

# The Statistical Interpretation of Entropy: An Activity

Todd Timberlake, Berry College, Mount Berry, GA

The second law of thermodynamics, which states that the entropy of an isolated macroscopic system can increase but will not decrease, is a cornerstone of modern physics. Ludwig Boltzmann argued that the second law arises from the motion of the atoms that compose the system. Boltzmann's statistical mechanics provides deep insight into the functioning of the second law and also provided evidence for the existence of atoms at a time when many scientists (like Ernst Mach and Wilhelm Ostwald) were skeptical.<sup>1</sup>

Occasionally the fundamental concepts of statistical mechanics are taught in the introductory calculus-based physics course.<sup>2</sup> In courses for non-science majors, the concept of entropy may be introduced as a measure of "disorder,"<sup>3</sup> but typically no attempt is made to provide a real definition of entropy or a statistical explanation of the second law. This paper describes an activity that presents the statistical approach to entropy and irreversibility in a way that is accessible to non-science majors and high school students. The activity uses highly simplified models that allow students to explore important concepts without sophisticated mathematics. The activity also introduces students to the historical development of these ideas.

This activity occupies two and a half to three hours of class time and requires some knowledge of Newtonian mechanics and energy. The computer simulations described in the article,<sup>4</sup> as well as worksheets to guide students through the activity, are available for free as part of the Open Source Physics collection on the ComPADRE digital library.<sup>5</sup>

## Multiplicity, probability, and entropy

To understand Boltzmann's approach to entropy, we must first introduce two ways of describing the state of a system: the *microstate* and the *macrostate*. A microstate specifies all possible information about the state of the system, while a macrostate gives only coarse-grained information about the system. In general, a macrostate will contain many microstates. A simple way to introduce students to these terms is to consider a model system consisting of a row of coins. Each coin is fixed in position but can show either heads or tails.<sup>6</sup> If we state for each coin whether it is showing heads or tails, then we have specified the microstate of the system. One way to specify a macrostate for this system is to give only the total number of heads and tails. This macrostate tells us how the different components of the system are distributed among their possible states, but it does not provide information about the specific state of any component.

Students easily can write down all of the possible microstates for systems of two, three, and four coins. They can then

determine the number of microstates that correspond to each of the possible macrostates, a quantity known as the *multiplicity* of the macrostate and symbolized by  $\Omega$ . For example, a system of two coins has four microstates: HH, HT, TH, and TT. Two of these microstates corresponds to the macrostate (1H,1T), so the multiplicity of this macrostate is  $\Omega(1H,1T) = 2$ . Similarly  $\Omega(2H,0T) = 1$ , etc. As students work their way up to a system of four coins, they will see that the macrostates with roughly equal numbers of heads and tails (macrostates near equilibrium) have the greatest multiplicities, while macrostates that have all heads or all tails have the smallest multiplicities. The multiplicities are given by the binomial coefficients and, by arranging the multiplicities for the cases of two, three, and four coins in the proper pattern, students can be led to recognize (or remember) Pascal's triangle. Once they see the pattern they can extend the triangle to determine the multiplicities for systems with larger numbers of coins.

What is the probability of choosing a microstate associated with a given macrostate if we select the microstate at random? This probability can be computed by dividing the multiplicity of the macrostate by the total number of possible microstates. Since the macrostates at or near equilibrium have the largest multiplicities, they will be the most probable. In a system of 10 coins, the probability of choosing a microstate in one of the five macrostates closest to equilibrium (3-7 heads) is about 89%, while the probability of choosing a microstate in one of the other six macrostates is only 11%.

