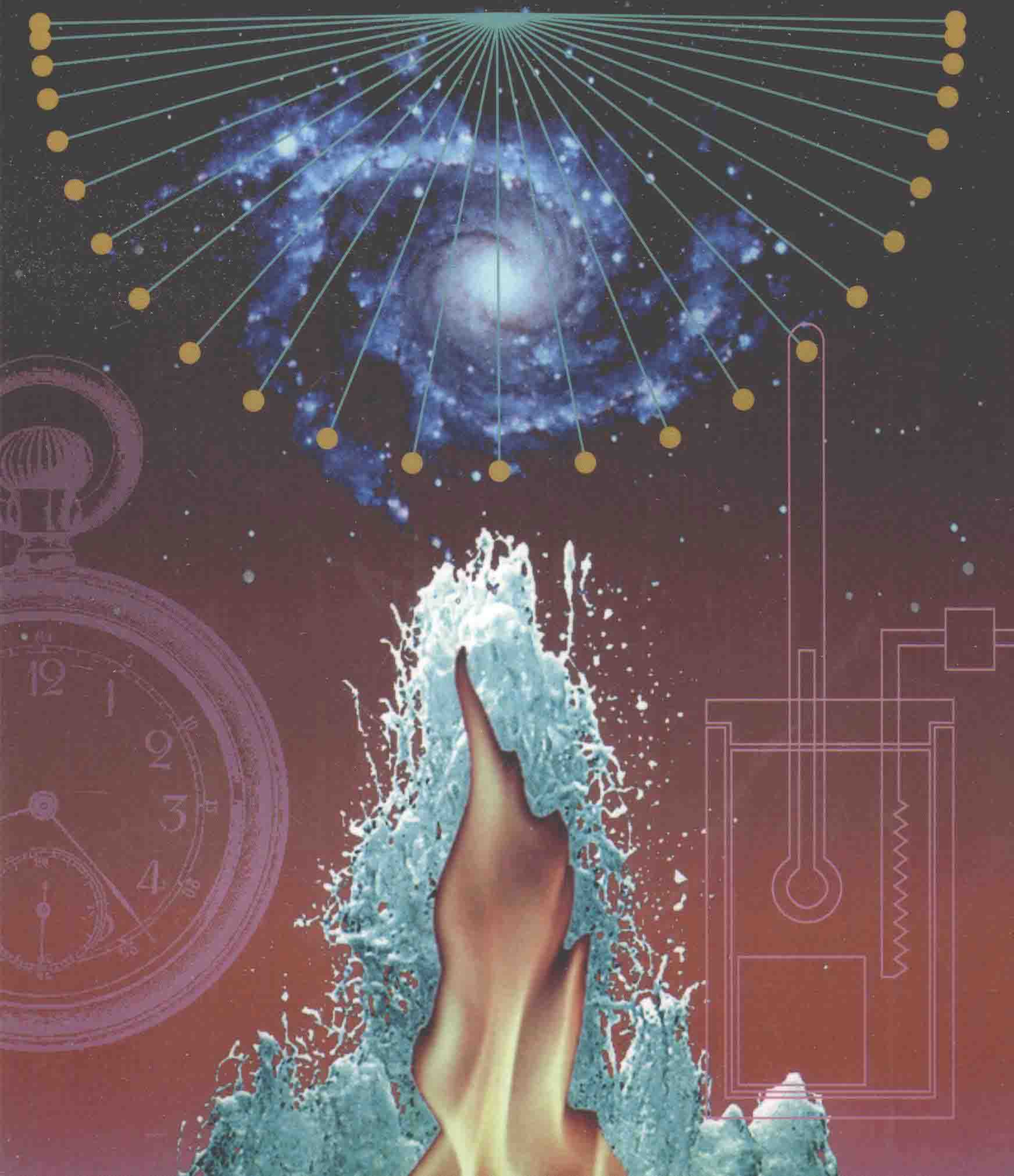
THE REFRIGERATOR AND THE UNIVERSE

UNDERSTANDING THE LAWS OF ENERGY

MARTIN GOLDSTEIN AND INGE F. GOLDSTEIN



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MARTIN GOLDSTEIN

INGE F. GOLDSTEIN

Harvard University Press
Cambridge, Massachusetts
London, England

Printed in the United States of America
Third printing, 1998

First Harvard University Press paperback edition, 1995

Library of Congress Cataloging in Publication Data

Goldstein, Martin, 1919 Nov. 18– .
The refrigerator and the universe: understanding the laws
of energy / Martin Goldstein, Inge F. Goldstein.
p. cm.
Includes bibliographical references and index.
ISBN 0-674-75324-0 (alk. paper) (cloth)
ISBN 0-674-75325-9 (pbk.)
1. Entropy. 2. Force and energy. 3. Entropy (Information theory)
I. Goldstein, Inge F. II. Title.
QC318.E57G65 1993
530'.7—dc20

