas.



energy with its surroundings, can increase its own order without violating the second law, for the entropy of the surroundings will increase.

The flow of energy through a system that is not closed may tend to increase the order in the system. The existence of highly organized structures that have life may be a result of supplying energy to them, as from the Sun. But the organizing phenomenon resulting in life does have its cost



FIGURE 7.19 A living system appears to contradict the second law of thermodynamics by bringing order out of disorder.

in terms of the effect on the rest of the total system. This point is expressed vividly in the following passage from a UNESCO document on environmental pollution:

Some scientists used to feel that the occurrence, reproduction, and growth of order in living systems presented an exception to the second law. This is no longer believed to be so. True, the living system may increase in order, but only by diffusing energy to the surroundings and by converting complicated molecules (carbohydrates, fats) called food into simple molecules (CO_2 , H_2O). For example, to maintain a healthy human being at constant weight for one year requires the degradation of about 500 kilograms (one-half ton) of food, and the diffusion into the surroundings (from the human and the food) of about 500,000 kilocalories (two million kilojoules) of energy. The “order” in the human may stay constant or even increase, but the order in the surroundings decreases much, much more.

7.8 TWO CHALLENGES

Late in the nineteenth century, a small but influential group of scientists began to question the basic philosophical assumptions of Newtonian mechanics. They even questioned the very idea of atoms. The Austrian physicist Ernst Mach argued that scientific theories should not depend on assuming the existence of things (such as atoms) which could not be directly observed.

Critics of kinetic theory pointed to two apparent contradictions between kinetic theory and the second law of thermodynamics. These contradic-

tions are known as the *reversibility paradox* and the *recurrence paradox*. Both paradoxes were based on possible exceptions to the second law; both were thought to cast doubt on the kinetic theory.

The Reversibility Paradox

Lord Kelvin and Josef Loschmidt, both of whom supported atomic theory, discovered the reversibility paradox during the 1870s. It was not regarded as a serious objection to the kinetic theory until the 1890s. The paradox is based on the simple fact that Newton's laws of motion are reversible in time. For example, if you watch a video of a bouncing ball, it is easy to tell whether the video tape is being run forward or backward: You know that the collisions of the ball with the floor are inelastic and that the ball rises less high after each bounce. (See Figure 7.16.) If, however, the ball made perfectly elastic bounces, it would rise to the same height after each bounce. Then you could not tell whether the tape was being run forward or backward. In the kinetic theory, molecules *are* assumed to make perfectly elastic collisions. Imagine that you could make a video recording of gas molecules colliding elastically according to this assumption. (See Figure 7.20.) When showing this video, there would be no way to tell whether it was being run forward or backward. Either way would show valid sequences of collisions. But here is the paradox: Consider videos of interactions involv-

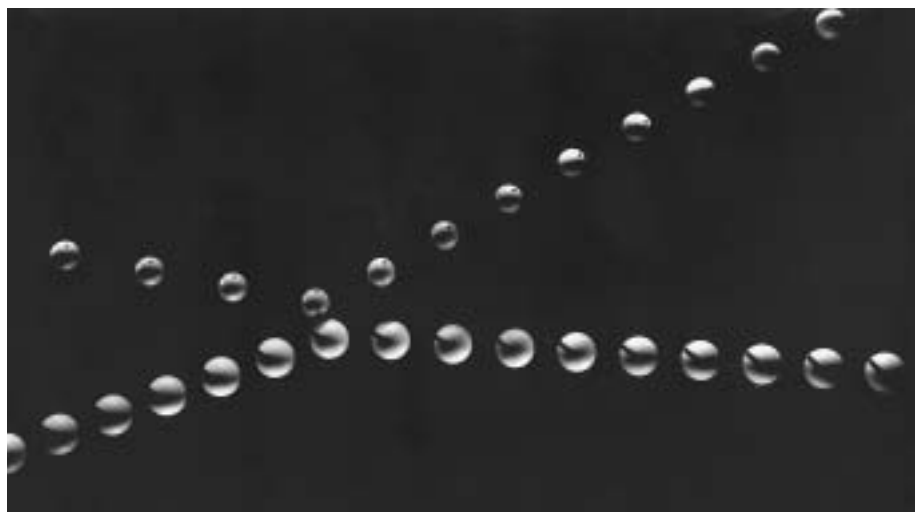


FIGURE 7.20 Two balls colliding elastically. Since no kinetic energy is lost, the process is reversible. The reversibility paradox: Can a model based on reversible events explain a world in which so many events are irreversible?