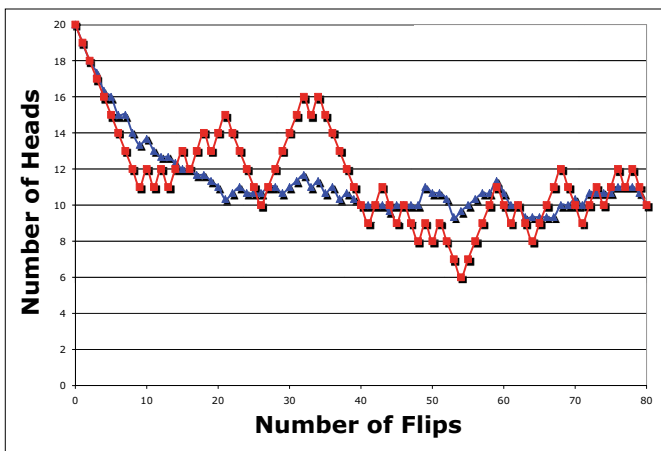
After they have examined the multiplicities and probabilities of a few macrostates, students can be introduced to Boltzmann's definition of entropy:

$$S = k_B \ln \Omega,$$

where  $S$  is the entropy of a macrostate and  $k_B$  is a proportionality constant.<sup>7</sup> Students can compute the entropy for various macrostates to see that macrostates with greater multiplicity have higher entropy.

## Flipping coins

Suppose we start with a row of 20 heads-up coins. What will happen to the macrostate of the system if we begin choosing coins at random and flipping them over? Will the system bounce around among the various macrostates, or will it tend toward one particular macrostate? What will happen to the entropy of the system? To explore this behavior we can roll a 20-sided die<sup>8</sup> and then flip over the coin that corresponds to the result of the die roll. If we repeat this procedure for 80 rolls of the die, we will get a result like that shown by the red squares in Fig. 1. It is clear that the system moves generally



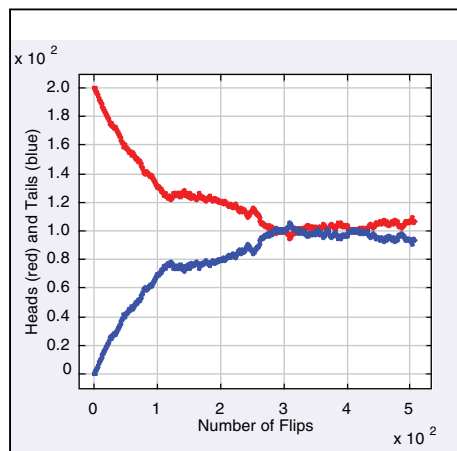
**Fig. 1.** Data from the coin flip experiment. The red squares show data generated by a single group with 20 coins, while the blue triangles show the average for six groups.

toward equilibrium (10H, 10T), but it experiences significant fluctuations away from equilibrium. This behavior is not hard to understand. Let's say the system is in the macrostate (17H,3T). When we roll the die there is a 17/20 chance that the result will lead to a macrostate that is closer to equilibrium (16H,4T) and only a 3/20 chance that it will lead to a macrostate farther from equilibrium (18H,2T). So the system will tend toward the equilibrium state. But moving away from equilibrium, though unlikely, is not impossible, and we should expect to see fluctuations away from equilibrium as shown in Fig. 1. If we average the data from six experiments (shown by the blue triangles in Fig. 1), we find that the fluctuations are smaller.

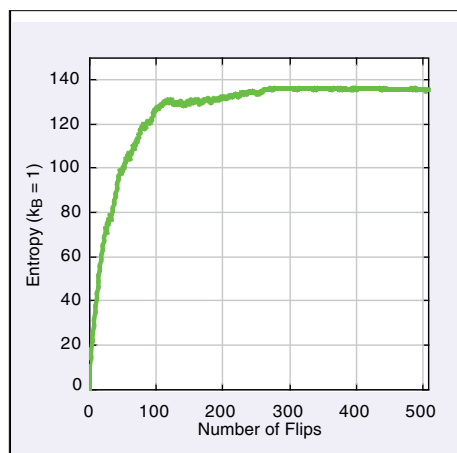
Students can use a computer simulation to explore the behavior of this model with a larger number of coins. The simulation provides a visual display of the state of the system as well as graphs of both the number of heads/tails [Fig. 2(a)] and the entropy [Fig. 2(b)] as a function of the number of coin flips. If students run the simulation with an increasing number of coins, they will quickly see that in all cases the system approaches the equilibrium state, which is also the state of maximum entropy. They will also observe that the relative size of the fluctuations (the size of the fluctuations as a fraction of the total number of coins) decreases as they use more and more coins. Students can then be led to see that this behavior is predicted by their multiplicity calculations, which show that as the number of coins is increased the probability becomes concentrated into a smaller fraction of the macrostates near equilibrium.