93-2084
CIP

To Theodore Saul Miller,
and any others
who come along

Acknowledgments

This book might be said to have been started when one of the authors took a correspondence course in thermodynamics while serving in the U.S. Army. In the years since, we have both been inspired by the various professors from whom we have learned—and the various students to whom we have taught—thermodynamics as well as other branches of science.

We have profited particularly from discussions with Professor James L. Anderson of Stevens Institute of Technology on the irreversibility paradox and on relativity, with Professor George Schmidt of the same institution on irreversibility and on chaos, and with Professor Erick Weinberg of Columbia University on cosmology.

We thank our son Michael Z. Goldstein for making a number of line drawings. Computer graphics were prepared by Ms. Vaun Hatch of the Center for Biomedical Communications, Columbia University.

It was a pleasure to work with Kate Schmit of Harvard University Press, who gave the book a thorough and critical editing.

Our children have been kind enough to tell us that they did not feel neglected while we were writing it.

The Refrigerator and the Universe

Contents

1
Energy and Entropy in Everyday Terms

Some people want to know how a refrigerator works. Others want to know the fate of the universe. The purpose of this book is to show that the answers to the two questions are related. The science that relates them is thermodynamics, and we can illustrate its laws with an even simpler device than a refrigerator: a spring-driven wristwatch.

We take the watch and wind it up. The hands begin to move and a ticking is heard, which continues for a little more than a day, and then the watch stops. The spring is unwound, and the hands no longer move. Except for one day's wear and tear, the watch is in the same condition as before we wound it. What has happened to the effort, small as it was, that we put into the winding of the spring? Has it disappeared with the sound of the ticking, or is it in some way still around?

Thermodynamics is the science that deals with energy; its transmission from one body to another and its transformations from one form to another. The bodies we will apply it to—watches, refrigerators, microbes, the earth, the stars—all can gain energy from other bodies or lose it to them. Energy comes in different forms—the energy of water stored behind a dam, of chemical or nuclear fuels, of electric currents, of those electromagnetic waves we call "light" or "microwaves," and the energy stored in the moving atoms of which matter is composed—and it can be changed from one form to another.

The first law of thermodynamics says that among all these transmissions and transformations, the net quantity of energy does not change. The second law says that while energy is never lost, it can be wasted, in the sense that it can become unavailable for further transformation, and thus unavailable for human use.

The spring-driven watch serves not only as an illustration of the laws of energy but as a metaphor for them as well. Invented in the fifteenth century, such watches had been developed to a state of high accuracy by the nineteenth century. In the twentieth century, though, they became obsolete: the new electric clocks and quartz watches are just as cheap to manufacture and more accurate than any spring-driven watch can be (although some of us, out of habit or nostalgia, still wear them). The laws of thermodynamics are among the nineteenth century's greatest scientific achievements. New scientific discoveries made in the twentieth century required that these laws be modified and identified limits on their applicability, but within those limits they have extraordinary power, generality, and accuracy.

We will describe these laws first in their nineteenth-century form. The reader may reasonably ask why we have chosen to take this approach. We have three reasons:

First, the laws of thermodynamics are more easily understood that way, because they are in accord with the common experiences and intuition of even twentieth-century individuals, who are more familiar with refrigerators, batteries, and automobile engines than with the interiors of stars.

Second, like spring-driven watches, the laws in their earlier form are sufficiently reliable and accurate for most purposes.

Third, one can get some sense of the significance of the revolutionary discoveries of the twentieth century—quantum mechanics and the theory of relativity—by comparing what we know now with what we knew then. In the last part of the book, we will discuss how the laws of thermodynamics and our understanding of what they mean have been changed by these discoveries. We will also describe how the laws apply to nuclear explosions and to an expanding universe.

