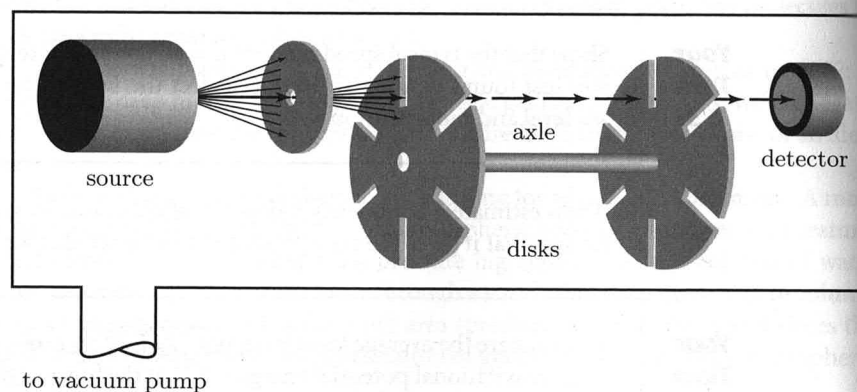


In this section, we have seen how the hypothesis of random molecular motion with an average kinetic energy proportional to the absolute temperature, explains the ideal gas law and a number of other facts. Other questions, however, come to mind. For example, if heating a pan of water raises the kinetic energy of the water molecules, why don't they all suddenly fly away when the temperature gets to some critical value, the one giving them enough energy to escape? To understand questions like this one, we need to keep in mind that the average kinetic energy is far from the whole story. We also want to know about the full *distribution* of molecular velocities, not just its mean-square value.

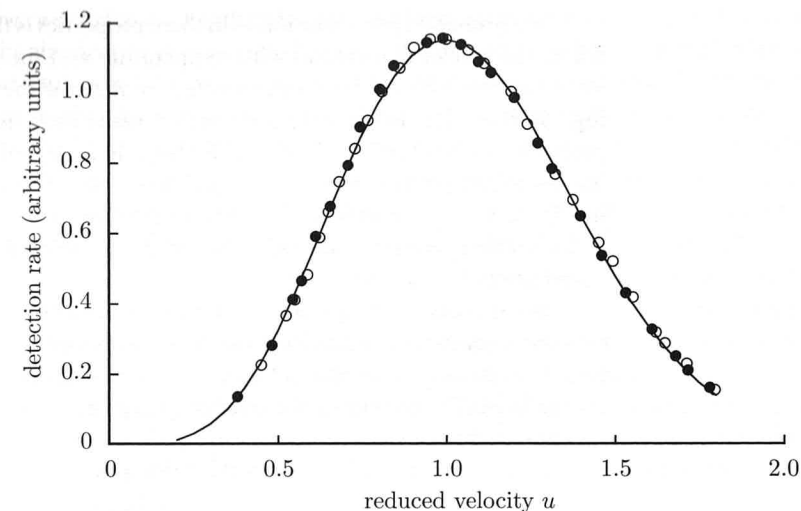
### 3.2.2 The complete distribution of molecular velocities is experimentally measurable

The logic in the previous subsection was a bit informal, in keeping with the exploratory character of the discussion. But we ended with a precise question: What is the full distribution of molecular velocities? In other words, how many molecules are moving at  $1000 \text{ m s}^{-1}$ ; how many at  $10 \text{ m s}^{-1}$ ? The ideal gas law implies that  $\langle v^2 \rangle$  changes in a very simple way with temperature (Idea 3.21), but what about the complete distribution?

These are not just theoretical questions. One can measure directly the distribution of speeds of gas molecules. Imagine taking a box full of gas (in practice, the experiment is done using a vaporized metal) with a pinhole that lets gas molecules emerge into a region of vacuum (Figure 3.6). The pinhole is made so small that the escaping gas molecules do not disturb the state of the others inside the box. The emerging molecules pass through an obstacle course, which only allows those with



**Figure 3.6:** (Schematic.) An experimental apparatus to measure the distribution of molecular speeds by using a velocity filter consisting of two rotating slotted disks. To pass through the filter, a gas molecule must arrive at the left disk when a slot is in the proper position, then also arrive at the right disk exactly when another slot arrives at the proper position. Thus, only molecules with one selected speed pass through to the detector; the selected speed can be set by adjusting how fast the disks spin. [Adapted from Reif, 1965.]