### From coins to ideal gases

After their detailed investigation of the coin model students are ready to explore a more realistic system: an ideal gas in a box. Figure 3(a) shows the output from a simulation of a classical ideal gas initially confined to the left side of a box. The graph shows the number of particles on the left and right sides of the box as a function of time. The results are



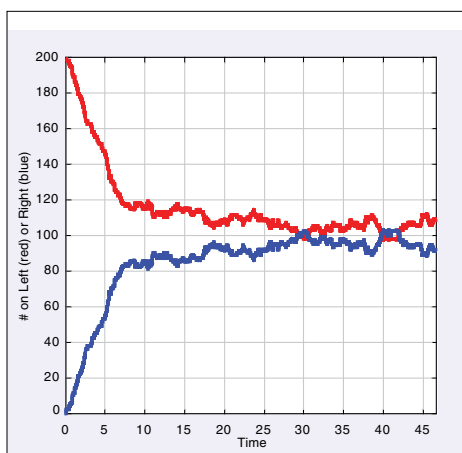
**Fig. 2(a).** Results of a coin flip simulation with 200 coins. The graph shows the number of heads (red) and tails (blue) vs the number of coin flips.



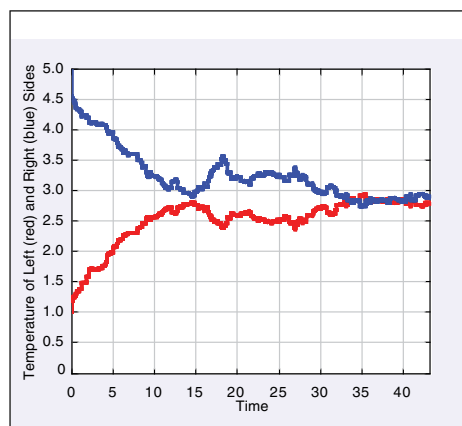
**Fig. 2(b).** Graph of entropy vs number of coin flips for the simulation with 200 coins. The entropy approaches the maximum value of  $S_{\max} = \ln\Omega(100H,100T) = \ln(200!/(100!)^2) \approx 135.75$ .

qualitatively the same as those of the coin model, showing the approach to equilibrium and fluctuations away from equilibrium. Increasing the number of particles in the gas, students will find that the gas approaches equilibrium steadily with no noticeable fluctuations. By analogy with the coin model, students can conclude that the entropy of this ideal gas increases as it approaches the equilibrium state.

It is not hard to understand why the behavior of the gas should mimic that of the coin model. Let each coin represent a particle, with heads indicating the particle is on the left side of the box and tails indicating it is on the right side. A particle moving from one side of the box to the other then corresponds to flipping over a coin. Particles pass from side to side at random (because of their random initial conditions), just as the coins to be flipped are chosen by a random die roll. In spite of these similarities, it is important to point out the differences between an ideal gas and the simple coin model. The



**Fig. 3(a).** Simulation of a gas of 200 particles, initially confined to the left side of a box, showing the number of particles on the left (red) and right (blue) sides as a function of time.



**Fig. 3(b).** Simulation of mixing hot and cold gases showing the temperature of the gas on the left (red) and right (blue) sides of the box as a function of time. Initially the hot gas is confined to the right side while the cold gas is confined to the left.

microstate of an ideal gas is given by stating, for each particle, the exact position and velocity of that particle rather than just stating which side of the box it occupies. The entropy of an ideal gas depends on the temperature and volume of the gas and therefore cannot be calculated with the method used for the coin model, but the behavior of the two systems is similar since the entropy of a gas at constant temperature increases with increasing volume.<sup>9</sup>