FIGURE 7.21 Example of an irreversible process.

ing large objects, containing many molecules. You can immediately tell the difference between forward (true) and backward (impossible) time direction. For example, a smashed light bulb does not reassemble itself in real life, although a video run backward can make it appear to do so.

The kinetic theory is based on laws of motion that assume the motions are reversible for each individual molecular interaction. How, then, can it explain the existence of *irreversible* processes on a large scale, involving many molecular collisions? The existence of such processes seems to indicate that time flows in a definite direction, that is, from past to future. This contradicts the possibility, implied in Newton's laws of motion, that, when it comes to observing physical phenomena, it does not matter whether we think of time as flowing forward or backward. As Kelvin expressed the paradox:

If . . . the motion of every particle of matter in the Universe were precisely reversed at any instant, the course of nature would be simply reversed for ever after. The bursting bubble of foam at the foot of a waterfall would reunite and descend into the water; the thermal motions would reconcentrate their energy, and throw the mass up the fall in drops reforming into a close column of ascending water. Heat which had been generated by the friction of solids and dissipated by conduction, and radiation with absorption, would come again to the place of contact, and throw the moving body back against the force to which it had previously yielded. . . . But the real phenomena of life infinitely transcend human science; and speculation regarding consequences of their imagined reversal is utterly unprofitable.

Kelvin himself, and later Boltzmann, used statistical probability to explain why we do not observe such large-scale reversals. There are almost

FIGURE 7.22 A bonfire—another example of an irreversible process.



infinitely many possible disordered arrangements of water molecules at the bottom of a waterfall. Only an extremely small number of these arrangements would lead to the process described by Kelvin. Reversals of this kind are possible *in principle*, but for all practical purposes they are out of the question.

The Recurrence Paradox

Another small possibility allowed in kinetic theory leads to a situation that seems unavoidably to contradict the second law. The *recurrence paradox* revived an idea that appeared frequently in ancient philosophies and is present also in Hindu philosophy to this day: the myth of the “eternal return.” According to this myth, the long-range history of the world is cyclic. All historical events eventually repeat themselves, perhaps many times. Given enough time, even the matter that people were made of will eventually reassemble by chance. Then people who have died may be born again and go through the same life. The German philosopher Friedrich Nietzsche was convinced of the truth of this idea.

The recurrence paradox begins with the fact that the number of molecules in the world is finite, hence there is only a finite number of possible arrangements of molecules. Therefore, if time continues infinitely, the same combination of molecules is bound to come up again. At some instant, all

The World's great age begins
anew,
The golden years return.
The earth cloth like a snake
renew
His winter weeds outworn . . .
Another Athens shall arise
And to remoter time
Bequeath, like sunset to the
skies,
The splendour of its prime . . .

[Percy Bysshe Shelley,
"Hellas" (1822)]

the molecules in the Universe would reassemble exactly the same arrangement they had at some previous time. All events following this point would then be exactly the same as the events that followed it before. That is, if any single instant in the history of the Universe is ever *exactly* repeated, then the entire history of the Universe will be repeated from that instant on. As a little thought shows, it would then be repeated over and over again to infinity. Thus, energy would *not* endlessly become dissipated as required by the second law. Nietzsche claimed that this view of the eternal return disproved the "heat-death" theory.

At about the same time, in 1889, the French mathematician Henri Poincaré published a theorem on the possibility of recurrence in mechanical systems. According to Poincaré, even though the Universe might undergo a heat death, it would ultimately come alive again:

A bounded world, governed only by the laws of mechanics, will always pass through a state very close to its initial state. On the other hand, according to accepted experimental laws (if one attributes absolute validity to them, and if one is willing to press their consequences to the extreme), the Universe tends toward a certain final state, from which it will never depart. In this final state, from which will be a kind of death, all bodies will be at rest at the same temperature.