**Figure 3.7:** (Experimental data with fit.) Speeds of atoms emerging from a box of thallium vapor, at two different temperatures. *Open circles:*  $T = 944 \text{ K}$ . *Solid circles:*  $T = 870 \text{ K}$ . The quantity  $\bar{u}$  on the horizontal axis equals  $u\sqrt{m/4k_B T}$ ; both distributions have the same most probable value,  $\bar{u}_{\text{max}} = 1$ . Thus  $u_{\text{max}}$  is larger for higher temperatures, as implied by Idea 3.21. The vertical axis shows the rate at which atoms hit a detector after passing through a filter like the one sketched in Figure 3.6 (times an arbitrary rescaling factor). *Solid line:* Theoretical prediction (see Problem 3.5). This curve fits the experimental data with *no* adjustable parameters. [Data from Miller & Kusch, 1955.]

speeds in a particular range to pass. The successful molecules then land on a detector, which measures the total number arriving per unit time.

Figure 3.7 shows the results of such an experiment. Even though individual molecules have random velocities, clearly the *distribution* of velocities is predictable and smooth. The data also show clearly that a given gas at different temperatures will have closely related velocity distributions; two different data sets lie on the same curve after rescaling the molecular speed  $u$ .

### 3.2.3 The Boltzmann distribution

Let's use the ideas of Section 3.2.1 to understand the experimental data in Figure 3.7. We are exploring the idea that, even though each molecule's velocity cannot be predicted, there is nevertheless a definite prediction for the *distribution* of molecular velocities. One thing we know about that probability distribution is that it must fall off at large velocities: Certainly there won't be any gas molecules in the room moving at a million meters per second! Moreover, the average speed must increase as we make the gas hotter, because we've argued that the average kinetic energy is proportional to  $T$  (see Idea 3.21). Finally, the probability of finding a molecule moving to the left at some velocity  $v_x$  should be the same as that for finding it moving to the right at  $-v_x$ .

One probability distribution with these properties is the Gaussian (Equation 3.8) where the spread  $\sigma$  increases with temperature and the mean is zero. (If the mean were nonzero, there'd be a net, directed, motion of the gas, that is, a wind blowing.) Remarkably, this simple distribution really does describe any ideal gas! More precisely, the probability  $P(v_x)$  of finding that a given molecule at a given time has its  $x$ -component of velocity equal to  $v_x$  is a Gaussian, like the form shown in Figure 3.2, but centered on 0. Each molecule is incessantly changing its speed and direction. What's unchanging is not the velocity of any one molecule but the distribution  $P(v_x)$ .

We can replace the vague idea that the variance  $\sigma^2$  of  $v_x$  increases with temperature by something more precise. Because the mean velocity equals zero, Your Turn 3B on page 74 says that the variance of  $v_x$  is  $\langle v_x^2 \rangle$ . According to Idea 3.21, the mean kinetic energy is  $\frac{1}{2}k_B T$ . Combining these statements gives

$$\sigma^2 = k_B T/m. \quad (3.24)$$

Section 1.5.4 on page 27 gave the numerical value of  $k_B T$  at room temperature as  $k_B T_r \approx 4.1 \cdot 10^{-21}$  J. That's pretty small, but so is the mass  $m$  of one gas molecule, so  $\sigma$  need not be small. In fact, you showed in Your Turn 3I that the quantity  $\sqrt{k_B T_r/m}$  corresponds to a large velocity.

Now that we have the probability distribution for one component of the velocity, we can follow the approach of Section 3.1.4 to get the three-dimensional distribution,  $P(\mathbf{v})$ . Your result in Your Turn 3F on page 77 then gives the distribution of molecular speeds, a function similar to the one shown in Figure 3.3.<sup>3</sup>

**Your  
Turn  
3L**

Find the most probable value of the speed  $u$ . Find the mean speed  $\langle u \rangle$ . Looking at the graph you drew in Your Turn 3F (or the related function in Figure 3.3), explain geometrically why these are/aren't the same.