This behavior is also connected to heating. Another simulation shows a box that initially has a cold ideal gas on the left side and a hot gas on the right side. The particles of each gas have randomly assigned initial positions (within their respective sides of the box) and random initial velocities distributed according to the Maxwell-Boltzmann distribution. When the simulation is run, each gas expands to fill the box, so that the initially cold side gets hotter and the initially hot side gets cooler [as shown in Fig. 3(b)], while the entropy of the system

increases. Note that here the temperature shown is really just a measure of the average kinetic energy of the particles on each side of the box because the ideal gases overlap without interacting and thus never reach a final Maxwell-Boltzmann distribution. In real gases the molecules interact. Faster-moving molecules are more likely to transfer energy to slow-moving molecules than vice versa, so real gases eventually reach a Maxwell-Boltzmann distribution at an intermediate temperature. The entropy of real gases would increase because energy gets spread and shared more evenly among the molecules (and among the various degrees of freedom, internal and external, of each molecule).<sup>10</sup> For the ideal gases in the simulations, the entropy increases solely as a result of the spreading of energy as each gas expands.

All of these examples illustrate that the second law of thermodynamics is a probabilistic law. Indeed, violations of the second law are possible, as shown by the fluctuations away from equilibrium in the simulations. But motion toward equilibrium, and thus toward higher entropy, is much more likely. As the number of molecules in the gas is increased, the probability that the gas will follow the second law becomes overwhelming. As Boltzmann put it, the second law “means nothing else than that . . . the system of bodies goes from a more improbable to a more probable state.”<sup>11</sup>

### Exploring historical objections

In 1872 Boltzmann used a statistical analysis of the motion of gas molecules to derive his “H-theorem,” which indicated that the reversible dynamics of an ideal gas produces an irreversible increase in the entropy of the gas. The H-theorem implied that the second law was absolute: entropy must *always* increase. What led Boltzmann to abandon this absolute view of the second law in favor of the probabilistic view presented above?

Doubts about the absolute nature of the second law had been expressed even before 1872. James Clerk Maxwell, in an 1869 letter to his friend P. G. Tait, expressed concern about possible violations of the second law. He imagined a gas confined to a box and monitored by an entity (later known as Maxwell’s Demon<sup>12</sup>) that would allow only fast-moving molecules to pass from the right side to the left side of the box and only slow-moving molecules to pass the other way. If the gas is initially in equilibrium, then the Demon will cause the left side to become hotter while the right side gets colder. This would be a clear violation of the second law, except that the gas is no longer an isolated system (because it interacts with the Demon). Maxwell thought that the natural motion of the molecules might coincidentally produce the same effects as the Demon, and therefore true violations of the second law might be possible (though presumably rare).

Students can explore the effects of Maxwell’s Demon using a modified version of the ideal gas simulation described above. The simulation begins with a mixture of hot and cold ideal gases spread throughout a box, but the actions of the Demon cluster the faster particles on the left and the slower

particles on the right, making one side get steadily hotter while the other side gets colder. The Demon can be turned off so that students can see that the system quickly returns to equilibrium. Note that the Demon in the simulation is not constrained by the laws of physics. If the Demon must obey the laws of physics, then it could take millions of years to generate a noticeable temperature difference.<sup>13</sup>

In 1876 Josef Loschmidt raised another famous objection that casts doubt not only on the absolute nature of the second law but also on its statistical interpretation. He pointed out that for any motion allowed by Newton's laws, the time-reversed motion must also be allowed. So for every set of motions that cause the entropy of a gas to increase, there must be another equally valid set that causes the entropy of the gas to decrease. Students can explore Loschmidt's argument using the ideal gas simulations described previously, each of which includes a button that reverses the velocities of all particles. If students run the simulation until it reaches equilibrium, reverse the velocities, and run the simulation again, the resulting time-reversed motion will violate the second law.

Boltzmann developed his probabilistic interpretation of the second law partially in response to these criticisms. In the 1877 papers in which he introduced his statistical approach to entropy, he admitted that violations of the second law were possible, but he claimed that such violations would be rare and brief. It seems intuitively unlikely that the natural motion of gas molecules would mimic the effects of Maxwell's Demon. Boltzmann claimed that the time-reversed behavior pointed out by Loschmidt also would be unlikely to occur, since the system would rarely evolve into a state like the velocity-reversed states described above. Furthermore, he claimed that any violations of the second law would only last for a short time before the entropy would start increasing again. This last point can be illustrated using the computer simulations discussed above. The decrease in entropy that occurs for the time-reversed gas lasts only until the gas reaches its initial condition. After that the entropy of the gas starts to increase again, so the violation of the second law is only temporary.