The First Law

The first law, known as the law of the conservation of energy, states that energy is indestructible and uncreatable. The idea that there is a "something" that cannot be created and cannot be destroyed is not of itself difficult to comprehend, but we need to know more about what scientists mean by the term *energy* and how they established the impossibility of making some of it out of nothing. Scientists are hard-nosed about such matters. Energy for them is not the vague and mutable entity it is in ordinary speech—"vigor or power in action, vitality or intensity of expression, the capacity for action or accomplishment," as the *American Heritage Dictionary* (1969) defines it. They want precise definitions and quantitative measurements. Some crass bookkeeping is involved: the statement that energy is conserved means that it is conserved to the last penny, or whatever units energy is measured in.

Because the concept of energy is a difficult one, we will have to approach its meaning slowly. One problem is that energy comes in many different forms, and for most of history the different forms were defined in different ways and measured in different units. Let us give a short list of familiar examples of energy. First, energy is associated with matter in motion: an apple falling from a tree or a wrecker's ball swinging toward its target. This kind of energy is most easily visualized and is closest to the common meaning of the term. But there may be energy where there is no motion but only the potentiality of producing it—the energy of water stored behind the dam of a hydroelectric power plant, the chemical energy of gasoline, the nuclear energy of plutonium or hydrogen. From any of these we can produce the energy of motion as needed—the motion of automobiles, chain saws, or food processors. Sometimes we use the stored energy to heat our immediate environment rather than to produce motion, which tells us that "heat," whatever we mean by the term, is in some sense also a form of energy. Then there is electrical energy, often a medium by which the potential energy of fuels or water is transmitted to a new setting, where it is transformed into another form of energy: the motion of a fan or the heating of a stove.

We measure, and pay for, electrical energy in kilowatt-hours (costing approximately 10 cents per kwh in New Jersey in 1992). If energy is both convertible and indestructible, it must be possible to measure all forms of it in kilowatt-hours and show that, whatever changes in the form of energy have occurred, the total number of kilowatt-hours has not changed. As we have indicated, other units for measuring energy are also used, some quite familiar: Calories, for the energy value of foods, and British thermal units (BTU), as an indication of the power of air conditioners and refrigerators. Less familiar units are the foot-pounds of the engineer and the joule and electron-volt of the scientific laboratory. There are fixed factors for converting quantities of energy from one system of measurement to another: unlike currency conversion rates, however, they do not fluctuate from day to day. A dieter's booklet we consulted gave the energy content of a banana split as 1,165 Calories: this translates to 1.35 kwh.

Let us now apply the principle of the conservation of energy to the burning of a log of wood. A quantity of chemical energy is stored in the wood and the oxygen of the surrounding air, and this energy is released when the log is burned. Chemically, wood and oxygen are converted to carbon dioxide, water, and ashes. The chemical energy has been released and the surrounding environment has been heated. In more scientific language, the "thermal energy" of the environment has been increased, as a thermometer would show us. Kilowatt-hour for kilowatt-hour, the chemical energy released can be accounted for by the increase in the energy of the surroundings.

We can trace the chemical energy stored in the wood back through previous forms. The living tree converted carbon dioxide, water, and minerals into living cells with the aid of the energy of light from the sun. The sun emits light because it is hot: its surface temperature is about 6,000°C (about 10,000°F). The source of the sun's energy is the nuclear fusion reaction in which hydrogen atoms in the core of the sun are converted to helium.

Having traced the chemical energy of the wood this far back, we will change direction now and follow the sun's energy to other destinations. Not all plants are used for firewood. Some are grown by human beings for food and for fodder; some grow wild, die, and are converted by molds and bacteria back to carbon dioxide and water. Food and fodder give both humans and animals the chemical energy needed for their muscles and their internal temperature-regulating systems to function. Thus some of the food energy goes to motion and some to keeping the body warm. But not all the sun's energy falling on the earth goes to grow plants—only about 0.1 percent does. Of the rest, some 35 percent is reflected or re-radiated back into space. Some, most strongly the ultraviolet light, is absorbed in the atmosphere, increasing its temperature and thus its energy but also producing some chemical reactions. The remainder warms the surface of the earth, evaporating water and warming air next to the surface. The warmed air rises, winds follow, the atmosphere of the earth circulates, rain and snow fall, tradewinds blow, and sometimes hurricanes. All is powered by the energy radiated by the sun.