Still assuming that the molecules move independently and are not subjected to any external force, we can next find the probability that *all*  $N$  molecules in the room have specified velocities  $\mathbf{v}_1, \dots, \mathbf{v}_N$ , again using the multiplication rule:

$$P(\mathbf{v}_1, \dots, \mathbf{v}_N) \propto e^{-m\mathbf{v}_1^2/(2k_B T)} \times \dots \times e^{-m\mathbf{v}_N^2/(2k_B T)} = e^{-\frac{1}{2}m(\mathbf{v}_1^2 + \dots + \mathbf{v}_N^2)/k_B T}. \quad (3.25)$$

James Clerk Maxwell derived Equation 3.25 and showed how it explained many properties of gases. The proportionality sign,  $\propto$ , reminds us that we haven't bothered to write down the appropriate normalization factor.

Equation 3.25 applies only to an ideal gas, free from any external influences. Chapter 6 will generalize this formula. Although we're not ready to prove this generalization, we can at least form some reasonable expectations:

<sup>3</sup>  $T_2$  The curve fitting the experimental data in Figure 3.7 is almost, but not quite, the one you found in Your Turn 3F(b). You'll find the precise relation in Problem 3.5.

- If we wanted to discuss the whole atmosphere, for example, we'd have to understand why the distribution is spatially nonuniform—air gets thinner at higher altitudes. But Equation 3.25 gives us a hint. Apart from the normalization factor, the distribution given by Equation 3.25 is just  $e^{-E/k_B T}$ , where  $E$  is the kinetic energy. When altitude (potential energy) starts to become important, it's reasonable to guess that we should just replace  $E$  by the molecule's *total* (kinetic plus potential) energy. Indeed, we then find the air thinning out, with density proportional to the exponential of minus the altitude (because the potential energy of a molecule is  $mgz$ ).
- Molecules in a sample of air hardly interact at all—air is nearly an ideal gas. But in more crowded systems, such as liquid water, the molecules interact a lot. There the molecules are not independent and we can't simply use the multiplication rule. But again we can form some reasonable expectations. The statement that “the molecules interact” means that the potential energy isn't just the sum of independent terms  $U(x_1) + \dots + U(x_N)$  but instead is some joint function  $U(x_1, \dots, x_N)$ . Calling the corresponding total energy  $E \equiv E(x_1, v_1; \dots; x_N, v_N)$ , let's substitute *that* into our provisional formula:

$$P(\text{state}) \propto e^{-E/k_B T}. \quad \text{Boltzmann distribution} \quad (3.26)$$

We will refer to this formula as the **Boltzmann distribution**<sup>4</sup> after Ludwig Boltzmann, who found it in the late 1860s.

We should pause to unpack the very condensed notation in Equation 3.26. To describe a state of the system, we must give the location  $\mathbf{r}$  of each particle, as well as its speed  $\mathbf{v}$ . The probability of finding particle  $a$  with its first coordinate lying between  $x_{1,a}$  and  $x_{1,a} + dx_{1,a}$  and so on, and its first velocity lying between  $v_{1,a}$  and  $v_{1,a} + dv_{1,a}$  and so on, equals

$$dx_{1,a} \times \dots \times dv_{1,a} \times \dots \times P(x_{1,a}, \dots, v_{1,a}, \dots). \quad (3.27)$$

For  $K$  particles, the probability distribution  $P(x_{1,a}, \dots, v_{1,a}, \dots)$  is a function of  $6K$  variables given by Equation 3.26.

Equation 3.26 has some reasonable features: At very low temperatures, or  $T \rightarrow 0$ , the exponential is a very rapidly decreasing function of  $\mathbf{v}$ : The system is overwhelmingly likely to be in the lowest energy state available to it. (In a gas, this state is the one in which all of the molecules are lying on the floor at zero velocity.) As we raise the temperature, thermal agitation begins; the molecules begin to have a range of energies, which gets broader as  $T$  increases.