## Conclusion

Boltzmann's statistical approach to entropy provides deep insight into the behavior of macroscopic systems. Moreover his interpretation of the second law as a probabilistic law introduced a radical new view of the nature of scientific laws. The activity described above is intended to make these important concepts accessible to high school students and non-science majors in college. Although the activity makes use of models that are highly simplified and lack many features of real gases, it can help students to understand the statistical interpretation of entropy and irreversibility while requiring only a minimal background in mathematics and physics. Computer simulations and worksheets for this activity are available for free in the Open Source Physics collection at [www.compadre.org/osp/](http://www.compadre.org/osp/).<sup>5</sup>

## Acknowledgments

The author would like to thank Dan Robb, Chuck Lane, and the anonymous referee for their helpful comments, and Wolfgang Christian for help with the computer simulations.

## References

1. An accessible account of the history of Boltzmann's work is given in David Lindley, *Boltzmann's Atom* (The Free Press, New York, 2001).
2. Ralph Baierlein, "Entropy and the second law: A pedagogical alternative," *Am. J. Phys.* **62**, 15-26 (Jan. 1994); Marcelo Alonso and Edward J. Finn, "An integrated approach to thermodynamics in the introductory physics course," *Phys. Teach.* **33**, 296-310 (May 1995); Thomas A. Moore and Daniel V. Schroeder, "A different approach to introducing statistical mechanics," *Am. J. Phys.* **65**, 26-36 (Jan. 1997); David C. Schoepf, "A statistical development of entropy for the introductory physics course," *Am. J. Phys.* **70**, 128-136 (Feb. 2002).
3. The analogy between entropy and disorder can be misleading. See D. F. Styer, "Insight into entropy," *Am. J. Phys.* **68**, 1090-1096 (Dec. 2000) for a discussion and a better analogy.
4. The simulations were created using Easy Java Simulations (EJS) by Francisco Esquembre (see [www.um.es/fem/Ejs/](http://www.um.es/fem/Ejs/)). Parts of the simulations are based on the MultipleCoinToss and PartitionedBox EJS models by Wolfgang Christian and Mario Belloni. See [www.compadre.org/osp/](http://www.compadre.org/osp/) for these and other EJS models.
5. A package containing all of the simulations is available at [www.compadre.org/osp/items/detail.cfm?ID=10161](http://www.compadre.org/osp/items/detail.cfm?ID=10161). Worksheets for the activity are available as supplemental documents on the same page.
6. This model is equivalent to the double-urn model first introduced by Paul and Tatiana Ehrenfest and presented as the dog-flea model in V. Ambegaokar and A. A. Clerk, "Entropy and time," *Am. J. Phys.* **67**, 1068-1073 (Dec. 1999).
7. The activity uses dimensionless units with  $k_B = 1$ , so that  $S = \ln\Omega$ .
8. These dice are used in role-playing games and can be found at hobby stores.
9. For a detailed discussion of entropy and irreversibility in an ideal gas, see R. H. Swendsen, "Explaining irreversibility," *Am. J. Phys.* **76**, 643-648 (July 2008).
10. H. S. Leff, "Thermodynamic entropy: The spreading and sharing of energy," *Am. J. Phys.* **64**, 1261-1271 (Oct. 1996).
11. William F. Magie, *A Source Book in Physics* (McGraw-Hill, New York, 1935), p. 263.
12. For an extensive list of references on Maxwell's Demon, see H. S. Leff and A. F. Rex, "Resource Letter MD-1: Maxwell's Demon," *Am. J. Phys.* **58**, 201-209 (March 1990).
13. Harvey S. Leff, "Maxwell's demon, power, and time," *Am. J. Phys.* **58**, 135-142 (Feb. 1990).

**Todd Timberlake** received his PhD in physics from the University of Texas at Austin in 2001 and is currently an associate professor of physics and astronomy at Berry College. His courses for nonscience students are activity-based and make use of computer simulations and historical material.

PO Box 5004, Mount Berry, GA 30149; [timberlake@berry.edu](mailto:timberlake@berry.edu)