. . . the kinetic theories can extricate themselves from this contradiction. The world, according to them, tends at first toward a state where it remains for a long time without apparent change; and this is consistent with experience; but it does not remain that way forever; . . . it merely stays there for an enormously long time, a time which is longer the more numerous are the molecules. This state will not be the final death of the Universe, but a sort of slumber, from which it will awake after millions of centuries.

According to this theory, to see heat pass from a cold body to a warm one, it will not be necessary to have the acute vision, the intelligence, and the dexterity of Maxwell's demon; it will suffice to have a little patience.

Poincaré was willing to accept the possibility of a violation of the second law after a very long time has passed. Others refused to admit even this possibility.

FIGURE 7.23 The ruins of the pyramid of Zosher (a step pyramid in Saggara, Egypt) testify to the continual encroachment of disorder.



The outcome of the dispute between the defenders and the critics of the kinetic theory was that both sides were partly right and partly wrong. Mach and his followers were correct in believing that Newton's laws of mechanics cannot fully describe molecular and atomic processes. We will come back to this subject when we discuss quantum mechanics in Chapter 15. For example, it is only approximately valid to describe gases in terms of collections of frantic little balls. But Boltzmann was right in defending the usefulness of the molecular model. The kinetic theory is very nearly correct except for those properties of matter that involve the structure of molecules themselves.

The new success of the kinetic theory in Einstein's account of Brownian motion, along with discoveries in radioactivity and atomic physics, persuaded almost all the critics that atoms and molecules do, in fact, exist. But the problems of irreversibility and of whether the laws of physics must distinguish between past and future survived. In a new form, these issues still interest physicists today.

SOME NEW IDEAS AND CONCEPTS

Boyle's law	kinetic-molecular theory of heat
Brownian motion	Maxwell's "demon"
density	model
diffusion	open system
entropy	pressure
ideal gas	recurrence paradox
ideal gas law	reversibility paradox
irreversible processes	reversible processes

IMPORTANT EQUATIONS

$$P = \frac{F_{\perp}}{A},$$

$$D = \frac{m}{V},$$

$$PV = kT.$$

FURTHER READING

G. Holton, and S.G. Brush, *Physics, The Human Adventure* (Piscataway, NJ: Rutgers University Press, 2000), Chapters 18–22.

H.C. von Baeyer, *Maxwell's Demon: Why Warmth Disperses and Time Passes* (New York: Random House, 1998). Softcover: *Warmth Disperses and Time Passes: A History of Heat* (New York: Modern Library, 1999).

STUDY GUIDE QUESTIONS

A. THE KINETIC THEORY

7.1 An Ideal Gas

1. Early forms of the kinetic-molecular theory were based on the assumption that heat energy is (select one of the following):
 - (a) a liquid;
 - (b) a gas;
 - (c) the kinetic energy of molecules;
 - (d) made of molecules.
2. The relationship between the volume and the pressure of a gas expressed by Boyle's law, $P = a/V$, holds true
 - (a) for any gas under any conditions;
 - (b) for some gases under any conditions;
 - (c) only if the temperature is kept constant;
 - (d) only if the volume is constant.
3. How is it possible for the pressure on the floor under a spiked heel to be greater than the pressure under an elephant's foot?
4. State the "ideal gas law" in your own words.
5. What is "ideal" about the ideal gas law?

6. The text states that the three proportionalities among P , V , and T can be combined into one equation, the ideal gas law. Confirm that by holding one of the variables constant, the equation does indeed yield each of the three proportions.
7. Explain why the ideal gas law is not a law of physics in the same sense as the law of conservation of energy.
8. Assuming the ideal gas law holds to the lowest temperatures, what happens to a gas at absolute zero?