It's almost unbelievable, but the very simple formula Equation 3.26 is exact. It's not simplified; you'll never have to unlearn it and replace it by anything more complicated. (Suitably interpreted, it holds without changes even in quantum mechanics.) Chapter 6 will derive it from very general considerations.

<sup>4</sup>Some authors use the synonym “canonical ensemble.”

## 3.2.4 Activation barriers control reaction rates

We are now in a better position to think about a question posed at the end of Section 3.2.1: If heating a pan of water raises the kinetic energy of its molecules, then why doesn't the water in the pan evaporate suddenly, as soon as it reaches a critical temperature? For that matter, why does evaporation cool the remaining water?

To think about this puzzle, imagine that it takes a certain amount of kinetic energy  $E_{\text{barrier}}$  for a water molecule to break free of its neighbors (because they attract one another). Any water molecule near the surface with at least this much energy can leave the pan; we say that there is an **activation barrier** to escape. Suppose we heat a covered pan of water, then turn off the heat and momentarily remove the lid, allowing the most energetic molecules to escape. The effect of removing the lid is to *clip* the Boltzmann probability distribution, as suggested by the solid line in Figure 3.8a. We now replace the lid of the pan and thermally insulate it. Now the constant jostling of the remaining molecules once again pushes some up to higher energies, regrowing the tail of the distribution as shown by the dashed line of Figure 3.8a. We say that the remaining molecules have **equilibrated**. But the new distribution is not quite the same as it was initially. Because we removed the most energetic molecules, the average energy of those remaining is less than it was to begin with: Evaporation cooled the remaining water. Moreover, rearranging the distribution takes time: Evaporation doesn't happen all at once. If we had assumed the water to be hotter initially, however, its initial distribution of energies would have been farther to the right (Figure 3.8b), and more of the molecules would have been ready to escape. In other words, evaporation proceeds faster at higher temperature.

The idea of activation barriers can help make sense of our experience with chemical reactions, too. When you flip a light switch, or click your computer's mouse, there is a minimal energy, or activation barrier, which your finger must supply. Tapping the switch too lightly may move it a fraction of a millimeter but doesn't click it over to its "on" position. Now imagine drumming your finger lightly on the switch, giving a series of random light taps with some distribution of energies. Given enough time, eventually one tap will be above the activation barrier and the switch will flip.

Similarly, one can imagine that a molecule with a lot of stored energy, say hydrogen peroxide, can only release that energy after a minimal initial kick pushes it over an activation barrier. The molecule constantly gets kicks from the thermal motion of its neighbors. If most of those thermal kicks are much smaller than the barrier, however, it will be a very long time before a big enough kick occurs. Such a molecule is practically stable. We can speed up the reaction by heating the system, just as in evaporation. For example, a candle is stable, but it burns when we touch it with a lighted match. The energy released by burning in turn keeps the candle hot long enough to burn some more, and so on.

We can do better than these simple qualitative remarks. Our argument implies that the rate of a reaction is proportional to the fraction of all molecules whose energy exceeds the threshold. Consulting Figure 3.8, we see that we want the *area* under the part of the original distribution that gets clipped when molecules escape over the barrier. The fraction of molecules represented by this area is small at low temperatures (see Figure 3.8a). In general, the area depends on the temperature with a factor of