Throughout all the transformations that take place, the bookkeeping goes on: kilowatt-hour for kilowatt-hour, all the energy can be accounted for. The total amount remains the same regardless of the changes of form. According to the first law, the total energy of the universe will remain the same for all time, the same as it is today, and the same as it was in the distant past. Forward or backward, it makes no difference.

The Second Law

But forward or backward must make a difference somehow. Think of the log of wood burning: the flames start out and spread; slowly the wood blackens, glows, and then turns to ashes. The heated gases from the combustion rise and warm the surrounding air while they mix with it. Gradually it all dies down as the gases and the thermal energy spread out more and more in the atmosphere. Eventually nothing is left except a pile of ashes.

But can the clock be turned backward to reverse this process? We have mentioned that plants convert carbon dioxide, water, and minerals into wood. Are we not back at the starting point again? Not quite. The reconstitution of the log of wood from ashes and the other products of combustion—or, in other words, the growth of a new tree—requires an input of the sun's energy. Turn off the sun and the ashes remain ashes. Well, then, could we not reconstitute the wood by other means: powerful lamps to take the place of sunlight, for example? Yes, but we need a source of energy for the lamps. To reverse the burning, a price must be paid in energy. Note that there was no external energy cost to burn the wood. True, we needed a match to start the fire, but one match can burn down a forest; we can leave it out of the bookkeeping. There is a natural direction to processes in the universe, and no energy cost is required to make them go in this direction. To make them go in the opposite direction we must pay.

Imagine that we had made a film of the burning of the log and then projected it backward. First we see a pile of cold ashes. Gradually warm air containing carbon dioxide and moisture descends on the ashes, which begin to get warm. The rate of descent of warm air, now mixed with smoke, increases: the ashes begin to glow, then break into flame. As the flames rise, wood is formed. Soon the flames die down again, and the log has been recreated.

No one watching this film would believe for a moment that it represents a possible event in the real world. Yet nothing that has happened violates the first law: the energy can be accounted for, kilowatt-hour by kilowatt-hour, whichever direction the film is projected. We need a new law of nature to tell us which is the natural direction and which the impossible direction for things to happen. This is the second law of thermodynamics.

The second law can be stated in a number of different ways that reflect different perspectives on its meaning, implications, and consequences. We will use various statements as we go along. Let us give one here, one related to the question of which way to run the film through the projector.

In the nineteenth century, Rudolf Clausius, a German physicist and one of the discoverers of the second law, formulated that law in an almost innocuous-sounding statement that heat will flow spontaneously from hot bodies to cold ones, never the reverse (heat flows from cold bodies to hot ones in the operation of refrigerators, but not spontaneously: an expenditure of electrical energy is required to make it happen). From this starting point, he was able by logical analysis to prove that matter must have a previously unrecognized property, which he called *entropy,* that can be readily determined in the laboratory. He further showed that in all natural processes the total entropy of everything involved in the process can never decrease: it can remain unchanged in certain idealized processes, but in all real changes, the entropy will always increase. Note the contrast to the total energy in any real change, which neither increases nor decreases. It led Clausius to formulate the second law in a new form: *the entropy of the universe tends to a maximum.*

The universe of the twentieth century—now expanding, perhaps infinite in extent, and obeying the theory of relativity—raises questions about Clausius's formulation. We will discuss them only briefly here, but we will discuss them in more detail in a later chapter. Dealing with the whole universe at once is an awesome project anyway, and we more commonly deal with processes taking place in small pieces of it at a time, pieces the size of a laboratory. To the extent that we can imagine each process carried out in isolation from all others, the total entropy within such isolated small regions must necessarily increase. Let us consider a few examples:

1. The flow of heat (thermal energy) from hot bodies to cold ones, leading to an equalization of temperature.
2. Any process involving friction, in which the energy of motion is converted to a heating of the moving body and its environment.
3. The expansion of a compressed gas into ordinary air, as when a tire is punctured.

4. An ice cube melting in a glass of warm water.
5. A teaspoon of sugar dissolving in a cup of hot coffee.
6. The combustion of gasoline in an auto engine.

We immediately recognize a film of any of these processes run backward as representing an impossible event. In all of them it can be shown that the total entropy of everything involved in the process has increased. The total entropy thus tells us objectively whether the film is being run forward or backward. Entropy has been called "the arrow of time."