7.2 A Model for the Gaseous State

1. What is meant by a “model of a gas”?
2. What kind of a model is a test model of a bridge made of balsa wood? a computer program that simulates the forces acting on a bridge? What are the differences between “theoretical” and “working” models? How are theoretical models tested?
3. What are some of the assumptions in the kinetic theory of gases?
4. Read the following description of a model of a gas and give a suitable numerical estimation for each underlined phrase: “a large number of small particles in rapid, disordered motion.”
5. In the kinetic theory, particles are thought to exert significant forces on one another:
 - (a) only when they are far apart;
 - (b) only when they are close together;
 - (c) all the time;
 - (d) never.
6. Why was the kinetic theory first applied to gases rather than to liquids or solids?
7. Why do we have to use statistics in studying gases? Why can't we just follow the motion of each atom?

7.3 The Speeds of Molecules

1. In the kinetic theory of gases, it is assumed that the pressure of a gas on the walls of the container is due to:
 - (a) gas molecules colliding with one another;
 - (b) gas molecules colliding against the walls of the container;
 - (c) repelling forces exerted by molecules on one another.
2. The idea of speed distribution for gas molecules means that:
 - (a) each molecule always has the same speed;
 - (b) there is a wide range of speeds of gas molecules;
 - (c) molecules are moving fastest near the center of the container of the gas.
3. What happens to the speed distribution as the temperature increases? As the temperature reaches absolute zero?
4. The average speed of a molecule in a gas at 900°C is about 1 km/s. Is it possible that there are molecules in the gas at speeds of 10 km/s? With zero speed?

7.4 The Sizes of Molecules

1. What was the objection raised against Clausius' kinetic theory for a gas?
2. In his revised kinetic-theory model Clausius assumed that the particles have a finite size, instead of being mathematical points, because:
 - (a) obviously everything must have some size;
 - (b) it was necessary to assume a finite size in order to calculate the speed of molecules;
 - (c) the size of a molecule was already well known before Clausius' time;
 - (d) a finite size of molecules could account for the slowness of diffusion.

B. APPLYING THE KINETIC THEORY

7.5 Kinetic-Theory Explanation of the Ideal Gas Law

1. Using the kinetic theory of gases, explain in your own words each of the three empirical relationships between P , V , and T for an ideal gas.
2. Does your response to Question 1 prove that the kinetic theory of gases is valid? Explain.
3. Using the concept of work and the kinetic theory of gases, explain why the temperature of a gas and the kinetic energy of its molecules both increase if a piston is suddenly pushed into the container holding the gas.
4. What are the limits under which the ideal gas law describes the behavior of real gases?

7.6 Kinetic-Theory Explanation of the Second Law

1. Which of the following statements agrees with the second law of thermodynamics?
 - (a) Heat does not naturally flow from cold bodies to hot bodies.
 - (b) Energy tends to transform itself into less useful forms.
 - (c) No engine can transform all its heat input into mechanical energy.
 - (d) Most processes in nature are reversible.
2. If the water in a pot placed on a hot stove suddenly froze, Newton's laws would not have been violated. Why would this event violate the second law of thermodynamics? If an extremely small volume of the total water in the pot cooled for a moment, would this violate the second law?
3. What is a reversible process?

7.7 Maxwell's Demon and the Statistical View of the Second Law

1. In each of the following pairs, which situation is more ordered?
 - (a) an unbroken egg; a scrambled egg;
 - (b) a glass of ice and warm water; a glass of water at uniform temperature;
 - (c) a falling ball; a ball that has hit a tabletop, bounced, and come to rest.
2. What is Maxwell's "demon" and what is it supposed to do?

3. True or false?
 - (a) Maxwell's demon was able to get around the second law of thermodynamics.
 - (b) Scientists have made a Maxwell's demon.
 - (c) Maxwell believed that his demon actually existed.
4. How did Boltzmann account for the entropy version of the second law?
5. How does the kinetic theory account for the fact that heat does not flow by itself from cold objects to hot objects?
6. Is it ever possible for a scrambled egg to unscramble itself? Why don't we observe this happening occasionally?
7. A growing plant takes in nutrients from the soil to create the increasingly complete structure of its stem, roots, leaves, flowers, etc. Order seems to be emerging by itself out of disorder. Is this a violation of the second law of thermodynamics? Explain.