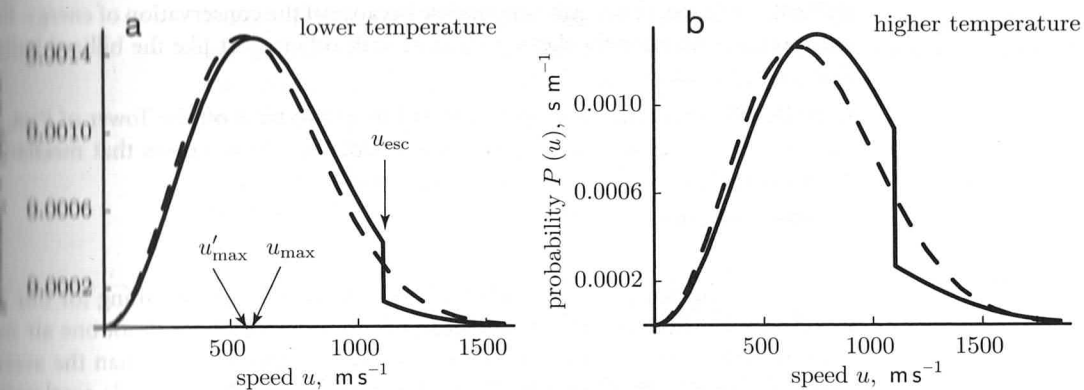


Figure 3.8: (Mathematical functions.) (a) *Solid line*: The distribution of molecular speeds for a sample of water, initially at 100°C, from which some of the most energetic molecules have suddenly been removed. After we reseal the system, molecular collisions bring the distribution of molecular speeds back to the standard form (*dashed line*). The new distribution has regenerated a high-energy tail, but the average kinetic energy did not change; accordingly, the peak has shifted slightly, from  $u_{\text{max}}$  to  $u'_{\text{max}}$ . (b) The same system, with the same escape speed; but this time the system starts at a higher temperature. The fraction of the distribution removed is now greater than in (a), and hence the shift in the peak is larger, too.

$e^{-E_{\text{barrier}}/k_{\text{B}}T}$ . You already found such a result in a simpler situation in Your Turn 3E on page 77: Substituting  $u_0$  for the distance  $R_0$  in that problem, and  $k_{\text{B}}T/m$  for  $\sigma^2$ , indeed gives the fraction of molecules over threshold as  $e^{-mu_0^2/(2k_{\text{B}}T)}$ .

The preceding argument is rather incomplete. For example, it assumes that a chemical reaction consists of a single step, which certainly is not true for many reactions. But there are many elementary reactions between simple molecules for which our conclusion is experimentally true:

*The rates of simple chemical reactions depend on temperature mainly via a factor of  $e^{-E_{\text{barrier}}/k_{\text{B}}T}$ , where  $E_{\text{barrier}}$  is some temperature-independent constant characterizing the reaction.* (3.28)

We will refer to Idea 3.28 as the **Arrhenius rate law**. Chapter 10 will discuss it in greater detail.

## 3.2.5 Relaxation to equilibrium

We are beginning to see the outlines of a big idea: When a gas, or other complicated statistical system, is left to itself under constant external conditions for a long time, it arrives at a situation where the probability distributions of its physical quantities don't change over time. Such a situation is called thermal equilibrium. We will define and explore equilibrium more precisely in Chapter 6, but already something may be troubling you, as it is troubling Gilbert:

**Gilbert:** Very good, you say the air doesn't fall on the floor at room temperature because of thermal motion. Why then doesn't it slow down and eventually stop (and then fall on the floor), as a result of friction?



**Sullivan:** Oh, no, that's quite impossible because of the conservation of energy. Each gas molecule makes only elastic collisions with others, just like the billiard balls in first-year physics.

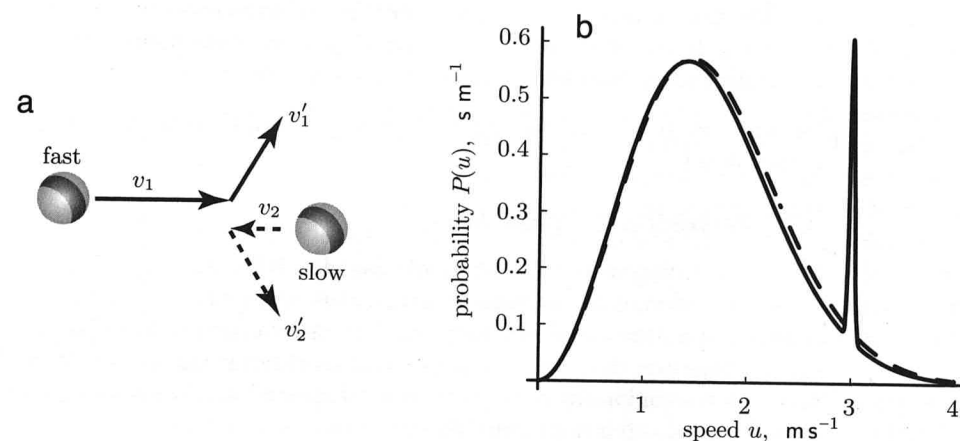
**Gilbert:** Oh? So then, what *is* friction? If I drop two balls off the Tower of Pisa, the lighter one gets there later, because of friction. Everybody knows that mechanical energy isn't conserved; eventually it winds up as heat.