The Molecular View of Entropy

Just what is entropy, and what does it mean to say that it is a property of matter? Entropy was discovered by an analysis of the conversion of the chemical energy of fuels into the energy of motion by steam engines. But the concept is more easily understood from the viewpoint of the molecular theory of matter, so we will set aside our burning logs and melting ice cubes for a moment.

Matter is made up of atoms of various kinds, usually combined together in stable aggregates called *molecules* (for example, H_2O is a molecule). Atoms and molecules are very small, and even a small amount of matter—an ounce or a gram—contains an enormous number of them. Further, they are in constant motion, colliding with each other repeatedly and therefore undergoing frequent changes in speed and direction. We may imagine them to act something like billiard balls colliding elastically on a billiard table. It would be difficult to predict the path of one ball when there are as few as 10 others on the table for it to collide with, but nevertheless we are able to study the millions of molecules in a vial of gas, say, or a drop of liquid, if we ask different kinds of questions: we cannot know the path of a particular molecule but we can describe the *average* behavior of enormous numbers of them. This is just the kind of problem for which the theory of probability was designed, and while it may seem easier to apply it to the tosses of a coin or to the shuffling of a deck of cards than to the motion of atoms, the theory has allowed us to make successful predictions of molecular behavior. Let us first talk about cards, though.

A deck of fifty-two cards can be arranged in order of suit and value. When shuffled, the deck tends toward a more disordered arrangement. A disordered deck of cards can also be shuffled, and it is not impossible that it could be shuffled into a perfectly ordered arrangement. But it is highly unlikely; it is much more likely to go from one disordered arrangement to another. The tendency of systems to approach a state of maximum disorder, and once there to stay there, is an example of the operation of what is often called the *law of averages*. It takes no deep grasp of the theory of probability to see that if we repeat the experiment with decks of trillions or quadrillions of cards, the tendency to go from an ordered arrangement to a disordered one is even more overwhelming, and the likelihood of any large deck ending up in a neat order after shuffling is inconceivably small.

Just like decks of cards, large collections of atoms or molecules can be classed as being either in ordered or disordered arrangements, and the vast numbers of disordered arrangements involved ensure with virtual certainty that they will end up disordered.

To return to our example of the burning log of wood: it can be shown that there was more order in the arrangement of the molecules of the wood and the air than there is, after burning, in the molecules of the ashes, the combustion products, and the heated environment. Entropy is related in a very simple way to the degree of disorder. The law of increasing entropy is thus equivalent to the statement that ordered systems tend to disorder while disordered systems tend to stay that way. The outcome is not inevitable, only very, very probable, but the probability can be overwhelming. It is safer to gamble that the tendency to disorder will prevail.

Quantum Mechanics and Relativity

A quantitative calculation of how much disorder there is in a particular collection of molecules, and therefore of the entropy of the collection, requires us to know how molecules move under the influences of whatever forces they exert on each other. The assumption was made in the nineteenth century that molecules move according to the same Newtonian laws as falling apples do, but the results of such calculations were often in stark disagreement with experimental measurements. In the twentieth century, the new quantum mechanics was shown to describe the experimentally observed properties of molecules, including their entropies, with, as far as we can tell, complete accuracy.

The theory of relativity, also a product of twentieth-century science, provided a framework for studying the history of the universe, from its beginning to its ultimate end. One of its most remarkable implications is that the universe is not static: it must be either expanding or contracting. Astronomical observations show in fact that the universe is now expanding. The theory of relativity shows it will either continue to expand forever or at some point turn around and begin to collapse.

The most significant consequence of relativity for thermodynamics is that energy is not always conserved. When the universe expands, the total amount of energy we can account for decreases, and if the universe were ever to contract, the total amount would increase. This does not deprive energy of an important role in our unstable universe; the energy content of the universe determines its rate of expansion and whether it will ultimately contract or not.

The second law must also be modified to apply to the unstable and possibly infinite universe of the theory of relativity, but there is as yet no good reason to doubt the inexorable increase of entropy. It is still, as far as we know, time's arrow.

In what follows we have three goals: to tell how the concepts of energy and entropy were discovered; to explain how they apply in a variety of fields—for example, in the study of radiation (including the "greenhouse effect"), chemistry (the synthesis of diamonds), biology (how the muscles do work), and geology (the age of the earth); and to describe how the concepts of energy and entropy have been modified by quantum mechanics and the theory of relativity, and how they apply to the expanding universe.