7.8 Two Challenges

1. What is the "reversibility paradox" and how did Boltzmann resolve it?
2. What is the "recurrence paradox" and how was it finally resolved?
3. The kinetic energy of a falling stone is transformed into heat when the stone strikes the ground. Obviously, this is an irreversible process; you never see the heat transform into kinetic energy of the stone, so that the stone rises off the ground. Scientists believe that the process is irreversible because:
 - (a) Newton's laws of motion prohibit the reversed process;
 - (b) the probability of such a sudden ordering of molecular motion is extremely small;
 - (c) the reversed process would not conserve energy;
 - (d) the reversed process would violate the second law of thermodynamics.
4. What is Brownian motion? How did it provide convincing evidence for the existence of atoms and molecules?

DISCOVERY QUESTIONS

1. Using the kinetic theory, explain why when exposed to room temperature, hot water near boiling cools down faster than cold water, initially near freezing, warms up?
2. An ice cube is dropped into an insulated cup of hot water. Describe what happens and why, based on the laws of thermodynamics.
3. Explain the results in Question 2 using the kinetic theory, including the fact that this process does not reverse itself.
4. Using material in this chapter, how would you answer this question: "How do we know that atoms really do exist?"
5. The idea of randomness can be used in predicting the results of flipping a large number of coins. Give some other examples where randomness is useful.

6. A drop in barometric pressure is often a signal that cold, wet weather is on the way. A rise in air pressure indicates warm, dry weather. Why do you think this is so?
7. At sea level, water boils at 100°C , while at higher elevations it boils at slightly lower temperature. Using the kinetic theory, how would you explain this?
8. Why is the melting of an ice cube considered to be an irreversible process, even though it could easily be refrozen?
9. Explain why you feel cold on getting out of a shower, even if the room is not cold.
10. Consider these aspects of the curves showing Maxwell's distribution of molecular speeds:
 - (a) all show a peak;
 - (b) the peaks move toward higher speed at higher temperatures.Explain these characteristics on the basis of the kinetic model.
11. State the ideal gas law. What three proportionalities are contained in this law? What are the limitations of this law?
12. Starting from the definition of density, $D = m/V$ (where m is the mass of a sample and V is its volume), write an expression relating pressure P , temperature T , and density D of a gas.
13. Distinguish between two uses of the word "model" in science.
14. What would you expect to happen to the temperature of a gas that was released from a container into empty space (i.e., with nothing to push back)?
15. List some of the directly observable properties of gases.
16. What aspects of the behavior of gases can the kinetic-molecular theory be used to explain successfully?
17. When a gas in an enclosure is compressed by pushing in a piston, its temperature increases. Explain this fact in two ways:
 - (a) by using the first law of thermodynamics;
 - (b) by using the kinetic theory of gases.
18. Since all the evidence is that molecular motions are random, you might expect that any given arrangement of molecules will recur if you just wait long enough. Explain how a paradox arises when this prediction is compared with the second law of thermodynamics, viewed as an absolute law of nature.
19.
 - (a) Explain what is meant by the statement that Newton's laws of motion are time-reversible.
 - (b) Describe how a paradox arises when the time-reversibility of Newton's laws of motion is compared with the second law of thermodynamics.
20. Where did Newtonian mechanics run into difficulties in explaining the behavior of molecules?
21. What are some advantages and disadvantages of theoretical models?

Quantitative

1. Benjamin Franklin observed in 1773 that a teaspoonful of oil would spread out to form a film of about $22,000\text{ ft}^2$ on a pond near London. This helped to give him an estimate of the upper limit of the size of a molecule. Suppose that

1 cm³ of oil forms a continuous layer one molecule thick that just covers an area on water of 1000 m².

- (a) How thick is the layer?
 - (b) What is the size of a single molecule of the oil (considered to be a cube for simplicity)? (See the Laboratory Exploration “Avogadro’s Number and the Size and Mass of a Molecule,” in the *Student Guide*.)
2. How high could water be raised with a lift pump on the Moon?
 3. (a) The pressure of a gas in a container is 100 N/m². If the temperature is doubled while the volume is made to shrink to one-third, what is the new pressure?
 - (b) The temperature of a gas is 100°C. If the pressure is doubled and the volume is also doubled, what is the new temperature?