**Sullivan:** Uh, um, . . .

As you can see, a little knowledge proves to be a dangerous thing for our two fictitious scientists. Suppose that, instead of dropping a ball, we shoot one air molecule into the room with enormous speed, say, 100 times greater than the average molecular speed. (One can actually do this experiment with a particle accelerator.) What happens?

Soon this molecule bangs into one of the ones that was in the room to begin with. There's an overwhelming likelihood that the latter molecule will have kinetic energy much smaller than the injected one and, indeed, probably not much more than the average. When they collide, the fast one transfers a lot of its kinetic energy to the slow one. Even though the collision was elastic, the fast one lost a lot of energy. Now we have two medium-fast molecules; each is closer to the average than it was to begin with. Each one now cruises along till it bangs into another, and so on, until they all blend into the general distribution (Figure 3.9).

Even though the total energy in the system is unchanged after each collision, the original *distribution* (with one molecule way out of line with the others) will settle down to the equilibrium distribution (Equation 3.26), by a process of sharing the



**Figure 3.9:** (Schematic; sketch graph.) (a) When a fast billiard ball collides with a slow one, in general both move away with a more equal division of their total kinetic energy than before. (b) An initial molecular speed distribution (solid line) with one anomalously fast molecule (or a few, creating the bump in the graph) quickly reequilibrates to a Boltzmann distribution at slightly higher temperature (dashed line). Compare with Figure 3.8.

energy in the original fast molecule with all the others.<sup>5</sup> What has changed is not energy but the *ordering* of that energy: The one dissident in the crowd has faded into anonymity. Again, the directed motion of the original molecule has been degraded to a tiny increase in the average random motion of its peers. But, average random velocity is just temperature, according to Equation 3.26. In other words, *mechanical energy has been converted to thermal energy* in the process of reaching equilibrium. **Friction** is the name for this conversion.

### 3.3 EXCURSION: A LESSON FROM HEREDITY

Section 1.2 outlined a broad puzzle about life (the generation of order) and a correspondingly broad outline of a resolution. Many of the points made there were elegantly summarized in a short but enormously influential essay by the physicist Erwin Schrödinger in 1944. Schrödinger then went on to discuss a vexing question from antiquity: the *transmission* of order from one organism to its descendants. Schrödinger noted that this transmission was extremely accurate. Now that we have some concrete ideas about probability and the dance of the molecules, we can better appreciate why Schrödinger found that everyday observation to be so profound. In fact, careful thought about the physical context underlying known biological facts led Schrödinger's contemporary Max Delbrück to an accurate prediction of what the genetic carrier would be like, decades before the discovery of the details of DNA's structure and role in cells. Delbrück's argument rested on ideas from probability theory, as well as on the idea of thermal motion.

#### 3.3.1 Aristotle weighs in

Classical and medieval authors debated long and hard about the material basis of the facts of heredity. Many believed that the only possible solution was that the egg contains somewhere inside itself a tiny but complete chicken, which needed only to grow. In a prescient analysis, Aristotle rejected this view, pointing out, for example, that certain inherited traits can skip a generation entirely. Contrary to Hippocrates, Aristotle argued,

The male contributes the *plan of development* and the female the substrate. . . . The sperm contributes nothing to the material body of the embryo, but only communicates its program of development . . . just as no part of the carpenter enters into the wood in which he works.

Aristotle missed the fact that the mother also contributes to the "plan of development," but he made crucial progress by insisting on the separate role of an *information carrier* in heredity. The organism uses the carrier in two distinct ways:

<sup>5</sup>What if we take one molecule and slow it down to much *smaller* speed than its peers? Now, the molecule tends to *gain* energy by collisions with average molecules, until once again it lies in the Boltzmann distribution.